



Attraction between identical colloidal particles caused by collective electrostatic repulsion

Eli Ruckenstein

*Chemical Engineering Department, State University of New York at Buffalo, Buffalo, NY 14260,
USA*

Abstract

The goal of this article is threefold: (i) To demonstrate that, within the framework of the Poisson–Boltzmann equation, the interparticle electrostatic interaction in a system containing only two identical particles immersed in an infinite or finite size reservoir of an electrolyte solution is repulsive at all distances. It cannot lead to a short-range repulsion and a long-range attraction as suggested by Sogami and Ise. (ii) To explain Ise's experimental observations that the electrostatic interactions in systems containing many identical colloidal particles can lead to attraction. (iii) To note that an effective attraction between two neighboring particles can be generated by the DLVO pair repulsion exerted on them by all the other particles of the system. © 1998 Elsevier Science B.V.

Keywords: Colloidal particles; Electrostatic interactions; Attraction via collective electrostatic interactions; Attraction via collective repulsion

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1. Introduction

It has been known for some time that sufficiently concentrated solutions of monodisperse latex spheres exhibit iridescence [1,2]. This phenomenon is a result of the Bragg diffraction of visible light by the ordered arrangement of the spheres [3–5]. The beautiful color of the natural colloidal crystals, such as the opals, is due to the equality between their lattice parameter and the optical wavelength. At such distances, the van der Waals interactions are, however, negligible and the only interactions which can be responsible for the crystalline order are the electrostatic ones. For this reason, the phase behavior of a system of colloidal particles interacting through the approximate repulsive screened Yukawa potential (which was corrected by replacing the charge and ion density by renormalized effective values) was examined theoretically in a number of articles [6–10]. The calculated phase diagram contains a transition from fcc to bcc crystalline phases as well as a melting transition, and is in agreement with experiments on colloidal suspensions of polystyrene spheres [10]. Microscopy experiments with dilute solutions of identical latex particles, carried out by Ise and coworkers [11–13], revealed that, when the particles were not highly charged, the interparticle distance was approximately equal to that calculated for a uniform distribution; for large charges, the measured distance between some of the particles was, however, smaller than that calculated for a uniform distribution. In the latter case, ordered regions coexisted with disordered ones. Ise rightly noted that the formation of ordered regions can occur only if attractive interactions between particles are also present. Since, the distance between particles was larger than the range of the van der Waals interactions, Ise concluded that the electrostatic interactions between two identical particles immersed in an electrolyte solution should be attractive at large distances and repulsive at short ones. He attributed these attractive interactions to the attraction exerted by the counterions on the particles which, as a result, attract one another, an idea which he borrowed from Langmuir [14]. A theory was developed by Sogami and Ise [15,16] which predicts, on the basis of the Poisson–Boltzmann (PB) equation, that the electrostatic interactions in a system containing only two identical colloidal particles immersed in an electrolyte solution generate a short-range repulsion and a long-range attraction. This result contradicts the DLVO theory, which predicts that the electrostatic force is repulsive at all distances [17]. The Sogami and Ise theory was criticized by Overbeek [18] and this was followed by arguments in its favor, by Smalley [19,21] and Sogami et al. [20], and against, by Woodward [22], Levine and Hall [23], Ettelaie [24] and Overbeek [25].

The scope of the present article is threefold. First, it will be demonstrated that, within the framework of the Poisson–Boltzmann equation, the electrostatic interactions between two identical parallel plates immersed in an electrolyte solution are always repulsive at all distances, and that the basic equations of the DLVO theory [17] are correct. While the arguments are in essence similar to those of Verwey and Overbeek [17], and the results are the same, a more formal thermodynamic treatment is employed which I hope will facilitate the understanding of the issue. Second, the attention will be drawn to a few articles we published a few years

ago [26–28] in which it was concluded that the collective Coulomb interactions among all the charged species (anions, cations, and identical colloidal particles) can lead to attraction. A similar conclusion was also reached by Chu and Wasan [29]. Of course, this result can explain the experimental observations of Ise. Third, it will be noted that even a pair repulsive potential, such as the pair DLVO electrostatic repulsion can lead, in a sufficiently large group of particles, to an effective attraction between two particles.

