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# The structure of molten $\text{ZnCl}_2$ and $\text{MgCl}_2$

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## Abstract

The structures of molten  $\text{MgCl}_2$  and  $\text{ZnCl}_2$  have been modelled using the reverse Monte Carlo method, based on neutron and x-ray diffraction data. We show that, although the structures are similar in terms of two-body correlations (e.g. partial radial distribution functions, average coordination numbers), there are important differences in the higher order correlations (e.g. bond angle and coordination number distributions). We have also analysed the models using bond-constraint counting. All of the results are consistent with the fact that  $\text{ZnCl}_2$  has a high viscosity and is a glass former (intermediate between strong and fragile), whereas  $\text{MgCl}_2$  is not a glass former, and with their different crystal structures.

## 1. Introduction

On the basis of most of the microscopic information that is available one would expect molten  $\text{ZnCl}_2$  and  $\text{MgCl}_2$  to be very similar. The number densities are 0.03 and  $0.0317 \text{ \AA}^{-3}$ , and the ionic radii of the doubly charged cations are 0.88 and 0.86  $\text{\AA}$ , respectively. The partial structure factors (psf),  $A_{\alpha\beta}(Q)$ , and partial radial distribution functions (prdf),  $g_{\alpha\beta}(r)$ , determined by neutron diffraction studies using isotopic (Cl) substitution [1, 2] are also very similar. However molten  $\text{ZnCl}_2$  is a highly viscous liquid that easily forms a glass. Its crystalline phases are characterized by the tetrahedral coordination of four  $\text{Cl}^-$  around  $\text{Zn}^{2+}$ .  $\text{MgCl}_2$ , on the other hand, has a relatively low viscosity, does not form a glass, and crystallizes in the layered  $\text{CdCl}_2$  structure with octahedral coordination.

The anomalous properties of molten  $\text{ZnCl}_2$  have led to a number of diffraction and modelling/simulation studies [1, 3–5].  $\text{MgCl}_2$  has been relatively ignored [2, 3]. In the present paper we make a comparison of the two liquids; this is an extension of an earlier study [3]. We show that, despite their apparent similarity, the diffraction data do indeed reveal a subtle but important difference between the two liquids that can be correlated with their physical properties and crystal structures. We also demonstrate that the reverse Monte Carlo (RMC) method of structural modelling is capable of revealing such a subtlety.

## 2. RMC modelling and results

The RMC modelling method and its application to studies of molten salts, including  $\text{MgCl}_2$  and  $\text{ZnCl}_2$ , has been described elsewhere [3, 6]. Here we will only give relevant details. Models consisted of 1200 cations and 2400 anions in a cube of side 48.42 Å for  $\text{MgCl}_2$  and 49.32 Å for  $\text{ZnCl}_2$ , with periodic boundary conditions. Atomic closest approach constraints were applied: Mg–Mg 3.3 Å, Mg–Cl 1.8 Å, Zn–Zn 3.5 Å, Zn–Cl 1.8 Å and Cl–Cl 2.7 Å. The data that were fitted were the total structure factors for samples with different isotopic Cl compositions as measured using neutron diffraction for  $\text{ZnCl}_2$  [1] and  $\text{MgCl}_2$  [2], and x-ray diffraction for  $\text{ZnCl}_2$  [4].

The total structure factor (tsf),  $F(Q)$ , measured in an experiment for a binary system is a linear combination of the three partial structure factors (psf),  $A_{\alpha\beta}(Q)$ ,

$$F(Q) = \sum_{\alpha=1}^N \sum_{\beta=1}^N \gamma_{\alpha\beta}(Q)(A_{\alpha\beta}(Q) - 1) \quad (1)$$

which are related to the partial radial distribution functions (prdf),  $g_{\alpha\beta}$ , by Fourier transform

$$g_{\alpha\beta}(r) - 1 = \frac{1}{(2\pi)^3 \rho} \int 4\pi Q^2 (A_{\alpha\beta}(Q) - 1) \frac{\sin Qr}{Qr} dQ \quad (2)$$

