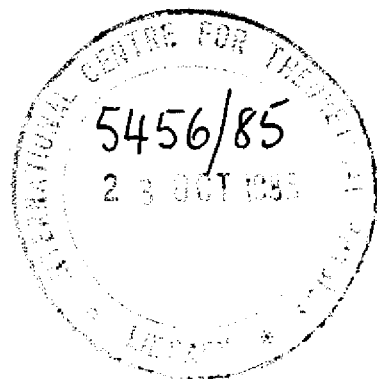


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**INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS**

IONIC PAIRING IN BINARY LIQUIDS OF CHARGED HARD SPHERES
WITH NON-ADDITIVE DIAMETERS

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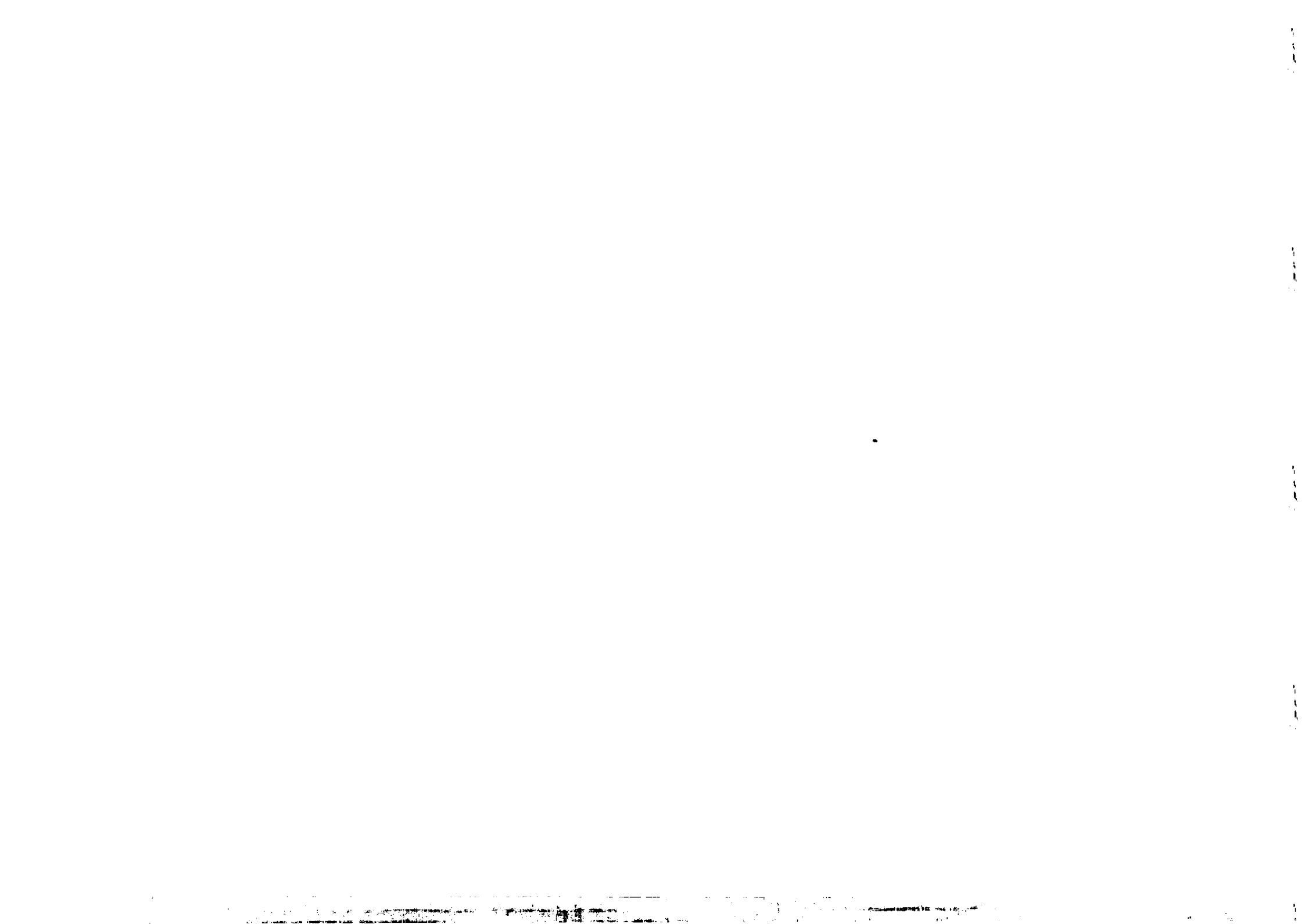


