Long-Range Electrostatic Attractions between Identically Charged Particles in Confined Geometries and the Poisson−Boltzmann Theory

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There has been much speculation about the origin of long-range electrostatic attractions between identical colloidal particles in confined geometries. Recently, we proved that such attractive interactions are not to be found in the well-established Poisson−Boltzmann theory, when the particles are immersed in a 1:1 electrolyte whose average ion concentrations are equal. A subsequent approximate analytical investigation (*Europhys. Lett.* **1999**, *46*, 407−413) has suggested that such attractive interactions result from a combination of the effects of confinement, imbalance of the average ionic concentrations, and polarization effects in the confining surface. Consequently, we extend our previous proof to encompass the general case of an electrolyte possessing any number of ionic species, where there is no restriction on their average concentrations. In so doing, we rigorously prove that within the framework of the Poisson−Boltzmann theory the interaction between identical colloidal particles is never attractive, irrespective of whether the particles are isolated or confined. Furthermore, we establish a necessary condition for the existence of attractive interactions, which indicates the possibility that an osmotically driven process is behind the observed attractive interactions.

1. Introduction

Recently, a great deal of effort has focused on understanding the mechanism behind the phenomenon of long-range electrostatic attraction between identically charged colloidal particles that are immersed in an electrolyte and confined by a third charged body.[1−13] It has been noted that this surprising phenomenon is at odds with the well-established theory of Derjaguin−Landau−Verwey−Overbeek (DLVO),[14,15,16] for the pairwise interaction of two isolated identically charged particles, which predicts a purely repulsive interaction. A significant clue to the mechanisms involved, however, lies in the experimental observation that the interaction returns to a purely repulsive one, when the particles are isolated from the confining surface.[3,6] Consequently, many workers have suggested that such attractive interactions are to be found naturally within the framework of the well-known Poisson−Boltzmann theory, upon which DLVO theory is founded, provided the effects of the confining charged body

are rigorously taken into account. Indeed, this was the contention of a recent numerical study,[10] which examined the behavior of two colloidal spheres confined in a cylindrical tube. In particular, the study in ref 10 considered the special case where the particles are immersed in a 1:1 electrolyte and all surfaces are of the constant potential type. The governing equation for the electric potential ψ in the electrolye used in ref 10 is the usual Poisson−Boltzmann equation

$$\nabla^2 \psi = \left(\frac{k_B T}{e_0}\right)\kappa^2 \sinh\left(\frac{e_0 \psi}{k_B T}\right) \qquad (1)$$

where κ is the Debye screening parameter, e_0 is the proton charge, k_B is the Boltzmann constant, and T is the absolute temperature. We emphasize that within eq 1 is the implicit assumption that the system is connected to a reservoir of electrolyte, for which the average concentrations of co-ions and counterions are equal.

In ref 13 we proved that eq 1 cannot lead to an attractive interaction, irrespective of whether the particles are confined or isolated. This finding is independent of the shape and charge of the colloidal particles and is valid for all boundary conditions on the particles and confining surfaces. We emphasize that the only restriction on the confining surface is that its sides must be parallel to the line joining the centers of the particles. At this stage, we note that Neu[12] gave a proof similar to ours[13] but only considered the case where the confining surface is of the constant potential type. However, Neu[12] made no restriction on the composition and average concentrations of ionic species in the electrolyte and again found that the interaction is purely repulsive. Note that an imbalance in the average concentrations of ionic species can be induced in a closed system that is not connected to a reservoir of electrolyte.

Approximate theoretical work on the Poisson−Boltzmann theory,[11] however, has suggested that attractive

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interactions can arise from the combination of three effects:

(a) geometrical confinement by a charged surface,

(b) imbalance in the average ionic concentrations of the electrolyte, and

(c) polarization effects in the confining surface resulting from its finite permittivity.

Such cases are not completely covered by either proof in refs 12 and 13. In particular, ref 12 considers cases a and b, but not c, whereas ref 13 considers cases a and c but not b. Consequently, in this paper we extend our proof in ref 13 and relax any restrictions on the ionic composition of the electrolyte, such as those implicit in eq 1. In particular, we allow for any number and type of ionic species in the electrolyte and make no restriction on the average concentration of ionic species. In so doing, we give a complete and general rigorous proof that the full Poisson–Boltzmann theory cannot account for the observed attractive interactions discussed above; i.e., within the framework of the Poisson–Boltzmann theory the interaction between identically charged particles is never attractive. We emphasize that this proof is valid for all boundary conditions on the surface and particles and is independent of the average concentration of ionic species. The only restriction is that the sides of the confining surface must be parallel to the line joining the centers of the particles. Consequently, our results prove that the experimentally observed attractive interactions[1-6] are not to be found within the theoretical framework of the Poisson–Boltzmann theory and suggest either (a) the need for revision of the existing and established colloidal theories or (b) a reassessment of the experimental techniques and the corresponding interpretation of experimental observations.

In addition to proving that the Poisson–Boltzmann theory cannot account for the observed attractive interactions, we also give a necessary condition for the existence of an attractive interaction between identically charged particles, which until now has remained elusive. This condition provides insight into the relevant mechanisms involved by indicating the possibility that an osmotically driven process underlies the phenomenon. Such a mechanism supports the observation that attractive interactions between confined identical particles are only observed when the particles are many Debye lengths apart,[1-6] where the electrical component of the force is expected to be negligible. It remains to be seen whether higher-order corrections to the Poisson–Boltzmann theory, such as the inclusion of ion–ion correlation and finite ion size effects, can induce such necessary osmotic effects.

