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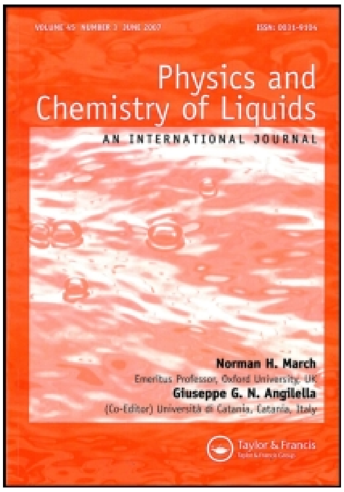

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Model and Experimental Direct Correlation Functions in Dense Charged Fluids

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LETTER

Model and Experimental Direct Correlation Functions in Dense Charged Fluids

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The Pearson–Rushbrooke relations are used to calculate partial direct correlation functions $c_{ij}(r)$ for:

a) A neutral mixture of point ions and charged hard spheres, using the mean spherical approximation;
b) Molten RbCl just above the freezing point, from diffraction data.

Some common features emerge from (a) and (b). The relevance of (b) to extraction of pair potentials is stressed.

KEY WORDS: Direct correlation function, molten salts, mean spherical approximation.

One of us (SAE)[1] has been concerned with the use of electron gas potentials for certain ionic crystals[2]. Presently, however, it is difficult to quantify the accuracy of such electron theory force laws. Therefore, the present work makes a modest start on a programme of generalizing the inversion of experimental structural data[3] for mainly monatomic liquid metals[4] to a binary ionic melt, namely RbCl, for which structural data is already available[5,6].

Experience on liquid metals has highlighted the importance of having measured structural data which is sufficiently refined to allow calculation of the direct correlation function $c(r)$ over a substantial range of r. Therefore, the focus of the present work is to demonstrate in molten RbCl just above the freezing point how well the three partial direct correlation functions $c_{ij}(r)$ are determined by the diffraction data, plus the basic physics associated with long-range Coulomb interactions.

The main tool to be employed stems from the Pearson-Rushbrooke relations[7] for $c_{ij}(r)$. However, before inputting diffraction data for RbCl into these relations, it is instructive to use them in conjunction with a simple model of a mixture of point ions and charged hard spheres. The structural features of this model have been studied previously by Gillan *et al*[8]. This study employed both the mean spherical approximation (MSA), which relates the c_{ij}'s to the pair potentials $\phi_{ij}(r)$ outside a core

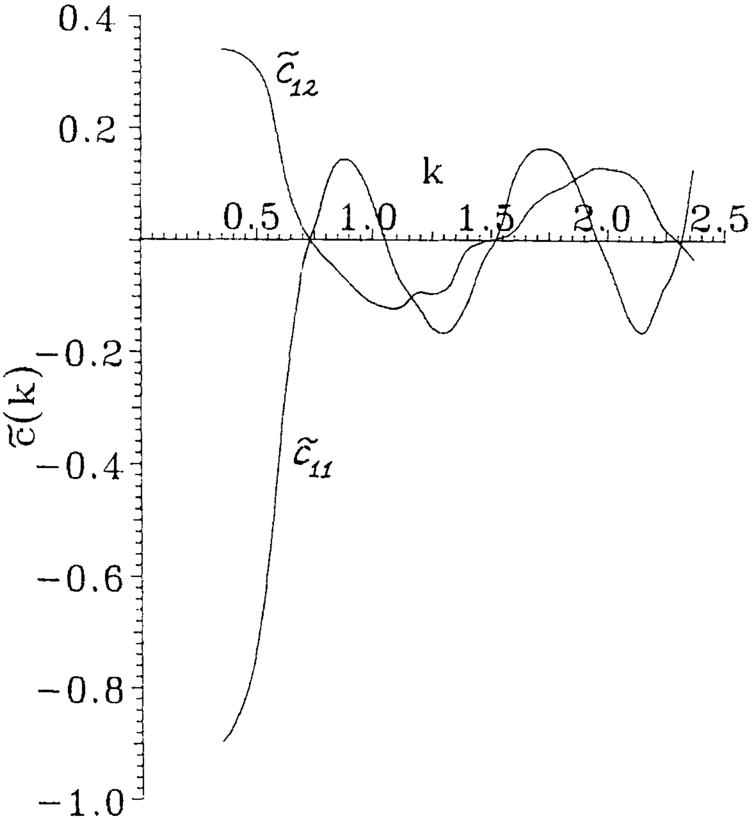

Figure 1 MSA k space forms of direct correlation functions for point ion—hard sphere model. Point ion–point ion correlation function, being proportional to k^{-2} in MSA, is not depicted.

