

Computer Simulation
of Spectral Properties
of Ionic Systems

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Abstract

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The technique of Molecular Dynamics (MD) computer simulation is coupled with the interrelated theories of light scattering and atomic polarisability to develop and test models for the Raman scattering from alkali halide systems. The primary interest is in the spectrum and intensity of the scattering from melts, but scattering from crystals is also considered.

Two computationally tractable models for the Raman scattering are developed. One, a qualitative model capable of reproducing light scattering lineshapes in NaI, is based on approximations to the quantum-mechanical transition rates for the scattering processes and relies on the *shell model* interionic potentials from lattice dynamics to give insight into the dynamics of ionic dipole moment fluctuations, from which the scattering behaviour is extracted.

The second model is a quantitative one capable of reproducing absolute scattering intensities as well as lineshapes for NaCl melts. This model is based on a detailed parameterisation of the variation of individual ion polarisabilities with the instantaneous local ionic configuration. The model parameters are extracted from the results of electronic structure calculations on ionic systems performed elsewhere. This model has additionally been applied with some success to NaCl crystal systems. The scattering behaviour of LiF has also been considered, although no experimental comparison is available. The primary failure of the second model is its inability to predict the correct depolarisation ratio for the scattering from NaCl; reasons for this are offered.

In developing the models, computer simulation techniques and the light scattering and polarisability theories are reviewed, as are aspects of alkali halide systems, especially interionic potentials suitable for use in simulations. Numerous improvements and extensions to the models are suggested.

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To my parents

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1 Introduction

1.1 Simulation: theory or experiment?

Computer simulation has opened many new doors in all areas of science and engineering: no longer need dense analytical or tedious calculation preclude the understanding of many physical processes. Originally viewed by many as a “last resort” for use only on problems where “real” (i.e. analytical) methods had failed, simulation has proved to be a useful tool for theoretician and experimentalist alike, aiding both in the understanding of their results. Simulation is indeed widely regarded now as a fully fledged third member of the traditional theory–experiment club.

Direct simulation of atomic and molecular systems from knowledge (or a good guess) of the interactions between their constituents is a powerful way to understand many properties of matter in all its phases. The present work uses methods from the large family of computer simulation techniques known as “molecular dynamics” (MD) to study some structural and dynamical properties of solid and molten alkali halides, specifically LiF, NaCl, NaI, and CsCl. The primary goal is an understanding of the mechanisms governing the Raman light scattering from molten salts, but a study of such a complex property necessarily involves consideration of many others, including scattering from crystals, along the way.

1.2 Motivation

There has been ongoing research into molten salts via molecular dynamics

(MD) computer simulation in this department for a number of years. Earlier workers in this field, both in this department and elsewhere, have studied the structure of molten alkali halide salts and such properties as their neutron scattering spectra via MD. Some computational studies have also been made of molten salt mixtures, as well as of alkali–earth halide melts and superionic solids (e.g., SrCl_2). Parallel experimental work at Oxford’s Clarendon Laboratory and elsewhere has provided for a healthy exchange of views between experimentalist and theoretician / simulator.

Many of the “simple” MD calculations have been done. There are well-known methods for extracting, say, the pair distribution functions and related partial structure factors from simulations; these quantities (described in chapter 2) define the structure of a condensed system. There is now a good understanding of the structure and many of the static properties of the simple molten salts, but even the structure remains controversial in the case of CsCl ; this particular problem is discussed in chapter 7. Many dynamical properties, including phonon properties and many neutron scattering–related correlation functions, have also been studied via MD.

The structure factors and associated pair distribution functions have been measured for some of the molten salts via neutron scattering, providing a basis for evaluating the validity and physical reasonableness of the simulation models. Clearly, if the simulations are unable to reproduce the known structure of the systems properly, any attempt to extract meaningful dynamical information from such simulations must be highly suspect. The scattering of virtually all kinds of radiation from alkali halide crystals has been well documented in the experimental literature.

A further property of interest to both theorists and experimentalists is the Raman scattering spectra of the alkali halide melts, and this is the primary subject of this work. Raman scattering from these systems is a sensitive probe

of the short time dynamical processes acting in these systems; the development of computational models capable of reproducing these measurements promises new insight into the microscopic behaviour of these systems. Specifically, the Raman scattering work complements the neutron scattering experiments already performed on some melts: the neutrons, with wavelengths on the order of interionic distances, probe local excitations, while the comparatively long wavelength light scattering probes sample-wide fluctuations and relaxations in dynamical quantities. Additionally, most of the alkali halides are accessible to detailed Raman measurements, while only a few are suitable for neutron studies. Raman scattering from both molten and crystalline salts is intimately related to the theory of ionic polarisability; development of computational models capable of accounting for the Raman scattering necessitates parallel development of models for the variation of ionic polarisability in changing condensed environments.

A variety of mechanisms are possible for the light scattering in ionic systems. It is known that the mechanisms at work in the ionic melts are different from those responsible for the scattering from another class of simple liquid, the inert liquids such as argon. Simulation work promises the opportunity to study several possible light scattering mechanisms for the ionic systems separately and in combination with others, which should help to further the understanding of the differences between the scattering from the two families of simple liquids.

1.3 The hardware

Various computers have been used in the course of this work. The molecular dynamics work has been carried out primarily on the IBM/Fujitsu mainframe complex at the Rutherford Appleton Laboratory, with some simple analysis performed on the Oxford Nuclear Physics Lab HEP VAX 11/780 and the Oxford University Computing Service VAX 11/785. Some lattice dynamics calculations

were also performed with the Daresbury Laboratory central computing facility.

1.4 Organization

The complexity of this topic requires that several fields be reviewed in some detail. Chapters 2 to 4 provide the necessary background information for the development of two models for the Raman scattering from alkali halides in chapters 5 and 6.

Specifically, Chapter 2 introduces and discusses MD techniques in general and the specific methods used in this work.

Chapter 3 presents the theoretical background of the main problem of interest: the determination of the Raman scattering spectra of molten salts.

Chapter 4 discusses the interionic potential models used in the MD studies of both crystalline and molten alkali halides and reviews some established structural and dynamical properties of alkali halide systems. The MD simulations performed during the course of this work are documented here.

Chapter 5 develops a qualitative model for the lineshape and relative polarised and depolarised scattering intensity for the molten salts based on approximations to the second-order quantum-mechanical transition rates for scattering processes. This model makes use of polarisable ion model potentials in simulations to provide information on dipole moment fluctuations in the melts. The model is applied to a system of molten NaI.

Chapter 6 constructs a quantitative model for the light scattering from ionic systems based on a detailed model for the variation of ionic polarisability in condensed environments. The three-part ionic polarisability model accounts for three separate mechanisms for the light scattering from these systems. The model is applied to crystal and melt systems of LiF and NaCl.

Chapter 7 concludes the thesis with a discussion of the results and of several as yet unresolved and/or unstudied related problems. A program for further study of ionic systems by MD is suggested.

The work reported here is successful in reproducing and explaining many important aspects of the Raman scattering from the salts studied.

1.5 Notation

In this thesis, vector quantities are indicated by a bold, slanted font: $\mathbf{a}_i(t)$, $\mathbf{V}(\mathbf{r})$. Scalars are denoted by lighter faced slanted type: $g_{\alpha\beta}(\mathbf{r})$, $v(\mathbf{r})$. Tensor quantities are underscored: $\underline{\mathbf{T}}$. Lower case superscripts or subscripts, as in $\mathbf{a}_i(t)$, usually denote a property for particle i in some set; Greek subscripts, as in p_α^i , usually indicate the cartesian components in directions x , y , or z of the corresponding vector.

References are cited in the abbreviated style [SAN76], where the letters are the first three of the (first) author's name, and the digits are the last two of the year of publication. All references are given at the end of the thesis.

2 Introduction to computational methods

2.1 MD vs. MC?

The computational methods for performing simulation studies of atomic and molecular systems fall into two broad classes: stochastic, or *Monte Carlo* (MC) methods, and dynamical methods such as Molecular Dynamics (MD). MC methods were developed first; stochastic methods in fact far predate the computer age. Fermi apparently invented but did not publish what are now known as MC methods while studying neutron diffusion in the 1930's and early 1940's, performing his calculations on a mechanical adding machine [WOO86]. Earlier, in what might be regarded as a precursor of both MC and MD calculations, Lord Kelvin had his assistant determine 5000 trajectories for particles in collision with the walls of a container from stochastic initial conditions as part of investigations into the kinetic theory in 1901 [KEL01].¹

2.1.1 Monte Carlo methods

MC as it is known today was pioneered by Metropolis *et al.* in the early 1950's [MET49, 53]. Binder [BIN79, 84] has edited a two volume review of current techniques and applications of the MC method; the articles of Levesque *et al.* [LEV79, 84] are particularly relevant to the simulation of particles in condensed phases.

These methods essentially work by making a random walk through the

¹ Wood [WOO86] has just written a history of the development of machine computation techniques (both MC and dynamical) in the 1950's from the perspective of one of the first practitioners of modern MC.

configuration space of a system. MC studies of particle systems typically work like this: given a system of particles with known positions and energies at some “time” t , the energy E of the configuration is determined via some Hamiltonian. A particle i is picked at random and given a random displacement, perhaps in both position and momentum space. (Many variations on the theme are possible here.) The energy E' of the new ‘trial’ configuration is computed, and the MC trial is accepted or rejected on the basis of the difference between E and E' . The Metropolis MC methods always accept the new configuration if $E' < E$, that is, if the new configuration is energetically favourable. Repeated application of this procedure, however, would drive the system to its ground state (or at least to a low-energy metastable state); this is not physical for any finite temperature. Energetically unfavourable configurations where $E' > E$ are therefore accepted or rejected according to their Boltzmann weights at the temperature of interest: a random number x such that $0 \leq x < 1$, is generated, and compared to the value $\exp[(E - E')/k_B T]$. The configuration is accepted if x is less than the weight factor. The system thus samples higher energy states with exponentially decreasing probability, proportional to their occurrence in the system at the desired temperature.

Statistical averages of properties of interest are taken over the accepted configurations in a typical MC study. Since the configurations have already been subjected to a Boltzmann weighting test before being accepted, a simple average over the accepted configurations should give thermodynamically sound values (usually in the canonical ensemble) if the number of configurations is large enough that the thermodynamic limit has been approximated, that is if the random walk through the system’s phase space has been long enough. The “if” here requires careful statistical consideration before results can be considered meaningful.

These methods are particularly useful for studying structural and configura-

tional properties of a system, and for gaining insight into the critical behaviour of systems near to and at points of phase transitions. There is, however, no proper “time” in such simulations; the accept/reject cycles, or *Monte-Carlo steps*, do not preserve the true dynamical behaviour of the system: particles are making random walks rather than following deterministic dynamical trajectories. Although sometimes certain “tricks” can be used, time-dependent, or dynamical studies are difficult via MC techniques.

2.1.2 Molecular dynamics

Molecular dynamics (MD) is conceptually a simple technique for exploring the dynamics of many body systems. It was introduced by Alder and Wainwright in 1957 [ALD57, 59] for studies of the equation of state of hard sphere systems,² and first applied to systems with more realistic “soft” potentials by Rahman in 1964 [RAH64] in a study of liquid argon with a Lennard–Jones (12–6) potential (see chapter 4).

In MD calculations, particles (atoms, ions, or molecules) of the system of interest are placed in a (usually cubic) simulation cell, and some appropriate boundary conditions are applied at the cell walls (section 2.2 below). Given a force law describing the interactions between these particles, or its corresponding potential law,³ and a suitable initial configuration representative of the state point (temperature, pressure, and phase) of interest, the classical equations of motion for the particles in the system are integrated numerically. Since continuous time cannot be modelled directly, a discrete timestep algorithm is

² Hard sphere systems have a potential law $V(r) = \infty$ for $r \leq a$, and $V(r) = 0$ otherwise; this is a model for non-interacting, infinitely rigid spheres which undergo elastic collisions with each other.

³ Pairwise, isotropic, central two-body potentials or force laws are usually employed. Many-body terms have been incorporated through three-body angle dependent and local density dependent terms in some calculations, including static calculations on alkali halides, but they have not yet been used for dynamical simulations of alkali halides. Chapter 4 discusses these and related points.

used to perform the integration. Properties of interest are computed by averaging or correlating over the set of generated configurations; as a trivial example, temperature fluctuations in time can be monitored by computing the total kinetic energy of the system at each timestep from knowledge of the velocities and masses of all particles. Further details of some aspects of MD calculations are given in the rest of this chapter; most topics (all except “algorithms” in section 2.4 and “timesteps” in section 2.5) are also relevant to MC simulations.

2.1.3 Relative merits of MC and MD

MD and MC are complementary, rather than competing, methods for gaining insight into the behaviour of systems at the particle level. A simulator must decide what he wants to learn about a system when choosing which technique to use. Sometimes either will do; both techniques are highly successful in studies of many static, structural, and configurational properties. Both can also assess the magnitude of fluctuations of thermodynamic quantities about their equilibrium values. MC methods can have a slight speed advantage in some such calculations. If time-dependent properties are important, dynamical methods must be used. MD work gives access to actual physical particle trajectories in space and time, thus allowing the determination of time correlation functions and the temporal development of system properties. The timescale of thermodynamic fluctuations can also be recovered from MD calculations.

Some work combines aspects of both methods. Some of the algorithms described below in section 2.4 for performing MD simulations at constant temperatures, for instance, involve a MC-like procedure for reassigning the velocities of particles in a non-dynamical way.

Car and Parrinello [CAR85] have recently developed a technique combining aspects of density functional theory with MD that involves an MD calculation

for ion dynamics and then either an MC- or MD-like calculation to evaluate the electronic structure of the system at each timestep, thus deriving interparticle forces in an *ab initio* manner from the combined ionic and electronic configuration. This technique promises extension of the usefulness of MD techniques to metallic and covalent systems where empirical, two body interparticle potentials are inappropriate.

2.2 Boundary conditions and “infinite systems”

The size of the MD simulation cell is chosen to agree with the experimentally known system density (in solids or melts) and/or lattice parameter (in crystals). One is usually interested in the properties of the bulk, or *infinite*, system, but current computers severely restrict the number of particles that can be included in a simulation to between hundreds and thousands (section 2.7 below), far below what could be reasonably regarded as a macroscopic “chunk” of the system. The simulation cells are therefore small enough that no particle is far from the surface; such a sample cannot be expected to represent adequately the bulk. To overcome surface effects, and to insure that the number of particles is conserved as atoms try to drift into and out of the simulation cell, *periodic boundary conditions* (PBCs) are usually applied to simulation samples so that a relatively small simulation cell can approximate an infinite bulk system [MET53].

The effect of PBCs in two dimensions is illustrated in figure 2.1. The “real” simulation cell (solid lines in the figure) where the calculations are actually performed is replicated in space in all directions. Particles can then interact not only with other particles in the “real” box, but also with *images* of “real” particles in the replicated boxes. The image particles shadow the movements of their real counterparts. As the trajectory of a real particle evolves, it may want to leave the central cell at some point on the cell wall. If it does so, one of its

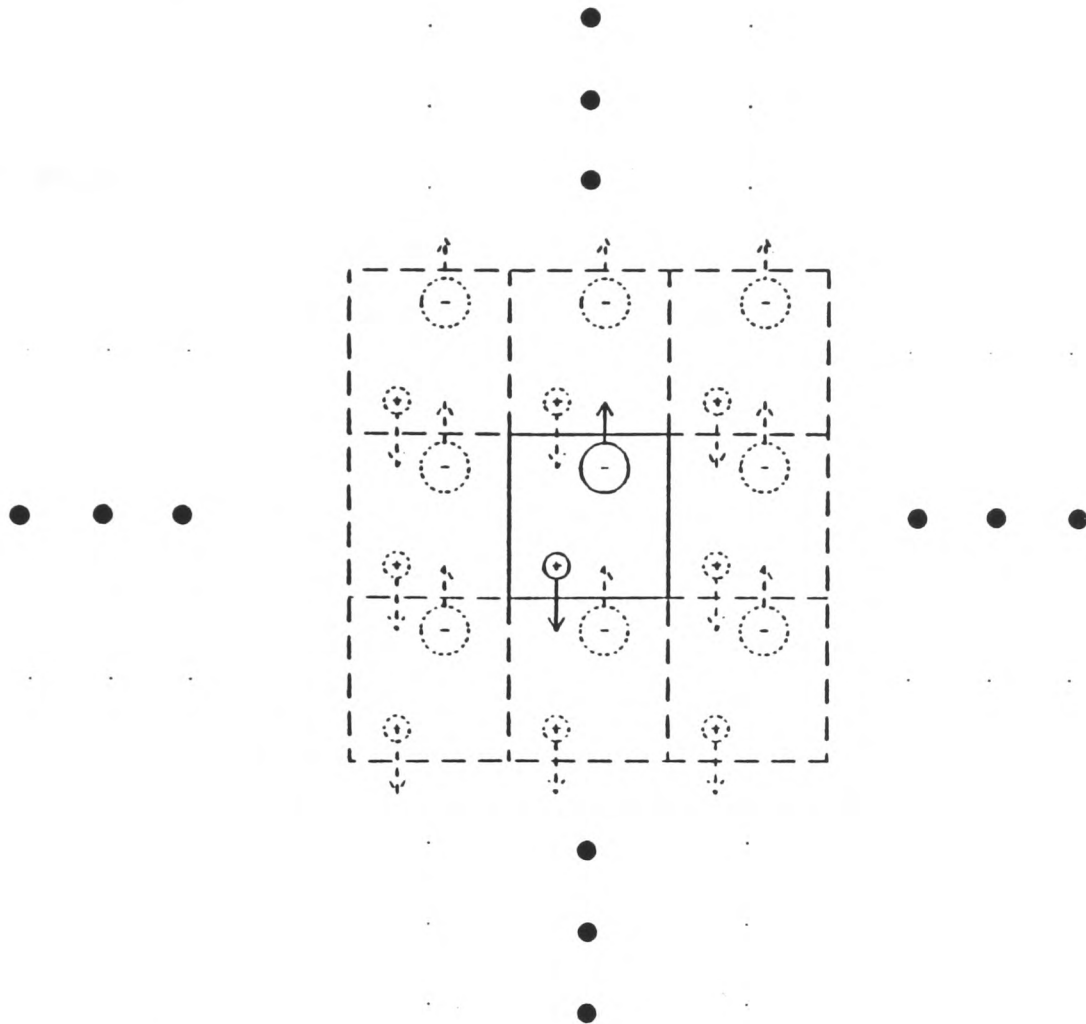


Figure 2.1 : The effect of Periodic Boundary Conditions in two dimensions: as particles move out of the “real” central cell, their images move in to replace them.

image particles in an adjacent cell enters the real cell to take its place, as in the figure. A bonus of PBCs is that particle momentum conservation is maintained automatically as particles enter and exit the central cell, as the images have the same momenta as their real counterparts. Strict (as opposed to time-average) particle number conservation is another benefit of the method.

If long-range forces (e.g., Coulomb forces) are present in the system, when considering the force on particle i due to particle j , one must in principle take account of *all* periodic images of j out to infinity. Indeed the closest approach (and thus the most important short-range interaction) may be between an image particle of j and i , as in figure 2.1, where the central cation is closer to the lower image of the anion than to the anion itself. If only short-range forces are important, a single conceptual “layer” of periodic cells around the main cell may suffice.

Effects arising from the computationally enforced unnatural periodicity of

PBCs can be important in some studies, e.g., of dielectric properties [DEL80a, b; 81]. In studies of liquids, for example, the PBCs effectively define a “crystal” with a large (N -particle) and constantly changing cubic unit cell. PBCs restrict the minimum wavevector that can be reliably studied to $\frac{2}{a}$ where a^3 is the volume of the system box, since $\frac{a}{2}$ is the maximum length in the simulation that can be considered to be free of the artificial periodicity. Simulations of 216 alkali halide ions have box sizes of about $20\text{\AA}$, so the minimum wavenumbers that can be studied are about $0.1\text{\AA}^{-1}$ [DIX83a]. This limitation on q does not render MD useless; in fact, it allows study of q -dependent properties such as neutron scattering in ranges consistent with those available to experimentalists [MCG84]. Particle dynamics in the molten salt systems do not seem to be affected by the wavevector restriction; chapter 4 shows that vibrational properties of crystals, for instance, can be reproduced quite well by these MD methods. Whether any constructive use of this artificial “superlattice” can be made remains to be seen.

Certain types of simulations require use of alternate types of boundary conditions. Studies of surfaces, for instance, would be ruined by application of PBCs on all sides; the “infinite” bulk system would be present again. So on the surface of interest, it is common to apply a *reflecting boundary*, where if a particle attempts to leave it is reflected back into the cell, or an *absorbing boundary*, which acts as a particle sink (a useful model for surface evaporation). Both of these types of boundary conditions introduce problems in maintaining momentum conservation, and in the absorbing case, particle number conservation, but these can be overcome.

2.3 Thermodynamics

Simulations performed in this work correspond to the microcanonical, or NVE , thermodynamic ensemble, as the number of particles N and the sys-

tem volume V are strictly conserved, and the time-average total energy $\langle E \rangle$ is conserved to high accuracy (1 part in 10^5 or 10^6 is typical). The kinetic and potential energies are not conserved separately in this ensemble, so the temperature and pressure, for example, fluctuate as the simulation progresses. The fluctuations are N -dependent and can be quite dramatic in small systems. The total (kinetic plus potential) energy remains quite stable, however, as the separate fluctuations in the kinetic and potential parts of the energy very nearly cancel (see figure 2.2 later in this chapter). As the current interest is in the properties of the bulk liquid and not the solid-liquid phase transition *per se* in this work, good results are obtained by targetting the simulations for a temperature about 50°K above melting. This corresponds with experimental practice in, for example, Raman and neutron scattering work [MIT83, MCG84].

It is possible to perform simulations in other ensembles, such as with constant temperature, or pressure, or indeed both. Close temperature and pressure control is needed in studies of properties very close to phase transitions, for instance. A review of all of the methods described briefly below and their uses, along with many variants on the standard methods, has recently appeared [AND85].

Constant temperature can be maintained in a number of ways. Andersen developed a method whereby temperature can be controlled with occasional “stochastic collisions” [AND80] between the simulation particles and an imagined “heat bath” surrounding them. This technique introduces a Monte Carlo flavour into the MD simulation, and causes some concern over the particle dynamics [AND85]. Nosé has developed a method of controlling the temperature through introduction of an additional degree of freedom with an associated “mass” that is coupled to the “real” atomic degrees of freedom [NOS84]. The equations of motion can also be constrained in various ways to give conserved temperature [HOO82, EVA83a, HAI83]. Both of these techniques have the ad-

vantage of producing dynamical trajectories [AND85]. *Ad hoc* velocity rescaling [WOO71b] can be used to control temperature, and is used in the equilibration phase in this work; this method is thermodynamically dubious, but is acceptable in the equilibration phase prior to data collection, and in the limit of small timesteps is equivalent to some of the constrained dynamics methods above [AND85].

Constant pressure can be maintained in similar ways. In a technique also due to Andersen [AND80], the size of the simulation cell fluctuates in response to internal dynamical fluctuations. The cell size has a dynamical “mass” associated with it, and the cell size then can be treated just like any other dynamical variable in the simulation: it has a trajectory that, in this case, corresponds to changes in the system volume. This technique complicates the accumulation of position- or wavevector-dependent properties, as all lengths in the problem are being constantly renormalised.

The constant temperature and pressure methods described above can be combined in the same simulation [AND80, EVA83b]; one further extension due to Parrinello and Rahman [PAR80] allows not only the size but also the shape of the simulation cell to vary in response to internal fluctuations. Here, the three box lengths a , b , and c , as well as the box angles α , β , and γ are all treated as dynamical variables with associated “masses.” External stress can be applied to a system with this method. This method has been very successful in investigating the occurrence and in some cases possible mechanisms of phase transitions in, for instance, metals under compressive and tensile loads [PAR81].

2.4 Algorithms

The basic problem in MD is to integrate the Newtonian equations of motion for the position $\mathbf{r}_i(t)$ of particle i in a system with a pairwise additive, central

interparticle potential law $\phi(r)$:

$$m_i \ddot{\mathbf{r}}_i(t) = - \sum_{j \neq i}^N \nabla \phi_{ij}(\mathbf{r}_{ij}), \quad (2.1)$$

where $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between particles i and j . There are many algorithms in the literature for integrating the equations of motion in a MD simulation; perhaps the most widely known is the “leap-frog” due to Verlet [VER67]. A different form due to Beeman [SCH73, BEE76] which has been shown to give better energy conservation is used in this work. The relations to determine the state of the system (e.g., the positions $\mathbf{r}_i$, velocities $\mathbf{v}_i$, and accelerations $\mathbf{a}_i$ for particles i) at timestep $(t + \Delta t)$ given the state at times t and $(t - \Delta t)$ are found in the Beeman scheme (following the derivation in Sangster and Dixon [SAN76]) by constructing the Taylor series for the particle position at time $t + \Delta t$:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + (1/2)\mathbf{a}_i(t)(\Delta t)^2 + (1/6)\mathbf{a}'_i(t)(\Delta t)^3 + \dots \quad (2.2)$$

where $\mathbf{a}'_i(t)$ is the time derivative of the acceleration. The approximation

$$\mathbf{a}'_i(t) \approx (\mathbf{a}_i(t) - \mathbf{a}_i(t - \Delta t))/\Delta t \quad (2.3)$$

results in the relation

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + (1/6)[4\mathbf{a}_i(t) - \mathbf{a}_i(t - \Delta t)](\Delta t)^2 \quad (2.4)$$

Given the new positions $\mathbf{r}_i(t + \Delta t)$, the equations of motion (2.1) show that the new accelerations can be calculated as a function only of the new configuration and the potential law:

$$\mathbf{a}_i(t + \Delta t) = F\left(\{\phi_{ij}(\mathbf{r}_{ij}(t + \Delta t))\}\right) \quad (2.5)$$

The Verlet and Beeman algorithms have been shown [SAN76, BER86] to be equivalent to this point, although at first glance the relations in the two schemes

look different. They are equivalent in the sense that they will give the same particle trajectories, and therefore the same development of particle potential energy in time. The Verlet relation for the particle position is usually written as

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \mathbf{a}_i(t)(\Delta t)^2 \quad (2.6)$$

where it is seen that the position calculation at $(t + \Delta t)$ does not depend on $\mathbf{v}(t)$. The Verlet scheme then determines the velocity at t using the knowledge of the new positions at $(t + \Delta t)$:

$$\mathbf{v}_i(t) = \frac{1}{2} [\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)] / \Delta t \quad (2.7)$$

This evaluation of $\mathbf{v}_i(t)$ after that of $\mathbf{r}_i(t + \Delta t)$ accounts for the popular name of the Verlet algorithm: the “leap frog.”

The Beeman method uses the “trick” of evaluating the velocity at the half timestep:

$$\mathbf{v}_i(t + \frac{1}{2}\Delta t) \approx [\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)] / \Delta t \quad (2.8)$$

which, on substituting eq. (2.4) for both $\mathbf{r}_i(t)$ and $\mathbf{r}_i(t + \Delta t)$ results in

$$\mathbf{v}_i(t + \frac{1}{2}\Delta t) \approx \mathbf{v}_i(t) + (1/6) [4\mathbf{a}_i(t) - \mathbf{a}_i(t - \Delta t)] \Delta t \quad (2.9)$$

By adding Δt to all terms in the above,

$$\mathbf{v}_i(t + \frac{3}{2}\Delta t) \approx \mathbf{v}_i(t + \Delta t) + (1/6) [4\mathbf{a}_i(t + \Delta t) - \mathbf{a}_i(t)] \Delta t \quad (2.10)$$

Approximating $\mathbf{a}_i(t + \Delta t)$ with $[\mathbf{v}_i(t + \frac{3}{2}\Delta t) - \mathbf{v}_i(t + \frac{1}{2}\Delta t)] / \Delta t$, the desired relation for the velocity at time $(t + \Delta t)$ is found:

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + (1/6) [2\mathbf{a}_i(t + \Delta t) + 5\mathbf{a}_i(t) - \mathbf{a}_i(t - \Delta t)] \Delta t \quad (2.11)$$

The two equations (2.4) and (2.11) comprise the usual Beeman algorithm; they are easily programmed to perform simulations. Note that the accelerations

at $(t + \Delta t)$ are determined from knowledge of only the positions at the new time and the potential law for the system; the new velocities are computed as a function only of the new positions and accelerations. The Beeman method's advantage over the Verlet scheme is that its velocity computation is more accurate, thus energy conservation in simulations with the Beeman method is improved [SAN76].

More complicated (and more accurate) integration algorithms can be derived by considering the relations above as first guesses or *predictions* of the values of the state variables at $(t + \Delta t)$; relations to give the first and indeed n^{th} order *corrections* to these initial predictions have been derived. Such *predictor-corrector schemes* (some are known as Gear methods) are discussed by Beeman [BEE76] and Berendsen [BER86]. These methods are sometimes needed when, for instance, a potential has a very hard repulsive core; in such simulations, trajectories must be computed more accurately to maintain adequate energy conservation. Many other standard mathematical methods for integrating the equations of motion, such as the Runge-Kutta methods, are unsuitable for machine implementation, since they involve multiple particle force evaluations per iteration, and thus excessively large amounts of computer time [SAN76].

The elaborate schemes beyond the Beeman method have been found to be unnecessary in this work; these systems are well enough behaved and the potentials sufficiently inexact that the more elaborate correction schemes for the particle trajectories would add nothing significant to the understanding of these systems. Indeed the extra computing time required to implement the predictor/corrector schemes would adversely affect the ability to simulate adequately large systems for long enough to form useful averages. Berendsen has recently [BER86] pointed out a minor change in the velocity evaluation within the Beeman scheme that reduces the noise in the velocity calculation slightly, and it should be considered for future work. This change has no impact on the particle

trajectories, however.

2.5 Timesteps

The choice of the timestep Δt is crucial to the success of MD simulations. Too long a timestep will result in errors in the integration procedures, thus giving non-physical trajectories for the ions and poor energy conservation for the system as a whole. Unnecessarily short timesteps will reduce the amount of “real time” ($\Delta t \times \text{\#timesteps}$) modelled in the simulation for a fixed amount of computer time and reduce the phase space explored by the simulation, thereby lowering the statistical accuracy of the values of properties determined. The timestep must be short compared with any dynamical process of the system such as lattice vibrations. In alkali halide crystals lattice frequencies of up to about 8 THz are important, and dynamical processes on a similar timescale are expected in melts. Timesteps on the order of 5×10^{-15} sec are about an order of magnitude faster than any vibrations and have been shown to give good energy conservation for runs of many thousands of timesteps [SAN76] and to reproduce faithfully the lattice vibrations of the alkali halide crystals when used with realistic potentials (see chapter 4).

Figure 2.2 shows typical simulation results for energy conservation, indicating the choice of the Beeman algorithm and timesteps of the order of 5×10^{-15} sec is suitable here. Though the kinetic and potential energies fluctuate, their sum remains very nearly constant, and there is no significant drift in the average total energy $\langle E \rangle$ of the system after many thousands of timesteps (5000 here).

2.6 Long-range forces

The infinite range of the Coulomb force is the major complication for sim-

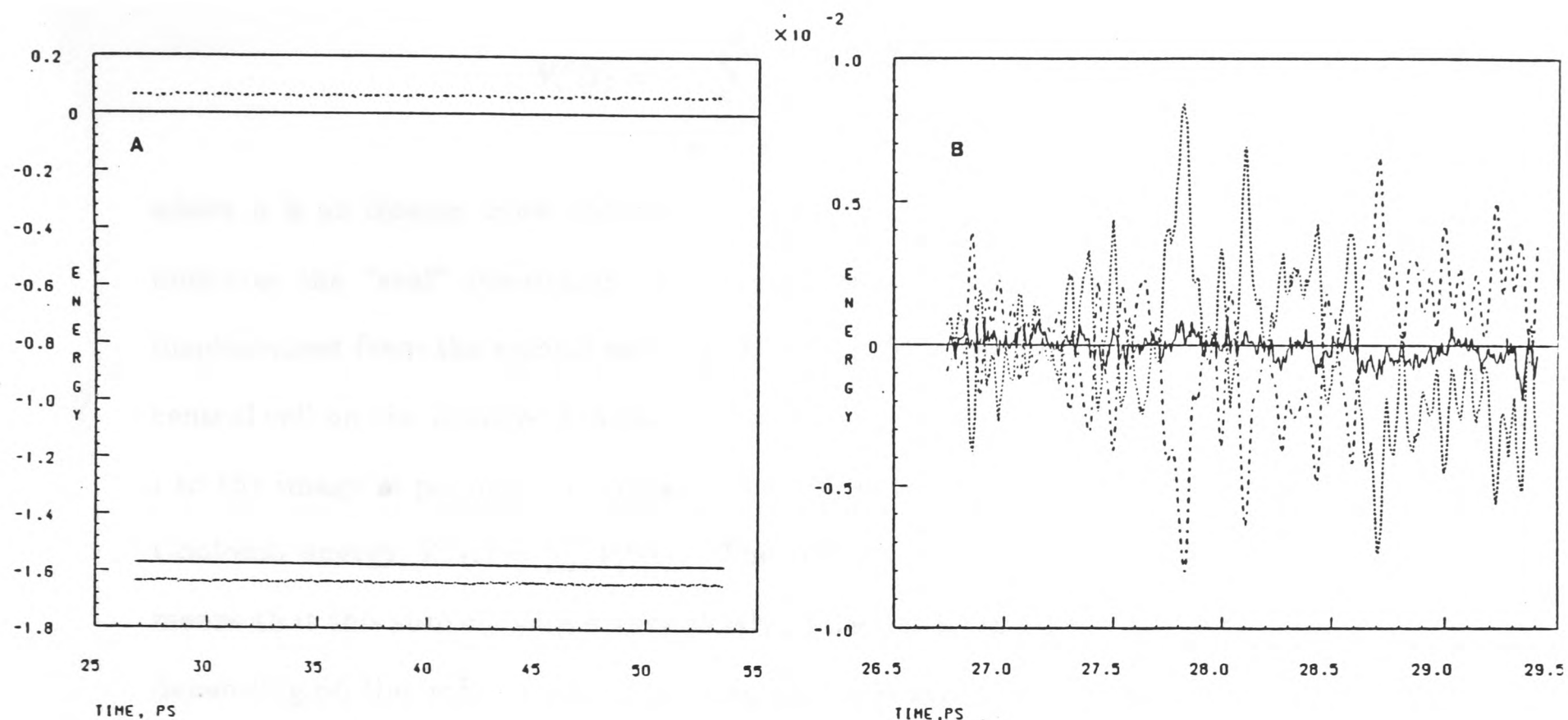


Figure 2.2 : Energy conservation in a typical MD simulation. a) The total energy (solid line), and its kinetic (dashed) and potential (dotted) components remain stable for 5000 timesteps ($\Delta t = 5.384 \times 10^{-15}$ sec) in the middle of a simulation of 216 ions of molten NaI at 973°K. b) A close-up of the fluctuations in the total energy (solid line) and its kinetic (dashed) and potential (dotted) components about their respective mean values for the first tenth of a). The kinetic and potential energy fluctuations very nearly cancel, leaving the total energy very stable.

ulations of alkali halides over, say, argon. The presence of long-range forces makes all possible pairwise interactions between particles in a system significant, thus vastly increasing the complexity of simulations. A simulation of any charged system will spend almost all of its time ($> 90\%$ in this work) evaluating long-range forces, so clearly an efficient way of doing so is crucial.

Given the periodic boundary conditions needed for modelling the bulk with a small system, for a simulation sample with N ions in the “real” simulation cell the total Coulomb energy of particle i due to its interactions with all particles

j and with all images of all particles j can be written as the infinite sum

$$V_i^c(t) = \sum_{\substack{j=1 \\ j \neq i \text{ if } \mathbf{n}=\mathbf{o}}}^N \sum_{\mathbf{n}} \frac{Z_i Z_j}{r_{i,j\mathbf{n}}} \quad (2.12)$$

where $\mathbf{n}$ is an integer triple identifying a particular image cell: $\mathbf{n} = \mathbf{o} = (0, 0, 0)$ indicates the “real” simulation cell, and all other cells are identified by their displacement from the central cell, i.e., $\mathbf{n} = (1, 0, 0)$ is the image cell next to the central cell on the positive x -axis. $r_{i,j\mathbf{n}} = |\mathbf{r}_i - \mathbf{r}_{j\mathbf{n}}|$ is the distance from particle i to the image of particle j in image cell $\mathbf{n}$. Z_i is the charge on ion i . The total Coulomb energy $V^c(t) = \sum_i V_i^c(t)$. The infinite range of the Coulomb force means that this sum converges very slowly; indeed it is conditionally convergent, depending on the order in which the sum over $\mathbf{n}$ is taken, or equivalently, on the shape of the infinitely remote boundary [DEL80a, HAN86].

The Coulomb energy cannot be approximated well by restricting the summation to the “real” cell, nor by truncating the summation after a reasonable number of “layers” of image cells. Quite distant image particles make a measurable difference to the Coulomb energy. Early attempts to use a truncated Coulomb potential in alkali halide simulations [WOO71a] resulted in disasterously low Coulomb energies. On the other hand inclusion of even one layer of image cells in a direct summation of the series above would increase the number of pairwise interactions considered by a factor of 26, a prohibitive increase in computational complexity. Clearly, alternatives to “brute-force” real space summation must be sought.

The summation technique of Ewald [EWA21] (explained at length by Born and Huang [BOR54] and Ziman [ZIM72]; its computer implementation is described by Sangster and Dixon [SAN76] and Hansen [HAN86]), developed for doing lattice sums, provides one relatively expensive but highly accurate way of performing this infinite, slowly converging real-space sum by recasting it as two converging sums, one in real space and one in reciprocal space. The result

is that one can write the Coulomb energy for a single particle i (2.12) in three parts:

$$V_i^c = V_{i1}^c + V_{i2}^c + V_{i3}^c \quad (2.13)$$

with

$$V_{i1}^c = \sum_{\substack{j=1 \\ j \neq i \text{ if } \mathbf{n}=0}}^N \sum_{\mathbf{n}} Z_i Z_j \frac{\text{erfc}(\alpha r_{i,j\mathbf{n}})}{r_{i,j\mathbf{n}}} \quad (2.14)$$

$$V_{i2}^c = -Z_i^2 \alpha \sqrt{\pi} \quad (2.15)$$

and

$$V_{i3}^c = \frac{1}{\pi L} \sum_{j=1}^N \sum_{\mathbf{h} \neq 0} Z_i Z_j \frac{\exp\left(-\frac{\pi^2 |\mathbf{h}|^2}{\alpha^2 L^2}\right)}{|\mathbf{h}|^2} \cos\left(\frac{2\pi}{L} \mathbf{h} \cdot \mathbf{r}_{ij}\right) \quad (2.16)$$

where $\mathbf{h}$ is a reciprocal lattice vector and L is the cell size. This form is obtained by recognizing the identity

$$\frac{2}{\sqrt{\pi}} \int_0^\infty \exp(-r_{ij}^2 x^2) dx = \frac{1}{r_{ij}}$$

and breaking the integral into two parts: one from 0 to α (yielding the erfc term in V_1^c (2.14)), and one from α to ∞ , which is then Fourier transformed to give V_3^c (2.16). The term V_2^c (2.15) is just the $\mathbf{h} = 0$ term of V_3^c . α is an arbitrary parameter: the total energy V_i^c is independent of its value, but the convergence rates of the two sums here depend quite strongly on α . A careful choice of α can yield two very rapidly converging sums, one in real space over $\mathbf{n}$ and one in reciprocal space over $\mathbf{h}$ [SAN76]. Woodcock and Singer [WOO71a] interpret the various sums in the Ewald expansion in terms of auxiliary, self-cancelling Gaussian charge distributions which improve the convergence rate of the sums dramatically.

Note that since with periodic boundary conditions in force, a liquid configuration at any specific timestep is actually a “crystal” with a unit cell encompassing the entire “real” simulation cell, this derivation for infinite crystals is

also valid for evaluating the Coulomb energy in melts. The degree to which this is really true is one measure of how well PBCs model the bulk.

In this work, values of the Coulomb force calculated via the Ewald method as a function of interparticle distance have been tabulated on a dense grid. Forces at a specific position are interpolated from this stored grid at run time and not determined from the Ewald series as the simulation progresses.⁴

Despite the early failures [WOO71a], approximate effective field and potential cutoff techniques for handling the Coulomb forces have been developed that are faster than Ewald summation but less accurate. Andrea *et al.* [AND83] have used spherically truncated potentials in simulations of water. The recent work of Clarke *et al.* [CLA86] neglects long-range forces completely, replacing the full potential with a short-range effective potential. They suggest that charge cancellation negates the effect of Coulomb forces at long range. Simulations employing these potentials have demonstrated that long-range charge ordering in alkali halide melts is possible even with short-range potentials. These simulations have achieved good qualitative agreement on the melt structure and thermodynamic quantities with work employing full treatment of the Coulomb forces, but at the cost of adjusting a free parameter. It is not yet clear how well these potentials will work for dynamical properties, but the advantage of being able to simulate far larger samples is significant (see next section).

2.7 System sizes

In materials with only short-range forces (such as argon), fairly large systems (10^3 – 10^4 particles) can be simulated routinely, since each particle interacts

⁴ This procedure is efficient for scalar machines, but when using a vector processor such as a Cray or Cyber205, it is actually more efficient to compute the Ewald series on the fly, since a table look-up is not a vectorisable operation [IMP85, HAN86]. The sum for V_3^c can be cast as two sums over N rather than one sum over N^2 [SAN76, HAN86].

significantly only with those particles lying inside a sphere of a few interatomic spacings' radius, centred on the particle of interest. Thus the complexity of the simulation grows only linearly with the size of the sample. This general rule is true of MC as well as MD, and maximum system sizes for the two methods are similar.⁵

Another advantage of simulations of argon is that a relatively simple potential law — the Lennard–Jones potential (see chapter 4) — is available that nevertheless gives very good results. This potential has only polynomial terms in the interparticle distances; no computationally expensive exponential or trigonometric terms, or square roots, enter into it. Simulations of short-range force solids have an additional advantage in that the neighbours of a given particle are fixed (in the absence of diffusion), so that a neighbour list can be computed once at the beginning of a simulation to determine with which particles a given particle can be expected to interact. With liquids, or indeed with superionic solids, such a neighbour list scheme can still be used to reduce the number of pairwise interactions considered for each particle at each timestep, but the neighbour lists have to be updated frequently as particles move around in the system.

The long-range Coulomb forces present in ionic systems cause severe complications as now all pairwise interactions are significant, i.e., no cutoff sphere can be used, at least in this work where very accurate evaluation of the long range forces is needed to reproduce vibrational properties of the systems. The complexity of the simulation thus grows as N^2 in the number of particles. The situation is actually worse than this, as all periodic images of each particle out to infinity must be considered to account properly for the Coulomb energy of an ionic system, but use of a scheme such as the Ewald method described above

⁵ The current record for largest MD simulation samples is apparently held by Abraham at IBM, who recently studied two-dimensional melting on quasi-two-dimensional samples of up to 161,604 krypton atoms on a graphite substrate [ABR85, ABR86].

limits the complexity to N^2 .

For crystals of binary systems such as the alkali halides, system sizes of $(2n)^3$ particles (n an integer) must be used if the periodic simulation cells are to fill space properly. The same sizes are generally used for simulations of melts to avoid unphysical packing or grouping of particles due to the PBCs. The complexity of the Ewald method has limited the system size that can be simulated with available computers to 216 ions for binary salts, although the next largest size system (512 ions) is feasible with the larger mainframe computers available today [CLA86]. A properly vectorised code for ionic simulations running on a vector processor could allow still larger samples to be studied, but such resources were not available for this work. Simulations with as few as 64 ions have been useful in this work; the periodic boundary conditions allow even such small samples to give very good agreement with experiment on such fundamental properties as the structure ($g_{\alpha\beta}(r)$ – see section 2.9). In this work, exploratory calculations have always been performed first on 64-ion samples, and then repeated for 216-ion samples when satisfactory results have been obtained with the smaller systems.

The approximate techniques for evaluating Coulomb forces described in the previous section have permitted ionic systems as large as 4000 ions to be studied [CLA86], but with the subsequent loss of precision in the calculation of some properties, and unknown (as yet) effect on the determination of dynamical properties.

2.8 Initialization

To begin a simulation of a solid, ions are usually placed on or slightly and randomly displaced from lattice sites, and they are assigned random initial velocities from a distribution that corresponds to the desired temperature of the

simulated system, subject to the constraint that the total momentum $P = \sum_i p_i$ of the system is zero. As the initial configuration is presumably non-physical, typically several hundred or thousand timesteps must be allowed for the system to come into proper equilibrium, and thus correspond to the desired thermodynamic state.

