A theory of void formation in charge-stabilised colloidal suspensions at low ionic strength

Patrick B. Warren

Unilever Research Port Sunlight, Bebington, Wirral, CH63 3JW, UK.

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Using a carefully justified development of Debye-Hückel theory for highly asymmetric electrolytes, one finds that a region of expanded phase instability, or miscibility gap, can appear for charge-stabilised colloidal suspensions at high charges and low ionic strengths. It is argued that this is offers a straightforward explanation for the observations of void structures and other anomalies in such suspensions in this region. The nature of the interface between coexisting phases, and general arguments that many-body attractions form a key part of the underlying physical picture, are also examined. The present analysis may also generate new insights into old problems such as coacervation in oppositely charged colloid or protein / polyelectrolyte mixtures, and suggests interesting new possibilities such as the appearance of charge density wave phases in colloidal systems in the vicinity of the critical solution points.

I. INTRODUCTION

For the past fifty years or so, our understanding of the stability of lyophobic colloids has been guided by the seminal works of Derjaguin and Landau,1 and Vervey and Overbeek2 (DLVO). The focus is on pair potentials between colloid particles, which are comprised of van der Waals attractions and electrostatic repulsions. If the electrostatic repulsions are sufficiently large, the suspension is stable. On the other hand if the electrostatic repulsions are reduced in some way, by screening by added electrolyte for example, a suspension is rendered unstable towards flocculation. The DLVO theory gives a clear explanation for this ‘salting out’ effect, first studied in detail by Faraday.3 Although the DLVO theory is aimed squarely at understanding the kinetic stability of dilute colloidal suspensions, the DLVO pair potentials are often used to rationalise many other properties of colloidal suspensions.

The unquestioning use of the DLVO pair potentials has been challenged over the last decade by experiments on dilute suspensions of highly charged colloids at low ionic strength (where the pair potential would predict absolute colloidal stability). Void structures,4 vapour-liquid coexistence5 or biphasic regions,6 and other anomalies7–12 have been cited as evidence that under these conditions an attractive minimum develops in the pair potential at large distances, not captured by DLVO theory. Several reviews are available.13 Until recently, the only theoretical explanation of the observed phenomena has been a modification of the DLVO theory advanced by Sogami and Ise (SI)14–15 although their analysis has been challenged by other workers.16
Very recently though, van Roij, Dijkstra and Hansen (RDH)\textsuperscript{17,18} and Graf and L"owen\textsuperscript{19} have pointed out the existence of so-called volume terms in the free energy of a colloidal suspension, which can profoundly influence the stability of such a suspension without affecting the pair potential of mean force between colloid particles. (The possible importance of volume terms was first noted by Grimson and Silbert.\textsuperscript{20}) The key idea is that pair potentials are not the sole arbiters of phase stability, in the presence of these volume terms. Using these ideas, RDH found that there could exist expanded regions of phase instability in the phase diagram, at low volume fractions and ionic strengths, and argued that this may provide an explanation of the anomalous phenomena.

Actually, as early as 1938, Langmuir had sounded a note of caution about the pair potential approach. He advanced three criticisms of “the use of energy diagrams [pair potentials] to analyse the stability of colloids.”\textsuperscript{21} These insights deserve to be quoted verbatim from his paper:

“(A) No direct account is taken of the thermal agitation which by itself would tend to cause the colloid particles and the ions to be dispersed throughout the liquid giving an osmotic pressure $p = \sum nkT$.

“(B) The attraction between the charged micelles and the ion atmosphere of opposite sign which extends throughout the intervening liquid is ignored or neglected although it exceeds the repulsive force between micelles.

“(C) The electric charges on the micelles are assumed to be constant, whereas they must be, in general, dependent on the concentration of the micelles.”\textsuperscript{21}

Langmuir argues that the electrostatic free energy, or more crucially the electrostatic contribution to the osmotic compressibility, should be negative, corresponding to an effective attraction. This is because in an electrically neutral suspension, correlations between unlike charges lower the free energy relative to a state where all charges are distributed at random. He supports this argument with the physical examples of a salt crystal, and an electrolyte solution. Further, he argues that to explain the stability of charged colloidal suspensions (given that the van der Waals forces are also attractive) one either requires “some new kind of repulsive force”\textsuperscript{21} or that the charge on the surfaces of the colloid particles decreases sufficiently rapidly with increasing concentration so as to make the suspension stable again. The latter seems to be Langmuir’s preferred explanation, hence point (C) above. He spends some time trying to set up a simple theory along these lines using the ideas of Debye and H"uckel\textsuperscript{22} (DH) for simple electrolytes, including a macroion contribution to the screening length.

Vervey and Overbeek raise several criticisms of Langmuir’s approach, pointing out that the DH linearisation approximation fails severely, and also noting that “[the double layer] thickness is determined by the electrolyte concentration in the sol medium, far from any particle, and is, therefore, independent of the sol concentration (in dilute sols).”\textsuperscript{2} In other words, the macroions are too far apart to contribute to the screening length. They conclude that “Langmuir’s theory of the attraction force between particles is untenable.”\textsuperscript{2} These criticisms are correct (and below we shall have to address them in developing a new version of the theory) but they also appear to have had the adverse effect of driving Langmuir’s general arguments into obscurity.\textsuperscript{2} In fact, as I shall argue below, Langmuir’s general points are well made.

The purpose of this paper therefore is to present a relatively simple analysis of the free
energy of a charge stabilised colloidal suspension, treated as a highly asymmetric colloidal electrolyte, but avoiding the problems associated Langmuir’s original application of Debye-Hückel theory. In so doing we will find that the stability of charge stabilised colloidal suspensions can be explained solely by the first two of Langmuir’s points. The principal factors are the translational entropy of the small ions and finite macroion size effects. A more detailed examination though shows that these stabilising mechanisms can fail, at low salt, low volume fractions, and high macroion charge. This is the origin of the phase instability discovered recently by RDH, which in the present model appears as a closed-loop miscibility gap—a region in the phase diagram in which phase separation occurs into colloid rich and colloid depleted phases.

The analysis is partly inspired by the recent application of DH theory to the critical behaviour of the so-called ‘restricted primitive model’ (RPM) of symmetric electrolytes by Fisher and co-workers, and a much earlier analysis of the stability of parallel charged rods by Michaeli et al. The miscibility gap in the present case is the analogue of the vapour-liquid phase transition found at low densities and low temperatures in the RPM. There are many parallels between the present approach to the colloid problem and the above cited approaches to the RPM: for instance it is known that DH theory captures the phase transition in the RPM provided the essential role of finite ion size effects is acknowledged and that the prediction of the critical density can be inaccurate due to non-linear effects, largely captured in the case of the RPM by the Bjerrum pairing model. These features will recur below.

The programme will be as follows. First I specify a ‘primitive’ model of a colloidal suspension as a highly asymmetric electrolyte, by analogy to the RPM. Next I analyse the domains of applicability of various approximations, before obtaining a tractable analytic expression for the free energy. As well as explaining the stability of colloidal suspensions, this free energy also predicts the closed-loop miscibility gaps at low ionic strength and high charge, which are analysed in some detail. The nature of interface between coexisting phases is also examined, as are arguments for the existence of many-body attractions.

As well as presenting this theory in some detail, I will also try to relate the ideas to the existing body of work which is quite extensive. In particular, in appendices, I present comparisons with the Sogami-Ise theory, the recent work by van Roij, Dijkstra and Hansen, and that by Levin, Barbosa and Tamashiro.

II. A PRIMITIVE MODEL FOR COLLOIDAL SUSPENSIONS

Suppose that the colloid particles or macroions have diameter $\sigma = 2a$, positive charge $Z \gg 1$ and number density $n_m$. The macroion volume fraction is $\phi = 4\pi a^3 n_m/3$. There are small coions and counterions at number densities $n_+$ and $n_-$ respectively. I suppose there is only one species of counterion and all small ions are univalent, and of a size sufficiently small to be negligible in the analysis which follows. The solvent is taken to be a dielectric continuum of permittivity $\epsilon$. The Coulomb interaction between a pair of univalent charges in units of $kT$ is $l_B/r$ where $l_B = e^2/4\pi\epsilon kT$ is the Bjerrum length (0.72 nm in water at room temperature)—this is one of the natural length scales for the problem. The effects of temperature can be subsumed into the weak temperature dependence of $l_B$. The densities
are slaved by the electroneutrality condition $Zn_m + n_+ = n_-$, which actually plays a rather important role as discussed further below. It will be convenient to write $n_+ = n_s$ to bring out the fact that it represents the added salt or electrolyte concentration.

Much work has been done applying integral equation methods to this model. The mean spherical approximation (MSA) can be solved analytically, and it has been noticed that this predicts a region of phase instability for the salt-free system. Similarly, solutions for the hypernetted chain (HNC) approximation have been computed, and Belloni and others also found indications of a phase instability. Various improved approximations have also been studied. Other workers have considered the problem using the random phase approximation (RPA) an analogue of the Fisher-Levin approach to the RPM, various local density approximations, and most recently field-theoretical methods. Because of the difficulty in extracting solutions though, a full phase diagram does not appear to have been constructed. In addition, the physics underlying the various approximations is often obscure, and it may not be easy to distinguish numerical artifacts from real effects.

