On the fluid-fluid phase separation in charged-stabilized colloidal suspensions

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We develop a thermodynamic description of particles held at a fixed surface potential. This system is of particular interest in view of the continuing controversy over the possibility of a fluid-fluid phase separation in aqueous colloidal suspensions with monovalent counterions. The condition of fixed surface potential allows in a natural way to account for the colloidal charge renormalization. In a first approach, we assess the importance of the so called “volume terms”, and find that in the absence of salt, charge renormalization is sufficient to stabilize suspension against a fluid-fluid phase separation. Presence of salt, on the other hand, is found to lead to an instability. A very strong dependence on the approximations used, however, puts the reality of this phase transition in a serious doubt. To further understand the nature of the instability we next study a Jellium-like approximation, which does not lead to a phase separation and produces a relatively accurate analytical equation of state for a deionized suspensions of highly charged colloidal spheres. A critical analysis of various theories of strongly asymmetric electrolytes is presented to assess their reliability as compared to the Monte Carlo simulations.

I. INTRODUCTION

There is a long standing debate in the field of colloidal science concerning a possibility of phase separation in aqueous colloidal suspensions containing monovalent counterions. Charged colloids provide a particular challenge to the theorists. The long ranged Coulomb interaction and the extremely large asymmetry between the polyions and the counterions makes it very difficult to apply to this system the traditional methods of the liquid state theory. In particular, such a well established tool of condensed matter theorists as integral equations is found to be useless when applied to strongly asymmetric electrolytes at large couplings (low temperatures). For a wide range of parameters of physical interest the integral equations fail to even converge. The original hope of associating the lack of convergence with an underlying physical instability has proven to be unfounded.

Recently, a linearized density functional theory has been used to study charged colloidal suspensions. The theory predicted a thermodynamic instability which manifested itself as a fluid-fluid phase separation. However, the underlying approximation of the theory put its conclusions in doubt. Specifically the linearization of the density functional lowers the statistical weight of the configurations in which the counterions are in a close vicinity of the polyions. This effect can be partially accounted for through the renormalization of the bare colloidal charge. Unlike the bare charge, the effective (renormalized) charge is found to be very large, the potential near the colloidal surface is

\[ \beta q \phi_{\text{sat}} \approx 4. \]

This simple observation allows of the Debye length, does not increase beyond \( \beta q \phi \simeq 4 \). This simple observation is sufficient to construct a consistent thermodynamic description of colloids with a state dependent effective charge. Since the WS cell description of colloidal suspension does not lead to a fluid-fluid phase separation (see for a general argument), to further understand the mechanism of the instability observed within the linearized theories, we focus on this alternative treatment.

We shall first (section II), study the effect of charge renormalization on the polyion-microion interaction free

\[ \frac{1}{kT} \approx \frac{1}{k_B T} \]

Relevance of the constant potential ensemble follows from the observation that unlike the bare charge, the effective charge of colloidal particles does not grow indefinitely but instead saturates. The saturation value is such that the effective electrostatic potential \( \phi_{\text{sat}} \) in the vicinity of colloidal surface is

\[ \beta q \phi_{\text{sat}} \approx 4, \]

where \( \beta = 1/k_B T \) and \( q \) is the elementary charge. Thus, although the colloidal charge can be very large, the potential near the colloidal surface, i.e. within the Debye length, does not increase beyond \( \beta q \phi_{\text{sat}} \approx 4 \).
energy, i.e. the volume term that appears when the original mixture of colloids, coions and counterions is mapped onto an effective one component system of dressed colloids [1, 2, 4]. In section III an alternative derivation of the thermodynamic equation of state based only on the far field considerations is presented. The corresponding pressure-density isotherms, in this case, do not exhibit criticality at any salt concentration. In order to assess the reliability of various approaches, in section IV we compare the corresponding pressures to the results of the Monte Carlo simulations of Linse [6]. We also consider the, recently proposed, symmetric Poisson-Boltzmann [10] and the “boot-strap” Poisson-Boltzmann [11] theories. Conclusions are drawn in section V.

