Dielectric Constants of Simple Gases
Determined Using Microwave Cavity Resonators

A thesis submitted to the University of London
for the Degree of Doctor of Philosophy
by
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Dedication

This work is dedicated to my parents Vera and Derek Royal.
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Abstract

The dielectric constants of simple, non-polar gases have been measured with fractional uncertainties on the order of ±1 ppm using two microwave cavity resonators. A spherical resonator with internal radius of 40 mm was used to make measurements on argon at four temperatures between 215 K and 300 K, nitrogen at 300 K, the mixture (0.5 Ar + 0.5 N\textsubscript{2}) at 300 K, and xenon at eight temperatures between 189 K and 360 K, for pressures below 1 MPa. A newly-designed cylindrical resonator, with internal radius of 9.5 mm and length 20.0 mm, was used to make measurements on nitrogen at ten temperatures between 243 K and 323 K, for pressures up to 4.015 MPa.

The $\varepsilon(p, T)$ measurements were combined with published $(p, V_m, T)$ virial coefficients and fitted to a form of the density-explicit expansion of the Clausius-Mossotti function to obtain estimates of the dielectric virial coefficients. The first dielectric virial coefficients were always in excellent agreement with published values (generally within 0.1 %). The second dielectric virial coefficients of xenon tended to be higher than the few published results although they generally agreed within the combined uncertainties, whilst the second dielectric virial coefficients of nitrogen were in good agreement with published results and enabled the determination of the quadrupole moment of nitrogen in superb agreement with values in the literature. The sphere measurements were also fitted to obtain estimates of the second $(p, V_m, T)$ virial coefficients in very good agreement with the most recently published results.
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Chapter 1  Introduction

This thesis is concerned with the accurate measurement of the relative permittivity or dielectric constant \( \varepsilon \) of gases, and the use of such measurements in determining the properties of the molecules and the interactions between them. The dielectric constant of a medium is a function of its density and temperature, but is formally independent of the amount of substance. For a non-magnetic, linear, isotropic, homogeneous medium (such as a gas used in this work), \( \varepsilon \) is related to the phase speed of light \( c \) in the medium by \( \varepsilon = \left(\frac{c_0}{c}\right)^2 \), where \( c_0 \) is the speed of light in vacuo. The physical origins of the dielectric constant of a medium and a number of related ideas and results that are important in understanding the work contained in this thesis are briefly covered in chapter 2.

The majority of published measurements of the dielectric constant of gases have been taken using capacitance cells operated at low frequencies (typically about 10 kHz). The most common factors limiting the accuracy of such measurements are mechanical hysteresis and cell geometry distortion caused by the need for insulating spacers. Microwave cavity resonators have no insulating spacers, and their use in measuring the dielectric constants of gases has begun to be seriously investigated in recent years and is developed further in this work. The achievement of accurate measurements using microwave resonators demands a comprehensive understanding of the relevant electromagnetic theory, and so the requisite theoretical background is detailed in chapters 3 and 4.

The resonance frequencies of an ideal resonator are exactly proportional to the phase speed of light in the medium filling the cavity, and so the measured resonance frequencies of a gas-filled and evacuated cavity can be used to determine \( \varepsilon \). The accuracy of the \( \varepsilon \) measurements can be improved by correcting for the effects of cavity non-ideality using perturbation theory. The more detailed the perturbation modelling, the more accurate will be the final \( \varepsilon \) values and the more reliable will be the uncertainties placed on such measurements, and so much time is spent, in chapter 4, considering the various sources of non-ideality affecting experimental resonators and the perturbation theory used to correct for their effects. An original and highly
accurate method of calculating the effect of openings in a cavity resonator wall is presented for the first time.

The measurements of $\varepsilon$ are related to the electrical and thermophysical properties of the gases through the various equations of state given in chapter 5. The density-dependence of the dielectric constant of a gas is related to its dielectric virial coefficients, which are functions of temperature alone. The first dielectric virial coefficient $A_2(T)$ depends on the polarisability and dipole moment of the individual gas molecules, while the second, and higher, dielectric virial coefficients are related to the properties of clusters of interacting molecules; in particular, the second dielectric virial coefficient $B_2(T)$ is directly related to the intermolecular pair potential of the gas. However, in general, the density-dependence of $\varepsilon$ is dominated by the first dielectric virial coefficient and so isothermal $(\varepsilon, p)$ measurements can be used to determine the first dielectric virial coefficient and estimates of the second, and higher, $(p, V_m, T)$ virial coefficients by neglecting $B_2$ and the higher dielectric virial coefficients or estimating them from theoretical calculations. Such a method is of particular interest for gases where adsorption gives rise to significant errors in traditional $(p, V_m, T)$ measurements.

In this work, the dielectric constants of argon, nitrogen, xenon and the mixture $\{0.5\,\text{Ar} + 0.5\,\text{N}_2\}$ were measured over a range of temperatures and pressures using two different microwave cavity resonators. The first was an existing aluminium alloy spherical resonator with a nominal 40 mm internal radius; the second was a newly-designed brass cylindrical resonator with internal radius of 9.5 mm and length 20 mm (these dimensions made it the smallest cavity resonator reported to date). The resonator designs and the experimental procedures followed are given in chapter 6. The new cylindrical resonator was pressure-compensated by enclosing it within a stainless-steel pressure vessel, specially designed and constructed for the purpose. The thermal and mechanical stability of the pressure-compensated cylinder was considerably better than that of other cavity resonators and capacitance cells described in the literature.

The spherical resonator was used to make isothermal measurements on argon at four temperatures between 215 and 300 K, on nitrogen and the mixture $\{0.5\,\text{Ar} + 0.5\,\text{N}_2\}$ at 300 K, and on xenon at eight temperatures between 189 and
360 K, for pressures up to about 1 MPa. These measurements are described in chapter 7. The \((\epsilon, p, T)\) data were analysed to provide estimates of the first dielectric virial coefficients and the second \((p, V_m, T)\) virial coefficients of argon, nitrogen and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\), and the first and second dielectric virial coefficients and the second and third \((p, V_m, T)\) virial coefficients of xenon. The first dielectric virial coefficients were in good agreement with published results, where available, and were often more precise. The second dielectric virial coefficients of xenon were higher than the very limited number of published measurements (although the discrepancies were not so large compared to the uncertainties), but showed a very similar temperature-dependence. A simple theoretical model for \(B_x\) gave values significantly smaller than ours, but, again, showed a very similar temperature-dependence. The second \((p, V_m, T)\) virial coefficients were also in good agreement with values in the literature, particularly for xenon, where the equation for \(B(T)\) derived from our measurements between 189 and 360 K gave very good agreement with the most reliable of other workers’ measurements at temperatures far higher than 360 K.

The cylindrical resonator was used to take measurements on nitrogen at 10 temperatures between 243 and 323 K, for pressures up to 4.015 MPa. The experimental data, reported in chapter 8, were used to determine first and second dielectric virial coefficients in good agreement with literature values. The second dielectric virial coefficients were analysed in terms of a more detailed, semi-empirical model for \(B_x\) to obtain an estimate of the permanent quadrupole moment of nitrogen in excellent agreement with literature values obtained using a variety of different experimental methods.
Chapter 2  Fundamentals of Electromagnetism

2.1 Introduction

The purpose of this brief chapter is to explain the principles of electromagnetism that lie at the foundation of this work. A number of assumptions about the nature of the gases used are also discussed because they are essential to the detailed analysis of later chapters.

2.2 Dielectric materials

Dielectrics or insulators contain very few free charged particles under ordinary conditions. They consist of neutral atoms or molecules, as in argon and nitrogen, or of ions held in a highly structured lattice, as in solid sodium chloride. The electrons in a dielectric are strongly bound to the nuclei and so, under the influence of an applied electric field, these particles move only small distances in opposite directions. An applied electric field also tends to direct permanent dipole moments. The field is said to polarise the dielectric.

The familiar concept of electric polarisation is quantified by defining a dipole density or electric polarisation $P$ as

$$\delta \mu = P \delta V$$  \hspace{1cm} (2.2.1)

where $\delta \mu$ is the dipole moment of an infinitesimal volume element $\delta V$ in a polarised dielectric. There may also be contributions to the electric polarisation from higher multipole moments such as quadrupoles or octupoles, but such contributions are generally small [1]. It is clear that $P$ depends on the electric field $E$ and this dependence is expressed by

$$P = \varepsilon_0 \chi_k E$$  \hspace{1cm} (2.2.2)

where $\varepsilon_0$ is the permittivity of free space $(8.8541872 \times 10^{-12} \text{ F m}^{-1} [2])$ and $\chi_k$ is the electric susceptibility.

The relative permittivity or dielectric constant $\varepsilon$ is given by

$$\varepsilon = 1 + \chi_k$$  \hspace{1cm} (2.2.3)

and is an intensive function of density and temperature for a given dielectric. For most dielectrics $\chi_k$ and $\varepsilon$ are independent of the magnitude of $E$ for moderate field
strengths; such dielectrics are described as linear. In the simplest of dielectrics, such as gases, $\chi_{E}$ and $\varepsilon$ are independent of the direction of $E$ and so are termed isotropic. Further, in materials such as gases, $\chi_{E}$ and $\varepsilon$ will be independent of position in the dielectric and such dielectrics are called homogenous. The low field strengths and simple gases used in this work ensure that the assumption of linear, isotropic, homogeneous (LIH) media employed throughout the analysis is entirely reasonable [1].

With the exception of ionic solids there are, in general, three contributions to the electric polarisation: the orientational contribution corresponds to the directing of permanent molecular dipole moments by the electric field, the atomic contribution corresponds to the motions of atoms during intramolecular vibrations, and the electronic contribution corresponds to the motions of electrons with respect to the nuclei. These motions have different characteristic times, the exact values of which depend on the nature of the dielectric. Representative values are $10^{-9} \text{s}$ for the dipoles, $10^{-13} \text{s}$ for the atoms, and $10^{-15} \text{s}$ for the electrons [3]. Characteristic frequencies of field variation can therefore be attributed to the three different parts of the polarisation. Representative frequencies for the orientational, atomic, and electronic contributions lie in the microwave, infrared, and optical parts of the electromagnetic spectrum, respectively. If the frequency of electric field is comparable to any of the characteristic frequencies then the relevant motion begins to lag behind the field variations and the polarisation is no longer in phase with the field. The corresponding contribution to the polarisation is altered and there is energy loss in the dielectric. This situation is described by introducing a complex, frequency-dependent dielectric constant [3]

$$\varepsilon(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega)$$

(2.2.4)

where $\omega = 2\pi f$ is the angular frequency of electric field of frequency $f$, $\varepsilon'$ is the real part of the dielectric constant, and the imaginary part $\varepsilon''$ is a measure of the energy loss in the dielectric [see section (4.9)]. Figure (2.1) shows the typical frequency-dependence of the dielectric constant for polar and non-polar media.
The gases used in this work are non-polar and so there is no orientational contribution to the polarisation. Therefore the measurements at microwave frequencies should provide $\varepsilon$ equal to the static-field value and significant dielectric energy losses are not expected.

### 2.3 Maxwell’s equations

The laws of electromagnetism are summarised in four equations which have come to be known as Maxwell’s equations. The differential forms, to apply at any point in a medium, are

\[
\nabla \cdot \boldsymbol{D} = q_v \quad (2.3.1)
\]

\[
\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \quad (2.3.2)
\]

\[
\nabla \cdot \boldsymbol{B} = 0 \quad (2.3.3)
\]

\[
\nabla \times \boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t} + \boldsymbol{J} \quad (2.3.4)
\]

where $t$ is time, $\nabla$ is the del vector, $q_v$ is the conduction charge density, $\boldsymbol{J}$ is the conduction current density, $\boldsymbol{E}$ is the electric field, $\boldsymbol{H}$ is the magnetic field, $\boldsymbol{D}$ is the
electric induction or electric displacement, and $B$ is the magnetic induction or magnetic flux density.

Maxwell's equations alone do not permit solutions of problems in electromagnetism. They are complemented by the constitutive relations which define the relations between the various field quantities:

\[ D = \varepsilon_{\varepsilon_0} E \] (2.3.5)
\[ B = \mu\mu_0 H \] (2.3.6)
\[ J = \sigma E \] (2.3.7)

where $\mu$ is the relative permeability, $\mu_0$ is the permeability of free space \( (4\pi \times 10^{-7} \text{ H m}^{-1} \text{ exactly [2]} \) and $\sigma$ is the electrical conductivity.

The relative permeability $\mu$, which is an intensive function of density and temperature for a given medium, is related to the magnetisation $M$ in a way analogous to the relation between the dielectric constant $\varepsilon$ and the electric polarisation $P$ [4]. For many important media, $\mu$ is not significantly different from unity. For these non-magnetic materials the $B$ field behaves as though in vacuo and the treatment is simplified. Fractional errors in $\varepsilon$ of the order \( (\mu - 1) \) are introduced by assuming $\mu = 1$ for the experimental analysis used in this work. Table (2.1) shows that such errors are insignificant for the gases used although $O_2$ is an example of a gas where they may be significant.

---

**Table (2.1)** \( 10^6 (\mu - 1) \) for a number of simple gases at 300K, 500kPa [5, 6]

<table>
<thead>
<tr>
<th>Gas</th>
<th>( 10^6 (\mu - 1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>-0.05</td>
</tr>
<tr>
<td>N₂</td>
<td>-0.03</td>
</tr>
<tr>
<td>Xe</td>
<td>-0.11</td>
</tr>
<tr>
<td>O₂</td>
<td>+8.70</td>
</tr>
</tbody>
</table>

The electrical conductivities of simple gases are extremely small under all but the most extreme conditions of temperature and electric field [5, 7]. We introduce fractional errors in $\varepsilon$ on the order of \( \left( \sigma/2\omega\varepsilon_0 \right)^2 \) if \( \sigma/\omega\varepsilon_0 \) is neglected for the
experimental analysis [see section (4.9)]. Such errors are negligible for the microwave frequency \((\omega > 10^{10} \text{ s}^{-1})\) measurements on the simple gases used in this work.

If we consider fields of time-dependence \(\exp(i\omega t)\), for which \(\left(\partial / \partial t\right) = i\omega\), in an insulating, non-magnetic, LIH medium then equations (1) to (4) become

\[
\begin{align*}
\nabla \cdot E &= 0 \quad (2.3.8) \\
\nabla \times E &= -i\omega \mu_0 H \quad (2.3.9) \\
\nabla \cdot H &= 0 \quad (2.3.10) \\
\n\nabla \times H &= i\omega \varepsilon \varepsilon_0 E \quad (2.3.11)
\end{align*}
\]

where we have used the constitutive relations, equations (5), (6) and (7), and the assumed time-independence of \(\varepsilon\) and \(\mu\) in obtaining these equations. Equations (8) to (11) are valid in all insulating, non-magnetic, LIH media for fields with a time variation of any single angular frequency \(\omega\). Maxwell’s equations are linear and therefore the superposition of any number of solutions will itself be a solution of the equations [4]. Fourier’s theorem states that any continuous periodic function may be expressed as the sum of a number of harmonic functions, each with different amplitude and frequency and suitable phase. Clearly then, the restriction of monochromatic fields imposed by equations (8) to (11) is not a serious one [8]. For magnetic media \(\mu_0\) is simply replaced by \(\mu \mu_0\) in equation (9) although this will not be necessary for our analysis.

### 2.4 Electromagnetic waves

Taking the curl of both sides of equation (2.3.9) and using the vector identity

\[
\nabla \times \nabla \times A = \nabla (\nabla \cdot A) - \nabla^2 A
\]

and equation (2.3.8) we obtain, after rearrangement

\[
\nabla^2 E + \omega^2 \varepsilon \varepsilon_0 \mu_0 E = 0
\]

(2.4.2)

where we have used equation (2.3.11) to eliminate \(H\). Similarly, taking the curl of both sides of equation (2.3.11) to eliminate \(E\). Using identity (1) and equation (2.3.10) we obtain, after rearrangement

\[
\nabla^2 H + \omega^2 \varepsilon \varepsilon_0 \mu_0 H = 0
\]

(2.4.3)
where equation (2.3.9) has been used to eliminate $E$. Comparison of equations (2) and (3) with the partial differential wave equation

$$\nabla^2 \psi + \omega^2 \left( \frac{1}{v^2} \right) \psi = 0$$

(2.4.4)

where $v$ is the speed of the $\psi$ wave, shows that equations (2) and (3) are wave equations for $E$ and $H$ fields propagated with the same speed

$$c = \left( \frac{1}{\varepsilon \varepsilon_0 \mu_0} \right)^{\frac{1}{2}}$$

(2.4.5)

That is, they are equations for electromagnetic waves. The speed of electromagnetic wave propagation in free space (where $\varepsilon = \mu = 1$) is

$$c_0 = \left( \frac{1}{\varepsilon_0 \mu_0} \right)^{\frac{1}{2}}$$

(2.4.6)

which is defined to be $2.99792458 \times 10^8$ m s$^{-1}$ [2]. The ratio of this speed to the phase speed in a given medium is its refractive index $n$, which in this case is given by

$$n = \frac{c_0}{c} = \varepsilon^{\frac{1}{2}}$$

(2.4.7)

or, equivalently

$$n^2 = \varepsilon$$

(2.4.8)

Equation (8) is known as Maxwell’s relation and is valid for all insulating, non-magnetic, LIH media provided the frequency of measurement for $n$ and $\varepsilon$ is the same [9].

The form of equation (8) is retained for lossy media by using the complex dielectric constant and a complex refractive index [3]:

$$\left[ n'(\omega) - in''(\omega) \right]^2 = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

(2.4.9)

where $n'$ is the real part of the complex refractive index and the imaginary part $n''$ is a measure of energy loss in the medium. However, as was discussed in section (2.2), dielectric losses are not to be expected for the microwave frequency measurements on the non-polar gases of this work and so the simple form of equation (8) is valid and sufficient.
2.5 Resonance in electrical circuits

Combinations of an inductance $L$ and a capacitance $C$ in series (where the current is common) or in parallel (where the potential difference is common) produce circuits that display the phenomenon of resonance. Figure (2.2(a)) shows a series $LC$ circuit, driven by an harmonic voltage supply with angular frequency $\omega$. The impedances $Z_C = (1 / i\omega C)$ and $Z_L = i\omega L$ are combined in series to give a total impedance of

$$Z_{LC} = i \left( \frac{\omega^2 LC - 1}{\omega C} \right)$$  \hspace{1cm} (2.5.1)

**Figure (2.2) Resonant electrical circuits**

(a) \hspace{1cm} (b)

Ohm’s law, expressed as $I = V / Z$, shows that for a given potential difference $V$, the reciprocal of equation (1), which is equal to the admittance of the circuit, shows the frequency-dependence of the current $I$ and this clearly goes to a maximum for $\omega = \omega_0 = 1/\sqrt{LC}$. The angular frequency $\omega_0$ is the resonance frequency of the series $LC$ circuit, which is the supply or drive angular frequency at which there is maximum current and, therefore, maximum power transfer in the circuit. The impedance of the circuit is purely imaginary, for real $L$ and $C$, and so there is no power dissipation, but merely reversible power transfer, and the resonance frequency is purely real.

The loss-free series $LC$ combination can be made to more closely resemble a practical circuit by the addition of a resistance $R$ in series with the inductance and capacitance, as shown in figure (2.2(b)). This resistance represents the energy losses.
that arise in practical circuits and it will be found that the resonance frequency of the circuit is modified by its presence.

The total impedance of the LCR combination shown in figure (2.2(b)) is

\[
Z_{LCR} = R + i \left( \frac{\omega^2 LC - 1}{\omega C} \right)
\]  

and the reciprocal of this, which is the admittance of the circuit, goes to a maximum when the drive angular frequency is [11]

\[
\omega = \omega_0 \left[ 1 - \left( \frac{R}{2\omega_0 L} \right)^2 \right]^{\frac{1}{2}} + i \left( \frac{R}{2L} \right)
\]  

where \( \omega_0 = 1/\sqrt{LC} \). At the angular frequency given in equation (3), the circuit current is maximized and so it is the resonance angular frequency. The resonance angular frequency is now complex and its real part is clearly shifted from the loss-free value of \( \omega_0 \), due to the presence of the energy losses in the circuit represented by the resistance \( R \).

The variation of circuit current \( I \) with the applied angular frequency \( \omega \) is shown in figure (2.3) where a very small value of \( R \) has been assumed. The small value of \( R \) gives rise to a sharp resonance and the sharpness is described by

\[
Q = \left( \frac{\omega_0}{\Delta\omega} \right)
\]

where \( Q \) is known as the quality factor of the resonance and \( \Delta\omega \) is the difference between the two values of angular frequency for which \( I = (1/\sqrt{2})I_{\text{max}} \). These are the angular frequencies at which the power developed in the circuit is half the maximum power (which occurs at the resonance angular frequency) and so \( (\omega_0 - \Delta\omega/2) \) and \( (\omega_0 + \Delta\omega/2) \) are called the half-power angular frequencies. The \( Q \) of the resonance can be shown to be equal to \( (\omega_0 L/R) \) for small \( R \) (i.e., large \( Q \)) and so equation (3), for the complex resonance angular frequency, can be rewritten as [11]

\[
\omega = \omega_0 \left[ 1 - \left( \frac{1}{2Q} \right)^2 \right]^{\frac{1}{2}} + i \left( \frac{\omega_0}{2Q} \right)
\]  

24
Although a theory of resonant cavities requires the application of a full electromagnetic field analysis, as will be discussed in section (2.6), the central ideas of a complex resonance (angular) frequency, arising from the introduction of energy losses in the system, and a quality factor $Q$, used as a measure of resonance sharpness, remain valid and a very similar equation to equation (5) arises naturally from a consideration of a resonant cavity containing a lossy dielectric [see section (4.9)].

2.6 The limitations of lumped component theory

The analyses of section (2.5) have treated the inductors, capacitors and resistors as discrete or lumped components connected by wires which play no other part in the circuit save that of merely connecting the components. We have been concerned only with the potential differences and currents that may be measured at the terminals of the components, and whilst this approach works well at low frequencies, there are a number of problems at microwave frequencies [4], such as the finite time taken for the transmission of electromagnetic signals, and the leakage of electric and magnetic fields outside the confines of the components, leading to radiation losses. For a
circuit with typical dimensions of a few centimetres, the time delay for signals will be on the order of $10^{-10}$ s, which is comparable to the period of a microwave frequency of a few gigahertz. Therefore, the variations of current and potential difference along a connecting wire will be significant and $I$ and $V$ must be treated as waves. As the wavelength becomes comparable with component dimensions the conducting surfaces of the components become relatively efficient radiating antennae and so need to be completely shielded. This is also true for the connecting wires and so, at microwave frequencies, they are replaced by coaxial cables where the shielding is in-built. The design of capacitors and inductors would be very different if they were intended for operation at microwave frequencies. If a resonant circuit were to resonate at a microwave frequency, the inductance $L$ and capacitance $C$ would have to be extremely small. This would require an inductor coil of perhaps only one loop of wire and a capacitor with very widely separated plates or plates with a tiny surface area. In both cases, radiative losses would be extremely large at microwave frequencies and the accurate analysis of the resulting circuit would be very difficult indeed [4].

These problems are solved by replacing connecting wires with electromagnetic waveguides and resonant circuits by resonant cavities. The problem of time delays is addressed by using a wave theory for the analysis, and the shielding required to stop excessive radiation is inherent in the system. Waveguides and cavity resonators can be described using transmission-line theory originally intended for much lower frequency circuits, and a number of authors take this approach [12, 13]. However, as Waldron [8] points out, such an approach does not bring out the full detail of the variations of electric and magnetic fields in the system and, perhaps more importantly, its application requires that a field treatment be applied, in any case, in order to calculate the equivalent capacitances and inductances required for such a circuit analysis. It is more enlightening, and no more complicated, to analyse the resonant microwave cavities using a full electromagnetic field theory and, as will be seen in chapter 3, the analysis of waveguides and cavity resonators begins with a return to Maxwell’s equations.
Chapter 3  The Theory of Ideal Waveguides and Cavity Resonators

3.1 Introduction

In the brief discussion of electromagnetic waves in section (2.4), no mention was made of the extent of the medium in which waves propagated; it was implicit that the medium was unbounded. If the region in which the electromagnetic fields exist contains two or more different media with boundary surfaces separating them, then solutions to Maxwell’s equations must satisfy the requisite boundary conditions. If a boundary surface has a large extension in at least one dimension, then the energy of an electromagnetic wave will be broadly concentrated close to the surface as a result of satisfying these boundary conditions and the wave will tend to propagate parallel to the surface [8]. The electromagnetic wave is now guided by the surface which is consequently acting as a waveguide.

One of the most common types of waveguide is a cylindrical pipe made of a highly conducting material, and section (3.2) considers the theory of an idealised cylindrical waveguide. It will be found that there are a number of discrete modes of propagation for electromagnetic waves travelling along the waveguide that satisfy Maxwell’s equations within the guide and the requisite boundary conditions at the cylindrical wall. The frequency of excitation for these modes must be above certain mode-dependent ‘cut-off’ frequencies for propagation to occur and, for typical guides with radii of a few centimetres, these frequencies lie in the microwave region of the spectrum.

Closing the ends of a cylindrical waveguide produces a cylindrical cavity resonator and the theory of an idealised case is given in section (3.3). Now the electromagnetic waves reflect from the end plates and standing waves are established within the cavity. The resonance frequencies of the ideal cavity are calculated and again lie in the microwave region for cavities with normal laboratory dimensions of a few centimetres.

The ideal spherical cavity resonator is considered in section (3.4). As with the cylindrical cavity, it will be found that there are a discrete number of resonant microwave frequencies for which standing waves are established.
In all cases, it is found that the characteristic frequencies, whether 'cut-off' or resonant, are proportional to the phase speed of light in the medium that fills the idealised waveguide or resonant cavity. This idea is central to this work and, whilst chapter 4 explains the differences between the resonant behaviour of practical cavities and the ideal ones, many of these differences turn out to be unimportant to a very high degree of accuracy if only relative, rather than absolute, speeds of light are required. The theory of ideal waveguides and resonators is therefore of great importance in this work and is presented in some detail.

The chapter closes with appendix A3.1, which contains many important mathematical relations relevant to waveguide and cavity theory.

### 3.2 The cylindrical waveguide

The ideal cylindrical waveguide is a long, perfectly cylindrical pipe of internal radius \( r = a \). It has a smooth, perfectly conducting wall with no openings and contains a perfectly insulating, non-magnetic, LH medium with dielectric constant \( \varepsilon \).

Cylindrical coordinates \((r, \theta, z)\), which are related to the Cartesian coordinates \((x, y, z)\) by

\[
\begin{align*}
  x &= r \cos \theta \\
  y &= r \sin \theta \\
  z &= z
\end{align*}
\]

are the best choice for the analysis, and in this case the \( \text{div}, \text{curl} \) and \( \text{Laplacian} \) are given by [8]

\[
\nabla \cdot F = \frac{1}{r} \frac{\partial}{\partial r} \left( r F_r \right) + \frac{1}{r} \frac{\partial F_\theta}{\partial \theta} + \frac{\partial F_z}{\partial z}
\]

(3.2.2)

\[
\nabla \times F = \left\{ \frac{1}{r} \frac{\partial F_\theta}{\partial z} - \frac{\partial F_z}{\partial \theta} \right\} \hat{r} + \left\{ \frac{\partial F_z}{\partial r} - \frac{\partial F_r}{\partial z} \right\} \hat{\theta} + \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r F_\theta \right) - \frac{\partial F_r}{\partial \theta} \right\} \hat{z}
\]

(3.2.3)

\[
\nabla^2 F = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial F}{\partial r} \right) + \frac{1}{r^2} \left( \frac{\partial^2 F}{\partial \theta^2} \right) + \frac{\partial^2 F}{\partial z^2}
\]

(3.2.4)

where \( F = \left( F_r \hat{r} + F_\theta \hat{\theta} + F_z \hat{z} \right) \) is any vector, expressed in the cylindrical coordinate system, where \( \hat{r}, \hat{\theta} \) and \( \hat{z} \) are the unit vectors in the direction of increasing \( r, \theta \) and \( z \), respectively. The coordinates are chosen such that the longitudinal axis of the waveguide is coincident with the \( z \) axis.

Monochromatic waves with time-dependence \( \exp(i \omega t) \) are to be considered and so equations (2.3.8) to (2.3.11) are the appropriate forms of Maxwell's equations.
Equations (2.3.9) and (2.3.11) can be expressed in cylindrical coordinates using the curl equation (3), and the \( \hat{r} \) and \( \hat{\theta} \) components separated. The four resulting partial differential equations can be substituted one into another to produce the four new equations [8]

\[
\left( \frac{\partial^2}{\partial z^2} + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) E_z = \left( \frac{\partial^2 E_z}{\partial z^2} \right) - \frac{i\omega \mu_0}{r} \left( \frac{\partial H_z}{\partial \theta} \right) \tag{3.2.5}
\]

\[
\left( \frac{\partial^2}{\partial z^2} + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) E_\theta = \frac{1}{r} \left( \frac{\partial E_z}{\partial \theta} \right) + i\omega \mu_0 \left( \frac{\partial H_z}{\partial r} \right) \tag{3.2.6}
\]

\[
\left( \frac{\partial^2}{\partial z^2} + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) H_r = \frac{i\omega \varepsilon_0}{r} \left( \frac{\partial E_z}{\partial r} \right) + \left( \frac{\partial^3 H_z}{\partial z \partial \theta} \right) \tag{3.2.7}
\]

\[
\left( \frac{\partial^2}{\partial z^2} + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) H_\theta = \frac{1}{r} \left( \frac{\partial^2 H_z}{\partial z \partial \theta} \right) - i\omega \varepsilon_0 \left( \frac{\partial E_z}{\partial r} \right) \tag{3.2.8}
\]

These give the transverse field components in terms of the longitudinal components alone and so calculation of \( E_z \) and \( H_z \) will provide all the other field components.

Calculation of the longitudinal fields begins with the appropriate forms of the wave equations for \( E \) and \( H \) fields which are given by equations (2.4.2) and (2.4.3). Using the Laplacian equation (4), the wave equation (2.4.2) becomes [14,15]

\[
\hat{r} \left( \nabla^2 E_r - \frac{2}{r^2} \frac{\partial E_r}{\partial r} - \frac{E_r}{r^2} \right) + \hat{\theta} \left( \nabla^2 E_\theta + \frac{2}{r^2} \frac{\partial E_r}{\partial \theta} - \frac{E_\theta}{r^2} \right)
\]

\[
+ \hat{z} \left( \nabla^2 E_z \right) + \omega^2 \varepsilon \varepsilon_0 \mu_0 \left( \hat{r} E_r + \hat{\theta} E_\theta + \hat{z} E_z \right) = 0
\]

and a similar equation for \( H \) can be derived from equation (2.4.3). The \( \hat{z} \) components of the two equations are separated to obtain

\[
\left( \nabla^2 + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) E_z = 0 \tag{3.2.10}
\]

for the \( E \) field and

\[
\left( \nabla^2 + \omega^2 \varepsilon \varepsilon_0 \mu_0 \right) H_z = 0 \tag{3.2.11}
\]

for the \( H \) field. Equations (10) and (11) are recognised as three-dimensional scalar Helmholtz equations and can be solved by separating the variables to obtain three ordinary second-order differential equations for which the solutions are well known.

For the longitudinal electric field, a product solution \( E_z = R(r)\Theta(\theta)Z(z) \) is proposed and substituted into equation (10). With the Laplacian expressed in
cylindrical coordinates using equation (4), the resulting expression separates into the three ordinary differential equations [8]

\[
\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + \left( k^2 - \frac{p^2}{r^2} \right) R = 0
\]

\[
\frac{d^2 \Theta}{d\theta^2} + p^2 \Theta = 0
\]

\[
\frac{d^2 Z}{dz^2} + \beta^2 Z = 0
\]

in which \(-p^2\) is the separation constant for \( \Theta \), \(-\beta^2\) is the separation constant for \( Z \) and \( k^2 = \left( \omega^2 \varepsilon \varepsilon_0 \mu_0 - \beta^2 \right) \). General solutions for equations (13) and (14) have the similar forms

\[
\Theta = Ae^{ip\theta} + Be^{-ip\theta}
\]

\[
Z = Fe^{i\beta z} + Ge^{-i\beta z}
\]

where \(A\), \(B\), \(F\) and \(G\) are constants. The independent variable \(r\) in equation (12) can be replaced by a new independent variable \((kr)\) to obtain

\[
\frac{d^2 R}{d(kr)^2} + \frac{1}{(kr)} \frac{dR}{d(kr)} + \frac{1}{(kr)^2} \left( 1 - \frac{p^2}{(kr)^2} \right) R = 0
\]

which is recognised as Bessel’s equation of order \( p \). The solution is [8]

\[
R = CJ_p(kr) + D Y_p(kr)
\]

where \( J_p \) is the cylindrical Bessel function of the first kind of order \( p \), \( Y_p \) is the cylindrical Bessel function of the second kind of order \( p \) (written \( N_p \) in some texts), and \( C \) and \( D \) are constants. Graphs of some low-order Bessel functions are shown in figure (3.1). The same procedure can be used to find a general solution for the longitudinal magnetic field. Therefore the general solution of the Helmholtz equation for \( E_z \) is

\[
E_z = R(r)\Theta(\theta)Z(z)
\]

\[
= \left\{ CJ_p(kr) + D Y_p(kr) \right\} \cdot \left\{ Ae^{ip\theta} + Be^{-ip\theta} \right\} \cdot \left\{ Fe^{i\beta z} + Ge^{-i\beta z} \right\}
\]

with a similar solution for the \( H_z \) equation:

\[
H_z = \left\{ C'J_p(kr) + D' Y_p(kr) \right\} \cdot \left\{ A'e^{ip\theta} + B'e^{-ip\theta} \right\} \cdot \left\{ F'e^{i\beta z} + G'e^{-i\beta z} \right\}
\]
where $A', B', C', D', F'$ and $G'$ are different constants to $A, B, C, D, F$ and $G$. Equations (19) and (20) give the spatial variation of $E_Z$ and $H_Z$ and it should be noted that the time variation $\exp(i\omega t)$ is implicit in both cases.

If the field components $E_Z$ and $H_Z$, from equations (19) and (20), are substituted into the set of partial differential equations (5) to (8) then all the field components can be obtained. No restrictions or boundary conditions have yet been imposed on these solutions and so they represent the field variations for unbounded, or free, electromagnetic waves. The generality of equations (19) and (20), in conjunction with equations (5) to (8), is such that they can be used to calculate the electromagnetic fields in any insulating, non-magnetic, LIH medium where cylindrical coordinates are appropriate. In particular, they are used together with the appropriate boundary conditions to calculate the fields in the ideal cylindrical and coaxial waveguides and the corresponding resonant cavities [8, 16, 17].

For the cylindrical waveguide, if the direction of propagation is defined to be in the positive $z$ direction then $F$ and $F'$ in equations (19) and (20) are zero. The $E$ and $H$ fields must, of course, be finite everywhere inside the waveguide and so $\ell_p(kr)$ which has a singularity at $r = 0$ cannot contribute to the solutions. (Note that the coaxial waveguide is an example where $r = 0$ does not lie within the region in which
the waves propagate, due to the presence of the central conductor, and so would require the $Y_p(kr)$ as part of the solutions [8, 17]. Therefore $D$ and $D'$ in equations (19) and (20) are also zero. The acceptable longitudinal fields are therefore

$$E_z = NJ_p(kr)\{Ae^{ip\theta} + Be^{-ip\theta}\}e^{-ipz}$$  \hspace{1cm} (3.2.21)

$$H_z = N'J_p(kr)\{A'e^{ip\theta} + B'e^{-ip\theta}\}e^{-ipz}$$  \hspace{1cm} (3.2.22)

where the new constants $N$ and $N'$ are related to those of equations (19) and (20) by $N = CF$ and $N' = C'F'$.

No electric potential difference can exist between two points in a perfect conductor and so there can be no electric field within the wall of an ideal waveguide. The well-known boundary condition, that the tangential component of an electric field is continuous across any boundary surface, therefore requires that the tangential electric field within the waveguide vanishes at the perfectly conducting wall $r = a$ [16]. The corresponding boundary condition for the magnetic field is readily seen from Maxwell’s equation (2.3.9). If the tangential component of electric field has vanished at the boundary wall, then equation (2.3.9) implies that the normal component of magnetic field must also vanish there. That is, if $E_{\tan} = \hat{r} \times E = 0$ at the boundary wall $r = a$, then $H_{\text{norm}} = \hat{r} \cdot H \sim \hat{r} \cdot (\nabla \times E) = -\nabla \cdot (\hat{r} \times E) = 0$ at the boundary wall $r = a$. This requires that $E_z, E_\theta$ and $(\partial H_z/\partial r)$ [by equations (6) and (7)] must be zero at $r = a$, for all $\theta$ and $z$, and thus the equations

$$J_p(ka) = 0$$  \hspace{1cm} (3.2.23)

and

$$\frac{d}{d(ka)}J_p(ka) = J'_p(ka) = 0$$  \hspace{1cm} (3.2.24)

must be satisfied simultaneously [8, 17]. The prime in equation (24) indicates differentiation with respect to the argument [in this case $(ka)$] and this shorthand notation, for the differentials of the Bessel functions, will be used from now on, without further comment. The zeroes of $J_p(ka)$ and the extrema of $J'_p(ka)$ do not coincide [see figure (3.1)] and so the only way both boundary conditions can be satisfied at the same time is if either $E_z = 0$ or $H_z = 0$. There are therefore two families of modes of propagation in the ideal cylindrical waveguide. Those for
which \((E_z = 0, H_z \neq 0)\) have zero longitudinal component of electric field and so are called transverse electric (TE) modes of propagation (some authors use the term magnetic or H type modes). Modes for which \((E_z \neq 0, H_z = 0)\) have zero longitudinal component of magnetic field and so they are called transverse magnetic (TM) modes of propagation (some authors use the term electric or E type modes). The case of \((E_z = 0, H_z = 0)\) is trivial since all field components vanish and so transverse electric and magnetic (TEM) modes do not propagate in the ideal cylindrical waveguide [16, 17].

Since there are no modes with both \(E_z\) and \(H_z\) non-zero, we are free to choose values for the arbitrary constants \(A, B\) in equation (21), and \(A', B'\) in equation (22), independently of each other. If we put \(A = A' = (1 - i)/2\) and \(B = B' = (1 + i)/2\), then the longitudinal fields become

\[
E_z = NJ_p(kr)[\cos p\theta + \sin p\theta]e^{-\beta z} \quad (3.2.25)
\]

\[
H_z = N'J_p(kr)[\cos p\theta + \sin p\theta]e^{-\beta z} \quad (3.2.26)
\]

where \(N\) and \(N'\) are normalisation constants such that for TM modes \((N \neq 0, N' = 0)\), whilst for TE modes \((N = 0, N' \neq 0)\). The fields must be single-valued within the waveguide and so the components must have the same values at \(\theta\) as at \((\theta + 2\pi)\) [8]. This requires that the mode index \(p\) is limited to the real integral values \(p = 0, \pm 1, \pm 2, \ldots\).

If the axial coordinate \(z\) in equation (25) or (26) is increased by a single wavelength \(\lambda\), then the phase of the corresponding wave will have increased by one full cycle of \(2\pi\) radians, and so we must have \(\beta = 2\pi/\lambda\). \(\beta\) is therefore called the phase constant of the mode.

There are an infinite number of solutions \((ka)\) of the characteristic equations (23) and (24). The \(q\)-th solution of the characteristic equation for TM modes, equation (23), is \((ka) = \chi_{pq}\), and these 'eigenvalues', \(\chi_{pq}\), are given, for selected values of \(p\) and \(q\), in table (3.1). The modes are labelled TM \(pq\) and have phase constants [8]

\[
\beta_{pq} = \frac{2\pi}{\lambda_{pq}} \sqrt{\omega^2 \varepsilon \varepsilon_0 \mu_0 - \left(\frac{\chi_{pq}}{c}\right)^2} \quad (3.2.27)
\]
where $\lambda_{pq}$ is the wavelength in the guide and is larger than unbounded waves of the same frequency would have in the medium. The phase speed of the guided waves is therefore higher than that of unbounded waves. The $q$-th solution of the characteristic equation for TE modes, equation (24), is $(ka) = \chi_{pq}'$, where the prime is to distinguish these solutions from those of the TM modes, and these eigenvalues $\chi_{pq}'$ are given, for selected values of $p$ and $q$, in table (3.2). The modes are labelled TEP$q$, and the phase constants are given by equation (27) if $\chi_{pq}$ is replaced by $\chi_{pq}'$. For both TM and TE modes, the mode indices $p$ and $q$ are restricted to the values $p = 0, \pm 1, \pm 2, \ldots$ and $q = 1, 2, 3, \ldots$ [8]. The index $q$ may not be zero since the zeroth order solutions of equations (23) and (24) are either non-existent or are equal to zero. If the eigenvalue is zero, then $k$ must be zero and this makes all field components vanish. Therefore modes with $q = 0$ do not propagate in the ideal cylindrical waveguide. These modes might exist in practical waveguides, although with very small amplitudes, and so it is, perhaps, more correct to say that a number of modes with $q = 0$ do exist in the ideal waveguide, but they do so with zero amplitude [17].

**Table (3.1)** Selected cylinder TM mode eigenvalues $\chi_{pq}$ [8]

<table>
<thead>
<tr>
<th>$\chi_{pq}$</th>
<th>$q = 1$</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p = 0$</td>
<td>2.40483</td>
<td>5.52008</td>
<td>8.65373</td>
<td>11.79153</td>
</tr>
<tr>
<td>1</td>
<td>3.83171</td>
<td>7.01559</td>
<td>10.17347</td>
<td>13.32369</td>
</tr>
<tr>
<td>2</td>
<td>5.13562</td>
<td>8.41724</td>
<td>11.61984</td>
<td>14.79595</td>
</tr>
</tbody>
</table>

**Table (3.2)** Selected cylinder TE mode eigenvalues $\chi_{pq}'$ [8]

<table>
<thead>
<tr>
<th>$\chi_{pq}'$</th>
<th>$q = 1$</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p = 0$</td>
<td>3.83171</td>
<td>7.01559</td>
<td>10.17347</td>
<td>13.32369</td>
</tr>
<tr>
<td>1</td>
<td>1.84118</td>
<td>5.33144</td>
<td>8.53632</td>
<td>11.70600</td>
</tr>
<tr>
<td>2</td>
<td>3.05424</td>
<td>6.70613</td>
<td>9.96947</td>
<td>13.17037</td>
</tr>
</tbody>
</table>
Having calculated the longitudinal fields $E_z$ and $H_z$ it is a simple matter to obtain the transverse components $E_r$, $E_\theta$, $H_r$ and $H_\theta$ by substituting $E_z$ and $H_z$ into equations (5) to (8) where $\partial/\partial z$ can be replaced by $-i\beta$, since we have $z$-dependence $\exp(-i\beta z)$, and recalling that for TM modes $H_z = 0$ whilst for TE modes $E_z = 0$. The full sets of field components for TM and TE modes are given below:

**TMpq modes**

\[
E_z = NJ_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.28)

\[
E_r = \frac{-i\beta}{k} NJ'_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.29)

\[
E_\theta = \frac{i\beta p}{k^2 r} NJ_p(kr)[\sin p\theta - \cos p\theta] 
\]

(3.2.30)

\[
H_z = 0 
\]

(3.2.31)

\[
H_r = \frac{-i\omega \varepsilon_0 p}{k^2 r} NJ_p(kr)[\sin p\theta - \cos p\theta] 
\]

(3.2.32)

\[
H_\theta = \frac{-i\omega \varepsilon_0}{k} NJ'_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.33)

**TEpq modes**

\[
E_z = 0 
\]

(3.2.34)

\[
E_r = \frac{i\omega \mu_0 p}{k^2 r} N'J'_p(kr)[\sin p\theta - \cos p\theta] 
\]

(3.2.35)

\[
E_\theta = \frac{i\omega \mu_0}{k} N'J'_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.36)

\[
H_z = N'J'_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.37)

\[
H_r = \frac{-i\beta}{k} N'J'_p(kr)[\cos p\theta + \sin p\theta] 
\]

(3.2.38)

\[
H_\theta = \frac{i\beta p}{k^2 r} N'J'_p(kr)[\sin p\theta - \cos p\theta] 
\]

(3.2.39)

In equations (28) to (39), the factors $\exp(-i\beta z)$ and $\exp(i\omega t)$ are implicit in all cases.

The mode indices $p$ and $q$ have the physical significance that $p$ is the number of full wave variations of electric and magnetic field around a circumferential path and also the number of radial nodal planes within the guide, and that $q$ is the number of
cylindrical nodal surfaces concentric with the \( z \) axis [13]. Field patterns for some modes of propagation within the ideal cylindrical waveguide are presented in figure (3.2).

The average power flow along the wave guide in a particular mode is given by

\[
P = \int \int_S \mathbf{E} \times \mathbf{H} \cdot d\mathbf{S}
\]

(3.2.40)

where the integration is taken over the cross-section of the waveguide. The quantity \( \mathbf{E} \times \mathbf{H} \) is the Poynting vector \( \mathbf{P} \), which represents the instantaneous power flow per unit area. The power flow for the modes of the ideal cylindrical waveguide is calculated in detail in the literature [8] and will not be required here. Equation (40) is used to demonstrate the orthogonality of the modes by showing that the integral over the guide cross-section is zero if \( \mathbf{E} \) is taken from one mode and \( \mathbf{H} \) from another. Therefore power is only transmitted in the normal modes and not by waves whose fields belong to different modes [8].

Using equations (27), (2.4.5) and the relation \( \omega = 2\pi f \), it can be shown that

\[
\beta_{pq} = \frac{2\pi}{c} \sqrt{f^2 - \left( \frac{\chi_{pq} c}{2\pi a} \right)^2}
\]

(3.2.41)

where \( c \) is the speed of unbounded waves in the medium. It can be seen from equation (41) that if \( f \) is less than \( \left( \frac{\chi_{pq} c}{2\pi a} \right) \), then the phase constant \( \beta \) will be purely imaginary and equal to

\[
-\left( \frac{2\pi}{c} \right) \sqrt{\left( \frac{\chi_{pq} c}{2\pi a} \right)^2 - f^2},
\]

where the negative root of equation (41) has been taken because we are considering propagation in the positive \( z \) direction. In this case, it can be seen from equations (25) and (26) that the amplitude of the waves will decay exponentially with increasing \( z \) and there will not be significant power flow along the waveguide. The critical frequency limit, \( \left( \frac{\chi_{pq} c}{2\pi a} \right) \), below which there is no significant propagation in the mode characterised by \( p \) and \( q \) is called its cut-off frequency \( f_{o\alpha} \) and is inversely proportional to the radius of the waveguide for a given mode. The dimensions of practical waveguides are often chosen to eliminate the possibility of propagation of unwanted higher modes [18-20].
Figure (3.2) Cylindrical waveguide field patterns [8, 13]

- **TM01**
  - Electric field
  - Magnetic field

- **TM11**

- **TE01**

- **TE11**
3.3 The cylindrical cavity

The ideal cylindrical cavity is derived from the ideal cylindrical waveguide by simply closing the ends, at \( z = 0 \) and \( z = L \), with perfectly conducting planes perpendicular to the \( z \) axis. The cavity therefore has an internal radius \( a \), as for the waveguide, and an internal length \( L \), and contains an insulating, non-magnetic, LIH medium as before. The end plates will modify the \( z \)-dependence of the longitudinal fields but the radial and angular dependence will be exactly the same as that of the waveguide. It is therefore immediately apparent that TM and TE modes will be supported by the cavity, just as was found for the waveguide, but that TEM modes will not \cite{8, 16, 17}.

Standing waves are produced in the cavity by the interference of waves propagating in the \(+z\) and \(-z\) directions. Therefore the solutions for these guided waves are superposed and made to obey the additional boundary conditions at \( z = 0 \) and \( z = L \) to find the fields in the cavity. The required longitudinal fields are therefore

\[
E_z = NJ_\rho(kr)[\cos p\theta + \sin p\theta][Fe^{i\beta z} + Ge^{-i\beta z}] \tag{3.3.1}
\]

\[
H_z = NJ_\rho(kr)[\cos p\theta + \sin p\theta][F'e^{i\beta z} + G'e^{-i\beta z}] \tag{3.3.2}
\]

where the factors \( e^{i\beta z} \) represent wave motion in the \(-z\) direction and the factors \( e^{-i\beta z} \) represent wave motion in the \(+z\) direction.

The boundary conditions of zero tangential electric field and zero normal magnetic field must be obeyed at the perfectly conducting end plates and so we must have \( E_r = E_\theta = 0 \) and \( H_z = 0 \) at \( z = 0 \) and \( z = L \). Substituting \( z = 0 \) into equation (2) for \( H_z \) and equating the result to zero, for all \( r \) and \( \theta \), shows that \( G' = -F' \) and so

\[
H_z = BJ_\rho(kr)[\cos p\theta + \sin p\theta]\sin \beta z \tag{3.3.3}
\]

where the constant \( B = (2iF'N') \). Substituting \( z = L \) into equation (3) and equating to zero, for all \( r \) and \( \theta \), shows that \( \sin \beta L = 0 \) and so

\[
\beta = \left(\frac{s\pi}{L}\right); \quad s = 0, 1, 2, \ldots \tag{3.3.4}
\]

Therefore the phase constant is restricted to integral multiples of \( (\pi/L) \) due to the presence of the perfectly conducting end plates \cite{8}. An expression for \( E_r \) is obtained by substituting for \( E_z \) and \( H_z \), from equations (1) and (3), respectively, into equation
(3.2.5) for \( E_r \). This is then equated to zero at \( z = 0 \), for all \( r \) and \( \theta \), to show that \( F = G \) in equation (1). Therefore

\[
E_z = AJ_p(kr)(\cos p\theta + \sin p\theta)\cos\left(\frac{s\pi z}{L}\right) \tag{3.3.5}
\]

where the constant \( A = 2FN \) and equation (4), for \( \beta \), has been used.

The restriction of \( \beta \) to integral multiples of \( (\pi/L) \) for standing waves in the cavity means that there are a number of natural frequencies of the cavity satisfying

\[
f_{pq} = \frac{\omega_{pq}}{2\pi} = c\sqrt{\left(\frac{\chi_{pq}}{2\pi a}\right)^2 + \left(\frac{s}{2L}\right)^2} \tag{3.3.6}
\]

where \( c = \sqrt{1/\varepsilon\mu_0} \) is the phase speed in the medium filling the cavity and \( f_{pq} \) is a natural frequency. Equation (6) is obtained from equations (4) and (3.2.41), and has been written for TM modes. The equation for TE modes is obtained by replacing \( \chi_{pq} \) by \( \chi'_{pq} \). At a natural frequency \( f_{pq} \): there is constructive interference of positive and negative going waves, reflecting back and forth between the end plates, and standing waves are generated within the cavity; the cavity is then at resonance.

If the wave frequency does not satisfy equation (6) then there is completely destructive interference of the positive and negative going waves and the electromagnetic fields vanish [19].

The transverse field components are obtained by substituting the longitudinal field equations (3) and (5) into equations (3.2.5) to (3.2.8), where

\[
k^2 = \left[\left(\frac{\partial^2}{\partial z^2}\right) + \omega^2\varepsilon\mu_0\right] \tag{3.3.7}
\]

\[
\begin{align*}
H_z &= 0 \quad \text{for TM modes} \\
E_z &= 0 \quad \text{for TE modes}
\end{align*} \tag{3.3.8}
\]

The full sets of field components are given below:

**TMpq\text{ modes}**

\[
E_z = AJ_p(kr)(\cos p\theta + \sin p\theta)\cos\left(\frac{s\pi z}{L}\right) \tag{3.3.9}
\]

\[
E_r = -\frac{s\pi}{kL} AJ'_p(kr)(\cos p\theta + \sin p\theta)\sin\left(\frac{s\pi z}{L}\right) \tag{3.3.10}
\]
where \( k^2 = \left( \frac{\chi_{pq}}{a} \right)^2 \), and the mode indices \( p, q \) and \( s \) are restricted to the values
\( p = 0, \pm 1, \pm 2, \ldots ; q = 1, 2, 3, \ldots ; s = 0, 1, 2, \ldots \) [8].

**TEpq{s} modes**

\[
E_z = 0 \tag{3.3.15}
\]

\[
E_r = \frac{i \omega \mu_0}{k^2 r} BJ_p(kr) \left[ \sin p\theta - \cos p\theta \right] \sin \left( \frac{s\pi z}{L} \right) \tag{3.3.16}
\]

\[
E_\theta = \frac{i \omega \mu_0}{k} BJ'_p(kr) \left[ \cos p\theta + \sin p\theta \right] \sin \left( \frac{s\pi z}{L} \right) \tag{3.3.17}
\]

\[
H_z = BJ_p(kr) \left[ \cos p\theta + \sin p\theta \right] \sin \left( \frac{s\pi z}{L} \right) \tag{3.3.18}
\]

\[
H_r = \frac{s\pi}{kL} BJ'_p(kr) \left[ \cos p\theta + \sin p\theta \right] \cos \left( \frac{s\pi z}{L} \right) \tag{3.3.19}
\]

\[
H_\theta = -\frac{p\pi}{k^2 r L} BJ_p(kr) \left[ \sin p\theta - \cos p\theta \right] \cos \left( \frac{s\pi z}{L} \right) \tag{3.3.20}
\]

where \( k^2 = \left( \frac{\chi_{pq}}{a} \right)^2 \), and the mode indices \( p, q \) and \( s \) are restricted to the values
\( p = 0, \pm 1, \pm 2, \ldots ; q = 1, 2, 3, \ldots ; s = 1, 2, 3, \ldots \) [8]. The index \( s \) cannot be zero for TE modes since this value makes all the field components vanish.

The cylindrical Bessel functions of the first kind of integer order \( p \) have the property [21, 22]

\[
J_{-p}(x) = (-1)^p J_p(x) \tag{3.3.21}
\]

and therefore the zeros and extrema of \( J_p(ka) \) are the same as those of \( J_{-p}(ka) \). This important fact means that, provided \( p \neq 0 \), mode TMpq{s} will have the same resonance frequency as TM(-p)qs but will have different electromagnetic fields due to the angular function \( \left[ \cos p\theta + \sin p\theta \right] \). We say that mode TM pq{s} is doubly
degenerate in the ideal cylindrical cavity. This is also clearly the case for TE \( pqs \) modes with \( p \neq 0 \) and so all modes in the ideal cylinder, except those for which \( p = 0 \), are doubly degenerate. Modes TM0qs and TE0qs, where \( p = 0 \), are non-degenerate [22].

The indices \( p \) and \( q \) have the same physical significance in the cylindrical cavity as in the waveguide. The mode index \( s \) is equal to the number of half-wave variations of field along the axis of the cavity. Field patterns for some of the resonant modes are shown in figure (3.3).

The total electromagnetic energy \( W \) stored in an ideal cavity at resonance is constant and is given by [8]

\[
W = \frac{1}{2} \iint \left( \varepsilon \varepsilon_0 |E|^2 + \mu_0 |H|^2 \right) dV
\]  
(3.3.22)

where \( \frac{1}{2} \iint \varepsilon \varepsilon_0 |E|^2 dV \) is the electric energy stored, \( \frac{1}{2} \iint \mu_0 |H|^2 dV \) is the magnetic energy stored, and the integration is taken over the cavity volume \( V_0 \). If the cavity contains a loss-free medium, the time-averaged electric and magnetic energies are equal [11, 19] and we can write

\[
\frac{1}{2} \iint \varepsilon \varepsilon_0 (|E|^2/2) dV = \frac{1}{2} \iint \mu_0 (|H|^2/2) dV
\]  
(3.3.23)

where the r.m.s. fields, \( (E/\sqrt{2}) \) and \( (H/\sqrt{2}) \), have been used to ensure that the correct average energies are calculated. Equation (23) shows that

\[
\frac{1}{2} \iint \varepsilon \varepsilon_0 |E|^2 dV = \frac{1}{2} \iint \mu_0 |H|^2 dV
\]  
(3.3.24)

and so the total electromagnetic energy \( W \) is also given by

\[
W = \iint \varepsilon \varepsilon_0 |E|^2 dV
\]  
(3.3.25)

and

\[
W = \iint \mu_0 |H|^2 dV
\]  
(3.3.26)

The total energy \( W \) can be calculated using equation (22), (25), or (26), whichever is the most convenient to complete the calculation at hand.

For the cylindrical cavity, \( V_0 = \pi a^2 L \) and \( dV = r dr d\theta dz \), where \( 0 \leq r/a \leq 1 \), \( 0 \leq \theta < 2\pi \), and \( 0 \leq z/L \leq 1 \).
Figure (3.3) Cylindrical cavity field patterns [8, 18, 19]

- Electric field
- Magnetic field
TM pq modes

Equation (26) is the simplest to use for this calculation and the required $H$ field components are given in equations (12) to (14). Substituting these into equation (26), and collecting terms, gives

$$W_{TMpq} = \frac{\omega^2 (\varepsilon \varepsilon_0) \mu_0}{k^2} A^2 \int_{r=0}^{r=p} \int_{\theta=0}^{\theta=\pi} \int_{z=0}^{z=L} \left[ \frac{p^2}{k^2 r^2} J_p^2(kr) + J_p^2(kr) \right]$$

$$\cdot \left[ \sin p \theta + \cos p \theta \right]^2 \cos^2 \left( \frac{s \pi z}{L} \right) r dr d\theta dz$$

where we have used equation (A3.1.31) in order to simplify equation (27). The integral over $r$ is given by equation (A3.1.18), the integral over $\theta$ is given by equation (A3.1.31), and the integral over $z$ is given by equation (A3.1.27). Using these results, equation (27) becomes

$$W_{TMpq} = \frac{1}{2} \varepsilon \varepsilon_0 A^2 V_0 J_p^2 \left( \chi_{pq} \right) \left( 1 + \frac{s^2 \pi^2}{k^2 L^2} \right)$$

where this result is to be multiplied by 2 if $s = 0$. We have used $(ka) = \chi_{pq}$, the Tmpq mode eigenvalue, the relation $k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0 - \left( s \pi / L \right)^2$, and the characteristic equation for TM modes, $J_p(ka) = 0$, to simplify equation (28).

TE pq modes

Equation (25) is the easiest to use in this case, and the required $E$ field components can be found in equations (15) to (17). Substituting these into equation (25) gives

$$W_{TEpq} = \frac{\omega^2 (\varepsilon \varepsilon_0 \mu_0)^2}{k^2} B^2 \int_{r=0}^{r=p} \int_{\theta=0}^{\theta=\pi} \int_{z=0}^{z=L} \left[ \frac{p^2}{k^2 r^2} J_p^2(kr) + J_p^2(kr) \right]$$

$$\cdot \left[ \sin p \theta + \cos p \theta \right]^2 \sin^2 \left( \frac{s \pi z}{L} \right) r dr d\theta dz$$

where we have used equation (A3.1.31) to simplify equation (29). The integral over $r$ is given by equation (A3.1.18), the integral over $\theta$ is given by equation (A3.1.31), and the integral over $z$ is given by equation (A3.1.27). Using these results, equation (29) becomes
\[ W_{\text{TEpq}} = \frac{1}{2} \mu_0 B^2 V_0 \left( 1 - \frac{p^2}{\chi_{pq}^2} \right) \int_0^{\infty} \left( 1 + \frac{s^2 \pi^2}{k^2 L^2} \right) \right) \]

where we have used \( (ka) = \chi_{pq}' \), the TEpq mode eigenvalue, the relation \( k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0 - (s \pi / L)^2 \), and the characteristic equation for TE modes, \( J_p'(ka) = 0 \), to simplify equation (30). The mode index \( s \) cannot be zero for TE modes.

Equations (28) and (30) can be used to calculate the normalisation constants \( A \) and \( B \) for some given level of energy in the cavity, and will also be employed for the treatment of cavity perturbations in chapter 4.

### 3.4 The spherical cavity

The ideal spherical cavity is a perfectly spherical cavity of radius \( r = a \) bounded by a perfectly conducting wall without openings. The cavity contains a perfectly insulating, non-magnetic, LH medium with dielectric constant \( \varepsilon \).

Spherical coordinates \((r, \theta, \phi)\), which are related to the Cartesian coordinates \((x, y, z)\) by

\[ x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta \]

are the most suitable for the analysis and in this case the \( \nabla \cdot F \), \( \nabla \times F \) and \( \nabla^2 F \) are given by [8]

\[ \nabla \cdot F = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 F_r \right) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \left( F_\theta \sin \theta \right) + \frac{1}{r \sin \theta} \frac{\partial F_\phi}{\partial \phi} \]

\[ \nabla \times F = \frac{1}{r \sin \theta} \left\{ \frac{\partial}{\partial \theta} \left( F_\phi \sin \theta \right) - \frac{\partial F_\theta}{\partial \phi} \right\} \hat{r} + \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left( r F_\phi \right) - \frac{\partial F_r}{\partial \phi} \right\} \hat{\theta} + \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left( r F_\theta \right) - \frac{\partial F_r}{\partial \theta} \right\} \hat{\phi} \]

\[ \nabla^2 F = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial F}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 F}{\partial \phi^2} \]

where \( F = (F_r \hat{r} + F_\theta \hat{\theta} + F_\phi \hat{\phi}) \) is any vector, expressed in spherical coordinates, where \( \hat{r}, \hat{\theta} \) and \( \hat{\phi} \) are the unit vectors in the direction of increasing \( r, \theta \) and \( \phi \), respectively.

It was seen in sections (3.2) and (3.3) that, in the case of the cylindrical waveguide and cavity, the wave equations for the longitudinal components of electric
and magnetic field could be separated from the vector wave equations because there exists an axis (the longitudinal, or $z$, axis) perpendicular to which the cross-section is uniform along its entire length. No such axis can be identified for the spherical cavity and an alternative approach has to be taken [8, 14, 15].

Using the vector identities

\[ \nabla \cdot (\nabla \times \mathbf{F}) = 0 \]
\[ \nabla \times \nabla \times \mathbf{F} = \nabla (\nabla \cdot \mathbf{F}) - \nabla^2 \mathbf{F} \]

where $\mathbf{F}$ is any vector, it is a simple matter to show that, if $\psi$ is a solution of the scalar Helmholtz equation

\[ (\nabla^2 + k^2)\psi = 0 \]

where $\nabla^2$ is the Laplacian for any coordinate system, then the corresponding vector Helmholtz equation

\[ (\nabla^2 + k^2)\mathbf{C} = 0 \]

where $\mathbf{C}$ is a vector field, is satisfied by the three independent solutions [14, 15]

\[ \mathbf{L} = \nabla \psi \]
\[ \mathbf{M} = \nabla \times a\psi \]
\[ \mathbf{N} = \frac{1}{k} \nabla \times \mathbf{M} = \frac{1}{k} \nabla \times \nabla \times a\psi \]

where $a$ is a constant vector. Using the same identities, the solutions $\mathbf{L}$, $\mathbf{M}$ and $\mathbf{N}$ can also be demonstrated to have the following properties [14, 15]

\[ \nabla \cdot \mathbf{L} = \nabla^2 \psi = -k^2 \psi \quad \nabla \cdot \mathbf{M} = 0 \quad \nabla \cdot \mathbf{N} = 0 \]
\[ \nabla \times \mathbf{L} = 0 \quad \mathbf{L} \cdot \mathbf{M} = 0 \]
\[ \mathbf{M} = \frac{1}{k} \nabla \times \mathbf{N} \]

The wave equations for $\mathbf{E}$ and $\mathbf{H}$ fields given in equations (2.4.2) and (2.4.3) are recognised as vector Helmholtz equations, of the form of equation (8). That is, the equations to be solved are

\[ (\nabla^2 + k^2)\mathbf{E} = 0 \]
\[ (\nabla^2 + k^2)\mathbf{H} = 0 \]

where the Laplacian is given by equation (4) and $k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0$. Reference to Maxwell's equations (2.3.8) to (2.3.11) shows that the vector solutions $\mathbf{M}$ and $\mathbf{N}$
have similar vector properties to the $E$ and $H$ fields. That is, $\nabla \cdot H = \nabla \cdot E = 0$ and $\nabla \cdot M = \nabla \cdot N = 0$, and that $E$ is proportional to $(\nabla \times H)$ and $H$ is proportional to $(\nabla \times E)$, just as $M$ is proportional to $(\nabla \times N)$ and $N$ is proportional to $(\nabla \times M)$. Therefore, the electric field in any given region may be represented as a superposition of fields of the form

$$E_j = A(a_j M_j + b_j N_j)$$

and the magnetic field as a superposition of fields of the form

$$H_j = \frac{i}{\omega \mu_0} \nabla \times E_j = \frac{ikA}{\omega \mu_0} (a_j N_j + b_j M_j)$$

where $A$ is a scalar constant and $a_j$ and $b_j$ are coefficients that describe the contribution to the electric and magnetic field from the vectors $M_j$ and $N_j$ associated with the $j$-th solution $\psi_j$ of the scalar Helmholtz equation. The vector solution $L$ cannot contribute to the field expansions because $\nabla \cdot L \neq 0$ and so Maxwell’s equations (2.3.8) and (2.3.10) could not be satisfied [14, 15].

The boundary conditions for electric and magnetic fields in the vicinity of perfect conductors were discussed in section (3.2). It was seen that the tangential component of electric field and the normal component of magnetic field were required to vanish at the boundary wall of the ideal cylindrical waveguide and these boundary conditions in the ideal spherical cavity will require that the constant vector $a$ be replaced by the (non-constant) radial vector $r$ in equations (10) and (11). {In the case of the ideal cylindrical cavity $a$ would be replaced by the (constant) unit vector $\hat{z}$ for satisfaction of the boundary conditions [14, 15]}. There is no problem in replacing $a$ by $r$ in equations (10) and (11) and it is readily shown that $M$ and $N$ remain perfectly valid solutions of equation (8). Putting $a = r$ in equations (10) and (11) and using the curl equation (3) gives

$$M_j = \nabla \times r \psi_j = \left\{ \frac{1}{\sin \theta} \frac{\partial \psi_j}{\partial \phi} \right\} \hat{\theta} - \left\{ \frac{\partial \psi_j}{\partial \theta} \right\} \hat{\phi}$$

$$N_j = \frac{1}{k} \nabla \times M_j = \frac{1}{k} \nabla \times \nabla \times r \psi_j$$

$$= \left\{ \frac{\partial^2 (r \psi_j)}{k \partial r^2} + k (r \psi_j) \right\} \hat{r} + \left\{ \frac{1}{kr} \frac{\partial (r \psi_j)}{\partial \theta} \right\} \hat{\theta} + \left\{ \frac{1}{kr \sin \theta} \frac{\partial^2 (r \psi_j)}{\partial r \partial \phi} \right\} \hat{\phi}$$

(3.4.20)
Therefore, by a combination of equations (17), (18), (19) and (20), we already have the vector fields \( \mathbf{E} \) and \( \mathbf{H} \) in the sphere in terms of scalar eigenfunctions \( \psi_j \). Further progress requires that the solutions \( \psi_j \) for the scalar Helmholtz equation in spherical coordinates be found.

The scalar Helmholtz equation in spherical coordinates is solved by separating the variables. A product solution

\[
\psi = R(r)\Theta(\theta)\Phi(\phi)
\]

is proposed and substituted into equation (7). With the Laplacian expressed in spherical coordinates, the equation separates into three ordinary second-order differential equations with well-known solutions. The equations are

\[
\left( \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left\{ k^2 - \frac{l(l+1)}{r^2} \right\} R \right) = 0 \tag{3.4.22}
\]

\[
\left( \frac{d^2 \Theta}{d\theta^2} + \cot \theta \frac{d\Theta}{d\theta} + \left\{ l(l+1) - \frac{m^2}{\sin^2 \theta} \right\} \Theta \right) = 0 \tag{3.4.23}
\]

\[
\left( \frac{d^2 \Phi}{d\phi^2} \right) + m^2 \left( \frac{d\Phi}{d\phi} \right) = 0 \tag{3.4.24}
\]

where \(-m^2\) is the separation constant for \( \Phi \), \(-l(l+1)\) is the separation constant for \( \Theta \) and \( k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0 \).

If the substitution \( X = \sqrt{r} R \) is made in equation (22), and the independent variable changed from \( r \) to \( (kr) \), then it becomes \[8\]

\[
\left( \frac{d^2 X}{d(kr)^2} \right) + \frac{1}{(kr)} \left( \frac{dX}{d(kr)} \right) + \left[ 1 - \frac{(l+1/2)^2}{(kr)^2} \right] X = 0 \tag{3.4.25}
\]

which is Bessel’s equation of order \((l+1/2)\). The solution which is finite at \( r = 0 \) is \( X = J_{l+1/2}(kr) \), the Bessel function of the first kind of order \((l+1/2)\). Bessel functions of the second kind, which become infinite at the origin, cannot contribute. Therefore we have the radial solution \[8\]

\[
R(r) = \frac{1}{\sqrt{r}} J_{l+1/2}(kr) \tag{3.4.26}
\]

Equation (23) becomes the associated Legendre equation if the independent variable is changed from \( \theta \) to \( \cos \theta \). The solution which is finite within the whole range of \( \theta \) is \[8\]
\[ \Theta(\theta) = P_l^{m}(\cos \theta) \]  \tag{3.4.27}

\( P_l^{m}(\cos \theta) \) is the \(|m|\)-th associated Legendre function of the first kind of order \( l \). The index \( l \) is restricted to the values \( l = 0, 1, 2, \ldots \) in order that the solution is finite at \( \theta = 0 \) and \( \theta = \pi \). It will be seen later that \( l = 0 \) is not acceptable due to more general field considerations. The index \( m \) must take values such that \(|m| \leq l\) since \( P_l^{m}(\cos \theta) \) vanishes for \(|m| > l\). Therefore \( m \) is restricted to the values \( m = 0, \pm 1, \pm 2, \ldots, \pm l \).

The appropriate solution of equation (24) is simply [22]
\[ \Phi = [\cos m\phi + \sin m\phi] \]  \tag{3.4.28}

Therefore the required solutions to the scalar Helmholtz equation in spherical coordinates are
\[ \psi_{lm} = \frac{1}{r} J_{l+1/2}(kr)P_l^{m}(\cos \theta)[\cos m\phi + \sin m\phi] \]  \tag{3.4.29}

The Bessel functions \( J_{l+1/2} \) can be replaced by the spherical Bessel functions \( j_l \), with integer order \( l \), where the relation between \( j_l \) and \( J_{l+1/2} \) is [8]
\[ J_{l+1/2}(kr) = \frac{2kr}{\pi} j_l(kr) \]  \tag{3.4.30}

The spherical Bessel functions \( j_l(kr) \) are elementary functions which can be expressed in terms of \( \sin(kr) \), \( \cos(kr) \) and powers of \( (kr) \) [8]:

\[
\begin{align*}
&l = 0 \quad j_0(kr) = \frac{\sin(kr)}{(kr)} \\
&l = 1 \quad j_1(kr) = \frac{\sin(kr)}{(kr)} - \frac{\cos(kr)}{(kr)} \\
&l = 2 \quad j_2(kr) = \frac{\sin(kr)}{(kr)} \left( \frac{3}{(kr)^2} - 1 \right) - \frac{3\cos(kr)}{(kr)^2} \\
&l = 3 \quad j_3(kr) = \sin(kr) \left( \frac{15}{(kr)^4} - \frac{6}{(kr)^2} \right) + \frac{\cos(kr)}{(kr)} \left( 1 - \frac{15}{(kr)^2} \right)
\end{align*}
\]

It is therefore often simpler to use these functions rather than the series solutions that are the (cylindrical) Bessel functions \( J_{l+1/2} \). This is especially the case when it comes to solving the characteristic equations that provide the resonance frequencies of the cavity. Some low-order functions \( x_j \) are plotted in figure (3.4). In addition, the angular parts of the solution can be taken together to give the spherical harmonics [22]
\[
Y_l^m(\theta, \phi) = l^m_l(\cos \theta)[\cos m\phi + \sin m\phi] \tag{3.4.31}
\]
So, the solutions in terms of spherical Bessel functions and spherical harmonics are
\[
\psi_{lm} = \sqrt{\frac{2k}{\pi}} j_l(kr) Y_l^m(\theta, \phi) \tag{3.4.32}
\]
As will be recalled, the boundary conditions require that the tangential electric field and the normal magnetic field must vanish at \( r = a \), for all \( \theta \) and \( \phi \), and so the equations
\[
E_{\text{tan}}\big|_{r=a} = \hat{r} \times E_{\text{in}}\big|_{r=a} = A \sqrt{\frac{2k}{\pi}} \left[ a_{lm} \left\{ j_l(kr) \frac{\partial Y_l^m}{\partial \theta} \hat{\theta} + \frac{1}{\sin \theta} j_l(kr) \frac{\partial Y_l^m}{\partial \phi} \hat{\phi} \right\} \right. \\
+ b_{lm} \left\{ \frac{1}{kr} \left[ (kr) j_l(kr) \right] \frac{\partial Y_l^m}{\partial \theta} \hat{\theta} \right. \\
\left. - \frac{1}{kr \sin \theta} \left[ (kr) j_l(kr) \right] \frac{\partial Y_l^m}{\partial \phi} \hat{\phi} \right\} \bigg|_{r=a} = 0 \tag{3.4.33}
\]
and
\[ H_{\text{norm}}|_{r=a} = \hat{r} \cdot H_{\text{lm}}|_{r=a} = \frac{ikA}{\omega \mu_0} \sqrt{\frac{2k}{\pi}} a_{lm} \left\{ \frac{l(l+1)}{kr} j_l(kr) y_n^m \right\} = 0 \quad (3.4.34) \]

must be satisfied simultaneously. The primes in equation (33) indicate differentiation with respect to the argument \((kr)\), and so

\[ [(kr) j_l(0)] = \frac{d}{d(kr)} [(kr) j_l(0)]. \]

Equations (33) and (34) are obtained using equations (17) to (20) and equation (32).

