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Phase coexistence in colloidal suspensions: An analytic Poisson-Boltzmann treatment

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We solve the linearized Poisson-Boltzmann equation analytically, subject to justifiable approximations, for a suspension containing a large number of identical spherical macroions under conditions of constant surface charge and zero added salt, in order to investigate the phase behavior of charge-stabilized colloidal suspensions. Our results for the electrostatic part of the Helmholtz free energy lead to an interaction which resembles the intermolecular interaction in the theory of molecular fluids. When combined with the ideal gas free energy of the counterions, this produces a van der Waals loop in the pV diagram, indicating coexistence between phases with different densities, for certain values of the macroion radius and charge. We also derive an expression for the surface potential of the macroions, and clarify the interpretation of the Poisson-Boltzmann equation.

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I. INTRODUCTION

One of the main theoretical tools which has been used to describe the physics of charged colloidal suspensions is the Poisson-Boltzmann theory. This treats the simple ions (microions) as point particles responding to a mean field electrostatic force; their equilibrium arrangement is then given by a balance, described by a Boltzmann factor, between the electrostatic potential governed by Poisson's equation, and the chemical potential.

Applied to just two colloidal particles (macroions or polyions), the linearized version of the Poisson-Boltzmann theory leads to the Derjaguin-Landau-Verwey-Overbeek potential [1], which predicts a purely repulsive interaction between the macroions, in qualitative agreement with experimental results [2] for this system. However, the situation in large suspensions of macroions is more complicated. Under certain circumstances, coexistence is observed [3–9] between a dense phase and a rarefied phase or void, analogous to the coexistence between solid/liquid and gaseous phases in molecular matter. This raises the question of how such an effect could arise from electrostatic interactions.

An attempt to describe the phenomenon theoretically within the framework of the linearized Poisson-Boltzmann theory was made by Sogami and Ise [10], who proposed an attractive effective interaction between macroions. More recently, van Roij and co-workers [11–13] used density functional methods, applied to a model whose assumptions are identical to those of the linearized Poisson-Boltzmann theory, to derive a free energy which contains a repulsive effective interaction between macroions and an additional volume-related term; together, these can lead to coexistence. Warren [14] has also shown that phase coexistence can result from a model based on similar assumptions.

Sogami and Ise argued that the correct thermodynamic potential for the description of a colloidal suspension is not the Helmholtz free energy but the Gibbs free energy. It has been pointed out [15,16] that there are problems with this aspect of the theory, associated with the difficulty of calculating the Gibbs free energy in an inhomogeneous system; however, the theory includes the backbone of a method for the solution of the linearized Poisson-Boltzmann equation for a large suspension. A problem with this method is that it permits microions to penetrate the interiors of the macroions [11], but in the present paper we eliminate this difficulty, enabling the Helmholtz free energy of some region of a suspension, as well as the surface potential of a macroion in such a region, to be found analytically. This requires us to make a small number of justifiable approximations, based around the idea that the environments of all the macroions in the region are approximately identical and spherically symmetric, if we ignore boundary effects.

The organization of the remainder of this paper is as follows. In Sec. II we define the theoretical model on which our investigations are based. We also discuss the interpretation of terms in the Poisson-Boltzmann equation, a point that is rarely made clear. In Sec. III the linearized Poisson-Boltzmann equation is solved, first for a single macroion and then for a suspension, and expressions for the electrostatic part of the free energy are derived; the calculations are set out in some detail in order to make the development as clear as possible. In Sec. IV we consider the application of our results and their consequences for the phase behavior of macroionic suspensions. We give our conclusions in Sec. V.

We use SI electromagnetic units throughout.

II. THE POISSON-BOLTZMANN EQUATION

A. The model

The theoretical model to be considered treats a constant number N_M of identical spherical macroions of radius a, each of which has a constant charge Ze distributed uniformly over its surface (e is the elementary charge). Associated with the macroions are a constant number N_i of each species i of microions, which are regarded as point charges of value $z_i e$. The system overall is charge neutral, so that $N_M Z + \Sigma_i N_i z_i = 0$. The ions are suspended in a solvent which is maintained at constant temperature and which is described according to a ''primitive model''; that is, it is a continuum with permittivity $\epsilon = \epsilon_r \epsilon_0$, which is unaffected by the ions. Here, ϵ_0 is the permittivity of the vacuum, and ϵ_r the relative permittivity, which is around 80 for water. We consider the behavior of the macroions to be adiabatically separated from that of the microions, as the macroions are much larger; the microions will be allowed to take up their equilibrium configuration about a ‘‘fixed’’ system of macroions, and only then will the effect on the macroions be considered. (To simplify the following discussion about the interpretation of the Boltzmann factor, we shall temporarily forget about the macroions altogether.) We ignore correlations between the microions, so that they do not interact directly with one another, and respond instead to a mean field. We also ignore kinetic energy, so the phase space for the microions is just the volume V available to them. The probability density $p_i(\mathbf{r})$ for each ion of species i within this phase space is given by the canonical distribution

$$p_i(\mathbf{r})=\frac{e^{-\beta H_i(\mathbf{r})}}{\int dVe^{-\beta H_i(\mathbf{r})}}, \tag{1}$$

where the volume integral is taken over the whole available volume. $H_i(\mathbf{r})$ is the Hamiltonian, and $\beta=1/k_BT$, where k_B is the Boltzmann constant and T the absolute temperature. Assume that there are N_i identical ions in the space; their number density will be given by a Boltzmann factor

$$n_i(\mathbf{r})=\frac{N_ie^{-\beta H_i(\mathbf{r})}}{\int dVe^{-\beta H_i(\mathbf{r})}}=n_{i0}e^{-\beta H_i(\mathbf{r})}, \tag{2}$$

where $n_{i0}=N_i/\int dVe^{-\beta H_i(\mathbf{r})}$. The Hamiltonian is taken to be $H_i(\mathbf{r})=z_ie\psi(\mathbf{r})$, where $\psi(\mathbf{r})$ is the electrostatic potential.

