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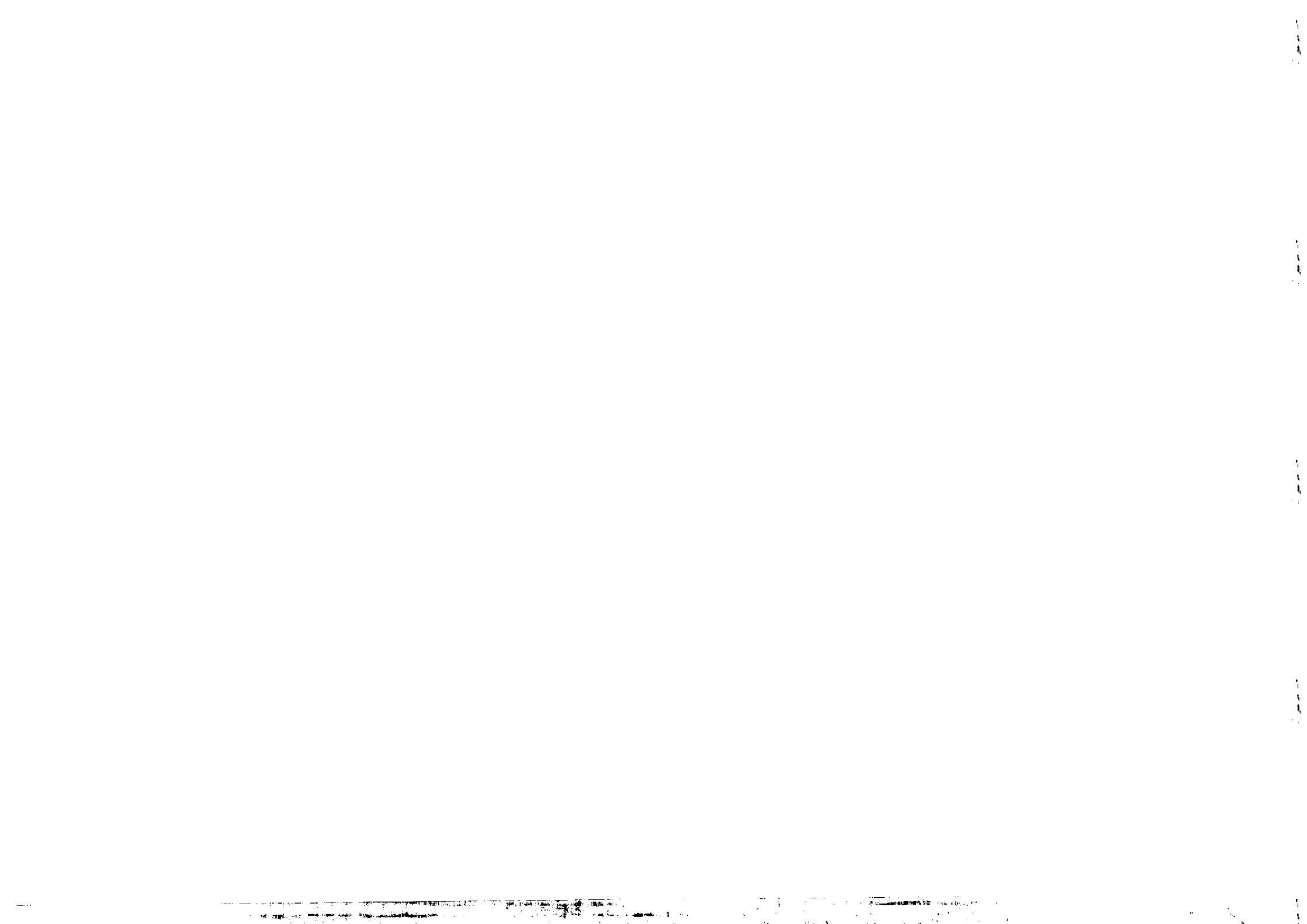


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STRUCTURE AND THERMODYNAMIC PROPERTIES OF MOLTEN STRONTIUM CHLORIDE *