II. ROLE OF VOLUME TERMS

A. State dependent effective charges

Consider a colloidal suspension at concentration $\rho_p$, containing spherical polyions of charge $-Zq$ and radius $a$ in contact with a monovalent salt reservoir at concentration $c_s$. Now suppose one colloid is fixed at $r = 0$. In a continuum approximation consisting of smearing out the charge of other colloids and linearizing the Poisson-Boltzmann equation [22], the electrostatic potential at distance $r$ from the center of colloid is

$$\phi(r) = -\frac{Zq\theta(\kappa a)e^{-\kappa a r}}{\epsilon r}$$

where the inverse Debye length is

$$\kappa = \sqrt{\frac{4\pi \lambda_B(\rho_+ + \rho_-)}{\epsilon}}$$

and the Bjerrum length is

$$\lambda_B = \frac{q^2}{\epsilon k_B T}.$$  \hspace{1cm} (2)

The mean densities of coions and counterions inside the suspension are respectively $\rho_-$ and $\rho_+$. When $\rho_p \to 0$, $\kappa^2 \to \kappa^2_s = 8\pi \lambda_B c_s$.

For highly charged polyions, Eq. (1) strongly overestimates the real electrostatic potential. However, it can be made consistent with the full non-linear PB, if instead of the bare charge $Z$ an effective, renormalized, charge $Z_{\text{eff}}$ is used. The observation that for large surface potentials the electrostatics away from the colloidal surface is completely insensitive to the surface charge density allows for the “far-field” definition of the effective charge. Specifically, viewed from a distance larger than the Debye length, and provided that $\kappa a > 1$, the surface potential of a strongly charged colloidal particle appears to be $\beta q\phi(a) \approx -4$ [19, 20, 22]. Combining this with Eq. (1) leads directly to [19, 22]

$$Z_{\text{eff}} = \frac{4a}{\lambda_B}(1 + \kappa a).$$

We should note that this is the saturated value of the effective charge relevant for the highly charged colloidal particles. For weekly charged particles there is little or no charge renormalization. In the infinite dilution limit [23] of one colloid immersed in a 1:1 electrolyte of concentration $c_s$, the exact result for the saturation limit of $Z_{\text{eff}}$ is

$$Z_{\text{eff}} = \frac{4a}{\lambda_B} \left(\frac{3}{2} + \kappa a\right).$$

This expression –valid up to corrections of order $(\kappa a)^{-1}$, which turn out to be quite small as soon as $\kappa a > 1$, is very close to the approximation [4], derived from the matching procedure detailed in [21, 22].

The effective charge depends strongly on the electrolyte concentration inside the suspension. Salt screens the electrostatic interactions between the counterions and the polyions and leads to an increase in the colloidal effective charge. While the effective charge of colloidal particles is a strongly state dependent function, the effective surface potential is not. Therefore, inside suspension, colloids behave as if their surface potential was effectively fixed. It is interesting, therefore, to study the thermodynamics of colloidal particles at fixed surface potential.
B. Thermodynamics of particles at fixed surface potential

The change of the thermodynamic ensemble from the constant charge to the constant surface potential allows us in a natural way to explore the role of charge renormalization in the framework of a linear theory. The surface potential is related to the effective colloidal charge through the Eq. (1)

\[ \varphi = -\beta q \phi(a) = \frac{Z \lambda_B}{a(1 + \kappa a)} . \]  

As mentioned above, the reduced surface potential within the non-linear Poisson-Boltzmann theory is found to saturate at \( \varphi = 4 \). For the sake of generality we shall, however, keep its value arbitrary. In the subsequent analysis, \( Z \) will refer to the saturation value of the colloidal effective charge. An implicit assumption is therefore that the bare charge largely exceeds the effective one.