We commence by defining the problem under consideration in section 2. This will be followed in section 3 with a derivation of the governing equations for the electric potential and osmotic pressure, within the framework of the Poisson–Boltzmann theory. In section 4, we will derive an exact and explicit expression for the force between the particles that is valid for any electrolyte model. In section 5, the implications of the results presented in sections 3 and 4 will be examined. In particular, an examination of the predictions of the Poisson–Boltzmann model will be given in section 5a, whereas in section 5b we will present a necessary condition for an attractive interaction that is valid for any electrolyte model. A listing of all variables and symbols is given in the Glossary.

2. Problem Statement

We consider the problem of two identically charged particles that are immersed in an electrolyte and confined
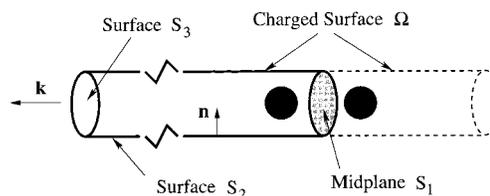
Figure 1. Schematic diagram of two identically charged particles (filled spheres) confined in a charged cylindrical pore Ω. The particles are immersed in an electrolyte which is bounded by the surface Ω. The region exterior to the electrolyte has constant permittivity. The integration surface S used in the evaluation of the force encloses one of the particles, and its subsurfaces S_1, S_2, and S_3 are indicated. Also indicated are the unit vectors $\mathbf{k}$ and $\mathbf{n}$.

to or in the vicinity of an arbitrary charged surface Ω which is parallel to the line connecting the centers of mass of the two particles. The particles need not be spherical and may have arbitrary charge properties. The only requirement is that the electric potential possesses mirror symmetry about the midplane between the particles. The electrolyte may have any number of ionic species and we make no restriction on the average concentrations of each ionic species, but only require the entire system be charge neutral; i.e., the total charge due to the colloidal particles, the confining surface, and the ionic species sum to zero. Consequently, the following analysis is applicable to systems that are connected to a "reservoir" of electrolyte and to systems which are in themselves closed. In the latter case, the average ionic concentrations are determined by requiring the closed system to be charge neutral, whereas in the former case charge neutrality in the reservoir is invoked. The electrolyte is confined to the interior of the surface Ω where the particles lie, and the region exterior to the electrolyte has constant permittivity. The surface Ω maintains either constant potential or constant charge density or is charge regulating.[17-19]

We emphasize that the above specifications encompass many cases of practical interest including that of two particles in the vicinity of a single planar wall,[6] particles confined between two walls,[1-5] or particles confined in a cylindrical pore[10] (see Figure 1). In the following sections we derive completely general and exact expressions for the force of interaction between the particles, for each of the boundary conditions on the confining surface Ω.

3. Poisson–Boltzmann Model

To begin, we derive the governing equations for the electric potential ψ and osmotic pressure Π in the electrolyte, within the framework of the Poisson–Boltzmann theory, and give the governing equation for the electrostatic potential ϕ in the region exterior to the electrolyte. For clarity, all results derived within the framework of the Poisson–Boltzmann theory shall henceforth be indicated using the symbol PB.

The electric potential ψ in the electrolyte is determined by the Poisson equation

$$\nabla^2 \psi = -\rho/\epsilon \qquad (2)$$

where ϵ is the permittivity of the electrolyte and ρ is the local volume density of charge in the electrolyte which is

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given by

$$\rho = \sum_i n_i \, z_i \, e_0 \tag{3}$$

The summation in eq 3 is over all ionic species, whereas z_i is the valency of ionic species i, and n_i is the local ion number density of species i. To calculate the local ion number density n_i, we use the Boltzmann equation, neglecting all ion–ion correlation and finite ion size effects. This results in the following approximate mean-field expression for the ith ionic species

$$n_i = n_i^{(0)} \exp\left(-\frac{z_i e_0}{k_B T}\psi\right) \tag{4}$$

where $n_i^{(0)}$ is the average ion number density of the ith species of the electrolyte, whose value is specified by the charge neutrality condition for the system. Because we are considering a completely general system, which may or may not be in contact with a reservoir of electrolyte, we make no restrictions on $n_i^{(0)}$ but simply note that they are nonnegative numbers; i.e., $n_i^{(0)} \geq 0$.

The governing equation for the scaled electric potential $y = e_0\psi/(k_B T)$ in the electrolyte is then obtained by substituting eqs 3 and 4 into eq 2, which gives the required result

$$\nabla^2 y_{PB} = -\lambda \sum_i n_i^{(0)} \, z_i \exp(-z_i \, y_{PB}) \tag{5}$$

where

$$\lambda = e_0^2/(\epsilon \, k_B T) \tag{6}$$

In the region outside the confining surface Ω (i.e., exterior to the electrolyte), whose permittivity is constant, the electric potential ϕ is determined by the Laplace equation

$$\nabla^2 \phi = 0 \tag{7}$$

Next we turn our attention to the osmotic pressure Π in the electrolyte, which is calculated by considering only the "ideal gas" contribution

$$\Pi = k_B T \sum_i n_i \tag{8}$$

This approach implicitly neglects all ion–ion correlation and finite ion size effects and is chosen to ensure consistency with the approximate Boltzmann distribution for the ion densities in the electrolyte (eq 4). Substituting eq 4 into eq 8 and defining a scaled osmotic pressure $G = \Pi/(k_B T)$, we then obtained the required result

$$G_{PB} = \sum_i n_i^{(0)} \exp(-z_i \, y_{PB}) \tag{9}$$

Equations 5, 7, and 9 are the governing equations we seek for (a) the electric potential in the electrolyte, (b) the electric potential in the dielectric medium exterior to the electrolyte, and (c) the osmotic pressure in the electrolyte, which have been obtained within the framework of the Poisson–Boltzmann theory. To determine the general nature of the force between the particles, however, we do not need to solve eqs 5 and 7, as we shall discuss below.

