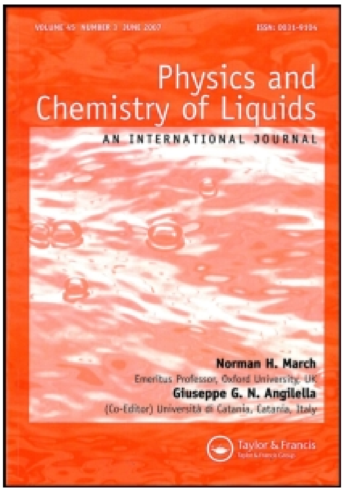

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Evidence for Many-Body Interactions in the Structure of Molten Alkali Chlorides

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Evidence for Many-Body Interactions in the Structure of Molten Alkali Chlorides

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An inversion of the measured partial structure factors of molten sodium chloride is attempted in order to assess some qualitative features of interionic forces in the melt. We start from a calculation of liquid structure and thermodynamic properties by means of a refined theory based on interionic pair potentials determined from properties of the solid phase. This yields very good agreement with the measured values of the internal energy and the compressibility of the liquid, whereas discrepancies with the observed structure are mainly localized in the region of interionic distances *outside* the minimum of the cation–anion potential. These discrepancies, when interpreted in terms of effective pair potentials in the melt through inversion of the structural data, strongly suggest the presence of many-body effects, insofar as such effective pair potentials oscillate with the local liquid structure and are inconsistent with the measured thermodynamic quantities. A similar analysis of data on molten rubidium and cesium chloride, though harder to carry out quantitatively, supports the above conclusion.

I INTRODUCTION

In the phenomenological models of cohesion in ionic crystals stemming from the early work of Born,[1] the "static-crystal" contribution to the internal energy is expressed as the sum of interionic pair potentials. It is well known that such effective pair potentials depend to some extent on the many-ions configuration—on crystal structure, in particular.[2] This was demonstrated theoretically by Löwdin,[3] who, starting from Hartree-Fock free-ion wave functions, showed that orthogonalization of overlapping orbitals centred on neighbouring lattice sites results in many-body short-range contributions to the binding energy of the static crystal. Configuration-dependent forces are also well known to arise in harmonic lattice vibrations around the static crystal configuration, the electron density deformations which accompany such small lattice distortions being commonly treated phenomenologically by the shell model in a dipolar approximation.[4] Considerable progress has been made recently by means of density-functional methods in assessing the nature of the electronic density distribution in ionic crystals[5,6] and in developing first-principles calculations of their structural phase transitions and phonon frequencies.[7]

Melting is clearly a large structural distortion. The residual short-range order in a typical molten salt, as measured by neutron diffraction,[8] still reflects the existence of a shell of unlike first neighbours and of a second shell of like neighbours around any given ion in the melt. These shells are rather broad and exchange of ions with the surrounding medium is clearly occurring to an appreciable extent. Nevertheless, the available evidence, coming mostly from detailed comparisons of results of computer simulation work with experimental data, shows that a rigid transfer of pair potentials from the solid to the liquid provides already a very reasonable description of the short-range order and of the thermodynamic properties of the liquid, at least for molten alkali halides.[9] Much more sensitive to the detailed microscopic model are the dynamical properties of the melt and, presumably, the small-angle scattering region in the partial structure factors.

We discuss in this paper the residual discrepancies between the above rigid-transfer approach and the available data on short-range order and thermodynamic properties of the melt. Ideally, one would wish to invert the liquid structure data to extract effective pair potentials in the melt. This task is notoriously delicate even for monatomic liquids and seems well-nigh impossible to carry out at present with quantitative confidence in a molten salt, where several pair potentials are involved and, furthermore, accurate data are still lacking in the small-angle scattering region. We shall therefore aim only at correlating some observed features of the short-range order in the ionic melt with gross features of effective pair potentials that would reproduce them, and also use calculations of thermodynamic properties as a qualitative gauge of the many-body effects which underlie such effective pair potentials. Our analysis will be mainly focussed on molten sodium chloride, for which we use the neutron diffraction data of Edwards *et al.*[10] as re-analyzed by Biggin and Enderby.[11]

