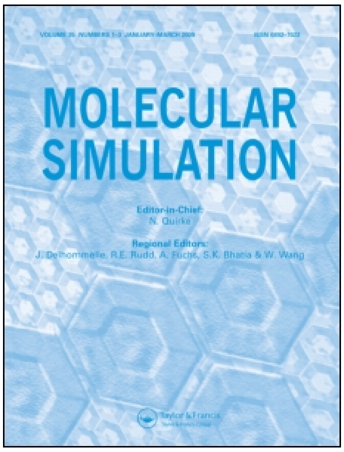

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Dynamics with the Shell Model

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DYNAMICS WITH THE SHELL MODEL

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Potentials for ionic materials are among the best classical models currently available, giving very realistic descriptions of many physical properties. The key feature in providing this realism has been found to be the inclusion of ion polarisability, most often via the shell model. Until recently though, the dynamical properties of such models, and their comparison with experiment, have received little attention due to the computational workload involved in dealing with the extra degrees of freedom.

We discuss here recent progress in the dynamical simulation of ionic materials using shell-model potentials. This includes the approaches which have successfully been developed to deal with the central problem, which is the requirement that the system obeys the Born-Oppenheimer principle with respect to the polarisation. The results of extensive simulations of UO_2, using the best potentials available, and comparison with neutron-scattering and other experimental data reveal the feasibility of shell-model MD, and also shed new light on the capabilities of the potentials.

KEY WORDS: Shell-model potentials, Ionic materials, Molecular dynamics, conjugate gradients, superionic conduction, melting.

1 INTRODUCTION

For many years now there has been a concerted effort to improve and refine potential models for ionic materials, and to use such models is computer simulation studies. Often this has been motivated by the need for a sound theoretical understanding of technologically important materials in the (near) absence of reliable experimental data. An excellent example is UO_2, a constituent of nuclear fuel. Safety considerations demand knowledge of physical properties at extraordinarily high temperatures (in excess of 5000 K), where experimental control and ability is extremely limited. The wealth of detail afforded by simulations is of equal importance to the ability to probe experimental difficult regimes. For example, the precise mechanisms involved in superionic conduction in fluorites were established through molecular dynamics (MD) studies of CaF_2 [1,2].

The quality of a potential determines the value of conclusions and predictions drawn and made in simulation studies. For ionic materials, *rigid-ion* pair potentials have been refined to the point of providing reasonably adequate descriptions, most notably for the alkali-halides, and have been used extensively in MD simulations [3,4,5] due to their simplicity. These models suppose that the ions carry their formal charges and have no internal structure. However for some ionic materials, most noticeably oxides, such a description is seriously flawed. The problem is that, commonly, oxides have a large high-frequency dielectric constant ϵ_∞, arising from the polar response of the ions. The lack of polarisability in rigid-ion models fixes ϵ_∞ as unity, and therefore (through the Lyddane-Sachs-Teller relation [6]) they predict the wrong vibrational spectrum for materials with polarisable ions. In UO_2, for example, a rigid-ion description predicts phonons in error by 40–50% when compared with experiment [7], and this failure obviously limits confident use in simulation.

The problems outlined can be largely overcome through use of the shell model [8]. In this model the ion is composed of a core and shell, both charged, which are linked by a harmonic spring, which is their only means of interaction. The core carries the mass of the ion, and the short-range (i.e. non-Coulombic) forces act between shells of different ions. Separation of the core and shell of an ion results in a dipole moment on that ion; importantly this polarisation can arise from both the electric field the ion experiences, and the forces on the shell due to its short-range interactions[1]. The shell is massless because the extra degrees of freedom must obey the Born-Oppenheimer principle, i.e. the system must always be in its electronic ground-state. In practise this means that the net force on each shell must be zero, with the shells responding adiabatically to the movement of the ions. This empirical means of introducing polar response brings a great increase in the realism of the model, attested to by numerous successful studies in which predicted vibrational properties, defect formation and migration energies and subtle structural details (such as surface relaxations and reconstructions) have compared well with experiment [10, 11]. However, until recently the vast majority of these studies were static (zero K)[2] simulations, due to the problem of solving the equations of motion for the massless shells in a computationally efficient manner. The unsatisfactory situation is that MD studies of ionic materials have been limited to the use of rigid-ion models which are much inferior to the shell models used in static studies. The subject of this short paper is to summarise techniques that have been developed and used to overcome this imbalance, and to show some results from MD simulations with shell-model potentials. In section 2 we briefly outline the two techniques used in shell-model MD; section 3 presents some recent results obtained for UO_2; and section 4 in conclusion discusses the state of shell-model MD and where progress may be anticipated.