Moreover, in the integral equation approaches to the primitive model, it may not be sensible to treat the macroion-macroion interactions on the same footing as the macroion-small ion or small ion-small ion interactions because of the gross asymmetry. This is why it can be desirable to integrate out the small ion degrees of freedom and treat what remains as an effective one-component system with a different approximation scheme. The effective one component model has traps for the unwary though: we shall see below that three of the most important contributions to the overall free energy are volume terms, and as such easily omitted. (These are the background electrolyte free energy, the interaction between the small ions and the macroions, and most subtle of all, a background subtraction counterterm that cancels most of the mean field macroion-macroion interaction.)

Very recently, direct numerical simulation of one particular realisation of this model has been undertaken by Lobaskin and Linse despite the difficulty in accessing relevant system sizes and time scales. This work confirms Langmuir’s insight that the pressure in these systems is reduced by the electrostatic interactions.

To describe the physics of the model, it will be convenient to draw analogies with the physics of classical plasmas and liquid metals. Other authors, particularly Grimson and co-workers, have recognised the benefits of these analogies.

A. Domains of behaviour of the model

My first aim is to establish the domain of applicability of the various linearisation and mean-field approximations underpinning Debye-Hückel theory. To this end I introduce the following two screening lengths: $\kappa^{-1}$ which is the Debye screening length from the small ions, and $\kappa_T^{-1}$ which is the screening length assuming the macroions also contribute. It seems something of a heresy to introduce $\kappa_T$ but the analysis below will indicate precisely the limits of validity of this concept. The two screening lengths are given by $\kappa^2 = 4\pi l_B(n_+ + n_-) = 4\pi l_B(Zn_m + 2n_s)$, and $\kappa_T^2 = 4\pi l_B(Z^2n_m + n_+ + n_-) \approx 4\pi l_B(Z^2n_m + 2n_s)$. It is also convenient to introduce the Wigner-Seitz cell radius $r_0$ as a measure of the typical distance between macroions, defined by $4\pi r_0^3n_m/3 = 1$. Noting that $\kappa_T^{-1} < \kappa^{-1}$ finds three distinct regions
of behavior depending on the relative magnitudes of $\kappa^{-1}$, $\kappa_T^{-1}$ and $r_0$: (I) $\kappa_T r_0 < 1$, (II) $\kappa r_0 < 1 < \kappa_T r_0$ and (III) $1 < \kappa r_0$.

If there is no added salt, then $\kappa^{-1} \sim Z^{-1} n^{-1/2}_m$, $\kappa^{-1} \sim Z^{-1/2} n^{-1/2}_m$, and $r_0 \sim n^{-1/3}_m$. As the macroion concentration increases therefore, the two screening lengths decrease more rapidly than the mean distance between macroions. Thus region I is obtained at the lowest macroion concentration, followed by region II and then region III. The crossovers occur at $l_B^3 n_m \sim Z^{-6}$ and $l_B^3 n_m \sim Z^{-3}$ respectively (restoring factors of $l_B$).

If salt is added, it acts to reduce both screening lengths. For instance one has a crossover from $\kappa \sim Z^{1/2} n^{-1/2}_m$ for $n_s \ll Z n_m$ to $\kappa \sim n^{-1/2}_s$ for $n_s \gg Z n_m$, and there is a similar crossover for $\kappa_T$. This competes with the crossovers discussed in the preceding paragraph but when the dust settles a fairly simple picture emerges, shown in Fig. 1. If $Z \gg 1$ the crossovers are well separated. Note that the analysis in the strict absence of salt fails to capture the re-entrant behaviour of region III.

![FIG. 1. Generic classes of behaviour of a charge stabilised colloidal suspension, treated as a highly asymmetric electrolyte: (I) weakly coupled OCP, (II) strongly coupled OCP, (III) screened Coulomb interaction divided into (III-a) added electrolyte dominates screening and (III-b) colloid counterions dominate screening.](image)

What is the physics behind this classification? In region I there are sufficient macroions in a screening volume for a DH mean-field approximation to be correct, since $\kappa_T r_0 \ll 1$ implies $\kappa^{-3} n_m \gg 1$. Below we shall see that the DH linearisation approximation is also valid. In region I therefore, Langmuir’s picture of DH theory applied to the system as a whole is valid. In regions II and III though, the spacing between macroions is much greater than the associated screening length ($r_0 \gg \kappa_T^{-1}$), and in fact both of the approximations underlying Langmuir’s picture break down. (Thus it is only in region I that $\kappa_T$ has any validity.) Note that this explanation of the ineffectiveness of the macroions in contributing to the screening length in regions II and III is not dependent on any time scale separation between the dynamics of the macroions and the small ions (Born-Oppenheimer or adiabatic approximation).

Indeed, I would argue this dynamic effect should play no role in determining the equilibrium properties of a colloidal suspension, but I shall return to this point below.
In both regions I and II, the macroions are interacting with effectively an unscreened Coulomb law, $Z^2 l_B/r$, since the small ion screening length is still much greater than their mean separation ($\kappa^{-1} \gg r_0$). In these regions it is reasonable to treat the macroions as a one-component plasma (OCP) in a neutralising background of electrolyte solution, where the polarisation of this background by the macroions is a weak perturbation. On entering region III though, the screening length from the small ions becomes less than or comparable to the distance between neighbouring macroions, resulting in a strongly screened macroion interaction. The polarisation of the background electrolyte is no longer weak and the macroions become surrounded with a double layer of small ions. Here it makes sense to follow Verwey and Overbeek, and treat the macroions and their accompanying double layers as composite objects. In particular, Verwey and Overbeek show that the original Coulomb interaction between macroions is replaced by the well known DLVO screened Coulomb interaction $Z^2 l_B e^{-\kappa r}/r$, possibly with $Z$ replaced by $Z_{\text{eff}} = Z e^{\kappa a}/(1 + \kappa a)^2$.

Let us return to the linearisation approximation. In regions I and II, I have argued above that one can consider the macroions as an OCP. Since the macroion charge is $Z$, the corresponding plasma coupling constant is $\Gamma = Z^2 l_B/r_0 \sim Z^2 l_B n_m^{1/3}$. Thus the crossover from weak to strong coupling occurs at $\Gamma \sim 1$ or $l_B n_m \sim Z^{-6}$, which is precisely where the crossover between regions I and II is found. Thus region I corresponds to an OCP in the weak coupling regime where the DH linearisation approximation is valid, whereas region II corresponds to the strong coupling regime where correlation effects are important. In fact in region II one would expect a freezing transition (colloidal crystals) at $\Gamma \sim 180$. The crossover from II to III occurs at $\Gamma \sim Z$ so this transition should be accessible. The width of the transition is determined by the free energy of the background in a manner discussed recently by Stishov.

The situation is summarised in Fig. 1. In regions I and II, the macroions are well approximated by an OCP in a neutralising and weakly polarisable background. Region I (II) corresponds to the weak (strong) coupling regime. In region III, the polarisation of the background becomes severe, and the Coulomb law is screened on distances less than the mean spacing between macroions.

Let us put some typical numbers into the problem, for example $Z = 1000$ and $\sigma = 200 \text{ nm}$. The upper apex of region II corresponds to $\phi \sim 10^{-2}$ and $[\text{salt}] \sim 10^{-6} \text{ M}$, and the upper apex of region I corresponds to $\phi \sim 10^{-11}$ and $[\text{salt}] \sim 10^{-12} \text{ M}$. These results are typical. We see that region I occurs at physically inaccessible concentrations, and in this sense Verwey and Overbeek’s criticism of Langmuir is made very precise. Region II is accessible at very low salt concentrations, and is where the anomalous behavior is observed. Most colloidal suspensions sit in region III though, where the DLVO picture is expected to be valid.

In the next section therefore I will develop a closed form expression for the free energy appropriate to regions II and III. Debye-Hückel approximations will be used to handle the small ion-small ion and small ion-macroion interactions, but, as the above analysis shows, the macroions may be in a strong coupling regime. For instance the macroion pair correlation function may develop strong oscillations, which can never be reproduced in a simple DH theory. To handle the macroion-macroion interactions therefore, I will turn to a variational method first introduced by Firey and Ashcroft and applied to colloidal suspensions by Shih and Stroud.
FIG. 2. Schematic dependence of effective charge on a macroion as the bare charge on a macroion is increased. Above a certain point, counterion condensation effectively takes place. This point is $Z_{\text{max}} \approx \alpha \sigma/l_B$ where $\alpha$ is a prefactor of order unity. For the purposes of the present work, $\alpha \approx 4$ is assumed, to correspond with previous work.\cite{27,51,52}. When fluctuation and correlation effects are taken into account, the situation may correspond more closely to the dashed line (see Fig. 7 in Ref. 52).

