THE SPEED OF SOUND IN GASES

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BY

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ABSTRACT

The speed of sound in various gases was measured using two different acoustic resonators. The first, a fixed-pathlength variable-frequency cylindrical resonator, was operated between 50 and 100 kHz, while the second, a spherical resonator of radius 60 mm, was operated between 2 and 15 kHz. The temperatures and pressures of the gases were accurately controlled and measured.

Measurements were made on argon, xenon, helium, and 2,2-dimethylpropane at various temperatures between 250 and 340 K, and at pressures below 110 kPa.

The results obtained in 2,2-dimethylpropane were used to derive values of the perfect-gas heat capacity and the second acoustic virial coefficient at temperatures between 250 and 340 K. The second acoustic virial coefficients determined using the spherical resonator have a precision of about ±0.1 per cent and have been used to calculate second virial coefficients. Measurements of the acoustic losses in the spherical resonator indicate that the vibrational relaxation time of 2,2-dimethylpropane at 298.15 K and 100 kPa is 4 ns.

Detailed measurements of the speed of sound in argon indicate that a precision approaching $1 \times 10^{-6}$ is possible in acoustic thermometry using a spherical acoustic resonator. The second acoustic virial coefficients obtained in argon are in close agreement with values calculated from the interatomic pair-potential-energy function.
# TABLE OF CONTENTS

**CHAPTER 1** INTRODUCTION 1

**CHAPTER 2** LINEAR ACOUSTICS 4

2.1 Introduction 4

2.2 The equation of continuity 5

2.3 The unperturbed wave equation 7

2.4 Thermal conduction and viscous drag 10

2.5 The Navier-Stokes equations 14

2.6 Simple-harmonic wave motion 17

2.7 Molecular thermal relaxation 28

References 36

**CHAPTER 3** ACOUSTIC RESONANCE 38

3.1 Introduction 38

3.2 The normal modes of an acoustic cavity 38

3.3 The cylindrical cavity 52

3.4 The spherical cavity 58

3.5 Speed of sound measurements by
   the resonance technique 64

Appendix A3.1 68

Appendix A3.2 78

References 85

**CHAPTER 4** ELECTROACOUSTIC TRANSDUCERS 86

4.1 Introduction 86

4.2 Electrostatic transducers 91

4.3 Piezoelectric transducers 96
CHAPTER 5 THE EQUATION OF STATE AND INTERMOLECULAR FORCES

5.1 Introduction
5.2 The virial equation of state
5.3 Intermolecular forces
   Appendix A5.1
   References

CHAPTER 6 THE CYLINDRICAL RESONATOR

6.1 Introduction
6.2 The apparatus
6.3 Experimental procedure
6.4 Sample results
   References

CHAPTER 7 THE SPHERICAL RESONATOR

7.1 Introduction
7.2 The acoustic resonator
7.3 Instrumentation and measurement technique
7.4 The acoustic model
7.5 Sample results
   Appendix A7.1
   References

CHAPTER 8 EXPERIMENTAL RESULTS

8.1 Introduction
8.2 Argon
8.3 2,2-dimethylpropane
   References
CHAPTER 9  METROLOGICAL APPLICATIONS OF SPHERICAL RESONATORS 247

9.1 Introduction 247
9.2 Sample results 248
9.3 Conclusion 260
References 261

LIST OF TABLES

6.1 Resonance frequencies ($f_1$/Hz) in argon 149
6.2 ($u/L$) for argon at 290.262 K 151
6.3 Resonance frequencies ($f_1$/Hz) in 2,2-dimethylpropane 154
6.4 ($u/L$) for 2,2-dimethylpropane at 290.039 K 157
6.5 Analysis of ($u/L$) for 2,2-dimethylpropane at 290.039 K 159

7.1 Resonance frequencies and half widths in argon at 298.15 K 182
7.2 Analysis of ($u/a)^2$ for argon at 298.15 K 189
7.3 Analysis of ($u/a)^2$ corrected for the temperature jump, argon at 298.15 K 189
7.4 Resonance frequencies and half widths in xenon at 298.15 K 192
7.5 Analysis of ($u/a)^2$ for xenon at 298.15 K 197
7.6 Analysis of ($u/a)^2$ corrected for the temperature jump, xenon at 298.15 K 197
7.7 Resonance frequencies and half widths in helium at 298.15 K 200
7.8 Resonance frequencies and half widths in 2,2-dimethylpropane at 262.61 K 203
7.9 Analysis of ($u/a)^2$ for 2,2-dimethylpropane at 298.15 K 209
8.1 ($u/L$) for argon at various temperatures and pressures 218
8.2 \((u/a)\) for argon at various temperatures and pressures 219
8.3 \(\beta_a\) for argon and \(L\) for cylindrical resonator at various temperatures 220
8.4 \(\beta_a\) for argon and \(a\) for spherical resonator at various temperatures 220
8.5 \((u/L)\) for 2,2-dimethylpropane at various temperatures and pressures 223
8.6 \((u/a)\) for 2,2-dimethylpropane at various temperatures and pressures 226
8.7 \(C_{p,m}^{pg}/R, \beta_a,\) and \(\gamma_a\) for 2,2-dimethylpropane at various temperatures obtained from unconstrained three-term fits. Cylindrical resonator 228
8.8 \(C_{p,m}^{pg}/R, \beta_a,\) and \(\gamma_a\) for 2,2-dimethylpropane at various temperatures obtained from unconstrained three-term fits. Spherical resonator 228
8.9 \(C_{p,m}^{pg}/R\) and \(\beta_a\) for 2,2-dimethylpropane at various temperatures obtained from three-term fits with \(\gamma_a\) constrained. Cylindrical resonator 232
8.10 \(C_{p,m}^{pg}/R\) and \(\beta_a\) for 2,2-dimethylpropane at various temperatures obtained from three-term fits with \(\gamma_a\) constrained. Spherical resonator 232
8.11 Second virial coefficients of 2,2-dimethylpropane 243
8.12 \(\gamma_a(T) - G(T)\) for 2,2-dimethylpropane 243
8.13 Third virial coefficients of 2,2-dimethylpropane 243

9.1 Results in argon at 273.1600 K, Set 1 251
9.2 Results in argon at 273.1600 K, Set 2 252
9.3 Results in argon at 273.1600 K, Set 3 254
9.4 \((u/a)^2\) for argon at 273.1600 K 255
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Dispersion in CO$_2$ at 300 K and 100 kPa</td>
<td>35</td>
</tr>
<tr>
<td>2.2</td>
<td>Absorption in CO$_2$ at 300 K and 100 kPa</td>
<td>35</td>
</tr>
<tr>
<td>3.1</td>
<td>Real and imaginary components of a Lorentzian resonance</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>Amplitude and phase of a Lorentzian resonance</td>
<td>45</td>
</tr>
<tr>
<td>4.1a</td>
<td>Mean displacement amplitude of a driven membrane as a function of frequency</td>
<td>89</td>
</tr>
<tr>
<td>4.1b</td>
<td>Mean displacement amplitude of a driven plate as a function of frequency</td>
<td>89</td>
</tr>
<tr>
<td>4.2</td>
<td>An electrostatic transducer</td>
<td>91</td>
</tr>
<tr>
<td>4.3</td>
<td>Electrostatic transducers</td>
<td>95</td>
</tr>
<tr>
<td>4.4</td>
<td>A piezoelectric transducer</td>
<td>97</td>
</tr>
<tr>
<td>5.1</td>
<td>A modified Boyle's tube apparatus</td>
<td>107</td>
</tr>
<tr>
<td>5.2</td>
<td>A differential Burnett apparatus</td>
<td>107</td>
</tr>
<tr>
<td>5.3</td>
<td>A Joule-Thompson calorimeter</td>
<td>110</td>
</tr>
<tr>
<td>5.4</td>
<td>The Mayer function of argon at various temperatures</td>
<td>123</td>
</tr>
<tr>
<td>5.5</td>
<td>Numerical inversion of second virial coefficients</td>
<td>126</td>
</tr>
<tr>
<td>6.1</td>
<td>The cylindrical resonator</td>
<td>137</td>
</tr>
<tr>
<td>6.2</td>
<td>External pipework (cylindrical resonator)</td>
<td>139</td>
</tr>
<tr>
<td>6.3</td>
<td>The electric thermostat</td>
<td>143</td>
</tr>
<tr>
<td>6.4</td>
<td>Instrumentation (cylindrical resonator)</td>
<td>145</td>
</tr>
<tr>
<td>6.5</td>
<td>$&lt;\delta(u/L)^2/\delta p&gt;$ as a function of $&lt;p&gt;$ for 2,2-dimethyl-propane at 290.039 K</td>
<td>159</td>
</tr>
<tr>
<td>7.1</td>
<td>The spherical resonator</td>
<td>167</td>
</tr>
</tbody>
</table>
7.2 Containment vessel  169
7.3 External pipework (spherical resonator)  170
7.4 Instrumentation (spherical resonator)  174
7.5 In-phase and quadrature components of \( \omega \) as a function of \( f \) near \( f_{01} \) in xenon at 298.15 K and 40 kPa  177
7.6 Shell response at an arbitrary phase  178
7.7 Various contributions to \( g \) and \( \Delta f \) in argon at 298.15 K and 100 kPa  185
7.8 Excess half widths and deviations of \( (u/a) \) for argon at 298.15 K and various pressures.  186
7.9 Fractional deviations of \( (u/a)^2 \) from regression lines for argon at 298.15 K  188
7.10 Excess half widths and deviations of \( (u/a) \) for xenon at 298.15 K and various pressures  195
7.11 \( (u/a)^2 \) vs. \( p \) and deviations of \( (u/a)^2 \) from regression lines for xenon at 298.15 K  196
7.12 \( (u/a)^2 \) vs. \( p \) and deviations of \( (u/a)^2 \) from regression lines for helium at 298.15 K  201
7.13 Half widths, deviations of \( (u/a) \), and deviations of \( (u/a)^2 \) from regression line for 2,2-dimethylpropane at 262.61 K  208
7.14 Power amplifier (circuit diagram)  212
7.15 Preamplifier (circuit diagram)  212
7.16 Bandpass amplifier (circuit diagram)  213

8.1 \( \beta_a(T) \) for argon  221
8.2 \( \beta_a(T) \) for 2,2-dimethylpropane from unconstrained three-term fits  229
8.3 \( \gamma_a(T) \) for 2,2-dimethylpropane  230
8.4 \( \beta_a(T) \) for 2,2-dimethylpropane from constrained three-term fits  233
8.5 \( C_{p,m}^{\text{pg}}(T)/R \) for 2,2-dimethylpropane 235
8.6 Deviations of \( \beta_a \) from equation (8.3.2) 239
8.7 \( B(T) \) for 2,2-dimethylpropane from various sources 242

9.1 \((u/a)^2\) vs. \(p\) for argon at 273.1600 K 256
9.2 Deviations of \((u/a)^2\) from regression lines for argon at 273.1600 K 258

Plate 1 The spherical resonator Inside back cover
CHAPTER 1 INTRODUCTION

The speed of sound in a gas is closely related to the thermodynamic properties of that gas, and its accurate measurement can therefore be used to gain detailed information about the equation of state. Conventionally, this information comes from measurements of the volumes occupied by a given mass of gas at various temperatures and pressures. Such measurements are subject to a number of significant systematic errors; some, but not all, of which may be reduced by use of more elaborate experimental techniques. Speed-of-sound measurements are subject to quite different systematic errors, and these are usually more easily identified and can be greatly reduced. Nevertheless, it is only recently that very accurate measurements have been made in which proper attention has been paid to the elimination of sources of uncertainty.

In view of the importance of a detailed understanding of the performance of acoustic resonators used in speed-of-sound measurements, two chapters of this thesis are devoted to acoustic theory. In chapter two the relation between the speed and attenuation of sound in a fluid and the equilibrium and transport properties of the medium is described. The influence of the presence of a solid boundary on the equations of acoustic wave motion is discussed in detail. Equations relating the resonance frequencies and widths of an acoustic cavity to the speed and attenuation of sound in the fluid it contains are derived in chapter three. These are sufficiently general to allow a detailed description of the performance of acoustic resonators under a wide range of conditions, and for an assessment of their systematic errors to be made.

A detailed study of the equation of state of a gas at low pressures over a wide range of temperatures is one method by which information about pair-wise intermolecular forces may be gained. Use of the pressure
dependence of the sound speed in determining the equation of state is discussed in chapter five, together with the question of what information about intermolecular forces such an equation contains. In addition, the speed of sound in the zero-pressure limit is simply related to the heat capacity of the gas, and to the product $RT$ of the universal gas constant $R$ and the thermodynamic temperature $T$. The principles of acoustic thermometry and of an acoustic redetermination of the gas constant are introduced in chapter five.

This work has employed two different pieces of apparatus. The first was an ultrasonic cylindrical resonator operating with a fixed pathlength and a variable excitation frequency. This is described in chapter six and has been used to study the equation of state of 2,2-dimethylpropane at temperatures between 250 and 340 K and at pressures below 110 kPa. The lowest temperature studied here is about 30 K below the normal boiling temperature, and at such low reduced temperatures conventional volumetric measurements would be subject to large systematic errors arising from adsorption of the gas on the walls of its container. Results at these low temperatures are essential if a direct calculation of the intermolecular pair-potential-energy function is to be undertaken for this substance. If similar measurements can be extended to the lower temperatures necessary for much simpler molecules then some progress in the field of intermolecular forces can be expected.

Although capable of high precision, a resonator operating at high frequencies is subject to systematic errors arising from the ill-defined nature of the wavefield. It was therefore decided to construct a new apparatus, based on a spherical acoustic resonator for use at audio frequencies, in which such uncertainties were eliminated. This apparatus is described in chapter seven and was capable of a precision approaching $1 \times 10^{-6}$ in the speed of sound. Measurements were made of the speed of sound in 2,2-dimethylpropane as a function of pressure at five
temperatures between 262.7 and 325 K, and the results indicate that systematic errors in the earlier measurements of the pressure dependence of the speed of sound were small in comparison with their imprecision. The results are presented in chapter eight where second virial coefficients of 2,2-dimethylpropane between 260 and 340 K have been calculated. These are believed to be of substantially higher accuracy than previous determinations. Values of the perfect-gas heat capacity of 2,2-dimethylpropane have also been obtained with a precision of 0.1 per cent and these are in close agreement with a previous determination at 298.15 K.

Detailed measurements of the speed of sound in argon divided by the mean internal radius of the spherical resonator were performed at the temperature of the triple point of water. The results are reported in chapter nine and suggest that a redetermination of the gas constant with a statistical imprecision of just a few parts per million should be possible. The problem of determining the mean internal radius of the resonator remains but, since it would be sufficient to know the volume of the cavity, a calibration by weighing the resonator firstly in air and secondly when filled with water of mercury should be capable of very high precision.
CHAPTER 2 LINEAR ACoustics

2.1 INTRODUCTION
2.2 THE EQUATION OF CONTINUITY
2.3 THE UNPERTURBED WAVE EQUATION
2.4 THERMAL CONDUCTION AND VISCIOUS DRAG
2.5 THE NAVIER-STOKES EQUATIONS
2.6 SIMPLE HARMONIC ACOUSTIC WAVE MOTION
2.7 MOLECULAR THERMAL RELAXATION

2.1 INTRODUCTION

In order to investigate the relation between the speed of sound in a fluid medium and the thermodynamics of that medium, the dynamics of wave motion must be examined. This will necessarily introduce the link between relevant mechanical and thermodynamic properties. It must be recognised that, while the mechanical processes involved in the passage of sound are intimately related to time, the equilibrium thermodynamic properties of the medium are not. The involvement of non-equilibrium processes, such as thermal conduction, will be seen to be the determinant between a simple wave equation and a much more complicated description of the acoustic cycle. However, the effects of such processes are usually small and can be treated as minor perturbations to the results of a simplified analysis. This simple treatment is given in section 3, and the remainder of this chapter deals with the various mechanisms by which acoustic energy is dissipated. Inclusion of the corresponding terms in the hydrodynamic equations reveals that the speed of sound differs from that predicted in section 3, but that under a wide range of conditions
these effects are negligible in the bulk of the fluid; small attenuations damp the wave motion but leave the speed of sound unperturbed. However, in the case of molecular relaxation phenomena the perturbations can be large and cause dispersion.

2.2 THE EQUATION OF CONTINUITY

In the discussion that follows, the Eulerian description of the fluid will be adopted. In this notation the co-ordinate system is fixed in space and a property of the fluid $f$, for example, refers to the portion of the fluid which happens to be at the position $\mathbf{r}$ of interest, at the time $t$. After a small interval $\Delta t$ of time, a new portion of the fluid may have reached $\mathbf{r}$; $(\partial f/\partial t)\Delta t$ expresses the excess in its $f$ over that in the first portion. In the alternative notation of the Lagrangian description, the total derivative $(df/dt)$ expresses the rate of change in $f$ at a point which is not fixed in space but moves with the fluid.

The fluid velocity is denoted by the vector $\mathbf{U} = U(r,t)$, and

$$
(\partial f/\partial t) = \left\{ f(r + \mathbf{U} \Delta t, t + \Delta t) - f(r, t) \right\}/\Delta t
= \left\{ \partial f/\partial t + U_x (\partial f/\partial x) + U_y (\partial f/\partial y) + U_z (\partial f/\partial z) \right\},
$$

(2.2.1)

where $(x,y,z)$ are the Cartesian components of $\mathbf{r}$, and $(U_x, U_y, U_z)$ are the components of $\mathbf{U}$. The relation between the total and partial derivatives of $f$ with respects to time is therefore

$$
(\partial f/\partial t) = (\partial f/\partial t) + (\mathbf{U} \cdot \nabla) f,
$$

(2.2.2)

where the operator $(\mathbf{U} \cdot \nabla)$ is the scalar product of the fluid velocity and the differential vector operator $\nabla$.†

The equation of continuity states that if $f = f(r,t)$ is an extensive property of the fluid then any change in the amount of $f$ within a closed
surface must be caused either by fluid flow or by creation of \( f \) within that region. The current density of \( f \) is a vector \( \mathbf{J}(\mathbf{r}, t) \) which represents the flow of that property. If \( q \) is a Cartesian co-ordinate then the component \( J_q \) of \( \mathbf{J} \) is the amount of \( f \) crossing a unit area perpendicular to the \( q \) axis, in unit time. Thus the total current density of \( f \) near \( \mathbf{r} \) is the vector \( \mathbf{J} = f' \mathbf{U} \), where \( f' = f'(\mathbf{r}, t) \) is the density of \( f \). The net rate at which \( f \) is lost from the volume \( dV \) around \( \mathbf{r} \) is

\[
\nabla \cdot \mathbf{J} dV = dydz(\partial J_x/\partial x)dx + dxdz(\partial J_y/\partial y)dy + dx dy(\partial J_z/\partial z)dz, \tag{2.2.3}
\]

where \( \nabla \cdot \mathbf{J} \) is the divergence of \( \mathbf{J} \). If in addition \( f \) is created at a rate \( H(\mathbf{r}, t) \) per unit volume then the net rate of change of \( f' \) at \( \mathbf{r} \) is

\[
(\partial f'/\partial t) = H - \nabla \cdot \mathbf{J} = H - f' \nabla \cdot \mathbf{U} - (\mathbf{U} \cdot \nabla) f'. \tag{2.2.4}
\]

Equation (4) is called the equation of continuity for the density of \( f \). If necessary the total derivative can be found by the combination of (2) and (4) which yields

\[
(\partial f'/\partial t) = H - f' \nabla \cdot \mathbf{U}. \tag{2.2.5}
\]

† The symbol \( \nabla \) is used to represent the differential vector operator \( \{\hat{\xi}(\partial/\partial x) + \hat{\jmath}(\partial/\partial y) + \hat{\kappa}(\partial/\partial z)\} \), where \( \hat{\xi}, \hat{\jmath}, \) and \( \hat{\kappa} \) are the \( x,y, \) and \( z \) pointing unit base vectors. The product \( \nabla f \) of \( \nabla \) and the scalar function of position \( f \) is the gradient of the scalar field \( f \). Similarly, the scalar product \( \nabla \cdot \mathbf{g} \), where \( \mathbf{g} \) is a vector function of position, is the divergence of the vector field \( \mathbf{g} \).
2.3 THE UNPERTURBED WAVE EQUATION

It is now possible to derive an equation to describe acoustic wave motion for the limiting case in which the amplitude of the sound is small. The simplified description of sound propagation presented in this section is strictly applicable to an idealised fluid that has no viscosity or thermal conductivity, that is uniform in its properties, at rest, and that is in thermodynamic equilibrium except for the disturbance caused by the passage of sound. In the presence of sound the pressure exerted by the fluid will be \( p + p_a(r, t) \), where \( p \) is the equilibrium pressure and \( p_a \) is the small acoustic pressure. In a similar manner, the temperature will be \( T + T_a(r, t) \) and the mass density \( \rho + \rho_a(r, t) \). The essential assumptions of linear acoustics are that the acoustic contributions to the pressure, temperature, and density are small compared with their equilibrium values, and that the fluid speed is small compared with the sound speed.

The wave equation is obtained by application of Newton's second law of motion and the equation of mass-density continuity to an element of volume in the fluid:

\[
\begin{align*}
- \nabla p_a &= (\rho + \rho_a) \left( \frac{\partial \mathbf{U}}{\partial t} \right) = (\rho + \rho_a) \left( \frac{\partial \mathbf{U}}{\partial t} + (\mathbf{U} \cdot \nabla) \mathbf{U} \right), \\
(\partial \rho_a / \partial t) &= -(\rho + \rho_a) \nabla \cdot \mathbf{U} - (\mathbf{U} \cdot \nabla) \rho_a,
\end{align*}
\]

(2.3.1) (2.3.2)

where \( \nabla p_a \) is the gradient of the acoustic-pressure field.

A consequence of the assumption of linear acoustics is that the compressibility \( \kappa = (1/\rho) (\partial \rho / \partial p) \) of the fluid is independent of \( p_a \) (although it may be dependent upon \( p \)) and therefore equation (2) may be expressed as

\[
\kappa \rho (\partial \rho_a / \partial t) = -(\rho + \rho_a) \nabla \cdot \mathbf{U} - (\mathbf{U} \cdot \nabla) \rho_a.
\]

(2.3.3)

Since \( \rho_a \ll \rho \), and \( \mathbf{U} \cdot \nabla \rho_a \) is the product of two small quantities, equation
(3) may be approximated by
\[ \kappa(\partial p_a / \partial t) = -\hat{\nabla} \cdot \hat{U}, \] (2.3.4)
correct to first order in \( p_a, \rho_a, \) and \( \hat{U}, \) and equation (1) may be written
\[ \rho(\partial \hat{U} / \partial t) = -\hat{\nabla} p_a, \] (2.3.5)
to the same degree of approximation. Taking the divergence of equation (5), and applying equation (4) to eliminate \( \hat{U} , \) gives the wave equation:
\[ \{ \nabla^2 - \kappa \rho(\partial^2 / \partial t^2) \} p_a(r, t) = 0, \] (2.3.6)
where \( \nabla^2 = \hat{\nabla} \cdot \hat{\nabla} \) is the Laplacian operator. This equation describes the propagation of a small-amplitude acoustic disturbance in an infinite and uniform fluid. The absence of frictional terms in equation (1) strictly limits this form of the wave equation to a non-viscous fluid. The problem is not yet completely specified because the compressibility \( \kappa \) is a function of the path of the acoustic cycle. It is assumed in this simple treatment that the transport of heat between one region of the fluid and another is absent, and that therefore the acoustic cycle is adiabatic. To specify the acoustic cycle thermodynamically, the first law is applied with the portion of fluid under consideration as the system:
\[ dE = Q + W, \] (2.3.7)
where \( E \) is the energy, \( Q \) is the heat, and \( W \) the work done on the system. Since the composition of the system is constant, the second law states
\[ dE = TdS - pdV, \] (2.3.8)
where \( S \) and \( V \) are the entropy and volume of the system. Combination of equations (7) and (8) gives
\[ TdS = Q + W + pdV, \] (2.3.9)
and since the acoustic cycle is assumed to be adiabatic, $Q$ is zero. Thus if internal friction is absent $\dot{W} + p dV = 0$ and the entropy is constant. The isentropic compressibility $\kappa_S$ is therefore appropriate in the wave equation.

A particular solution of the wave equation is given by $p_a(\mathbf{r}, t) = f_1(\mathbf{r} + ut\hat{h})$ and defines a wave travelling in a direction parallel to that of the unit vector $\hat{h}$, at a speed $u$. Insertion of $f_1$ into the wave equation yields

$$\left(\frac{\partial^2 f_1}{\partial \mathbf{q}^2}\right) = -\kappa_S u^2 \left(\frac{\partial^2 f_1}{\partial \mathbf{q}^2}\right); \quad \mathbf{q} = \mathbf{r} + ut\hat{h}, \quad (2.3.10)$$

and the general result that $u^2 = (1/\rho \kappa_S)$. In this example the wavefronts are planar and perpendicular to the direction of $\hat{h}$; such a wave is called a plane wave. Since equation (6) is a second-order partial-differential equation, it must have as its solutions two independent functions. For the plane-wave example cited here a second solution is $p_a(\mathbf{r}, t) = f_2(\mathbf{r} - ut\hat{h})$, defining a plane wave travelling in the opposite direction to the first. A general solution of the wave equation for plane waves is therefore a linear combination of $f_1$ and $f_2$.

Before proceeding to discuss the influence of viscous and thermal conductivity perturbations in the linearized equations of motion, it is useful to recast the description of the unperturbed wave field. In the absence of friction the fluid flow must be irrotational and in consequence the fluid velocity may be expressed as the gradient of a scalar function. This scalar function is the velocity potential and will be denoted as $\Psi(\mathbf{r}, t)$ so that

$$U(\mathbf{r}, t) = -\nabla \Psi(\mathbf{r}, t). \quad (2.3.11)$$

Substitution in equation (5) reveals that, to first order in the acoustic variables, the acoustic pressure is given by

$$p_a(\mathbf{r}, t) = \rho (\partial \Psi(\mathbf{r}, t)/\partial t). \quad (2.3.12)$$
This description is especially convenient because it relates both the fluid velocity and the acoustic pressure to the single quantity $\Psi$.

In this discussion two classes of assumption have been made: those that are common to all of linear acoustics, namely that the acoustic variables are sufficiently small for their cross products and higher powers to be negligible; and those adopted to obtain the simple solution, namely that viscous drag and thermal conduction can be neglected, and that local thermodynamic equilibrium is established instantaneously in the fluid. The approximations of linear acoustics are exact in the limit $p_a \to 0$ and in practice the small-amplitude limiting behaviour is easily achieved. In contrast, the approximations adopted for simplicity are not exact in the small-amplitude limit and require further discussion, although the result that the speed of sound is $(1/\rho_0)^{1/2}$ is a good approximation for a real gas.

2.4 THERMAL CONDUCTION AND VISCOUS DRAG

If there is a temperature gradient in the fluid then heat will flow irreversibly from the regions of higher temperature to those of lower temperature. Similarly, if there is a velocity gradient in the fluid then momentum will flow irreversibly from the regions of higher velocity to those of lower velocity. Gradients of both kinds exist in the presence of sound, and thus the acoustic cycle can never be exactly adiabatic or frictionless.

The current density of heat $\mathbf{j}_H$ is proportional to the gradient of the temperature:

$$\mathbf{j}_H = -k \nabla T_a,$$  \hspace{1cm} (2.4.1)

where the constant of proportionality is the coefficient of thermal
conductivity. In the absence of friction, $w = -pdV$ and equation (2.3.9) becomes

$$dS = \frac{1}{T}dQ, \quad (2.4.2)$$

where the heat is now an infinitesimal quantity. If it is assumed that at every instant in time there is local thermodynamic equilibrium within any infinitesimal element of volume $dV$ in the fluid, then equation (2) may be differentiated with respect to time $t$ to obtain

$$\left(\frac{\partial S}{\partial t}\right) = \frac{1}{T}\left(\frac{\partial Q}{\partial t}\right). \quad (2.4.3)$$

The quantity $\left(\frac{\partial Q}{\partial t}\right)$ can be obtained directly from the equation of heat-density continuity,

$$\left(\frac{\partial Q}{\partial t}\right) = -\nabla \cdot \mathbf{J}_H, \quad (2.4.4)$$

when there are no source terms. Combination of equations (1), (3), and (4) gives

$$\left(\frac{\partial S_a}{\partial t}\right) = \left(KV_m/T\right)\nabla^2 T_a, \quad (2.4.5)$$

where $S_a$ is the small acoustic contribution to the molar entropy, and $V_m$ is the molar volume of the fluid. This equation can be used to calculate the transfer of energy as heat, from the sound wave, arising

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† Equation (2.3.9), and therefore equation (2.4.2), is applicable only to a closed system. The Eulerian description does not refer to a fixed amount of the fluid and cannot be applied directly. Instead the total derivative $dS/dt$ must be found, and equation (2.4.3) obtained from equation (2.2.2) by neglecting the second-order term $(\mathbf{U} \cdot \nabla)S$. Thus the difference between the total and partial derivatives vanishes to first order in the acoustic variables.

* The neglect of frictional source terms in the equation of heat-density continuity is justified because such terms are of the second order in the acoustic variables.
from thermal conduction.

The effects of viscosity enter directly into the equations of motion. Let us again consider the fluid within an element of volume $\Delta x\Delta y\Delta z$ around $\mathbf{r}$. The force acting across the face $\Delta y\Delta z$ perpendicular to $x$, is $\mathbf{F}_x(\mathbf{r},t)\Delta y\Delta z$ where $\mathbf{F}_x$ is a vector representing the fluid stress on that face. In a non-viscous fluid $\mathbf{F}_x = \mathbf{i}p(\mathbf{r},t)$ and is normal to the surface ($\mathbf{i}$ is the $x$-pointing unit base vector). However, in a viscous fluid the interaction between any two regions which are separated by a plane surface is no longer normal to that surface. Thus the vector $\mathbf{F}_x$ has three components:

$$\mathbf{F}_x = \mathbf{i}p_{xx} + \mathbf{j}p_{xy} + \mathbf{k}p_{xz}, \quad (2.4.7)$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the $x$, $y$, and $z$-pointing unit base vectors. The resultant force on the element of volume $\Delta V = \Delta x\Delta y\Delta z$, transmitted across the faces perpendicular to the $x$ axis, is $(\partial \mathbf{F}_x / \partial x)\Delta V$. Similar terms arise for the stress and net force acting across the other faces of the element, and thus the total resultant force acting on the element of fluid requires nine terms, rather than three, to describe it. The resultant force acting at $\mathbf{r}$ is therefore given by

$$\mathbf{F}(\mathbf{r},t) = -\Delta V \left[ \frac{\partial}{\partial x} \mathbf{F}_x + \frac{\partial}{\partial y} \mathbf{F}_y + \frac{\partial}{\partial z} \mathbf{F}_z \right]. \quad (2.4.8)$$

Equation (8) may be given a matrix representation:

$$\begin{bmatrix} \mathbf{F}(\mathbf{r},t) \end{bmatrix} = -\Delta V \begin{bmatrix} \partial/\partial x & \partial/\partial y & \partial/\partial z \end{bmatrix} \begin{bmatrix} \mathbf{F}_x \\ \mathbf{F}_y \\ \mathbf{F}_z \end{bmatrix}, \quad (2.4.9)$$

in which the trio of vectors $\mathbf{F}_x', \mathbf{F}_y', \mathbf{F}_z'$ are given by

$$\begin{bmatrix} \mathbf{F}_x' \\ \mathbf{F}_y' \\ \mathbf{F}_z' \end{bmatrix} = \mathbf{P} \begin{bmatrix} \mathbf{i} \\ \mathbf{j} \\ \mathbf{k} \end{bmatrix} = \begin{bmatrix} p_{xx} & p_{xy} & p_{xz} \\ p_{yx} & p_{yy} & p_{yz} \\ p_{zx} & p_{zy} & p_{zz} \end{bmatrix} \begin{bmatrix} \mathbf{i} \\ \mathbf{j} \\ \mathbf{k} \end{bmatrix}. \quad (2.4.10)$$
where $\mathbb{P}$ is the scalar tensor of the fluid stress. The element $P_{ij}$ of $\mathbb{P}$ is the $q_j$ component of the vector $P_{iq_i}$, where $i, j = 1, 2, 3$, and $q_1 = x$, $q_2 = y$, $q_3 = z$. For a non-viscous fluid $\mathbb{P}$ is very simple, having $p_a$ on its diagonal elements and zeros elsewhere. The formulation of the viscous-stress tensor has been discussed in detail, but here it will be sufficient to say that there are three contributions to $\mathbb{P} = \mathbb{P}' + \mathbb{P}'' + \mathbb{P}'''$. The first, $\mathbb{P}'$, is a scalar representing the acoustic pressure and has the elements

$$P_{ii}' = p_a, \quad P_{ij}' = 0; \quad i \neq j. \quad (2.4.11)$$

$\mathbb{P}''$ is a proper symmetric tensor of the second rank representing the fluid stress resulting from shear viscosity, and has the elements

$$P_{ii}'' = -2\eta\{U_{i1}/\partial q_1 - (1/3)\mathbf{v} \cdot \mathbf{v}\},$$
$$P_{ij}'' = -\eta\{U_{i1}/\partial q_j + (\partial U_j/\partial q_1)\}; \quad i \neq j, \quad (2.4.12)$$

where $U_{i1}$ is the $q_i$ component of $\mathbf{U}$, and $\eta$ is the coefficient of shear viscosity. It should be noted that the classical shear viscosity can contribute to the normal stress as well as to the shear stress. The third contribution, $\mathbb{P}'''$, is a scalar representing a friction proportional to the rate of compression $(\partial p_a/\partial t)$. To first order in the acoustic variables, $(\partial p_a/\partial t)$ is proportional to the divergence of the fluid velocity and $\mathbb{P}'''$ is therefore defined to have the elements

$$P_{ii}''' = -\eta_b \mathbf{v} \cdot \mathbf{v} = \eta_b \nabla_S (\partial p_a/\partial t),$$
$$P_{ij}''' = 0; \quad i \neq j, \quad (2.4.13)$$

and $\eta_b$ is called the coefficient of bulk viscosity. The origin of this bulk or volume viscosity will be investigated in section 7 of this chapter.

The total stress tensor $\mathbb{P}$ is given by the combination of equations (11) to (13) and has the elements
This introduces viscous forces into the equations of motion.

2.5 THE NAVIER-STOKES EQUATIONS

The Navier-Stokes equations of hydrodynamics for a viscous compressible fluid are obtained by use of the full stress tensor $\mathbf{P}$ of equations (2.4.14) in the expression (2.4.9) for the force acting on the element of volume $dV$ around $\mathbf{x}$. The mass of the fluid within this region is $(\rho + \rho_a) dV$, and application of Newton's second law of motion results in

$$\nabla \mathbf{P} + \rho \mathbf{a} = (\rho + \rho_a) \partial \mathbf{u} / \partial t,$$

in place of (2.3.1). The problem is simplified by separating $\mathbf{P}$ into the sum

$$\mathbf{P} = \mathbf{P}_a - 4 \eta \mathbf{I} + \mathbf{T},$$

where $\mathbf{I}$ is the nine-component tensor with elements $\delta_{ij}$ ($\delta_{ii} = 1$, $\delta_{ij} = 0$; $i \neq j$) and $\mathbf{T}$ has the components

$$T_{ii} = -2\eta \partial^2 \mathbf{u} / \partial t^2,$$

$$T_{ij} = -\eta \partial \mathbf{u} / \partial t^2; i \neq j.$$

Since

$$\nabla \mathbf{P} + \rho \mathbf{a} = \eta \nabla^2 \mathbf{u} - \mathbf{v} \times (\mathbf{v} \times \mathbf{u})$$
where the vector product $\vec{\nabla} \times \vec{U}$ is the Curl of $\vec{U}$, equation (1) becomes

$$\rho \left( \frac{\partial \vec{U}}{\partial t} \right) = -\vec{\nabla} p_a + (\eta_b + 4\eta/3) \vec{\nabla} (\vec{\nabla} \cdot \vec{U}) - \eta \vec{\nabla} \times (\vec{\nabla} \times \vec{U}),$$

(2.5.5)
correct to first order in the acoustic variables. This separation of the stress terms is useful because any vector function of position, such as $\vec{U}$, can be resolved into the sum of a longitudinal component $\vec{U}_l$ for which $\vec{\nabla} \times \vec{U}_l = 0$, and a rotational (or transverse) component $\vec{U}_r$ for which $\vec{\nabla} \cdot \vec{U}_r = 0$. Since the longitudinal component is irrotational, it can be represented by the gradient of a velocity potential. In addition, the gradient of a scalar function is entirely longitudinal and therefore $\vec{\nabla} p_a$ can contribute only to the longitudinal component of $(\partial \vec{U}/\partial t)$.

Consequently the equation of motion (1) can be separated into a pair of uncoupled equations:

$$\rho \left( \frac{\partial \vec{U}_l}{\partial t} \right) = -\vec{\nabla} p_a + (\eta_b + 4\eta/3) \vec{\nabla} (\vec{\nabla} \cdot \vec{U}_l),$$

(2.5.6)$$\rho \left( \frac{\partial \vec{U}_r}{\partial t} \right) = -\eta \vec{\nabla} \times (\vec{\nabla} \times \vec{U}_r) = \eta \vec{\nabla}^2 \vec{U}_r.$$ (2.5.7)

Furthermore, equation (7) is quite unrelated to the acoustic pressure and may be neglected in the bulk of the fluid, although it will be important when there are boundary conditions to be satisfied.

The description now contains five unknowns: the acoustic pressure $p_a$, temperature $T_a$, density $\rho_a$, and molar entropy $S_a$, and the longitudinal fluid velocity $\vec{U}_l$. Five equations are required to specify a solution.

The first two equations are the Navier-Stokes equation for irrotational fluid flow, equation (6), and equation (2.4.6), the equation of continuity for entropy density. The third expression is the equation of mass-density continuity

$$\left( \frac{\partial \rho_a}{\partial t} \right) + \rho \vec{\nabla} \cdot \vec{U}_l = 0.$$ (2.5.8)

The thermodynamic equation of state is the fourth expression and interrelates $\rho_a$, $p_a$, and $T_a$. For a phase of fixed composition
\[ p_a = (\partial p / \partial T)_{T p a} + (\partial p / \partial T)_{p a} \]
\[ = \rho \kappa_T p_a - \rho \alpha_T a = \rho (\gamma \kappa_S p_a - \alpha T_a), \]
(2.5.9)

where \( \kappa_T = \gamma \kappa_S \) is the isothermal compressibility, \( \gamma = C_p / C_V \) is the ratio of the heat capacity of the fluid at constant pressure to the heat capacity at constant volume, and \( \alpha = (1/V)(\partial^2 V / \partial T) \) is the isobaric expansivity of the fluid. The final equation,

\[ S_a = (\partial S_m / \partial T)_{p a} + (\partial S_m / \partial p)_{T p a} \]
\[ = (C_{p m} T_a / T) - \alpha V_m p_a, \]
(2.5.10)

relates the acoustic entropy to \( T_a \) and \( p_a \).

The modified wave equation is obtained by the elimination of \( \bar{U}_1 \) between (6) and (8) to give

\[ \nabla^2 p_a = (\partial^2 p_a / \partial t^2) - (1/\rho)(\eta_b + 4\eta/3)\nabla^2 (\partial p_a / \partial t), \]
(2.5.11)

followed by the elimination of \( \rho_a \) using equation (9) to yield

\[ \nabla^2 p_a = \gamma \kappa_S \{(\partial^2 / \partial t^2) - (1/\rho)(\eta_b + 4\eta/3)(\partial / \partial t) \nabla^2\}(p_a - \beta T_a), \]
(2.5.12)

where \( \beta = (\partial p / \partial T)_p = (\alpha / \gamma \kappa_S) \) is the thermal pressure coefficient. In the case of isentropic flow, equation (10) shows that \( T_a = (T a u / C_{p m}) p_a = (\kappa_T - \kappa_S)p_a / \alpha = \{(\gamma - 1)/\gamma \beta\} p_a \) and thus when \( S_a = 0 \) and \( \eta_b = \eta = 0 \) equation (12) reduces to the simple wave equation of section 3.

If equations (2.4.6) and (10) are combined to eliminate \( S_a \) the equation:

\[ (K_{n m} / C_{p m}) \nabla^2 T_a = \{(\partial / \partial t)\{T_a - \{(\gamma - 1)/\gamma \beta\} p_a\}, \]
(2.5.13)

results which may be solved simultaneously with (12) for \( T_a \) and \( p_a \). If it is required, the longitudinal fluid velocity may be found from

\[ \rho (\partial \bar{U}_1 / \partial t) = -\bar{V}(p_a + (\eta_b + 4\eta/3)\gamma \kappa_S (\partial / \partial t)(p_a - \beta T_a), \]
(2.5.14)

the combination of (6), (8), and (9) which eliminates \( \rho_a \).
While an exact solution of the modified wave equation is possible, the effects of viscosity and thermal conductivity are small and it is sufficient to consider solutions that are correct to first order in \( \eta, \eta_b, \) and \( K. \)

### 2.6 Simple-Harmonic Wave Motion

The solutions of the modified wave equation are frequency dependent and it is convenient to adopt a harmonic analysis. The time dependent factor for such motion is \( \exp(-i\omega t) \) where \( \omega/2\pi \) is the frequency of the sound. The acoustic pressure will be required to satisfy the equations:

\[
\left( \frac{\partial}{\partial t} \right) p_a = -i \omega p_a, \quad \text{and} \quad \nabla^2 p_a = -k^2 p_a, \tag{2.6.1}
\]

in which \( k \) is the propagation constant. Since the acoustic temperature is proportional to the acoustic pressure, identical relations must exist for the spatial and time derivatives of \( T_a \). The ratio \( (k/\omega) \) is to be determined; its inverse gives the wave speed and attenuation. These are quite general properties of damped simple-harmonic waves.

The notation is simplified if equations (2.5.12) and (2.5.13) are recast as

\[
\nabla^2 p_a = \left( \frac{\gamma}{u_0^2} \right) \left( \partial^2/\partial t^2 \right) - \lambda_v u_0 \left( \partial/\partial t \right) \nabla^2 \left( p_a - \beta T_a \right), \quad \text{and} \quad \nabla^2 T_a = \left( 1/\lambda_h u_0 \right) \left( \partial/\partial t \right) \{ T_a - (\gamma-1) p_a / \gamma \beta \}, \tag{2.6.2}
\]

in terms of the characteristic thermal and viscous lengths

\[
\lambda_h = (K/u_0 c_p) = (K V_m u_0 C_p)_m, \quad \text{and} \quad \lambda_v = (\eta_b + \Delta \eta / 3) / \rho u_0, \tag{2.6.3}
\]

where \( c_p \) is the specific heat capacity at constant pressure, and
For gases, $Z_h$ and $Z_v$ are of the same order as the molecular mean free path.

Insertion of $-k^2$ for $\nabla^2$, and $-i\omega$ for $(\partial/\partial t)$, into the first of equations (1), yields

$$\{k^2 - (\omega^2 \gamma / u_o^2) - i(\omega k \lambda_v \gamma / u_o)\} p_a + \{(\omega^2 \gamma / u_o^2) + i(\omega k \lambda_v \gamma / u_o)\} \beta T_c = 0.$$  \hspace{1cm} (2.6.4)

Similarly, from the second of equations (2) the expression

$$\{(k^2 \lambda_h u_o) - i\omega\} T_c + \{i(\gamma - 1) \omega p_a / \gamma \beta\} = 0,$$  \hspace{1cm} (2.6.5)

is obtained. If equations (4) and (5) are solved simultaneously for $p_a$ then the result is

$$\{(k/\omega)^4[(\omega^2 \lambda_v \gamma) + i(\omega k \lambda_v u_o)] + (k/\omega)^2[1 - i(\gamma \omega k \lambda_v u_o) - i(\omega k \lambda_v u_o)] - \{1/u_o^2\}\} p_a = 0.$$  \hspace{1cm} (2.6.6)

This quadratic expression in $(k/\omega)^2$ is subject, again, to the principle condition that the amplitude of the sound be small. However, full account has now been taken of the effects of thermal conductivity and viscosity, so that equation (6) is essentially exact in the small-amplitude limit. It should be noted that this is a quadratic expression with two roots and that, together with the solution of the rotational wave equation, there are now three valid solutions in place of the simple result of section 3. Each of these solutions will yield a pair of solutions for $(k/\omega)$, but only the positive roots will be retained.

The solutions of equation (6) are given by

$$\frac{k}{\omega} = \frac{1}{2u_o L_h} \{(1 - iL_v - i\gamma L_h \pm D)/(1 - i\gamma L_v)\},$$  \hspace{1cm} (2.6.7)

where

$$L_h = \omega \lambda_h / u_o \quad \text{and} \quad L_v = \omega \lambda_v / u_o,$$  \hspace{1cm} (2.6.8)

and $D^2 = (1 - iL_v + i\gamma L_h)^2 + 4i(1 - \gamma)L_h$. If $L_v$ and $L_h$ are small in
in comparison with \( l \) then \( D \) may be expanded in a binomial series. Thus

\[
D = 1 - iL_v - i\gamma L_h - 2(\gamma - 1)L_h^2 + 2iL_h + 2(\gamma - 1)L_h L_v, \tag{2.6.9}
\]

correct to first order in \( L_v \) and second order in \( L_h \); since \( L_h \) occurs in the denominator of (7), equation (9) must be second order in \( L_h \) to provide a first-order solution for equation (7). Thus the first solution of the longitudinal wave equation (with \(-D\) in equation 7) is

\[
(k/\omega)^2 = (1/u_0)^2(1 + iL_v + i(\gamma - 1)L_h), \tag{2.6.10}
\]

and is called the propagational mode of sound. Thus the propagation constant \( k \) has a real part equal to \((\omega/u_0)\) and a small imaginary term, which is proportional to \( \omega^2 \), representing energy loss from the wave. The phase speed is identical with \( u_0 \) and the attenuation is small, provided that \( L_v \) and \( L_h << 1 \). However, if the sound frequency is sufficiently high (or if \( L_v \) and \( L_h \) sufficiently large), then \( L_v^2 \) and \( L_h^2 \) can no longer be neglected and the phase speed is found to differ from \( u_0 \) by an amount that is confined to terms of the second and higher orders in \( L_v \) and \( L_h \). For argon at 300 K and 100 kPa, \( L_h = 1.3 \times 10^{-4} \) and \( L_v = 1.1 \times 10^{-4} \) when the sound frequency is 100 kHz.\(^3\) Thus even at quite high frequencies the phase speed does not differ from \( u_0 \) by more than a few part in \( 10^8 \). Since \( L_h \) and \( L_v \) are approximately proportional to \( p^{-1} \), sound attenuation will increase at lower pressures, but even at the low pressure of 1 kPa dispersion of audio-frequency sound is slight.

The second solution of the longitudinal wave equation is given by

\[
(k_h/\omega)^2 = i/L_h u_0^2, \tag{2.6.11}
\]

and is called the thermal mode. Since \((k_h/\omega)^2\) is imaginary the thermal waves are very rapidly attenuated and can be neglected in the bulk of the fluid. However, this mode must be included when there are boundary conditions to be satisfied.
A third solution arises from the rotational terms in the hydrodynamic equations. This is called the shear mode and, since no changes in the acoustic temperature or pressure are involved, it can be neglected in the bulk of the fluid. Again, however, shear waves must be considered when there are boundary conditions to be satisfied. If a harmonic solution \( \frac{\partial \mathbf{U}}{\partial t} = -i \omega \mathbf{U} \), and \( \nabla^2 \mathbf{U} = -k^2 \mathbf{U} \) is imposed on equation (2.5.7) then the result is

\[
\left( \frac{k_s}{\omega} \right)^2 = \frac{i}{L_s u_0^2} ,
\]

where

\[
L_s = \frac{\omega L_s}{u_0} \quad \text{and} \quad l_s = \frac{\eta}{\rho u_0} ,
\]

and now the characteristic shear length \( l_s \) does not include the bulk viscosity. Clearly this mode is attenuated as rapidly as the thermal mode.

The energy withdrawn from the propagational wave is partitioned between the thermal and shear modes which are, in effect, the diffusion of heat and momentum from the propagating wave. Since the loss is so small, and the attenuation of the thermal and shear waves is so high, the amplitudes of these modes are negligible in the bulk fluid where they have no other means of support.

Equations (5) and (2.5.14) reveal that

\[
T_p = \left( \frac{\gamma-1}{\gamma \beta} \right) \left( 1 - i L_h \right) p_p , \quad \text{and} \quad \mathbf{U}_l, p = \left( 1 - i \omega \right) \left( 1 - i L_v \right) \mathbf{V}_p ,
\]

are the propagational wave's contribution to the acoustic temperature and longitudinal fluid velocity, where \( p_p \) is the acoustic pressure of the propagational mode.

Substitution of \( k_h \) in equation (2) shows that

\[
p_h = i \gamma \beta (L_h - L_v) T_h , \quad \text{and hence that} \quad \mathbf{U}_l, h = (\gamma \ell_h / \omega) \mathbf{V}_T ,
\]

(2.6.15)
are the contributions of the thermal wave to the acoustic pressure and fluid velocity, where \( T_h \) is the contribution to the acoustic temperature. All three are small in the bulk of the fluid.

