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A mean spherical approximation study of phase stability in charged colloidal solutions

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Abstract: The phase stability of charged hard sphere fluid mixtures modelling colloidal solutions is studied through the Mean Spherical Approximation (MSA). The isothermal compressibility and the Gibbs free energy of mixing are calculated, and from them, the liquid-vapor and the liquid-liquid decomposition spinodal line are determined, respectively.

The MSA results favorably compare with those available from other theories as far as the liquid-vapor instability is concerned. For liquid-liquid decomposition the theory allows one to construct the full temperature - concentration spinodal which shows an upper consolution point in temperature. Discussion and interpretation of this and related features of the phase stability line are reported.

Several simplified modelizations of charged colloidal systems have been proposed in recent years in order to obtain a theoretical description of the structural properties of these systems. One of these approaches, probably the first in order of time, is based on the reduction of these multicomponent fluids to a 'one component' system in which the colloidal macroparticles are assumed to interact via an effective potential which takes into account, in an averaged form, the presence of the counterions, of the solvent, and possibly of other ionic species. Once the model potential is so fixed one resorts to the application of some liquid structural theory¹ which allows one to calculate thermodynamic and structural properties of the colloidal solution; these last are eventually compared with experimental data or with computer simulation results, if available.

It is implicit in the one component representation that correlations between macroparticles and the other ionic species are so small that the presence of these last can be taken into account in terms of a 'mean field' interaction.

This approach is qualitatively accurate for the description of the structural properties of a number of real colloidal systems¹⁻²; its main deficiencies have however also been

evidentiated, thanks to calculations¹⁻⁷ which take the full multicomponent nature of the fluid into account. For instance, one can represent the system in terms of the well known primitive model (PM) of electrolytes^{2,4}, in which the different ionic species are assumed to be charged hard spheres interacting via a coulomb potential; in general, the coulombic forces are also assumed to be screened by a macroscopic dielectric constant through which all the solvent effects are taken into account.

Theoretical studies of the structural properties of the PM as applied to colloidal systems have been performed by different authors within the hypernetted-chain (HNC) approximation², the more sophisticated HNC-Soft Mean Spherical Approximation (HMSA)³ of Zerah and Hansen⁸, and the so called Rescaled Mean Spherical Approximation (RMSA)¹⁻⁶. Computer simulations have also been performed for different system configurations and results compared with structural theories⁶.

Some of these results concern HNC estimates of the 'liquid-vapor' spinodal and critical point of a colloid-counterion solution^{3,4} and also structural properties of charged solutions with more than two ionic species^{3,4}. We report below results obtained through the Mean Spherical Approximation (MSA) for the phase stability, both of liquid-vapor and of consolute type, of charged hard sphere multicomponent fluids, in a parameter regime which is close to that typical of real colloidal solutions.

It is known that liquid state theories whose solution is based on iterational procedures, as Percus-Yevick, HNC and all-HNC based theories, tend to show an highly unstable behaviour in the approach to phase boundaries. The algorithm of solution tends to converge slowly, and eventually no solution at all can be found⁹. More specifically, the numerical routine ceases to work when a certain thermodynamic state is reached which in some case can confidently be identified as close to, or located on, a true phase stability boundary; opposite examples exist, however, in which the instability has been found to be purely numerical in nature, and thermodynamic quantities (typically the isothermal compressibility) do not show any 'singular' behaviour.

Approximate structural theories of liquids are also known to yield critical exponents which do not take the correct value known from the experiment or renormalization group (RG) calculations^{9,10,11}. In what follows we try to illustrate the type of information that can be gained also in this respect through the use of MSA. This theory, as is well known, is analytically solvable and this makes it particularly well suited for the purpose earlier exposed. Moreover, it has the advantage that its solution can be implemented even in the presence of very large asymmetry of charges and sizes of the ionic species, whilst this is not the case with iterational approaches like the HNC^{3,4}.

The MSA is known to yield unphysical radial distribution functions at short range^{1,2,5,6} and to be affected by a serious thermodynamic inconsistency; it has been shown¹², however, that when the PM equation of state is calculated in the MSA via the

'energy route' ¹³ one obtains qualitatively good predictions for thermodynamic quantities. The explanation for this behavior rests in a compensation of errors taking place between contributions to the internal energy calculated through radial distribution functions which are oppositely wrong in the short range limit ¹⁴.

In what follows we shall confine ourselves to the MSA determination of the spinodal curves of a PM 'colloidal' solution, without dealing with structural properties and with their possible assessment, amply reported elsewhere¹⁻⁶.