Before moving on to this, I should discuss the approximation involved in treating the small ion-macroion interaction (the double layer) using DH theory. In this case, the DH approximation amounts to linearising $e^{-Zl_B/r}$ in the space around the macroion. This should be valid provided $Zl_B/r < 1$ for $r > a = \sigma/2$, or $Zl_B/\sigma < \alpha$ where $\alpha$ is a numerical constant of order unity. If $Zl_B/\sigma > \alpha$, the effective charge on the macroion (as gauged by comparing with the DH result at large distances for example) saturates around $Z_{\text{max}} \approx \alpha \sigma/l_B$ by a kind of counterion condensation effect. This effect gives an indication of the limit of validity of DH theory applied to the problem. Using Poisson-Boltzmann (PB) theory, Alexander et al suggest that the maximum charge is of order $15a/l_B$ suggesting that $\alpha \approx 7$ (Eq. (1.7) in Ref. 51). Simulations by Groot though suggest that PB theory overestimates the effective charge, and correlation effects may actually reduce the effective charge for $Z > Z_{\text{max}}$.\cite{52} Results resembling PB theory are also obtained in a variational approach by Levin et al.\cite{27} The general phenomenon is illustrated in Fig. 2 where I have compromised on $\alpha \approx 4$ as representative of the literature as a whole. Note that the more conservative criterion, $\alpha \approx 1$, ignores the fact that most of the double layer lies at a distance of order $\kappa^{-1}$ from the macroion surface (see below); a point discussed in early work by Hartley.\cite{53} Experimentally, the effect is broadly confirmed in a number of studies,\cite{54} and very recently for one $Z$ and $\sigma$ it has been checked in direct numerical simulations.\cite{42}

B. Analytic expression for the free energy

To get a tractable expression for the free energy of the system, I follow the development in Landau and Lifshitz\cite{55} and start with an exact expression for the electrostatic energy in terms of the pair correlation functions $g_{ij}(r)$
\[
\frac{E}{VkT} = \frac{1}{2} \sum_{i,j} n_i n_j \int d^3r \frac{z_i z_j l_B}{r} g_{ij}(r)
\]

where \(z_i = Z, 1, -1\) as \(i, j\) range over \(m, +, -\), and \(V\) is the volume of the system. We can replace \(g_{ij}\) by \(h_{ij} = g_{ij} - 1\) in the this expression by virtue of the electroneutrality condition, and split the energy into \(E = E_{ss} + E_{ms} + E_{mm}\) where

\[
\frac{E_{ss}}{VkT} = \frac{1}{2} \int d^3r \frac{l_B}{r} [n_i^2 h_{++}(r) + n_i^2 h_{--}(r) - 2 n_i n_j h_{+-}(r)],
\]

\[
\frac{E_{ms}}{VkT} = n_m \int d^3r \frac{Z l_B}{r} [n_i h_{m+}(r) - n_i h_{m-}(r)],
\]

\[
\frac{E_{mm}}{VkT} = \frac{n_m^2}{2} \int d^3r \frac{Z^2 l_B}{r} h_{mm}(r).
\]

To calculate these requires expressions for the \(g_{ij}\). As discussed above, with care we can use DH theory to derive \(g_{ss}\) and \(g_{ms}\). The DH approximations are inapplicable for \(g_{mm}\), which can exhibit strong structural features in the regimes of interest. The macroion contribution will therefore be handled separately by the aforementioned variational method.

I now proceed by analogy with the DH theory for the RPM, taking into account the analysis of the preceding section. We solve for the electrostatic potential around an ion of charge \(z\) by solving the linearised Poisson-Boltzmann equation \(\nabla^2 \psi + \kappa^2 \psi = 0\) in the space around the ion, where \(\kappa^2 = 4\pi l_B (Z n_m + 2 n_s)\) is from the small ions only (regions II and III), and \(\psi\) is the electrostatic potential. Next the potential of mean force between the ions is given by \(g(r) = e^{-z' \psi/kT} \approx 1 - z' \psi(r)/kT\), applying the linearisation approximation again.

For the small ions this leads to \(g_{++} = g_{--} = 1 - l_B e^{-\kappa r}/r\) and \(g_{+-} = 1 + l_B e^{-\kappa r}/r\) where the size of the ions has been neglected. In the energy integral above this results in

\[
\frac{E_{ss}}{VkT} = -\frac{2\pi l_B^2 (n_+ + n_-)^2}{\kappa} = -\frac{\kappa^3}{8\pi}
\]

which is recognised as the DH internal energy in a simple electrolyte solution.

For small ions around a large ion, the finite size of the macroion should be taken into account. Solving the linearised Poisson-Boltzmann equation with the condition that the electric field at the surface matches the surface charge density \((\partial \psi/\partial r = Z/4\pi a^2\) at \(r = a\)) results in an electrostatic potential

\[
\psi(r) = \frac{Z l_B kT e^{-\kappa(r-a)}}{r} \frac{1}{1 + ka}.
\]

Writing \(g_{m\pm}(r) = 1 \mp \psi(r)/kT\) in the above energy integral gives

\[
\frac{E_{ms}}{VkT} = -\frac{Z^2 l_B^2 n_m (n_+ + n_-)}{1 + ka} \int_a^\infty 4\pi r^2 dr \frac{e^{-\kappa(r-a)}}{r^2} = -\frac{Z^2 l_B \kappa n_m}{1 + ka}
\]

which is recognised as the energy of a finite sized macroion in DH theory. Note that the integral has been truncated at \(r = a\) since the hard core repulsion should not contribute
to the internal energy (it will be accounted for later). Per macroion, this energy takes the form $-Z^2 l_B kT/(a + \kappa^{-1})$ which has a well known interpretation—it is the electrostatic energy between the macroion and a counterion shell of equal and opposite charge situated a distance $\kappa^{-1}$ away from the surface.

![Diagram](image)

**FIG. 3.** (a) Electrostatic potential field around a macroion due to the double layer of small ions, at $\kappa a = 1$. The macroion polarises the surrounding electrolyte and sits in a potential well of its own making. (b) Depth of well as a function of $\kappa a$. In both plots, the units of potential are $Zl_B kT/a$.

This result can also be obtained directly from the potential in Eq. (6) by recognising that $\psi(r) - Zl_B kT/r$ is the potential field due to the small ions around the macroion. This is illustrated in Fig. 3(a), which clearly shows that each macroion sits in a potential well due to the double layer of small ions. The interaction energy between the macroion and its double layer is given by

$$Z\psi(a) - \frac{Z^2 l_B kT}{a} = -\frac{Z^2 l_B kT\kappa}{1 + \kappa a}. \quad (8)$$

Multiplying by the number of macroions recovers Eq. (7). In plasma language, Eq. (8) is the DH estimate of the *polarisation energy* when a macroion is placed in an electrolyte solution. The depth of this well is shown as a function of $\kappa a$ in Fig. 3(b). Note that it increases with increasing ionic strength (increasing $\kappa$). This means that there is a tendency for macroions to drift towards areas of enhanced ionic strength.

The free energy contributions corresponding to $E_{ss}$ and $E_{ms}$ are most readily obtained by the Debye charging procedure which in the present case takes the form

$$\frac{F}{VkT} = \int_0^1 \frac{d\lambda}{\lambda} \left( \frac{E}{VkT} \right)_{\lambda \to \lambda_B}. \quad (9)$$

Thus one obtains

$$\frac{F_{ss}}{VkT} = -\frac{\kappa^3}{12\pi}, \quad \frac{F_{ms}}{VkT} = -\frac{2}{3} Z^2 l_B kN_m f(\kappa a), \quad (10)$$

where the finite macroion size correction factor is $f(x) = (3/x^3)[\log(1 + x) - x + x^2/2]$ (note that $f(x) \to 1$ as $x \to 0$). The behaviour of $F_{ms}$ as a function of $\kappa a$ is similar to $E_{ms}$.  

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Now let us return to the macroion-macroion contribution. The energy integral Eq. (4) is still correct, except that we can no longer use DH theory for \( g_{mm}(r) \) and are forced to turn to another approach. Before doing so, first note that we might reasonably approximate \( Z_l \) with \( Z_l e^{-\kappa r}/r \) in Eq. (4). This is because we would expect \( h_{mm} \approx 0 \) for \( r > \kappa^{-1} \), which is the region where the approximation is most severe. Then we can write

\[
\frac{E_{mm}}{V k T} \approx \frac{n_m^2}{2} \int d^3r \frac{Z^2_l e^{-\kappa r}}{r} g_{mm}(r) - \frac{2\pi Z^2_l n_m^2}{\kappa^2}.
\]  

We recognise the first term in this as the internal energy of a system consisting solely of macroions interacting with the potential of mean force \( Z^2_l k T e^{-\kappa r}/r \), since in the true system \( g_{mm}(r) \) does correspond to this screened Coulomb potential. Such a system is well defined even in the absence of oppositely charged counterions. The second term is a reminder that in the real system, we should correct for the uniform neutralising background by subtracting off the mean field \( g_{mm} = 1 \) term. The present analysis shows quite clearly that such a term exists; another proof is described by RDH.