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IONIC PAIRING IN BINARY LIQUIDS OF CHARGED HARD SPHERES
WITH NON-ADDITIVE DIAMETERS †

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ABSTRACT

We examine types of short range order that arise in binary liquids from a combination of Coulombic interactions and non-additivity of excluded volumes. The initial motivation being observations of complex formation by hydrated ions in concentrated aqueous solutions. The model is a fluid of charged hard spheres with contact distances $\sigma_{+-} \neq \frac{1}{2}(\sigma_{++} + \sigma_{--})$, its structural functions being evaluated in the mean spherical approximation and in the hypernetted chain approximation. Cation-anion pairing is clearly seen in the calculated structural functions for negative deviations from additivity ($\sigma_{+-} < \sigma_{++} = \sigma_{--}$), though the absence of true chemical bonding in the model does not allow long-lived complexes. Positive deviations from additivity ($\sigma_{+-} > \sigma_{++} = \sigma_{--}$) favour long-wavelength concentration fluctuations and demixing in a neutral mixture: these are suppressed by Coulombic interactions in favour of microscopic intermixing of the two species in the local liquid structure, up to like-ion pairing. Contact is made with diffraction from concentrated aqueous solutions of cadmium sulphate and other instances of possible applicability of the model are pointed out.

1. INTRODUCTION

Recent X-ray diffraction measurements on concentrated aqueous solutions of cadmium and nickel phosphate¹⁾ and of cadmium sulphate²⁾ have produced evidence of complex formation by hydrated ions. Further evidence has been obtained from measurements of diffusion coefficients in solutions with various concentrations of cadmium and sulphate ions, where deviations from stoichiometry were introduced through addition of ammonium sulphate³⁾. Even in stoichiometric solutions a high percentage of the sixfold hydrated cadmium ions is found to be modified by replacement of a water molecule by an oxygen atom of a sulphate group. The distance between sulphur and cadmium within a complex is appreciably shorter than the sum of the radii of the two separate ionic solutes, i.e. hydrated cadmium ions and sulphate groups.

A primitive model to describe the above system is a fluid of charged hard spheres in a dielectric continuum with the property that the distance of closest approach for oppositely charged ions (σ_{+-} , say) is appreciably shorter than the average of the diameters of the two ionic species (σ_{++} and σ_{--} , say). In fact such a model has already been discussed, in the case of neutral hard spheres and in the Percus-Yevick approximation, by Levesque *et al.*⁴⁾ (see also Nixon and Silbert⁵⁾) in relation to some aspects of chemical ordering in liquid binary alloys. Some simulation results have also been reported in this case⁶⁾. Though the model lacks true features of chemical bonding as needed to form permanently bound complexes, it leads to pairing between unlike ions in a charged binary liquid, as we demonstrate by calculations of liquid structure in the mean spherical approximation (MSA) and in the hypernetted chain approximation (HNC).

In the opposite situation where σ_{+-} is appreciably larger than the average of σ_{++} and σ_{--} , one expects in a neutral liquid alloy an enhanced tendency to demixing. A phase transition with a critical point has been shown to occur in a related model⁷⁾ and phase separation has been demonstrated by simulation work on a mixture⁸⁾. We show below that Coulombic interactions due to charge transfer sharply stabilize such a binary liquid against demixing, inducing in its stead microscopic fluctuations of concentration of

The first step is to develop a model for the liquid structure. The structural richness of the present simple model, combining Coulombic interactions with non-additivity of excluded volumes, suggests extensions and applications to some complex liquids and phase separation phenomena.

2. DESCRIPTION OF THE MODEL AND ITS SOLUTION

We consider an equimolar mixture of oppositely charged hard spheres with equal diameters ($\sigma_{++} = \sigma_{--} = \sigma$, say). Non-additivity of contact distances is measured by a parameter α defined by

$$\sigma_{+-} = (1+\alpha)\sigma. \quad (2.1)$$

The strength of Coulombic coupling is measured by the parameter

$$\Gamma = Ze^2 / (\epsilon \alpha k_B T) \quad (2.2)$$

where Ze is the ionic charge, ϵ is the dielectric constant of the medium and a is the ion-sphere radius defined in terms of the total ionic density n by $a = (4\pi n/3)^{-1/3}$. We use a as the unit of length throughout the paper.