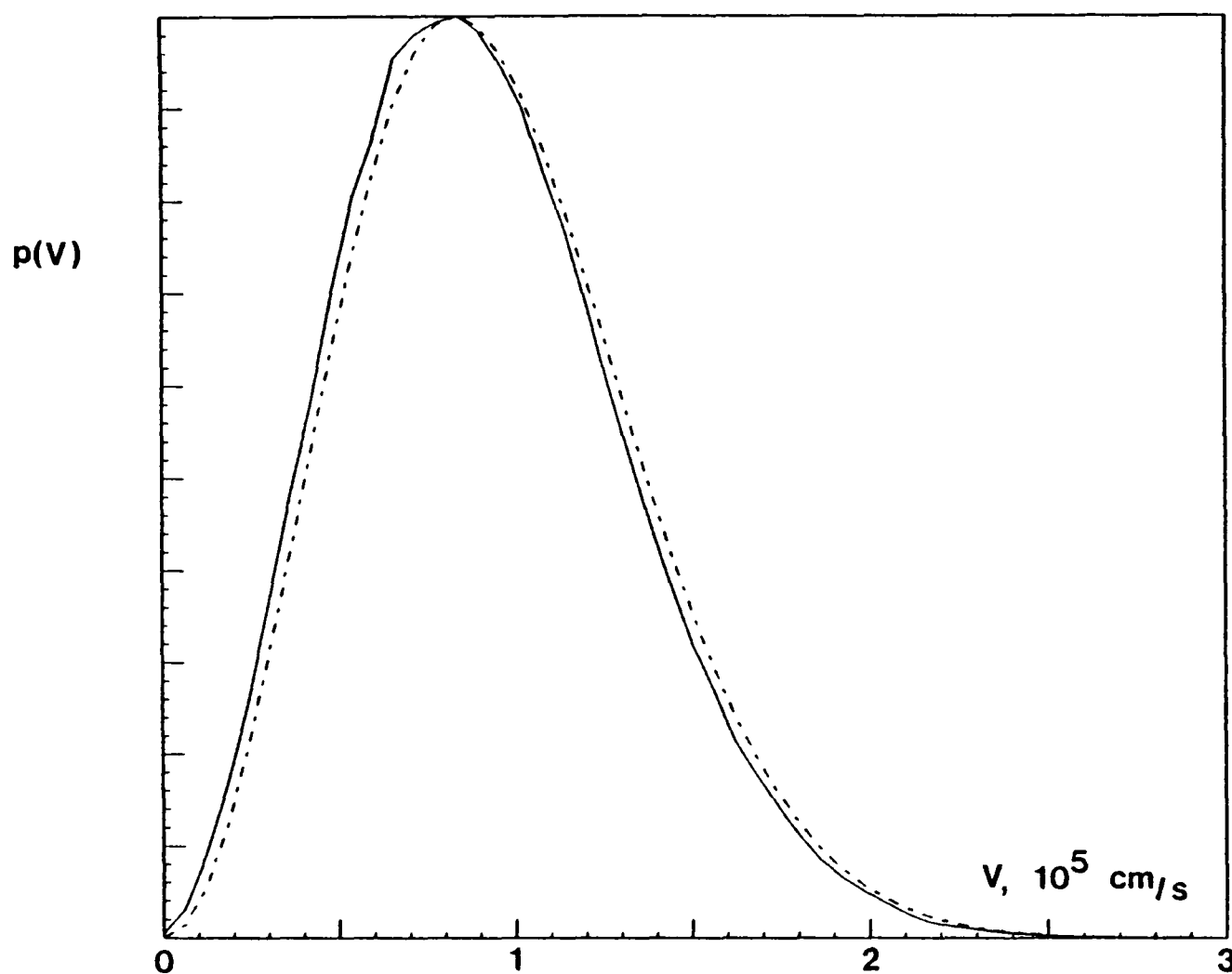


Figure 2.3 : Distribution of cation velocities after equilibration (solid curve) compared with expected Maxwellian distribution at the target temperature (dashed curve) for a typical MD run. The data was taken from timesteps 5001 – 10000 of a 216 ion simulation of molten NaI at 973°K.

Signs that equilibrium has been reached include the system's time averaged temperature remaining stable, and the velocity distribution of the particles approaching a Maxwellian appropriate to the desired temperature. When equilibrium is reached, equipartition should apply, *i.e.*, vibrational modes should be populated according to their Boltzmann weights for the temperature of the system. The density of phonon modes, as calculated in chapter 4 from ion displacement- or velocity-autocorrelation functions, confirms that reasonable

vibrational properties are present at equilibrium. Figure 2.3 shows an example of a typical velocity distribution for cations after equilibration, compared with the expected Maxwellian distribution. The very slight shift from the Maxwellian indicates that the simulation is probably a few degrees cooler than the target temperature, but the shape of the curves indicates that good energy distribution has been achieved.

During the equilibration phase, the velocities of the particles are rescaled frequently (while maintaining momentum conservation) to guide the system to the desired temperature. This rescaling interferes with the dynamics of the system, however, so properties of interest must be determined solely from configurations produced after the equilibration phase, which in turn must last well beyond the last velocity rescaling operation to allow any transients so induced to die out.

Solids and liquids each pose special problems in the equilibration phase. Here follow two examples of the types of problems that can plague MD simulations; both appeared in the early stages of this work.

Especially at low temperatures, say 100°K, simulated solids are subject to poor distribution of energy among modes. If one ion gets hot compared with the system as a whole, it tends to stay hot and not come into equilibrium with the system. Hot ions were an occasional artifact of the procedure formerly used to ensure momentum conservation in the initial configuration: for a system with n cations, say, the velocity of the n^{th} cation was determined from the others as

$$v_n^\alpha = - \sum_{i=1}^{n-1} v_i^\alpha \quad (2.17)$$

for all directions α . The first $(n - 1)$ velocities were drawn independently from a distribution appropriate to the desired temperature. Cations and anions were initialised separately to account for their different masses. Figure 2.4 shows a time-dependent histogram of ion velocities for a low-temperature crystal simu-

lation of NaI; notice how a single ion is locked in an unphysical high temperature state, thereby significantly distorting thermal averages for the system. In liquids (for which the programs were originally written) this was not a problem as the ions were active enough to exchange energy fairly readily amongst themselves, so any “hot” ions soon returned to the desired temperature range. This problem was corrected by adopting a new three-step prescription for assigning the initial velocities: again assuming n cations,

1. All $3n$ velocity components are initialized independently from an appropriate distribution.
2. The excess momentum

$$P^\alpha = \sum_{i=1}^n p_i^\alpha$$

is computed in each direction α , and each velocity component is then corrected by an amount $p_i^\alpha = p_i^\alpha - \frac{1}{n}P^\alpha$. This gives a net momentum of zero.

3. The new average temperature of the cations is computed, and the velocities are corrected by a factor to return the system to the desired average temperature. Scaling by a factor does not destroy the momentum conservation. The procedure is then repeated for the anions.

The problems in liquid simulations are different. Sometimes it is difficult to get a liquid simulation to “melt:” especially when the ions have started on lattice sites they can get trapped in a metastable, unphysical crystalline or superionic state at temperatures far above the melting point. This condition is readily detectable from examination of the ionic mean-squared displacement function. Figure 2.5 shows a case of metastable “superionic” NaI, where the cations have melted but the anions are still trapped on their lattice sites at a temperature well above the melting point. The easiest way to avoid this problem is to initialize new melt simulations from well-aged configurations of earlier melt simulations, but this just begs the question. To initiate a completely new melt simulation,

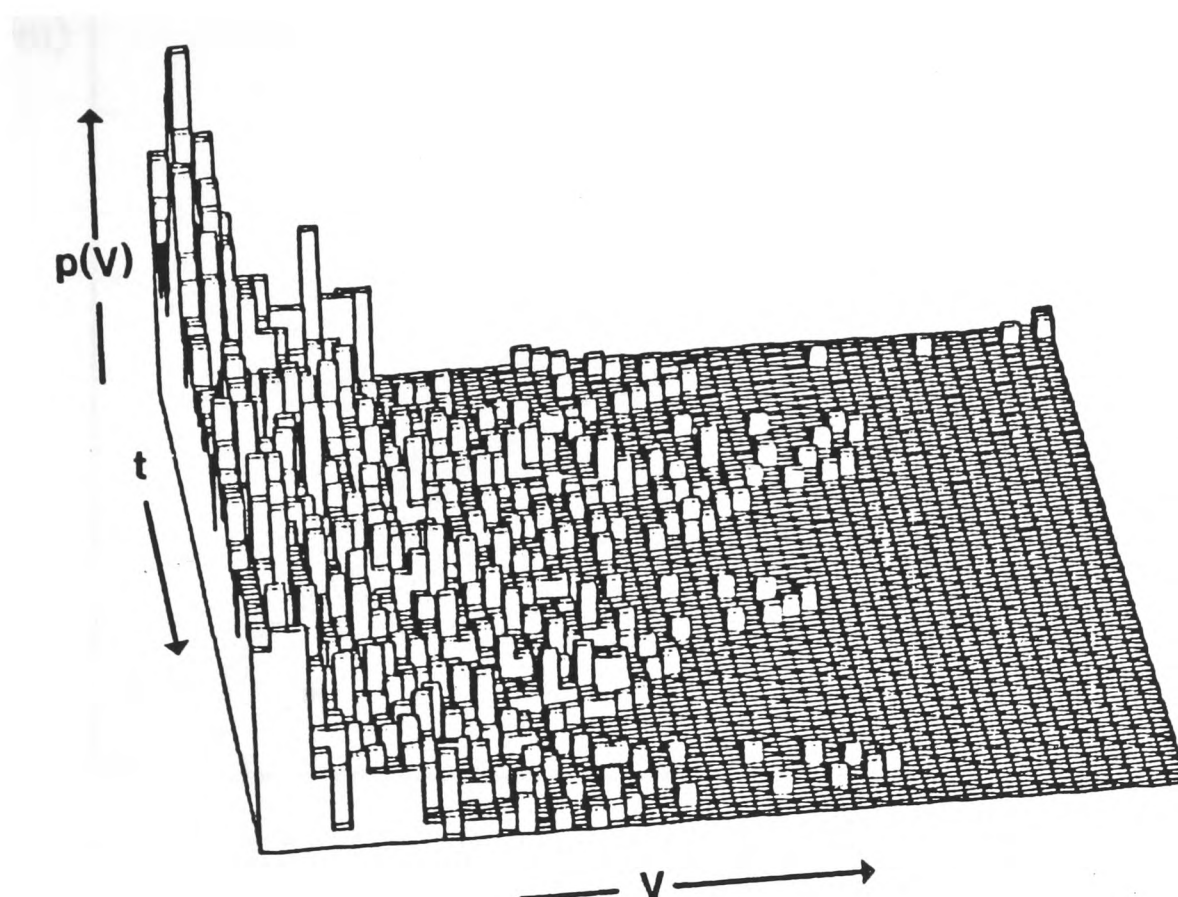


Figure 2.4 : Time-dependent histogram of ion velocities in a poorly behaved simulation of NaI at 100°K. One very hot ion is not coming into equilibrium with the rest of the system, thereby distorting the thermodynamics. Even a single hot ion was found to be able to ruin a simulation.

it is necessary to “kick” the system by heating it far beyond the melting point (up to twice the MP is typical) when the system does truly melt despite any metastability, and then cool it back down to the desired temperature. Once the system has melted, it does not tend to “refreeze” except when it should at temperatures below the real melting point.

2.9 What can MD calculate?

In these MD studies, the system configuration (positions, velocities, and accelerations) is written to tape after each timestep. Some instantaneous system properties such as the temperature, pressure, Coulomb and short-range energy, and total momentum are computed at each timestep and also written to tape.

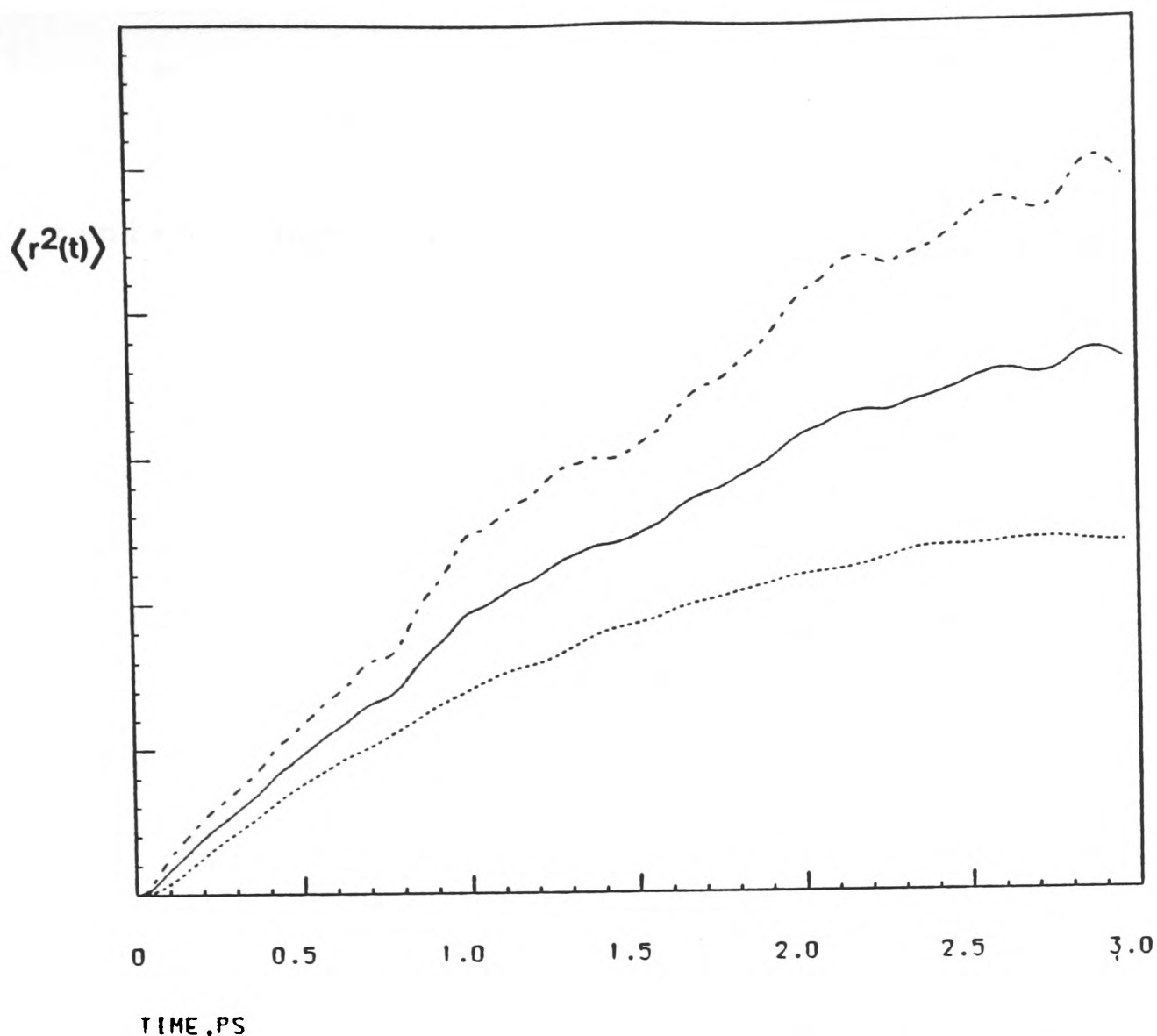


Figure 2.5 : “Superionic” NaI, from a simulation exhibiting metastability of the solid state at a temperature well ($\approx 100^\circ\text{K}$) above the melting point. In this plot of the mean-square displacement function for cations (dashed) and anions (dotted), the cations are diffusing readily while the anions are trapped on their lattice sites. The solid curve is the averaged cation and anion mean square displacement.

These are all straightforward to calculate: the temperature, for instance, is just

$$T = \frac{1}{3Nk_B} \sum_{i=1}^N m_i v_i^2, \quad (2.18)$$

where k_B is Boltzmann’s constant, and $3N$ is the number of degrees of freedom in the system of N particles.

Sangster and Dixon [SAN76] list many of the properties accessible to MD simulations. One of the most natural things to calculate in an MD study is the *radial distribution function* (rdf) $g(r)$ and the related *partial radial distribution functions* $g_{\alpha\beta}(r)$. The rdf gives the deviation of the density of particles at a distance r from a given particle from the bulk value of the number density ρ , where $\rho = V/N$, for a system of volume V with N particles. Equivalently, $g(r)$ is related to the likelihood of finding any particle at a distance r from a given particle. If $n(r)\Delta r$ is the average number of particles found at distances between

r and $r + \Delta r$ from a given particle, then

$$g(r) = \rho \frac{n(r)}{4\pi r^2}. \quad (2.19)$$

Defined in this way, $g(r) \rightarrow 1$ as $r \rightarrow \infty$. The partial rdf's $g_{\alpha\beta}(r)$ reflect the probability of finding a particle of type β (in ionic systems, β is either a cation (+) or an anion (-)) at a distance r from a given particle of type α (also + or - for ionic systems). There are three different rdf's to consider for an alkali halide system: the two like-ion distributions (cation-cation and anion-anion, or $g_{++}(r)$ and $g_{--}(r)$), and the unlike-ion distribution $g_{+-}(r)$. The different partial rdf's and the total rdf are easily accumulated during a simulation run by taking a histogram of the ion pair separations in the inner force computation loop over all pairs of ions. Chapter 4 contains examples of the partial rdf's for some alkali halide crystals and melts.

The *pair correlation functions* $h_{\alpha\beta}(r)$ are closely related to the partial radial distribution functions; $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$. The *partial structure factors* $S_{\alpha\beta}(q)$ are defined in terms of the spatial fourier transforms $h_{\alpha\beta}(q)$ of the real-space pair correlation functions $h_{\alpha\beta}(r)$:

$$S_{\alpha\beta}(q) = 1 + \rho h_{\alpha\beta}(q). \quad (2.20)$$

These are of particular interest, as they are accessible to neutron scattering experiments for some alkali halide melts [MCG84], and knowledge of them yields significant information about the nature of the liquid state. There are numerical difficulties in performing this transform in simulation work, since simulations have access only to $g(r)$'s for $r \leq \frac{a}{2}$ [SAN76], but these can be overcome [DIX83a].

The particle energies in the system must be determined at each timestep as part of the force calculation; these are easily reported on a per-particle or total-system basis. The energy is conveniently reported broken down into its

various components (kinetic, and Coulomb and short-range potential energies). With the standard microcanonical MD methods, the total energy is a conserved quantity, even though the individual components vary, as in figure 2.2.

The system pressure is easily accumulated at each timestep; such bulk properties as the specific heat and the compressibility can be determined by monitoring the fluctuations in time of the temperature and pressure, respectively. Such collective properties are, however, often subject to poor statistics [SAN76].

As configuration details (particle positions, velocities, accelerations) are written to tape after each timestep in this work, it is convenient to determine time-dependent properties via post-processing of the configuration tapes. Such quantities as the *normalised velocity autocorrelation function* for cations or anions ($\alpha = +$ or $-$)

$$\text{VACF}_\alpha(t) = \frac{\sum_{i=1}^{N_\alpha} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle}{\sum_{i=1}^{N_\alpha} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle} \quad (2.21)$$

are easily determined in this manner; the VACF and the related displacement autocorrelation function are intimately related to the vibrational properties of systems, and are discussed further in chapter 4.

The *mean square displacement function* $\langle r^2(t) \rangle_\alpha$ for particles of type α ,

$$\langle r^2(t) \rangle_\alpha = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle, \quad (2.22)$$

is a useful probe of the behaviour of a simulation, as was shown in figure 2.5. Particle diffusion constants can be related to the slope of this curve [SAN76]. Sangster and Dixon enumerate further accessible properties that are not of interest in this work [SAN76].

Quantities of spectroscopic interest include the electric field and field gradient on each ion at each timestep. The field is readily available from the Ewald summation procedure described above in section 2.6; the field gradient can also be found and recorded (chapter 6). Chapter 6 discusses how the Raman spectra of simulated systems can be related to time-correlation functions over these

field and field gradient terms and other quantities available from the simulation. Before these matters can be considered, however, it is necessary to discuss the specific issues relevant to simulations of alkali halide systems with the general methods outlined in this chapter; such matters, especially the form of the interionic potentials used, are the subject of chapter 4. First, however, a general discussion of Raman scattering follows in chapter 3.

3 Introduction to light scattering

3.1 The Raman effect

Raman spectroscopy is a powerful technique for probing the excitations of matter in all states. Although there exist classical approaches to the explanation of Raman scattering, the Raman effect can only be properly understood within the framework of the quantum theory. This fact was appreciated from the first observation of the Raman effect in 1928 [RAM28].

In modern laser–light Raman scattering experiments, monochromatic photons are scattered *inelastically* from the sample under study by exchanging energy with various excitations (e.g., vibrational modes) of a sample. Note the fundamental difference between the inelastic Raman scattering process which is purely a quantum–mechanical phenomenon, and *elastic* Rayleigh scattering of photons, which yields more readily to a classical treatment, although it, too is a result of quantum–mechanical transitions. The inelastically scattered Raman photons undergo a frequency shift; the amount of the shift is a direct measure of the energy of the mode(s) excited (or de–excited) by the photon in the exchange. Raman scattering is a very weak phenomenon, several orders of magnitude weaker than Rayleigh scattering, but laser sources provide light of sufficient intensity to measure the effect quite readily.

In vibrational Raman scattering in crystals, the excitations involved are phonons. In *Stokes* scattering, one or more phonons are created as a result of the scattering event; in *anti–Stokes* scattering, phonons are absorbed. The Stokes scattering is the more intense of the two: whereas the Stokes scattering involves exciting a system out of a ground state through the creation of some excitation,

anti-Stokes processes involve de-exciting an already excited state. Since the population of excited states of energy E falls off by a factor of $\exp(-E/k_B T)$, there are far fewer states available to participate in the anti-Stokes scattering.

1

The requirement for energy conservation leads to energy selection rules for Raman processes. Given an incident laser photon with frequency ω_L and energy $\hbar\omega_L$, and a scattered photon at shifted frequency ω_S with energy $\hbar\omega_S$, Stokes processes require that a phonon of frequency $\omega_O^S = \omega_L - \omega_S$ be created, and anti-Stokes process that a phonon of frequency $\omega_O^{AS} = \omega_S - \omega_L$ be destroyed, or absorbed, in the interaction.

Similarly, momentum conservation requires that, if the incident and scattered photons have momenta in the scattering medium of $\hbar n \mathbf{q}_L$ and $\hbar n \mathbf{q}_S$ respectively, then

$$\hbar n \mathbf{q}_S = \hbar n \mathbf{q}_L \pm \hbar \mathbf{k} + \hbar \mathbf{K}, \quad (3.1)$$

where $\mathbf{k}$ is the phonon wave vector and $\mathbf{K}$ is a reciprocal lattice vector; n is the index of refraction in the scattering medium. The anti-Stokes process involves the ‘+’ sign; the ‘−’ sign is the Stokes process. In practice, the free space photon wavevectors $\mathbf{q}_S$ and $\mathbf{q}_L$ are small compared with the reciprocal lattice vector $\mathbf{K}$, so momentum conservation requires that $\mathbf{K} = 0$, i.e., all wavevectors involved are well within the first Brillouin zone [ASH76].

A typical experimental arrangement is shown in figure 3.1a; the scattering geometry is given in figure 3.1b. Laser light of a certain polarisation is incident on the sample along the z -axis; the intensity of the scattered light (which may be polarised or depolarised with respect to the incident light) as a function of the frequency shift is measured along the y -axis with a spectrometer, a polarisation analyser, and a photon counter.

¹ Other factors also help to suppress anti-Stokes scattering; see, for example, Woodward [WOO72].

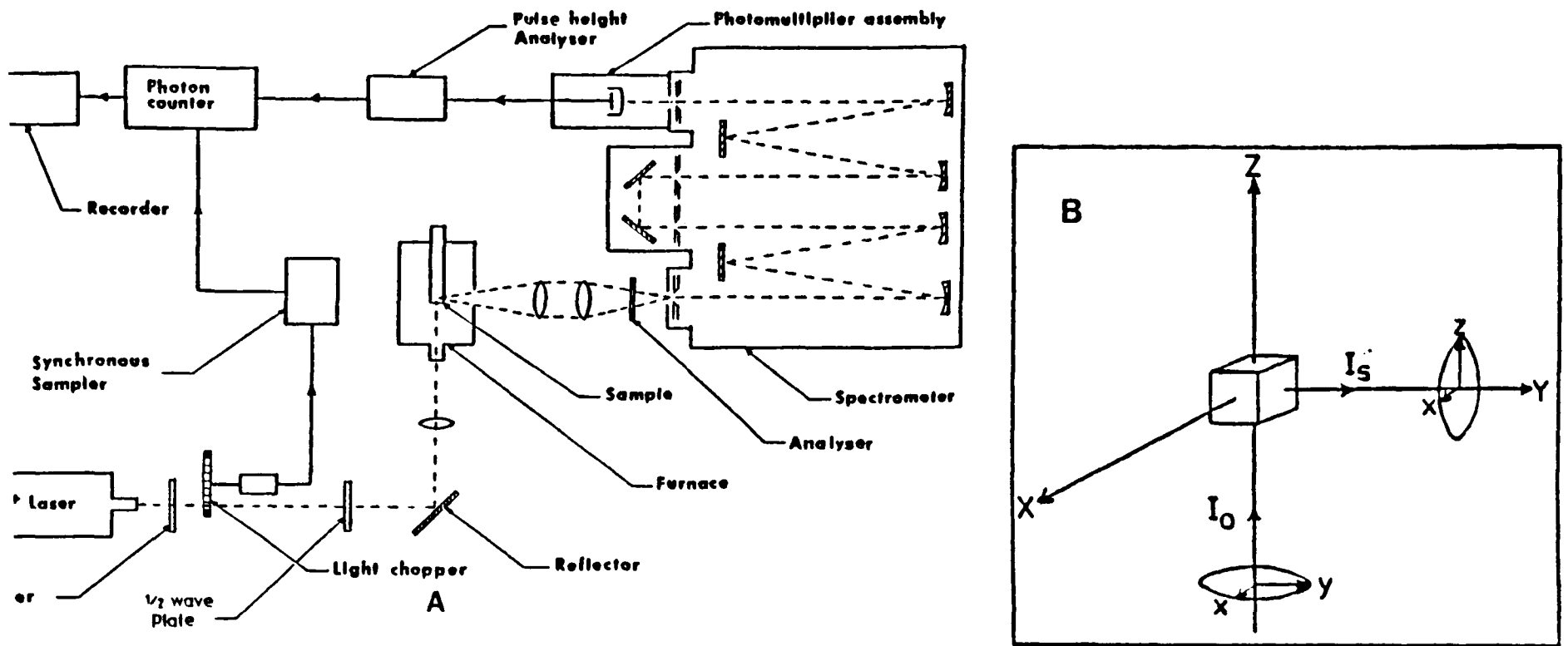


Figure 3.1 : a) Typical experimental set-up for Raman spectroscopy, from Mitchell and Raptis [MIT83]. b) The scattering geometry: light is incident along the z axis, and the scattered photons are counted along the y axis. The incident light is of a known polarisation; scattered light can have the same polarisation (*polarised scattering* or orthogonal polarisation *depolarised scattering*).

The theory of Raman scattering can be approached from two directions: upwards from a purely quantum-mechanical formulation, or downwards from a semi-classical atomic polarisability foundation. Both approaches have proved useful in this work, so a summary of each will be presented in this chapter.

3.2 Terms and definitions

Here are defined several related but distinct terms that figure in the theory of Raman spectroscopy. Some of these definitions are cast in the language of ionic systems, but it should be understood that equivalent formulations exist for atomic and molecular systems.

An incident electric field can distort the “electron cloud” about an ion, thus

inducing a dipole moment $\boldsymbol{\pi}$ on an otherwise dipole-free ion. The polarisability α of an ion i at position $\mathbf{r}$ connects the induced dipole moment $\boldsymbol{\pi}^i(\mathbf{r})$ to the total electric field $\mathbf{E}(\mathbf{r})$ acting on the ion. In an isotropic, extensive medium, the average polarisability can be written as a scalar:

$$\boldsymbol{\pi}^i(\mathbf{r}) = \alpha \mathbf{E}^i(\mathbf{r}) . \quad (3.2)$$

In general however, and certainly at the atomic level, α is a tensor quantity, $\underline{\alpha}$, so one must write

$$\pi_x^i(\mathbf{r}) = \alpha_{xx}^i(\mathbf{r}) E_x(\mathbf{r}) + \alpha_{xy}^i(\mathbf{r}) E_y(\mathbf{r}) + \alpha_{xz}^i(\mathbf{r}) E_z(\mathbf{r}), \quad \text{etc.}$$

or

$$\boldsymbol{\pi}^i = \underline{\alpha}^i \mathbf{E}^i . \quad (3.3)$$

All components of $\underline{\alpha}^i$ can themselves be sensitive to the instantaneous local environment about ion i , so one must treat $\underline{\alpha}$ in general as varying in time and space. The average polarisability α , then, is a suitably time-averaged sum of the polarisabilities of the constituents of a unit cell of the medium:

$$\alpha = \left\langle \sum_{\substack{\text{unit} \\ \text{cell}}} \underline{\alpha}^i(\mathbf{r}, t) \right\rangle . \quad (3.4)$$

The tensor $\underline{\alpha}$ can readily be shown to be symmetric (within certain approximations for the scattering process) [WOO72], and its transformation properties under coordinate axis rotations yield two invariant scalar quantities, the mean polarisability $\bar{\alpha}$, and the polarisability anisotropy γ_0 :

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3.5)$$

$$\begin{aligned} \gamma_0^2 &= \frac{1}{2} \{ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \} \\ &= \frac{1}{2} \left\{ \frac{1}{2} (2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})^2 + \frac{3}{2} (\alpha_{xx} - \alpha_{yy})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right\} \end{aligned} \quad (3.6)$$

These invariants give rise to the *isotropic* and *anisotropic* scattering respectively; the more familiar and experimentally accessible polarised and depolarised scattering are related to these through simple expressions (section 3.5). The second form of (3.6) above can be shown ([SCH65] and chapter 6) to give rise to five orthogonal representations of the anisotropic scattering.

The induced electronic dipole moment π should not be confused with the *configuration electronic dipole* μ , which is the electronic dipole resulting from the configuration of charges in a system. In molecular systems, μ can have contributions both from the configuration of charges within a molecule, and from the relative configuration of charges on different molecules. For ionic systems, there is no internal configuration dipole moment, but a system of ions has a configuration dipole moment due to the relative positions of their charges. As will be seen below, μ is central to the infra-red absorption problem, but π is crucial to Raman scattering.

Sometimes it is necessary to refer to the *total dipole moment* p^i of ion i ; $p^i = \mu^i + \pi^i$.

The Gaussian (CGS) unit for polarisability is a volume (cm^3); a convenient unit for polarisability is the cubic angstrom ($\text{\AA}^3$), since a zero-th order view of polarisability is the volume of the electron “cloud” around an ion [ASH76].² Chemists often use *atomic units* (au) to report polarisabilities;³

$$1\text{au} \doteq .1482\text{\AA}^3.$$

The *total polarisability operator* $\underline{\Pi}(t)$ is a collective property of a system and contains, in general, contributions from all single ions in the system, and all pairs of ions (through the dipole-induced dipole interaction discussed in chap-

² The SI unit for polarisability involves an extra factor of the free space permittivity, ϵ_0 , and is rarely used.

³ Atomic units are those in which length is measured in bohrs ($1\text{bohr} = 1a_0 \doteq 0.5292\text{\AA}$), charge in units of the electron charge e , mass in electron masses m_e , and energy in Hartrees ($1\text{H} = 4.359 \cdot 10^{-18}\text{J}$)

ter 6), and higher many-body multipole contributions. The total polarisability operator can include non-electronic effects, such as the effect of electron cloud compression from overlap repulsion (chapter 6). Π can be given as the sum of atomic polarisability operators: $\Pi = \sum_i \Pi^i$. Specific analytical forms for Π will be developed in chapter 6.

The *polarisation*, or *dipole density* $\mathbf{P}(\mathbf{r})$ of a system at position $\mathbf{r}$ is the local dipole-moment density of a small volume about $\mathbf{r}$. In the approximation of localised electrons about ions, $\mathbf{P}(\mathbf{r}) = \sum_i \mathbf{p}^i \delta(\mathbf{r} - \mathbf{r}^i)$. This total polarisation includes all the many-body effects (dipole-induced dipole and higher multipole interactions) mentioned above. In a crystal, or in a melt simulation with periodic boundary conditions, the average polarisation $\mathbf{P}$ can be defined as the average dipole-moment density of a unit cell or some sample volume. Fluctuations in $\mathbf{P}$, or equivalently in Π will be shown to govern light scattering in chapter 6.

One can also define *electronic hyperpolarisabilities* to extend the induced dipole moment expansion (3.3) beyond the linear term in the applied field. The electronic *dipole hyperpolarisability* $\underline{\gamma}$ and *quadrupole hyperpolarisability* $\underline{\mathbf{B}}$ are defined from [BUC67; FOW84b, 85]

$$\mu_{\alpha}^i = \alpha_{\alpha\beta}^i F_{\beta} + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta}^i F_{\beta} F_{\gamma} F_{\delta} + \frac{1}{3} B_{\alpha\beta,\gamma\delta}^i F_{\beta} F_{\gamma\delta} + \dots, \quad (3.7)$$

for ion i with the summation convention for repeated indices, where $\underline{\gamma}$ and $\underline{\mathbf{B}}$ are both tensor quantities, and F_{α}^i and $F_{\alpha\beta}^i$ are the components of the field and field gradients acting on ion i . In the spherical symmetry appropriate to ionic melts, the tensors $\underline{\gamma}$ and $\underline{\mathbf{B}}$ are shown [BUC67] each to depend on only one parameter:

$$\gamma_{\alpha\beta\gamma\delta} = \frac{1}{3} \gamma (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \quad (3.8)$$

and

$$B_{\alpha\beta,\gamma\delta} = \frac{3}{4} B (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} - \frac{1}{2} \delta_{\alpha\beta} \delta_{\gamma\delta}). \quad (3.9)$$

In crystals, the higher symmetry invalidates these relations, but relations specific

to each symmetry family are known which reduce the tensors to a few parameters [BUC67].

Further hyperpolarisabilities for higher terms in the dipole moment expansion, and equivalent operators for higher multipole operators (e.g., quadrupole moment expansions) can be similarly defined [BUC67].

3.3 Overview of scattering processes

Rayleigh and Raman scattering and infra-red absorption are related, complementary tools for probing atomic and molecular systems. The characteristics of each will be introduced here, following closely the clear exposition of Woodward [WOO72].

3.3.1 Infra-red absorption

If light from the infra-red part of the spectrum is incident on a sample, one finds on analysing the light transmitted through the sample that certain wavelengths of the incident light have been selectively *absorbed* by the sample. Further, the wavelengths absorbed are particular to each substance studied. The absorption frequencies are found to correspond to certain of the characteristic excitations (vibrations or rotations) of the sample, and the theory that explains this *infra-red absorption* is that of radiating electric dipoles.⁴

It is easiest to cast the description of IR processes in terms of molecules, but the following is true for ionic systems as well. Given a molecule i with a configuration dipole moment μ^i , the instantaneous value of μ will in general depend on the configuration of the atoms in the molecule and its neighbours,

⁴ The “infra-red” is simply a result of the fact that typical normal mode frequencies in a system are in the infra-red range.

thus

$$\boldsymbol{\mu}^i = \boldsymbol{\mu}^i(\mathbf{X}(t)), \quad (3.10)$$

where $\mathbf{X}$ is the set of atomic coordinates in the vicinity of i . In the simple harmonic approximation for vibrations in the sample, all oscillations are simply superpositions of the normal modes Q_k with frequencies ω_k characteristic of the sample. The dipole moments $\boldsymbol{\mu}^i$, then, can oscillate with lattice vibrations *only* at the mode frequencies ω_k , and an oscillating dipole emits radiation at the frequency of oscillation. The molecular dipoles can be *excited* to oscillate by absorbing incident photons at these frequencies ω_k (and only at these frequencies, within the approximations made).

Only certain mode frequencies show up as absorption lines in an IR spectrum, however. To understand why, one can write down a Taylor expansion of the dipole moment in the normal mode coordinates:

$$\boldsymbol{\mu}^i = \boldsymbol{\mu}_0^i + \sum_k \left\{ \left(\frac{\partial \boldsymbol{\mu}^i}{\partial Q_k} \right)_0 Q_k \right\} + \text{higher terms}, \quad (3.11)$$

where the subscript “0” denotes the equilibrium configuration. The higher terms will be neglected. The term $\boldsymbol{\mu}_0$ is constant for any given molecule, indeed $\boldsymbol{\mu}_0 = 0$ for ions, so $\boldsymbol{\mu}_0$ does not contribute to radiation or absorption. A collection of ions does, however, have a collective configuration dipole moment $\boldsymbol{\mu}$, so infra-red processes are still possible. A normal mode k can be reflected in the IR spectrum only if the term $(\partial \boldsymbol{\mu} / \partial Q_k)_0 \neq 0$. This condition is a *restricted selection rule* for the mode, restricted because of the two approximations made: simple harmonic motion and neglecting higher order terms in the Taylor series. Despite the approximations, this “rule” is quite authoritative for predicting which modes will not appear in a spectrum; these are referred to as *forbidden modes*. Some modes that are allowed by the rule, though, have an absorption amplitude too low to be observed in practice.

3.3.2 Raman and Rayleigh scattering

In Raman scattering, the incident light is deliberately chosen *not* to correspond to excitation frequencies of the sample under test.⁵ Instead monochromatic light, usually from the visible region of the spectrum, is incident on the sample; in the scattered radiation are found lines at frequencies *shifted* from the incident frequency ω_L (for Laser) by amounts corresponding to excitation frequencies of the sample.

The quantity of interest now is the induced dipole moment π^i of ion (or molecule) i . Recalling (3.3),

$$\pi^i = \underline{\alpha}^i E^i. \quad (3.3)$$

Again making the simple harmonic approximation for the vibrational modes, the polarisability tensor $\underline{\alpha}$ can be expanded in a Taylor series about the normal modes, yielding for a typical component $\alpha_{\alpha\beta}^i$

$$\alpha_{\alpha\beta}^i = (\alpha_{\alpha\beta}^i)_0 + \sum_k \left\{ \left(\frac{\partial \alpha_{\alpha\beta}^i}{\partial Q_k} \right)_0 Q_k \right\} + \text{higher terms}, \quad (3.12)$$

which is similar to (3.11) above. Again, the subscripts “0” denote the equilibrium configuration. The polarisability derivatives $(\partial \alpha / \partial Q_k)_0$ are called the *derived polarisabilities* of the k^{th} mode; they also constitute a tensor which is usually denoted $\underline{\alpha}'$. As $\underline{\alpha}$ is symmetric, it follows that $\underline{\alpha}'$ is also symmetric.

Now write

$$\pi^i = \underline{\alpha}_0^i E^i + \sum_k \underline{\alpha}'^i E^i Q_k. \quad (3.13)$$

The term in $\underline{\alpha}_0$ is a constant of the ion and is independent of any normal mode frequencies; the quantity $\underline{\alpha}_0 E$ oscillates at the frequency of the incident field, and therefore induces dipole oscillations at the incident frequency. These are re-radiated, giving rise to elastic Rayleigh scattering at the frequency of the incident radiation.

⁵ Resonant Raman scattering is a separate subject; see, for example, Long [LON77].

The components of $\underline{\alpha}'$ for mode k are also constant for that mode. The term involving $\underline{\alpha}'$ also involves the product of Q_k and E^i ; as these oscillate at frequencies ω_k and ω_L respectively, the law of cosine products gives us the desired result that these terms give rise to oscillations in $\underline{\alpha}'$, and thus in π^i , at the frequencies $\omega_L \pm \omega_k$. Thus the radiation emitted from these oscillating dipoles will contain photons shifted by amounts ω_k from the incident frequency ω_L . The different signs account for the Stokes and anti-Stokes lines in observed spectra.

Again, not all mode frequencies are reflected in the Raman spectrum of a sample; following the arguments in the section on IR absorption above, Raman active modes will be those for which at least one component of $\underline{\alpha}'$ is non-zero. Rayleigh scattering is never forbidden; there will always be deformation of the ion's electron cloud at the incident frequency giving rise to the elastic scattering.

3.3.3 Scattering geometries and intensities

One can measure both the *polarised* and *depolarised* scattering in an experiment; these can be understood in terms of the scattering geometry of figure 3.1b. If the laser light (incident along the z -axis) is polarised in the x direction, scattered light along the y -axis can be measured with either the same or different polarisation as the incident light. The polarised scattering is that with the same (i.e., x) polarisation; following experimental practice [MIT83] this is referred to as the Z(XX)Y scattering, and its intensity is labelled $I_{\parallel}$. The depolarised scattering is that scattered light with z or y polarisation; viewed along the y -axis, only the z -polarised light contributes; this configuration is denoted Z(XZ)Y. The intensity of the depolarised scattering is denoted as $I_{\perp}$.

The ratio of the intensity of the depolarised to the polarised scattering is

the *depolarisation ratio*, ρ_D :

$$\rho_D = \frac{I_{\perp}}{I_{\parallel}}. \quad (3.14)$$

Simple arguments show that the maximum possible value for ρ_D with polarised incident light perpendicular to the scattering plane is $\frac{3}{4}$, and with unpolarised, or “natural” light, $\frac{6}{7}$ [WOO72]. The depolarisation ratio can also be expressed as a function of frequency; if the scattering intensities at some frequency ω have been measured, then

$$\rho_D(\omega) = \frac{I_{\perp}(\omega)}{I_{\parallel}(\omega)}. \quad (3.15)$$

3.3.4 Raman scattering in alkali halide crystals

When the selection rules for Raman scattering are applied to the cubic structures of alkali halide crystals, it is found that *no* modes are Raman active. This is a general result for crystals with a centre of inversion symmetry [HAY78]. Although all one-phonon processes are thus forbidden, there is higher order Raman scattering from these crystals, the dominant component being the *two-phonon scattering*. This can be accounted for in the simple derivations above by extending the Taylor series to the next term, involving pieces like

$$\frac{\partial^2 \alpha}{\partial Q_{k_1} \partial Q_{k_2}} Q_{k_1} Q_{k_2},$$

and thus involving the simultaneous interaction of two phonons of modes k_1 and k_2 . An approach to the theory of the two-phonon scattering involves consideration of the two-phonon density of states, which for alkali halides has been considered at length by Hardy and Karo [HAR69, 79]. Bruce and Cowley have also considered the two-phonon scattering problem in alkali halides [BRU72a, b]. The details of these processes will not, however, be relevant to this work.

3.4 Quantum-mechanical theory of Raman scattering

A full treatment of the Raman effect involves a many-body theory of electron-photon-phonon interactions, as the Raman process is a result of complex interactions between both incident and scattered radiation and matter. Clearly, many approximations will have to be made to arrive at any more than a completely formal statement of the quantum interpretation of the Raman effect.

The main objective of this work is to understand the Raman spectra of simple ionic melts. In practical terms, the goal is to reproduce and understand the lineshapes that the Raman spectroscopists in the Clarendon lab and elsewhere see in alkali halide crystal samples heated slightly ($\approx 50^\circ\text{K}$) above the melting point. Previous experimental and simulation work has demonstrated the existence of regions of $\approx 25\text{\AA}$ radius in the melts with significant solid-like local ordering (see chapter 4), so one should not be surprised to see some vestige of the solid's scattering behaviour in the melts. The theory is introduced, therefore, with a description of scattering in crystals.

The scattering theory will be treated in the framework of a semi-classical approximation for the electrons, i.e., the electrons in the system will have definite position and momentum coordinates. The individual electrons will eventually drop out of the formalism.

The total Hamiltonian $\mathcal{H}_{tot}$ appropriate to light scattering in crystals can be broken down into several parts:

$$\mathcal{H}_{tot} = \mathcal{H}_{rad} + \mathcal{H}_{matter} + \mathcal{H}_{int} \quad (3.16)$$

where $\mathcal{H}_{rad}$ is the radiation Hamiltonian, $\mathcal{H}_{matter}$ describes the crystal, and $\mathcal{H}_{int}$ the interactions between matter and electromagnetic radiation. Each of these terms will be discussed in turn below, introducing appropriate approximations where necessary. Then expressions for the somewhat simpler infra-red absorption problem, and later for the complete Raman scattering problem will be

assembled.