Rather than proceeding further with the internal energy expression, we will instead use the variational approach of Firey and Ashcroft to obtain the free energy directly. This approach replaces the free energy by the variational minimum of

\[
\frac{F_{mm}}{V k T} = n_m \eta (4 - 3\eta)/(1 - \eta)^2 + \frac{2\pi Z^2_l n_m^2}{\kappa^2} [\lambda^2 G(\lambda) - 1].
\]

The first term is the free energy of the hard sphere reference state, and the second is \( \langle U \rangle_0 \) evaluated in closed form using the Percus-Yevick pair correlation function for hard spheres. Note that the background subtraction counterterm is incorporated in this. Again, one may wish to use \( Z_{eff} = Z e^{\kappa a}/(1 + \kappa a) \) instead of \( Z \) in which case a factor \( e^{2\kappa a}/(1 + \kappa a)^2 \) should be inserted in front of \( \lambda^2 G(\lambda) \). However it is important to note that the background subtraction counterterm should not be similarly corrected.

In Eq. (12) the variational parameter is the effective volume fraction \( \eta \), a parameter \( \lambda = 2\kappa r_0 \)^{1/3} is introduced, and the following functions are defined:

\[
G(\lambda) = \lambda L(\lambda)/[12\eta (L(\lambda) + \overline{S}(\lambda) e^\lambda)],
\]

\[
L(\lambda) = 12\eta [(1 + \eta/2)\lambda + (1 + 2\eta)],
\]

\[
\overline{S}(\lambda) = (1 - \eta)^2 \lambda^3 + 6\eta (1 - \eta) \lambda^2 + 18\eta^2 \lambda - 12\eta (1 + 2\eta).
\]

The variational minimum is found by solving the equation \( \partial F_{mm}/\partial \eta = 0 \) which has to be done numerically.

The final pieces in the free energy are the ideal gas or translational entropy terms:

\[
\frac{F_{id,he}}{V k T} = n_m \log n_m + n_+ \log \frac{n_+}{1 - \phi} + n_- \log \frac{n_-}{1 - \phi}
\]

where the previously omitted small ion-macroion hard core repulsion is captured by inserting correction factors of \( 1/(1 - \phi) \). We should not make a similar correction for the macroion.
hard core interactions since it is already in the hard sphere reference free energy in Eq. (12).
It is convenient to split this into the proper ideal term and a hard-core excluded volume term, and write (replacing \( n_+ \) and \( n_- \) by \( n_s \) and \( (Zn_m + n_s) \) respectively)

\[
\frac{F_{id}}{VkT} = n_m \log n_m + n_s \log n_s + (Zn_m + n_s) \log(Zn_m + n_s), \tag{17}
\]

\[
\frac{F_{hc}}{VkT} = (Zn_m + 2n_s) \log \frac{1}{1 - \phi}. \tag{18}
\]

We now have a closed form analytic free energy which consists of five terms:

\[
F = F_{id} + F_{hc} + F_{ss} + F_{ms} + F_{mm}, \tag{19}
\]

given in Eqs. (17), (18), (10), and (12) respectively (plus associated definitions). Note that this final result is very close in spirit to the approach of Fisher and Levin to the free energy of the RPM of simple electrolytes. To summarise, the five terms in Eq. (19) are respectively: an ideal solution term, a small ion-macroion hard core exclusion term, the small ion electrostatic free energy identical to the DH free energy of the background electrolyte, the small ion-macroion interaction free energy or background electrolyte polarisation energy, and the macroion-macroion interaction free energy which incorporates the background subtraction counterterm.

Before discussing the consequential phase behaviour, let me recap the nature of the approximations underlying this free energy. Firstly, it is useful to contrast it with Langmuir’s attempt to use DH theory for the same problem. In the present theory, DH type approximations involve the small ions only, and are applied to the small ion excess free energy and the small ion-macroion interaction energy or polarisation energy. The macroion-macroion interactions are treated separately by an established variational procedure, and tied in to the other contributions by the exact split of the internal energy in Eqs. (2)–(4).

The analysis is consistent with the preceding section which shows that in regions II and III only the small ions contribute to the screening length, and that macroion-macroion interactions are either strongly screened (region III) or in a strong coupling limit (region II). Additionally, the use of DH theory for the small ion-macroion contribution is valid provided \( Zl_B/\sigma \) is not too large.

It might appear that the variational approach to the macroion interactions should break down in region II (\( \kappa^{-1} \gg r_0 \)) where one might expect \( \eta > 1 \), supposing that the variational macroion radius is of order \( \kappa^{-1} \). In fact the variational estimate is good for this region too as can be seen from the following argument. In region II the macroions are essentially an OCP, corresponding to the limit \( \kappa \to 0 \) in Eq. (12), which reduces to

\[
\frac{F_{mm}}{N_m kT} = \frac{\eta (4 - 3\eta)}{(1 - \eta)^2} - 3\Gamma \frac{\eta^{2/3} \eta/5 + \eta^2/10}{1 + 2\eta}, \tag{20}
\]

where \( \Gamma = Z^2l_B/r_0 \) is the plasma coupling constant introduced earlier and \( N_m = Vn_m \) is the number of macroions. The variational minimum gives the following implicit equation for \( \eta \)

\[
\Gamma = 2\eta^{1/3} \frac{(1 + 2\eta)^2 (2 - \eta)}{(1 - \eta)^5 (2 + \eta)}. \tag{21}
\]
For instance, this places the freezing transition (estimated by setting $\eta = 0.5$) at $\Gamma \approx 122$ which is within 40% of the known value $\Gamma \approx 180$. Stroud and Ashcroft have examined the accuracy of this approximation in some detail and found that it is good provided $\Gamma > 10$ or so.

To summarise using the classification in the preceding section, the free energy in Eq. (19) is valid for colloidal systems in regions II and III provided the ratio $Zl_B/\sigma$ is not too large.

### III. Phase Behaviour

The most remarkable thing about the free energy in Eq. (19) is that it can have a region of negative osmotic compressibility, indicating that a phase instability is present. In a phase diagram, this appears as a closed-loop miscibility gap. Before discussing this in detail, it is worthwhile noting that all three electrostatic pieces act to destabilise the system, just as Langmuir surmised. This includes the macroion-macroion interaction term which is usually supposed responsible for the system’s overall thermodynamic stability. But it too is destabilising because of the background subtraction counterterm. A closer examination (see below) shows that it is the ideal translational entropy of the counterions, and to a lesser extent the hard core exclusion term, that are responsible for the system’s stability. A miscibility gap opens up where these stabilising mechanisms fail.

#### A. Phase instability or miscibility gap

Within the miscibility gap, coexistence compositions are calculated by standard methods corresponding to conditions of equality of chemical potential and osmotic pressure between coexisting phases. In deriving expressions for the chemical potentials and osmotic pressure, care has to be taken to account fully for the state point dependence of all parameters such as $\kappa$ in Eqs. (10), etc, and $\lambda$ and $\eta$ in Eq. (12), and also the fact that the free energy should be evaluated at a variational minimum with respect to $\eta$. Phase diagrams are shown in the $(n_m,n_s)$ plane. Typical results are shown in Figs. 4 and 5.

The interpretation of these diagrams is standard. Outside the miscibility gap, a colloidal suspension is predicted to remain stable and homogeneous. Within the miscibility gap, an initially homogeneous suspension is predicted to phase separate into colloid rich and colloid depleted regions along the tie lines indicated in these diagrams. The relative amounts of the two phases will be determined by the lever rule. Typically, though, the colloid volume fraction in the depleted phase is vanishingly small and this phase is essentially pure brine. Also, if the mean colloid volume fraction is nearer the right hand binodal, the second phase will appear as droplets of pure brine within the colloid-rich phase. This, it is argued, is a natural explanation for the void structures described in the introduction.

Within the miscibility gap one finds a spinodal region, demarcated by the short-dashed lines in Figs. 4 and 5. In this region, the osmotic compressibility is negative, indicating spinodal decomposition will occur. Also shown in Figs. 4 and 5 are long-dashed lines where the variational volume fraction $\eta = 0.5$. This is an indication of the location of the freezing transition to an ordered colloidal crystal phase. The width of this transition is determined essentially by the compressibility of the supporting electrolyte, and is expected
to be narrow in general, but widen considerably as the spinodal line in the miscibility gap is approached. This is indeed found by van Roij, Dijkstra and Hansen[18] whose calculations are superior in this respect to the present theory, since they explicitly include the possibility of an ordered phase. The proximity of the freezing transition is not entirely a coincidence, since the miscibility gap occurs close to the point where the system starts to behave as a strongly coupled OCP (region II) where the plasma coupling constant $\Gamma \sim Z$. Experimentally, it has also been noted that anomalous behaviour in the static structure factor starts close to the point where the ordered phase appears at low ionic strengths[9].

![Phase diagrams](image)

**FIG. 4.** Phase diagrams showing closed loop miscibility gaps for several colloid particle sizes, at charges roughly corresponding to $Z_{\text{max}} \approx 4\sigma/l_B$. The solid lines are binodals and tie lines. The short-dashed lines are spinodal lines. The long-dashed lines show where the variational volume fraction is 50%, and give an indication of the location of the freezing transition. See Table I for details of the upper critical solution point.

In general terms, the miscibility gap appears at low ionic strengths, low volume fractions and high macroion charges. Fig. 4 shows what happens to the miscibility gap for various macroion diameters, at charges roughly corresponding to $4\sigma/l_B$ which is the estimate of the maximum charge at which the linearised DH approximation for the macroion polarisation energy starts to break down severely. As the macroion size increases, the miscibility gap moves to lower salt concentrations, but remains approximately in the same place with regard to macroion volume fraction.