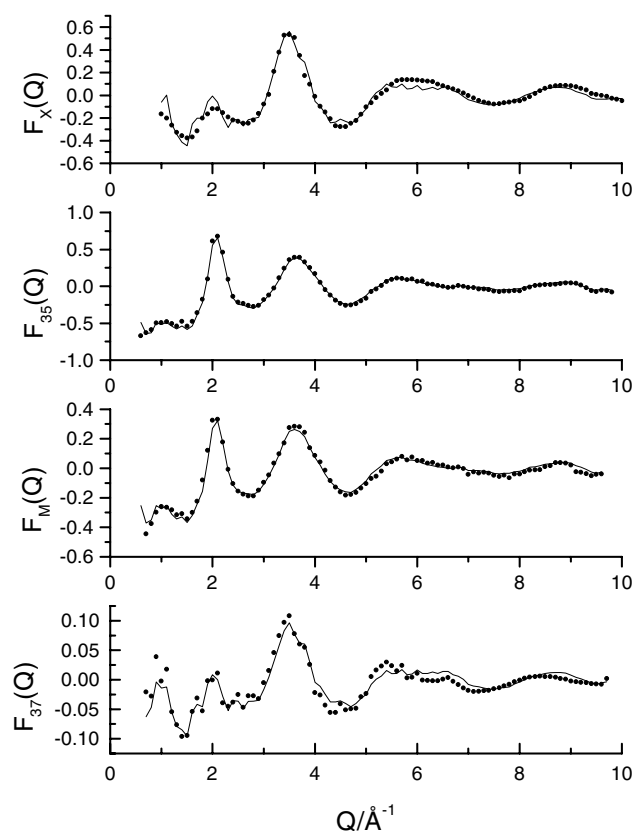
where  $\gamma_{\alpha\beta}$  are coefficients (see table 1), which is  $Q$  dependent an x-ray diffraction and is constant for neutron diffraction, and  $\rho$  is the atomic number density.

**Table 1.** Weighting coefficients of partial structure factors corresponding to the total structure factors shown in figure 1.

Radiation	Sample	$\gamma_{++}$	$\gamma_{+-}$	$\gamma_{--}$
$\text{ZnCl}_2$				
Neutron	$F_{37}$	0.0359	0.0837	0.0487
Neutron	$F_N$	0.0359	0.2255	0.3540
Neutron	$F_{35}$	0.0359	0.2942	0.6028
X-ray ( $Q = 0$ )	$F_X$	0.21	0.5	0.29
$\text{MgCl}_2$				
Neutron	$F_{37}$	0.0321	0.1085	0.0916
Neutron	$F_M$	0.0321	0.1937	0.2923
Neutron	$F_N$	0.0321	0.2289	0.4079
Neutron	$F_{35}$	0.0321	0.2695	0.5655

The following RMC models were produced.

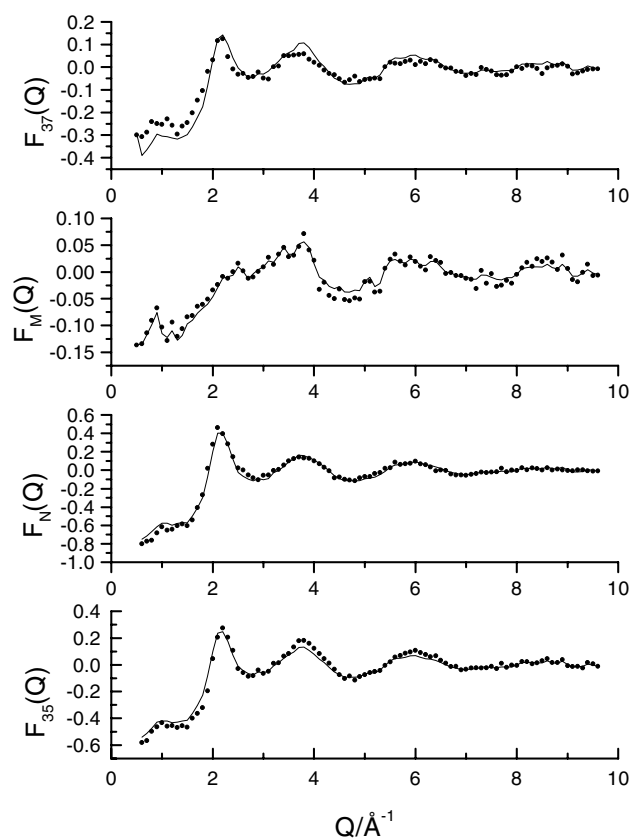
- (A) Starting from a random arrangement of ions and modelling neutron diffraction data with no constraints on coordination.
- (B) A model for  $\text{ZnCl}_2$  starting from the  $\text{MgCl}_2$  model produced in (A), and one for  $\text{MgCl}_2$  starting from the  $\text{ZnCl}_2$  model produced in (A), modelling neutron diffraction data with no constraints on coordination.
- (C) As (A) but with a constraint to maximize the fraction of fourfold cation–anion coordination up to 3.0 Å.
- (D) As (B) but with a constraint to maximize the fraction of fourfold cation–anion coordination up to 3.0 Å.
- (E) As (D) for  $\text{ZnCl}_2$  but also fitting to x-ray diffraction data.



