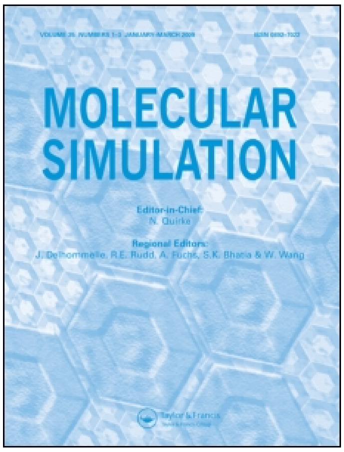

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MONTE-CARLO SIMULATION OF MOLTEN CsCl USING A 'DEFORMATION DIPOLE' POLARISABLE ION POTENTIAL

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We have simulated the structure of molten CsCl at 943 K using a form of interionic potential, based on the deformation dipole model of Hardy and Karo, where ions have both point charges and dipoles. The magnitude of the dipole on an ion is determined by two factors, one being the local electric field and the other the repulsive potential due to overlap with neighbouring ions. Parameters are determined directly from the crystal lattice constant, compressibility and dielectric constants. Good agreement with experimental results is obtained. The potential is compared to the shell model of ionic polarisability which does not produce good agreement with experiment.

KEY WORDS: Monte Carlo, polarisable ion, deformation dipole, shell model, molten salt

INTRODUCTION

Computer simulations of molten alkali chlorides using phenomenological rigid ion potentials such as those due to Born, Mayer and Huggins [1] or Narayanan et al. [2] have succeeded in producing structures which generally agree well with experiment [3, 4, 5]. However in the case of CsCl [6] there are significant deviations from the experimental partial radial distribution functions, $g_{\alpha\beta}(r)$, which may be summarised as follows:

(a) All peak heights and minima depths are respectively too high and too low.

(b) The second peak in $g_{+-}(r)$ is at too high an r value with respect to the first.

(c) Both $g_{++}(r)$ and $g_{--}(r)$ exhibit a shoulder on the high r side of their first peak (equivalent to the second like neighbour distance in the NaCl crystal structure).

The experimental result is compared in Figure 1 with a simulation by Baranyai et al. [7] using the rigid ion potential that forms the basis of the polarisable ion potential discussed in this paper.

In order to correctly simulate the dynamics of such a system some account must be taken of the ionic polarisability, e.g. both longitudinal and transverse optic mode frequencies in the crystal cannot be obtained correctly with rigid ion potentials. It has been suggested [6] that the deviation in the case of CsCl structure may be due to charge screening by the highly polarisable Cs^+ and Cl^- ions. However a simulation [8] using the shell model of ionic polarisability [9] produced no significant improvement. Indeed shell model results for the structures of molten salts are generally very similar to the equivalent rigid ion results [9] (there are however significant differences

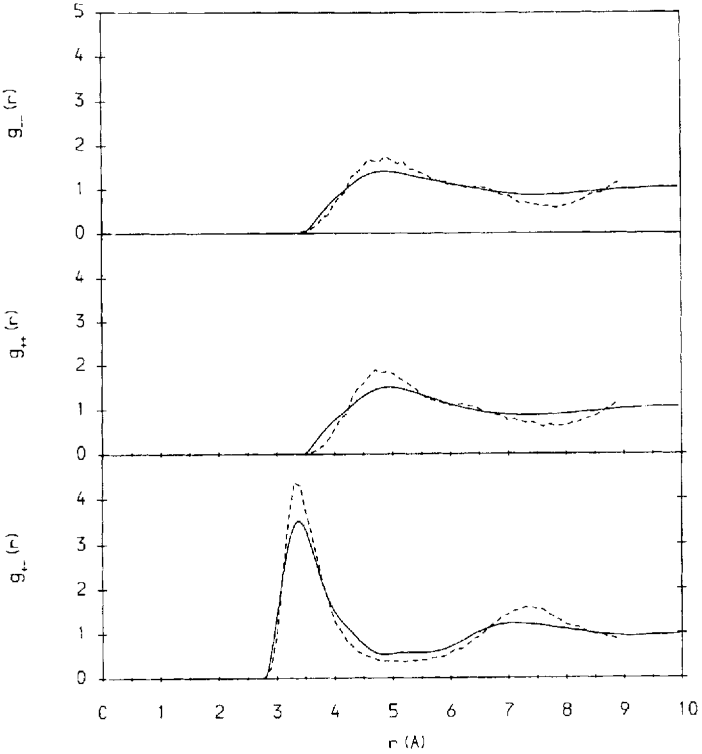

Figure 1 Partial radial distribution functions for molten CsCl; comparison of experiment [6] (solid curve) and rigid ion simulation [7] (broken curve).

in dynamics); a comparison is made for CsCl in Figure 2. The use of an empirical screened Coulomb potential [10] was also unsuccessful. An alternative model of ionic polarisability is therefore required.