To illustrate these phenomena, the behaviour of plane simple-harmonic waves of sound will be considered. It is first assumed that there are no boundaries and that the sound is propagating parallel to the \( z \) axis. For the propagational mode, the acoustic pressure will be

\[
p_p(z,t) = f(z)\exp(-i\omega t) \quad \text{where} \quad \omega = \omega / 2\pi \text{ is the real frequency}. \]

Since the waves are plane, there will be no dependence on the other spatial coordinates. Equation (1) requires that \( f(z) \) be an eigenfunction of the Laplacian operator and that the corresponding eigenvalue be \(-k^2\). Thus

\[
f(z) = A\exp(\pm ikz) \quad \text{are the two independent solutions and define positive- and negative-going waves of amplitude} \ A. \]

The positive-going wave is therefore,

\[
p_p(z,t) = A \exp(ikz - i\omega t) = A \exp(-\alpha z) \exp\{i(\omega / u_0)(z - u_0 t)\}, \quad (2.6.16)
\]

where \( \alpha \) is the imaginary component of \( k \), and \( \exp(-\alpha z) \) clearly describes the attenuation of the sound. The expression

\[
k = (\omega / u_0)\{1 + (iL_v/2) + i(\gamma - 1)L_h/2\}; \quad (2.6.17)
\]

may be obtained from equation (10) without further approximation and thus

\[
\gamma = (\omega / 2u_0)\{L_v + (\gamma - 1)L_h\} \quad (2.6.18)
\]

is the coefficient of absorption. For pure monatomic, and for many other gases, \( \eta_b = 0 \), \( L_v = L_s \), and \( \alpha \) is determined by the purely classical mechanisms of heat conduction and shear viscosity. In this case the classical absorption coefficient \( \alpha_{CL} \) is about \( 2 \times 10^{-11} \text{ m}^{-1} (f/\text{Hz})^2 \) at 100 kPa, \(^3\) and so attenuation at audio frequencies is very small.

The longitudinal component of the fluid velocity is given by

\[
\tilde{u}_{1,p}(z,t) = \tilde{\zeta}\{1 + \frac{1}{2}i(\gamma - 1)L_v - \frac{1}{2}iL_v\}\{p_p(z,t) / \rho u_0\}. \quad (2.6.19)
\]
Equation (19) illustrates the quite general analogy between the quotients $p/U$, in acoustics, and potential difference divided by electric current, in a.c. circuit theory. The quantity $\rho u_o$ is called the characteristic resistance of the medium.

The wavefunction of the associated thermal wave must also be an eigenfunction of $\nabla^2$ and in this case the eigenvalue must be $-k_h^2$. Thus

$$T_h(z,t) = B \exp(ik_n z - iwt)$$
$$= B \exp[(i-1)(\omega/u_o)(2L_h)^{-\frac{1}{2}} z - iwt)$$

(2.6.20)

describes a positive-going thermal wave. The real part of the exponential describes a very rapid attenuation.

For the associated shear wave $\nabla \times \vec{U}$ must be zero by definition, and $\vec{U}$ must be a vector eigenfunction of $\nabla^2$ with the scalar eigenvalue $-k_s^2$. Since the primary sound wave is plane and propagates parallel to the $z$ axis, the components $U_x$ and $U_y$ of $\vec{U}$ must be equal, and $U_z$ must be zero. Thus the positive-going shear wave's fluid velocity is

$$\vec{U}_r(z,t) = (\hat{\imath} + \hat{j}) C \exp(ik_s z - iwt)$$
$$= (\hat{\imath} + \hat{j}) C \exp[(i-1)(\omega/u_o)(2L_s)^{-\frac{1}{2}} z - iwt),$$

(2.6.21)

and again there is rapid attenuation.

When the fluid is confined to a particular region by a surface, the solutions of the wave equation must satisfy certain boundary conditions at that surface. If the wall is perfectly rigid then the normal component of the fluid velocity must vanish there. For a non-rigid wall, it is often possible to assume that the motion of any element of the surface is determined solely by the acoustic pressure acting there. In this case the boundary is said to be of local reaction, and a mechanical impedance $Z(r_s,t)$ may be defined for each position $r_s$ on the surface by $Z = p_a(r_s)/\vec{U}_n(r_s)$ where $U_n(r_s)$ is the wall-pointing normal component of $\vec{U}$ at $r_s$. If $U_n$ is zero then $Z$ is infinite. A more convenient quantity is the
acoustic admittance \( Y = Z^{-1} = \Gamma - i \Theta \), whose real component is the acoustic conductance \( \Gamma \), and whose imaginary component is the acoustic susceptance \( \Theta \) of the boundary surface. The general boundary condition for the total normal fluid flow is therefore

\[
U_n(\hat{r}_S) = p_a(\hat{r}_S)Y(\hat{r}_S, f),
\]

(2.6.22)

at each position \( \hat{r}_S \) on the surface.

In a viscous fluid the tangential component \( U_t \) of \( \hat{U} \) must vanish at the surface. A second boundary condition is therefore

\[
U_t(\hat{r}_S) = 0.
\]

(2.6.23)

In a thermally conducting fluid the temperature must be a continuous function of position. Since the heat capacity and thermal conductivity of the boundary material are usually much greater than those of the fluid, the third boundary condition is taken to be

\[
T_a(\hat{r}_S) = 0,
\]

(2.6.24)

so that the temperature is constant at the wall. In the case of the interface between a dilute gas and a metal wall this condition should be closely obeyed. However, if the fluid is dense or has a high thermal conductivity then the discontinuity in the thermal impedances at the surface will not be so large, and thermal waves may penetrate into the wall.

The propagational mode cannot, on its own, satisfy all three of the boundary conditions simultaneously and a combination of the three modes is required. At the boundary surface, additional energy is withdrawn from the propagating mode, and the amplitudes of the other modes are greatly increased so that the temperature fluctuations and tangential velocity of the propagational mode are cancelled. In the bulk of the fluid, the amplitudes of the thermal and shear waves decay
exponentially, by their characteristic decay lengths $\delta_h$ and $\delta_s$, from their maxima at the surface. Equations (20) and (21) give these decay lengths as

$$\delta_h = \left( \frac{u_0}{\omega} (2L_h) \right)^{\frac{1}{h}} = \left( \frac{2L_h u_0}{\omega} \right)^{\frac{1}{h}} = \frac{1+i}{k_h}, \quad \text{and}$$

$$\delta_s = \left( \frac{u_0}{\omega} (2L_s) \right)^{\frac{1}{s}} = \left( \frac{2L_s u_0}{\omega} \right)^{\frac{1}{s}} = \frac{1+i}{k_s}.$$  \hspace{1cm} (2.6.25)

The regions in which the thermal and shear waves are important are called the boundary layers; equations (25) show that the widths of these layers are usually much less than the wavelength $\lambda = 2\mu u/\omega$ of the sound.

If the plane waves under consideration are confined to the half space $z < 0$ by an infinite plane wall of local reaction then, in addition to the positive-going waves, there will be reflected waves which will give rise, together with the source waves, to a composite wave field. If the source waves are driven at an angle to the $z$ axis such that the motion is perpendicular to the $y$ axis, then the pressure in the composite wave field, due to the propagational mode, must be

$$p = f_1(x)f_2(y)\exp(-i\omega t), \hspace{1cm} (2.6.26)$$

where $f_1$ and $f_2$ are functions of their arguments. $f_1$ describes the tangential motion, while $f_2$ determines the motion that is normal to the surface. Since $f_1 f_2$ must be an eigenfunction of $\nabla^2$ with the eigenvalue $-k^2$, the second derivative of both functions with respect to their arguments must be constant, and if

$$\nabla^2 f_1 = -k^2_t f_1, \quad \text{then}$$

$$\nabla^2 f_2 = (k^2_t - k^2) f_2,$$  \hspace{1cm} (2.6.27)

where $k_t < k$ is the tangential wavenumber. Neglecting the small thermal and shear corrections to the propagational mode, the other acoustic variables are given by
\[
T_p = \frac{1}{(\gamma-1)/\gamma\beta} f_1 f_2 \exp(-i\omega t)
\]
\[
U_{p,z} = \frac{1}{i\omega\rho} \frac{df_2}{dz} f_1 \exp(-i\omega t)
\]
\[
U_{p,x} = \frac{1}{i\omega\rho} \frac{df_1}{dx} f_2 \exp(-i\omega t).
\]

(2.6.28)

In order to satisfy the thermal boundary condition of equation (24) at every point on the surface, the thermal wave must have the same dependence on \(x\) as the propagational wave. Thus

\[
T_h = f_1(x) f_3(z) \exp(-i\omega t),
\]

(2.6.29)
in which \(f_3(z)\) is to be determined. Since \(T_h\) is an eigenfunction of \(\nabla^2\) with the eigenvalue \(-k_h^2\),

\[
\nabla^2 f_3 = -(k_h^2 - k_t^2) f_3,
\]

(2.6.30)

where \(k_h = (i/L_h)(\omega/\nu_0)^2 = 2i/\delta_h^2\). Thus the required solution is \(f_3 = B \exp(-ik_3 z)\) where \(k_3 = (k_h^2 - k_t^2)^{1/2}\), but \(k_t^2 < k^2\), \(k_h^2 \gg k^2\), and an approximate solution is

\[
f_3(z) = B \exp(-ik_h z) = B \exp\left\{\frac{(1-i)z}{\delta_h}\right\}.
\]

(2.6.31)

This approximation will be valid when the wavelength of the sound is much greater than the characteristic thermal length \(\delta_h\) (i.e. when \(1>>L_h\)), and this condition is readily met. Comparison of equations (28) and (29) reveals that the amplitude \(B\) of the thermal wave that satisfies the boundary condition is

\[
B = -\frac{1}{(\gamma-1)/\gamma\beta} f_2(0).
\]

(2.6.32)

The contribution of the thermal mode to the other acoustic variables cannot be neglected in the boundary layer, without further examination, because of the greatly increased amplitude in this region. The contribution to the acoustic pressure, given by the first of equations (15), has the factor \((L_h - L_v)\) and is therefore negligible, and likewise the contribution to the tangential fluid velocity can be neglected.
However, the normal derivative of the thermal mode's temperature field is very large, and the second of equations (15), shows that

$$U_{h,z} = (i-1)(\gamma-1)f_1f_2(0)(\omega\delta_h/2\rho u_0^2)\exp(-i\omega t + (1-i)z/\delta_h)$$  \hspace{1cm} (2.6.33)$$
is linear in $\delta_h$ (rather than $L_h = \delta_h^2$). Thus the thermal mode must be considered when satisfying the boundary condition for normal fluid flow.

The shear mode must cancel the tangential component of the fluid velocity arising from the propagating waves. Clearly $U_{r,y} = 0$, and $U_{r,x} = -U_{p,x}$ when $z = 0$. Thus, since $\nabla \times \nabla \cdot U = 0$ and $\nabla^2 U = -k_S^2 U$, the shear wave with velocity components

$$U_{r,x} = (-1/i\omega p)(\frac{df_1}{dx})f_2(0)\exp(-i\omega t - ik_y z),$$
$$U_{r,z} = (-k_t^2/k_{\omega p})f_1f_2(0)\exp(-i\omega t - ik_y z),$$

is generated at the surface. When $\lambda >> \lambda_s$, as is usually the case, $k_s^2 >> k_t^2$ and thus $k_t$ can be neglected to obtain

$$U_{t,z} = (i-1)(k_t^2u_0/\omega)^2(\omega \delta_s/2\rho u_0^2)f_1f_2(0)\exp(-i\omega t + (1-i)z/\delta_s).$$  \hspace{1cm} (2.6.35)$$

The normal component of the total fluid velocity is the sum of the contributions of the three modes:

$$U_z = (f_1/i\omega p)\{(\frac{df_2}{dz}) - (-i+1)f_2(0)(\omega^2/2u_0^2)\{(k_t u_0/\omega)^2 \delta_s \exp(-ik_h z) + (\gamma-1)\delta_h \exp(-ik_h z)\}\}\exp(-i\omega t),$$  \hspace{1cm} (2.6.36)$$

provided that $\lambda_s$ and $\lambda_h << \lambda$. Equation (22) requires that

$$U_z(0) = (f_1/i\omega p)\{(\frac{df_2}{dz})\}_{z=0} - (1+i)f_2(0)(\omega^2/2u_0^2)\{(k_t u_0/\omega)^2 \delta_s + (\gamma-1)\delta_h\}\exp(-i\omega t)$$
$$= Y_m p_a(z=0),$$  \hspace{1cm} (2.6.37)$$

where $Y_m$ is the mechanical admittance of the wall. Since, to a very good approximation, $p_a = p_p = f_1f_2\exp(-i\omega t)$, the boundary conditions
reduce to a single condition which must be satisfied by the acoustic pressure. Substitution of $f_1^2(0)Y_m \exp(-i\omega t) = U_z(0)$ in equation (37) shows that this condition is

$$\left\{ \frac{1}{p_a} \frac{\partial p_a}{\partial n} \right\} = i\omega \{ Y_m + \left\{ \frac{(1-i)}{\rho u_o} \right\} \left\{ (\gamma-1) \frac{\omega \delta_h}{2u_o} + \frac{k_t u_o}{\omega} \right\} \}$$

$$= i\omega (Y_m + Y_h + Y_s), \quad \text{on } r = r_s, \quad (2.6.38)$$

where $(\partial p_a/\partial n)$ is the normal derivative of the acoustic pressure, and $Y_h$ and $Y_s$ are the effective acoustic admittances of the thermal and shear boundary layers respectively, given by

$$Y_h = \left\{ \frac{(1-i)}{\rho u_o} \right\} (\gamma-1) \left\{ \frac{\omega}{2u_o} \right\} \delta_h,$$  \quad \text{and}  \\
$$Y_s = \left\{ \frac{(1-i)}{\rho u_o} \right\} \left( \frac{k_t u_o}{\omega} \right)^2 \delta_s. \quad (2.6.39)$$

The ability to combine the boundary conditions into a simple expression relating the acoustic pressure and its normal derivative at the boundary, to an effective admittance of the boundary surface will be useful when acoustic cavities are considered. Although this result has been obtained for the simple case of the interaction between a plane wave and a plane surface, it is not restricted to this case. In particular, equation (38) can be applied to calculate the phase speed and attenuation of plane sound waves propagating in ducts. The case of the infinite cylindrical wave-guide was first considered by Helmholtz who found that viscous drag at the walls causes the phase speed of plane waves propagating along the tube to be less, and the coefficient of absorption to be higher, than in free space. The additional effect of thermal conduction at the boundary was included by Kirchhoff, and his results may be stated in the form

$$k_{KH} = k + (1+i)\alpha_{KH} \quad (2.6.40)$$

where $k_{KH}$ is the propagation constant for plane waves propagating in a tube of radius $b$, $k$ is the free-space propagation constant given by
equation (17), and

$$
\alpha_{KH} = (\omega/2u_0 b)\{\delta_s + (\gamma-1)\delta_h\}
$$

(2.6.41)

is the Kirchhoff-Helmholtz tube attenuation parameter.\textsuperscript{6} The derivation of equation (41) does involve some further approximation because, in effect, Kirchhoff and Helmholtz have assumed that the acoustic admittance of the cylindrical boundary layer is identical with that at a plane surface. This approximation is valid in the wide tube limit $b \rightarrow \infty$, but direct numerical solution of the boundary-layer problem shows that the approximation is generally accurate provided that $\delta_s$ and $\delta_h \ll b$.\textsuperscript{7}

Equations (38) and (39) can also be applied to specify the boundary conditions for a standing wave within a cavity, provided that the radii of curvature of the surfaces are large compared with the characteristic decay lengths $\delta_h$ and $\delta_s$. These decay lengths are proportional to $(\omega \rho)^{-1/2}$ and hence the effects of the boundary layers become increasingly important at low frequencies and low densities. In contrast, the losses throughout the bulk of the fluid are usually only important at high frequencies.

2.7 MOLECULAR THERMAL RELAXATION

In formulating the equations of acoustic wave motion it has so far been assumed that the relation between the density and pressure in the fluid is primarily a thermodynamic one. At each point in the acoustic cycle the temperature and pressure in a small element of the fluid are assumed to be those that would be achieved if that portion were suddenly isolated (so that no further density fluctuations could occur) and allowed to reach internal equilibrium. In practice there may be a delay between the imposition of a density change and the establishment of the
equilibrium temperature and pressure. It will be shown that, if this delay is short compared with $1/\omega$, the internal friction of bulk viscosity results. If this viscous friction is included in the problem then the thermodynamic equations can be applied with confidence. It has already been shown that the effects of shear viscosity, bulk viscosity, and thermal conduction enter independently. In gases the classical mechanisms of shear viscosity and thermal conduction are small; thus if $\eta_b$ is small its origin may be considered without the inclusion of the classical losses. If the delay in the attainment of local equilibrium in the fluid is of the order of $1/\omega$, then the effects will be sufficiently large for the other perturbations to be negligible in comparison. In either case it will not be necessary to include $\eta$ or $K$ in the following discussion.

In the absence of thermal conduction $T_a = (\gamma - 1) p_a / \gamma \beta$ and equation (2.5.9) gives

$$p_a = (\rho \kappa_T / \gamma) p_a, \quad \text{or} \quad p_a = (\gamma \rho_a / \rho \kappa_T). \quad (2.7.1)$$

This thermodynamic equation tells us what the change in pressure would be, following a change in density, if sufficient time had elapsed for equilibrium to be achieved. In the presence of sound the density is continuously fluctuating, and it is the instantaneous acoustic pressure $p_i$, rather than the value $p_a$ that would be obtained from thermodynamics, that is required in the equations of motion. In section 4 the results of this discussion were anticipated by the inclusion of the term $\eta_b \kappa_S (\partial p_a / \partial t)$ in the symmetric elements of the stress tensor $\tau$. It remains to show that the difference $(p_i - p_a)$ can indeed be expressed in this form. The discussion will be limited to gases of low or moderate density. In dense fluids empirical values of $\eta_b$ may be found but theoretical interpretation is complicated.

The pressure exerted by a gas depends only upon its translational
modes of motion. If the gas density is suddenly altered then these
degrees of freedom, and thus the gas pressure, will adjust almost
immediately because few molecular collisions are required for the
equilibration of translational energy. In other words, the time
constant for the exchange of translational kinetic energy is of the
order of the time between molecular collisions. The instantaneous
pressure $p_i$, just after a change in density, will not necessarily be
equal to $p_a$ because of the finite time required for the exchange of
energy between translational and internal modes of molecular motion.
In consequence, the instantaneous pressure will decay in the time
following an instantaneous compression, towards the value $p_a$ of
equation (1). This will occur at a rate which is governed by the time
constants of the relaxing degrees of freedom. The exchange of energy
between translational and internal modes can only occur, to a first
approximation, during molecular collisions and so this relaxation
phenomenon is called thermal relaxation.

Under the influence of sound the gas density is not instantaneously
altered but is fluctuating continuously at a frequency $\omega/\omega_0$. If $\omega$ is
small, equilibrium will be achieved at each instant in the acoustic
cycle. If $\omega$ is large then some or all of the internal degrees of
freedom may cease to participate altogether in the acoustic cycle, and
consequently the relation between $p_i$ and $p_a$ will differ from that
implied by equation (1). It will first be assumed that the translational,
intermolecular, and all the internal energies are independent. The
fluctuation in the energy content of the $n^{th}$ degree of freedom within
the molecules may be calculated on the assumption that equilibrium is
instantaneous. If these fluctuations have amplitudes $\epsilon_n$, and it is
assumed that the $n^{th}$ degree of freedom approaches its equilibrium
state in accordance with the first-order equation:

$$\frac{\partial E_n}{\partial t} = -\frac{\Delta E_n}{\tau_n},$$

(2.7.2)
where $E_n$ is the energy content of the mode, and $\Delta E_n$ is the difference between this and the equilibrium energy, then equation (2) defines the relaxation time $\tau_n$ of the $n$th degree of freedom. The amplitude of the actual energy fluctuations in the $n$th degree of freedom is therefore reduced to $\varepsilon_n/(1 - i\omega_n)$ when the sound is harmonic and of angular frequency $\omega$. It follows that the contribution of the $n$th degree of freedom to the heat capacity of the gas is also modified by the factor $(1 - i\omega_n)^{-1}$. The relaxation times for rotational degrees of freedom are short, usually not more than a factor of ten greater than those of translational motion, and, assuming them to be zero, the effective molar heat capacity at constant volume is given by

$$C_{V,m}^{\text{eff}}(T,p,\omega) = \left\{ C_{V,m}(T,p) - \sum_n C_n^{\text{vib}}(T) \right\} + \sum_n C_n^{\text{vib}}(T)/(1 - i\omega_n), \quad (2.7.3)$$

where $C_{V,m}(T,p)$ is the equilibrium value, and $C_n^{\text{vib}}(T)$ is the contribution of the $n$th vibrational mode of motion. Equation (3) assumes that the molecular degrees of freedom are independent of each other, but in reality coupling between vibrational modes can be strong. In this case intramolecular energy exchange occurs much more rapidly than molecular collisions, and a single relaxation time may be employed to account for all the vibrational modes.

If the molar heat capacity at constant pressure has the same form as equation (3) then the effective ratio of heat capacities $\gamma(\omega)$ will be

$$\gamma(\omega) = \frac{C_{p,m} - C_{V,m}^{\text{vib}} + \sum_n \left\{ C_n^{\text{vib}}/(1 - i\omega_n) \right\}}{C_{V,m}^{\text{vib}} + \sum_n \left\{ C_n^{\text{vib}}/(1 - i\omega_n) \right\}}$$

$$= \frac{C_{p,m} + \sum_n \left\{ i\omega_n C_n^{\text{vib}}/(1 - i\omega_n) \right\}}{C_{V,m} + \sum_n \left\{ i\omega_n C_n^{\text{vib}}/(1 - i\omega_n) \right\}} = \frac{\gamma + \sum_n \left\{ i\omega_n/(1 - i\omega_n) \right\} C_n^{\text{vib}}/C_{V,m}}{1 + \sum_n \left\{ i\omega_n/(1 - i\omega_n) \right\} C_n^{\text{vib}}/C_{V,m}}.$$

(2.7.4)
where \( C_{\text{vib}, m} = \sum_n C_{n, m}^{\text{vib}} \) is the total vibrational contribution to the equilibrium molar heat capacity. Since \( |i\omega_n/(1 - i\omega_n)| < 1 \) and \( C_{\text{vib}, m} < C_{V, m} \), the denominator of equation (4) may be expanded in a binomial series to give

\[
\gamma(\omega)/\gamma = 1 - i(\gamma - 1)\sum_n (\omega_n/(1 - \omega_n^2)) C_{n, m}^{\text{vib}}/C_{p, m} + (\gamma - 1)\sum_n (\omega_n^2/(1 - \omega_n^2)) C_{n, m}^{\text{vib}}/C_{p, m} + \cdots \tag{2.7.5}
\]

Thus if \( \omega_n \ll 1 \) for all \( n \), then the effect of vibrational relaxation is to add a small imaginary term to the effective heat-capacity ratio. This expression can be used to evaluate the difference \((p_i - p_a)\) in the acoustic cycle.

For simple harmonic sound

\[
(\partial p_a/\partial t) = -i\omega_a (1/\rho k_S) = (1/\rho k_S)[-i\omega_0 \exp(-i\omega t)], \tag{2.7.6}
\]

where \( \rho_0 \) is the amplitude of the density fluctuations, and the true rate of change of pressure is

\[
(\partial p_i/\partial t) = (1/\rho k_S)[-i\omega_0 \exp(-i\omega t)]\gamma(\omega)/\gamma, \tag{2.7.7}
\]

and therefore

\[
(p_i - p_a) = (1/\rho k_S)(1 - \gamma(\omega)/\gamma)i\omega_0 \exp(-i\omega t)dt = -\rho_a (1/\rho k_S)(1 - \gamma(\omega)/\gamma). \tag{2.7.8}
\]

If \( \omega_n \ll 1 \) for all \( n \) then the terms in \( (\omega_n)^2 \) and all higher powers may be neglected in the expansion for \( \gamma(\omega) \). In this case \( (1 - \gamma(\omega)/\gamma) \) is purely imaginary and hence

\[
(p_i - p_a) = -i\omega(\rho_a/\rho k_S)(\gamma - 1)\sum_n n C_{n, m}^{\text{vib}}/C_{p, m} = k_S(\partial p_a/\partial t)((\gamma - 1)/k_S)\sum_n n C_{n, m}^{\text{vib}}/C_{p, m}. \tag{2.7.9}
\]

Thus \((p_i - p_a)\) is indeed proportional to \( k_S(\partial p_a/\partial t) \) and the constant of proportionality
\[ \eta_{rel} = \frac{(\gamma-1)/\kappa}{1 + \frac{C_{vib,m}^2}{C_{p,m}}} \]  

(2.7.10)

is independent of the sound frequency provided that \( \omega t_n \ll 1 \) for all \( n \).

In the single-relaxation-time approximation

\[
\gamma(\omega) = \frac{\gamma + i\omega t_{vib} C_{vib,m}}{1 + i\omega t_{vib} C_{vib,m}} \frac{C_{vib,m}}{C_{p,m}}
\]

(2.7.11)

where \( t_{vib} \) is the vibrational relaxation time. If \( \omega t_{vib} \) is not much less than unity then \( 1 - \gamma(\omega)/\gamma \) will contain real terms and vary with the frequency of the sound. In this case, a single coefficient of bulk viscosity, independent of frequency, cannot account for the effects of relaxation. Unless \( C_{vib,m} \) is very small, these effects will be large and the phase speed will differ from \( u_0 \). Other dissipative effects will be comparatively small and \( \gamma(\omega) \) can be used directly to find an effective compressibility \( \gamma(\omega) \kappa_T \) which will be complex and dependent upon the frequency. The propagation constant of simple harmonic sound will be

\[
k(\omega) = \left( \frac{\omega}{u_0} \right) \left( \frac{\gamma(\omega)}{\gamma} \right)^{\frac{3}{2}},
\]

(2.7.12)

where \( \text{Re}(\omega/k(\omega)) \) is the phase speed and \( \text{Im}(k) \) is the coefficient of absorption. The phase speed increases from \( u_0 \) at low frequencies, where \( C_{V,m}^{\text{eff}}(\omega) = C_{V,m} \), and approaches a somewhat higher value asymptotically at high frequencies, where \( C_{V,m}^{\text{eff}}(\omega \to \infty) = C_{V,m} - C_{vib,m} \), passing through a point of inflexion at an angular frequency that is related to \( 1/t_{vib} \).

For a perfect gas this inflexion occurs at

\[
\omega_{inf} = \frac{C_{p,vib}^p}{C_{p,vib}^p} \frac{C_{vib,m}}{C_{vib,m}} C_{p,vib}^p - C_{vib,m} \text{.}
\]

(2.7.13)
where $C_{p}^{m}$ is the perfect-gas molar heat capacity at constant volume. The attenuation of the sound reaches a maximum at an angular frequency close to $\omega_{\text{inf}}$. For a perfect gas the angular frequency at which the relaxation-attenuation is a maximum is

$$\omega_{\text{max}} = \omega_{\text{inf}}(u_{0}/u_{\infty}),$$

(2.7.14)

where $u_{\infty}$ is the phase speed in the limit $\omega \to \infty$. If necessary the total absorption coefficient may be obtained by taking the sum of the relaxation absorption coefficient $\alpha_{\text{rel}}$ and the classical absorption coefficient $\alpha_{\text{CL}}$. Usually at angular frequencies near $\omega_{\text{max}}$, the relaxation attenuation is far in excess of that due to the classical mechanisms. For example for CO$_2$ gas at 300 K and 100 kPa $\omega_{\text{max}}/2\pi = 33$ kHz and, at that frequency, $\alpha_{\text{CL}} = 1.5 \times 10^{-2}$ m$^{-1}$ and $\alpha_{\text{rel}}$ is approximately 16 m$^{-1}$.

The phase speed is dramatically affected and $u_{\infty}^2$ exceeds $u_{0}^2$ by some 10 per cent. Figures 1 and 2 show the dispersion and absorption for CO$_2$ at 300 K and 100 kPa. These are based on a single relaxation time of 6.5 $\mu$s and the heat capacities given in reference 8. It should be noted that the relaxation time is proportional to the inverse of the gas density and so the frequencies at which dispersion is significant are even lower at lower pressures. Under these conditions accurate thermodynamic results cannot be obtained even if accurate speed of sound measurements can be made. This is because, in addition to the relaxation time, a detailed knowledge of the equation of state is required to calculate the dispersion and hence to obtain $u_{0}$. If measurements can be made at frequencies well below $\omega_{\text{inf}}$, where the dispersion is slight, then the extrapolation to zero frequency can be made using crude estimates of $\tau_{\text{vib}}$ and $C_{\text{vib}}$. This would also be true if $C_{\text{vib}}$ were very small as might be the case at low temperatures.

Relaxation is not the only possible contribution to $\tau_{\text{b}}$, and in gas mixtures diffusion causes additional sound absorption. There are
FIGURE 2.1. DISPERSION IN CO$_2$ AT 300 K & 100 kPa.

FIGURE 2.2. ABSORPTION IN CO$_2$ AT 300 K & 100 kPa. sound intensity attenuation per wavelength.
two processes which cause a periodic separation of the components of the mixture. These are the alternating density gradients which cause preferential flow of the lighter molecules, and the alternating temperature gradients which cause thermal diffusion. In the absence of binary diffusion this separation is reversible, but in reality the concentration gradients are damped by irreversible diffusion, and there is a loss of energy from the acoustic cycle. In the case of the binary gas mixture \( \{ xA + (1-x)B \} \), this effect can be accounted for by an additional contribution

\[
\eta_{\text{diff}} = \{ \gamma^2 x(1-x) pD_{12}/u_0^2 \} \left\{ \left( \frac{M_A - M_B}{M} \right) + \left( \frac{\gamma-1}{\gamma D_T} \right) (-y-1) D_{12} x(1-x) \right\}^2 , \tag{2.7.15}
\]

where \( D_{12} \) is the binary diffusion coefficient, \( D_T \) is the thermal diffusion coefficient, \( M \) is the mean molar mass of the mixture, and \( M_A \) and \( M_B \) are the molar masses of components A and B respectively.

REFERENCES


3.1 INTRODUCTION

When sound is generated continuously within a closed cavity, a steady state is attained and the wave motion is that of a standing wave. If the frequency of the source is coincident with a natural frequency of the enclosure then resonance will occur. If the enclosure is of simple geometry, and the properties of the walls are known then solutions of the wave equation can be found that satisfy the boundary conditions. These provide expressions which relate the resonance frequencies to the speed and absorption of sound in the medium.

3.2 THE NORMAL MODES OF AN ACOUSTIC CAVITY

Since the time dependence of a simple-harmonic standing wave is spatially uniform, the velocity potential $\Psi$ for the region $R$ of the cavity may be separated into the product

$$\Psi(r,t) = A \Phi(r) \exp(-i\omega t),$$  

(3.2.1)
where \( \omega/2\pi \) is the frequency. The factor \( \Phi(\mathbf{r}) \) is a dimensionless wavefunction which gives the spatial variation of the wave field, and \( A \) is a constant which determines its overall amplitude. The wave equation for a damped simple-harmonic wave,

\[
\{\nabla^2 + (k/\omega)^2 (\partial^2/\partial t^2)\} \Psi(\mathbf{r}, t) = 0, \tag{3.2.2}
\]

will be satisfied if

\[
\nabla^2 \Phi(\mathbf{r}) = -k^2 \Phi(\mathbf{r}), \tag{3.2.3}
\]

where \( k = (\omega/\mu) + i\alpha \), and \( \alpha \) is the coefficient of sound absorption. The solutions of equation (3), which are allowed within the closed region \( R \), are the eigenfunctions of \( \nabla^2 \) that satisfy the boundary conditions at the surface \( S \) of the enclosure. The corresponding eigenvalues are the allowed values of \( -k^2 \), and the natural frequencies of the cavity are the complex quantities

\[
F = (\mu/2\pi)(k-i\alpha). \tag{3.2.4}
\]

If the allowed wavenumbers \( k \) can be found then measurement of a complex natural frequency can serve to determine both the speed and absorption coefficient of the sound.

Since equation (3) is homogeneous, any linear combination of its solutions is also a solution. We shall seek an infinite set of solutions which are mutually orthogonal, finite, and continuous, within the region \( R \); these will define the normal modes of the cavity. All other solutions of equation (3) which are not formed by linear combination of the normal modes, fail to be of physical significance and are rejected. Since the problem is three dimensional, a set of three indicies will be required
to distinguish between the set of normal solutions. The eigenfunctions and their corresponding eigenvalues will therefore be denoted by

\[ \Phi_N(\mathbf{r}, \omega) \] and \[-K_N^2(\omega)\] respectively, where \( N \) stands for the necessary trio of indices. If the boundary conditions vary with the frequency of the sound then the solutions will also be frequency dependent. Each of the normal modes obeys the orthogonality condition

\[ \int \int \int_R \Phi_N(\mathbf{r}, \omega) \Phi_M(\mathbf{r}, \omega) dV = V \Lambda_N(\omega) \delta(n_1 - m_1) \delta(n_2 - m_2) \delta(n_3 - m_3), \] (3.2.5)

where the integral is performed over the whole of the region \( R \), \( V \) is the volume of the cavity, \((n_1, n_2, n_3)\) are the indices \( N \), and \((m_1, m_2, m_3)\) are the indices \( M \). By definition, the Dirac delta function \( \delta(\chi) \) has the following properties:

\[ \delta(\chi=0) = 1, \quad \delta(\chi \neq 0) = 0, \quad \text{and} \]
\[ \int_{-\infty}^{\infty} f(\chi) \delta(\chi-a) d\chi = f(a) \quad \text{for any function } f(\chi). \] (3.2.6)

Thus equation (5) vanishes, unless \( N=N \) when the integral evaluates to the product \( V \Lambda_N(\omega) \) of the volume of the cavity and the \( N^{th} \) normalization constant \( \Lambda_N \). The functions \( \{\Phi_N(\mathbf{r}, \omega)/\sqrt{\Lambda_N(\omega)}\} \) therefore form a complete orthonormal set.

It will be assumed that the surface \( S \) of the enclosure is of local reaction (this is in fact a condition for the existence of a complete set of orthogonal solutions), and so the sole boundary condition is

\[ U_n(\mathbf{r}_S^+) = p_a(\mathbf{r}_S^+) Y(\mathbf{r}_S^+, \omega) \quad \text{or,} \]
\[ \{\partial/\partial n\} \Phi_N(\mathbf{r}, \omega)|_{\mathbf{r}=\mathbf{r}_S^+} = i(\omega/\mu) \Phi_N(\mathbf{r}_S^+, \omega) Y(\mathbf{r}_S^+, \omega), \] (3.2.7)

where \( n \) is the component of \( \mathbf{r}^+ \) which points outwards from \( R \) normal to \( S \).
\( \hat{r}_S \) is a position on \( S \), and \( y(\hat{r}_S, \omega) = c_{\omega i}(\hat{r}_S, \omega) \) is the effective specific acoustic admittance of the boundary. The effect of the boundary condition is to restrict the eigenvalues to the discrete set \(-k^2_N(\omega)\), each member of which corresponds to an eigenfunction \( \hat{r}_N(\hat{r}, \omega) \).

These normal modes define only the form of the free oscillations that are allowed within the cavity and, as yet, nothing about forced oscillations which may be imposed at any frequency. However, all the acoustic properties of the cavity, including both the transient and steady-state response to a source of sound, can be expressed in terms of the wavefunctions and their characteristic wavenumbers. Since a source of finite size may alter the form of the wavefunctions, it will be useful to consider the response to a simple-harmonic source of infinitesimal size. The response to a source of finite size, whose influence on the normal modes is negligible, can be simulated by summing the effects of infinitesimal sources.

The velocity potential for the cavity in the steady state, arising from an infinitesimal source of frequency \( \omega/2\pi \) and strength \( S_{\omega} \) placed at the source point \( \hat{r}_0 \) will be denoted by

\[
\Psi_{\omega}(\hat{r}, \hat{r}_0, t) = S_{\omega} G_{\omega}(\hat{r}, \hat{r}_0) \exp(-i\omega t),
\]

where the function \( G_{\omega}(\hat{r}, \hat{r}_0) \), defining the spatial distribution of the driven wave field, is to be determined. \( \Psi_{\omega}(\hat{r}, \hat{r}_0, t) \) differs from the velocity potential \( \Psi \) of the undriven cavity because it is discontinuous at the source point. Thus \( G_{\omega}(\hat{r}, \hat{r}_0) \) is not a solution of the homogeneous wave equation; it can be shown that \( G_{\omega} \) is in fact a solution of the inhomogeneous equation

\[
\{\nabla^2 + k^2\} G_{\omega}(\hat{r}, \hat{r}_0) = -\delta(\hat{r} - \hat{r}_0),
\]

(3.2.9)
and is therefore an eigenfunction of $\nabla^2$ everywhere except at $r_0$.

$G_\omega$ must also satisfy the boundary condition,

$$
(\partial/\partial n)G_\omega(r, r_0) = i(\omega/u)G_\omega(r_0, r)\gamma(r_0, \omega),
$$

(3.2.10)

analogous to equation (7). Whatever the form of $G_\omega$, it may be expanded in an infinite series of the normal modes:

$$
G_\omega(r, r_0) = \sum \phi_N(r, \omega),
$$

(3.2.11)

where the coefficients $\phi_N$ are to be determined. Substitution of (11) in (9), and replacement of $N$ by $M$, gives

$$
\sum_{M} \phi_M(r, \omega) \{K_M^2(\omega) - k^2\} = \delta(r - r_0),
$$

(3.2.12)

which, on multiplication by $\phi_N(r, \omega)dV$ and integration over $R$, reduces to

$$
C_N = \{\phi_N(r_0, \omega)/V\Lambda_N(\omega)\{K_M^2(\omega) - k^2\}\}.
$$

(3.2.13)

The function $G_\omega(r, r_0)$ is called a Green's function, and its expansion in terms of the normal modes,

$$
G_\omega(r, r_0) = \sum \phi_N(r, \omega)\phi_N(r_0, \omega)/V\Lambda_N(\omega)\{K_M^2(\omega) - k^2\},
$$

(3.2.14)

ensures that the boundary condition is automatically satisfied. An important property of $G_\omega$ is that it is symmetric with respect to the exchange of the measurement point $r$ and the source point $r_0$.

The general formula for the spatial distribution of the acoustic pressure $p_\omega$ in the cavity is obtained by operating on $\psi_\omega$ with $\rho(\partial/\partial t)$, and then dropping the time-dependent factor, with the result
\[ p_\omega(\vec{r}, \vec{r}_0) = -i\omega \rho S \sum_N \{ \hat{\phi}_N(\vec{r}, \omega) \hat{\phi}_N(\vec{r}_0, \omega) / V_N(\omega) \{ k_N^2(\omega) - k^2 \} \} \]
\[ = -i\omega \rho S \sum_N \{ \hat{\phi}_N(\vec{r}, \omega) \hat{\phi}_N(\vec{r}_0, \omega) / V_N(\omega) \{ \omega_N^2(\omega) - \omega^2 \} \}, \quad (3.2.15) \]

where \( f = \omega / 2\pi \) is the real source frequency, and \( F_N(f) = \omega_N(\omega) / 2\pi \) is the complex natural frequency of the \( N \)th normal mode. If the \( N \)th resonance is clearly resolved, and if \( f \) is close to the real part of \( F_N(f) \), then the \( N \)th term of equation (15) will predominate. \( p_\omega(\vec{r}, \vec{r}_0) \) is also complex; the real part describes the component of the acoustic pressure which is in phase with the driving source, and the imaginary term is the component that is in quadrature with the source. Since the frequency dependence of the normal modes is slight, \( F_N \) is effectively constant for \( f \) close to \( \text{Re}[F_N] \) and is therefore the solution of the implicit equation

\[ f_N - ig_N = F_N(f_N); \quad f_N, g_N \text{ positive-real.} \quad (3.2.16) \]

Clearly, if a measurement of \( f_N - ig_N \) is to be made by a study of the resonant behaviour of the cavity, then the contributions of the other modes must be small when \( f \) is close to \( f_N \). This is the case at low frequencies (i.e. where \( N \) are small) where the background contribution of the other terms may be expanded in a Taylor series about \( f = f_N \), and equation (15) simplified to

\[ p_f(\vec{r}, \vec{r}_0) = \{ iA_N f / (f_N^2 - f^2) \} + B_N + C_N (f - f_N) + \cdots, \quad (3.2.17) \]

for \( f \) close to \( f_N \), where \( A_N, B_N, C_N \cdots \) are complex constants. The leading term is dominant, and \( A_N \) is proportional to \( S \hat{\phi}_N(\vec{r}, \omega) \hat{\phi}_N(\vec{r}_0, \omega) \). If either \( \vec{r} \) or \( \vec{r}_0 \) coincides with a node of the standing wave then resonance will not be observed. The complex natural frequency \( F_N = f_N - ig_N \), and the remaining constants in equation (17), may be determined from measurements of \( \text{Re}[p_f(\vec{r}, \vec{r}_0)] \) and \( \text{Im}[p_f(\vec{r}, \vec{r}_0)] \) over a range of
frequencies close to \( f_N \). A condition for precise measurements is that \( g_N \ll f_N \); this being so the denominator of the leading term in equation (17) may be approximated by

\[
(f_N^2 - f^2) = -2f_N \{(f - f_N) + ig_N\},
\]

(3.2.18)
correct to first order in \( g_N \) and \( f - f_N \). If the background terms are negligible then the Lorentzian formula

\[
\{p_F(\vec{r}, \vec{r}_0)/f\} = \{a/[g_N - i(f - f_N)]\}, \quad a \text{ constant},
\]

(3.2.19)
results. For a purely Lorentzian resonance, the response of the cavity reaches a maximum when the source frequency is coincident with the resonance frequency \( f_N \). The maximum amplitude is inversely proportional to \( g_N \) and, when \( f = f_N \pm ig_N \), the amplitude of \( \{p_F(\vec{r}, \vec{r}_0)/f\} \) is reduced to \( 1/\sqrt{2} \) of its maximum value. The variation of the real and imaginary components of equation (19) are illustrated in figure 3.1, and the corresponding amplitude and phase are shown in figure 3.2. The width of the in-phase-response-versus-frequency curve at half its maximum height is \( 2g_N \) and thus \( g_N \) is referred to as the resonance half width. The much used quantity \( Q_N = f_N/2g_N \) is a parameter that describes the sharpness of the \( N \)th resonance peak. Although the true form of the resonance is not quite Lorentzian, and the background terms are not usually negligible, equation (17) has the same general behaviour as the Lorentzian formula. It should be noted that the background terms can shift the apparent resonance frequency and their neglect could be a source of systematic errors in acoustic measurements.

In contrast to this situation of forced oscillations where the frequency is real and continuously variable, free oscillations occur at the discrete complex natural frequencies of the system. If the source
FIGURE 3.1. REAL & IMAGINARY COMPONENTS OF A LORENTZIAN RESONANCE.

FIGURE 3.2. AMPLITUDE & PHASE OF A LORENTZIAN RESONANCE.
is suddenly shut off then the cavity will reverberate, each mode oscillating in proportion to \( \exp(-2\pi f_N t) \). Thus, in the time domain, 

\[ 2\pi g_N \]

is the time constant with which free oscillations of the \( N^{th} \) standing wave decay. The amplitudes and phases of the reverberating modes which result when a simple-harmonic source is shut off can be obtained by the appropriate Fourier analysis. If the source had a frequency close to one of the resonance frequencies \( f_N \), then the reverberation consists mainly of that mode, and a measurement of the characteristic reverberation time can serve to determine \( g_N \).

The usefulness of these formulae clearly depends upon a detailed knowledge of the normal modes and their corresponding wavenumbers. However, if the geometry of the cavity is not particularly simple, or if the surface admittance is irregular, then these eigenfunctions and eigenvalues cannot be expressed in closed form, and a direct solution of the problem is not possible. From a practical point of view a simple geometry will always be chosen, and the mechanical compliance of the surface can be made small and uniform by proper construction. Nevertheless, infinitely fine tolerances cannot be achieved, and the geometry will always deviate slightly from the ideal. Furthermore, the effective acoustic admittance of the boundary layers is a function of the thermophysical properties of the fluid under study and therefore varies from one experimental situation to another. What is required is a method by which the normal modes and the corresponding eigenvalues, of a slightly imperfect cavity filled with a real fluid, can be related to those of an ideal enclosure containing the ideal fluid. Such a method allows verification that a particular resonator has been fabricated to the required tolerance and takes account of slight surface imperfections such as might be caused by a real source or detector of sound. It also allows the eigenvalues for the cavity to be expressed as the sum of an idealized component which is invariant, and a small component that varies
with the properties of the fluid under study.

For the idealized case in which perfect geometry and zero admittance are both assumed, the normal modes are easily found and obey the conditions:

$$\nabla^2 \phi_N^N(\mathbf{r}) = -k_N^2 \phi_N^N(\mathbf{r}) \quad \text{within } R_0,$$
$$\int \phi_N^N(\mathbf{r}) \, dV = V_{N}^0,$$
$$\left( \partial \phi_N^N / \partial n \right) = 0 \quad \text{on } S_0,$$

(3.2.20)

where $\phi_N^N(\mathbf{r})$ and $-k_N^2$ are independent of $\omega$, and $S_0$ and $R_0$ are the surface and region of the ideal cavity. The Green's function, representing the spatial distribution of the radiation from a point $\mathbf{r}_0$ in the idealized cavity, will be the solution of

$$\{\nabla^2 + k^2\} G(\omega, \mathbf{r}, \mathbf{r}_0) = -\delta(\mathbf{r} - \mathbf{r}_0) \quad \text{within } R_0,$$ and
$$\left( \partial / \partial n \right) G(\omega, \mathbf{r}, \mathbf{r}_0) = 0 \quad \text{on } S_0.$$  

(3.2.21)

Again, $G$ may be expanded in a series of the solutions of the corresponding homogeneous equation, with the result

$$G(\omega, \mathbf{r}, \mathbf{r}_0) = \sum_N \{ \phi_N^N(\mathbf{r}) \phi_N^N(\mathbf{r}_0) / V_{N}^0 (k_N^2 - k^2) \}.$$  

(3.2.22)

The normal modes of the real cavity can be expressed in an infinite series of orthogonal functions. Equations (20) show that the normal modes of the ideal cavity form a suitable basis set although they do not satisfy the required boundary condition of equation (10). The Green's function is a useful tool for solving this problem. Following Morse and Ingard, the first of equations (21) is written for an eigenvalue $K_N(\omega)$ of the real cavity, and multiplied by $-\phi_N^N(\mathbf{r}, \omega)$ with the result
\[-\phi^I_N(\vec{r},\omega) \nabla^2 G_N(\omega,\vec{r},\vec{r}_0) - k_N^2(\omega) \phi^I_N(\vec{r},\omega) G_N(\omega,\vec{r},\vec{r}_0) = \phi^I_N(\vec{r},\omega) \delta(\vec{r} - \vec{r}_0), \quad (3.2.23)\]

where \( \phi^I_N \) is the \( N^{th} \) eigenfunction for the real cavity, and

\[G_N(\omega,\vec{r},\vec{r}_0) = \sum_N \{ \phi_N(\vec{r}) \phi_N(\vec{r}_0) / V^0_N \{ k_N^2 - k_N^2(\omega) \} \}. \quad (3.2.24)\]

Equation (3) is now written for the same eigenvalue, multiplied by \( G_N(\omega,\vec{r},\vec{r}_0) \), and the result is combined with equation (23), the terms in \( K_N(\omega) \) being eliminated, to obtain

\[\{ G_N(\omega,\vec{r},\vec{r}_0) \nabla^2 \phi^I_N(\vec{r},\omega) - \phi^I_N(\vec{r},\omega) \nabla^2 G_N(\omega,\vec{r},\vec{r}_0) = \phi^I_N(\vec{r},\omega) \delta(\vec{r} - \vec{r}_0). \quad (3.2.25)\]

The position vectors \( \vec{r} \) and \( \vec{r}_0 \) are now interchanged, making use of the symmetry of the functions \( G_N(\omega,\vec{r},\vec{r}_0) \) and \( \delta(\vec{r} - \vec{r}_0) \) with respect to such an exchange, and equation (25) integrated in the co-ordinates of \( \vec{r}_0 \) over the entire region \( R \). This integration is readily performed using the Divergence theorem† for the left-hand side and the definition (equations 6) of the Dirac delta function for the right-hand side, with the result

\[\phi^I_N(\vec{r},\omega) = \iint_S \{ G_N(\omega,\vec{r},\vec{r}_S)(\partial/\partial n) \phi^I_N(\vec{r},\omega) - \phi^I_N(\vec{r}_S,\omega)(\partial/\partial n) G_N(\omega,\vec{r},\vec{r}_S) \} \, dS, \quad (3.2.26)\]

† The Divergence theorem relates the volume integral of the divergence of a vector to the surface integral of the vector over the surface \( S \) that bounds the region \( R \)

\[\iint_R \nabla \cdot \vec{F} \, dV = \oint_S \vec{n} \cdot \vec{F} \, dS\]

where \( \vec{n} \cdot \vec{F} \) is the outward-pointing normal component of \( \vec{F} \). A special case of this theorem is

\[\iint_R \nabla^2 f(\vec{r}) \, dV = \oint_S \vec{n} \cdot \nabla f(\vec{r}) \, dS = \iint_S (\partial/\partial n) f(\vec{r}) \, dS,\]

where \( (\partial/\partial n) f(\vec{r}) \) is the outward-pointing normal gradient of \( f(\vec{r}) \).
where $\mathbf{r}_0$ has been replaced by $\mathbf{r}_S$. Equations (25) and (26) are valid only when $k = k_N$ and so their solution must yield not only the required eigenfunctions, but also the corresponding eigenvalues. Since the Green's function for the ideal cavity has been employed, the second term in equation (26) will vanish when the surface $S$ is coincident with the surface $S_0$. In addition, the normal gradient of $\phi_N(\mathbf{r}, \omega)$ is specified on $S$ by the boundary condition. Thus,

$$\phi_N^t(\mathbf{r}, \omega) = \int \int_S \phi_N^t(\mathbf{r}_S, \omega) \{iK_N(\omega)G_N(\omega, \mathbf{r}, \mathbf{r}_S)Y(\mathbf{r}_S, \omega) - (\partial/\partial n)G_N(\omega, \mathbf{r}, \mathbf{r}_S)\} dS,$$

(3.2.27)

where the integral is in the co-ordinates of $\mathbf{r}_S$. Equation (27) is the homogeneous integral equation which exactly specifies the solutions of the homogeneous differential equation (3) that satisfy the boundary condition of equation (7). Again following Morse and Ingard, equation (24) is substituted in equation (27), and the large term in $\{\phi_N(r)/\{k^2_N - k^2_N(\omega)\}\}$ is separated, with the result

$$\phi_N(\mathbf{r}, \omega) = \int \int_S \phi_N^t(\mathbf{r}_S, \omega) \{iK_N(\omega)G_N(\omega, \mathbf{r}, \mathbf{r}_S)Y(\mathbf{r}_S, \omega) - (\partial/\partial n)G_N(\omega, \mathbf{r}, \mathbf{r}_S)\} dS + \{\int \int_S \phi_N^t(\mathbf{r}_S, \omega) \{iK_N(\omega)\phi_N(\mathbf{r}_S)Y(\mathbf{r}_S, \omega) - (\partial/\partial n)\phi_N(\mathbf{r}_S)\} dS\}\phi_N(\mathbf{r})/V\lambda_0(\{k^2_N - k^2_N(\omega)\})$$

(3.2.28)

where

$$G_N(\omega, \mathbf{r}, \mathbf{r}_S) = \sum_{M \neq N} \phi_M(\mathbf{r})\phi_M(\mathbf{r}_S)/V\lambda_0(\{k^2_N - k^2_N(\omega)\}).$$

(3.2.29)

Since equation (28) is homogeneous, the coefficient of $\phi_N(\mathbf{r})$ is constant for given $y(\mathbf{r}_S, \omega)$ and $\omega$, and $\phi_N(\mathbf{r}, \omega) = a\phi_N(\mathbf{r}, \omega)$, where $a$ is constant, is also a solution. If equation (28) is multiplied by the inverse of the
then the result,

\[ \Phi_N(\mathbf{r}, \omega) = \Phi_N(\mathbf{r}) + \int_S \Phi_N(\mathbf{r}_S, \omega) \{ iK_N(\omega) \Phi_N(\mathbf{r}_S) y(\mathbf{r}_S, \omega) - (\partial/\partial n) \Phi_N(\mathbf{r}_S) \} dS, \]  

defines the set of normal modes \( \Phi_N \) which tend to \( \Phi_N \) as \( y \to 0 \) and \( S \to S_0 \). The corresponding eigenvalues are obtained directly from equation (30) by recalling that \( \Phi_N = a \Phi_N' \):

\[ -k_N^2(\omega) = -k_N^2 + (1/V\mathbf{A}_N^0) \int_S \Phi_N(\mathbf{r}_S, \omega) \{ iK_N(\omega) \Phi_N(\mathbf{r}_S) y(\mathbf{r}_S, \omega) - (\partial/\partial n) \Phi_N(\mathbf{r}_S) \} dS, \]  

Equations (31) and (32) may now be solved simultaneously to any desired degree of accuracy.