We consider a system of particles interacting via the potential:

$$\begin{aligned} v_{ij}(r) &= \infty & r < R_{ij} = \frac{R_i + R_j}{2} \\ v_{ij}(r) &= \frac{Z_i Z_j e^2}{\epsilon r} & r > R_{ij} \end{aligned} \quad (1);$$

in (1) R_i is the charged hard sphere diameter, Z_i is the charge number in the i -th ionic species, while ϵ is the dielectric constant of a continuous medium in which the particles are supposed to be merged.

Potential (1) roughly embodies two basic ingredients of the classical Fumi-Tosi potential for alkali-halide crystals¹⁵, namely the harsh repulsion between ionic cores at short range, and the coulombic interaction at long range and, as it has been shown some time ago ¹⁶ it can be used successfully for the description of the structural properties of molten alkali-halides.

In what follows we shall make use of the dimensionless temperature $T^* = (k_B T \epsilon R_p / e^2)$, where R_p is the biggest ionic diameter (the colloidal particle diameter R_p in this case), and of its inverse, the so called plasma coupling parameter $\Gamma = 1/T^*$; we shall also make use of the packing fraction $\eta = \sum_i \rho_i R_i^3$, where ρ_i is the number density of particles in the i -th species. The solution of the MSA we use is that due to Blum¹⁷ and Blum and Hoyer¹⁷, who also gave a set of analytical expressions for thermodynamic quantities as derived via the 'energy route'.

We first consider the case of a colloid + counterion solution. The ionic sizes are such that

$$\alpha_c \equiv \frac{R_{\text{counter}}}{R_p} = 0.1;$$

we further assume $Z_c = -1$ while $Z_p \geq 20$ (electron charge units are used throughout).

The MSA locus of critical temperatures vs Z_p , as deduced from the spinodal determined through the divergence of the isothermal compressibility, is shown in a log-log plot in fig. 1. The straight line behaviour visible in the figure can be represented by the equation $T_{cr}^* = 0.116 Z_p^{0.937}$. This result is reasonably accurate in respect to the HNC estimate $T_{cr}^* = 0.123$

$Z_p^{1.18}$ obtained by Belloni³ also reported in fig.1. It is also worth observing that more refined HMSA calculations predict a displacement^{4,6} of the two phase region toward lower temperatures; unfortunately, the corresponding critical temperature locus is not reported in ref. 3, so to make possible a detailed comparison; the implication, however, is that the MSA result could be more accurate than it appears in fig. 1. Another remarkable feature of the MSA calculation is that, as discussed by Belloni³, one expects 1 as a value

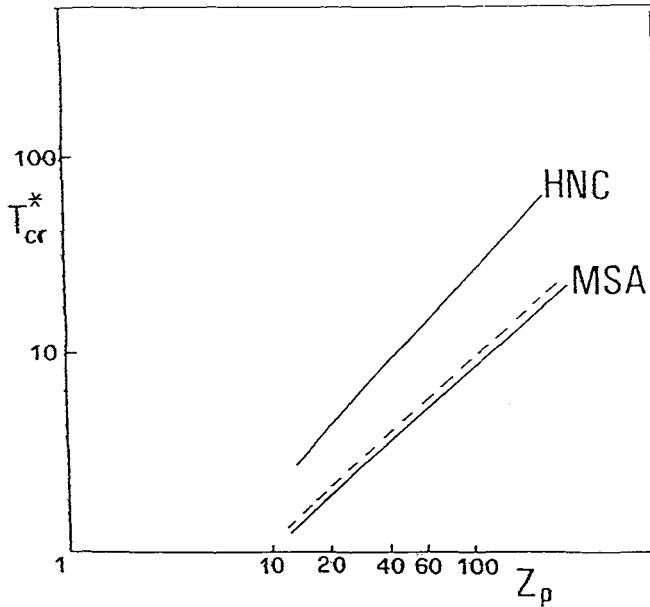


Fig. 1: Logarithmic scale representation of the reduced critical temperature locus as a function of the colloid charge Z_p for a colloid+counterion solution. HNC results correspond to $\alpha_c=0$. (ref.3); MSA results: full line, $4\alpha_c=0.1$; dashed line: $\alpha_c=0.01$.

for the exponent of Z_p , and 0.937, the MSA results (see above) is closer to 1 than 1.18 obtained through the HNC.

