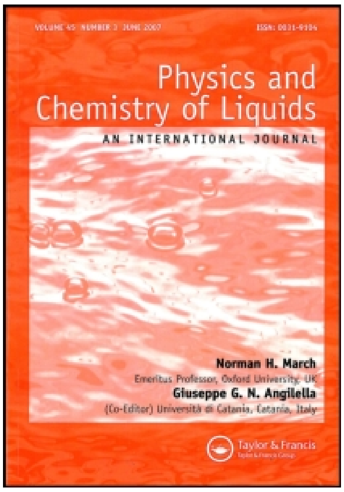

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Z. Badirkhan[a]; M. P. Tosi[b]
[a] International School for Advanced Studies, Trieste, Italy [b] Department of Theoretical Physics, University of Trieste and International Centre for Theoretical Physics, Trieste, Italy

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ON CONDENSATION DRIVEN BY ELECTROSTATIC INTERACTIONS IN MACROIONIC SOLUTIONS

Z. BADIRKHAN* and M. P. TOSI†

**International School for Advanced Studies, Trieste, Italy.*
†Department of Theoretical Physics of the University of Trieste and International Centre for Theoretical Physics, Trieste, Italy.

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Liquid-vapour phase separation, as it normally follows from attractive interactions, is demonstrated under pure Coulomb interactions for the primitive model of macroionic solutions in the mean spherical approximation and related to observations on dilute solutions of highly charged latex particles. It is stressed that, the corresponding effective pair potential between macro-ions being of the Verwey–Overbeek repulsive type, this effective interaction does not need to be supplemented by an attractive tail in order to deal with condensation phenomena, as was done in recent work by Sogami and Ise.

KEY WORDS: Charged hard spheres, osmotic pressure, spinodal curve.

1. INTRODUCTION

It is well known that suspended charged particles in aqueous solutions can form ordered structures, which are revealed by light diffraction and light scattering or directly observed by microscopy.[1] In the case of dilute solutions of highly charged, monodisperse latex particles Ise and coworkers[2,3] have observed coexistence between ordered and disordered regions and measured appreciable reductions of the interparticle distance in the ordered regions below the average value that would be calculated from the particle concentration. Further observations of separation of dilute suspensions into a dense phase with crystalline or liquid-like order and a rarefied structureless phase have been reported by Arora *et al.*[4]

Ise *et al.*[2,3] emphasized that the observed phenomena of macro-ion condensation are inconsistent with purely repulsive effective interactions between the like charged macro-ions. In view of the rather large values of the interparticle distance R_0 compared with the particle radius a in their experiments, they argued that the main agent for macro-ion condensation should be sought in an effective attractive tail of Coulombic origin, mediated by the counter-ions in the solution. Sogami[5] and Sogami and Ise[6] have attempted to construct such an interparticle pair potential, using the primitive model and the linearized Poisson–Boltzmann equation. Calculation of the Helmholtz free energy for each given spacial configuration of macro-ions leads to pair-wise contributions, which are repulsive and of the usual Verway–Overbeek (DLVO) type. The subsequent insertion of an attractive tail through a Gibbs free energy calculation has been critized by Overbeek[7] on themodynamic grounds.

Independent justification for a DVLO-type effective interaction is given in the work of Kahn *et al.*,[8] who show that it follows from liquid structure theory once the point-ion limit is taken for the counter-ions and all correlations other than those between macro-ions are treated in the mean spherical approximation (MSA). Such an effective pair potential depends on the correlations between macro-ions, as well as on density and temperature through the screening length. It is not, therefore, a standard state-independent repulsive interaction of the types that can only show a fluid-to-solid transition driven by the container size.[9] The crucial question is whether the repulsive, but state dependent, DLVO interaction can yield condensation as it occurs in a vapour-to-liquid transition, which commonly requires attractive forces.[9]

2. MACRO-ION CONDENSATION IN THE PRIMITIVE MODEL

As long as one assmes that the primitive model has at least qualitative relevance to real macroionic solutions, it is possible to bypass the question of the effective pair potential and to directly enquire whether the model shows condensation under pure electrostatic interactions. Indeed, relevant work has already been reported by Belloni,[10] who solves the model in the hypernetted chain approximation (HNC) and numerically finds that for certain choices of model parameters the osmotic compressibility seems to diverge as a function of concentration. This has led him to construct a spinodal curve for phase separation, which has been further tested by calculations transcending the HNC.[11]

We explicitly derive below the phase coexistence curve associated with Belloni's spinodal curve for the primitive model by resorting to the MSA, which is less accurate than the HNC but is fully solved analytically.[12,13] The coexistence is of the liquid-vapour type—namely, the model shows condensation in a suitable region of its parameters.[14] We then discuss the connection between the region of parameters for phase separation in the model and the experiments of Ise *et al* and return in the end to the question of the effective pair potential between macro-ions.

