

Structure and Dynamics in Network Liquids

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A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy of the University of Oxford

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Abstract

The onset of the Glass Transition in tetrahedral network liquids is associated with the over-constrained nature of the structure and the low ability of the ions to move relative to one another. We investigate the interplay between the structure and dynamics in BeF_2 , a template for the ideal tetrahedral system. We see that the ionic diffusion coefficients can be predicted from the calculated viscosity of the system using the Eyring hopping model of diffusion, with a diffusive jump length approximately corresponding to the radius of the first coordination sphere. Novel correlation functions are developed which enable us to identify the events responsible, on an atomistic level, for the structural rearrangements which correspond to the barrier crossing in this hopping model of diffusion, and we find that these events can be identified as the exchange of ions in the local coordination polyhedra, or *cage*, of the cations. The calculation of the rate of the decay of these cages allows us to predict the macroscopic diffusion coefficients with the definition of a jump length over which the diffusive hops occur, and to scale the behaviour of the system at different temperatures by setting the cage lifetime as an effective *clock* for the system. Comparison between simulations performed with and without the inclusion of the effects of anion polarisation suggest that the polarisation plays an important role in the ability of the system to undergo the cage decay events and to create the *defect* sites which facilitate a decrease in the number of constraints acting in the system.

The decay of the cages describes the local rearrangement of the ions in the first coordination shell of a given ion. The development of other correlation functions allows us to investigate the spatial relationship between these cage decay events over longer length and time scales, and also to investigate how the local structure of the first coordination shells of the cations relates to their ability to undergo the cage decay events and to form the defects.

These functions are then used to investigate the link between the structure and the dynamics in some molten trichloride systems, which have different network structures, and hence a different relationship between the cage decay and the diffusion.

Finally, we investigate the effect of changing the potential parameters in BeF_2 , and we find that the effective polarisability of the system can be controlled such that a less diffusive system may be described, giving a good representation of both structural and dynamical experimental data.

To my parents

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Chapter 1

Introduction

1.1 Barely diffusing systems: towards the Glass Transition

Many fluids, of vastly different chemical composition and internal structure, display an ability to form *glasses* on cooling. A glass is a supercooled liquid state, which is characterised by having an internal structure similar to that of the liquid state which persists at temperatures below the melting point. As the system cools, it effectively gets *trapped* in a liquid-like configuration, at temperatures below which crystallisation should occur. This trapping may occur due to the cooling rate being such that the system does not have time to sample enough of the *phase space* relating to its internal degrees of freedom, *i.e.* to access the whole of the *potential energy surface* governing the internal motion, so that the system finally rests in a configuration which is at an energy above that of the global minimum. This can be understood by expressing the many degrees of freedom of the system as a single coordinate, and examining the potential energy surface [1], as shown in figure 1.1. The global minimum energy configuration of the system is the crystal, as it has the lowest potential energy on the surface. However, as the system cools it is not necessarily able to sample those configurations which would lead to the crystalline configuration on further cooling. This is because the rate of cooling leads to there being a short time available to sample these configurations. There are not very many of these configurations, and this is represented by the narrow neck of the fun-

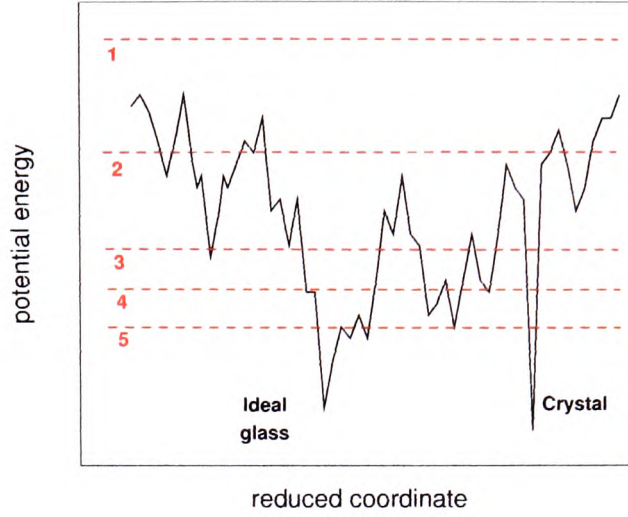


Figure 1.1: A representation of the Potential Energy Surface for a glass-forming liquid, the *reduced coordinate* representing the multi-dimensional motion over this surface. The red dashed lines denote energy regimes as discussed in section 1.1.

nel which leads to the crystal in figure 1.1. This scenario is referred to as the system being *non-ergodic*, which means simply that a situation of internal non-equilibrium has been attained. This leads to the general definition of a glass, proposed by Angell [2], as *a condensed state of matter which has become non-ergodic by virtue of the continuous slow down of one or more of its internal degrees of freedom*.

When a system with the potential energy surface given by figure 1.1 cools, it passes from configurations in regime 1 to those in regime 5. During this cooling, the system will spend more time sampling those configurations which correspond to local minima of energy, such as those in the shallow valley below regime 2. Further cooling results in the system undergoing *barrier crossings* until the glassy regime 5 is reached. Hence during the cooling into a glassy state, the system may get trapped temporarily into shallow valleys which are themselves at relatively high energy, before being able to mount the valley walls and move into another, lower energy valley. The structural relaxation within the fluid depends upon the occurrence of these barrier crossings, and this type of glass is usually referred to as a *structural glass*, as

there needs to be some rearrangement, or relaxation, of the different particles within the system relative to one another in order for the barrier crossings to occur. The *global* minimum energy configuration still corresponds to the crystal, but the probability of crossing the barrier between the valley corresponding to the *ideal glass* to that for the crystal is effectively zero.

1.1.1 The Glass Transition

The term *Glass Transition* refers to the change between the liquid phase and the kinetically stable glassy phase where structural relaxation of the system is arrested. The characteristic property of a liquid which gives a measure of the magnitude of the structural relaxation processes occurring, and which is measurable experimentally, is the viscosity. The Glass Transition is usually defined as occurring at the point at which the viscosity of the liquid reaches a certain high value, that is 10^{13} poise. This transition occurs over a wide range of temperatures in real systems, but the common definition of the point at which a substance becomes a glass upon supercooling is the *Glass Transition Temperature*, T_g . The value of T_g is very dependent on the nature of the material, but can generally be related to the melting point of that material, T_m , by the relation $T_g \approx 0.6T_m$, and so when we evaluate the temperature dependence of the viscosity of a range of materials in terms of the reduced temperature, $\frac{T}{T_g}$, we find that materials with very different temperature ranges of their diffusive behaviour may be more easily compared, as is shown in figure 1.2. In this figure, the Angell plot, the variation of viscosity with inverse reduced temperature is shown for a range of glass forming liquids.

1.1.2 Strong and Fragile Liquids

The behaviour of a glass forming liquid can be broadly classified into that of *Strong* or *Fragile* [5]. A strong liquid is one which has a logarithmic dependence of the viscosity, η , with the inverse reduced temperature, *i.e.* $\log \eta \propto \frac{T_g}{T}$, which means that it exhibits Arrhenius behaviour of the viscosity and related properties such as

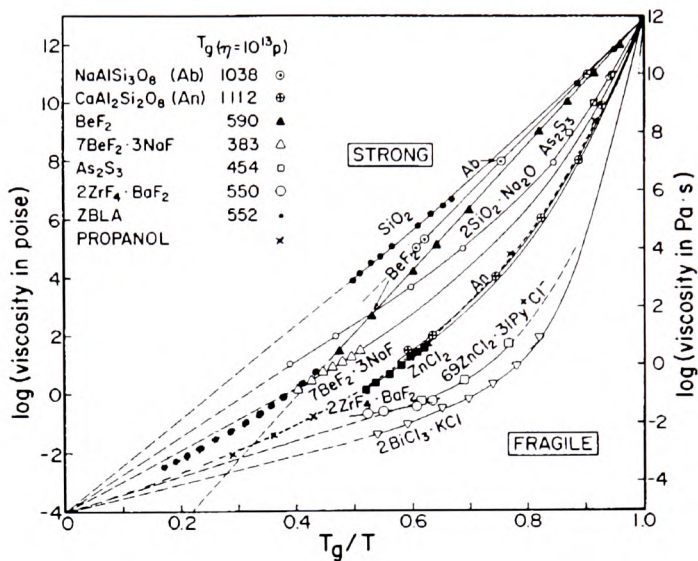


Figure 1.2: The Angell plot showing the dependence of the viscosity on the reduced inverse temperature, $\frac{T_g}{T}$, for a range of glass formers. The Glass Transition temperature, T_g , the temperature at which the viscosity equals 10^{13} poise, is shown for a selection of these materials in the legend. The classification as *Strong* or *Fragile* is determined by the curvature of this plot, the strong liquids being those, such as SiO_2 and BeF_2 , which exhibit Arrhenius behaviour of viscosity over an extended temperature range, and the fragile liquids are those which are strongly non-Arrhenius. This figure is reproduced from [3], which was itself adapted from [4].

the structural relaxation times and the self-diffusion coefficients. On the other hand, a fragile liquid is one in which the dependence of the viscosity on inverse reduced temperature is strongly *non-Arrhenius*, and in which there are discontinuities of properties such as its heat capacity at the glass transition temperature. The greater the curvature of the line in the $\log \eta$ against $\frac{T_g}{T}$ plot, then the more fragile the liquid. As can be seen from figure 1.2, strong liquids are typically those which form network structures. SiO_2 is the primary example, and it has crystal structures based upon the vertex sharing of SiO_4 tetrahedra, and these units persist in the liquid at ambient pressures. Fragile glasses are typically aromatic hydrocarbons or more highly coordinated ionic solids, and also Van der Waals' materials, which do not contain

strongly directional forces. Further discrimination between strong and fragile behaviour is possible if we introduce the idea of the *intermediate* liquid: here, there is some degree of network formation, but now effects other than the simple linking of polyhedra are important. One such liquid is ZnCl_2 [6, 7].

The *strength* of a liquid is related to the shape of the energy landscape, which is determined by the interactions within the system. Strong glasses have energy landscapes with relatively wide and deep energy wells. The presence of these wide valleys can be related to the *intermediate range order* (IRO) within the system [6, 7]; intermediate range order means that there is ordering of the network on a length scale beyond the nearest neighbour length scale, and implies the formation of extended *network strings* which are hard to break, and which therefore prohibit extensive structural rearrangement, due to the high energy barriers associated with this IRO.

1.2 Network Liquids

As suggested above, the strong liquids, those that exhibit Arrhenius dependence of the viscosity on temperature, are *network liquids*. A network liquid is generally an ionic melt, in which the cations are surrounded by anions to make up a series of polyhedra. In SiO_2 and BeF_2 , for example, these are MX_4 tetrahedra. The stoichiometry of these compounds dictates, though, that these species may not exist independently, and so the polyhedra are linked, by sharing vertices, edges or, much less frequently, faces. This linking of polyhedra extends throughout the liquid, and it is this extended structural motif which gives the liquids their strength. An example of the extended network structure can be seen for BeF_2 in figure 1.3.

To understand how the system relaxes, we have to identify the method of barrier crossings as the potential energy surface is traversed, and thus identify the physical processes which correspond to the multidimensional events that the surface represents.

Computer simulations of amorphous silica [9] have shown that it may undergo a

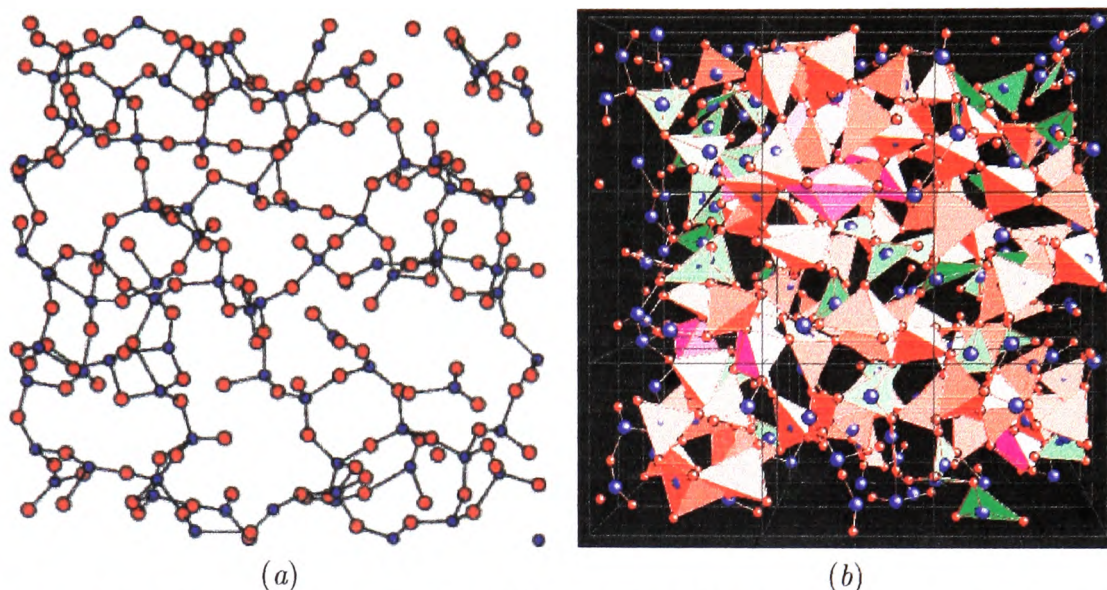


Figure 1.3: The network structure of BeF_2 . The Be^{2+} ions are shown as blue and the F^- ions as red. *Bonds* are drawn between cations and anions whose separation is smaller than the position of the first minimum in the cation-anion partial radial distribution function (see section 3.2.1). Panel (a) shows a slice through a simulation of BeF_2 at 700 K, with the slab thickness equal to 15 au: we can see the predominance of 4-coordinate cations and 2-coordinate anions, and also the vertex sharing of the coordination polyhedra. Panel (b) shows the vertex sharing polyhedra structure at 1300 K. Tetrahedra are drawn in red around four-coordinate cations. The purple and green polyhedra are drawn around five- and three-coordinate cations respectively. Note that the ions at the edges of the simulation cell are shown without their polyhedra, as the faces of these polyhedra penetrate the cell walls, being made up with vertices which are the *periodic images* of ions at the opposite faces of the cell (see section 2.4.1 on the use of periodic boundary conditions). This figure has been produced using a modified version of the *MDview* program of S. Hull [8].

reversible compaction (local density increase) upon Ultraviolet irradiation in the 200 nm range. This has been explained in terms of a model which relates the compaction to the fate of energy absorbed on irradiation. In this model, the absorbed energy is assumed to break a single Si-O bond, and then be converted into the increased kinetic energy of the now non-bonded Si and O ions¹. It is found that this description of the bond breaking being responsible for the dissipation of energy and the driving force for the structural relaxation which occurs on producing the higher

¹The exact mechanism involves modelling the bond breaking process as an increase in the kinetic energy of the two ions involved in the bond by adding momenta to these two ions involved such that the increase in energy of the two atoms is equal to the energy of the UV photons of interest, and makes no effort to represent the excited states of the ions which are formed immediately on the bond breaking. This is justified because it is assumed that the dissociated ions will return to their ground states as they separate.

density silica glass is a good one, and as such it may be assumed that the bond breaking process is important in network liquids in general.

We might assume that the barrier crossing events start with the fission of a cation-anion bond in the network melt, resulting in increased kinetic energy of the ions associated with the bond. In the network, though, each of these excited ions is surrounded by a local environment of counter ions. For the excited ions to move throughout the extended network there must be some rearrangement of this local structure to allow the diffusion of the excited ions to occur. This local neighbourhood of counter ions is often referred to as the *cage*, and this local rearrangement as the *cage decay*. The mechanism of this cage decay has been investigated by means of the *cage correlation function*: this is discussed in chapter 4, and it will be seen that the diffusivity in the network liquid, BeF_2 , can be predicted from an understanding of the cage decay.

If we interpret the bond fission as part of the barrier crossing event, then we must also observe that this is a local property. The experimentally determined viscosity is a property of the system as a whole, and hence we need to investigate how a local property such as the bond fission event relates to the dynamic behaviour of the system as a whole. For example, we might imagine that individual bond fission events will be correlated throughout space. The spatial correlation of the dynamical structural decay events is discussed in chapter 6.

1.3 Beryllium Fluoride

The principal compound of interest in this thesis is beryllium fluoride, which has been used both to investigate the role of polarisation in these network systems, and also as a means of developing the novel correlation functions which we will see are useful in developing an understanding of the processes occurring during structural relaxation.

1.3.1 Theoretical importance of BeF₂

Molecular Dynamics simulations of BeF₂ have a long history. Early work of Narten [10] using a potential due to Busing [11] described the structure of BeF₂, and this was reproduced by Woodcock [12] using a simpler, two-term potential. More recently, Angell *et al.* have also shown [3] that BeF₂ displays a range of interesting thermodynamic properties. These include a predicted *strong to fragile* transition at temperatures just above the limits of experimental measurement, which can be related to the presence of a density maximum at 2000 K and a predicted density minimum, such as that displayed by water, at 1250 K.

One of the principal ways in which BeF₂ is important is the similarity of its structure to SiO₂. SiO₂ is made up of vertex sharing tetrahedra, the stoichiometry being the same as BeF₂ and the radius ratio of the ions similar, but the forces acting in BeF₂ are much smaller, due to the reduced charges on the ions. This reduction in forces, and the smaller size of the F⁻ ion which means that polarisation effects are smaller in magnitude in BeF₂ than in SiO₂ (the polarisability of the fluoride ion versus the oxide ion is discussed in section 2.3, and the importance of including oxide ion polarisation on the properties of SiO₂ is discussed in [13, 14]), means that BeF₂ is easier to study via computer simulations. The predictions made from simulations of BeF₂ may be transferred to SiO₂. Figure 1.4 shows an example of the how experimental data on SiO₂ can be reproduced from a suitable scaling of the equivalent BeF₂ result. This figure shows the reduced intensity function, as described in section 3.2, for BeF₂ at 650 K compared to that measured experimentally for the room temperature glass [15]. The reduced intensity function for SiO₂ has been calculated simply by scaling that for BeF₂ by an appropriate length scale and by using X-ray scattering factors appropriate for SiO₂ rather than BeF₂, and we can see that there is reasonable agreement with experiment [15]².

²The SiO₂ reduced intensity function was calculated by taking the partial radial distribution functions for BeF₂, and the scattering factors for SiO₂ (see section 3.2.3), and then scaling the k -values by the ratio of the Si-Si to Be-Be distances, as given by the position of the first maximum in the M-M partial radial distribution function (see section 3.2.1 for BeF₂ and [15] for SiO₂).

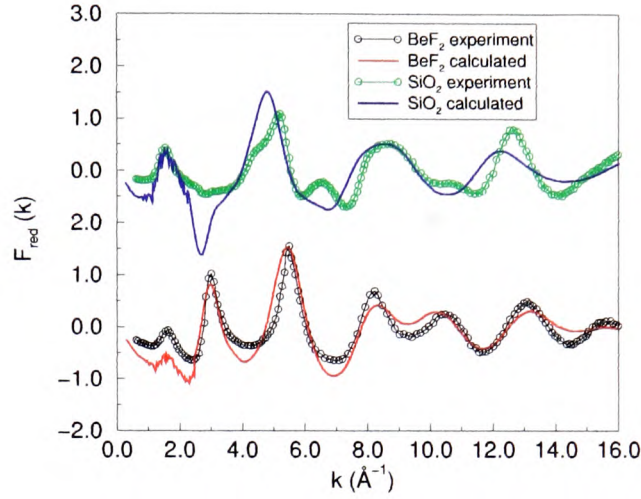


Figure 1.4: A comparison of the calculated and experimental reduced intensity functions for BeF_2 , and the experimental SiO_2 with scaled BeF_2 reduced intensity function, at 650 K.

1.3.2 Technological importance of BeF_2

BeF_2 has been studied mostly as a part of the Molten Salt Reactor Experiment in the 1960's, and more recently as its mixture with LiF , known as Flibe. These salts find use in nuclear reactors as a tritium breeding material because of a variety of suitable properties, such as:

- It suffers less radiation damage than other materials
- It has a high chemical stability
- It is easy to maintain
- It has a possible use as a coolant
- It has low electrical conductivity

1.3.3 The microscopic structure of BeF_2

As described previously, BeF_2 is made up of vertex shared BeF_4 tetrahedra. Panel (a) in figure 1.3 shows a slice through a typical configuration of BeF_2 , simulated using the Polarisable Ion Model (see section 2.3) at 700 K, giving a slab of thickness 15 au in which the tetra-coordinate nature of the Be^{2+} ions and the bi-coordinate nature of the F^- ions, and the vertex sharing of the cation coordination polyhedra, can be seen. It can also be seen that the system does not have a uniform ionic density, and can support holes, or *voids*. Bonds are drawn between ions separated by a distance smaller than the position of the first minimum in the cation-anion partial radial distribution function (see section 3.2.1), and they help to define the network connectivity.

Panel (b) in figure 1.3 shows the way these tetrahedra link together to form the extended network. We can also see, however, that not all the Be^{2+} ions are tetra-coordinate, and those ions which are under-coordinated (3-coordinate, shown by green trigonal planar species) and over-coordinated (5-coordinate, shown by purple polyhedra) are also shown. On the bond breaking event, the ions must be left in under-coordinated states, and then go on to form other species in the network. The presence of these defect sites is therefore inherent in our description of network relaxation by bond breaking, and hence the presence of longer lived defect sites may be expected to play a role in the structural relaxation. The importance of the defect sites is that they reduce the constraints (see section 4.3.2) imposed by the network structure, and increase the fluidity of the system, and the behaviour of these defect sites is discussed in section 4.4.

1.3.4 The Effect of Dipole Polarisation

The earlier simulation studies of BeF_2 were performed using Rigid Ion Models, as outlined in section 2.2, where the ions are treated as non-deformable species. However, the fluoride anion possesses a dipole polarisability, albeit small, of ~ 6 au,

and we might reasonably expect this to be important in simulating its properties, particularly in situations where the fluoride ion is asymmetrically coordinated, such that it is subject to a local electric field which will cause the polarisable anion to support a dipole. Systems similar to BeF_2 have been studied [16], and it has been found that the inclusion of the effects of dipole polarisation into the computer simulation model is vital for a proper understanding of the behaviour of materials of this kind.

The ground state crystal structure of BeF_2 is the quartz structure [17], and this is shown in figure 1.5. It can be seen that the Be-F-Be units are bent, and the inclusion of dipole polarisation is vital in describing the interactions in this system. In the absence of dipole polarisation, the bent Be-F-Be unit is destabilised, because the charge ordering will always mean that linear units are formed such that the Be^{2+} ions are as far apart as possible in order to reduce electrostatic repulsion. This triplet bond bending effect has been seen in previous studies on BeCl_2 , ZnCl_2 and SiO_2 [7, 6, 18].

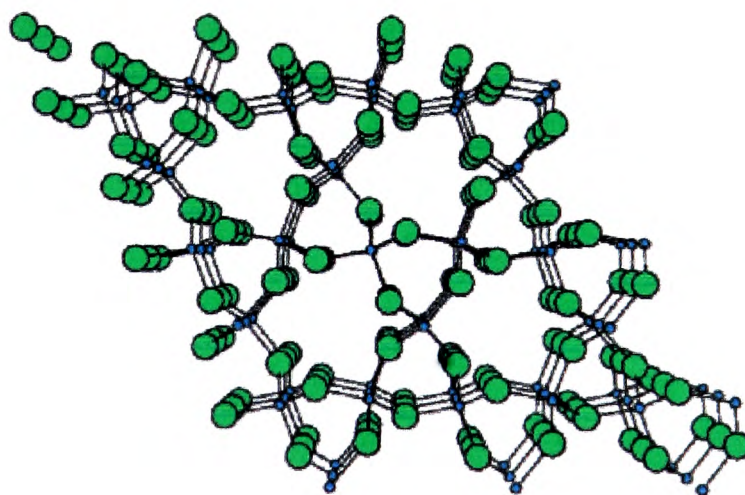


Figure 1.5: The crystal structure of the quartz isomorph of BeF_2 , shown in perspective down the c -axis. The Be^{2+} ions are shown in blue and the F^- ions in green. The bent Be-F-Be units can be clearly seen.

The main feature of the inclusion of dipole polarisation is the rationalisation of

what are classically referred to as *covalent* effects as resulting from purely *ionic* interactions between the ions due to the extended nature of the potential model. For example, the presence of bent Be–F–Be units in solid and liquid BeF₂ is explained by the introduction of F[−] electron density into the inter-Be-Be region when a dipole is formed on the F[−] ion. This introduced electron density screens the Be²⁺–Be²⁺ repulsion and allows the two Be²⁺ ions to move closer together and form a stable, bent Be–F–Be unit that would not exist if we did not include the effect of the polarisability of the F[−] ion.

Chapter 2

Computer Simulation Techniques

2.1 The use of computer simulation

Although techniques for experiments become ever more advanced, and the insight to be attained from them into the behaviour of materials grows, only in a very few cases it is possible to directly observe the motion of the atoms or ions within the material. Experimental measurements in some materials, such as BeF_2 , remain hard to acquire because the experimental conditions are difficult to achieve, such as high temperatures, or dangerous, perhaps due to toxicity. It is also difficult to attain anything other than an average picture of the system from an experiment on a macroscopic sample.

In a computer simulation, however, the positions and velocities of all the particles are precisely known at all times, and hence we can directly examine the motion of these particles, and then explore any link between the structure of the system and its dynamical properties.

In performing a simulation, we must establish a suitable model by which to describe the interactions within the system, and from which to reproduce the experimentally observed properties of the system. This *interaction model* will be controlled by various parameters, and we can vary these parameters independently and examine how characteristic elements of the interaction model relate to the properties of interest within the system.

A greater understanding of the properties of a material, gained from simulation,

can help to explain experimentally observed phenomena, and also provide predictions for improving the characteristics of a material, for example by changes in the composition of or preparation procedures for that material.

2.2 The Interaction Model

The simplest ionic model consists of a potential describing the interaction between ions i and j in the Born-Mayer form as described by

$$U_{ij}(r_{ij}) = \frac{Q_i Q_j}{r_{ij}} + B_{ij} e^{-\alpha_{ij} r_{ij}} - \sum_{n=6,8} \frac{C_{ij}^n}{r_{ij}^n} f_{ij}^n(r_{ij}) \quad (2.1)$$

This treats the ions as spherical, closed-shell species which carry formal valence charges. The $\frac{Q_i Q_j}{r_{ij}}$ term describes the Coulombic interaction between these charged species, and the $B_{ij} e^{-\alpha_{ij} r_{ij}}$ term describes the short-range repulsion between the species and reflects the fact that ions of opposite charges do not coalesce due to the Pauli exclusion principle, which prevents the overlap of their electron density at small separations. B_{ij} controls the magnitude of the repulsion at a given separation, r_{ij} , and α_{ij} describes how the repulsion decays with that separation. These are parameters which may be chosen to control the behaviour of the interaction model. α_{ij} is known as the *hardness parameter*, due to the fact that the short-range repulsion between *hard* ions, such as Be^{2+} and F^- , is much greater than that between *soft* ions, such as Pb^{2+} and I^- , which have a much more appreciable degree of electron-cloud overlap.

The C_{ij}^n terms are attractive, and model the dispersion interactions between ions, the C_{ij}^6 term referring to the dipole-dipole dispersion interaction and the C_{ij}^8 term to the dipole-quadrupole dispersion interaction. These dispersion coefficients are given by the Slater-Kirkwood formula [19], for the C_{ij}^6 coefficients,

$$C_{ij}^6 = \frac{\frac{3}{2} \alpha_i \alpha_j}{\left(\frac{\alpha_i}{P_i}\right)^{\frac{1}{2}} + \left(\frac{\alpha_j}{P_j}\right)^{\frac{1}{2}}}, \quad (2.2)$$

where α_i is the in-crystal polarisability of ion i , and P_i is its electron number, and by the Starkschall-Gordon formula [20], for the C_{ij}^8 coefficients,

$$C_8^{ij} = \frac{\frac{3}{2}C_6^{ij} \langle r_{ij}^4 \rangle}{\langle r_{ij}^2 \rangle}. \quad (2.3)$$

In the work on BeF₂ presented in this thesis, the C_{ij}^n coefficients have been set equal to zero, leading to a simpler expression for the potential. Omitting the dispersion effects in this way has been shown to have little effect on the micro-structure [21], although the pressure of the system may be affected, as discussed in section 9.5.

The $f_{ij}^n(r_{ij})$ are functions which damp the dispersion interactions, and are given by the Tang-Toennies formula [22],

$$f_{ij}^n(r_{ij}) = 1 - e^{-br_{ij}} \sum_{k=0}^n \frac{(br_{ij})^k}{k!} \quad : \quad n \text{ even}. \quad (2.4)$$

The parameter b controls the magnitude of the damping function at a given ionic separation, and so is an effective *range parameter* for this damping function. In the simulation model, different values of b may be chosen for the damping of the different C_{ij}^n terms.

In the simplest systems, this model contains all the interactions terms required to fully describe the behaviour of the system. In real systems, however, the ions may deform due to the effect of their surroundings (see section 2.2.1), and of major importance in improving the *transferability* of these types of potentials is the inclusion of the effects of *polarisation* (see section 2.3).

2.2.1 The nature of ions in the condensed phase

It is a rather crude approximation to envisage an ion as a spherical entity, unaffected by changes in its environment. The O²⁻ ion, for example, does not exist in the gas phase, as the second electron affinity of O is unfavourable (*i.e.* $O^{2-} \rightarrow O^- + e^-$ is spontaneous), yet it exists commonly in the condensed phase. The Madelung potential of the surrounding ions in the condensed phase serves to stabilise the addition of the second electron to the O⁻ ion.

The electrostatic potential, $V(\mathbf{r}_{i\alpha})$, experienced by an electron, α , on a given ion, i , due to the electrostatic interactions with the charges on other ions in a crystal is given by

$$V(\mathbf{r}_{i\alpha}) = - \sum_j \frac{Q_j}{|\mathbf{r}_{i\alpha} - \mathbf{r}_j|}, \quad (2.5)$$

where Q_j is the charge on ion j , and $\mathbf{r}_j$ is the position vector of ion j relative to the given ion. This potential can be decomposed into a spherical contribution, $V_0(r)$, and an angular dependent contribution which varies with the position of the electron on the given ion, $\mathbf{r}_{i\alpha}$. The ground electronic state of a closed shell ion, such as F^- and Be^{2+} , however, has S symmetry in a cubic crystal, and the angular contribution to this electrostatic potential is only significant if G symmetry states (those with angular momentum $l = 4$) are mixed in, as there can be no contributions from angular momenta with lower l . These states, though, are generally very much higher in energy, and so are unable to mix significantly with the ground state, and hence the electrostatic potential for closed shell ions can be considered to be spherical.

Let us consider the effect of the electrostatic potential on an electron on a central anion. The spherical distribution of cations as nearest neighbours has the effect of introducing enhanced positive charge acting at the anion's nucleus (according to Gauss's theorem), and this results in the electron experiencing increased attraction towards the central anion's nucleus. Therefore, the spherical potential acts to *compress* the electron density on the central anion, and so is a confining potential. The neighbouring ions are not merely point charges, however, and themselves have electrons which may be close to the central anion, and as the Pauli exclusion principle requires that the electrons may not occupy the same space, this causes the central anion to be compressed further. These effects are illustrated in figure 2.1.

A similar argument may be applied to the effect of the confining potential on a central cation, but because of the sign reversal of the charge on the nearest neighbours the Madelung potential now becomes a destabilising influence, as the electron now experiences increased repulsion at the central cation's nucleus. The Pauli exclusion

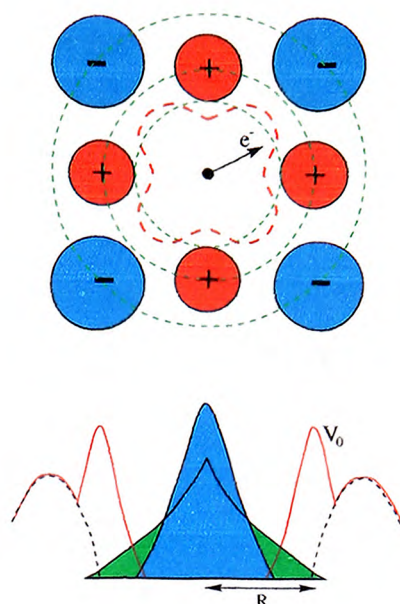


Figure 2.1: The origin of the spherically confining potential, V_0 , in a cubic crystal. The lower diagram shows a cross section through the spherical potential, with the Madelung contribution represented by the red line; the exclusion due to electrons on other ions is represented by the dashed line. The uncompressed electron density is shown in green, with the electron density resulting from the additional effects of the compression is shown in blue.

principle, however, still has the same effect, and the two factors oppose each other. These effects are outlined in table 2.1. This cancellation of effects on the central cation means that compression effects are much less important for cations than for anions. In addition, because electron distributions are much less diffuse in cations in the gas phase, they are much less likely to be affected by environmental considerations.

Central Ion	Madelung potential	Pauli exclusion principle
anion	towards	towards
cation	away	towards

Table 2.1: This table shows the direction of motion of the electron on a central ion relative to the nucleus of that ion due to the different contributions to the confining potential. The Pauli exclusion principle results in a short range repulsion between the electron density on the central ion and that on surrounding ions, which always serves to contract the central ion, but the effect of the Madelung potential depends upon the charge on the central ion.

Unlike O^{2-} , F^- is stable in the gas phase, but it must still be expected that the effects of both the confining potential and the Pauli exclusion principle will have an influence. In fact, the polarisability of a fluoride ion drops by around 60% on entering the condensed phase [23, 24], indicating that the ion is affected by its environment, although not as significantly as the oxide ion, for which the gas phase polarisability is infinite (corresponding to the loss of an electron to form O^- , *i.e.* ionisation). This means that a simulation potential parameterised in the condensed phase would not transfer accurately to the gas phase, without considering the effects of ion compression. However, simulation studies of CaF_2 [25] have shown that compression effects have very little effect on the ionic size of F^- in the condensed phase, and thus their inclusion would not merit the increase in computational time in the simulation, quite apart from the need to obtain extra parameters to quantify the phenomenon. In the fluoride ion studies presented in this thesis a potential is used which takes no account of the varying size of the fluoride ion as its environment changes, and the compressional effects change accordingly, *i.e.* the fluoride ion is modelled as if it has a single, constant, size and polarisability.

2.3 The Polarisable Ion Model

The Born-Mayer model outlined above treats the ions as spherical units which cannot change shape to adapt to changes in their surroundings as they move, and as such is often referred to as the **Rigid Ion Model (RIM)**. There is no way that this model can allow for the fact that an ion may have a non-spherical electron distribution caused by polarisation due to the local electric field created by neighbouring ions, and in the absence of the dispersion terms, which have been omitted in the simulations of BeF_2 , *polarisation effects* may not be treated at all.

The **Polarisable Ion Model (PIM)** [26], is an extension of the RIM in which the ions are treated as deformable, polarisable species which can adapt to the local electric field they experience. If an ion i of polarisability α_i is placed in an electric

field, $\mathbf{E}_i$, the dipole moment induced upon the ion, $\boldsymbol{\mu}_i$, is

$$\boldsymbol{\mu}_i = \alpha_i \mathbf{E}_i. \quad (2.6)$$

The ions are allowed to possess dipoles which interact with both the ionic charges and with other dipoles, which determine the local electric field. When the separations between a given ion, i , and the other interacting ions and dipoles are large, the dipole induced on that ion is due only to Coulombic interactions. This *asymptotic dipole moment*, so called because it corresponds to the dipole moment when the inter-ionic separation is large and thus the electron-cloud overlap is negligible, is given by

$$\boldsymbol{\mu}_i^{\text{asymptotic}} = \alpha_i \left(\sum_{j \neq i} \frac{Q_j \mathbf{r}_{ij}}{r_{ij}^3} - \sum_{j \neq i} \left[\frac{\boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)}{r_{ij}^5} \right] \right) \quad (2.7)$$

This expression is valid when the ionic separations are large, but in condensed phases these induced dipoles are moderated by short-range interactions due to the overlap of the electron-clouds of the given ion with those associated with adjacent ions. The effect of these short-range interactions is to deform the confining potential.

Consider the arrangement of an anion surrounded by cations and next shell anions in a crystal as shown in figure 2.2. In this arrangement, the right-hand cation has been displaced away from the central anion, compared to the perfect crystal, and now the charge density around the central anion is asymmetric, and a dipole is induced on the central anion which has a negative end pointing towards the cation opposite to that which has been displaced. This is the asymptotic dipole, as it depends only on the relative displacement of the central anion and displaced cation.

However, the effect of the cation moving away is to also generate a reduction in the electron density on that side of the central anion, which allows the anion electron density to distort to take advantage of the reduced electron-electron repulsion, and therefore relax to reduce the compression effect acting on the central anion due to the spherical confining potential (see section 2.2.1). These short-range effects have been demonstrated in electronic structure calculations [23, 24, 27], and also by empirical comparison of PIM simulations with experiment.

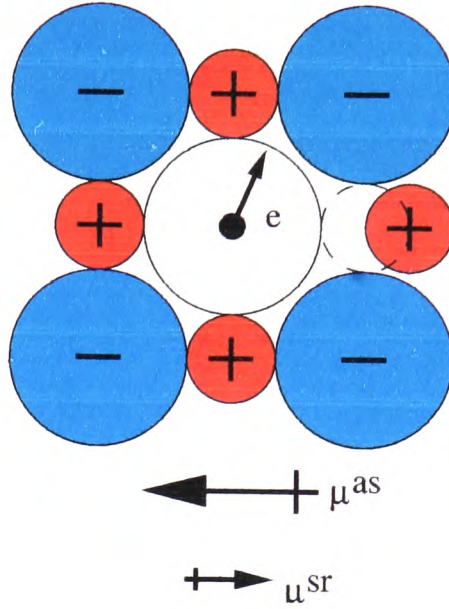


Figure 2.2: The origin of the *asymptotic* and *short-range* dipole moments on the central ion. The arrow representing the dipole points in the $\delta^+ \rightarrow \delta^-$ direction.

This flow of electron density generates another dipole, the *short-range* dipole, and for an anion it always points in the *opposite* direction to the asymptotic dipole, as shown in figure 2.2. For a cation the two dipoles are aligned and reinforce each other, as discussed in section 2.2.1, and the short-range dipole acts to *enhance* the asymptotic dipole.

The short-range dipole is given by

$$\mu_i^{\text{s-r}} = \alpha_i \sum_{j \neq i} f_{ij}(r_{ij}) \frac{Q_j \mathbf{r}_{ij}}{r_{ij}^3}, \quad (2.8)$$

where $f_{ij}(r_{ij})$ is the *short-range damping function*. It has been shown by electronic structure calculations that the best form of this damping function is a modified Tang-Toennies function [22],

$$f_{ij}(r_{ij}) = -ce^{-br_{ij}} \sum_{k=0}^4 \frac{(br_{ij})^k}{k!}. \quad (2.9)$$

This function tends to $-c$ as $r_{ij} \rightarrow 0$, and to 0 as r_{ij} becomes large. In anions, this leads to almost complete cancellation of the asymptotic dipole by the short-range

dipole at small separations (c is chosen to be 1 in our simulations), whilst at large separations the short-range damping function vanishes and the overall dipole on the central ion is simply the asymptotic dipole. In cations, as $c > 1$, the short-range dipole will increase the asymptotic dipole, as can be seen in equation 2.12.

The variable b , in the expression for the modified Tang-Toennies damping function (equation 2.9), controls the magnitude of the damping function, and is known as the *short-range induction damping parameter*. It depends upon the the sum of the ionic radii [28] according to the relation

$$b = \frac{\kappa}{\sigma_i + \sigma_j}, \quad (2.10)$$

where κ is a constant for a given class of compounds.

The total dipole moment, $\boldsymbol{\mu}_i$, is therefore given by the sum of the asymptotic and short range contributions [23, 24],

$$\boldsymbol{\mu}_i = \boldsymbol{\mu}_i^{\text{asymptotic}} + \boldsymbol{\mu}_i^{\text{s-r}}, \quad (2.11)$$

and hence

$$\boldsymbol{\mu}_i = \alpha_i \left(\sum_{j \neq i} (1 - f_{ij}(r_{ij})) \frac{Q_j \mathbf{r}_{ij}}{r_{ij}^3} - \sum_{j \neq i} \left[\frac{\boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)}{r_{ij}^5} \right] \right). \quad (2.12)$$

Comparing equations 2.6 and 2.12 it can be seen that the local field acting on an ion i , $\mathbf{E}_i$, where

$$\mathbf{E}_i = \sum_{j \neq i} (1 - f_{ij}(r_{ij})) \frac{Q_j \mathbf{r}_{ij}}{r_{ij}^3} - \sum_{j \neq i} \left[\frac{\boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)}{r_{ij}^5} \right], \quad (2.13)$$

depends upon the charges and dipoles on all the other ions. Hence, the dipole moment is *many body* in nature, and is not simply pairwise additive, unlike the charge-charge and short-range interactions in the RIM, which depend solely upon the separations between pairs of ions. Calculating the dipole on a given ion, $\boldsymbol{\mu}_i$, therefore depends upon a knowledge of the dipoles upon the other ions, $\boldsymbol{\mu}_j$, and so a *self-consistent* set of dipoles must be calculated.

2.3.1 The Car-Parrinello Scheme in the PIM

The inclusion of dipoles in the interaction potential leads to a substantial increase in computer time as we need to follow an iterative procedure to generate a set of self-consistent dipoles. This iterative procedure is known as **pseudo-conjugent gradient annealing**. In this procedure, the dipole orientations are allowed to change, thus generating an effective *velocity* on the dipole along a potential energy surface, and an associated kinetic energy. When this kinetic energy reaches a maximum, *i.e.* the dipole velocities are at a maximum and the dipoles are at a local *minimum* of potential energy, the dipole velocities in the current direction of motion along the surface are quenched. Then the dipoles are allowed to re-orientate along the dipole potential energy surface in the direction of the unquenched velocity until a new maximum of kinetic energy is reached, and so on until the dipole velocities are zero in all directions along the potential energy surface. This corresponds to the minimum potential energy of the dipoles, and hence the forces acting on the dipoles are zero, and a set of self-consistent dipoles has been generated.

Once this set of self-consistent dipoles is generated, the ions may be moved according to the forces acting on them, but now the dipoles on the ions in the new configuration will no longer be self-consistent, and so the annealing procedure required to generate a set of self-consistent dipoles will need to be repeated. Performing this iterative procedure every time step would be prohibitively computationally expensive, and so a method has been devised, according to the scheme of Car and Parrinello [29], to eliminate the need to perform this iterative procedure at every time step.

The dipoles are treated as extra degrees of freedom and are integrated according to equations of motion separate from, but parallel to, the equations of motion governing the motion of the ions, in an *extended Lagrangian* formalism.

The potential energy, $\mathcal{U}$, of a set of ions with dipole moments, μ_i , is given by

$$\mathcal{U} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[U'_{ij}(r_{ij}) + T_{ij} Q_i Q_j + T_{ij}^{\alpha} (Q_j \mu_i^{\alpha} - Q_i \mu_j^{\alpha}) - T_{ij}^{\alpha\beta} \mu_i^{\alpha} \mu_j^{\beta} \right] + k^{\mu} \sum_{i=1}^N \mu_i^2, \quad (2.14)$$

where a simple pair potential, $U'_{ij}(r_{ij})$, has been assumed to account for the short range repulsive and dispersion interactions, *i.e.* by comparison with equation 2.1,

$$U'_{ij}(r_{ij}) = B_{ij}e^{-\alpha_{ij}r_{ij}} - \sum_{n=6,8} \frac{C_{ij}^n}{r_{ij}^n} f_{ij}^n(r_{ij}). \quad (2.15)$$

The interaction tensors, T_{ij} , are given by

$$T_{ij}^{\alpha\beta\gamma\delta} = \nabla_\alpha \nabla_\beta \nabla_\gamma \nabla_\delta \dots \frac{1}{r_{ij}}. \quad (2.16)$$

Q_i is the charge on ion i and μ_i^α ($\alpha \in x, y, z$) is the α^{th} Cartesian component of the dipole on ion i . The $k^\mu \sum_{i=1}^N \mu_i^2$ term is the *self energy* term representing the energy necessary to induce a dipole on an ion.

If the energy $\mathcal{U}$ is minimised with respect to each dipole, μ_i^α , then we reach the condition

$$2k^\mu \mu_i^\alpha = E_i^\alpha, \quad (2.17)$$

where E_i^α is the α^{th} component of the electric field at ion i ,

$$E_i^\alpha = \sum_{j \neq i}^N -T_{ij}^\alpha Q_j + T_{ij}^{\alpha\beta} \mu_j^\beta. \quad (2.18)$$

By choosing the parameter $k^\mu = \frac{1}{2\alpha'}$, where α' is the ionic polarisability, the induced dipole acquires the physical value,

$$\mu_i^\alpha = \alpha' E_i^\alpha. \quad (2.19)$$

Substituting this value for the dipole back into the expression for $\mathcal{U}$ gives the contribution of the induction of dipoles onto the ions, U^{ind} , to the total energy,

$$U^{\text{ind}} = -\frac{1}{2} \sum_i \alpha' E_i^2. \quad (2.20)$$

We notice that it costs energy to induce the dipoles on the ions, *i.e.* the *self-energy* which is $\frac{1}{2} \sum_i \alpha' E_i^2$, as there is a rearrangement of the electrons in the ions, but this energy is recovered by the interaction of the dipoles with their local electric fields, which is $-\sum_i \mu_i E_i = -\sum_i \alpha' E_i^2$ with μ_i as given by equation 2.19.

The kinetic energy, $\mathcal{T}$, is similarly composed of separate contributions due to the ionic and the dipolar motions

$$\mathcal{T} = \frac{1}{2} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i^2 + \frac{1}{2} \sum_{i=1}^N m_i^\mu \dot{\boldsymbol{\mu}}_i^2, \quad (2.21)$$

where m_i^μ is the *fake mass* of ion i , and governs the magnitude the inertia of the dipolar degrees of freedom. This does not correspond to a *physical* mass, but is a necessity of this extended Lagrangian formalism.

The equation of motion for the ions in Lagrangian form is given by

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0, \quad (2.22)$$

which reduces to Newton's second law

$$m_i \ddot{\mathbf{r}}_i = - \frac{\partial U}{\partial \mathbf{r}_i}. \quad (2.23)$$

and the equation of motion for the dipoles is similarly

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{\mu}}_i^\alpha} \right) - \frac{\partial \mathcal{L}}{\partial \boldsymbol{\mu}_i^\alpha} = 0, \quad (2.24)$$

which reduces to

$$m_i^\mu \ddot{\boldsymbol{\mu}}_i^\alpha = \sum_{j \neq i}^N -T_{ij}^\alpha Q_j + T_{ij}^{\alpha\beta} \mu_j^\beta - 2k^\mu \mu_i^\alpha. \quad (2.25)$$

When the dipole acceleration, $\ddot{\boldsymbol{\mu}}_i$, is zero, equation 2.25 reduces to the conditions, equations 2.17 and 2.19, for obtaining the dipoles that minimise $\mathcal{U}$. Thus if the dipole acceleration remains small then the dipoles will remain approximately self-consistent. The dipoles are not necessarily exactly self-consistent, but oscillate around their self-consistent, or *adiabatic*, values. The degree of oscillation is controlled by the choice of the dipolar fake mass, and maintaining a suitably low dipolar kinetic energy, such that the motion of the dipoles around their adiabatic values makes little contribution to the energy of the system. The maintenance of the dipolar motion at a low temperature can be ensured by the use of a thermostat, as described in section 2.4.3.

2.4 The Basics of Molecular Dynamics

A **Molecular Dynamics (MD)** simulation involves calculating the forces on each ion due to the presence of the other ions, by differentiating the expression for the potential energy between the ions as described by the interaction model, as given by equations 2.1 and 2.14, and then moving the ions by integrating Newton's laws of motion to calculate the new positions and velocities of the ions as time evolves. These positions and velocities are re-calculated every *time step*, a period of time whose length depends upon the properties of the system being investigated, but which is generally of the order of 10^{-15} seconds.

In performing an efficient MD simulation, there are various techniques which allow accurate calculations to be performed on long time scales and large system sizes, in an acceptable amount of computer time. These are outlined in the following sections.

2.4.1 The simulation cell

The simulations presented in this thesis contain between 500 and 1000 ions. These ions are placed inside a *simulation cell*. However, in a cubic simulation cell of length x , approximately 50% of the particles are contained in the space within $0.1x$ of the walls of the cell. This means that the properties investigated will be dominated by *surface effects*, and to avoid this, and to enable us to study the *bulk* properties of the system, the simulation cell is replicated and repeated infinitely throughout space in all directions.

During the course of the simulation, it is likely that at least some of the ions will move out of the simulation cell. The application of **periodic boundary conditions** [30], ensures that the composition of the simulation cell is conserved. The simulation cell is surrounded on all faces by images of itself, and when a particle leaves the cell through one face, the image of this particle from the equivalent cell on the *opposite* face enters the cell, as shown in figure 2.3.

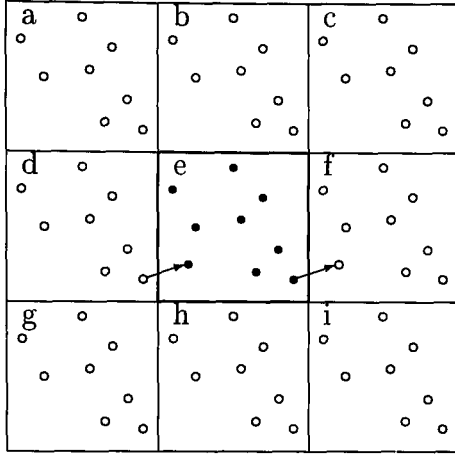


Figure 2.3: The application of Periodic Boundary Conditions. When an ion leaves the simulation cell, for example the ion at the bottom right of cell e moving from cell e to the image cell f , it is replaced by the equivalent ion from the image cell, which for this ion is cell d , which moves in through the opposite face.

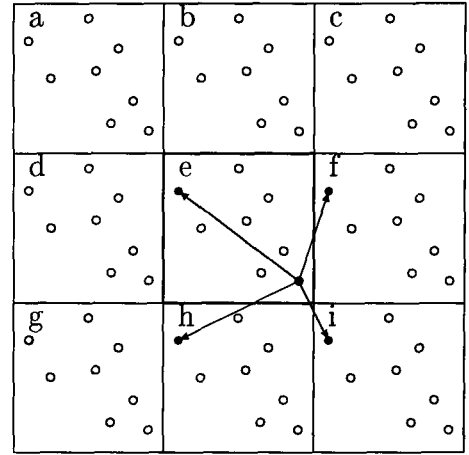


Figure 2.4: The calculation of the identity of *Nearest Neighbours*. The ion j at the bottom right hand corner of cell e is closer to the image of ion k (at the top left hand corner of cell e), in cell i , than to ion k itself.

Replicating the simulation cell throughout space in this way means that each ion has many images of itself. When calculating short-range interaction terms, such as the short-range repulsion term in the RIM, $B_{ij}e^{-\alpha_{ij}r_{ij}}$ (see section 2.2), only one interaction needs to be considered for each pair of ions as the lengths of the simulation cell are generally much larger than the length scale over which the short-range repulsion has an appreciable magnitude. For two ions, j and k , it is possible that j will be nearer to one of the images of k than to k itself, and in this case the short range interaction for the jk pair should be calculated between j and the nearest image of k . In this situation, the short range effect should only be calculated between an ion and its *nearest neighbour* ions or their images, and this is achieved by applying the **minimum image convention** as shown in figure 2.4. Here the short range repulsion should be calculated between the ion at the bottom right hand corner of cell e , ion j , and the image of the ion from the same cell which is found in the top left hand corner of cell i , ion k .

However, the Coulombic term, $\frac{Q_i Q_j}{r_{ij}}$ (see section 2.2) acts over a much larger range

of ionic separations, and this means, for example, that an ion, i , will interact with ion j and all of its images because the magnitude of the interaction does not decrease to zero over the length scale of the simulation cell. The summation of long range interactions is treated in reciprocal space, by a method known as the **Ewald Summation** [31], which is outlined in appendix B.

2.4.2 Conserved Hamiltonian equations of motion in Molecular Dynamics: the use of thermostats

The MD procedure outlined above is based upon the solution of Newton's equations of motion. For a system of N particles moving under the influence of the potential described by the interaction model, whose positions and velocities are denoted $\mathbf{r}_1, \dots, \mathbf{r}_N$ and $\mathbf{v}_1, \dots, \mathbf{v}_N$, and whose masses are denoted $m_1, \dots, m_N$, the motion of the particles will be determined by the Hamiltonian, given by (in the absence of any external field),

$$H(\mathbf{p}, \mathbf{r}) \equiv H(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (2.26)$$

where $\mathbf{p}_1, \dots, \mathbf{p}_N$ are the particle momenta ($\mathbf{p}_i = m_i \mathbf{v}_i$) and $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the inter-particle potential (see equation 2.1). The forces on the particles are given in terms of the inter-particle potential by

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i}. \quad (2.27)$$

We can recover Newton's equations of motion in terms of the system Hamiltonian according to

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i} \quad (2.28)$$

and

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = -\frac{\partial U}{\partial \mathbf{r}_i} = \mathbf{F}_i(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (2.29)$$

An important property of these equations of motion is that they conserve the Hamiltonian, *i.e.* $\frac{dH}{dt} = 0$, and hence the energy of the system, E , is a constant. An MD simulation of this kind, with constant energy, and with the number of particles,

N , and the volume, V , assumed to be fixed, will therefore generate a trajectory of a series of configurations each with fixed N , V , and E , which corresponds to the micro-canonical ensemble.

However, in general we perform simulations at constant temperature, corresponding to the canonical ensemble, or at constant temperature and pressure, corresponding to the isothermal-isobaric ensemble. We do this because experiments are usually performed at constant temperature, or at constant temperature and pressure, rather than at constant energy. Simulations of this nature therefore involve an energy, and hence a Hamiltonian, which is not conserved, and so these simulations depend upon unconserved Hamiltonian equations of motion. To recover the constant energy situation, we can include an energy reservoir with which the system can exchange energy. This is achieved by implementing a thermostating procedure, the so-called Nosé-Hoover chain (NHC) dynamics method, as proposed by Nosé [32] and Hoover [33] and extended by Martyna [34]. This involves incorporating additional degrees of freedom into the equations of motion. These extra degrees of freedom represent the heat reservoir, which adds energy to or subtracts energy from the system as required.

In the NHC method, the Newtonian equations of motion are replaced by Nosé-Hoover equations, which extend the ordinary particle degrees of freedom, the positions, $\mathbf{r}_1, \dots, \mathbf{r}_N$, and velocities, $\mathbf{v}_1, \dots, \mathbf{v}_N$, to include a set of M thermostat variables, $\zeta_1, \dots, \zeta_M$, with conjugate momenta, $p_{\zeta_1}, \dots, p_{\zeta_M}$. The equations of motion become

$$\begin{aligned}
\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\
\dot{\mathbf{p}}_i &= \mathbf{F}_i - \frac{p_{\zeta_1}}{Q_1} \mathbf{p}_i \\
\dot{\zeta}_k &= \frac{p_{\zeta_k}}{Q_k} \quad : \quad k = 1, \dots, M \\
\dot{p}_{\zeta_k} &= G_k - \frac{p_{\zeta_{k+1}}}{Q_{k+1}} p_{\zeta_k} \quad : \quad k = 1, \dots, M-1 \\
\dot{p}_{\zeta_M} &= G_M,
\end{aligned} \tag{2.30}$$

where the thermostat forces, G_k , are

$$\begin{aligned} G_1 &= \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - g k_B T \\ G_k &= \frac{p_{\zeta_{k-1}}^2}{Q_{k-1}} - k_B T \quad : \quad k = 2, \dots, M, \end{aligned} \quad (2.31)$$

where g is the number of ionic degrees of freedom, and the parameters, Q_k , given by $Q_1 = g k_B T \tau^2$ and $Q_k = k_B T \tau^2$ are effective *masses* which relate the magnitude of the thermostat force to its acceleration, and which determine the time scale over which the thermostat force acts through the single parameter, τ .

The Nosé-Hoover equations of motion are applied using the Velocity-Verlet finite difference algorithm [30], and so the ionic coordinates, where $\mathbf{r}_i$, $\mathbf{v}_i$ and $\mathbf{a}_i$ are the position, velocity and acceleration of ion i respectively, are updated according to

$$\begin{aligned} \mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \mathbf{a}_i(t) \frac{\Delta t^2}{2}, \\ &= \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \left[\frac{\mathbf{F}_i(t)}{m_i} - \mathbf{v}_i(t) v_{\zeta_1}(t) \right] \frac{\Delta t^2}{2}, \end{aligned} \quad (2.32)$$

where $v_{\eta_1}(t) = \dot{\zeta}_1(t)$, and

$$\begin{aligned} \mathbf{v}_i(t + \Delta t) &= \mathbf{v}_i(t) + [\mathbf{a}_i(t) + \mathbf{a}_i(t + \Delta t)] \frac{\Delta t}{2} \\ &= \mathbf{v}_i(t) + \left[\left\{ \frac{\mathbf{F}_i(t)}{m_i} - v_{\zeta_1}(t) \mathbf{v}_i(t) \right\} \right. \\ &\quad \left. + \left\{ \frac{\mathbf{F}_i(t + \Delta t)}{m_i} - v_{\zeta_1}(t + \Delta t) \mathbf{v}_i(t + \Delta t) \right\} \right] \frac{\Delta t}{2}. \end{aligned} \quad (2.33)$$

We can see from equations 2.32 and 2.33 that $\mathbf{v}_i(t + \Delta t)$ must be iterated self consistently.

The thermostat variables are integrated according to

$$v_{\zeta_k}(t + \Delta t) = v_{\zeta_k}(t) + \left[\ddot{\zeta}_k(t) + \ddot{\zeta}_k(t + \Delta t) \right] \frac{\Delta t}{2}, \quad (2.34)$$

where $v_{\zeta_k}(t) = \dot{\zeta}_k(t)$, which, using equations 2.30, gives

$$\begin{aligned} \ddot{\zeta}_k(t) &= \frac{G_k(t)}{Q_k} - \dot{\zeta}_k(t) \dot{\zeta}_{k+1}(t) \quad : \quad k = 1, M - 1 \\ \ddot{\zeta}_k(t) &= \frac{G_M(t)}{Q_M} \quad : \quad k = M, \end{aligned} \quad (2.35)$$

which, using the expression for the thermostat forces, G_k , equations 2.31, gives

$$\begin{aligned}\ddot{\zeta}_1(t) &= \frac{\sum_{i=1}^N \frac{\mathbf{p}_i^2(t)}{m_i} - gk_B T}{Q_1} - v_{\zeta_1}(t)v_{\zeta_2}(t) \quad : \quad k = 1 \\ \ddot{\zeta}_k(t) &= \frac{Q_{k-1}v_{\zeta_{k-1}}^2(t) - k_B T}{Q_k} - v_{\zeta_k}(t)v_{\zeta_{k+1}}(t) \quad : \quad k = 2, M-1 \\ \ddot{\zeta}_M(t) &= \frac{Q_{M-1}v_{\zeta_{M-1}}^2(t) - k_B T}{Q_M} \quad : \quad k = M.\end{aligned}\tag{2.36}$$

Substitution of the thermostat coefficient accelerations, equations 2.36, into the thermostat coefficient integrator, equation 2.34, shows that the thermostat coefficients, too, need to be integrated self-consistently.

2.4.3 Thermostatting the dipoles in the PIM

In section 2.4.2, the use of thermostats as extra degrees of freedom to make the simulation one with a constant temperature rather than a constant energy was described. In the Car-Parrinello scheme, the dipolar degrees of freedom may also be thermostatted to a target temperature in addition to the ionic degrees of freedom in order to control the transfer of energy between the ionic and dipolar degrees of freedom.

Without thermostatting the kinetic energy of the ions would eventually equilibrate with the fake kinetic energy of the dipoles, leading to an equipartition of energy between the ion and dipolar systems. Since the dipoles are required to observe a much lower *fake* temperature than the *real* simulation temperature, the dipolar motion must be thermostatted separately. This is done by introducing another degree of freedom, $\xi_\mu(t)$, which is analogous to $\zeta_1(t)$ in equation 2.30, which acts as a heat bath for the dipolar system only. The effect of this thermostat is to introduce a frictional force which counteracts deviations of the dipolar kinetic energy from the target dipolar temperature, T_μ . This force can be measured in terms of the dipolar friction coefficient, $\xi_\mu(t)$.

In the ionic system we use the Nosé-Hoover Chain to thermostat the ionic motion. In the dipolar system we use the somewhat simpler Nosé-Hoover thermostat [33]

itself. This is effectively the NHC approach but with a chain length of unity. If the dipolar degrees of freedom are the dipoles, $\boldsymbol{\mu}_i, \dots, \boldsymbol{\mu}_N$, with dipole velocities, $\mathbf{v}_i^\mu, \dots, \mathbf{v}_N^\mu$, and we include an extra degree of freedom, ξ_μ , with momentum, p_{ξ_μ} to represent the dipole thermostat, the equations of motion for the dipole on a given ion, i , become, on the inclusion of the thermostating force,

$$\begin{aligned}\dot{\boldsymbol{\mu}}_i &= \frac{\mathbf{p}_i}{m_i^\mu} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \dot{\xi}_\mu \mathbf{p}_i \\ \dot{\xi}_\mu &= \frac{p_{\xi_\mu}}{Q_\mu} \\ \dot{p}_{\xi_\mu} &= G_{\xi_\mu}\end{aligned}\tag{2.37}$$

where $\mathbf{p}_i$ is the dipolar momentum, *i.e.* $\mathbf{p}_i = m_i^\mu \dot{\boldsymbol{\mu}}_i$, where m_i^μ is the dipolar *fake mass* of ion i , and where the dipolar thermostat force, G_{ξ_μ} , is given by

$$G_{\xi_\mu} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i^\mu} - g k_B T, \tag{2.38}$$

where g is now the number of dipolar degrees of freedom, and Q_μ is the effective dipole thermostat mass, given by $Q_\mu = g k_B T_\mu \tau_\mu^2$, where T_μ is the target temperature of the dipolar system, and τ_μ is the dipole thermostat relaxation time, and controls the magnitude of the dipole thermostat force and the time scale over which it acts. The integrator equations for the dipoles and dipolar velocities are therefore analogous to those for the ionic positions and dipoles, equations 2.32 and 2.33, with ζ_1 being now replaced by ξ_μ , and the integrator equation for the dipole thermostat coefficient is

$$v_{\xi_{mu}}(t + \Delta t) = v_{\xi_{mu}}(t) + \frac{1}{Q_\mu} [G_{\xi_\mu}(t) + G_{\xi_\mu}(t + \Delta t)] \frac{\Delta t}{2}, \tag{2.39}$$

where $v_{\xi_{mu}}(t) = \dot{\xi}_\mu(t)$, and $G_{\xi_\mu}(t)$ is as given by equation 2.38.

The effect of the thermostats is to cause the simulated dipoles to oscillate around their adiabatic values, as shown in figure 2.5. From the inset of this figure, which shows μ_α and $\alpha' E_\alpha$ ($\alpha \in x, y, z$) for one of the fluoride ions in a BeF₂ system simulated at 700 K using the PIM, we can see that the period of oscillation of the

simulated dipole around its adiabatic value is approximately 10 simulation time steps.

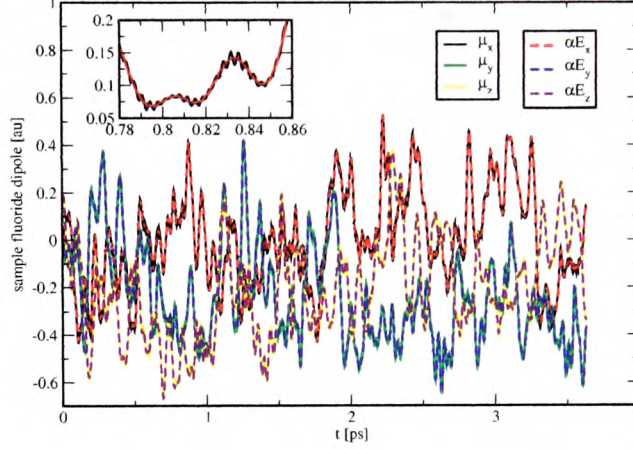


Figure 2.5: The comparison of the evolution of a ionic dipole with that predicted from the electric field acting on the anion, for a fluoride ion in BeF_2 at 700 K, simulated using the PIM. The solid lines show the Cartesian components of the dipole on a fluoride ion, μ_α where $\alpha \in x, y, z$, and the dashed lines show those predicted from the electric field acting on the ion, $\alpha'E_\alpha$, where α' is the dipole polarisability of the ion. The inset shows μ_x and $\alpha'E_x$ over a shorter time range with $\alpha'E_x$ now being the solid red line. The *time step* is 15 au, which corresponds to 0.36 fs. The dipole thermostat parameters for the fluoride ions are $T_\mu^F = 2$ au, $m_\mu^F = 100$ au and $\tau_\mu^F = 5000$ au, where these values are given in atomic units. The choice of thermostat parameters is discussed in section 2.4.4.

