Partial structures and compressibilities of ions in fused potassium bromide

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Abstract. Treating the coulomb interaction between ion species as a perturbation on the Waisman-Lebowitz solution for direct correlation function within the hard core region, the total direct correlation function in K–space has been formulated, which gives a direct method of evaluating the partial structure factors between different ion species of the fused salts through the use of Pearson-Rushbrooke equations. The partial structure factors so obtained have been applied to evaluate the partial radial distribution functions of ion pairs. In addition, many other important associated functions such as the static correlations of total number, mass and charge densities have been computed by particular linear combination of partial structure factors. The charge neutrality relate the partial structure factors to the isothermal compressibility for the wavevector $K \to 0$ and hence the evaluation of the compressibilities of ions in fused KBr is possible, which agrees well with the observed value. As such the present method is very useful in investigating the structure of molten salts since only the parameters σ_{ij}, the distances of closest approach between ions and ε, the effective dielectric constant (which can be estimated from the literature) are enough for this work.

1. Introduction

Basic interest in correlations in ionic melts arises from their nature as a dense liquid of charged atomic constituents. Work on the correlation in fused salts has so far been focussed on the determination of static pair correlation functions. Work is being done extensively through the use of x–ray, neutron diffraction and computer simulation studies (Rhodes 1972; Page and Mika 1971; Woodcock and Singer 1971; Tosi and Fumi 1964; Dixon and Sangster 1976; Enderby and Neilson 1980; Derrien and Dupuy 1975) to unravel the correlations between the various ion pairs in molten salts. It has been acknowledged by various workers (Rhodes 1972; Edwards *et al* 1975) that the simulation studies and even the x-ray diffraction or neutron scattering technique cannot resolve the correlations between the various ion-pairs.

This paper will be exclusively concerned with the evaluation of the partial static structure factors of the molten potassium bromide (KBr) in a purely analytical way so as to decipher the structural features of the melt. The three partial structure factors in the limit $K \to 0$ are equal in magnitude and are connected with the isothermal compressibility (χ_T) through the compressibility sum rule equation, which enable us to evaluate the isothermal compressibility of the concerned fused salt. Then we will focus our attention on the particular linear combinations of the partial structure factors,

which correspond to the correlations between total number, mass and charge densities respectively. In addition, the partial structure functions (PSF) so evaluated are utilised to compute the partial pair distribution functions between the ion species. The present method yields quite satisfactory results. In this connection it may be pointed out that the determination of PSF is not easy since it involves complete enrichment of an atom of the salt with a particular species of isotope which is not always possible. This is necessary because three sets of results are needed for evaluating the three partial structures.

2. Formulation of the method

Waisman-Lebowitz (WL) (Waisman and Lebowitz 1972a, b) solution for the direct correlation function (DCF) leads to the formulation of the present important method. According to them, the DCF within the region of hard core for the molten salt can be written as follows:

$$C_{ij}^{WL}(r) = [C_s(r)]_{ij}^{WT} - \frac{\beta' Q_i Q_j}{\varepsilon \sigma_{ij}} \left[2B_{ij} - \frac{rB_{ij}^2}{\sigma_{ij}} \right], \quad \text{for } r \leq \sigma_{ij} \tag{1}$$

whereas the DCF outside the hard core region is simply the mean spherical model (MSM) approximation given by Lebowitz and Percus (1966) as follows:

$$C_{ij}(r) = \frac{\beta' Q_i Q_j}{\varepsilon} (1/r), \quad \text{for } r > \sigma_{ij}, \tag{2}$$

where Q_i, Q_j are the charges of ions i and j; ε is the effective dielectric constant of the fused salt; β' is the reciprocal of $K_B T$ with K_B as the Boltzmann constant and T, the working temperature and σ_{ij} are the equilibrium distances of approach between two ions.

$$B_{ij} = \frac{1}{\xi} [1 + \xi - (1 + 2\xi)^{1/2}]. \tag{3}$$

$$= K_D \sigma. \tag{4}$$

$$K_D^2 = \frac{4\pi}{K_B T \varepsilon} \sum_i \rho_i q_i^2. \tag{5}$$

Here ρ_1 and ρ_2 are the number densities of the ith and jth type of ions. In uni-univalent salts $\rho_1 = \rho_2 = \rho$ and $(C_s(r))_{ij}^{WT}$ is Percus-Yevick solution obtained by Wertheim and Thiele, the details of which are discussed in the next paragraph.

