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Shell model simulations by adiabatic dynamics

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Abstract. A method is introduced by which molecular dynamics simulations of ionic materials can incorporate the shell model of ionic polarizability. The shells are given a small mass and their motion integrated in the same way as that of the cores, by numerical integration of the classical equations of motion. We argue that results should be in agreement with the conventional massless shell model providing that the frequency of the spring linking the core and the shell is much higher than the lattice vibrational frequencies. It is always possible to satisfy this condition by making an appropriate choice of the shell mass. The method is tested in simulations of diffusion in molten NaCl and superionic CaF₂, and of phonon frequencies in MgO. The method works well, is easy to implement, and is computationally efficient.

1. Introduction

In the theoretical study of ionic materials shell model potentials for interactions between the ions are widely used (Catlow and Mackrodt 1982). These models incorporate electronic polarizability by representing an ion in terms of a charged core and a charged shell, linked by a harmonic spring. The shell is taken to be massless. The inclusion of polarizability is essential in many materials to obtain reliable results for defect and surface energies and lattice vibrational frequencies. However, in molecular dynamics simulation, important in the study of many dynamical processes in solids, particularly superionic conduction (see, e.g., Gillan 1986), rigid-ion potentials are most commonly employed. Shell model molecular dynamics, though it has a long history (Jacucci *et al* 1974, Sangster and Dixon 1976), has a reputation for being difficult to use. Most workers (see, e.g., Dixon 1983, Board and Elliott 1989, O'Sullivan and Madden 1991) have used a steepest descents method to relax the shell positions iteratively to zero-force positions on each time step of the molecular dynamics. Recently Lindan and Gillan (1992) have developed an improved method based on conjugate gradient relaxation of the shells. In this paper we study an alternative approach in which the shells are given a mass and their motion, like that of the cores, is found by conventional numerical integration of their equations of motion. In section 2 we describe the method and discuss the circumstances under which it should give results in agreement with the massless shell model. In section 3 the method is tested in comparison with the results of Sangster and Dixon (1976) on molten sodium chloride and Lindan and Gillan (1992) on superionic calcium fluoride. We also compare phonon frequencies in magnesium oxide with conventional lattice dynamics. Our conclusions follow in the final section.

2. Method

In the shell model the cores and shells are linked by a harmonic spring with constant k . The shell carries a charge y . In the models discussed here the core charge is chosen so that the total charge, core charge plus shell charge, has the full ionic value. The Coulombic interaction between a core and its own shell is excluded. Short-range potentials act between the shells only, and take the usual form

$$u_{\alpha\beta}(r) = A_{\alpha\beta} \exp(-r/\rho_{\alpha\beta}) - C_{\alpha\beta}/r^6 - D_{\alpha\beta}/r^8. \quad (1)$$

In the conventional shell model the shells are assumed to be massless. In our approach we put a proportion x of the ion mass on the shell, and $(1 - x)$ on the core. We then integrate the motions of the cores and shells by conventional molecular dynamics techniques.

The introduction of massive shells can be justified as follows. The shell model is not intended to represent realistically internal degrees of freedom of the ion. Rather, the aim is to study the motion of the ions as entities, and the shells are a device designed to introduce polarizability into the model of interactions between ions. The motion of the centre of mass of the ion depends only on the total force on the ion, and is not affected by the internal core-shell interaction. In the massless shell model the ions are polarized by instantaneous relaxation of the shells to zero-force position, with no inertial delay. In a model in which the shells have mass their motion, and the resulting polarization, will correspond to that in the massless case to a good approximation, providing that the shells can respond sufficiently quickly to the changing electric field experienced by the ions: in other words, providing that the frequency of the core-shell spring is well above that of the ionic vibrational frequencies.

