SIMULATION STUDIES OF SURFACE AND BULK PROPERTIES OF MATERIALS

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Abstract

This thesis addresses three related problems of substantial interest in contemporary Chemistry: first, crystal growth inhibition; second, molecular diffusion in microporous materials and third, the interaction of sucrose at the ice-water interface which is of importance in the development of commercial ice-cream.

The crystal growth studies have involved the utilisation of robust modelling methodologies which included energy minimisation and molecular dynamics methods. The mode of interaction of a selection of newly designed phosphonate crystal inhibitors was modelled in order to elucidate their mode of interaction with respect to the stepped and planar \{10\bar{1}4\} planes of calcite. The phosphonates were chosen to elucidate the variation in their activity as a function of structure. It has also been shown in this study that; a] poisons have a greater affinity for the defect containing surfaces compared to planar surfaces in accordance with experimental observations; b] the presence of a hydrophobic functional group depletes poison efficacy; c] the presence of electronegative atoms promotes the operation of the poison; d] the diphosphonate HEDP is a superior poison to monophosphonate species. The mechanism of action for these phosphonates is proposed.

Insights into long-range molecular diffusion have been investigated in the purely siliceous form of Faujasite and CIT-I zeolites. Atomistic simulation studies involving the diffusion routes of molecules and the calculation of diffusion coefficients, obtained from the Einstein relation, have been undertaken for the rigid ion and shell model descriptions of the zeolites using NVT, NVE and NPT simulation protocols. Inclusion of oxygen polarizability via the shell model gives rise to decreased calculated diffusion coefficients as well as enhanced molecular contact with the zeolite channel walls, in contrast to the rigid ion model.

In appendix A, a representation of the ice-water interface has been produced enabling the favourable sucrose interaction modes to be predicted.
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Chapter 1  Introduction

1.0  Prologue

The work described in this thesis addresses surface, interfacial and bulk properties of solids using computer simulation techniques.

A dramatic growth has occurred in the area of molecular modelling within the past fifteen years, making it both a valuable if not indispensable tool to the scientific community. This growth has been driven by developments in techniques and algorithms and by faster computer processors making the modelling of thousands of atoms achievable. The bulk and surface single processor simulations described in Chapters 4 and 5 of this thesis, utilized Tyndall situated at the Royal Institution. Tyndall, comprises a 14 processor Silicon Graphics Origin 2000 machine with each processor containing a MIPS R12000 300Mhz chip. Such a facility greatly exceeds in cpu powered memory the national supercomputers of the 1980s.

A range of multi-purpose packages are now in use which provide today's modeller with the choice of using codes ranging from commercial software packages such as Cerius$^3$, [used in the interfacial study of Appendix A] which have sophisticated graphical interfaces to academic codes such as MARVIN and DLPOLY_2.0 [used in Chapters 4 and 5 respectively], containing no ‘front end’ but which offer greater flexibility and user control.
The systems on which we focus in this thesis each necessitated the modelling of thousands of atoms. Consequently, 'force-field' or interatomic potential techniques were necessary for these calculations to be viable. The thesis exploits the capability of modern molecular modelling techniques to examine systems of great complexity.

Regarding our first theme, crystal growth inhibition, few modelling studies of the processes involved in the inhibition of mineral growth have been documented within the past twenty years. There is, therefore, huge scope for designing efficient poisons and characterizing further structure/activity relationships for many of the systems of importance to the water and petroleum industries.

Our second theme of diffusion within zeolites has been studied extensively within the past thirty years due to increased numbers of synthesized zeolites and the development of a variety of catalytic processes and adsorption/separation processes. Theoretical studies have been particularly useful in the elucidation of zeolite/hydrocarbon mechanisms which are operational within shape selective catalysis.

The fact that the taste of commercially engineered ice-creams is impaired after re-refrigeration offers another example of how simulations have been applied to commercially important problems. In the third theme, our aim was to build an ice/water interface and determine feasible sucrose conformations at the interface.

The aims of the three components of this project are now explained in greater detail.
1.1 Surface phenomena: crystal growth inhibition

This component of the thesis has the central aim of elucidating a mechanism of action for a variety of the phosphonate class of crystal poison, ultimately resulting in the crystal growth inhibition of the \{10\overline{1}4\} surface of calcite. These calculations were performed by using the classic simulation methodologies of energy minimization and molecular dynamics. Specifically, the following systems and features of additive/calcite systems were modelled:

- Totally deprotonated poisons of the phosphonate class of poison.
- Variation of the functionality of the additive backbone.
- The roles of terrace, step and kink nucleation sites in the growth of calcite.
- The roles of terrace, step and kink nucleation sites in the inhibition of calcite growth.
- The relationship between additive selectivity and functionality.
- The differences in additive interaction between acute and obtuse steps on the \{10\overline{1}4\} calcite surface.
- The mechanisms of replacement and binding processes.
- The differences in interaction between diphosphonates and monophosphonates.

Our calculations performed in Chapter 4 revealed that: calcium carbonate unit attachment to kink sites was impeded by the presence of a pre-poisoned step site; stepped calcite surfaces furnished superior modes of attachment when compared to the ideal calcite substrate as demonstrated by their respective energetically favourable binding energies; inhibitors containing electronegative groups formed superior attachments than those without; calculated replacement and binding energies
suggested that diphosphonate class of poison was able to associate with the calcite stepped surface via binding rather than double carbonate ion replacement; the diphosphonate ion enabled higher calculated binding energies compared to the singly substituted monophosphonate counterparts.

1.2 Bulk phenomena: molecular diffusion in zeolites

As noted, sorbate diffusion in microporous materials is a crucial process controlling their operation in catalysis and molecular sieves.

In this thesis, diffusion studies in purely siliceous zeolites have been investigated using rigid ion and shell model descriptions. The zeolite frameworks studied were the Faujasite and siliceous CIT-1. Systems under observation included CIT-1/para-xylene, CIT-1/ortho-xylene and Faujasite/benzene. The topics and problems investigated included:

- The application and effect of the inclusion of polarizability on the magnitude of the diffusion coefficient.
- The application of the rigid ion model to zeolite/molecule systems and the calculation of corresponding diffusional properties.
- The effect of simulation temperature on the magnitude of the diffusion coefficient.
- The effect of molecular loading on the magnitude of the diffusion coefficient.
- The investigation of the role of ensemble choice on the magnitude of the diffusion coefficient.
- The elucidation of any change in molecular mechanism behaviour through zeolite channels due to the inclusion of the polarisability to the model.
The elucidation of any differences apparent in the effect of inclusion of the polarizability via the shell model for Faujasite compared to the lower density CIT-1 framework.

1.3 Interfacial phenomena

Ice crystal growth formation is important in the re-refrigeration of commercial ice-creams. The interaction of sucrose at the ice/water interface was simulated and the calculated binding energies and observations are reported in the appendix of this thesis.
Chapter 2 Theoretical techniques

2.0 Overview

The molecular modelling methods used throughout this work employed force-fields which allow the simulation of large complex systems containing several thousand atoms. The applications reported refer to bulk or surface simulations using periodic boundary conditions. Such methods do not model electronic effects explicitly, hence features such as bond-breaking and bond-formation are not described. The origins of these force-field\(^1\) based procedures are discussed in detail in this chapter.

2.1 Introduction

Quantum mechanics is the most fundamental approach for the theoretical determination of molecular properties. It relates molecular properties to the behaviour of electrons in atoms and molecules. The solution of the Schrödinger equation allows the calculation of electronic, structural and spectroscopic properties and can be used to predict chemical behaviour including reactivity.

The solution of the Schrödinger equation becomes rapidly more demanding as the size of the system increases scaling usually at \(N^3\), \(N^4\) or higher (where \(N = \) the number of atoms). The systems studied during this work consist typically of thousands of atoms. For this reason, interatomic potentials or force-fields based ultimately on the Born-Oppenheimer approximation\(^2\) (described in section 2.2) were used exclusively. The simulation of these systems is thus made computationally achievable.
2.2 Interatomic potentials

The potential energy surface, described in equation 2.1 below, is a mathematical representation of the potential energy, \( V(R) \), of a molecule as a function of nuclear coordinates or structural parameters such as bond lengths, bond angles and torsion angles, \((r_{1}, \ldots, r_{n})\):

\[
V(R) = f(r_{1}, \ldots, r_{n})
\]  \hspace{1cm} (2.1)

\( V(R) \), is usually represented by analytical functions that are parametrized via ab-initio calculations or from experimental results.

At the heart of the concept is, of course, the Born-Oppenheimer approximation. This is based on the assumption that electrons respond instantaneously to changes in nuclear co-ordinates. Therefore, the motion of the electrons and the nuclei can be resolved into two equations. Equation 2.2 describes the electronic motion, \( H \) is the Hamiltonian operator, \( \psi \) can be described as a function of the co-ordinates of the nuclei \( (R) \) and of the electrons \( (r) \):

\[
H\psi(r; R) = E\psi(r; R)
\]  \hspace{1cm} (2.2)

Equation 2.3 represents the motion of the nuclei, which is defined by the Hamiltonian \( H(\phi) \), and the energy \( E(\phi) \):

\[
H(\phi) = E(\phi)
\]  \hspace{1cm} (2.3)
The next approximation made in "classical" simulations is that the motion of the nuclei on the potential energy surface follows classical dynamics. Hence the classical equation for the movement of nuclei is described in equation 2.4 where $V$ is the potential energy, $m$ is the mass and $R$ the position of the nuclei and $t$ the time.

$$\frac{dV}{dR} = m \frac{d^2R}{dt^2}, \tag{2.4}$$

Methods based on interatomic potentials normally use an analytical and differentiable potential energy function. For molecular systems, the potentials are often referred to as the force field.

### 2.3 Molecular force fields

The concept of a force field, originally emerged from analysis of vibrational spectra. However, these early force fields did not originally include interactions between non-bonded atoms and were not parameterized with structure and energy calculations in mind. Modern force-fields include van der Waals and other non-bonded interactions.

The molecular force field describes the potential energy of a molecule, relative to the energy of some reference geometry. The force field contains parameters including the force constants, which are derived from a systematic comparison of calculated and observed properties and/or from ab-initio calculations. In performing molecular mechanics calculations, it is desirable to validate the force-field with respect to a wide range of molecular structures and properties.
Generally, a molecular force field includes terms, which describe:

(i) the energy of stretching each bond from the equilibrium value (2 body term);
(ii) the energy of bending bonds from their standard values (3 body term);
(iii) the energy required to twist the molecule about a bond i.e. a change in torsion angle (4 body term);
(iv) the cross terms of the above.
(v) the non-bond interactions between atoms.

2.3.1 Form of the force field

As noted, the form of the force field can be described in terms of bonded, non-bonded and cross term interactions.

The bonding interactions usually refer to atoms in the following relationships:

- Those which are directly bonded to each other, i.e. a 1-2 bond stretch: a two body term, $E_r$.
- Those in which atoms are bound to a common atom, i.e. 1-3 angle bending: a three body term, $E_\theta$.
- Those in which atoms are separated by 3 bonds, i.e. a 1-4 dihedral angle rotation: a four body term, $E_\phi$.

The non-bonded interactions usually include the following terms:

- An exchange repulsion term which acts when atomic charge clouds overlap.
- A long range attractive interaction due to dispersive forces.
Electrostatic interactions resulting from the interactions of charges.

The repulsive and attractive terms combine in what are referred to as van der waals terms.

Thus the valence or bonded terms, $E_{\text{val}}$, comprise $E_R$, $E_\theta$, $E_\phi$, $E_\psi$, see equation 2.5:

$$E_{\text{val}} = \left( E_R + E_\theta + E_\phi + E_\psi \right), \quad (2.5)$$

The non-bonded interactions, $E_{\text{nb}}$, comprises the van der Waals, $E_{\text{vdw}}$ and electrostatic $E_{\text{el}}$ terms which are shown in equation 2.6:

$$E_{\text{nb}} = \left( E_{\text{vdw}} + E_{\text{el}} \right), \quad (2.6)$$

The total potential energy, $V$, is the sum of the two terms: see equations 2.5 and 2.6:

$$V = \left( E_R + E_\theta + E_\phi + E_\psi + E_{\text{vdw}} + E_{\text{el}} \right), \quad (2.7)$$

Each of the analytical functions will now be discussed.

### 2.3.1.1 Bond stretching term

The energy associated with the small displacements of a bond from its equilibrium value can be described by an harmonic function, see equation 2.8, where $k_b$ is the
force constant describing the stiffness of the bond, \( r_0 \) is the equilibrium bond length and \( r \) is the deformed bond length:

\[
E_{\text{bond}} = \sum_{\text{bonds}} k_b (r - r_0)^2,
\]  

(2.8)

The Morse function, shown in equation 2.9, is used for long bond lengths and greater deviations from equilibrium bond lengths as the harmonic term becomes inappropriate under these conditions. The Morse function contains an exponential component which rises more steeply than the Harmonic potential at short bond lengths. This feature can be important during simulations in which a molecule is directed away from a potential minimum.

\[
E_{\text{Morse}} = \sum D \left( e^{-A(r - r_0)} - 1 \right)^2,
\]  

(2.9)

where \( D \) is the bond dissociation energy, \( r_0 \) is the equilibrium bond length, \( r_0 \) is the deformed bond length and \( A \) is the force constant parameter.

2.3.1.2 Angle bending term

The term defined by equation 2.10 is normally taken to be harmonic and represents deviations from equilibrium bond angles:

\[
E_\theta = \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2,
\]  

(2.10)
where \( k_0 \) is the bond bending force constant and \( \theta_0 \) is the equilibrium bond angle.

2.3.1.3 Torsion term

The torsional term, equation 2.11, is described with a small cosine Fourier expansion in \( \phi \)

\[
E_\phi = \sum k_\phi \left( l + s \cos(p\phi) \right), \tag{2.11}
\]

where \( k_\phi \) is represented by half the barrier height, \( p \) is the periodicity and \( s \), the sign, is used to determine whether the maximum of the term occurs at \( 0^\circ \) or \( (360^\circ/n) \); \( \phi \) is the torsional angle.

2.3.1.4 Inversion term

The term shown in equation 2.12 represents the out of plane interactions present in molecules such as carbonate ions. The potential involves the estimation of the angle between a bond from the central atom and the plane defined by the central atom and two atoms. When all four atoms assume a coplanar geometry, the energy value is zero; \( \psi \) is the torsional angle and \( k_\psi \) the force constant.

\[
E_\psi = k_\psi \left( l - 2 \cos(\psi) \right), \tag{2.12}
\]
2.3.1.5  Van der Waals term

The Lennard Jones 12-6 potential (equation 2.13), has been used in many molecular mechanics calculations,

\[ E_{LJ} = \sum \left( \frac{A}{r_{ij}^{12}} \right) - \left( \frac{C}{r_{ij}^{6}} \right), \quad (2.13) \]

where \( r_{ij} \) is the non bonded distance between two atoms \( i \) and \( j \). \( A \) and \( C \) are van der Waals parameters for the interacting pair of atoms. Dispersive interactions arise from the correlation between the motions of electrons on different atomic or molecular sites. The correlations result in instantaneous dipoles arising on each species. The \( r_{ij}^{-6} \) term describes the latter interactions while the \( r_{ij}^{-12} \) term describes the repulsive interactions between the overlapping atomic charge clouds.

Often, the repulsive part of the 12-6 term is too steep or hard to describe interactions between atoms in organic molecules. The Buckingham term, in equation 2.14, may act as a more accurate alternative to the Lennard-Jones potential since it contains a more realistic exponential component which describes the short range repulsion.

\[ E_{Buckingham} = \sum A_{ij} \exp \left( - \frac{r_{ij}}{\rho_{ij}} \right) - \left( \frac{C_{ij}}{r_{ij}^{6}} \right), \quad (2.14) \]

where \( A_{ij}, \rho_{ij} \) and \( C_{ij} \) are van der Waals parameters for the interacting pair of atoms.
2.3.1.6 Electrostatic term

The electrostatic interactions are calculated using point charges; $q_i$ and $q_j$, (the assignment of which are discussed in section 2.5 of Chapter 2) separated by the distance $r_{ij}$ of atoms i and j. The analytical expression for this term is shown in equation 2.15 below.

$$E_{\text{electrostatic}} = \sum \left( \frac{q_i q_j}{r_{ij}} \right),$$

(2.15)

In systems where solvents are present this interaction may be screened using an effective dielectric constant $\varepsilon$.

2.4 Interatomic potentials for ionic and semi-ionic solids

2.4.1 Introduction

Relatively simple models work well in modelling ionic crystals due to the relative simplicity of the nature of the bonding. Ionic solids can be modelled as charged points between which Coulomb and non-bonded interactions act. Most models are based on the simple pair potential approximation, although bond-bending, three body terms may also be added in systems with some degree of covalency e.g. silicates.
2.4.2 *The rigid ion model*

Rigid ion models are the simplest class of ionic model. This model does not take into account ionic polarizability within the system, a limitation of which precludes accurate modelling of the dielectric and dynamical properties of lattices.

The basic form for the potential describing the interaction of a pair of ions is shown below in equation 2.16, which is the sum of Coulombic and Buckingham functions discussed earlier:

\[
V(r_{ij}) = \left( \frac{q_i q_j}{r_{ij}} + A_{ij} \exp\left( - \frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} \right),
\]  
(2.16)

2.4.3 *The shell model*

The shell model, developed originally by Dick and Overhauser, was used in this work to model the polarisation of oxygen. The model is a simple mechanical model of a polarizable atom or ion which comprises a core (containing all the mass) and a massless shell which describes the polarizable valence shell electrons. The core and shell are connected by an harmonic spring. The short-range interactions are then defined between the shells, on the assumption that short-range repulsion is caused by interactions between valence shell electrons. The sum of the charges on the shell and core give rise to the total ionic charge. Polarization is modelled by the displacement of the shells from the cores, the self-energy of which is given by the term,

\[
E_{shell} = k_{sh} r_{c-s}^2,
\]

where \( k_{sh} \) is the shell force constant and \( r_{c-s}^2 \) is the core-shell...
distance. Accounting for the effect of polarization significantly improves the accuracy of the simulation as shown by the results presented later in Chapter 5 of this thesis.

Early applications of the shell model were in the lattice dynamics studies performed by Jaccucci et al.\textsuperscript{8} and Dixon and Sangster\textsuperscript{9} in the mid-seventies. It should be noted that whilst the rigid ion technique was sufficient to reproduce static properties of systems such as pair correlation functions, shell model methods were proven to reproduce the dynamical properties of systems more accurately.\textsuperscript{10}

Problems in the original implementation of shell model molecular dynamics included the high computational expense of the calculations\textsuperscript{11} caused by the fact that it was necessary to equilibrate the shell position for all nuclear co-ordinates consistent with the zero mass of the shells.\textsuperscript{12} This was achieved by systematically relaxing all the shells at each molecular dynamics time step via the conjugate gradient technique (explained later in this chapter). Inherent problems within this latter technique included lack of energy conservation, which was rectified by the inclusion of a procedure for the prevention of energy drift in 1993 by Lindan and Gillan.\textsuperscript{12}

Calculations including polarization were later further improved with the introduction by Fincham and Mitchell\textsuperscript{13} of their shell model molecular dynamics technique in which a small mass was assigned to the shells as well as the cores of the atoms, which together with increased computer power resulted in an increase in its use.
The shell model potential\textsuperscript{14} used during this work comprised electrostatic, repulsive and three body terms. The form of the force field for the shell model is described in equation (2.17) below:

\[
V = \sum \left[ \frac{q_i q_j}{r_{ij}} + A_{ij} \exp \left( -\frac{r_{ij}}{\rho_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6} + \sum_{\text{angles}} k_{\theta} (\theta - \theta_0)^2 + \sum_{\text{shells}} k_{sh} r_{c-s}^2 \right], \tag{2.17}
\]

where \( i \) and \( j \) represent the interacting ions, \( q_i \) and \( q_j \) are their respective charges and \( A_{ij}, \rho_{ij} \) and \( C_{ij} \) are short-range potential parameters, \( k_{\theta} \) and \( k_{sh} \) are the force constants.

Having outlined the methods used in treating polarizability, we now consider the key question of the assignment of charges in both molecular and ionic potentials.

2.5 Charges

2.5.1 Phosphonate charges

Preliminary studies conducted in order to elucidate which charge calculation scheme to use for the phosphonates involved 1] the Mulliken Population analysis\textsuperscript{15} of the results of calculations using a range of semi-empirical techniques\textsuperscript{16-18} which included PM3, AM1, MNDO and 2] the Gasteiger and Marsili\textsuperscript{19} method available from within Cerius\textsuperscript{2}. The charge distributions calculated via the Gasteiger method gave rise to the most isotropic distribution so this method was chosen to calculate the phosphonate charges used in the simulations. Further details of these approaches are now presented.
2.5.2 *Semi-empirical methods*

Semi-empirical methods have been very widely used in computational Chemistry. They differ in the various approximations which they make. The Neglect of Differential Overlap (NDO) methods, i.e. MNDO, PM3 and AM1 replace key integrals in the Hamiltonian by parameterized terms. The terms partially compensate for considering only valence electrons. They may also incorporate, again partially, the effects of electron correlation. In the present study the aim was simply to obtain charges using the Mulliken population analysis technique.

2.5.2.1 *Mulliken population analysis technique*

This widely used technique attempts to assign charges between different atoms in molecules using a standard prescription based on the coefficients of the atomic basis functions in the LCAO molecular orbital\(^{17}\). There are, however, many limitations of the method, including the fact that the charge between two nuclei is divided equally irrespective of electronegativity. The representation of charge distribution is more realistic when derived from a minimal basis set computation compared to an extended basis set.

An account of the application of semi-empirical methods to the computation of charge on a phosphonate molecule using a Mulliken population approach is given in Appendix B.
2.5.3 The Gasteiger and Marsili charge calculation method

Mulliken’s definition of electronegativity relates the ionization potential to the electron affinity, which is also a characteristic of a particular valence state. This idea was expanded by Hinze et al. by introducing the concept of orbital electronegativity which is defined as the electronegativity of a particular orbital in a particular valence state. Orbital electronegativities depend not only on hybridization but also on the occupation of an orbital. An empty orbital has a greater ability to attract electrons than an occupied orbital. Using the terminology of Gasteiger and Marsili, the difference between the orbital charge density of an atom with partial orbital occupancy and that of the corresponding atom in a molecule is defined as a partial charge, \( q_{\nu} \) in the orbital \( \nu \) of atom \( A_i \). Orbital electronegativity therefore depends not only upon the charge in one orbital but also the charge of neighbouring orbitals.

The driving force for the charge transfer between two bonded atoms is the difference in electronegativity. However, charge transfer leads to the generation of an electrostatic field which impedes further transfer. A simple damping procedure is therefore invoked by implementing the iterative formula below in equation 2.18:

\[
q^{(\alpha)} = \frac{\chi_B^{(\alpha)} - \chi_A^{(\alpha)}}{\chi_A^+} \left( \frac{1}{2} \right)^\alpha,
\]

(2.18)

where \( q \) is the charge transferred on atom \( A_i \) in each iteration step, \( \chi_A^+ \) is the orbital electronegativity of an atom in the +1 state, \( \alpha \) gives the iteration step number. Hence when \( \alpha = 1 \), a damping factor of \( \frac{1}{2} \) is applied to the charge transfer. When \( \alpha = 2 \),
new electronegativities are calculated and a damping factor of $\frac{1}{4}$ is applied. The total charge is calculated as the sum of the individual charge transfers, see equation 2.19:

$$Q_i^{(a)} = \sum_a q_i^{(a)} ,$$  \hspace{1cm} (2.19)

An adaptation of the procedure is used for polyatomic molecules. This method was used to assign charges in the simulations of phosphoante-calcite interactions reported in Chapter 4. A detailed discussion of this charge calculation method is given in reference [19].
2.6 Minimization

2.6.1 Introduction

Having outlined the main features of the interatomic potentials employed in the study we now consider the main simulation techniques used in the thesis.

Energy minimizations or geometry optimizations\textsuperscript{22} aim to generate the structural configurations which correspond to the minimum energy of the system. Minimization techniques have been extensively used in this thesis employing the GULP\textsuperscript{23} and MARVIN\textsuperscript{24} codes. The former, models 3D periodic systems and the latter 2D periodic systems.

2.6.2 The technique

The minimization technique searches for a minimum, defined by the gradient in the energy being zero with respect to all variables. A wide variety of iterative minimization algorithms are available. The most efficient use the past history of points sampled from the potential surface in order to determine the next point on the potential energy surface. The techniques fall into the different categories depending upon whether the first or second derivatives are calculated. The former include the steepest descent and conjugate gradient methods. Second derivative techniques, such as the quasi-Newtonian BFGS technique are the more rapidly convergent. All of these methods have been used throughout the present work. These algorithms will now be discussed in greater detail.
As stated previously, performing an energy optimization on a molecule is always a useful starting point for subsequent simulations. The aim is normally, if possible, to locate the global energy minimum. However, local minima are a pervasive problem. For example, each of the torsional terms in the energy expression has more than one minimum; therefore, since the torsions are the variables which define the conformation of the molecule, there are many conformations with local energy minima for large molecules. It follows then that no minimization algorithm can really guarantee that the lowest energy conformation that it finds is the global minimum which is known as the local minimum problem. Sophisticated procedures including simulated annealing and genetic algorithms may partially overcome the problem, but the location of the global minimum can never be guaranteed.