In the simplest approximation, the Helmholtz free energy of the suspension is a sum of entropic and electrostatic contributions

\[ \beta F = N_+ [\ln \rho_+ \Lambda^3 - 1] + N_- [\ln \rho_- \Lambda^3 - 1] + \beta F_{el} , \]  

where \( \Lambda \) is the de Broglie thermal wavelength, and \( N_+ \) and \( N_- \) refer to the number of counterions and coions inside the suspension.

The electrostatic free energy results from the polyion-microion, microion-microion and the polyion-polyion interactions. For suspensions containing monovalent counterions the polyion-counterion interaction is the dominant contribution and will be the only one kept in the present exposition (we come back to this point in section IV). We find \[22\]

\[ \beta F_{el} = \frac{Z^2 \lambda_B N_p}{2a(1 + \kappa a)} . \]  

This expression can be obtained through the usual Debye charging process in which all the particles are simultaneously charged from 0 to their final charge \[22\]. Alternatively a surface charging process, at constant Debye length can be employed \[24\]. It is noteworthy that in the salt free case, we recover precisely the volume term obtained in Refs \[1, 4\].

If the suspension is in contact with a salt reservoir of chemical potential \( \mu_s \), the effective charge of colloidal particles, as well as the number of counterions and coions, is determined by the minimum of the grand potential function

\[ \beta \Omega = \beta F - \beta \mu_s (N_+ + N_-) - (\varphi + \gamma) Z N_p - \omega N_p \left[ \varphi (1 + \kappa a) - \frac{Z \lambda_B}{a} \right] - \gamma (N_+ - N_- - Z N_p) . \]  

In this equation, \( \omega \) and \( \gamma \) are the Lagrange multipliers: \( \gamma \) ensures the charge neutrality of the system, while \( \omega \) enforces the relationship between the surface potential and the effective charge, Eq. (6). In the biophysics literature \( \gamma \) is known as the Donnan potential. It results from the inability of macroions to diffuse through a semi-permeable membrane. This is precisely the situation that we have in mind, while the microions are assumed to be in a free exchange with the reservoir, the polyions are confined to the interior of suspension. This restriction on the polyion mobility results in a potential difference \( \gamma \), between the bulk of suspension and the reservoir. The colloids are then held at potential \( \varphi + \gamma \) with respect to the reservoir, or equivalently at potential \( \varphi \) with respect to the bulk of the suspension. Within the WS cell model, a similar prescription of constraining the potential difference between the colloidal surface and the outer (reservoir) boundary has been shown to yield a surprisingly good agreement with the full non-linear Poisson-Boltzmann equation \[26\].

Minimizing the grand potential with respect to \( N_+ \), \( N_- \) and \( Z \), we find

\[ \frac{\partial \beta \Omega}{\partial N_\pm} = \frac{\partial \beta F}{\partial N_\pm} - \mu_s - \omega \left[ \frac{2\pi \varphi \lambda_B \rho_p}{\kappa} \right] \mp \gamma = 0 , \]  

\[ \frac{\partial \beta \Omega}{\partial Z} = \frac{\partial \beta F}{\partial Z} - \omega N_p \left[ \lambda_B \rho_p \right] - \varphi N_p = 0 , \]  

and the charge neutrality condition reads

\[ N_+ - N_- = \frac{\varphi a(1 + \kappa a)}{\lambda_B} N_p . \]
Noting that
\[
\frac{\partial \beta F}{\partial Z} = \varphi N_p ,
\] (13)
Eq. 11 simplifies to
\[
\omega = 0 .
\] (14)
Eliminating the Lagrange multiplier between Eqs. 10, we are left with two equations which govern the concentrations of counterions and coions inside suspension,
\[
\rho_+ - \rho_ - = \frac{\varphi a (1 + \kappa a)}{\lambda_B} \rho_p .
\] (16)

C. The equation of state

The osmotic pressure inside suspension of colloids at fixed surface potential is
\[
P = - \frac{d\Omega}{dV} \bigg|_{N_p,N_+,N_-,Z,\mu_s,\omega,\gamma,\varphi} .
\] (17)