We aim to evaluate the liquid structure by solving the Ornstein-Zernike integral equations

$$h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \frac{1}{2}n \sum_{\gamma} \int d\mathbf{r}' c_{\alpha\gamma}(r-\mathbf{r}') h_{\gamma\beta}(r'), \quad (2.3)$$

which relate the pair correlation functions $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ and the direct correlation functions $c_{\alpha\beta}(r)$. The appropriate hard-sphere boundary conditions are

$$h_{\alpha\beta}(r) = -1 \quad (r < \sigma_{\alpha\beta}). \quad (2.4)$$

We have used alternatively the closure imposed in the MSA, i.e.

$$c_{\alpha\beta}(r) = -\Gamma Z_{\alpha} Z_{\beta} / (\epsilon r) \quad (r > \sigma_{\alpha\beta}), \quad (2.5)$$

or the HNC closure,

$$g_{\alpha\beta}(r) = \exp \left[-\frac{\Gamma Z_{\alpha} Z_{\beta}}{\epsilon r} + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) \right]. \quad (2.6)$$

Both closures are known to be useful approximations in the calculation of liquid structure for dense Coulomb fluids, the MSA being however rather poorer at distances close to contact where it can yield unphysically negative values for $g_{\alpha\beta}(r)$. The evaluation of thermodynamic quantities is subject to inconsistencies with either closure.

The closed sets of equations consisting of eqs. (2.3)-(2.5) or of eqs. (2.3), (2.4) and (2.6) have been solved numerically by means of the algorithm developed by Gillan⁹⁾ to stabilize and speed up convergence. A mesh of 512 point has been found to suffice for solutions of good precision, some care being needed in handling discontinuities at contact. No noticeable difficulty has been met in obtaining the solution of the model for values of its parameters (i.e. σ , α and Γ) inside the region of stability of the homogeneous phase. With regard to the extent of this region, the isothermal compressibility from the fluctuation formula tends to diverge in the HNC at higher values of Γ when the effective packing n^* increases, the latter being defined e.g. by

$$\eta^* = \frac{\pi}{6} n \sigma^3 [1 + (1+\alpha)^3]. \quad (2.7)$$

We present below various illustrative results for the pair distribution functions $g_{\alpha\beta}(r)$ and for the liquid structure factors of the model. The latter are defined either as the partial structure factors $S_{\alpha\beta}(k)$,

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} + \frac{1}{2}n \int d\mathbf{r} h_{\alpha\beta}(r) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad (2.8)$$

or as the Bhatia-Thornton¹⁰⁾ structure factors,

$$S_{NN}(k) = \frac{1}{2} [S_{++}(k) + S_{--}(k) + 2 S_{+-}(k)] \quad (2.9)$$

and

$$S_{QQ}(k) = \frac{1}{2} [S_{++}(k) + S_{--}(k) - 2 S_{+-}(k)] \quad (2.10)$$

The charge-charge structure factor $S_{QQ}(k)$ defined in eq.(2.10) is fully equivalent to the concentration-concentration structure factor $S_{CC}(k)$ introduced by Bhatia and Thornton for neutral mixtures, in the present case of an equimolar binary liquid. Of course, the restriction $\sigma_{++} = \sigma_{--}$ implies $S_{++}(k) = S_{--}(k)$, until we shall transcend it in discussing a cadmium sulphate solution in sect.5.

3. RESULTS FOR NEGATIVE NON-ADDITIVITY

Before we proceed to illustrate the structural effects of negative deviations from additivity of contact distances ($\alpha < 0$) in the presence of Coulombic forces, let us recall the main results reported by Nixon and Silbert⁵⁾ in the limiting case of a neutral equimolar mixture ($P=0$).

Two main effects arise in the liquid structure:

- (i) while at $\alpha = 0$ the fluid is a completely random mixture of two equivalent species, a new type of short range order gradually develops for $\alpha < 0$ from entropic reasons tending to favour a more efficient packing. The overall mixing of the two species is greatly enhanced as revealed, for instance, by a sharp decrease of $S_{CC}(0)$ relative to its value for an ideal mixture.
- (ii) The combination of inner penetration of unlike spheres with enhanced mixing increases the available free volume. The reduced effective packing induces an overall depression of structural correlations.

