NOVEL SIMULATIONS OF MOLTEN SALTS

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ABSTRACT

It has long been assumed that the long range charge ordering in ionic liquids is a direct consequence of the strength and long range of the coulomb interactions. In this paper we demonstrate, using molecular dynamics computer simulation, that short range effective pair (SHREP) potentials can be used to reproduce the structural and transport properties of many molten salts. The thermodynamic properties of the ionic liquids can be obtained rather simply using first order perturbation theory. SHREP potential simulations of molten KCl, SrCl₂ and NaAlCl₄ generate structures and properties which compare favourably with the results of previous simulations and with experiment.

INTRODUCTION

The main aim of this paper is to demonstrate that the essential structural and dynamic features of molten salts are not a consequence of the long range coulomb interactions. Charge ordering, which was originally discovered by computer simulation studies [1] and which has now been observed in neutron diffraction measurements [2,3,4] as the familiar signature of ionic liquids, is reproduced to good accuracy using short range effective pair (SHREP) potentials with a range of about three ionic diameters. This work extends previous studies of molten potassium chloride [5] to SHREP potential simulations of molten strontium chloride and molten sodium tetrachloroaluminate. Each of these systems has been examined recently using diffraction techniques and also by computer simulation.
The development of an understanding of molten salts at the microscopic level depends on an important mixture of theory and experiment. While detailed experimental data on molten salt structure is now becoming available from neutron and X-ray scattering measurements, development of analytical theories is frustrated by the need to make simplifying and sometimes incorrect assumptions regarding the statistical mechanical behaviour of the system. Success has been limited to calculations on alkali halides using the hypernetted chain (HNC) [6] and mean spherical approximations (MSA) [7].

Computer simulation techniques, both Monte Carlo and molecular dynamics (MD), occupy an important position between theory and experiment. They can provide a complete numerical solution to the classical many body problem while avoiding many unnecessary assumptions. On the one hand they can be employed to evaluate theoretical predictions using simplified but well defined models for the particle interactions. On the other hand the aim can be to reproduce accurately the properties of a particular molten salt and to enhance the interpretation of experimental data. We are thus lead to the real current theoretical challenge - that of providing an accurate description of particle interactions in a molten salt.

Substantial effort has been expended in the last 10 or 15 years in developing semi-empirical interaction potentials for molten salt simulations. To date all have been firmly based on the Born model in which the dominant interaction is the \(r^{-1}\) coulomb term. With few exceptions all these potentials require the use of lattice summation methods, in conjunction with the usual periodic boundary conditions, to overcome the divergence problem of the \(r^{-1}\) term. These methods are computationally expensive and impose severe practical limitations on the size of system. There is a variety of experimental evidence, however, which suggests that at long range there is almost complete cancellation of coulomb effects in molten salts. For instance it is possible completely to neglect the reciprocal space sums, which account for long range effects in the Ewald representations of the coulomb potential, without damaging the essential physics of the liquid [8]. These cancellation effects were also found in a recent approximate theoretical treatment of the hard sphere electrolyte [9]. In simulations of molten alkali halides it is found [10] that the force correlations describing the ion dynamics are dominated by contributions from the immediate neighbours. Indeed it was postulated many years ago that coulomb forces have little influence on dynamic properties in molten salts [11].

Aside from this practical evidence there are also theoretical objections to a rigid adherence to the Born model. The total potential energy \(\Phi_T\) of a system of \(N\) interacting particles can be written as follows:
\[ \Phi_T(N) = \Phi(2) + \Phi(3) + \Phi(4) + \ldots \Phi(N) \quad (1) \]

where \( \Phi(m) \) is the isolated \( m \)-body contribution to the total energy. To date it has been usual practise, in both computer simulations and theoretical studies, to assume that 3- and higher-body interactions are sufficiently weak so that their effects can either be neglected or incorporated in an effective pairwise additive interaction \( \Phi_{\text{eff}}(2) \) so that

\[ \Phi_T = \Phi_{\text{eff}}(2) \quad (2) \]

