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Long-range electrostatic interactions between like-charged colloids: Steric and confinement effects

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Within the framework of a modified Poisson-Boltzmann theory accounting for steric effects of microions, we prove analytically that the effective pair interactions between like-charge colloids immersed in a confined electrolyte are repulsive. Our approach encompasses and extends previously known results to the case of complete confinement, and further incorporates the finite size of the microions which is absent in the standard Poisson-Boltzmann theory. [S1063-651X(99)12012-9]

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Recent experiments show convincingly the existence of long-range electrostatic attractions between like-charge colloids immersed in an electrolyte, in particular in the vicinity of a charged wall or when the particles are confined in a slit [1,2]. These striking observations are inconsistent with the well established theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) [3], and constitute an important controversy in colloid science. Inasmuch as direct measurements of the effective pair interactions in the *bulk* of a suspension confirm the validity of DLVO theory with repulsive interactions [4], confinement effects are thought to play a major role and have been included in numerical [5] and theoretical [6] investigations of the electrostatic forces between colloidal spheres. These studies reported a range of interparticle distances for which the computed forces were attractive. However, Neu [7] rigorously proved that the Poisson-Boltzmann (PB) model considered in Ref. [5] necessarily leads to repulsion. His proof applies within PB theory (which forms the basis of the DLVO potential) in the specific case of Dirichlet boundary conditions (constant electrostatic potential ψ on the confining surface, the experimental relevance of which is dubious). Sader and Chan extended the PB argument to a broader class of boundary conditions [8].

The PB theory is a continuum mean-field approach neglecting statistical correlations between microions, that are assumed to be pointlike. It is known to grossly overestimate counterion concentrations close to a charged surface (e.g., that of a polyion). A modified Poisson-Boltzmann (MPB) theory including steric effects was put forward to overcome this shortcoming [9–12]. This approach retains the simplicity of the original PB theory, and is more tractable than the other attempts to improve upon PB theory by inclusion of steric repulsion [13,14].

In this paper, we consider the MPB model in the situation of a mixture of microions (with overall global electroneutrality). Within this framework, we analyze the interactions between a pair of like-charge polyions immersed in a confined electrolyte of permittivity ε. The colloids may be of arbitrary shape, and the confining region $\mathcal{R}$ is a cylinder of arbitrary cross section. As in Refs. [7,8], the only requirement is that the electrostatic potential ψ possesses mirror symmetry with respect to the midplane $z=0$ between the colloids. Unlike in Refs. [7,8], where $\mathcal{R}$ is of infinite lateral extension, we allow the confining region to be of finite volume (a situation hereafter referred to as finite confinement, which can be that of a pore or of a closed Wigner-Seitz cell). The geometry considered here encompasses many cases of experimental relevance, such as two colloids confined in a slit, in a charged pore or in the vicinity of a wall [1,2,6]. We consider boundary conditions where the medium $\mathcal{R}'$ outside $\mathcal{R}$ is a dielectric continuum of permittivity ε' with the possibility of a uniform density of surface charges σ on the boundary $\partial\mathcal{R}$ (as in Ref. [6]). This class of boundary conditions is large, as for $\sigma=0$ the limit $\varepsilon'\to 0$ reduces to Neuman boundary conditions with a vanishing normal electric field on $\partial\mathcal{R}$, whereas $\varepsilon'\to\infty$ corresponds to the standard Dirichlet condition on $\partial\mathcal{R}$. We show rigorously that the inclusion of excluded volume effects within the MPB approach does not change the sign of the force which remains repulsive as in the PB approach. As the MPB approach gives back the PB theory in the well behaved limit where steric effects disappear, our results also include those reported in Refs. [7,8], and extend them to the situation of finite confinement.

The MPB theory can be obtained from the free energy functional $\mathcal{F}=\mathcal{F}_{\text{Coul}}+\mathcal{F}_{\text{ent}}$ of the inhomogeneous fluid of microions contained in $\mathcal{R}$. Given N species α with a local density $c_\alpha(\boldsymbol{r})$ and charge number z_α, the Coulombic energy contribution to $\mathcal{F}$ reads

$$\mathcal{F}_{\text{Coul}}=\frac{1}{2}\int_{\mathcal{R}}\rho_c(\boldsymbol{r})G(\boldsymbol{r},\boldsymbol{r}')\rho_c(\boldsymbol{r}')d\boldsymbol{r}d\boldsymbol{r}', \tag{1}$$

where $\rho_c(\boldsymbol{r})=\Sigma_\alpha z_\alpha e c_\alpha(\boldsymbol{r})$ is the local charge density and $G(\boldsymbol{r},\boldsymbol{r}')$ is the Green's function inverting the Laplacian inside $\mathcal{R}$ with the required boundary conditions. In the absence