The same qualitative structural changes are observed in the presence of Coulombic interactions and indeed are strongly enhanced for energetic reasons with increasing Γ . Figure 1 illustrates these effects at $\alpha = -0.5$

for $\alpha = 1.2$ and Γ increasing from 0 to 10, i.e. in a regime appropriate to concentrated electrolyte solution at rather high packing. HNC results are reported only for $\Gamma = 10$, where the differences between the two closures are largest. With regard to the number-density correlations described by $S_{NN}(k)$ (Figure 1a), electrostatic coupling strongly increases the liquid compressibility and greatly reduces its short range order. The accompanying changes in the concentration correlations ($S_{QQ}(k)$, Figure 1b) are the suppression of long-wavelength fluctuations by electroneutrality and the sharp depression and shift of the main peak. As is well known, the main peak in $S_{QQ}(k)$ at $\alpha = 0$ reflects an essentially alternating distribution of oppositely charged shell of ions around a reference ion. This type of short-range order is modified towards pairing of unlike ions, as is more evident from the partial structure factors and pair distribution functions shown in Figs. 2 for $\Gamma = 10$ and $\alpha = -0.5$. The oscillations in $S_{+-}(k)$ reflect a preferred distance which is the contact distance between unlike ions ($\sigma_{+-} = 0.6$ in this case) while the main preferred distance reflected, somewhat more weakly, in $S_{++}(k)$ is twice as large. Unlike-ion pairing is evident in the HNC pair distribution functions in Figure 2b.

A quantitative measure of pairing is afforded by the cation-anion coordination number N_{+-} reported in Table 1, from the definition

$$N_{+-} = 4\pi n \int_0^R r^2 g_{+-}(r) dr \quad (3.1)$$

where R is the minimum in $g_{+-}(r)$. Though, of course, the precise numerical values have little meaning, Table 1 shows the disgregation of an essentially sixfold local coordination geometry into a twofold one. Values of N_{+-} approaching unity can be reached with further increases in the coupling strength or by lowering the packing.

Finally, Figure 3 illustrates the effects of varying α on the partial structure factors in a lower packing regime. A set of results for positive non-additivity ($\alpha = 0.333$) is already included for comparison.

4. RESULTS FOR POSITIVE NON-ADDITIVITY

The main physical consequence of a positive deviation from additivity of contact distances in an equimolar mixture is the strong enhancement of long-wavelength concentration fluctuation, as is shown by the value of $S_{cc}(0)$ in Fig. 4 for $\Gamma=0$ relative to $S_{cc}^{ideal}(0)=0.25$. Demixing up to phase separation is being favoured. Fig.4 also shows the sharp stabilization of the homogeneous phase by Coulombic forces via electroneutrality. Long-wavelength concentration fluctuations are suppressed while a tendency of like particles to cluster on a microscopic scale sets in, giving rise to enhanced fluctuations of concentration at finite wave number.

The above microscopic behaviour is better visualized from the HNC pair distribution functions shown in Fig.5 for $\Gamma=10$, $\sigma=1.2$ and values of α in the range $-0.5 \leq \alpha \leq 0.5$. At $\alpha=0.5$ like particles penetrate inside the shell of unlike particles around a given reference ion, the contact value of $g_{+-}(r)$ being also somewhat enhanced by the need to screen the excess charge contained inside σ_{+-} . For $\alpha=-0.5$, as we saw already in Fig.2, pairing of unlike ions has overscreened the central ion, leading indirectly to an enhancement in the contact value of $g_{++}(r)$.

It is interesting to follow the behaviour of $g_{++}(r)$ for $\alpha>0$ with increasing Γ . The balance between non-additivity and Coulombic interactions is fairly delicate and the short-range order turns out to be very sensitive to the competition between the two. As is shown in Fig.6, in the strong coupling regime ($\Gamma=50$, as appropriate to molten salts) and for relatively modest values of α ($\alpha=0.176$), the electrostatic repulsion digs out a sharp Coulomb hole between like ions, followed by a double-peak structure. This is still qualitatively similar to the well-known shape of $g_{++}(r)$ for additive charged hard spheres¹¹⁾, where the two peaks are believed to reflect two groups of like neighbours at approximate distances $\sqrt{2}\sigma_{++}$ and $2\sigma_{++}$. On increasing α (e.g. at $\alpha=0.258$), like ions start to transfer from the second into the first neighbour shell until a crossover occurs at $\alpha \approx 0.3$. As is shown in Fig.6, at $\alpha=0.328$ a switch-over of unlike and like ions between the first and the second neighbour shell has taken place. These changes in local structure accompanied by a strong reduction of the liquid compressibility.

5. APPLICATION TO A MODEL OF A CADMIUM SULPHATE SOLUTION

As we have already mentioned in the introduction, the present model for $\alpha < 0$ should be useful as a primitive model for ionic correlations in electrolyte solutions where complex formation between hydrated ions is taking place. We consider here in particular the 2M solution of $CdSO_4$ in water at 62°C, studied by Caminiti²⁾ by X-ray diffraction. He interprets a peak at $r = 3.5 \text{ \AA}$ in the Fourier transform of the total X-ray scattered intensity as due to the formation of $[Cd(H_2O)_{6-Z}(OSO_3)_Z]^{2-2Z}$ groups in concentration $Z \approx 0.64$ from the $[Cd(H_2O)_6]^{2+}$ and $[SO_4]^{2-}$ ionic constituents.

