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A computer simulation study of transport coefficients in alkali halides

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Abstract. We report the first application of molecular dynamics simulation to the calculation of the thermal conductivity of ionic solids. Results are presented for the thermal conductivity of solid NaCl and KCl at a range of temperatures between room temperature and the melting point, and also for a number of transport coefficients in the liquid state. The calculations are based on simulations in full thermal equilibrium, and make use of the Green–Kubo relations. The simulations reproduce the experimental measurements with satisfactory accuracy (generally to within 10%), except for the solids near the melting point.

1. Introduction

The technique of molecular dynamics (MD) simulation has been widely used to study the transport coefficients of liquids and, to a much smaller extent, of solids (for reviews, see e.g. Evans and Morriss 1984, Allen and Tildesley 1987). Much of the work reported so far has been concerned with matters of technique, and has focused on simple model systems such as the hard-sphere and Lennard-Jones fluids, although work has been reported on liquid metals (Cummins and Morriss 1988), molecular liquids (e.g. Evans 1981, Allen and Kivelson 1981) and fluids of charged particles (Bernu and Hansen 1982, Pierleoni *et al* 1987). The purpose of the present paper is to describe MD calculations of the transport coefficients in two alkali halides. We shall show that the simulations give results in quite satisfactory agreement with experiment for both the solid and liquid states.

The work we report is of both scientific and technological interest. The alkali halides are among the simplest ionic materials, and have been very intensively studied. MD simulation has been very successful in exploring their static and dynamical properties (Sangster and Dixon 1976). Apart from one very brief study (Bazhenov and Desyatnik 1983), however, no simulation work has previously been reported on their thermal conductivity. The viscosity of several alkali halides has been computed from non-equilibrium simulations by Ciccotti *et al* (1976), but the efficiency of equilibrium simulations has not been investigated. The technological motivation for the work is connected with our interest in the nuclear reactor fuel UO₂, whose transport coefficients are of

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practical importance. This is an ionic material in which the thermal conductivity is known to behave anomalously near the melting point (Washington 1973, Brandt *et al* 1976, Martin 1982), and the change of thermal conductivity on melting has been the subject of recent controversy (Fink and Leibowitz 1985). We have recently shown that UO_2 can be successfully modelled by MD simulation (Sindzingre and Gillan 1988, Gillan 1989), and it seems likely that further simulation work will shed light on the behaviour of the high-temperature transport coefficients. Our present calculations on the alkali halides are intended to prepare the way for such work.

Several techniques have been developed for calculating transport coefficients by MD simulation. The most obvious approach is perhaps to simulate a system with boundaries to which an appropriate perturbation is applied, and to calculate the induced steady state flux. An example of this is the work of Tenenbaum *et al* (1982) on the thermal conductivity of the Lennard-Jones liquid, in which opposite boundaries of the simulation cell are maintained at different temperatures, and the heat flow across the system is measured. Such a method would not be suitable for the work on solids which interests us here. Meaningful results by this technique could not be expected unless the phonon mean free path was small compared with the distance between the boundaries, and this would require an inordinately large simulated system, except possibly near the melting point (Mountain and MacDonald 1983). To avoid the problem of boundaries, some authors have studied the response to a perturbation varying periodically in space. This method suffers from the difficulty of extrapolating to long wavelengths (Ciccotti *et al* 1978). We believe that the only satisfactory non-equilibrium methods are those based on the use of a steady translationally-invariant perturbation, for example the Evans–Gillan technique for calculating the thermal conductivity (Evans 1982, Gillan and Dixon 1983). However, even these methods suffer from serious drawbacks, such as the need to extrapolate to zero perturbation (Gillan 1987). In view of these problems with non-equilibrium methods, we have based the present calculations entirely on the equilibrium Green–Kubo formulae. These express transport coefficients as the time integral of correlation functions of the fluxes that arise by spontaneous fluctuations in full thermal equilibrium. In this approach, all that is required is a standard—though perhaps lengthy—MD simulation, from which we can obtain all the transport coefficients of interest.

