

Phase Separation in Deionized Colloidal Systems: Extended Debye–Hückel Theory

Derek Y. C. Chan,^{*,†} Per Linse,[‡] and Simon N. Petris[†]

Particulate Fluids Processing Centre, Department of Mathematics & Statistics, The University of Melbourne, Parkville VIC 3010, Australia, and Physical Chemistry 1, Center of Chemistry and Chemical Engineering, Lund University, P.O. Box 124, S-22100 Lund, Sweden

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Using an extension of the Debye–Hückel theory for strong electrolytes, the thermodynamics, phase behavior, and effective pair colloidal potentials of deionized charged dispersions have been investigated. With the inclusion of colloid size effects, this model predicts the possibility of the existence of two critical points, one of which is thermodynamically metastable but can exhibit interesting behavior at high colloid charges. This analytic model also serves as a pedagogic demonstration that the phase transition is driven by cohesive Coulomb interactions between all charged species in the system and that this cohesion is not inconsistent with a repulsive effective pair potential between the colloidal particles.

Introduction

In a series of very careful experimental studies, Ise et al.¹ demonstrated that stable deionized aqueous dispersions of polystyrene latex colloids exhibit simultaneously regions of high and low colloid densities. When the density of the latex particles is carefully matched with that of the suspending aqueous medium (with a H₂O/D₂O mixture), large void regions of low particle concentration were observed to coexist with a phase of high particle concentration. In both the high and low particle concentration regions, the colloidal particles remain as individual particles—there is no coagulation or flocculation between the particles. The observed coexistence of low and high particle number density phases is reminiscent of a gas–liquid-phase equilibrium.

If the dispersion is regarded as a one-component system comprised of colloidal particles interacting via an effective pair potential, then the familiar van der Waals picture of vapor–liquid equilibrium will require the existence of an attractive interaction between the particles. However, even in the more concentrated region, the interparticle separations are sufficiently large that attractive dispersion forces are totally negligible and therefore only Coulomb interactions among the charged colloidal particles and their neutralizing counterions are important in such systems. Therefore, within the one-component paradigm it must follow that the like-charged colloidal particles must have an attractive component in their effective pair potential. This point of view led to the development of the Sogami² pair potential to explain the observed phase separation. While the Sogami potential exhibits the required attraction between like-charged particles at large separations, its theoretical foundation is not without controversy.³ In the traditional model for colloidal inter-

actions based on the Deryaguin–Landau–Verwey–Overbeek⁴ (DLVO) picture, the colloidal dispersion is treated as a one-component fluid of colloidal particles interacting under a combination of attractive dispersion forces and repulsive electrical double layer forces. In particular, the electrical double layer interaction between identically charged particles is repulsive for all separations. In this situation, the purely repulsive double layer interaction due to Coulomb interaction between the colloidal particles cannot, within the van der Waals picture, give rise to a vapor–liquid equilibrium. This is the dilemma that one faces in attempting to reconcile the observed phase separation behavior with the well-tested DLVO theory.

We propose to study phase behavior in a deionized colloidal dispersion or in a dispersion with added electrolyte, by going beyond the one-component paradigm, which only focuses on the separation dependent effective pair potential between colloidal particles, as in the Sogami–Ise approach. Instead, we consider the total free energy of the system that arises from Coulomb interactions between all species in the system—between the colloidal particles and the small ions as well as between the small ions. By focusing on the free energy of the entire system, there is in fact no conflict between the picture of a purely repulsive effective interaction between any pair of colloidal particles and the possible existence of vapor–liquid equilibrium for the whole system.

In this paper, we use a simple extension of the Debye–Hückel theory for strong electrolytes to provide a simple and transparent illustration of how Coulomb interactions alone are sufficient to drive a vapor–liquid like phase transition in deionized colloidal systems and to resolve the apparent paradox of the existence of phase separation behavior between like-charged colloidal particles that only experience mutual repulsion over all interparticle separations. While this approach may have the limited utility of being able to provide accurate quantitative predictions, its analytic nature is still very instructive in helping to illuminate two different ways of thinking about Coulomb interactions in colloidal systems. Furthermore, this extended Debye–Hückel theory of de-ionized colloidal systems predicts the existence of a critical point as well

* Author for correspondence. E-mail: D.Chan@ms.unimelb.edu.au.

[†] The University of Melbourne.

[‡] Lund University.

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as an interesting metastable phase behavior that can be long-lived at high colloid charges. There is the possibility that the vapor–liquid like phase separation observed in deionized latex systems corresponds to this long-lived metastable state.

The present work also provides a clear analytic demonstration that while there are different equivalent methods of calculating the thermodynamic properties of Coulomb systems, those approaches that use an effective pair potential between the colloids will involve cancellations between terms of similar magnitude that arise for instance from one-body and two-body terms, and therefore these should be evaluated in a consistent manner.

The study of the statistical thermodynamics of systems involving long-ranged Coulomb interactions can be quite subtle, and sometimes well-established approximations that are valid in treating systems with short-ranged potentials can lead to incorrect conclusions. We therefore also attempt a comparison between the present work and the work of van Roij et al. and of Warren, who took similar approaches to study the phase separation problem. The general physical content invoked in explaining the phase separation phenomenon in these papers is very similar to that discussed here. However, the technical details of each approach are quite different in each case, so that in special known limits, there are significant quantitative differences between the results obtained via different approaches.

Very recently, computer simulation studies of the structure and thermodynamics of charged colloidal systems using a model of discrete small ions and discrete charged colloidal particles have been performed.^{5,6} While it is not yet feasible at present to carry out simulations for system parameters that are within the range where phase separation has been observed in experimental systems, the simulation results clearly indicate the existence of a Coulomb-interaction-driven phase separation.

Colloidal System as an Asymmetric Electrolyte

Our starting point for considering phase behavior of Coulomb dispersions is to calculate the Helmholtz free energy and the pressure of the system, and hence we first summarize the necessary standard formalism.⁹ For a deionized colloidal dispersion stabilized only by Coulomb interactions, we model the colloidal particles as hard spheres of radius R_0 and valence z_0 that are neutralized by counterions of radius R_1 and of valence z_1 . Later we will study in detail the limits $z_0 = Z \gg 1$, $z_1 = -1$, and $R_1 = 0$. We assume N_0 colloidal particles and N_1 counterions in a volume V and that the amount of residual electrolyte or added salt is negligible. The number densities of the colloids $n_0 = N_0/V$ and of the counterions $n_1 = N_1/V$ that neutralize the colloidal charge are related by the bulk electroneutrality condition: $n_0 z_0 + n_1 z_1 = 0$. The aqueous solvent is treated as a dielectric continuum with a relative dielectric permittivity ϵ .