We therefore take $\sigma_{+-} = 3.5 \text{ \AA}$ for the distance of closest approach of doubly-charged cations and anions. From the same data we also estimate $\sigma_{++} \approx 4.6 \text{ \AA}$ and $\sigma_{--} \approx 3.0 \text{ \AA}$ for the diameters of hydrated cadmium ions and of sulphate ions, respectively. The resulting MSA structure factors are shown in Fig. 7. The value of Γ has been taken to be $\Gamma = 6.53$, as estimated from the dielectric constant of water and from the density and temperature of the solution.

Focussing in particular on the shape of $S_{+-}(k)$ in Fig.7, we notice that the period of the oscillations in this function reflects directly the preferred contact distance σ_{+-} between a cation and an anion inside a complex, which as already noted appears as a peak in the total X-ray pair distribution function. The phase of the oscillations, on the other hand, carries information on longer-range correlations. For instance, a model which were to include only the intra-complex correlations would shift the oscillations in $S_{+-}(k)$ by approximately a quarter of a period. Unfortunately we have not been able to ascertain whether longer-range interionic correlations appear in the measured scattered intensity, since the latter is dominated by contributions from the solvent in the important region of wave number corresponding to the first minimum in $S_{+-}(k)$. An experimental test of these predictions would thus require a more sensitive probe of the structure of the electrolyte solution than provided by standard X-ray diffraction techniques.

6. SUMMARY AND DISCUSSION

We have explored in this paper the changes brought about by deviations from additivity of excluded volumes in the liquid structure factors and radial distribution functions of a simple model for Coulomb fluids. Both negative and positive deviations from additivity simulate structural features that the presence of some chemical bonding, between unlike ions or between like ions respectively, would induce. Of course, this statement refers to a snapshot picture of local structure, where dynamics appears only indirectly through the broadness of the main peak in the radial distribution functions. True chemical bonding would also suppress exchanges between paired states and the surrounding liquid.

Negative deviations from additivity induce reductions of the cation-anion coordination number up to cation-anion pairing. We have used this model to discuss partial diffraction patterns for values of the parameters appropriate to a concentrated cadmium sulphate solution, pointing out that at this level of structural analysis one could distinguish between the mere presence of a preferred intra-complex distance and the existence of longer-range charge ordering. Other possible applications of a non-additive MSA have been suggested in connection with liquid structure calculations on molten alkali-halides¹²⁾ and alkaline-earth dihalides¹³⁾, as well as for concentrated solutions of alkali metals in molten alkali-halides. In the latter systems, of course, the excess of metal ions prevents pairing: non-additivity would help in handling the interplay of anion-cation attractions and cation-cation repulsions in a screening sea of electrons.

In the case of positive deviations from additivity, we have seen that the tendency to demixing that they favour in a liquid mixture is suppressed by Coulomb interactions and converted into microscopic fluctuations of concentration in the first neighbour shell, up to the formation of anion-anion and cation-cation microscopic clusters. Such a model liquid shows strong "rigidity" and is under some aspects reminiscent of structural characteristics that one might associate with an ionic glass-forming liquid. Among such liquids molten $ZnCl_2$ has been structurally analyzed experimentally in detail¹⁵⁾ and may be amenable to theory by a suitable asymmetric non-

additive model. Other potentially interesting systems are the alkali iodide-iodine solutions¹⁶⁾ and the molten alkali hyperoxides¹⁷⁾, though we do not know of structural studies having as yet been carried out on these liquids. Finally, it may be possible to model the phenomena of phase separation that have been observed in electrolyte solutions brought to supercritical conditions¹⁸⁾ by allowing for non-additivity in solvent-solvent and solvent-solute interactions.

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HNC cation-anion coordination number at $\sigma = 1.2$ for varying α and Γ

