



Structure of the network glass-former ZnCl_2 : From the boiling point to the glass



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ABSTRACT

The structure of the network glass-forming material ZnCl_2 was measured using both neutron and high-energy x-ray diffraction for the glass at 298(1) K and for the liquid over the temperature range 601(1)–977(2) K. Intermediate range order, as manifested by the appearance of a first-sharp diffraction peak in the measured diffraction pattern for the glass at a scattering vector $k_{\text{FSDP}} \approx 1 \text{ \AA}^{-1}$, is retained in the liquid state even at temperatures close to the boiling point. The correlation lengths associated with both the intermediate and extended range ordering are found to be inversely proportional to temperature. The reverse Monte Carlo (RMC) method was used to model the material, and the results at two different temperatures are compared to those obtained from RMC models based on the partial structure factors measured by using the method of isotope substitution in neutron diffraction. The models show temperature dependent structural variability in which there is an interplay between the fractions of corner-sharing versus edge-sharing ZnCl_4 tetrahedra. Corner-sharing motifs are predominant in the glass, and edge-sharing motifs become more numerous in the liquid as the temperature is increased. The appearance of a first-sharp diffraction peak in the Bhatia–Thornton concentration–concentration partial structure factor is discussed in the context of classifying the different network types for glass-forming materials.

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1. Introduction

The structure of network glass-forming liquids over multiple length scales, and the evolution of this structure with temperature, is important for understanding the physical properties of these technologically important materials [1–5]. In the case of tetrahedral glass-forming systems with the MX_2 stoichiometry, the structure is described by two length scales at distances larger than the nearest-neighbor distance [6], and there is a competition between the ordering on these length scales that affects a melt's ‘fragility’ [7]. The length scales are associated with atomic-scale ordering on the intermediate and extended ranges, and manifest themselves in the measured diffraction patterns by the appearance of a first-sharp diffraction peak (FSDP) and a principal

peak. These peaks appear at scaled positions of $k_{\text{FSDP}}r_{\text{MX}} \approx 2.5$ and $k_{\text{PP}}r_{\text{MX}} \approx 4.8$ where k_{FSDP} and k_{PP} are the scattering vectors for the FSDP and principal peak, respectively, and r_{MX} is the nearest-neighbor distance for unlike chemical species [8–12]. The competition between the ordering on these length scales manifests itself in terms of the relative importance of the FSDP versus the principal peak in the Bhatia–Thornton [13] number–number partial structure factor $S_{\text{NN}}^{\text{BT}}(k)$ which describes the topological ordering. The FSDP in $S_{\text{NN}}^{\text{BT}}(k)$ is more prominent than the principal peak for ‘strong’ glass formers such as GeO_2 , whilst the converse holds true for more ‘fragile’ glass formers such as ZnCl_2 and GeSe_2 [7,12,14]. The ‘strong’ versus ‘fragile’ taxonomy for glass-forming liquids originates from the temperature dependence of the viscosity near the glass transition temperature T_g [15]. Fragile materials show a particularly rapid increase of viscosity near T_g which affects their manipulability, e.g. it may be necessary to supercool a fragile liquid in order for its viscosity to become sufficiently large to enable fiber-pulling [16].

In this paper we explore the evolution with temperature of the atomic scale ordering in the glass-forming system ZnCl_2 [6,17–34] by using a combination of neutron and high energy x-ray diffraction to investigate the glass at 298(1) K and the liquid at several temperatures in