2.6.3 The algorithms

The minimization algorithms described are:

- Steepest descent technique
- Conjugate gradient technique
- BFGS technique

2.6.3.1 The steepest descent algorithm

This algorithm was developed over thirty years ago. It is one of the simplest methods of optimization. The direction of steepest descent, $g$, described in equation 2.20 is the negative of the gradient vector, $\nabla$:
\[ g = -\nabla E = \left\{ \frac{\partial E}{\partial x_i}, \frac{\partial E}{\partial y_j}, \ldots, \frac{\partial E}{\partial z_n} \right\}, \quad (2.20) \]

The steepest descent method may provide a reasonably good procedure to begin an optimization when the starting point is far from the minimum. However, it converges slowly near the minimum and it is principally recommended only to initiate optimization from a poor starting point.

A major limitation of steepest descent, is that the successive directions of search, \( g_i \), \( g_{i+1} \) etc. are not conjugate directions. Searching along the successive directions of steepest descent might, for example, keep going back and forth across a long, narrow valley. Conjugate gradient methods are a considerable improvement over steepest descent methods and involve searching down conjugate directions rather than steepest descent directions.

2.6.3.2 The conjugate gradient algorithm

This algorithm was developed by Fletcher et al.,\(^{27}\) in 1969. In the steepest descent method, the first derivative is recomputed each time, but the way in which these derivatives are changing is not taken into consideration. The core of the conjugate methods is to use knowledge of derivatives in previous iterations.

Conjugate gradient methods compute the conjugate directions \( h_i \), by iterative computation, involving the gradient \( g_i \) without recourse to computation of second derivatives.
The steps in a gradient minimization are:

(a) A starting point is defined and the initial conjugate direction is chosen to be the steepest descent direction, $h_0 = g_0$.

(b) Along the conjugate direction, $h_i$, a line minimization is carried out until a minimization is found that defines the next point, where the gradient is re-evaluated as $g_{i+1}$.

$$h_{i+1} = g_{i+1} + \lambda_{i+1} h_i$$

where the coefficient $\lambda_{i+1}$ given in equation 2.21, is calculated from the new and the old gradients $g_{i+1}$ and $g_i$.

$$\lambda_{i+1} = \left[ \frac{g_{i+1}^T g_{i+1}}{g_i^T g_i} \right], \quad (2.21)$$

The procedure is terminated when the convergence threshold is reached.

2.6.3.3 The Broyden-Fletcher-Goldfarb-Shanno (BFGS) Algorithm

The BFGS algorithm is a quasi-Newtonian method which involves evaluation of the Hessian matrix, i.e. the inverse of the second derivative matrix. This may be a lengthy procedure; in addition the calculation of analytical second derivatives may not be easy. To alleviate these problems quasi-Newton methods gradually build up the inverse Hessian matrix, $H$, in successive iterations.
At each iteration $k$, the new positions $x_{k+1}$ shown in equation 2.22, are obtained from the current positions $x_k$, the gradient $g_k$ and the current approximation to the inverse Hessian matrix $H_k$

$$x_{k+1} = x_k - H_k g_k,$$  \hspace{1cm} (2.22)

$H$ will be updated at new positions $x_{k+1}$ from its value at the previous step according the BFGS formula. This method converges to a minimum, for a quadratic function of $M$ variables, in $M$ steps.

The BFGS update formula is described below in equation 2.23:

$$H_{k+1} = H_k + \left[ \frac{(x_{k+1} - x_k)}{(x_{k+1} - x_k) \cdot (g_{k+1} - g_k)} \right]$$

$$\left[ \frac{H_k \cdot (g_{k+1} - g_k)}{(g_{k+1} - g_k) \cdot H_k \cdot (g_{k+1} - g_k)} \right] + \left[ (g_{k+1} - g_k) \cdot H_k \cdot (g_{k+1} - g_k) \right] \mu \otimes \mu$$

(2.23)

where:

$$u = \left[ \frac{(x_{k+1} - x_k)}{(x_{k+1} - x_k) \cdot (g_{k+1} - g_k)} \right] - \left[ \frac{H_k \cdot (g_{k+1} - g_k)}{(g_{k+1} - g_k) \cdot H_k \cdot (g_{k+1} - g_k)} \right]$$

Note that the symbol, $\otimes$, when placed between two vectors demonstrates that a matrix is to be formed.
The matrix, $H$, is often initialized to the unit matrix $I$, although the performance of the quasi-Newtonian algorithms can be improved by using a better initial estimate of the inverse Hessian.

2.6.3.4 Summary

The minimization algorithms attempt to find a minimum in the energy, $E$ as a function of specified co-ordinates. The process yields no guarantee that a global minimum as opposed to a local minimum will be identified. More sophisticated sampling algorithms based on simulated annealing techniques are needed to identify global minima in complex systems. However, for many of the applications reported in this thesis straightforward minimization methods were the effective and appropriate techniques.
2.7 Molecular dynamics

2.7.1 Introduction

Molecular dynamics includes the kinetic energy explicitly into simulations by modelling the motion of an ensemble of atoms, ions, or molecules over the potential energy surface. The motion of the molecules over this surface is treated classically, i.e. as governed by Newton's Second Law of Motion. After an initial set of conditions velocities and co-ordinates are defined. Newton's Second Law is solved in a numerical, iterative fashion using a specified "time-step" to yield the time evolution of the system.

The first applications of molecular dynamics techniques,\(^{29,30}\) pioneered by Alder and Wainwright in 1959, were made to simple fluids. Rahman and Stillinger\(^{31}\), followed later with their simulations for liquids such as water, with one of the first molecular dynamics simulations of a bio-molecule performed by McCammon \textit{et al.}\(^{32}\) Since then, the method has been applied to an enormous variety of systems\(^{33}\) ranging from proteins to zeolites.

Molecular dynamics also has a role in searching for global minima and by using the technique we can overcome conformational barriers. But the chances of locating the global minimum are increased only when activation barriers do not greatly exceed kT. In this context, a popular technique when employing molecular dynamics is to search conformational space in order to select conformations at regular intervals from the trajectory and to minimize them to their associated minimum energy structures, a technique known as quench dynamics. If a sufficiently large number of time intervals
are used and the temperature is high enough to enable all the barriers to rotation to be overcome, then, in principle all potential energy minima could be identified.

The real power of the method is, however, exploited when approaching dynamical phenomena such as diffusion described later in the thesis.

2.7.2 Methodology

Molecular dynamics simulations calculate the future positions and velocities of atoms based on their current values. A simulation, first determines the force, $F_i$, in equation 2.24 below:

$$ F_i = \left( -\frac{\partial V_i(r_1, r_2, \ldots, r_n)}{\partial r_i} \right), $$

(2.24)

acting on each atom as a function of time, which is equal to the gradient of the potential energy, as in equation (2.24), where $V$ is the potential energy and $r_i$ is the position of atom $i$.

The acceleration, $a_i$, of each atom is determined by dividing the force acting on it by the mass of the atom: consider equation (2.25)

$$ a_i = \frac{F_i}{m_i}, $$

(2.25)

where $a_i$ is the acceleration of the atom and $m_i$ is the mass of the atom.
The change in velocities, \( v_i \), is equal to the integral of acceleration over time. The change in position, \( r_i \), is equal to the integral of velocity over time. The kinetic energy, \( T \), is defined in terms of the velocities of the atoms (equation 2.26).

\[
T = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2, \tag{2.26}
\]

The total energy of the system is described by the Hamiltonian, which is the sum of the potential and kinetic energies; see equation 2.27

\[
H(r, p) = T(p) + V(r), \tag{2.27}
\]

where \( H \) is the Hamiltonian operator, \( r \) is the set of cartesian co-ordinates, \( p \) is the momenta of the atoms, \( T \) is the kinetic energy and \( V \) is the potential energy.

A molecular dynamics simulation proceeds by updating positions and velocities at each time step. The key problem in the technique is to ensure that the updating procedure does not lead to significant and cumulative errors.
2.7.3 Molecular dynamics algorithms

2.7.3.1 The Verlet algorithm

A variety of algorithms exist to integrate the equations of motion, including the Verlet algorithm and the leapfrog algorithm.

The Verlet algorithm uses the positions and accelerations at time \( t \) and positions, \( r \) from the previous step \( r(t - \delta t) \) to calculate the position at time \( (t + \delta t) \) to give

\[
r(t + \delta t), \text{ where } \delta t \text{ is the time step (equations 2.28 and 2.29).}
\]

At time \( t \), forward step

\[
r(t + \delta t) = r(t) + \delta tv(t) + \frac{1}{2} (\delta t^2 a(t)) + \ldots \quad (2.28)
\]

reverse step

\[
r(t - \delta t) = r(t) - \delta tv(t) + \frac{1}{2} (\delta t^2 a(t)) - \ldots, \quad (2.29)
\]

adding the two previous expressions gives:

\[
\Rightarrow r(t + \delta t) = 2r(t) - r(t - \delta t) + \delta t^2 a(t)
\]

Velocities do not appear in the Verlet integration algorithm. The velocities are calculated by the division of the difference in positions at times \( r(t + \delta t) \) and \( r(t - \delta t) \) by 2 to give equation 2.30:
The leapfrog algorithm

A simple modification of the Verlet algorithm is the leapfrog algorithm. The positions in equation (2.31) at time \((t + \delta t)\) are deduced from the velocities at time \((t + \frac{1}{2} \delta t)\).

The velocities in equation (2.32) are calculated at time \((t + \frac{1}{2} \delta t)\) from velocities at time \((t - \frac{1}{2} \delta t)\) and acceleration at time \(t\).

\[
\begin{align*}
\mathbf{r}(t + \delta t) &= \mathbf{r}(t) + \delta t \mathbf{v}(t + \frac{1}{2} \delta t), \\
\mathbf{v}(t) &= \frac{1}{2} \left[ \mathbf{v}(t + \frac{1}{2} \delta t) + \mathbf{v}(t - \frac{1}{2} \delta t) \right],
\end{align*}
\]

Velocities therefore 'leapfrog' over the positions to give their values at time \((t + \frac{1}{2} \delta t)\). The positions then 'leapfrog' over the velocities to give a new value at \((t + \delta t)\), ready for the velocity at \((t + \frac{3}{2} \delta t)\).

Leapfrog and Verlet algorithms are mathematically equivalent numerical methods of determining the positions and velocities of systems at \(t \to 0\). However, the Verlet approach is slightly more accurate, less sensitive to numerical error according to Swope and co-workers\(^{37}\), and more efficient when velocities must be adjusted. The
leapfrog method explicitly includes the velocity; however, positions and velocities are not synchronised compared to the Verlet algorithm.

A common concern is the choice of the timestep. The time step, must be shorter than the smallest frequency motion of the molecule. Hence, a time step of 1fs is commonly used. Methods have evolved, however, notably the SHAKE algorithm\textsuperscript{34} developed by Berendsen \textit{et al.}, in 1977, which constrained the high-frequency bonds to fixed lengths, which can usually allow the step size to be increased to 2fs or larger. Also Gibson and Scheraga\textsuperscript{35} have reported that with the ECPP potential function, where all bond lengths and angles are fixed, that it may be possible to use time steps as long as 15fs.

2.7.4 Equilibration

In molecular dynamics simulations, a suitable starting configuration is determined initially at time $t = 0$. The velocities are assigned in order for the average kinetic energy to match with the specified simulation temperature. The initial forces acting on the atoms are determined from the assigned force field. The system proceeds using Newton's Second Law of Motion. The positions and velocities are calculated using the Verlet numerical algorithm. An initial so-called equilibration period ranging typically between 10-35ps is necessary in order for the randomized positions and velocities to reach thermal equilibrium. This equilibration period is followed by a longer so-called production period which can evolve for hundreds of thousands of time steps representing a simulation run of the order of hundreds of picoseconds to nanoseconds. This production period contains the averaged values of the system.
which are subsequently used for analysis. The codes used to perform the molecular
dynamics calculations reported in Chapter 4 and Chapter 5 were MARVIN and
DL_POLY, general purpose simulation programs.

2.7.5 Ensembles

The molecular dynamics calculations performed during this work utilized ensembles
which enabled the temperature, energy or pressure to be controlled. The commonest
procedure in molecular dynamics is the constant energy [NVE] dynamics (employing
the microcanonical ensemble), where N, V and E represent the constant number of
atoms, constant volume and constant energy of a simulated system. Constant
temperature [NVT] dynamics (employing the canonical ensemble), is defined by N, V
and T which represent the number of atoms, volume and temperature kept constant in
a simulated system. Finally, constant pressure [NPT] dynamics may be employed,
where N, P and T represent the atoms, pressure and temperature which remain
constant.

In the microcanonical ensemble [NVE], a simulated system undergoes molecular
dynamics without any rescaling of velocities; this is straightforward, providing that
the system is sufficiently relaxed during the equilibration phase mentioned earlier in
this chapter. Problems arise, however, when the temperature of the system oscillates
without any external controlling mechanism. Such temperatures are inevitable for
finite systems but may be exaggerated by the effects arising from the truncation of
long-range electrostatic forces.
The canonical ensemble, [NVT], enables the temperature of a system to be controlled, which is achieved by coupling the simulated system to a heat bath, thus enabling a dynamic exchange of heat to and from the system. The method does however introduce energy drifts. Another method used to control the temperature involves rescaling the temperature at every step using \( \lambda \), which defines the factor \( (T_{\text{desired}}/T_{\text{actual}})^{1/2} \) in each time step of the desired temperature, as defined in equation 2.35 below:

\[
\lambda = \sqrt{1 + \frac{\Delta t}{\tau} (\frac{T_{\text{desired}}}{T_{\text{actual}}} - 1)}, \tag{2.35}
\]

where \( \lambda \) is the scaling factor, \( t \) is the time and \( \tau \) is the coupling parameter which is representative of the relaxation time of the system. The coupling parameter is adjustable and determines exactly how precise the velocity re-scaling is.

The desired temperature of a simulation can be initially calculated from the average of the kinetic energy [left hand side of equation 2.36] of all of the atoms in the system:

\[
\frac{1}{2} \sum m v_i^2 = \frac{3}{2} N k_B T_{\text{desired}}, \tag{2.36}
\]

where \( m \) and \( v \) are the mass and the velocity respectively; and \( N \), \( k_B \) and \( T_{\text{desired}} \) are the atom number, Boltzmann distribution constant and the temperature respectively.
From equation 2.36 at time $t = 0$, no velocities are known. Assigning random velocities to atoms via a Boltzman distribution for the given temperature enables the system to be heated. After the random velocities have been assigned the molecular dynamics method continues with the equilibration phase. The kinetic energy of both scaling methods can be modified by scaling the velocities, with the rate of heat transfer controlled by the coupling parameter $\tau$.

The NPT ensemble can be enabled by a similar procedure to that already explained above for the NVT ensemble, that is, by coupling to a pressure bath. The volume [as opposed to the velocities] of the atoms are changed by scaling the co-ordinates by a factor, $\lambda$, defined by the difference of the desired and actual pressure, $(P_{\text{desired}} - P_{\text{actual}})$, see equation 2.37 below

$$
\lambda = 3 \left[ 1 - \kappa \left( \frac{\Delta t}{\tau} \right) \left( P_{\text{desired}} - P_{\text{actual}} \right) \right], 
$$

(2.37)

where, $\kappa$ defines the compressibility of the system, and $\tau$ the coupling parameter as described above.
2.7.6 Calculation of the diffusion coefficient

A defined force field such as the type described previously in this was used directly in the molecular dynamics algorithms to generate the molecular trajectory over time. From this trajectory, diffusivities, $D$, are easily calculated via the Einstein relation, $D = \frac{1}{6} \langle r^2 \rangle / t$, described in Chapter 3, section 3.5.1 of this thesis, where $\langle r^2 \rangle$ is the mean square distance travelled by the diffusing molecules during a period $t$. 
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Chapter 3 Experimental techniques

3.0 Overview

This chapter summarizes the relevant experimental data relating to the two main themes of the thesis, namely the simulation of crystal growth inhibition and the modelling of molecular diffusion in zeolites. The former area is discussed first.

3.1 Mineral crystal growth

3.1.1 Introduction

Calcium carbonate is intrinsic to several areas of fundamental and applied significance. These include its presence in very high concentrations in seawater, which leads to its precipitation in oil pipes, the scale of which blocks and compromises efficient petroleum engineering. The precipitation within water also makes calcite scale conspicuous in domestic water heaters. The nuisance of calcite accumulating in unwanted places therefore provided an incentive for rational investigations into how its growth may be controlled over the past century. Calcium carbonate occurs in several forms; calcite, vaterite and aragonite. The most stable of these forms is calcite, the rhombohedral form of which was used in the Chapter 4 study. The rhombohedral form of calcite takes the form of a distorted rock salt structure. The distortion occurs in the direction of one of the three diagonals that run through the structure. The structure has six faces and six mirror planes.

Prior to discussing the literature pertinent to crystal growth inhibition, an overview of the crystal growth process will be presented. The literature indicates that crystal
surfaces can be defined by three growth regimes,\textsuperscript{14} that is, continuous growth, nucleation mediated growth and spiral growth which occurs via the development of screw dislocations.

3.1.2 Overview of crystal growth

The basis of growth theory can be charted back to the early part of the last century and is mainly attributed to Stranski’s work\textsuperscript{5} on crystal fine structure. The processes\textsuperscript{6} in figure 3.1, illustrate the dynamical features present in a basic cubic crystal. The cubes represent the mineral growth units, labelled G, attaching themselves to terraces, labelled T, step sites, labelled S and kink sites, labelled K. The model shown in figure 3.1, provided a remarkable insight into the processes thought to govern growth. The etch pits, labelled E, are usually formed due to crystal dissolution usually which experimentalists have shown to occur primarily at kink sites.\textsuperscript{8,9}

Figure 3.1. This schematic details the dynamic nature of a growing crystal surface.\textsuperscript{7} (E: etch pit, S: step, T: terrace, K: kink, G: growth unit)
Disparate crystal faces have different surface free energies, which implies various structures to be present at the microscale. The surfaces of crystals are commonly classified as terraced, stepped and kinked as previously stated. Terraces have been shown to grow via so-called ‘layer growing’ mechanisms;\textsuperscript{10} whilst steps and kinks are produced via the accumulation of steps generated on two or three terraced faces, giving rise to stepped and kinked surfaces. These two sites in particular have high free energies and offer high energy sites for growth; that is, it is more likely that a growth unit will attach itself at these locations than to terraces. Ions are therefore attached to terraces by a single bond and hence they are ‘easily’ detached into solution. The kink sites, however, provide the least favourable desorption route since the ions are attached via three bonds. Crystal growth is therefore mainly effected by growth via the addition of species to kink sites as exemplified by experimental and theoretical studies.

### 3.1.3 Mechanisms of calcite surface \{10 \bar{1} 4\} crystal growth

The advent of sophisticated microscopy techniques and apparatus during the latter part of the twentieth century gave unparalleled insight into actual in-situ crystal growth mechanisms operating in real time over a variety of reaction conditions. Information including the actual nature of the species present on a freshly cleaved surface was exposed.\textsuperscript{11}

The studies by Gratz \textit{et al.}\textsuperscript{12} and Hillner \textit{et al.}\textsuperscript{13} using atomic force microscopy (AFM), uncovered the fact that minerals such as calcite did not grow entirely according the widely accepted mechanism proposed in the Burton, Cabrera and Frank (BCF) model.\textsuperscript{6} In fact, the so-called ‘surface diffusion’ mechanism was not observed.
to operate in an important way for calcite and certainly did not control the rate of crystal growth. The surface diffusion mechanism assumes that step growth was governed by step surface area. Hence, growth units were thought to adsorb from steps which were a large distance apart and added to the front of approaching steps. The larger the distance between the steps, the faster the steps were thought to move. In fact, AFM studies showed that steps moved via mononuclear growth and that, at longer reaction times, the mechanism changed to spiral growth due to the presence of screw dislocations. The velocity of step motion was calculated to be faster than spiral growth and therefore the latter was stated as the rate determining step of the mechanism. Spiral growth centres were therefore determined as the sources of step nucleation.

Nanonocollas et al.\textsuperscript{7} state that a screw axis is created due to the fact that the angular velocity is larger closer to the dislocation. The surface over time was predicted to be covered by a series of steps in a spiral pattern\textsuperscript{6,14,15} demonstrating a realistic crystal surface.

Calcite has been initially observed\textsuperscript{16,17} to start growing as rhombohedral shaped nuclei. Two types of steps are present; these are called obtuse steps and acute steps. The obtuse step edges grow towards a side face which forms an obtuse angle with the \{10 \overline{1} 4\} face. Acute step edges grow toward a side face that forms an acute angle, with the \{10 \overline{1} 4\} face.

AFM imaging\textsuperscript{17} showed that the growth ‘hillocks’ present grew in clockwise, as well as anti-clockwise motions. The obtuse steps were observed to be growing in a
straight, uniform manner. The acute steps grew appreciably slower and hence step-bunching and macro step formation occurred due to the fact that the positive steps were able to grow up behind these slower growing steps before they [the acute] steps had time to ‘grow outwards’. The steps grew outwards via monomolecular growth and by the addition of growth units from the solution medium. Gratz et al.\textsuperscript{13} determined that the growth units were added to the obtuse kink sites, faster than any other kink sites during their observations of the calcite \{10\overline{1}4\} cleavage surface.

The work by Dove and Hochella\textsuperscript{17}, used scanning force microscopy [SFM] in order to study the various growth regimes of calcite under different degrees of saturation. Their studies contradicted earlier observations that calcite exclusively grew via the spiral growth mechanism. Dove and Hochella, observed the polynuclear ‘birth and spread’ mechanism\textsuperscript{18} to be operational initially. This particular mechanism was not observed by Gratz et al. It must also be noted that Dove and Hochella only observed the spiral growth mechanism to operate and in-fact dominate at longer reaction times. Hence it was deduced that several mechanisms were operational and governed the growth of calcite at different reaction times and under different reaction conditions.

Dove and Hochella\textsuperscript{15} also observed that calcite growth was generated by topographic protrusions, which were thought to be due to spiral growth being initiated on such areas. They also observed the dynamic surface of calcite with simultaneous dissolution and growth occurring.

Several experimentalists\textsuperscript{11,13,17,120-22} who have used microscopy techniques have therefore observed calcite growth phenomena to include the following features: the
presence of initial rhombohedral nuclei; the eventual coalescence of nuclei to form a monolayer; the onset of the ‘birth and spread’ mechanism; the onset of the spiral growth mechanism; the presence of straight, faster moving positive steps and etch pit formation during the onset of dissolution.

3.2 Crystal growth inhibition

3.2.1 Introduction

There have been several studies on the inhibition of calcite growth by organic as well as inorganic ions. The impetus for poison mechanism elucidation is derived from the oil and water industries\textsuperscript{23-24} both of which cite calcite scale as a major operational hazard. Some of the most widely used inhibitors are organic phosphonate ions and it is generally considered that diphosphonates and polyphosphonates are more efficient crystal growth poisons than monophosphonates and that their major mode of interaction is electrostatic,\textsuperscript{25} via the phosphonate head group; such interactions deplete potential as well as actual impurity sites such as kinks, preventing step flow and propagation and thereby alter crystal morphology as well as inhibiting crystal growth. Monophosphonates offer a milder poisoning capacity enabling more precise control on the accumulation of calcite scale.

3.2.2 Background

The early studies into the effects of phosphorus based poisons on crystal growth and morphology were performed by numerous workers including Brooks \textit{et al.}\textsuperscript{26} Calcite/poison processes were identified by Hatch and Rice\textsuperscript{27} and Reitmeier and
Buehrer as surface controlled events which required a very small concentration of poison to facilitate total crystal growth inhibition; these observations were supported much later by Nancollas et al. and Weigen et al. This surface controlled crystal growth mechanism was later shown to have a rate determining step governed by the rate of kink formation (Christofferson and Christofferson). Possible mechanisms of the interaction of organo-phosphorus based crystal poisons with various mineral surfaces including calcite have been explored using a variety of surface characterisation and experimental techniques including X-ray photoelectron spectroscopy, XPS, AFM, SEM by many workers including Ralston et al., Dunning et al., Davey, Sears, Vetter, Gratz et al., Mann et al., Walters et al., Stipp et al., Dove and Hochella, Austin et al. and Teng et al. Studies of the processes involved in the crystal growth mechanism were published almost a century ago and still form the foundations of contemporary crystal growth theory.

Over the last decade, de Leeuw and Parker et al. have made a major contribution to the elucidation of mineral crystal growth phenomena using atomistic simulation techniques. Simulations leading to insight into the effects of cations, phosphate anions, temperature and water on mineral growth, as well as morphological predictions which agree well with experiment have also been reported. In addition, they have also successfully modelled aspects of the calcite growth phenomena, in particular the modelling of screw dislocations and calcium carbonate unit dissolution from calcite steps using molecular dynamics. Rohl et al. also successfully simulated a variety of flexible diphosphonate ions and predicted their impact on the stabilization and resulting expression of specific surfaces of the barite crystal.
A previous study by Nygren et al.\textsuperscript{53} demonstrated how atomistic computer simulation techniques could be used to model the interaction of diphosphonate inhibitors with defects in terrace and step sites on the \{10\bar{1}4\} surface of calcite. They determined that it was unlikely for a diphosphonate ion to become incorporated into the calcite framework via the simultaneous blocking of step and terrace sites. Instead, they proposed that a diphosphonate ion was more likely to become reversibly associated with the calcite framework, thereby inhibiting crystal growth by preventing successive adsorption of \(\text{CaCO}_3\) units.

The present study builds on this previous work by simulating a variety of monophosphonate inhibitor ions at terrace and step defect sites (illustrated in figure. 3.2), with the overall aim of developing models for the inhibition mechanism and its dependence on the structural properties of the inhibitor molecules.