$\Gamma \backslash \alpha$	0	1	10
0	4.5	5.5	5.5
- 0.5	2.4	2.5	1.6

FIGURE CAPTIONS

- Fig.1 Bhatia-Thornton structure factors $S_{NN}(k)$ (Fig. 1a) and $S_{QQ}(k)$ (Fig.1b) versus ka for $\sigma = 1.2$. Full lines (broken lines) give MSA results for $\alpha = 0$ and $\alpha = -0.5$, respectively, at $\Gamma = 0, 1$ and 10. Dots and triangles are HNC results at $\Gamma = 10$ for $\alpha = 0$ and $\alpha = -0.5$, respectively.
- Fig.2 (a): partial structure factors $S_{++}(k)$ and $S_{+-}(k)$ versus ka at $\Gamma = 10$ and $\sigma = 1.2$. Full lines (dots) are MSA (HNC) results at $\alpha = 0$; broken lines (triangles) are MSA(HNC) results at $\alpha = -0.5$. (b): HNC pair distribution functions $g_{+-}(r)$ and $g_{++}(r)$ versus r/a at $\Gamma = 10$ and $\sigma = 1.2$, for $\alpha = 0$ (full lines) and $\alpha = -0.5$ (broken lines).
- Fig.3 Partial structure factors $S_{++}(k)$ and $S_{+-}(k)$ versus ka in the MSA at $\Gamma = 10$ and $\sigma = 0.6$, for $\alpha = 0.333, 0, -0.333$ and -0.667 .
- Fig.4 $S_{QQ}(k)$ versus ka in the MSA for $\sigma = 1.2$ and $\alpha = 0.167$ at $\Gamma = 0$ (full curve) and $\Gamma = 1$ (broken curve).
- Fig.5 HNC pair distribution functions $g_{+-}(r)$ and $g_{++}(r)$ versus r/a at $\Gamma = 10$ and $\sigma = 1.2$. For $\alpha = -0.5$ (broken curves) $\alpha = 0$ (full curves) and $\alpha = 0.5$ (dots).
- Fig.6 HNC pair distribution function $g_{++}(r)$ versus r/a at $\Gamma = 50$ and $\sigma = 1.31$, for $\alpha = 0.176, 0.233$ and 0.328 .
- Fig.7 MSA partial structure factors versus ka for model of cadmium sulphate in aqueous solution at 2M and 62C.