These expressions for the eigenfunctions and eigenvalues of the real cavity are of considerable importance in both the design and use of acoustic resonators. Equation (31) shows that if the surface admittance or geometry is irregular, then the normal modes of the cavity are coupled together, and the eigenfunctions of the real enclosure differ in form from the unperturbed set. The terms arising from the failure of \( S \) to coincide with \( S_0 \) can usually be made negligibly small by careful design and construction; detailed mechanical measurements and the appropriate integration can verify that this is so. If the surface admittance is uniform over the whole of \( S \) or piecewise uniform over sections of \( S \), and if \( S \) is close to \( S_0 \) then most of the terms in the integral on the right of equation (31) will be negligible and \( \Phi_N \) will have the same form.
as $\phi_N$. A first-order solution of equation (32) is then appropriate and this is obtained by setting $\phi_N = \phi_N$. Thus if $S = S_0$ then

$$-k_N^2(\omega) = -k_N^2 + \{iK_N(\omega)/\sqrt{V_N N_0^0}\} \int_S y(\tau_S, \omega) c_N^2(\tau_S) dS,$$  

(3.2.33)

which is quadratic in $K_N(\omega)$ and leads to

$$\{K_N(\omega)/k_N\} = 1 - \{(i/2k_N V_N N_0^0) \int_S y(\tau_S, \omega) c_N^2(\tau_S) dS\}$$  

(3.2.34)

correct to first order in the surface admittance. The frequency dependence of the eigenfunctions and eigenvalues arises from the dependence of the surface admittance on the frequency. The natural frequencies $\omega_N/2\pi$ will be predominantly determined by the speed of sound in the fluid. However, in reality the two are not quite in proportion because of the frequency shifts arising from the boundary-layer admittance. It should be noted that (31) and (32) are implicit equations, for $y$ is a function of $\omega$ and, to obtain the correct solution, the appropriate frequency must be used in its calculation. In the case of the free vibrations of the $N^{th}$ standing wave, $\omega = \omega_N = 2\pi(f - i\gamma_N)$ is appropriate but, when the motion is driven, $\omega = 2\pi f$, where $f$ is the frequency of the source.

If the surface admittance (or geometry) is not regular then $\phi_N$ will differ in form from $\phi_N$, and equation (34) will only constitute a first approximation to the required eigenvalues. A variational calculation can yield a second approximate solution. An additional complication may arise when the state of the system is degenerate. In this case a number of the eigenfunctions have the same idealized eigenvalue $-k_N^2$, and the effects of any irregularities in the surface admittance or geometry are greatly amplified by the large terms

$$\{k_N^2 - k_N^2(\omega)\}^{-1}$$

that remain in $G_N^1$. This problem can be overcome by
recasting the degenerate wavefunctions in appropriate linear combinations, and thereby forming a new basis set. These linear combinations must be weighted so that the offending integrals in equation (31) vanish.

It is now possible to consider the wavefunctions and resonance frequencies of the cylindrical and spherical cavities of interest, on the assumptions that the geometry is perfect and that the surface admittance is zero. The results of that analysis can then be combined with equation (34) to obtain the eigenvalues of the cavities when they are filled with a real fluid.

3.3 THE CYLINDRICAL CAVITY

The cavity is defined as a cylinder of radius $b$, concentric with the $z$ axis and extending from $z = 0$ to $z = L$; and it is assumed that the walls are rigid, the geometry perfect, and that the thermal and shear boundary layers are negligible. The wavefunctions $\phi_N(r)$ of the cavity will be expressed as the product

$$\phi_N(w, \psi, z) = X_N(w)Y_N(\psi)Z_N(z), \quad N = (l, m, n),$$

in terms of the cylindrical co-ordinates $(w, \psi, z)$ which are related to the usual Cartesian set $(x, y, z)$ by

$$x = w \cos \psi, \quad y = w \sin \psi, \quad \text{and} \quad z = z,$$

and for which the Laplacian operator is given by

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} \right) + \left( \frac{\partial^2}{\partial y^2} \right) + \left( \frac{\partial^2}{\partial z^2} \right)$$

$$= \left( \frac{\partial^2}{\partial w^2} \right) + \left( \frac{1}{w} \frac{\partial}{\partial w} \right) + \left( \frac{1}{w^2} \frac{\partial^2}{\partial \psi^2} \right) + \left( \frac{\partial^2}{\partial z^2} \right).$$

The wavefunctions must satisfy the orthogonality condition of equations (3.2.5), which for equation (1) reduces to

\[ \int_0^B X_N(w)Y_M(w)dw = \int_0^{2\pi} Y_M(\psi)Y_N(\psi)\psi^L Z_N(z)Z_M(z)dz = V_N^0 \delta_{MN}, \quad (3.3.4) \]

where \( \delta_{MN} = \delta(m - m')\delta(n - n') = \delta_{11'}\delta_{mm'}\delta_{nn'} \).

Substitution of (1) in the time-independent wave equation (3.2.3) separates the problem into three independent differential equations:

\[
\begin{align*}
(1/x)(d^2X/dw^2) + (1/wX)(dX/dw) + (k_N^2 - q^2) - (m^2/w^2) &= 0, \\
(d^2Y/dw^2) + m^2Y &= 0, \\
(d^2Z/dz^2) + q^2Z &= 0, \quad (3.3.5)
\end{align*}
\]

where \(-m^2\) is the separation constant for \(Y\) and \(-q^2\) is the separation constant for \(Z\). The substitution \(w = x(k_N^2 - q^2)^{-\frac{1}{2}}\) reveals that the first of equations (5) is identical with Bessel's equation

\[
(\frac{d^2X}{dx^2}) + (\frac{1}{x})(\frac{dX}{dx}) + (1 - m^2/x^2)X = 0, \quad (3.3.6)
\]

for which one solution is \(X = J_m(x)\), the cylindrical Bessel function of order \(m\). However, equation (6) is of the second order and there must be two independent solutions. The second of these \(X = N_m(x)\), the cylindrical Newmann function of order \(m\), is infinite along the line \(w = 0\) and therefore fails to be of physical significance and is rejected. The valid radial wavefunction \(J_m[(k_N^2 - q^2)^{\frac{1}{2}}w]\) must satisfy the boundary condition

\[
\{\frac{d}{dw}[J_m[(k_N^2 - q^2)^{\frac{1}{2}}w]]/dw\}_{w=b} = 0 \quad (3.3.7)
\]

and \((k_N^2 - q^2)^{\frac{1}{2}}\) is therefore restricted to a discrete set of values.
Successive roots \((k_n^2 - q^2)^{1/2} b = \chi_{mn}\) of equation (7) will be labelled \(n = 0, 1, 2, \ldots\); the first few are given below.

<table>
<thead>
<tr>
<th>(\chi_{mn})</th>
<th>(n = 0)</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<td>7.015</td>
<td>10.174</td>
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<tr>
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<td>5.331</td>
<td>8.526</td>
<td>11.706</td>
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<td>6.706</td>
<td>9.969</td>
<td>13.170</td>
</tr>
<tr>
<td>3</td>
<td>4.201</td>
<td>8.015</td>
<td>11.346</td>
<td>14.586</td>
</tr>
</tbody>
</table>

The properties of the cylindrical Bessel functions that are relevant to this chapter are reviewed in the appendix A3.2.

Two independent solutions of the angular equation are \(Y^+ = \cos(m\psi)\) and \(Y^- = \sin(m\psi)\), where the superscript indicates the symmetry of the function with respect to the sign of \(\psi\). Since the solutions are required to be continuous and periodic such that \(Y(m\psi) = Y(m(\psi + 2\pi))\), \(m\) is restricted to zero and integer values. The completeness of the set of normal modes is not compromised by taking the linear combination \(\{Y^+(m\psi) + Y^-(m\psi)\}\) and this is preferable because a single series of functions results.

In the case of the longitudinal equation there are again two independent solutions: \(Z^+ = \cos(qz)\) and \(Z^- = \sin(qz)\). However, \(Z\) must satisfy the boundary condition \((dZ/dz) = 0\) on the surfaces \(z = 0\) and \(z = L\), and hence the antisymmetric wavefunction \(Z^-\), which cannot satisfy this condition, is rejected. In order that the remaining symmetric wavefunction satisfies the boundary conditions, \(q\) is restricted to the values

\[ q = l\pi/L, \quad l = 0, 1, 2, \ldots \]

Thus, combining these solutions, the eigenfunctions of \(\nabla^2\) which
satisfy the boundary conditions in the idealized cylindrical cavity are

\[ \phi_N(w, \psi, z) = J_m(\chi_{mn} w/b)(\cos(m\psi) + \sin(m\psi))\cos(l\pi z/L), \quad N = (l, m, n), \]

(3.3.10)

where \( l, m, \) and \( n \) may take zero and positive-integer values (negative values are allowed but not required). The corresponding eigenvalues are

\[-k_N^2 = -(l\pi/L)^2 - (\chi_{mn}/b^2), \]

(3.3.11)

and hence the natural frequencies of the cavity are

\[ F_N(f_N) = (f_N - ig_N) = (w/2\pi)\left\{[(l\pi/L)^2 + (\chi_{mn}/b)^2]^{1/2} - i\alpha(f_{mn}) \right\}, \]

(3.3.12)

where the only damping is that arising from the bulk attenuation. In this idealized model the eigenvalues are independent of the frequency, and the resonance frequencies \( f_N \) are directly proportional to the speed of sound. The \( N^{th} \) mode has \((l+1)\) plane longitudinal nodal surfaces \((l > 0), m \) plane radial nodes, and \((n+1)\) cylindrical nodes \((n > 0)\).

Using the appropriate properties of the Bessel and trigonometric functions, the orthogonality of the normal modes can be verified, and the normalization constants shown to be

\[ \Lambda_N^0 = (1/\varepsilon_1)\{1 - (m/\chi_{mn})^2\}J_m^2(\chi_{mn}), \quad \varepsilon_0^0 = 1, \quad \varepsilon_1^0 = 2. \]

(3.3.13)

The walls of practical resonators are not perfectly rigid, nor are the effects of thermal and viscous damping in the boundary layers negligible. The perturbations to the idealized eigenvalues, which are the result of these non-ideal boundary conditions, are given to a first approximation by the leading term of equation (3.2.34). The surface
integral involved may be separated into the sum

$$\iint_{S} y_{S}(r_{S}, \omega) d_{N}^{2}(r_{S}) dS = \int_{0}^{L} \int_{0}^{2\pi} y(w = b, \psi, z, _{=}) d_{N}^{2}(w = b, \psi, z) b d\psi dz + \int_{0}^{L} \int_{0}^{2\pi} y(w, \psi, z = L, \omega) d_{N}^{2}(w, \psi, z = L) d\psi dw + \int_{0}^{L} \int_{0}^{2\pi} y(w, \psi, z = 0, \omega) d_{N}^{2}(w, \psi, z = 0) d\psi dw \quad (3.3.16)$$

of the integrals over the side and two ends of the cylindrical cavity.

Since the specific acoustic admittance of the viscous boundary layer is a function of the tangential component $k_t$ of the wavenumber at the wall, the total boundary admittance will depend upon the mode of the cavity's excitation. For the longitudinal modes ($m = n = 0$), $k_t = k$ at the side walls, and $k_t = 0$ at the end walls. Thus the effective specific-acoustic-admittances $y_{1,s}$ of the side and $y_{1,e}$ of the ends are

$$y_{1,s}(f) = (1 - i)(\pi f / u)((\gamma - 1)\delta_h + \delta_s) + y_{m,s}(f), \quad \text{and}$$

$$y_{1,e}(f) = (1 - i)(\pi f / u)((\gamma - 1)\delta_h + \delta_s) + y_{m,e}(f), \quad (3.3.17)$$

in accordance with (2.6.39). The thermal and shear penetration lengths are given by equations (2.6.25), and have the frequency dependence of $f^{-1}$.

$y_{m,s}$ and $y_{m,e}$ are the specific acoustic admittances of the side and end walls that arise from their non-zero mechanical compliance. These terms are usually very small and can be estimated from mechanical measurements.

For the radial modes ($l = m = 0$) the situation is reversed; $k_t$ is zero along the side walls, and equal to $k$ at the end plates. Thus the effective side-wall and end-wall specific-acoustic-admittances are

$$y_{r,s}(f) = (1 - i)(\pi f / u)((\gamma - 1)\delta_h + y_{m,s}(f)), \quad \text{and}$$

$$y_{r,e}(f) = (1 - i)(\pi f / u)((\gamma - 1)\delta_h + \delta_s) + y_{m,e}(f), \quad (3.3.18)$$

in accordance with (2.6.39). The thermal and shear penetration lengths are given by equations (2.6.25), and have the frequency dependence of $f^{-1}$. $y_{m,s}$ and $y_{m,e}$ are the specific acoustic admittances of the side and end walls that arise from their non-zero mechanical compliance. These terms are usually very small and can be estimated from mechanical measurements.
respectively. For both the radial and longitudinal modes \( y(r, s) \) is a constant for each of the separated surface integrals. This would not be so for the compound modes \( (m \neq 0) \).

For the longitudinal modes \( \lambda_{10}^0 = 1 \), \( \phi_{10} = \cos(l \pi z/L) \), and therefore the corrected eigenvalues are

\[
K_{10}(f) = k_{10} - (i/b)y_{1s}(f) - (2i/L)y_{1e}(f). \tag{3.3.20}
\]

The natural frequencies are obtained by substitution of \( K_{10}(f) \) in equation (3.2.4) and solving the resulting implicit equation for \( (f_{10} - ig_{10}) \):

\[
F_{10}(f_{10}) = (f_{10} - ig_{10}) = (u/2\pi)(K_{10}(f_{10}) - i\alpha(f_{10})). \tag{3.3.21}
\]

In the case of the radial modes \( \lambda_{0n}^0 = J_0^2(x_{0n}) \) and \( \phi_{0n} = J_0(x_{0n} w/b) \). Use of the appropriate properties of the cylindrical Bessel functions shows that

\[
K_{0n}(f) = k_{0n} - (i/b)y_{0s}(f) - (i/L)y_{0e}(f), \tag{3.3.22}
\]

and the corresponding natural frequencies are therefore

\[
F_{0n}(f_{0n}) = (f_{0n} - ig_{0n}) = (u/2\pi)(K_{0n}(f_{0n}) - i\alpha(f_{0n})). \tag{3.3.23}
\]

In both equations (20) and (22), the dominant frequency dependent terms are those that arise from the viscous and thermal boundary-layer losses. These terms are proportional to \( f^{\frac{1}{2}} \) and usually make only a small contribution to the eigenvalues which may therefore be taken as constant over a small interval of frequency.
3.4 THE SPHERICAL CAVITY

The cavity is defined as a sphere of radius \( a \), centred at the origin; and it is again assumed that the walls are rigid, the geometry perfect, and that the thermal and shear boundary layers are negligible. The wavefunctions are separated into the product

\[
\phi_N(r, \theta, \zeta) = R_N(r)P_M(\theta)Q_N(\zeta), \quad N = (l, m, n),
\]

in terms of the spherical co-ordinates \((r, \theta, \zeta)\), where \( r \) is the magnitude of the position vector, the co-latitude \( \theta \) is the angle made with the Cartesian \( z \) axis, and the azimuth \( \zeta \) is the angle made with the Cartesian \( x \) axis. Thus,

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

and the Laplacian operator is given by

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

The wavefunctions are required to obey the orthogonality condition

\[
\int_0^{2\pi} \int_0^\pi \int_0^{2\pi} R_N(r)R_M(r) \sin \theta \sin \zeta \frac{\partial^2 Q_N(\zeta)Q_M(\zeta)}{\partial \zeta^2} d\zeta = \delta_{NN} \delta_{MM},
\]

and substitution of (1) in the wave equation yields the three independent differential equations

\[
(1/R)(d^2R/dr^2) + (2r/R)(dR/dr) + k_N^2 - 1(l + 1)/r^2 = 0,
\]

\[
(d^2P/d\theta^2) + (\cos \theta/\sin \zeta)(dP/d\theta) + (1(l + 1) - m^2/\sin^2 \theta)P = 0,
\]

and
\[ (\frac{d^2 Q}{d r^2}) + m^2 Q = 0, \quad (3.4.5) \]

in which \(-m^2\) is the separation constant for \(Q\) and \(-1(1+1)\) is the separation constant for \(P\). The substitution \(r = x/k_N\) reveals that the first of equations (5) is

\[ (\frac{d^2 R}{d x^2}) + \frac{2}{x} (\frac{d R}{d x}) + \{1 - 1(1+1)/x^2\} R = 0. \quad (3.4.6) \]

The solution of (6) is finite at the origin is \(X = j_1(k_Nr)\), the spherical Bessel function of order 1. The radial boundary condition requires that

\[ \{\frac{dj_1(k_Nr)}{dr}\}_{r=a} = 0, \quad (3.4.7) \]

and successive roots \(k_Na = \nu_{1n}\) of this equation are labelled \(n = 0, 1, 2, \ldots\); the first few are given below.

<table>
<thead>
<tr>
<th>(\nu_{1n})</th>
<th>(n = 0)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000000</td>
<td>4.493409</td>
<td>7.725252</td>
<td>10.90412</td>
<td>14.06619</td>
</tr>
<tr>
<td>1</td>
<td>2.081576</td>
<td>5.940370</td>
<td>9.205840</td>
<td>12.40445</td>
<td>15.57924</td>
</tr>
<tr>
<td>2</td>
<td>3.342094</td>
<td>7.289932</td>
<td>10.61386</td>
<td>13.84611</td>
<td>17.04290</td>
</tr>
<tr>
<td>3</td>
<td>4.514100</td>
<td>8.583755</td>
<td>11.97273</td>
<td>15.24451</td>
<td>18.46815</td>
</tr>
</tbody>
</table>

(3.4.8)

A more extensive list of solutions, and some of the important properties of the spherical Bessel functions, are given in the appendix A3.2.

The solutions of the angular-dependent equations are well known and will not be discussed in detail here. The solution of the second of equations (5) that is finite and continuous is
and the solutions of the third of equations (5), \( \cos(m\zeta) \) and \( \sin(m\zeta) \), may be combined with (9) to define the spherical harmonics

\[
Y_{lm}(\theta, \zeta) = \{ \cos(m\zeta) + \sin(m\zeta) \} P_l^m(\cos \theta). \tag{3.4.10}
\]

The function \( P_l^m \) is the \( |m| \)th associated Legendre polynomial of order \( l \); its important properties are reviewed in appendix A3.2.

Equation (10) may be combined with the spherical Bessel function to define the normal modes of the cavity as

\[
\phi_N(r, \theta, \zeta) = j_l(\nu_{ln} r/a) Y_{lm}(\theta, \zeta), \quad N = (l, m, n). \tag{3.4.11}
\]

The corresponding eigenvalues and natural frequencies are

\[
-k_N^2 = - (\nu_{ln}/a)^2, \quad \text{and}
F_N(f_N) = (f_N - i\sigma_N) = (u/2\pi)(\nu_{ln}/a) - i\alpha(f_N), \tag{3.4.12}
\]

respectively. All the states with a given \( l \) are \((2l+1)\) fold degenerate, and the \( n \)th mode has \( l \) plane longitudinal nodal surfaces, \( m \) axial nodes, and \((n+1)\) spherical nodal surfaces (except for \( l=0 \) when there are \( n \) spherical nodes). Using the appropriate properties of the function \( j_l \) and \( Y_{lm} \) the normal modes of equation (11) can be shown to satisfy the orthogonality condition of equation (4), with the normalization constants

\[
N_N^0 = \{3/2(2l+1)}(1-1(1+1)/\nu_{ln}^2)((1-|m|)/(1+|m|)! \}, \tag{3.4.13}
\]

The eigenvalues must be modified to account for the non-ideal boundary conditions which are found in a real resonator. In the case of
the radially symmetric modes, the surface corrections are particularly simple because the motion is normal to the wall and no viscous damping occurs. For these modes the specific acoustic admittance of the boundary is

\[ y_r(f) = (1 - i)(\pi f/u)(\gamma - 1)\delta_h + y_{m,r}(f), \]  

(3.4.14)

where \( y_{m,r} \) is the contribution of the mechanical compliance of the wall. The surface integral in equation (3.2.34) is

\[
\int_S y_r(f) j_0^2(\nu_{0n}) dS = y_r(f)a^2 j_0^2(\nu_{0n}) \int_0^{2\pi} \int_0^{\pi} \sin \theta d\theta d\zeta \\
= 4\pi a^2 y_r(f) j_0^2(\nu_{0n}),
\]

(3.4.15)

and hence

\[
K_{0n}(f) = K_{0n} - (i/a)y_r(f),
\]  

and

\[
F_{0n}(f_{0n}) = (f_{0n} - ig_0) = (u/2\pi)\{K_{0n}(f_{0n}) - i\alpha(f_{0n})\},
\]

(3.4.16)

correct to first order in the surface admittance.

The \( l \)th order \((l > 0)\) non-radial modes of a spherical cavity are (2l + 1) fold degenerate, and the tangential fluid flow at the surface is generally a complicated function of the co-latitude and azimuth angles. However, in the case of those non-radial modes that are of axial symmetry \((m = 0)\) the motion is independent of \( \xi \). The tangential wave-number \( k_t \) is given by

\[
\nabla^2 p_0^0(\cos \theta) = -k_t^2 n_1(\cos \theta) = -(l(l + 1)/r^2)p_1^0(\cos \theta),
\]

(3.4.17)

and is constant over the surface \( r = a \) of the enclosure. The effective specific-acoustic-admittance of the thermal and viscous boundary layers
of the axial modes is

\[ y_a(f) = (1 - i)((\pi f/u)(\gamma - 1))e^{\delta S} + i(1 + 1)u\delta S/4\pi a^2 f, \]  

(3.4.18)

and the required surface integral is

\[ y_a(f)e^{-2i2(\nu_{1n})}\int_{0}^{2\pi} \int_{0}^{\pi} (\nu_1^0(\cos\theta))^2 \sin\theta d\theta d\xi = (4\pi a^2/(2l + 1))y_a(f)j_{11}^2(\nu_{1n}) \]  

(3.4.19)

The first-order corrected eigenvalues corresponding to the axially-symmetric non-radial wavefunctions are therefore

\[ K_{1n}(f) = k_{1n} - (i/a)[1 - l(1 + l)/\nu_{1n}^2]^{-1}y_a(f). \]  

(3.4.20)

The effects of boundary-shape perturbations can be estimated from equation (3.2.32) which gives

\[ (K_N/k_N) = 1 + (1/2V_Nk_N^2)\int_S \phi_N(r_S)(\partial/\partial n)\phi_N(r_S)\partial S, \]  

(3.4.21)

to a first-order approximation. For a near spherical surface, \((\partial/\partial n)\) may be replaced by \((\partial/\partial r)\) and hence the fractional shift in the eigenvalues of the radial modes is

\[ (k_N - k_N)/k_N = -(a/3\nu_{0n}j_0^2(\nu_{0n}))\int_S j_0(\nu_{0n}r/a)j_1(\nu_{0n}r/a)\partial S. \]  

(3.4.22)

Since \(j_1(\nu_{0n}) = 0\), the perturbation vanishes as \(S \rightarrow S_0\), the ideal surface \(r = a\). To proceed, \(j_0(\nu_{0n}r/a)\) and \(j_1(\nu_{0n}r/a)\) are both expanded in a Taylor's series about \(r = a\) with the results

\[ j_0(\nu_{0n}r/a) = j_0(\nu_{0n}) \{1 - (\nu_{0n}^2/2)((r - a)/a)^2 + \cdots\} \]
\[ j_1(\nu_{On} r/a) = \nu_{On} j_0(\nu_{On}) \{((r-a)/a) - ((r-a)/a)^2 \]
\[ + (2/3)((r-a)/a)^2 \{20 - 19\nu_{On}^2\}/30 \} + \cdots \] (3.4.23)

where the derivatives have been reduced to zero-order Bessel functions using the properties set out in appendix A3.2. Substitution of (23) in (22) yields

\[ (K_N - k_N)/k_N = -(a/3V) \int_S \{((r-a)/a) - ((r-a)/a)^2 \]
\[ + ((r-a)/a)^3 \{20 - 19\nu_{On}^2\}/30 \} \} \text{d}S, \] (3.4.24)

where \( \text{d}S = \rho_s^2(\theta, \zeta) \sin \theta \text{d}\theta \text{d}\zeta \) and \( \rho_s(\theta, \zeta) \) is the radial co-ordinate of a position on the surface. If \( \varepsilon \) is a small parameter describing a geometric deformation of the perfect cavity by which the volume remains unchanged, then the leading term in the surface integral of \( ((r-a)/a) \) will be of the order of \( \varepsilon^2 \). Thus the radial modes are insensitive to geometric imperfections. However, the non-radial wavefunctions are weighted by the factors \( Y_{1m}(\theta, \zeta) \) and are sensitive in the first order to a parameter describing a deformation. A specific example is the case in which the cavity is constructed from two hollow hemispheres of unequal radii. If the radius of one half is \( a(1 + \varepsilon)N \) and the radius of the other half is \( a(1 - \varepsilon)N \), where \( N^3 = (1 + 3\varepsilon^2)^{-1} \), then the volume is exactly independent of \( \varepsilon \) and the first two terms in equation (24) show that the fractional perturbation is \( 15\varepsilon^4 \). Thus, in this highly symmetric case the perturbation is vanishing to third order in \( \varepsilon \) and a fine tolerance is not required.
3.5 SPEED OF SOUND MEASUREMENTS BY THE RESONANCE TECHNIQUE

In principle, the speed of sound can be found from a time-of-flight measurement, in which the time taken for a pulse of sound to travel an accurately measured distance is determined. Methods of this type are of practical advantage in the study of liquids and dense gases, but if the characteristic acoustic resistance $\rho u$ of the fluid is small then the generation of a pulse with a useful amplitude becomes difficult. In dilute gases $\rho u$ is indeed small and the resonance technique, with its continuous excitation, is clearly superior.

The purpose of this section is to briefly review the relative merits of the various types of acoustic interferometer. Essentially, there are two types of interferometer, classified either according to the use of fixed geometry, and consequently variable frequency, or variable geometry and fixed operating frequency. These are further classified according to the use of high frequencies ($N$ large) or low frequencies ($N$ small).

The variable geometry experiment is restricted to the use of the longitudinal modes of a cylindrical interferometer. The cavity is driven at a fixed frequency by a transducer which usually forms one end of the cylinder. The remaining end is closed by a piston which is moved in the bore of the tube in order to tune the cavity. The resonance condition is detected either by a second transducer acting as a detector, or by measurement of the mechanical impedance of the loaded source transducer (this may be achieved by measurement of the corresponding electrical impedance). In either case the measured quantity is proportional to the Green's function of equation (3.2.14) where the excitation frequency $f$ is fixed and $L$ is tuned until $f_{\text{res}}$ is coincident with $f$. The resonance half-widths are obtained from the displacement of the reflector necessary to reduce the amplitude of the standing wave to $1/\sqrt{2}$ of its maximum.
value. This method has the substantial advantage that the absolute length of the cavity is not required; the speed of sound is obtained from the travel $\Delta L$ of the piston necessary to shift from one order of resonance to the next. Optical techniques can be used to measure $\Delta L$ with a relative accuracy approaching $1 \times 10^{-6}$. In contrast, absolute knowledge of the pathlength is required for absolute measurements by the constant-geometry variable-frequency technique. However, in many applications absolute measurements of sound speeds are not required, and the simpler arrangement of a fixed-geometry resonator is advantageous.

In any cavity the range of operating frequencies is important. If measurements are made at high frequencies, where $\lambda$ is much less than the characteristic dimensions of the resonator, then the boundary layer corrections are minimised at the expense of increased attenuation throughout the bulk of the fluid ($g_s/f = f^{-1/2}, \alpha/f = f$). However, as the operating frequency is raised, the number of resonances occurring in a given range of frequencies increases dramatically, and overlap between adjacent modes can be a serious source of systematic error. This is particularly severe in a cylindrical interferometer when the longitudinal modes are driven at frequencies well above $u(2\pi)/(X_{10}/b)$ because the compound modes are often unresolved from the purely longitudinal resonances. In addition, vibrational-relaxation absorption and dispersion can be large at high frequencies. The systematic errors prevalent in the various types of cylindrical interferometer have been discussed in detail by Colclough,\(^3\) who concludes that low-frequency measurements in a variable pathlength interferometer are preferable when high absolute accuracy is required. Nevertheless many workers have used interferometers for sound speed measurements at high ultrasonic frequencies to good effect and found that the problem of unresolved modes is not generally important at the usual $1 \times 10^{-4}$ level of accuracy.

Low-frequency measurements are usually unaffected by dispersion,
and overlap between adjacent resonances can be avoided. However, the boundary layer corrections are much larger, and accurate knowledge of the gas transport properties is required for a calculation of these corrections. A relative correction of $1 \times 10^{-3}$ is not uncommon at audio frequencies, where the precision of the measurements may be better than $1 \times 10^{-5}$. Fortunately the contribution $g_b$ of bulk absorption to the total resonance half-widths is usually small at low frequencies, and the contribution $g_S$ of the boundary-layer losses is easily found from the measured half-width. The difference $\Delta f_S$ between an idealized resonance frequency and the measured value is equal to $g_S$ (in the absence of other perturbations), and hence the measured half-widths can be employed to make the corrections. These half-widths can also be used to find the coefficients of thermal conductivity and shear viscosity from measurements of several resonances which have differing symmetry.

The choice of transducers, and the method by which they are coupled to the cavity, is crucial. If a large transducer is used as the end plate of a cylindrical resonator then the boundary condition there will differ from that assumed in the derivation of the normal modes; the fluid velocity at the end in motion must match that of the moving surface. The theory of cylindrical interferometers that operate with this type of transducer has been discussed in detail by Colclough and Quinn. Measurements of the mechanical admittance (or impedance) of the loaded transducer are essential in accurate work of this kind. It is generally desirable to use a small transducer which approximates to a point source, and has a negligible influence on the normal modes. Unfortunately, a point source is very inefficient, and the amplitude of the standing wave generated by such a device may be too small for sensitive measurements.

A spherical interferometer is necessarily of fixed geometry, and absolute knowledge of the radius is required for absolute measurements. Fortunately, the resonance frequencies of the radially symmetric modes of
a sphere are insensitive to geometric imperfections, and knowledge of the mean radius is sufficient. Because of the absence of viscous damping, and the favourable surface area to volume ratio in a sphere, the radial modes have $Q$'s which are about a factor of ten greater than those of a comparable cylinder. The boundary-layer corrections are therefore smaller, and less severe demands are placed on the quality of the gas transport data required to calculate these corrections. Again the measured half-width may be used to evaluate the corrections, and to determine the coefficient of thermal conductivity for the fluid under study. Quite inefficient transducers may be used, and the area of the surface perturbed by the source need only be a small fraction of the total.

In summary, low-frequency interferometry avoids the problems of overlapping modes and vibrational relaxation, but large boundary layer corrections must be made. However, while the influence of the former effects are difficult to assess, the latter are measurable. In addition, resonance width measurements can provide accurate gas transport quantities.
APPENDIX A3.1

The calculation of the boundary-layer corrections is crucial to the accuracy of low-frequency measurements of the speed of sound in dilute gases. The expressions derived in chapter 2 (equations 2.6.39), for the acoustic admittance of the boundary layers, and in this chapter (equation 3.2.34), for the corresponding perturbations to the resonance frequencies of a cavity, form a consistent first-order approximation to the exact solution of the problem. By this approximation the thermal and shear corrections to the propagational wave are neglected in the boundary layers, $k_h^2 - k_t^2$ is set equal to $k_h^2$, and $k_s^2 - k_t^2$ is set equal to $k_s^2$. It has also been assumed, without proof, that the results obtained for a plane surface may be applied to curved surfaces without modification. In addition to these approximations there is the overall assumption that a dilute gas may be considered as a classical continuum fluid. Without this assumption the boundary conditions of continuous temperature and vanishing tangential velocity do not apply. The molecular nature of the fluid is responsible for the breakdown of these boundary conditions at low densities, and for the resulting phenomena of molecular slip and the temperature jump.

All these possible sources of error have been investigated by Weston\textsuperscript{5} for the case of plane waves propagating along an infinite cylindrical waveguide. He considered the approximations made by Kirchhoff in the derivation of the orthodox tube propagation-constant of equation (2.6.40), and derived some more exact formulae which are applicable to a number of limiting cases. The approximations of Kirchhoff are the same as those made in the application of equations (2.6.39) to the solution of the boundary-value problem at the side walls of a cylindrical interferometer operating in the longitudinal modes. Shields, Lee, and Wiley\textsuperscript{6} have obtained direct numerical solutions for
the same problem, which are valid over a wide range of frequencies and tube radii. The relative errors introduced into sound-speed measurements, by the neglect of their second-order corrections, are of the order of the square of the relative first-order correction itself. Unless the first-order corrections are very large (as they would be for very narrow tubes) the second-order corrections are negligible in all but the most precise measurements. The effects of molecular slip were also found to be a source of error, but the temperature-jump effect, which Weston suggests is as large, was neglected. These latter effects are of greater importance than the approximations in the Kirchhoff-Helmholtz theory because relatively wide tubes \( b > \delta_h, \delta_s \) are employed for speed-of-sound measurements.

Second-order corrections have not been investigated for the radial resonances of a spherical interferometer and will therefore be considered here. To begin with it will be assumed that the non-classical temperature-jump effect is negligible, and that thermal waves do not propagate in the wall. Thus, the thermal boundary condition is the same as was adopted in chapter 2. However, the thermal and shear corrections to the propagational mode will not be neglected, and hence

\[
p_p(r) = A j_0(K_{On} r) \exp(-i\omega t) \\
T_p(r) = A \{(\gamma - 1)/\gamma \beta\}(1 - iL_h) j_0(K_{On} r) \exp(-i\omega t), \quad \text{and} \\
\vec{u}_p(r) = -A(\delta/\omega \epsilon)(1 - iL_v) K_{On} j_1(K_{On} r) \exp(-i\omega t),
\]

are the contributions to the acoustic pressure, temperature, and fluid velocity of the \( n^{th} \) radial mode, where \( A \) is a constant, and \( \hat{\epsilon} \) is the radial unit base vector. The thermal mode must satisfy the wave equation

\[
\nabla^2 T_h(r) = -k_h^2 T_h(r),
\]
and the total acoustic temperature \( T_a = T_p + T_h \) must satisfy the boundary condition

\[
T_a(r = a) = 0
\]

at the surface \( r = a \) of the enclosure. The radially symmetric eigenfunction of \( \nabla^2 \), which is finite at the origin and has the time dependence of \( \exp(-i\omega t) \), is

\[
T_h(r) = B j_0(k_h r)\exp(-i\omega t), \quad (A3.1.4)
\]

where the amplitude

\[
B = -A(1 - iL_h)(\gamma - 1)/\gamma j_0(k_h a)
\]

is determined by the thermal boundary condition. The thermal wave makes a small contribution to the acoustic pressure, given by

\[
p_h(r) = i\gamma \beta (L_h - L_v)T_h(r)
= -iA(L_h - L_v)(\gamma - 1)j_0(K_{on} a)j_1(k_h a)\exp(-i\omega t), \quad (A3.1.6)
\]

and a contribution to the fluid velocity, given by

\[
\vec{u}_t = \hat{\epsilon}(\gamma \beta L_h/\omega \rho)(dT_r/\bar{r})
= \hat{\epsilon}A(1 + iL_h)(\omega/2c_0^2)(1 - iL_h)(\gamma - 1)j_0(K_{on} a)j_1(k_h r)/j_0(k_h a). \quad (A3.1.7)
\]

Thus, the magnitude of the total fluid velocity at the surface \( r = a \) is

\[
|\vec{u}|(r = a) = A\{\exp(-i\omega t)/i\omega\}((1 - iL_h)(\omega^2 \xi_h/2c_0^2)(1 - iL_h)(\gamma - 1)j_1(k_h a)/j_0(k_h a)
- (1 - iL_v)K_{on}j_1(k_{on} a))
\]
\[ \gamma_m p_a(r = a) = \gamma_{-1}(a) \exp(-i\omega t). \]  

Elimination of \( \exp(-i\omega t) \) from equation (8), and some rearrangement yields

\[ \{K_{-1} j_1(K_{-1} a)/j_0(K_{-1} a)\} = \text{ii} \omega \{1 + iL_v + (L_h - L_v)(\gamma - 1)\}{Y_m + Y'_m}, \]  

where

\[ Y'_m = -i\{(1 - i)/\nu u_0\}(\gamma - 1)(\omega/2u_0)\delta_h\{1 - iL_h + (L_v - L_h)(\gamma - 1)\}j_1(k_h a)/j_0(k_h a), \]  

is the effective acoustic-admittance of the thermal boundary layer. The term \( \delta_h\{1 - iL_h + (L_v - L_h)(\gamma - 1)\} \) which is partially third order in \( \delta_h \) may be replaced by \( \delta_h \), and by the same reasoning \( \{1 + iL_v + (L_h - L_v)(\gamma - 1)\} \) may be replaced by \( 1 \) in equation (9). Since \( j_1(z)/j_0(z) = z^{-1} - \cot(z) \), and \( k_h = (1 + i)/\delta_h \), the ratio of spherical Bessel functions can be expanded as

\[ \{j_1(k_h a)/j_0(k_h a)\} = \{1 - i\delta_h/2a\} - \cot((1 - i)a/\delta_h) \]

\[ = \{(1 - i)\delta_h/2a\} + \frac{i\tan(a/\delta_h)\tanh(a/\delta_h) - 1}{\tan(a/\delta_h) + i\tanh(a/\delta_h)}, \]  

where

\[ \tanh(z) = \{(e^z - e^{-z})/(e^z + e^{-z})\} \xrightarrow{z \to \infty} 1. \]  

The limiting behaviour of \( \tanh(z) \) is reached very rapidly; \( \tanh(a/\delta_h) = 1 \pm 10^{-6} \) for \( (a/\delta_h) > 10 \), and hence.
\[ \{j_1(k_h a)/j_0(k_h a)\} = i(1 - (1 + i)\delta_h/2a). \]  
\[ (A3.1.13) \]

Thus, the specific acoustic admittance of the thermal boundary layer is

\[ y'_h = y_h \{1 + (1 + i)\delta_h/2a\} = y_h - (\gamma - 1)(\omega/2u_0)(\delta_h^2/a), \]

\[ (A3.1.14) \]

correct to second-order in \( \delta_h \), where \( y_h = (1 - i)(\gamma - 1)(\omega/2u_0)\delta_h \) is the first-order approximation. The second-order term in equation (14) arises from the curvature of the surface, and vanishes as \( a \to \infty \). The additional effect of this term can be demonstrated by the first-order equation (3.4.16), which shows that the imaginary components of the eigenvalues are perturbed by the fraction \( i(\gamma - 1)(\delta_h^2/a)^2 \), and that the resonance frequencies are not shifted. Clearly when \( (a/\delta_h)^2 > 10^3 \) the second-order term in equation (14) is negligible. However, a direct numerical solution of equation (9) is desirable in order to verify that the predictions of the first-order theory are sufficiently precise. In the present context, the required solution is the one obtained when \( \omega = 2\pi f_{0_n} \), and corresponds to the situation where the cavity is driven at its \( n \)th radial resonance frequency. Setting \( K_{0_n} a = \nu_{0_n} + i\chi_{0_n} \), and \( y'_h = (\zeta - i\sigma)/\rho u_0 \), where \( \zeta \) and \( \sigma \) are the specific acoustic-conductance and susceptance of the boundary, and substituting in (9) the equations

\[ (\nu_{0_n} + i\chi_{0_n}) = n\pi + \tan^{-1}(c+id), \]

\[ c = \{\nu(1+\nu\sigma) + \chi(\nu\zeta)\}/[(\bar{\zeta} + \nu\sigma)^2 + (\nu\zeta)^2], \quad \text{and} \]

\[ d = \{\chi(1+\nu\sigma) - \nu(\nu\zeta)\}/[(\bar{\zeta} + \nu\sigma)^2 + (\nu\zeta)^2], \]

\[ (A3.1.15) \]

may be obtained. The required eigenvalues are found by iteration; if \( \nu^{(m)} \) and \( \chi^{(m)} \) are the \( m \)th approximations to \( \nu \) and \( \chi \) then the \( (m+1) \)th improved approximation is \( n\pi + \tan^{-1}(c^{(m)}+id^{(m)}) \), where \( c^{(m)} \) and \( d^{(m)} \) are calculated from the \( n \)th approximations. For example, in argon at
$T = 273$ K and $p = 10$ kPa, $\delta_h = 124.0 \mu m$ at 3.7 kHz, and hence $y_h = (1 - i)0.00312_3$. The first-order theory of equation (3.4.16) predicts that $v_{01} = 4.49028_6$ and $\chi_{01} = -0.00312_3$, while an exact solution gives $v_{01} = 4.49028_9$ and $\chi_{01} = -0.00312_1$ (two iterations of equation 15 are required if the first-order estimates are the starting values). Since $f_{01}$ will occur at 3.7 kHz in a resonator of radius 60 mm filled with argon at $T = 273$ K and $p = 10$ kPa, the second-order correction implied by equation (14) indicates that $y^\prime_h = y_h - 0.000000_6$. If $v^{(0)}_{01} = 4.5$ and $\chi^{(0)}_{01} = 0$ are taken as the zeroth approximations to $v_{01}$ and $\chi_{01}$, then four iterations of equation (15) are required using $y^\prime_h$, with the result $v_{01} = 4.49028_9$ and $\chi_{01} = -0.00311_4$. Similarly close agreement, between first-order theory and the prediction of equations (14) and (15), is found for the higher-frequency modes. Clearly, even at the low pressure of 10 kPa, the neglect of second-order terms in the boundary theory has a negligible effect on the resonance frequencies. However, the first-order theory does slightly overestimate the resonance half-widths (by about 0.3 per cent in this example), and this may be marginally significant when a measured boundary-layer correction is applied, or in a measurement of the thermal conductivity of the medium.

Errors arising from the failure of continuum theory can be significant if the gas pressure is low because the mean free path $\lambda$ can become a significant fraction of the thermal and shear decay lengths. The resulting phenomena of molecular slip and the temperature jump have been discussed in a number of publications.\textsuperscript{4,5,6} Since there is no tangential motion, molecular slip will not be of importance for the radial modes of a spherical resonator. The temperature jump is an apparent discontinuity in the temperature, which occurs over the thin layer of gas within a few mean free paths of a gas-to-solid interface when there is a heat current. The temperature $T_e$ of the gas at the boundary, as estimated from the uniform temperature gradient in the bulk
of the fluid, differs from the true temperature $T_S$ of the surface. At sufficiently high pressures, the apparent discontinuity in the temperature is given by\(^7\)

\[
(T_e - T_S) = \left(\frac{J_H}{p}\right) \left(\frac{\pi M T_e}{2R}\right)^\frac{1}{2}(2 - h)/2h)

= \left(\frac{J_H}{p}\right) 
\]

\[
(\text{A3.1.16})
\]

for a monatomic gas of thermal conductivity $K$, where $J_H$ is the component of the heat current density which points into the surface, and the thermal accommodation length is given by

\[
I_t = \left(\frac{K}{p}\right) \left(\frac{\pi M T_e}{2R}\right)^\frac{1}{2}(2 - h)/2h)
\]

\[
(\text{A3.1.17})
\]

The accommodation coefficient $h$ is defined as the fraction of molecules which are diffusely reflected from the surface, and can be measured in the hot-wire type of thermal conductivity experiment.\(^8\)

Fortunately a more fundamental boundary condition can be imposed which does not require the temperature of the fluid at the interface to be specified but instead simply requires the heat current density in the gas just outside the accommodation layer to equal the heat current density in the wall at its surface. It will be sufficient to return to the case of the plane wall confining the gas to the half space $z \leq 0$. The heat current density in the wall is given by

\[
\dot{J}_H = -K_w \nabla T_w,
\]

\[
(\text{A3.1.18})
\]

where $T_w$ is the temperature, and $K_w$ is the thermal conductivity, of the wall material. The equation of continuity for energy density is

\[
C_{V_w} \rho_w (\partial T_w/\partial t) + \nabla \cdot \dot{J}_H = 0,
\]

\[
(\text{A3.1.19})
\]
where $C_{V_w}$ is the specific heat capacity at constant volume, and $\rho_w$ is the density, of the wall material. Combination of (18) and (19) results in the thermal wave equation

\[ \nabla^2 - (1/D_t)(\partial/\partial t)T_w(r,t) = 0, \]  
\[ \text{(A3.1.20)} \]

where $D_t = (K_w/\rho_w C_{V_w})$ is the thermal diffusivity of the wall. The plane-wave solution of equation (20), which is equal to $T + T_0 \exp(-i\omega t)$ at the surface $z=0$, and $T$ in the limit $z \to \infty$, is

\[ T_w(z,t) = T + T_0 \exp(-i\omega t + (i - 1)(\omega/2D_t)^{1/2}z), \]  
\[ \text{(A3.1.21)} \]

where $T$ is the equilibrium temperature. By analogy with the thermal mode in the gas, a thermal decay length $\delta_w$ may be defined for the wall:

\[ \delta_w = (2D_t/\omega)^{1/2} = (2K_w/\rho_w C_{V_w})^{1/2}, \]  
\[ \text{(A3.1.22)} \]

and $\exp(-z/\delta_w)$ describes a rapid attenuation of the thermal oscillations in the wall.