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The interaction potential between two ionic species at a distance r between their centers is taken to be made up of a hard-sphere (hs) part and a Coulomb (coul) part $u_{\alpha\beta}(r) = u_{\alpha\beta}^{\text{hs}}(r) + u_{\alpha\beta}^{\text{coul}}(r)$ where α and β denote either a colloidal particle (0) or a counterion (1). The hard-sphere and the Coulomb interactions are given by

$$u_{\alpha\beta}^{\text{hs}}(r) = 0, \quad r \geq (R_\alpha + R_\beta) \\ = \infty, \quad r < (R_\alpha + R_\beta) \quad (1)$$

$$u_{\alpha\beta}^{\text{coul}}(r) = \frac{z_\alpha z_\beta e^2}{\epsilon r}, \quad r > 0 \quad (2)$$

with e denoting the protonic charge. This is the specification of our primitive asymmetric electrolyte model for the deionized colloidal dispersion.

The configurational part of the Hamiltonian of this system is a sum of hard-sphere interactions, H^{hs} , and Coulomb interactions, H^{coul} , where the latter has the form

$$H^{\text{coul}} = \sum_{\alpha > \beta} \sum_{\substack{j \in \alpha \\ j \neq i}} u_{\alpha\beta}^{\text{coul}}(r_{ij}) \quad (3)$$

The (excess) electrostatic internal energy, E^{coul} , arising from the Coulomb interactions is given in terms of the pair distribution functions, $g_{\alpha\beta}(r)$, between various species

$$\frac{E^{\text{coul}}}{V} = \frac{1}{2} \sum_{\alpha, \beta} n_\alpha n_\beta \int u_{\alpha\beta}^{\text{coul}}(r) g_{\alpha\beta}(r) \mathbf{d}\mathbf{r} \quad (4)$$

$$= \frac{2\pi e^2}{\epsilon} \sum_{\alpha, \beta} n_\alpha z_\alpha n_\beta z_\beta \int_{R_\alpha + R_\beta}^{\infty} r h_{\alpha\beta}(r) \mathbf{d}\mathbf{r} - \\ \frac{\pi e^2}{\epsilon} \sum_{\alpha, \beta} n_\alpha z_\alpha n_\beta z_\beta (R_\alpha + R_\beta)^2 \quad (5)$$

Taken individually, each integral in eq 4 diverges because of the long-ranged nature of the Coulomb potential. But using the total correlation function $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ and the bulk electroneutrality condition, the divergences in eq 4 cancel to give finite integrals in eq 5. The second term in eq 5 follows from the exact condition $h_{\alpha\beta}(r) = -1$ which must hold for $r < (R_\alpha + R_\beta)$ and arises from the combined effects of size differences and Coulombic interactions between the charged species.

The configurational part of the Helmholtz free energy F can accordingly be separated as a sum of the hard-sphere free energy F^{hs} and the (excess) electrostatic free energy F^{coul} . By employing a coupling constant or charging integration, F^{coul} can be evaluated from E^{coul} using the formally exact relation

$$F^{\text{coul}} = \int_0^1 \langle H^{\text{coul}} \rangle_\lambda \frac{d\lambda}{\lambda} = \int_0^1 E^{\text{coul}}(\lambda) \frac{d\lambda}{\lambda} \quad (6)$$

where $E^{\text{coul}}(\lambda) \equiv E^{\text{coul}}(e^2 \rightarrow \lambda e^2)$.

The pair distribution functions, $g_{\alpha\beta}(r)$, obey the local electroneutrality condition about an ionic species of valence z_α

$$z_\alpha = - \sum_{\beta} n_\beta z_\beta \int g_{\alpha\beta}(\mathbf{r}) \mathbf{d}\mathbf{r} \quad (\text{local electroneutrality}) \quad (7)$$

This condition expresses the requirement that the total

net charge surrounding a particular particle of valence z_α must cancel the charge on that particle exactly. This condition provides a check on approximate expressions for $g_{\alpha\beta}(r)$. Also as a consequence of the long-ranged $1/r$ form of the Coulomb potential, the Stillinger–Lovett second moment condition should also hold for the $g_{\alpha\beta}(r)$:¹⁰

$$\frac{3\epsilon kT}{2\pi e^2} = -\sum_{\alpha,\beta} n_\alpha z_\alpha n_\beta z_\beta \int r^2 g_{\alpha\beta}(r) dr \quad (\text{Stillinger–Lovett}) \quad (8)$$

Up till now, all the results are completely general and we are in the position to investigate various approximate methods of calculating the free energy of a system of deionized colloidal dispersions and, from that, study the phase behavior of such systems. In general, one only has available approximate expressions for $g_{\alpha\beta}(r)$, so the accuracy of any approximation will depend on the method that one uses to compute the relevant thermodynamic quantities. Equations 4 and 6 provide one such method, but equally, one can calculate the pressure directly using the virial equation⁹ or one may choose a free energy density functional formalism⁷ or some other approach. The very general local electroneutrality and Stillinger–Lovett conditions, both of which are consequences of the Coulomb potential, provide simple checks on the internal consistency of the approximate pair distribution functions $g_{\alpha\beta}(r)$.

Point-Ion Debye–Hückel Theory

Thermodynamics. While the thermodynamics of an electrolyte described by the Debye–Hückel theory is well-known, its analytic nature means that one can readily make explicit the subtle cancellations that arise when trying to describe a colloidal system in terms of effective pair potentials when it is treated as an asymmetric electrolyte. For point colloids and point ions ($R_0 = 0 = R_1$), the potential, $\phi_\beta(r)$, at r given that there is a point charge ($z_\beta e$) at the origin satisfies the Poisson equation:

$$\nabla^2 \phi_\beta(r) = -\frac{4\pi e}{\epsilon} \sum_\gamma n_\gamma z_\gamma g_{\gamma\beta}(r) - \frac{4\pi z_\beta e}{\epsilon} \delta(\mathbf{r}), \quad r \geq 0 \quad (9)$$

which together with the linearized mean-field approximation, $g_{\alpha\beta}(r) \cong 1 - z_\alpha e \phi_\beta(r)/kT$, gives the approximate total correlation function

$$h_{\alpha\beta}(r) = -\frac{z_\alpha z_\beta e^2}{\epsilon kT} \frac{\exp(-\kappa_D r)}{r}, \quad r > 0 \quad (\text{DHLL}) \quad (10)$$

where κ_D is the inverse Debye screening length of the asymmetric electrolyte

$$\begin{aligned} \kappa_D^2 &= \frac{4\pi e^2}{\epsilon kT} (n_0 z_0^2) + \frac{4\pi e^2}{\epsilon kT} (n_1 z_1^2) \\ &\equiv \kappa_0^2 + \kappa_1^2 \end{aligned} \quad (11)$$

The inverse Debye screening length has contributions from both the colloidal particles, κ_0 , and the counterions, κ_1 . The total correlation functions, eq 10, satisfy the local electroneutrality condition, eq 7, as well as the Stillinger–Lovett condition, eq 8.

