

The structure of molten ZnCl_2 : A new analysis of some old data

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Abstract. Using a recently derived method, based on empirical potential structure refinement (EPSR), the structure of molten zinc chloride (ZnCl_2) is re-analysed. Contrary to the picture given in some early analyses, the results indicate that there are significant uncertainties in the extracted site–site radial distribution functions, particularly the Zn–Zn distribution. These are derived from the small weighting of this partial structure factor in the measured diffraction data and from systematic uncertainties in the original data. The simulated atom distributions are used to discuss the three-dimensional structure of this molten salt.

Keywords. Neutron diffraction; liquids; computer simulation.

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1. Introduction

In a recent paper [1], I have described a method of extracting the partial structure factors (PSFs) and site–site radial distribution functions (SSRDFs) from the diffraction data of disordered materials. The method makes use of the empirical potential structure refinement procedure (EPSR) [1–3] and, by means of a ‘confidence’ factor, f , where $0 < f < 1$, a range of solutions to the problem of inverting the differential cross-section data to PSFs and SSRDFs can be found which fit the diffraction data to a greater or lesser extent. Solutions which give the best fit are then used to analyse the simulated atom ensembles for structural characteristics. Since the basics of the method have already appeared in [1], only a summary of the technique will be reported here. The main part of the present paper is devoted to an analysis of the extracted structure of molten ZnCl_2 , as determined from the neutron diffraction work of Biggin and Enderby [4]. The present structural conclusions are then compared with some previous studies of this material [4–11].

In a diffraction experiment the observed diffraction pattern, $D(Q)$, can be represented as a weighted sum of PSFs, $S_{\alpha\beta}(Q)$, with weights determined by the products of the atomic fraction, c_α , and scattering length (or X-ray form factor), b_α , of each component,

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$$D(Q) = \sum_{\alpha, \beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(Q), \quad (1)$$

where Q is the wave vector change in the diffraction experiment, and the partial structure factors are related to their real space counterparts, the SSRDFs, $g_{\alpha\beta}(r)$, by a three-dimensional Fourier transform:

$$S_{\alpha\beta}(Q) = 4\pi\rho \int_0^{\infty} r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} dr. \quad (2)$$

For neutrons the scattering length of a particular atom can often be altered by changing the isotopic composition of that atom. By measuring the diffraction patterns for a sufficient number of isotope variants of the same sample, the set of total diffraction patterns, $D(Q)$, can be inverted in principle to produce a complete set of partial structure functions. The question is however, given the likely systematic uncertainties in the diffraction data and the different weighting of individual PSFs in the total diffraction pattern, what is the reliability of this direct inversion? In [1] I argue that it can lead to inaccurate or unjustified conclusions.

The essence of the EPSR technique is to perform a computer simulation of the material in question at the correct atomic number density and composition of the real sample. The initial structure is determined by imposing a ‘reference’ potential energy function which serves to meet certain constraints, such as the likely minimum separation of particular atom pairs, the likely ionic charges if ions are present, and the likely molecular structures if molecules are present. This reference potential is then perturbed by an empirical potential (EP) which attempts to drive the simulated diffraction profiles as close as possible to the measured diffraction data. Thus the empirical potential is derived solely from the diffraction experiment, and there is a separate empirical pair potential for each distinct atom pair in the material. For a material containing J distinct components there are $N = J(J + 1)/2$ PSFs, SSRDFs and site–site pair potentials. If diffraction data are to be inverted directly to PSFs it must be possible to measure at least $M = N$ distinct versions of the diffraction data, where M is the number of isotope variant sets of diffraction data available.

In EPSR the quality of fit is determined by means of the unweighted R -factor, R_f , where

$$R_f = \frac{1}{M} \sum_i \frac{1}{n_Q} \sum_Q (D_i(Q) - F_i(Q))^2, \quad (3)$$

where $(D_i(Q) - F_i(Q))$ is the difference between data and fitted structure factor for the i th set of data. The value of R_f is determined as a function of the confidence factor, f , and those simulations which produce the best (smallest) R_f are then chosen for further analysis of the structure.