The model is a two-component fluid of charged hard spheres representing macro-ions (with valence z_1, diameter σ_1 and number density ρ_1) and counter-ions (of valence z_2, diameter σ_2 and number density ρ_2, with $z_1\rho_1 + z_2\rho_2 = 0$), embedded in a uniform dielectric of dielectric constant ε. The osmotic pressure (namely, the pressure of the system of active particles relative to the uniform dielectric background) is the sum of contributions from hard spheres and from Coulomb interactions,[12]

$$P = P_{\text{hs}} + P_{\text{ex}} \tag{1}$$

We evaluate P_{hs} from the Percus-Yevick compressibility of the hard spheres fluid mixture,[15]

$$P_{\text{hs}} = \frac{6k_BT}{\pi}\left[\frac{\zeta_o}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{3\zeta_2^3}{(1-\zeta_3)^3}\right] \tag{2}$$

with $\zeta_m = (\pi/6)\Sigma_i\rho_i\sigma_i^m$, and take the excess pressure due to Coulomb interactions from the MSA solution[13] as

$$P_{\mathrm{ex}} = -\frac{k_B T \Gamma^3}{3\pi} - \frac{\pi e^2 P_n^2}{2\varepsilon(1-\zeta_3)^2} \tag{3}$$

Here, Γ is a generalized inverse screening length to be determined from the equation

$$\Gamma = \left[\frac{\pi e^2}{\varepsilon k_B T} \sum_i \rho_i \left\{ \frac{z_i - \frac{1}{2}(\pi\sigma_i^2 P_n^2)/(1-\zeta_3)}{1+\Gamma\sigma_i} \right\}^2 \right]^{1/2} \tag{4}$$

and the explicit expression for P_n can be found in Ref. 13. The corresponding Helmholtz free energy F is found from the above expressions for the osmotic pressure P by integration over density and the Gibbs free energy G is obtained as $G = F + PV$. Clearly, P_{ex} in Eqn. (3) is intrinsically negative and may thus lead to phase separation at small values of the volume fraction of macro-ions, by bending the ideal gas isotherms downwards before the positive excess term in P_{hs} takes over. We also remark that the total pressure of the solution is distinct from the osmotic pressure P and includes an explicit contribution of the solvent, as discussed by Overbeek.[7]

Figure 1 illustrates the calculated isotherms (with pressure and temperature in reduced units $P^* = \varepsilon P\sigma_1^4/e^2$ and $T^* = \varepsilon\sigma_1 k_B T/2e^2$) against volume fraction $\Phi = \pi\rho_1\sigma_1^3/6$, for a particular choice of model parameters already considered by Belloni[10].

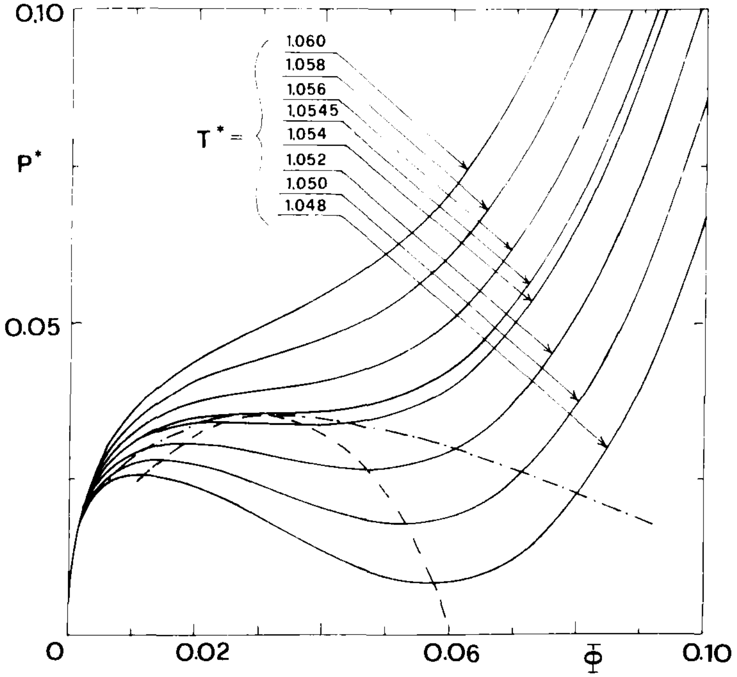

Figure 1 Isotherms versus volume fraction for the primitive model in the MSA at the indicated values of the reduced temperature T^* (full curves). The spinodal curve (dashed) and the phase coexistence curve (dot-dashed) are also shown. The model parameters are $z_1 = 20$, $z_2 = -1$ and $\sigma_2/\sigma_1 = 0$.