It is important to keep in mind that as \( \Omega \) changes with volume, the number of coions, counterions, as well as the charge of colloidal particles are all varying. This is the reason for writing the total derivative in the expression (17)
\[
\frac{d\Omega}{dV} \bigg|_{N_p,N_+,N_-,Z,\mu_s,\omega,\gamma,\varphi} = \frac{\partial \Omega}{\partial N_+} dN_+ + \frac{\partial \Omega}{\partial N_-} dN_- + \frac{\partial \Omega}{\partial Z} dZ + \frac{\partial \Omega}{\partial V} .
\] (18)
Recalling that at the thermodynamic equilibrium
\[
\frac{\partial \Omega}{\partial N_+} = \frac{\partial \Omega}{\partial N_-} = \frac{\partial \Omega}{\partial Z} = 0
\] (19)
expression for pressure simplifies to
\[
P = - \frac{d\Omega}{dV} \bigg|_{N_p,N_+,N_-,Z,\mu_s,\omega,\gamma,\varphi} = - \frac{\partial F}{\partial V} \bigg|_{N_p,N_+,N_-,Z} .
\] (20)
Equation 20 beautifully illustrates the thermodynamic principle of ensemble equivalence. The functional form of the pressure is the same weather the calculation is done in the fixed potential ensemble using the grand potential function \( \Omega \), or in the fixed colloidal charge ensemble using the Helmholtz free energy \( F \). We stress that simply inserting \( Z_{\text{eff}}(V) \) with its state dependence into \( F \) and then differentiating it with respect to volume will lead to an incorrect result. If the Helmholtz free energy is used, the variation must be performed at fixed colloidal charge.

In general it can be very difficult to find a suitable thermodynamic potential for a constrained system. The calculation of pressure, on the other hand, can be done very straightforwardly using the constant \( Z \) ensemble, and enforcing the constraint \textit{a posteriori}. Evaluating the partial derivative in Eq. 20, the osmotic pressure inside the suspension takes a particularly simple form
\[
\beta P = \rho_+ + \rho_ - - \frac{1}{4 \lambda_B} \varphi^2 \kappa a \rho_p ,
\] (21)
where the concentrations of coions and counterions are determined from Eqs. 15 and 16.

In the special case of vanishing salt concentration, Eqs. 15 and 16 simplify to
\[
\rho_+ = 0 ,
\] (22)
\[
\rho_+ = \varphi \rho_p a \frac{a}{\lambda_B} \left[ 1 + \frac{3}{2} \eta \varphi + \frac{1}{2} \sqrt{3\eta \varphi (4 + 3\eta \varphi)} \right],
\]
and the ratio of colloidal size to Debye length is
\[
\kappa a = \frac{3\eta \varphi}{2} + \frac{1}{2} \sqrt{3\eta \varphi (4 + 3\eta \varphi)},
\]
where \(\eta = 4\pi \rho_p a^3/3\) is the macroion volume fraction. For salt-free suspensions pressure becomes
\[
4\pi \lambda_B a^2 \beta P = 3\eta \varphi \left( 1 + \kappa a - \frac{1}{4} \varphi \kappa a \right).
\]
If \(\varphi < 4\) the osmotic pressure is a convex up function of colloidal density. For real colloids with \(\varphi = 4\), the pressure is a linear function of colloidal density, \(\beta P = 4\rho_p a/\lambda_B\). For surface potentials strictly above 4, a thermodynamic instability appears. It is very curious to note that the instability sets in precisely at \(\varphi = 4\), which is the saturation value for the surface potential obtained within the non-linear Poisson-Boltzmann theory. Renormalization of the electrostatic free energy is, therefore, sufficient to stabilize a salt free real colloidal suspension (\(\varphi = 4\)) against a fluid-fluid phase separation.