3.4.1 Crystal Hamiltonian for alkali halides

The most general form for the matter (crystal) Hamiltonian is [BIL84]

$$\mathcal{H}_{matter} = T_e + T_i + \Phi_e + \Phi_i + \Phi_{ei} \quad (3.17)$$

where the subscripts e and i refer to electrons and ions (strictly to the bare nuclei), and the operators T and Φ are for kinetic and potential energy respectively. In a non-relativistic formulation, the kinetic energy terms are simply

$$T_e = \sum_l \frac{\mathbf{p}_l^2}{2m_e} ; \quad T_i = \sum_n \frac{\mathbf{p}_n^2}{2M_n} . \quad (3.18)$$

Here, the sums are over the electrons l with momenta $\mathbf{p}_l$ and mass m_e , and ions n with momenta $\mathbf{p}_n$ and masses M_n .

The potential energy terms are those appropriate to a Coulomb interaction between electrons and ions:

$$\Phi_i = \frac{1}{2} \sum'_{n,n'} \frac{Z_n Z_{n'} e^2}{|\mathbf{r}_n - \mathbf{r}_{n'}|} \quad (3.19)$$

$$\Phi_e = \frac{1}{2} \sum'_{l,l'} \frac{e^2}{|\mathbf{r}_l - \mathbf{r}_{l'}|} \quad (3.20)$$

$$\Phi_{ei} = - \sum_{l,n} \frac{Z_n e^2}{|\mathbf{r}_l - \mathbf{r}_n|} \quad (3.21)$$

where the primed sums exclude $l = l'$, etc., and ion n has net charge Z_n ($Z_n = \pm 1$ if the ion is fully “ionic”).

The *adiabatic approximation* is usually introduced at this stage, which says that the electron and ion parts of the states of the matter Hamiltonian are separable [BIR74]:

$$|\Psi\rangle_{adiabatic} = |\Psi\rangle_{electron} |\Psi\rangle_{lattice} . \quad (3.22)$$

This approximation effectively asserts that the much heavier and slower ion nuclei cannot follow the rapid motion of the smaller and faster electrons; on the timescale of ion motion, all the ions see is an “average” electronic configuration, and not the instantaneous electronic configuration.

3.4.2 Electromagnetic interactions

The standard approach (Bilz *et al.* [BIL84]) is to treat the electromagnetic field, described by its 4-vector potential $(\mathbf{A}, \phi)$, in the *radiation gauge* ⁶ so that the full potential can be written in terms of a non-divergent vector potential $\mathbf{A}$ without a scalar part:

$$\nabla \cdot \mathbf{A} = 0 ; \quad \phi = 0. \quad (3.23)$$

Writing a gauge-invariant form for the electron and ion kinetic energies (including the interactions with the field): ⁷

$$T_e(\mathbf{A}) = \frac{1}{2m_e} \sum_l (\mathbf{p}_l - \frac{e}{c} \mathbf{A})^2 \quad (3.24)$$

and

$$T_i(\mathbf{A}) = \sum_n \frac{1}{2M_n} (\mathbf{p}_n - \frac{eZ_n}{c} \mathbf{A})^2. \quad (3.25)$$

As the free, or non-interacting, part of the kinetic energy has been included in $\mathcal{H}_{matter}$ above in eq. (3.17), the interaction Hamiltonian becomes

$$\begin{aligned} \mathcal{H}_{int} = & \frac{e}{m_e c} \sum_l \left(-\mathbf{A} \cdot \mathbf{p}_l + \frac{e}{2c} \mathbf{A}^2 \right) \\ & + \frac{e}{c} \sum_n \frac{Z_n}{M_n} \left(-\mathbf{A} \cdot \mathbf{p}_n + \frac{eZ_n}{2c} \mathbf{A}^2 \right). \end{aligned} \quad (3.26)$$

This separation of the free and interacting parts leaves $\mathcal{H}_{int}$ non gauge-invariant, but introducing the *dipole approximation* for the interaction restores

⁶ The radiation gauge, which is usually derived for sourceless regions [BJO65], can be used in a crystal when the internal field can be taken as a weak perturbation.

⁷ Birman [BIR74] chooses (3.24) with a ‘+’ sign to conform to the Lorentz gauge, but the end result is the same. Expressed as written above, the gauge momenta can be thought of as those of quasiparticles called polaritons.

invariance and makes the formalism usable. It can be shown that neglecting the terms in A^2 is valid for insulators without a significant free-carrier density (such as alkali halides), but would be wrong for metals, where it would neglect momentum exchange between the photons and the free carriers [BIR74, BIL84]. The dipole approximation effectively neglects contributions to the interaction Hamiltonian from higher electronic multipoles and all magnetic moments by making the substitution [BIL84]

$$-\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \longrightarrow -e\mathbf{r} \cdot \mathbf{E}, \quad (3.27)$$

where $\mathbf{E}$ is the electric field. This substitution is valid because, in the radiation gauge, $\mathbf{E} = -(1/c)\partial\mathbf{A}/\partial t$, and in a long wavelength limit, $\mathbf{A}$ and $\mathbf{E}$ are only weakly dependent on $\mathbf{r}$, so one can write

$$\frac{d}{dt} \mathbf{A}(\mathbf{r}, t) \longrightarrow \frac{\partial}{\partial t} \mathbf{A}(\mathbf{r}, t), \quad (3.28)$$

and then commute the order of time-differentiation in (3.26) after discarding the terms in A^2 (justified in [BIL84]).

3.4.3 Radiation Hamiltonian

For completeness, the free radiation Hamiltonian $\mathcal{H}_{rad}$ in the radiation gauge (3.23) is given by

$$\mathcal{H}_{rad} = 2\pi c^2 M^2 + \frac{1}{8\pi} (\nabla \times \mathbf{A})^2, \quad (3.29)$$

[BIR74], although it will not directly enter into the expressions below. Here, M is the conjugate momentum to $\mathbf{A}$ treated as a “generalised coordinate,”

$$M = \frac{1}{4\pi c^2} \frac{\partial \mathbf{A}}{\partial t}.$$

3.4.4 Infra-red absorption

The appropriate total Hamiltonian for the scattering processes, between whose eigenstates $|i\rangle$ the scattering transitions of interest occur, is $\mathcal{H}_{tot}$ (3.16), with the various terms given by expressions above. If the interaction term (3.26) is written in terms of the dipole approximation (3.27), then

$$\mathcal{H}_{int} = e \sum_l \mathbf{r}_l \cdot \mathbf{E}(\mathbf{r}_l) + e \sum_n Z_n \mathbf{R}_n \cdot \mathbf{E}(\mathbf{R}_n) \quad (3.30)$$

with sums over the electrons l and nuclei n . Grouping together the coordinate terms for the electrons l_i and nucleus of each ion i ,

$$-e(Z^i \mathbf{R}^i + \sum_{l_i} \mathbf{r}_{l_i}) = \mathbf{p}^i, \quad (3.31)$$

the interaction can be represented in terms of the total dipole moments of the ions i :

$$\mathcal{H}_{int} = - \sum_i \mathbf{p}^i \cdot \mathbf{E}(\mathbf{r}^i), \quad (3.32)$$

since the relative electron and nuclear coordinates of an ion, weighted by the appropriate charge value, gives the total electronic dipole moment within the semiclassical electron approximation.

An IR absorption event involves the absorption of one photon by the matter system, and is therefore a first-order process in the interaction Hamiltonian $\mathcal{H}_{int}$. Using first-order time dependent perturbation theory, a rate law [BIR74] for the transitions from some initial state $|i\rangle$ to a final state $|f\rangle$ can be written down as

$$\omega_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}_{int} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega_0), \quad (3.33)$$

where the incident photon has energy $\hbar\omega_0$.

3.4.5 Raman scattering

Following the approach originally due to Placzek [PLA34],⁸ an expression for the Raman scattering process in terms of transition rates between initial and

⁸ A modern treatment is in Birman [BIR74].

final states of the total Hamiltonian mediated by inelastic photon scattering can be found. The Raman scattering is (at least) a two photon process, involving interactions (via $\mathcal{H}_{int}$) with both an incident and a scattered photon. Making Placzek's approximation that the matter system's electrons begin and end each scattering event in a ground state, the rate $\omega_{i \rightarrow f}$ for transitions out of an initial state $|i\rangle$ to a final energy conserving state $|f\rangle$ can be written as

$$\omega_{i \rightarrow f} = \left| \frac{\sum_{EX} \langle f | \mathcal{H}_{int} | EX \rangle \langle EX | \mathcal{H}_{int} | i \rangle}{E_i - E_{EX}} \right|^2 \delta(E_i - E_f). \quad (3.34)$$

$|EX\rangle$ is an intermediate excited state of the system with energy E_{EX} , and E_i is the energy $\hbar\omega_i$ of state $|i\rangle$. This formalism will not be directly useful in the calculations, as the intermediate excited states are not accessible to the simulations performed. Chapter 5 introduces a simplified (*i.e.*, tractable for machine computation) model for the transition rates that still reproduces some of the features of the Raman spectrum.

3.5 Atomic polarisation theory of Raman scattering

In semi-classical approaches to light scattering, the quantum mechanical nature of the process is masked by attributing the scattering to fluctuations in the electronic dipole moments and polarisabilities of the constituent atoms, ions, or molecules of the sample. The fundamental nature of these fluctuations is, of course, quantum mechanical, but various approximations can be made to yield a classically consistent, if somewhat empirical, theory. The empirical nature comes from having to supply values of various constants, *e.g.*, polarisabilities and hyperpolarisabilities, which are not in general known from first principles but which can often be measured experimentally or estimated accurately from, for example, electronic structure calculations.

This introductory discussion follows those of Fowler and Madden [FOW85], Buckingham [BUC67], and Woodward [WOO72]; “ion” here means molecule,

atom, or ion, as appropriate for a given situation.

The basic expression needed is for the instantaneous polarisation density $P(t)$ in the sample cell. By making the dipole approximation [FOW85 and (3.27)], that is, by neglecting the contributions to the polarisation from higher-order multipoles, the average polarisation per ion can be written as

$$P(t) = \frac{1}{N} \sum_i^N p^i(t) \quad (3.35)$$

where N is the number of ions in the unit cell, p^i is the total dipole moment of ion i and r^i is its position:

$$p^i(t) = \mu^i(t) + \pi^i(t). \quad (3.36)$$

In ionic systems, $\mu^i = 0$. There is a collective configuration dipole μ for a system of ions, but this term contributes only very weakly to Raman scattering. Effectively, therefore, $p^i(t) = \pi^i(t)$, i.e., only the induced dipole contributes to the total dipole moment of interest. The simplest approximation that can be made for $\pi^i(t)$ is to assume that the polarisability tensor $\underline{\alpha}^i(t)$ (which varies with the local environment of ion i) has a constant, average “in-crystal” value α_{CRYS}^i ,⁹ thus

$$p^i(t) = \alpha_{CRYS}^i \cdot E(r^i, t), \quad (3.37)$$

where $E(r^i, t)$ is the applied external field on ion i at time t . In a modern light scattering experiment, E is the laser field.

Elaborations of this oversimplified representation of the dipole moment, and thus of the polarisation, will occupy chapter 6. Whatever the elaboration, the relation between the dipole moment and the applied external field E can be represented through a *polarisability operator* $\underline{\Pi}$, such that for ion i ,

$$p_\alpha^i(t) = \sum_\beta \Pi_{\alpha\beta}^i(t) E_\beta(r^i, t) \quad (3.38).$$

⁹ The value of polarisability constants in condensed environments is discussed in chapter 6.

The desired polarised and depolarised scattering intensities and lineshapes can be found from appropriate manipulations of this operator $\underline{\Pi}$. At any given time, the various forms for $\underline{\Pi}$ that will be presented in chapter 6 can be thought of as polarisability tensors; the values of the components of the effective tensor will have the same invariants as $\underline{\alpha}$: a mean value (3.5) and an anisotropy (3.6). The isotropic and anisotropic components of the scattering are determined from these invariants and then combined in ways to be described below to give the polarised and depolarised scattering.

The isotropic scattering intensity, $I^{ISO}(\omega)$, is given by the Fourier transform of the time correlation of the isotropic fluctuations in the polarisability operator $\underline{\Pi}$:

$$I^{ISO}(\omega) = G_c \int_0^\infty dt e^{-i\omega t} \langle \frac{1}{3} \text{Tr}(\Delta \underline{\Pi}(0)) \frac{1}{3} \text{Tr}(\Delta \underline{\Pi}(t)) \rangle; \quad (3.39)$$

G_c is a known geometrical factor depending on the scattering geometry used, and $\Delta \underline{\Pi}(t)$ is the deviation of $\underline{\Pi}$ at time t from its average value $\langle \underline{\Pi} \rangle$. This is the scattering from the totally symmetric part of the polarisability fluctuations. The anisotropic scattering, $I^{ANI}(\omega)$, can be expressed as

$$I^{ANI}(\omega) = G_c \int_0^\infty dt e^{-i\omega t} \langle \mathcal{A}(\Delta \underline{\Pi}(0)) \mathcal{A}(\Delta \underline{\Pi}(t)) \rangle. \quad (3.40)$$

The operator $\mathcal{A}$, analogous to the $\frac{1}{3} \text{Tr}$ operator in (3.39), projects the anisotropic part of the polarisability fluctuations in the operator $\underline{\Pi}$. $\mathcal{A}$ is related to the anisotropy γ_0^2 ; the five terms in (3.6) each contribute a representation of $\mathcal{A}$, so, for example,

$$\mathcal{A}^1 \underline{\Pi} = 2\Pi_{zz} - \Pi_{xx} - \Pi_{yy}. \quad (3.41)$$

All five anisotropic operators are given in chapter 6. In spherical symmetry, all five operators are degenerate; in higher crystal symmetries, different operators correspond to different group representations of vibrational modes [SCH65 and chapter 6].

The polarised part of the spectrum is given directly by the sum of the isotropic and anisotropic parts, that is,

$$I_{\parallel}(\omega) = I^{ISO}(\omega) + I^{ANI}(\omega). \quad (3.42)$$

In laser scattering experiments with polarised incident radiation, the depolarised part is given by

$$I_{\perp}(\omega) = \frac{3}{4}I^{ANI}(\omega). \quad (3.43)$$

From this form, it is easy to see that the maximum depolarisation ratio ρ_D of $\frac{3}{4}$ occurs when the isotropic intensity vanishes [LON77]. This is found to be the case in simple inert liquids such as liquid argon, but some of the alkali halide melts have been shown experimentally to possess significant isotropic components in their scattering.

In chapter 6, several forms for Π will be used in such expressions to calculate Raman spectra from simulation data.

4 Simulations of alkali halides

4.1 Interparticle potentials: pair potentials and more

An MD simulation can produce physically meaningful results only if the interparticle potential model used adequately reflects the interactions in a system. Computational constraints today force almost all MD simulations to employ central, two-body, isotropic potentials, although consideration of the many-body effects present in real systems would suggest that non-central potentials including three- and indeed many-body terms, angle-dependent terms, etc., would be more realistic. Axilrod and Teller recognized the inadequacy of simple two-body force laws in modelling realistic many-body systems (rare gas systems) long ago [AXI43], and introduced three-body effects through angle-dependent potentials. Potential laws incorporating many-body effects for rare gas systems have been continuously improved since then [BAR76]. Clementi [CLE83, DIE84] has included four-body terms in simulations of water, a calculation made possible only through use of an exotic, experimental supercomputer [CLE85]. Local density-dependent potentials have been used to improve representation of many-body effects in metals [TAY85], and directional potentials have been used to model oxides [CAT85].

There have been numerous attempts to include many-body effects in potentials for ionic systems; Singh [SIN82] reviews many of these, and Leslie [LES85] has done more recent work involving explicit treatment of three-body angle-dependent terms. Although these potentials have proved useful in static lattice calculations, potentials incorporating explicit many-body terms have not yet been used in any simulation work on ionic systems due to their computational

complexity. Gordon and Kim have derived *ab initio* pair potentials for alkali halide systems [GOR72], but these suffer from the same limitations as other two-body potential models [DIX82] and have not been considered in this work. Potentials which incorporate many-body effects indirectly (such as the polarisable ion, or “shell model,” potentials described below) have, however, been of great use in dynamical simulation work [DIX76a, SAN76, CAT82].

Potential models for alkali halides suitable for use in simulation work have been reviewed by Sangster and Dixon [SAN76, DIX82]. The specific potential models used in this work will be described in more detail below. Justification of such simple models lies in the success of their use, however.

4.2 Potentials for simpler systems — argon

The inert elements of row VIII (Ar, Kr, etc.) are simpler systems to work with than the alkali halides; the absence of uncompensated atomic charges in these closed-shell systems means that atoms interact only via weak, short-ranged mutual induction (van der Waals) attractive forces and repulsive forces reflecting opposition to electron orbital overlap, arising from the exclusion principle. For these systems, a simple potential of the Lennard-Jones type [LEN24] has been shown to work fairly well in all three phases, within the limitations of a two-body model [SAN76]. The form often used is the so-called “12-6” form, where

$$\Phi^{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right), \quad (4.1)$$

and the two parameters ϵ and σ have the units of energy and distance, respectively. The attractive r^{-6} term properly represents the van der Waals dipole-induced dipole interaction between closed-shell atoms, and the r^{-12} term is an arbitrary but convenient representation for the repulsive term.

Rahman used a potential of this form in the first MD simulation of a real-

istic physical system [RAH64]; Lennard–Jones potentials have since been used successfully in many dynamical and Monte Carlo [LEV79, 84] calculations on argon–like systems. The form of this potential, with only fairly low–order polynomial terms and no transcendental functions, makes it computationally attractive. The additional luxury of no long–range interactions means (as was pointed out in chapter 2) that only near neighbours of a given particle need be considered in force calculations, so the complexity of simulations employing such potentials grows only linearly with the size of the sample.

4.3 Potentials for charged systems — rigid ion models

Modern potential models suitable for application to alkali halide systems were developed starting in the 1930’s with the work of Born, Huggins and Mayer on interatomic distances in crystals [BOR32, HUG33]. Improvements were made in the 1950’s and 1960’s to explain the newly observable (via neutron scattering) vibrational properties of crystalline salts. Various potential models were developed for use in lattice dynamics calculations [BOR54, COC71]; the potentials used today in simulation work are derived from these early lattice dynamics models. That potentials developed for use in static phonon dispersion and mode density calculations should also work well in dynamical simulations is not obvious; some of the complications induced by using them will be described.

Potential models for alkali halides are necessarily more complex than those for inert systems. In a first approximation, though, an alkali halide ion can be modelled as a closed shell atom like argon, etc., with the addition of an uncompensated unit charge. The first alkali halide chosen for a simulation study, KCl, was in fact picked because both its ions are isoelectronic with argon [WOO71a]. This description leads to the *rigid ion model* for interionic potentials. This model treats the ions as structureless (and thus isotropic), massive, rigid, charged point

particles; the ions interact via a long-range Coulomb force in addition to the attractive van der Waals and repulsive electron overlap forces. With two species of ion present, there are three different types of interactions to consider: *cation-cation* ($++$), *cation-anion* ($+-$), and *anion-anion* ($--$). The rigid ion model for alkali halides is often attributed to Kellermann. His original alkali halide lattice dynamics work used a potential model of this form, but he required only the force constants of the Coulomb and short range parts of the potential at the equilibrium distance, and not a parameterized form of the potential as a function of distance [KEL40, 41]. Computer simulation work requires knowledge of the potential over a significant distance range; even like ions can pass fairly close together in a melt. The earlier work of Born, Huggins, and Mayer [BOR32, HUG33] is invoked to provide a suitable starting point.

The energy Φ^C of the Coulomb interaction of ions i and j separated by the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is given by

$$\Phi^C(r_{ij}) = Z_i Z_j \frac{e^2}{r_{ij}} \quad (4.2)$$

where e is the electronic charge and Z_i is the ionic charge of ion i : $Z_i = \pm 1$ if the system is fully ionic. The alkali halides, especially those composed of the smaller ions, can generally be treated as fully ionic [SAN76], although the larger ions probably exhibit some non-ionic behaviour (see discussion of CsCl in chapter 7).

The total potential energy $\Phi(r_{ij})$ will be the sum of this Coulomb part and a short-range part. A potential model must therefore have terms like

$$\Phi(r) = \Phi^C(r) + \Phi^{REP}(r) + \Phi^{VDW}(r), \quad (4.3)$$

for the Coulomb, overlap repulsion, and Van der Waals terms. The Born-Huggins-Mayer form [HUG33] for the short-range interaction is often used. This takes the repulsive term in an exponential form, and uses polynomials to represent the first two van der Waals terms — the dipole-dipole (r^{-6}) and dipole-quadrupole (r^{-8}) attractive induction terms. These terms combine to yield

a pair potential of the form

$$\Phi_{\alpha\beta}(r) = Z_{\alpha}Z_{\beta}\frac{e^2}{r} + B_{\alpha\beta}\exp\left(-\frac{r}{\sigma_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r^6} - \frac{D_{\alpha\beta}}{r^8} \quad (4.4)$$

for species α and β (i.e., for the cation–cation interaction, $\alpha = \beta = '+'$).

The 12 phenomenological parameters $B_{\alpha\beta}$, $C_{\alpha\beta}$, $D_{\alpha\beta}$, and $\sigma_{\alpha\beta}$ in (4.4) are fitted to a variety of experimental data in some systematic way, usually across the entire family of alkali halides [SAN76]. Woodcock and Singer [WOO71a, b] used potentials in this form in the first MC and MD simulations of alkali halide melts. The values of the parameters used in this work are usually those of Fumi and Tosi [FUM64, TOS64]; a set due to Dixon and Sangster [DIX76a, b, 77b] has also been used occasionally in some test calculations. Several other sets of parameters in this form, resulting from different fitting procedures for the experimental data and different assumptions about how properties of a given ion transfer between salts, can be found in a catalogue of potentials compiled by Stoneham [STO79].

The rigid ion model potentials can reproduce the cohesive energy of alkali halides quite well [BOR54]. They have been used in simulations of all of the alkali halides, and have been found to model well the static and structural properties of most of these systems [SAN76, BAR86]. The rigid ion potentials perform nearly as well as the more complex “shell model” potentials described below in determining these properties.¹ For many salts, however, the rigid ion potentials perform quite poorly in the determination of dynamical properties.

Rigid ion potentials fail to model one important aspect of alkali halide ions. As they hypothesize *rigid* ions, they do not model the distortions that ions undergo as other ions come near them. These distortions, however, affect the ions’ short-range interactions with their neighbours, and *vice versa* [LYD38, WOO60].

¹ CsCl is a salt for which both the rigid and shell model potentials agree quite closely on a melt structure, but both disagree sharply with experiment [LOC85]. This is discussed further in the final chapter.

These models are thus incapable of capturing the effect of *ionic polarisability* (chapter 3) on the behaviour of the ions as their local environments change. This polarisability has both electronic (from the mutual electrostatic interactions of ions) and “mechanical” (from the distortions caused by ionic collisions or overlap repulsion) components [DIX76a].

As polarisability is related to the degree to which the outer electron shell is bound to the core, anions are in general more polarisable than cations, and larger anions more so than smaller ones. The effect of the neglect of polarisability is thus most severe in salts with large anions, as will be seen in the next section. The effect on the dynamical behaviour of such systems is severe. It is necessary to introduce some details of phonon properties to understand how and why the rigid ion potentials go wrong, and what can be done to improve matters.

4.4 Dispersion relations and density of phonon states

One measure of merit of a potential model is its ability to reproduce the vibrational properties of a system. For crystal systems, the well established techniques of *lattice dynamics* calculations and a given potential model allow determination of the phonon frequencies at any point in the Brillouin zone through solution of an eigenvalue problem for the system’s *dynamical matrix* of force derivatives [BOR54, COC67, COC71, BRU82]. From this knowledge, the traditional phonon dispersion curves in high symmetry directions can be determined, as can the *density of phonon states* (DOS) throughout the zone. The latter is obtained by constructing a histogram from a large number of phonon frequencies at positions chosen from a dense grid in k -space [COC67]. Kellermann determined the first realistic phonon spectrum for an alkali halide crystal (NaCl) using these techniques in 1940 [KEL40, 41]. Today, established computational packages such as the AERE Harwell PHONONS program automate these kinds

of calculations.

4.4.1 Dispersion relations and failure of the rigid ion model

Inelastic neutron scattering techniques have allowed the phonon properties of many real systems to be measured with high accuracy [LOV84]. Alkali halide crystals at low temperature were the subject of early neutron scattering studies [WOO60, 63]; lattice dynamics calculations of phonon properties from model potentials in this period led to the refinement of potential models to account for the new experimental data [WOO60, 63]. The phonon dispersion relations of many insulators, including all the alkali halides, have been collected by Bilz [BIL79], where model-potential dispersion relations from lattice dynamics calculations are also collected for comparison. Hardy and Karo [HAR79] also document the phonon properties of the alkali halides. For some salts with smaller ions, especially the alkali fluorides such as KF, (figure 4.1) rigid ion potentials provide quite a good characterization of phonon properties when compared with neutron experiments [BUH70]. For other salts, such as NaI (figure 4.2), rigid ion models go disastrously wrong.

As was indicated in the previous section, the principal reason for this is the neglect of polarisability in the rigid ion model. Specifically, the assumption of rigid ions is equivalent to assuming that the high frequency dielectric constant $\epsilon_{\infty} = 1$ [DIX76a]. As the actual high frequency dielectric constant is between about 2 and 3 for most alkali halides, the Lyddane–Sachs–Teller relation [LYD41] between the low and high frequency dielectric constants and the longitudinal and transverse and optic mode frequencies requires that the rigid ion models produce too great a splitting between the two optic branches of the phonon spectrum. One can adjust the parameters so that either the longitudinal or transverse branches are fairly well represented, but the separation will remain too great, as

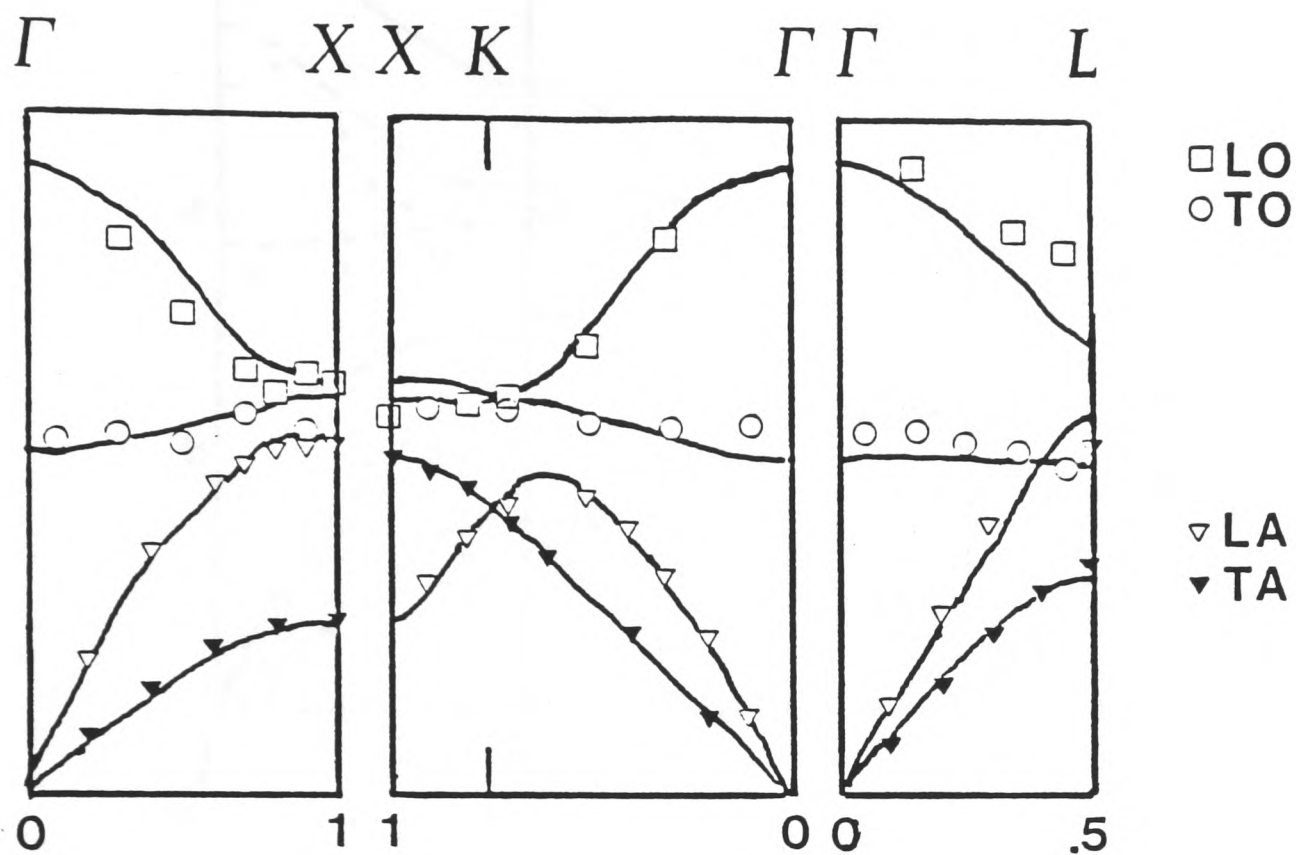


Figure 4.1 : Dispersion relations for KF at 300°K for which a rigid ion model potential (solid curve) reproduces the experimental values (points) well, after Büher [BUH70].

in figure 4.2. The fluorine ion in KF (figure 4.1) has a polarisability only about one fourth or less that of the iodine ion in NaI [WIL70]; both of the cations have a very small polarisability. ϵ_{∞} for KF is about 1.86 [LOW69], so the rigid ion approximation is not so bad. The NaI potential in figure 4.2 was fit to the transverse optic frequency, and the reproduction of that branch, as well as the acoustic branches, is fair. The longitudinal optic branch, however, is poorly represented. One could fit to the longitudinal optic frequency instead, but then the transverse modes would be out; Dixon demonstrates this for the case of NaI [DIX76a].

4.4.2 Density of phonon modes

The “experimental” phonon density of states for alkali halide crystals is determined by fitting a many-parametered (as many as 14) empirical poten-

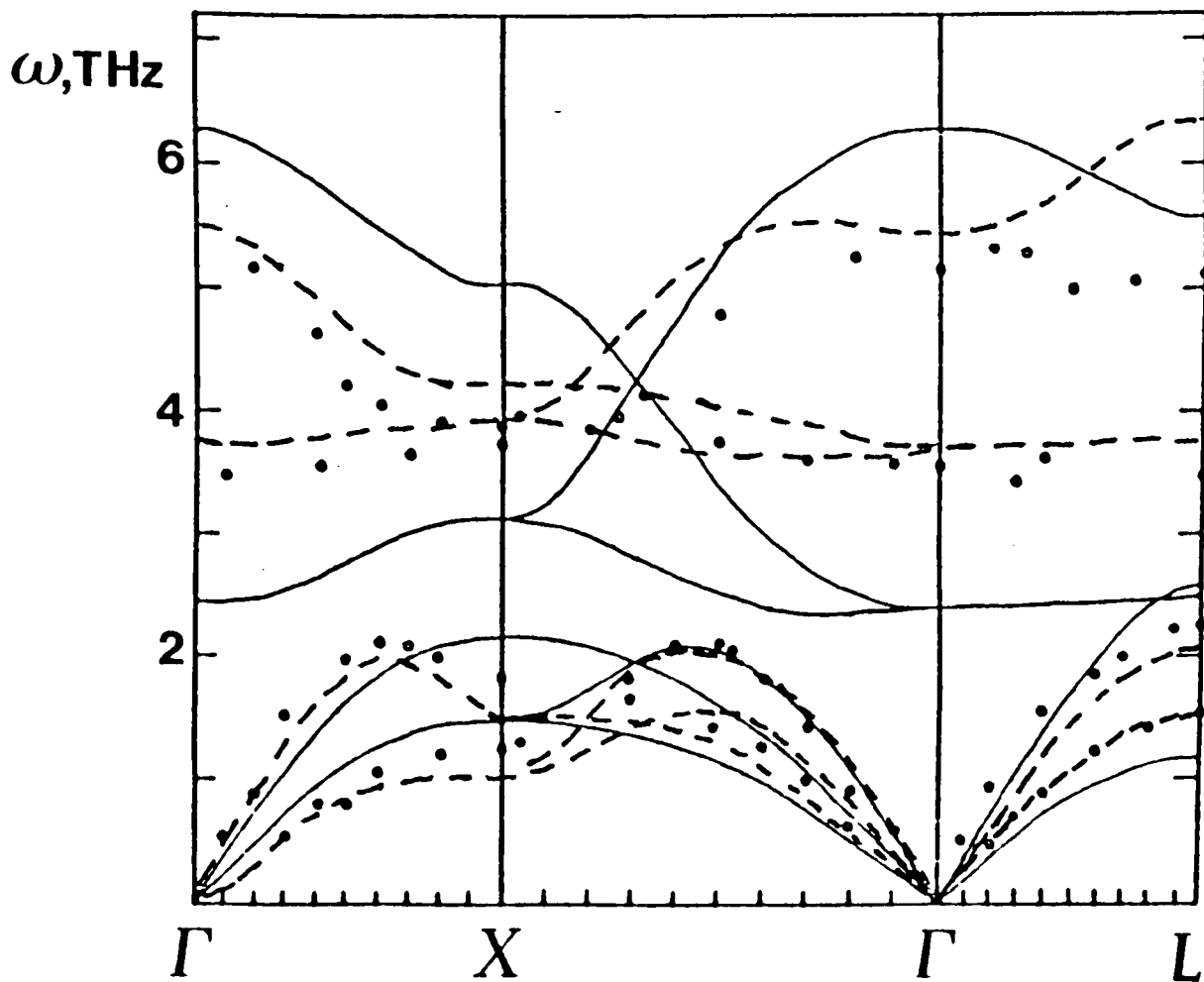


Figure 4.2 : Phonon dispersion relations for NaI at 100°K, after Dixon [DIX76a]. The rigid ion potential (solid curve) is unable to reproduce the experimentally observed phonon behaviour of this salt (points), especially in the optical branches. A shell model potential (dashed curve) can account for the ionic polarisability and model the phonon behaviour successfully.

tial (usually of the shell model type discussed below) to the measured phonon dispersion data [BIL79]. Standard lattice dynamics calculations are performed on this potential. The assumption is that the fitted potential will interpolate between the measured high symmetry points for phonon frequencies at arbitrary positions in the Brillouin zone.

The DOS is also accessible in MD simulations via the ion displacement or velocity autocorrelation functions [DIC69]. The theory of double-time thermal Green functions [ZUB60, ELL74, RIC80] within the harmonic approximation relates the spectrum of correlation functions to the trace of the related Green function, which in turn is shown to give the energy spectrum of excitations in the system. The mass-weighted velocity autocorrelation function for ions i of

mass m_i is given by

$$C_v(t) = \sum_i m_i \langle \mathbf{v}_i(0) \mathbf{v}_i(t) \rangle. \quad (4.5)$$

Its Fourier transform gives the density of phonon modes $\rho(\omega)$, weighted by frequency and thermal weighting factors:

$$\int_0^\infty \sum_i m_i \langle \mathbf{v}_i(0) \mathbf{v}_i(t) \rangle e^{-i\omega t} dt = \omega n(\omega) \rho(\omega) \quad (4.6)$$

where $n(\omega)$ is the Bose-Einstein factor:

$$n(\omega) = \frac{1}{\exp(\frac{\hbar\omega}{k_B T}) - 1} \quad (4.7)$$

The equations of motion of the displacement and velocity Green functions are related in a simple way [ELL74], leading to the similar result for the displacement autocorrelation function in the displacements $\mathbf{u}_i$ of ions i about their equilibrium positions:

$$\int_0^\infty \sum_i m_i \langle \mathbf{u}_i(0) \mathbf{u}_i(t) \rangle e^{-i\omega t} dt = \frac{n(\omega)}{\omega} \rho(\omega) \quad (4.8)$$

The separate contributions to the density of states from the cations and anions can easily be determined by restricting the sums in (4.6) or (4.8) to the desired species. This can be useful for recognizing and attributing features in optical spectra, such as the Raman spectrum.

The density of states is thus a computationally inexpensive but quite informative probe of the detailed dynamical behaviour of a simulation. Figure 4.3 shows the density of states collected from simulations of NaI crystals at 100°K with both a rigid ion and a more sophisticated potential, compared with “experiment.” The rigid ion density of states reflects the inadequacies in the dispersion curves above in figure 4.2; the energy gap in the density of states is missing, and only the lowest frequency acoustic phonons are modelled successfully. The *shell model* potential (discussed below) is much more successful; all the essential

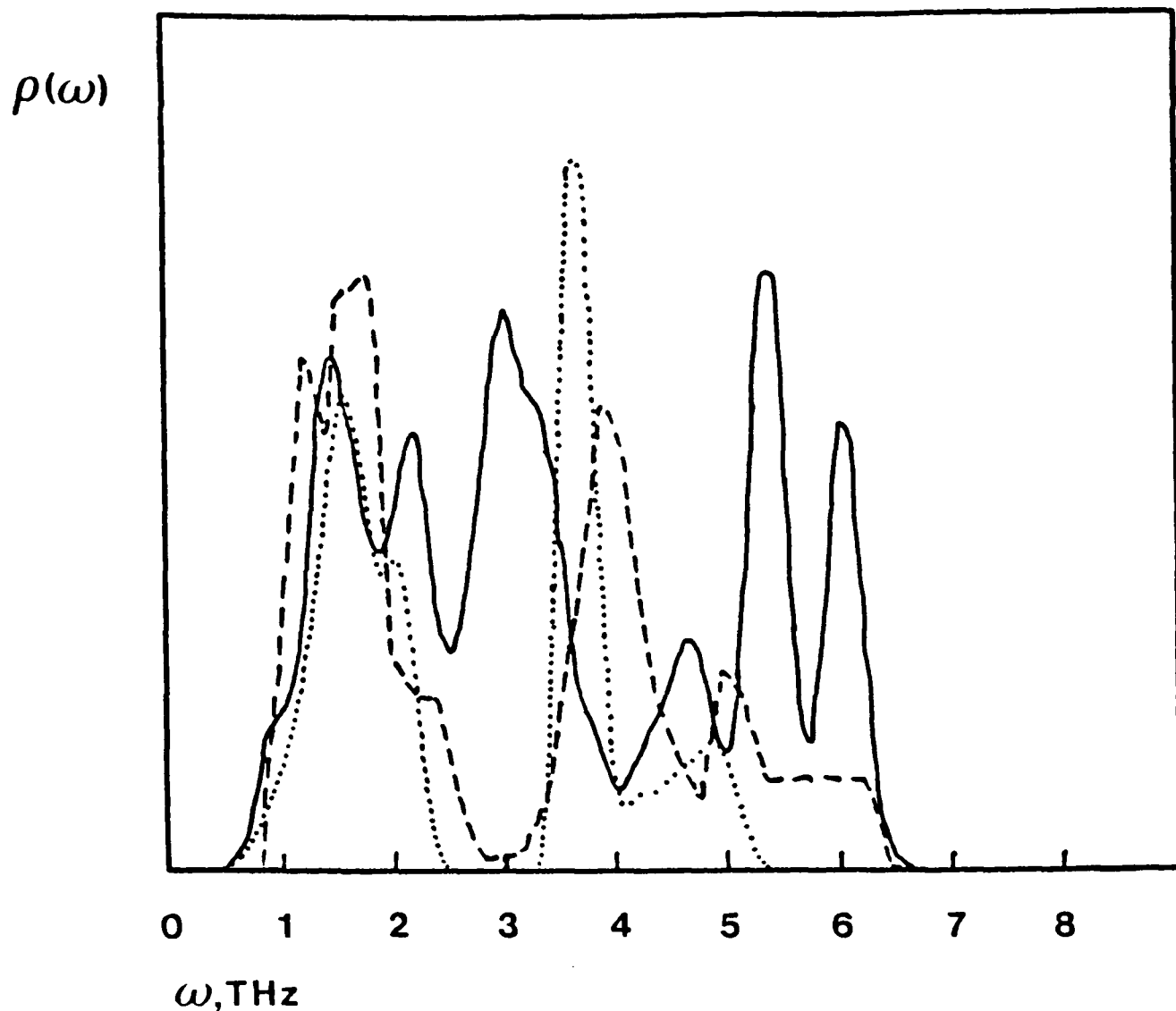


Figure 4.3 : Density of phonon states for NaI from experiment near 0°K (dotted line [BIL79]) and from simulations at 100°K using rigid ion (solid curve) and shell model (dashed curve) potentials. The simulation DOS curves were calculated from the displacement autocorrelation function (4.8).

features of the experimental spectrum including the energy gap are reproduced, although there is some broadening and frequency shift due to the temperature difference, and a high frequency tail to the density of states representing one failure of the simple shell model (also discussed below).

4.4.3 “Phonons” in liquids

In liquids, phonons do not exist. Nevertheless, there are measurable (via neutron scattering) collective excitations in ionic liquids [MCG84, 85]. When the frequency vs neutron wavenumber relation of these excitations is plotted for some alkali halides, the results are much like the phonon dispersion relations in high temperature crystals. The experimental demonstration of significant solid-like ordering in such melts suggests that it is not improper to treat these

excitations as “quasi-phonons” [MCG84, 85]. The spectrum of these excitations in melt simulations can be calculated in the same way as for crystals via the velocity auto-correlation function (4.6).

4.5 Polarizable ion, or shell model potentials

The failure of rigid ion models to reproduce accurately the phonon properties of most of the alkali halides led to the development of better potential models. These models include the ionic polarizability in some way, allowing especially for improved representation of the optic vibrational modes in these systems. As the polarizability is partly an electronic effect, and partly a mechanical one (due to ionic compression on collision), the successful models find ways of coupling electronic and mechanical degrees of freedom. Lyddane and Herzfeld failed in 1938 to account properly for the properties of alkali halides by considering only electronic polarizability and realised the need to treat both aspects [LYD38].

To avoid the complexity of the models that follow, attempts were made in this work to improve the vibrational properties of rigid ion potentials for NaI by exploiting the Lyddane–Sachs–Teller relation. By altering the mass of the ions (e.g., from 23 to 20 a.u. for Na) or their charges (e.g., to $\pm 0.75e$ instead of the usual fully ionic value of $\pm e$) it was indeed possible to bring the longitudinal and transverse optic frequencies both nearer the experimentally known values in low-temperature crystals (cf figure 4.2). When such potentials were used in room-temperature crystal simulations, however, the resulting DOS was not significantly improved over the actual Fumi–Tosi rigid ion potential results, although the errors were distributed differently. The unphysical basis of this approach and the lack of significant success with it led to its abandonment in favour of the “proper” polarizable ion potentials described next.

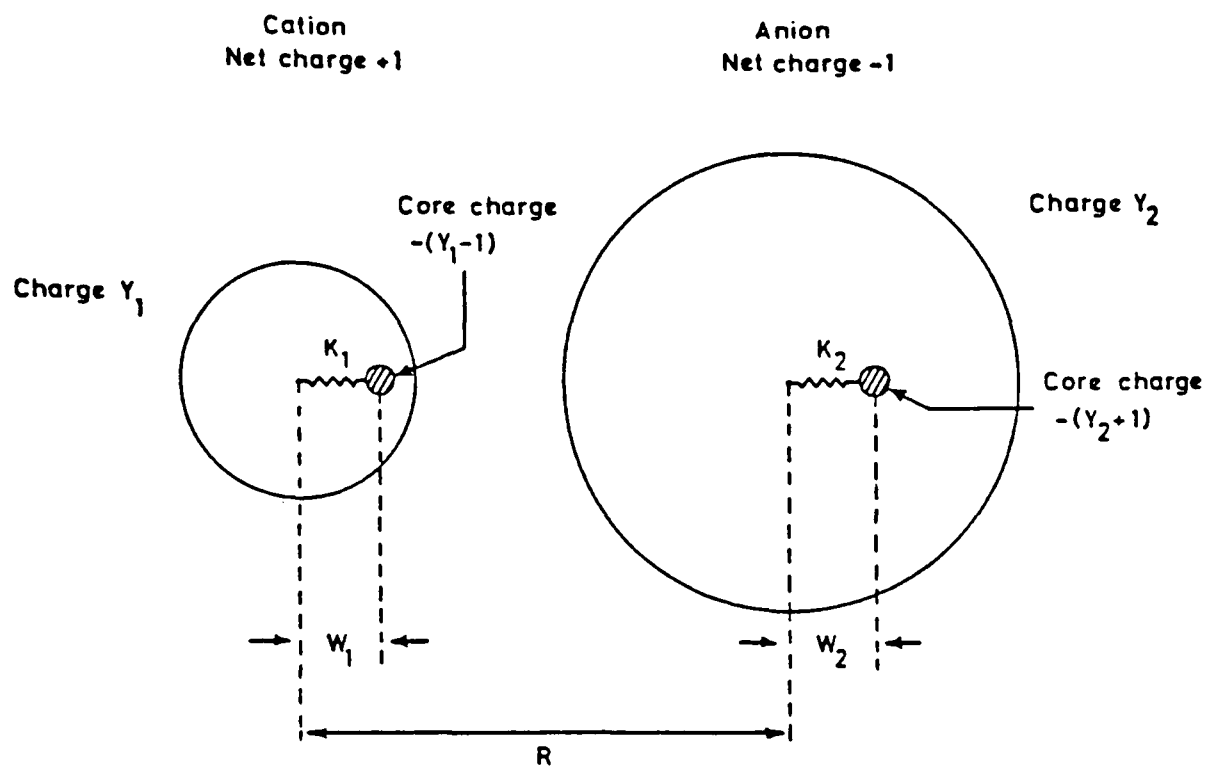


Figure 4.4 : Shell model potentials model ions as rigid, massive, charged cores surrounded by and attached via ‘springs’ to charged, massless shells, representing the outer electrons. From Sangster and Dixon [SAN76].