Substitution of eqs 2 and 10 into eq 5 gives the Coulomb contribution to the internal energy per unit volume

$$\begin{aligned} \frac{E^{\text{coul}}}{V} &= -\frac{2\pi e^2}{\epsilon^2 kT \kappa_D} \{n_0^2 z_0^4 + 2(n_0 z_0^2)(n_1 z_1^2) + n_1^2 z_1^4\} \\ &= -\frac{kT \kappa_D^3}{8\pi} \quad (\text{DHLL}) \end{aligned} \quad (12)$$

When $|z_0| \gg |z_1|$, the dominant contribution is from the first (colloid–colloid) term. It follows from eq 6 that the Coulomb contribution to the free energy per unit volume is

$$\begin{aligned} \frac{F^{\text{coul}}}{V} &= \int_0^1 \left(-\frac{kT \kappa_D^3 \lambda^{3/2}}{8\pi} \right) \frac{d\lambda}{\lambda} \\ &= -\frac{kT \kappa_D^3}{12\pi} \sim n_0^{3/2} Z^3 \quad (\text{DHLL}) \end{aligned} \quad (13)$$

and the Coulomb contribution to the pressure is

$$P^{\text{coul}} \equiv -\frac{\partial F^{\text{coul}}}{\partial V} = -\frac{kT \kappa_D^3}{24\pi} \quad (\text{DHLL}) \quad (14)$$

From eq 12 we see that the Coulomb contributions due to colloid–colloid, colloid–counterion, and counterion–counterion interactions are always *negative*. In other words, the bare Coulomb repulsions between the colloid–colloid species and between the counterion–counterion species are outweighed by the bare Coulomb attraction between the colloid–counterion species with the net effect that the Coulomb interaction provides a *cohesive* effect that will tend to collapse the ionic system; this cohesive effect counter-balances the ever-present entropic effects.

For a deionized colloidal dispersion with monovalent counterions, modeled as a $Z:1$ electrolyte with $z_0 = Z (> 0)$ and $z_1 = -1$, the inverse Debye screening length $\kappa_D^2 = 4e^2 n_0 Z(Z+1)/(\epsilon kT)$ is dominated by the highly charged ($Z \gg 1$) colloidal particles. The explicit expressions for the total pressure, P , which in the present model will include an entropic contribution from colloids and counterions treated as an ideal gas mixture, is

$$\begin{aligned} P &= P^{\text{ideal}} + P^{\text{coul}} \\ &= n_0(Z+1)kT - \frac{kT}{24\pi} \left(\frac{4\pi e^2}{\epsilon kT} \right)^{3/2} [n_0 Z(Z+1)]^{3/2} \end{aligned} \quad (15)$$

The simple treatment provided by the point-ion Debye–Hückel theory demonstrates the existence of a cohesive contribution to the free energy due to Coulomb interactions and therefore signals the possibility of a vapor–liquid phase equilibrium. Indeed, this is precisely the point of view adopted by Langmuir¹¹ in considering phase behavior in strongly interacting dispersions and by Michaeli et al.¹² in considering phase separation in polyelectrolytes.

However, this simple instructive treatment cannot as yet predict a phase transition. This is evident from the pressure in eq 15, where at low densities ($n_0 \rightarrow 0$) the ideal gas term dominates as expected but at high densities the cohesion due to Coulomb interactions ($\sim n_0^{3/2}$) overwhelms the ideal gas term. This offers no great surprise, as the point-ion Debye–Hückel theory is only expected to be valid at low concentrations. In a later section, we will provide an attempt to remedy this shortcoming.

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We can understand the origin of this cohesion in more detail by considering the forms of the pair distribution functions within the point-ion model. Equation 12 showed that when $|z_0| \gg |z_1|$, the dominant term in the cohesive contribution to the internal energy is from the colloid–colloid term. Since the total correlation function $h_{00}(r)$ given by eq 10 is negative, this implies that there is a depletion of other colloidal particles in the neighborhood of any given colloidal particle; or equivalently, the colloidal particles *repel* each other. The apparent paradox that a *repulsion* between colloidal particles can give rise to a *cohesion* in the system can be explained as follows. The total bare Coulomb interaction between colloidal particles is obviously repulsive. However, bulk electroneutrality has enforced the cancellation of the effects of the bare Coulomb repulsions between colloidal particles that are far apart, assuming a homogeneous distribution. Now since there is a depletion of other colloidal particles in the neighborhood of any given colloid, this depletion means that the repulsion is now *less* than what would be there if the colloid–colloid distribution is uniform. It is this *absence* of repulsion that is manifested as a negative contribution to the energy.

Effective Pair Potential. Given the traditional picture of colloidal interactions, which, according to the DLVO picture, can be understood in terms of an effective pair potential between colloidal particles, the natural questions that arise are as follows: Within the point-ion Debye–Hückel theory, what is the nature of the interaction between any two colloidal particles in a deionized dispersion? Do the colloidal particles attract each other as in the Sogami theory? If an effective pair potential can be defined between colloidal particles, how is it related to the colloid–colloid correlation function, $h_{00}(r)$? And how should this pair potential be used to calculate thermodynamic properties of the colloidal dispersion and used to study phase separation?

This question of an effective pair potential between colloidal particles in a deionized dispersion has been considered in an earlier paper.¹³ We summarize the results here for completeness and refer the reader to that paper for technical details.

A consistent way to define the effective interaction among colloidal particles is to consider a fixed spatial configuration of colloidal particles and average over all possible configurations of the counterions. This is achieved by writing the configurational integral of the system as follows

$$\frac{1}{V^{N_0+N_1}} \int \exp[-(H^{\text{hs}} + H^{\text{coul}})/kT] d\{\mathbf{r}\} d\{\mathbf{R}\} \equiv \frac{1}{V^{N_0}} \int \exp[-H_{\text{eff}}(\{\mathbf{R}\})/kT] d\{\mathbf{R}\} \quad (16)$$

where $H_{\text{eff}}(\{\mathbf{R}\})$, defined by eq 16, is the potential of mean force⁹ of a fixed configuration of colloidal particles at positions $\{\mathbf{R}\} = \{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_0}\}$. This definition will guarantee that the system of colloidal particles interacting with the effective Hamiltonian $H_{\text{eff}}(\{\mathbf{R}\})$ will give the same thermodynamic properties as the original system of colloids and counterions. However, $H_{\text{eff}}(\{\mathbf{R}\})$ will be both number density and temperature dependent and so will vary from state point to state point.