2 TECHNIQUES FOR SHELL-MODEL DYNAMICS

We have already mentioned the problem inherent in shell-model MD simulation–how do we generate the trajectories of the shells as the system evolves in time? The most obvious solution is to use a relaxation method, at each time-step of the integration of the motion of the cores, to find the energy minimum with respect to the shell positions. The advantages of a shell-model description have been recognised for many years now, and early attemps in MD used just such a relaxation approach [3, 12]. However, the computational demand proved prohibitive, and the method was considered to be unpractical.

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[1] The latter mechanism accounts for the limiting effect of an ion's environment on its freedom to polarise in response to an electric field, and avoids the so-called "polarisation catastrophe" [9].

[2] Finite temperature effects have been addressed in a limited way through quasi-harmonic calculations. These do not, of course, simulate the dynamical behaviour of systems of polarisable ions.

There are two main reasons why, recently, shell-model MD based on relaxation has been successfully used. Firstly there has been a huge increase in computer power available to the simulator. Thus, for example, extensive studies have been undertaken [13] to determine the effect of polarisation on calculated Raman spectra from molten NaCl using essentially the same techniques as in earlier work. Secondly, through the adoption of a conjugate gradients relaxation method instead of the crude steepest descents algorithm used previously [3, 13], a considerable increase in robustness and efficiency has been gained. As will be shown later, it is now feasible to perform large-scale simulations with shell-model potentials on a modest computer budget.

Much promise is offered by a different approach to generating the time evolution of a polarisable system. Borrowing from ideas used in quantum-mechanical simulations, the polarisation of each ion or molecule can be governed by the dynamical behaviour of a fictitious mass associated with it. In this approach, equations of motion for both the ions (or molecules) *and* the fictitious masses can be derived from an extended Lagrangian. The evolution of the system from an initial, ground-state configuration proceeds through simulatneous integration of all the equations of motion. If the fictitious masses, which have no physical significance, are sufficiently small, the additional polarisation variables are updated (via the motion of the fictitions masses) in the correct way to maintain the ground state for each subsequent configuration–the fictitious masses (and hence the system polarisation) follow the motion of the real masses adiabatically. Sprik has successfully applied this method to pure water and also to the solvation of a chlorine ion [14, 15]. Wilson and Madden [16] examined the effect of polarisation on the simulated properties of solid and liquid LiF and liquid NaCl, using a method which allows for generalisation to higher- order induced multipoles. The shell model has also been used in the framework of an extended Lagrangain method. Mitchell and Fincham [17] incorporated the extra degrees of freedom by dividing the ionic mass between shell and core. They found that such an approach yielded good agreement with shell-model MD performed by relaxation methods for the diffusion coefficients in molten NaCl and CaF_2, and for the phonon frequencies in MgO when compared with a lattice dynamics calculation.

3 SOME RECENT RESULTS FOR SHELL-MODEL UO_2

We turn now to the presentation of results obtained for the superionic fluorite UO_2, simulated by shell-model MD using conjugate gradients relaxation. UO_2 is a particularly difficult ionic material to model [18, 19, 20], not least because the highly polarisable O^{--}-ion results in a high-frequency dielectric constant of 5.3 [22]. However, good quality (as gauged by static simulation) shell models do exist for UO_2 [18], which combined with the clear inadequacies of rigid-ion models [19] provide ample encouragement for shell-model MD studies. Little is known about shell- model dynamics in its own right, which provides additional interest.

We will consider two topics: first, how well does the shell model reproduce the superionic behaviour in UO_2, as characterised by neutron scattering experiments and examined through previous rigid-ion simulations? Second, what is the melting point of the shell-model UO_2 system? The simulations we report here were all performed at constant number, volume and energy, with a time step of 3fs, on HP and IBM RISC workstations. Full details of the UO_2 shell model [18] and the conjugate gradients code [21, 7] appear in the literature.