\textbf{Figure 3.2.} Schematic of the terrace and step sites at a calcite \{10\bar{1}4\} surface with inhibitor ion interacting at a nucleation site.
3.2.3 Role of characterization techniques on inhibition mechanism elucidation

Sophisticated structural characterisation techniques such as scanning electron microscopy and atomic force microscopy have been used to understand the molecular basis of the models for the inhibition mechanism.\cite{11,17} Gratz et al. and Hillner et al.\cite{12-13} introduced the application of atomic force microscopy (AFM), to observe crystal growth inhibition processes, which was achieved by performing real-time, \textit{in situ} AFM imaging; they observed that a significant location of the diphosphonate poison HEDP, was at the step-edge sites of the calcite crystal as opposed to terrace sites, at high, medium and low poison concentrations, (see figure 3.3 below.)

![Figure 3.3](image)

**Figure 3.3.** The evolution of poison traits on a growing calcite \{10\overline{1}4\} surface. 

*From left to right; normal, straight steps becoming grizzled after a small amount of poison and step growth is eventually halted entirely at large HEDP concentrations. Topographical highlights in the final plate show the location of the poison. Taken from references \cite{12,13}.*
Scanning force microscopy studies\textsuperscript{17} determined that after phosphate addition to fledgling, calcite surfaces, the rhombohedra shaped nuclei which were observed to spread and to coalesce [Birth and Spread Model] via straight steps in an unpoisoned solution, now gave rise to rounded nuclei. In turn, the newly rounded, quasi-rhombohedra shaped nuclei generated irregular, ragged edged steps. This observation was direct evidence of the poisons directly adsorbing to and pinning back the growing steps thus hindering their velocity and growth.

When the poisoned solution was added to the growing surface after the initial nucleation stage, that is when several rhombohedra had spawned their characteristic straight, uniformly growing steps, the poison destroyed the regular step shape by adsorbing directly at step edges resulting in non-uniformly growing steps. Hence the imaging techniques used in these studies provided compelling evidence for anionic poison affinity to the kink and step regions. Unfortunately, the resolution of these images meant that neither kinks nor water molecules were observed at all.

3.2.4 Factors controlling crystal inhibition by anionic poisons

Although the processes involved in crystal growth inhibition are acknowledged as complex, there is a general consensus that the three main factors influencing the interaction of organic phosphorus containing compounds with respect to various calcite crystal planes are: charge distribution, stereochemistry and geometry as reported by Davey\textsuperscript{54}, Mann et al.\textsuperscript{55} Austin et al.\textsuperscript{41} and Teng et al.\textsuperscript{42}
It has been noted that poison specificity can be enhanced by functionalization (Rohl et al., Black et al., Davey et al., Mann et al., Falini et al., Gill et al.), as will be underlined by the calculations reported in the present study. Indeed, the phosphonates in this work were selected in order to investigate the extent to which electrostatic interactions between monophosphonates and calcite surfaces were enhanced or decreased by specific functional groups, which may donate or withdraw electron density from the phosphonate oxygen atoms.

The five phosphonate poisons modelled during this work are discussed further in Chapter 4 of this thesis, and listed below in table 3.1.

<table>
<thead>
<tr>
<th>ion</th>
<th>formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>$(\text{PO}_3)_2\text{CH(\text{CH}_3)(\text{OH})}^4$-</td>
</tr>
<tr>
<td>HEMP</td>
<td>$(\text{PO}_3)\text{CH(\text{CH}_3)(\text{OH})}^2$-</td>
</tr>
<tr>
<td>DHMP</td>
<td>$(\text{PO}_3)\text{CH(\text{OH})}_2^2$-</td>
</tr>
<tr>
<td>PMP</td>
<td>$(\text{PO}_3)\text{Ph}^2$-</td>
</tr>
<tr>
<td>PEMP</td>
<td>$(\text{PO}_3)\text{CH(CH}_3)_2^2$-</td>
</tr>
</tbody>
</table>

Regarding morphology, the preferential distribution of additive ions e.g. transition metal and Group 1A metal ions on certain crystal faces has been shown to cause a change in crystal morphology due to a structural stabilisation (Mann et al., Kiryanova et al., Black et al., Didymus et al., Sears, Davey, Parker et al., Austin et al., Ralston et al., Vetter, Rohl et al., Parkman et al., Reeder, De Leuize et al. and Weigen et al.).
Wulff’s Theorem\(^6\) can be used to calculate the equilibrium crystal morphology, the idea was conceived by Curie\(^6\) in 1885. Wulff stated that if faceted crystals were successful in lowering the surface free energy, then the perpendicular distance from the crystal face to the crystal centre divided by the surface free energy of that particular face would be a constant for all faces of a crystal. Since symmetrically non-equivalent faces have different surface free energies, different structures are ultimately expressed. Hence the growing crystal can become altered and the surface energies can be used to predict the crystal morphologies.

The rigidity of an additive ion might be expected to limit ion location to particular defect sites and hence the respective binding ability and consequently the impact on morphology, as will be shown in Chapter 4 of this thesis. Mann \(\textit{et al.}^{54}\) supported this proposal and stated that low molecular weight additive ions that interact with inorganic crystal surfaces will do so \textit{via} electrostatic and stereochemical processes. Additives, which are structurally different from the calcite surface plane, may be limited to terrace sites (Davey\(^3^5\)). These factors are compared in Chapter 4 by calculating the replacement energies of a variety of phosphonate ions at step and terrace sites of calcite.

Since DHMP has two electron withdrawing groups, giving rise to additional hydrogen bonding thus aiding anionic/calcite interaction. It may be expected that it would be amongst the most effective of the monophosphonates in inducting any morphological changes during the crystallization process, with HEDP having a greater effect due to the presence of two phosphonate groups through which it can interact electrostatically with the calcite surface.
3.2.5 Role of pH, temperature and ionic strength on growth inhibition

Inhibition is also, it is clear, strongly determined by external factors such as pH, temperature and supersaturation (Suzuki et al., Teng et al., Dove and Hochella, van der Weijden et al., Weigen and Rosmalen, Kiryanova et al., Jonasson et al., Black et al., Mann et al., Parisieglia et al., Adams et al., Davey et al., Stumm and Morgan, Nancollas et al., Didymus et al., Zieba, Hoch et al., and Amjad et al.). Conformational fluctuations aid specificity in binding (Gill et al., Mann et al., and Rohl et al.). Smaller, narrower steps are observed after the additive interacts with crystal planes that are not otherwise expressed in the pure calcite structure and hence the morphology is altered. Rounded steps are caused by the slower step growth due to the adsorbed layer of additive ions on the terraces of stepped surfaces, (Walters et al. and Teng et al.)

The requirement of a solution to have a pH in the range 4 to 8, in order for morphological disturbances to be observed, has been documented in several studies, including that of van der Weigen et al., Rosmalen et al. and Nancollas et al. who amongst others showed that a neutral-alkaline pH is required for optimal calcite growth inhibition to take place. No morphological changes, have been observed to take place at acidic pH levels below pH 3. This is explained by protonation of the additive and calcite surface at low pH (Davey et al., Black et al., Didymus et al., Mann et al. and Nancollas et al.) Therefore, only doubly charged additive ions might be expected to interact with the growing crystal surface electrostatically, (Mann et al., Austin et al., Weigen and Rosmalen and Davey et al.).
As noted, various inhibitor/surface systems have been studied for many years. Suzuki et al. reported early work on the co-precipitation of calcite with the anionic phosphate ion ($\text{PO}_4^{2-}$) even at very low pH values where protonated phosphate ions would be expected to be in the highest concentration. Cabrera et al. showed how perfectly smooth, flat crystal surfaces in contact with supersaturated solution showed no crystal growth whereas adjacent stepped faces showed rapid growth.

Regarding the molecular basis of the inhibition mechanism, two routes are thought to operate: 1] Inhibitor ions adsorb onto kinks [active growth sites], thus making them unavailable for growth. 2] The additive ions adsorb onto terraces of steps of a growing crystal, thus impeding the advancement of that step, as proposed by Cabrera-Vermilyea who imply an irreversible adsorption of the additive in contact with the surface. Gutjar et al. argue that the advancement of steps are caught by the additives on the terrace whilst they grow in between them. Steps therefore become bent as the velocity is decreased. A major aim of this thesis is of course, to advance our understanding of the molecular mechanisms of calcite growth inhibition.

3.2.6 Experimental methods used to observe crystal growth and inhibition

The experimental techniques used to study crystal growth and inhibition mechanisms and the corresponding kinetics of these reactions include the constant composition technique, the free drift method and the potentiostatic method. Each of these methods is now briefly reviewed.
3.2.6.1 The constant composition technique

This method was developed by Tomson and Nancollas\textsuperscript{82} and has been widely used by several workers\textsuperscript{38,40,43,46,51,52,65} to establish the rates of crystal growth processes in order to determine their likely mechanisms. As the title suggests, the method enables the activities of the reactants in solution to remain constant for the duration of the experiment. The popularity of this method is due also to the advantages it holds over other mechanistic predictor methods, which include the following:

- The effect of crystal growth poisons on the rate of a reactions can be followed for long reaction times whilst maintaining a constant concentration of calcium carbonate ions and poisons.\textsuperscript{83}
- The rates of growth and dissolution processes may be accurately evaluated at very low saturation levels.
- Changes in the surface reactivity may be followed as a function of time.
- Analyses can be achieved at exact points corresponding to a phase diagram thus avoiding side reactions from occurring.\textsuperscript{84}

3.2.6.2 The free drift method

The free drift method was developed by Davies and Jones\textsuperscript{85} in the early part of the last century. The kinetics of a particular process are elucidated by measuring concentration variations with time via various sensor or analytical methods. These sensors include photometric, conductometric and potentiometric methods.\textsuperscript{83}
3.2.6.3 The potentiostatic method

In order to ascertain the processes governing a reaction at a particular pH for example, typical pH maintenance procedures are invoked\textsuperscript{84,85}, which is achieved via the addition of acidic or basic titrant solutions controlled by a potentiostat incorporating a glass and reference electrode.\textsuperscript{86} The corresponding rate of reaction can be determined from the volume of titrant depletion with time.
3.3 Diffusion in microporous zeolites

3.3.1 Introduction

In this section, we summarize the experimental background relevant to our simulation studies on hydrocarbon diffusion in zeolites reported in Chapter 5. Zeolites are defined as crystalline, porous aluminosilicalites which are constructed from corner sharing tetrahedra. The silicon or aluminium atoms are co-ordinated to four oxygen anions at the four corners of the tetrahedron. They are also commonly protonated and contain extra framework cations. Zeolites are microporous materials; recently mesoporous silicas have been synthesized. Microporous zeolites have pore dimensions of less than 20Å whereas the pore dimensions of mesoporous silicas are between 30Å<d<60 Å.

Barrer\textsuperscript{87,88} performed some of the earliest studies on microporous zeolites by characterizing their structure, synthesis and their shape selective catalysis applications. Naturally formed zeolites can be described as volcanic minerals formed when volcanic ash was deposited in ancient alkaline lakes. The resulting alkaline silica rich solutions led to zeolite synthesis.

Modern zeolite chemistry has been characterized by the variety of synthetic zeolites which can now be designed with a view to specific, desirable applications. Molecular diffusion in zeolites is an important area of industrial significance particularly in the areas of shape selective catalysis and gas separation. The ion exchange properties\textsuperscript{89-90} are also of key industrial importance. Typical zeolite structures\textsuperscript{91} are shown in figure 3.4.
Zeolite frameworks can be purely siliceous or of the aluminosilicalite variety; for example, silicalite is the siliceous form of H-ZSM5. A high aluminium to silicon framework ratio may be indicative of a stable framework, as suggested by the work of Ooms et al. The variation of the ratio can lead to changes in the number of rings present in the lattice.

Zeolites have enormous internal surface areas such that only one gram of zeolite provides up to several hundred square meters of internal surface. This characteristic of zeolites has given them excellent applications as sorbants and promotes their use in the area of shape selective catalysis. This process is of importance to the petroleum industry including major application in hydrocarbon cracking.

As noted, zeolites can contain extra framework cations such as Ca$^{2+}$ or Na$^+$ as a result of which they have the ability to exchange cations. This substitution of ions enables them to adsorb selectively certain harmful or unwanted elements from soil, water and air. A classic example is the removal of calcium from hard water where they exchange sodium for calcium ions. A further application of zeolites is in landfills and at industrial sites, where they aid the prevention of the release of a number of harmful or unwanted elements into the environment.
Figure 3.4. From top: (A) zeolite zinc silicalite [ZSM-48], (A1) unit cell of zinc silicalite.; from bottom: (B) zeolite ABW, (B1) zeolite ABW unit cell and middle diagram: (C) zeolite siliceous Faujasite.
Molecular diffusion is a key phenomenon in many systems. In zeolites it is a property of major importance, influencing shape selectivity in petrochemical catalysis and of course, controlling gas separation. For example, the inequality of diffusion migration coefficients of two of the xylene isomers (para and ortho) is exploited in the area of catalysis where the faster diffusivity of para-xylene can be leveraged. Typically, ortho-xylene is not able to travel as quickly or via all channel systems as the para-xylene isomer. This feature is modelled and reported in Chapter 5 of this thesis. Figure 3.5 shows a snapshot taken of a para-xylene molecule residing within a 12 MR channel.

![Figure 3.5. Snapshot of a para-xylene molecule diffusing within a CIT-1 12MR channel [viewed along the [010] projection].](image)

Self diffusion in microporous zeolites such as CIT-1 used in the present study, can be followed by a variety of experimental techniques [explained later in this section] or computationally by tracing the paths of motion of a sample of molecules in which the
mean square displacement (MSD), is calculated as the average distance moved per unit of time in the three co-ordinate directions of space. The rate of the molecule's self diffusivity can be evaluated by equation 3.1, the Einstein relation.  \(^{103}\)

\[
\langle r^2_\alpha(t) \rangle = 6Dt ,
\]

(3.1)

where \(\alpha\) is the atom or molecule type, The slope of the MSD versus time, \(t\), graph therefore allows the diffusion coefficient, \(D\) to be calculated.

### 3.4 Experimental techniques and self diffusion

The mechanism by which molecules diffuse through pores has been shown by various workers\(^{105-108}\) to be governed by factors including pore size, pore wall, structure and molecular size and thermodynamics factors.

The experimental techniques\(^{109-112}\) which have been used to determine the diffusivity in microporous zeolites include uptake methods, pulsed field gradient nuclear magnetic resonance (PFG NMR), neutron scattering, zero length column (ZLC) and chromatography. However, chromatography, uptake and ZLC methods are very slow and calculated diffusion coefficients evaluated by the Einstein relation after molecular dynamics simulations\(^{113}\) [explained later in this chapter] cannot be directly compared with diffusivities generated from these methods.

Self-diffusion of molecules under equilibrium conditions such as benzene through microporous zeolites such as Faujasite, has been determined by the development of spectroscopic diffusion measurement techniques. These experimental molecular tracer
techniques include NMR gradient methods such as [PFG NMR], as well as thermal neutron scattering techniques such as quasi-elastic neutron scattering [QENS]. The results of experiments using these methods are more comparable with simulations and a more detailed account therefore follows.

3.4.1 Overview of experimental techniques

The PFG NMR technique is generally considered to be more flexible than that of neutron scattering due to the larger time scales over which self diffusion can be monitored by the former. Typically, PFG NMR can track diffusion over distances between micrometers to millimetres. Neutron scattering techniques however, can only trace diffusion at the nanosecond time-scale. Both techniques are able to trace directly the actual route of the molecule. NMR methods achieve this by the interaction of a magnetic dipole moment of the nuclei of molecule with their surroundings, which generates information about the location of the nuclei and their dynamic environment. The aim of both techniques is to measure self-diffusion which the PFG NMR technique is able to determine directly. Auerbach et al.\textsuperscript{114} state that PFG NMR is preferable to other experimental techniques since long time scale transitions such as movement of a molecule from a sorption site to a window can be followed whereas shorter time scale methods would only measure intra-cage molecular movements.

3.4.2 Self diffusion and neutron scattering

Neutron scattering is governed by the interaction of diffusing molecules with the neutron beam. Diffusion measurements are therefore enabled by the fact the energy
exchange between the neutron beam and the ensemble of molecules is influenced by the molecular mobility.

The analysis of experimental data assumes that the self-correlation factor, the quantity accessible from incoherent scattering measurements is of the Gaussian form shown in equation 3.2:

$$G_s(r, t) = \frac{1}{4\pi \gamma(t)^2} \exp\left[-\frac{r^2}{4\gamma(t)}\right], \quad (3.2)$$

Where $\gamma(t)$ can be correlated to the mean square displacement, $\langle r^2(t) \rangle$ of a particle during time $t$, see equation 3.3

$$\langle r^2(t) \rangle = \int r^2 G_s(r, t) dr = 6 \gamma t \quad (3.3)$$

from which the diffusion coefficient can be calculated by evaluating the gradient of the plot.

3.4.3 Self diffusion and NMR methods

Intracrystalline diffusion coefficients have been reliably determined using PFG NMR.\textsuperscript{115,116} The basis of this technique relies on the application of a $\pi/2$ pulse which shifts the vector sum of the magnetic moments into the plane perpendicular to the direction of the constant magnetic field where it rotates at the Larmor frequency. The Larmor condition can be described by the way in which the nuclear spins rotate
around the direction of the constant applied magnetic field, with a constant angular velocity and hence a constant inclination to the field.

Therefore, the phase angle derived from the nuclear spins as a result of their motion is position dependent. The evaluation of the phase angle determines the actual position of the molecular nuclei and hence the magnitude of their diffusion path over a given time.

In the pulsed field gradient technique, the field gradient is superimposed on the magnetic field (B) over two short time intervals. It is assumed that the field gradient pulses are of identical length and size but of opposite sign. The motion of the transverse magnetization [vector sum of magnetic moments of individual nuclei] is depends on the spatial co-ordinate, z, when influenced solely by the field gradient pulse.

The initial gradient pulse hence generates the dephasing of the vectors of the transverse magnetization at various locations within the molecule. This dephasing results in a decay of the magnetization. If the molecule's position remains unchanged during the interval between the two gradient pulses, the magnetization vector becomes restored to its original value. If on the other hand, the molecule's location changes in between the time interval of the two pulses, the magnetization will not be fully returned to the original value as before. The greater the mean squared displacement, the greater the decrease in the NMR signal. The self-diffusion coefficient and the molecular mean squared displacement can then be evaluated from the following relation described in equation 3.4:
\[ \varphi = (A, \delta g) = \exp \left[ -\gamma' \delta^2 g^2 \left( \langle r^2(d) \rangle \right) / 6 \right], \quad (3.4) \]

Equation 3.4 generates a slope after plotting the signal intensity or \( \varphi \) versus \( \langle \delta g \rangle^2 \).

Here \( \varphi \) represents the ratio of the intensity of the spin echo signal in the presence, \( A(G) \), and in the absence, \( A(0) \), of a gradient field, \( \gamma \), denotes the gyromagnetic ratio and \( g \) is the field gradient, \( [g \text{ may vary in experiments whilst keeping } \delta \text{ and } \Delta \text{ constant}] \).

### 3.4.4 Chromatography

The application of this method to calculate diffusion in zeolites have been reported in, for example, reference (104). Here, a continuous flow of argon which is non-adsorbing is used as a carrier. The chromatography column containing the adsorbate to be studied is then filled with argon. At the beginning of the experiment a short stream of sorbate is injected at the inlet of the column. The concentration of the output is then monitored closely. The average retention time is a measure of the adsorption equilibrium. The width of the response peak can be elucidated via the dual effects of mass transfer resistance and axial mixing within the chromatographic column. If measurements are taken across a range of conditions then contributions to the pulse widening can be attributed to either mass transfer resistance or axial mixing, hence intraparticle or intracrystalline diffusivities can be calculated. A major advantage of this method is that by establishing a high carrier rate through the column, external mass and heat transfer resistances are eliminated more successfully than in a static system.
3.4.5 Zero length column [ZLC] method

This method has also been used to determine intracrystalline diffusion in zeolites.\textsuperscript{104} High diffusivity values can be measured and only a small amount of the adsorbate is required for the measurement to be taken. ZLC was developed in order to over-ride the major disadvantage of the chromatographic method, which arises from the fact that the dispersion width of the response peak is governed by the mass transfer resistance as well as axial dispersion. To measure the mass transfer resistance and therefore the intraparticle diffusivity, the contribution from the axial dispersion must be discarded or included. If the contribution from the axial dispersion is too dominant then this implies that intraparticle diffusion is too rapid and the integrity of the measurements are compromised.

In ZLC, a small quantity of the adsorbant is equilibrated at a uniform sorbate concentration. The adsorbate is then desorbed by using an inert gas at a flow rate which is able to maintain zero sorbate concentration at the surface of the crystals. The rate of desorption is measured by following the composition of the discharged gas. A moisture sensitive flame ionization detector [FID] for organic sorbates is used due to its sensitivity.
3.4.6 Summary

A wide variety of techniques is therefore available for the measurement of diffusion in zeolites. Widely differing results are obtained from these different approaches. There is, therefore a clear need for guidance from theoretical methods as discussed in the next section.

3.5 Theoretical techniques and self diffusion

3.5.1 Molecular dynamics and self diffusion

The method of molecular dynamics discussed in the previous chapter has been extensively applied to the study of diffusion in zeolites. Mean square displacement plots yield diffusion coefficients and trajectory analysis conveys direct mechanistic information. Results of molecular dynamics simulations can be usefully compared to PFG NMR and neutron scattering methods of diffusion processes in zeolites, and the molecule’s trajectory can be visualized.

A limitation of molecular dynamics and diffusion processes is that the length of time diffusion can be followed is currently limited to the order of nanoseconds. Therefore, corresponding diffusion coefficients less than \( \sim 10^{-8} \text{cm}^2 \text{s}^{-1} \) are not evaluated.

Other theoretical techniques such as the kinetic Monte Carlo method have been utilized by Fitchthorn et al.,\textsuperscript{121} to simulate the diffusion of molecules within cationic and acidic zeolites in conjunction with PFG NMR. Forester and Smith.,\textsuperscript{122} combated the problem of slow diffusion phenomena as observed for benzene/Faujasite and benzene/silicalite systems, by employing the ‘Bluemoon’ ensemble in which
constrained reaction co-ordinate dynamics characterise the free energy profiles of for example benzene in silicalite along the mean reaction path for diffusion. The path of the molecule in a particular direction corresponding to a particular framework window was successfully plotted and the corresponding diffusion coefficients were evaluated.

The results reported in Chapter 5 are based on classical NVE, NVT and NPT ensemble molecular dynamics using standard sets of interatomic potentials details of which have been already presented in Chapter 2.

3.6 Diffusion in microporous zeolites: characteristics

As was stated earlier in this chapter, many factors govern the diffusion of hydrocarbon molecules through a zeolite framework system. Computational and experimental techniques together have generated an insight into the mechanisms and magnitude of diffusion. The factors highlighted include those of:

- framework flexibility,
- effect of sorbate loading,
- effect of system temperature,
- effect of varying simulation time,
- effect of atomic polarisability,

Although some theoretical studies have shown a close correlation to reliable long timescale experimental techniques, others [including this work] report deviations by as much as three orders of magnitude for calculated diffusion
coefficients.\textsuperscript{119,125-126} Discrepancies such as these may be attributable in part to processes occurring on the external surfaces of the zeolite which are externally protonated.\textsuperscript{127-130} Extra framework cations might be also expected to have a substantial effect on molecular diffusion processes. Clearly, any diffusion process will be influenced strongly by such physical factors. Therefore, purely siliceous systems such as those modelled during this work for bulk CIT-1/xylene and Faujasite/benzene systems might be expected to yield high diffusion coefficients. Care must also be taken in comparison of experimentally determined diffusion coefficients with theoretical values since only the neutron scattering techniques and PFG NMR experimental methods directly evaluate this property.

Incorporating the effect of framework fluctuations within simulations is now widespread.\textsuperscript{129-134} Many workers now acknowledge that the extra computational expense incurred actually is necessary in reproducing realistic zeolite frameworks. Early work, however, often omitted these effects. Goodbody \textit{et al.}\textsuperscript{135} reported close correlation with experimental diffusion values for their fixed framework study. Since the randomness of molecular jumps can be attributed to the interactions between diffusing molecules, the framework rigidity may not be a relevant factor. The fixed framework study of June \textit{et al.}\textsuperscript{136} neglected the contributions of momentum and energy transfer by proposing that the thermal equilibrium could be maintained by the intense interaction between diffusing molecules. Some of the earliest studies to include this factor were those of Demonitis \textit{et al.}\textsuperscript{129} and Catlow \textit{et al.}\textsuperscript{130} It was Demonitis \textit{et al.}\textsuperscript{131} and Raj \textit{et al.}\textsuperscript{132} who determined that the effect of including framework fluctuations within their molecular dynamics calculations increased the diffusivity by approximately twenty percent. This observation was supported by
Ruthven and Kärger\textsuperscript{104} who state that self diffusion would be expected to be affected by the zeolite pore walls due to the fluctuation [size] of microporous zeolite channels. Increased temperatures lead as expected to higher diffusion coefficients. Elevated temperatures have also been shown by several studies\textsuperscript{132,133} to give rise to changes in molecule routes within zeolite channels. For example Raj \textit{et al.}\textsuperscript{132} determined from analysis of diffusion coefficients in $x$, $y$ and $z$ directions for the octane/silicalite system, that octane entered straight channels at higher temperatures [450K] as opposed to sinusoidal channels at lower temperatures [300K]. The study of benzene within siliceous Faujasite performed by Henson \textit{et al.}\textsuperscript{119} also observed the coupling of lattice vibrations with sorbate motion. It was determined that the increase in temperature distorted the 12-ring window to such an extent that the molecular motion was aided through macrocell movement. The higher temperature simulations were deemed to cause a change in the sorbate migration mechanism since extra rate processes were isolated by inspection of the generated MSD versus time plots and inspection of trajectory plots with time. Hence, it can be assumed that alternative channel directions were followed.

