Moments of the Bhatia–Thornton partial pair-distribution functions

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Abstract
Topological versus chemical ordering in disordered binary systems is investigated by using the Bhatia–Thornton formalism. The moments of the partial pair-distribution functions are considered and are related to relevant thermodynamic and other properties of the system. The results are illustrated by using the measured partial-pair distribution functions for the network forming glasses $ZnCl_2$ and $GeSe_2$.

1. Introduction

The formalism of Bhatia and Thornton [1] offers a convenient means of investigating the topological and chemical ordering in binary mixtures [2, 3]. In a neutron diffraction experiment, the measured intensity can be decomposed into its contributions from the so-called number–number, $S_{NN}(k)$, concentration–concentration, $S_{CC}(k)$, and number–concentration, $S_{NC}(k)$, partial structure factors, where k is the magnitude of the scattering vector. These Bhatia–Thornton $S_{IJ}(k)$ (where I, J = N, C) have a simple interpretation in the thermodynamic ($k = 0$) limit, and their Fourier transforms, the partial pair-distribution functions $g_{IJ}(r)$, describe (i) the sites of the scattering nuclei irrespective of the chemical species that occupy those sites ($g_{NN}(r)$), (ii) the chemical ordering ($g_{CC}(r)$), and (iii) the correlation between sites and their occupancy by a given chemical species ($g_{NC}(r)$) [3]. The $g_{IJ}(r)$ may be obtained directly from computer simulation studies (see e.g. [4]) and, in the case of colloidal systems, from three-dimensional fluorescence confocal microscopy [5]. Recently, it has been found that both the topological and chemical ordering in the network forming glasses $ZnCl_2$ and $GeSe_2$ extend to large length scales, up to ≈ 60 Å in the case of $ZnCl_2$ [6]. The object of this paper is to examine the moments of the measured $g_{IJ}(r)$ for these systems and the nature of the information they should reveal. For definiteness it will be assumed that expressions which hold for the liquid phase carry over to the glassy phase.

2. Theory

In a neutron diffraction study on a binary A–X compound, the coherent scattered intensity can be represented by the total structure factor

$$F(k) = \langle b \rangle^2 [S_{NN}(k) - 1] + c_A c_X (b_A - b_X)^2 [S_{CC}(k)/c_A c_X - 1] + 2\langle b \rangle (b_A - b_X) S_{NC}(k)$$

(1)

where c_α, b_α represent the atomic fraction and bound coherent scattering length of chemical species α respectively, and $\langle b \rangle = c_A b_A + c_X b_X$ is the average scattering length. Since $F(k) + \langle b \rangle^2$ is a measured intensity, and must therefore be positive or zero, the $S_{IJ}(k)$ must satisfy the conditions $S_{NN}(k) \geqslant 0$, $S_{CC}(k) \geqslant 0$ and $S_{NN}(k)S_{CC}(k) \geqslant [S_{NC}(k)]^2$ [1]. The number–number partial structure factor is related to the corresponding partial pair-distribution function by the Fourier transform

$$S_{NN}(k) - 1 = \frac{4\pi n_0}{k} \int_0^\infty dr \, [g_{NN}(r) - 1] r \sin(kr)$$

(2)

where n_0 is the atomic number density. Equivalent Fourier transforms relate $[S_{CC}(k)/c_A c_X - 1]$ to $g_{CC}(r)$ and $S_{NC}(k)/c_A c_X$ to $g_{NC}(r)$. In terms of the partial pair-distribution functions for the atomic species A and X,

$$g_{NN}(r) = c_A^2 g_{AA}(r) + c_X^2 g_{XX}(r) + 2c_A c_X g_{AX}(r)$$

(3)

$$g_{CC}(r) = c_A c_X [g_{AA}(r) + g_{XX}(r) - 2g_{AX}(r)]$$

(4)

$$g_{NC}(r) = c_A [g_{AA}(r) - g_{AX}(r)] - c_X [g_{XX}(r) - g_{AX}(r)].$$

(5)

For an ionic A–X system the imposition of overall charge neutrality implies $c_A Z_A + c_X Z_X = 0$, where $Z_\alpha e$ is the charge on an ion of type α. Charge–charge, $S_{ZZ}(k)$, and number–charge, $S_{NZ}(k)$, partial structure factors can then be defined, where $S_{CC}(k) \equiv c_A c_X S_{ZZ}(k)$ and $S_{NC}(k) \equiv (c_X/Z_A)S_{NZ}(k)$.