In general, the effective Hamiltonian $H_{\text{eff}}(\{\mathbf{R}\})$ will comprise of a sum of one-, two-, three-, ...-body terms: $H_{\text{eff}}(\{\mathbf{R}\}) = N_0 W_1 + \sum_{i<j} W_2(\mathbf{R}_i, \mathbf{R}_j) + \sum_{i<j<k} W_3(\mathbf{R}_i, \mathbf{R}_j, \mathbf{R}_k) +$

.... Within the point-ion Debye–Hückel theory, the expansion ends exactly after two terms:

$$H_{\text{eff}}^{\text{coul}} = N_0 W_1 + \sum_{i<j} W_2(r_{ij}) \quad (17)$$

with $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$. The one-body term W_1 takes the form¹³

$$W_1 = -\frac{\kappa_1(z_0 e)^2}{2\epsilon} + \frac{\kappa_1 z_0 z_1 e^2}{3\epsilon} + \frac{z_0 kT}{2z_1} \quad (18)$$

and since z_0 and z_1 have opposite signs, W_1 is always *negative*. While the W_1 term is position independent, it is both temperature and density dependent through κ_1 (eq 11), and the term can be interpreted as the change in the free energy in bringing a single colloidal particle into the presence of all other colloidal particles and their counterions at a given density; however, all the colloidal particles are very far away from each other. The two-body $W_2(r)$ term takes the form¹³

$$W_2(r) = \frac{(z_0 e)^2}{\epsilon} \frac{\exp(-\kappa_1 r)}{r} \quad (19)$$

and possesses an explicit dependence on the colloid–colloid separations as well as a temperature and density dependence through κ_1 . The effective pair potential, $W_2(r)$, is the bare Coulomb potential screened by the counterions Debye parameter, κ_1 (see eq 11), rather than the Debye parameter of the whole system, κ_D . An alternative derivation of this effective two-body potential is to begin with a formal asymptotic analysis of the Ornstein–Zernike equations for the asymmetric electrolyte system.¹³ This effective pair potential, derived by two very different methods, is the same and is *repulsive* for all separations.

Within the Debye–Hückel model, $W_2(r)$ is the effective colloid–colloid pair potential to use if one wishes to use the paradigm of a one-component system comprising interacting colloidal particles. This pair potential is the repulsive pair interaction between like-charged particles that one would expect from the DLVO picture. We will now recover the excess electrostatic free energy (eq 13) by treating the dispersion as a one-component system with the effective one- and two-body potentials W_1 and $W_2(r)$ given above. This will also demonstrate that while $W_2(r)$ is a short-ranged and exponentially screened potential, it is nonetheless a density dependent potential, and so care must be exercised in order to obtain the correct density dependent contribution of this term to the thermodynamics.

According to eq 17, the excess electrostatic free energy possesses two terms:

$$F^{\text{coul}} = F_1 + F_2 = N_0 W_1 + F_2 \quad (20)$$

The one-body term is given by¹³

$$\frac{F_1}{V} = n_0 W_1 = -\frac{kT\kappa_0^2 \kappa_1}{8\pi} - \frac{kT\kappa_1^3}{12\pi} + \frac{n_0 z_0 kT}{2z_1} \quad (21)$$

where all three contributions in eq 21 are negative. The two-body potential $W_2(r)$ is screened exponentially and appears to be short-ranged, but because of the Coulombic nature of the system and the fact that $W_2(r)$ is a density dependent potential, the following steps are needed to recover the expected result in eq 13. The two-body term F_2 can be written formally as a coupling constant integral of an “internal energy” of the effective one-component

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system with the pair potential $W_2(r)$:

$$\begin{aligned} \frac{F_2}{V} &= \int_0^1 \left(\frac{1}{2} n_0^2 \int [\lambda W_2(r)] g(r, \lambda) \, d\mathbf{r} \right) \frac{d\lambda}{\lambda} \\ &= \frac{1}{2} n_0^2 \int W_2(r) \, d\mathbf{r} + \int_0^1 \left(\frac{1}{2} n_0^2 \int [\lambda W_2(r)] h(r, \lambda) \, d\mathbf{r} \right) \frac{d\lambda}{\lambda} \\ &= -\frac{n_0 z_0 kT}{2z_1} + \int_0^1 \left(\frac{1}{2} n_0^2 \int [\lambda W_2(r)] h(r, \lambda) \, d\mathbf{r} \right) \frac{d\lambda}{\lambda} \end{aligned} \quad (22)$$

where $g(r, \lambda) = 1 + h(r, \lambda)$ is the pair distribution function of a one-component system that interacts via the pair potential $[\lambda W_2(r)]$. To ensure we collect all terms of the same order in density n_0 , we sum simple ring diagrams⁹ by calculating the Fourier transform of $h(r, \lambda)$, namely $\tilde{h}(k, \lambda)$, which is a function of wavenumber, k , by the Ornstein–Zernike equation:

$$\tilde{h}(k, \lambda) = \frac{\tilde{c}(k, \lambda)}{1 - n_0 \tilde{c}(k, \lambda)} \quad (23)$$

with

$$c(r, \lambda) = -\lambda \frac{W_2(r)}{kT} = -\lambda \frac{(z_0 e)^2 \exp(-\kappa_1 r)}{\epsilon kT r}, \quad r > 0 \quad (24)$$

This gives¹³

$$h(r, \lambda) = -\lambda \frac{(z_0 e)^2 \exp(-\kappa_D(\lambda) r)}{\epsilon kT r}, \quad r > 0 \quad (25)$$

where

$$\kappa_D(\lambda) = (\lambda \kappa_0^2 + \kappa_1^2)^{1/2} \quad (26)$$

Using eqs 25 and 26 in the second integral of eq 22, we obtain for the two-body free energy, F_2

$$\frac{F_2}{V} = \left(\frac{kT \kappa_0^2 \kappa_1}{8\pi} + \frac{kT \kappa_1^3}{12\pi} - \frac{n_0 z_0 kT}{2z_1} \right) - \frac{kT \kappa_D^3}{12\pi} \quad (27)$$

All terms in parentheses are positive (since z_0 and z_1 have opposite signs) while the last term is negative.

The substitution of eqs 21 and 27 into eq 20 gives the total excess electrostatic Helmholtz free energy from the effective one-component pair potential description

$$\frac{F^{\text{coul}}}{V} = \frac{F_1}{V} + \frac{F_2}{V} = -\frac{kT \kappa_D^3}{12\pi} \quad (28)$$

which is exactly the point-ion Debye–Hückel result (eq 13) that we expect to recover. Notice how the terms in the two-body free energy F_2 that arise from the effective pair potential $W_2(r)$ cancel out all three terms in the one-body or volume term F_1 to give the point-ion Debye–Hückel result.

While this calculation is for the idealized case of point ions, the analytic result suggests that computing thermodynamic quantities using eqs 4 and 6 is likely to be more robust numerically. On the other hand, using the effective one-component approach will require the evaluation of one- and two-body and possibly higher body potentials between the colloids as well as the calculation of the contributions to the free energy from the effective colloid–colloid potentials. Indeed, in the effective one-component approach for point ions, while the final answer

originates from the part of F_2 that arises from the effective pair potential $W_2(r)$, the significant cancellation between contributions from the one- and two-body terms means that there is a risk of errors arising from incomplete cancellations when inconsistent approximations are used in different parts of the calculation. This appears to be the case in the work of Levin, Barbosa, and Tamashiro,¹⁴ who used different approximations to calculate the contributions to the free energy from colloid–colloid, colloid–counterion, and counterion–counterion interactions and as a result concluded that phase separation cannot arise from Coulomb interactions in such systems.