The miscibility gap is bounded above and below by critical solution points. Note that in the present theory, a strictly salt-free system has no phase instability. As the charge on the
macroions is reduced, the miscibility gap reduces in size and finally vanishes once the charge falls below some minimum value $Z_{\text{min}}$, illustrated in Fig. 5 for one particular macroion size. At the point where the miscibility gap vanishes, the upper and lower critical solution points coincide. This point is identified as a double critical point or hypercritical point.

![Graphs showing miscibility gap](image)

FIG. 5. As the charge on the colloid particles is reduced, the miscibility gap shrinks and finally disappears for $Z < Z_{\text{min}} \approx 565$ in this case. At $Z = Z_{\text{min}}$ the upper and lower critical solution points meet at a double critical point or hypercritical point.

The upper critical solution point can be taken as approximately representative of the position of the miscibility gap as a whole, and Fig. 5(a) shows what happens to it as $Z$ varies between $Z_{\text{max}} \approx 4\sigma/l_B$ and $Z_{\text{min}}$, for various particle diameters. As $Z$ is reduced, in general the upper critical solution point moves to lower volume fractions and ionic strengths, before vanishing at the double critical point.

Fig. 5(b) shows the region in parameter space where the phenomenon of a closed-loop miscibility gap is found. The solid line with circles in this plot indicates where the miscibility gap just disappears, where a double critical point arises in the phase diagram. The behaviour is plotted in the space $(\sigma, Zl_B/\sigma)$ which serves to bring out an important point. At low macroion size, the value of $Z_{\text{min}}$ required to observe the miscibility gap approaches $Z_{\text{max}}$, where non-linear effects start to become important. This may explain why anomalous effects are only observed for larger colloid particles where a sufficient gap opens up between $Z_{\text{min}}$ and $Z_{\text{max}}$ for the phenomena to be experimentally accessible.

Some representative numerical data on the upper critical solution points are collected in Table I and the double critical points in Table II. These tables show the small ion
The Debye screening length $\kappa^{-1}$ in relation to other lengths in the problem, at the critical point in question. The first point to note is that the upper critical solution point always lies approximately at $\kappa a \sim 1$. This fact has been noticed before and interpreted as evidence in support of the SI theory (see appendix)—for example one might compare the measured $\kappa X_{\text{min}}$ of Ref. 9 with $\kappa r_0$ in Table I, although the two systems are not the same. Here $\kappa a \sim 1$ emerges naturally and is seen to reflect the particular importance of the finite macroion size correction factor, $f(x)$ in the second of Eqs. (10), around $x = \kappa a \sim 1$ (see also Fig. 3). The second point to note is that, to $O(Z)$, the miscibility gap occurs at $\kappa r_0 \sim Zn_m/n_s \sim 1$. This places the miscibility gap at the apex of region II where it meets with regions III-a and III-b in the state diagram in Fig. 1.

| $\sigma$/nm | $Z$ | $Zl_B/\sigma$ | $\phi$ | [salt]/M | $\kappa^{-1}$/nm | $\kappa a$ | $\kappa r_0$ | $2n_s/Zn_m$ |
|-------------|-----|---------------|--------|----------|-----------------|------------|-------------|-------------|
| 50          | 250 | 3.60          | 1.62 x 10^{-2} | 8.74 x 10^{-4} | 9.96           | 2.51       | 9.92        | 17.0        |
| 100         | 500 | 3.60          | 1.36 x 10^{-2} | 2.49 x 10^{-4} | 18.8           | 2.66       | 11.1        | 23.1        |
| 200         | 1000 | 3.60        | 1.09 x 10^{-2} | 6.74 x 10^{-5} | 36.3           | 2.75       | 12.4        | 31.1        |
| 200         | 800  | 2.88         | 9.93 x 10^{-3} | 4.08 x 10^{-5} | 46.6           | 2.15       | 9.99        | 25.9        |
| 200         | 600  | 2.16         | 5.51 x 10^{-3} | 1.51 x 10^{-5} | 76.3           | 1.31       | 7.42        | 23.0        |
| 500         | 2500 | 3.60         | 7.82 x 10^{-3} | 1.15 x 10^{-5} | 88.5           | 2.83       | 14.2        | 46.3        |
| 1000        | 5000 | 3.60         | 5.91 x 10^{-3} | 2.95 x 10^{-6} | 175            | 2.86       | 15.8        | 63.0        |

**TABLE I.** Location of upper critical solution point for various macroion charges and diameters. Also shown is the Debye screening length and its relation to the macroion radius $a$ and mean spacing between macroions $r_0$. The last column gives the ratio of contributions to $\kappa$ from the salt ions ($2n_s$) and the macroion counterions ($Zn_m$), at the state point in question.

| $\sigma$/nm | $Z_{\text{min}}$ | $Z_{\text{min}}l_B/\sigma$ | $\phi$ | [salt]/M | $\kappa^{-1}$/nm | $\kappa a$ | $\kappa r_0$ | $2n_s/Zn_m$ |
|-------------|-----------------|-----------------------------|--------|----------|-----------------|------------|-------------|-------------|
| 50          | 175             | 2.52                        | 6.08 x 10^{-3} | 1.59 x 10^{-4} | 23.0           | 1.09       | 5.95        | 11.8        |
| 100         | 314             | 2.26                        | 4.21 x 10^{-3} | 3.48 x 10^{-5} | 49.9           | 1.00       | 6.21        | 16.6        |
| 200         | 565             | 2.03                        | 2.99 x 10^{-3} | 7.78 x 10^{-6} | 106           | 0.94       | 6.53        | 23.3        |
| 500         | 1233            | 1.78                        | 2.01 x 10^{-3} | 1.12 x 10^{-6} | 282            | 0.89       | 7.02        | 35.6        |
| 1000        | 2225            | 1.60                        | 1.28 x 10^{-3} | 2.25 x 10^{-7} | 633            | 0.79       | 7.27        | 49.6        |

**TABLE II.** Location of double critical solution points for various macroion diameters, which occur when the upper and lower critical solution points coincide and the miscibility gap just appears, at $Z = Z_{\text{min}}$. 

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FIG. 6. (a) Fate of the upper critical solution point as $Z$ varies between $Z_{\text{max}} \approx 4\sigma/l_B$, and $Z_{\text{min}}$ where it meets the lower critical solution point (open circles). Data for various particle diameters are shown. (b) State diagram showing where a miscibility gap is found. The open circles indicate the points where $Z = Z_{\text{min}}$ for various $\sigma$, where the miscibility gap just disappears. Essentially this is a line indicating where double critical points occur in the phase diagram (see Table II). The dashed line shows where $Z = 4\sigma/l_B$, which is one possible criterion for acceptability of the Debye-Hückel approximation for the polarisation energy.

These results are in broad agreement with recent detailed experiments of Yoshida, Yamakana and co-workers. For instance Fig. 2 in Ref. 8 indicates that for $\sigma \approx 120\, \text{nm}$, $Z \approx 200$ particles (sample KE-P10W), a biphasic region appears around $\phi \approx 1$–5% and $n_s \approx 10$–20 $\mu\text{M}$. For these values of $\sigma$ and $Z$, the present theory does not predict a miscibility gap, although it does so at somewhat higher $Z$ (Table II). However, one would expect a region of greatly lowered osmotic compressibility to persist in that area of the phase diagram for smaller values of $Z$. If the freezing transition comes close to such a region, one would expect it to broaden considerably. This is seen for instance in the calculations of RDH who include the possibility of an ordered phase. The measured biphasic region lies at $Z n_m \approx (0.2$–$1) \times 10^{-5}\, \text{nm}^{-3}$ and $n_s \approx (0.5$–$1) \times 10^{-5}\, \text{nm}^{-3}$, both of which are close to the apex of region II in Fig. 4, located at $Z^{-2}l_B^3 \approx 7 \times 10^{-5}\, \text{nm}^{-3}$. To $O(Z)$, this is the same place that the miscibility gap appears in the present theory. Whilst far from conclusive, one can argue that this is evidence the theories are on the right track. Similarly one can calculate $\kappa^{-1} \approx 80\, \text{nm}$ and thus $\kappa a \approx 0.7$, in agreement with the above general observations. Some of the detailed trends reported by Yoshida et al are not seen in the present theory, perhaps because detailed account is not made of the ordered phase. Similarly, there are remarkable kinetic phenomena which are not covered in this equilibrium theory, and which I will touch on briefly again below.

B. Relative importance of free energy contributions

We can determine the relative importance of the various contributions to the free energy in Eq. (19) simply by recalculating the phase instability regions in the presence or absence of one or more of these terms. In this way the following sequence of importance is discovered:

$$F_{\text{id}}, F_{\text{ms}} > F_{\text{mm}} > F_{\text{hc}} \gg F_{\text{ss}}.$$  (22)
The driving force for phase separation is mainly due to the polarisation term, the second of Eq. (10), and to a lesser extent the macroion interaction term Eq. (12), whereas it is the ideal translational entropy term Eq. (17) that is the main driving force for stability. When the translational entropy is insufficient to balance the electrostatic free energy, a miscibility gap appears. The relative importance of the macroion-small ion interaction contribution has been confirmed very recently by direct numerical simulation.42

If any of the polarisation term, the macroion interaction term, or the background subtraction counterterm in the latter, is omitted, the phase instability moves to much higher $Z$ and lower salt concentration. On the other hand, the presence or absence of the small ion electrostatic free energy, the first of Eqs. (10) has essentially no effect on the location of the phase transition. This is because it has a similar state point dependence to the polarisation term but is diminished in magnitude relative to this by a factor $Z$.