2.4.4 Thermostat parameters and the ionic and dipolar dynamics in the PIM

In the dipolar dynamics, the forces introduced on the dipoles which control their behaviour are governed by the choice of the dipolar fake mass, m_μ , and in the thermostating procedure by the target dipolar temperature, T_μ , which controls the magnitude of the energy in the dipolar system, and the dipole thermostat relaxation time, τ_μ , where the dipolar force $F_\mu \propto \frac{1}{\tau_\mu^2}$ (see equations 2.37 and 2.38, which give $F_\mu \propto \frac{G_{\epsilon_\mu}}{Q_\mu}$, where $Q_\mu = gk_B T_\mu \tau_\mu^2$), which helps to determine the magnitude of the

thermostatting forces which act to maintain the dipoles around their values on the adiabatic surface. Changing these parameters can affect not only the dynamics of the dipolar system, but also those of the ionic system. As our aim is to understand the effect that the inclusion of polarisation has on the ionic dynamics, it is imperative that the dynamics of the ionic system are not dominated by those of the dipolar system.

The effect of the target dipolar temperature, T_μ , and the dipolar fake mass, m_μ , on the kinetic temperatures of the ionic and dipolar systems

Panel (a) in figure 2.6 shows the time evolution of the dipolar kinetic temperature for various values of the fake mass at two target dipolar temperatures. We can see that at low target dipolar temperature ($T_\mu = 1$ K) low fake masses result in smaller deviations of the actual dipolar temperature from its target temperature. At higher target temperatures ($T_\mu = 9$ K), this result is reversed.

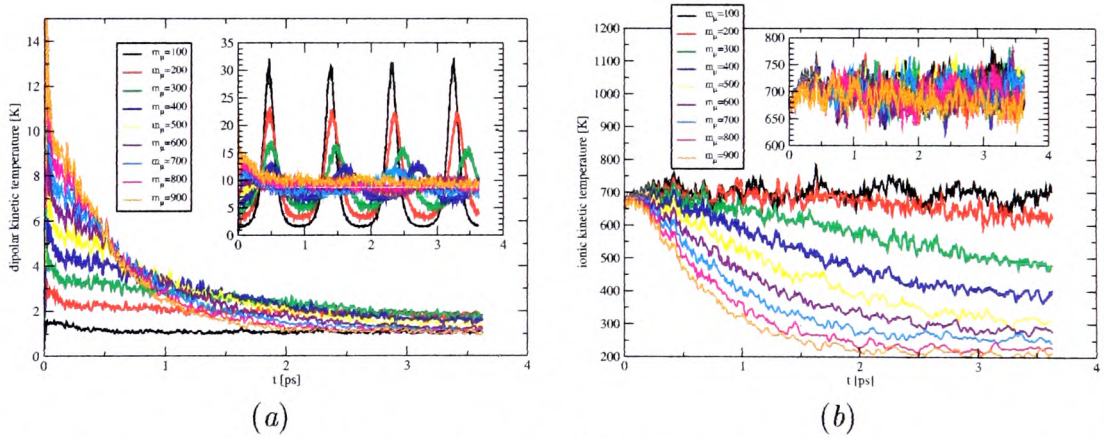


Figure 2.6: Panel (a) shows the variation of *dipolar* kinetic temperature, and panel (b) shows the variation of the *ionic* kinetic temperature with dipolar fake mass, m_μ as given in the legend, for a target dipolar thermostat temperature T_μ , of 1 K (and of 9 K in the inset), for a BeF₂ PIM simulation at 700 K, of 10000 time steps ($\Delta t = 15$ au), with a dipole thermostat relaxation time, τ_μ , of 5000 au.

At low fake mass, the *natural* energy of the dipolar system is much lower than the target temperature, and the thermostat works to *drive* the dipolar system to a higher energy, resulting in the periodic variation of the dipolar temperature. This periodic

motion can be understood by noting that at low fake mass, the inertia of the dipoles is small, and they are able to respond quickly to the forces, both due to the electric field and due to the thermostats, acting on them. When the fake mass is small, the accelerations are large¹ and the dipoles tend to overshoot the values required under adiabatic conditions, and then the thermostat tries to correct this overshoot; as the inertia is small, the dipoles again respond quickly, and now overshoot in the opposite direction, and the continuous overcorrection of the deviation of the dipoles from their adiabatic values leads to the periodic behaviour. At higher fake mass, the dipolar accelerations are smaller, and this continual overshooting is much reduced. In panel (b) in figure 2.6 we can also see the effect that changing the fake mass of the dipolar system has on the temperature of the ionic system, which has a target temperature of 700K. At low dipolar temperature, energy is withdrawn from the ionic system through the dipolar thermostat, and this effect increases with fake mass, such that conservation of ionic temperature is only possible for $m_\mu = 100, 200$ au at $T_\mu = 1$ K. At the higher dipolar target temperature ($T_\mu = 9$ K) the temperature conservation in the ionic system is much improved, and it oscillates around the target temperature for all choices of fake mass.

Panel (a) in figure 2.7 shows the time evolution of the dipolar temperature for a series of target dipolar temperatures, for fake masses of $m_\mu = 100$ au and, in the inset, $m_\mu = 900$ au. At low mass, we can see that increasing the target dipolar temperature leads to a change over from the dipolar temperature oscillating around the target temperature (for $T_\mu = 1, 2$ K), where the *natural* temperature of the dipolar system is similar to the target temperature, to a periodic regime (for $T_\mu > 2$ K), where the thermostat is trying to drive the dipolar degrees of freedom to a higher energy than that which corresponds to their ordinary motion on the dipolar potential energy surface. At high fake mass ($m_\mu = 900$ au) the inertia of the dipoles is larger, and hence they respond more slowly to the thermostating forces and the periodic variation of the dipolar temperature disappears.

¹“ $\mathbf{F} = m\mathbf{a}$ ”, so decreasing the mass leads to an increase in the acceleration.

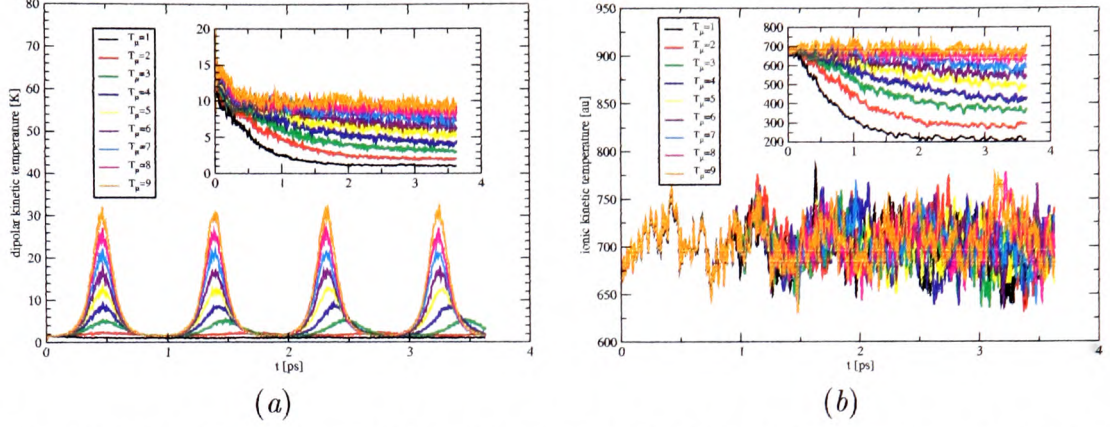


Figure 2.7: Panel (a) shows the variation of dipolar kinetic temperature, and panel (b) shows the variation of the ionic kinetic temperature, with target dipolar thermostat temperature, T_μ as given in the legend, with a dipolar fake mass, m_μ , of 100 au (and of 900 au in the inset). The other simulation conditions are as given in figure 2.6.

In panel (b) in figure 2.7, though, we see that in the ionic system, low dipolar fake mass allows good agreement of the ionic temperature with its target temperature, for all target dipolar temperatures, while at high dipolar fake mass a low target dipolar temperature results in the temperature of the ionic motion decreasing to a value far below the target ionic temperature.

The effect of the dipolar temperature and the dipolar fake mass on the time evolution of a sample dipole

In the Car-Parrinello (CP) scheme, we integrate the motion of the dipoles, and so we know the values of the dipoles on the ions $\mu_i(t)$. We can also calculate the self-consistent electric field acting on the ion, $\mathbf{E}_i(t)$, and hence compare the actual dipole from the CP scheme with the adiabatic dipole, given by $\alpha_i \mathbf{E}_i(t)$, where α_i is the dipole polarisability of ion i . Figure 2.8 shows the time evolution of $\mu_1^x(t)$ and $\alpha_1 \mathbf{E}_1^x(t)$ (*i.e.* the x-component of the actual and adiabatic dipoles for the first fluoride ion) under a range of different thermostatting conditions.

Panels (a) and (b) in figure 2.8 show the time evolution of the actual and adiabatic dipoles for $T_\mu = 1, 5, 9$ K with a fake mass of 100 au and 900 au respectively.

In panel (a), we can see that changing the temperature at which the dipoles are thermostatted actually leads to a change in the potential energy surface along which the dipoles move. At around $t = 0.6$ ps, the ion moves from one local potential energy minimum to another, and the dipole changes accordingly. This change is different, however, depending upon the temperature of the dipolar system, and after this time the dipoles follow different trajectories. This behaviour is seen again in panel (b), although now the divergence of the dipolar trajectories starts at around $t = 0.4$ ps. If we look at the behaviour on a short time scale as shown in the insets of these figures, we can see a change in the way the dipoles respond to the changing electric field. At low fake mass ($m_\mu = 100$ au, panel (a)), when the dipoles have low inertia and are able to respond quickly to the changing forces, the actual dipoles (shown as solid lines) do oscillate around their adiabatic values (shown as dashed lines), while at high fake mass ($m_\mu = 900$ au, panel(b)), the dipoles no longer oscillate but *lag behind* the adiabatic dipoles, and the degree of lag increases as the target dipole thermostat temperature decreases, from ~ 1 time step at $T_\mu = 9$ K to ~ 3 time steps at $T_\mu = 1$ K. When the dipoles are oscillating around their adiabatic values, the deviations between the real and desired dipoles produce random, fluctuating restoring forces on the dipoles (to restore them to their adiabatic values) which will cancel, on average, for each dipole. When the dipoles are constantly lagging behind their desired values, there will always be non-zero restoring forces, which will not necessarily have a zero mean field effect, and so this lagging-type behaviour is undesirable.

Panels (c) and (d) in figure 2.8 show the time evolution of the actual and adiabatic dipoles at target dipole temperatures of $T_\mu = 1$ K and $T_\mu = 9$ K respectively. At $T_\mu = 1$ K and $m_\mu = 100$ au there is excellent agreement between the actual and required dipoles, and as the fake mass increases, the lagging behaviour again becomes apparent, seen most clearly in the inset, the lag varying from ~ 1 time step at $m_\mu = 500$ au to ~ 2.5 time steps at $m_\mu = 900$ au. At the higher temperature,

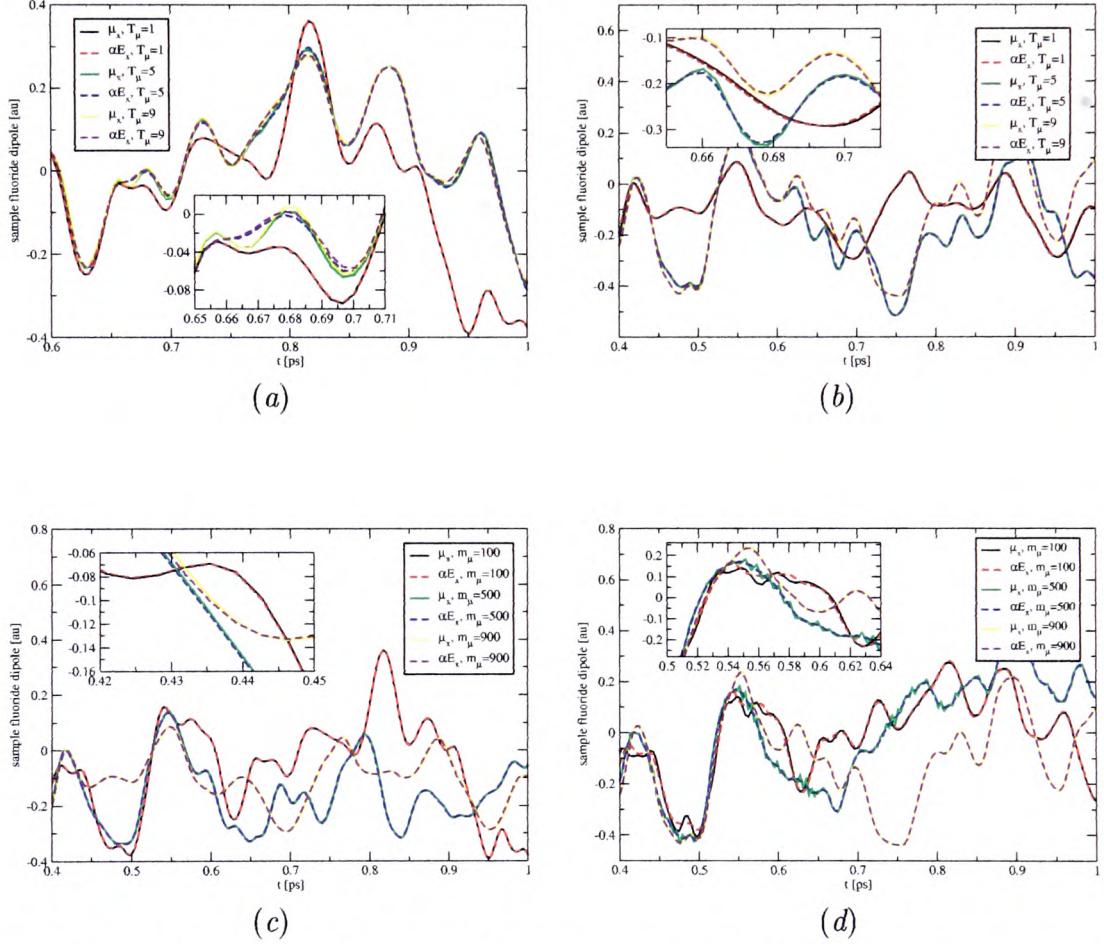


Figure 2.8: The time evolution of the x-component of the dipole, μ_x , on ion F^1 compared to its adiabatic value, αE_x , for: panels (a) and (b), dipolar fake masses of 100 au and 900 au respectively, with target dipolar thermostat temperatures as given by the legends, and panels (c) and (d), target dipolar thermostat temperatures of 1 K and 9 K respectively, with dipolar fake masses as given by the legends. The other simulation conditions are as given in figure 2.6.

the desired oscillatory behaviour of the actual dipole around the adiabatic dipole is observed at all but the highest target dipolar temperature, although from the inset we can see that the oscillations may be quite large.

The effect of the dipolar temperature and the dipolar fake mass on the measurement of the ionic diffusion coefficients: the ionic mean squared displacements

The object of investigating the dipole thermostat parameters is to give the dipolar system properties which do not influence the properties of the ionic system too much, such that we do not get a false idea of the ionic dynamics. The most readily calculated measurement of the ionic dynamics is the diffusion coefficient, as defined in equation 3.10, which relates the ionic diffusion coefficient to the mean squared displacements of the ions. The diffusion coefficient is essentially the long time gradient of the mean squared displacement when plotted against time.

In panel (a) in figure 2.9, the cationic mean squared displacements are shown for a set of target dipolar temperatures with two fake masses, $m_\mu = 100, 900$ au, while panel (b) shows the cationic mean squared displacements for a set of dipolar fake masses with two target dipolar temperatures, $T_\mu = 1, 9$ K. The anionic mean squared displacements follow similar patterns, and are omitted for clarity in the figure.

The length of the simulation runs used for the investigation of the thermostat parameters here is 10000 time steps, which is equivalent to 3.6282 ps. Whilst this is long enough to understand the effects on the temperatures of the ionic and dipolar systems, and to examine the time evolution of the actual and adiabatic dipoles, it is not really long enough to look at the long time behaviour of the gradient of the mean squared displacement plots, as can be seen from the nature of the curves in figure 2.9. Whilst it would be inappropriate to calculate a diffusion coefficient from simulations of these lengths, we can examine how the mean squared displacements vary with changing thermostat parameters.

At $T_\mu = 1$ K, in panel (a) of figure 2.9, we can see that the mean squared displacements fall broadly into two regimes, for $m_\mu < 500$ au and for $m_\mu \geq 500$ au,

with gradients of approximately $0.4 \text{ au}^2 \text{ ps}^{-1} = 1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $0.3 \text{ au}^2 \text{ ps}^{-1} = 8.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ respectively, and as the temperature increases, to $T_\mu = 9 \text{ K}$ in the inset, the difference between the mean squared displacements of runs with different fake masses decreases and the curves lie increasingly on top of each other.

For a given fake mass, there is little difference between the mean squared displacements as the target dipolar temperature is changed, as shown in panel (b) of figure 2.9, for $m_\mu = 100 \text{ au}$ (and $m_\mu = 900 \text{ au}$ in the inset). At the high dipolar target temperature, the main difference between different simulations is those that have higher fake masses tend to have a higher initial mean squared displacement (the difference is approximately 2 au^2 to 1.5 au^2 , which corresponds to a difference in mean displacement of $\sim 0.2 \text{ au}$, compared to the ionic radius of the Be^{2+} ion of 0.64 au), but the longer time gradient is similar, and hence there will be little difference in the calculated diffusion coefficients.

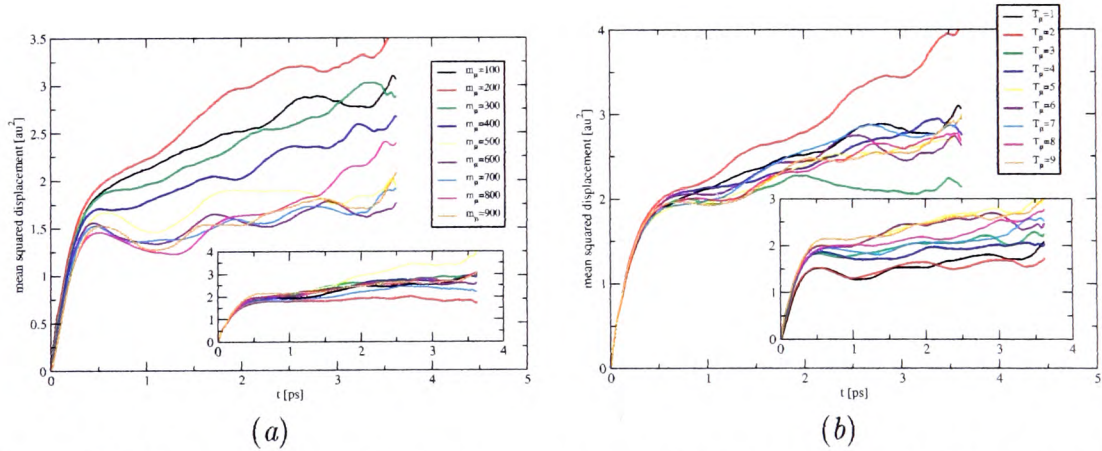


Figure 2.9: The variation of cationic mean squared displacements, $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$, with, in panel (a) the dipolar fake mass, m_μ , as given in the legend, with a target dipolar thermostat temperature, T_μ , of 1 K (and of 9 K in the inset), and in panel (b) target dipolar thermostat temperature, T_μ , as given in the legend, with a dipolar fake mass, m_μ , of 100 au (and of 900 au in the inset). The other simulation conditions are as given in figure 2.6.

Overall, the changing target dipolar temperature and dipolar fake mass has little effect on the observed ionic mean squared displacements, especially on the longer

time gradients, from which we calculate the diffusion coefficient.

The importance of the dipole thermostat relaxation time

We have seen that the thermostat forces acting on the dipoles, to reduce their deviation from their adiabatic values, is proportional to the inverse square of the dipole thermostat relaxation time, τ_μ . The results presented in this section on the effects of changing the fake mass and the target dipole thermostat temperature have used a dipole thermostat relaxation time of $\tau_\mu = 5000$ au.

A similar investigation was undertaken with a dipole thermostat relaxation time of $\tau_\mu = 700$ au, and the trends of the behaviour on changing the fake mass and target dipolar temperature were the same. The forces are larger, by a factor of $\left(\frac{5000}{700}\right)^2 \approx 50$, and so the deviations from the desired behaviour occurred more quickly.

In general, we would like to keep the thermostating forces as small as possible, and hence to have as large a value of the dipole thermostat relaxation time as possible. In BeF_2 , the dipoles fluctuate quickly due to the low value of the fluoride ion polarisability (which means that the fluoride ion is reasonably *hard* and subject to high frequency oscillations). This means that we may not have dipole thermostat relaxation times as long as those used in simulations of *softer* anions, which have lower frequency oscillations, such as the chloride anion, where commonly used values of the thermostat parameters are $m_\mu \approx 30$ au, $T_\mu \approx 0.3$ K, and $\tau_\mu = 10000$ au, but where the dipole polarisability is now $\alpha_{Cl} = 20$ au.

Summary of the choice of dipole thermostat parameters

The investigation into the effects that the various thermostat parameters have in simulations of PIM BeF_2 as outlined above led to a best (combined) choice set of: $m_\mu = 100$ au, $T_\mu = 2$ K, and $\tau_\mu = 5000$ au. Other values are used in simulations of other materials, and these are summarised in appendix F.

Chapter 3

BeF₂: Characterisation of the Polarisable Ion Model

3.1 Introduction

The analysis of the output from computer simulations enables comparison of calculated properties with *experimental* and other *theoretical* results. We have been interested in linking the microscopic structure of a network liquid to its macroscopic dynamical properties. In this chapter, we describe how the structural and dynamical properties calculated for our Polarisable Ion Model simulations of BeF₂ compared with those measured experimentally.

3.1.1 Details of the simulations

The PIM simulations of BeF₂ were performed on a system of 648 ions, in a cubic simulation cell of side 38.55 au, which corresponds to the density of 1.986 gcm⁻³ for the glass at room temperature[15]. The potential parameters are based on those used in earlier simulations [11, 35] and are as given in tables 3.1 and 3.2.

The systems were set up with a *velocity rescale*¹ at a given temperature, and then run on for 100000 time steps at that temperature to achieve equilibration. The runs are then continued for another 500000 time steps, each of 15 au length, or 3.6282×10^{-16} ps, without any further velocity rescaling, and the trajectories from these runs are used for the data analysis. In the course of this thesis, time scales are

¹The ionic velocities are set up on a Maxwell-Boltzmann distribution at the required temperature.

often discussed in terms of *configurations*: one configuration corresponds to the time between the output of ionic positions, velocities, *etc.* from the simulation. This is done every 100 time steps, so one configuration is equal to 0.036282 ps.

The parameterisation of the model of BeF₂ is described in [36], and gives very good agreement between the calculated and experimentally observed *reduced intensity functions* (see equation 3.9), as described in section 3.2.

We should note from table 3.1 that dispersion effects are excluded, *i.e.* $C_{\alpha\beta}^6 = f_{\alpha\beta}^6 = C_{\alpha\beta}^8 = f_{\alpha\beta}^8 = 0$: the small size and polarisability of the fluoride ion and the very small size and near-zero polarisability of the beryllium ion mean that the dispersion effects will be small, and are ignored in the interests of simplifying the interaction potential².

B_{FF}	16.62	B_{BeF}	13.10	B_{BeBe}	8.245
α_{FF}	1.823	α_{BeF}	1.823	α_{BeBe}	1.823
C_{FF}^6	0.0	C_{BeF}^6	0.0	C_{BeBe}^6	0.0
C_{FF}^8	0.0	C_{BeF}^8	0.0	C_{BeBe}^8	0.0
f_{FF}^6	0.0	f_{BeF}^6	0.0	f_{BeBe}^6	0.0
f_{FF}^8	0.0	f_{BeF}^8	0.0	f_{BeBe}^8	0.0

Table 3.1: Born-Mayer parameters in the PIM simulation of BeF₂, as described by equation 2.1.

α_F	5.983
b_{BeF}	2.00
c_{BeF}	1.0
m_μ	100.0
T_μ	2.0
τ_μ	5000.0
τ_{ion}	5000.0

Table 3.2: Other parameters in the PIM simulation of BeF₂. α_F is the polarisability of the fluoride ion, in *au*; b_{BeF} , in bohr⁻¹, and c_{BeF} are the short range damping parameters for use in equation 2.9; m_μ is the dipolar fake mass in *au*, and T_μ is the target dipole thermostat temperature, in K, and τ_μ the dipolar thermostat relaxation time, in *au*; τ_{ion} is the ionic thermostat relaxation time, in *au*.

²The relative unimportance of dispersion effects in CaF₂ has previously been observed [37].

3.2 Static Structure

3.2.1 Radial distribution functions

The structure of a fluid can be most generally expressed in terms of the **radial distribution function**, (RDF), which is defined as

$$g_{ij}(r) = \frac{n_{ij}(r)}{n_{id}(r)}, \quad (3.1)$$

where n_{ij} is the number of ions of species, j , in the distance interval $r \rightarrow r + \delta r$ from the central ion of species, i , and n_{id} is the number of ions in the same interval in an ideal gas at the same density. This can also be expressed as

$$g_{ij}(r) = \frac{1}{\rho N} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle, \quad (3.2)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\rho = \frac{N}{V}$ is the number density of the ions. It can be seen that in a binary mixture, containing ions α and β , we can construct three *partial* radial distribution functions, $g_{\alpha\alpha}(r)$, $g_{\alpha\beta}(r)$ and $g_{\beta\beta}(r)$. A typical set of radial distribution functions for BeF₂, simulated using the PIM at 700 K, are shown in figure 3.1.

The radial distribution function can tell us the average separations of the nearest neighbours, as the locations of the maxima, and we may also use the heights of the *minima* as an idea of the degree of ion motion. For example, in figure 3.1, the first minimum in the Be–F partial radial distribution function has a height of only ~ 0.05 , and this would imply that there is very little motion of ions between the first and second coordination shells around the central Be or F ion: on moving between shells, an ion would take up intermediate positions between the average distances corresponding to the first and second coordination shells, and so appreciable motion would lead to a significant intensity in the region of the first minimum. The dashed green line in figure 3.1 shows the Be–F partial radial distribution function for the PIM at 1300 K, and now we can see much higher intensity in this region, and hence a much greater degree of transfer between coordination shells.

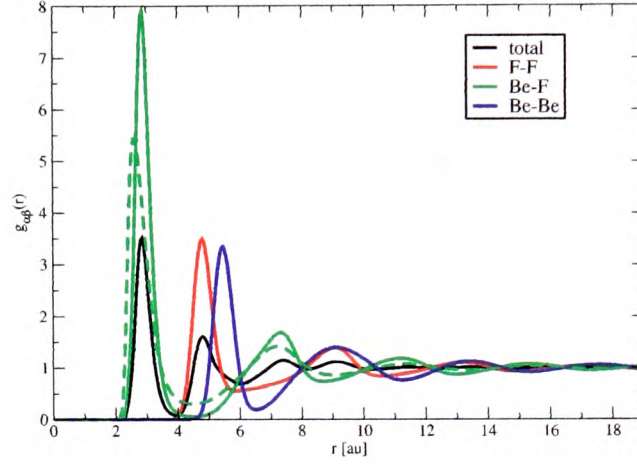


Figure 3.1: The total and partial radial distribution functions in BeF_2 , simulated using the PIM at 700 K. The dashed green line is the Be-F partial radial distribution function for the PIM at 1300 K.

The integrated (partial) radial distribution function, given by

$$\int P_{\alpha\beta}(r)dr = 4\pi\rho_\beta \int r^2 g_{\alpha\beta}(r)dr, \quad (3.3)$$

where $\rho_\beta = \frac{N_\beta}{V}$ is the number density of ions of type β and $P_{\alpha\beta}(r)$ is the probability distribution function, is a measure of the number of particles of a given type β within a distance r of a central ion α . This is shown for the PIM at 700K in figure 3.2. The *Coordination Number*, N^c , of a given ion is defined as the number of ions within a sphere of a given radius around the ion. This radius is generally chosen to be the location of the first minimum in the relevant partial radial distribution function.

Choosing these radial cut-offs, the coordination number of the Be ions at 700 K is ~ 3.9 , which reflects the almost ideal tetrahedral coordination of Be ions by F ions in the melt. At 1300 K, the average Be coordination number has fallen to ~ 3.5 , suggesting that the number of non-tetrahedral Be species has increased substantially. Typically, there will be a range of coordination environments occupied by the cations: table 3.3 gives the number of $N^c = 3$, $N^c = 4$, and $N^c = 5$ species

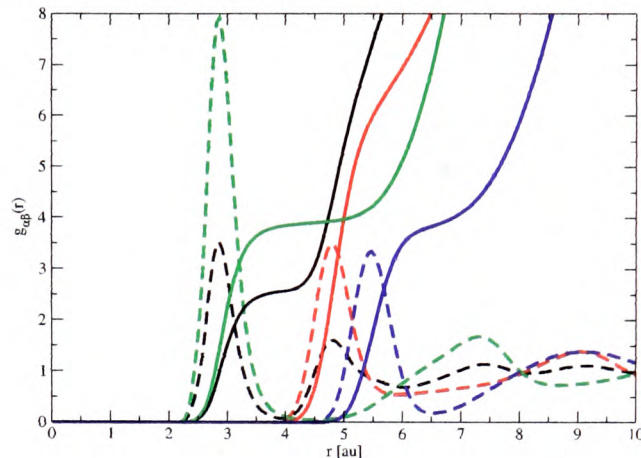


Figure 3.2: The integrated total and partial radial distribution functions in BeF_2 , simulated using the PIM at 700 K. The dashed lines show the radial distribution functions, as in figure 3.1, and the full lines are the integrated radial distribution functions, $4\pi\rho \int r^2 g_{\alpha\beta}(r) dr$.

for a series of BeF_2 simulations over a range of temperatures, and we can see that the number of non-tetrahedral sites increases with temperature.

System	$N^c = 3$	$N^c = 4$	$N^c = 5$
700K	9.66%	89.77%	0.53%
800K	16.83%	81.98%	1.07%
900K	23.94%	73.93%	1.77%
1000K	29.81%	67.02%	2.46%
1100K	34.10%	61.70%	3.02%
1300K	41.18%	52.66%	3.56%

Table 3.3: The variation with temperature of the populations of the different cation coordination numbers in PIM BeF_2 .

3.2.2 The Tetrahedrality of the network

The ideality of the network can be expressed not only in terms of the number of tetrahedra present, of which the average coordination number is a crude measurement, but also in the *regularity* of the tetrahedra themselves. This regularity of a

tetrahedron has two possible measurements: an angular part and a radial part [38], for which two measures, S_g and S_k , are given by equations 3.4 and 3.5.

$$S_g = \frac{3}{32} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\mathbf{r}_j \cdot \mathbf{r}_k + \frac{1}{3} \right)^2 \quad : \quad 0 \leq S_g \leq 1 \quad (3.4)$$

$$S_k = \frac{1}{3} \sum_{k=1}^4 \frac{(r_k - \bar{r})^2}{4\bar{r}^2} \quad : \quad S_k \geq 0. \quad (3.5)$$

S_g is a measurement of the angular distortion of the BeF_4 tetrahedra, *i.e.* the deviation of the F–Be–F bond angles from the tetrahedral angle of 109.5° , for which $\cos \theta = -\frac{1}{3}$, and S_k , which is the variance of the distances from the central Be^{2+} ion to the F^- ions at the vertices, *i.e.* the variance in the Be–F bond length, is a measurement of the radial distortion. Both quantities are zero for a perfect tetrahedron, and these expressions are strictly valid only for four-coordinate species. Figure 3.3 shows the variation in these values over the course of a simulation of PIM BeF_2 at 700 K. Both quantities are close to zero, suggesting that the tetrahedra are very close to perfect.

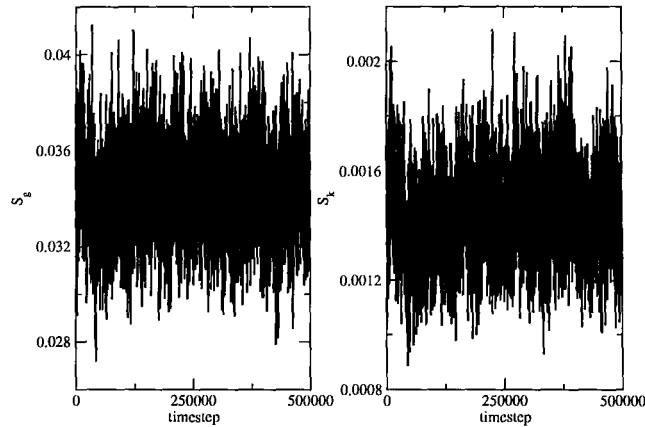


Figure 3.3: The variation of the tetrahedrality parameters, S_g as given by equation 3.4 and S_k as given by equation 3.5, over the course of the BeF_2 PIM simulation at 700K.

Table 3.4 gives the tetrahedrality parameters for PIM BeF₂ simulations, and figure 3.4 gives the temperature dependence of the fraction of a given type of coordination environment present and the values of the tetrahedrality parameters. The combination of these two measurements gives an idea of the *ideality* of the tetrahedral network.

T [K]	S_g	S_g^4	S_k	S_k^4
700	0.0387	0.0343	0.00156	0.00143
800	0.0475	0.0389	0.00205	0.00178
900	0.0562	0.0424	0.00247	0.00202
1000	0.0639	0.0447	0.00280	0.00215
1100	0.0706	0.0466	0.00307	0.00223
1300	0.0788	0.0473	0.00331	0.00216

Table 3.4: The temperature dependence of the tetrahedrality parameters in PIM BeF₂. S_g and S_k are the angular and radial parameters calculated for all BeF_n species, and S_g^4 and S_k^4 for the four-coordinate, BeF₄, species, for which the parameters are only strictly defined.

Across a wide range of temperatures, the tetrahedrality parameters are close to zero. We should therefore not consider deviations from the perfect tetrahedron in ions which remain four coordinate as having a major contribution to the *non-ideality* of the network. Disruption of the ideal network comes in the form of non-tetrahedral cations (or non-bi-coordinate anions), and it will be seen that these *defect* species have an important role to play in the dynamics of the network liquid.

3.2.3 Structure Factors

The radial distribution function gives us the average relative positions of the ions in the melt, but is not directly measurable. The calculated radial distribution function can, however, be related to experimentally observed properties such as the *X-ray structure factors* and the *reduced intensity function*, as described below.

X-ray and neutron diffraction experiments give data which can be related directly to the **structure factors** calculated from simulation. The (*partial*) structure factor

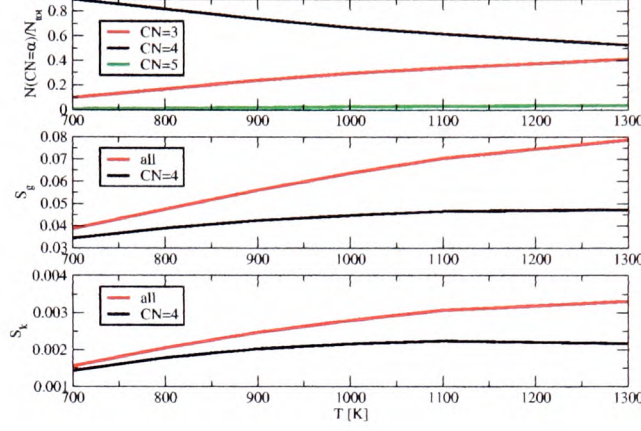


Figure 3.4: The temperature dependence of the tetrahedrality parameters and the number of given coordination species for PIM BeF₂. The combination of the number of tetrahedral sites combined with the value of the tetrahedrality parameters gives an idea of the overall *ideality* of the tetrahedral network.

is the Fourier transform of the (*partial*) radial distribution function, and may be expressed as

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + 4\pi\rho \int_0^\infty r^2 \frac{\sin(kr)}{kr} [g_{\alpha\beta}(r) - 1] dr. \quad (3.6)$$

Structure factors are measured in diffraction experiments, using X-rays and neutrons as the irradiating beam. The experimentally measured *X-ray structure factor* can be cast in terms of the partial structure factors according to

$$S_{\text{X-ray}}(k) = f_+^2(k)x_+[S_{++}(k)-1]+2f_+(k)f_-(k)\sqrt{x_+x_-}[S_{+-}(k)]+f_-^2(k)x_-[S_{--}(k)-1], \quad (3.7)$$

where x_α is the mole fraction of species α and f_α is the *form factor*, as described below, with + and – referring to cations and anions respectively, and the partial structure factors are as given by equation 3.6 ³.

³Note that $S_{+-}(k)$ is usually normalised such that it tends to zero at large k , i.e. $\delta_{+-} = 0$ in equation 3.6, and hence we do not subtract 1 from it when using it in equation 3.7.

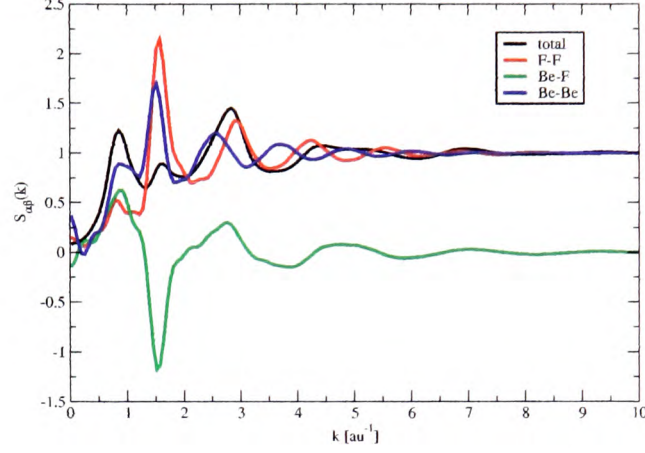


Figure 3.5: The total and partial structure factors in PIM BeF₂ at 700 K, as calculated using equation 3.6.

When an X-ray beam is incident on a sample, the X-rays are scattered by the electron clouds within the individual ions, and the intensity of the scattered radiation depends upon the angle of incidence, θ , of the X-rays. The scattered intensity will also depend on the ability of the ion to interfere with the path of the X-ray: this ability is expressed in terms of the form factor, f_α (see equation 3.7), for the species α which has the angular dependence given by

$$f_\alpha \left(\frac{\sin\theta}{\lambda} \right) = \sum_{i=1}^4 a_{i\alpha} \exp \left\{ -b_{i\alpha} \left(\frac{\sin\theta}{\lambda} \right)^2 \right\} + c_\alpha. \quad (3.8)$$

The values of the *scattering factors*, $\{a_{i\alpha}, b_{i\alpha}, c_\alpha\}$, in BeF₂ are given in table 3.5, and k can be related to $\sin\theta$ by the expression $k = 4\pi \left(\frac{\sin\theta}{\lambda} \right)$.

Experimental X-ray data is also often presented in terms of the *Reduced Intensity function*, $k.i(k)$, where $i(k)$ is the intensity of the scattered radiation, and which is given by

$$F_{\text{red}}(k) = k.i(k) = k. \left\{ \frac{S_{\text{X-ray}}(k)}{\sum_{\alpha} f_{\alpha}^2(k)} - 1 \right\}. \quad (3.9)$$

Scattering Factor	Be ²⁺	F ⁻
a ₁	6.2603	3.6322
a ₂	0.8849	3.51057
a ₃	0.7993	1.26064
a ₄	0.1647	0.940706
b ₁	0.0027	5.27756
b ₂	0.8313	14.7353
b ₃	2.2758	0.442258
b ₄	5.1146	47.3437
c	-6.1092	0.653396

Table 3.5: X-ray scattering factors for Be²⁺ and F⁻ for use in determining the form factor using equation 3.8 [39].

Figure 3.6 shows the calculated reduced intensity function for the PIM at 700 K and 1300 K, compared with the experimental results for the glass at room temperature [15]. There is good agreement between the experimental reduced intensity function and that calculated for the PIM at 700 K (the lowest temperature simulated), particularly in peak positions, across the whole range of k values. The intensities do not match so well at low k , but the agreement becomes very good at high k , and we conclude that our potential gives a very good representation of the structure of BeF₂.

3.3 Transport properties and the motion of ions

The diffusion coefficient may be calculated in a computer simulation from the Einstein relation,

$$D_{\alpha} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_{i\alpha}(t) - \mathbf{r}_{i\alpha}(0)|^2 \rangle. \quad (3.10)$$

In this equation the diffusion coefficient is defined as the limiting value of the gradient of the mean squared displacement of the ions at *infinite* time. In a simulation, we find that the diffusion coefficient acquires an approximately constant value typically after a few picoseconds, the time scale of the structural relaxation. The structural relaxation time is expected to be very temperature dependent, and to vary in an approximately Arrhenius fashion. The value of the structural relaxation time can

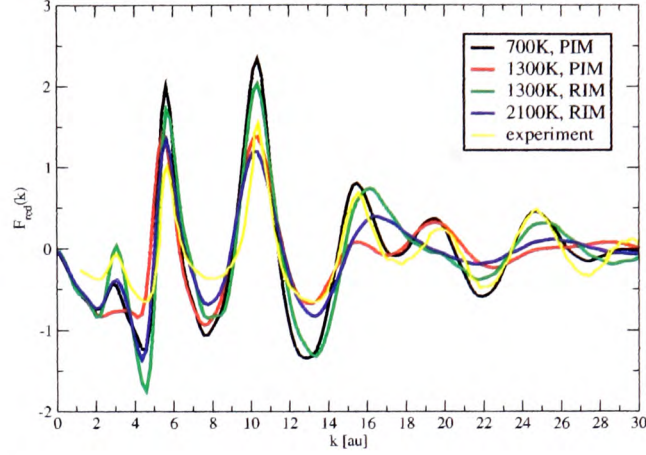


Figure 3.6: The reduced intensity functions for PIM, at 700 K and 1300 K, and RIM, at 1300 K and 2100 K, BeF₂ compared to that measured experimentally for the room temperature glass [15]. A discussion of the RIM results will follow in chapter 5.

be obtained from a consideration of the viscosity of the system.

Experimental measurements of the mobility of a network system have focused on the viscosity. The coefficient of shear viscosity, η , may be defined as the time integral of the autocorrelation function of an off-diagonal element of the stress tensor in the limit $k \rightarrow 0$ [40]⁴,

$$\begin{aligned}\eta &= \frac{1}{kTV} \int_0^\infty \langle \sigma_0^{xz}(0) \sigma_0^{xz}(t) \rangle dt \\ &= \int_0^\infty \eta(0, t) dt,\end{aligned}\tag{3.11}$$

where

$$\eta(0, t) = \frac{1}{kTV} \lim_{k \rightarrow 0} \langle \sigma_{\mathbf{k}}^{xz}(0) \sigma_{-\mathbf{k}}^{xz}(t) \rangle.\tag{3.12}$$

The stress tensor is a property of the whole system, and so the statistical imprecision in its calculation can be large, especially for systems with a low mobility, or at low

⁴This relationship is true when the z-axis is in the direction of $\mathbf{k}$, but this is not a unique choice of direction, and we average over the different stress tensor off-diagonal elements, as given in figure 3.7, to find a final value of the shear viscosity.

temperature. In figure 3.7, the running integral of the stress tensor correlation function is shown, and it can be seen that it approaches a steady plateau value, shown with a dashed orange line, at around 10 ps. The time taken to reach this plateau value is a measure of the structural relaxation time of the fluid, and this is the time scale beyond which the diffusion coefficient should be measured when calculated using equation 3.10.

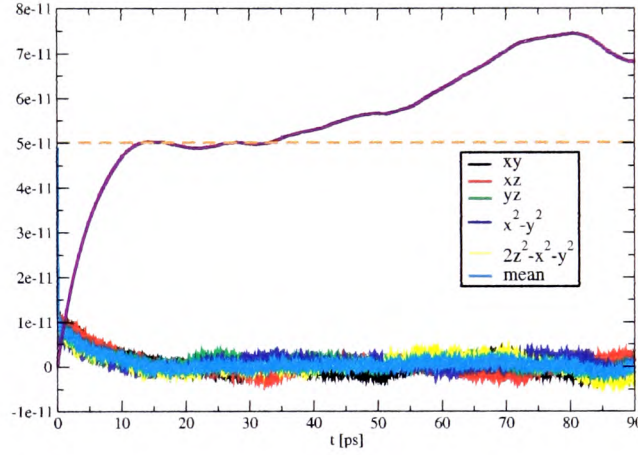


Figure 3.7: The time evolution of the individual contributions and the mean stress tensor correlation function in PIM BeF₂ at 700 K. The plateau value, *i.e.* the integrated stress tensor correlation function, is taken as the first levelling off of the running integral of the mean stress tensor correlation function, and is shown with the dashed orange line.

The viscosity can be related to the self-diffusion coefficient, D_α , through two models, the Stokes-Einstein relation,

$$D_\alpha = \frac{kT}{6\pi\eta a_\alpha} \quad (3.13)$$

where a_α is the hydrodynamic radius of an ion of species α , and the Eyring relation,

$$D_\alpha = \frac{kT}{\eta\lambda_\alpha} \quad (3.14)$$

where λ_α is an effective jump length for an ion of species α in a hopping mechanism of diffusion.

If we compare equations 3.10 and 3.11, we can see that the viscosity is a property of the system as a whole, whereas the diffusion coefficient depends upon the mean squared displacements of individual ions, and so now the averaging is over all ions and over time origins. Hence, the statistics are much better for the diffusion coefficient.

The prediction of the diffusion coefficient from the viscosity using either of these relationships requires the prescription of an appropriate length scale: in the Stokes-Einstein relation the hydrodynamic radii are typically taken to be the in-crystal ionic radii, whereas the choice of jump length in the Eyring relation is somewhat more arbitrary. Earlier studies [41] on silicates⁵ have suggested a value of $\lambda_\alpha = 2r_\alpha$, where r_α are the ionic radii, but we feel that a more appropriate *a priori* choice of jump length is the position of the first minimum in the cation-anion partial radial distribution function: for structural relaxation to occur via a hopping mechanism we might postulate that an ion needs to change its local coordination environment, and the simplest way of doing this is by moving out of its first coordination shell, *i.e.* beyond the first minimum in the partial radial distribution function, and so we propose this as the jump length in a network fluid. The previous use of the Eyring relation on the silicates with a jump length of $\lambda_\alpha = 2r_\alpha$ would give a diffusion coefficient higher for the cation than the anion, which is not observed. The accuracy of the anionic diffusion coefficient in that work, however, when calculated with this jump length lies in the fact that this value lies close to the position of the first minimum in the M–O (M=Al,Si) partial radial distribution function, *i.e.* $2r_O \approx r_{MO}^{\min}$ (indeed, in our system $2r_F = 5.14$ au compared to $r_{BeF}^{\min} = 4.5$ au), whereas this relationship is not true for the cations, which are very small ($r_{Si} = 0.41$ Å, $r_{Al} = 0.50$ Å). The jump length in the network fluids should therefore be taken as $r_{\alpha\beta}^{\min}$.

Figure 3.8 shows the variation of the ionic diffusion coefficients for PIM BeF₂ with

⁵Here, the authors argue that “previous studies of O²⁻ diffusion in silicate liquids have reported good correlation [of the calculated diffusion coefficient with that obtained from the experimental viscosity] if the Eyring equation is used with this [the diameter of the O²⁻ ion] jump distance [42, 43]”.

inverse temperature, calculated using the Einstein relation, and as converted from the calculated viscosity using the Stokes relation and the Eyring relation. The agreement between the anionic diffusion coefficients calculated from the Einstein relation and the Eyring relation is excellent when we use the position of the first minimum in the BeF partial radial distribution function, $r_{BeF}^{\min}$, as the jump length, particularly at low temperature. This is the first time that this calculation has been performed, and we can conclude that the suggestion that the Eyring relation is the best way of calculating the diffusion coefficient from the viscosity in these network systems [41], as used for BeF₂ by Angell [3], is a good one.

If we use the same value of the jump length, $r_{BeF}^{\min}$, for each species we must obtain the same diffusion coefficient for each species when using the Eyring relation: this is approximately the case, as the diffusion coefficients calculated from the Einstein relation give us $D_F \approx 1.1D_{Be}$. If we were to use the Stokes-Einstein relation to predict the diffusion coefficients using the in-crystal ionic radii as the hydrodynamic radii then we would obtain diffusion coefficients which would not only be very different for the two species, as the Be²⁺ ion is much smaller than the F⁻ ion ($r_{Be} = 0.34 \text{ \AA}$, compared to $r_F = 1.36 \text{ \AA}$), but which would also be too small, as shown in figure 3.8. The Stokes-Einstein relation is not appropriate for network systems, whereas it has been shown to work very well in unassociated ionic melts [44, 45]. This suggests a very different mechanism for diffusion in these different types of liquid.

3.3.1 Comparison of the proposed with the observed diffusive length scales

Using the diffusion coefficients calculated using the Einstein relation and the viscosity calculated from the stress tensor correlation function, equations 3.13 and 3.14 can be adapted to give effective values for the hydrodynamic radii and jump lengths,

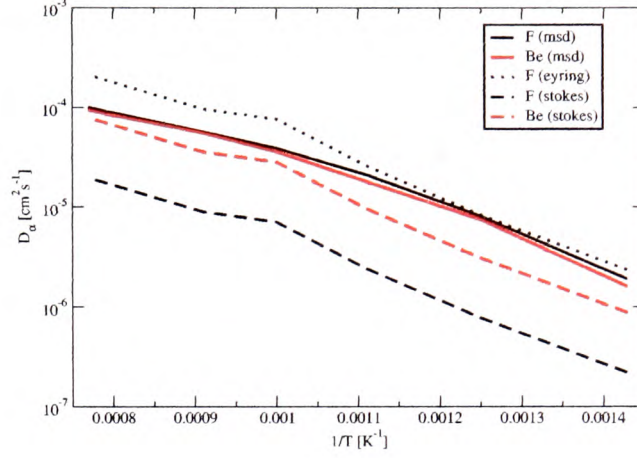


Figure 3.8: The inverse temperature dependence of the ionic diffusion coefficients calculated from the Einstein relation, and converted from the viscosity using the Eyring and Stokes relations. The line for the cationic diffusion coefficient calculated from the Eyring relation is omitted as the cationic and anionic Eyring diffusion coefficients are equal, as $\lambda_{Be} = \lambda_F$.

as given by

$$a_\alpha = \frac{kT}{6\pi\eta D_\alpha} \quad (3.15)$$

$$\lambda_\alpha = \frac{kT}{\eta D_\alpha}. \quad (3.16)$$

Figure 3.9 shows the variation of hydrodynamic radii and jump lengths calculated using equations 3.15 and 3.16. The hydrodynamic radii and jump lengths are greater for Be than F, which reflects the lower diffusivity of Be than F.

The mean hydrodynamic radius of Be, which is 0.403 au across the temperature range shown, is less than the ionic radius of 0.64 au, and this is unphysical and confirms that the Stokes-Einstein relation is not appropriate for calculating the diffusion coefficient: this observation is exaggerated for F, where the calculated mean hydrodynamic radius of 0.369 au is *much* smaller than the bare ionic radius of 2.57 au. In unassociated ionic melts the Stokes-Einstein relation is good at predicting the diffusion coefficients, with hydrodynamic radii being the in-crystal radii, or

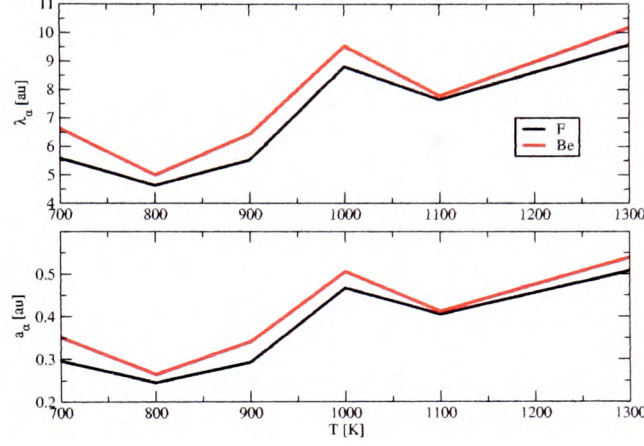


Figure 3.9: The upper panel shows the temperature dependence of the ionic jump lengths, calculated using equation 3.16, and the lower panel shows the hydrodynamic radii, calculated using equation 3.15, for PIM BeF₂. The ionic radii are $r_F = 2.57$ au and $r_{Be} = 0.64$ au.

corresponding to some well defined larger unit such as a complex ion, *e.g.* LaCl₆³⁻ species in dilute solutions of LaCl₃ in [Li,K]Cl mixtures [45]. The unphysically small value of the hydrodynamic⁶ radii here means that there is more ionic motion than would be expected from the decay of the stress tensor correlation function, and this is a signature of the network behaviour.

The mean jump lengths are $\lambda_{Be} = 7.59$ au and $\lambda_F = 6.96$ au. We can compare these jump lengths with the characteristic length scales in the system: the positions of the first peaks and first minima in the partial radial distribution functions for PIM BeF₂ at 700K, as shown in figure 3.1, are given in table 3.6.

The structural units in BeF₂ are the vertex sharing BeF₄ tetrahedra. The size of these tetrahedra can be estimated from taking $r_{BeF}^{\min}$, the position of the first minimum if the Be–F partial radial distribution as the radius of the circumsphere of the tetrahedron. In order for an ion to diffuse via the hopping mechanism implied

⁶We have to use a very small value for a_0 to obtain the correct value for η .

$\alpha - \beta$	first maximum [au]	first minimum [au]	jump length, λ_α [au]
F-F	4.85	5.90	–
F-Be	2.90	4.50	6.96
Be-F	2.90	4.50	7.59
Be-Be	5.50	6.50	–

Table 3.6: The positions of the first maxima and the first minima in the partial radial distribution functions in PIM BeF₂ at 700 K. These constitute the *characteristic length scales* in the system. These values are relatively constant for PIM BeF₂ across a range of temperatures. The final column gives the values of the ionic jump lengths calculated from equation 3.16.

by the use of the Eyring equation it must make a hop over a distance given by the jump length. We can see from table 3.6 that the calculated jump lengths are comparable to the diameter of the tetrahedral units, and this agrees with the idea that the ions jump from one tetrahedral unit to another.

3.4 Dynamical properties and the Static Structure in PIM BeF₂

Figure 3.10 shows the diffusion coefficients calculated from our simulations using equation 3.10, compared with those predicted from experimental viscosity measurements [46, 47], using equation 3.14 with jump lengths given by $\lambda_\alpha = r_{\alpha\beta}^{\min}$, and with other theoretical calculations [3]. We can see that the diffusivities of our systems simulated using the PIM are much too high, and hence that the systems are much too fluid.

Figure 3.10 also shows the ionic diffusion coefficients calculated from simulations performed using the RIM. The RIM simulations are performed using the *same* Born-Mayer potential as the PIM. The agreement between the calculated values and the experimental values is much better for the RIM than for the PIM. This observation is also in good agreement with the conclusions of Angell *et al.* [3] whose TRIM model (*Transferable*-RIM) of BeF₂ does not include the effects of polarisation, and whose calculated diffusion coefficients match up with the high temperature experimental measurements, as deduced from the viscosities using the Eyring equation.

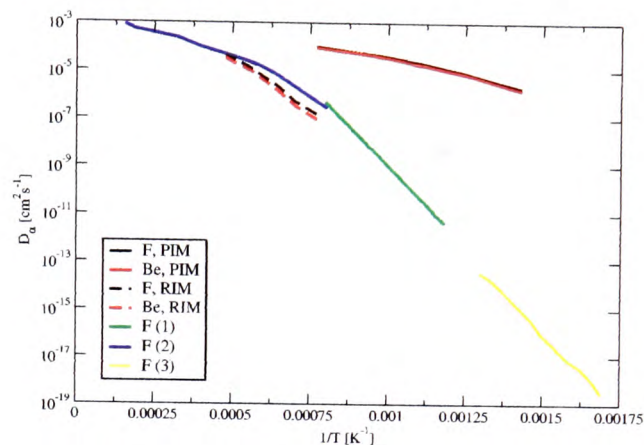


Figure 3.10: The comparison of the inverse temperature dependence of the calculated diffusion coefficients in Beryllium Fluoride for the Polarisable Ion Model, PIM (see section 2.3), and for the Rigid Ion Model, RIM (see section 2.2), with experimental data, set (1) from [46] and set (3) from [47], and other theoretical data, set (2) from [3].

This result would appear to suggest that the RIM is the better model to study the *dynamical* behaviour of molten BeF_2 . However, we can see from figure 3.6 that the reproduction of the experimental *structural* data, in the form of the reduced intensity function, is much better for the PIM than the RIM, particularly at large k , or short r (for example, the RIM does not predict the double peak in the 15 – 20 au region at all). The dramatic effect that including polarisation has suggests that we can learn about the network dynamics from the comparison of the behaviours of the PIM and RIM.

One problem associated with the calculation of the diffusion coefficient from simulation is that the structural relaxation times at the low temperatures at which the experimental measurements have been made become comparable with the time over which a simulation may be performed in a reasonable amount of computer time. In this case, the calculated statistics will be relatively poor, as the system will spend

much of its time in a relatively few configurations as it approaches the glass transition. This is why the temperature range of the calculated diffusion coefficients does not quite overlap with the experimental measurements: on the other hand, the higher temperatures more suitable for study by computer simulation are hard to attain under experimental conditions.

The higher diffusivities calculated using the PIM are unphysical, but correspond to structural relaxation times which are relatively short compared to the time scale of the simulation. We can therefore generate good statistics on the dynamical processes that are responsible for the diffusive events.

Although the polarisability of the Fluoride anion is small, we can see that the inclusion of polarisation does give improved agreement between the calculated and experimental structural measurements. The Born-Mayer parameters used in our Rigid Ion simulation model are the same as those for the Polarisable Ion Model, as outlined in table 3.1 and hence our Rigid Ion Model is not necessarily the best available. However, our aim is to understand the effect that including polarisation has on the dynamical properties of the system, and hence to understand why the PIM gives a good structural representation of the real system, and the RIM a good dynamical representation of the system.

Chapter 4

Diffusion in BeF₂: novel analysis methods

4.1 Introduction

The proposed mechanism of diffusion in a network fluid is one dependent upon *bond breaking* events. The way these events interact or propagate throughout the fluid should determine the mobility, or fluidity, of the system, but no detailed picture has been given.

However, in order to investigate this relationship, we need to characterise the motion of the particles over a range of time scales, and link this to the observed diffusion coefficient. This motion can also be separated into different length scales: for example, the use of the Eyring relation implies the importance of the *jump length*, and the relation of this length scale to the structural length scales present allows us to probe the effect of changes in structure on the dynamics.

The dynamics are usually considered to be *exponentially dependent on structure*¹, and hence small changes in the structure can be responsible for large changes in the dynamics, and so the interpretation of the dynamical properties in terms of the structural properties will be a sensitive one. On the other hand, the relationship between structure and dynamics is implicitly assumed in much of science. For example, the action of drugs and the rates of their reactions are often interpreted in terms of the local structure of the drug-substrate binding site. Therefore, the existence of

¹This is summarised by the Arrhenius relationships which govern the dynamics.

a link in network fluids is a tantalising prospect but the means of forging it are by no means clear: the problem will need to be examined from many standpoints.

4.2 The van Hove correlation function

The Diffusion Coefficient is our main means of comparing dynamical results of simulations with those measured experimentally, but it gives us little information about the motions of individual ions within the system, other than the mean distance moved in a given time. In order to better understand the types of motion occurring on the microscopic level in the liquid, we must look at other measures of that motion. These need not, however, necessarily be measurable experimentally.

The **van Hove correlation function** is one such function which gives a description of the microscopic dynamical behaviour of a liquid. It is constructed as described in reference [40] (see appendix C), and can be defined as

$$G(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle. \quad (4.1)$$

This can be separated into two parts, the *self*, $G_s(r, t)$, and *distinct*, $G_d(r, t)$, parts,

$$G(r, t) = G_s(r, t) + G_d(r, t), \quad (4.2)$$

where

$$G_s(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)] \right\rangle, \quad (4.3)$$

$$G_d(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1, i \neq j}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle. \quad (4.4)$$

The **van Hove self-correlation function**, $G_s(r, t)$, therefore gives the probability of finding a particle at a distance r from its position at $t = 0$.

The van Hove correlation function, $G(\mathbf{r}, t)$, contains all the information about the motion within the system. If we know the positions of all the particles at $t = 0$, and we know $G(\mathbf{r}, t)$ then we will know, on average, the magnitude and the direction of how each of the particles has moved relative to every other particle.

The problem now is that this function contains so much information as to prohibit simple understanding of the types of motion occurring, particularly on the nearest and next nearest neighbour length scales which turn out to be important in these network liquids.

When investigating the behaviour of the particles, we are generally interested in the *probability distribution* of positions of particles relative to their own positions at different times, and to the positions of other particles, and hence we multiply the van Hove self-correlation function by a volume factor, $4\pi r^2$, *i.e.* the volume of a thin shell at a distance r from the ion. The function $4\pi r^2 G_s(r, t)$ is shown for the Be^{2+} ions in a PIM simulation of BeF_2 at 700 K in figure 4.1.

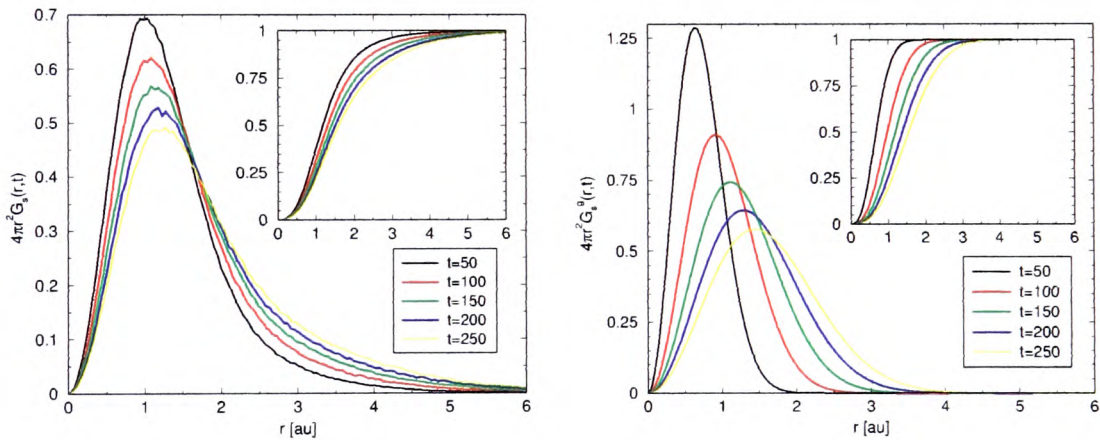


Figure 4.1: The van Hove self-correlation function, $4\pi r^2 G_s(r, t)$, (in the left-hand panel), and its Gaussian approximation, $4\pi r^2 G_s^g(r, t)$, (in the right-hand panel), for Be^{2+} ions in a PIM simulation of BeF_2 at 700 K. The times given in the legend are in terms of the configurations outputted in the simulation, where the time between outputs is 36.3 fs (*i.e.* $t = 50$ corresponds to a real time of 1.814 ps). The insets show the integrated probability functions, $4\pi r^2 \int G_s(r, t) dr$ and $4\pi r^2 \int G_s^g(r, t) dr$, respectively. Note that the number of particles in the system is conserved, and so if we integrate the van Hove self-correlation functions over space we find, irrespective of time, that $\int G_s(r, t) dr = 1$.

The time scales shown in figure 4.1 are relatively short when compared to the typical structural relaxation times in the system. These structural relaxation times can be characterised by the time over which the plateau in the integrated stress tensor

correlation function develops, and this is of the order of 10 ps at 700 K, as can be seen in figure 3.7. The 10 ps approximately corresponds to the 250 configuration time scale, and so figure 4.1 shows the behaviour of the system up to the time when it just moves into the diffusive limit. At longer time, the van Hove self correlation function has less structure, as discussed in section 4.2.4.

4.2.1 The van Hove self-correlation function in the diffusive limit

The motion in a liquid is characterised at very short time by the free motion of particles prior to collisions between the particles, whilst at long time the motion crosses over to diffusive behaviour.

In the diffusive limit, we can predict the form of the van Hove self-correlation function by noting that, if r and t are macroscopic quantities, $G_s(r, t)$ will be governed by the diffusion equation

$$\frac{d}{dt}G_s(\mathbf{r}, t) = D\nabla^2 G_s(\mathbf{r}, t) \quad (4.5)$$

where D is the self-diffusion coefficient. If we solve this equation, noting that $G_s(r, 0) = \delta(r)$, we find

$$G_s(r, t) = \frac{1}{(4\pi Dt)^{\frac{3}{2}}} \exp\left(\frac{-r^2}{4Dt}\right). \quad (4.6)$$

This form of $G_s(r, t)$ is a Gaussian in r , and we shall label it $G_s^g(r, t)$. The probability function, $4\pi r^2 G_s^g(r, t)$, is also shown in figure 4.1 for Be^{2+} ions in PIM BeF_2 at 700 K. In order to calculate the Gaussian approximation to the van Hove self correlation function, we need to choose a value of the self diffusion coefficient, D , for use in equation 4.6. We must use the value calculated beyond the time scale of the structural relaxation as observed in the calculation of the viscosity from the stress tensor correlation function.

The short time free motion limit also gives rise to a Gaussian form of the van Hove self-correlation function, as described in section 4.2.2. Any deviation of $G_s(r, t)$ from $G_s^g(r, t)$ means that the diffusive motion in the system is not in the short time

free particle limit nor in the long time hydrodynamic limit, and this deviation is a signal that there is some sort of co-operative motion occurring in the structural rearrangement which accompanies the particle motion.