The equation \([14, 15]\]

\[ (3.4.35) \]

has also been used to obtain equation (34), and equation (35) itself follows from equation (22). The satisfaction of equations (33) and (34) requires that

\[ j_l(ka) = 0 \] provided \(a_{lm} \neq 0\)

and

\[ [(ka) j_l(ka)]' = 0 \] provided \(b_{lm} \neq 0\)

But the zeros of \(j_l(ka)\) and the extrema of \([(ka) j_l(ka)]\) do not coincide [see figure (3.4)] so the only way both boundary conditions can be satisfied at the same time is if \((a_{lm} = 0 \text{ and } b_{lm} \neq 0)\) or \((a_{lm} \neq 0 \text{ and } b_{lm} = 0)\) and consequently there are two classes of resonant modes.

The combination of equations (18) and (19) shows that the modes with \((a_{lm} = 0, b_{lm} \neq 0)\) have no radial component of magnetic field and so are called transverse magnetic (TM) modes. The characteristic equation for TM modes is

\[ [(ka) j_l(ka)]' = 0 \quad (3.4.36) \]

The \(n\)-th solution of equation (36) is \((ka) = \nu_n'\) and these eigenvalues \(\nu_n'\) are given, for selected values of \(l\) and \(n\), in table (3.3). Therefore, since \(k^2 = \omega^2 \varepsilon_\varepsilon_0 \mu_0\), we have, for the TM\(ln\) mode [8],

\[ f_{ln} = \frac{\nu_n' c}{2\pi a} \quad (3.4.37) \]

where \(c = \sqrt{1/\varepsilon_\varepsilon_0 \mu_0}\) is the phase speed in the medium filling the cavity and \(f_{ln}\) is the resonance frequency of the TM\(ln\) mode in the ideal cavity.

The fields of the TM\(lnm\) mode are
and the individual field components are obtained by using equations (19), (20) and (35). The factor \( \exp(i\omega t) \) is implicit in equations (40) to (45).

**TM\(lm\) modes**

\[
E_r = \frac{l(l+1)}{kr} B j_l(kr) l^{(k)}[\cos \theta][\sin m\phi + \cos m\phi] \tag{3.4.40}
\]

\[
E_\theta = \frac{1}{kr} B (kr) j_l(kr) \frac{d}{d\theta} P_l^{\text{in}}(\cos \theta)[\sin m\phi + \cos m\phi] \tag{3.4.41}
\]

\[
E_\phi = \frac{-m}{kr \sin \theta} B (kr) j_l(kr) \frac{d}{d\theta} P_l^{\text{in}}(\cos \theta)[\sin m\phi - \cos m\phi] \tag{3.4.42}
\]

\[
H_r = 0 \tag{3.4.43}
\]

\[
H_\theta = -\frac{i\omega \varepsilon \kappa m}{k \sin \theta} B j_l(kr) \frac{d}{d\theta} P_l^{\text{in}}(\cos \theta)[\sin m\phi - \cos m\phi] \tag{3.4.44}
\]

\[
H_\phi = -\frac{i\omega \varepsilon \kappa}{k} B j_l(kr) \frac{d}{d\theta} P_l^{\text{in}}(\cos \theta)[\sin m\phi + \cos m\phi] \tag{3.4.45}
\]

where the normalisation constant \( B = \sqrt{\frac{2k}{\pi}} (Ab_{lm}) \).

As can be seen from a combination of equations (17) and (19), the modes with \((alm \neq 0, blm = 0)\) have no radial component of electric field and so are called transverse electric (TE) modes. The characteristic equation for TE modes is

\[
j_l(ka) = 0 \tag{3.4.46}
\]

and the solutions, or eigenvalues, \((ka) = \nu_{ln}\) are given, for selected values of \(l\) and \(n\), in table (3.4). The resonance frequency of the TE\(ln\) mode is found using equation (37) with \(\nu_{ln}'\) replaced by \(\nu_{ln}\). The fields of the TE\(lnm\) mode are

\[
E_{lnm} = Aa_{lnm} M_{lnm} \tag{3.4.47}
\]

\[
H_{lnm} = \frac{ik}{\omega \mu_0} Aa_{lnm} N_{lnm} \tag{3.4.48}
\]

and the individual field components are found using equations (19), (20) and (35). The factor \( \exp(i\omega t) \) is implicit in equations (49) to (54).
Table (3.3) Selected sphere TM mode eigenvalues $\nu'_{ln}$ [8]

<table>
<thead>
<tr>
<th>$\nu'_{ln}$</th>
<th>$n = 1$</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = 1$</td>
<td>2.7437</td>
<td>6.1168</td>
<td>9.3166</td>
<td>12.4859</td>
</tr>
<tr>
<td>2</td>
<td>3.8702</td>
<td>7.4431</td>
<td>10.7130</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.9734</td>
<td>8.7199</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (3.4) Selected sphere TE mode eigenvalues $\nu_{ln}$ [8]

<table>
<thead>
<tr>
<th>$\nu_{ln}$</th>
<th>$n = 1$</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l = 1$</td>
<td>4.4934</td>
<td>7.7253</td>
<td>10.9041</td>
<td>14.0662</td>
</tr>
<tr>
<td>2</td>
<td>5.7635</td>
<td>9.0950</td>
<td>12.3229</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.9879</td>
<td>10.4171</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TElm modes**

$$E_r = 0$$

$$E_\theta = \frac{-m}{\sin \theta} C j_i(kr) P^{|l|}_i(\cos \theta) \sin m \phi - \cos m \phi$$

$$E_\phi = -C j_i(kr) \frac{d}{d \theta} \{ P^{|l|}_i(\cos \theta) \} \sin m \phi + \cos m \phi$$

$$H_r = \frac{i \omega \mu_0 (l+1)}{k^2 r} C j_i(kr) P^{|l|}_i(\cos \theta) \sin m \phi + \cos m \phi$$

$$H_\theta = \frac{i \omega \mu_0}{k^2 r \sin \theta} C [(kr) j_i(kr)]' \frac{d}{d \theta} \{ P^{|l|}_i(\cos \theta) \} \sin m \phi + \cos m \phi$$

$$H_\phi = -\frac{i \omega \mu_0 m}{k^2 r \sin \theta} C [(kr) j_i(kr)]' P^{|l|}_i(\cos \theta) \sin m \phi - \cos m \phi$$

where the normalisation constant $C = \sqrt{\frac{2k}{\pi} (\lambda a_{lnm})}$.

The case of $(a|l|m = 0, b|l|m = 0)$ is a trivial solution for which $E$ and $H$ vanish completely, and so the ideal spherical cavity does not support transverse electric and magnetic (TEM) modes.

The permissible values of $l$, $n$ and $m$ for both TM and TE modes are $l = 1, 2, 3, \ldots$; $n = 1, 2, 3, \ldots$; $m = 0, \pm 1, \pm 2, \ldots, \pm l$ [8]. The index $l$ cannot be zero since this requires $m$ to be zero also and so all field components would vanish.
The third mode index \( m \) does not appear in the characteristic equations for either TM or TE modes due to the high degree of symmetry of the cavity and so the resonance frequencies of an ideal spherical cavity do not depend on \( m \). However, for a given value of \( l \), there are \((2l+1)\) permissible values of \( m \) and each of these corresponds to a different mode with its individual arrangement of electric and magnetic fields, and so the resonant modes of the ideal spherical cavity are \((2l+1)\)-fold degenerate [23, 24].

The term 'TM\( \ell n \) mode', which is used throughout this work and the relevant literature, is a shorthand notation for the \((2l+1)\) TM modes, each with a different value of \( m \), that have the same values of \( l \) and \( n \), and therefore the same resonance frequency in the ideal spherical cavity. These are commonly referred to as the \((2l+1)\) 'components' of the TM\( \ell n \) mode, although they are, of course, resonant modes in their own right. If it is important to know which component is being discussed, for example when considering the \( E \) and \( H \) field arrangements or discussing the effects of non-ideality, then the mode will be labelled with its full set of three indices ('TM\( \ell nm \)'), or the component in question will be made clear in some other way. Similarly, the term 'TE\( \ell n \) mode' refers to the \((2l+1)\) TE modes, each with a different value of \( m \), that have the same values of \( l \) and \( n \), and therefore the same resonance frequency in the ideal spherical cavity. They are referred to as the \((2l+1)\) components of the TE\( \ell n \) mode and, as indicated for the TM\( \ell n \) mode components, it will be made clear which TE\( \ell n \) mode component is being discussed whenever necessary.

The mode indices \( l \), \( n \) and \( m \) have a definite significance with respect to the patterns of electric and magnetic fields in the cavity for a given mode. There are \( l \) conical radial nodal surfaces, \( n \) spherical radial nodal surfaces and \(|m|\) radial nodal planes parallel to the sphere's equatorial plane for the electric and magnetic fields. Field patterns for some modes in the ideal spherical cavity are shown in figure (3.5).

The total energy \( W \) stored in the electromagnetic fields in the ideal spherical cavity can be calculated, for a particular mode, and used to obtain the relevant normalisation constant, \( B \) or \( C \), as was seen with the cylindrical cavity in section (3.3), using equation (3.3.22), (3.3.25), or (3.3.26). For the spherical cavity, the
Figure (3.5) Spherical cavity field patterns [8, 25]. The fields of the \( m = 0 \) components are shown in a plane of constant \( \phi \) and only the \( E \) or \( H \) field alone is shown for clarity. The \( E \) and \( H \) fields are mutually orthogonal everywhere.

\[ \begin{align*}
\text{Electric field} & \quad \text{Magnetic field} \\
\hline
\text{TM 110} & \quad \text{TM 210} \\
\text{TM 120} & \quad \text{TM 310} \\
\text{TM 130} & \quad \text{TE 110}
\end{align*} \]
volume \( V_0 = \frac{4}{3} \pi a^3 \) and the volume element \( dV = r^2 \, dr \, \sin \theta \, d\theta \, d\phi \), where \( 0 \leq r/a \leq 1 \), \( 0 \leq \theta \leq \pi \), and \( 0 \leq \phi < 2\pi \).

**TMlnm modes**

Equation (3.3.26) is the simplest to use for this calculation, and the required \( H \) field components can be found in equations (43) to (45). Substituting these field components into equation (3.3.26), and collecting terms, gives

\[
W_{TMlnm} = \frac{\omega^2 (\varepsilon \varepsilon_0)^2 \mu_0 B^2}{2} \int_0^\pi \int_0^\pi \int_0^{2\pi} \frac{r^2}{j^2 (kr)} (\sin m \phi + \cos m \phi)^2 \sin^2 \theta \, dr \, d\theta \, d\phi \tag{3.4.55}
\]

where we have used equation (A3.1.31) in order to simplify equation (55). The integral over \( r \) is given by equation (A3.1.25) and the integral over \( \phi \) is given by equation (A3.1.31). Using these results, equation (55) becomes

\[
W_{TMlnm} = \frac{3 \varepsilon \varepsilon_0 B^2 V_0}{4} \left[ 1 - \frac{l(l+1)}{v'_{ln}^2} \right] j^2 (v'_{ln}) \int_0^\pi \int_0^\pi \left\{ \frac{|m|^2}{\sin \theta} \left[ P_{ln}^{\text{im}}(\cos \theta) \right]^2 + \left[ \frac{d}{d\theta} \left\{ P_{ln}^{\text{im}}(\cos \theta) \right\} \right]^2 \sin \theta \right\} d\theta \sin \theta \, d\theta \tag{3.4.56}
\]

where we have used \((ka) = v'_{ln}\), the TMln mode eigenvalue, and the relation \( k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0 \) to simplify. The integral over \( \theta \) in equation (56) can be evaluated for an individual mode or a limited family of modes.

**TMln0 modes**

If \( m = 0 \) then equation (56) becomes

\[
W_{TMln0} = \frac{3 \varepsilon \varepsilon_0 B^2 V_0}{4} \left[ 1 - \frac{l(l+1)}{v'_{ln}^2} \right] j^2 (v'_{ln}) \cdot \int_0^\pi \left[ P_{ln}^0(\cos \theta) \right]^2 \sin \theta \, d\theta \, d\theta \tag{3.4.57}
\]

where equation (A3.1.38) has been used to simplify the integral over \( \theta \). The integral over \( \theta \) in equation (57) is given by equation (A3.1.40) and so \( W_{TMln0} \) is
\[
W_{TM_{ln0}} = \frac{3\epsilon\epsilon_0 B^2 V_0}{4} \left[ 1 - \frac{l(l+1)}{V_{ln}^2} \right] j^2_i(v'_{in}) \left[ \frac{2}{2l+1} \frac{(l+1)!}{(l-1)!} \right]
\] (3.4.58)

**TM1nm modes**

If \( l = 1 \) then \( m \) is restricted to the values 0, ±1. \( W_{TM_{ln0}} \) can be calculated using equation (58), so we need only consider the \( l = 1, m = \pm 1 \) components.

In general, the integral over \( \theta \) in equation (56) can be written

\[
I(\theta) = I_1 + I_2
\] (3.4.59)

where

\[
I_1 = \int_0^\pi \left[ P_i^{\text{inl}+1}(\cos \theta) \right]^2 \sin \theta d\theta
\] (3.4.60)

and

\[
I_2 = \int_0^\pi \left[ m^2 \left[ P_i^{\text{inl}}(\cos \theta) \right] \left( \frac{1}{\sin \theta} + \frac{\cos^2 \theta}{\sin \theta} \right) - 2m \cos \theta P_i^{\text{inl}}(\cos \theta) P_i^{\text{inl}+1}(\cos \theta) \right] d\theta
\] (3.4.61)

where we have used equation (A3.1.38) to obtain equations (60) and (61). The integration in equation (60) can be evaluated using equation (A3.1.40) for any values of \( l \) and \( m \) such that \(|m| + 1\) ≤ \( l \). If \(|m| = l \) then \( P_i^{\text{inl}+1}(\cos \theta) = 0 \), from the definition of \( P_i^{\text{inl}}(x) \) given in equation (A3.1.33), and this is the case for \( l = 1, m = \pm 1 \) considered here. Therefore \( I_1 = 0 \) and \( I_2 \) is given by

\[
I_2 = \int_0^\pi \left[ P_i^{\text{inl}}(\cos \theta) \right]^2 \left( \frac{1}{\sin \theta} + \frac{\cos^2 \theta}{\sin \theta} \right) d\theta
\] (3.4.62)

The associated Legendre function \( P_i^l(\cos \theta) = \sin \theta \) [see equations (A3.1.36)] and so the integral \( I_2 \) can be evaluated:

\[
I_2 = \int_0^\pi (\sin \theta + \sin \theta \cos^2 \theta) d\theta = \frac{8}{3}
\] (3.4.63)

Therefore, equation (59) gives \( I(\theta) = 8/3 \) and this is substituted into equation (56) to finally give

\[
W_{TM_{ln1}} = 2\epsilon\epsilon_0 B^2 V_0 \left[ 1 - \frac{2}{V_{ln}^2} \right] j^2_i(v'_{in})
\] (3.4.64)
**TE\(lnm\) modes**

Equation (3.3.25) is the simplest to use for this calculation, and the required \(E\) field components are given in equations (49) to (51). These are substituted into equation (3.3.25) to give

\[
W_{TE\text{h}0} = \varepsilon\varepsilon_0 C^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 j_1^2 (kr) (\sin m\phi + \cos m\phi)^2 \\
\times \left\{ \frac{|m|^2}{\sin \theta} \right\} \left[ P_{l}^{\text{inh}}(\cos \theta) \right]^2 + \left[ \frac{d}{d\theta} \left\{ P_{l}^{\text{inh}}(\cos \theta) \right\} \right]^2 \sin \theta \right\} dr \, d\theta \, d\phi
\]

(3.4.65)

where equation (A3.1.31) has been used to simplify equation (65). The integral over \(r\) is given by (A3.1.26) and the integral over \(\phi\) is given by equation (A3.1.31). Using these results, equation (65) becomes

\[
W_{TE\text{h}0} = \frac{3\varepsilon\varepsilon_0 C^2 V_0}{4} j_1^2 (v_m) \left\{ \frac{|m|^2}{\sin \theta} \right\} \left[ P_{l}^{\text{inh}}(\cos \theta) \right]^2 + \left[ \frac{d}{d\theta} \left\{ P_{l}^{\text{inh}}(\cos \theta) \right\} \right]^2 \sin \theta \right\} d\theta
\]

(3.4.66)

where we have used \((ka) = v_m\), the TE\(lnm\) mode eigenvalue, to simplify. The integral over \(\theta\) in equation (66) is equal to \(I(\theta)\) in equation (59), and can be evaluated for an individual mode or a limited family of modes, as was seen before.

**TE\(ln0\) modes**

If \(m = 0\) then \(I(\theta)\) is the same as that found for TM\(ln0\) modes and so the total energy is given by

\[
W_{TE\text{h}0} = \frac{3\varepsilon\varepsilon_0 C^2 V_0}{4} j_1^2 (v_m) \left[ \frac{2}{2l + 1} \frac{(l + 1)!}{(l - 1)!} \right]
\]

(3.4.67)

**TE\(1nm\) modes**

If \(l = 1\) then \(m\) is restricted to the values 0, \(\pm 1\). \(W_{TE1\text{h}0}\) can be found using equation (67) so the only additional components that need to be considered are those with
l = 1, m = ±1. If \( |m| = 1 \) then \( I(\theta) \) is the same as that found for TM1n±1 modes and so the total energy is given by

\[
W_{TE_{l=1}} = 2\varepsilon\varepsilon_0 C^2 V_0 j_1^2(\nu_m) \quad (3.4.68)
\]

### A3.1 Mathematical appendix

#### Bessel functions [8, 21, 26]

Bessel’s equation of order \( p \) is

\[
\frac{d^2\psi}{dx^2} + \frac{1}{x} \frac{d\psi}{dx} + \left(1 - \frac{p^2}{x^2}\right)\psi = 0 \quad (A3.1.1)
\]

This equation often arises in wave motion problems where the system of interest has circular symmetry. In such problems, it is usually the case that \( x = (kr) \) where \( r \) is the radial coordinate and \( k \) is a separation constant which arises from the separation of the (three-dimensional) partial differential wave equation into three ordinary differential equations, each involving only one coordinate.

A series solution of Bessel’s equation is \( J_p(x) \) which is called Bessel’s function of the first kind of order \( p \). For integer order \( p \), \( J_p(x) \) is

\[
J_p(x) = x^p \sum_{m=0}^{\infty} \frac{(-1)^m x^{2m}}{2^{2m+p} m!(p+m)!} 
\]

(A3.1.2)

The zeros of \( J_p \) are the eigenvalues \( \chi_{pq} \) for TM modes in the cylindrical waveguide and cavity, and the turning points of \( J_p \) are the eigenvalues \( \chi'_{pq} \) for TE modes in the cylindrical waveguide and cavity. A second series solution of Bessel’s equation is \( Y_p(x) \) which is called Bessel’s function of the second kind of order \( p \), or Neumann’s function of order \( p \). \( Y_p(x) \) is defined in terms of Bessel functions of the first kind by

\[
Y_p(x) = \frac{1}{\sin p\pi} \left[ J_p(x) \cos p\pi - J_{-p}(x) \right] 
\]

(A3.1.3)

A general solution of Bessel’s equation is a linear combination

\[
Z_p(x) = AJ_p(x) + BY_p(x) 
\]

(A3.1.4)

where \( A \) and \( B \) are constants to be determined for the problem at hand.

The functions \( J_p(x) \), \( Y_p(x) \), and the linear combinations \( Z_p(x) \), satisfy a large number of relations, the most useful of which are given here in terms of \( Z_p(x) \) for
convenience of presentation. In these relations the order $p$ may be integral or non-integral, negative or positive. A prime indicates differentiation with respect to the argument $x$.

**Differential and recurrence relations**

\[
Z_{p-1}(x) + Z_{p+1}(x) = \frac{2p}{x} Z_p(x) \tag{A3.1.5}
\]

\[
Z_{p-1}(x) - Z_{p+1}(x) = 2Z'_p(x) \tag{A3.1.6}
\]

\[
Z'_p(x) = Z_{p-1}(x) - \frac{p}{x} Z_p(x) \tag{A3.1.7}
\]

\[
Z'_p(x) = \frac{p}{x} Z_p(x) - Z_{p+1}(x) \tag{A3.1.8}
\]

\[
Z''_p(x) = -\frac{1}{x} Z'_p(x) - \left(1 - \frac{p^2}{x^2}\right) Z_p(x) \tag{A3.1.9}
\]

Equation (5) is useful for expressing Bessel functions of high order in terms of functions of low order, and has been used for compiling tables of Bessel functions.

**Linear dependence**

\[
Z_{-p}(x) = (-1)^p Z_p(x) \tag{A3.1.10}
\]

Bessel functions of the first kind $J_p(x)$ also satisfy the following very useful relations:

**Approximation for small $x$**

\[
J_p(x) \approx \frac{x^p}{2^p \cdot p!} \left\{1 - \frac{x^2}{4(p+1)}\right\} \tag{A3.1.11}
\]

**Approximations for large $x$**

\[
J_p(x) \approx \left(\frac{2}{\pi x}\right)^{\frac{1}{2}} \left(\cos u + \frac{1-4p^2}{8x} \sin u\right) \tag{A3.1.12}
\]

\[
J'_p(x) \approx \left(-\left(\frac{2}{\pi x}\right)^{\frac{1}{2}} \left(\sin u + \frac{4p^2 + 3}{8x} \cos u\right) \tag{A3.1.13}
\]

where $u = x - [(2p+1)\pi/4]$. 

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Integral properties

Lommel’s integral is given by

\[ \int_0^\infty r J_p^2(kr) \, dr = \frac{a^2}{2} \left\{ J_p^2(ka) + \left( 1 - \frac{p^2}{(ka)^2} \right) J_p^2(ka) \right\} \]  
(A3.1.14)

Integration by parts, using Lommel’s integral, and use of the recurrence relations can provide a variety of integrals involving products of Bessel functions. The most useful are

\[ \int_0^\infty - \frac{1}{r} J_p^2(kr) \, dr = \frac{1}{2} p \left\{ 1 + J_0^2(ka) + J_p^2(ka) - 2 \sum_{q=0}^p J_q^2(ka) \right\} \text{ for } p \geq 1 \]  
(A3.1.15)

\[ \int_0^\infty J_p(kr) J_{p+1}(kr) \, dr = \frac{1}{2k} J_{p+1}^2(ka) + \frac{p+1}{k} \int_0^\infty J_{p+1}^2(kr) \frac{dr}{r} \]  
(A3.1.16)

\[ \int_0^\infty r^2 J_{p-1}(kr) J_p(kr) \, dr = \frac{a^2}{2k} J_p^2(ka) \]  
(A3.1.17)

\[ \int_0^\infty r \left\{ J_p^2(kr) + \frac{p^2}{k^2 r^2} J_p^2(kr) \right\} dr \]  
(A3.1.18)

\[ = \frac{a^2}{2} \left\{ J_p^2(ka) + \frac{2p}{ka} J_p(ka) J_p'(ka) + \left( 1 - \frac{p^2}{(ka)^2} \right) J_p^2(ka) \right\} \]

Spherical Bessel functions [8, 26]

The spherical Bessel function of the first kind of integer order \( l \), which is represented by the symbol \( j_l \), is related to \( J_{l+1/2} \), the Bessel function of the first kind of order \( (l+1/2) \), by

\[ j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+1/2}(x) \]  
(A3.1.19)

The spherical Bessel function of the second kind of integer order \( l \), denoted by the symbol \( y_l \), is defined in a similar way:

\[ y_l(x) = \sqrt{\frac{\pi}{2x}} Y_{l+1/2}(x) \]  
(A3.1.20)
where $Y_{\nu+1/2}(x)$ is the Bessel function of the second kind of order $(l + 1/2)$. The $y_{\nu}(x)$ has a singularity at $x = 0$. The function $j_{l}(x)$, where $x = kr$, appears in the solutions of the wave equation in spherical coordinates and, therefore, in the expressions for the field components of the TM and TE modes within the spherical cavity.

**Differential and recurrence relations**

These are obtained from the differential and recurrence relations of the Bessel functions $J_{l+1/2}$ using equations (5) to (9) and the relation of equation (19).

\[
j_{l-1}(kr) + j_{l+1}(kr) = \frac{2\left(l + \frac{1}{2}\right)}{(kr)} j_{l}(kr)
\]

\[
j_{l-1}(kr) - j_{l+1}(kr) = \frac{1}{(kr)} j_{l}(kr) + 2 j_{l}^2(kr)
\]

\[
j_{l}^\prime(kr) = j_{l-1}(kr) - \frac{(l+1)}{(kr)} j_{l}(kr)
\]

\[
j_{l}^\prime(kr) = \frac{1}{(kr)} j_{l}(kr) - j_{l+1}(kr)
\]

**Integral properties**

The useful integral $\int_{0}^{\alpha} r^2 j_{l}^2(\alpha) d\alpha$ can be found by replacing $[r^2 j_{l}^2(\alpha)]$ by $[(\pi/2k)rJ_{l+1/2}(\alpha)]$, using equation (19), and then evaluating the resulting integral using Lommel’s integral, equation (14). The results for TM and TE spherical cavity modes are considered separately since the characteristic equations can be used to simplify the derivations.

**TM modes:**

The characteristic equation is $[(ka)j_{l}(ka)] = 0$ and the integral is given by

\[
\int_{0}^{\alpha} r^2 j_{l}^2(\alpha) d\alpha = \frac{\alpha^3}{2} \left[1 - \frac{l(l+1)}{(ka)^2}\right] j_{l}^2(ka)
\]

**TE modes:**

The characteristic equation is $j_{l}(ka) = 0$ and the integral is given by

\[
\int_{0}^{\alpha} r^2 j_{l}^2(\alpha) d\alpha = \frac{\alpha^3}{2} j_{l}^2(ka)
\]

where the prime denotes differentiation with respect to the argument $(ka)$. 
Trigonometric functions [8]

Most of the simple differential and integral properties of the trigonometric functions are well-known and so only a small number of useful integrals are given here.

\[
\int_0^L \sin^2\left(\frac{s\pi z}{L}\right) dz = \int_0^L \cos^2\left(\frac{s\pi z}{L}\right) dz = \frac{L}{2} \quad \text{for real integral values of } s \neq 0 \quad (A3.1.27)
\]

\[
\int_0^\pi \sin^2 p\theta d\theta = \pi \quad \text{for real integral values of } p \neq 0 \quad (A3.1.28)
\]

\[
\int_0^\pi \cos^2 p\theta d\theta = \pi \quad \text{for real integral values of } p \neq 0 \quad (A3.1.29)
\]

\[
\int_0^\pi \sin p\theta \cos p\theta d\theta = 0 \quad \text{for all } p \quad (A3.1.30)
\]

Equations (28), (29) and (30) can be used to show that

\[
\int_0^\pi \left[\sin p\theta - \cos p\theta\right]^2 d\theta = \int_0^\pi \left[\sin p\theta + \cos p\theta\right]^2 d\theta = 2\pi \quad (A3.1.31)
\]

for any real integer \( p \).

Associated Legendre functions [8, 26]

Legendre's associated equation of order \( l \) is

\[
\left(1 - x^2\right) \frac{d^2\psi}{dx^2} - 2x \frac{d\psi}{dx} + \left[l(l + 1) - \frac{m^2}{1 - x^2}\right] \psi = 0 \quad (A3.1.32)
\]

This equation commonly occurs in wave motion problems where the system of interest has spherical symmetry, e.g., the solution of the Schrödinger equation for the hydrogen atom, and the analysis of acoustic and electromagnetic waves in a spherical cavity. In these cases the independent variable \( x = \cos\theta \), where \( \theta \) is the polar angle between the polar, or \( z \), axis and the radial vector. The solution that is finite over the range of \( \theta \), between 0 and \( \pi \), is \( P_l^m(\cos\theta) \) which is the \(|m|\)-th associated Legendre function of the first kind of order \( l \). The associated Legendre function of the second kind \( Q_l^m(\cos\theta) \) has singularities at \( \theta = 0 \) and \( \theta = \pi \), and so is of no interest to the current work where finite solutions within the whole range of \( \theta \) are required. The \(|m|\)-th associated Legendre function of the first kind of order \( l \) is defined by
\[ P_{l}^{m}(x) = \left(1 - x^2\right)^{|m|/2} \frac{d^{|m|} P_{l}(x)}{dx^{|m|}} \]  
(A3.1.33)

\[ l = 0, 1, 2, 3, \ldots \quad \text{and} \quad |m| = 0, 1, 2, 3, \ldots, l \]

where \( x = \cos \theta \) and \( P_{l}(x) \) is the Legendre function of order \( l \) which is equal to the zeroth associated Legendre function \( P_{l}^{0}(x) \) and is given by Rodrigue’s formula:

\[ P_{l}(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} \left(x^2 - 1\right) \]  
(A3.1.34)

It will be noted from the definition of \( P_{l}^{m}(x) \), equation (33), that \( m \) is limited to the values \( 0, \pm 1, \pm 2, \ldots, \pm l \) since \( P_{l}^{l+1}(x) = 0 \).

The first few Legendre functions are

\[
\begin{align*}
P_{0}(x) &= 1 \\
P_{1}(x) &= x \\
P_{2}(x) &= \frac{1}{2} \left(3x^2 - 1\right) \\
P_{3}(x) &= \frac{x}{2} \left(5x^2 - 3\right)
\end{align*}
\]

and so the first few associated Legendre functions are

\[
\begin{align*}
P_{0}^{0}(\cos \theta) &= 1 \\
P_{1}^{0}(\cos \theta) &= \cos \theta \\
P_{1}^{1}(\cos \theta) &= \sin \theta \\
P_{2}^{0}(\cos \theta) &= \frac{1}{2} \left(3\cos^2 \theta - 1\right) \\
P_{2}^{1}(\cos \theta) &= 3\cos \theta \sin^2 \theta \\
P_{2}^{2}(\cos \theta) &= 3\sin^2 \theta \\
P_{3}^{0}(\cos \theta) &= \frac{1}{2} \cos \theta \left(5\cos^2 \theta - 3\right) \\
P_{3}^{1}(\cos \theta) &= \frac{3}{2} \sin \theta \left(5\cos^2 \theta - 1\right) \\
P_{3}^{2}(\cos \theta) &= 15\cos \theta \sin^2 \theta \\
P_{3}^{3}(\cos \theta) &= 15\sin^3 \theta
\end{align*}
\]

where the substitution \( x = \cos \theta \) has been made.
Differential relations

\[ \frac{d}{dx} P_l^{\text{inl}}(x) = (1 - x^2)^{-\frac{l}{2}} P_l^{\text{inl+1}}(x) - \frac{1}{|m|} x (1 - x^2)^{-1} P_l^{\text{inl}}(x) \]  \hspace{1cm} (A3.1.37)

\[ \frac{d}{d\theta} P_l^{\text{inl}}(\cos \theta) = |m| \frac{\cos \theta}{\sin \theta} P_l^{\text{inl}}(\cos \theta) - P_l^{\text{inl+1}}(\cos \theta) \]  \hspace{1cm} (A3.1.38)

Integral properties

\[ \int_{-1}^{1} \left[ P_l^{\text{inl}}(x) \right]^2 dx = \frac{2}{(2l + 1)(l - |m|)!} \]  \hspace{1cm} (A3.1.39)

\[ \int_{0}^{\pi} \left[ P_l^{\text{inl}}(\cos \theta) \right]^2 \sin \theta d\theta = \frac{2}{(2l + 1)(l - |m|)!} \]  \hspace{1cm} (A3.1.40)

L’Hôpital’s rule [27]

L’Hôpital’s rule is used to evaluate the formally indeterminate limiting form \((0/0)\). If there are two differentiable functions \(f(x)\) and \(g(x)\) such that \(f(0) = g(0) = 0\), then L’Hôpital’s rule states that

\[ \lim_{x \to 0} \left[ \frac{f(x)}{g(x)} \right] = \frac{f'(0)}{g'(0)} \]  \hspace{1cm} (A3.1.41)

where the prime indicates differentiation with respect to the argument \(x\). If \([f'(0)/g'(0)] = (0/0)\) then L’Hôpital’s rule should be applied again, provided \(f''(x)\) and \(g'(x)\) are differentiable.
Chapter 4  Non-ideality and the Application of Perturbation Theory

4.1 Introduction

This chapter explains the differences between the resonant behaviour of practical spherical and cylindrical cavity resonators and the corresponding idealised cavities discussed in chapter 3. Section (4.2) contains an outline of common sources of non-ideality encountered, the most important of which, for the measurements taken in this work, is the compliance of the resonators, discussed in section (4.3). First order perturbation theory is considered in section (4.4), and a number of applications of the theory are presented in subsequent sections. Section (4.5) considers the perturbation due to the finite conductivity of the boundary wall, section (4.6) is concerned with smooth departures from perfect geometry, and localised boundary shape deformations, such as indentations or openings, are discussed in section (4.7). An original method of calculating the effect of openings in a cavity resonator wall is presented in section (4.7), and the theory is shown to be in excellent agreement with experimental measurements on the cylindrical resonator. Section (4.8) deals with the perturbation caused by the external coupling of a resonator, and, in section (4.9), the effects of energy losses in the material within a cavity resonator are explained. The chapter closes with an assessment of the relative importance of the corrections for the various sources of non-ideality, presented in section (4.10).

4.2 Non-ideality

For an ideal cavity resonator, the medium is perfectly loss-free, the walls are perfectly conducting and perfectly smooth, and there is not even the smallest of openings through which radiation may occur. There are, then, no mechanisms for energy loss and so the resonances of an ideal cavity would be perfectly sharp. Further, the ideal cavity resonator has perfect geometry and there are no discontinuities in the boundary wall to perturb the electromagnetic fields. The fields will be exactly as calculated in chapter 3 and any degeneracies will be perfectly preserved. If we imagine being able to excite and detect the resonances of an ideal...
cavity, we would find that the resonance frequencies could be determined with perfect precision.

The situation with practical cavity resonators is, of course, somewhat different. Practical resonators are made of a material which has a high, but finite, electrical conductivity and this gives rise to energy losses in the walls [8, 11]. The geometry will not be perfect, even with highly-skilled machining, and so degeneracies will be partially, or fully, lifted [23, 24, 28]. Resonators are made in at least two pieces which are joined together to form the enclosed cavity, and imperfect alignment will give rise to further geometric deformations. For a resonator to be useful, there must be a number of openings made in the wall; these allow the resonator to be filled with a gas sample, and subsequently evacuated, and allow coupling structures (e.g., probe antennae) to be inserted so that the resonances can be excited and detected. Indeed, the connection of a resonator to the instrumentation necessary to make the measurements, demands that factors external to the resonator itself be taken into account [11, 29, 30]. Finally, the gas in a practical cavity will not be perfectly loss-free, as is assumed to be the case in an ideal resonator. These many sources of non-ideality give rise to energy loss and shift the resonance frequencies from the calculated ideal cavity values. We observe, then, shifted resonances with a finite halfwidth.

Exact solutions for non-ideal cavities would be difficult to calculate and cumbersome to use, and so an alternative approach is taken. This involves relating the resonance frequencies of a practical resonator, which can be measured, to those of the corresponding ideal cavity by treating the sources of non-ideality as perturbations on the ideal cavity solutions and calculating the effects using perturbation theory. The calculated corrections are applied to the measured resonance frequencies to obtain estimates of the ideal cavity resonance frequencies.

The sources of non-ideality in practical resonators give rise to complex resonance frequencies $F_N$, which are related, using first order perturbation theory, to the purely real resonance frequencies of the ideal cavity $f_N^0$ by [31, 32]

$$F_N = f_N + ig_N = f_N^0 + \sum_j \left( \Delta f_j + ig_j \right)_N$$

(4.2.1)

In equation (1), $N$ is equal to the mode indices $lmn$ for a spherical resonator mode and $pq$s for a cylindrical resonator mode, $f_N$ is a measured resonance frequency of
the practical resonator and $g_N$ is the corresponding resonance halfwidth, defined in
this work as half the resonance linewidth at half maximum power, which is a
measure of total energy loss in the system for the mode in question [11]. The
summation in equation (1) is taken over the number of different perturbations to the
cavity resonator which give rise to the shifts in resonance frequency $\Delta f_j$ and
contributions to the resonance halfwidth $g_j$ for a mode characterised by the mode
indices $N$.

A quality factor $Q_N$ can be calculated for each mode of a practical cavity
resonator: it is defined as [11]

$$Q_N = \frac{f_N}{2g_N}$$  \hspace{1cm} (4.2.2)

and is a measure of the sharpness of the resonance. The energy losses that arise due
to the different perturbations are additive [11] and so the total halfwidth $g_N$ of a
mode is the sum of the individual contributions $g_j$:

$$g_N = \sum_j g_j$$  \hspace{1cm} (4.2.3)

Therefore the mode quality factor $Q_N$ is given by [11]

$$\frac{1}{Q_N} = \sum_j \left( \frac{1}{Q_j} \right)_N$$ \hspace{1cm} (4.2.4)

where $Q_j$ is the quality factor for an individual perturbation to the resonance. In
reality, the resonator is difficult to characterise accurately enough to take account of
all sources of energy loss and so we obtain a calculated halfwidth $g_N^{\text{calc}}$, which is
equal to the sum of the calculated halfwidth contributions from the perturbations that
are actually considered. The difference between the measured and calculated
halfwidth, $(g_N - g_N^{\text{calc}})$, is called the excess halfwidth of the mode, and it would be
zero if all losses were brought to account. In any case, the excess halfwidth of a
resonance is a measure of the ignorance of the loss mechanisms in the resonator.

The rest of this chapter is concerned with the estimation of the first order shifts
in resonance frequency $\Delta f_j$ and the halfwidth contributions $g_j$, for the modes of
cylindrical and spherical cavity resonators, caused by the most significant
perturbations.
The first source of non-ideality to be considered, however, is not treated as a perturbation and its effects are simple to calculate without recourse to perturbation theory. It is however, the most important correction to be considered in this work and so is included here rather than elsewhere, and is presented first.

4.3 Compliance

If the pressure exerted on the internal surface of the wall of a resonator exceeds the pressure exerted on the external surface then the resonator will dilate. The increase in the cavity dimensions will depend on the original dimensions, the mechanical properties of the material from which the resonator is constructed, at the temperature of operation, and the internal and external pressures. If the resonator is pressure-compensated, where the internal and external pressures are equal, there will still be a change in the cavity dimensions. In fact, the dimensions will decrease since the external surface area of the resonator wall must be larger than the internal surface area and so there will be a resultant force, directed inwards. However, in this case, the change in dimensions is smaller than would be found if the internal and external pressures were unequal. The fractional change in a dimension per unit increase in pressure is the compliance \( \chi \), and this can be calculated for the dimensions of a spherical and cylindrical shell using formulae given in the literature [33, 34]. Both of the resonators used in this work are considered thick-walled shells, by the definition of reference 33, in that the wall thickness of each resonator is greater than one-tenth of its radius.

The Sphere

In operation, the sphere was subjected to a uniform internal gas pressure \( p \), whilst the outer surface of the wall was maintained under vacuum. Assuming that the spherical wall is perfectly isotropic, this gives rise to a uniform dilation, where the fractional increase in the internal radius \( a \) relative to the vacuum-radius \( a_0 \) is given, correct to first order, by

\[
\frac{(a - a_0)}{a_0} = \chi p
\]

(4.3.1)
where $\chi$ is the compliance given by [33]

$$\chi = \frac{1}{E} \left[ \frac{(1-\sigma)(b^3 + 2a^3)}{2(b^3 - a^3)} + \sigma \right]$$

(4.3.2)

In equation (2), $E$ is the Young's modulus or modulus of elasticity of the wall material (Aluminium alloy 6082, condition T6, for the sphere used in this work) at the temperature of interest, $\sigma$ is Poisson's ratio for the wall material, $b$ is the external radius of the sphere at pressure $p$, and $a$ is the internal radius of the sphere at pressure $p$. The resonance frequencies of an ideal spherical cavity are inversely proportional to $a$, and so the presence of a gas, with a dielectric constant of unity, at a pressure $p$ inside the cavity, will reduce the resonance frequencies by a factor $\left[1/(1 + \chi p)\right]$ relative to the corresponding resonance frequencies of the cavity when evacuated, if the external surface of the spherical wall is maintained under vacuum. The fractional shift in any resonance frequency is therefore

$$\frac{\Delta f_x}{f^\|_N} = -\frac{\chi p}{(1 + \chi p)}$$

(4.3.3)

if the external surface of the spherical resonator is maintained under vacuum. The shift in resonance frequency $\Delta f_x$ is to be subtracted from a measured resonance frequency to give an estimate of that resonance frequency in absence of dilation. That is,

$$f^\|_N = f_N + \frac{f_N \chi p}{(1 + \chi p)}$$

(4.3.4)

where $f^\|_N$ is a (corrected) cavity resonance frequency in absence of dilation and $f_N$ is the resonance frequency of the same mode in the dilated resonator. In practice, the correction was estimated as $-\Delta f_x = [f_N \chi p/(1 + \chi p)]$ since we did not know $f^\|_N$, but $f_N$ was close enough to $f^\|_N$ to make no significant difference.

The internal radius of the evacuated sphere $a_0$ over a range of temperatures between $T = 90.06$ K and $T = 373.15$ K has been determined with a fractional uncertainty of 2 to 3 ppm (1 ppm = $1.0 \times 10^{-6}$) using speed of sound measurements in argon [35], and this can be used as an estimate of $a$ in equation (2) without introducing significant error. A linear regression of $\ln(a_0/m)$ on the Celsius
temperature \((t/°C)\), where \((t/°C) = (T/K) - 273.15\), using the data given in reference 35, gave

\[
\ln(\alpha_0 / m) = -(3.2190778 ± 0.0000094) + (2.273 ± 0.011) \times 10^5 (t / °C) + (1.32 ± 0.12) \times 10^4 (t / °C)^2 - (6.09 ± 0.82) \times 10^{11} (t / °C)^3 \quad (4.3.5)
\]

Equation (5) fitted the data with an overall standard deviation of \(\ln(\alpha_0 / m)\) of \(12 \times 10^6\). This is approximately five times as large as the uncertainty in an individual value of \(\ln(\alpha_0 / m)\), propagated from the estimated experimental uncertainty in \(\alpha_0\), because there was large curvature in \(\alpha_0(T)\) at \((T / K) \leq 118.88\), which was difficult to accommodate with such a polynomial fit. Higher terms in \((t/°C)\) were not individually significant, even at the 0.95 probability level, although the addition of a \((t/°C)^4\) term reduced the overall standard deviation to \(5 \times 10^6\). However, equation (5) can be expected to give \(\alpha_0\) with an estimated fractional uncertainty of \(12 \times 10^6\), for \(90.06 ≤ T / K ≤ 373.15\), which is more than sufficient for estimating \(\chi\) in equation (2), since such a small uncertainty contributes only \(29 \times 10^6\) to the fractional uncertainty of \(\chi^1\).

The wall thickness was known to be \((10.2 ± 0.1) mm\) [36], giving an external radius of \(b = (\alpha_0 + 10.2 mm) ± 0.1 mm\), and this uncertainty contributes only 0.5% to the fractional uncertainty of \(\chi\). Poisson's ratio \(\sigma\) was taken to be 0.355, which is the value for aluminium given in reference 5, and was assumed independent of temperature over the range of interest. Values of Young's modulus \(E\), at seven temperatures between \(T = 80\) K and \(T = 350\) K, were obtained from reference 37 where the individual values are estimated to have a fractional uncertainty of better than \(±5\%\). Linear regression of these values of \((E / GPa)\) on \((t/°C) = (T/K) - 273.15\) gave

\[
(E / GPa) = (71.59 ± 0.21) - (0.0381 ± 0.0018) (t/°C) \quad (4.3.6)
\]

Equation (6) fitted the data with a standard deviation of \(0.46\) GPa, which is only 0.7% of the smallest individual value of \(E\) (68 GPa at 350 K), and therefore much smaller than the estimated uncertainty in the individual values of \(E\) from which equation (6) is obtained. Higher terms in \((t/°C)\) did not significantly reduce the standard deviation of the fit, even at the 0.95 probability level. Equation (6) can,

\footnote{Uncertainties quoted in this work are at the one standard deviation level unless otherwise indicated.}
therefore, be expected to provide $E$, with an estimated fractional uncertainty of ±5 %, over the temperature range $80 \leq T / K \leq 350$, and a short extrapolation to the highest temperature used in this work, 360.3 K, should be possible without significantly increasing the uncertainty. The fractional uncertainty in $E$ makes a similar contribution to the fractional uncertainty in $\chi$, and so it is estimated that the fractional resonance frequency shift given in equation (3) can be calculated accurate to about ±5 %. For example, at 273 K, $\chi$ is calculated to be $(23.4 \pm 1.2) \times 10^{-12}$ Pa$^{-1}$, and so, at the highest experimental pressure of 800 kPa, $(\Delta f_x / f_N^a) = -(18.7 \pm 0.9)$ ppm where the uncertainty is likely to be rather pessimistic.

A second order correction to equation (1), which arises if we include the pressure-dependence of the compliance ($\chi$ depends on $a$ and $b$ which are, themselves, pressure-dependent), contributes only $-4 \times 10^{-10}$ to $(\Delta f_x / f_N^a)$ at 273 K for a pressure of 800 kPa.

The cylinder

The cylindrical resonator was designed to be pressure-compensated in use, which means that the same gas pressure was exerted on the internal and external surfaces of the resonator wall. However, the larger external surface area leads to an imbalance of forces on the cylinder wall, even though the internal and external pressures are equal, and the cylinder contracts when pressurised. Considering the resonator as a perfectly cylindrical, thick-walled shell with capped ends, subject to a uniform pressure $p$ inside and outside, the fractional change in internal radius $a$ and internal length $L$ is given by

$$\left(\frac{a-a_0}{a_0}\right) = \left(\frac{L-L_0}{L_0}\right) = \chi P$$  \hspace{1cm} (4.3.7)

where $\chi$ is the compliance, given by [33]

$$\chi = -\frac{(1-2\sigma)}{E}$$  \hspace{1cm} (4.3.8)
In equation (7), \( a \) and \( L \) are the internal radius and internal cavity length at pressure \( p \) and \( a_0 \) and \( L_0 \) are the radius and length when the system is under vacuum. In equation (8), \( \sigma \) is Poisson’s ratio and \( E \) is Young’s modulus for the wall material.

For the pressure-compensated cylinder, \( \chi \) is negative, because the cylinder contracts under pressure, and it is independent of the cavity dimensions, so we do not need accurate measurements of \( a \) and \( L \) to estimate the fractional shift in the resonance frequencies. The resonance frequencies of an ideal cylindrical cavity are given by

\[
\frac{f^0_{pq}}{c} = \sqrt{\left( \frac{Z_{pq}}{2\pi a} \right)^2 + \left( \frac{s}{2L} \right)^2},
\]

where \( Z_{pq} \) represents a TM or TE mode eigenvalue, and it is simple to show that the fractional shift in the resonance frequencies, caused by the contraction, is given by equation (3), where, in this case, \( \left( \frac{\Delta f_x}{f^0_N} \right) > 0 \) because \( \chi < 0 \). Thus, the corrected resonance frequencies, in absence of the contraction, are given by equation (4), although, just as was seen with the sphere, the actual correction applied was \( -\Delta f_x = f_N \chi p / (1 + \chi p) \) since \( f_N \equiv f^0_N a_{\chi} \).

The cylindrical resonator was machined from an extruded rod of free-cutting brass BSS 2874 CZ 121, and, for this type of brass, values of the Young’s modulus \( E \) are available at only two different temperatures [38, 39]. Fortunately, these two temperatures are \( t = -30 \, ^\circ\text{C} \) (at which \( E = 97.3 \, \text{GPa} \)) and \( t = +20 \, ^\circ\text{C} \) (at which \( E = 95.7 \, \text{GPa} \)), both of which lie within the experimental temperature range, and, on advice from the Copper Development Association, Young’s modulus was estimated, at intermediate temperatures, by assuming a linear decrease in \( E \) with increase in the Celsius temperature \( t \). Hence \( E \) was estimated from the equation

\[
(E / \text{GPa}) = 96.34 - 0.032 (t/\degree\text{C}) \tag{4.3.9}
\]

This equation was applied over the temperature range of measurements with the cylinder in this work (-30 °C to +50 °C), and it is reasonable to estimate that equation (9) gives \( E \), within this temperature range, with a fractional uncertainty of \( \pm2\% \), at worst, since there is very little change in \( E \) over the range of interest and the published values of \( E \), at -30 °C and +20 °C, have an estimated fractional uncertainty of \( \pm1\% \). Poisson’s ratio \( \sigma \) was taken to be 0.35 [38] and was assumed to be independent of temperature.
At 273 K, \( \chi \) is calculated to be \((-3.11 \pm 0.06) \times 10^{12} \text{ Pa}^{-1} \), which is nearly a factor of eight smaller in magnitude than that calculated for the sphere at the same temperature. The Young’s modulus of the brass is only about 34% larger than that of Aluminium alloy 6082 at the same temperature, so clearly the huge reduction in the magnitude of the compliance is principally due to pressure-compensation. It is noted, in this respect, that if the external surface of the cylinder were maintained under vacuum then the compliance would be approximately \(+24 \times 10^{12} \text{ Pa}^{-1} \), assuming the nominal dimensions \( a = 9.5 \text{ mm}, \ L = 20 \text{ mm} \). For the pressure-compensated cylinder used in this work, the fractional shift in a resonance frequency at 273 K and a pressure of 4 MPa is calculated to be \(+\left(12.4 \pm 0.2\right) \text{ ppm} \). For the uncompensated cylinder at this pressure we could expect a fractional shift of approximately \(-96 \text{ ppm} \). Pressure compensation offers the benefits of smaller corrections and, consequently, smaller contributions to the overall uncertainty in \( f_N^{\text{u},\text{i}} \), estimates. There are also benefits to be had with respect to mechanical stability, but these will be discussed in chapter 6.

### 4.4 Perturbation theory

Cavity perturbation theory is used to relate the resonance frequencies of a non-ideal resonator to those of the corresponding ideal resonator. For the theory to be reliably applied, the sources of non-ideality (the perturbations) must be either very small over a large region (e.g. the ideal resonator has a perfectly conducting wall, the non-ideal has a wall with a high but finite conductivity) or large over a very small region (e.g. the ideal resonator has a smooth continuous wall, the non-ideal may have an indentation) for the theory to be reliably applied [8, 40].

If the unperturbed electric and magnetic fields, in the ideal cavity, are \( E_0 \) and \( H_0 \), respectively, and the corresponding perturbed cavity fields are assumed to be \( (E_0 + E_i) \) and \( (H_0 + H_i) \), then Waldron [8, 40] gives the fractional complex resonance frequency shift, for a given mode, due to any perturbation as

\[
\left( \frac{\Delta f_i}{f_N^0} \right) = \left( \frac{\Delta f_j + ig_j}{f_N^0} \right) = \frac{1}{2} \iiint_V \left\{ \left( E_i \cdot D_0 - E_0 \cdot D_i \right) - \left( H_i \cdot B_0 - H_0 \cdot B_i \right) \right\} dV
\]

\[
\frac{1}{2} \iiint_V \left\{ \varepsilon_0 |E|^2 + \mu_0 |H|^2 \right\} dV
\]

(4.4.1)
where the subscript \( j \) is used to label the individual perturbations, and the shift has been given correct to first order. \( D_0 \) and \( B_0 \) are the unperturbed electric and magnetic induction, respectively, and \( D_1 \) and \( B_1 \) are the additions to these for the perturbed cavity. The integrations in numerator and denominator are taken over the cavity volume \( V_0 \). Equation (1) assumes that the perturbation is small which requires that \( D_1 \ll D_0 \) and \( B_1 \ll B_0 \). In cases where \( D_1 \) and \( B_1 \) are large (e.g. an indentation in the wall), they are only so over a very small part of the cavity volume and so the integral in the numerator would remain small. The denominator of equation (1) is recognised as the total electromagnetic energy stored in the unperturbed cavity at resonance, which was discussed in chapter 3. The numerator represents the difference between the changes in the electric and magnetic field energy due to the perturbation.

The perturbation formula, equation (1), can therefore be understood in the following terms: a perturbation shifts the resonance frequency of a given mode because it causes a change in the balance between the energy stored in the electric and magnetic fields. In an unperturbed cavity at resonance, the time-averaged electric and magnetic field energies are equal. If there is a change in, say, the electric energy due to some perturbation then the fields adopt a new configuration so as to make the energies stored in the electric and magnetic fields equal again. This new field configuration will be reflected by a new and different resonance frequency.

### 4.5 Finite conductivity of the boundary wall

The boundary condition for an electric field dictates that the tangential component vanishes at the perfectly conducting boundary wall of an ideal cavity [16]. If the cavity wall has a high but finite electrical conductivity \( \sigma \), as would be the case for materials such as brass or aluminium alloy, then there will be a small tangential component of electric field at the boundary surface [11]. Maxwell’s equation (2.3.9) shows that, in this event, there must also be a small normal component of magnetic field at the boundary surface. These fields decay exponentially within the wall, the decay being characterised by a skin-depth \( \delta \), which is defined as the depth at which the tangential electric field has fallen to \( (1/e) \approx 0.37 \) of its initial value at the boundary surface. Clearly then, the electromagnetic fields can now penetrate the
wall, but are confined to a thin layer or skin with a thickness on the order of $\delta$. For monochromatic fields of frequency $f_N$ (a resonance frequency), the skin-depth is given by [8, 11]

$$
\delta = \left( \frac{1}{\pi f_N \mu \mu_0 \sigma} \right)^{\frac{1}{3}} \tag{4.5.1}
$$

where $\mu$ is the relative permeability of the boundary wall material and can be assumed equal to 1 for the materials used in this work without introducing any significant error.

The penetration of the electromagnetic fields into the boundary wall causes conduction currents to flow, within the skin-depth region, which dissipate energy. In addition, the field configurations will change to take account of the modified boundary conditions. Therefore, for any given mode, there will be both a contribution to the resonance halfwidth $g_\delta$ and a corresponding shift in the resonance frequency $\Delta f_\delta$. Applying the perturbation formula, equation (4.4.1), to this problem, Waldron [8] shows that, for any cavity operating in any mode, the fractional complex resonance frequency shift is given by

$$
\frac{\Delta f_\delta}{f_N^0} = \frac{\Delta f_\delta + ig_\delta}{f_N^0} = \frac{(-1 + i)\delta \int \mu_0 |H|^2 dS}{4W} \tag{4.5.2}
$$

where $W$ is the total energy stored in the cavity at resonance, $H$ is the unperturbed magnetic field in the cavity, and the integral in the numerator is taken over the boundary surface of the cavity. Therefore, the resonance frequency, of a given mode, is reduced by an amount equal to the halfwidth contribution, and so $\Delta f_\delta = -g_\delta$, where $g_\delta$ is related to the corresponding quality factor $Q_\delta$ by

$$
Q_\delta = \frac{f_N}{2g_\delta} = \frac{2W}{\delta \int \mu_0 |H|^2 dS} \tag{4.5.3}
$$

The total energy $W$ is equal to $\int \int \int \mu_0 |H|^2 dV$, as shown in chapter 3. Thus equation (3) becomes

$$
Q_\delta = \frac{2}{\delta} \left( \frac{I_\nu}{I_S} \right) \tag{4.5.4}
$$

where
\[ I_v = \iiint_{V} \mu_0 |H|^2 \, dV \]  
(4.5.5)

and

\[ I_s = \iint_{S} \mu_0 |H|^2 \, dS \]  
(4.5.6)

The sphere

It was seen in chapter 3 that general expressions for the total energy \( W \) of TM\( lnm \) and TE\( lnm \) sphere modes could not be obtained, but, rather, that \( W \) had to be evaluated for a particular mode or small family of modes. However this is not a problem here, and we can calculate \( (Q_\theta)N \) for all TM and TE modes whatever the values of \( N = lnm \), using equation (4). This is because the resulting integrals over the \( \theta \) and \( \phi \) coordinates cancel out in the numerator and denominator as will now be demonstrated.

TM\( lnm \) modes

The TM\( lnm \) mode field components, in an ideal spherical cavity, are given in equations (3.4.40) to (3.4.45) of chapter 3. The volume integral \( I_v \) is given by

\[ I_v = \mu_0 \iiint_{V} |H_\theta|^2 + |H_\phi|^2 \, dV \]  
(4.5.7)

since \( H_\theta = 0 \) for TM modes, and the surface integral \( I_s \) is given by

\[ I_s = \mu_0 \iint_{S} |H_\theta|^2 + |H_\phi|^2 \, dS \]  
(4.5.8)

For the sphere, the required surface and volume elements are \( dS = a^2 \sin \theta \, d\theta \, d\phi \) and \( dV = r^2 \, dr \, \sin \theta \, d\theta \, d\phi \), and the radial coordinate \( r \) in the surface integral \( I_s \) is put equal to the cavity radius \( a \). If the field components \( H_\theta \) and \( H_\phi \), as given by equations (3.4.44) and (3.4.45), along with the expressions for the volume and surface elements, are substituted into equations (7) and (8), then it becomes clear that the integral

\[
B^2 \frac{\omega^2 (\varepsilon \varepsilon_0)^2}{k^2} \mu_0 \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \left\{ \frac{m^2}{\sin^2 \theta} \left[ P_{lm}^{\text{ml}}(\cos \theta) \right]^2 \left( \sin m\phi - \cos m\phi \right)^2 \right. \\
+ \left[ \frac{d}{d\theta} P_{lm}^{\text{ml}}(\cos \theta) \right]^2 \left( \sin m\phi + \cos m\phi \right)^2 \right\} \sin \theta \, d\theta \, d\phi
\]
is common to both $I_N$ and $I_S$, and can, therefore, be cancelled out in the numerator and denominator of equation (4) for $Q_\delta$. If this is done, we are left with

$$Q_\delta = \frac{2}{\delta} \int_{r_0}^R r^2 j_1^2(kr)dr$$

where the $a^2$ in the denominator arises from the surface element $dS$. The integral in the numerator of equation (9) is given by equation (A3.1.25), and so, after rearrangement, equation (9) becomes

$$Q_\delta = \frac{a}{\delta} \left\{ 1 - \frac{l(l+1)}{\nu_m'^2} \right\}$$

where $\nu_m'$ is the TM$ln$ mode eigenvalue. Therefore, substituting the expression for $Q_\delta$ into equation (3), and rearranging, gives the contribution to the resonance halfwidth for TM$lnm$ sphere modes as [24]

$$g_\delta = \frac{f_N \delta}{2a} \left\{ 1 - \frac{l(l+1)}{\nu_m'^2} \right\}$$

and the corresponding resonance frequency shift is given by

$$\Delta f_\delta = -g_\delta = -\frac{f_N \delta}{2a} \left\{ 1 - \frac{l(l+1)}{\nu_m'^2} \right\}$$

**TE$lnm$ modes**

For the calculation of the halfwidth contribution for TE$lnm$ modes it is more convenient to calculate the total energy $W$, that appears in equation (3) for $Q_\delta$, by using

$$W = \iiint \varepsilon \varepsilon_0 |E|^2 dV$$

instead of the integral over magnetic fields used in the calculation of $Q_\delta$ for TM$lnm$ modes. Therefore, in the case of TE$lnm$ modes we have

$$I_N = \iiint \varepsilon \varepsilon_0 |E|^2 dV$$

and

$$I_S = \int \mu_0 |H|^2 dS$$

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In so doing, it is found that a common integral, over the angular coordinates $\theta$ and $\phi$, arises in $I_{\nu_s}$ and $I_{\gamma}$ which cancels out when they are substituted into equation (4). Using the $E$ and $H$ field components for TE$lmn$ modes from equations (3.4.49) to (3.4.54) in $I_{\nu_s}$ and $I_{\gamma}$, and substituting these into equation (4) gives

$$Q_s = \frac{2\varepsilon_0 \int_0^\infty J_i^2(\kappa r) r^2 dr}{\delta \frac{\varepsilon_0^2}{k^4} \frac{\mu_0}{[(\kappa a) j_i'(\kappa a)]^2}}$$  \hspace{1cm} (4.5.16)

where the integrals over $\theta$ and $\phi$ have cancelled out in numerator and denominator, and the characteristic equation for TE modes, $j_i(\kappa a) = 0$, has been used. The integral in the numerator is given by equation (A3.1.26), and the denominator is equal to $\delta \frac{\varepsilon_0^2}{k^4} (\kappa a)^2 j_i^2(\kappa a)$, where we have used $k^2 = \omega^2 \varepsilon_0 \mu_0$ and $j_i(\kappa a) = 0$ in order to simplify. Therefore

$$Q_s = \frac{2\varepsilon_0 \left(\frac{\kappa}{2}\right) j_i^2(\kappa a)}{\delta \frac{\varepsilon_0^2}{k^4} (\kappa a)^2 j_i^2(\kappa a)} = \frac{a}{\delta}$$  \hspace{1cm} (4.5.17)

and substituting this final expression for $Q_s$ into equation (3), and rearranging, gives the contribution to the halfwidth for TE$lmn$ sphere modes as [24]

$$\sigma_s = \left(\frac{f_N \sigma}{2a}\right)$$  \hspace{1cm} (4.5.18)

The corresponding resonance frequency shift is therefore

$$\Delta f_s = -\sigma_s = -\left(\frac{f_N \sigma}{2a}\right)$$  \hspace{1cm} (4.5.19)

In order to calculate the halfwidth contributions and the resonance frequency shifts due to the skin-depth perturbation, it is necessary to know the electrical conductivity $\sigma$ of the sphere wall material, aluminium alloy 6082 in the T6 condition. The reciprocal of the conductivity is the resistivity $\rho = (1 / \sigma)$, and this was estimated from the equation

$$10^8 (\rho / \Omega \text{ m}) = 3.938 \{1 + 0.00294 (t / {}^\circ \text{C})\}$$  \hspace{1cm} (4.5.20)

where $(t / {}^\circ \text{C}) = (T / \text{K}) - 273.15$, which is based on an equation, given in reference 28, for the resistivity of aluminium alloy 6081 in the T6 condition, derived from the
measurements of Clark et al. [41]. This alloy has the same condition and a very similar composition to alloy 6082, and can therefore be assumed to have a similar resistivity. Equation (20), and the equation from which it has been obtained, is derived from measurements of \( \rho \) between 77 K and 273 K, but the reported linearity of the measurements over this temperature range [41] gives weight to the assumption that equation (20) can be used to estimate \( \rho \) over the whole temperature range of the sphere measurements in this work (189 K to 360 K).

The cylinder

\textbf{TM}_{pqs} modes}

The calculation of \( Q_{\delta} \) for \textbf{TM}_{pqs} cylinder modes is similar to that for \textbf{TM}_{lnm} modes in the sphere. The volume integral \( I_{V_0} \) is given by

\[
I_{V_0} = \iiint \mu_0 |H|^2 dV
\]  

and the surface integral \( I_S \) by

\[
I_S = \iiint_\delta \mu_0 |H|^2 dS
\]

The \( H \) field components required for these integrals are found in equations (3.3.12) to (3.3.14). The volume integral is simply taken over the cavity volume \( V_0 \) and the volume element is \( dV = r dr d\theta dz \). The surface integral must be taken over the cylindrical wall where \( r = a \) and \( dS = a d\theta dz \), and also over the two end plate surfaces where \( z = 0, L \) and \( dS = r dr d\theta \).

If the appropriate substitutions are made in equations (21) and (22), and the resulting expressions for \( I_{V_0} \) and \( I_S \) are substituted into equation (4) for \( Q_{\delta} \), it becomes clear that the integrals over the \( \theta \) coordinate in the numerator and denominator of the resulting equation are equal and can thus be cancelled out. We are left with

\[
Q_{\delta} = \frac{1}{2} \int_{r=0}^{r=a} \left\{ \frac{p^2}{k^2 r^2} J_n^2(kr) + J_n^2(kr) \right\} \cos\left( \frac{s\pi z}{L} \right) r dr \frac{dz}{dz}
\]

\[
\frac{1}{a J_n^2(ka)} \int_{z=0}^{L} \cos^2\left( \frac{s\pi z}{L} \right) dz + 2 \int_{r=0}^{r=a} \left\{ \frac{p^2}{k^2 r^2} J_n^2(kr) + J_n^2(kr) \right\} r dr
\]  

\[
Q_{\delta} = \frac{1}{2} \int_{r=0}^{r=a} \left\{ \frac{p^2}{k^2 r^2} J_n^2(kr) + J_n^2(kr) \right\} \cos\left( \frac{s\pi z}{L} \right) r dr \frac{dz}{dz}
\]

\[
\frac{1}{a J_n^2(ka)} \int_{z=0}^{L} \cos^2\left( \frac{s\pi z}{L} \right) dz + 2 \int_{r=0}^{r=a} \left\{ \frac{p^2}{k^2 r^2} J_n^2(kr) + J_n^2(kr) \right\} r dr
\]  

(4.5.23)
where the first integral of the denominator has arisen from the surface of the cylindrical wall and the second integral from the two end plate surfaces. The remaining integrals in equation (23) are straightforward and are given by

\[
\int_{z=0}^{l} \cos^3 \left( \frac{s \pi z}{L} \right) dz = \frac{L}{2} \quad \text{for } s \neq 0
\]

and

\[
\int_{z=0}^{l} \cos^3 \left( \frac{s \pi z}{L} \right) dz = L \quad \text{for } s = 0
\]

and

\[
\int_{r=0}^{a} \left( \frac{p^2}{kr^2} J_\nu^2 (kr) + J_\nu^2 (kr) \right) r dr = \frac{a^2}{2} J_\nu^2 (ka)
\]

Equation (26) comes from the use of equation (A3.1.18), and recalling that \( J_\nu (ka) = 0 \) for TM modes. Making the appropriate substitutions in equation (23), and rearranging, gives

\[
Q_\delta = \frac{aL}{\delta (L+2a)} \quad \text{if } s \neq 0
\]

\[
Q_\delta = \frac{aL}{\delta (L+a)} \quad \text{if } s = 0
\]

The halfwidth contribution and resonance frequency shift are therefore

\[
\Delta f_\delta = -g_\delta = -\frac{f_\nu \delta (L+2a)}{2aL} \quad \text{if } s \neq 0
\]

\[
\Delta f_\delta = -g_\delta = -\frac{f_\nu \delta (L+a)}{2aL} \quad \text{if } s = 0
\]

TE\( pqs \) modes

Inspection of the \( H \) field components for TE\( pqs \) modes, given in equations (3.3.18) to (3.3.20), reveals that, in a calculation of \( Q_\delta \) using the current method, the integrals over the \( \theta \) coordinate would cancel out in numerator and denominator of equation (4), just as was seen for TM\( pqs \) modes. Therefore, the \( \theta \)-dependence of the field components need not be included in the calculations. The method is exactly as for the TM mode calculation and requires the use of equation (A3.1.18) where, this time, \( J'_\nu (ka) = 0 \) since TE modes are now being treated. The final result for \( \Delta f_\delta \) and \( g_\delta \) is
\[ \Delta f_s = -g_s = -\frac{f_s \delta \left\{ \frac{ak^2 L + \frac{p^2 s^2 \pi^2}{k^2 aL}}{L^2} \left( 1 - \frac{p^2}{\chi_{pq}^2} \right) \right\}}{2a^2 L \left( 1 - \frac{p^2}{\chi_{pq}^2} \right) \omega^2 \varepsilon_\varepsilon_0 \mu_0} \]  

(4.5.31)

where \( \chi_{pq} \) is the \( TE_{pq} \) mode eigenvalue. The mode index \( s \) cannot be zero for \( TE_{pq} \) modes.

The electrical conductivity \( \sigma \) of the free-cutting brass BSS 2874 CZ121, of which the cylindrical resonator was made, was estimated using data supplied by the Copper Development Association [38]. The electrical resistivity \( \rho = (1 / \sigma) \) at 20 °C is \( 6.25 \times 10^8 \ \Omega \cdot m \), and the temperature coefficient of resistivity between 0 °C and 100 °C is \( +0.0017 \ \degree C^{-1} \). Therefore, the resistivity between 0 °C and 100 °C can be estimated from the equation

\[ 10^8 \left( \frac{\rho}{\Omega \cdot m} \right) = 6.25 \left\{ 1 + 0.0017 \left[ (t / \degree C) - 20 \right] \right\} \]  

(4.5.32)

The resistivity at \(-30 < t / \degree C < 0\) was also estimated using equation (32), where the linearity of \( \rho \), shown by equation (32), has been assumed to extend below 0 °C. The conductivity was then simply obtained from \( \sigma = (1 / \rho) \).

4.6 Smooth departures from perfect geometry

The fractional resonance frequency shift, for a given mode, due to a deformation of the resonator which removes a volume \( \Delta V \) from the unperturbed cavity volume \( V_0 \) by pushing in the boundary wall is given by [11, 19, 23]

\[ \frac{\Delta f}{f_0} = \frac{1}{2} \iint_{\Delta V} \left( \mu_0 |H|^2 - \varepsilon_\varepsilon_0 |E|^2 \right) dV \]  

\[ = \frac{1}{2} \iint_{\Delta V} \left( \varepsilon_\varepsilon_0 |E|^2 + \mu_0 |H|^2 \right) dV \]  

(4.6.1)

where the integral in the numerator is taken over the excluded volume \( \Delta V \) which lies between the boundary surfaces of the perturbed and unperturbed cavities, and the denominator is recognised as the total energy stored in the unperturbed cavity.

Equation (1) can be derived from the general perturbation formula, equation (4.4.1), by employing the boundary conditions for \( D, E, B \) and \( H \) at a perfectly conducting surface, to find that \( D_1 = H_1 = 0, E_1 = -E_0 \) and \( B_1 = -B_0 \) [8]. Equation (1) gives a purely real resonance frequency shift, since it considers deformations of a perfectly
conducting boundary wall and these will not give rise to energy losses. Therefore, provided only small deformations of the perfectly conducting wall of an ideal cavity are being considered, there will be no contribution to the resonance halfwidths. However, if holes are made in the boundary wall then there may be a contribution to the halfwidth arising from radiative loss [12, 42]; this will be considered in section (4.7).

Equation (1) can be used to calculate the effects of smooth departures from the perfect geometry of ideal cavities, such as are caused by imperfect machining, as well as more abrupt, localised deformations, such as those due to holes, indentations or protrusions (e.g. antennae). However, it will prove useful to consider these perturbations separately. This is principally because the effects of smoothly-varying geometric deformations on acoustic resonances have been considered in some detail by other workers and the equations that describe acoustic and microwave resonances in the same cavities are sufficiently similar that it is profitable to work by analogy with the published work rather than begin anew. Also, the treatment of the more abrupt, localised deformations can be simplified by the assumption that the fields remain approximately constant over the perturbed region $\Delta V$; this is not the case for the smooth departures from perfect geometry which usually occur over a much larger region of the boundary wall. The effects of smooth departures from ideal geometry are considered in this section. The effects of localised deformations such as small indentations, holes or protrusions are considered in section (4.7).

**The sphere**

Boundary shape perturbation theory has been successfully applied by Mehl [43, 44] to estimate the effects of smoothly-varying geometric imperfections on the resonance frequencies of spherical acoustic resonators. The perturbed surface is described by a function

$$r(\theta, \phi) = a \left(1 - \varepsilon \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} Y_{lm}^{*}(\theta, \phi)\right)$$

(4.6.2)

where $r$ is the internal radius of the deformed sphere at a point on the perturbed surface, $a$ is the internal radius of the corresponding unperturbed (geometrically perfect) sphere, $\varepsilon$ is a small, positive parameter that indicates the magnitude of the...
deformation and the coefficients $c_{lm}$ describe its shape. The $Y_{lm}(\theta, \phi)$ are the spherical harmonics and the terms $c_{lm} Y_{lm}(\theta, \phi)$ are generally of order unity. The $c_{0m}$ terms in equation (2) describe a change in the volume of the sphere, which would lead to the same fractional shift for all modes, and this will be zero for volume-preserving deformations.

Mehl shows that the resonance frequencies of the non-degenerate $l = 0$ acoustic modes are unaffected, to first order in $\epsilon$, by any smooth deformation that does not change the cavity volume; the first non-zero fractional shift in the resonance frequencies is on the order of $\epsilon^2$. With high quality machining, $\epsilon$ is generally on the order of $5 \times 10^{-4}$ (i.e. the cavity is spherical to within about 1 part in 2000) [36, 45-48] and fractional shifts on the order of $\epsilon^2$ (typically 0.25 ppm) are small compared to usual experimental accuracy.

The situation for degenerate modes ($l \geq 1$) is more complicated. Although the individual $(2l + 1)$ components of an acoustic mode characterised by the mode index $l$ will suffer resonance frequency shifts of order $\epsilon$, the average fractional shift in resonance frequency of all $(2l + 1)$ components is zero, to first order in $\epsilon$, for smooth, volume-preserving deformations [44]. This most important result means that if one can determine the perturbed resonance frequencies of all $(2l + 1)$ individual components of the mode, then the average of these is equal to the corresponding unperturbed (geometrically perfect) cavity resonance frequency to order $\epsilon^2$. Thus the average resonance frequency of a set of $(2l + 1)$ components is no more sensitive to geometric imperfections than are the resonance frequencies of the $l = 0$ non-degenerate modes [44].