The *polarisable ion*, or *shell model potentials* are another class of two-body potentials that have proved useful in lattice dynamics studies. They were first introduced by Dick and Overhauser [DIC58], and generalised to their now standard form by Cochran [COC59, COC67]. They were invented to help understand the dielectric behaviour of alkali halides but were soon used to clarify the phonon properties of those salts for which the rigid ion models had proven inadequate [WOO60]. They have been used in simulation work since their introduction by Dixon and Sangster in 1975 in a study of NaI [DIX75, 76a].

The shell model hypothesizes a rigid, charged, massive ion core (as in the rigid ion model) surrounded by a charged, massless shell that is connected to the core via a “spring” (usually harmonic); see figure 4.4. The shells serve to represent some of the properties of the outer electrons of the ions and are free to move (subject to the constraint of the springs) separately from the cores. The short-range interactions, the result of overlap repulsion and Van der Waals attraction due to distortions of the electron “cloud”, are taken to act only between shells, and not cores, and are taken in the same functional form (Born–Huggins–Mayer) as for the rigid ion model potentials (4.4). In this way, both mechanical

and electronic polarisability are catered for. If the shell and core of ion i are displaced from each other by an amount w_i , this corresponds to an induced dipole moment $w_i e$ on the ion. In simulation work, this dipole moment is a dynamical quantity.

The shells interact with all other shells and cores via Coulomb forces. The cores interact with all other objects (shells and cores) in the system through Coulomb forces, and through harmonic springs with their own shells (anharmonic springs have also been considered in static calculations [BRU72a, b]). As the shells and cores respond to both electronic (through Coulomb forces) and mechanical (through short-range interactions between shells coupled to the cores by springs) effects, the model can hope to account for both the electronic and mechanical polarisability of the ions. As the local environment of an ion alters its interactions with other ions, the shell model is a means of incorporating many-body effects indirectly into simulation work. Basu describes the three- and four-body effects manifested in the simple shell models [BAS74].

The net charge on each core-shell unit is ± 1 , or nearly so, but there is freedom in choosing the actual value of the core and shell charges, subject to the constraint that their difference is about 1. These charges and the spring constants are fitted to such experimental data as the high and low frequency dielectric constants, and the $q = 0$ transverse optic frequency [SAN76]. This extra freedom in the shell model to fit to both the high and low frequency dielectric constants allows the model to overcome the inherent limitations of the rigid ion model on optic branch separation. The fitting criteria for shell model potentials used in simulation work are necessarily different from those used to parameterise static lattice dynamics shell model potentials [SAN76].

For a salt such as NaI with a small cation and a large anion, only the highly polarisable iodine ion need be given a shell; the much smaller and less polarisable sodium ion can be treated as rigid, resulting in a significant savings

in computation in simulation work. A proper treatment of a salt such as CsCl, however, requires that both ions be given shells. Dispersion relations for such potentials are far superior to those obtained from the simpler rigid ion potentials; the ability to fit to both optic frequencies results in substantial improvement in the calculation of phonon properties. Results for NaI are shown in figure 4.2; compare with the rigid ion results there.

The simple shell models are not the final word in alkali halide potentials, however. Examination of the simple shell model dispersion curves for NaI (figure 4.2) reveals poor agreement on the longitudinal optic branch in the $[\zeta\zeta\zeta]$ direction between the symmetry points Γ and L. This branch accounts for the high frequency tail in the shell model DOS in figure 4.3. These particular modes can be improved through use of the *breathing shell model* of Schröder [SCH66], introduced in a treatment of the Γ -L branch of NaI, which allows the shells as in the simple shell model described above to expand and contract, or “breathe,” isotropically. There are new potential parameters associated with this breathing, which in some ways represents isotropic distortions of the electron cloud around an ion, although the developers of the model are reluctant to ascribe too serious a physical interpretation to the breathing action [SAN76]. Inclusion of this effect in lattice dynamics calculations leads to complete agreement with the measured phonon dispersion curves for most salts within experimental error. Dixon wrote code to implement the breathing shell model in simulation work for NaI but deemed it too expensive to run, given the minor improvement in phonon properties expected and the large uncertainties involved in extrapolating any lattice potentials for use in melts [DIX83d].

The *deformable shell model* [SAN74] has been used in some lattice dynamics work; this allows the shells to distort anisotropically in addition to breathing. This is the only model described here capable of accounting properly for the Cauchy violation in the elastic constants of some alkali halides [SAN76] but is

too complex to use in simulation work. Further potential models additionally allow charge transfer between ions; these and other extensions are reviewed by Basu [BAS74].

For simulation work, an alternative to the shell model approach for accounting for ionic polarisability was advanced by Jacucci [JAC74, 76]. This method expands the polarisability in a power series in the ionic displacements. Some results were obtained this way, but the approximations involved are significant; this path has not been followed in the present work.

Shell model potentials have been used successfully in simulation work, but they are much more expensive (about an order of magnitude in computer time) than the simpler rigid ion models. There are a number of complications induced by adapting these lattice dynamics potentials to dynamical simulation work; most centre on the nature of the shells.

As the shells are a representation of the outer electrons of an ion, it is sensible to treat them within the *adiabatic approximation*, which asserts that the light electrons move on a timescale orders of magnitude faster than that of the heavy ion cores. As the simulations are carried out in “ionic time” rather than “electronic time,” the electrons should feel no net force on the timescale of a simulation timestep. The electrons, and thus the shells, are taken to be able to relax instantaneously to adapt to changes in the ionic configuration. In lattice dynamics work, the shells are taken to be completely massless so they cannot experience a net force. The prescription to achieve the same effect in simulation work is more involved [DIX76a]. ²

Dixon developed this procedure to allow the shells to relax to their equilibrium configuration at each timestep [DIX76a]:

² The shells are conceptually massless in the shell model potentials for simulations, but a shell mass value never enters into the dynamical equations for ionic motion. The “masslessness” assumption is simply a restatement of the adiabatic approximation, and must be implemented by the procedure described here.

- 1 The ion cores (only) at each timestep are moved according to the MD algorithm in use, as for rigid ion model simulations.
- 2 The shells are given initial displacements equivalent to those of their cores.
- 3 The force F_i on each shell i is determined.
- 4 The position of each shell is relaxed against its own core through the “spring” connecting the two in a direction to relieve the net force, by an amount $\Delta w_i = aF_i/K$. (K is the spring constant.)
- 5 The force on each shell is recalculated, and the shell movement procedure iterated until the net force on all shells is arbitrarily small.

The above procedure is found to work well if the relaxation constant a is about .75; this avoids “overshoot” and excessive oscillation in the shell relaxation process that tend to appear when $a = 1$. Typically four or five iterations of the procedure are needed at each timestep to achieve satisfactory shell relaxation. The procedure is expensive in computer time and accounts for the order of magnitude increase in computation needed to simulate with shell models instead of rigid ion models.

In his alkali halide work, Dixon considered only melt systems. It was necessary in the current work to investigate the behaviour of shell model potentials in crystal simulations, to confirm that these potentials really did improve the vibrational properties of simulations over rigid ion model work. It proved challenging to use these potentials in crystals; equilibration between ion species was especially difficult to obtain. No simple explanation is offered for why it is harder to achieve equilibrium with shell model potentials than for rigid ion ones; the shell motion prescription (above) perhaps interferes with energy exchange between species as all the short range interaction energy is calculated at the shell positions, and transmitted to the cores via the springs. Satisfactory results were obtained by performing velocity rescaling (section 2.8) separately on cations and

anions for a time at the beginning of the equilibration phase of a new run.

4.6 Temperature dependence of phonons and potentials

A fundamental assumption of this simulation work on melts is that the potential models initially derived for use in low temperature crystals will also model the interactions in a high temperature melt. As proper vibrational behaviour is essential for good ion dynamics, it is necessary to examine the properties of phonons and potential models at elevated temperatures in crystals and in melts.

There is a substantial body of experimental data on the phonon properties of low-temperature alkali halide crystals. There is not, however, much data to illuminate the behaviour of the lattice vibrations at higher temperature. There are experimental difficulties in taking neutron spectra at higher temperatures; some vibrational modes experience very significant broadening as the temperature increases [WOO63]. What is known from the high temperature data available is that the effect of temperature is not trivial; different branches of the phonon dispersion relation move at different rates as a crystal is heated [WOO63]. Anharmonicity in the interionic potentials as well as environmentally varying ionic polarisability can cause these effects. As there is not much high temperature data even for the crystals, other means must be derived for judging the quality of melt simulations.

It is possible to determine whether or not the simulations are consistent with the expected behaviour of the model potentials at elevated temperatures. In an investigation of the anion-only shell model of NaI, the AERE Harwell PHONONS program was used to calculate the dispersion relation for this potential as the lattice parameter was varied to account for observed expansion of the crystal at high temperature. The results are in figure 4.5; as the temperature rises, the different branches of the dispersion relation do move significantly,

and at different rates. The energy gap between the optic and acoustic modes, an important feature of low temperature optical studies of NaI, apparently disappears at around 800°K. Simulations were performed at corresponding temperatures and the density of states calculated; the shift in peak positions and the disappearance of the energy gap indicated that the simulations continued to represent properly the dynamical behaviour of the potential model even at elevated temperature. Analysis of the “DOS” in the melt compared with the high temperature crystal shows a gradual, rather than dramatic, change in the excitation spectrum on melting, after allowing for low-frequency diffusive motion. So one concludes that the vibrational properties of the melt simulations are reasonable, given the potential model.

The important question, of course, is whether or not the shell model’s high temperature behaviour, which the simulations reproduce faithfully, is an accurate representation of what happens in NaI at elevated temperature. There is no direct answer to that question. Indirect evidence that the model’s behaviour is reasonable comes from consideration of other dynamical properties successfully reproduced by the simulations, especially the dynamical structure factors [DIX83a, b, c]. Confidence would increase if agreement in some dynamical high-temperature properties was found to improve dramatically when shell models, rather than rigid ion models, were used in simulation work. There is, as of yet, no single property that provides a convincing demonstration of this; the work in chapter 5 on the Raman spectrum is an attempt to find one.

The primary justification of the use of lattice potentials in melts remains the success of the results obtained. Systematic study of the high-temperature phonon properties of alkali halides could help to improve this situation.

4.7 Structure of alkali halide melts

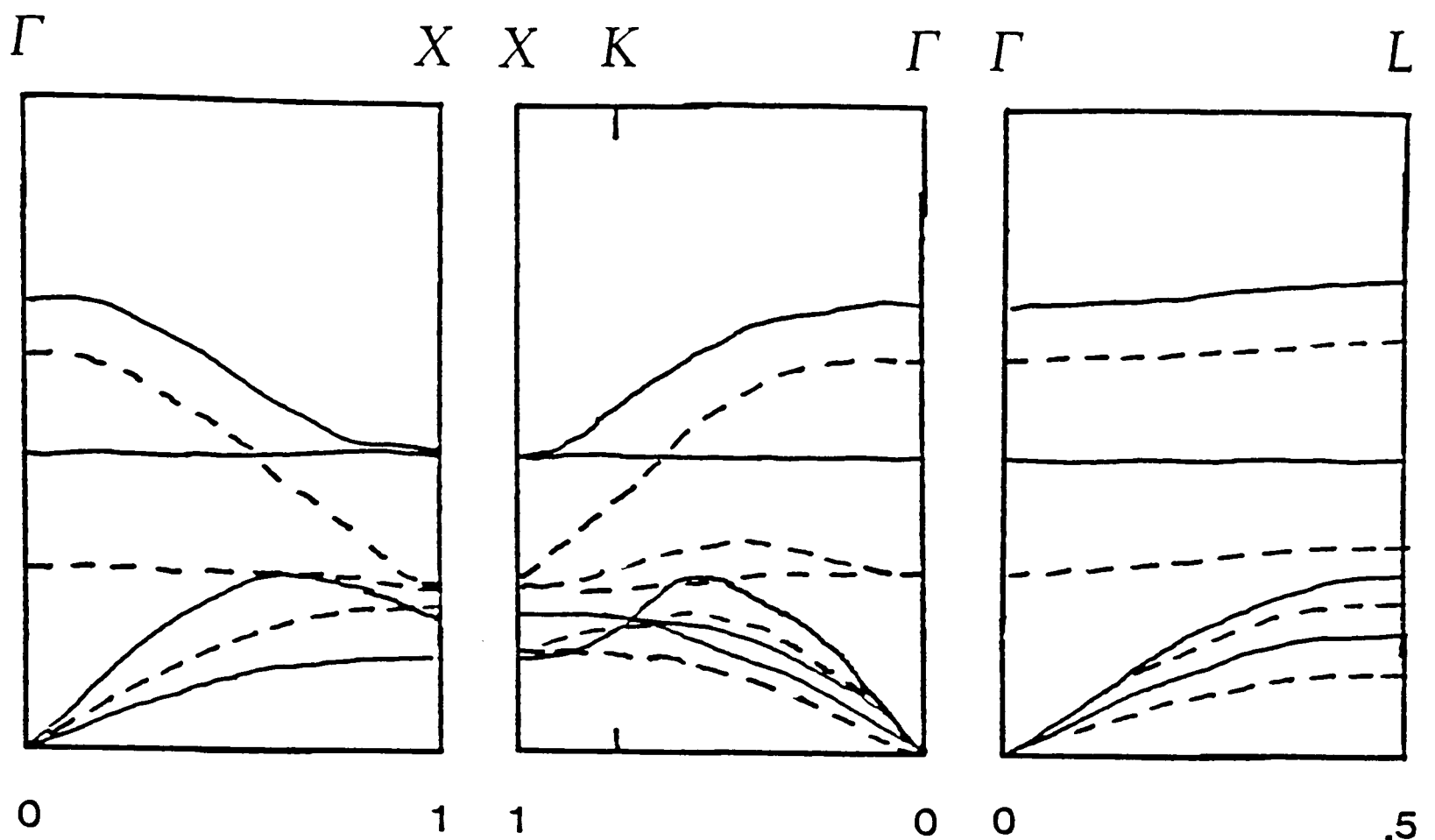


Figure 4.5 : Temperature dependence of phonon dispersion relations of a good shell model potential for NaI. Phonon dispersion relations calculated at 0°K (solid lines) shift significantly when the lattice parameter in the lattice dynamics calculations is changed to a value appropriate to about 800°K (dashed lines). Different branches move at different rates as the lattice expands on heating; the pronounced 0°K energy gap is gone at 800°K. Systematic experimental studies of high temperature phonon dispersion have not been performed.

Much has been learned about the structure and physical properties of alkali halide melts since the first MC and MD simulation studies in 1971 [WOO71a, b]. Sangster and Dixon [SAN76] survey all simulation work on alkali halides through 1976, and Baranyai *et al.* [BAR86] review all information on static and structural properties gathered from simulations through early 1985.

The most important result of the simulation studies of melts is that these systems are charge ordered. The radial distribution functions of these melts indicate that each ion, on average, is surrounded by spherical shells of ions of the other charge, as in the crystal. The distances of these charge shells are consistent with those found in high temperature crystals as well. Neutron studies

of some alkali chloride melts [DER75, EDW75, MIT76, BIG82, LOC85]³ have confirmed this picture of the melts as “hot crystals,” rather than completely disordered systems. Figure 4.6 is a typical example of what is found; here, the experimental and computationally determined radial distribution functions of RbCl are compared. This charge ordering is quite long ranged, extending noticeably in both the neutron and simulation observations for at least four or five atomic shells (the limit of computer simulation system sizes). Clarke has recently shown [CLA86] that, contrary to the common assumption that this long-range ordering was mediated primarily by the long-range Coulomb force, the charge ordering can be a consequence only of short-range forces.

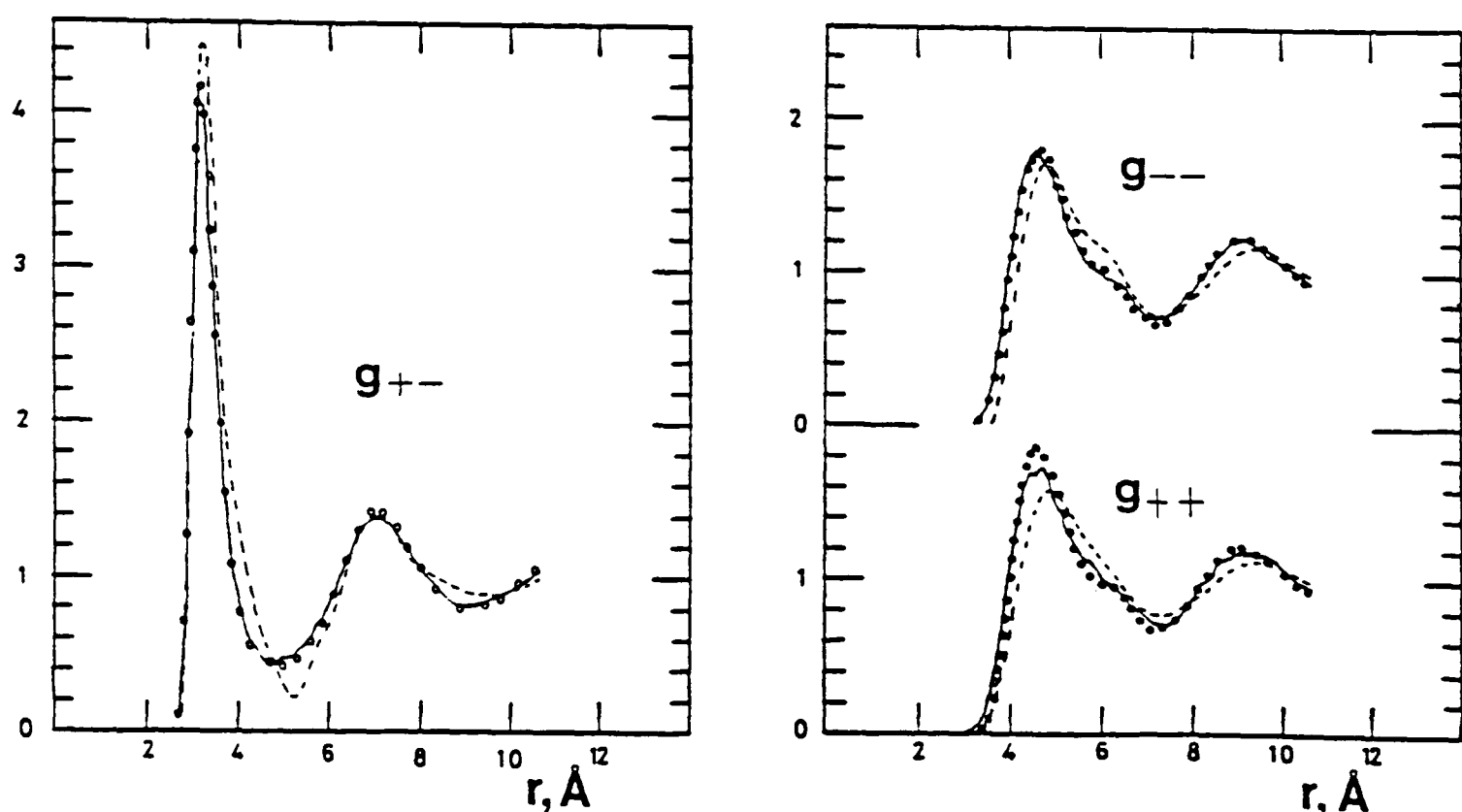


Figure 4.6 : Partial radial distribution functions for RbCl from neutron experiment of Mitchell *et al.* [MIT76] (dashed lines) and MD simulations of Dixon and Sangster [DIX77a] using shell model (solid lines) and rigid ion model (open circle) potentials. Charge ordering for at least four ionic shells is evident. From Dixon and Sangster [DIX77a].

³ The partial radial distribution functions $g_{\alpha\beta}(r)$ are available for those materials for which the technique of *isotopic substitution* can be used to separate the contributions due to each atomic interaction type [LOC85]. The chlorides are the only alkali halides accessible to these studies to date.

Closely related to the radial distribution functions are the structure factors $S_{\alpha\beta}(k)$; these are also available experimentally for some salts and from computer simulation [SAN76]. The dynamical structure factors, available from simulations and neutron work, allow determination of quasi-dispersion curves for alkali halide melts [DIX83a; MCG84, 85]. Dixon has exhaustively studied further dynamical properties of NaI via simulation, such as the mass, charge, particle number, and current correlations [DIX83b, c].

As indicated above in section 4.5, this work has demonstrated that it is possible for melt simulations to reflect realistically the dynamical properties of the potential models used in them. Although there are problems associated with performing shell-model simulations of alkali halides, they can be overcome to the point that reasonable ion dynamics can be obtained. It is certainly possible to model the dynamics in crystals well with these techniques.

4.8 Simulations performed

In the course of this work, simulations have been performed on a number of alkali halide systems, in solid and liquid states, with several potential models at various temperatures. Many of these simulations were developmental, however, and have yielded no new results. The work reported on in this thesis is based on simulations of LiF, NaCl, NaI, and CsCl. Details of these simulations, including the potentials and all other parameters used, are given here, along with a physical characterization (e.g., $g_{\alpha\beta}(r)$), of each.

NaI has been the object of particular study in chapter 5, where attempts are made to connect the shell model potentials with ionic polarisability and thereby the Raman scattering via the shell-core dipole moment. As was pointed out above, NaI is computationally attractive since the cations can be treated as rigid, leaving only the anions with shells, resulting in a significant savings in

computer time. Nevertheless, the large polarisability of the anion leads to expectations of significant effects on inclusion of this polarisability through the shell model. The interesting properties of the low-temperature phonons, especially the pronounced energy gap (figures 4.2 and 4.3), are another reason for choosing NaI.

LiF and NaCl are the subject of investigations in chapter 6 of possible mechanisms for Raman scattering in melts from an atomic polarisability viewpoint. These salts are accessible to electronic structure calculations; NaCl represents the current state of the art in this field, as is discussed in chapter 6. At present, LiF and NaCl are the only salts for which polarisability data from electronic structure calculations are available; this explains their choice.

CsCl is a difficult case discussed briefly in the final chapter; the weight of experimental and simulation evidence suggests that it is not proper to regard CsCl as a fully ionic system.

Physical data for the simulations has come from several sources. For crystal simulations, the cell size is determined by the lattice parameter, which has been accurately measured as a function of temperature with and tabulated in crystal structure handbooks [HEL73]. For melts, temperature-dependent density data has been compiled in Janz's *Molten Salt Handbook* [JAN67], a valuable source of physical data. An error in the labelling of the density table in this handbook, however, necessitated consultation of the original research reports, especially [YAF56], to confirm the values found in the handbook. All physical parameters relevant to the seven simulations are given in table 4.1.

Table 4.2 reports all potential parameters used in the seven simulations. All of the potentials used are documented in the literature; references are given in the table. Note that the same potential parameters apply regardless of temperature, so, for instance, a single set of potential parameters in table 4.2 characterises both of the LiF simulations. The differences between crystal and melt

Physical Parameters for Simulations							
salt	temp °K	# ions	box Å	timestep 10^{-14} sec	# timestep	cation mass amu	anion mass amu
LiF xtal	298	216	12.079	.2815	5600	6.941	18.9984
LiF melt	1170	216	13.824	.3447	5600	6.941	18.9984
NaCl xtal	300	216	16.920	.4667	19600	23.0	35.45
NaCl melt	1181	216	19.125	.5609	16800	23.0	35.45
CsCl melt	968	216	22.255	.5633	2150	132.9054	35.45
NaI melt1	973	216	21.500	.5348	10000	23.0	126.9
NaI melt2	973	216	21.500	.5348	10000	23.0	126.9

Table 4.1 : Physical parameters for simulations. The seven simulations from which results have been obtained in this thesis are characterized by these values. The box size for crystals is determined from X-ray data; box sizes for melts are determined from density data.

simulations are solely in the physical parameters in table 4.1. The shell model simulations of CsCl and NaI use the same form of potential for the short range interactions as the rigid ion simulations; this form is given by equation (4.4), and all parameters in the top portion of table 4.2 refer to that equation.

The additional parameters for the shell model are the shell charges Y and spring constants K . Both the cation and anion have shells in the CsCl simulation; only the anion has a shell in the NaI simulations. The two NaI simulations are quite similar; the potential used in the first NaI simulation is known to be slightly mis-parameterised [DIX76a], but Dixon and Sangster continued to use this potential in addition to the corrected second potential as a check of the sensitivity of measured quantities to changes in the potential parameters. The two NaI potentials differ most sharply in the anion-anion interaction; note the differences in $g_{--}(r)$ in the subsequent figures. The net charge of each ion-shell combination is given in the rows labelled Z_+ and Z_- ; for all of these salts, $Z = \pm 1$. The actual charge on the core is such that the sum of the core and

shell charges Y_+ or Y_- is ± 1 as appropriate.

The spring constants are reported in terms of the quantity K/V to conform with the convention in lattice dynamics work; V is the volume of the unit cell of the salt at 0°K. Note that $V = 2a_0^3$ for NaCl structure salts, and $V = 8a_0^3$ for CsCl structure salts.

Each simulation is further characterized by plots of the radial distribution functions, the mean-square displacements, the energy fluctuations, and the vibrational mode spectrum (except for CsCl, as the simulation is too short for good statistics on such a dynamical property). For all except CsCl, the plots are from the “production” section of the simulation, after the equilibration phase. For CsCl; $g(r)$ is taken from a few hundred timesteps after the equilibration; the mean-square displacement and energy fluctuations are plotted for the duration of the simulation. For CsCl, the effects of intervention during the equilibration phase are evident: the temperature is deliberately set too high at the beginning of the simulation to ensure melting; it is gradually lowered as the simulation progresses (thus the falling kinetic energy). The changing temperature is responsible for the changing slope of the mean-square displacement function, which is related to the ionic conductivity.

These pictures indicate that the simulation tools developed for melt simulations also work quite well for crystal systems if proper precautions are taken during the equilibration phase.

Values for parameters relevant to the ionic polarisability models used in the determination of Raman spectra which do not affect the dynamics of the simulations are reported in chapter 6.

Potential Parameters for eq. (4.4)					
	LiF	NaCl	CsCl	NaI 1	NaI 2
Potential Type†	FTM	FTM	2PIM	1PIM	1PIM
Reference	[SAN76]	[SAN76]	[DIX77b]	[DIX76a]	[DIX76a]
Z_+, e	+1	+1	+1	+1	+1
Z_-, e	-1	-1	-1	-1	-1
$B_{++}, 10^{-12}\text{erg}$	158.514	679.35	30506.58	500.8	1753.3
$B_{+-}, 10^{-12}\text{erg}$	366.876	2012.87	37198.73	8530.59	2884.7
$B_{--}, 10^{-12}\text{erg}$	673.684	5591.25	42524.0	136228	4449.5
$C_{++}, 10^{-12}\text{erg } \text{\AA}^6$	0.073	1.68	152.0	1.68	1.68
$C_{+-}, 10^{-12}\text{erg } \text{\AA}^6$	0.8	11.2	129.0	19.1	19.1
$C_{--}, 10^{-12}\text{erg } \text{\AA}^6$	14.5	116.0	129.0	392.0	392.0
$D_{++}, 10^{-12}\text{erg } \text{\AA}^8$	0.03	0.8	278.0	0.8	0.8
$D_{+-}, 10^{-12}\text{erg } \text{\AA}^8$	0.6	13.9	250.0	31.0	31.0
$D_{--}, 10^{-12}\text{erg } \text{\AA}^8$	17.0	233.0	260.0	1100	1100
$\sigma_{++} = \sigma_{+-} = \sigma_{--}, \text{\AA}^{-1}$	0.2990	0.3170	0.2847	0.2980	0.3427
†FTM: Fumi-Tosi rigid ion mode 2PIM: Shell Model (cation and anion) 1PIM: Shell Model (anion only)					
Shell Model Charges Y and Spring Constants K					
Y_+, e	-	-	-7.754	-	-
Y_-, e	-	-	-2.3320	-3.045	-3.045
$K_+/V, \text{\AA}^{-3}$	-	-	23.102	-	-
$K_-/V, \text{\AA}^{-3}$	-	-	1.675	1.312	1.312

Table 4.2 : Potential Parameters. Discussed in text.

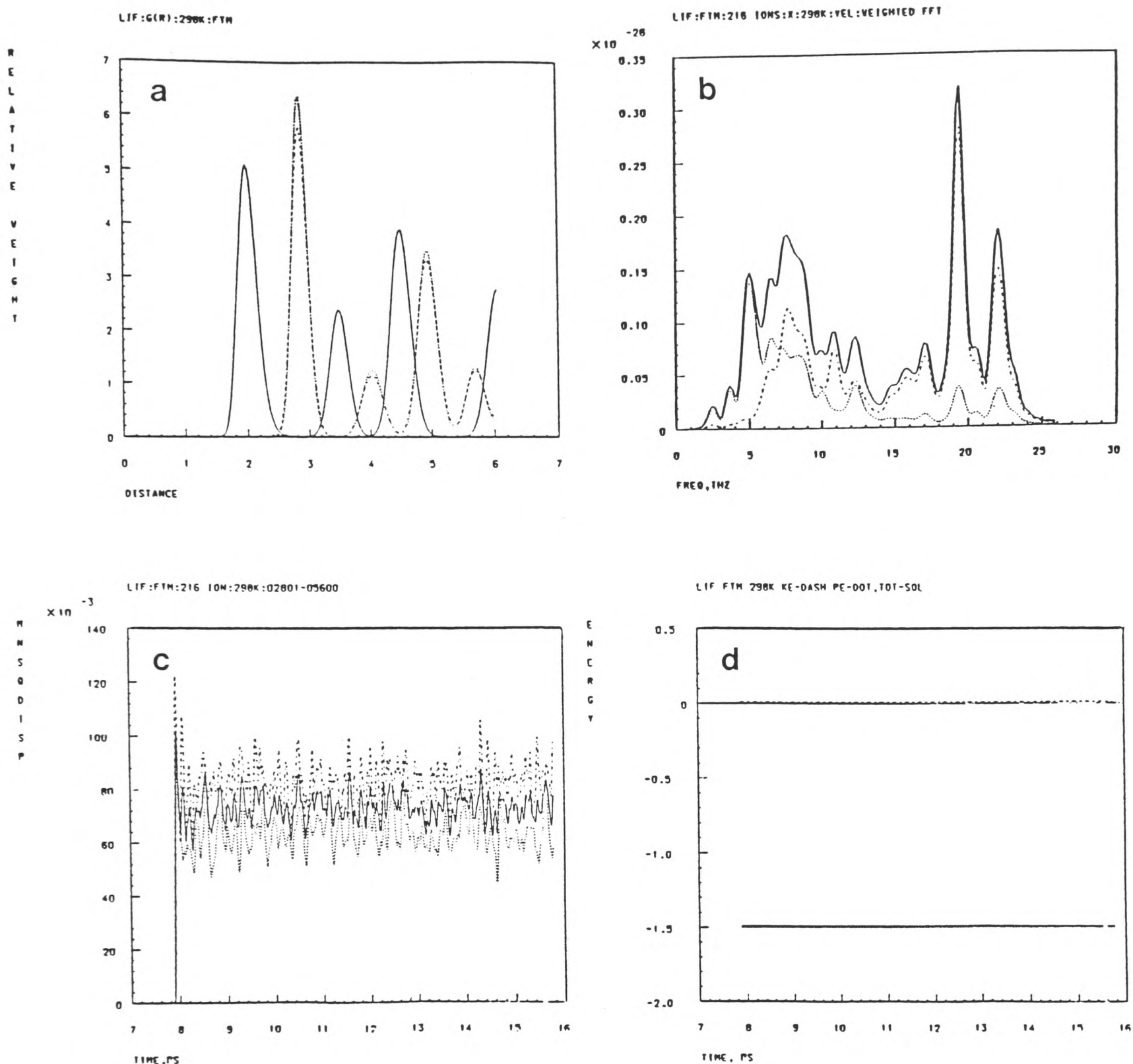


Figure 4.7 : Figures characterizing simulation of 216 ions of LiF crystal with a Fumi-Tosi rigid ion model potential, at 298°K. a) Radial distribution functions $g_{+-}(r)$ (solid), $g_{++}(r)$ (dashed), $g_{--}(r)$ (dotted). b) Phonon density of states $\rho(\omega)$: total (solid), cation (dashed), anion (dotted). c) Mean square displacement $\langle r^2 \rangle(t)$: total (solid), cation (dashed), anion (dotted). d) Energy stability: total (solid), kinetic (dashed), potential (dotted).

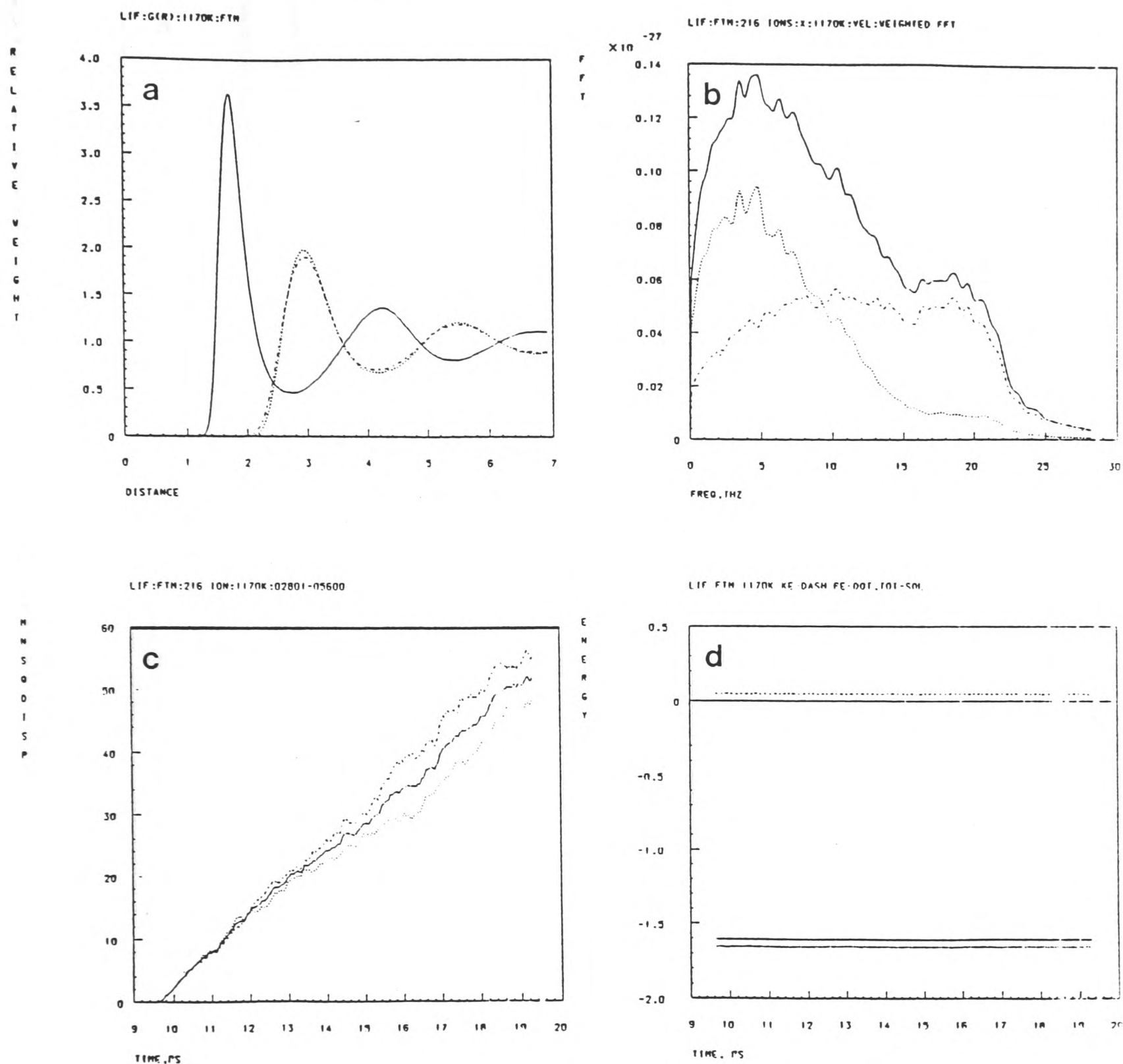


Figure 4.8 : Figures characterizing simulation of 216 ions of LiF melt with a Fumi-Tosi rigid ion model potential, at 1170°K. As figure 4.7.

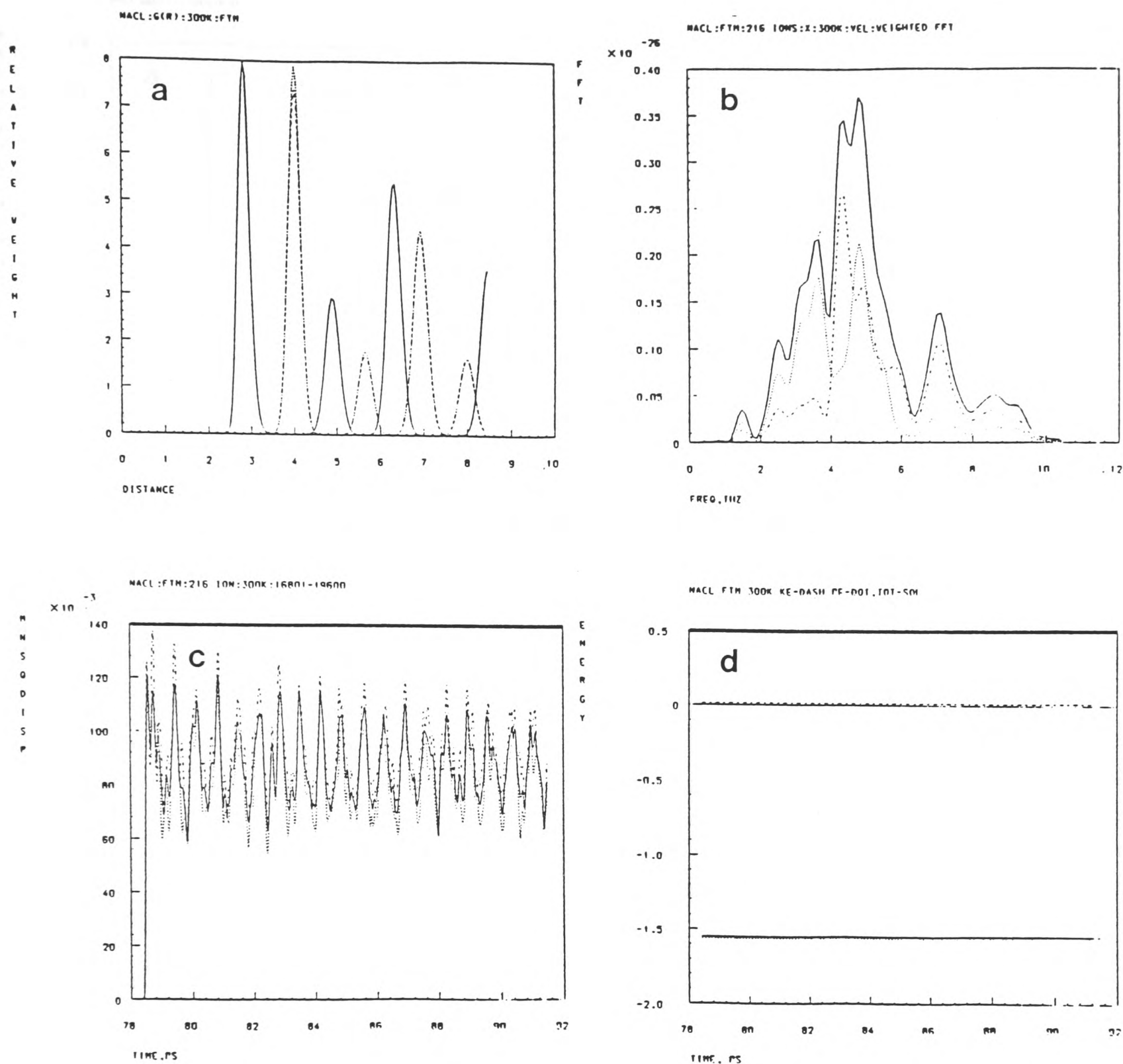


Figure 4.9 : Figures characterizing simulation of 216 ions of NaCl crystal with a Fumi-Tosi rigid ion model potential, at 300°K. As figure 4.7.

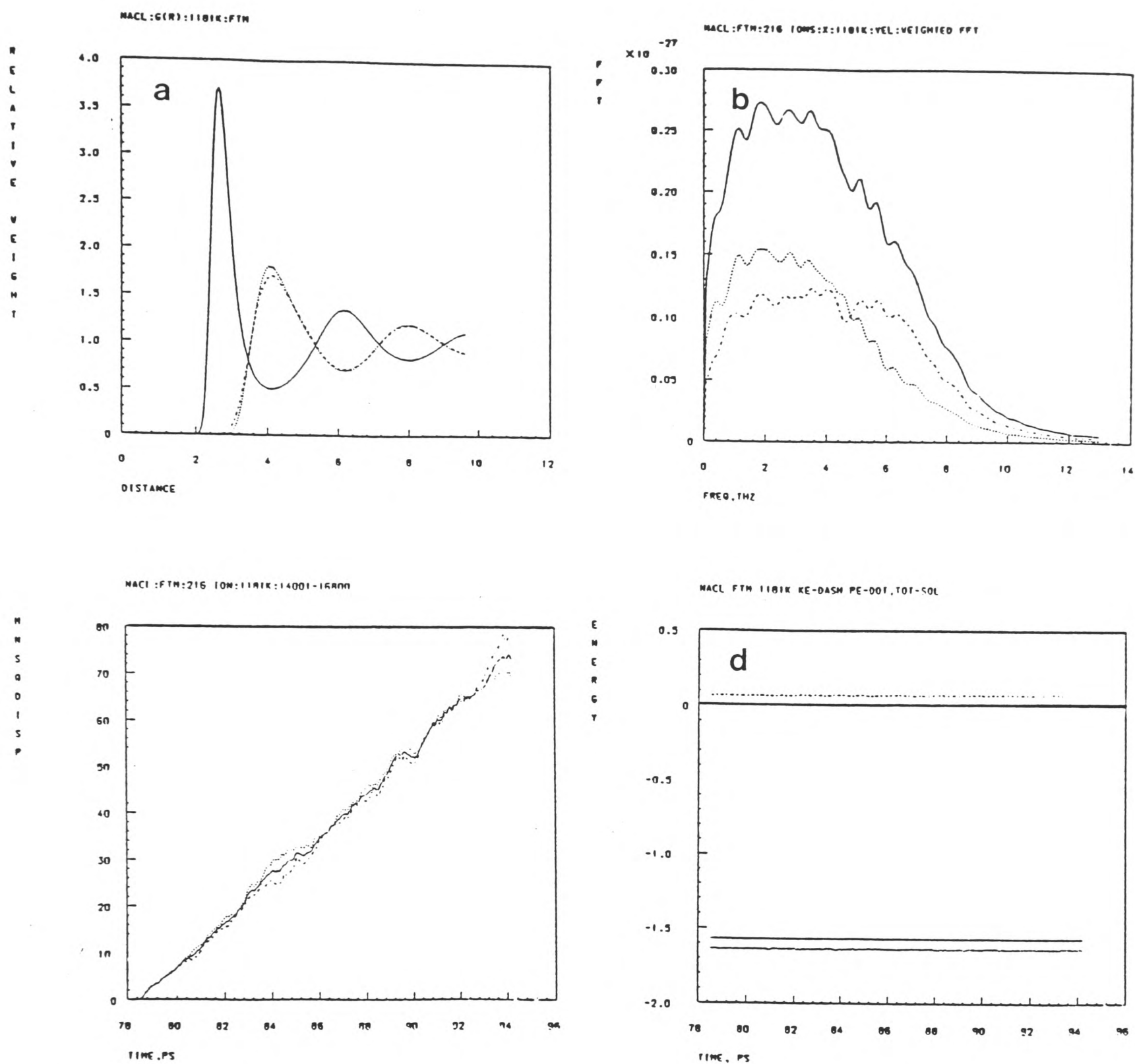


Figure 4.10 : Figures characterizing simulation of 216 ions of NaCl melt with a Fumi-Tosi rigid ion model potential, at 1181°K. As figure 4.7.