4. Exact Expression for the Force

In this section we derive an exact expression for the force between the two particles that is valid for any electrolyte model and any boundary conditions on the particles and confining surface Ω. We emphasize that the Poisson–Boltzmann or any other approximation is not used at any stage in this general derivation.

To begin, we note that a formally exact expression for the electrostatic force f between the particles, acting along their line of centers, is obtained by integrating the Maxwell stress tensor[17] over an appropriate surface S enclosing one of the particles within the electrolyte

$$f = \int_S \mathbf{n} \cdot \left[\left(\Pi + \frac{1}{2}\epsilon E^2\right)\mathbf{I} - \epsilon \mathbf{EE}\right] \cdot \mathbf{k} \, dS \tag{10}$$

where Π is the osmotic pressure in the electrolyte and $\mathbf{E} = -\nabla\psi$ is the electric field in the electrolyte, $\mathbf{n}$ is the unit normal vector directed toward the enclosed particle from the surface S, and $\mathbf{k}$ is the unit normal vector pointing away from the unenclosed particle, that is in the line joining the centers of the particles. A repulsive force between the particles corresponds to f being positive.

The choice of the surface S is completely arbitrary and will give the same result provided it completely encloses one of the particles. For convenience we choose the surface S to be a cylinder of arbitrary cross section with the following:

(a) One face of S coincides with the midplane between the particles, denoted S_1.

(b) The sides of cylinder S, denoted S_2, are parallel to the line of centers of the particles and are either lying on the charged surface Ω or at an infinite distance from the particles (e.g., in the case Ω is a single flat wall).

(c) The remaining face of S, denoted S_3, is identical and parallel to the face at the midplane S_1 but located at an infinite distance along the cylinder axis from S_1 and the interacting particles.

A graphical example of this surface for two particles confined in a cylindrical pore is given in Figure 1.

To calculate the force f, we first note that the electric potential is symmetric about the midplane S_1 and does not vary in the $\mathbf{k}$ direction at S_3. It then follows that the components of the electric field in the $\mathbf{k}$ direction at S_1 and S_3 are zero. Using these properties, we then separate eq 10 into three integrals over S_1, S_2, and S_3, giving

$$f = f_1 + f_2 + f_3 \tag{11}$$

where f_i is the component of the surface integral in eq 10 over surface S_i and is given by

$$f_1 = \epsilon \left(\frac{k_B T}{e_0}\right)^2 \int_{S_1} \lambda G + \frac{1}{2}|\nabla_t \, y|^2 \, dS_1 \tag{12a}$$

$$f_2 = -\epsilon \left(\frac{k_B T}{e_0}\right)^2 \int_{S_2} \mathbf{n} \cdot \left(\frac{\partial y}{\partial z}\nabla y\right) dS_2 \tag{12b}$$

$$f_3 = -\epsilon \left(\frac{k_B T}{e_0}\right)^2 \int_{S_3} \lambda G + \frac{1}{2}|\nabla_t \, y|^2 \, dS_3 \tag{12c}$$

where z is the spatial coordinate that is parallel to and increasing in the $\mathbf{k}$ direction and ∇_t is the gradient operator in directions transverse to the $\mathbf{k}$ direction, i.e., directions parallel to the midplane between the particles.

To obtain insight into the nature of the force between the particles, we first express the scaled electric potential y as the sum of the potential y_3 in the electrolyte due to

the charged surface Ω in isolation (i.e., with the particles removed), and a correction potential $\hat{y}$ that accounts for the presence of the particles, i.e.

$$y \equiv y_3 + \hat{y} \tag{13}$$

We emphasize that this decomposition of the potential y is completely general and is exact. Furthermore, we note that y_3 is independent of z and is identical to the potential at the surface S_3. Substituting eq 13 into eq 12, we then obtain

$$f_1 = \epsilon\left(\frac{k_B T}{e_0}\right)^2 \int_{S_1} \lambda G + \frac{1}{2}|\nabla_t(y_3 + \hat{y})|^2 \, dS_1 \tag{14a}$$

$$f_2 = -\epsilon\left(\frac{k_B T}{e_0}\right)^2 \int_{S_2} \mathbf{n}\cdot\left(\frac{\partial\hat{y}}{\partial z}\nabla(y_3 + \hat{y})\right) dS_2 \tag{14b}$$

$$f_3 = -\epsilon\left(\frac{k_B T}{e_0}\right)^2 \int_{S_3} \lambda G + \frac{1}{2}|\nabla_t y_3|^2 \, dS_3 \tag{14c}$$

We now expand the integrands of eqs 14 to eliminate any repeated terms. To begin, we expand the second term in the integrand of eq 14a using the vector identity for the dot product

$$\frac{1}{2}|\nabla_t(y_3 + \hat{y})|^2 = \frac{1}{2}|\nabla_t \hat{y}|^2 + \frac{1}{2}|\nabla_t y_3|^2 + \nabla_t\cdot(\hat{y}\nabla_t y_3) - \hat{y}\nabla_t^2 y_3 \tag{15}$$