The details of the miscibility gap also rely on the finite size correction factor appearing in the second of Eq. (11). If $f(x)$ is set to unity in this, the phase instability may not be bounded from above in $n_m$. In this respect, the present theory resembles the finite-size corrected DH theory of simple electrolytes.25 Similarly we can check the influence of the finite size corrected macroion charge in the macroion interaction term (a factor $e^{2\kappa a}/(1 + \kappa a)^2$ in Eq. (12)). The presence or absence of this factor is found to have only a weak effect on the location of the phase transition. Other finite size corrections might be applied for instance to the screening length expression itself, to take account of the increased concentration of small ions due to the volume excluded by the macroions. These effects have not been seriously explored since $\phi$ is small at the point where the phase instability appears. On the other hand, since the small ion entropy is so significant, the factors $1/(1 - \phi)$ appearing in Eq. (18) do play a role in suppressing the phase instability at high $\phi$.

The role of the ideal translational entropy of the counterions, in stabilising the suspension at higher salt concentrations, can be seen in an elementary way by noting that at high $n_s$ the small ion entropy term in Eq. (17) becomes

$$(Zn_m + n_s) \log(Zn_m + n_s) \approx \text{consts.} + \frac{Z^2n_s^2}{n_s}. \quad (23)$$

It is seen that this contributes an effective positive term $Z^2/n_s$ to the effective second virial coefficient between the macroions. Since $Z \gg 1$ this represents a strong stabilising influence. Note also that if $n_s \gg Zn_m$, the screening length is dominated by $n_s$ and is not strongly dependent on $n_m$. This means that the macroion polarisation term becomes approximately linearly proportional to $n_m$, and acts simply to shift the macroion chemical potential, rather than destabilise the suspension.

The conclusion is that the appearance of the miscibility gap is driven by the electrostatic free energy but opposed principally by the translational entropy of the counterions. Remarkably, it is precisely these two effects which were identified by Langmuir in his 1938 analysis. A similar conclusion has also been reached for charged plates recently.60 The exact location and width of the miscibility gap depends on a subtle combination of finite size effects though, and in contrast to Langmuir’s conclusion, the general stability of a colloidal suspension does not depend on anything more esoteric than the domination of small ion entropy in the free energy.
FIG. 7. Donnan potential between coexisting phases for \( Z = 1000 \) and \( d = 200 \) nm (see Fig. 3 for actual phase diagram), plotted as a function of the salt concentration in the macroion-poor phase, which is essentially pure brine. The sign is such that the macroion-rich phase is at a higher potential than the macroion-poor phase.

C. Donnan potential difference

The phase behaviour has been calculated using \( n_m \) and \( n_s \) as dependent variables. An alternative is to use \( n_m, n_+ \) and \( n_- \) as variables and replace the electroneutrality condition by a Donnan potential term,

\[
\frac{F_{\text{Donnan}}}{VkT} = \frac{e}{kT} (Zn_m + n_+ - n_-),
\]

added to the free energy density. The Donnan potential or mean electrostatic potential in each phase, \( \overline{\psi} \), is chosen to ensure electroneutrality in any bulk phase. One could view it as a Lagrange multiplier for the electroneutrality condition, although it does have a physical significance. Since this potential will in general be different in coexisting phases, it means that there is in general a Donnan potential difference, \( \Delta \overline{\psi} \), between coexisting phases. This is like a membrane equilibrium, where the interface between the two phases plays the role of the membrane. Clearly, much insight into the nature of the phase transition can be gained by examining the structure of this interfacial region, and a knowledge of \( \Delta \overline{\psi} \) throws some light on this.

It is fairly easy to derive an expression for \( \Delta \overline{\psi} \). First one can show that

\[
\mu_\pm = \pm e\overline{\psi} + kT \log(fn_\pm)
\]

where the activity coefficient \( f \) is the same for both species since the excess free energy only depends on the combination \( (n_+ + n_-) \). From the constancy of \( \mu_+ - \mu_- \), the Donnan potential difference between a pair of coexisting phases is

\[
\Delta \overline{\psi} = \overline{\psi}^{(ii)} - \overline{\psi}^{(i)} = \frac{1}{2} \frac{kT}{e} \left[ \log \left( 1 + \frac{Zn_m}{n_s} \right) \right]^{(ii)} - \left[ \log \left( 1 + \frac{Zn_m}{n_s} \right) \right]^{(i)}
\]

This allows easy determination of \( \Delta \overline{\psi} \) given the compositions of a pair of coexisting phases, and a typical result is shown in Fig. 7. Note that the macroion-rich phase is at a higher
potential than the macroion-poor phase, and given the previous observation that $Zn_m \sim n_s$, the potential difference between the phases is of order $kT/e \approx 25$ mV.

FIG. 8. Postulated structure of the interface between two coexisting phases in a miscibility gap. The macroion-poor phase (left hand side) is essentially pure brine. The macroion-rich phase has a large excess of counterions to match the electrostatic charge of the macroions. These spill across the interface and set up a macroscopic double layer raising the mean potential in the macroion-rich phase and consequently depleting it of coions. The dashed line is the ionic strength, $(n_+ + n_-)/2$. The known coexistence compositions have been smoothly connected across the interface here.

IV. THE NATURE OF THE INTERFAcial REGION

As mentioned above, much insight into the nature of the above phase transition can be gained by studying the interface between coexisting phases. Such a study would require the generalisation of the present theory to inhomogeneous states. This has not yet been attempted, but is clearly possible, perhaps using methods described by Rowlinson and Widom, density functional theory, and the generalised DH theory of Lee and Fisher for the polarisation free energy in a salt gradient. Nevertheless, there is enough information in the present calculations to make an informed guess as to the structure of the interfacial region in this charged system.

Fig. 8 shows a postulated structure of the interface between two co-existing phases in the middle of the miscibility gap for $\sigma = 200$ nm and $Z = 1000$ (see Fig. 5 for actual phase diagram). In drawing this structure, one is guided by the calculated Donnan potential difference between the two phases. This potential difference can only be explained by a macroscopic electric field across the interface. The sign of the potential difference indicates that a kind of macroscopic super-double layer forms because of an excess of counterions spilling out into the macroion-dilute phase. In fact, this is entirely to be expected from consideration of the translational entropy terms discussed above. The co-ions are depleted from the macroion rich phase by the well known Donnan common ion effect (from Eq. (25) we see that the product of the small ion activities $(fn_+)(fn_-)$ is common to the two coexisting phases). Since the co-ions can be taken as representing the salt concentration, this also
corresponds to the salt partitioning seen in the full phase diagrams. Although the salt partitions to some extent out of the macroion rich phase, it is easy to check that the ionic strength, 
\[ \frac{n_+ + n_-}{2} \]
is increased in this phase.

Before leaving this subject, one should mention that it is entirely possible for oscillatory density profiles to develop across the interface, instead of the smoothly interpolated densities suggested by Fig. 8. This might be expected in the neighbourhood of the critical point, corresponding to the possible appearance of charge density wave phases mentioned below.

V. MANY-BODY ATTRACTIONS?

The theory thus presented is self contained, yet it seems to the present author that the story, if it stops here, is not quite complete. The phase instability appears despite the fact that the macroion pair interactions remain repulsive, as discussed at length by RDH17,18. The instability is driven by volume terms which don’t feature in the pair potentials. Simple arguments below though suggest that the volume terms should have an alternative interpretation in terms of an *attractive many-body interaction*. The interpretation of the void phenomena by many-body attractions has been championed by Schmitz,19 who considers the interactions of a macroion with a collection of other macroions at set positions in a Poisson-Boltzmann theory. The arguments below are partly motivated by these calculations.

Of course, it is well known that an attractive component can appear in the pair interactions due to correlation effects not captured in the present mean field theories. In the simplest picture, the attraction arises from correlated fluctuations of the ion clouds around the macroions, and is the classical analogue of the London-van der Waals forces. The effect can be very significant for multivalent electrolytes,38 and in certain circumstances can be sufficiently strong to drive phase separation.70 For colloidal systems in the present regime though, this mechanism seems ruled out.20

Beyond the pair level, a hint of the existence of many-body attractions is provided by experiments which seem to show an attractive interaction between pairs of charged colloid particles in the presence of wall(s).21,22 Theoretically, the situation in these geometries is not clear cut. Non-linearities in Poisson-Boltzmann theory23,24 seemed to provide an explanation of these observations until challenged by subsequent work25 and density functional theory26,27 which argue for the absence of attractions. However other theoretical work,28 and recent simulations, are seen to show that attractions might appear beyond mean field theory.