II LIQUID PROPERTIES FROM STATIC-CRYSTAL PAIR POTENTIALS

The relation between interionic pair potentials $\phi_{\alpha\beta}(r)$ and partial pair distribution functions $g_{\alpha\beta}(r)$ in the liquid can be written through the equations[12]

$$g_{\alpha\beta}(r) = \exp[-\beta\phi_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - b_{\alpha\beta}(r)]. \tag{2.1}$$

Here, a Greek suffix labels the ionic species, $\beta = 1/k_B T$, $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$, and $c_{\alpha\beta}(r)$ are the Ornstein-Zernike direct correlation functions, defined through the integral equations

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

n_α being the density of ions of species α. Finally, the functions $b_{\alpha\beta}(r)$ in Eq. (2.1) give the contributions coming from the so-called bridge diagrams.

An approximate scheme has been proposed recently by three of us[13] for the evaluation of the bridge functions $b_{\alpha\beta}(r)$ in a molten salt (this earlier work will be referred to henceforward as I). Very briefly, these functions are taken in the form

$$b_{\alpha\beta}(r) = \exp(-r^2/\xi_{\alpha\beta}^2) b_{PY}(r; \eta_{\alpha\beta}) + [1 - \exp(-r^2/\xi_{\alpha\beta}^2)] b_{\alpha\beta}^{(4)}(r), \tag{2.3}$$

which interpolates between the bridge functions $b_{PY}(r; \eta_{\alpha\beta})$ of a mixture of hard spheres with non-additive radii in the Percus-Yevick approximation at short interionic distances and the leading bridge term $b_{\alpha\beta}^{(4)}(r)$ at large distances, as determined by four-point bridge diagrams. The essential parameter of this approach is the packing fraction η_{+-} for cation-anion pairs, which is fixed through the requirement of consistency on the isothermal compressibility from the virial theorem and from thermodynamic fluctuations theory. The other parameters are determined from the positions of the main peak in $g_{\alpha\beta}(r)$ as evaluated in the hypernetted-chain approximation ($b_{\alpha\beta}(r) = 0$).

It was shown in I that the results obtained in this way for the pair functions $g_{\alpha\beta}(r)$, as well as those for the internal energy and the pressure of the liquid, are in very close agreement with those obtained by computer simulation with the same set of interionic pair potentials. This fact, combined with the weak sensitivity of the calculated bridge functions to reasonable changes in the pair potentials, gives us some confidence that this approach can be usefully employed to examine the connection between structure and interionic forces.

We first assess in this section the quality of theoretical results from static-crystal pair potentials against experimental data on liquid structure and thermodynamic properties (excess internal energy U_{exc}, pressure p and isothermal compressibility K_T). We use pair potentials of the Born–Mayer form,

$$\phi_{\alpha\beta}(r) = \frac{Z_\alpha Z_\beta e^2}{r} + \varphi_{\alpha\beta}(r), \tag{2.4}$$

where Z_α is the ionic valence and the short-range potentials $\varphi_{\alpha\beta}(r)$ are given by

$$\varphi_{\alpha\beta}(r) = A_{\alpha\beta}\exp(-r/\rho) - \frac{c_{\alpha\beta}}{r^6} - \frac{d_{\alpha\beta}}{r^8}. \tag{2.5}$$

The van der Waals coefficients $c_{\alpha\beta}$ and $d_{\alpha\beta}$ are taken from the work of Mayer[14] and the overlap repulsive parameters $A_{\alpha\beta}$ and ρ from the work of Tosi and Fumi.[15] The results for thermodynamic properties of both NaCl and KCl are compared with experiment in Table I, while the calculated pair distribution functions of NaCl are shown in Figure 1 (full lines) together with neutron diffraction data reported by Biggin and Enderby[11] (circles). The density of each system was taken to be the measured density[16] at atmospheric pressure and the indicated temperature.