2. Application of EPSR to molten zinc chloride data

The diffraction data from [4] were digitised using a scanner and then used in an EPSR simulation of molten ZnCl_2 . A cubic box of 1000 Zn atoms and 2000 Cl atoms

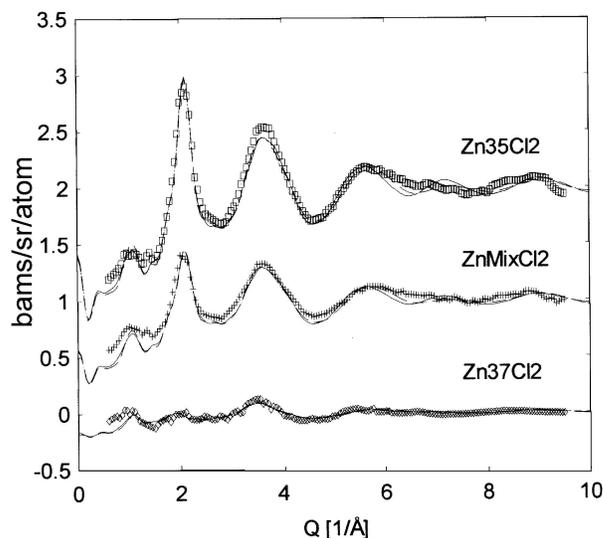


Figure 1. Diffraction data (points) for molten ZnCl_2 as obtained by scanner from Biggin and Enderby [1]. The lines show two EPSR fits to these data with different confidence factors, $f = 0.95$ (solid) and $f = 0.8$ (dashed). The two fits are almost indistinguishable from each other.

was set up, box dimension 44.7085 \AA , corresponding to an assumed number density of 0.03357 atoms per \AA^3 . As Biggin and Enderby did not state their assumed density, this value has been taken from the X-ray work of Triolo and Narten [5]. The reference potential between atom pairs was built up from a combination of Lennard–Jones and Coulomb potentials. All atoms were given a Lennard–Jones potential well depth, $\varepsilon_{\text{Zn}} = \varepsilon_{\text{Cl}} = 0.8$ kJ/mole, with Coulomb charges of $+2e$ on the Zn atoms and $-e$ on the Cl atoms. The Lennard–Jones σ values were adjusted repeatedly until the first peak in the Zn–Cl RDF occurred at about 2.29 \AA , and the first peak in the Cl–Cl RDF occurred at about 3.2 \AA , as was derived in the earlier experiment [7]. This process gave $\sigma_{\text{Zn}} = 1.12 \text{ \AA}$ and $\sigma_{\text{Cl}} = 4.54 \text{ \AA}$ respectively.

The Monte Carlo simulation itself follows the traditional pattern [8,9], with application of periodic boundary conditions, use of the minimum image convention and neighbour lists. To save computing time no correction is made for the long range forces. Instead, the derivative of the potential energy functions were truncated smoothly with a decaying exponential function of the form

$$T(r) = 1.0 \quad r \leq 9, \\ = \exp\left[\frac{r-9}{3}\right] \quad r > 9, \quad (4)$$

where r is in \AA . The potential energy functions were obtained by integrating this modified derivative backwards (i.e., to lower r values) from $r = r_{\text{max}}$, assuming the potential energy at $r = r_{\text{max}}$ and beyond is zero. In the present case r_{max} was set to 12 \AA .