While this may be a reasonable assumption for many non-ionic liquids, it would be surprising if the intense particle interactions in a molten salt did not give rise to significant non-pairwise additive effects, especially at short range. The most obvious of these is the first order induction energy due to ion polarisation. Although attempts have been made to take account of this effect by use of the shell model \[12\] the majority of simulations to date have made use of semi-empirical rigid ion effective pair potentials with parameters fitted using either low temperature crystal data \[13\] or gas-phase spectroscopic data \[14\]. If one compares results for simple ionic molten salts such as the alkali halides obtained using these different potentials, the structural differences turn out to be quite small and often within the limits of accuracy of the experimental data available for comparison. It can be regarded as fortuitous, however, that these models should be adequate as effective pair potentials in molten salts.

Simulations employing SHREP potentials are computationally highly efficient, enabling studies of systems containing more than 10000 particles such as are desirable for the simulation of mixtures or interfacial phenomena. Like the parent Born model these potentials are as yet still semi-empirical in basis. Their relative simplicity emphasises, however, the minimum requirements for the successful simulation of ionic liquids. Essential parameters are the unlike particle separations, \( r_0 \), at the respective potential energy minima, the curvatures of the potentials in the region of \( r_0 \) and the depths \( \epsilon \) of the minima. All of these parameters can be obtained from gas phase spectroscopic data. This approach, coupled with more extensive experimental data, may provide a route to the empirical evaluation of specific short range many body interactions.

**SHREP POTENTIALS**

The idea underlying the use of Short Range Effective Pair potentials is that it is only necessary to consider interactions between immediate like and unlike neighbours, beyond which the potentials are smoothly and symmetrically truncated to zero. An important property of ionic interactions that must be retained in the
model is the balance, at medium range, of attractions and repulsions between like and unlike particles respectively. Aside from this the only essential features are the distance parameters r_0 which in the case of unlike particles are the separations at the potential energy minima, and the curvatures of the potentials in the region of near neighbour separations. One particularly simple form of SHREP potential that we have used \[5\] is

\[
E(r) = \varepsilon(k,l) \left[ A \left( \frac{r_0(k,l)}{r} \right)^n + B \left( \frac{r_0(k,l)}{r} \right)^m \right] \quad \ldots(3)
\]

where \(A = m/(n-m), B = n/(m-n). \ \varepsilon(k,l)\) and \(r_0(k,l)\) are energy and distance parameters characterising the interaction between particles of species \(k\) and \(l\). The switching parameter \(\chi\) is set equal to \(-1\) for particles of like charge and \(\chi = +1\) for particles of unlike charge. It is convenient to add a term \((ar+b)\) to equation (3), where \(a\) and \(b\) are constants, in order to provide smooth truncation of the potential at, typically, \(3r_0\). This modification has been shown to cause only minor distortions in the form of the potential \[5\].

The balance of like and unlike particle interactions appears partly (and automatically) in the stoichiometry of the sample but is also determined by the relative values of \(\varepsilon\) for the different pair types. It is well recognised that the depth of ion pair potential energy minima are orders of magnitude greater than \(kT\). Consequently the absolute values of \(\varepsilon\) are not critical to the simulation as long as the condition is upheld that \(\varepsilon \gg kT\). A much more important property is the force constant at \(r_0\) (or, for like particles, the curvature of the interaction potential in the region of near neighbours) which for the simple SHREP potential are proportional to \(\varepsilon\). These features determine the magnitude of structural fluctuations which are reflected in the sharpness of peaks in \(g(r)\) and the values of dynamic properties such as the diffusion coefficient.

The form of potential in equation (3) was used recently in simulations of molten potassium chloride \[5\] with \(n=8\) and \(m=4\). It is compared with the corresponding BHM potential in Fig.1. The value of \(r_0\) is the same in both cases and the force constants are also very similar although the depths of the energy minima are quite different. It is important to note that the ratios of the unlike and like particle interaction energies are very similar for all distances corresponding to the most probable nearest neighbour separations (see Fig.1).