**Figure 1.** Total structure factors,  $F(Q)$ , for neutron diffraction from three samples of molten  $\text{ZnCl}_2$  with different isotopic chlorine compositions (see table 1 for details) and for x-ray diffraction. Points; experimental data [1, 4]. Curves, RMC fit (model (E)).

The experimental data are shown in figures 1 and 2 together with the RMC fits for model (D) for  $\text{MgCl}_2$  and model (E) for  $\text{ZnCl}_2$ . The quality of fit is the same for all the models. Note that the neutron diffraction data were measured some years ago and are not of the high statistical accuracy that might now be expected. However, we estimate that the systematic errors are reasonably low, and this is usually more important. The x-ray diffraction data for  $\text{ZnCl}_2$  show a deviation at high  $Q$  that might be expected due to, e.g., an incorrect background subtraction (this being more important at high  $Q$  due to the fall off of the form factor in this region). A similar deviation is evident in the modelling study of Bassen *et al* [5]. We have therefore not used data above  $10 \text{ \AA}^{-1}$ . The inclusion of x-ray diffraction data does not make a significant difference to the model for  $\text{ZnCl}_2$ . As can be seen from table 1, the relative weighting factors for the psf's are similar to those for neutron diffraction from  $\text{Zn}^{37}\text{Cl}_2$ , so little extra information is provided by the additional data. The fitting merely then serves to confirm that the neutron and x-ray data are consistent.

The psf's and prdf's are shown in figures 3 and 4, respectively. These are very similar for  $\text{ZnCl}_2$  and  $\text{MgCl}_2$ , as noted previously, so the first expectation is that there is no significant difference between the models. The first diffraction peak (FDP) at  $\sim 1 \text{ \AA}^{-1}$  occurs dominantly in the cation–cation psf, consistent with the fact that it is strongest for tsf's with a greater weighting of the relevant coefficient. This FDP indicates some intermediate range ordering (IRO) of the

