Structure of liquid and glassy $ZnCl_2$

A basic question in glass science concerns the nature of the glass transition and, while this process is intimately related to the dynamical properties of a system on cooling [1], it is nevertheless important to understand the atomic ordering in the liquid and glass. Within the family of binary network glass forming systems, $ZnCl_2$ is an exemplar whose basic properties can be understood in terms of an ionic interaction model, provided that anion polarisation effects are taken into account, i.e. it is possible to model this material by using large scale molecular dynamics methods [2]. We have therefore applied a combination of neutron and X-ray diffraction techniques to measure the full set of partial structure factors for liquid and glassy $ZnCl_2$, thus maximising the information that can be obtained at the pair correlation function level [3,4].

The neutron diffraction experiments employed the method of isotope substitution and were made using the instrument D4c at the Institut Laue-Langevin in Grenoble, France. The high energy X-ray diffraction experiments used beamline **BL04B2** at SPring-8 with an incident wavelength of 0.2 Å. The sample for the X-ray experiments was held in a silica capillary tube which was loaded by using the "Hummingbird" method in which anhydrous beads of $ZnCl_2$ are first sealed under vacuum in a silica tube connected to the capillary (Fig. 1). The beads are then evaporated in an oven, condensed into a liquid within the capillary, and quenched to form a glass. The capillary containing the sample is finally sealed under vacuum. The full set of partial structure factors were extracted from the neutron diffraction data sets by using the method of singular value decomposition [4]. Their accuracy was assessed by using them to reconstruct the expected X-ray diffraction pattern, making a correction for the effect of the resolution function of the neutron diffractometer [5]. A comparison between the measured and reconstructed X-ray diffraction patterns for liquid and glassy $ZnCl_2$ is shown in Fig. 2.

The diffraction patterns were used to construct three-dimensional models (Fig. 3) for liquid and glassy $ZnCl_2$ by employing the reverse Monte Carlo (RMC) method [4]. The results show that the predominant structural motif in both phases is the corner sharing $ZnCl_4$ tetrahedron where the average

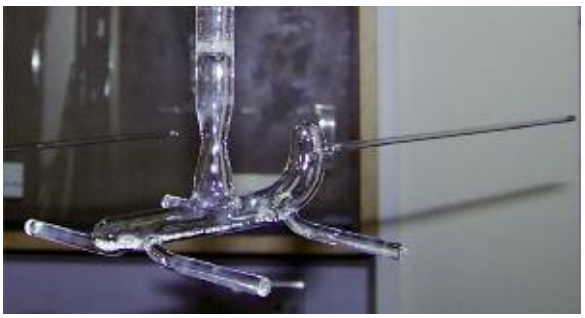

Fig. 1. The "Hummingbird" apparatus, made from silica, which was used to load a capillary tube with the $ZnCl_2$ sample for the X-ray diffraction experiments. The sample is initially in the form of white anhydrous beads which can be seen in the "body" of the bird while a long thin capillary tube forms the "beak" of the bird on the right hand side. The vertical tube, which is used to load the beads into the bird, is initially connected to a vacuum line but is sealed prior to placing the apparatus into an oven.