At this juncture however it is important to point out that (1) was originally derived for ions of equal size. For ions of unequal size seven parameters enter into the calculation (Waisman and Lebowitz 1972a, b). Moreover some approximations have to be made with respect to the dielectric constant (ε). Hence a search is felt necessary for numerical computation of partial structure function ($S_{ij}(K)$) with less parameters and arbitrary assumptions for ions of approximately equal radii. Some preliminary calculations have revealed that the primary form of the direct correlation functions (DCF) for primitive model electrolytes as derived by Waisman-Lebowitz does not change if the ionic diameters are not differing by about 50% or so. Waisman-Lebowitz

(WL) perturbed the hard sphere potential and obtained the direct correlation function $C_{ij}^{WL}(r)$, inside the core σ_{ij} following essentially the technique developed by Wertheim and obtained (1).

In (1) $(C_s(r))_{ij}^{WT}$ as already stated is the well-known Wertheim-Thiele solution of neutral hard spheres and can be written as

$$C_s(r)_{ij}^{WT} = \alpha - \beta (r/\sigma) + \gamma(r/\sigma)^3, \tag{6}$$

where
$$\alpha = -\frac{(1+2\eta)^2}{(1-\eta)^4}, \tag{7}$$

$$\beta = -\frac{6\eta(1+\eta/2)^2}{(1-\eta)^4}, \tag{8}$$

and
$$\gamma = -\eta/2 \frac{(1+2\eta)^2}{(1-\eta)^4}, \tag{9}$$

with
$$\eta = \frac{\pi\rho\sigma^3}{6} \text{ and } N/V = \rho. \tag{10}$$

Now perturbing the hard-sphere potential outside the core WL obtained (1) for $C_{ij}(r)$ inside the core σ_{ij} and this equation can be rearranged as

$$C_{ij}^{WL}(r) = \alpha_1 - \beta_1(r/\sigma) + \gamma(r/\sigma)^3, \quad r \leqslant \sigma \tag{11}$$

where
$$\alpha_1 = \alpha - 2K, \tag{12}$$

$$\beta_1 = -6\eta \frac{(1+\eta/2)^2}{(1-\eta)^4} + KB_{ij}, \tag{13}$$

$$K = \frac{Q_i Q_j B_{ij}}{K_B T \varepsilon \sigma_{ij}}. \tag{14}$$

Thus one immediately sees that the form $C_{ij}^{WT}(r)$ and $C_{ij}^{WL}(r)$ in (6) and (11) is alike. Thus no quadratic or any such terms of r enter into $C_{ij}(r)$ inside the core. Only the constants α and β (which are functions of the packing fraction and hence of σ_{ij}) change to α_1 and β_1. Hence we believe that as long as the perturbation is the same *i.e.* coulombic in nature the form of $C_{ij}(r)$ remain the same inside the charged hard sphere. *Hence we put forward the working hypothesis that the form of $C_{ij}(r)$ does not change in spite of different ion sizes.* Only the constant term and the coefficient of r and r^3 change. This is confirmed by the fact that by suitably choosing σ thereby changing η and hence the constant term and the coefficients of r and r^3, good agreement between calculated and experimental $S_{ij}(K)$ curves can be achieved.

Further recent studies of Harada *et al* (1982) have shown that the ion size ratio if it varies between $0.75 < (\sigma_+/\sigma_-) < 1.5$ the configuration integral does not change and hence the present working hypothesis that by a suitable choice of σ_{ij} one can obtain satisfactory $S_{ij}(K)$ curves with (1).

