

## Attraction or repulsion between charged colloids? A connection with Debye–Hückel theory

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**Abstract.** We discuss the phase behaviour of suspensions of charged colloidal particles, specifically at low salt concentrations. The total free energy  $F$  of a three-component system of charged colloids and positive and negative salt ions can be expressed as  $F = F_{\text{DLVO}} + F_0$ , where  $F_{\text{DLVO}}$  is the free energy of a one-component system of colloidal particles interacting via the DLVO pair potential, and  $F_0$  consists of density-dependent contributions from the salt ions. We argue that  $F_0$  drives a gas–liquid spinodal at low salt concentrations, in accordance with several experimental observations. The underlying mechanism is equivalent to that of the well-established gas–liquid transition in simple electrolytes. The present theory connects directly the classic linearized Poisson–Boltzmann theories for simple electrolytes (Debye–Hückel) and colloidal suspensions (DLVO).

It is well known that the phase behaviour of classical fluids is determined by the interplay between repulsive and attractive forces between particles. It is often a good approximation to describe the steric repulsion between spherically symmetric particles by the hard-sphere pair potential  $v_{\text{HS}}(r)$ , and its contribution to the total Helmholtz free energy of the fluid,  $F$ , by that of the hard-sphere fluid,  $F_{\text{HS}}$ . The contribution to  $F$  from the non-steric pair interactions depends on the nature of the system. As an illustration we consider Van der Waals' mean-field treatment of the dispersion interactions in simple fluids [1, 2], and Debye and Hückel's treatment of the Coulomb interactions in simple electrolytes [3, 4]. Denoting the number density of spherical particles by  $n$ , the temperature by  $T$ , and the total macroscopic volume of the fluid by  $V$ , one can express these standard results as

$$\frac{F - F_{\text{HS}}}{Vk_B T} = \begin{cases} -\frac{1}{2} \frac{a}{k_B T} n^2 \propto -n^2 & \text{(simple fluid)} \\ -\frac{\kappa_D^3}{12\pi} \propto -n^{3/2} & \text{(simple electrolyte).} \end{cases} \quad (1)$$

Here  $a > 0$  is the integrated strength of the Van der Waals dispersion interaction in simple fluids, and  $1/\kappa_D$  is the Debye screening length given by

$$\kappa_D^2 = 8\pi e^2 n_s / \epsilon k_B T$$

for a monovalent 1:1 electrolyte with equal densities  $n_s = n/2$  of positive and negative salt ions. The dielectric constant of the electrolyte is  $\epsilon$ , and  $e$  is the proton charge. The main difference between the two expressions is the power of the  $n$ -dependence, the  $\mathcal{O}(n^2)$  term being

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typical for integrable (short-ranged) interactions, and the  $\mathcal{O}(n^{3/2})$  term typical for long-ranged Coulomb forces (in three dimensions). More important for the present purposes, however, is the common negative sign and curvature (as a function of  $n$ ) of the right-hand sides of equation (1). The negative *sign* signals that both the dispersion and the Coulomb interactions provide cohesive energy. This cohesive energy is easily understood in terms of the attractions between each particle pair in the case of simple fluids, and in terms of the closer proximity, on average, of oppositely charged particles than of equally charged particles in simple electrolytes. The negative *curvature* signals the possibility of a spinodal instability [5]. Indeed, it is well established that Van der Waals' theory for simple fluids and the Debye–Hückel theory for simple electrolytes explain the essence of the coexistence of a dilute gas phase and a dense liquid phase below a critical temperature (although finer details such as the exact shape of the coexistence curve require better theories [4]). In both types of fluid, the liquid phase is stabilized by the cohesive energy provided by the non-steric interactions, and the gas phase by high entropy (or a low contribution  $F_{\text{HS}}$  to  $F$ ).

The notion of the importance of the interplay between attractions and repulsions is not limited to the field of simple fluids and simple electrolytes; it has also been recognized for a long time in the field of *colloidal fluids*. The classic work of Derjaguin and Landau [6] and Verwey and Overbeek [7] in the 1940s explains the stability of colloidal suspensions on the basis of an effective potential,  $v_{\text{DLVO}}(r)$ , between pairs of charged colloidal particles at separation  $r$ . This DLVO potential—named after its discoverers—consists of a steric hard-sphere repulsion  $v_{\text{HS}}(r)$ , an electrostatic double-layer repulsion of screened Coulomb form, and a dispersive Van der Waals–London–Hamaker attraction. For monodisperse colloidal spheres of diameter  $D = 2R$  and total charge  $-Ze$ , suspended in a simple 1:1 electrolyte of dielectric constant  $\varepsilon$  and Debye screening length  $1/\kappa_{\text{D}}$ , the explicit form of the pair interaction reads