From equation (2), a series expansion of $\sin(kr)$ leads to the expression

$$S_{NN}(k) - 1 = M_{NN}^{(0)} + M_{NN}^{(2)}k^2 + M_{NN}^{(4)}k^4 + \cdots$$

(6)

where we define the running moments of $[g_{NN}(r) - 1]$ by

$${}^{run}M_{NN}^{(2m)}(r_{max}) = \int_0^{r_{max}} dr \, \rho_{NN}^{(2m)}(r)$$

(7)

and weighted pair-distribution functions by

$$\rho_{NN}^{(2m)}(r) = \frac{4\pi n_0 (-1)^m}{(2m+1)!}[g_{NN}(r) - 1]r^{2m+2}$$

(8)

where $m = 0, 1, 2, \ldots$. Hence the moments $M_{IJ}^{(2m)}$ of equation (6) are obtained by extending r_{max} to infinity in equation (7) and the coefficient of k^{2m} denotes the $(2m + 2)$th moment of $[g_{NN}(r) - 1]$. Equivalent expressions define the running moments ${}^{run}M_{CC}^{(2m)}(r_{max})$ and ${}^{run}M_{NC}^{(2m)}(r_{max})$ and the weighted pair-distribution functions $\rho_{CC}^{(2m)}(r)$ and $\rho_{NC}^{(2m)}(r)$ that correspond to $g_{CC}(r)$ and $g_{NC}(r)$ respectively. Note that this approach does not lead to odd powers of k that can nevertheless occur; for example, dispersion forces for which the pair-potential decays as r^{-6} lead to terms proportional to k^3 in equation (6) [7–9].

The $S_{IJ}(k)$ are readily linked with the thermodynamic properties of a binary system when $k = 0$ [1], namely

$$S_{NN}(0) = n_0 k_B T \kappa_T + \delta^2 S_{CC}(0)$$

(9)

$$S_{CC}(0) = k_B T/(\partial^2 G/\partial c_A^2)_{T,p,N}$$

(10)

$$S_{NC}(0) = -\delta S_{CC}(0)$$

(11)

where k_B, T, p, N are the Boltzmann constant, absolute temperature, pressure and total number of particles respectively, G is the Gibbs free energy per particle, κ_T is the isothermal compressibility, the dilation factor $\delta \equiv n_0(v_A - v_X)$, and v_α is the partial molar volume
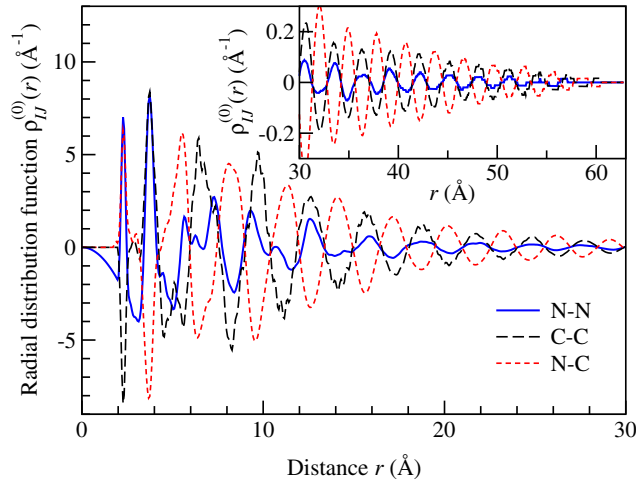
Figure 1. The weighted pair-distribution functions $\rho_{NN}^{(0)}(r) = 4\pi n_0 r^2 [g_{NN}(r) - 1]$ (solid (blue) curve), $\rho_{CC}^{(0)}(r) = 4\pi n_0 r^2 g_{CC}(r)$ (broken (black) curve) and $\rho_{NC}^{(0)}(r) = 4\pi n_0 r^2 g_{NC}(r)$ (dotted (red) curve) for glassy ZnCl$_2$. The inset shows the data at larger distances on an expanded scale.