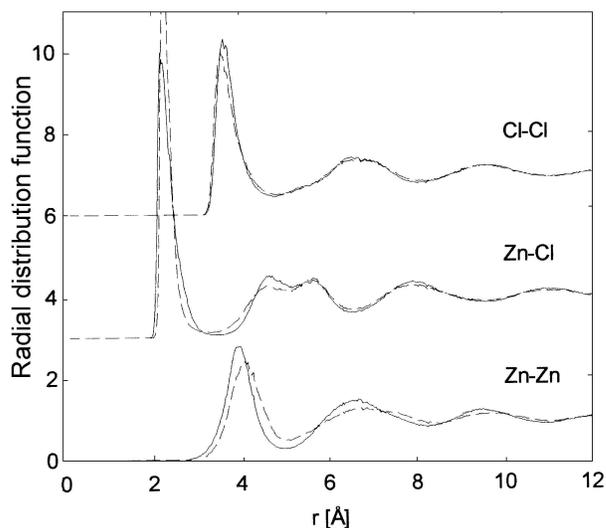


Figure 2. Estimated SSRDFs for molten ZnCl_2 as derived by EPSR using 95% confidence in the data ($f = 0.95$). The dashed line corresponds to 80% confidence in the data ($f = 0.8$). Note that the Zn–Zn peak is at slightly higher r values than the corresponding Cl–Cl peak, particularly for $f = 0.8$, and is much more uncertain as the degree of confidence in the data is lowered.

The values of R_f as a function of the confidence factor, f , that were obtained in this simulation are given in table IV of [1]. Figure 1 shows the simulated diffraction pattern vs. the diffraction data for two values of f which gave the lowest values of R_f , namely $f = 0.95$ and $f = 0.8$. It can be seen that these two values give almost indistinguishable fits. Figure 2 shows however that the simulated SSRDFs for these two cases are not identical, particularly for the Zn–Zn term, which is weakly weighted in the total diffraction pattern of ZnCl_2 . This therefore is an indication that simply being able to measure a set of diffraction data with isotope substitution will not guarantee a unique set of SSRDFs being extracted, and the EPSR method has enabled the range of possible solutions to be determined.

In addition to the SSRDFs, other quantities can be calculated from the atom ensembles. Table 1 for example summarises the coordination numbers for the four cases $f = 0.0, 0.8, 0.95$, and 1.0 . We see that for all the four cases, Zn is four-fold coordinated by Cl, indicating a likely strong tetrahedral arrangement of anions around the cation. The Cl–Cl and the Zn–Zn values are almost unchanged with f , indicating a general lack of sensitivity of coordination number to the details of the radial distribution functions.

Further information can be gleaned by plotting triplet angle distributions. In this case the Cl–Zn–Cl angle distribution (figure 3), is used to describe the local (tetrahedral) anion order around the cation, while the Zn–Cl–Zn angle distribution (figure 4), can be used to illustrate the ordering between adjacent cation tetrahedra.

From figures 2–4 it is clear that an unambiguous structure determination for molten ZnCl_2 will in practice be difficult to achieve. This is because different levels

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Table 1. Coordination numbers for each of the site–site radial distributions in molten ZnCl₂ as derived from EPSR analysis. The integration range is shown under respective SSRDF heading. The standard deviations show the variation from one site to the next, and so indicate the spread of values found in the liquid.

Confidence factor <i>f</i>	Zn–Zn (Integration range 0–5 Å)	Zn–Cl (Integration range 0–3 Å)	Cl–Cl (Integration range 0–5 Å)
0.00	5.0±1.0	4.2±0.5	12.2±1.0
0.80	5.2±0.9	4.4±0.6	11.2±1.1
0.95	4.9±0.9	4.5±0.7	11.1±1.2
1.00	4.5±1.0	4.3±0.6	11.0±1.2

of confidence in the data yield somewhat different SSRDFs, while giving equivalent fits to the diffraction data. But some general trends do emerge. There is for example clear evidence for ZnCl₄ tetrahedra in the melt, but they are probably quite distorted in practice, and although most are corner sharing a certain fraction of them will be edge sharing.

3. Discussion: Comparison with previous results on molten ZnCl₂

Following the publication of the first X-ray [5] and neutron [4] data on molten ZnCl₂, there were a number of subsequent studies on this system, both experimental and theoretical, and so far the present discussion has made no reference to, or comparison with these studies. It is intriguing therefore to discover how the present results from EPSR compare with other interpretations. Certainly, in terms of the original Biggin and Enderby results, the present SSRDFs (figure 2), show qualitative agreement with figure 3 of [4], but the position of the first Zn–Zn peak is less certain than implied by [4]. In particular a fit where this distance is significantly larger than the corresponding Cl–Cl distance gives an equally good representation of the original diffraction data as a fit where the first Zn–Zn peak distance is shorter.