In this way, molecular dynamics has also demonstrated the anisotropy of diffusion in zeolites. For instance in dynamics studies of methane in silicalite,\textsuperscript{137} which has both straight and sinusoidal channels, the movement of molecules is not uniform. Instead, methane was calculated to diffuse via straight channels approximately four times more than sinusoidal channels a result, which has been verified by the diffusion random walk model.\textsuperscript{108} It must also be noted that for translational hopping motion, higher temperatures and longer simulation times are necessary otherwise so-called reverse hops were only observed.
Bull et al.\textsuperscript{138} studied the siliceous Faujasite/benzene simulation system. Benzene was observed to be in close contact with the wall of the zeolite channel again proving that zeolite framework fluctuations have a vital role to play in self diffusion of some. Bull et al. also found that systems such as benzene/siliceous Faujasite require appreciable simulation times and temperature elevation before appreciable molecular mobility was observed. At shorter simulation times of only 25ps, only intra cavity motion was observed as opposed to inter cavity jumping due to higher molecule mobility observed as the route was tracked for longer times. However a close correlation between PFG NMR and molecular dynamics diffusivities was made.

Generally, workers including Sastre et al.\textsuperscript{125} and Pickett et al.\textsuperscript{139} have observed that an increased loading\textsuperscript{132,140} of molecules yields a lower value of the diffusion coefficient which is attributable to the fact that the average residence times between molecule jumps increases with loading. This property was tested during the current work, the results of which are reported in Chapter 5. However, Catlow et al.\textsuperscript{130} reported the opposite effect. That is, for increased methane loading the diffusion coefficients increased dramatically. The effect remains unexplained.

Intuitively, one would expect that molecule size and channel aperture also have roles to play in the diffusion of molecules in microporous zeolites, as demonstrated in several studies. For example, the work of Sastre et al.\textsuperscript{141} and Nagy et al.\textsuperscript{142} modelled the mixture of para-xylene and ortho-xylene. It was observed that the ortho isomer had difficulty entering the 10 membered ring [MR] successfully compared to the tapered para-xylene, which had no problems diffusing at significantly higher rates down both 10 and 12 MR channels of CIT-1. This difference in isomeric size causing
selective behaviour has been exploited in the area of molecular sieve catalysis as a means of separating the isomers. The work of Raj et al.\textsuperscript{132} showed that longer hydrocarbon molecules preferentially diffused down sinusoidal channels of ZSM5 at higher temperatures compared to straight channels at lower temperatures. The presence of moisture has also been shown by Tezel et al.\textsuperscript{143} and Beagley et al.\textsuperscript{144} to cause a decrease in diffusivity. It is speculated that this effect is due to water-cation complex formation.

The factors modelled during Chapter 5 of this thesis were effect of loadings, effect of time scales and the effect of molecular structure. In addition we examined the effect of including oxygen polarizability in the simulation – a factor which had not been considered previously.
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Chapter 4  Calcite crystal growth inhibition by phosphonates: simulation studies

4.0  Introduction

The background to this study was given in Chapter 3. Here, we report detailed simulations of phosphonate/calcite interactions. In particular, the interaction of monophosphonate and diphosphonate mineral growth inhibitor ions with the planar and stepped \{10\bar{1}4\} surfaces of calcite were simulated using the MARVINS\textsuperscript{1} surface simulation code. The mechanisms of poison/substrate replacement and binding were modelled. The energy minimization and molecular dynamics techniques were employed throughout the work which was performed in order to determine the following:

- Which phosphonate inhibitor ion had a greater affinity for the planar \{10\bar{1}4\} surface as opposed to the stepped \{10\bar{1}4\} plane?

- The structural factors controlling the predominant mode of interaction of the inhibitors with respect to the real and ideal surfaces.

- Whether monophosphonate inhibitor ions possessing heteroatom substituents demonstrated a greater binding to the calcite lattice in contrast to the organic functional groups contained in phenyl monophosphonate.

- The most feasible mechanism operational during calcite mineral inhibition by the mono-substituted and the di-substituted class of phosphonate poison.
4.1 Phosphonate ions used in this study

The five phosphonates modelled during this work are listed in table 4.0 and are depicted in Figure. 4.0. Three of the monophosphonates studied were the mono-substituted analogues of the diphosphonates previously modelled. The HEMP ion has a methyl as well as a hydroxyl group; the PEMP ion contains two methyl groups, whilst the DHMP ion has two hydroxyl functionalities; HEDP is the diphosphonate analogue of HEMP ion whilst PMP contains a phenyl functional group attached to the phosphonate motif. Their inclusion allowed further exploration of the effect of different functional groups on the mode of crystal growth inhibition effected by the phosphonates. Modelling of the interactions of these five inhibitors with the calcite surface will therefore allow us to investigate the impact of both steric and electrostatic factors on the inhibition mechanism. The phenyl substituted monophosphonate was included to allow a comparison to be made with experimental observations regarding its influence on the calcite crystallization.

Table 4.0. The five phosphonate ions modelled during this work are shown below.

<table>
<thead>
<tr>
<th>ion</th>
<th>formula for replacement calculations</th>
<th>formula for binding energy calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>[(PO₃)₂CH(CH₃)(OH)]⁺⁺⁺⁺</td>
<td>[(PO₃)₂CH(CH₃)(OH)]⁰⁺⁺⁺⁺</td>
</tr>
<tr>
<td>HEMP</td>
<td>[(PO₃)CH(CH₃)(OH)]⁻⁻⁻⁻</td>
<td>[(PO₃)CH(CH₃)(OH)]⁰⁻⁻⁻⁻</td>
</tr>
<tr>
<td>DHMP</td>
<td>[(PO₃)CH(OH)₂]⁻⁻⁻⁻</td>
<td>[(PO₃)CH(OH)₂]⁰⁻⁻⁻⁻</td>
</tr>
<tr>
<td>PEMP</td>
<td>[(PO₃)CH(CH₃)₂]⁻⁻⁻⁻</td>
<td>[(PO₃)CH(CH₃)₂]⁰⁻⁻⁻⁻</td>
</tr>
<tr>
<td>PMP</td>
<td>[(PO₃)Ph]⁻⁻⁻⁻</td>
<td>[(PO₃)Ph]⁰⁻⁻⁻⁻</td>
</tr>
</tbody>
</table>
**Figure 4.0.** The five phosphonate ions modelled during this study: from top hydroxyethylidene monophosphonate (HEMP), propyl ethyldene monophosphate (PEMP), dihydroxymonophosphonate (DHMP), phenyl monophosphonate (PMP) and hydroxyethylidene diphosphonate (HEDP).
4.2 Computational method

The interaction of phosphonate molecules with the calcite surface was simulated using the [Minimization and Relaxation of Vacancies Interstitials for Neutral Surfaces] MARVINS simulation code. MARVIN uses a small finite number of atoms that are duplicated in two dimensions. This basic 2-D cell has 2-D periodic boundary conditions parallel to the interface. The 2-D lattice vectors are used to generate the 'full' surface by being applied to the co-ordinates of each atom within the small finite cell. The co-ordinate system has been chosen so that the z axis is normal to the surface. This 2-D surface simulation cell is shown below in figure 4.1.

![Figure 4.1. Schematic of the MARVIN simulation model. Region I atoms are allowed to relax whereas those in region II are kept fixed.](image)

The software is effective at modelling crystals containing molecular ions since it prevents them from being cleaved during the surface generation process. It is also
suitable for modelling molecules on surfaces as it includes of molecular mechanics potentials with parameters being determined by connectivity.

The 2-D surface simulation cell as depicted in figure 4.1 consists of one or more blocks divided into regions [I and II]. Each region contains structural units which may be ions or molecules consisting of one or more atoms. The atoms of the region I are relaxed to zero force. Those in region II are kept fixed to reproduce the semi-infinite crystal. The total energy of the system is defined as the energy of all the region I structural units, which interact with each other, the region II units and the periodic images of both regions. The extended MARVINS code used within this work includes a molecular dynamics routine implemented by Catlow et al.⁵

The simulated surface [see figure 4.2] consists of one block A with the structural units near the surface in its region I [region IA] and the underlying region II [region IIA]. A periodic array of phosphonate molecules to be docked onto a surface is formally in region I of another block [B], while the corresponding region II is empty.
Figure 4.2. The MARVIN simulation cell used to dock the phosphonate poisons onto a calcite surface. The cell is repeated infinitely in the x and y directions. The region I atoms are allowed to relax whilst those in region II are kept fixed.
4.3 Interatomic potentials

4.3.1 Calcite

The Born-model potential was used to model calcite interactions. It was developed by Pavese et al.\textsuperscript{6,7} The Ca and CO\textsubscript{3} ions were assigned formal charges. Fractional charges were assigned to the carbon and oxygen atoms of 0.587 and −1.632 respectively. Non-bonding interatomic potentials were described by the standard Buckingham function [equation 2.14], while the intra-ionic covalent interactions between the carbon and oxygen atoms of the CO\textsubscript{3}\textsuperscript{2−} ions were modelled using a Morse function [equation 2.9]. The carbonate ions, were assigned a harmonic angle-bending term of the type given in equation 2.10 with an equilibrium angle of 120°. An additional term which expressed the energy increase, $E_\psi$, of the CO\textsubscript{3} unit due to out of plane displacements of the carbon atom was also added, this term was described by equation 2.12.

Oxygen atom polarizability was modelled using the shell model of Dick and Overhauser\textsuperscript{8} [explained in Chapter 2] in which each ion is harmonically represented as a core connected by a spring to a shell. The shells were assigned a small nominal mass. It should be noted that Pavese et al.\textsuperscript{6} found that the shell model described the lattice properties and vibrational spectra of calcite adequately.

4.3.2 Modelling of phosphonates

The monophosphonates were modelled using the consistent-valence force field [CVFF]\textsuperscript{9} available from within Discover. This is a generic, first generation force field which was originally developed in order to model biomolecules. The parameters have been determined by the fitting of experimental properties. The analytical terms present include
harmonic bond and harmonic angle expressions; a Fourier expansion in theta to represent the torsional term as well as the Coulombic and Lennard-Jones expressions describing the non-bonded electrostatic and van der Waals terms respectively. The sum of these analytical terms are shown in equation 4.1 below and have been discussed in Chapter 2 of this thesis:

\[
V = \sum_{\text{bonds}} k_b \left( b - b_0 \right)^2 + \sum_{\text{angles}} k_\theta \left( \theta - \theta_0 \right)^2 + \sum_{\text{torsion}} k_\phi \left( I + \cos \phi \right) + \sum \left[ \left( \frac{r_j}{r} \right)^{12} - 2 \left( \frac{r_j}{r} \right)^6 \right] + \sum \left( \frac{q_i q_j}{r_{ij}} \right) \tag{4.11}
\]

4.3.3 Charges

A key requirement for modelling phosphonate ions is a suitable representation of the charge distribution. The method of Gasteiger et al.,\textsuperscript{10} discussed in Chapter 2, and obtained from the Cerius\textsuperscript{2} package was employed, since the method gave the same charge distribution on all the oxygen atoms of the phosphonate group.

The neutral phosphonic acid species have the formula [R_3CPO_3H_2]^0. However, within an alkaline biased medium, the fully deprotonated [R_3CPO_3]^2- ion is present. In order to calculate accurately the binding energy of the fully deprotonated ion to the neutral calcite surface (with no defects present), a charge of zero was applied to the deprotonated ion approximating it to [R_3CPO_3]^0.
4.4 **Inhibitor Docking on Planar and Stepped \(10\overline{1}4\) surfaces**

The two steps of the \(10\overline{1}4\) calcite surface were defined by surface vectors of \((4 -2)\) and \((-4 -6)\), with half of the top layer of ions missing, as shown in figure 4.3. A distance of approximately 23Å separated the obtuse \([2\overline{1}]\) and acute \([21]\) steps. Calculations were performed with the MARVIN code.

![Obtuse step Acute step](image)

**Figure 4.3.** Calcite \(10\overline{1}4\) plane showing location of \([2\overline{1}]\) obtuse and \([21]\) acute steps.

These calculations were repeated with both planes being relaxed using a quasi-Newtonian energy minimization algorithm described in Chapter 2. The relaxed configurations were used for the subsequent calculation of binding and replacement at the ideal and defective surfaces.
4.5 Simulation protocol for phosphonate docking

Before docking each phosphonate species onto the calcite surface, a quasi-Newtonian energy minimization was performed in order to generate the equilibrated conformation of the inhibitor molecule. The phosphonates were then randomly ‘docked’ onto the planar calcite \{10\bar{1}4\} surface. This phosphonate/planar \{10\bar{1}4\} system was then subjected to 500 steps of quasi-Newtonian energy minimization and allowed to relax with respect to the planar calcite surface. The relaxed phosphonate/planar \{10\bar{1}4\} system was further subjected to 15ps of constant temperature molecular dynamics at 298K. The simulation yielded a catalogue of conformations; the three of lowest energy were extracted for further quasi-Newtonian energy minimizations, in order to generate the most favourable energy conformation. This procedure was repeated for the stepped \{10\bar{1}4\} surface/phosphonate systems and in the calculation of replacement energies.

4.6 Steric matching

The calculated equilibrium distance between the phosphonate groups within the HEDP ion of 4.1\text{Å} is significant since of the three closest carbonate-carbonate calcite distances of 4.05\text{Å}, 4.80\text{Å} and 6.29\text{Å} on the \{10\bar{1}4\} calcite surface, clearly, a pair of carbonate ions separated by 4.05\text{Å} provides the best match for replacement by the fully deprotonated diphosphonate ion. These simple predictions have been investigated by performing the requisite calculations for replacement processes on the planar \{10\bar{1}4\} calcite surface for the HEDP ion. Following previous work\textsuperscript{11,12} the reaction schemes below may be proposed for the replacement by a monophosphonate ion of a surface \text{CO}_3^{2-} species;
for which the corresponding replacement energy is given by equation 4.2 below:

\[ E_{\text{replacement}} = E_{\text{solution}} \left( \text{CO}_3^{2-} \right) + E_{\text{surface}} \left( \text{monoPO}_3^{2-} \right) - E_{\text{solution}} \left( \text{monoPO}_3^{2-} \right) - E_{\text{surface}} \left( \text{CO}_3^{2-} \right), \quad (4.2) \]

In order to evaluate the replacement energy, an estimate of the solvation energies is required for all the species present in the system. These solvation calculations were performed using Discover® within InsightII, using the CVFF potential, as will be now be discussed in greater detail in the following section.

### 4.7 Solvation calculations

Initially, an isolated phosphonate ion was subjected to 1000 steps of conjugate-gradient/steepest descent minimization followed by 15ps of NVT dynamics performed at 298K followed by 1000 steps of energy minimization. Next, the ion was soaked within an equilibrated water sphere of radius 15Å and the entire phosphonate/water sphere system was subjected to the same simulation regime. Solvent molecules, which overlapped with the atoms in the poisons that were being solvated, were removed. Finally, the phosphonate ion was removed from the water sphere and the identical simulation procedure was repeated on the solvent alone. This procedure was repeated five times for each ion/water sphere system. The calculated solvation energies are reported in table 4.1. They are calculated as the difference between the energy of the solvation species and that of the solvent sphere.
Table 4.1. Calculated solvation energies of anionic phosphonate ions. Simulations were performed using DISCOVER® and included energy minimization and 15ps of molecular dynamics performed at 298K.

<table>
<thead>
<tr>
<th>phosphonate ion</th>
<th>solvation energy/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[HEDP]$^{4-}$</td>
<td>-3079.8</td>
</tr>
<tr>
<td>[HEMP]$^{2-}$</td>
<td>-1367.2</td>
</tr>
<tr>
<td>[DHMP]$^{2-}$</td>
<td>-1414.4</td>
</tr>
<tr>
<td>[PEMP]$^{2-}$</td>
<td>-1275.5</td>
</tr>
<tr>
<td>[PMP]$^{2-}$</td>
<td>-797.9</td>
</tr>
<tr>
<td>[CO$_3$]$^{2-}$</td>
<td>-1109.6</td>
</tr>
</tbody>
</table>

4.8 Replacement energy calculation at the planar calcite surface

Replacement energies were calculated for the HEDP ion, at the three nearest carbonate-carbonate distances present in the planar {10$ar{1}$4} plane for the HEDP ion in order to elucidate the most favourable steric match.

Table 4.2. Calculated replacement energies used to establish most feasible CO$_3$-CO$_3$ distances occurring within the planar {10$ar{1}$4} surface.

<table>
<thead>
<tr>
<th>CO$_3$-CO$_3$ distance</th>
<th>replacement energy/ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.29Å</td>
<td>1154.0</td>
</tr>
<tr>
<td>4.80Å</td>
<td>336.7</td>
</tr>
<tr>
<td>4.05Å</td>
<td>43.4</td>
</tr>
</tbody>
</table>
From table 4.2, the least unfavourable replacement energy of 43.4 kJmol$^{-1}$ corresponds as expected to the closest match of the phosphonate group separation (of 4.1Å) with the carbonate-carbonate spacing of 4.05Å. Moreover, the replacement energies, for all the carbonate distances were positive, suggesting that diphosphonates are more likely to be sorbed onto the calcite surface rather than permanently incorporation into the calcite framework using two fully deprotonated phosphonate groups. The experimental literature is inconclusive on this crucial point$^{13-15}$, since external factors such as pH play a major role. However, it is likely that one singly protonated phosphonate group is required to facilitate optimum binding of a diphosphonate poison to calcite whilst one fully deprotonated phosphonate group becomes incorporated via CO$_3$ replacement.

4.9  
**Phosphonate interactions at the ideal and stepped calcite \{10\bar{1}4\} surfaces**

The binding energy of a neutral phosphonate species with respect to the planar \{10\bar{1}4\} calcite surface which contained no defects, was calculated for all five phosphonates; the results are reported in table 4.3. All calculated binding energies were favourable, reinforcing the point made above that binding to rather than incorporation is the main mode of interaction of HEDP to the planar surface. The polar nature of the hydroxyl groups present within HEMP and DHMP enabled the ions additionally to use these groups in binding to the surface and in doing so form closer contacts to the planar surface - see figure. 4.4. Moreover, it has been noted experimentally that changes within the additive's molecular structure consequently give rise to dramatic changes in crystal morphology.$^{16-23}$
Table 4.3. Calculated binding energies for the phosphonate ions at the planar \( \{10\overline{1}4\} \) surface after 20ps NVT dynamics performed at 298K.

<table>
<thead>
<tr>
<th>Phosphonate</th>
<th>binding energy/ kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>-85.9</td>
</tr>
<tr>
<td>PEMP</td>
<td>-41.5</td>
</tr>
<tr>
<td>DHMP</td>
<td>-47.3</td>
</tr>
<tr>
<td>HEMP</td>
<td>-54.0</td>
</tr>
<tr>
<td>PMP</td>
<td>-18.4</td>
</tr>
</tbody>
</table>

The results of the simulations clearly showed that each of the phosphonate ions was predominantly bound via electrostatic interactions; that is, the calcium atoms were interacting with the oxygen atoms of the phosphonate group. Indeed, an analysis of the contributions from the energy expression found that the electrostatic term contributed over 95% of the total binding energy. Figure 4.4 shows the configurations, at the end of a typical 15-20ps NVT simulation, for the five phosphonates; the oxygen atoms of the phosphonate group interact with the calcium atoms within calcite whilst the hydroxyl oxygen atom is situated in order to maximize the interaction with the surface and with water.
Figure 4.4. Conformations of a)HEDP ion [top diagram] and b)DHMP ion [bottom diagram] at the planar calcite surface after simulation.

Trends within the calculated binding energies are also consistent with the major mode of interaction with the surface being via the phosphonate oxygen atoms, with the binding energy of the diphosphonate being approximately twice that of the monophosphonates with the exception of PMP.

Next, binding energies for the phosphonates at the obtuse stepped \{10\bar{1}4\} calcite surface were calculated; the results are given in table 4.4.

Table 4.4. Calculated binding energies for the phosphonate ions at the stepped, obtuse calcite plane after 20ps NVT dynamics performed at 298K.

<table>
<thead>
<tr>
<th>phosphonate</th>
<th>binding energy/ kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>-276.0</td>
</tr>
<tr>
<td>PEMP</td>
<td>-140.9</td>
</tr>
<tr>
<td>DHMP</td>
<td>-182.4</td>
</tr>
<tr>
<td>HEMP</td>
<td>-166.9</td>
</tr>
<tr>
<td>PMP</td>
<td>-118.7</td>
</tr>
</tbody>
</table>

The phosphonates were more strongly bound to the stepped surface\(^{20,21}\) compared to the planar surface as has been predicted.\(^{24}\) In all cases, the phosphonate group interacts electrostatically with the terrace, whilst the side functional groups bind to the step. Indeed, the calculated binding energies were approximately three-times those previously calculated on the planar \{10\bar{1}4\} surface.

The order of effectiveness of the monophosphonate ions would be expected to be dependent upon pH. Fully deprotonated phosphonate groups exist in alkaline
environments where their potency would then be governed strongly by the type of functional groups attached to them. From table 4.4, we note that PMP has the lowest calculated binding energy since the phenyl ring does not facilitate a strong association with the calcite lattice in contrast to DHMP which has two hydroxyl groups which increase the binding to calcite by approximately 60 kJmol⁻¹. Within a neutral pH environment the DHMP, HEMP and PMP would probably have a high concentration of singly protonated species. The dual factors of enhanced charge localization together with an extra proton on the ions might facilitate an increased binding to the surface and therefore increase their impact on calcite inhibition and morphology.¹⁴,²⁵,²⁶

Surface characterization techniques including X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED)²⁷,²⁸ have proven that the calcite {1014} surface exists in vacuum and air as an electrical double layer. That is, the CO₃H and CaOH species are known to exist in close contact to the surface bulk calcite layer. The CaOH species in particular, has been shown by Stipp et al., to be present even after prolonged drying periods and irrespective of pH conditions. The representation of the calcite surface used in this work does not include these hydrated species; however it can be envisaged that upon approach to the hydrated calcite surface that a phosphonate of high charge is able to disrupt the hydration sphere enclosing the calcium atoms thus exposing them and enabling a strong interaction via their phosphonate oxygen atoms. We can also propose that this process will occur less readily with poisons which are weakly acidic.
4.10 Incorporation of monophosphonate ions into terrace, steps and step edge defect sites.

4.10.1 An overview

We next investigated the interaction of the monophosphonates with defect sites created by the removal of carbonate ions from both the terrace and step as well as the ‘edge’ (lower step) sites of the stepped surface, as illustrated in Figure. 4.5. From the calculation of replacement energies at the obtuse step, it was shown that the closest form of attachment of the monophosphonate ion to calcite was at the vicinity of the step. An obstruction at this region would be expected to impede the flow of the step outwards over the terrace and cause an irregularity in the calcite morphology, since the normal movement of the step would be altered by the presence of the monophosphonate. Certainly, binding of the monophosphonate would cause a decrease in the velocity of the step as it grew outwards over the terrace.

In order to obtain a balanced idea of the possible mechanism of monophosphonate crystal growth inhibition, a variety of such processes were simulated. The models investigated were based on the following: blocking of a terrace, step or edge defect site with a monophosphonate ion followed by binding of a CaCO₃ kink next to the range of pre-docked monophosphonate ions, the latter model being necessary to establish which ion may be more damaging to the actual step assembly and consequently the flow rate.
Figure 4.5. Schematic showing sites of the three surface defects.
4.10.2 Results for the incorporation process

The calculated replacement energies reported in table 4.5 are mostly negative and therefore represent favourable occlusion of the impurity into the calcite surface. Overall the impurities at the stepped site yielded the most favourable replacement energies for ions other than PMP. The hydroxy groups of DHMP furnished a favourable replacement energy at the calcite step site of \(-386.99\) kJmol\(^{-1}\), see figure 4.6C. In accordance with AFM studies\(^{21}\), it was observed that the primary location of the diphosphonate ion HEDP was in the vicinity of the step. However the double phsphonate substitution seen in figure 4.6D is energetically unlikely, see table 4.5. The most favourable replacement energy calculated for the PMP ion was at the terrace site, see Figure. 4.6A, and was probably due to the fact that the steric bulk of the phenyl group facilitated a successful replacement only at this site. At the edge site defect, the anionic phosphonate functionality was not successfully incorporated into the calcite lattice vacancy due to a significant repulsion at step and edge sites by the bulky and relatively inflexible ring which prevented favourable replacement energies from being calculated.