We therefore write the DCF as

$$C_{ij}(r) = C_{ij}^{WL}(r) \qquad r \leqslant \sigma_{ij}$$

as given by (1) and outside the core we use (2). Hence the total direct correlation

function in K-space can be obtained through the following equation:

$$\hat{C}_{ij}(K) = \frac{4\pi}{K} \int_0^{\sigma_{ij}} r \cdot \sin Kr \cdot \left[\{C_s(r)\}_{ij}^{WT} - \frac{\beta' Q_i Q_j}{\varepsilon \sigma_{ij}} \left(2B_{ij} - \frac{rB_{ij}}{\sigma_{ij}} \right)^2 \right] dr$$

$$+ \frac{4\pi}{K} \int_{\sigma_{ij}}^{\infty} \frac{\beta' Q_i Q_j}{\varepsilon} (1/r) \cdot r \sin Kr \, dr. \tag{16}$$

After simplification and multiplying with the factor ρ on both sides of (16) one can immediately write the exact form of $C_{ij}(K)$ as follows:

$$\hat{C}_{ij}(K) = 24\eta_{ij}(\alpha)_{ij} \left[(K\sigma_{ij}\cos K\sigma_{ij} - \sin K\sigma_{ij})/K^3\sigma_{ij}^3 \right]$$

$$+ 24\eta_{ij}\beta_{ij} \left[(K^2\sigma_{ij}^2 \cos K\sigma_{ij} - 2K\sigma_{ij}\sin K\sigma_{ij} \right.$$

$$- 2\cos K\sigma_{ij} + 2)/K^4\sigma_{ij}^4 \right] + 24\eta_{ij}\gamma_{ij} \left[(K^4\sigma_{ij}^4 \cos K\sigma_{ij} \right.$$

$$- 4K^3\sigma_{ij}^3 \sin K\sigma_{ij} - 12K^2\sigma_{ij}^2 \cos K\sigma_{ij}$$

$$+ 24K\sigma_{ij}\sin K\sigma_{ij} + 24\cos K\sigma_{ij} - 24)/K^6\sigma_{ij}^6 \right]$$

$$+ \frac{4\eta_{ij}\beta'(Q_i Q_j)}{\varepsilon} \times B_{ij}^2/\sigma_{ij} \left[12\cos K\sigma_{ij}/K^4\sigma_{ij}^4 - 12/K^4\sigma_{ij}^4 \right.$$

$$+ 12\sin K\sigma_{ij}/K^3\sigma_{ij}^3 - 6\cos K\sigma_{ij}/K^2\sigma_{ij}^2 \right] + 48\eta_{ij}\left(\frac{Q_i Q_j \beta'}{\varepsilon} \right)$$

$$\times (B_{ij}/\sigma_{ij}) \left[\cos K\sigma_{ij}/K^2\sigma_{ij}^2 - \sin K\sigma_{ij}/K^3\sigma_{ij}^3 \right]$$

$$- 24\eta_{ij}(Q_i Q_j \beta'/\varepsilon) \times \frac{1}{\sigma_{ij}} (\cos K\sigma_{ij}/K^2\sigma_{ij}^2), \tag{17}$$

where
$$\alpha_{ij} \equiv -\frac{(1 + 2\eta_{ij})^2}{(1 - \eta_{ij})^4}, \tag{18}$$

and
$$\gamma_{ij} \equiv -\frac{\eta_{ij}}{2} \frac{(1 + 2\eta_{ij})^2}{(1 - \eta_{ij})^4}. \tag{19}$$

$$\beta_{ij} \equiv -6\eta_{ij}(1 + \eta_{ij}/2)^2 (1 - \eta_{ij})^{-4}$$

and $K = $ wavevector (Å^{-1}).