per particle of chemical species α. For a single-component system, $S_{NN}(k)$ describes the structure since $b_A = b_X$ in equation (1) and $M_{NN}^{(0)} + 1 = S_{NN}(0)$ is given by equation (9) with $\delta = 0$. For an ionic A–X material, the Stillinger–Lovett [10] conditions give (a) $M_{CC}^{(0)} = S_{CC}(0)/c_A c_X - 1 = -1$ such that $S_{CC}(0) = 0$, $M_{NN}^{(0)} + 1 = S_{NN}(0) = n_0 k_B T \kappa_T$ and $M_{NC}^{(0)} = S_{NC}(0)/c_A c_X = 0$, and (b) $M_{CC}^{(2)} = \Lambda_D^2$, where Λ_D is the Debye screening length

$$\Lambda_D^{-2} = \frac{4\pi n_0}{k_B T \epsilon} \sum_\alpha c_\alpha (Z_\alpha e)^2, \tag{12}$$

$\epsilon \equiv 4\pi \epsilon_r \epsilon_0$, ϵ_r is the dimensionless relative dielectric constant and ϵ_0 is the vacuum permittivity. By comparison, if A and X are equally sized spherical particles of identical molar volume and amplitude of thermal motion and if they form a random substitutional alloy wherein there is no energy penalty in interchanging one particle for another then $M_{CC}^{(0)} = 0$, $M_{NN}^{(0)} + 1 = n_0 k_B T \kappa_T$ and $M_{NC}^{(0)} = 0$. Other analytical expressions for the moments can be deduced using simple theories for simple model pair-potentials [8, 11].

3. Results

The $g_{IJ}(r)$ for glassy ZnCl$_2$ were obtained by spline fitting and Fourier transforming the $S_{IJ}(k)$ of [6] after smoothly truncating at $k_{max} = 23.5$ Å^{-1} by using a Lorch function $\mathcal{M}(k) = \sin(\pi k/k_{max})/(\pi k/k_{max})$ [12]. Note that the area under the r-space representation of $\mathcal{M}(k)$ is unity since $\int_{-\infty}^{\infty} dr\, \mathcal{M}(r) = \mathcal{M}(k = 0) = 1$. The resultant $\rho_{IJ}^{(0)}(r)$ are shown in figure 1. The $g_{IJ}(r)$ for glassy GeSe$_2$ were obtained similarly from the $S_{IJ}(k)$ of [13, 14] except that $k_{max} = 15.9$ Å^{-1}. The running second moments, $^{run}M_{IJ}^{(0)}(r_{max})$, are shown in figure 2 and converge at $r_{max} = 60(2)$ Å for glassy ZnCl$_2$ and at $r_{max} = 44(1)$ Å for glassy GeSe$_2$. Hence values for $M_{NN}^{(0)}$, $M_{CC}^{(0)}$ and $M_{NC}^{(0)}$ of $-0.95, -0.98, 0.10$ are obtained for ZnCl$_2$ and $-0.89, -0.90, 0.07$ are obtained for GeSe$_2$ respectively, with an estimated error of ± 0.03. The measured reciprocal space data sets can also be used to obtain the $M_{IJ}^{(0)}$ and $M_{IJ}^{(2)}$ directly by, for example, plotting $[S_{NN}(k) - 1]$ versus k^2 at small-k and fitting a straight line (see equation (6)). Hence
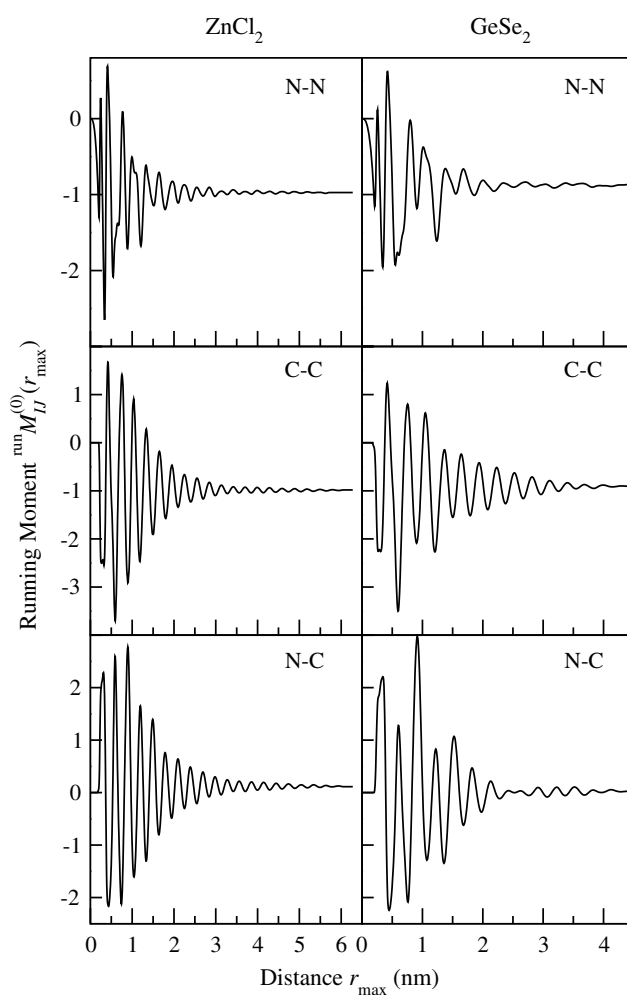
Figure 2. The running second moments of the Bhatia–Thornton partial pair-distribution functions as measured for glassy $ZnCl_2$ and $GeSe_2$.

