

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Monte-Carlo Simulations of the Structure of Molten CsCl Using Screened Coulomb Potentials

P. R. Gartrell-mills^a; R. L. McGreevy^a

^a Clarendon Laboratory, Oxford, UK

To cite this Article Gartrell-mills, P. R. and McGreevy, R. L. (1987) 'Monte-Carlo Simulations of the Structure of Molten CsCl Using Screened Coulomb Potentials', *Physics and Chemistry of Liquids*, 17: 3, 201 – 207

To link to this Article: DOI: 10.1080/00319108708078557

URL: <http://dx.doi.org/10.1080/00319108708078557>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Monte-Carlo Simulations of the Structure of Molten CsCl Using Screened Coulomb Potentials

P. R. GARTRELL-MILLS and R. L. MCGREEVY

Clarendon Laboratory, Parks Road, Oxford, UK

(Received 18 May 1987)

Monte-Carlo simulations of the structure of molten CsCl have been performed using a screened Coulomb potential. The partial radial distribution functions are found to be largely insensitive to even a high degree of screening, though the small variations are consistent with the proposal that screening may account for some of the differences between experiment and simulation. Some evidence is found that the method of treatment of long range image charge interactions, e.g. Ewald sum or cut-off sphere, and the shape of the simulation cell may be equally important.

KEY WORDS: Monte-Carlo simulations, molten CsCl, screened Coulomb potential.

Computer simulations of the structures of molten alkali halides have succeeded in reproducing the main structural features observed experimentally.¹ There remain, however, small differences between simulation and experimental results, most notably in the case of CsCl.²

- i) All peaks in the radial distribution functions $g_{ij}(r)$ are too high.
- ii) The second peak in g_{+-} is too high relative to the first and at too large an r value.
- iii) The first peak in g_{++} and g_{--} has a distinct shoulder on the high r side.

It was suggested that these differences may be due to charge screening by ionic polarisation but simulations which include ionic polarisability through the shell model³ produce only small structural changes and are, if anything, in worse agreement with experiment. (Larger changes are produced in dynamical behaviour by the use of polarisable ion potentials.⁴)

Copestake and Evans⁵ have examined the difference (for hard spheres) between a short range screened Coulomb (Yukawa) potential and the full long range interaction, and have shown that long range interactions are not necessary in order to obtain a strongly charge ordered system. One of the effects of the screening is to lower and shift the second peak in g_{+-} , an effect similar to difference (ii) noted above. Clarke *et al.*⁶ showed that it is possible to obtain charge ordering using an empirical short range potential, but the structures that they obtained are not in good quantitative agreement with experiment.

Baranyai *et al.*⁷ have performed simulations in which the long range Coulomb interactions are treated in a reaction field corrected cut-off sphere approximation, producing slightly closer agreement with experiment than the simulations of Dixon and Gillan³ which used the more common Ewald summation method. The essential difference between these methods is that the former uses a cut-off in real space, i.e. screening charges at long distances (which are image charges of the central simulation box), while the latter uses a cut-off in reciprocal space, i.e. no screening (image charges are treated out to infinity).

In the simulations of Baranyai *et al.*⁷ the cut-off was chosen to be the smallest possible that did not alter the simulated structure. Noting that there are still disagreements between experiment and simulation we have speculated that a smaller effective cut-off, i.e. greater screening, may be required. However the imposition of a sharp cut-off at short distances introduces a discontinuity into the Coulomb potential that may produce discontinuities in the structure. Yukawa (exponential) screening introduces a similar discontinuity into the potential gradient unless screening is applied from $r = 0$. We have therefore empirically modified the Coulomb potential to be of the form

$$V_{ij}^C(r) = Z_i Z_j' e^2 / r$$

where

$$\begin{aligned} Z_j' &= Z_j & r < r_1 \\ &= Z_j \sin(\pi(r - r_1)) / (\pi(r_2 - r_1)) & r_1 < r < r_2 \\ &= 0 & r_2 < r \end{aligned}$$

There are no discontinuities in this function or its derivatives and in the limit $r_1 = r_2$ it reproduces the sharp cut-off sphere approximation. To account for uncompensated charges within the cut-off sphere the energy of each particle is corrected by an amount

$$\Delta u_i = -Z_i \frac{e^2}{r_2} \frac{\kappa r_2}{1 + \kappa r_2} \sum_j Z_j'$$

where κ is the Debye screening parameter. This essentially assumes that the "missing" charge is uniformly distributed.