A similar result has been obtained, by Mehl and Moldover [23], for the resonant modes of a spherical microwave cavity resonator. There are no $l = 0$ non-degenerate modes in the microwave cavity, but it has been demonstrated that the average resonance frequency shift of a microwave multiplet of $(2l + 1)$ components is zero, to first order in $\epsilon$, for all perturbations which do not change the cavity volume. This result is of great significance, but demands that the individual resonance frequencies of all $(2l + 1)$ components of a given multiplet be unambiguously determined for its application. In practice, this may be difficult despite the detail revealed in the experimental resonances due to the very high quality factors of the microwave
modes. It is therefore useful to know the estimated first order shifts of the individual components within a microwave multiplet since it should be simpler to measure the resonance frequency of a single chosen component than all \((2l + 1)\) components. Further, theoretical knowledge of the first order shifts, combined with experimental measurements, can provide information on the very small second order shifts of the mean multiplet resonance frequencies [44].

The first-order fractional resonance frequency shifts of the individual components of acoustic modes with \(l = 1\) and \(l = 2\) has also been considered in some detail by Mehl [44] for a number of common geometric deformations which preserve the volume of the spherical cavity. A spherical resonator is machined in two hemispherical pieces which are subsequently joined together. It is likely that, individually, the two hemispheres are highly axisymmetric, provided there was no wobble in the spindle whilst machining. However, during machining, it is useful to have a cylindrical extension at the ‘equator’ of each hemisphere, and this has to be subsequently cut off by the machinist, perpendicular to the axis of the hemisphere and at the correct distance from the ‘pole’. It is likely that the extension will be cut off too long or too short, albeit by a very small amount. This may produce a sphere where the polar diameter is different to the equatorial diameter, and such deformations are described by a \(c_{20}\) term in equation (2) [44]. Another common geometric deformation can occur if, in joining the two hemispherical pieces together, there is some misalignment, giving shoulders at the equatorial join. This would produce a sphere which has imperfect axial symmetry overall even though the individual hemispheres may, themselves, show axial symmetry; such deformations are described by a \(c_{21}\) term in equation (2) [44]. The first proposed deformation, where only the equatorial and polar diameters differ, still retains overall axial symmetry, and so the \((2l + 1)\) degeneracy is only partially removed to give \((l + 1)\) degeneracy [44]. For example, if acoustic \(l = 1\) modes are considered, the triply degenerate multiplet in the unperturbed sphere becomes a singlet and a degenerate doublet. The singlet will be at the higher frequency if the polar diameter is smaller than the equatorial diameter and vice-versa. The second proposed deformation, where there is misalignment of the two hemispheres, is non-axisymmetric and the \((2l + 1)\) degeneracy is completely lifted [44]. For example, if \(l = 1\) modes are
considered, the triply degenerate multiplet in the unperturbed sphere becomes three
discrete, non-degenerate singlets in the perturbed sphere - one component is shifted
to lower frequency, one to higher frequency by the same amount, and one component
is unaffected.

Published material on the resonance frequency shifts of the individual \((2l + 1)\)
components of a microwave mode is more scarce. Working by analogy with Mehl's
acoustic work [44], Boyes, Ewing and Trusler [28] have calculated the fractional
shifts in resonance frequency of the components of a TM \(1n\) mode for volumepreserving deformations. In this case, only terms in \(c_{20}\) and \(c_{21}\) need to be considered
and the fractional shifts are given, correct to first order, by

\[
\frac{\Delta f_{1mn}^0}{f_{1n}^0} = \frac{f_{1mn} - f_{1n}^0}{f_{1n}^0} = -\frac{\epsilon c_{20} \lambda_m}{2\sqrt{20\pi}} \left( \frac{\nu_{1n}^2 + 4}{\nu_{1n}^2 - 2} \right)
\]

(4.6.3)

where \(f_{1n}^0\) is the unperturbed TM \(1n\) mode resonance frequency, \(\nu_{1n}\) is the TM \(1n\)
mode eigenvalue and \(\lambda_m\), where \(m = 0, \pm 1\), is given by

\[
\lambda_0 = -1
\]

\[
\lambda_1 = \frac{1}{2} + \frac{3}{2} \sqrt{1 + \frac{3}{8} \left( \frac{c_{21}}{c_{20}} \right)^2}
\]

\[
\lambda_{-1} = \frac{1}{2} - \frac{3}{2} \sqrt{1 + \frac{8}{3} \left( \frac{c_{21}}{c_{20}} \right)^2}
\]

(4.6.4)

Equation (3) is in accordance with the expression given in reference 24, where only
axisymmetric deformations are considered. The sign of \((\Delta f / f_{1n}^0)\), for the TM \(1n\)
mode components, is opposite in sign to that for the acoustic \(\{1,n\}\) mode
components, but the fractional shifts are of similar magnitude [24, 44].

For axisymmetric shape perturbations, \(c_{21}\) will be zero and equations (4) give
\(\lambda_0 = \lambda_{-1} = -1\) and \(\lambda_{+1} = +2\). Therefore the degeneracy of the three components will
be only partially lifted since \(\lambda_0 = \lambda_{+1} = -1\) and so the perturbed resonance frequencies
will be

\[
f_{1n-1} = f_{1n0} = f_{1n}^0 \left[ 1 + \frac{\epsilon c_{20}}{2\sqrt{20\pi}} \left( \frac{\nu_{1n}^2 + 4}{\nu_{1n}^2 - 2} \right) \right]
\]

(4.6.5)

\[
f_{1n+1} = f_{1n}^0 \left[ 1 - \frac{2\epsilon c_{20}}{2\sqrt{20\pi}} \left( \frac{\nu_{1n}^2 + 4}{\nu_{1n}^2 - 2} \right) \right]
\]

(4.6.6)
demonstrating that a two-fold degeneracy is retained for axisymmetric shape perturbations.

Therefore, for an axisymmetric perturbation, it is expected that a degenerate doublet and a separate singlet will be observed in measured TM_{1n} resonances. This has been confirmed experimentally by measurements using the same aluminium alloy sphere as was used in this work [28]. From measurements on the TM_{11} mode, it was possible to estimate $\varepsilon c_{20}$ as $(+114 \pm 3) \times 10^6$, where the plus sign corresponds to the observation that the singlet occurred at lower frequency than the assumed doublet. The ordering of components as low frequency singlet and high frequency doublet was arrived at by comparing the measured halfwidths with those estimated from the theory of the skin-depth perturbation, and by attempting data fits which considered all three components within the multiplet rather than treating the singlet as one component and the (nearly) degenerate doublet as another. The details of such analyses are explained further in chapter 7.

The fractional resonance frequency shifts, due to axisymmetric deformations, for the components of a TE_{1n} mode are given in reference 24 in the form $(f_{\text{singlet}} - f_{\text{doublet}})/f_{1n}^0$ and are

$$\left( \frac{f_{\text{singlet}} - f_{\text{doublet}}}{f_{1n}^0} \right) = -\frac{3 \varepsilon c_{20}}{2\sqrt{20\pi}}$$

(4.6.7)

which implies that the individual fractional shifts for the components are

$$\frac{\Delta f_{1mn}}{f_{1n}^0} = \frac{f_{1mn} - f_{1n}^0}{f_{1n}^0} = -\frac{\varepsilon c_{20} \lambda_m}{2\sqrt{20\pi}}$$

(4.6.8)

where $f_{1n}^0$ is the unperturbed TE_{1n} mode resonance frequency and $\lambda_m$, where $m = 0, \pm 1$, is given by $\lambda_0 = \lambda_{-1} = -1$ and $\lambda_{+1} = +2$. The derivation of equation (8) from equation (7) has relied on the requirement that the fractional shift of the singlet is twice as large as that of the (degenerate) doublet, which must be satisfied if the average resonance frequency shift is to remain zero to first order in $\varepsilon$.

The calculated fractional resonance frequency shifts of the components of microwave modes with $l \geq 2$ have not been published. However, certain features of the predicted shifts can be reliably deduced by analogy with the theory for acoustic modes [44], just as has been demonstrated for the $l = 1$ modes. Axisymmetric shape perturbations will give rise to a partially lifted $(l + 1)$ degeneracy so, for an $l = 2$
microwave mode, given sufficient resolution, we should observe three ‘peaks’ in the experimental response: one will consist of a single component and the other two will both be degenerate doublets. By inference from the calculations for the \( l = 1 \) microwave modes \([\text{equations (5) to (8)}]\), the single component will appear at higher frequencies if \( c_{20} < 0 \), which corresponds to the polar diameter being larger than the equatorial diameter. For non-axisymmetric perturbations the degeneracy will be fully lifted, although the degeneracy of the doublet furthest removed from the singlet will not be removed so much as that of the doublet nearest in frequency to the singlet, for a given degree of non-axisymmetric perturbation.

A similar set of observations for \( l = 3 \) modes is expected [44]. For an axisymmetric perturbation, there are predicted to be four ‘peaks’ in the experimental response which ought to be observed if there is sufficient resolution. These consist of three pairs of individually degenerate doublets and a separate singlet, giving the \((3 \times 2) + 1 = 7\) components overall, and the singlet may be expected to appear at the highest frequency if \( c_{20} < 0 \). For non-axisymmetric perturbations, the degeneracies of the three doublets can be expected to lift, if only by some small amount.

To extract accurate information regarding the size and shape of the deformations of practical spheres from measured splittings of components would require that the actual orientations of the electromagnetic fields with respect to the symmetry axes of the sphere be known. An analogous difficulty has been noted by Trusler in acoustic work [22]. There are no natural zeros of the polar angle \( \theta \) and the azimuthal angle \( \phi \) and, whilst one could assume that the fields adopt the same angular orientations in the practical cavity as are predicted in the ideal cavity [this assumption is implicit in the calculated fractional resonance frequency shifts of equations (3) to (8)], there are many factors such as antennae size and position, and position of other perturbations such as openings in the boundary wall, that could influence the field orientations. For example, if we consider the TM \( 1n \) mode and assume that the antennae are positioned such that the mode is excited, in the cavity, with the zero of \( \theta \), for the fields, coincident with the physical north pole of the resonator, then we could expect a single component to lie at high frequency and a doublet at low frequency for an axisymmetric perturbation in which the polar diameter is larger than the equatorial \((c_{20} < 0)\). If this is, indeed, observed we may conclude that, as suggested, the polar
diameter is larger than the equatorial diameter and that the observed frequency
difference between the singlet and the doublet corresponds to the difference in
diameters. However, if, despite the positioning of the antennae, the orientations of
the fields are shifted by an angle $\pi/2$ with respect to the expected orientations,
which is perfectly plausible, then we would observe the complete opposite, and find
a singlet at low frequency and a degenerate doublet at high frequency, for the same
physical deformation of the sphere. Whilst the $\pi/2$ rotation of fields is plausible, it
is more likely that the fields will be rotated by an angle between 0 and $\pi/2$ and, in
many respects, this is a greater problem. With the $\pi/2$ rotation we could, at least in
principle, measure the ‘correct’ magnitude of the deformation even if its ‘direction’
was misinterpreted, but if the fields rotate by some angle between 0 and $\pi/2$ then
the magnitudes of the observed resonance frequency shifts would be smaller than
those predicted for a given $|\epsilon_{c_{20}}|$ and we would then calculate $|\epsilon_{c_{20}}|$ too small.

However, some very successful applications of the boundary shape perturbation
theory described in this section have been reported [24, 47], with the measured
splittings of $l=1$ acoustic and microwave modes, in the same spherical resonator,
being used to independently predict values of $\epsilon_{c_{20}}$ that agree within a few parts per
million. Such close agreement suggests that the same physical deformation was
responsible for the acoustic and microwave splittings [24], and gives weight to the
assumption that the perturbed fields had approximately the same orientations within
the cavity as would be expected for unperturbed cavity fields.

Calculations given in sections (4.7) suggest that some part of the observed
splitting could be due to other perturbations such as the localised deformations of
openings in the resonator wall and the antennae that protrude into the cavity to excite
and detect the modes. However these are demonstrated to be quite small and it is
very likely that smooth geometric deformations, such as were considered in this
section, are responsible for the majority of observed splittings.

The cylinder

The effects of volume-preserving deformations of the cylindrical resonator on the
microwave resonance frequencies can also be estimated by analogy with published
work on acoustic modes [22]. Such published material is, however, limited to a
consideration of the effects on the non-degenerate \( p = 0 \) modes and the doubly degenerate modes with indices \( p \neq 0, q, s = 0 \). Fortunately, this is sufficient to cover the three modes of interest here: the TM 010, TM 011 and TM 110 modes.

The cylinder used in this work was constructed from three pieces - two flat end plates and a short, cylindrical section - which were tightly screwed together to form the enclosed cavity. The most likely geometric imperfections are non-parallelism of the end-plates and an eccentricity of the cylindrical bore, and Trusler [22] notes that the resonance frequencies of the non-degenerate \( p = 0 \) acoustic modes are unaffected to first order, by such geometric imperfections, if the cavity volume is preserved. That this will also be true for the non-degenerate \( p = 0 \) microwave modes can be readily seen from the form of equation (1), which gives the first order fractional resonance frequency shift, for a given mode, due to a deformation of the boundary wall which removes a volume \( \Delta V \) from the cavity by pushing in the boundary wall. For deformations that increase the cavity volume by an amount \( \Delta V \) by pushing out the boundary wall, the fractional resonance frequency shift is given by a change of sign of equation (1) [11]. Therefore, the first order fractional shift is given by

\[
\left( \frac{\Delta f}{f^0} \right)_N = \frac{1}{2} \frac{\iiint (\varepsilon_\varepsilon_0 |E|^2 - \varepsilon_\varepsilon_0 |E|^2) dV}{\frac{1}{2} \iiint (\varepsilon_\varepsilon_0 |E|^2 + \varepsilon_\varepsilon_0 |H|^2) dV} \tag{4.6.9}
\]

for deformations that increase the cavity volume by an amount \( \Delta V \) by pushing the boundary wall outwards. Indeed, if we adopt the convention that \( \Delta V \) is positive for deformations that increase the cavity volume by pushing the wall outwards, and negative for deformations that decrease the cavity volume by pushing the wall inwards, then equation (9) can be applied to any boundary deformation. The unperturbed \( E \) and \( H \) fields of the non-degenerate \( p = 0 \) modes have no angular dependence and, therefore, have rotational symmetry about the longitudinal axis of the cylinder. They are also symmetric about a plane through the middle of the cylinder perpendicular to the longitudinal axis. These symmetry properties, combined with the \( \pi/2 \) phase difference between the fields which causes the \( E \) field to be strong in a region where the \( H \) field is weak, mean that any boundary deformation which increases the cavity volume by an amount \( \Delta V \) will give rise to a
resonance frequency shift that is equal in magnitude but opposite in sign to that caused by any deformation that decreases the cavity volume by the same amount. Thus the resonance frequencies of the non-degenerate $p = 0$ modes are unaffected, to first order, by any volume-preserving deformation of the boundary wall, including non-parallelism of the end-plates and an eccentricity of the bore.

The effects of smooth, volume-preserving deformations on the resonance frequencies of the doubly degenerate acoustic modes with indices $p \neq 0$, $q$, $s = 0$ have been considered by Trusler [22]. A model deformation of the boundary wall was considered, such that the perturbed surface is given by

$$r(\theta) = a \left(1 - \varepsilon \sum_{m=-\infty}^{\infty} c_m e^{im\theta}\right)$$

(4.6.10)

where $a$ is the radius of the unperturbed cavity, $\varepsilon$ is a small, positive parameter that indicates the magnitude of the deformation, and the coefficients $c_m$ describe its shape. It can be shown that, for such a boundary shape perturbation, the components of the mode suffer first order shifts which split the two resonance frequencies symmetrically about that of the ideal cylinder by an amount proportional to $\varepsilon |c_{(\ell \rho)}|$, provided the cavity volume is unchanged by the deformation. Thus the average of the two perturbed resonance frequencies will be equal to the unperturbed resonance frequency correct to first order in $\varepsilon$. This is a very similar result to that found for the degenerate modes, both acoustic and microwave, of a spherical resonator and so it is reasonable to expect the same result for the $p \neq 0$ doubly-degenerate microwave modes of the cylindrical resonator. Therefore it can be predicted that the average resonance frequency of a microwave doublet, in a cylinder perturbed by a volume-preserving deformation, will be equal to the unperturbed resonance frequency, correct to first order in $\varepsilon$.

### 4.7 Localised deformations of the boundary wall

In section (4.6), it was demonstrated how boundary shape perturbation theory can be applied to estimate the fractional shifts in resonance frequencies due to smooth departures from ideal geometry. In this section the same theory is used to calculate the resonance frequency shifts caused by deformations which are more abrupt but are usually localised in one, or a small number of regions on the boundary wall. These
deformations include indentations, or full-thickness holes, in the wall and also protrusions into the cavity, such as are caused by antennae. It is important to be able to assess the effects of such perturbations since without openings in the wall the cavity can neither be filled nor evacuated, and without antennae, or other coupling structures, the resonances could not be excited or detected.

The first order fractional resonance frequency shifts caused by any small deformation of the perfectly conducting boundary wall is given by

\[
\frac{\Delta f}{f_N^0} = -\frac{1}{2} \int \int \int_A \left( \mu_0 |H|^2 - \varepsilon \varepsilon_0 |E|^2 \right) dV
\]

which can be derived from the general perturbation formula, equation (4.4.1), as described in section (4.6). The integral in the numerator is taken over the perturbed region \( \Delta V \) and is equal to the difference between the changes in electric and magnetic energy stored in the cavity due to the deformation; the denominator is recognized as the total electromagnetic energy \( W \) stored in the unperturbed cavity at resonance. This interpretation is very similar to that for the general perturbation formula of equation (4.4.1) from which equation (1) can be derived. As previously noted, this expression gives a purely real resonance frequency shift since it is only concerned with deformations of a perfectly conducting boundary and these are will not make any contribution to the resonance halfwidth. However, as will be demonstrated shortly, equation (1) can also be used to estimate the resonance frequency shifts caused by actual holes in the resonator wall and, in such cases, there might be radiative losses which could make some contribution to the resonance halfwidth. These losses will be discussed separately.

All the calculations in this section rest on the validity of two simple but important assumptions, which are that the deformations occur over a sufficiently small region of the boundary surface that the \( E \) and \( H \) fields may be considered to be constant over the perturbed region, and the perturbation is sufficiently small that the fields in the perturbed region are not significantly different from unperturbed fields in the same region. The first assumption allows us to treat the integral in the numerator of equation (1) as an integration over the sum of two constants, \( \left( \mu_0 |H|^2 \right) \) and \( \left( -\varepsilon \varepsilon_0 |E|^2 \right) \), which can therefore be taken outside the integral, leaving
\begin{align}
\iiint dV = \Delta V, \text{ the volume change caused by the perturbation. The second assumption means that } |H| \text{ and } |E| \text{ in the numerator are given by the ideal cavity fields, given in chapter 3, in the region of the perturbation. Thus equation (1) is to be used in the form}
\begin{align}
\left( \frac{\Delta f}{f_0} \right) &= -\frac{1}{2} \left( \mu_0 |H_{\Delta r}|^2 - \epsilon \epsilon_0 |E_{\Delta r}|^2 \right). \Delta V / W 
\end{align}
\end{align}

where \( W = \frac{1}{2} \iiint \left( \epsilon \epsilon_0 |E|^2 + \mu_0 |H|^2 \right) dV \) is the total energy stored in the unperturbed cavity at resonance, and \( H_\Delta V \) and \( E_\Delta V \) are the magnetic and electric fields, respectively, in the perturbed region, which are obtained from the relevant ideal cavity field expressions of chapter 3 by substituting in the coordinates at the perturbed region.

The first order fractional shifts in resonance frequency caused by deformations in regions of the cavity commonly used for inlet openings and coupling structures such as antennae will now be considered for the modes of the sphere and cylinder. Calculations for the sphere are limited to the TM\( l m 0 \) and TE\( l m 0 \) modes, and the TM\( l m m \) and TE\( l m m \) modes, since these are the mode families for which general expressions for the total energy stored, \( W \), can be readily derived. This allows estimation of the perturbations on all \((2l + 1)\) components of the TM\( l m \) modes and also the \( m = 0 \) components of all TM\( l m \) modes. The calculations could easily be extended to any component of any mode in the sphere if the total energy \( W \) is calculated on a mode-by-mode basis, as explained in chapter 3. The calculated resonance frequency shifts in the cylinder are given, in each case, for all TM\( p q s \) and TE\( p q s \) modes since the calculation of general expressions for \( W \) in the cylinder presents no difficulty. The regions of deformation to be considered in the sphere are areas on the boundary surface \( r = a, \) with any value of the polar angle \( \Theta, \) and azimuthal angle \( \phi = 0 \) or \( \pi. \) Although \( \phi \) is restricted to \( 0 \) or \( \pi, \) there is nothing in the unperturbed cavity to define a zero of \( \phi \) and so we can choose \( \phi = 0 \) (or \( \pi \)) to coincide with the location of the deformation to enable the results given here to be applied to a perturbation at any angle \( \phi. \) However, once the \( 0 \) or \( \pi \) for \( \phi \) has been chosen it must be adhered to if other perturbation calculations are considered for the same cavity.
For the cylinder, deformations in the end plates and the cylindrical wall must be considered separately. In the end plates, at $z = 0$ and $z = L$, deformations anywhere along a radial line, between $r = 0$ and $r = a$, at an angle $\theta$ of $0$ or $\pi$ are considered. In the cylindrical wall, at $r = a$, deformations anywhere along the length of the wall, at an angle $\theta$ of $0$ or $\pi$, are treated. Although $\theta$ is restricted to $0$ or $\pi$, there is nothing in the unperturbed cavity to define a zero of $\theta$ and so we can choose $\theta = 0$ (or $\pi$) to coincide with the location of the deformation and so the results given here can be applied to a deformation at any angle $\theta$. However, as has been noted for the angle $\phi$ in the sphere, once the zero (or value of $\pi$) for $\theta$ has been chosen it cannot be chosen again for the calculation of other perturbation corrections.

The calculations in this section assume an angular orientation of the $E$ and $H$ fields, with respect to the locations of the deformations, that is in accordance with the ideal cavity fields given in chapter 3, and yet the actual orientations of the fields, within the perturbed cavity, may be different. This problem, if it arises, is more likely to be the case for the sphere, due to its higher order of symmetry, than for the cylinder. In the cylinder, the orientations of the electromagnetic fields are more restricted (e.g. the electric field lines for the TM110 mode must run from one end-plate to the other) and there are, of course, non-degenerate modes which have fields with no angular dependence and so the problem does not arise. Measurements of the resonance frequency shifts of the non-degenerate TM010 and TM011 modes, caused by a small hole in the centre of an end plate of the cylindrical resonator used in this work, are presented and shown to be in excellent agreement with the shifts calculated using first order perturbation theory. This agreement not only inspires confidence in the methods of calculations used but also supports the assumptions that are made, concerning the nature and orientation of the fields, in deriving the calculated shifts.

The calculated first-order fractional resonance frequency shifts due to localised boundary shape deformations are now presented, beginning with those for the spherical cavity.
The sphere

Deformations of the boundary wall, which change the cavity volume by an amount $\Delta V$, in the region $(r = a, \theta = \xi, \phi = 0$ or $\pi$) are considered.

Sphere $TM_{ln0}$ modes

In the perturbed region, the field components are given by substituting $(r = a, \theta = \xi, \phi = 0)$ into equations (3.4.40) to (3.4.45). Therefore, in the region of the perturbation

$$E_r = \frac{l(l+1)}{ka} B_j(ka) P_l^{\theta}(\cos\xi)$$

$$E_\phi = E_\theta = H_r = H_\theta = 0$$

$$H_\phi = \frac{+i\omega\varepsilon_0}{k} B_j(ka) P_l^{\theta}(\cos\xi)$$

where we have used the characteristic equation for TM modes, $[\nu_n^l(ka)]' = 0$, and the relation $d[P_l^{\theta}(\cos\theta)]/d\theta = -P_l^{\theta}(\cos\theta)$, in obtaining equations (3) to (5).

These field components are substituted into equation (2), along with the expression for the total energy $W_{TMln0}$ from equation (3.4.58), to give

$$\left(\frac{\Delta f}{f_{ln0}}\right) = -\frac{2}{3} \frac{[P_l^{\theta}(\cos\xi)]^2 - \frac{l(l+1)}{\nu_n^l} [P_l^{\theta}(\cos\xi)]^2}{\left[1 - \frac{l(l+1)}{\nu_n^l} \right] \frac{2}{2l+1} \frac{(l+1)!}{(l-1)!}} \left(\frac{\Delta V}{V_0}\right)$$

where we have used $k^2 = \omega^2 \varepsilon_0 \mu_0$ and $(ka) = \nu_n^l$, the TM$ln$ mode eigenvalue, to simplify. The azimuthal coordinate has been assumed to be $\phi = 0$ at the perturbed region, for this calculation, but exactly the same result is given for $\phi = \pi$.

In the case of $\xi = 0$ (or $\pi$), which corresponds to a deformation at the north (or south) pole of the spherical cavity wall, equation (6) becomes

$$\left(\frac{\Delta f}{f_{ln0}}\right) = \frac{\nu_n^l}{\nu_n^l} \frac{\left[\frac{l(l+1)}{\nu_n^l}\right]^2}{\left[1 - \frac{l(l+1)}{\nu_n^l} \right] \frac{2}{2l+1} \frac{(l+1)!}{(l-1)!}} \left(\frac{\Delta V}{V_0}\right)$$

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where we have used \( P^1_l(\pm 1) = 0 \) for all \( l \) and \( [P^0_l(\pm 1)]^2 = 1 \) for all \( l \), both of which follow from the definition of \( P^\text{ind}_l(x) \) given by equation (A3.1.33).

**Sphere TE/\( n0 \) modes**

In the perturbed region, the field components are obtained by substituting \( r = a, \theta = \xi, \phi = 0 \) into equations (3.4.49) to (3.4.54). This gives

\[
E_r = E_\theta = E_\phi = H_r = 0
\]  (4.7.8)

\[
H_\theta = \frac{-i\omega \varepsilon \varepsilon_0}{k^2 a} C\left[(ka)j,l(ka)\right] P^l_1(\cos \xi)
\]  (4.7.9)

\[
H_\phi = 0
\]  (4.7.10)

where we have used the characteristic equation for TE modes, \( j_l(ka) = 0 \), and the relation \( d[P^0_l(\cos \theta)]/d\theta = -P^1_l(\cos \theta) \). These field components are substituted into equation (2), along with the expression for \( W_{TE/\text{n}0} \) from equation (3.4.67), to give

\[
\left( \frac{\Delta f_{/n0}}{f_{/n0}} \right) = -\frac{2}{3} \left( \frac{P^1_1(\cos \xi))^2}{l+1 (l-1)!} \frac{(\Delta V)}{V_0} \right)
\]  (4.7.11)

where we have used \( [(ka)j,l(ka)]=j_l(ka) + (ka)j'_l(ka) = (ka)j_l(ka) \) for TE modes, \( k^2 = \omega^2 \varepsilon \varepsilon_0 \mu_0 \) and \( (ka) = \nu_{\text{n}} \), the TE mode eigenvalue, to simplify. Equation (11) has been obtained by assuming \( \phi = 0 \) at the perturbed region, but exactly the same result is obtained for \( \phi = \pi \).

In the case of \( \xi = 0 \) (or \( \pi \)), which corresponds to a deformation at the north (or south) pole of the spherical wall, equation (11) becomes

\[
\left( \frac{\Delta f_{/n0}}{f_{/n0}} \right) = 0
\]  (4.7.12)

since, if \( \xi = 0, P^l_1(\cos \xi) = P^1_1(1) = 0 \) for all \( l \), by the definition of \( P^\text{ind}_l(x) \) given by equation (A3.1.33). Therefore, there is no first order resonance frequency shift due to deformations at the poles for TE/\( n0 \) modes.
Sphere TM1nm modes

If \( l = 1 \) then \( m = 0, \pm 1 \) and so we need only consider the resonance frequency shifts for modes with \( |m| = 1 \) since the results for TM1n0 modes have already been given. In the perturbed region, the field components are obtained by substituting \((r = a, \theta = \xi, \phi = 0)\) into equations (3.4.40) to (3.4.45). This gives

\[
\begin{align*}
E_r &= \frac{2}{ka} B_j(ka) \sin \xi \\
E_\theta &= E_\phi = H_r = 0 \\
H_\theta &= \frac{+i\omega \varepsilon_0}{k \sin \xi} B_j(ka) \sin \xi \\
H_\phi &= \frac{-i\omega \varepsilon_0}{k} B_j(ka) \cos \xi
\end{align*}
\]

where we have used the characteristic equation for TM modes, \([k \sin \xi j'_n(k a)] = 0\), and \( P^1_l(\cos \theta) = \sin \theta \). The field components are substituted into equation (2), along with the expression for \( W_{\text{TM}1n} \) from equation (3.4.64), to give

\[
\left( \frac{\Delta f}{f_{1n}^0} \right) = \left[ \frac{1 + \cos^2 \xi}{4 \left( 1 - \frac{2}{\nu_{1n}^2} \right)} \right] \left( \frac{\Delta V}{V_0} \right)
\]

where we have used \( k^2 = \omega^2 \varepsilon_0 \mu_0 \) and \((ka) = \nu_{1n}\), the TM1n mode eigenvalue, to simplify. This result has been obtained for \( m = +1 \) and taking \( \phi = 0 \), but exactly the same result is obtained for \( m = \pm 1 \) and \( \phi = 0 \) or \( \pi \).

For deformations at the poles, \( \xi = 0 \) (or \( \pi \)) is substituted into equation (17) to give

\[
\left( \frac{\Delta f}{f_{1n}^0} \right) = -\frac{1}{2(1 - 2/\nu_{1n}^2)} \left( \frac{\Delta V}{V_0} \right)
\]

Sphere TE1nm modes

As for the TM1nm modes, we need only consider modes with \( |m| = 1 \) since the results for TE1n0 modes have already been given. The field components in the perturbed
region are obtained by substituting \((r = a, \theta = \xi, \phi = 0)\) into equations (3.4.49) to (3.4.54). This gives

\[
E_r = E_\theta = E_\phi = H_r = 0 \quad (4.7.19)
\]

\[
H_\theta = \frac{+i\omega \varepsilon_\varepsilon_0}{k^2 a} C[(ka)j_1(ka)\] \cos \xi \quad (4.7.20)
\]

\[
H_\phi = \frac{+i\omega \varepsilon_\varepsilon_0}{k^2 \sin \xi} C[(ka)j_1(ka)\] \sin \xi \quad (4.7.21)
\]

where we have used the characteristic equation for TE modes, \(j_1(ka) = 0\), and \(P_1'(\cos \theta) = \sin \theta\). These field components are substituted into equation (2), along with the expression for \(W_{\text{TE}1n}\) from equation (3.4.68), to give

\[
\left( \frac{\Delta f}{f_{in}} \right) = -\frac{1}{4} \left( \cos^2 \xi + \frac{1}{\nu_{in}^2} \right) \frac{\Delta V}{V_0} \quad (4.7.22)
\]

where we have used \([(ka)j_1(ka)\]' = j_1(ka) + (ka)j_1(ka) = (ka)j_1(ka)\) for TE modes, \(k^2 = \omega^2 \varepsilon_\varepsilon_0 \mu_0\) and \((ka) = \nu_{in}\), the TE1n mode eigenvalue, to simplify. Equation (22) has been derived by assuming \(\phi = 0\) and \(m = +1\), but exactly the same result is obtained for \(m = \pm 1\) and \(\phi = 0\) or \(\pi\). For deformations at the poles, \(\xi = 0\) or \(\pi\) is substituted into equation (22) to give

\[
\left( \frac{\Delta f}{f_{in}} \right) = -\frac{1}{4} \left( 1 + \frac{1}{\nu_{in}^2} \right) \frac{\Delta V}{V_0} \quad (4.7.23)
\]

The cylinder

Deformations in the end plates of the cylinder at \(z = 0\) and \(z = L\), and those in the cylindrical wall at \(r = a\) must be considered separately. The fractional shifts in resonance frequency for deformations in the end plates are considered first.

(1) End plate deformations

Deformations are considered which change the cavity volume by an amount \(\Delta V\) in the region \((r = x, \theta = 0\) or \(\pi, z = 0\) or \(L\))
(a) Cylinder TMpq$ns$ modes

In the perturbed region, the field components are given by substituting 
($r = x$, $\theta = 0$, $z = 0$) into equations (3.3.9) to (3.3.14) to give

$$E_z = AJ_p(kx)$$  \hspace{1cm} (4.7.24)

$$E_r = E_\theta = H_z = 0$$  \hspace{1cm} (4.7.25)

$$H_r = \frac{+i\omega \varepsilon \varepsilon_0 p}{k^2 x} AJ_p(kx)$$  \hspace{1cm} (4.7.26)

$$H_\theta = \frac{-i\omega \varepsilon \varepsilon_0}{k} AJ_p'(kx)$$  \hspace{1cm} (4.7.27)

These field components are substituted into equation (2), along with the expression 
for $W_{TMpqns}$ from equation (3.3.28), to give

$$\frac{\Delta f}{f_0} = \frac{\omega^2 \varepsilon \varepsilon_0 \mu_0}{k^2} \left\{ \left[ \frac{p^2}{2k^2 x^2} - \frac{k^2}{\omega^2 \varepsilon \varepsilon_0 \mu_0 k_0} \right] J_p^2(kx) + J_p'^2(kx) \right\} \left[ \frac{\Delta V}{V_0} \right]$$  \hspace{1cm} (4.7.28)

where this expression is to be divided by 2 if $s = 0$. The expression for the resonance 
frequency shift can be evaluated by substituting the value of $x$ at the region of the 
perturbation and using the equation $J_p'(kx) = 1/2 \left[ J_{p-1}(kx) - J_{p+1}(kx) \right]$ to simplify 
the calculation. Equation (28) has been obtained using $z = 0$ and $\theta = 0$ but exactly 
the same result is obtained using $z = 0$ or $L$ and $\theta = 0$ or $\pi$. For perturbations at the 
centre of an end plate we put $x = 0$ into equation (28). However, equation (28) 
contains the terms $p^2 \left[ J_p(kx)/(kx) \right]^2$ and $J_p'^2(kx)$, and some caution is required to 
evaluate these for $x = 0$. There are three cases of interest which must be considered 
individually:

(i) $p = 0$ modes

In this case the term $p^2 \left[ J_p(kx)/(kx) \right]^2 = 0$ since $p = 0$, and $J_p'^2(kx) |_{x=0} = 0$ since 
$J_0'(kx) = -J_1(kx)$, and $J_1(kx) = 0$ for $x = 0$. Also, we can put $J_p(kx) = J_0(kx) = 1$ 
for $x = 0$ to give the fractional resonance frequency shift as

$$\left( \frac{\Delta f}{f_0} \right)_{q, p=0} = \left[ \left( 1 + \frac{s^2 \pi^2}{k^2 L^2} \right) J_0'^2(\chi_{p0}) \right]^{-1} \left[ \frac{\Delta V}{V_0} \right]$$  \hspace{1cm} (4.7.29)

where this is to be divided by 2 if $s = 0$.  

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(ii) $p = 1$ modes

In this case $p^2 \left[ J_p(kx)/(kx) \right]^2 \big|_{x=0} = \left[ J_1(kx)/(kx) \right]^2 \big|_{x=0}$. This is indeterminate since it gives $[0/0]^2$ and so L'Hôpital's rule, equation (A3.1.41) must be used. Now, $J'_1(kx) = 1/2 \left[ J_0(kx) - J_2(kx) \right]$, using equation (A3.1.6), and therefore $J'_1(kx) = 1/2$ for $x = 0$ since $J_0(0) = 1$ and $J_2(0) = 0$. The differential of $(kx)$ with respect to $(kx)$ is, of course, simply 1 and so, in this case, $p^2 \left[ J_p(kx)/(kx) \right]^2 \big|_{x=0} = 1/4$. Also, we have just seen that for $p = 1$, $J'_p(kx) \big|_{x=0} = J'_1(0) = 1/2$, and therefore the fractional resonance frequency shift is

$$
\left( \frac{\Delta f}{f_{pp'}} \right) = -\frac{1}{2} \left( \frac{\omega^2 \epsilon_0 \mu_0}{k^2} \right) \frac{\Delta V}{V_0} \left( \frac{\Delta V}{V_0} \right)
$$

where this is to be divided by 2 if $s = 0$.

(iii) $p > 1$ modes

The term $p^2 \left[ J_p(kx)/(kx) \right]^2 \big|_{x=0} = 0$, where we have used L'Hôpital's rule and the equation $J'_p(kx) = 1/2 \left[ J_{p-1}(kx) - J_{p+1}(kx) \right]$, together with the fact that $J_p(0) = 0$ for $p \geq 1$. Also, using the same differential relation for $J_p(kx)$ we have $J'_p(kx) \big|_{x=0} = 0$ for $p > 1$. Hence, the numerator of the resonance frequency shift formula, equation (28), vanishes for $p > 1$ which means that

$$
\left( \frac{\Delta f}{f_{pp'}} \right) = 0 \text{ for } p > 1
$$

(b) Cylinder TE$_{pq}$ modes

In the perturbed region, the field components are given by substituting $(r = x, \theta = 0, z = 0)$ into equations (3.3.15) to (3.3.20) to give

$$
E_z = E_\theta = H_\theta = H_z = 0
$$

$$
H_r = \frac{s \pi}{kL} BJ'_p(kx)
$$

$$
H_\theta = \frac{+p_\theta s \pi}{k^2 x L} BJ'_p(kx)
$$

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These field components are substituted into equation (2), along with the expression for $W_{\text{TE}pq}$ from equation (3.3.30), to give

$$\left(\frac{\Delta f}{f_{pq}^0}\right) = \left(\frac{s^2 \pi^2}{k^2} \left[\frac{J^2_p(kx) + \frac{p^2}{k^2 x^2} J^2_p'(kx)}{1 - \frac{p^2}{\chi_{pq}^2}}\right]\right) \left(\frac{\Delta V}{V_0}\right)$$

(4.7.35)

where $\chi_{pq}$ is the TE$\text{pq}$ mode eigenvalue. The mode index $s$ cannot be zero for TE modes. Equation (35) has been obtained using $z = 0$ and $\theta = 0$, but exactly the same result is obtained using $z = 0$ or $L$ and $\theta = 0$ or $\pi$. As was seen for the TM$\text{pq}$ modes, the special case of $x = 0$ has to be evaluated with caution and there are, again, three cases of interest to be considered individually.

(i) $p = 0$ modes

From sub-section (1.a.i.) we have $p^2 \left[J_p^2(kx)/(kx)\right] = 0$ and $J_p^2(kx)|_{x=0} = 0$ for $p = 0$, and therefore the numerator of equation (35) vanishes, giving

$$\left(\frac{\Delta f}{f_{pq}^0}\right) = 0$$

(4.7.36)

(ii) $p = 1$ modes

From sub-section (1.a.ii.) we have $p^2 \left[J_p^2(kx)/(kx)\right]|_{x=0} = 1/4$ and $J_p^2(kx)|_{x=0} = 1/4$, for $p = 1$, and so the fractional resonance frequency shift is given by

$$\left(\frac{\Delta f}{f_{pq}^0}\right) = \frac{-\left(s^2 \pi^2}{2k^2}\right)}{\omega^2 \varepsilon \varepsilon_0 \mu_0 \left(1 - \frac{1}{\chi_{pq}^2}\right)} \left(\frac{\Delta V}{V_0}\right)$$

(4.7.37)

where $\chi_{pq}$ is the TE$\text{pq}$ mode eigenvalue.

(iii) $p > 1$ modes

From sub-section (1.a.iii) we have $p^2 \left[J_p^2(kx)/(kx)\right]|_{x=0} = 0$ and $J_p^2(kx)|_{x=0} = 0$ for $p > 1$, and so the fractional resonance frequency shift is zero, to first order. That is,

$$\left(\frac{\Delta f}{f_{pq}^0}\right) = 0 \text{ for } p > 1$$

(4.7.38)
2) Cylindrical wall deformations

Deformations are considered which change the cavity volume by an amount \( \Delta V \) in the region \( (r = a, \theta = 0 \text{ or } \pi, z = d) \).

a) Cylinder TM\( pqs \) modes

In the perturbed region, the field components are given by substituting \( (r = a, \theta = 0 \text{ or } \pi, z = d) \) into equations (3.3.9) to (3.3.14) to give

\[
E_z = 0 \tag{4.7.39}
\]

\[
E_e = \frac{-s\pi}{kL} A J_p'(ka) \sin \frac{s\pi d}{L} \tag{4.7.40}
\]

\[
E_\theta = H_z = H_r = 0 \tag{4.7.41}
\]

\[
H_\theta = -\frac{i\omega \varepsilon_0 \mu_0}{k} A J_p'(ka) \cos \frac{s\pi d}{L} \tag{4.7.42}
\]

where we have used the characteristic equation for TM modes, \( J_p(ka) = 0 \).

Substituting these field components into equation (2), along with the expression for \( W_{\text{TM}pqs} \) from equation (3.3.28), we obtain

\[
\left( \frac{\Delta f}{f_{p0}} \right) = \left[ \frac{\omega^2 \varepsilon_0 \mu_0 k^2}{L^2} \cos^3 \left( \frac{s\pi d}{L} \right) - \frac{s^2 \pi^2}{L^2} \sin^3 \left( \frac{s\pi d}{L} \right) \right] \left( \frac{\Delta V}{V_0} \right) \tag{4.7.43}
\]

where this fractional shift is to be divided by 2 if \( s = 0 \). This resonance frequency shift formula has been obtained using \( \theta = 0 \) but exactly the same result is obtained for \( \theta = \pi \). For modes with \( s = 0, k^2 = \omega^2 \varepsilon_0 \mu_0 \) and, recalling that for these modes the fractional shift is to be divided by 2, we obtain

\[
\left( \frac{\Delta f}{f_{p0}} \right) = -\frac{1}{2} \left( \frac{\Delta V}{V_0} \right) \tag{4.7.44}
\]

Thus the resonance frequency shift is the same for all \( s = 0 \) modes wherever the deformation lies along the cylindrical wall.
b) Cylinder TEpq modes

In the perturbed region, the field components are given by substituting 
\((r = a, \theta = 0, z = d)\) into equations (3.3.15) to (3.3.20) to give

\[
E_z = 0
\]

\[
E_r = \frac{-i\omega \mu_0 p}{k^2 a} BJ_p(ka) \sin \frac{s\pi d}{L}
\]

\[
E_\theta = 0
\]

\[
H_z = BJ_p(ka) \sin \frac{s\pi d}{L}
\]

\[
H_r = 0
\]

\[
H_\theta = \frac{ps \pi}{k^2 a L} BJ_p(ka) \cos \frac{s\pi d}{L}
\]

where we have used the characteristic equation for TE modes, \(J'_p(ka) = 0\).

Substituting these field components into equation (2), along with the expression for \(W_{TEpq}\) from equation (3.3.30), we obtain

\[
\frac{\Delta f}{f_{TEpq}} = \frac{-p^2}{k^2 a^2} \left[ \frac{s^2 \pi^2}{L^2} \cos^2 \left( \frac{s\pi d}{L} \right) - \omega^2 \varepsilon \varepsilon_0 \mu_0 \sin^2 \left( \frac{s\pi d}{L} \right) \right] \left( \frac{\Delta V}{V_0} \right) \]

\[
\omega^2 \varepsilon \varepsilon_0 \mu_0 \left( 1 - \frac{p^2}{\chi_{pq}^2} \right)
\]

where \(\chi_{pq} = (ka)\) is the TEpq mode eigenvalue and the mode index \(s\) cannot be zero for TE modes. Equation (51) has been obtained for \(\theta = 0\) but exactly the same result is obtained for \(\theta = \pi\). It can be seen from the fractional resonance frequency shift formula that the shift will be zero, correct to first order, for modes with \(p = 0\) (i.e. TE0qs modes), for all values of \(d\).

If a full-thickness hole is made through a boundary wall then, clearly, the cavity volume has been increased rather than decreased and so \(\Delta V > 0\) due to this perturbation, but this leaves the question of the magnitude of \(\Delta V\). It is probably this question that has hitherto prevented a successful solution to the problem of calculating the resonance frequency shift due to holes in the boundary wall from being published, since the perturbation formulae of equations (4.4.1) and (4.6.1) are widely known [8, 11, 19, 23, 40]. An account of one attempt to estimate the effects of this perturbation is given in reference 49, but the calculated resonance frequency...
shift is an order of magnitude smaller than the measured shift presented in the paper. The authors acknowledge, but cannot account for, the difference.

The estimation of the effective increase in cavity volume due to the presence of a small hole, presented here, comes from treating the cylindrical opening, caused by drilling the hole, as a section of cylindrical waveguide with radius equal to the hole radius and length equal to the thickness of the resonator wall. The radius of the hole is likely to be so small in comparison to the cavity dimensions that the frequency of electromagnetic fields at resonance within the cavity will be far below the lowest cut-off frequency for modes of propagation in the waveguide. Therefore, there will be rapid exponential decay of the fields within the waveguide (i.e. the hole) and so the fields will only propagate a very small distance \( h_{\text{co}} \) out of the cavity and into the hole. The change in cavity volume is then given by \( \Delta V = \pi b^2 h_{\text{co}} \) where \( b \) is the radius of the hole and \( h_{\text{co}} \) is the 'cut-off length'. This value of \( \Delta V \) can then be substituted into the appropriate resonance frequency shift formula to estimate the shift due to the presence of the hole. It will now be shown how such calculations lead to predicted shifts in resonance frequency which are in excellent agreement with measured values.

If a full-thickness opening or hole with a circular cross-section of radius \( b \) is made in the boundary wall of a resonant cavity, where the wall has a thickness \( t \), then the opening can be considered as a section of cylindrical waveguide of radius \( b \) and length \( t \). As discussed in section (3.2), a particular waveguide mode will only propagate freely if the frequency of the fields is above the cut-off frequency in the waveguide for that mode. If we consider that the field frequency is \( f \) the resonance frequency of a cavity mode, and that the medium filling the cavity and waveguide section is such that the speed of light is \( c = \left(1/\varepsilon\varepsilon_0\mu_0\right)^{1/2} \), then equation (3.2.41) gives the phase constant for propagation of a cylindrical waveguide mode, with eigenvalue \( \chi \), within the waveguide section as

\[
\beta = \frac{2\pi}{c} \sqrt{f^2 - \left(\frac{\chi c}{2\pi b}\right)^2}
\]

(4.7.52)

If the cavity resonance frequency \( f \) is smaller than the cut-off frequency \( \left(\chi c/2\pi b\right) \) then the phase constant \( \beta \) will be purely imaginary. For a small hole, it will
generally be the case that \( f^2 \ll \left( \frac{\chi c}{2\pi b} \right)^2 \) (e.g. the lowest frequency mode measured using the cylinder in this work, the TM010 mode, has \( f = 12 \text{ GHz} \), and this is much smaller than the lowest possible cut-off frequency of 185 GHz for a hole of radius 0.475 mm) and so we can put

\[
\sqrt{f^2 - \left( \frac{\chi c}{2\pi b} \right)^2} = -i \left( \frac{\chi c}{2\pi b} \right)
\]

in equation (52) without significant error, where the negative square root is taken because we are considering propagation along the waveguide, away from the cavity, to be in the \(+z\) direction with respect to the waveguide [see section (3.2)]. Thus the purely imaginary phase constant is \(-i(\chi/b)\). We are considering propagation (albeit cut-off) to be directed in the \(+z\) direction of the waveguide and, as seen in section (3.2), this is characterised by the function \(\exp(-i\beta z)\). With the purely imaginary phase constant \(\beta = -i(\chi/b)\), this function becomes \(\exp(-\left(\chi/b\right)z)\), and this gives the dependence of the amplitudes of the \(\mathbf{E}\) and \(\mathbf{H}\) fields, within the waveguide, on the distance \(z\) along the waveguide, going away from the cavity. If the amplitudes of the \(\mathbf{E}\) and the \(\mathbf{H}\) fields within the waveguide are proportional to \(\exp(-\left(\chi/b\right)z)\) then the power flow, along the waveguide, which goes as \((\mathbf{E} \times \mathbf{H})\), must decay as \(\exp(-2\left(\chi/b\right)z)\). It is important to consider the power, or energy flow rate, contained in the fields of the waveguide mode rather than just the field amplitudes, because, in considering the cavity resonance frequency shift due to this perturbation, we are really considering the energy changes that occur due to the presence of the opening. When the waveguide electromagnetic fields have propagated a distance \(z = h_{co} = \left(\frac{b}{2\chi}\right)\), away from the cavity, the power contained in the fields within the waveguide will have fallen to \((1/e)\) of its initial level at the start of the opening (the inner surface of the cavity boundary wall), and this 'cut-off length' \(h_{co} = \left(\frac{b}{2\chi}\right)\) can be considered as the depth of penetration into the opening by the electromagnetic fields of the cavity. Thus the effective increase in cavity volume \(\Delta V\), due to the opening in the boundary wall, is simply given by

\[
\Delta V = \pi b^2 h_{co} = \pi \left(\frac{b^3}{2\chi}\right)
\]
This value of $\Delta V$ is substituted into the appropriate resonance frequency shift formula given in this section to estimate the fractional shift in resonance frequency caused by the opening. In general this gives

$$\left(\frac{\Delta f}{f_N^0}\right) = -\frac{1}{2} \left(\mu_0|H_{\Delta v}|^2 - \varepsilon\varepsilon_0|E_{\Delta v}|^2\right) \cdot \left[\pi\left(b^3/2X\right)\right]/W$$

(4.7.55)

where $E_{\Delta v}$ and $H_{\Delta v}$ are the (unperturbed) cavity fields in the vicinity of the region for which we are considering the perturbation. The same result can be obtained by an alternative approach which does not assume that the $E$ and $H$ fields remain constant over the region of the perturbation. If the fields in the region of the small perturbation (i.e. the hole) at the cavity wall are assumed to approximate to the unperturbed fields in the same region, $E_{\Delta v}$ and $H_{\Delta v}$, then the fields within the waveguide section formed by the opening will be $E' = E_{\Delta v} e^{-i\beta z}$ and $H' = H_{\Delta v} e^{-i\beta z}$, where $\beta$ is the phase constant for wave propagation in the waveguide. These must be the waveguide fields, since it is the cavity fields that couple to and excite the (cut-off) waveguide mode. As before the phase constant $\beta = -i\left(\chi/b\right)$ and so

$$E' = E_{\Delta v} \exp(-i\beta z) = E_{\Delta v} \exp(-\left(\chi/b\right)z)$$

(4.7.56)

$$H' = H_{\Delta v} \exp(-i\beta z) = H_{\Delta v} \exp(-\left(\chi/b\right)z)$$

(4.7.57)

and these fields, in the region of the perturbation, are substituted into the resonance frequency shift formula, equation (1), to give

$$\left(\frac{\Delta f}{f_N^0}\right) = -\frac{1}{2} \int \int \int_{\Delta v} \left(\mu_0|H_{\Delta v}|^2 - \varepsilon\varepsilon_0|E_{\Delta v}|^2\right) \exp(-2\left(\chi/b\right)z) dV$$

$$\int \int \int_{\Delta v} \left(\frac{1}{2} \int \int \left(\varepsilon\varepsilon_0|E|^2 + \mu_0|H|^2\right) dV\right)$$

(4.7.58)

The fields $E_{\Delta v}$ and $H_{\Delta v}$ are constant with respect to the integration over the perturbed volume since they represent the fields at the start of the opening and are equal to the unperturbed cavity fields at that part of the boundary wall, and the denominator of equation (58) is, of course, the total stored energy $W$. The remaining integral in the numerator is taken over the perturbed region, which is the waveguide formed by the opening, and is given by

$$\int \int \int_{\Delta v} \exp\left[-2\left(\chi/b\right)z\right] dV = \pi b^2 \int_{-\infty}^{+\infty} \exp\left[-2\left(\chi/b\right)z\right] dz = +\pi\left(\frac{b^3}{2\chi}\right)$$

(4.7.59)
The integration over the $z$ coordinate of the waveguide extends from zero (the beginning of the opening at the cavity surface) to infinity, and yet the result is finite because the amplitudes of the $E$ and $H$ fields fall off so quickly in the opening. The result of this integration is substituted into equation (58) to give the fractional shift in a cavity resonance frequency as

$$\frac{\Delta f}{f} = -\frac{1}{2} \left( \frac{\mu_0 |H_{\alpha \nu}|^2 - \varepsilon \varepsilon_0 |E_{\alpha \nu}|^2}{\pi \left( \frac{b^3}{2 \chi} \right) \frac{1}{W}} \right)$$

(4.7.60)

which is exactly the same result as obtained before. Thus we can put $\Delta V = +\pi \left( b^3 / 2 \chi \right)$, for the deformation due to an opening with circular cross-section of radius $b$, and this can be substituted into the appropriate resonance frequency shift formula to calculate the resonance frequency shift for a given mode. To a first approximation, the eigenvalue $\chi$ that appears in the expression for $\Delta V$ is that for the (cut-off) waveguide mode which dominates in the waveguide section formed by the opening in the resonator wall, and is most likely to be the eigenvalue of the waveguide mode, with the lowest cut-off frequency, whose $E$ and $H$ fields couple most efficiently with the cavity fields in the region of the opening. The value of $\chi$ used will therefore depend on the cavity mode under consideration and the position of the opening in the cavity wall. To assess which waveguide mode is most likely to dominate and therefore which value of $\chi$ is to be used, for a given location of opening, we can use the field patterns for the resonant modes given in section (3.3) for the cylinder and (3.4) for the sphere. For example, if we are considering the TM010, TM011, and TM110 cylindrical cavity modes and the opening lies in the centre of an end plate at $(r = 0, z = L)$ then inspection of the field patterns of the cylindrical cavity and cylindrical waveguide modes, in figures (3.3) and (3.2), respectively, shows that the lowest waveguide mode that would couple efficiently with these resonant cavity modes is the TM01 mode, and this has an eigenvalue of $\chi_{01} = 2.40483$. The opening is in the centre of an end plate, and so the appropriate resonance frequency shift formulae are equation (29) for TM010 and TM011 (the shift must be divided by 2 for TM010, since $s = 0$), and equation (30) for TM110, where the shift must be divided by 2 because $s = 0$. 
The brass cylindrical resonator used in this work was used to test the validity of the resonance frequency shift formulae as follows. Before final polishing of the internal surfaces, a circular hole, with a diameter of \((0.95 \pm 0.03)\) mm, determined from the best available mechanical measurements, was drilled through the exact centre of the bottom end plate. This opening was to serve as a gas inlet hole for the resonator. On the external side of the endplate (i.e. that which faces outwards when the resonator is assembled), a thread was tapped in the hole to a depth of approximately 2 mm and a brass plug with a threaded section near its shoulder was carefully machined so that when screwed into the hole, it left no discernible gap on the inner surface when viewed with a jeweller’s eyeglass. The end of the plug was smoothed, whilst the plug was screwed into the endplate, to leave it perfectly flush with the surface of the endplate. Thus, when the plug was carefully screwed into place, up to its shoulder, the endplate inner surface was without any discernible deformation, and when the plug was removed a circular opening of diameter \((0.95 \pm 0.03)\) mm was revealed. Thus, by inserting and removing the plug, the differences between the resonance frequencies of the TM010 and TM011 modes in the absence of, and in the presence of, the opening could be measured under ambient conditions. These differences were equal to the shifts in resonance frequencies due to the presence of the opening and were expected to agree with the shifts calculated using equations (29) and (30).

The measurements were taken very carefully, using the procedure described in chapter 6, and the plug was handled whilst wearing disposable gloves to help reduce heat transfer and ensure cleanliness. Two series of measurements were taken, for both modes, on consecutive days. For the first series, presented in tables (4.1) and (4.2), measurements were taken with the plug alternately inserted and removed, and the corresponding resonance frequency shifts were estimated by subtracting each measurement of resonance frequency from the average of the measurements taken before and after it. For the second series of measurements, presented in tables (4.3) and (4.4), a number of measurements were taken with the plug inserted, followed by a number of measurements with the plug removed, followed by another set of measurements with the plug inserted; in this way the variation of the measurements of \(f_N\) and \(g_N\) with time (and, therefore, ambient temperature variation) could be
followed. These two methods of measurement allowed two different means of estimating the corrections for ambient temperature drift and, it was hoped, helped to reduce the effects of any unknown systematic errors. The fractional resonance frequency shifts given in tables (4.1) to (4.4) have been corrected, in the manners indicated above, for drift in ambient temperature. The average of the 12 determinations of the fractional shift in resonance frequency, due to the presence of the opening, for the TM010 mode was (+22.9 ± 0.8) ppm, and the average of the 11 determinations of the fractional shift in resonance frequency, due to the presence of the opening, for the TM011 mode was (+32.7 ± 0.3) ppm, where the uncertainties are single standard deviations.

In order to calculate the fractional shifts for the perturbation due to the opening it was necessary to know the internal radius $a$ and length $L$ of the cavity. These were nominally $a = 9.5$ mm and $L = 20.0$ mm, but they were determined more accurately by using the average measured resonance frequencies of the TM010 and TM011 modes with the plug inserted.

For the purposes of this determination of $a$ and $L$ it was assumed that the measured halfwidths $g_N$ were equal to the reductions in the resonance frequencies due to all other perturbations, including the skin-depth perturbation, and so the halfwidths were added to the measured resonance frequencies to obtain estimates of the unperturbed resonance frequencies $f_N^0$. The unperturbed resonance frequencies of the TM010 and TM011 modes are related to the dimensions $a$ and $L$ by

$$f_{010}^0 = \left( f_{010} + g_{010} \right) = \frac{X_{01}c}{2\pi a}$$  \hspace{1cm} (4.7.61)

$$f_{011}^0 = \left( f_{011} + g_{011} \right) = c\left[ \left( \frac{X_{01}}{2\pi a} \right)^2 + \left( \frac{1}{2L} \right)^2 \right]^{\frac{1}{2}}$$  \hspace{1cm} (4.7.62)

where $f_{010}$ and $f_{011}$ are the measured resonance frequencies and $g_{010}$ and $g_{011}$ are the measured halfwidths. Thus the cavity radius $a$ was calculated from the measured TM010 resonance frequency and halfwidth, and found to be $a = (9.520 ± 0.001)$ mm, where the estimated uncertainty is principally due to the uncertainty in ambient temperature and air pressure. The cavity length was obtained from the measured TM011 resonance frequency and halfwidth and using $a = (9.520 ± 0.001)$ mm from
Table (4.1) Cylinder gas inlet perturbation measurements for the TM010 mode (first series)

<table>
<thead>
<tr>
<th>plug position</th>
<th>$f_{010} / \text{MHz}$</th>
<th>$g_{010} / \text{MHz}$</th>
<th>$10^6 \left( \Delta f / f_{010}^0 \right)$</th>
</tr>
</thead>
<tbody>
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<td>1.5654</td>
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Table (4.2) Cylinder gas inlet perturbation measurements for the TM011 mode (first series)

<table>
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<th>plug position</th>
<th>$f_{011} / \text{MHz}$</th>
<th>$g_{011} / \text{MHz}$</th>
<th>$10^6 \left( \Delta f / f_{011}^0 \right)$</th>
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Table (4.3) Cylinder gas inlet perturbation measurements for the TM010 mode (second series)

<table>
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<th>plug position</th>
<th>time / mins.</th>
<th>$f_{010}$ / MHz</th>
<th>$g_{010}$ / MHz</th>
<th>$10^6(\Delta f/f_{010}^0)$</th>
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Table (4.4) Cylinder gas inlet perturbation measurements for the TM011 mode (second series)

<table>
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<th>time / mins.</th>
<th>$f_{011}$ / MHz</th>
<th>$g_{011}$ / MHz</th>
<th>$10^6(\Delta f/f_{011}^0)$</th>
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110
the TM010 measurements, and was found to be \( L = (19.956 \pm 0.004) \text{mm} \), where the uncertainty principally arises from the uncertainties in ambient temperature and air pressure, and the uncertainty in \( a \).

The calculated fractional shift in resonance frequency for the TM010 mode is given by equation (29) as

\[
\left( \frac{\Delta f}{f_{010}^0} \right) = \left[ \frac{1}{2} J_0^2 \left( \chi_{01} \right) \right] \left( \frac{\Delta V}{V_0} \right) = \left[ \frac{1}{2} J_0^2 \left( \chi_{01} \right) \right] \left( \frac{b^3/2 \chi_{01}}{a^2 L} \right)
\]  

(4.7.63)

where \( J_0 \left( \chi_{01} \right) = -0.51915 \) [8], \( \chi_{01} = 2.40483 \) [see table (3.1)], \( b = (0.475 \pm 0.015) \times 10^{-3} \text{m} \), \( a = (9.520 \pm 0.001) \times 10^{-3} \text{m} \) and \( L = (19.956 \pm 0.004) \times 10^{-3} \text{m} \). This gives a calculated fractional shift of \( \left( \frac{\Delta f}{f_{010}^0} \right) = (+22.9 \pm 2.2) \text{ppm} \), in perfect agreement with the average measured fractional shift of \((+22.9 \pm 0.8) \text{ppm}\). The calculated fractional shift in resonance frequency for the TM011 mode is given by equation (30) as

\[
\left( \frac{\Delta f}{f_{011}^0} \right) = \left[ \left( 1 + \frac{\pi^2}{k^2 L^2} \right) J_0^2 \left( \chi_{01} \right) \right]^{-1} \left( \frac{\Delta V}{V_0} \right) = \left[ \left( 1 + \frac{\pi^2}{k^2 L^2} \right) J_0^2 \left( \chi_{01} \right) \right]^{-1} \left[ \frac{b^3/2 \chi_{01}}{a^2 L} \right]
\]  

(4.7.64)

where \( k = \chi_{01}/a = (252.608 \pm 0.027) \text{m}^{-1} \), and the other parameters are as given before. This gives a calculated fractional shift of \( \left( \frac{\Delta f}{f_{011}^0} \right) = (+32.9 \pm 3.2) \text{ppm} \) which is in excellent agreement with the average measured fractional shift of \((+32.7 \pm 0.3) \text{ppm}\).

The excellent level of agreement between the calculated and measured fractional shifts in resonance frequency for these cylinder modes is perhaps somewhat fortuitous since the important hole radius \( b = (0.475 \pm 0.015) \text{mm} \) used is a best estimate from simple mechanical measurements of the hole diameter at the inner surface of the endplate. However, the agreement is sufficiently good that the theory presented in this section would appear to be satisfactory for the treatment of small openings in the cavity wall.
The resonance halfwidths, with the plug inserted and removed, were routinely measured with the resonance frequencies, using the procedure described in chapter 6, and are also shown in tables (4.1) to (4.4). It was found that there was no significant change in the halfwidth of either mode when the plug was removed: the average change in halfwidth when the plug was removed was \((0.0005 \pm 0.0072)\) MHz for the TM010 mode, where the largest change was \((0.0019 \pm 0.0071)\) MHz, and \((0.0007 \pm 0.0115)\) for the TM011 mode, where the largest change was \((0.0037 \pm 0.0113)\) MHz. The resonance frequency shift formula of equation (1), used to calculate the fractional shift in the resonance frequencies, gives purely real resonance frequency shifts since it is concerned with deformations of a perfectly conducting boundary which do not contribute to the resonance halfwidth. However, in the case of openings, there may be radiative losses. For small openings of radius \(b \ll a\) (the cavity radius), we have seen that any waveguide mode that may attempt to propagate along the opening is cut-off and there will, therefore, be no significant power flow through the waveguide section formed by the opening and, thus, no additional energy loss. This argument is borne out by the failure to detect a significant change in resonance halfwidth in the presence of the opening. An expression for the quality factor \(Q_{hole}\) for a given mode, due to the presence of an opening in the side of a square-prismatic resonator is given in reference 12 as

\[
Q_{hole} = \left(\frac{f_N}{2g_{hole}}\right) = \frac{27\pi^3}{16\sqrt{2}} \left(\frac{a^3}{A}\right) \frac{L}{2a}
\]

(4.7.65)

where \(f_N\) is the measured resonance frequency of the mode, \(g_{hole}\) is the contribution to the resonance halfwidth due to radiative losses through the hole, \(a\) is half the length of a side of the resonant cavity, \(L\) is its height and \(A\) is the cross-sectional area of the hole. The resonance frequencies and halfwidths due to electrical losses in the resonator walls of cylindrical and square-prismatic resonators of comparable dimensions are similar and so equation (65) might be used to estimate \(g_{hole}\) for the TM010 and TM011 modes of the cylindrical resonator used in this work, by replacing \(a\) by the radius of the cylinder and \(L\) by the length of the cylinder. Using the dimensions for \(a, b\) and \(L\) given previously, we calculate \(Q_{hole} = 8.1 \times 10^7\) which, using \(f_{010} = (12051.4874 \pm 0.0030)\) MHz and \(f_{011} = (14199.3362 \pm 0.0050)\) MHz as typical measured resonance frequencies with the plug inserted, gives
\[ g_{010}^{\text{hole}} = 0.00007 \text{ MHz} \] and \[ g_{011}^{\text{hole}} = 0.00009 \text{ MHz}. \] These contributions are much smaller than the uncertainties in the measured halfwidths, which were typically \( \pm 0.0050 \text{ MHz} \) for \( g_{010} \) and \( \pm 0.0080 \text{ MHz} \) for \( g_{011} \), and so equation (65) is in accordance with the observation that an opening as small as the one in the wall of the brass cylinder would make no significant contribution to the halfwidth of the resonances, and this is very likely to be the case for all openings with \( b \ll a \).

In order to verify further the resonance frequency shift formula of equation (1), another brass plug was fashioned, which also fitted very tightly into the opening when inserted, but in this case the length of the plug was kept overlong so that, when inserted, the end of the plug (which was machined smooth and perpendicular to the shaft of the plug) protruded by some small amount into the cylindrical cavity space. The plug was fully inserted into the hole in the end plate and the resonance frequencies and halfwidths of the TM010 and TM011 modes were measured. Small pieces of stainless-steel shim of accurately known thicknesses were placed under the shoulders of the plug to lift the plug end by an accurately known amount and, thereby, decrease the amount by which the plug protruded into the cavity space. Shim of thicknesses 0.10 mm, 0.15 mm and 0.20 mm were available and so, by combining pieces of shim of different thicknesses, it was possible to make measurements of resonance frequency and halfwidth for the following displacements of the plug: fully inserted (0 mm) and removed by the amounts 0.10 mm, 0.15 mm, 0.20 mm, 0.25 mm, 0.30 mm, 0.35 mm and, finally, 0.40 mm. These displacements correspond to a protrusion, and then an indentation of increasing depth, in the centre of the end plate. Thus the measurements of \( f_N \) and \( g_N \), at each of the plug positions, should provide a rigorous test of the ability of equation (29) to also predict the resonance frequency shifts due to a protrusion and an indentation (the equation has already been demonstrated to very accurately predict the resonance frequency shift caused by a full-thickness hole). The measured fractional shifts in resonance frequency, relative to the initial resonance frequency where the plug is fully inserted and thus protrudes by a small unknown amount into the cavity space, are presented graphically in figure (4.1).
Figure (4.1) Fractional shifts in the resonance frequencies of TM010 and TM011 modes caused by a plug displacement $\Delta h$

It is important to understand that these measurements are 'raw', and represent the fractional resonance frequency shifts with respect to the initial position of the plug where it protrudes into the cavity space, and not with respect to an initial position where the plug end is flush with the inner surface of the end plate, as was the case for the measurements with the first brass plug described. Thus, the overall fractional shifts of +39.2 ppm for TM010 and +54.3 ppm for TM011 were the fractional shifts in resonance frequency from an initial state where the plug protruded by some small amount to the final state where the plug had been lifted by 0.40 mm. It is clear from the measurements that the fractional shifts in resonance frequency for both modes increased steadily as the plug was progressively removed from the cavity space, until the plug had been lifted by approximately 0.18 mm from its initial position and then there were no further shifts in the resonance frequencies. This is in qualitative agreement with the predictions from equations (29), (63) and (64), in that they predict that as the plug is removed from the cavity, and $\Delta V$ in equation (29) reduces, the measured resonance frequencies should approach the unperturbed resonance frequencies [having initially been lower than the unperturbed resonance
frequencies by an amount in accordance with equation (29)] and then the measured resonance frequencies should begin to exceed the unperturbed resonance frequencies, again in accordance with equation (29), as the plug continues to be lifted and an indentation appears, until it reaches a position where the indentation has a depth approximately equal to the cut-off length $h_{co} = \left(\frac{b}{2}\chi_{01}\right)$, at which point there ought to be no further shift as the plug is removed. If our ideas about the cut-off nature of the indentation (or opening) were false we should see no plateau in the measurements.

The quantitative agreement between the measurements and the theory presented in this section can also be shown to be very good. We know from the earlier measurements that the fractional resonance frequency shifts corresponding to displacement of a closely fitting plug from a position where its end is flush with the inner surface of the end plate to a state where it has been completely removed are $(+22.9 \pm 0.8)$ ppm for the TM010 and mode $(+32.7 \pm 0.3)$ ppm for the TM011 mode (these are, of course, the measured fractional resonance frequency shifts due to the presence of the opening). Therefore if these fractional shifts are subtracted from the overall fractional shifts of $+39.2$ ppm for TM010 and $+54.3$ ppm for TM011, the remaining fractional shifts, of $+16.3$ ppm for TM010 and $+21.6$ ppm for TM011, can be attributed to the changes in the resonance frequencies that occur due to the movement of the plug from its initial position where it protruded by some amount into the cavity space to the position where its end was flush with the inner surface of the end plate. The plug was very close fitting in the opening and a best estimate of its radius was $(0.475 \pm 0.015)$ mm, the same as the opening, and, using this radius, it is possible to estimate, from equation (29), the extent to which the plug was protruding into the cavity space when fully inserted. Equation (29) is written for the TM010 mode as

$$\left(\frac{\Delta f}{f_{010}}\right) = \left[\frac{1}{2}J_0^2(\chi_{01})\right]\left(\frac{r^2 d}{a^2 L}\right)$$  \hspace{1cm} (4.7.66)

and for the TM011 mode as
\[
\left( \frac{\Delta f}{f_{010}} \right) = \left[ \left( 1 + \frac{\pi^2}{k^2 L^2} \right) J_0^2 \left( \chi_{01} \right) \right]^{1/4} \frac{r^2 d}{a^2 L} \quad (4.7.67)
\]

where, in both of these equations, \( J_0 \left( \chi_{01} \right) = -0.51915 \) \[8\], \( a = (9.520 \pm 0.001) \) mm, \( L = (19.956 \pm 0.004) \) mm, \( r = (0.475 \pm 0.015) \) mm is the radius of the brass plug, and \( d \) is the length of protrusion to be calculated. The fractional resonance frequency shifts due to the protrusion are substituted into the appropriate equation, (66) or (67), to give estimates of \( d = (0.070 \pm 0.006) \) mm from the TM010 mode data and \( d = (0.065 \pm 0.006) \) mm from the TM011 mode data, where the uncertainties are estimated from the propagation of the uncertainties of the parameters in equations (66) and (67). The difference between these two values of \( d \) and the mean value of \( (0.068 \pm 0.004) \) mm corresponds to a fractional shift in \( f_{010}^0 \) on the order of 0.7 ppm and a fractional shift in \( f_{011}^0 \) on the order of 0.8 ppm, which shows the sensitivity of the determined values of \( d \) on the measured fractional resonance frequency shifts.

The mean value \( d = (0.068 \pm 0.004) \) mm will be taken as the best estimate of the amount by which the plug was protruding into the cavity when fully inserted. The magnitude of the fractional resonance frequency shifts due to this protrusion, 16.3 ppm for the TM010 mode and 21.6 ppm for the TM011 mode, must be subtracted from all the measured fractional shifts of the respective modes, and the length \( d = (0.068 \pm 0.004) \) mm should be subtracted from the plug displacements \( \Delta h \), to 'normalise' the measurements presented in figure (4.1). In doing this, we obtain the graphs presented in figure (4.2), which represent the fractional resonance frequency shifts relative to the resonance frequencies of the undeformed cavity.