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the range 601(1)–977(2) K, i.e. close to the melting and boiling points at 563 and 1005 K, respectively [35]. This material is a prototypical example of a glass-former with structure-related properties that can be understood in terms of an ionic interaction model, provided that anion polarization effects are taken into account [23,27,29–31]. The basic structure of the glass can be thought of in terms of a random close-packed distribution of Cl atoms where the Zn atoms occupy tetrahedral holes and are arranged in a way that maximizes the number of corner-sharing ZnCl_4 tetrahedra [21]. The structure can also be thought of in terms of a network of corner-sharing ZnCl_4 tetrahedra in which the Cl atoms are densely packed. For example, molecular dynamics simulations on MX_2 systems show that a SiO_2 -like structure can be transformed to a ZnCl_2 -like structure via a systematic increase of the anion polarizability [36,37]. Thus, ZnCl_2 can also be regarded as a network glass-former albeit with a topology that is different to materials such as SiO_2 , e.g. at ambient pressure the coordination number of the electronegative species can vary from two (Section 5.1). The fragility of liquid ZnCl_2 is intermediate between strong glass-forming systems such as SiO_2 and GeO_2 and more fragile glass forming systems such as KCl-BiCl_3 and $\text{Ca}_2\text{K}_3(\text{NO}_3)_7$ [15,24,38,39].

Part of the motivation for the present study is a search in glass-forming systems for a growing static length scale which should accompany a slowdown in the dynamics as the glass transition is approached, i.e. the time taken for a system to relax increases because correlated regions of growing size need to rearrange [40]. The alterations to the measured structure factors for glass-forming liquids as T_g is approached are, however, small as compared to dynamical properties such as the viscosity and diffusion coefficients which change by many orders of magnitude [41,42]. Nevertheless, it is of value to measure the temperature dependent structural changes in ZnCl_2 because this system is ionic and is therefore amenable to investigation by molecular dynamics methods using a polarizable ion model [23,27,29,30,37,43]. Such methods allow for access to several of the pertinent length and time-scales, e.g. the extended range ordering in tetrahedral MX_2 glasses can persist to nanometer length-scales of 20–30 Å [6,7,12,44,45].

The diffraction data were modeled by using the reverse Monte Carlo (RMC) method [46], and the full set of partial structure factors were extracted for several temperatures, together with the associated bond angle distributions and ring statistics. We find that the network structure of the glass is made predominantly from corner-sharing ZnCl_4 tetrahedra, although there are also edge-sharing tetrahedra which become more numerous in the liquid with increasing temperature. The structural motifs organize on an intermediate length scale to give an FSDP in the measured diffraction patterns at $k_{\text{FSDP}} \approx 1 \text{ Å}^{-1}$ which remains a significant feature of the liquid state even at temperatures close to the boiling point. The appearance of edge-sharing motifs is consistent with molecular dynamics work on tetrahedral glass-forming MX_2 systems which suggests that by disrupting networks of corner-sharing tetrahedra they promote melts with increased fragility [36].

The manuscript is organized as follows. In Section 2, the essential theory is described for understanding the diffraction results. In Section 3, an outline is given of the sample preparation and characterization methods, the neutron and x-ray diffraction experiments, and the RMC procedure used to model the structure. The resolution function correction applied to the neutron diffraction data is also described. Next, in Section 4, the neutron and x-ray diffraction results for the glass and liquid are presented, and the results obtained from the RMC models are compared to those obtained from previous RMC work in which the full set of partial structure factors were measured by using neutron diffraction with isotope substitution (NDIS) for the glass at 298(1) K and for the liquid at 605(5) K [32]. In Section 5, the results are discussed in terms of the temperature dependence of the structural motifs, bond angle distributions and ring statistics, and also in terms of the Bhatia–Thornton [13] partial structure factors which separate the topological from the chemical ordering. Finally, in Section 6 the conclusions are summarized.

2. Theory

In a neutron or x-ray diffraction experiment on glassy or liquid ZnCl_2 the total structure factor [47]

$$F(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} f_{\alpha}(k) f_{\beta}^*(k) [S_{\alpha\beta}(k) - 1] \quad (1)$$

is measured, where α and β denote the chemical species, c_{α} represents the atomic fraction of chemical species α , $f_{\alpha}(k)$ and $f_{\alpha}^*(k)$ are the form factor (or scattering length) for chemical species α and its complex conjugate, respectively, $S_{\alpha\beta}(k)$ is a Faber–Ziman [48] partial structure factor, and k is the magnitude of the scattering vector. $S_{\alpha\beta}(k)$ is related to the partial pair-distribution function $g_{\alpha\beta}(r)$ via the Fourier transform

$$g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^{\infty} dk k [S_{\alpha\beta}(k) - 1] \sin(kr) \quad (2)$$

where ρ is the atomic number density and r is a distance in real space. The mean coordination number of atoms of type β , contained in a volume defined by two concentric spheres of radii r_i and r_j centered on an atom of type α , is given by

$$\bar{n}_{\alpha}^{\beta} = 4\pi \rho c_{\beta} \int_{r_i}^{r_j} dr r^2 g_{\alpha\beta}(r). \quad (3)$$