Then the partial structure functions can be computed through the use of the Pearson-Rushbrooke equations (Abramo *et al* 1977)

$$S_{ii}(K) = \frac{1 - \rho C_{ij}(K)}{[1 - \rho C_{11}(K)][1 - \rho C_{22}(K)] - \rho^2 C_{12}^2(K)}, i = 1, 2 \tag{20}$$

$$S_{12}(K) = \frac{C_{12}(K)}{[1 - \rho C_{11}(K)][1 - \rho C_{22}(K)] - \rho^2 C_{12}^2(K)}. \tag{21}$$

Here '1' and '2' correspond to K^+ and Br^- ions respectively. Thus the present method gives an expression for $\rho C_{ij}(K)$ involving the parameters σ_{ij} and ε, which yields a direct method of evaluating the partial structure functions $[S_{ij}(K)]$ in an analytical way. The parameters have been determined by fitting (20) and (21) with the available values of the partial structure functions at the first maximum or at the first minimum. The partial

structure functions determined from the Pearson-Rushbrooke equations are shown in figure 1a, b.

The partial radial distribution functions between ion pairs can be obtained from the partial structure factors $[S_{ij}(K)]$ through Fourier inversion using the well-known equation (Bhuiyan 1979):

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2 r (\rho_i \rho_j)^{1/2}} \int_0^\infty [S_{ij}(K) - \delta_{ij}] K \sin Kr \, dK, \tag{22}$$

where δ_{ij} is the Kronecker delta. The $[g_{ij}(r)]$ so computed are given in figure 2. The other structure factors can also be calculated through particular combination of the partial structure functions. In particular, the charge, mass and number correlation structure factors are defined as follows (Adams *et al* 1977; Simon *et al* 1978).

$$S^{QQ}(K) = \frac{1}{2}(S_{11}(K) + S_{22}(K) - 2S_{12}(K)), \tag{23}$$

$$S^{MM}(K) = 1/m^2 [m_+^2 S_{11}(K) + m_-^2 S_{22}(K) + 2m^2 S_{12}(K)], \tag{24}$$

and $$S^{NN}(K) = \frac{1}{2}(S_{11}(K) + S_{22}(K) + 2S_{12}(K)), \tag{25}$$

where $m = (m_+ m_-)^{1/2}$ with m_+ and m_- as the masses of the potassium ion and bromide ion respectively. The $S^{NN}(K)$, $S^{QQ}(K)$ and $S^{MM}(K)$ so computed are shown in figures 3-5, respectively.

The behaviour of $S_{ij}(K)$ in the long wave limit is related with the isothermal compressibility (χ_T) of the fused potassium bromide (KBr) through the well-known compressibility sum rule equation (Bhuiyan 1979)