TABLE I

Thermodynamic properties of molten NaCl and KCl

	NaCl (1148K)		KCl (1043K)	
	Theory	Expt	Theory	Expt
U_{exc}(KJ/mol)	−713.8	−714.3[a]	−649.4	−650.5[a]
P(kbar)	1.3	0.0	1.3	0.0
K_T(10^{-12} cm^2 dyn^{-1})	31.7	32.4[b]	39.0	36.7[b]

[a] From D. J. Adams and I. R. McDonald, Ref. 17, after correction for temperature difference.

[b] From G. J. Janz, Ref. 16.

With regard to the results in Table I, we should first of all point out that the density dependence of the bridge functions turns out to be important in the calculation of the compressibility. This density dependence, which was omitted in I, is included in the present calculations, all the results being almost completely insensitive to it except for the value of K_T. The close agreement with the measured values of K_T shown in the table is particularly remarkable. The excellent values yielded by such a pair-potentials model for the internal energy, and its overestimate of the equilibrium pressure (or equivalently the underestimate of the equilibrium density at atmospheric pressure), were already known from computer simulation work.[17]

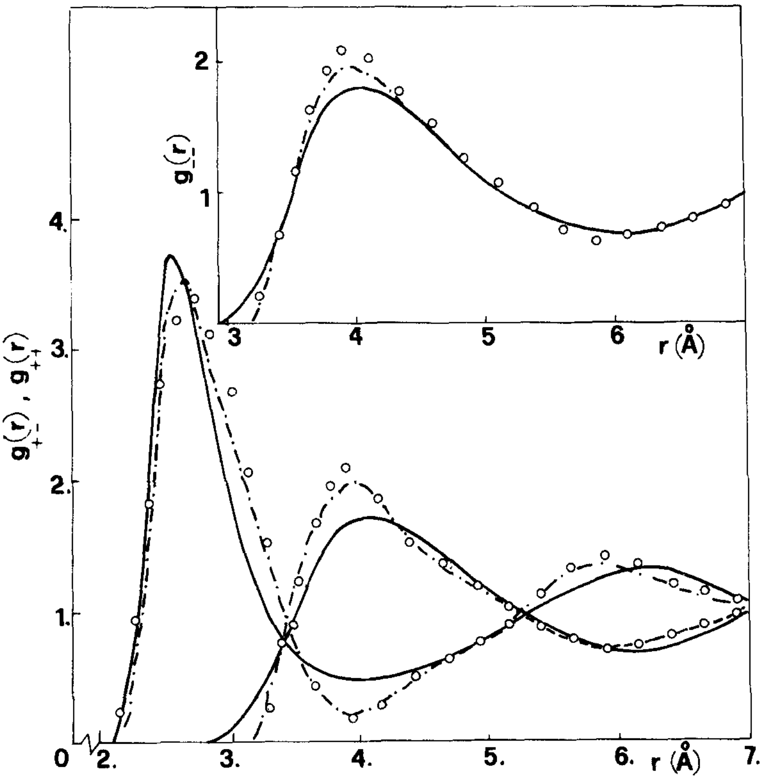

Figure 1 Pair distribution functions $g_{\alpha\beta}(r)$ in molten NaCl at 1148 K. Full curves are theoretical results from static-crystal pair potentials and circles are experimental data of Biggin and Enderby.[11] The dashed curves give "empirical" $g_{\alpha\beta}(r)$ constructed as described in the text.

In fact, a shift of the parameter ρ in Eq. (2.5) by about 1 %, which is hardly significant, suffices to reduce the calculated pressure to zero. On considering the effects of such uncertainties in the model parameters and of the residual discrepancies between calculated and observed liquid structure in Figure 1, we estimate an uncertainty of roughly ± 10 kJ/mol in the calculated internal energy. We stress that this uncertainty is a consequence of the model, *not* of the statistical-mechanical approach for a given set of pair potentials (cf. the discussion in I).