Let us discuss two arguments for the existence of many-body attractions, even in the mean field theory. The first argument is essentially due to Smalley.29 Start with a homogeneous distribution of macroions such that the mean composition lies within the two phase region identified above. Next move the macroions collectively so that we have a void region coexisting with a homogeneous distribution of macroions at an enhanced density and the appropriate ordered crystal or strongly correlated fluid structure. If the compositions and relative volumes of the two regions are chosen correctly, the final state will correspond to a pair of coexisting state points in the phase diagram. The free energy must decrease in such a process, therefore there must be a many-body thermodynamic force tending to accumulate macroions in the manner suggested. This argument is rather general, and indicates a \( N \)-body attraction appears for \( 2 < N < 10^{11} \) or so (see below for a more refined estimate).
A general argument in the text indicates that, in the interfacial region, there should be a net attraction of an isolated macroion to a correlation hole in the macroion-rich phase.

The second argument concerns the forces acting on macroions in the vicinity of the interfacial region. Note that this region does resemble the experimental situation mentioned above, given an excess of counterions in vicinity of the interfacial region that extends some way into bulk of the macroion-poor phase. Thus an attraction between pairs of macroions adjacent to the macroion-rich phase might be expected. However, in the interfacial region, there ought to be a net attraction between an isolated macroion and the macroion-rich phase. To see this, imagine introducing a tracer macroion into the interfacial region. In equilibrium, the probability distribution, $P(z)$, for the position of the tracer particle across the interface should be proportional to the macroion number density profile, $n_m(z)$, otherwise the particle isn’t doing its job as a tracer. Now consider $P(z)$ as the stationary solution of some Smoluchowski equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial z} \left( \frac{1}{\xi} \left( kT \frac{\partial P}{\partial z} + P \frac{\partial U}{\partial z} \right) \right)$$

in which $\xi$ is the local friction coefficient for the tracer particle, and $-\partial U/\partial z$ is the force acting on the tracer macroion due to the interfacial profile structure. Inserting $P(z) \propto n_m(z)$ and requiring stationarity shows that this force is simply $(kT/n_m) \partial n_m/\partial z$. Since the macroion density increases through the interface, this means that there must be a net attraction between the tracer particle and the macroion-rich phase.

What is the origin of this force? Clearly we can decompose it into a number of effects. The electric field (potential gradient $\partial \psi/\partial z$) acts to repel the tracer macroion from the macroion-rich phase, since the tracer is positively charged. However there is also a gradient in the ionic strength (Fig. 8), leading to a force attracting the tracer towards the macroion-rich phase, due to the polarisation energy discussed earlier (Fig. 3). In fact, in this case we can show that this is not quite sufficient to overcome the electrostatic repulsion, essentially because the miscibility gap does not appear at these parameter values if only the polarisation term is included in the free energy.

The final contribution which tips the balance in favour of an attraction towards the macroion-rich phase derives from the macroion-macroion correlations represented by the free energy Eq. (12) in the bulk. Note that the background subtraction counterterm in this
corresponds to the fact that there is no net interaction between the tracer and macroions deep in the bulk of the macroion-rich phase. The only force acting over such large distances, the Coulomb force, is exactly cancelled by the net charge of the small ions since the bulk is electrically neutral (which is another way to see that \( Z \) rather than \( Z_{\text{eff}} \) should appear in the background counterterm). The macroion-macroion contribution to the force therefore corresponds to a pure correlation effect: the electrostatic repulsion between the tracer and neighbouring macroions causes them to move away leaving an excess of counterions in the vicinity of the tracer. It is the attraction of the tracer to this ‘correlation hole’, the centre of which is displaced towards the macroion-rich phase in the interfacial region, that appears to be the final piece in the jigsaw. This is illustrated in Fig. 9, but clearly the lack of a proper theory for the inhomogeneous state is most keenly felt in formulating this notion more precisely.

In the theory for void formation presented above, or the RDH theory, these many-body effects are apparently not present. In fact a kind of many-body interaction has crept in by sleight-of-hand via the electroneutrality condition. This condition means that it is impossible to vary the macroion number density in the bulk without a concomitant variation in the small ion densities. The consequent effect, via changes to \( \kappa \) for instance, feeds back through otherwise innocuous terms in the free energy to influence the thermodynamic properties of the system in a non-trivial manner. As the discussion on the interfacial region shows though, the electroneutrality condition corresponds to the appearance of a Donnan potential difference between the phases, hence an electrostatic potential gradient and a macroscopic double layer. Therefore the rather innocent-looking electroneutrality condition conceals some rather important physical effects. In fact, Sogami and Ise already identified the crucial importance of this condition—see appendix.

Whilst in an ordinary liquid, many-body interactions are generally insignificant, the same conclusion is not necessarily true in ionic systems. Although pair interactions may be screened, the long range nature of the Coulomb law is never far from the surface, and reappears on whatever length scale is necessary as soon as inhomogeneous charge distributions arise.

The co-operative nature of many-body attractions may shed some light on one of the mysteries of the void phenomenon mentioned in passing above, namely the length of time it appears to take for voids to form. It is easy to estimate times for macroions to diffuse distances of order the interparticle spacing. These times \((r_0^3/D)\) are of the order of 10–100 seconds or less, even for the largest (1 \( \mu \)m) particles, whereas the void formation time is measured in 10–100 hours. This certainly appears to present a difficulty for theories based on attractive minima in pair potentials, and arguments which rely on a time scale separation between the small ion and macroion dynamics, but can be explained rather easily in the present theory. For example, in the spinodal instability region, one might expect that only density fluctuations of sufficiently long wavelengths \( \lambda \) to incorporate sufficiently many macroions will be unstable and grow. The growth rate decreases as \( \lambda^{-2} \), and the difference in the above time scales (a factor of \( 10^3 \) or so) can be explained by supposing that the minimum fluctuation size is of order \((10^3)^{1/2} \sim 30 \) or so particles in linear dimensions. In the above terms, this implies \( N \)-body attractions start to be significant around \( N \sim 30^3 \sim 10^4 \) particles.

At present though, no immediate explanation seems forthcoming for the elaborate time
sequences of phase transformations that have sometimes been observed. Uncharged colloid-polymer mixtures with vapor-liquid and freezing transitions in their phase diagram have recently been demonstrated to have a rich kinetic behaviour. In the present case where the vapour-liquid phase transition is driven at least in part by many-body attractions, even more varied novel kinetic pathways seem possible.

VI. GENERAL DISCUSSION

We have seen how a carefully justified Debye-Hückel (DH) theory can be constructed for the free energy of a charge stabilised colloidal suspension, treated as a highly asymmetric electrolyte or plasma. Linearisation and mean-field approximations are justified and applied to the interactions of small ions with small ions, and of small ions with macroions. These approximations cannot be supported for the macroion-macroion interactions, which are treated separately by a well-established variational method.

The most remarkable prediction that emerges from the analysis is the appearance of a phase instability in the form of a closed-loop miscibility gap, at low ionic strengths, low volume fractions, and high macroion charges. This gap appears to be the analogue, for the highly asymmetric electrolyte, of the vapour-liquid coexistence region in the RPM. The present theory confirms the recent calculations of van Roij, Dijkstra and Hansen (RDH) who use a different approximation method. Void formation and other anomalies in highly charged colloidal suspensions at low ionic strengths would appear to have a natural explanation in terms of this phase instability.

The phase instability is driven by the electrostatic correlation free energy, and is principally opposed by the counterion translational entropy acting in concert with the condition of bulk phase electroneutrality. The precise location and extent of the instability depends on more subtle details, such as finite macroion size correction factors in the various terms in the free energy.

The above analysis has not exhausted the list of possible phases that might form in charge stabilised colloidal suspensions. As well as ordered colloidal phases (colloidal crystals) that have been included by RDH there is a rather general argument based on a Landau theory that charge-density-wave phases might be expected in the vicinity of critical points in charged systems, in other words in the vicinity of the upper and lower critical solution points in the present theory. This possibility arises because such modulated phases can break the electroneutrality condition that applies in bulk phase separation, and allow the density of small ions to be more uniformly spread than the macroion density. To decide whether such a phase is stable or not requires that the present theory be elaborated to treat such inhomogeneous states though.

The extension to treat inhomogeneous states is also a critical step in constructing a theory for the interfacial region, from which many insights might be gained into the nature of the phase transition and the role of many-body attractions, which are concealed to some extent in the homogeneous theory by the use of the electroneutrality condition.

The theory can be extended in a number of other directions too. One extension is to improve the DH approximation for the polarisation free energy taking into the saturation effect indicated in Fig. and avoid the charge that the interesting effects in the present theory
lie at the margin of its validity (see appendix C). Another extension is to see what happens if the present fixed-charge macroions are replaced with fixed-surface-potential macroions, or replaced with a more physical charge-regulating model for the surface thereby addressing Langmuir’s point (C) in the introduction.