An alternative approach is to start with the full ionic potential of the Born-Huggins-Mayer form (with or without dispersion energy terms):

\[
V(r) = \frac{q_i q_j}{4\pi \varepsilon_0 r} + b \exp \left[ \sigma_i + \sigma_j - r_{ij} \right] \quad \ldots(4)
\]
and to truncate the long range interactions by multiplying with a function \( P(r) \) (a third order polynomial), so that

\[
\begin{align*}
E(r) &= V(r) ; \quad r < r_1 \\
E(r) &= V(r) P(r) ; \quad r_1 < r < r_c \\
E(r) &= 0 ; \quad r > r_c
\end{align*}
\] ....(5)

and \( P(r) \) is chosen to be 1 at \( r_t \), 0 at \( r_c \) and \( dP/dr = 0 \) at both \( r_t \) and \( r_c \). The simplest procedure is to identify \( r_t \) with \( r_0 \).

For the simulations reported here we have used only the SHREP potential formulation given in equation (3).

**DETAILS OF COMPUTER SIMULATIONS**

Molecular dynamics simulations using the SHREP potentials have been carried out at constant volume on equilibrated samples of 500, 750 or 4000 particles using link cell coding to increase the efficiency of the computations. Equations of motion were integrated using the leapfrog forms of the Verlet algorithm for either constant energy or constant temperature (damped force) dynamics. The time step was \( 0.5 \times 10^{-14} \) s. Details of the procedure with the simulations has been described elsewhere [5].

The full ionic calculations with the BHM potential were carried out using the program MIONS from the SHREC CCP5 program library. For 512 ions each time step consumed 2.65 s of CPU time on a CDC 7600 computer, compared to 0.8 s for 500 particles and 4.6 s for 4000 particles using the n=m SHREP potentials.

**RESULTS AND DISCUSSION**

1. **Molten Alkali Halides**

SHREP potential simulations of molten alkali halides are exemplified by the case of potassium chloride. The results at 1300 K preented here are compared with those generated using Born-Huggins-Mayer (BHM) potential with Tosi-Fumi parameters [1]. For the short range part of this potential the values of these parameters are very similar for \( K^+ - Cl^- \), \( K^+ - K^+ \) and \( Cl^- - Cl^- \) interactions. To gain simplicity, therefore, the same values of \( r_0 \) and \( \epsilon \) were used for each of the three types of interaction in the SHREP potential. The value of \( r_0 \) was 0.2589 nm which is the unlike ion separation at the minimum of the BHM potential. It has already been shown [5] that the main structural features are not very sensitive to \( \epsilon \). Its value (0.2 of the depth of the BHM minimum) was chosen so that the force constant (curvature at \( r_0 \)) was approximately the same as that obtained from spectroscopic data on the gas phase K-Cl ion pair (this
is also very close to the value for the BHM potential. The potentials were truncated at 3\(r_0\).

The partial radial distribution functions generated by the SHREP and BHM potentials are compared in Fig. 2 and the indiscriminate (particle-particle) functions are shown in Fig. 3. The SHREP potentials are seen to generate 'charge' oscillations remarkably similar to those of the true ionic liquid but nevertheless produce the same strong damping of particle-particle correlations beyond the second nearest neighbour shell. It should be noted that the 'charge' oscillations occur out to much larger distances than the range of the potential showing that they are clearly a long range manifestation of short range interactions. Observation of these oscillations out to distances of the order 10\(r_0\) emphasises the advantage of being able to use large samples in the computer simulation. The potential of mean force, \(E_m(r)\), on an ion in the BHM liquid can be calculated from the particle-particle distribution function in Fig. 3, since

\[
E_m(r) = -kT \ln g(r) \quad \ldots \ldots (5)
\]

It is clear that \(E_m(r)\) decays to zero within three particle diameters, emphasising the dominance of short range interactions.