comparable values for $M_{NN}^{(0)}$, $M_{CC}^{(0)}$ and $M_{NC}^{(0)}$ of $-0.954(6)$, $-0.98(7)$, $0.09(2)$ are found for $ZnCl_2$ and $-0.890(4)$, $-0.89(3)$, $0.05(1)$ are found for $GeSe_2$ respectively. The corresponding values for $M_{NN}^{(2)}$, $M_{CC}^{(2)}$ and $M_{NC}^{(2)}$ are $0.37(2)$, $-0.1(2)$, $0.35(6)$ Å^2 for $ZnCl_2$ and $0.21(2)$, $0.1(1)$, $0.28(3)$ Å^2 for $GeSe_2$ respectively.

4. Discussion

4.1. The second moments $M_{IJ}^{(0)}$

$ZnCl_2$ is usually regarded as a prototypical ionic network forming glass, provided that ion polarization effects are taken into account [15], whereas $GeSe_2$ is a generic covalently bonded network material [13, 14]. For example, $GeSe_2$ shows typical semiconducting behaviour and the ionicity of the A–X bond is 7% for $GeSe_2$ as opposed to 43% for $ZnCl_2$. Furthermore, although the predominant structural motif in glassy $GeSe_2$ is also the $A(X_{1/2})_4$ tetrahedron,

edge-sharing configurations are common and homopolar bonds are a characteristic feature that enables glass formation in the Ge–Se system over a wide composition range. This viewpoint for the interatomic interactions in $ZnCl_2$ and $GeSe_2$ is consistent with the measured $M_{CC}^{(0)}$ values.