2. The electrostatic interactions between two identical parallel plates immersed in an electrolyte solution

As emphasized by Verwey and Overbeek [17], two ways can be used to derive an expression for the force between two identical very large parallel plates, immersed in a large reservoir containing an electrolyte. One of them starts from the equality between the gradient of the hydrostatic pressure and the electrostatic force acting on the space charge. The combination of this equation with the PB equation leads to the Langmuir [14] expression

$$F = 2c_{\infty}kT[\cosh(e\psi_m/kT) - 1] \quad (1)$$

where F is the force acting per unit area, $2c_{\infty}$ is the concentration of all the ions (assumed in this article univalent), k is the Boltzmann constant, T the temperature in K, e the protonic charge and ψ_m the midpoint electrical potential.

In the second way, the Langmuir equation was derived using either the expression

$$F = \frac{\partial}{\partial \ell} \int_0^{\psi_s} \sigma(c_{\infty}, \ell, \psi) d\psi \quad \text{at constant } \psi_s \text{ and } c_{\infty} \quad (2a)$$

or the expression

$$F = - \frac{\partial}{\partial \ell} \int_0^{\sigma_s} \psi(c_{\infty}, \ell, \sigma) d\sigma \quad \text{at constant } \sigma_s \text{ and } c_{\infty} \quad (2b)$$

where ℓ is the half distance between the plates, ψ_s is the surface potential, σ_s the surface charge density and σ the surface charge density for a surface potential ψ . Combined with the PB equation, Eqs. (2a) and (2b) lead to the Langmuir equation [Eq. (1)] and hence indicate that the electrostatic interactions between the two plates is repulsive at all distances. The derivation by Verwey and Overbeek of Eqs. (2a) and (2b), while absolutely rigorous from a thermodynamic point of view, can be followed with some difficulty. A more formal approach due to Everett and Radke [30] and Ruckenstein [31] is presented below.

The Gibbs free energy, G , of the entire system is given by the expression

$$G = A\gamma + \sum n_i \mu_i \quad (3)$$

where A is the area of the inner faces of both plates, γ is the interfacial free energy of the inner faces, n_i the number of molecules (or ions) of species i and μ_i is their electrochemical potential. For the sake of simplicity, the outer faces of the plates are considered uncharged.

For a reversible change, at constant temperature, of the distance 2ℓ between the plates, one can write

$$dG = \gamma dA - AFd\ell + \sum \mu_i dn_i + Vdp \quad (4)$$

where V is the volume of the system, p is the external pressure and the force, F , is assumed positive for repulsion.

Differentiating Eq. (3) and combining with Eq. (4) yields the following Gibbs–Duhem equation

$$Ad\gamma + AFd\ell + \sum n_i d\mu_i - Vdp = 0 \quad (5)$$

Denoting by $c_{i\infty}$ the concentration of species i in the large reservoir, one can write, at constant temperature, the Gibbs–Duhem equation

$$\sum Vc_{i\infty} d\mu_i - Vdp = 0 \quad (6)$$

Combining Eqs. (5) and (6), leads to

$$d\gamma + Fd\ell + \sum \Gamma_i d\mu_i = 0 \quad (\text{at constant temperature}) \quad (7)$$

where

$$\Gamma_i = \frac{n_i - Vc_{i\infty}}{A} \quad (8)$$

is the surface excess of species i . For a transformation that occurs at constant ℓ and temperature, one obtains the Gibbs adsorption equation

