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Charge renormalization and phase separation in colloidal suspensions

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Abstract. – We explore the effects of counterion condensation on fluid-fluid phase separation in charged colloidal suspensions. It is found that formation of double layers around the colloidal particles stabilizes suspensions against phase separation. Addition of salt, however, produces an instability which, in principle, can lead to a fluid-fluid separation. The instability, however, is so weak that it should be impossible to observe a fully equilibrated coexistence experimentally.

Colloidal suspensions present an outstanding challenge to modern theories of statistical mechanics. In spite of the work extending all the way to the beginning of previous century, our understanding of these complex systems remains far from complete. Even such basic questions as what is the form of the interaction potential between two colloidal particles inside a solution, still remain controversial [1]. The suspensions most often studied experimentally consist of polystyrene sulphate spheres with diameter in the range of 10^{-6} – 10^{-4} cm, and 10^3 – 10^4 ionisable surface groups. The typical solvent is water at room temperature. The main stumbling blocks are the presence of long-range Coulomb interactions and the tremendous asymmetry existing between the polyions and their counterions. The ratio of the bare charge of a colloidal particle to that of its counterion can be as high as 10000:1. This large asymmetry completely invalidates most of the methods of liquid state theory, which have proven so successful in the studies of simple molecular fluids.

A particularly interesting question that has provoked much controversy over the last two decades concerns itself with the possibility of fluid-fluid phase separation in charged colloidal suspensions. A naive argument, based on the theory of simple molecular fluids, suggests that fluid-fluid (or liquid-gas) coexistence is only possible in the presence of sufficiently long-ranged attractive interactions. Thus, it has been proposed by some authors that a phase separation, or

even existence of voids in charged colloidal lattices requires attraction between the polyions [2]. Although appealing intuitively, this point of view is difficult to justify within the framework of statistical mechanics. The fundamental observation is that colloidal suspension is a complex fluid for which many-body effects play the fundamental role. It is, therefore, erroneous to confine attention to pair interactions between the colloidal particles while ignoring the significantly larger contributions to the free energy arising from the presence of counterions [3]. This point has also been emphasized by van Roij and Hansen (RH) [4] who demonstrated, in the context of the linearized density functional theory, the existence of “volume” terms, which can drive phase separation even for pairwise *repulsive* interactions [5]. The prediction of a liquid-gas phase separation in an aqueous solution of like-charged colloidal particles seems, however, to be contradicted by the recent simulations of Linse and Lobaskin [6], who did not find any indication of phase transition in suspensions with monovalent counterions. This apparent discrepancy between the simulations and the density functional theory suggests that a closer look at the mechanism of phase separation is worth while. Since the first simulations were performed in the absence of salt, as a starting point, we shall concentrate our attention on this regime.

Our model consists of $N_p = \rho_p V$ spherical polyions of radius a , inside a homogeneous medium of volume V and dielectric constant D . Each polyion carries Z ionized groups of charge $-q$ uniformly distributed over its surface. A total of ZN_p monovalent counterions of charge $+q$ are present in order to preserve the overall charge neutrality of solution. In the absence of salt, the counterions can be treated as point-like.

All the thermodynamic properties of colloidal suspensions can be determined given the free energy. Unfortunately due to the complexity of these systems, no exact calculation is possible and approximations must be used. We construct the total free energy as a sum of the most relevant contributions: electrostatic, entropic, and hard core, $f = F/V = f_{\text{el}} + f_{\text{ent}} + f_{\text{hc}}$. The electrostatic free energy, f_{el} , is the result of polyion-counterion, f_{pc} , and the polyion-polyion, f_{pp} , interactions. Interactions between the monovalent microions are insignificant for aqueous solutions and can be ignored [3].