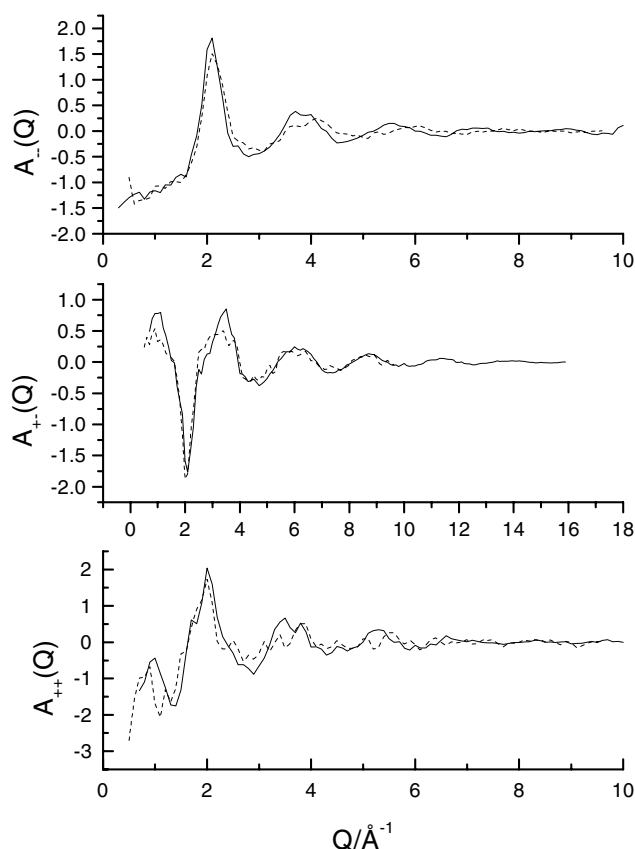


**Figure 2.** Total structure factors,  $F(Q)$ , for neutron diffraction from four samples of molten  $\text{MgCl}_2$  with different isotopic chlorine compositions (see table 1 for details). Points, experimental data [2]. Curves, RMC fit (model (D)).

cations. The cation–cation pdf's have a first peak at the same distance as the anion–anion pdf's,  $\sim 3.6$  Å, which is unexpected because the cation is doubly charged. There is an apparent small split in the first peak of the cation–cation pdf for both  $\text{ZnCl}_2$  and  $\text{MgCl}_2$ . However, we have no reason to believe that this is 'real'—probably it is an artefact caused by the data quality. Typically such artefacts occur in the partial for which there is least information in the data.

In models (A) and (B) the dominant cation–anion coordination is fourfold; hence we have also produced models (C), (D) and (E) with constrained fourfold coordination. This has been achieved to a level of 97% for  $\text{ZnCl}_2$  and 99% for  $\text{MgCl}_2$ .

In figure 5 we show bond angle correlation functions,  $P_{\alpha\beta\gamma}(\cos\theta)$ , for various triplets of neighbours. Ions are defined as neighbours if their separation is less than 5.0 Å (++) , 3.0 Å (+−) or 4.8 Å (−−), the distances being taken from the approximate positions of the first minima in the corresponding  $g_{\alpha\beta}(r)$ . The results for  $P_{+++}$  and  $P_{---}$  are very similar. The largest differences occur for  $P_{+-+}$ .  $\text{MgCl}_2$  has a very broad distribution, peaking at about  $90^\circ$ .  $\text{ZnCl}_2$  has a sharper distribution which peaks close to the inter-tetrahedral angle,  $109^\circ$ . Given that both materials have fourfold coordination this leads to the conclusion that there is a similar basic anion structure, but in  $\text{ZnCl}_2$   $\text{Zn}^{2+}$  favour the occupation of tetrahedral interstices, whereas in  $\text{MgCl}_2$   $\text{Mg}^{2+}$  favour the occupation of interstices where the co-ordination is more square planar. The IRO occurs because of correlations between the cation sites.