McGreevy and Pusztai [6] performed a series of reverse Monte Carlo (RMC) studies on a number of molten salts and concluded that for ZnCl₂ there was some degree of covalency in the melt, as indicated by the sharpness of the tetrahedral coordination of the Zn ion. In addition, they claimed that the prepeak or ‘first sharp diffraction peak’ (FSDP) arose primarily from zinc clustering, as seen in the Zn–Zn partial structure factor. The present analysis does not appear to disagree with that interpretation in any significant way.

Subsequently, Salmon [7] produced an analysis in terms of the density–density, density–concentration and concentration–concentration structure factors, and concluded that the FSDP was a consequence of direction dependent (i.e. three-body) interactions. This was followed by Wilson and Madden [8], who introduced the polarisable ion model to the computer simulation, and demonstrated that polarisation of the anion could partly shield the cations from their mutual Coulomb repulsion,

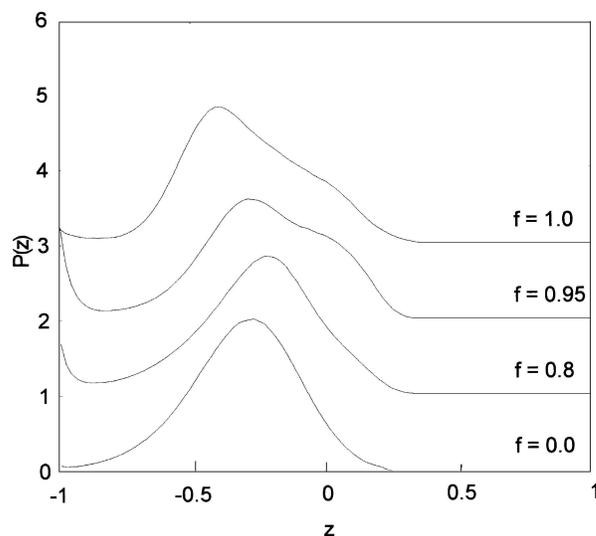


Figure 3. Cl-Zn-Cl angle distributions, $P(z)$, vs. the included angle $z = \cos(\theta)$ as a function of the confidence factor, f , for molten ZnCl_2 . Bonded pairs of Zn and Cl are defined when they lie within 3 Å of each other. It can be seen that this distribution, which has a pronounced peak near the tetrahedral angle, $z = -0.33$, changes appreciably for different levels of confidence in the data, and indicates a greater degree of distortion in the ZnCl_4 tetrahedra at high confidence levels.

allowing them to approach closer than they would otherwise do. Indeed, inspection of the EPSR empirical potentials for this work (figure 5) reveals a broad minimum in the region near $r = 2\text{--}3$ Å, which would indeed counteract the Coulomb repulsion in that region. They distanced themselves from an interpretation that invoked covalency in the melt, though it has to be noted that their results show mainly qualitative agreement with the experiment, rather than the quantitative comparison reported here and by McGreevy and Pusztai [6]. However, as we have seen the precise value of the Zn-Zn distance is not well-determined by the experiment, and if it is further out in distance than suggested originally by Biggin and Enderby, then the extent of polarisation in structuring the liquid need to be reassessed.

Bassen *et al* [9] published a combined Monte Carlo and RMC study of molten ZnCl_2 where they tried to use an effective pair potential to perform the function of the anion polarisation. In addition, instead of using the existing neutron data for the RMC calculations, they used their own new X-ray diffraction data. They found in all their simulations that the nearest-neighbour Zn-Zn distance was about 0.3 Å longer than Cl-Cl distance. They felt that the earlier neutron data had overemphasised the prepeak in the Zn-Zn PSF, though they also concluded that this prepeak was dominated by this term. Hence, discrepancies with the earlier work were emerging here, particularly the observation of a longer Zn-Zn distance, and the sharpness of the prepeak.