At this point, we can compare our result with that of van Roij, Dijkstra, and Hansen (vRDH)^{7,8} for a $Z:1$ ($Z > 0$) electrolyte with point colloids and point counterions in the limit of no salt. Using a density functional formulation, their treatment of electrostatic interactions is nearly identical to the present work. In their effective one-component treatment, they also obtained a negative one-body term, which in our notation has the form

$$\frac{F_1}{V} = -\frac{kT \kappa_0^2 \kappa_1}{8\pi} - \frac{n_0 Z kT}{2} \quad (\text{van Roij, Dijkstra, and Hansen}) \quad (29)$$

This result differs from our one-body potential given by eq 21 by the term $kT \kappa_1^3 / (12\pi)$. Noting that the order in density and charge dependence of the three terms in eq 21 is $\sim n_0^{3/2} Z^{5/2}$, $\sim n_0^{3/2} Z^{3/2}$, and $\sim n_0 Z$, respectively, we see that the term $kT \kappa_1^3 / (12\pi)$ omitted by vRDH is of the same order ($\sim n_0^{3/2}$) in the colloid density as is the leading term but has an intermediate dependence ($\sim Z^{3/2}$) on the colloid charge. From a comparison with the work of Beresford-Smith et al.,¹³ it is evident that this omitted term arises from contributions to the free energy due to counterion–counterion correlations effects. This effect has been ignored explicitly at the outset in the density functional formulation of vRDH. The second term in eq 29 was also omitted in an earlier paper by vRDH.⁷

Another difference in the vRDH approach is that the contribution to the free energy from the two-body effective potential between colloidal particles was estimated numerically by a variational method. In the low-density limit, they obtained⁸

$$\frac{F_2}{V} \approx \frac{1}{2} n_0^2 \int d\mathbf{r} W_2(r) = \frac{n_0 Z kT}{2} \quad (\text{van Roij, Dijkstra, Hansen, Evans}) \quad (30)$$

instead of retaining *both* terms in eq 22.

In the point-ion limit, their excess electrostatic free energy, obtained as the sum of eqs 29 and 30 according to eq 20, becomes⁸ (again in our notation)

$$\frac{F^{\text{coul}}}{V} = -\frac{kT \kappa_0^2 \kappa_1}{8\pi} \sim n_0^{3/2} Z^{5/2} \quad (\text{van Roij, Dijkstra, Hansen, Evans}) \quad (31)$$

which differs from the point-ion Debye–Hückel limiting law (eq 13) by a factor $(2/3)Z^{1/2}$, a difference that can be significant when $Z \gg 1$, as in typical colloidal systems.¹ The reason for this difference is thus traced to the way in which the free energy contributions F_1 and F_2 were calculated.

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In their density functional formulation, vRDH neglected the ion–ion correlation term in the one-body potential as well as omitted the important ring diagram contributions to the electrostatic free energy from the two-body term,⁹ so their result will not reduce to the Debye–Hückel limiting law expected in the point-ion and point-colloid limit or at low densities. In their calculation that included effects of finite colloid size and added salt, the free energy contribution from the colloid–colloid effective pair potential is calculated using a variational approach based on a hard-sphere reference system. Since some of the interesting phase behavior founded by vRDH occurs at very low colloid densities, it seem important to be able to recover known low-density limiting behavior.

Warren¹⁵ also studied phase separation of a colloidal dispersion under only Coulombic interactions. The physical model and initial assumptions are very similar to that of vRDH and that in this paper. Warren also started the analysis with expressions for the internal energy as given by eq 4. However, all the approximate pair distribution functions used by Warren to calculate internal energies do not satisfy the local electroneutrality condition (eq 7). Also, like vRDH, he also used a variational method to calculate the contribution of the effective pair potential to the colloid–colloid free energy, but he did not give a detailed justification of the form of the pair potential he used. As a consequence, it is not possible to make a more detailed comparison with the work of Warren.

For finite colloid size, the exact term that arises from the combined effects of size differences and Coulombic interactions between the charged species—the second term in eq 5—is not present in the treatments of vRDH or Warren.

Extended Debye–Hückel Theory—Finite Colloid Size

Thermodynamics. The Debye–Hückel theory for electrolytes can be extended to include hard-sphere radii $R_\alpha > 0$. Due to the hard-sphere repulsion, $g_{\alpha\beta}(r) = 0$ (or equivalently $h_{\alpha\beta}(r) = -1$) for $r < (R_\alpha + R_\beta)$. An approximation for the total correlation functions $h_{\alpha\beta}(r)$ for $r > (R_\alpha + R_\beta)$ is to retain the Debye–Hückel form $h_{\alpha\beta}(r) \approx -z_\alpha z_\beta \phi_\beta(r)/kT$, for $r > (R_\alpha + R_\beta)$, where $\phi_\beta(r)$ is the potential at r given that there is a point charge ($z_\beta e$) at the origin and satisfies $\nabla^2 \phi_\beta(r) - \kappa_D^2 \phi_\beta(r) = 0$, $r > (R_\alpha + R_\beta)$. In other words, the size effect is taken into account by assuming that the point charge model remains valid up to the distance of closest approach ($R_\alpha + R_\beta$) between species. This gives

$$h_{\alpha\beta}(r) = -1, \quad r < (R_\alpha + R_\beta)$$

$$= -\frac{z_\alpha z_\beta e^2}{\epsilon kT(1 + \kappa_D(R_\alpha + R_\beta)) \exp[-\kappa_D(r - (R_\alpha + R_\beta))]} \times \frac{1}{r}, \quad r > (R_\alpha + R_\beta) \quad (32)$$

These correlation functions satisfy the local electroneutrality condition (eq 7) but not the second moment condition (eq 8). Equation 32 for the colloid–counterion correlation function is identical to that in the treatment of vRDH.

Insertion of $z_0 = Z$, $z_1 = -1$, $R_0 = R$, and $R_1 = 0$ into eq 32 gives the excess electrostatic internal energy from eq 5

$$\frac{E^{\text{coul}}}{V} = -\frac{2\pi(n_0 Z)^2 e^4}{\epsilon^2 \kappa_D kT} \left(\frac{Z^2}{1 + 2\kappa_D R} + \frac{2Z}{1 + \kappa_D R} + 1 \right) - \frac{2\pi(n_0 Z e R)^2}{\epsilon} \quad (33)$$

in which all terms are negative, with the colloid–colloid term being dominant when $Z \gg 1$. The last term in eq 33, which is exact, arises from the contributions from the domains $r < 2R$ and $r < R$ in the colloid–colloid and colloid–counterion integrals, respectively.

The excess electrostatic free energy can again be found by a coupling constant integration over λ . Substitution of eq 33 into eq 6 and remembering that $\kappa_D \rightarrow \lambda^{1/2} \kappa_D$ and $e^2 \rightarrow \lambda e^2$ leads to

$$\frac{F^{\text{coul}}}{V} = -\frac{4\pi(n_0 Z)^2 e^4}{3\epsilon^2 \kappa_D kT} [Z^2 f(2\kappa_D R) + 2Z f(\kappa_D R) + 1] - \frac{2\pi(n_0 Z e R)^2}{\epsilon} \quad (34)$$

where $f(x) \equiv (3/x^3)(\log(1+x) - x + x^2/2)$, and in the point-colloid limit $R \rightarrow 0$, eq 34 reduces to the point-ion Debye–Hückel result of eq 13, since $f(0) = 1$.