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of confinement, G reduces to the Coulomb potential $1/[4\pi\varepsilon|\boldsymbol{r}-\boldsymbol{r}'|]$. The entropic contribution is

$$\mathcal{F}_{\rm ent}=kT\int_{\mathcal{R}} d\boldsymbol{r}\left\{\sum_{\alpha} c_\alpha[\ln(\Lambda_\alpha^3 c_\alpha)-1] + \frac{1}{a^3}\left[1-\sum_{\alpha} a^3 c_\alpha\right]\ln\left(1-\sum_{\alpha} a^3 c_\alpha\right)\right\}, \tag{2}$$

where Λ_α are irrelevant length scales and $kT\equiv\beta^{-1}$ is the thermal energy. For the sake of simplicity, all types of microions are assumed to have the same size a. The last term in Eq. (2) mimics the entropy of the solvent molecules, while the remaining ones are the ideal entropies of the mixture of coions and counterions. In the limit where $a\to 0$, the steric correction disappears and the classical PB expression is recovered. The equilibrium density profiles are those which minimize the free energy functional $\mathcal{F}$ subject to the constraint that

$$\int_{\mathcal{R}} c_\alpha(\boldsymbol{r})d\boldsymbol{r}=N_\alpha, \tag{3}$$

with N_α the total number of ions α inside $\mathcal{R}$. The minimization yields:

$$c_\alpha(\boldsymbol{r})=\frac{p_\alpha\exp(-\beta e z_\alpha\psi)}{1+\sum_{\alpha} a^3 p_\alpha \exp(-\beta e z_\alpha\psi)}, \tag{4}$$

where $\psi(\boldsymbol{r})=\int_{\mathcal{R}}\rho_c(\boldsymbol{r}')G(\boldsymbol{r},\boldsymbol{r}')d\boldsymbol{r}'$. Since the potential ψ can be shifted by an arbitrary constant, the prefactors p_α have individually no physical significance. In the limit where $\mathcal{R}$ is of infinite extension, ψ is conveniently chosen to vanish far from the polyions and we obtain $p_\alpha=c_\alpha^{\rm bulk}/(1-\Sigma_\alpha a^3 c_\alpha^{\rm bulk})$. In the case of complete confinement, two experimental situations can be distinguished: (a) the solution is of fixed ionic composition (canonical description) and the prefactors p_α are determined by the normalization constraint (3); or (b) the dispersion is in osmotic equilibrium with a salt reservoir, treated within MPB theory for consistency. We then have $p_\alpha=c_\alpha^r/(1-\Sigma_\alpha a^3 c_\alpha^r)$, where c_α^r denotes the concentration of species α in the reservoir (subject to the electroneutrality constraint $\Sigma_\alpha z_\alpha c_\alpha^r=0$). As expected, the density profiles tend to their PB counterparts as the excluded volume $a^3\to 0$.

The force acting on a colloidal particle follows from integration of the stress tensor $\boldsymbol{\Pi}$ over the surface S of the polyion (see Fig. 1),

$$\boldsymbol{F}=\oint_S \boldsymbol{\Pi}\cdot\hat{\boldsymbol{n}}dS, \tag{5}$$

where $\hat{\boldsymbol{n}}$ is the unit vector pointing outward from the surface of integration. The stress tensor can be obtained by considering the mechanical equilibrium condition of a fluid element of microions: the balance between the electric force and the osmotic constraint can be written

$$-\boldsymbol{\nabla}P+\rho_c\boldsymbol{E}=\boldsymbol{0} \tag{6}$$

$$\Leftrightarrow \partial_\psi P=-\rho_c, \tag{7}$$

from which we deduce the expression for the osmotic pressure:

$$P(\psi)=\frac{kT}{a^3}\ln\left[1+\sum_{\alpha} a^3 p_\alpha\exp(-\beta e z_\alpha\psi)\right]. \tag{8}$$

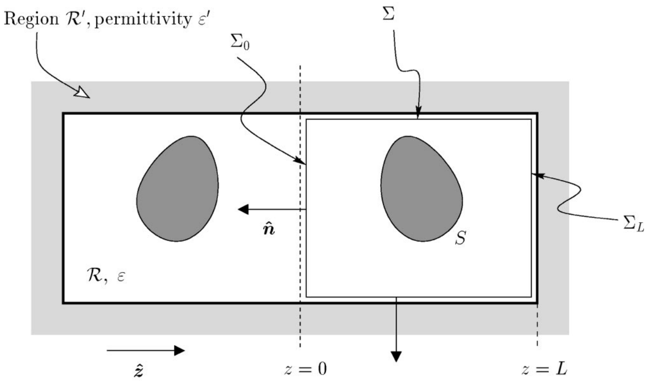

FIG. 1. Schematic side view of the geometry considered. The closed cylinder S' is made of the lateral surface Σ and the two cross sections perpendicular to the Oz axis (Σ_0 and Σ_L). The thick line denotes the boundary $\partial\mathcal{R}$.