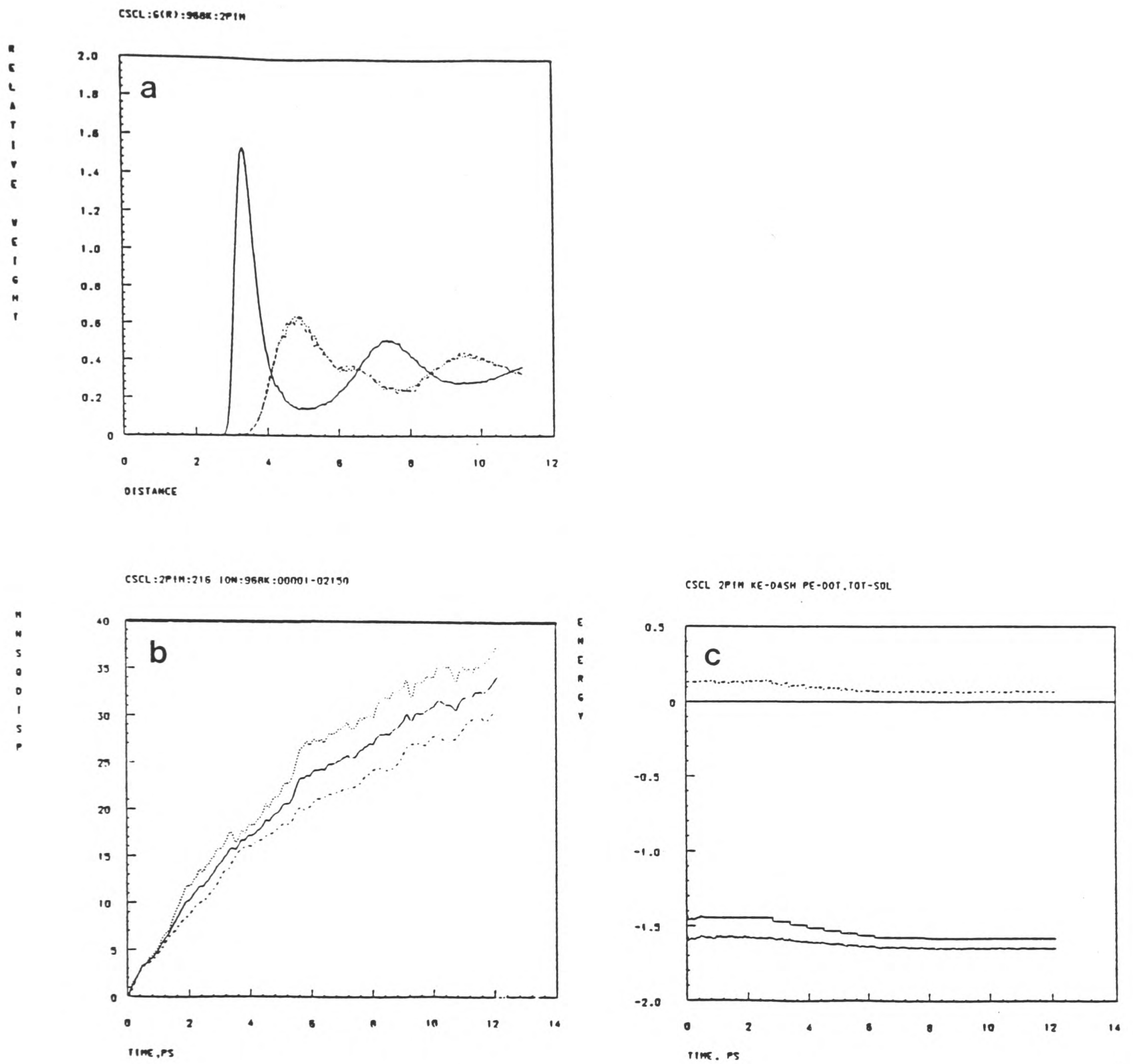


Figure 4.11 : Figures characterizing simulation of 216 ions of CsCl melt with a cation and anion shell model potential, at 968°K. As figure 4.7, except no density of modes.

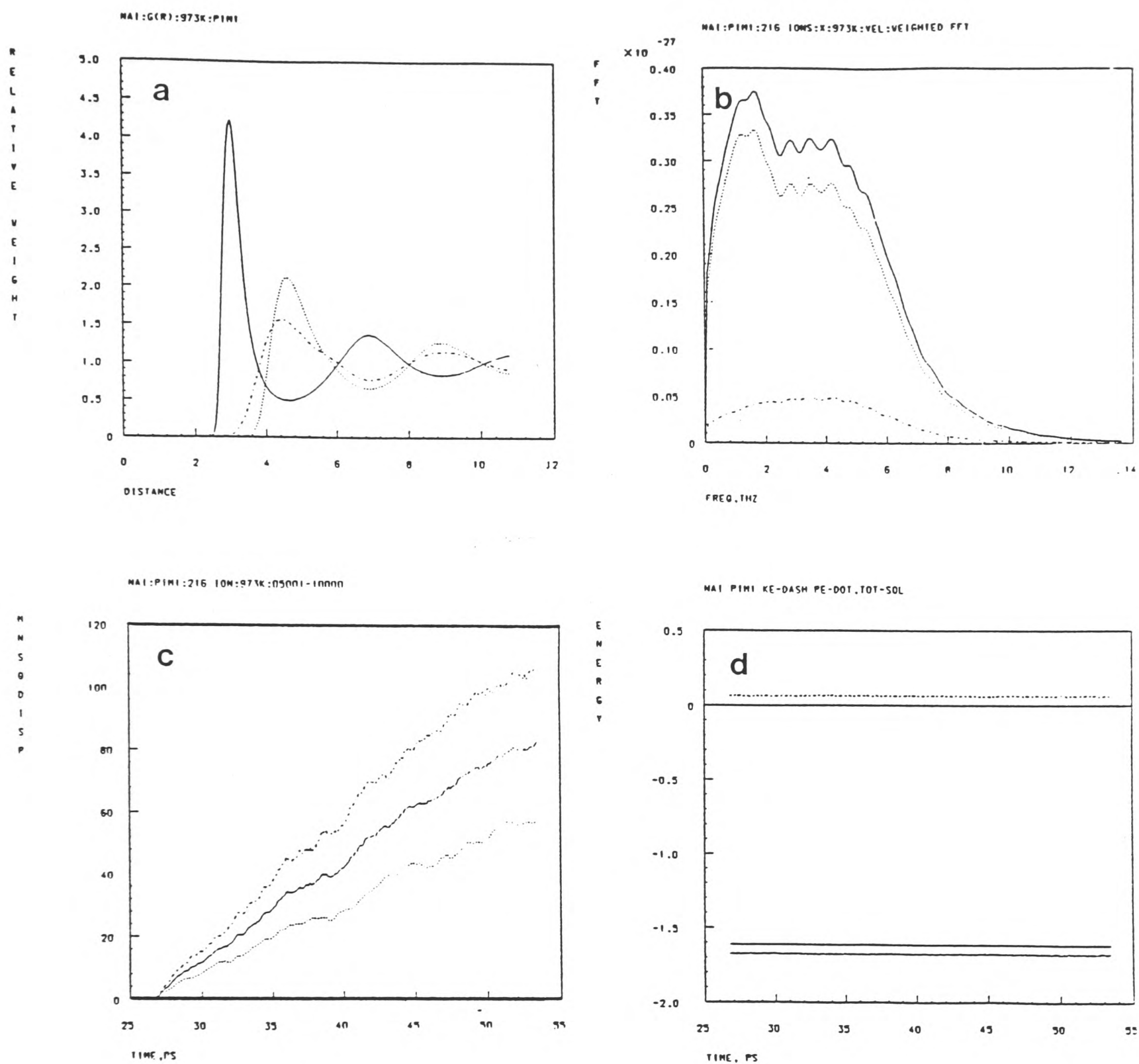


Figure 4.12 : Figures characterizing simulation of 216 ions of NaI melt with anion-only shell model potential # 1, at 973°K. As figure 4.7.

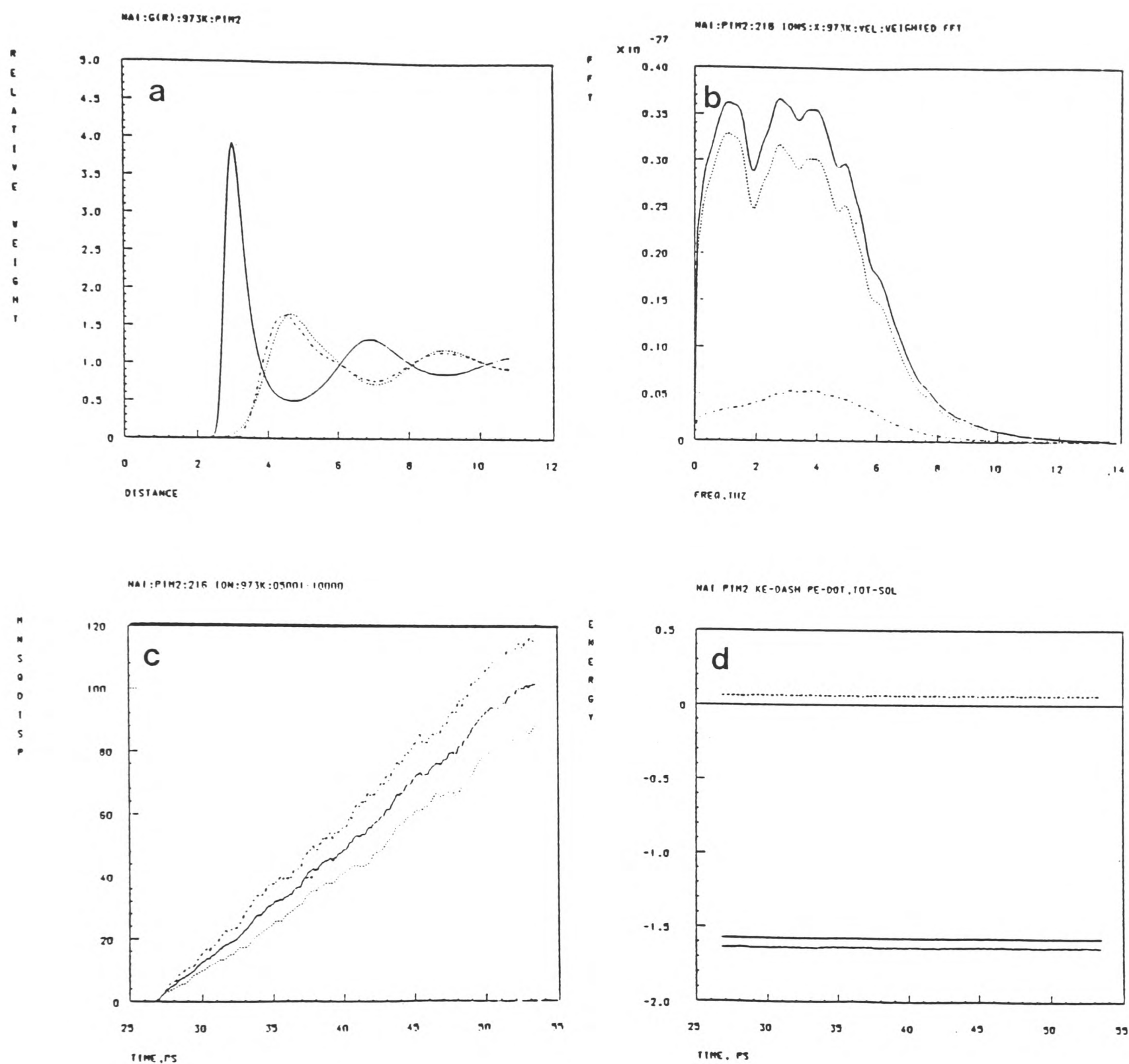


Figure 4.13 : Figures characterizing simulation of 216 ions of NaI melt with anion-only shell model potential # 2, at 973°K. As figure 4.7.

5 Shell model Raman calculations

5.1 Shell model dipoles

The previous chapter established the need to use polarisable ion, or shell model, potentials in MD simulations of some alkali halides with at least one highly polarisable ion if proper lattice dynamics are to be obtained. The extreme polarisability of the I^- ion in NaI, and the dramatic difference in the dispersion relations of rigid and polarisable ion potentials (figure 4.2) for this salt make it a good candidate for shell model studies. Differences in results for calculated values of properties between the two potential models, if any, should be most pronounced for NaI. NaI is also computationally attractive for MD simulation work, since only the anions need be given shells, thus saving greatly on computer time compared with full (cation and anion) polarisable ion simulations.

As a result of performing shell model simulations of a salt such as NaI, the coordinates for both the ion cores and their electron shells (for the anions) are available for each ion at each timestep. The difference of these two for a given ion i is just that ion's instantaneous fluctuating electronic dipole moment μ_i within the approximations of the shell model. Note that this is not the same as the induced dipole moment π_i , since there is no external field present in the simulation to cause any induction. μ_i is the result of local, instantaneous electric field fluctuations within the sample as well as short range interactions with neighbouring ions. It is reasonable to seek to take advantage of the presence of this extra data, beyond that which the rigid ion potentials can provide, in the formation of calculable models for ion properties. Whether or not this calculated dipole moment is a reasonable representation of the “real” dipole moment, or

simply an unphysical artifact of the simulation method, is a result that is sought. The greatest cause for concern is the shell relaxation procedure (section 4.5), which implements the adiabatic approximation for the electrons; the relaxed shell positions may or may not represent satisfactorily the dipole moment of a given ion at a given timestep.

The goal of this chapter is the development of a model for light scattering processes in alkali halide melts which, given an independently parameterised potential model (*i.e.*, not “rigged” for light scattering work), is free from additional phenomenological parameters, and which takes fullest advantage of the presence of the anion dipole moment data provided by the shell model calculations. This approach puts maximum faith in the artifact anion dipole moments as reasonable, “real” ion dipole moments. The model will be developed from fundamental quantum-mechanical considerations, but some severe approximations will be made.

5.2 Terminology for scattering from melts

There is some confusion in the literature as to the terminology appropriate for the light scattering in melts. What is referred to here as “Raman scattering” from these ionic systems is equivalently termed “depolarised Rayleigh scattering”¹, or perhaps most appropriately, “Rayleigh wing scattering” [CLA78]. Some workers reserve the term “Raman scattering” in liquids work for scattering from intramolecular degrees of freedom; for ionic systems, this distinction is irrelevant.

5.3 Standard model for induced dipole scattering

¹ This is the usual term in argon work, since the polarised spectrum is of little interest as it is simply $\frac{4}{3}$ times the depolarised spectrum.

The usual treatment of light scattering in liquids [CLA78] proceeds from the calculation of transition rates for processes involving the spontaneous emission of a photon from a system excited by the presence of an induced dipole moment $\mathcal{M}(t) = \sum_i \boldsymbol{\pi}^i(t)$.² Within the approximations of a linear response of the induced dipole $\mathcal{M}$ to the applied field, and of a uniform scattering system initially at thermal equilibrium and only weakly perturbed by the incident field of frequency ω_0 , the appropriate transition rate for spontaneous emission at a frequency shift of ω from the incident frequency ω_0 is [CLA78]

$$\omega_{i \rightarrow f} = \frac{\omega_{if}^3}{3c^3 \hbar} |\langle f | \mathcal{M} | i \rangle|^2 \delta(\omega - \omega_{if}), \quad (5.1)$$

where ω_{if} is the frequency corresponding to the difference in the energies of the initial state $|i\rangle$ and the final state $|f\rangle$: $\hbar\omega_{if} = \hbar\omega_i - \hbar\omega_f$.

The total probability of any transition giving rise to scattering at a frequency $(\omega_0 \pm \omega)$ (“−” for Stokes scattering, “+” for anti-Stokes) is obtained by summing (5.1) over all possible initial states $|i\rangle$ and final states $|f\rangle$. Since the system is assumed to be at thermal equilibrium, the sum over the states i is weighted by their Boltzmann weights ρ_i . Thus, [CLA78]

$$P(\omega_0 \pm \omega) = \frac{(\omega_0 \pm \omega)^3}{3c^3 \hbar} \sum_{i,f} \rho_i |\langle f | \mathcal{M} | i \rangle|^2 \delta(\omega - \omega_{if}). \quad (5.2)$$

For the scattering processes of interest, the incident light is in the visible part of the spectrum, and the observed frequency shifts of the scattered light are a few THz, or a few hundred cm^{-1} , so the factor in $(\omega_0 \pm \omega)$ can be taken as constant to a good approximation. If the scattered radiation with polarisation $\mathbf{n}_s$ is measured in a direction perpendicular to the incident radiation (as in figure 3.1), then the scattered Stokes intensity $I(\omega)$ at frequency shift ω is given by

$$I(\omega) \sim \sum_{i,f} \rho_i |\langle f | \mathcal{M} \cdot \mathbf{n}_s | i \rangle|^2 \delta(\omega - \omega_{if}). \quad (5.3)$$

² $\mathcal{M}$ can be written this way if the wavelength of the incident light is large with respect to the sample size; the phase factor can then be safely ignored.

The “constant” of proportionality contains factors in $(\omega_0 - \omega)$ and a *local field correction factor*, which corrects for the difference between the radiation field in the sample and the applied field [CLA78]. Polarised scattering results when $\mathbf{n}_s$ is parallel to $\mathbf{n}_0$, the polarisation of the incident field; depolarised scattering occurs when $\mathbf{n}_s$ is perpendicular to $\mathbf{n}_0$.

Clarke [CLA78] demonstrates how to transform (5.3) from the Schrödinger representation, where the states are time-dependent, to the Heisenberg representation, where the time-dependence is in the operator $\mathcal{M}(t)$. Only the result of this transformation will be given here, as a similar result will be derived in detail in the next section. The Stokes intensity $I(\omega)$ is shown to be dependent on the Fourier transform of the time correlation function of the dipole operator $\mathcal{M}(t)$:

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mathcal{M}(0) \mathcal{M}(t) \rangle. \quad (5.4)$$

This model is not useful to the current simulation work, however, since it depends on the induced dipoles $\boldsymbol{\pi}_i$; this data is not available from the simulation programs at present. The simulations do, however, give information about the thermally fluctuating electronic dipoles $\boldsymbol{\mu}_i$. The standard model gives an indication of how to proceed in order to develop a calculable model based on $\boldsymbol{\mu}_i$ instead of $\boldsymbol{\pi}_i$.

5.4 A second order treatment

The model above disregards the absorption of the incident photon as the origin of the induced dipole $\mathcal{M}$, and thus ignores the second order (in the electron-photon interaction) nature of the Raman transitions. To treat this aspect of the scattering more accurately, a reduction to time correlation functions (similar to that sketched above) is here performed on the second order Raman transition probability expression given in chapter 3. The model so derived will be

calculable in terms of the available simulation data.

The second order (in the electron–photon interaction) quantum transition probability for Raman processes was given in (3.34) as

$$\omega_{i \rightarrow f} = \left| \frac{\sum_{EX} \langle f | \mathcal{H}_{int} | EX \rangle \langle EX | \mathcal{H}_{int} | i \rangle}{E_i - E_{EX}} \right|^2 \delta(E_i - E_f). \quad (3.34)$$

This is the probability of a Raman-type transition from state $|i\rangle$ to an energy conserving final state $|f\rangle$, mediated by an intermediate excited electronic state $|EX\rangle$. The states $|i\rangle$ and $|f\rangle$ here are combined electron–photon–phonon states, and Placzek’s approximation that the electrons are in their ground states before and after the scattering is in force, so the energy shift $\hbar\omega$ of the scattered photon of frequency ω_S from the incident laser photon frequency ω_L represents a gain or loss of energy in the phonon system of the sample (with “phonon” meaning some phonon-like mode in a melt).

To make the frequency dependence of the scattering more explicit, the states $|i\rangle$ and $|f\rangle$ are here redefined to be matter system states only (electron–phonon states) so that the delta function in (3.34) can look like that in (5.1): for scattering at a frequency shift of ω ,

$$\omega_{i \rightarrow f} = \left| \frac{\sum_{EX} \langle f | \mathcal{H}_{int} | EX \rangle \langle EX | \mathcal{H}_{int} | i \rangle}{E_i - E_{EX}} \right|^2 \delta(\omega - \omega_{if}). \quad (5.5)$$

The difference in the energy of the initial and final matter states, $\hbar\omega_{if}$, must be the same as the energy imparted to or from the scattered photon, $\hbar\omega$.

The total probability of Stokes scattering processes at a frequency shifted by ω from the incident frequency, analogous to (5.2) above, is found by taking a Boltzmann weighted sum over all initial states $|i\rangle$, and a sum over all energy conserving final states $|f\rangle$, so that

$$P(\omega) = \sum_{i,f} \rho_i \left| \frac{\sum_{EX} \langle f | \mathcal{H}_{int} | EX \rangle \langle EX | \mathcal{H}_{int} | i \rangle}{E_i - E_{EX}} \right|^2 \delta(\omega - \omega_{if}). \quad (5.6)$$

The scattering intensity $I(\omega)$ will be proportional to $P(\omega)$ if the shifts ω are small when compared with ω_0 .

As was pointed out in section 3.4, this expression is not useful for MD calculations, as there is no knowledge of intermediate excited electronic states in these MD calculations. The explicit treatment of the intermediate excited state $|EX\rangle$, and the separate inclusion of the incident and scattered photons, are the differences between this expression and (5.2) above. The excited state is a manifestation of the induced dipole moment of (5.2), but its origin is clearer here.

In the spirit of the shell model, it is asserted that there is *one important, dominant, excited electronic state* $|E\rangle$ in the system. This is equivalent to a harmonic (in the shell-core restoring force) shell model with a single frequency for shell-core oscillations; all polarisability effects are represented through one process. In lieu of the sum over all excited states $|EX\rangle$, an “average energy denominator” $\frac{1}{\Delta E} = \frac{1}{E_i - E_E}$ is introduced, and the sum over $|EX\rangle$ is reduced to a projection into the single state $|E\rangle$. Removing the (now constant) projection into $|E\rangle$, and substituting the dipole approximation representation (3.32) of the interaction Hamiltonian $\mathcal{H}_{int}$, the scattering intensity can be rewritten as

$$I(\omega) \sim \frac{1}{\Delta E} \sum_{i,f} \rho_i \left| \langle f | \left(\sum_{j,\beta} E_{S,\beta}^j \cdot \mu_{\beta}^j \right) \left(\sum_{i,\alpha} E_{L,\alpha}^i \cdot \mu_{\alpha}^i \right) | i \rangle \right|^2 \delta(\omega - \omega_{if}), \quad (5.7)$$

where E_L^i is the incident laser field on ion i ; E_S^j is the scattered field acting on ion j , and μ^i is the instantaneous dipole moment of ion i . Note that μ is simply the instantaneous electronic dipole moment; its origin (i.e., via external field induction or not) is irrelevant. The incident laser field interaction mediates the transition from the initial state $|i\rangle$ to the (now fixed) intermediate state; the scattered field is involved in the transition to the final state $|f\rangle$.

The electric fields in this expression are non-interacting; the effect of the fields in a melt (where ion positions and dipole orientations are random to some approximation) can be captured by averaging over all field directions and

lumping the result into a constant prefactor, which is dropped, leaving

$$I(\omega) \sim \sum_{i,f} \rho_i \sum_{\alpha\beta} |\langle f | M_\beta M_\alpha | i \rangle|^2 \delta(\omega - \omega_{if}), \quad (5.8)$$

where $M = \sum_i \mu^i$.

To put the proper time-dependence in this formulation, the Heisenberg picture [CLA78] is invoked. The delta function $\delta(\omega - \omega_{if})$ can be Fourier transformed as

$$\begin{aligned} \delta(\omega - \omega_{if}) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i(\omega - \omega_{if})t} \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} e^{\frac{iE_i t}{\hbar}} e^{\frac{-iE_f t}{\hbar}} \end{aligned} \quad (5.9)$$

Substitution of (5.9) in (5.8) and expansion of the squared matrix elements leads to

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i,f} \rho_i \sum_{\alpha\beta} \langle i | M_\beta M_\alpha | f \rangle e^{\frac{-iE_f t}{\hbar}} \langle f | M_\beta M_\alpha | i \rangle e^{\frac{iE_i t}{\hbar}}. \quad (5.10)$$

Since the states $|i\rangle$ and $|f\rangle$ are eigenstates of the total Hamiltonian $\mathcal{H}$, (5.10) can be rewritten as

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i,f} \rho_i \sum_{\alpha\beta} \langle i | M_\beta M_\alpha | f \rangle \langle f | e^{\frac{i\mathcal{H}t}{\hbar}} M_\beta M_\alpha e^{\frac{-i\mathcal{H}t}{\hbar}} | i \rangle. \quad (5.11)$$

In the Heisenberg representation, the time development of operator $\mathcal{A}$ at time t is given by

$$\mathcal{A}(t) = e^{\frac{i\mathcal{H}t}{\hbar}} \mathcal{A}(0) e^{\frac{-i\mathcal{H}t}{\hbar}}. \quad (5.12)$$

Applying (5.12) to (5.11), the intensity can now be written

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{i,f} \rho_i \sum_{\alpha\beta} \langle i | M_\beta(0) M_\alpha(0) | f \rangle \langle f | M_\beta(t) M_\alpha(t) | i \rangle. \quad (5.13)$$

Performing the central sum over states $|f\rangle$ (which are assumed to be a complete set, thus $\sum_f |f\rangle \langle f| = 1$), the scattering intensity is now

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_i \rho_i \sum_{\alpha\beta} \langle i | M_\beta(0) M_\alpha(0) M_\beta(t) M_\alpha(t) | i \rangle. \quad (5.14)$$

This expression, involving the sum over states $|i\rangle$ weighted by their Boltzmann factors ρ_i , is simply the Fourier transform of the thermal average of the four dipole operator:

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha\beta} \langle M_\beta(0) M_\alpha(0) M_\beta(t) M_\alpha(t) \rangle_T, \quad (5.15)$$

where $\langle \dots \rangle_T$ denotes the equilibrium thermal average. The ensemble average is simply given by the corresponding time correlation function [CLA78], so finally for the scattering intensity $I(\omega)$,

$$I(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha\beta} \langle M_\beta(0) M_\alpha(0) M_\beta(t) M_\alpha(t) \rangle. \quad (5.16)$$

The expression (5.16) means that the probability of a Raman event involving an emission of a photon of frequency $(\omega_0 - \omega)$, that is, shifted by ω from the incident frequency, is proportional to the time correlation of the dipole product $M_\alpha(t) M_\beta(t)$. There are two distinct types of scattering events to consider, those with $\alpha = \beta$, and those with $\alpha \neq \beta$. An example of the first type of event is when $\alpha = \beta = X$: this corresponds to a *polarised* scattering event, since the dipole moments involved at the incident and scattering events are in the same direction. An example of the second type of event is when $\alpha = X$ and $\beta = Y$; this corresponds to a *depolarised* scattering event, since orthogonal polarisation components are involved. Thus,

$$I_{\parallel}(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha} \langle M_\alpha(0) M_\alpha(0) M_\alpha(t) M_\alpha(t) \rangle \quad (5.17)$$

$$I_{\perp}(\omega) \sim \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_{\alpha \neq \beta} \langle M_\beta(0) M_\alpha(0) M_\beta(t) M_\alpha(t) \rangle \quad (5.18)$$

Although the scattering intensities given by these expressions are in arbitrary units, their relative values should be consistent, so the ratio of $I_{\perp}$ to $I_{\parallel}$ should give the frequency-dependent depolarisation ratio $\rho(\omega)$:

$$\rho_D(\omega) = \frac{I_{\perp}(\omega)}{I_{\parallel}(\omega)}. \quad (5.19)$$

The integrated depolarisation ratio ρ_D is available from the $t = 0$ values of the correlation functions in (5.17) and (5.18) [FAI86].

5.5 Calculations on NaI

The above model has been tested on shell model simulations of molten NaI. Two separate simulations of 216-ion systems of NaI, with different potentials, have been performed. These potentials were discussed in chapter 4: one of them is known to be erroneous, but Dixon and Sangster found it useful to continue to use the incorrect version as a test of the sensitivity of calculations to potential parameters [DIX76a]. The incorrect potential, labelled as *PIM1* here (for *polarisable ion model #1*), misrepresents the anion–anion interaction significantly, as a comparison of the anion–anion radial distribution functions in figures 4.12 and 4.13 indicates. The corrected potential is labelled *PIM2*. The differences in the results from the two potentials will give some indication as to how sensitive the results are to the details of the local ionic environment.

5.6 Experimental data

Recent Raman measurements of most of the alkali halide melts have been performed by Mitchell *et al.* [MIT83, RAP83], and by Giergiel *et al.* [GIE84]. Both groups have measured $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ for molten NaI, and the former have given $\rho_D(\omega)$. The two groups are in close agreement on most details of their measurements; this will enable reliable comparison of the results from the model calculation with experiment.

The experimental intensities of Raptis, Buntin, and Mitchell [RAP83] for NaI at 968°K are given on a semi-log scale in figure 5.1. The results of Giergiel *et al.* [GIE84] are very similar. Both the polarised and depolarised spectra are characterised by long, high frequency exponential tails (straight lines in figure 5.1). The polarised spectrum has a pronounced shoulder at about 4 THz, marking a transition to a more complex low frequency behaviour. A

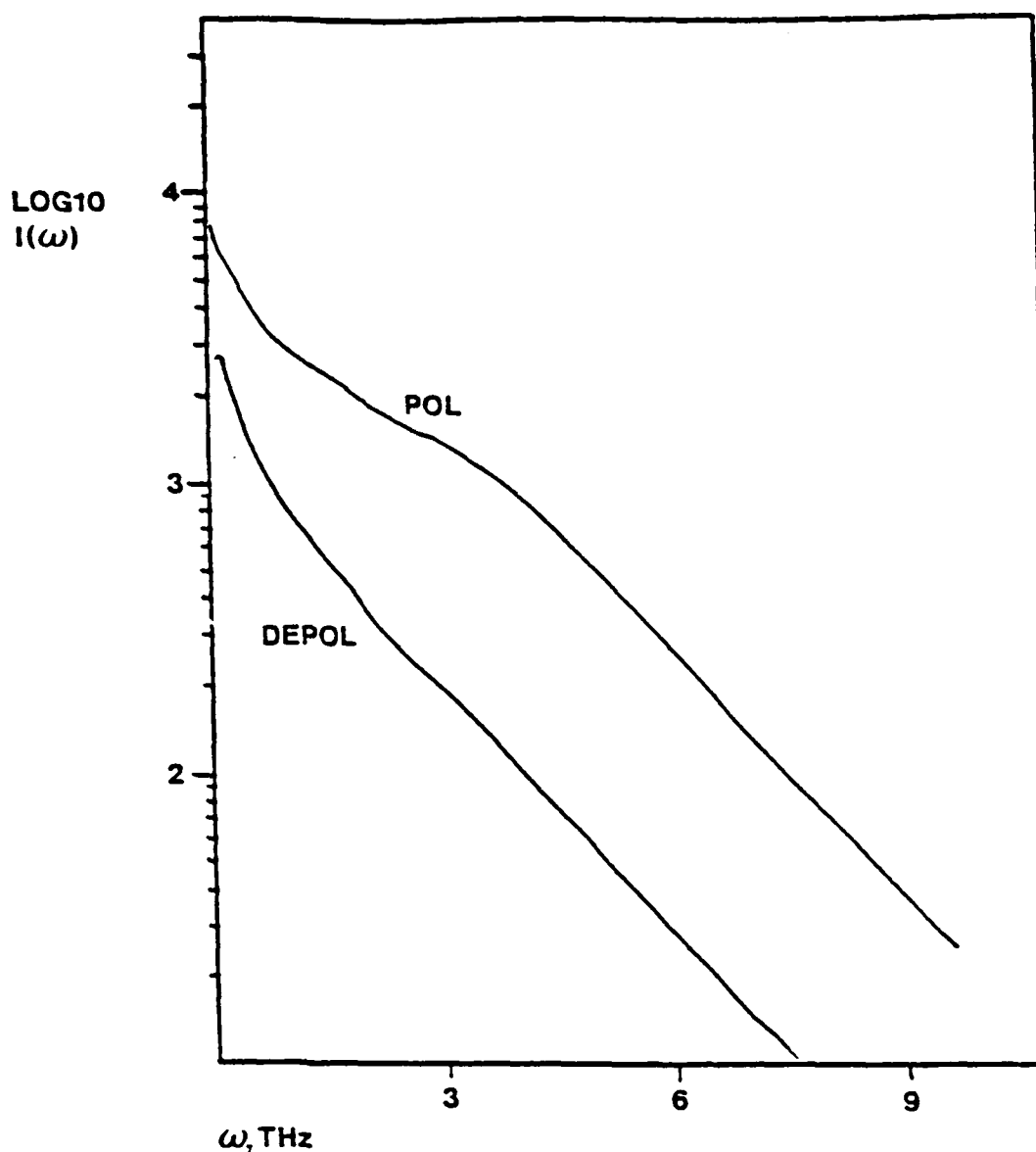


Figure 5.1 : Experimental polarised (POL) and depolarised (DEPOL) Raman scattering intensities from molten NaI at 968°K, after Raptis *et al.* [RAP83].

second exponential with a different decay constant can characterise the lineshape between about 1 and 4 THz; Raptis *et al.* claim the low frequency region up to about 1 THz is also exponential in character with yet another characteristic decay, although this is less clear from the figure. The depolarised spectrum also has complex behaviour below about 1 THz, but a single exponential characterises the high frequency portion; there is no shoulder here [RAP83].

The exponential decays of the various regions of the spectra have been characterised [RAP83] by time constants τ_s with $\tau_s = 1/\omega_s$ (ω_s in THz), and

$$I(\omega) = I_0 e^{-\omega/\omega_s}. \quad (5.20)$$

5.7 Results and discussion

Plots of the calculated lineshapes $I_{\perp}(\omega)$ and $I_{\parallel}(\omega)$ from simulations using

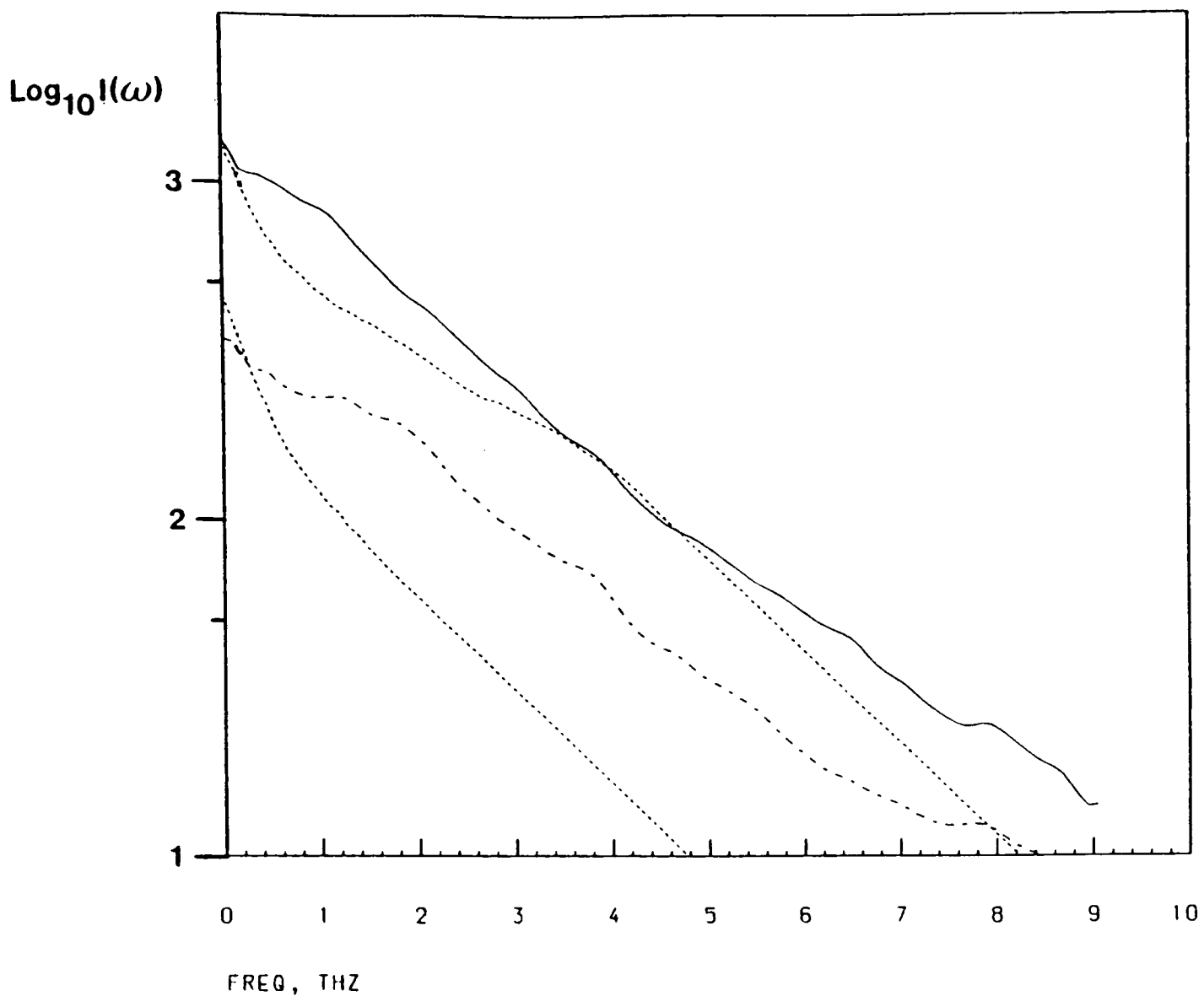


Figure 5.2 : Smoothed semi-log plot of the polarised (solid line) and depolarised (dashed line) scattering as given by (5.17) and (5.18) for a 216 ion simulation of molten NaI with shell model potential PIM1 at 973°K, compared with the experimental results of Raptis *et al.* [RAP83] (dotted lines). The two polarised curves have been normalised to the same arbitrary intensity at $\omega = 0$; the depolarised curves are plotted at their known relative intensities with respect to the polarised curves.

both shell model potentials PIM1 and PIM2 are given on a semi-log scale in figures 5.2 and 5.3; both are compared with experiment.

5.7.1 Data analysis

The determination of the depolarised spectra is straightforward; the time correlation function (5.18) is well-behaved in that it decays to zero fairly rapidly, and taking its Fourier transform presents no problems (figure 5.4). The polarised correlation function (5.17), however, has a non-zero long-time value (figure 5.4); since it is the product of two squares, it is guaranteed always to be non-negative. The long-time average value must be subtracted off and the amplitude rescaled before taking the Fourier transform. As the time spectra are quite noisy, the

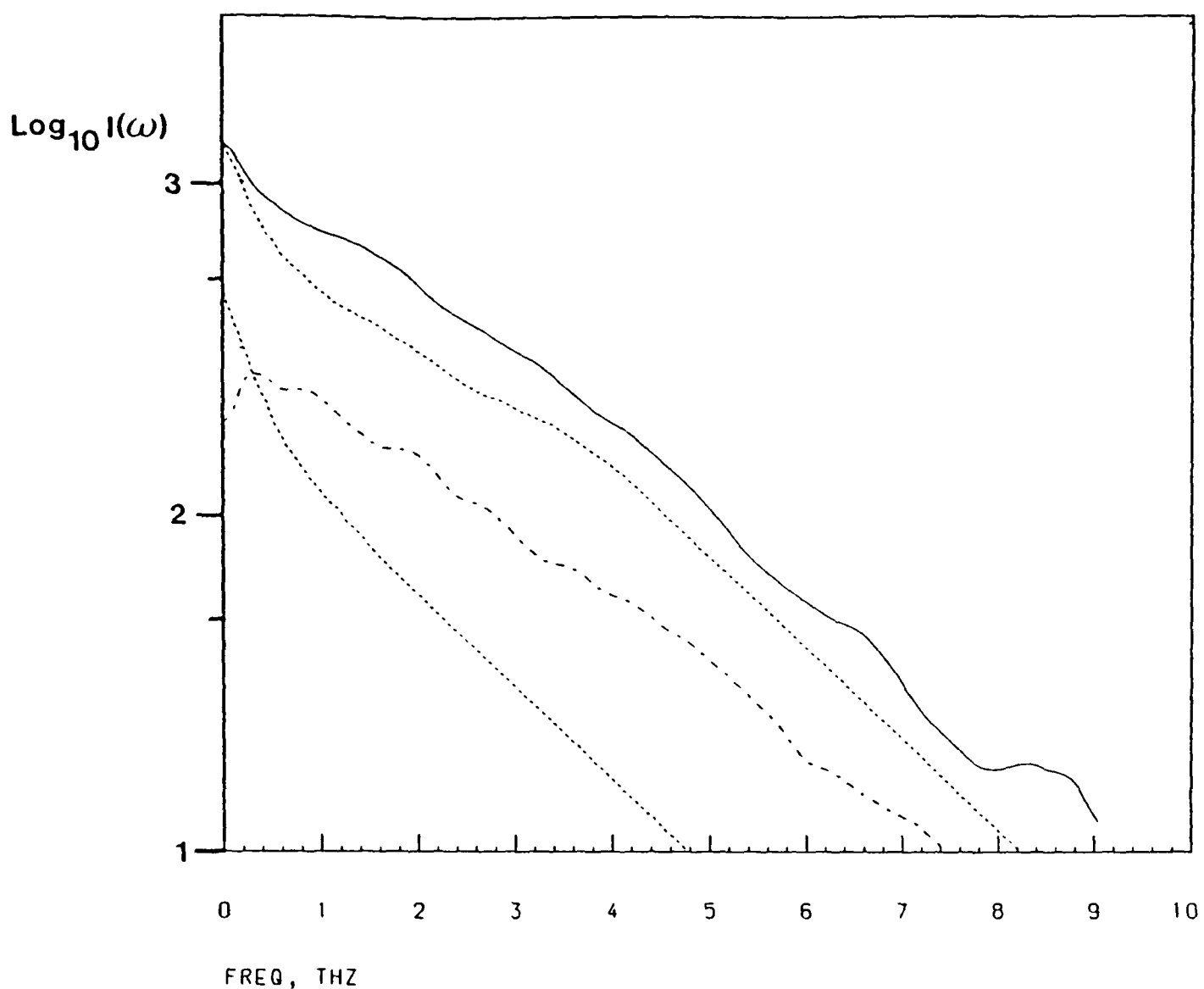


Figure 5.3 : Smoothed semi-log plot of the polarised and depolarised scattering as given by (5.17) and (5.18) for a 216 ion simulation of molten NaI with shell model potential PIM2 at 973°K, compared with the experimental results of Raptis *et al.* [RAP83]. The curves are normalised and labelled as in figure 5.2. The time correlation functions giving rise to these curves are given in figure 5.4; the unsmoothed version of these curves is given in figure 5.5.

best value of this long-time average is a subjective judgement, but the resulting spectra were found not to be very sensitive to small changes in the value of this long-time average.