3.1 Superionic conduction and neutron quasielastic scattering

One of the most striking high-temperature features of solid UO_2 is the superionic state, the transition to which occurs above 2000 K. Superionic conduction is a general characteristic of fluorite-structured materials: an impressive series of papers by Gillan [1, 2] reported extensive rigid-ion MD studies of CaF_2 which provide the most detailed theoretical understanding of the mechanisms involved in the liquid-like diffusion on the highly disordered anion sublattice. Neutron scattering is a powerful experimental tool in the study of such behaviour, and has been applied to UO_2 [24, 25]:diffraction reveals the onset of oxygen disorder at 2000 K, while the quasielastic scattering

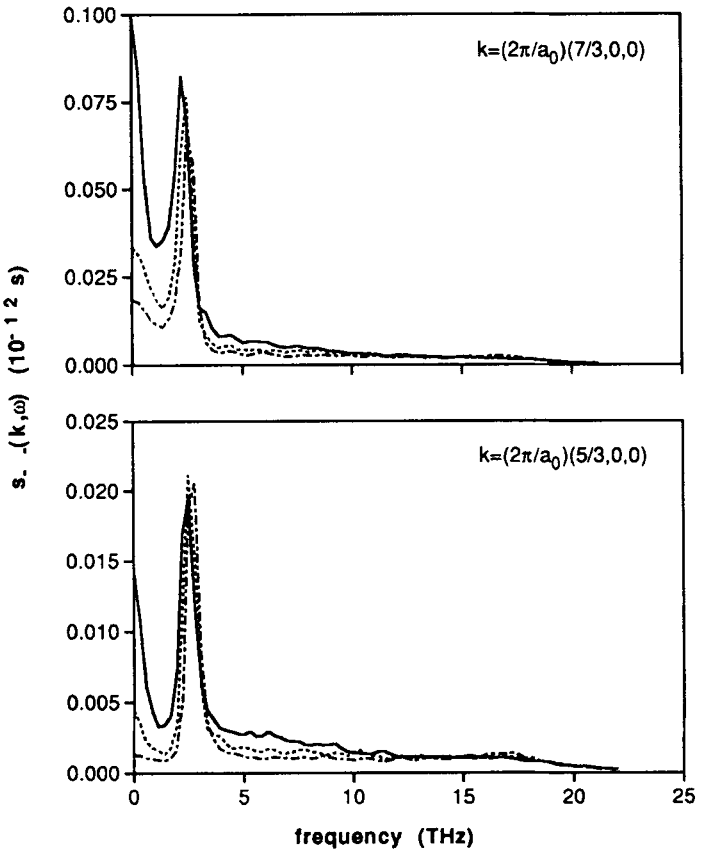

Figure 1 Simulation results for the oxygen-oxygen dynamical structure factor, $S_{--}(\mathbf{k}, \omega)$, calculated at the wavevectors $k = (2\pi/a_0)(5/3, 0, 0)$ and $k = (2\pi/a_0)(7/3, 0. 0)$. In each case, results are shown for temperatures of 2493 K (chain curve), 2658 K (dotted curve) and 3060 K (solid curve).

observed above this temperature is associated with the creation, movement and annihilation of defects, and is a signature of superionic conduction. Recently we have investigated how well shell-model MD reproduces superionic behaviour in CaF_2 [21] and UO_2 [7]. Here we focus on our UO_2 results, and their comparison with neutron scattering measurements.

In Figure 1 we show the calculated anion-anion dynamical structure factors in the (100) direction for three temperatures and two wavevectors, for a system of 324 ions. In addition to the prominent longitudinal acoustic phonon peaks around 2.5 THz, a strong peak, centred on zero frequency, appears as the temperature of the simulations is increased. This quasielastic scattering increases dramatically with temperature in the simulations. Experimentally, as well as the strong dependence on temperature, the intensity of this feature varies very rapidly with wavevector. Our simulations reproduce this trend, showing a maximum at $\mathbf{k} = (2\pi/a_0)(7/3, 0, 0)$. (The experimental maximum occurs at $\mathbf{k} = (2\pi/a_0)(2.15, 0, 0)$). In Figure 2 we show an absolute comparison of the quasielastic intensity predicted by our simulations with that form experiment [7, 24]. Bearing in mind that this comparison involves some approximations, there is reasonable agreement between the two results, although the simulated intensities do lie rather below the experimental ones.

Overall these studies showed that the dynamical behaviour of shell-model UO_2 reproduced faithfully many of the features of the superionic state. However, the transition to superionic behaviour was at too high a temperature, and the extent of oxygen disorder and the mobility were rather too low, indicating the necessity for further potential development.