Had it been possible to take an accurate measurement of the protrusion of the plug when fully inserted this procedure would not have been necessary, but this was found to be difficult without potentially scratching the inner surface of the end plate in the process. However, it is certainly the case that the protrusion was less than 0.1 mm, in accordance with the semi-empirical value of \( d = (0.068 \pm 0.004) \) mm.
Figure (4.2) Normalised fractional shifts in the resonance frequencies of TM010 and TM011 modes caused by a normalised plug displacement $\Delta h_{\text{corr}}$

Also shown in figure (4.2) are lines of calculated fractional resonance frequency shifts, obtained using equation (29), with $\Delta V$ replaced by $\pi b^2 \Delta h_{\text{corr}}$ where $b$ is the radius of the plug, which is also the estimated radius of the opening, and $\Delta h_{\text{corr}}$ is the depth of indentation in the end plate due to withdrawal of the plug ($\Delta h_{\text{corr}}$ is negative for positions of the plug where the end protrudes into the cavity space since $\Delta V$ must be negative in this case). The lines have been calculated for the same values of the parameters in equation (29) as have already been given and the agreement between the calculated fractional resonance frequency shifts and the measured values is seen to be very good. As a final indication of the accuracy of this theory, the three fractional shifts, for each of the modes, which appear at the three lowest values of $\Delta h_{\text{corr}}$ in the measurements presented in figure (4.2), and which are presumed to correspond to displacements of the plug where $\Delta h_{\text{corr}} < h_{\text{co}}$, were fitted to the corresponding values of $\Delta h_{\text{corr}}$ using linear regressions without any constant terms [since $(\Delta f / f_N^0)$ must be zero for $\Delta h_{\text{corr}} = 0$]. The results were
where the regression on the TM010 data, equation (68), had a standard deviation of 1.3 and that on the TM011 data, equation (69), had a standard deviation of 0.3. The gradients indicated in equations (68) and (69) ought to correspond to

\[ 10^6 \left( \frac{\Delta f}{f_{010}} \right) = (221.2 \pm 7.2) \times 10^3 \left( \frac{\Delta h}{m} \right) \quad (4.7.68) \]

\[ 10^6 \left( \frac{\Delta f}{f_{011}} \right) = (330.0 \pm 1.4) \times 10^3 \left( \frac{\Delta h}{m} \right) \quad (4.7.69) \]

Using the previously quoted values for the other parameters, we can use the expressions to estimate values of \( b \) from the gradients obtained by the regressions on the measured fractional resonance frequency shifts. Therefore we obtain \( b = (0.464 \pm 0.014) \text{ mm} \), from the TM010 data, and \( b = (0.472 \pm 0.002) \text{ mm} \), from the TM011 data, both of which agree, within their combined uncertainties, with the estimate of \( b \) from mechanical measurements. These two estimates of \( b \) are both very slightly smaller than the value of \( b \) that has been used in the calculations of \( \left( \Delta f / f_0^0 \right) \) presented in this section. If we had used these values in the calculations of the fractional resonance frequency shifts due to the presence of the opening earlier in this section, we would have obtained \( \left( \Delta f / f_{010}^0 \right) = (+21.3 \pm 2.0) \text{ ppm} \), and \( \left( \Delta f / f_{011}^0 \right) = (+32.1 \pm 0.4) \text{ ppm} \), which are still in very good agreement with the measured fractional shifts of \( (+22.9 \pm 0.8) \text{ ppm} \) and \( (+32.7 \pm 0.3) \text{ ppm} \) for the TM010 and TM011 modes, respectively.

The very small differences between these newly calculated shifts and the corresponding measurements are most likely to be due to the small clearance space, which must necessarily exist, between the wall of the opening and the shaft of the second brass plug (i.e. that which was used for the plug displacement measurements), which would give rise to smaller shifts being measured for a given
displacement of the plug, or the end of the first brass plug being very slightly proud of the inner surface of the end plate when fully inserted, which would give rise to larger than expected shifts being measured when the plug was completely removed.

Equations (68) and (69) can also be used to estimate the cut-off length $h_{co}$ by calculating the plug displacement $\Delta h_{cor}$ for which $\left( \Delta f / f_{010}^0 \right) = (+22.9 \pm 0.8) \text{ ppm}$ and $\left( \Delta f / f_{011}^0 \right) = (+32.7 \pm 0.3) \text{ ppm}$, which are the measured fractional shifts in resonance frequency of the TM010 and TM011 modes, respectively; due to the presence of the opening. Substituting these fractional shifts into the appropriate equation, (68) or (69), gives $h_{co} = (0.108 \pm 0.007) \text{ mm}$ from the TM010 mode data, and $h_{co} = (0.099 \pm 0.001) \text{ mm}$ from the TM011 mode data. These estimates of $h_{co}$, from the measured shifts alone, are in very good agreement with $\left( b / 2 \chi_{01} \right) = (0.099 \pm 0.003) \text{ mm}$, calculated from the theory of the perturbation, and provide very good support for the theory as a whole and, in particular, the assumption that it is the (cut-off) TM01 cylindrical waveguide mode that dominates in the waveguide section formed by the opening in the end plate.

The resonance halfwidths of both modes were also measured, for each displacement of the brass plug, and are presented in figures (4.3) and (4.4). Clearly the halfwidths did not significantly change as the brass plug was progressively removed from the cavity, in accordance with the fractional resonance frequency shift formula of equation (1) which predicts purely real resonance frequency shifts.

It would appear from the work presented, that equation (29) is capable of very accurate predictions of the fractional shifts in resonance frequency of cylinder TM01s modes for protrusions, indentations and even full-thickness holes [where equation (29) is supplemented by equation (54)] in the centre of an end plate. The theory presented has been rigorously tested and appears capable of predicting the fractional shifts to within about 5% of the measured fractional shifts, which corresponds to about 1.5 ppm, or better, in resonance frequency for the quite large resonance frequency shifts discussed (a 0.95 mm diameter deformation is quite large for such a small cylindrical resonator). The agreement should become even better if the resonator and the deformation(s) can be characterised with greater accuracy. Although the other resonance frequency shift formulae presented in this section have not been verified experimentally, they nevertheless arise from the same type of
Figure (4.3) Halfwidth of the TM010 mode at a normalised plug displacement $\Delta h_{\text{corr}}$

![Graph of Figure 4.3](image1)

Figure (4.4) Halfwidth of the TM011 mode at a normalised plug displacement $\Delta h_{\text{corr}}$

![Graph of Figure 4.4](image2)
analysis as equation (29), and so we might expect that they will be just as accurate if carefully applied. Great care is particularly necessary, if an opening is to be considered, in employing the correct waveguide mode eigenvalue \( \chi \) for use in equation (54), since the wrong choice can lead to very different calculated resonance frequency shifts. A further difficulty can arise for degenerate \( p \neq 0 \) cylindrical cavity modes, which have angular dependence of electromagnetic fields. The orientation of the \( E \) and \( H \) fields may not be same as that predicted from the unperturbed cavity theory, in which case the predicted resonance frequency shifts may differ somewhat from the actual shifts. It is difficult to imagine how such a problem could be completely avoided. The same problem may, of course, arise in estimating the shifts in resonance frequency caused by deformations of spherical cavity boundary walls as has previously been noted in this section and in section (4.6). However, it is still instructive to estimate the effect of the opening on the resonance frequency of the doubly-degenerate TM110 cylinder mode.

The cut-off length \( h_{co} \) is the same as that for the TM010 and TM011 modes, since we assume that it is the (cut-off) TM01 waveguide mode that dominates within the opening and so \( \Delta V = \pi b^2 h_{co} = \pi (b^2/2 \chi_{01}) \), as before. This expression for \( \Delta V \) is substituted into equation (30) to give

\[
\left( \frac{\Delta f}{f_0^{10}} \right) = \left\{ \frac{1}{2} \left[ 2 J_1^2 \left( \chi_{11} \right) \right] \right\} \left[ \frac{(b^3/2 \chi_{01})}{a^2 L} \right]
\]  

(4.7.70)
since \( \omega^2 \varepsilon \varepsilon_0 \mu_0 = k^2 \) for \( s = 0 \) modes. Substituting \( J_1^1(\chi_{11}) = -0.40276 \) \( [8] \), \( b = (0.475 \pm 0.015) \) mm, \( a = (9.520 \pm 0.001) \) mm, \( L = (19.956 \pm 0.004) \) mm and \( \chi_{01} = 2.40483 \) into this expression gives a predicted fractional shift of \( (\Delta f/f_0^{10}) = -(19.0 \pm 1.8) \) ppm. Thus, we would predict that the opening causes a reduction in the resonance frequency by 19 ppm of the unperturbed resonance frequency, a shift of a similar magnitude but opposite ‘direction’ to that calculated and measured for the TM010 mode. The shifts for the TM010 and TM011 modes are positive because it is the electric field that dominates in the vicinity of the perturbation (the opening), whereas for the TM110 mode, the magnetic field is stronger in the region of the perturbation. Equation (30) gives the fractional resonance frequency shift for both the \( p = +1 \) and \( p = -1 \) components of the TM110
mode, since equation (30) is exactly the same whether \( p \) is positive or negative, and so we predict that the two components are shifted by exactly the same amount, correct to first order. The opening itself is not expected to make any contribution to the resonance halfwidth, as discussed earlier, and, as the two components will ‘move together’, the measured halfwidth ought to be the same in the presence of the opening as it is in absence of the opening. Unfortunately, measurements on the TM1110 mode were not taken before final assembly of the cylindrical resonator, in order to verify the predicted resonance frequency shift, but it is likely to be accurate to about 1 ppm of the unperturbed resonance frequency, if the orientation of the fields within the perturbed cavity is similar to that expected in an unperturbed cavity.

The spherical resonator used in this work has a 1 mm diameter gas inlet hole drilled through the wall at its north pole (polar angle \( \theta = 0 \)) [36]. Equation (7) enables the prediction of the first-order fractional shift in resonance frequency for any TM\( mn0 \) mode (i.e. the \( m = 0 \) component of any TM\( mn \) mode) and equation (18) predicts the fractional shifts for the \( m = \pm 1 \) components of any TM\( mn \) mode. Using these two equations, we can estimate the fractional shifts in resonance frequency due to the presence of the gas inlet hole for all three components of the TM\( 1n \) modes measured in this work (TM11, TM12 and TM13) and also the \( m = 0 \) components of the TM21 and TM31 modes measured in this work. For the purposes of these calculations it is assumed that the orientations of the \( E \) and \( H \) fields in the perturbed cavity are the same as we would expect in the corresponding unperturbed cavity [this assumption was used to derive equations (7) and (18)]. It is difficult to estimate the accuracy of this assumption since detailed measurements of the resonance frequency shift due to such perturbations in the sphere have not been reported in the literature, but we could expect that the calculated shifts will have the same order of magnitude as the actual shifts. The additional volume \( \Delta V \), which arises due to the presence of the hole, will be given by equation (54) as \( \Delta V = \pi(b^3/2 \chi) \), where \( b \) is the hole radius and \( \chi \) is the eigenvalue of the dominant (cut-off) waveguide mode that is excited within the opening by the cavity fields. For the \( m = 0 \) components it is most likely that \( \chi = \chi_{01} \), as was found for the cylindrical resonator, since the TM01 waveguide mode is that mode with the lowest cut-off frequency whose \( E \) and \( H \) fields are likely to couple most efficiently with the spherical cavity \( E \) and \( H \) fields of
the $m = 0$ components [see figures (3.2) and (3.5)]. Thus, for the TM$n0$ modes, the best estimate of $\Delta V$ is $\pi \left( b^3/2 \chi_{01} \right)$. For a TM$n$ mode, the $m = +1$ and $m = -1$ components have similar $E$ and $H$ fields to the $m = 0$ component but the fields are orthogonal to those of the $m = 0$ component and mutually orthogonal to each other. Therefore, for the $m = \pm 1$ components, the most likely value of $\chi$ will not be $\chi_{01}$, for a hole at $\theta = 0$, but is more likely to be $\chi'_{11}$, the cylindrical waveguide TE11 mode eigenvalue, since the $E$ and $H$ fields of the TE11 mode are more likely to couple efficiently with the $E$ and $H$ fields of the $m = \pm 1$ components of a spherical cavity TM$n$ mode in the vicinity of a hole at $\theta = 0$.

The calculation of the unperturbed cavity volume $V_0$ requires the spherical cavity radius $a$ and for these calculations the evacuated cavity radius $a_0$, at temperature $T = 273 \text{ K}$, will be used. Equation (4.3.5) gives $a_0(273 \text{ K}) = (39.99178 \pm 0.00048) \times 10^{-3} \text{ m}$ and thus $V_0 = \left( 4/3 \right) \pi a_0^3 = (267.9173 \pm 0.0057) \times 10^{-6} \text{ m}^3$. Using $\Delta V = \pi \left( b^3/2 \chi_{01} \right)$ for the TM$n0$ modes and $\Delta V = \pi \left( b^3/2 \chi_{11}' \right)$ for the TM$n \pm 1$ modes, the first order fractional shifts in resonance frequency for the sphere modes used in this work were calculated and are presented in table (4.5).

<table>
<thead>
<tr>
<th>$10^6 \left( \Delta f_{\text{hole}} / f_{\text{beam}}^0 \right)$</th>
<th>$m = 0$</th>
<th>$m = \pm 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM11$m$</td>
<td>+0.11</td>
<td>-0.27</td>
</tr>
<tr>
<td>TM12$m$</td>
<td>+0.02</td>
<td>-0.21</td>
</tr>
<tr>
<td>TM13$m$</td>
<td>+0.001</td>
<td>-0.20</td>
</tr>
<tr>
<td>TM21$m$</td>
<td>+0.34</td>
<td></td>
</tr>
<tr>
<td>TM31$m$</td>
<td>+0.67</td>
<td></td>
</tr>
</tbody>
</table>
The estimated accuracy of the calculated fractional shifts in resonance frequency presented in table (4.5) is ±5%, provided the perturbed cavity fields in the region of the opening approximate to those of the corresponding unperturbed cavity in the same region. Even if the accuracy is only ±30%, then it is only for the TM31 mode that the calculated fractional resonance frequency shift will be in error by more than 0.1 ppm of the unperturbed resonance frequency, which is on the order of the experimental uncertainty of the measured resonance frequencies. The fractional resonance frequency shifts for TM1n0 modes with $n \geq 4$ will be smaller than 0.007 ppm, and those for TM1n ±1 modes with $n \geq 4$ will be −0.20 ppm, correct to 2 significant figures. As was predicted, and measured, for the cylinder modes, the presence of the gas inlet opening in the wall of the spherical resonator is not expected to make a significant contribution to the resonance halfwidth of any mode.

The boundary shape perturbation formula of equation (1) has been shown to be capable of accurately predicting the fractional shifts in resonance frequency due to localised protrusions, indentations and openings in the resonator wall and it may be expected to predict the fractional shifts caused by any form of such perturbations provided their dimensions and positions within the boundary wall can be determined accurately. Although the experimental verification of equation (1) has been limited to two resonant modes in one cylindrical resonator, the agreement between theory and experiment was shown to be so good, particularly for such a large perturbation, that it is expected that it will be the accurate characterisation of deformations rather than the validity of equation (1), and all those equations carefully derived from it, which will prove to be the limiting factor in determining the effect of boundary shape deformations on the resonance frequencies of resonant cavity modes.

4.8 Coupling

The measured microwave resonance frequency $f_N$ and halfwidth $g_N$, of a resonant cavity mode, depend on the electrical admittances of the microwave generator (the source) and the instrumentation to measure the output power (the load). An admittance $Y$ is the reciprocal of the corresponding impedance $Z$ and is defined as
where $G$ is the conductance and $B$ is the susceptance. If the reduced admittance of the source is $G_S + iB_S$, and the reduced admittance of the load is $G_L + iB_L$, where 'reduced' means that the admittance is expressed as a fraction of the corresponding characteristic admittance, then the first order fractional shift in a resonance frequency is given by [11, 50]

$$\frac{\Delta f_{\text{ext}}}{f_N^0} = -\frac{1}{2Q_{\text{ext}}}$$

and the contribution to the resonance halfwidth is [11, 50]

$$g_{\text{ext}} = \frac{G_S + G_L}{2Q_{\text{ext}}}$$

where $Q_{\text{ext}}$ is the external quality factor, which arises from the energy losses in the resistive parts of the source and load impedances.

If the source and load are perfectly matched to the coaxial lines attached to the resonant cavity, then we can put $B_S = B_L = 1$ and $G_S = G_L = 1$, and equations (2) and (3) become

$$\frac{\Delta f_{\text{ext}}}{f_N^0} = -\frac{1}{2Q_{\text{ext}}}$$

$$g_{\text{ext}} = \frac{f_N}{2Q_{\text{ext}}}$$

Therefore, if $f_N \equiv f_N^0$, there is a reduction in the resonance frequencies which is equal to the corresponding contributions to the halfwidth.

The insertion loss $I$ of a given mode, which is a measure of the decrease in power on transmission through the cavity resonator for that mode, is defined as [11]

$$I = 10\log_{10}\left(\frac{P_{\text{in}}}{P_{\text{out}}}ight) = 10\log_{10}\left(1/\eta_c\right)$$
where $P_{in}$ is the input power, $P_{out}$ is the output power and $\eta_c = \left( P_{out}/P_{in} \right)$ is called the circuit efficiency, for the mode. The circuit efficiency is related to the external quality factor of the mode by [11]

$$\eta_c = \frac{1}{1 + (Q_{ext}/Q_u)} \quad (4.8.7)$$

where $Q_u$ is the unloaded quality factor of the mode. This is the quality factor of the mode for an isolated cavity, and is that due to all other losses except those which contribute to $Q_{ext}$. $Q_u$ is related to the total or loaded quality factor of the mode $Q_N$ by

$$\frac{1}{Q_N} = \left( \frac{1}{Q_u} + \frac{1}{Q_{ext}} \right)_N \quad (4.8.8)$$

Therefore the total measured halfwidth of the mode $g_N$ is given by

$$g_N = \left( g_u + g_{ext} \right)_N \quad (4.8.9)$$

where $g_u$ is the halfwidth of the unloaded cavity and $g_{ext}$ is the contribution to the halfwidth due to the losses in the resistive parts of the source and load impedances.

Although we were unable to calculate the fractional resonance frequency shift of equation (4), for either of the cavities used in this work, measurements, described in reference 51, on a brass cylindrical cavity, coupled by simple probe antennae and with total quality factors of approximately 3000 for the modes of operation (which is very similar to the quality factors of the modes of the cylinder used in this work) suggest that the fractional shifts could be on the order of 1 ppm or less if the source and load are very accurately matched to the coaxial lines attached to the resonant cavity. A general procedure for measuring the insertion loss of equation (6) is given in reference 52.

This work is concerned with the measurement of relative, rather than absolute, speeds of light and, therefore, we are more concerned with changes in the resonance frequency than the absolute resonance frequencies themselves. Therefore, even if the (unknown) resonance frequency shifts due to these external effects is much larger than suspected, the accuracy of the dielectric constant measurements presented in
this work should not be compromised if $Q_{\text{ext}}$, which appears in equation (4) does not alter significantly with frequency and/or pressure. This important point is explained more fully in section (4.10).

In this work, the resonant modes were excited and detected by means of short, straight, probe antennae which were formed by extending the central conductors of coaxial microwave cables into the cavity space. The antennae were positioned so as to be aligned with the $E$ field lines of the modes which were to be excited and detected. Generally, antennae are placed in a region of strong $E$ field (high density of $E$ field lines) so as to strongly excite/detect the mode, although this will give rise to larger perturbations due to the presence of the antennae themselves. There is, then, a compromise to be made between sensitivity and perturbation [11]. Alternative means of coupling include inserting loops, formed from the inner conductors of coaxial cables, into the cavity space to link the magnetic flux of the $H$ fields of the resonant modes, or waveguides (commonly cylindrical) are inserted into the walls of the resonator in positions such that the $E$ and $H$ fields of the waveguide mode couple effectively with the $E$ and $H$ fields of the resonant cavity mode [11, 18, 20]. Both of these alternative methods are likely to give rise to larger perturbations than small probe antennae because the physical disturbance they cause to the cavity fields would be greater [11].

The microwave cable on the input side transmits power from the source to the resonator and the radiation from the input antenna excites the resonant mode within the cavity. The output antenna is inserted so as to couple only loosely with the resonator mode so that the power flowing out into the output cable is a very small but constant fraction of the power dissipated within the cavity (principally in the wall of the cavity) [11]. The loose coupling is realised by using only very short probe antennae. Longer antennae would give rise to ‘tighter’ coupling which would increase the power transferred, and thus the circuit efficiency $\eta_C$, but at the expense of the external quality factor $Q_{\text{ext}}$. That is, if $\eta_C$ in equation (7) is large then the ratio $(Q_{\text{ext}}/Q_u)$ must be small and so $Q_{\text{ext}}$ must be small if $Q_u$ has remained relatively constant. So tight coupling, such as would be produced by long antennae, would give rise to a small $Q_{\text{ext}}$ and thus a large contribution to the halfwidth $e_{\text{ext}}$, for a given mode. This would degrade the resonance and make the precise measurement of
resonance frequency difficult. Therefore we use loose coupling given by short antennae, and compensate for the lower circuit efficiency by using higher input power and very sensitive detection and measurement equipment.

Measurements of the resonance frequency and halfwidth of modes TM010 and TM011 were taken, using the brass cylinder, under ambient conditions of temperature and pressure, for different lengths of probe antennae. Figure (4.5) shows the fractional difference, for each mode, between the resonance frequency for a given length of antennae \( l \), and that measured with antennae of nominally zero length (where the inner conductors are cut off flush with the ends of the coaxial cables). Also shown in figure (4.5) are the calculated fractional shifts due to the boundary shape deformation caused by the presence of the probe antennae, obtained using equation (4.7.29). The differences between the measured and calculated fractional shifts are mainly attributed to the effects of the resistive parts of the source and load impedances. Figure (4.6) shows the corresponding fractional changes in the measured halfwidths, and figure (4.7) shows the ratios of the output power, measured at the diode, to the input power, from the microwave generator, for both modes (see schematic of microwave electronics in chapter 6). This ratio approximates to the circuit efficiency \( \eta_C \) and the correlations between \( \eta_C \), for a given length of antennae, and the fractional resonance frequency shifts and fractional changes in halfwidth are clearly seen. It was necessary to open the resonator, by unscrewing the top plate, in order to shorten the antennae after each measurement of \( f_N \) and \( g_N \), and therefore the length and average diameter of the cylinder were very slightly different for each of the measurements. This gave rise to shifts in \( f_N \) and, perhaps, changes in \( g_N \) itself, and so the presented resonance frequency shift measurements should only be considered accurate to approximately \( \pm 100 \text{ ppm in } f_N \) since this is the estimated inaccuracy introduced.

The smaller halfwidths were measured with antennae of nominally zero length and it was found, for such antennae, that the resonances of the TM010, TM011 and TM110 cylinder modes could still be excited and detected with sufficient power to enable precise measurement of the resonance frequencies and halfwidths in the presence of any background signals. Thus, potentially, the most precise
Figure (4.5) Fractional changes in the resonance frequencies of TM010 and TM011 modes for antennae of length \( l \)

![Graph showing fractional changes in resonance frequencies](image)

Figure (4.6) Fractional changes in the halfwidths of TM010 and TM011 modes for antennae of length \( l \)

![Graph showing fractional changes in halfwidths](image)
Figure (4.7) Approximate values of circuit efficiency of TM010 and TM011 modes for antennae of length \( l \)

![Graph showing approximate values of circuit efficiency for TM010 and TM011 modes.](image)

measurements of \( f_N \) and \( g_N \) could be made using antennae of nominally zero length in the cylinder.

The probe antennae used in the sphere were nominally 2 mm long and no measurements were made with shorter antennae. It might be possible to still excite and detect the sphere resonances, with sufficient strength, using antennae of nominally zero length, but it is likely that the success of such antennae in the cylinder was, in most part, due to the very small volume of the cavity, giving rise to appreciable \( E \) and \( H \) field amplitudes for relatively low levels of input power or cavity energy [see equations (3.3.28) and (3.4.56)].

As indicated in section (4.7), there was a boundary shape perturbation due to the physical presence of the antennae themselves, considered as protrusions into the cavity space. The first order fractional shifts in resonance frequency, \( \left( \frac{\Delta f_{an}}{f_N^0} \right) \), for the modes of the cylinder can be calculated using the appropriate forms of equations (4.7.29) and (4.7.30), where \( \Delta V \) is the volume of the cavity excluded by the presence of an antenna, i.e. the volume of an antenna. The antennae of nominally zero length
do not protrude into the cavity, to a first approximation, and if the ends of the coaxial cables are fitted to be perfectly flush with the inner surface of the end plate then $\Delta V$ will be zero. Thus, provided the cable ends remain flush with the inner surface of the end plate, we do not predict any shift in the resonance frequencies due to the physical structures of the antennae (although the presence of the coaxial cable ends in the end plate surface may shift the resonance frequencies). The 2 mm long probe antennae used in the sphere will exclude a volume $\Delta V = (\pi b^2) \times 2 \times 10^3$ m for each antenna, and we expect non-zero resonance frequency shifts. The antennae are placed at polar angles of $\pm (\pi/4)$, and separated by an azimuthal angle $\pi$, so the appropriate forms of equations (4.7.6) and (4.7.17) can be used to estimate the fractional resonance frequency shifts, $\left( \Delta f_{\text{ant}} / f_N^0 \right)$, on the TM sphere modes, caused by their physical presence.

4.9 Bulk losses

As described in chapter 2, above given frequencies of field variation the dielectric constant of a medium becomes complex and energy losses will arise. In addition, poor dielectrics may have a significant electrical conductivity $\sigma$, and this contributes an imaginary part, $-i(\sigma/\omega \varepsilon_0)$, to the dielectric constant $\varepsilon$, which also gives rise to energy dissipation within the dielectric. These energy losses can be grouped together under the heading of 'bulk losses', and they give rise to a first order contribution to the resonance halfwidth and a second order fractional shift in the resonance frequency.

In general, the dielectric constant for all LIH media, whether conducting or non-conducting, can be written [3]

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) - i\left(\sigma/\omega \varepsilon_0\right) = \varepsilon'(\omega) - i \left[\varepsilon'' + \left(\sigma/\omega \varepsilon_0\right)\right]$$  \hspace{1cm} (4.9.1)

for monochromatic field variations of angular frequency $\omega = 2\pi f$. Slater [11] suggests that the fractional shift in any resonance frequency due to non-zero $\left[\varepsilon'' + \left(\sigma/\omega \varepsilon_0\right)\right]$ for the medium within a resonant cavity is given by
where \( \omega_0^0 = 2\pi f_0^0 \). Therefore, the first non-vanishing resonance frequency shift is second order in \( (\sigma/\omega_0^0) \) and \( \epsilon'' \). This is negligible for all the gases used in this work and, indeed, would be negligible for the vast majority of gases under ordinary conditions of temperature and pressure. The contribution to the resonance halfwidth is [11]

\[
\Delta f_{\text{bulk}} = -\frac{1}{2} \left( \frac{\sigma}{2\omega_0^0 \epsilon' \epsilon_0} + \frac{\epsilon''}{2\epsilon'} \right)^2
\]

(4.9.2)

and so is first order in \( (\sigma/\omega_0^0) \) and \( \epsilon'' \). Neither \( \sigma \) nor \( \epsilon'' \) are expected to be significant for the simple, non-polar gases employed in this work [5, 7] and \( \Delta f_{\text{bulk}} \) is expected to be insignificant for all the measurements taken.

### 4.10 Summary

It is a general observation that all perturbations cause calculated fractional resonance frequency shifts, correct to first order, of the form

\[
\frac{f_N(p) - f_N^0(p)}{f_N^0(p)} = \frac{\Delta f_N(p)}{f_N^0(p)} = K[p, f_N(p)]
\]

(4.10.1)

where \( p \) is the gas pressure; \( f_N^0(p) \) is the unperturbed resonance frequency at pressure \( p \), \( f_N(p) \) is the perturbed resonance frequency at pressure \( p \), and \( K[p, f_N(p)] \) is a factor, determined from perturbation theory, that may be pressure and/or frequency-dependent. This dependence may be explicit, as in the skin-depth perturbation where \( \Delta f \propto f^{1/2} \), or implicit, as in the perturbation due to the presence of a gas inlet opening, where the cavity dimensions which appear in the resonance frequency shift formulae are, themselves, functions of pressure.

For a particular perturbation, equation (1) can be re-written as

\[
f_N(p) = f_N^0(p) + K[p, f_N(p)] f_N^0(p)
\]

(4.10.2)
and if it is assumed that $K[p, f_n(p)]f_{N0}^0(p) = K[p, f_n(p)]f_n(p)$ then equation (2) can be re-arranged to give

$$f_{N0}^0(p) = f_n(p)\left[1 - K[p, f_n(p)]\right]$$

(4.10.3)

Equation (3) will give $f_{N0}^0(p)$ too small by $K^2[p, f_n(p)]f_{N0}^0(p)$ which is only significant in comparison with the typical experimental precision of 0.1 ppm if $|K|$ is on the order of 300 ppm or larger. This would represent a much larger perturbation than the largest individual perturbation calculated for either resonator in this work. Equation (3) can also be written for the case when pressure $p = 0$ (when the cavity is evacuated):

$$f_{N0}^0(0) = f_n(0)\left[1 - K[0, f_n(0)]\right]$$

(4.10.4)

Equation (4) gives $f_{N0}^0(0)$ too small by $K^2[0, f_n(0)]f_{N0}^0(0)$ which, again, is likely to be insignificant in comparison with experimental precision. Hence, the squared ratio $\left[f_{N0}^0(0)/f_{N0}^0(p)\right]^2$, which is equal to the dielectric constant $\varepsilon$ of the gas at pressure $p$, is

$$\varepsilon = \left[\frac{f_{N0}^0(0)}{f_{N0}^0(p)}\right]^2 = \left[\frac{f_n(0)\left[1 - K[0, f_n(0)]\right]}{f_n(p)\left[1 - K[p, f_n(p)]\right]}\right]^2$$

(4.10.5)

There are two important observations to be made about equation (5). The first is that the errors on the order of $-K^2$, which arose in deriving equations (3) and (4), will virtually cancel out in equation (5) and so equation (5) can be considered accurate, within experimental precision in $\varepsilon$, for $|K|$ much larger than 300 ppm. The second, and most important, observation is that if $K[0, f_n(0)] = K[p, f_n(p)]$ then the squared ratio of perturbed resonance frequencies $\left[f_n(0)/f_n(p)\right]^2$ will be equal to the squared ratio of unperturbed resonance frequencies $\left[f_{N0}^0(0)/f_{N0}^0(p)\right]^2$, and thus the dielectric constant $\varepsilon$. In other words, if the calculated fractional shift $\left(\Delta f / f_{N0}^0\right)$, which is equal to $K$, does not show strong pressure and/or frequency-dependence, then the squared ratio of the uncorrected, measured resonance frequencies will be
very nearly equal to the squared ratio of unperturbed resonance frequencies, or the 'true' dielectric constant \( \varepsilon \). The implication of this is that if the resonator can be designed so as to minimise the pressure or frequency-dependence of perturbations, even at the expense of the absolute magnitudes of the perturbations themselves (provided they are not so large as to make the first-order analysis invalid), then the accuracy of the dielectric constant values derived from the measurements could be increased. This fact depends on relative, rather than absolute, speeds of light being measured, and yet because the speed of light in vacuo is defined, one can nevertheless obtain absolute speeds of light from the measurements, if required. The explicit temperature-dependence of perturbations has not been included in equations (1) to (5) because this work is concerned with isothermal measurements of \( \varepsilon \).

A similar equation to equation (1) can be written, in general, for the halfwidth contribution due to any perturbation:

\[
\frac{g_s(p)}{f_N^2(p)} = Y[p, f_N(p)]
\]

(4.10.6)

where \( Y[p, f_N(p)] \) is a positive factor (possibly zero), determined from perturbation theory, that may be pressure and/or frequency-dependent. For perturbations such as the skin-depth perturbation \( g_N(p) = -\Delta f_N(p) \), and so \( (g_s) \) and \( (\Delta f) \) have the same frequency and pressure-dependence. It is also likely to be the case that other perturbations, including those which have not been explicitly considered in the preceding sections of this chapter, give rise to resonance frequency shifts and halfwidth contributions with similar frequency and pressure-dependence. Therefore the pressure and frequency-dependence of the measured halfwidth \( g_N \) can be used to estimate the degree of pressure and frequency-dependence of \( \Delta f_N \). It was demonstrated earlier in this section that provided a particular perturbation (or a number of perturbations) is not strongly pressure and/or frequency-dependent then accurate relative speeds of light could be obtained from uncorrected, measured resonance frequencies. This suggests that only those calculated resonance frequency shifts which are significantly pressure and/or frequency-dependent need to be applied to correct the measured resonance frequencies. The corresponding calculated

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halfwidth contributions are subtracted from the measured halfwidth to obtain an 'excess halfwidth', \( \Delta g_N = g_N - \sum_j \Delta g_j \), which is often expressed as a fraction of the resonance frequency to give a fractional excess halfwidth \( \Delta g_N / f_N \). The measured variation of \( \left( \Delta g_N / f_N \right) \) with pressure and frequency, over the course of an isotherm, gives an indication of the pressure and frequency-dependence of those perturbations which have not been explicitly considered, either due to mathematical difficulties or the inability to fully characterise imperfections in the practical resonator. Thus we have a useful probe of the importance of any perturbations which have not been considered in the analysis. It is the changes in \( \left( \Delta g_N / f_N \right) \), and therefore \( \left( \Delta f_N / f_N^0 \right) \), over the course of an isotherm that are important, and not just the absolute magnitudes of \( \left( \Delta g_N / f_N \right) \) and \( \left( \Delta f_N / f_N^0 \right) \), if we are interested in relative speeds of light. In this respect, the uncertainty in resonance frequency caused by our ignorance of all the unconsidered perturbations that exist in a resonator can be estimated from the variation in \( \left( \Delta g_N / f_N \right) \) over the course of an isotherm.

Some workers [24, 53] have used the experimental halfwidths \( g_N \) to correct the measured resonance frequencies by assuming that \( \Delta f_N = -g_N \) and therefore \( f_N^0 = (f_N - g_N) \), but this assumes that all perturbations give rise to resonance frequency shifts of the same magnitude as the corresponding halfwidth contributions, and reduce the resonance frequencies by these amounts. This has been demonstrated to be strictly false by the results of sections (4.6), (4.7) and (4.9), but if absolute speeds of light are required (particularly in vacuo) then this procedure may give greater accuracy than using just the calculated resonance frequency shifts if the corresponding fractional excess halfwidths are large (suggesting that there are significant perturbations which have not been accounted for).
Chapter 5 Equations of State

5.1 Introduction

Gibbs phase rule dictates that a system consisting of a single phase of one component, subject to no extra restrictions, has two thermodynamic degrees of freedom. Therefore, any intensive property of the system, $X_1$, can be expressed as a function of any two other intensive properties, $X_2$ and $X_3$:

$$X_1 = X_1(X_2, X_3)$$  \hspace{1cm} (5.1.1)

which is a general equation of state for the system. The most common choice of properties for $X_1$, $X_2$, and $X_3$, for gaseous equations of state, are pressure $p$, thermodynamic temperature $T$, and molar volume $V_m$ or amount-of-substance density $\rho = (1 / V_m)$.

The most simple proposed equation of state for a gas is the perfect or ideal gas equation

$$pV_m = RT$$  \hspace{1cm} (5.1.2)

where $R$ is the molar gas constant \{(8.314471 ± 0.000014) J mol$^{-1}$ K$^{-1}$ [47]\}, and the molar volume $V_m$ is given by

$$V_m = \frac{V}{(m/M)}$$  \hspace{1cm} (5.1.3)

where $V$ is the volume and $(m/M)$ is the amount of substance (i.e., the number of moles of the gas sample), with $m$ being the mass of the gas sample, and $M$ being the molar mass of the gas. The behaviour of real gases was found to deviate from equation (2), particularly at low temperatures and high pressures, and, ever since this discovery, much effort has been expended to develop more accurate empirical and semi-empirical $(p, V_m, T)$ equations. A number of alternative $(p, V_m, T)$ equations of state to the perfect gas equation, all of which are based on the Van der Waals equation, are described in section (5.2). However, the equations of state of all real gases tend to equation (2) in the limit of zero density or pressure [54], and so it is still of great importance and lies at the heart of many accurate determinations of thermodynamic temperature $T$. 
Gas imperfections [i.e., deviations from equation (2)] are evidence for the existence of interactive forces between the gas molecules, and measurements of the equation of state for real gases can provide information on the nature of such forces. The most important equation of state if one is concerned with investigating intermolecular interactions is the well-known virial equation of state, and this is discussed in detail in section (5.3).

A number of better-known experimental methods used to determine gaseous equations of state are described in section (5.4). The traditional \((p, V, T)\) measurements can suffer from systematic error due to adsorption, and so a number of alternative methods where the measured function of \(T\) and \(p\) is formally independent of the amount of substance have been used: flow calorimetry and measurements of the speed of sound are discussed in section (5.4). Section (5.5) is concerned with equations of state based on the dielectric constant and the refractive index, two properties which are also formally independent of the amount of substance. Such equations are based on the Clausius-Mossotti and the Lorentz-Lorenz functions, and a full account is given of the virial expansion of the Clausius-Mossotti function due to Buckingham and Pople [85], forms of which were used to fit all of the measurements in this work. Finally, in section (5.6), methods of measuring the dielectric constant and refractive index of gases, and of determining the coefficients of the corresponding equations of state, are described; a brief introduction to the measurement of dielectric constants using cavity resonators forms part of the discussion.

5.2 \((p, V_m, T)\) equations of state

The earliest reported attempt to develop an alternative \((p, V_m, T)\) equation of state to the perfect gas equation was that due to van der Waals, published in 1873. The van der Waals equation of state can be written [55]

\[
p = \left( \frac{RT}{V_m - b} \right) - \left( \frac{a}{V_m^2} \right)
\]

(5.2.1)

where \(-\left( a/V_m^2 \right)\) represents the reduction in pressure due to attractive intermolecular interactions, and \(b\) is a parameter which represents the (molar) volume excluded due to repulsive intermolecular interactions, with the molecules considered as
impenetrable or 'hard' spheres; the parameters $a$ and $b$ may be determined experimentally for individual gases. Equation (1) was shown to be capable of qualitatively explaining the $(p, V_m, T)$ behaviour of real gases, but the quantitative agreement was found to be less good, and more sophisticated equations of state were sought.

Many equations of state have been developed by modifying the attractive or repulsive terms of equation (1), to produce equations which are still cubic in $V_m$, a simple example of which is the Berthelot equation [56]

\[
p = \left( \frac{RT}{V_m - b} \right) - \left( \frac{a}{TV_m^2} \right)
\]

(5.2.2)

where the attractive term has been modified by introducing a very simple form of temperature-dependence. Many other closed, cubic equations have been proposed to improve agreement between experimental and calculated behaviour, and details of these can be found in reference 56.

Modification of both the attractive and repulsive terms of the van der Waals equation produces an equation which is no longer cubic in $V_m$, the best-known example of which is the Beattie-Bridgman equation [56, 57]:

\[
p = \frac{(1 - \gamma)RT(V_m + \beta) - \alpha}{V_m^2}
\]

(5.2.3)

where

\[
\alpha = a_0 \left(1 + \frac{a}{V_m}\right)
\]

\[
\beta = b_0 \left(1 - \frac{b}{V_m}\right)
\]

(5.2.4)

\[
\gamma = \frac{c_0}{V_m T^3}
\]

The parameters $a, b, a_0, b_0$ and $c_0$ in equations (4) may be determined experimentally for individual gases. This equation was shown to provide satisfactory representation
of \((p, V_m, T)\) behaviour only below the critical density. More sophisticated non-cubic equations have been proposed, most of which contain exponential terms, and details can be found in the literature [58-60]. Such equations are capable of fitting experimental \((p, V_m, T)\) measurements, over wide ranges of temperature and pressure, to within a few per cent of the experimental compression factor \(Z = (pV_m/RT)\).

Although very many equations of state have been used to fit experimental data, often with great success, there is one equation that is of central importance if the relation between intermolecular forces and the equation of state is of prime interest; this is the so-called virial equation of state.

### 5.3 The virial equation of state

The virial equation of state is given by

\[
\frac{pV_m}{RT} = 1 + B(T)p + C(T)p^2 + D(T)p^3 + \cdots
\]  

(5.3.1)

which can also be written as a pressure series:

\[
\frac{pV_m}{RT} = 1 + B'(T)p + C'(T)p^2 + D'(T)p^3 + \cdots
\]  

(5.3.2)

The coefficients \(B, C, D, \cdots\) in equation (1) are the second, third, fourth, \(\cdots\) \((p, V_m, T)\) virial coefficients and are functions of temperature alone. They are defined by the limiting relations

\[
RTB = \lim_{\rho \to 0} \left[ \frac{\partial(pV_m)}{\partial \rho} \right]
\]

\[
RTC = \frac{1}{2} \lim_{\rho \to 0} \left[ \frac{\partial^2(pV_m)}{\partial \rho^2} \right]
\]

\[
RTD = \frac{1}{6} \lim_{\rho \to 0} \left[ \frac{\partial^3(pV_m)}{\partial \rho^3} \right]
\]

(5.3.3)

and so on for the higher coefficients. The coefficients \(B', C', D', \cdots\) in equation (2) are uniquely related to the coefficients of equation (1) by the relations [61]
although equations (4), and the more complicated expressions for higher coefficients, are only exactly correct for the infinite series of equations (1) and (2).

The great importance of the virial equation of state lies in its theoretical connection with the forces between molecules, since considered as an empirical equation it has a number of shortcomings [61]: the convergence of equations (1) and (2) may only be good at moderate densities, and there is evidence that the two series may even diverge at very high densities. Further, to describe measurements up to high densities requires the inclusion of many terms in the series and this means that many virial coefficients must be determined. In many cases, other equations of state with fewer parameters can be used to fit particular sets of data just as adequately. However, the virial equation is the only gaseous equation of state that has a thoroughly sound theoretical foundation and, whilst originally suggested on an empirical basis, it has been found that equations (1) and (2) can be rigorously determined using statistical mechanics [61-63].

The connection between the virial equation of state and the interactions between gas molecules is simple. The values of the virial coefficients $B$, $C$, $D$, ... are related to the potential energy of interaction between clusters of two, three, four, ... molecules, respectively, which is shown by the statistical mechanical derivation of equations (1) and (2). For example, the second virial coefficient of a pure gas is given by [63]

$$B(T) = -\frac{N_A}{2V\Omega^2} \oint f_{12} d\tau_1 d\tau_2$$

(5.3.5)

where $f_{12} = \left[ \exp\left(-U_{12}/kT\right)/-1 \right]$ is the Mayer $f$ function, $N_A$ is Avagadro’s constant, $\Omega$ is a normalisation constant, and $\tau_1$ and $\tau_2$ are the orientations of molecules 1 and 2, respectively. For molecules with no internal degrees of freedom, and assuming the pair potential energy $U_{12}$ to be dependent on intermolecular separation $r$ only (central forces), $B$ is simply given by [55]
Expressions for higher coefficients, relating to the potential energies of clusters of three or more molecules, are more complicated due to the non-additivity of pair potential energies [55, 61].

The second virial coefficient of a mixture of \( c \) components is given by [61]

\[
B_{\text{mix}}(T) = \sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j B_{ij}(T)
\]

where \( x_i \) and \( x_j \) are the mole fractions of components \( i \) and \( j \), and \( B_{ij} \) is the second virial coefficient arising from interactions between the molecules of components \( i \) and \( j \). Equation (7) can be written for a binary mixture of components A and B, with the composition \( \{(1-x)A + xB\} \), as

\[
B_{\text{mix}}(T) = (1-x)^2 B_{AA}(T) + x^2 B_{BB}(T) + 2(1-x)x B_{AB}(T)
\]

where \( B_{AA} \) and \( B_{BB} \) are the second virial coefficients for pure A and pure B, respectively, and \( B_{AB} \) is the cross virial coefficient, which arises from interactions between the molecules of A and B.

The determination of virial coefficients from experimental \((p, V_m, T)\) measurements is not as simple as it may, at first, appear. The ideal situation is to have highly precise measurements extending down to very low densities, and determine the virial coefficients using equations (3) [61, 64]. In practice, the measurements are rarely sufficiently precise, and a polynomial fit to the data is often attempted by using a truncated form of equation (1) or (2). There are a number of difficulties with this approach [61]. The virial coefficients, as given in equations (1) and (2), are for the infinite series only, and if a truncated series is used then the coefficients determined may differ from the 'true' virial coefficients; in particular, the relations of equations (4) only hold exactly for the infinite series. For example, if a series is truncated at the third virial coefficient term, then the derived second virial coefficient \( B \) may be a good estimate of the true value of \( B \), but the value of \( C \) obtained should only be considered as an 'apparent' third virial coefficient, which may be significantly different from the true value of \( C \). If the measurements are extended to sufficiently high gas densities that the contributions from the third and higher virial coefficients are significant then it might be difficult to disentangle these contributions from that due to the second virial coefficient, but if the maximum gas
density at which measurements are taken is kept low then there is not much of a measureable effect from which to determine \( B \). It is a common observation that a particular set of \( (p, V_m, T) \) data may be represented by a smaller number of terms using equation (1) than are required using equation (2), or, put another way, for a given number of terms, it is often found that the density series of equation (1) gives a better representation of the data than the pressure series of equation (2). This presents a difficulty since the coefficients from the polynomial with the larger number of terms may differ considerably from the corresponding coefficients of the polynomial with the smaller number of terms.

A common shortcoming in measurements reported in the literature is that the lowest density used is often so high that the definitions of the virial coefficients in equations (3) can hardly be realised. Thus it is difficult to maintain that the coefficients determined can be identified with the limiting values of equations (3) [61]. It would appear that many workers do not take full account of these problems, and the values of \( B \), and more especially higher coefficients, reported by different workers often do not agree within their combined estimated uncertainties [65].

5.4 Experimental methods

\( (p, V_m, T) \) methods

Most equation of state information has come from isothermal \( (p, V_m, T) \) measurements. The measurement of pressure \( p \) and temperature \( T \) present little difficulty, but the molar volume \( V_m \) or the amount-of-substance density \( \rho = (1 / V_m) \) cannot be measured directly. In traditional methods, measurements of the vessel volume \( V \) and amount of substance are combined to provide \( V_m \). However, much care is needed to avoid introducing systematic errors in these measurements.

Probably the earliest apparatus for \( (p, V_m, T) \) measurements is the Boyle’s tube apparatus which dates from the seventeenth century. In this apparatus, the gas sample is confined by mercury in the closed, shorter arm of a J-shaped piece of tubing whose diameter is uniform and accurately known. Mercury is added (usually at the bottom of the J-tube) to increase the pressure. The volume of the sample is inferred from the length of the confined sample and the pressure is determined by the difference in the mercury levels in the long and short arms of the J-tube. The
amount of substance is determined either by weighing and using the molar mass of the gas \( M \), or from the limiting value of \( \frac{pV}{RT} \) at low pressures. The limitations of this method are obvious. It is only useful at low pressures where the mercury column is of a manageable length, and for temperatures at which mercury is a liquid but has an acceptably low vapour pressure. The uniformity of the tube diameter is very important, and allowance must be made for capillary depression in measuring the mercury levels [55].

Improved versions of the apparatus, with a number of carefully calibrated volumes into which the confined sample is allowed to expand, have been used and measurements below the freezing point of mercury have been made by using differential pressure transducers to isolate the sample from the manometers. If care is taken to determine the volumes of the connecting tubes and valves, then uncertainties in \( B \) of as little as \( \pm 5 \text{ cm}^3 \text{ mol}^{-1} \) can be achieved [66].

The requirement for absolute measurements of pressure can be eliminated by the use of differential techniques [67, 68], where the behaviour of a sample is compared with that of a reference gas whose virial coefficients are considered to be accurately known (and are generally small). The sample and the reference gases are made to undergo similar volume changes and the difference in resulting pressures is measured, or the volume change needed to restore pressure equilibrium following similar large expansions is measured to give a direct indication of the difference in imperfection of the reference and sample gases.

The Burnett multiple-expansion method, introduced in 1936 [69], avoids the need for measurements of volume and amount of substance altogether. The method involves the use of two fixed volumes, a larger volume \( V_1 \) and a smaller volume \( V_2 \), separated by a valve \( T \). Initially, \( V_1 \) contains the gas sample at a high pressure \( p_0 \), which is accurately measured using a pressure gauge, and \( V_2 \) is evacuated. Then \( T \) is opened and the gas allowed to expand into \( V_2 \); once equilibrium has been re-established, the new lower pressure \( p_1 \) is measured. \( T \) is closed and \( V_2 \) is re-evacuated. \( T \) is then re-opened, the gas expands and the new, lower pressure \( p_2 \) is measured. The cycle is repeated until the pressure is too low to be measured accurately. The experimental data are, then, the series of pressures \( p_0, p_1, p_2, \ldots, p_j \) which are used to determine the virial coefficients of the sample gas. Determination
of the compression factor ratio \( Z_j / Z_{j+1} = \left[ p_j / \left( x p_{j+1} \right) \right] \), where \( Z_j \) is the compression factor at pressure \( p_j \), requires that the apparatus constant \( x = [(V_1 + V_2) / V_1] \) be evaluated. This constant can be found from the limiting value of \( p_j / p_{j+1} \) as the pressure tends to zero since \( Z \to 1 \) as \( p \to 0 \). Thus it can be shown that a plot of the pressure ratio \( p_j / p_{j+1} \) against \( p_j \) has the intercept \( x \) and the limiting slope \( B(x-1) / RT \). Higher virial coefficients can be estimated from the limiting curvature.

At pressures approaching the vapour pressure, the accuracy of the \((p, V_m, T)\) methods considered may be seriously compromised by adsorption of the gas onto the walls of the vessel which reduces the amount-of-substance in the gas phase [70]. The degree of adsorption depends on the surface area to volume ratio, the quality of surface finish and the pressure, and differs from one apparatus to another. High polishing of the vessel surfaces can reduce adsorption, and models of adsorption have been used to estimate corrections.

In recent years, Wagner et al. have made direct measurements of the mass density, as a function of temperature and pressure, of a number of pure gases using a method based on the Archimedes' buoyancy principle [71]. The gas density is measured using a two-sinker densimeter: one sinker is a gold-coated quartz glass sphere, the other is a ring of solid gold. The ring has exactly the same mass and surface area as the sphere, but a very different volume, and so the problematic effects of adsorption can be compensated. The apparatus is capable of a fractional uncertainty in gas density of better than \( 1 \times 10^{-4} \) over very wide ranges of temperature, and can also be used to make measurements in the homogeneous liquid phase, and along the (vapour + liquid) coexistence curve [72, 73].

Adsorption problems can also be avoided by using alternative equations of state where the measured function of \( T \) and \( p \) is formally independent of the amount of substance.

**Calorimetric methods**

The equation of state

\[
H_m = H_m(T, p)
\]  (5.4.1)
can be investigated using a flow calorimeter consisting of a throttling device across which a gas pressure gradient is maintained.

The isenthalpic Joule-Thomson coefficient \( \mu_{\text{jT}} = \left( \partial T / \partial p \right)_H \) is determined by measuring the change in temperature of the gas \( \Delta T \) on adiabatic expansion through the throttle across which the pressure gradient is \( \Delta p \). The value of \( \left( \Delta T / \Delta p \right) \) in the limit of zero pressure gradient gives an estimate of \( \mu_{\text{jT}} \), which is related to the virial coefficients of the gas by [55]

\[
\mu_{\text{jT}} C_{p,m}^0 = -\left( B - T \frac{dB}{dT} \right) + \frac{1}{V_m} \left[ 2B^2 - 2TB \frac{dB}{dT} - 2C + T \frac{dC}{dT} - \frac{RT^2}{C_{p,m}^0} \left( B - T \frac{dB}{dT} \right) \frac{d^2 B}{dT^2} \right] + \ldots
\]

(5.4.2)

where \( C_{p,m}^0 \) is the molar perfect gas heat capacity at constant pressure. Therefore the zero density limit is \(-[B - T(dB/dT)]\) and so measurements of \( \mu_{\text{jT}} \) can provide information on \( B \) and its temperature derivative, although the elimination of heat leaks in order to realise the isenthalpic requirements can be difficult.

If an electrical heater is introduced on the low pressure side of the throttle, then the heating power \( P \) required to maintain the same gas temperature either side of the throttle, for a known gas-flow-rate \( f \), can be measured to determine the isothermal Joule-Thomson coefficient \( \phi_{\text{jT}} = \left( \partial H / \partial p \right)_T \). This is related to the virial coefficients by [55]

\[
\phi_{\text{jT}} = B - T \frac{dB}{dT} + \frac{2\langle p \rangle}{RT} \left( C - B^2 + TB \frac{dB}{dT} - \frac{1}{2} T \frac{dC}{dT} \right) + \ldots
\]

(5.4.3)

where \( \langle p \rangle \) is the mean pressure, and so the limit as the mean pressure tends to zero is \( B - T(dB/dT) \). Although equation (3) suggests that isothermal Joule-Thomson measurements would be an excellent approach for studies of gas imperfections, the experiment has proved to be extremely difficult in practice [56]

The principal advantage of these calorimetric methods is that they are unaffected by adsorption effects and have been used for studying regions where adsorption may be a serious problem in \( (p, V_m, T) \) methods [74].
The speed of sound

The speed of sound $u$ in a gas is formally independent of the amount-of-substance and so equations of state of the form

$$u^2 = u^2(T, p)$$  \hspace{1cm} (5.4.4)

have been studied as alternatives to $(p, V_m, T)$ equations, with the expectation that the measurements will be unaffected by adsorption and will be successful in regions where problems with $(p, V_m, T)$ measurements arise. However, at pressures approaching the vapour pressure, a 'precondensation' effect has been recognised [75], which reduces the measured speed of sound below its expected value, and its avoidance requires that the maximum pressure of measurements be limited to about 60% to 70% of the vapour pressure. The speed of sound is also a function of the frequency of the sound wave in dispersive gases but measurements are usually taken at low frequencies ($< 20 \text{ kHz}$) where dispersive effects are negligible for most gases [45].

The fundamental relation between the speed of sound and the thermodynamic properties of a fluid is

$$u^2 = \frac{1}{M} \left( \frac{\partial p}{\partial \rho} \right)_S$$  \hspace{1cm} (5.4.5)

where $\rho$ is the amount-of-substance density, $M$ is the molar mass of the gas and $S$ is the entropy. The perfect gas value of the speed of sound $u_0$ is given by

$$u_0^2 = \frac{RT \gamma_{pe}}{M}$$  \hspace{1cm} (5.4.6)

where $\gamma_{pe} = C_{p,m}^{PE} / C_{V,m}^{PE} = C_{p,m}^{PE} / (C_{p,m}^{PE} - R)$ is the ratio of the perfect gas molar heat capacities. Departures from equation (6), at high pressures, are described by the pressure-explicit series

$$u^2 = A_0(T) + A_1(T)p + A_2(T)p^2 + \cdots$$  \hspace{1cm} (5.4.7)

where $A_0 = u_0^2 = RT \gamma_{pe} / M$. Thus a series of isothermal $(u^2, p)$ measurements can be extrapolated to zero pressure to obtain $u_0^2$, and thus any one of the properties on the right-hand-side of equation (6) can be determined if the other properties are known. Rayleigh used such a method to determine the molar masses of simple gases, and the same method has been used for very high accuracy primary thermometry [76] and a recent determination of the gas constant $R$ [47]. An alternative equation of state
involving \( u^2 \) can be written in the form of an amount-of-substance density-explicit series:

\[
u^2 = u_0^2 \left( 1 + \beta_\rho(T) \rho + \gamma_\rho(T) \rho^2 + \delta_\rho(T) \rho^3 + \cdots \right) \tag{5.4.8}
\]

where \( u_0^2 \) is given by equation (6), and \( \beta_\rho, \gamma_\rho, \delta_\rho, \ldots \) are the second, third, fourth, \ldots acoustic virial coefficients, which are functions of \( T \) alone. These coefficients are related to those of equation (7) by

\[
A_1 = \left( \frac{\gamma_{\text{pg}}}{M} \right) \beta_\rho.
\]

\[
A_2 = \left( \frac{\gamma_{\text{pg}}}{M} \right) \frac{\gamma_\rho - B \beta_\rho}{RT}.
\tag{5.4.9}
\]

and so isothermal \((u^2, p)\) measurements can be used to determine the acoustic virial coefficients.

The acoustic virial coefficients are related to the corresponding \((p, V_m, T)\) virial coefficients by second-order differential equations. For example \( \beta_s \) is given by

\[
\beta_s = 2B + 2T(\gamma_{\text{pg}} - 1) \frac{dB}{dT} + T^2 \left( \frac{\gamma_{\text{pg}} - 1}{\gamma_{\text{pg}}} \right) \left( \frac{d^2 B}{dT^2} \right) \tag{5.4.10}
\]

and so, in principle, \( B \) can be obtained by measuring the temperature-dependence of \( \beta_s \) and performing a numerical integration of equation (10) [77]. Alternatively, a simple temperature-dependence is assumed for \( B \) (e.g., that given by assuming a square-well pair potential energy) and the differentiations in equation (10) are performed to produce an expression for \( \beta_s \) as a function of \( T \) whose parameters can be optimised using the experimental \((\beta_s, T)\) data, using a non-linear least squares regression. Therefore a functional form of \( B(T) \) is obtained which can be used to calculate \( B \) at any temperature within the range of the \( \beta_s \) measurements [36, 45, 78-82]. If we are only interested in the form of the pair potential energy \( U_{12} \), then \( \beta_s \) can be related directly to \( U_{12} \) and there is no need to attempt to obtain values of \( B \) from the speed of sound measurements [35, 83].

The speed of sound in gases is most accurately measured using resonant acoustic cavities with carefully calibrated volumes. The most common geometries are cylindrical, where a fixed frequency sound source can be used with a variable pathlength resonator or a variable frequency source can be used with a fixed
pathlength resonator, and spherical, where a variable frequency source is used. With careful modelling of the various perturbations on the acoustic waves and the use of phase-sensitive detection equipment, the speed of sound in gases has been routinely determined with estimated fractional uncertainties of better than 10 ppm using the high-quality radial modes of spherical resonators. Clearly, then, the measurement of \( u \) with sufficient accuracy presents few problems, and the speed of sound method has been used to obtain values of \( B \) for a number of pure gases [35, 36, 78] and gas mixtures [83] with uncertainties smaller than \( \pm 2 \, \text{cm}^3 \, \text{mol}^{-1} \), over appreciable ranges of temperature.

5.5 The dielectric constant and the refractive index

The speed of light \( c \), and the related properties the refractive index \( n \), and the dielectric constant \( \varepsilon \) of a gas are functions of its temperature \( T \) and amount-of-substance density \( \rho \), but are formally independent of the amount of gas. Thus measurements of \( n \) and \( \varepsilon \) should be immune from the effects of adsorption that cause problems in \( V_m \) determinations, and alternative gaseous equations of state for \( n \) and \( \varepsilon \) have been developed.

In general, \( n \) and \( \varepsilon \) are functions of the frequency of measurement. Most measurements of \( n \) are taken at optical frequencies and it is important to ensure that the same frequencies of measurement have been used when comparing the measurements of different workers because \( n \) increases rapidly in this region of normal dispersion [84]. The majority of \( \varepsilon \) measurements are taken at sufficiently low frequencies that the static-field values are obtained [see section (2.2)] and the measurements of different workers are directly comparable.

The dielectric constant

The earliest attempt to calculate the density-dependence of the static dielectric constant \( \varepsilon \) for a pure non-polar gas used simple arguments [1, 3, 4], based on the definition of the dipole density or electric polarisation \( P \) [see section (2.2)] of a cluster of non-interacting spherical molecules, to give the Clausius-Mossotti formula

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where \( \alpha \) is the mean static polarisability of an individual gas molecule. A modification of equation (1), after Debye [1, 3], gave the expression

\[
\left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V_m = \frac{N_A \alpha}{3\varepsilon_0} \tag{5.5.1}
\]

where \( \alpha \) is the permanent dipole moment of an individual gas molecule and \( k \) is Boltzmann’s constant. Thus equation (2) allowed pure polar and non-polar \( (\mu_0 = 0) \) gases to be considered. However, the dielectric constant of real gases showed deviations from equation (2) at high gas densities and, in 1955, Buckingham and Pople [85] proposed an expansion of the Clausius-Mossotti function or ‘total polarisation’ \( \tau P = \left[ (\varepsilon - 1)/(\varepsilon + 2) \right] V_m \), in powers of the amount-of-substance density \( \rho = \left( 1/V_m \right) \):

\[
\tau P = \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V_m = A_\varepsilon(T) + B_\varepsilon(T) \rho + C_\varepsilon(T) \rho^2 + \cdots \tag{5.5.3}
\]

where \( A_\varepsilon, B_\varepsilon, C_\varepsilon, \cdots \) are the first, second, third, \cdots dielectric virial coefficients. They are functions of temperature alone and are defined by the limiting relations

\[
A_\varepsilon = \lim_{\rho \to 0} \left\{ \left[ \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V_m \right] \right\}
\]

\[
B_\varepsilon = \lim_{\rho \to 0} \left\{ \frac{\partial}{\partial \rho} \left[ \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V_m \right] \right\} \tag{5.5.4}
\]

\[
C_\varepsilon = \frac{1}{2} \lim_{\rho \to 0} \left\{ \frac{\partial^2}{\partial \rho^2} \left[ \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) V_m \right] \right\}
\]

\( A_\varepsilon \) is the contribution to \( \tau P \) from the molecules in the absence of intermolecular interactions, and, for a pure gas, is given by

\[
A_\varepsilon = \frac{N_A}{3\varepsilon_0} \left( \alpha + \frac{\mu_0 \cdot \mu_0}{3kT} \right) \tag{5.5.5}
\]

The higher dielectric virial coefficients \( B_\varepsilon, C_\varepsilon, D_\varepsilon, \cdots \) represent the contributions to \( \tau P \) from interacting pairs, triplets, quartets, \cdots of molecules, respectively. Using statistical mechanics, Buckingham and Pople [85, 86] obtained an expression for the second dielectric virial coefficient of a pure gas which may be written [87]
\[ B_e = \frac{N^2}{3\Omega\varepsilon_0} \int \left\{ \left[ \frac{1}{2} \alpha_{12} - \alpha \right] + \frac{1}{3kT} \left[ \frac{1}{2} \mu_{12} \cdot \mu_{12} - \mu_0 \cdot \mu_0 \right] \right\} \exp \left( -U_{12}/kT \right) dr_{12} d\xi_{12} \]

(5.5.6)

where \( \alpha_{12} = \alpha_{12}(r_{12}, \xi_{12}) \) is the total polarisability of a pair of interacting molecules 1 and 2, \( \alpha \) is the polarisability of an individual isolated molecule, \( \mu_{12} = \mu_{12}(r_{12}, \xi_{12}) \) is the total dipole moment of the interacting molecules 1 and 2, \( \mu_0 \) is the permanent dipole moment of an individual isolated molecule, and \( U_{12} = U_{12}(r_{12}, \xi_{12}) \) is the intermolecular pair potential energy. The integration in equation (6) is taken over all possible separations \( r_{12} \) and relative angular orientations \( \xi_{12} \) of the molecular pair, and the normalisation factor \( \Omega \) is defined by \( \int dr_{12} d\xi_{12} = \Omega V_m \).

There are a number of effects that may make \( B_e \) non-zero [85-87]:

1. If the polarisability of a molecule is altered by interaction with a neighbouring molecule then \( \left( \alpha_{12}/2 \right) - \alpha \neq 0 \) in equation (6).

2. The applied electric field polarises each individual molecule and the resulting induced dipole moment may induce an additional dipole moment in a neighbouring molecule. This ‘dipole-induced-dipole’ (DID) effect makes a contribution to \( \alpha_{12} \) in equation (6), and is thought to be the principal contribution to \( B_e \) for most non-polar gases. The contribution to \( B_e \) will be positive.

3. If a pair of interacting molecules possesses a resultant dipole moment in the absence of an external field then there will be a non-zero contribution to \( \mu_{12} \) in equation (6), even if \( \mu_0 = 0 \) (non-polar gases), and the resulting contribution to \( B_e \) will be positive. This effect will not arise with spherically symmetric molecules such as those of monatomic gases.

4. Molecules which have no permanent dipole moment but possess higher multipoles, such as a quadrupole or octupole, can induce dipoles in neighbouring molecules, and these induced dipoles make a contribution to \( \mu_{12} \) in equation (6).

5. For polar gases, the dominant contribution arises from the term \( \left[ \left( \mu_{12} \cdot \mu_{12} \right)/2 - \mu_0 \cdot \mu_0 \right] \) in equation (6). If all relative orientations of the dipole
moments of neighbouring molecules were equally probable then the average value of this term would be zero. However, there are preferred relative orientations of neighbouring polar molecules and these give rise to non-zero $\left(\frac{\mu_{12} \cdot \mu_{12}}{2} - \mu_0 \cdot \mu_0\right)$ and thus a non-zero contribution to $B_\varepsilon$. If a like arrangement of dipoles is preferred then the contribution to $B_\varepsilon$ will be positive; if an opposed arrangement of dipoles is preferred then the contribution to $B_\varepsilon$ will be negative.

Contributions 1 to 4, detailed above, can arise for both polar and non-polar gases, but contribution 5 can arise only for polar gases. In the absence of other considerations, the energetically most favourable arrangement of dipoles is the simple head-to-tail arrangement and this always gives a positive contribution to $B_\varepsilon$. However, measured values of $B_\varepsilon$ for polar gases are both positive and negative [88] and so the shape of the molecules must have an important impact on the preferred orientations [86], since the negative contributions from effects 1 and 4 are likely to be small. For example, two rod-like polar molecules will tend to adopt the arrangement shown in figure (5.1(a)), with anti-parallel dipoles, giving an overall dipole $\mu_{12} = 0$. Thus the contribution to $B_\varepsilon$ will be negative. Two plate-like molecules with dipole moments along the axis will tend to adopt the orientation shown in figure (5.1(b)), with a head-to-tail arrangement of dipoles, giving an overall dipole $\mu_{12} = 2 \mu_0$, and thus a positive contribution to $B_\varepsilon$. Therefore, measurements of $B_\varepsilon$ for polar molecules may provide useful information on the angular components of molecular interactions [86, 87].

**Figure (5.1) Orientations of polar molecules**

![Figure 5.1](image)
For pure, noble gases, equation (6) simplifies to [89]

\[ B_e = \frac{N_A^2}{3 \Omega \varepsilon_0} \int \left[ \frac{1}{2} \alpha_{12} (r) - \alpha \right] \exp \left( \frac{-U_{12} (r)}{kT} \right) r^2 \, dr \]  

(5.5.7)

since the term \( \left[ (\mu_{12} \cdot \mu_{12})/2 - \mu_0 \cdot \mu_0 \right] \) can make no contribution to equation (6), and a central force law can be used. Although \( B_e \) is directly related to the centrally symmetric pair potential \( U_{12} \), there is still no satisfactory way of calculating \( \alpha_{12} \) for even the atomic gases and so measurements of \( B_e \) for such gases are more profitably considered as a source of information on \( \alpha_{12} \) [89, 90], using the relatively well characterised pair potentials for atomic gases [55], determined using other measurements and \textit{a priori} theoretical arguments.

The first and second dielectric virial coefficients of gaseous mixtures are given by [87]

\[ A_{\varepsilon, \text{mix}} = \sum_i x_i A_{\varepsilon, i} \]  
\[ B_{\varepsilon, \text{mix}} = \sum_{i,j} x_i x_j B_{\varepsilon, ij} \]  

(5.5.8)

where \( x_i \) is the mole fraction of the \( i \)-th component, \( A_{\varepsilon, i} \) is the first dielectric virial coefficient of the \( i \)-th component and \( B_{\varepsilon, ij} \) is the second dielectric virial coefficient that arises from interactions between the molecules of components \( i \) and \( j \). For a binary mixture of components \( A \) and \( B \) with the composition \( \{(1-x)A + xB\} \), equations (8) become

\[ A_{\varepsilon, \text{mix}} = (1-x)A_{\varepsilon, A} + xA_{\varepsilon, B} \]  
\[ B_{\varepsilon, \text{mix}} = (1-x)^2 B_{\varepsilon, AA} + x^2 B_{\varepsilon, BB} + 2(1-x)x B_{\varepsilon, AB} \]  

(5.5.9)

where \( A_{\varepsilon, A} \) and \( A_{\varepsilon, B} \) are the first dielectric virial coefficients for pure \( A \) and \( B \), respectively, \( B_{\varepsilon, AA} \) and \( B_{\varepsilon, BB} \) are the second dielectric virial coefficients for pure \( A \) and pure \( B \), respectively, and \( B_{\varepsilon, AB} \) is the cross dielectric virial coefficient, which arises from interactions between the molecules of \( A \) and \( B \). There are contributions to \( B_{\varepsilon, AB} \) which arise from the effects discussed previously as well as an additional effect due to transient dipoles during bimolecular collisions [87].
The expansion of the Clausius-Mossotti function, equation (3), is expressed in powers of amount-of-substance density and, as has been previously noted, this property is not directly measureable. The \((p, V_m, T)\) virial equation of state, given in equation (5.3.1) can be re-written in the form
\[
\rho = \frac{P}{RT} - B \rho^2 - C \rho^3 - \cdots
\] (5.5.10)
and successive substitutions of this expression for \(\rho\) into equation (3) gives a pressure-explicit expansion of the function \(\left[(\varepsilon - 1)/\varepsilon + 2\right]RT/p:\)
\[
\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{RT}{p} = A'_\varepsilon + B'_\varepsilon \left(\frac{P}{RT}\right) + C'_\varepsilon \left(\frac{P}{RT}\right)^2 + \cdots
\] (5.5.11)
where the coefficients \(A'_\varepsilon\), \(B'_\varepsilon\) and \(C'_\varepsilon\) are related to those of expansions (5.3.1) and (5.5.3) by
\[
\begin{align*}
A'_\varepsilon &= A_\varepsilon \\
B'_\varepsilon &= B_\varepsilon - A_\varepsilon B \\
C'_\varepsilon &= C_\varepsilon - A_\varepsilon C + 2A_\varepsilon^2 B^2 - 2B_\varepsilon B \\
\end{align*}
\] (5.5.12)
Equations (12) are exact for the infinite series only but can be considered accurate for carefully truncated series. Therefore, isothermal measurements of \(\varepsilon\) and \(p\) can be fitted, using equation (11), to determine the coefficients in equations (12). In principle, this could provide values of the first dielectric virial coefficient \(A_\varepsilon\) and the higher dielectric virial coefficients \(B_\varepsilon\), \(C_\varepsilon\) \(\cdots\) if the \((p, V_m, T)\) virial coefficients \(B\), \(C\), \(\cdots\) were known, or values of the first dielectric virial coefficient \(A_\varepsilon\) and the \((p, V_m, T)\) virial coefficients \(B\), \(C\), \(\cdots\) if \(B_\varepsilon\), \(C_\varepsilon\) \(\cdots\) were known. Equation (11) also forms the basis of dielectric constant gas thermometry using absolute \(\varepsilon(p)\) measurements [91, 92].

In the second of equations (12), it is generally found that \(|B_\varepsilon| \ll |A_\varepsilon B|\) for measurements away from the Boyle temperature (at which \(B = 0\)) [88, 93]. Therefore, the accurate determination of \(B_\varepsilon\), for a particular gas, from absolute \(\varepsilon(p)\) measurements requires that very accurate values of \(B\) are available, since even reasonably small errors in \(B\) can give rise to very large errors in \(B_\varepsilon\) [88]. The determination of \(C_\varepsilon\) by such a method requires that accurate values of \(C\) are also available. The scarcity of highly precise measurements of \(B\) in the published literature has led some [94] to dismiss this method of measuring second, and higher,
dielectric virial coefficients, although the first dielectric virial coefficient \( A_e \) is invariably determined from such measurements. Absolute \( \varepsilon(p) \) measurements can also be used to determine dielectric virial coefficients by using the measured pressures, with published values of the \((p, V_m, T)\) virial coefficients, to calculate the molar volumes and amount-of-substance densities required to fit the \( \varepsilon \) measurements to equation (3). In principle, this method of analysis is equivalent to fitting the data to equation (11), followed by the use of published \((p, V_m, T)\) virial coefficients to extract the dielectric virial coefficients, as previously described, so it suffers from the same difficulties, but if both methods are used to analyse the same measurements then the effect of truncating the infinite series can be investigated.

The small magnitudes of the higher dielectric virial coefficients may be turned to our advantage if we are interested in determining the \((p, V_m, T)\) virial coefficients, rather than the dielectric virial coefficients, from absolute \((\varepsilon, p)\) measurements, since the terms in equations (12) involving \( B_e \) and \( C_e \) can be neglected, or estimated using calculated values for \( B_e \) and \( C_e \).

An alternative expansion of \( [(\varepsilon - 1)/(\varepsilon + 2)]RT/p \), in terms of \( [(\varepsilon - 1)/(\varepsilon + 2)] \), can also be derived [95, 96] from the combination of equations (3) and (5.3.1):

\[
\left( \frac{\varepsilon - 1}{\varepsilon + 2} \right) \frac{RT}{p} = A_e + \left[ \frac{B_e - A_e B}{A_e} \right] \frac{\varepsilon - 1}{\varepsilon + 2} + \left[ \frac{A_e C_e - B_e^2 (B^2 - C)}{A_e^3} \right] \frac{\varepsilon - 1}{\varepsilon + 2}^2 + \ldots
\]

Thus equation (13) can be used to fit isothermal \((\varepsilon, p)\) measurements, in place of equation (11), to determine \( A_e \) and \( B_e, C_e, \ldots \) if \( B, C, \ldots \) are known, or \( A_e \) and \( B, C, \ldots \) if \( B_e, C_e, \ldots \) are known. Equation (13) may be preferred to equation (11) if the majority of suspected error lies in the measurements of \( p \) rather than \( \varepsilon \), since it is generally the case that all the error is assumed to reside in the dependent variable in least-squares regressions.

Care must be taken in fitting dielectric constant measurements to truncated forms of equations (3) and (11), as was urged before with respect to the fitting of \((p, V_m, T)\) measurements, and all the caveats of the earlier discussion are equally valid here.
From equation (3), it can be shown that the amount of substance density $\rho$ is given by

$$\rho = Z - \frac{B_e}{A_e} Z^2 + \frac{2B_e^2 - A_e C_e}{A_e^2} Z^3 + \cdots$$ (5.5.14)

where $Z = \{[(\varepsilon - 1)/(\varepsilon + 2)]/A_e\}$, and so the density can be determined from absolute measurements of $\varepsilon$ provided that the dielectric virial coefficients $A_e, B_e, C_e, \ldots$ are known. Indeed, the terms higher than $Z$ in equation (14) contribute only about 1% of $\rho$, and so reasonable estimates of $\rho$ can be achieved from just $\varepsilon$ and $A_e$.