It is important to stress that even a minor modification of the approximations employed may have a dramatic effect on the predicted phase instability. One may wish for instance to use Eq. (5) for the effective charge instead of Eq. (4). It is important to note, however, that such a modification means that colloid is no longer held at fixed potential. Therefore, the grand potential \(\Omega\), as written in (9), can no longer be used. However, we can compute the functional dependence of \(P\) on \(\frac{\kappa a}{3.2}\) by differentiating the Helmholtz free energy \(F\) with respect to volume at constant \(\varphi\), and enforcing the constraint \(\varphi = a (4\kappa a + 6)/\lambda_B a\) post aliori. Following this route, we recover the same equation of state as before [i.e. Eq. (25) in the salt free case but with now a different salt dependence of \(\varphi\)] and the critical salt concentration above which the instability sets in (see Figure 3), decreases by a factor of four to \(\kappa_s^* a \simeq 1.77\).

III. AN ALTERNATIVE APPROACH : A JELLIUM APPROXIMATION

In the previous section, we have found a fairly accurate expression for the effective colloidal charge at saturation and used it to renormalize the electrostatic free energy. It is important to remember, however, that the effective
charge, is by definition related to the “far field” asymptotic properties of the electrostatic potential. Its use for the renormalization of electrostatic free energy is, therefore, questionable, since not only far field but also the near field properties of the electrostatic potential may be relevant. We now turn our attention to a simple approach which relies only on the far field features of the electrostatic potential to obtain the equation of state. As within the WS cell picture, use will be made of contact theorem, which relates the osmotic pressure to the concentration of counterions in the region where the electric field is zero\cite.

We now reconsider the approach put forward at the beginning of section\cite. Consider one colloidal particle fixed at the origin of coordinate system. As before the charge of other microions is uniformly smeared throughout the solution. On the other hand, positions of counterions are strongly correlated with those of colloids. The system then forms a jellium, where the electrostatic potential far from the colloid $\phi_{\infty}$ (bulk) differs from that in the reservoir (chosen to vanish). The solution of the linearized Poisson-Boltzmann equation for $\delta \phi = \phi - \phi_{\infty}$ is again given by Eq.\cite, where the screening length is related to the bulk salt concentration, $\kappa^2 = 4\pi\lambda_B(\rho_+(\infty) + \rho_-(\infty))$. In the spirit of the previous discussion, the colloidal particles are held at constant surface potential $\phi = 4$ with respect to the bulk $\phi_{\infty}$, which again imposes $Z = 4a(1 + \kappa a)/\lambda_B$. The counterions and coions are distributed inside the jellium in accordance

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**FIG. 2:** Comparison between the effective charge (solid line) found using our variational approach, to that obtained within the Poisson-Boltzmann cell theory (circles), following the prescription proposed by Alexander et al.\cite,\cite.

**FIG. 3:** Pressure isotherms for different reservoir salt concentrations, making use of Eq.\cite instead of Eq.\cite. The situation is now different from that of the previous constant $\phi$ ensemble. Working is the constant $Z$ ensemble with the Helmholtz free energy\cite nevertheless allows to compute the pressure.
TABLE I: Equation of state with (third column) and without (fourth column) renormalization of volume terms, as a function of electrostatic coupling $\lambda_B/a$, for a packing fraction $\eta = 0.00125$. The quantity $n$ denotes the mean total density of counterions $n = \rho_p/Z_{\text{bare}}$. The MC data (second column) are taken from reference [6]. Since the previous parameters do not correspond to the saturation regime of effective charges but only approach it, we have used the effective charge given by Alexander’s prescription [18] to compute the pressure from Eq. (25) in the third column. The corresponding ratio $Z/Z_{\text{bare}}$ is indicated in the last column.