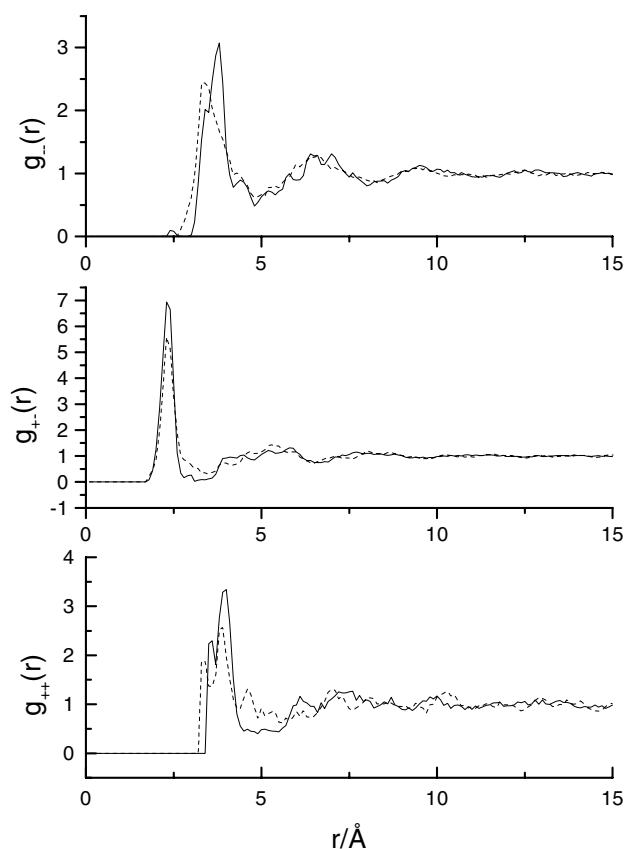


**Figure 3.** Partial structure factors,  $A_{\alpha\beta}(Q)$ , calculated from RMC models for molten ZnCl<sub>2</sub> (full curves, model (E)) and MgCl<sub>2</sub> (broken curves, model (D)).

Figure 6 shows the coordination number distributions,  $C_{\alpha\beta}(N)$ , for model (D) for MgCl<sub>2</sub> and model (E) for ZnCl<sub>2</sub>. Because of the constraint applied  $C_{+-}$  (i.e. the number of anions which are neighbours of a given cation) is four for almost every cation. However, there is a significant difference between the anion–cation coordination number distributions. Although the average value  $\bar{C}_{-+} = \bar{C}_{+-}/2 \approx 2$  for both MgCl<sub>2</sub> and ZnCl<sub>2</sub>, ZnCl<sub>2</sub> has significantly more twofold coordinated anions (78%) than MgCl<sub>2</sub> (45%).  $C_{++}(N)$  and  $C_{--}(N)$  are also more sharply peaked for ZnCl<sub>2</sub> than for MgCl<sub>2</sub>.

### 3. Discussion

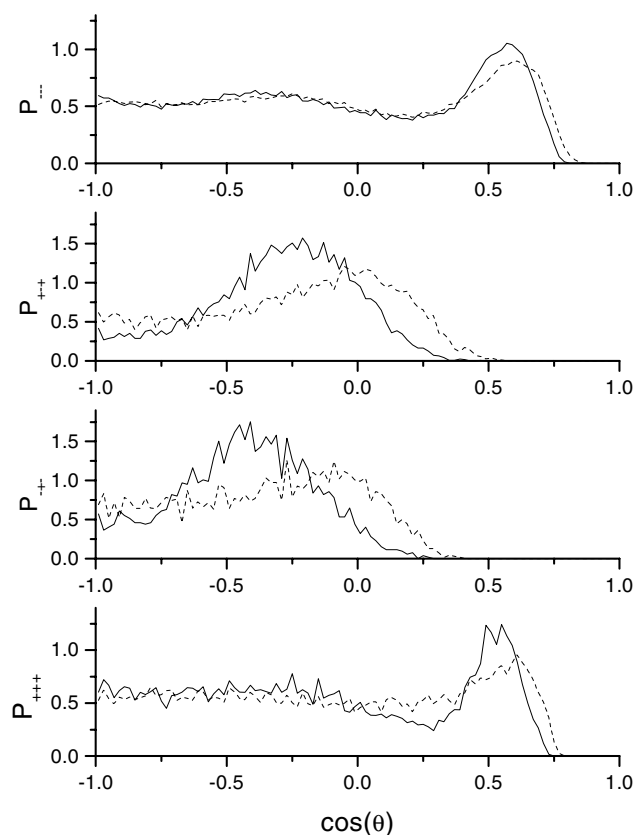
Bassen *et al* [5] have recently reported a RMC and MC modelling study of molten ZnCl<sub>2</sub>. Their conclusions as to the basic structure are no different from ours. They also conclude that ‘the RMC method should be applied with much care when used for the structural modelling of molten salts’. We would entirely agree with this statement. However Bassen *et al* are implying that the RMC results are in some sense unreliable since they do not reproduce the high definition of tetrahedral units that the MC simulations do. We would point out the following. First of all Bassen *et al* have modelled only x-ray diffraction data, and over a very limited  $Q$  range (0.5–7  $\text{\AA}^{-1}$ ). In fact above 4  $\text{\AA}^{-1}$  the agreement with the data can only be considered as