Information on the compressibility of glassy $ZnCl_2$ does not appear to be available. However, in the case of glassy $GeSe_2$, longitudinal and transverse sound velocities of $v_L = 2800$ ms^{-1} and $v_T = 1620$ ms^{-1} are estimated from ultrasonic experiments [16] and the mass density $\rho = 4260$ kg m^{-3} [17]. An adiabatic compressibility $\kappa_S = 5.4 \times 10^{-11}$ Pa^{-1} is then obtained by using $\kappa_S^{-1} = \rho[3v_L^2 - 4v_T^2]/3$ [18]. Also, by plotting the molar volume of Ge–Se glasses obtained from density measurements versus c_{Ge} and taking the tangent to the resultant curve at $c_{Ge} = 1/3$ [19], it is found that Ge and Se have equal partial molar volumes at the $GeSe_2$ composition, i.e. $\delta = 0$. Since $\kappa_T \geqslant \kappa_S$ [20] it follows from equations (6) and (9) that $M_{NN}^{(0)} = S_{NN}(0) - 1 \geqslant -0.993$, in keeping with the neutron diffraction results. Incidentally, the density data of [21] give partial molar volumes of $v_{Ge} = 16.3(8)$ Å^3 and $v_{Se} = 40.0(8)$ Å^3 for the liquid phase of $GeSe_2$ at 750 °C such that $\delta = -0.74(4)$.

4.2. The fourth moments $M_{IJ}^{(2)}$

For an ionic system, $M_{CC}^{(2)} = \Lambda_D^2$ where Λ_D is given by equation (12). At frequencies that are high relative to lattice vibrational energies but low compared with atomic excitation frequencies, the electronic polarizability will provide the dominant contribution to the dielectric constant. In equation (12), ϵ_r is often set to this 'high-frequency' electronic dielectric constant ϵ_∞ [8] which can usually be obtained by measuring the refractive index, n, of the medium at optical frequencies where $n^2 = \epsilon_\infty$ [22]. For an isotropic medium or cubic lattice, the Clausius–Mossotti relation gives

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3} n_0 \sum_\alpha c_\alpha P_\alpha \qquad (13)$$

where P_α is the polarizability of chemical species α.

For $ZnCl_2$, $P(Zn^{2+}) \approx 0.74$ Å^3, $P(Cl^-) \approx 2.96$ Å^3 [23] and for the glass at room temperature $n_0 = 0.0359(1)$ Å^{-3} [24]. Use of equation (13) then gives $n = 1.584$. By comparison, the refractive index of liquid $ZnCl_2$ at 320 °C measured using light of wavelength 0.5461 μm is 1.588(1) [25] and for the crystalline solid at a wavelength of 0.5893 μm values of $n = 1.687$ and 1.713 are quoted [26]. Hence Λ_D^2 is in the range 0.0050–0.0058 Å^2 or $\Lambda_D \approx 0.070$–0.076 Å for glassy $ZnCl_2$. Comparable Debye screening lengths are found for the molten alkali halides near freezing [8]. For glassy $GeSe_2$ at room temperature, $n_0 = 0.0334(1)$ Å^{-3} [17] and the refractive index measured using light of wavelength 10 μm is 2.345 [27] such that $\Lambda_D^2 = 0.012$ Å^2 or $\Lambda_D = 0.108$ Å. The Clausius–Mossotti relation yields $n = 2.33$ if $P(Ge^{4+}) = 0.60$ Å^3 [28] and $P(Se^{2-}) = 6.1$ Å^3, the latter being at the lower end of the range of polarizabilities quoted for Se^{2-} [26]. For both glasses, the measured $M_{CC}^{(2)}$ and calculated Λ_D^2 values are in agreement within the experimental error, although $GeSe_2$ is not considered to be an ionic material.

5. Conclusion

The running moments $^{run}M_{IJ}^{(0)}(r_{max})$ of the measured Bhatia–Thornton $g_{IJ}(r)$ for glassy $ZnCl_2$ and $GeSe_2$ confirm that the ordering in these materials extends to large distances of about 60(2) and 44(1) Å respectively [6]. However, the measured moments, $M_{IJ}^{(2m)}$, are sensitive to the details of the partial structure factors at small-k and new small-angle neutron scattering

experiments, employing the method of isotopic substitution, are necessary to improve the accuracy. Nevertheless, the manner in which the running moments converge may give some insight into the structure of these materials. The general results should also prove useful for deducing parameters such as Λ_D directly from calculated $g_{IJ}(r)$ [29] and for analysing the $g_{IJ}(r)$ measured for colloidal systems using confocal microscopy [5] once equations (9)–(11) are rewritten in terms of appropriate thermodynamic functions.

Acknowledgments

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