| $\lambda_B/a$ | $\beta P/n$, MC | $\beta P/n$, $Z = Z_{\text{eff}}$ | $\beta P/n$, $Z = Z_{\text{bare}}$ | $Z_{\text{eff}}/Z_{\text{bare}}$ |
|-------------|-------------|------------------|------------------|------------------|
| 0.022       | 0.98        | 0.99             | 0.99             | 1.0              |
| 0.044       | 0.95        | 0.96             | 0.97             | 0.99             |
| 0.089       | 0.89        | 0.88             | 0.92             | 0.95             |
| 0.178       | 0.71        | 0.68             | 0.78             | 0.82             |
| 0.356       | 0.45        | 0.41             | 0.46             | 0.53             |
| 0.712       | 0.26        | 0.21             | -0.32            | 0.29             |

with the Boltzmann distribution

$$\rho_+(r) = c_s e^{-\beta q\phi(r)}$$

$$\rho_-(r) = c_s e^{\beta q\phi(r)}$$

where $\phi(r)$ is the local electrostatic potential with respect to the reservoir. Taking the product of Eqs. (26) and (27) we find the familiar condition for Donnan equilibrium

$$\rho_+(\infty) = \rho_-(\infty) + Z\rho_p.$$ 

The total concentration of microions inside the suspension is then related to their concentration inside the salt reservoir through

$$(\kappa a)^4 = (\kappa_s a)^4 + [12\eta^2(1 + \kappa a)^2].$$

The osmotic pressure, within the non-linear PB theory, is determined from the concentration of microions in the region where the electric field is zero. Since the electrostatic potential decays exponentially with $r$, the electric field vanishes when $r \to \infty$. Within the jellium approximation the osmotic pressure then takes a particularly simple form,

$$\beta P = \rho_+(\infty) + \rho_-(\infty) = \frac{\kappa^2}{4\pi\lambda_B}.$$ 

One can show that solution of Eq. (28) obeys the inequality

$$\frac{\partial \kappa}{\partial \eta} \bigg|_{\kappa_s} > 0$$

which ensures that the compressibility is always positive and that suspension is stable against the phase separation. In the absence of salt, we obtain a simple analytic expression

$$4\pi\lambda_B a^2 \beta P = 12\eta \left[1 + 6\eta + \sqrt{12\eta(1 + 3\eta)}\right],$$

that will be tested against experimental data in section IV.

IV. DISCUSSION

A. Comparison with the Monte Carlo simulations

The above analysis shows that different routes to thermodynamic pressure lead to very different results. In order to decide which route is the most reliable, a comparison with “exact results” is welcome. As a benchmark, we can use the Monte Carlo (MC) pressure data of Linse [6] for salt-free asymmetric electrolytes consisting of highly charged spherical...
macroions and point counterions. At high electrostatic couplings, this system exhibits an instability and separates into two coexisting phases of different electrolyte concentration. We shall argue that a minimum requirement for a reliable theory of phase behavior is its ability to reproduce reasonably accurately the MC equation, at least up to the transition point. This appears to be a stringent test and a necessary condition to trust any instability that a theory might predict.

We first test in Table 1 the equation of state (25) for a charge asymmetry \( Z_{\text{bare}} = 40 \) between colloids and counterions. It is evident that renormalization of colloidal charge significantly improves upon complete neglect of nonlinearities. The latter approach consists in considering \( Z = Z_{\text{bare}} \) and severely fails at high \( \lambda_B/a \), giving negative pressures. Our renormalized volume term captures the main effect of nonlinearities, but the agreement with MC, even if decent in view of the simplicity of the approach is nevertheless only qualitative, and does not reach the level of accuracy required to discuss phase stability.

The jellium equation of state derived in section III only holds for saturated effective charges, i.e. in a regime of coupling that the Monte Carlo simulations, so far, have not reached (which corresponds to a very high bare charge with a large separation of scales between Bjerrum length and colloid radius, see below). We therefore directly turn to the comparison of the relative performances of the Poisson-Boltzmann cell model, symmetric PB \([10]\) and boot-strap PB (see \([11]\) for details), with respect to Monte Carlo data (see Figures 4 and 5).