MODELS OF IONIC POLARISABILITY

In the shell model [11] each ion is considered to be composed of a core and a shell connected by a 'spring.' Both the core and the shell are charged, the sum of the charges being that of the ion. For two ions there are core–core, shell–shell and core–shell Coulomb interactions. The parameters, i.e. core and shell charges and spring constants, are determined, together with the parameters in the repulsive potential, by fitting to crystal properties such as the elastic and dielectric constants [9]. The repulsive interactions are assumed to take place between ion shells. It should be noted that individual parameters obtained in such a fitting often have 'unphysical' values.

An alternative to the shell model is the 'deformation dipole' model used by Hardy and Karo [12] in their calculations of the lattice dynamics of alkali halide crystals. In this model there are two separate contributions to ionic polarisation.

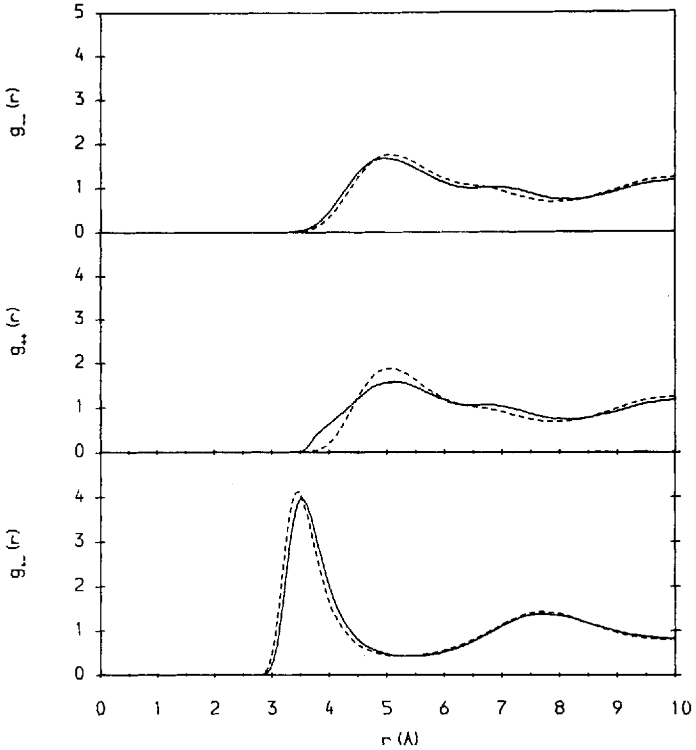

Figure 2 Partial radial distrubiton functions for molten CsCl; comparison of rigid ion (solid curve) and shell model polarisable ion (broken curve) simulations [8].

(a) It is assumed that rather than a rigid shell there is a soft deformable shell into which holes are 'punched' by neighbouring ions, thus distorting the previously isotropic electron distribution and creating a dipole. This is point dipole which is situated at the ion centre.

(b) Ions are polarised in the normal manner by the local electric field; again it is assumed that the induced dipole is a point dipole situated at the ion centre. The local field contains contributions from both charges and dipoles, so there are many-body terms in the interionic potential.

Saboungi et al. [13] have, at the same time as this work, adopted a similar approach to ionic polarisation in a simulation of molten MAX_4 (e.g. $NaCl$–$AlCl_3$). They have considered only field induced dipoles, i.e. terms (b), but have included them as dynamical variables within a Molecular Dynamics simulation by a very elegant method which results in considerable saving in computer time. While the results of this simulation are important in indicating the structural changes that are brought about by polarisation, particularly with regard to ionic complex formation, the form of the polarisable ion potential itself cannot be evaluated since they are not compared to experimental results for any real system. Tosi and Doyama [14] and Brumer [15] have also adopted essentially the same approach to ionic polarisation in calculations concerning alkali halide molecules.