The Coulomb contribution to the pressure is

$$P^{\text{coul}} = -\frac{2\pi(n_0 Z)^2 e^4}{3\epsilon^2 \kappa_D kT} [Z^2 p(2\kappa_D R) + 2Z p(\kappa_D R) + 1] - \frac{2\pi(n_0 Z e R)^2}{\epsilon}$$

$$\equiv P_{\text{cc}}^{\text{coul}} + P_{\text{ex}}^{\text{coul}} \quad (35)$$

where $p(x) \equiv (3/x^3)((1+x) - 1/(1+x) - 2 \log(1+x))$. In eq 35, we have identified for later discussion the contribution from charge correlations $P_{\text{cc}}^{\text{coul}}$ that arises from the three integrals involving correlation functions in eq 33 and the exact term $P_{\text{ex}}^{\text{coul}}$, which arises from the size difference between the charged species. In the point-colloid limit $R \rightarrow 0$, eq 35 reduces to the point-ion Debye–Hückel result of eq 14, since $p(0) = 1$.

Critical Points and Phase Diagrams. We will now investigate the phase behavior of the extended Debye–Hückel theory by examining the critical points of the equation of state. The state of the $Z:1$ colloidal system can be characterized by the following three nondimensional variables: the colloid charge Z , the colloid volume fraction ϕ , and the coupling strength or inverse temperature Γ defined by⁶

$$\phi \equiv \frac{4\pi R^3}{3} n_0 \quad \Gamma \equiv \frac{e^2}{\epsilon kTR} \quad (36)$$

and all other nondimensional parameters can be constructed from these, for example, $(\kappa_D R)^2 = 3\phi\Gamma Z(Z+1)$.

To analyze the critical behavior of the system, we use the Carnahan–Starling formula⁹ for the contribution to the pressure, P^{hs} , from the reference system of uncharged hard sphere colloids and uncharged point ions:

$$P^{\text{hs}} \equiv n_0 kT \Phi(\phi, Z) \equiv n_0 kT \left(\frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} + \frac{Z}{1 - \phi} \right) \quad (37)$$

All thermodynamic functions can now be written in terms of the three nondimensional parameters (Z , ϕ , and Γ):

Electrostatic Internal Energy

$$\frac{E^{\text{coul}}}{N_0 kT} = -\frac{Z\Gamma\kappa_D R}{2(Z+1)} \left(\frac{Z^2}{1+2\kappa_D R} + \frac{2Z}{1+\kappa_D R} + 1 \right) - {}^{3/2}\phi Z^2 \Gamma \quad (38)$$

Helmholtz Free Energy

$$\frac{F}{N_0 kT} = \Theta(\phi, Z) - \frac{Z\Gamma\kappa_D R}{3(Z+1)} \times [Z^2 f(2\kappa_D R) + 2Z f(\kappa_D R) + 1] - {}^{3/2}\phi Z^2 \Gamma \quad (39)$$

where

$$\Theta(\phi, Z) \equiv (Z+1) \log(\phi) + \frac{2}{1-\phi} + \frac{1}{(1-\phi)^2} - Z \log(1-\phi)$$

Pressure

$$\begin{aligned} \frac{4\pi R^3 P}{3kT} &= \phi \Phi(\phi, Z) - \frac{\phi Z \Gamma \kappa_D R}{6(Z+1)} \times \\ & [Z^2 p(2\kappa_D R) + 2Z p(\kappa_D R) + 1] - {}^{3/2}\phi Z^2 \Gamma \\ &\equiv \frac{4\pi R^3 P^{\text{hs}}}{3kT} + \frac{4\pi R^3 P^{\text{cc}}}{3kT} + \frac{4\pi R^3 P^{\text{ex}}}{3kT} \end{aligned} \quad (40)$$

Chemical Potential

$$\frac{\mu}{kT} \equiv \frac{1}{kT} \frac{dF}{dN_0} = \frac{1}{\phi} \frac{4\pi R^3 P}{3kT} + \frac{F}{N_0 kT} \quad (41)$$

Equation 41 is a standard thermodynamic relation for the chemical potential μ of a single colloid particle plus its neutralizing counterions.

Critical points can be located by solving $(\partial P/\partial V) = 0 = (\partial^2 P/\partial V^2)$. For $Z \gg 1$, we can retain only the leading term in Z in P^{cc} in eq 40 and write the pressure as

$$\frac{4\pi R^3 P}{3kT} \approx \phi \Phi(\phi, Z) - \frac{1}{48} \left((1+2\kappa_D R) - \frac{1}{1+2\kappa_D R} - 2 \log(1+2\kappa_D R) \right) - {}^{3/2}\phi Z^2 \Gamma \quad (42)$$

There are two density regimes of interest: $\kappa_D R \leq 1$ and $\kappa_D R \gg 1$ that we can examine. When $\kappa_D R \leq 1$, the second term on the RHS of eq 42 is of order $(\kappa_D R)^3 \sim \phi^{3/2} \Gamma^{3/2} Z^3$ and is therefore the larger of the two negative terms when $Z \gg 1$. So by retaining only the first two leading terms in eq 42 and approximating $\Phi(\phi, Z)$ by 1, we have

$$\frac{4\pi R^3 P}{3kT} \approx \phi Z - \frac{1}{48} \left((1+2\kappa_D R) - \frac{1}{1+2\kappa_D R} - 2 \log(1+2\kappa_D R) \right) \quad (43)$$

The critical parameters can now be estimated by solving $(\partial P/\partial V) = 0 = (\partial^2 P/\partial V^2)$ to give approximate expressions for the *low density* critical parameters.

Extended Debye–Hückel Theory Low-Density Critical Point ($Z \gg 1$)

$$\kappa_D^{\text{Lcr}} R \approx \frac{1}{2} \quad \phi^{\text{Lcr}} \equiv \frac{4\pi R^3}{3} n_0^{\text{Lcr}} \approx \frac{1}{384Z}$$

$$\Gamma^{\text{Lcr}} \equiv \frac{e^2}{\epsilon kT^{\text{Lcr}} R} \approx \frac{32}{Z} \quad \frac{4\pi R^3 P^{\text{Lcr}}}{3kT^{\text{Lcr}}} \approx \frac{(16 \log(2) - 11)}{3 \times 2^7} \quad (44)$$

These analytical results demonstrate qualitatively the possibility of the existence of a vapor–liquid-phase transition in a deionized dispersion driven by Coulomb interactions and ideal gas entropy. For $Z \gg 1$, this critical point occurs at a very low volume fraction. If the critical temperature is to be around room temperature and the relative dielectric permittivity ϵ is to be the aqueous value of 78, the present extended Debye–Hückel theory with finite-sized colloids would predict a colloidal charge $Z \sim 2200$ for a colloidal radius of 50 nm. Experimental colloidal charges are estimated to be around this order of magnitude.¹

The above estimates for the low-density critical values have the same form as that obtained earlier for a Debye–Hückel treatment of symmetric electrolyte with equal size ions.¹⁶ For this restrictive primitive model electrolyte, the third term ($P^{\text{ex, coul}}$) in eq 40 for the pressure that originates from size differences between the charged species is identically zero. Indeed, the study of phase transitions in symmetric electrolytes is covered very extensively in the literature, and the general consensus is that while the Debye–Hückel theory is able to provide instructive analytical results, it has only qualitative accuracy¹⁷ because of the inherent linearization assumptions.