4.2.2 The differences between the van Hove self-correlation function and its Gaussian approximation

The differences between the calculated van Hove self-correlation function and its Gaussian approximation, which are indicative of co-operative motion occurring in the rearrangement of the ions, are best seen in the functions $4\pi r^2 \Delta G_s(r, t)$, given by

$$4\pi r^2 \Delta G_s(r, t) = 4\pi r^2 G_s(r, t) - 4\pi r^2 G_s^g(r, t), \quad (4.7)$$

and $\Gamma_s(r, t)$, given by

$$\begin{aligned} \Gamma_s(r, t) &= \frac{4\pi r^2 G_s(r, t) - 4\pi r^2 G_s^g(r, t)}{4\pi r^2 G_s^g(r, t)} \\ &= \frac{G_s(r, t)}{G_s^g(r, t)} - 1. \end{aligned} \quad (4.8)$$

$4\pi r^2 \Delta G_s(r, t)$ is simply the difference between the calculated van Hove self-correlation function and its Gaussian approximation, while $\Gamma_s(r, t)$ takes into account that the typical probability of finding a particular value of the displacement, r , decreases as the distribution of observed displacements gets broader. This allows better comparison of the difference between the actual and Gaussian approximation over a wide range of times. These functions are shown in figure 4.2 for the Be^{2+} ions in PIM BeF_2 at 700 K.

In figure 4.2, an excess of probability of the particles having moved a distance r in time t compared to the Gaussian approximation is seen as a positive contribution to $4\pi r^2 \Delta G_s(r, t)$ and $\Gamma_s(r, t)$, while a deficiency in the probability is seen as a negative contribution. It can be seen that at short times there is a deficiency of particles which have moved a short distance, *i.e.* $4\pi r^2 \Delta G_s(r, t)$ and $\Gamma_s(r, t)$ are negative at low r , and an excess of particles which have moved a larger distance. This suggests that fewer particles have remained close to their initial positions than predicted by

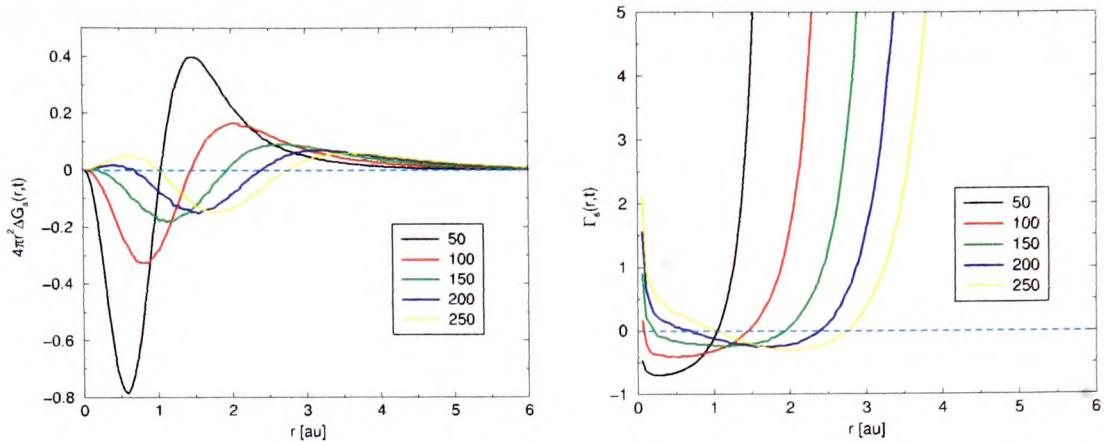


Figure 4.2: The difference between the van Hove self-correlation function and its Gaussian approximation for the system outlined in figure 4.1. $4\pi r^2 \Delta G_s(r, t)$ is shown in the left-hand panel and $\Gamma_s(r, t)$ in the right-hand panel, and the dashed cyan lines show $4\pi r^2 \Delta G_s(r, t) = 0$ and $\Gamma_s(r, t) = 0$.

the diffusion model. This difference is principally due, however, to the fact that although the short time/short r , free-flight model of diffusion gives rise to a Gaussian form of $G_s^g(r, t)$, it is not the same form as the long time/large r , hydrodynamic limit. The free-flight (FF) form of the van Hove self correlation function is given by [40]

$$G_s^{g,FF}(r, t) = \left(\frac{\beta m}{2\pi t^2} \right)^{\frac{3}{2}} \exp \left(\frac{-\frac{1}{2}\beta m r^2}{t^2} \right), \quad (4.9)$$

where $\beta = \frac{1}{kT}$, compared with the hydrodynamic limit form, given by equation 4.6. The main difference between the two limits is that the free-flight diffusivity is higher than the hydrodynamic diffusivity, and this is observed in $G_s^g(r, t)$ as an excess of particles which have moved further than predicted by the hydrodynamic limit. This accounts for much of the deficit of particles which have moved a small distance at short time.

At longer time, however, as we move into the diffusive regime, there is an excess of particles both at very small r and at longer r , which is more suggestive of a *bimodal* behaviour in the particle diffusivity. This means that some particles have essentially not moved, and others have moved a long way. The fact that the particles may be

split up into two groups, the *immobile* and the *mobile* particles, *may* mean that the different types of particles are in *spatially* separated regions of the system, *i.e.* that there may be some heterogeneity in the fluidity of the network, such that particles in some regions may be relatively immobile while in other regions the network may be able to relax much more easily with accompanying larger mobility. This *dynamical heterogeneity* is investigated further in chapter 6.

4.2.3 The van Hove self-correlation function for the different species

Figure 4.3 shows the van Hove self-correlation function and its Gaussian approximation for the F^- ions in PIM BeF_2 at 700 K, for the same time scale as the cations in figure 4.1, and also shows the direct comparison of the cation and anion van Hove self correlation functions. The form of the functions is the same for both species, but the anions have a mean displacement greater than that for the cations.

The diffusion coefficient is, according to the Einstein relation, proportional to the square of the displacements, and this higher mean anionic displacement is reflected in the higher anionic diffusion coefficient, *i.e.* $D_F \approx 1.1D_{Be}$ across all temperatures. This $\sim 10\%$ increase in diffusivity corresponds to a $\sim 5\%$ increase in the mean displacement. In figure 4.3, it can be seen, however, that the positions of the maxima in the van Hove self-correlation functions for the anions and the cations differ by more than $\sim 5\%$, in fact having a ratio of 1.25 for $t = 50$ configurations. This can be understood by looking at figure 4.4 which shows the time evolution of the diffusion coefficient over the course of the simulation run. The short time scales observed figures 4.1 to 4.3 correspond to the time scale shown in the inset of figure 4.4 (250 configurations ≈ 9 ps). Over the first picosecond, the calculated *effective* diffusion coefficient of the anions is approximately double that of the cations, and this is reflected in the much higher ratio of the mean displacement of the anions to the cations in the van Hove self-correlation function plot at $t = 50$ configurations. For $t < 250$ configurations ($t = 250$ is the time scale of the structural relaxation) we

may calculate an *effective* value of the diffusion coefficient from the mean squared displacements, but this will not be representative of the true long time limit diffusion coefficient because we are largely probing the vibrational motion of the system. During the vibrational motion, the F ions oscillate more about their sites in the network as they are only bonded to two Be ions, whereas the Be ions are each bonded to four F ions, and hence the F ions may move more freely. This extra freedom is observed as a higher *effective* diffusion coefficient over this intermediate time scale. Overall, as we approach the diffusive limit, the qualitative behaviour of the van Hove self-correlation functions is the same for both species, and the quantitative difference is due to the 10% higher diffusivity of the anions.

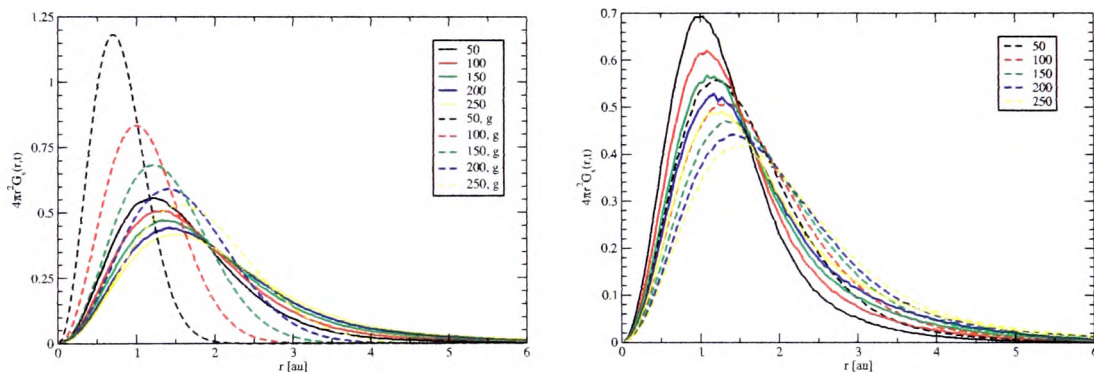


Figure 4.3: The left-hand panel shows the van Hove self-correlation function and its Gaussian approximation (denoted in the legend by g), for the F^- ions, and the right-hand panel shows the comparison between the van Hove self-correlation functions for the cations (in full lines) and anions (in dashed lines), in PIM BeF_2 at 700 K.

4.2.4 Timescales in and Temperature dependence of the van Hove self-correlation function

The time scales studied so far in our analysis of the van Hove self-correlation function have been just moving into the diffusive regime at the longer time, $t = 250$ configurations. We have seen, though, evidence of a splitting of the particle behaviour into two groups, the mobile and immobile. Figure 4.5 shows the van Hove

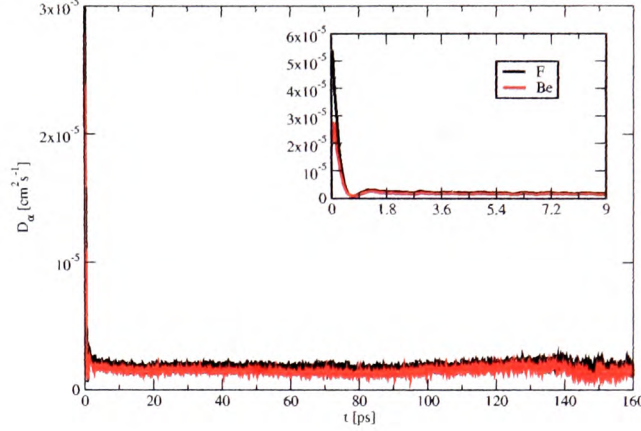


Figure 4.4: The time evolution of the ionic self-diffusion coefficients in PIM BeF₂ at 700 K. The main plot shows the slope of the mean squared displacement versus time, interpreted as a diffusion coefficient using the Einstein relation, and the inset shows the same data but over only a 9 ps section of the simulation. This time corresponds to the time scales shown as $t = 50 \rightarrow 250$ in figures 4.1 to 4.3.

self-correlation function for the Be²⁺ ions in PIM BeF₂ at 700 K over time scales which are now (much) beyond the structural relaxation time of $t \approx 250$ configurations, and hence in the hydrodynamic limit where we would expect the Gaussian approximation to work well. We can see, however, from the behaviour of the difference function, $4\pi r^2 \Delta G_s(r, t)$, and the ratio function, $\Gamma_s(r, t)$, shown in figure 4.6 that there are differences between $G_s(r, t)$ and $G_s^q(r, t)$ even at very long time². The bimodal behaviour exists even at $t = 3000$ configurations, and the excess correlation in the $r < 4$ au region for $t = 3000$ suggests that some particles have remained relatively immobile even over this time scale. This suggests that, although the relaxation of the stress tensor is complete on this time scale, other longer lived structural correlations persist in the network which affect the diffusive dynamics.

To analyse the contributions that any excess correlation of particles, whether mo-

²The noise in the calculated functions at long time is due to the fact that these times are approaching the total length of the simulation, 5000 configurations, and hence the number of time origins over which the function is calculated is small.

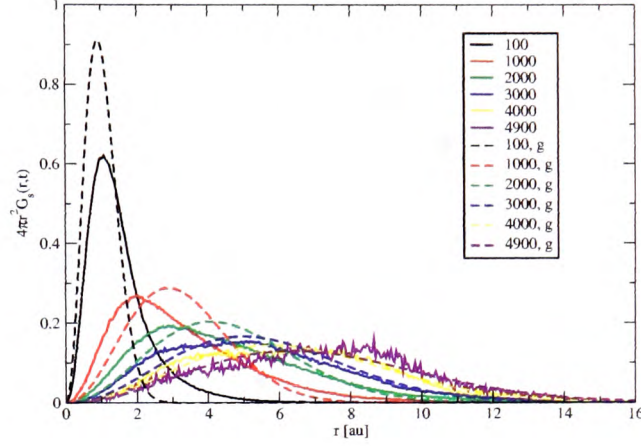


Figure 4.5: The van Hove self-correlation function and its Gaussian approximation (denoted in the legend by g) for the Be^{2+} ions in PIM BeF_2 at 700 K over a longer time scale.

mobile or immobile, makes to the diffusivity, we must choose an appropriate time scale on which to examine the van Hove self-correlation function. We would anticipate that this would be strongly temperature dependent, and we can see from figure 4.7, which shows the van Hove self-correlation function and the ratio function for the Be^{2+} ions in PIM BeF_2 at 1300 K, that the difference between the calculated and Gaussian approximated functions is negligible at 1300 K over the time scales where we observed excess correlation at 700 K. This *washing out* of the excess structure at high temperatures and long times is as expected from the predictions made for simple liquids [40].

The persistence of excess correlations at 700 K to times longer than the 10 ps that was identified as the structural relaxation time at that temperature suggests that we cannot simply use that time scale as our characteristic time scale of investigation. To choose an appropriate time scale, we must examine the typical displacements of the particles.

The maximum in the van Hove self-correlation function corresponds to the most

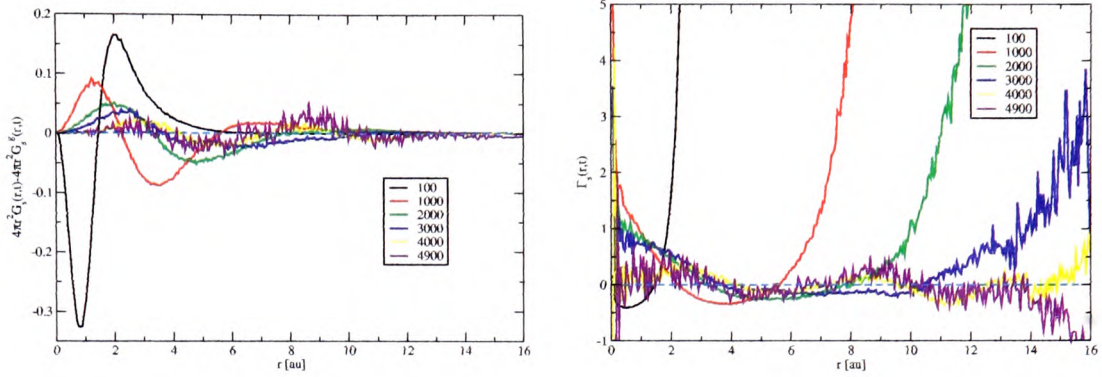


Figure 4.6: The left-hand panel shows the difference function, $4\pi r^2 \Delta G_s(r, t)$, and the right-hand panel shows that ratio function, $\Gamma_s(r, t)$, for the Be^{2+} ions in PIM BeF_2 at 700 K, over the longer time scales.

probable ionic displacement, and the width of the distribution is a measure of the spread of the displacements. If we consider the (partial) radial distribution functions for the system, as shown in figure 3.1, we can see that the typical ionic separations (cation to nearest neighbour anion) are $r_{\text{BeF}}^{\text{max}} \approx 3.0$ au and that the distance to the first minimum, which defines the furthest extreme of the first coordination shell, is $r_{\text{BeF}}^{\text{min}} = 4.5$ au (as summarised in table 3.6). From figure 4.5 we can see that the time when the most probable displacement is equal to the typical ionic separation is around 1000-2000 configurations, and that at these times the excess correlation in particle displacements occurs for displacements greater than (approximately) the size of the first coordination shell, *i.e.* $G_s(r, t) > G_s^q(r, t)$ for $r > r_{\text{BeF}}^{\text{min}}$. This is consistent with the majority of particles having moved as far as their nearest neighbours, and a few, the mobile particles, having moved beyond the cutoff distance for the first coordination shell, and hence beyond their nearest neighbours, over this 1000-2000 configuration time scale.

In using the Eyring equation to calculate the diffusivity from the viscosity, we have proposed a mechanism for motion characterised by a typical *jump length*, and these observations also suggest that the mobile particles, over a given time scale, are those

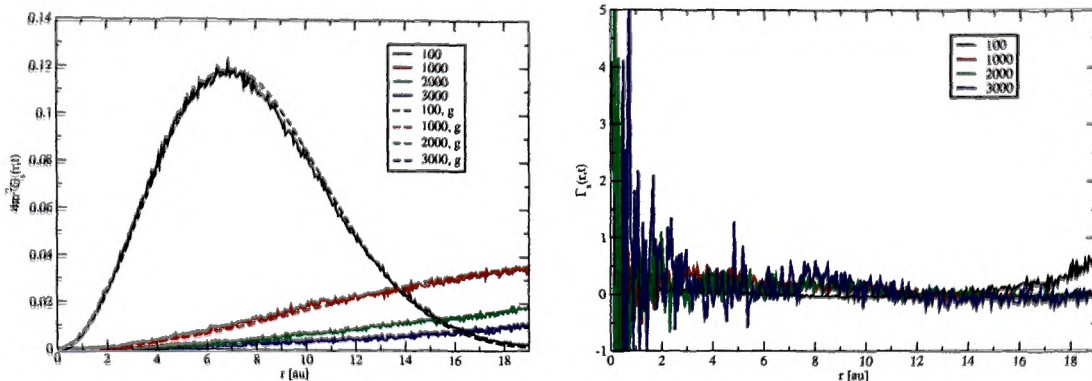


Figure 4.7: The left-hand panel shows the van Hove self-correlation function and its Gaussian approximation (denoted in the legend by g), and the right-hand panel gives the ratio function, $\Gamma_s(r, t)$, for the Be^{2+} ions in PIM BeF_2 at 1300 K.

which have moved further than a typical cutoff distance. The type of microscopic dynamical behaviour which could give rise to these observations is discussed in section 4.3, where we shall see that we may choose our cutoff length scale unambiguously, and thence calculate the characteristic diffusive time scale, which we will see agrees with the proposed 1000-2000 configuration time scale on the basis of the excess correlation of the particle displacements in the PIM BeF_2 at 700 K.

4.2.5 The incoherent scattering function

The discussion so far has focused on the van Hove self-correlation function, and while this gives us valuable insight it is not directly measurable in scattering experiments. The incoherent scattering function, $F_s(k, t)$, is, however, directly accessible from these experiments³. $F_s(k, t)$ is the space-Fourier transform of the van Hove self-correlation function [40]⁴,

$$F_s^\alpha(k, t) = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} \langle \exp\{i\mathbf{k} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]\} \rangle, \quad (4.10)$$

³The scattering experiments measure the time-Fourier transform of the incoherent scattering function, $S(k, \omega)$, so $F(k, t)$ can be calculated from the back-transform of this.

⁴The *coherent scattering function*, $F(k, t)$, corresponds to the space-Fourier transform of the total van Hove correlation function, $G(r, t)$.

where the α reflects the fact that the incoherent scattering function may differ between the ionic species. Panel (a) in figure 4.8 shows the variation with temperature of the incoherent scattering function for the cations and anions in PIM BeF₂, evaluated at the k -vector whose magnitude corresponds to the position of the *first sharp diffraction peak* in the static structure factor, which is shown in panel (b) of figure 4.8. The intermediate range order in the system gives rise to the first sharp diffraction peak (see *e.g.* [6, 7] for a discussion for ZnCl₂ and [48] for SiO₂), and is on the length scale corresponding to the distance between the centres of adjacent tetrahedra. Figure 4.9 shows the equivalent functions for the anions in SiO₂ (reproduced from [48], in panel (a)) and for a simple fluid (reproduced from [49], in panel (b)).

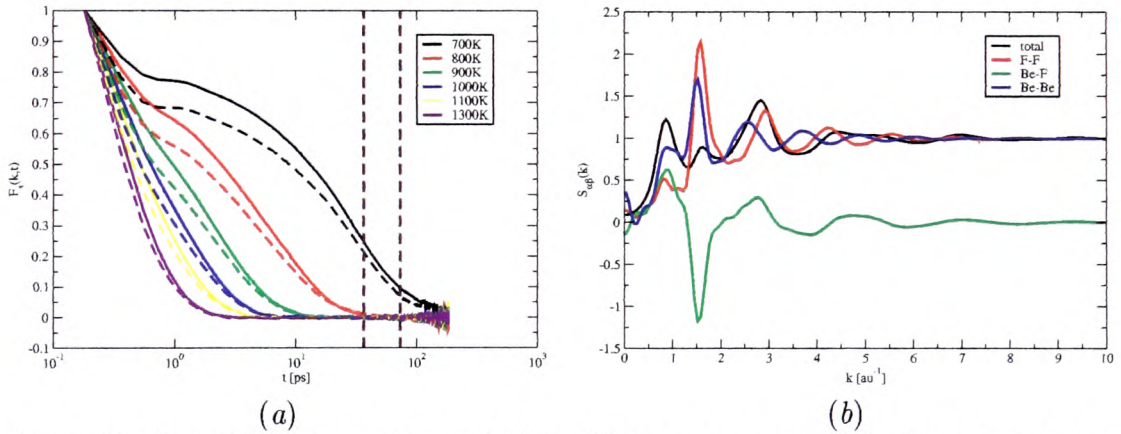


Figure 4.8: Panel (a) shows the variation with temperature of the incoherent scattering function, $F_s(k, t)$, for the cations (in solid lines) and anions (in dashed lines) in PIM BeF₂. The function is given for $|k| = 0.9 \text{ \AA}^{-1}$, which corresponds to the position of the *first sharp diffraction peak* in the static structure factor, $S(k)$, which is shown in panel (b) for PIM BeF₂ at 700 K. The dashed maroon lines in panel (a) correspond to the 1000-2000 configuration time scale which is proposed as the important diffusive time scale.

The qualitative behaviour of the incoherent scattering function in BeF₂ is the same as that in SiO₂, and is the same for the anions and cations within BeF₂ except that the anion function decays faster, reflecting the fact that these are more weakly bound. There is a very short time ballistic regime, followed by some vibrational decay, out to about 1 ps at 700 K, which corresponds to the rattling motion of the

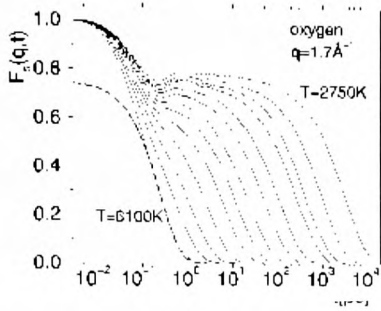


FIG. 1. Time dependence of the incoherent intermediate scattering function for the oxygen atoms for all temperatures investigated. The wave vector q is $1.7 \text{ \AA}^{-1}$, the location of the first peak in the structure factor. The dashed line is a fit to the curve for 6100 K with an exponential function

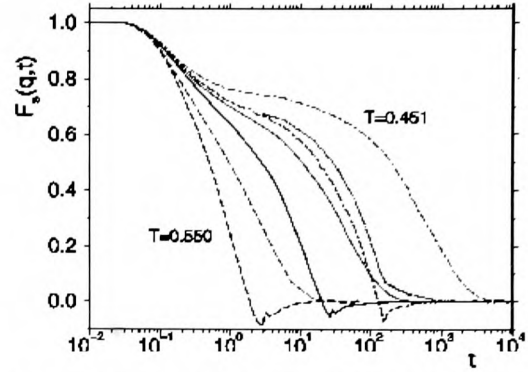


FIG. 4. The incoherent intermediate scattering function for the mobile (bold lines) and the bulk particles (thin lines) for $T = 0.550$ (dashed line), $T = 0.480$ (solid line), and $T = 0.451$ (dash-dotted line).

(a)

(b)

Figure 4.9: Panel (a) shows the variation with temperature of the incoherent scattering function evaluated for k corresponding to the first sharp diffraction peak in SiO_2 (reproduced from [48]), and panel (b) shows the same for a Lennard-Jones fluid, this time evaluated for k corresponding to the position of the principle peak in the static structure factor (reproduced from [49]). The temperatures in panel (b) are given in terms of *reduced units*, T^* , given by $T^* = \frac{k_B T}{\epsilon}$, where ϵ is the depth of the potential energy well.

ions within the cages formed by their neighbours, termed the β -relaxation, followed at longer time by the α -relaxation corresponding to the particles beginning to leave their cages. This β -relaxation is observed as a plateau in the incoherent scattering function, and we can see that the length of the plateau decreases rapidly with temperature, such that at higher temperature we see essentially exponential decay of the incoherent scattering function.

The diffusive time scale range of 1000-2000 configurations at 700 K proposed as being important from a consideration of the van Hove self-correlation function is shown between the dashed maroon lines in panel (a) of figure 4.8, and we can see that it is well into the α -relaxation regime, and corresponds to a time when many of the particles have left their cages. This provides us with further evidence that the important time scale for diffusion corresponds to one in which many ions have undergone a change in their local surroundings, *i.e.* have changed their local cages. This is discussed further in the next section, and the behaviour of the incoherent scattering function in chapter 5.

4.3 The cage correlation function

4.3.1 Introduction

The local structure of an ionic liquid is often described in terms of a network of linked polyhedra, which themselves are made up an ion (usually the cation), surrounded by its counter-ions. These polyhedra are linked together by sharing vertices, edges or faces, and these linkages constrain how the network may move.

BeF_2 is made up of vertex shared BeF_4 tetrahedra. In an *ideal* network, each BeF_4 tetrahedron is linked through each of its vertices to four further tetrahedra, and so the network structure propagates. For an ion to move through such an ideal network, there must be a change in the local structure, normally associated with the breaking of a Be-F bond and the creation of a *defect* site, followed by the relaxation of the local network around this defect. This defect is an ion which does not have the usual, tetrahedral coordination environment, such as 3- or 5-coordinate Be^{2+} ion or a uni-coordinate F^- ion. Figure 4.10 shows the typical types of local ionic motion which we might anticipate.

We might imagine the cation-centred polyhedra as decaying by the central cation moving out of the polyhedron through one of the faces, with the anions relatively *immobile* during the passage of the cation, and this is shown in panel (a) in figure 4.10. This is the type of motion observed in *fast-ion conductors* such as AgI: these materials are crystalline, but one of the ionic sub-lattices is essentially molten, the Ag^+ sub-lattice in AgI, and the crystalline nature is maintained by the I^- ions remaining on their lattice sites. The other extreme of behaviour is observed, for example, in a dilute solution of LaCl_3 in KCl, where the La^{3+} ion moves whilst keeping its first coordination sphere intact, *i.e.* the La^{3+} ion diffuses as a LaCl_n^{3-n} species ($6 \leq n \leq 9$) and only slowly exchanges its neighbour ions with the bulk [45]. In BeF_2 both species are molten, and the F^- ions in fact move slightly faster than the Be^{2+} ions ($D_F \approx 1.1D_{Be}$). It is therefore probably better to think of the cation polyhedra relaxing due to the motion of the anions at the vertices. Panel (b) in

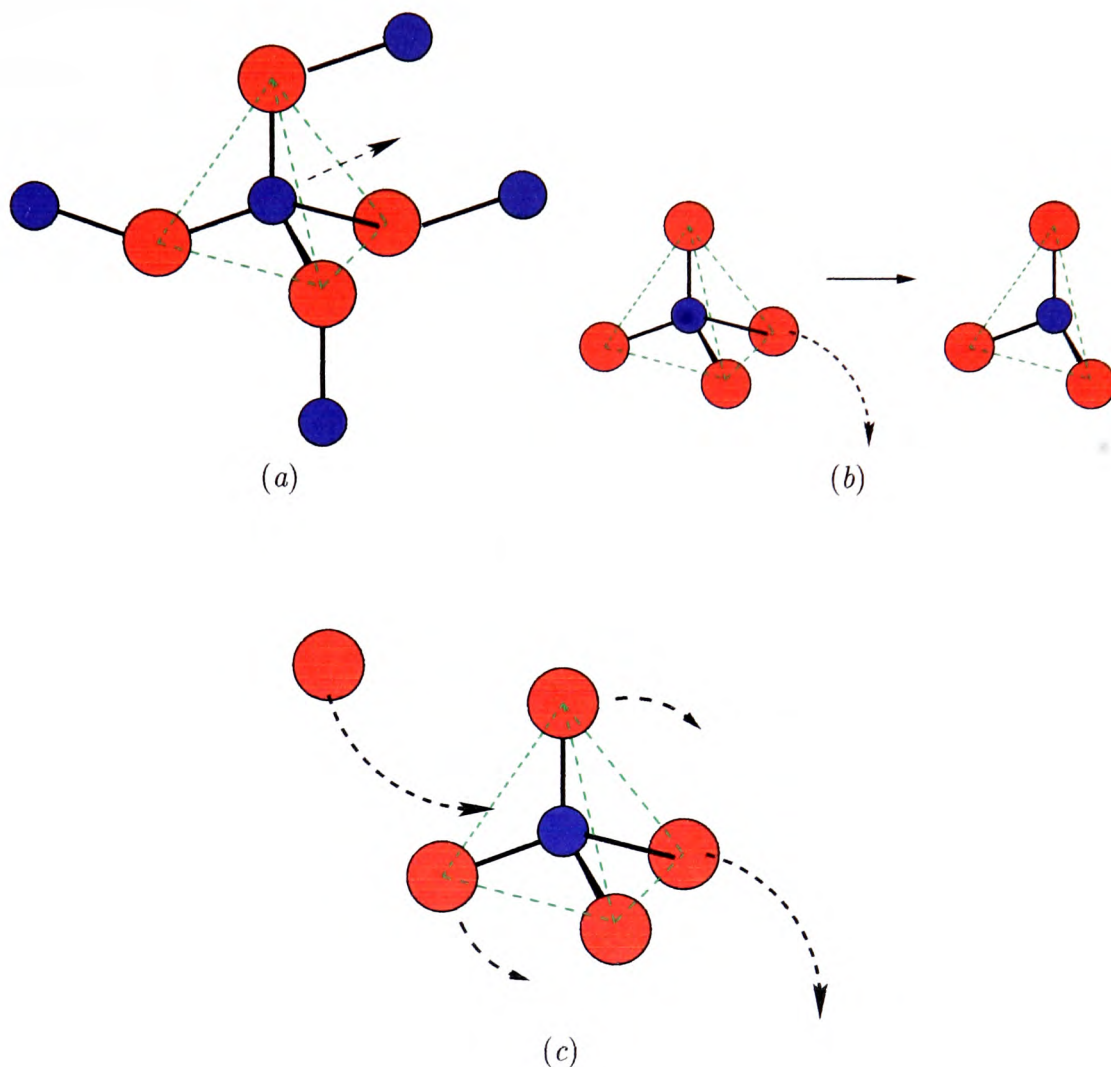


Figure 4.10: Panel (a) shows the structural decay of a BeF_4 tetrahedron through the loss of the central cation, shown in blue, through one of the faces of the tetrahedron, made up of the anions shown in red (the dashed green lines represent the tetrahedron). The tetrahedron itself is part of an extended network, as shown by the linking of the anions to further cations, which themselves are *bonded* to further anions. Panel (b) shows the structural decay of a BeF_4 tetrahedron through an S_N1 -like mechanism. The right-hand-most anion departs the first coordination sphere of the central cation, as depicted by the dashed arrow, leaving behind a 3-coordinate cation. Panel (c) shows the structural decay of a BeF_4 tetrahedron through an S_N2 -like mechanism. The long dashed arrows imply large scale ionic motion, resulting in the breaking or formation of a bond, while the short dashed arrows imply motion without changing the bonding. The anion at the top left of the figure enters the coordination sphere of the central cation as the right-hand-most anion leaves the coordination sphere. At the same time, there is a rearrangement of the positions of the other bonded anion to accommodate the new anion and to remove the *vacancy* left by the departing anion. This mechanism will proceed through a 5-coordinate intermediate.

figure 4.10 shows a simple example of this type of motion, where the tetrahedron decays through the loss of one of the ions at the vertices, to leave behind a cation coordinated to only three anions. This is reminiscent of the S_N1 -like reactions in substitution in organic compounds. Panel (c) in figure 4.10 shows an example of the decay through a more concerted type of motion: the departing anion at the vertex of the tetrahedron only leaves when the entering anion is very close to the central cation, and ready to form a bond. This is similar to the S_N2 -like reactions of substitution of organic compounds.

The relative importance of these different types of decay can be linked to the rigidity of the network. The S_N2 -like decay involves the approach of an anion from outside the cation polyhedron, and it is likely in the extended network that this anion will also be part of another polyhedron. Hence, this type of rearrangement requires the concerted motion of more than just a single coordination shell. However, the S_N1 -like rearrangement involves only the first coordination shell, *i.e.* the anions making up the polyhedron, and to a much lesser degree further coordination shells (there must be some further relaxation around the departing anion in order for there to be some empty space into which it can move in the dense fluid).

4.3.2 Constraints and Rigidity in the Network

The atomistic relaxation processes outlined above are all mechanisms which might be envisaged to lead to the structural relaxation of the network. The common theme is that there will be some bond-breaking in the local coordination polyhedra, leading to some local loss of rigidity within these polyhedra, which increases the fluidity of the network as a whole.

The link between the rigidity of the network and the bonding patterns within it has been investigated [50, 51, 52, 53, 54, 55] in terms of the *constraints* on the ionic motion imposed by the network. This analysis states that an ion is only free to move when the number of constraints on the ion, n_c , such as bond length and bond angle constraints, is less than the number of degrees of freedom of the ion, n_d .

The constraints can be expressed in terms of the mean bonding number, or mean coordination, of an ion, $\langle r \rangle$, where the mean bonding number is given by

$$\langle r \rangle = \frac{\sum_r r n_r}{\sum_r n_r}, \quad (4.11)$$

where r is the number of bonds formed by a given ion, and n_r is the number of ions which form r bonds. It is found [56, 54] in various numerical simulations of $\text{Si}_x\text{O}_{1-x}$ systems that there is a critical mean coordination, $\langle r \rangle_c = 2.40$, where the number of constraints per atom equals the number of degrees of freedom per atom ($n_c = n_d$). Raman scattering experiments on $\text{Ge}_x\text{X}_{1-x}$ ($\text{X}=\text{S}, \text{Se}$) systems [57] have been interpreted as being consistent with a critical mean coordination closer to $\langle r \rangle_c = 2.46$.

This critical mean coordination provides a means of discriminating between types of network: for $\langle r \rangle_c < 2.4(6)$ the network contains rigid and floppy regions, and for $\langle r \rangle_c > 2.4(6)$ the network is an amorphous solid which is mechanically rigid. For example, experiments on chalcogenide glasses [58] have shown that their glass-forming ability is optimised when $\langle r \rangle_c$ is approached, *i.e.* as the network approaches mechanical rigidity.

In order to examine the rigidity of our network, we must calculate the mean bonding numbers of the ions within our system. We define $\langle r_\alpha \rangle$ as

$$\langle r_\alpha \rangle = 4\pi\rho_\beta \int_0^{r_{\alpha\beta}^{\min}} r^2 g_{\alpha\beta}(r) dr, \quad (4.12)$$

where $\langle r_\alpha \rangle$ is the mean bonding number of species α , ρ_β is the number density of the counter ion to species α , and $g_{\alpha\beta}(r)$ is the partial radial distribution function for β ions around a central α ion. The integral is performed up to the position of the first minimum in the partial radial distribution function, $r_{\alpha\beta}^{\min}$. The mean bonding number in BeF_2 is then

$$\langle r \rangle = \frac{1}{3}\langle r_{Be} \rangle + \frac{2}{3}\langle r_F \rangle, \quad (4.13)$$

but $\langle r_F \rangle$ is simply related to $\langle r_{Be} \rangle$ by $\langle r_F \rangle = \frac{1}{2}\langle r_{Be} \rangle$ (because $\rho_{Be} = \frac{1}{2}\rho_F$ in our definition of $\langle r_\alpha \rangle$ in equation 4.12) and so $\langle r \rangle = \frac{2}{3}\langle r_{Be} \rangle$. The temperature depen-

dence of the mean coordination is given in tables 4.1 and 4.2 for the PIM and RIM respectively. We can see that our PIM simulations pass through the critical mean coordination of $\sim 2.4(6)$ in the region 1000-1300 K, whereas our RIM simulations are well into the rigid regime at all simulated temperatures.

T [K]	$r_{BeF}^{\min}$ [au]	$4\pi\rho_F \int_0^{r_{BeF}^{\min}} r^2 g_{BeF}(r) dr$	$\langle r \rangle$
700	4.50	3.91	2.61
800	4.50	3.84	2.56
900	4.50	3.77	2.51
1000	4.50	3.71	2.47
1100	4.50	3.67	2.45
1300	4.45	3.57	2.38

Table 4.1: The temperature dependence of the mean bond number, $\langle r \rangle$, in PIM BeF₂.

T [K]	$r_{BeF}^{\min}$ [au]	$4\pi\rho_F \int_0^{r_{BeF}^{\min}} r^2 g_{BeF}(r) dr$	$\langle r \rangle$
1300	4.45	4.00(6)	2.67(1)
1425	4.45	4.00(5)	2.67(0)
1550	4.50	4.01(0)	2.67(3)
1800	4.50	4.00(8)	2.67(2)
2100	4.55	4.01(3)	2.67(5)

Table 4.2: The temperature dependence of the mean bond number, $\langle r \rangle$, in RIM BeF₂.

We can see from figure 3.8, which shows the temperature dependence of the ionic diffusion coefficients in PIM BeF₂, that the agreement between the anionic diffusion coefficient calculated from the mean squared displacements and that scaled from the viscosity using the Eyring equation is excellent below ~ 900 K, and is slightly poorer at higher temperature. This might suggest that the hopping model on which the use of the Eyring equation is based is compromised in the higher temperature region when the system is no longer *over-constrained*: in the RIM, there is good agreement (for the anions) between the diffusion coefficients calculated by both means across the whole simulated temperature range (see figure 5.3).

When a bond is broken, the coordination numbers of the ions which formed the

bonds decrease, and so the rigidity of the local network decreases (as $\langle r \rangle$ decreases). The types of local coordination sphere rearrangements outlined in section 4.3.1 are vital in generating the bond breaking events, which in the *constrained* network are required for any structural relaxation, and on the longer time scale diffusive motion, to occur.

4.3.3 Construction of the cage correlation function

The common theme of these proposed rearrangement schemes is that there is a change in the identity of the ions which make up the first coordination sphere of the central cation as it moves. In the rearrangement represented by panel (a) in figure 4.10, after the cation has moved out from the centre of the tetrahedron, it will no longer be coordinated to the anion at the far vertex, and in the rearrangements represented by panels (b) and (c) in figure 4.10, one anion has left, and one anion has left and another entered the first coordination sphere of the central cation respectively. Hence the decay of the cation polyhedra may be characterised by a change in the identity of the *surrounding* ions of the cation at the centre of the tetrahedron. The rate of this change in atomic surroundings can be measured by calculating the **cage correlation function** [59, 60]. The immediate surroundings of a given ion can be described as the set of neighbouring ions, or *cage*. This cage can be envisaged as the nearest neighbours in a crystal or the first solvation sphere in liquids. When a diffusive event occurs, there is a change in the set of neighbouring ions, as shown in figure 4.11.

In the extended system, we need to identify the ions which make up the cage of each given ion, and these are defined in terms of the *neighbour list*, ℓ_i , which is a vector, for ion i , of length N in an N ion system, where

$$\ell_i = \begin{pmatrix} f(r_{i1}) \\ \vdots \\ f(r_{iN}) \end{pmatrix} \quad (4.14)$$

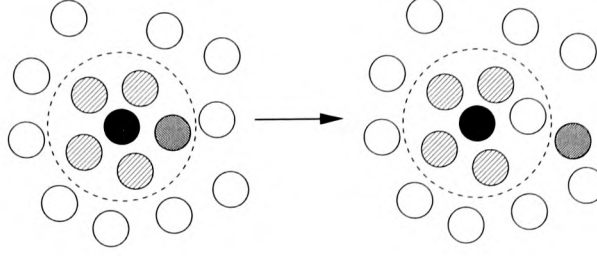


Figure 4.11: The *cage* of the black ion is shown as the dotted line. At time t the grey counter-ion is inside the cage of the black ion, but at time $t + \delta t$ it is outside, and has been replaced by a white counter-ion. The cage of the black ion has decayed and the cage correlation function is assigned a value of zero, even though four of the five original *cage ions* remain in the cage.

and where $f(r_{ij})$ is the Heaviside function,

$$f(r_{ij}) = \Theta(r_{\text{cutoff}} - r_{ij}) = \begin{cases} 1 & \text{if } |r_{ij}| \leq r_{\text{cutoff}} \\ 0 & \text{otherwise} \end{cases}. \quad (4.15)$$

The length scale, r_{cutoff} , defines the shell of counter-ions which surround a given ion, and is generally taken to be the position of the first minimum in the radial distribution function.

When the network relaxes as an ion moves out of one cage and into another, the neighbour list of the central ion will change, but most of the original counter-ions will still remain in the cage. We need a correlation function which relates the number and identity of neighbouring ions at time t to those at time $t + \delta t$, and hence is a measure of how much the cage has changed. We need to know the number of ions which have entered or left the cage. The number of ions which have left a given ion's cage at time t is given by

$$n_i^{\text{out}}(t, t + \delta t) = |\ell_i(t)|^2 - \ell_i(t) \cdot \ell_i(t + \delta t), \quad (4.16)$$

whilst the number of ions which have entered the cage is given by

$$n_i^{\text{in}}(t, t + \delta t) = |\ell_i(t + \delta t)|^2 - \ell_i(t) \cdot \ell_i(t + \delta t). \quad (4.17)$$

In these equations, $|\ell_i(t)|^2$ is the number of ions in the cage of ion i at time t , and $\ell_i(t) \cdot \ell_i(t + \delta t)$ is the number of ions in the cage of ion i at both time t and time

$t + \delta t$.

As we are interested in how much the cage has changed, we need to define the number of cage-ions which must change, c , either by entering or leaving the cage, for that cage to be considered as having decayed. Only when this desired number of ions have entered or left the central ion's neighbour list can we consider the cage to have decayed, and so we may variously define the cage correlation functions as

$$C_{cage}^{in}(t) = \langle \Theta(c - n_i^{in}(0, t)) \rangle, \quad (4.18)$$

$$C_{cage}^{out}(t) = \langle \Theta(c - n_i^{out}(0, t)) \rangle, \quad (4.19)$$

$$C_{cage}^{in-out}(t) = \langle \Theta(c - n_i^{in}(0, t)) \Theta(c - n_i^{out}(0, t)) \rangle, \quad (4.20)$$

where the averages, $\langle \dots \rangle$, are over all ions, i , and multiple time origins, and Θ is again the Heaviside function,

$$\Theta(c - n_i(0, t)) = \begin{cases} 1 & \text{if } n_i(0, t) < c \\ 0 & \text{otherwise} \end{cases}. \quad (4.21)$$

$C_{cage}^{in}(t)$ refers to cage decay processes which occur by $n \geq c$ ions entering the cage, $C_{cage}^{out}(t)$ to those processes where $n \geq c$ ions leave the cage, and $C_{cage}^{in-out}(t)$ to processes where there is an overall change in the neighbour list of $n \geq c$ ions, regardless of whether the change is by ions entering or leaving the cage.

The most general cage decay process is that in which a neighbour ion changes by leaving or entering, and most of the discussions in this thesis will focus on the behaviour of $C_{cage}^{in-out}(t)$, as discussed in section 4.3.4.

4.3.4 The cage correlation function in multi-component systems

In multi-component systems, the situation is more complicated. Ions are usually surrounded by their counter-ions, but in certain configurations ions of the same type may enter the cage, as the separation of the like ions may be smaller than the cut-off distance. We need to construct the neighbour list for a given ion to take account of the fact that the ions within the cut-off distance may be of different species. This

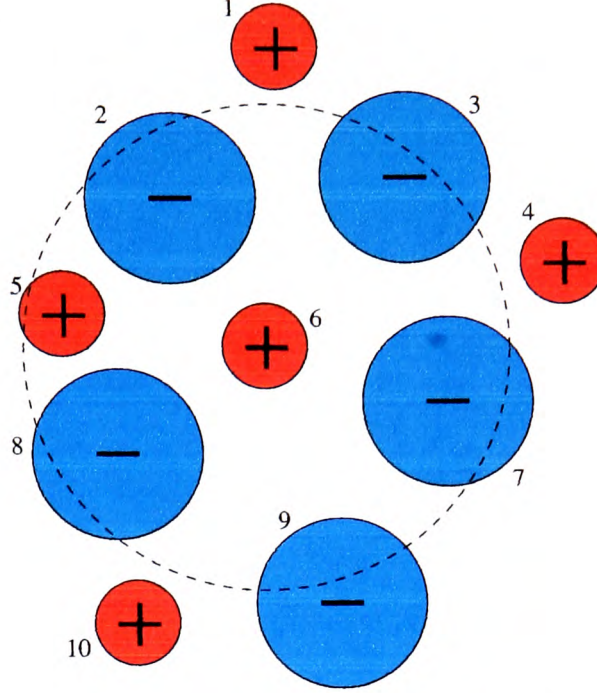


Figure 4.12: This is an example of the calculation of the neighbour list, ℓ_i , for a multi-component system, here showing cations in red and anions in blue. The dashed line indicates the cut-off radius, r_{cutoff} , around the central cation, **6**. Ion **9** does not contribute to the neighbour list since its centre lies outside the cut-off radius. The calculation of the mixed cage correlation function, as defined in equation 4.22, requires that the neighbour list of the central cation runs over only the anions, and so ion **5** will also not contribute to the neighbour list even though it lies inside the cut-off radius.

situation is shown in figure 4.12.

In the multi-component system, we can define the cage correlation function according to the nature of the ion at the centre, α , and those making up the neighbours, β , e.g. for the *in-out* function, according to

$$C_{\alpha\beta}^{\text{in-out}}(t) = \langle \Theta(c_\alpha - n_{i_\alpha\beta}^{\text{in}}(0, t)) \Theta(c_\alpha - n_{i_\alpha\beta}^{\text{out}}(0, t)) \rangle, \quad (4.22)$$

where the averages, $\langle \dots \rangle$, run over ions of species α , i_α , and multiple time origins, and where c_α is now dependent on the nature of the ion at the centre of the cage, i.e. for an $\alpha\beta_n$ cage, where there are n β ions surrounding a central α ion, the maximum c_α value is n . $n_{i_\alpha\beta}^{\text{out}}(0, t)$ refers to the number of ions of species β which have left the neighbour list of the central ion, i , of species α , in time, t . In a two

component system, such as BeF_2 , we can therefore construct a total of four (in-out) cage correlation functions, $C_{FF}^{in-out}(t)$, $C_{FBe}^{in-out}(t)$, $C_{BeF}^{in-out}(t)$, and $C_{BeBe}^{in-out}(t)$.

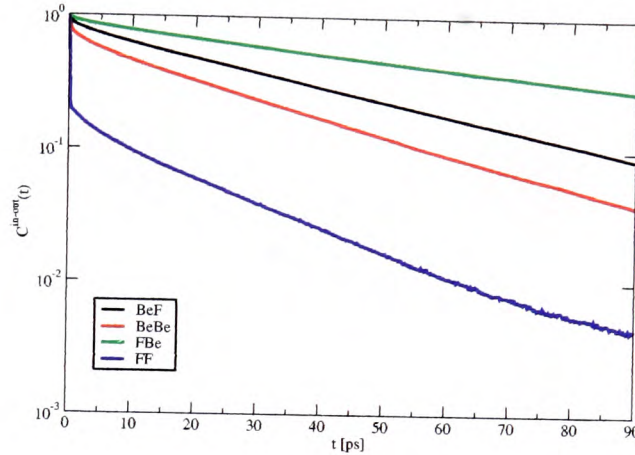


Figure 4.13: The different cage correlation functions, $C_{\alpha\beta}^{in-out}(t)$, in a two component system, shown for PIM BeF_2 at 700K.

From equation 4.22, it can be seen that calculating the BeBe and FF cage correlation functions involves no knowledge of the neighbour lists of the F and Be ions respectively. In these cases, we examine the decay of the individual sub-systems of ions, and, in effect, the counter ions act only as an oppositely charged background. The structural decay of the cations, for example, relative to each other, will necessarily involve the motion of the anions, as for one cation polyhedron to decay to allow the motion of its central cation (such that it may move relative to the other cations) there needs to be some motion of the anions making up that polyhedron. However, we can construct the cage correlation functions as given by equation 4.22, and then we can interpret the relative decay behaviour of, for example, the BeF function to the BeBe function in terms of the ionic motion occurring.

The different cage decay functions, $C_{\alpha\beta}^{in-out}(t)$, are shown, for $c_\alpha = 1$, in figure 4.13, for PIM BeF_2 at 700 K. The relative order of cage decay is $FF > BeBe > BeF > FBe$.

A striking feature of these functions is the very large initial decay in $C_{FF}(t)$. We can understand this by noting that this vibrational decay may occur without any change in the bonding topology of the network, *i.e.* there may be a change in the positions of the F^- ions relative to the other F^- ions, and hence a decay in the FF cage correlation function, without there being any bond breaking events. This kind of motion corresponds to a rotation of the Be-F-Be triplet about the Be-Be axis, as shown in figure 4.14.

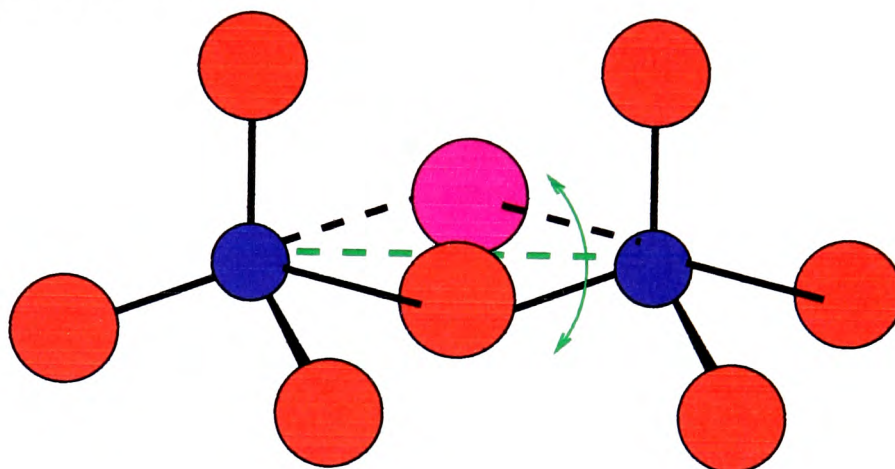


Figure 4.14: The fast decay in the anion-anion cage correlation function. The central anion, in red, is part of a Be-F-Be triplet, which may rotate about the Be-Be axis, shown with the dashed green line, to a new position, shown in magenta, which results in a change in the anion-anion neighbour list of this anion and/or surrounding anions. The two Be-F bonds remain intact during this motion, so it is relatively facile, and hence there is a very large initial rate of anion-anion cage decay.

Figure 4.15 shows the relative ionic motion which might lead to the decay of the cation-cation sub-system or the cation-anion cage. In this figure green arrows represent ionic motion. Let us consider two scenarios. The first scenario involves the bridging fluoride ion moving as shown by the arrow, resulting in the fission of the dashed BeF bond, which corresponds to a decay of the BeF cage around the right-hand Be ion. However, the separation of the two Be ions does not change, and their relative orientations do not change and so the BeBe cage remains intact. In the second scenario, the right-hand Be ion moves as shown, again resulting in the fission of

the dashed BeF bond, and again the BeF cage of the right-hand Be ion decays, but as there is a resultant separation of the two Be ions, now the BeBe cage also decays. The comparison of the behaviour of $C_{BeF}^{in-out}(t)$ and $C_{BeBe}^{in-out}(t)$ might therefore give some information on the relative importance of these two decay processes.

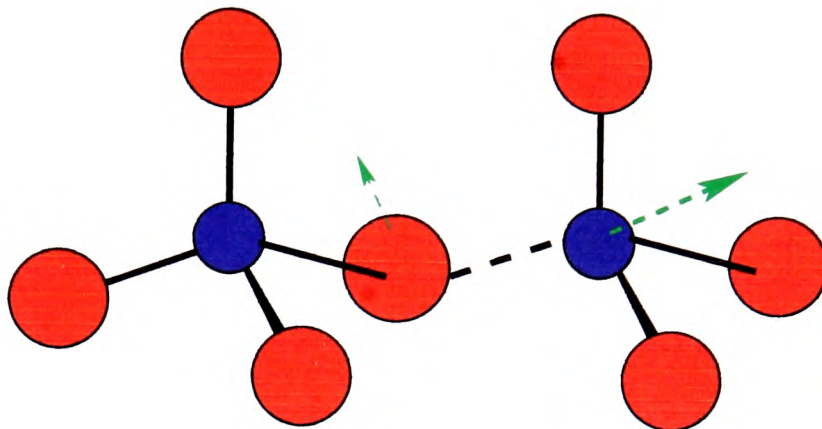


Figure 4.15: The relative ionic motions responsible for the cage decay of the different sub-systems. Ionic motion is implied by a dashed green arrow, and the BeF bond which gets broken as a result of these ionic motions is shown with a dashed black line. We may envisage two scenarios: i) The bridging fluoride ion moves as shown by the arrow, resulting in the fission of the dashed BeF bond, which corresponds to a decay of the BeF cage around the right-hand Be ion. The separation of the two Be ions does not change, and so the BeBe cage remains intact; and, ii) The right-hand Be ion moves as shown, again resulting in the fission of the dashed BeF bond and the decay of the BeF cage of the right-hand Be ion, but as there is now also a resultant separation of the two Be ions, the BeBe cage also decays.

From figure 4.13, we can see that the BeBe cage correlation function decays more quickly than the BeF function, and this implies that the second type of decay process is the more important: the first type of decay process allows BeF decay without BeBe decay, and hence the BeF decay would proceed more quickly, which is not what is observed.

4.3.5 Comparison of the out only and in-out functions in a multi-component system

Figure 4.16 shows the cage correlation functions, C_{BeF}^{in-out} and C_{BeF}^{out} , for PIM BeF₂ at 700 K, for $c_{Be} = 1, 2, 3, 4$. It can clearly be seen that the decay of the *out only*

function closely resembles that of the *in-out* function, particularly that the long time gradient of the two cage correlation functions for each c -value are the same. The principal difference between the two forms of the function is that the short time decay of the *in-out* function is faster than that for the *out only* function. This is because the structural decay may be decomposed into two contributions: the short time vibrational decay as ions move around in their local potential energy wells, and the longer time decay, responsible for the structural rearrangement proper, when the ions move from one potential energy well to an adjacent well. The diffusion coefficient reflects the motion of ions from one well to another. In the *in-out* function, we observe more of the short time vibrational decay, as a decay event is registered when an ion enters the cage of a given ion *and* when an ion leaves the cage of a given ion, whereas the *out only* function only records decay events when an ion leaves the cage of the given ion. The extra decay of the *in-out* function relative to the *out only* function therefore corresponds to the *in* decay events.

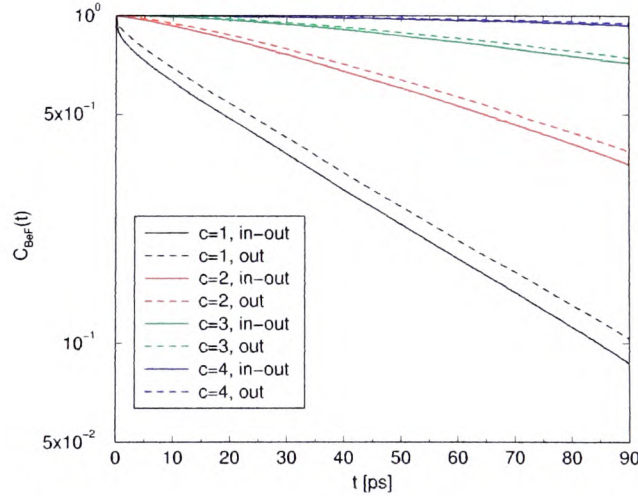


Figure 4.16: The C_{BeF}^{in-out} and C_{BeF}^{out} functions for different c_{Be} -numbers, where c_{Be} is the number of F^- ions which must change in the neighbour list of the central Be^{2+} ion for the cage to be considered as having decayed. The results shown are for PIM BeF_2 at 700 K. Note that the plot is shown with a logarithmic scale for the cage decay.

This similarity in the long time behaviour of the *in-out* and *out only* functions means that we need only consider one of them in interpreting the behaviour of the structural decay, and the properties of the cage correlation function, and we choose the *in-out* function as it contains all the relaxation events.

4.3.6 The dependence of the cage correlation function on the value of r_{cutoff}

The cut-off distance, r_{cutoff} , has so far been chosen as the first minimum in the relevant partial radial distribution function, $r_{\alpha\beta}^{\text{min}}$. This is not, however, a unique choice. Figure 4.17 shows the variation of the *in-out* and *out only* cage correlation functions with the choice of r_{cutoff} , for a small range of values around the first minimum in the BeF partial radial distribution function ($r_{\text{BeF}}^{\text{min}} = 4.5$ au), for PIM BeF₂ at 700 K. The inset of the figures show the long time behaviour of the cage correlation function, whilst the main plots show the short time, vibrational behaviour. The main difference between the behaviour with different r_{cutoff} values is the magnitude of the very short time drop in the value of the cage correlation function. This is a minimum when the cutoff is chosen as the first minimum in the partial radial distribution function, and increases as the cutoff value is moved away from the minimum, in either direction.

The most important observation, though, is that the long time behaviour of the cage correlation function is almost invariant on changing the value of the cutoff. The long time rate of cage decay is stable to small variations in the choice of r_{cutoff} around the minimum in the relevant partial radial distribution function. The reason for this is that the value of the BeF partial radial distribution function changes very little over a small range around the first minimum. Furthermore, the fact that the long time decay is independent of these small changes in r_{cutoff} means that it does not reflect the short-range motion of the ions around the first minimum: it corresponds to motion which is insensitive to the precise form of the partial radial distribution functions in this range, and hence corresponds to motion between different coordination

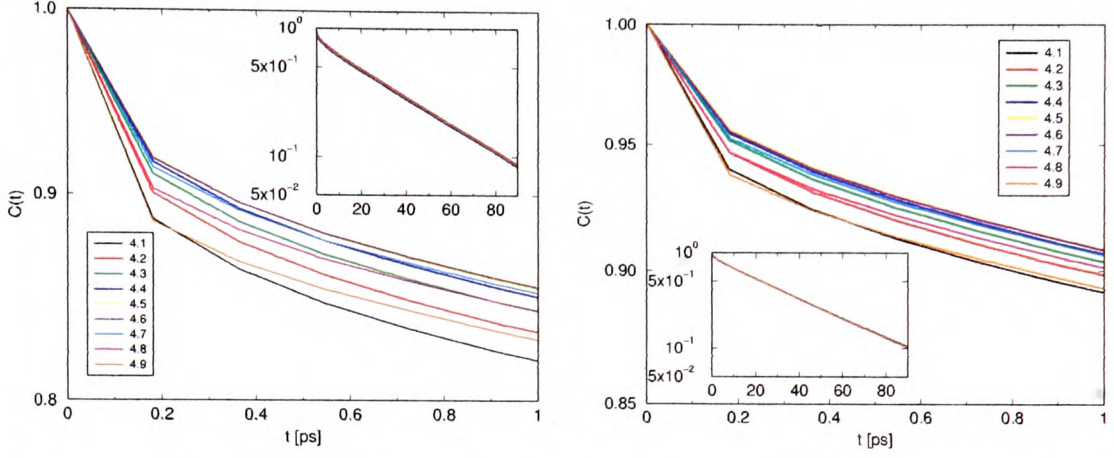


Figure 4.17: The $C^{in-out}_{BeF}(t)$ (in the left-hand panel) and $C^{out}_{BeF}(t)$ (in the right-hand panel) functions for $c_{Be} = 1$, for PIM BeF₂ at 700 K, with r_{cutoff} taking the values, in au, as shown in the legend. The main panels show the behaviour of the cage correlation functions over the first picosecond, whilst the insets show the behaviour over much longer time.

spheres.

4.3.7 The rate of cage decay

We define the cage decay rate, $k_{\alpha\beta}$, as the gradient of the long time part of the cage correlation function when expressed in exponential form. That is, we write the cage correlation function as

$$C^{in-out}_{\alpha\beta}(t) = C_0 \exp(-k_{\alpha\beta}t). \quad (4.23)$$

Figure 4.18 shows the cage correlation functions, $C^{in-out}_{BeF}(t)$ for $c_{Be} = 1$, in PIM BeF₂ across the range of simulated temperatures, together with the exponential fit of the form given in equation 4.23. Table 4.3 gives the fitted cage decay rates, $k_{\alpha\beta}$, for the *in-out* cage correlation function, for $c = 1, 2, 3, 4$.

The variation of the cage decay rate, $k_{\alpha\beta}$, with temperature is shown, for $C^{c=1,in-out}_{\alpha\beta}(t)$, in figure 4.19, together with the ionic diffusion coefficients. We can see that the temperature dependence of the cage decay rates closely resembles that of the diffusion coefficients, and so it is reasonable to conclude that by understanding the behaviour of the cage correlation function we may understand the diffusivity. Alternatively,

$c_\alpha = 1$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.0248	0.0316	0.0128	0.0415
800	0.106	0.166	0.0566	0.224
900	0.328	0.413	0.151	0.609
1000	0.524	0.728	0.245	1.50
1100	0.838	1.19	0.349	2.93
1300	1.29	1.70	0.584	5.96
$c_\alpha = 2$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.0117	0.0175	0.00326	0.0331
800	0.0727	0.0963	0.0217	0.175
900	0.189	0.241	0.0487	0.511
1000	0.283	0.404	0.0848	0.990
1100	0.473	0.574	0.130	1.58
1300	0.763	0.896	0.208	3.72
$c_\alpha = 3$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.00385	0.00789	–	0.0242
800	0.0381	0.0498	–	0.135
900	0.0981	0.126	–	0.402
1000	0.155	0.218	–	0.759
1100	0.235	0.339	–	1.27
1300	0.378	0.557	–	2.73
$c_\alpha = 4$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.000685	0.00187	–	–
800	0.0144	0.0181	–	–
900	0.0348	0.0436	–	–
1000	0.0583	0.0730	–	–
1100	0.0868	0.110	–	–
1300	0.123	0.199	–	–

Table 4.3: The fitted cage decay rates, of the form $C_{\alpha\beta}^{in-out}(t) = C_0^T \exp(-k_{\alpha\beta}^T t)$, for PIM BeF₂ across the simulated temperature range. Note, for example, that each F ion is (on average) bound to *only* two Be ions, and hence the FBe cage only contains two ions, and the cage correlation function, $C_{FBe}^{c=3,in-out}(t)$, will have little meaning and it has not been calculated.

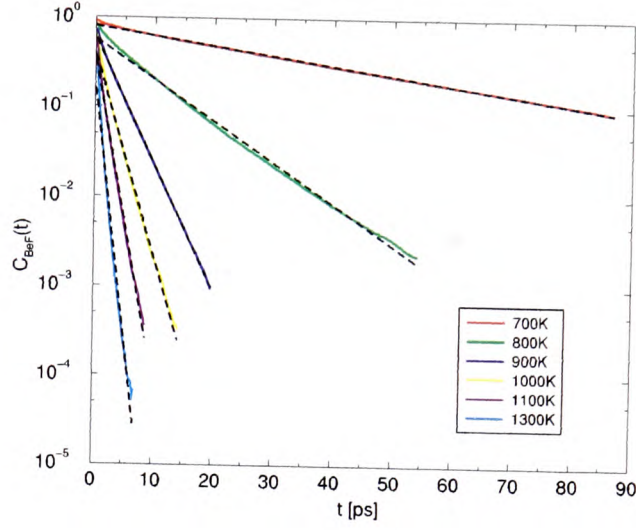


Figure 4.18: The cage correlation functions, $C_{BeF}^{c=1,in-out}(t)$, for PIM BeF₂ across the simulated temperature range. The dashed black lines are the exponential fit to the cage correlation function, of the form $C_{BeF}^{c=1,in-out}(t) = C_0^T \exp(-k_{BeF}^T t)$ in each case.

we can conclude that our proposed model of diffusion being controlled by the bond breaking or cage decay events is a good one, as the temperature dependence of the diffusion coefficients follows that of the cage decay rates. The link between the diffusion coefficient and the cage decay rate is explored further in section 4.3.9.