THE FORM OF THE INTERIONIC POTENTIAL

As a basis for this simulation we have taken the rigid ion potential of Narayanan et al. [2], as used by Baranyai et al. [7] in their simulations of molten alkali halides. This has the form

$$U_i = \sum_{i \neq j} A_{ij} \exp(-k_{ij} r_{ij})\, r_{ij} + z_i \sum_{i \neq j} z_j\, e^2/r_{ij} \tag{1}$$

where z_i is the charge on ion i (in units of e) and $\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i$ is the separation of ions i and j. A_{ij} and k_{ij} are obtained from ab initio coefficients calculated by Harrision [16] and then fitting to the crystal lattice parameter and compressibility [2].

Szigetti [17] has shown that the consistent application of the dipolar approximation in alkali halide crystals leads to values of the static dielectric constant approximately twice as large as those observed. An 'effective' ionic charge

$$e^* = \pm\,(e - p) \tag{2}$$

is therefore required. This may be calculated using the expression

$$\frac{e^*/(Mv)^{1/2}}{1 - (4\pi/3)[(\alpha_+ + \alpha_-)/v]} = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{4\pi}\right)^{1/2} \omega_{TO} \tag{3}$$

where M is the reduced ionic mass, v the unit cell volume, ω_{TO} the transverse optic (zone centre) frequency, ε_0 and ε_∞ the high and low frequency dielectric constants respectively and α_+ and α_- the ionic polarisabilities.

Hardy and Karo [12] have related the reduction in effective charge to the dipole moment $\mu(r_0)$ produced by ionic deformation in each of the nearest neighbour bonds. For the CsCl structure this has the form

$$p = -4\,[\mu'(r_0) + 2^{1/2}\,\mu(r_0)/r_0] \tag{4}$$

the prime indicating differentiation with respect to r.

We have modelled the deformation dipole using the repulsive term in the rigid ion potential in the following way:

$$\boldsymbol{\mu}_{ij}^{D} = \alpha_{ij}^{D} A_{ij} \exp(-k_{ij} r_{ij})\, \mathbf{r}_{ij} \tag{5}$$

We have assumed that $\alpha_{ii} = \alpha_{jj} = 0$ and $\alpha_{ij} = \alpha_{ji}$. The former is a reasonable approximation in a crystal but less so in a melt, where there may be significant overlap between like ions. The latter is a reasonable approximation for ions of similar size such as Cs^+ and Cl^-. If these approximations are not made then there is some empirical choice to the α_{ij}, since there is only one value of p from which to obtain four coefficients.

The total deformation dipole induced on an ion is then

$$\boldsymbol{\mu}_i^{D} = \sum_{i \neq j} \boldsymbol{\mu}_{ij}^{D} \tag{6}$$

The dipole induced on an ion due to the local electric field of all charges is

$$\boldsymbol{\mu}_i^{z} = \alpha_i \sum_{i \neq j} z_j\, \mathbf{r}_{ij}/r_{ij}^3 \tag{7}$$

where α_i is the (high frequency) polarisability of ion i. We must also include dipole terms induced by the field due to other dipoles, which can only be done by an iterative procedure. We express the pairwise additive terms $\boldsymbol{\mu}_i^z$ and $\boldsymbol{\mu}_i^D$ which will be constant in the iteration as

$$\boldsymbol{\mu}_i^c = \boldsymbol{\mu}_i^D + \boldsymbol{\mu}_i^z \tag{8}$$

The field at ion i due to all other dipoles is

$$\mathbf{E}_i^\mu = \sum_{i \neq j} 3\, \boldsymbol{\mu}_j \cdot \mathbf{r}_{ij}\, \mathbf{r}_{ij}/r_{ij}^5 - \boldsymbol{\mu}_j/r_{ij}^3 \tag{9}$$

The dipole on ion *i* is the sum of the constant term and the dipole-induced-dipole term

$$\boldsymbol{\mu}_i' = \boldsymbol{\mu}_i^c + \alpha_i\, \mathbf{E}_i^\mu \tag{10}$$

We then iterate

$$\boldsymbol{\mu}_i'' = \boldsymbol{\mu}_i^c + \alpha_i\, \mathbf{E}_i^{\mu'} \tag{11}$$

until convergence is achieved. (In the present case we have found three iterations to be sufficient. This step obviously dominates the time required for such a simulation.)