The alkali halides we have chosen for study are NaCl and KCl. Our calculations employ the ionic pair potentials due to Tosi and Fumi (1969), which are known to give reliable results for the thermodynamic quantities, radial distribution functions and diffusion coefficients of the salts in the molten state (Sangster and Dixon 1976).

The paper is organised as follows. We summarise in section 2 the theoretical relations on which the work is based. In section 3, we then describe the simulations we have performed, give results for the correlation functions and their time integrals for the solid and liquid salts, and present the values we deduce for the transport coefficients. We discuss the comparison of these results with experimental data in section 4. In the final section, we present our conclusions.

2. Theoretical relations

We summarise here the formulae on which our calculations are based.

In a binary ionic system, the local fluxes j_z and j_q of charge and heat are described by the phenomenological transport equations:

$$j_z = -\beta L_{zz}(\nabla\mu_z)_T - L_{zq}\nabla(-\beta) \quad j_q = -\beta L_{qz}(\nabla\mu_z)_T - L_{qq}\nabla(-\beta) \quad (1)$$

where μ_z is the electrochemical potential, β is $1/k_B T$, and L are the phenomenological coefficients; the notation $()_T$ indicates that the gradient is taken under isothermal conditions.

Statistical-mechanical theory shows that the coefficients $L_{\alpha\beta}$ ($\alpha, \beta = z, q$) can be expressed in terms of time correlation functions of the dynamical variables J_α representing the total fluxes of charge and heat in the system

$$L_{\alpha\beta} = \frac{1}{3\Omega} \int_0^\infty dt \langle J_\alpha(t) \cdot J_\beta(0) \rangle \quad (2)$$

where Ω is the volume of the system, and angle brackets indicate the average in full thermal equilibrium (Green 1954, Kadanoff and Martin 1963, Kubo 1966, Bernu and Vieillefosse 1978, Bernu and Hansen 1982, Allen and Tildesley 1987).

The electrical conductivity σ , i.e. the ratio between the electric current density and the negative gradient of μ_z under isothermal conditions, is given by $\sigma = \beta L_{zz}$. Taking the thermal conductivity λ to mean the ratio between the heat flux and the negative temperature gradient when the electric current is zero, we obtain the formula

$$\lambda = (L_{qq} - L_{qz}^2/L_{zz})/k_B T^2. \quad (3)$$

The transport coefficients L_{qz} and L_{zq} (which are equal by the Onsager reciprocal relation), describe thermoelectric effects, which will not concern us here.

For simulation purposes, it is easier to work with the energy flux j_e rather than the heat flux j_q . The two are related by

$$j_q = j_e - h_1 j_1 - h_2 j_2 = j_e - h_z j_z \quad (4)$$

where j_ν is the flux of ions of species ν in the centre of mass frame, and h_ν is the partial enthalpy of species ν ; the explicit expression for h_z in terms of h_1 and h_2 will not be needed here. The phenomenological relations can be re-expressed in terms of the fluxes j_z and j_e

$$j_z = -L_{zz}\nabla(\beta\mu_z) - L_{ze}\nabla(-\beta) \quad j_e = -L_{ez}\nabla(\beta\mu_z) - L_{ee}\nabla(-\beta) \quad (5)$$

the coefficients $L_{\alpha\beta}$ being given by formula (2), with correlation functions now involving the fluxes J_z and J_e . It is readily shown that the thermal conductivity is equivalently given by

$$\lambda = (L_{ee} - L_{ze}^2/L_{zz})/T^2. \quad (6)$$

More generally, one can work with any flux $j_x = j_e - x j_z$ instead of j_q or j_e . In terms of the corresponding phenomenological coefficients defined in the obvious way, λ is given by

$$\lambda = (L_{xx} - L_{zx}^2/L_{zz})/T^2. \quad (7)$$

The usefulness of these alternative expressions will be apparent later. We shall see that the autocorrelation function of the energy current in the solid shows a prominent oscillatory behaviour arising from fluctuations of the electric current at the transverse optic frequency. These oscillations can be suppressed by working with the appropriate flux j_x .