We have performed Monte-Carlo simulations of the structure of molten CsCl that were in all other respects identical to those of Baranyai *et al.*⁷ ($T = 973$ K; 112 particles in a cubic box, side $L = 17.895$ Å, with periodic boundary conditions.) Starting from a simulation at $r_1 = r_2 = L$ (hereafter referred to as I) we have reduced r_1 to zero. We have then set $r_1 = 0$ and reduced r_2 . The potential V_{+-} is shown in Figure 1 for various values of r_1 and r_2 with the partial radial distribution functions, relative to I, in Figure 2 for $r_2 = L$ and in Figure 3 for $r_1 = 0$.

The most general conclusion that may be drawn is that, except in the most extreme case of change in the potential ($r_1 = 0$, $r_2 = 4.895$ Å) there are only small changes in the structure. This clearly demonstrates the insensitivity of the main structural features to the details of the potential. It cannot therefore be assumed that a potential will give a satisfactory description of the dynamics of a system, which are more sensitive to changes in potential, even if the experimental structure is adequately reproduced.

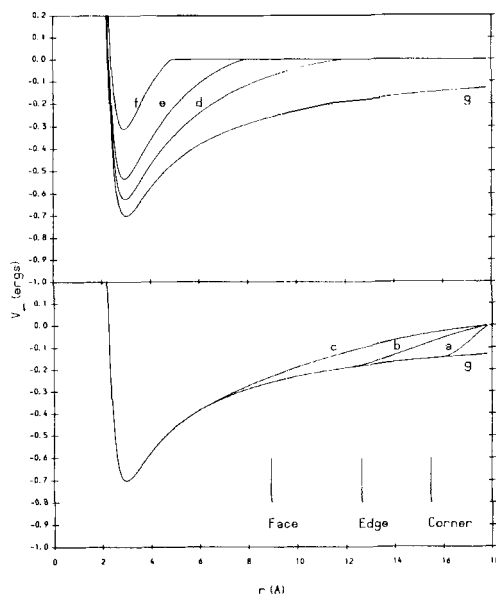


Figure 1 Pair potentials for unlike ions for simulations at $r_2 = 17.895$ Å with $r_1 =$ (a) 15.895 Å, (b) 11.895 Å, and (c) 5.895 Å, at $r_1 = 0$ with $r_2 =$ (d) 11.895 Å, (e) 7.895 Å and (f) 4.895 Å and (g) with $r_1 = r_2 = 17.895$ Å. The face, edge and corner positions of the simulation box are also shown.

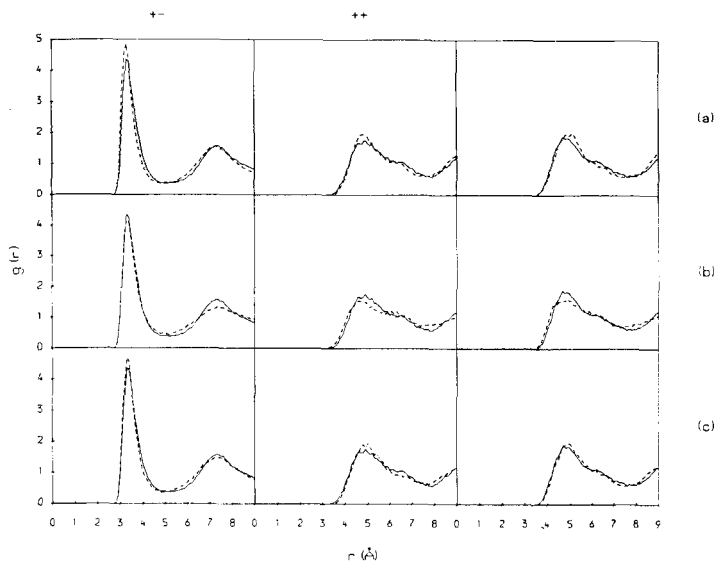


Figure 2 Partial radial distribution functions for $r_2 - r_1 =$ (a) 2 Å, (b) 6 Å, and (c) 12 Å with $r_2 = 17.895$ Å, (broken curves) compared with the results for $r_1 = r_2 = 17.895$ Å (solid curves)⁷.