The magnitude of the heat current density into the wall at the surface is

\[ J_H = (1 - i)K_w(\omega/2D_t)^{1/2}T_0 \exp(-i\omega t) \]
\[ = (1 - i)(K_w/\delta_w)T_0 \exp(-i\omega t), \]  
\[ \text{(A3.1.23)} \]

which must equal the magnitude of the heat current density in the gas adjacent to the wall. The gradient $(\partial/\partial z)T_a(z = -L_t)$ of the acoustic temperature in the gas just outside the accommodation layer gives

\[ J_H = -K(\partial/\partial z)T_a(z = -L_t), \]  
\[ \text{(A3.1.24)} \]
and equation (16) shows that the acoustic temperature extrapolated to the wall $T_e^' = (T_e - T)$ differs from the true acoustic temperature of the surface by

$$T_e^' - T_0 \exp(-i\omega t) = -l_t \left( \partial / \partial z \right) T_a (z = -l_t).$$  \hfill (A3.1.25)

Combination of equations (23) and (24) gives

$$T_0 \exp(-i\omega t) = -(1 + i) \delta_w (K/2K_w) \left( \partial / \partial z \right) T_a (z = -l_t),$$  \hfill (A3.1.26)

and elimination of $T_0 \exp(-i\omega t)$ in (25) results in

$$T_e^' = -(1 + (1 + i) \delta_w (K/2K_w)) \left( \partial / \partial z \right) T_a (z = -l_t).$$  \hfill (A3.1.27)

Equation (27) is the thermal boundary condition which must be satisfied by the thermal and propagational waves in the gas. The gradient of the acoustic temperature is evaluated in the gas just outside the accommodation layer, where classical heat flow should occur, and the behaviour of the acoustic temperature within the accommodation layer is not specified. $T_e^'$ is the acoustic temperature of the fluid at $z = 0$ that would be calculated with the assumption that continuum theory applied right up to the interface. As $l_t \rightarrow 0$ and $\delta_w (K/K_w) \rightarrow 0$ the boundary condition reverts to $T_a (z = 0) = 0$, but in the range of pressures where $l_t (= \delta_h)$ is a small, but significant, fraction of $\delta_h$, the normal gradient of $T_a$ must be adjusted to satisfy (27). Since the gradient of the acoustic temperature is very nearly linear at $z = -l_t$, the normal gradient at $-l_t$ may be replaced by the gradient $(\partial T_e^' / \partial z)_{z = 0}$ that would be found at the interface if continuum theory applied. It then follows, using the methods by which equations (2.6.39) were derived, that the specific acoustic admittance of the thermal boundary layer is modified by the
factor \{1 - (1 - i)(1_t/\delta_h) - (\delta_w/\delta_h)(K/K_w)\}. The fractional correction to the radial eigenvalues, which results from this modification, is

\[(K'_{On} - K_{On})/K_{On} = (\gamma - 1)(1_t/\alpha) + (1 + i)(\gamma - 1)(\delta_w/2a)(K/K_w),\]  

(A3.1.28)

where \(K'_{On}\) is the \(n^{th}\) corrected radial eigenvalue. Since the thermal conductivity of metals is greater than that of gases by a factor of about \(10^4\), and \(\delta_w\) is of the same order as \(\delta_h\), the fractional shifts in the resonance frequencies, arising from thermal propagation in the wall, are negligible under all likely conditions. However, at very high gas densities the resonance half-widths are small, and there may be a significant effect on measurements of the coefficient of thermal conductivity.\(^9\)

For argon at 273 K the accommodation coefficient at a clean metal surface is close to unity,\(^4\) and thus \(1_t = 0.59 \mu m\) at \(p = 20\) kPa (c.f. \(\lambda = 0.51 \mu m\)). At that pressure the fractional shift in the resonance frequencies of a resonator of radius 60 mm is \(7 \times 10^{-6}\), which is significant by comparison with the possible precision of \(1 \times 10^{-6}\). It should be noted that the resonance half-widths are not perturbed, and that the relative effect on the resonance frequencies is independent of the mode number \(n\).
This appendix lists some of the properties of the following mathematical functions:

(a) the cylindrical Bessel functions of integer order,\(^{10}\)
(b) the trigonometric functions \(\cos(m\psi) + \sin(m\psi)\) for integer \(m\),
(c) the spherical Bessel functions of integer order,\(^{11}\) and
(d) the associated Legendre functions.\(^{12}\)

A. The Cylindrical Bessel Functions

The general solution of the second-order differential equation:

\[
\frac{d^2Z}{dz^2} + \left(\frac{1}{z}\right)\left(\frac{dZ}{dz}\right) + \left\{1 - \left(\frac{m}{z}\right)^2\right\}Z = 0
\]

is \(Z(z) = AJ_m(z) + RN_m(z)\), where \(A\) and \(B\) are arbitrary constants, \(N_m(z)\) is the cylindrical Neumann function of order \(m\), and \(J_m(z)\) is the cylindrical Bessel function of order \(m\). The Neumann functions are infinite at \(z=0\) and are not required in the formulation of equations to describe acoustic motion in a region containing the origin. When \(m\) is a positive integer or zero, \(J_m(z)\) may be represented by the infinite series:

\[
J_m(z) = \sum_{j=0}^{\infty} \frac{1}{(m+j)!}(z/2)^{m+2j},
\]

which, for large values of \(z\), has the asymptotic form

\[
J_m(z) \xrightarrow{z \to \infty} \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \cos\left[z - \frac{(2m+1)}{4}\right].
\]

Negative-order functions are defined by
\[ J_{-m}(z) = (-1)^m J_m(z), \quad z > 0, \quad (A3.2.4) \]

and some additional properties of the cylindrical Bessel functions are:

\[ 2(\frac{d}{dz})J_m(z) = J_{m-1}(z) - J_{m+1}(z) \]
\[ J_{m-1}(z) + J_{m+1}(z) = (2m/z)J_m(z) \]
\[ J_m(az)J_m(bz)zdz = \frac{z}{(a^2 - b^2)^{1/2}}[bJ_m(az)J_{m-1}(bz) - aJ_m(bz)J_{m-1}(az)] \]
\[ J_m^2(z)zdz = (z^2/2)[J_m^2(z) - J_{m-1}(z)J_{m+1}(z)]. \quad (A3.2.5) \]

The turning points \( z = \chi_{mn} \) of the \( m \)th order function are the solutions of \((\frac{\partial}{\partial z})J_m(z) = 0\), and may be obtained numerically with the aid of the first of equations (5) and equation (2). The set of functions \( \chi_{mn} \), \( n = 0, 1, 2, \ldots, \infty \), are mutually orthogonal in the interval \( 0 \leq z \leq 1 \); since

\[ J_{m-1}(\chi_{mn}) = (m/\chi_{mn})J_m(\chi_{mn}), \quad (A3.2.6) \]

the third of equations (5) shows that

\[ \int_0^1 J_m(\chi_{mn}z)J_m(\chi_{mn}z)zdz = 0, \quad n \neq n', \quad (A3.2.7) \]

and the fourth of equations (5) that

\[ \int_0^1 J_m^2(\chi_{mn}z)zdz = (1/2)J_m(\chi_{mn})[1 - (m/\chi_{mn})^2]. \quad (A3.2.8) \]

B. The Trigonometric Functions \( \{\cos(m\psi) + \sin(m\psi)\} \).

The general solution of the second-order differential equation

\[ (\frac{d^2y}{d\psi^2}) - m^2y = 0 \quad (A3.2.9) \]
is \( Y(\psi) = A \cos(m\psi) + B \sin(m\psi) \), where \( A \) and \( B \) are arbitrary constants. If \( m \) is an integer then the solution is periodic with a period of \( 2\pi \). The set of particular solutions \( \{\cos(m\chi) + \sin(m\chi)\} \), \( m = 0, 1, 2, \cdots \infty \), are mutually orthogonal in the interval \( 0 < \psi/2\pi < 1 \):

\[
\int_0^{2\pi} \{\cos(m\psi) + \sin(m\psi)\} \{\cos(m'\psi) + \sin(m'\psi)\} d\psi = 2\pi \delta_{mm}'.
\]  

(A3.2.10)

C. The Spherical Bessel Functions

The second-order differential equation:

\[
\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left\{ \frac{r^2 + 1}{2} \frac{2 + 1}{2} \right\} R/r^2 = 0,
\]

(A3.2.11)

has the general solution \( R(r) = A j_1(r) + B n_1(r) \), where \( A \) and \( B \) are arbitrary constants, \( n_1(r) \) is the spherical Neumann function of order \( 1 \), and \( j_1(r) \) is the spherical Bessel function of order \( 1 \). The particular solution \( h_1(r) \), obtained when \( A = 1 \) and \( B = 0 \), is called the spherical Hankel function of order \( 1 \), and is given by the finite series:

\[
h_1(r) = (i^{-1}/ir)^{1/2} \sum_{s=0}^{\infty} \frac{(1+s)!}{s!(1-s)!} (i/2r)^s \exp(ir),
\]

(A3.2.12)

which may be resolved into real and imaginary terms to obtain

\[
j_1(r) = (\sigma_1/r)^{1/2} \sum_{s=0}^{\infty} \frac{(1+s)!}{s!(1-s)!} (1/2r)^s (-1)^{s/2} \sin r
\]

\[
+ \sum_{s=1}^{\infty} \frac{(1+s)!}{s!(1-s)!} (1/2r)^s (-1)^{(s+1)/2} \cos r
\]

(A3.2.13)

where \( \sigma_1 = (-1)(1+2)/2 \) for even \( l \) and \( \tau_1 = (-1)(1+1)/2 \) for odd \( l \). When \( r \) is large \( j_1(r) \) may be approximated by the asymptotic form
Some important properties of the spherical Bessel functions of integer order are:

\[
(d/dr)j_1(r) = \frac{1}{r}(2j_{1-1}(r) - (1 + \frac{1}{2})(j_{1+1}(r))
\]

\[
j_{1-1}(r) + j_{1+1}(r) = \frac{(2I + 1)}{r} j_1(r)
\]

\[
j(1)(ar)j_{1}(br)r^2dr = \{r^2/(a^2 - b^2)\}(b_j_{1}(ar)j_{1-1}(br) - a_j_{1}(br)j_{1-1}(ar))
\]

\[
j(1)^2(r)r^2dr = \{r^3/2\}(j_{1}(r)^2 - j_{1-1}(r)j_{1+1}(r)).
\]

The turning points \(r = \nu_{1n}\) of the \(l^{th}\) order function are the solutions of \((d/dr)j_1(r) = 0\), and may be obtained numerically with the aid of the first of equations (15) and equation (13). The following values are accurate to \(\pm 1\) in the last digit:

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<td>28.823 65</td>
<td>29.854 85</td>
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<td>31.914 95</td>
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The set of functions $rj_1(\nu_{ln}r)$, $n = 0, 1, 2, \ldots \infty$, are mutually orthogonal in the interval $0 \leq r \leq 1$: since

$$
\begin{align*}
J_{l-1}(\nu_{ln}) &= \{(1 + 1)/\nu_{ln}\}j_1(\nu_{ln}) \quad \text{and} \\
J_{l+1}(\nu_{ln}) &= (1/\nu_{ln})j_1(\nu_{ln}),
\end{align*}
$$

(A3.2.16)

the third of equations (15) shows that

$$
f_0^1j_1(\nu_{ln}r)j_1(\nu_{ln}, r)r^2 dr = 0, \quad n \neq n',
$$

(A3.2.17)

and the fourth of equations (15) that

$$
f_0^1j_2(\nu_{ln}r)r^2 dr = (1/2)j_1(\nu_{ln})\{1 - 1(1 + 1)/\nu_{ln}^2\}.
$$

(A3.2.18)

D. The Associated Legendre Functions

The solution of the second-order differential equation

$$
\left(\frac{d^2P}{d\theta^2}\right) + \left(\frac{\cos \theta}{\sin \theta}\right)\left(\frac{dP}{d\theta}\right) + \left\{1(1 + 1) - \frac{m^2}{\sin^2 \theta}\right\}P = 0
$$

(A3.2.19)

that is finite and continuous in the interval $0 \leq \theta \leq \pi$ is $P(\theta) = P_m^l(\cos \theta)$, the $m^{th}$ associated Legendre function of order $l$, where $l$ is restricted to zero and positive integer values and $m$ to values $0, \pm 1, \pm 2, \ldots \pm l$. The $P_m^l(x)$ are related to the Legendre functions $P_l(x)$ by

$$
P_m^l(x) = (1 - x^2)^{1/2} \frac{d^m}{dx^m}(x^m P_l(x)),
$$

(A3.2.20)

and hence $P_0^l(x) = P_l(x)$. The Legendre functions themselves are defined by
\( P_1(x) = (1/2^11!) (d^1/dx^1)(x^2 - 1)^1 \), \( \text{(A3.2.21)} \)

and have the following properties:

\[
\begin{align*}
(d/dx)[P_{1+1}(x) - P_{1-1}(x)] &= (2l + 1)P_1(x) \\
(1 + 1)P_{1+1}(x) + 1P_{1-1}(x) &= (2l + 1)\lambda P_1(x) \\
\int_{-1}^{1} P_1(x) P_{1,1}(x) dx &= 2\delta_{11}/(2l + 1).
\end{align*}
\( \text{(A3.2.22)} \)

The first few Legendre functions of \( \cos \theta \) are:

\( P_0(\cos \theta) = 1, \ P_1(\cos \theta) = \cos \theta, \ P_2(\cos \theta) = (1/4)(2 \cos 2\theta + 1), \) and
\( P_3(\cos \theta) = (1/8)(5 \cos 3\theta + 3 \cos \theta). \) \( \text{(A3.2.23)} \)

The last of equations (22) show that the set of functions \( P_1(x) \),
\( l = 0,1,2,\cdots \infty, \) are mutually orthogonal in the interval \(-1 \leq x \leq 1\). It

can also be shown\(^{12} \) that the associated Legendre functions obey the

condition

\[
\int_{0}^{\pi} |P_1^m(\cos \theta)|^2 \sin \theta d\theta \delta_{m,1} = 2(1 + |m|)! (2l + 1)!/(2l + 1)(1 - |m|)!, \ (A3.2.24)
\]

and hence that the set of functions \( (\sin \theta)^{1/2} P_1^m(\cos \theta), \ l = 0,1,2,\cdots \infty, \)

are mutually orthogonal in the interval \( 0 \leq \theta \leq \pi. \)
REFERENCES


4.1 INTRODUCTION

Electroacoustic transducers are crucial components in the design and use of acoustic resonators. Many different schemes are possible for the excitation and detection of acoustic resonance, but here the emphasis will be placed upon two-transducer arrangements in which the frequency is variable. The latter requirement places considerable constraints on the type of transducers that may be used and, in particular, excludes the use of resonant devices at their natural frequencies. In a two-transducer variable-frequency interferometer it is assumed that the source strength $S_\omega$ is constant as the frequency is varied near to a resonance of the cavity, and the electrical output from a separate detector is assumed to be proportional to the acoustic pressure at the measurement point. This is in contrast to the

For a simple-harmonic source of arbitrary shape, $S_\omega$ is defined by

$$S_\omega \exp(-i\omega t) = \int \hat{n} \cdot \vec{U} \delta S,$$

where $\vec{U}$ is the surface velocity, and $\hat{n}$ is the outward-pointing unit vector normal to the surface element $\delta S$. 
arrangement in which the resonance is detected by measurement of the variation of the mechanical impedance of the loaded source transducer as a function of the frequency (or of displacement in a variable-path interferometer).

The transducers may form part of the wall of the acoustic cavity, in which case their non-zero mechanical admittance can influence the response of the resonator. Alternatively, the transducers may be installed outside the cavity and coupled to the interior by waveguides, but these too can perturb the normal modes. An advantage of this latter method is that the resonator may be operated at an extreme temperature, while the transducers are near to the ambient temperature. In either case, careful design is required to reduce the perturbations to a measurable or calculable level. A compromise is usually required between a system which offers small perturbations but low electroacoustic efficiency, and a more efficient arrangement which has a correspondingly large influence on the resonance frequencies and widths.

The active surface of a non-resonant transducer is usually either a membrane or a thin plate because, when suitably mounted, the displacement amplitude of these systems in response to a driving force is independent of the frequency of that force, provided that this is below the frequency of the fundamental resonance. Thus vibrating plates and membranes are well suited to application in a wide range of frequencies; the system is usually designed so that the resonance frequency is somewhat above the maximum required operating frequency.

In the absence of damping, the mean transverse displacement amplitude $\langle \omega M \rangle_S$ over the surface of a uniform circular membrane fixed at its rim, and driven by a uniform acoustic pressure $P\exp(-i\omega t)$ on one side only, is given by

$\dagger$ Since the driving force is uniform over the surface of the membrane, only the circularly symmetric vibrations will be considered here.
where \( T_m \) is the tension, \( a \) is the radius, and

\[
\dot{k}_m^2 = \frac{\omega^2 \rho_S}{T_m},
\]

where \( \rho_S \) is the mass per unit area. At low frequencies, such that \( k_m a \) is less than unity, the Bessel functions may be approximated by the leading terms in their series expansions, and equation (1) reduced to

\[
<\psi_m> = \frac{p a^2}{8T_m}, \quad k_m a < \frac{1}{\chi_1}.
\]

At higher frequencies, the response of the membrane is punctuated by sharp resonances which occur at the frequencies

\[
f_n = \left( \frac{\chi_n}{2\pi a} \right) \left( \frac{T_m}{\rho_S} \right), \quad \chi_1 = 2.4059
\]

where \( \chi_n \) are the values of \( \chi a \) for which \( J_0(\chi a) = 0 \). Clearly, the range of frequencies over which the response is uniform may be extended by an increase in the tension, but the sensitivity is thereby reduced.

Figure 4.1a shows \( <\psi_m> \) as a function of the driving frequency, for frequencies up to twice the fundamental. Damping may be introduced to reduce the amplitude at resonance to a finite value, and it is possible to extend the range of fairly uniform response up to slightly above the first resonance frequency.

The corresponding mean surface-displacement amplitude of an edge-clamped circular plate of radius \( a \) and thickness \( d \) is

\[
<\psi_p> = \frac{12P(1-\sigma^2)}{\pi \Delta \alpha d^2} \left[ \frac{L}{\pi a} \frac{I_1(\chi a)}{I_0(\chi a) I_1(\chi a) + I_0(\chi a) I_1(\chi a)} \right]^{-1}
\]
FIGURE 4.1. MEAN DISPLACEMENT AMPLITUDES AS A FUNCTION OF THE FREQUENCY.

A. driven membrane.

B. driven plate.
where \( Y \) is Young's modulus, \( \sigma \) is Poisson's ratio, \( I_0(ix) = J_0(ix) \) and \( I_1(ix) = -iJ_1(ix) \) are the zeroth- and first-order hyperbolic Bessel functions, and

\[
k^4 = \left\{12\omega^2(1-\sigma^2)/Yd^2\right\},
\]

(4.1.6)

where \( \rho \) is the density. At low frequencies, such that \( Ka \) is less than unity, the term in square brackets in equation (5) may be approximated by \( (Ka)^4/192 \), and hence \( \langle \psi_p >_S \) is approximately

\[
\langle \psi_p >_S = \left\{a^4\rho(1-\sigma^2)/16Yd^3\right\}, \quad Ka < 1.
\]

(4.1.7)

The resonance frequencies of the plate are

\[
f_n' = \left(\chi_n'd/2\pi a^2\sqrt{12}\right)\{Y/\rho(1-\sigma^2)\}^{\frac{1}{4}}, \quad \chi_1' = 10.2,
\]

(4.1.8)

where \( \chi_n' + (n\pi)^2 \) for large values of \( n \). Increasing the radius, or decreasing the thickness, will improve the sensitivity at low frequencies, but lower the frequency of the fundamental resonance. Figure 4.1b shows \( \langle \psi_p >_S \) as a function of the driving frequency, for frequencies up to six times the fundamental.

In the following two sections the use of plates and membranes in electrostatic and piezoelectric transducers will be described, and in the final section of this chapter the effects of waveguides on the performance of a resonator will be investigated.
4.2 ELECTROSTATIC TRANSDUCERS

The electrostatic transducer is essentially a parallel plate capacitor in which one plate, the backplate, is held stationary while the other is an edge-clamped plate or membrane and moves in response to a mechanical or electrostatic force. Figure 4.2 shows a typical arrangement and an appropriate electrical circuit, in which $E_0$ is a d.c. polarization potential difference, $C_B$ is a capacitance preventing direct current from flowing in the external circuit, and $R_B$ is a large resistance preventing alternating current from flowing in the polarization source. Since $C_B \gg C$, the capacitance of the transducer, and $R_B \gg 1/\omega C$, the blocking capacitor and resistor have a negligible influence on the behaviour of the network.

![Figure 4.2. An Electrostatic Transducer.](image)

The capacitance of the transducer is

$$C = \varepsilon S/x = Q/E$$  \hspace{1cm} (4.2.1)

where $\varepsilon$ is the dielectric constant of the gas between the plates, $S$ is
the surface area of the diaphragm, \( x \) is the separation of the plates, \( Q \) is the charge, and \( E \) is the total potential difference between the plates. If the diaphragm is set in motion by an incident sound wave then the capacitance of the transducer will fluctuate in proportion to the displacement, and if no current flows in the circuit (\( Q \) remains constant) then an alternating potential difference

\[
E - E_0 = \frac{Q}{\varepsilon S} \langle \psi \rangle_S \exp(-i\omega t)
= \left( \frac{E_0}{x_0} \right) \langle \psi \rangle_S \exp(-i\omega t)
\]

(4.2.2)

is generated across the external circuit, where \( \langle \psi \rangle_S \) is the mean surface-displacement amplitude, and \( x_0 \) is the static separation. Constant charge operation of the transducer is achieved by connection to an amplifier having a very high input impedance, using leads with a minimum of stray capacity. The displacement amplitude may be calculated for low-frequency operation from equation (4.1.3) or (4.1.7), and when operating in a dilute gas the true response will be fairly close to the calculated value. Membranes are usually preferred to plates because they can offer much higher sensitivity, and the fundamental resonance can be easily damped.

The transducer is reversible; if an alternating potential difference \( E_\perp \exp(-i\omega t) \) is applied to the network then the static charge is modulated, and the total electrostatic force between the diaphragm and the backplate is

\[
F_e = -\frac{Q^2}{\varepsilon S} = \left( E_0 + E_\perp \exp(-i\omega t) \right)^2 (\varepsilon S / x^2)
\]

(4.2.3)

Since the force depends upon the square of the potential difference, sound will be produced both at the applied angular frequency \( \omega \) and the first overtone \( 2\omega \). Usually \( E_0 \gg E_\perp \) and the driving frequency
\(\frac{\omega}{2\pi}\) predominates, but if \(E^t = 0\) then sound is produced at twice the driving frequency. The latter case has sometimes been used to avoid direct electromagnetic 'crosstalk' between the source and detector; the electrical drive signal is provided at half the required acoustic frequency, and the crosstalk can be filtered from the output of the detector.

Equations (2) and (3) show that the sensitivity of the transducer is increased by reducing the static separation of the plates, or by increasing the d.c. bias. No direct account has been taken of damping arising from internal friction, or from the fluid around the diaphragm. At low frequencies, such that the wavelength is greater than the diameter of the transducer, the loading of the transducer is slight. However, the static gap \(x_0\) is usually very small (20 \(\mu\text{m}\) for example) and the volume of fluid trapped between the plates is therefore also very small. Unless precautions are taken to increase the available volume, the motion of the diaphragm will be strongly damped by the fluctuations in the pressure between the plates. The transducer shown in figure 4.2 is provided with a vent hole so that the pressure behind the diaphragm remains nearly constant (unless the vent hole is also exposed to the sound field).

The transducer's diaphragm does not have to be all metal, and metallized plastic membranes are frequently used. In the electret capacitance transducer, a plastic membrane is used in which permanent dielectric polarization has been induced by heat treatment in a strong electric field. The external polarization supply is not required for these transducers, but the polarization is lost if the membrane is exposed to a high temperature. Stretched membranes cannot be expected to operate over a wide range of temperatures without drastic alterations.

† This type of transducer is really a piezoelectric device.
occurring in the tension, but diaphragms machined in solid metals (in the walls of the resonator, for example) should exhibit good mechanical stability over a wide range of temperatures.

An alternative to stretched membranes or plates is the use of an untensioned membrane which lies freely over the surface of the backplate. The small volume of gas trapped in the surface irregularities of the backplate exerts critical damping of the resonances of the membrane, and the response is uniform (though rather small) up to high ultrasonic frequencies. The efficiency of the system can be greatly increased by roughening of the surface of the backplate, or by the provision of grooves or holes. Critical damping still occurs at low frequencies (the membrane simply moves until the increase in the pressure in the trapped volume balances the incident acoustic pressure), but at high frequencies, such that the dimensions of the trapped space are no longer small compared to the wavelength, the system is again resonant. Figure 4.3 shows two transducers of that type which have been used in this work. The membrane material is 12 μm thick Melinex that has been metallized with a layer of aluminium approximately 50 nm thick. The small transducer has been used in the spherical resonator with a 200 V d.c. bias and up to 60 V r.m.s. driving signal. Both devices operate over the entire audio-frequency range. Because of their simple construction, high sensitivity, and wide frequency range, this type of electrostatic transducer with solid dielectric has been widely used in acoustic measurements. At high temperatures mica and quartz dielectrics have been used, although it is difficult to obtain a metallic coating that does not flake off. An alternative would be to use a separate metal foil membrane.

† Polyester film (polyethylene terephthalate), Imperial Chemical Industries p.l.c.
FIGURE 4.3. ELECTROSTATIC TRANSDUCERS.

SECTION ON X-X' (exploded view showing diaphragm)
- bolt hole
- diaphragm
- copper pin
- vent
- nylon insulator
- PTFE case
- diaphragm
- copper backplate
- PTFE insulation
- copper electrode

SECTION ON Y-Y' (exploded view)
- screen
- PTFE case
- copper backplate
- PTFE insulation
- copper electrode
4.3 PIEZOELECTRIC TRANSDUCERS

The piezoelectric effect, by which a dipole moment is induced in a solid when it is subjected to a mechanical stress, is exhibited by certain crystals that lack inversion symmetry. At low temperatures, ferroelectric materials can exist in two phases, one of which lacks inversion symmetry and is piezoelectric. Above the ferroelectric critical temperature (the Curie point) only the symmetric phase occurs, and below that temperature the symmetric phase is usually of lower energy, but the piezoelectric state may be metastable. Thus ferroelectric materials may be rendered piezoelectric by cooling from a temperature above the Curie point, in the presence of a strong electric field which stabilizes the piezoelectric structure. At sufficiently low temperatures the crystal structure will not revert to the symmetric form when the electric field is switched off, and the material is permanently polarized. However, if exposed to a temperature above the Curie the material will depolarize. Quartz is one of the few crystals in which the piezoelectric phase is truly stable below its Curie temperature, and it does not therefore require polarization.

If a piezoelectric crystal is subjected to a mechanical force then the resulting deformation causes a change in the dipole moment, and hence alters the internal electric field. Conversely, if the crystal is subjected to an external field then a force is generated within it, and a deformation occurs. Both these effects are linear and reversible (at least for small changes). For practical purposes, metal electrodes are deposited on opposite faces of the crystal; application of an alternating force produces an alternating potential difference between the electrodes, and vice versa. Unfortunately, unless the frequency is near to a natural frequency of the crystal the effect is very small, and hence single crystals, acting directly on the fluid, are usually only operated at
these discrete natural frequencies. Quartz crystals have very high quality factors \(Q \approx 10^6\) and are highly efficient as resonant transducers, especially at high ultrasonic frequencies (crystals for use below 100 kHz are rather too large for most purposes). The Curie temperature of quartz is about 850 K and thus a wide range of operating temperatures are possible.

In order to obtain a useful output from a non-resonant piezoelectric transducer, the active element is usually coupled to a diaphragm. Two arrangements are possible; firstly a piezoelectric disc may be cemented to the diaphragm, or secondly, the motion of the diaphragm may be coupled to the element by a mechanical linkage. In both cases the piezoelectric element operates in a bending mode with the motion parallel to the direction of polarization. Piezoelectric ceramics are preferable to quartz because of their high mechanical compliance, low resonance frequencies, and low quality factors. Figure 4.4 shows a typical piezoelectric transducer in which a ceramic element (PXE5, Mullard Ltd.) is bonded to the diaphragm with epoxy resin (One component type AV1566, Ciba-Geigy Ltd.). The fundamental frequency of the unloaded aluminium alloy (6082) diaphragm would be 23 kHz, but the presence of the piezoelectric ceramic lowers the fundamental resonance to about 20 kHz, and introduces considerable damping. Thus the transducer has a fairly even

---

**FIGURE 4.4. A PIEZOELECTRIC TRANSDUCER.**

- aluminium alloy 6082
- piezoelectric ceramic

- circular section
- 50 mm
response between resonances as well as in the low-frequency limit (f < 10 kHz). This device is used in the cylindrical interferometer at frequencies somewhat above and below the first overtone (71 kHz), with a sufficiently high efficiency being obtained between about 50 and 95 kHz. The quality factor of the transducer at its first overtone is about 50, and the static capacitance is 1.8 nF (thus stray capacitance in the connecting leads does not lead to a great loss of signal). The maximum operating temperature is about 370 K, and this is determined by both the stability of the epoxy cement and the risk of thermal depoling of the piezoelectric.

4.4 ACOUSTIC WAVEGUIDES

For a number of reasons, it may be desirable to install the transducers outside the resonator, and to transmit and receive the sound through hollow tubes. These waveguides may have a small cross-sectional area, and therefore behave as approximately a point source and a point detector. The tubes may terminate either in small chambers containing the transducers, or at the more or less rigid surfaces of the transducers themselves. The former arrangement allows the use of quite large transducers, and if the waveguides extend to a region of ambient temperature then there are many commercial transducers that can be used.

In order to calculate the effects of an opening in the cavity wall on its resonance frequencies and widths, the effective acoustic impedance $Z_0$ of its opening must be found. Narrow tubes (radius $b < length l$) are used, and the frequency must be below $\chi_{\lambda 0}^u/2\pi b$, the first cut-off frequency, so that only plane waves propagate. This being the case and letting $z$ be the distance from the tube's opening into the cavity, the impedance $Z_0$ can be expressed in terms of the tube
propagation constant $k_{KH}$ (see equation 2.6.40), and the terminal impedance $Z_L$ at the end $z=L$ of the tube. Whatever $Z_L$ might be, it can be compactly expressed in the form

$$Z_L = (p_a/U)_{z=L} = \rho u \tanh(\gamma_L - i\delta_L) = -i\rho u \tan(\delta_L + i\gamma_L), \quad (4.4.1)$$

where $\exp(-2\gamma_L)$ is the reflection coefficient at $z=L$, and $(2\delta_L + \pi)$ is the phase shift accompanying reflection.\(^7\) The corresponding impedance at $z=0$ is given by

$$Z_0 = \rho u \tanh(\gamma_L - i\delta_L - iK_{KH}L) = -i\rho u \tan(\delta_L + i\gamma_L + K_{KH}L), \quad (4.4.2)$$

and hence the specific acoustic admittance at $z=0$ is

$$y_0 = \rho u /Z_0 = i \cot(\delta_L + i\gamma_L + K_{KH}L). \quad (4.4.3)$$

If the tube is open at $z=L$ then to a first approximation the acoustic pressure there is zero and hence $Z_L = (p_a/U)_{z=L} = 0$. In this approximation, $\gamma_L = \delta_L = 0$; the specific acoustic admittance is very large at measurement frequencies close to the open tube resonance frequencies ($KL = n\pi/l$, $n = 0,2,4,\cdots$), but is very small near the antiresonances ($KL = m\pi/l$, $m = 1,3,5,\cdots$). At frequencies sufficiently far from the tube resonances for $K_{KH}L \ll |\tan(KL)|$, the specific acoustic admittance of the opening is given by

\(^7\) These formulae are consistent with a time dependence of $\exp(-i\omega t)$ (rather than the positive exponential $e^{i\omega t}$), and the definition of acoustic impedance as acoustic pressure divided by fluid speed (rather than acoustic pressure divided by total fluid current).
\[ y_0^0 = i \cot(kL) + (\alpha_{KH} L) \csc^2(kL). \tag{4.4.4} \]

The true terminal impedance of a tube open to free space differs from zero because of the effects of radiation. In the case of a flanged opening to free space the terminal impedance is given by

\[ Z_L = \rho u \left\{ \frac{1}{4}(kb)^2 - i \frac{8(kb)}{3\pi} \right\}, \] and hence
\[ \gamma_L = \frac{1}{4}(kb)^2, \quad \text{and} \]
\[ \delta_L = \frac{8(kb)}{3\pi}, \tag{4.4.5} \]

provided that \( \frac{1}{4}(kb)^2 \ll \frac{8(kb)}{3\pi} \ll 1 \) (consistent with the low frequency conditions), and hence equation (4) may be replaced by

\[ y_0^0 = i \cot(kL') + (\alpha_{KH} L') \csc^2(kL'), \] where
\[ L' = L + \frac{8b}{3\pi}, \quad \text{and} \]
\[ L'' = L + \frac{(kb)^2}{2\alpha_{KH}} \tag{4.4.6} \]

are effective tube lengths. If, instead of opening to free space, the tube ends in a chamber of volume \( V \), whose internal dimensions are much less than the wavelength, then the terminal impedance may be estimated from a Helmholtz-resonator model. \(^9\) Provided that there are no losses within the chamber,

\[ Z_L = i \rho u \frac{n}{kV}, \] and hence
\[ \gamma_L = 0, \quad \text{and} \]
\[ \delta_L = \tan^{-1}\left(\frac{\pi b^2}{kV}\right), \tag{4.4.7} \]

where \( \delta_L \) is an additional phase shift. At frequencies such that \( (\pi b^2/kV) \ll 1 \), \( \delta_L = (\pi b^2/kV) \), and equation (4) may be replaced by
$$y^0 = i \cot(kL''') + (\alpha_{KH} L) \csc^2(kL'''),$$ \text{ where} \\
$L''' = L + \delta_L / k \approx L + \pi b^2 / k^2 v$. \hspace{1cm} (4.4.8)

Alternatively, the tube may be closed at $z = L$ by a rigid wall, such as the backplate of a capacitance transducer. The terminal impedance and reflection parameters may be obtained from equation (7) by allowing $V \to 0$. Since the wall is assumed rigid (as was the Helmholtz resonator), $\gamma_L = 0$ as before, but now $\delta_L = \pi/2$ and the total phase shift on reflection reverts to zero. In this case the specific acoustic admittance of the open end is given by

$$y^c = -i \tan(kL) + (\alpha_{KH} L) \sec^2(kL),$$ \hspace{1cm} (4.4.8)

provided that $\alpha_{KH} L \ll |\tan(kL)|$. The perturbation arising from a closed tube is very small near to the tube resonance frequencies ($kL = n\pi/2$, $n = 0, 2, 4, \cdots$), but is large at frequencies close to the antiresonances ($kL = m\pi/2$, $m = 1, 3, 5, \cdots$).

Clearly, when waveguides are used care must be taken to ensure that $y_0$ is small at frequencies close to the resonances of interest. Fortunately, the relation between cavity and tube resonances is independent of the speed of sound in the fluid, and is not strongly affected by the temperature and pressure. If a long waveguide were used, along which there was a temperature gradient, then the calculations would be more complicated than indicated here.

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CHAPTER 5  THE EQUATION OF STATE AND INTERMOLECULAR FORCES

5.1 INTRODUCTION

This chapter deals with the equation of state for dilute gases. The virial equation of state is introduced in section two and some experimental techniques by which it can be studied are reviewed. The role of the second virial coefficient as a determinant of intermolecular potential energies is discussed in section three. Acoustic measurements are seen to provide accurate information about the equation of state which may be related directly, or indirectly through the second virial coefficient, to intermolecular potential energies.

5.2 THE VIRIAL EQUATION OF STATE

For a single gas phase of fixed composition there are two degrees of freedom, and hence if any two intensive properties are held constant then the thermodynamic state of the gas is invariant. However, in order to specify that state, an equation of state is required to relate the values of two independent variables to the other equilibrium properties of the gas. Explicitly, the equation of state:
\[ Q(y, x_1, x_2) = 0 \]  

relates a third intensive quantity \( y \) to the quantities \( x_1 \) and \( x_2 \) which are chosen as the independent variables. Specification of any other intensive thermodynamic property requires a different mathematical form of the equation of state in which the required property is the dependent variable but, at least in principle, transformation from one form to another simply requires the application of the appropriate thermodynamic identities. Since equation (1) relates only intensive variables, it contains no information about the extent of the phase.

The exact mathematical form of the function \( Q_{v_m}(V_m, T, p) \) in the equation of state

\[ Q_{v_m}(V_m, T, p) = 0 \]  

is known to be

\[ Q_{v_m} = (pV_m / RT) - \{ 1 + B(T)/V_m + C(T)/V_m^2 + D(T)/V_m^3 + \cdots \}, \]  

where \( p \) is the pressure, \( V_m \) is the molar volume, and \( T \) is the temperature, and where \( R \) is the gas constant. Equation (3) is the virial equation of state and \( B, C, D, \cdots \) are the second, third, fourth, \cdots virial coefficients and, for a gas of fixed composition, are functions of the temperature only. In a sufficiently dilute gas, the series on the right of equation (3) is found to converge rapidly. The importance of the virial equation of state lies in its theoretical basis; the virial coefficients \( B, C, D, \cdots \) are related to the intermolecular potential energies of clusters of two, three, four, \cdots molecules at a time. For this reason precise measurements of the second virial coefficient can be used to infer information about the intermolecular pair-potential-
energy functions of the interacting molecules. In a gas mixture \( B \) will
depend upon interactions between both like and unlike molecules, and
hence on more than one intermolecular pair-potential-energy function.
In particular, the second virial coefficient \( B(T, x) \) of the binary gas
mixture \( \{(-- - x)A + xB\} \) is given by

\[
B(T, x) = (1 - x)^2 B_{AA} + 2(1 - x)x B_{AB} + x^2 B_{BB},
\]

(5.2.4)

where \( B_{AA} \) and \( B_{BB} \) are the second virial coefficients of pure \( A \) and of
pure \( B \), and \( B_{AB} \) is the second virial coefficient that arises from the
unlike interactions between molecules of \( A \) and of \( B \).

From an experimental point of view the best choices for the
independent variables are often the temperature and the pressure of the
gas because both can be measured and controlled with high precision.
Thus a pressure-explicit expansion of the molar volume may be preferable
in the equation of state:

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

(5.2.5)

in which the coefficients \( \mathcal{B}, \mathcal{C}, \mathcal{D}, \cdots \) are related to the virial
coefficients by

\[
\mathcal{B} = B, \quad \mathcal{C} = (C - B^2)/RT, \quad \mathcal{D} = (D - 3BC + 2B^3)/(RT)^2, \cdots.
\]

(5.2.6)

Both equation (3) and equation (5) contain infinite series which
must be truncated for practical purposes. It is not usually difficult
to find the finite series which best represents a given set of \( (p, V_m, T) \)
measurements, but the problem of finding the values of the virial
coefficients which are closest to the true values in the infinite series
is more subtle. It is not always possible to obtain accurate results
at sufficiently low pressures for all of the coefficients above the second to be neglected, and incorrect truncation of the series can introduce large systematic errors into the determination of the second virial coefficient. This problem is eased if precise measurements can be extended to as low a fraction of the maximum pressure as is possible.

The difficulties that are inherent in any direct study of the equation of state in the form of (3) or (5) stem mainly from the measurement of molar volume. A direct measurement of that quantity is not possible and it is necessary to know both volume and amount of substance \( n \) separately, although \( n \) may be inferred from the value of
\[
\lim_{p \to 0}(pV/RT).
\]

The simplest apparatus used in the study of the equation of state is Boyle's tube in which the pressures exerted by a fixed amount of substance are measured at known volumes while the temperature is held constant. A variant on this apparatus is shown in figure 5.1. In this apparatus a fixed amount of substance is confined above mercury and allowed to expand into several previously calibrated volumes under isothermal conditions, the pressure being measured after each expansion. A null-reading pressure transducer is used to isolate the sample from the external pressure gauge, but the accessible temperatures are still limited to those at which mercury is a liquid and has an acceptable vapour pressure. Although the amount of substance in the apparatus is constant throughout the experiment, the amount in the gas phase will depend upon the extent to which the material adsorbs on the walls, and that is a function of the pressure. At low reduced temperatures gas adsorption can be severe under experimental conditions and large systematic errors in the second virial coefficient can result.

In order to separate the effects of the second virial coefficient from those of the higher-order terms in the virial equation of state,\(^\dagger\)

\(^\dagger\) In this context the reduced temperature \( T_R = T/T_c \), where \( T_c \) is the critical temperature of the fluid.
FIGURE 5.1. A MODIFIED BOYLE'S TUBE APPARATUS

FIGURE 5.2. A DIFFERENTIAL BURNETT APPARATUS
it is desirable to pursue measurements at low pressures. However, at
low pressures the gas imperfections are slight (usually contributing
less than 5 per cent of $V_m$ at a pressure of 100 kPa) and very precise
measurements of the dependent variable are required in order to resolve
$B$ with useful precision.

Many of the difficulties outlined above may be overcome or reduced
in more sophisticated experiments, such as the one devised by Burnett.\footnote{ Burnett, J. B. (1970) The measurement of the heat of reaction.

In this method two vessels $A$ of volume $V_A$ and $B$ of volume $V_B$ are
connected via valve 1 as shown in figure 5.2. The smaller vessel $B$ is
connected via valve 2 to a vacuum pump, and vessel $A$ is connected to a
null-reading pressure transducer 3 which isolates the sample gas from
an external manometer or pressure balance. Initially, vessel $A$ contains
the sample gas at the highest pressure to be studied, valve 1, is closed,
and vessel $B$ is evacuated. The pressure $p_0 = p_0(n_0, V_A)$ corresponding to
the amount of substance $n_0$ occupying the volume $V_A$ is measured. Valve 2
is then closed and the gas allowed to expand through valve 1 so that the
same amount of substance occupies the volume $V_A + V_B$. Once thermal
equilibrium has been achieved, valve 1 is closed and the new pressure
$p_1 = p_1(n_0, V_A + V_B) = p_1(n_1, V_A)$ is measured. Valve 2 is then opened to
evacuate vessel $B$ and an amount of substance $n_1$ remains in the apparatus.
This procedure is repeated until a low pressure is achieved. Since the
pressure $p_{q-1}$ before the $q^{th}$ expansion is

$$p_{q-1} = \{n_{q-1}RT/V_A\}[1 + B(p_{q-1}/RT) + \cdots] \quad (5.2.7)$$

and the pressure $p_q$ following the $q^{th}$ expansion is

$$p_q = \{n_{q-1}RT/(V_A + V_B)\}[1 + B(p_q/RT) + \cdots], \quad (5.2.8)$$

the ratio $(p_{q-1}/p_q)$ is given by
\[
(p_{q-1}/p_q) = N_a + N_a(N_a-1)B(p_q/RT) + \ldots,
\]  

(5.2.9)

where the apparatus constant \( N_a = (V_A + V_B)/V_A \). Thus a plot of \((p_{q-1}/p_q)\) against \( p_q \) has the slope \( N_a(N_a-1)B/RT \) and the value \( N_a \) in the limit \( p_q \to 0 \), and hence such measurements can determine the second virial coefficient without the need to measure either amount of substance or volume. Unfortunately, very accurate measurements of the pressure are required and it is not easy to meet this requirement over a wide range of pressures. A differential method\(^2\) can be employed to reduce the influence of random errors in the measurement of pressure. Again referring to figure 5.2, a second Burnett apparatus consisting of vessels C and D, and valves 4 and 5, is connected in parallel with the manometer, and the null-reading pressure transducer 3 is replaced by a differential manometer. The reference apparatus is filled with a gas whose equation of state is accurately known, and the experiment proceeds as before on each side of the differential manometer. However, it is now only necessary to measure one of the pressures accurately with the external manometer; the other pressures are calculated from the small measured pressure differences \( \Delta p_q \) across the differential manometer and the equation of state of the reference gas. This technique is one of the best methods of studying the molar-volume-explicit equation of state and may be used over a wide range of temperatures and pressures. A precision of \( 1 \text{ cm}^3\text{ mol}^{-1} \) in \( B \) is possible from measurements conducted at pressures below 100 kPa. However, adsorption may still cause systematic errors in the measurements. In the Burnett method, the effects of adsorption can be reduced by design of vessels having equal surface-area-to-volume ratios; the increase in available surface for adsorption following an expansion is than approximately balanced by the reduction in the total pressure. In any \((p, V_m, T)\) experiment the microscopic surface area available for adsorption may be reduced by careful polishing
of the interior walls. If the remaining effects of adsorption are small then corrections can be calculated from a model, but at temperatures below the normal boiling point (where the pressures are necessarily a fairly large fraction of the saturated vapour pressure) such corrections become large and accurate second virial coefficients are very difficult to obtain.

Full accounts of $(p,V_m,T)$ measurements can be found in the literature.

In order to obtain accurate values of the second virial coefficient under conditions where adsorption is significant an alternative to $(p,V_m,T)$ measurements must be found. The equation of state is written explicitly in terms of another measurable property of the gas ostensibly independent of the amount of substance. For example, the equation of state in the form

$$0 = [H_m(p \rightarrow 0,T) - H_m(p,T)] + \int_0^p (\partial H_m/\partial p)_T \, dp$$

$$= [H_m(p \rightarrow 0,T) - H_m(p,T)] + (B - TB')p + \frac{1}{2}(C - TC')p^2 + \cdots \quad (5.2.10)$$

in which $H_m$ is the molar enthalpy, $B' = (\partial B/\partial T)$, and $C' = (\partial C/\partial T)$, can be studied by adiabatic flow calorimetry. Figure 5.3 shows an adiabatic flow calorimeter suitable for Joule-Thompson measurements. In this

![FIGURE 5.3. A JOULE-THOMPSON CALORIMETER.](image)
apparatus, the gas under study flows at a constant rate \((dn/dt)\) through a thermally insulated tube fitted with a throttle and an electric heater. The temperatures \(T_1\) and \(T_2\), and the pressures \(p_1\) and \(p_2\), on each side of the throttle are measured, together with the molar flow rate. In the isothermal Joule-Thompson experiment, an electrical power \(P\) is dissipated in the heater so as to maintain \(T_2 = T_1\). The isothermal Joule-Thompson coefficient is defined by

\[
\phi_{JT} = (\partial H/\partial p)_T = \lim_{p_1 \to p_2} \frac{\{H(T, p_2) - H(T, p_1)\}}{(p_2 - p_1)}, \tag{5.2.11}
\]

and measurements of \(p_1\), \(p_2\), \(P\), and \((dn/dt)\) under steady-state conditions can serve to determine

\[
\{H_m(T, p_2) - H_m(T, p_1)\} = P/(dn/dt)
\]

\[
= (\mathcal{B} - T\mathcal{B}')(p_2 - p_1) + \frac{\mathcal{C}}{2}(C - T\mathcal{C}')(p_2^2 - p_1^2) + \ldots, \tag{5.2.12}
\]

and hence to obtain \((\mathcal{B} - T\mathcal{B}')\) from such measurements over a range of pressures. Once the steady state is established, these measurements should be independent of adsorption but are nevertheless very difficult in practice. The main experimental difficulties arise from the presence of temperature gradients near the throttle and the need to maintain very steady gas flow. However, despite the considerable experimental difficulties, reliable measurements of \((\mathcal{B} - T\mathcal{B}')\) have been made under conditions where adsorption would have been a serious problem in a conventional \((p, V_m, T)\) apparatus.\(^6\)

The speed of sound in a gas is also formally independent of the amount of substance and can be measured with high accuracy. The equation:

\[
u_0^2 = (1/\rho \kappa_S) \tag{5.2.13}
\]
provides a link between a directly measurable mechanical property of the gas and the thermodynamic property \( \kappa_S \) of that gas. In order to specify the state of a gas from \((u_0^2, T, p)\) measurements, an equation of state is required that is explicit in \(u_0^2\). This may be achieved by expanding both \( \Phi \) and \( \kappa_S = \gamma \kappa_T \) in terms of equation (5) with the result:

\[
u_0^2 = A_0(T) + A_1(T)p + A_2(T)p^2 + \cdots, \tag{5.2.14}\]

where

\[
A_0(T) = \left( RT \gamma_{pg}/\gamma \right),
\]

\[
A_1(T) = \left( \gamma_{pg}/\gamma \right) \left( 2B + (\gamma_{pg} - 1)TB' + (\gamma_{pg} - 1)^2 T^2B''/\gamma_{pg} \right), \text{ and}
\]

\[
A_2(T) = \left( \gamma_{pg}/\gamma \right) \left\{ (\gamma_{pg} + 2)\mathcal{C} + 2(\gamma_{pg} - 1)T\mathcal{C}' + (\gamma_{pg} - 1)^2 T^2\mathcal{C}''/2\gamma_{pg} \right\} + G(T). \tag{5.2.15}\]

In equations (15) \( B'' = (d^2B/dT^2) \) and \( \mathcal{C}'' = (d^2\mathcal{C}/dT^2) \), \( G(T) \) is given by

\[
G(T) = \left( 1/RT \right) \left\{ B^2 - \{ (\gamma_{pg} - 1) + 4(\gamma_{pg} - 1)^2 \} T^2(B')^2 + \{ (\gamma_{pg} - 1)^3/\gamma_{pg} \} T^4(B'')^2 - 4(\gamma_{pg} - 1)TB'B' + 2\{ (\gamma_{pg} - 1)^2/\gamma_{pg} \} T^2BB'' \right\} + 2\{ (\gamma_{pg} - 1)^2(2\gamma_{pg} - 1)/\gamma_{pg} \} T^2BB'' \right\} \tag{5.2.16},
\]

and

\[
\gamma_{pg} = \lim_{p \to 0} \left( C_p m/C_m \right) \tag{5.2.17}
\]

is the perfect-gas value of \( \gamma \). In a sufficiently dilute gas, equation (14) is found to converge rapidly. The coefficients \( A_1, A_2, A_3, \cdots \) are functions of the temperature only (for a gas of fixed composition) and the related quantities

\[\dagger\] The algebraic complexity of this transformation increases dramatically with the inclusion of higher powers of the pressure. A treatment of the problem, correct to second order in \( p \), is given in appendix A5.1.
\[ \beta_a = (M/\gamma^p g)A_1, \quad \gamma_a = (M/\gamma^p g)A_2, \ldots \] (5.2.18)

will be referred to here as the second, third, \ldots acoustic virial coefficients. The second acoustic virial coefficient may be related to the intermolecular pair-potential-energy functions of the gas molecules in a similar manner to \( \beta \), but a single measurement is insufficient to determine \( \beta \) which instead may be obtained from measurements of \( \beta_a \) over a range of temperatures. Numerical techniques have been devised for this purpose, and for the purpose of computing a wide range of thermodynamic properties of gases from their \( u_0^2 \)-explicit equations of state. Thus equation (14) retains both the experimental and the theoretical advantages of the virial equation of state while allowing speed-of-sound measurements to be substituted for the difficult measurements of the molar volume.