The bulk and shear viscosities ζ and η are similarly given in terms of phenomenological coefficients expressing the linear relation between the momentum flux (stress tensor) and velocity gradients. The corresponding Green–Kubo formulae are (Kadanoff and Martin 1963, Allen and Tildesley 1987):

$$\zeta + \frac{4}{3}\eta = \frac{1}{\Omega k_B T} \int_0^\infty dt \langle (\sigma_{xx}(t) - p\Omega)(\sigma_{xx}(0) - p\Omega) \rangle \quad (8)$$

$$\eta = \frac{1}{\Omega k_B T} \int_0^\infty dt \langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle$$

where p is the equilibrium pressure, and $\sigma_{\alpha\beta}$ are the cartesian components of the stress tensor.

The microscopic expressions for the stress tensor and energy current for ionic systems have been discussed before in the literature (Bernu and Vieillefosse 1978, Bernu and Hansen 1982, Bernu 1983).

3. The calculations

The interactions between the ions in NaCl and KCl are represented by the Tosi–Fumi (1969) rigid-ion pair potentials. Several previous simulation studies have shown that these potentials give a very satisfactory account of the properties of these salts both in the solid and the liquid phase (Sangster and Dixon 1976).

We have made simulations on systems containing 64 and 216 ions. The simulations were performed at constant volume and constant temperature, using the Nosé (1984) technique. Integration of the equations of motion was performed with the algorithm used in our recent simulations on UO_2 (Sindzingre and Gillan 1988). The time step was

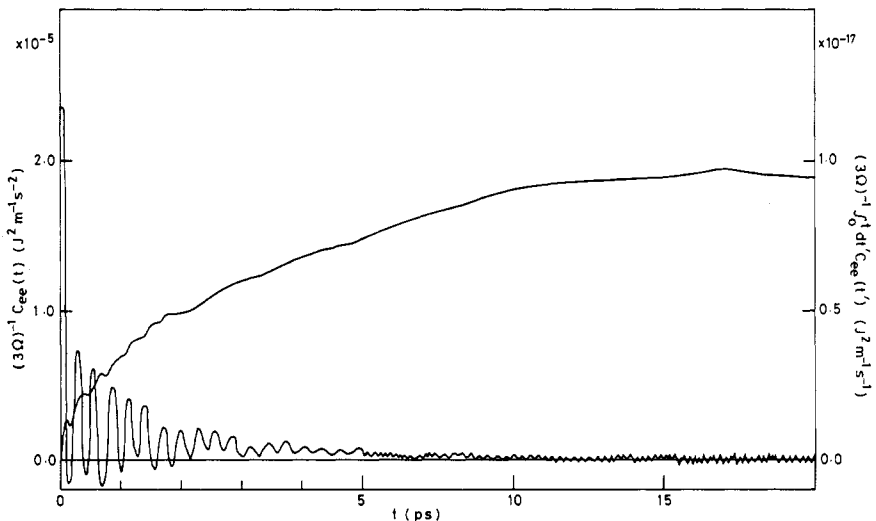


Figure 1. Autocorrelation function $\langle J_e(t) \cdot J_e(0) \rangle$ and its time integral $\xi_{ee}(t)$ (see equation (9)) for solid KCl at 500 K. The results were obtained in a simulation of 1.4×10^5 time steps performed on a system of 64 ions.