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (\text{at constant temperature and } \ell) \quad (9)$$

and for a transformation that occurs at constant temperature and μ_i , the expression

$$F = -\frac{\partial \gamma}{\partial \ell} \quad (\text{at constant temperature and } \mu_i) \quad (10)$$

first employed by Mackor and van der Waals in their theory of steric repulsion [32]. The electrochemical potential μ_i can be written as the sum

$$\mu_i = \mu_i' + \nu_i e \psi_s \quad (11)$$

where μ_i' is the chemical component of μ_i at the surface and $\nu_i e \psi_s$ (with ν_i the

ion valency, positive for cations) the electrical component also at the surface. Because of the overall electroneutrality

$$\Sigma \Gamma_i d\mu_i = \Sigma \Gamma_i d\mu_i'$$

and one can write

$$d\gamma = -\Sigma \Gamma_i d\mu_i' \quad (\text{at constant temperature and } \ell) \quad (12)$$

and

$$F = -\frac{\partial \gamma}{\partial \ell} \quad (\text{at constant temperature and } \mu_i') \quad (13)$$

For illustrative purposes, let us assume that the solution contains one electrolyte A^+E^- and that only the ion E^- is adsorbed on the surface because of its strong interactions with the plate. Consequently,

$$-d\gamma = \Gamma_A d\mu_A + \Gamma_E d\mu_E + \Gamma_S d\mu_S, \quad (14)$$

where the subscripts A and E stand for the respective ions and the subscript S for the solvent.

Since at constant temperature and pressure

$$\Sigma x_i d\mu_i = 0, \quad (15)$$

where x_i is the molar (ionic) fraction of species i in the reservoir, one can eliminate the chemical potential of the solvent from Eq. (14) to obtain

$$-d\gamma = \Gamma_{AS} d\mu_A + \Gamma_{ES} d\mu_E \quad (16)$$

with

$$\Gamma_{iS} = \Gamma_i - \frac{x_i}{x_S} \Gamma_S$$

Because $x_i \ll x_S$ and $|\Gamma_S| \ll |\Gamma_i|$, Eq. (16) becomes

$$-d\gamma = \Gamma_A d\mu_A + \Gamma_E d\mu_E \quad (17)$$

Denoting by Γ_E' the surface density due to the preferential adsorption of ion E^- and by D_E the deficiency of the same ion in the double layer, one can write

$$\Gamma_E = \Gamma_E' - D_E \quad (18)$$

and Eq. (17) becomes

$$-d\gamma = \Gamma_E' d\mu_E' + \sigma_s d\psi_s + \Gamma_A d\mu_A - D_E d\mu_E \quad (19)$$

Since μ_A and μ_E are not independent quantities, let us introduce the quantity Γ defined by

$$\Gamma d\mu_A \equiv \Gamma_A d\mu_A - D_E d\mu_E \quad (20)$$

Eq. (19) can be rewritten as

$$-d\gamma = \Gamma_E' d\mu_E' + \sigma_s d\psi_s + \Gamma d\mu_A \quad (21)$$

The cross differentiation yields

$$\frac{\partial \sigma_s}{\partial \mu_A} = \frac{\partial \Gamma}{\partial \psi_s} \quad (22)$$

from which results that

$$\Gamma = \int_0^{\psi_s} \frac{\partial \sigma(\psi)}{\partial \mu_A} d\psi \quad (23)$$

Combining Eqs. (21) and (23) and taking into account that

$$d \int_0^{\psi_s} \sigma d\psi = \sigma_s d\psi_s + \left(\int_0^{\psi_s} \frac{\partial \sigma}{\partial \mu_A} d\psi \right) d\mu_A \quad (24)$$