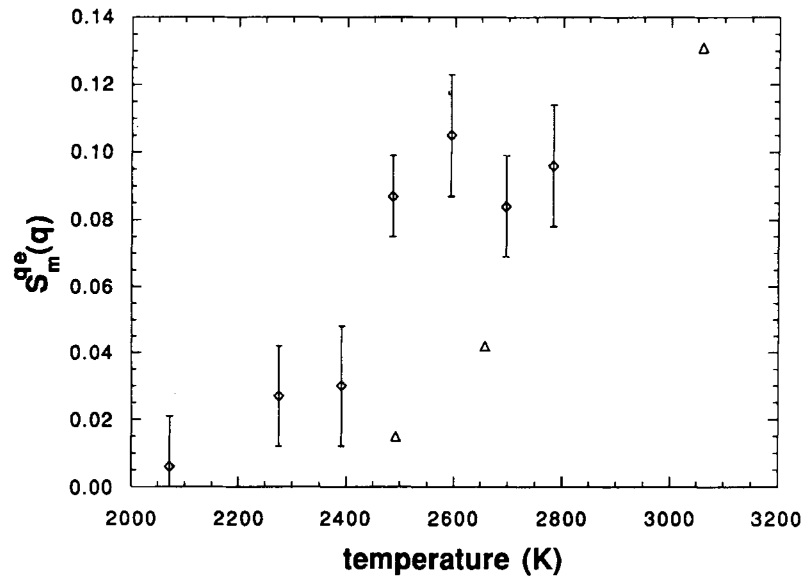

Figure 2 Comparison of experimental (open diamonds with error bars) and simulation (open triangles) result for the quasielastic intensity $S^{qe}_m(\mathbf{q})$ as a function of temperature. The results are for the wavevector $k = (2\pi/a_0)(7/3, 0, 0)$.

3.2 *A preliminary estimate of the melting point*

A fundamental property we wish a potential to reproduce when used in MD is the melting point of the solid. For UO_2 this is particularly relevant since there is much interest in the liquid state, and while previous rigid-ion studies found reasonable agreement with the experimental melting temperature of 3120 K, the predicted properties of the liquid were poor [19]. We therefore have a keen interest in the melting of shell-model UO_2, and the behaviour of the liquid.

As is well known by now [26, 27], finding the melting point in MD simulation is not entirely straightforward. This is because of the excessive superheating and supercooling that occurs in simulation, even in the N, P, T ensemble. The usual route taken to accurately locate the melting point is to determine the state point where the solid and liquid phases have equal free energies [26]. However, it is also understood that surfaces (along with other interruptions of periodicity, such as grain boundaries) play a crucial role in the melting of a real crystal, and this is true also in simulation [28]. By including a free surface in a simulated system it is possible to obtain a reasonable estimate of the melting point.

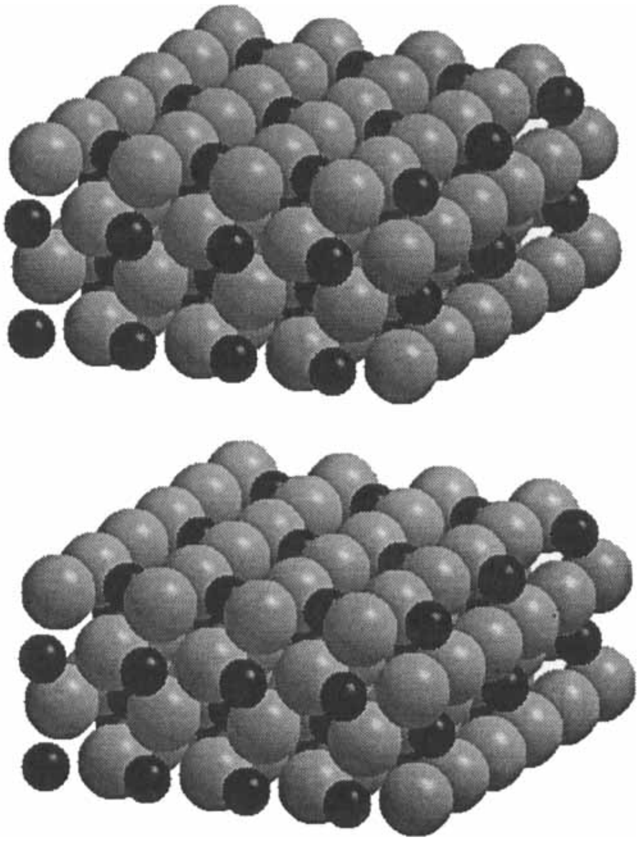

Figure 3 Slab geometry used to determine the shell-model UO_2 melting point. The figure shows how the periodic boundary conditions are applied in the z-direction to create alternate slabs of the material, separated by vacuum. The simulation box contains 48 cations (small black spheres) and 96 anions (large grey spheres).