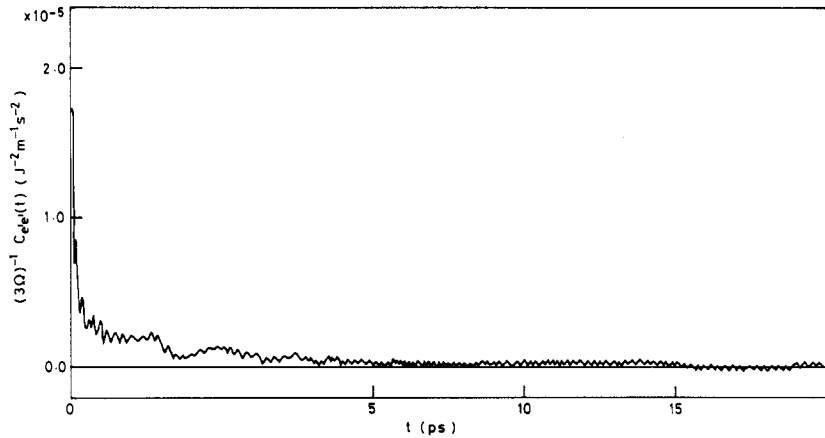


Figure 2. Autocorrelation function $\langle J_e(t) \cdot J_e(0) \rangle$ of the modified energy current J_e for solid KCl at 500 K. The results were obtained from the simulation referred to in figure 1.

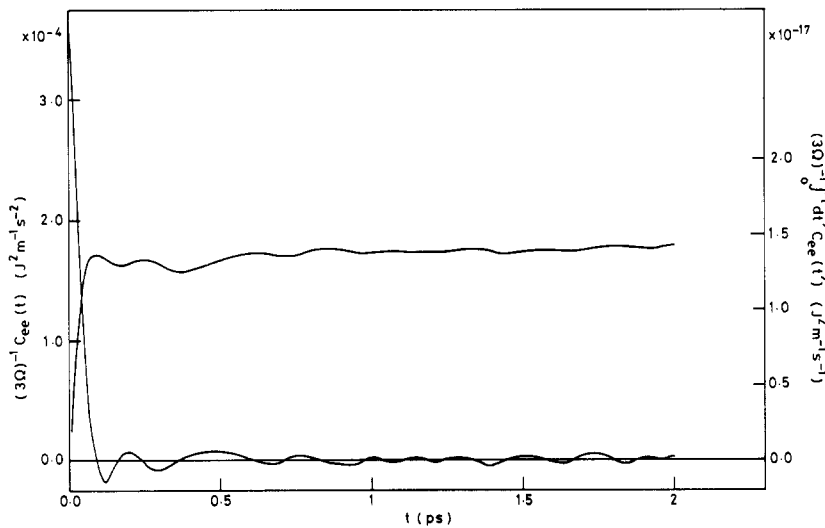


Figure 3. Autocorrelation function $\langle J_e(t) \cdot J_e(0) \rangle$ and its time integral for liquid NaCl at 1100 K. The results were obtained in a simulation of 3.8×10^4 time steps performed on a system of 216 ions.

8.1×10^{-15} s. The Coulomb interactions were treated using the normal Ewald method (Allen and Tildesley 1987).

For comparison with experimental data for the thermal conductivity, we studied the solids at moderate and high temperatures, and for experimental values of the volume. Simulations were done for solid NaCl at 400 and 1050 K, and for solid KCl at 300, 500 and 1000 K. The melting points T_f of NaCl and KCl are respectively 1073 and 1045 K, so that the temperatures of our simulations range from roughly $T_f/3$ up to nearly T_f . The lowest temperatures considered are above the Debye temperature, and quantum