Turning now to the structural results shown in Figure 1, the good agreement between theory and experiment for $g_{+-}(r)$ at short interionic distances confirms that the overlap repulsive cation-anion potential in Eq. (2.5) is approximately correct in the thermodynamic conditions of present interest. The most prominent discrepancies occur in the region between 3 and 4 Å, i.e. well *outside* the minimum of the cation-anion potential. In particular, the first-neighbour shell in the molten salt is, relative to the model, both broader and more stable against ionic exchange with the surrounding medium. This immediately suggests that additional restoring forces are acting on unlike ions as they move out of close contact with the central ion. We shall proceed in the next section to give some quantitative assessment of these forces in terms of effective pair potentials in the melt.

III INVERSION OF STRUCTURAL DATA AND RESULTS FOR EFFECTIVE PAIR POTENTIALS

The use of Eq. (2.1) to derive effective pair of potentials in the molten salt from the measured liquid structure requires, first of all, the determination of $c_{\alpha\beta}(r)$ from $g_{\alpha\beta}(r)$ through Eq. (2.2). This equation in Fourier transform yields

$$(n_\alpha n_\beta)^{1/2} c_{\alpha\beta}(k) = \delta_{\alpha\beta} - S_{\alpha\beta}^{-1}(k) \tag{3.1}$$

where $S_{\alpha\beta}^{-1}(k)$ denotes the inverse of the matrix of partial structure factors. The latter are known experimentally for NaCl only over a limited range of wave number k, not including, most importantly, the low-k region.

It was pointed out in I, however, that the discrepancies between the theory and experiment in the $g_{\alpha\beta}(r)$'s that we have seen in Figure 1 are correlated with the behaviour of the partial structure factors in the region of wave number between 2 and 4 Å^{-1}. We have therefore supplied to the incompleteness of the data for the estimation of $c_{\alpha\beta}(r)$ by making use of the theoretical structure factors both at very small and at very large wave number. As shown in Figure 1, the "empirical" $g_{\alpha\beta}(r)$ that we have been able to reconstruct in this way (dashes) mimick the observed ones reasonably well beyond about 3 Å. We shall next ask what effective pair potentials can reproduce these "empirical" $g_{\alpha\beta}(r)$. Clearly, we are thereby renouncing an evaluation of effective pair potentials at large interionic distances and also inside the minimum of the cation-anion potential, and focussing only on the region between 3 and 5 Å.

The bridge functions in the above region are largely determined by the contribution $b_{\alpha\beta}^{(4)}(r)$ in Eq. (2.3), which is given by

$$b_{\alpha\beta}^{(4)}(r) = -\frac{1}{2}\sum_{\gamma,\delta} n_\gamma n_\delta \iint d\mathbf{r}'\, d\mathbf{r}''\, h_{\alpha\gamma}(r') \times h_{\alpha\delta}(r'') h_{\gamma\delta}(|\mathbf{r}' - \mathbf{r}''|) h_{\gamma\beta}(|\mathbf{r} - \mathbf{r}'|) h_{\delta\beta}(|\mathbf{r} - \mathbf{r}''|) \tag{3.2}$$

These integrals show little sensitivity to the details of the structural input and their values can, at least as a first approximation, be taken from the results of