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ABSTRACT

Self-consistent calculations of pair distribution functions and thermodynamic properties are presented for a pair-potentials model of molten strontium chloride. The calculations extend to a strongly asymmetric ionic liquid an earlier assessment of bridge diagrams in a modified hypernetted chain approach to the liquid structure of alkali halides. Good agreement is found with computer simulation data obtained by de Leeuw with the same set of pair potentials, showing that the present approach incorporates genuine general features of liquid structure theory for multicomponent liquids with strong relative ordering of the component species. It is further shown that the strong correlations between the divalent cations, both in the model and in real molten strontium chloride, can be approximately reproduced on the basis of a simple one-component plasma model, provided that dielectric screening is allowed for in the real liquid. This allows us to tentatively attribute the significant level of disagreement between a pair potentials model of this liquid and the neutron diffraction data of McGreevy and Mitchell to many-body distortions of the electronic shells of the ions.

I. INTRODUCTION

The technique of thermal neutron scattering from isotopically enriched samples has been employed in recent years to unravel the liquid structure of several divalent-cation chlorides (BaCl_2 : Edwards, Enderby, Howe and Page 1978; ZnCl_2 : Biggin and Enderby 1981a; CaCl_2 : Biggin and Enderby 1981b; SrCl_2 : McGreevy and Mitchell 1982). The rather interesting physical behaviours of these systems in the hot solid phase, which go from fast-ion conduction in BaCl_2 and SrCl_2 to the existence of a glassy state of ZnCl_2 , provide added motive for studying the structure of their liquid phase near freezing. The most revealing structural feature of the liquid is in this respect the cation-cation partial structure factor, as contrasted with the anion-anion partial structure factor. In particular, in molten BaCl_2 and SrCl_2 the strong correlations in the cationic component are reflected in a strong main peak of its partial structure factor, though the mean distance between first neighbour cations lies as far out as 5 \AA . Within a density wave theory of freezing these correlations drive the freezing transition into a crystal with a high degree of disorder in the anionic component, which is responsible for the observed superionic behaviour. (D'Aguanno, Rovere, Tosi and March 1983).

The observed liquid structure and solid state disorder are, of course, ultimately determined by the nature of the interionic forces. In this connection, McGreevy and Mitchell (1982) have also presented a detailed comparison of their neutron scattering results on molten SrCl_2 with computer simulation data reported earlier by de Leeuw (1976, 1978a and b) as well as with unpublished simulation results of Dixon. The simulation work is based on pair potentials models and shows a significant level of disagreement with the neutron data. A discussion of the origin of these discrepancies between model and observation is one of the aims of the present work.

The simulation results of de Leeuw on the other hand, though referring to a model which clearly provides quantitatively a rather poor representation for the structure of real molten SrCl_2 , are interesting in their own right from a statistical mechanical viewpoint. In parallel with the observations of McGreevy and Mitchell, the model liquid of divalent cations and monovalent anions shows both relative ordering of the two species and strong asymmetry between the like-ion correlation functions. Thus, de Leeuw's data offer the opportunity of a test of liquid structure theory for ionic systems where the short-range order is well spread out in space. As it turns out, the Sr-Sr correlations also appear from the comparisons presented by McGreevy and Mitchell to be most sensitive to the model for the interionic forces.

In recent work we have developed a modified hypernetted chain (MHNC) approach to liquid structure in binary liquids with strong relative ordering of the component species, involving a specific thermodynamically consistent assessment of the bridge diagram corrections to the hypernetted chain approximation (Ballone, Pastore and Tosi 1984a and b, hereafter referred to as I). The approach was successfully tested on a nearly symmetric ionic liquid (RbCl) and also on systems such as NaCl where size differences between the ionic species are appreciable, though the cation-cation and anion-anion correlation functions are still similar. The other main aim of the present work is to test this approach against de Leeuw's data in the strongly asymmetric case provided by SrCl₂.