**Figure 4.** Partial radial distribution functions,  $g_{\alpha\beta}(r)$ , calculated from RMC models for molten  $\text{ZnCl}_2$  (full curves, model (E)) and  $\text{MgCl}_2$  (broken curves, model (D)).

poor. The information supplied to RMC is therefore extremely limited. Even if one would expect that the RMC model would be intrinsically more disordered than the real system (this has been discussed many times elsewhere, e.g. [6]), the conclusion should be that RMC has done a remarkable job to produce a structure that is in such good general agreement with MC on the basis of the small amount of information supplied. It might also be noted that in the MC models some of the expectations are ‘built in’ through the potential—hence it is hardly surprising that the results agree with the expectations. RMC methods should indeed be applied with care, and one point of care is not to have an unrealistic expectation on the basis of inadequate information.

The models produced here confirm that the cation–cation nearest-neighbour distance is similar to the corresponding anion–anion distance, despite the higher cation charge. Wilson and Madden [7] have shown that this can arise in the following way. The small cation polarizes the neighbouring anion(s). In certain atomic arrangements this polarization can produce an additional attraction for a second cation, which may be considered as an effective reduction in the cation–cation repulsion. Since there are fewer cations than anions, but the first neighbour distance is the same, this implies that the cation density in some regions must be higher than in others, i.e. the cations tend to cluster. This density fluctuation gives rise to the FDP in  $A_{++}(Q)$ . The same behaviour is observed for both salts, so cation clustering has no direct relationship



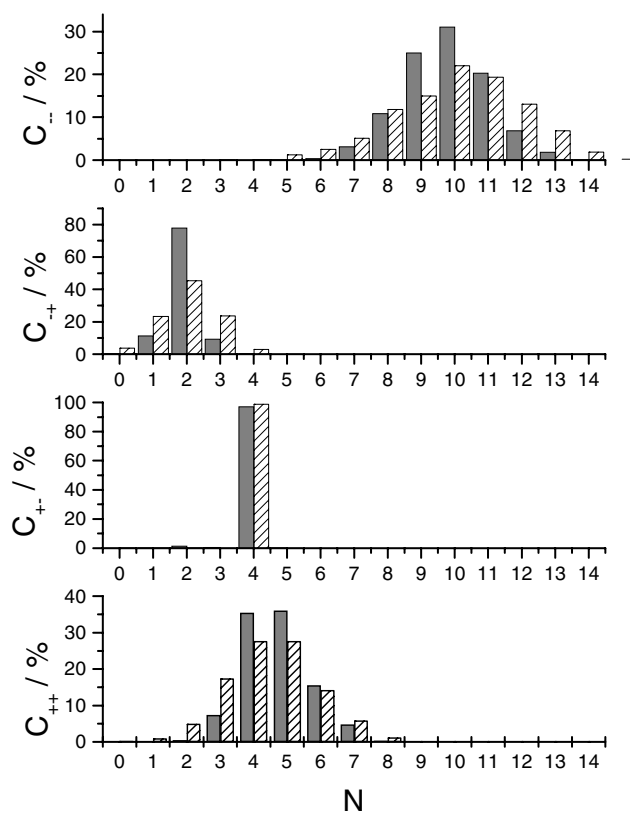
**Figure 5.** Bond-angle correlation functions,  $P_{\alpha\beta\gamma}(\cos\theta)$ , between nearest neighbours for molten ZnCl<sub>2</sub> (full curves, model (E)) and MgCl<sub>2</sub> (broken curves, model (D)).

to the fact that MgCl<sub>2</sub> has high mobility (low viscosity) and ZnCl<sub>2</sub> has low mobility (high viscosity). Indeed it might be noted that there is evidence of short cation–cation distances in other salts where the cations are specifically associated with high mobility (fast ion conduction) (e.g. [8–11]). In these cases the cation–cation distance is comparable with the cation–anion distance, and has again been related to polarization of the anions [12].