one finally obtains

$$-d\gamma = \Gamma_E' d\mu_E' + d \int_0^{\psi_s} \sigma d\psi \quad (25)$$

The derivative $\frac{\partial \gamma}{\partial \ell}$ is given by

$$\begin{aligned} -\frac{\partial \gamma}{\partial \ell} &= \Gamma_E' \frac{\partial \mu_E'}{\partial \ell} + \sigma_s \frac{\partial \psi_s}{\partial \ell} + \int_0^{\psi_s} \frac{\partial \sigma}{\partial \ell} d\psi + \int_0^{\psi_s} \frac{\partial \sigma}{\partial \mu_A} \frac{\partial \mu_A}{\partial \ell} d\psi \\ &= \Gamma_E' \frac{\partial \mu_E}{\partial \ell} + \Gamma_A \frac{\partial \mu_A}{\partial \ell} - D_E \frac{\partial \mu_E}{\partial \ell} + \int_0^{\psi_s} \frac{\partial \sigma}{\partial \ell} d\psi \\ &= \Sigma \Gamma_i \frac{\partial \mu_i}{\partial \ell} + \int_0^{\psi_s} \frac{\partial \sigma}{\partial \ell} d\psi \equiv \Sigma \Gamma_i \frac{\partial \mu_i'}{\partial \ell} + \int_0^{\psi_s} \frac{\partial \sigma}{\partial \ell} d\psi. \end{aligned} \quad (26)$$

Consequently,

$$F = \int_0^{\psi_s} \frac{\partial \sigma}{\partial \ell} d\psi \quad (\text{at constant } \mu_i \text{ or } \mu_i') \quad (27)$$

Eq. (27) can be rewritten in the following form, which emphasizes the surface

charge density

$$F = \frac{\partial}{\partial \ell} \int_0^{\psi_s} \sigma d\psi - \sigma_s \frac{\partial \psi_s}{\partial \ell} = \frac{\partial}{\partial \ell} (\sigma_s \psi_s) - \frac{\partial}{\partial \ell} \int_0^{\sigma_s} \psi d\sigma - \sigma_s \frac{\partial \psi_s}{\partial \ell} \quad (28)$$

from which one obtains

$$F = - \int_0^{\sigma_s} \frac{\partial \psi}{\partial \ell} d\sigma \quad (\text{at constant } \mu_i \text{ or } \mu'_i) \quad (29)$$

Eqs. (27) and (29) can be rewritten as

$$F = \frac{\partial}{\partial \ell} \int_0^{\psi_s} \sigma d\psi - \sigma_s \frac{\partial \psi_s}{\partial \ell} \quad (27a)$$

and

$$F = - \frac{\partial}{\partial \ell} \int_0^{\sigma_s} \psi d\sigma + \psi_s \frac{\partial \sigma_s}{\partial \ell} \quad (29a)$$

The results provided by Eqs. (27a) and (29a) are the same as those provided by the Verwey and Overbeek expressions

$$F = \frac{\partial}{\partial \ell} \int_0^{\psi_s} \sigma d\psi \quad (\text{at constant } \psi_s) \quad (30)$$

and

$$F = - \frac{\partial}{\partial \ell} \int_0^{\sigma_s} \psi d\sigma \quad (\text{at constant } \sigma_s) \quad (31)$$

Each of the Eqs. (27) and (29)–(31) combined with the Poisson–Boltzmann equation leads to the Langmuir equation (Eq. (1)). The latter equation clearly shows that the electrostatic interactions between two infinite, parallel plates immersed in a large reservoir is repulsive at all distances.

Can a finite size reservoir change the sign of the force? In this case a part of the solution constitutes a finite size or in the limit a zero size reservoir. Neglecting edge effects as well as any effect of the double layer on the ions in the finite reservoir, the treatment employed for a large reservoir can be extended also to the present case. Of course, in order to ensure the constancy of the chemical potential μ_i during the change of ℓ , required to calculate the force F , the concentrations of ions A^+ and E^- in the reservoir must be kept constant and equal to their values in the final state. There is a single important difference between the infinite and finite size reservoirs. Whereas for infinite reservoirs these concentrations are given, for finite size reservoirs they must be calculated from mass balances and the condition of equilibrium. Let us denote by V the total volume of the solution, by V_r the volume of the reservoir and use the subscript a for the ionic concentration in

the solution before immersing the plates and the subscript r for those in the reservoir in the final state. Assuming Boltzmann distributions, mass balances lead to the equations

$$A \left[\Gamma'_E + \int_{\delta}^{\infty} c_{Er} \exp(e\psi/kT) dz \right] + c_{Er} V_r = V c_{Ea} \quad (32)$$

and

$$A \int_{\delta}^{\infty} c_{Ar} \exp(-e\psi/kT) dz + c_{Ar} V_r = V c_{Aa} \quad (33)$$

where δ is the thickness of the monolayer of E^- ions adsorbed on the surface, z the distance to the plate, $c_{Aa} = c_{Ea}$, $c_{Ar} = c_{Er}$ and $V_r = V - A\ell - At$, with t the thickness of the plates.