Extended Debye–Hückel Theory High-Density Critical Point ($Z \gg 1$). At higher densities for which $\kappa_D R \gg 1$, the second term for the pressure in eq 42 is of order $(\kappa_D R) \sim \phi^{1/2} \Gamma^{1/2} Z$, and so it is small compared to the third term. Hence for $Z \gg 1$ we can neglect the second term in eq 42 to give

$$\frac{4\pi R^3 P}{3kT} \approx \phi \left(\frac{Z}{1-\phi} \right) - {}^{3/2}\phi Z^2 \Gamma \quad (45)$$

and we find a second critical point characterized approximately by

$$\begin{aligned} \kappa_D^{\text{Hcr}} R &\approx \frac{3Z^{1/2}}{2} & \phi^{\text{Hcr}} &\approx \frac{1}{3} \\ \Gamma^{\text{Hcr}} &\approx \frac{9}{4Z} & \frac{4\pi R^3 P^{\text{Hcr}}}{3kT^{\text{Hcr}}} &\approx \frac{Z}{8} \end{aligned} \quad (46)$$

This high-density critical point occurs at a volume fraction ϕ^{Hcr} of around 33%, and it is determined by the hard-sphere contribution P^{hs} and the exact Coulomb contribution $P^{\text{ex, coul}}$ due to the size-difference effects between the colloids and the ions.

The general form of the pressure isotherm is shown in Figure 1 for a colloid charge $Z = 100$. Note the location of the two critical points at very different volume fractions: one at around $\phi \sim 10^{-4}$ (eq 44) and one at around $\phi \sim 10^{-1}$ (eq 46) separated by a region of near ideal gas behavior at $\phi \sim 10^{-3}$. At $Z = 10$, only the high-density critical point is present (see Figure 2). In fact, in this model, the system only exhibits two critical points provided $Z \geq$

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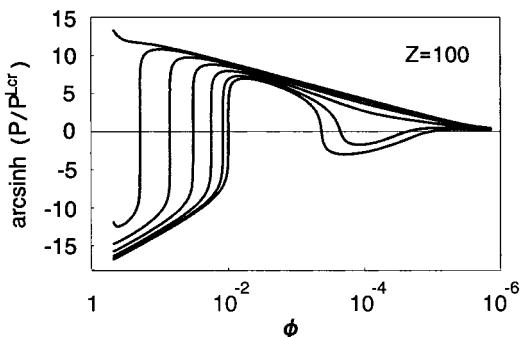


Figure 1. Pressure (P) scaled by the approximate low-density critical pressure P^{Lcr} (see eq 44) as a function of the colloid volume fraction ϕ at colloid charge $Z = 100$. From bottom to top, the isotherms are at $\Gamma = (e^2/kTR) = 32/(ZT^*)$ for $T^* = 0.8, 0.9, 1.2, 2, 4, 9,$ and 15 . The pressure is plotted on an arcsinh scale.

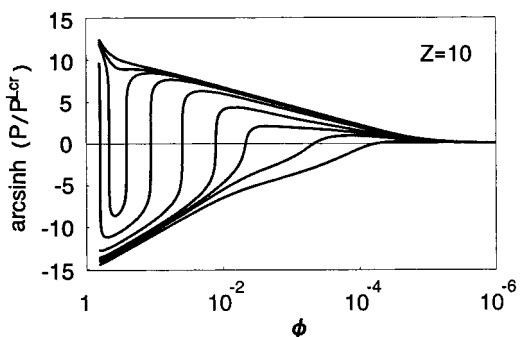


Figure 2. Pressure (P) scaled by the approximate low-density critical pressure P^{Lcr} (see eq 44) as a function of the colloid volume fraction ϕ at colloid charge $Z = 10$. From bottom to top, the isotherms are at $\Gamma = (e^2/kTR) = 32/(ZT^*)$ for $T^* = 0.8, 1.1, 1.25, 1.5, 2.5, 5, 8, 10,$ and 15 . The pressure is plotted on an arcsinh scale.

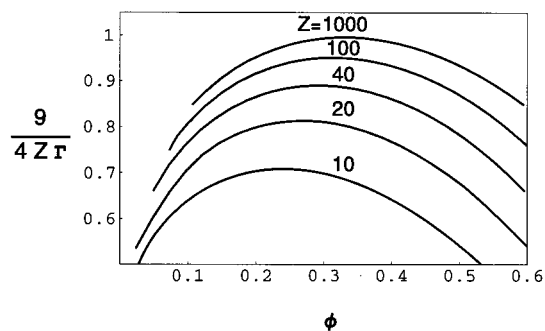


Figure 3. Scaled temperature $\Gamma^{Hcr}/\Gamma = 9/(4ZT) = 9kTR/(4Ze^2)$ versus volume fraction ϕ phase diagram corresponding to colloid charges of $Z = 10-1000$.

11. From the magnitude of the pressure, only the high-density critical point around $\phi \sim 10^{-1}$ is thermodynamically stable and examples of the temperature–volume fraction phase diagram for a range of colloid charges Z are given in Figure 3. For the case $Z = 10$, the present theory predicts a critical point at $\phi_c = 0.24$ and $\Gamma_c = 0.32$, and for $Z = 20$, $\phi_c = 0.27$ and $\Gamma_c = 0.14$. These modest colloid charges are certainly accessible by simulation studies.⁶

The critical point at low volume fraction is in the metastable region of the pressure isotherm. This general feature of the pressure isotherm is illustrated schematically in Figure 4. The portion of the isotherm between points A and B is in a thermodynamically metastable region. At the composition S , the system may phase

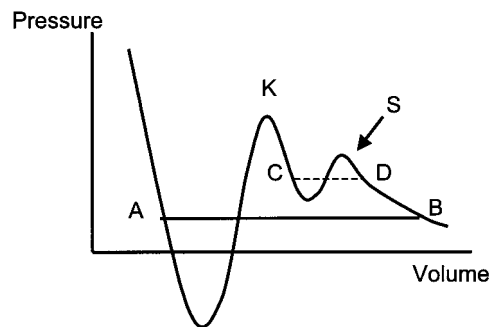


Figure 4. Schematic illustration of the pressure isotherm with two critical points.