In the massless shell model there can be no kinetic energy in the core-shell relative motion. The separation of frequencies just described is also the necessary condition to ensure that, if the shells are given mass, they move adiabatically, without equipartition of thermal energy into the internal degree of freedom. (Of course, there must be *some* kinetic energy in the core-shell relative motion, or the ion would never polarize, but the hope is that this will be small.) The period of the spring depends on the reduced mass, and is given by

$$T_x = 2\pi[x(x-1)M/k]^{1/2} \quad (2)$$

where M is the ion mass. We can always ensure that the frequency T_x^{-1} is well above the vibrational frequencies of the ions by choosing x small enough. Providing that this condition is satisfied, the behaviour of the model should be independent of x . The method of adiabatic dynamics has previously been used by Sprik (1991) to develop a polarizable model for water molecules.

Care needs to be taken when equilibrating the simulation to introduce no thermal energy into the core-shell relative motion. Equilibration involves thermostating, i.e. the scaling of velocities to produce the desired temperature. We usually use the heat bath method of Berendsen *et al* (1984), in which on each time step the velocities are multiplied by a scaling factor β given by

$$\beta = [1 + (T_r/T_a - 1)(\Delta/\tau)]^{1/2} \quad (3)$$

where T_r is the required temperature, T_a is the actual 'instantaneous temperature' on this step, Δ is the time step and τ is a relaxation time, for which we usually take the value 0.4 ps. Initially the core velocities are selected from a Gaussian distribution corresponding to the required temperature. The total momentum of the system is subtracted out, and the core-shell relative velocities are set to zero. We define the temperature of the system to be that of the motion of the centres of mass of the ions. To thermostat this temperature we modify the core and shell velocities in such a way that the centre-of-mass velocity of each ion is scaled by the appropriate factor, and the core-shell relative velocity remains unchanged. This method also ensures that the total momentum remains at zero.

In other respects our simulations are conventional. We use cubic periodic boundaries with an accurate Ewald sum for the electrostatic forces. We remember to correct for the fact that the reciprocal space part of the Ewald sum would otherwise introduce interactions between a core and its own shell. Motions are integrated with a leapfrog algorithm. To check that the shell relaxation is truly adiabatic we monitor the temperature of the core-shell relative motion.

3. Results

3.1. Molten sodium chloride

As the first test of our method we compare with the results of Sangster and Dixon (1976) on molten sodium chloride. The parameters of the model are given in table 1.

Table 1. Shell model parameters for sodium chloride.

	y $ e $	k (eV Å ⁻²)			
Na ⁺	-0.5056	63.014			
Cl ⁻	-2.5005	25.724			
	A (eV)	ρ (Å)	C (eV Å ⁶)	D (eV Å ⁸)	
Na-Na	487	0.237 68	1.05	0.5	
Na-Cl	145 134	0.237 68	6.99	8.7	
Cl-Cl	405 774	0.237 68	72.40	145.4	

With these parameters for the Na⁺ ion the largest possible value for T_x is $T_{0.5} = 19.5$ fs corresponding to a frequency of 51 THz, already well above that of any ionic motion. For the Cl⁻ ion we have $T_{0.5} = 38$ fs and by reducing x to 0.1 we can make the Cl⁻ spring frequency similar to the lowest possible Na⁺ spring frequency, since $T_{0.1} = 23$ fs. We have accordingly performed two simulations with $x_{Cl} = 0.1$, and with $x_{Na} = 0.1$ and 0.5 respectively. The target temperature was 1427 K and the molar volume was 39.006 cm³. We took a timestep of 2 fs: rigid ion simulations would normally use 8 fs for this system. The simulations used 216 ions. We equilibrated the simulations using the Berendsen thermostat, and then performed measurement runs of 20 ps with no thermostat, i.e. using conventional energy conserving dynamics.