The polyion-counterion contribution to the total free energy can be obtained in the framework of Debye-Hückel theory [3, 7]. Fixing one colloidal particle at the origin, it is possible to show that the electrostatic potential in its vicinity satisfies the Helmholtz equation $\nabla^2 \psi = \kappa^2 \psi$, where $\kappa a = (4\pi Z \rho_p^* / T^*)^{1/2}$, and the reduced temperature and density are $T^* = k_B T q^2 D / a$ and $\rho_p^* = \rho_p a^3$, respectively. The electrostatic free energy can be obtained from the solution of the Helmholtz equation followed by the Debye charging process, yielding

$$\beta f_{\text{pc}} = \frac{Z^2}{2T^*(1 + \kappa a)} \rho_p. \quad (1)$$

We note that this expression would be identical to the one obtained by RH using the density functional theory [4], but for the self-energy contribution, $\beta f_{\text{self}} = Z^2 \rho_p / 2T^*$, which we include and RH excluded. Since f_{self} is proportional to the density, it is irrelevant for any thermodynamic calculations, *as long as* the effects of charge renormalization are neglected. Thus, contrary to some earlier claims [8], the Debye-Hückel theory is fully consistent with the density functional theory.

The polyion-polyion contribution to the free energy is calculated within the variational approach proposed by Mansoori and Canfield [9]. The electrostatic DLVO potential [10] is used to describe the effective pair interactions between the colloidal particles inside the suspension. Based on the Gibbs-Bogoliubov inequality $F \leq F_0 + \langle U \rangle_0$, Mansoori and Canfield replace the free energy by the lowest variational bound. The subscript 0 denotes the reference

system of hard spheres whose diameter plays the role of a variational parameter. The polyion-polyion free energy is given by [11]

$$\beta f_{\text{pp}}(\eta) = \rho_{\text{p}} \frac{\eta(4-3\eta)}{(1-\eta)^2} + \frac{Z\rho_{\text{p}}}{2} [\lambda^2 G(\lambda) - 1]. \quad (2)$$

The first term is the free energy of the reference hard-sphere system, while the second is the electrostatic contribution evaluated using the Percus-Yevick pair correlation function for hard spheres. The volume fraction, η , plays the role of a variational parameter. The functions

$$\begin{aligned} G(\lambda) &= \frac{\lambda L(\lambda)}{12\eta[L(\lambda) + \bar{S}(\lambda)e^\lambda]}, \\ L(\lambda) &= 12\eta \left[\left(1 + \frac{\eta}{2}\right) \lambda + (1 + 2\eta) \right], \\ \bar{S}(\lambda) &= (1-\eta)^2 \lambda^3 + 6\eta(1-\eta)\lambda^2 + 18\eta^2 \lambda - 12\eta(1+2\eta), \end{aligned} \quad (3)$$

are given in terms of $\lambda = 2\kappa r_0 \eta^{1/3}$, where r_0 is a measure of the typical distance between the macroions and is given by $4\pi\rho_{\text{p}}r_0^3/3 = 1$. The variational minimum $\bar{\eta}$ is found by solving the equation $\partial f_{\text{pp}}/\partial\eta = 0$, this has to be done numerically. The polyion-polyion contribution to the total free energy is $f_{\text{pp}}(\bar{\eta})$. Again we observe that this calculation is very similar to the one performed by RH using the density functional theory. We also note that eq. (2) already includes the background subtractions emphasized by Warren [12].

The contribution to the total free energy arising from the hard-core repulsion between the colloidal particles can be approximated by the Carnahan-Starling form [13],

$$\beta f_{\text{hc}} = \rho_{\text{p}} \frac{\phi_{\text{p}}(4-3\phi_{\text{p}})}{(1-\phi_{\text{p}})^2}, \quad (4)$$

where $\phi_{\text{p}} = 4\pi\rho_{\text{p}}^*/3$ is the volume fraction of polyions. The final contribution to the total free energy is due to the entropic motion of counterions and polyions and can be expressed using the Flory theory [14]

$$\beta f_{\text{ent}} = \rho_{\text{p}} \ln \left(\frac{\phi_{\text{p}}}{\zeta_{\text{p}}} \right) - \rho_{\text{p}} + Z\rho_{\text{p}} \ln \left(\frac{\phi_{\text{c}}}{\zeta_{\text{c}}} \right) - Z\rho_{\text{p}}, \quad (5)$$