The refractive index

The density-dependence of the refractive index $n = n(\omega, \rho, T)$ of a gas is given by an expansion of the Lorentz-Lorenz function or molar refraction $R_m$:

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right) \nu_m = A_R(\omega, T) + B_R(\omega, T) \rho + C_R(\omega, T) \rho^2 + \cdots$$ (5.5.15)

the form of which can be obtained from equation (3) by replacing $\varepsilon$ by $n^2$. In equation (15), $\omega$ is the angular frequency of the measurements of $n$, and $A_R, B_R, C_R, \ldots$ are the first, second, third, \ldots refractivity virial coefficients of the gas, which are functions of frequency and temperature only. The majority of refractive index measurements are taken at optical frequencies and it is usually assumed that such frequencies are implied when the term 'refractive index' is used although, strictly, the term can be applied to the ratio of the speed of light in vacuum to the phase speed of light in a medium for light of any frequency.

The first two refractivity virial coefficients are given by

$$A_R = \frac{N_A \alpha(\omega)}{3\varepsilon_0}$$

$$B_R = \frac{N_A}{3\Omega\varepsilon_0} \int \left[\frac{1}{2} \alpha_{12}(\omega) - \alpha(\omega)\right] \exp(-U_{12}/kT) d\xi_{12} d\xi_{21}$$ (5.5.16)

which are very similar to the expressions for $A_\varepsilon$ and $B_\varepsilon$ for noble gases, since at optical frequencies any contributions due to molecular dipole moments have vanished. The molecular polarisability is now the dynamic, rather than the static, polarisability and so $A_\varepsilon \neq A_R$, although they are generally found to be very similar for
non-polar gases. It has also been found that $B_\varepsilon$ and $B_R$ are of very similar magnitude for non-polar gases, and the same is likely to be true of the higher coefficients [93].

Equation (15) can be recast with the $(p, V_m, T)$ virial equation of state to give

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) \frac{RT}{p} = A'_R(\omega, T) + B'_R(\omega, T)\left(\frac{P}{RT}\right) + C'_R(\omega, T)\left(\frac{P}{RT}\right)^2 + \cdots \quad (5.5.17)$$

where

$$A'_R = A_R$$

$$B'_R = B_R - A_R B$$

$$C'_R = C_R - A_R C + 2 A_R B^2 - 2 B_R B \quad (5.5.18)$$

Therefore, absolute measurements of $n$ and $p$ can provide estimates of the refractivity virial coefficients and the $(p, V_m, T)$ virial coefficients in a similar way to that seen for absolute $(\varepsilon, p)$ measurements. Equation (17) also forms the basis of refractive index gas thermometry using absolute $(n, p)$ measurements [91].

The amount-of-substance density-dependence of the refractive index of a gas can also be expressed by the series [98]

$$(n - 1)V_m = A_n(\omega, T) + B_n(\omega, T) \rho + C_n(\omega, T) \rho^2 + \cdots \quad (5.5.19)$$

where $A_n, B_n, C_n, \ldots$ are the first, second, third, $\ldots$ refractive index virial coefficients, which are functions of angular frequency $\omega$ and temperature $T$ only. Equation (19) can also be recast with the $(p, V_m, T)$ virial equation of state to give the series

$$(n - 1) \frac{RT}{p} = A'_n(\omega, T) + B'_n(\omega, T)\left(\frac{P}{RT}\right) + C'_n(\omega, T)\left(\frac{P}{RT}\right)^2 + \cdots \quad (5.5.20)$$

where

$$A'_n = A_n$$

$$B'_n = B_n - A_n B$$

$$C'_n = C_n - A_n C + 2 A_n B^2 - 2 B_n B \quad (5.5.21)$$

The refractive index virial coefficients are related to the refractivity virial coefficients by the relations

$$A_R = 2 A_n / 3$$

$$B_R = 2 B_n / 3 - A_n^2 / 9 \quad (5.5.22)$$

$$C_R = 2 C_n / 3 - 2 A_n B_n / 9 - 4 A_n^3 / 27$$

with more complicated expressions for the higher coefficients [98].
5.6 Experimental methods for determining the refractive index and dielectric constant of gases

The dielectric constant

Capacitance cells

The simplest method of determining absolute values of \( \varepsilon \) is the use of a capacitance cell. The capacitor is commonly of the parallel or cylindrical plate type and its capacitance is most often measured using a bridge circuit operated at, typically, 10 kHz. The capacitance \( C \) is measured with the gas at pressure \( p \) between the plates and also under vacuum conditions. The ratio \( C(p) / C(0) \) gives the dielectric constant \( \varepsilon \) for the gas at pressure \( p \). Modern capacitance measuring bridges can provide a fractional resolution in \( C \) of better than 1ppm, without difficulty, and so fractional uncertainties in \( \varepsilon \) on this level are, in principle, attainable. Unfortunately, this is not often achieved due to mechanical hysteresis [99]. This gives rise to changes in capacitance as the temperature and/or gas pressure is varied that are not entirely due to the change in dielectric constant, but are partly due to small, irreversible changes in the capacitor dimensions. Similar errors can occur if the capacitor geometry is distorted when the temperature and/or pressure is changed due to the different mechanical properties of the capacitor plate material and the insulating material that must be used to separate the plates. It should be noted that such effects are quite distinct from the reversible changes in dimensions that are normally expected when the temperature or pressure is changed: reversible changes can be corrected for either by calibration with a gas of known \( \varepsilon \), or using the published mechanical properties of the capacitor materials.

The unpredictable hysteresis and distortion effects can be the limiting factors in the accuracy of absolute measurements of \( \varepsilon \) using capacitance cells, although careful design, including the use of very thin insulators, can produce cells that are capable of an estimated fractional uncertainty in \( \varepsilon \) of as little as 10 ppm at pressures above 10 MPa [99]. However, changes in \( \varepsilon \) can be measured with much smaller uncertainties.
Capacitance cells have been used for the majority of published measurements of the dielectric constant of gases. Measurements of capacitance are generally taken, under isothermal conditions, at a series of gas pressures. The vacuum capacitance measurement is then combined with these to provide the required absolute values of dielectric constant. These can be combined with the measured pressures to determine dielectric and/or \((p, V_m, T)\) virial coefficients as described in section (5.5). This procedure is used to obtain values of the first dielectric virial coefficient \(A_e\) with estimated uncertainties of a few parts in \(10^4\), and has been used to estimate \(B_e\) [101], but expansion techniques are more commonly used to measure \(B_e\) and the higher coefficients [94-96, 100, 102, 103].

The first of the expansion methods employs the Burnett technique to allow measurements at a series of gas densities in a fixed ratio \(r\) such that \(\rho_{i+1} = r \rho_i\). This is achieved by successive expansions from the capacitance cell to a smaller fixed volume which is evacuated before each expansion. The measurements are analysed in terms of the series

\[
\frac{Z_i}{Z_{i+k}} = r^{-k} + \left( r^{-k} - 1 \right) \frac{B_e}{A_e^2} Z_i + \left( r^k - r^{-k} \right) \left( \frac{C_e}{A_e^3} - \frac{B_e^2}{A_e^4} \right) Z_i^2 + \ldots
\]

(5.6.1)

where \(Z_i = \left( (\varepsilon - 1)/(\varepsilon + 2) \right)\), and \(r\) is the expansion ratio which is a constant for the individual apparatus. Therefore, a series of \(2k\) expansions gives \(k\) independent values of \((Z_i / Z_{i+k})\) which are fitted to equation (1) to determine \(r\) and \((B_e / A_e^2)\). \(A_e\) may be determined from the same measurements if the gas pressure is also measured; \(B_e\) can then be found. This method has been used to measure \(B_e\) for a number of simple gases with reported uncertainties of about \(\pm5\%\) [102, 103]. A number of values of \(C_e\) have also been reported [102] with typical estimated uncertainties larger than \(\pm\ 50\%\).

The main disadvantage of this method is that the expansion ratio \(r\) must be determined to within a few parts per million in order to determine \(B_e\) with useful precision, and this makes the method vulnerable to drifts in the capacitance of the cell during the expansion run. The measurements reported using this and other expansion methods tend to begin at very high pressures (above 10 MPa) and extend down only as far as 200 kPa or so; often the lowest pressure is much higher.
Therefore, it may be questionable whether the determined value of $B_\varepsilon$ truly corresponds to the value in the limit of zero density, which is the definition of $B_\varepsilon$.

The differential-expansion method, developed by Buckingham et al. [104], employs two similar capacitance cells A and B, one of which is filled with the gas at density $\rho$ and the other evacuated. The sum of the capacitances of the two cells is measured and then the gas is allowed to expand into the evacuated cell. The gas density is approximately halved as a result of the expansion, and the sum of the cell capacitances is measured again. This procedure is repeated until a low density is reached. Finally, a measurement of the evacuated cell capacitances is taken. The linear term in density of the total capacitance remains the same before and after each of the expansions but the quadratic and higher order terms change. Thus the second and third dielectric virial coefficients can be determined from the measured changes in the total capacitance. The effect of the mismatches in volume and capacitance of the similar, but not identical, cells are reduced by performing two expansion runs, one involving expansions from A to B and the other involving expansions from B to A. This eliminates the effects of reversible changes in capacitor dimensions and geometry due to cell pressurisation, but does not eliminate hysteresis effects.

The working equation for analysis of the measurements can be written [94]

\[
\frac{D_A}{C_0(\varepsilon_1 - 1)} + \frac{D_B}{C_0(\varepsilon_2 - 1)} = \left( \frac{B_\varepsilon + A_\varepsilon^2}{6A_\varepsilon^2} \right) \left[ (\varepsilon_1 - 1) + (\varepsilon_2 - 1) \right]
\]

\[
+ \frac{1}{2} \left( \frac{4B_\varepsilon^2 - 3A_\varepsilon C_\varepsilon + 2B_\varepsilon A_\varepsilon^2 + A_\varepsilon^4}{36A_\varepsilon^4} \right) \left[ (\varepsilon_1 - 1) + (\varepsilon_2 - 1) \right]^2 + \ldots
\]

(5.6.2)

where $D_A$ is the change in capacitance when the gas ($\varepsilon_1, \rho_1$) in cell A is expanded into the evacuated cell B, $D_B$ is the change in capacitance when the gas ($\varepsilon_2, \rho_2$) is expanded into the evacuated cell A (when the expansion run is reversed), and $C_0$ is the average geometric capacitance of the two cells. The experimental measurements can be fitted to equation (2) to obtain $B_\varepsilon$ and $C_\varepsilon$ provided that $A_\varepsilon$ is known. $A_\varepsilon$ can be obtained from the same set of measurements, if the pressure is measured, by fitting absolute measurements of $\varepsilon_1$ or $\varepsilon_2$ to equation (5.5.11), but, even if $A_\varepsilon$ is obtained from separate measurements, it is necessary to determine the absolute values of $\varepsilon_i$.
and $\varepsilon_2$ for the regression of equation (2). These measurements are just as vulnerable to the effects of capacitor hysteresis and deformation as the simpler measurements using a single capacitance cell described earlier. Nevertheless, the majority of recent determinations of $B_\varepsilon$ and $C_\varepsilon$ have employed this method and uncertainties of as little as $\pm 2\%$ in $B_\varepsilon$ and $\pm 9\%$ in $C_\varepsilon$ have been reported [94-96].

### Cavity resonators

Cavity resonators are made of a single, highly-conducting material and can, therefore, be designed to have a very high degree of mechanical stability. These resonators can be broadly divided into re-entrant and simple geometry types [19].

Re-entrant cavity resonators are usually based on a simple cylindrical cavity, but have a post which protrudes, from one of the end plates, into the cavity space. The post, which most commonly has a cylindrical section, can be turned in the solid so that it forms an integral part of the end plate. The post can either extend almost the full length of the cavity, leaving just a small gap at the end to form a parallel plate capacitor [105-109], as shown in figure (5.2(a)), or can be made to widen within the cavity so as to leave a small annular gap between itself and the boundary wall, forming a cylindrical capacitor [110-112], as shown in figure (5.2(b)). In either case, part of the cylindrical post acts as an inductance $L$ and so, to a first approximation, a re-entrant resonator can be considered as a perfectly shielded, parallel $LCR$ circuit.

The lowest resonance frequency lies in the radio frequency region for cavities with dimensions of a few centimetres and is very nearly inversely proportional to $\sqrt{\varepsilon}$ for the gas filling the cavity. Thus, the dielectric constant of the gas is given by $\left[ f(0)/f(p) \right]^2$, to a very good approximation, where $f(p)$ is the resonance frequency when the gas is at a pressure $p$ in the cavity, and $f(0)$ is the resonance frequency of the evacuated cavity. The resonance frequencies can be determined by measuring the transmission characteristics of the resonator using an impedance analyser. The reversible changes in capacitance and inductance, and therefore resonance frequency, arising from dimensional changes due to pressurisation, can be taken into account by calibration using a gas with accurately known $\varepsilon$. This provides a correction factor which is used to relate $\varepsilon$ and $\left[ f(0)/f(p) \right]^2$ accurately [111].
Re-entrant resonators do not suffer from the problem of differential expansion caused by the presence of insulating spacers, found in conventional capacitance cells, but may suffer from small hysteresis effects. However, measurements with an estimated fractional uncertainty in $\varepsilon$ on the order of 1ppm at pressures up to 300 kPa have been reported [110, 111]. There is every reason to believe that this level of precision could be maintained at higher pressures. Changes in $\varepsilon$ can be measured with even higher precision, and a re-entrant resonator has been used for accurate dew and bubble point studies at pressures above 5 MPa by detecting the changes in $\varepsilon$ at phase boundaries [110, 111]. The lack of insulating spacers makes very wide ranges of temperature possible, and the same recently designed resonator is suitable for use with corrosive fluids at temperatures up to 400 °C.

Simple geometry cavity resonators, such as are used in this work, have seen only limited use for measuring the dielectric constant of gases [50, 113, 114]. They have no insulating spacers or re-entrant parts and are operated at microwave frequencies. A number of resonant modes can be used and they all have much higher quality factors than the modes of a re-entrant resonator of similar dimensions, which enables the resonance frequencies to be determined with greater precision. The absence of re-entrant corners allows a fully analytical theory of the cavity fields to be developed (there are singularities of field at re-entrant corners), and so an understanding of the
resonance frequencies and halfwidths to a level approaching 1ppm can be gained. This allows absolute measurements of \( \varepsilon \) to be made without the need for calibration.

There has been no reported attempt to apply the Burnett expansion method, or a differential-expansion technique, to measurements with cavity resonators, but it is likely that such measurements would lead to more accurate measurements of the higher dielectric virial coefficients than have been reported to date.

The refractive index

In early measurements [115, 116], the first and higher refractivity virial coefficients were determined by fitting absolute measurements of \( n \) and \( p \), taken along an isotherm, to equation (5.5.17), but, in recent years, this method has only been used to obtain \( A_n \), with the higher refractivity virial coefficients being determined using a differential-expansion technique [84, 98] similar to that described for the measurement of dielectric virial coefficients. Such differential-expansion measurements are analysed using an equation derived from equation (5.5.19).

In recent work, the absolute measurements of \( n \), at optical frequencies, are taken using a grating interferometer with a monochromatic, linearly-polarised laser light source. The laser light is 'split' to produce coherent beams, one of which is made to pass through a sample cell containing the gaseous sample at pressure \( p \) and temperature \( T \). The other beam does not pass through the sample, but acts as a reference. The beams are recombined at the detector end of the interferometer to produce interference fringes. The light of the 'sample beam' is slowed down as it passes through the sample cell, and so the wavelength of the light within the sample cell is smaller than that of the reference beam. Thus a phase difference between the reference and sample beams appears at the detector. If the phase difference between the reference and sample beams at the detector is \( \Delta \phi \) then the change in the fringe count whilst venting the gas sample to vacuum is given by \( \Gamma = - (\Delta \phi / 2\pi) \). Therefore, the refractive index of the sample, at pressure \( p \) and temperature \( T \), is given by

\[
n(p, T) = \left[ \Gamma(p, T) \frac{\lambda_0}{L} \right] + 1 \tag{5.6.3}
\]
With a fringe count sensitivity of $10^{-3}$ of a fringe and sample cell lengths of a few centimetres, a precision in $n$ of a few parts in $10^5$ is, in principle, possible. However, uncertainties in the effects of temperature variation, mechanical vibration and sample cell distortion under pressurisation, give rise to estimated accuracies of about 0.5 ppm at pressures below 1 MPa and 20 ppm at pressures above 30 MPa for the most carefully taken measurements [98]. Absolute $(n, p)$ measurements of this type can provide $A_8$ with an estimated fractional uncertainty of about $2 \times 10^{-4}$.

The differential-expansion technique [117, 118] used to measure $B_n$ and higher refractivity virial coefficients employs two similar cells A and B, arranged in series, within the interferometer region such that the sample beam passes through both. Initially, cell A contains the gaseous sample at pressure $p$ and cell B is evacuated. A valve connecting the two cells is opened and the gas expands to fill both A and B. The density of the gas is approximately halved, but the sample length is doubled (for perfectly matched cells A and B) and so the $\rho^i$ term of the change in fringe count is the same before and after the expansion, as can be seen by the combination of equations (3) and (5.5.19). Therefore, the change in fringe count is determined solely by the quadratic and higher terms in $\rho$ of equation (5.5.19), and thus by the values of the higher refractive index virial coefficients $B_n, C_n, \ldots$. In practice, it is impossible to produce identical cells and so, just as was seen with the differential-expansion measurements of $\varepsilon$, two expansion runs are carried out (the first from cell A to cell B, the second from cell B to cell A) to eliminate the effects of mismatch. However, any irreversible cell distortion effects will not be eliminated by this procedure.

Full details of the differential-expansion method can be found in the literature [117, 118], and only the final working equation is given here:

$$\Delta \Gamma_{\text{red}} = \left( \frac{B_n}{2A_n^2} \right) [(n_A - 1) + (n_B - 1)] + \left( \frac{3A_n C_n - 4B_n^2}{4A_n^4} \right) [(n_A - 1) + (n_B - 1)]^2 + \cdots$$

(5.6.4)

where $\Delta \Gamma_{\text{red}}$ is the fractional difference between the initial and final values of the change in fringe counts of cells A and B referred to vacuum, for a given expansion, and $n_A$ and $n_B$ are the absolute values of refractive index of the gas within cells A and B following an expansion. Thus a least-squares regression of $\Delta \Gamma_{\text{red}}$ on $[(n_A - 1) + (n_B - 1)]$ can provide estimates of $B_n$ and $C_n$ (and, possibly, higher
coefficients) if an accurate value of $A_n$ can be obtained from absolute $(n, p)$ measurements at the same temperature. The refractivity virial coefficients $B_R, C_R, ...$ can then be evaluated using equations (5.5.22). Uncertainties of $\pm 3\%$ in $B_R$ [84, 98] and $\pm 6\%$ in $C_R$ [98] have been reported using the differential-expansion technique described. A limited number of $D_R$ values have also been reported [98] with uncertainties of about $\pm 45\%$.

Laser interferometers are expensive and their use has generally been limited to measurements of refractive index and refractivity virial coefficients at temperatures greater than 273 K. Temperature control at much lower temperatures is likely to require apparatus (e.g., a liquid-nitrogen flow system) that could easily disturb the measurements since interferometers are extremely sensitive to mechanical vibrations, thermal shock and other physical disturbances [98, 117].
Chapter 6 Experimental Apparatus and Techniques

6.1 Introduction

A brief description of the spherical resonator and its thermostat, previously used for measurements of the speed of sound in a number of gases, is given in section (6.2). Adaptations made to facilitate the measurement of the speed of light, and, therefore, the refractive index and dielectric constant, at microwave frequencies are set forth in some detail.

The design and fabrication of the new, brass cylindrical resonator and its stainless-steel pressure vessel are described in section (6.3). The cylindrical resonator, which has an internal volume of less than 5.7 cm$^3$ (cf. 268.1 cm$^3$ for the spherical resonator), is significantly smaller than any reported to date and is demonstrated to be highly stable with respect to changes in temperature and pressure.

The instrumentation used to measure the resonance frequencies and halfwidths of the modes of both resonators is outlined in section (6.4), and the experimental procedures are given in section (6.5); the gas samples for which measurements were taken are described in section (6.6). Section (6.7) contains an account of the statistical analysis used to extract the resonance frequencies and halfwidths from the experimental data. It is shown that the resonance frequencies of the cylinder were determined with a fractional precision which compares well with that found for the modes of the sphere.

6.2 The spherical resonator

A full account of the fabrication of the spherical resonator, originally designed by Goodwin for measurements of the speed of sound in gases at pressures up to 7 MPa, is given in references 36 and 119, and the thermostat, intended for operation between 80 and 373 K, is described in references 78 and 120, and so only a brief account of these parts of the apparatus is given here. The resonator was adapted for measurements of the speed of light at microwave frequencies by replacing the acoustic transducers with probe antennae housed in mounts designed by Bailey and
Ewing [121], and such adaptations, which have not yet been reported in the literature, are covered in some detail.

The spherical resonator and its thermal environment are shown in figure (6.1). Two highly-polished aluminium alloy 6082 (T6 condition) hemispheres, each with a nominal internal radius of 40 mm and thickness of 10 mm, welded together in an electron beam for a vacuum and pressure-tight seal, formed the basic spherical resonator. The microwave probe antennae were housed in mounts machined to fit the transducer ports that had been used for the previous acoustic measurements. Thus the antennae were located at a polar angle of $\pi/4$, separated by an azimuthal angle of $\pi$, with a 1 mm diameter gas inlet tube, of length 40.9 mm, at a polar angle of 0. A cross-sectional diagram of one of the microwave probe mounts is shown in figure (6.2).

Cryogenic semi-rigid coaxial cables, used to prevent heat leaks, transmitted the microwave signals to and from the resonator, and 2 mm lengths of the inner conductors of the cables (silver-coated copper-clad steel wires of diameter 0.5 mm) protruded into the cavity to act as the probe antennae. PTFE dielectric (o.d. 1.68 mm) separated the inner conductors from the 304 stainless-steel outer sheaths (o.d. 2.14 mm) which had copper-coated interior surfaces. The two probes were joined to SMA connectors using 1.4 m lengths of the coaxial cable, which were coiled three times around the temperature control block above the resonator. The cables were not thermally anchored to the control block, but it was estimated that the total heat leak along the cables was about 4 mW at 189 K, and that the temperature of the resonator wall at the equator and the south pole was about 1 and 3 mK, respectively, below the temperature at the microwave probes. Such temperature differences imply variations of less than 0.07 ppm in the radius of the resonator since the linear coefficient of thermal expansion of the resonator has been estimated to be $(22.03 \pm 0.06) \times 10^6 \text{ K}^{-1}$ from microwave measurements on the evacuated cavity from 90 to 373 K [28]. The effect of such temperature differences on the isothermal measurements of refractive index and dielectric constant carried out in this work was negligible.
Figure (6.1) The spherical resonator and its thermal environment. Description on following page

[Diagram showing a spherical resonator and its components, labeled A, B, C, D, E, F, G, H, J, K.]
A Polystyrene block
B Inlet tube
C Access tube
D Dewar
E Temperature control block
F Copper block
G Microwave probe mount
H The spherical resonator
J Vacuum can
K Radiation shield

**Figure (6.2)** A microwave probe mount in the spherical resonator [121]
The resonator was linked by a copper post to the copper temperature control block which was bolted to the lid of a 3 mm thick copper radiation shield. The outer edge of the control block was wound with a 22.5 Ω manganin-wire heater which was varnished to provide improved thermal contact between itself and the block. A 50 Ω manganin-wire heater, which could be energised as required, was wound around the equator of the sphere so that the resonator temperature could be recovered more quickly following a pressure reduction [see section (6.5)]. This heater was also varnished to improve thermal contact between itself and the resonator. The sides and bottom of the radiation shield were uniformly wound with a manganin-wire heater (although this was not energised during the measurements in this work) and the whole was covered with 100 layers of superinsulation. An outer stainless-steel can, sealed with indium wire, formed a vacuum enclosure; with continual pumping by an oil diffusion pump, the pressure inside the can was less than 1 mPa. Several copper braids connected the control block to the lid of the can to provide a heat link. The apparatus was immersed in a large dewar, and the temperature could be reduced by heaping dry ice on top of the can or by filling the dewar with liquid nitrogen, the level of which was sensed by thermistors coupled to a flow controller.

The control block temperature was sensed by four 100 Ω (near 273 K) platinum resistance thermometers, thermally coupled to a copper block anchored to the resonator and connected in series with a fixed resistance of 400 Ω which was also thermally coupled to the block. Three manganin wires (two current, one potential) led from the thermostat to an external potential divider which completed a Wheatstone bridge that was excited by 1 V rms at 1025 Hz. The error signal from the bridge was amplified and fed to a proportional-integral controller which, in turn, energised the heater on the temperature control block. Typical short-term temperature fluctuations at the control block were on the order of 0.1 mK and since the thermal coupling between the resonator and the block had a characteristic time constant of 45 min, short-term fluctuations at the resonator were not considered to be a problem. The longer-term stability of the resonator temperature was also good, with only 1 to 2 mK drifts being recorded over a 24 h period, even when controlled at temperatures far from ambient.
The temperature of the resonator, and therefore of the enclosed gas at thermal equilibrium, was measured using a single 25 Ω (near 273 K) capsule-type platinum resistance thermometer (Tinsley B145) mounted in an aluminium block [not shown in figure (6.1)] bolted to the outside of the resonator at a polar angle of π/4 and in a plane separated from that of the microwave probes by an azimuthal angle of π/2. Vacuum grease was used to improve thermal contact between the thermometer and the block and between the block and the resonator. The thermometer leads were thermally anchored to the temperature control block, before connection to the thermometers, to reduce heat leaks. There was a second aluminium thermometer mount, bolted to the outside of the resonator at a location diametrically opposite to the first, but no thermometer was available at the time of the measurements for use in this mount.

The capsule-type platinum resistance thermometer (PRT) was calibrated on the International Practical Temperature Scale of 1968 (IPTS-68) [122], over the temperature range 90.188 to 903.89 K, at the National Physical Laboratory (NPL).

In the range 90.188 to 273.15 K, \( T_{68} \) is defined by

\[
W(T_{68}) = W_{\text{CCT-68}}(T_{68}) + \Delta W_{4}(T_{68})
\]

(6.2.1)

where \( W(T_{68}) \) is the measured resistance ratio given by

\[
W(T_{68}) = \left\{ R(T_{68})/R(273.15 \text{ K}) \right\}
\]

(6.2.2)

and \( W_{\text{CCT-68}}(T_{68}) \) is the resistance ratio given by the reference function

\[
\frac{T_{68}/K}{3.28} = \sum_{j=0}^{10} a_j \left( \frac{\ln W_{\text{CCT-68}}(T_{68}) + 3.28}{3.28} \right)^j
\]

(6.2.3)

where the coefficients \( a_j \) are defined constants [122]. The deviation function \( \Delta W_{4}(T_{68}) \), in equation (1), is given by

\[
\Delta W_{4}(T_{68}) = b_4(T_{68} - 273.15 \text{ K}) + e_4(T_{68} - 273.15 \text{ K})^3(T_{68} - 373.15 \text{ K})
\]

(6.2.4)

where the thermometer constants \( b_4 \) and \( e_4 \) are determined by the measured deviations at the normal condensation point of oxygen or the triple point of argon (to determine \( e_4 \)) and the normal boiling point of water (to determine \( b_4 \)). Thus, the values of \( T_{68} \) in this range were determined by iterative solution of equation (1) using equations (3) and (4).

In the range 273.15 K to 903.89 K, \( T_{68} \) is defined by
\[
\left( T_{68}/K \right) = 273.15 + \left( t'/\,{}^oC \right) + 0.045 \left( \frac{t'}{100\,{}^oC} \right) \left( 1 - 1 \right) \left( \frac{t'}{419.58\,{}^oC} \right) - 1 \left( \frac{t'}{630.74\,{}^oC} \right) - 1
\]  

(6.2.5)

where \( t' \) is defined by the Callendar equation

\[
t' = \frac{1}{\alpha} \left[ W(t') - 1 \right] + \delta \left( \frac{t'}{100\,{}^oC} \right) \left( 1 - 1 \right) \left( \frac{t'}{100\,{}^oC} \right)
\]  

(6.2.6)

with \( W(t') = \{ R(t')/R(0\,{}^oC) \} \). The ice point resistance \( R(0\,{}^oC) \), the fundamental coefficient \( \alpha \) and the Callendar constant \( \delta \) are determined from measurements of the thermometer resistance at the triple point of water and the normal melting points of tin and zinc. All the required thermometer constants, obtained from the NPL calibration, are given in table (6.1).

**Table (6.1) NPL calibration constants for the Tinsley B145 capsule-type PRT**

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R(0,{}^oC)/\Omega )</td>
<td>24.88161</td>
</tr>
<tr>
<td>( 10^3 \alpha/,{}^oC )</td>
<td>3.925708</td>
</tr>
<tr>
<td>( \delta/,{}^oC )</td>
<td>1.4967</td>
</tr>
<tr>
<td>( 10^5 b_4/,{}^oK )</td>
<td>-2.588</td>
</tr>
<tr>
<td>( 10^7 e_4/,{}^oK )</td>
<td>4.846525</td>
</tr>
</tbody>
</table>

During the temperature measurements, the resistance of the thermometer was measured using an a.c. resistance bridge (Tinsley model 5840), with a resolution of 10 \( \mu \Omega \) (0.1 mK), operated at 375 Hz and a current of 1 mA. A standard 10 \( \Omega \) resistor (Wilkins 5685A) was used to monitor small drifts in the bridge.

All the IPTS-68 temperatures recorded for the sphere measurements have been converted to temperatures on the International Temperature Scale of 1990 (ITS-90) [123] using a polynomial representation of the differences \( (t_{90} - t_{68}) \), due to R. L. Rusby of the NPL, given by [124]

\[
(t_{90} - t_{68})/\,{}^oC = \sum_{j=1}^{8} a_j \left( t_{68}/630\,{}^oC \right)^j
\]  

(6.2.7)
where \( (\frac{t_{90}}{^\circ C}) = [(T_{90}/K) - 273.15], \quad (\frac{t_{e8}}{^\circ C}) = [(T_{e8}/K) - 273.15], \) and the coefficients \( a_j \) are constants. The polynomial is not part of the ITS-90, but it has been estimated to be accurate to 1 mK above 0 °C and 1.5 mK below 0 °C.

The gas pressure was measured with a differential capacitance manometer ('Baratron', MKS type 310CD) with a resolution of 13 Pa and a full-scale of 1.3 MPa, connected in the external pipework; the reference port of the Baratron was continually evacuated by a rotary pump to a pressure not exceeding 1 Pa. The Baratron was calibrated against a nitrogen-lubricated standard pressure balance (Ruska type 2465-751-000) which had a manufacturer's estimated accuracy of the greater of 0.015 % of reading and 10 Pa [high pressure range of 13.796 ≤ (\( p / \) kPa) ≤ 4301.069] or 0.7 Pa [low pressure range of 1.3800 ≤ (\( p / \) kPa) ≤ 108.5882]. Calibration measurements were taken at 11 (descending) pressures from 782.964 kPa to vacuum, and the data could best be accommodated by the equation

\[
(\Phi / \text{mV}) = (999.957 \pm 0.042) + (7.71206 \pm 0.00028)(p/\text{kPa}) \\
- (3.5522 \pm 0.0035) \times 10^{-5}(p/\text{kPa})^2
\]  

where \( \Phi \) was the Baratron output potential and \( p \) was the pressure generated at the pressure balance, corrected for imperfect bell-jar vacuum ('absolute' measurements were made, with the mass/piston arrangement enclosed within a bell-jar evacuated by a rotary pump to a pressure of about 13 Pa). The calibration data fitted equation (8) with a standard deviation of 0.06 mV (8 Pa), which was only 60 % of the ultimate resolution of the Baratron, and was found to be reproducible to about 0.02 %; the deviations of the measured outputs of the Baratron from equation (8) are shown in figure (6.3). Equation (8) was solved by iteration to determine all the gas pressures measured using the Baratron in this work.
Figure (6.3) Deviations of the Baratron output potential from equation (6.2.8)

There was invariably some small drift in the Baratron zero (on the order of 0.5 mV) over the course of an isotherm, and the measured pressures were corrected by assuming that the zero drifted linearly in time from its initial setting. Given the 0.015 % of accuracy of the pressure balance pressures and the 0.02 % reproducibility of the calibration data used to determine equation (8), it is estimated that pressures determined using the Baratron were accurate to approximately 0.03 %, which is similar to previous estimates [78, 120], and compares well with the manufacturer’s estimate of 0.05 %.

6.3 The cylindrical resonator

The small brass resonator, within its stainless-steel pressure vessel, is shown in figure (6.4). The resonator consisted of a short, open-ended cylindrical section and top and bottom flat end-plates, all machined from a single cylindrical length of extruded free-cutting brass rod (BSS 2874 CZ121) of 32 mm diameter (finally turned down to 31 mm). The final adjustment of the cylindrical section was made by carefully passing a 19 mm diameter bit through the centre of the rod, using single passes, one
Figure (6.4) The cylindrical resonator and its pressure vessel

- A: Copper gas inlet tube
- B: Swagelok male connector
- C: Stainless-steel bolt
- D: Viton O-ring
- E: Microwave coaxial cable
- F: Grub screw
- G: The stainless-steel pressure vessel
- H: The brass cylindrical resonator
- J: Transparent plastic tubing housing the thermometer leads
- K: Cylindrical resonator gas inlet hole
- L: Swagelok elbow connector
- M: The Rosemount 162D capsule-type PRT
from each end. The rod was then cut to the final length of 20 mm. This procedure helped to reduce eccentricity of the bore and ensured that the edges were not rounded at the section ends. Each end-plate was drilled out for 6 countersunk brass screws, at \( \pi/3 \) centres, and the top and bottom edges of the cylindrical wall were tapped to accept them. Two circular openings were drilled through the top-plate, at diametrically-opposed positions 5.0 mm from the centre of the plate, to house the microwave coaxial cables (Radio Spares RG405, nominal o.d. 2.17 mm) snugly, and a 0.95 mm diameter gas inlet hole was drilled in the centre of the bottom plate. Two 2 mm diameter threads were tapped into the edge of the top-plate, passing through the line of the microwave cable openings, to a sufficient depth that grub screws could be inserted and gently tightened onto the outer conductors of the microwave cables when in position, to reduce the movement of the cables during final assembly. The majority of the toolmarks were removed from the inner surfaces of the cylinder with progressively finer grades of emery paper, following which the cylinder had a nominal internal radius of 9.5 mm and an internal length (when closed) of 20.0 mm, with a cylindrical wall thickness of 6.0 mm and end-plate thicknesses of 6.0 mm. These thicknesses allowed firm positioning of the securing screws and microwave cables without making the external dimensions unnecessarily large. Following the gas inlet perturbation measurements described in section (4.7), the inner surfaces of the cylinder were polished with ‘Solvol’ chrome polish to a good, but not mirror, finish (further polishing threatened to produce small dips in the end-plates around the microwave cable and gas inlet openings, and distort the cylindrical bore), but feint, circular toolmarks were still visible on the inner surface of the cylindrical wall following the final polishing.

The design of the austenitic stainless-steel 321-S12 pressure vessel was governed by the following requirements:

- The pressure vessel should be as small and simple as possible, and yet be able to accommodate three Swagelok male connectors in the lid (one to accept a 3 mm o.d. copper tube for connection to the external pipework and two to allow the insertion of the input and output microwave cables), and a capsule-type platinum resistance thermometer in its base.
• The design should conform to section 3 of BS5500 (1991) [125], the recommended design codes for pressure vessels, for a maximum internal working pressure of 12 MPa at 150 °C.

A brief account follows of how the final design, shown in figure (6.4), was arrived at, before the fabrication of the pressure vessel, to this design, is described. All the design equations used can be found in reference 125, but, due to limitations on space, only a few of the more important equations used have been reproduced here. References 126 to 128 were also useful sources of information during the design process.

The minimum required thickness $t_{min}$ of the wall of the pressure vessel was the larger of

$$t_{min} = \left( \frac{pR}{SE - 0.6p} \right) \text{ or }$$

$$t_{min} = \left( \frac{pR}{2SE - 0.2p} \right)$$

(6.3.1)

where $p = 12$ MPa is the maximum working pressure, $R$ is the internal radius, $S = 1.57 \times 10^8$ Pa is the maximum design stress of the pressure vessel wall material (austenitic stainless-steel 321-S12) at the design temperature [129], and $E$ is the joint efficiency factor (1.0 for the initial assumption of a seamless shell). The internal radius $R$ was chosen to be 17 mm to allow a 1.5 mm clearance gap around the brass resonator when placed in the pressure vessel. The first of equations (1) arises from a consideration of circumferential stresses, and gave $t_{min} = 1.4$ mm, whilst the second of equations (1) arises from a consideration of longitudinal stresses and gave $t_{min} = 0.7$ mm. The largest of these, 1.4 mm, is clearly much smaller than the wall thickness of the final design which was determined by the chosen method of closure and the spacing of the three 9mm diameter openings for the Swagelok male connectors in the lid. In accordance with sub-section 3.5.4 of BS5500 (1991) [125], the centres of the openings for the connectors had to be at least 18 mm apart (this being twice the diameter of one opening), and similar considerations for the spacing of bolt openings in the lid required that a bolt circle diameter $C$ of 55 mm be used. Therefore, to provide space for an O-ring groove between the bolt circle and the pressure vessel cavity space, a gasket (O-ring) circle diameter $G$ of 42.5 mm was
chosen, where the availability of viton O-rings was taken into account to arrive at the final figure of 42.5 mm.

Rather than use a flanged and bolted method of closure in an attempt to keep the wall thickness (in some regions) as small as approximately 1.4 mm, it was felt simpler and much more satisfactory to use a simple bolted closure as shown in figure (6.4). Preliminary calculations, using design formulae given in references 125 and 126, had shown that the flanges would have had to be approximately 15 mm thick and 40 mm in length, radially from the lip of the pressure vessel cavity space, to comply with the given values of bolt and gasket circle diameters. Such flanges would have made the vessel very top-heavy, encouraging discontinuity stresses [128] in the vessel, and temperature gradients at the cylindrical resonator since the thermal time constants for the flanged end of the pressure vessel would be very different from those at other parts of the vessel. To allow a simple bolted closure, the wall thickness was chosen to be 41.5 mm, giving 7 mm external clearance (the thickness of wall between the bolt threads and the external surface of the pressure vessel) for each of the 6 mm diameter bolts. The minimum required bolt load for the operating conditions was given by

\[ W_{m1} = \pi \left( \frac{G}{2} \right)^2 p + m\pi G(2b)p \]

(6.3.2)

where the gasket factor \( m = 0.25 \) for viton O-rings, and the effective gasket width \( b = 0.75 \) mm for the selected O-ring. The value of \( W_{m1} = 17616 \) N, calculated using equation (2), gave a required total bolting area \( A_m \) of 112 mm\(^2\) (where the maximum design stress for the stainless-steel bolts was taken to be \( 1.57 \times 10^8 \) Pa, the same as that for the pressure vessel wall material). A single 6 mm diameter bolt provided a bolting area of 22 mm\(^2\), and so it was clear that six 6 mm diameter bolts were required, and that these offered an additional safety factor of 18 % over the calculated number of 5.1 bolts. The six bolts had a spacing \( B_w = \left( \pi C/b \right) = 28.8 \) mm around the bolt circle diameter \( C \), and this was greater than the minimum required spacing of 18 mm for 6 mm diameter bolts. The minimum lid thickness \( e \) was calculated using

\[ e = \sqrt{\frac{0.3G^2p}{S} + \frac{1.909W_{m1}h_C}{GS}} \]

(6.3.3)
where

\[ h_o = \frac{(C - G)}{2} \quad (6.3.4) \]

Substitution of \( G = 42.5 \text{ mm} \), \( C = 55 \text{ mm} \), \( W_{m1} = 17616 \text{ N} \), \( S = 1.57 \times 10^4 \text{ Pa} \), and \( p = 12 \text{ MPa} \) into equations (3) and (4) gave \( e = 8.5 \text{ mm} \). However, the lid had to be reinforced because of the presence of the 9 mm diameter openings for the Swagelok male connectors, and thus the area replacement method [125] was used to estimate that an extra reinforcing thickness of at least 1.4 mm was required. Consideration of the further openings for the bolts in the lid led to a thickness of 13 mm being arrived at. A 4 mm locating step in the underside of the lid meant that the thickness was increased to 17 mm in the region of the openings for the Swagelok connectors, providing yet further reinforcement.

The final important design consideration was the depth of the cavity space in the pressure vessel, to house the brass cylindrical resonator. The resonator was to be suspended, within the pressure vessel, from the microwave cables, and so it was necessary for the cables to be bent towards the openings in the top-plate of the resonator from their positions of entry through the pressure vessel lid. These bends required 10 mm clearance space above the resonator top-plate, when in position. A further 2 mm clearance was allowed between the resonator bottom-plate and the bottom of the pressure vessel cavity. Thus, a pressure vessel cavity space of height 44 mm (with the pressure vessel lid in position) was selected.

The pressure vessel and its lid were machined, in accordance with the given design, from a single billet of austenitic stainless-steel 321-S12. The threaded openings for the three Swagelok male connectors (metric 3 mm connectors with NPT threads) were drilled and tapped into the lid at \( 2\pi/3 \) centres around a circle of diameter 23 mm. The pressure vessel base had a thickness of 15 mm which was sufficient to house the capsule-type PRT in a 6.2 mm diameter cylindrical opening drilled horizontally through the centre of the base from the side of the vessel [see figure (6.4)]; the thermometer leads were taken through a Swagelok elbow connector (NPT metric 3 mm). Sharp edges on the pressure vessel, which may have acted as fatigue crack initiators [128], were rounded. The pressure vessel was sealed with a viton O-ring (Pimseal 0410-15), chosen to allow work from about \(-40 \degree C\) to 225 \degree C.
with a large variety of fluids, which was lightly covered with vacuum grease and seated in a groove machined to the manufacturer's specification.

In the final assembly process, the microwave cable ends were smoothed using fine-grade emery paper (a jig was used to ensure the ends were kept perpendicular to the cable lengths) before being bent into the shape shown in figure (6.4). The cable ends were cleaned with 1,1,1-trichloroethane, inserted into the openings in the resonator top-plate, so that the ends were flush with the inner surface of the plate, and the grub-screws tightened. The resonator top-plate was then screwed to the cylindrical wall, to which the bottom-plate had already been screwed; particular care was taken not to disturb the microwave cables. The free ends of the 1 m long cables were then fed through the Swagelok connectors in the pressure vessel lid until the resonator top-plate was 10 mm from the inner surface of the pressure vessel lid. For the nitrogen isotherm at 300 K, the seals between the cables and the connectors were made by wrapping PTFE tape around those sections of the cables within the connectors, before fitting PTFE ferrules. For the rest of the measurements, the tape and ferrules were replaced by 1.7 cm lengths of silicon-rubber tube with a 1 mm diameter bore (actually the insulator of heavy-duty electrical wire).

Once assembled, the pressure vessel and resonator were fully immersed in the centre of a thermostatted bath (HAAKE K type 000-3295 with HAAKE F3 type 001-4202 thermostating unit), which had an operating temperature range of approximately 240 to 423 K with a suitable choice of bath liquid. For the measurements from 243 to 323 K taken in this work, a mixture of ethanol, water and antifreeze, in approximately equal volumes, was employed. The pressure vessel was supported in the bath on a small, stainless-steel platform designed such that the bath liquid could flow freely underneath, and come into direct thermal contact with, the pressure vessel base. The liquid mixture level came approximately 3 cm above the top of the Swagelok connectors in the pressure vessel lid when the bath was fully filled (required approximately 10.4 dm³). Short-term fluctuations in the temperature of the bath liquid were typically ±3 mK between 243 and 323 K, with drifts of up to 15 mK being recorded over the course of an individual isotherm. The short-term fluctuations were presumably damped by the convective heat transfer between the bath liquid and the pressure vessel (which was characterised by a thermal time
constant of about 20 min) because typical short-term fluctuations of only ±1 mK were measured by the capsule-type PRT buried in the base of the pressure vessel; the longer-term drifts in the bath liquid temperature were reproduced at the capsule-type PRT. Small corrections (≤ 0.2 ppm) were made to the measured resonance frequencies to take account of the longer-term drifts in temperature.

During the course of this work, the bath lost its ability to reach temperatures lower than ambient (possibly due to refrigerant leak) and so a separate dip cooler (Techne RU-500) was used in conjunction with the bath to complete the low temperature measurements. The thermostatting ability was not at all affected; in particular, there was no noticeable change in the short and long-term stability of the pressure vessel temperature over the course of an isotherm.

The temperature of the pressure vessel, and thus the resonator and the enclosed gas at thermal equilibrium, was measured using a single 25.5 Ω (near 273 K) capsule-type PRT (Rosemount 162D S/N 1249) embedded in the pressure vessel base, as previously described. Its housing within the base had been machined such that, when fully inserted, the centre of the thermometer was in line with the axis of the pressure vessel and resonator, to reduce errors in temperature measurement due to any radial temperature gradients, and was only about 2.6 cm from the centre of the resonant cavity; vacuum grease was used to improve thermal contact between the thermometer and the wall of the housing. The thermometer resistance was measured on the same bridge used to determine the resistance of the spherical resonator's capsule-type PRT.

The thermometer was calibrated on the International Temperature Scale of 1990 (ITS-90) [123] from 234.3156 to 423.0264 K.

In the range 13.8033 to 273.16 K, $T_{90}$ is defined by

$$\ln[W_r(T_{90})] = A_0 + \sum_{i=1}^{12} A_i \left[ \ln\left(\frac{T_{90}}{273.16K}\right) + 1.5 \right]^{i/15}$$  \hspace{1cm} (6.3.5)

and in the range 273.15 to 1234.93 K, $T_{90}$ is defined by

$$W_r(T_{90}) = C_0 + \sum_{i=1}^{9} C_i \left[ \frac{T_{90}/K - 745.15}{481} \right]^{i}$$  \hspace{1cm} (6.3.6)

where the $A_i$ and $C_i$ are defined constants and $W_r(T_{90})$ is a resistance ratio given by
\[ W_r(T_{90}) = W(T_{90}) - \Delta W(T_{90}) \]  

In equation (7), \( W(T_{90}) = \frac{R(T_{90})}{R(273.16 \text{ K})} \) is a measured resistance ratio, and \( \Delta W(T_{90}) \) is a deviation function, the form of which depends on the temperature sub-range considered. The ITS-90 comprises a number of sub-ranges throughout each of which temperatures \( T_{90} \) are defined; several of these sub-ranges overlap. Two such sub-ranges are from \( T_{90} = 234.3156 \text{ K} \) (the triple point of mercury) to \( T_{90} = 302.9146 \text{ K} \) (the melting point of gallium), and from \( T_{90} = 273.15 \text{ K} \) to \( T_{90} = 429.7485 \text{ K} \) (the melting point of indium). These were seen to cover the requirements for measurements using the cylinder in this work.

In the sub-range 273.15 to 429.7485 K, \( \Delta W(T_{90}) \) is defined as

\[ \Delta W(T_{90}) = a W(T_{90}) - 1 \]  

where the thermometer constant \( a \) is usually determined from the measurement of \( W(T_{90}) \) and the defined value of \( W(T_{90}) \) at the melting point of indium. Unfortunately, the apparatus for realisation of the melting point was not available, so an alternative approach was adopted. Calibration measurements at the melting point of indium were replaced by comparing the capsule-type PRT with a long-stem PRT (Tinsley 5187SA S/N 253124), calibrated on the ITS-90 from 273.15 to 903.15 K at the NPL, using a pair of stainless-steel comparative ebulliometers [130], both of which contained equal volumes of triple-distilled water. The water in each was boiled and the condensation temperature of the water in the reference ebulliometer (423.0264 K at the elevated pressure near 476 kPa), measured at the long-stem PRT, was associated with the measured resistance of the capsule-type PRT housed in the thermometer pocket of the other ebulliometer, following a +0.3 mK correction for the difference in water vapour heads at the thermometers and a systematic correction of −3.6 mK which was measured reproducibly using a second long-stem PRT (Tinsley 5187SA S/N 245064), also calibrated on the ITS-90 at the NPL, in place of the capsule-type PRT. Therefore, the thermometer constant \( a \), in equation (8), was determined using the value of \( W(T_{90}) \) obtained from equation (6) and the resistance ratio \( W(423.0264 \text{ K}) = \frac{R(423.0264 \text{ K})}{R(273.16 \text{ K})} \), where \( R(423.0264 \text{ K}) \) was measured using the comparative ebulliometers and \( R(273.16 \text{ K}) \) was measured in a triple point of water cell.
In the sub-range 234.3156 to 302.9146 K, \( \Delta W(T_{90}) \) is defined as

\[
\Delta W(T_{90}) = b[W(T_{90}) - 1] + c[W(T_{90}) - 1]^2
\]  

Measurements of the capsule-type PRT resistance in a triple point of mercury cell and a triple point of water cell were combined to determine \( W(234.3156 \text{ K}) \), whilst \( W(302.9146 \text{ K}) \) was obtained using equations (6), (7) and (8), employing the thermometer constant \( a \) determined in the calibration from 273.15 to 423.026 K. These two values of \( W(T_{90}) \) enabled the thermometer constants \( b \) and \( c \), of equation (9), to be found. The triple point of water resistance \( R(273.16 \text{ K}) \) and the thermometer constants \( a, b \) and \( c \) are given in table (6.2).

Table (6.2) Calibration constants for the Rosemount 162D capsule-type PRT

<table>
<thead>
<tr>
<th>( R(273.16 \text{ K})/\Omega )</th>
<th>25.51402</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^4a )</td>
<td>-2.0146</td>
</tr>
<tr>
<td>( 10^4b )</td>
<td>-2.0041</td>
</tr>
<tr>
<td>( 10^6c )</td>
<td>-8.84</td>
</tr>
</tbody>
</table>

As a check on the accuracy of the calibration procedure adopted, the capsule-type PRT and one of the NPL-calibrated long-stem PRTs (S/N 245064) were placed in hexane-filled glass tubes immersed in the thermostatted bath such that their sensing elements were about 1.5 cm apart. The thermometers were compared at six temperatures from 248.764 to 322.807 K, and the temperature differences \( \Delta T = T_{\text{capsule}} - T_{\text{long-stem}} \) are shown in table (6.3). The uncertainties are due to short-term fluctuations in the bath liquid temperature. The temperature differences were never larger than 2 mK, and even these were likely to have been due to transitory temperature gradients rather than errors arising from the calibration procedure. A further set of comparison measurements were taken at 373.1216 K using the water-filled comparative ebulliometers, and, as can be seen from table (6.3), the temperature difference was only 0.1 mK. In short, there was every indication that the calibration had been successful in allowing the measurement of true ITS-90 temperatures to within about 1 mK (and at worst 2 mK) over the calibration range.
Table 6.3 Differences $\Delta T = T_{\text{capsule}} - T_{\text{long-stem}}$ between temperatures on the Rosemount capsule-type PRT and an NPL-calibrated long-stem PRT

<table>
<thead>
<tr>
<th>$T_{\text{long-stem}}$/K</th>
<th>$\Delta T$/mK</th>
</tr>
</thead>
<tbody>
<tr>
<td>248.764</td>
<td>0 ± 3</td>
</tr>
<tr>
<td>253.619</td>
<td>-2 ± 2</td>
</tr>
<tr>
<td>258.621</td>
<td>0 ± 2</td>
</tr>
<tr>
<td>263.594</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>268.582</td>
<td>+2 ± 1</td>
</tr>
<tr>
<td>322.806</td>
<td>+2 ± 1</td>
</tr>
<tr>
<td>373.1215</td>
<td>+0.1 ± 0.1</td>
</tr>
</tbody>
</table>

The pressure of gas contained within the cylindrical resonator and its pressure vessel was measured using the pressure balance described in section (6.2) and, since it was only used for measurements on nitrogen, there was no need to separate it from the resonator using a differential pressure gauge as is normally the case when other sample gases are used (the pressure balance itself had been calibrated by the manufacturers using nitrogen).

Following assembly, the thermal and mechanical stability of the cylindrical resonator was investigated. The resonance frequencies $f_N$ and halfwidths $g_N$ of modes TM010, TM011 and TM110 were measured in the evacuated cylinder at nine equally-spaced temperatures in the range 243.284 to 323.002 K, first in the direction of increasing temperature and then in the direction of decreasing temperature. The measurements are presented in table (6.4).

The resonance frequencies of each mode, for the measurements in the direction of increasing temperature, were fitted to equations of the form

$$\ln\left[\frac{f_N(t)}{\text{MHz}}\right] = \ln b_0 + b_1 t + b_2 t^2 + \cdots$$

(6.3.10)

where $f_N(t)$ is the measured resonance frequency, of a given mode, at the Celsius temperature $t$. It was found, for each mode, that only the first three terms of equation (10) were significant at the 0.995 probability level, and the addition of a term in $t^3$ did
not significantly reduce the overall standard deviation of the fit for any mode. The values of the coefficients of equation (10), for each mode, are given in table (6.5), together with the standard deviations of the fits $\sigma(\ln f_N)$. The deviations, $10^6\Delta(\ln f) = 10^6\{[\ln (f_N/\text{MHz})]_{\text{meas}} - [\ln (f_N/\text{MHz})]_{\text{eqn. (6.3.10)}}\}$, of the measured values of $\ln[f_N(t)/\text{MHz}]$ from equation (10), using the appropriate coefficients from table (6.5), are shown in figure (6.5).

Although no values were available for the particular brass used for fabrication of the resonator, the estimates of the linear coefficient of thermal expansion, $(-b_t)$, were in good agreement with published values for brasses of similar composition [39, 131].

### Table (6.4) Resonance frequencies $f_N$ and halfwidths $g_N$ of the evacuated cylinder

#### Measurements in direction of increasing temperature (‘inc’ measurements)

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$t$/°C</th>
<th>$f_{010}$/MHz</th>
<th>$g_{010}$/MHz</th>
<th>$f_{011}$/MHz</th>
<th>$g_{011}$/MHz</th>
<th>$f_{110}$/MHz</th>
<th>$g_{110}$/MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.284</td>
<td>-29.866</td>
<td>12059.8466</td>
<td>1.3858</td>
<td>14206.4077</td>
<td>2.1579</td>
<td>19211.3196</td>
<td>2.1860</td>
</tr>
<tr>
<td>253.246</td>
<td>-19.904</td>
<td>12057.6011</td>
<td>1.3989</td>
<td>14203.7891</td>
<td>2.1684</td>
<td>19207.7466</td>
<td>2.2073</td>
</tr>
<tr>
<td>263.189</td>
<td>-9.961</td>
<td>12055.3365</td>
<td>1.4078</td>
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<td>2.1898</td>
<td>19204.1456</td>
<td>2.2309</td>
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<tr>
<td>273.170</td>
<td>0.020</td>
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<td>1.4214</td>
<td>14198.4685</td>
<td>2.2154</td>
<td>19200.5064</td>
<td>2.2723</td>
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<td>283.142</td>
<td>9.992</td>
<td>12050.7424</td>
<td>1.4275</td>
<td>14195.7666</td>
<td>2.2234</td>
<td>19196.8324</td>
<td>2.2958</td>
</tr>
<tr>
<td>293.096</td>
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<td>14193.0329</td>
<td>2.2432</td>
<td>19193.1171</td>
<td>2.3092</td>
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<td>303.063</td>
<td>29.913</td>
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<td>14190.2455</td>
<td>2.2642</td>
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<td>2.3297</td>
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<td>39.888</td>
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#### Measurements in direction of decreasing temperature (‘dec’ measurements)

<table>
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<tr>
<th>$T$/K</th>
<th>$t$/°C</th>
<th>$f_{010}$/MHz</th>
<th>$g_{010}$/MHz</th>
<th>$f_{011}$/MHz</th>
<th>$g_{011}$/MHz</th>
<th>$f_{110}$/MHz</th>
<th>$g_{110}$/MHz</th>
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Table (6.5) Coefficients of equation (6.3.10)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>TM010</th>
<th>TM011</th>
<th>TM110</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10^6 \sigma(\ln f_0))</td>
<td>0.40</td>
<td>0.57</td>
<td>0.95</td>
</tr>
<tr>
<td>(\ln b_0)</td>
<td>((9.39707281 \pm 0.00000019))</td>
<td>((9.56088920 \pm 0.00000027))</td>
<td>((9.86269189 \pm 0.00000044))</td>
</tr>
<tr>
<td>(10^4 b_1/\circ C^{-1})</td>
<td>((-19.1237 \pm 0.0067))</td>
<td>((-19.0370 \pm 0.0095))</td>
<td>((-19.164 \pm 0.016))</td>
</tr>
<tr>
<td>(10^2 b_2/\circ C^{-2})</td>
<td>((-8.71 \pm 0.23))</td>
<td>((-11.55 \pm 0.32))</td>
<td>((-12.52 \pm 0.54))</td>
</tr>
</tbody>
</table>

Figure (6.5) Deviations of \(\ln[f_0(t)/\text{MHz}]\) from equation (6.3.10).

Figure (6.6) Fractional differences between the resonance frequencies measured in the directions of decreasing and increasing temperatures.
In any case, the estimates presented here refer to a particular artifact (the resonator) operating in a particular mode, and so need not necessarily be reliable estimates of the linear expansivity of the material used for its fabrication.

The fractional differences $10^6 \left( \frac{\Delta f}{f} \right) = 10^6 \left( \frac{f_{\text{dec}}(t) - f_{\text{inc}}(t)}{f_{\text{inc}}(t)} \right)$, between the resonance frequencies in the directions of decreasing (dec) and increasing (inc) temperatures are shown in figure (6.6), where corrections of up to 0.5 ppm have been made to take account of the small temperature differences between the ‘dec’ and ‘inc’ measurements. The largest differences were only $-1.5$ ppm for the TM010 mode, $-1.8$ ppm for the TM011 mode, and $-4.2$ ppm for the TM110 mode, all at 20 °C, demonstrating the excellent stability shown by the resonator during the temperature cycle. Such small levels of hysteresis compare favourably with those shown by other high-stability resonant cavities [110] and capacitance cells [99], and even if the hysteresis had been larger, the accuracy of the dielectric constant measurements in this work would not have been compromised because isothermal measurements were always taken. The greater hysteresis found for the TM110 mode, compared with the other two modes, may have been due to small movements of the microwave cable ends during the temperature cycle: for a given movement of one, or both, antennae from their initial positions, it can be shown, using equation (4.7.28), that the TM110 mode resonance frequency would suffer a fractional shift 2.9 times larger than that of the TM010 mode and 6.9 times larger than that of the TM011 mode.

To assess the mechanical stability with respect to changes in pressure, the resonator was subjected to a number of pressure changes along an isotherm near 243 K. Initially, the vacuum resonance frequencies and halfwidths of modes TM010, TM011 and TM110 were measured, following which the system was pressurised to 4.015 MPa and allowed to stabilise for 1 h. The system pressure was then reduced to 3.001, 2.000, 1.200, 0.400, and 0.079 MPa, with a 1 h stabilisation period allowed after each pressure change; this sequence of pressure changes was chosen to be similar to that undergone during a full set of microwave measurements using the cylindrical resonator. Finally, the system was re-evacuated and allowed to settle before the vacuum resonance frequencies and halfwidths were re-measured. The measured fractional changes in the vacuum resonance frequencies and halfwidths are given in table (6.6).
Table (6.6) Fractional changes in the vacuum resonance frequencies and halfwidths of the cylinder at 243 K following the pressurisation cycle up to 4.015 MPa

<table>
<thead>
<tr>
<th></th>
<th>TM010</th>
<th>TM011</th>
<th>TM110</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6 (\Delta f / f)$</td>
<td>(-0.2 ± 0.2)</td>
<td>(+0.3 ± 0.3)</td>
<td>(+0.7 ± 0.2)</td>
</tr>
<tr>
<td>$10^2 (\Delta g / g)$</td>
<td>(-0.6 ± 0.3)</td>
<td>(-0.3 ± 0.3)</td>
<td>(-0.3 ± 0.3)</td>
</tr>
</tbody>
</table>

It was only for the TM110 mode that any significant change in the vacuum resonance frequency was detected, and even this change was very small indeed by normal standards. Similarly, the change in resonance halfwidth was only significant for the TM010 mode, and barely significant at that.

Such mechanical stability came from the pressure-compensated design where, in operation, the same gas pressure was exerted on the inner and outer walls of the resonator. The level of mechanical hysteresis shown by the pressure-compensated brass cylinder (on the order of 0.5 ppm in the resonance frequencies and, therefore, the cavity dimensions) was almost two orders of magnitude smaller than that shown by an uncompensated brass re-entrant resonator recently used to make accurate dielectric constant measurements on argon at pressures up to only 300 kPa [110], and was still at least one order of magnitude smaller than that shown by a pressure-compensated capacitance cell used to measure the dielectric constant of hydrogen at pressures up to 10.554 MPa [99]. The hysteresis shown by the stainless-steel pressure vessel was, no doubt, considerably larger than 0.5 ppm (perhaps even two orders of magnitude larger), but this was of no consequence since the behaviour of the pressure vessel had no effect on the resonance frequencies and halfwidths measured, and, with the very small dimensions of the resonator, the whole apparatus was still small enough to allow simple methods of temperature control such as the electrically-thermostatted bath used.
6.4 Microwave electronics

A schematic of the microwave electronics used to measure the resonance frequencies and halfwidths for the spherical and cylindrical resonators is shown in figure (6.7). The measurements were computer-controlled over an IEEE standard 488 interface. For the measurements on the spherical resonator, the microwave frequency signal from a Hewlett Packard (HP) 8671B continuous wave (CW) generator, which could provide an internally-levelled output from −120 to +13 dBm over its frequency range of 2.0 to 18.0 GHz, was passed through a pulse (amplitude) modulator (HP11720A) controlled at 1025 Hz by a separate CW synthesiser (HP3320A, +13 dBm output). For the measurements on the cylindrical resonator, a Hewlett Packard 8673B CW generator, which could provide an internally-levelled output from −100 to +13 dBm over its larger frequency range of 2.0 to 26.0 GHz, was used to generate the microwave signal, and since this synthesiser was capable of its own pulse modulation (once provided with the 1025 Hz reference), the separate HP11720A pulse modulator was not used. For both microwave synthesisers, the output signals were achieved by the multiplication of a fundamental 2.0 to 6.6 GHz, with a 1 kHz resolution, by a factor of 1, 2, 3 or 4 (2.0 to 26.0 GHz synthesiser only), giving a fractional frequency resolution of 0.15 to 0.50 ppm, whilst the frequency stability of both synthesisers was guaranteed by the manufacturers to be better than ±0.01 ppm over 24 h continuous operation; this stability was more than sufficient for our measurements which never lasted more than 12 h.

The microwave signal, pulsed at 1025 Hz, was transmitted through the resonant cavity and detected at the diode (HP8472B, low-level sensitivity > 0.4 mV μW⁻¹), the output potential of which (< 100 μV) was amplified at the lock-in amplifier (Scitec Instruments 500Mc) and measured at the digital voltmeter (Keithley 192 Programmable); the measured potential was assumed proportional to the power transmitted through the cavity. The reference signal for the lock-in amplifier was supplied by the HP3320A synthesiser which controlled the pulse modulation of the microwave signal. It was found that the power transmitted through the resonators varied from mode to mode, and so the microwave synthesiser output and the sensitivity scale of the lock-in amplifier were adjusted so that the maximum potential measured at the diode, for a given resonant mode, was within 20% of the full-scale.
Figure (6.7) Schematic of microwave electronics

- **Cylindrical or spherical resonator**
- **Diode**
- **Pulse modulator**
- **Schmitt trigger output**
- **Lock-in amplifier output**
- **TTL output**
- **±1V square wave output**
- **CW microwave synthesiser**
  - 2.0 - 18.0 GHz
  - 2.0 - 26.0 GHz
- **1025 Hz synthesiser**
- **Digital voltmeter**
- **IEEE standard 488 interface**
- **Personal computer**

The diagram illustrates the connections and components involved in microwave electronics, including the use of pulse modulators, Schmitt triggers, lock-in amplifiers, and synthesisers, as well as the interaction with digital voltmeters and IEEE 488 interfaces.
deflection at the lock-in for the chosen sensitivity scale. Typical synthesiser output and lock-in sensitivity settings used for measurements of the modes of the sphere and cylinder are given in tables (6.7) and (6.8), respectively. The time constant (signal averaging time) of the lock-in was always set to 0.1 s, and a delay time of 0.4 s (four time constants) was allowed before each measurement of transmitted power was recorded during the sweeping of all the resonances of the sphere and the cylinder.

| Table (6.7) Typical synthesiser output and lock-in amplifier sensitivity settings for the modes of the sphere |
|---|---|---|---|---|---|
|  | TM11 | TM12 | TM13 | TM21 | TM31 |
| Output power/dBm | -5 | 7 | 7 | -7 | -8 |
| Sensitivity/mV | 0.1 | 0.03 | 0.03 | 0.1 | 0.1 |

| Table (6.8) Typical synthesiser output and lock-in amplifier sensitivity settings for the modes of the cylinder |
|---|---|---|
|  | TM010 | TM011 | TM110 |
| Output power/dBm | -10 | -10 | -20 |
| Sensitivity/mV | 0.1 | 0.1 | 0.1 |

6.5 Experimental procedures

Refer to figure (6.8) during the following description.

The spherical resonator

Essentially the same procedure was used for all isotherms in the spherical resonator. In the preliminary stages, the resonator and external pipework were evacuated by the oil diffusion pump until the pressure indicated by the Penning gauge had been below 1 mPa for at least 24 h. The potential divider was set to attain the desired temperature at the control block, with liquid nitrogen or dry ice being used, as required, to reduce the temperature below ambient. The resonator and pipework
were thoroughly flushed with the sample gas before being re-evacuated to a pressure not exceeding 10 mPa. The Baratron zero was set and the system was then filled with the sample gas to the initial maximum pressure $P_{\text{max}}$. For the measurements on argon and xenon, $P_{\text{max}}$ was the largest pressure achievable using the available gas cylinder (about 750 kPa for argon and 540 kPa for xenon), except for the xenon isotherm near 189 K, where $P_{\text{max}}$ was restricted to about 300 kPa to avoid condensation within the resonator. The maximum pressure for the measurements on nitrogen and the mixture $\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}$ was chosen to be approximately the same as that used for the argon isotherms. After filling with sample gas, the apparatus was left overnight to reach thermal and hydrostatic equilibrium.

Measurements were taken for the five modes TM11, TM12, TM13, TM21 and TM31, always in that order; modes TM11, TM12 and TM13 were the three lowest frequency triply-degenerate TM modes (the lowest order of degeneracy for modes of the sphere), and TM21 and TM31 were the lowest frequency TM modes with five-fold and seven-fold degeneracies, respectively. For each mode, the quarter-power-point frequency range (the frequency range over which the power transmitted through the cavity was greater than, or equal to, one quarter of the maximum
transmitted power for that resonance) was found by manual adjustment of the microwave synthesiser, with the sensitivity scale of the lock-in amplifier and output power of the synthesiser being set as described in section (6.4). The initial temperature and pressure were recorded immediately before the microwave measurements began.

Under computer control, the power transmitted through the sphere was measured at 31 discrete, equally-spaced frequencies over the quarter-power-point range of a resonance, with a delay of 0.4 s (four time constants) allowed after each frequency change for equilibrium to be established. The sweep was then reversed and the transmitted power was re-measured at each frequency. The powers measured at each frequency were averaged to take account of any small changes in conditions (e.g., temperature drift) during the scan. The average of the squared differences between the up and down-sweep powers at each frequency was used as an estimate of the variance of the data for the reduced chi-squared statistic employed in the analysis of each resonance [see section (6.7)]. Once measurements for all five modes had been completed, the final temperature and pressure were immediately taken and the averages of the initial and final values were assigned to the set of microwave measurements; if the temperature or pressure had changed significantly during the measurements then all five modes were scanned again.

The gas pressure was reduced by about \( p_{\text{max}}/10 \) and the sphere was electrically heated, if required, to help recover the initial temperature - the expansion of sample gas into the vacuum line, used to reduce the pressure, took place almost adiabatically. The apparatus was left for about 25 min, in order that equilibrium could be established (the resonance frequencies were usually within about 1 ppm of their final, equilibrium values after only 5 mins), and then microwave measurements were taken again. This procedure was repeated until measurements had been made at, usually, 10 pressures, from \( p_{\text{max}} \) to \( p_{\text{max}}/10 \).

A set of measurements was also taken at a pressure of about \( p_{\text{max}}/20 \) for all isotherms, and at pressures of about \( p_{\text{max}}/40 \) and \( p_{\text{max}}/80 \) for the xenon isotherms at 273 and 300 K, to more thoroughly investigate the behaviour at low pressures. Finally, the resonator and external pipework were evacuated to a pressure not exceeding 10 mPa and the last of the microwave measurements were taken. The
final Baratron output potential was noted, during the vacuum measurements, to ascertain whether there had been any drift in its zero setting over the course of the isotherm.

**The cylindrical resonator**

The procedure for the isothermal measurements in the cylinder was very similar to that followed for the sphere and so only a brief account is given here.

Following the initial evacuation of the cylinder and external pipework to 1 mPa, the thermostatted bath was set to control at the desired temperature; the system was then thoroughly flushed with nitrogen and re-evacuated to 10 mPa. The resonator and pipework were filled to the maximum pressure $p_{\text{max}}$, which was about 4.015 MPa for all of the isotherms, and then the apparatus was left overnight to attain equilibrium.

Measurements were taken for the three modes TM010, TM011 and TM110, always in that order; modes TM010 and TM011 were the two lowest frequency non-degenerate TM modes and TM110 was the lowest frequency doubly-degenerate TM mode. The resonances were swept exactly as described for the sphere measurements, with a lock-in time constant of 0.1 s and delay times of 0.4 s (four time constants) being allowed for all three modes. The initial and final temperatures and pressures were recorded and averaged as before.

The gas pressure was determined using the pressure balance which was floated whilst the resonances were scanned. Microwave measurements were usually taken at pressures near 4.015, 3.504, 3.001, 2.501, 2.000, 1.500, 1.200, 0.800, 0.400, 0.200 and 0.079 MPa, and under vacuum ($p \leq 10$ mPa), with a 30 min period being allowed for the system to return to equilibrium following each pressure reduction (the resonance frequencies were usually within 1 ppm of their final, equilibrium values after 7 mins).
6.6 Materials

All the gas samples were supplied by B.O.C. Gases Ltd. and were used without further purification.

The 'zero-grade' argon and nitrogen, previously used for speed of sound measurements [35], from 80 to 373 K, in the same spherical cavity adapted for speed of light measurements in this work, were of a certified minimum 0.99998 purity. Data provided by the suppliers indicated that the gases each contained less than 3 ppm of oxygen, less than 2 ppm of water, and less than 1 ppm of each of carbon monoxide, carbon dioxide, hydrogen and hydrocarbons; the 'zero-grade' argon also contained up to 6 ppm of nitrogen. It is estimated that the stated impurities would alter the refractive index of argon, at 215 K and 724 kPa, by less than 0.1 ppm, and that of nitrogen, at 243 K and 4.015 MPa, by less than 0.3 ppm.

The argon and nitrogen gas mixture was prepared by the suppliers, from pure components of the same 'zero-grade' specification, to a nominal composition of \{0.5 \text{Ar} + 0.5 \text{N}_2\}. The mole fraction of nitrogen was accurately determined to be \((0.50178 \pm 0.00006)\), from measurements of the speed of sound in the mixture, at temperatures from 90 to 373 K, using the same spherical cavity used in this work [83].

The 'research-grade' xenon had a certified minimum purity of 0.99995. The suppliers stated that the gas contained up to 40 ppm of krypton, less than 5 ppm of nitrogen, and less than 1 ppm of each of argon, oxygen, hydrogen, water, carbon dioxide and hydrocarbons, all of which impurities would alter the refractive index of xenon, at 189 K and 294 kPa, by less than 0.1 ppm.

6.7 Resonance analysis

As described in section (6.5), the resonance frequencies and halfwidths of the modes of the spherical and cylindrical resonators were determined by measuring the transmitted power over the quarter-power-point frequency range of the resonances. The power \(P\) transmitted through the spherical or cylindrical resonator was assumed to be proportional to the potential measured at the diode, and was, therefore, fitted to the theoretically-predicted function [24, 132]
\[ P(f) = \left| \sum_{N} \left( \frac{A_N}{g_N + i(f - f_N)} \right) + B + Cf \right|^2 \]  

(6.7.1)

using non-linear least-squares regression, where \( f \) is the microwave drive frequency and \( f_N, g_N \) and \( A_N \) are the resonance frequency, halfwidth and complex amplitude, respectively, of a component, denoted by the subscript \( N = lnm \) for a sphere mode and \( N = pq\) for a cylinder mode. The expression in parentheses \{\ldots\} is a Lorentzian function, and \( B \) and \( Cf \) are the first two terms of a complex Taylor series used to take account of any background which may include the 'tails' of other, nearby resonances, and the effects of electronic cross-talk.