The spectra in figures 5.2 and 5.3 have been smoothed through the application of a low-pass filter to reduce the statistical noise that is the result of the relatively short length of the simulation runs. Each of these simulations was equilibrated for 5000 timesteps, and the data collected over the next 5000 timesteps. The great similarity of the spectra for the two potentials gives confidence that this filtering is reasonable, *i.e.*, that the runs are long enough to produce reasonable and consistent results, albeit noisy ones. The similarity of the two sets of results also indicates that the model is not extremely sensitive to changes in the potential parameters, although the differences that are evident

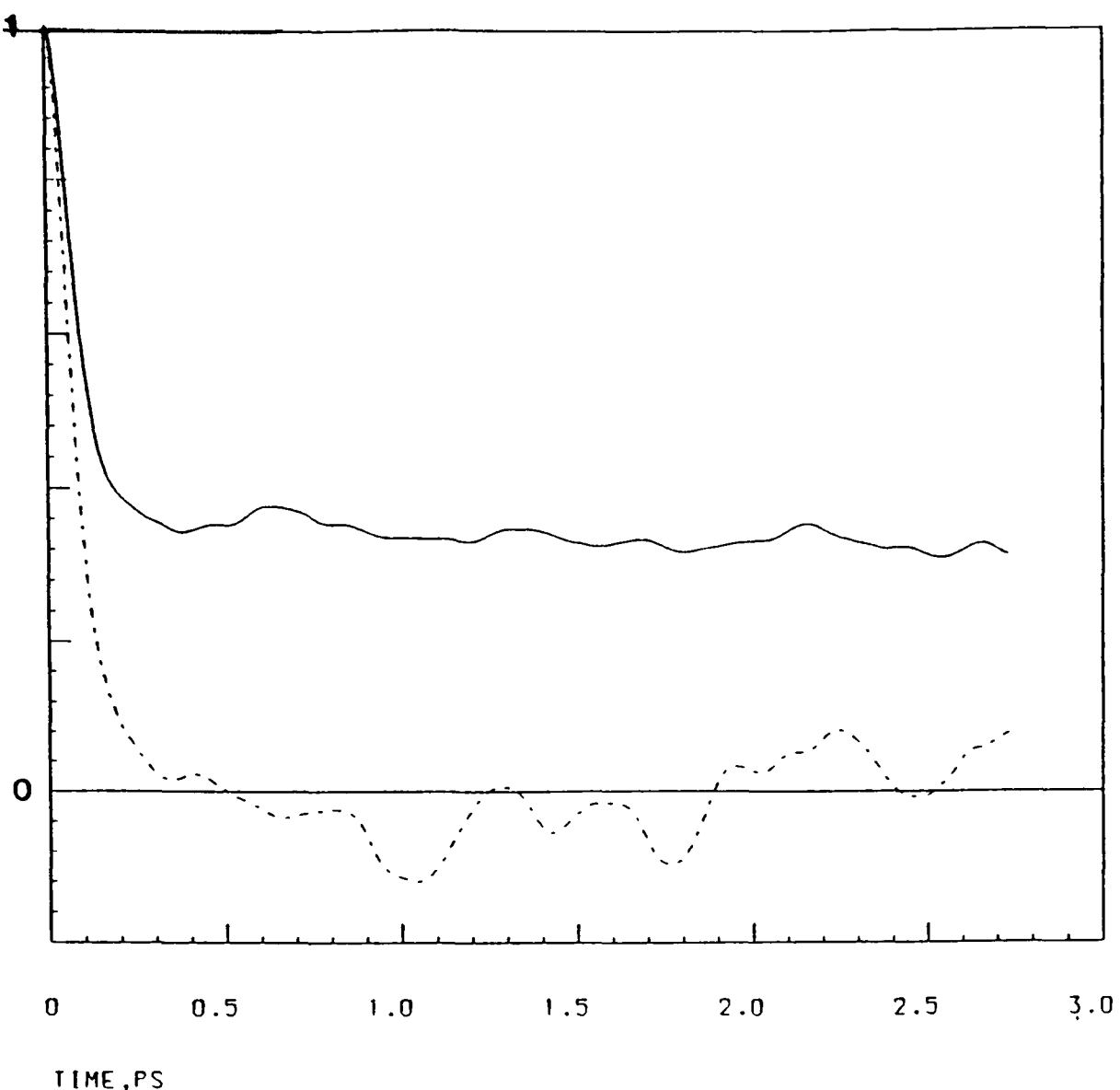


Figure 5.4 : Time correlation functions for the simulation using the potential PIM2 whose Fourier transforms give the Raman spectra in figures 5.3 and 5.5. The solid curve gives rise to the polarised scattering, the dashed curve to depolarised scattering. The long-time average value of the polarised curve must be subtracted off and its amplitude rescaled prior to taking the Fourier transform.

demonstrate that the choice of potential model is important. Figure 5.5 gives an example of the unsmoothed spectra used to generate figure 5.3.

5.7.2 Scattering intensities and depolarisation ratios

The absolute scattering intensity is not available from this model, since much violence was done to the prefactors of the intensity expressions (5.17) and (5.18). The polarised and depolarised spectra are calculated in the same way, however, so the relative intensity of the two is valid. Specifically, the integrated intensities are related to the $t = 0$ values of the time correlation functions in (5.17) and (5.18); the total (integrated) depolarisation ratio for the model is therefore available. The frequency-dependent depolarisation ratio $\rho_D(\omega)$ can

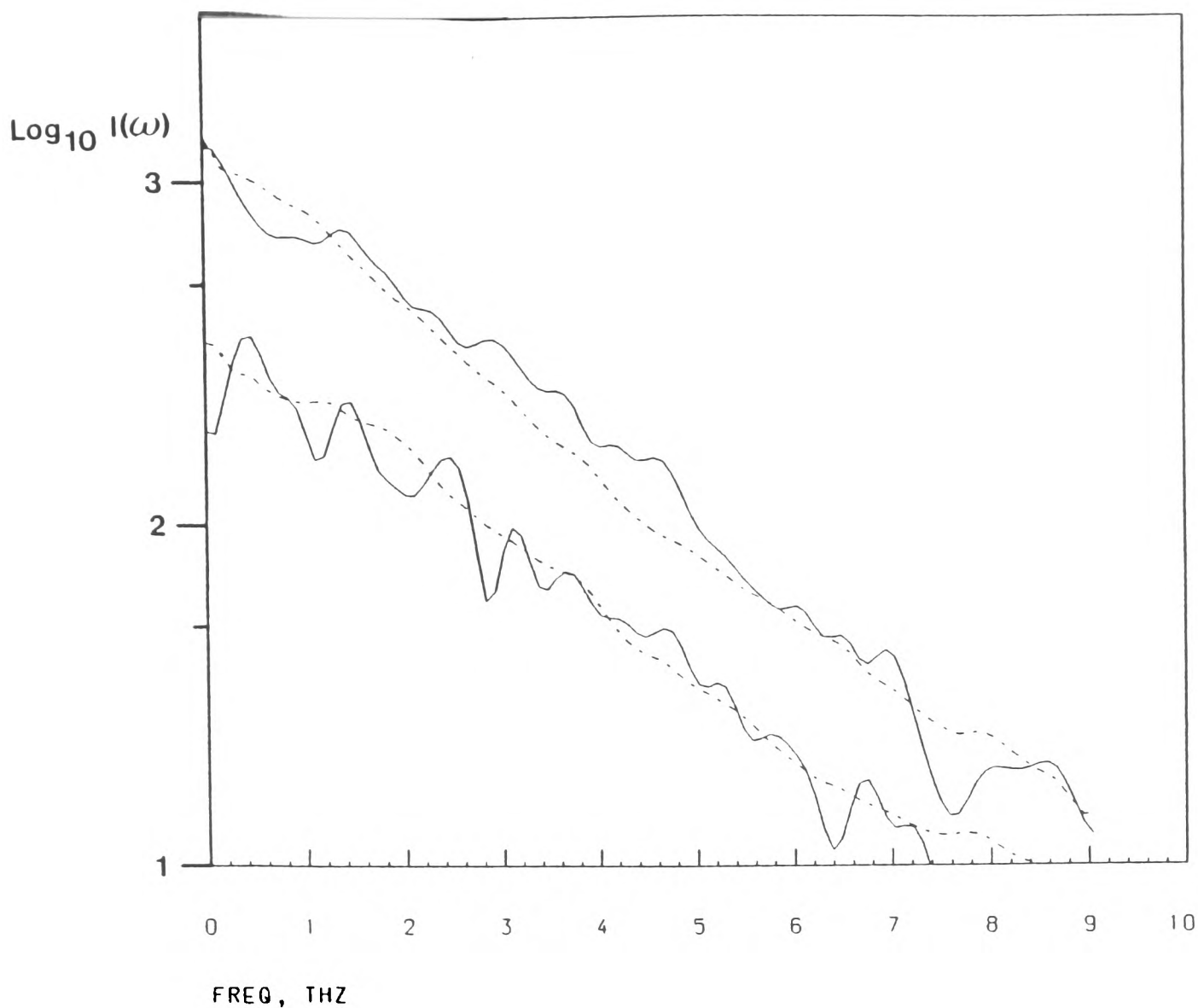


Figure 5.5 : Semi-log plots of the unsmoothed Fourier transforms of the time correlation functions for the PIM2 simulation in figure 5.4. The smoothed versions of these curves (dotted lines) from a low-pass filtering operation are the polarised and depolarised spectra of figure 5.3.

be determined from the ratio of the curves in figures 5.2 and 5.3. These quantities are also available experimentally; the results are summarized in table 5.1. Figure 5.6 gives $\rho_D(\omega)$ for the simulations and experiment. Note that the behaviour of $\rho_D(\omega)$ for potential PIM2 is anomalous at low frequency; this is due to the unfiltered “bump” in the depolarised spectrum for that simulation at low frequency (figure 5.3); the entry for $\rho_D(0)$ for PIM2 in table 5.1 is based on extrapolation of the higher frequency behaviour back to $\omega = 0$. The higher frequency (> 7 THz) behaviour for both simulations is also anomalous; numerical problems in taking the ratio of small numbers may be to blame. The values of $\rho_D(\infty)$ in table 5.1 ignore this region.

5.7.3 Spectral lineshapes and time constants

The lineshapes are described by time constants for the exponential decay

Depolarisation Ratios from Simulation and Experiment				
	PIM1	PIM2	EXPT [RAP83, FAI86]	EXPT [GIE84]
$I_{\perp}$	91	135	1.46	—
$I_{\parallel}$	279	446	6.65	—
ρ_D	0.33	0.30	0.219	—
$\rho_D(0)$	0.3	0.3	0.34	0.3
$\rho_D(\infty)$	0.4	0.3	0.11	0.125

Table 5.1 : Scattering intensities and depolarisation ratios. The integrated polarised $I_{\parallel}$ and depolarised $I_{\perp}$ intensities from simulation (in arbitrary units) and experiment (in $10^{-29}\text{cm}^2\text{sr}^{-1}\text{ion pair}^{-1}$) give the total (integrated) depolarisation ratio ρ_D . Giergiel *et al.* did not report absolute intensities. The low frequency ($\rho_D(0)$) and high frequency ($\rho_D(\infty)$) limits, as extrapolated from figures 5.2 and 5.3, are also given.

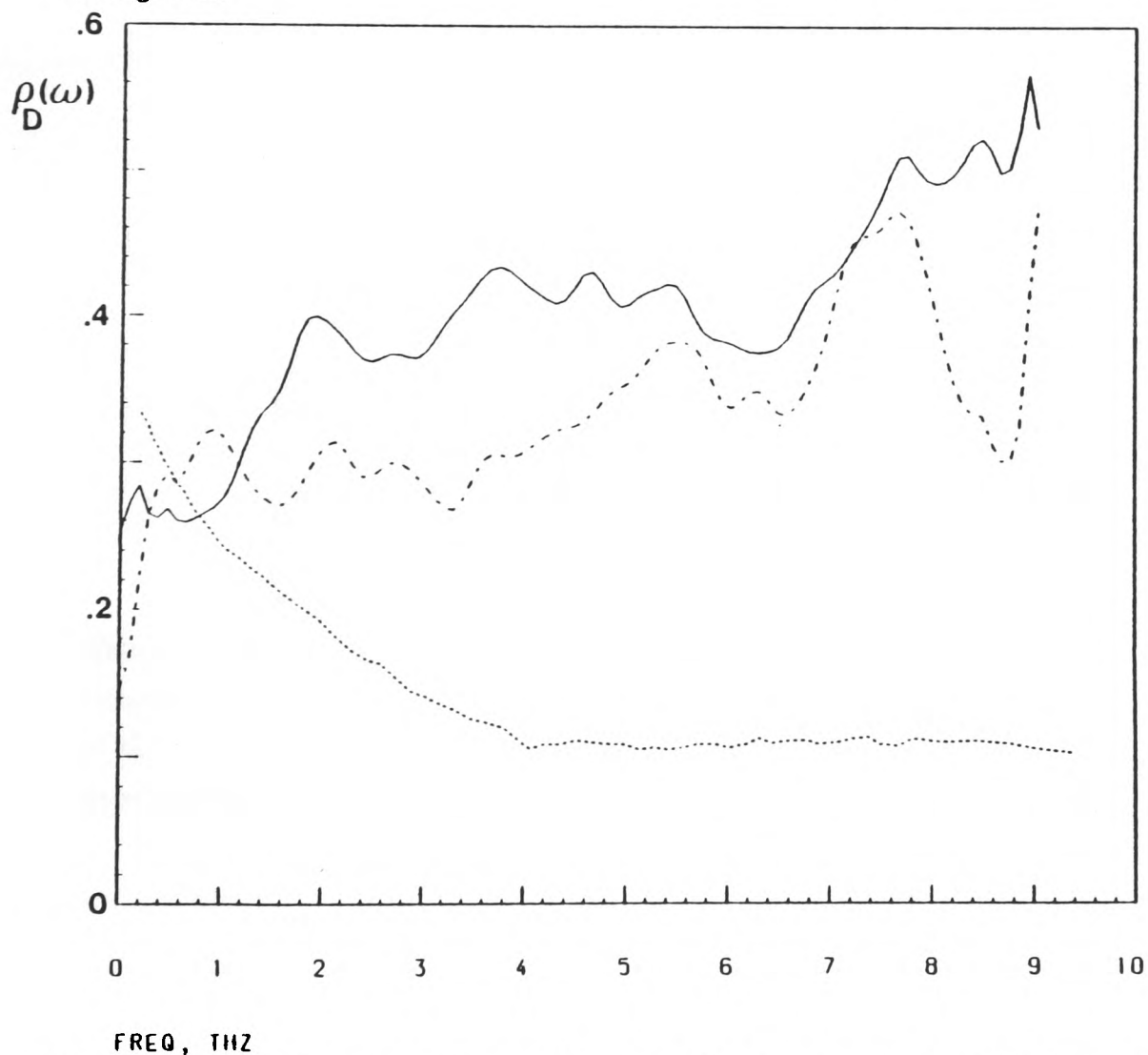


Figure 5.6 : Frequency dependent depolarisation ratio $\rho(\omega)$ from simulations of molten NaI at 973°K with potential PIM1 (solid line) and PIM2 (dashed line), and from experiment of Raptis *et al.* at 968°K [RAP83] (dotted line).

of the spectra, as in (5.20). A single exponential dominates the behaviour from about 1 THz onwards in both the polarised and depolarised spectra from both simulations. The lineshape below 1 THz lacks detail due to the statistics of the simulation and should not be regarded as accurate. There is perhaps a very weak shoulder and consequent change in slope in the polarised spectrum of the simulation with potential PIM2 at about 3 THz, but it is clearly not as strong as in the experimental spectrum (figure 5.3). For the simulation with potential PIM1, the polarised and depolarised spectra have almost the same slope on the semi-log plot, indicating that the same time constant governs both. The curves for PIM2 are not parallel; their slow convergence is responsible for the rise in $\rho_D(\omega)$ with ω for this simulation (figure 5.6).

The time constants governing the high frequency decay of the exponential intensity lineshapes are given in table 5.2 for the simulations and the experiment of Raptis *et al.* [RAP83].

Time constants of scattering lineshapes			
	PIM1	PIM2	EXPT [RAP83]
$I_{\parallel} : \tau_{\infty}$	.5 ps	.6 ps	.64 ps
$I_{\perp} : \tau_{\infty}$	.5 ps	.5 ps	.64 ps

Table 5.2 : Time constants for spectral lineshapes. The time constants, as defined in (5.20), for the high-frequency exponential decay of the polarised and depolarised spectra for the two simulations and the experiment of Raptis *et al.* [RAP83].

5.7.4 Discussion

The model is capable of reproducing the lineshape and relative intensity of the polarised and depolarised scattering from molten NaI to an encouraging extent. The first conclusion is that the instantaneous dipole moments as provided

by shell model simulations are indeed fairly good representations of the “real” system dipole moments.

The depolarisation ratios given by the model calculation are significantly lower than the completely anisotropic scattering value of 0.75, but are not low enough to match experiment. The low frequency $\rho_D(0)$ is not too far off, but the lack of the distinct experimentally observed shoulder in the polarised spectrum prevents the value from coming down to the observed high frequency value of about 0.1. The polarised and depolarised spectra in the simulations in fact stay roughly parallel (PIM1) or indeed converge slightly (PIM2), resulting in a rise of $\rho_D(\omega)$ with frequency.

The high frequency depolarised lineshape, as characterised by the time constant τ_∞ is in quite good agreement with experiment for both simulations; the mid frequency region is less satisfactory, and the statistics are poor on the low frequency region. The polarised lineshape is significantly wrong, but curiously less so for the “bad” potential (PIM1).

Figure 5.7 gives the time domain picture of the scattering lineshape. The experimental spectra have been back-transformed to the time domain, as have the *smoothed* simulation spectra from the simulation using potential PIM2. The simulation curves should be compared with the original time correlation functions for that simulation in figure 5.4 to see the effect in the time domain of the filtering operation. For the polarised correlations (figure 5.7a), the short-time behaviour of the two is in good agreement; the initial decay of the two curves is nearly identical. This is the time domain equivalent to the good high frequency agreement of the corresponding spectra in figure 5.3. The lack of good agreement between about 0.2 ps and 0.5 ps is consistent with the failure to observe the mid-frequency shoulder in the simulation spectra. The agreement for the depolarised curves (figure 5.7b) is much worse, reflecting the divergence of the simulation and experimental depolarised spectra in figure 5.3 and table 5.2.

The corresponding picture for the simulation using the potential PIM1 is not given but is similar, except that the depolarised correlations are in slightly better agreement at short times, reflecting the closer agreement in the high frequency spectra (figure 5.2).

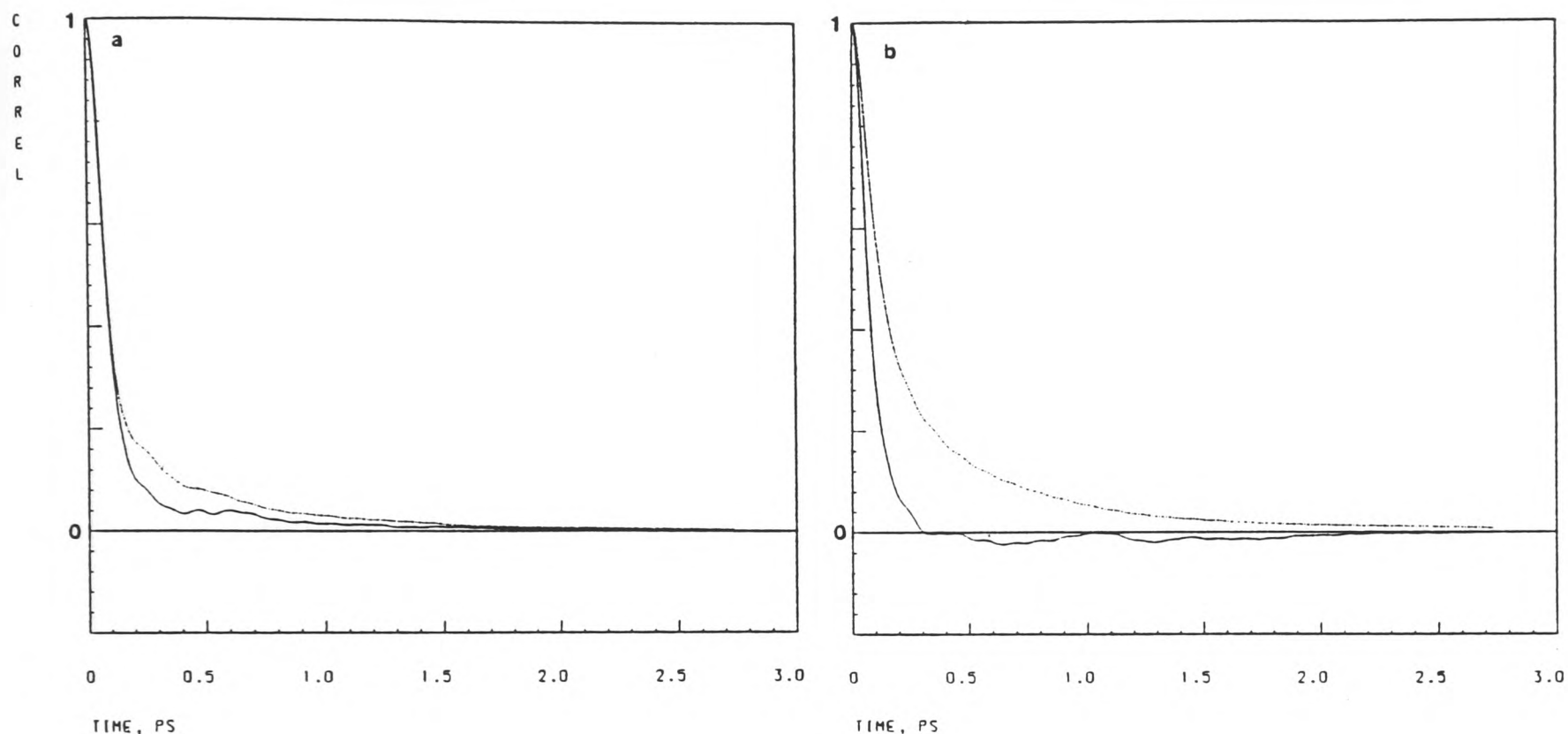


Figure 5.7 : Time-domain scattering picture. The polarised (a) and depolarised (b) experimental spectra (figure 5.1) have been back-Fourier transformed to give the dashed curves, which are compared with the back-transforms of the smoothed spectra from the simulation using the potential PIM2 (solid curves). The simulation curves should be compared with figure 5.4 to see the time domain effect of the smoothing operation.

To understand these spectra further, the timescales of various processes in the NaI simulations are given in table 5.3. The characteristic times of vibrational, optical, and diffusive processes are given as calculated from the simulations.

Diffusive processes are apparently too slow to be of much importance to the light scattering, except perhaps at very low frequency, where the experimental lineshape time constant goes up to about 1.6 ps for depolarised scatter-

Time scales in NaI melts, in ps		
Process	PIM1	PIM2
$\sum_{i+} m_i \langle \mathbf{u}_i(0) \mathbf{u}_i(t) \rangle$	0.07	0.07
$\sum_{i-} m_i \langle \mathbf{u}_i(0) \mathbf{u}_i(t) \rangle$	0.07	0.07
$\langle (\sum_i \boldsymbol{\mu}_i(0)) (\sum_j \boldsymbol{\mu}_j(t)) \rangle$	0.21	0.21
τ_d^+ [DIX76a]	1.9	1.9
τ_d^- [DIX76a]	3.4	2.8

Table 5.3 : Time scales of processes in NaI melts. The first two rows give the characteristic relaxation time (to e^{-1} of the initial value) of the velocity autocorrelation function for cations and anions, reflecting the timescale of phonon-like vibrational processes. The third row gives the relaxation time of the dipole-dipole correlation function, which is related to infra-red absorption. The last two rows give the diffusion times (time to diffuse one near-neighbour spacing) for cations and anions.

ing [RAP83], and the simulation results are inconclusive. Vibrational processes, however, are too fast to be responsible for the characteristic decay of the light scattering processes.

The dipole-dipole correlation function relaxation time is roughly equal to the known plasma period of molten NaI of 0.20 ps without polarisation effects and 0.28 ps with polarisation included [RAP83]. As the dipole-dipole correlation is one component of the infra-red absorption, the plasma time should characterise its decay. This is one more indication that the shell model dipole moments are reasonable. This agreement is probably responsible for the success of the model in reproducing the high frequency lineshape, since the correlation functions (5.17) and (5.18) are roughly (but not exactly) the square of the dipole-dipole correlation, and the Raman relaxation times are roughly twice the plasma time, as would be expected for the square of an exponential. Thus, plasma modes are indicated as important mediators of the light scattering re-

laxation.

5.7.5 Going further

The model developed in this chapter includes only dipole scattering. One would also expect a contribution from higher multipoles; the quadrupole term is the obvious first candidate. It is hoped that the quadrupole scattering might behave differently (*i.e.*, have a different lineshape) than the dipole contribution, so that some combination of the two might improve the overall result.

Elliott and Dixon [ELL81] estimated the lineshape of the quadrupole contribution to the scattering in NaI from consideration of the local polarisation correlation

$$\langle P_{\alpha\beta}(0)P_{\alpha\beta}(t) \rangle. \quad (5.21)$$

Here, $P_{\alpha\beta}$ is the polarisation due to the field components E_{α}^L and E_{β}^S of the laser and scattered field. The Fourier transform of this correlation is related to the Raman scattering.

The polarisation in (5.21) can be approximated as

$$P_{\alpha\beta} = \sum_{ij} q^i r_{\alpha}^i q^j r_{\beta}^j, \quad (5.22)$$

where $\mathbf{r}^i$ is the relative electron coordinate of ion i , and q^i its charge. The terms with $i \neq j$ are related to the dipole scattering; the local terms with $i = j$ give the quadrupole term.

Elliott and Dixon estimated the local polarisation with an exponential term in the ion displacements $\mathbf{r}_{ij}$ taken from the short range part of the Born–Mayer potential from (chapter 4) such that the polarisation $q^i \mathbf{r}^i = \mathbf{p}^i$ is given by

$$\mathbf{p}^i = \sum_j A e^{-r_{ij}/\rho} \hat{\mathbf{r}}_{ij}. \quad (5.23)$$

This approach thus estimates the polarisation induced by the short range repulsive interactions.

Substituting (5.23) into (5.21), they found that the statistics of the dipole contributions ($i \neq j$) were very poor. The quadrupolar contribution ($i = j$) gave reasonable results and provided lineshapes somewhat different from those found in this chapter. Specifically, there was some higher frequency structure, albeit at the wrong frequency, that gave hope of finding in a more accurate calculation and in combination with the dipolar terms the shoulder observed in the polarised experimental spectrum.

The shell model allows a crude approximation of (5.22) from knowledge of the relative shell coordinate on the anions. The product $r_\alpha r_\beta$ in (5.22) should be determined from the quantum-mechanical average of the incident and scattered fields over the electron distribution of the ion in question. An approximation in terms of the shell-core separation is equivalent to asserting that the average $\langle r_\alpha^i r_\beta^i \rangle$ is the same as the independently averaged terms $\langle r_\alpha^i \rangle \langle r_\beta^i \rangle$. In this work, correlation functions of the form

$$\langle (\sum_i \mu_\alpha^i(0) \mu_\beta^i(0)) (\sum_j \mu_\alpha^j(t) \mu_\beta^j(t)) \rangle \quad (5.24)$$

were calculated; this is equivalent to taking only the local ($i = j$) term in (5.7).

The statistics of the terms with $\alpha = \beta$, which are related to the polarised scattering, were too poor to use. The terms with $\alpha \neq \beta$, which give three representations of the depolarised scattering, were better behaved and could be used. On Fourier transforming these functions, however, the disappointing result was a lineshape almost identical to that found via (5.18) (figures 5.2 and 5.3). Improvement may be possible through a more precise treatment of the quadrupolar contribution, as the terms used here are only an approximation to it; some other possibilities for extending the model are discussed in the final chapter.

6 Models for ionic polarisability

6.1 Raman scattering and polarisation theory

Section 3.5 indicated how it is possible to understand light scattering in terms of fluctuations in atomic polarisabilities and polarisation densities. As an alternative to chapter 5's procedure of accessing polarisabilities indirectly through consideration of ionic dipole moments in an "*ab initio*" (within the approximations made) manner, this chapter will consider an explicit model for the variation of ionic polarisabilities in dynamically changing condensed environments.

This approach is more empirical than that of the preceding chapter, in the sense that more phenomenological constants need to be supplied to parameterise the various models. The physical values required, however, are quite well known from both experimental and theoretical work, so there is the hope of developing accurate models from which absolute light scattering intensities from melts, in addition to the lineshapes as determined in chapter 5, will be accessible. Light scattering lineshapes and intensities from crystals will also be available. This program promises intimate comparison with experimental details, and greater insight into the mechanisms of the scattering.

As the effective polarisability of an ion in a condensed environment is determined by several effects acting in concert (discussed below), the computational work provides the opportunity to determine the relative importance of several possible scattering mechanisms by considering them separately, as well as the degree to which the mechanisms are independent (or not). To presage the results that follow, this procedure is quite successful in reproducing the scattering

intensities and lineshapes of some of the simple alkali halide melts; the relative efficacy of several scattering mechanisms is also revealed.

6.2 Polarisability in condensed environments

The discussion in chapter 3 on the Raman effect described how Raman scattering is the result of time-dependent variations in atomic or molecular polarisabilities and, in condensed systems, polarisation densities. Specifically in crystals, the vibrational Raman scattering was shown to depend on terms like $d\alpha/dQ_k$ for polarisability α and normal modes Q_k . In disordered systems (and indeed in crystals), the scattering is related to time correlation functions of the form $\langle P(0)P(t) \rangle$, where P is the polarisation density in the sample.

From Raman and many other types of measurements, it is clear that atomic polarisabilities and local polarisation densities do vary, sometimes quite dramatically, with instantaneous surroundings in a condensed system. Fowler and Madden [FOW83; 84a, b; 85] have studied the sensitivity of the polarisabilities of some alkali halide ions to these effects in detail. The first significant phenomenon to note is the substantial reduction in anion polarisability from isolated ion values when ions are brought together in a crystal or melt. For example, Fowler and Madden [FOW83] found that the polarisability of the F^- ion in LiF is reduced from a free ion value of about 15 a.u. to about 6 a.u. in a crystal. They ascribe the reduction to compression and stabilisation of the “electron cloud” around the ion under a combination of electronic and “mechanical” forces, corresponding to the various types of interionic forces present — Coulomb, van der Waals, and overlap repulsion (chapter 4).

Cations have much smaller polarisabilities than anions; having lost an electron, their electronic structure is more compact and more stable, and less likely to vary with the environment. At least for the smaller cations studied so far

(Li^+ and Na^+), the *in-crystal* polarisability is nearly the same as the free ion value; the magnitude and the fluctuations of cation polarisability are both small compared with anions. Their contribution to scattering processes is usually minimal. In terms of the shell model used in chapter 5, these cations can be treated as rigid particles.

The actual instantaneous values of the anion *in-crystal* polarisabilities are found to fluctuate quite significantly as the local environment varies. These effects have been quantified in studies of disordered crystal lattices [FOW85]. These studies are a good starting point for understanding the instantaneous variation of ionic polarisabilities in melts, but a much wider range of local ionic configurations is sampled in the melt than in the still relatively ordered distorted crystal, so any parameterisation based on crystal data must be regarded with some restraint. Nevertheless, these crystal polarisability fluctuations are a necessary first step. To understand how the magnitude of these fluctuations is assessed, it is necessary to discuss briefly the electronic structure calculations used to determine them.

6.2.1 Electronic structure calculations of polarisabilities

Fowler and Madden have published a number of studies of the behaviour of ionic polarisabilities [FOW83, 84a] and hyperpolarisabilities [FOW84b] in condensed environments, as determined from electronic structure calculations. They have also studied explicitly the fluctuations of dipole moments in these systems [FOW85]. Their calculations are conducted in stages to allow evaluation of the relative importance of different mechanisms in determining the polarisability.

The work on LiF is typical [FOW83]. They begin with a free ion (figure 6.1a), whose electronic structure is represented by a large basis set. The po-

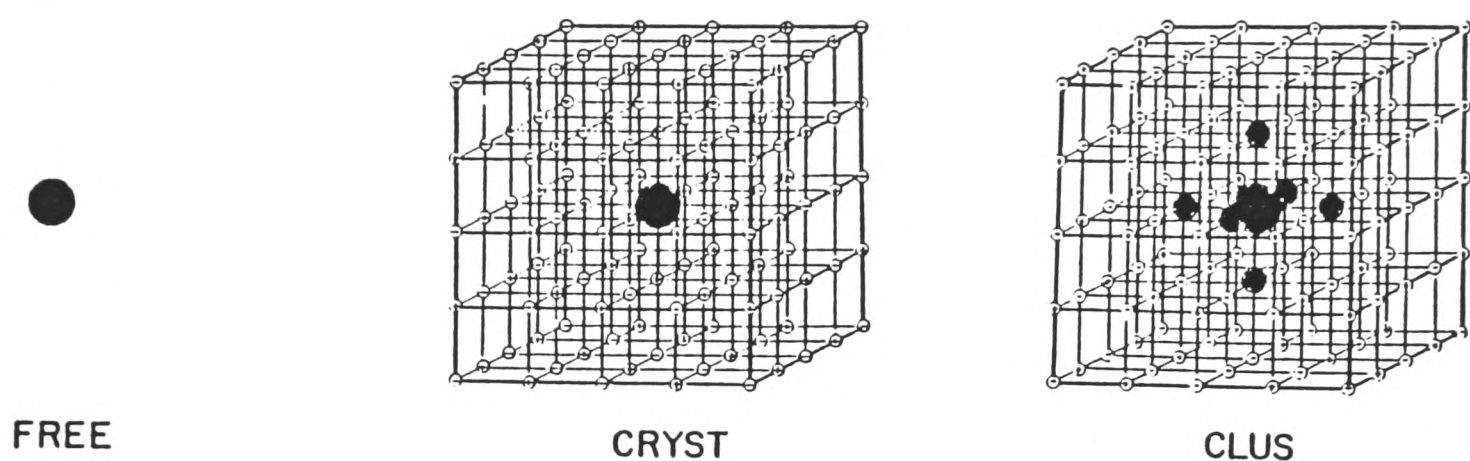


Figure 6.1 : Ion environments for electronic structure calculations: a) the FREE ion environment; b) the XTAL environment where the ion of interest is centered in a $5 \times 5 \times 5$ lattice of point charges; c) the CLUS (for cluster) environment, where the ion of interest is surrounded by six near neighbours represented by proper electronic basis sets; the cluster is embedded in the same point charge lattice as for b). From Fowler and Madden [FOW84a]

larisability of this free ion is calculated with standard techniques and compared with theoretically established values to confirm the performance of the basis set. The ion is then placed in a $5 \times 5 \times 5$ lattice of point charges (figure 6.1b); the lattice corresponds to the crystal lattice at the desired temperature, and the charge on each site corresponds to the species occupying that site in the crystal. This allows the effect of electrostatic compression (or expansion in the case of cations) to be measured; the result is a significant reduction in anion polarisability (from 16 a.u. to about 9 a.u. for F^- in a LiF lattice) and a very slight ($< 0.1\%$) increase in cation polarisability (for Li^+ , Na^+ , and K^+) [FOW84a]. Finally, the six (in the case of NaCl crystal structure salts) nearest neighbour sites to the given ion are occupied with proper ions (figure 6.1c), represented by good electronic basis sets; the rest of the lattice is occupied by point charges. This allows the additional effect of electron cloud “compression” for both cations and anions due to overlap repulsion interactions with neighbouring ions to be calculated; in LiF, this results in a further fall in polarisability of about 3 a.u. to 6.18 a.u. for F^- but no significant change to the cation. Similar results have

been found for NaCl [FOW86, MAD86], with the Cl^- polarisability falling from a free ion value of about 36 a.u. to 20.9 a.u. in the crystal (table 6.1 later in this chapter).

This work confirms the observations of Lyddane and Herzfeld long ago [LYD38] that electronic effects alone are inadequate to represent the polarisability of ions in crystals. The total in-crystal polarisabilities are accessible experimentally via refractive index measurements and the Clausius–Mossotti relation [FOW84a]; the calculations are in good agreement with experiment. As the basis sets used are large and quite accurate, much confidence can be placed in the separation, achieved by the calculations, of these polarisabilities into component parts due to various mechanisms.

Since the interatomic distances in melts are similar to those crystals, it is expected that qualitatively similar modifications of the free ion polarisability will occur in melts, but the disordered environment makes such a detailed calculation as was possible for crystals difficult. Specifically, the ions in the melt sample a much broader range of possible configurations than do the ions in the solid, so naive application of results obtained from crystals is potentially misleading. Certainly in the melts, the contribution to the ionic polarisability from hyperpolarisability terms (which vanish in the perfect crystal and are small in disordered crystal environments) must be assessed. Close approaches by like ions also can occur in melts and must be treated in any model.

What is possible in the crystal environment is the measurement of changes in the relative contributions of the different polarisability modifying mechanisms as the neighbouring ions are shifted from their equilibrium positions. Fowler, Madden, and Board have done this for disordered crystals of LiF [FOW85] and NaCl [FOW86, MAD86]. From knowledge of the behaviour of the polarisability components in these disordered environments, models for the polarisability in general disordered environments (and thus in melts) can be drawn up and

parameterised. After a discussion of the simpler case of argon, such models for alkali halide ions will be developed and used.

6.3 Simpler systems — argon revisited

As for the development of potential models described in chapter 4, early work on the light scattering from liquids concentrated on simpler systems, such as argon. Only recently, however, has a clear picture for the situation of liquid argon emerged. The light scattering from liquid argon has been extensively studied experimentally [VAR81, CLA81b] and via simulation [LAD80, VAR81, CLA81a]. The most striking result from the experimental work is that the scattering is almost completely depolarised; that is, in experiments with linearly polarised laser light, the measured depolarisation ratio ρ_D is almost .75. This means that there can be no isotropic contribution to the scattering; only traceless operators can contribute to the polarisation (section 3.5). This would be reasonably expected for an inert system, as the very weak atomic interactions do not alter the electronic configuration of the atoms significantly.

6.3.1 The dipole–induced dipole mechanism

The most obvious source for contributions to the polarisation density of systems of argon atoms is the dominant multipole interaction, the dipole–induced dipole (or DID) interaction. The overlap repulsion force is not very effective in altering the polarisability in argon [LAD80, VAR81]; it would contribute a trace term, and thus an isotropic intensity, to the scattering, which would lead to departures from the measured depolarisation ratio of .75. It is thought that the DID mechanism accounts for at least 90% of the scattering, with the rest coming from higher multipole mechanisms [VAR81].

Within the approximation of localised electrons about argon atoms, the polarisation $\mathbf{P}(\mathbf{r})$ at position $\mathbf{r}$ can be written as depending only on the total dipole moments $\mathbf{p}^i$ of the ions i [FOW85],

$$\mathbf{P}(\mathbf{r}) = \sum_i \mathbf{p}^i \delta(\mathbf{r} - \mathbf{r}^i), \quad (6.1)$$

where the total dipole moments within the dipole approximation are given by

$$\mathbf{p}^i = \boldsymbol{\mu}^i + \underline{\boldsymbol{\alpha}}^i \cdot \left(\mathbf{E}^0(\mathbf{r}^i) + \sum_{j \neq i} \underline{\mathbf{T}}^{ij} \cdot \mathbf{p}^j \right). \quad (6.2)$$

Here, $\mathbf{E}^0(\mathbf{r})$ is the external field at position $\mathbf{r}$, and $\underline{\mathbf{T}}^{ij}$ is the dipole–dipole tensor for atoms i and j [KIR36];

$$\mathbf{T}_{\alpha\beta}^{ij} = \left(\nabla \nabla \mathbf{r}_{ij}^{-1} \right)_{\alpha\beta} = \frac{1}{r_{ij}^3} \left(\delta_{\alpha\beta} - \frac{3r_{ij}^\alpha r_{ij}^\beta}{r_{ij}^2} \right); \quad (6.3)$$

$\mathbf{r}_{ij}$ is the position vector between atoms i and j . This self-consistent expression for $\mathbf{p}^i$ in terms of the $\mathbf{p}^j$'s is the sum of the polarisation due to the free atom plus all pair interactions involving the given atom mediated by the dipole tensor and the intrinsic atomic polarisability $\underline{\boldsymbol{\alpha}}^i$.

There are several great simplifications that can now be made for argon. First, there is no configurational dipole moment $\boldsymbol{\mu}$. Second, the light scattering from argon can be explained well by replacing the configuration dependent atomic polarisability tensors $\underline{\boldsymbol{\alpha}}^i$ with the constant, spherically averaged isolated atom polarisability α_0 . This reflects the fact that the intrinsic polarisability of argon atoms is almost completely unaffected by the local environment, and the atoms in melts over time experience approximate spherical symmetry. In the same spirit, the self-consistent expression can be reduced to a simpler form by truncating this series at first order, that is, by replacing the $\mathbf{p}^j$ by $\alpha_0 \mathbf{E}^0(\mathbf{r}^j)$. Finally, in the limit of slowly varying fields (on the distance scales of scattering processes),

$$\mathbf{E}^0(\mathbf{r}^i) = \mathbf{E}^0(\mathbf{r}^j) = \mathbf{E}^0.$$

The complete polarisability operator $\underline{\Pi}^i$ for atom i can now be written as ($\underline{\mathbf{I}}$ is the unit tensor)

$$\underline{\Pi}^i = \alpha_0 \underline{\mathbf{I}} + \alpha_0^2 \sum_{j \neq i} \underline{\mathbf{T}}^{ij}. \quad (6.4)$$

6.3.2 Lineshapes and absolute intensities

Given the polarisation density as calculated above in the DID model, the absolute intensity in melts and lineshape of the scattering in crystals and melts can be obtained. The absolute intensity is related to the mean square value of the fluctuation of the polarisability density from its average value. As the dipole tensor is by construction traceless, there will be no isotropic term proportional to the trace of this tensor, and thus no isotropic intensity. The anisotropic intensity is proportional to $\langle \beta^2 \rangle$, the mean-square value of the fluctuations in the anisotropic part of the total polarisability $\underline{\Pi}$ (cf (3.6) and [ALD73a]):

$$I^{ANI} \propto \langle \beta^2 \rangle$$

$$\langle \beta^2 \rangle = G_c \alpha_0^4 \sum_{\substack{i \\ \alpha \neq \beta}} ((\Pi_{\alpha\alpha}^i - \Pi_{\beta\beta}^i) - \langle \Pi_{\alpha\alpha}^i - \Pi_{\beta\beta}^i \rangle)^2 + 6(\Pi_{\alpha\beta}^i - \langle \Pi_{\alpha\beta}^i \rangle)^2 \quad (6.5)$$

where the constant term in α_0 has been discarded since only the fluctuating part is relevant. G_c is a geometrical constant resulting from the spherical averaging; its value depends on the exact scattering geometry used, but these values are well known [LON77]. Note the average values have been subtracted away to give the fluctuating part. The mean square value can be written this way since the two diagonal and three off-diagonal representations of the tensor are all mutually orthogonal [SCH65]. The intensity due to the DID mechanism is proportional to the fourth power of the polarisability, and so calculations based on the DID model are quite sensitive to the value of the polarisability used.

The absolute scattering intensity for polarised and depolarised light is measured as a scattering cross section in experimental work; the absolute cross sec-

tion of a given sample must be determined by referring the (arbitrary) scattering intensities obtained from a given instrument to the intensity from a reference standard of known cross section. This may be done by having minute amounts of the reference material present in the sample of interest or by performing separate experiments on the sample and reference under identical conditions. The reference materials themselves have been calibrated fundamentally against hydrogen, for which the scattering cross sections are known from *ab initio* calculations [VAR81].

In simulation work, a vaguely similar “calibration” technique can be used to find the absolute scattering intensity. The polarised and depolarised intensities measured experimentally can be converted to the isotropic and anisotropic intensities accessible to the simulation (or vice versa). For example, the mean square polarisability anisotropy $\langle\beta^2\rangle$ is accessible to simulation (as described above) and experiment, from knowledge of the absolute intensity of, say the depolarised scattering, since with polarised incident light and completely depolarised scattering appropriate to argon,

$$I^{DEPOL} = \frac{4}{45}K\langle\beta^2\rangle; \quad (6.6)$$

K is an internal field correction factor. Thus a conversion factor from $\langle\beta^2\rangle$ to absolute intensities can be determined; Clarke and Bruining found it to be $1\text{a.u.}^2 = 1.02 \times 10^{-30}\text{cm}^2\text{sr}^{-1}\text{atom}^{-1}$ [CLA81b]. The scattering intensity of other materials as determined from simulation can be referred to this argon standard if $\langle\beta^2\rangle$ is determined in the same way.

The absolute intensity of scattering from crystals is much more difficult to determine, as all parameters are directional, and there is no simple way in general to incorporate a reference material in the sample. For most materials, including the alkali halides, absolute intensities for crystals are not available experimentally. The simulation work, however, is able to overcome these difficulties, so the absolute intensity of the scattering from crystals can be predicted

through this work. The anisotropic scattering from crystals is usually separated into components arising out of different representations of the symmetry group of the crystal; these representations, which are equivalent in the spherical symmetry of melts, are not all equivalent in crystals.