We have recently performed a trial calculation on shell-model UO_2 using slab geometry N, V, E MD to estimate the melting point. Figure 3 shows the system, which consists of 144 ions oriented so as to form an orthorhombic array. Periodic boundary conditions are applied in the usual way along the x and y directions, while in the z direction the periodic images are separated by a region of vacuum. In our studies, this vacuum region was the same thickness as the slab, 8.07 Ångström. This is a fairly small distance, but by calculating the system energy as a function of the vacuum region thickness it can be shown that there is in fact little interaction between the slab and its images with this separation. The surfaces formed perpendicular to the z-direction are the (110) faces of the conventional unit cell. This choice is partly dictated by the need to eliminate charge separation on the surfaces, which leads to mechanical instability [29, 30]. The simulation then proceeded as follows. First, we equilibrated the system for 1000 steps at 2800 K, a temperature below the expected melting point. Then a production run of 4000 steps was made, followed by 1000 steps in which we re-scale velocities to increase the temperature, and another 1000 steps of equilibration, in readiness for the next production run.

By measuring the time-dependent mean-squared displacement of both cations and anions during the production runs we can confirm whether the system is solid or liquid. Figure 4 shows the mean-squared displacements calculated at 2933 and 3095 K. Superionic conduction is evident through the liquid-like mobility of the anions at both temperatures[3]. The cations, though, are not diffusing at the lower temperature, while at the higher value they are clearly mobile-the crystal has melted. Further confirmation of