<table>
<thead>
<tr>
<th>defect</th>
<th>DHMP</th>
<th>PEMP</th>
<th>HEMP</th>
<th>PMP</th>
<th>HEDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>STEP</td>
<td>-386.99</td>
<td>-235.42</td>
<td>-362.78</td>
<td>51.14</td>
<td>695.65</td>
</tr>
<tr>
<td>TERRACE</td>
<td>-308.75</td>
<td>-176.56</td>
<td>-111.92</td>
<td>-89.92</td>
<td>695.65</td>
</tr>
<tr>
<td>EDGE</td>
<td>-215.16</td>
<td>134.14</td>
<td>-75.16</td>
<td>261.14</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.5. Calculated replacement energies/ kJmol\(^{-1}\) at the \(\{10\bar{1}4\}\) calcite obtuse step. [N.B. EDGE=lower step site, see Figure. 4.5]
We found that, generally, the step site defects enabled the monophosphonates to interact strongly and were energetically favourable processes. Classical terrace sites are surrounded by fewer interaction sites once the ion becomes irreversibly anchored into the calcite framework, i.e far away from the steps. However, the ions replaced in terrace site defects during the present set of calculations were situated sufficiently close to interact with the front step. The PMP ion contained a bulky phenyl substituent which precluded it from successfully interacting with any of the defect sites to a great degree. Hence, specificity was lost by the inclusion of the bulky phenyl ring. Overall, the DHMP ion was observed to form the closest contacts with the calcite surface, due to the polar nature of the hydroxyl groups, compared to the bulky methyl and phenyl groups present in the remaining ions. The most effective replacement process for the PMP ion is at the terrace site, which yielded a replacement energy of $-89.92 \text{kJmol}^{-1}$. This conformation, shown in figure 4.6A, resulted in the ion binding via the oxygen atoms of the phosphonate group with the calcium atoms within the calcite framework. The phenyl group was slightly orientated at an angle from the front step of calcite.

The HEMP ion yielded a favourable replacement energy of $-362.8 \text{kJmol}^{-1}$ at the step site, owing to the interaction between the hydroxyl and phosphonate oxygen atoms with the calcite framework as illustrated in figure 4.6E. The DHMP formed close contacts to the calcite surface at the terrace site by employing the hydroxyl and phosphonate oxygen atoms to bind with the calcium atoms within the calcium surface. The step and terrace sites were also found to be favourable interaction centres for the PEMP ion as shown in figure 4.6B.
From the calculated favourable replacement energies we can propose that substitution of a carbonate ion by a monophosphonate ion into the calcite framework at either step or terrace sites are feasible mechanisms and hence we can assume that both impurity sites operate to prevent the progression of crystal growth.
Figure 4.6. Snapshots of a)PMP, b)PEMP, c)DHMP, d)HEDP and e)HEMP ions interacting at lower step ‘edge’, step and terrace defects, after 5ps of constant temperature dynamics performed at 298K using MARVIN.

4.11 Binding of CaCO₃ kink sites to steps containing phosphonate inhibitor ions

A further mechanism of crystal growth inhibition referred to earlier was via a kink site annihilation¹¹,²⁹ by a monophosphonate ion. The results of modelling this process are reported in table 4.6. Initially, a single CaCO₃ unit was bound and relaxed to equilibrium to the calcite framework at the step site. The binding energy calculated for the bound CaCO₃ unit was −955.2 kJmol⁻¹, and is calculated with respect to a relaxed step geometry (which is kept fixed during the simulation) and a CaCO₃ unit in the vacuum. A further CaCO₃ unit was subsequently placed next to the initial relaxed CaCO₃ unit at the newly formed kink site and this was then relaxed with respect to the step. A calculated binding energy of −1539.8 kJmol⁻¹ was generated, strongly suggesting that successive CaCO₃ units are more strongly bound to each other as they
bind along a step, that is, the second CaCO$_3$ unit is bound approximately 578.9 kJmol$^{-1}$ stronger than the initial CaCO$_3$ unit. As stated by Nygren et al.,$^{11}$ the rate determining process is that of step assembly, i.e. the binding of individual calcium carbonate units to kink sites along a step.

Next, we elucidate the strength of interaction of a CaCO$_3$ unit at a kink impurity site which has a pre-bound monophosphonate impurity bound to the step. We therefore calculate the binding energy of a CaCO$_3$ unit at this step site with the monophosphonate ion impurity as a neighbour. The calculated binding energies of CaCO$_3$ units bound next to a variety of monophosphonate ions are reported in table 4.6. Previously, binding energies have been calculated for neutral monophosphonates ions at the stepped calcite surface. We noted earlier, that binding an impurity ion to a step site has been found to be a favourable process with negative binding energies obtained for all ions, (see table 4.4). A comparison with the binding energies of CaCO$_3$, table 4.6, at stepped sites show this latter process to be a considerably more favourable process.

Table 4.6. Calculated binding energies of CaCO$_3$ units bound to kink sites containing phosphonate ions at the stepped{1014} surface.

<table>
<thead>
<tr>
<th>kink ion</th>
<th>binding energy/ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$, first</td>
<td>-955.2</td>
</tr>
<tr>
<td>CaCO$_3$, second</td>
<td>-1539.9</td>
</tr>
<tr>
<td>HEDP</td>
<td>-22.2</td>
</tr>
<tr>
<td>HEMP</td>
<td>-113.8</td>
</tr>
<tr>
<td>PEMP</td>
<td>-104.2</td>
</tr>
<tr>
<td>DHMP</td>
<td>-124.5</td>
</tr>
<tr>
<td>PMP</td>
<td>-226.7</td>
</tr>
</tbody>
</table>
The binding energy of a CaCO$_3$ unit at a step can be compared with that for a CaCO$_3$ unit bound next to a pre-docked inhibitor at the same site. From table 4.6 it can be established that the process of binding successive CaCO$_3$ units to a step is more energetically feasible in a pure crystal and a substantially more exothermic process, when compared to a poisoned crystal in which CaCO$_3$ units have inhibitors as neighbours. From these results, it is proposed that the formation of the kink site is frustrated but not totally thwarted by the presence of the monophosphonate ion. If the method used to calculate binding energies in table 4.6 were explicitly to include solvation effects, the effect of binding a CaCO$_3$ next to a pre-bound inhibitor would be an endothermic process; that is, kink site formation at a poisoned step would become energetically unfeasible. Step assembly and flow would cease altogether.

4.12 Discussion and conclusion

The mechanisms by which an adsorbed monophosphonate ion impurity could block the growth of a crystal such as calcite can be described as follows: first, by the interaction with a CaCO$_3$ kink site hence disrupting further step assembly; secondly by the incorporation of a monophosphonate ion at step sites of the surface; and thirdly by the incorporation of a monophosphonate ion at the terrace site of the surface.

4.12.1 Mechanism for prevention of step flow and assembly

By binding each CaCO$_3$ unit to a pre-docked monophosphonate ion separately and then comparing the magnitude of the binding energy obtained to the binding energy for a CaCO$_3$ unit to the stepped calcite surface, we have shown that it is more
energetically favourable to bind successive CaCO₃ units to steps than for a CaCO₃ unit to bind next to a pre-bound monophosphonate inhibitor ion.

Whichever route the inhibitor takes to become attached to the step, its presence acts as a barrier for the attachment of further CaCO₃ units, a trend which this study has shown is more effective with the diphosphonate, HEDP. For the kink site mechanism, given the assumption that the inhibitor lifetime at a step is long enough for competition between CO₃²⁻ and the poison anion for nucleation sites, we can expect that this behaviour would lead to increased distances between kink sites and a decrease in kink-kink annihilation velocity, due to the steric hindrance of monophosphonate poisons at defect sites, leading to a decrease in step assembly and flow. In fact, according to Davey et al.¹⁰ desorption of an inhibitor interacting at the kink site would require such a huge activation energy for kink site entry that the kink site would be rendered totally inactive for further growth. Morphologically, this process would lead to jagged steps of decreased velocity.²¹,²⁸,³¹

4.12.2 Phosphonate interaction modes as a function of structure

In order to locate the optimal equilibrium geometry of the inhibitor in the step vacancy, it was necessary to use a combination of molecular dynamics (at 298K) and energy minimization techniques. All monophosphonate ions, with the exception of the dihydroxy-substituted ion interacted with the step via the tripod of oxygen atoms attached to the phosphonate motif (see Figure 4.4). The dihydroxy-substituted ion, DHMP, was able to interact additionally using the oxygen atom of an hydroxyl, enabling it to co-ordinate to a calcium ion at a step site hence leading to stronger
binding, which is reflected in the results reported table 4.3 and table 4.4. The HEMP ion demonstrated a similar mode of interaction, see figure 4.6E.

The PMP inhibitor exhibits an inflexible phenyl ring [figure 4.6A], the steric bulk of which prevents favourable replacement at step sites. Additionally, the phenyl ring delocalizes electron density away from the phosphonate group oxygen atoms thus depleting the strength of electrostatic attraction the between poison and the calcite surface: hence the fully deprotonated PMP is the most weakly bound monophosphonate (see table 4.3 and table 4.4) and consequently would be less useful at effecting inhibition. Retardation of step growth is also possible through occasional incorporation into the terrace (table 4.5) or binding via the singly protonated phosphonate moiety, though given the observations of Didymus et al., this poison is more likely to interact more favourably with and therefore stabilize the \{01\bar{1}2\} plane as opposed to the \{10\bar{1}4\} plane.

4.12.3 Binding and replacement processes

Monophosphonate ions can either bind to a step, terrace or kink sites or become irreversibly incorporated into the calcite surface at terrace or stepped sites by replacing carbonate groups. The calculated binding and replacement energies of an inhibitor ion to a step site are favourable processes. Therefore, it is conceivable that at high concentrations, fully deprotonated monophosphonates impede crystal growth and alter crystal morphology by i) successively interacting at step sites [where they bind more strongly than to terrace sites] the strength of which increases when heteroatom functional groups are present as these provide additional interactions to the calcite lattice, ii) interacting and poisoning kink sites thus rendering them inactive
iii) association with the step via binding or replacement processes, causing a decrease in further CaCO₃ kink formation. Deprotonated monophosphonates operate via a similar mechanism to that of the deprotonated diphosphonates in that they can both bind to or become incorporated into the lattice.

HEDP is unlikely to replace two carbonate defects at once, as demonstrated by the positive replacement energy calculated in table 4.5; it can however undergo a favourable incorporation of a single phosphonate group whilst the oxygen atoms of the remaining phosphonate group bind with the calcium atoms since both binding and replacement of a single phosphonate group have been shown to be favourable processes (see tables 4.4 and 4.5). The diphosphonate ion, HEDP, has a greater impact on preventing step assembly at kink nucleation sites (table 4.6) compared to the monophosphonate ions and calculations show it to be more effective at halting the flow of steps by its ability to electrostatically interact to a stronger degree than monophosphonate ions (table 4.4).

4.12.4 Correlation with experiment

Experimental studies,²,³,¹⁶ have reported that the calcite morphology is altered by phenyl phosphonate. The morphological distortions reported, exemplified by curved steps for instance, may be due to the fact that once the PMP ion has undergone a replacement reaction at a step or a terrace site, further CaCO₃ units would bind weakly next to the impurity, creating large gaps between kink sites due to steric factors and hence disrupting the assembly of steps.
The phenyl substituted monophosphonate, PMP, demonstrated the least interaction towards the calcite \{1\overline{0}1\overline{4}\} surface for all mechanisms modelled. Since the potency of this poison has been recorded to increase with pH, the singly protonated version has proven to yield optimum inhibitor properties. It can be assumed that it may give rise to the dual expression of both positive \{1\overline{0}1\overline{4}\} and negative \{01\overline{1}2\} rhombohedral faces of calcite by stabilizing these faces as predicted experimentally and theoretically by Didymus et al.\textsuperscript{2}

In the case of non-aromatic monophosphonates, it has been shown that the reversible binding and irreversible replacement [see tables 4.3-4.6] are both energetically favourable. Moreover, in the absence of knowledge of the activation energies, the replacement energy of \(\text{CO}_3^{2-}\) can be inferred to be far greater than that of any of the monophosphonates. Since the binding energy of \(\text{CO}_3^{2-}\) can be expected to be far greater than that of any of the monophosphonates, the competition for a low concentration of vacancies at steps and terrace sites would be expected to be dominated by the carbonate ion at low poison concentrations facilitating crystal growth as opposed to inhibition.

The exothermic replacement and binding energies calculated showed the step site to be a favourable location for this process, a result which has been corroborated for HEDP via AFM.\textsuperscript{21,32,33} It has also been reported in experimental studies that the presence of inhibitors at the step decreases the velocity[and hence the step flow] of a step, as the ion is irreversibly incorporated into the crystal lattice. Therefore, in order for the step to proceed it must grow past the monophosphonate obstructions. It can also be envisaged that as the step grows past the monophosphonate, the steps become
jagged at low poison concentrations, a feature that has been widely observed by experimentalists.\textsuperscript{20,21,34}

Replacement energies calculated at terrace sites were some of the smallest, see table 4.5. The poisons interacted with the terrace site vacancy by the tripod of oxygen atoms. The replacement energy of a monophosphonate ion for a carbonate ion represented the irreversible incorporation of a monophosphonate impurity ion into the calcite lattice. In this process, the monophosphonate ion is rooted into the calcite crystal framework where it is in a strategic location to impede sterically the propagation of the step, thus decreasing the step velocity. Also, the surface area for kink formation would become depleted due to the presence of the phosphonate ions at terraces. The overall effect of several ions attached at the terrace site impurity would be to stunt the movement of the step. However, for morphological effects to occur the impurity lifetime would have to exceed the kink unit lifetime\textsuperscript{11} and the impurity ion would be required to be in a sufficiently high concentration for this process to be effective.

The calculations have shown that the overall mode of interaction of a fully deprotonated monophosphonate ion with the calcite surface is predominantly \textit{via} the electrostatic interaction of the de-protonated oxygen atoms of the phosphonate group interacting with the Ca\textsuperscript{2+} ions. A larger concentration of fully deprotonated phosphonate groups may be expected for alkaline experimental conditions, in which monophosphonate ions, when in sufficiently high concentrations, would be expected to cause varying degrees of morphological disturbances to calcite surfaces. Since phosphonate inhibition is at a maximum\textsuperscript{14,34} between pH 5-7, singly protonated
phosphonate groups are likely to be present at higher concentrations thus facilitating additional hydrogen bonding to the calcite surface. In this pH range HEDP and PMP have been shown to be more potent in smaller concentrations.\textsuperscript{13,14,16,26} Under acidic experimental conditions, although the inhibitor ions still interact electrostatically with the protonated calcite surface, they have less opportunity to directly interact with the calcite surface to disturb the normal mode of calcite crystal growth at steps. These morphological effects are known to be concentration, temperature and pH dependent and hence further work encompassing these effects would provide a more detailed description of inhibition phenomena.

\textbf{4.13 Summary}

Simulations involving the effect of irreversible incorporation and the reversible association via binding of the monophosphonate ions to the \{10\overline{1}4\} planar and stepped calcite plane have been shown in this work to relate to kinetic and morphological studies; chiefly that stepped and kink sites are the prime areas of phosphonate activity necessary to optimize calcite poisoning, expressed in a decrease and/or stoppage of step flow and assembly; the diphosphonate HEDP is a more powerful poison than the four monophosphonates modelled, as demonstrated by their respective calculated binding energies; the presence of heteroatoms such as oxygen which electrostatically interacts with calcium atoms present in calcite, facilitates a stronger binding with the calcite lattice; the presence of an aromatic ring depreciates poison efficacy; it is more energetically feasible for a single phosphonate to become incorporated into the calcite lattice than for both phosphonate groups in the case of HEDP.\textsuperscript{14,15,21,26,35} This work is summarized in reference 36.
References


19. G.W. Sears in *Growth of Crystals from Solution*, 1959 441


*Nature* 1991 353 549

Chapter 5 Diffusion in microporous zeolites: simulation studies

5.0 Overview

The background to the importance of molecular diffusion in zeolites is discussed in Chapter 3. In this chapter we report the results of dynamic, long simulation time diffusion studies of the small molecules, para-xylene, ortho-xylene and benzene in high density CIT-1 and low density purely siliceous Faujasite using both the GULP\(^1\) code and the multi-functional DL_POLY\(^2\) software package.

5.1 Introduction

This work explores methodological aspects of the effect of ensemble choice and simulation duration as well as the potential model on the diffusion mechanism determined for different types of zeolite/hydrocarbon systems. Calculated diffusion coefficients show that the rigid ion model possibly overestimates the molecule’s diffusivity when compared to the shell model for molecular dynamics simulations performed on identical systems. A notable feature of the simulations was that long diffusion time scales were explored using extended simulation times which revealed new and interesting mechanistic aspects relating to molecular diffusion in zeolites.
5.2 **Para - xylene/CIT-1 and ortho-xylene/CIT-1 systems**

5.2.1 **Background**

This system had been studied previously by Sastre *et al.* However, the methodology used in their study differs from that of the present in two pivotal respects. Sastre’s relaxed simulation cell was restrained at 0K for a 25ps period. After this ‘initialization’ stage, the lattice restraints were removed and a 100ps NVT molecular dynamics production run at 500K ensued. The procedure of fixing the framework at 0K and subsequently allowing relaxation at 500K led to structural changes absent in the current work. During the present study, all frameworks remained flexible during equilibration and production phases. Secondly and more importantly, the rigid ion model was used throughout Sastre’s work. We are also, as noted earlier, able to extend the simulation times considerably when compared with the previous work.

5.2.2 **CIT-1 zeolite model**

Lobo *et al.* synthesized the microporous zeolite CIT-1 which can be characterized in terms of interconnecting 10 and 12 member ring channels, which are shown in figures 5.1-5.3. A 2x2x2 CIT-1 macrocell was generated from a relaxed (energy minimized) unit cell. The resulting simulation box comprised 672 atoms.

Implementation of the shell model involved the application a small mass of 0.99 to the oxygen shell of charge $-2.86$ and a mass of 15.00 to the oxygen core of charge $0.86$. The motions of the shells as well as the cores were then calculated as normal by molecular dynamics. The shell mass was chosen specifically to ensure that the
frequency of the core-shell spring was higher than the frequencies of the lattice. The separation of frequencies guaranteed that the shells moved adiabatically; hence no additional thermal energy was introduced into the core-shell motion. The chosen core-shell mass distribution gave rise to a period of vibration which was smaller than the time-step used for the molecular dynamics simulations, which was 1fs.

**Figure 5.1.** Snapshot of CIT-1 macrocell showing 10MR channels parallel to [010] crystallographic axis.
Figure 5.2. Zeolite CIT-1: 12MR channels parallel to [010] crystallographic axis.

Figure 5.3. Snapshot of CIT-1 macrocell: 12MR channels parallel to [001] crystallographic axis.
5.3 Simulation methodology

The unit cell of CIT-1 was first relaxed using the BFGS technique within GULP. Cell geometry parameters were $a = 26.84\text{Å}$, $b = 26.84\text{Å}$, $c = 25.06\text{Å}$, $\alpha = 107.88^\circ$, $\beta = 72.11^\circ$, $\delta = 118.16^\circ$. Following this, the optimized 2x2x2 macro-cell of 672 atoms for the rigid ion system was generated. The shell model system involved the further addition of 448 Oxygen shell sites to the previously described system of 448 Oxygen and Silicon cores resulting in a total system of 1120 sites. The relaxed system was subsequently imported into DL_POLY with potentials and charges for simulation times between 100ps [equilibration time: 20ps, production time: 80ps] and 440ps [equilibration time: 55ps, production time: 385ps]. NVT, NPT and NVE ensembles were employed with loadings of 0.25 molecules/unit and 0.125 molecules/unit at temperatures of 400K, 450K and 500K. The latter loading was calculated from a single molecule in a 2x2x2 zeolite supercell; the former was calculated from two molecules in a 2x2x2 zeolite supercell. The diffusion coefficient, $D$, was evaluated from the mean squared displacement utility within DL_POLY using the Einstein relation described in Chapter 3. The small number of molecules in the simulation box resulted in a substantial error arising in our calculated diffusion coefficients. However, the results are still of value for explaining the effect of interaction potentials, molecular structure and loading on diffusion and for investigating transport.
5.3.1 Potentials

As in the Sastre et al. study, four types of interatomic potentials, shown in equation 5.1, were required to model the zeolite/molecule systems analytical terms all of which have been explained in Chapter 2 and Chapter 3 of this thesis:

\[ V_{total} = V_{zeolite} + V_{xylene} + V_{xylene-xylene} + V_{zeolite-xylene} \]  

The rigid ion potential for the framework, \( V_{zeolite} \) was developed originally by Catlow et al. The derivation of a more accurate, shell model potential to represent the zeolite framework was reported by Jackson et al. The Born model potential comprised of a three-body interaction, short-range terms, and a long range Coulomb interaction. The shell model potential consisted of electrostatic, repulsive, three body and a harmonic core-shell terms. The potential for the xylene molecules was taken from Oie et al. It comprised of two, three and four body interactions with Coulomb terms. Four different atom types were assigned to the xylene isomers, namely CA HA CB HB denoting equatorial (A) and axial (B) atoms. The charges assigned to the atoms were: \( q(CA) = -0.153, q(HA) = 0.483, q(CB) = 0.153, q(HB) = -0.110 \). In total 18 bond terms, 30 angle terms and 36 torsion terms are described. The 12-6 Lennard-Jones potentials, taken from Catlow et al as well as Coulomb interactions were used to describe the hydrocarbon-hydrocarbon [xylene-xylene] and framework-hydrocarbon [zeolite-xylene] interactions.
5.3.2 Trajectories

The purely siliceous zeolite CIT-1 consists of a framework of interlinked 10 and 12 MR channels. During the course of each simulation performed, the trajectory route of each xylene isomer was plotted using the InsightII® program. A history file of configurations generated from DL_POLY was used to plot the trajectory path of each molecule. Analysis of the trajectories revealed ‘molecule hopping’ of para-xylene between the 10 and 12 MR channels. The hopping was punctuated by ‘stationary’ modes where translational molecular motion was constricted. The periods of low molecular diffusion were associated with ‘bottlenecks’ or intersections between the 10 and 12 MR channels. The stationary modes were typically found to be 7ps in duration which was indicative of the time taken to surmount significant activation barriers for the transport of molecules via the 10MR and 12MR intersection into the next channel. Residence times within the actual ring systems compared to the intermediate channels were dependent upon the xylene isomer.

In the following sections, the results of the effect of xylene loading, xylene isomer, simulation time and interatomic potential type are described.

5.4 Diffusion of para-xylene isomers within zeolite CIT-1:
rigid ion model, NVT, NVE dynamics

5.4.1 Function of isomer for 0.25 xylene molecules/unit cell systems

The para-xylene isomer was calculated to diffuse with greater speed through the channels and to permeate a larger surface area than the bulkier ortho-xylene. This diffusion is shown by the calculated diffusion coefficients which are reported in table 5.1 and graph 5.1. The ortho isomer/CIT-1 system shown in graph 5.1 are
characterized by a downturn after 80ps corresponding to decreased translational motion of the isomer at this point of the simulation. The NVT ensemble was employed for these calculations. The ortho xylene isomer was determined to travel at almost half the speed of the para isomer, due to the steric limitations of the former isomer see graph 5.2. The trend for higher para activity was also observed during the NVE ensemble simulations, see graph 5.2. The MSD plots shown in graph 5.2 yielded significantly higher diffusion coefficients than those calculated via the NVT ensemble due to temperature fluctuations. These observations are explained in the discussion. The diffusion coefficients were calculated by evaluating the gradient of the MSD/simulation time plots between 0ps to 100ps by using the Einstein relation described in section 2.7.6.

Table 5.1. Diffusion coefficients of ortho versus para isomers of xylenes for DL_POLY runs of 100ps performed at 450K, NVT dynamics.

<table>
<thead>
<tr>
<th></th>
<th>para-xyylene</th>
<th>ortho-xyylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coeff, D</td>
<td>$15.0 \times 10^{-6}$ cm$^2$s$^{-1}$</td>
<td>$8.7 \times 10^{-6}$ cm$^2$s$^{-1}$</td>
</tr>
</tbody>
</table>

Graph 5.1. MSD versus simulation time for 100ps NVT ensemble performed at 450K for CIT-1/para isomer [black line] and MSD versus simulation time for 100ps NVT ensemble performed at 450K for CIT-1/ortho isomer [white line].
Graph 5.2. MSD versus simulation time for 100ps NVE ensemble performed at 450K for CIT-1/para isomer [black line] and MSD versus simulation time for 100ps NVE ensemble performed at 450K for CIT-1/ortho isomer [white line].

5.4.2 Function of loading for CIT-1/para-xylene system

Simulations were set up in which two of the same isomers were added to the zeolite framework [0.25 molecules/unit cell]. Both molecules were located inside and between the 10MR and 12 MR over the course of the longer simulation runs performed using NVT and NVE ensembles. The increased loading resulted in lower calculated diffusion coefficients as reported in table 5.2. Inspection of the trajectory plots generated showed that the increased loading produced smaller co-ordinate oscillations in accordance with the lower calculated diffusion coefficient.

Table 5.2. Calculated diffusion coefficients for one and two molecular CIT-1/para xylene systems; NVT simulations were performed at 400K.

<table>
<thead>
<tr>
<th></th>
<th>2 x para-xylene [loading 0.25]</th>
<th>1 x para-xylene [loading 0.125]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coeff.</td>
<td>3.3 x 10^{-6} cm^2 s^{-1}</td>
<td>1.7 x 10^{-6} cm^2 s^{-1}</td>
</tr>
</tbody>
</table>

The effect of doubling the load on the diffusion rate can also be observed by a comparison with a previous study for the para CIT-1 system run for 100ps for
identical simulation conditions, see table 5.3. These simulations were run at a higher temperature of 500K using the NVE ensemble.

Table 5.3. Comparison table for D values calculated for higher loadings of 0.25 para-molecules/unit cell in the Sastre et al study [3] and the lower loading of 0.125 para-molecules/unit cell for NVE simulations performed at 500K.