With the notable exception of a few simple fluids such as CO\(_2\), which can exhibit marked dispersion at audio frequencies, \( u_0 \) may easily be obtained from low frequency (below 20 kHz) measurements of \( u \) because \( u + u_0 \) as \( \omega \to 0 \). In the remainder of this work it will be assumed that the speed of sound is identical with \( u_0 \) and the subscript will be dropped. An important advantage of the acoustic technique is that measurements of \( u^2 \) with a precision of \( 1 \times 10^{-5} \) or better may be extended to pressures well below 100 kPa and, in favourable circumstances, to below 10 kPa. As a result a precision of \( \pm 0.1 \text{ cm}^3\text{ mol}^{-1} \) in \( \beta_a \) can be attained and measurements over a wide range of temperatures should provide a severe and reliable test for any proposed intermolecular potential-energy function.

Although formally independent of the amount of substance, it has become apparent recently that in some circumstances speed-of-sound measurements are affected by gas adsorption or precondensation. Both experimental and theoretical evidence shows that substantial
errors occur in low-frequency measurements when the pressure is close to the saturated vapour pressure. The theoretical work also suggests that a smaller effect may occur at much lower pressures, but as yet there appears to be no supporting experimental evidence. These effects arise from condensation and evaporation from the adsorbed film during the acoustic cycle and make a contribution to the effective acoustic admittance of the resonator's walls. At pressures approaching saturation, this excess wall admittance becomes very large, particularly at low frequencies, and the resonance half widths increase greatly. Such discrepant results can easily be identified and rejected but, in order to verify that low-pressure results are truly unaffected by adsorption, it is necessary to study the same gas in resonators having different surface-area-to-volume ratios. This possible source of error in low-pressure acoustic measurements should be investigated with caution, but it must be noted that the magnitude of the predicted effects at low pressures are very much smaller than either the proven systematic errors in conventional \( (p, V, T) \) measurements, or the errors in low-pressure Joule-Thompson measurements.

Acoustic interferometry in gases is also of importance in metrology. Measurement of \( A_0 \) at the temperature of the triple point of water, where \( T = 273.16 \) K by exact definition, in a gas for which \( N \) and \( \gamma^p \) are accurately known, can serve to determine the universal gas constant \( R \). The currently accepted value of the gas constant has a fractional random uncertainty of some \( 93 \times 10^{-6} \), but recent measurements of \( A_0 \) in argon have provided a new value which is numerically close to the accepted value but with a fractional random uncertainty of only \( 18 \times 10^{-6} \) (and a similar level of systematic uncertainty). These measurements were performed in a variable-pathlength cylindrical interferometer operating.

\[ \text{\textsuperscript{+}} \] These uncertainties are based on three standard deviations.
at 5.6 kHz. New measurements in a spherical resonator should be capable of defining $R$ with even higher precision. The most probable source of error on such measurements, namely the determination of the mean radius of the resonator, is quite different to the sources of error in the variable-path interferometer, and hence new measurements would provide independent verification of the earlier work.

Measurement of the ratio $A_0(\Theta)/A_0(T=273.16 \text{ K})$, where $\Theta$ is an empirical temperature, can be used to evaluate the true thermodynamic temperature $T(\Theta)$ without exact knowledge of $R$ and $M$. Alternatively if both $R$ and $M$ are treated as known constants then a single measurement of $A_0(\Theta)$ is sufficient to determine $T(\Theta)$. At temperatures below about 20 K the uncertainty in $R$ is unimportant and measurements of the speed of sound in helium have been used to obtain the true thermodynamic temperatures of a number of 'fixed-points' between 4.2 and 20 K. It seems likely that future measurements will be extended into a wider range of temperatures, and that spherical resonators will be preferred to the conventional variable-pathlength cylindrical instruments. At temperatures below the critical (5.4 K for helium, 151 K for argon) precondensation may lead to systematic errors that are significant in comparison with the random uncertainties, but these are expected to be much smaller than the corresponding effects in a conventional gas thermometer. At any temperature desorption of impurities from the walls of the resonator can change the mean molar mass and give rise to a systematic error.
5.3 INTERMOLECULAR FORCES

The imperfection of gases is direct evidence for the existence of intermolecular forces. The virial equation of state can be related to the molecular interactions in a quantitative manner, and hence allows the study of these microscopic phenomena by measurement of the properties of the bulk gas. The methods of statistical mechanics can be used to derive the virial equation of state and to find expressions that relate the virial coefficients $B$, $C$, $D$, $\cdots$ to the forces between molecules in clusters of two, three, four, $\cdots$ at a time.$^{15}$

The intermolecular force $\mathbf{F}_{AB} = \mathbf{F}_{AB}(\mathbf{r}_{AB}, \tilde{\omega}_{AB})$ between the isolated pair of molecules $A$ and $B$ is conveniently given by

$$\mathbf{F}_{AB}(\mathbf{r}_{AB}, \tilde{\omega}_{AB}) = -\nabla U_{AB}(\mathbf{r}_{AB}, \tilde{\omega}_{AB}), \tag{5.3.1}$$

where $U_{AB}(\mathbf{r}_{AB}, \tilde{\omega}_{AB})$ is the intermolecular pair-potential-energy function of the molecules $A$ and $B$, $\mathbf{r}_{AB} = \mathbf{r}_A - \mathbf{r}_B$, $\mathbf{r}_A$ and $\mathbf{r}_B$ are the positions of the centres of mass of molecules $A$ and $B$, and $\tilde{\omega}_{AB}$ is their relative orientation. The second virial coefficient $B_{AB}(T)$ corresponding to the interactions between molecules of $A$ and of $B$ is given by

$$B_{AB}(T) = \frac{-L}{2Q_A Q_B} \int f_{AB}(T, \mathbf{r}_{AB}, \tilde{\omega}_{AB}) d\mathbf{r}_{AB} d\tilde{\omega}_A d\tilde{\omega}_B, \tag{5.3.2}$$

where

$$f_{AB}(T, \mathbf{r}_{AB}, \tilde{\omega}_{AB}) = \exp\{-U_{AB}(\mathbf{r}_{AB}, \tilde{\omega}_{AB})/kT\} - 1 \tag{5.3.3}$$

is called the Mayer function, $L$ is Avogadro's constant, $\tilde{\omega}_A$ and $\Omega_A$, and $\tilde{\omega}_B$ and $\Omega_B$ are the sets of co-ordinates and their corresponding normalization constants necessary to specify the orientation in space.
of molecules A and B, and the integration is performed over all possible positions and orientations. The Eulerian angles $\theta$, $\phi$, and $\psi$ may be used to specify the orientation of a molecule. For a monatomic molecule no orientational angles are required and $\Omega = 1$ and $d\omega = 1$. Two angles are required for a linear molecule ($d\omega = \sin \theta d\phi d\zeta$, $\Omega = 4\pi$), and for a non-linear molecule three are required ($d\omega = \sin \theta d\phi d\zeta d\psi$, $\Omega = 4\pi^2$).

In describing intermolecular forces with a pair-potential-energy function, it is assumed that the intermolecular degrees of freedom are distinct and independent from the remaining degrees of freedom of the particles in the system $A + B$. However, in a formal sense a different intermolecular pair-potential-energy function is required to correspond to each of the allowed internal states of the molecules. This is certainly the case with the electronic degrees of freedom, but electronic excitation from the molecular ground state is slight at all accessible temperatures for most simple molecules and can therefore be neglected. Since intermolecular forces are electrostatic in origin, they are coupled to the vibrational and rotational states of the interacting molecules by the effects of anharmonicity and centrifugal distortion, but these phenomena usually have only a slight influence on the geometry and electron distribution of the molecules. In consequence, it is a reasonable approximation to separate the internal and intermolecular degrees of freedom and to seek a single potential-energy function. The dimensionality of that function, and hence the number of co-ordinates over which it must be integrated in order to obtain $B_{AB}$, depends upon the nature of the interacting species:

- Atom + atom: 1 degree of freedom, $\Omega_{A,B} = 1$
- Atom + linear molecule: 2 degrees of freedom, $\Omega_{A,B} = 4\pi$
- Atom + non-linear molecule: 3 degrees of freedom, $\Omega_{A,B} = 8\pi^2$
- Linear molecule + linear molecule: 4 degrees of freedom, $\Omega_{A,B} = 16\pi^2$
linear molecule + non-linear molecule : 5 degrees of freedom, $\Omega_A^B = 32\pi^3$

non-linear molecule + non-linear molecule : 6 degrees of freedom,

$\Omega_A^B = 64\pi^4$.

In the case of the interaction between like atoms, equation (2) is greatly simplified because $f_{AA} = \{\exp[-U(r)/kT] - 1\}$, $\bar{r}_{AA} = r^2 \sin \theta \sin \theta \sin \zeta$, and thus

$$B(T) = -\frac{kL}{\pi} \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \int_0^\infty \{\exp[-U(r)/kT] - 1\} r^2 dr$$

$$= -2\pi L \int_0^\infty \{\exp[-U(r)/kT] - 1\} r^2 dr,$$

(5.3.4)

where $r$ is the interatomic separation. Since $U(r) \to 0$ as $r \to \infty$, the Mayer function falls off to zero at large separation and the integration in equation (4) presents no difficulty.

The derivation of the virial equation of state is based entirely on classical mechanics, and it is known that for light molecules at low temperatures the wave-like properties of the particles cannot be neglected. For $H_2$ and He the classical theory fails completely at low temperatures and a full quantum mechanical treatment is required. However, for all other substances this is unnecessary and a semi-classical approach is successful. The second virial coefficient may be expanded in a series of powers of $(\hbar^2/m)$:

$$B = B_{q0} + B_{q1}(\hbar^2/m) + B_{q2}(\hbar^2/m)^2 + B_{q3}(\hbar^2/m)^3 + \cdots,$$

(5.3.5)

where $m$ is the mass of one molecule, $\hbar = \hbar/2\pi$, and $\hbar$ is Planck's constant. The leading term in equation (5), $B_{q0}$, is the result of the classical

† Here $(r, \theta, \zeta)$ are the spherical co-ordinates introduced in chapter 2. The origin is located at the centre of mass of one of the interacting molecules and the angles are measured relative to laboratory fixed axes.
treatment, and expressions for the next three coefficients are all known for spherically symmetric potential-energy functions.\textsuperscript{18,19} This series is found to converge within three terms for all substances other than hydrogen and helium at low temperatures.

Equation (3) is readily differentiated with respect to the temperature and it is therefore a simple matter to relate the acoustic virial coefficient to the intermolecular pair-potential-energy function of the molecules making up the gas. Thus for a pure monatomic gas (for which $\gamma_{pg} = 5/3$ exactly) at the temperature $T$

$$\beta_a(T) = -4\pi U \int_0^\infty \{1 + (6/15)(U/kT) + (2/15)(U/kT)^2\} \exp(-U/kT) - 1\} r^2 dr, (5.3.6)$$

where $U = U(r)$. It has been suggested by Blatt that the methods of statistical mechanics may be unreliable in a system subject to displacements from equilibrium that occur at frequencies above the ternary molecular collision frequency.\textsuperscript{20} Blatt predicts that $\beta_a$ is a function of the frequency and that the value of equation (6) is attained in the limit $\omega \to 0$. Substantially above the ternary collision frequency, $\beta_a$ is predicted to be zero. This effect should be quite obvious in accurate measurements of $u$ in the heavier monatomic gases but there is no experimental evidence to suggest that it does in fact occur.

Expressions may also be derived to relate the higher virial coefficients to intermolecular energies, but these are complicated by the need to evaluate the energy of clusters containing more than two molecules. In such clusters the pair-wise interaction energies are perturbed by the presence of other molecules, and the total energy of a system of $N$ molecules is given by

$$U_{\text{Total}} = \sum_{i<j}^N U^{(2)}(r_{ij}, \bar{\omega}) - \sum_{i<j<k}^N U^{(3)}(r_{ij}, r_{jk}, r_{ki}, \bar{\omega}) + \ldots$$

$$+ \sum_{i<j<\ldots}^N U^{(N)}(r_{ij}, r_{jk}, \ldots, \bar{\omega})$$

(5.3.7)
where \( U(2), U(3), \ldots \) are the pair-, triplet-, \ldots potential-energy functions, \( r_{ij} \) is the distance between molecules \( i \) and \( j \), and \( \hat{\omega} \) stands for the relative orientation of the molecules in the cluster. Thus the third virial coefficient is determined not only by the three pair-wise interaction energies of a triplet of molecules, but also by a fourth term uniquely associated with the presence of three molecules. Although equation (7) converges rapidly in dilute systems, many-body interactions are important in determining the properties of solids and dense fluids, and are a limitation on the information about pair-interaction energies that can be gained from a study of such properties.

The wide range of experimental and theoretical methods by which pair-wise intermolecular forces are studied have been reviewed in detail by Maitland, Rigby, Smith, and Wakeham in their recent monograph;\(^{21}\) here it will be sufficient to concentrate on the role of the second virial coefficient.

The traditional approach to the determination of intermolecular potential energies from measurements of \( B(T) \) was to assume some simple functional form for the intermolecular energy, usually of spherical symmetry, containing two or more disposable parameters which are then varied in order to achieve the best fit to the experimental results. This usually tells one little about intermolecular forces because different assumed functional forms can show widely different shapes for \( U(r) \) while retaining a good fit to the second virial coefficient. For example the crude 'square-well potential':

\[
U(r) = \begin{cases} 
\infty & r < \sigma \\
-\varepsilon & \sigma \leq r \leq g\sigma \\
0 & r > g
\end{cases}
\]

(5.3.8)

which on substitution in (4) gives
\begin{align*}
B(T) &= (2\pi Lo^3/3)\left(\frac{g^3}{(g^3 - 1)}\exp(\varepsilon/kT)\right), \quad (5.3.9)
\end{align*}

shows good agreement with the second virial coefficients of argon between 150 and 1000 K with $\sigma = 0.3021$ nm, $g = 1.641$, and $(\varepsilon/k) = 105.6$ K.\textsuperscript{22} While equation (9) is useful for the correlation of second virial coefficients it is of only limited value in the determination of intermolecular potential energies. The function

\begin{align*}
U(r) &= \varepsilon \left\{ \frac{(n - m)(r_e/r)^n - (n/(n - m))(r_e/r)^m}{(m/(n - m))} \right\}, \quad (5.3.10)
\end{align*}

attributed to Lennard-Jones,\textsuperscript{23} but first proposed by Mie,\textsuperscript{24} contains four adjustable parameters: $\varepsilon$ and $r_e$, the depth of the potential-energy well and the intermolecular separation at which $U(r) = -\varepsilon$, are scaling parameters, while $m$ and $n$ are shape parameters and determine the steepness of the attractive and repulsive branches respectively. Often $m$ is taken as 6, in accordance with the known long-range dependence of the intermolecular energy, and $n$ as 12. Although clearly more realistic than equation (8), and useful in model calculations and for modest extrapolations of experimental results, the Lennard-Jones function is a poor representation of those intermolecular potential-energy functions that are known in detail. However, the modified form suggested by Maitland and Smith,\textsuperscript{25} in which $m = 6$ and $n$ is a linear function of $r$, does give a good account of the known intermolecular potential-energy functions of the noble gases.\textsuperscript{26}

The problem is one of uniqueness: $U$ as a function of $r$ uniquely defines $B$ as a function of $T$ (for a spherically symmetric system), but the reverse is not true. This becomes apparent when equation (4) is recast in the form

\begin{align*}
B(T) &= (2\pi Lo^3/3T)\int_0^{\Delta(\phi)} \exp(-\phi/kT) d\phi \quad (5.3.11)
\end{align*}
where $\Delta(\phi) = r_L^3 - r_R^3$, $\alpha = \exp(\epsilon/kT)/k$, $\phi = U - \epsilon$, and $r_L$ and $r_R$ are the inner and outer co-ordinates of the potential-energy well at a given energy. In the repulsive region $r > \epsilon$, $\phi = r^3(\phi)$. Since $\frac{TB(\phi)}{\frac{1}{2}\pi L^2}$ is the Laplace transform of $\Delta(\phi)$, $B(T)$ can in principle determine $\Delta(\phi)$. Thus $B$ as a function of $T$ can only define $\phi$ as a function of $r$ uniquely in the repulsive region; elsewhere only $r_L^3 - r_R^3$ as a function of $\phi$ may be obtained. Unfortunately this formal inversion fails in practice because the discontinuity in $\Delta(\phi)$ at $\phi = \epsilon^*$ causes numerical instability, and unrealistically accurate data are required.

The apparent insensitivity of the second virial coefficient to the detailed shape of the intermolecular pair-potential-energy function arises partly from the range of temperatures over which it has been reliably studied. The Mayer function $f(T, r)$ of argon is shown for a number of temperatures in figure 5.4. Since the second virial coefficient is obtained by integration of this function, it is evident that over a fairly wide range of intermediate temperatures much information is lost by cancellation between the attractive ($f > 0$) and repulsive ($f < 0$) parts of the function. At very high temperatures ($T \gg \epsilon/k$) $B(T)$ becomes sensitive to the repulsive branch of $U(r)$, while at low temperatures there is an exponential growth in the sensitivity to the attractive region. Unfortunately these high temperatures are experimentally inaccessible except for hydrogen and helium, and many low-temperature measurements of $B(T)$ are unreliable due to the effects of adsorption. The repulsive branch can be obtained from other sources, and low-temperature acoustic measurements should be capable of overcoming the insensitivity in the attractive region. In fact, second virial

* $\Delta(\phi) \to \infty$ as $\phi \to \epsilon$ from $\phi < \epsilon$, and at $\phi = \epsilon$ there is a jump-discontinuity from $\Delta = -\infty$ to $\Delta = r^3$.

† For example, molecular-beam experiments, and direct calculation of the short-range energies.
FIGURE 5.4. THE MAYER FUNCTION OF ARGON AT VARIOUS TEMPERATURES

$\phi(T, r)$

- 75 K
- 150 K
- 300 K
- 600 K

$r$/nm
coefficients can be a much more sensitive probe of intermolecular energies than either the results obtained with simple functional forms or the formal inversion suggest. In recent years a number of inversion methods have been devised by which the intermolecular pair-potential-energy functions of spherically symmetric molecules may be extracted from second virial coefficients which span an accessible range of temperatures with a realistic accuracy.\textsuperscript{27,28,29} The most sophisticated of these methods can yield the complete function $U(r)$ between upper and lower limits of $r$ that are determined by the temperature range of the experimental results, although the function obtained is not formally unique. It has been established that the method works but the reasons for its success are less clear.

The basis of the successful inversion technique is to relate the intermolecular potential energy $U(\bar{r})$ at the characteristic intermolecular distance

$$\bar{r} = \left\{3(B + TB')/2\pi L\right\}^{1/3}, \quad (5.3.12)$$

determined by the experimental $B(T)$ results, to $kT$ by

$$U(\bar{r}) = F(T)kT, \quad (5.3.13)$$

where the inversion function $F(T)$ is to be determined. A first approximate value $F_0(T)$ of the inversion function is calculated from an initial approximate potential-energy function $U_0(r)$ for each of the experimental temperatures by setting

$$F_0(T) = U_0(\bar{r}_0)/kT, \quad (5.3.14)$$

where $\bar{r}_0$ is calculated from equation (12) using $B + TB'$ calculated from
The inversion function is not highly sensitive to the details of the initial approximate potential-energy function. New estimates \( U_1(r) \) of the intermolecular potential energy at \( r \) are given by

\[
U_1(r) = U_0(r_0) = F_0(T)kT, \tag{5.3.15}
\]

where \( r \) is determined by the experimental results and \( r_0 \) by \( U_0 \), and these are found to be closer to the true potential-energy at \( r \) than \( U_0(r) \). The first improved function \( U_1(r) \) is then used to calculate values of \( B + TB' \), and hence of \( F_1(T) \) at each of the experimental temperatures. A second improved function

\[
U_2(r) = U_1(r_1) = F_1(T)kT, \tag{5.3.16}
\]

is then obtained from \( U_1 \) by interpolation. This procedure is repeated until convergence; three iterations usually suffice. Although the procedure is insensitive to the details of \( U_0(r) \) and will converge for any reasonable approximation, the depth of the potential-energy well is not modified and remains as an adjustable parameter. However, comparison of the second virial coefficients calculated from the potential-energy function and the experimental results serves to determine \( \varepsilon \), and thus \( U(r) \) is completely determined from \( B(T) \) alone.

Figure 5.5 compares the HFD-C function for argon with the results of a numerical inversion of 45 values of \( B + TB' \) in the range \( 84 < T/K < 700 \) calculated with high accuracy from that function. The initial approximation was an 11-6-8 function with \( (\varepsilon/k) = 143 \text{ K} \), the true value, and the results are shown after the third iteration. Also shown are the r.m.s. deviations of the second virial coefficients generated by the recovered function from the 45 pseudo-experimental values for different assumed well depths. Clearly, the well depth is defined to within 1
FIGURE 5.5. NUMERICAL INVERSION OF SECOND VIRIAL COEFFICIENTS.

- HFD-C function
- Inversion results $U_3(\tilde{r})$

Insert: rms deviations of calculated $B$'s for different $\epsilon$
per cent of the true value, and both the attractive and repulsive branches are recovered with high accuracy. Since each measurement of \((B + TB')\) is related to an individual point on \(U(r)\), the range of separations over which that function is obtained is determined by the range of temperatures that can be studied. At each step in the inversion procedure \((B + TB')\) must be calculated by integration between \(r = 0\) and \(r \to \infty\), and \(U(r)\) must be extrapolated outside the range of the experimental results for this purpose. Fortunately the long-range form of the intermolecular potential-energy function is known but, nevertheless, it is desirable to obtain results at reduced temperatures \(T^* = kT/\varepsilon\) down to 0.6 or below. The extrapolation at short ranges will present few problems if the measurements can be extended to reduced temperatures of 4 or above. The inversion procedure is not highly sensitive to random experimental errors, and tests with pseudo-experimental data containing errors of a realistic magnitude drawn at random from a Gaussian distribution indicate that the precision of the best experimental techniques \((1 \text{ cm}^3 \cdot \text{mol}^{-1} \text{ or } 1 \text{ per cent of } B, \text{ whichever is greater})\) is adequate.\(^{32}\) Smoothing of the results is conveniently performed by fitting \(B(T)\) with

\[
B(T) = B_0(T) + P(T) \tag{5.3.17}
\]

where \(B_0(T)\) is calculated from an approximate potential-energy function constrained to give the best fit to \(B(T)\), and \(P(T)\) is a suitable polynomial to describe the deviation of \(B(T)\) from \(B_0(T)\). Equation (17) can be differentiated to obtain \(B'(T)\) as required, and the approximate potential-energy function can serve as the initial function \(U_0(r)\) for the inversion. Experimental values of \(B_a(T)\) obtained from acoustic measurements could be analysed in a similar manner to obtain \((B + TB')\) and \(U_0\).
Using the inversion procedure as outlined above, the second virial coefficients of argon in the range $2 \leq T/k \leq 1000$ have been inverted to obtain $U(r)$. The results lie close to the HFD-C function, although the well depth ($\epsilon/k = 150 \pm 5$ K) is some $5$ per cent greater than expected. It seems likely that the low-temperature second virial coefficients of argon suffer from slight systematic errors, possibly arising from adsorption.

To date our detailed knowledge of intermolecular forces is limited to a number of monatomic species. For these systems second virial coefficients, gas transport properties, atomic-beam scattering results, and spectroscopic studies can all provide definitive information about parts of $U(r)$. In practice, the best functions have been obtained from a wide range of differing properties and, when such results are available, a functional form of sufficient flexibility to accommodate all the data may be assumed and unrealistic constraints are not imposed on the form of $U(r)$. For polyatomic molecules inversion techniques cannot define $U(r,\theta)$ for all relative orientations, but $B(T)$ may be used to obtain the angle averaged function by the method described above. This will exhaust all the information about intermolecular energies that is contained in the $B(T)$ results, and the angle-averaged function can only be related to the true angular dependent function by use of additional information. Considerable information about the long-range energies can be gained by calculation of the dispersion energies, and by inclusion of terms describing the interactions of permanent electric moments. Calculation of the repulsive branch may also provide useful information, but interpretation of gas transport properties of polyatomic molecules still presents theoretical and computational difficulties. In addition, spectroscopic studies of the bound-state dimers can provide detailed information about the well region. Measurements of $B(T)$ and $\beta_a(T)$ have an important role to play in future work and, in combination with spectroscopic and theoretical studies, it does not seem unreasonable to
expect some progress for diatomic and simple polyatomic molecules. However, the usefulness of the second virial coefficient does depend upon the availability of accurate results over a wide range of temperatures. The required range is accessible for simple molecules, and it must be recognised that any serious investigation of intermolecular forces cannot be based upon studies that are restricted in this respect.

APPENDIX A5.1

The purpose of this appendix is to relate the equation of state in the form

$$u^2 = A_0 + A_1 p + A_2 p^2 + \cdots \quad (A5.1.1)$$

to the pressure explicit expansion of the molar volume:

$$V_m = (RT/p)(1 + \mathcal{B}(p/RT) + \mathcal{C}(p^2/RT) + \cdots). \quad (A5.1.2)$$

The fundamental relation derived in chapter two is

$$u^{-2} = \frac{\partial \kappa}{\partial p}$$

$$= (\partial \rho/\partial p)_S = (\partial \rho/\partial p)_T + (\partial \rho/\partial T)_p (\partial T/\partial p)_S, \quad (A5.1.3)$$

and use of the relation

$$(\partial T/\partial p)_S = - (\partial S/\partial T)_T/(\partial S/\partial T)_p, \text{ in which}$$

$$(\partial S/\partial p)_T = - (\partial V/\partial T)_p, \text{ and}$$

$$C_p = \frac{\partial \rho}{\partial T}_p, \quad (A5.1.4)$$
\[ u^{-2} = (\frac{\partial p}{\partial \rho})_p + (\frac{\partial \rho}{\partial T})_p \frac{(\partial \rho}{\partial \rho})_T (T/C_p) \]  
\[ = -MV_m^{-2} \left\{ (\frac{\partial V_m}{\partial p})_T + (\frac{\partial V_m}{\partial T})_p^2 (T/C_p, p, m) \right\}. \] (A5.1.5)

\[ V_m^2 \] and the required derivatives can be obtained from equation (2):
\[ V_m^2 = (\frac{RT}{p})^2 \left\{ 1 + 2B(p/RT) + (2C + B^2/RT)(p^2/RT) + \cdots \right\} \]
\[ (\frac{\partial V_m}{\partial p})_T = \frac{-RT}{p} + C + \cdots \]
\[ (\frac{\partial V_m}{\partial T})_p = \frac{R}{p} + B' + C'p + \cdots. \] (A5.1.6)

Equations (5) and (6) may be combined to obtain
\[ u^{-2} = -M \left\{ 1 + \frac{2B(p/RT)}{p} \right\} \left\{ (R/p)^2 + (2RB'/p) + 2RC' + (B')^2 + \cdots \right\} \]
\[ \times (\frac{RT}{p})^2 \left\{ 1 + 2B(p/RT) + (2C + B^2/RT)(p^2/RT) + \cdots \right\}^{-1} \]
\[ = \{ M(C_{p, m} - R)/RTC_{p, m} \} \left\{ \left[ 1 - \{ 2B'(p/RT) + 2RTC' + (B')^2 \} \right] \times (\frac{RT}{C_{p, m} - R}) + \cdots \right\} \left\{ 1 + 2B(p/RT) + (2C + B^2/RT)(p^2/RT) + \cdots \right\}^{-1}, \] (A5.1.7)

and \( u^2 \) may be found using a binomial expansion, with the result:
\[ u^2 = \left\{ RTC_{p, m}/M(C_{p, m} - R) \right\} \]
\[ + \left\{ RTC_{p, m}/M(C_{p, m} - R) \right\} \left\{ 2C + B^2/RT \right\} \]
\[ \times (\frac{RT}{C_{p, m} - R}) + \cdots \]
\[ = \left\{ \frac{RTC_{p, m}}{M(C_{p, m} - R)} \right\} \left\{ (2C + B^2/RT)(1/RT) + \{ 2BB'/RT(C_{p, m} - R) \} \right\} + \left\{ 2RTC_{p, m}/M(C_{p, m} - R) \right\} \left\{ 2C' + (B')^2/RT \right\} \left\{ 1/(C_{p, m} - R) \right\} + \left\{ 4(B')^2(1/RT) \right\} \]
\[ + \cdots. \] (A5.1.8)

However, the task is not yet complete because \( C_{p, m} \) is also a function of the pressure:
\[ C_{p, m} = C'_{p, m} + \int_{0}^{p} (\partial C_{p, m}/\partial p)_T \, dp = C'_{p, m} + \int_{0}^{p} (\partial H_{m}/\partial p)_T \, dp, \] (A5.1.9)
where \( (\partial H_m/\partial p)_T = \{V_m - T(\partial V_m/\partial T)_p \} \) and may be expanded as

\[
(\partial H_m/\partial p)_T = (\bar{B} - TB') + (\bar{C} - TC')p + \cdots, \quad \text{(A5.1.10)}
\]

and the superscript "pg" denotes the perfect-gas value. Thus

\[
C_{p,m} = C_{p,m}^{pg}\left\{1 - (TB''p/c_{p,m}^{pg}) - \frac{1}{2}(TC''p^2/c_{p,m}^{pg}) + \cdots\right\}
\]

\[
= C_{p,m}^{pg}\left\{1 - \{TB''(\gamma_{pg} - 1)p/R\gamma_{pg}^2\} - \frac{1}{2}\{TC''(\gamma_{pg} - 1)p^2/R\gamma_{pg}\} + \cdots\right\}, \quad \text{(A5.1.11)}
\]

\[
(C_{p,m} - R) = C_{V,m}^{pg}\left\{1 - (TB''p/C_{V,m}^{pg}) - \frac{1}{2}(TC''p^2/C_{V,m}^{pg}) + \cdots\right\}
\]

\[
= C_{V,m}^{pg}\left\{1 - \{TB''(\gamma_{pg} - 1)p/R\} - \frac{1}{2}\{TC''(\gamma_{pg} - 1)p^2/R\gamma_{pg}\} + \cdots\right\}, \quad \text{(A5.1.12)}
\]

and hence \(1/(C_{p,m} - R)\) and \((C_{p,m}/(C_{p,m} - R))\) are given by

\[
(C_{p,m} - R)^{-1} = \gamma_{pg}\left\{1 + \{TB''(\gamma_{pg} - 1)p/R\gamma_{pg}^2\} + \frac{1}{2}\{TC''(\gamma_{pg} - 1)p^2/R\gamma_{pg}\} + \cdots\right\}
\]

\[
\quad + \{TB''(\gamma_{pg} - 1)p/R\}^2 + \cdots, \quad \text{(A5.1.13)}
\]

\[
C_{p,m}(C_{p,m} - R)^{-1} = \gamma_{pg}\left\{1 + \{TB''(\gamma_{pg} - 1)p/R\gamma_{pg}^2\} + \frac{1}{2}\{TC''(\gamma_{pg} - 1)p^2/R\gamma_{pg}\} + \cdots\right\}
\]

\[
\quad + \{TB''(\gamma_{pg} - 1)p/R\}^2 + \cdots. \quad \text{(A5.1.14)}
\]

Finally combining equations (6), (13), and (14) we obtain

\[
u^2 = (RT\gamma_{pg}/M)\left\{1 + \{TB''(\gamma_{pg} - 1)p/R\gamma_{pg}^2\} + \frac{1}{2}\{TC''(\gamma_{pg} - 1)p^2/R\gamma_{pg}\} + \cdots\right\}
\]

\[
\quad + \{TB''(\gamma_{pg} - 1)p/R\}^2 + \cdots \quad \text{(A5.1.15)}
\]

and collecting powers of \(p\) find
\[ A_0 = \left( \frac{RT^\gamma}{\gamma} \right) \]  

\[ A_1 = \left( \frac{RT^\gamma}{\gamma} \right) \{ 2B + 2(\gamma - 1)T\hat{B}' + (\gamma - 1)^2 T^2 B'' / \gamma \} \]  

\[ A_2 = \left( \frac{RT^\gamma}{\gamma} \right) \{ (\gamma + 2)C + 2(\gamma - 1)T\hat{C}' + (\gamma - 1)^2 / 2 \gamma T^2 C'' + G(T) \}, \]  

(A5.1.16)

where

\[ G(T) = \left( \frac{1}{RT} \right) \{ B^2 + ((\gamma - 1) + 4(\gamma - 1)^2)T^2 (B')^2 + ((\gamma - 1)^3 / \gamma)T^4 (B'')^2 + 4(\gamma - 1)TBB' + 2((\gamma - 1)^2 / \gamma)T^2 BB'' + 2((\gamma - 1)^2 (2\gamma - 1) / \gamma)T^2 B'B'' \}, \]  

(A5.1.17)

and where the higher-order terms are even more complicated.

REFERENCES


18. Reference 21, p. 115.
26. Reference 21, p. 582.
27. Reference 21, p. 139.
32. Smith, E. B.; Tindell, A. R.; Wells, B. H.; Crawford, B. W.
6.1 INTRODUCTION

The apparatus described in this chapter is a constant-pathlength, variable-frequency cylindrical resonator, that had been constructed previously in this laboratory. Its design was based on the following criteria:

(A) The main requirement is for precise measurements of the second acoustic virial coefficient $\beta_a$ and therefore for relative speeds of sound as a function of pressure along a series of isotherms, rather than for absolute measurements of the sound speed. $\gamma^g$ is also required, and can be obtained from the ratio of $A_0^g$ for the gas under study to that for a monatomic gas. Thus a constant-pathlength interferometer is preferable, and independent measurement of the pathlength is unnecessary.

(B) A wide cavity and ultrasonic frequencies can be used to reduce boundary-layer corrections to a negligible level.

(C) A wide range of operating frequencies can be used to check that dispersion arising from residual boundary-layer effects, or from thermal relaxation in the gas, is absent.
(D) Resonance frequencies can be obtained from observations of the received amplitude as a function of the excitation frequency. Phase-sensitive detection and measurement of resonance widths are unnecessary for relative accuracy of $1 \times 10^{-4}$.

(E) Although the resonances in the wide cavity at ultrasonic frequencies are not purely longitudinal (there will be unresolved higher modes), the relation between the group speed obtained with the assumption that the waves are plane and the speed of sound in the unbounded gas should be approximately independent of the state of the gas. Thus the small errors arising from the ill-defined nature of the wavefield tend to cancel in a ratio of speeds of sound.

In this chapter the detailed design of the cylindrical resonator, and the experimental procedures used, will be described. Sample measurements in argon and 2,2-dimethylpropane will be presented here, and the bulk of the results are reported in chapter eight.

6.2 THE APPARATUS

Figure 6.1 shows a cross-section through the acoustic cavity of the cylindrical resonator. The transducers are as described in chapter four, except that the electrical connection to the rear electrode of each was made by means of a small spring-located screw head exerting light pressure on the piezoelectric element. The remaining connection to each transducer was made to the brass mounting frame, and the three leads were connected to tungsten rods that were sealed through glass-to-metal seals in the lid of the vessel. Prior to the final assembly, the transducers were carefully aligned on their mounting frame, and the
FIGURE 6.1. THE CYLINDRICAL RESONATOR.

thermometer well

leadthrough

transducer

mounting frame (brass)

50 mm

copper wall
pathlength adjusted to about 100 mm.

The lid of the containment vessel was sealed with a viton rubber 'O'-ring, while the remaining joints were silver soldered. The resonator was mounted on blocks inside a concentric-shield electric furnace.

A single 3.2 mm internal diameter stainless-steel pipe connected the vessel to the external pipework and was used both for filling and pressure measurement. The external pipework is shown schematically in figure 6.2. The vacuum pumps consisted of a 75 mm diameter oil-vapour diffusion pump operating in conjunction with a rotary mechanical pump, and the ultimate low pressure that could be achieved in the whole system, as measured by a Penning gauge in the vacuum line, was 0.1 mPa. Gas samples could be introduced either directly from a cylinder or by distillation from a detachable glass ampoule.

The pressure of the sample gas was measured indirectly using a quartz-spiral gauge (Ruska model DDR 6000) with a resolution of 1 Pa and a full-scale reading of 115 kPa. The gauge was isolated from the sample gas by a differential capacitance manometer (Baratron model 90M) which was used as a null-reading instrument. Argon was used to pressurise the Ruska gauge and a separate mechanical vacuum pump was used to lower the pressure. Both gauges could be connected through to the main vacuum pumps in order to achieve a high vacuum and set their zero-pressure readings. The Ruska gauge was calibrated by the manufacturers to an accuracy of 1 Pa.

The temperature was measured using a capsule-type platinum resistance thermometer (Tinsley type 5187 SA, serial number 223 708) located in the re-entrant well in the lid of the vessel. This thermometer had been calibrated on the International Practical Temperature Scale of 1968 (IPTS-68) for use above 273.15 K prior to installation. Measurements of the ratio $R(T_{68})/(R(T_{68})+R_s)$ where $R(T_{68})$ is the resistance of the thermometer at the IPTS-68 temperature $T_{68}$ and $R_s$ is a
FIGURE 6.2. EXTERNAL PIPEWORK (cylindrical resonator).

- Ruska gauge
- Penning gauge
- Cold trap
- To main vacuum
- To gas cylinder
- Baratron
- Main vessel
- Drying ampoule
- Sample ampoule
- To argon supply
- To secondary vacuum
- Rotoflo Teflon-in-glass valve.
reference resistance, were performed using an automatic resistance comparison bridge (Automatic Systems Laboratories Ltd., model A7) with a resolution of $10^{-7}$, and operating with an alternating current of 1 mA r.m.s. at 375 Hz. The standard resistor (Tinsley model 3404D, nominal value 100 Ω) was housed in a stirred oil bath, and $R_s$ is given by the equation:

$$R_s/Ω = 100.0011 - 5.06 \times 10^{-5}(T_s/K) - 296.15)^2,$$  \hspace{1cm} (6.2.1) 

determined by the manufacturer, where $T_s$ is the temperature of the resistor and was measured with an accuracy of ±0.2 K using a mercury-in-glass thermometer. The value of equation (1) is strictly only applicable to a direct current measurement because the resistor was not designed for a negligible reactance at 375 Hz. Since the thermometer was calibrated using the same apparatus for the resistance measurements, the small error in assuming that equation (1) is applicable cancels. The IPTS-68 temperatures above 273.15 K were calculated using the standard algorithm:

$$T_{68} = 273.15 K + t + 0.045(t/100 ^{\circ}C) \times (t/100 ^{\circ}C) - 1) \times (t/630.74 ^{\circ}C) - 1) ^{\circ}C,$$  \hspace{1cm} (6.2.2) 

where $t$ is a Celsius temperature given by

$$t = ((W - 1)/\alpha) + \delta(t/100 ^{\circ}C)(t/100 ^{\circ}C) - 1),$$

in which

$$W = [R(T_{68})/R(273.15 K)] = [R(T_{68})/R_0]_7,$$  \hspace{1cm} (6.2.3) 

using the constants

$$R(273.15 K) = R_0 = 22.1790 \, Ω, \quad \alpha = 3.0039255 \, ^{\circ}C^{-1}, \quad \text{and} \quad \delta = 1.501 \, ^{\circ}C.$$  \hspace{1cm} (6.2.4)
Equation (3) was solved by iterations using \((\ln{\gamma} - 1)/\alpha\) as the initial estimate of \(\gamma\). Between 13.81 and 273.15 K the IPTS-68 temperature is given by

\[
T_{68} = \sum_{j=0}^{20} a_j \left( \frac{\ln W_{\text{CCT-68}} + 3.28}{3.28} \right)^j K, \tag{6.2.5}
\]

where

\[
W_{\text{CCT-68}} = W - \Delta \gamma
\]

(6.2.6)

and \(\Delta \gamma\) is a deviation function representing the deviations of a given thermometer from the reference resistance ratio \(W_{\text{CCT-68}}\), and where \(a_j\) \((j = 0, 20)\) are a set of 21 defined constants.\(^2\) Between 90.18 K and 273.15 K \(\Delta \gamma\) is given by

\[
\Delta \gamma = b_4 (T_{68} - 273.15 K) + e_4 (T_{68} - 273.15 K)^3 (T_{68} - 373.15 K), \tag{6.2.7}
\]

where \(b_4\) and \(e_4\) are calibration constants. Unfortunately, the thermometer used in this apparatus had not been calibrated for use at temperatures below 273.15 K. Rather than assume \(\Delta \gamma = 0\) or guess \(b_4\) and \(e_4\), the simpler equation (2) was employed with

\[
t = \left\{ \frac{(W - 1)}{\alpha} \right\} + \beta_t \left( \frac{t}{100 \degree C} - 1 \right)^2 \left( \frac{t}{100 \degree C} \right) + \beta_t \left( \frac{t}{100 \degree C} \right)^3 \left( \frac{t}{100 \degree C} - 1 \right), \tag{6.2.8}
\]

where \(\beta_t = 0.11 \degree C\) was assumed, in accordance with the 1948 International Practical Temperature Scale for the range 90.18 to 273.15 K.\(^3\) At 250 K (the lowest temperature studied in this work) the third term in equation (8) contributes just 3 mK, and hence the assumption of a typical value for \(\beta_t\) (rather than one determined by calibration) should not lead to
significant error. Small corrections were applied to convert the
temperatures determined in this way to the 1968 scale. The total
uncertainty in the measured $T_{68}'s$ is estimated to be $\pm 20$ mK in the
range $250 < T/K < 340$.

The electric thermostat is illustrated in figure 6.3, with the
shields cut away to reveal the location of the acoustic cavity. The
inner shield, the control shield, was wound uniformly over its length with
a $600 \, \Omega$ (at $300 \, K$) enamelled copper-wire resistance thermometer. Six
sets of $380 \, \Omega$ enamelled Manganin wire heating coils were non-inductively
wound directly over the copper thermometer. This thermometer formed one
arm of a d.c. Wheatstone bridge which provided the error signal for the
integrating proportional temperature controller that switched the
alternating current in the six heaters. The control temperature was set
by adjustment of the fixed resistors in the Wheatstone bridge. The
excellent thermal contact between the shield, thermometer, and heating
coils resulted in a fast response by the control system to a change in
power demand. This, combined with the fairly long time constant for heat
exchange between the shield and the resonator (several hours in air)
provided excellent temperature stability. When left unperturbed, the
temperature as measured by the platinum resistance thermometer could be
stable to $\pm 0.5$ mK for 1 h at $320 \, K$. A set of thermocouples on the
control shield enabled the vertical temperature gradient to be measured,
and this could be reduced to $\pm 0.1$ K by altering the division of power
between the heaters. The temperature gradients on the outside of the
resonator could not be measured, but should have been much smaller than
on the control shield.

The outer shield, the radiation shield, was also provided with six
sets of $380 \, \Omega$ Manganin heating coils non-inductively wound over its
length, and there were additional $2 \, \Omega$ heaters wound, one over each end.
These were all used to provide additional power and were operated with a
FIGURE 6.3. THE ELECTRIC THERMOSTAT
constant alternating current. Thermocouples were used to measure the vertical temperature gradients (which could also be reduced to $\pm 0.1$ K by variation of the power distribution between the heaters), and also to measure the difference in the temperatures of the control and radiation shields. The control shield was usually operated between 0.5 and 5 K above the radiation shield.

The whole assembly was mounted inside a brass vessel which was sealed with a PTFE 'O'-ring and could be evacuated in order to reduce the heat loss from the apparatus. This was not found to be necessary and the thermostat was operated in air. For operation below room temperature, the apparatus was immersed in a refrigerated fluid bath and temperatures down to 250 K were possible.

A number of glass tubes were sealed through the lid of the outer vessel with glass-to-metal seals. The wires to the transducers, heaters, and thermometers passed up these tubes to emerge through fine holes sealed with vacuum wax. The stainless-steel inlet pipe passed up a 10 mm internal-diameter stainless-steel tube sealed through the lid of the outer vessel, and an 'O'-ring seal between the two was provided about 100 mm above the lid. A heater was wound over the inlet pipe so that heat loss to the refrigerated bath could be compensated, and a thermocouple was provided to measure the vertical temperature gradient in this region.

The instrumentation used to detect the resonances is shown schematically in figure 6.4. The signal supplied to the source transducer was derived from a sine-wave signal synthesizer (Hewlett-Packard model 3320 A) that has a continuously variable frequency. The frequency was measured using a frequency counter (Hewlett-Packard model 5381 A) incorporating a quartz-crystal oscillator as its time base. Although the crystal was not housed in a thermostat, variations in the ambient temperature altered the frequency by an insignificant amount (fractionally $5 \times 10^{-7}$ K$^{-1}$). The source signal was amplified to about 10 V r.m.s. so as
FIGURE 6.4. INSTRUMENTATION (cylindrical resonator).

resonator

oscilloscope (dual trace)

amplifier 40 dB

amplifier 20 dB

signal source

counter
to obtain adequate output from the transducer. The receiving transducer was connected to an amplifier having a forward potential-difference gain of 100. The input resistance of this amplifier was deliberately reduced to 1 kΩ in order to reduce the sensitivity to audio-frequency noise. The amplified signal was displayed on an oscilloscope for observation of its amplitude. Under typical conditions, the signal at the input to the oscilloscope was about 50 mV r.m.s. at frequencies close to a resonance frequency. Much larger signals were observed when the frequency was also close to the resonance frequency of the transducers themselves.

6.3 EXPERIMENTAL PROCEDURE

Before beginning each set of measurements, the quartz-spiral gauge was evacuated and its zero-pressure reading adjusted in accordance with the manufacturers instructions. The zero-pressure reading of the Baratron was also set under vacuum.

Samples of 2,2-dimethylpropane held in the sample ampoule were degassed by repeatedly freezing the liquid (by immersion in liquid nitrogen), evacuating the remaining vapour, and then remelting the sample. Water was removed by transfer of the material to a second ampoule containing grade 4A molecular sieves, previously dried by baking at 550 K and 1 mPa for 12 h, where it was left for 24 h before transfer to the resonator. Samples could also be introduced directly from a gas cylinder. The connecting pipe and gas-cylinder pressure regulator were flushed with the gas to avoid contamination with air. The pressure regulators used (British Oxygen Company Ltd, type 80B) were not vacuum tight and hence flushing was the only method by which contamination could be reduced.

Prior to filling, the main vessel was evacuated until the pressure in the vacuum line as indicated by the Penning gauge fell below 1 mPa.
During filling, the reference side of the Baratron was slowly pressurised with argon so that the pressure difference was close to zero and the Ruska gauge indicated the approximate sample pressure. The vessel was initially pressurised to about 100 kPa or 80 per cent of the saturation pressure, which ever was the smaller. The apparatus was then usually left overnight for thermal equilibrium to be re-established before the measurements were begun.

Each set of measurements was performed under near isothermal conditions and at, typically, ten pressures above 10 to 20 kPa. The observed resonance frequencies $f_1$ of the cavity between 50 and 100 kHz were assumed to be given by

$$f_1 = \frac{1}{2}(u/L)(1 + \delta),$$

(6.3.1)

where $l$ is a positive integer, and $\delta$ is the phase shift that arises from the non-zero fluid velocity at the faces of the transducers (and also from the effects of direct electromagnetic coupling between the source and detector circuits). By locating and measuring two adjacent resonance frequencies, $(u/L)$ and the $(1 + \delta)'s$ could be estimated and used to locate the remaining resonances. The temperature and pressure were then recorded, and all of the resonance frequencies between about 50 and 90 to 100 kHz measured with a resolution of 1 Hz. Random noise limited the precision of an individual determination to about ±5 Hz. At each resonance, the driving frequency was adjusted until the amplitude of the received signal, as observed on the oscilloscope was at a maximum (for even values of $l$), or at a minimum (for odd values of $l$), and the frequencies at which this occurred were taken as the resonance frequencies. Alternate resonances result in an observed minimum in the received amplitude because of the strong direct electromagnetic coupling (crosstalk) between the source and detector circuits. This usually
contributed more than half of the received signal, and was in phase with
the signal of acoustic origin for even values of $\lambda$ (hence the observed
maxima) but approximately $\pi$ out of phase for odd values of $\lambda$ (hence the
observed minima). About 20 to 30 min were required to record each set
of resonance frequencies, and the temperature was measured for a second
time on completion of the measurements; where there was significant drift
the mean of the two measurements was taken as the true temperature.
Usually the temperature drift was less than 5 mK. Typical results are
discussed in section 4.