B. Interpretation of the Boltzmann factor

The microion number density is

$$n_i(\mathbf{r})=n_{i0}e^{-\beta z_ie\psi(\mathbf{r})}. \tag{3}$$

It is clear that if n_{i0} is replaced by some different value $n_{i0}+\Delta n_{i0}$, the same ion distribution can still be produced, provided that $\psi(\mathbf{r})$ is also shifted by the appropriate constant amount. There is no physical significance in such a constant shift in $\psi(\mathbf{r})$, since the physics depends only on the gradient of the potential; the potential has no natural zero value, and its absolute value is of no importance. Consider

$$n_i'(\mathbf{r})=(n_{i0}+\Delta n_{i0})e^{-\beta z_ie[\psi(\mathbf{r})+\Delta\psi(\mathbf{r})]}. \tag{4}$$

This will be the same density distribution as $n_i(\mathbf{r})$ provided that

$$\Delta\psi(\mathbf{r})=\frac{1}{\beta z_ie}\ln\left(1+\frac{\Delta n_{i0}}{n_{i0}}\right), \tag{5}$$

which is independent of $\mathbf{r}$ and therefore represents a constant shift $\Delta\psi$.

This shifting of the electrostatic potential is a little like a gauge transformation [17], with the ‘‘gauge condition’’ being a condition on an integral of the potential

$$\int dVe^{-\beta z_ie\psi(\mathbf{r})}=\frac{N}{n_{i0}}, \tag{6}$$

which can be satisfied by setting the potential zero to the appropriate value. As an example of a gauge, consider that in which n_{i0} is equal to $\overline{n_i}$, the mean density of ions of species i. This requires the zero of the potential to be set so that

$$\int dVe^{-\beta z_ie\psi(\mathbf{r})}=V. \tag{7}$$

Note that since the ion density can be represented in the $n_{i0}=\overline{n_i}$ gauge as

$$n_i(\mathbf{r})=\overline{n_i}e^{-\beta z_ie\psi(\mathbf{r})}, \tag{8}$$

it can also be represented as

$$n_i(\mathbf{r})=n_{i0}e^{-\beta z_ie[\psi(\mathbf{r})+\Delta\psi]}, \tag{9}$$

where $n_{i0}=c_i\overline{n_i}$, with $c_i=e^{\beta z_ie\Delta\psi}$, for any $\Delta\psi$. This means that, whatever gauge is being used, n_{i0} is some constant multiple of the mean ion density. This is significant for the consideration of colloidal suspensions: in the present model, the total number of microions (and therefore their mean density) is a constant, independent of the macroion configuration. Therefore, in a given fixed gauge, n_{i0} is also a constant.

In systems containing several species of microions it is impossible, in any given gauge, to have $c_j=c_i$ unless $z_j=z_i$. That is, Eq. (6) can only be satisfied simultaneously for ion species having unequal charges if we interpret n_{i0} differently for each species. For example, we could define the potential zero so as to make the n_{i0} associated with ions of charge z_i equal to the mean density $\overline{n_i}$, but then the n_{j0} associated with ions of charge $z_j\neq z_i$ would not be equal to $\overline{n_j}$. This point would need to be taken into account in the application of solutions to the full Poisson-Boltzmann equation.

C. The linearized Poisson-Boltzmann equation

Poisson’s equation for the electrostatic potential states that

$$\nabla^2\psi(\mathbf{r})=-\frac{1}{\epsilon}\rho(\mathbf{r}), \tag{10}$$

where $\rho(\mathbf{r})$ is the charge density. If we consider a system in which the only charges are those on the microions, this charge density is

$$\rho(\mathbf{r})=\sum_i z_ien_i(\mathbf{r})=\sum_i z_ien_{i0}e^{-\beta z_ie\psi(\mathbf{r})}. \tag{11}$$

Inserting this into Poisson’s equation gives the Poisson-Boltzmann equation for the electrostatic potential in an ionic system

$$\nabla^2\psi(\mathbf{r}) = -\frac{1}{\epsilon}\sum_i z_i e n_{i0} e^{-\beta z_i e\psi(\mathbf{r})}. \tag{12}$$

The full Poisson-Boltzmann equation is, unfortunately, too difficult to solve analytically for any but the simplest geometries. However, we can expand the exponential as a power series, and if we assume that the potential is everywhere sufficiently close to zero for the conditions $|\beta z_i e\psi(\mathbf{r})| \ll 1$ to be met (the Debye-Hückel approximation), we can keep only the first two terms, leading to the linearized Poisson-Boltzmann equation

$$\nabla^2\psi(\mathbf{r}) = -\frac{1}{\epsilon}\sum_i z_i e n_{i0}[1-\beta z_i e\psi(\mathbf{r})]. \tag{13}$$

It is clear that the extent to which this linearized equation is a good approximation to the original depends not only on the gradient of the potential, but also on the gauge. The equivalence between gauges that exists in the full equation is lost: it is no longer true that an arbitrary change Δn_{i0} can be compensated for by a constant shift $\Delta\psi$ in $\psi(\mathbf{r})$. The best gauge to use, if we wish to convert to the linearized equation, is one that keeps $\psi(\mathbf{r})$ as close as possible to zero in as much of the system as possible. The one mentioned above, in which $n_{i0} = \overline{n_i}$, seems to be quite a good candidate: if we integrate the density (using a linearized Boltzmann factor),

$$N_i = \int dV n_i(\mathbf{r}) = n_{i0}V - \beta z_i e n_{i0}\int dV\psi(\mathbf{r}), \tag{14}$$

we see that this gauge correponds to the condition $\int dV\psi(\mathbf{r}) = 0$, or $\overline{\psi} = 0$.

Now it can be seen that this linearized system possesses an advantage to set against the disadvantage of the restriction on our choice of potential zero. It is possible to write $n_{i0} = c\overline{n_i}$, where c is the same for every species of microion, provided that the gauge used is $\overline{\psi} = 0$ (so $n_{i0} = \overline{n_i}$ and $c = 1$). This means that we can put the same interpretation on n_{i0} for each ion species.

There is a third, and conclusive, reason for choosing $\overline{\psi} = 0$ in the linearized system (and this also applies, in fact, to the nonlinear system). We shall later wish to calculate the Helmholtz free energy of a colloidal system from the electrostatic energy using Eq. (51), Debye's charging-up equation. This involves integrating the elementary charge e from zero to its physical value. Therefore, we should consider the behavior of a system of ions described by a Boltzmann factor as e is changed. The ion density at some charge $e^{(1)}$ is given by the linearized Boltzmann factor as

$$n_i^{(1)}(\mathbf{r}) = n_{i0}^{(1)}[1-\beta z_i e^{(1)}\psi^{(1)}(\mathbf{r})]. \tag{15}$$

There is no reason to expect the density distribution to remain the same as e changes to $e^{(2)}$; however, we require the total number of ions to remain the same

$$n_{i0}^{(1)}\left(V - \beta z_i e^{(1)}\int dV\psi^{(1)}(\mathbf{r})\right) = n_{i0}^{(2)}\left(V - \beta z_i e^{(2)}\int dV\psi^{(2)}(\mathbf{r})\right). \tag{16}$$

During the e integration, we wish to keep n_{i0} constant, that is, $n_{i0}^{(2)} = n_{i0}^{(1)}$; applying this condition and considering the situation when $e^{(1)}$ is equal to zero, we see that Eq. (16) can only be satisfied if $\overline{\psi^{(2)}} = \overline{\psi^{(1)}} = 0$. It appears that Debye's charging-up theorem only makes sense if $\overline{\psi} = 0$, so we shall assume this gauge in the remainder of the paper.