One of the most interesting developments is to replace the supporting simple electrolyte by a more complex fluid, such as a polyelectrolyte solution. Let us suppose that the polyelectrolyte chains have an opposite charge from the macroions. Whilst there are effects on all components in the electrostatic free energy, perhaps the single most important effect might be the reduction in importance of the translational entropy of the counterions. This can be captured by replacing \((Zn_m + n_s) \log(Zn_m + n_s)\) of Eq. (17) by \((n_p/N_p) \log(n_p/N_p) + (Zn_m + n_s - fn_p) \log(Zn_m + n_s - fn_p)\), where \(n_p\) is the additional polyelectrolyte segment density, \(N_p\) is the degree of polymerisation, and \(f\) is the charge per segment. Preliminary investigations show that the effect of the polyelectrolyte in this model is to strongly amplify the phase instability, particularly around the charge stoichiometry plane \(Zn_m = fn_p\), in accordance with expectations. This simple picture might lead to new insights into the phase behaviour (coacervation) of mixtures of oppositely charged polyelectrolytes and colloids or proteins.

A final extension might be to re-introduce van der Waals attractions between macroions. This should result in the re-appearance at high salt concentrations of a second phase instability, corresponding to the salting out phenomenon presently captured by the DLVO theory. Indeed such a theory has been constructed by Victor and Hansen and Grimson et al for related models. In this way, one might hope for a truly general theory that encompasses all aspects of the stability of lyophobic colloids.

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APPENDIX A: COMPARISON WITH THE SOGAMI-ISE THEORY

By making a distinction between the ‘Helmholtz pair potential’ and the ‘Gibbs pair potential’, Sogami and Ise (SI) introduce an ingenious twist to the standard DLVO theory. In their theory, the Gibbs pair potential acquires an attractive tail which can overcome the electrostatic repulsions at large distances. Sogami and Ise argue that this is the explanation for the void structures and other anomalies seen in colloidal suspensions at low ionic strengths.

Of course, the actual forces must be independent of the thermodynamic ensemble used, the force experienced by \(i\)’th macroion at position \(r_i\) is \(F_i = -(\partial F/\partial r_i)_{V,T} = -(\partial G/\partial r_i)_{p,T}\). It is easy to dismiss the SI theory therefore, on the grounds that an elementary mistake has been made. However, if it is claimed that the SI potential is only an “effective pair potential,” then what the SI theory actually does is to capture the state point dependence of
the Debye screening length. This is most clearly illustrated in the derivation by Schmitz. In fact, this model (charged particles with pairwise screened Coloumb interactions and a state point dependent screening length) has been shown to have vapour-liquid coexistence, in direct simulations by Dijkstra and van Roij, thus vindicating the SI attraction mechanism.

Such a model omits the volume terms described in the main text though, and I would argue only captures a small part of the physics of the real situation. Nevertheless, one should credit Sogami and Ise with identifying the essential electrostatic origin of the effective attraction mechanism. For instance: “the attraction in question is a logical consequence of the principle of electric neutrality.”

APPENDIX B: COMPARISON WITH THE VAN ROIJ AND HANSEN THEORY

More recently, van Roij, Dijkstra and Hansen (RDH) have studied charge stabilised colloids by density functional theory. By making what is essentially a random phase approximation (RPA) in the inhomogeneous density functional, they are able to solve the problem analytically at least as far as computing a closed form expression for the free energy. The resulting free energy is basically the same as the present DH free energy, in the sense that for each important term in Eq. (19), there is a corresponding term in the RDH theory with more or less the same functional dependence. They report phase diagrams for only a few parameters, which are compared with the present theory in Table III. (It should be noted that the longer paper corrects the initially reported calculations.) The predictions from both theories for the critical salt concentration are in good agreement, but the critical volume fractions are as much as an order of magnitude higher in RDH at the high Z end. At the highest Z, RDH do not appear to find even metastable fluid-fluid coexistence. The trends are not the same either: in the present theory the critical φ increases with increasing Z, whereas the reverse holds for RDH. Similarly, the present theory always predicts a lower critical salt concentration, albeit at very low salt concentrations. It is not clear if this also holds for RDH. These differences in detail though should not mask the overall similarity between the predictions of the two theories.

| σ/μm | Z   | ZlB/σ | φ           | [salt]/M        | φ       | [salt]/M       |
|------|-----|-------|-------------|-----------------|---------|----------------|
| 652  | 7300| 8.06  | 4.08 × 10⁻³ | 2.78 × 10⁻⁵     | —       | —              |
| 461  | 3650| 5.70  | 6.29 × 10⁻³ | 3.10 × 10⁻⁵     | 7.6 × 10⁻² | 2.0 × 10⁻⁵     |
| 349  | 2086| 4.30  | 8.48 × 10⁻³ | 3.25 × 10⁻⁵     | 3.8 × 10⁻² | 2.1 × 10⁻⁵     |
| 266  | 1217| 3.29  | 9.81 × 10⁻³ | 3.25 × 10⁻⁵     | 1.4 × 10⁻² | 1.9 × 10⁻⁵     |

TABLE III. Upper critical solution points for van Roij, Dijkstra and Hansen macroion parameters.
In the theory, the differences lie in three places. Firstly, in the macroion-small ion interaction term, RDH end up with an expression very similar to the present one in Eq. (10), but with a somewhat different finite size scaling factor: \( f(x) = \frac{3}{4(1+x)} \) (note that \( f(x) \rightarrow 1 \) as \( x \rightarrow 0 \)). Which is closer to the true free energy depends on whose approximations are most believable; for example one can compare the difference to the two approximations introduced for the MSA by Groh et al. Secondly there are minor differences in macroion-small ion hard core interaction term—their expression can be derived from the present theory by setting \( \log(1/(1-\phi)) = \log(1+\phi/(1-\phi)) \approx \phi/(1-\phi) \) and making a similar adjustment in the prefactor. Thirdly, the small ion interaction term is absent from RDH although it makes no practical difference to the results. This term can be recovered if one actually carries out the functional integration over the small ion density fluctuations.

A point of fundamental interest remains though. In their longer paper, RDH claim that the long wavelength macroion-macroion structure factor, \( S_{cc}(q \rightarrow 0) \), should not diverge at the critical point because the pair interactions between macroions remain purely repulsive, although in a later article they modify this position somewhat. The counter-argument is that the spinodal line (including the critical point) is the locus of points where the determinant of second partial derivatives of the free energy vanishes. Since the long wavelength structure factor matrix is the inverse of the matrix of second partial derivatives of the free energy, one would expect every component of the structure factor matrix including \( S_{cc}(q \rightarrow 0) \) to diverge on the spinodal line, barring accidental cancellations.

What, then, is missing from the pair potential argument? Firstly, we have seen that many-body effects are undoubtedly present, although concealed in the present theoretical approaches by the apparent simplicity of the electroneutrality constraint. Secondly, the use of the RPA itself can be misleading. Frequently, the RPA is used to derive an \( S(q) \) which is at a lower level of approximation (zeroth order in a loop expansion to be precise) than the free energy (first order in a loop expansion). If the phase instability only appears at the higher level of approximation, as is the case for DH theory for example, then it will not be seen in \( S(q) \). This does not uncover any profound physics though, rather it represents an inconsistent level of approximation between \( S(q) \) and the free energy. To get consistent results, one should either compute \( S(q) \) to first order in a formal loop expansion (which may be a hard calculation), or invert the matrix of second partial derivatives of the free energy (which only gives \( S(q \rightarrow 0) \)). I have also emphasised these considerations in relation to polyelectrolytes: see appendix to.

APPENDIX C: COMPARISON WITH THE THEORY OF LEVIN, BARBOSA AND TAMASHIRO.

In a series of papers, Levin, Barbosa and Tamashiro (LBT) introduce a theory for charge stabilised colloidal suspensions which is very close to the present studies. The theory is studied in the absence of added salt though, and unfortunately this may have led the authors to miss the existence of the miscibility gap which only appears at a finite added salt concentration (according to the present theory, at least). A novel feature of the LBT approach is an attempt to account for the counterion condensation phenomenon. Their results for the effective charge resemble the PB theory of Alexander et al. and Groot.
Thus Fig. 1 in Ref. 27 shows counterion condensation starting effectively for $Zl_B/\sigma \approx 3$ (their reported calculation is for $Z \approx 600$ and $a/l_B = T^* = 100$, where $T^*$ is their reduced temperature).

The LBT approach is motivated by analogy to the work on the RPA by Fisher and Levin. The free energy is split into contributions similar to those identified here, and the incorporation of the counterion condensation is motivated by the importance of Bjerrum pairing in the RPM. The counterion contribution to the free energy is that of an OCP, which reduces to the first of Eqs. (10) here in the relevant limit where the ion concentration is $\ll 1 \text{ M}$. The macroion-counterion contribution is identical to that in RDH, except that the self energy of the macroion, $Z^2l_BkT/2a$, is also included. This is essential for the LBT theory where the effective charge $Z$ is variable, whereas in theories where $Z$ is fixed the self energy just shifts the macroion chemical potential. The macroion contribution is treated via a mean field-van der Waals approximation omitting the background subtraction counterterm. As described in the main text, this omission can have quite a significant effect on the location of the miscibility gap, and it would be quite important to rectify this in any future work.

It seems that progress might be made by combining the variational approach to the counterion condensation phenomenon advocated by LBT, with the more careful treatment of the free energy of the whole system considered in the present paper (or by RDH). It certainly would be interesting to see whether the miscibility gap appears when added salt is included in such a theory, which can legitimately be pushed to much higher values of the bare macroion charge than have been considered in the present study.

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