After each set of frequency measurements, the gas pressure was
reduced for the next point on the isotherm. Condensable samples were
transferred back to the sample ampoule under vacuum, while others were
simply pumped away. Such an expansion of gas from the vessel is nearly
adiabatic and resulted in the cavity cooling by, typically, 3 mK. About
1 h would have been required for the temperature to return to the set
point but, because the drift was slow, it was not usual practice to wait
for more than about 10 min before the next set of measurements were begun.
The lowest pressure at which measurements of useful precision could be
performed was between 10 and 20 kPa because the signal of acoustic origin
became obscured by the crosstalk and random noise at lower pressures.

6.4 SAMPLE RESULTS

The following sample results were obtained at temperatures close
to 290 K in argon and 2,2-dimethylpropane.

The isotherm in argon covers ten pressures between 21.3 and 102.5
kPa at a mean temperature of 290.262 K. The resonance frequencies,
temperatures, and pressures are given in table 6.1. The frequency range
of the measurements was determined by the range over which the transducers
<table>
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<tr>
<th>$p$/Pa</th>
<th>102469</th>
<th>93483</th>
<th>84743</th>
<th>74552</th>
<th>66575</th>
<th>57449</th>
<th>48116</th>
<th>39322</th>
<th>29934</th>
<th>21292</th>
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</thead>
<tbody>
<tr>
<td>$(T - T_m)/mK$</td>
<td>13</td>
<td>23</td>
<td>17</td>
<td>13</td>
<td>4</td>
<td>0</td>
<td>-13</td>
<td>-18</td>
<td>-22</td>
<td>-19</td>
</tr>
</tbody>
</table>

TABLE 6.1. Resonance frequencies ($f_i$/Hz) in argon. Cylindrical resonator, mean temperature $T_m = 290.262$ K.
operated with a useful efficiency. At the lower pressures, where acoustic losses are greatest and coupling between the source transducer and the gas is least efficient, some of the resonances that were observed at higher pressures became obscured by the crosstalk and random noise. In addition, some of the recorded resonance frequencies are clearly inconsistent with the bulk of the measurements and have been rejected from the analysis. The frequencies that have been rejected (underlined in Table 6.1) yield values of $(u/L)$ that differ by more than two standard deviations from the mean value of the remaining results at the same pressure. Some of the worst affected resonances were not recorded at the lower pressures.

In order to calculate $(u/L)$, the $\delta$ parameter must be found. Both $(u/L)$ and $\delta$ can be found by a linear least-squares regression analysis in which the equation:

$$f_1 = \frac{1}{2}(u/L)\delta + \frac{1}{2}(u/L)I$$

(6.4.1)

is fitted to $f_1$. For example, the results at 93.483 kPa yield $\delta = (0.158 \pm 0.005)$ and $(u/L) = (3156.05 \pm 0.36) \text{s}^{-1}$, and the standard deviation of the fit is 5 Hz. Values of $\delta$ obtained from the results at other pressures do not differ significantly and $\delta = 0.158$ is the optimum value for the isotherm. Mean values of $(u/L)$ and $(u/L)^2$ at each pressure, obtained with $\delta = 0.158$ and adjusted to 290.262 K (assuming $u^2(T_1)/u^2(T_2) = T_1/T_2$), are given in Table 6.2.

† Unless otherwise stated, all quoted uncertainties in this work are ±one standard deviation only. In the case of the coefficient $a_j$ of the $j^{th}$ independent variable, estimated in a multiple linear regression analysis with $\nu$ degrees of freedom, the confidence interval at the probability level $\alpha$ is $[a_j \pm t_\nu(\alpha)\sigma_j]$, where $\sigma_j$ is the standard deviation of $a_j$ and $t_\nu(\alpha)$ is given by the $t$ distribution for $\nu$ degrees of freedom in a 'two-sided' test.
<table>
<thead>
<tr>
<th>p/kPa</th>
<th>((u/L)/s^{-1})</th>
<th>((u/L)^2/s^{-2})</th>
<th>((\Delta_2/s^{-2})^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>102.469</td>
<td>3156.02 ± 0.18</td>
<td>9960460 ± 1140</td>
<td>-90</td>
</tr>
<tr>
<td>93.483</td>
<td>3155.93 ± 0.20</td>
<td>9959890 ± 1260</td>
<td>-180</td>
</tr>
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<td>84.743</td>
<td>3155.89 ± 0.18</td>
<td>9959640 ± 1140</td>
<td>40</td>
</tr>
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<td>74.882</td>
<td>3155.79 ± 0.20</td>
<td>9959010 ± 1260</td>
<td>-70</td>
</tr>
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<td>66.578</td>
<td>3155.77 ± 0.21</td>
<td>9958880 ± 1330</td>
<td>240</td>
</tr>
<tr>
<td>57.449</td>
<td>3155.66 ± 0.20</td>
<td>9958190 ± 1260</td>
<td>40</td>
</tr>
<tr>
<td>48.116</td>
<td>3155.61 ± 0.22</td>
<td>9957870 ± 1390</td>
<td>220</td>
</tr>
<tr>
<td>39.322</td>
<td>3155.53 ± 0.25</td>
<td>9957370 ± 1580</td>
<td>180</td>
</tr>
<tr>
<td>29.934</td>
<td>3155.46 ± 0.26</td>
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</tr>
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<td>21.292</td>
<td>3155.28 ± 0.26</td>
<td>9955790 ± 1640</td>
<td>-440</td>
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</table>

Two term fit. Standard deviation of \(f_1^2 = 0.760 \text{ kHz}^2\)

\[
(A_0/L^2)^+ = (9955130 ± 230)s^{-2}
\]

\[
(A_1/L^2) = (52.9 ± 4.0) \times 10^{-3}s^{-2}\cdot\text{Pa}^{-1}
\]

Three term fit. Standard deviation of \(f_1^2 = 0.762 \text{ kHz}^2\)

\[
(A_0/L^2) = (9955070 ± 510)s^{-2}
\]

\[
(A_1/L^2) = (55.4 ± 21.9) \times 10^{-3}s^{-2}\cdot\text{Pa}^{-1}
\]

\[
(A_2/L^2) = (-0.2 ± 1.7) \times 10^{-7}s^{-2}\cdot\text{Pa}^{-1}
\]

Weighted two term fit. Standard deviation of \(f_1^2 = 0.753 \text{ kHz}^2\)

\[
(A_0/L^2) = (9955110 ± 260)s^{-2}
\]

\[
(A_1/L^2) = (53.2 ± 4.0) \times 10^{-3}s^{-2}\cdot\text{Pa}^{-1}
\]

Weighted three term fit. Standard deviation of \(f_1^2 = 0.755 \text{ kHz}^2\)

\[
(A_0/L^2) = (9955170 ± 540)s^{-2}
\]

\[
(A_1/L^2) = (55.4 ± 21.9) \times 10^{-3}s^{-2}\cdot\text{Pa}^{-1}
\]

\[
(A_2/L^2) = (-0.2 ± 1.7) \times 10^{-7}s^{-2}\cdot\text{Pa}^{-2}
\]

\[\Delta_2 = ((u/L)^2 - (A_0/L^2) - (A_1/L^2)) \quad \text{from weighted two term fit.}\]
The 173 selected resonance frequencies were analysed by fitting the leading two and three terms of the equation:

\[ f^2_1 = \left( \frac{A_0}{L^2} \right)^2 (1 + \delta)^2 + \left( \frac{A_1}{L^2} \right)^2 (1 + \delta)^2 P + \left( \frac{A_2}{L^2} \right)^2 (1 + \delta)^2 P^2 + \cdots \quad (6.4.2) \]

to \( f^2_1 \), using the method of least squares. The coefficients \( \left( \frac{A_0}{L^2} \right) \), \( \left( \frac{A_1}{L^2} \right) \), and \( \left( \frac{A_2}{L^2} \right) \), and their standard deviations, as estimated from two- and three-term fits to equation (2), are given in table 6.2. In the initial regression analysis each pressure on the isotherm was given equal weighting; the frequencies \( f_1 \) at each pressure were weighted by \( w_p = N(n/n_p) \), where \( n \) is the total number of frequencies in the analysis, \( n_p \) is the number at that pressure, and \( N = n/\sum_{i=1}^{n} w_i \) is a normalisation constant. In the weighted regression analysis the frequencies at each pressure were weighted by \( N(n/n_p)(1/s_p^2) \), where \( s_p^2 \) is the variance of \( 2f_1/(1 + \delta) \) at that pressure. This takes account of the random scatter among the measurements. Clearly the results are well represented by a two-term fit; inclusion of the third term actually increases the standard deviation of the fits. The results of the weighted and unweighted analyses are in excellent agreement. The weighted two-term fit has been used to generate the fourth column of the table which gives the deviations of the experimental results from the line of best fit. The best estimate of the second acoustic virial coefficient, \( \beta_a = 12.9 \text{ cm}^3\text{ mol}^{-1} \), compares reasonably well with the value \( 9.1 \text{ cm}^3\text{ mol}^{-1} \) obtained by differentiation of equation (5.3.9), the square-well formula for \( B(T) \), and with the value \( 9.7 \text{ cm}^3\text{ mol}^{-1} \) obtained by numerical integration of the HFD-C pair-potential-energy function for argon in accordance with equation (5.3.6).

The weighted two-term fit estimate of \( \frac{A_0}{L^2} \) has been combined with the calculated value of \( A_0 \) to find the pathlength of the interferometer at 290.26 K. The sample gas was Matherson grade argon (Cambrian gases Ltd) and the manufacturers claimed that the total mole fraction of
impurities was less than $5 \times 10^{-6}$. Thus $\gamma_{pg}$ may be taken as exactly $5/3$, and the only significant uncertainty in the molar mass $M = 0.039948$ kg mol$^{-1}$ should be that arising from the uncertainty in the isotopic composition: $\delta M = 3 \times 10^{-6}$ kg mol$^{-1}$. If the uncertainty $\delta T$ in the measured IPTS-68 temperature is taken to be $\pm 20$ mK, and the uncertainty $\delta R$ in the gas constant $R = 8.31441$ J K$^{-1}$ mol$^{-1}$ is taken to be $\pm 0.00026$ J K$^{-1}$ mol$^{-1}$ ($\pm$ one standard deviation), then the relative uncertainty in $A_0(290.262)$ $= 100$ 687 m$^2$ s$^{-2}$ is

$$\frac{\delta A_0}{A_0} = \left(\frac{\delta R}{R}\right)^2 + (\delta T/T)^2 + (\delta M/M)^2 \right)^{\frac{1}{2}} = 1.1 \times 10^{-4}. \quad (6.4.3)$$

The relative uncertainty in the estimation of $(A_0/L^2)$ that arises from the random scatter in the measurements is $0.7 \times 10^{-4}$ (99 per cent confidence interval with 171 degrees of freedom), and hence

$$L = (100.569 \pm 0.007) \text{ mm.} \quad (6.4.4)$$

This result is sensitive to the value chosen for $\delta$; a change of 0.005 would correspond to about 0.01 mm in $L$.

The isotherm in 2,2-dimethylpropane covers ten pressures between 17.5 and 99.2 kPa at a mean temperature of 290.039 K (about 7.4 K above the normal boiling temperature). The measured resonance frequencies, temperatures, and pressures are given in table 6.3. The underlined entries have been rejected from the final analysis by the same criterion as was applied to the measurements in argon. There is no evidence in the measurements to suggest that there was any significant dispersion at the experimental frequencies. The mean value of $\delta$ obtained by fitting equation (1) to the results at each pressure is $(0.158 \pm 0.008)$. If the results at the two lower pressures are neglected then the optimum value is $(0.155 \pm 0.005)$. Since the values obtained for $(u/L)$ are sensitive to
TABLE 6.3. Resonance frequencies \( f_1 / \text{Hz} \) in 2,2-dimethylpropane.

Cylindrical resonator, mean temperature \( T_m = 290.039 \text{ K} \).

<table>
<thead>
<tr>
<th>( p )/( \text{Pa} )</th>
<th>99214</th>
<th>90781</th>
<th>82230</th>
<th>73693</th>
<th>63386</th>
<th>54052</th>
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<th>35361</th>
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<tbody>
<tr>
<td>( T - T_m )/mK</td>
<td>31</td>
<td>-16</td>
<td>2</td>
<td>-1</td>
<td>4</td>
<td>9</td>
<td>4</td>
<td>-12</td>
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</tr>
<tr>
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<td>79</td>
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<th>74479 74725 74954 75190</th>
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</tr>
<tr>
<td>82</td>
<td>74930 75173</td>
</tr>
<tr>
<td>83</td>
<td>74850 75066 75306 75539</td>
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| 75826 76080 76325 76574 76809 77041 |
| 84      | 76675 76898 77141 77381 77673 77939 |
| 85      | 78182 78443 78675 78916 |

| 77614 77837 78050 78326 78618 78874 79128 79389 79614 79873 |
| 86      | 78505 78733 78981 79230 79530 79791 |
| 87      | 80042 80310 80555 80804 81236 81489 |

| 81731 80150 80453 80719 80974 |
| 88      | 80329 80561 80819 81069 81379 81648 |
| 89      | 81902 82182 82428 |
| 90      | 81244 81475 81731 81988 82297 82565 |
| 91      | 82827 83098 83366 |

| 8364 84036 84283 |
| 92      | 82153 82387 82644 82910 83213 83488 |
| 93      | 83764 84036 84283 |
| 94      | 83067 83305 83568 83830 84144 84419 |
| 95      | 84694 84963 85217 |
| 96      | 83964 84208 84474 84744 85058 85344 |
| 97      | 85617 85899 86162 |
| 98      | 84888 85130 85402 85669 85994 86273 |
| 99      | 86547 86833 87090 |

| 87911 86037 86312 86582 86912 87196 87470 87772 88020 |
| 94      | 85791 86037 86312 86582 86912 87196 87470 87772 88020 |
| 95      | 86709 86960 87233 87507 87845 88120 88412 88695 |
| 96      | 87620 87872 88145 88427 88755 89050 89337 89632 |
| 97      | 88521 88779 89066 89341 89680 89970 90260 90554 |
| 98      | 89444 89693 89953 90271 90601 |
| 99      | 90341 90605 90592 91170 91521 |
the chosen \( \delta \), and since \( L \) was eliminated using the results obtained in argon, the value 0.158 which is in agreement with that found for argon has been adopted for the analysis. Mean values of \( (u/L) \) and \( (u/L)^2 \) at each pressure, adjusted to 290.039 K, are given in table 6.4 together with their standard deviations.

The 324 selected frequencies have been analysed by fitting equation (2), and the results of weighted and unweighted two- and three-term fits are given in table 6.4. By analysing all of the frequencies, rather than just the mean values of \( (u/L)^2 \) at each pressure, the influence of random experimental error on the estimation of the coefficients is minimised. The question of which order of fit to select is not so easily answered in this case; a two-term fit gives a good account of the results, but inclusion of a third term leads to a significant reduction in the standard deviation of the fit, and the third coefficient is significant at a probability level of 0.1 per cent: \( |A_2/\sigma(A_2)| = 6.9 \) is greater than \( t_{321}(0.001) = 3.3 \). The fourth and fifth columns of table 6.4 contain the deviations of the mean values of \( (u/L)^2 \) from the weighted two- and three-term fits, and the r.m.s. deviations are 420 s\(^{-1}\) and 310 s\(^{-1}\) respectively. It is noteworthy that the coefficients estimated in the weighted and unweighted two-term regressions differ significantly, but that those obtained from the three-term analyses are in close agreement. These results suggest that the coefficients obtained in the weighted three-term regression analysis are the best estimates of the true values, and that a 99 per cent confidence interval for the second acoustic virial coefficient is \( \beta_a = (-1609 \pm 14) \text{cm}^2\text{mol}^{-2} \). The results obtained by fitting the equation:

\[
(u/L)^2 = (A_0/L^2) + (A_1/L^2)p + (A_2/L^2)p^2 - \cdots \tag{6.4.5}
\]

to the mean values of \( (u/L)^2 \) at each pressure do not differ significantly,
**Table 6.4** \((u/L)\) for 2,2-dimethylpropane at 290.039 K.

<table>
<thead>
<tr>
<th>(p/\text{kPa})</th>
<th>((u/L)/\text{s}^{-1})</th>
<th>((u/L)^2/\text{s}^{-2})</th>
<th>((\Delta_2/\text{s}^{-2})^\dagger)</th>
<th>((\Delta_3/\text{s}^{-2})^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.214</td>
<td>1822.18 ± 0.13</td>
<td>3320340 ± 470</td>
<td>120</td>
<td>430</td>
</tr>
<tr>
<td>90.781</td>
<td>1827.63 ± 0.12</td>
<td>3340230 ± 440</td>
<td>-490</td>
<td>-410</td>
</tr>
<tr>
<td>82.230</td>
<td>1833.31 ± 0.13</td>
<td>3361030 ± 460</td>
<td>-470</td>
<td>-560</td>
</tr>
<tr>
<td>73.693</td>
<td>1839.11 ± 0.14</td>
<td>3382330 ± 520</td>
<td>80</td>
<td>-110</td>
</tr>
<tr>
<td>63.386</td>
<td>1846.04 ± 0.14</td>
<td>3407860 ± 520</td>
<td>560</td>
<td>330</td>
</tr>
<tr>
<td>54.052</td>
<td>1852.11 ± 0.11</td>
<td>3430310 ± 410</td>
<td>330</td>
<td>130</td>
</tr>
<tr>
<td>44.899</td>
<td>1858.06 ± 0.13</td>
<td>3452390 ± 460</td>
<td>160</td>
<td>80</td>
</tr>
<tr>
<td>35.361</td>
<td>1864.25 ± 0.13</td>
<td>3475430 ± 490</td>
<td>20</td>
<td>130</td>
</tr>
<tr>
<td>26.390</td>
<td>1869.90 ± 0.18</td>
<td>3496530 ± 670</td>
<td>-680</td>
<td>-320</td>
</tr>
<tr>
<td>17.519</td>
<td>1875.65 ± 0.24</td>
<td>3518060 ± 900</td>
<td>-710</td>
<td>-40</td>
</tr>
</tbody>
</table>

Two term fit. Standard deviation of \(f_1^2 = 1.041 \text{ kHz}^2\)

\[
(A_0/L^2) = (3560980 ± 80)\text{s}^{-2}
\]

\[
(A_1/L^2) = (-2.4253 ± 0.0014)\text{s}^{-2}\text{Pa}^{-1}
\]

Three term fit. Standard deviation of \(f_1^2 = 0.955 \text{ kHz}^2\)

\[
(A_0/L^2) = (3559630 ± 160)\text{s}^{-2}
\]

\[
(A_1/L^2) = (-2.3702 ± 0.0071)\text{s}^{-2}\text{Pa}^{-1}
\]

\[
(A_2/L^2) = (-4.62 ± 0.59) \times 10^{-7}\text{s}^{-2}\text{Pa}^{-2}
\]

Weighted two term fit. Standard deviation of \(f_1^2 = 0.970 \text{ kHz}^2\)

\[
(A_0/L^2) = (3561350 ± 90)\text{s}^{-2}
\]

\[
(A_1/L^2) = (-2.4304 ± 0.0014)\text{s}^{-2}\text{Pa}^{-1}
\]

Weighted three term fit. Standard deviation of \(f_1^2 = 0.906 \text{ kHz}^2\)

\[
(A_0/L^2) = (3559850 ± 200)\text{s}^{-2}
\]

\[
(A_1/L^2) = (-2.3759 ± 0.0080)\text{s}^{-2}\text{Pa}^{-1}
\]

\[
(A_2/L^2) = (-4.28 ± 0.62) \times 10^{-7}\text{s}^{-2}\text{Pa}^{-2}
\]

\(\dagger\) \(\Delta_2 = [(u/L)^2 - (A_0/L^2) - (A_1p/L^2)]\) from weighted 2 term fit.

\(*\) \(\Delta_3 = [(u/L)^2 - (A_0/L^2) - (A_1p/L^2) - (A_2p^2/L^2)]\) from weighted 3 term fit.
but the influence of random errors is more pronounced in such an analysis. For example, the results of unweighted two- and three-term fits are given in table 6.5, and the three-term fit gives $\beta_a = (-1607 \pm 55) \text{ cm}^3 \text{ mol}^{-1}$ (99 per cent confidence interval with seven degrees of freedom). Clearly, the effects of random errors on the estimated coefficients are much smaller in the two-term regression analyses, but the results are subject to a systematic error arising from the neglect of $A_2$. Conversely, if the third term is included then random errors give rise to a much larger statistical uncertainty in the estimation of $\beta_a$, and this is particularly severe when only the mean values of $(u/L)^2$ are analysed. An alternative method of analysing the results is to employ a number of two-term regressions in which the measurements at the highest pressures are progressively neglected. Such an analysis yields the mean value of $(\partial(u/L)^2/\partial p)$ over the experimental range of pressures, but the required quantity is $\lim_{p \to 0} (\partial(u/L)^2/\partial p)$. The results obtained from unweighted analyses at different mean pressures are given in table 6.5, and also plotted in figure 6.5. Clearly, $(\partial(u/L)^2/\partial p)$ is a linear function of the mean pressure $<p>$ to within the resolution of the measurements, and a linear extrapolation gives $\lim_{p \to 0} (\partial(u/L)^2/\partial p) = (A_1/L^2) = (-2.354 \pm 0.005) \text{ s}^{-2} \text{ Pa}^{-1}$, and $\frac{1}{2}(\partial^2(u/L)^2/\partial p^2) = (A_2/L^2) = (6.5 \pm 0.5) \times 10^{-7} \text{ s}^{-2} \text{ Pa}^{-2}$. This result implies that $\beta_a = (-1595 \pm 13) \text{ cm}^3 \text{ mol}^{-1}$ (99 per cent confidence interval with six degrees of freedom), and this differs from the result of three-term regression analysis by 0.9 per cent.

The perfect-gas heat capacity ratio $\gamma^{Pd}(C_{5}, 290.04 \text{ K})$ of 2,2-dimethylpropane at 290.04 K has been obtained by combining the best estimate of $A_0/L^2$, namely $(3559850 \pm 200) \text{ s}^{-2}$, with that obtained in argon. The value of $(A_0/L^2)$ obtained in argon at 290.26 K was adjusted to 290.04 K with the assumption that the temperature dependence of the pathlength is determined by the thermal expansion of the brass transducer mounting frame (using $\partial L/\partial T = 2 \times 10^{-5} L \text{ K}^{-1}$), with the result
TABLE 6.5 Analysis of $(u/L)$ for 2,2-dimethylpropane at 290.039 K.

Two terms. Standard deviation of $(u/L)^2 = 460 \text{ s}^{-2}$

$A_0/L^2 = (3561000 \pm 360) \text{ s}^{-2}$

$A_1/L^2 = (-2.426 \pm 0.006) \text{ s}^{-2} \cdot \text{Pa}^{-1}$

Three terms. Standard deviation of $(u/L)^2 = 370 \text{ s}^{-2}$

$A_0/L^2 = (3559740 \pm 610) \text{ s}^{-2}$

$A_1/L^2 = (-2.372 \pm 0.023) \text{ s}^{-2} \cdot \text{Pa}^{-1}$

$A_2/L^2 = (-4.62 \pm 1.97) \times 10^{-7}\text{ s}^{-2} \cdot \text{Pa}^{-2}$

<table>
<thead>
<tr>
<th>$&lt;p&gt;/\text{kPa}$</th>
<th>$&lt;A_0/L^2&gt;/\text{s}^{-2}$</th>
<th>$&lt;\delta(u/L)^2/\delta p&gt;/\text{s}^{-2} \cdot \text{Pa}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.753</td>
<td>3561000 ± 360</td>
<td>-2.426 ± 0.006</td>
</tr>
<tr>
<td>54.257</td>
<td>3561020 ± 400</td>
<td>-2.427 ± 0.007</td>
</tr>
<tr>
<td>49.691</td>
<td>3560800 ± 410</td>
<td>-2.421 ± 0.008</td>
</tr>
<tr>
<td>45.043</td>
<td>3560430 ± 300</td>
<td>-2.411 ± 0.006</td>
</tr>
<tr>
<td>40.268</td>
<td>3560100 ± 180</td>
<td>-2.401 ± 0.004</td>
</tr>
<tr>
<td>35.644</td>
<td>3560040 ± 230</td>
<td>-2.399 ± 0.006</td>
</tr>
<tr>
<td>31.042</td>
<td>3559920 ± 300</td>
<td>-2.394 ± 0.009</td>
</tr>
<tr>
<td>26.423</td>
<td>3559810 ± 550</td>
<td>-2.389 ± 0.020</td>
</tr>
</tbody>
</table>

FIGURE 6.5.
\[ A_0(\text{Ar}, 290.04 \text{ K})/L^2(290.04 \text{ K}) = (9947350 \pm 260) \text{ s}^{-2}. \text{ Thus} \]

\[ A_0(\text{C}_5\text{H}_{12}, 290.04 \text{ K})/A_0(\text{Ar}, 290.04 \text{ K}) = \frac{(3/5)[M(\text{Ar})/M(\text{C}_5\text{H}_{12})]}{\gamma_{\text{pg}}(\text{C}_5\text{H}_{12}, 290.04 \text{ K})} = (0.35786 \pm 0.00002), \text{ (6.4.6)} \]

where both the pathlength and the gas constant are eliminated, as are systematic uncertainties in the measured IPTS-68 temperatures. In order to calculate \( \gamma_{\text{pg}} \) the molar mass of the sample is required. The chemical purity will be discussed in chapter eight, but if purity is assumed then the molar mass is \( (0.072150 \pm 0.000006) \text{ kg mo}^{-1} \), and hence \( \gamma_{\text{pg}}(\text{C}_5\text{H}_{12}, 290.04 \text{ K}) = (1.07722 \pm 0.00021). \) The corresponding value for the perfect-gas molar heat capacity at constant pressure is

\[ C_{p,m}^{\text{pg}}(\text{C}_5\text{H}_{12}, 290.04 \text{ K})/R = 13.95 \pm 0.04, \text{ (6.4.7)} \]

where the uncertainties in the molar masses have been combined in quadrature with a 99 per cent confidence interval for the value of equation (6) to obtain the quoted uncertainty.

These results may be compared with the recent work of Hossenlopp and Scott who measured the vapour heat capacity and enthalpy of vapourisation \( \Delta H^{\text{m}}_V \) of 2,2-dimethylpropane by vapour-flow calorimetry.\(^5\) The heat-capacity measurements were used to obtain values of \( C_{p,m}^{\text{pg}}/R \) at ten temperatures between 298.15 and 523.15 K, and these may be represented by the empirical equation:

\[ C_{p,m}^{\text{pg}}(T)/R = 1.296 + 4.2808 \times 10^{-2}(T/K) + 1.4274 \times 10^{-5}(T/K)^2 \]
\[ - 3.0308 \times 10^{-8}(T/K)^3, \text{ (6.4.8)} \]

with a standard deviation of 0.009 (well within the experimental
uncertainties of \( \pm 0.2 \) per cent). The short extrapolation to 290.04 K yields \( \frac{C^p_{\text{pg}}}{R} = 14.18 \), and that value exceeds the value of equation (7) by 1.6 per cent. This discrepancy could arise from a systematic error of 0.13 per cent in the measured ratio \( A_0(C_5H_{12}, 290.04 \text{ K})/A_0(\text{Ar}, 290.04 \text{ K}) \). The enthalpies of vapourisation, obtained at eight temperatures between 264.81 and 303.50 K, were combined with values of the derivative \( (dp^{1+g}/dT) \) of the vapour pressure (derived from the literature) to obtain the differences \( \Delta_{1m}^{\text{gV}} \) between the molar volumes of the liquid and vapour at each temperature using Clapeyron's equation:

\[
(dp^{1+g}/dT) = \frac{\Delta_{1m}^{\text{gH}}}{T} \Delta_{1m}^{\text{gV}}. \tag{6.4.9}
\]

These were then combined with estimates of the molar volume of the liquid to obtain the molar volume of the coexisting vapour, and hence to find the second virial coefficients by neglecting the higher-order terms in the equation of state. The results were represented by

\[
B(T)/ \text{cm}^3\cdot\text{mol}^{-1} = 494 - (373260 \ K/T) + 552\{1 + (1622.5 \ K/T) - \exp(1622.5 \ K/T)\} \tag{6.4.10}
\]

with an estimated uncertainty of \( \pm 30 \text{ cm}^3\cdot\text{mol}^{-1} \) at 264.81 K, decreasing to \( \pm 10 \text{ cm}^3\cdot\text{mol}^{-1} \) at 303.50 K. The second acoustic virial coefficient at 290.04 K obtained by differentiation of equation (10) using \( \gamma_{\text{pg}} = 1.076 \), namely \( (-1600 \pm 20) \text{ cm}^3\cdot\text{mol}^{-1} \), is in good agreement with the acoustic result. However, the closeness of this agreement may be fortuitous in view of the neglect of the third virial coefficient in the determination of equation (10).
REFERENCES

1. Ewing, M. B. To be published.


7.1 INTRODUCTION

The advantages of spherical resonators in comparison with the conventional cylindrical designs for low-frequency (2 to 20 kHz) measurements of sound speeds have been discussed in chapter three. Briefly, the absence of shear boundary-layer damping for the radial modes, and the favourable surface area to volume ratio in a sphere, lead to very high quality factors (as high as 25 000 in this work), and to boundary-layer corrections that are about a factor of 10 smaller than for a comparable cylinder. In addition, the radial resonance frequencies are insensitive to geometric imperfections in the resonator, and hence for practical purposes only the volume of the cavity need be known. In recent years M. R. Moldover and J. B. Mehl have demonstrated that speeds of sound can be measured to a relative precision approaching $1 \times 10^{-6}$ using a spherical resonator with phase-sensitive detection. $^{1,2,3,4}$ It was therefore decided to construct a similar apparatus in this laboratory, initially for use in a limited range of temperatures. The apparatus has been used to obtain highly precise speeds of sound in argon at the temperature of the triple point of water (such as would be required in a re-determination of the gas constant), and to supplement the results...
obtained in 2,2-dimethylpropane using the cylindrical resonator.

7.2 THE ACOUSTIC RESONATOR

In the design of the resonator, three important factors were considered: the radius of the sphere, the wall material and thickness, and the location of the transducers.

The size of the resonator determines the range of operating frequencies and the magnitude of the thermal-boundary-layer corrections. The fractional correction \( g_S/f_{On} \) to the frequency of the \( n \)th radial resonance that arises from damping in the thermal boundary layer is related to the radius \( a \) by

\[
(g_S/f_{On}) = (1/a)^{\frac{1}{2}}(\gamma - 1)(D_t/2\nu_{On} u)^{\frac{1}{2}},
\]

where \( D_t = (K/\rho c_p) \) is the thermal diffusivity of the gas, and hence a large cavity is favoured. Use of higher-order resonances would also reduce the magnitude of the correction, but at the expense of increased bulk losses and overlap between modes. The choice \( a = 60 \) mm was felt to be a suitable compromise between the conflicting requirements for small boundary-layer perturbations and a uniform temperature in the cavity. With \( u = 300 \) m·s\(^{-1} \) the first five radial resonances occur at frequencies between 3.6 and 13.7 kHz, sufficiently low to avoid vibrational-relaxation dispersion in most polyatomic gases.

The walls of the resonator, having a finite mechanical compliance, vibrate in response to an acoustic pressure. In the approximation that the fundamental 'breathing mode' resonance of the spherical shell is isolated, Greenspan derived the following expression for the specific acoustic admittance of the wall when excited by radial waves:
\[
y_{m,r} = -i2\pi f_0 u_A \{1 - (f/f_{\text{res}})\}, \tag{7.2.2}
\]

where

\[
A = \frac{(1 + 2t^3)}{2(t^3 - 1)}\rho \frac{u_s^2}{a}, \tag{7.2.3}
\]

and the breathing-mode resonance frequency is given by

\[
f_{\text{res}} = \frac{\left(\frac{3}{2} - 1\right)/2\pi^2(t - 1)(1+2t^3)}{(u_s/a)}, \tag{7.2.4}
\]

and where \( t = \frac{b}{a} \), \( b \) is the outer radius, \( \rho \) is the density of the wall, and \( u_s \) is the speed of longitudinal sound waves in the wall. The effect of this motion is to reduce the ideal resonance frequencies by the fraction

\[
(\Delta f_{\text{el}}/f_0) = A\rho u^2/[1 - (f_0/f_{\text{res}})^2]. \tag{7.2.5}
\]

Equation (5) is applicable at frequencies below \( f_{\text{res}} \) provided that the motion is purely radial. Brass and aluminium alloys were considered as possible materials for construction, but with brass \( f_{\text{res}} \) would be rather low (about 15 kHz with \( a = 60 \text{ mm} \) and \( t = 1.2 \)), and so aluminium was chosen. The resonance frequency \( f_{\text{res}} \) is not very sensitive to the thickness of the wall, which primarily determines the magnitude of \( A \). The choice of aluminium alloy 6082 with \( a = 60 \text{ mm} \) and \( b = 72 \text{ mm} \) gives \( A = 2.7 \times 10^{-11} \text{ Pa}^{-1} \) and \( f_{\text{res}} = 21.2 \text{ kHz} \). Thicker walls could have been used to reduce the elastic response, but with the chosen dimensions \( (\Delta f_{\text{el}}/f) \) is typically less than \( 1 \times 10^{-5} \) for the first five radial modes at a gas pressure of 100 kPa and vanishes as \( \rho \to 0 \). Thus equation (4) constitutes a very small

\[\text{†} \quad \text{The sign of equation (4) is consistent with the time dependence } \exp(-i\omega t) \text{ used here.}\]
correction to $A_1$ and does not affect measurements of $A_0$.

The most efficient means of exciting the radial resonances of a spherical resonator is to place the source at the centre. Moldover et al.\(^1\) found that high order radial resonances could then be detected by another transducer at the surface with very high signal-to-noise ratios. However the presence of the transducer and its wires perturbs the resonance frequencies in a manner which is difficult to calculate. Following Moldover, it was decided to install both the transducers in the wall of the resonator, and to place them $\pi/2$ apart in order to avoid overlap between the first radial mode $(0,1)$ and the adjacent non-radial mode $(3,0)$ ($\nu_{30}/\nu_{01} = 1.005$).

The resonator is shown in cross-sections in figure 7.1. Its design was based on the one described by Moldover and Mehl.\(^2\) The two hemispheres were turned from aluminium alloy 6082 using a simple pivoting tool for the inner surface, and a special spherical turning tool for the outer surface. Prior to the final cutting, the two halves were annealed to relieve stress, and then retempered by precipitation treatment. Use of a tool of constant radius to turn each hemisphere insured that a very close match in the radii was achieved (better than 5 $\mu$m). Mechanical measurements on the finished resonator indicated that the true radius of curvature was $(60.16 \pm 0.01)$ mm at 293 K. The depths of the two hemispheres differed by 0.09 mm, but their mean was $(60.17 \pm 0.02)$ mm at 293 K. The two halves met at an interlocking step which insured that they were concentric when bolted together, and they touched only on the inner edge. The internal surface was polished by hand using an abrasive paste. Although some tooling marks remained (especially near to the opening of each half where chatter in the lathe caused more serious scoring) the surface had a near-mirror finish, as can be seen in plate 1. Unfortunately the polishing eroded the sharp corners between the inner surfaces and the rims; the radius of curvature appeared to be
FIGURE 7.1 THE SPHERICAL RESONATOR.

vent

coupling - tube adaptor

transducer port

bolt hole

two perpendicular cross-sections.

50 mm
about 0.5 mm and that would lead to a fractional increase in the volume of the resonator of $3 \times 10^{-5}$.

The transducer mounting holes shown in figure 7.1 allowed for various types of transducer to be installed. In this work, a small electrostatic capacitance transducer (see figure 4.3) was used as the source. The active surface of this device came flush with the interior of the cavity and, because the backplate was rigid, there should have been no perturbation to the normal modes. The detector was a small commercially-available electret capacitance microphone with its own built-in preamplifier. This device was mounted in the wall of the resonator and coupled to the interior using a 1 mm diameter waveguide of length 6 mm machined in a close fitting adaptor. A small space between the end of the waveguide and the active surface of the microphone was sufficiently large for the tube to be treated as open in the calculation of the coupling tube corrections. This transducer arrangement is non-selective; all modes of the cavity are excited, but because all have high quality factors the lower order resonances are clearly resolved and no serious overlap occurs. The measurement technique used does not rely on single-mode excitation.

The cavity was not sealed, but instead the gas was allowed to flow freely into and out of the resonator through a single 1 mm diameter hole drilled in the wall. The resonator was suspended on fine wires inside a brass vessel sealed with viton rubber '0'-rings, as shown in figure 7.2. Two access ports in the side of the vessel are provided so that the transducers may be changed without disassembly of the vessel. The electrical connections to the detector are made across vacuum leadthroughs in the cover of one of these access ports, while those to the source pass through similar leadthroughs in the lid of the vessel.

The temperature of the cavity was measured using a long-stem standard platinum resistance thermometer (Leads and Northrup, serial
FIGURE 7.2. CONTAINMENT VESSEL.
number 780308) recently calibrated on IPTS-68. The thermometer was inserted into the well shown in figure 7.2. The upper part of this well was a thin walled (1 mm wall, 8 mm inside diameter) stainless-steel tube silver soldered to the lower part, which consisted of a large copper block with a spherical surface bolted to the resonator. With the exception of the measurements described in chapter 9, all resistance measurements were performed using the A.S.L. A7 resistance comparison bridge with the Tinsley 100 Ω standard resistor (see chapter 6). The constants in equation (6.4.3) for the Leads and Northrup thermometer were

\[ R_0 = 25.56002 \, \Omega, \quad \alpha = 0.00392578 \, ^{\circ}C^{-1}, \quad \text{and} \quad \delta = 1.49578 \, ^{\circ}C \text{ at 1 mA,} \]

(7.2.6)

and the constants in the IPTS-68 deviation function for use between 90.188 K and 273.15 K were

\[ b_4 = -2.3 \times 10^{-5} \, K^{-1} \quad \text{and} \quad e_4 = 5.0 \times 10^{-5} \, K^{-4}. \]

(7.2.7)

The pressure of the sample gas was measured indirectly using a differential capacitance manometer (Baratron, model 221AH-A-10) to isolate the system from the pressure gauge. Pressures up to 115 kPa were measured with a precision of 1 Pa using the Ruska quartz-spiral gauge (see chapter 6), while those between 115 and 260 kPa were measured with a bronze-spiral gauge (Budenberg Ltd.) to an accuracy of 0.5 kPa and a precision of 0.1 kPa, using a Fortin barometer to measure the ambient pressure.

The vessel was connected via a stainless-steel bellows valve (sealed to the vessel using a Cajon VCR coupling and a nickel compression gasket) to the vacuum system, gas cylinders, and a sample ampoule. The pipework is shown schematically in figure 7.3. The 50 mm diameter oil-
FIGURE 7.3. EXTERNAL PIPEWORK (spherical resonator).

VALVES: 1 Edwards PV10 bellows-sealed diaphragm valve.  
2 Nupro SS-8BAW-TW all-welded stainless-steel valve, bellows-sealed.  
3 Nupro SS-4BW-TW.  
4 ‘o’-ring-sealed control valve.
vapour diffusion pump had an ultimate low pressure of 0.1 mPa, and the main vessel could be pumped down to an ultimate low pressure of about 0.3 mPa as indicated by an ionisation gauge in the connecting pipe.

The main vessel was immersed in a well-stirred water bath in which the temperature was controlled to ±1 mK by a commercial temperature controller driving a 500 W heater. The stirring efficiency was very high and as a result temperature gradients in the water bath were negligible. Unfortunately, the stirrer motor caused so much vibration that it was usually necessary to turn it off while the acoustic measurements were performed but, with a time constant between the bath and the resonator of several h, a few min (usually less than 2) without stirring generally caused no detectable change in the temperature of the resonator. When left unperturbed the temperature of the sphere would be constant to within a few tenths of a mK for 1 h or longer. A small 1 W heater was attached to the outer surface of the resonator and used to compensate for the fall in its temperature following a reduction in the gas pressure. If this had not been installed many hours would have been required for thermal equilibrium to be re-established following an expansion. With temperature differences between one part of the water bath and another of, at most, 10 mK and with a long time constant for heat exchange between the sphere and its container (about 4 h in argon and 30 min in helium) significant temperature gradients of the resonator can be discounted. Every indication implied that the measured temperature was indeed the true (IPTS-68) temperature of the gas.
The instrumentation used to measure resonance frequencies and widths is shown schematically in figure 7.4. The system was based in the Hewlett-Packard HP4192A impedance analyser, which consists of a digital frequency synthesiser and an amplitude and phase comparator. This instrument was operated under the remote control of a small computer (Hewlett-Packard HP87A with HP-IB interface). The internal time base of the HP4192A was phase locked to a calibrated 10 MHz quartz-crystal oscillator (this was housed in a thermostat built-in to a Hewlett-Packard HP5315B opt. 004 frequency counter). Since all synthesised frequencies had the relative accuracy of the 10 MHz reference signal, and since this was stated to be better than $1 \times 10^{-7}$, it was not necessary to employ a separate frequency counter.

The output signal of the HP4192A, which was variable between 0.005 and 1.100 V r.m.s., was amplified to a maximum 70 V r.m.s. and used to drive the source transducer. A resistive potential-difference divider in parallel with the output of the power amplifier was used to supply a reference signal of 1 V r.m.s. to the amplitude and phase comparator.

The detector had a sensitivity of about $10 \text{ mV} \cdot \text{Pa}^{-1}$ at audio frequencies, and was connected by a screened cable to a low-noise amplifier having a forward potential-difference gain of 1000. The signal was then further amplified, and filtered to remove low- and high-frequency noise, by a bandpass amplifier (potential difference gain 10; passband 1 to 100 kHz) and fed to the measurement channel of the amplitude and phase comparator. Under typical conditions near resonance, the signal at the input to the HP4192A was between 0.1 and 1 V r.m.s., and its amplitude and phase could be measured with a resolution of 0.01 per cent and 0.0002 rad, with a time constant of 1 s.

Circuit diagrams of the amplifiers constructed in this work are
FIGURE 7.4. INSTRUMENTATION (spherical resonator)

- Resonator
- Amplifier 60 dB
- Bandpass amplifier
- Oscilloscope
- Potential-difference divider
- Amplifier 36 dB
- Signal source, amplitude & phase comparator
- HB-1B interface
- HP-87 computer

Input: 200 V d.c.
- Received signal
- Ref. signal
- O/P 10 MHz

Flowchart details:
- Amplifier 60 dB connected to resonator.
- Bandpass amplifier connected to oscillator.
- Oscilloscope connected to potential-difference divider.
- Amplifier 36 dB connected to oscillator.
are given in appendix A7.1. Since the reference signal for the amplitude and phase measurements was derived from the output of the drive amplifier, the frequency response of the source electronics was not critical to the accuracy of the measurements. The amplitude-and-phase response of the bandpass amplifier used in the detector circuit was measured, but only the phase shift varied in the passband and this variation was too small to introduce significant systematic error into the measurements reported here.

The measurement procedure, which was similar to that adopted by Moldover and Mehl, was as follows. The centre frequencies $f_{cn}$ and half widths $g_{cn}$ of each of the lowest five radial modes were first estimated by sweeping the source frequency and observing the received signal on the oscilloscope. Then, under the control of the computer, the relative amplitude $\bar{a}$ and phase $\phi$ of the received signal were measured at a number of discrete frequencies in the vicinity of each resonance. Starting at a frequency near $f_{cn} - g_{cn}$, the frequency was increased to one near $f_{cn} + g_{cn}$ in ten even increments of $g_{cn}/5$, and then the sign of the increment was reversed and the frequency stepped back down to its initial value. At each frequency, the system paused for a time $1.4/g_{on}$ during which the amplitude at the detector settled to within 0.02 per cent of its final value, before recording the amplitude and phase. The measured values of $\bar{a}$ and $\phi$ were converted into the real and imaginary parts of the complex potential-difference ratio of the received and reference signals,

$$w = \bar{a} \cos(\phi) - i\bar{a} \sin(\phi), \quad (7.3.1)$$

and used to evaluate the constants $f_{cn}$, $A$, $B$, and $C$ in the theoretical form of the resonance:

$$w = \{Af/(f_{cn}^2 - f^2)\} + B - Cf. \quad (7.3.2)$$
The non-linear fitting procedure used in this analysis has been described in detail by Mehl. The twenty-two measurements of the complex variable $w$ are used to evaluate four complex constants in equation (2). In that equation, $F_{On} = f_{On} - i g_{On}$ in the complex resonance frequency, $A$ is a complex amplitude, and $B + Cf$ are the leading terms of a Taylor's series that accounts for the background signal from other modes and from direct coupling between source and detector. Use of careful screening reduced the electromagnetic crosstalk to a low level, and for the lowest three modes $|B + Cf|$ usually accounted for only a few per cent of the received signal. The background level was higher for the other modes (as much as 50 per cent at the lowest pressures in argon) and if resonances above the fifth had been employed then more terms in the Taylor's expansion may have been required. Figure 7.5 shows a typical set of results and their deviations from equation (2). With a precision of about 0.1 per cent in $w$, and with $Q$'s of several thousand, a resolution of about $10^{-7} f_{On}$ was achieved. The values of $f_{On}$ and $g_{On}$ obtained in this way were not sensitive to the range of frequencies studied: measurements between $f_{On} + 2 g_{On}$ and $f_{On} + 2 g_{On}$ yielded virtually identical values. No evidence was found that suggested that $f_{On}$ or $g_{On}$ were dependent on the amplitude of the standing wave.

No detailed investigation of the elastic response of the resonator's shell was undertaken in this work. However, the spectrum shown in figure 7.6 was obtained with the resonator evacuated, and it shows that the expected resonance in the vicinity of 20 kHz is very complex. Perhaps this was due to the presence of the thermometer well bolted to the resonator. There is some evidence of resonances at lower frequencies, particularly near 8.6 and 15 kHz.
FIGURE 7.5. Top: in-phase and quadrature components of \( w \) as a function of \( f \) near \( f_{01} \) in xenon at 298.15 K and 40 kPa. Bottom: deviation from equation (7.7.2) as a fraction of the maximum amplitude; □ in-phase  ○ quadrature
FIGURE 7.6. SHELL RESPONSE AT AN ARBITRARY PHASE.

ARBITRARY UNITS
7.4 THE ACOUSTIC MODEL

The various corrections that must be applied to the measured resonance frequencies in order to obtain accurate speeds of sound have been discussed in the previous chapters and in reference 2; they are simply collected here in a convenient form for ease of reference.

The observed complex resonance frequency $F_{0n}$ of the $n^{th}$ radial mode is given by

$$F_{0n} = f_{0n} - ig_{0n} = (\nu_{0n} u/2\pi a) - \sum_{j}(\Delta f + ig)_{j}, \quad (7.4.1)$$

where $(\nu_{0n} u/2\pi a)$ is the unperturbed resonance frequency, and $(\Delta f + ig)_{j}$ is the $j^{th}$ perturbation. Four mechanisms that lead to perturbation of the resonance frequencies are included in this model. The first, and for many gases the most important, is damping in the thermal boundary layer. This surface effect gives rise to a perturbation,

$$\Delta f_{S} + ig_{S} = (1 + i)(\gamma - 1)/2a(D_{t} f_{0n}/\pi)^{\frac{1}{2}}, \quad (7.4.2)$$

that has equal real and imaginary components. The classical mechanisms of thermal conductivity and shear viscosity combine with vibrational-relaxation absorption to give rise to an attenuation throughout the bulk of the fluid. In the absence of significant dispersion, only the resonance widths are perturbed and the contribution is

$$\Delta = ((D_{v}/3) + (\gamma - 1)D_{t} + (n_{b}/\zeta), \quad (7.4.3)$$

where $D_{v} = (n/\rho)$ is the viscous diffusivity, and the vibrational-relaxation contribution to the bulk viscosity $n_{b}$ is given by equation (2.7.10). At sufficiently high frequencies the real part of $F_{0n}$ would
also be perturbed, but such effects contribute less than $10^{-6} f_{On}$ in this work and have been neglected. The third perturbation arises from the presence of the filling and coupling tubes, which are both of diameter 1 mm. The detector's coupling tube is 6 mm long, while the filling tube is 12 mm long. Combination of equations (4.4.4), (3.4.12), and (3.2.24) shows that for one open tube of length $L$ and cross-sectional area $S$

$$\Delta f_t - ig_t = -(u/2\pi a)(S/4\pi a^2)\{\cot(\nu_{On} L/a) - i\alpha_{KH} L \cosec^2(\nu_{On} L/a)\}, \quad (7.4.4)$$

provided that the tube resonance is well separated from the resonances of the cavity. The fundamental resonance of the filling tube is approximately midway between the fourth and fifth modes, and for the detector's coupling tube the fundamental resonance is well above the range of operating frequencies. Under the conditions of the measurements reported here $g_t/f_{On}$ was always less than $10^{-6}$ and has been neglected. The total relative shifts in the resonance frequencies are $-11.1 \times 10^{-6}$ for the first mode, $-2.3 \times 10^{-6}$ for the second, $+0.3 \times 10^{-6}$ for the third, $+3.3 \times 10^{-6}$ for the fourth, and $-3.1 \times 10^{-6}$ for the fifth mode. The final perturbation arises from the elastic response of the resonator's walls and is given by equation (7.2.5), which for the chosen dimensions and material reduces to

$$\Delta f_{el} = 2.7 \times 10^{-11} f_{On} (pu^2/\text{Pa})/[1 - (f_{On}/21.2 \text{ kHz})^2]. \quad (7.4.5)$$

Greenspan has found the contributions to $g$ arising from losses in the wall and radiation from its outer surface to be negligible. 