After a summary of the essential points of the theory in Sec.II, our theoretical results for de Leeuw's model of SrCl₂ are presented in Sec.III and successfully compared with his data on thermodynamic properties, pair correlation functions and partial structure factors. The discussion of the model against experimental data on thermodynamics and structure is taken up in Sec.IV. Focussing on the Sr-Sr correlations, it is there shown that the gross discrepancies between model and observation in this pair function can be understood in terms of electronic screening of the Coulomb repulsions between cations. Sec.V closes the paper with some final remarks.

II. MHNC APPROACH AND EVALUATION OF BRIDGE FUNCTIONS

A diagrammatic expansion for the pair distribution functions $g_{\alpha\beta}(r)$ in an ionic fluid relates them to the interionic pair potentials $\phi_{\alpha\beta}(r)$ through the equations

$$g_{\alpha\beta}(r) = \exp \left[-\beta \phi_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - b_{\alpha\beta}(r) \right], \quad (2.1)$$

where a Greek suffix denotes the ionic species, $\beta = (k_B T)^{-1}$ and $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ (Morita and Hiroike 1960; Meeron 1960). The Ornstein-Zernike direct correlation functions $c_{\alpha\beta}(r)$ are related to $h_{\alpha\beta}(r)$ by the further equations

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_{\gamma} n_{\gamma} \int d\mathbf{r}' c_{\alpha\gamma}(|\mathbf{r}-\mathbf{r}'|) h_{\gamma\beta}(r'), \quad (2.2)$$

where n_{α} is the number density of particles of each species. The bridge functions $b_{\alpha\beta}(r)$, on the other hand, are formally related to $h_{\alpha\beta}(r)$ by diagrams involving clusters of four or more particles. Eqs.(2.1) and (2.2)

become a closed set for the evaluation of liquid structure from given pair potentials once a suitable approximation is introduced for the evaluation of the bridge functions.

A standard form for pair potentials in ionic systems is the Born-Mayer interaction

$$\phi_{\alpha\beta}(r) = \frac{Z_{\alpha} Z_{\beta} e^2}{r} + \varphi_{\alpha\beta}(r), \quad (2.3)$$

where Z_{α} is the ionic valence and $\varphi_{\alpha\beta}(r)$ describes short-range contributions, usually a repulsion between the closed-shell ionic cores supplemented by a van der Waals attractive tail. The approximation developed in I for the bridge functions in such a model binary fluid accounts empirically in their construction for (i) the excluded volume region for cation-anion pairs as determined by $\varphi_{+-}(r)$, (ii) the excluded volume regions for cation-cation and anion-anion pairs coming mostly from their Coulombic repulsions $Z_{\alpha}^2 e^2 / r$, and (iii) the approach to large- r behaviours in a fluid with long-range Coulombic interactions. The different physical origins of the excluded volume regions for the various types of pairs, as noted above, are primarily responsible for the relative ordering of the two ionic species (i.e. charge ordering) and for asymmetry in the like-ion distribution functions in the case $Z_{+} \neq |Z_{-}|$.

Features (i) and (ii) are included in the evaluation of $b_{\alpha\beta}(r)$ through reference to a fluid mixture of hard spheres with strongly non-additive diameters $\sigma_{\alpha\beta} (\sigma_{+-} \ll \frac{1}{2} (\sigma_{++} + \sigma_{--}))$, whereas feature (iii) is accounted for through evaluation of the leading four-point bridge diagrams in the ionic liquid. Interpolation between short and long range behaviours yields

$$b_{\alpha\beta}(r) = \exp(-r^2/\xi_{\alpha\beta}^2) b_{\alpha\beta}^{HS}(r) + [1 - \exp(-r^2/\xi_{\alpha\beta}^2)] b_{\alpha\beta}^{(4)}(r), \quad (2.4)$$

where $b_{\alpha\beta}^{HS}(r)$ are the bridge functions for the mixture of hard spheres while $b_{\alpha\beta}^{(4)}(r)$ is given by

$$b_{\alpha\beta}^{(4)}(r) = -\frac{1}{2} \sum_{\gamma, \delta} n_{\gamma} n_{\delta} \iint d\mathbf{r}' d\mathbf{r}'' h_{\alpha\gamma}(|\mathbf{r}-\mathbf{r}'|) h_{\gamma\delta}(|\mathbf{r}'-\mathbf{r}''|) h_{\delta\beta}(|\mathbf{r}-\mathbf{r}''|) h_{\alpha\beta}(|\mathbf{r}'-\mathbf{r}|). \quad (2.5)$$