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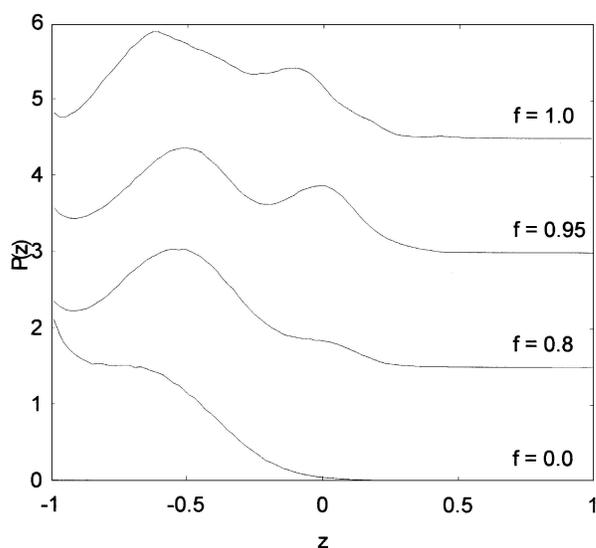


Figure 4. Zn-Cl-Zn angle distributions, $P(z)$, versus the included angle $z = \cos(\theta)$ as a function of the confidence factor, f , for molten ZnCl_2 . Bonded pairs of Zn and Cl are defined when they lie within 3 \AA of each other. As in figure 3, a marked dependence on the confidence factor, f , is observed. For $f = 0.0$ the two cations appear to lie in a straight line with greatest probability, but with a broad distribution about this line. For higher confidence factors this angle is bent to near 120° ($\cos \theta = -0.5$), but a second angle at $\sim 90^\circ$ also appears, suggesting that there may be edge to edge contacts between neighbouring ZnCl_4 tetrahedra.

This was followed by Neufeind [10], who reported yet another X-ray study, using high energy X-rays to go to large Q , and combined this with recent high precision neutron data. He too found a longer Zn-Zn near-neighbour distance than Cl-Cl distance and concluded that the prepeak arises primarily from the Zn-Cl PSF, not Zn-Zn. In addition, the region beyond the first peak in Zn-Zn looks different from the same region in Cl-Cl, to some extent in contrast to the Biggin and Enderby result.

A very recent study from Belashchenko and Ostrovskii [11] reports an analysis of the original Biggin and Enderby data, using a process that appears closely analogous to the EPSR method adopted here. However the EP calculation is made in r space, and once again the data are given a 100% confidence level. The empirical potentials they extract have several features in common with the empirical potentials produced in this work, particularly the minimum in the Zn-Zn term around 3 \AA . Apart from the observation that molten ZnCl_2 is a networked liquid, there do not seem to be any new conclusions about the structure in this work.

Overall therefore somewhat divergent views of the structure of molten ZnCl_2 have emerged recently. Perhaps the present EPSR analysis, which in many ways is consistent with all the existing analyses of molten ZnCl_2 , can help to reconcile the different approaches. It can now be said with some confidence that while the Cl-Cl

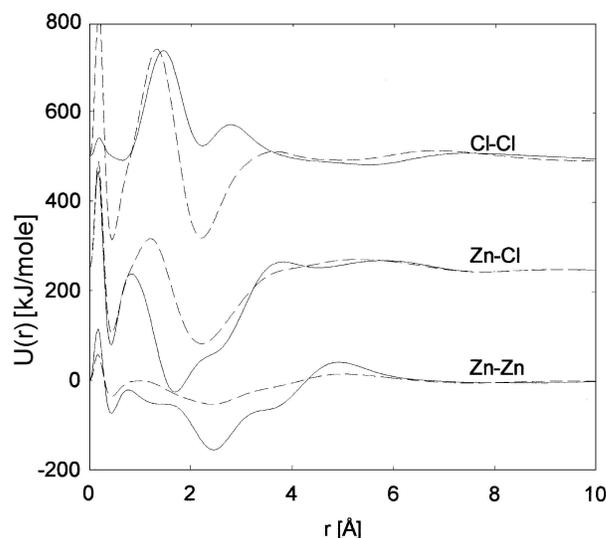


Figure 5. Derived site-site empirical potentials for molten ZnCl_2 from EPSR analysis for the cases $f = 0.95$ (solid lines) and $f = 0.8$ (dashed lines). Note how at short distances (2–3 Å) the empirical potentials generally imply additional attraction between ions, compared to the bare ion model. According to the Wilson and Madden analysis [8] this extra attractive potential at short distances arises from ionic polarisation shielding the cations from their direct Coulomb interactions.