A fifth perturbation, in effect a second-order correction to equation (2), arising from the temperature-jump effect may be significant at low gas pressures. A simple theory for monatomic gases is suggested in appendix A3.1, and will be compared with the experimental results in the following section.
7.5 SAMPLE RESULTS

The results presented in detail in this section were obtained in argon, xenon, and helium at temperatures close to 298.15 K, and in 2,2-dimethylpropane at temperatures close to 262.61 K (20 K below the normal boiling temperature).

The gas-handling procedures used were similar to those described in chapter six and will not be repeated here. No special precautions were taken in these experiments to insure rigorously high chemical purity, but the system was evacuated to 1 mPa (as indicated by an ionisation gauge in the vacuum line) and flushed with the gas prior to filling, except for the measurements in xenon where there was insufficient gas to flush the apparatus. Random errors in the measured temperatures are less than ±0.5 mK in these experiments, and were later reduced to ±0.1 mK by replacing the ageing A.S.L resistance bridge with a new instrument (see chapter nine). The rather limited precision of the pressure measurements above 115 kPa was just adequate for argon and helium, but was a definite limitation with xenon. All the measurements on 2,2-dimethylpropane were performed at lower pressures using the precise quartz-spiral gauge.

The argon was supplied by Cambrian gases Ltd. who estimated that the total mole fraction of impurities was less than $5 \times 10^{-6}$. Measurements were performed at 13 pressures between 20 and 241 kPa, at a mean temperature of 298.1495 K. The measured values of $T$, $p$, $f_{0n}$, and $g_{0n}$ are given in table 7.1. The uncertainties in $f_{0n}$ and $g_{0n}$, as estimated by the non-linear regression analysis, were always less than 0.2 per cent of $g_{0n}$, and the quality factors range from $Q_{01} = 920$ at the lowest pressure to $Q_{05} = 5500$ at the highest pressure studied.

The measured half-widths in argon may be compared with the directly-measured values of the transport coefficients $\eta(298.15 \text{ K}, p \to 0) = 22.6 \text{ mPa}\cdot\text{s}$ and $K(298.15 \text{ K}, p \to 0) = 17.7 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ taken from a recent review.9
TABLE 7.1 Resonance frequencies and half widths in argon at 298.15 K.

<table>
<thead>
<tr>
<th>p/kPa</th>
<th>T/K</th>
<th>n</th>
<th>$f_{On}$/Hz</th>
<th>$g_{On}$/Hz</th>
<th>$g_{S}$/Hz</th>
<th>$g_{b}$/Hz</th>
<th>$10^6\Delta_g/f$ (u/a)/10^3 s⁻¹</th>
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<td>T/K</td>
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<td>( g_{on}/\text{Hz} )</td>
<td>( g_s/\text{Hz} )</td>
<td>( g_b/\text{Hz} )</td>
<td>( 10^6 \Delta B/f )</td>
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Values of \((u/a)\) are adjusted to the mean temperature of 298.1495 K.
These are believed to be accurate to ± 0.2 per cent. The effects of pressure on both quantities are quite negligible under the conditions of these measurements, and perfect-gas values of $u$, $\rho$, and $c_p$ are sufficient for the calculation of $g_S$ and $g_b$; the results of such calculations are given in table 7.1. Typical contributions to the resonance half widths are shown as a continuous function of frequency in figure 7.7. The dominance of the surface term is evident. The measured half widths exceed those calculated by just a few per cent, but this additional loss remains unexplained. The 'excess' half widths $\Delta g = (g - g_S - g_b)$ are listed as fractions of the resonance frequencies in table 7.1, and selected values are plotted on figure 7.8. For the second and third modes, $\Delta g/f$ is less than $3 \times 10^{-6}$ and decreases with the pressure while, for the first and fourth modes, $\Delta g/f$ is systematically higher and tends to increase at low pressures. The larger excess half widths observed for the fifth mode are not typical; the usual behaviour was closer to that of the second and third modes. The rapid increase in $\Delta g_{05}/f_{05}$ with the pressure may be the result of a minor shell resonance near that frequency. There is some evidence for this in figure 7.6.

The resonance frequencies were corrected according to equation (7.4.1), adjusted to the mean temperature, and used to generate the values of $(u/a)$ listed in table 7.1. Typical contributions to the relative frequency shifts $\Delta f/f$ are shown as a continuous function of frequency in figure 7.7. Uncertainties in the thermal conductivity of dilute argon at 298.15 K should not lead to errors of more than $1 \times 10^{-6}$ in the corrected frequencies. Relative deviations of $(u/a)$ from the mean value for the first five modes at selected pressures are plotted on figure 7.8, and are at worst $-6 \times 10^{-6}$, and typically $\pm 2 \times 10^{-6}$. For the second, third, and fifth modes the deviations are consistently small and do not depend systematically on the pressure, while those of the first and fourth modes show greater scatter. It is significant that the excess
FIGURE 7.7. VARIOUS CONTRIBUTIONS TO 
g AND Δf IN ARGON AT 298.15 K AND 100 kPa.
FIGURE 7.8. TOP: excess half widths as a fraction of the resonance frequencies. BOTTOM: fractional deviations of ($\frac{u}{\mu}$) from the mean value for the first five radial modes. $\Delta u = u - u(\text{mean})$. 

× Ar, 121 kPa. △ Ar, 79 kPa. ◁ Ar, 40 kPa 
298.15 K.
half widths at the fifth mode do not appear to be associated with a
frequency shift; if the anomaly in $g_{55}$ does arise from a vibration in the
wall of the resonator then that motion must be out of phase with the
standing wave in the gas.

The mean values of $(u/a)^2$ obtained at each of the 13 pressures have
been analysed by fitting the equation:

$$(u/a)^2 = (A_0/a^2) + (A_1/a^2)p + (A_2/a^2)p^2 + \cdots , \quad (7.5.1)$$

and the results of two- and three-term analyses are given in table 7.2.
The first two terms of equation (1) fit the measurements with a standard
deviation of $5 \times 10^{-6}$ and, taking $\gamma = 0.039948 \text{ kg mol}^{-1}$ and $R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$, give $a = 60.1799 \text{ mm}$ in close agreement with the value $(60.17 \pm 0.02) \text{ mm}$ obtained by direct mechanical measurements. The value $\beta_a = (11.5 \pm 0.1) \text{ cm}^3 \text{ mol}^{-1}$, obtained for the second acoustic virial coefficient, is
in excellent agreement with those obtained by numerical integration of
the HFD-C$^{10}$ potential-energy function of argon $(11.5 \text{ cm}^3 \text{ mol}^{-1})$, and
from the square-well formula, equation (5.3.9), for the second virial
coefficients $(10.9 \text{ cm}^3 \text{ mol}^{-1})$. However, the deviations of $(u/a)^2$ from
the regression line, shown in figure 7.9, are clearly systematic and
inclusion of the third term of equation (1) in the analysis reduces the
standard deviation by a factor of 3. The three-term fit gives $\beta_a = (10.8
\pm 0.1) \text{ cm}^3 \text{ mol}^{-1}$ and $A_2 = (11.6 \pm 1.3) \times 10^{-11} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-2}$. This latter
value may be compared with the precise speed-of-sound measurements of El-
Hakeem,$^{11}$ which extend up to 7 MPa and give $A_2 = (273.15 \text{ K}) = (6.1 \pm 0.4) \times
10^{-11} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-2}$ and $A_2 (294.26 \text{ K}) = (5.5 \pm 0.8) \times 10^{-11} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-2}$.
Linear extrapolation gives $A_2 (298.15 \text{ K}) = 5.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-2}$, and
suggests that the value obtained above from this work is in significant
error. Since this discrepancy could arise from the neglect of the
temperature jump-effect, the results have been reanalysed after adjust-
FIGURE 7.9. Fractional deviations \( \Delta u^2/u^2 = (u^2 - u^2_{\text{calc.}})/u^2 \) of \( u^2 \) from regression lines. ○ unmodified two-term fit, □ three-term fit adjusted for the temperature-jump effect. Argon at 298.15 K.
### TABLE 7.2 Analysis of \((u/a)^2\) for argon at 298.15 K.

Two terms. Standard deviation of \((u/a)^2 = 150 \, s^{-2}\)

\[
\begin{align*}
(A_0/a^2) &= (2.855726 \pm 0.000007) \times 10^7 \, s^{-2} \\
(A_1/a^2) &= (1.326 \pm 0.006) \times 10^{-1} \, s^{-2} \cdot Pa^{-1}
\end{align*}
\]

Three terms. Standard deviation of \((u/a)^2 = 50 \, s^{-2}\)

\[
\begin{align*}
(A_0/a^2) &= (2.855755 \pm 0.000004) \times 10^7 \, s^{-2} \\
(A_1/a^2) &= (1.248 \pm 0.009) \times 10^{-1} \, s^{-2} \cdot Pa^{-1} \\
(A_2/a^2) &= (3.20 \pm 0.37) \times 10^{-8} \, s^{-2} \cdot Pa^{-2}
\end{align*}
\]

Uncertainties are one standard deviation.

### TABLE 7.3 Analysis of \((u/a)^2\) corrected for the temperature jump, argon at 298.15 K.

Two terms. Standard deviation of \((u/a)^2 = 90 \, s^{-2}\)

\[
\begin{align*}
(A_0/a^2) &= (2.855697 \pm 0.000004) \times 10^7 \, s^{-2} \\
(A_1/a^2) &= (1.341 \pm 0.004) \times 10^{-1} \, s^{-2} \cdot Pa^{-1}
\end{align*}
\]

Three terms. Standard deviation of \((u/a)^2 = 50 \, s^{-2}\)

\[
\begin{align*}
(A_0/a^2) &= (2.855713 \pm 0.000004) \times 10^7 \, s^{-2} \\
(A_1/a^2) &= (1.295 \pm 0.009) \times 10^{-1} \, s^{-2} \cdot Pa^{-1} \\
(A_2/a^2) &= (1.84 \pm 0.34) \times 10^{-8} \, s^{-2} \cdot Pa^{-2}
\end{align*}
\]

Uncertainties are one standard deviation.
ment according to equation (A3.1.25) using an accommodation coefficient \( \hbar = 1 \). This lowers \( (u/a)^2 \) by \( 15 \times 10^{-6} \) at the lowest pressure studied. The results of two- and three-term fits of equation (1) are given in table 7.3. Again, the three-term fit appears to be justified and the remaining differences between the measurements and the regression curve shown in figure 7.9 are clearly random. The value \( A_2 = (6.7 \pm 1.2) \times 10^{-11} \text{m}^2 \cdot \text{s}^{-2} \cdot \text{Pa}^{-2} \) obtained from this analysis does not differ significantly from the one estimated from El-Hakeem's results, and the second acoustic virial coefficient \( \beta_a = (11.2 \pm 0.1) \text{cm}^3 \cdot \text{mol}^{-1} \) is still in excellent agreement with independent estimations of the highest quality.

The research grade xenon was supplied by the British Oxygen Company who estimated that the total mole fraction of impurities was less than \( 5 \times 10^{-5} \). The actual purity of the gas must have been much worse than this because the gas mixed with air in the cylinder-head pressure regulator several times when samples were withdrawn for other purposes. Measurements were performed at 14 pressures between 15 and 237 kPa, at a mean temperature of 298.149 K. Most of the results were taken at pressures below 100 kPa to facilitate a comparison with the predictions of the temperature-jump theory. In addition, if the failure of kinetic theory predicted by Blatt actually occurred then the higher frequency modes should yield speeds of sound that approached the ideal-gas value much more rapidly than those obtained at lower frequencies. Unfortunately, the measurements were much less precise at the lower pressures where the above effects might be observed. The decline in precision was caused by instability in the source transducer which became quite pronounced at low pressures where the damping was slight and the excursions of the diaphragm large. In later work the Helinex membrane was replaced and the problem did not recur.

Nevertheless, at pressures above 50 kPa the random errors in \( f_{0n} \) and \( g_{0n} \) arising from this instability are estimated to be less than
1 \times 10^{-6} f_{on} \) (except for the first mode at the two highest pressures where fractional errors of about \( 5 \times 10^{-6} \) were estimated). At lower pressures the uncertainties increase to about \( 20 \times 10^{-6} f_{on} \) in the worst case. The measured values of \( T, p, f_{on}, \) and \( g_{on} \) are given in table 7.4, together with calculated values of \( g_5 \) and \( g_b \) based on the published low-pressure gas transport properties of xenon. The quality factors range from \( Q_{01} = 1100 \) at the lowest pressure to \( Q_{05} = 7800 \) at the highest pressure studied.

The excess half widths \( \Delta g \) are listed as fractions of the resonance frequencies in table 7.4, and selected values are plotted on figure 7.10. The general pattern is similar to that found in argon; the second, third, and fifth modes tend to exhibit smaller \( \Delta g \)'s than the first and fourth. Relative deviations of \( (u/a) \) from the mean value for the first five radial modes at selected pressures are also plotted on figure 7.10. The first mode is systematically low by a fraction of about \( 3 \times 10^{-6} \), while the remaining resonances are in very close agreement. The increased role of random errors in both the resonance frequencies and widths is evident at the lower pressure, but there is no evidence of dispersion to support Blatt's theory.

The mean values of \( (u/a)^2 \) are plotted as a function of the pressure for \( p \leq 100 \) kPa in figure 7.11, and the results of two- and three-term fits of these values to equation (1) are given in table 7.5. Derivatives of the measured values of \( (u/a)^2 \) from the regression lines are also shown on figure 7.11. Although the deviations of \( (u/a)^2 \) from the two-term fit are not excessive in view of the rather large random uncertainties in the resonance frequencies, they are clearly systematic and vary rapidly at low pressures. The three-term fit is able to accommodate much of this curvature and reduce the standard deviation to \( 4.5 \times 10^{-6} \) (from \( 8.5 \times 10^{-6} \)). The estimated values of the second acoustic virial coefficient are \( \beta_a = (-101.3 \pm 0.3) \text{ cm}^2 \cdot \text{mol}^{-1} \), from the two-term fit, and
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Values of $(u/a)$ are adjusted to the mean temperature of 298.1498 K.
FIGURE 7.10. TOP: excess half widths as a fraction of the resonance frequencies. BOTTOM: fractional deviations of \((u/a)\) from the mean value for the first five radial modes.

- O Xe, 236 kPa.
- O Xe, 200 kPa.
- O Xe, 160 kPa.
- X Xe, 120 kPa.
- Δ Xe, 80 kPa.
- V Xe, 40 kPa.

298.15 K.
FIGURE 7.11. TOP: $(u/a)^2$ vs. $p$ showing two-term fit. BOTTOM: fractional deviations of $(u/a)^2$ from regression lines. ○ two-term fit, □ three-term fit. Xenon at 298.15 K.
TABLE 7.5 Analysis of \((u/a)^2\) for xenon at 298.15 K.

Two terms. Standard deviation of \((u/a)^2\) = 74 s\(^{-2}\)

\[
(A_0/a^2) = (8.689659 \pm 0.00047) \times 10^6 \text{ s}^{-2}
\]

\[
(A_1/a^2) = (-3.553 \pm 0.009) \times 10^{-1} \text{ s}^{-2} \cdot \text{Pa}^{-1}
\]

Three terms. Standard deviation of \((u/a)^2\) = 39 s\(^{-2}\)

\[
(A_0/a^2) = (8.689874 \pm 0.003052) \times 10^6 \text{ s}^{-2}
\]

\[
(A_1/a^2) = (-3.654 \pm 0.022) \times 10^{-1} \text{ s}^{-2} \cdot \text{Pa}^{-1}
\]

\[
(A_2/a^2) = (7.02 \pm 1.93) \times 10^{-8} \text{ s}^{-2} \cdot \text{Pa}^{-2}
\]

Uncertainties are one standard deviation.

TABLE 7.6 Analysis of \((u/a)^2\) corrected for the temperature jump, xenon at 298.15 K.

Two terms. Standard deviation of \((u/a)^2\) = 60 s\(^{-2}\)

\[
(A_0/a^2) = (8.689578 \pm 0.000038) \times 10^6 \text{ s}^{-2}
\]

\[
(A_1/a^2) = (-3.544 \pm 0.007) \times 10^{-1} \text{ s}^{-2} \cdot \text{Pa}^{-1}
\]

Three terms. Standard deviation of \((u/a)^2\) = 32 s\(^{-2}\)

\[
(A_0/a^2) = (8.689752 \pm 0.000044) \times 10^6 \text{ s}^{-2}
\]

\[
(A_1/a^2) = (-3.627 \pm 0.019) \times 10^{-1} \text{ s}^{-2} \cdot \text{Pa}^{-1}
\]

\[
(A_2/a^2) = (7.28 \pm 1.62) \times 10^{-8} \text{ s}^{-2} \cdot \text{Pa}^{-2}
\]

Uncertainties are one standard deviation.
\( \beta_a = (-104.2 \pm 0.6) \text{ cm}^3 \cdot \text{mol}^{-1} \), from the three-term fit. Inclusion of the temperature-jump correction with an accommodation coefficient of unity does lead to a marginal improvement, but does not account for all the observed curvature at low pressures. The results of two- and three-term analyses are given in table 7.6. Unfortunately, the marginal improvement does not provide much evidence to support the temperature-jump theory. The higher pressure results have not been included so far because of the relatively large uncertainties in the measured pressures. However, all the results obtained with \( p \geq 25 \text{ kPa} \) may be represented by a linear isotherm with a standard deviation of \( 4 \times 10^{-6} \), and inclusion of the third term does not improve the fit. This analysis gives \( a = 60.176 \text{ mm} \) (using \( M = 0.13130 \text{ kg} \cdot \text{mol}^{-1} \)), fractionally \( 6 \times 10^{-5} \) below that obtained using argon, and \( \beta_a = (-101.10 \pm 0.04) \text{ cm}^3 \cdot \text{mol}^{-1} \). The values obtained for the second acoustic virial coefficient may be compared with that calculated from the interatomic potential-energy function of xenon. The value obtained from the simple form advocated by Maitland and Smith\(^{12}\) is \(-101.6 \text{ cm}^3 \cdot \text{mol}^{-1} \) at \( 298.15 \text{ K} \), while the square-well formula with \( g = 1.641, \sigma = 0.3534 \text{ nm}, \text{ and } \varepsilon/k = 202.9 \text{ K} \), giving the best fit to the second virial coefficients, predicts \( \beta_a(298.15 \text{ K}) = -101.8 \text{ cm}^3 \cdot \text{mol}^{-1} \). These values favour the results of two-term fits and suggest that the measurements at the lower pressures are in error.

Technical grade helium was supplied by the British Oxygen Company without specification of its purity. While high chemical purity was not felt to be important in these trial measurements, slow outgassing into the sample during the course of the experiment would alter the apparent shape of the isotherm. Since the speed of sound in helium is so high (about \( 1000 \text{ m} \cdot \text{s}^{-1} \) at \( 300 \text{ K} \)) even small amounts of heavier gases would have a serious consequence. In order to reduce this risk, the system was pressurised with helium to \( 250 \text{ kPa} \) and evacuated several times before filling. A high-purity gas-cylinder pressure regulator was used to avoid
contamination by air. The measurements were performed at seven pressures between 50 and 253 kPa using the first two radial modes only. The measured values of $T$, $p$, $f_{on}$, and $g_{on}$ are given in Table 7.7, together with the calculated contributions to the half widths (again based on published dilute-gas transport properties$^9$) and the corrected values of $(u/a)$ at the mean temperature of 298.1476 K.

These results are particularly interesting because the second radial resonance occurred at frequencies very close to a major resonance of the shell. While the $(\Delta g/f)'s$ for the first mode are very similar to those found in argon and xenon, the excess half width of the second mode increases rapidly with the pressure. Even more marked are the differences between the values of $(u/a)^2$ obtained from the two modes, as can be seen in Figure 7.12. At 252.3 kPa $(u/a)^2$ calculated from $f_{02}$ exceeds that calculated from the first mode by $310 \times 10^{-6}$, but the two modes differ by just $14 \times 10^{-6}$ as $p \to 0$ (on the basis of linear extrapolations). That the second mode yielded speeds of sound greater than those of the first (rather than less) is not surprising in view of the complexity of the shell's vibrations near 20 kHz. In fact, Figure 7.6 shows that $f_{02}$ was just above a shell resonance (rather than just below as predicted by simple theory). The very large perturbation to $f_{02}$ and the comparatively small change in $g_{02}$ is characteristic of wall motion that is in phase with the standing wave in the gas.

These results are also interesting because, in contrast to the heavy monatomic gases, the thermal accommodation coefficient at a perfectly smooth metal surface is much less than unity. There is good experimental evidence that $h \approx 0.17$ for helium at a bright platinum surface near 300 K.$^{13}$ If that value were applicable to the wall of the resonator then an accommodation length of 7.9 $\mu$m at 50 kPa would result, and the resonance frequencies would be shifted by about $88 \times 10^{-6}$. Surface imperfections increase the accommodation coefficient, but one
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Values of $(u/a)$ are adjusted to the mean temperature of 298.1476 K.
FIGURE 7.12. TOP: $(u/a)^2$ vs. $p$ from first (○) and second (□) modes showing two-term fits. BOTTOM: fractional deviations of $(u/a)^2$ from a two-term fit. Helium at 298.15 K.
cannot predict by how much. On this basis the deviations of \((u/a)^2\) from a two-term fit of equation (1) are simply accepted as experimental error and no correction has been attempted. These deviations are shown for the first mode, which should be reliable in every other respect, in figure 7.12. The regression analysis gives \(\beta_a = (21.9 \pm 0.1) \text{ cm}^3\text{ mol}^{-1}\) and \(a = 60.183 \text{ mm}\) or, if the lowest pressure is neglected, \(\beta_a = (22.01 \pm 0.03) \text{ cm}^3\text{ mol}^{-1}\) and \(a = 60.184 \text{ mm}\). Thus the second acoustic virial coefficient is in excellent agreement with the value \((21.93 \pm 0.01) \text{ cm}^3\text{ mol}^{-1}\) obtained by Gammon using pressures of up to 15 MPa.\(^{14}\) The contribution of \(A_2\) is quite negligible under the conditions reported here.\(^{15}\) The values of \(a\) obtained using argon and helium differ by a fraction of about \(6 \times 10^{-5}\). While this difference is rather more than expected on the basis of the uncertainties in the molar masses, it could easily arise from impurities in the helium. For example, a mole fraction \(3 \times 10^{-5}\) of neon or \(1.2 \times 10^{-5}\) of argon would increase the molar mass of the gas by a fraction \(12 \times 10^{-5}\) and thereby account for the differing values of \(a\).

The 2,2-dimethylpropane was supplied by Cambrian gases Ltd. The liquid was degassed by vacuum sublimation and dried over molecular sieves. Measurements were performed at 10 pressures between 4.9 and 31.7 kPa, at a mean temperature of 262.60 \(\pm\) 0 K. The maximum pressure is about 69 percent of the saturated vapour pressure, and was therefore sufficiently low to avoid the systematic errors, arising from the presence of adsorbed vapour on the walls of the resonator, that were observed by Moldover and Mehl.\(^3\) The measured values of \(T, p, f_{On}\), and \(g_{On}\) are given in table 7.8, and the quality factors vary from \(Q_{05} = 2900\) at 4.9 kPa to \(Q_{02} = 12900\) at 31.7 kPa.

In order to analyse the various contributions to the resonance half widths, the shear viscosity and thermal conductivity of 2,2-dimethylpropane were required. The viscosity was taken from the measurements by Diaz Peña et al\(^{16}\) which cover the range \(263.35 \leq T/\text{K} \leq 393.15\) and fit
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Values of $(u/a)$ are adjusted to the mean temperature of 262.6090 K.
\[ \eta(T) / \mu \text{Pa}\cdot\text{s} = 1.14 + 0.01985(T/K) \] (7.5.3)

with a standard deviation of 0.06 \( \mu \text{Pa}\cdot\text{s} \). Unfortunately, there are very few published measurements of the thermal conductivity, but the values \( K(323.15 \text{ K}) = 18.2 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \) and \( K(373.15 \text{ K}) = 23.5 \text{ mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1} \) obtained by Parkinson and Gray are thought accurate to \( \pm 2 \) per cent.\(^{17}\) Four different techniques were investigated for extrapolation of these data to lower temperatures. Two of these rely on a correlation between the thermal conductivity and the viscosity, and are the Eucken formula

\[ K = (\eta/M)(C_{V,m} + 9R/4), \] (7.5.4)

which is very nearly exact for monatomic gases, and the modified Eucken expression

\[ K = (\eta/M)(1.32C_{V,m} + 1.77R). \] (7.5.5)

Direct comparisons between the published results and the predictions of these methods at 323.15 \( \text{K} \) and 373.15 \( \text{K} \) are possible using the heat capacities given by equation (6.6.8). The Eucken formula predicts thermal conductivities of 2,2-dimethylpropane that are too low by about 20 per cent, but those of the modified method agree with the measurements to better than 1 per cent. The method of Roy and Thodos\(^{19}\) is based on the principle of corresponding states and, in the case of a saturated hydrocarbon, predicts

\[ \frac{\Gamma K}{\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}} = 41.6\{\exp(0.0464T_r) - \exp(-0.2412T_r)\} + C(-0.152T_r + 1.191T_r^2 - 0.039T_r^3), \] (7.5.6)

where \( \Gamma = (T_c/K)^{1/6}(M/\text{kg}\cdot\text{mol}^{-1})^{1/2}(p_c/\text{kPa})^{-2/3} \), \( T_r = T/T_c \), and \( T_c \) and \( p_c \)
are the critical temperature and pressure: 433.7 K and 3200 kPa for 2,2-dimethylpropane.\textsuperscript{20} The constant $c$ in equation (6) may be calculated on the basis of group contributions with the result $c = 62.7$.\textsuperscript{19} This method is in close agreement with the experimental value at 373.15 K but predicts a value that is too low by about 2 per cent at 323.15 K. The final extrapolation method, that due to Owens and Thodos,\textsuperscript{21} predicts that $K$ is proportional to $T^{-1.786}$. Thus, using the experimental value at 323.15 K, the Owens-Thodos method gives

$$K(T)/\text{mW\cdot m}^{-1}\cdot\text{K}^{-1} = 18.22(T/323.15\text{ K})^{-1.786} \quad (7.5.7)$$

for 2,2-dimethylpropane and this expression is in exact agreement with the experimental value at 373.15 K. This latter method was finally adopted and predicts $K(262.61\text{ K})/\text{mW\cdot m}^{-1}\cdot\text{K}^{-1} = 12.6$, 0.2 below the prediction of the modified Eucken formula and 0.7 above the value of equation (6).

The gas transport coefficients given by equations (3) and (7) were used in the calculations of the surface contributions $g_S$ and the classical bulk contributions

$$g_{CL} = (\pi f^2/u^2)[(4D_v/3) + (\gamma - 1)D_t] \quad (7.5.8)$$

to the resonance half widths. A 10 per cent error in the thermal conductivity would correspond to an error of about $6 \times 10^{-6}$ in $(g_S/f)$ in the worst case. The remaining excess half width $\Delta g = g - g_S - g_{CL}$ should equal the vibrational-relaxation contribution to the bulk attenuation:

$$g_{rel} = (\pi f^2/u^2)(\eta_{rel}/\rho). \quad (7.5.9)$$

In order to achieve the highest precision it was necessary to allow for the gas imperfections in these calculations. The second virial
coefficients and their first two temperature derivatives were estimated from equation (6.6.10), while $\gamma^p$ and $u^2$ were estimated from the uncorrected results. The results of these calculations are given in table 7.8, together with the $\Delta g$'s and corrected values of $(u/a)$ at the mean temperature. Typical contributions to the resonance half widths are illustrated in figure 7.13. The dominant contribution at the higher frequencies arises from the relaxation bulk attenuation, and the curve is drawn using $(g_{rel}/f^2) = 7.7$ ns (obtained from the fifth mode). Again, the first and fourth modes appear to have slightly increased half widths.

If $C_{pg}$ is taken as 13.0 R and $\gamma$ as 1.083 then equation (2.7.10) yields a single relaxation time of 42 ns at 8 kPa, which corresponds to $\tau(100$ kPa) = 3.4 ns. The value found at 298.15 K and 100 kPa was 4.2 ns.

Typical relative deviations of $(u/a)$ from the mean value for the first five modes are plotted in figure 7.13. Generally the agreement is very close, but the deviations of $(u/a)$ obtained with the first mode from the mean value depend systematically on the pressure. The maximum deviation of $7 \times 10^{-6}$ occurs at 14 kPa, about 30 per cent of the saturation pressure, and in the region where a precondensation anomaly has been predicted. If the observed deviations represent the full extent of the precondensation effect then no significant error should arise, but the predicted anomaly would have the same relative effect on each of the modes and hence would not be revealed by their comparison.

The isotherm was analysed by fitting equation (1) to the 50 individual determinations of $(u/a)^2$, and the results of two- and three-term fits are given in table 7.9. Clearly, three terms are required, and the deviations of the mean values of $(u/a)^2$ at each of the ten pressures from that fit are shown in figure 7.13. Inclusion of a fourth term did not improve the standard deviation of the fit, and there is no evidence to suggest that the temperature-jump effect is significant in these measurements. The coefficients estimated from the regression
FIGURE 7.13. TOP: various contributions to $g$ at 8 kPa. MIDDLE: fractional deviations of $(u/a)$ from the mean value for the first five radial modes. BOTTOM: fractional deviations of $(u/a)^2$ from a three-term fit. 2,2-Dimethylpropane at 262.61 K.
TABLE 7.9 Analysis of $(u/a)^2$ for 2,2-dimethylpropane at 298.15 K.

Two terms. Standard deviation of $(u/a)^2 = 424 \text{ s}^{-2}$

$$(A_0/a^2) = (9.06786 \pm 0.00014) \times 10^6 \text{ s}^{-2}$$

$$(A_1/a^2) = (-8.196 \pm 0.007) \text{ s}^{-2} \cdot \text{Pa}^{-1}$$

Three terms. Standard deviation of $(u/a)^2 = 65 \text{ s}^{-2}$

$$(A_0/a^2) = (9.06619 \pm 0.00004) \times 10^6 \text{ s}^{-2}$$

$$(A_1/a^2) = (-7.963 \pm 0.005) \text{ s}^{-2} \cdot \text{Pa}^{-1}$$

$$(A_2/a^2) = (-6.33 \pm 0.14) \times 10^{-6} \text{ s}^{-2} \cdot \text{Pa}^{-2}$$

Uncertainties are one standard deviation.
analysis using \( a = (60.137 \pm 0.0023) \) mm (see chapter eight) are

\[
\begin{align*}
A_0 &= (32.780.6 \pm 2.5) \text{ m}^2\text{s}^{-2}, \\
A_1 &= (-2.8791 \pm 0.0049) \times 10^{-2} \text{ m}^2\text{s}^{-2}\text{Pa}^{-1}, \text{ and} \\
A_2 &= (-2.29 \pm 0.14) \times 10^{-8} \text{ m}^2\text{s}^{-2}\text{Pa}^{-2},
\end{align*}
\tag{7.5.10}
\]

where the estimated uncertainties are based on 99 per cent confidence intervals with 47 degrees of freedom combined in quadrature with the uncertainty in the molar mass of the argon calibration gas. The molar heat capacity derived from \( A_0 \) is

\[
C_{p,m}^\text{pg}(\text{C}_5\text{H}_{12}, 262.16 \text{ K}) = (13.018 \pm 0.019)R,
\tag{7.5.11}
\]

and the second acoustic virial coefficient is

\[
\beta_a(\text{C}_5\text{H}_{12}, 262.16 \text{ K}) = (-917.7 \pm 3.3) \text{ cm}^3\text{mol}^{-1}.
\tag{7.5.12}
\]

Thus it would appear to be possible to obtain \( \beta_a \)'s with an accuracy of 0.2 per cent even under conditions where the accessible range of pressures is limited and a three-term fit is required. The value obtained for \( C_{p,m}^\text{pg}/R \) exceeds that extrapolated from the results of Hossenlopp and Scott (using equation 6.6.5) by 0.4 per cent. This small difference probably arises from the empirical nature of the extrapolation; the results obtained at 298.15 K agree with Hossenlopp's and Scott's direct measurements to well within the estimated error in the latter.
This appendix provides brief descriptions of the amplifiers constructed in this work. Figure 7.14 is a circuit diagram of the power amplifier used to drive the source transducer. The first stage consisted of two type-759 power operational amplifiers coupled in a bridge arrangement to give a total potential difference gain of 5. The signal was further boosted by a 1:12.6 step-up transformer to give an overall gain of 63 (36 dB) between 0.04 and 25 kHz. Figure 7.14 also shows the potential-difference divider used to supply the reference signal for the amplitude and phase measurements.

Capacitance transducers have very high impedances at audio frequencies; the commercial microphone used as the detector had its own built-in F.E.T preamplifier with an output of 1 kΩ. However, this device only serves as an impedance converter and provides no gain. A second preamplifier, based on the ZN459CP integrated circuit, was used to boost the output of the detector by a factor of 1000, and the circuit is shown in figure 7.15.

The circuit diagram of the bandpass amplifier is shown in figure 7.16. The input stage was generally used with unit gain so that the overall gain of the amplifier was 20 dB. Above 100 kHz and below 1 kHz, the frequency response fell off at 30 dB per octave, but between 2 and 20 kHz the response was flat to ±0.01 dB.

REFERENCES

FIGURE 7.14. POWER AMPLIFIER

FIGURE 7.15. PREAMPLIFIER

60 dB gain
15 MHz bandwidth.
FIGURE 7.16 BANDPASS AMPLIFIER.

OVERALL SCHEME

$E_{\text{in}}$ 1 MΩ, a.c. coupled.

Input stage

High-pass filter

Low-pass filter

$E_{\text{out}}$ 50 Ω, d.c. coupled.

Variable gain 0, 10, 20, & 30 dB

1 kHz cut-off, 30 dB/octave.

100 kHz cut-off, 30 dB/octave.

Passband gain 20 dB

INPUT STAGE

$E_{\text{in}}$

0.01 µF

1 MΩ

$E_{\text{out}}$


12. Reference 9, p. 582.


19. Reference 18, p. 481.


8.1 INTRODUCTION

The bulk of the experimental results obtained in argon and 2,2-dimethylpropane are reported in this chapter. In order to reduce the information to a manageable proportion, the individual frequency measurements at each temperature and pressure have been combined to yield mean values of \((u/L)\) or \((u/a)\). The results obtained in the cylindrical resonator fall into two groups: those below 295 K for which \(\delta = 0.158\), and those above 295 K for which \(\delta = 0.128\).\(^\dagger\) There appears to be a reversible change on the optimum value of \(\delta\) that occurred when the temperature passed through 295 K. The results obtained in the sphere also fall into groups because the resonator was disassembled several times during the course of the measurements and each reassembly resulted in a slight reduction of the effective mean radius.

All quoted temperatures refer to the International Practical Temperature Scale of 1968. Again, unless otherwise stated, all quoted uncertainties are ± one standard deviation only.

\(^\dagger\) The measurements from which the latter are derived were made in previous work, and that was presented for examination at University College London as part of the B.Sc. degree in 1980.
8.2 ARGON

Argon was used as the calibration gas for both resonators, and was supplied by Cambrian gases Ltd, except for the measurements at 273.16 K which were performed on high purity argon supplied by the British Oxygen Company Ltd.

The mean values of \((u/L)\), and their standard deviations, obtained in the cylindrical resonator are given in table 8.1. The pathlengths and second acoustic virial coefficients obtained from two-term weighted regression analyses of all the frequencies are given in table 8.3. The weighting scheme was described in chapter six, and there were at least 120 degrees of freedom in each of the analyses. The systematic uncertainties in \(R\), \(T\), and \(M\) have not been included in the estimated errors.

The results obtained in argon at 277, 287, 297, and 298.15 K using the spherical resonator are given in table 8.2, while those obtained at 273.16 K are given in chapter nine. The values given in table 8.2 are adjusted for the temperature-jump effect using an accommodation coefficient \(h=1.0\), and the results of two-term regression analyses of \((u/a)^2\) are given in table 8.4. Again, the systematic uncertainties in \(R\), \(T\), and \(M\) have been neglected. The neglect of \(A_2\) should lead to a systematic error of no more than \(+0.6\,\text{cm}^3\cdot\text{mol}^{-1}\) in \(\beta_a\). Values of \(\beta_a\) for argon between 270 and 330 K obtained from various sources are compared in figure 8.1, where the curve represents the results of numerical integration of the HFD-C pair-potential-energy function of argon.²

The results at 277, 287, and 297 K were obtained without disassembly of the sphere and the corresponding radii are consistent with an expansivity \((1/a)(\partial a/\partial T) = 22.8 \times 10^{-6}\,\text{K}^{-1}\) over that temperature range, which is almost identical with the expansivity of pure aluminium at 287 K.³
<table>
<thead>
<tr>
<th>$T = 251.156 , \text{K}$</th>
<th>$T = 290.262 , \text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p / \text{kPa}$</td>
<td>$(u/L)/s^{-1}$</td>
</tr>
<tr>
<td>96.137</td>
<td>2936.82 ± 0.23</td>
</tr>
<tr>
<td>86.996</td>
<td>2936.85 ± 0.21</td>
</tr>
<tr>
<td>77.849</td>
<td>2936.95 ± 0.22</td>
</tr>
<tr>
<td>68.845</td>
<td>2936.94 ± 0.23</td>
</tr>
<tr>
<td>59.288</td>
<td>2936.80 ± 0.24</td>
</tr>
<tr>
<td>50.744</td>
<td>2936.84 ± 0.26</td>
</tr>
<tr>
<td>41.805</td>
<td>2936.86 ± 0.21</td>
</tr>
<tr>
<td>33.330</td>
<td>2936.92 ± 0.21</td>
</tr>
<tr>
<td>24.676</td>
<td>2936.90 ± 0.24</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = 298.690 , \text{K}$</th>
<th>$T = 325.611 , \text{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p / \text{kPa}$</td>
<td>$(u/L)/s^{-1}$</td>
</tr>
<tr>
<td>97.660</td>
<td>3202.60 ± 0.23</td>
</tr>
<tr>
<td>86.845</td>
<td>3202.56 ± 0.24</td>
</tr>
<tr>
<td>74.791</td>
<td>3202.49 ± 0.22</td>
</tr>
<tr>
<td>65.327</td>
<td>3202.42 ± 0.24</td>
</tr>
<tr>
<td>56.103</td>
<td>3202.33 ± 0.27</td>
</tr>
<tr>
<td>43.264</td>
<td>3202.26 ± 0.27</td>
</tr>
<tr>
<td>30.629</td>
<td>3202.09 ± 0.22</td>
</tr>
<tr>
<td>19.688</td>
<td>3202.04 ± 0.32</td>
</tr>
</tbody>
</table>
TABLE 8.2 (u/a) for argon at various temperatures and pressures.

<table>
<thead>
<tr>
<th>T = 277.000 K</th>
<th>T = 287.000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p/kPa</strong></td>
<td><strong>(u/a)/10^3s^-1</strong></td>
</tr>
<tr>
<td>200.0</td>
<td>5.154721 ± 0.000012</td>
</tr>
<tr>
<td>170.0</td>
<td>5.154483 ± 0.000013</td>
</tr>
<tr>
<td>140.0</td>
<td>5.154262 ± 0.000008</td>
</tr>
<tr>
<td>110.10</td>
<td>5.154036 ± 0.000009</td>
</tr>
<tr>
<td>80.00</td>
<td>5.153816 ± 0.000009</td>
</tr>
<tr>
<td>50.00</td>
<td>5.153606 ± 0.000012</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T = 297.000 K</th>
<th>T = 298.150 K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p/kPa</strong></td>
<td><strong>(u/a)/10^3s^-1</strong></td>
</tr>
<tr>
<td>103.11</td>
<td>5.334860 ± 0.000011</td>
</tr>
<tr>
<td>88.99</td>
<td>5.334675 ± 0.000012</td>
</tr>
<tr>
<td>79.84</td>
<td>5.334565 ± 0.000013</td>
</tr>
<tr>
<td>70.02</td>
<td>5.334444 ± 0.000012</td>
</tr>
<tr>
<td>60.01</td>
<td>5.334331 ± 0.000015</td>
</tr>
<tr>
<td>50.01</td>
<td>5.334211 ± 0.000012</td>
</tr>
<tr>
<td>40.01</td>
<td>5.334086 ± 0.000014</td>
</tr>
<tr>
<td>29.99</td>
<td>5.333968 ± 0.000014</td>
</tr>
</tbody>
</table>

All values adjusted for the temperature-jump effect.
TABLE 8.3  $\beta_a$ for argon and $L$ for cylindrical resonator at various temperatures.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
<th>$L/\text{mm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>251.143</td>
<td>0.3 ± 0.9</td>
<td>100.500 ± 0.002</td>
</tr>
<tr>
<td>290.262</td>
<td>12.9 ± 1.0</td>
<td>100.569 ± 0.002</td>
</tr>
<tr>
<td>298.690</td>
<td>12.1 ± 1.0</td>
<td>100.531 ± 0.002</td>
</tr>
<tr>
<td>325.611</td>
<td>20.6 ± 1.3</td>
<td>100.593 ± 0.002</td>
</tr>
</tbody>
</table>

TABLE 8.4  $\beta_a$ for argon and $a$ for spherical resonator at various temperatures.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
<th>$a/\text{mm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.160</td>
<td>5.61 ± 0.02</td>
<td>60.1449 ± 0.0001</td>
</tr>
<tr>
<td>277.000</td>
<td>6.64 ± 0.06</td>
<td>60.1525 ± 0.0001</td>
</tr>
<tr>
<td>287.000</td>
<td>9.19 ± 0.04</td>
<td>60.1663 ± 0.0001</td>
</tr>
<tr>
<td>297.000</td>
<td>11.22 ± 0.08</td>
<td>60.1797 ± 0.0001</td>
</tr>
<tr>
<td>298.150</td>
<td>11.64 ± 0.03</td>
<td>60.1799 ± 0.0001</td>
</tr>
</tbody>
</table>

Two-term fits adjusted for the temperature-jump effect.
FIGURE 8.1 $\beta_a(T)$ for argon.

$\beta_a$ (cm$^3$ mol$^{-1}$)

$T/K$

- Sphere, 2 term fit.
- Sphere, 3 term fit.
- Cylinder.
- Colclough et al. (1)
- Numerical integration of HFD-C.
All the measurements on 2,2-dimethylpropane were performed using samples taken from a single cylinder supplied by Cambrian gases Ltd. The chemical purity was investigated by gas chromatography using a 46 m × 0.5 mm, surface-coated open-tubular column with a carbowax stationary phase (SCOT type GSC/CW20M, 35 500 effective plates) operating at 340 K. The injector was operated at 355 K and the flame-ionization detector at 400 K. With the helium carrier gas flowing at 2 cm³ min⁻¹, 5 mm³ samples of 2,2-dimethylpropane vapour were eluted in 240 s and a single impurity was detected with a retention time 1.08 times that of 2,2-dimethylpropane. The impurity peak was clearly resolved and, assuming equal sensitivity of the detector, the mole fraction was $(5 ± 1) \times 10^{-4}$. Samples that had been used in the cylindrical resonator gave identical results to those taken directly from the cylinder. Since the impurity was most probably a hydrocarbon of similar molar mass to 2,2-dimethylpropane, the relative effects on the measured heat capacities and acoustic virial coefficients should be less than 0.05 per cent.

The results obtained with the cylindrical resonator along 20 isothersms in the range $250 \leq T/K \leq 340$ are given in table 8.5. In order to avoid the adverse effects of adsorption, all the values reported here were obtained at pressures below 80 per cent of the saturation pressure. Measurements were attempted at high fractions of the saturation pressure, and showed a significant apparent dispersion and increased attenuation. For example, at 49 kPa and 265 K (96 per cent of the saturation pressure) the value of $(u/L)$ obtained near 60 kHz was lower than that obtained near 80 kHz by nearly 0.1 per cent.

The resonance frequencies have been analysed by fitting the first three terms of equation (6.4.2) using the weighting scheme described in chapter six. For the results obtained at temperatures below 295 K, the
<table>
<thead>
<tr>
<th>$T = 251.245$ K</th>
<th>$T = 255.056$ K</th>
<th>$T = 260.038$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$/kPa</td>
<td>$(u/L)/s^{-1}$</td>
<td>$p$/kPa</td>
</tr>
<tr>
<td>22.151</td>
<td>1744.35 ± 0.22</td>
<td>25.443</td>
</tr>
<tr>
<td>20.015</td>
<td>1746.48 ± 0.23</td>
<td>22.873</td>
</tr>
<tr>
<td>17.362</td>
<td>1749.19 ± 0.25</td>
<td>19.723</td>
</tr>
<tr>
<td>15.183</td>
<td>1751.34 ± 0.27</td>
<td>16.833</td>
</tr>
<tr>
<td>13.184</td>
<td>1753.08 ± 0.20</td>
<td>13.900</td>
</tr>
<tr>
<td>10.825</td>
<td>1755.39 ± 0.30</td>
<td>10.940</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.970</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = 264.972$ K</th>
<th>$T = 270.042$ K</th>
<th>$T = 275.086$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$/kPa</td>
<td>$(u/L)/s^{-1}$</td>
<td>$p$/kPa</td>
</tr>
<tr>
<td>40.855</td>
<td>1776.13 ± 0.13</td>
<td>48.070</td>
</tr>
<tr>
<td>36.450</td>
<td>1779.84 ± 0.22</td>
<td>44.362</td>
</tr>
<tr>
<td>32.510</td>
<td>1783.15 ± 0.19</td>
<td>40.340</td>
</tr>
<tr>
<td>28.403</td>
<td>1786.55 ± 0.19</td>
<td>36.642</td>
</tr>
<tr>
<td>24.473</td>
<td>1789.73 ± 0.17</td>
<td>32.262</td>
</tr>
<tr>
<td>20.147</td>
<td>1793.40 ± 0.19</td>
<td>28.314</td>
</tr>
<tr>
<td>15.073</td>
<td>1797.44 ± 0.17</td>
<td>24.068</td>
</tr>
<tr>
<td>10.212</td>
<td>1801.43 ± 0.20</td>
<td>19.701</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.408</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.263</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = 275.056$ K</th>
<th>$T = 275.086$ K (cont.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$/kPa</td>
<td>$(u/L)/s^{-1}$</td>
</tr>
<tr>
<td>61.398</td>
<td>1795.22 ± 0.13</td>
</tr>
<tr>
<td>55.195</td>
<td>1800.08 ± 0.13</td>
</tr>
<tr>
<td>48.869</td>
<td>1804.88 ± 0.13</td>
</tr>
<tr>
<td>42.513</td>
<td>1809.72 ± 0.13</td>
</tr>
<tr>
<td>38.458</td>
<td>1812.72 ± 0.14</td>
</tr>
<tr>
<td>34.496</td>
<td>1815.64 ± 0.17</td>
</tr>
<tr>
<td>30.406</td>
<td>1818.72 ± 0.15</td>
</tr>
</tbody>
</table>
TABLE 8.5 continued.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>p/kPa</th>
<th>(u/L)/s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 280.241 K</td>
<td>74.216</td>
<td>1803.91 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>66.915</td>
<td>1809.39 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>58.844</td>
<td>1815.32 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>51.363</td>
<td>1820.79 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>43.574</td>
<td>1826.34 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>35.854</td>
<td>1831.77 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>28.005</td>
<td>1837.26 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>20.252</td>
<td>1842.67 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>20.261</td>
<td>1842.68 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>14.771</td>
<td>1846.46 ± 0.22</td>
</tr>
<tr>
<td></td>
<td>9.686</td>
<td>1849.84 ± 0.20</td>
</tr>
<tr>
<td>T = 284.050 K</td>
<td>79.544</td>
<td>1813.75 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>70.492</td>
<td>1820.27 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>61.911</td>
<td>1826.31 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>53.250</td>
<td>1832.37 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>44.485</td>
<td>1838.46 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>35.494</td>
<td>1844.56 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>26.580</td>
<td>1850.59 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>17.770</td>
<td>1856.43 ± 0.24</td>
</tr>
<tr>
<td>T = 290.039 K</td>
<td>99.214</td>
<td>1822.19 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>90.781</td>
<td>1827.63 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>82.230</td>
<td>1833.32 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>73.693</td>
<td>1839.11 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>63.386</td>
<td>1846.03 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>54.152</td>
<td>1852.11 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>44.899</td>
<td>1858.06 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>35.361</td>
<td>1864.25 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>26.390</td>
<td>1869.91 ± 0.18</td>
</tr>
<tr>
<td>T = 290.293 K</td>
<td>87.818</td>
<td>1830.34 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>86.860</td>
<td>1836.63 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>75.779</td>
<td>1841.93 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>65.779</td>
<td>1847.68 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>56.528</td>
<td>1852.84 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>47.424</td>
<td>1859.99 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>40.116</td>
<td>1865.51 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>31.370</td>
<td>1870.92 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>23.365</td>
<td>1874.68 ± 0.16</td>
</tr>
<tr>
<td>T = 294.963 K</td>
<td>97.538</td>
<td>1840.28 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>86.860</td>
<td>1847.31 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>75.779</td>
<td>1854.24 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>65.779</td>
<td>1860.55 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>56.528</td>
<td>1866.38 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>47.424</td>
<td>1872.05 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>40.116</td>
<td>1876.66 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>31.370</td>
<td>1881.96 ± 0.19</td>
</tr>
<tr>
<td>T = 300.280 K</td>
<td>101.042</td>
<td>1857.37 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>92.034</td>
<td>1862.96 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>83.203</td>
<td>1868.35 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>74.736</td>
<td>1873.53 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>65.967</td>
<td>1878.75 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>57.259</td>
<td>1884.19 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>48.117</td>
<td>1889.59 ± 0.13</td>
</tr>
<tr>
<td></td>
<td>39.603</td>
<td>1894.54 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>30.357</td>
<td>1899.97 ± 0.14</td>
</tr>
<tr>
<td>T = 304.176 K</td>
<td>96.319</td>
<td>1874.32 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>86.166</td>
<td>1880.24 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>74.893</td>
<td>1886.86 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>67.170</td>
<td>1891.36 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>57.177</td>
<td>1897.23 ± 0.16</td>
</tr>
<tr>
<td>T = 304.176 K (cont.)</td>
<td>48.776</td>
<td>1902.02 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>39.486</td>
<td>1907.21 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>29.730</td>
<td>1912.21 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>20.176</td>
<td>1918.04 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>11.145</td>
<td>1922.86 ± 0.42</td>
</tr>
</tbody>
</table>
TABLE 3.5 continued.