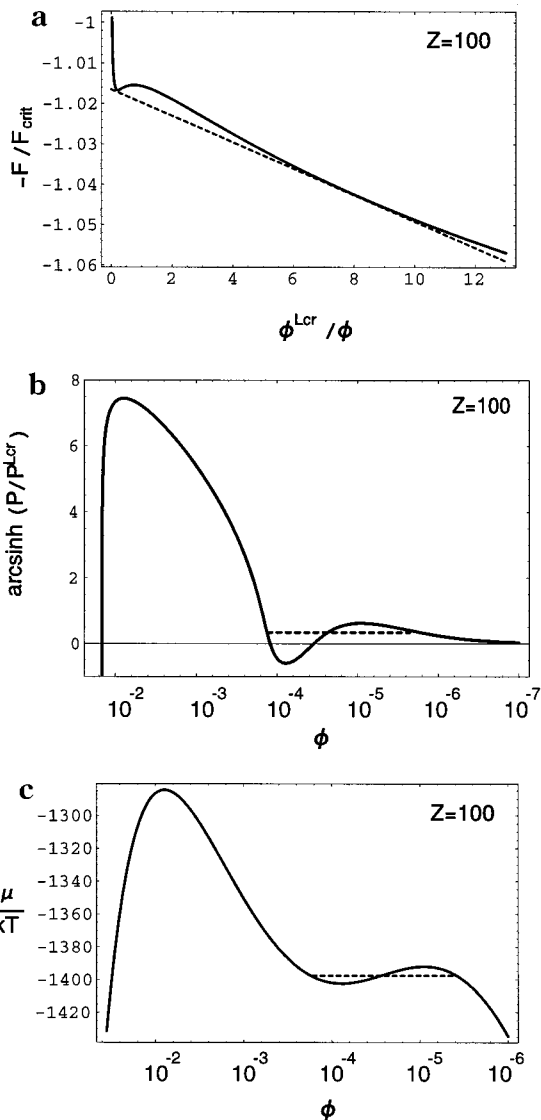


Figure 5. Free energy (F/F^{Lcr}), pressure (P/P^{Lcr}), and chemical potential (μ/kT) versus volume fraction ϕ at the scaled temperature of $1/\Gamma = (kTR/e^2) = 0.95(1/\Gamma^{Lcr}) = 0.95(Z/32)$ near the metastable critical point for a colloid charge of $Z = 100$. F^{Lcr} is the free energy (eq 39) evaluated at the state point given by eq 44. Horizontal tie lines and the common tangent construction between the equilibrium densities are shown.

separate into the metastable points C and D, and will finally attain thermodynamic equilibrium at the equilibrium state points A and B. To obtain a simple measure of the “stability” of the metastable states C and D, we consider the variation of the chemical potential in the neighborhood of the metastable low-density critical point.

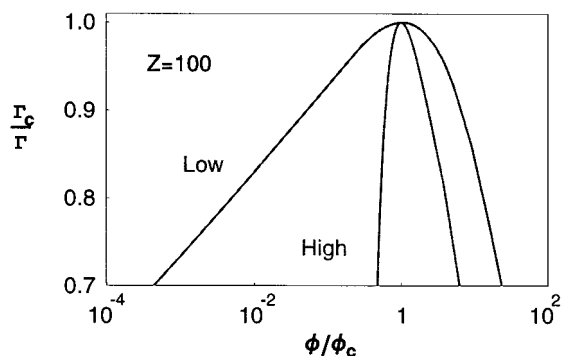


Figure 6. Temperature–volume fraction phase boundaries at the low- and high-density critical points. The colloid charge $Z = 100$. Each curve is scaled with respect to its own critical values.

In Figure 5 we show the variation of the free energy, pressure, and chemical potential with volume fraction for a system with colloid charge $Z = 100$ at a reduced temperature of $(1/T) = 0.95(Z/32)$. The usual common tangent construction for the free energy (Figure 5a) and the Maxwell equal area construction for the pressure (Figure 5b) are indicated by the dotted lines. We observe that there is a large barrier in the chemical potential associated with the pressure maximum (point K in Figure 4). We note from Figure 5c that, at $Z = 100$, the chemical potential barrier is of the order $100kT$ and, at $Z = 50$ (not shown), the chemical potential barrier still has a magnitude of about $30kT$. While considerations of the lifetime of the metastable states are beyond a simple equilibrium study undertaken here, this observation would suggest that, at large colloid charges, the low-density critical point offers the possibility of the existence of long-lived metastable states that may be manifested as the vapor–liquid like phase separation observed in deionized latex dispersions.¹ Finally, we observe that the variation of the free energy between the two metastable states is only around 2–3%, which gives an indication of the numerical precision needed if this metastable region is to be explored by simulation studies.

In Figure 6, we compare the characteristics of the temperature–volume fraction coexistence phase boundaries about the low-density and high-density critical points for a colloid charge $Z = 100$. The results have been scaled with respect to their own critical values for comparison. The phase boundaries corresponding to the low-density (metastable) critical point have a very large density difference between the metastable states which is reminiscent of the low particle densities observed within the void regions in deionized dispersions¹.

Clearly, the reliability of the above results obtained from the extended (linear) Debye–Hückel model is difficult to gauge without further work. We can gain some insight by comparing with earlier studies of the critical behavior of the restricted primitive model (RPM) electrolyte—a symmetric electrolyte in which the anions and cations have equal hard sphere radii. For this system, the extended

Debye–Hückel model gave a scaled critical temperature $(kT_c \epsilon R / e^2) = 1/32$, which is within about 10% of the best estimate from Monte Carlo simulations.¹⁷ However, the predicted critical density is too low by over a factor of 5. This would suggest that the extended Debye–Hückel model may also be reasonable in estimating the critical temperature of the $Z:1$ system. Hopefully, the results obtained herein will stimulate further theoretical and simulation studies.

Conclusion

Using an extension of the Debye–Hückel theory of an asymmetric electrolyte, we have demonstrated how a vapor–liquid phase separation can be driven by Coulomb interactions between the charged species because the overall Coulomb interaction is cohesive. We also showed that this cohesive contribution to the free energy due to Coulomb interactions is consistent with a purely repulsive effective pair interaction potential between the colloidal particles in the system within the primitive model. While the DLVO paradigm of regarding a colloidal system as a one-component system of colloidal particles interacting with pair potentials has been extremely successful in understanding colloidal stability, the phase separation phenomenon requires consideration of the thermodynamic state of the whole system. In low salt or deionized systems where Coulomb interactions dominate, a consideration of the colloid–colloid pair interaction alone will not provide sufficient insight into the phase behavior of the system; instead it is necessary to consider additional contributions from the small ions.

As with other studies,^{7,13,15} our consideration of the point–ion, point–colloid Debye–Hückel model indicates that, in using the effective pair potential paradigm to calculate thermodynamic properties, there will be significant cancellations between contributions from the one- and two-body terms because both contribute to the same order in the colloid density. More generally, with finite colloid size, higher body terms will appear although their contributions to the thermodynamics may remain small. Nonetheless, it is important to ensure that all types of terms are calculated in a consistent manner. On the other hand, a direct approach to calculate the internal energy in terms of distribution functions does not involve such cancellations and may provide a numerically more stable route to system thermodynamics.

So far, previous theories^{7,13,15} of such colloidal systems are based on variants of the linear Debye–Hückel theory. However, it is possible to go beyond the linear Debye–Hückel theory by exploiting the idea of effective pair potentials between colloidal particles to include nonlinear effects in the Coulomb interaction. This will be presented in the next paper in this series.

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