Eqs. (32) and (33) are not independent, because of the electroneutrality condition. Any of the Eqs. (32) and (33) can be used to calculate c_{Er} and the electrostatic interaction is given by the expression

$$F = 2c_{Er} [\cosh(e\psi_m/kT) - 1] \quad (34)$$

with

$$c_{Er} = \frac{V c_{Ea}}{A \int_{\delta}^{\infty} \exp(-e\psi/kT) dz + V_r} \quad (35)$$

Since $c_{Er} > 0$, the electrostatic interaction between two identical plates is repulsive at all distances when the reservoir has a finite or zero size.

It is now clear that, if Eq. (11) for the chemical potential and the Poisson–Boltzmann equation for the electrical potential are employed, the interparticle electrostatic interaction between two particles immersed alone in a finite or infinite reservoir containing an electrolyte cannot become attractive. Therefore the experimental findings of Ise and coworkers require another explanation than the one provided by Sogami et al.

3. Attractive electrostatic interactions among identical charged colloidal particles

In contrast to the DLVO theory which considered two colloidal particles as macroscopic bodies immersed in an electrolyte solution, in our treatment [26–28] the colloidal particles were considered a component of the mixture, a kind of macroions, and the Coulomb interactions among all the charged species (anions, cations and colloidal particles) were taken into account. The Ornstein–Zernike equation in its zero-order approximation (symmetrized Poisson–Boltzmann equation) was employed. The calculations indicated the existence of a critical particle

concentration above which the pair correlation function of the particles became greater than unity, indicating an effective attraction between particles. A similar model was employed by Chu and Wasan [29]. They solved the Ornstein–Zernike equation with the mean spherical-approximation closure and concluded that the collective electrostatic interactions can generate a long-range attraction and a short-range repulsion. Consequently, the collective interactions among colloidal particles, anions and cations can generate a long range attraction. I do not disagree with Ise from this point of view. I disagree that this attraction can be obtained in the framework of the Poisson Boltzman equation, by considering two colloidal particles immersed alone in an electrolyte solution.

It is of interest to note that the collective behavior of colloidal particles interacting via pair repulsive potentials can also lead to an effective attraction. As noted in the introduction, such a pair potential sometimes constitutes a good approximation, since it can predict the phase behavior of a suspension of colloidal particles. Let us consider two neighboring colloidal particles, 1 and 2, in a sea of identical charged particles. The repulsion to which the right-hand particle 1 is subjected by the other particles except particle 2 can be dominated by the particles at its right. As a result, particle 1 is pushed to the left. Similarly, the repulsion experienced by the left-hand particle 2 from the other particles except particle 1 can be dominated by the particles at its left, and particle 2 is pushed to the right. In this manner, an attraction between particles 1 and 2 is generated. In other words, the collective repulsion exerted by the other particles of the system on two selected neighboring particles can have, as a result, an effective attraction between the latter two. This is expected to occur only if the concentration of particles is not too small. Of course, the two particles are also subjected to the repulsion between them. If the repulsive forces pushing particle 1 to the left and particle 2 to the right overcome the repulsion between particles 1 and 2, an effective attractive force is generated. The above explanation implies that the ions affect only the pair repulsion between particles and that the pair repulsion is long range.