<table>
<thead>
<tr>
<th>$T = 309.980 , K$</th>
<th>$T = 320.075 , K$</th>
<th>$T = 325.225 , K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p/kPa$</td>
<td>$(u/L)/s^{-1}$</td>
<td>$p/kPa$</td>
</tr>
<tr>
<td>102.144</td>
<td>1890.60 ± 0.11</td>
<td>99.153</td>
</tr>
<tr>
<td>91.005</td>
<td>1896.82 ± 0.12</td>
<td>91.485</td>
</tr>
<tr>
<td>82.218</td>
<td>1901.76 ± 0.13</td>
<td>83.951</td>
</tr>
<tr>
<td>73.438</td>
<td>1906.62 ± 0.12</td>
<td>76.870</td>
</tr>
<tr>
<td>64.668</td>
<td>1911.40 ± 0.13</td>
<td>68.714</td>
</tr>
<tr>
<td>55.734</td>
<td>1916.31 ± 0.13</td>
<td>61.322</td>
</tr>
<tr>
<td>46.514</td>
<td>1921.26 ± 0.13</td>
<td>52.415</td>
</tr>
<tr>
<td>37.530</td>
<td>1926.04 ± 0.15</td>
<td>44.085</td>
</tr>
<tr>
<td>28.075</td>
<td>1931.22 ± 0.17</td>
<td>35.026</td>
</tr>
<tr>
<td>19.267</td>
<td>1935.90 ± 0.24</td>
<td>26.205</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T = 329.955 , K$</th>
<th>$T = 334.934 , K$</th>
<th>$T = 340.170 , K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p/kPa$</td>
<td>$(u/L)/s^{-1}$</td>
<td>$p/kPa$</td>
</tr>
<tr>
<td>100.232</td>
<td>1957.31 ± 0.15</td>
<td>101.059</td>
</tr>
<tr>
<td>90.930</td>
<td>1961.76 ± 0.12</td>
<td>91.734</td>
</tr>
<tr>
<td>81.914</td>
<td>1965.87 ± 0.12</td>
<td>82.393</td>
</tr>
<tr>
<td>72.538</td>
<td>1970.27 ± 0.11</td>
<td>73.590</td>
</tr>
<tr>
<td>64.591</td>
<td>1973.90 ± 0.14</td>
<td>67.717</td>
</tr>
<tr>
<td>58.036</td>
<td>1976.92 ± 0.15</td>
<td>59.042</td>
</tr>
<tr>
<td>50.228</td>
<td>1980.49 ± 0.12</td>
<td>49.116</td>
</tr>
<tr>
<td>41.062</td>
<td>1984.60 ± 0.13</td>
<td>39.444</td>
</tr>
<tr>
<td>32.093</td>
<td>1988.67 ± 0.13</td>
<td>30.996</td>
</tr>
<tr>
<td>24.043</td>
<td>1992.45 ± 0.14</td>
<td>21.045</td>
</tr>
<tr>
<td>19.001</td>
<td>1994.81 ± 0.11</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 8.6 (u/a) for 2,2-dimethylpropane at various temperatures and pressures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (kPa)</th>
<th>(u/a)/10^3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>262.609</td>
<td>31.717</td>
<td>2.967696 ± 0.000003</td>
</tr>
<tr>
<td></td>
<td>29.005</td>
<td>2.971525 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>25.974</td>
<td>2.975750 ± 0.000005</td>
</tr>
<tr>
<td></td>
<td>22.954</td>
<td>2.979946 ± 0.000008</td>
</tr>
<tr>
<td></td>
<td>20.037</td>
<td>2.983977 ± 0.000008</td>
</tr>
<tr>
<td></td>
<td>17.013</td>
<td>2.988113 ± 0.000009</td>
</tr>
<tr>
<td></td>
<td>14.022</td>
<td>2.992218 ± 0.000012</td>
</tr>
<tr>
<td></td>
<td>11.020</td>
<td>2.996265 ± 0.000017</td>
</tr>
<tr>
<td></td>
<td>7.995</td>
<td>3.000343 ± 0.000005</td>
</tr>
<tr>
<td></td>
<td>4.931</td>
<td>3.004467 ± 0.000004</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (kPa)</th>
<th>(u/a)/10^3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>277.001</td>
<td>60.003</td>
<td>3.012715 ± 0.000008</td>
</tr>
<tr>
<td></td>
<td>49.993</td>
<td>3.025277 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>39.990</td>
<td>3.037630 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>29.953</td>
<td>3.049823 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>19.976</td>
<td>3.061767 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>9.981</td>
<td>3.073573 ± 0.000007</td>
</tr>
<tr>
<td></td>
<td>4.973</td>
<td>3.079437 ± 0.000009</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (kPa)</th>
<th>(u/a)/10^3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.002</td>
<td>72.915</td>
<td>3.055658 ± 0.000007</td>
</tr>
<tr>
<td></td>
<td>56.954</td>
<td>3.073880 ± 0.000007</td>
</tr>
<tr>
<td></td>
<td>42.979</td>
<td>3.089534 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>26.983</td>
<td>3.107113 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>12.984</td>
<td>3.122229 ± 0.000008</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T (K)</th>
<th>p (kPa)</th>
<th>(u/a)/10^3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.147</td>
<td>75.986</td>
<td>3.116241 ± 0.000005</td>
</tr>
<tr>
<td></td>
<td>70.044</td>
<td>3.122366 ± 0.000005</td>
</tr>
<tr>
<td></td>
<td>65.018</td>
<td>3.127515 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>60.046</td>
<td>3.132579 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>55.004</td>
<td>3.137686 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>49.988</td>
<td>3.142738 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>45.016</td>
<td>3.147727 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>40.036</td>
<td>3.152689 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>34.940</td>
<td>3.157766 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>30.013</td>
<td>3.162623 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>25.020</td>
<td>3.167528 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>20.053</td>
<td>3.172375 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>15.027</td>
<td>3.177262 ± 0.000004</td>
</tr>
<tr>
<td></td>
<td>9.977</td>
<td>3.182137 ± 0.000006</td>
</tr>
<tr>
<td></td>
<td>5.001</td>
<td>3.186988 ± 0.000009</td>
</tr>
</tbody>
</table>
pathlengths were interpolated between the calibration results at 251.16 and 290.26 K while, for the remaining results, the interpolation was between the values at 298.69 and 325.61 K (see table 8.3). Values of $C_{p,m}^R$, $\beta_a$, and $\gamma_a$ obtained from these analyses are listed in table 8.7. The estimated error limits are based on 99 per cent confidence intervals with $\infty$ degrees of freedom and, for the heat capacities, include the uncertainties propagated from the calibration measurements and the uncertainty in the molar masses (combined in quadrature). Values obtained from unweighted regressions do not differ significantly from those given in table 8.7.

The results obtained using the spherical resonator are given in table 8.6, and the heat capacities and acoustic virial coefficients derived from three-term fits are listed in table 8.8, where the quoted error limits were calculated as for table 8.7. Full details of the analyses are given in chapter seven. The radius $a$ of the sphere at 277, 287, and 298.15 K was obtained by calibration measurements in argon at those temperatures. The values required at 262.61 and 325.04 K were extrapolated from the measurements in argon at 273.16 and 298.15 K respectively using the expansivity of pure aluminium.$^3$ The values obtained for the second acoustic virial coefficient are plotted on figure 8.2 and show good agreement between the two resonators although there is much greater scatter in the results obtained using the cylindrical resonator.

The $\gamma_a$'s obtained in the spherical resonator are plotted on figure 8.3 and the equation:

$$\gamma_a(T)/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1} = 0.429 - 4.458 \times 10^{-3} \exp(1600 K/T)$$ (8.3.1)

fits the results with a standard deviation of 0.016 cm$^3$\cdot mol$^{-1}$\cdot kPa$^{-1}$ (with two degrees of freedom); equation (1) was used to draw the curve shown
### Table 8.7

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$C_{pg}^{m}/R$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
<th>$\gamma_a/(\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>251.245</td>
<td>12.59 ± 0.29</td>
<td>-1886 ± 511</td>
<td>-11.83 ± 15.10</td>
</tr>
<tr>
<td>255.056</td>
<td>12.67 ± 0.12</td>
<td>-1957 ± 173</td>
<td>-5.63 ± 4.83</td>
</tr>
<tr>
<td>260.038</td>
<td>12.74 ± 0.10</td>
<td>-2050 ± 115</td>
<td>-0.45 ± 2.52</td>
</tr>
<tr>
<td>264.972</td>
<td>12.94 ± 0.04</td>
<td>-1933 ± 40</td>
<td>-1.00 ± 0.74</td>
</tr>
<tr>
<td>270.042</td>
<td>13.23 ± 0.04</td>
<td>-1782 ± 33</td>
<td>-1.77 ± 0.52</td>
</tr>
<tr>
<td>275.066</td>
<td>13.27 ± 0.08</td>
<td>-1850 ± 52</td>
<td>0.05 ± 0.68</td>
</tr>
<tr>
<td>275.086</td>
<td>13.47 ± 0.03</td>
<td>-1734 ± 15</td>
<td>-1.24 ± 0.20</td>
</tr>
<tr>
<td>280.241</td>
<td>13.67 ± 0.03</td>
<td>-1670 ± 15</td>
<td>-1.06 ± 0.16</td>
</tr>
<tr>
<td>284.050</td>
<td>13.83 ± 0.04</td>
<td>-1628 ± 17</td>
<td>-0.90 ± 0.16</td>
</tr>
<tr>
<td>290.039</td>
<td>13.95 ± 0.04</td>
<td>-1610 ± 15</td>
<td>-0.29 ± 0.11</td>
</tr>
<tr>
<td>290.293</td>
<td>14.00 ± 0.04</td>
<td>-1573 ± 15</td>
<td>0.67 ± 0.15</td>
</tr>
<tr>
<td>294.963</td>
<td>14.27 ± 0.04</td>
<td>-1534 ± 13</td>
<td>-0.43 ± 0.10</td>
</tr>
<tr>
<td>300.280</td>
<td>14.50 ± 0.04</td>
<td>-1474 ± 12</td>
<td>-0.49 ± 0.09</td>
</tr>
<tr>
<td>304.176</td>
<td>14.60 ± 0.04</td>
<td>-1427 ± 15</td>
<td>-0.48 ± 0.12</td>
</tr>
<tr>
<td>309.980</td>
<td>14.87 ± 0.04</td>
<td>-1383 ± 12</td>
<td>-0.32 ± 0.09</td>
</tr>
<tr>
<td>320.075</td>
<td>15.33 ± 0.04</td>
<td>-1288 ± 15</td>
<td>-0.27 ± 0.07</td>
</tr>
<tr>
<td>325.225</td>
<td>15.45 ± 0.04</td>
<td>-1274 ± 12</td>
<td>-0.10 ± 0.10</td>
</tr>
<tr>
<td>329.955</td>
<td>15.65 ± 0.04</td>
<td>-1234 ± 10</td>
<td>-0.07 ± 0.09</td>
</tr>
<tr>
<td>334.934</td>
<td>15.84 ± 0.04</td>
<td>-1185 ± 15</td>
<td>-0.18 ± 0.12</td>
</tr>
<tr>
<td>340.170</td>
<td>15.97 ± 0.04</td>
<td>-1152 ± 15</td>
<td>-0.24 ± 0.12</td>
</tr>
</tbody>
</table>

### Table 8.8

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$C_{pg}^{m}/R$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
<th>$\gamma_a/(\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>262.609</td>
<td>13.018 ± 0.019</td>
<td>-1917.7 ± 3.4</td>
<td>-1.524 ± 0.090</td>
</tr>
<tr>
<td>277.001</td>
<td>13.669 ± 0.021</td>
<td>-1723.0 ± 1.9</td>
<td>-0.980 ± 0.028</td>
</tr>
<tr>
<td>287.002</td>
<td>14.087 ± 0.023</td>
<td>-1601.3 ± 1.7</td>
<td>-0.740 ± 0.018</td>
</tr>
<tr>
<td>298.147</td>
<td>14.545 ± 0.024</td>
<td>-1484.8 ± 1.1</td>
<td>-0.530 ± 0.013</td>
</tr>
<tr>
<td>325.041</td>
<td>15.600 ± 0.028</td>
<td>-1260.5 ± 2.4</td>
<td>-0.167 ± 0.028</td>
</tr>
</tbody>
</table>
FIGURE 8.2. $\beta_d(T)$ for 2,2-dimethylpropane from unconstrained three-term fits.
FIGURE 8.3 $\gamma_a(T)$ for 2,2-dimethylpropane.
in figure 8.3. Values of $\gamma_a$ calculated from equation (1) were used to systematically adjust the measured resonance frequencies which were then reanalysed to obtain the final results listed in tables 8.9 (cylindrical resonator) and 8.10 (spherical resonator), where the quoted error limits were calculated as for table 8.7. While the constraint of $A_2$ has little effect on the already precise results of the spherical resonator, the second acoustic virial coefficients calculated from the results of the cylindrical resonator are much smoother, and this can be seen in figure 8.4. The curve shown in figure 8.4 is based on a Taylor's series expansion:

$$
\beta_a(T) = \beta_a(T_0) + \delta T \beta'_a(T_0) + \frac{1}{2} (\delta T)^2 \beta''_a(T_0) + \frac{1}{6} (\delta T)^3 \beta'''_a(T_0)
$$

(8.3.2)

in which $\delta T = (T - T_0)$, $T_0 = 325.041$ K, and the first three temperature derivatives of $\beta_a$ and their standard deviations at $T = T_0$, given by

$$
\beta'_a(T_0) = (7.20 \pm 0.19) \text{ cm}^3\text{mol}^{-1}\text{K}^{-1}
$$

$$
\beta''_a(T_0) = (-0.0766 \pm 0.0180) \text{ cm}^3\text{mol}^{-1}\text{K}^{-2}
$$

$$
\beta'''_a(T_0) = (0.00146 \pm 0.00060) \text{ cm}^3\text{mol}^{-1}\text{K}^{-3}
$$

(8.3.3)

were determined by least-squares regression analysis of the five determinations of $\beta_a$ in the spherical resonator. The standard deviation of those values from equation (2) is 0.9 cm$^3$mol$^{-1}$ with two degrees of freedom, and the maximum deviation is 1.0 cm$^3$mol$^{-1}$ at 277 K. The second acoustic virial coefficients determined in the cylindrical resonator with $\gamma_a$ constrained by equation (1) are in remarkably good agreement with equation (2), except below 265 K where they are increasingly more negative. If the three lowest temperatures in table 8.9 are neglected then the remaining values are lower than those of equation (3) by an average of 6 cm$^3$mol$^{-1}$, or about 0.4 per cent.
<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$C_{p,m}^{pg}/R$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>251.245</td>
<td>$12.41 \pm 0.08$</td>
<td>$-2210.3 \pm 47.3$</td>
</tr>
<tr>
<td>255.045</td>
<td>$12.60 \pm 0.04$</td>
<td>$-2089.0 \pm 25.7$</td>
</tr>
<tr>
<td>260.030</td>
<td>$12.78 \pm 0.04$</td>
<td>$-1996.1 \pm 18.2$</td>
</tr>
<tr>
<td>264.967</td>
<td>$12.96 \pm 0.03$</td>
<td>$-1910.5 \pm 6.8$</td>
</tr>
<tr>
<td>270.040</td>
<td>$13.20 \pm 0.03$</td>
<td>$-1815.1 \pm 6.2$</td>
</tr>
<tr>
<td>275.066</td>
<td>$13.37 \pm 0.03$</td>
<td>$-1765.4 \pm 7.0$</td>
</tr>
<tr>
<td>275.086</td>
<td>$13.45 \pm 0.03$</td>
<td>$-1747.6 \pm 3.4$</td>
</tr>
<tr>
<td>280.241</td>
<td>$13.66 \pm 0.03$</td>
<td>$-1683.2 \pm 2.9$</td>
</tr>
<tr>
<td>284.050</td>
<td>$13.81 \pm 0.03$</td>
<td>$-1637.6 \pm 3.1$</td>
</tr>
<tr>
<td>290.039</td>
<td>$14.05 \pm 0.03$</td>
<td>$-1562.1 \pm 2.6$</td>
</tr>
<tr>
<td>290.293</td>
<td>$14.00 \pm 0.03$</td>
<td>$-1571.7 \pm 2.9$</td>
</tr>
<tr>
<td>294.963</td>
<td>$14.30 \pm 0.03$</td>
<td>$-1517.0 \pm 2.6$</td>
</tr>
<tr>
<td>300.280</td>
<td>$14.50 \pm 0.03$</td>
<td>$-1475.2 \pm 2.1$</td>
</tr>
<tr>
<td>304.176</td>
<td>$14.59 \pm 0.03$</td>
<td>$-1433.9 \pm 2.9$</td>
</tr>
<tr>
<td>309.980</td>
<td>$14.88 \pm 0.03$</td>
<td>$-1380.2 \pm 2.1$</td>
</tr>
<tr>
<td>320.075</td>
<td>$15.31 \pm 0.03$</td>
<td>$-1298.1 \pm 2.3$</td>
</tr>
<tr>
<td>325.225</td>
<td>$15.47 \pm 0.03$</td>
<td>$-1265.0 \pm 2.3$</td>
</tr>
<tr>
<td>329.955</td>
<td>$15.67 \pm 0.03$</td>
<td>$-1227.5 \pm 2.1$</td>
</tr>
<tr>
<td>334.934</td>
<td>$15.84 \pm 0.03$</td>
<td>$-1195.0 \pm 3.1$</td>
</tr>
<tr>
<td>340.170</td>
<td>$15.97 \pm 0.03$</td>
<td>$-1174.4 \pm 2.6$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$C_{p,m}^{pg}/R$</th>
<th>$\beta_a/(\text{cm}^3\cdot\text{mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>262.609</td>
<td>$13.018 \pm 0.019$</td>
<td>$-1917.7 \pm 1.8$</td>
</tr>
<tr>
<td>277.001</td>
<td>$13.670 \pm 0.021$</td>
<td>$-1722.1 \pm 0.5$</td>
</tr>
<tr>
<td>287.002</td>
<td>$14.086 \pm 0.023$</td>
<td>$-1601.7 \pm 0.2$</td>
</tr>
<tr>
<td>298.147</td>
<td>$14.544 \pm 0.024$</td>
<td>$-1486.0 \pm 0.2$</td>
</tr>
<tr>
<td>325.041</td>
<td>$15.601 \pm 0.026$</td>
<td>$-1259.7 \pm 0.5$</td>
</tr>
</tbody>
</table>
FIGURE 8.4. $\beta_d(T)$ for 2,2-dimethylpropane from constrained three-term fits.

- $\beta_d$ (cm$^3$ mol$^{-1}$)
- $T/K$

- Cylindrical resonator.
- Spherical resonator.

---
equation (8.3.2)
The values of \( C_{p,m}^{pg} / R \) given in tables 8.9 and 8.10 are plotted on figure 8.5; the curve is given by

\[
C_{p,m}^{pg}(T) / R = -3.309 + 7.9084 \times 10^{-2} (T/K) - 6.4340 \times 10^{-5} (T/K)^2
\]  

(8.3.4)

and fits the results of the spherical resonator with a standard deviation of 0.008. Equation (3) is in excellent agreement with the direct measurements by Hossenlopp and Scott at 298.15 K, but is lower by 0.37 per cent at 323.15 K. This discrepancy is significant in view of the estimated uncertainty of less than ±0.2 per cent in the calorimetric result. It could arise in part from an error in the assumed expansivity of the resonator between 298.15 and 325.04 K, or from contamination of the gas sample. The heat capacities are sensitive to small errors in the speeds of sound; the fractional error induced in \( C_{p,m}^{pg} \) by an error in \( A_0 \) is greater by a factor of \( 1/(\gamma_{pg} - 1) \approx 15 \) at 325 K.

The heat capacities obtained using the cylindrical resonator appear to be systematically too low by about 1 per cent, and this suggests that the speeds of sound obtained were systematically too high by about 0.07 per cent. Such an error is consistent with the presence of unresolved higher modes in the cavity.

The relation between the second virial coefficient and \( \beta_a \), namely

\[
\beta_a(T) = 2B(T) + F_1(T)B'(T) + F_2(T)B''(T)
\]  

(8.3.5)

in which

\[
F_1(T) = 2(\gamma_{pg} - 1)T, \quad \text{and}
\]

\[
F_2(T) = \{(\gamma_{pg} - 1)^2 / \gamma_{pg}\}T^2,
\]  

(8.3.6)

is an inhomogeneous linear second-order differential equation containing
FIGURE 8.5. $C_{p,m}^{0g}(T)/R$ for 2,2-dimethylpropane.
variable coefficients. In principle, if $\beta_a(T)$, $F_1(T)$, and $F_2(T)$ were known functions then an exact particular solution $B_p(T)$ of equation (5) could be found and that would exactly specify $\beta_a(T)$. However, the general solution for $B(T)$ is given by the sum of a particular solution $B_p(T)$ and the complementary solution $B_c(T)$ of the corresponding homogeneous equation in which $\beta(T) = 0$ and, to be general, the solution of the homogeneous equation must involve two arbitrary constants. Thus equation (5) cannot be solved unless boundary conditions are imposed in order to specify these constants. Suitable boundary conditions are values of $B$ at two temperatures of values of $B$ and $B'$ (or even $B''$) at a single temperature. If such results are available from another source then an approximate solution can be obtained for $B(T)$ by numerical means using values of $\beta(T)$ and $\gamma_{pg}(T)$ determined at a number of temperatures.

Alternatively, if the functional form of $B(T)$ were known then the numerical values of the constants in that form could be determined from measurements of $\beta_a(T)$ and $\gamma_{pg}(T)$ at a sufficient number of temperatures, without the need to draw on information from other sources. While the exact functional form of $B(T)$ is again unknown, empirical representations are known that accurately fit second virial coefficients over limited ranges of temperature. In an extended range of temperatures a less empirical approach may be required, such as the use of $\beta_a(T)$ to determine a set of adjustable parameters in an assumed intermolecular pair-potential energy function. A very simple analysis of this type is to use the 'square-well potential' of equation (5.3.8). Substitution of the square-well formula for $B$ (equation 5.3.9) in equation (5) gives

$$
\beta_a = 2a + 2b\{1 - (c/T)(\gamma_{pg} - 1) + [(\gamma_{pg} - 1)^2/2\gamma_{pg}](c/T)(2 + (c/T))\}\exp(c/T),
$$

(8.3.7)

where
\[ a = \left(2\pi \sigma^3 / 3\right)g^3, \quad b = \left(2\pi \sigma^3 / 3\right)(1 - g^3), \quad \text{and} \quad c = (\varepsilon / k). \quad (8.3.8) \]

Equation (7) fits the five determinations of \( \beta_a \) made with the spherical resonator with a standard deviation of 1.1 cm\(^3\) mol\(^{-1}\) (two degrees of freedom) when \( a, b, \) and \( c \) are adjusted in a non-linear regression analysis, and the resulting expression for the second virial coefficient is

\[ B(T) / \text{cm}^3 \cdot \text{mol}^{-1} = 206.9 - 187.08 \exp(520 K/T). \quad (8.3.9) \]

The values of \( \gamma_{pg} \) determined in this work were used in the above analysis, but replacement of the suspect value at 325 K with the value 1.0681 interpolated from the results of Hossenlopp and Scott has a negligible effect on the virial coefficients.

Non-linear regression analysis can be avoided if \( B \) is assumed to have a polynomial representation of the form:

\[ B(T) = \sum_j a_j (T/K)^j, \quad (8.3.10) \]

which when substituted in (5) gives

\[ \beta_a(T) = 2 \sum_j a_j \left\{1 + j(\gamma_{pg} - 1) + j(j - 1)(\gamma_{pg} - 1)^2 / 2\gamma_{pg}\right\}(T/K)^j. \quad (8.3.11) \]

The coefficients \( a_j \) may then be determined by multiple linear regression analysis. The series with \( j = 0, -1, \) and \(-2\) can be an accurate representation of second virial coefficients and, in common with the square-well formula, has the correct behaviour for \( T \to 0 \). The same five values of \( \beta_a \) are accommodated with a standard deviation of 1.0 cm\(^3\) mol\(^{-1}\) and give

\[ B(T) / \text{cm}^3 \cdot \text{mol}^{-1} = -520.8 + 354.480 (T/K)^{-1} - 1.36220 \times 10^8 (T/K)^{-2}; \quad (8.3.12) \]
inclusion of an additional term in $T^{-3}$ did not improve the fit. However, the series with $j=0$, $1$, and $2$ fits the five $\beta_a$'s with a standard deviation of 2.1 cm$^3$ mol$^{-1}$ and gives

$$B(T)/\text{cm}^3\text{ mol}^{-1} = -5504.3 + 24.78C2(T/K) - 3.0948 \times 10^{-2}(T/K)^2$$

(8.3.13)

despite the unrealistic constraint of $B''(T)$ to a constant value. Second virial coefficients calculated at various temperatures from equations (9), (12), and (13) are compared in table 8.11. Although the three functional forms all fit the second acoustic virial coefficients closely, quite large differences exist between the values obtained for $B$ at 260 K. This may arise in part from the use of three adjustable parameters to fit just five values but must also indicate the inadequacy of assuming any arbitrary functional form. Nevertheless, equation (9) and (12) are in close agreement, and the maximum difference of 2.9 cm$^3$ mol$^{-1}$ at 260 K amounts to just 0.2 per cent; a very small imprecision for second virial coefficients. The inadequacy of equation (13) is clearly shown in figure 8.6 where $\beta_a(T)$ calculated in turn from equations (9), (12), and (13), using equation (4) to evaluate the coefficients of $B'$ and $B''$, is compared with the smoothed measurements as represented by equation (2). The original measurements are also plotted in figure 8.6. The series of negative powers gives results that are almost coincident with equation (2), while equation (9) shows only slightly greater deviations, but equation (13) provides a much poorer representation.

Analyses of this type do not necessarily provide complete solutions for $B(T)$ because explicit account of the complementary solution $B_c(T)$ has not been taken. Formally, when $\beta_a(T)$ in equation (5) is replaced by the functional representation given by equation (7) a new, approximate, differential equation is obtained whose exact particular solution is $B_p(T) = a + b \exp(c/T)$. Similarly, when $\beta_a(T)$ is replaced by the right-
FIGURE 8.6. Deviations $\Delta \beta_a = \beta_a - \beta_a$ (equation 2) of calculated second acoustic virial coefficients and of the experimental values from equation (8.3.2).
hand side of equation (11) a new differential equation is obtained whose exact particular solution is given by equation (10). The close agreement between equation (12) and the experimental results is only proof that a good approximation to the particular solution has been found.

In order to find the required complementary solution, the solution of the homogeneous equation:

\[ 0 = 2B_c(T) + F_1(T)B_c'(T) + F_2(T)B_c''(T) \]  

(8.3.14)

is required such that \( B_p(T) + B_c(T) \) satisfies two independent initial or boundary conditions. Unfortunately there are wide variations among the published second virial coefficients of 2,2-dimethylpropane below 350 K which make it very difficult to choose an initial value for \( B \) and quite impossible to place any realistic constraint on an initial value of \( B' \). However, the heat capacity measurements by Hossenlopp and Scott provide independent values of \( B'' \) at two temperatures in the range studied here:

\[
B''(298.15 \text{ K}) = (-0.089 \pm 0.016) \text{ cm}^3\text{ mol}^{-1}\text{K}^{-2} \\
B''(323.15 \text{ K}) = (-0.056 \pm 0.010) \text{ cm}^3\text{ mol}^{-1}\text{K}^{-2} \]  

(8.3.15)

and hence by differentiation, the complementary solution accompanying equation (12) must satisfy

\[
B''_c(298.15 \text{ K}) = (-0.012 \pm 0.016) \text{ cm}^3\text{ mol}^{-1}\text{K}^{-2} = 0, \text{ and} \\
B''_c(323.15 \text{ K}) = (-0.003 \pm 0.010) \text{ cm}^3\text{ mol}^{-1}\text{K}^{-2} = 0 \]  

(8.3.16)

Thus \( B''_c(323.15 \text{ K}) \) and all higher derivatives at that temperature may be taken as zero, and differentiation of equation (5) then shows that \( B'_c(323.15 \text{ K}) = 0 \) and hence that \( B_c(T) = 0 \) for all \( T \). The same result is obtained for the complementary solution accompanying equation (9), but
equation (13) gives $B''(T) = -0.062 \text{ cm}^3/\text{mol} \cdot \text{K}^{-2}$ for all $T$ and this differs significantly from the boundary value at 298.15 K.

The use of functional forms can be completely avoided in a direct numerical integration of equation (5) using the Adams method with appropriate initial or boundary conditions. This technique provides an approximate solution of the exact differential equation, based on Taylor's series expansions of $B$ spanning the intervals between the experimental temperatures, rather than the exact solutions of approximate differential equations found above. A condition for numerical stability is that the three terms in equation (5) must be of comparable magnitude, but here at 325 K: $2B = -1439 \text{ cm}^3/\text{mol}$, $F_1 B' = 204 \text{ cm}^3/\text{mol}$, and $F_2 B'' = -25 \text{ cm}^3/\text{mol}$ (from equation 12). Trial solutions using initial values taken from equation (12) or equation (9) were indeed found to be highly sensitive to the starting values. For substances with smaller heat capacities the coefficients $F_1$ and $F_2$ would be much larger and this instability would not arise.

Thus, in the absence of more precise boundary conditions, equation (12) appears to be the best representation of the second virial coefficients over the range of temperatures studied. Random errors in $\beta_a$ are about $\pm 1 \text{ cm}^3/\text{mol}$ and should cause errors no greater than that in the derived second virial coefficients. Perhaps the small differences (less than $3 \text{ cm}^3/\text{mol}$) between equations (9) and (12) represent the likely systematic errors arising from the imposition of the chosen functional form. The values of equation (12) are compared with second virial coefficients taken from the literature in figure 8.7. There are clearly wide discrepancies between the reported values but those of Hamann and Lambert lie close to the present results. The values recommended by Dymond and Smith appear to be too low by about 70 cm$^3$/mol at 300 K. Below that temperature, only the results obtained by Hossenlopp and Scott are available for comparison. These are more
FIGURE 8.7. $B(T)$ for 2,2-dimethylpropane from various sources.

- reference 5, 2 term fits.
- reference 5, 3 term fits.
- reference 6.
- reference 7.
- reference 8.
- reference 9.
- reference 10.
- reference 11.

1 reference 4.
2 equation (8.3.12)
### TABLE 8.11  Second virial coefficients of 2,2-dimethylpropane.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$B/(\text{cm}^3\cdot\text{mol}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>equ. (9)</td>
</tr>
<tr>
<td>260</td>
<td>-1175.4</td>
</tr>
<tr>
<td>280</td>
<td>-991.4</td>
</tr>
<tr>
<td>300</td>
<td>-851.9</td>
</tr>
<tr>
<td>320</td>
<td>-743.2</td>
</tr>
<tr>
<td>340</td>
<td>-656.6</td>
</tr>
</tbody>
</table>

### TABLE 8.12  $\gamma_a(T) - G(T)$ for 2,2-dimethylpropane.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$G/(\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1})$</th>
<th>$(\gamma_a - G)/(\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>262.609</td>
<td>0.410</td>
<td>-1.934</td>
</tr>
<tr>
<td>277.001</td>
<td>0.312</td>
<td>-1.292</td>
</tr>
<tr>
<td>287.002</td>
<td>0.261</td>
<td>-1.001</td>
</tr>
<tr>
<td>298.147</td>
<td>0.215</td>
<td>-0.745</td>
</tr>
<tr>
<td>325.041</td>
<td>0.140</td>
<td>-0.307</td>
</tr>
</tbody>
</table>

### TABLE 8.13  Third virial coefficients of 2,2-dimethylpropane.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$C/(\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1})$</th>
<th>$C/(\text{cm}^6\cdot\text{mol}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>-1.02</td>
<td>-830 000</td>
</tr>
<tr>
<td>280</td>
<td>-0.58</td>
<td>-370 000</td>
</tr>
<tr>
<td>300</td>
<td>-0.34</td>
<td>-120 000</td>
</tr>
<tr>
<td>320</td>
<td>-0.19</td>
<td>50 000</td>
</tr>
<tr>
<td>340</td>
<td>-0.10</td>
<td>150 000</td>
</tr>
</tbody>
</table>
negative than equation (12) by between 20 and 50 cm$^3$·mol$^{-1}$, and this is consistent with the neglect of the third virial coefficient in that work.

The third virial coefficient can also be estimated in the range of temperatures studied. $\gamma_a$ is related to the coefficient $\tilde{C}$ in the pressure explicit equation of state (equation 5.2.5) by

$$\gamma_a = (\gamma^p + 2)\tilde{C} + 2(\gamma^p - 1)T\tilde{C}' + ((\gamma^p - 1)^2/2\gamma^p)\tilde{C}'' + G,$$

(8.3.17)

where $G(T)$ is the function defined by equation (5.2.16). Equation (12) was used to calculate $G$ at the five temperatures studied in the spherical resonator, and the resulting values of $G$ and $\gamma_a - G$ are given in table 8.12; equation (9) yields virtually identical results. $\tilde{C}$ was constrained to the form

$$\tilde{C} = a + b \exp(c/T),$$

(8.3.18)

which on substitution in (17) gives

$$\left(\gamma_a - G\right)/(\gamma^p + 2) = a + b\{1 - 2\{(\gamma^p - 1)/(\gamma^p + 2)\}(c/T) + \{(\gamma^p - 1)^2/2\gamma^p(\gamma^p + 2)\}(c/T)\{2 + (c/T)\}\} \exp(c/T),$$

(8.3.19)

and the coefficients $a$, $b$, and $c$ were determined by non-linear regression analysis with the result:

$$\tilde{C}(T)/\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1} = 0.148 - 1.689 \times 10^{-3}\exp(1700 K/T).$$

(8.3.20)

Values of $\tilde{C}$ and the third virial coefficient $C = RT\tilde{C} + B^2$ at various temperatures are listed in table 8.13. Uncertainties arising from random errors in the third acoustic virial coefficients are quite small;
equation (19) fits \((\gamma_a - G)\) with a standard deviation of \(0.015 \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{kPa}^{-1}\). However, systematic errors arising from the neglect of the fourth acoustic virial coefficient, and from the imposition of the chosen functional form on \(C\), may be rather larger. Variations amongst the reported values of \(C\) are very large. For example at 303.2 K, Ewing and Marsh give \((-9.4 \pm 3.0) \times 10^5 \text{ cm}^6\cdot\text{mol}^{-2}\), Silderberg et al give \((2.82 \pm 0.14) \times 10^5 \text{ cm}^3\cdot\text{mol}^{-2}\), while equations (12) and (20) yield \(C = -0.9 \times 10^5 \text{ cm}^6\cdot\text{mol}^{-2}\). Adsorption may well be responsible for the discrepancies between the reported values, and the results obtained here should be reliable to \(\pm 1 \times 10^{-5} \text{ cm}^6\cdot\text{mol}^{-2}\).

REFERENCES

CHAPTER 9  METROLOGICAL APPLICATIONS OF SPHERICAL RESONATORS

9.1 INTRODUCTION

9.2 SAMPLE RESULTS

9.3 CONCLUSION

9.1 INTRODUCTION

It was noted in chapter five that accurate measurements of $A_0$ in gases have applications in metrology. Probably the most challenging of these is a redetermination of the gas constant because, for this purpose, accurate knowledge of the mean molar mass of the sample gas is required. In addition, an absolute measurement of $A_0$ must be performed rather than measurements of the ratio $A_0(T_1)/A_0(T_2)$ that are sufficient in acoustic thermometry. Thus use of a spherical resonator will require an accurate measurement of its effective internal radius. Since the radial resonance frequencies are insensitive to small geometric imperfections in the resonator, it would be sufficient to measure the volume of the cavity, and this could be accomplished by weighing, first with the resonator empty and then with it filled with a fluid of known density. It would probably be most convenient to perform such measurements at room temperature and then to measure the expansivity between that temperature and the temperature of the triple point of water, $T(s+1+g,H_2O)$. If water is used as the calibration fluid then its isotopic composition must be known, but the density of standard mean ocean water is known with a fractional uncertainty of only a few parts per million at temperatures between 273.16 and 300 K. The density of mercury is known
with even higher precision, and its use would avoid the problems of dissolved air but a stainless-steel resonator would probably be required to avoid corrosion. A calibration of the volume of the resonator used in this work has not been attempted, mainly because it became apparent that there was a misfit between the two halves. This increases the volume available to the calibration fluid (perhaps by as much as $1 \times 10^{-4}$) and could have caused slow leakage during the lengthy weighing procedure. Nor has the isotopic and chemical purity of the sample gas been investigated in detail. Nevertheless detailed trial measurements of the speed of sound in argon divided by the mean radius of the resonator have been performed at temperatures very close to $T(s+1+g,H_2O)$. These results are reported here and represent the highest precision that can currently be attained with the equipment used.

9.2 SAMPLE RESULTS

The gas used in these measurements was research grade argon supplied by the British Oxygen Company (B.O.C. special gases Ltd). B.O.C. state that the total mole fraction of impurities is less than $5 \times 10^{-6}$ and give the following assay:

\[
\begin{array}{cccccc}
\text{Impurity B:} & N_2 & O_2 & H_2 & CO_2 & H_2O & \text{Hydrocarbons} \\
10^6 x_B & 2 & <1 & <1 & 0.5 & 1 & 0.5 \\
\end{array}
\]

(9.2.1)

and the combined influence of these is to increase $A_0$ by no more than $5 \times 10^{-6}$. The gas used by Quinn et al.\textsuperscript{3} in their acoustical redetermination of $R$ came from the same source and was found to have a molar mass $M = (39.9476 \pm 0.0002)$ g·mol\textsuperscript{-1}. Unless production techniques at B.O.C. have been altered it seems unlikely that the molar mass of the gas used
in this work differs significantly from their value.

Before filling with the sample gas the system was baked under vacuum for 48 h to reduce the risk of outgassing during the course of the experiment. The pipework, valves, and Baratron were baked at 375 K, while the temperature of the main vessel was held at 335 K (higher temperatures would have depolarised the detector). The pressure as measured by the ionization gauge was reduced to 0.3 mPa, and the system was then flushed three times with the gas before finally filling to 250 kPa. A high-purity stainless-steel pressure regulator was used with the gas cylinder so that contamination with air during filling was avoided.

A new resistance measuring bridge was also obtained for this work (Tinsely model 5840) with its own built-in thermostatically controlled reference resistor. The thermometer was calibrated in a triple-point cell before, during, and after these measurements and each time \( R_0 \) was found to be \( (25.56009 \pm 0.00001) \) \( \Omega \) when the measurement current was 1 mA r.m.s. Increasing the current by a factor of \( \sqrt{2} \) resulted in an increase of 150 \( \mu \Omega \) in the resistance of the thermometer, and exactly the same self-heating effect was found in the apparatus. Ethanol was used in the thermometer well to promote good thermal contact. The lower 200 mm of the thermometer was inside the vessel (see figure 7.2) and the effect of depth of immersion was checked by slowly raising the thermometer; no change in the temperature was detected over the bottom 50 mm. The precision of the temperature measurements was \( \pm 0.1 \) mK and the total uncertainty in the thermodynamic temperature should not exceed 0.3 mK. Methanol was added to the water bath to prevent freezing and to reduce the viscosity; cooling was provided by a commercial refrigerator with its heat-exchanger's coil immersed in the bath. Temperature gradients in the bath around the vessel were again negligible.

Three sets of measurements were made covering a total of 30
pressures between 15 and 253 kPa at temperatures within ± 2.5 mK of
\( T_{(s+1+g,H_2O)} \). The results obtained using the first four radial modes are
given in tables 9.1, 9.2, and 9.3 (small corrections have been applied
to refer all values to 273.16 K exactly). The fifth mode was also used,
but was rejected for the final analysis because \( f_{05} \) was again close to a
minor shell resonance. The resonance frequency was lowered by \( 1 \times 10^{-5} \)
at 250 kPa but this discrepancy between the fifth and the lower four
modes decreased as \( p \rightarrow 0 \). The listed values of \( (u/a) \) include the
corrections for the thermal boundary layer, coupling and filling tubes,
and the elastic response of the shell. The thermal conductivity of
dilute argon at 273.16 K was taken as 16.4 mW·m\(^{-1}\)·K\(^{-1}\) and the viscosity
as 21.0 \( \mu \)Pa·s.\(^4\) Random errors in the resonance frequencies are typically
\( \pm 2 \times 10^{-7} \) and never more than ten times that. Again the excess half
widths are smaller for the second and third modes than for the first and
fourth and, while the former show a tendency to decrease at low pressures,
the latter increase as the pressure is reduced. The total range of the
corrected results at each pressure is typically \( 4 \times 10^{-6} (u/a) \) and there
is no significant reduction in precision even at 15 kPa. Measurements
at 8 kPa showed significant random errors and were rejected. The mean
values of \( (u/a)^2 \) obtained at each pressure are listed in table 9.4

\[ A_2 = (6.96 \pm 0.73) \times 10^{-11} \text{ m}^2\cdot\text{s}^{-2}\cdot\text{Pa}^{-2}, \]

obtained
TABLE 9.1 Results in argon at 273.1600 K. Set 1.

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**TABLE 9.2** Results in argon at 273.1600 K. Set 2.

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**TABLE 9.4** \((u/a)^2\) for argon at 273.1600 K.

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<th>((u/a)^2/10^6 \text{s}^{-2})</th>
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+ These values corrected for the temperature-jump effect.
FIGURE 9.1. \((u/a)^2\) vs. \(p\) for argon at 273.1600 K. •: unmodified results.
○: results adjusted for the temperature-jump effect and for \(A_2\).
by Colclough, Quinn, and Chandler using pressures up to 1.3 MPa, has been assumed and $A_0$ and $A_1$ constrained by

$$(u/a)^2 - (A_2/a^2)p^2 = (A_0/a^2) + (A_1/a^2)p.$$  \hspace{1cm} (9.2.2)

The estimated error in this value of $A_2$ is based on three standard deviations and corresponds to less than $5 \times 10^{-6} (u/a)^2$ at the maximum pressure studied in this work. Equation (2) fits the results unmodified for the temperature jump with a standard deviation of $3.5 \times 10^{-6}$; the resulting coefficients and their standard deviations are

$$(A_0/a^2) = (26.19466 \pm 0.00004) \times 10^6 \text{ s}^{-2}, \text{ and}$$  
$$(A_1/a^2) = (5.894 \pm 0.023) \times 10^{-2} \text{ Pa}^{-1}. \hspace{1cm} (9.2.3)$$

Deviations of the measurements from the constrained quadratic fit are shown in figure 9.2 and provide strong evidence for a systematic effect increasing in proportion to a low power of $(1/p)$. It is unlikely that this arises from outgassing from the walls of the resonator; the final set of measurements (set 3) were performed over 2 d and after 12 h at 50 kPa $(u/a)$ had changed by less than $5 \times 10^{-7}$. In addition, the three sets of measurements are entirely consistent with a single isotherm. Equation (2) fits the results corrected for the temperature jump with a standard deviation of $1.7 \times 10^{-6}$ and yields the following coefficients and standard deviations:

$$(A_0/a^2) = (26.19445 \pm 0.000018) \times 10^6 \text{ s}^{-2}, \text{ and}$$  
$$(A_1/a^2) = (5.987 \pm 0.011) \times 10^{-2} \text{ Pa}^{-1}. \hspace{1cm} (9.2.4)$$

The value of $(A_0/a^2)$ is lower than that of equation (3) by $8.0 \times 10^{-6}$ and has a standard deviation of only $0.7 \times 10^{-6}$. Thus random errors in these
FIGURE 9.2. Fractional deviations $\Delta u^2/u^2 = [u^2 - u^2(\text{calc.})]/u^2$ of $u^2$ from constrained three-term fits. TOP: unmodified results. BOTTOM: results corrected for the temperature-jump effect.
measurements are much less than the systematic temperature-jump correction. The corresponding deviations of the modified results from the constrained fit are shown in figure 9.2, and \( ((u/a)^2 - (A_2/a^2)p^2) \) is plotted on figure 9.1. The increased scatter in the results above 110 kPa can be attributed to the lower precision of the pressure measurements. Clearly, the lower pressure results are smooth on the scale of \( 10^{-6}(u/a)^2 \) and the theoretical temperature-jump correction accounts for almost all the observed curvature in this region. Had an accommodation coefficient \( h = 0.9 \) been adopted, the remaining deviations would have been purely random and \( (A_0/a^2) \) would be lowered by a further \( 2 \times 10^{-6} \). This latter figure is perhaps a fair estimation of the systematic uncertainty associated with adopting equation (4) as the best estimate of \( (A_0/a^2) \). With the accepted value of the gas constant, the effective radius at 273.16 K is found to be 60.145 mm.

The value \( A_1 = (2.166 \pm 0.012) \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{Pa}^{-1} \) (± three standard deviations) obtained from equations (4) is in good agreement with the values \( 2.23 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{Pa}^{-1} \), obtained by numerical integration of the HFD-C pair-potential-energy function of argon,\(^6\) and \( (2.02 \pm 0.09) \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-2} \cdot \text{Pa}^{-1} \), obtained by Colclough et al.\(^5\). However, it is notable that the small difference between the latter value and the one obtained here is rather more than the combined statistical uncertainty (estimated as ± three standard deviations). This difference is comparable to the effect of the correction applied here for the elastic response of the resonator's wall (which increases \( A_1 \) by about 5 per cent in this case), but amounts to just 0.35 cm\(^3\)\text{ mol}^{-1} in \( \beta_a \). Colclough et al used a much heavier walled interferometer and applied no correction for its elastic response. Since the difference could also arise from the constraint of \( A_2 \), an unconstrained three-term fit has been performed and the resulting coefficients and standard deviations are
\[ \frac{(A_0/a^2)}{a^2} = (26.19450 \pm 0.00002) \times 10^6 \text{ s}^{-2}, \]
\[ \frac{(A_1/a^2)}{a^2} = (5.890 \pm 0.046) \times 10^{-2} \text{ s}^{-2} \text{ Pa}^{-1}, \text{ and} \]
\[ \frac{(A_2/a^2)}{a^2} = (2.28 \pm 0.17) \times 10^{-8} \text{ s}^{-2} \text{ Pa}^{-2}; \] (9.2.5)

the standard deviation of the fit is \(1.6 \times 10^{-6}\). This value of \(A_0/a^2\) does not differ significantly from that given by the first of equations (4), and the values of \(A_1\) and \(A_2\) are found to be:

\[ A_1 = (2.13 \pm 0.05) \times 10^{-4} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-1}, \text{ and} \]
\[ A_2 = (8.3 \pm 1.8) \times 10^{-11} \text{ m}^2 \text{ s}^{-2} \text{ Pa}^{-2}. \] (9.2.6)

Both these estimates agree with those of Colclough, Quinn, and Chandler to within the combined statistical uncertainties.

9.3 CONCLUSION

These results show that \(A_0/a^2\) can be measured with a standard deviation of about \(1 \times 10^{-6}\), and with systematic uncertainties substantially less than \(1 \times 10^{-5}\). The three sets of measurements are consistent with a single isotherm to within \(1 \times 10^{-6}\) (in as much as the mean deviation of \((u/a)^2\) from the combined isotherm is less than \(1 \times 10^{-6}\) for each set taken separately) and there was no evidence that the modest precautions taken here against outgassing were insufficient. It would be desirable in future work to use transducers that were either physically isolated from the sample gas (by a diaphragm) or that could withstand a higher baking temperature. A mass spectrometer would be useful in assessing the chemical purity of the gas used. Higher precision is required in the measurement of pressure, and it might be better to perform the measurements between, say, 50 and 500 kPa in order
to avoid systematic uncertainties arising from the temperature-jump correction.

It is disappointing to have no accurate knowledge of the mean radius of the cavity. In future work it would be necessary to pay more attention in the design of the resonator to the problems involved in a calibration of its volume by weighing. Misfit between the two halves could have been avoided if, instead of meeting at an interlocking step, they were simply butted together and aligned using the outer surface. This would also make mechanical measurements of the depths of the hemispheres much easier. Each half could be machined to a depth greater than its radius of curvature, polished, and finally lapped down to the correct depth. Any damage caused to the edge during polishing would then be removed, and a water tight seal should be achieved.

REFERENCES