where ζ_{p} and ζ_{c} are the internal partition functions of the polyions and the counterions, and ϕ_{c} is the ‘‘effective’’ volume fraction of counterions. Since both the polyions and the counterions are rigid, without any internal structure, $\zeta_{\text{p}} = 1$ and $\zeta_{\text{c}} = 1$. Although we have assumed the counterions to be point-like, the strong electrostatic repulsion will prevent them from approaching too close to one another. The distance of characteristic approach d can be obtained by comparing the electrostatic and the thermal energies. More specifically from the theory of one-component plasma [15] we find that $d = [(1 + 3\kappa a/T^*)^{1/3} - 1]/\kappa$. The volume fraction occupied by the counterions is then $\phi_{\text{c}} = 4\pi Z\rho_{\text{p}}d^3/3$. Combining all these contributions, we obtain the total free energy $f = f_{\text{ent}} + f_{\text{pc}} + f_{\text{pp}} + f_{\text{hc}}$ of a colloidal suspension. We observe that when $Z\lambda_{\text{B}}/a$ is bigger than approximately 15, the Helmholtz free energy is no longer a convex function of colloidal density and the separation into two coexisting phases becomes thermodynamically favorable. Here $\lambda_{\text{B}} = a/T^*$ is the Bjerrum length and is equal to 7.2 Å in water at room temperature. In fig. 1 we demonstrate some characteristic pressure-density isotherms, exhibiting the familiar van der Waals loop, indicating the presence of a first-order phase transition.

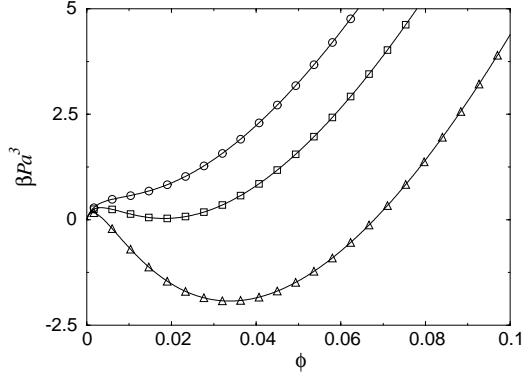


Fig. 1 – The pressure-volume fraction, $\phi = \frac{4}{3}\pi a^3 \rho_p$, isotherms for salt-free colloidal suspensions at room temperature, $\lambda_B = 7.2 \text{ \AA}$. The circles are for $Z = 2000$, squares for $Z = 2200$ and triangles for $Z = 2500$. The radius of polyions is $a = 1000 \text{ \AA}$. Note the presence of the van der Waals loop for $Z = 2200$ and $Z = 2500$.

Is the phase transition found above consistent with the underlying approximations of the Debye-Hückel and the linearized density functional theory? Clearly the fact that the transition is located at $Z/T^* \approx 15$, *i.e.*, the strong coupling regime, should leave us concerned. Certainly, in this regime the charge renormalization due to strongly associated counterions should play a significant role [16]. Fortunately, it is fairly straightforward to include the effects of counterion condensation directly into the theory presented above [3, 17]. To achieve this, we separate counterions into condensed and free. For simplicity we shall assume that each polyion has an equal number n of condensed (associated) counterions [3]. The density of free counterions is then $\rho_f = (Z - n)\rho_p$. We shall suppose that the only effect of condensed counterions is to renormalize the bare charge of colloidal particles, while the screening is performed by the *free* microions. The effective charge of a polyion-counterion complex is then $Z_{\text{eff}} = Z - n$. The free energy $f(n)$, taking into account the charge renormalization, is obtained by replacing $Z \rightarrow Z - n$ in all formulas, including the inverse screening length κ . In addition, since the complexes now have structure [3], their internal partition function can be approximated by $\zeta_p = [Z! / ((Z - n)! n!)] e^{-\beta E_n}$, where E_n is the electrostatic energy of n counterions condensed onto the surface of a polyion. The electrostatic energy of association can be obtained through the charging process [3], yielding $\beta E_n = -(Zn - n^2/2)/T^*$.

For fixed volume and number of particles, the equilibrium state of a colloidal suspension is determined by the minimum of Helmholtz free energy, $f_{\text{ren}} = \min_n f(n)$. Predictions of this theory for Z_{eff} have been recently tested and found to be in a semi-quantitative agreement with the experiments [18]. We find that the charge renormalization, fig. 2b, has a most profound effect on the free energy. The f_{ren} is a convex function of colloidal density *for all values of Z* , see fig. 2a. We conclude that *counterion condensation stabilizes salt-free colloidal suspension against phase separation*.