radius by

$$c_{ij}(r) = -\frac{\phi_{ij}(r)}{k_B T}, \tag{1}$$

and, in the extreme strong coupling regime, Monte Carlo computer simulation. Below, to expose some features of the c_{ij}'s we shall be content to use the MSA results. Before presenting the c_{ij}'s for this model, we emphasize that the point ion limit is only quantitatively useful when there is a substantial difference between the ionic radii involved. This is true for CuCl, studied experimentally by Page and Mika[9], where the copper ion has about half the diameter of the chloride ion. Figure 1 shows the hard sphere—hard sphere correlation function $\tilde{c}_{11}(k)$ for the point ion—charged hard sphere model, together with the cross-correlation function $\tilde{c}_{12}(k)$. We merely note at this point the oscillatory character of these 'model' partial direct correlation functions.

With the above model designed to provide a preliminary orientation, we turn

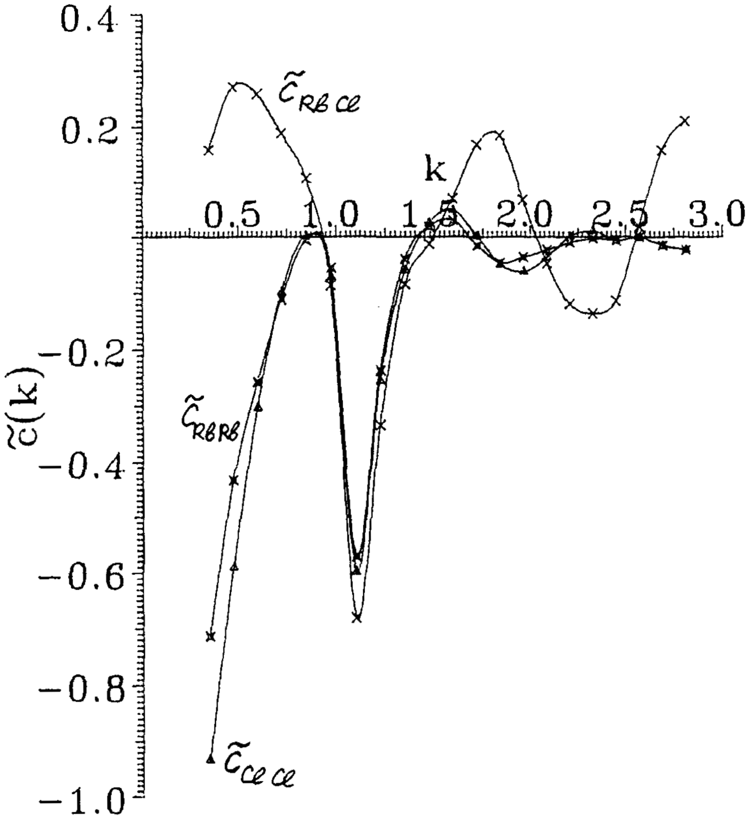

Figure 2 Similar to Figure 1, but now for molten RbCl just above freezing: derived from measured structure factors via Pearson–Rushbrooke relations.

immediately to discuss the results in Figure 2. These have been obtained from the tabulated partial structure factors $S_{ij}(k)$ in Ref. 6, kindly supplied to us by Dr. R. McGreevy. From this diffraction data, the Pearson–Rushbrooke relations were employed in k space to calculate the three $\tilde{c}_{ij}(k)$* which are displayed in Figure 2:

$$c_{12}(k) = \frac{S_{12}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}, \qquad c_{ii} = 1 - \frac{S_{jj}(k)}{S_{11}(k)S_{22}(k) - S_{12}^2(k)}, \tag{2}$$
$$i = 1 \Leftrightarrow j = 2$$

These functions were then Fourier transformed numerically to obtain the **r** space forms shown in Figure 3.

We note immediately the close resemblance of $c_{\mathrm{Rb-Rb}}(r) \equiv c_{11}(r)$ and $c_{\mathrm{Cl-Cl}}(r) \equiv c_{22}(r)$, due to the rather similar ionic radii of Rb^+ and Cl^-. As in Figure 1 (for $\tilde{c}_{11}(k)$

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* $\tilde{c}_{ij}(k)$ and $c_{ij}(k)$ are related precisely by Eq. (3).