4.3.8 The dependence of the cage correlation function on the value of the number of neighbour ions which must change, c_α

Figure 4.16 shows the variation in the cage decay with the choice of c_α , that is the number of ions in the neighbour list of a given ion which must change for that cage to be considered as having decayed for PIM BeF₂ at 700 K. The variation of the cage decay rate with temperature is shown for the different c -values in figure 4.20 for the cation cage correlation functions, $C_{Be\beta}^{in-out}(t)$, and for the anion functions, $C_{F\beta}^{in-out}(t)$ (where $\beta \in \text{Be}, \text{F}$ in each case). The shape of the plot is approximately independent of the function chosen, and hence we can calculate the mean ratio of decay rates for

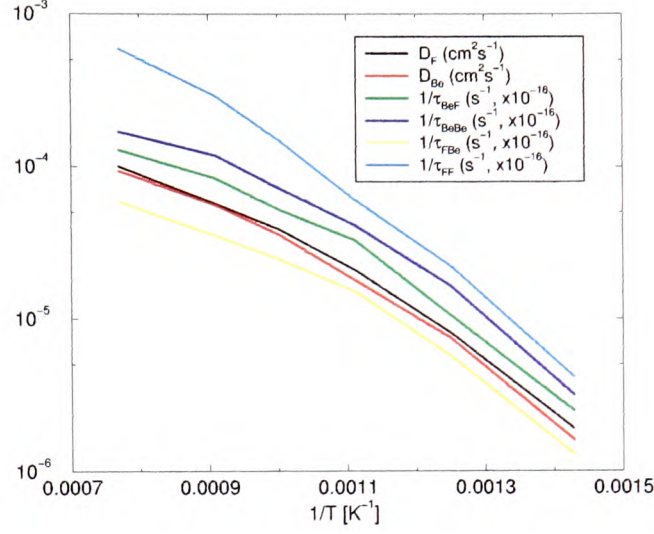


Figure 4.19: The temperature dependence of the cage decay rate for the $c = 1$ -*in-out* function in PIM BeF₂ across the simulated temperature range. Also shown for comparison are the ionic diffusion coefficients.

different functions across the whole temperature range without these ratios being dominated by the individual ratios at any given temperature. The inset to figure 4.20 shows the variation with temperature of the ratios of the rate of the BeF cage decay to the rate of the BeBe cage decay for the different c_{Be} values.

The ratio of the decay rate for changing one neighbour ion in the anion cage around a central cation to the decay rate for changing two neighbour ions, for example, can be calculated (for the *in-out* function) as

$$\begin{aligned}
 \frac{k_{BeF}^{c=1}}{k_{BeF}^{c=2}} &= \frac{1}{N_T} \sum_1^{N_T} \frac{k_{BeF}^{c=1}(T)}{k_{BeF}^{c=2}(T)} \\
 &= \frac{1}{6} \left\{ \frac{0.0248}{0.0117} + \frac{0.106}{0.0727} + \frac{0.328}{0.189} + \frac{0.524}{0.283} + \frac{0.838}{0.473} + \frac{1.29}{0.763} \right\} \\
 &= \frac{1}{6} \{ 2.12 + 1.46 + 1.73 + 1.85 + 1.77 + 1.69 \} \\
 &= 1.77,
 \end{aligned}$$

where N_T is the number of values of the temperature considered. The ratios of the different decay rates for all possible cages are given in tables E.1 and E.2, but we

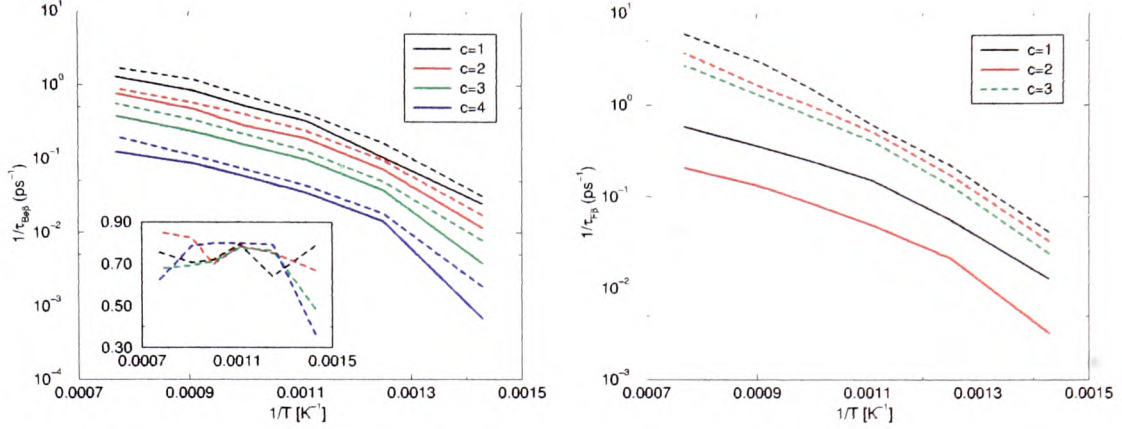


Figure 4.20: The temperature dependence of the cage decay rates for the cation (in the left-hand panel) and the anion (in the right-hand panel) cage correlation functions; k_{BeF}^{in-out} and k_{FBe}^{in-out} are shown with the full lines, and k_{BeBe}^{in-out} and k_{FFe}^{in-out} are shown with the dashed lines, for the c_α values as given in the legend. The inset shows the ratio of the BeF cage decay rate to the BeBe cage decay rate, $\frac{k_{BeF}^{in-out}}{k_{BeBe}^{in-out}}$, for the c_{Be} values as given by the legend.

should note primarily that $\frac{k_{BeF}^{c=1}}{k_{BeF}^{c=2}} = 1.77$ and $\frac{k_{BeF}^{c=1}}{k_{BeBe}^{c=1}} = 0.73$.

We can define the *cage lifetime* as the inverse of the cage decay rate, *i.e.* $\tau_{\alpha\beta} = \frac{1}{k_{\alpha\beta}}$: the cage lifetimes for the $c = 1$ -*in-out* cage correlation functions are given for PIM BeF₂ in table 4.4. As we might expect, these vary strongly with temperature, changing by around three orders of magnitude over a 600K range of temperature.

As calculated above, $\frac{k_{BeF}^{c=1}}{k_{BeF}^{c=2}} = 1.77$ which means that the rate of decay of the BeF cage by changing one neighbour ion is not simply twice the rate of decay of the BeF cage by changing two neighbour ions. If we measure the decay of the system in terms of the time taken to change one ion, $\tau_{BeF}^{c=1,in-out}$, and we assume that each change of c_α ions occurs by a series of *one-ion* changes, then we would expect the time taken to change two ions to be proportional to the probability of two of the *original* cage ions being changed multiplied by the time taken to change the first ion. For a four coordinate ion, there is a $\frac{1}{4}$ chance of changing a given first neighbour ion. After this change, there are only $\frac{3}{4}$ of the initial cage ions present, and hence the *effective* time taken to change one of these ions is $\frac{4}{3}$ the time taken to change the first cage ion

$c = 1$				
T [K]	τ_{BeF} [ps]	τ_{BeBe} [ps]	τ_{FBe} [ps]	τ_{FF} [ps]
700	40.3	31.6	78.2	24.1
800	9.44	6.04	17.7	4.46
900	3.05	2.42	6.64	1.64
1000	1.91	1.37	4.08	0.665
1100	1.19	0.843	2.86	0.342
1300	0.776	0.587	1.71	0.168
$c = 1$				
T [K]	τ_{BeF} [configs]	τ_{BeBe} [configs]	τ_{FBe} [configs]	τ_{FF} [configs]
700	1111	872	2156	665
800	260	166	487	123
900	84	67	183	45
1000	53	38	112	18
1100	33	23	79	9
1300	21	16	47	5

Table 4.4: The cage Lifetimes for the $c = 1$ -in-out cage correlation function in PIM BeF₂. The top half of the table shows the cage lifetimes in picoseconds, and the bottom in terms of the number of configurations outputted in the simulation to the nearest whole number (the *real* time elapsed between outputted configurations is 36.3 fs).

(as the time required is $1/\frac{3}{4}$ times the time required to change the first ion) because changing the incoming ion from the first cage decay event would represent no further decay of the *original* cage (although it would, of course, represent a decay of the cage from the *intermediate time*). This would result in a relative rate of $\frac{k_{BeF}^{c=1}}{k_{BeF}^{c=2}} = 2.33$. A similar increase of the relative rate above 2 would be predicted if, having changed one cage ion, the change of the second cage ion occurred by interchanging with the first-changed ion (which we might anticipate occurring as the first-changed ion is still likely to be fairly close by in space), as this situation again represents no further decay of the *original* cage.

However, the actual relative rate of changing two cage ions to changing one cage ion is *less* than 2, and this suggests that the changing of the second ion is *promoted* by the changing of the first ion, *i.e* it takes less time to change the second ion than to change the first ion. This may be suggestive of changes in the cage occurring when

there is a relatively large disruption of the local network; this large local disruption allows the change of the first ion and accompanying fast(er) change of the second ion.

We also calculated that $\frac{k_{BeF}^{c=1}}{k_{BeBe}^{c=1}} = 0.73 < 1$, *i.e.* the BeBe cage breaks up faster than the BeF cage. We can understand this by noting that the BeBe cage can decay, like the FF cage described earlier, without the need for bond-breaking events to occur. If the bent Be–F–Be triplet straightens, then the increase in separation of the Be ions may be enough to cause a change in the BeBe neighbour list and hence for the BeBe cage to decay. The constraints in the BeBe sub-system come from considerations of the Be–F–Be bond angle, rather than from direct Be–Be bonds, and the system is therefore less constrained than the BeF network. The fact that the relative rates are not too far from 1 suggests, however, that a large proportion of the BeBe cage decay events occur directly as a result of the decay of a BeF cage⁵.

The cage lifetime for the cage correlation function $C_{BeF}^{c=1,in-out}(t)$ is $\tau_{BeF} = 1111$ configurations at 700 K. This corresponds to the 1000-2000 configuration time scale proposed as being important from our analysis of the van Hove self-correlation function (see section 4.2.4). This suggests that we can use this cage lifetime, which varies with temperature, as the fundamental *clock* of the system: the diffusive processes proceed via a series of steps, each taking, on average, the cage lifetime to occur.

Figure 4.21 shows the van Hove self correlation function and the hydrodynamic approximation to it calculated at the cage decay time across the simulated temperature range for PIM BeF₂. The agreement between the functions at the different temperatures is very good, *i.e.* if we scale the dynamics in terms of the time taken for the characteristic diffusive hop to take place then the temperature variation of the diffusive time scales is eliminated. The temperature dependence of the cage decay rate accounts for the temperature dependence of the diffusive dynamics as a whole.

⁵Compare the value of $\frac{k_{BeF}^{c=1}}{k_{FF}^{c=1}} = 0.41$ (see table E.2) which means that the majority of FF cage decay occurs in the absence of any BeF cage decay.

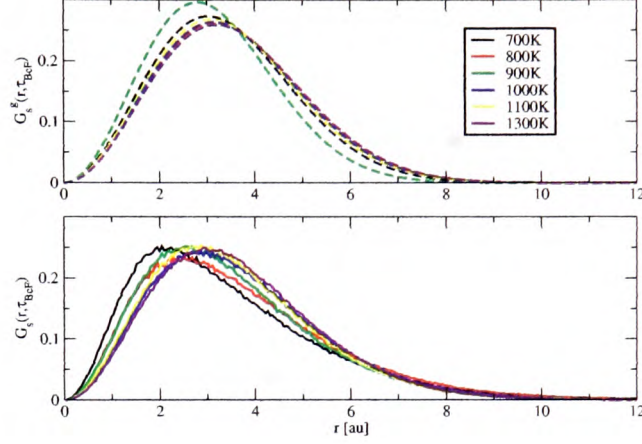


Figure 4.21: The van Hove self-correlation function, $G_s(r, \tau_{BeF})$, in the lower panel, and its hydrodynamic approximation, $G_s^g(r, \tau_{BeF})$, in the upper panel, for the Be^{2+} ions in PIM BeF_2 evaluated at the BeF cage decay time.

4.3.9 Calculating the diffusion coefficient from the cage decay rate

The van Hove self-correlation function analysis suggests that the important length scale is approximately the position of the first minimum in the partial radial distribution function. Over this length scale there is an excess of particle motion compared to the hydrodynamic limit. The diffusive process occurs in a series of steps, and we can use the length scale suggested by the van Hove self-correlation function as the length used to define the cage, or first coordination sphere, in calculating the cage correlation function and hence the cage decay rate. As the cage relaxation occurs by a series of jumps, and as those jumps are involved in the diffusive hops, we should be able to relate the cage decay rate to the diffusion coefficient. The diffusion coefficient of species α is defined according to the Einstein relation (equation 3.10). Using the cage lifetime, $\tau_{\alpha\beta}$, as the time scale in this equation, and defining the *jump length*, $\lambda_{\alpha\beta}$, as the distance an ion of species α surrounded by a cage of ions of species β must move in order for the cage to be considered as having decayed, we can relate

the diffusion coefficient to the cage lifetime according to

$$D_\alpha = \frac{1}{6\tau_{\alpha\beta}} \lambda_{\alpha\beta}^2. \quad (4.24)$$

This relationship is derived by replacing the mean ionic displacement by the jump length in the Einstein relation. We can then use the diffusion coefficient calculated using the Einstein relation to calculate the effective jump length

$$\begin{aligned} \lambda_{\alpha\beta} &= (D_\alpha \cdot 6\tau_{\alpha\beta})^{\frac{1}{2}} \\ &= \left(\frac{6D_\alpha}{k_{\alpha\beta}} \right)^{\frac{1}{2}}. \end{aligned} \quad (4.25)$$

Figure 4.22 shows ratio of the diffusion coefficients to the cage decay rates, $\frac{D_\alpha}{1/\tau_{\alpha\beta}}$, for the $c = 1$ -*in-out* function, from which the jump lengths may be calculated using equation 4.25. We can see that the ratio of the diffusion coefficients to the cage decay rates are approximately independent of temperature, and this suggests that the mechanism of diffusion is also independent of temperature. The similarity of the trends of the ratios for the BeF and BeBe cage decay rates show that these functions both reflect the same dynamical event, whereas the different temperature dependence of the FF ratio shows that this describes more the *wobbling* of the FF sub-system and is not related to diffusion.

Cage CF	λ_{BeF} [au]	λ_{FBe} [au]
$c = 1$ - <i>in-out</i>	3.77	5.75
$c = 2$ - <i>in-out</i>	5.01	9.93
$c = 3$ - <i>in-out</i>	7.36	—
$c = 4$ - <i>in-out</i>	13.9	—

Table 4.5: The *effective jump lengths*, $\lambda_{\alpha\beta}$, calculated from the ratio of the diffusion coefficient to the cage decay rate, for PIM BeF₂.

The jump length is the distance an ion has to move for the cage to decay. These values, given in table 4.5⁶, are comparable with the positions of the first minima

⁶The jump lengths for the cage correlation functions with $c > 1$ are *effective 1-ion* jump lengths, *i.e.* the distance one ion would have to jump to contribute all of the diffusive behaviour associated with the cage decay, which is actually due to the chance of multiple ions in the local coordination environment.

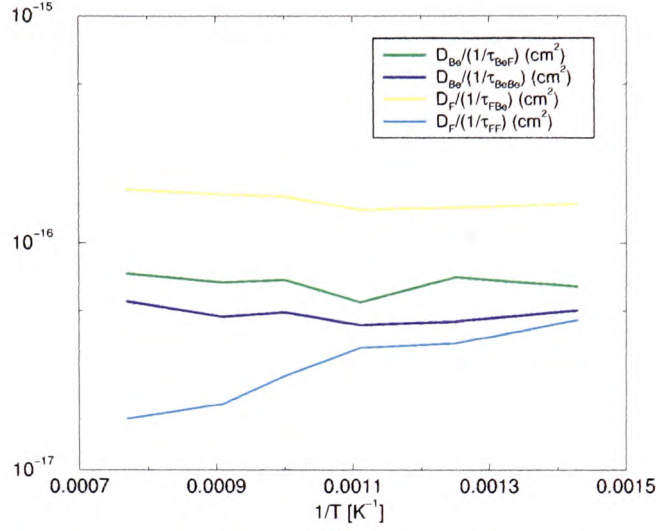


Figure 4.22: The ratio of the Diffusion Coefficients to the cage decay rate, from which the jump lengths may be calculated using equation 4.25. This figure shows the ratio of the diffusion coefficients to the cage decay rates shown in figure 4.19.

in the partial radial distribution functions, and consistent with the choice of these as our cutoffs for the calculation of the cage decay rate⁷. The jump lengths are actually *less* than the cage cutoff distances, $r_{\alpha\beta}^{\min}$, and this implies that there is some degree of *cooperative* motion in the network: an ion does not have to move quite the cutoff distance for the bond to break and the cage to decay as there is some cooperative rearrangement of the network whilst it remains intact which facilitates the ion changing cages.

Table 4.6 shows the jump lengths calculated from the cage correlation functions and with those calculated from the Eyring equation, compared with the important structural dimensions in the network.

The Eyring jump length is that calculated as being required to give precise agreement between the viscosity and the diffusion coefficient, and corresponds to the distance

⁷The difference between λ_{BeF} and λ_{FBe} can be accounted for by the fact that the rate of the BeF cage decay is double that of the FBe cage decay (there are *twice* as many FBe cages but the *same* number of cage decay events), and that the anion diffusion coefficient is slightly larger than that for the cation, $D_F \approx 1.1D_{Be}$, and so $\lambda_{FBe} \approx 1.1 \times \sqrt{2} \times \lambda_{BeF}$.

$\alpha - \beta$	first maximum [au]	first minimum [au]	Eyring jump length, λ_α [au]	cage jump length, $\lambda_{\alpha\beta}$ [au]
F-Be	2.90	4.50	6.96	5.75
Be-F	2.90	4.50	7.59	3.77

Table 4.6: The cage correlation function predicted and the Eyring equation predicted ionic jump lengths, compared with the typical structural dimensions in PIM BeF₂.

moved by an ion during the hopping event which the Eyring equation describes. We can see from table 4.6 that the Eyring jump length is approximately double that of the cage jump length ($\frac{\lambda_{\text{Eyring}}}{\lambda_{\text{cage}}} = \frac{7.59}{3.77} = 2.01$). In the hopping mechanism, the ion moves from one energy minimum to an adjacent minimum, or in terms of the structure of the network we might imagine a Be ion moving from the centre of one BeF₄ tetrahedron to the centre of the next. In order for this BeF₄ cage to decay, however, the central Be ion only has to move to the edge of the first coordination shell⁸, and does not have to travel the remainder of the distance into the centre of the adjacent coordination sphere. This simple relationship predicts that the Eyring hopping jump length should be around double that of the cage decay jump length, and this is as calculated.

4.4 The coordination number dependent cage correlation function

The cage correlation function allows us to define the important time and length scales over which the ionic jumps which correspond to the diffusive hops occur, and hence to relate the changes in the local coordination environments, or cage decay, to the ionic diffusion coefficients. However, we do not know how these cage decay events occur, other than being able to compare, for example, how the rate of the decay of the cage of second neighbour ions compares to that of first neighbour ions. An ideal network system, with every cation being four coordinate, is not free to move as the system is *over-constrained*, as described in section 4.3.2. When a cage

⁸Here we consider a cage to decay by the central ion moving out of the polyhedron rather than by losing one of the cage ions at the vertices.

decay event occurs, there is a change in the local environment of the ion and this allows the network to change its configuration and for the ions to move. The question now arises as to how the cage decay event itself occurs. Two scenarios can be envisaged. If the network is connected by strong bonds, such that the spontaneous breaking of the bond in the ideal tetrahedral network is unlikely, then the relaxation of a particular cage will be promoted by the migration of a coordination defect to its vicinity. In this picture the coordination defects, the populations of which were discussed in chapter 3, act as promoters of cage decay events and hence diffusion. The coordination defects would be present in the network because of its topology, perhaps because the bending of the Be–F–Be bond was incompatible with the existence of an ideal 4-coordinate network. In the alternative scenario, the Be–F bond is intrinsically weak and may be broken by the thermal agitation of the network, essentially *unimolecularly*. In this case the coordination defects arise simply as the transient consequences of bonds spontaneously breaking.

We can hope to distinguish between these scenarios by studying the lifetimes of the coordination defects themselves, and to this end we can construct the **coordination number dependent cage correlation function**, *i.e.* we calculate the cage correlation function as already outlined, but now we only consider those ions of a given coordination number.

In the definition of the cage correlation function, we have to consider the change in the identity of the ions in the neighbour list of a given ion in a time interval δt , *i.e.* we have to calculate the neighbour list at times t and $t + \delta t$. During the cage decay event, the coordination number of the central ion will change⁹, and so we need to consider the coordination number of the central ion at only one of the times used to calculate the neighbour lists. Hence the coordination number dependent cage

⁹The coordination number is defined as the average number of ions within a sphere of radius r_{cutoff} around a given ion, and we choose this radial cutoff as the position of the first minimum in the partial radial distribution function, *i.e.* the same as the radial cutoff for the calculation of the neighbour list, so as an ion moves out of the neighbour list, there will be a change in the coordination number of the central ion, unless the loss of one ion is compensated by the gain of another, or *vice versa*.

correlation function can be defined as

$$C_{cage}^{in}(t) = \langle \Theta'(N_i^c(0)) \Theta(c - n_i^{in}(0, t)) \rangle, \quad (4.26)$$

$$C_{cage}^{out}(t) = \langle \Theta'(N_i^c(0)) \Theta(c - n_i^{out}(0, t)) \rangle, \quad (4.27)$$

$$C_{cage}^{in-out}(t) = \langle \Theta'(N_i^c(0)) \Theta(c - n_i^{in-out}(0, t)) \rangle, \quad (4.28)$$

by comparison with equations 4.18, 4.19, and 4.20, where the averages, $\langle \dots \rangle$, are over all ions, i , and multiple time origins, and where $\Theta'(N_i^c(0))$ is again the Heaviside function,

$$\Theta'(N_i^c(0)) = \begin{cases} 1 & \text{if } N_i^c(0) = N^{c*} \\ 0 & \text{otherwise} \end{cases}, \quad (4.29)$$

where N^{c*} is the coordination number of interest.

Figure 4.23 shows the coordination number dependent cage correlation functions for $N^c = 3, 4, 5$ for the Be^{2+} ions in PIM BeF_2 at 700 K and 1300 K, for each of the *in only*, *out only* and *in-out* functions, and for $c = 1$. The relative concentrations of each type of coordination number, for 3-, 4-, and 5-coordinate ions respectively, are 9.7%, 89.8%, and 0.5% at 700 K, and 41.2%, 52.7%, and 3.6% at 1300 K. The very low concentration of 5-coordinate defect sites leads to the poor statistics for the $N^c = 5$ function, particularly at low temperature, but we can see that these species decay predominantly through the *out* mechanism, *i.e.* by losing an ion from the extended coordination shell. We can also see that the decay of the 5-coordinate sites occurs principally via the vibrational pathway, as shown by the very fast decay at very short time. For these reasons, it would appear that the 5-coordinate defect does not play a major role in diffusion in the PIM calculations, and arises only through the vibration of an ion into the coordination shell.

The decay of the 3-coordinate function at 700 K is more interesting. This is dominated by the *in*-process, restoring the 3-coordinate site to a 4-coordinate one. There is a very fast initial decay, which is to be associated with sites which are only transiently 3-coordinate as a consequence of a particularly large stretch of one of the Be-F bonds at a 4-coordinate site. This only accounts for about 30% of the decay of the correlation function. The remainder of the decay reflects the dynamics of

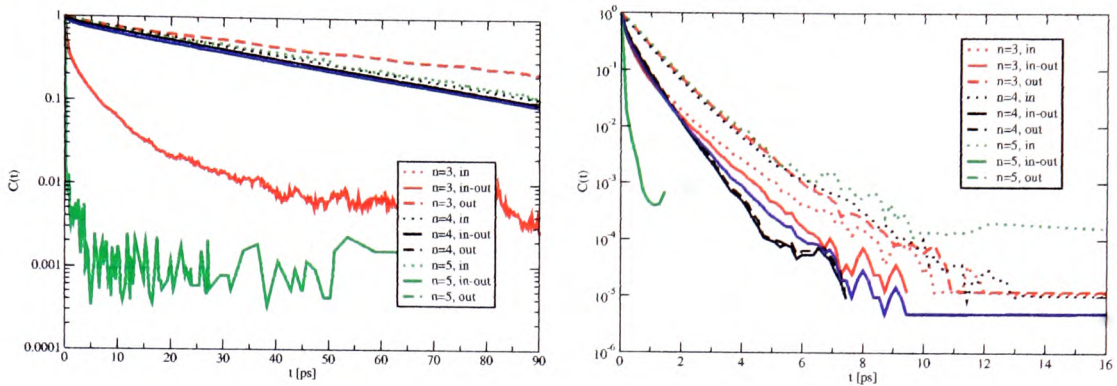


Figure 4.23: The coordination number dependent cage correlation function for Be^{2+} ions in PIM BeF_2 at 700 K (in the left-hand panel) and at 1300 K (in the right-hand panel). The $N^c = 3$ -in function is hidden behind the $N^c = 3$ -in-out function at 700 K, and the $N^c = 5$ -out functions are hidden behind the and $N^c = 5$ -in-out functions at both temperatures. The blue line shows the coordination number *independent* cage correlation function for comparison.

defect sites which are sufficiently long-lived to have an influence upon the diffusive process. As panel (a) of figure 4.23 shows, the bulk of this decay, from about 0.5 ps to 25 ps and relaxing the correlation function to about 1% of its initial value, is non-exponential and occurs on a considerably faster time scale than the relaxation of the dominant 4-coordinate species. As the temperature is raised to 1300 K the distinction between the relaxation rates of the different functions is much less marked, suggesting that any particular dynamical role for the 3-coordinate sites is much reduced compared to the lower temperature.

At the longest times all of the coordination number dependent cage correlation functions relax exponentially, as shown in figure 4.24. This exponential portion dominates the relaxation of the 4-coordinate function but accounts for only a small part of the relaxation of the 3- and (in particular) the 5-coordinate functions. As table 4.7 shows, the associated decay constants for the 3- and 4-coordinate functions are quite similar, as also reflected by the inverse temperature dependence of the cage decay rates for the different species shown in figure 4.25. The existence of a distinc-

tive intermediate time scale relaxation process for the 3-coordinate sites, at least at the lowest temperatures, is compatible with a model in which the 3-coordinate defects act as promoters of cage relaxation, and hence diffusion in the network, at these temperatures. If, say, the proportion of 3-coordinate sites was 10% and such a site was involved in every cage relaxation of a 4-coordinate site, then the 3-coordinate cage decay rate would be ten times greater than that of the 4-coordinate site. As the temperature rises (and consequently the proportion of defect sites increases) the distinction between the two time scales diminishes, and when the proportion becomes very large it becomes meaningless to invoke the defects in the network relaxation.

$N_{Be}^c = 3$			
T [K]	k_{BeF} [ps^{-1}]	τ_{BeF} [ps]	τ_{BeF} [configs]
700	0.0549	18.2	502
800	0.0770	13.0	358
900	0.256	3.91	108
1000	0.444	2.25	62
1100	0.722	1.39	38
1300	1.20	0.831	23
$N_{Be}^c = 4$			
T [K]	k_{BeF} [ps^{-1}]	τ_{BeF} [ps]	τ_{BeF} [configs]
700	0.0250	39.9	1101
800	0.107	9.33	257
900	0.339	2.95	81
1000	0.542	1.85	51
1100	0.875	1.14	31
1300	1.73	0.579	16
$N_{Be}^c = 5$			
T [K]	k_{BeF} [ps^{-1}]	τ_{BeF} [ps]	τ_{BeF} [configs]
700	0.223	4.48	124
800	0.428	2.34	64
900	0.834	1.20	33
1000	1.01	0.988	27
1100	2.12	0.472	13
1300	4.36	0.230	6

Table 4.7: The coordination number dependent cage correlation function long time cage decay rates and cage lifetimes for $N^c = 3, 4, 5$, for PIM BeF₂.

The role of the defects in promoting diffusion can also be examined by comparing

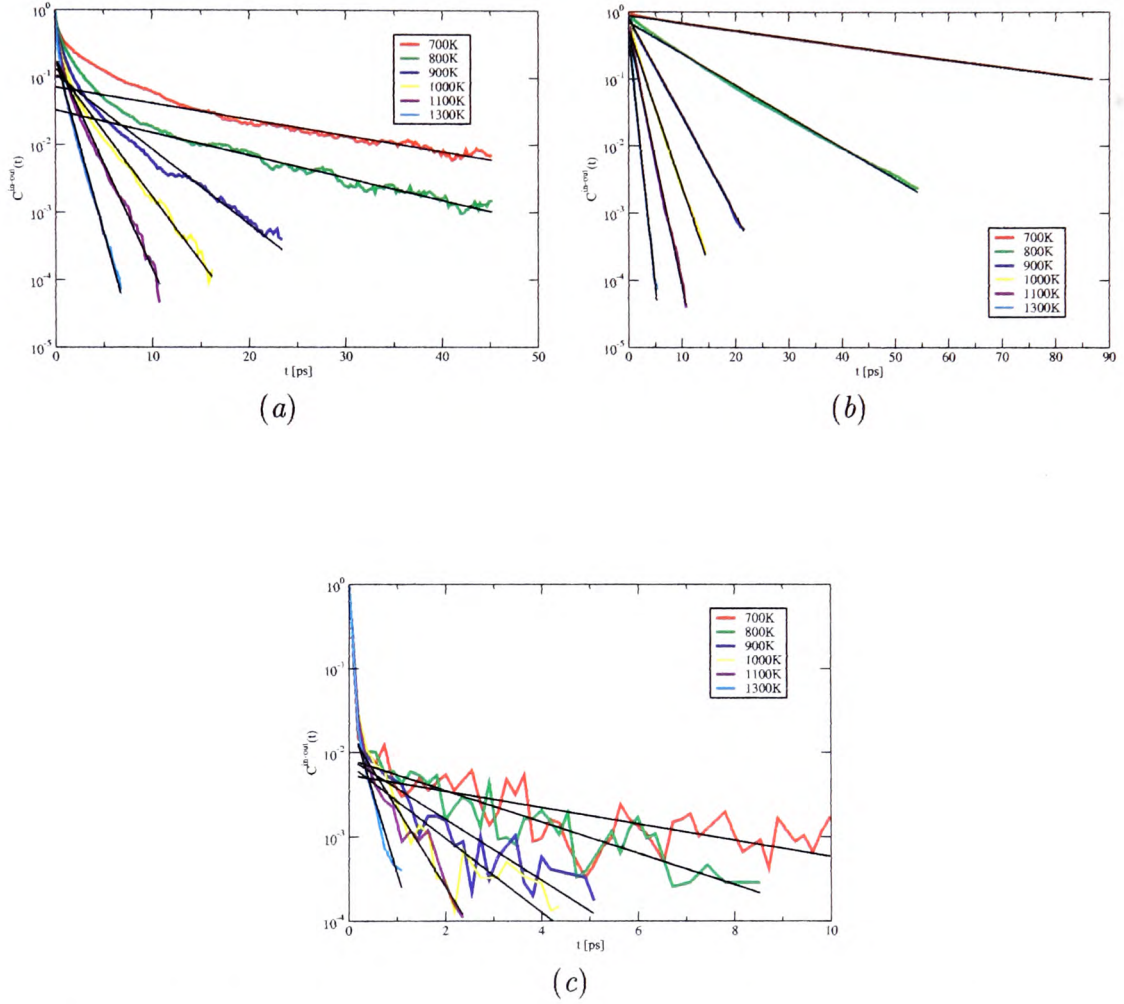


Figure 4.24: The temperature dependence of the coordination number dependent cage correlation function, $C_{BeF}^{c=1,in-out}(t)$, for (a) 3-coordinate, (b) 4-coordinate, and (c) 5-coordinate Be^{2+} ions in PIM BeF_2 . The exponential fits to the long time decay of the functions are shown in black.

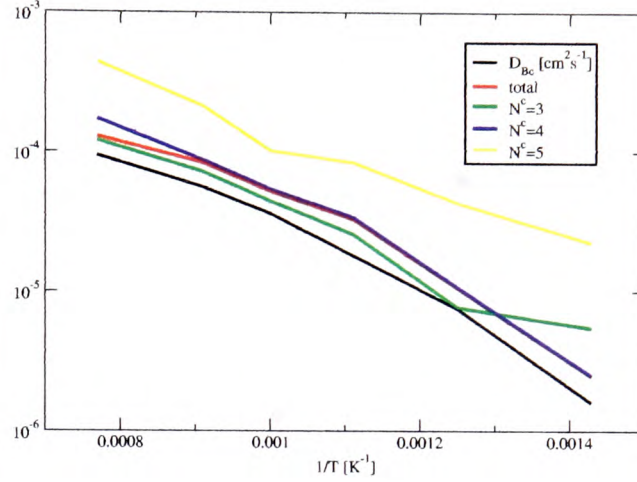


Figure 4.25: The variation of long time cage decay rate with inverse temperature, for the coordination number dependent cage correlation functions, $C_{BeF}^{c=1,in-out}(t)$, for $N^c = 3, 4, 5$, for PIM BeF₂. The cage decay rates are in ps⁻¹ ($\times 10^{-4}$). Also shown is the cation diffusion coefficient, in cm²s⁻¹ and in black, and the cage decay rate for the coordination number *independent* cage correlation function, in red.

the temperature dependencies of the diffusion coefficients with that of the number of coordination defects. We may express the fraction of the cations which are defect sites, F_D , the mobility of the ions, and hence the overall diffusivity in an exponential, Arrhenius form, as given by

$$F_D \propto \exp\left(-\frac{E_A^{\text{form}}}{RT}\right), \quad (4.30)$$

$$D \propto F_D \exp\left(-\frac{E_A^{\text{mig}}}{RT}\right), \quad (4.31)$$

and therefore

$$D \propto \exp\left(-\frac{E_A^{\text{diff}}}{RT}\right). \quad (4.32)$$

Writing the diffusion coefficients in this form allows us to investigate the effect that the presence of the defect sites has, and then try to separate this from the motion of the ions in the absence of the defects. Figure 4.26 shows the variation of the

diffusion coefficient and defect populations with inverse temperature¹⁰.

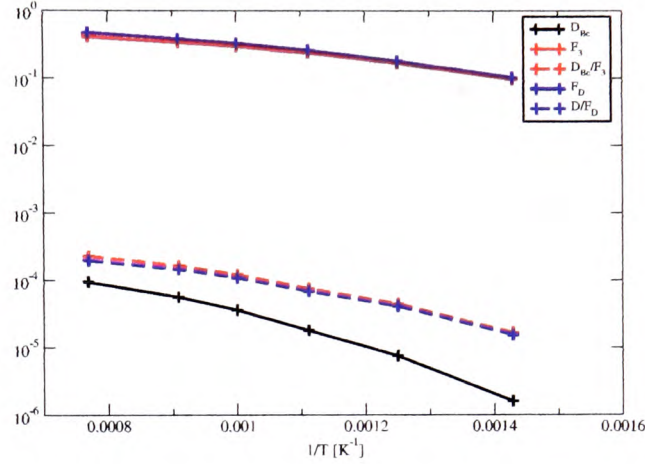


Figure 4.26: The variation of the cationic diffusion coefficients, populations of the different defect sites, and ratios of the diffusion coefficients to defect site populations with inverse temperature, for PIM BeF₂. F_D is the fraction of non-tetrahedral cation sites, $1 - F_4$, *i.e.* the total population of defect sites, and D_{Be} is given in cm²s⁻¹.

From fits of the calculated data in figure 4.26 to the Arrhenius forms in equations 4.30 to 4.32, we may obtain the activation energies for the formation of the defects, E_A^{form} , for the migration of the ions once the defects have been formed, E_A^{mig} , and for the overall activation energy of diffusion, E_A^{diff} ¹¹. The calculated activation energies are given in table 4.8. Note that the functions labelled with F_D refer to the total number of defects, *i.e.* $F_D = 1 - F_4$. We can see that the activation energy for the formation of a 3-coordinate defect is approximately half that for the ion migration in the presence of a 3-coordinate defect. That the activation energy for the formation of the 3-coordinate defect sites is slightly lower than for the formation of any defect suggests that the formation of the 3-coordinate sites is the easiest, and we will see in chapter 6 that the ability of the 3-coordinate site to promote structural

¹⁰We have not considered the 5-coordinate sites as *true* defects as we have seen that they largely exist only vibrationally.

¹¹Note that the Arrhenius form of these equations means that $E_A^{\text{diff}} = E_A^{\text{form}} + E_A^{\text{mig}}$.

rearrangement and ionic mobility in the surrounding network is enhanced compared to the 4- and 5-coordinate sites.

Function	E_A [kJmol ⁻¹]
D	51.5
F_3	18.3
F_D	19.3
$\frac{D}{F_3}$	33.2
$\frac{D}{F_D}$	32.1

Table 4.8: The activation energies for the formation of defects, the migration of ions after defects have formed, and for the overall diffusion coefficients. F_D is the total population of non-tetrahedral sites, *i.e.* $1 - F_4$.

In calculating the activation energies above, we have made a best fit of the Arrhenius form to the temperature variation of the diffusion coefficients and the numbers of defects: this assumes a linear dependence of $\log D_\alpha$ on $\frac{1}{T}$. However, there is actually some curvature in the plot of diffusion coefficient against inverse temperature. This curvature has been interpreted as the transition to *fragile* behaviour in the otherwise strong glass material [3]. When we divide out the population of defect sites, the curvature, on the logarithmic scale, of the reduced diffusion coefficient, $\frac{D}{F_D}$, decreases (this is the dashed blue line in figure 4.26). This suggests that the fragility in PIM BeF₂ is associated with the presence of non-tetrahedral cation sites. This curvature also means that the activation energies for defect creation and ion migration in the low temperature regime, where the diffusion is truly controlled by the action of the defect sites, will actually be higher than the values given in table 4.8. If we calculate the activation energies by fitting the curves in the low temperature regime (by using the 700 K and 800 K points only) we find $E_A^{\text{form}} = 26.4 \text{ kJmol}^{-1}$, $E_A^{\text{mig}} = 45.6 \text{ kJmol}^{-1}$, and $E_A^{\text{diff}} = 71.9 \text{ kJmol}^{-1}$. It may be more appropriate to discuss the activation energies which determine the role of the defects in the tetrahedral network in terms of these values, those calculated when the network is closest to being in the ideal regime with the PIM.

Figure 4.27 shows a set of configurations of PIM BeF₂ at 1300 K, which has the

highest defect concentration, each separated by 5 configurations, or 0.18141 ps, in comparison with the defect cage lifetimes of $\tau_{BeF}^{N^c=3} = 23$ and $\tau_{BeF}^{N^c=5} = 6$ configurations. As the simulation snapshots in this figure, running (a) through to (f), are separated by a time approximately equal to the cage lifetime of the 5-coordinate species, which are shown as magenta polyhedra, we might expect very few of these species to persist from one snapshot to the next (they are likely to decay to four coordinate species, which have not been drawn for clarity). This does appear to be the case, with only the $N^c = 5$ species at the bottom left of snapshots (e) and (f) persisting (shown in the *red* circles). The cage lifetime for the 3-coordinate species is longer, at approximately 4-5 snapshots, and we do appear to see these species persisting from one snapshot to another much more often. The 3-coordinate species in the *green* circles persists from snapshots (a) to (b), is absent in snapshot (c), but returns for snapshots (d) to (f). This an instance of what appears to be a cage decay when looked at by the naked eye, but what is probably a vibrational process being observed, *i.e.* an anion temporarily comes into the first coordination shell of the 3-coordinate cation to form a 4-coordinate cation ((b)→(c)) and is then lost to regenerate the 3-coordinate cation ((c)→(d)).

The use of molecular graphics techniques to look on the atomistic level can, therefore, give us some understanding of the types of motion occurring, but even on this small scale it is difficult to pick out the important events from the whole snapshot. The statistical analysis of the system as a whole by the cage correlation function approach affords us much more insight, and in turn aids us when as we search through the molecular graphics images for snapshots which show the important dynamical events.

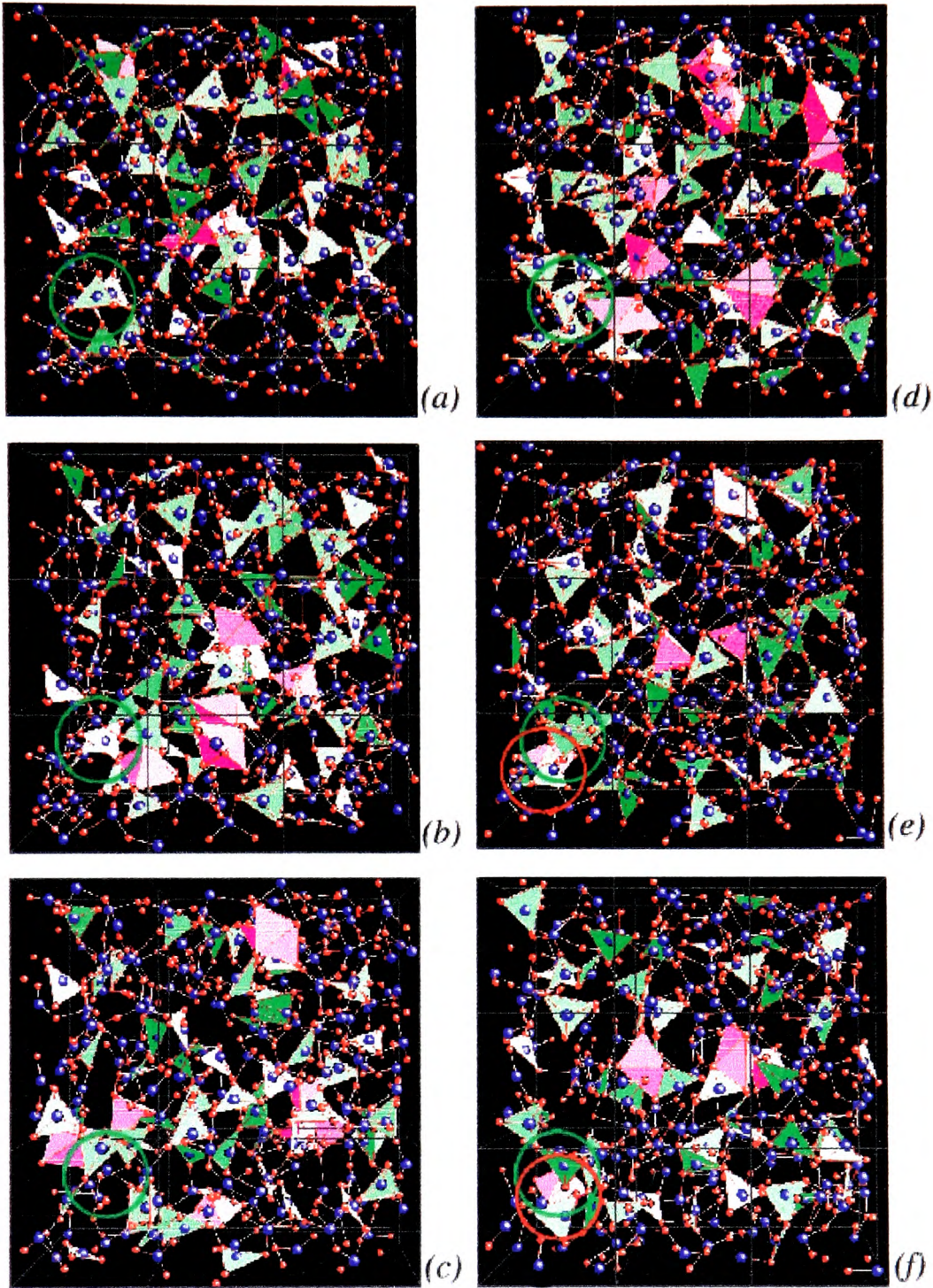


Figure 4.27: Snapshots of PIM BeF_2 at 1300 K, running (a) to (f), each separated by 5 configurations, or 0.18141 ps, with the Be^{2+} ions in blue and the F^- ions in red, and showing the 3-coordinate Be^{2+} ions as green planar triangles, and the 5-coordinate Be^{2+} ions with magenta polygons (triangular faces are drawn with the anions as the vertices). The cage lifetimes are $\tau_{\text{BeF}}^{N^c=3} = 23$ and $\tau_{\text{BeF}}^{N^c=5} = 6$ configurations. These figures have been produced using a modified version of the *MDview* program from S. Hull [8]. Note that the apparent defect concentration appears lower in these images than in the system (there are 40% 3-coordinate cations at this temperature) because those species with coordination shells which overlap the simulation cell boundaries have not been drawn, although the analysis takes these into account through the use of *periodic images* (see figure 2.3).

4.5 Summary of the cage correlation function results

The cage correlation function analysis identifies the processes leading to the structural breakdown of the local network around a given ion, and from this it has been shown that we can predict the diffusion coefficient from the cage decay rate, using the cutoff length for the cage as a jump length for the diffusive motion. We can conclude from this that the model of diffusion being controlled by a series of local cage break-ups which lead to further structural relaxation is a good one: the hopping of the system from one local energy minimum to the next on the potential energy surface for the system can therefore be identified with these cage decay events. It has also been shown that the high diffusivity of the PIM for BeF_2 seems to be linked to the high number of defect cation sites present, *i.e* the high number of non-tetrahedral sites.

The cage correlation function is, though, essentially a function of one coordination sphere: consideration of, for example, the cation-cation cage correlation function allows us to probe the second coordination sphere of cations around the central cation, but we cannot probe the second sphere of anions around the central cation. The analysis of the cage correlation function does not tell us, for example, how the defect sites relate to the *mobile* ions. We saw from the van Hove self-correlation function that there was an excess of particles with high displacements over a time scale of the cage lifetime when the mean displacement was of the order of the cage cutoff. It is these mobile particles which contribute most to the diffusion coefficient, and we would like to know what relation these mobile ions have to the defect ions, *e.g.* are they the same ions, or are the mobile ions, for example, in the first coordination sphere of the defect ions?

The relationship through space of the defect ions to mobile ions, and of mobile ions to other mobile ions, for example, has been examined using another set of correlation functions. The importance of the defect sites can be separated into the effect

on the magnitude of the diffusion coefficient, which we have seen is much higher in the PIM than the RIM, and which is discussed further in chapter 9, and also the effect on the nature of the species which are responsible for the high diffusivity, and this is discussed further in chapter 6.

Chapter 5

BeF₂: The Rigid Ion Model, and the comparison with the PIM

In chapter 3 we described how the RIM seems to give a good account of the dynamics of BeF₂, whereas the static structure is better described by the PIM. In this section, we present some of the results observed when BeF₂ is simulated using the RIM. It should be noted that the RIM Born-Mayer potential used is the same as the for the PIM, and the difference is that now no attempt is made to include the effects of polarisation in our model.

The main difference in the method of performing the RIM simulations to that outlined for the PIM is that we may use a longer time step. The fastest motion in the PIM is the oscillation of the dipoles, and hence we must use a time step short enough to allow accurate integration of the *dipolar* forces. In the RIM there are no dipoles, and the fastest motion is now the oscillation of the ions themselves, and we can use a longer time step and still integrate the *ionic* forces accurately. The time step used in the RIM simulations is 50 au; the positions, velocities, *etc.*, are still outputted every 100 time steps, so a *configuration* now corresponds to 0.121 ps, compared to 0.036 ps in the PIM.

5.1 The static structure of RIM BeF₂

The reduced intensity function for RIM BeF₂ at 1300 K and 2100 K is shown in figure 3.6. It has been described how the agreement with the experimental reduced

intensity function for the room temperature glass is poorer for the RIM than for the PIM. What, then, are the main differences in the structure between the RIM and the PIM?

Figure 5.1 shows the total and partial radial distribution functions for RIM BeF_2 at 1300 K. Also shown for comparison is the Be–F partial radial distribution function for PIM BeF_2 at 1300 K: on going from the PIM to the RIM, the height of the first peak in the Be–F partial radial distribution function increases and the width decreases, and the intensity in the region between the first and second peaks is also much reduced, with $g_{\text{BeF}}^{\text{RIM}} \approx 0$ in this region whereas $g_{\text{BeF}}^{\text{PIM}} \approx 0.3$. The running integral of the Be–F partial radial distribution function, shown in the inset to figure 5.1, also shows that the mean cation coordination number in the RIM is much closer to the ideal value of 4. These observations all suggest a *tightening* of the first coordination shell in the RIM.

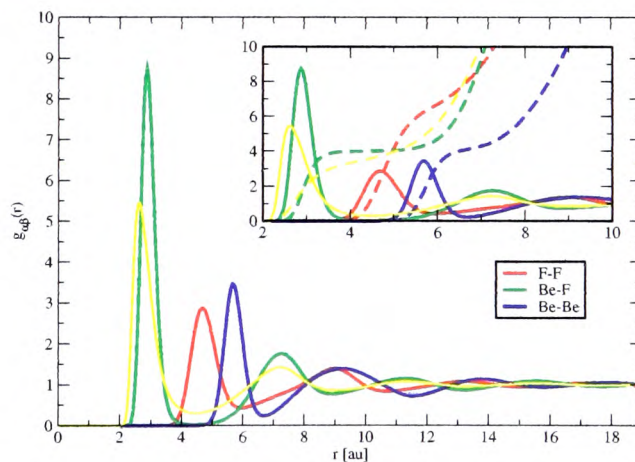


Figure 5.1: The total and partial radial distribution functions in RIM BeF_2 at 1300 K. Also shown, in yellow, is the Be–F partial radial distribution function for PIM BeF_2 at 1300 K. The inset shows the running integral of the partial probability distribution functions, from which the coordination number, N^c , where $N^c = 4\pi\rho_F \int_0^{r_{\text{BeF}}^{\text{min}}} r^2 g_{\text{BeF}}(r) dr$, may be calculated (the integral running up to the position of the first minimum of the partial radial distribution function, $r_{\text{BeF}}^{\text{min}}$).

Tables 5.1 and 5.2 show the variation with temperature of the population of the different cation coordination types and the tetrahedrality parameters respectively. The number of defect sites in the RIM is much lower ($F_D^{1300K} = 1.94\%$ compared to 47.34% in the PIM), and the low values of the tetrahedrality parameters also indicate a network in which the ions are much closer to being *ideally coordinated* than in the PIM.

System	$N^c = 3$	$N^c = 4$	$N^c = 5$
1300K	0.68%	98.06%	1.25%
1425K	1.27%	96.80%	1.92%
1550K	2.17%	94.54%	3.27%
1800K	5.66%	87.85%	6.40%
2100K	10.53%	79.25%	9.96%

Table 5.1: The temperature dependence of the populations of the different types of cation coordination environment in RIM BeF_2 .

System	S_g	S_g^4	S_k	S_k^4
1300K	0.0502	0.0452	0.00106	0.00100
1425K	0.0548	0.0477	0.00121	0.00111
1550K	0.0601	0.0496	0.00140	0.00124
1800K	0.0768	0.0561	0.00184	0.00151
2100K	0.1007	0.0624	0.00247	0.00181

Table 5.2: The temperature dependence of the tetrahedrality parameters in RIM BeF_2 , as shown for the PIM in table 3.4.

The RIM system, then, resembles much more closely the constrained system which relies upon the creation of defect sites for motion to occur.

The bond angle distribution functions for RIM and PIM BeF_2 are shown in figure 5.2. The main effect on the structure of the network of including the effects of polarisation is to reduce the Be-F-Be bond angle, as the bent unit becomes stabilised by the dipole which forms on the fluoride anion. However, as we can see from the radial distribution functions and the populations of the different types of coordination environment that another effect of polarisation is to (greatly) reduce the definition of the first coordination shell of anions around the cation, and to facilitate the

transfer of ions between coordination shells. The ability of the ions to move from one shell to another is very dependent on the precise locations of the ions within the coordination shells, and this is investigated further in chapter 7.

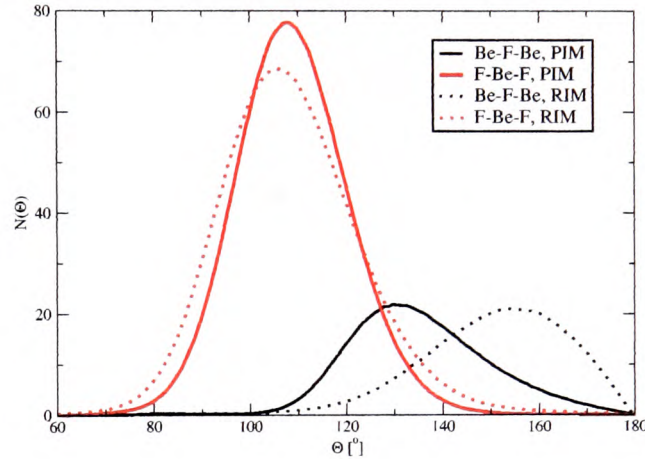


Figure 5.2: The bond angle distributions in BeF_2 , shown with full lines for the PIM at 700 K, and with dashed lines for the RIM at 1550 K. These temperatures are chosen for comparison due to the similarity of the ionic diffusion coefficients (see section 3.3). It can be seen that the main effect of including polarisation is a reduction in the Be–F–Be bond angle.

5.2 The diffusivity of RIM BeF_2

Figure 5.3 shows the diffusion coefficients calculated in the RIM using the Einstein relation, and those scaled from the calculated viscosities using the Eyring equation with jump lengths equal to the position of the first minimum in the partial radial distribution function, *i.e.* $\lambda_F = r_{\text{BeF}}^{\text{min}} = \lambda_{\text{Be}}$ which means that $D_F = D_{\text{Be}}$. The agreement between the calculated and viscosity-scaled diffusion coefficients is again very good, as in the PIM, suggesting that the hopping mechanism of diffusion described by the Eyring relation is a good model, and that, despite the differences in defect numbers, the type of dynamical behaviour is similar in the two fluids.

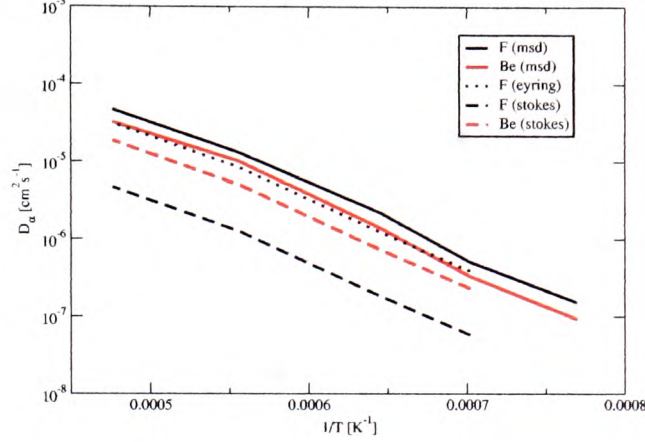


Figure 5.3: The ionic diffusion coefficients in RIM BeF₂ calculated from the Einstein relation, and scaled from the viscosity using the Eyring and Stokes equations, with the Eyring jump lengths being the position of the first minimum in the Be–F partial radial distribution function. The Eyring diffusion coefficient for the cations is omitted because the choice of identical Eyring jump lengths for the cations and anions means that the Eyring diffusion coefficients for the cations and anions are identical. The scaled values are not shown for the lowest temperature, 1300 K, because the stress tensor correlation function at this temperature does not converge, and so we cannot reliably calculate the viscosity.

If we use the viscosity and the diffusion coefficient to calculate the effective jump lengths required by the Eyring relation, then we obtain jump length values of $\lambda_F = 4.75$ au and $\lambda_{Be} = 6.95$ au, which are given in table 5.3 with the other characteristic dimensions in the system. The jump lengths in the PIM were $\lambda_F = 6.96$ au and $\lambda_{Be} = 7.59$ au.

5.3 The van Hove self-correlation function of RIM BeF₂

The van Hove self-correlation function and its Gaussian approximation are shown in figure 5.4 for the Be²⁺ ions in RIM BeF₂ at 2100K. The inset shows the difference between the two functions, $4\pi r^2 \Delta G_s(r, t)$. The time scales given in the legend are

$\alpha - \beta$	first maximum [au]	first minimum [au]	jump length, λ_α [au]
F-F	4.70	6.09	–
F-Be	2.86	4.49	4.74
Be-F	2.86	4.49	6.95
Be-Be	5.69	6.78	–

Table 5.3: The mean positions of the first minima and maxima in the partial radial distribution functions in RIM BeF₂ across the simulated temperature range, and compared with the jump lengths calculated from the Eyring relation.

in terms of numbers of configurations elapsed, where 14 configurations corresponds to the cage relaxation time, τ_{BeF} , in this system. If we compare the behaviour of the difference function with that shown for PIM BeF₂ at 700 K in figure 4.6¹ we can see that the PIM has a higher tendency to exhibit the bimodal behaviour, *i.e.* to have mobile and immobile particles.

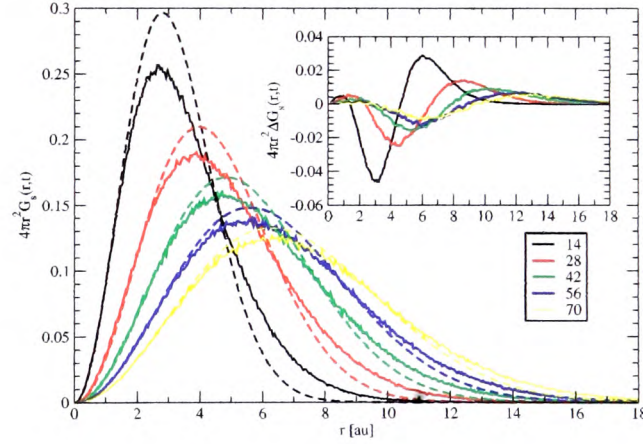


Figure 5.4: The van Hove self-correlation function, shown with full lines, and its Gaussian approximation, shown with dashed lines, in RIM BeF₂ at 2100 K. The inset shows the difference function, $4\pi r^2 \Delta G_s(r, t)$, and the time scales given in the legend are in terms of configurations, where 14 configurations is equal to the cage relaxation time, τ_{BeF} .

¹The cage relaxation time in the 700 K PIM system is 1111 configurations, and so the red to purple lines in figure 4.6 approximately correspond to 1-5 times the cage relaxation time, and in figure 5.4 the lines exactly correspond to 1-5 times the cage relaxation time.

The extra intensity, evaluated at τ_{BeF} , at small r , which corresponds to the immobile particles, is higher in the PIM than the RIM: the maximum value of $4\pi r^2 \Delta G_r(r, \tau_{BeF})$ in this region is ~ 0.08 in the PIM but only ~ 0.004 in the 2100 K². In the mobile region, *i.e.* at larger r where the particles have moved further than predicted by the hydrodynamic model, the maximum value of $4\pi r^2 \Delta G_r(r, \tau_{BeF})$ is ~ 0.015 in the PIM and ~ 0.028 in the RIM, so there is a higher probability of having moved further than expected in the RIM than in the PIM, although the difference between the two models here is less than in the immobile region, and this is a signature of the stronger network character in the RIM.

5.3.1 The incoherent scattering function in RIM BeF₂

The variation with temperature of the incoherent scattering functions for the cations and anions in RIM BeF₂ is shown in panel (a) of figure 5.5, and should be compared with figure 4.8 which shows the same functions for the PIM. The form of the functions is the same as that for the PIM, and the cage relaxation times correspond to the systems being well into the α -relaxation regime (as shown by the dashed lines in figure 5.5). The plateau persists longer in more of the simulations here, and this is because we are considering less diffusive systems ($D_{RIM}^{1550K} \approx D_{PIM}^{700K}$) and so in effect we are considering *colder* systems, closer to the glass transition, and hence with longer relaxation times. At higher temperature, though, we still recover the essentially exponential decay.

The dashed vertical lines representing the cage relaxation times at each temperature (see section 5.4), and we can see that the incoherent scattering function has decayed to approximately the same value, of around 0.2 – 0.3, at each temperature at the cage relaxation time, and that this value is the same as that in the PIM (see figure 4.8 which shows the approximate cage decay time for PIM BeF₂ at 700 K).

²We can compare these values directly because we have scaled the time in terms of the cage relaxation time, and we have seen that expressing the van Hove self-correlation function in terms of the cage relaxation time allows the systems at different temperatures to be reduced to a single curve (see figure 4.21).

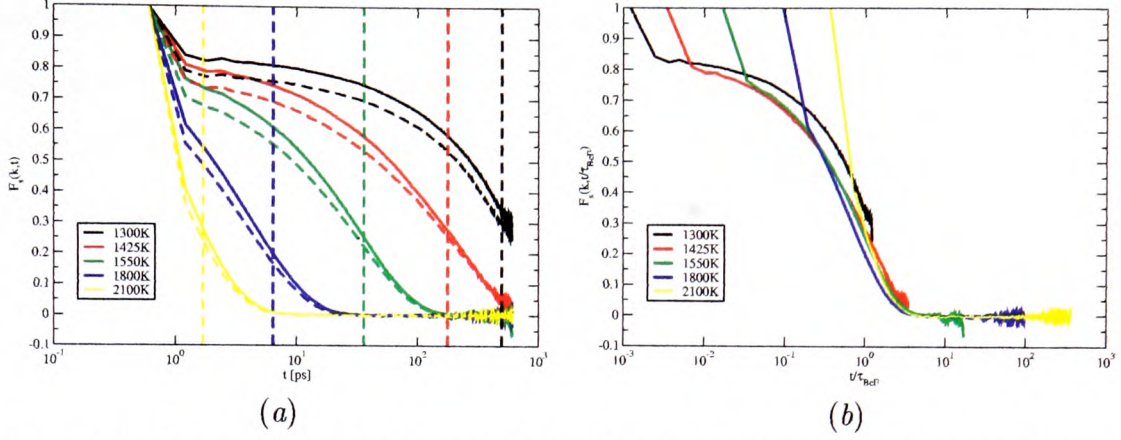


Figure 5.5: Panel (a) shows the variation with temperature of the incoherent scattering function, $F_s(k, t)$, for the cations (in solid lines) and anions (in dashed lines) in RIM BeF_2 . The function is given for $|k| = 0.9 \text{ au}^{-1}$, which corresponds to the position of the *first sharp diffraction peak* in the Static Structure factor, $S(k)$. The vertical dashed lines correspond to the cage relaxation times, τ_{BeF} , at each temperature. In panel (b), the same data is shown, for the cations only, but now the time is scaled in terms of the cage relaxation time at each temperature.

At all temperatures, and in both models, the β -relaxation has finished, *i.e.* the plateau has been reached, well before the cage relaxation time. This relaxation therefore corresponds to a gentle unwinding of the network, such as the flexing of bonds, and occurs without any gross structural change, *i.e.* before there have been bond-breaking, or cage decay events. On this time scale, very few of the particles have diffused over the length scale being probed by k (which corresponds to the cation-cation separation), and so there has been relatively little decay of $F_s(k, t)$ and the network is still largely intact.

The fact that the incoherent scattering function has decayed to approximately the same value after the cage relaxation time has elapsed at each temperature suggests that we can scale the function in terms of this typical time scale for decay. The incoherent scattering function scaled in terms of the cage relaxation time at each temperature, $F_s(k, t/\tau_{\text{BeF}})$, is shown, for the cations, in panel (b) of figure 5.5. We can see that the curves all fall approximately on top of each other in the α -relaxation

regime when scaled in this way, so we may scale the relaxation of the system in terms of the time taken for the cage decay to occur, as suggested from our analysis of the van Hove self-correlation function in PIM BeF₂ (see section 4.3.8 and figure 4.21). This agrees with one of the predictions from Mode Coupling Theory, that of the time temperature superposition principle (TTSP), such that a correlator may be expressed as

$$\phi(t, T) = \hat{\phi}(t/\tau(T)), \quad (5.1)$$

where $\tau(T)$ is the typical time scale for decay of the correlation function at the temperature, T , and $\hat{\phi}$ is a master function³. Previous studies have used the α -relaxation time, the time taken for the correlator to have fallen to e^{-1} of its initial value, as this scaling time. As discussed, the α -relaxation regime relates to the approximate time scale over which exchange of particles between cages occurs, and so the use of the cage relaxation time, which is exactly the time scale over which the particle exchange occurs, is a sensible unambiguous alternative.

The curves do not collapse onto a master curve in the region of the β -relaxation, as has previously been observed in simulations of SiO₂ [48]: the dominance of the vibrational dynamics over this time scale mask the effects of the TTSP.

5.4 The cage correlation function of RIM BeF₂

The cage decay rates for RIM BeF₂ are given in table 5.4 for the *in-out* functions with $c = 1, 2, 3, 4$ (where c is the number of cage-ions which must change for the cage to decay) for the BeF, BeBe, FBe, and FF sub-systems. Table 5.5 shows the cage relaxation times for the $c = 1$ -*in-out* function for the different sub-systems. The cage decay rates are much lower in the RIM than the PIM at the same temperature. We can understand why this might be so by considering the ionic motion during the cage decay processes. At these times the ions are likely to move through regions of space which correspond to unstable configurations (*e.g.* at the top of the barrier

³The use of the term master function to describe the function for a particular correlator means that that function is now independent of temperature.

in the barrier crossing mechanism of structural relaxation). The passage of the ion over the barrier in the PIM is subject to a lower activation energy because the the dipoles on the the ions can evolve as the barrier is traversed in such a way as to stabilise what is likely to be an asymmetric ionic environment in the region of the transition state. This scenario is illustrated in figure 5.6, where the passage of the cation between the two anions is facilitated by the distortion of the anions to create dipoles which point towards the cation and which increase the favourable electrostatic interaction with the cation as it passes over the barrier. In the RIM this is not possible, and so the barrier crossing, and hence the cage decay, occurs much more slowly. Similar stabilisation of the transition states associated with the migration of the anions themselves would also be anticipated.

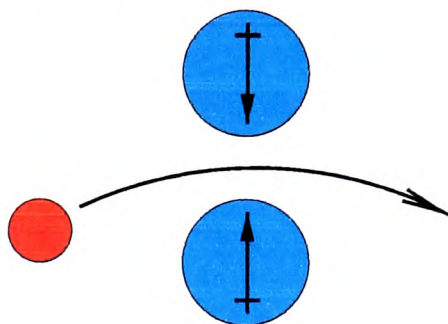


Figure 5.6: The motion of a cation between two anions will be stabilised in the PIM due to the ability of the anions to distort and produce dipoles which have a favourable electrostatic interaction with the cation.