distribution can be measured with good reliability, the other RDFs, particularly Zn–Zn, are not so reliable and different versions of this functions can be found which are consistent with the diffraction experiment. The conventional Biggin and Enderby result, which puts the Zn–Zn near-neighbour peak at the same distance as the Cl–Cl peak, followed by a deep minimum, is not the only distribution which fits the measured data, and a range of Zn–Zn RDFs can be found which give equally good representations of the data.

A particular controversy concerns the origin of the prepeak near $Q = 1 \text{ \AA}^{-1}$ which appears in all total diffraction patterns. Originally this was associated with the Zn–Zn PSF, but, as seen in figure 6, by not placing 100% confidence in the data it is possible to generate a slightly different version of the PSFs where the Zn–Cl PSF contributes to this peak as well (compare $f = 0.95$ with $f = 0.8$). Certainly in the present analysis it does not appear that the prepeak is as well-defined in the Zn–Zn PSF as originally suggested by Biggin and Enderby [4] (see their figure 2).

4. Conclusion

It has been shown here how, by placing different levels of confidence in a set of diffraction data while performing a computer simulation of the system they relate to, it is possible to assess the reliability with which any given structural aspect of a

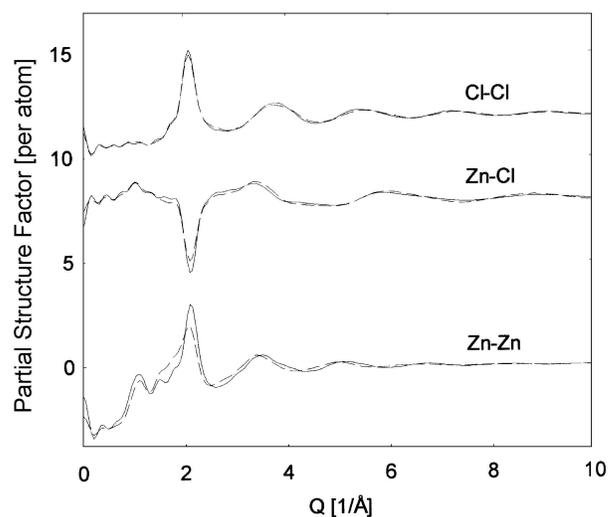


Figure 6. Estimated partial structure factors for molten ZnCl_2 for different confidence factors $f = 0.95$ (solid lines) and $f = 0.8$ (dashed lines). Note how the height of the prepeak (1 \AA^{-1}) in the Zn–Zn PSF is dependent on the degree of confidence in the data.

system can be determined. Perhaps not surprisingly we have found that quantities that are weakly weighted in the diffraction experiment are not likely to be determined unambiguously, but at least limits can be defined on the possible values of those quantities, based on the quality of fit for different confidence levels. Certainly it is not adequate to assume, as has frequently been done in the past, that diffraction data are 100% perfect. The present EPSR analysis of molten ZnCl_2 diffraction data has highlighted some of these questions. In particular it is found that the Zn–Zn partial structure factor, which is weakly weighted in the total diffraction pattern, and some of the related quantities such as triplet angle distributions, are not well-determined by the diffraction experiment. However by assuming that the diffraction data are not 100% reliable, a range of possible structures which are quantitatively compatible with the data can be generated, and these are used to set the boundaries of possible structural properties. It is the range of structural parameters found here that probably explains why a series of investigations of the structure of molten ZnCl_2 do not come to the same conclusions: depending on how the data are analysed they will give somewhat different interpretations. It is only when armed with the knowledge of what the data are sensitive to and what they are not sensitive to that an experimenter can make definitive statements about the structure of a material that has been investigated by diffraction.

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