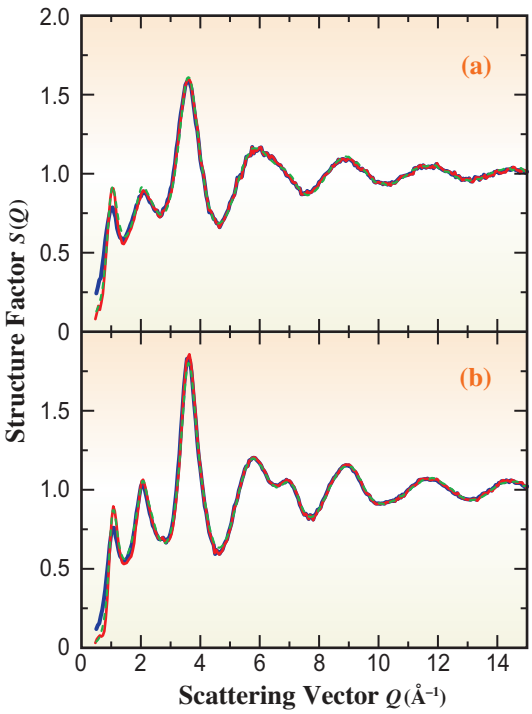

Fig. 2. Comparison between the X-ray and neutron diffraction results for **(a)** liquid $ZnCl_2$ at 330°C and **(b)** glassy $ZnCl_2$ at room temperature. For each panel, the broken (green) curve corresponds to the structure factor $S(Q)$ measured by using X-ray diffraction, the solid dark (blue) curve corresponds to the X-ray structure factor reconstructed from the neutron diffraction results, and the solid light (red) curve corresponds to this data after correction for the resolution function of the neutron diffractometer. The resolution function correction improves agreement between the neutron and X-ray data sets, especially in the region around the first sharp diffraction peak at $Q \approx 1$ Å^{-1}.

Zn-Cl coordination number is 3.96 for the liquid and 3.99 for the glass. There is also a small number of edge sharing configurations, these being more abundant in the liquid. The fraction of fourfold coordinated Zn atoms in corner and edge sharing configurations was estimated at 82% and 18% for the glass and at 63% and 37% for the liquid, respectively. The tetrahedra organize on an intermediate length scale to give a so-called first sharp diffraction peak in the measured diffraction patterns at a scattering vector $Q \approx 1$ Å^{-1} that is most prominent for the Zn-Zn correlations i.e. this peak arises from the ordering associated with the tetrahedron centres. An analysis of the connectivity profiles for the models shows an absence of odd membered rings which is a characteristic of a chemically ordered network (Zn-Cl-Zn-Cl connections), as befits an ionic system. Sixfold rings containing three Zn and three Cl atoms are a significant feature of both the liquid and glass networks.

The relative ''fragility'' of glass forming materials is a measure of the rate at which the dynamical properties of a liquid change on approaching the glass transition. In the case of $ZnCl_2$, the temperature dependence of the liquid viscosity shows behavior that is intermediate between "strong" glass forming systems such as SiO_2 and GeO_2 and "fragile" glass forming systems such as KCl-$BiCl_3$ and $Ca_2K_3(NO_3)_7$. Recent molecular dynamics work on tetrahedral glass forming liquids with the MX_2 stoichiometry suggests that the fragility of a melt increases with the number of edge sharing configurations [2]. The present results for liquid $ZnCl_2$ are consistent with this notion since they show the presence of edge sharing units, these conformations being absent in strong liquids such as SiO_2 and GeO_2.

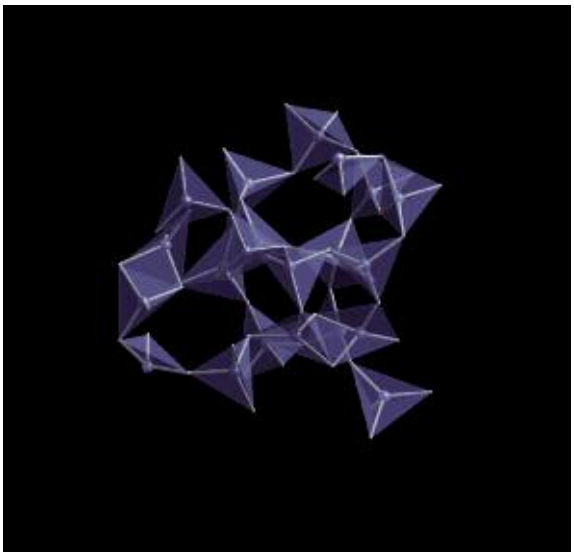

Fig. 3. A representative atomic configuration in glassy $ZnCl_2$ as extracted from the RMC model. Corner sharing $ZnCl_4$ tetrahedra are the predominant structural motifs where a Zn atom (large sphere) resides at the centre of a tetrahedron and four Cl atoms (small spheres) reside at its vertices. A few edge sharing $ZnCl_4$ tetrahedra also occur.

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