To produce these figures (providing a similar comparison as Table 1), we have chosen the lowest and the highest packing fractions investigated by Linse in \([6]\). The striking feature revealed by Figs 4 and 5 is the remarkably good agreement between the PB cell pressures \([26, 27]\) and the MC simulations, even at \( \eta = 0.00125 \) where the cell model could have been anticipated to fail (see also \([28]\)). The only competitive approach at \( \eta = 0.08 \) seems to be the boot strap PB theory \([11]\), but this theory severely fails for low volume fractions, see Fig 4 necessary to study colloidal phase-stability. At this volume fraction, the simple treatment of section III [Eq. 25], provides a better equation of state than the boot strap PB or symmetric PB (see Table II and Fig. 4). Within the PB cell, polyion-polyion as well as counterion-counterion correlations are discarded ; Figs 4 and 5 show that as far as the pressure is concerned, these contributions are small or negligible, for the parameters investigated, even at the highest couplings. This justifies their neglect in our analytical treatment.

Given the accuracy of the PB cell model, we are now in the position to assess the quality of the jellium approximation of section III. The corresponding pressures are compared in Fig. 6 with their PB cell counterparts for highly charged colloids (where the effective charge saturates to its upper threshold), both with and without added salt. The simple analytical expression \([31]\) for salt free suspensions is found to be in good agreement with the PB data. Unfortunately the agreement deteriorates when \( \kappa_s a > 1 \) (see the inset).
At this point, we must conclude that the PB theory, even restricted to the cell, is superior to the competing approaches for aqueous suspensions with monovalent counterions. At high electrostatic couplings, corresponding to multivalent counterions in water, the MC simulations of Linse [6] find an instability. This transition, however, has nothing to do with the volume terms, but is the result of strong correlations between the double layers of colloidal particles [22], which produce attraction between like-charged colloids at sufficiently short separations [29, 30]. So far, this attraction has not been properly included in any of the thermodynamic theories of colloidal stability.

Validity of PB theory. To quantify the range of validity of the PB theory one may construct a dimensionless parameter $\Gamma_{cc}$ characterizing the importance of microions correlations, discarded within the PB theory. For monovalent microions, $\Gamma_{cc} \propto \beta q^2/\langle \ell \rangle$ where $\ell$ is the characteristic mean distance between the microions in the double layer. If the number of condensed counterions is such as to almost completely neutralize the colloidal charge, which is the case for strongly charged colloids, $\ell \simeq a/\sqrt{Z_{bare}}$, and $\Gamma_{cc}$ becomes [22, 29]

$$\Gamma_{cc} = \frac{\lambda_B}{a} \sqrt{\frac{Z_{bare}}{4\pi}}.$$ (32)
When $\Gamma_{cc}$ exceeds unity, PB theory is expected to break down. The value $\Gamma_{cc} \simeq 2$ has been reported to correspond to the instability threshold [29, 31], which and has been observed in the simulations of Linse [6]. The field theoretic treatment of Netz also corroborates this conclusion [32]. For particles with $Z_{\text{bare}} = 40$, $\Gamma_{cc} \simeq 2$ corresponds to $\lambda_B/a \simeq 1.1$. Thus the PB theory can be expected to work quite well up to very high surface charge concentrations. Indeed, comparing the predictions of the PB cell model to the MC simulations, an excellent agreement is observed up to $\lambda_B/a \simeq 0.7$ where the MC data stop, rather close to the expected point of instability $\lambda_B/a \simeq 1.1$, see Figs. 4 and 5.

**Validity of the saturation picture within the PB.** The constant potential approach used in sections II and III relies on the phenomenon of effective charge saturation exhibited by the PB theory, when $Z_{\text{bare}}$ is large enough. The saturation occurs when the electrostatic energy of the condensed counterion is significantly larger than $k_B T$. This can be characterized by a dimensionless parameter

$$\Gamma_{\text{sat}} = \frac{Z_{\text{bare}}}{Z_{\text{eff}}} = \frac{Z_{\text{bare}} \lambda_B}{4a(1 + \kappa_s a)}.$$  

When $\Gamma_{\text{sat}}$ becomes larger than 1 [20, 23], linearized theory fails and charge renormalization becomes important.