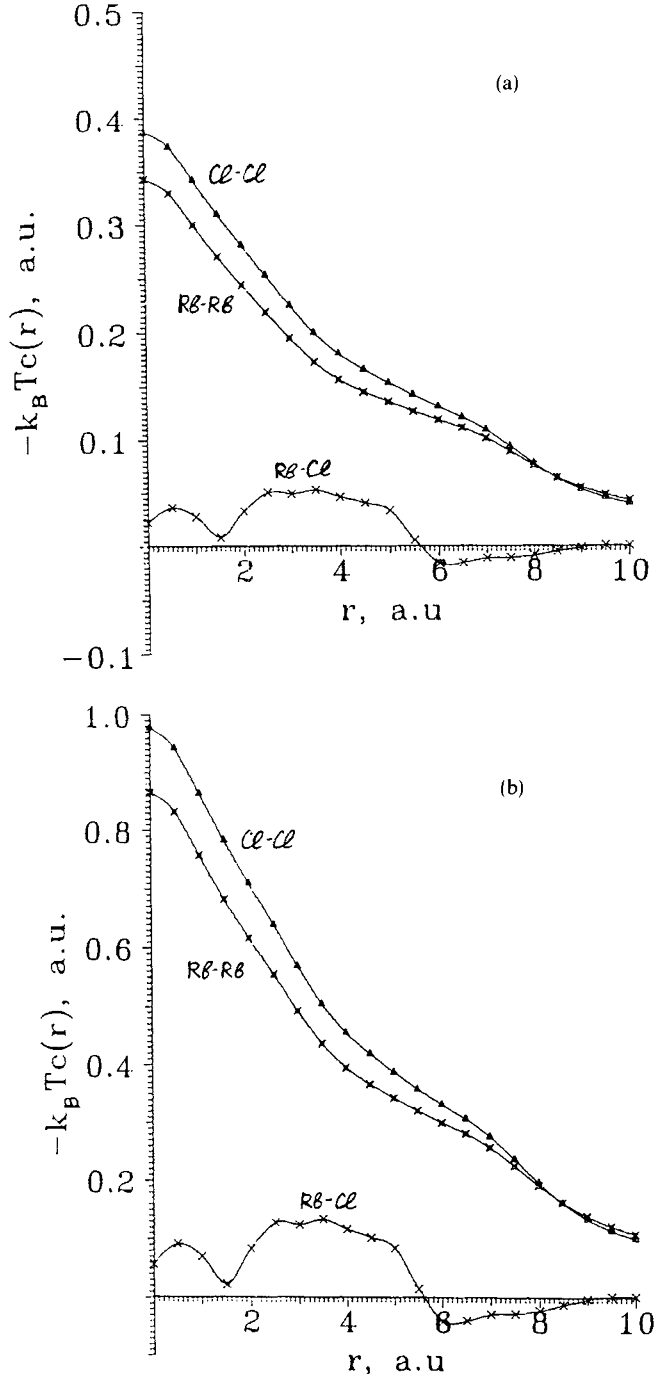

Figure 3 r space forms of $c_{ij}(r)$ from Fourier transform of Figure 2. (a) Without Coulomb restriction; (b) With Coulomb restriction. (Quantity actually plotted is $-k_BTc_{ij}(r)$: compare Eq. (1)).

and $\tilde{c}_{12}(k)$) oscillations are in evidence in the empirically derived $\tilde{c}_{11}(k)$ and $\tilde{c}_{12}(k)$ for RbCl. In **r** space, the cross-correlation function $c_{12}(r)$ is numerically smaller.

In a little more detail, Figure 3(a) was constructed simply from the measured data, without any attempt to incorporate further physics associated with long-range Coulomb interactions. As a second step, therefore, let us return to the asymptotic result (1), valid for large r, and note that in Fourier transform therefore, with $\phi_{ij}(r) \sim \pm(e^2/r)$ in RbCl, again, of course, asymptotically:

$$\tilde{c}_{ij}(k) = \mp \frac{k_B T c_{ij}(k)}{4\pi e^2 k^2 \sqrt{\rho_i \rho_j}}, \quad k \to 0 \tag{3}$$

Thus we have next imposed on the $\tilde{c}_{ij}(k)$'s derived from the diffraction data that $k^2\tilde{c}_{ij}(k)$ tends to a constant, where the constants in this relation are known from Eq. (3). Figure 3(b) has been constructed: though the general shape of the $c_{ij}(r)$'s remains intact, it will be noted that major quantitative changes result for small r. This might