<table>
<thead>
<tr>
<th></th>
<th>Sastre et al (^2) [loading:0.25]</th>
<th>present work [loading:0.125]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>(25 \times 10^{-6} \text{ cm}^2 \text{s}^{-1})</td>
<td>(56 \times 10^{-6} \text{ cm}^2 \text{s}^{-1})</td>
</tr>
</tbody>
</table>

5.4.3 Self-diffusion as a function of simulation time

Longer simulation times were required to facilitate extended molecular migration through the zeolite framework. Analysis of simulation runs lasting up to 100ps suggested restricted molecular diffusion. Typically the para-xylene molecule would remain localized in a 10 or a 12 MR for the duration of the 100ps experiments. Simulations of up to 440ps for NVT and NVE ensembles demonstrated greater movement throughout the rings and interconnected channels. Several discrete diffusion rates within a single simulation were calculated. These gave rise to MSD plots, graph 5.3, which exhibited two regimes. The first which had a large, positive gradient [which is linear] and other regimes, where the gradient of the line approaches zero, where the molecules are stationary. These MSD plots were correlated to the exact molecule location. That is, the molecular diffusion in a ring system corresponded to the linear region of the MSD plot; whereas a plateau region reflected slower hydrocarbon movement via the smaller interconnecting rings, indicated by the
region labelled I, shown in figure 5.4. The calculated diffusion coefficients reflecting the diffusion regimes are depicted in table 5.4.

**Table 5.4.** Diffusion coefficients of para-xylene in the 10MR, 12MR and intra-connecting region of CIT-1 for 300ps of NVT dynamics performed at 500K for 0.125 loading.

<table>
<thead>
<tr>
<th></th>
<th>10MR</th>
<th>12MR</th>
<th>intra-region</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>$11.7 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
<td>$17.3 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
<td>$11.0 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
</tr>
</tbody>
</table>

**Figure 5.4.** Outlines the area of the framework in which molecules are confined temporarily in transit to 10MR or 12MR channels.

*NB: the ‘intra-region, I’ refers to the network connecting the 10MR and 12MR channels.*
Graph 5.3. Mean squared diffusion profile for the CIT-1/para xylene NVT ensemble system performed at 500K.

The trend of the results reported in table 5.4 corroborate previous studies;\textsuperscript{9-11} in particular that the para-xylene isomer has a greater diffusivity in the larger 12MR system than the 10MR system. The plateau [flat] regions of the diffusion plot shown in graph 5.3 are consistent with a ‘cooling off’ period’ for the molecule reflected in the slight decrease in diffusion coefficient.

A 360ps, 450K dynamics simulation was performed using the NVE ensemble. The results are reported in table 5.5. In this simulation significantly higher diffusion rates were reached. The diffusion plot in graph 5.4 displayed clear regions of molecular mobility and relatively static periods within the smaller channel system. An initial linear relationship between MSD and simulation time was observed from 0ps-100ps. Observations revealed the para-xylene to be located within the 10MR channel at this point. The calculated diffusion coefficient was 76.6 x10\(^{-6}\) cm\(^2\)s\(^{-1}\). A large deceleration in diffusivity [41.7 x10\(^{-6}\) cm\(^2\)s\(^{-1}\)] occurred between 133ps and 220 ps where the molecule was ‘hopping’ between the ‘inter’ ring regions and the 10MR channel.
Therefore between 133ps and 145ps the molecule was in the 10MR channel system; the diffusion coefficient was $34.7 \times 10^{-6} \text{cm}^2\text{s}^{-1}$, the molecule was then observed to move out into the ‘interconnecting channel’ region between 161ps and 219ps. This led to a value of $44.5 \times 10^{-6} \text{cm}^2\text{s}^{-1}$. However, from 225ps to 360ps a linear increase in diffusion occurred representing the increased para-xylene mobility in the 12MR. The diffusion coefficient calculated here was $67.9 \times 10^{-6} \text{cm}^2\text{s}^{-1}$. Snapshots of the superimposed molecule’s locations as described above are shown in figures 5.5-5.7.

**Table 5.5.** Diffusion coefficients of para-xylene in the 10MR, 12MR and intra-connecting region of CIT-1 for up to 360ps of NVE dynamics performed at 500K.

<table>
<thead>
<tr>
<th></th>
<th>10MR</th>
<th>12MR</th>
<th>Intra-region</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>$41.7 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
<td>$67.9 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
<td>$34.7 \times 10^{-6} \text{cm}^2\text{s}^{-1}$</td>
</tr>
</tbody>
</table>

**Graph 5.4.** MSD versus simulation time plot for approximately 360ps NVE CIT-1/para system performed at 450K demonstrating distinct diffusion processes.
Figure 5.5. Snapshot of overlaid para-xylene molecules within the 10MR channel showing molecule location during the course of an NVE simulation performed at 450K for 360ps.

Figure 5.6. Snapshot of overlaid para-xylene molecules within the 12MR channel viewed along the [010] projection showing molecule location during the course of an NVE simulation performed at 450K for 360ps.
Figure 5.7. Snapshot of overlaid para-xylene molecules within the 12MR channel viewed along the [001] projection showing molecule location during the course of an NVE simulation performed at 450K for 360ps.

5.4.4 Diffusion of ortho-xylene isomers within zeolite CIT-1: rigid ion model dynamics

Molecular dynamics simulations lasting 440ps and using NVT dynamics at 450K were run for the ortho-xylene isomer. The calculated diffusion coefficients were lower than those for the streamlined para-xylene molecule as reported in table 5.6 below.

Table 5.6. Comparison of aggregate diffusion coefficients for the two xylene isomers after 440ps of NVT dynamics.

<table>
<thead>
<tr>
<th></th>
<th>ortho-xylene [440ps]</th>
<th>para-xylene [440ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>8.3 x10^{-6} cm^2 s^{-1}</td>
<td>18.6 x10^{-6} cm^2 s^{-1}</td>
</tr>
</tbody>
</table>
The MSD graph 5.5, shows diffusion regimes are present, providing evidence of non-uniform molecule diffusion within the CIT-1 macro-cell. Diffusion coefficients generated from the simulation at 100ps, 200ps and 300ps have been evaluated.

From 0ps to 100ps the MSD/simulation time relationship is linear except for a deviation between 32ps to 47ps. The diffusion coefficient calculated for this period was approximately $18 \times 10^{-6}\text{cm}^2\text{s}^{-1}$. At this point, the molecule had passed into the inter-channel region and moved into the 12MR channel; hence diffusion was uninterrupted by the constriction of the 12MR aperture. In the following 100ps, the diffusion rate was maintained until the molecule moved out into smaller channels at 168ps and remains there until 201ps. After this point [201ps-440ps] a marked decrease in diffusion coefficient was determined of $8.3\times10^{-6}\text{cm}^2\text{s}^{-1}$ up until the end of the simulation. This deceleration in diffusivity over a very long time-scale is characterised by a parabolic region of the MSD plot, which remained linear until 201ps. After the ‘post’ 201ps dynamics, the molecule was observed to ‘hop’ around the macro-cell network and did not reside in any of the larger cells for any appreciable length of time.

Graph 5.5. Mean squared diffusion profile for the CIT-1/ortho-xylene system performed at 450K.
5.5 **Diffusion of xylene isomers within zeolite CIT-1: shell model**

5.5.1 *Function of isomer and potential type*

The trend for the para-isomer of xylene having higher mobility when compared to the ortho-isomers is again demonstrated for the shell model simulations performed at 550K, which included the polarisability of the oxygen atoms within the siliceous zeolite framework. Inspection of the trajectory plots for the ortho/CIT-1 simulation show that the molecule movement is localized in the 12MR channel which is parallel to the [001] crystallographic axis, see figure 5.3. The isomer was seen to undergo only intra channel exploration for the 100ps simulation period; as reflected by the smaller diffusion coefficient of $8.16 \times 10^{-6}\text{cm}^2\text{s}^{-1}$. The non-linear diffusion plot corroborates this observation - see graph 5.6. This behaviour may be compared to linear plot generated for the ortho/CIT-1 rigid ion simulation in graph 5.7, which resulted in a high diffusion coefficient of $13.5 \times 10^{-6}\text{cm}^2\text{s}^{-1}$ implying a faster transport route - see table 5.7. The para-xylene isomer yielded a larger self-diffusion coefficient over the same simulation time range compared to the ortho counterpart. The calculated self-diffusion coefficient for the para-isomer was approximately double the magnitude of that for the ortho-xylene molecule- see table 5.8.

**Table 5.7.** Comparison of diffusion coefficients for the ortho-xylene isomers after 100ps of NVT dynamics performed at 550K for the two models.

<table>
<thead>
<tr>
<th></th>
<th>ortho-xylene [shell]</th>
<th>ortho-xylene [r.i.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>$8.2 \times 10^{-6}\text{cm}^2\text{s}^{-1}$</td>
<td>$13.5 \times 10^{-6}\text{cm}^2\text{s}^{-1}$</td>
</tr>
</tbody>
</table>
Table 5.8. Comparison of aggregate diffusion coefficients for the xylene systems after 500ps of NVT dynamics performed at 550K at loadings of 0.25 molecules/unit cell.

<table>
<thead>
<tr>
<th></th>
<th>ortho-xylene [shell]</th>
<th>para-xylene [shell]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>11.6 x10^{-6}cm^2s^{-1}</td>
<td>25.5 x10^{-6}cm^2s^{-1}</td>
</tr>
</tbody>
</table>

Graph 5.6. MSD plot for the shell model ortho/CIT-1 simulation for 100ps.

Graph 5.7. MSD plot for the rigid ion model ortho/CIT-1 simulation for 100ps.

5.5.2 Function of simulation time: shell model

At loadings of 0.25 molecules/simulation cell, the calculated diffusion coefficients for the ortho-xylene isomer were shown in table 5.8 and graph 5.8. This result can be compared with previous work,\textsuperscript{12} that demonstrates increased molecular loading leads
to lower diffusivity because of greater residence times between jumps. Moreover, inspection of the history plots generated for the shorter 100ps runs and the longer 500ps runs showed that the different diffusion mechanisms were operating at extended simulation times. These distinct regimes are shown by inspection of graphs 5.8 and 5.9 and are highlighted by the discontinuities of the linear plots. The ortho-isomer was restricted within a single channel system for the duration of the 100ps simulation. However, at prolonged simulation times the molecule was observed to hop back and forth between two 12MR channels parallel to the [001] crystallographic plane, as can be shown by the increased diffusivity after 350ps, see graph 5.8. The movement of the ortho-isomer is clearly restricted in comparison to the large mobility and high diffusivity exhibited by the para-isomer simulation. In this case, the para-isomer was observed to sample the entire simulation framework and the interconnecting channel systems by jumping between the 10MR and 12MR channels as demonstrated in graph 5.9.

Graph 5.8. MSD plot for the shell model ortho-xylene/CIT-1 440ps NVT simulation.
Graph 5.9. MSD plot for the shell model para-xylene/CIT-1 440ps NVT simulation.

Plots 5.1-5.3 show the movements of the individual molecular systems throughout the shell model molecular dynamics runs for the x, y and z co-ordinates. Inspection of these plots shows that the ortho isomer moved with smaller displacements than the para isomer, in line with the previous discussion.
Plots 5.1-5.3 Trajectory plots of history files showing the evolution of the molecule paths with simulation time for the x, y and z co-ordinates for the CIT1/ortho and CIT1/para systems using the shell model.
5.6 Effect of shell model on xylene/CIT-1 systems

In all simulation cases, the shell model was calculated to have a significant influence on the magnitude of the diffusion coefficients. The overall effect was to reduce the diffusion coefficients by around fifty percent of their rigid ion model values. The shell model provides a more accurate description of the zeolite. The inclusion of the polarizability of oxygen influences molecular diffusion rates at least in part because it modifies the dynamics of the zeolite cage.

An artefact of the shell model simulations was that although the total energy of the system was outwardly conserved in all simulations, the oxygen cores did lose energy to the oxygen shells. This leakage from the cores to the shells resulted in an overall 'cooling' of the zeolite lattice. However, this effect of lattice cooling is rather small. In a typical simulation of 100ps duration, approximately 4K leached into the core-shell unit. The effect is unlikely to influence significantly the calculated diffusion coefficients. Much more significant is the fact that the pore apertures were slightly smaller for the shell model compared with the rigid ion simulations due to the dynamic fluctuation of the shells, and the oxygen shells were polarised into the channel system. The combined effect of these factors furnished lower calculated molecule diffusivities compared to the rigid ion model systems.
5.7 Summary

This work has been performed to elucidate the effect of key factors on molecular transport. The factors included:

5.7.1 Extended simulation times of up to half a nanosecond

Long periods of molecular dynamics enabled greater insights into the molecular pathways taken throughout the zeolite framework to be critically analysed. In particular, the xylene molecules were found to associate closely with the zeolite walls and in the case of both isomers to orientate themselves randomly within the network of channels, interspersed by stationary periods at channel intersections. The extended simulation times allowed observation of distinct diffusion regimes which are not always observed over very short simulation periods. For instance figure 5.8 demonstrates the separate transport modes undertaken by para-xylene during a prolonged simulation run of 0.4ns. The varied framework locations of the molecule are evident and of course yielded distinct diffusion coefficients, as explained elsewhere in this chapter.

Figure 5.8. The disparate locations and diffusivities of the para-xylene molecule can be distinguished by inspection of the regimes, labelled G, operating during the extended NVT simulation.
5.7.2 *Inclusion of the shell model*

An investigation of the effects of implementing shell model molecular dynamics on the size of diffusion and the mechanism of molecular activity within microporous zeolites was undertaken and compared to the standard rigid ion approach. All shell model systems yielded lower diffusion coefficients than rigid ion systems irrespective of ensemble, simulation times or loading concentration. The reasons for these differences are linked to the effects of including polarization on the dynamics of the zeolite lattice.

5.8 *Benzene/siliceous Faujasite systems*

5.8.1 *Introduction*

This study was performed chiefly to compare the effect of shell model inclusion on the mode of the benzene/Faujasite interaction and its corresponding diffusion coefficient with the rigid ion model potential representation. A defect free form of Faujasite was used throughout the work and the benzene molecule was placed randomly in the 12MR zeolite window [indicated as region A in figure 5.9] before the simulations commenced.

5.8.2 *Siliceous Faujasite: structural information*

The purely siliceous, defect free form of Faujasite comprises a 12MR window and 6 and 4 MR windows. The three-dimensional channel system comprises circular 12-ring 7.4Å interconnecting windows and spherical 11.8Å cavities. Hence the framework consisted of a tetrahedral arrangement of double 6-rings. The structure in figure 5.9 is
dominated by the central cage and formed by ten sodalite units. Only two of the four tetrahedrally spaced 12MR’s are visible in the snapshot below.

Figure 5.9. Snapshot of purely siliceous Faujasite showing the 12MR window labelled: A and 6 and 4 ring cages labelled: B and C respectively.

5.9 Benzene/Faujasite system: simulation methodology

The siliceous Faujasite simulation unit cell used consisted of 576 atoms. The simulation cell parameters were \( a = b = c = 24.23 \text{Å} \), \( \alpha = \beta = \delta = 90^\circ \). The potentials of Henson et al.\(^{11}\) were used to model the benzene-framework interactions since the framework used formal rather than scaled charges. The scaled charges used for the benzene molecule for the two atom types were \( q(\text{CB}) = -0.153 \) and \( q(\text{HB}) = 0.153 \). A total of 12 bond terms, 18 angle terms and 24 dihedral terms were described...
One molecule of benzene was placed in region A [figure 5.9] of the simulation cell. Periodic boundary conditions were applied to the entire system. The DL_POLY program was again used to perform the molecular dynamics simulations. The zeolite systems were relaxed prior to dynamics using the GULP code. All molecular dynamics calculations were performed at 300K. An equilibration period of 35ps was applied and a production period of 100ps was performed using the NVT, NVE and NPT ensembles. The MSD quantity was evaluated as explained in Chapter 3 of this thesis using the utility available from the DL_POLY code. A fully flexible framework model was invoked for the rigid ion and the shell model systems.

5.10 Benzene/Faujasite system: rigid ion model

5.10.1 Effect of simulation length

In Chapter 3 of this thesis, it was reported that the benzene/Faujasite system was characterized as possessing a relatively slow diffusion pathway and consequently sensitive spectroscopic methods can be used to calculate the self diffusion coefficient values for the benzene molecule. This trend of sluggish molecule mobility was a feature of the 100ps simulations carried out at 300K. From 0-100ps the molecule was localized within the sodalite cages and 6MR cages only. No movement into the central cage was observed. The corresponding calculated diffusion coefficient [table 5.9] was $1.03 \times 10^{-9} \text{m}^2\text{s}^{-1}$; the MSD plot is shown in graph 5.10. This result can be compared to the experimental value, which was obtained via the PFG NMR of
4.5±3.3x10^{-10} \text{m}^2\text{s}^{-1} \text{ by Bull et al}^{13}. Reasons for this discrepancy are discussed in section 5.12.3.

**Graph 5.10.** MSD plot for the benzene/Faujasite system generated at 300K using the NVT ensemble.

**Table 5.9.** Comparison of the diffusion coefficients for the Faujasite/benzene systems after 100ps of NVT dynamics performed at 300K.

<table>
<thead>
<tr>
<th></th>
<th>present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>1.0x10^{-9} \text{m}^2\text{s}^{-1}</td>
</tr>
</tbody>
</table>

5.10.2 *Effect of ensemble*

Comparison of diffusivities calculated for different ensembles appeared to reflect an alteration of the molecular diffusion mechanism. The fastest diffusion routes calculated involved the NVE ensemble at 300K, which generated a diffusion coefficient of 1.83x10^{-9} \text{m}^2\text{s}^{-1}. The lowest calculated diffusivity was for the NPT ensemble, which yielded a diffusion coefficient of 0.94x10^{-9} \text{m}^2\text{s}^{-1}, see
graphs 5.11, 5.12 and table 5.10. However, the results imply perhaps a more complicated relationship between the diffusion pathways.

**Graph 5.11.** MSD plot of NVE ensemble for benzene/Faujasite system performed at 300K.

**Graph 5.12.** MSD plot of NPT ensemble for benzene/Faujasite system performed at 300K.
Table 5.10. Comparison of the diffusion coefficients for the benzene/Faujasite systems after 100ps of NVE dynamics and NPT dynamics performed at 300K.

<table>
<thead>
<tr>
<th></th>
<th>(NVE) dynamics</th>
<th>(NPT) dynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, (D)</td>
<td>(1.8 \times 10^{-2}) m(^2)s(^{-1})</td>
<td>(0.9 \times 10^{-9}) m(^2)s(^{-1})</td>
</tr>
</tbody>
</table>

The snapshot taken in figure 5.10 shows the movement of benzene during the course of the simulation for constant temperature simulation conditions. It is of interest that for constant temperature dynamics the benzene molecules remain relatively localized within the main 12MR window of Faujasite as opposed to traversing a greater surface of the Faujasite structure, for example to one of the six membered rings.\(^{14,15}\)

Figure 5.10. Snapshot of Faujasite/benzene for NVT ensemble performed at 300K.
5.11 Benzene/Faujasite system - shell model

5.11.1 Effect of simulation time

Longer simulation allow rare events such as supercage to supercage hopping via the 12MR window, to be sampled more frequently. Inspection of the MSD plot over 100ps demonstrated decreased movements of the benzene molecule within the 12MR window of Faujasite compared to the rigid ion model behaviour, which was reflected in the corresponding diffusion coefficient of $0.66 \times 10^{-9} \text{m}^2 \text{s}^{-1}$, see table 5.11. Intrachannel movement within this 12MR cage was observed; movement into the surrounding smaller cage networks was not observed. A close interaction of benzene with the macrocell walls was apparent, see figure 5.10; which was in agreement with literature observations citing the importance of the zeolite wall on the activity of the molecule diffusivity.

The increased simulation periods at the temperature of 298K resulted in molecular ‘flipping’ during the course of which a greater area of the 12MR was explored. The overall diffusion coefficient for the shell model potential at 298K was $0.5 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. No ‘skateboard’ motions such as those described by previous workers\textsuperscript{13} were observed at this temperature using the shell model, which was not an expected result since benzene has been reported only to follow other activated mechanistic pathways at enhanced temperatures. Analysis of the history plots 5.5 and 5.6, of the x, y and z co-ordinates of benzene also provide evidence of reduced translational mobility at shorter simulation periods for shell model simulation.
Table 5.11. Comparison of the diffusion coefficients for the benzene/Faujasite systems at different simulation times using of NVT dynamics.

<table>
<thead>
<tr>
<th></th>
<th>100ps</th>
<th>450ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coeff, D</td>
<td>$0.6 \times 10^{-3}$ m$^2$s$^{-1}$</td>
<td>$0.5 \times 10^{-3}$ m$^2$s$^{-1}$</td>
</tr>
</tbody>
</table>

Plots 5.5-5.6. Faujasite/benzene history plot during NVE dynamics at 300K showing variation of x,y,z co-ordinates with simulation times for rigid ion model top plot and shell model bottom plot.

5.11.2 Effect of ensemble

Diffusivities calculated for the three ensembles varied with constant pressure molecular dynamics yielding a diffusion coefficient of $0.5 \times 10^{-9}$ m$^2$s$^{-1}$ and NVE dynamics a value of $0.6 \times 10^{-9}$ m$^2$s$^{-1}$ see graph 5.13. The higher diffusion coefficient obtained from the NVE ensemble, see figure 5.11, was attributed to the temperature fluctuations enabling the molecules to undergo increased thermal vibrations, which triggered further molecular motion. At extended simulation times increased flipping
of the benzene was observed. Snapshots taken during the simulations corroborate these calculations.

Figure 5.11. Shell model simulation for Faujasite/benzene system after NVE dynamics showing superimposed benzene ring snapshots taken along the duration of the simulation.

Graph 5.13. MSD plot of NVE shell model simulation performed at 300K, increased benzene ring rotations occur after 375ps.
Plot 5.7  Faujasite/benzene history plot during NVE dynamics at 300K showing variation of x co-ordinates with simulation times for shell model versus rigid ion model for 100ps and 500ps runs.

Plots 5.5, 5.6 and 5.7 all reinforce the facts described previously, specifically that molecular transport in the shell model systems gives rise to retarded molecule diffusivity in contrast to the rigid ion model.

5.12 Discussion

5.12.1 Overview: effect of oxygen polarization inclusion on diffusion

Here we attempt to draw together some of the general features obtained from the simulations reported in this chapter. Differences between the rates of molecular transport within the microporous zeolite channels of CIT-1 and Faujasite zeolites have been observed for the simulations employing the rigid ion potential and the polarization inclusive shell model.

In both frameworks the consequence of applying the shell model resulted in self-diffusion coefficients, which were approximately fifty percent lower than those calculated via the rigid ion model. It must be noted that this decrease in diffusivity was calculated irrespective of ensemble, loading, temperature or simulation length proving that it was an artefact of the model. An important relationship exists between
the dynamics of the walls of microporous zeolites and diffusing molecules; the results presented in this work provided proof of that relationship.

5.12.2 *Simulation and experimental studies: CIT-1/xylene systems.*

Comparison of the diffusion data generated via molecular dynamics and zero length chromatography (ZLC) are difficult. A direct comparison between the two cannot be made since only the former method utilizes the Einstein relation to evaluate the mean squared displacement. It must also be noted that the sample constituents used during experimental studies, varied from the siliceous systems which were simulated. The zeolite CIT-1 is synthesized as a borosilicate and converted to an aluminosilicate after the addition of aqueous HCL and aqueous aluminium nitrate. This latter form of Al-CIT-1 has aluminium atoms present in the tetrahedral and octahedral positions of the framework, giving rise to an Si:Al ratio of 35. The aluminosilicate version of CIT-1 was used to carry out the ZLC diffusion studies\(^\text{16}\), which yielded diffusivity values of the order \(10^{-9}\text{cm}^2\text{s}^{-1}\). The PFG NMR method would be envisaged to generate even higher self diffusion coefficients.

The documented effect of protonation, cation presence and high Al:Si on molecule transport into the 10 and 12 MR pores has been to cause a significant decrease in diffusion coefficient. Therefore, because the present values obtained for self-diffusion coefficients are of the order \(10^{-6}\text{cm}^2\text{s}^{-1}\), a significantly faster transport process has been calculated due to the fact that CIT-1 has been modelled in a purely siliceous form as is apparent from the data summarized below in table 5.12.
Table 5.12. A comparison of diffusion coefficients determined theoretically and experimentally for the xylene/CIT-1 system.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>56.0 x10^{-6} cm^2 s^{-1}</td>
<td>25.5 x10^{-6} cm^2 s^{-1}</td>
<td>3.7 x10^{-7} cm^2 s^{-1}</td>
</tr>
</tbody>
</table>

5.12.3 Simulation and experimental studies: Faujasite/benzene systems

Turning now to the Faujasite/benzene system, calculated mean squared displacements - see table 5.13, which included polarisation effects were closer to the experimentally determined value of 4.4±3.3x10^{-10} m^2 s^{-1} obtained by Bull et al.\textsuperscript{13} who used \textsuperscript{2}H NMR spin-lattice relaxation experiments on a sample of purely siliceous Faujasite at 298K.

The simulated value obtained from the molecular dynamics study of Henson et al. was 2.7x10^{-9} m^2 s^{-1}. This value was larger than our polarization inclusive simulated value of 0.6x10^{-9} m^2 s^{-1} obtained using the microcanonical ensemble. This is consistent with the greater molecular migration frequency observed during their study. Our simulated value is also plausible when compared to PFG NMR data for Zeolite Y of 1x10^{-10} m^2 s^{-1} and the earlier simulated values\textsuperscript{17} of 4x10^{-9} m^2 s^{-1}. The purely siliceous Faujasite gives rise to the highest diffusivity due to no impediments to the transport process by extra framework cations which benzene is known to form strong attachments to thus impeding its diffusion. Table 5.13 compares the current simulated values with those discussed for previous simulated and experimental work.

Table 5.13. A comparison of diffusion coefficients determined theoretically and experimentally for the benzene/Faujasite system.