Charge charge structure factors \(S_{QQ}(k)\) were also computed from direct Fourier transforms of the radial distributions. In this representation

\[
S_{QQ}(k) = \frac{1}{2} \{S_{++}(k) + S_{--}(k) - 2S_{+-}(k)\} \quad \ldots \ldots (7)
\]

Fig. 4 demonstrates the clear similarity between \(S_{QQ}(k)\) for the SHREP potential liquid and for the BHM liquid. The sharp main peak (often referred to as the 'coulomb' peak) and strong oscillations are the well established signatures of 'charge ordering' [9]. In a coulomb system overall charge neutrality demands [15] that \(S_{QQ}(k) \propto k^2\) as \(k \to 0\). As a result of the limited sample size the small \(k\) region is not accessible in our simulations. The results for the SHREP potential liquid show that the trend in \(S_{QQ}(k)\) is, however, not inconsistent with the above requirement.

It has been shown previously that the thermodynamic properties of the ionic liquid can be calculated from the structure generated by the SHREP potential using first order perturbation theory [5]. In Table I we compare the predicted values of \(U_{ionic}\) and \(P_{ionic}\) with experimentally measured values and with those obtained for an ionic simulation using the BHM potential. The agreement is extremely good since it is unlikely that the experimentally measured value of the internal energy \(U\) is known to better than a few per cent.

Values of the particle self diffusion coefficients computed from plots of the mean squared displacements against time are included in
Table I: Thermodynamic properties and mean ion diffusion coefficients for liquid potassium chloride at 1300 K and 54 cm³ mol⁻¹. For the SHREP potential simulation U and p were calculated using first order perturbation theory [5].

Table I. The statistical error in the computed values of D and also accuracy of the experimental values is only about ± 10%. Within margin there is excellent agreement between diffusion coefficients computed for the SHREP potential, the ionic simulation and experiment.

Simulations of other alkali chlorides have been made using SHREP potentials of the form in equation (3). The changes in structural features, as compared to KC1, are much the same as has been obtained from previous studies utilising BHM potentials and show good agreement with experimental data on the respective systems. The position of the first peak in the Cl–Cl distribution, for instance, moves very slightly to larger r values as the cation size increases. In molten lithium chloride, as expected [1], the unlike nearest neighbour peak in the radial distribution function sharpens and moves to shorter distances.

So far we have discussed simulations of the bulk properties of molten alkali chlorides. An additional and remarkable demonstration of the successful use of SHREP potentials is found in the simulation of interfacial properties of molten potassium chloride. We have previously reported studies of thin films of the ionic liquid confined between rigid planar walls, in a first attempt to simulate the electrode–molten salt interface [16]. Several interesting
predictions emerged from these studies. The rigid boundary induces a partially layered structure of the liquid which rapidly decays into the bulk of the liquid and which is very similar in form to that for simple atomic liquids such as argon. This result was compared with that obtained after applying an electric field of $3.6 \times 10^7$ V cm$^{-1}$ across the film. This is the same magnitude of field strength thought to exist near a metal electrode in a molten salt. Interestingly there was no change in the overall particle density profile although clearly the distribution of anions and cations in the interfacial layers changed in response to the perturbation. This is illustrated in the density profiles shown in Fig. 5. The asymmetric distribution of ions is perhaps more clearly revealed in the oscillation of the excess charge, the form of which broadly confirms theoretical predictions [17]. The problem was that we could not be sure that the charge oscillations at the two ‘electrodes’ were not mutually disturbed by long range coulomb interactions across these very thin films. Recent simulations using a SHREP potential [10] show clearly that this is not the case and that the phenomena observed are likely to be reproduced for films of macroscopic thickness.

