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Effective interaction between confined colloids: repulsion or attraction?

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Abstract Using computer simulations of the primitive model, we calculate the effective force acting onto a single macroion and onto a macroion pair in the presence of slit-like confinement between charged plates. For moderate Coulomb coupling, we find that this force is repulsive. Under strong coupling conditions, however, the sign of the force depends on the distance to the plates and on the interparticle distance. In particular, the particle-plate interaction becomes strongly attractive for small distances, which leads to colloidal crystalline layers near the plates as observed in recent experiments.

Key words Charged colloids · Effective interaction · Screening · Computer simulation address

Introduction

Recent experiments [1–3] have revealed that the effective interaction between like-charged colloidal particles ("macroions") is sensitively affected by a confinement between two parallel charged glass plates. For aqueous polystyrene suspensions studied in experiment, the effective force between two colloidal macroions is found to be repulsive far away from the plates but becomes attractive when the like-charge macroions are located close to an equally charged plate. These findings are surprising as nonlinear Poisson–Boltzmann theory results in a purely repulsive interaction, which was recently shown independently by Neu [4] and Sader and Chan [5]. Assuming an equilibrium situation and neglecting the discrete structure of the solvent and any chemical details, it is tempting to explain the mutual attraction between macroions near plates by counterion fluctuations and correlations which are ignored in the Poisson–Boltzmann approach but fully included in the primitive model of strongly asymmetric electrolytes.

In this paper, we use "exact" computer simulations to calculate the effective interaction between confined charged colloids within the primitive model. We study one or two macroions confined between two parallel charged plates and find that the wall-particle and the interparticle interaction is repulsive for weak Coulomb coupling. For stronger coupling, the behavior of the force changes from repulsive to attractive and back to repulsive as the interparticle distance is varied. In particular, the plate-particle interaction exhibits a short-range attraction for a small distances. This may explain the occurrence of long-lived crystalline colloidal layers on top of the glass plates found in recent experiments [6–8].

The model and target quantities

We consider $N_m = 1, 2$ macroions with bare charge $q_m = Ze > 0$ ($e > 0$ denoting the elementary charge) and mesoscopic diameter d_m confined between two parallel plates that carry a surface charge density $\sigma > 0$. The separation distance between plates is $2L$. For convenience, we choose the z axis to be perpendicular to the plate surface. The origin of the coordinate system is located on the surface of one plate. Image charges are neglected, and there is no added salt. Typically we use a periodically repeated square cell in x and y direction which possesses an area S_p. Hence the macroion number density is $\rho_m = N_m/2LS_p$. The counterions from the plates and the colloids have a microscopic diameter d_c

and carry an opposite charge $q_c = -qe$ where $q > 0$ denotes the valency. Typically, $q = 1, 2$. The total counterion number N_c in the cell is fixed by the condition of global charge neutrality.

The interactions between the particles are described within the framework of the primitive model. We assume the following pair interaction potentials $V_{\mathrm{mm}}(r)$, $V_{\mathrm{mc}}(r)$, $V_{\mathrm{cc}}(r)$ between macroions and counterions, r denoting the corresponding interparticle distance and ϵ the dielectric constant of the solvent:

$$V_{\mathrm{mm}}(r) = \begin{cases} \infty & \text{for } r \leq d_{\mathrm{m}} \\ \frac{Z^2 e^2}{\epsilon r} & \text{for } r > d_{\mathrm{m}} \end{cases} \quad (1)$$

$$V_{\mathrm{mc}}(r) = \begin{cases} \infty & \text{for } r \leq (d_{\mathrm{m}} + d_{\mathrm{c}})/2 \\ -\frac{Zqe^2}{\epsilon r} & \text{for } r > (d_{\mathrm{m}} + d_{\mathrm{c}})/2 \end{cases} \quad (2)$$

$$V_{\mathrm{cc}}(r) = \begin{cases} \infty & \text{for } r \leq d_{\mathrm{c}} \\ \frac{q^2 e^2}{\epsilon r} & \text{for } r > d_{\mathrm{c}} \end{cases} \quad (3)$$

The interaction between the particles and the wall is zero as the plates are equally charged.