D. Representation of the macroions

Before we can model a colloidal suspension, we must add the macroions. The total surface charge density $\rho_M(\mathbf{r})$ is given [10] by a sum over a set of spherical delta functions of radius a, the nth of which represents a macroion centered on $\mathbf{R}_n$

$$\rho_M(\mathbf{r}) = \sum_n \rho_n(\mathbf{r}) = \sum_n \frac{Ze}{4\pi a^2}\delta(|\mathbf{r}-\mathbf{R}_n| - a). \tag{17}$$

The next step is to modify the available volume (and hence the phase space) to exclude microions from the interior of the macroions. We encode this exclusion by multiplying the Boltzmann factor by a product of Heaviside step functions $\Pi_n\theta_n \equiv \Pi_n\theta(|\mathbf{r}-\mathbf{R}_n| - a)$,

$$n_i(\mathbf{r}) = n_{i0}[1-\beta z_i e\psi(\mathbf{r})]\prod_n \theta_n. \tag{18}$$

This change requires the volume integrals mentioned above to be taken over all space except the interiors of the macroions.

Introducing a constant quantity κ^2, defined, in the same way as the square of the inverse screening length in the Debye-Hückel theory to be

$$\kappa^2 \equiv \frac{\beta}{\epsilon}\sum_i z_i^2 e^2 n_{i0}, \tag{19}$$

allows the linearized Poisson-Boltzmann equation, taking the macroions into account, to be written as

$$\left(\nabla^2 - \kappa^2\prod_n \theta_n\right)\psi(\mathbf{r}) = -\frac{1}{\epsilon}\sum_n \rho_n(\mathbf{r}) - \frac{1}{\epsilon}\sum_i z_i e n_{i0}\prod_n \theta_n. \tag{20}$$

The dielectric constant of the macroion interiors will obviously be different from that of the solution, but in these regions the charge density, and therefore $\nabla^2\psi$, will be zero, so the difference in the dielectric constants will have no effect on our results. Consequently, we use for ϵ its value in the solution.

III. SOLUTION OF THE POISSON-BOLTZMANN EQUATION

A. A shifted potential

The first step is to simplify Eq. (20) by changing variables to a new potential $\phi(\mathbf{r})$, which is given by

$$\phi(\mathbf{r})=\psi(\mathbf{r})-\frac{e}{\epsilon\kappa^2}\sum_i z_i n_{i0}, \tag{21}$$

so that

$$\left(\nabla^2-\kappa^2\prod_n \theta_n\right)\phi(\mathbf{r})=-\frac{1}{\epsilon}\sum_n \rho_n(\mathbf{r}). \tag{22}$$

Since the shift is a constant, the gradient of $\phi(\mathbf{r})$ is equal to that of $\psi(\mathbf{r})$. This shift in the potential is not the same as the gauge transformation introduced in Sec. II B. There, we shifted the potential in order to describe the system with the same form of equation, but with a different value for n_{i0}. Here, we shift the potential in order to describe the system with a different, simpler form of equation, but with the *same* value for n_{i0}.

What is the interpretation of this shifted potential $\phi(\mathbf{r})$? The value of $\psi(\mathbf{r})$ at some (possibly hypothetical) location far from any macroions can be found from the condition of local charge neutrality

$$\sum_i z_i n_i(\mathbf{r})=0 \tag{23}$$

to be

$$\psi_\infty=\frac{1}{\beta\epsilon}\frac{\sum_i z_i n_{i0}}{\sum_i z_i^2 n_{i0}}=\frac{e}{\epsilon\kappa^2}\sum_i z_i n_{i0}. \tag{24}$$

So $\phi(\mathbf{r})=\psi(\mathbf{r})-\psi_\infty$; that is, $\phi(\mathbf{r})$ is the potential relative to a zero point located at some point far outside the system of macroions. This is the potential zero used by Verwey and Overbeek [1]; however, the n_{i0} in the definition of the κ^2 that appears in Eq. (22) is still to be interpreted as the mean microion density.

B. Solving for the potential in Fourier space

In order to solve Eq. (22), we follow Sogami and Ise [10] in Fourier transforming it; our convention for the Fourier transform $\mathcal{F}[\alpha(\mathbf{r})]$ of a function $\alpha(\mathbf{r})$ is

$$\mathcal{F}[\alpha(\mathbf{r})]=\frac{1}{(2\pi)^{3/2}}\int d^3\mathbf{r}\,\alpha(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}, \tag{25}$$

where the volume integral is to be taken over the whole of the system. The term involving ∇^2 is easily dealt with using $\mathcal{F}[\nabla^2\phi(\mathbf{r})]=-k^2\tilde{\phi}(\mathbf{k})$, where the meaning of the tilde is that $\tilde{\alpha}(\mathbf{k})\equiv\mathcal{F}[\alpha(\mathbf{r})]$. For the second term in Eq. (22), we use the fact that $\Pi_n\theta_n$ is zero inside macroions and unity outside to write

$$\mathcal{F}\left[\kappa^2\prod_n \theta_n\phi(\mathbf{r})\right]=\kappa^2\tilde{\phi}(\mathbf{k})-\frac{\kappa^2}{(2\pi)^{3/2}}\int_{\mathrm{int}} dV\phi(r)e^{-i\mathbf{k}\cdot\mathbf{r}}, \tag{26}$$

where the integral is over the interiors of all the macroions. To perform this integration, we introduce an approximation by assuming that the field surrounding each macroion is spherically symmetric. Then the potential inside the macroions will be constant, and will in fact be equal to the surface potential ϕ_s. If we also write $\mathbf{r}=\mathbf{R}_n+\mathbf{r}'$, the integral can be rewritten as

$$\int_{\mathrm{int}} dV\phi(r)e^{-i\mathbf{k}\cdot\mathbf{r}}=\phi_s\sum_n e^{-i\mathbf{k}\cdot\mathbf{R}_n}\int_{|\mathbf{r}'|=0}^{a} d^3\mathbf{r}'e^{-i\mathbf{k}\cdot\mathbf{r}'}. \tag{27}$$