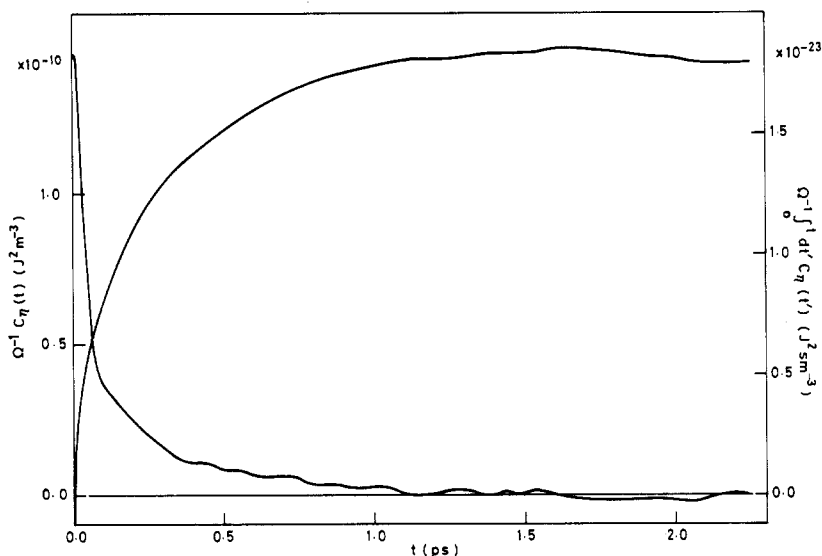


Figure 4. Autocorrelation function $\langle \sigma_{xy}(t)\sigma_{xy}(0) \rangle$ and its time integral for liquid NaCl at 1100 K. The results were obtained from the simulation referred to in figure 3.

corrections are expected to be very small. For the liquids, we have performed simulations only at 1100 K for NaCl and at 1096 K for KCl.

In figures 1–4 we show examples of our results for the autocorrelation functions of the fluxes J_z and J_e , and their time integrals

$$\xi_{\alpha\beta}(t) = \frac{1}{3\Omega} \int_0^t dt' C_{\alpha\beta}(t') \quad (9)$$

where $C_{\alpha\beta}(t) = \langle J_\alpha(t) \cdot J_\beta(0) \rangle$.

Figure 1 displays the autocorrelation function $\langle J_e(t) \cdot J_e(0) \rangle$ in solid KCl at 500 K and its time integral $\xi_{ee}(t)$. The correlation function exhibits the prominent slowly decaying oscillations referred to in section 2. We find that these oscillations remain clearly visible up to the melting point, though their decay rate increases with temperature. The oscillation frequency agrees closely with the frequency of the electric current correlation function $\langle J_z(t) \cdot J_z(0) \rangle$, in other words the transverse optic frequency. This indicates that we are seeing energy current fluctuations associated with transverse optic vibrations at zero wavevector. These vibrations do not contribute to the long-range transport of energy. When considering the thermal conductivity, it is therefore convenient to consider the modified energy flux $J_{e'}$ defined so as to suppress these oscillations. It is straightforward to show that the appropriate definition of $J_{e'}$ is $J_{e'} = J_e - h_z^0 J_z$ where the ‘enthalpy’ h_z^0 is

$$h_z^0 = (m_2 h_1^0 - m_1 h_2^0) / e(m_2 z_1 - m_1 z_2) \quad (10)$$

where m_α is the mass of ions of species α , z_α is the charge on ions of species α in units of the elementary charge, e , and the quantities h_α^0 are given by

Table 1. Simulation results for the thermal conductivity λ in solid NaCl and KCl for different temperatures T at the experimental value of the molar volume V . The number of ions in the simulated system is N , and the duration of the simulation is given by the number of time steps n . Experimental values of λ are from Petrov *et al* (1976).

	T (K)	V (cm ³ mol ⁻¹)	N	n (10 ⁴)	λ_{calc} (W m ⁻¹ K ⁻¹)	λ_{exp}
NaCl	400	27.35	64	18	4.08 ± 0.44	4.25
	1050	30.42	64	12	0.87 ± 0.07	1.24
KCl	300	37.53	64	18	5.45 ± 0.67	6.42
	500	38.42	64	14	2.78 ± 0.46	3.27
	500	38.42	216	5	3.52	
	1000	41.63	64	12	0.88 ± 0.07	1.37
	1000	41.63	216	4	0.78	

$$h_{\alpha}^0 \mathbf{I} = \frac{1}{2} \sum_{\beta} \sum_j \left(V_{\alpha\beta}(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) \mathbf{I} - \frac{V'_{\alpha\beta}(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j})}{|\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}|} (\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j})(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) \right). \quad (11)$$

Here, $V_{\alpha\beta}(r)$ is the pair potential acting between ions of species α and β , $V'_{\alpha\beta}(r)$ is its first derivative, $\mathbf{R}_{\alpha i}$ is the regular lattice position of ion i of species α , and \mathbf{I} is the unit matrix; the prime on the summation over j indicates exclusion of the term $i = j$ for $\alpha = \beta$. In writing equation (11), we have made use of the cubic symmetry of the crystal.