Our target quantities are the effective forces $\mathbf{F}_j$ acting onto the jth macroion at position $\mathbf{R}_j$ which embody three different parts [9–11]:

$$\mathbf{F}_j = \mathbf{F}_j^{(1)} + \mathbf{F}_j^{(2)} + \mathbf{F}_j^{(3)} \quad (4)$$

The first term, $\mathbf{F}_j^{(1)}$, is the direct Coulomb repulsion stemming from neighboring macroions and the plates:

$$\mathbf{F}_j^{(1)} = -\nabla_{\mathbf{R}_j} \left(\sum_{i=1; j \neq i}^{N_{\mathrm{m}}} V_{\mathrm{mm}}(|\mathbf{R}_i - \mathbf{R}_j|) \right) \quad (5)$$

The second part $\mathbf{F}_j^{(2)}$ involves the electric part of the counterion-macroion interaction and has the statistical definition:

$$\mathbf{F}_j^{(2)} = \left\langle \sum_{i=1}^{N_c} \nabla_{\mathbf{R}_j} \frac{Zqe^2}{\epsilon |\mathbf{R}_j - \mathbf{r}_i|} \right\rangle_{\mathrm{c}} \quad (6)$$

where $\langle \cdots \rangle_{\mathrm{c}}$ is the canonical average over the counterion positions $\{\mathbf{r}_i\}$ in the field of fixed macroions. Finally, the third term $\mathbf{F}_j^{(3)}$ describes a depletion (or contact) force arising from the hard-sphere part in $V_{\mathrm{mc}}(r)$, which involves a surface integral over the counterion equilibrium number density field $\rho_{\mathrm{c}}^{(0)}(\mathbf{r})$:

$$\mathbf{F}_j^{(3)} = k_{\mathrm{B}} T \int_{S_j} \mathrm{d}\mathbf{f}\, \rho_{\mathrm{c}}^{(0)}(\mathbf{r}) \quad (7)$$

Here S_j is the spherical surface of the jth macroion and $\mathbf{f}$ is a surface vector pointing towards the macroion center and $k_{\mathrm{B}}T$ is the thermal energy.

We define the strength of Coulomb coupling via the dimensionless coupling parameter [11]:

$$\Gamma = \frac{Z}{q} \frac{2\lambda_{\mathrm{B}}}{d_{\mathrm{m}} + d_{\mathrm{c}}} \quad (8)$$

where the Bjerrum length is $\lambda_{\mathrm{B}} = q^2 e^2 / \epsilon k_{\mathrm{B}} T$.

Results from computer simulation

We have calculated the counterion averages needed to obtain the effective forces between the macroions by computer simulations. We take divalent counterions ($q = 2$) throughout our investigations and fixed the temperature to $T = 293$ K and the width of the slit to $2L = 5d_{\mathrm{m}}$. The dielectric constant is that for water at room temperature ($\epsilon = 78.3$) but we have also investigated the case $\epsilon = 3.9$ in order to enhance the Coulomb coupling Γ formally.

Let us first consider a *single macroion* at position $\mathbf{R}_1 = (0, 0, Z_1)$. The total force $\mathbf{F}_1$ acting on the macroion only depends on the distance Z_1 and points along the unit vector $\mathbf{e}_z$ of the z-axis. Results for $F_1 = \mathbf{F}_1 \cdot \mathbf{e}_z$ are shown in Fig. 1. All data are scaled by the (arbitrary) unit $F_0 = e^2/d_{\mathrm{m}}^2$. For weak Coulomb coupling ($\Gamma = 11$, dashed line), it is repulsive but it exhibits repulsive, attractive and repulsive parts as a function of Z_1 for larger coupling ($\Gamma = 110$, solid line). In the latter case,