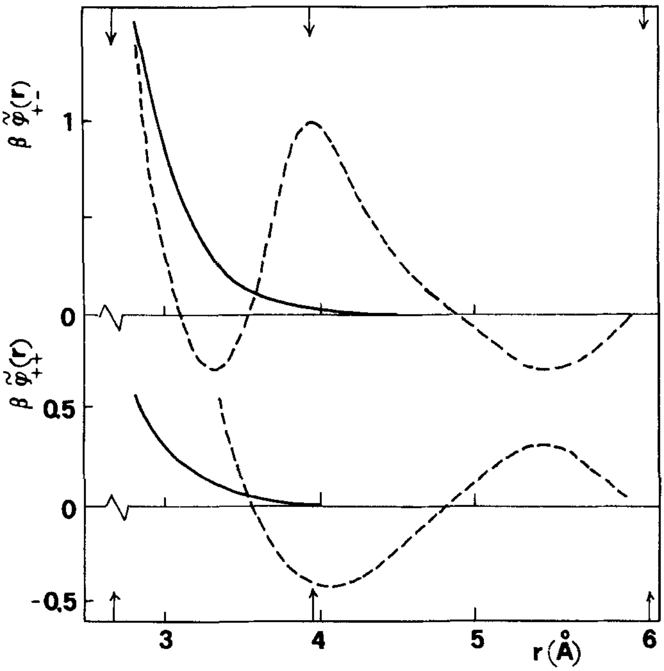

FIGURE 2 Effective short-range pair potentials $\tilde{\varphi}_{\alpha\beta}(r)$ determined by inversion of the "empirical" $g_{\alpha\beta}(r)$ in Figure 1 (dashed curves). The full curves report the static crystal potentials of Eq. (2.5), the long-range van der Waals tail being not visible on the present scale. The arrows correspond to the positions of the first peak, first minimum and second peak in $g_{+-}(r)$.

Section II. Effective pair potentials in the melt are then immediately obtained from Eq. (2.1). Figure 2 reports as dashed lines the effective short-range potentials $\tilde{\varphi}_{+-}(r)$ and $\tilde{\varphi}_{++}(r) \approx \tilde{\varphi}_{--}(r)$ which, after addition of the Coulomb term $Z_\alpha Z_\beta e^2/r$, reproduce the reconstructed "empirical" $g_{\alpha\beta}(r)$ in Figure 1. The full lines in Figure 2 give the corresponding static crystal potentials.

Bearing in mind that these results can only have at best semiquantitative value, we notice first that the bridge functions in this region of interionic distances are smaller than $\beta\tilde{\varphi}_{\alpha\beta}(r)$ by roughly an order of magnitude, justifying the approximation on $b_{\alpha\beta}(r)$ that we have made above. The cation–anion effective potential $\tilde{\varphi}_{+-}(r)$ shows, as surmised in Section II, an attractive part in the outer region of the first neighbour shell, which turns out to be much larger, by a factor of order 5, than the van der Waals attractive terms of Eq. (2.5) in this region. Further oscillations of the effective pair potentials, in phase with the local structure of the liquid, are suggested by the results at larger interionic distances.

The above features strongly suggest that these effective pair interactions reflect many-body distortions of the electronic shells of the ions occurring on a microscopic scale. This interpretation is further supported by the fact that large errors are found in a calculation of thermodynamic properties if the effective pair potentials extracted from the liquid structure are treated as true pair potentials. We find, in particular, a shift of U_{exc} by about -30 kJ/mol from the values given in Table I, which we feel is beyond the reasonable uncertainty that may affect a calculation of this quantity in molten NaCl from a pair-potentials model.

IV CONCLUDING REMARKS

Experimental data on liquid structure of comparable quality to those used above for molten NaCl are available also for molten RbCl[18] and CsCl.[19] A static-crystal-potentials approach to liquid structure yields progressively worse results in these systems, which are composed of increasingly more polarizable ions. An analysis of the data for RbCl and CsCl is consequently much more difficult to carry out quantitatively by the method that we have used above. Qualitative features of effective pair potentials in these systems seem nevertheless to parallel those that we have illustrated for molten NaCl.

While in the framework of a viable statistical-mechanical theory one can only discuss liquid structure in terms of effective pair potentials, we believe that our results are displaying the effects of many-body distortions of the electron density distribution in the molten salt. Given the oscillatory nature of ionic screening around any given ion in the molten salt, a similar oscillatory character for the electronic screening seems possible on the microscopic scale that we have been concerned with. At any rate, the construction of interionic pair potentials for polarizable-ion models from data on dielectric constants and lattice vibrational frequencies may have little relevance on a microscopic scale corresponding to wave numbers in the range $2 \div 4$ Å^{-1}. Such models should instead be useful to describe the small-angle scattering and the large-distance correlations. An analysis of data on the Sr–Sr distribution function in molten $SrCl_2$[20] lends support to this view.[21]

In conclusion, our results draw attention to interionic forces in a region of interionic distances that has so far received little attention in the literature. Useful insight could come from quantum-mechanical calculations on ionic molecules and small ionic aggregates under stretch.

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