Then we note that the surface integral over S_1 of the third term on the right-hand side of eq 15 can be reduced to a line integral over the perimeter of S_1 using Green's theorem,[20] from which we obtain

$$\int_{S_1} \nabla_t\cdot(\hat{y}\nabla_t y_3) \, dS_1 = -\oint_{l_1} \mathbf{n}\cdot\hat{y}\nabla_t y_3 \, dl_1 \tag{16}$$

where l_1 is the perimeter of surface S_1. Using eqs 15 and 16, the expression for f_1 in eq 14a becomes

$$f_1 = \epsilon\left(\frac{k_B T}{e_0}\right)^2\left[\int_{S_1}\left(\lambda G + \frac{1}{2}|\nabla_t \hat{y}_1|^2 + \frac{1}{2}|\nabla_t y_3|^2 - \hat{y}_1\nabla_t^2 y_3\right) dS_1 - \oint_{l_1} \hat{y}_1\mathbf{n}\cdot\nabla_t y_3 \, dl_1\right] \tag{17}$$

where $\hat{y}_1$ is the scaled correction potential evaluated at the surface S_1.

Next, we turn our attention to the integrand for f_2 in eq 14b. To begin, we express the surface integral over S_2 as a double integral whose components are over the length and perimeter of S_2, i.e., $dS_2 = dz \, dl_2$, where l_2 is the perimeter of S_2. At this stage we note that the perimeter (or path) l_1 is identical with l_2, because the sides of S_2 are parallel to the line of centers of the particles. Using this property and noting that y_3 is independent of the spatial coordinate z, it then follows that eq 14b can be rewritten as

$$f_2 = \epsilon\left(\frac{k_B T}{e_0}\right)^2\left[-\int_{S_2}\mathbf{n}\cdot\left(\frac{\partial\hat{y}}{\partial z}\nabla\hat{y}\right) dS_2 + \oint_{l_1} \hat{y}_1\mathbf{n}\cdot\nabla_t y_3 \, dl_1\right] \tag{18}$$

Substituting eqs 14c, 17, and 18 into eq 11 and noting that S_1 and S_3 are identical surfaces which have been

(20) Jeffreys, H.; Jeffreys, B. *Methods of Mathematical Physics*; Cambridge University Press: Cambridge, U.K., 1992.

shifted in z, it then follows that the line integrals in eqs 17 and 18 cancel and we obtain the following expression for the force

$$f = \epsilon\left(\frac{k_B T}{e_0}\right)^2\left[\int_{S_1}\left(\lambda[G_1 - G_3] - \hat{y}_1\nabla_t^2 y_3 + \frac{1}{2}\left|\nabla_t \hat{y}_1\right|^2\right) dS_1 - \int_{S_2}\mathbf{n}\cdot\left(\frac{\partial\hat{y}}{\partial z}\nabla\hat{y}\right) dS_2\right] \tag{19}$$

where G_1 and G_3 are the scaled osmotic pressures evaluated at the surfaces S_1 and S_3, respectively.

We now turn our attention to the surface integral over S_2, henceforth denoted I,

$$I = -\int_{S_2}\mathbf{n}\cdot\left(\frac{\partial\hat{y}}{\partial z}\nabla\hat{y}\right) dS_2 \tag{20}$$

and examine the nature of its behavior for various boundary conditions on the surface Ω (because S_2 is a subsurface of Ω). In particular, we consider the boundary conditions of (a) constant surface potential, (b) constant surface charge density, and (c) charge regulation. We emphasize that these boundary conditions encompass all possible cases that are encountered in practice.

4a. Constant Potential Surface Ω. To begin, we examine the case where Ω is held at constant surface potential. Here the electric potential at the surface Ω is unchanged by the presence of the particles, i.e., $\hat{y} = 0$ at Ω. Because S_2 is a subsurface of Ω, it also follows that $\hat{y} = 0$ at S_2. Substituting $\hat{y} = 0$ into eq 20, we then obtain the trivial result

$$I = 0 \tag{21}$$

Therefore, for constant potential boundary conditions on the surface Ω, the integral I does not contribute to the force.

4b. Constant Charge Surface Ω. Next we consider the case where Ω is held at a constant charge density σ. This corresponds to requiring that (a) the tangential components of the electric field interior and exterior to the electrolyte be continuous across Ω, and (b) the difference in the interior and exterior components of the dielectric displacement, which are normal to the surface Ω, be equal to the charge density at Ω. Expressed in terms of the electric potential, these conditions become

$$\frac{\partial y}{\partial z} = \frac{\partial p}{\partial z} \quad \text{at } \Omega \tag{22a}$$

$$\epsilon_{\text{ext}}\mathbf{n}\cdot\nabla p - \epsilon\mathbf{n}\cdot\nabla y = \sigma_s \quad \text{at } \Omega \tag{22b}$$

where $p = e_0\phi/(k_B T)$, $\sigma_s = e_0\sigma/(k_B T)$, and ϵ_{ext} is the permittivity of the region exterior to the electrolyte. Because Ω is held at a constant surface charge density, it follows that the isolated electric potentials (in the absence of the particles) interior and exterior to the electrolyte also satisfy eqs 22, i.e.,

$$\frac{\partial y_3}{\partial z} = \frac{\partial p_3}{\partial z} \quad \text{at } \Omega \tag{23a}$$

$$\epsilon_{\text{ext}}\mathbf{n}\cdot\nabla p_3 - \epsilon\mathbf{n}\cdot\nabla y_3 = \sigma_s \quad \text{at } \Omega \tag{23b}$$

where $p_3 = p - \hat{p}$ is the isolated electric potential exterior to the electrolyte and $\hat{p}$ is the correction potential that accounts for the presence of the particles. Subtracting eqs 23 from eqs 22, it then follows that the required boundary

conditions for the correction potentials $\hat{y}$ and $\hat{p}$ at the surface Ω are

$$\frac{\partial \hat{y}}{\partial z} = \frac{\partial \hat{p}}{\partial z} \quad \text{at } \Omega \quad (24a)$$

$$\epsilon_{\text{ext}} \mathbf{n} \cdot \nabla \hat{p} = \epsilon \mathbf{n} \cdot \nabla \hat{y} \quad \text{at } \Omega \quad (24b)$$