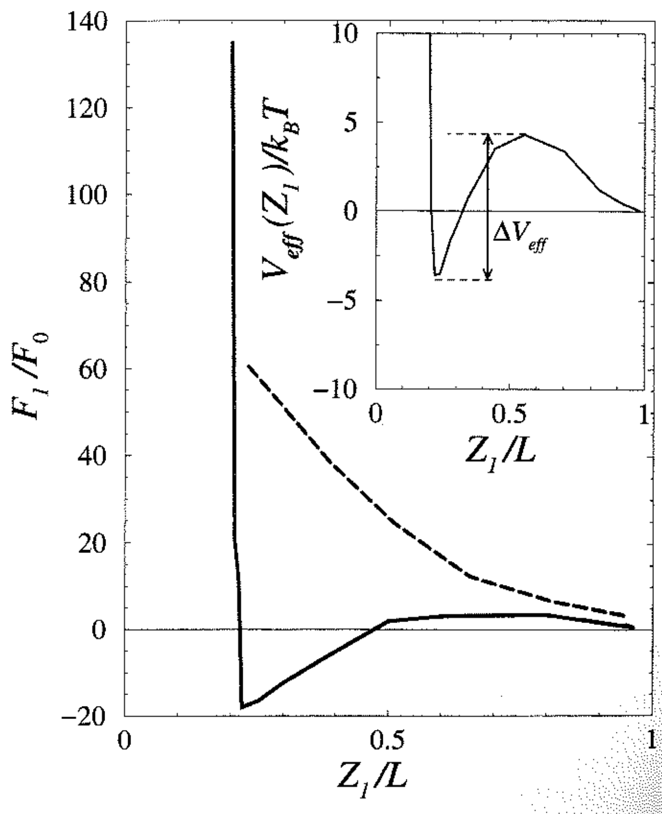

Fig. 1 Force $F_1 = \mathbf{F}_1 \cdot \mathbf{e}_z$ acting on a single macroion versus reduced macroion distance Z_1/L. *Dashed line*: $Z = 200$, $\sigma = 1.24 \times 10^{11}$ (e/cm^2), $\epsilon = 78.3$, $\rho_{\mathrm{m}} = 1.0 \times 10^{12} (1/\mathrm{cm}^3)$, $d_{\mathrm{m}} = 5.32 \times 10^{-6}$ (cm), $d_{\mathrm{c}} = 5.32 \times 10^{-8}$(cm). *Solid line*: $Z = 100$, $\sigma = 1.49 \times 10^{11}$ (e/cm^2), $\epsilon = 3.9$, $\rho_{\mathrm{m}} = 1.7 \times 10^{12} (1/\mathrm{cm}^3)$, $d_{\mathrm{m}} = 5.32 \times 10^{-6}$(cm), $d_{\mathrm{c}} = 5.32 \times 10^{-8}$ (cm). The *inset* shows the effective potential in units of $k_{\mathrm{B}}T$ versus reduced macroion distance Z_1/L together with the energy barrier ΔV_{eff}

the electrostatic part $F_1^{(2)} = \mathbf{F}_1^{(2)} \cdot \mathbf{e}_z$ and the depletion part $F_1^{(3)} = \mathbf{F}_1^{(3)} \cdot \mathbf{e}_z$ behave qualitatively different: $F_1^{(3)}$ is always repulsive and increases with decreasing Z_1, at least if the macroion is not too close to the surface when the counterion depletion between the macroion and the wall induced by the finite counterion core is negligible. This is an expected behavior, since in general there are more counterions close to the walls. The pure electrostatic contribution, $F_1^{(2)}$, on the other hand, exhibits a more subtle behavior. If the macroion is close to the midplane, it is repulsive, then it becomes attractive as the macroion is getting closer to the plates.

For strong coupling, the macroion has three equilibrium positions, two of them are stable, namely the midplane and a position in the vicinity of the plate. In order to extract more information, we have calculated the effective wall-particle potential defined by:

$$V_{\rm eff}(Z_1) = -\int_0^{Z_1} F_1(h)\mathrm{d}h \tag{9}$$

by integrating our data with respect to the macroion altitude h. This quantity is shown as an inset in Fig. 1. One first sees that the global minimum is in the vicinity of the walls. Furthermore, the barrier height $\Delta V_{\rm eff}$ to escape from there is about $8k_BT$. This implies that the time for a colloidal particle to escape from the position close to the surface is roughly $\tau_0 \exp(\Delta V_{\rm eff}/k_BT) = e^8\tau_0 \approx 3000\tau_0$ [12, 13], where τ_0 is a Brownian time scale governing the decay of dynamical correlations of the macroion.