**The modes of the spherical resonator**

In principle, the sum in equation (1) should run over all \((2l + 1)\) components of a mode but some components may overlap (geometric deformations of the cavity were small and, it would seem, approximately axisymmetric) or they might be weakly excited or detected because of the positions of the microwave probes. In any case, even for the TM1\(n\) modes, with only 3 components, the number of adjustable parameters in equation (1) could be as large as 15 if the sum ran over all components. Of the five modes measured, it was only for the three-component TM1\(n\) modes that there was a real possibility of satisfactorily resolving the components and, consequently, obtaining reliable estimates of the component halfwidths \(g_N\). The observed values of quality factor for individual components, 

\[ Q_N = f_N / (2g_N) \]

varied from about 14000 for TM11 at 360 K to 37400 for TM13 at 189 K. It is difficult to maintain, with confidence, that individual components of the TM21 and TM31 modes were properly resolved, but, if we were, indeed, successful in doing so, then it appears that the quality factors of individual components varied from about 10500 at 360 K to 14250 at 189 K for TM31, and from about 18250 at 360 K to 22600 at 189 K for TM21.

Superficially, the resonances of the sphere appeared to consist of either one component ('singlets') or a pair of components ('doublets'), as can be seen in figure (6.9) where the responses of the evacuated sphere near 189 and 360 K are shown; the measurements were taken at the end of the respective isotherms in xenon. The
appearance of the responses was very similar in the evacuated and the gas-filled cavity at each temperature, and was reasonably consistent with an approximately axisymmetric deformation of the spherical resonator [see section (4.6)]. Therefore, modes TM12 and TM13, which ought to consist of three components, were always analysed as singlets, whilst modes TM11, TM21 and TM31, which ought to consist of three, five and seven components, respectively, were always analysed as doublets. This approach invariably led to convergent and stable fits of the transmitted powers to equation (1), which was never found to be the case when triplet fits were used; higher orders of fit, for modes TM21 and TM31, were never attempted. The number of parameters in the singlet and doublet fits was chosen on the basis of whether there was a statistically-significant reduction, at the 0.995 probability level, in the overall standard deviation of the fit, and a similar reduction in the reduced chi-squared statistic $\chi^2$, on addition of extra (background) parameters. In the context of this work, $\chi^2$ was defined as

$$\chi^2 = \frac{1}{\langle (\Delta P)^2 \rangle} \sum_{i=1}^{M} \frac{[P_i^{\text{exp}}(f) - P_i^{\text{calc}}(f)]^2}{M - n}$$  \hspace{1cm} (6.7.2)$$

where $[P_i^{\text{exp}}(f) - P_i^{\text{calc}}(f)]$ was the difference between the measured power and the power calculated using equation (1) at drive frequency $f$, $M$ was the number of data points (always 31 in this work), $n$ was the number of parameters in the fit, and $\langle (\Delta P)^2 \rangle$ was the average squared difference between the up and down-sweep powers at each point, which was used as an estimate of the variance of the data [see section (6.4)]. With an appropriate number of parameters, it was usually possible to fit equation (1) to the data for any of the five modes with $\chi^2$ less than unity (the ideal value). That $\chi^2$ was generally much smaller than unity implies that the estimated variance $\langle (\Delta P)^2 \rangle$ provided a rather pessimistic account of the collected data. It was also necessary for any extra parameters to be significantly different from zero for their inclusion in the fit, and this was assessed by comparing the magnitude of the ratio $(Z/\sigma_Z)$, where $Z$ is a parameter value and $\sigma_Z$ is its standard deviation, with the tabulated value of the Student t-statistic at the 0.995 probability level.
Figure (6.9) Measured responses of the evacuated sphere at 188.5533 and 360.2599K
The singlet fits, for modes TM12 and TM13, could contain three, five or seven (adjustable) parameters: $|A_N|$, $f_N$ and $g_N$ for the three-parameter fits without background, $|A_N|$, $f_N$, $g_N$, $|B|$ and $\text{arg}(B)$ for the five-parameter fits with a constant background, and $|A_N|$, $f_N$, $g_N$, $|B|$, $\text{arg}(B)$, $|C|$ and $\text{arg}(C)$ for the seven-parameter fits with a combination of constant and frequency-dependent background. For all the TM13 mode measurements taken in this work, the five parameters $|A_N|$, $f_N$, $g_N$, $|B|$ and $\text{arg}(B)$ were always required to satisfactorily accommodate the data, but the extra background terms $|C|$ and $\text{arg}(C)$ were rarely deemed to be significant. To promote consistency along individual isotherms and between the measurements at different temperatures, the five-parameter fits were always used. With five adjustable parameters, equation (1) could be generally made to fit TM13 mode data with a fractional standard deviation $[\sigma(P)/P_{\text{max}}]$ of about 0.5 %, where $\sigma(P)$ was the standard deviation of the power obtained in the regression with equation (1) and $P_{\text{max}}$ was the maximum transmitted power. As will be seen in
chapter 7, it seems that only one of the three TM13 mode components was predominant in the experimental responses, with the remaining two (weaker) components at higher frequency than the quarter-power-point range over which measurements were taken. This accounts for the success of the singlet fits, with the low-frequency 'tail' of the weaker components being accounted for by the background terms. By analogy with calculations given in reference 132, an estimate of the fractional random uncertainty in the halfwidth of a component is given by \[ \frac{\sigma(g_N)}{g_N} = 2\frac{\sigma(P)}{P_{\text{max}}}, \] and an estimate of the fractional random uncertainty in the resonance frequency of a component is given by \[ \frac{\sigma(f_N)}{f_N} = \frac{\sigma(g_N)}{f_N} = \frac{\sigma(P)}{P_{\text{max}}}/Q_N. \] With quality factors of between about 30300 at 360 K and 37400 at 189 K, \[ \frac{\sigma(f_N)}{f_N} \] was generally less than 0.2 ppm for the TM13 mode. Such estimates of \[ \frac{\sigma(g_N)}{g_N} \] and \[ \frac{\sigma(f_N)}{f_N} \] were always at least as large as the fractional standard deviations of repeated measurements of \( g_N \) and \( f_N \), for any mode of the sphere or cylinder, whilst the temperature and pressure were kept constant.

For the TM12 mode, the number of significant parameters was generally more ambiguous. For the measurements on nitrogen, xenon and the mixture \( \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} \) at 300 K and argon at 215, 260 and 300 K, the full seven parameters \( A_N, f_N, g_N, |B|, \text{arg}(B), |C| \) and \( \text{arg}(C) \) were deemed to be significant, whereas for the remaining measurements on xenon at temperatures from 189 to 360 K, only five parameters were required, although there was often some ambiguity in choosing between the five and seven-parameter fits. The reason for such changes in the order of fit is not entirely clear, but it was necessary to renew the indium seal on one of the microwave probe mounts, before the measurements on xenon between 189 and 360 K (apart from that at 300 K) could be taken, and its replacement presumably gave rise to a subtly different background, rendering the inclusion of the \( |C| \) and \( \text{arg}(C) \) parameters unnecessary. In any case, provided the same order of fit was used for all points along an isotherm, the differences between the estimates of refractive index obtained from the five and seven-parameter fits was generally less than 1 ppm. Using five or seven adjustable parameters, as appropriate, it was generally possible to fit equation (1) to the TM12 data with a fractional standard deviation \[ \frac{\sigma(P)}{P_{\text{max}}} \] of between 0.5 and 2.0 \%. As will be further discussed in chapter 7, it appears that the experimental responses for mode TM12
consisted of a poorly-resolved superposition of all three components, with $|A_N|$, $f_N$ and $g_N$ being relied upon to fit the strongest component, or a combination of strong components, and the background terms accommodating the remaining (weaker) component(s). If the observed halfwidths are regarded as estimates of single component halfwidths, then the quality factor of mode TM12 varied between about 24700 at 360 K to about 28000 at 189 K, giving estimated fractional precisions in the resonance frequency of between 0.2 and 0.8 ppm.

The number of statistically-significant terms for the doublet fits, for modes TM11, TM21 and TM31, was never ambiguous. For the TM21 and TM31 modes, only six adjustable parameters in equation (1) were ever required to accommodate the data: the component resonance frequencies ($f_c - x$) and ($f_c + x$) [where $f_c$ was the mean resonance frequency of the two components and $x$ was half the frequency difference between them], the halfwidths $g_{\text{low}}$ and $g_{\text{high}}$ of the components at the lower and higher frequency, respectively, and the two amplitudes $|A_{\text{low}}|$ and $|A_{\text{high}}|$; the phase difference between the two components was fixed at $\pi$. There was never a significant reduction in the overall standard deviation of the fit, or the $\chi^2$, on addition of background terms. It was generally found possible to fit equation (1) to TM21 and TM31 data with $[\sigma(P)/P_{\text{max}}]$ of about 1.5 % and 0.6 %, respectively, giving an estimated fractional precision in the resonance frequencies for both modes usually better than 0.7 ppm. For the TM11 mode, the additional background parameters $|B|$ and $\text{arg}(B)$ were also required to achieve the best fits, and it was usually found that equation (1) could accommodate the data with a fractional standard deviation of less than 0.15 %. With measured quality factors between about 14000 at 360 K and 19100 at 189 K, the TM11 resonance frequencies could generally be determined with an estimated fractional precision of better than 0.1 ppm.

As will be shown in chapter 7, the halfwidth analysis for the TM11 measurements strongly suggests that the stronger, higher-frequency 'peak' in each experimental response comprises a single component of the mode, whilst the lower-frequency peak (or shoulder) contains (the remaining) two closely-spaced components, overlapping in phase. This assignment of TM11 mode components is consistent with an axisymmetric deformation of the sphere, such that the polar diameter is larger than the equatorial diameter if the orientations of the
electromagnetic fields of the components are reasonably consistent with the theory of the unperturbed cavity [see section (4.6)].

It was, of course, more difficult to assign the larger number of components of the TM21 and TM31 modes to the two peaks in the experimental responses. An axisymmetric deformation of the sphere of the magnitude suggested by the TM11 measurements is expected to give rise to three peaks in the experimental responses for mode TM21, and four peaks for mode TM31, with the highest frequency peak consisting of a single component if the polar diameter was larger than the equatorial diameter [refer to section (4.6)]. The observation of only two peaks in the TM21 and TM31 resonances was, presumably, the result of overlap of the components and/or the weak excitation and detection of one, or more, components.

The modes of the cylindrical resonator

The responses of modes TM010, TM011 and TM110, for the evacuated cylinder at temperatures near 243 K and 323 K, are shown in figure (6.10); the measurements were taken at the end of the respective isotherms in nitrogen. The profiles of the resonances are typical of all those measured between 243 and 323 K, whether in the evacuated or gas-filled cavity. The responses for all three modes seemed to consist of only one component, which was as expected for the non-degenerate TM010 and TM011 modes, and could be readily explained for the two-component TM110 mode by reasoning that the components must have been nearly degenerate and that the halfwidths of the individual components were sufficiently large that they could not be resolved. The resonances of all three cylinder modes were treated as singlets, with only the five parameters $|A_N|$, $f_N$, $g_N$, $B$ and $\arg(B)$ of equation (1) generally deemed to be significant. On occasion, there was some ambiguity in choosing between the five and seven-parameter fits. However, this posed little problem since the fractional difference between the resonance frequencies obtained from the two fits was never larger than 0.2 ppm, for any of the modes, in such circumstances. Further, provided the same order of fit was used, for a given mode, at all gas pressures along an isotherm, the fractional differences between the estimates of refractive index determined from the five and seven-parameter fits were, generally,
Figure (6.10) Measured responses of the evacuated cylinder at 243.334 and 323.072K.
even smaller than 0.2 ppm, since the resonance frequencies from the seven-parameter fits were either all systematically larger, or all systematically smaller, than those from the five-parameter fits. Therefore, the simpler five-parameter fits were used in every case, giving typical fractional standard deviations $[\sigma(P)/P_{\max}]$ of only 0.15 % for modes TM010 and TM011, and 0.2 % for mode TM110. Such small standard deviations for the five-parameter fits compare very well with those of the eight-parameter fits to TM11 data in the sphere, demonstrating the benefit of the high symmetry of the responses of the non-degenerate and doubly-degenerate cylinder modes [see figure (6.10)]. The single-component cylinder TM01s modes offered another real advantage over the multi-component sphere modes, since it was possible to obtain unambiguous estimates of single component halfwidths. As will be seen in chapter 8, the halfwidths $g_N$, and therefore the quality factors $Q_N = f_N/(2g_N)$, of the cylinder modes varied somewhat for different assemblies of the resonator (it was occasionally necessary to open the resonator, between isotherms, to replace the microwave cables). The highest quality factors observed in gas measurements were those determined along the nitrogen isotherms at 283 and 303 K, with $Q_{010} \approx 4100$, $Q_{011} \approx 3100$ and $Q_{110} \approx 4800$ (assuming the observed $g_{110}$ was approximately that of a single component). In general, however, $Q_{010}$ varied from about 3600 at 323 K to 3800 at 243 K, $Q_{011}$ varied from about 2650 at 323 K to 2800 at 243 K, and $Q_{110}$ varied from about 3500 at 323 K to about 3600 at 243 K. Therefore, the resonance frequencies could generally be determined with an estimated fractional precision of better than 0.4 ppm for mode TM010, and better than 0.6 ppm for modes TM011 and TM110.

Higher quality factors than those reported in this section were observed for the evacuated cylinder, during the temperature-cycle measurements presented in table (6.4): $Q_{010}$ varied from about 4350 at 243 K to about 4100 at 323 K, $Q_{011}$ varied from about 3300 at 243 K to about 3100 at 323 K, and $Q_{110}$ varied from about 4400 at 243 K to about 4100 at 323 K. These were the highest quality factors ever observed for the cylinder, being about 75 % of the theoretical quality factor for the TM010 mode, about 68 % of the theoretical quality factor for the TM011 mode, but only about 59 % of the theoretical quality factor for the TM110 mode because the
measured halfwidth $g_{110}$ was, presumably, that of a poorly-resolved doublet and, therefore, larger than that of a single, fully-resolved TM110 component.
Chapter 7 Measurements Using the Spherical Resonator

7.1 Introduction

This chapter contains the measurements taken using the 40 mm radius spherical resonator. The isothermal \((\varepsilon, p)\) measurements taken for argon at four temperatures between 215 and 300 K, and for nitrogen and the binary mixture \(0.5 \text{Ar} + 0.5 \text{N}_2\) at 300 K, are reported in section (7.2). The isothermal \((\varepsilon, p)\) measurements for xenon at eight temperatures between 189 and 360 K are described in section (7.3).

The dielectric constant measurements had an estimated random uncertainty better than ±0.3 ppm for the TM11 mode and better than ±2.3 ppm for all of the five modes measured. The measurements were fitted to three different series derived from the Clausius-Mossotti virial expansion of Buckingham and Pople [85] to determine estimates of the first and second (only for xenon) dielectric virial coefficients \(A_\varepsilon\) and \(B_\varepsilon\), and the second and third (xenon only) \((p, V_m, T)\) virial coefficients \(B\) and \(C\).

The first dielectric virial coefficient of argon was independent of temperature between 215 and 300 K, and was estimated to be \((4.14293 ± 0.00052) \text{ cm}^3 \text{ mol}^{-1}\), which was in good agreement with values in the literature and had a smaller uncertainty than the most recent and precise of the published work [133]. Our \(A_\varepsilon(215 \text{ K})\) was at a temperature 27 K lower than that of any other reported \(A_\varepsilon\) measurement for argon. The estimated second \((p, V_m, T)\) virial coefficients for argon were also in good agreement with published results, although our uncertainties were higher than those of the most recent measurements in the literature. Our results for \(B\) were \((-40.72 ± 0.56) \text{ cm}^3 \text{ mol}^{-1}\) at 215 K, \((-23.77 ± 0.66) \text{ cm}^3 \text{ mol}^{-1}\) at 260 K, and \((-15.61 ± 0.81) \text{ cm}^3 \text{ mol}^{-1}\) at 300 K, where the highest temperature result is a mean of the two values determined near 300 K. The quoted uncertainties in \(B\) were derived from the standard deviations and the estimated truncation errors.

Our \(A_\varepsilon(300 \text{ K})\) for nitrogen \([(4.39198 ± 0.00034) \text{ cm}^3 \text{ mol}^{-1}]\) was in excellent agreement with the measurement taken using the cylindrical resonator in this work.
[see chapter 8], and was in good agreement with a published value at 298.15 K [134] \((A_e\) for nitrogen is not independent of temperature). The estimated second \((p, V_m, T)\) virial coefficient \([-4.48 \pm 0.55] \text{ cm}^3 \text{ mol}^{-1}\) was in excellent agreement with recently reported, very precise values [35, 135]. The \(A_e(300 \text{ K})\) for the mixture \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\), found to be \(4.26597 \pm 0.00087 \text{ cm}^3 \text{ mol}^{-1}\), was in good agreement with a value calculated from the pure component first dielectric virial coefficients, and the estimated \((p, V_m, T)\) virial coefficient \([-11.7 \pm 2.3] \text{ cm}^3 \text{ mol}^{-1}\) was in satisfactory agreement with the published results of speed of sound measurements on the same gas mixture [83].

The first dielectric virial coefficient of xenon was independent of temperature between 189 and 360 K, and was found to be \((10.1305 \pm 0.0028) \text{ cm}^3 \text{ mol}^{-1}\), which was only 0.084\% higher than the only other reported value [94]. The second dielectric virial coefficients, which were determined with standard deviations of 3.5 to 8.7 \text{ cm}^3 \text{ mol}^{-1}\, were found to have a similar temperature-dependence to the theoretical values calculated using the simple dipole-induced dipole model, but were about 20 \text{ cm}^6 \text{ mol}^{-2}\ systematically higher. The very limited number of published measurements of \(B_e\) for xenon between 189 and 360 K were 6 to 12 \text{ cm}^6 \text{ mol}^{-2}\ lower than our results, but such differences were not very large in terms of their uncertainties. The estimated second \((p, V_m, T)\) virial coefficients of xenon between 189 and 360 K determined in this work were accurately described by

\[
B_{\text{est}}(T)/\text{cm}^3\cdot\text{mol}^{-1} = 242.7 - 190.1 \exp(200.08/T) \tag{7.1.1}
\]

where the total uncertainty on a value of \(B_{\text{est}}\) determined from the equation was about \(\pm 3 \text{ cm}^3 \text{ mol}^{-1}\). This equation was in very good agreement with the most reliable published measurements, even at temperatures far higher than the maximum experimental temperature of 360 K.
7.2 Argon, nitrogen and the mixture \{0.5 \text{ Ar} + 0.5 \text{ N}_2\}

Measurements are reported for argon at four temperatures between 215 and 300 K and for nitrogen and the mixture \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} at 300 K.

**Excess halfwidths and splitting parameters**

The excess halfwidths $\Delta g$ were determined, at each state point, by subtracting the calculated skin-depth perturbation contributions $g_\delta$ obtained from equation (4.5.11), from the corresponding measured halfwidths $g$. The fractional excess halfwidths $10^4 \left( \frac{\Delta g}{f} \right) = 10^4 \left( \frac{\{g - g_\delta\}}{f} \right)$, where the $f$ are the corresponding measured resonance frequencies, are presented graphically in figures (7.1) to (7.6), for all the modes measured along each isotherm: mode TM21 was not measured for the argon isotherm at 260 K, and mode TM31 was not measured for the argon isotherms at 215 and 260 K. As described in section (4.5), $g_\delta$ is the estimated contribution to a single component halfwidth due to energy dissipation in the imperfectly-conducting resonator wall, so if there were no other sources of energy loss and all components had been fully resolved then one should expect all $(\Delta g/f)$ to be zero.

The observed $(\Delta g/f)$ values for the high-frequency peak of the TM11 mode ('TM11 high') were almost invariably less than 3 ppm, compared to about 11 to 19 ppm for the low-frequency peak ('TM11 low'), and were not systematically dependent on pressure along the individual isotherms. This is consistent with the high-frequency peak being a single component of the mode. Given this assignment, the excess halfwidths of the high-frequency TM11 components can be ascribed to energy losses not accounted for by $g_\delta$ which may include losses in the resistive parts of the source and load impedances within the microwave circuit, as described in section (4.8), direct antenna-antenna coupling, and losses in the annular PTFE insulators surrounding the probe antennae. It appeared that $(\Delta g/f)$ for the high-frequency component was slightly dependent on temperature [the mean $(\Delta g/f)$ values for the argon isotherms at 215, 260 and 299.9728 K were (1.36±0.25), (2.64±0.05) and (2.69±0.25) ppm, respectively], indicating that the additional energy losses were temperature-dependent. The mean $(\Delta g/f)$ of the high-frequency component for the argon isotherm at 299.9654 K was only (1.73±0.14) ppm, but this isotherm was taken following replacement of the indium seal around one of the microwave probe
Figure (7.1) $10^6(\Delta g/f)$ for argon at 214.9658 K

Figure (7.2) $10^6(\Delta g/f)$ for argon at 259.9583 K
Figure (7.3) $10^6(\Delta g/f)$ for argon at 299.9654 K

Figure (7.4) $10^6(\Delta g/f)$ for argon at 299.9728 K
Figure (7.5) $10^6(\Delta g/f)$ for nitrogen at 299.9819 K

Figure (7.6) $10^6(\Delta g/f)$ for the mixture $\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}$ at 299.9887 K
mounts, and it is expected that the subtly different position of the microwave probe would give rise to different \((\Delta g/f)\) values. As was expected for the non-polar gases used in this work, the \((\Delta g/f)\) values for this component did not appear to depend on the identity of the gas sample: the mean \((\Delta g/f)\) values for the argon isotherm at 299.9728 K, the nitrogen isotherm at 300 K, and the \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\) isotherm at 300 K, were \((2.69\pm0.25), (2.64\pm0.22)\) and \((2.71\pm0.41)\) ppm, respectively.

If it is assumed that the high-frequency peak of each TM11 resonance corresponded to a singlet then, if all three components of the mode were present, the low-frequency peak was made up of the remaining two components, closely spaced and overlapping in phase since \((\Delta g/f)\) for this peak was generally about seven times larger than that of the assumed singlet. This assignment of components was further supported by the greater scatter in the \((\Delta g/f)\) values for the low-frequency peak, for an individual isotherm, compared to that observed for the high-frequency peak: the standard deviation of \((\Delta g/f)\) values for the low-frequency peak was typically 10 times larger than that for the high-frequency peak, for a given isotherm. Such scatter was presumably the result of variations in the overlap or relative intensities of the components within the low-frequency doublet as the pressure was changed.

As will be seen later, in the final analysis for the TM11 mode we used the estimated single component resonance frequencies (the high-frequency peak resonance frequencies) to obtain the values of dielectric constant. Although our assumption of high-frequency singlet and low-frequency doublet would appear to be justified, it was possible that the low-frequency peak was the singlet, with the high-frequency peak consisting of the remaining two components overlapping out of phase to give rise to a halfwidth smaller than that of the singlet. However, even if we had used the low-frequency peak resonance frequencies then, in general, the estimates of refractive index derived from the TM11 measurements in this work would have changed by less than 2 ppm.

The \((\Delta g/f)\) values for the TM12 mode were generally less than 5 ppm, apart from those along the argon isotherm at 299.9654 K which varied reasonably smoothly from about 8 ppm at low pressures to about 4 ppm at high pressures. Such small fractional excess halfwidths may suggest that the measured resonances consisted of fully-resolved single components, with the excess halfwidths accounted for by
energy losses other than those represented by \( g_{\phi} \). However, although the fractional excess halfwidths along the argon isotherms at 215, 260 and 299.9728 K and the nitrogen and \{0.5 Ar + 0.5 N\_2\} isotherms at 300 K showed little, if any, systematic pressure-dependence (in accordance with such an assignment), this was clearly not the case for the argon isotherm at 299.9654 K. Thus it may appear that the experimental responses for mode TM\(_{12}\), at least for argon at 299.9654 K, consisted of a superposition of two or, perhaps, all three of the expected components; this is supported by a doublet analysis of TM\(_{12}\) mode data and calculations of the splitting parameter \( \chi_{12} \), as will be described later in this section.

The fractional excess halfwidths \((\Delta g/f)\) for the TM\(_{13}\) mode were nearly always less than 5 ppm and, as with the TM\(_{11}\) high-frequency component, showed no systematic dependence on pressure along any of the individual isotherms. This suggests that single components have been fully-resolved within the TM\(_{13}\) resonances; the high-frequency tail of each resonance can be attributed to the low-frequency tail of the remaining two components which overlap in phase. As will soon be shown, this assignment of components - single resolved component at low frequency and two overlapping components at high frequency (lying mainly outside the normal frequency range of measurements) - although opposite to that for the TM\(_{11}\) resonances, is consistent with doublet analyses of TM\(_{13}\) mode data taken over twice the normal frequency range and the magnitudes of calculated splitting parameters \( \chi_{13} \).

The observed \((\Delta g/f)\) values for the low-frequency peak of the TM\(_{21}\) mode ('TM\(_{21}\) low') were always larger than 17 ppm and showed significant systematic pressure-dependence along all six isotherms. For the argon isotherm at 215 K, \((\Delta g/f)\) decreased smoothly from about 36 ppm at the lowest pressure to about 17 ppm at the highest pressure, whilst, for the other four isotherms for which mode TM\(_{21}\) was measured, \((\Delta g/f)\) increased smoothly from about 19 ppm at the lowest pressures to about 21 ppm at the highest pressures. Such large fractional excess halfwidths (at least five times larger than those observed for the assumed TM\(_{11}\) single component) and their pressure-dependence suggest that two or more of the five TM\(_{21}\) components, of which at least two must have been overlapping in phase, were present in the low-frequency peak of the resonances. The \((\Delta g/f)\) values for the high-
frequency TM21 peak ('TM21 high') were significantly smaller in magnitude than those for the low-frequency peak, but were generally negative, suggesting that two or more TM21 components, at least two of which must have been overlapping out of phase, were present in the high-frequency peak of the resonances. Apart from along the argon isotherm at 215 K, the \((\Delta g/f)\) values for the high-frequency TM21 peak did not show systematic pressure-dependence, although their standard deviations were two to three times larger than those observed for the assumed TM11 and TM13 singlets.

The fractional excess halfwidths of the low-frequency peaks of the TM31 mode ('TM31 low') were very large (36 to 74 ppm) and showed systematic pressure-dependence along each isotherm, suggesting, again, that these low-frequency peaks were composed of two, or more, of the seven TM31 components, at least two of which must have been overlapping in phase. The \((\Delta g/f)\) values for the high-frequency peaks of the TM31 mode ('TM31 high') were smaller (9 to 18 ppm) than those for the low-frequency peaks but also showed some systematic pressure-dependence (although much smaller) along all isotherms for which the mode was measured. As before, it is assumed that this is the result of the superposition of two, or more, of the TM31 components, with at least two overlapping in phase.

As indicated in section (6.7), the splittings \(x_{11}\) of the TM11 resonances were reasonably consistent with an approximately axisymmetric deformation of the spherical resonator, and they can be analysed using boundary shape perturbation theory [see section (4.6)]. Using equations (4.6.5) and (4.6.6), and recalling that \(2x = (f_{\text{high}} - f_{\text{low}})\), it can be shown that

\[
\frac{x_{1n}}{f_{1n}^0} = \frac{-3 \varepsilon c_{20}}{4\sqrt{20\pi}} \left( \nu_{2n}^2 + 4 \right) \left( \nu_{2n}^2 - 2 \right)
\]

(7.2.1)

where the minus sign arises from the assumption that the singlet of the TM11 mode lies at high frequency and the degenerate doublet at low frequency. The measured values of \(10^6(x_{11}/f_{11})\) in the evacuated resonator \((p = 0)\), for each isotherm, along with the values of \(10^6(\varepsilon c_{20})\), calculated using equation (1), are given in table (7.1). Apart from the anomalously low value for the argon isotherm at 260 K, the estimates of \(10^6(\varepsilon c_{20})\) are in good agreement, and the average of the values for the argon
Table (7.1) Splitting parameters of the evacuated spherical resonator following the Ar, N\textsubscript{2} and \{0.5 Ar + 0.5 N\textsubscript{2}\} isotherms

<table>
<thead>
<tr>
<th>Gas sample</th>
<th>T/K</th>
<th>10\textsuperscript{6}(x\textsubscript{11}/f\textsubscript{11})</th>
<th>10\textsuperscript{6}(\varepsilon\textsubscript{c\textsubscript{20}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>44.58</td>
<td>-225.9</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>41.11</td>
<td>-208.3</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>46.99</td>
<td>-238.1</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>46.65</td>
<td>-236.4</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>299.9819</td>
<td>45.55</td>
<td>-230.8</td>
</tr>
<tr>
<td>{0.5 Ar + 0.5 N\textsubscript{2}}</td>
<td>299.9887</td>
<td>45.34</td>
<td>-229.8</td>
</tr>
</tbody>
</table>

Isotherms at 215, 299.9654, 299.9728 K and the nitrogen and \{0.5 Ar + 0.5 N\textsubscript{2}\} isotherms at 300 K is \(\langle 10^6(\varepsilon c_{20}) \rangle = (-232.2 \pm 5.0)\). This is approximately twice the magnitude and of opposite sign to the estimate of \(\langle 10^6(\varepsilon c_{20}) \rangle = (+114 \pm 3)\) determined by Boyes, Ewing and Trusler from their TM11 mode measurements on the same evacuated spherical resonator between 90 and 373 K [28]; the difference in sign is due to the assumption of Boyes \textit{et al.} that the single component was at low frequency and the degenerate doublet was at high frequency, an assumption, based in part on an analysis of excess halfwidths similar to that used in this work, that appears to be correct for their data. The change in the magnitude of \(10^6(\varepsilon c_{20})\), between the measurements of Boyes \textit{et al.} in 1994 and those taken in this work, may be due to a genuine increase in the geometric deformation of the sphere, since the resonator has been used by a number of workers in the intervening period over a wide range of temperatures and pressures.

Mehl [44] gives the fractional changes in the polar and equatorial diameters of the sphere, due to the geometric deformation, as \((- \varepsilon c_{20}/2) \sqrt{5/\pi}\) and \((\varepsilon c_{20}/4) \sqrt{5/\pi}\), respectively. Using \(\langle 10^6(\varepsilon c_{20}) \rangle = (-232.2 \pm 5.0)\), determined in this work, it can be shown that the polar and equatorial diameters differed by just 17.6 \(\mu\text{m}\), where the polar diameter was larger than the equatorial diameter if it can be assumed that the high-frequency TM11 peak was the singlet and if the
electromagnetic fields of the mode had the same angular orientations as would be expected for unperturbed cavity fields [see section (4.6)].

Equation (1) suggests that a given axisymmetric geometric deformation should give the same distribution of components for all TM\(1\Pi\) modes, and if \(\langle 10^6(c_{x20}) \rangle = (-232.2 \pm 5.0)\) then we can calculate \(10^6(x_{12}/f_{13}) = (25.69 \pm 0.55)\) and \(10^6(x_{13}/f_{13}) = (23.52 \pm 0.51)\), where the single components are expected at high frequency, as for the TM11 mode. Doublet analyses of TM12 and TM13 data (taken over twice the normal frequency range for TM13), recorded for the evacuated sphere near 300 K, gave the experimental values {TM12: \(f_c = (7294.0850 \pm 0.0283)\) MHz, \(g_{\text{low}} = (0.4180 \pm 0.0498)\) MHz, \(g_{\text{high}} = (0.1242 \pm 0.0059)\) MHz, \(10^6(x_{12}/f_{12}) = (24.5 \pm 2.9)\)} and {TM13: \(f_c = (11109.8539 \pm 0.0551)\) MHz, \(g_{\text{low}} = (0.1641 \pm 0.0063)\) MHz, \(g_{\text{high}} = (0.2873 \pm 0.0941)\) MHz, \(10^6(x_{13}/f_{13}) = (26.1 \pm 5.6)\)} and so the experimental values of \((x/f)\) are apparently in good agreement with those predicted from the TM11 measurements. However, whereas the excess halfwidths suggested that the single component was at high frequency for the TM12 data, in accordance with the TM11 measurements, the TM13 mode halfwidths indicated that the single component was at low frequency. This can be explained by a \((\pi/2)\) rotation of the fields of the TM13 mode with respect to the orientation that would be expected in an unperturbed cavity, giving rise to an opposite ordering of components for exactly the same geometric deformation of the sphere. Such rotation of the fields may simply be the result of the TM13 mode having a preferred angular orientation within the perturbed resonator that was orthogonal to that preferred by the TM11 and TM12 modes. Clearly, then, we cannot say from these measurements alone whether the polar or equatorial diameter was the greater, but, since the experimental and predicted values of \((x_{12}/f_{12})\) and \((x_{13}/f_{13})\) were in such good agreement, we can say with some confidence that there was a difference of about 17.6 \(\mu\)m between the diameters.

The scaled fractional splitting parameters \(10^6(x/f)\), at each state point along the six isotherms, are presented graphically for modes TM11, TM21 and TM31 in figures (7.7), (7.8) and (7.9), respectively. In general, apart from the argon isotherm at 260 K, \((x_{11}/f_{11})\) showed little, if any, significant pressure-dependence whilst \((x_{21}/f_{21})\) and \((x_{31}/f_{31})\) were significantly pressure-dependent along all the isotherms for
Figure (7.7) $10^6(x_1/f_{11})$ for the Ar, N$_2$ and {0.5 Ar + 0.5 N$_2$} isotherms

Figure (7.8) $10^6(x_2/f_{21})$ for the Ar, N$_2$ and {0.5 Ar + 0.5 N$_2$} isotherms
which these modes were measured [although $(x_{31}/f_{31})$ varied much less along the argon isotherm at 299.9654 K than was found for the other isotherms]. The apparent pressure-dependence of $(x_{21}/f_{21})$ and $(x_{31}/f_{31})$ was likely to have been because neither the high nor low-frequency peaks of these resonances were singlets and so the components within the peaks may have shifted or their relative intensities changed as the pressure was changed, complicating the analysis. This is reasonably consistent with the observed pressure-dependence of the excess halfwidths for these modes, with the TM21 low-frequency peak fractional excess halfwidth generally increasing as $(x_{31}/f_{31})$ decreases, and the TM31 low and high-frequency peak fractional excess halfwidths generally decreasing as $(x_{31}/f_{31})$ increases.
Dielectric constants

The combination of equations (2.4.7), (2.4.8) and (3.4.37) shows that the dielectric constant at pressure $p$ and temperature $T$ is given by

$$\varepsilon(p,T) = \left[ \frac{f^0_N(0,T)}{f^0_N(p,T)} \right]^2 \quad (7.2.2)$$

where $f^0_N(0, T)$ and $f^0_N(p, T)$ are the unperturbed resonance frequencies for the evacuated cavity ($p = 0$) and the gas-filled cavity at pressure $p$, respectively. Using the results of section (4.10), we can put

$$\varepsilon(p,T) = \left[ \frac{f_N(0,T)}{f_N(p,T)} \left(1 - \sum_j \left( K_j[0,T,f_N(0,T)]_N \right) \right) \right]^2 \quad (7.2.3)$$

which is a form of equation (4.10.5) generalised to take all sources of non-ideality into account. In equation (3), $f_N(0,T)$ and $f_N(p,T)$ are the perturbed resonance frequencies of the evacuated cavity and the gas-filled cavity at pressure $p$, respectively, and $K_j = \left[ \Delta f_j / f^0_N \right]$ is the fractional frequency shift due to the $j$-th perturbation. As indicated in section (4.10), only those perturbations for which $K_j$ is significantly pressure or frequency-dependent need be included in equation (3) to determine accurate estimates of $\varepsilon(p, T)$ from the perturbed (experimental) resonance frequencies $f_N$. The fractional precision of $\varepsilon$ measurements in this work was on the order of 0.1 ppm, so only those perturbations for which $|K_j[0,T,f_N(0,T)] - K_j[p,T,f_N(p,T)]| \geq 0.05$ ppm, or whose cumulative effect was of a similar order, needed to be taken into account.

The fractional frequency shifts due to the gas-inlet opening [equations (4.7.7) and (4.7.18), and see table (4.5)] and the physical presence of the probe antennae [equations (4.7.6) and (4.7.17)], which only showed pressure-dependence through the variation of the sphere radius, contributed only a few parts per billion to $\varepsilon$, even at the highest pressures, and so were neglected. The fractional frequency shift due to the sphere compliance [equation (4.3.3)] was explicitly pressure-dependent, and that due to the skin-depth perturbation [equation (4.5.12)] was significantly frequency-dependent (through the frequency-dependence of $\delta$), so corrections for these perturbations were made to the measured resonance frequencies $f_N$. 

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In equation (3), the frequencies $f_N$ are the resonance frequencies of the perturbed cavity, including the effect of geometric deformations. As explained in section (4.6), Mehl and Moldover [23] have demonstrated that, for volume-preserving deformations, the average resonance frequency of the $(2l+1)$ components of a given perturbed mode is equal to the corresponding geometrically perfect cavity resonance frequency, correct to first order in the deformation parameter $\varepsilon$. Therefore, the effect of geometric deformations of the sphere could be taken into account by employing the mean multiplet resonance frequencies

$$f_N = [1/(2l + 1)] \sum_{nm=1}^{nm+l} f_{nm}. $$

Alternatively, we can use estimates of the perturbed resonance frequency of a given single component within each multiplet. Given the previously described difficulties in identifying all $(2l+1)$ components within each multiplet, particularly for modes TM21 and TM31, it was much simpler to determine the resonance frequency of one component than of all the components (even assuming they were all represented in the responses). This approach could be expected to fully account for the effects of geometric deformation to the extent that the true shape and magnitude of the deformation under vacuo was the same as that at pressure $p$; given the limited pressure range of 1 MPa for a resonator designed to withstand 7 MPa without distortion, it is reasonable to assume that no significant changes took place (the expected uniform dilation of the resonator was already accounted for by the compliance correction).

There was generally a great improvement in consistency between the estimated values of $\varepsilon(p, T)$ from the different modes if estimated singlet rather than mean multiplet resonance frequencies were used. Assuming the following distribution of components:

- TM11 low-frequency degenerate doublet, high-frequency singlet
- TM12 low-frequency degenerate doublet, high-frequency singlet
- TM13 low-frequency singlet, high-frequency degenerate doublet
- TM21 low-frequency degenerate doublet, high-frequency degenerate triplet
  (there must be more than one component at high frequency and the distribution of components for an axisymmetric deformation is 2-2-1)
- TM31 low-frequency degenerate quartet, high-frequency degenerate triplet
  (again, there must be more than one high-frequency component and
the component distribution for an axisymmetric deformation is 2-2-2-1)

the mean multiplet resonance frequencies were estimated as

\[
\langle f \rangle_{11} = \left[ 2(f_{c,11} - x_{11}) + (f_{c,11} + x_{11}) \right] / 3 = f_{c,11} - (x_{11} / 3) \\
\langle f \rangle_{12} = \left[ 2(f_{12} - 2x_{12}) + f_{12} \right] / 3 = f_{12} - (4x_{12} / 3) \\
\langle f \rangle_{13} = \left[ f_{13} + 2(f_{13} + 2x_{13}) \right] / 3 = f_{13} + (4x_{13} / 3) \\
\langle f \rangle_{21} = \left[ 2(f_{c,21} - x_{21}) + 3(f_{c,21} + x_{21}) \right] / 5 = f_{c,21} + (x_{21} / 5) \\
\langle f \rangle_{31} = \left[ 4(f_{c,31} - x_{31}) + 3(f_{c,31} + x_{31}) \right] / 7 = f_{c,31} - (x_{31} / 7)
\]

where \( f_{c,11}, f_{c,21}, f_{c,31}, \) and \( x_{11}, x_{21}, x_{31} \) were the central resonance frequencies and splitting parameters from the doublet fits to modes TM11, TM21 and TM31, and \( f_{12} \) and \( f_{13} \) were the estimated single component resonance frequencies determined from the singlet fits to modes TM12 and TM13. The TM12 and TM13 splitting parameters \( x_{12} \) and \( x_{13} \) were calculated from equation (1), where \( \varepsilon c_{20} \) was determined using \( x_{11} \). The estimated single component resonance frequencies were

\[
\begin{align*}
\langle f \rangle_{11} & = f_{c,11} + x_{11} \\
\langle f \rangle_{12} & = f_{12} \\
\langle f \rangle_{13} & = f_{13} \\
\langle f \rangle_{21} & = f_{c,21} + x_{21} \\
\langle f \rangle_{31} & = f_{c,31} + x_{31}
\end{align*}
\]

where the TM211 and TM311 components were assumed to lie at high frequency, as for the TM111 component; this also gave better agreement between the estimates of \( \varepsilon \) from the three TM/1 modes than if the resonance frequencies of the low-frequency TM21 and TM31 peaks were used.

For the purposes of comparing the two different approaches, the estimates of \([(\varepsilon-1)/(\varepsilon+2)]\) for the \( N_{2} \) isotherm at 300 K were fitted to equation (9), where all five modes were included in each case and the individual measurements were weighted as \( ([(\varepsilon-1)/(\varepsilon+2)]) / \sigma^2 \), where \( \sigma \) was the estimated random uncertainty of an individual value of \([(\varepsilon-1)/(\varepsilon+2)]\) calculated from equation (11) below. Only the term in \( \rho \) was significant for each fit, with \( A_{\varepsilon} = (4.3975 \pm 0.0015) \) cm\(^3\) mol\(^{-1}\) and a standard deviation in \([(\varepsilon-1)/(\varepsilon+2)]\) of 2.070x10\(^{-6}\) when the mean multiplet resonance frequencies were used, and \( A_{\varepsilon} = (4.39328 \pm 0.00038) \) cm\(^3\) mol\(^{-1}\) and a standard deviation in \([(\varepsilon-1)/(\varepsilon+2)]\) of only 0.537x10\(^{-6}\) when the singlet resonance frequencies
were used. Such a dramatic reduction in the overall standard deviation of the fit (almost a factor of four) was typical of that observed for every isotherm in the sphere. The deviations $10^6 \Delta \{(\varepsilon - 1)/(\varepsilon + 2)\} = 10^6 \{(\varepsilon - 1)/(\varepsilon + 2)\}_{\text{meas}} - \{(\varepsilon - 1)/(\varepsilon + 2)\}_{\text{fit}}$, of the individual measurements of $\{(\varepsilon - 1)/(\varepsilon + 2)\}$ from each fit, are shown in figure (7.10). The improvement in consistency when using the singlet resonance frequencies was particularly marked for the highly-degenerate TM21 and TM31 modes, for which we could never reliably identify all the components, but even the agreement between the reasonably well-resolved TM1n modes was significantly improved. In this respect it is noted that even if only the three TM1n modes were included for the example isotherm then the overall standard deviation of the fit was $0.389 \times 10^{-6}$ when the mean multiplet resonance frequencies were used, but only $0.195 \times 10^{-6}$ when the singlet resonance frequencies were used.

Using the estimated single component resonance frequencies [equations (5)] and making the skin-depth perturbation and sphere compliance corrections as previously indicated, the estimates of $\varepsilon(p, T)$ were determined from equation (3) for each mode along all six isotherms and are presented in table (7.2). The fractional random uncertainty in $\varepsilon$, $\sigma(\varepsilon)/\varepsilon$, was estimated from

$$
\frac{\sigma(\varepsilon)}{\varepsilon} = 2\sqrt{\left(\frac{\sigma(f_N)}{f_N}\right)^2_{p=0} + \left(\frac{\sigma(f_N)}{f_N}\right)^2_p} \quad (7.2.6)
$$

where $\sigma(f_N)/f_N = [\sigma(P)/P_{\text{max}}]/Q_N$ was the fractional random uncertainty in a measured resonance frequency $f_N$ [see section (6.7)]. Estimates of $\sigma(\varepsilon)/\varepsilon$ for all five modes are given in table (7.3). A further contribution (always less than 2.4 ppm) to the total fractional uncertainty in $\varepsilon$, approximately given by $(\chi \varepsilon / 10)$, arose from the estimated $\pm5\%$ uncertainty in the compliance $\chi$, but this was not included in the estimates of the fractional random uncertainty $\sigma(\varepsilon)/\varepsilon$ in table (7.3) because every mode was subject to the same fractional error and so it does not form part of the random uncertainty and does not account for any part of the differences between the estimates of $\varepsilon$ determined using the different modes. The uncertainty in the skin-depth perturbation correction contributed no more than 0.02 ppm to the fractional uncertainty in $\varepsilon$ for any mode at any pressure and temperature.
Figure (7.10) Deviations of \( [(\varepsilon - 1)/(\varepsilon + 2)] \) from the regression equations for data using mean multiplet frequencies (empty symbols) and single component frequencies (solid symbols).

Table (7.2) Experimental values of \( 10^6(\varepsilon - 1) \) for \( \text{Ar} \), \( \text{N}_2 \) and \( \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} \). The uncorrected vacuum resonance frequencies \( f_0 \) and splitting parameters \( x \) are also given so that the original resonance frequencies at each pressure and temperature can be calculated if desired.

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The table shows the experimental values of \( 10^6(\varepsilon - 1) \) for Argon, Nitrogen, and a mixture of 50% Argon and 50% Nitrogen. The vacuum resonance frequencies \( f_0 \) and splitting parameters \( x \) are also given for each pressure level.
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$f_0$/MHz = 3274.1009  7299.6574  11117.8706

$x$/MHz = 0.1346

## Argon $T/K = 299.9654$

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$f_0$/MHz = 3271.1665  7293.1694  11108.1025  4613.6172  5926.9297

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## Argon $T/K = 299.9728$

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$f_0$/MHz = 3271.1587  7293.1362  11107.8350  4613.6123  5926.9106

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$\frac{x}{MHz} = 0.1490 \quad 0.5012 \quad 1.1502$

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<td>2546.90</td>
<td>2557.07</td>
</tr>
<tr>
<td>416.08</td>
<td>2139.28</td>
<td>2136.57</td>
<td>2141.91</td>
<td>2141.34</td>
<td>2148.50</td>
</tr>
<tr>
<td>338.17</td>
<td>1741.87</td>
<td>1735.53</td>
<td>1740.27</td>
<td>1739.24</td>
<td>1745.38</td>
</tr>
<tr>
<td>260.00</td>
<td>1336.49</td>
<td>1334.66</td>
<td>1338.03</td>
<td>1335.63</td>
<td>1341.31</td>
</tr>
<tr>
<td>181.93</td>
<td>933.83</td>
<td>932.40</td>
<td>936.50</td>
<td>934.62</td>
<td>937.68</td>
</tr>
<tr>
<td>103.69</td>
<td>533.56</td>
<td>531.65</td>
<td>534.83</td>
<td>533.75</td>
<td>534.49</td>
</tr>
<tr>
<td>51.68</td>
<td>266.62</td>
<td>264.77</td>
<td>267.35</td>
<td>265.66</td>
<td>266.84</td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

$\frac{f_0}{MHz} = 3271.1614 \quad 7293.1348 \quad 11107.8096 \quad 4613.6011 \quad 5927.0347$

$\frac{x}{MHz} = 0.1483 \quad 0.5042 \quad 1.0408$

**Table (7.3)** Estimated fractional random uncertainties in the dielectric constant $\varepsilon$ for the sphere measurements
Regression equations

The dielectric constant measurements were fitted to three different series derived from the Clausius-Mossotti virial expansion of Buckingham and Pople [85]. If equation (5.5.3) is multiplied by $\rho$ then we obtain

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) = A_\varepsilon \rho + B_\varepsilon \rho^2 + C_\varepsilon \rho^3 + \cdots$$

(7.2.7)

where the dielectric virial coefficients are defined by the limiting relations

$$A_\varepsilon = \lim_{\rho \to 0} \left\{ \frac{\partial}{\partial \rho} \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \right\}$$

$$B_\varepsilon = \frac{1}{2} \lim_{\rho \to 0} \left\{ \frac{\partial^2}{\partial \rho^2} \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \right\}$$

(7.2.8)

$$B_\varepsilon = \frac{1}{6} \lim_{\rho \to 0} \left\{ \frac{\partial^3}{\partial \rho^3} \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \right\}$$

which are equivalent to those in equations (5.5.4). Equation (7) is more well-behaved when fitting experimental data than equation (5.5.3) because as the independent variable $\rho$ tends to zero on the right-hand side, the dependent function $[(\varepsilon - 1)/(\varepsilon + 2)]$ on the left-hand side also tends to zero. By contrast, as $\rho$ tends to zero on the right-hand side of equation (5.5.3), on the left-hand side $[(\varepsilon - 1)/(\varepsilon + 2)]$ tends to zero, but $V_m$ tends to infinity.

In both equations (5.5.3) and (7), the function $[(\varepsilon - 1)/(\varepsilon + 2)]$ is constrained to be zero in the limit of zero molar density, as would be expected in the ideal case because $\varepsilon$ is exactly equal to unity in vacuo. However, we are fitting experimental data, and the introduction of a dimensionless 'deviation term' $\Delta_0$ on the right-hand side of equation (7) means that no such constraints are placed on the experimental values of $[(\varepsilon - 1)/(\varepsilon + 2)]$ in the limit of zero molar density:

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) = \Delta_0 + A_\varepsilon \rho + B_\varepsilon \rho^2 + C_\varepsilon \rho^3 + \cdots$$

(7.2.9)

Thus, $\Delta_0$ can take account of systematic errors in $\varepsilon$ such as are caused by an unobserved zero error in the pressure measurements or by irreversible changes in cavity dimensions, cavity geometry and/or the positions of antennae, without such errors affecting the values of the determined dielectric virial coefficients. It will be noted, in this respect, that the dielectric virial coefficients in equation (9) are still
given exactly by the definitions of equations (8), and it is these that we were concerned to determine. An insignificant value for $\Delta_0$ simply implied that systematic errors of the type mentioned were much smaller than the random uncertainties in the measurements, and so the 'deviation term' was best left out of the regression equation.

In an analogous way, the pressure-explicit virial expansion of equation (5.5.11) can be written

$$\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) = \Delta_0 + A_\varepsilon \left(\frac{P}{RT}\right) + B_\varepsilon \left(\frac{P}{RT}\right)^2 + C_\varepsilon \left(\frac{P}{RT}\right)^3 + \cdots \quad (7.2.10)$$

where $\Delta_0$ represents the same type of errors as previously described, and the coefficients are still given by equations (5.5.12). As before, equation (10) is to be preferred to equation (5.5.11) for the fitting of experimental $(\varepsilon, p, T)$ data.

The virial expansion of $\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)RT/p$ in terms of $\left(\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right)$, given in equation (5.5.13), cannot be rearranged in the same way as equations (5.5.3) and (5.5.11), and so there is no possibility of a dimensionless $\Delta_0$ term in the regressions. If, for a given set of measurements, the deviation term has been found to be significant from a regression using equation (9) or (10), then the errors that gave rise to the $\Delta_0$ term can be expected to affect the coefficients of equation (5.5.13). However, for data where a $\Delta_0$ term has been demonstrated to be insignificant, equation (5.5.13) is perfectly satisfactory, and may even be preferred to equation (10) if the majority of suspected error lies in the measurements of $p$ rather than $\varepsilon$, because, in our least-squares regressions, all the error was assumed to be in the dependent variables.

**Dielectric virial coefficients**

The experimental values of $\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)$ along each isotherm were fitted, using least-squares regressions, to equation (9) to obtain estimates of the dielectric virial coefficients. The fits were performed using the full sets of results (i.e. with separate dielectric constants determined from each mode) and the individual values of $\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)$ were weighted as $\left(\frac{(\varepsilon - 1)(\varepsilon + 2)}{\sigma}\right)^2$, where $\sigma$ was the estimated random uncertainty of an individual value of $\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)$ given by
\[ \sigma = \frac{3\sigma(\varepsilon)}{(\varepsilon + 2)^2} \]  
(7.2.11)

where \( \sigma(\varepsilon) \) was given by equation (6). The amount-of-substance densities \( \rho = (1/V_n) \) were calculated, correct to \( C'(T) \), from equation (5.3.2). The coefficients \( B'(T) \) and \( C'(T) \) were calculated from equations (5.3.4), where the second and third \( (\rho, V_n, T) \) virial coefficients \( B(T) \) and \( C(T) \) were determined at the temperatures of the microwave isotherms using the results of least-squares regressions on published measurements; the chosen form of the regression equations for \( B(T) \) and \( C(T) \) were derived from a square-well potential model.

For argon, the recent determinations of \( B(T) \) and \( C(T) \) by Gilgen, Kleinrahm and Wagner [72] were used, and unweighted least-squares regressions on their measurements from 190 to 340 K gave the equations

\[ B(T)/\text{cm}^3\text{mol}^{-1} = 191.1148 - 153.7674\exp\left(\frac{88.29K}{T}\right) \]  
(7.2.12)

\[ C(T)/\text{cm}^6\text{mol}^{-2} = 718 + 292x + 2485x^2 \]  
(7.2.13)

where \( x = \{\exp\left(\frac{88.29K}{T}\right) - 1\} \)

The measurements of \( B \) fitted equation (12) with a standard deviation of 0.05 cm\(^3\) mol\(^{-1}\) and the measurements of \( C \) fitted equation (13) with a standard deviation of 1.3 cm\(^6\) mol\(^{-2}\). These were considerably smaller than the respective reported total uncertainties of \( \pm 0.25 \) cm\(^3\) mol\(^{-1}\) for the individual measurements of \( B \) and \( \pm 70 \) cm\(^6\) mol\(^{-2}\) for the individual measurements of \( C \), which were taken as the estimated uncertainties of values of \( B \) and \( C \) determined using equations (12) and (13). Gilgen, Kleinrahm and Wagner further indicate that a density calculation using only their values of \( B \) and \( C \), and neglecting the higher virial coefficients, has an estimated total uncertainty less than \( 1.5\times10^4 \rho \) for \( \rho < 4\times10^3 \) mol cm\(^{-3}\). Equation (12) also fits the values of \( B \) obtained by Ewing and Trusler from their acoustic measurements [35] to within 0.1 cm\(^3\) mol\(^{-1}\), in the temperature range 190 to 340 K, suggesting that the estimated \( \pm 0.25 \) cm\(^3\) mol\(^{-1}\) uncertainty in the values of \( B \) calculated using equation (12) may be slightly pessimistic.

For nitrogen, the measurements of \( B \) and \( C \) by Novak, Kleinrahm and Wagner [135] were used to determine the equations

\[ B(T)/\text{cm}^3\text{mol}^{-1} = 189.6676 - 144.3465\exp\left(\frac{89.1634K}{T}\right) \]  
(7.2.14)
\[ C(T)/\text{cm}^6\text{mol}^{-2} = 1402 - 1494x + 5615x^2 - 2221x^3 \quad (7.2.15) \]

where \( x = \left\{ \exp\left(89.1634 \text{K}/T\right) - 1 \right\} \)

which were the results of unweighted least-squares regressions on their measurements from 150 to 340 K. The measurements fitted equations (14) and (15) with standard deviations of 0.03 cm\(^3\) mol\(^{-1}\) and 4.8 cm\(^6\) mol\(^{-2}\), respectively, which were, again, much smaller than the quoted uncertainties in the individual measurements of \( B \) and \( C \) of ±0.25 cm\(^3\) mol\(^{-1}\) and ±100 cm\(^6\) mol\(^{-2}\), respectively. Wagner et al. indicate that a density calculation using their values of \( B \) and \( C \) alone will have a total uncertainty less than 5×10\(^{-5}\) for \( \rho < 1\times10^3 \text{ mol cm}^{-3} \). Equation (14) fits the values of \( B \) obtained by Ewing and Trusler from their acoustic measurements \[35\] to within 0.4 cm\(^3\) mol\(^{-1}\), in the temperature range 150 to 340 K, which is within their estimated uncertainties.

For the \( \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} \) isotherm at 300 K, the value \( B_{\text{mix}} = (-10.11 \pm 0.12) \) cm\(^3\) mol\(^{-1}\) was calculated using equation (5.3.8), where, for consistency, both the pure component second virial coefficients and the cross second virial coefficient were taken from the acoustic measurements of Ewing and Trusler \[35, 83\]. The cross third virial coefficient was not determined by Ewing and Trusler, and so the approximation \( C_{\text{mix}} = \left\{ -B_{\text{mix}}^2/(RT)^2 \right\} \) was made in equation (5.3.2), where \( C_{\text{mix}} \) was neglected. This approximation can be seen as the result of considering pair interactions alone within the gas mixture and neglecting the effects of triplet interactions. It is estimated that such an approach caused an error no greater than 0.0005 cm\(^3\) mol\(^{-1}\) in the value of \( A_e \) determined from the least-squares fit to equation (9), and yet significantly improved the accuracy of the determined value of \( A_e \) over that which would have been obtained had \( C_{\text{mix}} \) been entirely neglected.

The molar gas constant was taken to be \( R = (8.314471 \pm 0.000014) \text{ J mol}^{-1}\text{K}^{-1} \), which was determined at the National Bureau of Standards from measurements of the speed of sound in argon as a function of pressure at the temperature of the triple point of water \[47\], and is only 4.7 ppm smaller than the value from the 1986 adjustment of the fundamental constants \[2\].

The number of terms of equation (9) included in each of the finally adopted regressions was chosen on the basis of whether there was a statistically significant
reduction, at the 0.995 probability level, in the overall standard deviation of the fit on
the addition of extra terms. It was also necessary for any additional coefficients to be
significantly different from zero for their inclusion, and this was assessed by
comparing the magnitude of the ratio \((Z/\sigma Z)\), where \(Z\) was the value of a dielectric
virial coefficient and \(\sigma Z\) was its standard deviation, with the tabulated value of the
Student t-statistic at the 0.995 probability level. Individual data points were
neglected in the final analyses if they deviated by more than five standard deviations
from the corresponding regression curves and if their removal significantly changed
the dielectric virial coefficients obtained. Those modes for which the majority of the
data points were candidates for removal on such a basis were completely removed
from the final analyses since it was judged that such modes were likely to be
suffering from significant systematic error and that the inclusion of any data from
these modes could only reduce the accuracy of the final regression results. Those
data points neglected in the final analyses have been underlined in table (7.2).

Only one term fits \((A_\rho\rho\text{ alone})\) were ever statistically significant for the \(\text{Ar, N}_2\)
and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\) measurements at the 0.995 probability level, and the zero
density deviation term \(\Delta_0\) in equation (9) was never required. There was never a
significant reduction in the standard deviation of the fit on the addition of terms in \(\rho^2\),
and the values of \(B_\varepsilon\) so determined were never significantly different from zero, even
at the 0.95 probability level. The estimates of \(A_\varepsilon\) obtained from the one term fits,
along with their individual standard deviations and the overall standard deviations of
the fits, are shown in table (7.4).

The deviations \(10^6\Delta\{(\varepsilon-1)/(\varepsilon+2)\} = 10^6\{[(\varepsilon-1)/(\varepsilon+2)]_{\text{meas}} - [(\varepsilon-1)/(\varepsilon+2)]_{\text{fit}}\}\), of the
individual measurements of \([(\varepsilon-1)/(\varepsilon+2)]\) from the one term fits (i.e., the regression
residuals), are presented in figures (7.11) to (7.16); those data points neglected in the
final analyses are represented by empty symbols. It is simple to show that for
materials with a dielectric constant very close to unity the corresponding deviations
in the values of \(\varepsilon\) are approximately three times the deviations in \([(\varepsilon-1)/(\varepsilon+2)]\). In
figures (7.11) to (7.16), it can be seen that the deviations of \([(\varepsilon-1)/(\varepsilon+2)]\) for those
data points included in the final analyses are generally less than 0.5 ppm,
corresponding to deviations less than 1.5 ppm in \(\varepsilon\). Such small deviations are in
Table (7.4) First dielectric virial coefficients of Ar, N\textsubscript{2} and \{0.5 Ar + 0.5 N\textsubscript{2}\} from the \[(\varepsilon - 1)/((\varepsilon + 2)]\) on \(\rho\) regressions

<table>
<thead>
<tr>
<th>Sample Gas</th>
<th>(T/K)</th>
<th>(10^6\sigma)</th>
<th>(A_\varepsilon /\text{cm}^3\text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>0.124</td>
<td>(4.143446 \pm 0.000098)</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>0.153</td>
<td>(4.14360 \pm 0.00014)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>0.356</td>
<td>(4.14227 \pm 0.00024)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>0.162</td>
<td>(4.14195 \pm 0.00013)</td>
</tr>
<tr>
<td>(N\textsubscript{2})</td>
<td>299.9819</td>
<td>0.196</td>
<td>(4.39198 \pm 0.00016)</td>
</tr>
<tr>
<td>{0.5 Ar + 0.5 (N\textsubscript{2})}</td>
<td>299.9887</td>
<td>0.712</td>
<td>(4.26597 \pm 0.00064)</td>
</tr>
</tbody>
</table>

accord with the estimates of fractional random uncertainty in \(\varepsilon\) given in table (7.3). It is also clear from figures (7.11) to (7.16) that the individual measurements from the different modes agree within small multiples (generally less than three) of their combined estimated random uncertainties. As previously discussed in detail, there was some ambiguity in component identification for modes TM12 and TM31, and it is to this that the necessary removal of one of these modes from each of the regressions is attributed.

As expected for an atomic gas, the measurements of \(A_\varepsilon\) for argon were not significantly dependent on temperature. Weighted least-squares regression on the four values of \(A_\varepsilon\) in table (7.4), where the values were weighted as \([1/\sigma(A_\varepsilon)]^2\), gave

\[
A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (4.1468 \pm 0.0020) - (1.49 \pm 0.76) \times 10^{-5}(T/K) \quad (7.2.16)
\]

with an overall weighted standard deviation of 0.00043 cm\(^3\) mol\(^{-1}\), whilst an unweighted least-squares fit gave

\[
A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (4.1475 \pm 0.0021) - (1.73 \pm 0.78) \times 10^{-5}(T/K) \quad (7.2.17)
\]

with an overall standard deviation of 0.00055 cm\(^3\) mol\(^{-1}\). Neither of the temperature-dependent terms in equations (16) and (17) was statistically significant, even at the 0.95 probability level, and so the best estimate of \(A_\varepsilon\) for argon between 215 K and
Figure (7.11) Residuals of the \[\frac{(g-l)}{(g+2)}\] on \(\rho\) regression for argon at 214.9658K

Figure (7.12) Residuals of the \[\frac{(e-1)}{(e+2)}\] on \(\rho\) regression for argon at 259.9583K
Figure (7.13) Residuals of the \([f/(l + 2)]\) on \(\rho\) regression for argon at 299.9654K

Figure (7.14) Residuals of the \([|\varepsilon - 1|/(\varepsilon + 2)]\) on \(\rho\) regression for argon at 299.9728K
Figure (7.15) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for nitrogen at 299.9819K

Figure (7.16) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for {0.5 Ar + 0.5 N$_2$} at 299.9887K

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$300 \text{ K}$ is given by the mean of the four values in table (7.4). The weighted mean value, using the same weighting scheme, was found to be $(4.14293 \pm 0.00043) \text{ cm}^3 \text{ mol}^{-1}$, which was in excellent agreement with the unweighted mean of $(4.14282 \pm 0.00083) \text{ cm}^3 \text{ mol}^{-1}$.

Figure (7.17) shows the deviations $\Delta A_e = (A_e - 4.14293 \text{ cm}^3 \text{ mol}^{-1})$ of the individual measurements of $A_e$ for argon taken in this work, as well as those published by a number of other workers, from the weighted mean of $4.14293 \text{ cm}^3 \text{ mol}^{-1}$. The error bars on our measurements in figure (7.17) are the single standard deviations of $A_e$ determined from the least-squares regressions only. While none of the measurements of $A_e$ taken in this work differ by more than $0.001 \text{ cm}^3 \text{ mol}^{-1}$ from the weighted mean, they deviate by as many as 7.5 individual standard deviations from the weighted mean. However, there were further contributions to the total uncertainties in $A_e$ from the uncertainties of $\pm0.25 \text{ cm}^3 \text{ mol}^{-1}$ and $\pm70 \text{ cm}^6 \text{ mol}^{-2}$ in the values of $B$ and $C$, respectively, used to obtain the molar densities. It was estimated that the uncertainty in $B$ contributed about $0.00030 \text{ cm}^3 \text{ mol}^{-1}$ to the total uncertainty in a measurement of $A_e$, whilst the uncertainty in $C$ contributed less than $0.00003 \text{ cm}^3 \text{ mol}^{-1}$. Given this, it is estimated that the total uncertainties in our four values of $A_e$ were typically about $\pm0.00035 \text{ cm}^3 \text{ mol}^{-1}$, and it is clear that all four of the determinations of $A_e$ for argon differed by less than three such uncertainties from the weighted mean value. It would seem, therefore, that our best estimate of $A_e$ for argon between $215 \text{ K}$ and $300 \text{ K}$ is $(4.14293 \pm 0.00052) \text{ cm}^3 \text{ mol}^{-1}$, where the quoted uncertainty was obtained by combining in quadrature the standard deviation of the weighted mean $(0.00043 \text{ cm}^3 \text{ mol}^{-1})$ and the contributions due to the uncertainties in $B$ $(0.00030 \text{ cm}^3 \text{ mol}^{-1})$ and $C$ ($<0.00003 \text{ cm}^3 \text{ mol}^{-1}$).

Although published measurements of $A_e$ for argon are scarce, particularly at temperatures below $280 \text{ K}$ or above $323.15 \text{ K}$, our measurements are generally in good agreement with those of other workers. The graph has been extended to well above $300 \text{ K}$ since the majority of published measurements are at higher temperatures. The recent determination of Goodwin, Mehl and Moldover [111] is a mean value based on their measurements between $280 \text{ K}$ and $330 \text{ K}$, but it has been placed at $280 \text{ K}$ to aid the clarity of figure (7.17). The error bars on the
measurements taken from references 100, 102 and 136 represent standard deviations from the least-squares regressions alone, whilst those from references 103, 111 and 133 represent estimated total uncertainties, including contributions from suspected systematic errors. The measurements of Orcutt and Cole in reference 102 which extend to 423 K are systematically lower than our weighted mean of $(4.14293 \pm 0.00052) \text{ cm}^3 \text{ mol}^{-1}$, by about 0.006 cm$^3$ mol$^{-1}$, but show no significant temperature-dependence within themselves. They probably suffered from an unsuspected systematic error, caused by the lack of measurements below 130 kPa, which made it more difficult to determine accurately the limiting (as $\rho \rightarrow 0$) intercept ($A_e$) and gradient ($B_e$) of the Clausius-Mossotti function. However, since their measurements extend to sufficiently high pressures (>13 MPa), precise estimates of $B_e$ were determined [e.g., $(2.2 \pm 0.1) \text{ cm}^6 \text{ mol}^{-2}$ at 323.15K], and their values for $A_e$ should be given due regard, at least until other measurements have been
taken at such high temperatures, because they are unlikely to suffer from serious truncation errors. Our measurements are in excellent agreement with those presented in references 103, 111 and 106, which agree within their individual uncertainties or standard deviations with our weighted mean. Our results are also in very good agreement with those of reference 100, which are scattered evenly about our weighted mean and lie just slightly more than their single standard deviations from it. The very precise result of Bose and Cole [133] is 0.0032 cm$^3$ mol$^{-1}$ below the weighted mean, but this difference is still less than three combined uncertainties.

The single measurement of $A_\varepsilon$ for nitrogen at 300 K, given in table (7.4), is compared in figure (8.24) with the measurements taken in this work using the cylindrical resonator as well as those published by other workers. The result using the sphere is in excellent agreement with that using the cylinder at 300 K, being just 0.00013 cm$^3$ mol$^{-1}$ smaller. This difference is less than the standard deviation of $A_\varepsilon$ arising from the regression, which is particularly encouraging because the cylinder measurement arises from a fit to equation (9) in which $B_\varepsilon$ was significant, indicating that the sphere result, which is derived from a fit with $A_\varepsilon$ only, does not suffer from significant truncation error. As was the case for argon, the estimated total uncertainty in the nitrogen sphere measurement must also include contributions due to the uncertainties in $B$ and $C$ (contributions estimated at $\pm$ 0.0003 cm$^3$ mol$^{-1}$ and $\pm$ 0.00003 cm$^3$ mol$^{-1}$, respectively), and as such is estimated to be $\pm$ 0.00034 cm$^3$ mol$^{-1}$. Our measurement was in excellent agreement with that published by Vidal and Lallemand [134] at 298.15 K, being well within their estimated uncertainty. The measurements of Johnston, Oudemans and Cole [100] at 296 K and 306 K are about 0.011 cm$^3$ mol$^{-1}$ and 0.008 cm$^3$ mol$^{-1}$ smaller than our value at 300 K suggesting that their work may be subject to some important unidentified systematic error, although their measurements on argon using the same apparatus and method were in very good agreement with ours, and, indeed, their result for nitrogen at 242 K was in very good agreement with our cylinder measurement at 243 K.

There are no published measurements of the dielectric virial coefficients of the gas mixture \{0.5 Ar + 0.5 N$_2$\}, but our $A_\varepsilon$ at 300 K can be compared with the value calculated using equation (5.5.9) and the values of $A_\varepsilon$ for the pure components at
300 K. The value for argon at 299.9728 K was used for the calculation, because this isotherm was taken over much the same pressure range as those of the mixture and pure nitrogen, and the modes included in the final analyses were the same. The mole fraction of nitrogen was taken to be \((0.50178 \pm 0.00006)\), which is the weighted mean value from Ewing and Trusler's speed of sound measurements on the same mixture between 90 and 373 K [83], and differs from their determination at 300.62 K by just 0.00006. Thus, we calculated the value for the binary gas mixture of \(A_e(300 \text{ K}) = (4.26741 \pm 0.00010) \text{ cm}^3 \text{ mol}^{-1}\), where the uncertainty was derived solely from the standard deviations of the pure component values in table (7.4). The difference between measured and calculated values was therefore just \(-0.00144 \text{ cm}^3 \text{ mol}^{-1}\), which was less than twice their combined standard deviation of \(0.00074 \text{ cm}^3 \text{ mol}^{-1}\). Had the argon measurement at 299.9654 K been used instead, then the calculated \(A_e\) for the mixture would have been larger by just \(0.00016 \text{ cm}^3 \text{ mol}^{-1}\). The contribution to the uncertainty in \(A_e\) due to that in the second virial coefficient \(B\) used for the isotherm fit was again about \(\pm0.0003 \text{ cm}^3 \text{ mol}^{-1}\), and that due to the approximation used for \(C_{\text{min}}\) was estimated at \(\pm0.0005 \text{ cm}^3 \text{ mol}^{-1}\), giving an estimated total uncertainty in \(A_e\) of \(\pm0.00087 \text{ cm}^3 \text{ mol}^{-1}\).