$$v_{\text{DLVO}}(r) = v_{\text{HS}}(r) + \frac{Z^2 e^2}{\varepsilon} \left( \frac{\exp[\kappa_{\text{D}} R]}{1 + \kappa_{\text{D}} R} \right)^2 \frac{\exp[-\kappa_{\text{D}} r]}{r} - \frac{A}{12} \left[ \frac{D^2}{r^2 - D^2} + \frac{D^2}{r^2} + 2 \ln \left( 1 - \frac{D^2}{r^2} \right) \right] \quad (2)$$

where the Hamaker constant  $A$  is a measure of the strength of the dispersion interaction between the colloidal particles [6–8]. Typical values for colloidal suspensions are  $Z \simeq 10$ – $10^4$ ,  $D \simeq 10$ – $1000$  nm, and  $A \simeq 10^{-20}$ – $10^{-18}$  J. For an aqueous electrolyte at room temperature we have  $e^2/\varepsilon k_{\text{B}} T \simeq 0.72$  nm, and  $1/\kappa_{\text{D}} \simeq 0.3, 10, 300$  nm for salt concentrations  $n_{\text{s}} = 1$  M, 1 mM, and 1  $\mu\text{M}$ , respectively. The potential of equation (2), together with these typical numbers, gives rise to strong screening (and hence attractions dominating the repulsions) under high-salt conditions, and, conversely, repulsions dominate the attractions under low-salt conditions. The DLVO theory thus explains the experimental observations of colloidal instability and irreversible aggregation at high salt concentrations, say  $n_{\text{s}} \simeq 1$  M, and colloidal stability and reversible gas–liquid transitions at lower salt concentrations, say  $n_{\text{s}} < 1$  mM [7, 9]. The screened Coulomb repulsion of the DLVO potential also explains the experimental observation of colloidal crystals, in the repulsion-dominated stable regime, at packing fractions of a few per cent [10]. For these reasons, and many more, the DLVO theory is considered to be one of the cornerstones of colloid science.

Since the 1980s, however, several experimental observations for colloidal suspensions have been reported that seem to be inconsistent with the DLVO theory. Invariably these experiments have been performed at extremely low salt concentrations  $n_{\text{s}} = 1$ – $10$   $\mu\text{M}$ , i.e. in the regime where the screened Coulomb repulsions completely mask the dispersion

forces according to the DLVO theory<sup>†</sup>. In contrast, the low-salt observations of gas–solid coexistence [11], ‘voids’ in otherwise homogeneous suspensions [12], fully developed gas–liquid coexistence [13], re-entrant fluid–solid transitions [14], and long-lived metastable crystallites [15] appear to call for strong colloid–colloid attractions. Many attempts to find a theoretical basis for attractions between like-charged colloids have been reported over the years [16, 17], but recent direct measurements of the colloid–colloid pair interaction under the low-salt conditions of interest are perfectly consistent, at least for bulk, with the purely repulsive screened Coulomb form described by the DLVO theory [18]. The theory presented in detail in reference [19] explains this puzzling state of affairs quite straightforwardly. Here we summarize the salient features of our approach, and by making connection with the theory of phase separation in simple electrolytes provide some further insight into the mechanism which drives phase separation in low-salt suspensions of charged colloids.

Instead of regarding a colloidal suspension as a one-component fluid of colloids with effective DLVO pair interactions from the start, we calculate the total Helmholtz free energy  $F$  of a three-component system of colloids (density  $n_c$ , charge  $-Ze$ ), negative salt ions (density  $n_- = n_s$ , charge  $-e$ ), and positive salt ions (density  $n_+ = n_s + Zn_c$ , charge  $+e$ ). Dispersion interactions are ignored completely. We regard the mixture as an inhomogeneous system of salt ions in the external field of the colloidal particles, and retain the colloid–salt-ion correlations at the linearized Poisson–Boltzmann level. The salt-ion–salt-ion interactions are treated at the Hartree-like mean-field level. In reference [19] we showed (i) that the salt ions form a diffuse ‘cloud’ of thickness  $1/\kappa$  and total charge  $+Ze$  around the surface of each colloid, with  $\kappa^2 = 4\pi e^2(2n_s + Zn_c)/\epsilon k_B T$ , and (ii) that  $F = F_{\text{DLVO}} + F_0$ . Here  $F_{\text{DLVO}}$  is the free energy of a one-component fluid of density  $n_c$  with pairwise DLVO interactions given in equation (2), but with  $A = 0$  and  $\kappa_D$  replaced by  $\kappa$ . Clearly, there is *no* cohesive energy contribution in  $F_{\text{DLVO}}$  because the pair interactions are purely repulsive. The other contribution to  $F$ ,  $F_0$ , is the so-called volume term given by