The ordered, crystalline organization of the colloidal particles can be explained by noting that the symmetry thus achieved can easily result in a zero force at each site of the lattice. Let us consider again the two neighboring marked particles 1 and 2. Assuming that only pair screened electrostatic repulsions are acting between particles, particles 1 and 2 are subjected to the pair repulsion between them, but also to the effective attraction generated by the collective repulsion of all the other particles of the system. At equilibrium, the attraction and repulsion should be equal. To demonstrate that this equilibrium is stable, let us perturb the distance between the marked neighboring particles. If the distance between the two is increased, the repulsion between them is decreased, but the collective repulsion due to all other particles (which generates the effective attraction between the two) is increased. As a result, the two particles will be moved back to their initial positions. If the distance is decreased, the repulsion between the two is increased and the effective attraction decreased, and the particles will be moved again back to the equilibrium sites. Of course, the above considerations are valid only at 0 K, since the harmonic and anharmonic oscillations around the sites should be also

included at higher temperatures. They provide, however, some qualitative understanding of the problem.

The above qualitative explanation as well as the theoretical approaches regarding the colloidal crystals [6–10] suggest that the DLVO pair repulsive potential can sometimes constitute a reasonable approximation of the pair potential for a dispersion of colloidal particles.

For completeness let us mention that a short-range attraction due to electrostatic interactions was suggested by Oosawa [33] and calculations carried out by various authors [34–38]. When two similarly charged particles approach one another, the fluctuations in the counterion concentrations around them generate, because they are correlated, an attraction similar to the London forces, which is significant for multivalent counterions. The attractive force of concern in the present article has, obviously, a different origin.

4. Discussion of Ise's experiments

As already mentioned, ordered clusters dispersed in a disordered phase were observed by Ise and coworkers. This can represent the beginning of a slow separation into ordered and disordered phases; it is, however, also possible for the dispersion to be more stable thermodynamically than the separate phases. Indeed, assuming pairwise additivity of a repulsive potential, the free energy may be decreased by the splitting of the ordered phase into small domains dispersed in the disordered phase. The splitting decreases the free energy contribution due to the interaction between particles and increases, via dispersion, the entropy of the system. Of course, the free energy contribution due to the interfacial tension between the ordered clusters and the disordered phase, which has to be positive, must be overcome for the dispersion to be stable. Because it is long range, the repulsion due to the other particles may dominate that due to the particles present in the relatively small aggregate of the ordered phase and this may ensure the stability of the interface. The minimization of the free energy with respect to the size and volume fraction of the ordered domains provides their dimension and their number density. If an attractive component is also included in the pair potential, the dispersion may become thermodynamically stable if the entropic effect dominates the interfacial free energy contribution.

Interesting experiments have been published recently by Ise [39] and Tata et al. [40]. These authors observed the formation of large voids (25–50 μm), with large volume fractions (0.33–0.63), in highly charged aqueous poly(chlorostyrene-styrene sulfonate) suspensions of low particle (180 nm size) volume fraction (< 0.06). The voids were very stable, since they reappeared within 16 h after shaking. The authors suggested that the coexistence of voids with a disordered (amorphous) colloidal dispersion can be viewed as a phase separation. Because of the stability of the voids, it is, however, possible that the system constitutes a thermodynamically stable giant emulsion of water droplets in a colloidal dispersion. While the repulsive pair potential may provide a reasonable approximation for the calculation

of the interactions among the particles, the interfacial tension between the voids and colloidal dispersion needs an interaction potential which has also an attractive component, in order to ensure the stability of the interface. Can (i) the entropy of dispersion of the droplets in the amorphous colloidal dispersion; (ii) the electrostatic interactions among the droplets; and (iii) the interfacial free energy have such values so as to ensure the thermodynamic stability of such an emulsion?

5. Conclusions

Contrary to the opinion of Sogami, Ise and Smalley, within the framework of the Poisson–Boltzmann equation, the interparticle electrostatic interaction between two identical particles is repulsive at all distances.

The electrostatic attractive interactions among a sufficiently large number of identical colloidal particles observed experimentally by Ise are a result of the collective interactions between all the charged species involved.

An effective attraction between two particles can be generated by the pair-repulsions exerted on them by the other particles of the system.

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