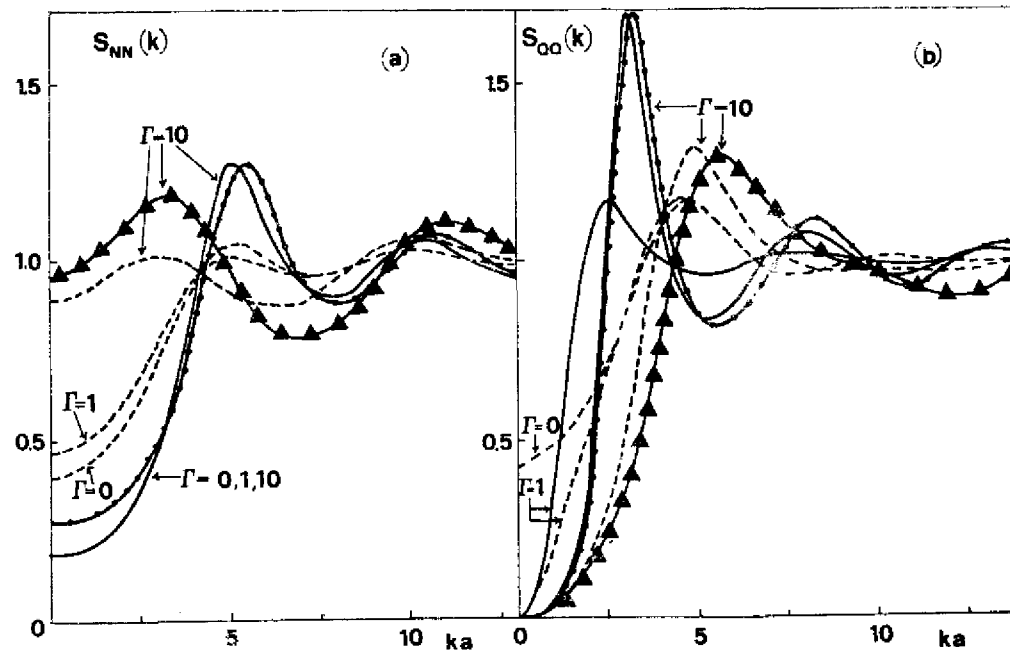


Fig.1

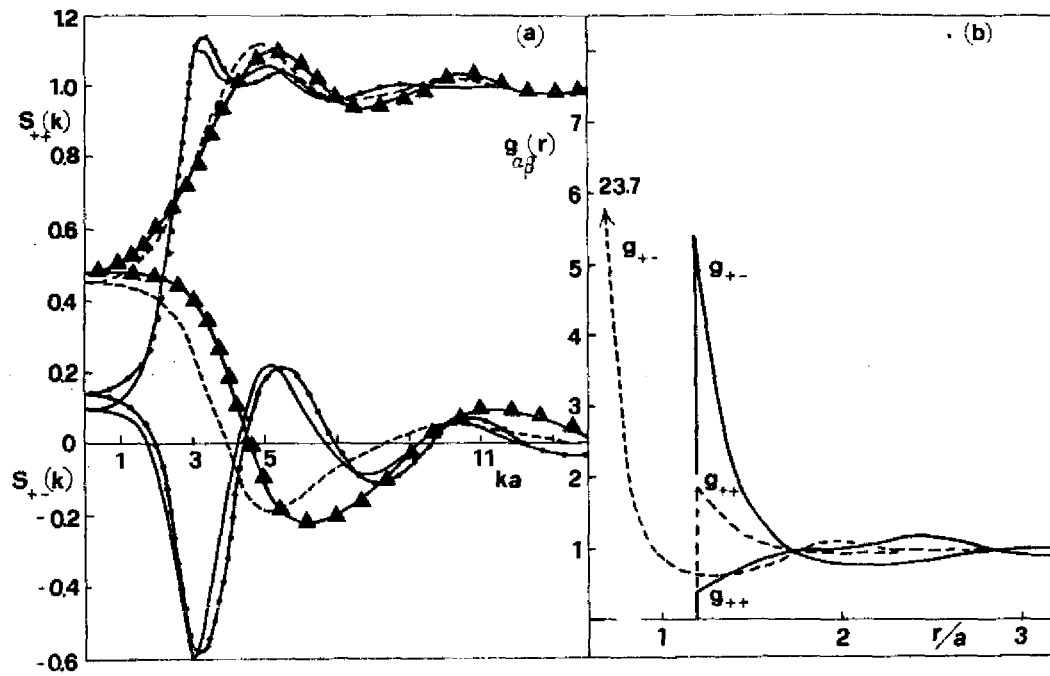


Fig.2

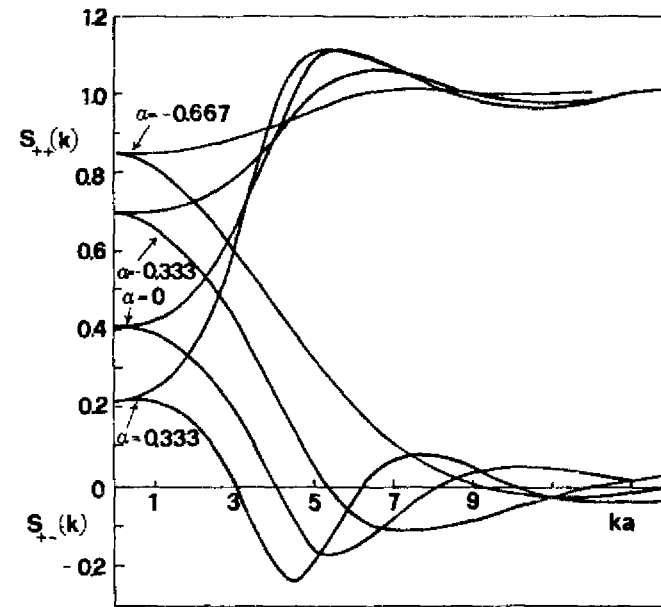


Fig.3

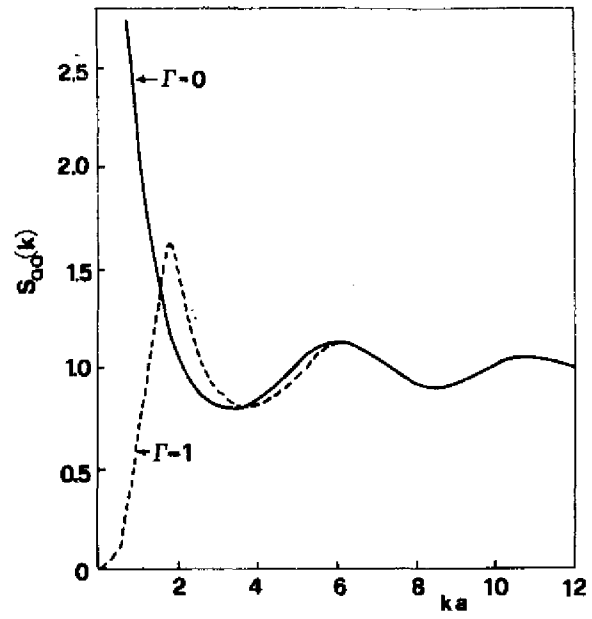