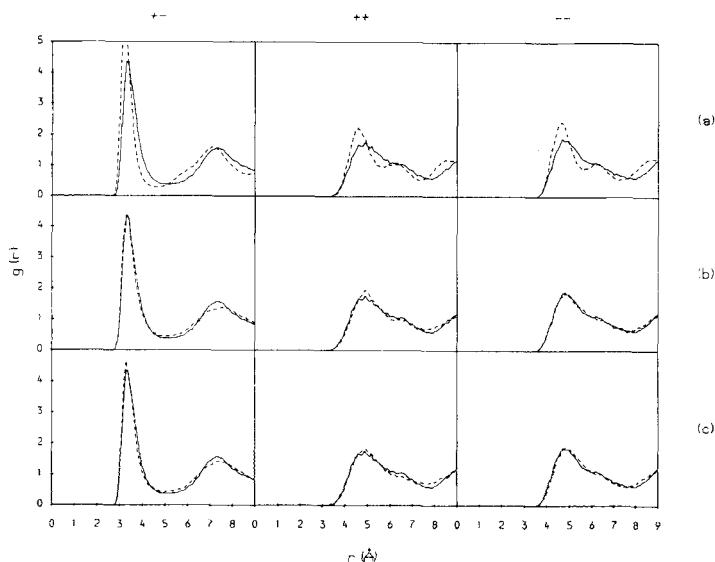


Figure 3 Partial radial distribution functions for $r_2 - r_1 =$ (a) 4.895 Å, (b) 7.895 Å, and (c) 11.895 Å with $r_1 = 0$, (broken curves) compared with the results for $r_1 = r_2 = 17.895$ Å (solid curves)⁷.

The set of simulations with $r_1 = 0$ is not meant to be physically realistic since even nearest neighbour charges are screened to some extent, and there is no experimental evidence to support partial ionic charges in alkali halides. It was performed purely to illustrate the high stability of the structure, exemplified by the fact that the resulting radial distribution functions are almost identical to those in I except for the lowest value of r_2 . In this case all peaks become sharper and the shoulder on the high r side of the first peak in g_{++} and g_{--} is resolved as a separate peak. This is consistent with the results of Clarke *et al.*⁶ who also find greater ordering as the depth of the potential minimum is decreased (see Figure 1). For the set with $r_2 = L$ the simulation with $r_2 - r_1 = 2 \text{ \AA}$ shows a small increase in all peak heights in $g_{ij}(r)$; the other simulations in the set show a consistent decrease in the height of the second peak in g_{+-} . The simulation with $r_2 - r_1 = 6 \text{ \AA}$ shows significant decrease in the heights of the first peak in g_{++} and g_{--} and improves the general level of agreement with experiment. As $r_2 - r_1$ is increased further the radial distribution functions revert back to those found for $r_2 = r_1 = L$.

The internal energies are shown in Figure 4 relative to the energy calculated for I (-615 kJ/mol). There is only a small change in energy as r_1 decreases but a larger change as r_2 decreases. This is to be expected since the major contribution comes from near neighbour interactions,

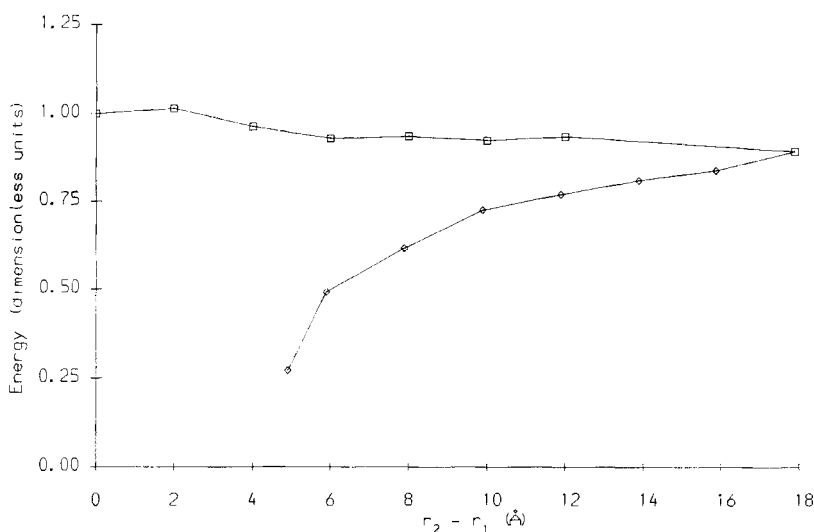


Figure 4 Internal energies of the simulations as a function of $r_2 - r_1$, for $r_2 = 17.895 \text{ \AA}$ (□) and $r_1 = 0$ (◇), relative to the simulation at $r_2 = r_1 = 17.895 \text{ \AA}$.

i.e. around the potential minimum, which only change in the latter case (see Figure 1). It should be noted that up to a 50% change in simulation energy can be accompanied by almost no change in structure. Whether the structures are "liquid" or not can only be tested by comparable molecular dynamics simulations.