<table>
<thead>
<tr>
<th></th>
<th>current work [300K]</th>
<th>Henson et al.\textsuperscript{11} [298K]</th>
<th>Bull et al.\textsuperscript{13} [298K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffusion coefficient, D</td>
<td>0.6 x10^{-9} m^2 s^{-1}</td>
<td>2.7 x10^{-9} m^2 s^{-1}</td>
<td>4.4 x10^{-10} m^2 s^{-1}</td>
</tr>
</tbody>
</table>
References

1. DL_POLY 2.0 User Manual; Forester T.R., Smith W., CCLRC Daresbury Laboratory 1995


Chapter 6 Conclusion

6.0 Epilogue

Simulation studies have been performed in order to explore surface, interfacial and bulk properties of specific systems of industrial significance. Aspects of the mechanisms of these reactions have been clarified by using the classic molecular modelling methodologies which included minimization, molecular dynamics and Monte Carlo calculations.

6.1 Surface properties – phosphonate scale inhibitors on calcite \{10\bar{1}4\} scale prevention.

We have successfully calculated the modes of interaction necessary for calcite scale inhibition via the phosphonate class of scale poisons. These simulations have focussed on inhibitor design in order to rationalize the structure function dynamics likely to occur in extreme alkaline conditions at active growth sites of the calcite crystal surface. Consequently, feasible mechanisms which operate calcite scale growth intervention have been proposed and corroborated. The chief observations established include the fact that the calculated binding energies prove that the poisons are predominantly electrostatically associated with the dynamic crystal surface. Poisons were shown to favour energetically step and kink sites along the crystal surface; the phosphonates initially made contact with the calcite surface via the phosphonate moiety. Smaller concentrations of HEDP were required to retard kink-kink annihilation than for single phosphonate group poisons. Calcium carbonate units formed endothermic attachments to step edges containing phosphonate neighbours.
6.2 **Bulk properties – self diffusion of hydrocarbon within microporous zeolites**

Fully flexible framework, long-range diffusion studies were performed on the two purely siliceous versions of the zeolites Faujasite and CIT-1. These simulations have been performed with a view to determining the effect of simulation model, simulation time, molecule loading and ensemble choice on the transport dynamics of the hydrocarbon molecules para-xylene, ortho-xylene and benzene through such macrocells. Distinct diffusion rates have been calculated to operate over long simulation production runs. Calculated diffusion coefficients have been proven to be influenced by the introduction of polarization effects into the model.
6.3 Further work

Further insights into the mechanisms of phosphonate poisons on step retardation and kink-kink suppression may be determined by performing an examination of the importance of phosphonate protonation on surface binding. A study into the effects of phosphonate inhibition of other commercially important minerals such as hydroxyapatite may also be useful.

Shell model simulations studies in excess of a nanosecond would definitively determine the most realistic transport routes of small molecules such as benzene. A study across a range of zeolites such as silicalite and MCM-22 comparing rigid ion model diffusivities to those calculated using shell model would be of interest and would be expected to reinforce the results found in Chapter 5, namely that the rigid ion model overestimates properties such as diffusion coefficients.
Appendix A  Sucrose and ice-water interface interactions : simulation studies

A.0  Overview

The aims of this study were two-fold:

• to observe the orientation and the conformational behaviour of sucrose at the ice/water interface at 273K;

• to determine the interaction of sucrose with respect to the smooth, naturally occurring basal plane of hexagonal ice, the (001) plane.

These aims were achieved by simulating an ice/water interfacial system which was modelled at 273K with sucrose at the interface. The simulations were performed using the Cerius\textsuperscript{2} software package.\textsuperscript{1} Characterization of the ice-water interface was performed using the Software Developers's Kit (SDK). The classic molecular modelling techniques of energy minimization and molecular dynamics explained in Chapter 2 of this thesis, were applied to simulate the molecular behaviour of sucrose both in bulk [extended single point charge, SPC/E] water and whilst adsorbed at the ice/water interface. The Monte Carlo technique was used to locate initial starting conformations for sucrose. Both NVE and NVT molecular dynamics methods were employed throughout the work.
A.1 Introduction

Sucrose, α-D-glucopyranosyl-β-D furanoside, is one of the most widespread sugars encountered in nature. It is produced commercially from sugar cane and sugar beets and is a crucial ingredient in ice-creams manufactured by Unilever®. A sensible starting configuration for sucrose was found via the Boltzmann jump sampling technique.

The water and ice/water interface systems were both characterized by calculating:

- The radial distribution function
- The oxygen density profiles

The present chapter will discuss:

- details of the simulation systems used during this investigation, that is, the water, ice/water and sucrose systems and how these simulations were performed.
- details of the analysis procedures used to investigate the simulation;
- observations and results of the simulations

A.2 Ice

There are several polymorphic forms of ice in existence, however, the most common forms² investigated by researchers are the hexagonal I_h and the cubic I_c structures. This is due to the fact that they are both very stable over a wide range of temperatures and pressures. The phase diagram for water is shown in figure A.1. For these reasons, hexagonal ice was the polymorph chosen for this phase of the work. The tetrahedral
packing found in the cubic polymorph of ice gives rise to a structure with plenty of space and will lead to the structure being more sensitive to pressure.

Each of the phases of ice which exist are stable over a limited range of pressure and temperature. The phase diagram indicates that at high pressures, liquid water can freeze at temperatures of $80^\circ C$. All phases possess the common feature of being tetrahedrally bound by hydrogen bonding. The variations in the structures arise from an increased degree of hydrogen bonding as the pressure is increased. This will facilitate deformation of the ice lattice by causing an increase in the oxygen-oxygen distances and a decrease in the next nearest neighbour distances. At very high pressures, phases VII and VIII are surrounded by eight nearest neighbours.

![Figure A.1](image_url)  

**Figure A.1.** The phase diagram of water [3]. Solid lines indicate a stable phase, hatched lines indicate a metastable phase and dotted lines represent estimated boundaries.
The (001) external plane of hexagonal ice was studied during this work. The ice surface was constructed from the unit cell of ice using the *surface builder* module within *Cerius*². The space group used for ice, *Iₜ*, was *P63/mmc*. The unit cell parameters were \( a = b = 4.616 \, \text{Å} \), \( c = 7.364 \, \text{Å} \), \( \alpha = \beta = 90° \), \( \gamma = 120° \).

The structure of ice has been investigated using different experimental techniques.⁴⁻⁶ The crystal structure of ice *Iₜ* is hexagonal in which each oxygen atom is H-bonded to four neighbouring oxygen atoms. The lattice consists of puckered layers which are normal to the c-axis, which contain hexagonal rings of water molecules in the chair conformation. The hexagonal rings formed by three molecules of one layer and the three of the adjacent layer exist in a boat conformation. The surface of the hexagonal unit comprises eight faces: two are basal faces normal to the c-axis and prism faces. The basal face is known as the c-axis (001) due to the fact that it is normal to the c-axis. The c-axis is defined and explained in section A.2.1 and illustrated in figure A.2.

### A.2.1 Generation of the ice crystal: simulation methodology

The raw hexagonal unit cell contained four water molecules in an anti-ferromagnetic structure. The unit cell was converted into a super-lattice. This change eradicated any space group operations within the unit cell. The unit cell was dismantled and the H atoms were subsequently re-adjusted.

Periodicity was restored to the hexagonal ice unit and SPC/E charges⁷ were assigned to the model and the multi-purpose DREIDING 2.21 force field was assigned to the model. Using atomic constraints, the oxygen atoms were fixed whilst the remainder
were rendered movable. The entire system was energy minimized. A period of 0.6ps NVT dynamics was performed on the relaxed system at an elevated temperature of 800K.

A (6x6x3) supercell of ice was generated. During subsequent simulations all oxygen atoms present within the ice slab remained fixed, allowing the hydrogen atoms the freedom to rotate and vibrate.

A.2.2 The (001) plane

The c-face is characterized by a hexagonal arrangement of the oxygen atoms on it with a repeat distance of 4.6Å – see figure A.2. A similar repeat distance can also be found on the prism face. Another common feature of the two faces is that they are flat.

A.2.3 The (201) plane

Amongst the numerous internal planes in the hexagonal crystal, the a-plane (normal to an a-axis) and the (201) plane [shown in figure A.3] have attracted much attention due to their probable involvement in the anti-freeze mechanism. Any insight into the behaviour of sucrose with respect to this plane would be valuable in predicting competitive inhibition at the ice/water interface between antifreeze proteins [AFP] and sucrose.
Figure A.2. [top] Sketch of the hexagonal unit of the ice crystal structure. The shaded area is the c-face; the hatched area is the prisms face; Figure A.3 [bottom] schematic represents the internal (201) plane in the hexagonal unit cell of ice $I_h$. 
A.2.4 Water

The bulk water used during this work was fitted to the SPC/E model devised by Berendsen, Grigera and Straatsma. The SPC/E model comprises of three point masses (as opposed to four in the TIPS4P model) a tetrahedral water structure with an O-H bond distance of 1 Å and a HOH angle of 109.47; with a charge of -0.8476 | e | on the oxygen atom and 0.4238 | e | on the hydrogen atom. A Lennard Jones interaction term was applied to represent the interactions between the oxygen atoms. Table A.1 includes a comparison of the input parameters for the SPC/E, SPC and TIPS4P model.

| Table A.1 | Potential parameters for water models.  

<table>
<thead>
<tr>
<th></th>
<th>SPC/E</th>
<th>SPC</th>
<th>TIP4P</th>
<th>experiment.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(OH) (Å)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9672</td>
<td>0.9672</td>
</tr>
<tr>
<td>(HOH)°</td>
<td>109.47</td>
<td>109.47</td>
<td>104.62</td>
<td>104.62</td>
</tr>
<tr>
<td>(10^{-6}A(\text{kJ}Å^2\text{mol}^{-1}))</td>
<td>2.663</td>
<td>2.663</td>
<td>2.610</td>
<td></td>
</tr>
<tr>
<td>(10^{-3}C(\text{kJ}Å^6\text{mol}^{-1}))</td>
<td>2.167</td>
<td>2.167</td>
<td>2.662</td>
<td></td>
</tr>
<tr>
<td>q(O) (</td>
<td>e</td>
<td>)</td>
<td>-0.8476</td>
<td>-0.82</td>
</tr>
<tr>
<td>q(H) (</td>
<td>e</td>
<td>)</td>
<td>0.4238</td>
<td>0.41</td>
</tr>
<tr>
<td>q(M) (</td>
<td>e</td>
<td>),q(OM) (</td>
<td>e</td>
<td>)</td>
</tr>
<tr>
<td>(\mu/D)</td>
<td>2.36</td>
<td>2.274</td>
<td>2.177</td>
<td>1.86 (vac)</td>
</tr>
</tbody>
</table>

The extended single point charge SPC/E model was chosen to model bulk water during this study because it accurately reproduces many properties of liquid water. Indeed all water models in existence are derivations of the original model developed by Bernal and Fowler in 1933. Other models which model bulk water include SPC.
and TIPS4P. Each of the water model’s parameters differ in number, position and value of applied charges, O-H bond lengths and tetrahedral bond angles. Following the implementation of the SPC/E model in this work, preliminary studies were carried out on the water simulation to ensure that the model was correctly implemented. The following characterization techniques were used:

- Internal energy;
- Radial distribution function

### A.3 Reproduction of the SPC/E model: preliminary work

The amended ice slab described in section A.2.1 of this chapter possessed the following statistics:

- Cell parameters: $a = 22 \, \text{Å}, \, b = 22 \, \text{Å}, \, c = 21 \, \text{Å}$;
- Cell angles: $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
- Cell density: $1.023 \, \text{gcm}^{-3}$.

Simulations were initially performed on both hexagonal and cubic periodic systems of 216 and 300 water molecules (exclusively using $I_h$ system later in the study), using a time step of 1fs and a cut-off radius of 9Å. Long range forces were treated using the Ewald summation technique. Microcanonical (NVE) dynamics were employed. The direct scaling method was used to maintain a constant temperature of 273K. Each system was equilibrated for a period of approximately 6ps followed by a production period of 40ps simulation time, prior to analysing the trajectories.
Table A.2 below includes the results from Berendsen et al.\textsuperscript{10} compared with the simulation results obtained from this work.

Table A.2. Preliminary results from SPC/E model.

<table>
<thead>
<tr>
<th></th>
<th>SPC/E model [10]</th>
<th>SPC/E model, (present work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.998 g cm(^{-3})</td>
<td>1.023 g cm(^{-3})</td>
</tr>
<tr>
<td>Pressure</td>
<td>6 kPa</td>
<td>6.6 Gpa</td>
</tr>
<tr>
<td>Potential Energy</td>
<td>-41.7 kJ mol(^{-1})</td>
<td>-41.3 kJ mol(^{-1})</td>
</tr>
</tbody>
</table>

The calculated values were obtained by performing constant NVT molecular dynamics on a bulk water system of density approximately 1 g cm\(^{-3}\) at a temperature of 300K for 60ps. The radial distribution functions calculated in this study from the water model are almost identical to the radial distribution functions calculated by Berendsen et al., whose own data was in good agreement with experimental data.

A.3.1 Rationale

The justification for using an ice/water interface as opposed to an ice/vacuum interface is that the latter system is an unacceptable oversimplification. McDonald et al.,\textsuperscript{14} state that the ice/water interface describes the environment experienced by the 'real' molecule in situ more accurately than the artificial environment used in simplified docking studies. However, adsorption studies utilizing an ice/vacuum system have proved insightful.\textsuperscript{8}
A.4  Generation of the ice-water interface: simulation method

A.4.1 Methodology

The generation of the ice-crystal was explained previously in section A.2.1. The smooth, external (001) plane of the ice slab was modelled initially, a logical choice, since it occurs naturally in hexagonal ice.

A large block of ice was made by duplicating a unit cell of hexagonal ice. A custom made force field, containing the optimum parameter set was implemented [Table A.1] in order to reproduce the SPC/E water model. The large block of ice was orientated, displaying the [001] plane. The slab was rotated so that its smallest dimension was set to the z-direction. At this point, the slab contained four molecular layers of width 3.6Å each in the z direction.

The co-ordinates in the slab of ice containing 300 molecules was duplicated in the ± z directions in order to provide the co-ordinates for what would become the liquid water region of the structure. The ice/water interface was equilibrated in two stages of NVE dynamics. The top and bottom portions of the ice-slab were heated to 300K and equilibrated for 10ps to produce a liquid phase. The positions of all the atoms in the central (ice) portion were constrained during this stage. The system was then cooled to 273K and equilibrated for a further 6ps. The ice region was modified to constrain all oxygen atoms whilst allowing the hydrogen atoms to move and the entire system was finally equilibrated for a further 10ps at 273K. This resulted in an overall ice/water interface of 2700 atoms in total. The resulting ice/water interface is shown in figure A.4.
Figure A.4. The simulated ice/water interface.
A.5 Sucrose

A.5.1 Background

Although sucrose is a critical ingredient in commercially developed ice-creams, little is understood about its behaviour at a molecular level, both in a vacuum and at the ice/water interface. Sucrose is a disaccharide, composed from one D-glucose and one D-fructose unit, which are joined by an acetal linkage, an $\alpha\beta(1-2)$ glycosidic link between two anomeric carbon atoms$^{15}$. The glucose unit is in the pyranose form and the fructose is in the furanose form. Since both the anomeric carbons are bound in the acetal form, sucrose is a non-reducing sugar, that is, no carbonyl groups are available to participate in chemical reactions.

The two torsional angles phi and psi were subtended at both of the anomeric carbon centres of the molecule. Figure A.5 shows a strained high energy conformation of sucrose in which the functional groups are in extremely close proximity to each other leading to severe steric hindrance. Figure A.6 shows a less strained ‘anti’ conformation with less steric bulk. Figure A.7 shows the positions of the phi/psi torsional angles whose flexibility lead to conformational changes.
A.5.2 Sucrose conformational search methods: simulation details

A number of suitable low energy conformers of the sucrose were generated before the simulations could proceed. These were achieved by undertaking extensive conformer search analysis.

Three methods\(^1\) were used to determine the lowest energy conformation. They included.

(i) Boltzmann jump
(ii) Random sampling
(iii) Grid search

<table>
<thead>
<tr>
<th>search method</th>
<th>Universal Force Field /kcalmol(^1)</th>
<th>Dreiding Force Field /kcalmol(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann jump</td>
<td>219</td>
<td>93</td>
</tr>
<tr>
<td>Grid scan</td>
<td>236</td>
<td>102</td>
</tr>
<tr>
<td>Random sampling</td>
<td>241</td>
<td>161</td>
</tr>
</tbody>
</table>

These choices were further subdivided into two classes of search procedure: systematic and stochastic procedures.

Types (i) and (ii) are classed as stochastic procedures. These involved the random generation of conformations. Monte Carlo methods\(^16\) are in this category. Random
perturbations to a given conformation are used as a method of exploring conformational space. This method is confined to medium and larger molecules. The nature of the random moves and the criteria used for accepting the moves is dependent on the search procedure.

Type (iii) is a systematic search method which produces several conformations by the systematic varying of sets of specified torsion angles. Within this method, the option of relaxing the torsion angles to their nearest local conformational energy minimum is available. This method is especially suited for exploring a small number of degrees of freedom.

A.5.2.1 Grid scan

The grid scan method was used to perform a simple systematic search where each specified torsion angle is varied over a grid of equally spaced values (if more than one torsion angle is involved, the variation of the torsion angles is nested). For example, for two angles A and B at each given value of A, the angle B is varied systematically. A itself also varies systematically. It is impractical to employ grid scan for more than four torsion angles since too many conformations are generated. Typically 1728 conformations were generated from four torsion angles. Energy minimizations were performed on the lower energy conformations. Figure A.8 depicts the lowest energy conformers obtained for this search method using UNIVERSAL$^{17}$ and DREIDING$^{18}$ 2.21 force fields. The lowest energy conformers generated by the force fields were the ‘anti’ conformations in which the furanose and pyranose rings were oriented away from each other.
A.5.2.2 Random sampling

In the random sampling method, the starting conformation was perturbed by randomly altering the values of all possible torsion angles. Each torsion angle $\theta$ was randomly assigned a value in the range $(\theta - 0.6w)$ to $(\theta + 0.6w)$, where $w$ is the torsion angle window, $60^\circ$. The lowest energy conformers generated by this method were energy minimized.

Random sampling could be performed with:

- Each perturbation being performed on the same reference conformation;
- Each perturbation being performed on the previously generated random conformation.

Certain specifications were applied to the random sampling method. These specifications comprised of:

- The total number of conformations generated;
- The torsion angle window value;
- Making the choice of whether minimization was performed on each generated conformation.

The results of the sucrose conformations generated by the random sampling method are shown in figure A.9.
The performance of the Boltmann jump search method can be influenced by:

- **torsion angle window**: the magnitude of the torsion angle window determines the magnitude of the conformational change produced by a single trial move. A larger window increased the chances of producing higher energy conformations and thus increased the rate of conformation rejection. When the angular window was decreased, the rate of acceptance of conformations increased.

- **temperature**: the higher the temperature, the more uphill moves will be accepted. If the temperature is taken to be zero, no upward jumps in energy are allowed. This special case is a simple energy minimization using the random search method.

*A.5.2.3 Boltzmann jump*

The Boltzmann jump method was chosen to generate the lowest energy conformers. These are shown in figure A.10. The figures show that the force fields have generated almost identical conformers with the pyranose and furanose rings in the 'anti' conformation.

The Boltzmann Jump method involved the following procedure:

Torsion angles were randomly altered within a specified angular window of 60°. After each random move. If \( \Delta E \) was negative, the move was selected, however, if \( \Delta E \) was positive then the Boltzmann factor was calculated see equation A.1:


\[ F = \exp\left(\frac{-\Delta E}{RT}\right), \quad (A.1) \]

Equation (A.1) was calculated and a random number from 0 to 1 subsequently generated. If the random number was greater than F, the move was selected, if not the move was rejected. These trial moves were repeated \(10^6\) times.

At the end of the sequence, the conformation was energy minimized and the minimized conformation was retained for further use during molecular dynamics simulations.
Figure A.8. Snapshots of the lowest energy conformers of sucrose using *top:* the grid search/Dreiding force field model; *bottom:* the grid search/Universal force field model.
Figure A.9. Snapshots of the lowest energy conformers of sucrose using top: the random search/Universal force field model; bottom: the random search Dreiding force field model.
Figure A.10. Snapshots of the lowest energy conformers of sucrose using top: the Boltzmann Jump/Dreiding force field model; bottom: the Boltzmann Jump/Universal force field model.
A.6 Characterization of the ice-water interface and water model

It has already been stated that an important component of this study was to characterize the water and ice/water interface models by radial distribution functions and oxygen density profiles respectively.

A.6.1 Radial distribution functions

The radial distribution function, \( g(r) \), can be defined as the probability of finding a site (atom) a distance \( r \) from another atom at the origin compared to the probability in the ideal gas. For molecular liquids, the partial distribution function gives a reasonable account of the complete structure of the fluid.

Consider the following formula shown in equation A.2 which represents the calculation of the partial distribution function for a molecular liquid:

\[
g(r) = \frac{\left( \sum_{i} \sum_{j(i)} H\left( r_j - \left( r + \frac{\Delta r}{2}\right) \right) H\left( \left( r + \frac{\Delta r}{2}\right) - r_i \right) \right)}{4\pi r^2 \rho \left( \frac{N}{2} \right)}
\]

(A.2)

where \( H \) is the Heavyside function, \( r_{ij} \) is the interatomic distance between two atoms \( i \) and \( j \), \([4\pi r^2 \text{dr}]\), is the volume of the spherical shell of an atom, \( \rho \), is the density of the system and \( N \) represents the number of atoms in a simulation.
The above expression for \( g(r) \), can be modified in order to define the partial distribution functions for the hydrogen-hydrogen atoms, \( g_{HH}(r) \), the oxygen to hydrogen atoms, \( g_{OH}(r) \) and the oxygen to oxygen atoms, \( g_{OO}(r) \).

The radial distribution function expression for oxygen-oxygen distances are described in equation A.3:

\[
g_{oo}(r) = \frac{\sum_{a,o} \sum_{b,o} H\left(r_{ab}\left(r + \frac{\Delta r}{2}\right)\right)H\left(r + \frac{\Delta r}{2} - r_{ab}\right)}{4\pi r' dr_o N_o} \tag{A.3}
\]

The radial distribution function expression for hydrogen-hydrogen distances is shown in equation A.4:

\[
g_{HH}(r) = \frac{\sum_{a,H} \sum_{b,H} H\left(r_{ab}\left(r + \frac{\Delta r}{2}\right)\right)H\left(r + \frac{\Delta r}{2} - r_{ab}\right)}{4\pi r' dr_H N_H} \tag{A.4}
\]

The radial distribution function expression for the oxygen-hydrogen distances: is shown in equation A.5:

\[
g_{OH}(r) = \frac{\sum_{a,H} \sum_{b,O} H\left(r_{ab}\left(r + \frac{\Delta r}{2}\right)\right)H\left(r + \frac{\Delta r}{2} - r_{ab}\right)}{4\pi r' dr_H N_O} \tag{A.5}
\]

The calculated \( g(r) \) plots for the SPC/E water model are shown in the following profiles: \( g_{HH}(r) \): figure A.11, \( g_{OH}(r) \): figure A.12, \( g_{HH}(r) \): figure A.13.
For short, repulsive distances, which are less than the atomic diameter, \( g(r) \) is zero, due to strong repulsive forces. This characteristic is found in each of the following profiles. The largest peaks at 1.9 Å and 1.6 Å seen in the \( g_{HH}(r) \) and \( g_{OH}(r) \) profiles illustrate the greater probability that two atoms would have these separations than in an ideal gas. The minima found in all the \( g(r) \) profiles, indicate the probability of finding two atoms with a separation of 3.2 Å. For example, in the \( g_{HH}(r) \) profile, it would be less than for an ideal gas. At long distances, \( g(r) \) tends to the ideal gas value of one which indicates no remaining long range order in the system.
Figure A.11. Radial distribution function of hydrogen-hydrogen distances for SPC/E water at 300K.
Figure A.12. Radial distribution function of oxygen-hydrogen distances for SPC/E water at 300K.
Figure A.13. Radial distribution function of oxygen-oxygen distances for SPC/E water at 300K.
A.6.2 Oxygen density profile

A key feature when simulating systems such as the ice/water interface which include waters explicitly, is the calculation of a density profile along a particular direction of the simulation box. The variation in density along the z axis shows how well the system has been equilibrated. This profile shown in figure A.14 was achieved by the implementation of a Fortran program (see appendix C) into the SDK application of Cerius².