$$\lim_{K \to 0} S_{ij}(K) = \rho K_B T \chi_T. \tag{26}$$

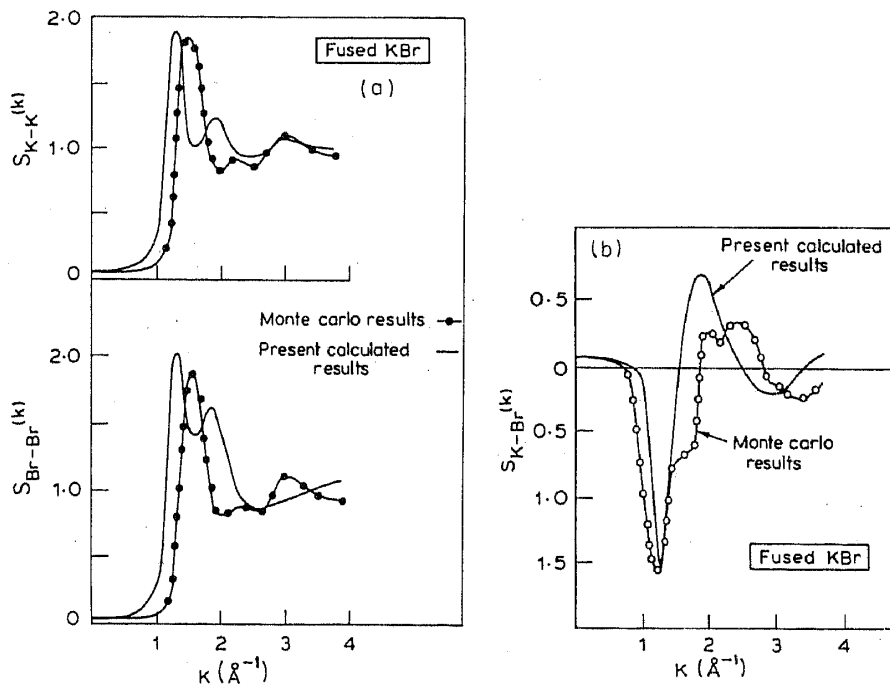**Figure 1a.** Partial structures of: (i) potassium–potassium (ii) bromide–bromide.
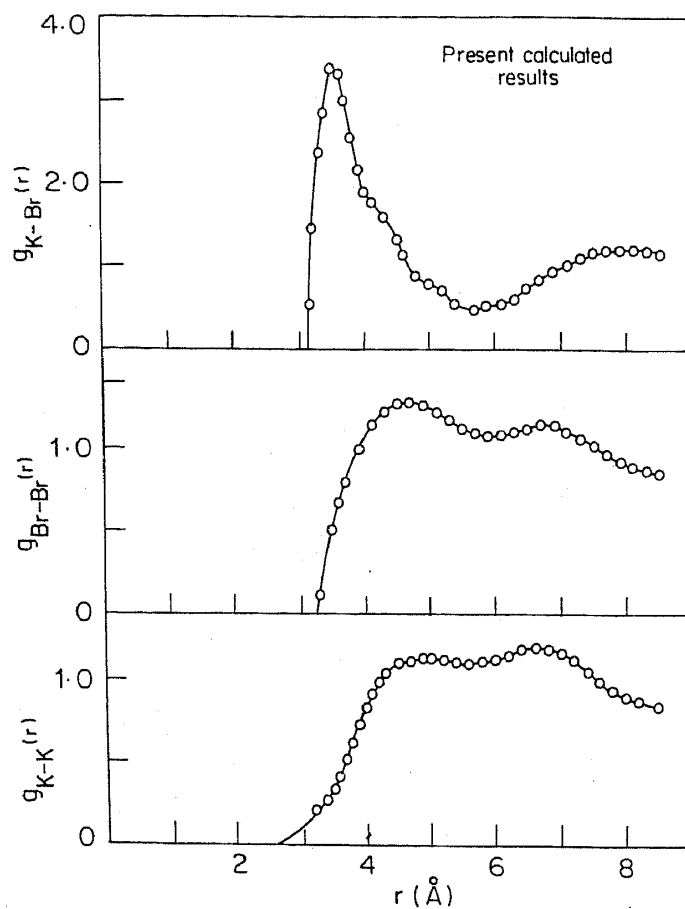**Figure 1b.** Partial structures of: potassium–bromide.

Figure 2. Partial radial distribution functions of: (a) potassium–bromide (b) bromide–bromide (c) potassium–potassium.
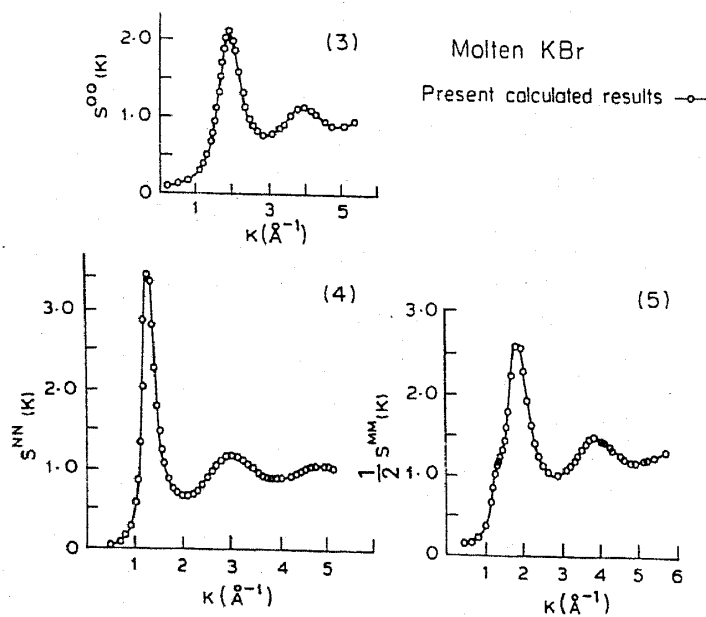