The functions $b_{\alpha\beta}^{HS}(r)$ in Eq.(2.4) are further approximated by

$$b_{\alpha\beta}^{HS}(r) = b_{PY}(r; \eta_{\alpha\beta}), \quad (2.6)$$

the Percus-Yevick bridge function for a monatomic fluid of hard spheres at packing fraction $\eta_{\alpha\beta}$, with the restriction

$$\eta_{\alpha\alpha} = n_{\alpha} (\sigma_{\alpha\alpha}/\sigma_{+-})^3 \eta_{+-} / \sum_{\alpha} n_{\alpha} \quad (2.7)$$

allowing for the various concentration factors.

The expression (2.4)-(2.7) for the bridge functions involves six parameters for a binary fluid (the packing fraction η_{+-} , the diameter ratios σ_{++}/σ_{+-} and σ_{--}/σ_{+-} , and the interpolation lengths $\xi_{\alpha\beta}$), but only the first of these has crucial importance. It is determined by enforcing consistency between the values of the isothermal compressibility from the virial theorem and from thermodynamic fluctuation theory, i.e. from the long-wavelength values of the partial structure factors. The values of the other parameters are read from the positions of the main peak in $g_{\alpha\beta}(r)$ as obtained from the initial solution of Eqs.(2.1) and (2.2) in the hypernetted chain approximation (i.e. with $b_{\alpha\beta}(r) = 0$). The numerical results are stable against small variations of these latter parameters.

In the calculations reported below we have also included, at variance from I, an account of the density dependence of the bridge functions. The thermodynamically consistent value of the compressibility is quite sensitive to this effect, whereas all the other calculated properties, both thermodynamic and structural, are almost completely insensitive. The above density dependence enters the calculations through the dependence of $b_{PY}(r)$ on the packing fraction and through the dependence of $b_{\alpha\beta}^{(b)}$ in Eq.(2.5) on the density factors in front of the integrals. The evaluation of these integrals, which is by far the most time-consuming step, can be made with sufficient accuracy by using $h_{\alpha\beta}(r)$ from the hypernetted chain solution of Eqs.(2.1) and (2.2) and by omitting their implicit density dependence.

III. RESULTS FOR A PAIR-POTENTIALS MODEL OF MOLTEN STRONTIUM CHLORIDE

In the calculations reported in this section we have adopted, following de Leeuw (1978a), the set of pair potentials of the general form (2.3) which were derived for $SrCl_2$ by Busing (1970) from an analysis of

crystal data for alkaline-earth halides. The temperature of the melt is taken as 1150K and the molar volume is taken as $V_M = 61.94 \text{ cm}^3/\text{mole}$, which is the value determined by de Leeuw's Monte Carlo simulation at the same temperature and zero pressure. This value is somewhat larger than the measured molar volume in the same thermodynamic state ($V_M = 58.16 \text{ cm}^3/\text{mole}$, Janz 1967).

Table I reports our results for thermodynamic properties of the model, namely the pressure P calculated from the virial theorem, the excess internal energy U_{exc} per mole, with its contributions U_{Coul} from Coulombic interactions (Madelung energy) and U_{sr} from short-range interactions, and the isothermal compressibility K_T . These results are compared in the table with de Leeuw's simulation data (1978a) and with the results of the hypernetted chain approximation (HNC). As in the case for models of molten alkali halides discussed in I, our estimate of the bridge functions leads to a major improvement on the HNC results and to very good agreement with the simulation data for the same set of pair potentials.