Rewriting Eq. (6) as $\boldsymbol{\nabla}\cdot\boldsymbol{\Pi}=\boldsymbol{0}$ finally yields

$$\boldsymbol{\Pi}=-[P(\psi)+\tfrac{1}{2}\boldsymbol{D}\cdot\boldsymbol{E}]\boldsymbol{I}+\boldsymbol{D}\otimes\boldsymbol{E}, \tag{9}$$

where $\boldsymbol{E}=-\boldsymbol{\nabla}\psi$ is the electrostatic field, and $\boldsymbol{D}=\varepsilon\boldsymbol{E}$ and $\boldsymbol{I}$ denotes the identity tensor. It is worthwhile to mention that Poisson's equation can be written in the form

$$\boldsymbol{\nabla}^2\psi=\frac{1}{\varepsilon}\frac{\partial P}{\partial\psi}. \tag{10}$$

As the mechanical equilibrium condition invoked above implies that $\boldsymbol{\Pi}$ is divergence free, the surface of integration in Eq. (5) can be deformed to any surface S' enclosing colloid S only, as stressed in Refs. [7,8]. It is convenient to choose $S'=\Sigma_0\cup\Sigma\cup\Sigma_L$ (see Fig. 1). The z component of the force $\boldsymbol{F}$ then reads

$$F_z=\int_{\Sigma_0\cup\Sigma_L}\hat{\boldsymbol{z}}\cdot\boldsymbol{\Pi}\cdot\hat{\boldsymbol{n}}dS+\int_{\Sigma}\hat{\boldsymbol{z}}\cdot\boldsymbol{\Pi}\cdot\hat{\boldsymbol{n}}dS. \tag{11}$$

On the cross sections Σ_0 and Σ_L, $\hat{\boldsymbol{z}}\cdot\boldsymbol{\Pi}\cdot\hat{\boldsymbol{n}}=[D_zE_z-\boldsymbol{D}\cdot\boldsymbol{E}/2-P(\psi)]\hat{\boldsymbol{z}}\cdot\hat{\boldsymbol{n}}$, while on the lateral surface Σ, $\hat{\boldsymbol{z}}\cdot\boldsymbol{\Pi}\cdot\hat{\boldsymbol{n}}=-\sigma E_z+D_n'E_z'$. In the previous expression, primed symbols refer to the region $\mathcal{R}'$ outside $\mathcal{R}$ (with permittivity ε'), and the dielectric boundary conditions have been used ($D_n'-D_n=\sigma$ and $E_z=E_z'$). The last term in Eq. (11) can be recast by considering the divergence free tensor $\boldsymbol{\Pi}'$ in $\mathcal{R}'$ obeying similar constitutive relations like Eqs. (9) and (8) [we allow the continuum in $\mathcal{R}'$ to contain an electrolyte solution; on the other hand, if no salt is present outside $\mathcal{R}$, the corresponding pressure $P(\psi')$ vanishes in Eq. (8)]. We obtain

$$\int_{\Sigma} D'_n E'_z dS = \int_{\Sigma'_0} \left[\left(D'_z E'_z - \frac{1}{2} \boldsymbol{D}' \cdot \boldsymbol{E}' - P(\psi') \right)_{z=L} - \left(D'_z E'_z - \frac{1}{2} \boldsymbol{D}' \cdot \boldsymbol{E}' - P(\psi') \right)_{z=0} \right] dxdy, \tag{12}$$

where $\Sigma_0 \cup \Sigma'_0$ is the Oxy plane.