In figure 2, we display our results for the correlation function $\langle \mathbf{J}_e'(t) \cdot \mathbf{J}_e(0) \rangle$ in solid KCl at 500 K. The oscillations have now been completely suppressed.

Figure 3 shows the autocorrelation function of the energy current in liquid NaCl at 1100 K and its time integral. The correlation function decays rapidly to zero, so that its time integral quickly attains the plateau value needed to calculate the thermal conductivity. The behaviour of the stress correlation function involving σ_{xy} for the liquid is illustrated in figure 4, which shows $C_{\eta}(t) = \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle$ and its time integral for liquid NaCl at 1100 K. The correlation function decays rapidly to zero, and the estimation of the plateau value of its time integral presents no problem.

From the plateau values of the time integrals, we have obtained results for the transport coefficients σ , λ , ζ and η . Results for the thermal conductivity of the two solid salts at a number of temperatures are reported in table 1, and results for all four transport coefficients for the liquids are given in tables 2 and 3. Statistical errors have been estimated by the usual method of studying the spread of results from sub-averages; they are typically of order 10%. We have not studied size effects in a systematic way, but the differences between the results for the systems containing 64 and 216 ions are in all cases comparable to the statistical errors; this suggests that size effects are probably not very significant.

4. Discussion of results

4.1. Comparison with experimental data

Our most extensive results are for the thermal conductivity, and we concentrate mainly on the comparison of these results with experimental values, which are shown for both solid and liquid phases in tables 1–3.

Table 2. Comparison of simulation results with experimental values for thermal conductivity λ , bulk and shear viscosities ζ and η and electrical conductivity σ of liquid NaCl. References for the experimental values are: (a) Golyshev *et al* 1983; (b) Young and O'Connell 1971; (c) Tørklep and Øye 1979; (d) Van Artsdalen and Yaffe 1955.

	Calculated results		Experimental results
T (K)	1100		
V (cm ³ mol ⁻¹)	38.01		
N	64	216	
n (10 ⁴)	14	3.8	
λ (W m ⁻¹ K ⁻¹)	0.65 ± 0.06	0.67	0.41 ^(a)
ζ (cp)	2.2 ± 0.7	1.6	
η (cp)	1.05 ± 0.05	1.16	1.24 ^(b,c)
σ (Ω ⁻¹ cm ⁻¹)	3.3 ± 0.3	2.8	3.58 ^(d)

Table 3. Comparison of simulation results with experimental values for thermal conductivity λ , bulk and shear viscosities ζ and η and electrical conductivity σ of liquid KCl. References for the experimental values are: (a) MacDonald and Davies (1971); (b) Young and O'Connell (1971); (c) Jal *et al* (1980); (d) Van Artsdalen and Yaffe (1955).

	Calculated results		Experimental results
T (K)	1096		
V (cm ³ mol ⁻¹)	49.88		
N	64		
n (10 ⁴)	14		
λ (W m ⁻¹ K ⁻¹)	0.41 ± 0.04		0.37 ^(a)
ζ (cp)	2.1 ± 0.7		
η (cp)	1.24 ± 0.08		1.03 ^(b,c)
σ (Ω ⁻¹ cm ⁻¹)	2.5 ± 0.3		2.28 ^(d)

The simulation results are in close agreement with experiment for the solid at lower temperatures. As one approaches the melting point, the agreement becomes somewhat less satisfactory, the experimental values being some 40% higher than the simulation values for NaCl, and 70% higher for KCl near the melting point. In the liquid, we find close agreement for KCl, but there appears to be a discrepancy of around 30% for NaCl.