The full expression for the potential is then

$$\begin{aligned} U_i = {} & z_i \sum_{i \neq j} z_j\, e^2/r_{ij} + \sum_{i \neq j} \exp(-k_{ij} r_{ij})\, r_{ij} \\ & + \sum_{i \neq j} \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j / r_{ij}^3 - 3 \sum_{i \neq j} (\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})/r_{ij}^5 \\ & + \sum_{i \neq j} (z_i \boldsymbol{\mu}_j - z_j \boldsymbol{\mu}_i) \cdot \mathbf{r}_{ij}/r_{ij}^3 \end{aligned} \tag{12}$$

It is also possible to include van der Waal's terms, i.e. $C_{ij}/r_{ij}^6 + D_{ij}/r_{ij}^8$. However these are considered to be relatively unimportant and have been neglected. Values of the coefficients A_{ij}, k_{ij}, α_{ij}^D and α_i are given in Table 1.

SIMULATION DETAILS

The simulation is in all respects apart from the potential identical to that of Baranyai et al. [7]. 112 ions are contained in a cubic box of dimension $L = 17.895$ Å (equivalent to the density at the experimental temperature of 943 K) with periodic boundary conditions. We have used Markov chain Boltzmann sampling. The starting point was an equilibrium configuration obtained for the rigid ion potential. We have run 12500 accepted particle displacements to achieve a new equilibrium and then subsequent 12500 displacements. One in fifty of these are then averaged over to produce the result. The individual terms $\boldsymbol{\mu}_{ij}^D$, $\boldsymbol{\mu}_{ij}^z$ and $\mathbf{r}_{ij}$ are saved in an array so that only those related to the displaced particle need to be calculated at each step. This saves a

Table 1

	++	+−	−−
$A_{ij}(10^7 \mathrm{J\,m^{-1}})$ [7]	563.3	446.0	346.2
$k_{ij}(\text{Å}^{-1})$ [7]	4.401	4.072	3.742
$\alpha_{ij}^D(\mathrm{C\,m\,J^{-1}})$	0	$1.316\,10^{-10}$	0
$\alpha_i(\text{Å}^3)$ [18]	3.0	0	3.2

considerable amount of time but the program still takes approximately 5 times as long as with the rigid ion potential, largely because of the dipole iteration. Since the aim of the simulation is purely to test the potential it was not felt worthwhile to run a larger simulation, the only effective gain being an increase in statistical accuracy.

The correction of the long range Coulomb interaction is performed using the reaction field corrected cut-off sphere method [7, 10]. Coulomb interactions are calculated directly within a sphere of radius L centred on an ion i. The net charge and dipole within the sphere are given by

$$\Delta z_{\mathrm{i}} = \sum_{i \neq j} z_{\mathrm{j}}, \Delta \boldsymbol{\mu}_{\mathrm{i}} = \sum_{i \neq j} \boldsymbol{\mu}_{\mathrm{j}}, r_{\mathrm{ij}} < L \tag{13}$$

These are compensated for by an opposite charge and dipole situated on the surface of the sphere, the Coulomb interaction with the central ion being screened. The energy correction is therefore given by

$$\Delta U_{\mathrm{i}} = -z_{\mathrm{i}} \Delta z_{\mathrm{i}} e^2 \alpha / L - \boldsymbol{\mu}_{\mathrm{i}} \cdot \Delta \boldsymbol{\mu}_{\mathrm{i}} \beta / L^3 \tag{14}$$

where κ is the Debye screening length

$$\kappa = 4\pi e^2 \varrho / k_{\mathrm{B}} T \tag{15}$$

and

$$\alpha = \kappa L/(1 + \kappa L), \beta = 2\kappa L/(1 + 2\kappa L) \tag{16}$$

RESULTS AND DISCUSSION

The partial radial distribution functions obtained using the potential described above are shown in Figure 3 in comparison with the experimental result. The agreement is within the experimental error, though it may possibly be improved slightly by decreasing the ionic polarisabilities. However it must be emphasised that the present level of agreement has been achieved without any empirical adjustment of parameters, which were all obtained directly from crystal data. The deformation dipole model is therefore, in this case at least, considerably better than the shell model.