The integral on the right hand side of Eq. (27) is identical for each macroion, and can be evaluated by elementary methods, yielding

$$\mathcal{F}\left[\kappa^2\prod_n \theta_n\phi(\mathbf{r})\right]=\kappa^2\tilde{\phi}(\mathbf{k})-\left(\frac{2}{\pi}\right)^{1/2}\kappa^2\phi_s\times\left(\frac{\sin ka}{k^3}-\frac{a\cos ka}{k^2}\right)\sum_n e^{-i\mathbf{k}\cdot\mathbf{R}_n}. \tag{28}$$

To find the Fourier transform of the right hand side of Eq. (22), we once again introduce $\mathbf{r}=\mathbf{R}_n+\mathbf{r}'$, resulting in an integral which is the same for each macroion. After we integrate over the angular coordinates of $\mathbf{r}'$, a delta function picks out the value $r'=a$ in the r' integration, with the result

$$\tilde{\rho}_n(\mathbf{k})=\frac{1}{(2\pi)^{3/2}}\frac{Ze\sin ka}{ka}e^{-i\mathbf{k}\cdot\mathbf{R}_n}. \tag{29}$$

Collecting Eqs. (22), (28), and (29) leads to the result for the Fourier transform of the potential

$$\tilde{\phi}(\mathbf{k})=\frac{1}{(2\pi)^{3/2}}\frac{Ze}{\epsilon}\frac{1}{k^2+\kappa^2}g(k)\sum_n e^{-i\mathbf{k}\cdot\mathbf{R}_n}, \tag{30}$$

where, to lighten the equations, we have defined $g(k)$ by

$$g(k)\equiv\frac{\sin ka}{ka}+\frac{4\pi\epsilon\kappa^2\phi_s}{Ze}\left(\frac{\sin ka}{k^3}-\frac{a\cos ka}{k^2}\right). \tag{31}$$

C. The potential around a single macroion

Before considering a large suspension, it is instructive to apply the results derived above to the calculation of the electrostatic field around a single isolated spherical macroion, although this can, of course, be calculated more simply [1]. The assumption that the field surrounding the particle is spherically symmetric will be exactly true for a single macroion. Without loss of generality, we can assume that the center of the macroion is at $\mathbf{R}=0$, so that from Eq. (30)

$$\tilde{\phi}(\mathbf{k})=\frac{1}{(2\pi)^{3/2}}\frac{Ze}{\epsilon}g(k)\frac{1}{k^2+\kappa^2}. \tag{32}$$

Now we use the inverse Fourier transform

$$\phi(\mathbf{r})=\frac{1}{(2\pi)^{3/2}}\int d^3\mathbf{k}\tilde{\phi}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}; \tag{33}$$

substituting Eq. (32) into this and integrating over the angular part of $\mathbf{k}$ gives

$$\phi(r)=\frac{1}{2\pi^2}\frac{Ze}{\epsilon r}\int_0^\infty dk\frac{k}{k^2+\kappa^2}g(k)\sin kr. \tag{34}$$

This integral can be evaluated by contour integration in the complex plane. We rewrite it as a sum of two separate contour integrals, of which one contains terms of the form e^{ikC}, where C is a positive constant, while the other contains terms of the form e^{-ikC}. The former must be integrated around the upper half plane, the latter around the lower. However, which group a given term falls into depends on the relative values of a and r, with the result that Eq. (34) has two different solutions: one valid for $r<a$ (that is, inside the macroion)

$$\phi_{r<a}(r)=\phi_s+\left[\frac{Ze}{4\pi\epsilon\kappa a}-\phi_s\left(\frac{1}{\kappa}+a\right)\right]\frac{\sinh\kappa r}{r}e^{-\kappa a}, \tag{35}$$

which results from poles at zero and $+i\kappa$ in the upper half plane and at zero and $-i\kappa$ in the lower half plane, and one for $r>a$ (outside the macroion)

$$\phi_{r>a}(r)=\left[\left(\frac{Ze}{4\pi\epsilon\kappa a}-\frac{\phi_s}{\kappa}\right)\sinh\kappa a+a\phi_s\cosh\kappa a\right]\frac{e^{-\kappa r}}{r}, \tag{36}$$

which results from poles at $+i\kappa$ in the upper half plane and at $-i\kappa$ in the lower half plane. To make the link between the two solutions, we consider the boundary condition on the second solution at the surface

$$\phi_{r>a}(a)=\phi_s. \tag{37}$$

This leads to the condition

$$\frac{Ze}{4\pi\epsilon\kappa a}=\phi_s\left(\frac{1}{\kappa}+a\right); \tag{38}$$

applied to the first solution this condition produces, as expected, a constant potential $\phi_{r<a}=\phi_s$, while applied to the second solution it produces

$$\phi_{r>a}(r)=\phi_s a e^{\kappa a}\frac{e^{-\kappa r}}{r}, \tag{39}$$

which is the potential derived by Verwey and Overbeek [1]. It is also worth noting that the boundary condition is equivalent to

$$\phi_s=\frac{Ze}{4\pi\epsilon a}\frac{1}{1+\kappa a}; \tag{40}$$

allowing for differences in the electromagnetic units, this is Verwey's and Overbeek's relation between the surface potential ϕ_s and the surface charge Ze.

D. The surface potential in a suspension

Now we wish to consider the surface potential of a macroion in a suspension of identical macroions. The main motivation for doing this is to provide an approximate expression for ϕ_s which can be used in calculations of the free energy of such a system. The inverse Fourier transform is applied to Eq. (30), but now with many macroions. This leads to

$$\phi(\mathbf{r})=\frac{1}{(2\pi)^3}\frac{Ze}{\epsilon}\sum_n\int d^3\mathbf{k}\frac{1}{k^2+\kappa^2}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_n)}g(k), \tag{41}$$

which is a sum of potentials, the nth of which has the same form of equation as the single macroion potential in Eq. (34), but centered on $\mathbf{R}_n$ rather then on zero. Thus, we can use the results derived in Sec. III C to express the solutions for the potential in real space as sums of the single macroion solutions, as follows: inside macroion m, we have a sum of the internal solution for macroion m and the external solutions for all the other macroions