Although the actual decay rates themselves are much lower in the RIM than in the PIM, the trends in the rates are similar. If we write the diffusion coefficient in terms of the cage relaxation time, we can again calculate an effective jump length from the Einstein relation, and these are given in table 5.6, which we can compare with the PIM values given in table 4.5. The jump lengths in the RIM are shorter than in the PIM, and this reflects the fact that the jump lengths calculated from the Eyring equation were also shorter than in the PIM. We previously interpreted the fact that the effective jump length was shorter than the cutoff distance used to define the cage, *i.e.* $\lambda_{BeF} < r_{BeF}^{\min}$, as a signature of the cooperative motion within

$c = 1$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
1300	0.00202	0.00237	0.00111	0.00309
1425	0.00568	0.00642	0.00307	0.00819
1550	0.0280	0.0346	0.0129	0.0447
1800	0.157	0.215	0.0721	0.271
2100	0.591	0.704	0.241	1.01
$c = 2$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
1300	0.000666	0.00108	0.000214	0.00234
1425	0.00265	0.00337	0.000961	0.00641
1550	0.0172	0.0196	0.0053	0.0379
1800	0.0996	0.123	0.0300	0.241
2100	0.330	0.432	0.0912	0.827
$c = 3$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
1300	0.000208	0.000361	–	0.00157
1425	0.00112	0.00174	–	0.00491
1550	0.00905	0.00977	–	0.0290
1800	0.0542	0.0619	–	0.187
2100	0.188	0.215	–	0.647
$c = 4$				
T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
1300	0.0000281	0.0000767	–	–
1425	0.000367	0.000725	–	–
1550	0.00345	0.00432	–	–
1800	0.0244	0.0266	–	–
2100	0.0791	0.125	–	–

Table 5.4: The fitted cage decay rates in RIM BeF₂ across the simulated temperature range.

T [K]	k_{BeF} [ps ⁻¹]	τ_{BeF} [ps]	τ_{BeF} [configs]
1300	0.00202	496	4098
1425	0.00568	176	1455
1550	0.0280	35.8	256
1800	0.157	6.36	53
2100	0.591	1.69	14

Table 5.5: The variation with temperature of the cage decay rates and the cage relaxation times in RIM BeF₂.

the network⁴ and so we can conclude that the degree of cooperative motion within the RIM system is higher.

Cage CF	λ_{BeF} [au]	λ_{FBe} [au]
$c = 1-in-out$	3.43	6.05
$c = 2-in-out$	4.25	10.60
$c = 3-in-out$	7.37	–
$c = 4-in-out$	15.4	–

Table 5.6: The *effective jump lengths*, $\lambda_{\alpha\beta}$, calculated from the ratio of the diffusion coefficient to the cage decay rate, for RIM BeF₂.

5.5 The coordination number dependent cage correlation function of RIM BeF₂

The number of defect sites in the RIM is very low, but we can still investigate the role these defect sites play in the diffusion using the coordination number dependent cage correlation function. Figure 5.7 shows the variation with temperature of the cage correlation functions for the $c = 1-in-out$ functions, and for the $N^c = 3$ and $N^c = 5$ cations respectively in RIM BeF₂. The BeF cage decay rates and relaxation times, calculated from an exponential fit to the long time section of the decay curves, for the $c = 1-in-out$ function, for the 3-, 4- and 5-coordinate species are given in table 5.7, and figure 5.8 shows the temperature dependence of those cage decay rates and also of the cation diffusion coefficient, as shown for the PIM in figure 4.25. The low concentration of defect sites in the RIM means that the statistics here are somewhat poorer than in the PIM, especially at the lower temperatures; however, the trends in the behaviour of the different types of defect may still be compared to the PIM. Again we see the increased importance of the intermediate time scale relaxation at low temperature, which we associated with the particular importance of the defects in promoting the cage relaxation and diffusion in the network in the low defect concentration regime, but now the behaviour of the 3- and 5-coordinate sites in the

⁴An ion does not have to make the jump over the whole of the cage cutoff distance because cooperative rearrangement of the network facilitates a cage decay event with a smaller jump length.

RIM is much more similar than in the PIM, suggesting that the 5-coordinate sites play a relatively more important role in facilitating the diffusion in the RIM than in the PIM. The 5-coordinate site still decays faster than the 3-coordinate, but now the difference between the decay rates of the two types of defect is much smaller: this suggests that the 5-coordinate site is relatively more stable in the RIM than the PIM, although it is still less stable than the 3- and 4-coordinate site. Overall, the behaviour of the cage decay rates in the two models is similar, suggesting that the relationship between the cage decay and the diffusion is the same in both models; and it is only the relative ease of the cage decay that is enhanced by the polarisation. This can be seen by examining the activation energy for diffusion in the RIM.

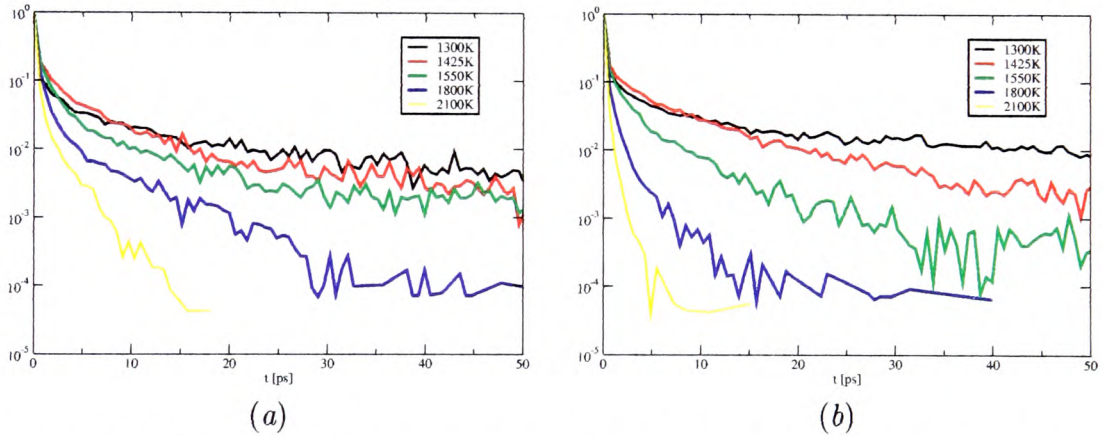


Figure 5.7: The temperature dependence of the coordination number dependent cage correlation function, $C_{BeF}^{c=1,in-out}(t)$, for (a) 3-coordinate and (b) 5-coordinate Be^{2+} ions in RIM BeF_2 .

If we fit D , F_D , and $\frac{D}{F_D}$ to the Arrhenius form, as shown in figure 5.9, we can again calculate an activation energy for diffusion, and split this up into contributions for the formation of the defects and for the migration of the ions when the defects have been created. These contributions are shown in table 5.8. We can see that the activation energy for diffusion is 171 kJmol^{-1} , which is much higher than the 51.5 kJmol^{-1} observed in the PIM. This reflects the fact that the transition state in the RIM is no longer stabilised by the favourable dipole reorganisation as the

$N_{Be}^c = 3$			
T [K]	k_{BeF} [ps ⁻¹]	τ_{BeF} [ps]	τ_{BeF} [configs]
1300	0.0408	24.5	203
1425	0.0493	20.3	168
1550	0.0457	21.9	181
1800	0.157	6.27	53
2100	0.358	2.79	23
$N_{Be}^c = 4$			
T [K]	k_{BeF} [ps ⁻¹]	τ_{BeF} [ps]	τ_{BeF} [configs]
1300	0.00203	493	4079
1425	0.00568	176	1455
1550	0.0280	35.69	295
1800	0.151	6.62	55
2100	0.591	1.69	14
$N_{Be}^c = 5$			
T [K]	k_{BeF} [ps ⁻¹]	τ_{BeF} [ps]	τ_{BeF} [configs]
1300	0.0110	90.9	751
1425	0.0484	20.7	171
1550	0.115	8.70	72
1800	0.304	3.29	27
2100	1.03	0.972	8

Table 5.7: The coordination number dependent cage correlation function decay rates and cage lifetimes for $N_{Be}^c = 3, 4, 5$ in RIM BeF₂.

ion passes through the transition state environment. This higher value is also much more appropriate for the energy required to break a Be–F bond compared with the low PIM value.

Although the activation energy for diffusion has increased, the relative contributions to the overall activation energy from the defect formation and ionic migration components remain the same, *i.e.*

$$\frac{E_A^{\text{mig,PIM}}}{E_A^{\text{diff,PIM}}} = \frac{32.1}{51.5} = 0.62$$

$$\frac{E_A^{\text{mig,RIM}}}{E_A^{\text{diff,RIM}}} = \frac{102.0}{171.0} = 0.60.$$

Approximately 60% of the total activation barrier to diffusion is due to the ionic migration and 40% to the defect formation which facilitates the ionic migration, and these proportions are the same in both models. The fact that the proportions are the same in both models suggests that the effect of polarisation cannot simply be

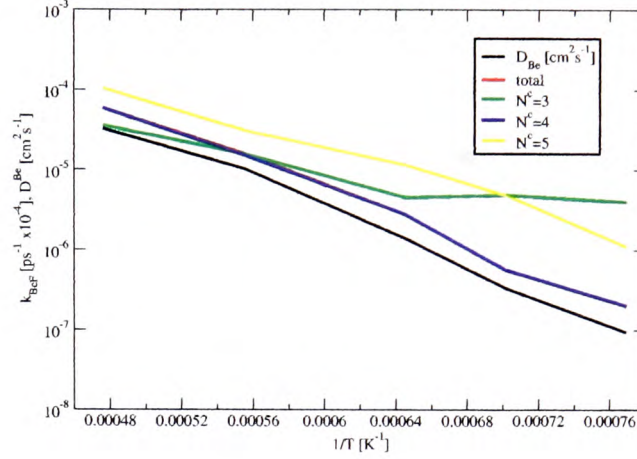


Figure 5.8: The variation in cage decay rate with inverse temperature for the coordination number dependent cage correlation functions, $C_{BeF}^{c=1, in-out}(t)$, for $N^c = 3, 4, 5$ in RIM BeF₂. The cage decay rates are in ps⁻¹ ($\times 10^{-4}$). Also shown is the cationic diffusion coefficient and the coordination number independent cage decay rate, in red and labelled *total*.

ascribed to one part of the diffusive process: the inclusion of polarisation makes it easier both to create the defects and to move afterwards, but it does not change the relative importance of each of these components in the overall diffusive scheme.

Figure 5.10 shows a series of snapshots from RIM BeF₂ at 1550 K, at which temperature the diffusion coefficients are approximately equal to those in PIM BeF₂ at 700 K. The snapshots are separated by 70 configurations, or 8.466 ps, which is approximately the cage relaxation time for the 5-coordinate cations, $\tau_{BeF}^{N^c=5}$, which are the fastest relaxing cation species in the system. Over these snapshots, the mean number of 5-coordinate sites is 10.5, whereas it is 7.0 over the whole simulation, so these snapshots correspond to a time in the system when there is a relatively high defect activity (note that the mean number of 3-coordinate defect sites over the snapshots is 5 compared to an overall mean of 4.7). However, there is little evidence of defect species persisting from one frame to the next even in this regime of high defect activity.

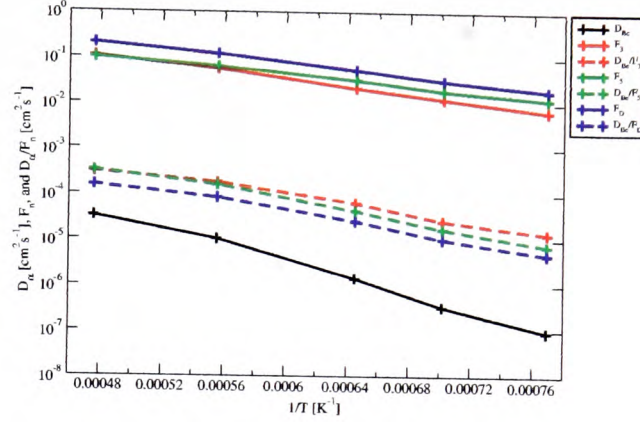


Figure 5.9: The variation of the cationic diffusion coefficients, populations of the different defect sites, and ratios of the diffusion coefficients to defect site populations with inverse temperature, for RIM BeF₂. F_D is the fraction of non-tetrahedral cation sites, $1 - F_4$, *i.e.* the total population of defect sites, and D_{Be} is given in cm²s⁻¹.

Function	E_A^{PIM} [kJmol ⁻¹]	E_A^{RIM} [kJmol ⁻¹]
D	51.5	171.0
F_3	18.3	79.2
F_5	24.7	60.6
F_D	19.3	68.9
$\frac{D}{F_3}$	33.2	91.7
$\frac{D}{F_5}$	26.8	110.3
$\frac{D}{F_D}$	32.1	102.0

Table 5.8: The activation energies for the formation of defects, the migration of ions after defects have formed, and for the overall diffusion coefficients. F_D is the total population of non-tetrahedral sites, *i.e.* $1 - F_4$. The middle column is reproduced from table 4.8.

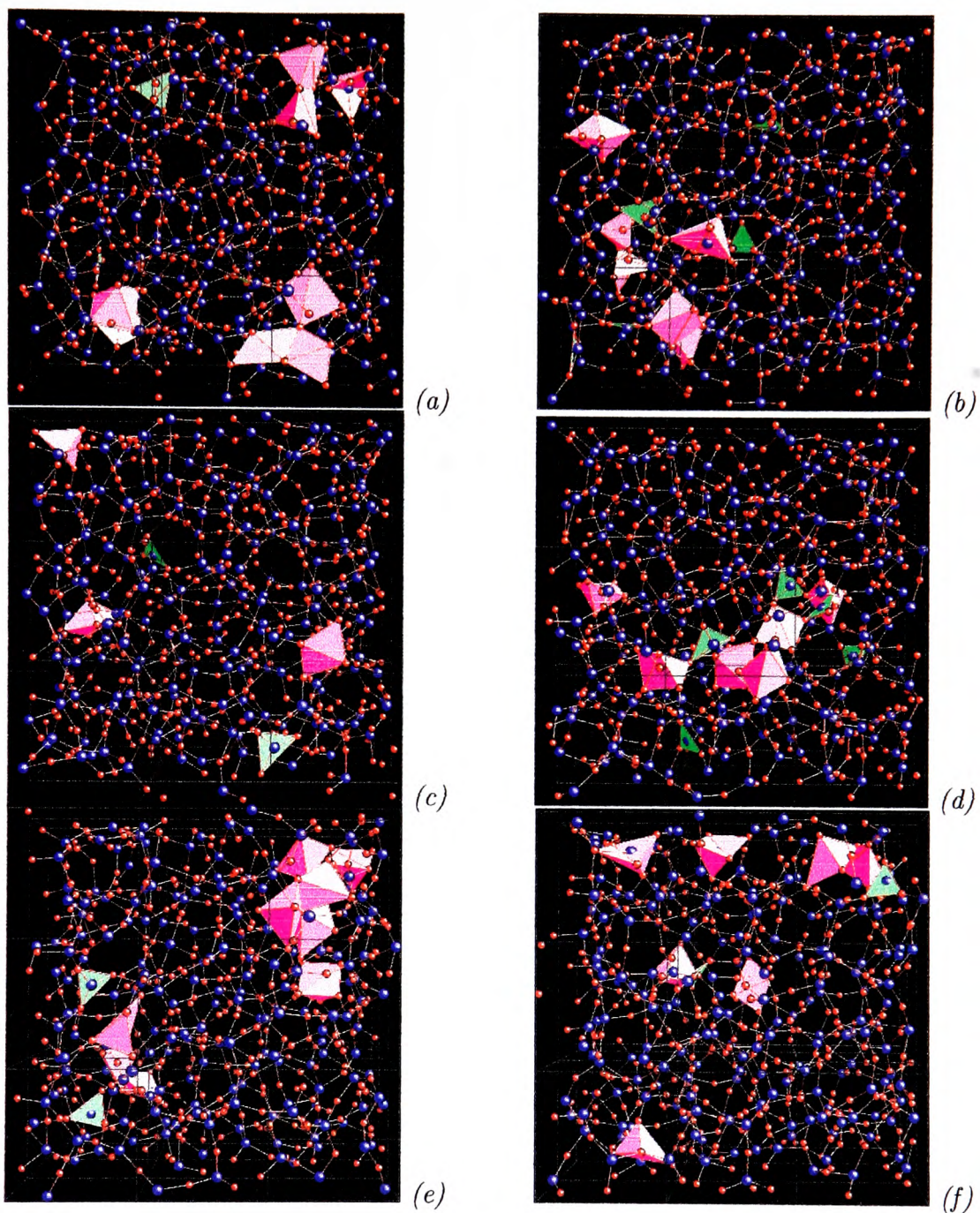


Figure 5.10: Snapshots of RIM BeF₂ at 1550 K, running (a) to (f), each separated by 70 configurations, or 8.466 ps, with the Be²⁺ ions in blue and the F⁻ ions in red, and showing the 3-coordinate Be²⁺ ions as green planar triangles, and the 5-coordinate Be²⁺ ions with magenta polygons (triangular faces are drawn with the anions as the vertices). The cage lifetimes are $\tau_{BeF}^{N^c=3} = 181$ and $\tau_{BeF}^{N^c=5} = 72$ configurations. These figures have been produced using a modified version of the *MDview* program from S. Hull [8].

Chapter 6

BeF₂: The spatial distribution of dynamical events

6.1 Introduction

The analysis of the van Hove self-correlation function in chapter 4 suggested that, over appreciable periods of time, there are two types of particle, the mobile and the relatively immobile. We might postulate that these may form *spatially distinct* regions within the system, *i.e.* at a given time some volume of the liquid will be mobile while another volume will be immobile, and that over time the relative sizes and positions of these regions with different mobilities will change.

The analysis of the cage correlation function, and particularly the Coordination Number dependent cage correlation function suggested the importance of defect sites, *i.e.* non-tetrahedral cations, in promoting the mobility of the system. The cage correlation function analysis is, however, limited to the local coordination shell around a given ion, and tells us nothing about how the cage decay events are distributed throughout space. The splitting up of the system into mobile and immobile regions might be connected to different regions of the fluid having high and low concentrations of defects, and we need some way of probing the fluid to determine the link between the spatial distribution of defects and mobility.

The idea of this *dynamically heterogeneous* system has been investigated in simple liquids by Glotzer *et al.* [61, 62, 63] with the development of functions which look at the spatial distribution of mobile particles, and in this chapter we will exam-

ine the behaviour of these functions in the tetrahedral network systems. We will also develop the ideas expressed in these Glotzer functions to analyse the spatial distributions of other properties within the system.

6.2 The Displacement-Displacement weighted radial distribution function

We can define the displacement, $\boldsymbol{\mu}_i(t, \Delta t)$, of particle i , over the time interval, Δt , starting from the reference time origin, t , as

$$\boldsymbol{\mu}_i(t, \Delta t) = \mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t). \quad (6.1)$$

We can investigate the spatial correlations of these displacements by weighting the radial distribution function by the displacements of the ions, to give the displacement-displacement weighted radial distribution function,

$$g_u(\mathbf{r}, \Delta t) = \frac{V}{\bar{\mu}^2 N^2} \left\langle \sum_{i=1}^N \sum'_{j=1}^N \boldsymbol{\mu}_i(t, \Delta t) \cdot \boldsymbol{\mu}_j(t, \Delta t) \delta[\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t)] \right\rangle, \quad (6.2)$$

where the ' indicates that terms in which $i = j$ in the double sum are excluded. We are primarily interested in spatial correlations in the *magnitude* of the ionic displacements, and so equation 6.2 can be replaced with

$$g_u(r, \Delta t) = \frac{V}{\bar{\mu}^2 N^2} \left\langle \sum_{i=1}^N \sum'_{j=1}^N \mu_i(t, \Delta t) \mu_j(t, \Delta t) \delta[\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t)] \right\rangle, \quad (6.3)$$

where $\mu_i(t, \Delta t) = |\boldsymbol{\mu}_i(t, \Delta t)|$ and $\bar{\mu} = \left\langle \frac{1}{N} \sum_{i=1}^N \mu_i(t, \Delta t) \right\rangle$. We can see that this function depends on the separations of the ions, r , and also the time interval, Δt , over which the displacements of the ions are calculated. Figures 6.1 and 6.2 show the total and cation-anion *partial*¹ displacement-displacement weighted radial distribution functions respectively for PIM BeF₂ at 700 K.

The form of the weighted distribution function is very similar to the ordinary pair

¹As the function depends on the identities of the ions, in a multi-component system we can construct the functions for the different combinations of ion species, just as in the usual pair distribution function.

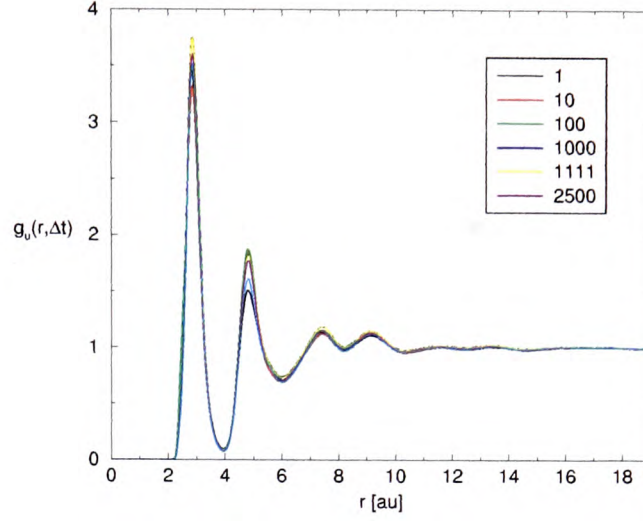


Figure 6.1: The displacement-displacement weighted total radial distribution function for PIM BeF₂ at 700 K. The ordinary total radial distribution function, $g(r)$, is shown in cyan for comparison. The legend gives the time, Δt , in units of *configurations*, where one configuration has a time of 0.036282 ps. The cage relaxation time in this system is $\tau_{BeF} = 1111$ configurations, which corresponds to the function plotted in yellow in the figure.

distribution function, and this means it is difficult to see the differences between $g_u(r, \Delta t)$ and $g(r)$. However, if the displacement of each of the particles over the time interval Δt were the same, then this weighted function would reduce to the standard pair distribution function, $g(r)$, and so it is the differences between the weighted and unweighted radial distribution functions which describe any *excess* spatial correlations of displacements. The excess displacement-displacement correlation function, $\Gamma(r, \Delta t)$, is defined as

$$\Gamma(r, \Delta t) = \frac{g_u(r, \Delta t)}{g(r)} - 1. \quad (6.4)$$

The excess displacement-displacement correlation functions are shown in figures 6.3 and 6.4 for the total and cation-anion partial radial distribution functions respectively. If we consider these figures, we can see that the positive excess correlations dominate and hence that the integrated excess correlation functions, $\int_0^\infty \Gamma(r, \Delta t) dr$,

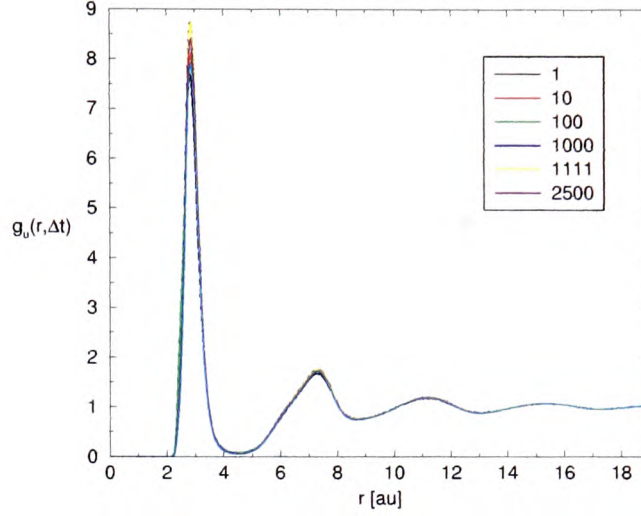


Figure 6.2: The displacement-displacement weighted cation-anion partial radial distribution function for PIM BeF₂ at 700 K, over time scales, Δt , as given by the legend. The ordinary cation-anion partial radial distribution function, $g_{BeF}(r)$, is shown in cyan for comparison.

are positive.

From figure 6.4 we can see that there is only intensity in $\Gamma_{BeF}(r, \Delta t)$ over the length scale of the first peak in the partial radial distribution function, which is shown in the figures for clarity, and rather less intensity in the region of the second peak, out to approximately $r = 8.5$ au. This behaviour is reflected in the behaviour of the other partial excess correlation functions, $\Gamma_{FF}(r, \Delta t)$ and $\Gamma_{BeBe}(r, \Delta t)$, though it is somewhat confused in the total function, shown in figure 6.3, as the peaks in the total radial distribution contain contributions from more than one partial function, so the excess correlation appears to extend beyond the second coordination shells. At large r , the intensity is zero in all of the excess correlation functions. This suggests that any spatial correlation of high mobilities is limited to only one or two coordination shells, and that there are *not* large patches of the fluid that are highly mobile.

The location of the length scale over which the excess correlation of the displace-

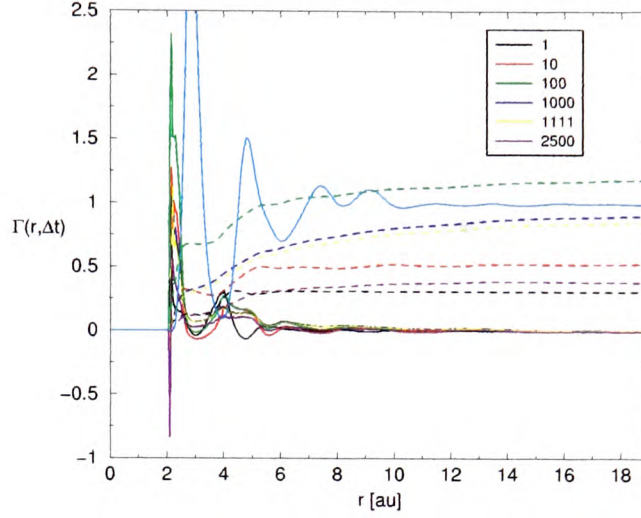


Figure 6.3: The ratio of the displacement-displacement weighted to the ordinary total radial distribution function, $\Gamma(r, \Delta t)$, for PIM BeF₂ at 700 K. The dashed lines show the running integrals of $\Gamma(r, \Delta t)$, and the total radial distribution function, $g(r)$, is again shown in cyan.

ments decays to zero can be identified from the position of the appearance of the plateau in the running integral of the excess correlation function. At very short time ($t = 1$) and at long time ($t = 2500$), the plateau in $\int_0^\infty \Gamma_{BeF}(r, \Delta t) dr$ appears at about the first minimum in the Be-F partial radial distribution function, and so excess correlation is displacements is limited to only the first coordination shell: on these time scales the motion of the tetrahedral unit as a whole is dominant. However, at intermediate time scales, up to approximately the cage decay time, τ_{BeF} (which is 1111 configurations in PIM BeF₂ at 700 K and which corresponds to the functions shown in yellow in figures 6.1 to 6.4), the plateau appears after approximately the position of the second minimum in the partial radial distribution function. Over these time scales, there is an increased likelihood of finding mobile particles over a length scale of the second nearest neighbour, *i.e.* the mobility is correlated out into the tetrahedral units bonded to the central unit. This suggests that in the course of the cage decay event, the mobility of the network increases

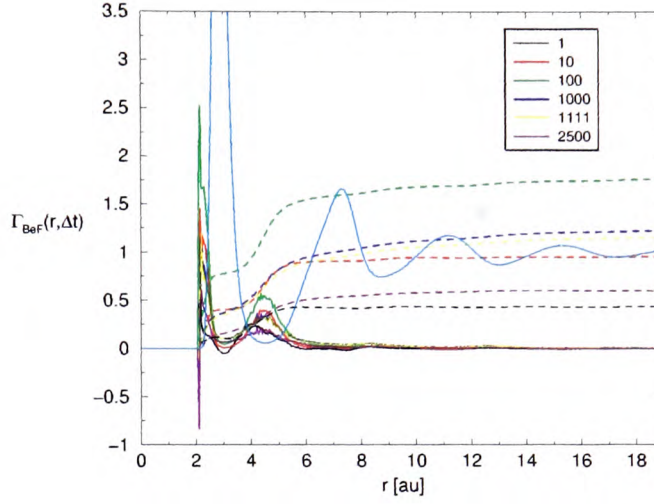


Figure 6.4: The ratio of the displacement-displacement weighted to the ordinary cation-anion partial radial distribution function, $\Gamma_{BeF}(r, \Delta t)$, for PIM BeF_2 at 700 K. The dashed lines show the running integrals of $\Gamma_{BeF}(r, \Delta t)$, and the cation-anion partial radial distribution function is again shown in cyan.

over a longer range than just the cage that is decaying, and hence that a mobile ion has an influence on the mobility of the network over an intermediate spatial range. The conclusion that mobility is correlated over an intermediate length scale over the time scale corresponding to the cage decay does not tell us, however, how the cage decay event is directly related in space to the increased correlation in mobility. We might imagine that the increased local mobility would be due to a cage decay event occurring at the origin, but this cannot be directly inferred from the analysis of the displacement-displacement weighted radial distribution function. Section 6.3 describes extensions to the idea of the weighting of the radial distribution function which allow us to further probe the spatial relation between the cage decay event and the excess correlation in mobility.

The time dependence of the excess spatial correlation function, $\Gamma(r, \Delta t)$, can be investigated by measuring the variation of the integrated excess spatial correlation

function, or *total excess correlation*, $A(\Delta t)$, which is defined as

$$A(\Delta t) = \int_0^\infty \Gamma(r, \Delta t) dr. \quad (6.5)$$

Figure 6.5 shows the total excess correlation against time for the system as a whole, and for each of the partial contributions.

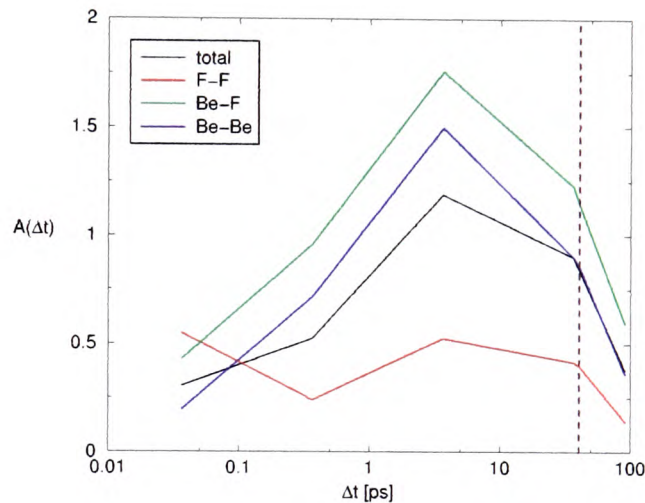


Figure 6.5: The integrated ratio of the displacement-displacement weighted to the ordinary radial distribution functions, $A_{BeF}(r, \Delta t)$, for PIM BeF₂ at 700 K. The dashed maroon line corresponds to the cage relaxation time, τ_{BeF} , at this temperature.

We can define a time, τ^* , as the time when the total excess correlation is at a maximum. This time scale is around 100 configurations, corresponding to approximately 4 ps. This is shorter than the cage decay time, τ_{BeF} , which we have previously stated can be considered as our clock for the diffusive processes. The total excess correlation builds up as the system is approaching a cage decay event, and this suggests that the mobility is highest as the cage decay event is occurring (note that when the cage decay time has elapsed, the cage decay event has already occurred). The importance of the cage decay time can be understood by noticing that the total excess correlation decays to zero very quickly after this time, *i.e.* once the diffusive

event has occurred, the homogeneity of the fluid is restored.

The total excess correlation of the fluid is highest in the cation-anion sub-system, and is very small in the anion-anion sub-system. This reflects the cage decay results, where we saw that the slowest decay was in the cation-anion sub-system, corresponding to the persistence of the local Be–F cages after the extended Be–Be and F–F cages had decayed, and also where there was the very rapid decay in the F–F cage, corresponding to the ability of the ions in this sub-system to move relative to each other without any breaking of bonds; this ease of decay of the F–F sub-system is observed as there being only a small amount of structure in the excess correlation function for this sub-system.

6.2.1 Temperature dependence of the displacement-displacement weighted radial distribution functions

In the cage correlation function analysis, we saw that the cage decay behaviour was approximately independent of temperature, when scaled in terms of the cage decay time, $\tau_{BeF}(T)$, *i.e.* the cage decay jump lengths were approximately temperature independent, and the diffusion coefficient could be predicted from the cage decay rate, $k_{BeF}(T)$, and the cage decay jump length, across the whole simulated temperature range.

The temperature variation of the excess correlation function for the Be–F partial distribution evaluated at the cage relaxation time, $\Gamma_{BeF}(r, \tau_{BeF}(T))$, is shown in figure 6.6. The total excess correlation reduces as temperature increases as we might expect: as the temperature increases, the entire fluid becomes more homogeneous, and so any excess dynamical structure is reduced. However, the form of the distribution is independent of temperature, with the furthest extent of the positive correlation being the second coordination shell for all temperatures ($\Gamma_{BeF}(r, \tau_{BeF}(T))$ being approximately zero beyond the second minimum in $g_{BeF}(r)$ for all T).

The variation with temperature of the total excess correlation evaluated at the cage decay time, for the total system and the partial sub-systems, $A_{\alpha\beta}(\tau_{BeF}(T))$, is shown

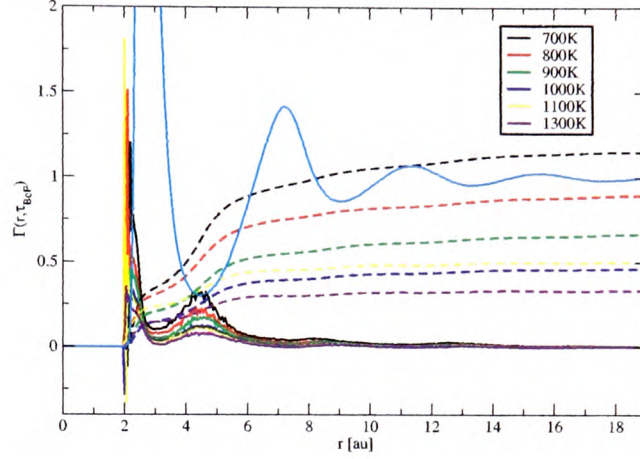


Figure 6.6: The variation with temperature of the excess correlation function, $\Gamma_{BeF}(r, \tau_{BeF})$, for the cation-anion sub-system, evaluated at the cage relaxation time, τ_{BeF} , in PIM BeF₂. The partial radial distribution, $g_{BeF}(r)$ at 1300 K, is again shown in cyan.

in figure 6.7. We can see that there is not a sudden increase in the total excess correlation in each of the sub-systems, and rather a smooth, continuous increase as the temperature decreases and the glass transition is approached, although the increase is highest in the cation-anion partial sub-system, reflecting the dominant nature of the cation-anion polyhedra in the structure. Figure 6.8 shows the variation with temperature of the time dependence of the total excess correlation, in the system as a whole and in the partial sub-systems, for PIM BeF₂. We can see that there is no evidence of a rapid build up in collectivity as the temperature drops, and that the exponential variation with temperature of the total excess correlation at the cage relaxation time is typical of that at all times (though the absolute magnitudes of $A(\Delta t)$ do vary with time).

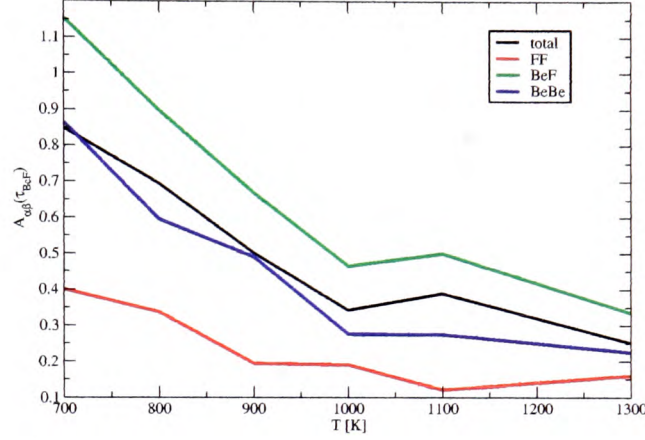


Figure 6.7: The variation with temperature of the total excess correlation function, $A_{\alpha\beta}(\tau_{BeF})$, for the total system and the partial sub-systems, evaluated at the cage relaxation time, τ_{BeF} , in PIM BeF₂.

6.2.2 The displacement-displacement weighted radial distribution function in RIM BeF₂

Figure 6.9 shows the ratio of the displacement-displacement weighted to the ordinary cation-anion partial radial distribution functions for RIM BeF₂ at 2100 K. We can see that the general form of these functions in RIM BeF₂ at 2100 K is as in the PIM at 700 K, although the running integrals, the total excess correlation, have lower plateau values, reflecting the lower level of total excess correlation at the higher temperature. These plateaus are reached on the length scale of the second peak, although the excess correlation does not extend to as large a value of r for this system as for PIM BeF₂ at 700 K. This again reflects the higher temperature². The time dependence of the total excess correlation, $A_{\alpha\beta}(\Delta t)$, is shown for RIM BeF₂ at 2100 K in figure 6.10, and again we can see (on comparing this figure with

²The temperature of the two models should not be directly compared, as we are actually considering the fluidity of the models. We should compare a *reduced temperature* of the systems in terms of an effective fluidity, but when we do this the RIM 2100K system is still more fluid, and hence *hotter* than the PIM 700K system ($D_{Be}^{PIM} = 1.6 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ and $D_{Be}^{RIM} = 3.7 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$).

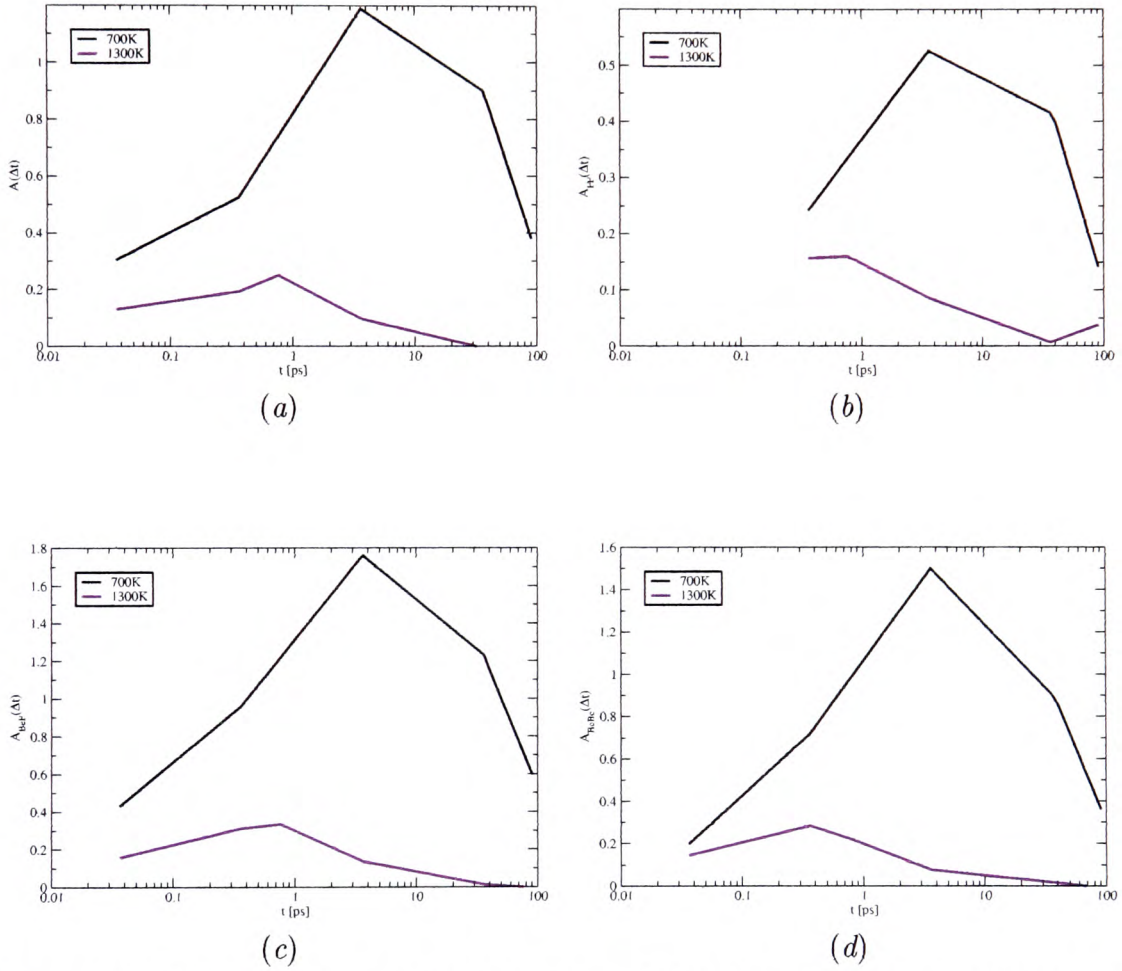


Figure 6.8: The variation with temperature of the time dependence of the total excess correlation, for the whole system in panel (a), and for partial sub-systems, anion-anion in panel (b), cation-anion in panel (c) and cation-cation in panel (d), in PIM BeF₂.

figure 6.5 which shows the equivalent data for PIM BeF₂ at 700 K) that the form of the variation is the same in the RIM as the PIM. The time, τ^* , is again smaller than the cage decay time, τ_{BeF} , which in this system is 45 configurations, or ~ 5.4 ps, and again we see the rapid reduction in the excess correlation after the cage decay time has elapsed. This suggests that the spatial distribution of the mobile particles in the two systems is broadly similar, and enhances our conclusion from the cage correlation function analysis that the same events are responsible for the diffusion in each of the models, with the difference between the models which is responsible for the huge difference in fluidity being the concentration of the defect species primarily responsible for the decay events.

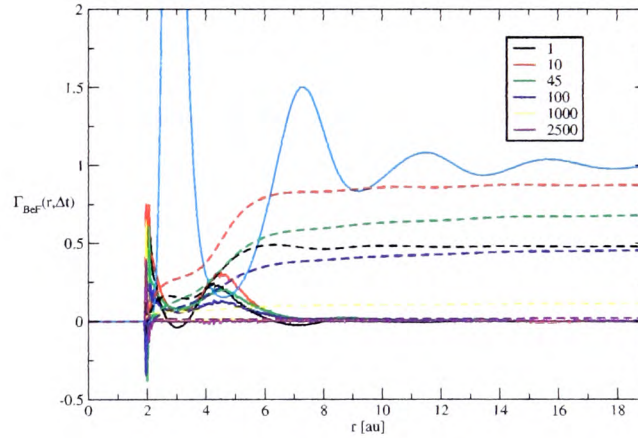


Figure 6.9: The ratio of the displacement-displacement weighted to the ordinary cation-anion partial radial distribution function, $\Gamma_{BeF}(r, \Delta t)$, for RIM BeF₂ at 2100 K. The dashed lines show the running integrals of $\Gamma_{BeF}(r, \Delta t)$, and the cation-anion partial radial distribution function is shown in cyan. Compare this with figure 6.4, which shows the equivalent data for PIM BeF₂ at 700 K.

The temperature dependence of the excess correlation function in the Be-F partial distribution evaluated at the cage relaxation time, $\Gamma_{BeF}(r, \tau_{BeF}(T))$, is shown for RIM BeF₂ in figure 6.11, and the variation with temperature of the total excess

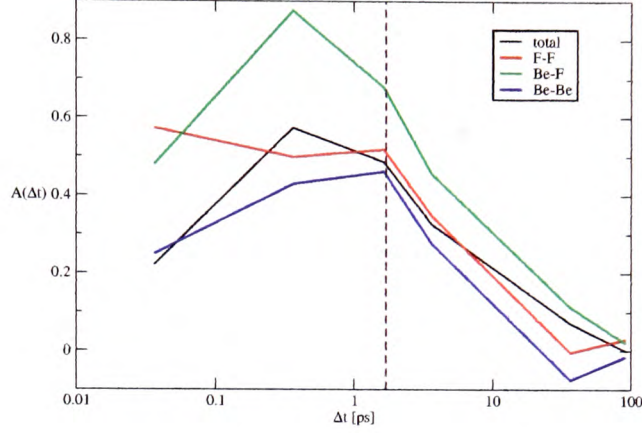


Figure 6.10: The integrated ratio of the displacement-displacement weighted to the ordinary radial distribution functions, $A_{BeF}(r, \Delta t)$, for RIM BeF_2 at 2100 K. The dashed maroon line corresponds to the cage relaxation time, τ_{BeF} , at this temperature. Compare this with figure 6.5 which shows the equivalent data for PIM BeF_2 at 700 K.

correlation evaluated at the cage decay time, for the total system and the partial sub-systems, $A_{\alpha\beta}(\tau_{BeF}(T))$, is shown for RIM BeF_2 in figure 6.12. The qualitative description of the behaviour here is again the same as in the PIM system. There is again a smooth increase in the total excess correlation as the temperature decreases, and now the contribution of the excess correlation in the cation-anion sub-system to the total is even more dominant. However, the motion in the RIM is more cooperative: if we compare the total excess correlation of the two models at the lowest simulated temperatures, we see that $A^{RIM, 1300K}(\Delta t) \approx 1.3$ whereas $A^{PIM, 700K}(\Delta t) \approx 0.8$. The polarisation increased the defect concentration, and it is the defects which appear to be largely responsible for the diffusion, which allows the homogeneity of the system to be restored. The increased ability to dissipate the spatial heterogeneity is observed as a lower degree of excess correlation in the PIM.

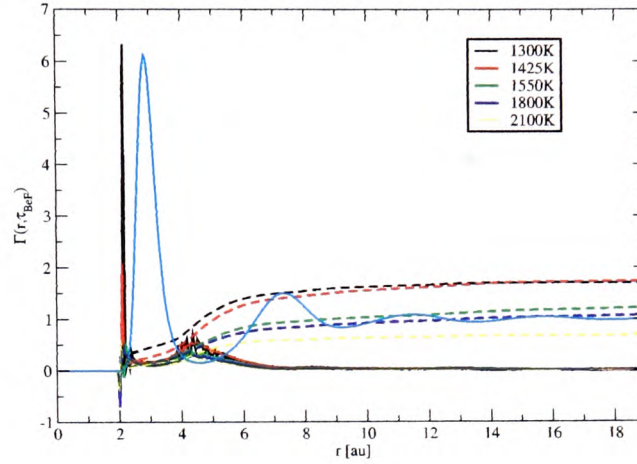


Figure 6.11: The variation with temperature of the excess correlation function, $\Gamma_{BeF}(r, \tau_{BeF})$, for the cation-anion sub-system, evaluated at the cage relaxation time, τ_{BeF} , in RIM BeF_2 . The partial radial distribution, $g_{BeF}(r)$ at 2100 K, is again shown in cyan. Compare with the PIM results shown in figure 6.6.

6.2.3 Comparison of the network fluid with a simple fluid

The original work on the displacement-displacement weighted radial distribution function by Glotzer *et al.* was on the simple fluid, Lennard-Jones systems [63]. Figure 6.13 shows the weighted and unweighted radial distribution functions for a Lennard-Jones fluid [64]. The time scale over which the displacement is calculated is the α -relaxation time, τ_α , which describes the decay of the self part of the incoherent scattering function, $F_s(k, t)$, and which corresponds to the decay time for the caging of the particles. The evaluation of $g_u(r, \Delta t)$ at τ_α for the simple fluid is therefore comparable with the evaluation of $g_u(r, \Delta t)$ at the cage relaxation time, τ_{BeF} , in the network fluid.

We can see immediately that the excess correlation, $\Gamma(r, \Delta t)$, extends over a more considerable range in the simple fluid than in the network fluid. $\Gamma(r, \Delta t)$ has intensity over 4-5 coordination shells in the simple fluid whereas it was only observed over 2-3 coordination shells in the network liquid. This long range excess correlation

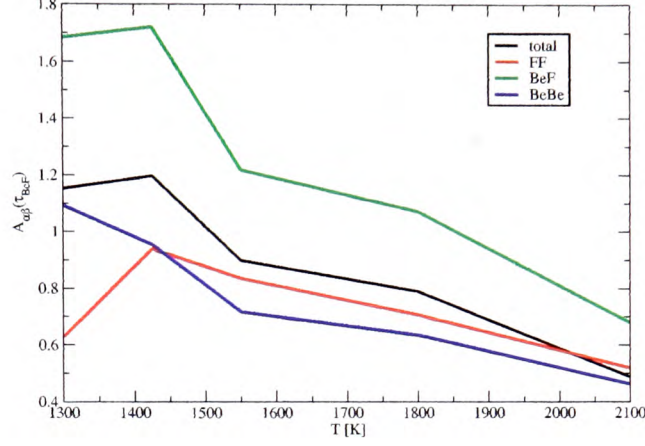


Figure 6.12: The variation with temperature of the total excess correlation function, $A_{\alpha\beta}(\tau_{BeF})$, for the total system and for the partial sub-systems, evaluated at the cage relaxation time, τ_{BeF} , in RIM BeF_2 . Compare with the PIM results shown in figure 6.7.

has been interpreted in the simple fluid in terms of clusters of mobile particles, and strings of mobile particles through the other regions consisting of immobile particles. The shorter range of the excess correlation in the network fluid suggests that the mobile regions are much smaller in size, as discussed above.

The upper panel in figure 6.14 shows the temperature dependence of the total excess correlation, $A(\Delta t)$, for the Lennard-Jones fluid. In the simple fluid $A(\Delta t)$ increases in magnitude and its maximum value with time moves to longer time as the temperature is reduced, and this is similar to the network fluid, as shown in figure 6.8 for PIM BeF_2 . However, if we consider the maximum values of $A(\Delta t)$, then we see these are approximately 0.2-0.3 in the simple fluid but 1.2 in the PIM at 700 K and 0.6 in the RIM at 2100 K (see figures 6.5 and 6.10 respectively). Hence there is a higher total excess correlation in the network fluid but it is shorter ranged in r . We can interpret this in terms of the structures adopted by the fluids: in the Lennard-Jones fluid each atom is surrounded by 11-12 others in a relatively diffuse cage, whereas in

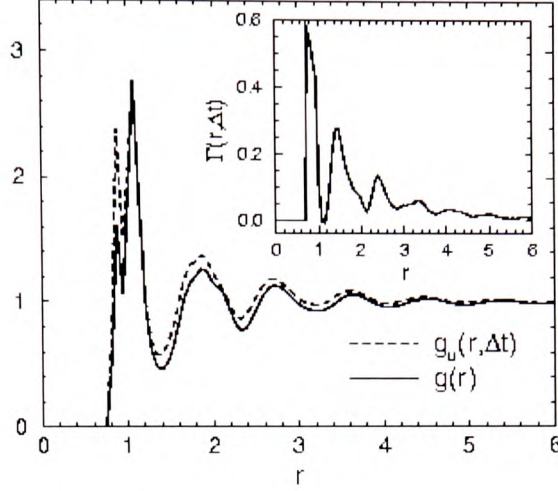


Figure 6.13: The displacement-displacement weighted and ordinary radial distribution functions, $g_u(r, \Delta t)$ and $g(r)$, for a Lennard-Jones fluid at $T = 0.451$. The inset shows the excess correlation function, $\Gamma(r, \Delta t)$. Δt is chosen to be of the order of τ_α . This figure is reproduced from [63].

the network fluid the ions have well defined, tightly bound coordination polyhedra. The excess correlation is higher in the network fluid due to the extra definition of the local structure.

6.3 Extension of the spatial correlation function to other dynamical properties

In the spatial correlation function outlined in section 6.2, we weight the standard pair distribution function by the displacements of the ions. In general, we can choose to weight by any structural or dynamical property of the ions. The general form of the weighted radial distribution function is

$$g_u(r, \Delta t) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \sum_{j=1}^N [\theta_i(t, \Delta t) \theta_j(t, \Delta t)] \delta[\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t)] \right\rangle, \quad (6.6)$$

where $\theta_i(t, \Delta t)$ is a function which describes the property of interest.

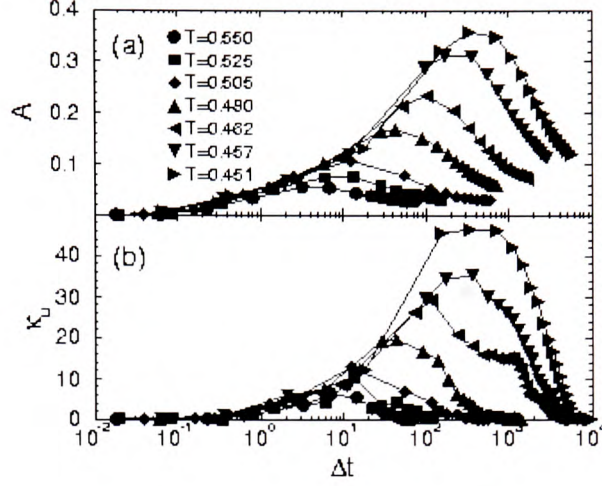


Figure 6.14: The upper panel, (a), shows the temperature dependence of the total excess correlation, $A(\Delta t) = \int \Gamma(r, \Delta t) dr$, in a Lennard-Jones fluid. This figure is reproduced from [63]. The temperatures are given in terms of *reduced units*, T^* , given by $T^* = \frac{k_B T}{\epsilon}$, where ϵ is the depth of the potential energy well.

6.3.1 The direction weighted radial distribution function

If $\theta_i(t, \Delta t) = \hat{\mu}_i(t, \Delta t)$ in equation 6.6, then we can define $g_u(r, \Delta t)$ as

$$g_u(r, \Delta t) = \frac{V}{N^2} \left\langle \sum_{i=1}^N \sum_{j=1}^{N'} [\hat{\mu}_i(t, \Delta t) \cdot \hat{\mu}_j(t, \Delta t)] \delta[\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t)] \right\rangle \quad (6.7)$$

which is the radial distribution function weighted by the scalar product of the unit vectors of the displacements of the ions, and so the excess correlation here gives a measure of the probability of ions moving in the same direction where the scalar product is most positive. If the motion is completely uncorrelated, then $g_u(r, \Delta t) = 0$ for all r and Δt . Note, therefore, that in this case the excess correlation function, $\Gamma(r, \Delta t)$, is simply the weighted distribution function itself.

Figure 6.15 shows the direction weighted radial distribution functions for PIM BeF₂ at 700 K. Again, we can see that the excess correlation has a maximum range in r out to the second minimum of the partial radial distribution function, and that the maximum excess correlation is observed at times shorter than the cage relaxation time, *i.e.* at $\Delta t = 100$ configurations compared to $\tau_{BeF} = 1111$ configurations. This behaviour is the same for each of the partial distribution functions. This suggests

that regions of the network of the order of a small number of tetrahedral units in size can move in the same direction until the cage decay event occurs, and then there is a decreased probability of the direction of the ionic motion within this region remaining correlated. Note also that the short time ($\Delta t = 1$ configuration) negative correlation on the large r side of the first peak in the anion-anion and cation-anion direction weighted partial radial distribution functions reflects the dominance of vibrational motion of the tetrahedra over this time scale, and that at the extreme of the vibration the ions are moving in opposite directions, resulting in a negative scalar product and a negative correlation in the weighted distribution function.

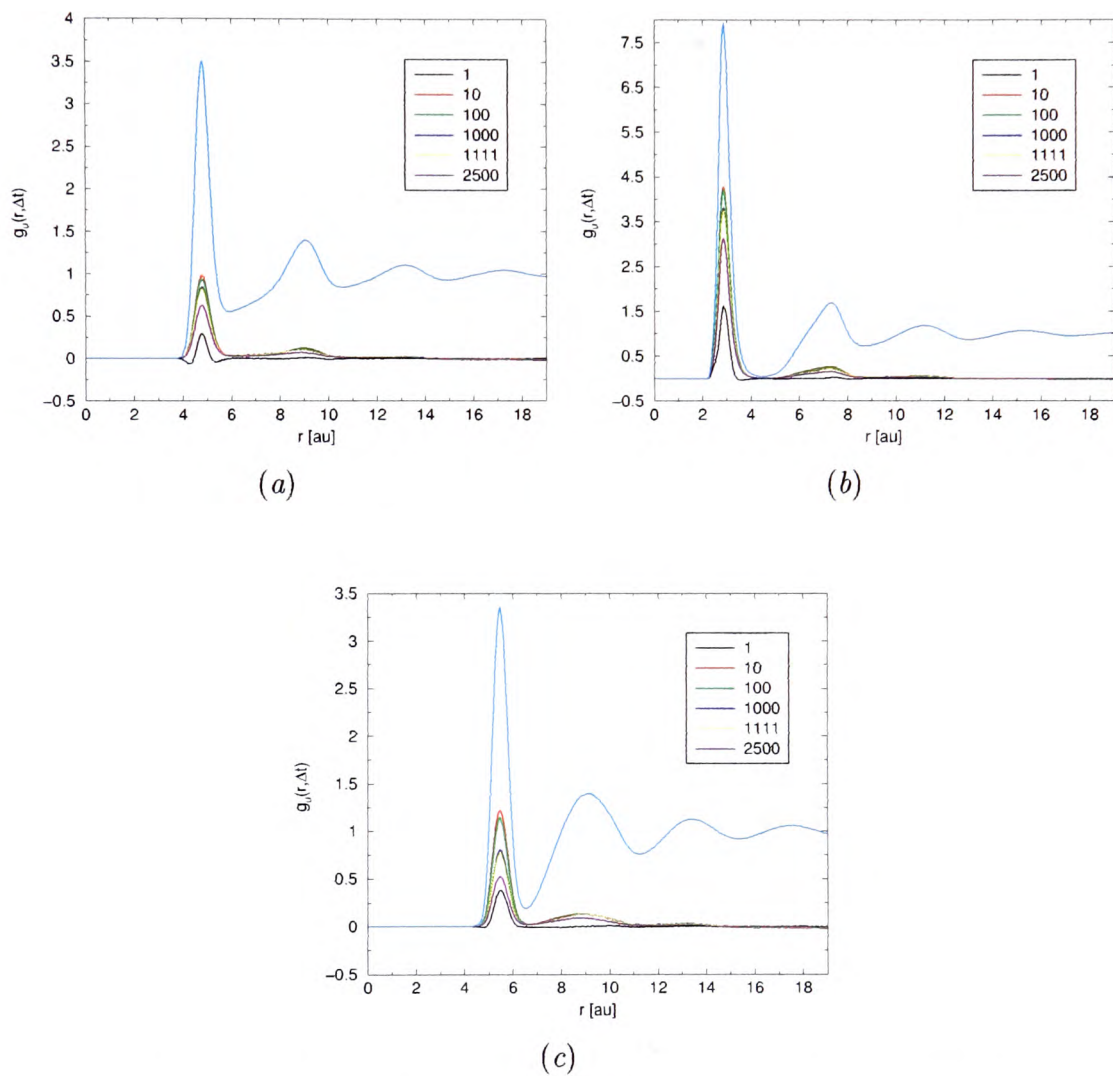


Figure 6.15: The partial direction weighted radial distribution functions for (a) the anion-anion, (b) the cation-anion, and (c) the cation-cation distributions in PIM BeF₂ at 700 K. The cyan lines show the relevant ordinary partial radial distribution function in each case.

6.3.2 The mobile ion weighted radial distribution function

If we define $\theta_i(t, \Delta t)$ in equation 6.6 according to the relations

$$\theta_i(t, \Delta t) = \begin{cases} 0 & \text{if } \mu_i(t, \Delta t) < r_{\text{cutoff}} \\ 1 & \text{if } \mu_i(t, \Delta t) \geq r_{\text{cutoff}} \end{cases}, \quad (6.8)$$

where r_{cutoff} is some length scale which an ion must have moved in order to be considered as *mobile*. This weighted radial distribution function is called the mobile-mobile weighted radial distribution, and emphasises the particles which have moved further than the cutoff length scale. This length scale has been chosen as the first minimum in the relevant partial radial distribution function, *i.e.* it is the same as the cutoff distance for the cage correlation function, such that a mobile ion here is considered to be one which has moved a distance greater than or equal to the ionic jump length required for a cage to be considered as having decayed, and hence this function describes the spatial distribution of the *very* mobile particles above and beyond the displacement-displacement weighted radial distribution function. As a mobile particle is one which has moved the cage decay jump length, we might reasonably expect that a mobile ion is one which has undergone cage decay, although this might not necessarily be the case if the mobile ion has moved with its immediate coordination shell remaining intact, and thus moving without any cage decay, as is seen for La^{3+} ions in dilute $[\text{Li}, \text{K}]\text{Cl}$ solution [45].

Figure 6.16 shows the partial mobile-mobile weighted radial distribution functions for PIM BeF_2 at 700 K. At short times, very few of the particles have moved further than the cutoff length scale, and hence the statistics for $g_u(r, \Delta t)$ are poor, and these distributions are not shown for $\Delta t < 100$ configurations. The excess correlation again extends over approximately two coordination shells, but there is a particularly high excess correlation in the first coordination shell, especially in the cation-anion partial distribution function; the maximum value of the weighted radial distribution function in the first coordination shell is $g_u^{\text{BeF}}(r, \Delta t = 100) \approx 100$, compared with $g_u^{\text{FF}}(r, \Delta t = 100) \approx g_u^{\text{BeBe}}(r, \Delta t = 100) \approx 17$, and this suggests that the excess correlation of the mobile particles is particularly important within the

tetrahedral units.

At long time, *i.e.* $\Delta t > \tau_{BeF}$, the difference between the weighted and unweighted functions is small: at $\Delta t = 2500$ configurations, compared with $\tau_{BeF} = 1111$ configurations, around 90% of the network will have undergone a cage decay event, and so we would expect the spatial heterogeneity to be decreased, and that $g_u(r, \Delta t)$ would approach $g(r)$, and this is as observed, *i.e.* the purple and cyan lines in figure 6.16 largely coincide.

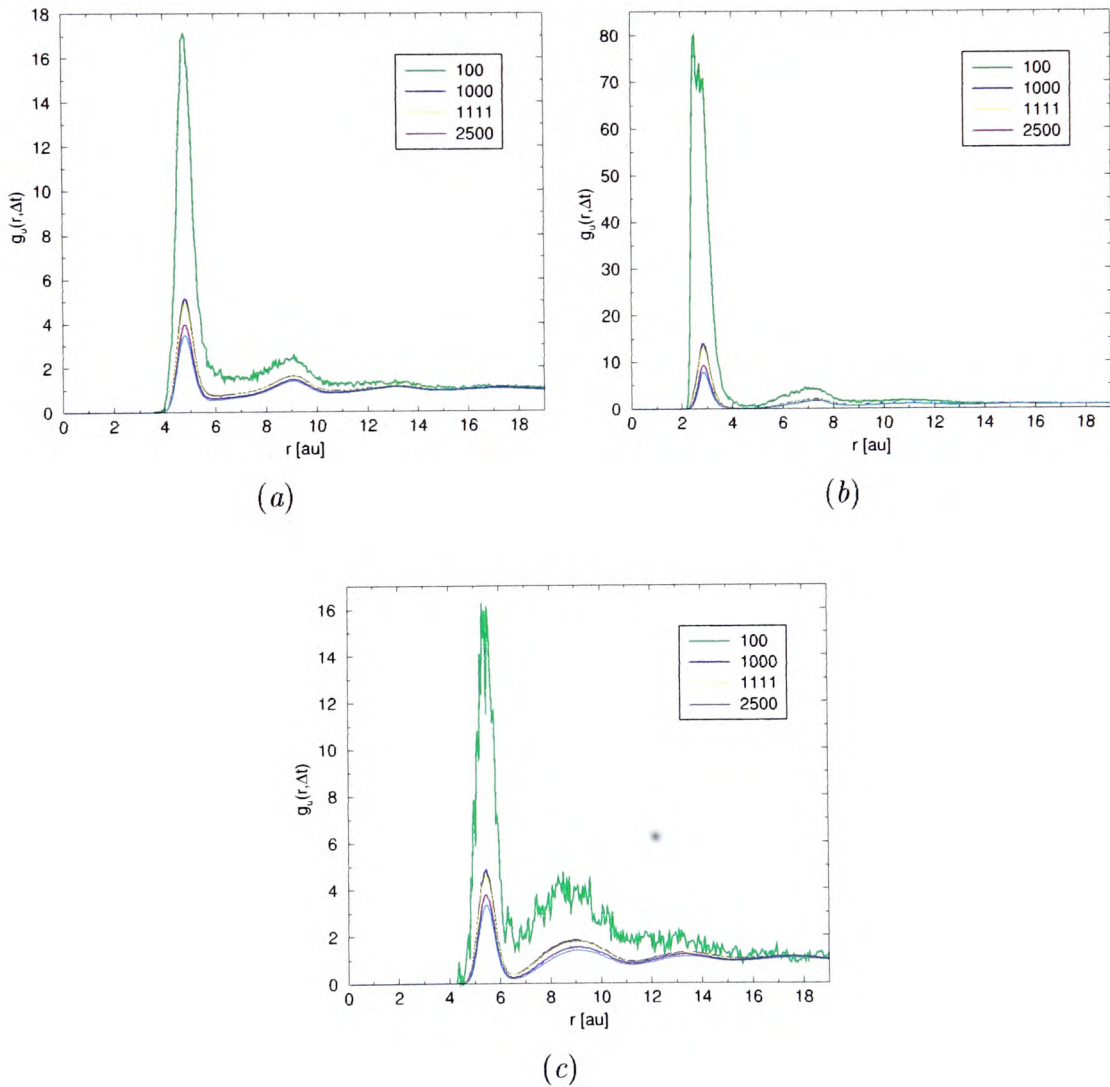


Figure 6.16: The partial mobile-mobile weighted radial distribution functions for (a) the anion-anion, (b) the cation-anion, and (c) the cation-cation distributions in PIM BeF₂ at 700 K. The cyan lines show the relevant ordinary partial radial distribution function in each case.