The scattering lineshape is obtained from the Fourier transform of the time correlation of the polarisability fluctuations projected into the appropriate symmetry. Again for argon there is no isotropic scattering; the spectrum of the anisotropic polarisability fluctuations is given by

$$I^{ANI}(\omega) \propto \int_0^\infty \langle \beta(0)\beta(t) \rangle e^{-i\omega t} dt. \quad (6.7)$$

$\beta(t)$ is the instantaneous value of the fluctuating part of the polarisability anisotropy at time t ; its form depends on the symmetry of the system. A general expression for the polarisability correlation, isotropic or anisotropic, analogous to $\langle \beta(0)\beta(t) \rangle$ above, is

$$\left\langle \left(\sum_{i=1}^N \mathcal{O} \Pi^i(0) - \langle \mathcal{O} \Pi^i \rangle \right) \cdot \left(\sum_{j=1}^N \mathcal{O} \Pi^j(t) - \langle \mathcal{O} \Pi^j \rangle \right) \right\rangle. \quad (6.8)$$

The operator $\mathcal{O}$ projects out the appropriate combination of the elements of Π^i for the scattering of interest (isotropic or anisotropic). Such properties are called *coherent* properties of the system, as they depend on the collective behaviour of the entire system, through the separate sums over i and j . The statistics of such collective properties as collected in simulations are known to be quite poorly behaved; extremely long runs are required to obtain accurate estimates of coherent properties from simulation work. *Incoherent* properties are found from equations of the same form, but with the second sum restricted to terms with $j = i$. Sometimes a coherent property can be approximated by the related incoherent one, since the statistics of incoherent correlations are usually better.

Note that the intensity is just the $t = 0$ value of this correlation function. The experimentally available polarised and depolarised scattering lineshapes

and the isotropic and anisotropic lineshapes from the simulation can be interconverted.

Early computer simulations of liquid argon employing the DID model were performed by Berne *et al.* [BER73], and Alder *et al.* [ALD73a, b]; the failure of these workers to reproduce the experimentally “known” values of the argon scattering intensity led to refutation of the DID model as incomplete for even the simplest inert systems (see, for example, [ALD79]). Much work was devoted to the construction of more elaborate models for the scattering in simple liquids, but new experiments on the absolute scattering intensity from argon lowered the previously established intensity value by a considerable amount, bringing experiment and simulation with the simple DID model in close agreement [VAR81, CLA81b]. The absolute intensity experiments are indeed difficult; the simulation work with the DID model is also subject to problems induced by the boundary conditions of the simulation cells [CLA81a]. Both simulation and experiment, however, are now thought to be correct. Lineshapes for argon scattering have also been obtained from simulation and agree well with experiment [ALD73b].

6.4 Polarisability mechanisms in alkali halides

The situation in ionic systems, not surprisingly, is more complex than for the inert systems. The DID mechanism is again a very important part of the scattering, but now the polarisabilities should properly be taken as variable, since they are known to fluctuate strongly with the environment. The polarisability fluctuations due to overlap repulsion must also be taken into account; indeed they are responsible for most of the isotropic scattering that reduces the depolarisation ratio below the fully depolarised value of .75. The longer range effects of disorder can be accounted for through consideration of the effects of higher order electric field and field gradient contributions to the ionic polaris-

ability. In the perfect crystal, these terms cancel, but these hyperpolarisability contributions could be important in disordered environments.

Clarke and Woodcock [CLA72] realised the importance of going beyond the DID term in an early attempt to model light scattering from KCl. Their *charge-induced anisotropy* model for anion polarisability includes an *ad hoc* treatment of isotropic polarisability fluctuations induced by the total electrostatic field acting on an ion, and is successful in reproducing a portion of the lineshape of the polarised scattering from this melt. The new data now available from the electronic structure calculations will allow a quantification of these early ideas.

6.4.1 Dipole-induced dipole scattering

The formalism for the DID scattering in ionic systems is similar to that for inert systems described above, with the difference that now the polarisabilities vary not only with ionic species, but also with the instantaneous environment of each ion. In the dipole approximation, the instantaneous total electronic dipole moment $\mathbf{p}^i(t)$ of ion i at time t should be determined from an expression

$$\mathbf{p}^i(t) = \underline{\alpha}^i(\mathbf{R}^N(t)) \cdot \left(\mathbf{E}^0(\mathbf{r}^i) + \sum_{j \neq i} \underline{\mathbf{T}}^{ij} \cdot \mathbf{p}^j(t) \right). \quad (6.9)$$

(Compare with (6.2) for argon.) In simulation work, this full, self-consistent calculation is too expensive. In the spirit of the argon work, though, a number of approximations can be made, although the same approximations are more severe when applied to these systems. In lieu of the configuration dependent, instantaneous values of $\underline{\alpha}^i(\mathbf{R}^N(t))$, the constant, spherically averaged in-crystal values α_{CRYS}^i as calculated by Fowler and Madden [FOW83, 84a] (table 6.1) have been used for each species in both melt and crystal simulations. The self-consistent series in the $\mathbf{p}^j$ has again been truncated at first order, giving $\mathbf{p}^j \approx \alpha_{CRYS}^j \mathbf{E}^0(\mathbf{r}^j)$, and again the slowly varying field assumption is made.

Thus the effective DID polarisability operator $\underline{\Pi}^{i,DID}$ is given by (cf (6.4))

$$\underline{\Pi}^{i,DID} = \alpha_{CRY S}^i \left(\underline{\mathbf{I}} + \sum_{j \neq i} \underline{\mathbf{T}}^{ij} \alpha_{CRY S}^j \right). \quad (6.10)$$

When the initial melt simulations had been completed with this model and the other effects below included, the actual average value of the polarisability of each species in the melt could be assessed. Not surprisingly, the actual average anion polarisability is higher than the in-crystal value, since the interionic distances are greater on average so that the electron cloud is not compressed quite as much as in the crystal. The value of the cation polarisabilities remains virtually unaffected by the change in environment. The average anion crystal and melt polarisabilities are reported in table 6.1. The calculated Cl^- melt polarisability of 21.8 a.u. should be compared with the experimentally found (from the refractive index) value of 21.9 a.u. [MIT83]. As the DID scattering intensity is proportional to the mean square of the fluctuating part of the DID polarisability, and thus to the fourth power of the polarisabilities, the DID contributions to the intensity and lineshape calculations for melts were enhanced by a factor of $(\alpha_{MELT}^i / \alpha_{CRY S}^i)^4$

Ion	$\alpha_{CRY S}$, a.u.	α_{MELT} , a.u.
F^- in LiF	6.18	6.62
Cl^- in NaCl	20.9	21.8

Table 6.1 : In-crystal and average melt values of the anion polarisability. The in-crystal values are taken from Fowler and Madden [FOW84a]; the average melt values were found in this work. The value of α_{MELT} for Cl^- in NaCl has been found experimentally to be 21.9 a.u. [MIT83].

6.4.2 Hyperpolarisability contribution to dipole density

In the disordered environment appropriate to studies of melts, and possibly in finite temperature crystals, the effect of terms in the electronic polarisability expansion of (3.7) higher than the dipole polarisability must be considered. These hyperpolarisability terms should reflect the effect of disorder at long range (greater than about near neighbour spacing) on the electronic structure of a given ion, since the higher order electric field and field gradient terms, which vanish in the perfect (0°K) crystal, can become significant when the perfect lattice symmetry is broken. The terms are measurable in finite temperature crystals, and could become quite significant in melts. As these terms should capture the deviation of total electronic polarisability from the dipole polarisability alone in the presence of disorder in the limit of large separations, Fowler and Madden have called them the *asymptotic terms* [FOW85]. At short distances, the additional effect of ion compression due to overlap repulsion, a “mechanical” rather than electronic effect, must be considered; this is treated in the next section.

Fowler and Madden have performed electronic structure calculations similar to those used to assess the in-crystal polarisability to evaluate the leading hyperpolarisabilities contributing to the dipole density. Recall from (3.7) that the electronically induced dipole on ion i can be expanded in powers of fields and field derivatives; the first few terms in the series are

$$\mu_{\alpha}^i = \alpha_{\alpha\beta}^i F_{\beta} + \frac{1}{6} \gamma_{\alpha\beta\gamma\delta}^i F_{\beta} F_{\gamma} F_{\delta} + \frac{1}{3} B_{\alpha\beta,\gamma\delta}^i F_{\beta} F_{\gamma\delta} + \dots \quad (3.7)$$

The term in $\underline{\gamma}$ is the *dipole hyperpolarisability*, and the term in $\underline{B}$ is the *quadrupole hyperpolarisability*. The term in $\underline{B}$ is traceless, and thus will not contribute to the isotropic scattering intensity. $\underline{\gamma}$ is not traceless, however, so it will contribute an isotropic intensity. Sources of isotropic intensity are needed to account for the observed low depolarisation ratio in NaCl. Unfortunately, it will turn out that the $\underline{\gamma}$ term is very weak in the present parameterisation. Written in terms of an operator $\underline{\Pi}^{ASY,i}$ and the pair separations $\mathbf{r}_{ij}$, the asymptotic

polarisability terms for ion i are [MAD86]

$$\underline{\Pi}_{\alpha\beta}^{ASY,i} = \delta_{\alpha\beta}\bar{\alpha} + \frac{1}{2}\gamma_{\alpha\beta\gamma\delta}\left(\sum_j q_i \nabla_\gamma r_{ij}^{-1}\right)\left(\sum_k q_k \nabla_\delta r_{ik}^{-1}\right) + \frac{1}{3}B_{\alpha\beta,\gamma\delta} \sum_j q_j \nabla_\gamma \nabla_\delta r_{ij}^{-1}. \quad (6.11)$$

In spherically symmetric environments (appropriate to melts), each of these tensors can be shown on average to depend only on one parameter, as given in (3.8) and (3.9) [BUC67]. These relations can be restated as [FOW84b]

$$\gamma_{xxxx} = \gamma_{yyyy} = \gamma_{zzzz} = \gamma_1 = \gamma, \quad (6.12)$$

$$\gamma_{xxyy} = \gamma_{xxzz} = \gamma_{yyzz} = \gamma_2 = \frac{1}{3}\gamma, \quad (6.13)$$

$$B_{xx,xx} = -2B_{xx,yy} = -2B_{xx,zz} = B_1 = B \quad (6.14)$$

$$B_{xy,xy} = B_{xz,xz} = B_{yz,yz} = B_2 = \frac{3}{4}B \quad (6.15)$$

In a crystal, however, the cubic symmetry destroys the simple relation between the on- and off-diagonal terms of each tensor [FOW84b], so that $\gamma_1 \neq 3\gamma_2$ and $B_1 \neq \frac{4}{3}B_2$. Fowler and Madden have calculated the values γ_1 , γ_2 , B_1 , and B_2 for F^- in LiF and Cl^- in LiCl; the results are in table 6.2. The deviation from the simple spherical symmetry relations between the two sets of values are clearly violated, but not drastically.

Ion	γ_1 , a.u.	γ_2 , a.u.	$\bar{\gamma}$, a.u.	B_1 , a.u.	B_2 , a.u.	$\bar{B}$, a.u.
F^- in LiF	209	119	283	-48 ± 6	-45 ± 1	-54
Cl^- in LiCl	2090	815	2270	-317 ± 1	-275 ± 10	-342

Table 6.2 : In-crystal values of ionic hyperpolarisabilities In the crystal, the spherical symmetry relations (6.12) — (6.15) are broken, but not catastrophically. The mean values $\bar{\gamma}$ and $\bar{B}$ are formed from a weighted average of γ_1 and γ_2 (6.16), and B_1 and B_2 (6.17) respectively, as if spherical symmetry still applied. From Fowler and Madden [FOW84b].

In the simulation work, since the spherical symmetry relations were not violated enormously, especially for the Cl^- in LiCl, the spherical averages $\bar{\gamma}$ and

$\bar{B}$ were formed from the relations

$$\bar{\gamma} = \frac{1}{2}(\gamma_1 + 3\gamma_2) \quad (6.16)$$

$$\bar{B} = \frac{1}{2}(B_1 + \frac{4}{3}B_2). \quad (6.17)$$

These average values, also given in table 6.2, were then used in the simulation work to calculate the hyperpolarisability contribution to the dipole density from the reconstructed spherically symmetric tensors $\underline{\gamma}$ and $\underline{B}$ described by (6.12) — (6.15). The LiCl value for the Cl^- hyperpolarisabilities have been used for NaCl simulations, as hyperpolarisability data on NaCl is not yet available. For both LiF and NaCl, the cation hyperpolarisabilities are thought to be negligible.

Evaluation of these terms required some modification to the simulation programs. It is necessary to have available the electric field and field gradient on each ion at each timestep. The field was available as an artifact of the Ewald summation used to evaluate the Coulomb energy of each ion (chapter 2), so it was easy to write out the field along with the configuration data.

The field gradient was not directly determined before. An attempt was made to write down the Ewald-like expansion for the field gradient, essentially by taking the derivative of the usual Coulomb energy Ewald series, but this approach proved to be numerically difficult. Specifically, the quadrupole hyperpolarisability term in $\underline{B}$, which involves the field gradient, should be traceless, since $\underline{B}$ itself is traceless. The interpolation procedure used to evaluate the gradient at an arbitrary position given the values stored on a real-space grid gave a consistently small but non-zero isotropic term, however. The results given here for LiF were determined with this method, and could therefore be improved.

Since the field gradient converges much more rapidly than the field, and since absolute accuracy was not needed in the first instance when interest was in assessing whether or not the quadrupole hyperpolarisability term was significant or not (noting also that the gradient terms do not affect the ion dynamics),

the gradient was instead found by evaluating the gradient directly within a spherically cut off radius:

$$\mathbf{F}^i = \sum_{j:r_{ij} < r_a} q_j \nabla \nabla r_{ij}^{-1}. \quad (6.18)$$

This representation involves the same terms in $(\nabla \nabla r^{-1})$ as the DID scattering above, so the two terms were conveniently computed with much common code, with a common truncation length.

In the simulation of molten NaCl, the cutoff r_a was chosen at the third node of the like-ion distribution functions $g_{++}(r) \sim g_{--}(r)$ (figure 4.10); at 7.08 Å, or 0.37 of the box size. In the NaCl crystal simulation, the cutoff was taken after the fifth peak in the combined radial distribution function (figure 4.9), at 6.60 Å, or 0.39 of the box size.

This procedure of extracting the mean spherical value of the hyperpolarisabilities from crystal data seems a sensible first approximation for the evaluation of these effects on melt simulations. It is less satisfactory to use this spherical form in crystal simulations, but this has been done to get a qualitative assessment of the importance of these terms in the crystal as well as melt scattering. It would be desirable to improve these calculations through use of NaCl data rather than relying on the transferrability of the LiCl data, and to repeat the calculations in an environment more appropriate to the melts. In crystals, it would be better to use the separate γ_1 , γ_2 , B_1 , and B_2 terms in the evaluation of the hyperpolarisability induced dipole density, but the small deviations of the crystal values from the spherically symmetric ones in LiCl did not seem to warrant the necessary modifications to the simulation programs. These terms are found (below) to be extremely important to the scattering intensity in both crystals and melts. This is gratifying, since the electronic structure calculations to date indicate that they should be important.

6.4.3 Short range repulsion distortions

At short range, i.e., within about near neighbour distances, the effect on an ion's polarisability due to the proximity of a neighbour is primarily “mechanical” rather than electronic, as the overlap repulsion locally “squeezes” the electron clouds of the interacting ions. This results in what Fowler and Madden call a *dent in the wall* of the confining potential for the electrons, and thus a reduction in the ionic polarisability. As the dipole hyperpolarisability $\underline{\gamma}$ described above was found to give only a very weak isotropic contribution to the scattering, and no other mechanism considered in this model contributes an isotropic term, this “dent” effect must account for the significant isotropic scattering observed in highly polarised melts like NaCl.

To capture the effects of this short range distortion in simulation work in a computationally tractable model, a pairwise additive parameterisation of the effect for general ionic configurations is needed. The electronic structure calculations identifying and quantifying the effect, however, have only been performed for a few carefully chosen configurations in disordered (but not severely so) crystals.

A generalised classical Drude model for the polarisability [HIR54] is a convenient vehicle with which to perform this parameterisation. The Drude model, somewhat in the spirit of the polarisable ion shell model interionic potentials described in chapter 4, treats the polarisability of an isolated ion in terms of a harmonic spring of force constant k connecting an ion core to the charge q (in fully ionic systems) associated with it. In the presence of an electric field $\mathbf{E}$, the polarisability is represented as $\alpha = q/k$, since $q\mathbf{E}/k$ gives the induced dipole moment on the ion.

In a condensed system, the polarisability and thus the Drude “spring” must be tensor quantities. The second rank tensorial generalisation of the Drude

model to an operator $\underline{\Pi}^{SR,i}$ (for Short Range polarisability distortion operator) is

$$\underline{\Pi}^{SR,i} = q \left(\underline{\mathbf{k}}^i(\mathbf{R}^N) \right)^{-1}, \quad (6.19)$$

where $\underline{\mathbf{k}}$ and thus the operator $\underline{\Pi}^{SR,i}$ are symmetric, as is required physically. The $\mathbf{R}^N$ dependence indicates that the polarisability of a given ion is, in general, a function of the configuration of all ions in the system. The assumption of constant charge q is equivalent to assuming that no significant charge transfer between ions takes place; this is consistent with the findings of the electronic structure calculations for the salts studied here [FOW83, 84a].

The most general form that can be adopted for $\underline{\mathbf{k}}^i$ consistent with a pairwise additive model is

$$\underline{\mathbf{k}}^i(\mathbf{R}^N) = \left(k_0 + \sum_{j \neq i} A(r_{ij}) \right) \underline{\mathbf{I}} + \sum_{j \neq i} B(r_{ij}) (3\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} - \underline{\mathbf{I}}). \quad (6.20)$$

$\underline{\mathbf{I}}$ is the unit tensor, and $A(r)$ and $B(r)$ are functions describing the effect of the overlap repulsion on the isotropic and anisotropic parts, respectively, of the “spring,” and thus of the polarisability. $\hat{\mathbf{r}}_{ij}$ is a unit vector in the direction $\mathbf{r}_{ij}$. $A(r)$, describing the variation of the isotropic part, in some ways captures the same “breathing modes” of the electron shell as the breathing shell model potentials (chapter 4). Bruce and Cowley have used breathing shell model potentials to study the Raman scattering from alkali halide crystals [BRU72a, b]; much of their work could be recast in this language.

In the spirit of the Born–Huggins–Mayer form for the overlap repulsion term as used in the potential models described in chapter 4, it seems sensible to assume an exponential form for the functions A and B . Elliott and Dixon [ELL81] used an exponential form in a study of the lineshape of the quadrupole moment fluctuation contribution Raman scattering from molten NaI (chapter 5); they did not, however, separate the polarisability distortion into separate isotropic and anisotropic parts, and their *ad hoc* parameterisation was not based on detailed

knowledge of the electronic behaviour of the ions. For the functions $A(r)$ and $B(r)$, the most general parameterisation is

$$A(r_{ij}) = a_{ij} \exp(-c_{ij}(r_{ij} - \sigma_{ij})) \quad (6.21)$$

$$B(r_{ij}) = b_{ij} \exp(-c_{ij}(r_{ij} - \sigma_{ij})) \quad (6.22)$$

In each of these expressions, there are two independent parameters; the σ_{ij} are simply the sum of the interionic radii for ions i and j ; the Fumi–Tosi values [SAN76] are used here (table 6.3). To be consistent with the treatment of the repulsive term in the Fumi–Tosi parameterisation of the potential model that is used in these simulations, the range parameters c_{ij} and d_{ij} should also be reasonably close to the Fumi–Tosi values.

The cation–cation terms can be eliminated from the discussion at the start; as the cation polarisability is virtually unaffected by repulsion, the cations are assumed not to contribute to the short range polarisability fluctuations. It remains to obtain values for the remaining eight parameters for this model (two each for $A(r)$ and $B(r)$ for the cation–anion and anion–anion interactions). The electronic structure calculations described in section 6.2 only include near neighbour ions explicitly, so there is no direct data from which to extract anion–anion parameters. The like–ion contribution should be far less important than the cation–anion term, so its parameterisation should be less critical. The anion–anion parameters, then, are set in an *ad hoc* manner to values similar to the cation–anion ones; the different distances appropriate to the like–ion interaction are counted on to reduce the effect of this term to the proper level. Clearly there is room for improvement here.

The crucial cation–anion parameters are fitted to the polarisability distortions calculated in the electronic structure work. The distortions underdetermine these parameters, so some choices based on physical reasoning must still be made. The special lattice distortions chosen allow separation of the isotropic

$A(r)$ and anisotropic $B(r)$ terms. For NaCl, three distortions were used (figure 6.2). The known value of the in-crystal anion polarisability α_{CRYS}^- (table 6.1) fixes the quantity $(k_0 + 6a_{+-})$. The bending distortion (#3 in figure 6.2) fixes the amplitude b_{+-} of the anisotropic distortions, since no change in the distance r_{ij} results from this distortion. The values of c_{+-} and d_{+-} , and the ratio (a_{+-}/k_0) are then adjusted to fit the stretching distortions (1 and 2 in figure 6.2) [MAD86].

The values for all these parameters as determined by the above procedure are given in table 6.3. When put back into equations (6.19 – 6.22), these values reproduce the known (via electronic structure calculations) distortions in figure 6.2 quite accurately [MAD86]. The configurations used for LiF were similar but slightly different; the same fitting procedure is used, with the same uncertainties, resulting in the values in table 6.3.

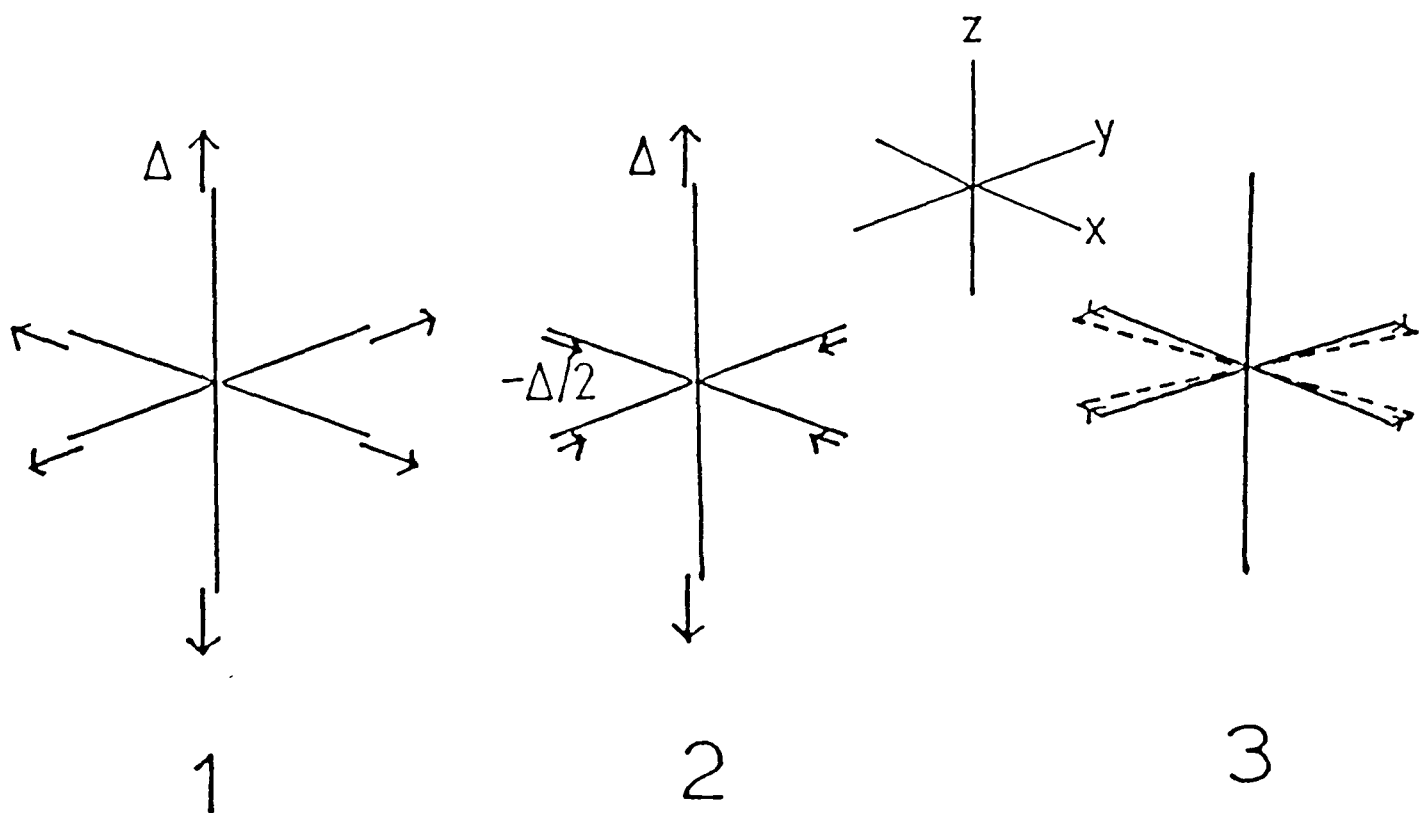


Figure 6.2 : Distorted ion configurations used to parameterise the “dent in the wall” terms for NaCl. From Madden and Board [MAD86].

Salt	a_{+-} a.u. ⁻¹	a_{--} a.u. ⁻¹	b_{+-} a.u. ⁻¹	b_{--} a.u. ⁻¹	c_{+-} Å ⁻¹	c_{--} Å ⁻¹	d_{+-} Å ⁻¹	d_{--} Å ⁻¹	σ_+ Å	σ_- Å	k_0^{-1} a.u.
LiF	0.00841	0.00564	0.00564	0.00564	2.3702	3.3434	3.3434	3.3434	0.816	1.179	9.622
NaCl	0.0024	0.0011	0.00203	0.0011	1.97	3.43	1.65	3.43	1.170	1.585	28.212

Table 6.3 : Parameters for “dent in the wall” model. These values for eqns. (6.19 – 6.22) reproduce the known electronic distortion data quite accurately.

6.5 Results: Raman intensities and lineshapes

The salts chosen for study with the three-part model derived above were LiF and NaCl; these are the only salts so far for which the electronic structure calculations needed to parameterise the models have been done. Section 4.8 presents details of the simulations themselves. The models were first tested on short 64-ion simulations; the NaCl data reported here were taken from long (about 100ps, or 20000 timesteps) 216-ion simulations. The 216-ion LiF simulations were much shorter (5600 timesteps). Extensive experimental work has been performed on NaCl melts (and those of many other alkali halides) by Raptis *et al.* [RAP83] and by Giergiel *et al.* [GIE84]. The Raman spectrum of NaCl crystals has been measured by Krauzman [KRA68] and Raptis *et al.* [RAP86], and considered theoretically by Karo and Hardy [KAR66] and Bruce [BRU72b]. The NaCl results can, therefore, be compared in some detail with experiment. There are no experimental data available on LiF with which to compare the simulation results. There are apparently experimental difficulties working with this salt (it attacks cells used to contain it). Although some phonon data are known from which good pair potentials can be extracted, there are no experimental light scattering data for this salt from either the crystal or the melt. Results for LiF can only be judged qualitatively as to their reasonableness, given what is known about other alkali halides.

6.5.1 Absolute scattering intensities

Using a procedure similar to that described for argon in section 6.3, the absolute scattering intensity of each of the three mechanisms detailed in section 6.4, as well as the intensity of the interference, or “cross terms,” between each pair of mechanisms, has been calculated. By collecting appropriate combinations of terms from the polarisability tensor, the isotropic and anisotropic contributions have been determined separately; appropriate combinations of these two values gives the more conventionally reported polarised and depolarised scattering intensity.

The polarisability operator for ion i appropriate to this calculation is

$$\underline{\Pi}^i(t) = \underline{\Pi}^{SR,i}(t) + \underline{\Pi}^{DID,i}(t) + \underline{\Pi}^{ASY,i}(t), \quad (6.23)$$

for the short range, dipole-induced dipole, and asymptotic mechanisms described above by equations (6.19), (6.10), and (6.11) respectively. All three terms will turn out to be important, although the γ contribution to the asymptotic term will be quite small.

The scattering intensity is determined from the mean square of the polarisability anisotropy $\langle\beta^2\rangle$, or equivalently from the $t = 0$ value of the polarisability correlation function $\langle(\sum_i \delta \mathcal{O} \underline{\Pi}^i(0)) \cdot (\sum_j \delta \mathcal{O} \underline{\Pi}^j(t))\rangle$, where the operator $\mathcal{O}$ projects out the desired isotropic or anisotropic representation and δ indicates that the fluctuating part of this quantity is of interest. The Fourier transform of this correlation function gives the scattering lineshape.

Specifically, the isotropic intensity is determined from the function

$$I^{ISO}(\omega) = \frac{G_c}{9} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left\langle \left(\sum_{i=1}^N \text{Tr} \underline{\Pi}^i(0) - \langle \text{Tr} \underline{\Pi}^i \rangle \right) \left(\sum_{j=1}^N \text{Tr} \underline{\Pi}^j(t) - \langle \text{Tr} \underline{\Pi}^j \rangle \right) \right\rangle. \quad (6.24)$$

G_c is a known factor resulting from the spherical averaging and the scattering geometry.

The five representations of the anisotropic intensity are obtained from the operators $\mathcal{A}^1 - \mathcal{A}^5$, given by [SCH65]

$$\begin{aligned}\mathcal{A}^1 \underline{\Pi}^i &= 2\Pi_{zz}^i - \Pi_{xx}^i - \Pi_{yy}^i \\ \mathcal{A}^2 \underline{\Pi}^i &= \sqrt{3}(\Pi_{xx}^i - \Pi_{yy}^i) \\ \mathcal{A}^3 \underline{\Pi}^i &= \sqrt{12}\Pi_{xy}^i \\ \mathcal{A}^4 \underline{\Pi}^i &= \sqrt{12}\Pi_{xz}^i \\ \mathcal{A}^5 \underline{\Pi}^i &= \sqrt{12}\Pi_{yz}^i\end{aligned}\tag{6.25}$$

In melts, due to the spherical symmetry, all five independent representations should be equivalent. In crystals, however, the different representations correspond to different scattering geometries: the *on-diagonal* representations $\mathcal{A}^1$ and $\mathcal{A}^2$ are equivalent to each other, and the *off-diagonal* representations $\mathcal{A}^3 - \mathcal{A}^5$ are also equivalent, but the two classes of representation are not equivalent. In a given representation r , the anisotropic intensity is given by

$$I^{ANI,r}(\omega) = \frac{G_c}{9} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left\langle \left(\sum_{i=1}^N \mathcal{A}^r \underline{\Pi}^i(0) - \langle \mathcal{A}^r \underline{\Pi}^i \rangle \right) \left(\sum_{j=1}^N \mathcal{A}^r \underline{\Pi}^j(t) - \langle \mathcal{A}^r \underline{\Pi}^j \rangle \right) \right\rangle.\tag{6.26}$$

To convert these intensities into experimental units for scattering cross sections per ion pair, a value derived from the argon work of Clarke and Bruining [CLA81b] of $1\text{a.u.}^2 = 1.02 \times 10^{-30} \text{cm}^2 \text{sr}^{-1} \text{pair}^{-1}$ has been used.

The contributions from each mechanism separately and the two-mechanism interference terms can be computed by restricting $\underline{\Pi}$ to include only the desired term or terms. Additionally, the separate contributions due to cation-cation, cation-anion, and anion-anion interactions can be determined by restricting the sums in (6.24) or (6.26) over the appropriate species.

From the discussion of the three mechanisms above, the isotropic scattering should be zero except for the short range and dipole hyperpolarisability mechanisms for anions, and their interference term. The field gradient and dipole-

induced dipole terms are strictly traceless, so they have no isotropic component, and the intensity of fluctuations due to the effect of short range forces on cations is taken to be zero for these salts, reflecting the results of the electronic structure calculations. The intensities are reported here for the three mechanisms separately, their pairwise interference, and in total.

6.5.2 Summary of absolute intensity results for melts

The major results for the scattering intensity from melts are given here. The total polarised and depolarised intensities, the depolarisation ratio, and the total isotropic and anisotropic intensities are presented in table 6.4. The anisotropic intensity given is the average of the five independent representations (6.25). The NaCl results are compared with experiment. The simulation results for the intensities are broken down into the constituent parts for each mechanism and symmetry representation in the next section; a discussion of the results follows.

6.5.3 Detailed results for intensity of melt scattering

The isotropic and anisotropic results presented in table 6.4 are broken down per-mechanism in table 6.5. The anisotropic terms are further broken down on a per-representation basis in table 6.6. The notation for tables 6.5 and 6.6 is as follows. The three scattering mechanisms — short-range distortions, DID, and asymptotic hyperpolarisabilities — are denoted by SR , DID , and ASY , respectively. The scattering due to one mechanism alone is denoted by, for instance, $I^{ANI,SR}$ for the anisotropic scattering due to the short range distortions. The interference terms are denoted by, for instance, $I^{ANI:SR,DID}$ for the interference between the short-range distortion and DID mechanisms for the anisotropic scattering. Only the SR and γ part of the ASY terms contribute to the isotropic scattering; the other terms are all zero and are not reported.

Melt scattering intensities, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$			
	LiF, 1170°K	NaCl, 1181°K	NaCl, 1118°K
	Simulation	Simulation	Experiment
I^{POL}	2.0	12.9	24.4
I^{DEPOL}	0.5	3.8	4.1
I^{ISO}	1.4	7.7	19.0
I^{ANI}	0.6	5.1	5.4
Depolarisation ratios			
ρ_D	.25	.30	.17

Table 6.4 : Principal results for scattering intensities from melts. The polarised (POL) and depolarised (DEPOL) intensities are related to the isotropic (ISO) and anisotropic (ANI) intensities by (3.42) and (3.43). The anisotropic intensities for the simulations here are averages from the five representations, as given in table 6.6. Experimental results for NaCl are from Raptis *et al.* [RAP83] and Fairbanks *et al.* [FAI86]. See text for a discussion of the errors appropriate to this and similar tables.

The values in tables 6.4–6.6 are quoted to the first decimal place in the units employed. Examination of the degree of variation in the values between different independent anisotropic representations in table 6.6 indicates that this is an overly generous estimate of the accuracy of the calculation; specification to two-digit accuracy would probably be more appropriate. The overspecified values, however, give a better indication of the subtlety of the interaction between mechanisms. Similar comments apply to the tables of crystal values (tables 6.7–6.9) later in this chapter.

6.5.4 Lineshapes for melt scattering

The lineshapes for the scattering are obtained from expressions like (6.7);

Melt scattering intensity by mechanism, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$		
	LiF, 1170°K simulation	NaCl, 1181°K simulation
$I^{ISO,SR}$	1.0	7.6
$I^{ISO,ASY}$	0.8	1.8
$I^{ISO:SR,ASY}$	-0.3	-1.7
$I^{ANI,SR}$	8.9	16.6
$I^{ANI,DID}$	0.5	12.4
$I^{ANI,ASY}$	9.5	20.7
$I^{ANI:SR,DID}$	-3.0	-10.4
$I^{ANI:SR,ASY}$	-17.4	-33.2
$I^{ANI:DID,ASY}$	2.1	-0.9

Table 6.5 : Isotropic and anisotropic scattering in melts by mechanism. See text for notation. The anisotropic values here are the averages of the five representations given separately in table 6.6.; these values sum to give the totals reported in table 6.4

lineshapes for the isotropic and mean anisotropic scattering are presented in figure 6.3a for LiF and figure 6.4a for NaCl. The experimentally accessible (for NaCl) polarised and depolarised spectra are formed from appropriate combinations of the isotropic and anisotropic scattering, viz. (3.42 and 3.43),

$$I^{POL}(\omega) = I^{ISO}(\omega) + I^{ANI}(\omega)$$

$$I^{DEPOL}(\omega) = \frac{3}{4}I^{ANI}(\omega)$$

These spectra are given in figures 6.3b and 6.4b for LiF and NaCl, respectively; the latter are also compared with experiment (figure 6.4c). The frequency-dependent depolarisation ratio $\rho_D(\omega)$ is also given for NaCl and compared with experiment (figure 6.4c).

6.5.5 Intensity of crystal scattering

Anisotropic intensity by representation					
LiF, 1170°K, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$					
	$\mathcal{A}^1$	$\mathcal{A}^2$	$\mathcal{A}^3$	$\mathcal{A}^4$	$\mathcal{A}^5$
I^{ANI}	0.7	0.8	0.5	0.6	0.5
$I^{ANI,SR}$	8.5	10.1	8.4	9.2	8.2
$I^{ANI,DID}$	0.5	0.6	0.5	0.5	0.5
$I^{ANI,ASY}$	9.3	11.4	8.3	9.7	8.6
$I^{ANI:SR,DID}$	-3.1	-3.2	-3.0	-3.0	-2.7
$I^{ANI:SR,ASY}$	-16.9	-20.4	-15.9	-18.0	-15.9
$I^{ANI:DID,ASY}$	2.3	2.4	2.2	2.2	1.9

Anisotropic intensity by representation					
NaCl, 1181°K, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$					
	$\mathcal{A}^1$	$\mathcal{A}^2$	$\mathcal{A}^3$	$\mathcal{A}^4$	$\mathcal{A}^5$
I^{ANI}	5.8	6.1	4.5	4.6	4.4
$I^{ANI,SR}$	15.8	17.3	17.2	16.2	16.3
$I^{ANI,DID}$	13.2	13.4	11.5	12.1	11.6
$I^{ANI,ASY}$	21.7	22.7	20.3	19.3	19.6
$I^{ANI:SR,DID}$	-9.1	-11.4	-10.8	-10.9	-9.9
$I^{ANI:SR,ASY}$	-32.9	-35.3	-33.9	-31.7	-32.3
$I^{ANI:DID,ASY}$	-3.0	-0.6	0.2	-0.4	-0.9

Table 6.6 : Anisotropic scattering for each mechanism in each symmetry representation for melts. The representations are given in (6.25); the notation is described in the text. The total for each representation is given in the first row; its components in the next six. The values given in tables 6.4 and 6.5 are averages of these values.

Similar calculations of intensities and lineshapes have been performed with

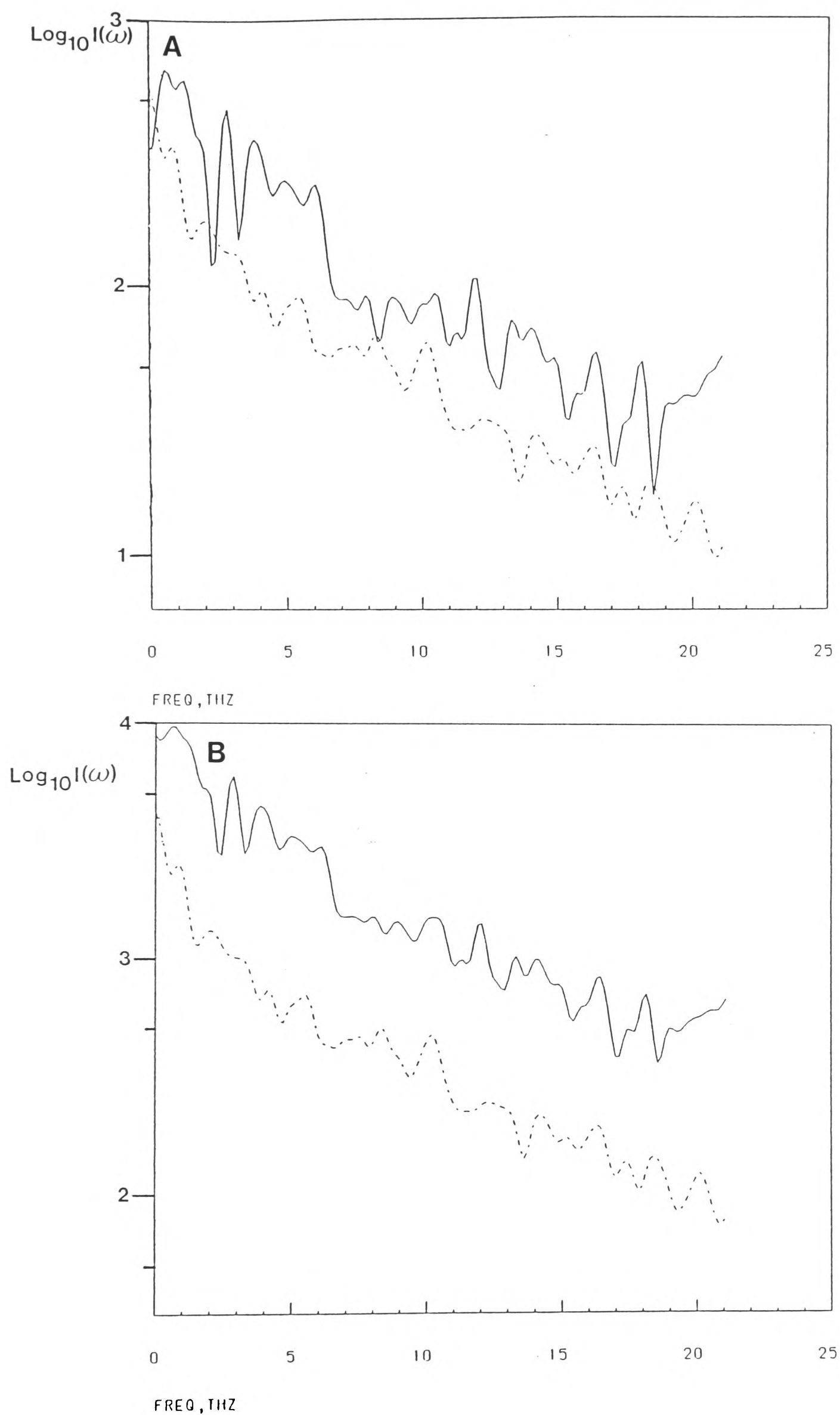


Figure 6.3 : Simulated light scattering lineshapes for LiF at 1170°K. (a) Isotropic (solid) and anisotropic (dashed) scattering. (b) Polarised (solid) and depolarised (dashed) scattering.