These discrepancies may be partly due to inadequacies of the Tosi–Fumi potentials, but it should be stressed that the experiments are not entirely straightforward, since radiative effects may give important corrections at high temperatures. Although Petrov *et al* (1976) attempted to correct for these effects in their measurements on solid NaCl and KCl, we suggest that residual corrections may account for some of the discrepancy in the high-temperature solid. The measurements of MacDonald and Davies (1971) on liquid KCl used the hot-wire technique, for which radiative corrections are negligible, and our close agreement with their result is therefore significant.

Our simulation results for the shear viscosity of the two liquid salts are in very satisfactory agreement with experiment for KCl, and in somewhat less good agreement for NaCl. Experimental results for the bulk viscosity are, of course, not available.

4.2. Comparison with previous simulations

Simulation has not been used previously to calculate the thermal conductivity of ionic solids, but a calculation of the thermal diffusivity D_T of liquid NaCl has been reported by Bazhenov and Desyatnik (1983), using the Tosi–Fumi model employed in the present work. The authors used a non-equilibrium technique in which the relaxation of an initial spatially periodic temperature disturbance is calculated. The thermal diffusivity is defined as $D_T = \lambda/\rho C_p$, where ρ is the density and C_p is the specific heat at constant pressure. From the value of D_T near 1200 K reported by Bazhenov and Desyatnik, and the value of C_p for the Tosi–Fumi NaCl reported by Lewis and Singer (1975) for a similar temperature, we deduce the value $\lambda \approx 1.2 \text{ W m}^{-1} \text{ K}^{-1}$. This is much higher than our value ($0.6 \text{ W m}^{-1} \text{ K}^{-1}$) at 1100 K, which itself is somewhat higher than the experimental value of $0.4 \text{ W m}^{-1} \text{ K}^{-1}$. Given the weak temperature dependence of λ indicated by experiment for the liquid, the discrepancy cannot be attributed to the difference of thermodynamic state. The work of Ciccotti *et al* (1978), however, demonstrates that finite-wavevector results for λ can depend strongly on wavevector. For the small system (64 ions) used by Bazhenov and Desyatnik, the smallest available wavevector is already large, and we believe that their result cannot be taken to refer to the observable macroscopic thermal conductivity.

Calculations of the shear viscosity and the electrical conductivity of liquid NaCl have been previously reported by Ciccotti *et al* (1976) at a temperature some 150 K above the one we have studied. Both η and σ vary significantly with temperature, so that their results are not directly comparable with ours. However, like us, they find rather close agreement with experiment for both quantities.

5. Conclusions

The present work is significant mainly in relation to the thermal conductivity of ionic materials, which has not previously been studied by MD simulation. We have shown that the equilibrium Green–Kubo technique gives reliable and reasonably accurate results for λ both in the solid and liquid states of the two alkali halides we have studied. Our calculations also indicate that it is not necessary to use very large simulated systems. Even though at low temperatures the phonon mean free path is certainly greater than the dimension of the repeating cell (i.e. the decay time of the correlation function is greater than the time for sound to cross the system), there is no indication of important size effects.

MD simulations avoid the use of statistical-mechanical approximations and, for a given interionic potential, yield essentially exact results for a classical system. This is of great advantage for the computation of the thermal conductivity, not only in liquid but also in solid systems, where this approach can now be considered as an attractive and efficient alternative to the methods based on the Boltzmann equation and anharmonic perturbation theory. The Boltzmann equation provides only an approximate description of energy transport, and further approximations are involved in its solution. In addition, as shown by Ladd *et al* (1986) in the case of a soft-sphere system, the validity of perturbation theory is questionable in high-temperature solids. The MD approach will be especially suited to the investigation of the thermal conductivity of superionic solids like UO_2 , which we plan to undertake in the near future.

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