We now turn our attention to suspensions in the presence of salt. Since a system containing point-like positive and negative particles is intrinsically unstable, we assign to each counterion and coion a characteristic radius a_c . The concentration of monovalent salt is designated by ρ_s . The calculation now proceeds as the one outlined above. The density of free microions is $\rho_f = (Z - n)\rho_p + 2\rho_s$ and $\kappa a = (4\pi\rho_f^*/T^*)^{1/2}$. The effective charge of a polyion-counterion complex is $Z_{\text{eff}} = Z - n$. The polyion-counterion and the polyion-polyion contributions to the

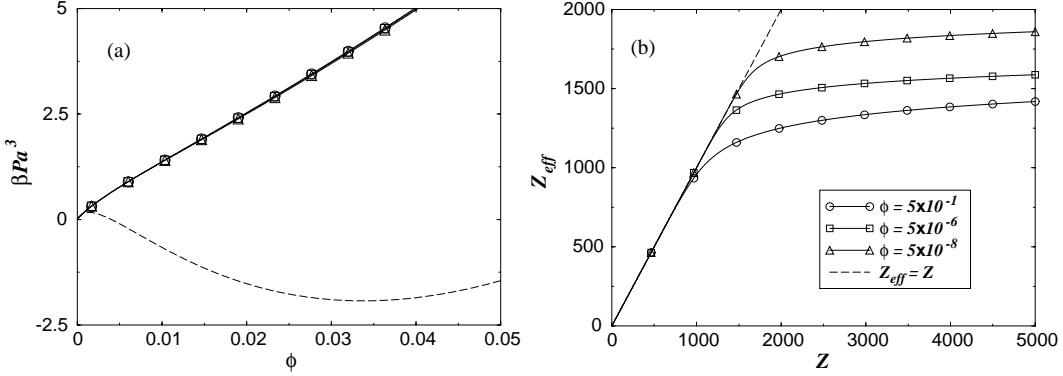


Fig. 2 – (a) The pressure-volume fraction isotherms for salt-free colloidal suspensions. All parameters are as in fig. 1. The solid curves are for $Z = 2000$ (circles), 2200 (squares), 2500 (triangles) *with counterion condensation* taken into account. Note that Z_{eff} is almost the same for all three bare charges, and the isotherms collapse onto one monotonically increasing curve. There is no phase separation. The dashed curve, included for comparison, *neglects* the counterion condensation, and demonstrates the presence of the van der Waals loop and the phase separation for $Z = 2500$. (b) The effective charge Z_{eff} vs. Z for various colloidal volume fractions. Note that the effective charge is quite insensitive to colloidal concentration.

total free energy are the same as for the case without salt, but with the new definition of κ , since all free microions contribute to screening. The entropic free energy is given by

$$\beta f_{\text{ent}} = \rho_p \ln \left(\frac{\phi_p}{\zeta_p} \right) - \rho_p + \rho_+ \ln \left(\frac{\phi_+}{\zeta_c} \right) - \rho_+ + \rho_- \ln \left(\frac{\phi_-}{\zeta_c} \right) - \rho_-, \quad (6)$$

where the density of free counterions is $\rho_+ = (Z - n)\rho_p + \rho_s$ and the density of coions is $\rho_- = \rho_s$. The volume fractions are $\phi_+ = 4\pi\rho_+a_c^3/3$ and $\phi_- = 4\pi\rho_-a_c^3/3$.