We now define $\hat{q}$ to be the correction potential exterior to the region enclosed by S, so that $\hat{q} = \hat{y}$ in the electrolyte and $\hat{q} = \hat{p}$ in regions exterior to the electrolyte. Using this definition and the boundary conditions in eqs 24, we are now able to simplify the expression for I in eq 20. First, we express the surface integral I in terms of the correction potential $\hat{q}$ exterior to the region enclosed by S

$$I = -\frac{\epsilon_{\text{ext}}}{\epsilon} \int_{S_2} \mathbf{n} \cdot \left(\frac{\partial \hat{q}}{\partial z} \nabla \hat{q} \right) \mathrm{d}S_2 \quad (25)$$

Note that, in arriving at eq 25, we have used the property that $\hat{q} = \hat{y} = 0$ on any section of S_2 that does not lie on Ω because these sections must be an infinite distance from the particles (see the definition for S_2 above).

Because the electric potential is symmetric about the midplane between the particles, it follows that the component of the electric field in the $\mathbf{k}$ direction at the midplane is identically zero

$$\partial \hat{q}/\partial z = 0 \quad (26)$$

Using eq 26 and the property that $\hat{q} = 0$ at an infinite distance from the particles, the integral over S_2 in eq 25 can be transformed into an integral over a closed surface S_c, which has the following topology: S_c is composed of four subsurfaces, with
(a) one subsurface of S_c being S_2
(b) another subsurface coinciding with the midplane between the particles that is exterior to the domain enclosed by S, henceforth denoted A,
(c) a third subsurface being the extension of S_3 exterior to the domain enclosed by S, and consequently is parallel to A, and
(d) an arbitrary surface running along the length of S_2, at an infinite distance from S_2, that connects the outer perimeters of the subsurfaces in b and c.

In simple terms: *The surface S_c encloses the domain exterior to that enclosed by S, that is, on the same side of the midplane as S.* A schematic illustration of this closed surface for the case of two particles confined to a cylindrical pore is given in Figure 2. Consequently, eq 25 becomes

$$I = -\frac{\epsilon_{\text{ext}}}{\epsilon} \oint_{S_c} \mathbf{n}_1 \cdot \left(\frac{\partial \hat{q}}{\partial z} \nabla \hat{q} \right) \mathrm{d}S_2 \quad (27)$$

where $\mathbf{n}_1$ is the outward unit normal vector to S_c, and is identical to $\mathbf{n}$ at the subsurface S_2. Note that the only subsurface of S_c which gives a nonzero contribution in eq 27 is S_2. However, by expressing I as an integral over a closed surface, we can now invoke Gauss's theorem[20] and replace the surface integral over S_c by a volume integral over the region V enclosed by the surface S_c

$$I = -\frac{\epsilon_{\text{ext}}}{\epsilon} \int_V \nabla \cdot \left(\frac{\partial \hat{q}}{\partial z} \nabla \hat{q} \right) \mathrm{d}V \quad (28)$$

Expanding the integrand of eq 28 using the product rule for the divergence operator and noting that (a) $\hat{q} = \hat{y} = 0$ in regions of V that lie in the electrolyte and (b) $\nabla^2 \hat{q} = \nabla^2 \hat{p} = 0$ in regions of V exterior to the electrolyte (which is
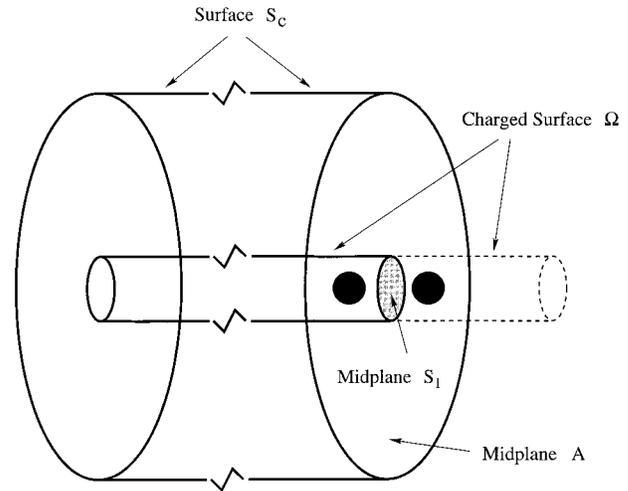
Figure 2. Schematic diagram showing the closed surface S_c in the region exterior to that enclosed by S, which is on the same side of the midplane as S. Also shown is the midplane S_1 and the midplane A exterior to the region enclosed by S.

exact for such regions, see eq 7), it is then very easy to show that

$$I = -\frac{\epsilon_{\text{ext}}}{\epsilon} \int_V \frac{1}{2} \frac{\partial}{\partial z} |\nabla \hat{q}|^2 \, \mathrm{d}V \quad (29)$$

Finally, we evaluate the volume integral in eq 29 by separating it into a line integral over the length of S_2 (i.e., with respect to the z coordinate) and a surface integral over the surface that is parallel to A. The integral with respect to z in eq 29 is then explicitly evaluated, and upon imposing the condition $\hat{q} = 0$ at an infinite distance from the particles, we obtain the required result

$$I = \frac{\epsilon_{\text{ext}}}{\epsilon} \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, \mathrm{d}A \quad (30)$$

Note that the integral in eq 30 is performed over the midplane A that is exterior to the domain enclosed by S. Because the integrand of eq 30 is always nonnegative, it follows that I is also always nonnegative. We shall discuss the implications of this finding below.