Our results for the liquid structure of the model are reported in Figs.1 and 2, together with the simulation data of de Leeuw (1978a and b, dots) and the experimental data of McGreevy and Mitchell (1982, circles). With regard to the pair distribution functions $g_{\alpha\beta}(r)$ shown in Fig.1, we note that the agreement with the simulation results is quite good. Some discrepancies are evident in the height of the main peak of these functions, where the cross-over between the two types of reference bridge functions is taking place in Eq.(2.4). The corresponding partial structure factors $S_{\alpha\beta}(k)$, defined by

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + (n_{\alpha}n_{\beta})^{1/2} \int d\mathbf{r} [g_{\alpha\beta}(r) - 1] \exp(i\mathbf{k}\cdot\mathbf{r}), \quad (3.1)$$

are shown in Fig.2. A discussion of the model against experiment will be given in the next section.

We conclude from the results presented above that our empirical approach to the estimation of bridge diagrams is of rather general applicability to liquids where a strong degree of relative ordering of the component species is induced by the interatomic forces, i.e. ionic liquids and presumably also "ordered" liquid alloys. In a further attempt to examine the approach in detail, we have also carried out a full Percus-Yevick calculation of $b_{\alpha\beta}^{HS}(r)$ in Eq.(2.4) for a mixture of non-additive hard spheres. This leads to small changes in the results that we have reported above, worsening somewhat their quality on the whole. Unfortunately, it is still difficult to

assess the quality of the Percus-Yevick approximation for such a reference model. Only a preliminary discussion of its equation of state has been given (Nixon and Silbert 1984) against simulation data of Adams and McDonald (1975).

IV. NATURE OF THE Sr-Sr CORRELATIONS AND COMPARISONS WITH EXPERIMENT

As we have already discussed in the introduction, the Sr-Sr correlations are in several respects the most remarkable structural feature of molten SrCl_2 . The character of these correlations (cf. Figs.1 and 2) suggests that a primitive representation may be obtained by schematizing the Sr component as a one-component classical plasma (OCP) floating in a uniform neutralizing background constituted by the smeared-out Cl component. This turns out indeed to be the case for de Leeuw's model of molten SrCl_2 , as shown in Fig.3. The full curves there give the pair distribution functions $g(r)$ and the structure factor $S(k)$ calculated for a fluid OCP at a coupling strength $\Gamma = 4e^2/(ak_B T) = 200$, as determined directly from the temperature $T = 1150\text{K}$ and the density $n_+ = (4\pi a^3/3)^{-1}$ of the cationic component. The MHNC approach given by Rosenfeld and Ashcroft (1979) for the OCP was used in these calculations. Considering the simplicity of the OCP model, the degree of agreement with de Leeuw's data for the Sr-Sr correlations (shown in Fig.3 as dots) is quite remarkable.

Bearing in mind the above result, we pass next to discuss de Leeuw's model of molten SrCl_2 against experiment. The model, we recall, assumes a rigid transfer of interionic pair potentials from the solid to the liquid. This yields quite reasonable agreement with the measured thermodynamic properties of the liquid (cf. the last row in Table I) and also with the observed $g_{+-}(r)$ in the region of close contact between cations and anions, for $r \lesssim 2.7 \text{ \AA}$ (cf. Fig.1). The discrepancies with the observed liquid structure in Fig.1 are instead quite substantial as one moves out in space, becoming very large in the Sr-Sr pair distribution function.

Returning now to our primitive OCP model for Sr-Sr correlations in Fig.3, we report there as dashed lines the results of a MHNC calculation of $g(r)$ and $S(k)$ for a screened OCP at a coupling strength $\Gamma = 4e^2/(\epsilon ak_B T) = 73$, where we have taken $\epsilon = 2.72$ which is the measured value for the electronic dielectric constant of crystalline SrCl_2 (Tessman, Kahn and Shockley 1953). These results are clearly in quite reasonable agreement with the observed Sr-Sr structural functions of the real liquid.

The calculations that we have just presented suggest that dielectric screening of the cation-cation Coulombic repulsions is occurring in molten SrCl_2 . Of course, while the use of the electronic dielectric constant may be justifiable at the rather large interionic separations involved in $\epsilon_{\text{SrSr}}(r)$, a detailed microscopic account of electron-shell deformations would be necessary for the other correlation functions.