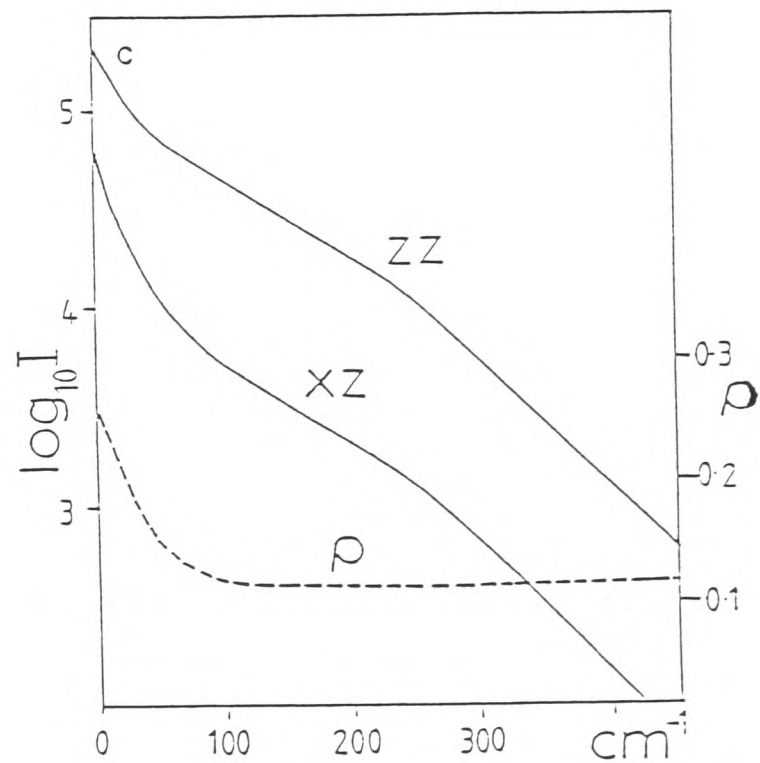
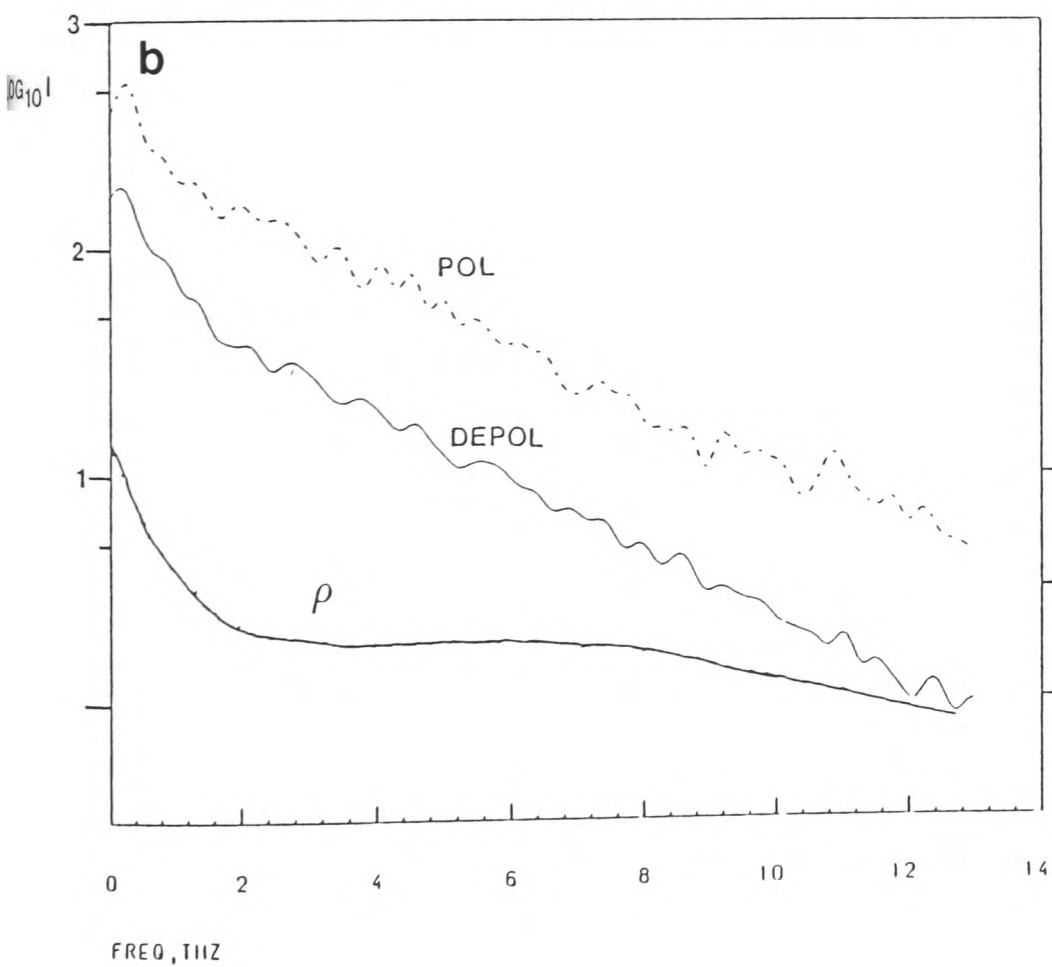
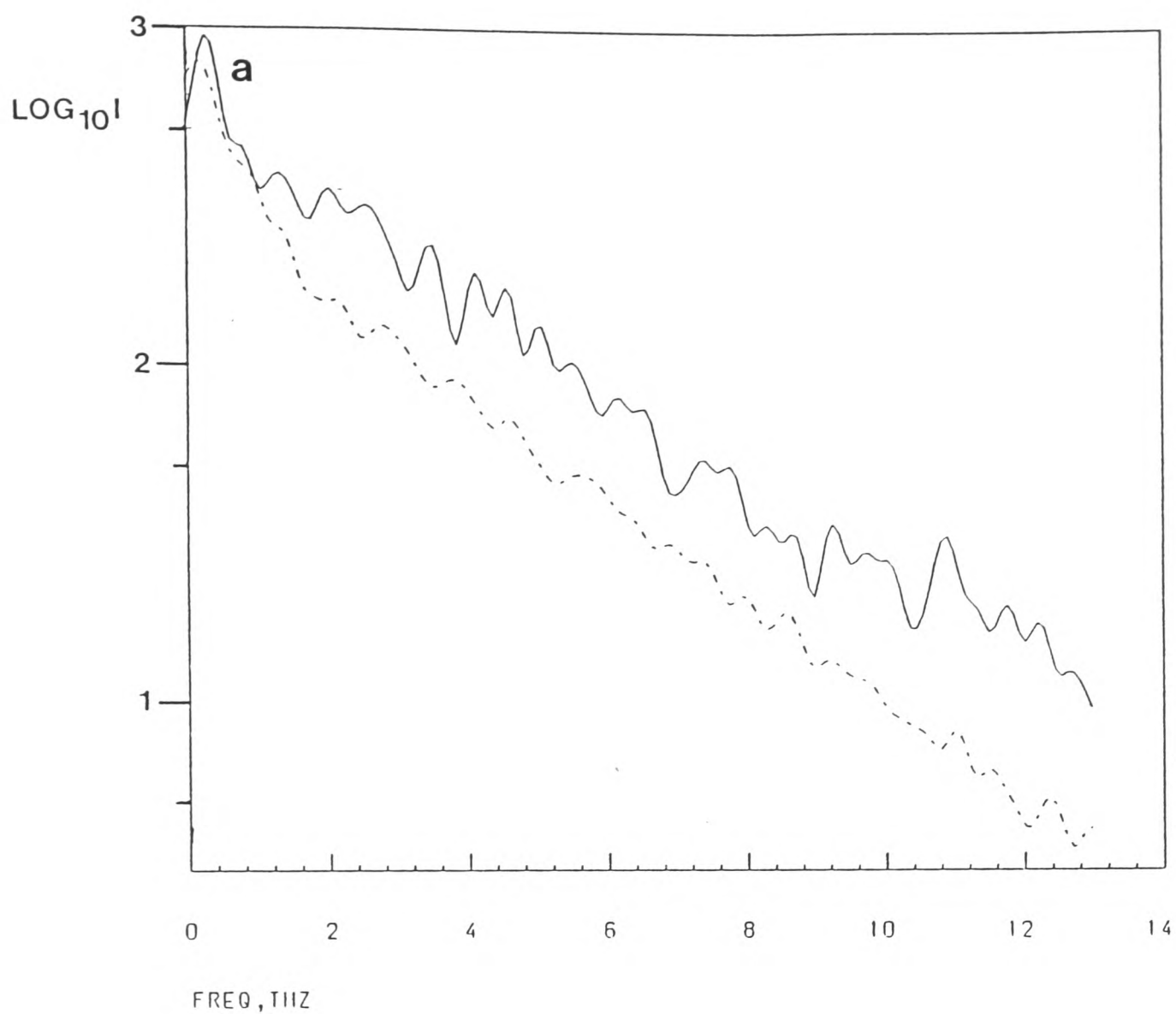


Figure 6.4 : Light scattering lineshapes for NaCl at 1181°K. (a) Simulated isotropic (solid) and anisotropic (dashed) scattering. (b) Polarised and depolarised scattering, and depolarisation ratio $\rho_D(\omega)$ from the simulation; from Madden and Board [MAD86]. (c) Experimental results of Raptis *et al.* [RAP83]; plotted as in (b); from Madden and Board [MAD86].

simulations of crystals of LiF and NaCl. In notation appropriate to crystal work, the isotropic scattering is denoted by “A”; in the absence of spherical symmetry and the averaging over angles implicit in it, the anisotropic scattering has two components, “E” and “F”. These letters correspond to the group theoretical representations giving rise to each type of scattering [BIR74]. The “E” scattering corresponds to the average of the on-diagonal anisotropy terms $\mathcal{A}^1$ and $\mathcal{A}^2$; in the conventions of this work, the scattering as calculated here is denoted “4E”. The “F” is the average of the off-diagonal terms $\mathcal{A}^3$, $\mathcal{A}^4$, and $\mathcal{A}^5$; with the crystallographic prefactor, the calculated quantity is “ $\frac{4}{3}$ F”. The results are first summarised and then broken down into component parts in the next section. There are no experimental determinations of the absolute intensity of crystal scattering available for comparison. As for melts, where the experimentally accessible quantities are the polarised and depolarised scattering, Raman lineshape measurements for crystals yield combinations of these terms in A, E, and F. In the notation of Krauzman [KRA67], these are

$$\begin{aligned}\delta &= A + 4E \\ \beta &= 3E \\ \gamma &= F.\end{aligned}\tag{6.27}$$

Although the absolute intensities of these spectra are not available, the experimental lineshape measurements below do indicate the relative intensity of these lines. The calculated intensity of each is reported here.

The crystal scattering is broken down into component parts in the same manner as the melt intensities in tables 6.7 – 6.9. The notation used is the same, except that “ISO” has become “A”, and “ANI” is now in two parts, “4E” and “ $\frac{4}{3}$ F”.

6.5.6 Lineshapes for crystal scattering

Crystal scattering intensities, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$		
	LiF, 298°K	NaCl, 300°K
	Simulation	Simulation
I^A	0.029	0.087
I^{4E}	0.018	0.137
$I^{\frac{4}{3}F}$	0.014	0.018
I^δ	0.047	0.224
I^β	0.014	0.103
I^γ	0.010	0.014

Table 6.7 : Principal results for scattering intensities from crystals. The results are given for the A, E, and F representations (corresponding to the isotropic and anisotropic components of the melt spectra) and the experimentally accessible (albeit only for relative intensities and lineshapes) δ , β , and γ combinations. Compare magnitude of corresponding terms with the melt results in tables 6.4 – 6.6.

The lineshapes for scattering from LiF and NaCl crystals are given in figures 6.5 and 6.6. The one isotropic (A) and two anisotropic ($4E$ and $\frac{4}{3}F$) lineshapes are given in part a of each figure; the observable scattering combinations δ , β , and γ , as given in (6.27), are given in part b. The NaCl results are compared with experiment (figure 6.6c).

6.6 Discussion of results for melt and crystal scattering

The results for LiF must stand on their own merit, as there is no experiment with which to compare them. What can be said is that the behaviour of LiF is broadly consistent with NaCl; the magnitudes of all intensities in LiF are much lower, though, reflecting the lower polarisability of the F^- ion. The DID scattering from LiF is, however, greatly reduced relative to its importance in

Crystal scattering intensity by mechanism, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$		
	LiF, 298°K simulation	NaCl, 300°K simulation
$I^{A,SR}$	0.032	0.071
$I^{A,ASY}$	0.025	0.036
$I^{A:SR,ASY}$	-0.028	-0.019
$I^{4E,SR}$	0.193	0.169
$I^{4E,DID}$	0.004	0.259
$I^{4E,ASY}$	0.261	0.201
$I^{4E:SR,DID}$	-0.016	-0.114
$I^{4E:SR,ASY}$	-0.429	-0.219
$I^{4E:DID,ASY}$	0.005	-0.158
$I^{\frac{4}{3}F,SR}$	0.067	0.071
$I^{\frac{4}{3}F,DID}$	0.004	0.044
$I^{\frac{4}{3}F,ASY}$	0.110	0.128
$I^{\frac{4}{3}F:SR,DID}$	-0.017	-0.016
$I^{\frac{4}{3}F:SR,ASY}$	-0.156	-0.168
$I^{\frac{4}{3}F:DID,ASY}$	0.005	-0.042

Table 6.8 : Scattering in crystals by mechanism for each representation A, E, and F. See text for notation. The 4E values here are the averages of the representations $\mathcal{A}^1$ and $\mathcal{A}^2$ given separately in table 6.9; the $\frac{4}{3}F$ values are the average of the off-diagonal representations $\mathcal{A}^3 - \mathcal{A}^5$. These values sum to give the totals reported in table 6.7.

NaCl. In the LiF crystal, the DID effects have nearly vanished, whereas for NaCl crystals they are a major contribution. In the melt, the DID scattering from LiF is an order of magnitude down on the short range distortion and asymptotic term scattering. For molten NaCl, all three are of the same order. This presumably reflects the lower polarisability of the F^- ion, since the DID scattering intensity

Anisotropic intensity by representation					
LiF, 298°K, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$					
	$\mathcal{A}^1$	$\mathcal{A}^2$	$\mathcal{A}^3$	$\mathcal{A}^4$	$\mathcal{A}^5$
I^{ANI}	0.019	0.018	0.013	0.014	0.016
$I^{ANI,SR}$	0.196	0.189	0.072	0.070	0.061
$I^{ANI,DID}$	0.004	0.004	0.004	0.004	0.004
$I^{ANI,ASY}$	0.268	0.255	0.109	0.109	0.112
$I^{ANI:SR,DID}$	-0.016	-0.016	-0.020	-0.018	-0.012
$I^{ANI:SR,ASY}$	-0.438	-0.419	-0.161	-0.157	-0.149
$I^{ANI:DID,ASY}$	0.005	0.005	0.009	0.007	< 0.001

Anisotropic intensity by representation					
NaCl, 300°K, $10^{-30}\text{cm}^2\text{sr}^{-1}\text{pair}^{-1}$					
	$\mathcal{A}^1$	$\mathcal{A}^2$	$\mathcal{A}^3$	$\mathcal{A}^4$	$\mathcal{A}^5$
I^{ANI}	0.135	0.139	0.017	0.018	0.018
$I^{ANI,SR}$	0.163	0.175	0.075	0.064	0.075
$I^{ANI,DID}$	0.257	0.260	0.044	0.044	0.043
$I^{ANI,ASY}$	0.201	0.202	0.134	0.117	0.134
$I^{ANI:SR,DID}$	-0.103	-0.125	-0.014	-0.015	-0.019
$I^{ANI:SR,ASY}$	-0.216	-0.223	-0.176	-0.150	-0.177
$I^{ANI:DID,ASY}$	-0.166	-0.151	-0.046	-0.042	-0.038

Table 6.9 : Anisotropic scattering for each mechanism in each symmetry representation for crystals. The representations are given in (6.25); the notation is described in the text. The total for each representation is given in the first row; its components in the next six. Representations $\mathcal{A}^1$ and $\mathcal{A}^2$ correspond to “4E”, and $\mathcal{A}^3 - \mathcal{A}^5$ to “ $\frac{4}{3}\text{F}$ ”. The values given in tables 6.7 and 6.8 are averages of these values.

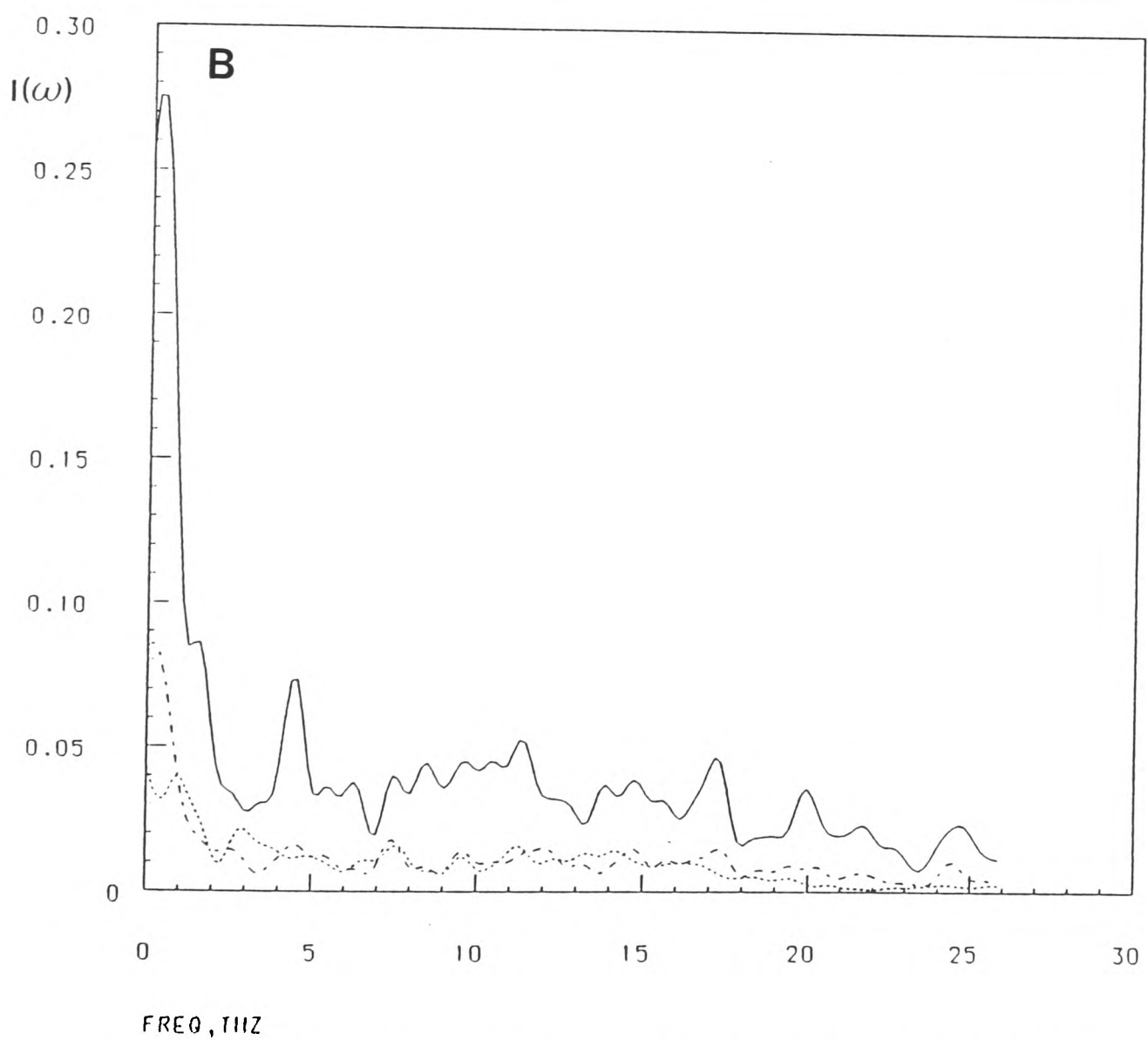
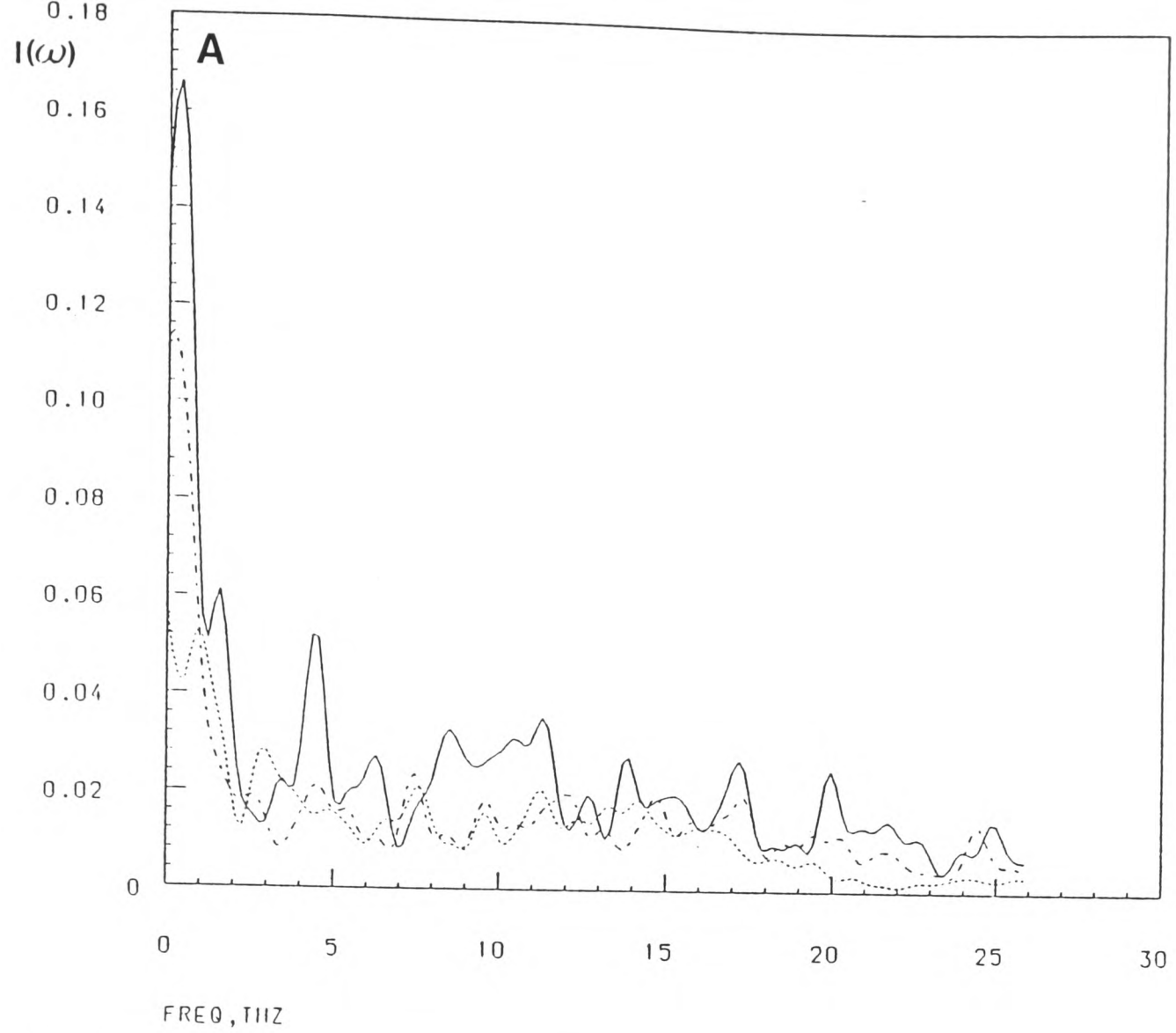


Figure 6.5 : Simulated light scattering lineshapes for crystalline LiF at 298°K. (a) Isotropic, or A (solid), 4E (dashed), and $\frac{4}{3}F$ (dotted) scattering. (b) Observable scattering combinations (6.27) δ (solid), β (dashed), and γ (dotted).

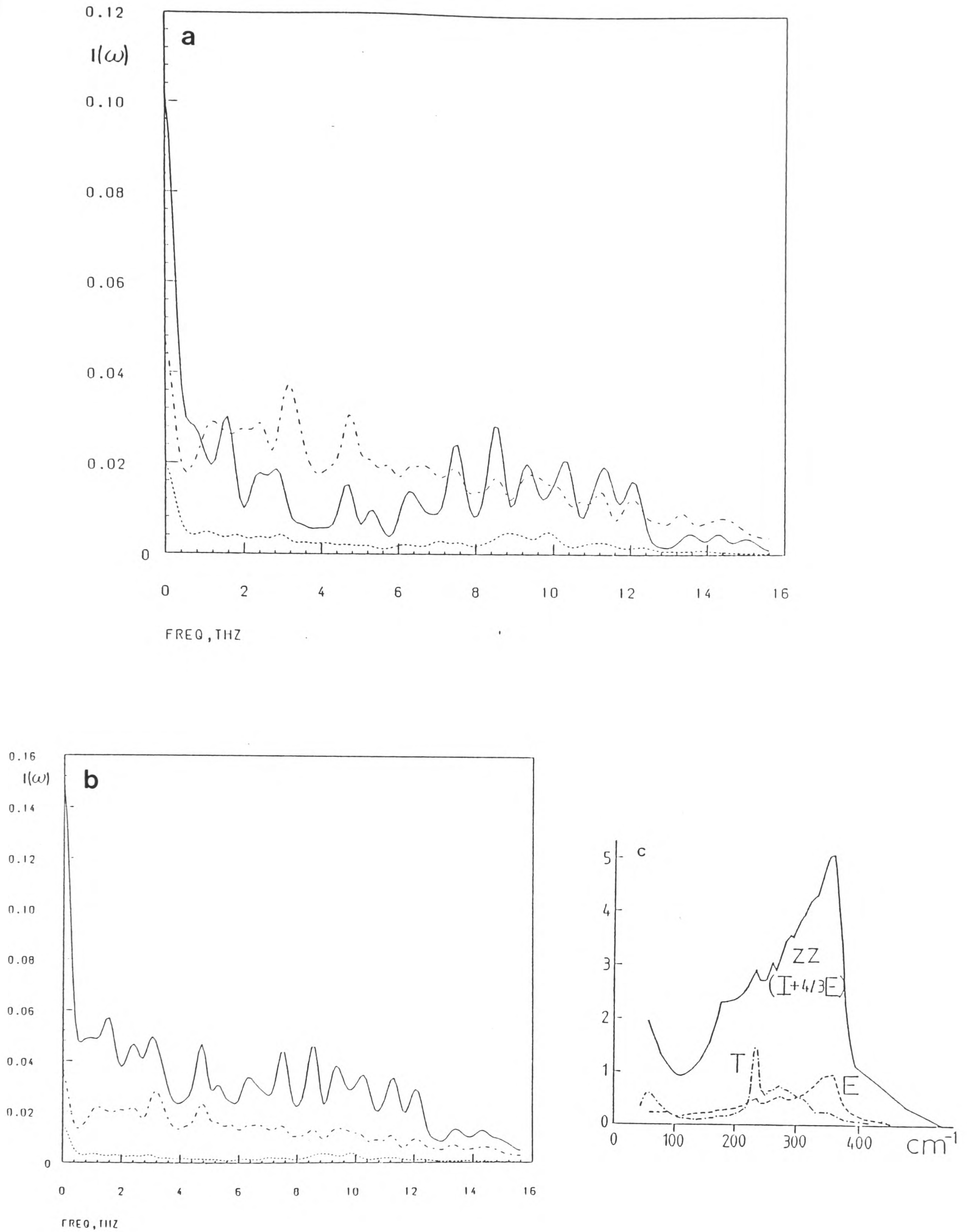


Figure 6.6 : Light scattering lineshapes for crystalline NaCl at 300°K. (a) Isotropic, or A (solid), 4E (dashed), and $\frac{4}{3}F$ (dotted) scattering from simulation. (b) Observable scattering combinations (6.27) δ (solid), β (dashed), and γ (dotted), from simulation. An artificially broadened version of the simulated polarised δ curve (thick solid line) is also included (see text). From Madden and Board [MAD86]. (c) Experimental results of Krauzman [KRA68], from Madden and Board [MAD86]; as (b).

goes as the fourth power of the polarisability. The magnitude of the other terms indicates that the fluctuations in this polarisability, however, are of the same order as those in NaCl. LiF certainly displays the dramatic cancellation effects between the mechanisms that characterizes the NaCl results.

The rest of this section will discuss the NaCl results; much of what is said applies equally to the LiF.

6.6.1 Melt intensities and lineshapes

The greatest success of this work is the reproduction of the experimentally observed polarised and depolarised light scattering intensity from molten NaCl to quite reasonable accuracy. The simulations predict a value of about $13 \times 10^{-30} \text{cm}^2 \text{sr}^{-1} \text{pair}^{-1}$ for the polarised intensity; the experiment of Raptis *et al.* gives $24.4 \times 10^{-30} \text{cm}^2 \text{sr}^{-1} \text{pair}^{-1}$. Both simulation and experiment give a value of about $4 \times 10^{-30} \text{cm}^2 \text{sr}^{-1} \text{pair}^{-1}$ for the depolarised scattering intensity. This is particularly satisfying since the experimental intensity nowhere enters into the parameterisation of the polarisability model developed in this chapter. The agreement of the mean anion polarisability in the melt with experiment (table 6.1) is also encouraging. Combined with the intensity data, this indicates that the simulation can reproduce the magnitude of and fluctuations in the sample's polarisation quite well.

The polarisability model has also succeeded in lowering the depolarisation ratio for NaCl from the fully depolarised value of 0.75 appropriate to argon, to about 0.3. This is clearly larger than the experimentally observed value of about 0.17 but is still a significant achievement. Again, nowhere did the observed ρ_D enter into the model parameterisation. In order for ρ_D to be lowered further in the simulation to the experimentally observed value, the anisotropic intensity would have to fall from 5.1 to $2.2 \times 10^{-30} \text{cm}^2 \text{sr}^{-1} \text{pair}^{-1}$. Given the

large size of the terms contributing to the anisotropic intensity, and the size of the cancellation terms, it is not unreasonable to hope that a reparameterisation of, say, the asymptotic contribution with values more appropriate to NaCl would achieve this reduction.

All three terms in the polarisability model contribute importantly to the scattering. It would not be acceptable to drop or more severely approximate any of the three terms in the model; indeed the results indicate that improvements in the parameterisation of all three are equally urgent. The extremely large cancellation terms between the three mechanisms indicate their interdependence; it is improper to regard them as independent effects.

The isotropic scattering is given almost entirely by the short range distortion effects; the small but measurable term in the dipole hyperpolarisability γ almost completely cancelled itself with the short range term.

The anisotropic scattering is smaller in magnitude than five of the six terms (table 6.5) comprising it; this is the best evidence of the need for a multiple mechanism model to explain the fluctuation of polarisability in ionic systems. The γ term is only a small part of the asymptotic scattering; the quadrupole hyperpolarisability B is the dominant single term in the scattering. Fowler and Madden have reported that the hyperpolarisabilities are even more sensitive to local configurations than the polarisabilities, so significant change in both γ and B is plausible.

The isotropic scattering intensity predicted by the short range distortion model is probably quite reasonable; the correct reproduction of the mean polarisability and its fluctuations argue for not altering the isotropic intensity too significantly in either direction. There is enough uncertainty in the experimental intensity measurements to be content with factor of two agreement in the polarised intensity between simulation and experiment. As was pointed out, however, there is some freedom in the determination of the parameters for the

model since the short range distortion model parameters are underdetermined by the electronic structure calculations. This flexibility could be exploited in a reparameterisation to increase or decrease the isotropic intensity significantly by biasing all selections with some freedom that way, if this were found to be desirable.

The DID term could be calculated more accurately if the polarisabilities in (6.10) were taken to be time-varying; this should be possible without undue increase in computational complexity. The approximation to the self-consistent expression (6.9) could be improved by taking into account the values of the dipole moments $\mathbf{p}^j$ at the previous timestep rather than retaining just the first-order truncation $\mathbf{p}^j \approx \alpha^j \mathbf{E}(\mathbf{r}^j)$. The effective polarisability on each ion at each timestep can be determined from the model as presented here; this could replace the spherically averaged value used in (6.9) at present.

There was reason to fear that the current parameterisation of the short range “dent” terms might exaggerate the importance of the anion–anion interaction. The parameters supplied in table 6.3 can allow the like-ion contribution from anions to become large if close approaches by like ions are frequent. A recalculation of the scattering intensities with a_{--} and b_{--} set to 0 was performed; the result was that there was no dramatic change in any of the components of the scattering. The small changes that did occur were sensible: a drop of about 15% in the isotropic intensity due to the reduction in the SR contribution, and about a 30% rise in the anisotropic intensity, due mostly to an increase in the SR contribution with the increased anisotropy of the environment without second near neighbours.

The lineshapes for both polarised and depolarised scattering are quite satisfactory. The polarised spectrum (figure 6.4b) changes slope at about 1 THz, as does the experimental curve (figure 6.4c). There is another change in behaviour at about 6 THz, albeit not as dramatic as in the experiment. The depolarised

spectrum also agrees well with the shape of the experimental curve at low frequencies, but lacks the shoulder at about 6 THz which is quite pronounced in the experimental depolarised spectrum.

The frequency-dependent depolarisation ratio $\rho_D(\omega)$ is too high across the frequency range, but the general behaviour of the curve is correct: it falls from an initial moderate value to a lower constant value from about 3 THz. There is another fall in ρ_D beyond 8 THz, but this may be due in part to numerical problems with the small numbers at these frequencies. This is a major improvement over the shell model results for NaI in chapter 5, where the calculated ρ_D actually went up with frequency in some cases.

All quantities considered here could be determined more precisely through longer simulation runs. The LiF simulation is really too short for good answers, but as comparison with experiment is not possible, semi-quantitative results are probably sufficient. The NaCl simulations do have quite reasonable statistics, as the agreement of the intensities as calculated from the independent anisotropic representations of the same type (better than 5%) indicates.

Given all the caveats here, the agreement of the scattering lineshape for NaCl (figure 6.4) is very satisfying. The simulations are apparently providing a realistic dynamical environment in which the polarisability fluctuates. Improvements in the model parameterisation that reduce the depolarisation ratio to more realistic levels should improve the lineshape agreement as well.

6.6.2 Crystal intensities and lineshapes

The results for the crystals, on first inspection, are much less impressive than those for the melts. There are, however, a number of encouraging features in the crystal results.

The intensities of all terms are down by about two orders of magnitude

from the melt values. Although absolute intensities for the crystals are not available, this is consistent with the recent findings of Raptis [RAP86] that the intensity of crystal scattering falls by about a factor of 20 at room temperature compared with the scattering just below the melting point. The polarised term is significantly larger than the two depolarised terms in the crystal, adding more weight to the argument that the high depolarisation ratios found in the melt simulations are a result of the environment change in going from crystal to melt.

All three mechanisms are again important in the melt; the cancellations between the three are such that the anisotropic intensities are less than or of the same order as all six of the terms comprising them (table 6.8).

The poor agreement of the NaCl crystal lineshapes can be improved through consideration of a few factors. The crystal symmetry of these systems admits only two-phonon and higher processes for Raman scattering. The limited system size (216 ions) of the simulations means that only a small number of discrete phonon modes, rather than the continuum appropriate to the infinite system, are represented in the solid simulation. The two-phonon density of states, which is the dominant factor governing the crystal scattering, is even more sparsely represented. Thus, it is not surprising that the simulation spectra are more peaked than the experimental ones.

The phonon properties in these crystal simulations are also not ideal, as rigid ion model potentials, which give at best only a fair representation of the phonon properties of NaCl, were used. A shell model calculation of the ion dynamics coupled with the polarisability model developed here would reveal the importance of better phonon properties.

Taking these factors into account, an artificially smoothed version of the polarised scattering is also given in figure 6.6, which is in somewhat better agreement with the experiment.

7 Conclusions

7.1 Summary of results

The work reported in this thesis is successful in accomplishing several things. Extensive molecular dynamics simulations have been carried out on ionic systems and it has been shown that the simulation methods originally developed for modelling molten ionic systems can also be used successfully on crystal systems if appropriate precautions are taken during equilibration.

Two computationally tractable models for the light scattering from ionic systems have been developed; both unify a number of separate simulation concepts and both are quite successful in many respects.

The first model exploits the shell model potentials from lattice dynamics work; the ionic dipole moments that are the result of the core-shell separation in these potentials are apparently fairly good representations of the “real” ionic dipole moments in these systems. An expression based on the reduction of second-order quantum-mechanical scattering process transition rates to time-correlation functions of ionic dipole moments is derived in chapter 5 and used to determine scattering lineshapes for molten NaI. The results are encouraging; the agreement with the known experimental lineshape is quite good, but the depolarisation ratio predicted by the model is far too high. The time constants of the exponential decay of the scattering intensity indicate the importance of plasma modes in mediating the scattering processes. The shell model potentials are parameterised to reproduce the known dielectric constant ϵ_0 ; this probably explains their ability to model polarisation effects successfully.

The second model, developed in chapter 6, uses results from a series of

detailed electronic structure calculations on various alkali halides to parameterise a description of the variation of ionic polarisability with local environment. The variation of ionic polarisability in the condensed state is shown to be the result of several mechanisms acting collectively to distort the electronic structure of an ion. Three mechanisms have been identified and a first attempt to quantify them has been made. The light scattering spectrum and intensity has been calculated from the time-correlation of fluctuations in the sample polarisation due to these ionic polarisability mechanisms. The known mean anion polarisability in the NaCl melt is reproduced quite accurately. The lineshape agreement is again quite good, and most satisfyingly the total absolute intensity measurements for the scattering as determined from simulation are in good agreement with experiment.

It is clear from the failure of the simulation to reproduce the correct depolarisation ratio that much improvement in the model's parameterisation must be sought. Many possible improvements in the parameterisation were suggested in chapter 6; most are dependent on further electronic structure calculations. The results obtained, however, indicate that the attempt to design and parameterise a model for the instantaneous variation of ionic polarisabilities in condensed environments is worthwhile and potentially quite fruitful.

7.2 Comparison of the models

The two models were developed from quite different underlying principles, but they do share many common features. Both recognize the importance of treating ionic polarisability as the result of electronic and mechanical effects. The shell model calculation includes these through the short-range forces acting on the shells; the Born-Mayer-Huggins potential form includes dipolar and quadrupolar electronic effects as well as overlap repulsion. The polarisability

model includes both types of effects explicitly.

Both models indicate the importance of the DID mechanism and short range overlap repulsion to light scattering from these systems; it is inadequate to treat these systems like argon by considering only DID effects. The polarisability model work permitted quantification of the relative contributions of the different mechanisms; it is important to note the significant cancellation between all three (short range, DID, and asymptotic) terms in the model, which indicates that they are highly correlated. The small contribution from the dipole hyperpolarisability term in γ was somewhat disappointing.

The shell model approach is incomplete in some ways. A great advantage of the ionic polarisability model is that it allows good estimation of absolute scattering intensities, whereas the shell model calculation does not. It should be possible to restore the prefactors in the shell model intensity expressions (5.17 and 5.18) at least to an order-of-magnitude level to estimate absolute intensities from this model.

An abortive attempt to incorporate quadrupolar effects in the shell model work was reported at the end of chapter 5; the results of chapter 6 seem to indicate that such effects should be fairly unimportant. The shell model approach could probably be improved through careful consideration of the effect of the shell relaxation procedure on the resulting dipole moments. A more realistic way of relaxing the shell positions should be sought; again the results of chapter 6 indicate the importance of accurately modelling the effect of short-range distortions, which the current shell relaxation procedure almost certainly disrupts.

The computation of the various polarisation models for the second model increases the computer time required by a rigid ion model simulation by about a factor of three; this still leaves the second model about three times faster than a shell model simulation. The polarisability model could as easily be applied to

a shell model simulation, resulting in no significant increase in the already long times required to perform such simulations.

A unification of the two models may be possible to some extent. Certainly in the NaCl crystal study, part of the disagreement is due to the inherent failings of the rigid-ion model potentials. A shell model simulation of a NaCl crystal employing the polarisability model could improve the agreement significantly. If, however, a shell model simulation were being performed, there should be some way of incorporating the instantaneous shell model dipoles into the polarisability model. The best ways of using the shell model dipole data have not yet been determined.

7.3 Further study of ionic systems

The experimental work on ionic systems has progressed much more rapidly than the theoretical and simulation work. The light scattering models developed here have only been applied to three salts, and only two of those are subject to reasonable comparison with experiment. The light scattering spectra of most of the alkali halides are available experimentally; simulation of additional salts should help both to refine the light scattering models and, through separation of the scattering mechanisms possible in the simulation work, help to explain the trends that are seen across families of alkali halides.

As has been mentioned in the text of this thesis, the salt CsCl cannot yet be modelled in simulation work, even to the extent of getting its structure correct. Figure 7.1 compares the radial distribution functions determined from the neutron experiments of Locke *et al.*[LOC85] with those from the simulation of Dixon and Gillan using a rigid ion potential. The experiment and simulation are clearly not in good agreement. The simulation of Dixon was performed several years ago at a slightly different state point than the recent neutron

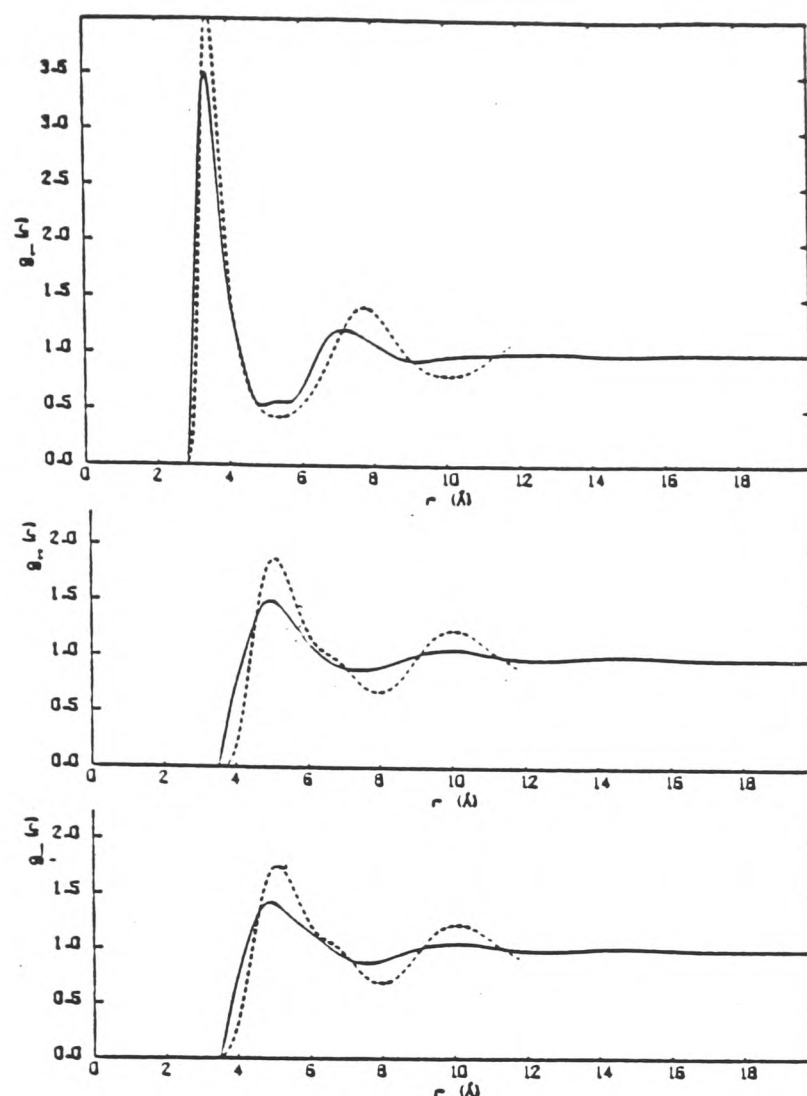


Figure 7.1 : Partial radial distribution functions $g_{\alpha\beta}(r)$ for CsCl from neutron experiment of Locke *et al.* [LOC85] (solid) and the simulation of Dixon and Gillan [DIX81] (dotted). The simulation used a rigid ion potential, but results from a full (cation and anion) polarisable ion simulation were almost identical, still in considerable disagreement with experiment. From Locke *et al.* [LOC85].

experiments. Dixon and Gillan also performed a full (cation and anion) shell model simulation of CsCl, but the structure results were virtually identical to these rigid ion results [DIX81, LOC85].

A new full shell model simulation of CsCl was undertaken in this work to investigate this difference in simulation and experimental results. Every effort was made to ensure the new simulation was performed at the same state point as the experiment; particular care was taken to ensure that the simulation was equilibrated properly, as the old procedure was sometimes unreliable (chapter 2). Despite this care, the result (figure 4.11) was virtually unchanged. The more accurate temperature matching did slightly shift the peak positions in the simulation $g(r)$, but simulation and experiment are still qualitatively different in their structures. These results indicate that a simple treatment of ionic polarisability

is inadequate for this salt, at least.

As CsCl is the only caesium salt accessible to the neutron structure measurements, it is not possible to say whether only CsCl is anomalous in this way. It is likely, however, that the other caesium salts are poorly modelled by simulations. Locke *et al.* conjecture on the basis of light scattering and other data for CsCl (its Raman spectrum is highly depolarised) that the polarisation of the Cs^+ ion may be anisotropic, and thus not adequately modelled by a simple shell model potential. There may be covalency or charge transfer or other non-ionic effects present in CsCl; these cannot be treated properly in simulations at present. The full, simple shell model simulations of CsCl represent the current state of the art in ionic simulation work, but these techniques are apparently inadequate. Development of computationally efficient ways of incorporating anisotropic polarisability effects and other complex non-ionic phenomena into simulation work is highly desirable. Molten CsCl has also been the subject of extensive inelastic neutron scattering studies [MCG85], so there is much data with which to test any simulation studies.

The experimentalists have gone beyond the Raman scattering; Brillouin scattering data are now available on some salts [QIU85]. Light and neutron scattering experiments have also been carried out on many of the alkaline earth halides [BUN86, MAR84, MCG85b, FAI86]. There has been some simulation work on these compounds, but the potential models used to date have been mostly *ad hoc* rigid-ion type parameterisations. The superionic state of some of these compounds, e.g. SrCl_2 , is especially interesting and has been the subject of some simulation work [DIX79, DIX80, GIL80], but much more could be done.

These computations are all quite expensive. The presence of the long-range forces complicates the task of writing efficient codes suitable for execution on vector (CRAY-type) supercomputers or large array processors. Progress on some of the problems mentioned above might be made through use of new “*ab*

initio” simulation techniques which combine MD calculations for ion dynamics with electronic structure calculations for the evaluation of interparticle forces [CAR85]. The computational requirements of these new techniques are orders of magnitude up on those of the current simulation methods, however. Investigation of new computer architectures suitable for efficient simulation of large ionic systems and/or for efficient execution of the dual electronic structure – ion dynamics codes promises to push back significantly the limits of what can be accomplished through atomic level simulation work.

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