Let us now consider *two equally charged macroions* at positions $\mathbf{R}_1 = (X_1, Y_1, Z_1)$ and $\mathbf{R}_2 = (X_2, Y_2, Z_1)$ with same altitude ($Z_1 = Z_2$). The distance between the macroion centers is $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$, where the difference vector $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ is the xy-plane. The total force acting on the two macroions can be split into a part pointing in z-direction and another contribution pointing along $\mathbf{R}_{12}$. Hence we write $\mathbf{F}_j = \mathbf{F}_j^{\parallel} + \mathbf{F}_j^{\perp}$ defining $\mathbf{F}_j^{\parallel} = (\mathbf{F}_j \cdot \mathbf{R}_{12}) \cdot \mathbf{R}_{12}/R_{12}^2$ and $\mathbf{F}_j^{\perp} = (\mathbf{F}_j \cdot \mathbf{e}_z) \cdot \mathbf{e}_z$ for $j = 1, 2$. Clearly, $\mathbf{F}_1^{\perp} = \mathbf{F}_2^{\perp}$, and $\mathbf{F}_1^{\parallel} = -\mathbf{F}_2^{\parallel}$.

Simulation results for $F_1^{\parallel} = \mathbf{F}_1^{\parallel} \cdot \mathbf{R}_{12}/R_{12}$ are shown in Fig. 2. For weak coupling ($\Gamma = 11$, dashed line) the force is repulsive, but for larger coupling ($\Gamma = 110$, solid line) there is attraction. In Fig. 3 we fixed the macroion distance and plotted the force perpendicular to the plates, $F_1^{\perp} = \mathbf{F}_1^{\perp} \cdot \mathbf{e}_z$ versus altitude Z_1. The parameters here correspond to strong coupling ($\Gamma = 100$) and again there