4c. Charge Regulating Surface Ω. The final boundary condition to be considered is that where the surface Ω is charge regulating; i.e., the charge density on the surface Ω is a function of the surface potential. In terms of the electric potential, this boundary condition becomes

$$\frac{\partial y}{\partial z} = \frac{\partial p}{\partial z} \quad \text{at } \Omega \quad (31a)$$

$$\epsilon_{\text{ext}} \mathbf{n} \cdot \nabla p - \epsilon \mathbf{n} \cdot \nabla y = \sigma_s(y) \quad \text{at } \Omega \quad (31b)$$

where σ_s is as defined in the preceding section but is now allowed to be a function of the potential y at the surface Ω. We remind the reader that constant potential and constant charge density boundary conditions are limiting cases of this very general boundary condition.[17−19]

The isolated potentials y_3 and p_3 also must satisfy eqs 31, i.e.,

$$\frac{\partial y_3}{\partial z} = \frac{\partial p_3}{\partial z} \quad \text{at } \Omega \quad (32a)$$

$$\epsilon_{\text{ext}} \mathbf{n} \cdot \nabla p_3 - \epsilon \mathbf{n} \cdot \nabla y_3 = \sigma_s(y_3) \quad \text{at } \Omega \quad (32b)$$

However, unlike the previous case, note that the right-hand sides of eqs 31b and 32b are unequal in general. Subtracting eqs 32 from eqs 31, we then obtain the required boundary conditions for the correction potentials $\hat{y}$ and $\hat{p}$

$$\frac{\partial \hat{y}}{\partial z} = \frac{\partial \hat{p}}{\partial z} \qquad \text{at } \Omega \qquad (33a)$$

$$\epsilon_{\text{ext}} \mathbf{n} \cdot \nabla \hat{p} - \epsilon \mathbf{n} \cdot \nabla \hat{y} = \sigma_s(y_3 + \hat{y}) - \sigma_s(y_3) \qquad \text{at } \Omega \quad (33b)$$

which will now be used to simplify the expression for I in eq 20. Substituting eqs 33 into eq 20 and noting that $\hat{y} = \hat{p}$ and $y_3 = p_3$ at the surface Ω then gives the following result for I:

$$I = -\frac{\epsilon_{\text{ext}}}{\epsilon} \int_{S_2} \mathbf{n} \cdot \left(\frac{\partial \hat{q}}{\partial Z} \nabla \hat{q} \right) dS_2 + \frac{1}{\epsilon} \int_{S_2} \frac{\partial \hat{q}}{\partial Z} (\sigma_s(p_3 + \hat{q}) - \sigma_s(p_3)) \, dS_2 \quad (34)$$

where $\hat{q}$ is the correction potential exterior to the region enclosed by S, as defined above, and we have again used the property that $\hat{q} = 0$ on any section of S_2 that does not lie on Ω.

The first integral in eq 34 is simplified in a manner identical to that performed in the previous section, resulting in

$$I = \frac{\epsilon_{\text{ext}}}{\epsilon} \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, dA + \frac{1}{\epsilon} \int_{S_2} \frac{\partial \hat{q}}{\partial Z} (\sigma_s(p_3 + \hat{q}) - \sigma_s(p_3)) \, dS_2 \quad (35)$$

Then the surface integral over S_2 in eq 35 is expressed as a double integral over the perimeter and length of S_2, i.e., $dS_2 = dz \, dl_2$. This enables the variables of integration to be changed, from which we obtain

$$I = \frac{\epsilon_{\text{ext}}}{\epsilon} \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, dA + \frac{1}{\epsilon} \oint_{l_2} \int_{\hat{q}_1}^{\hat{q}_3} (\sigma_s(p_3 + \hat{q}) - \sigma_s(p_3)) \, d\hat{q} \, dl_2 \quad (36)$$

where $\hat{q}_1$ and $\hat{q}_3$ are the correction potentials at the perimeters of subsurfaces S_1 and S_3, respectively. In eq 36 we have used the property that the perimeters of subsurface S_1 and S_3 form the boundaries of subsurface S_2 (see Figure 1). Noting that $\sigma_s(p_3)$ is independent of $\hat{q}$ and $\hat{q}_3 = 0$, as discussed above, we then obtain the required result for I

$$I = \frac{\epsilon_{\text{ext}}}{\epsilon} \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, dA + \frac{1}{\epsilon} \oint_{l_1} [\hat{q}_1 \sigma_s(p_3) - \int_0^{\hat{q}_1} \sigma_s(p_3 + \hat{q}) \, d\hat{q}] \, dl_1 \quad (37)$$

where we have used the property that l_1 and l_2 are identical paths.