$$\begin{aligned} \frac{F_0(n_c, n_s)}{V} = k_B T & \left[ n_+ (\ln n_+ - 1) + n_- (\ln n_- - 1) + \frac{\eta}{1 - \eta} \frac{2n_+ n_-}{n_+ + n_-} \right] \\ & - \frac{Z^2 e^2}{2\epsilon(R + 1/\kappa)} n_c - \frac{1}{2} \frac{4\pi Z^2 e^2}{\epsilon \kappa^2} n_c^2 \end{aligned} \quad (3)$$

with colloid packing fraction  $\eta = (4\pi/3)R^3 n_c$ . The first three terms of equation (3) represent the ideal-gas and excluded-volume entropy of the microions. The last two terms of equation (3) are of electrostatic nature, the fourth term being due to ‘inter’ colloid–cloud *correlations* and the fifth due to *mean-field* ‘intra’ colloid–cloud interactions. The correlation term is, for each colloidal particle, of the order of the Coulomb energy of charges  $\pm Ze$  separated by a distance  $R + 1/\kappa$ , and thus represents the ‘internal free energy’ of each colloidal particle with ‘its own’ oppositely charged cloud. The final term of equation (3) corrects for overcounting in  $F_{\text{DLVO}}$  by essentially cancelling its mean-field contribution; it may be interpreted as the Coulomb energy of the clouds in the mean field of other colloidal particles. Although all terms in  $F_0$  have a natural physical meaning, the volume term was not considered in early studies of the phase behaviour of colloidal suspensions. More recent treatments do consider free-energy contributions that are similar or equivalent to those contained in  $F_0$ ; see e.g. references [20].

<sup>†</sup> The dispersion contribution in the potential of equation (2) exhibits a (non-physical) negative divergence at contact, i.e. when  $r \rightarrow D^+$ , and decays algebraically as  $-r^{-6}$  when  $r \rightarrow \infty$ . One could therefore argue that the attractions always dominate the repulsions at contact (‘primary minimum’) and at sufficiently large separation (‘secondary minimum’). The point here is that the screened Coulomb repulsion, at low enough salt concentrations, forms an insurmountable barrier that prevents colloids from coming into contact (‘kinetic stabilization’) and shifts the secondary minimum to such a large colloid–colloid separation that its well depth is substantially less than  $k_B T$ .

The correlated cohesive energy term in  $F_0$ , together with the  $n_c$ -dependence of  $\kappa$ , turns out to be the key to the understanding of the experimental low-salt observations, and to establishing a direct connection between DLVO theory and Debye–Hückel theory. This is most easily seen for point colloids,  $R = 0$ , but the essence of the argument also holds for finite  $R$ . At sufficiently low salt concentrations  $n_s$  we have  $\kappa \propto n_c^{1/2}$ , and hence the cohesive energy term yields an  $\mathcal{O}(-n_c^{3/2})$  contribution to  $F_0/V$ . For exactly the same reasons and by exactly the same mechanism as in the Debye–Hückel theory for 1:1 electrolytes, this term can cause a gas–liquid spinodal, and stabilize coexistence of a dense colloidal liquid or solid with a dilute colloidal gas phase. The mechanism of this phase separation is *not* based on pairwise colloid–colloid attractions, but instead on the balance between a more compressed double layer in a dense colloidal liquid or crystalline phase (and hence a low electrostatic energy but a low entropy) and the more expanded double layer in a dilute colloidal gas (and hence a high entropy but a not-so-low electrostatic energy). At sufficiently high salt concentrations  $n_s$ , the double-layer thickness is essentially determined by  $n_s$  only, and does not noticeably depend on  $n_c$ . Then the cohesive energy contribution to  $F_0/V$  is essentially proportional to  $-n_c$ , and hence is irrelevant for the thermodynamics.

Full numerical calculations of  $F_{\text{DLVO}}$ , and hence of  $F$ , show that gas–liquid and gas–solid coexistence occur in aqueous suspensions, with typical colloidal charges  $Z \simeq 10^3$ – $10^4$  and diameters  $D \simeq 200$ – $700$  nm, at salt concentrations  $n_s \leq 25 \mu\text{M}$  [19]. These parameter values are in the regime of the experimental observations of gas–liquid and gas–solid coexistence [11–13, 15]. In addition, the theory predicts closed-loop gas–liquid coexistence, which may be related directly to the re-entrant phenomena observed in reference [14]. Finally, the present theory suggests that the observed phase transitions in low-salt colloidal suspensions are the analogues of the gas–liquid transition in simple 1:1 electrolytes. This could provide an interesting alternative opportunity to study Coulombic criticality experimentally [4].

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