To study a possibility of phase separation in this multicomponent system is significantly more difficult than for the case of salt-free suspensions. The clearest indication of phase transition can still be obtained from the pressure-density isotherms. A caution, however, must be taken since the two coexisting phases do not necessarily have the same concentration of salt, but *must have the same* chemical potential. This can be controlled by putting the suspension in contact with a hypothetical reservoir containing an aqueous solution of salt. In fig. 3, we present the pressure-density isotherms for suspensions with salt. We see that even an extremely low concentration of salt is sufficient to shift the phase transition to the region of parameter space where the charge renormalization plays only a marginal role. The suspension phase separates; however, the transition is much weaker than it would be in the absence of counterion condensation, fig. 3. The instability region forms a closed loop in the (ρ_s, ρ_p) -plane. For the values of Z , a , a_c , and λ_B used in fig. 3 the upper critical point is at $\rho_s^u \approx 64 \mu\text{M}$ and $\phi_p^u \approx 0.02$. For salt concentrations $\rho_s > \rho_s^u$ the suspension is completely stable. The lower critical point is located at $\rho_s^l \approx 0.28 \mu\text{M}$ and $\phi_p^l \approx 0.000025$. Since in practice it is impossible to deionise water below $\rho_s \approx 1 \mu\text{M}$, all aqueous suspension should —*in principle*— exhibit a miscibility gap at sufficiently low colloidal volume fractions and salt concentrations. From fig. 3, however, it is clear that fluid-fluid transition is so weak that it is highly unlikely that a fully equilibrated coexistence can be observed experimentally.

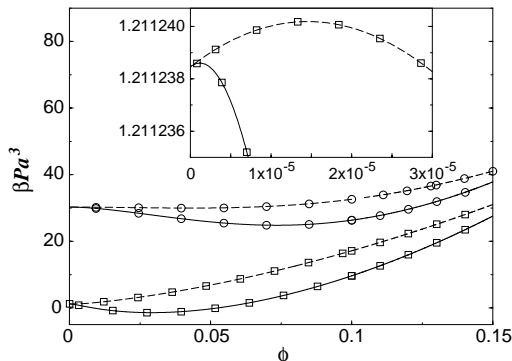


Fig. 3 – The pressure-volume fraction isotherms for colloidal suspensions with two different reservoir salt concentrations: circles for $\rho_s = 25 \mu\text{M}$ and squares for $\rho_s = 1 \mu\text{M}$; $\lambda_B = 7.2 \text{ \AA}$, $a = 1000 \text{ \AA}$, $a_c = 2 \text{ \AA}$, $Z = 2500$. The solid curves are when the charge renormalization is neglected, while the dashed curves are when the charge renormalization is taken into account. We note that in the presence of salt, the counterion condensation does not fully destroy the phase transition, but only makes it weaker. The inset amplifies the region of small densities, showing a part of the van der Waals loop for $\rho_s = 1 \mu\text{M}$. Note the scale of pressure.

We conclude that the non-linear effects associated with the presence of double layers strongly modify the critical phenomena of charged colloidal suspensions. In particular, we find that aqueous suspensions with monovalent counterions do not phase separate in the absence of salt. Addition of a small amount of 1:1 electrolyte produces a very weak instability. In fact the phase transition is so weak that it is unlikely to be observed experimentally. The metastable effects associated with the mathematical singularity, however, might indeed have been detected, appearing as dilute voids in homogeneously deionised suspensions [2].

We would like to stress that our conclusions are only applicable to *aqueous suspensions* with *monovalent* counterions. In the case of multivalent counterions, the correlations between the condensed counterions can become so strong as to lead to an effective attraction between the polyions [19], which in turn can drive a liquid-gas phase separation. Similarly, in organic solvents of low dielectric constant, the correlations between the condensed counterions can become sufficiently strong as to produce phase separation [20]. Unfortunately, this correlation-induced instability cannot be studied at the level of the theory presented in this letter, since the interactions between the polyions are described by the DLVO potential, which does not include correlations. The DLVO potential is sufficient as long as the attention is restricted to water with monovalent counterions, but most certainly fails if the electrostatic interactions between the condensed counterions are significant, as is the case for low dielectric solvents and multivalent counterions.

The theory presented above suggests that the counterion condensation stabilizes charged colloidal suspensions against fluid-fluid phase separation. It, however, says nothing about the possibility that suspension freezes, forming an ordered lattice. Fluid-solid transition will certainly occur at sufficiently large colloidal volume fractions and will depend on the concentration of salt in the system. To study this transition requires an accurate free energy of the crystalline state. This can be obtained using the density functional theory within a suitable cell geometry. The equality of pressure and chemical potential in the two phases will lead to a fluid-solid coexistence curve.

* * *

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