The nature of I in eq 37 can be examined by noting that if σ_s satisfies

$$\partial \sigma_s(y)/\partial y \leq 0 \qquad (38a)$$

then the following inequality always holds:

$$\hat{q}_1 \sigma_s(p_3) \geq \int_0^{\hat{q}_1} \sigma_s(p_3 + \hat{q}) \, d\hat{q} \qquad (38b)$$

We emphasize that this result is independent of the values of p_3 and $\hat{q}_1$. Because the inequalities in eqs 38 are always

satisfied, as we shall discuss below, it then follows that I is always nonnegative for a charge regulating surface Ω.

4d. Complete Expression for the Force. Combining eq 19 with the above results for the confining surface Ω held at (a) constant potential (eq 21) (b) constant charge density (eq 30), and (c) charge regulation (eq 37), we obtain the complete expression for the force between the two particles

$$f = \epsilon \left(\frac{k_B T}{e_0} \right)^2 \left[\int_{S_1} \left(\lambda [G_1 - G_3] - \hat{y}_1 \nabla_t^2 y_3 + \frac{1}{2} |\nabla_t \hat{y}_1|^2 \right) dS_1 + I \right] \quad (39)$$

where

$$I = \frac{\epsilon_{\text{ext}}}{\epsilon} \times$$

$$\begin{cases} 0 & \text{constant potential } \Omega \\ \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, dA & \text{constant charge } \Omega \\ \int_A \frac{1}{2} |\nabla \hat{q}|^2 \, dA + \frac{1}{\epsilon_{\text{ext}}} \oint_{l_1} [\hat{q}_1 \sigma_s(p_3) - \\ \qquad \int_0^{\hat{q}_1} \sigma_s(p_3 + \hat{q}) \, d\hat{q}] \, dl_1 & \text{charge regulating } \Omega \end{cases}$$

$$(40)$$

We emphasize that eqs 39 and 40 are exact results that are valid for any electrolyte model.

5. Theoretical Implications

An exact and explicit expression for the force of interaction f, which is valid for any electrolyte model and all boundary conditions of practical interest on the surface Ω, was evaluated in the previous section. In this section, we examine the implications of this result to the nature of the force between the particles.

5a. Poisson–Boltzmann Theory. To begin, we implement eqs 39 and 40 in examining the predictions of the Poisson–Boltzmann electrolyte model. Because y_3 is independent of the spatial coordinate z, it follows from eq 5 that

$$\text{(PB)} \qquad \nabla_t^2 y_3 = \nabla^2 y_3 = - \lambda \sum_i n_i^{(0)} z_i \exp(-z_i y_3) \quad (41)$$

Substituting eq 41 and the expression for the osmotic pressure that is consistent with the Poisson–Boltzmann approximation (eq 9) into eq 39 then gives the required result for the force

$$f_{\text{PB}} = \epsilon \left(\frac{k_B T}{e_0} \right)^2 \left[\int_{S_1} \left(\lambda \sum_i n_i^{(0)} \exp(-z_i y_3)(\exp(-z_i \hat{y}_1) + z_i \hat{y}_1 - 1) + \frac{1}{2} |\nabla_t \hat{y}_1|^2 \right) dS_1 + I \right] \quad (42)$$

where I remains unchanged from eq 40.

Next, we note that all known mechanisms and models for ionizable or charge regulating surfaces[21−24] satisfy

$$\partial\sigma_s(y)/\partial y \le 0 \tag{43}$$

Indeed, within the framework of the Poisson−Boltzmann theory, a unique solution to the electric potential exists only if this constraint is satisfied.[18,19] Consequently, upon returning to eqs 38, we find that $I \ge 0$, irrespective of whether the confining surface Ω is held at constant potential or constant charge density or is charge regulating. Furthermore, because (a) $\lambda > 0$, (b) $n_i^{(0)} \ge 0$, and (c) $\exp(-z_i\,\hat{y}_1) + z_i\,\hat{y}_1 - 1 \ge 0$ for all values of z_i and $\hat{y}_1$, it is then clear that all of the integrands in eq 42 are nonnegative. The implications of this finding are truly significant, because they prove that within the framework of the Poisson−Boltzmann theory f_{PB} is always nonnegative, indicating that the force between the particles is *never attractive*. We emphasize that this conclusion is independent of the boundary conditions on the confining surface Ω and on the particles and is valid for any particle shape and charge.

5b. Condition for Attraction. By examining the general expression for the force in eqs 39 and 40, we now establish a necessary condition for an attractive interaction. We remind the reader that eqs 39 and 40 are exact expressions that are valid for any electrolyte model. Consequently, from eqs 39 and 40, it then follows that a negative value for f (i.e., an attractive interaction) is only possible if either or both of the following conditions are satisfied:

$$\int_{S_1}(\lambda[G_1 - G_3] - \hat{y}_1\nabla_t^2 y_3)\,dS_1 < 0 \tag{44a}$$

$$\partial\sigma_s(y)/\partial y > 0 \tag{44b}$$

The second condition appears unlikely, because all known mechanisms and models for charge regulation satisfy the opposite condition, as discussed above. This leaves the inequality in eq 44a as the only plausible condition for an attractive interaction. We emphasize that the satisfaction of eq 44a does not guarantee an attractive interaction but indicates that the possibility exists. If the condition in eq 44a is not satisfied, however, then an attractive interaction is impossible.