The structures of molten ZnCl<sub>2</sub> and MgCl<sub>2</sub> can be considered as close-packed Cl<sup>−</sup> networks with cations occupying a fraction of the interstices. The fourfold cation–anion coordination and the positions of the peaks in  $P_{+-+}$  suggest that Zn<sup>2+</sup> prefer to occupy relatively regular tetrahedral interstices, while Mg<sup>2+</sup> prefer to occupy interstices with a more octahedral geometry with a pair of anion vacancies (square planar geometry is therefore one of these possibilities). This seems consistent with the fact that ZnCl<sub>2</sub> forms tetrahedrally coordinated structures in the glass and crystal while MgCl<sub>2</sub> forms a layer structure. It also seems consistent with the lower viscosity of MgCl<sub>2</sub>.

This can be given a more quantitative basis using bond-constraint counting ideas (e.g. [13, 14]). Ideally an  $N$ -fold coordinated atom has  $n_s = N/2$  bond stretching constraints and  $n_b = (2N - 3)$  bond-bending constraints. However, some constraints may be broken. For example, in vitreous SiO<sub>2</sub> ( $N_{SiO} = 4$ ,  $N_{OSi} = 2$ ) the bond-bending constraints for O atoms





**Figure 6.** Coordination number distributions,  $P_{\alpha\beta}(N)$ , of nearest neighbours for ZnCl<sub>2</sub> (grey, model (E)) and MgCl<sub>2</sub> (hatched, model (D)).

are broken (the Si–O–Si bond is very flexible) giving an average number of constraints

$$n_c = \frac{(N_{SiO}/2) + 2 \times (N_{Osi}/2) + (2 \times N_{SiO} - 3)}{3} = 3. \quad (3)$$

Since the number of constraints equals the number of degrees of freedom the system is optimally constrained and SiO<sub>2</sub> is an excellent glass former. To analyse the models for ZnCl<sub>2</sub> and MgCl<sub>2</sub> we will consider only ‘ideally’ coordinated cations and anions, i.e. cations with fourfold cation–anion coordination and anions with twofold anion–cation coordination. Anion centred bond-bending constraints are broken (as in SiO<sub>2</sub>). Cation centred bond-bending constraints are broken if Cl is not twofold coordinated. The number of constraints for ZnCl<sub>2</sub> is then similar to that for SiO<sub>2</sub> (though the structures are not topologically equivalent—there is no ‘short’ Si–Si distance)

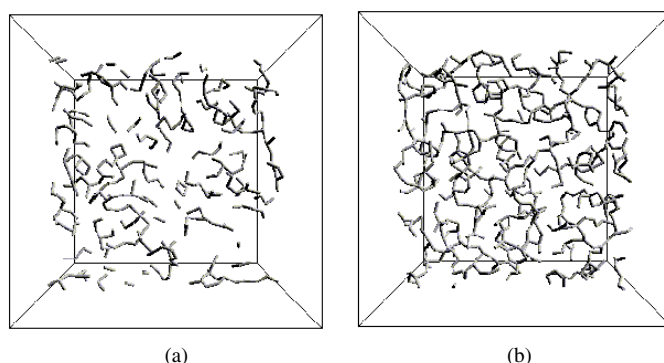
$$n_c = \frac{0.97 \times (4/2) + 0.78 \times 2 \times (2/2) + 0.78 \times (2 \times 4 - 3)}{3} = 2.47. \quad (4)$$

However for MgCl<sub>2</sub> the number of twofold coordinated anions is much lower, giving

$$n_c = \frac{0.99 \times (4/2) + 0.45 \times 2 \times (2/2) + 0.45 \times (2 \times 4 - 3)}{3} = 1.71. \quad (5)$$

If one includes all bonds for the bond-stretching constraints (i.e. not just the fourfold and twofold coordinated) the numbers rise to 2.61 and 2.08, respectively. In either case the numbers

suggest that  $\text{ZnCl}_2$  will be midway between a strong and fragile glass former and  $\text{MgCl}_2$  will be extremely fragile (i.e. effectively not a glass former), as is in fact the case.