6.3.3 The coordination number dependent, mobile ion weighted radial distribution function

We can define $\theta_i(t, \Delta t)$ and $\theta_j(t, \Delta t)$ according to the relations

$$\theta_i(t, \Delta t) = \begin{cases} 1 & \text{if } N_i^c(t) = N^{c*} \\ 0 & \text{if } N_i^c(t) \neq N^{c*} \end{cases}, \quad (6.9)$$

and

$$\theta_j(t, \Delta t) = \begin{cases} 0 & \text{if } \mu_j(t, \Delta t) < r_{\text{cutoff}} \\ 1 & \text{if } \mu_j(t, \Delta t) \geq r_{\text{cutoff}} \end{cases}, \quad (6.10)$$

where r_{cutoff} is the same length scale for an ion to be considered as mobile, and where $N_i^c(t)$ is the coordination number of ion i at time t , and N^{c*} is the coordination number of interest. This weighted radial distribution function is called the coordination number-mobile weighted radial distribution function. This function has been developed to examine the relative abilities of ions of different coordination types to promote motion within the network, both locally and over an extended range.

Figure 6.17 shows the *cation-cation* partial coordination number-mobile weighted radial distribution function for $N^c(\text{Be}^{2+}) = 3, 4, 5$ in PIM BeF_2 at 700 K³. There are relatively poor statistics for the $N^c = 5$ distributions due to the low concentration of $N^c = 5$ defect sites at this temperature, and particularly at short time when few particles have moved further than the cutoff distance, *i.e.* there are few mobile particles. However, it is clear that the degree of excess correlation is much higher for the $N^c = 3$ species than for $N^c = 4, 5$. This means that the ability of the 3-coordinate defect site to promote mobility in the local network is much enhanced compared to the other types of coordination species, and now the excess correlation extends beyond even the second coordination shell. Note that for $\Delta t > \tau_{\text{BeF}}$, the enhancement at large r can be somewhat accounted for by the decrease of $g_u(r, \Delta t)$ below $g(r)$ in the region of the first peak, as the mobile ions have moved out of the

³The ordinary partial distribution function, $g_{\text{BeBe}}(r)$, shown in these figures is the cation-cation partial radial distribution function for cations of all coordination numbers, and not just for a given coordination number. This allows better comparison of the effects of a cation having a given coordination number with the system as a whole.

first coordination shell to create extra intensity elsewhere.

Despite the poor statistics, we can see that there is negligible excess correlation for the $N^c = 4, 5$ species, and this suggests the pre-eminent role of the 3-coordinate defect site in promoting the fluidity of the network.

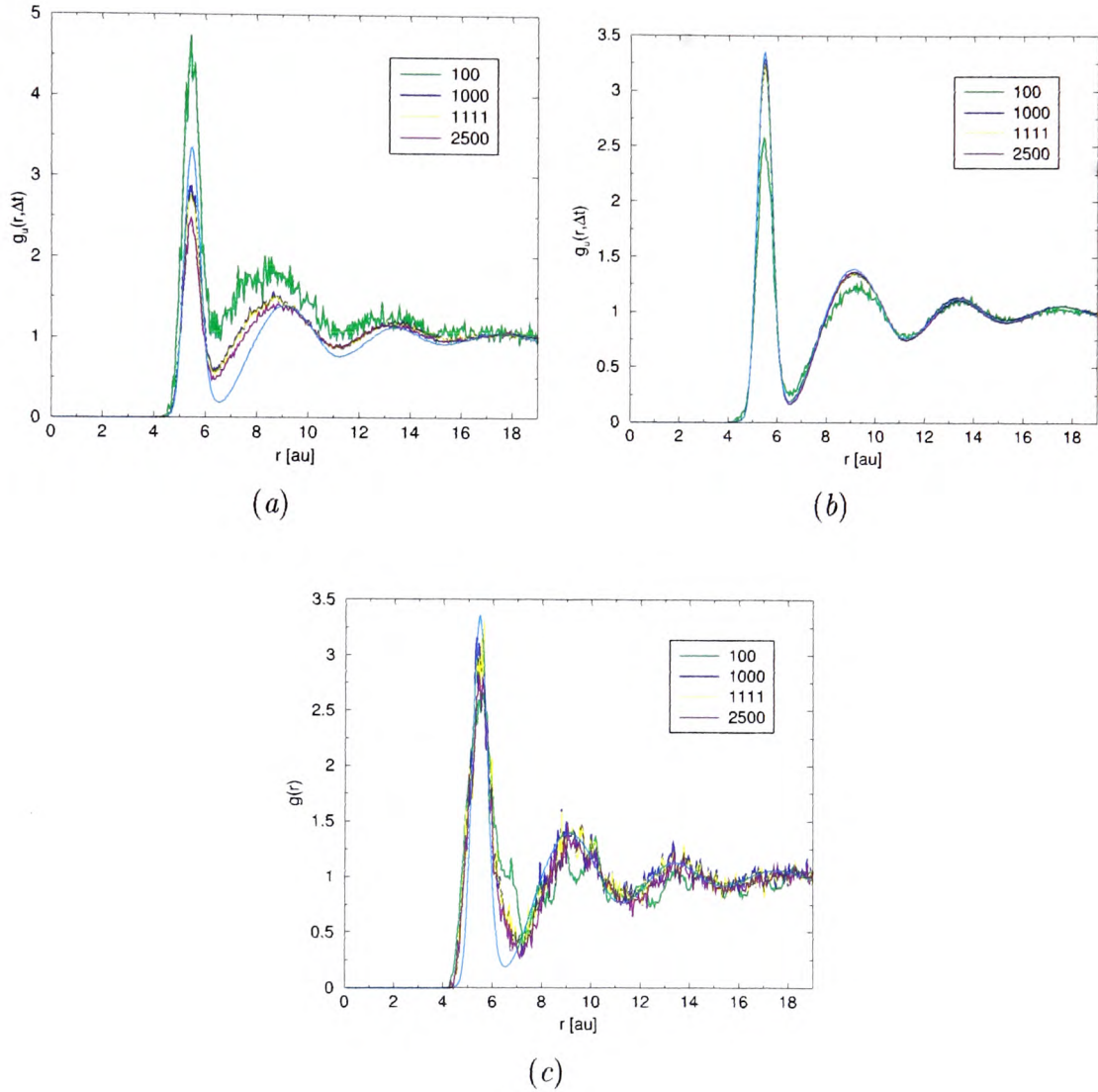


Figure 6.17: The cation-cation partial coordination number-mobile weighted radial distribution functions for (a) $N^c(Be^{2+}) = 3$, (b) $N^c(Be^{2+}) = 4$, and (c) $N^c(Be^{2+}) = 5$ in PIM BeF_2 at 700 K. The cyan lines show the ordinary cation-cation partial radial distribution function in each case.

6.3.4 The coordination number dependent, change in coordination number weighted radial distribution function

If we define $\theta_i(t, \Delta t)$ and $\theta_j(t, \Delta t)$ in equation 6.6 according to the relations

$$\theta_i(t, \Delta t) = \begin{cases} 1 & \text{if } N_i^c(t) = N^{c*} \\ 0 & \text{if } N_i^c(t) \neq N^{c*} \end{cases}, \quad (6.11)$$

and

$$\theta_j(t, \Delta t) = \begin{cases} 0 & \text{if } N_j^c(t) = N_j^c(t - \Delta t) \\ 1 & \text{if } N_j^c(t) \neq N_j^c(t - \Delta t) \end{cases}, \quad (6.12)$$

where N^{c*} is again the coordination number of interest, then we generate a radial distribution function weighted by those ions which change their coordination number over the time interval, Δt , subject to the condition that there is an ion of a given coordination number at the origin. This function is known as the coordination number-change in coordination number weighted radial distribution function. This function has been developed to examine the spatial relation of ions which are changing their coordination number, which corresponds to the creation or annihilation of a defect, to ions of a given coordination number, and hence to examine the spatial propagation of defects throughout the network.

Figure 6.18 shows the cation-cation partial coordination number-change in coordination number weighted radial distribution function for PIM BeF₂ at 700 K. The main observation here is that there is a higher probability of finding a cation changing its coordination number in the region between the first and second shells of a 3-coordinate cation than for 4- and 5-coordinate species over a time scale up to $\sim \tau_{BeF}$ (despite the poor statistics for the $N^c = 5$ functions again, due to the low concentration of $N^c = 5$ cation sites). There is an accompanying loss of intensity in the first shell peak, in the $N^c = 3$ function, as the ion changing its coordination number moves out of the first coordination shell. This suggests that the $N^c = 3$ species has a higher ability to cause the surrounding ions to change their coordination number, and hence to propagate the defect throughout the network. We saw from the analysis of the coordination number dependent-mobile ion weighted radial distribution function that the mobility was enhanced around a 3-coordinate defect

sites, and hence these sites also have a higher ability to promote mobility, and the spread of mobility throughout the network. The $N^c = 4, 5$ functions, however, have a similar form to $g(r)$ for all time scales, and hence these sites do not have any extra ability to promote defect propagation.

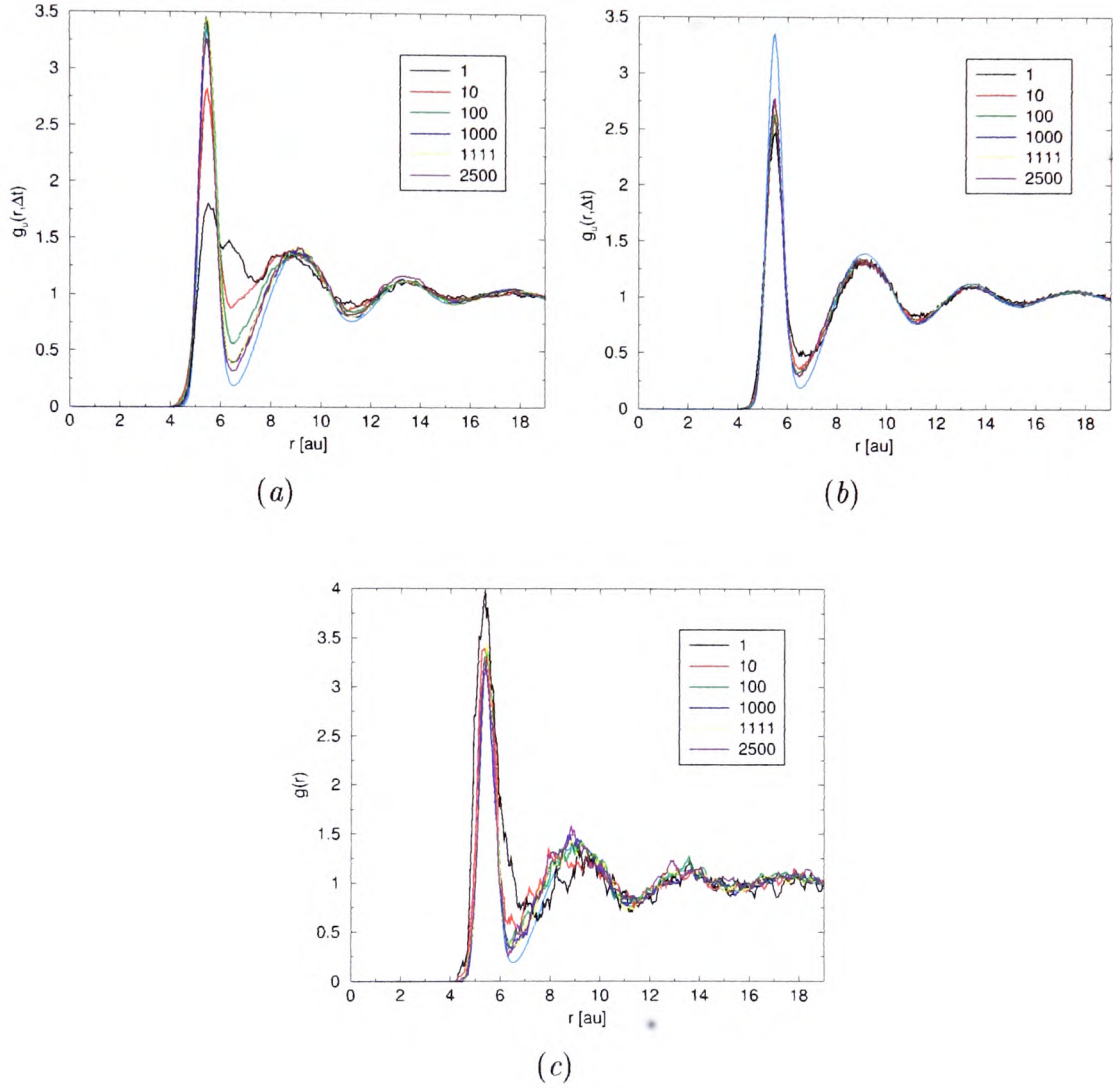


Figure 6.18: The cation-cation partial coordination number-change in coordination number weighted radial distribution functions for (a) $N^c(Be^{2+}) = 3$, (b) $N^c(Be^{2+}) = 4$, and (c) $N^c(Be^{2+}) = 5$ in PIM BeF_2 at 700 K. The cyan lines show the ordinary cation-cation partial radial distribution function in each case.

6.3.5 The temperature dependence of the extended weighted radial distribution functions

Figure 6.19 shows the cation-anion and figure 6.20 the cation-cation partial mobile-mobile weighted radial distribution functions for PIM BeF₂ at 700 K and 1300 K evaluated at the cage decay time, together with the ratio of the weighted to the unweighted function, $\Gamma(r, \tau_{BeF}(T))$, and the excess correlation function, $\int \Gamma(r, \tau_{BeF}(T)) dr$. This should be compared to figure 6.6 which contains the equivalent ratios for the displacement-displacement weighted radial distribution functions.

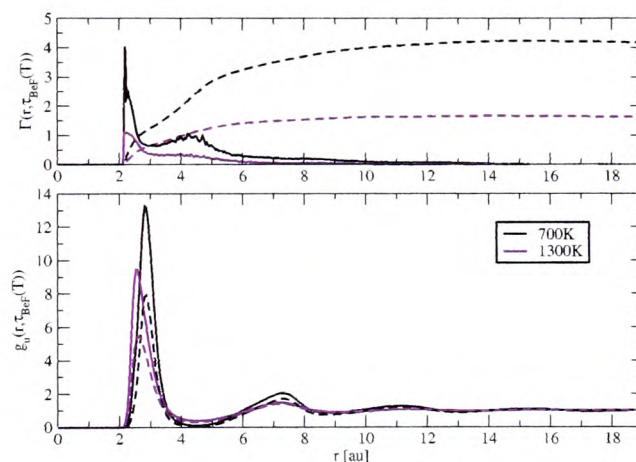


Figure 6.19: The cation-anion partial mobile-mobile weighted radial distribution function for PIM BeF₂ at 700 K and 1300 K, evaluated at the cage decay time, τ_{BeF} , and shown with the ordinary cation-anion partial radial distribution function, with dashed lines, for comparison. The upper panel shows the ratio of the weighted to unweighted functions, $\Gamma(r, \tau_{BeF})$, with the solid lines, and the excess correlation function, $\int \Gamma(r, \tau_{BeF}) dr$, with the dashed lines.

The forms of the distributions are the same as for the displacement-displacement weighted distribution, with the mobile-mobile weighted distribution also having additional intensity compared to the unweighted function over an r range extending to the second coordination shell, and with both the magnitude and the range of the excess correlation decreasing with temperature, *i.e.* as the system becomes more

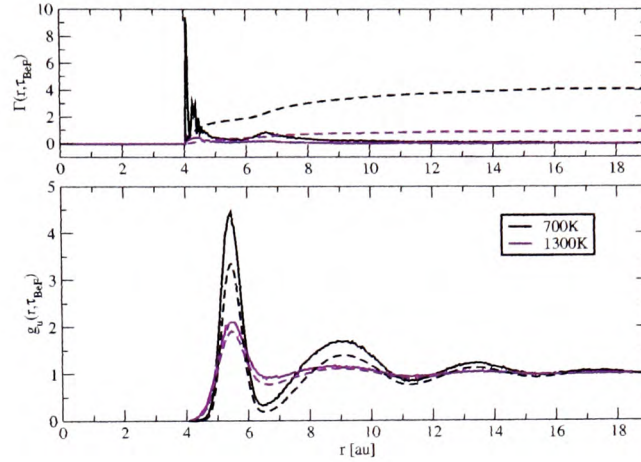


Figure 6.20: The cation-cation partial mobile-mobile weighted radial distribution function for PIM BeF₂ at 700 K and 1300 K. The key to the lines is the same as for figure 6.19.

spatially homogeneous. The absolute magnitude of the excess correlation is higher for the mobile-mobile weighted function, *e.g.* $A_{BeF}^{dd}(\tau_{BeF}(700\text{ K})) = 1.2$ whereas $A_{BeF}^{mm}(\tau_{BeF}(700\text{ K})) = 4.1$ (where *dd* refers to the displacement-displacement and *mm* refers to the mobile-mobile weighted distribution functions respectively). The *dd* function includes contributions from particles which have only moved small distances, as it includes all particles in its calculation, whereas the *mm* function includes only those particles which have made considerable displacements, and the higher value for the total excess correlation suggests that the mobile ions with large displacements have a greater degree of spatial correlation than those ions with a general value of the displacement⁴.

Figures 6.21 and 6.22 respectively show the cation-cation partial weighted radial dis-

⁴The different value of the total excess correlation may also be due, however, to the way it is calculated. When $\mu_i(t, \Delta t) > r_{\text{cutoff}}$ we add 1 to the count in the *mm* algorithm, and 0 if the reverse condition is satisfied, whereas in the *dd* algorithm we always add a contribution of $\frac{\mu_i(t, \Delta t)}{\bar{\mu}}$, which is likely to be smaller than 1, as we saw from the analysis of the van Hove self-correlation function (see section 4.2) that there are relatively few particles which have displacements larger than the cutoff distance.

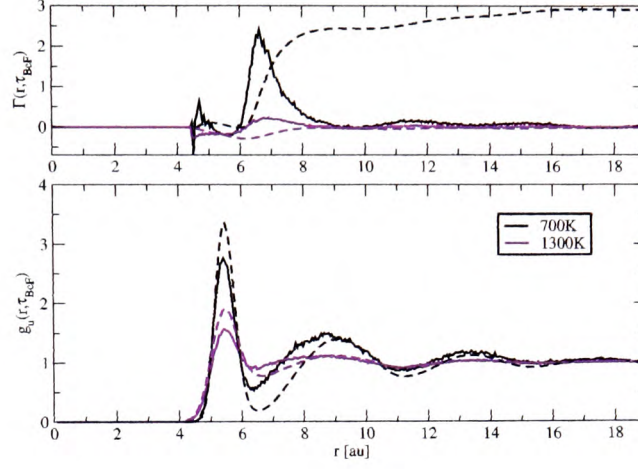


Figure 6.21: The cation-cation partial coordination number dependent-mobile ion weighted radial distribution function for 3-coordinate cations in PIM BeF_2 at 700 K and 1300 K, evaluated at the cage decay time, τ_{BeF} , and shown with the ordinary cation-anion partial radial distribution function, with dashed lines, for comparison. The upper panel shows the ratio of the weighted to unweighted functions, $\Gamma(r, \tau_{\text{BeF}})$, with the solid lines, and the excess correlation function, $\int \Gamma(r, \tau_{\text{BeF}}) dr$, with the dashed lines.

tribution functions for the coordination number dependent-mobile ion and coordination number dependent-change in coordination number functions, for 3-coordinate cations. Again, the form of these functions and the excess correlation is as seen with the other weighted functions, with the range and magnitude of the excess correlation decreasing with temperature. Now, at the highest temperature, 1300 K, there is very little excess correlation in these functions compared to the dd and mm functions described above, although the excess correlation at lower temperature is comparable. The values of the total excess correlation in the cation-cation sub-system at the lowest and highest temperatures are given in table 6.1.

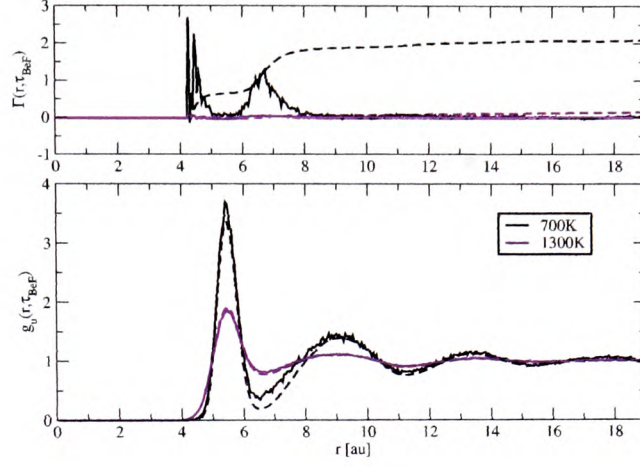


Figure 6.22: The cation-cation partial coordination number dependent-change in coordination number weighted radial distribution function for 3-coordinate cations in PIM BeF₂ at 700 K and 1300 K, evaluated at the cage decay time, τ_{BeF} , and shown with the ordinary cation-anion partial radial distribution function, with dashed lines, for comparison. The upper panel shows the ratio of the weighted to unweighted functions, $\Gamma(r, \tau_{BeF})$, with the solid lines, and the excess correlation function, $\int \Gamma(r, \tau_{BeF}) dr$, with the dashed lines.

6.4 Summary of the weighted radial distribution function analysis

The focus of the investigation of the behaviour of the weighted radial distribution functions has been with the results obtained from the PIM simulations. This is justified as the behaviour of the functions for the RIM is similar to that for the PIM when time scales are scaled in terms of the cage relaxation time for a given system. The main difference between the PIM and the RIM is the high 3-coordinate defect concentration in the former, though the spatial behaviour of the effect of this type of site is broadly similar in each type of model, as reflected in our investigation of the displacement-displacement weighted radial distribution function for RIM BeF₂ in section 6.2.2.

From our analysis of the extended weighted radial distribution functions in PIM

Temperature [K]	<i>dd</i>	<i>mm</i>	<i>cm</i>	<i>cc</i>
700	0.86	4.07	2.92	2.10
1300	0.23	0.91	~ 0	0.15

Table 6.1: The total excess correlation in the cation-cation sub-system evaluated at the cage relaxation time, $A_{BeBe}^{xx}(\tau_{BeF}(T)) = \int_0^\infty \Gamma_{BeBe}^{xx}(r, \tau_{BeF}(T)) dr$, for the different weighted radial distribution functions. *xx* refers to (i) *dd* for the displacement-displacement, (ii) *mm* for the mobile-mobile, (iii) *cm* for the coordination number dependent-mobile, and (iv) *cc* for the coordination number dependent-change in coordination number weighted functions. In (iii) and (iv) the cation coordination number is 3.

BeF₂, we see the vital role played by the 3-coordinate defect sites in the fluidity of the network. These species have an enhanced probability of being surrounded by mobile ions, as defined by the criteria that an ion is mobile over a given time period, Δt , if its displacement over that time scale, $\mu_i(t, \Delta t)$, is greater than the cage cutoff distance, r_{cutoff} , and also of being surrounded by those ions which are changing their coordination number, over a range of approximately two coordination shells. This probability is enhanced when compared to that of the 4- and 5-coordinate cation species, which are essentially indistinguishable in this analysis. We can also see that mobile ions have an enhanced probability of being found close to other mobile ions, and hence we can conclude that the 3-coordinate species is able to promote mobility in the region of the defect, and also to promote the propagation of the defect through the network and thus to promote the spread of the mobility and diffusivity. The particular importance of the 3-coordinate defect site compared to the 5-coordinate one is likely to be due to the *intermediate* cage relaxation time of the 3-coordinate species. The cage relaxation time of the 3-coordinate species, $\tau_{BeF}^{N^c=3}$, is approximately 3 to 4 times longer than that of the 5-coordinate species, $\tau_{BeF}^{N^c=5}$ (see table 4.7) and this allows the action of the defect, *i.e.* defect propagation and enhanced ionic mobility, to be observed before the defect itself is annihilated. The time scale over which the maximum excess correlation is observed, labelled τ^* in section 6.2, is shorter than the overall cage relaxation time, τ_{BeF} (which is 1111 configurations at

700 K), and in fact lies closer to the cage relaxation time of the 3-coordinate species ($\tau_{BeF}^{N^c=3} = 502$ configurations at 700 K).

The anomalously high mobility of our PIM simulation model can be traced back to the high concentration of 3-coordinate defect sites within the system, and the ability of these sites to promote high mobility of the surrounding ions over the range of two or three coordination shells around the defect. We have changed our PIM potential, as discussed in chapter 9, and one of the main results is a dramatic decrease in the concentration of non-tetrahedral cation sites (see, for example, figure 9.5), and this was accompanied by a huge reduction in diffusivity. The effective polarisability of the system therefore has an important role in stabilising the creation and persistence of the 3-coordinate defects, and this is examined in chapter 7.

Chapter 7

BeF₂: The mechanism of coordination shell exchange

7.1 Introduction

In the discussion of the cage correlation function, we investigate the time taken for there to be a change in the identity of one or more of the cage-ions surrounding the central ion. Only when there is a change do we describe the cage as having decayed, which we can associate with the diffusive event in the network relaxation via the introduction of the jump length of the cage decay, *i.e.* the diffusion coefficient can be calculated from the cage decay rate and the jump length. We have seen that the very high diffusivity associated with our original PIM potential (compared to the RIM potential or to subsequent PIM potentials, as described in chapter 9) can be linked to the presence of relatively large numbers of 3-coordinate defects cations which greatly enhance the fluidity of the network. We would like to be able to explain why the defect population is so high, and in particular link the characteristic structure of the first coordination shell to the ability of the system to form and sustain the high defect concentrations.

7.2 The neighbourhood radial distribution function

The **neighbourship radial distribution function** [65, 66, 67] offers us a description of the spatial arrangement of the cage-ions, and a way of linking the change in

position of the cage-ions to the rate at which the decay occurs.

The neighbourhood radial distribution function is simply the one-particle radial distribution function: the neighbours of a given ion can be ordered in terms of the separation of the neighbouring ion from that central ion and hence be defined as first neighbour, second neighbour, and so on. If we calculate the average distribution of these separations over all choices of the central ion, we get a set of pair distribution functions, $g(n, r)$, for each value of the neighbour number, n . If we were to then sum over all the neighbours, n , we would recover the standard radial distribution function, *i.e.*

$$g(r) = \sum_n g(n, r). \quad (7.1)$$

In general, we are interested in the probability of finding the n^{th} neighbour of the central ion at a given separation, and so we have to allow for the fact that the volume available changes with distance from the central ion, and hence we define the neighbourhood probability distribution function, $P(n, r)$, as

$$P(n, r) = 4\pi\rho r^2 g(n, r). \quad (7.2)$$

where ρ is the density. Note that for a given n , $\int P(n, r)dr = 1$, *i.e.* there is only 1 n^{th} neighbour. Again, the radial probability function, $P(r)$, is simply the sum over neighbours in the neighbourhood probability distribution function,

$$P(r) = 4\pi\rho r^2 g(r) = \sum_n P(n, r). \quad (7.3)$$

In a multicomponent system, we may define a set of neighbourhood partial radial distribution and probability functions, $g_{\alpha\beta}(n, r)$ and $P_{\alpha\beta}(n, r)$, where the integrated probability function, $\int P_{\alpha\beta}(n, r)dr$, need not now be 1 for a given n . This can be understood by looking at figure 7.1. This shows a segment of the *ideal* network in BeF_2 , with a central cation bonded to four neighbouring anions, the nearest neighbour cage, and then each of these anions is bonded to a further cation, the next nearest neighbours (because the anions are bi-coordinate bridging species), and so on, with the next nearest neighbour cations being bonded to three further

anions each.

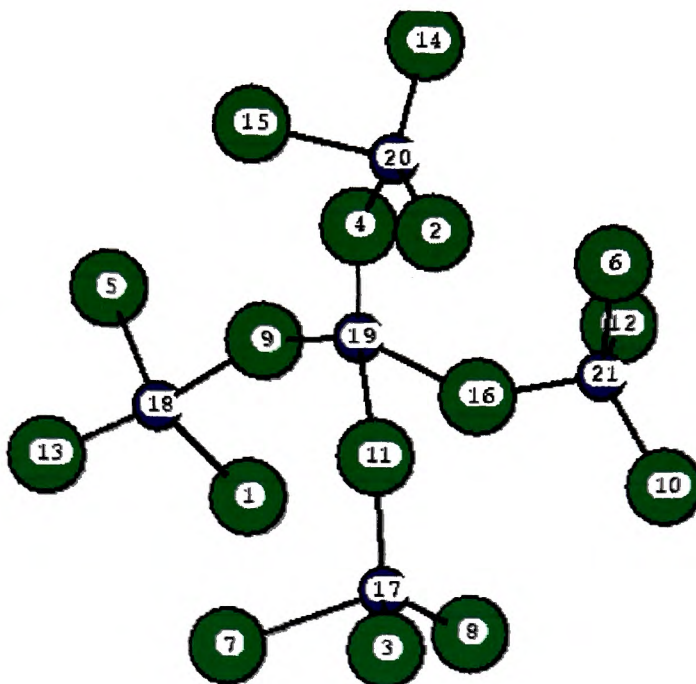


Figure 7.1: A section of the ideal tetrahedral network. Each of the cations, shown in blue, is tetrahedrally coordinated to four anions, shown in green, and these act as bridging species to four further cations, and so on. The numbers on the ions correspond to those given in tables 7.1 and 7.2.

In this ideal system, the arrangement of ions around a given cation will be as shown in table 7.1, and around a given anion as shown in table 7.2. Around the central cation, there will be very little intensity in the $g_{BeF}(5 \rightarrow 8, r)$ functions, as the $n = 5 \rightarrow 8$ positions around the central cation are principally occupied by the shell of next nearest neighbour cations. Any intensity we do observe is due to non-ideality in the network, and this can be related to the motion of the diffusing ions, because when the ions move they pass through the regions of space corresponding to the non-ideal positions, *i.e.* through the space between coordination shells.

Figures 7.2 and 7.3 show the total and partial neighbourship and probability radial distribution functions for each of the partial sub-systems in PIM BeF₂ at 700 K. We can see from $g_{BeF}(n, r)$, shown in panel (c) of figure 7.2, that the first peak in $g_{BeF}(r)$ contains the individual contributions from the first four anions, as expected,

neighbour, n	identity
1-4	F^4, F^9, F^{11}, F^{16}
5-8	$Be^{20}, Be^{18}, Be^{17}, Be^{21}$
9-20	$(F^2, F^{14}, F^{15}), (F^1, F^5, F^{13}), (F^3, F^7, F^8), (F^6, F^{10}, F^{12})$

Table 7.1: The identity and type of the neighbouring ions around a central cation in a segment of an ideal tetrahedral network, demonstrated for BeF_2 . The central ion is Be^{19} , where the number refers to the labels as shown in figure 7.1.

neighbour, n	identity
1-2	Be^{19}, Be^{21}
3-8	$(F^4, F^9, F^{11}), (F^6, F^{10}, F^{12})$
9-14	$Be^{20}, Be^{18}, Be^{17}, Be^{*1}, Be^{*2}, Be^{*3}$
15-32	$(F^2, F^{14}, F^{15}), (F^1, F^5, F^{13}), (F^3, F^7, F^8), 3F^{*1}, 3F^{*2}, 3F^{*3}$

Table 7.2: The identity and type of the neighbouring ions around a central anion in a segment of an ideal tetrahedral network, demonstrated for BeF_2 . The central ion is F^{16} , where the number refers to the labels as shown in figure 7.1. An ion labelled with a * refers to an ion not shown in figure 7.1.

but that the distribution for the fourth anion, $g_{BeF}(4, r)$, is much broader than that for the first three anions (this can be seen particularly in the inset). This is the origin of the high tendency to form the 3-coordinate defect species, in as much as the fourth anion spends a higher proportion of its time relatively far from the central cation, with a relatively high value of $g_{BeF}(4, r)$ in the region of the first minimum in $g_{BeF}(r)$, hence being more easily lost. Figure 7.4 shows the variation with temperature of the BeF partial neighbourship radial distribution function for the fourth anion neighbour around the central cation, $g_{BeF}(4, r)$, for the PIM and the RIM. The principal difference between the two models is the much greater extension of the high r tail of $g_{BeF}(4, r)$ out into the region of the first minimum in $g_{BeF}(r)$, the *inter-shell* region, in the PIM, particularly at higher temperatures, and this is emphasised when we consider the neighbourship probability functions, $P_{BeF}(4, r)$, which are shown in the insets in figure 7.4, where we can now see that there is a significant probability of finding an anion in the inter-shell region in the PIM, but that it is still small in the RIM.

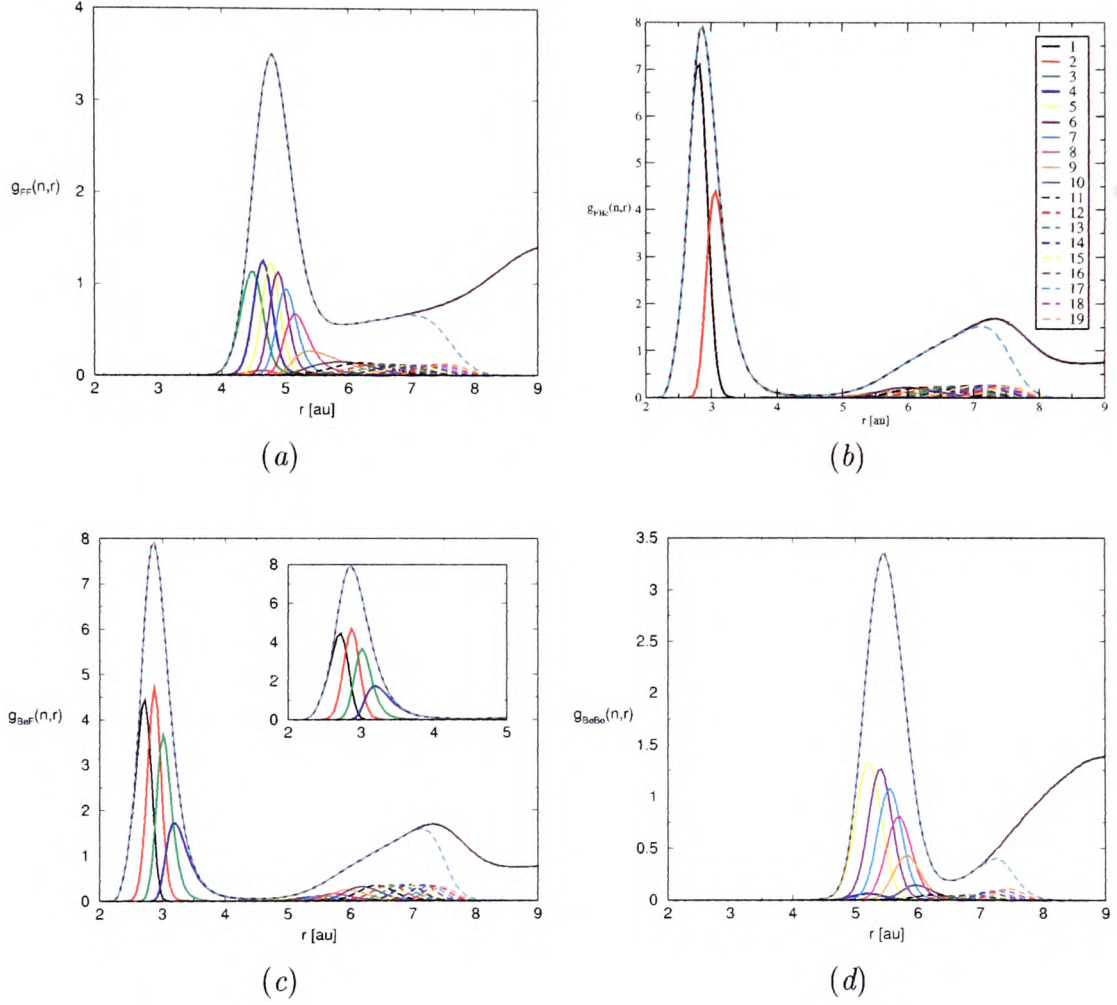


Figure 7.2: The neighbourhood radial distribution functions, for $n = 1 \rightarrow 19$, for PIM BeF₂ at 700 K. The maroon line shows the ordinary radial distribution function, $g_{\alpha\beta}(r)$, and the dashed turquoise line is the sum of the individual neighbourhoodship radial distribution functions, *i.e.* $\sum_{n=1}^{19} g_{\alpha\beta}(n, r)$, and the other colours are as given by the legend in panel (b), where the numbers refer to the values of n . The individual panels show (a) $g_{FF}(n, r)$, (b) $g_{FBe}(n, r)$, (c) $g_{BeF}(n, r)$, and (d) $g_{BeBe}(n, r)$. The inset of panel (c) shows the $g_{BeF}(r)$ neighbourhood function in the first shell environment, $n = 1 \rightarrow 4$, on a larger scale.

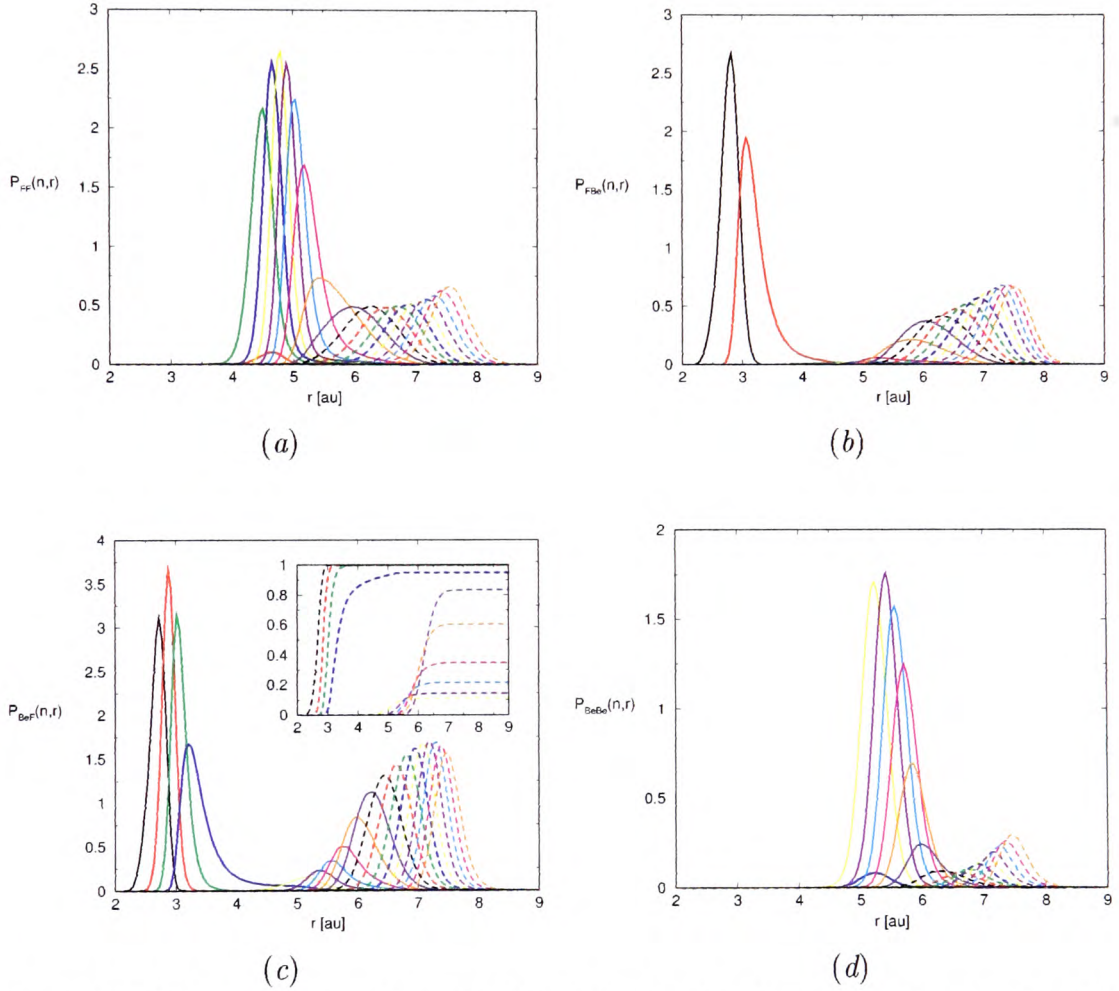


Figure 7.3: The neighbourship probability distribution functions, for $n = 1 \rightarrow 19$, for PIM BeF₂ at 700 K. The individual panels are as in figure 7.2. The inset to the panel (c) shows the running integral of the neighbourship probability distribution functions, $\int P_{BeF}(n, r) dr$, for $n = 1 \rightarrow 10$. The colours of the lines are as given in figure 7.2.

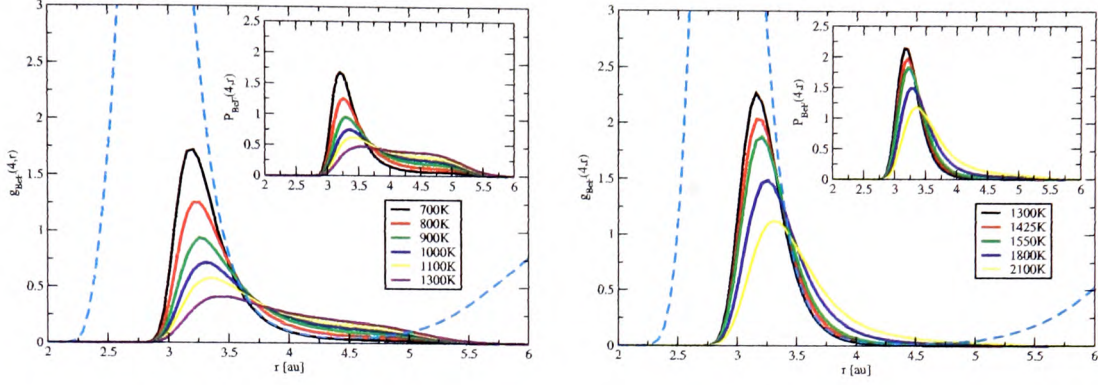


Figure 7.4: The variation with temperature of the cation-anion partial neighbour-ship radial distribution functions for the 4th nearest anionic neighbour around a central cation, $g_{BeF}(4, r)$, for the PIM (in the left-hand panel) and the RIM (in the right-hand panel). The insets show the relevant cation-anion partial neighbour-ship probability distribution functions, $P_{BeF}(4, r)$. The dashed cyan lines show the cation-anion partial radial distribution function, $g_{BeF}(r)$, for PIM at 700 K and RIM at 1300 K, respectively. The cutoff for the first shell is at the minimum in this function, $r_{BeF}^{\min}$.

7.2.1 The probability overlap function

The probability functions, $P_{\alpha\beta}(n, r)$, give the distributions of the separations of the central ion and the n^{th} neighbour. As the network relaxes, ions necessarily move into the space (formerly) occupied by other ions, and the ease of network relaxation will depend on how easy it is for a given ion to move into the space of surrounding ions. The probability of finding two neighbouring ions, the n and $n + 1$ neighbours, of type β around a central ion of type α , in the same space, $P_{\alpha\beta}([n, n + 1], r)$, is given by the product of finding the individual neighbours in that space,

$$P_{\alpha\beta}([n, n + 1], r) = P_{\alpha\beta}(n, r)P_{\alpha\beta}(n + 1, r). \quad (7.4)$$

This *probability overlap function* is shown in figure 7.5 for the Be–F partial probability overlap functions, $P_{BeF}(n, r)P_{BeF}(n + 1, r)$, in the PIM at 700 K and the RIM at 1550 K (the comparison is made between these systems because of the similarity of the ionic diffusion coefficients between the two models at these temperatures). The

probability overlap function emphasises the absence of intensity in the inter-shell region, as both $P_{BeF}(n, r)$ and $P_{BeF}(n + 1, r)$ are small in this region, but we can again see differences between the two models. This function is a measure of the amount of overlap of the $n \leftrightarrow n + 1$ positions, and hence the transfer between them, and we can see that these distributions are lower and broader in the first shell in the PIM than in the RIM. The broader distribution, which corresponds to increased transfer, is a sign that there is a more flexible first coordination shell in the PIM, and hence that there is a more flexible network as a whole, even though the diffusion coefficients are approximately comparable. This flexibility is seen in the value of the E -bending vibrational mode, which occurs at too low a frequency in the PIM (see section 9.2).

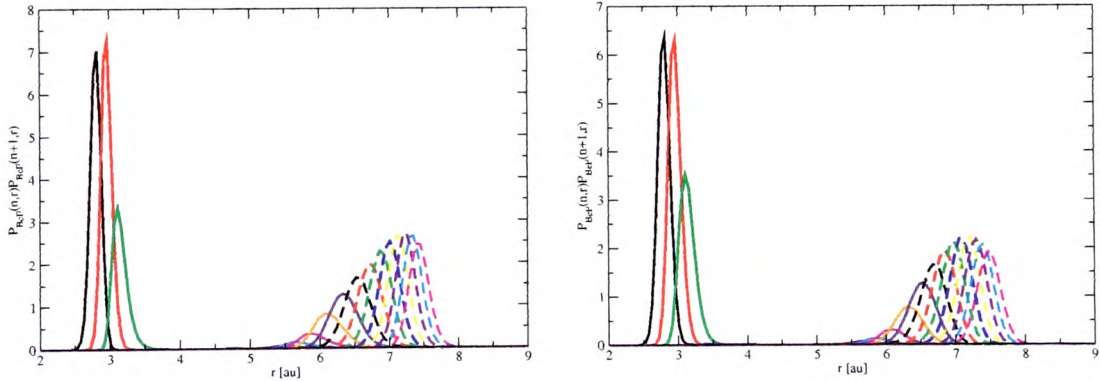


Figure 7.5: The cation-anion partial probability overlap function, $P_{BeF}(n, r)P_{BeF}(n + 1, r)$, for the PIM at 700 K (in the left-hand panel) and the RIM at 1550 K (in the right-hand panel).

7.2.2 The total and partial overlap integrals

When there is a change in the local coordination of an ion, there is likely to be a change in the ordering of the neighbours. As the network relaxes, the ease of diffusion depends upon the ease of transfer of one neighbour into the space occupied by another. We can measure this by constructing the *overlap integral*, $O_{\alpha\beta}(n, n + 1)$,

which is the probability overlap function integrated over all space,

$$\begin{aligned} O_{\alpha\beta}(n, n+1) &= \int P_{\alpha\beta}(n, r) P_{\alpha\beta}(n+1, r) dr \\ &= \int P_{\alpha\beta}([n, n+1], r) dr. \end{aligned} \quad (7.5)$$

This is the total probability of the n and $n+1$ neighbours being found in the same volume of space, and hence is related to the rate of interchange between the positions of those particles.

The overlap integral does not take into account the fact that the integrals of the individual partial probability distributions do not all equal 1; the relative weights of the $O_{BeF}(1, 2)$ and $O_{BeF}(2, 3)$ overlap integrals, for example, are much higher than those of $O_{BeF}(4, 5)$ and $O_{BeF}(5, 6)$ simply as a result of the topology of the network, *i.e.* very few anions are found, for example, in the 5th and 6th neighbour positions around a central cation (see figure 7.1), and hence, for example, $P_{BeF}(5, r)$, $P_{BeF}(5, r)P_{BeF}(6, r)$, and $O_{BeF}(5, 6)$ are all *always* small. The *normalised overlap integral*, $F_{\alpha\beta}(n, n+1)$, given by

$$\begin{aligned} F_{\alpha\beta}(n, n+1) &= \frac{\int P_{\alpha\beta}(n, r) P_{\alpha\beta}(n+1, r) dr}{\sqrt{\int P_{\alpha\beta}^2(n, r) dr \int P_{\alpha\beta}^2(n+1, r) dr}} \\ &= \frac{O_{\alpha\beta}(n, n+1)}{\sqrt{O_{\alpha\beta}(n, n) O_{\alpha\beta}(n+1, n+1)}}, \end{aligned} \quad (7.6)$$

scales $O_{\alpha\beta}(n, n+1)$ by the *self-overlap* probability integrals, $\int P_{\alpha\beta}^2(n, r) dr = O_{\alpha\beta}(n, n)$, which means that the intensity in these distributions is a measure of the migration of ions between the n and $n+1$ positions, and is not small in a particular region simply due to there being only a small probability of finding an ion of type β in the n^{th} neighbourhood position of the central ion of type α .

Figure 7.6 shows the variation with temperature of the cation-anion partial normalised overlap integral, $F_{BeF}(n, n+1)$, for PIM and RIM BeF₂. Now that the low partial overlap probability functions, $P_{BeF}([n, n+1], r)$, in the inter-shell region have been allowed for, we can see that there is a clear divide between the first shell region and beyond, at $n \approx 4$, and that there is also some evidence of the divide between the second and third coordination shells, *i.e.* between the first cation

shell and the second anion shell around the central cation, in the small decrease in $F_{BeF}(8, 9)$ compared to $F_{BeF}(7, 8)$ and $F_{BeF}(9, 10)$. This is only visible in the lowest temperature PIM simulation, at 700K, but it can be seen in the RIM even up to 1800K. This suggests that the network really is ideal even out as far as the third coordination shell in the RIM, and is relatively deformed in the PIM even down to low temperatures.

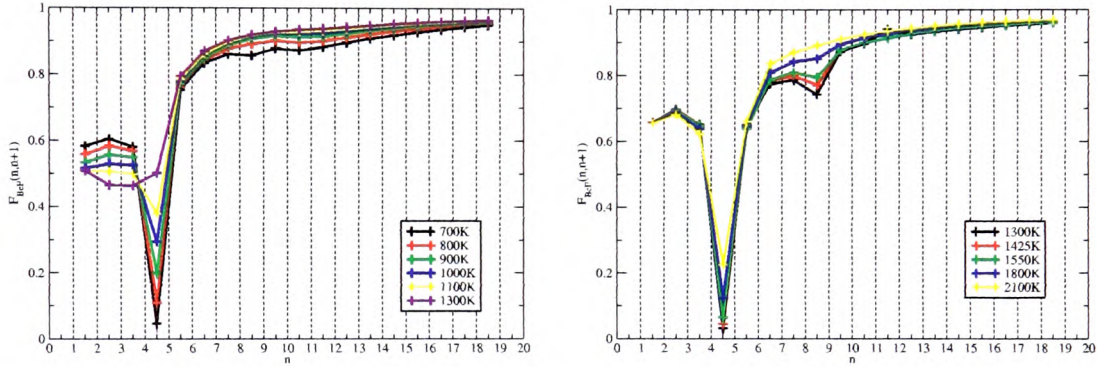


Figure 7.6: The variation with temperature of the cation-anion partial normalised overlap integral, $F_{BeF}(n, n + 1)$, in PIM (in the left-hand panel) and RIM (in the right-hand panel) BeF_2 .

7.2.3 The temperature dependence of the overlap integrals

We can see from figure 7.6 that the increase with temperature of the value of the normalised overlap integral for the boundary between first and second coordination shells, $F_{BeF}(4, 5)$, is faster in the PIM than the RIM. Figure 7.7 shows the variation with inverse temperature of $F_{BeF}(4, 5)$ for the PIM and the RIM, and it also includes the cationic diffusion coefficients (in cm^2s^{-1} , $\times 10^4$).

If we fit $F_{BeF}(4, 5)$ to the Arrhenius form, then we can effectively calculate an activation energy for the $n = 4 \rightarrow 5$ (first to second coordination shell) transfer, *i.e.*

$$F_{BeF}(4, 5)(T) = F_0 \exp \left(-\frac{E_A}{RT} \right), \quad (7.7)$$

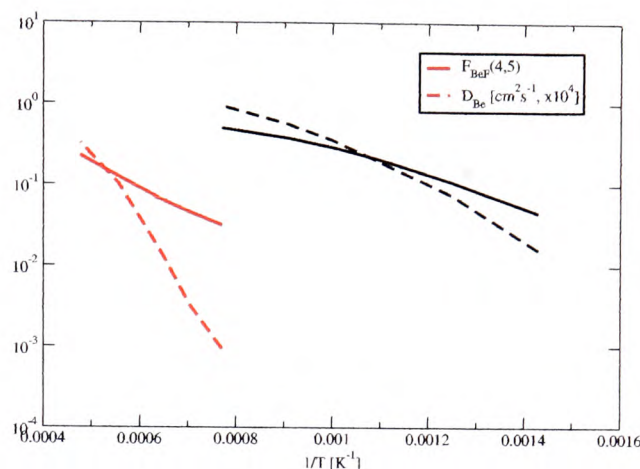


Figure 7.7: The variation with temperature of the cation-anion partial normalised overlap integral, $F_{BeF}(4,5)$, for the PIM (in black) and the RIM (in red), for the boundary between the first and second coordination shells around a central cation in BeF_2 . The cationic diffusion coefficients are also shown with dashed lines (in cm^2s^{-1} , $\times 10^4$).

and this activation energy is given in table 7.3 for the two models. Also shown in this table are the activation energies for the formation of the defects and migration of the ions, after the defects have been created, as given in tables 4.8 (for the PIM) and 5.8 (for the RIM). The overall activation energies for diffusion are $E_A^{PIM} = 51.5 kJmol^{-1}$ and $E_A^{RIM} = 170.1 kJmol^{-1}$. It appears, at least for the RIM model, that the activation energy for first to second shell transfer can be closely associated with the activation energy for defect formation: this suggests that the mechanism of defect creation by the simple loss of one of the coordinated anions, which is transferred from the first to second shell in the process, is the correct one, and that more complicated defect creation, or cage decay, schemes, such as the central cation jumping through one of the faces of the tetrahedron, can be eliminated. In the PIM, the situation is not so clear, as the agreement between the activation energy for defect creation now appears to be less closely associated with the activation

energy for first to second shell transfer: the increased curvature with temperature of these plots in the PIM compared to the RIM mean that the comparison is only valid in the low temperature regime in the PIM where the action of the defects in promoting diffusion in the network is most important, *i.e* where the tetrahedral network most closely approaches ideality (see the discussions of the action of the defects in sections 4.4 and 5.5).

Function	E_A [kJmol ⁻¹]
$F_{BeF}^{PIM}(4, 5)$	30.5
$F_{BeF}^{RIM}(4, 5)$	56.1
defect formation, PIM	19.3
defect formation, RIM	68.9
ionic migration, PIM	32.1
ionic migration, RIM	102.0

Table 7.3: The activation energies for first to second shell transfer in PIM and RIM BeF₂, calculated from an Arrhenius fit to the inverse temperature variation of $F_{BeF}(4, 5)$. Also shown are the activation energies for defect formation and ionic migration, as given in tables 4.8 (for the PIM) and 5.8 (for the RIM).

7.3 The coordination number dependent neighbourhood radial distribution function

Figure 7.8 shows the coordination number dependent cation-anion neighbourhood partial radial distribution function for 3-, 4-, and 5-coordinate cations in BeF₂, for the PIM at 700 K and the RIM at 1300 K. These functions are normalised such that $\int_0^\infty 4\pi r^2 g_{BeF}^{N^c=\alpha}(1, r) dr = 1$ for each coordination number, α , so that we may directly compare the intensities for different coordination types¹. In these systems, the number of defect sites is low, and the distribution functions for the 4-coordinate cations are almost entirely representative of the overall distribution functions, as shown in panel (c) of figure 7.2 for the coordination number *independent* distribution function in the PIM at 700 K. The location of the ions in the defect

¹This ensures that the fact that there are different populations of each type of coordination environment is taken into account, and is based on the assumption that the nearest neighbour ($n = 1$) for a cation is *always* an anion.

sites can also be seen: in the 3-coordinate species, the 4th anion has its highest probability of being located at distances just larger than the first minimum in the Be-F partial radial distribution function, whereas the 5th anion in the 5-coordinate species is most likely to be found just inside the position of the first minimum. The temperature dependence of the distribution functions is shown in figures 7.9 and 7.10 for the PIM and RIM systems respectively, focusing on the ions either side of the cutoff boundary, *i.e.* $n = 3, 4$ for $N^c = 3$, $n = 4, 5$ for $N^c = 4$, and $n = 5, 6$ for $N^c = 5$. The distribution functions for the defect ions are approximately independent of temperature, even though the distributions of the bound ions in the first coordination shell become broader, reflecting the increase in vibrational motion as the temperature increases. This suggests that the structure of the defects does not change with temperature; the relatively close proximity of the 4th anion to the 3-coordinate species, at all temperatures, suggests that we can consider the defect as a 3-coordinate cation with an associated nearby uni-coordinate anion.

If we also examine the distribution functions for the ions which are bound in the first shell, then we can see that there is some contraction of the first shell on the formation of the 3-coordinate species, *i.e.* the peaks for $n = 1, 2, 3$ are at lower r for $N^c = 3$ than $N^c = 4$, whereas there is little change on formation of the 5-coordinate species. The cage lifetimes for the different species suggested that the 3-coordinate site was the more stable of the defects in the PIM, *i.e.* it had a longer cage lifetime, and this reflects the formation of the shorter, stronger Be-F bonds, which does not occur in the formation of the 5-coordinate defect. The 5-coordinate defect appears to be approximately 4+1 in its coordination, as the 5th anion is found inside, but very near to the cutoff boundary. The penetration of the 5th anion into the first coordination shell, up to $n = 4$, is greater in the RIM than the PIM, and this may account for the change in the relative stability of the 3- and 5-coordinate defect sites in the two models: in the PIM the 3-coordinate defect is much more stable, whereas in the RIM, the cage lifetimes, and hence stability, of the two defect species are

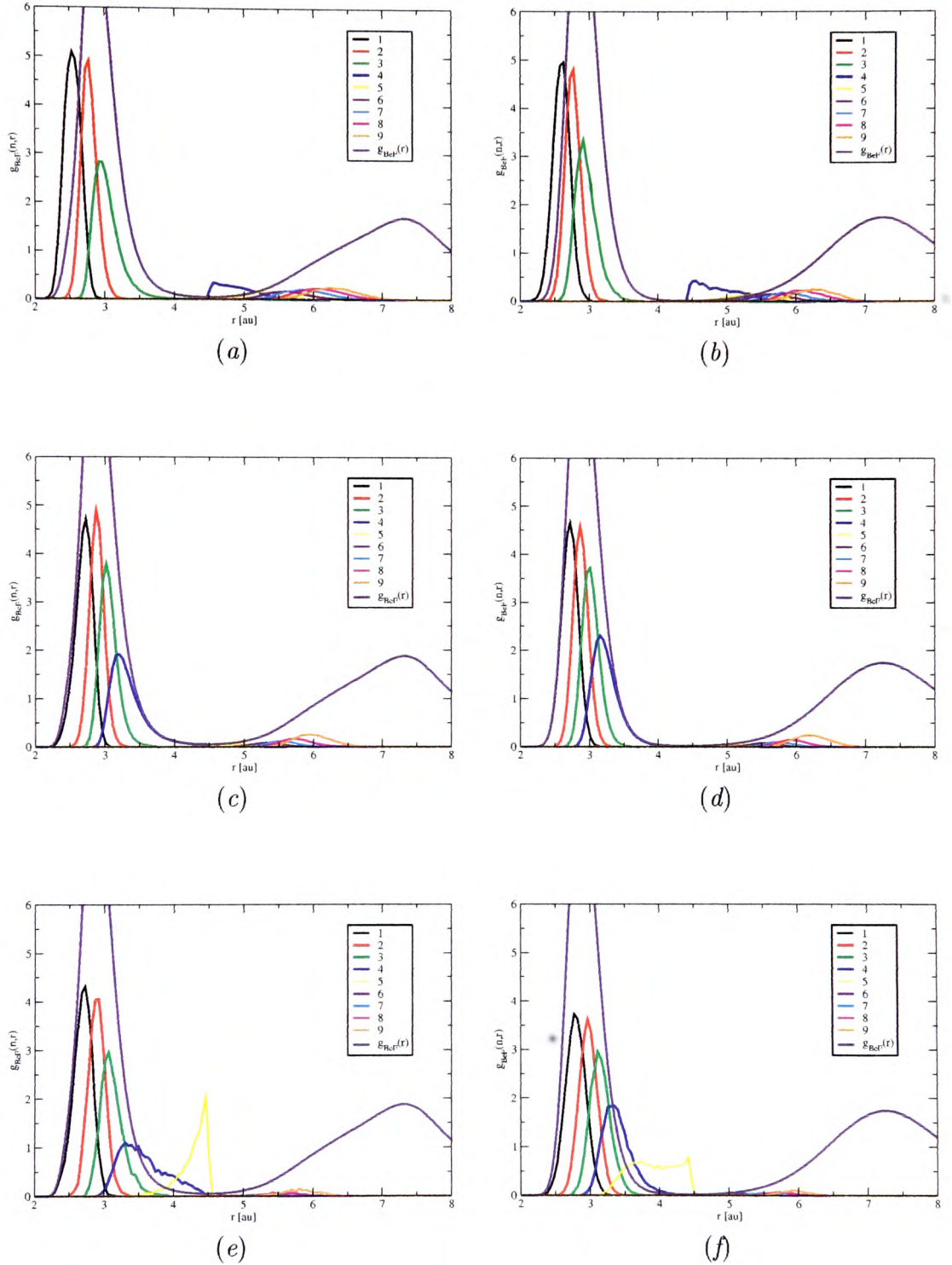


Figure 7.8: The coordination number dependent neighbourship partial radial distribution functions for PIM BeF_2 at 700 K and RIM BeF_2 at 1300 K: $g_{\text{BeF}}(n, r)$ for (a) $N^c(\text{Be}) = 3$, (c) $N^c(\text{Be}) = 4$, (e) $N^c(\text{Be}) = 5$ in the PIM, and for (b) $N^c(\text{Be}) = 3$, (d) $N^c(\text{Be}) = 4$, (f) $N^c(\text{Be}) = 5$ in the RIM. The indigo line shows the BeF partial radial distribution function (constructed for cations of all coordination numbers) for the given system in each case.

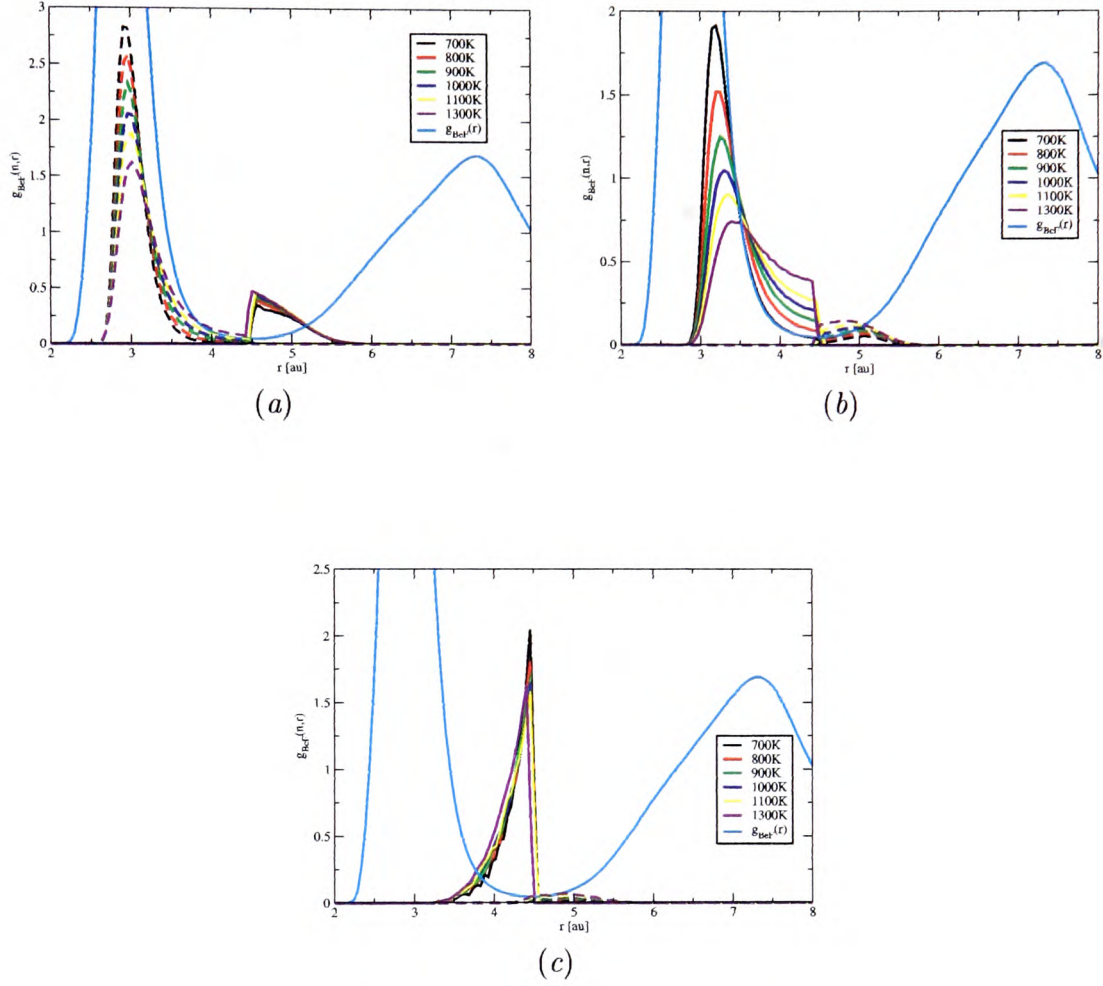


Figure 7.9: The temperature dependence of the coordination number dependent neighbourship partial radial distribution functions for PIM BeF₂ at the first shell boundary: $g_{BeF}(n, r)$ for (a) $N^c(Be) = 3$ and $n = 3, 4$, (b) $N^c(Be) = 4$ and $n = 4, 5$, (c) $N^c(Be) = 5$ and $n = 5, 6$.

much closer to each other, and this reflects that extra penetration of the 5th anion into the first coordination shell, and the accompanying increase in the Be–F bond strength, as the bond-length is shorter, making the 5-coordinate site comparable in stability to the 3-coordinate site in the RIM.