Figure 3. Charge–charge structure function.
Figure 4. Number–number structure function.
Figure 5. Mass–mass structure function.

The Fourier transform of the direct correlation functions $[C_{ij}(K)]$ computed with the parameters σ_{ij} and ε are shown in figure 6. The parameters σ_{ij} and ε are presented in table 1 along with the present calculated compressibility (χ_T) and other input data used in the computation. Table 2 gives the structural features of the pair distribution functions $[g_{ij}(r)]$ of the potassium bromide melt. The structural details of $S^{QQ}(K)$, $S^{NN}(K)$ and $S^{MM}(K)$ are presented in table 3.
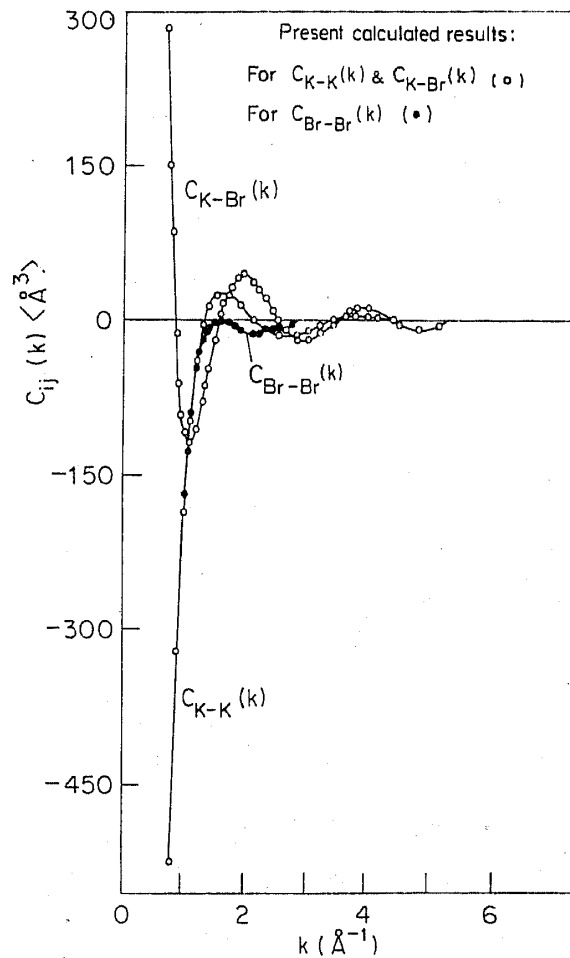

Figure 6. Partial direct correlation functions of (a) $C_{K-K}(K)$ (b) $C_{Br-Br}(K)$ (c) $C_{K-Br}(K)$.

Table 1. Molecular parameters, other input data and compressibility.

$\sigma_{Kr\text{-}Kr}$ (Å)	$\sigma_{Br\text{-}Br}$ (Å)	$\sigma_{K\text{-}Br}$ (Å)	Temperature (°K)	Dielectric constant (ε)	Number density (ρ) $(10^{24}\,cm^{-3})$	Present calculated $\chi_T(10^{-12}$ $cm^2/dyne)$	Observed χ_T $(10^{-12}\,cm^2/$ dyne)
2·5	3·75	3·25	1003	2·8	0·01078	32	38

Table 2. Structural features of the pair distribution function $[g_{ij}(r)]$.