In Fig. 5 we also show the excess ‘charge’ profile generated for a thin film of liquid in which the particles were made to interact with each other according to the SHREP potential in equation (3) with a truncation range of $3r_0$. They were made to respond to the applied electric field, however, as if they were $K^+$ and $Cl^-$ ions. Clearly there are no possible direct long range interactions in this system yet the excess charge profile is almost identical to that obtained for the ionic liquid. These striking interfacial phenomena are not, therefore, spurious effects due to the small thickness of the films and are indeed explainable in terms of minor perturbations (induced by the electric field) on short range packing effects in the molten salt.

2. Molten Strontium Chloride

This liquid was chosen in order to evaluate the use of a SHREP potential for simulating molten salts where the cations and anions have different charge numbers. The experimental structural characteristics of molten strontium chloride [18] have previously been explained in terms of the simple ionic model [3,4] and successful simulations using a Busing potential (very similar to BHM) have been reported [19].

We used the equation (3) form of SHREP potential. Values of $\varepsilon$ and $r_0$ were taken from gas phase spectroscopic data on the diatom SrCl, so that

$$\varepsilon(1,2) = 6.74 \times 10^{-19} \text{ J}$$

$$r_0(1,2) = 0.267 \text{ nm}$$
To ensure balance of attractions and repulsions at medium range 
\(\varepsilon(1,1) = 2.0 \times \varepsilon(1,2), \varepsilon(2,2) = 0.5 \times \varepsilon(1,1)\). The value of \(r_0\) for the 
like particle interactions is not critical and we have chosen 
\(r_0(1,1) = r_0(2,2) = r_0(1,2)\).

The simulations were performed for a temperature of 1150 K and a 
constant volume of \(61.95 \text{ cm}^3 \text{ mol}^{-1}\). This volume is the same as that 
used in the ionic potential simulations [19] and is about 5% larger 
than the experimental volume at the same temperature. The partial 
radial distribution functions generated by the SHREP potentials are 
shown in Fig.6. The same general pattern is observed as for molten 
potassium chloride although the distribution functions for the Sr and 
Cl are now quite different. Charge oscillations again clearly persist 
out to quite long range. Points on this figure show the peak 
positions obtained in the ionic potential simulations and the 
agreement is excellent. The structure generated by the SHREP 
potential shows all the detail observed experimentally for this 
liquid such as the strong penetration of the first coordination shell 
by like particles. To emphasise how accurately the SHREP potential 
reproduces the structure of strontium chloride, in Table II we 
compare the ionic internal energy (calculated using perturbation 
theory) with the values from the previous simulation and from 
experiment. The agreement is extremely good. Calculated diffusion 
coefficients are also shown for the various models. Values for the 
SHREP potential liquid actually agree rather better with experiment 
than do those from the ionic simulation, although this may be 
fortuitous.

| property       | SHREP potential | a BHM potential | a experiment |
|----------------|-----------------|-----------------|--------------|
| \(U_{\text{Ionic}}\) kJ mol\(^{-1}\) | -2025           | -2036           | -2029        |
| \(D_+\)        | 2.9±0.3         | 0.68            | 2.2          |
| \(D_-\)        | 6.3±0.5         | 1.71            | 4.3          |

\(a \text{ data from ref. 19}\)

Table II : Internal energies and diffusion 
coefficients (in \(10^{-9} \text{ m}^2 \text{ s}^{-1}\)) for liquid 
strontium chloride at 1150 K and \(61.95 \text{ cm}^3 \text{ mol}^{-1}\). 
For the SHREP potential simulation \(U_{\text{Ionic}}\) was 
calculated using first order perturbation theory [5].
Crystalline strontium chloride is an ionic superconductor due to a high mobility of the chloride ions in the lattice. Certainly chloride is far more mobile in the liquid. It has been suggested [20] that this property can be related to the strong damping of $g_{c}c_{1}c_{1}$ as compared to $g_{Sr}Sr$. (The damping of the former function is particularly noticeable because it shows such distinct short range structure). Our data (which extend out to nearly 6r_0) show that this is really a rather small differential effect.