The main differences between deformation dipole and shell models can be summarised as follows:

(a) Shell model.

(i) Dipoles are produced by separation of the core and shell charges.

(ii) The repulsive interactions take place between ion shells.

(iii) There is strong coupling between dipoles induced by the local electric field and by ionic overlap.

(iv) The parameters are intimately coupled together and may individually have unphysical values.

(b) Deformation dipole model.

(i) Point dipoles are used.

(ii) Repulsive interactions take place between ion cores.

(iii) There is no coupling between dipoles induced by the local electric field and by ionic overlap.

(iv) The parameters are weakly coupled and have physically realistic values.

The two models may be considered to represent extremes of real behaviour. Dipoles, and higher order multipoles, will be situated somewhere between the ion core and its shell; repulsive interactions will also occur between these two points. One might consider that in fact the field induced dipole should be placed at the ion core, with the overlap induced dipole being placed at the shell. There will be some degree of coupling between the different contributions to the dipoles. In this particular case the deformation dipole model has been shown to be applicable, though in general we will require a model that combines the features of both. However the deformation dipole model has certain advantages as a starting point for further development. It is faster and easier to code into a simulation (particularly when using the MD technique of Saboungi et al. [13]) and the independence of the parameters means that these can be altered individually and empirically if necessary, while still retaining an idea of the underlying physical mechanisms.

An attempt to simulate the structure of molten LiCl (in which effectively only the Cl^- ion is polarisable) using a potential derived in the same manner was unsuccesful. This could specifically be traced to the fact that the repulsive potential between unlike ions was too soft; including dipole terms resulted in an effective minimum in the two body potential at small separations, i.e. the formation of LiCl molecules. Because of

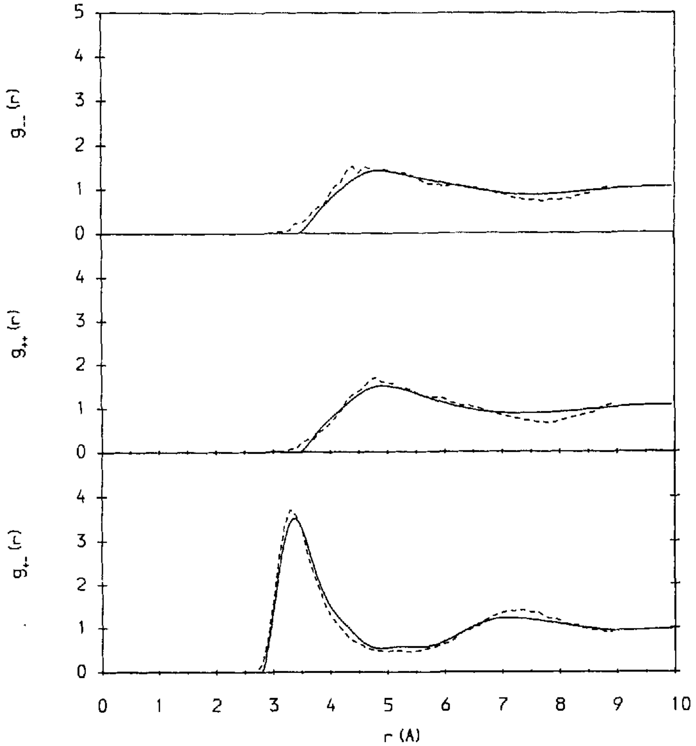

Figure 3 Partial radial distribution functions for molten CsCl; comparison of experiment [6] (solid curve) and deformation dipole polarisable ion simulation (broken curve).

the independence of the parameters an empirical increase of the repulsion is possible to overcome this problem, but this then results in a potential that does not correctly fit the crystal properties, and was therefore felt to be unjustified. It may be noted that the rigid ion potential of Narayanan et al.[2] does not produce satisfactory agreement with experiment for LiCl,[3] due to the softness of the repulsion. The shell model has not yet been succesfully applied to molten LiCl either. It is possible that potentials derived from crystal data are inappropriate in this case, since the local coordination in the melt is tetrahedral, whereas in the crystal it is octahedral. The deformation dipole model has not yet been applied to any other systems.

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