The scattering lengths in neutron diffraction are independent of k but the form factors in x-ray diffraction are k -dependent. In order to compensate for this k -dependence, the total structure factor is often rewritten as

$$S(k) - 1 = \frac{F(k)}{|\langle f(k) \rangle|^2} \quad (4)$$

where $\langle f(k) \rangle = c_{\text{Zn}} f_{\text{Zn}}(k) + c_{\text{Cl}} f_{\text{Cl}}(k)$ is the mean form factor. The corresponding real-space information is provided by the total pair-distribution function as obtained from the Fourier transform

$$G(r) - 1 = \frac{1}{2\pi^2 \rho r} \int_0^{\infty} dk k [S(k) - 1] \sin(kr). \quad (5)$$

In the case of x-ray diffraction experiments, the normalization defined by Eq. (4) has the advantage that it allows for a better resolution of the peaks in $G(r)$. For r values smaller than the distance of closest approach between the centers of two atoms $g_{\alpha\beta}(r) = g_{\alpha\beta}(r \rightarrow 0) = 0$ such that $G(r) = G(r \rightarrow 0) = 0$.

The total structure factor can also be written in terms of the Bhatia–Thornton [13] number–number, concentration–concentration and number–concentration partial structure factors denoted by $S_{NN}^{\text{BT}}(k)$, $S_{CC}^{\text{BT}}(k)$ and $S_{NC}^{\text{BT}}(k)$, respectively, where

$$F(k) = |\langle f(k) \rangle|^2 S_{NN}^{\text{BT}}(k) + |f_{\text{Zn}}(k) - f_{\text{Cl}}(k)|^2 S_{CC}^{\text{BT}}(k) + \{ \langle f(k) \rangle [f_{\text{Zn}}(k)^* - f_{\text{Cl}}(k)^*] + \langle f(k) \rangle^* [f_{\text{Zn}}(k) - f_{\text{Cl}}(k)] \} S_{NC}^{\text{BT}}(k) - [c_{\text{Zn}} |f_{\text{Zn}}(k)|^2 + c_{\text{Cl}} |f_{\text{Cl}}(k)|^2]. \quad (6)$$

The $S_{JJ}^{\text{BT}}(k)$ ($I, J = N, C$) and $S_{\alpha\beta}(k)$ ($\alpha, \beta = \text{Zn, Cl}$) partial structure factors are related by the equations

$$S_{NN}^{\text{BT}}(k) = c_{\text{Zn}}^2 S_{\text{ZnZn}}(k) + c_{\text{Cl}}^2 S_{\text{ClCl}}(k) + 2c_{\text{Zn}} c_{\text{Cl}} S_{\text{ZnCl}}(k), \quad (7)$$

$$S_{CC}^{\text{BT}}(k) = c_{\text{Zn}} c_{\text{Cl}} \{ 1 + c_{\text{Zn}} c_{\text{Cl}} [S_{\text{ZnZn}}(k) + S_{\text{ClCl}}(k) - 2S_{\text{ZnCl}}(k)] \}, \quad (8)$$

$$S_{NC}^{\text{BT}}(k) = c_{\text{Zn}} c_{\text{Cl}} \{ c_{\text{Zn}} [S_{\text{ZnZn}}(k) - S_{\text{ZnCl}}(k)] - c_{\text{Cl}} [S_{\text{ClCl}}(k) - S_{\text{ZnCl}}(k)] \}. \quad (9)$$

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