$$\begin{aligned}\phi_{\text{int}}(\mathbf{r})=\phi_s&+\left[\frac{Ze}{4\pi\epsilon\kappa a}-\phi_s\left(\frac{1}{\kappa}+a\right)\right]\frac{\sinh\kappa|\mathbf{r}-\mathbf{R}_m|}{|\mathbf{r}-\mathbf{R}_m|}e^{-\kappa a}\\&+\left[\left(\frac{Ze}{4\pi\epsilon\kappa a}-\frac{\phi_s}{\kappa}\right)\sinh\kappa a\right.\\&\left.+a\phi_s\cosh\kappa a\right]\sum_{n\neq m}\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_n|}}{|\mathbf{r}-\mathbf{R}_n|}\end{aligned} \tag{42}$$

while, outside all macroions, we have a sum over the external solutions for all the macroions

$$\begin{aligned}\phi_{\text{ext}}(\mathbf{r})=&\left[\left(\frac{Ze}{4\pi\epsilon\kappa a}-\frac{\phi_s}{\kappa}\right)\sinh\kappa a\right.\\&\left.+a\phi_s\cosh\kappa a\right]\sum_n\frac{e^{-\kappa|\mathbf{r}-\mathbf{R}_n|}}{|\mathbf{r}-\mathbf{R}_n|}.\end{aligned} \tag{43}$$

In this system, the assumption that the field around each macroion is spherically symmetric is only an approximation. Consequently, the potential inside the macroions will not be exactly constant, nor will the surface potential ϕ_s be constant over the surface. However, in the present approximate treatment we assume that it is constant, and consider the value taken at the surface of one particular macroion m by the external solution for the potential. We introduce the further approximation that the effect of the other macroions on the potential at this surface is the same as it is at the center (that is, $|\mathbf{r}-\mathbf{R}_n| \approx |\mathbf{R}_n-\mathbf{R}_m|$ for all n; this approximation can be justified by noting that the effect of a macroion located on one side of macroion m being nearer to an element of the surface of m than it is to the center of m, will be partially cancelled by the effect of a macroion on the opposite side being further from the surface than it is from the center). The result is

$$\phi_s = \left[\left(\frac{Ze}{4\pi\epsilon\kappa a} - \frac{\phi_s}{\kappa}\right)\sinh\kappa a + a\,\phi_s\cosh\kappa a\right]\frac{e^{-\kappa a}+\Sigma^Y}{a}, \tag{44}$$

where Σ^Y is the sum over the Yukawa potentials

$$\Sigma^Y \equiv a\sum_{n\neq m}\frac{e^{-\kappa R_{mn}}}{R_{mn}} = \sum_{n\neq m}\frac{e^{-\kappa a S_{mn}}}{S_{mn}}; \tag{45}$$

here $R_{mn} \equiv |\mathbf{R}_m-\mathbf{R}_n|$, and $S_{mn} \equiv R_{mn}/a$ is a dimensionless separation between the centers of macroions m and n. Equation (44) can be rearranged to yield a simple expression for the surface potential

$$\phi_s = \frac{Ze}{4\pi\epsilon a}\,\frac{e^{-\kappa a}+\Sigma^Y}{(1+\kappa a)e^{-\kappa a}+(1-\kappa a\coth\kappa a)\Sigma^Y}. \tag{46}$$

It is easy to see that in the limit of a single macroion ($\Sigma^Y = 0$), this expression for ϕ_s reduces to Eq. (40), as expected.

We can also introduce a dimensionless surface potential Φ_s, which is the ratio of the surface potential to that of an isolated macroion with the same charge

$$\Phi_s = \frac{4\pi\epsilon a(1+\kappa a)}{Ze}\,\phi_s; \tag{47}$$

then Eq. (46) takes the form

$$\Phi_s = \frac{(1+\kappa a)(e^{-\kappa a}+\Sigma^Y)}{(1+\kappa a)e^{-\kappa a}+(1-\kappa a\coth\kappa a)\Sigma^Y}, \tag{48}$$

while Eq. (31) becomes

$$g(k) = \frac{\sin ka}{ka} + \frac{\kappa^2\Phi_s}{a(1+\kappa a)}\left(\frac{\sin ka}{k^3} - \frac{a\cos ka}{k^2}\right). \tag{49}$$

E. The Helmholtz free energy of a suspension

In order to calculate the free energy F of the system, we first calculate the electrostatic energy U using the standard equation, which involves an integral over the square of the potential gradient

$$U = \frac{\epsilon}{2}\int dV[\nabla\phi(\mathbf{r})]^2, \tag{50}$$

and then calculate F by thermodynamic integration [18], using Debye's charging-up equation [19,20]

$$F = F_0 + \int_0^{e^2_{\text{phys}}} de^2\,\frac{U}{e^2}, \tag{51}$$

in which we integrate the elementary charge from zero to its physical value e_{phys}. F_0, the free energy of the system in the absence of charge, is a sum of two terms: the free energy F_{id} of an ideal gas of hypothetical uncharged microions, and a mildly repulsive entropic term F_{hs} due to uncharged colloidal particles, represented as hard spheres

$$F_0 = F_{\text{id}} + F_{\text{hs}}. \tag{52}$$

F_{hs} may be calculated using the Carnahan-Starling equation of state [21,22]; however, it is small in comparison with the electrostatic and ideal gas terms, and therefore we shall ignore it.

The first step in the calculation of the electrostatic free energy is to find the gradient of the potential. This is given by an inverse Fourier transform

$$\nabla\phi(\mathbf{r}) = \frac{1}{(2\pi)^{3/2}}\int d^3\mathbf{k}\,\mathcal{F}[\nabla\phi(\mathbf{r})]e^{i\mathbf{k}\cdot\mathbf{r}}; \tag{53}$$

using Eq. (30) and given that $\mathcal{F}[\nabla\phi(\mathbf{r})] = i\mathbf{k}\tilde{\phi}(\mathbf{k})$, this can be written explicitly as

$$\nabla\phi(\mathbf{r}) = \frac{1}{(2\pi)^3}\frac{Ze}{\epsilon}\sum_n\int d^3\mathbf{k}\frac{i\mathbf{k}}{k^2+\kappa^2}g(k)e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{k}\cdot\mathbf{R}_n}, \tag{54}$$

which leads, through Eq. (50), to

$$\begin{aligned} U = -\frac{1}{(2\pi)^6}\frac{Z^2e^2}{2\epsilon}\sum_m\sum_n\int d^3\mathbf{r}\int d^3\mathbf{k} \\ \times\int d^3\mathbf{k}'\frac{\mathbf{k}\cdot\mathbf{k}'}{(k^2+\kappa^2)(k'^2+\kappa^2)} \\ \times g(k)g(k')e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}}(e^{-i\mathbf{k}\cdot\mathbf{R}_n})(e^{-i\mathbf{k}'\cdot\mathbf{R}_m}). \end{aligned} \tag{55}$$