V. CONCLUDING REMARKS

There seems to be from our results a reasonable degree of control on the theory of liquid structure for ionic liquids with given pair potentials. Although alternative and possibly simpler approaches to the evaluation of bridge functions may yet be devised, the nature of these functions in interspecies-ordering liquids should reflect the general features that we have stressed in Sec.II. On the other hand, the adoption of rigid pair potentials is clearly insufficient for a fully quantitative account of the observed structure of these liquids. An important role of microscopic many-body distortions of the electronic shells of the ions is indicated by our results.

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Table I

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Thermodynamic properties of molten strontium chloride near freezing (a)

	P(kbar)	U_{exc} (kJ)	U_{Coul} (kJ)	U_{sr} (kJ)	$K_T (10^{-12} \text{ cm}^2/\text{dyn})$
HNC	9.5	-2062	-2237	175	8.6, 37.6 (b)
MHNC (c)	0.05	-2074	-2226	151	12
Simulation	0	-2078	-2228	150	11
Experiment (d)	0	-2044	-	-	13

(a) The first three rows refer to the liquid at 1150K and $V_M = 61.94 \text{ cm}^3/\text{mole}$, against $V_M = 58.16 \text{ cm}^3/\text{mole}$ from experiment.

(b) The two values for K_T in the HNC correspond to the use of the virial theorem and of thermodynamic fluctuation theory, respectively.

(c) The values of the parameters in the bridge function are $\sigma_{+-} = 2.72 \text{ \AA}$, $\sigma_{--} = 3.51 \text{ \AA}$, $\sigma_{++} = 4.69 \text{ \AA}$, $\xi_{+-} = 2.82 \text{ \AA}$, $\xi_{--} = 3.7 \text{ \AA}$ and $\xi_{++} = 4.9 \text{ \AA}$.

(d) The experimental value of U_{exc} is estimated from the crystal lattice energy at 298K reported by Busing (1970) on adding the measured enthalpy of the liquid at 1150K relative to the crystal at 298K. This enthalpy difference, as well as the compressibility of the liquid, are given by de Leeuw (1978a).

FIGURE CAPTIONS

Fig.1 Pair distribution functions $g_{+-}(r)$, $g_{--}(r)$ and $g_{++}(r)$ of molten SrCl_2 near freezing. Curves are present MHNC results at 1150K and dots are Monte Carlo simulation data of de Leeuw (1978a) at 1150K with the same pair potentials. Circles are neutron diffraction data at 1198K by McGreevy and Mitchell (1982).

Fig.2 Partial structure factors $S_{+-}(k)$, $S_{--}(k)$ and $S_{++}(k)$ of molten SrCl_2 near freezing. Curves are present MHNC results at 1150K and dots are molecular dynamics data of de Leeuw (1978b) at 1193K with the same pair potentials. Circles are neutron diffraction data at 1198K by McGreevy and Mitchell(1982).

Fig.3 Pair distribution function $g(r)$ (left) and structure factor $S(k)$ (right) of a classical one-component plasma at coupling strengths $\Gamma = 200$ (full curves) and $\Gamma = 73$ (dashed curves) . Dots and circles are simulation data of de Leeuw and neutron diffraction data of McGreevy and Mitchell, respectively, for the Sr-Sr correlations in molten SrCl_2 .