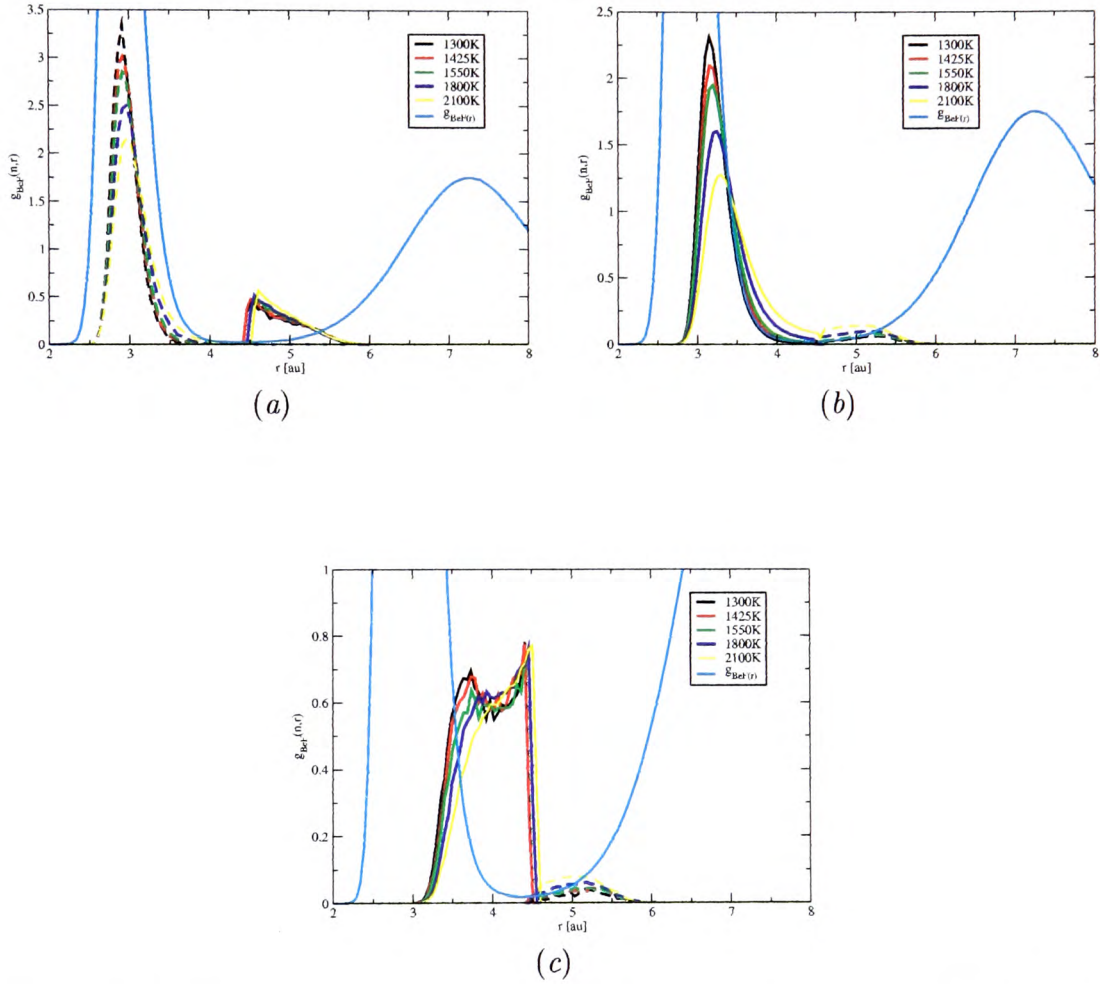


Figure 7.10: The temperature dependence of the coordination number dependent neighbourhood partial radial distribution functions for RIM BeF_2 at the first shell boundary: $g_{BeF}(n, r)$ for (a) $N^c(Be) = 3$ and $n = 3, 4$, (b) $N^c(Be) = 4$ and $n = 4, 5$, (c) $N^c(Be) = 5$ and $n = 5, 6$.

Chapter 8

MCl₃: Extension to other materials

8.1 Introduction

The focus so far has been on the tetrahedral glass forming fluid BeF₂. In this system, the diffusivity was controlled by the requirement that the network must become less constrained in order for any structural relaxation to occur, and this was facilitated by the formation of defect sites.

In this chapter, we will investigate the link between the structure and the dynamics in the molten trichloride systems, ScCl₃, YCl₃ and LaCl₃. The tri-valent metal halides are interesting because of the wide range of materials available for study, with a wide range of cation sizes, and also because there are a number of proposed or existing technologies, such as the electro-deposition of refractory materials [68] or electrolytic separation of nuclear waste [69], which involve solutions of tri-valent metal halides in molten alkali halides.

8.2 The structure of the Molten Trichlorides

Previous simulation studies [70, 71, 72] have shown that the structures of a range of molten trichloride systems may be accurately predicted using a single, transferable potential in the PIM scheme. The parameters for the different systems vary in a systematic way, being determined by the value of the cationic radius. The potential parameters used for these simulations of ScCl₃, YCl₃ and LaCl₃ are given in table

F.4. It was found, however, that the mobility of these melts was too low [72], as determined from the comparison of the calculated and experimental conductivities. Here we consider simulations of ScCl_3 , YCl_3 and LaCl_3 , which have in-crystal cation radii of $r_{\text{Sc}} = 0.81\text{\AA}$, $r_{\text{Y}} = 0.93\text{\AA}$, $r_{\text{La}} = 1.15\text{\AA}$. The chloride ion is anticipated to behave the same way in each of the systems, so that any change in behaviour is attributable to the changing cationic radius. The simulations were performed using a similar procedure to that outlined for BeF_2 (see, for example, section 3.1.1) but now the systems contain 500 ions, with densities of $\rho_{\text{ScCl}_3} = 1.643\text{ gcm}^{-3}$, $\rho_{\text{YCl}_3} = 2.491\text{ gcm}^{-3}$ and $\rho_{\text{LaCl}_3} = 3.173\text{ gcm}^{-3}$. The potential parameters for these simulations are given in table F.3. If we compare these with those used in the previous simulations, then we can see that the main difference is the large reduction in the values of α_{MCl} and α_{ClCl} , with an accompanying decrease in B_{MCl} and B_{ClCl} , and so we might anticipate that this softening of the potential would result in a more mobile system¹.

Figure 8.1 shows the comparison between the calculated and experimental neutron structure factors for ScCl_3 , YCl_3 and LaCl_3 , with experimental data from [73], [74, 75, 76], and [77] respectively. We can see that there is excellent agreement between simulation and experiment across the whole k -range, and moreover that the agreement has improved compared to the previous simulations [72]. The forms of the structure factors are very different, *e.g* the first sharp diffraction peak has high intensity in ScCl_3 but by LaCl_3 the principal peak is by far the dominant feature, and hence these systems adopt very different liquid structures.

Figure 8.2 shows molecular graphics snapshots of the structures adopted by the three materials. As the cation size increases, the mean cation coordination number increases and the degree of connectivity of the network increases. The main observation is that the structures of ScCl_3 and YCl_3 systems can be thought of as networks where the cation coordination number is ~ 6 , and the anion coordination

¹In BeF_2 , we *increased* the B_{ij} and α_{ij} parameters on going from potential 1 to potentials 2 and 4 (see chapter 9), and we generated a more rigid, less mobile system.

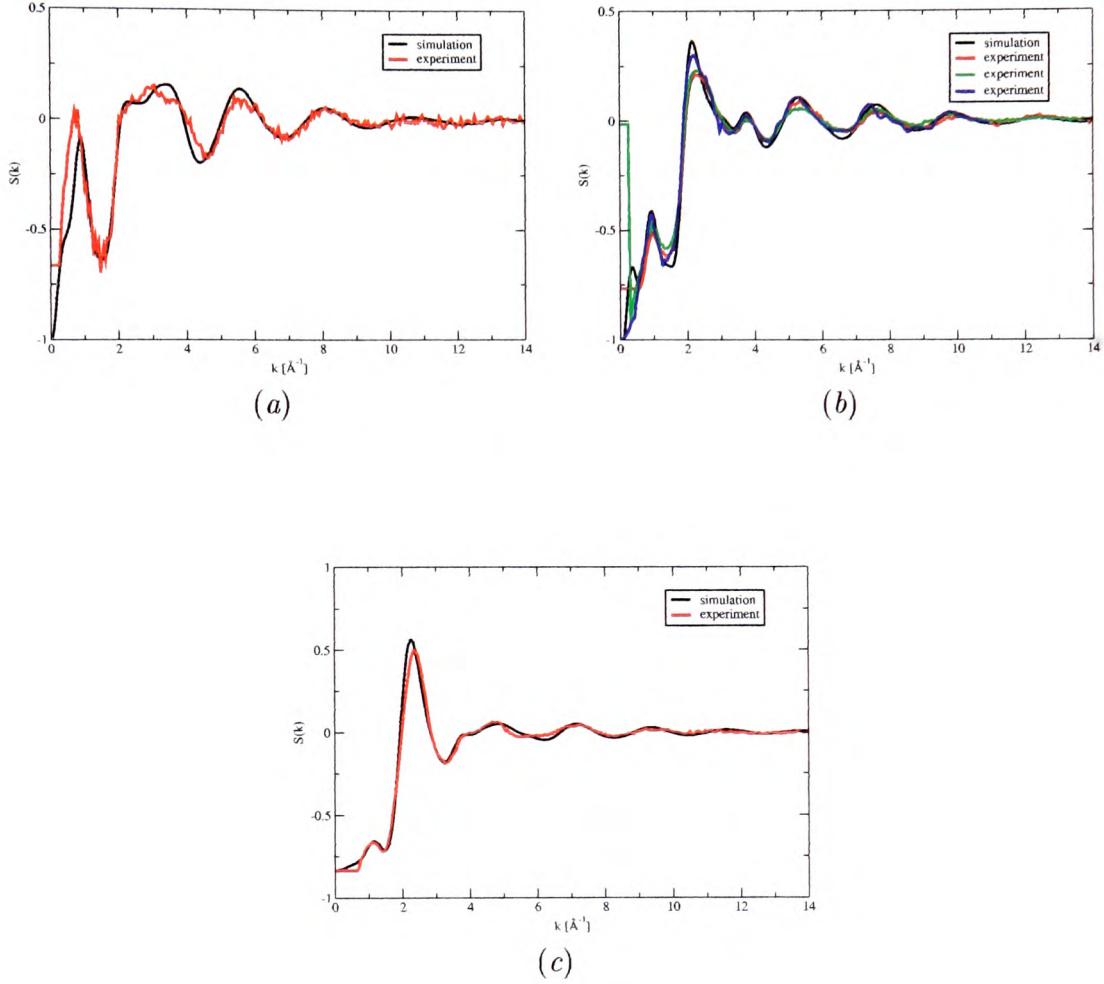


Figure 8.1: The calculated and experimental neutron weighted structure factors for (a) ScCl_3 at 1300 K, (b) YCl_3 at 1000 K, and (c) LaCl_3 at 1200 K. Experimental data from: (a) [73] (at 1253 K), (b) [74, 75, 76] (at 1033 K), and (c) [77] (at 1178 K).

number is therefore ~ 2 (as in the BeF_2 system). These comprise chains of edge sharing polyhedra, which percolate through the system, but with differing degrees of cross-linking between the chains. The LaCl_3 , on the other hand, has higher cation and anion coordination numbers and has more of the character of a densely packed ionic melt.

Interpretation of the experimental Raman spectra [78] and of simulations of dilute solutions of these cations in alkali chloride mixtures, *e.g.* M^{3+} in $[\text{Li}, \text{K}]\text{Cl}$ [45] sug-

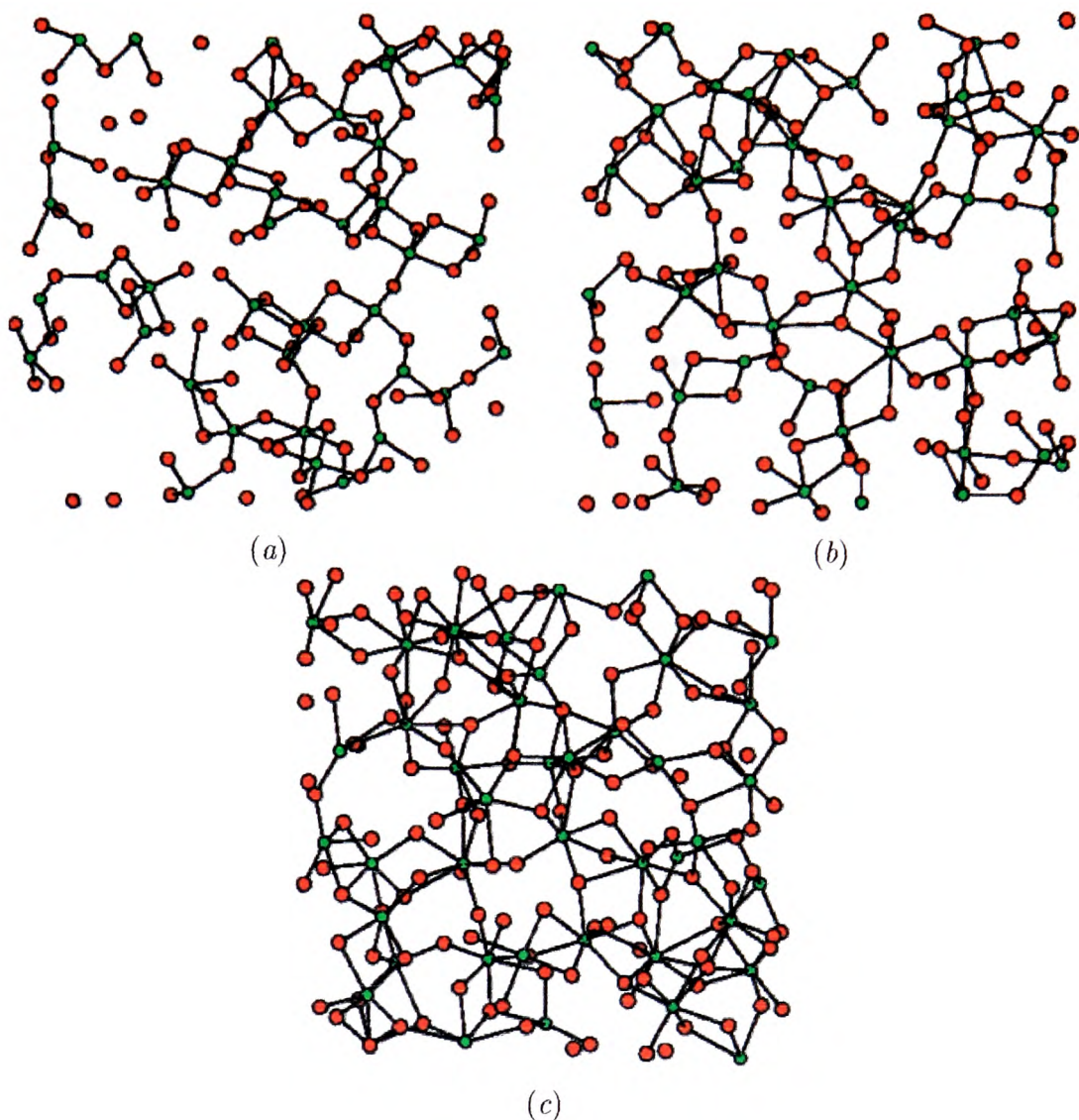


Figure 8.2: Molecular graphics snapshots, at 1000 K, of (a) ScCl_3 , (b) YCl_3 , and (c) LaCl_3 . The structure of ScCl_3 and YCl_3 is made up of chains of *edge-sharing* MCl_n units, but the degree of cross linking of these chains increases as the mean coordination number of the cation increases, and LaCl_3 is more like a densely packed melt. (Metal ions are shown in *green* and chloride ions in *red*).

gest that these cations are octahedrally coordinated. However, within the pure melts there is a range of cation coordination environments. The variation with temperature of the distributions of cation environments is given in table 8.1, and the mean coordination numbers, $\bar{N}_\alpha^c$, which are calculated according to

$$\bar{N}_\alpha^c = 4\pi\rho_\beta \int_0^{r_{\alpha\beta}^{\min}} r^2 g_{\alpha\beta}(r) dr, \quad (8.1)$$

where the total and partial radial distribution functions, $g_{\alpha\beta}(r)$, are as shown in figure 8.3 (at 1000 K), are given in table 8.2. From these distributions, we can see that ScCl_3 has a mean coordination number of ~ 5.5 , YCl_3 of ~ 6.5 , and LaCl_3 of ~ 7.5 ; the increased number of chloride ions around each cation leads to an increase in the degree of sharing of chloride ions between cations, and hence to an increase in the connectivity of the network.

ScCl_3						
T [K]	F_4	F_5	F_6	F_7	F_8	F_9
1000	0.016	0.233	0.728	0.023	–	–
1100	0.026	0.276	0.665	0.033	–	–
1200	0.049	0.357	0.557	0.036	–	–
1300	0.063	0.388	0.502	0.045	–	–
1400	0.085	0.420	0.451	0.042	–	–
YCl_3						
T [K]	F_4	F_5	F_6	F_7	F_8	F_9
900	–	0.028	0.667	0.277	0.028	–
1000	–	0.037	0.644	0.288	0.030	–
1100	–	0.051	0.600	0.311	0.037	–
1200	–	0.060	0.561	0.330	0.047	–
LaCl_3						
T [K]	F_4	F_5	F_6	F_7	F_8	F_9
1000	–	–	0.070	0.378	0.445	0.103
1100	–	–	0.072	0.369	0.437	0.115
1200	–	–	0.074	0.365	0.435	0.118
1300	–	–	0.080	0.367	0.426	0.118
1400	–	–	0.069	0.336	0.431	0.150

Table 8.1: The variation with temperature of the distribution of cation coordination environments for the MCl_3 systems. F_n is the fraction of cation sites which have a coordination number n .

	ScCl ₃		YCl ₃		LaCl ₃	
T [K]	$r_{MCl}^{\min}$	N^c	$r_{MCl}^{\min}$	N^c	$r_{MCl}^{\min}$	N^c
900	—	—	6.80	6.30	—	—
1000	6.70	5.76	6.80	6.31	7.50	7.59
1100	6.75	5.71	6.85	6.34	7.55	7.60
1200	6.70	5.58	6.95	6.36	7.55	7.61
1300	6.75	5.53	—	—	7.55	7.60
1400	6.70	5.45	—	—	7.65	7.70

Table 8.2: The variation with temperature of the mean cation coordination numbers in the MCl₃ systems. The mean cation coordination number, $\bar{N}^c$, is given by $\bar{N}^c = 4\pi\rho_{Cl} \int_0^{r_{MCl}^{\min}} r^2 g_{MCl}(r) dr$.

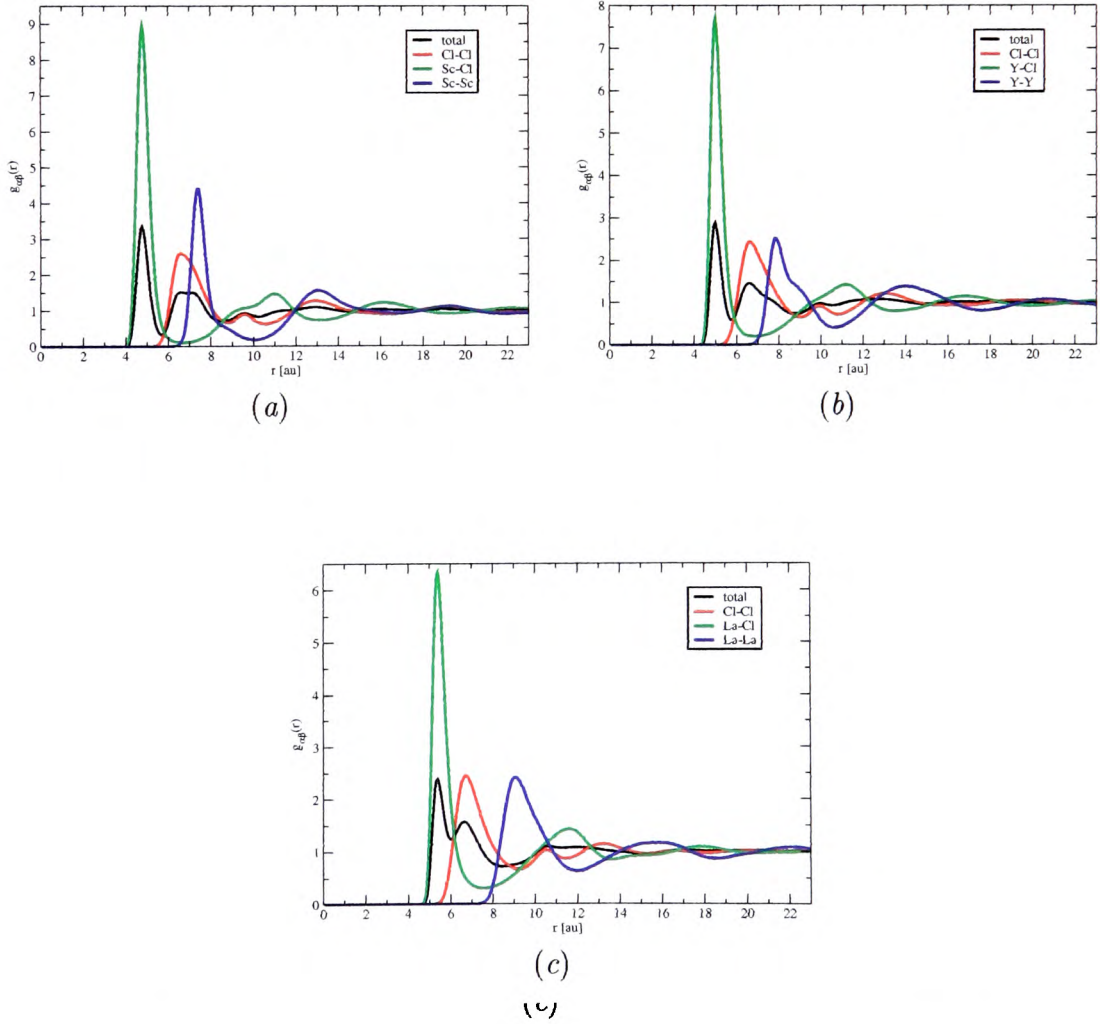


Figure 8.3: The total and partial radial distribution functions at 1000 K for (a) ScCl₃, (b) YCl₃ and (c) LaCl₃.

8.3 The vibrational dynamics of LaCl_3

The vibrational densities of states of the coordination polyhedra in the MCl_3 systems can be calculated by a process similar to that outlined in appendix D, except that in these systems the relevant vibrational modes are those corresponding to an octahedron, rather than the tetrahedron described there, to reflect the changed geometry (see also, for example, [79]). For LaCl_3 , the experimental Raman spectrum has a polarised band at 250 cm^{-1} (P_1) with a shoulder at 300 cm^{-1} (P_2) [78] which have been interpreted as the symmetric stretching modes of the LaCl_6 octahedra in the melt. We have seen that there is actually a distribution of cation coordination numbers in the melt, and the vibrational densities of states for the symmetric breathing modes for the cations of different coordination numbers are shown in figure 8.4 for LaCl_3 at 1300 K. The peaks in the calculated densities of states occur in the range $271 - 287\text{ cm}^{-1}$, depending on the coordination number considered, and hence are at a higher frequency than that observed experimentally. The peak frequency increases with decreasing coordination number ($\omega_{\text{max}}^{N^c=6} = 287\text{ cm}^{-1}$, $\omega_{\text{max}}^{N^c=7} = 284\text{ cm}^{-1}$, $\omega_{\text{max}}^{N^c=8} = 280\text{ cm}^{-1}$, and $\omega_{\text{max}}^{N^c=9} = 271\text{ cm}^{-1}$) and this is as we would expect from a consideration of the bond strengths in the LaCl_n complex (as the number of coordinated anions increases, the average distance of the anions from the central cation increases and hence the bond strength and the vibrational frequency of the complex decreases).

The calculated vibrational frequencies are therefore a little high compared with experiment. We might anticipate that this deviation results from having a potential that is too stiff. The potential does, though, give an excellent reproduction of the static structure. The stiff nature of the potential is likely to lead to a system which is less diffusive and which has a lower conductivity than observed experimentally, as discussed in section 8.4, since the coordination polyhedra are less likely to break up. The relatively narrow range of peak frequencies for the cations of different coordination numbers suggests, however, that the experimental polarised Raman band

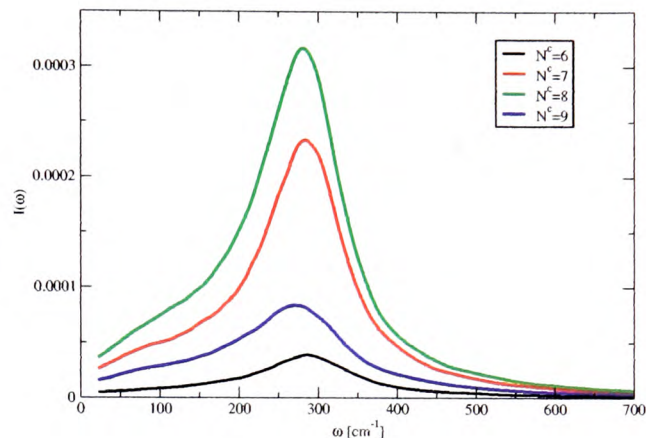


Figure 8.4: The calculated vibrational densities of states for the symmetric stretching modes of the different cation coordination numbers in LaCl_3 at 1300K.

could contain contributions from the symmetric stretches of all of the different cation coordination environments, and not simply the six coordinate cations as proposed [78].

8.4 The diffusive dynamics of the Molten Trichlorides

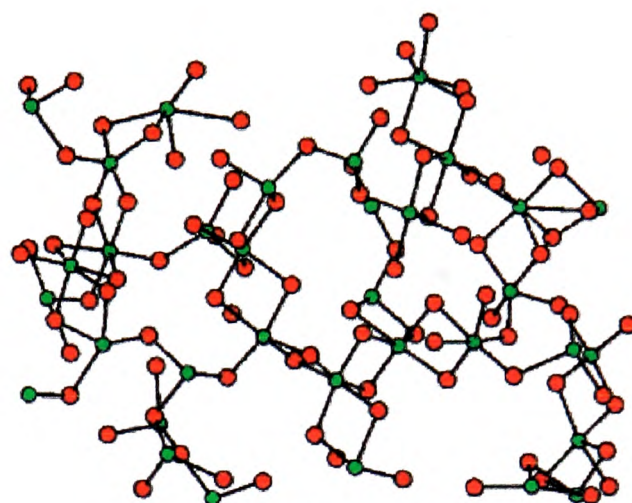
The MCl_3 systems, which are based upon the 6-coordinate cations, do not form glasses on cooling. Instead, they are observed to crystallise. We can use the techniques developed to examine the glass forming tetrahedral network systems to probe the link between the structure and the dynamics in these new systems.

We have seen that the structure varies with the size of the cation, but that it is still based upon chains of *edge sharing* MX_n units. This is different from the tetrahedral BeF_2 system which was constructed from *vertex sharing* MX_4 (and some MX_3) units: this is shown in figure 8.5, where the snapshot of ScCl_3 at 1000 K demonstrates very little vertex sharing, and that of the the PIM BeF_2 at 700 K shows *no* edge sharing.

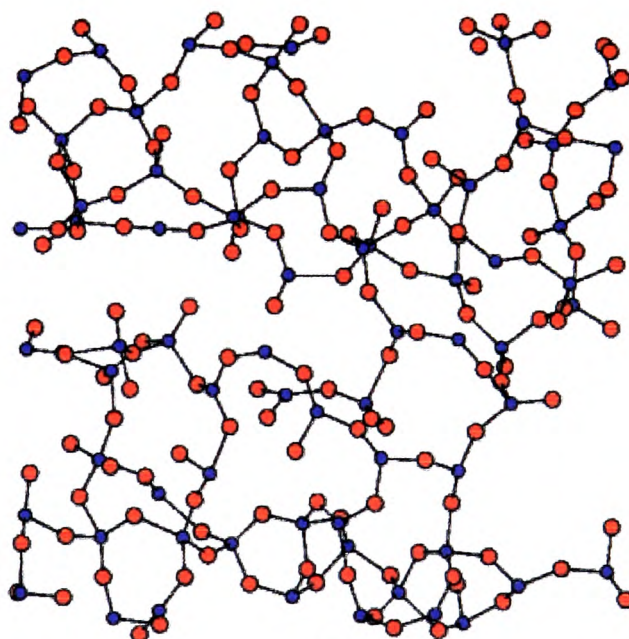
The vertex shared system is over-constrained, in the absence of defect sites, and we have seen that this dominates the structural relaxation, in as much as defects must be created by a cage decay event in order for the ions to move. In the MCl_3 systems, the nature of the constraints is rather different, because the structural motif is the chains of edge sharing units, and we might therefore expect the structural relaxation to be different.

Figure 8.6 shows the inverse temperature dependence of the ionic diffusion coefficients for the MCl_3 systems calculated using the Einstein relation, and scaled from the calculated viscosity using the Eyring relation with a jump length, λ_α , given by $r_{\alpha\beta}^{\min}$, *i.e.* the position of the first minimum in the partial radial distribution function, and also using the Stokes-Einstein relation with hydrodynamic radii, a_α , given by the in-crystal ionic radii.

In all cases, we can see that the diffusion coefficient calculated from the Stokes-Einstein relation, using the in-crystal ionic radii as the hydrodynamic radii, is too low, as also observed for BeF_2 . It would appear that this underestimation of the diffusion coefficient in the network systems using the Stokes-Einstein relationship is a general one, and not just limited to systems with the tetrahedral topology. The use of the Eyring relation in the network system contrasts with the successful use of the Stokes-Einstein relation in the unassociated melt. For the La^{3+} ion in a dilute solution of LaCl_3 in $[\text{Li},\text{K}]\text{Cl}$, the Stokes-Einstein relation predicts a hydrodynamic radius of ~ 6.6 au [45], which is much larger than the in-crystal ionic radius but comparable with the position of the first minimum in the cation-anion partial radial distribution function, *i.e.* in the dilute system the La^{3+} ion diffuses with its cage intact, as a complex ion. In the pure network, this formation of complex ions cannot lead to discreet complex ions because there are no longer enough chloride ions to form independent complexes of each cation, and the Stokes-Einstein relation ceases to describe the diffusive motion accurately.



(a)



(b)

Figure 8.5: Molecular graphics snapshots of (a) ScCl_3 at 1000 K, and (b) PIM BeF_2 at 700 K. The structure of ScCl_3 is dominated by *edge-sharing* octahedral ScCl_6 units, with some ScCl_5 species, whereas the BeF_2 system is made almost entirely from *vertex-sharing* BeF_4 species. Note that the image shows a slice through a simulation cell of BeF_2 , showing approximately one third of the cell. Many of the cations which appear 3-coordinate actually have a fourth coordinated anion (which is not shown because it is *outside* of the slice of the cell shown), and hence there appears to be too high a number of 3-coordinate species. (Sc ions are shown in *green*, Be ions in *blue*, and halide ions in *red*)

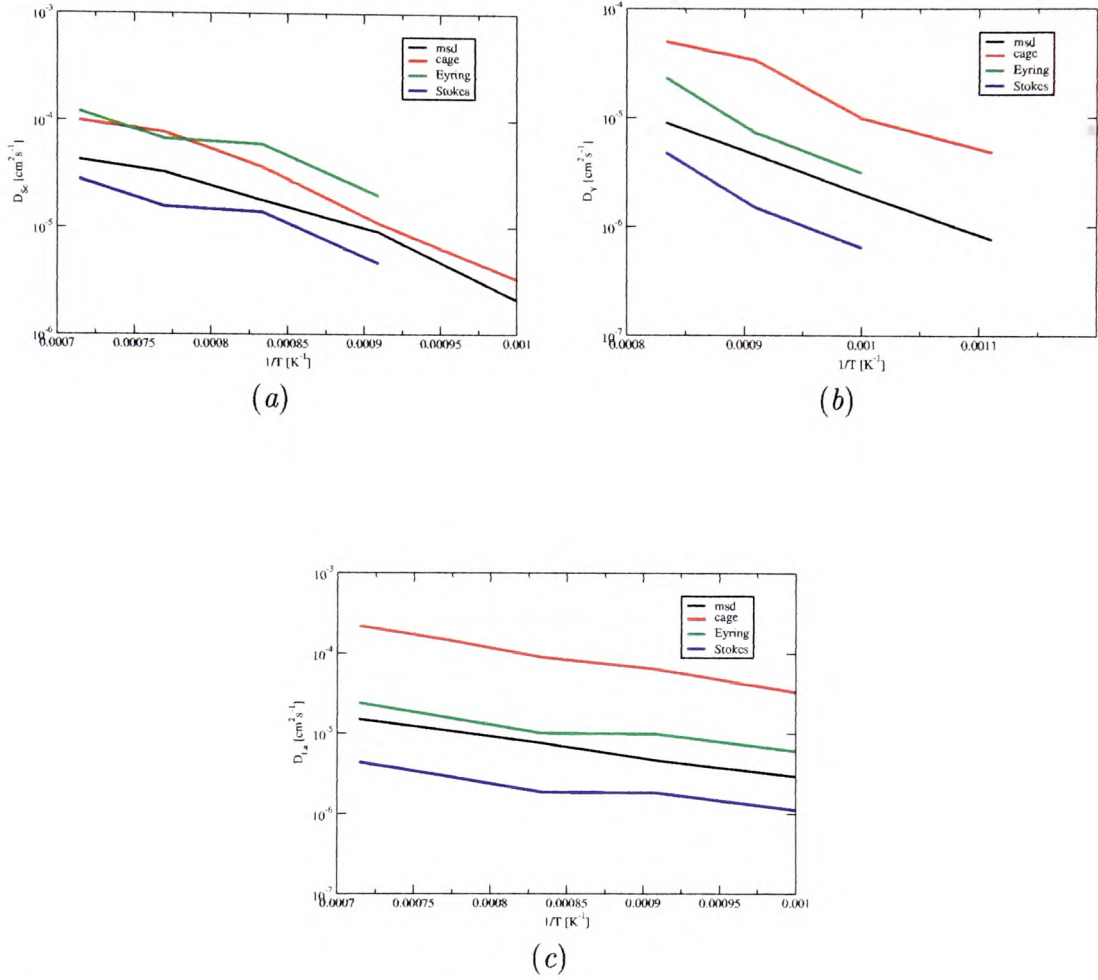


Figure 8.6: The inverse temperature dependence of the cationic diffusion coefficients calculated from the Einstein relation (black lines), and scaled from the Eyring relation with the jump lengths, λ_α , given by $\lambda_\alpha = r_{\alpha\beta}^{\min}$ (green lines) and from the Stokes-Einstein relation with the hydrodynamic radii, a_α , given by the in-crystal ionic radii (blue lines), and calculated from the cage decay rate and cage jump lengths (red lines), for (a) ScCl_3 , (b) YCl_3 , and (c) LaCl_3 .

8.4.1 The cage decay in the MCl_3 systems

The cationic diffusion coefficients and cage decay rates for the $c = 1$ -in-out M-Cl cage for the MCl_3 systems are given in table 8.3. If we consider the cage decay rates at a given temperature, we can see that the order is $k_{LaCl} > k_{YCl} > k_{ScCl}$, which reflects the increasing coordination number of the cation: as the number of cage ions increases, the bonding strength of each M-Cl bond decreases and so the bond is more easily broken and so the cage decays more quickly. Shown in table 8.4 are the ratios of the rates of decay of different cages, $\frac{k_{MCl}^{c=1}}{k_{MCl}^{c=2}}$ and $\frac{k_{MCl}^{c=1}}{k_{MM}^{c=1}}$, and these are compared to the results for PIM BeF_2 . The principal observation is that $\frac{k_{MCl}^{c=1}}{k_{MM}^{c=1}} < 1$ for BeF_2 but > 1 for all the MCl_3 systems, *i.e.* in these systems the M-M network persists even after the M-Cl cages decay. This can be understood by considering the linking of the polyhedra. In BeF_2 , there is only one bridging F anion between cation centres, and we interpreted the faster Be-Be decay as being due to the local *breathing* of the Be-F network which allowed a change in the separations of the Be species without breaking bonds. The fact that there was only one bridging F anion between the centres would, however, mean that the breaking of either of the Be-F bonds would be likely to result in a decay of the Be-Be cage. In the MCl_3 systems, whilst the local breathing of the M-Cl sub-system will still occur, of greater importance is the fact that now most of the M-M centres are coupled by two bridging Cl anions: when one of the M-Cl bonds breaks, resulting in an M-Cl cage decay event, the second M-Cl-M bridge may persist, and so the two M ions at either end of the bridge can maintain their relative positions, and so the M-M cage will remain intact. The edge-sharing nature is most pronounced in $ScCl_3$ and this is reflected in the $\frac{k_{MCl}^{c=1}}{k_{MM}^{c=1}}$ ratio being the highest in $ScCl_3$. The relative rate of changing two anions to changing one is still less than two, as it was for BeF_2 , which again suggests that the interchange of the second anion is (relatively) promoted by the interchange of the first anion.

ScCl ₃		
T [K]	D_{Sc} [cm ² s ⁻¹]	k_{ScCl} [ps ⁻¹]
1000	2.1×10^{-6}	0.0157
1100	9.1×10^{-6}	0.0498
1200	1.8×10^{-5}	0.176
1300	3.3×10^{-5}	0.366
1400	4.3×10^{-5}	0.499
YCl ₃		
T [K]	D_Y [cm ² s ⁻¹]	k_{YCl} [ps ⁻¹]
900	7.6×10^{-7}	0.0221
1000	2.0×10^{-6}	0.0461
1100	4.6×10^{-6}	0.155
1200	9.0×10^{-6}	0.223
LaCl ₃		
T [K]	D_{La} [cm ² s ⁻¹]	k_{LaCl} [ps ⁻¹]
1000	2.9×10^{-6}	0.126
1100	4.6×10^{-6}	0.242
1200	7.6×10^{-6}	0.338
1300	1.1×10^{-5}	0.577
1400	1.5×10^{-5}	0.791

Table 8.3: The variation with temperature of the cationic diffusion coefficients, calculated using the Einstein relation, and the cage decay rates, k_{MCl} , for the $c = 1$ -*in-out* function in the MCl₃ systems.

System	$\frac{k_{MCl}^{c=1}}{k_{MCl}^{c=2}}$	$\frac{k_{MCl}^{c=1}}{k_{MM}^{c=1}}$
ScCl ₃	1.33	1.39
YCl ₃	1.67	1.23
LaCl ₃	1.65	1.18
PIM BeF ₂	1.77	0.73

Table 8.4: The ratio of the mean rates of the decay of different cages within the MCl₃ systems, compared to those for PIM BeF₂.

8.4.2 Calculation of the diffusion coefficient from the cage decay rate in the MCl₃ systems

Figure 8.6 also shows the diffusion coefficients calculated from the cage decay rates and cage jump lengths, given by

$$D_{\alpha}(T) = \frac{k_{\alpha\beta}(T)\lambda_{\alpha\beta}^2(T)}{6}, \quad (8.2)$$

where the cage decay rate is for the $c = 1$ -in-out function for the cation-anion cage, as given in table 8.3², and the cage jump length is equal to the position of the first minimum in the relevant partial radial distribution function, *i.e.* $\lambda_{\alpha\beta}(T) = r_{\alpha\beta}^{\min}(T)$. The temperature dependence of the diffusion coefficient calculated from the cage decay rate is the same as that calculated from the Einstein relation, and hence we can link the diffusion to the cage decay in these systems as we did in the tetrahedral BeF₂. However, now the diffusion coefficient calculated from the cage decay rate systematically *overestimates* the diffusion coefficient calculated from the Einstein relation. This means that there are effectively some cage decay events which do not lead to diffusion, and this effect is greatest in LaCl₃ and least in ScCl₃. We can interpret this in terms of the degree of interconnectivity of the chains within the network. We saw in figure 8.2 that LaCl₃ had the highest degree of interconnectivity, and ScCl₃ the least. We can envisage the LaCl₃ system as a series of *hairy* LaCl_{*n*} balls, where the La–Cl bonds correspond to the *hairs*, which are all stuck together. The loss of one of the hairs on an individual unit, corresponding to the breaking of an La–Cl bond and a La–Cl cage decay event, reduces the ability to stick to other balls, but as the number of hairs is high there is still an appreciable degree of network interconnectivity, and hence the La³⁺ ion at the centre of the ball cannot yet diffuse. In the ScCl₃ system, where the chains extend throughout the system but where there is much less linking *between* chains, most of the Sc–Cl bond breaking events now result in an increased local mobility of the network, and the diffusion coefficient predicted from the cage decay rate bears a much closer resemblance to that calculated from the mean squared ionic displacements. YCl₃ has an intermediate degree of chain interlinking and an intermediate level of agreement.

In BeF₂, we saw that the idea of the *defect* site, or non-ideally coordinated ion, aided our description of the mechanism of diffusion. In systems where there is a larger range of coordination environments, the idea of a defect site within the system has

²The diffusion coefficients are very low for YCl₃ at the lowest simulated temperatures, and their non-Arrhenius variation with inverse temperature at low temperature is a symptom of systems which are still slowing down.

less meaning. Also, when we consider that our LaCl_3 system is better described in terms of a densely packed melt than a well organised network, we cannot really interpret the structure of the melt in terms of an ideal system with defect sites of the non-ideal coordination environment. The model of the diffusion being controlled by the creation of the defect site, and then motion resulting from the presence of the defect, is therefore not merited in these systems, where the underlying network structure is not an ideal linkage of polyhedra as it is in BeF_2 . This assumes that a defect is to be identified with a non-ideal coordination number site, while the relatively wide distribution of coordination numbers within these systems suggests that this definition is not enough to identify a defect. We may conclude that these systems are too far from the ideal 6-coordinate system to become glassy. This may be intrinsic of the real 6-coordinate systems, and is perhaps the reason that they do not form glasses.

8.4.3 The conductivity of the Molten Trichlorides

The conductivity can, like the ionic diffusion coefficients, be calculated from the ionic displacements according to the procedure outlined in appendix G, and may be summarised by

$$\lambda^K = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} [Q_+^2 \langle |\Delta_+(t)|^2 \rangle + Q_-^2 \langle |\Delta_-(t)|^2 \rangle + 2Q_+Q_- \langle \Delta_+(t) \cdot \Delta_-(t) \rangle], \quad (8.3)$$

and, the Nernst-Einstein relation,

$$\lambda^{NE} = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} [Q_+^2 N_+ \langle |\delta_+(t)|^2 \rangle + Q_-^2 N_- \langle |\delta_-(t)|^2 \rangle], \quad (8.4)$$

where $\Delta_\alpha(t)$ in equation 8.3 is the *net* displacement of *all* the ions of species α in time t , and $\delta_\alpha(t)$ in equation 8.4 is the displacement of a *single* ion of species α in time t (*i.e.* $\Delta_\alpha(t) = \sum_{i \in \alpha} \delta_i(t)$), and hence the requirement that it is multiplied by the number of ions of type α , N_α , in the system).

The difference between the two measures of conductivity is that the Nernst-Einstein expression takes no account of any cross-correlation of the motion of different ions

(i.e. it has no terms in $\langle \delta_+(t) \cdot \delta_-(t) \rangle$ or $\langle \delta_1(t) \cdot \delta_2(t) \rangle$, where $1, 2 \in \alpha$), whereas the first expression for the conductivity, equation 8.3, includes the contribution from the cross-correlation, and hence the conductivity there arises from the displacement of the set of cations relative to the set of anions.

The conductivities can be calculated from the gradients of the charge-scaled mean squared displacements, and figure 8.7 shows the charge-scaled mean squared displacements for the MCl_3 systems. The gradient has converged in the functions which give the Nernst-Einstein conductivity, shown with dashed lines, whereas the convergence is not so good in the functions which take into account the correlation of ionic motion, although we may still get a good estimate of the gradient and hence conductivity.

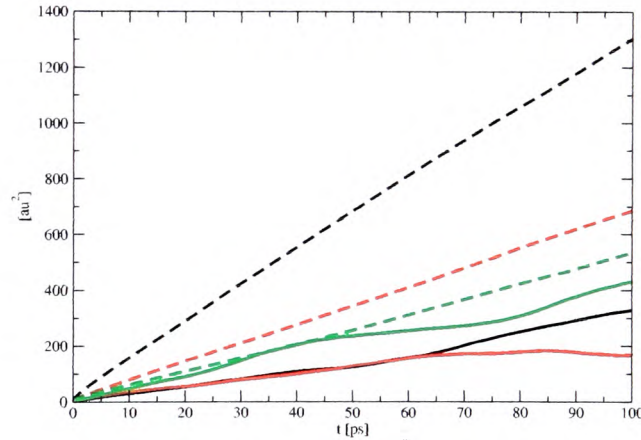


Figure 8.7: The time evolution of the charge-scaled mean squared displacements, in au^2 , in the molten trichlorides at 1200 K. The conductivities are calculated from the long-time gradients of these lines, according to equations 8.3 and 8.4. The solid lines give the conductivity taking into account the collective motion of the ions, and the dashed lines give the Nernst-Einstein conductivity, and the colours are ScCl_3 (black), YCl_3 (red), and LaCl_3 (green).

The Nernst-Einstein relation, then, is effectively the diffusion coefficient scaled by the charges on the ions, Q_α , and accounts for the fact that the Nernst-Einstein

conductivity, λ^{NE} , of the molten trichlorides is in the order $\text{ScCl}_3 > \text{YCl}_3 > \text{LaCl}_3$, as given in table 8.5, because this is also the order of the diffusion coefficients calculated from the analogous Einstein relation.

ScCl_3			
T [K]	$\lambda^K [\Omega^{-1}\text{cm}^{-1}]$	$\lambda^{NE} [\Omega^{-1}\text{cm}^{-1}]$	$\kappa [\Omega^{-1}\text{cm}^{-1}]$
1000	~ 0.10	0.4	
1100	~ 0.10	1.3	
1200	0.50	2.5	0.53 [†]
1300	0.60	3.5	0.67 [‡]
1400	0.30	4.5	
YCl_3			
T [K]	$\lambda^K [\Omega^{-1}\text{cm}^{-1}]$	$\lambda^{NE} [\Omega^{-1}\text{cm}^{-1}]$	$\kappa [\Omega^{-1}\text{cm}^{-1}]$
900	~ 0.10	0.15	–
1000	~ 0.10	0.40	0.431
1100	0.40	0.90	0.644
1200	0.60	1.50	–
LaCl_3			
T [K]	$\lambda^K [\Omega^{-1}\text{cm}^{-1}]$	$\lambda^{NE} [\Omega^{-1}\text{cm}^{-1}]$	$\kappa [\Omega^{-1}\text{cm}^{-1}]$
1000	~ 0.25	0.5	–
1100	0.65	0.9	–
1200	0.80	1.1	1.686
1300	0.90	1.5	–
1400	0.95	2.1	–

Table 8.5: The conductivities for the MCl_3 systems, as calculated according to equations 8.3 and 8.4, compared to the experimental conductivities, κ , where they have been measured [80] ([†] at 1223 K, and [‡] at 1273 K).

However, the interconnectivity in the network is such that we cannot describe the ions as unassociated entities, and this is reflected in the lower conductivity of the systems when this cross correlation of the ionic motion is taken into account, *i.e.* $\lambda^{NE} > \lambda^K$. Using this measure of conductivity, the order is now $\text{ScCl}_3 < \text{YCl}_3 < \text{LaCl}_3$, which is the order observed experimentally (at a given temperature) and this reflects the degree of association of the melt: in ScCl_3 , the chains which extend throughout the fluid are approximately charge *neutral*, and much of the diffusion occurs while these chains remain intact (and we have seen that the M–M network persists even when the M–Cl network has decayed), and the diffusion of a neutral species does

not contribute to the conductivity. The free chain-like structure decreases as the cation size increases, and λ^K approaches λ^{NE} , although λ^K remains lower than λ^{NE} for all the systems.

Also shown in table 8.5 are the experimental conductivities, κ , where they exist [80]. The conductivities calculated including the effects of correlation now bear a much closer comparison with those measured experimentally, particularly for the ions with the lowest coordination numbers, Sc and Y, than was the case in the previous simulations [72] which gave the results summarised in table 8.6. The new potentials, with their much reduced α_{ij} and B_{ij} values, have softened the systems and made them more mobile, and therefore increased the conductivities.

ScCl ₃		
T [K]	λ^K [$\Omega^{-1}\text{cm}^{-1}$]	λ^{NE} [$\Omega^{-1}\text{cm}^{-1}$]
1300	0.033	1.007
YCl ₃		
T [K]	λ^K [$\Omega^{-1}\text{cm}^{-1}$]	λ^{NE} [$\Omega^{-1}\text{cm}^{-1}$]
1100	0.279	0.323
1200	0.128	0.595
LaCl ₃		
T [K]	λ^K [$\Omega^{-1}\text{cm}^{-1}$]	λ^{NE} [$\Omega^{-1}\text{cm}^{-1}$]
1200	0.306	0.413

Table 8.6: The conductivities for the MCl₃ systems, as previously reported in [72].

8.5 The neighbourhood structure in the Molten Trichlorides

We have seen that the mean coordination numbers of the cation are ~ 5.5 in ScCl_3 , ~ 6.5 in YCl_3 , and ~ 7.5 in LaCl_3 , with a fairly wide distribution of coordination numbers in each system. The nature of the different species can be investigated by considering the form of the neighbourhood partial radial distribution functions. Figure 8.8 shows the cation-anion neighbourhood partial radial distribution functions for the first ten anion neighbours in the MCl_3 systems at 1000 K. The non-integral value of the mean coordination number corresponds to a distribution of the n^{th} neighbour, where $n = 6$ in ScCl_3 , 7 in YCl_3 , and 8 in LaCl_3 , which extends over the range of the position of the first minimum. In ScCl_3 , there are five tightly bound neighbours and the 6^{th} has significant intensity at large r , corresponding to an unbound species, whereas in YCl_3 there are six tightly bound neighbours and a 7^{th} which appears to be intermediate between the first and second shells. In LaCl_3 , the first six neighbours are tightly bound, with the 7^{th} weakly bound and now the 8^{th} in the intermediate region. The ability to form the higher coordination species in LaCl_3 and YCl_3 reflects the increased cation size, but it would still appear that the first six anions are tightly bound, as determined by the narrow width of their $g_{\text{MCl}}(n, r)$, with the other bound ions relatively further away from the cation and therefore much more weakly bound. In ScCl_3 , the small cation has difficulty accommodating even the 6^{th} anion neighbour.

We may construct the normalised probability overlap functions, $F_{\text{MCl}}(n, n+1)$, and these are shown in figure 8.9 for ScCl_3 , YCl_3 , and LaCl_3 , and compared to the functions for PIM BeF_2 , all at 1000 K. These functions show that there is a high degree of separation between the coordination shells in ScCl_3 and YCl_3 , and that the distinction between coordination shells comes at $n = 6$ for ScCl_3 and YCl_3 , but at $n = 7$ for LaCl_3 . This distinction between shells is much softer in LaCl_3 than the other two materials, as indicated by the much higher value of $F_{\text{LaCl}}(7, 8)$

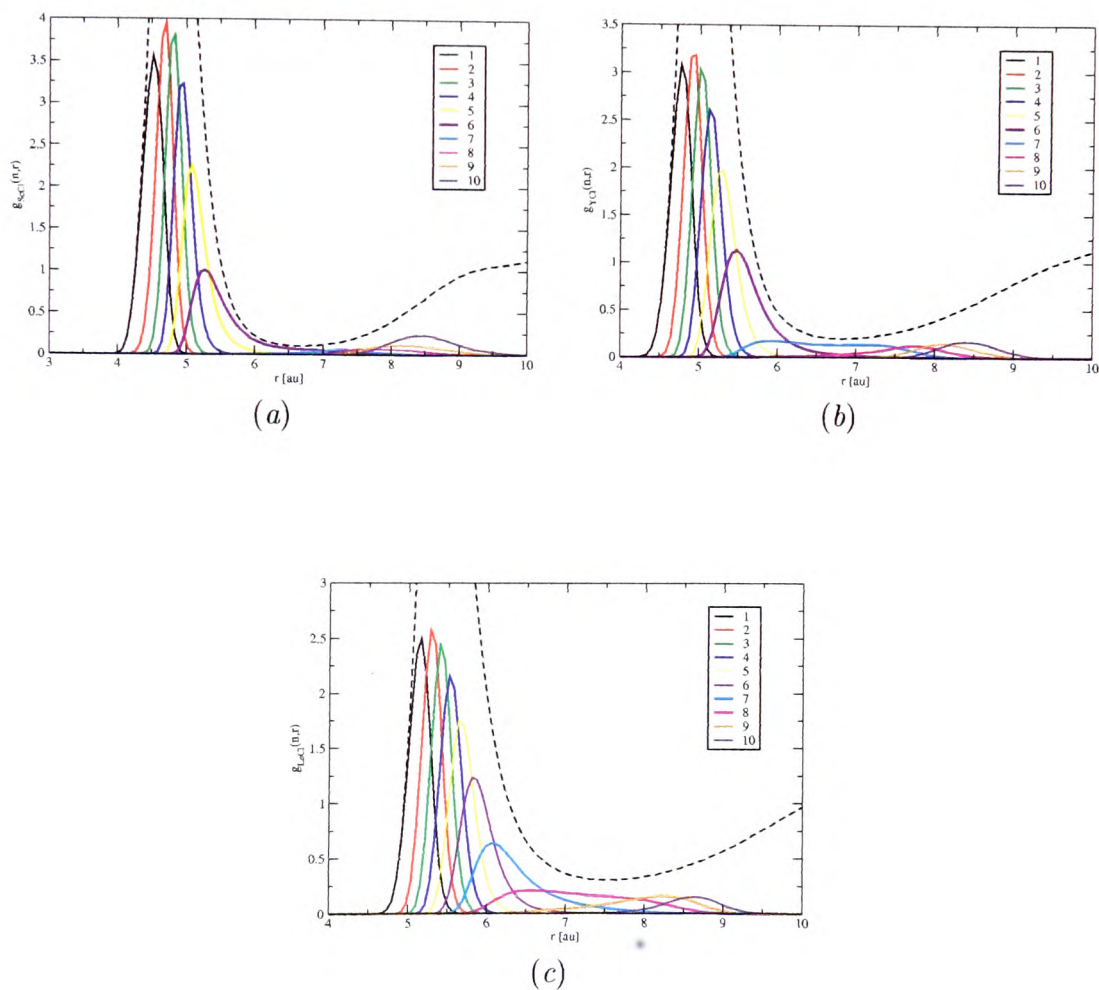


Figure 8.8: The cation-anion neighbourhood partial radial distribution functions at 1000K for (a) ScCl_3 , (b) YCl_3 , and (c) LaCl_3 .

than $F_{ScCl}(6, 7)$ and $F_{YCl}(6, 7)$. This emphasises the description of the structure of molten $LaCl_3$ as being made up of *hairy balls* rather than well defined coordination polyhedra. The much better definition in the cutoff between coordination shells in $ScCl_3$ and YCl_3 reflects the predominantly 6-coordinate nature of Sc and the $[6+n]$ -coordinate nature of Y, and the barrier depth is now comparable to that of PIM BeF_2 at the same temperature, where there was an appreciable degree of defect formation.

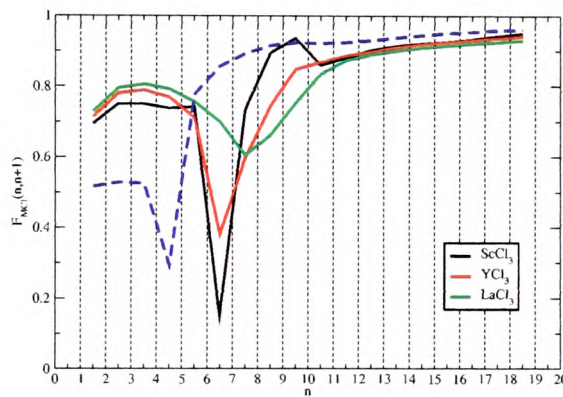


Figure 8.9: The normalised probability overlap functions, $F_{MCl}(n, n + 1)$, for the MCl_3 systems, at 1000 K. The dashed blue line shows $F_{BeF}(n, n + 1)$ for PIM BeF_2 at 1000K for comparison.

Chapter 9

BeF₂: Towards a less diffusive Polarizable Ion Model

9.1 Introduction

In our discussion of the molten trichlorides, we calculated the vibrational densities of states for the symmetric stretching modes of the cation polyhedra in LaCl₃. There was reasonable agreement with the experimental polarised Raman spectra, but the stretching frequencies were a little too high. We also saw that the systems were somewhat less diffusive, and had lower conductivities than observed experimentally. A vibrational frequency that is too high correlates with cation coordination polyhedra which are too stiff, and that with a slower cage decay rate and hence lower diffusivity. We can therefore perhaps link the difference in the calculated and experimentally observed vibrational frequencies with the changes in the potential which must be made in order to improve the representation of the dynamics.

In this chapter we investigate the effect that changing the potential has on the dynamics of PIM BeF₂. We scale the values of the potential parameters in order to improve the dynamical representation of PIM BeF₂ whilst retaining our good structural representation, and we find that the vibrational spectra can be used as our driving force for change, as explained below.

9.2 Construction of a better PIM potential

We have seen that the current BeF₂ potential gives good agreement with the experimental structural measurements when used in the PIM, and good agreement with the experimental diffusivity measurements when used in the RIM. The difference between the two models seems to be the large number of defect cation sites, *i.e.* non-tetrahedral cations, and so to get a better set of potential parameters for the PIM, such that we get good agreement with both experimental structural and dynamical data, we need to change the parameters in order to effectively reduce the number of defect sites present.

The potential is described by equation 2.1,

$$U_{ij}(r_{ij}) = \frac{Q_i Q_j}{r_{ij}} + B_{ij} e^{-\alpha_{ij} r_{ij}} - \sum_{n=6,8} \frac{C_{ij}^n}{r_{ij}^n} f_{ij}^n(r_{ij}), \quad (9.1)$$

and the local structure around a given ion is determined in particular by the short range repulsive part of the potential,

$$U_{ij}^{s-r}(r_{ij}) = B_{ij} e^{-\alpha_{ij} r_{ij}}. \quad (9.2)$$

The force acting on an ion, i , due to another ion, j , F_{ij} , is given by

$$F_{ij}(r_{ij}) = - \left(\frac{\partial U^{s-r}(r_{ij})}{\partial r_{ij}} \right) = \alpha_{ij} B_{ij} e^{-\alpha_{ij} r_{ij}}. \quad (9.3)$$

When we change the potential parameters, we want to keep the radial distribution functions as close to their current forms as possible, and particularly to keep the bond lengths the same. The local structure, which determines the bond-lengths, will be relatively unperturbed on changing the potential parameters if the local forces remain the same. We can ensure this by choosing the bond-length, which is taken to be the position of the first maximum in the partial radial distribution function, as a characteristic distance, r_{ij}^* , and applying the condition

$$\begin{aligned} F'_{ij}(r_{ij})|^{r_{ij}=r_{ij}^*} &= F_{ij}(r_{ij})|^{r_{ij}=r_{ij}^*} \\ \therefore \alpha'_{ij} B'_{ij} e^{-\alpha'_{ij} r_{ij}^*} &= \alpha_{ij} B_{ij} e^{-\alpha_{ij} r_{ij}^*}, \end{aligned} \quad (9.4)$$

such that the forces acting at the bond-length remain the same. α'_{ij} and B'_{ij} are the new choice of potential parameters, and α_{ij} and B_{ij} the original parameters.

In this scheme, the choice of new α_{ij} and B_{ij} parameters is arbitrary, such that equation 9.4 is satisfied. We need to direct our search through parameter space, and we do this by noting that the vibrational frequency of the local polyhedra is determined by the rate of change of the forces, as given by

$$\left(\frac{\partial F_{ij}(r_{ij})}{\partial r_{ij}} \right) = -\alpha_{ij}^2 B_{ij} e^{-\alpha_{ij} r_{ij}}. \quad (9.5)$$

We can therefore change the potential parameters such that a second condition is satisfied,

$$\begin{aligned} \left. \frac{\partial F'_{ij}(r_{ij})}{\partial r_{ij}} \right|^{r_{ij}=r_{ij}^*} &= n \left. \frac{\partial F_{ij}(r_{ij})}{\partial r_{ij}} \right|^{r_{ij}=r_{ij}^*} \\ \alpha_{ij}'^2 B_{ij}' e^{-\alpha_{ij}' r_{ij}^*} &= n \alpha_{ij}^2 B_{ij} e^{-\alpha_{ij} r_{ij}^*}, \end{aligned} \quad (9.6)$$

where n is a scaling factor such that the new rate of change of the forces gives better agreement of the calculated vibrational density of states with the experimental vibrational spectra. The calculation of the vibrational density of states is outlined in appendix D. Now, if $\alpha'_{ij} = n_{\alpha_{ij}} \alpha_{ij}$ and $B'_{ij} = n_{B_{ij}} B_{ij}$, where $n_{\alpha_{ij}}$ and $n_{B_{ij}}$ are scaling factors for the parameters α_{ij} and B_{ij} , then equation 9.4 becomes

$$(n_{\alpha_{ij}} \alpha_{ij}) (n_{B_{ij}} B_{ij}) e^{-n_{\alpha_{ij}} \alpha_{ij} r_{ij}^*} = \alpha_{ij} B_{ij} e^{-\alpha_{ij} r_{ij}^*}, \quad (9.7)$$

and equation 9.6 becomes

$$(n_{\alpha_{ij}} \alpha_{ij})^2 (n_{B_{ij}} B_{ij}) e^{-n_{\alpha_{ij}} \alpha_{ij} r_{ij}^*} = n \alpha_{ij}^2 B_{ij} e^{-\alpha_{ij} r_{ij}^*}, \quad (9.8)$$

and hence

$$n_{\alpha_{ij}} n_{B_{ij}} e^{-(n_{\alpha_{ij}} - 1) \alpha_{ij} r_{ij}^*} = 1 \quad (9.9)$$

$$n_{\alpha_{ij}}^2 n_{B_{ij}} e^{-(n_{\alpha_{ij}} - 1) \alpha_{ij} r_{ij}^*} = n. \quad (9.10)$$

From these expressions, it follows (from dividing equation 9.10 by equation 9.9) that

$$n_{\alpha_{ij}} = n.$$

The relationship expressed by equation 9.10 results from the requirement that we want to scale our α_{ij} parameters (by the factor $n_{\alpha_{ij}} = n$) in order to get better agreement of the frequencies of the modes in the vibrational density of states with those measured in the experimental Raman and Infra-Red spectra. Figure 9.1 shows the vibrational densities of states for PIM BeF₂ at 700 K and RIM BeF₂ at 1300 K respectively. The experimental Raman and Infra-Red densities of states for glassy BeF₂ at room temperature [81, 82] are also shown.

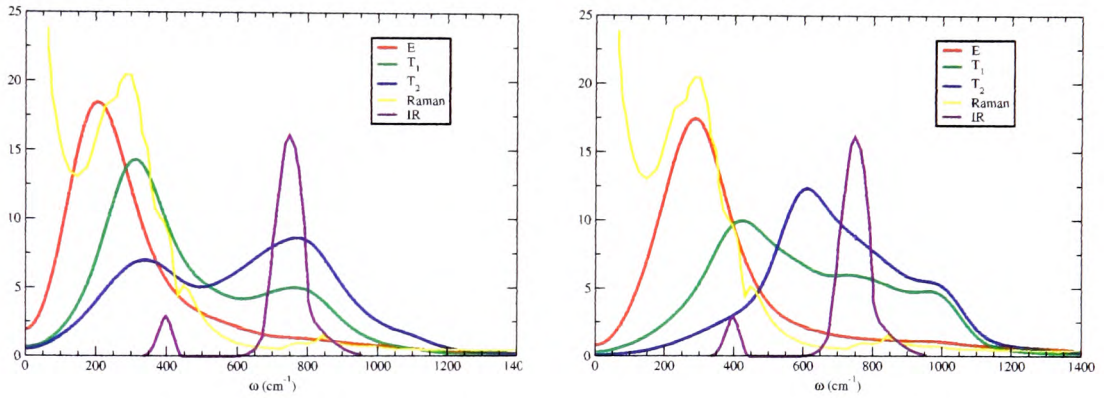


Figure 9.1: The calculated vibrational densities of states for PIM BeF₂ at 700 K (in the left-hand panel) and RIM BeF₂ at 1300 K (in the right-hand panel), compared with the HH-depolarised band from the experimental Raman spectrum, which represents the Raman density of states, and the experimental Infra-Red absorption spectrum for amorphous BeF₂ at room temperature [81, 82]. The experimental spectra are shown with arbitrary intensities.