Fig. 4

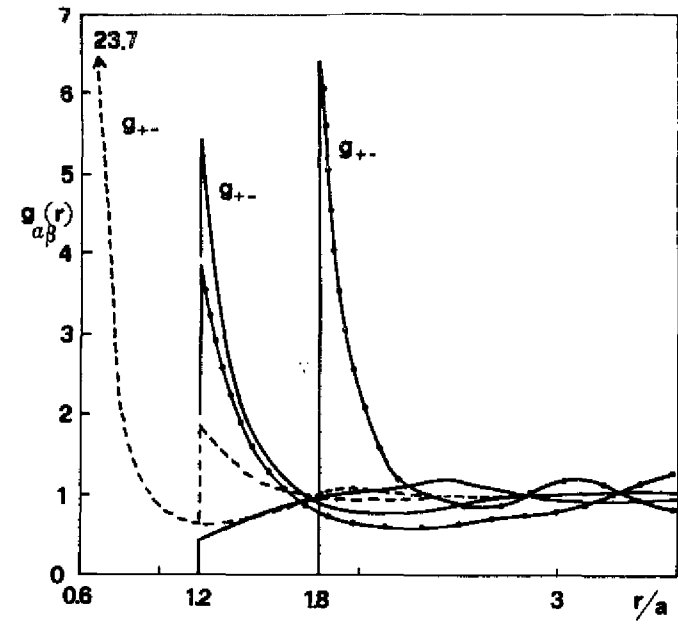


Fig. 5

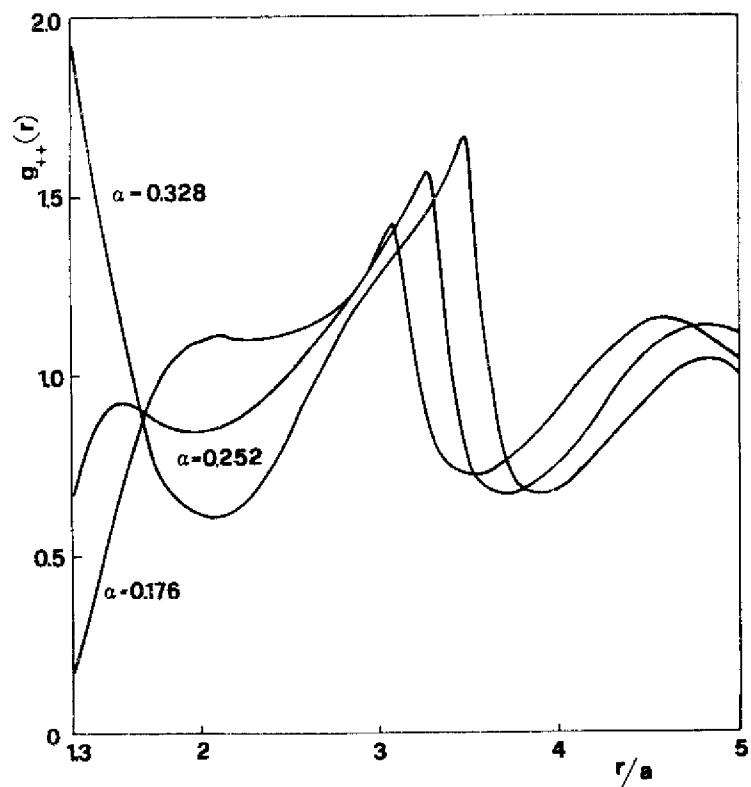


Fig.6

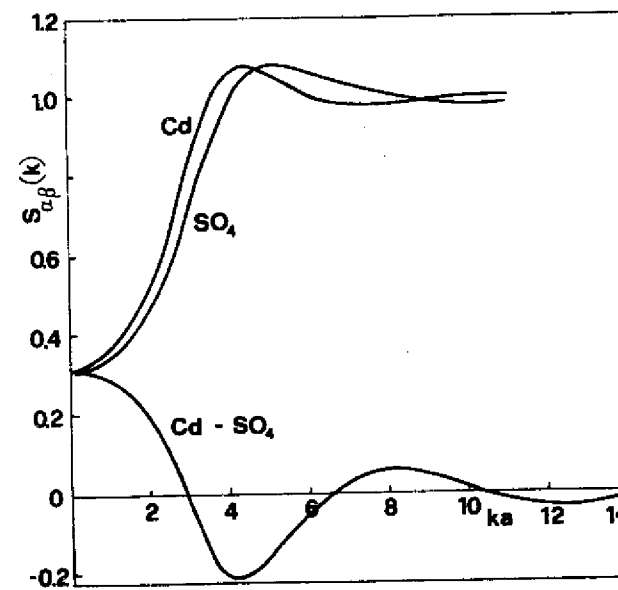


Fig.7