Performing the integral over $\mathbf{r}$, we get a delta function that picks out $\mathbf{k}' = -\mathbf{k}$ in the integral over $\mathbf{k}'$, giving, since $g(k)$ is an even function

$$\begin{aligned} U = \frac{1}{(2\pi)^3}\frac{Z^2e^2}{2\epsilon} \\ \times\sum_m\sum_n\int d^3\mathbf{k}\frac{k^2}{(k^2+\kappa^2)^2}[g(k)]^2e^{i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)}. \end{aligned} \tag{56}$$

For the range of parameters in which we will be interested, the term in $g(k)$ which depends on Φ_s is well approximated by

$$\frac{\kappa^2\Phi_s}{a(1+\kappa a)} \approx A\kappa^2 + B, \tag{57}$$

where $A = \ln v/9a$ and $B = 7/2va^3$. Now U/e^2 depends on the elementary charge e only through κ^2. Recalling that $\kappa^2 = \beta/\epsilon \Sigma_i z_i^2 e^2 n_{i0}$, we can perform the integral in Eq. (51), with the result

$$F = F_0 + \frac{1}{(2\pi)^3}\frac{Z^2e^2}{2\epsilon} \times \sum_m \sum_n \int d^3\mathbf{k}\left\{\frac{[g(k)]^2}{k^2+\kappa^2} - \kappa^2 Y + 2(X - k^2 Y) \times \left[\frac{k^2}{\kappa^2}\ln\left(1+\frac{\kappa^2}{k^2}\right) - 1\right]\right\} \times e^{i\mathbf{k}\cdot(\mathbf{R}_m - \mathbf{R}_n)}, \tag{58}$$

where

$$X = AB\left(\frac{\sin ka}{k^3} - \frac{a\cos ka}{k^2}\right)^2 + A\frac{\sin ka}{ka}\left(\frac{\sin ka}{k^3} - \frac{a\cos ka}{k^2}\right) \tag{59}$$

and

$$Y = A^2\left(\frac{\sin ka}{k^3} - \frac{a\cos ka}{k^2}\right)^2. \tag{60}$$

The electrostatic part of the free energy in Eq. (58) can be split into two sets of terms: terms where $m \neq n$ (pair free energy) and terms where $m = n$ (self free energy)

$$F = F_0 + F_{\text{pair}} + F_{\text{self}}. \tag{61}$$

After the angular integration, F_{pair} can conveniently be rewritten as

$$F_{\text{pair}} = -\frac{i}{(2\pi)^2}\frac{Z^2e^2}{2\epsilon} \times \sum_n \sum_{m\neq n}\left\{\int_{-\infty}^{\infty} k\,dk\left(\frac{[g(k)]^2}{k^2+\kappa^2} - \kappa^2 Y\right)\frac{e^{ikR_{mn}}}{R_{mn}} + 4i\int_0^{\infty} k\,dk(X - k^2 Y) \times \left[\frac{k^2}{\kappa^2}\ln\left(1+\frac{\kappa^2}{k^2}\right) - 1\right]\frac{\sin kR_{mn}}{R_{mn}}\right\}. \tag{62}$$

While the second integral must be evaluated numerically, the first can be evaluated by contour integration; since we do not wish the macroions to be able to interpenetrate one another, we can assume $R_{mn} > 2a$, and take into account only a pole at $+i\kappa$. Assuming all macroions to have identical environments, the pair free energy per macroion f_{pair} can be written

$$f_{\text{pair}} = \frac{Z^2e^2}{8\pi\epsilon a}\left\{\left[\frac{\sinh\kappa a}{\kappa a} + \frac{\Phi_s}{1+\kappa a}\left(\cosh\kappa a - \frac{\sinh\kappa a}{\kappa a}\right)\right]^2 \Sigma^{Y} + \frac{4\ln v}{9\pi\kappa^2 a}\sum_{m\neq n}\int_0^{\infty} I(k)\,dk\,\frac{\sin kaS_{mn}}{kaS_{mn}}\right\}, \tag{63}$$

where Φ_s is to be calculated from Eq. (48) and

$$I(k) = \left\{\left(\frac{7}{2v(ka)^2} - \frac{\ln v}{9}\right)(\sin ka - ka\cos ka)^2 + \sin ka(\sin ka - ka\cos ka)\right\}\left[\ln\left(1+\frac{\kappa^2}{k^2}\right) - \frac{\kappa^2}{k^2}\right]. \tag{64}$$

These results can be compared with the equivalent result of Sogami and Ise [10],

$$F_{\text{pair}} = \frac{Z^2e^2}{8\pi\epsilon}\left(\frac{\sinh\kappa a}{\kappa a}\right)^2 \sum_n \sum_{m\neq n}\frac{e^{-\kappa R_{mn}}}{R_{mn}}; \tag{65}$$

the effect of excluding the microions from the interiors of the macroions has just been to introduce additional terms.

In F_{self}, $\mathbf{R}_m = \mathbf{R}_n$, and so the exponential in Eq. (58) goes to unity. The result is a spherically symmetric function in k space, which is identical for each macroion; after the angular integration, we find

$$F_{\text{self}} = \frac{1}{(2\pi)^2}\frac{Z^2e^2}{2\epsilon}\sum_n\left\{\int_{-\infty}^{\infty} k^2 dk\left[\frac{[g(k)]^2}{k^2+\kappa^2} - \kappa^2 Y\right] + 4\int_0^{\infty} k^2 dk(X - k^2 Y)\left[\frac{k^2}{\kappa^2}\ln\left(1+\frac{\kappa^2}{k^2}\right) - 1\right]\right\}. \tag{66}$$

Once again, the second integral has to be evaluated numerically, while the first can be evaluated using contour integration. We split this first integral into three separate integrals, of which the first (containing no complex exponential terms) involves a pole at $+i\kappa$, the second (containing a positive complex exponential) involves poles at $+i\kappa$ and zero, and the third (containing a negative complex exponential) involves poles at $-i\kappa$ and zero. The result for the self free energy per macroion is

$$f_{\text{self}} = \frac{Z^2e^2}{8\pi\epsilon a}\left[\frac{1}{1+\kappa a} + \frac{1}{3}\left(\frac{\kappa a}{1+\kappa a}\right)^2\Phi_s^2 + \frac{e^{-\kappa a}}{1+\kappa a} \times \left(\frac{\sinh\kappa a}{\kappa a} - \cosh\kappa a\right)(\Phi_s - 1)^2 - \frac{1}{3}\left(\frac{\kappa a\ln v}{9}\right)^2 + \frac{4\ln v}{9\pi\kappa^2 a}\int_0^{\infty} I(k)\,dk\right]. \tag{67}$$

The role of the macroion surface potential is twofold. First, it provides a boundary condition to link the potential in the two regions (inside and outside macroions), in the same way as it did in the treatment of a single, isolated macroion. Second, it introduces many-body interactions. The linearized Poisson-Boltzmann equation is often considered to lead only to pairwise interactions, and to ignore many-body effects; however, while $F_{\rm pair}$ looks rather like a sum of pairwise interactions, it actually takes account through Φ_s of the positions of all the macroions in the suspension (as does $F_{\rm self}$; in this sense, the distinction we have made between $F_{\rm pair}$ and $F_{\rm self}$ is rather artificial, and is largely a consequence of the form of the equations rather than of any physical feature of the system).