\((p, V_m, T)\) virial coefficients

The experimental values of \([(\varepsilon -1)/(\varepsilon + 2)]\) for argon, nitrogen and the mixture \({0.5 \text{ Ar} + 0.5 \text{ N}_2}\) were also fitted, using least-squares regressions, to equation (10) to determine estimates of the first dielectric virial coefficients and the second \((p, V_m, T)\) virial coefficients. The full sets of results were used, as in the previous molar density fits, and the same weighting scheme was employed. The basis upon which individual data points (or complete sets of results for particular modes) were rejected from the final analyses was exactly as before, and, in this way, the same points were removed from the regressions on \((p/RT)\) as had been removed from those on \(\rho\). This was very helpful when comparing the estimates of \(A_e\) from the two sets of regressions, since it eliminated suspicion of systematic differences due to mode selection.
Only two term fits \([A_\epsilon(p/RT) + (B_\epsilon - A_\epsilon B)(p/RT)^2]\) to equation (10) were ever judged to be statistically significant, the zero pressure deviation term \(\Delta_0\) never being significantly different from zero. There was never a significant reduction in the overall standard deviation of the fit on addition of \((p/RT)^2\) terms, even at the 0.95 probability level, and the additional coefficients so derived were never themselves significant. The coefficients \(A_\epsilon\) and \(B'_\epsilon = (B_\epsilon - A_\epsilon B)\), along with their individual standard deviations and the overall standard deviations of the regressions, are given in table (7.5). The distribution and size of the residuals from the \((p/RT)\) regressions were essentially the same as those for the one term molar density fits to the same data [see figures (7.11) to (7.16)] despite the higher order of fit, and so, in the interests of space, are not reproduced here. Estimates of the second \((p, V_m, T)\) virial coefficients \(B^\text{est} = (-B'_\epsilon/A_\epsilon)\) are also given in table (7.5), along with their standard deviations calculated from the standard deviations of \(A_\epsilon\) and \(B'_\epsilon\). In calculating \(B^\text{est}\) in this way, we have assumed that the contribution from \((B_\epsilon/A_\epsilon)\) is negligible, an assumption which almost certainly leads to errors less than \(-0.3\) to \(-0.4\) cm\(^3\) mol\(^{-1}\) for the second \((p, V_m, T)\) virial coefficients of argon [using the recent measurements of \(B_\epsilon\) of \((1.84 \pm 0.07)\) cm\(^6\) mol\(^{-2}\) at 243 K and \((1.22 \pm 0.09)\) cm\(^6\) mol\(^{-2}\) at 303 K reported in reference 94], and an error of about \(-0.5\) cm\(^3\) mol\(^{-1}\) for the second \((p, V_m, T)\) virial coefficient of nitrogen at 300 K [using the measurement of \(B_\epsilon = (2.04 \pm 0.28)\) cm\(^6\) mol\(^{-2}\) at 300 K taken with the cylindrical resonator - see chapter 8]. It would, of course, have been possible to use such published values of \(B_\epsilon\) to 'improve' our estimates of \(B\), but data are available for only a small number of gases over limited ranges of temperature and there are significant differences (often more than 100\%), even for relatively well studied gases like argon) between the estimates of \(B_\epsilon\) from different workers [88]. Therefore, such small corrections will be neglected for the present measurements and the differences between our \(B^\text{est}\) values and the published second virial coefficients of other workers will help to indicate the resulting errors using this method. However, before such comparisons are made, the \([\epsilon - 1]/(\epsilon + 2)]RT/p\) on \([\epsilon - 1]/(\epsilon + 2)]\) regressions will be described because these too gave values of \(A_\epsilon\) and estimates of \(B\).
Table (7.5) Coefficients from the \( [(\varepsilon - 1)/(\varepsilon + 2)] \) on \( (p/RT) \) regressions for Ar, \( N_2 \) and \( \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} \)

<table>
<thead>
<tr>
<th>Sample Gas</th>
<th>( T/\text{K} )</th>
<th>( \sigma/\text{cm}^3 \text{ mol}^{-1} )</th>
<th>( A_f/\text{cm}^3 \text{ mol}^{-1} )</th>
<th>( B_f^*/\text{cm}^3 \text{ mol}^{-1} )</th>
<th>( B_{\text{est}}/\text{cm}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>0.124</td>
<td>(4.14309 ± 0.00036)</td>
<td>(172.6 ± 1.1)</td>
<td>(-41.66 ± 0.27)</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>0.148</td>
<td>(4.14450 ± 0.00051)</td>
<td>(99.6 ± 1.8)</td>
<td>(-24.03 ± 0.43)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>0.310</td>
<td>(4.13935 ± 0.00083)</td>
<td>(72.1 ± 2.7)</td>
<td>(-17.42 ± 0.64)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>0.157</td>
<td>(4.14303 ± 0.00053)</td>
<td>(58.1 ± 2.1)</td>
<td>(-14.02 ± 0.51)</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>299.9819</td>
<td>0.196</td>
<td>(4.39174 ± 0.00062)</td>
<td>(19.7 ± 2.4)</td>
<td>(-4.49 ± 0.55)</td>
</tr>
<tr>
<td>{0.5 \text{ Ar} + 0.5 \text{ N}_2}</td>
<td>299.9887</td>
<td>0.713</td>
<td>(4.2642 ± 0.0024)</td>
<td>(49.9 ± 9.8)</td>
<td>(-11.7 ± 2.3)</td>
</tr>
</tbody>
</table>

Table (7.6) Coefficients from the \( [(\varepsilon - 1)/(\varepsilon + 2)]RT/p \) on \( [(\varepsilon - 1)/(\varepsilon + 2)] \) regressions for Ar, \( N_2 \) and \( \{0.5 \text{ Ar} + 0.5 \text{ N}_2\} \)

<table>
<thead>
<tr>
<th>Sample Gas</th>
<th>( T/\text{K} )</th>
<th>( \sigma/\text{cm}^3 \text{ mol}^{-1} )</th>
<th>( A_f/\text{cm}^3 \text{ mol}^{-1} )</th>
<th>( B_f^*/\text{cm}^3 \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>0.00057</td>
<td>(4.14357 ± 0.00036)</td>
<td>(40.72 ± 0.26)</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>0.00071</td>
<td>(4.14462 ± 0.00050)</td>
<td>(23.77 ± 0.43)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>0.00136</td>
<td>(4.13942 ± 0.00083)</td>
<td>(17.27 ± 0.64)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>0.00085</td>
<td>(4.14306 ± 0.00053)</td>
<td>(13.95 ± 0.51)</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>299.9819</td>
<td>0.00105</td>
<td>(4.39174 ± 0.00062)</td>
<td>(4.48 ± 0.55)</td>
</tr>
<tr>
<td>{0.5 \text{ Ar} + 0.5 \text{ N}_2}</td>
<td>299.9887</td>
<td>0.00408</td>
<td>(4.2642 ± 0.0024)</td>
<td>(11.7 ± 2.3)</td>
</tr>
</tbody>
</table>

For all six isotherms, the experimental values of \( [(\varepsilon - 1)/(\varepsilon + 2)]RT/p \) were fitted to equation (5.5.13) using weighted least-squares regressions. The same modes and individual data points were included in the final analyses as were retained for the \( \rho \) and \( (p/RT) \) fits (adopting the same basis for data rejection as used previously), and the weighting scheme was similar, with each point being weighted as \( \left\{[(\varepsilon - 1)/(\varepsilon + 2)]RT/p\right\}/\sigma \), where \( \sigma \) was the estimated random uncertainty in an individual value of \( [(\varepsilon - 1)/(\varepsilon + 2)]RT/p \) given by

\[
\sigma = \frac{RT}{p} \left[ \frac{3\sigma(\varepsilon)}{(\varepsilon + 2)^2} \right] \quad (7.2.18)
\]

with \( \sigma(\varepsilon) \) being the random uncertainty in \( \varepsilon \). It may be noticed that the random uncertainty in \( [(\varepsilon - 1)/(\varepsilon + 2)]RT/p \) given by equation (18) is just the random uncertainty in \( [(\varepsilon - 1)/(\varepsilon + 2)] \) given by equation (11) multiplied by the factor \( RT/p \). The regression residuals were essentially the same as those from the \( \rho \) and \( (p/RT) \) fits, but each scaled by the factor \( RT/p \), and so are not repeated here. Again, as for
the \((p/RT)\) fits, only two terms were ever significant at the 0.995 probability level, with the addition of a third term never leading to a significant reduction in the overall standard deviation even at the 0.95 probability level. There was no possibility of a \(\Delta_0\) term in any of these regressions, but this should be of no consequence because such a term was never significant in the corresponding \(\rho\) and \((p/RT)\) fits. The resulting coefficients \(A_e\) and \(B''_e = \left[\left(\frac{B_e}{A_e}\right) - B\right]\) are shown in table (7.6), along with their individual standard deviations and the overall standard deviations of the fits. Clearly, the values of \(-B''_e\) directly give new estimates of the second \((\rho, V_m, T)\) virial coefficients if we neglect \((B_e/A_e)\).

The estimates of \(A_e\) from the three sets of regressions carried out on the \(\text{Ar}, \text{N}_2\) and \{0.5 \(\text{Ar} + 0.5 \text{N}_2\}\) measurements are compared in table (7.7). The values from the three regressions are in good agreement, the differences always being less than three combined standard deviations. This is particularly encouraging when it is recalled that the coefficients derive from both one and two term fits. The weighted mean value of \(A_e\) for argon between 215 and 300 K from the \((p/RT)\) fits is \((4.1425 \pm 0.0011)\, \text{cm}^3\, \text{mol}^{-1}\), whilst that from the \(\left[\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right] RT/p\) on \(\left[\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right]\) regressions is \((4.1427 \pm 0.0012)\, \text{cm}^3\, \text{mol}^{-1}\), both of which are in excellent agreement with the weighted mean of \((4.14293 \pm 0.00043)\, \text{cm}^3\, \text{mol}^{-1}\) from the \(\rho\) fits (the quoted uncertainties are single standard deviations only).

<table>
<thead>
<tr>
<th>Sample Gas</th>
<th>(T/K)</th>
<th>([A_e(2) - A_e(1)]/\text{cm}^3, \text{mol}^{-1})</th>
<th>([A_e(3) - A_e(1)]/\text{cm}^3, \text{mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>-0.00036</td>
<td>-0.00012</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>+0.00090</td>
<td>+0.00102</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>-0.00292</td>
<td>-0.00285</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>+0.00108</td>
<td>+0.00111</td>
</tr>
<tr>
<td>(N_2)</td>
<td>299.9819</td>
<td>-0.00024</td>
<td>-0.00024</td>
</tr>
<tr>
<td>{0.5 (\text{Ar} + 0.5 \text{N}_2)}</td>
<td>299.9887</td>
<td>-0.0018</td>
<td>-0.0018</td>
</tr>
</tbody>
</table>

\(A_e(1):\) first dielectric virial coefficient from the \(\rho\) regression
\(A_e(2):\) first dielectric virial coefficient from the \((p/RT)\) regression
\(A_e(3):\) first dielectric virial coefficient from the \(\left[\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right]RT/p\) on \(\left[\frac{(\varepsilon - 1)}{(\varepsilon + 2)}\right]\) regression
The estimates of the second \((p, V_m, T)\) virial coefficients \(B^{\text{est}}\) obtained from the \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] on \((p/RT)\) regressions agreed with those from the \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right] \frac{RT}{p}\] on \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] regressions within single standard deviations, except for the measurements on argon at 215 K, and these \(B^{\text{est}}\) values still agreed within two combined standard deviations. The small differences that occurred were presumably due to the systematic error caused by the truncation of two different virial expansions. A further indication of the error that may have been caused by series truncation at two terms was gained by comparing the results of several two term fits to each set of measurements over reduced \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] ranges by successively removing the highest pressure data. Each of the two term fits gave mean gradients [the coefficient \((B/A) - B\)] over the range of data used, but it was the limiting values of gradient that we were really concerned to determine; this is the problem of truncation error. However, for each isotherm there was no significant pressure-dependence shown by the gradients derived from the two term fits over successively reduced ranges and so the best estimates of the limiting \((p \rightarrow 0)\) gradients were the mean values. The means of the coefficients \([B/A) - B\] obtained from the \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right] \frac{RT}{p}\] on \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] regressions on successively reduced data ranges are given in table (7.8), and it can be seen that the largest difference between these values and those in table (7.6) was about 2 cm\(^3\) mol\(^{-1}\) for argon at 260 K. However, the coefficients in table (7.8) never differ by more than one standard deviation from those in table (7.6), and the typical difference for the six isotherms was only about 0.5 cm\(^3\) mol\(^{-1}\), which is comparable with the differences between the estimates of \(B\) determined from the \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] on \((p/RT)\) regressions and the \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right] \frac{RT}{p}\] on \[\left[\frac{(\varepsilon - 1)}{\varepsilon + 2}\right]\] regressions.

Figure (7.18) shows the deviations \(\Delta B = [B - B_{\text{eqn. (7.2.12)}}]\) of the estimates of \(B\) for argon determined in this work [tables (7.5) and (7.6)], as well as those published by a number of other workers, from equation (12). The error bars placed on our measurements represent the single standard deviations determined from the regressions only. The chosen published values are intended to be representative of the measurements reported since 1910. As can be seen from the close agreement of
Table (7.8) Means of the coefficients \([ (B_d/A_d) - B ] \) from the regressions over successively reduced ranges of \([(\varepsilon - 1)/(\varepsilon + 2)] \) for Ar, N\(_2\) and \(0.5 \text{ Ar} + 0.5 \text{ N}_2\). The uncertainties are single standard deviations.

<table>
<thead>
<tr>
<th>Gas Sample</th>
<th>T/K</th>
<th>Mean ([ (B_d/A_d) - B ] ) / cm(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>214.9658</td>
<td>(41.3 ± 1.3)</td>
</tr>
<tr>
<td>Ar</td>
<td>259.9583</td>
<td>(21.8 ± 2.0)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9654</td>
<td>(17.0 ± 1.1)</td>
</tr>
<tr>
<td>Ar</td>
<td>299.9728</td>
<td>(13.53 ± 0.66)</td>
</tr>
<tr>
<td>N(_2)</td>
<td>299.9819</td>
<td>(4.86 ± 0.47)</td>
</tr>
<tr>
<td>(0.5 \text{ Ar} + 0.5 \text{ N}_2)</td>
<td>299.9887</td>
<td>(11.7 ± 2.3)</td>
</tr>
</tbody>
</table>

the values from references 35, 137, 138, the recommended values from reference 65, and equation (12), the second \((p, V_m, T)\) virial coefficients of argon between 200 and 300 K are very well known. The measurements of Schramm et al. [139] are in slightly poorer agreement with equation (12), although they still agree within their quoted uncertainties. The values published by Kammerlingh-Onnes and Crommelin [140] are systematically high by 3.5 to 4.8 cm\(^3\) mol\(^{-1}\), but are included in figure (7.18) to give some indication of the errors in earlier measurements. The estimates of \(B\) determined from our \([(\varepsilon - 1)/(\varepsilon + 2)] \) \(RT/p\) on \([(\varepsilon - 1)/(\varepsilon + 2)] \) regressions all deviate by less than 3.1 of their individual standard deviations from equation (12), and are in good agreement with the measurements in references 35, 137, 138, 139, and the recommended values from reference 65. The determinations of \(B\) from the \((p/RT)\) fits are, perhaps, in slightly poorer agreement with equation (12), although the largest deviation, at 299.9654 K, is still only 3.3 standard deviations. The estimates of \(B\) obtained from the measurements at 299.9654 and 299.9728 K differ by about 3.4 cm\(^3\) mol\(^{-1}\), which is slightly less than three of their combined standard deviations, and therefore show satisfactory agreement, especially given the additional estimated 0.5 cm\(^3\) mol\(^{-1}\) truncation errors.
The values of $B$ for nitrogen at 300 K determined from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ and $[(\varepsilon - 1)/(\varepsilon + 2)]RT/p$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions [tables (7.5) and (7.6)] differed by just 0.15 and 0.16 cm$^3$ mol$^{-1}$, respectively, from equation (14), and were also well within the quoted uncertainties of the determination of Ewing and Trusler [35] at 300 K, as well as the recommended value of Dymond and Smith at 300 K [65]. Our estimates of $B_{\text{mix}}$ for the $\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}$ mixture [tables (7.5) and (7.6)] were not in such good agreement with the value of $(-10.11 \pm 0.12)$ cm$^3$ mol$^{-1}$ calculated from the virial coefficients of Ewing and Trusler [35, 83], but were fairly imprecise and so still agreed with it within their single standard deviations.

**Figure (7.18)** Deviations of measurements of the second $(p, V_m, T)$ virial coefficients of argon from equation (7.2.12)
7.3 Xenon

Measurements are reported for xenon at eight temperatures between 189 and 360 K.

Excess halfwidths and splitting parameters

As before, the excess halfwidths $\Delta g$ were determined, at each state point, by subtracting the calculated skin-depth perturbation contributions $g_\delta$ obtained from equation (4.5.11), from the corresponding measured halfwidths $g$. The fractional excess halfwidths $10^6 \left( \frac{\Delta g}{f} \right) = 10^6 \left( \frac{g - g_\delta}{f} \right)$, where the $f$ are the corresponding measured resonance frequencies, are presented in figures (7.19) to (7.26).

The trends in the excess halfwidths of the xenon isotherms were very much the same as those for the Ar, N$_2$ and $\{0.5$ Ar $+ 0.5$ N$_2\}$ isotherms. The $\left( \frac{\Delta g}{f} \right)$ values for the high-frequency peak of the TM11 mode were always less than 3 ppm, compared to about 8 to 18 ppm for the low frequency peak, and were not systematically dependent on pressure along any of the xenon isotherms. This was very similar to what was seen for the measurements in section (7.2), and indicated that the high frequency peak was a single component of the TM11 mode with the low frequency peak being made up of the remaining two components, overlapping in phase. Again, $\left( \frac{\Delta g}{f} \right)$ for the high frequency component was slightly dependent on temperature [see table (7.9)], suggesting that the sources of energy loss not accounted for by the skin-depth contribution were temperature-dependent. For a given xenon isotherm, the standard deviation of $\left( \frac{\Delta g}{f} \right)$ for the low frequency peak was typically seven times larger than that of the high frequency peak (the assumed singlet), presumably due to the variations in overlap and relative intensity of the two components within the low frequency doublet as the pressure was changed.

The $\left( \frac{\Delta g}{f} \right)$ values for the TM12 mode were always less than 10 ppm, but often showed a small but significant pressure-dependence along individual isotherms, suggesting that the TM12 responses were a superposition of two, or perhaps all three, of the mode components, as was concluded before. This is further supported by the negative excess halfwidths observed at 360 K, indicating that at least two of the components were overlapping out of phase.
Figure (7.19) $10^6(\Delta g/f)$ for xenon at 188.5533 K

Figure (7.20) $10^6(\Delta g/f)$ for xenon at 204.5894 K
Figure (7.21) $10^6(\Delta g/f)$ for xenon at 224.6757 K

Figure (7.22) $10^6(\Delta g/f)$ for xenon at 249.2879 K
Figure (7.23) $10^6(\Delta g/f)$ for xenon at 272.9014 K

Figure (7.24) $10^6(\Delta g/f)$ for xenon at 299.9935 K
Figure (7.25) $10^6(\Delta g/f)$ for xenon at 315.2844 K

Figure (7.26) $10^6(\Delta g/f)$ for xenon at 360.2599 K
The fractional excess halfwidths $(\Delta g/f)$ for the TM13 mode were almost invariably less than 4 ppm and never showed any pressure-dependence along an isotherm, indicating that single components had effectively been fully resolved. The high-frequency tails were, again, attributed to the remaining two components.

The $(\Delta g/f)$ values for the low frequency peak of the TM21 mode were always larger than 17 ppm and almost invariably showed significant pressure-dependence along the individual isotherms, suggesting that two or more of the five TM21 components must have been represented in the peak. The rate of decrease of $(\Delta g/f)$ with increasing pressure becomes smaller at higher temperatures, until, at 300 K and above, the $(\Delta g/f)$ values actually begin to increase with increasing pressure. The reason for this is not clear, but similar changes in the rate of change of $(\Delta g/f)$ with pressure were observed for the high frequency TM21 peaks as well as for both peaks of the TM31 responses. The $(\Delta g/f)$ values for the high frequency peak of the TM21 mode were always negative, indicating that two or more of the mode components were present, with at least two overlapping out of phase.

The fractional excess halfwidths of the low frequency peaks of the TM31 mode were always larger than 27 ppm, and generally showed significant pressure-
dependence. This implied that at least two of the seven TM31 components were present in the low frequency peak with two or more of them overlapping in phase. The \((\Delta g/f)\) values for the high frequency peaks of the TM31 mode were smaller (7 to 19 ppm) than those of the low frequency peaks but showed a significant pressure-dependence along the isotherms at 225 and 249 K, although this was not observed for the other isotherms. As with the measurements described in section (7.2), it was assumed that two or more components were present in the TM31 high frequency peaks, with at least two overlapping in phase.

The measured splittings \(x_{11}\) of the TM11 mode were consistent with the approximately axisymmetric geometric deformation of the sphere inferred in section (7.2). The measured values of \(10^6(x_{11}/f_{11})\) in the evacuated resonator, along with the corresponding values of \(10^6(\epsilon c_{\omega 0})\), calculated using equation (7.2.1), are given in table (7.10). The estimates of \(10^6(\epsilon c_{\omega 0})\) at the eight different temperatures were very similar, and the mean value of \(\left\langle 10^6(\epsilon c_{\omega 0}) \right\rangle = (-228.0 \pm 2.5)\) was in excellent agreement with the value of \((-232.2 \pm 5.0)\) determined from the Ar, \(N_2\) and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\) isotherms which were taken over a narrower temperature range. The determination of \(\left\langle 10^6(\epsilon c_{\omega 0}) \right\rangle\) from the xenon isotherms is consistent with there having been a difference of 17.3 \(\mu m\) between the polar and equatorial diameters of the sphere, in excellent agreement with the previously determined difference of 17.6 \(\mu m\). As before, it is not possible to state firmly which of the diameters was the larger because we cannot be sure about the angular orientation of the electromagnetic fields of the resonant modes within the resonator.

The fractional splitting parameters \(10^6(x/f)\) for modes TM11, TM12 and TM13 are presented graphically in figures (7.27) to (7.29). The measurements of \((x_{11}/f_{11})\) showed small but significant pressure-dependence along the isotherms at 205, 225 and 249 K, although this was less so for the other isotherms. This may be attributed to small changes in the positions and relative intensities of the two components in the low frequency peaks, but corresponding variations in the fractional excess halfwidths were not observed. The fractional splitting parameters \((x_{21}/f_{21})\) were between about
Table (7.10) Splitting parameters of the evacuated spherical resonator following the xenon isotherms

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$10^8(x_{11}/f_{11})$</th>
<th>$10^8(\varepsilon c_{20})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>45.14</td>
<td>-228.8</td>
</tr>
<tr>
<td>204.5894</td>
<td>44.69</td>
<td>-226.5</td>
</tr>
<tr>
<td>224.6757</td>
<td>44.96</td>
<td>-227.9</td>
</tr>
<tr>
<td>249.2879</td>
<td>44.89</td>
<td>-227.5</td>
</tr>
<tr>
<td>272.9014</td>
<td>45.80</td>
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<td>299.9935</td>
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<td>-230.1</td>
</tr>
<tr>
<td>315.2844</td>
<td>44.10</td>
<td>-223.5</td>
</tr>
<tr>
<td>360.2599</td>
<td>44.88</td>
<td>-227.5</td>
</tr>
</tbody>
</table>

Figure (7.27) $10^8(x_{11}/f_{11})$ for the xenon isotherms in the sphere
Figure (7.28) $10^6(x_{27}/f_{27})$ for the xenon isotherms in the sphere

![Graph showing $10^6(x_{27}/f_{27})$ for xenon isotherms at various temperatures](image)

Figure (7.29) $10^6(x_{31}/f_{31})$ for the xenon isotherms in the sphere

![Graph showing $10^6(x_{31}/f_{31})$ for xenon isotherms at various temperatures](image)
125 ppm at 189 K and 105 ppm at 360 K, and so were similar to those seen in section (7.2), where \((x_2/f_2)\) varied from about 117 ppm for argon at 215 K to 107 ppm for argon, nitrogen and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\) at 300 K. The values of \((x_3/f_3)\) for the xenon isotherms generally decreased with increasing pressure, consistent with the observations on the Ar, N\(_2\) and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\) isotherms. The values of \((x_3/f_3)\) were very similar to those measured in Ar, N\(_2\) and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\), and, as for \((x_2/f_2)\), tended to be slightly smaller at higher temperatures.

**Dielectric constants**

The trends in excess halfwidths and splitting parameters for the xenon isotherms were generally very similar to those seen for the measurements on Ar, N\(_2\) and \(\{0.5 \text{ Ar} + 0.5 \text{ N}_2\}\), and the same assignment of components within the experimental resonances was therefore assumed. The previously discussed difficulties in measuring the frequencies of all components within each resonance meant that the estimated single component resonance frequencies [equations (7.2.5)] were used to determine the dielectric constants using equation (7.2.3), after making the corrections for the skin-depth perturbation [equation (4.5.12)] and the sphere compliance [equation (4.3.3)], as before. The estimates of \(\delta(p, T)\) for each mode along the eight xenon isotherms are presented in table (7.11). The fractional random uncertainties in the dielectric constants were calculated from equation (7.2.6) and estimates are given in table (7.3). As explained in section (7.2), the uncertainties in table (7.3) do not include the contribution arising from the uncertainty in the sphere compliance, but this was estimated to be never greater than 1.5 ppm for the xenon isotherms.
Table (7.11) Experimental values of $10^6 (\varepsilon - 1)$ for xenon. The uncorrected vacuum resonance frequencies $f_0$ and splitting parameters $\alpha$ are also given.

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$f_0$/MHz = 3278.9341
$x$/MHz = 0.1480

$77K = 204.5894$

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$f_0$/MHz = 3277.9019
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$77K = 224.6757$

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$f_0$/MHz = 3275.5591
$x$/MHz = 0.1473

$77K = 224.6757$
### Table 1: Temperature Dependence of $\alpha$ and $\beta$

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$\alpha / \text{MHz} = \frac{3274.8542}{730.3661} \times 11120.5819 = 4618.7999 = 5933.6424$

$x / \text{MHz} = 0.1470$

#### $T/K = 272.9014$

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$\alpha / \text{MHz} = \frac{3273.1593}{7297.6002} \times 11114.8112 = 4616.4089 = 5930.5315$

$x / \text{MHz} = 0.1499$

#### $T/K = 299.9935$

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$\alpha / \text{MHz} = \frac{3271.1633}{7293.1344} \times 11107.8994 = 4613.6191 = 5927.0713$

$x / \text{MHz} = 0.1485$

255
The full sets of results of \( [(\varepsilon - 1)/(\varepsilon + 2)] \) along each isotherm were fitted to equation (7.2.9), with the individual data points being weighted exactly as in section (7.2), to determine estimates of the first and second dielectric virial coefficients \( A_\varepsilon \) and \( B_\varepsilon \). The amount-of-substance densities \( \rho \) were calculated, correct to \( C'(T) \), from equation (5.3.2). The required coefficients \( B'(T) \) and \( C'(T) \) were calculated from equations (5.3.4), where the second \( (\rho, V_m, T) \) virial coefficient \( B(T) \) was taken from the equation

\[
B(T)/\text{cm}^3\text{mol}^{-1} = 245.6 - 190.9 \exp\left(200.2 K/T\right)
\]  

Dielectric virial coefficients

\[
\rho/\text{kPa} \quad T_M11 \quad T_M12 \quad T_M13 \quad T_M21 \quad T_M31
\]

\[
521.57 \quad 6211.58 \quad 6211.42 \quad 6212.52 \quad 6213.26 \quad 6215.81
\]

\[
468.08 \quad 5559.43 \quad 5560.44 \quad 5559.67 \quad 5559.63 \quad 5564.06
\]

\[
415.71 \quad 4924.41 \quad 4926.04 \quad 4924.48 \quad 4924.92 \quad 4929.30
\]

\[
363.57 \quad 4295.28 \quad 4297.43 \quad 4295.40 \quad 4295.97 \quad 4300.72
\]

\[
311.59 \quad 3671.32 \quad 3674.02 \quad 3671.66 \quad 3671.76 \quad 3677.08
\]

\[
259.61 \quad 3050.63 \quad 3054.37 \quad 3051.43 \quad 3051.27 \quad 3056.21
\]

\[
207.65 \quad 2433.82 \quad 2436.69 \quad 2434.49 \quad 2434.23 \quad 2438.78
\]

\[
155.70 \quad 1820.67 \quad 1823.23 \quad 1821.41 \quad 1820.99 \quad 1825.16
\]

\[
103.72 \quad 1209.97 \quad 1213.24 \quad 1210.60 \quad 1209.88 \quad 1213.78
\]

\[
0.00 \quad 0.00 \quad 0.00 \quad 0.00 \quad 0.00 \quad 0.00
\]

\[
 f/\text{MHz} = 3270.0204 \quad 7290.5735 \quad 11104.1254 \quad 4612.0356 \quad 5925.0638
\]

\[
 x/\text{MHz} = 0.1442 \quad 0.5065 \quad 1.0418
\]

\[
\rho/\text{kPa} \quad T_M11 \quad T_M12 \quad T_M13 \quad T_M21 \quad T_M31
\]

\[
537.21 \quad 5556.45 \quad 5554.54 \quad 5557.45 \quad 5558.75 \quad 5556.05
\]

\[
483.56 \quad 4992.29 \quad 4991.03 \quad 4993.25 \quad 4994.27 \quad 4991.04
\]

\[
430.04 \quad 4432.44 \quad 4428.93 \quad 4432.03 \quad 4432.40 \quad 4429.84
\]

\[
376.75 \quad 3874.93 \quad 3874.21 \quad 3875.42 \quad 3876.51 \quad 3874.80
\]

\[
324.41 \quad 3319.80 \quad 3320.72 \quad 3320.40 \quad 3320.87 \quad 3319.60
\]

\[
270.19 \quad 2768.04 \quad 2767.72 \quad 2769.18 \quad 2769.74 \quad 2769.60
\]

\[
216.84 \quad 2218.00 \quad 2218.73 \quad 2218.52 \quad 2218.84 \quad 2219.62
\]

\[
163.59 \quad 1670.20 \quad 1672.70 \quad 1670.85 \quad 1671.42 \quad 1672.34
\]

\[
107.40 \quad 1094.41 \quad 1095.70 \quad 1095.19 \quad 1095.54 \quad 1096.17
\]

\[
56.18 \quad 571.78 \quad 569.25 \quad 571.66 \quad 572.24 \quad 572.78
\]

\[
28.66 \quad 291.25 \quad 291.05 \quad 291.32 \quad 291.48 \quad 292.52
\]

\[
14.38 \quad 146.12 \quad 146.29 \quad 146.78 \quad 146.07 \quad 146.75
\]

\[
7.23 \quad 73.30 \quad 73.11 \quad 73.97 \quad 73.74 \quad 73.40
\]

\[
0.00 \quad 0.00 \quad 0.00 \quad 0.00 \quad 0.00 \quad 0.00
\]

\[
 f/\text{MHz} = 3266.5517 \quad 7282.8434 \quad 11092.3862 \quad 4607.1538 \quad 5918.7596
\]

\[
x/\text{MHz} = 0.1466 \quad 0.4927 \quad 1.0552
\]
which was determined by Ewing from recent speed of sound measurements in xenon between 190 and 360 K [141] using the method described in section (5.4). The fractional uncertainty in a value of $B$ determined from equation (1) was estimated to be ±0.15 %, giving an uncertainty of ±0.5 cm$^3$ mol$^{-1}$ at 189 K and ±0.1 cm$^3$ mol$^{-1}$ at 360 K. The third virial coefficient $C$ has not been determined by Ewing from the speed of sound measurements due to the lack of well established methods of obtaining estimates of $C$ from the third acoustic virial coefficients $\gamma$, so, as with the measurements on \{0.5 Ar + 0.5 N$_2$\}, the approximation $C' = \left\{-B^2/(RT)^2\right\}$ was made in equation (5.3.2). Published measurements of $C$ for xenon are scarce, especially below 273 K, and it was felt preferable to use equation (1) for $B$, and accept the errors introduced by the approximation for $C'$, than use other published values of $B$ and $C$ which may well be less reliable and would not have covered more than half of our temperature range. However, other workers' measurements of $C$ can be used to assess the effects of the approximation for $C'$, and this will be considered later.

The same basis for rejection of modes from the final analyses was adopted for the xenon measurements as has been described in section (7.2). Those measurements neglected in the final analyses have been underlined in table (7.11). The measurements at 422, 478 and 526 kPa in the isotherm at 225 K were removed in the final analysis because there was excessive curvature in the data (especially for modes TM11 and TM12) which could not be satisfactorily accommodated by the addition of a term in $\rho^3$ in equation (7.2.9). The origin of this high pressure curvature is not known, but it was not a problem in any of the other isotherms.

For the isotherms between 189 and 273 K, and for the isotherm at 360 K, only two terms of equation (7.2.9), $A_0$ and $B_0$, were required to fit the measurements; the $A_0$ term was not statistically significant at these temperatures. For the isotherm at 315 K, the $A_0$, $A_4\rho$ and $B_4\rho^2$ terms were all significant. The second dielectric virial coefficient $B_\epsilon$ was not significant for the isotherm at 300 K, but the $A_0$ term was significant. The estimates of the first and second dielectric virial coefficients and the zero-pressure deviation terms $A_0$, along with the overall standard deviations of the fits, are given in table (7.12). The fit to the data at 300 K with $B_\epsilon$ included is also
presented in table (7.12), but, since the $B_\varepsilon$ coefficient was not significantly different from zero at the 0.995 probability level, the fit with only $\Delta_0$ and $A_\varepsilon$ has been considered in the following discussion.

The deviations $10^6\Delta((\varepsilon-1)/(\varepsilon+2)) = 10^6\{(\varepsilon-1)/(\varepsilon+2)\}_{\text{meas}} - \{(\varepsilon-1)/(\varepsilon+2)\}_{\text{fit}}$ of the individual measurements of $[(\varepsilon-1)/(\varepsilon+2)]$ from the fits are presented in figures (7.30) to (7.37); the measurements rejected in the final analyses are depicted by empty symbols. As discussed previously, the deviations in figures (7.30) to (7.37) are about three times smaller than the corresponding deviations in $\varepsilon$. In general, the measurements included in the final analyses were within three of their estimated random uncertainties [table (7.3)] of the regression lines. Mode TM31 was rejected from the final fit at 189, 300 and 315 K, whilst mode TM12 was rejected at 189, 249 and 315 K. The necessary removal of these modes is similar to the situation found in section (7.2), and is attributed, again, to the difficulties of component identification within the resonances.

Truncation errors for the isotherms with significant values of $B_\varepsilon$ were investigated by performing several fits over successively reduced ranges of molar density. In no case was there a significant change in the dielectric virial coefficients whilst $B_\varepsilon$ was required to accommodate the data, indicating that series truncation was not a significant source of error in our values of $B_\varepsilon$.

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$10^6\sigma$</th>
<th>$10^6\Delta_0$</th>
<th>$A_\varepsilon$/cm$^3$ mol$^{-1}$</th>
<th>$B_\varepsilon$/cm$^6$ mol$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>0.089</td>
<td></td>
<td>$(10.12588 \pm 0.00056)$</td>
<td>$(55.7 \pm 3.5)$</td>
</tr>
<tr>
<td>204.5894</td>
<td>0.233</td>
<td></td>
<td>$(10.1222 \pm 0.0012)$</td>
<td>$(47.4 \pm 8.0)$</td>
</tr>
<tr>
<td>224.6757</td>
<td>0.211</td>
<td></td>
<td>$(10.1380 \pm 0.0010)$</td>
<td>$(47.1 \pm 6.1)$</td>
</tr>
<tr>
<td>249.2879</td>
<td>0.216</td>
<td></td>
<td>$(10.13414 \pm 0.00081)$</td>
<td>$(41.2 \pm 3.7)$</td>
</tr>
<tr>
<td>272.9014</td>
<td>0.265</td>
<td></td>
<td>$(10.1248 \pm 0.0010)$</td>
<td>$(42.4 \pm 5.8)$</td>
</tr>
<tr>
<td>299.9935</td>
<td>0.161</td>
<td>$(0.199 \pm 0.034)$</td>
<td>$(10.13912 \pm 0.00030)$</td>
<td>$(17.0 \pm 4.5)$</td>
</tr>
<tr>
<td></td>
<td>0.143</td>
<td>$(0.286 \pm 0.038)$</td>
<td>$(10.13555 \pm 0.00099)$</td>
<td></td>
</tr>
<tr>
<td>315.2844</td>
<td>0.109</td>
<td>$(0.48 \pm 0.12)$</td>
<td>$(10.1326 \pm 0.0022)$</td>
<td>$(43.9 \pm 8.7)$</td>
</tr>
<tr>
<td>360.2599</td>
<td>0.173</td>
<td></td>
<td>$(10.13816 \pm 0.00087)$</td>
<td>$(38.3 \pm 6.0)$</td>
</tr>
</tbody>
</table>
Figure (7.30) Residuals of the \([(\varepsilon - 1)/(\varepsilon + 2)] \) on \( \rho \) regression for xenon at 188.5533K

Figure (7.31) Residuals of the \([(\varepsilon - 1)/(\varepsilon + 2)] \) on \( \rho \) regression for xenon at 204.5894K
Figure (7.32) Residuals of the \([\varepsilon - 1]/(\varepsilon + 2)\) on \(\rho\) regression for xenon at 224.6757K.

Figure (7.33) Residuals of the \([\varepsilon - 1]/(\varepsilon + 2)\) on \(\rho\) regression for xenon at 249.2879K.
Figure (7.34) Residuals of the \( [(\varepsilon - 1)/(\varepsilon + 2)] \) on \( \rho \) regression for xenon at 272.9014K.

Figure (7.35) Residuals of the \( [(\varepsilon - 1)/(\varepsilon + 2)] \) on \( \rho \) regression for xenon at 299.9935K.
Figure (7.36) Residuals of the \([\varepsilon-1]/(\varepsilon+2)\) on \(\rho\) regression for xenon at 315.2844K

![Figure 7.36](image)

Figure (7.37) Residuals of the \([\varepsilon-1]/(\varepsilon+2)\) on \(\rho\) regression for xenon at 360.2599K

![Figure 7.37](image)
Xenon is an atomic gas and so we did not expect the measurements of $A_\varepsilon$ to be systematically dependent on temperature. This was confirmed by both weighted and unweighted least-squares regressions on the values of $A_\varepsilon$ given in table (7.12). A weighted regression on all eight measurements, where the values were weighted as $[1/\sigma(A_\varepsilon)]^2$, gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (10.1091 \pm 0.0083) + (9.5 \pm 3.0) \times 10^{-3} (T / K) \quad (7.3.2)$$

with an overall weighted standard deviation of 0.0020 cm$^3$ mol$^{-1}$, whilst an unweighted regression gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (10.115 \pm 0.010) + (6.6 \pm 3.8) \times 10^{-3} (T / K) \quad (7.3.3)$$

with an overall standard deviation of 0.0059 cm$^3$ mol$^{-1}$. The temperature-dependent term in equation (2) was only significant at the 0.98 probability level and that of equation (3) was not significant even at the 0.95 probability level. The estimate of $A_\varepsilon$ at 300 K came from a linear fit [(\Delta_{\theta} + A_\varepsilon \varphi) only] to equation (7.2.9) and had a much smaller standard deviation, and correspondingly larger weight in the weighted regression, than the estimates of $A_\varepsilon$ at the other temperatures, even though it was much more likely to be suffering from truncation error. Leaving $A_\varepsilon(300 \text{ K})$ out of the fit, the weighted least-squares regression gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (10.1148 \pm 0.0082) + (6.4 \pm 3.3) \times 10^{-3} (T / K) \quad (7.3.4)$$

with an overall weighted standard deviation of 0.0032 cm$^3$ mol$^{-1}$, whilst the unweighted regression gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (10.116 \pm 0.011) + (5.7 \pm 4.0) \times 10^{-3} (T / K) \quad (7.3.5)$$

with an overall standard deviation of 0.0060 cm$^3$ mol$^{-1}$. Neither of the temperature-dependent terms in equations (4) and (5) was statistically significant, even at the 0.95 probability level, and so the best estimate of $A_\varepsilon$ for xenon between 189 and 360 K was given by the mean of the all the values except that at 300 K. The weighted mean was $(10.1305 \pm 0.0028)$ cm$^3$ mol$^{-1}$, which was in excellent agreement with the unweighted mean of $(10.1308 \pm 0.0065)$ cm$^3$ mol$^{-1}$. If $A_\varepsilon(300 \text{ K})$ had been included, then the weighted and unweighted means would have been $(10.1352 \pm 0.0010)$ cm$^3$ mol$^{-1}$ and $(10.1319 \pm 0.0067)$ cm$^3$ mol$^{-1}$, respectively, which were in poorer agreement than the means obtained when $A_\varepsilon(300 \text{ K})$ was neglected.
The deviations $\Delta A_e = (A_e - 10.1305 \text{ cm}^3 \text{ mol}^{-1})$ of the individual measurements of $A_e$ from the weighted mean of $(10.1305 \pm 0.0028) \text{ cm}^3 \text{ mol}^{-1}$ are shown in figure (7.38). Also shown is the only measurement of $A_e$ for xenon published in the literature [94]. The error bars on our measurements in figure (7.38) are the single standard deviations of $A_e$ from the regressions only. There was considerably larger scatter in our measurements of $A_e$ for xenon than was found for argon, even for temperatures where the order of fit in the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression was the same. This was partly caused by the approximation for $C'$ used in the regressions.

The error in $A_e$ caused by neglecting $C$ in the calculation of $C'$ was assessed by refitting the data at 273, 300, 315 and 360 K using values of $C$ estimated from a graphical interpolation of the measurements of Michels, Wassenaar and Louwerse [142] between 273.15 and 423.15 K. The values of $C$ used were 6255, 6432, 5741 and 4159 cm$^3$ mol$^{-1}$ at 273, 300, 315 and 360 K, respectively, and were estimated to be accurate to 300 cm$^3$ mol$^{-1}$. In the new fits, $A_e$ had changed by $-0.0013$, $+0.0027$, $-0.0022$ and $-0.0006$ cm$^3$ mol$^{-1}$ at 273, 300, 315 and 360 K, respectively. Hence, the neglect of $C$ gave rise to errors in $A_e$ of the magnitude of 0.001 to 0.003 cm$^3$ mol$^{-1}$, and this partly explains the large scatter observed because the error was different at each temperature. The contribution to the total uncertainty in a value of $A_e$ from the ±0.15% uncertainty in $B$ was found to be always smaller than ±0.00005 cm$^3$ mol$^{-1}$, and so was not responsible for a significant part of the scatter. There were apparently, then, some unidentified systematic errors in our measurements of $A_e$ for xenon, helping to give rise to the large scatter. However, these were included in the weighted standard deviation of the weighted mean, and so our best estimate of $A_e$ for xenon between 189 and 360 K was $(10.1305 \pm 0.0028) \text{ cm}^3 \text{ mol}^{-1}$. None of the individual measurements of $A_e$ deviated by more than $(3 \times 0.0028) \text{ cm}^3 \text{ mol}^{-1}$ from the weighted mean.
Figure (7.38) Deviations of measurements of $A_e$ for xenon from our weighted mean of 10.1305 cm$^3$ mol$^{-1}$

The only determination of $A_e$ for xenon published in the literature is that of Huot and Bose [94], which was $(10.122 \pm 0.002)$ cm$^3$ mol$^{-1}$ at 323.15 K. Although this is only 0.084% smaller than our best estimate (and such a difference represents only 1.8 combined uncertainties), the published measurement was determined from a two-term fit to equation (5.5.11), and the estimate of $B$ obtained from the fit was 17.5 cm$^3$ mol$^{-1}$ more negative than the value given by equation (1). This suggests that the published value of $A_e$ is too small, giving rise to the highly negative estimate of $B$. Further, Huot and Bose's result came from a single isotherm with a minimum pressure of about 350 kPa, which is considerably greater than our lowest pressures, and so there is doubt as to whether their $A_e$ truly represents the required limiting value.

The second dielectric virial coefficients from table (7.12) are presented graphically in figure (7.39). Also shown are the measurements of Huot and Bose.
[94] at 242.95, 323.15 and 407.6 K, which are the only values for xenon published in the literature to date, and were determined using Buckingham's differential expansion method [104]. The error bars on all the measurements in figure (7.39) are just the single standard deviations arising from the individual least-squares regressions.

The results of Huot and Bose at 242.95 and 323.15 K differed from our measurements at the nearby temperatures of 249 and 315 K by just 1.1 combined standard deviations. This represents good agreement given the considerable differences between the experimental methods used, and is particularly pleasing because Huot and Bose's $B_e$ at 323.15 K comes from data which extended to sufficiently high densities that the third virial coefficient $C_e = (-3482 \pm 310) \text{ cm}^3 \text{ mol}^{-1}$ was also determined, and so was unlikely to be suffering from significant series truncation error. Huot and Bose's measurement at 407.6 K is 20 cm$^6$ mol$^{-2}$ smaller than their measurement at 323.15 K, despite also arising from data for which a significant value of $C_e [(-1164 \pm 437) \text{ cm}^3 \text{ mol}^{-3}]$ was determined, and if the limited temperature-dependence of $B_e$ indicated by their measurements at 242.95 and 323.15 K was correct then their result at 407.6 K was in error by about 17 cm$^6$ mol$^{-2}$. Such a large error indicates that the standard deviations reported by Huot and Bose were a serious underestimate of the 'true' uncertainties of their measurements ($\pm 5$ to $\pm 10$ cm$^6$ mol$^{-2}$ would appear to be much more realistic, and would be similar to our standard deviations). Our value for $B_e$ at 189 K was, perhaps, too high by about 8 cm$^6$ mol$^{-2}$, given the trend of the other measurements, but such an error was only 2.3 standard deviations.

The contribution to the total uncertainty in each of our $B_e$ values due to the uncertainty in the second virial coefficient used to determine the amount-of-substance densities varied between $\pm 5.8$ cm$^6$ mol$^{-2}$ at 189 K and $\pm 1.1$ cm$^6$ mol$^{-2}$ at 360 K. The errors in our values of $B_e$ caused by neglecting the third virial coefficient $C$ in calculating the amount-of-substance densities were assessed by refitting the data at 273, 315 and 360 K using the estimates of $C$ determined from the measurements reported by Michels, Wassenaar and Louwerse [142]. In the new fits, $B_e$ was 61.1 cm$^6$ mol$^{-2}$ at 273 K, 64.6 cm$^6$ mol$^{-2}$ at 315 K, and 48.8 cm$^6$ mol$^{-2}$ at 360 K.
Therefore, the inclusion of $C$ significantly increased $B_\varepsilon$ at these temperatures and so worsened the agreement between our measurements and those of Huot and Bose. However, at the lowest isotherm temperatures $C$ is likely to be negative and so the agreement between our measurements and those of Huot and Bose would be more likely to improve.

Figure (7.39) The second dielectric virial coefficients of xenon

The theoretical expression of $B_\varepsilon$ for pure, atomic gases is given by equation (5.5.7). Using a dipole-induced dipole (DID) model [see section (5.5)], the incremental polarisability can be approximated by [85, 89]

$$\left( \alpha_{12} - 2\alpha \right) = \frac{4\alpha^3}{r^6}$$  \hspace{1cm} (7.3.6)

where it has been assumed that the atomic polarisability $\alpha$ is independent of the separation $r$ of a pair of atoms. If a Lennard-Jones (12-6) potential of the form
\[ U_{12}(r) = 4 \epsilon \left[ \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right] \]  

(7.3.7)

is assumed, then the integral in equation (5.5.7) can be evaluated and \( B_\epsilon \) is given by

\[
B_\epsilon = \frac{N_A^2}{18 \left( 4 \pi \epsilon_0 \right) \epsilon_0^2 \gamma_0} \left( \frac{\alpha}{r_0} \right)^3 \frac{H_6(y)}{y^4}
\]  

(7.3.8)

In equation (8), \( N_A \) is Avagadro’s number, \( \epsilon_0 \) is the permittivity of free space, \( y = 2 \sqrt{\left( \frac{\epsilon}{k T} \right)} \), where \( k \) is Boltzmann’s constant, and \( H_6(y) \) is a function whose value has been tabulated by Buckingham and Pople [143] for \( 0.6 \leq y \leq 3.2 \). The atomic polarisability for xenon was calculated to be \( \alpha = (4.4682 \pm 0.0012) \times 10^{-40} \) C^2 m^2 J^1 by substituting our weighted mean \( \Lambda_e = (10.1305 \pm 0.0028) \) cm^3 mol^-1 into equation (5.5.5). The values \( (\epsilon/k) = 229.0 \) K and \( r_0 = 4.055 \times 10^{-10} \) m were taken from reference 84. Equation (8) was used to calculate \( B_\epsilon \) for xenon at all eight isotherm temperatures and the results are given in table (7.13). Equation (8) is also compared with the experimental results in figure (7.39).

Table (7.13) Theoretical second dielectric virial coefficients of xenon, \( B_\epsilon(\text{calc.}) \), and the differences between the experimental results, \( B_\epsilon(\text{expt.}) \), and the theoretical values

<table>
<thead>
<tr>
<th>T/K</th>
<th>( B_\epsilon(\text{calc.})/\text{cm}^6 \text{ mol}^{-2} )</th>
<th>( [\text{B}<em>\epsilon(\text{expt.})-\text{B}</em>\epsilon(\text{calc.})]/\text{cm}^6 \text{ mol}^{-2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>26.70</td>
<td>29.00</td>
</tr>
<tr>
<td>204.5894</td>
<td>25.16</td>
<td>22.24</td>
</tr>
<tr>
<td>224.6757</td>
<td>23.70</td>
<td>23.40</td>
</tr>
<tr>
<td>249.2879</td>
<td>22.37</td>
<td>18.83</td>
</tr>
<tr>
<td>272.9014</td>
<td>21.36</td>
<td>21.04</td>
</tr>
<tr>
<td>299.9935</td>
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<td>N/A</td>
</tr>
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<td>20.19</td>
<td>23.71</td>
</tr>
<tr>
<td>360.2599</td>
<td>19.31</td>
<td>18.99</td>
</tr>
</tbody>
</table>
Our measurements were systematically higher than the calculated values of $B_e$, typically by about $20 \text{ cm}^6 \text{ mol}^{-2}$, but showed a very similar temperature-dependence. The results of Huot and Bose at 242.95 and 323.15 K were also higher than the calculated values, by about $12 \text{ cm}^6 \text{ mol}^{-2}$, but their $B_e$ at 407.6 K was much closer to the theoretical value, being just $6.7 \text{ cm}^6 \text{ mol}^{-2}$ smaller. However, since Huot and Bose's result at 407.6 K was suspected of being in serious error, the agreement between the experimental results and equation (8) was generally poor.

It is clear that equation (8) always gives a positive $B_e$ and yet this is not in accordance with the negative measurements of $B_e$ for helium and neon [94, 100]. Even though the measured values of $B_e$ for xenon were positive, the agreement with the DID theory has been shown to be unsatisfactory. The discrepancies occurred because the DID model is concerned with only one of a number of contributions to $B_e$. The DID model takes no account of the dispersion-type effect of the change in polarisability of one molecule in the presence of another and the short-range, 'electron exchange' contribution which arises due to the overlap of orbitals of two molecules in close proximity. These additional effects may be taken into account by using the following expression for the incremental polarisability [89]:

$$\left( \alpha_{12} - 2\alpha \right) = \frac{4\alpha^3}{r^5} - \frac{5\gamma C_6}{9\alpha r^6} - \lambda_i \exp\left(-r/r_f\right)$$  \hspace{1cm} (7.3.9)

where $\gamma$ is the second hyperpolarisability, $C_6$ is the dispersion force constant (which is negative by definition), and $\lambda_i$ and $r_f$ are fitting parameters whose values describe the electronic overlap and exchange effects; all these parameters may be determined from \textit{ab initio} calculations or from the polarised part of the collision-induced Raman spectra (CIS) [144]. The first and second terms of equation (9) make positive contributions to $B_e$, while the third term makes a negative contribution and is the term that dominates in smaller systems and therefore gives rise to the negative values of $B_e$ for helium and neon [94, 100]. By including the DID and dispersive contributions, and using the Self-Consistent Field (SCF) method for approximating the short-range effects, Dacre [145] calculated the second dielectric virial coefficient of xenon at 322 K to be $21.6 \text{ cm}^6 \text{ mol}^{-2}$. This is only $1.5 \text{ cm}^6 \text{ mol}^{-2}$ larger than the DID contribution alone, calculated from equation (8), and so it is not expected that
the inclusion of dispersive and short-range effects in calculating $B_e$ would significantly improve the agreement between the experimental and theoretical values. Achtermann et al. [93] have noted that the inclusion of higher-order positive terms in the DID expansion would help improve the accuracy of calculated values of the second refractivity virial coefficient $B_n$, and the same is true for $B_e$.

(p, $V_m$, $T$) virial coefficients

The experimental values of $\varepsilon$ were also fitted to equations (7.2.10) and (5.5.13) using least-squares regressions, exactly as described for the Ar, N$_2$ and {0.5 Ar + 0.5 N$_2$} data in section (7.2). The same weighting schemes were used, and, adopting the previously described method for deciding which points were rejected from the final analyses, the same data were removed from the fits to equations (7.2.10) and (5.5.13) as had been removed for the $\rho$ fits.

For the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ regressions, $A_\varepsilon$, $B'_\varepsilon$ and $C'_\varepsilon$ were required to fit the measurements between 189 and 300 K. The $C'_\varepsilon(p/RT)^2$ term was not significant, even at the 0.95 probability level, for the measurements at 315 and 360 K, but these fits were chosen in the final analyses because the $B'_\varepsilon$ values would be less likely to suffer from serious truncation error and the fits would be more comparable across the entire temperature range. The $\Delta_\varepsilon$ term was significant only for the isotherms at 300 and 315 K, exactly as was found for the $\rho$ fits. The estimates of the $A_\varepsilon$, $B'_\varepsilon$ and $C'_\varepsilon$ coefficients are given in table (7.14), along with the overall standard deviations of the fits. Also included for comparison in table (7.14) are the results of the fits, at 315 and 360 K, without the $C'_\varepsilon(p/RT)^2$ terms. The residuals from each of the $(p/RT)$ regressions were, again, essentially the same as those for the $\rho$ fits to the same data, despite the changes in the order of fit, and so are not reproduced here (the residuals of the fits to the measurements at 315 and 360 K were virtually unchanged when the $C'_\varepsilon(p/RT)^2$ term was included).

For the $[(\varepsilon - 1)/(\varepsilon + 2)]$ RT/$p$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions, $A_\varepsilon$, $B''_\varepsilon$ and $C''_\varepsilon$ were required to fit the measurements at 189 to 249 K and at 300 and 315 K. The $C''_\varepsilon[(\varepsilon - 1)/(\varepsilon + 2)]^2$ term was not significant, even at the 0.95 probability level, for the isotherms at 273 and 360 K, but, again, such fits were chosen for the final
analyses to improve consistency across the temperature range and reduce truncation errors. There was no possibility of a $\Delta_q$ term in any of the regressions to equation (5.5.13), and the effect of this on the virial coefficients for the isotherms at 300 and 315 K, for which the $\Delta_q$ term had been significant in the $\rho$ and ($p/RT$) fits, will be considered in due course. The estimates of the $A_\alpha$, $B''_\varepsilon$ and $C''_\varepsilon$ coefficients are given in table (7.15), along with the overall standard deviations of the fits. The results of the fits without the $C''_\varepsilon[(\varepsilon - 1)/(\varepsilon + 2)]^2$ terms, at 273 and 360 K, are also given in the table. The residuals from each of the regressions were essentially the same as those for the ($p/RT$) fits to the same data, but each scaled by a factor of $(RT/p)$.

To investigate the effects on the coefficients $B''_\varepsilon$ of series truncation and the pressure range used, the isotherm data was also analysed using a number of two term fits $\{A_\varepsilon + B''_\varepsilon[(\varepsilon - 1)/(\varepsilon + 2)]\}$ only over successively reduced pressure ranges, exactly as described in section (7.2). Such an analysis gave the mean value of gradient over each of the reduced pressure ranges, but the required quantity was the limiting value, and this was given for each isotherm by

$$\lim_{(\varepsilon) \to 0} \left\{ \frac{\partial}{\partial Z} \left[ \frac{RT}{p} \right] \right\},$$

where $(\varepsilon)$ was the average value of $Z = [(\varepsilon - 1)/(\varepsilon + 2)]$ for a reduced data set. For all the isotherms between 189 and 315 K, the mean gradient showed approximately linear dependence on $(\varepsilon)$ and their limiting values are given in table (7.16). For the isotherm at 360 K, the mean gradient showed no significant dependence on $(\varepsilon)$ and so the best estimate of the limiting value was given by the mean of the gradients of the successively reduced data sets, and this is also given in table (7.16). The limiting values of gradient derived from the two term fits were in very good agreement with the values of $B''_\varepsilon$ from the three term fits [given in table (7.15)] at 189 to 273 K and at 360 K, but in much poorer agreement at 300 and 315 K. This indicated that truncation error was not significant in the values of $B''_\varepsilon$ determined in the three term fits (as would be expected given the inclusion of a $C''_\varepsilon$ term) at 189 to 273 K and at 360 K, but that there was some systematic error in the values at 300 and 315 K. The source of this error was likely to have been the same as that which led to the requirement for $\Delta_q$ terms in the $\rho$ and ($p/RT$) fits at 300 and 315 K.
Table (7.14) Coefficients from the $\frac{(\varepsilon - 1)}{(\varepsilon + 2)}$ on $(p/RT)$ regressions for xenon

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$10^4\sigma$</th>
<th>$10^4\Delta_0$</th>
<th>$A^\varepsilon$/cm$^3$ mol$^{-1}$</th>
<th>$B^\varepsilon$'/cm$^6$ mol$^{-1}$</th>
<th>$10^4C^\varepsilon$'/cm$^9$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>0.088</td>
<td></td>
<td>(10.1298 ± 0.0015)</td>
<td>(3072 ± 24)</td>
<td>(2.472 ± 0.089)</td>
</tr>
<tr>
<td>204.5894</td>
<td>0.280</td>
<td></td>
<td>(10.1305 ± 0.0020)</td>
<td>(2548 ± 20)</td>
<td>(2.200 ± 0.045)</td>
</tr>
<tr>
<td>224.6757</td>
<td>0.213</td>
<td></td>
<td>(10.1403 ± 0.0027)</td>
<td>(2231 ± 41)</td>
<td>(1.24 ± 0.15)</td>
</tr>
<tr>
<td>249.2879</td>
<td>0.218</td>
<td></td>
<td>(10.1345 ± 0.0021)</td>
<td>(1860 ± 24)</td>
<td>(0.766 ± 0.066)</td>
</tr>
<tr>
<td>272.9014</td>
<td>0.265</td>
<td></td>
<td>(10.1276 ± 0.0030)</td>
<td>(1537 ± 42)</td>
<td>(0.66 ± 0.14)</td>
</tr>
<tr>
<td>299.9935</td>
<td>0.141</td>
<td>(0.240 ± 0.047)</td>
<td>(10.1394 ± 0.0025)</td>
<td>(1249 ± 28)</td>
<td>(0.498 ± 0.086)</td>
</tr>
<tr>
<td>315.2844</td>
<td>0.110</td>
<td>(0.82 ± 0.12)</td>
<td>(10.1214 ± 0.0023)</td>
<td>(1308.7 ± 9.3)</td>
<td>(0.19 ± 0.22)</td>
</tr>
<tr>
<td>360.2599</td>
<td>0.176</td>
<td></td>
<td>(10.1358 ± 0.00090)</td>
<td>(963.4 ± 6.3)</td>
<td>(0.23 ± 0.14)</td>
</tr>
</tbody>
</table>

Table (7.15) Coefficients from the $\frac{(\varepsilon - 1)}{(\varepsilon + 2)}RT/p$ on $\frac{(\varepsilon - 1)}{(\varepsilon + 2)}$ regressions for xenon

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$\sigma$/cm$^3$ mol$^{-1}$</th>
<th>$A^\varepsilon$/cm$^3$ mol$^{-1}$</th>
<th>$B^\varepsilon$'/cm$^6$ mol$^{-1}$</th>
<th>$10^3C^\varepsilon$'/cm$^9$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>0.0007</td>
<td>(10.1277 ± 0.0013)</td>
<td>(309.6 ± 1.9)</td>
<td>(9.43 ± 0.68)</td>
</tr>
<tr>
<td>204.5894</td>
<td>0.0012</td>
<td>(10.1232 ± 0.0015)</td>
<td>(264.9 ± 1.3)</td>
<td>(7.97 ± 0.28)</td>
</tr>
<tr>
<td>224.6757</td>
<td>0.0018</td>
<td>(10.1395 ± 0.0025)</td>
<td>(222.5 ± 3.6)</td>
<td>(5.2 ± 1.2)</td>
</tr>
<tr>
<td>249.2879</td>
<td>0.0014</td>
<td>(10.1335 ± 0.0019)</td>
<td>(185.6 ± 2.1)</td>
<td>(2.79 ± 0.55)</td>
</tr>
<tr>
<td>272.9014</td>
<td>0.0022</td>
<td>(10.1201 ± 0.0011)</td>
<td>(162.97 ± 0.60)</td>
<td>(3.2 ± 1.2)</td>
</tr>
<tr>
<td>299.9935</td>
<td>0.0016</td>
<td>(10.1489 ± 0.0019)</td>
<td>(114.9 ± 2.5)</td>
<td>(5.09 ± 0.77)</td>
</tr>
<tr>
<td>315.2844</td>
<td>0.0009</td>
<td>(10.1462 ± 0.0019)</td>
<td>(107.7 ± 2.7)</td>
<td>(4.08 ± 0.93)</td>
</tr>
<tr>
<td>360.2599</td>
<td>0.0017</td>
<td>(10.13708 ± 0.00087)</td>
<td>(92.86 ± 0.59)</td>
<td>(1.3 ± 1.3)</td>
</tr>
</tbody>
</table>

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Table (7.16) Limiting values of gradient for the two-term fits of the

\[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \frac{RT}{p} \] on \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \] regressions for xenon

<table>
<thead>
<tr>
<th>T/K</th>
<th>Limiting Gradient/cm^6 mol^{-2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>(308.76 ± 0.86)</td>
</tr>
<tr>
<td>204.5894</td>
<td>(265.6 ± 1.2)</td>
</tr>
<tr>
<td>224.6757</td>
<td>(220.37 ± 0.84)</td>
</tr>
<tr>
<td>249.2879</td>
<td>(182.42 ± 0.94)</td>
</tr>
<tr>
<td>272.9014</td>
<td>(153.04 ± 0.66)</td>
</tr>
<tr>
<td>299.9935</td>
<td>(107.1 ± 1.8)</td>
</tr>
<tr>
<td>315.2844</td>
<td>(83.4 ± 2.4)</td>
</tr>
<tr>
<td>360.2599</td>
<td>(89.3 ± 3.8)</td>
</tr>
</tbody>
</table>

The estimates of \( A_\varepsilon \) from the three sets of regressions carried out on the xenon isotherms are compared in table (7.17). The values from the \( \rho \) and \( (p/RT) \) regressions were in good agreement, the differences always being less than three combined standard deviations. The largest difference, at 205 K, came from an isotherm for which there is some evidence that the \( (p/RT) \) fit was in error (as will be discussed), and yet the difference in \( A_\varepsilon \) for this isotherm was still only 2.6 combined standard deviations. The estimates of \( A_\varepsilon \) from the \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \frac{RT}{p} \] on \( \rho \) regressions and those from the \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \frac{RT}{p} \] on \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \] regressions were in even better agreement, apart from the isotherms at 300 and 315 K where the large differences between the \( A_\varepsilon \) values were caused by the lack of a \( \Delta_\rho \) term for the \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \frac{RT}{p} \] on \[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} \] regressions.
Table (7.17) Differences between the estimates of the first dielectric virial coefficients arising from the three different regressions for xenon

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$[A_e(2) - A_e(1)]/\text{cm}^3 \text{ mol}^{-1}$</th>
<th>$[A_e(3) - A_e(1)]/\text{cm}^3 \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>0.0039</td>
<td>0.0018</td>
</tr>
<tr>
<td>204.5894</td>
<td>0.0083</td>
<td>0.0010</td>
</tr>
<tr>
<td>224.6757</td>
<td>0.0023</td>
<td>0.0015</td>
</tr>
<tr>
<td>249.2879</td>
<td>0.0004</td>
<td>-0.0006</td>
</tr>
<tr>
<td>272.9014</td>
<td>0.0028</td>
<td>0.0023</td>
</tr>
<tr>
<td>299.9935</td>
<td>0.0003</td>
<td>0.0098</td>
</tr>
<tr>
<td>315.2844</td>
<td>-0.0039</td>
<td>0.0136</td>
</tr>
<tr>
<td>360.2599</td>
<td>0.0008</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

$A_e(1)$: first dielectric virial coefficient from the $\rho$ regression

$A_e(2)$: first dielectric virial coefficient from the $(\rho/RT)$ regression

$A_e(3)$: first dielectric virial coefficient from the $[(\varepsilon - 1)/(\varepsilon + 2)]RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regression

The weighted mean value of $A_\varepsilon$ from the $(\rho/RT)$ fits was $(10.1336 \pm 0.0018) \text{ cm}^3 \text{ mol}^{-1}$, which was in excellent agreement with the weighted mean of $(10.1339 \pm 0.0037) \text{ cm}^3 \text{ mol}^{-1}$ from the $[(\varepsilon - 1)/(\varepsilon + 2)]RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions. The weighted mean from the $(\rho/RT)$ fits only increased by 0.0006 cm$^3$ mol$^{-1}$ if the value at 205 K was left out, whilst that from the $[(\varepsilon - 1)/(\varepsilon + 2)]RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions became $(10.1298 \pm 0.0030) \text{ cm}^3 \text{ mol}^{-1}$ if the measurements at 300 and 315 K were removed. All of these weighted mean values for $A_\varepsilon$ agreed with the weighted mean of $(10.1305 \pm 0.0028) \text{ cm}^3 \text{ mol}^{-1}$ determined from the $\rho$ fits (neglecting $A_\varepsilon$ at 300 K), within their combined standard deviations. However, there was particularly good agreement between the weighted mean obtained from the $[(\varepsilon - 1)/(\varepsilon + 2)]RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions if the measurements at 300 and 315 K were not included [i.e., $(10.1298 \pm 0.0030) \text{ cm}^3 \text{ mol}^{-1}$], and the weighted mean determined from the $\rho$ fits if the measurement at 300 K was neglected [i.e., $(10.1305 \pm 0.0028) \text{ cm}^3 \text{ mol}^{-1}$].
Since it was necessary to neglect $C$ in the calculations of $\rho$ for the molar density fits described earlier, it was interesting to compare the estimates of $B_\varepsilon$ that may be obtained from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ regressions, and those from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions, with the estimates of $B_\varepsilon$ from the $\rho$ fits. The estimates of $B_\varepsilon$ from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ regressions and the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions are given in table (7.18). These estimates were obtained by combining the values of the second $(p, V_m, T)$ virial coefficients $B$ from equation (1) with the coefficients $A_\varepsilon$ and $B_\varepsilon' = (B_\varepsilon - A_\varepsilon B)$, and $A_\varepsilon$ and $B_\varepsilon^* = [(B_\varepsilon - A_\varepsilon B)/A_\varepsilon]$, taken from tables (7.14) and (7.15), respectively.

The estimates of $B_\varepsilon$ from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ regressions and the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions always had much larger standard deviations than those determined from the $\rho$ fits because they were determined from regressions with higher orders of fit, and it is a general observation that the greater the number of terms included in a virial expansion, the larger the random uncertainties in the coefficients.

The estimates of $B_\varepsilon$ obtained from the $(p/RT)$ fits were generally in very poor agreement with those from the $\rho$ fits. However, ignoring the measurements at 300 and 315 K where the lack of $\Delta_0$ terms clearly gave rise to systematic error, the values of $B_\varepsilon$ from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions differed from those obtained from the $\rho$ fits by less than 1.1 combined standard deviations. Although such agreement was pleasing, it was only so because of the large standard deviations of the $B_\varepsilon$ values from the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions, and none of these values was considered to be significantly different from zero. However, the results of the $\rho$ fits were clearly more consistent with the results of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ $RT/\rho$ on $[(\varepsilon - 1)/(\varepsilon + 2)]$ regressions than with those of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ regressions, for those isotherms where $\Delta_0$ terms were not significant.
Table (7.18) Estimates of the second dielectric virial coefficients arising from the three different regressions for xenon

<table>
<thead>
<tr>
<th>T/K</th>
<th>$B_1(1)$/cm$^4$mol$^{-2}$</th>
<th>$B_1(2)$/cm$^4$mol$^{-2}$</th>
<th>$B_1(3)$/cm$^4$mol$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>(55.7 ± 3.5)</td>
<td>(-32 ± 25)</td>
<td>(32 ± 19)</td>
</tr>
<tr>
<td>204.5894</td>
<td>(47.4 ± 8.0)</td>
<td>(-109 ± 20)</td>
<td>(26 ± 13)</td>
</tr>
<tr>
<td>224.6757</td>
<td>(47.1 ± 6.1)</td>
<td>(2 ± 41)</td>
<td>(27 ± 37)</td>
</tr>
<tr>
<td>249.2879</td>
<td>(41.2 ± 3.7)</td>
<td>(30 ± 24)</td>
<td>(51 ± 21)</td>
</tr>
<tr>
<td>272.9014</td>
<td>(42.4 ± 5.8)</td>
<td>(-2 ± 42)</td>
<td>(10 ± 38)</td>
</tr>
<tr>
<td>299.9935</td>
<td>N/A</td>
<td>(-34 ± 28)</td>
<td>(-118 ± 25)</td>
</tr>
<tr>
<td>315.2844</td>
<td>(43.9 ± 8.7)</td>
<td>(79 ± 78)</td>
<td>(-70 ± 27)</td>
</tr>
<tr>
<td>360.2599</td>
<td>(38.3 ± 6.0)</td>
<td>(22 ± 36)</td>
<td>(24 ± 34)</td>
</tr>
</tbody>
</table>

$B_1(1)$: $B_1$ from the $\rho$ regression  
$B_1(2)$: $B_1$ from the $(p/RT)$ regression  
$B_1(3)$: $B_1$ from the $[(\epsilon - 1)/(\epsilon + 2)]\ RT/p$ on $[(\epsilon - 1)/(\epsilon + 2)]$ regression

Estimates of the second ($p$, $V_m$, $T$) virial coefficients $B^{\text{est}}$ were calculated from the coefficients $B_1' = B_1 - A_1 B$ and $B_1'' = \left( B_1 - A_1 B \right) / A_1$, given in tables (7.19) and (7.20) respectively, in a similar way to that described in section (7.2), but rather than simply neglect the contributions to $B_1'$ and $B_1''$ from the second dielectric virial coefficients [as was done for Ar, N$_2$ and {0.5 Ar + 0.5 N$_2$}], the theoretical values of $B_1$ from table (7.13) were used because the potential errors in $B^{\text{est}}$ caused by neglecting $B_1$ were more significant for xenon (the potential errors in $B^{\text{est}}$ were on the order of 2 cm$^3$ mol$^{-1}$). As can be seen from tables (7.19) and (7.20), the $B^{\text{est}}$ values from the $(p/RT)$ fits differed from those derived from the $[(\epsilon - 1)/(\epsilon + 2)]\ RT/p$ on $[(\epsilon - 1)/(\epsilon + 2)]$ regressions by less than one combined standard deviation at 225, 249, 273 and 360 K, and by less than two combined standard deviations at 189 K. The larger discrepancies at 300 and 315 K can be explained by the lack of $\Delta_0$ terms in the $[(\epsilon - 1)/(\epsilon + 2)]\ RT/p$ on $[(\epsilon - 1)/(\epsilon + 2)]$ regressions. The $B^{\text{est}}$ from the $(p/RT)$ fit at 205 K was significantly less negative than that from the $[(\epsilon - 1)/(\epsilon + 2)]\ RT/p$ on $[(\epsilon - 1)/(\epsilon + 2)]$ regression at the same temperature, presumably because $A_1$ was significantly larger in the $(p/RT)$ fit.
Table (7.19) Estimated second and third \((p, V_m, T)\) virial coefficients determined from the \([(\epsilon - 1)/(\epsilon + 2)]\) on \((p/RT)\) regressions for xenon

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(B_e^{\text{DID}}/\text{cm}^6\text{ mol}^{-2})</th>
<th>(B_e^{\text{est}}/\text{cm}^3\text{ mol}^{-1})</th>
<th>(10^4C_e^{\text{est}}/\text{cm}^6\text{ mol}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>26.70</td>
<td>(-300.6 ± 2.3)</td>
<td>(-6.17 ± 0.90)</td>
</tr>
<tr>
<td>204.5894</td>
<td>25.16</td>
<td>(-249.0 ± 2.0)</td>
<td>(-9.19 ± 0.45)</td>
</tr>
<tr>
<td>224.6757</td>
<td>23.70</td>
<td>(-217.7 ± 4.0)</td>
<td>(-2.6 ± 1.5)</td>
</tr>
<tr>
<td>249.2879</td>
<td>22.37</td>
<td>(-181.3 ± 2.3)</td>
<td>(-0.90 ± 0.86)</td>
</tr>
<tr>
<td>272.9014</td>
<td>21.36</td>
<td>(-149.7 ± 4.1)</td>
<td>(-1.8 ± 1.4)</td>
</tr>
<tr>
<td>299.9935</td>
<td>20.74</td>
<td>(-121.1 ± 2.7)</td>
<td>(-1.93 ± 0.86)</td>
</tr>
<tr>
<td>315.2844</td>
<td>20.19</td>
<td>(-120.4 ± 7.6)</td>
<td>(+1.1 ± 2.2)</td>
</tr>
<tr>
<td>360.2599</td>
<td>19.31</td>
<td>(-87.5 ± 3.5)</td>
<td>(-0.7 ± 1.4)</td>
</tr>
</tbody>
</table>

Table (7.20) Estimated second and third \((p, V_m, T)\) virial coefficients determined from the \([(\epsilon - 1)/(\epsilon + 2)]\) \(RT/p\) on \([(\epsilon - 1)/(\epsilon + 2)]\) regressions for xenon

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(B_e^{\text{DID}}/\text{cm}^6\text{ mol}^{-2})</th>
<th>(B_e^{\text{est}}/\text{cm}^3\text{ mol}^{-1})</th>
<th>(10^4C_e^{\text{est}}/\text{cm}^6\text{ mol}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>188.5533</td>
<td>26.70</td>
<td>(-307.0 ± 1.9)</td>
<td>(+0.0348 ± 0.0025)</td>
</tr>
<tr>
<td>204.5894</td>
<td>25.16</td>
<td>(-262.4 ± 1.3)</td>
<td>(-1.051 ± 0.037)</td>
</tr>
<tr>
<td>224.6757</td>
<td>23.70</td>
<td>(-220.2 ± 3.6)</td>
<td>(-0.322 ± 0.074)</td>
</tr>
<tr>
<td>249.2879</td>
<td>22.37</td>
<td>(-183.4 ± 2.1)</td>
<td>(+0.62 ± 0.12)</td>
</tr>
<tr>
<td>272.9014</td>
<td>21.36</td>
<td>(-150.9 ± 3.8)</td>
<td>(-0.90 ± 0.34)</td>
</tr>
<tr>
<td>299.9935</td>
<td>20.74</td>
<td>(-112.9 ± 2.5)</td>
<td>(-3.85 ± 0.58)</td>
</tr>
<tr>
<td>315.2844</td>
<td>20.19</td>
<td>(-105.7 ± 2.7)</td>
<td>(-2.98 ± 0.68)</td>
</tr>
<tr>
<td>360.2599</td>
<td>19.31</td>
<td>(-87.7 ± 3.4)</td>
<td>(-0.52 ± 0.52)</td>
</tr>
</tbody>
</table>

Also included in tables (7.19) and (7.20) are the estimated values of the third \((p, V_m, T)\) virial coefficients \(C_e^{\text{est}}\), determined using the equations

\[
C_e^{\text{est}} = \frac{- \left(2BB_e' + C_e'\right)}{A_e} \quad (7.3.10)
\]

\[
C_e^{\text{est}} = B_e'' - A_e C_e'' \quad (7.3.11)
\]

both of which assume that \(C_e\) makes a negligible contribution to \(C_e^{\text{est}}\). The \(C_e^{\text{est}}\) values from the \((p/RT)\) fits and the \([(\epsilon - 1)/(\epsilon + 2)]\) \(RT/p\) on \([(\epsilon - 1)/(\epsilon + 2)]\) regressions were generally in very poor agreement with each other, and were also extremely different to the limited number of published values [65], often being of opposite sign. This was not too surprising, because it was expected that our values of \(C_e'\) and \(C_e''\) would be suffering from truncation error, and their principal value was in reducing such error in the \(B_e'\) and \(B_e''\) coefficients.
The greater consistency between the \( \rho \) fits and the \([ (\varepsilon - 1)/(\varepsilon + 2) ] \) \( RT/p \) on \([ (\varepsilon - 1)/(\varepsilon + 2) ] \) regressions than between the \( \rho \) fits and the \( (p/RT) \) fits, as shown by the estimates for both \( A_\varepsilon \) and \( B_\varepsilon \), meant that more confidence was placed in the \( B^{\text{est}} \) values from the \([ (\varepsilon - 1)/(\varepsilon + 2) ] \) \( RT/p \) on \([ (\varepsilon - 1)/(\varepsilon + 2) ] \) regressions than those from the \( (p/RT) \) fits, and so the following discussion is concerned with the \( B^{\text{est}} \) estimates in table (7.20).