Both simulations gave good energy conservation. With $x_{\text{Na}} = 0.1$ the rate of total energy drift was $-0.008 \text{ kJ mol}^{-1} \text{ ps}^{-1}$ (compared with a value of around -700 kJ mol^{-1}) and the ratio σ_E/σ_U of total energy fluctuations to potential energy fluctuations was 0.03. With $x_{\text{Na}} = 0.5$ the total energy drift rate was $-0.06 \text{ kJ mol}^{-1} \text{ ps}^{-1}$ and σ_E/σ_U was 0.20. It has been argued (Fincham 1986) that this order of total energy fluctuations is quite acceptable providing there is no upward drift of energy and temperature. The actual average temperature in the $x_{\text{Na}} = 0.1$ simulation was 1428 K and in the $x_{\text{Na}} = 0.5$ simulation it was 1417 K.

The temperature of the internal core-shell degree of freedom increased steadily throughout the run, but at a very low rate. In the $x_{\text{Na}} = 0.1$ simulation the average rate of increase of the temperature of this degree of freedom was 0.4 K ps^{-1} with a final value of 17 K. It should be emphasized that we did not control this temperature in any way. The low rate of transfer of thermal energy from the motion of ion centres of mass into their internal degree of freedom is a consequence of the separation of frequencies described in the previous section. The $x_{\text{Na}} = 0.5$ simulation was not so good in this regard, thermalizing at 2.3 K ps^{-1} with a final temperature of 61 K.

We compared radial distribution functions from the $x_{\text{Na}} = 0.1$ and $x_{\text{Na}} = 0.5$ simulations, and found no detectable difference. Thermodynamic properties were also in excellent agreement, given the slight difference in temperature between the two simulations. Since shell model effects are most noticeable in dynamical properties we concentrate on presenting measurements of the diffusion coefficients. These were determined by linear fits to mean-square displacements over the time interval 1–6 ps and checked by integrating the velocity autocorrelation function. Based on the scatter of points around the linear fit and comparison with values obtained from the velocity autocorrelation functions we estimate that our values are accurate to within about $\pm 5\%$. Results are given in table 2.

Table 2. Diffusion coefficients in molten sodium chloride. Units are $10^{-9} \text{ m}^2 \text{ s}^{-1}$.

	Na ⁺	Cl ⁻
$x_{\text{Na}} = 0.1$	11.6	8.6
$x_{\text{Na}} = 0.5$	11.2	8.0
Sangster and Dixon	10.8	4.4
Conjugate gradient	11.7	7.0
Rigid	8.1	5.8

The values obtained with $x_{\text{Na}} = 0.1$ and $x_{\text{Na}} = 0.5$ are in excellent agreement with each other. The Cl⁻ diffusion coefficient does not agree with the result of Sangster and Dixon (1976). However, their diffusion values were obtained from fits out to only 0.8 ps and cannot be regarded as very reliable. We also show the diffusion coefficients calculated using the same model with the conjugate gradients relaxation program of Lindan and Gillan and obtain excellent agreement for the Na⁺ coefficient, though the Cl⁻ coefficient does not agree quite so well.

The small diffusion coefficient for Cl⁻ obtained by Sangster and Dixon has been puzzling since experimentally it is not much lower than the Na⁺ value. We have accordingly performed rigid-ion simulations using the same short-range parameters as in the shell model. These results are also given in table 2, and show that a low Cl⁻ diffusion is a feature of this model even in the absence of polarization. Overall the introduction of polarization enhances the cation diffusion coefficient by around

35%, with a somewhat smaller enhancement of the anion coefficient. A similar result was found for molten KI by Jacucci *et al* (1976).

3.2. Superionic calcium fluoride

As a second test of our method we compare it with the conjugate gradient relaxation results of Lindan and Gillan (1992) on the superionic conductor CaF_2 . Again we concentrate on the diffusion coefficient: in this case only the F^- ion diffuses. The model potential is given in table 3.