The features of the radial distribution function which vary most as a function of screening are (i) the heights of all peaks in g_{ij} (ii) the position of the second peak in g_{+-} and (iii) the definition of a shoulder on the high r side of the first peak in g_{++} and g_{--} . These are the same differences observed between experiment and simulations, which supports the suggestion that screening is important. Closest agreement with experiment is achieved for $r_2 = L$ and $r_2 - r_1 = 6 \text{ \AA}$. However the level of agreement is not yet sufficiently good to suppose that the form of screening used here is correct. Since anions are more polarisable than cations it may be necessary to screen them differently.

It is instructive to note that these simulations have been performed, in common with most liquid state simulations, using a cubic box with repeated images. For I all charges in the central box are considered together with some charges in the 26 surrounding image boxes. With $r_2 = L$ and $r_2 - r_1 > 2.4 \text{ \AA}$ the effect of charges in the corners of the central box begins to be reduced, and for $r_2 - r_1 > 9 \text{ \AA}$ the effect of charges at central box face centres is also reduced. (Corner, face and edge positions are indicated in Figure 1.) This may "soften" any cubic symmetry introduced into the liquid structure by the combination of long range interactions and the cubic symmetry of the simulation system. Since equally large structural changes are produced by a small amount of screening as by a large amount it is possible that some of the structural changes observed may be due to the method of treating the long range part of the Coulomb interaction in relation to images rather than specifically to the change in potential. The fact that simulations using the Ewald summation enhance the same features that are altered using our modified cut-off sphere approach also suggests that this may be part of the problem. Such effects can only be tested by simulations of systems containing an order of magnitude more particles, but this is prohibitively expensive in computer time.

The effects of polarisation and screening are more marked in the alkaline earth halides. There are large differences, notably in g_{++} , between simulation and experiment for these melts which are also not improved by the use of polarisable ion (shell model) potentials.⁸ Pastore *et al.*⁹ have shown that $g_{++}(r)$ for SrCl_2 may be predicted by considering the cations to be a plasma in a medium of uniform (chosen) dielectric constant. The uniform dielectric approach suggests consider-

able screening by the anions, even at short distances. Since this cannot be adequately represented by the shell model description of ionic polarisability it may be that the deformation dipole model¹⁰ is more appropriate. Any effects observed in simulations of molten alkali halides are likely to be more important in the alkaline earth halides because of the greater polarising power of the doubly charged cations. Further investigation of the treatment of long range Coulomb interactions is therefore required.

References

1. M. J. L. Sangster and M. Dixon, *Adv. Phys.*, **25**, 247, 1976.
2. J. Locke, R. L. McGreevy, S. Messoloras, E. W. J. Mitchell and R. J. Stewart, *Phil. Mag. B*, **51**, 301, 1985.
3. M. Dixon and M. J. Gillan, *Phil. Mag. B*, **43**, 1099, 1980.
4. M. Dixon, *Phil. Mag. B*, **47**, 509, 1983.
5. A. P. Copestake and R. Evans, *J. Phys. C*, **15**, 4961, 1982.
6. J. H. R. Clarke, W. Smith and L. V. Woodcock, *J. Chem. Phys.*, **84**, 2290, 1986.
7. A. Baranyai, I. Ruff and R. L. McGreevy, *J. Phys. C*, **19**, 453, 1986.
8. R. L. McGreevy and E. W. J. Mitchell, *J. Phys. C*, **15**, 5537, 1982.
9. G. Pastore, P. Ballone and M. P. Tosi, *J. Phys. C*, **19**, 487, 1986.
10. J. R. Hardy and A. M. Karo, *The Lattice Dynamics and Statics of Alkali Halide Crystals*, Plenum Press, 1979.