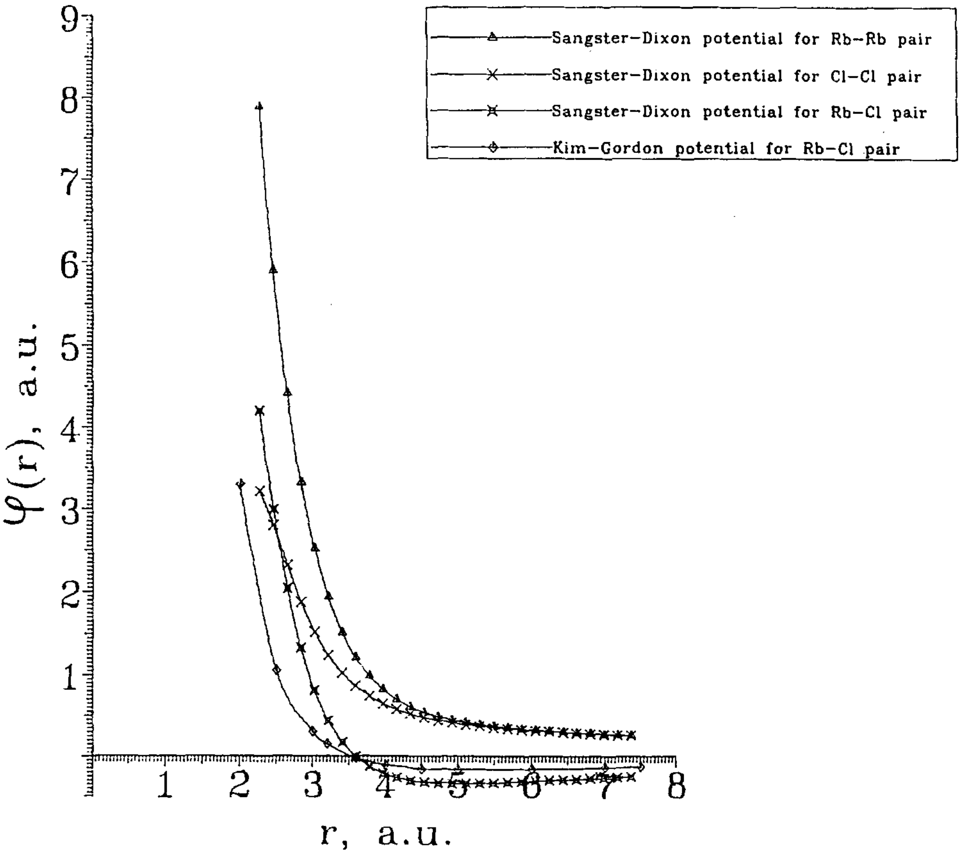

Figure 4 Electron gas and semi-empirical potentials $\phi(r)$ for RbCl.

seem, at first sight, to be surprising, since the modifications in Eq. (3) alter merely the small k behaviour. However, it should be borne in mind that $c_{ij}(r = 0)$ involves an integral over all k, and clearly this integral must be influenced appreciably by enforcing the small k behaviour (3) on the data.

Because of the quantitative differences between Figures 3(a) and 3(b), it would be premature to attempt to invert these $c_{ij}(r)$'s to derive the pair potentials $\phi_{ij}(r)$ at this stage. Before accuracy comparable with that achieved by the inversion by Reatto *et al*[10,4] of the structural data for liquid Na near melting, more systematic small-angle scattering data will be needed on molten RbCl. Given this, then a proper quantitative test of electron gas potentials[2], in comparison with semi-empirical potentials such as were used by Sangster and Dixon[11] in their computer simulation of RbCl should be entirely feasible (see Figure 4). In this context, and bearing in mind Eq. (1), we might have anticipated some agreement between $-k_B T c_{\mathrm{Rb-Cl}}(r)$ at large r, and $\phi_{\mathrm{Rb-Cl}}(r)$. This is not the case with either the electron gas potential[2] or the semiempirical potential of Sangster and Dixon. This cautions that one may have to go out to $r \sim 15$ atomic units, for $c_{\mathrm{Rb-Cl}}(r)$, before the asymptotic result (1) takes over. In contrast, for $c_{\mathrm{Rb-Rb}}(r)$ and $c_{\mathrm{Cl-Cl}}(r)$, the Coulomb tail is already in the evidence in the range of the plots in Figure 3(b).

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