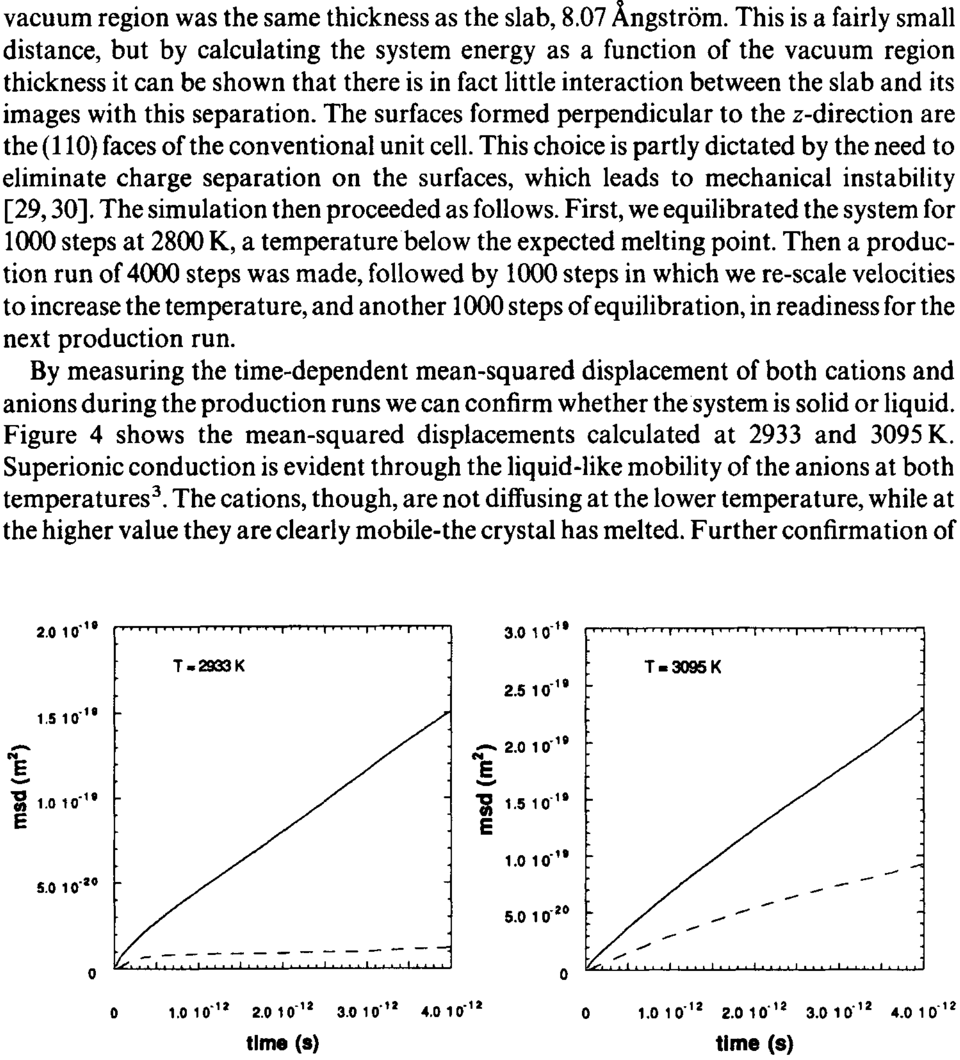

Figure 4 Means-squared displacements as a function of time for anions (solid curve) and cations (dashed-curve). At the lower temperature of 2933 K, the system is solid, as shown by the zero-slope of the cation curve (left). At 3095 K, the system has melted, and the cations are diffusing rapidly (right).

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[3] The actual values of the diffusion coefficients are significantly higher than those obtained using the same model at the same temperature in standard-geometry shell-model MD [7]. This is an artifact of the small system we use here, which has a large surface-to-volume ratio. Diffusion on the surface is considerably easier than in the bulk.

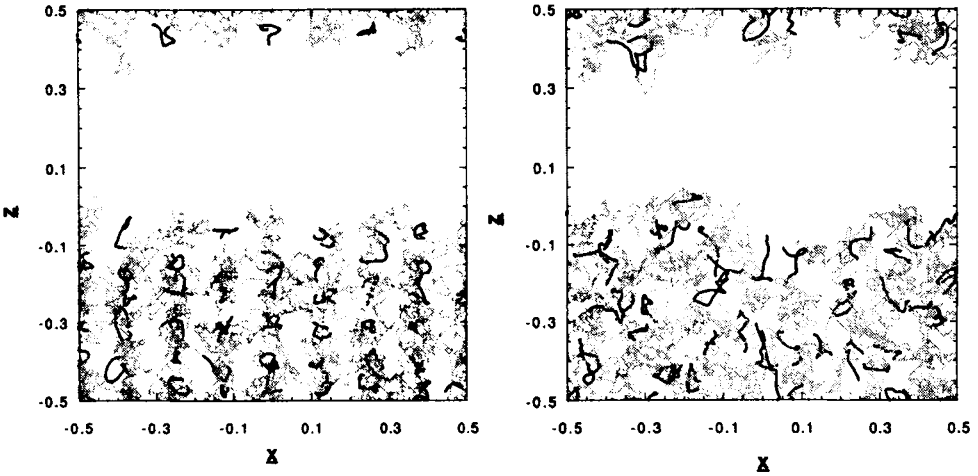

Figure 5 Traces of cation (black lines) and anion (grey lines) trajectories at two temperatures over 200 time-steps. The trajectories of all the ions are projected onto the x-z plane. At 2933 K the cation sublattice structure is clearly discernable, while the anions exhibit rapid diffusion (left). By 3095 K, there is no long-range cation order, and the slab is liquid (right).

this conclusion comes from inspection of the pair distribution functions (not shown here), and the trajectories shown in Figure 5. We tentatively conclude, then that shell-model UO_2 melts at around 3100 K, although system size effects may well alter this value considerably. The results of free-energy calculations we are presently performing will give a more accurate melting point.

4 CONCLUSIONS AND PERSPECTIVES

Use of the shell model in MD is now entirely practical, and represents a considerable advance in the realism of dynamical studies of ionic materials. This is not to claim that use of the shell model solves all problems in modelling ionics; for example, in UO_2 there is an urgent need to include the effects of electronic excitations [19, 23] and oxide compressibility [20] in potentials. However, the shell model provides a large first-order correction to crude rigid-ion models.

Shell-model MD studies of UO_2 have shown that current potentials compare well with experiment for the solid, though the onset of superionic behaviour occurs at too high a temperature. It well be interesting to examine the behaviour of the simulated liquid, since the rigid-ion model has proved rather poor in this respect [19]. While stressing the preliminary nature of the result it is encouraging to find that shell-model UO_2 melts very close to the experimental point, and we hope to report in detail on the liquid properties in the near future. It seems likely that the more significant differences in shell-model MD, as compared with rigid-ion studies, will occur in the liquid state [3, 16], and perhaps for lower symmetry solids.

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