Unweighted least-squares regression on the values of \( B^{\text{est}} \) in table (7.20) at all eight temperatures gave

\[
B^{\text{est}}(T) / \text{cm}^3 \text{ mol}^{-1} = 263.3 - 197.9 \exp\left(\frac{199.96 \text{ K}}{T}\right) \quad (7.3.12)
\]

which fitted the data with an overall standard deviation of 5.5 cm\(^3\) mol\(^{-1}\). However, ignoring the results at 300 and 315 K, which were suspected of systematic error due to the lack of \( \Delta_0 \) terms and showed significant deviations from equation (12), unweighted least-squares regression on the \( B^{\text{est}} \) values at 189, 205, 225, 249, 273 and 360 K gave

\[
B^{\text{est}}(T) / \text{cm}^3 \text{ mol}^{-1} = 245.3 - 191.1 \exp\left(\frac{200.12 \text{ K}}{T}\right) \quad (7.3.13)
\]

which had an overall standard deviation of 1.4 cm\(^3\) mol\(^{-1}\) [nearly four times smaller than that of equation (12)]. Weighted least-squares regression on the estimates of \( B^{\text{est}} \) at 189, 205, 225, 249, 273 and 360 K, where the individual values of \( B^{\text{est}} \) were weighted as \([1/\sigma(B^{\text{est}})]^2\), gave

\[
B^{\text{est}}(T) / \text{cm}^3 \text{ mol}^{-1} = 242.7 - 190.1 \exp\left(\frac{200.08 \text{ K}}{T}\right) \quad (7.3.14)
\]

with an overall weighted standard deviation of 0.58 cm\(^3\) mol\(^{-1}\). The measurements of \( B^{\text{est}} \) at 189, 205, 225, 249, 273 and 360 K agreed with the weighted least-squares regression of equation (14) within their single standard deviations. The values at 300 and 315 K were 14.8 and 10.2 cm\(^3\) mol\(^{-1}\) less negative than the estimates given by equation (14), differences which represented 5.9 and 3.8 standard deviations, respectively, indicating that these \( B^{\text{est}} \) values were suffering from systematic error as suspected. Given a typical individual standard deviation in \( B^{\text{est}} \) of 2.7 cm\(^3\) mol\(^{-1}\), and the weighted standard deviation of the fit of 0.58 cm\(^3\) mol\(^{-1}\), it is estimated that the standard deviation for a value of \( B^{\text{est}} \) calculated from equation (14) was about 3 cm\(^3\) mol\(^{-1}\) across the experimental temperature range of 189 to 360 K.
Figure (7.40) shows the deviations $\Delta B = [B - B_{eqn.(7.3.14)}]$ of the individual values of $B^{est}$ given in table (7.20), as well as those published by a number of other workers, from equation (14). The error bars on our measurements are the single standard deviations only. In general, the second $(p, V_m, T)$ virial coefficients of other workers are in very good agreement with equation (14).

**Figure (7.40) Deviations of the second $(p, V_m, T)$ virial coefficients of xenon from equation (7.3.14)**

Equation (1), which was determined by Ewing from speed of sound measurements, was in excellent agreement with equation (14), being just 0.3 cm$^3$ mol$^{-1}$ less negative at 189 K and 1.4 cm$^3$ mol$^{-1}$ less negative at 360 K. Even if equation (1) was extrapolated to 700 K, the discrepancy was still less than 2 cm$^3$ mol$^{-1}$, which was well within the estimated uncertainty of equation (14). Equation (1) was in even better agreement with the unweighted least-squares
regression on the $B_{\text{ext}}$ measurements in this work [equation (13)], being only about 0.6 cm$^3$ mol$^{-1}$ systematically higher between 189 and 700 K.

The measurements of Pollard and Saville [146] between 160 and 301 K had an estimated standard deviation of 5 cm$^3$ mol$^{-1}$ at 160 K and 2 cm$^3$ mol$^{-1}$ at all other temperatures, but were about 4 cm$^3$ mol$^{-1}$ more negative than equation (14) at low temperatures and about 7 cm$^3$ mol$^{-1}$ more negative than equation (14) at high temperatures. Such differences were presumably the result of some unidentified systematic errors in their work (possibly due to adsorption) because their results were about 5 cm$^3$ mol$^{-1}$ more negative than other, published measurements near 300 K. The measurements of Beattie et al. [147] varied smoothly between being 1.3 cm$^3$ mol$^{-1}$ more negative than equation (14) at 290 K and 1.1 cm$^3$ mol$^{-1}$ less negative than equation (14) at 373 K, differences which were similar to their typical uncertainty of ±1 cm$^3$ mol$^{-1}$ for the measurements in this temperature range, and were well within the estimated uncertainty of equation (14). The highest temperature measurement of Beattie et al., at 573 K, was still only 3.3 cm$^3$ mol$^{-1}$ less negative than the value given by equation (14), which is only a small difference given that equation (14) has been extrapolated by more than 200 K beyond its ‘valid’ temperature range. The determinations of Michels et al. [142] between 273 and 423 K were also in very good agreement with equation (14), never differing by more than 1.6 cm$^3$ mol$^{-1}$ (at 298 K). The results of Whalley, Lupien and Schneider [148] are up to 7.9 cm$^3$ mol$^{-1}$ less negative than equation (14), but are in quite good agreement between 373 and 473 K, even though this is outside the ‘valid’ range of equation (14). Dymond and Smith’s recommended values [65] agree with equation (14) within their estimated uncertainties between 160 and 450 K, except at 275 and 300 K, where the recommended values are 1.3 and 1.8 times their uncertainty more negative than equation (14); such discrepancies occur because of the undue weight given to Pollard and Saville’s measurements [146] at temperatures near 300 K, which are estimated to be up to 5 cm$^3$ mol$^{-1}$ too negative.

Although our estimates of $B$ were generally in very good agreement with those of other workers, it will be recalled that theoretical values of $B_{\alpha}$ calculated using just the simple dipole-induced dipole model, were used to determine $B_{\text{ext}}$ from $B_{e}^{\gamma}$, and it has already been demonstrated that the DID model cannot fully account for
experimental $B_e$ measurements. Should an alternative, independent source of $B_e$ values for xenon become available (e.g., using a more complete theoretical model, or experimental results from differential expansion measurements over a wider range of temperatures), then even better estimates of the second $(p, V_m, T)$ virial coefficients of xenon could be determined from our values of $B_e^n$ in table (7.15).

As previously stated, the $B_{est}$ values at 300 and 315 K [indicated by empty circles in figure (7.40)] were almost certainly in error and were consequently left out of the final analysis. It is worthy of note that the estimates of $B$ determined from the $(p/RT)$ fits at 300 and 315 K were in much better agreement with equation (14) than the values determined from the $[(\varepsilon - 1)/\varepsilon + 2)] \cdot RT/p$ on $[(\varepsilon - 1)/\varepsilon + 2)]$ regressions, supporting the hypothesis that $\Delta_0$ terms were required to fit the data accurately at these temperatures and yet such terms were not possible in the $[(\varepsilon - 1)/\varepsilon + 2)] \cdot RT/p$ on $[(\varepsilon - 1)/\varepsilon + 2)]$ regressions.
Chapter 8 Measurements Using the Cylindrical Resonator

8.1 Introduction

This chapter contains the \((\varepsilon, p)\) measurements on nitrogen taken using the cylindrical resonator. Isotherms were carried out near 243, 253, 263, 273, 283, 293, 300, 303, 313 and 323 K, at pressures up to 4015 kPa. The dielectric constants had estimated random uncertainties better than \(\pm 1.1\) ppm for the TM010 mode, and better than \(\pm 1.7\) ppm for the TM011 and TM110 modes, but systematic errors increased the typical total uncertainties to \(\pm 2\) ppm for the TM010 mode, \(\pm 4\) ppm for the TM011 mode, and about \(\pm 15\) ppm for the TM110 mode. The second and third \((p, V_m, T)\) virial coefficients of nitrogen are known to a high degree of accuracy [35, 135], and so our cylindrical resonator measurements were fitted using \([\varepsilon -1]/(\varepsilon +2)\) on \(p\) regressions only, to determine estimates of the first and second dielectric virial coefficients.

The first dielectric virial coefficient of nitrogen between 243 and 323 K was found to be temperature dependent and was best described by the equation

\[
A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (4.3632 \pm 0.0040) + (9.9 \pm 1.4) \times 10^{-5}(T/\text{K}) \tag{8.1.1}
\]

which fitted our individual \(A_\varepsilon\) measurements with a weighted standard deviation of 0.00061 cm\(^3\) mol\(^{-1}\). The total uncertainty in a value of \(A_\varepsilon\) calculated using equation (1) was estimated to be less than \(\pm 0.0025\) cm\(^3\) mol\(^{-1}\). Equation (1) was in good agreement with published results at 242 and 298.15 K, but was about 0.006 cm\(^3\) mol\(^{-1}\) higher than literature values near 323 K, and about 0.018 cm\(^3\) mol\(^{-1}\) higher than published measurements at 344 K. These discrepancies are discussed in detail.

Our measurements of the second dielectric virial coefficients of nitrogen were generally in good agreement with published results over the whole temperature range. Our most reliable results, between 273 and 303 K, were used to determine the quadrupole moment of nitrogen \(\Theta = (1.480 \pm 0.040) \times 10^{-26}\) e.s.u., in excellent agreement with published values determined using a large range of different methods.
8.2 Nitrogen

Measurements are reported for nitrogen at 10 temperatures between 243 and 323 K.

**Excess halfwidths**

As with the measurements using the sphere, the excess halfwidths $\Delta g$ were determined by subtracting the calculated skin-depth perturbation contributions $g_s$ determined using equations (4.5.29) and (4.5.30), from the corresponding measured halfwidths $g$. The fractional excess halfwidths $10^6(\Delta g/g)$ are presented graphically in figures (8.1) to (8.10), for all modes at the ten temperatures for which measurements were taken. As can be seen from the graphs, there was some systematic variation of the fractional excess halfwidths with pressure for all three modes at all temperatures. The average values and the standard deviations of the scaled fractional excess halfwidths for each mode at each temperature are given in table (8.1). The marked systematic variations in $(\Delta g/g)$ for the TM110 mode measurements are indicated by the significantly larger values of the standard deviation of $(\Delta g/g)$ for this mode than for modes TM010 and TM011. The systematic variations in $(\Delta g/g)$ over the course of an individual isotherm will be discussed presently.

---

Table (8.1) Mean values of $10^6(\Delta g/g)$ along the nitrogen isotherms in the cylinder. The uncertainties are single standard deviations.

<table>
<thead>
<tr>
<th>T/K</th>
<th>TM010</th>
<th>TM011</th>
<th>TM110</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.334</td>
<td>(45.04 ± 0.80)</td>
<td>(73.5 ± 1.2)</td>
<td>(68.6 ± 5.7)</td>
</tr>
<tr>
<td>253.323</td>
<td>(43.92 ± 0.66)</td>
<td>(71.4 ± 1.3)</td>
<td>(66.6 ± 5.2)</td>
</tr>
<tr>
<td>263.186</td>
<td>(44.20 ± 0.57)</td>
<td>(71.7 ± 1.2)</td>
<td>(66.3 ± 5.4)</td>
</tr>
<tr>
<td>273.190</td>
<td>(43.81 ± 0.59)</td>
<td>(71.4 ± 1.3)</td>
<td>(65.1 ± 6.0)</td>
</tr>
<tr>
<td>283.401</td>
<td>(32.24 ± 0.30)</td>
<td>(52.48 ± 0.33)</td>
<td>(32.2 ± 1.6)</td>
</tr>
<tr>
<td>293.186</td>
<td>(45.23 ± 0.81)</td>
<td>(73.8 ± 1.6)</td>
<td>(66.1 ± 6.4)</td>
</tr>
<tr>
<td>299.968</td>
<td>(37.58 ± 0.34)</td>
<td>(67.60 ± 0.50)</td>
<td>(46.5 ± 1.9)</td>
</tr>
<tr>
<td>303.409</td>
<td>(32.44 ± 0.31)</td>
<td>(53.57 ± 0.38)</td>
<td>(32.5 ± 1.6)</td>
</tr>
<tr>
<td>312.862</td>
<td>(45.56 ± 0.70)</td>
<td>(73.8 ± 1.2)</td>
<td>(65.9 ± 5.7)</td>
</tr>
<tr>
<td>323.072</td>
<td>(47.1 ± 1.0)</td>
<td>(76.5 ± 1.4)</td>
<td>(68.4 ± 6.2)</td>
</tr>
</tbody>
</table>
Figure (8.1) $10^6(\Delta g/\rho)$ for nitrogen at 243.334 K

Figure (8.2) $10^6(\Delta g/\rho)$ for nitrogen at 253.323 K
Figure (8.3) $10^6(Ag/f)$ for nitrogen at 263.186 K

Figure (8.4) $10^6(Ag/f)$ for nitrogen at 273.190 K
Figure (8.5) $10^6(\Delta g/f)$ for nitrogen at 283.401 K

Figure (8.6) $10^6(\Delta g/f)$ for nitrogen at 293.186 K
Figure (8.7) $10^6(\Delta g/f)$ for nitrogen at 299.968 K

Figure (8.8) $10^6(\Delta g/f)$ for nitrogen at 303.409 K
Figure (8.9) $10^6(\Delta g/f)$ for nitrogen at 312.862 K

Figure (8.10) $10^6(\Delta g/f)$ for nitrogen at 323.072 K
The fractional excess halfwidths for the resonant modes of the cylinder were much larger than the values found for the single components of those modes of the sphere for which the experimental resonances could be reliably decomposed (TM11 and TM13). This indicates that there were significant sources of energy loss other than the electrical losses within the brass walls of the cylinder. For the measurements near 243 K, 253 K, 263 K, 273 K, 293 K, 313 K and 323 K, the average fractional excess halfwidths of the TM010 mode were between 43.8 ppm (at 273 K) and 47.1 ppm (at 323 K), those of the TM011 mode were between 71.4 ppm (at 253 K and 273 K) and 76.5 ppm (at 323 K), and those of the TM110 mode were between 65.1 ppm (at 273 K) and 68.6 ppm (at 243 K). There was no significant temperature-dependence of the average \( \Delta g/f \) values for the measurements at these temperatures, indicating that the energy losses not accounted for by the skin-depth perturbation did not significantly change within this 80 K temperature range.

One important source of additional energy loss may have arisen from the resistive parts of the source and load impedances within the microwave circuit, giving rise to the halfwidth contributions \( g_{\text{ext}} \) as described in section (4.8). Unfortunately, it has not been possible to calculate the likely extent of this contribution for any mode, although it is possible that a significant part of the observed \( \Delta g/f \) values can be attributed to this effect. It is also likely that direct antenna-antenna coupling caused significant energy loss, especially because of the close proximity of the microwave cable ends in such a small resonator. Again, it was not possible to quantify such an effect, but it has been reported as playing a significant part in the loss mechanisms of other resonant cavities [110, 111]. Another possible source of energy loss was the physical presence of the cable ends in the lid of the cylinder, because the cable ends did not present a perfectly conducting surface to the cavity electromagnetic fields, especially at the PTFE dielectric which separated the inner and outer conductors of the cables, and so contributions to the resonance halfwidths were to be expected due to energy losses at these sites. However, the electrical conductivity of the copper conductors was not that different
to the cylinder brass [39], and the dielectric loss factor of PTFE is small [149], and so
the halfwidth contributions were expected to be small.

The average value of \( \Delta g/f \) for the TM011 mode was typically a factor of about
1.6 larger than that for the TM010 mode, and the average value of \( \Delta g/f \) for the
TM110 mode was typically a factor of about 1.5 larger than that for the TM010
mode, at a given temperature. This can partly be explained in terms of the difference
in the external halfwidth contributions \( g_{\text{ext}} \) that would be expected for a given circuit
efficiency \( \eta_c \) for the three modes. Equations (4.8.5) and (4.8.7) can be combined to
show that

\[
g_{\text{ext}} = g_u \left( \frac{1}{\eta_c} - 1 \right)^{-1} \tag{8.2.1}
\]

where \( g_u \) is the unloaded cavity halfwidth. If it is assumed that \( \eta_c \) was approximately
the same for all three modes at a given state point, then the external halfwidths \( g_{\text{ext}} \),
for the three modes, should be in the same ratio as the unloaded cavity halfwidths \( g_u \).
The unloaded halfwidths can be approximated by the skin-depth contributions \( g_\delta \)
alone, and it is a simple matter to show that \( g_\delta \) for the three modes will be in the
approximate ratio 1: 1.4: 1.3, for modes TM010, TM011 and TM110, respectively,
using equations (4.5.29) and (4.5.30). Thus, if the excess halfwidths were fully
accounted for by the external halfwidths \( g_{\text{ext}} \), then we should expect the \( \Delta g/f \) values
to be in the approximate ratio 1: 1.2: 0.8. Therefore, it is predicted that the values of
\( \Delta g/f \) for the TM011 mode should be larger than those of the TM010 mode, in
qualitative agreement with the observed values of \( \Delta g/f \) for these two modes. The
observed values of \( \Delta g/f \) for the TM110 mode were larger than expected partly
because the TM110 mode consists of two components, whereas the TM010 and
TM011 modes consist of single components. In-phase overlap of the two
components would give rise to increased excess halfwidths provided the degeneracy
of the two components has been lifted, as was expected due to the imperfect
geometry of the practical cylindrical resonator. Further differences between the
observed values of \( \Delta g/f \) and those predicted by the preceding discussion were,
presumably, the result of additional energy loss mechanisms such as have already
been discussed.
The fractional excess halfwidths of all three modes were notably smaller for the measurements near 300 K, and smaller still for the measurements near 283 K and 303 K. This was because it was necessary to open the resonator following the measurements near 300 K, and, also, before, and after, the measurements near 283 K and 303 K, in order to remove and, subsequently, replace the microwave cables. Following the measurements near 300 K, the temperature was reduced towards 243 K, whereupon a leak became evident (for \( p > 4 \) MPa) at one of the microwave cable seals in the pressure-vessel lid, brought about by the initial use of PTFE ferrules and tape to make these seals (PTFE undergoes a solid-solid phase transition near 288 K, causing volume changes which, presumably, led to the opening of the seal). The replacement of the PTFE ferrules and tape by 1.7 cm lengths of silicon-rubber tube with a 1 mm diameter bore (actually, the insulator of heavy-duty electrical wire) made it necessary to completely remove, and replace, the microwave cables. The silicon rubber seals were used for all other high-pressure measurements using the cylindrical resonator, and were apparently leak-free, at pressures up to at least 4.1 MPa, for all temperatures except near 243 K, for which there was a small leak at the highest pressure used (4.014 MPa), indicated by difficulty in balancing the dead-weight pressure gauge. This was, presumably, the result of shrinkage of the silicon-rubber seals at this (lowest) temperature. It was necessary to open the cylindrical resonator and renew the microwave cables following the measurements near 283 K and 303 K because the cables were accidentally severed by overtightening the Swagelok male connectors onto the silicon-rubber seals in preparation for measurements at lower temperatures.

In both cases, new cable ends were fashioned and cleaned, before being fitted flush with the inner surface of the cylinder lid, to act as ‘antennae of nominally zero length’, and secured in place by tightening the grub screws. However, it was quite possible that the cables were displaced during assembly of the cylinder and pressure-vessel, causing the cable ends to be either slightly proud of, or slightly shy of, the inner surface of the cylinder lid when the measurements were finally taken. This may have caused the cable ends to be in slightly different positions for each assembly of the cylindrical resonator, and, thus, to give rise to different perturbations in each case. Although, as discussed in section (4.7), small movements of the cable ends,
considered as deformations of a perfectly conducting boundary, were not expected to
give rise to significant halfwidth contributions (or changes in these contributions), it
was, nevertheless, highly likely that different positions of cable ends cause different
degrees of direct antenna-antenna coupling leading to different amounts of energy
loss and, therefore, different contributions to the resonance halfwidths. The different
cable end positions may also have led to different insertion losses for the microwave
circuit, giving rise to changes in the halfwidth contribution $g_{\text{ext}}$ for each mode [see
section (4.8)].

There is one further explanation which may, in part, account for the differences
in the mean excess halfwidths, for a given mode, for each assembly of the resonator:
the re-closing and screwing of the cylinder lid, following the renewal of the
microwave cables during each assembly, may have left very small gaps between the
lid and the cylinder wall, the sizes of which would, naturally, have been different in
each case. Such gaps could permit radiative energy loss although, as discussed in
section (4.7), it was very unlikely that such small openings (invisible to the naked
eye) were responsible for a significant part of either the absolute magnitudes of the
observed excess halfwidths, or the changes in average excess halfwidths following
each assembly.

There was some ambiguity regarding the systematic variation of $(\Delta g/f)$, for each
mode, along each isotherm. It can be seen from figures (8.1) to (8.10) that the
systematic variations in $(\Delta g/f)$ with pressure for the three modes did not clearly
follow the same trend. However, some light may be shed on the variations by a
consideration of the corresponding value of circuit efficiency $\eta_c$ for each
measurement of $(\Delta g/f)$ taken. As indicated in section (4.8), it was not possible to
make accurate measurements of insertion loss or circuit efficiency for the cylindrical
resonator, but useful relative approximations to $\eta_c$ can be obtained by calculating the
ratios of output power measured at the crystal detector to input power supplied from
the microwave synthesiser, at each state point. Such ratios were a serious
underestimate of the true circuit efficiencies, because no account has been taken of
signal attenuation and reflection along the microwave cables, but the variation of
such ratios along an isotherm might be expected to be similar to the variations of the
true circuit efficiency, for a given mode. Table (8.2) shows the fractional excess
halfwidths and approximated circuit efficiencies, of all three modes, for the isotherm near 293 K. The variations in \((\Delta g/f)\) and \(\eta_c\) were typical of those found at all temperatures for which measurements were taken using the cylinder.

**Table (8.2)** \(10^6(\Delta g/f)\) and approximated \(10^3\eta_c\) for the nitrogen isotherm at 293.186 K in the cylinder. A crystal detector rating of 2.5 \(\mu\)W mV\(^{-1}\) was assumed in estimating \(\eta_c\):

<table>
<thead>
<tr>
<th>(p/\text{kPa})</th>
<th>(10^6(\Delta g/f))</th>
<th>(10^3\eta_c)</th>
<th>(10^6(\Delta g/f))</th>
<th>(10^3\eta_c)</th>
<th>(10^6(\Delta g/f))</th>
<th>(10^3\eta_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4014.798</td>
<td>45.64</td>
<td>2.3</td>
<td>76.44</td>
<td>3.8</td>
<td>43.26</td>
<td>2.7</td>
</tr>
<tr>
<td>3504.340</td>
<td>46.82</td>
<td>3.2</td>
<td>75.92</td>
<td>3.3</td>
<td>55.07</td>
<td>4.0</td>
</tr>
<tr>
<td>3000.761</td>
<td>46.09</td>
<td>3.0</td>
<td>73.45</td>
<td>2.2</td>
<td>44.70</td>
<td>2.7</td>
</tr>
<tr>
<td>2500.635</td>
<td>45.28</td>
<td>2.4</td>
<td>72.96</td>
<td>1.9</td>
<td>36.25</td>
<td>1.9</td>
</tr>
<tr>
<td>2000.505</td>
<td>44.49</td>
<td>1.9</td>
<td>73.31</td>
<td>2.3</td>
<td>40.91</td>
<td>2.3</td>
</tr>
<tr>
<td>1500.394</td>
<td>44.02</td>
<td>1.9</td>
<td>75.22</td>
<td>3.5</td>
<td>53.06</td>
<td>3.6</td>
</tr>
<tr>
<td>1200.304</td>
<td>44.13</td>
<td>1.9</td>
<td>75.44</td>
<td>3.7</td>
<td>50.53</td>
<td>3.4</td>
</tr>
<tr>
<td>800.208</td>
<td>44.56</td>
<td>2.2</td>
<td>74.10</td>
<td>2.8</td>
<td>40.53</td>
<td>2.2</td>
</tr>
<tr>
<td>400.098</td>
<td>45.44</td>
<td>2.8</td>
<td>72.99</td>
<td>2.1</td>
<td>36.90</td>
<td>1.9</td>
</tr>
<tr>
<td>200.055</td>
<td>45.53</td>
<td>2.8</td>
<td>71.99</td>
<td>1.8</td>
<td>37.37</td>
<td>1.8</td>
</tr>
<tr>
<td>79.334</td>
<td>45.39</td>
<td>2.8</td>
<td>71.97</td>
<td>1.8</td>
<td>39.65</td>
<td>2.0</td>
</tr>
<tr>
<td>0.000</td>
<td>45.41</td>
<td>2.8</td>
<td>72.21</td>
<td>1.8</td>
<td>41.32</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Figures (8.11) to (8.13) show the variations of \((\Delta g/f)\) with \(\eta_c\) more clearly, and it can be seen that there was a strong correlation between \((\Delta g/f)\) and \(\eta_c\), for all three modes, with large circuit efficiencies being accompanied by large fractional excess halfwidths. This is in qualitative agreement with equation (4.8.7) and the accompanying discussion, given in section (4.8), concerning the relation between the circuit efficiency and the external halfwidth contribution \(g_{ext}\), for a given mode. Thus, it would appear that the variations in \((\Delta g/f)\) were due to the variations in \(g_{ext}\) caused by the changes in \(\eta_c\). However, it was difficult to fully account for the
Figure (8.11) Variation of $10^6(\Delta g_{010}/f_{010})$ with $\eta_c$ for nitrogen at 293.186 K

Figure (8.12) Variation of $10^6(\Delta g_{011}/f_{011})$ with $\eta_c$ for nitrogen at 293.186 K
changes in $\eta_c$ along an individual isotherm. The most likely explanation would seem to be small movements in the cable ends, caused by the pressure changes over the course of the measurements. Such movements would not only give rise to changes in $\eta_c$, but also in the degree of direct antenna-antenna coupling. The three modes may show different variations of $(\Delta g/f)$ with pressure because the cable ends were initially displaced by the pressure changes, and then relaxed back towards their original positions whilst the measurements were being taken. The variations in $(\Delta g/f)$ were likely to have been much larger for the TM110 mode than for the TM010 and TM011 modes because the electric field strength was much stronger in the vicinity of the cable ends for the TM110 mode than for the other two modes, for a given level of energy in the cavity, giving rise to greater changes in $\eta_c$, and thus $g_{\text{ext}}$ and $(\Delta g/f)$, for this mode than for modes TM010 and TM011.

Unfortunately, it has not been possible to quantify these effects in order to estimate the shifts in resonance frequency that accompany such perturbations. In this respect, it is noted that it would be particularly difficult to do so if the microwave cables had, indeed, been in the process of relaxing back into their original positions, following their initial displacement, during the measurements. In such
circumstances, the systematic variation in the fractional excess halfwidths of a given mode over the course of an individual isotherm - the measure of which was given by the appropriate value of the standard deviation of \( \Delta g/f \) given in table (8.1) - must be regarded as the systematic fractional uncertainty in the corrected resonance frequencies caused by our ignorance of the unaccounted for perturbations. This can then be propagated into an additional fractional uncertainty in the values of dielectric constant \( \varepsilon \) determined from the measurements.

**Dielectric constants**

The dielectric constants \( \varepsilon(p, T) \) were determined from the measured resonance frequencies of cylinder modes TM010, TM011 and TM110 using equation (7.2.3), and are presented in table (8.3). The perturbation due to the gas-inlet opening in the cylindrical resonator [equations (4.7.29), (4.7.30) and (4.7.54)] contributed less than two parts per billion to \( \varepsilon \), even at the highest pressures, and so was neglected. Compared to the difficulties encountered with the sphere, there was little problem in taking account of any geometric imperfections in the cylinder. Modes TM010 and TM011 were non-degenerate and so the measured resonance frequencies were simply those of the single components, and these were unaffected, to first order, by volume-preserving geometric deformations of the cylinder. Mode TM110 was doubly-degenerate, but the resonances were always fitted as singlets and the resulting resonance frequencies were the mean resonance frequencies of the two components. Therefore, for all three modes, the measured resonance frequencies needed no corrections for the effects of imperfect cavity geometry [see section (4.6)]. The fractional frequency shifts for the compliance of the cylinder [section (4.3)] and the skin-depth perturbation [equations (4.5.29) and (4.5.30)] were explicitly dependent on pressure and frequency, respectively, and so corrections for these imperfections were made to the measured cylinder resonance frequencies in equation (7.2.3).

The standard deviations of the fractional excess halfwidths, given in table (8.1), were combined in quadrature with typical values of the fractional random uncertainties in the resonance frequencies \( f_N \), estimated from

\[
\left[ \sigma(f_N)/f_N \right] = \left[ s(P)/P_{\max} \right]/Q_N
\]

, to obtain estimated total fractional uncertainties in
Table (8.3) Experimental values of $10^6(\varepsilon - 1)$ for nitrogen. The uncorrected vacuum resonance frequencies $f_0$ are also given.

**$T/K = 243.334$**

<table>
<thead>
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**$T/K = 253.323$**

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$f_0$/MHz = 12046.9269 14191.1722 19182.1605
### $T_{\text{K}} = 299.968$

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### $T_{\text{K}} = 303.409$

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$f_0$/MHz = 12046.6870 14190.9608 19195.6259

### $T_{\text{K}} = 312.862$

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$f_0$/MHz = 12042.2876 14185.7118 19174.7671
the experimental values of $\varepsilon$ given by

$$u(\varepsilon)/\varepsilon \equiv 2\sqrt{\left[\sigma(f_N)/f_N\right]_{\rho=0}^2 + \left[\sigma(f_N)/f_N\right]_{\rho}^2 + 2\sigma(\Delta f/g)^2}$$

(8.2.2)

where $\sigma(\Delta f/g)$ was the standard deviation of the fractional excess halfwidths for a given mode at a given temperature. Typical values of $[u(\varepsilon)/\varepsilon]$, calculated in this way, are given in table (8.4), at each experimental temperature.

A further contribution to the total fractional uncertainty in $\varepsilon$, approximately given by $(4\chi_p/100)$ and never larger than 0.5 ppm, which came about from the estimated $\pm2\%$ uncertainty in the compliance $\chi$, was not included in table (8.4) because every mode was subjected to the same fractional error and so it did not account for any part of the differences between the estimates of $\varepsilon$ from the three modes. As with the results for the sphere, the uncertainty in the skin-depth perturbation contributed no more than a few parts in $10^8$ to the total fractional uncertainty in $\varepsilon$.

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$T/K = 323.072$
Table (8.4) Typical total fractional uncertainties \(10^6[u(\varepsilon)/\varepsilon]\) in the dielectric constants along the nitrogen isotherms

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<td>283.401</td>
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<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>293.186</td>
<td>2.5</td>
<td>4.7</td>
<td>18.0</td>
</tr>
<tr>
<td>299.968</td>
<td>1.6</td>
<td>2.1</td>
<td>5.4</td>
</tr>
<tr>
<td>303.409</td>
<td>1.4</td>
<td>1.8</td>
<td>4.7</td>
</tr>
<tr>
<td>312.862</td>
<td>2.2</td>
<td>3.5</td>
<td>16.1</td>
</tr>
<tr>
<td>323.072</td>
<td>3.3</td>
<td>4.4</td>
<td>17.5</td>
</tr>
</tbody>
</table>

The estimated total fractional uncertainties in \(\varepsilon\) for the TM110 mode were typically a factor of six larger than those for the TM010 mode, and a factor of four larger than those for the TM011 mode, because there was much larger variation in the values of \((\Delta g/f)\) for the TM110 mode than for the other two modes, at all temperatures. Therefore, it was expected that much greater accuracy and precision would be achieved by relying on the TM010 and TM011 measurements alone.

**Dielectric virial coefficients**

The experimental values of \([(\varepsilon -1)/(\varepsilon +2)]\) along each isotherm were fitted to equation (7.2.9) to determine the dielectric virial coefficients of nitrogen. Just as with the regressions on the sphere measurements, the full sets of results were used with the individual data points being weighted as \([(\varepsilon -1)/(\varepsilon +2)]/\sigma^2\), where \(\sigma\) was the estimated random uncertainty of an individual value of \([(\varepsilon -1)/(\varepsilon +2)]\) given by equation (7.2.11), with \(\sigma(\varepsilon)/\varepsilon\) being given by equation (7.2.6). The amount-of-
substance densities $\rho$ were calculated correct to $C'(T)$ using equation (5.3.2), where the required second and third ($\rho, V_m, T$) virial coefficients $B(T)$ and $C(T)$ were given by equations (7.2.14) and (7.2.15) which were derived from the results of Novak, Kleinrahm and Wagner between 150 and 340 K [135].

The previously-described basis for identification of outliers was adopted, with measurements laying five or more standard deviations from the regression line being neglected if their removal gave rise to significant changes in the dielectric virial coefficients obtained. This approach led to the removal of the majority of TM110 measurements at 273, 283, 300 and 323 K, suggesting that all TM110 data should be neglected at these temperatures, but, for the remaining isotherms, only a minority of TM110 measurements were candidates for removal. However, the much larger scatter in the fractional excess halfwidths of the TM110 mode than for the TM010 and TM011 modes suggested that the accuracy and precision of the dielectric virial coefficients determined from the regressions could be improved by using the TM010 and TM011 measurements only in all of the final analyses. In this respect it was noted that the overall standard deviation of the fit for any of the isotherms was typically reduced by a factor of three if mode TM110 was neglected from the regression. Consequently, the finally adopted fits included modes TM010 and TM011 only, but the results of the regressions when all three modes were included will also be presented for comparison. All the measurements at 4015 kPa were neglected in the final regression for the isotherm at 243 K because there was a leak from the pressure vessel at this maximum pressure. The TM011 data at 4015 and 3504 kPa in the isotherm at 273 K were removed from the final analysis because these measurements were five and nine standard deviations from the regression line, respectively, and, most importantly, their removal had a significant effect on the dielectric virial coefficients obtained.

The results of the finally adopted regressions are given in table (8.5). The order of fit was ambiguous for the isotherms at 243 to 263 K, because there was a similar reduction in the overall standard deviation if either a deviation term $\Delta_\varphi$ or a $B_\varphi\rho^2$ term was included, and so the coefficients from both types of fit are given in table (8.5). Given the importance of taking into account the errors that give rise to a $\Delta_\varphi$ term, and the slightly smaller standard deviations that result at 253 and 263 K, the $[\Delta_\varphi + A_\varphi\rho]$
fits were considered to be the 'best' representations of the data at 243, 253 and 263 K. The regressions for the isotherms at 273 to 323 K were not so ambiguous. The first and second dielectric virial coefficients were significant at 273 K, but the $\Delta_0$ term was clearly not. The $\Delta_0$, $A_d\rho$ and $B_d\rho^2$ terms were all significant at 283, 300, 303 and 323 K, but only the $A_d\rho$ term was significant at 293 and 313 K [the results of the insignificant $(A_d\rho + B_d\rho^2)$ fits at 293 and 313 K are also given in table (8.5) for comparison]. The variation in the order of regression that gave the 'best' fits can be partly explained by the opening and re-closing of the resonator during the previously-described maintenance, giving rise to changes in the perturbations to the modes; this also explains the significantly lower standard deviations of the fits at 283, 300 and 303 K. The results of the regressions when modes TM010, TM011 and TM110 were all included are given in table (8.6) for comparison with the 'best' fits of table (8.5). The dielectric virial coefficients were considerably less precise when the TM110 data was included, but they always agreed with the results in table (8.5) within their combined standard deviations. The deviations $10^6\Delta\{(\varepsilon -1)/(\varepsilon +2)\} = 10^6\{[(\varepsilon -1)/(\varepsilon +2)]_{\text{meas}} -[(\varepsilon -1)/(\varepsilon +2)]_{\text{fin}}\}$ of the measured $[(\varepsilon -1)/(\varepsilon +2)]$ values from the final fits of table (8.5) are shown in figures (8.14) to (8.23); the TM110 mode measurements are represented by empty symbols to indicate that they were not included in the regressions. The $[(\varepsilon -1)/(\varepsilon +2)]$ measurements were almost invariably within three of their estimated uncertainties of the regression lines, even for mode TM110 whose data were not used in determining the fits. Truncation errors for the isotherms with significant values of $B_e$ were investigated by performing several fits over successively reduced ranges of molar density. In no case was there a significant change in the dielectric virial coefficients whilst $B_e$ was required to accommodate the data, indicating that series truncation was not a significant source of error in our values of $B_e$. 
Table (8.5) Coefficients from the \([(\varepsilon -1)/(\varepsilon +2)]\) on \(\rho\) regressions on the nitrogen data from modes TM010 and TM011 only

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(10^6\sigma)</th>
<th>(10^6\Delta_v)</th>
<th>(A_\varepsilon/cm^3\text{ mol}^{-1})</th>
<th>(B_\varepsilon/cm^6\text{ mol}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.334</td>
<td>1.185</td>
<td>(-1.48 ± 0.40)</td>
<td>(4.38769 ± 0.00046)</td>
<td>(4.3826 ± 0.0010)</td>
</tr>
<tr>
<td></td>
<td>1.144</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>253.323</td>
<td>1.281</td>
<td>(-2.34 ± 0.45)</td>
<td>(4.38818 ± 0.00045)</td>
<td>(4.3823 ± 0.0012)</td>
</tr>
<tr>
<td></td>
<td>1.529</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>263.186</td>
<td>1.202</td>
<td>(-1.91 ± 0.42)</td>
<td>(4.38954 ± 0.00043)</td>
<td>(4.3843 ± 0.0011)</td>
</tr>
<tr>
<td></td>
<td>1.349</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>273.190</td>
<td>0.982</td>
<td></td>
<td>(4.38651 ± 0.00093)</td>
<td></td>
</tr>
<tr>
<td>283.401</td>
<td>0.304</td>
<td>(1.23 ± 0.24)</td>
<td>(4.39210 ± 0.00064)</td>
<td></td>
</tr>
<tr>
<td>293.186</td>
<td>1.035</td>
<td></td>
<td>(4.39269 ± 0.00025)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.060</td>
<td></td>
<td>(4.39273 ± 0.00096)</td>
<td></td>
</tr>
<tr>
<td>299.968</td>
<td>0.296</td>
<td>(1.77 ± 0.14)</td>
<td>(4.39211 ± 0.00046)</td>
<td></td>
</tr>
<tr>
<td>303.409</td>
<td>0.362</td>
<td>(1.23 ± 0.17)</td>
<td>(4.39106 ± 0.00057)</td>
<td></td>
</tr>
<tr>
<td>312.862</td>
<td>1.058</td>
<td></td>
<td>(4.39465 ± 0.00027)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.070</td>
<td></td>
<td>(4.3939 ± 0.0010)</td>
<td></td>
</tr>
<tr>
<td>323.072</td>
<td>1.001</td>
<td>(3.95 ± 0.47)</td>
<td>(4.3913 ± 0.0017)</td>
<td></td>
</tr>
</tbody>
</table>
Table (8.6) Coefficients from the \([(\varepsilon -1)/(\varepsilon +2)]\) on \(\rho\) regressions on the nitrogen data from modes TM010, TM011 and TM110

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(10^6\sigma)</th>
<th>(10^6\Delta_0)</th>
<th>(A_\varepsilon/\text{cm}^3\text{mol}^{-1})</th>
<th>(B_\varepsilon/\text{cm}^6\text{mol}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.334</td>
<td>3.737</td>
<td>(-1.5 ± 1.0)</td>
<td>(4.3870 ± 0.0011)</td>
<td>(3.4 ± 1.4)</td>
</tr>
<tr>
<td></td>
<td>3.537</td>
<td></td>
<td>(4.3808 ± 0.0021)</td>
<td></td>
</tr>
<tr>
<td>253.323</td>
<td>2.835</td>
<td>(-2.01 ± 0.82)</td>
<td>(4.38771 ± 0.00078)</td>
<td>(3.7 ± 1.0)</td>
</tr>
<tr>
<td></td>
<td>2.606</td>
<td></td>
<td>(4.3804 ± 0.0016)</td>
<td></td>
</tr>
<tr>
<td>263.186</td>
<td>3.076</td>
<td>(-1.29 ± 0.85)</td>
<td>(4.38840 ± 0.00089)</td>
<td>(4.3 ± 1.3)</td>
</tr>
<tr>
<td></td>
<td>2.721</td>
<td></td>
<td>(4.3812 ± 0.0019)</td>
<td></td>
</tr>
<tr>
<td>273.190</td>
<td>4.908</td>
<td></td>
<td>(4.3846 ± 0.0034)</td>
<td>(0.5 ± 2.3)</td>
</tr>
<tr>
<td>283.401</td>
<td>1.102</td>
<td>(2.16 ± 0.69)</td>
<td>(4.3915 ± 0.0019)</td>
<td>(2.9 ± 1.0)</td>
</tr>
<tr>
<td>293.186</td>
<td>4.525</td>
<td></td>
<td>(4.39053 ± 0.00092)</td>
<td>(5.6 ± 2.3)</td>
</tr>
<tr>
<td></td>
<td>4.215</td>
<td></td>
<td>(4.3836 ± 0.0030)</td>
<td></td>
</tr>
<tr>
<td>299.968</td>
<td>1.153</td>
<td>(2.72 ± 0.45)</td>
<td>(4.3928 ± 0.0015)</td>
<td>(1.13 ± 0.90)</td>
</tr>
<tr>
<td>303.409</td>
<td>0.910</td>
<td>(1.51 ± 0.36)</td>
<td>(4.3899 ± 0.0012)</td>
<td>(2.68 ± 0.72)</td>
</tr>
<tr>
<td>312.862</td>
<td>3.392</td>
<td></td>
<td>(4.39311 ± 0.00071)</td>
<td>(4.3 ± 2.0)</td>
</tr>
<tr>
<td></td>
<td>3.220</td>
<td></td>
<td>(4.3880 ± 0.0025)</td>
<td></td>
</tr>
<tr>
<td>323.072</td>
<td>3.177</td>
<td>(2.7 ± 1.2)</td>
<td>(4.3891 ± 0.0044)</td>
<td>(8.5 ± 2.9)</td>
</tr>
</tbody>
</table>
Figure (8.14) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for nitrogen at 243.334K

($A_0 + A_2\rho$) fit:

($A_2\rho + B_2\rho^2$) fit:
Figure (8.15) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for nitrogen at 253.323K

$$(\Delta_0 + A_\rho \rho)\text{ fit:}$$

$$(A_\rho \rho + B_\rho \rho^2)\text{ fit:}$$
Figure (8.16) Residuals of the \([\epsilon - 1]/(\epsilon + 2)\) on \(\rho\) regression for nitrogen at 263.186K

\((\Delta_\epsilon + A_\epsilon \rho)\) fit:

\((A_\epsilon \rho + B_\epsilon \rho^2)\) fit:
Figure (8.17) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for nitrogen at 273.190K

Figure (8.18) Residuals of the $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $\rho$ regression for nitrogen at 283.401K
Figure (8.19) Residuals of the \([\varepsilon -1]/(\varepsilon +2)\) on \(\rho\) regression for nitrogen at 293.186K

![Figure (8.19)](image)

Figure (8.20) Residuals of the \([\varepsilon -1]/(\varepsilon +2)\) on \(\rho\) regression for nitrogen at 299.968K

![Figure (8.20)](image)
Figure (8.21) Residuals of the $[(\varepsilon -1)/(\varepsilon +2)]$ on $\rho$ regression for nitrogen at 303.409K

Figure (8.22) Residuals of the $[(\varepsilon -1)/(\varepsilon +2)]$ on $\rho$ regression for nitrogen at 312.862K
In contrast to the first dielectric virial coefficient of argon between 215 and 300 K, and of xenon between 189 and 360 K, the $A_\varepsilon$ for nitrogen between 243 and 323 K was found to be significantly dependent on temperature. Weighted least-squares regression on the values of $A_\varepsilon$ at all ten temperatures (the $(\Delta_\varepsilon+A_\varepsilon\rho)$ fits were used at 243 to 263 K, and each value was weighted as $[1/\sigma(A_\varepsilon)]^2$) gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (4.3632 \pm 0.0040) + (9.9 \pm 1.4) \times 10^{-5}(T/K)$$

(8.2.3)

which had an overall weighted standard deviation of 0.00061 cm$^3$ mol$^{-1}$. The temperature-dependent term in equation (3) was easily significant at the 0.995 probability level. An unweighted regression on the same values of $A_\varepsilon$ gave

$$A_\varepsilon(T)/\text{cm}^3\text{mol}^{-1} = (4.3692 \pm 0.0064) + (7.5 \pm 2.2) \times 10^{-5}(T/K)$$

(8.2.4)

which had an overall standard deviation of 0.0018 cm$^3$ mol$^{-1}$ and had coefficients in good agreement with those of the weighted least-squares regression. Only our estimates of $A_\varepsilon$ at 273 and 303 K deviated by more than three of their individual
standard deviations from equation (3), and even at these temperatures the differences were no larger than four standard deviations. Removing the values of $A_e$ at 273 and 303 K had no significant effect on the coefficients of the $A_e$ on $T$ regression. Using equation (5.5.5), equation (3) can be given in terms of molecular polarisability:

$$10^{40} \alpha(T)/C^2m^2J^{-1} = (1.92451 \pm 0.00093)\left[1 + \left\{(22.7 \pm 3.2) \times 10^{-6} K^{-1}\right\}T\right](8.2.5)$$

The temperature coefficient $(22.7 \pm 3.2) \times 10^{-6} K^{-1}$ determined from our measurements was some 12.6 times larger than that reported by Kerl, Hohm and Varchmin [150].

The contribution to the uncertainty in $A_e$ due to the $\pm 0.25 \text{ cm}^3 \text{ mol}^{-1}$ uncertainty in $B(T)$ was estimated to be about $\pm 0.002 \text{ cm}^3 \text{ mol}^{-1}$ for those fits where $B_e$ was not included, but less than only $\pm 0.00005 \text{ cm}^3 \text{ mol}^{-1}$ for the fits where $B_e$ was included. The contribution to the uncertainty in $A_e$ due to the $\pm 100 \text{ cm}^6 \text{ mol}^2$ uncertainty in $C(T)$ was estimated to be about $\pm 0.001 \text{ cm}^3 \text{ mol}^{-1}$ for the fits where $B_e$ was not included, but less than only $\pm 0.00006 \text{ cm}^3 \text{ mol}^{-1}$ for those fits where $B_e$ was included.

Figure (8.24) shows the deviations $\Delta A_e = \{A_e - A_e[\text{eqn. (8.2.3)}]\}$ of our measurements of $A_e$ as well as those published by a number of other workers, from equation (3). The error bars on our measurements are the single standard deviations arising from the least-squares regressions only. The error bar on the result of Orcutt and Cole [103] represents the estimated total uncertainty, whilst the error bars on the measurements of Johnston, Oudemans and Cole [100], Huot and Bose [151], and Vidal and Lallemand [134], are standard deviations from their data fits only. The measurement of Vidal and Lallemand at 298.15 K [134] was in excellent agreement with equation (3) and with our individual values of $A_e$ at 293 and 300 K, which was very pleasing because their $A_e$ came from a fit to absolute measurements of $\varepsilon$ and $p$ in which both the second and third dielectric virial coefficients were obtained, and so was not likely to be suffering from serious truncation error. The result of Orcutt and Cole at 322.15 K [103] was 0.005 cm$^3$ mol$^{-1}$ smaller than the value given by equation (3), but this difference was still only 2.5 times their estimated uncertainty. Huot and Bose's measurement at 323.15 K [151] was 0.0057 cm$^3$ mol$^{-1}$ smaller than equation (3), a difference which was about 11.4 times their standard deviation. However, the $A_e$ of Huot and Bose came from a two-term $[(\varepsilon - 1)/(\varepsilon + 2)]$ on $(p/RT)$ fit where the $B_e'$ coefficient was
found to be \((0.1 \pm 0.5) \text{ cm}^3 \text{ mol}^{-1}\), which was not statistically significant. Had the \(B'_e\) coefficient been left out of their data analysis, Huot and Bose's \(A_e\) would have been slightly larger, improving the agreement between their value and equation (3). Although our individual measurement of \(A_e\) at 323 K was in excellent agreement with those of Orcutt and Cole at 322.15 K and Huot and Bose at 323.15 K, our \(B_e\) at 323 K (which arose, of course, from the same regression) was suspected of systematic error so the agreement of the individual \(A_e\) values may not be all that significant. The discrepancy between equation (3) and the measurements of \(A_e\) reported by Johnston, Oudemans and Cole [100] generally increased with temperature, with their value at 344 K being about 0.015 to 0.018 cm\(^3\) mol\(^{-1}\) smaller than that given by equation (3). Their results were also derived from absolute measurements of \(\varepsilon\) and \(p\), and the only temperature at which they determined a statistically significant value of \(B_e\) was at 242 K where the agreement between their \(A_e\) and equation (3) was very good. At higher temperatures, Johnston, Oudemans and
Cole's $B_e$ estimates were not significantly different from zero, even at the 0.90 probability level, and so their $A_e$ values were more likely to be in error. Differences between the $(p, V_m, T)$ data used by Johnston, Oudemans and Cole to determine molar densities and the $(p, V_m, T)$ data of Novak, Kleinrahm and Wagner [135] used in this work also account for part of the discrepancy between our values of $A_e$ and those of Johnston, Oudemans and Cole.

The second dielectric virial coefficients $B_e$ determined from our dielectric constant measurements are also given in table (8.5), where the quoted uncertainties are just the single standard deviations obtained from the regressions. The contributions to the total uncertainty in $B_e$ from the $\pm 0.25 \text{ cm}^3 \text{ mol}^{-1}$ uncertainty in $B$ and the $\pm 100 \text{ cm}^6 \text{ mol}^{-2}$ uncertainty in $C$ were about $\pm 1.2 \text{ cm}^6 \text{ mol}^{-2}$ and $\pm 1.1 \text{ cm}^6 \text{ mol}^{-2}$, respectively, so the typical total uncertainty in one of our estimates of $B_e$ was about $\pm 1.7 \text{ cm}^6 \text{ mol}^{-2}$, where this figure was arrived at by combining in quadrature the contributions due to the uncertainties in the $(p, V_m, T)$ virial coefficients and the standard deviation from the regression.

The second dielectric virial coefficients determined in this work are compared with those measured by a number of other workers in figure (8.25); we have included the values of $B_e$ from the $[A_e \rho + B_e \rho^2]$ fits at 243 to 263 K, even though these fits were not considered to be the 'best' at these temperatures, to enable comparison with our results for $B_e$ at 273 to 323 K. The error bars on our measurements are single standard deviations from the regressions only. The error bar on the result of Orcutt and Cole [103] represents the estimated total uncertainty, whilst the error bars on the measurements of Johnston, Oudemans and Cole [100], Huot and Bose [151], and Vidal and Lallemant [134], are standard deviations from their data fits only.

The measurements of Johnston, Oudemans and Cole [100] were generally in good agreement with our values of $B_e$ over the temperature range. Their results at 296 and 306 K agreed with our values at 300 and 303 K within their single standard deviations, whilst their value at 242 K agreed with ours at 243 K within the combined standard deviation. Whilst such agreement was very pleasing, it must be recalled that it was only at 242 K that Johnston, Oudemans and Cole determined a statistically significant value of $B_e$, and their results came from absolute $\varepsilon$ and $p$.
measurements where a different source of \((p, V_m, T)\) data to that used in this work was employed to obtain the molar densities for the regressions. The two different measurements of Johnston, Oudemans and Cole at 344 K were outside our experimental temperature range, but it will be shown later that one of their values at 344 K was consistent with our results. Vidal and Lallemand’s \(B_e\) at 298.15 K [134] was 0.92 cm\(^6\) mol\(^{-2}\) smaller than our \(B_e\) at 300 K, but this difference was only 1.6 combined standard deviations. The measurements of Orcutt and Cole at 322.15 K [103], and Huot and Bose at 323.15 K [151], were significantly smaller than our value at 323 K, but, clearly, our \(B_e\) at 323 K was considerably higher than our values at lower temperatures and was likely to be suffering from systematic error caused by the poor temperature stability which was observed for this isotherm. It will soon be shown that Huot and Bose’s very precise result at 323.15 K was highly consistent with our more reliable measurements of \(B_e\) at lower temperatures.
The simple DID model was not expected to provide accurate theoretical values of $B_e$ for $N_2$, principally because, for a given molecular pair, the model only considered the interaction between the dipole induced on one molecule by the external field, with the additional dipole induced on the neighbouring molecule. Nitrogen molecules have significant quadrupole moments, and there will be an additional contribution to $B_e$ from the quadrupole-induced dipole (QID) interactions. The QID contribution arises from the interaction between the quadrupole moment on one molecule with the dipole induced in a neighbouring molecule by that quadrupole moment. Such an additional effect could be taken into account by using [85]

$$B_e(T) = B_e^{\text{DID}}(T) + B_e^{\text{QID}}(T) \quad (8.2.6)$$

where $B_e^{\text{DID}}$ was given by Buckingham and Pople's equation (7.3.8), as before, and $B_e^{\text{QID}}$ was

$$B_e^{\text{QID}}(T) = \frac{N_A^2}{18\left(4\pi\varepsilon_0\right)e_0^2} \left(\frac{\alpha^2\Theta^2}{8 \varepsilon r_0^3}\right) \frac{H_8(y)}{y^2} \quad (8.2.7)$$

Equation (7) was obtained by Buckingham and Pople [85], from their equation (5.5.6) for $B_e$ by using a point quadrupole-point induced dipole model and by employing an approximate pair potential of the form

$$u_{12} = u_{12}^{1-6}(r) + \text{quadrupole–quadrupole energy} \quad (8.2.8)$$

where $u_{12}^{1-6}(r)$ was the Lennard-Jones (12-6) potential of equation (7.3.7). In equation (7), $\Theta$ was the permanent quadrupole moment of a molecule and $H_8(y)$ was a function whose value has been tabulated by Buckingham and Pople [143] for $(0.6 \leq y \leq 3.2)$.

Using the Lennard-Jones parameters $(\varepsilon/k) = 91.5$ K and $r_0 = 3.681 \times 10^{-10}$ m, which were based on viscosity data and taken from reference 152, obtaining $\alpha$ from equation (5), and using the $N_2$ quadrupole moment $\Theta = 1.5 \times 10^{-26}$ e.s.u. [153, 154], values of $B_e$ between 240 and 350 K were calculated using equation (6), and are shown in figure (8.25) as a continuous curve. As can be seen, our measurements of $B_e$ between 243 and 303 K were about 1 cm$^6$ mol$^{-2}$ systematically lower than the values given by equation (6). As will be appreciated from the discussion in section (7.3) concerning the theoretical values of $B_e$ for xenon, equation (6) took no account of the dispersive or short-range effects, and so could never give highly accurate
values of $B_e$. A much better approach, taken from the work of Huot and Bose [151], was to use the equation

$$B_e(T) = B^\text{exp}_e(T) + B^\text{QID}_e(T) + \Delta B^\text{OR}_e(T)$$  \hspace{1cm} (8.2.9)

where $B^\text{exp}_e$ was the experimental value of the second refractivity virial coefficient [see section (5.5)], $B^\text{QID}_e$ was given by equation (7) as before, and $\Delta B^\text{OR}_e$ was the sum of a number of correction terms which accounted for such effects as the reaction fields of the molecules and polarisability anisotropy [151]. Equation (9) was expected to give improved estimates of $B_e$ because the measured second refractivity virial coefficient $B^\text{exp}_e$ should include all long- and short-range contributions to $B_e$ except those from QID interactions [$B^\text{QID}_e$ in equation (7)] and other ‘orientational’ effects [$\Delta B^\text{OR}_e$ in equation (9)] which do not contribute at the optical frequencies at which $B_e$ is measured. The caveat is that $B_e$ is frequency-dependent and so what we really require are values of $B_e$ at microwave frequencies (but, paradoxically, not including orientational contributions so we can still separate $B^\text{QID}_e$). However, given the size of uncertainties in experimental determinations of $B_e$ [84, 155, 156], the limited frequency-dependence [97] can be neglected without any serious errors.

Rather than simply using equation (9) and published measurements of $B_e$ to calculate estimates of $B_e$ for comparison with our experimental results, it was more interesting to follow the procedure of Huot and Bose [151] and use our measurements of $B_e$ with the published values of $B_e$ to determine the quadrupole moment of nitrogen. The correction term $\Delta B^\text{OR}_e$ in equation (9) was estimated, at each of our isotherm temperatures, from Huot and Bose’s detailed calculations at 323.15 K by considering the temperature-dependence of each contribution to $\Delta B^\text{OR}_e$ (explicitly given by Huot and Bose in their paper); the correction term was never greater than 0.17 cm$^6$ mol$^{-2}$, so we were not concerned that this simple procedure would lead to significant errors. The second refractivity virial coefficient of nitrogen was estimated at each experimental temperature by using the precise results of Montizi et al. [156] at 298.15 K [$B_e = (0.75 \pm 0.10)$ cm$^6$ mol$^{-2}$] and Achtermann et al. [155] at 323.15 K [$B_e = (0.64 \pm 0.08)$ cm$^6$ mol$^{-2}$], and assuming that the temperature variation of $B_e$ was the same as that of the DID contribution to $B_e$ [97]. The values
Table (8.7) Experimental values of the quadrupole moment of nitrogen

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$B_e$/cm$^6$ mol$^{-2}$</th>
<th>$B_R$/cm$^6$ mol$^{-2}$</th>
<th>$\Delta B_e^\text{OR}$/cm$^6$ mol$^{-2}$</th>
<th>$10^{26}$ $\Theta$/e.s.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>243.334</td>
<td>(2.86 ± 0.75)</td>
<td>0.80</td>
<td>0.17</td>
<td>(1.51 ± 0.28)</td>
</tr>
<tr>
<td>253.323</td>
<td>(2.73 ± 0.77)</td>
<td>0.77</td>
<td>0.16</td>
<td>(1.51 ± 0.30)</td>
</tr>
<tr>
<td>263.186</td>
<td>(2.58 ± 0.74)</td>
<td>0.76</td>
<td>0.15</td>
<td>(1.48 ± 0.30)</td>
</tr>
<tr>
<td>273.190</td>
<td>(2.72 ± 0.71)</td>
<td>0.75</td>
<td>0.15</td>
<td>(1.58 ± 0.28)</td>
</tr>
<tr>
<td>283.401</td>
<td>(2.69 ± 0.34)</td>
<td>0.74</td>
<td>0.14</td>
<td>(1.60 ± 0.14)</td>
</tr>
<tr>
<td>293.186</td>
<td>N/A</td>
<td>0.72</td>
<td>0.14</td>
<td>N/A</td>
</tr>
<tr>
<td>299.968</td>
<td>(2.04 ± 0.28)</td>
<td>0.72</td>
<td>0.13</td>
<td>(1.35 ± 0.13)</td>
</tr>
<tr>
<td>303.409</td>
<td>(2.47 ± 0.35)</td>
<td>0.71</td>
<td>0.13</td>
<td>(1.58 ± 0.16)</td>
</tr>
<tr>
<td>312.862</td>
<td>N/A</td>
<td>0.69</td>
<td>0.13</td>
<td>N/A</td>
</tr>
<tr>
<td>323.072</td>
<td>(7.1 ± 1.1)</td>
<td>0.68</td>
<td>0.12</td>
<td>(3.19 ± 0.26)</td>
</tr>
</tbody>
</table>

The value of $\Theta$ at 323 K was considerably higher than the results at lower temperatures, and was certainly in significant error. The unweighted mean of the estimates of $\Theta$ between 243 and 303 K was $(1.516 \pm 0.086) \times 10^{-26}$ e.s.u., whilst the weighted mean, where the individual values were weighted as $[1/\sigma(\Theta)]^2$, was $(1.445 \pm 0.037) \times 10^{-26}$ e.s.u. However, the estimates of $\Theta$ at 243, 253 and 263 K were determined from values of $B_e$ which came from fits not considered to be the best at those temperatures, so our best estimate of $\Theta$ for nitrogen was given by the mean of the values at 273, 283, 300 and 303 K only: the unweighted mean of these four values of $\Theta$ was $(1.53 \pm 0.12) \times 10^{-26}$ e.s.u., whilst the weighted mean was $(1.480 \pm 0.040) \times 10^{-26}$ e.s.u. None of the individual measurements of $\Theta$ between 243 and 303 K differed by more than one standard deviation from the weighted mean of $\Theta = (1.480 \pm 0.040) \times 10^{-26}$ e.s.u., and, as can be seen in table (8.8), our result was in excellent agreement with published values.
Table (8.8) Comparison with published values of the quadrupole moment of nitrogen

<table>
<thead>
<tr>
<th>Source</th>
<th>10^{38} \Theta/e.s.u.</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>(1.480 \pm 0.040)</td>
<td>(B_e - B_R - \Delta B_e^{\text{OR}})</td>
</tr>
<tr>
<td>Huot and Bose [151]</td>
<td>(1.47 \pm 0.07)</td>
<td>(B_e - B_R - \Delta B_e^{\text{OR}})</td>
</tr>
<tr>
<td>Buckingham et al. [157]</td>
<td>(1.47 \pm 0.09)</td>
<td>Induced birefringence</td>
</tr>
<tr>
<td>Budenholzer et al. [153]</td>
<td>(1.5 \pm 0.5)</td>
<td>Ion-molecule scattering</td>
</tr>
<tr>
<td>Poll and Hunt [154]</td>
<td>(1.5 \pm 0.1)</td>
<td>Collision-induced absorption</td>
</tr>
<tr>
<td>Dagg et al. [158]</td>
<td>1.51</td>
<td>Collision-induced absorption</td>
</tr>
<tr>
<td>Flygare and Benson [159]</td>
<td>(1.4 \pm 0.1)</td>
<td>Magnetizability anisotropy</td>
</tr>
<tr>
<td>Moon and Oxtoby [160]</td>
<td>1.541</td>
<td>Theory</td>
</tr>
</tbody>
</table>

All the quoted uncertainties in table (8.8) are estimates of the random errors only and take no account of systematic errors. However, given the estimated total uncertainty in each of our measurements of \(B_e\) of \(\pm 1.7 \text{ cm}^6 \text{ mol}^{-2}\), the total uncertainty in our value of \(\Theta\) was estimated to be \(\pm 0.58 \times 10^{-26} \text{ e.s.u.}\).

Using our best estimate of \(\Theta = 1.480 \times 10^{-26} \text{ e.s.u.}\), and the values of \(B_e^{\text{exp}}\) and \(\Delta B_e^{\text{OR}}\) from table (8.7), the discontinuous, semi-empirical \(B_e\) curve in figure (8.25) was obtained; \(B_e\) was also calculated at 350 K \([B_e = 0.67 \text{ cm}^6 \text{ mol}^{-2}, \Delta B_e^{\text{OR}} = 0.11 \text{ cm}^6 \text{ mol}^{-2}]\) so that the curve could be extended beyond Johnston, Oudemans and Cole’s measurements at 344 K [100]. Although we used the same correction terms \(\Delta B_e^{\text{OR}}\) as Huot and Bose [151], the contributions to our \(\Theta\) values in table (8.7) were small and so Huot and Bose’s experimental \(B_e(323.15\text{K}) = (2.1 \pm 0.1) \text{ cm}^6 \text{ mol}^{-2}\) still provided good independent confirmation of the accuracy of our \(B_e\) measurements at lower temperatures, and made it clear that our measurement of \(B_e\) at 323 K was in significant error. The excellent agreement of Huot and Bose’s measurement with our semi-empirical curve was particularly pleasing because Huot and Bose’s result came from a regression in which a significant value of the third dielectric virial coefficient was determined \([C_e = (-107 \pm 5) \text{ cm}^6 \text{ mol}^{-2}]\), and so their \(B_e\) was not likely to be suffering from
significant truncation error, suggesting that our measurements of $B_e$ from which the semi-empirical curve was obtained were equally free of such error. The result of Vidal and Lallemand at 298.15 K [134] was about 1.2 cm$^6$ mol$^2$ smaller than the semi-empirical value, although this difference was still less than two combined standard deviations, since we estimate that the standard deviation of a semi-empirical $B_e$ value was approximately the same as the standard deviations of the measured $B_e$ values between 273 and 303 K from which the semi-empirical curve was obtained. The measurement of Orcutt and Cole at 322.15 K [103] was about 1.6 cm$^6$ mol$^2$ smaller than the semi-empirical curve, but it was probably suffering from truncation error. Huot and Bose [151] have shown that $C_e$ for nitrogen at 323.15 K was negative and so Orcutt and Cole’s $B_e$ may have contained a hidden contribution from $C_e$ and was, therefore, too small. Johnston, Oudemans and Cole’s measurements at 344 K [100] were both smaller than the empirical curve, but their non-zero value agreed with the curve within its standard deviation. The results of Johnston, Oudemans and Cole between 242 and 306 K [100] were, of course, in good agreement with our semi-empirical curve, just as they were in good agreement with our individual $B_e$ measurements.
Chapter 9 Conclusions

In this work, spherical and cylindrical microwave cavity resonators have been used to measure the dielectric constants of gases at temperatures between 189 and 360 K, and at pressures up to 4.015 MPa, with total fractional uncertainties on the order of ±1 ppm, which are smaller than those reported for the majority of capacitance cell measurements and are comparable with the best of the published work using interferometers. It has been shown that the resonance frequencies and halfwidths of microwave cavity resonators can be modelled to a level approaching 1 ppm, and a completely novel theory for the perturbation due to openings in a cavity wall has been presented and shown to be in superb agreement with experimental measurements on the cylindrical resonator. All useful cavities require openings (e.g., for gas inlets/outlets) and such calculations as were presented in chapter four would prove to be of particular value if the highest accuracy was required in absolute measurements of the speed of light.

The spherical resonator used was originally designed to measure the speed of sound in gases, but it has been demonstrated that the simple introduction of a pair of microwave probes enabled highly-accurate speed of light, and, therefore, dielectric constant measurements using the same apparatus. The speed of sound and dielectric constant measurements on the same gas sample can both be analysed to provide information on the imperfections of the gas, in particular the intermolecular potential energies and the \((p, V_m, T)\) virial coefficients. In one resonator, then, we have the means to determine the same theoretically and industrially important properties exploiting two quite distinct phenomena, one mechanical in nature, the other electromagnetic.

The unprecedentedly small dimensions of the newly-designed cylindrical resonator meant that it could be pressure-compensated within a separate pressure vessel, whilst retaining an overall size suitable for employing a commercially available water bath for a simple means of highly-stable temperature control. This gave rise to a significantly greater mechanical stability than has been reported for any apparatus used to measure the dielectric constants of gases described in the literature to date. Since the mechanical stability of the cell or cavity is often the limiting factor
in dielectric constant measurements, our results were considered to be of superior quality to the majority of published work.

The spherical resonator has been used to determine the first dielectric virial coefficients of argon between 215 and 300 K, of nitrogen and the mixture \(\{0.5\text{ Ar} + 0.5\text{ N}_2\}\) at 300 K, and of xenon between 189 and 360 K, in good agreement with the relatively small number of measurements in the literature and often with higher precision than the most recently published. The second dielectric virial coefficients of xenon were also determined, and were found to be slightly higher than the only two published values within the temperature range; the comparison with theoretical values of \(B_x\) for xenon, calculated using the simple dipole-induced dipole model, was not so good, although the temperature-dependence was similar.

Estimates of the second \((p, V_m, T)\) virial coefficients of argon, nitrogen, \(\{0.5\text{ Ar} + 0.5\text{ N}_2\}\) and xenon determined in this work were generally in good agreement with recently published results. In particular, the smoothing equation determined from our xenon data gave \(B(T)\) in very good agreement with results from the literature at temperatures far outside our experimental range of 189 to 360 K, ably demonstrating the usefulness of the microwave cavity resonator method for estimating \((p, V_m, T)\) virial coefficients without the problems of adsorption that can reduce the accuracy of the more traditional \((p, V_m, T)\) measurements.

The cylindrical resonator was used to measure the first and second dielectric virial coefficients of nitrogen between 243 and 323 K. Our measurements of the first dielectric virial coefficient were in good agreement with literature results at the lower temperatures but were found to be increasingly larger than published measurements at higher temperatures. The discrepancies were attributed to differences in the data used to determine the amount of substance densities and to errors in the fitting of the published work. Our measurements of the second dielectric virial coefficients of nitrogen were generally in good agreement with published results over the whole temperature range. The most reliable of our measurements, between 273 and 303 K, were used to determine a value for the quadrupole moment of nitrogen which was in superb agreement with literature results obtained using a wide variety of experimental techniques, helping to confirm the accuracy of our \(B_x\) measurements.
Most of the gases measured in this work were chosen because their \((p, V_m, T)\) virial coefficients were well known (particularly argon and nitrogen) and because their dielectric virial coefficients had been previously measured by a number of workers, so that the reliability of our dielectric constant measurements using microwave cavity resonators could be confirmed. Argon and nitrogen are often chosen as test gases when developing theoretical models for the properties of industrially important fluids and are also often chosen as reference gases for the calibration and testing of a wide variety of scientific apparatus, and our dielectric virial coefficient measurements will allow the determination of \(\varepsilon\) for these important gases with a greater accuracy than has previously been possible. The measurements of \(B_e\) for xenon presented in this work represent a significant increase in the number of results available, and should enable a more thorough testing of theoretical expressions for \(B_e\) proposed in the future. Our measurements of the second \((p, V_m, T)\) virial coefficients of xenon will help to improve current knowledge of the equation of state for this gas since there are significant differences between many of the results published to date. Now that the high accuracy of the cavity resonator method for measuring the dielectric constant of gases over appreciable ranges of temperature and pressure has been established, gases of greater industrial interest can be measured with confidence. In this respect, it would have been particularly interesting to make measurements on a polar gas sample: the estimates of \((p, V_m, T)\) virial coefficients may not be seriously affected by adsorption errors, but the significantly larger dielectric virial coefficients would require that theoretical values for \(B_e, C_e, \text{ etc.}\) (or an independent source of experimental values), be used when estimating \(B, C, \text{ etc.}\), from the coefficients of the \([(\varepsilon-1)/(\varepsilon +2)]\) on \((p/RT)\) or \([(\varepsilon-1)/(\varepsilon +2)]RT/p\) on \([(\varepsilon-1)/(\varepsilon +2)]\) regressions, just as was done for xenon in chapter seven. Despite the difficulties in estimating second dielectric virial coefficients (especially using current simple models), it is hoped that the resulting estimates of the second \((p, V_m, T)\) virial coefficients would be more accurate than those from direct \((p, V_m, T)\) measurements, especially at low temperatures.

Future work along such lines could benefit from a number of improvements to the resonators. The quality factors of the sphere resonances could have been increased by using shorter microwave probes, perhaps even using antennae of
nominally zero length as in the cylinder, which would have reduced the random uncertainties in the resonance frequencies and the dielectric constants derived from them. This would allow any remaining systematic errors to be more easily identified and, perhaps, eliminated. The measurements taken using the spherical resonator could have been further improved by determining the gas pressure using a pressure balance, as was used for the cylinder measurements on nitrogen.

The cylinder measurements could have been significantly improved by fixing the microwave cables more securely, perhaps by using a commercially available adhesive cement, because it was suspected that the systematic undulations in the fractional excess halfwidths along each of the cylinder isotherms was the result of small movements of the antennae. Measurements taken since this work have supported such suspicions because it was found that when the grub screws were secured as tightly as possible against the cables, there was no systematic undulation in the fractional excess halfwidths as the gas pressure was changed [161]. Reducing the cable movements, and, thereby, the systematic undulations in the excess halfwidths, would reduce the systematic uncertainties in the dielectric constant measurements using the cylinder, and would, perhaps, allow the TM110 mode results to be included along with the TM010 and TM011 modes in the final data analyses. The random uncertainties could be reduced by increasing the quality factors of the modes: even if other contributions to the resonance halfwidths remained the same, the quality factors of the cylinder modes would be increased by an average of about 50% if the cavity walls were silver plated.
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