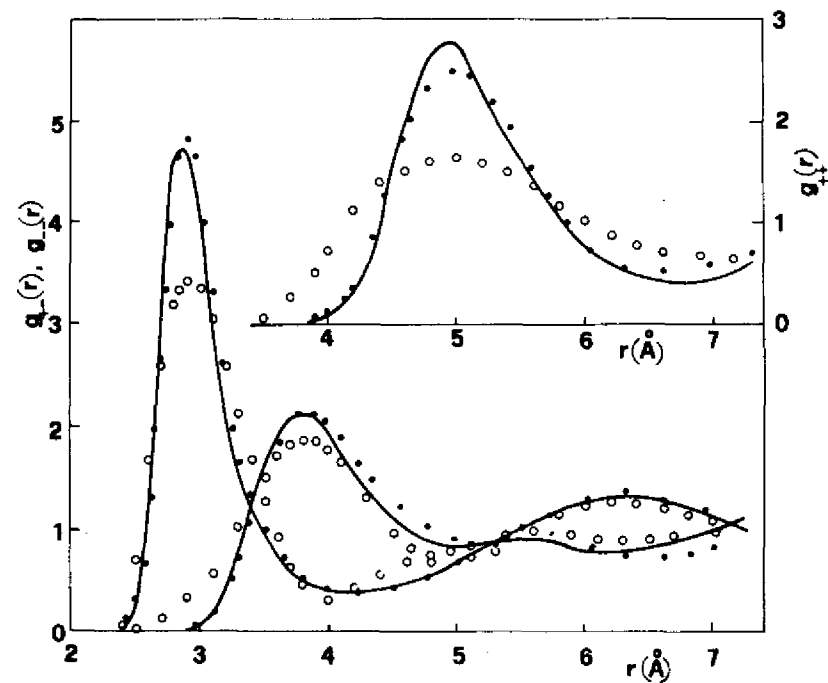


Fig.1

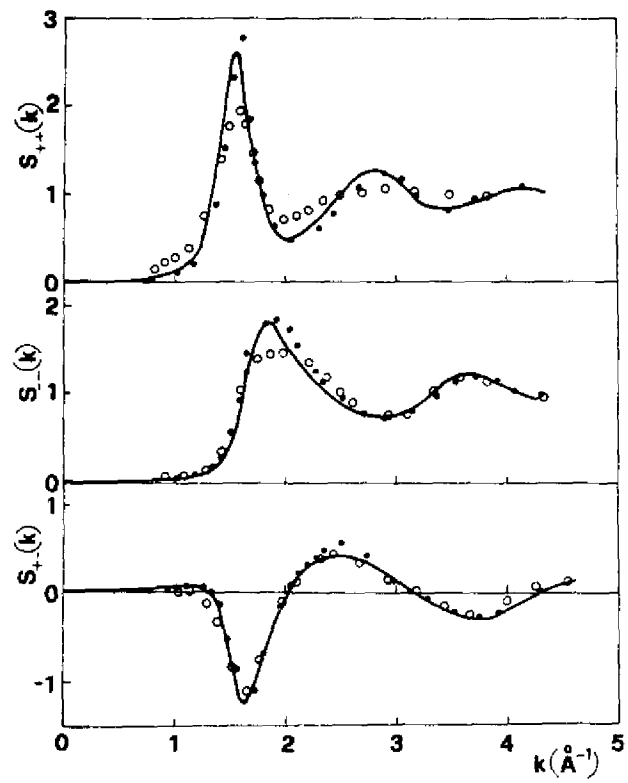


Fig. 7

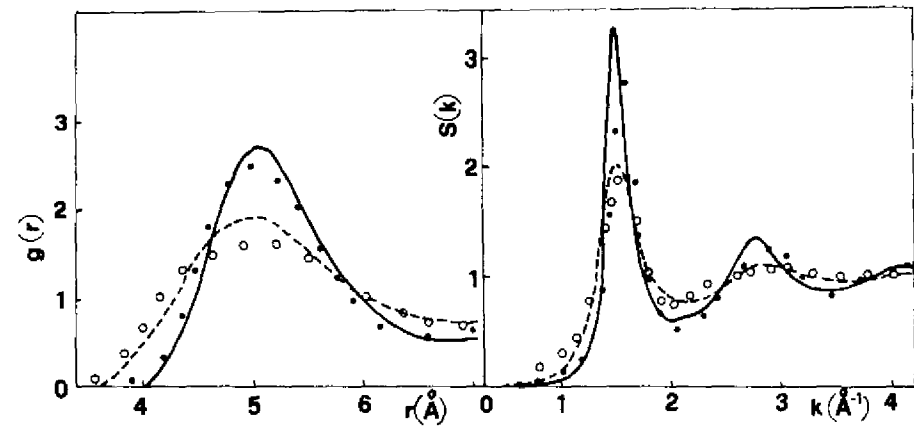


Fig. 8