The structural properties of molten strontium chloride are explainable in terms of straightforward ionic interactions. There are several other molten divalent metal chlorides, such as magnesium and zinc chloride, where this is not the case [4]. For instance the results of neutron diffraction experiments show that the most probable separations of positive ion and negative ion near neighbours are very similar, which would certainly not be expected from a simple ionic model (see Fig.6). If these effects are to be explained then it will be necessary to introduce additional short range (perhaps many-body) contributions to the interaction potential.

3. Molten sodium tetrachloraluminate

Finally we briefly discuss some preliminary simulations of liquid sodium tetrachloraluminate, NaAlCl$_4$, using a SHREP potential. This material has been examined recently using both X-ray [21] and neutron [22] diffraction techniques. These studies confirm the conclusions of previous spectroscopic observations - namely that there is little dissociation of the tetrahedral AlCl$_4^-$ unit in the liquid. Simulations have also been reported [23] based on an ionic model of interactions between Al$^{3+}$, Cl$^-$ and Na$^+$. Since little is known about the short range interactions between these ions, model BHM potentials were employed in order to explore the sensitivity of the melt structure to various parameters. The most important parameter turned out to be the 'size' assigned to the chloride ion. To illustrate just how sensitive the structure was to the value chosen we plot in Fig.7 the ratios of the interaction energies for various particle pairs relative to the Al-Cl energy at the same separation. Marked on this figure are the positions of the nearest neighbour peaks in g(r). The shaded area shows the small difference in the ratio of interactions required to cause a changeover in the melt structure from octahedral to tetrahedral coordination. At a separation corresponding to the first peak in $g_{c}c_{1}c_{1}$ this difference is hardly observable on the plot, although the difference in absolute energies is several times kT! Of course it is always possible a posteriori to choose parameters to give the correct structure. The much greater challenge to theory is the correct prediction of these small details of the interaction potential.
The above discussion shows that the structure adopted by this molten salt mixture is strongly dependent on a very delicate balance between on the one hand Al-Cl (and Na-Cl) unlike particle interactions and on the other hand the Cl-Cl repulsions. Consequently, realistic simulations of this liquid presents a stringent test for SHREP potentials, indeed for any set of potentials.

We have recently performed a SHREP potential simulation using the equation (3) form with $n = 8$, $m = 1$ but with a truncation range of only $3r_0(2,3)$, where we number the species in order Na,Al,Cl. The values used for the most important parameters were:

\[
\begin{align*}
\varepsilon(2,3) &= 16.0 \times 10^{-19} \text{ J} \\
r_0(2,3) &= 0.182 \text{ nm}
\end{align*}
\]

where the former value is about half the depth of the BHM potential but was chosen so that the force constants were the same. To maintain a close comparison with the ionic simulation the value of $r_0(2,3)$ was identical to that of the BHM potential [23]. Values for all the other parameters were chosen so as to maintain the same ratios as shown in Fig.7 for the potential c discussed by Saboungi Rahman and Blander. It must be stressed that the results are preliminary but they are nevertheless very encouraging. The coordination number for chloride around aluminium was, within the error limits, four and very well defined. Table III shows the positions and heights of the three main peaks in the partial radial distribution functions. There is generally good agreement with the data for the ionic potential.

| pair   | ht. pos./nm | this work | Saboungi et al ref 23 | experiment ref 22 |
|--------|-------------|-----------|-----------------------|-------------------|
| Cl-Cl  | h           | 3.2       | 3.5                   | 3.0               |
|        | r           | 0.35      | 0.34                  | 0.35              |
| Al-Cl  | h           | 13        | 16.5                  | 9.3               |
|        | r           | 0.21      | 0.21                  | 0.21              |
| Na-Cl  | h           | 4.2       | 3.8                   |                   |
|        | r           | 0.26      | 0.27                  |                   |

Table III: Nearest neighbour peak heights (h) and positions (r in nm) in the partial radial distribution functions obtained from a SHREP potential simulation of molten NaAlCl$_4$ at 500 K.
CONCLUSIONS

Evidence has been presented that the structure and many properties of molten salts are not determined by long range coulomb interactions. It has been shown that simulations of molten salts using SHEEP potentials preserve the same essential physics of the liquid as in the case of Born potentials. SHEEP potentials are a highly practical alternative for simulation studies. They permit more economic use of computer time and broaden the range of systems that can be examined. One problem in accurately modelling all but the simplest of molten salts, however, is our limited knowledge of the details of short range (repulsive) interactions, especially between unlike ions. This limitation applies both to SHEEP potentials and to those based on the Born model. There is a clear need for more fundamental work in this area.