We should also consider the role of the parameter κ defined in Eq. (19). Although this is defined in the same way as the inverse screening length in the Debye-Hückel theory, it has no physical meaning at any particular point in this inhomogeneous system, since it depends on the mean microion densities n_{i0} rather than on the local densities. In a sense, it is a ''mean inverse screening length.'' κ is related to the number of microions, and therefore, because of the overall neutrality of the system, to the total charge on the macroions, but it is also related to the choice of gauge (see Sec. II C). Changing the value of κ at constant macroion density can thus represent two possible situations. If accompanied by the appropriate change in the value of Z, it represents a change in the charge on the macroions, and therefore in the total number of microions. If κ is varied without changing Z, it represents a change of gauge, and the resulting alteration in the results is not an indication of any physical change in the system, but of an alteration in the extent to which the linearized Poisson-Boltzmann equation is a good approximation to the full version. However, changing the gauge away from $\bar{\psi}=0$ invalidates results for the free energy obtained using Eq. (51).

IV. APPLICATION OF THE RESULTS

Consider the simplest case, where the system contains only one species of microion, which is a monovalent counterion. The absence of coions implies that the suspension contains no added salt. We wish to specify the thermodynamics of a region which is homogeneous (with respect to the macroions), in order to investigate the possibility that two such regions, with different macroion densities, might coexist. Overall charge neutrality requires that $|Z|$ microions are associated with each macroion. We can disregard the possibility that the microions are distributed in such a way that the individual regions depart significantly from charge neutrality; this form of distribution would be energetically unfavorable. Regional charge neutrality will be satisfied if the number of microions in a given homogeneous region is equal to $|Z|$ multiplied by the number of macroions; we regard each microion as associated with a particular macroion, and confined to the region in which that macroion is located. That is, we consider each region to be approximately equivalent to a hypothetical system comprising an identical region surrounded by an impenetrable wall, which confines the microions to that region. The thermodynamic potential for this hypothetical system is the Helmholtz free energy. Then we can investigate how the free energy of the system depends on the density of the macroions.

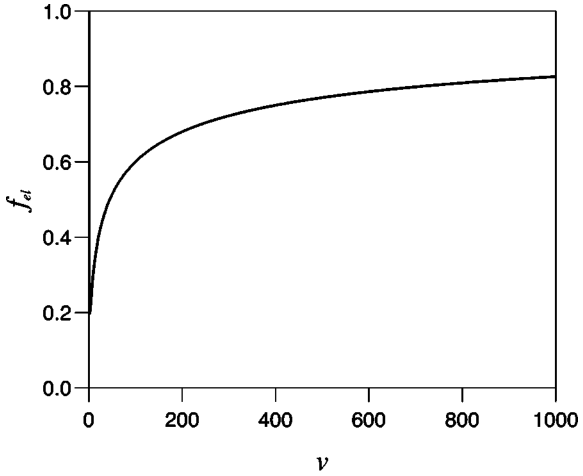

FIG. 1. The electrostatic part $f_{\rm el}$ of the free energy per macroion in units of $Z^2e^2/8\pi\epsilon a$, for $a=0.05$ μm and $|Z|=1076$.

In order to calculate the electrostatic part of the free energy per macroion, $f_{\rm el}=f_{\rm pair}+f_{\rm self}$, we use the results in Eqs. (45), (48), (63), (64), and (67). The parameter κa varies, through its dependence on n_{i0}, as a function of the volume

$$\kappa a=\left(\frac{3\beta|Z|e^2}{4\pi\epsilon a}\,\frac{1}{v-1}\right)^{1/2}. \tag{68}$$

Here, v is a dimensionless volume per macroion, in units of the volume of one macroion, $(4/3)\pi a^3$; it is equal to $1/\eta$, where η is the colloid volume fraction. The presence here of $(v-1)$ instead of v accounts for the exclusion of the microions from the interiors of the macroions. The relation between v and the dimensionless nearest neighbor macroion separation S (in units of a) depends on the structure, as does Σ^Y. We shall use a face centered cubic structure as an approximate model of both solidlike and fluidlike phases; for this structure we have

$$S=\left(\frac{4\sqrt{2}\pi}{3}v\right)^{1/3}. \tag{69}$$

Figure 1 shows $f_{\rm el}$ as a function of v, for a macroion radius of $a=0.05$ μm and a charge of $|Z|=1076$. This part of the free energy increases monotonically with increasing v; a hard core repulsion has also been added, as the macroions cannot interpenetrate.

The ideal gas free energy $f_{\rm id}$ of the microions associated with one macroion is

$$f_{\rm id}=\frac{|Z|}{\beta}\left\{\ln\left[\frac{3|Z|}{4\pi}\left(\frac{\Lambda}{a}\right)^3\right]-\ln(v-1)-1\right\}; \tag{70}$$

$\Lambda=(\beta h^2/2\pi m)^{1/2}$ is the thermal wavelength of the microions, where h is Planck's constant and m the mass of one microion. To simplify the calculations and to avoid having to choose a value for m, we shall consider only the v-dependent part of the ideal gas free energy, $\Delta f_{\rm id}=-(|Z|/\beta)\ln(v-1)$.