The calculation of the vibrational densities of states corresponding to the different vibrational modes of the tetrahedron, $A_1 + E + T_1 + T_2$, is explained in appendix D, and the assignment of the experimental spectra is outlined in section 9.3. The main conclusion from the analysis of the vibrational densities of states is that the frequency of the E vibration mode in the PIM is too low compared to experiment, whereas the agreement in the RIM is excellent. The ratio of the calculated frequency for the E band in the PIM to the frequency of the peak in the experimental Raman spectrum is our first choice of n , the scaling factor such that the vibrational

frequencies give better agreement with experiment. The positions of the peaks are $\omega_{max}^{E,PIM} = 210 \text{ cm}^{-1}$ and $\omega_{max}^{Raman} = 290 \text{ cm}^{-1}$, suggesting an n value of $\frac{290}{210} \approx 1.4$. We would anticipate that the new potential parameters, with $n = n_{\alpha_{ij}} \approx 1.4$, would generate a vibrational density of states with better agreement of the calculated E mode with experiment, and we would choose new B_{ij} values, by solving equations 9.9 and 9.10, such that the positions of the peaks in the partial radial distribution functions remain relatively unchanged and hence that the agreement of the calculated and experimentally observed reduced intensity functions remains good. The parameter sets investigated are given in table 9.1. The first four parameter sets correspond to solutions of equations 9.9 and 9.10, and the latter four to a more general sweep through the FF and BeF parameter space.

	Parameter Set							
Parameter	1	2	3	4	5	6	7	8
α_{FF}	1.823	2.28	2.28	2.05	2.28	2.28	2.28	2.28
B_{FF}	16.62	114.8	114.8	43.38	114.8	114.8	200.0	50.0
α_{BeF}	1.823	2.28	2.05	2.28	1.85	1.95	2.05	2.05
B_{BeF}	13.10	37.38	21.99	37.38	13.79	17.39	21.99	21.99
α_{BeBe}	1.823	2.28	2.28	2.28	2.28	2.28	2.28	2.28
B_{BeBe}	8.245	80.89	80.89	80.89	80.89	80.89	80.89	80.89

Table 9.1: The sets of Born-Mayer parameters considered, for PIM BeF₂, in improving the potential.

The simulations with these new sets of potential parameters were performed on short time scales (10000 time steps), and retained the thermostatting parameters and anion polarisability of the previous BeF₂ potential, as described in chapter 3 (which here corresponds to potential 1). The different temperature simulations were all started from a common start-up configuration with a velocity rescale to the desired temperature.

These simulations, although short, were used to calculate the reduced intensity functions, as shown in figure 9.2 for the 800 K simulations, the partial radial distribution functions, as shown in figure 9.3, again for the 800 K simulations, and the tempera-

ture dependence of the distribution of cation coordination numbers, shown in figure 9.5, and of the ionic diffusion coefficients, as shown in figure 9.6, across the 800-1000 K temperature range.

9.2.1 The reduced intensity function and partial radial distribution functions with the new potentials

In figure 9.2, the potential which corresponds to that used to generate the PIM results seen previously is labelled potential 1, and is shown as the function plotted with the *red* line. This gives the best agreement with the experimental reduced intensity function, especially at larger k , which corresponds to the small r local structure corresponding to the immediate ionic neighbourhood. However, it is noticeable that the agreement remains reasonable across all the potentials examined, apart from the smearing out of the minimum in the function in the 8-10 Å⁻¹ range; despite this smearing out, though, these potentials still give the splitting into two peaks, even though the peak at higher k may appear only as a shoulder of the lower k peak, in all but potential 8.

If we compare the behaviour here with that shown in figure 3.6, we can see that some of these new PIM potentials are starting to show a more RIM-like appearance of the reduced intensity function. The agreement is therefore becoming worse, but we can aim for a choice of potential parameters which given acceptable agreement with the reduced intensity function and much better agreement with the diffusive behaviour.

Figure 9.3 shows the partial radial distribution functions, $g_{\alpha\beta}(r)$, for the different potentials, with the inset emphasising the behaviour of the BeF partial radial distribution function in the region of the first minimum. The main effect of changing the potential seems to be that we can control the width of the first peaks in the distributions, and also the height at and position of the first minima.

The potentials which give the more RIM-like behaviour are those which have a narrower, taller first peak in the cation-anion partial radial distribution function, and

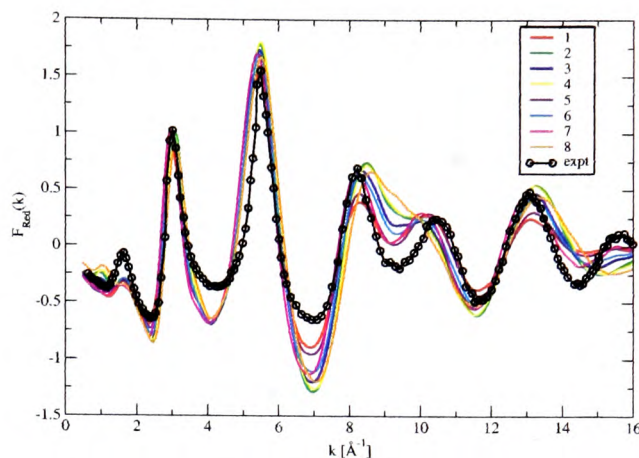


Figure 9.2: The calculated reduced intensity functions for the range of potential sets, for PIM BeF_2 at 800 K, compared with that measured experimentally. The numbers given by the legend refer to the potential set numbers in table 9.1.

which have the lowest intensity in the region between the first and second peaks. This was interpreted in the RIM as a tightening up of and increased definition in the first coordination sphere.

9.2.2 The bond angle distributions with the new potentials

The Be–F–Be and F–Be–F bond angle distributions are shown in figure 9.4 for the PIM, RIM, and potentials 2 and 4 at 1300 K. Potentials 2 and 4 are the least diffusive of the new potentials, as discussed below. The change in the structure in the new, less diffusive potentials corresponds to the *tightening* up of the first coordination shell, as described above, whilst retaining the bent Be–F–Be unit which is characteristic of a system with a polarisable anion. This can be seen from the maximum intensity in the bond angle distribution occurring at 130° in the new potentials, compared to 125° in the original PIM, but compared to the much straighter unit in the RIM where the maximum intensity occurs at 160° . The form of the intensity in the F–Be–F bond angle distribution is very much like the RIM with these new poten-

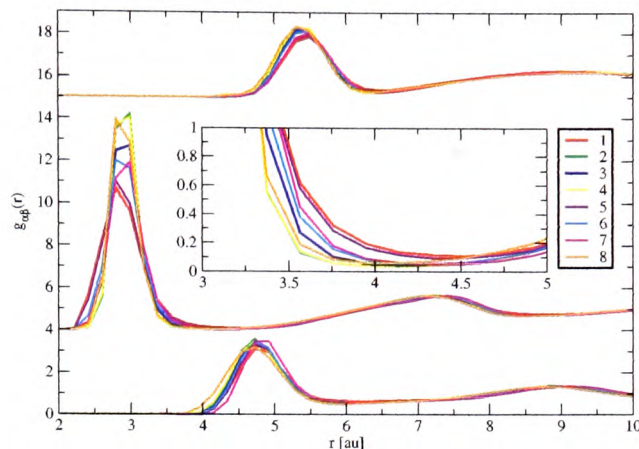


Figure 9.3: The calculated partial radial distribution functions for the range of potential sets, for PIM BeF_2 at 800 K. The lower set of functions is $g_{FF}(r)$, the middle set $g_{BeF}(r)$, and the top set $g_{BeBe}(r)$. The inset shows the BeF partial radial distribution function in the region of the first minimum in more detail.

tials, and this again is a signature of the tightening up of the first coordination shell compared to the PIM; this has a very broad F–Be–F bond angle distribution, due partly to the relatively high temperature, but also due to the ability of the anionic dipoles to stabilise less tetrahedral configurations. The new potentials, therefore, contain some of the characteristics of both the PIM and RIM potentials studied so far.

9.2.3 Coordination Numbers and Diffusion Coefficients with the new potentials

The mean coordination number, the number of ions of a given species around a central ion, is the value of the probability function integrated to the position of the first minimum in the relevant partial radial distribution function. The cationic coordination number distributions calculated in this way are shown in figure 9.5 for

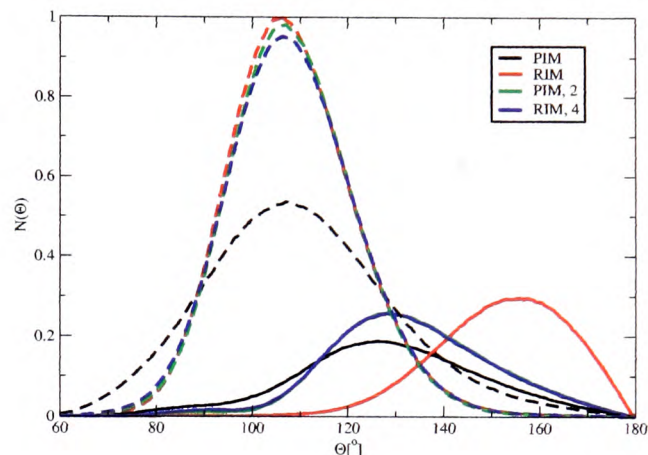


Figure 9.4: The F–Be–F (with dashed lines) and Be–F–Be (with solid lines) bond angle distributions in BeF₂ at 1300K, simulated using the PIM, RIM, and PIM with the new potentials 2 and 4.

the 3- and 4-coordinate cations¹. As we might expect, those potentials with the best defined first coordination shell, in terms of the shape of the first peak in the cation-anion partial radial distribution function, are those potentials which have the highest population of 4-coordinate cations. In chapter 4, we suggested that the high diffusivity of our current PIM simulations, corresponding to potential 1, could be linked to the high population of non-tetrahedral cations. The potentials examined here which result in a high fraction of 4-coordinate sites are also those which have a low diffusivity. This can be seen in figure 9.6, which shows the variation of the cationic diffusion coefficients² with inverse temperature for the different potentials. The simulations used to investigate the choice of potential parameters were short, at 10000 time steps corresponding to 3.6 ps of real time, and so we should not consider

¹Any remaining cation coordination number intensity is due to the small numbers of 5-coordinate cations present, and is not shown in this figure for clarity: the temperature dependence of the fraction of 5-coordinate cations present is similar to that for the fraction of 3-coordinate cations.

²The anionic diffusion coefficients follow the cationic behaviour, but are approximately 10% higher. They are not shown in figure 9.6 for clarity.

the absolute values of the diffusion coefficients calculated from these simulations as being totally accurate, as we have barely begun to probe the diffusive regime (especially in some of the less diffusive systems). However, the diffusion coefficients still span approximately an order of magnitude, and we can see the trends associated with the low defect concentration being repeated in the diffusion coefficients.

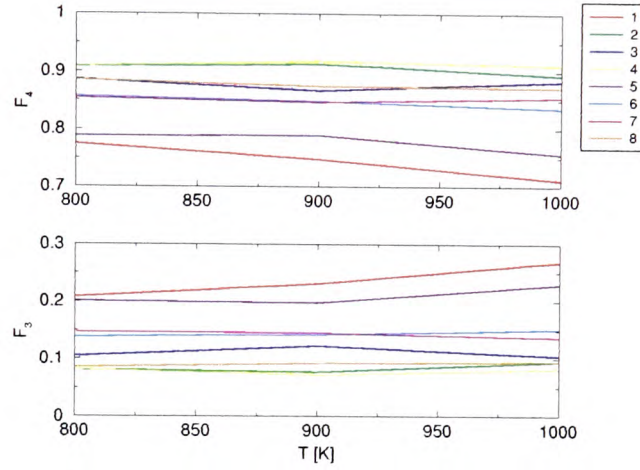


Figure 9.5: The variation of the fraction of sites with $N^c = 3$ (the lower panel) and $N^c = 4$ (the upper panel) with temperature, for the different potential sets for PIM BeF_2 .

9.2.4 What are the changes in the potential parameters responsible for the change in the structural and diffusive behaviour?

In our search for a less diffusive PIM system, we have changed the Born-Mayer parameters, α_{ij} and B_{ij} , and the main changes have focused on the values of α_{FF} , B_{FF} , α_{BeF} , and B_{BeF} . The potentials calculated according to equation 2.1 for the anion-anion and cation-anion interactions, $U_{FF}(r)$ and $U_{BeF}(r)$, are shown in figure 9.7. We can see that relatively small changes in the potential lead to large changes in the dynamics (as the *dynamics are exponentially dependent on the structure*), and

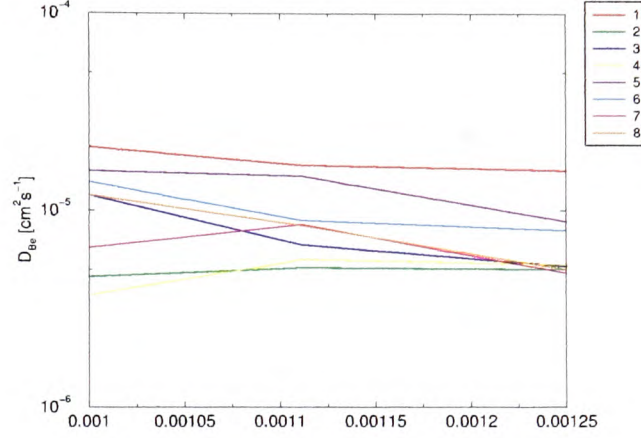


Figure 9.6: The variation of the ionic diffusion coefficients, D_{Be} , with inverse temperature for the different potential sets for PIM BeF_2 , as given by the legend.

that the dynamics are particularly sensitive to motion in regions where the short range repulsion is dominant, *i.e.* where the passage of an ion is closest to other ions, such as in the ionic motion described by figure 5.6.

Changing the values of α_{ij} and B_{ij} effectively changes the size of the ions and their *hardness*, *i.e.* the ability of their electron charge clouds to overlap. The higher α_{BeF} and B_{BeF} values which correspond to the least diffusive systems have had the effect of making the Be^{2+} ion bigger and the BeF interaction harder, thus favouring the 4-coordinate environment much more than the original potential, and hence decreasing the tendency to form 3-coordinate species and thereby reducing the diffusivity. This increase in size and hardness effectively counteracts the polarisation terms on the fluoride anions which tend to make the BeF interaction softer due to the ability of the F ions to distort as they approach the Be ions.

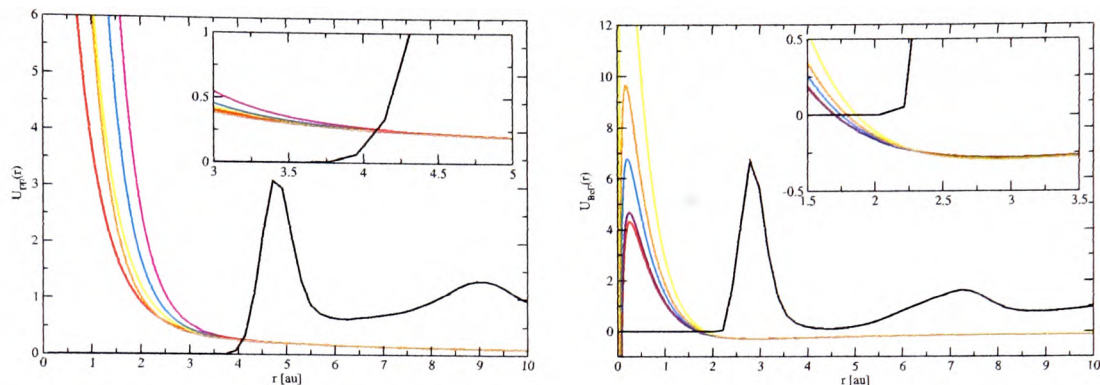


Figure 9.7: The anion-anion (in the left-hand panel) and the cation-anion (in the right-hand panel) Born-Mayer potentials for the new potential sets investigated in PIM BeF₂. The colours of the lines are as given in the legend to figure 9.6.

9.2.5 Summary of the effects of changing the potential parameters

The least diffusive potentials, then, are those labelled 2 and 4. Our initial guide to the choice of scaling factors was that we should obtain better agreement of the calculated vibrational densities of states whilst retaining the good agreement of the reduced intensity function. The calculated vibrational densities of states are shown in figure 9.8 for PIM BeF₂ with potentials 2 and 4 respectively, and should be compared to those shown in figure 9.1 for the original PIM and RIM potentials. Table 9.2 shows the positions of the peaks of the different modes in the calculated vibrational densities of states, compared with those measured experimentally, and these should be compared with the values given in table 9.3 which are for the original potential, potential 1, calculated for the PIM and RIM models.

Whilst the agreement of the T_2 peaks with the experimental IR spectrum are poorer³ in the calculated vibrational densities of states for potentials 2 and 4 compared to

³Note, though, that in all the modes there is a large amount of mixing between the T_1 and T_2 modes: the vibrations of all the modes are calculated on the basis of the tetrahedra being individual units, but in fact the vertex sharing nature of the network means that the units are not isolated, and so there will be correlation between the motions of adjacent tetrahedra, and hence a mixing of the modes of different symmetries.

the original potential, there is a marked improvement in the agreement of the E -bending mode with the experimental Raman spectrum. In section 9.3 we describe the origin of this mode, and we will see that it is likely to be most sensitive to the choice of B_{BeF} and B_{FF} parameters: the larger values used in potentials 2 and 4 give a better defined first coordination shell, and now a stiffer E -bending motion; this is characteristic of a more rigid, and therefore less diffusive, network.

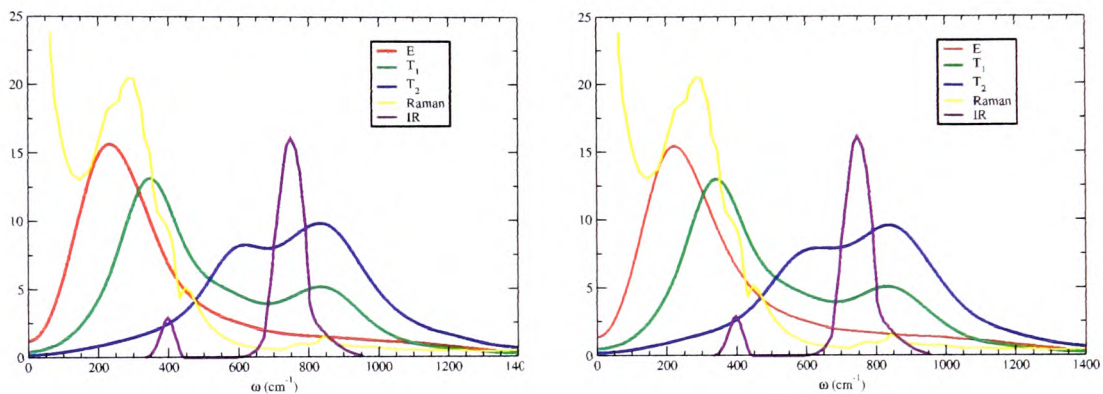


Figure 9.8: The calculated vibrational densities of states for PIM BeF_2 at 1300 K, simulated using potentials 2 (in the left-hand panel) and 4 (in the right-hand panel), as described in table 9.1.

Band	ω_{max} [cm^{-1}]		
	PIM, potential 2, 1300 K	PIM, potential 4, 1300 K	Experiment
A_1	580	580	—
E	235	225	—
T_1	345,835	345,830	—
T_2	620,840	595*,840	—
Raman	—	—	290,450*,840
IR	—	—	400,750

Table 9.2: The frequencies of the positions of maximum intensity, *i.e.* the *peaks*, in the calculated vibrational densities of states and experimental Raman and Infra-Red spectra, from figure 9.8. The values marked with a * are shoulders on the (rather broad) peaks.

9.3 Assignment of the experimental vibrational spectra

Table 9.3 shows the positions of the peaks in the calculated densities of states and the experimental spectra, as shown in figure 9.1. The vibrational densities of states for the simulated systems are calculated according to the procedure outlined in appendix D.

Band	ω_{max} [cm ⁻¹]		
	PIM, 700 K	RIM, 1300 K	Experiment
A_1	510	540	–
E	210	290	–
T_1	310,770	425,775*,965*	–
T_2	345,770	610,975*	–
Raman	–	–	290,450*,840
IR	–	–	400,750

Table 9.3: The frequencies of the positions of maximum intensity, *i.e.* the *peaks*, in the calculated vibrational densities of states and experimental Raman and Infra-Red spectra, from figure 9.1. The values marked with a * are shoulders on the (rather broad) peaks. The *Raman active* modes are $A_1 + E + T_2$. The presence of multiple peaks in the T_1 and T_2 bands is due to the mixing of the vibrations with these symmetries, which is possible because the tetrahedra are not isolated units and the linkages can break the symmetry of the vibrations.

In a simple tetrahedron, the T_2 mode is *Infra-Red active*, while the *Raman active* modes are $A_1 + E + T_2$. We note that the agreement between the positions of the peaks in the Infra-Red spectrum and the calculated T_2 mode are good, particularly for the PIM (as shown by comparing the blue and purple lines in figure 9.1). We may also make a tentative assignment that the main broad peak in the Raman spectrum contains contributions from the E and T_2 modes⁴. The agreement between the position of the E mode and the peak in the Raman spectrum is poorest in the PIM, but this agreement has become good in the RIM.

To understand this, we should consider the motion of the ions responsible for the E band. Equations D.5 describe the projections of the ionic motion used to calculate

⁴The experimental Raman spectrum is the HH-depolarised spectrum, and so the A_1 band does not contribute (this band will only be seen in the polarised spectrum).

this band, and these expressions correspond to the ionic motion shown in figure 9.9.

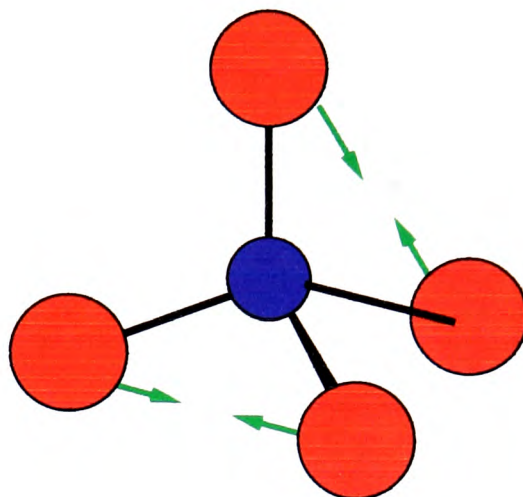


Figure 9.9: The ionic motion responsible for the E bending vibration in a tetrahedral MX_4 unit. The anions on opposite edges of the tetrahedron move towards and away from each other in a concerted *scissors* motion.

The E -bending motion involves F^- ions moving towards each other along opposite edges of the tetrahedron, and so is strongly dependent on the repulsion between the two F^- ions. This is governed by the $B_{FF}e^{-\alpha_{FF}r_{FF}}$ term, but the dependence of this term on r_{FF} does not change between the PIM and RIM. The difference between the two models can be accounted for by the fact that in the PIM the anion has a dipole which can change as the surroundings of the anion change. Thus, as two anions move closer together during the first part of the motion, the dipoles orientate to compensate for the fact that the negative charge on the anions is now closer together and therefore has a higher repulsion, and *vice versa* when the anions move apart during the second part of the motion. This results in the *scissors* motion of the E bending vibration having a lower energy in the PIM than the RIM, and hence being observed at a lower frequency.

9.4 The dynamical properties of the less diffusive BeF₂ systems

9.4.1 Details of the simulations

Longer simulations across a range of temperatures were carried out in order to better characterise the behaviour of the less diffusive PIM systems, potentials 2 and 4. The procedure for performing the simulations was the same as that outlined for the original PIM in section 3.1.1, *i.e.* a velocity rescale followed by a 100000 step run to attain equilibrium⁵, and then a 500000 step run to generate the trajectory from which the results are calculated. The time step was again 15 au, and the density 1.986 gcm⁻³.

9.4.2 The diffusion coefficients

Figure 9.10 shows the inverse temperature dependence of the calculated ionic diffusion coefficients for BeF₂ simulated using the PIM with potentials 2 and 4, compared with those calculated previously from PIM and RIM simulations with the original potential, and those measured experimentally, as shown in figure 3.10.

At the lower temperatures simulated with the new potentials, the diffusion coefficients are very small, and the fit to the Arrhenius form is very poor. This is because the low diffusion coefficients correspond to very long structural relaxation times, and hence over the course of the simulations structural equilibrium has not been attained. In fact we can see from the values of the diffusion coefficients in the 800-1000 K range that the values calculated here are lower than those for the short potential investigation simulations, shown in figure 9.6, which is evidence that the equilibration is continuing, and the system is slowing down as this occurs. At the highest temperature, 1300 K, we can see that the agreement between the calculated and experimental diffusion coefficients is now good, and we might anticipate that the agreement at lower temperature would also improve if proper equilibration could be

⁵The discussion in section 9.4.2 suggests that this is not necessarily long enough for equilibrium to be attained, but we may believe the trends in the results.

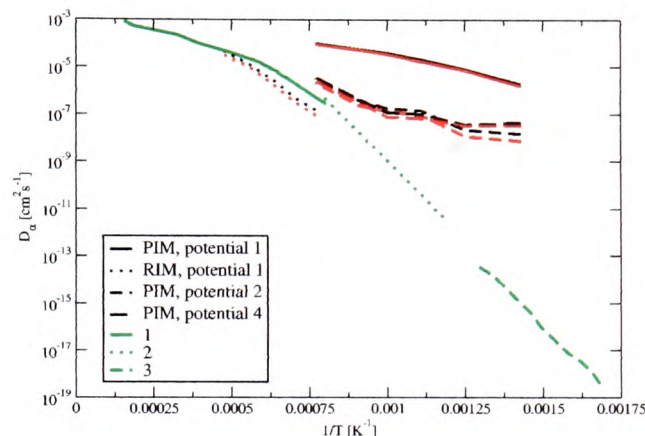


Figure 9.10: The comparison of the inverse temperature dependence of the calculated diffusion coefficients for BeF_2 simulated using potential 1, PIM in the solid line and RIM in the dotted line, and potentials 2, PIM in the dashed line, and 4, PIM in the long dashed line, with experimental data, set (1) from [46] and set (3) from [47], and other theoretical data, set (2) from [3] (see figure 3.10). The anion diffusion coefficients are shown with black and green lines (simulation and experiment respectively), and the cation diffusion coefficients with red lines.

achieved⁶. Note that the slope of the diffusion coefficients at the highest temperatures still gives an activation energy, at 125 kJmol^{-1} for potential 2 and 127 kJmol^{-1} for potential 4, which is small, although it is now closer to that previously obtained for the RIM.

9.4.3 The cage correlation functions

The cage decay rates for the $c = 1$ -in-out functions for the different subsystems are given in tables 9.4 and 9.5 for potentials 2 and 4 respectively, and the cage lifetimes are given in table 9.6. These values are obtained by fitting the cage decay function to the form $C(t) = C_0 \exp(-\frac{t}{\tau})$, and due to the small amount of cage decay occurring in these simulations it is difficult to achieve reliable fits; the small amount of cage decay

⁶The long structural relaxation times (see section 9.4.3) associated with these very low diffusivities mean that equilibration is not really feasible in a reasonable amount of computer time; we are moving into the glassy regime and so the diffusive statistics become very poor.

corresponds to the very long cage lifetimes (only the 1300 K simulations will really have sampled many cage decay events), and this in turn to the poor equilibration already described. Nevertheless, we may use the ratio of the diffusion coefficients to the cage decay rates to calculate the effective cage jump lengths, and these are given in table 9.7. If we compare these with the jump lengths for the PIM and RIM, given in tables 4.5 and 5.6 respectively, we can see that they are shorter than the PIM jump lengths and comparable with the RIM jump lengths. This implies an increase in the cooperativity of the cage decay events and also confirms the transition to a more RIM-like behaviour of the diffusivity with these new potentials.

T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.00549	0.000545	0.000278	0.00128
800	0.000241	0.000241	0.000107	0.00548
900	0.00237	0.00329	0.00114	0.00685
1000	0.00227	0.00334	0.00127	0.00478
1100	0.00591	0.00690	0.00295	0.0124
1300	0.0394	0.0499	0.0191	0.0720

Table 9.4: The cage decay rates for the $c = 1$ -in-out function, for the different subsystems in PIM BeF₂, simulated using potential 2.

T [K]	k_{BeF} [ps ⁻¹]	k_{BeBe} [ps ⁻¹]	k_{FBe} [ps ⁻¹]	k_{FF} [ps ⁻¹]
700	0.000549	0.000921	0.000249	0.00164
800	0.000602	0.00116	0.000361	0.00156
900	0.00171	0.00244	0.000883	0.00415
1000	0.00146	0.00204	0.000785	0.00291
1100	0.00529	0.00634	0.00310	0.0108
1300	0.0498	0.0636	0.0247	0.0875

Table 9.5: The cage decay rates for the $c = 1$ -in-out function, for the different subsystems in PIM BeF₂, simulated using potential 4.

9.5 The effect of dispersion in BeF₂

The BeF₂ potentials investigated so far have not included any effects due to the dispersion interaction between ions, as it has been anticipated that the small sizes

T [K]	Potential 2		Potential 4	
	τ_{BeF} [ps]	τ_{BeF} [configs]	τ_{BeF} [ps]	τ_{BeF} [configs]
700	1822	50216	1821	50196
800	4147	114311	1660	45754
900	423	11652	558	15384
1000	440	12134	683	18833
1100	169	4662	189	5211
1300	25.4	699	20.1	554

Table 9.6: The cage lifetimes for the $c = 1$ -in-out BeF function in PIM BeF₂, simulated using potentials 2 and 4.

Potential	λ_{BeF} [au]	λ_{FBe} [au]
2	3.04	5.42
4	3.41	5.49

Table 9.7: The cage jump lengths for the $c = 1$ -in-out BeF function in PIM BeF₂, simulated using potentials 2 and 4.

of the ions would mean that these effects would also be small. Simulations of the liquid-vapour interface in BeF₂ [83] have shown, however, that the dispersion forces must be included in constant *pressure* simulations to prevent the system expanding (our simulations are performed under constant *volume* conditions).

These simulations on the interface included dispersion terms in the F–F interaction taken from the *ab initio* values from studies on Cryolite (Na₃AlF₆) [84], and the potential used was derived from our potential 4⁷ and the Born-Mayer potential parameters for the interface potential, labelled 4*, are given in table 9.8. The simulations on the interface concluded that this potential resulted in overwhelmingly 4-coordinate cations, with the relatively small number of 3-coordinate species being found at the interface, and hence that the bulk liquid structure was very similar to that for the simulations with the basis potential 4.

A bulk liquid simulation was performed with potential 4* at 1300K, using the procedure outlined in section 3.1.1, and the diffusive properties of the system investigated.

⁷The adaptation of the potential to include the effects of dispersion followed a similar procedure to that outlined in section 9.2: the potential parameters were changed such that the positions of the first peaks in the partial radial distribution functions were retained.

$\alpha - \beta$	α [au]	B [au]	C_6 [au]	C_8 [au]	f_6 [au]	f_8 [au]
F-F	1.75	21.36	28.372	538.77	1.8	1.8
Be-F	2.28	37.28	0.0	0.0	1.0	1.0
Be-Be	2.28	10.89	0.0	0.0	1.0	1.0

Table 9.8: The Born-Mayer potential parameters for the simulations of the liquid-vapour interface in PIM BeF₂, including the effects of dispersion in the F-F interaction. This potential is based on the for potential 4, and all other simulation parameters were the same.

The results are summarised in table 9.9.

Potential	D_F	D_{Be}	k_{BeF}	k_{BeBe}	k_{FBe}	k_{FBe}
4	3.7×10^{-6}	2.6×10^{-6}	0.0498	0.0636	0.0247	0.0875
4*	6.5×10^{-6}	5.3×10^{-6}	0.0769	0.0927	0.0397	0.136
Potential			λ_{BeF}		λ_{FBe}	
4			3.41		5.49	
4*			3.84		5.93	

Table 9.9: Summary of the diffusive results for the 1300 K simulation with potential 4*, which includes the effects of dispersion, and compared with the results for the basis potential 4. Diffusion coefficients, D_α , are given in cm²s⁻¹, cage decay rates (for the $c = 1$ -in-out function), $k_{\alpha\beta}$, in ps⁻¹, and cage jump lengths (for the $c = 1$ -in-out function), $\lambda_{\alpha\beta}$, in au. Note that the cage jump lengths for potential 4 are averaged over all simulated temperatures, and for potential 4* are calculated from the 1300 K simulation only.

The main observation is that including the effects of dispersion leads to a doubling of the diffusion coefficient and an accompanying doubling of the cage decay rates. This, though, is a small change compared to the huge differences between the PIM and RIM results with the original potential, where the diffusion coefficients changed by several orders of magnitude. The cage jump lengths, which are calculated on the basis of this single simulation at 1300 K for potential 4* but which were averaged over temperature for potential 4, have increased slightly, but they are all still consistent with the choice of the first minimum in the BeF partial radial distribution function as the choice for the cage cutoff length and the diffusive length scale, and we conclude that our model for diffusion is not changed on the inclusion of the dispersion effects. Furthermore, the fact that there is only a change of a factor of

two in the diffusion coefficients between the simulations including and excluding the dispersion interaction suggests the dispersion effects are much less important in the bulk than they are at the liquid-vapour interface, and hence that we are justified in omitting them.

Chapter 10

Conclusions

We have investigated BeF_2 as a template for the ideal vertex shared tetrahedral network system in an attempt to identify the local events, on an atomistic scale, which determine the measurable, macroscopic diffusion coefficients. We have calculated the viscosity from the stress tensor correlation function, and then scaled this using the Eyring relation to give an estimate of the ionic diffusion coefficients. These compare favourably with those calculated from the Einstein relation, the *true* diffusion coefficients, and we conclude that the use of the Eyring relation, based upon the hopping model for diffusion, is appropriate for the network fluid. Furthermore, the hopping length scale is of the order of the first minimum in the cation-anion partial radial distribution function, suggesting that these hops correspond to the cation leaving its shell of nearest neighbours.

The definition of the *cage* of counter-ions as those ions which are inside the first coordination shell, after Gezelter *et al.*, allows us to calculate the rate of exchange one of these cage ions, by fitting the long time decay of the cage correlation function to an exponential form. We can use this cage decay rate, which can be associated with the rate of breaking a Be-F bond, together with the position of the first minimum in the cation-anion partial radial distribution function as a jump length, to calculate the diffusion coefficient using a modified version of the Einstein relation, and we find that this gives good agreement with the true diffusion coefficient. We conclude that the diffusive process in BeF_2 is wholly determined the need for an ion

to exchange its surroundings before it can diffuse. Comparison of the PIM and RIM suggests that the much enhanced diffusivity of the PIM is due to the much higher cage decay rates, which can be attributed to the increased ability of the PIM to stabilise asymmetric transition states during the passage of ions from one coordination shell to another.

The constrained network requires the formation of non-ideally coordinated species, or *defects*, in order for any relaxation to occur, and an analysis of the cage decay of different cation coordination types has shown that there is enhanced relaxation of the network on an intermediate time scale due to the 3-coordinate defects in the PIM, and to 3- and 5-coordinate defects in the RIM, in the low temperature regimes where the systems are most ideal. The 5-coordinate sites in the PIM exist only vibrationally and so do not aid structural relaxation. At higher temperatures, where defect concentrations become appreciable, the actions of the different types of site become comparable.

We have extended the weighted radial distribution function ideas of Glotzer *et al.* to allow us to probe the spatial distribution of the cage relaxation processes, which are only single coordination polyhedron events, and we have shown that the enhanced diffusive action of the 3-coordinate sites can be linked to their higher ability to promote changes in coordination number and high ionic mobility in their surrounding coordination shells. The increase in excess correlation of particle motion on time scales up to approximately the cage relaxation time suggests that concerted motion of ions is most important while the network remains largely intact.

The analysis of the neighbourhood radial distribution functions allows us to associate the rate of cage decay with the probability of finding the exchanging cage ions in the same region of space. We have also shown that the activation energy for defect formation can be closely associated with the activation energy for the first to second coordination shell transfer. From a consideration of the coordination number dependent neighbourhood radial distribution function we have seen that the enhanced

stability of the 5-coordinate cation in the RIM is due to the closer penetration into the first coordination shell by the 5th neighbour anion.

We have used the comparison of the calculated vibrational densities of states and experimental Raman and Infra-Red spectra as the driving force for changing our BeF₂ PIM potential, and we have shown that we can effectively control the effects of polarisation with our choice of Born-Mayer parameters, and we have thus been able to generate a potential which gives good agreement with both experimental structural and dynamical data in BeF₂.

Simulations of MCl₃ systems have shown that the ideas of a hopping model of diffusion transfer well to networks of very different structures to BeF₂. The fact that the rate of cage decay overestimates the diffusivity in these systems is attributable to the fact that the presence of edge sharing of the coordination polyhedra maintains the network connectivity even when a local cage decays. Calculation of the vibrational densities of states for the symmetric breathing modes of the cation coordination polyhedra with different coordination numbers in LaCl₃ suggests that the experimental data is consistent with there being the range of coordination environments seen in the simulation. Calculation of the conductivities has also shown that we have been able to generate new potentials for these systems which give a better representation of both the experimental structural and dynamical data.

We have seen, then, that the construction of novel correlation functions has allowed us to quantify the relationship between changes in the local structure around an ion and its diffusivity in a network fluid. The transferability of this approach across very different structures suggests that techniques are now available to probe the structure-dynamics link in a range of network and complex-ion forming fluids.

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Appendix A

Atomic Units

Due to the very small nature of the lengths, masses and time steps involved in computer simulations, the use of SI units often leads to loss of accuracy in computer calculations. Atomic units, au, are reduced variables based upon microscopic properties, such as the distance at which the electron orbits the nucleus in the hydrogen atom, and are a set of units much more suited to the length and time scales involved on an atomistic level. The table below gives the conversion factors for the common atomic units used in the simulations, and also less common units found in references.

Unit	Name	Conversion Factor
Mass	m_e	$9.1095 \times 10^{-31} \text{ kg}$
Time		$2.4188 \times 10^{-17} \text{ s}$
Charge	e	$1.6022 \times 10^{-19} \text{ C}$
Energy	Hartree	$4.3597 \times 10^{-18} \text{ J}$
Length	bohr	$0.529177 \times 10^{-10} \text{ m}$
Pressure		$2.942 \times 10^{13} \text{ Pa}$

Table A.1: Conversion factors to convert atomic units in *S.I.* units.

Appendix B

The Ewald summation

The Ewald sum [31] may be used in order to calculate the long range contributions to the potential energy in a system with periodic boundary conditions, where an ion interacts with all of its periodic images. The potential energy can be written as

$$U = \frac{1}{2} \sum_{\mathbf{n}}' \left(\sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\mathbf{r}_{ij} + \mathbf{n}|} Q_i Q_j \right), \quad (\text{B.1})$$

where the sum over $\mathbf{n}$ is the sum over all simple cubic lattice points, $\mathbf{n} = (n_x L, n_y L, n_z L)$ with n_x, n_y, n_z integers. The prime indicates that we omit $i = j$ for $\mathbf{n} = 0$, *i.e.* we do not count the interaction of an ion with itself.

The ideas behind the Ewald summation may be summarised:

- During the simulation the distribution of charges in the cell constitutes the unit cell for a neutral lattice which extends throughout space.
- Each point charge is surrounded by a Gaussian charge distribution of equal magnitude and opposite sign which spreads out radially.
- This extra charge distribution acts as an ionic atmosphere which screens the interaction between neighbouring charges.
- The screened interactions now become short-ranged, and the total screened potential is calculated by summing over all the ions in the central cell and all their images in the real space lattice of image cells.

- A second Gaussian charge distribution of the same sign as the original charge and the same shape as the first Gaussian charge distribution is also added, and this cancelling distribution reduces the overall potential to that due to the original set of charges.
- This means that the Fourier transforms of the cancelling distributions (one for each original charge) are added, and the total transformed back into real space.
- Finally, the interaction of the cancelling distribution with itself must be subtracted from the total.

Therefore, equation B.1 may be re-written in terms of a real space sum plus a reciprocal space sum minus a self term (representing the interaction of the ion with itself) to give

$$\begin{aligned}
U = & \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left(\sum_{|\mathbf{n}|=0}^{\infty} Q_i Q_j \frac{\text{erfc}(\eta|\mathbf{r}_{ij} + \mathbf{n}|)}{|\mathbf{r}_{ij} + \mathbf{n}|} \right. \\
& + \frac{1}{\pi V} \sum_{\mathbf{k} \neq \mathbf{0}} Q_i Q_j \left(\frac{4\pi^2}{k^2} \right) e^{\frac{-k^2}{4\eta^2}} \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) \Bigg) \\
& - \frac{\eta}{\pi^{\frac{1}{2}}} \sum_{i=1}^N Q_i^2 + \left(\frac{2\pi}{3V} \right) \left| \sum_{i=1}^N Q_i \mathbf{r}_i \right|^2, \tag{B.2}
\end{aligned}$$

where V is the volume of the simulation cell, and where $\text{erfc}(\eta r_{ij})$ is the complementary error function,

$$\text{erfc}(\eta r_{ij}) = \frac{2}{\pi^{\frac{1}{2}}} \int_{\eta r_{ij}}^{\infty} e^{-t^2} dt. \tag{B.3}$$

The complementary error function decreases to zero with increasing ηr_{ij} , and so we can vary our choice of η to control the contributions to the real and reciprocal space parts of the sum. If η is chosen to be large enough the only term which contributes to the sum in real space is that with $n = 0$, and so the first term reduces to the normal minimum image convention. The second term is a sum over reciprocal vectors $\mathbf{k} = \frac{2\pi\mathbf{n}}{L^2}$, where L is the simulation cell length, and a large value

of η means that we need to include many terms in the k -space summation because it corresponds to a very sharp screening charge distribution. Hence, the parameter η determines the rate of convergence of the real and reciprocal space parts of the sum; when η is large the former converges quickly, but when η is small the latter converges quickly. An appropriate value must therefore be chosen such that both terms converge reasonably quickly for the most efficient use of computer time. This is generally chosen to be just smaller than half the simulation cell length.

A full discussion of this method may be found in [30].

B.1 The Ewald summation in the PIM

In the RIM, the charge-charge interactions were sufficiently long ranged to require calculation using the Ewald sum method. In the Polarisable Ion Model, in addition to the charge-charge interactions, the charge-dipole and dipole-dipole terms are also sufficiently long-ranged to require treatment via the Ewald summation method.

The method here is the same as in the RIM case, but we replace the $U_{ij}^{\text{RIM}} = \frac{1}{|\mathbf{r}_{ij} + \mathbf{n}|} Q_i Q_j$ term from equation B.1 with the new long range interaction term, U_{ij}^{PIM} , which, from equation 2.14, is given by

$$U_{ij}^{\text{PIM}} = T_{ij} Q_i Q_j + T_{ij}^{\alpha} (Q_j \mu_i^{\alpha} - Q_i \mu_j^{\alpha}) - T_{ij}^{\alpha\beta} \mu_i^{\alpha} \mu_j^{\beta}. \quad (\text{B.4})$$

Appendix C

Construction of the van Hove correlation function

The van Hove correlation function gives a distribution of the motions of the particles around a given particle, and is constructed as follows (from [40]).

The density of particles in the liquid at a point $\mathbf{r}$ and at time t is given by

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t)]. \quad (\text{C.1})$$

We can construct a density-density time correlation function, $G(\mathbf{r}, \mathbf{r}', t)$ given by

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}', t) &= \frac{1}{N} \langle \rho(\mathbf{r}' + \mathbf{r}, t) \rho(\mathbf{r}', 0) \rangle \\ &= \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}_i(0) - \mathbf{r}'] \right\rangle. \end{aligned} \quad (\text{C.2})$$

By integrating over $\mathbf{r}'$ we can eliminate the dependence on the choice of origin, and we obtain the space and time dependent pair distribution function of van Hove,

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \int \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}_i(0) - \mathbf{r}'] d\mathbf{r}' \right\rangle. \quad (\text{C.3})$$

At $t = 0$, if the liquid is homogeneous, we can integrate over $\mathbf{r}'$ to give

$$G(\mathbf{r}, 0) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)] \right\rangle. \quad (\text{C.4})$$

If we separate the terms for $i = j$ and $i \neq j$, we find

$$G(\mathbf{r}, 0) = \delta(\mathbf{r}) + \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^{N'} \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)] \right\rangle \quad (\text{C.5})$$

$$= \delta(\mathbf{r}) + \rho g(\mathbf{r}), \quad (\text{C.6})$$

where the ' means that terms where $i = j$ are not included in the double sum, and where $g(\mathbf{r})$ is the *radial distribution function* (see section 3.2.1). Furthermore, $G(\mathbf{r}, t)$ may be given by

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle, \quad (\text{C.7})$$

or alternatively as

$$G(\mathbf{r}, t) = \frac{\langle \rho(\mathbf{r}, t) \rho(0, 0) \rangle}{\rho}. \quad (\text{C.8})$$

Equation C.7 can be obtained from equation C.3 by noting that the only terms which contribute to the integral are those where $\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t) = \mathbf{0}$, and hence where $\mathbf{r}' = \mathbf{r}_j(t) - \mathbf{r}$.

We can separate $G(\mathbf{r}, t)$ into two parts, the *self*, $G_s(\mathbf{r}, t)$, and *distinct*, $G_d(\mathbf{r}, t)$, parts,

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t), \quad (\text{C.9})$$

where

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)] \right\rangle, \quad (\text{C.10})$$

$$G_d(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1, i \neq j}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)] \right\rangle. \quad (\text{C.11})$$

Thus, $G_s(r, 0) = \delta(\mathbf{r})$ and $G_d(r, 0) = \rho g(\mathbf{r})$. $G(\mathbf{r}, t)$ is the probability of finding a particle i in the region $d\mathbf{r}$ around a point $\mathbf{r}$ at time t given that there was a particle j at the origin at time $t = 0$. The **van Hove self-correlation function**, $G_s(\mathbf{r}, t)$ corresponds to the case $i = j$, and so gives the distribution of particle displacements, $\mathbf{r}_i(t) - \mathbf{r}_i(0)$, in the time t .

As the number of particles in the system is conserved, we have a way of normalising the van Hove correlation functions. Integrating over $\mathbf{r}$ we find, independently of t , that

$$\int G_s(\mathbf{r}, t) d\mathbf{r} = 1, \quad (\text{C.12})$$

$$\int G(\mathbf{r}, t) d\mathbf{r} = N. \quad (\text{C.13})$$

Finally, when the fluid is *isotropic* the functions only depend on the magnitude of the particle separations, $|\mathbf{r}| \approx r$, and hence

$$G_s(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta[\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)] \right\rangle, \quad (\text{C.14})$$

and the quantities considered in this thesis are the probability functions $4\pi r^2 G_s(r, t)$.

Appendix D

Calculation of the vibrational densities of states of polyatomic molecules and ions

The vibrations of polyatomic molecules and ions can be considered to be the superposition of various *normal modes*. The motion of the atoms in a given normal mode is determined by the *symmetry species* of that normal mode, where the symmetry species are themselves determined by the point group of the polyatomic molecule¹. The motion of the ions in the tetrahedral BeF₄ units in BeF₂, however, is not correlated in such a simple way, as there are multiple normal modes and there will be a thermal distribution of the BeF₄ units in the different normal modes.

The motion of the ions may be decomposed into various normal modes which transform as the symmetry operations of the tetrahedron, and then a Fourier transformed velocity autocorrelation function for each of these modes will give the vibrational density of states for that mode. This approach is outlined below.

For the tetrahedral cation, i , at a given time, t , the four bonded anions are identified, $\alpha = 1, 2, 3, 4$. The positions and velocities of these neighbouring anions *relative to the central cation*, $\mathbf{r}_{i\alpha}$ and $\mathbf{v}_{i\alpha}$, are then calculated.

$$\hat{\mathbf{r}}_{i\alpha} = \frac{\mathbf{r}_{i\alpha}}{|\mathbf{r}_{i\alpha}|} = \frac{\mathbf{r}_i - \mathbf{r}_\alpha}{|\mathbf{r}_i - \mathbf{r}_\alpha|}, \quad (\text{D.1})$$

¹For example, in the symmetric stretch of the CH₄ molecules, all the H atoms move away from and then towards the central C atom in a simultaneous, concerted fashion.

where $\hat{\mathbf{r}}_{i\alpha}$ is the unit vector along the bond between cation i and anion α , and then the velocities are decomposed into components parallel to, $v_{i\alpha}^{\parallel}$, and perpendicular to, $\mathbf{v}_{i\alpha}^{\perp}$, the bonds, according to

$$v_{i\alpha}^{\parallel} = \mathbf{v}_{i\alpha} \cdot \hat{\mathbf{r}}_{i\alpha}, \quad (\text{D.2})$$

and

$$\mathbf{v}_{i\alpha}^{\perp} = \mathbf{v}_{i\alpha} - v_{i\alpha}^{\parallel} \hat{\mathbf{r}}_{i\alpha}. \quad (\text{D.3})$$

The symmetry species of the vibrational normal modes of the tetrahedral species are $A_1 + E + T_1 + T_2$. The velocity of the central cation, i , in the A_1 (stretching) mode, $V_i^{A_1}$, is then given by

$$V_i^{A_1} = \sum_{\alpha=1 \rightarrow 4} v_{i\alpha}^{\parallel}. \quad (\text{D.4})$$

The degenerate modes are more complicated, but we still describe them in terms of the relative positions and velocities of the central cation, i , and its neighbouring anions. The two components of the (doubly degenerate) E (bending) mode are given by

$$\begin{aligned} V_i^{E,1} &= (\mathbf{v}_{i1}^{\perp} - \mathbf{v}_{i2}^{\perp}) \cdot (\hat{\mathbf{r}}_{12}) + (\mathbf{v}_{i3}^{\perp} - \mathbf{v}_{i4}^{\perp}) \cdot (\hat{\mathbf{r}}_{34}) \\ V_i^{E,2} &= (\mathbf{v}_{i1}^{\perp} - \mathbf{v}_{i3}^{\perp}) \cdot (\hat{\mathbf{r}}_{13}) + (\mathbf{v}_{i2}^{\perp} - \mathbf{v}_{i4}^{\perp}) \cdot (\hat{\mathbf{r}}_{24}) \\ \therefore V_i^E &= V_i^{E,1} + V_i^{E,2}, \end{aligned} \quad (\text{D.5})$$

where $\hat{\mathbf{r}}_{\alpha\beta} = \frac{\hat{\mathbf{r}}_{i\alpha} - \hat{\mathbf{r}}_{i\beta}}{|\hat{\mathbf{r}}_{i\alpha} - \hat{\mathbf{r}}_{i\beta}|}$, *i.e.* $\hat{\mathbf{r}}_{\alpha\beta}$ is the unit vector along the line joining anions α and β . The three components of the (triply degenerate) T_1 (bending) mode are given by

$$\begin{aligned} V_i^{T_1,1} &= v_{i1}^{\parallel} - \{ \mathbf{v}_{i2}^{\perp} \cdot \hat{\mathbf{r}}_{i1} + \mathbf{v}_{i3}^{\perp} \cdot \hat{\mathbf{r}}_{i1} + \mathbf{v}_{i4}^{\perp} \cdot \hat{\mathbf{r}}_{i1} \} \\ V_i^{T_1,2} &= v_{i2}^{\parallel} - \{ \mathbf{v}_{i3}^{\perp} \cdot \hat{\mathbf{r}}_{i2} + \mathbf{v}_{i4}^{\perp} \cdot \hat{\mathbf{r}}_{i2} + \mathbf{v}_{i1}^{\perp} \cdot \hat{\mathbf{r}}_{i2} \} \\ V_i^{T_1,3} &= v_{i3}^{\parallel} - \{ \mathbf{v}_{i4}^{\perp} \cdot \hat{\mathbf{r}}_{i3} + \mathbf{v}_{i1}^{\perp} \cdot \hat{\mathbf{r}}_{i3} + \mathbf{v}_{i2}^{\perp} \cdot \hat{\mathbf{r}}_{i3} \} \\ \therefore V_i^{T_1} &= V_i^{T_1,1} + V_i^{T_1,2} + V_i^{T_1,3}. \end{aligned} \quad (\text{D.6})$$

Finally, the three components of the (triply degenerate) T_2 (stretching) mode are given by

$$\begin{aligned}
V_i^{T_2,1} &= v_{i1}^{\parallel} - \frac{1}{3} \left\{ v_{i2}^{\parallel} + v_{i3}^{\parallel} + v_{i4}^{\parallel} \right\} \\
V_i^{T_2,2} &= v_{i2}^{\parallel} - \frac{1}{3} \left\{ v_{i3}^{\parallel} + v_{i4}^{\parallel} + v_{i1}^{\parallel} \right\} \\
V_i^{T_2,3} &= v_{i3}^{\parallel} - \frac{1}{3} \left\{ v_{i4}^{\parallel} + v_{i1}^{\parallel} + v_{i2}^{\parallel} \right\} \\
\therefore V_i^{T_2} &= V_i^{T_2,1} + V_i^{T_2,2} + V_i^{T_2,3}.
\end{aligned} \tag{D.7}$$

The density of states for a given symmetry species, $C_{V\Gamma}(\omega)$ with $\Gamma \in A_1, E, T_1, T_2$, are then given by

$$C_{V\Gamma}(\omega) = \Re \left\{ \int_0^\infty dt e^{i\omega t} \frac{1}{N_i} \sum_i \langle V_i^\Gamma(t) V_i^\Gamma(0) \rangle \right\}, \tag{D.8}$$

where the average, $\langle \dots \rangle$, runs over multiple time origins, and the sum is over cations, i .

In the network liquid, the polyhedra are linked through vertex sharing of bridging anions, and hence there will be a considerable degree of correlation of the motion of one tetrahedron with those adjacent to it, and this analysis of the vibrational motion takes no account of this. The mixing of the T_1 and T_2 modes due to the correlated motion leading to symmetry breaking is evidence of this. Neither does this analysis include the motion of the ions in polyhedra which are not tetrahedral, and at high temperatures we have seen that there is a considerable proportion of non-tetrahedral sites present in BeF_2 , particularly in the PIM. However, we may use this analysis to generate densities of states which may be considered to be approximations to those measured experimentally in the Raman and Infra-Red spectra.

Appendix E

The relative cage decay rates for different cages in BeF₂

In the construction of the cage correlation function, as described in chapter 4, we calculate the cage decay rates for different values of the number of cage-ions which must change in order for the cage to be considered as having decayed, c_α , and also for the different subsystems in a multicomponent system.

The tables presented here give the ratios of the cage decay rates for different functions.

$k_{BeF}^{c=a}/k_{BeF}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.77	3.82	13.69	2.12	7.35	3.25
$k_{BeBe}^{c=a}/k_{BeBe}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.83	3.42	10.81	1.87	5.91	3.12
$k_{FBe}^{c=a}/k_{FBe}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
3.00	–	–	–	–	–
$k_{FF}^{c=a}/k_{FF}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.45	1.89	–	1.31	–	–

Table E.1: The ratio of the cage decay rates for different c -values for the four different types of cage in the bi-component system, PIM BeF₂.

$k_{BeF}^{c=a}/k_{BeBe}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.73	0.76	0.69	0.69
$k_{BeF}^{c=a}/k_{FBe}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
2.12	3.58	–	–
$k_{BeF}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.41	0.32	0.20	–
$k_{BeBe}^{c=a}/k_{FBe}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
2.90	4.70	–	–
$k_{BeBe}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.56	0.43	0.29	–
$k_{FBe}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.20	0.09	–	–

Table E.2: The ratio of the cage decay rates for different cages, with constant c -values, for the four different types of cage in the bi-component system, PIM BeF₂.

$k_{BeF}^{c=a}/k_{BeF}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.78	3.55	9.39	1.96	5.12	2.57
$k_{BeBe}^{c=a}/k_{BeBe}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.79	3.55	7.74	1.99	4.32	2.18
$k_{FBe}^{c=a}/k_{FBe}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
3.17	–	–	–	–	–
$k_{FF}^{c=a}/k_{FF}^{c=b}$					
$a = 1, b = 2$	$a = 1, b = 3$	$a = 1, b = 4$	$a = 2, b = 3$	$a = 2, b = 4$	$a = 3, b = 4$
1.22	1.63	–	1.33	–	–

Table E.3: The ratio of the cage decay rates for different c -values for the four different types of cage in the bi-component system, RIM BeF₂.

$k_{BeF}^{c=a}/k_{BeBe}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.81	0.81	0.78	0.64
$k_{BeF}^{c=a}/k_{FBe}^{c=a}$			
$a =$	$a = 2$	$a = 3$	$a = 4$
2.09	3.23	–	–
$k_{BeF}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.63	0.42	0.25	–
$k_{BeBe}^{c=a}/k_{FBe}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
2.60	4.01	–	–
$k_{BeBe}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.77	0.52	0.32	–
$k_{FBe}^{c=a}/k_{FF}^{c=a}$			
$a = 1$	$a = 2$	$a = 3$	$a = 4$
0.31	0.13	–	–

Table E.4: The ratio of the cage decay rates for different cages, with constant c -values, for the four different types of cage in the bi-component system, RIM BeF₂.

Appendix F

Born-Mayer Parameters for simulations in this thesis

The tables presented here give the potential parameters governing the ionic interactions for the simulations presented in this thesis, and also the thermostat parameters for the PIM simulations.

System	m_μ [au]	T_μ [K]	τ_μ [au]	τ [au]
BeF ₂	100	2	5000	5000
ZnCl ₂	30	0.2	20000	20000
LaCl ₃	30	0.27	10000	20000
ScCl ₃	30	0.2	20000	10000
YCl ₃	30	0.2	10000	10000

Table F.1: The thermostat parameters used in the PIM simulations presented in this thesis. m_μ is the fake mass, T_μ is the target dipole thermostat temperature, τ_μ is the dipole thermostat relaxation time, and τ is the ionic thermostat relaxation time.

Parameter	Value in atomic units			
	Potential 1	Potential 2	Potential 4	Potential 4*
Anion polarisability	5.983	5.983	5.983	5.983
Short-range damping, b	2.0	2.0	2.0	2.0
α^{FF}	1.823	2.28	2.05	1.75
B^{FF}	16.62	114.8	43.38	21.36
C_6^{FF}	0.0	0.0	0.0	28.372
C_8^{FF}	0.0	0.0	0.0	538.77
f_6^{FF}	0.0	0.0	0.0	1.8
f_8^{FF}	0.0	0.0	0.0	1.8
α^{BeF}	1.823	2.28	2.28	2.28
B^{BeF}	13.10	37.38	37.38	37.38
C_6^{BeF}	0.0	0.0	0.0	0.0
C_8^{BeF}	0.0	0.0	0.0	0.0
f_6^{BeF}	0.0	0.0	0.0	1.0
f_8^{BeF}	0.0	0.0	0.0	1.0
α^{BeBe}	1.823	2.28	2.28	2.28
B^{BeBe}	8.245	80.89	80.89	10.89
C_6^{BeBe}	0.0	0.0	0.0	0.0
C_8^{BeBe}	0.0	0.0	0.0	0.0
f_6^{BeBe}	0.0	0.0	0.0	1.0
f_8^{BeBe}	0.0	0.0	0.0	1.0

Table F.2: The Born-Mayer parameters in simulations of Beryllium Fluoride: potential 1 is the original PIM potential, and potentials 2 and 4 are adapted to give better agreement of the simulated and experimental diffusive behaviour. Potential 4* is adapted from potential 4 to investigate the effects of the inclusion of dispersion (see chapter 9 for a discussion of the implementation of potentials 2, 4, and 4*).

Parameter	Value in atomic units		
	LaCl ₃	ScCl ₃	YCl ₃
Anion polarisability	20.0	20.0	20.0
Short-range damping, b	1.258	1.39	1.336
α^{ClCl}	1.53	1.53	1.53
B^{ClCl}	100.0	100.0	100.0
C_6^{ClCl}	200.0	320.0	350.0
C_6^{ClCl}	5000.0	6000.0	7000.0
f_6^{ClCl}	1.5	1.5	1.5
f_8^{ClCl}	1.0	1.0	1.0
α^{MCl}	1.8	1.8	1.8
B^{MCl}	450.0	195.0	273.0
C_6^{MCl}	102.2	15.2	45.2
C_8^{MCl}	0.0	100.0	1000.0
f_6^{MCl}	1.5	1.5	1.5
f_8^{MCl}	1.51	1.51	1.51
α^{MM}	37.798	2.798	2.798
B^{MM}	0.0	10.0	15.0
C_6^{MM}	0.0	5.0	15.0
C_8^{MM}	0.0	20.0	200.0
f_6^{MM}	100.90	1.90	1.90
f_8^{MM}	100.8	1.8	1.8

Table F.3: The Born-Mayer parameters used in the simulations of Chlorides presented in this thesis.

Parameter	Value in atomic units		
	LaCl ₃	ScCl ₃	YCl ₃
Anion polarisability	20.0	20.0	20.0
Short-range damping, b	1.258	1.390	1.354
α^{ClCl}	1.260	1.260	1.260
B^{ClCl}	36.434	36.434	36.434
C_6^{ClCl}	200.0	200.0	200.0
C_6^{ClCl}	5000.0	5000.0	5000.0
α^{MCl}	2.439	2.250	2.439
B^{MCl}	10075.457	1011.98	3655.663
C_6^{MCl}	102.220	26.609	47.062
C_8^{MCl}	0.0	0.0	0.0
α^{MM}	37.798	2.798	2.798
B^{MM}	0.0	0.0	0.0
C_6^{MM}	666.66	16.217	666.66
C_8^{MM}	0.0	0.0	0.0

Table F.4: The Born-Mayer parameters used in the simulations of Chlorides presented in previous work [70, 71].

Appendix G

Calculating the conductivity

The ionic diffusion coefficients, D_α , are described by the Einstein relation, equation 3.10, as

$$D_\alpha = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}_{i_\alpha}(t) - \mathbf{r}_{i_\alpha}(0)|^2 \rangle, \quad (\text{G.1})$$

but they may also be described in terms of the velocity auto-correlation functions,

$$D_\alpha = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_{i_\alpha}(t) \cdot \mathbf{v}_{i_\alpha}(0) \rangle dt. \quad (\text{G.2})$$

The usual route for calculating the diffusion coefficients is via equation G.1, as it is difficult to judge when the velocity correlations have die away to zero, whereas the limiting value of the gradient of the mean squared displacement plot is more readily observed.

The ionic conductivity is normally expressed as a similar integral over the charge current correlation function [40]

$$\lambda^K = \frac{\beta e^2}{V} \int_0^\infty J(t) dt, \quad (\text{G.3})$$

where $\beta = 1/kT$, e is the electronic charge, and $J(t)$ is given by

$$\begin{aligned} J(t) &= \sum_{i=1}^N \sum_{j=1}^N Q_i Q_j \langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle \\ &= \sum_{i=1}^N Q_i^2 \langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \\ &\quad + \sum_{j=1}^N \sum_{i \neq j}^N Q_i Q_j \langle \mathbf{v}_i(t) \cdot \mathbf{v}_j(0) \rangle. \end{aligned} \quad (\text{G.4})$$

The conductivity therefore involves the relative motion of the cations and anions. It is much more difficult to calculate than the diffusion coefficient as it is a collective quantity. A frequently used approximation is to neglect all the correlations in the velocities of different ions, which leads to the so-called Nernst-Einstein relationship for the conductivity,

$$\lambda^{NE} = \beta e^2 (\rho_+ Q_+^2 D_+ + \rho_- Q_-^2 D_-), \quad (\text{G.5})$$

where ρ_α is the number density of species α .

It is convenient to re-express the conductivity in the form of a mean-square displacement. This expression is

$$\lambda^K = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle \left| \sum_i Q_i (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \right|^2 \right\rangle, \quad (\text{G.6})$$

as can be shown by substituting into equations G.3 and G.4 the relation

$$\mathbf{r}_i(t) - \mathbf{r}_i(0) = \int_0^t d\tau \mathbf{v}_i(\tau). \quad (\text{G.7})$$

Equation G.6 may also be written in the form

$$\lambda^K = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |Q_+ \Delta_+(t) + Q_- \Delta_-(t)|^2 \rangle, \quad (\text{G.8})$$

where $\Delta_\alpha(t)$ is the *net* displacement of all the ions of species α in time t . This equation makes it clear (bearing in mind the opposite signs of the cation and anion charges) that the conductivity involves the displacement of the set of cations relative to the set of anions. Equation G.8 may be re-written as

$$\lambda^K = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} [Q_+^2 \langle |\Delta_+(t)|^2 \rangle + Q_-^2 \langle |\Delta_-(t)|^2 \rangle + 2Q_+Q_- \langle \Delta_+(t) \cdot \Delta_-(t) \rangle]. \quad (\text{G.9})$$

The Nernst-Einstein approximation can be written in an equivalent form

$$\lambda^{NE} = \frac{\beta e^2}{V} \lim_{t \rightarrow \infty} \frac{1}{6t} [Q_+^2 N_+ \langle |\delta_+(t)|^2 \rangle + Q_-^2 N_- \langle |\delta_-(t)|^2 \rangle], \quad (\text{G.10})$$

where $\delta_\alpha(t)$ is the displacement of a *single* ion of species α (*i.e.* $\Delta_\alpha(t) = \sum_{i \in \alpha} \delta_i(t)$). The difference between the two expressions, G.9 and G.10, is that the second does not include the cross-correlation of the motion of the different species.