The isotherms have the classical van der Waals shape, as appropriate in a mean field theory. The spinodal curve is directly given by the location of the extremal points on the isotherms and the two-phase coexistence curve is obtained from the Gibbs free energy by the usual Maxwell construction. These curves are also shown in Figure 1. Of course, both phases are fluid in these calculations and hence the nearest known equivalent to their coexistence is the liquid-vapour one. The order parameter is the difference in volume fraction of the two coexisting phases and shows classical mean field behaviour near the critical temperature, as expected in the present theory.

For what concerns the dependence of the coexistence curve on model parameters, the critical value of T^* increases by almost a factor two on doubling the valence ratio z_1/z_2 at constant radius ratio, while the two-phase region shifts to lower volume fractions. The effect of changing the radius ratio at constant valency ratio on a specific isotherm is shown in Figure 2. Clearly, the critical T^* increases with the ratio σ_1/σ_2.

3. DISCUSSION

Our MSA results in Figure 1 can be compared with the HNC and MHNC results of Belloni[10,11] with regard to the location of the critical point and the shape of the spinodal curve. The comparison shows, in accord with past experience in this area,[16]

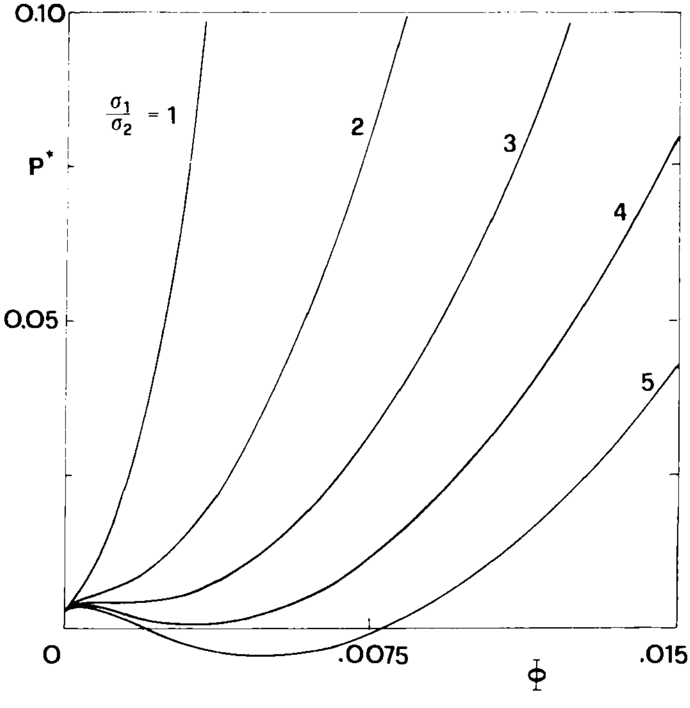

Figure 2 The $T^* = 0.895$ isotherm of the primitive model in the MSA for various values of the radius ratio σ_1/σ_2. The other model parameters are as in Figure 1.

that the MSA is not quantitatively valuable for fluids of strongly asymmetric ionic components. It gives nevertheless full agreement at the qualitative level with the more refined calculations.

We next make contact in orders of magnitude with the observations of Ise and coworkers[2,3] on macro-ion condensation in aqueous solutions. It is immediately satisfactory that phase separation in the theory of the primitive model and observed condensation occur at similar values of macro-ion concentration, of the order of a percent by volume. For what concerns temperature, in view of the widely different valency ratios in the two situations we propose that the relevant parameter is the Coulomb coupling strength between macro-ions and counter-ions, as measured by the "plasma parameter" $\gamma = |z_1 z_2| e^2/(\varepsilon R_o k_B T) = |z_1 z_2| a/(R_o T^*)$. The appropriate value of this parameter in the experiments is estimated to be of order 20, taking $|z_1 z_2| \approx 10^3$, $R_o/a \approx 5$ and $k_D a \approx 1$ for the Debye inverse length k_D. This is consistent with the indications given by the primitive model, for which γ is of the order of a few units at the critical point and increasing along the liquid branch of the coexistence curve. Solidification of the dense fluid phase will take place at still larger values of the coupling strength.

Finally, we stress that, while the foregoing results have in no way involved the notion of an effective pair potential between macro-ions, the theoretical arguments of Kahn *et al.*[8] show that the phase diagram in Figure 1 applies to an effective one-component fluid of macro-ions interacting via a DLVO-type potential. Therefore, this simple effective interaction is not only well founded at a precise level of approximation, but also quite rich in virtue of its state dependence. Of course, the effective pair potential has to be understood as appropriate for the evaluation of macro-ions statistical averages and structure, from which the thermodynamic functions follow by well established statistical mechanical procedures. Provided that this route is consistently followed, there is no need to invoke *ad hoc* attractive tails in order to describe phenomena of macro-ion condensation.

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