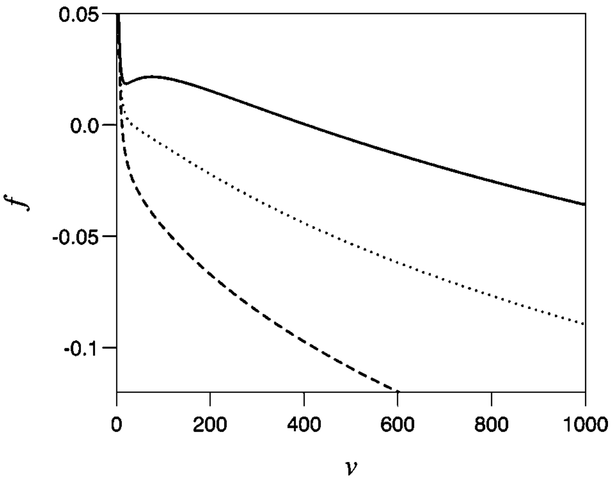

FIG. 2. The free energy *f* per macroion in units of $Z^2e^2/8\pi\epsilon a$, for $a=0.05$ μm. Dashed line: $|Z|=1000$; dotted line: $|Z|=1076$; solid line: $|Z|=1150$.

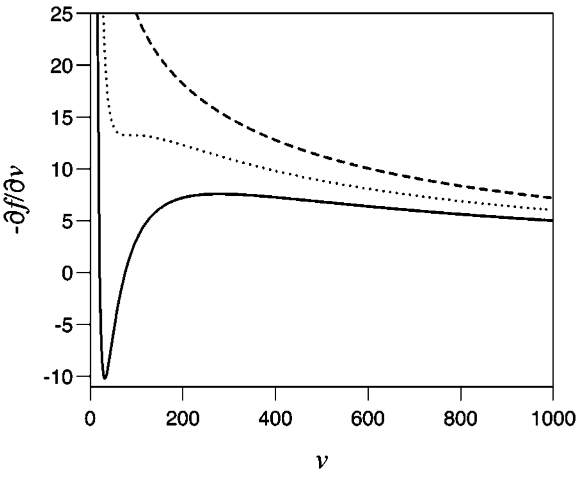

FIG. 3. pV diagram for macroions of radius $a=0.05$ μm, showing a van der Waals loop. $-\partial f/\partial v$ has units of $10^{-5}(3Z^2e^2/32\pi^2\epsilon a^4)$. Dashed line: $|Z|=1000$; dotted line: $|Z|=1076$; solid line: $|Z|=1150$.

In the theory of molecular fluids associated with van der Waals, the free energy contains two terms: an intermolecular interaction which is attractive at long distances and has a repulsive hard core, and the ideal gas term, which becomes more negative logarithmically as the volume *V* increases. At sufficiently low temperatures, so that the ideal gas term does not overwhelm the intermolecular interaction, the graph of the total free energy *F* as a function of *V* may develop an upward bulge, where $\partial^2F/\partial V^2$ becomes negative; since the pressure is given by $p=-\partial F/\partial V$, this leads to a van der Waals loop in the pV diagram. A horizontal line drawn across the loop ensures mechanical stability (the two phases are at the same pressure); drawing this line according to Maxwell's equal area construction ensures that the free energy is globally minimized (the two phases have the same chemical potential). In the present two-component system, the free energy per macroion *f* contains two important terms $f_{\rm el}$ and $\Delta f_{\rm id}$, which take similar forms and similar roles to the intermolecular interaction and the ideal gas term, respectively, in a molecular fluid. For certain values of the macroion radius a and charge number $|Z|$, an upward bulge appears in the graph of *f* as a function of v, resulting in a van der Waals loop, which indicates coexistence between two phases with different densities.

In Fig. 2, $f=f_{\rm el}+\Delta f_{\rm id}$ is plotted for macroions of radius 0.05 μm at three different values of $|Z|$: 1000, 1076, and 1150. Phase coexistence behavior emerges as the charge is increased above a critical charge Z_c of around 1076. Figure 3 shows the pV diagram for a system with the same physical parameters; at $|Z|=1150$, the model predicts coexistence between a rarefied region and a region with $v\approx 20$, which corresponds to a volume fraction η of about 0.05, or a nearest neighbor separation *S* of about 5.

The values of the charge used here are larger than some of the effective charges observed in recent experiments [9] in which phase coexistence was observed in suspensions of colloidal particles of about this size. The discrepancy is probably due to the simplifications in the present model: in addition to linearizing the Poisson-Boltzmann equation, we have assumed zero added salt, and ignored the possibility of phases differing in symmetry as well as in density.

V. CONCLUSIONS

We have solved the linearized Poisson-Boltzmann equation analytically, subject to justifiable approximations, for a suspension of identical spherical macroions at constant surface charge with no added salt. This is accomplished by an extension of the method used by Sogami and Ise; by taking account of the exclusion of microions from the interiors of the macroions, we correct and complete the result obtained in Ref. [10]. In this way, we have found expressions for both the surface potential ϕ_s and the electrostatic part $f_{\rm el}$ of the Helmholtz free energy per macroion. Through the surface potential, each term in $f_{\rm el}$ depends on the positions of all the macroions, so the results are not limited to pairwise interactions.

The electrostatic part of the free energy resembles the intermolecular interaction in the theory of a molecular fluid, and plays a similar role. To form the total free energy per macroion *f*, it must be combined with a term representing the free energy of an ideal gas of microions. We find that, for certain values of the macroion radius a and charge $|Z|$, an upward bulge appears in f expressed as a function of the volume per macroion v. As with a molecular fluid, this leads to a van der Waals loop in the pV diagram, and therefore to coexistence between phases with different densities. This result is qualitatively in line with experimental observations, and also with the calculations of van Roij and co-workers [11–13] and of Warren [14], which predict that phase coexistence (and, in particular, coexistence between a dense phase and a rarefied phase) arises from the linearized Poisson-Boltzmann theory.

We have clarified the interpretation of the Poisson-Boltzmann equation and of results obtained from it, and in particular of the constant n_{i0}. This can take any value in the full equation, but in the linearized version it is restricted to values that are consistent with the validity of the linearization. If we wish to calculate free energies using Debye's charging-up equation, there is a further restriction: the procedure makes sense only if n_{i0} is equal to the mean ion density $\overline{n_i}$.

By its very nature, the Poisson-Boltzmann theory ignores a number of effects, for example ionic correlations [16,23,24]. However, it should prove possible to extend the present treatment to take account of certain other effects that have been ignored here, and which would be important to a complete theoretical description of the phase behavior. More species of microion could be added, to allow the consideration of systems containing added salt. By changing the way that Σ^Y is calculated in Eq. (45), the model could be altered to take account of differences of symmetry (solidlike/fluidlike) in addition to density differences. Finally, the assumption that the macroion surface charge is independent of the configuration of the system, though often made, is not physically reasonable; since the charge is caused by dissociation of surface groups, it would be expected to depend on the local ion concentration in the solvent, which depends on the positions of the macroions.

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