Table 3. Shell model parameters for calcium fluoride.

	y $ e $	k (eV \AA^{-2})		
Ca^{++}	5.24	309.9		
F^-	-2.38	101.2		
	A (eV)	ρ (\AA)	C (eV \AA^6)	
Ca-Ca	0.0		0.0	
Ca-F	1329.61	0.2979	0.0	
F-F	1801.01	0.2930	109.1	

We take the same value of x for the Ca^{++} and F^- ions, and have performed simulations with $x = 0.1$ and $x = 0.2$. For Ca^{++} we have $T_{0.1} \approx 0.69$ fs, $T_{0.2} = 9.2$ fs, and for F^- we have $T_{0.1} = 8.4$ fs, $T_{0.2} = 11.2$ fs. The latter period corresponds to a frequency of 89 THz, well above the highest (LO) lattice frequency of 14 THz. Rather surprisingly, in view of the above spring periods, we were able to use a time step of 1.5 fs throughout: in fact the simulations are stable up to 1.8 fs time step. This is presumably because we do not energize these vibrations, and therefore do not need to integrate them very accurately. Lindan and Gillan used a timestep of 5 fs. We used a system of 324 ions, not being able to obtain reliable diffusion coefficients with a 96-ion system. We studied three state points: $T = 1500$ K, $V = 27.88$ cm³; $T = 1600$ K, $V = 28.00$ cm³; and $T = 1670$ K, $V = 28.06$ cm³. Since in this system the diffusion coefficients vary strongly with temperature we applied a heat bath thermostat (with a relaxation time of 1 ps) to control the system temperature during the measurement phase of the run. In every case the actual average temperature was within a degree or two of the target temperature. Simulations were for 36 ps at the lowest temperature, and 18 ps at the other temperatures. The thermalization of the internal core-shell degree of freedom was at a very low rate, in no case greater than 0.4 K ps⁻¹. Very possibly we could have used a larger value of x and consequently a larger time step. Results for F^- diffusion are shown in table 4, and compared with those of Lindan and Gillan (1992). Agreement is satisfactory throughout.

3.3. Phonon frequencies in magnesium oxide

One of the most noticeable effects of introducing polarizability into potential models for ionic materials is that on the frequencies of lattice vibrations. In MgO the frequency of the LO mode at the zone centre is reduced from around 32 THz to

Table 4. F^- diffusion coefficients in superionic calcium fluoride. Units are $10^{-9} \text{ m}^2 \text{ s}^{-1}$.

	Temperature (K)		
	1500	1600	1670
$x = 0.1$	2.2	3.1	4.5
$x = 0.2$	2.2	3.3	4.1
Lindan and Gillan	2.0	3.1	4.5

Table 5. Shell model parameters for magnesium oxide.

	y [e]	k (eV \AA^{-2})		
O^-	-2.9345	51.71		
	A (eV)	ρ (\AA)	C (eV \AA^6)	
Mg-Mg	0.0		0.0	
Mg-O	1346.6	0.2984	0.0	
O-O	22 764.5	0.1490	20.37	

around 22 THz. We have performed simulations on MgO using the shell-model potential of Stoneham and Sangster (1985) which is given in table 5. In this model only the O^- ion is polarizable.

We chose a value of 0.085 for x giving $T_x = 10$ fs, corresponding to a frequency of 100 THz, well above the LO frequency of 22 THz. The system consisted of 216 ions and was simulated for 15 ps after equilibration using a time step of 1 fs at a temperature of 100 K and volume corresponding to a lattice parameter of 4.228 \AA . The internal degree of freedom thermalized at a rate of 0.6 K ps^{-1} . The phonon frequencies were found by Fourier transformation of the correlation functions of the longitudinal and transverse mass and electric charge currents. (Because of the small system size and the use of periodic boundaries a limited number of wave vectors are accessible.) Results are shown in figure 1. They are compared with conventional lattice dynamics using the same potential model and lattice parameter, obtained from the CCP5 program PHONON at the SERC Daresbury Laboratory. Agreement is excellent.

4. Discussion

We have shown that, by giving the shells a small proportion of the ionic mass, it is possible to implement shell model molecular dynamics very simply using conventional simulation techniques. Stable simulations with very good energy conservation result. It is possible to ensure that the spring frequency lies well above the vibrational frequencies of the ionic system. In these circumstances, the core-shell relative motion thermalizes at a very low rate, in most cases not more than 1 K ps^{-1} . Results are then independent of the shell mass, and in agreement with those obtained using relaxation of massless shells.