We must stress that large values of $\Gamma_{\text{sat}}$ are fully compatible with small values of $\Gamma_{cc}$. Specifically, for any $a \gg \lambda_B$, there exists a range of bare colloidal charges $Z_{\text{bare}}$, such that $\Gamma_{cc} < 2 < \Gamma_{\text{sat}}$. For these values of $Z_{\text{bare}}$, the polyion-microion interaction is sufficiently strong that linearized theories, without charge renormalization, will certainly fail. On the other hand the counterion-counterion correlations are sufficiently weak, so that the PB theory is still applicable. To illustrate this point, we compare in Fig. 7 the pressure obtained at saturation within the PB cell model calculation (formally $Z_{\text{bare}} \rightarrow \infty$), to that measured experimentally by Reus et al, under the conditions very close to complete deionization (no salt). The agreement with PB theory had already been mentioned in [20, 33], but provides an illustration of the saturation phenomenon in real suspensions. It also shows that despite its simplicity, Eq. (31) is fairly accurate.

It is important to stress, however, that for any colloidal size $a$, there is a maximum value of $Z_{\text{bare}}$ above which the PB theory fails. In practice, however, this break down of the PB equation never occurs for aqueous suspensions containing only monovalent counterions. The reason for this is that the hydrated ionic size provides a lower cutoff for the length $\ell$ which appears in $\Gamma_{cc}$, i.e. $\ell > d$, where $d \approx 4 \text{ Å}$, is the hydrated ionic diameter. For aqueous suspension with monovalent counterions $\Gamma_{cc}$ is, therefore, always less than $\lambda_B/d$, so that $\Gamma_{cc} < 2$. For monovalent counterions in water, the PB theory, therefore, should apply without any restriction. Of course, this pleasant situation changes as soon as multivalent salt is added to suspension. In this case, hydrated ionic size is no longer sufficient to restrict the strength of microion-microion correlations and $\Gamma_{cc} > 2$. Under these conditions the PB theory will no longer apply and a more sophisticated approach must be used.

FIG. 7: Same as figure 6, including a comparison with osmotic pressures of deionized bromopolystyrene particles (shown by diamonds, from ref. [33]). The curve labeled “jellium” corresponds to the analytical prediction (31). No adjustable parameters have been used.
V. SUMMARY AND CONCLUSIONS

We have proposed (section II) a linear theory to investigate the phase behavior of colloidal suspensions. The nonlinear effects are partially taken into account through the postulate that highly charged polyions behave as if they were constant potential objects. The effective charge of colloidal particles is, therefore, a state dependent function. Our first goal was to develop a consistent thermodynamic approach for such state dependent charges. The results found in section II rely on a simple form for the electrostatic free energy (volume term), resulting from the polyion-microion interactions calculated using the linearized PB equation, for spherical colloids. The approach could be easily generalized to the case of cylindrical macroions. The critical behavior predicted is, however, spurious, which may be attributed to the simplicity of the volume term used, and/or the difficulty of renormalizing such terms. The jellium-like model of section III provides a more reliable route, and allows to obtain analytically a simple equation of state for highly charged colloids in the salt free limit, see Fig. 7. Unfortunately it is difficulty to see how this kind of approach can be extended to account for the polyion-polyion interactions.

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From our analysis, we conclude that for $\Gamma_{cc} = [Z_{bare}/(4\pi)]^{1/2} \lambda_B/a < 2$, Poisson-Boltzmann approach (PB), even restricted to the cell model, leads to more accurate predictions for the thermodynamic functions than the competing theories. This is quite remarkable, since it is by far the simplest (see the appendix of [34] for a “ready-to-use” implementation of PB cell model). However, there is clearly a need to go beyond the PB theory when dealing with the multivalent counterions, since it is the counterion-counterion correlations that drive a phase instability for $\Gamma_{cc} > 2$. Inclusion of these effects in a theoretical approach is a difficult task, since they have little signature on the pressure data up to the electrostatic coupling where suddenly they destabilize the system.

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