Upon substitution of Eq. (12) into Eq. (11), the axial force can be expressed in the form

$$F_z = \int_{Oxy} [P(\psi)_{z=0} - P(\psi)_{z=L}] dxdy + \frac{1}{2} \int_{Oxy} \times [(\boldsymbol{D} \cdot \boldsymbol{E})_{z=0} - (\boldsymbol{D} \cdot \boldsymbol{E})_{z=L}] dxdy - \sigma \int_{\Sigma} E_z dS + \int_{Oxy} [(D_z E_z)_{z=L} - (D_z E_z)_{z=0}] dxdy, \tag{13}$$

where primes have been omitted for the part of Oxy belonging to $\mathcal{R}'$ (i.e., Σ'_0): when unambiguous, the same notations are hereafter used for the fields inside and outside $\mathcal{R}$, with ϵ standing for the permittivity ε in $\mathcal{R}$ and for ε' in $\mathcal{R}'$. In the last term of Eq. (13), $(E_z)_{z=0} = 0$ due to the mirror symmetry, and $(E_z)_{z=L}$ vanishes only in the limit $L \to \infty$ considered in Refs. [7,8]. Expression (13) is conveniently recast, invoking the identity

$$[(\boldsymbol{D} \cdot \boldsymbol{E})_{z=0} - (\boldsymbol{D} \cdot \boldsymbol{E})_{z=L}] = \epsilon (\boldsymbol{E}_{z=0} - \boldsymbol{E}_{z=L})^2 + 2 \boldsymbol{E}_{z=L} \cdot (\boldsymbol{D}_{z=0} - \boldsymbol{D}_{z=L})$$

and the relation

$$\int_{Oxy} \boldsymbol{E}_{z=L} \cdot (\boldsymbol{D}_{z=0} - \boldsymbol{D}_{z=L}) dxdy = \int_{\partial \Sigma} (D_n - D'_n)_{z=L} (\psi_{z=0} - \psi_{z=L}) dl - \int_{Oxy} (\psi_{z=0} - \psi_{z=L}) \epsilon \boldsymbol{\nabla}^2 \psi_{z=L} dxdy \tag{14}$$

$$= \sigma \int_{\Sigma} E_z dS - \int_{Oxy} (\psi_{z=0} - \psi_{z=L}) \frac{\partial P}{\partial \psi} (\psi_{z=L}) dxdy. \tag{15}$$

Equation (14) follows from a standard Green identity. The line integral in Eq. (14) has been reexpressed remembering the dielectric boundary condition $D'_n - D_n = \sigma$ and that $\int_{\partial \Sigma} (\psi_{z=L} - \psi_{z=0}) dl = \int_{\Sigma} E_z dS$. Expression (15) was then obtained making use of Poisson's equation (10).

Gathering results, we finally obtain

$$F_z = \int_{Oxy} \left[P(\psi)_{z=0} - P(\psi)_{z=L} - (\psi_{z=0} - \psi_{z=L}) \times \frac{\partial P}{\partial \psi} (\psi_{z=L}) \right] dxdy + \frac{\epsilon}{2} \int_{Oxy} (\boldsymbol{E}_{z=0} - \boldsymbol{E}_{z=L})^2 dxdy + \epsilon \int_{Oxy} [(E_z)_{z=L}]^2 dxdy. \tag{16}$$

It can be checked that since the coefficients p_α are positive, the osmotic pressure P is a convex-up function of its argument ψ. Consequently, the first integral in Eq. (16) is positive, from which we conclude that $F_z \geqslant 0$. This rigorous result holds irrespective of the specific boundary conditions to be applied on the colloids, and is independent of the sign of the surface charge σ. The complete confinement of the electrolyte solution in $\mathcal{R}$ results in an enhanced repulsion with respect to the geometries considered in Refs. [7,8], for which the last term of Eq. (16) vanishes. As stressed by Neu [7], the nonconvexity of the pressure $P(\psi)$ is a necessary condition for attractive interactions. Note that this result holds beyond PB or MPB theories, in fact in any continuum description of the electrolyte solution relying on the local density approximation: once such a theory provides the functional dependence of the charge density ρ_c on the electrostatic potential ψ [or equivalently of the pressure P appearing in the stress tensor (9)], $\partial_\psi \rho_c \leqslant 0$ (or equivalently $\partial^2_\psi P \geqslant 0$) is a sufficient condition for repulsive pair interactions.

While the numerical results reported in Ref. [5] appear erroneous, the reason for the attraction found in Ref. [6] could lie in the effective charge assigned to the polyions to account for the presence of tightly bound counterions and polyion-microion excluded volume. Our alternative approach to incorporate steric effects gives rise to repulsion. A more definite answer could be obtained by considering the generic density functional of Biben *et al.* [15] for electric double layers, which allows one to cope with the finite size of the microions (treated as charged hard spheres) and the molecular nature of the solvent (considered to be a mixture of dipolar hard spheres). Our results nevertheless show the robustness of repulsive interactions within mean-field theories, and may point to the importance of correlated microion density fluctuations (neglected by density functional theories) in interpreting the experimental data.

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