Using the Poisson equation (eq 2), eq 44a can be written in terms of the volume charge density ρ_3 in the electrolyte due to the confining surface Ω in the absence of the particles,

$$\int_{S_1}(\Delta\Pi + \rho_3\Delta\psi)\,dS_1 < 0 \tag{45}$$

where $\Delta\Pi = \Pi_1 - \Pi_3$ is the difference in the osmotic pressure in the electrolyte at the midplane S_1 and an infinite distance from the midplane at S_3, whereas $\Delta\psi = \psi_1 - \psi_3$ is the difference in the electric potential in the electrolyte at the midplane S_1 and an infinite distance from the midplane at S_3. Equation 45 is the result we seek and is a necessary condition for an attractive interaction. We emphasize that eq 45 is valid, irrespective of whether the particles are confined or isolated, and indicates the

possibility that the osmotic pressure is primarily responsible for attractive interactions between identically charged particles.

6. Conclusions

We have given a complete and general proof that, within the framework of the Poisson−Boltzmann theory, the interaction between two identically charged particles is never attractive. This finding is independent of (a) the charge and shape of the particles, (b) the boundary conditions on the particles and confining surface, (c) the composition of the electrolyte, and (d) the average ion concentrations and (e) is valid whether the particles are confined or isolated. The only restriction is that the sides of the confining surface must be parallel to the line of centers of the particles. Consequently, the observed long-range electrostatic attraction between like-charged particles cannot be accounted for using this well-established theory, contrary to previous suggestions and theoretical calculations.[1,3,5,6,10,11,13] An alternative theory[7−9] has been proposed to explain this phenomenon, but its predictions are also inconsistent with experimental observations.[3,6]

We also established a necessary condition for the existence of an attractive interaction, which is valid for any electrolyte model. This condition indicates the possibility that an osmotically driven process is behind the observed attractive interactions between like-charged particles. It remains to be seen whether (a) the inclusion of ion−ion correlation and finite ion size effects, which are absent from the Poisson−Boltzmann theory, can produce such osmotic effects and result in an attractive interaction between like-charged particles or (b) the origin of such attractive interactions lies in experimental phenomena that have not been interpreted correctly.

Glossary

A	midplane between the particles, exterior to the region enclosed by S
e_0	proton charge
E	electric field vector
E	magnitude of electric field vector
f	force between the particles, acting along their line of centers
f_i	component of surface integral eq 10, over surface S_i
G	scaled osmotic pressure, $G = \Pi/(k_B T)$
G_i	scaled osmotic pressure at subsurface S_i
I	integral defined in eq 20
I	unit tensor
k	unit vector pointing away from the unenclosed particle in eq 2, which is in the line joining the centers of the particles
k_B	Boltzmann constant
l_i	perimeter of subsurface S_i
n_i	local ion number density of species i
$n_i^{(0)}$	average ion number density of species i
n	unit normal vector directed toward the enclosed particle from the surface S
$\mathbf{n}_1$	outward unit normal vector to surface S_c

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p	scaled electric potential exterior to electrolyte, $p = e_0\phi/(k_B T)$
p_3	scaled electric potential exterior to electrolyte in the absence of the particles
$\hat{p}$	difference between the scaled potential exterior to the electrolyte and that due to the surface Ω in isolation, $\hat{p} = p - p_3$
PB	use of the approximate Poisson–Boltzmann electrolyte model
$\hat{q}$	correction potential exterior to the region enclosed by S; $\hat{q} = \hat{y}$ in the electrolyte and $\hat{q} = \hat{p}$ in regions exterior to the electrolyte
$\hat{q}_i$	$\hat{q}$ evaluated at the perimeter of subsurface S_i
S	integration surface
S_1, S_2, S_3	subsurfaces of integration surface S
S_c	surface enclosing domain exterior to that enclosed by S, which is on the same side of the midplane as S
T	absolute temperature
V	region enclosed by the surface S_c
y	scaled electric potential in electrolyte, $y = e_0\psi/(k_B T)$
y_i	scaled electric potential in electrolyte at the surface S_i
$\hat{y}$	difference between the scaled potential in the electrolyte and that due to the surface Ω in isolation, $\hat{y} = y - y_3$
$\hat{y}_i$	$\hat{y}$ evaluated at surface S_i
z	spatial coordinate parallel to and increasing in the direction $\mathbf{k}$
z_i	valency of ionic species i
ϵ	permittivity of electrolyte
ϵ_{ext}	permittivity of region exterior to the electrolyte
κ	Debye screening parameter
λ	parameter that is proportional to the Bjerrum length, $\lambda = e_0^2/(\epsilon k_B T)$
ϕ	electric potential exterior to electrolyte
ψ	electric potential in electrolyte
ψ_i	electric potential in electrolyte at subsurface S_i
$\Delta\psi$	difference in electric potential at the midplane S_1 and subsurface S_3, $\Delta\psi = \psi_1 - \psi_3$
ρ	local volume charge density in the electrolyte
ρ_3	local volume charge density in the electrolyte at subsurface S_3
σ	surface charge density at surface Ω
σ_s	scaled surface charge density at surface Ω, $\sigma_s = e_0\sigma/(k_B T)$
$\sigma_s(y)$	scaled surface charge density at surface Ω, which is a function of the surface potential
Ω	confining surface
Π	osmotic pressure
Π_i	osmotic pressure at subsurface S_i
$\Delta\Pi$	difference in osmotic pressures at the midplane S_1 and subsurface S_3, $\Delta\Pi = \Pi_1 - \Pi_3$
∇	three-dimensional gradient operator
∇_t	transverse gradient operator parallel to the midplane between the particles
∇^2	three-dimensional Laplacian operator
∇_t^2	transverse Laplacian operator parallel to the midplane between the particles