Our estimate of the critical packing fraction at $Z_p=20$ is approximately 0.002, as reported in Table I., a value which qualitatively agrees with Belloni's one³ who obtained $\eta_{cr}=0.006$. The MSA critical pressure are also reported in Table I.

Table I

Z_p	T_{cr}^*	P_{cr}^*	η_{cr}	R_p	$T_{cr}(K)$	$p_{cr}(atm)$	Mol_{cr}
20	1.923	0.0072	~ 0.002	20	200	1.03	8×10^{-4}
				50	80	0.02	5×10^{-5}
40	3.57	0.004	~ 0.001	20	372	0.57	4×10^{-4}
100	8.69	0.017	$\sim 10^{-4}$	20	906	2.44	5×10^{-4}

Table I: Critical parameters for the PM modelling a charged colloidal solution. $\alpha_c = 0.1$ (see text) and varying colloidal charge are considered. Also illustrated is the correspondence induced by the choosing of R_p between thermodynamic reduced quantities and their real counterparts.

Note that both η_{cr} and P_{cr}^* map onto realistic molarities and pressures when R_p is taken ~ 50 Å, a reasonable lower bound for the size of colloidal particles. Also note that the critical temperature attains values comparable to room temperature only for $Z_p \sim 100$ and $R_p = 50$ Å.

We now come to the ionic size ratio effect on T_{cr}^* . We study this aspect by comparing the extreme case when $\alpha_c = 1$, that is when particles have all the same diameter, with the current one in which $\alpha_c = 0.1$. As it can be seen in Table II the critical temperature increases when $\alpha_c \rightarrow 0$. This result could have probably been anticipated on the basis of a paper by Stell *et al.*¹⁸ who first identified the presence of a critical point in the PM fluid. According to them phase separation in this system is basically driven by ion pairing phenomena. Now, a reduction of one ionic size favours closest approach between unlike charged particles, thus enhancing the pair stability because of the stronger electrostatic attraction. Therefore, in order to bring the system to a homogenous phase, more kinetic energy (with respect to the $\alpha_c = 1$ case) will be necessary to break tightly bound pairs, in agreement with what we find.

Table II

$Z_p \rightarrow$	1	40	100
α_c			
1.0	0.0785	3.14	7.85
0.1	0.1984	3.577	8.69

Table II: Effect of the ionic size ratio α_c on the reduced critical temperature in colloidal solutions with different charge number Z_p .

Another manner to investigate the role of coulombic forces in determining phase stability is to consider the effect of the addition of an ionic salt to the colloidal solution. Under usual experimental condition this operation results in a sudden lowering of the critical temperature. In our model calculation the addition of a 1-1 salt can be mimicked by assuming the presence in the fluid of another ionic species, termed 'coion', for which $Z_{co.}=+1$ and $R_{co.}=R_c.=0.1R_p$, while counterions belonging to the 1-1 salt are supposed to be the same as those present in the original colloidal solution.

In Fig. 2 the effect on T_{cr}^* of varying the concentration of the salt, (also expressible as the coion concentration $c = \frac{\rho_{co.}r}{\rho_{co.} + \rho_c}$) is reported. It appears that T_{cr}^* decreases when the coion number increases. This is essentially the result of screening that these charges now exert on the colloid-counterion interaction. Actually, it is known from previous studies that condensation of counterions on colloidal particles is reduced when coions are added to the solution¹⁻⁷.

We turn now to consider liquid-liquid phase separation in mixed charged colloidal solutions. The case we consider can be assumed as the prototype of a multicomponent system in which