The main steps in the Fortran program were as follows:

1] Identify the model
2] Open the trajectory file
3] Return periodicity of the model
4] Perform consistency checks
5] Get number of movable atoms in the trajectory
6] Obtain list of atom identities.
7] Loop over all atoms and get pointer array which points to the co-ordinates of all oxygen atoms in the trajectory file.
8] Sort over all trajectories, sort all oxygen co-ordinates into a histogram:

\[ I_{nx} = \text{int} \left( \frac{z_i}{\Delta z} \right) + 1 \]

where \( z_i \) is the co-ordinate of a particular oxygen atom in the z-direction

\( \Delta z \) is the difference in the z co-ordinates.
9] Calculate the density along the z axis.
The oxygen density profile across the ice/water interface in the z direction was determined by averaging over 60ps of NVE dynamics. By inspection of figure A.14, it can be seen that the oxygen density profile consists of six strong peaks corresponding to the bulk ice. The two peaks of intermediate height with non-zero minima were due to the interfacial region. A section with a density just below 1.0gcm$^{-3}$, corresponded to liquid water.
Figure A.14. Oxygen density profile of the ice-water interface after 60ps of NVE dynamics.
A.7  *Sucrose and the ice-water interface: simulation results and observations*

Four simulations were performed in order to elucidate the interaction of sucrose with respect to a known plane of hexagonal ice

The four simulations shown in figure A.15 were:

- Bulk SPC/E water was simulated for 40ps of constant NVE dynamics after an initial equilibration of 6ps at a constant temperature of 273K and a time step of 1fs.
- Bulk SPC/E water [equilibrated] was simulated for 40ps of constant NVE dynamics after an initial equilibration period of 40ps at a constant temperature of 273K and a time step of 1fs.
- The ice/water interface was equilibrated for 6ps prior to 40ps of constant NVE dynamics at constant temperature of 273K and a time step of 1fs.
- The interface/sucrose system was equilibrated for 60ps, finally 66ps of constant NVE dynamics was performed on the system at 273K with a time step of 1fs.
Bulk SPC/E water simulation performed at 273K using NVE dynamics for 40ps.

Water/sucrose simulation performed at 273K using NVE dynamics for 60ps

Ice/water interface simulation performed at 273K using NVE dynamics for 80ps.

Ice-water interface/sucrose simulation performed at 273Kk using NVE dynamics for 80ps.

**Figure A.15.** Simulation results: from top figure: simulation (1), simulation (2), simulation (3) and simulation (4).
A.7.1 Calculation of the sucrose / ice-water interaction energy

The strategy for calculating the overall energy of interaction between the sucrose molecule and the ice plane was as follows:

Calculate the energy of bulk SPC/E water, $E_w$, simulation (1), see figure A.15 and table A.4. For the same number of water molecules, calculate $E_{ws}$, simulation (2), see figure A.15 and table A.5. ($E_{ws} - E_w = E_{s, bulk}$), the interaction energy of a single sucrose molecule with bulk water. Calculate $E_{iw}$, the energy of the ice/water interface, simulation (3) – see figure A.15 and table A.6. For the same interface calculate $E_{iws}$, ($E_{iws} - E_{iw} = E_{s, interface}$), the interaction energy of a single sucrose molecule with the ice-water interface, simulation (4) - see figure A.15 and table A.7. Calculate $E_{adsorption} = (E_{s, surface} - E_{s, bulk})$, the adsorption energy of sucrose.

A.7.1.1 Normalization of energies

To convert the simulation energy calculated by Cerius$^2$ into kJmole$^{-1}$ of water, the equation A.6 was used:

$$U = \frac{4.184}{N}$$ \hspace{1cm} (A.6)

where $N$ is the number of water molecules in the system, and 4.184 is a conversion factor. In order to compare the previous simulation estimates for water it is necessary to add the polarization correction$^{27}$ of 5.22kJmol$^{-1}$ - see equation A.7 below.

$$U_{\text{normake}} = \frac{4.184}{N} + 5.22\text{kJmol}^{-1}$$ \hspace{1cm} (A.7)
A.7.1.2 Bulk SPC/E water simulation

The system contained 300 water molecules, density of SPC/E water was 1.023gcm\(^{-3}\).

Table A.4. Data obtained from the bulk SPC/E water simulation.

<table>
<thead>
<tr>
<th></th>
<th>average</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/kcalmol(^{-1}) of system</td>
<td>704</td>
<td>33.96</td>
</tr>
<tr>
<td>T/K</td>
<td>273</td>
<td>12.67</td>
</tr>
<tr>
<td>U/kcalmol(^{-1}) of system</td>
<td>-3376</td>
<td>64.83</td>
</tr>
<tr>
<td>Van der Waals/kcalmol(^{-1}) of system</td>
<td>661.7</td>
<td>36.97</td>
</tr>
<tr>
<td>Coulombic/kcalmol(^{-1}) of system</td>
<td>-4298.46</td>
<td>62.39</td>
</tr>
<tr>
<td>Total Energy/ kcalmol(^{-1})</td>
<td>-2471.297</td>
<td>64.81</td>
</tr>
</tbody>
</table>

A.7.1.3 Bulk water/sucrose simulation

The system contained 300 water molecules and a single sucrose molecule.

Table A.5. Data obtained from the bulk SPC/E water/sucrose simulation.

<table>
<thead>
<tr>
<th></th>
<th>average</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/kcalmol(^{-1}) of system</td>
<td>767.4</td>
<td>16.22</td>
</tr>
<tr>
<td>T/K</td>
<td>272.3</td>
<td>6.41</td>
</tr>
<tr>
<td>U/kcalmol(^{-1}) of system</td>
<td>-2236.3</td>
<td>17.46</td>
</tr>
<tr>
<td>Van der Waals/kcalmol(^{-1}) of system</td>
<td>388.96</td>
<td>21.40</td>
</tr>
<tr>
<td>Coulombic/kcalmol(^{-1}) of system</td>
<td>-3064.36</td>
<td>32.46</td>
</tr>
<tr>
<td>Total Energy/ kcalmol(^{-1})</td>
<td>-1467.88</td>
<td>12.00</td>
</tr>
</tbody>
</table>
**A.7.1.4 Ice/water interface simulation**

The system contained 600 water molecules and 300 ice molecules, density of SPC/E water: 1.023gcm$^{-3}$.

**Table A.6.** Data obtained from the bulk SPC/E water/sucrose simulation.

<table>
<thead>
<tr>
<th></th>
<th>average</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K /\text{kcalmol}^{-1}$ of system</td>
<td>2016.86</td>
<td>632.31</td>
</tr>
<tr>
<td>$T /\text{K}$</td>
<td>273</td>
<td>12.67</td>
</tr>
<tr>
<td>$U /\text{kcalmol}^{-1}$ of system</td>
<td>-7669661</td>
<td>646.61</td>
</tr>
<tr>
<td>Van der Waals/$\text{kcalmol}^{-1}$ of system</td>
<td>1644.36</td>
<td>66.11</td>
</tr>
<tr>
<td>Coulombic/$\text{kcalmol}^{-1}$ of system</td>
<td>-772414.12</td>
<td>226.77</td>
</tr>
<tr>
<td>Total Energy/ $\text{kcalmol}^{-1}$</td>
<td>-767646.12</td>
<td>1074.64</td>
</tr>
</tbody>
</table>

**A.7.1.5 Ice/water interface/sucrose simulation**

The simulation contained 600 water molecules, 300 ice molecules and sucrose, density of SPC/E water: 1.023gcm$^{-3}$.

**Table A.7.** Data obtained from the bulk SPC/E water/sucrose simulation.

<table>
<thead>
<tr>
<th></th>
<th>average</th>
<th>standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K /\text{kcalmol}^{-1}$ of system</td>
<td>1987.21</td>
<td>26.87</td>
</tr>
<tr>
<td>$T /\text{K}$</td>
<td>272.66</td>
<td>3.68</td>
</tr>
<tr>
<td>$U /\text{kcalmol}^{-1}$ of system</td>
<td>-769669</td>
<td>31.31</td>
</tr>
<tr>
<td>Van der Waals/$\text{kcalmol}^{-1}$ of system</td>
<td>1664.09</td>
<td>39.43</td>
</tr>
<tr>
<td>Coulombic/$\text{kcalmol}^{-1}$ of system</td>
<td>-772364.76</td>
<td>67.00</td>
</tr>
<tr>
<td>Total Energy/ $\text{kcalmol}^{-1}$</td>
<td>-767682</td>
<td>33.73</td>
</tr>
</tbody>
</table>

The simulations performed demonstrated that the interaction of sucrose with respect to the smooth, external (001) ice plane, was $E_{\text{adsorption}} = -1048.03\text{kcalmol}^{-1}$, which implied a favourable interaction between sucrose to the ice/water substrate.
A.8 Discussion

A.8.1 Water/sucrose simulation

The pyranose and furanose rings of the sucrose molecule experienced significant ring puckering throughout the simulation. A frequent transition and interchange from boat→chair→twist configurations was observed. The hydroxyl groups on both rings were inter-converted between axial and equatorial positions. Hence the sucrose freely vibrated and rotated and diffused through the bulk water system. Hydroxyl groups of the molecule seemingly interacted with free water molecules via extensive H bonding.

A.8.2 Interface/sucrose simulation

Considerably less interaction was observed between the sucrose at the ice/water interface. The sucrose molecule had been deliberately placed in an upright position with respect to the interface approximately 7Å above the ice section on the (001) plane of the hexagonal ice structure. Throughout the 66ps constant NVE simulation although vibration and rotation of the sucrose molecule was observed, limited translational movement and migration of sucrose towards the ice plane occurred.
A.9 Summary and further work

The molecular modelling techniques of energy optimization, molecular dynamics and
the Monte Carlo algorithm have been used in order to elucidate the interactions
between a sucrose molecule at the smooth (001) plane of an ice/water interface at
273K. The ice/water interface was accurately built as determined by the successful
implementation of the oxygen density profile functionality. A conformational study
of sucrose was achieved with a view to assessing eventually the competition between
low energy sucrose conformers and anti-flounder proteins at the growing ice-water
interface. The overall interaction energy of the sucrose molecule for the basal plane of
ice was large and exothermic, a more suitable force field such as AMBER-
HOMANS [especially parametized for carbohydrate molecules] would be expected to
furnish interaction energies of lower magnitude.

The interaction of the an increased concentration of sucrose low energy sucrose
conformers at an internal ice plane such as (201) for longer simulation times, using
the AMBER_HOMANS force field, specifically developed for carbohydrates, would
offer a suitable approach to solving the sucrose molecular interaction mechanism
which operates at the ice-water interface.
References

3. F. Franks, Water, Plenum Press, New York, 1972 1 Chapter 4
14. S.M. McDonald, A. White and P. Clancy, AICHE Journal 1995 41 4

Appendix B  Mulliken charge preliminary calculations

B.1  Comparison of semi-empirical methods

The modified neglect of differential overlap [MNDO], Austin model 1 [AM1] and parametric method number 3 [PM3] methods are all parameterized versions of the neglect of diatomic differential overlap [NDDO] model. The parameterization is in terms of atomic variables, which refer only to the properties of a single atom. The three methods are all derived from the same basic approximations. They differ only in the way the core-core repulsion is treated, and how the parameters are assigned. Each method considers only the valence s and p functions, which are taken as Slater type orbitals with corresponding exponents, $\zeta_s, \zeta_p$. The accuracy is known to increase in the order MNDO > AM1 > PM3. This is due to the fact that AM1 contains more adjustable parameters than MNDO. It must also be noted that PM3 can be considered as a version of AM1 with fully optimized parameters. It has been noted, however, that regarding the Mulliken population analysis, AM1 yields a higher quality wave function than the PM3 method.

The effective atomic charges deduced from the Mulliken population analysis for the charged diphosphonate, hydroxy ethylidene 1,1 diphosphonate, HEDP by the different methods is given in table B.1. The charges deduced for the neutral diphosphonate, 1 hydroxy-ethylidene 1,1 diphosphonate, HEDP by the different methods is given in table B.2.
Table B.1  Mulliken charges in $\text{[HEDP]}^+$ with different methods.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>AM1</th>
<th>PM3</th>
<th>MNDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2.6309</td>
<td>1.7169</td>
<td>1.1137</td>
</tr>
<tr>
<td>O</td>
<td>-1.3065</td>
<td>-1.0812</td>
<td>-0.9274</td>
</tr>
<tr>
<td>O</td>
<td>-1.2972</td>
<td>-1.0669</td>
<td>-0.9291</td>
</tr>
<tr>
<td>O</td>
<td>-1.3174</td>
<td>-1.0982</td>
<td>-0.9679</td>
</tr>
<tr>
<td>C</td>
<td>-1.0618</td>
<td>-0.5402</td>
<td>-0.2968</td>
</tr>
<tr>
<td>P</td>
<td>2.6128</td>
<td>1.6570</td>
<td>1.1135</td>
</tr>
<tr>
<td>O</td>
<td>-1.2989</td>
<td>-1.04089</td>
<td>-0.9284</td>
</tr>
<tr>
<td>O</td>
<td>-1.3106</td>
<td>-1.085</td>
<td>-0.9278</td>
</tr>
<tr>
<td>O</td>
<td>-1.3242</td>
<td>-1.0897</td>
<td>-0.9677</td>
</tr>
<tr>
<td>O</td>
<td>-0.3654</td>
<td>-0.4325</td>
<td>-0.3557</td>
</tr>
<tr>
<td>H</td>
<td>0.1532</td>
<td>0.2040</td>
<td>0.1542</td>
</tr>
<tr>
<td>C</td>
<td>-0.1719</td>
<td>-0.0754</td>
<td>0.1369</td>
</tr>
<tr>
<td>H</td>
<td>0.0415</td>
<td>0.0088</td>
<td>-0.0382</td>
</tr>
<tr>
<td>H</td>
<td>-0.0240</td>
<td>-0.0211</td>
<td>-0.0897</td>
</tr>
<tr>
<td>H</td>
<td>0.0393</td>
<td>-0.0477</td>
<td>-0.0897</td>
</tr>
</tbody>
</table>
Table B.2  Mulliken charges in [HEDP]$^0$ with different methods.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>AM1</th>
<th>PM3</th>
<th>MNDO</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>2.5171</td>
<td>2.1485</td>
<td>1.3162</td>
</tr>
<tr>
<td>O</td>
<td>-0.9684</td>
<td>-0.4694</td>
<td>-0.4846</td>
</tr>
<tr>
<td>O</td>
<td>-0.9213</td>
<td>-0.8162</td>
<td>-0.7177</td>
</tr>
<tr>
<td>O</td>
<td>-0.7220</td>
<td>-0.4482</td>
<td>-0.5844</td>
</tr>
<tr>
<td>C</td>
<td>0.5144</td>
<td>-0.7521</td>
<td>0.4938</td>
</tr>
<tr>
<td>P</td>
<td>2.5085</td>
<td>2.1098</td>
<td>1.4247</td>
</tr>
<tr>
<td>O</td>
<td>-1.0651</td>
<td>-0.8194</td>
<td>-0.5707</td>
</tr>
<tr>
<td>O</td>
<td>-1.0962</td>
<td>-0.4769</td>
<td>-0.6187</td>
</tr>
<tr>
<td>O</td>
<td>-0.7726</td>
<td>-0.4484</td>
<td>-0.4854</td>
</tr>
<tr>
<td>O</td>
<td>-0.4810</td>
<td>-0.2991</td>
<td>-0.2350</td>
</tr>
<tr>
<td>H</td>
<td>0.2720</td>
<td>0.2163</td>
<td>0.2572</td>
</tr>
<tr>
<td>C</td>
<td>-0.3292</td>
<td>-0.1311</td>
<td>0.0323</td>
</tr>
<tr>
<td>H</td>
<td>0.2045</td>
<td>0.0634</td>
<td>0.0637</td>
</tr>
<tr>
<td>H</td>
<td>0.1420</td>
<td>0.0745</td>
<td>0.0481</td>
</tr>
<tr>
<td>H</td>
<td>0.1972</td>
<td>0.0483</td>
<td>0.0605</td>
</tr>
</tbody>
</table>
Appendix C  Fortran code for the oxygen density profile calculation

C.1  Oxygen density profile program

SUBROUTINE GetOxy(ModelFile, TrjFile, ierr)

IMPLICIT NONE
CHARACTER(*) ModelFile  ! file containing model
CHARACTER(*) TrjFile    ! trajectory file name
INTEGER ierr            ! error flag
REAL rho(nalab),den(nslab),z(nalab)
REAL delz,nden,ib,A,Lx,Ly,Lz,dvol,Lz2

c......Includes
#include "madefa.inc"

C......Locals
INTEGER jerr,density,status
INTEGER Model, Period, ModelPeriod
INTEGER NMovAtoms, MAtomsCell, NFixed, NOxygen
INTEGER i, j, NGot, iframe
INTEGER TrjId
LOGICAL found, Reading

C......Pointers
DOUBLE PRECISION xys(3,l)
DOUBLE PRECISION Oxyz(3,l)
INTEGER AtIds(l)
INTEGER AtOIds(l)
INTEGER TrjAtIds(l)
INTEGER IndexList(l)
INTEGER AtACL(l)
INTEGER AtAtomicNo(l)
POINTER (pxys, xys)
POINTER (pOxyz, Oxyz)
POINTER (pAtIds, AtIds)
POINTER (pAtOIds, AtOIds)
POINTER (pTrjAtIds, TrjAtIds)
POINTER (pIndexList, IndexList)
POINTER (pAtACL, AtACL)
POINTER (pAtAtomicNo, AtAtomicNo)

C......Code
C......Expect SUCCESS
ierr = SUCCESS

C......Initialize variables
pxys = NullPtr
pOxyz = NullPtr
pAtIds = NullPtr
pAtOIds = NullPtr
pTrjAtIds = NullPtr
pIndexList = NullPtr
pAtACL = NullPtr
pAtAtomicNo = NullPtr
TrjId = m8A_TRJ_NullId
pAtIds = ms_MEM_Alloc(NAtomsCell*ms_BYTE_INTEGER)
pAtOIds = ms_MEM_Alloc(NAtomsCell*ms_BYTE_INTEGER)
pAtACL = ms_MEM_Alloc(NAtomsCell*ms_BYTE_INTEGER)
pTrjAtIds = ms_MEM_Alloc(NMovAtoms*ms_BYTE_INTEGER)
pIndexList = ms_MEM_Alloc(NAtomsCell*ms_BYTE_INTEGER)

C.....Get list of Atom OIDs
CALL msD_MOD_AtomList(Model, ms_SYM_ALL, AtOids, NAtomsCell, > NGot, jerr)

C.....Get a list of atoms ids
CALL msD_Id(AtOids, NAtomsCell, AtIds, jerr)

C.....Get ACL for each atom
CALL msD_Type(AtOids, NAtomsCell, AtACL, jerr)

C.....Get atomic number of each atom
CALL msD_ACL_AtomicNumber(AtACL, NAtomsCell, AtAtomicNo, jerr)

C.....Get atom id order saved in trajectory
CALL msA_TRJ_ValueInt(TrjId, msA_TRJ_MOVABLEATOMIDS, TrjAtIds, > NMovAtoms, NGot, jerr)

C.....Loop over all atoms and get a pointer array which points to
C.....coordinates of all O atoms

NFixed = 0
NOxygen = 0
DO i = 1, NAtomsCell
  C......If atom i is an oxygen
  IF (AtAtomicNo(i) .EQ. 8) THEN
    found = .FALSE.
    DO j = 1, NMovAtoms
      IF (AtIds(i) .EQ. TrjAtIds(j)) THEN
        NOxygen = NOxygen+1
        IndexList(NOxygen) = j
        found = .TRUE.
      ENDIF
    ENDDO
  ENDIF
  C......If atom not saved in trajectory assume it was fixed and get
  C.....coordinates from model. May actually want to test that the
  C.....atom really is fixed ....
  IF (.NOT.found) THEN
    NFixed = NFixed+1
    CALL msD_Xyz(AtOids(i), 1, xyz(1,NMovAtoms+NFixed), jerr)
    NOxygen = NOxygen+1
    IndexList(NOxygen) = NMovAtoms+NFixed
  ENDIF
ENDIF
ENDDO

C........At this stage all of the oxygens are indexed. We know where to find them!
C.....Allocate memory for O coordinates
pOxyz = ms_MEM_Alloc(3*NOxygen*ms_BYTE_DOUBLE)

C.....Loop over all frames in trajectory
  iframe = 0
  Reading = .TRUE.
c.....Get current model
CALL msD_MOD_Current(Model, jerr)
IF (jerr .NE. SUCCESS) THEN
  WRITE(*,*) 'ERROR: getting current model'
ierr = FAILURE
GOTO 999
ENDIF

C.....Attempt to load Model file
CALL msD_FILE_ImportModel(ModelFile, msD_FMT_MSI,
  > msD_REPLACE_MODEL, Model, jerr)
IF (jerr .NE. SUCCESS) THEN
  WRITE(*,*) 'ERROR: Loading model'
ierr = FAILURE
GOTO 999
ENDIF

C.....Attempt to open trajectory
CALL msA_TRJ_Open(TrjFile, msA_TRJ_OPENREADFILE, TrjId, jerr)
IF (jerr .NE. SUCCESS) THEN
  WRITE(*,*) 'ERROR: Opening trajectory file'
ierr = FAILURE
GOTO 999
ENDIF

C.....Some consistency checks
C.....(1) same periodicity
CALL msD_MOD_PeriodicType(Model, ModelPeriod, jerr)
CALL msA_TRJ_ValueInt(TrjId, msA_TRJ_PERIODICITY, Period, 1, NGot,
  > jerr)
IF (((Period .EQ. 0) .AND. (ModelPeriod .NE. msD_NONPERIODIC))
  > .OR.
  > ((Period .EQ. 1) .AND. (ModelPeriod .NE. msD_PERIODIC_1D))
  > .OR.
  > ((Period .EQ. 2) .AND. (ModelPeriod .NE. msD_PERIODIC_2D))
  > .OR.
  > ((Period .EQ. 3) .AND. (ModelPeriod .NE. msD_PERIODIC_3D)))
  > THEN
  WRITE(*,*) 'ERROR: Periodicity mismatch between model and trj'
ierr = FAILURE
GOTO 999
ENDIF

C.....(2) same number of atoms in unit cell
CALL msD_MOD_NuImAtoms(Model, msD_SYM_ALL, NatomsCell, jerr)
CALL msA_TRJ_ValueInt(TrjId, msA_TRJ_TOTALNOATOMS, I, 1, NGot,
  > jerr)
IF (NAtomsCell .NE. I) THEN
  WRITE(*,*) 'ERROR: Atom mismatch between model and trj'
ierr = FAILURE
GOTO 999
ENDIF

C.....FROM NOW ON SKIP DOING ANY ERROR CHECKING - REALLY SHOULD CHECK
RETURN STATUS FROM ANY API CALL ...

C.....Get number of movable atoms in trj
CALL msA_TRJ_ValueInt(TrjId, msA_TRJ_NOMOVABLEATOMS, NMovAtoms, 1,
  > jerr)

C.....Allocate some dynamic memory
pxyz = msS_MEM_Alloc(3*NAtomsCell*msS_BYT_DOUBLE)
DO i=1,nslab
    den(i) = 0.0
    rho(i) = 0.0
ENDDO

c........histogram array set to zero
C........define some geometry variables
Lx=22.0144
Ly=22.0345
Lz=64.0415
Lz2=Lz/2.0
A=SQRT(3.0)*Lx*Ly/2.0

delz = Lz/real(nslab)
dvol = delz*A
write (6,*) 'Area = ',A
write (6,*) ' dvol = ',dvol

DO WHILE (Reading)

C ........Read next frame
CALL msA_TRJ_ReadFrame(TrjId, iframe+1, jerr)

IF (jerr .NE. SUCCESS) THEN
C ..........If error reading frame end loop (end of file is an error)
Reading = .FALSE.
ELSE
C ........Frame read successfully
C ........increment frame counter
 iframe = iframe+1
write(6,*) 'frame No', iframe
C ........Get coordinates from trajectory
CALL msA_TRJ_ValueDouble(TrjId, msA_TRJ_COORDINATES, xyz, >
3*NNovAtoms, NGot, jerr)

C ........extract coordinates of oxygens
DO i = 1, NOxygen
    Oxyz(1,i) = xyz(1,IndexList(i))
    Oxyz(2,i) = xyz(2,IndexList(i))
    Oxyz(3,i) = xyz(3,IndexList(i))
    Oxyz(3,i) = Oxyz(3,i) -Lz2
    Oxyz(3,i) = Oxyz(3,i) - Lz * ANINT (Oxyz(3,i)/Lz)
write (6,*) Oxyz(3,i)
ENDDO

IF (iframe .EQ.1) then
write (6,*) (Oxyz(3,i), i=1,NOxygen)
ENDIF

DO i = 1, NOxygen
    ib = int((Oxyz(3,i) + Lz2)/delz) + 1
    den(ib) = den(ib) + 1.0
ENDDO

C ...........Sorts into slab ib
C ...........DO WHATEVER YOU WANT WITH THE O COORDINATES !!!!
ENDIF
ENDDO

DO i = 1, nslab
    rho(i) = den(i)/real(iframe)/dvol
ENDDO
rho(i) = rho(i) * 18.0 * 10.0 / 6.023
z(i) = (real(i) - 0.5) * delz - Lz2
ENDDO

write (6, '(3E15.6)') (z(i), den(i), rho(i), i=1, nslab)
c..........ends loop over trajectory
c........Exit
999 CONTINUE

c........Close trajectory
   IF (TrjId .NE. msA_TRJ_NullId) CALL msA_TRJ_Close(TrjId, jerr)

c........Free memory
   IF (pxyz .NE. NullPtr) jerr = msS_MEM_Free(pxyz)
   IF (pOxyz .NE. NullPtr) jerr = msS_MEM_Free(pOxyz)
   IF (pAtIds .NE. NullPtr) jerr = msS_MEM_Free(pAtIds)
   IF (pAtIds .NE. NullPtr) jerr = msS_MEM_Free(pAtOids)
   IF (pAtACL .NE. NullPtr) jerr = msS_MEM_Free(pAtACL)
   IF (pAtAtomicNo .NE. NullPtr) jerr = msS_MEM_Free(pAtAtomicNo)
   IF (pTrjAtIds .NE. NullPtr) jerr = msS_MEM_Free(pTrjAtIds)
   IF (pIndexList .NE. NullPtr) jerr = msS_MEM_Free(pIndexList)
RETURN
END

* By M Pinches, D.J. Tildesley and S.A. Ojo.