	$g_{11}(r)$ (Å)		$g_{12}(r)$ (Å)		$g_{22}(r)$ (Å)	
	Position of first					
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
Present calculated results	5·0	5·6	3·5	5·6	4·7	6·0
Monte-Carlo results	4·8	—	3·2	—	4·8	—

Table 3. Structural details of $S^{QQ}(K)$, $S^{NN}(K)$ and $S^{MM}(K)$.

	First maximum		First minimum	
	Position KÅ^{-1}	Height	Position KÅ^{-1}	Height
$S^{QQ}(K)$	1·25	6·88	2·05	1·36
$S^{NN}(K)$	1·85	4·12	2·85	1·58
$S^{MM}(K)$	1·85	5·23	2·80	2·00

3. Results and discussion

In figure 1a, b we have compared the present calculated results of the partial structure functions $[S_{ij}(K)]$ with the values obtained through Fourier inversion of the partial pair correlation functions $[g_{ij}(r)]$ determined by (Lewis *et al* 1975) using the Monte-Carlo (MC) method. In our present calculated results there is shift in positions of the main peaks of the structure factor curves with reference to the MC results. It is worthwhile to mention that there is good agreement between the present compressibility (χ_T) calculated through the present extrapolated values of $S_{ij}(0)$ using (26) and the observed χ_T value (Abramo *et al* 1973). An exactly similar method has been applied to fused NaCl and RbBr (Rao and Pal 1984) and the results obtained were promising and satisfactory. Moreover the values of all the $S_{ij}(K)$ in the limit $K \to 0$ are nearly equal which supports the compressibility sum rule equation. In addition, the overall charge neutrality of the system ensures that $\lim_{K \to 0} S^{QQ}(K) = 0$. Because of the opposing phases of the 'like' and 'unlike' structure factors, $S^{QQ}(K)$ has a very pronounced first peak whereas $S^{NN}(K)$ displays very little structure with a weak main peak for the same reason. The pair distribution functions $[g_{ij}(r)]$ of the fused potassium bromide agree favourably well with the MC results presented by Abramo *et al* (1973). It is gratifying to note that the σ_{ij} and ε values obtained through the present method are comparable to those available in literature (Janz 1967). Thus it can be inferred that the present method constitutes an important and simpler method in evaluating the static structure functions and associated correlation function.

It is important to point out that with the present working hypothesis we give a method to compute $S_{ij}(K)$ even when sufficient data is not available. WL defined the parameter a_{ij} (Waisman and Lebowitz 1972a, b) as

$$a_{ij} = 1 - 4\pi\Sigma\rho_i \int_0^{(\sigma_{11}+\sigma_{22})/2} r^2\,dr \left[C_{ij}(r) + \frac{Q_i Q_j}{K_B Tr\varepsilon} \right]. \qquad (27)$$

These are in fact related to the partial molar volumes V_j by

$$a_j = V_j/K_B T\chi_T\varepsilon. \qquad (28)$$

Choosing σ_{ij} and ε around literature values along with the appropriate $C_{ij}(r)$ as given by (17) it should be possible to evaluate through (27) a_j values which in turn are related to $S(0)$ as

$$S(0) = (a_1 + a_2)^{-1}. \qquad (29)$$

Hence a set of σ_{ij}'s may be scanned to give the correct $S(0)$. Further the σ_{ij} along with Pearson-Rushbrooke partial structures should produce equal $S_{ij}(0)$ for 1–1 type electrolyte.

We also have another important relation for 1–1 type electrolyte

$$\lim_{K\to 0} \left[C_{11}(K) = C_{22}(K) = -C_{12}(K) \right],$$

which should be satisfied simultaneously. This is exactly seen to be the case by taking a quick glance of figure 6 regarding $C_{K-K}(r)$ and $C_{Ba-Br}(r)$ at low K values. All these tests confirm the proper choice of σ_{ij} which can then be used to evaluate partial structure functions.

3. Conclusions

It is satisfying to note that there is a general agreement of the present calculations, the structural information obtained from this method as well as the compressibility value. This is important if we remember that the partial structures as determined from experiment need not be taken as accurate because of the experimental difficulties.

Acknowledgement

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