REFERENCES

1. L.V.Woodcock and K.Singer, J.Chem.Soc.Farad. Trans. II, 67, 12 (1971).
2. L.V.Woodcock, Chem.Phys.Lett., 10, 257 (1971).
3. E.W.J.Mitchell, P.F.J.Poncet and R.J.Stewart, Phil.Mag., 34, 721 (1976).
4. S.Biggin and J.E.Enderby, Adv. Molten Salt Chem., Vol 5 (Ed. G.Mamantov, Elsevier, Amsterdam 1983)
5. J.E.Enderby, Contemp. Phys., 24, 561 (1983).
6. J.H.R.Clarke, W.Smith and L.V.Woodcock, J.Chem.Phys. (in press)
7. J.C.Hansen and I.R.McDonald, Phys.Rev., All, 2111 (1975).
8. M.Gillan, B.Larsen, M.P.Tosi and N.H.March, J.Phys. C, 9, 889 (1976).
9. L.V.Woodcock, Adv. Molten Salt Chem., Vol 3 (Ed. J.Braunstein, G.Mamantov and G.P.Smith, Plenum, NY 1975)
10. A.P.Copestake and R.Evans, J.Phys.C, 15, 4961 (1982)
11. J.H.R.Clarke, unpublished data, 1985
12. S.A.Rice, Trans.Farad.Soc., 58, 499 (1962).
13. M.J.L.Sangster and M.Dixon, Adv. Physics, 25, 247 (1976).
14. M.P.Tosi and F.G.Fumi, J.Phys.Chem.Sol., 25, 31 (1964).
15. L.V.Woodcock, J.Chem.Soc.Farad.Trans. 2, 70, 1405 (1974).
16. F.H.Stillinger and R.Lovett, J. Chem. Phys., 48, 3858 (1968)
17. D.M.Beyes and J.H.R.Clarke, J.Chem.Soc.Farad.Trans. 2, 77, 1089 (1981).
18. A.D.Graves and D.Inman, Electroanal.Chem.Interfac.Electrochem., 25, 349 (1970).
19. R.L.McGreevy and E.W.J.Mitchell, J.Phys. C, 15, 5537 (1982).
20. S.W.de Leeuw, Mol.Phys., 36, 103,765 (1978).
21. J.E.Enderby and G.W.Neilson, Adv. Physics, 29, 323 (1980).
22. S.Biggin, S.Cummings and J.E.Enderby, private communication.
23. M.L.Saboungi, A.Rahman and M.Blander, J.Chem.Phys., 80, 2141 (1984).
Fig. 1: SHREP and BHM interaction potentials for liquid KCl. u - unlike, L - like particles

Fig. 2: Partial radial distribution functions for model KCl at 1300 K.

Fig. 3: Particle-particle distribution functions for the BHM and SHREP potential liquids at 1300 K.

Fig. 4: Charge-charge structure factors for the two models of molten KCl at 1300 K.
Fig. 5: Density and Charge distributions across a thin film of molten KCl at 1050 K constrained by rigid boundaries and a uniform electric field.

Fig. 6: Partial radial distribution functions for strontium chloride. Circles show peak positions for an ionic simulation [19].

Fig. 7: BHM potentials [23] for NaAlCl₄. Shown is the ratio of interaction energies and the position of the Cl-Cl nearest neighbour peak. The shaded area shows the difference in interactions giving rise to octahedral and tetrahedral coordination of Cl around Al.