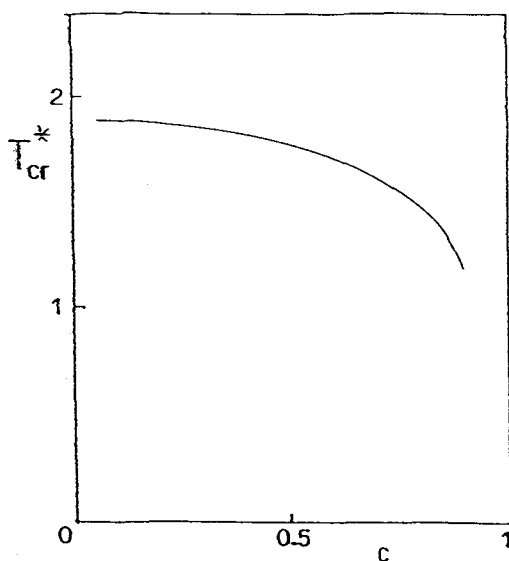


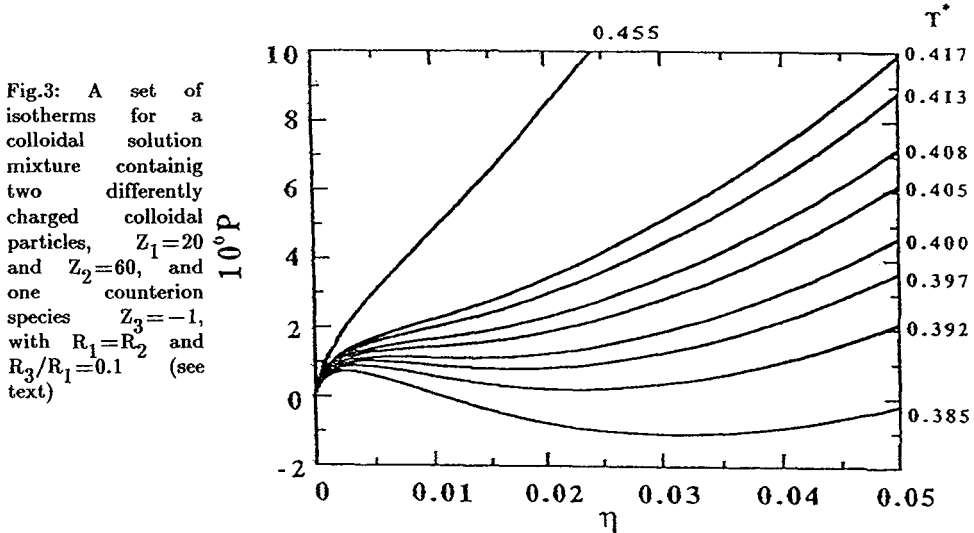
Fig.2 : Variation of the reduced critical temperature as a function of the 1-1 added salt for a system in which $R_c. = R_{co.} = 0.1 R_p$ and $Z_p = 20$ (see text).

charge polydispersity exist for the big colloidal particles. The results we report are part of a larger investigation of phase stability and phase coexistence in multicomponent charged

fluids, recently undertaken in cooperation with other authors¹⁹.

We consider a three component charged hard sphere mixture in which the two colloidal particles, labelled as species 1 and 2, respectively, have number charges $Z_1=20$, $Z_2=60$, and in which species 3 is constituted by counterions with $Z_3 = -1$; the hard sphere diameters are such that $R_1=R_2=10 R_3$, so that colloidal particles are of equal size, and ten times bigger than counterions. We characterize the composition of the mixture in terms of the concentration $c=\rho_1/(\rho_1+\rho_2)$.

Liquid-liquid decomposition in such a mixture is investigated in terms of the Gibbs free energy of mixing, G_m , vs. the concentration, calculated at constant pressures, a condition this last, which is imposed in order to reproduce as much as possible the actual experimental conditions. To this aim, the pressure vs. packing fraction has to be determined at fixed temperature for every concentration. A typical set of isotherms is shown in fig. 3 for the case $c=0.65$.



(note that only the low density portion of the isotherm is displayed in order to detail the evolution from non-monotonic to monotonic increase of the pressure with the packing fraction; also note that all calculations reported below have been performed at pressures high enough that P is monotonically increasing with η ; see ref.20 for more details on this and related points).

As is well known the temperature-concentration spinodal for the mixture is defined by the condition

$$\left(\frac{\partial^2 G_m}{\partial c^2} \right)_{T,P} = 0$$

which corresponds to the occurrence of concavity changes in the G_m vs. c pattern.

Fig. 4 reports G_m at different constant Γ 's (or T^* 's).

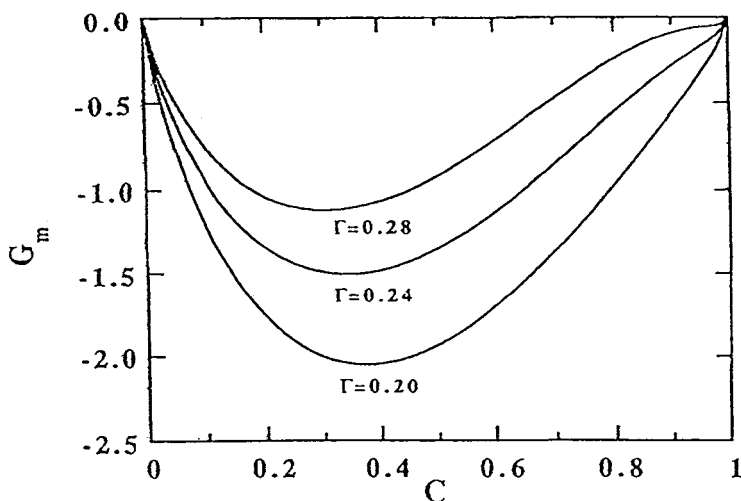


Fig. 4: Gibbs free energy of mixing G_M vs. concentration at fixed pressure $P = 0.01$ (in reduced e^2/R_p^4 units) and different fixed Γ 's, for the mixture of fig. 3