**Figure 7.** Sections of RMC models (10 Å thick) for molten  $\text{MgCl}_2$  ((a), model (D)) and  $\text{ZnCl}_2$  ((b), model (E)). Bonds are drawn between cation–anion pairs less than 3 Å apart where cations have fourfold anion coordination and anions have twofold cation coordination.

It can be noted that normally bond-constraint calculations are made on the basis of ‘ideal’ or average coordination numbers which are determined on the basis of simple chemical ideas and the composition of the material. However, this would predict similar properties for  $\text{ZnCl}_2$  and  $\text{MgCl}_2$ . It is therefore necessary to account for the coordination number distribution. To our knowledge this is the first time that such an idea has been applied. For relatively symmetric coordination number distributions the bond-stretching constraints will be the same whether the distribution or the average is used. It is less obvious how to deal with bond-bending constraints. In order to be able to make some simple calculations we have had to make a slightly arbitrary choice of which bond-stretching constraints to include. Whatever choice is made would still lead to the conclusion that  $\text{ZnCl}_2$  is more ‘ $\text{SiO}_2$  like’, in the sense that it has the ‘perfect’ combination of fourfold cation–anion coordination and twofold anion–cation coordination to a higher degree, and  $\text{MgCl}_2$  is less ‘ $\text{SiO}_2$  like’. It is therefore reasonable to conclude that one might expect  $\text{ZnCl}_2$ , on a purely structural basis, to be a better glass former. A fuller discussion of how to apply bond-constraint calculations in such ‘non-ideal’ structures should be left to a separate paper.

The difference between  $\text{MgCl}_2$  and  $\text{ZnCl}_2$  can also be shown visually. In figure 7 we show sections from the models where bonds are drawn between neighbouring cation–anion pairs if cations have fourfold anion coordination and anions have twofold cation coordination. It is clear that the  $\text{ZnCl}_2$  bond network percolates, i.e. connects across the entire model, whereas the  $\text{MgCl}_2$  network is fragmented.

It then remains to consider the origin of the differences between the two salts. As noted earlier, the similarity in number density and ionic radii would lead to similar structures and properties on the basis of a simple ionic potential. With the inclusion of ‘first order’ polarization effects, as done by Wilson and Madden [7], one would still expect similarity since the anions are identical and the polarization effect is to first-order dependent on the cation size and charge. However, if one looks at the trends then for even smaller cation size the expected structure becomes more similar to that for molten  $\text{NiI}_2$  [15], which is associated with a relatively high mobility ( $\text{NiI}_2$  is a fast ion  $\text{Ni}^{2+}$  conductor at high temperature in the solid state). The trend from  $\text{Zn}^{2+}$  to  $\text{Mg}^{2+}$  is therefore in the ‘right direction’. Madden [16] has suggested that higher order polarization effects may play some role. We would also suggest that  $\text{ZnCl}_2$  is in fact anomalous because it falls into a special ‘window’ where the cation size and polarization

effects produce a bond network that has long-range connectivity, but is just to one side of a percolation threshold. Only a small change in the bonding is required to place  $\text{MgCl}_2$  on the other side of the threshold.

#### 4. Conclusions

We have shown that in terms of two-body correlations, e.g. prdf's, the structures of molten  $\text{MgCl}_2$  and  $\text{ZnCl}_2$  are very similar. However they are not identical and the differences become more visible when one considers higher order correlations, e.g. bond angle distributions and bonding networks. We have then shown that there is a structural basis for the high viscosity and good glass forming ability of molten  $\text{ZnCl}_2$ , and why this is not the same for  $\text{MgCl}_2$ .

These results occur *entirely on the basis of the data*, independently of the starting configuration and the imposition of coordination constraints. It might be argued that, since the data are not of the highest quality, these differences might be driven by residual errors. While this cannot be discounted, it would be an extraordinary coincidence that the results produced by such errors were nevertheless consistent with what might be expected on the grounds of viscosity and crystal structures. We are therefore inclined to believe that they are real. The reverse Monte Carlo method has demonstrated the advantage that it is potential independent. Any potential based method would have to use a very complex potential in order to be able to produce the same results.

#### Acknowledgments

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