The efficiency of the method in terms of computer time can be roughly analysed as follows. The time step required in a rigid ion simulation is determined by the

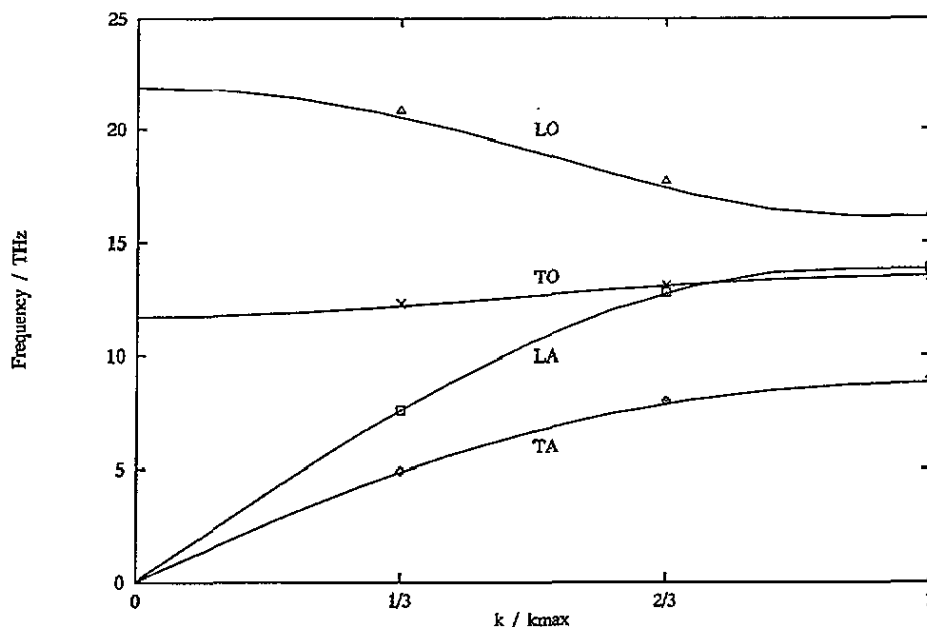


Figure 1. Phonon frequencies in MgO in the [100] direction using a shell model potential. The lines are results from conventional lattice dynamics; the points from a molecular dynamics simulation at 100 K.

necessity to resolve the fastest ionic vibrations. In our method, it is determined by the spring frequencies which are necessarily higher, and we therefore need a smaller time step. From the previous section it appears that typically our time step would be a factor of three smaller than in the rigid ion case. The inter-ion interaction is also more complicated to evaluate because of the core-core, core-shell, shell-core and shell-shell electrostatic contributions (but only one set of short-range forces). Overall, one should allow for roughly an order of magnitude increase in computer time compared with a rigid-ion simulation lasting for the same real time. In the conjugate gradient method the time step can be the same as in a rigid-ion simulation since only core motions are integrated by the molecular dynamics. Typically about 10 iterations of conjugate gradient relaxation (Lindan and Gillan 1992) are required on each time step, each involving re-evaluation of the forces (except the core-core electrostatic interactions since the cores do not move). This suggests that the present method may be two to three times faster than conjugate gradient relaxation, as well as being much simpler to implement.

The thermalization of the internal degree of freedom, though occurring at a very low rate, could be a nuisance in very long simulations. Since completing the work for this paper we have been experimenting with the introduction of a small frictional damping term in the core-shell spring motion. To compensate for the resulting loss of energy the system temperature is thermostatted, and the overall energy conservation is then excellent. The temperature of the core-shell degree of freedom rises to a few kelvin and then remains constant. Preliminary indications are that this amount of energy is sufficient to enable the ion to polarize, and to give reliable results.

It is possible that the efficiency of the method could be further improved by the

use of two time steps: a short time step to integrate the fast core-shell motions, and a larger time step for the ion centre-of-mass motions.

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