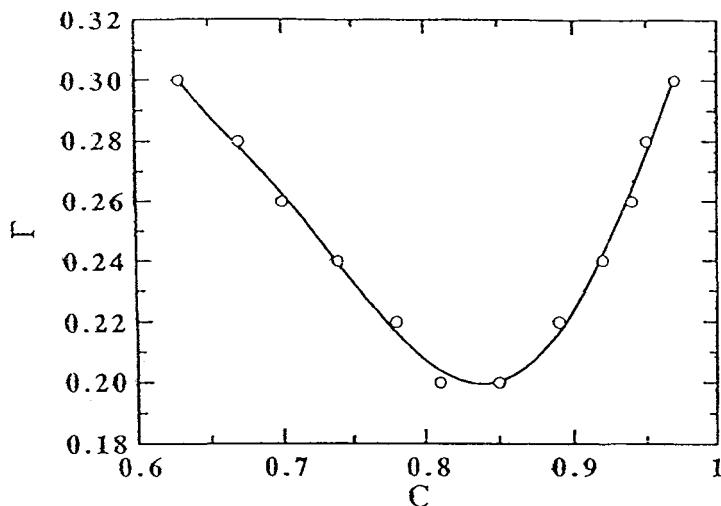


Fig.5: Inverse-temperature vs. concentration spinodal for the mixture of fig.3.

It can be appreciated that at sufficiently high coupling, that is for sufficiently low reduced temperature, inflection points appear in the G_m pattern thus indicating the occurrence of phase instability with respect to concentration fluctuations. The locus of these points is reported in fig. 5 and constitutes the liquid-liquid spinodal for the present system.

The main feature of fig. 5 is the presence of a lower consolute point in Γ , corresponding to an upper consolution point in temperature, and the shift of consolute critical point toward the lower-charge component (species 1) rich-end.

These results can be interpreted in terms of the different effect that the addition of 1 or 2 particle has on the equilibrium of the mixture, and on the competition between different physical contribution to the Gibbs thermodynamic potential.

In fact, the process of segregation is obviously accompanied by a decrease in the total entropy of the system; this amounts to inducing a *positive* variation in the Gibbs free energy

$$\Delta G_m = \Delta U - T\Delta S + P\Delta V \quad (2) ;$$

on the other hand, the same segregation favors the formation, with respect to the mixture where positive charges are more randomly distributed, of well defined and highly packed clusters of oppositely charged particles (we mean particles 2 with 1, or particles 3 with 1), and these clusterization implies a decrease of the configurational energy $\Delta U < 0$ which more than compensate for the entropic increase in ΔG_m before envisaged. There is obviously an extra-term associated with volume variation (see eq.2); however, we have shown in a previous paper²¹ that this contribution is not able to modify the qualitative aspect of the aforementioned competition between entropic and coulombic energy effects.

The presence of a l.c.p. in fig. 5 can now be understood if one considers that the role of coulombic interactions is enhanced when Γ increases (or T^* decreases); it is also reasonable that the spinodal is asymmetric toward the less charged species rich-end since relatively few highly charged 2 particles affect the properties of the fluid more than an equivalent amount of low charged particles 1.

The conclusion that can be drawn from the present study is that despite the serious shortcomings of the MSA, a judicious use of this approximation might reveal fruitful in the context of phase stability behavior investigation, especially if the 'energy route' is used to construct thermodynamics from the structure. At this proposal it could be worth trying to assess the performances of this approximation against more refined theories and/or computer simulation results, in a limited number of representative cases of ionic fluids. This would allow one to establish well defined benchmarks to the MSA

predictions as far as the stability of thermodynamic states is concerned. Such a qualitative knowledge of the phase behaviour of ionic fluids could be useful, e.g., to experimentalists interested to define broad intervals of physical parameters where phase equilibria or decomposition of colloidal systems may take place.

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