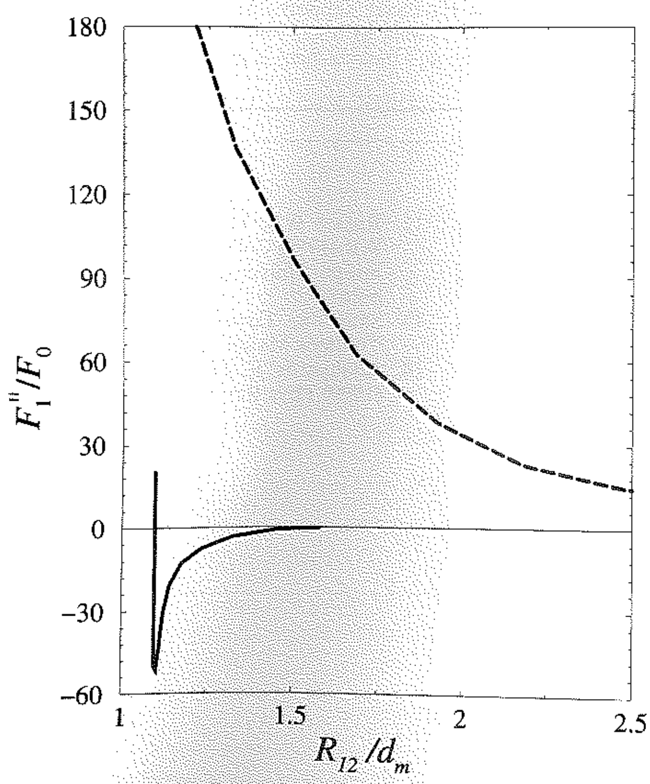

Fig. 2 Parallel part of the effective force acting onto a macroion pair, $F_1^{\parallel}$ versus reduced interparticle distance $R_{12}/d_{\rm m}$. The altitude of macroions is $Z_1 = 0.6\,d_{\rm m}$. *Dashed line*: $Z = 200$, $\sigma = 1.24 \times 10^{11}$ $(e/{\rm cm}^2)$, $\epsilon = 78.3$, $\rho_{\rm m} = 2.34 \times 10^{13} (1/{\rm cm}^3)$, $d_{\rm m} = 5.32 \times 10^{-6}$ (cm), $d_{\rm c} = 5.32 \times 10^{-8}$(cm). *Solid line*: $Z = 100$, $\sigma = 2.98 \times 10^{11}$ $(e/{\rm cm}^2)$, $\epsilon = 3.9$, $\rho_{\rm m} = 2.34 \times 10^{13}$ $(1/{\rm cm}^3)$, $d_{\rm m} = 5.32 \times 10^{-6}$(cm), $d_{\rm c} = 5.32 \times 10^{-8}$(cm)

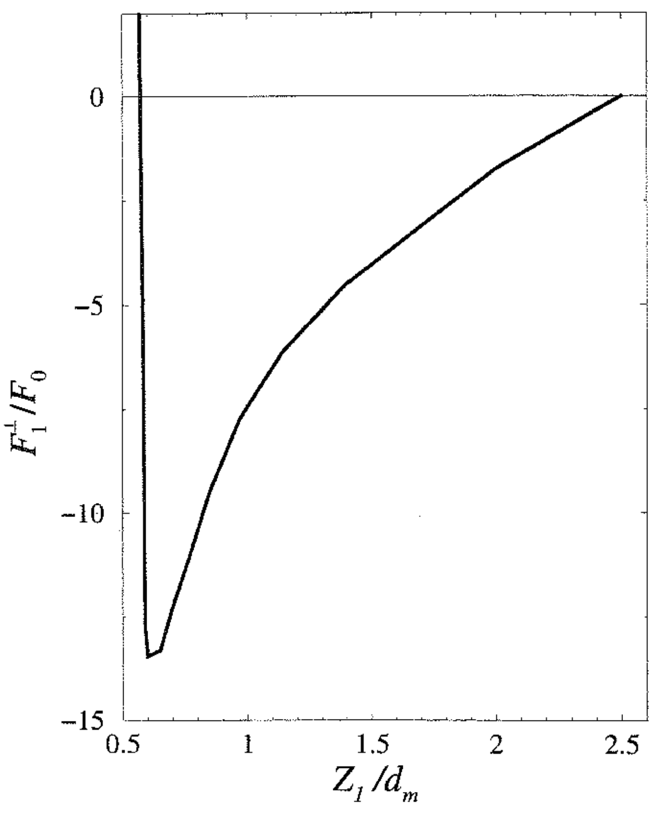

Fig. 3 Perpendicular part of effective force, $F_1^{\perp} = \mathbf{F}_1^{\perp} \cdot \mathbf{e}_z$ versus reduced altitude $Z_1/d_{\rm m}$ for fixed interparticle spacing $R_{12} = 1.2\,d_{\rm m}$. System parameters are: $Z = 100$, $\sigma = 2.38 \times 10^{14} (e/{\rm cm}^2)$, $\epsilon = 78.3$, $\rho_{\rm m} = 1.87 \times 10^{17} (1/{\rm cm}^3)$, $d_{\rm m} = 2.66 \times 10^{-7}$(cm), $d_{\rm c} = 2.66 \times 10^{-8}$(cm)

is attraction. Both the interparticle attraction and the wall-particle attraction become stronger in the vicinity of the plate. The depth in the effective wall-particle interaction potential for the perpendicular part is much more than twice as large as in the single macroion case [14]. Thus, a pair of macroions near a planar surface is more stable than a single macroion. Hence, the attraction between the wall and a single macroion is enhanced if more macroions are close to the wall. This gives evidence that the macroions will assemble on top of the surface forming two-dimensional colloidal layers.

Conclusions

In conclusion, we have simulated the effective force between macroions confined in a slit geometry. An effective attraction due to counterion correlations was found for strong Coulomb coupling. In particular, the effective potential of a single macroion confined between two parallel charged plates was found to have two stable minima where the total force vanishes: the first is in the mid-plane, the second close to the walls. This result was confirmed for two macroions. In this case the attraction towards the walls was even stronger than for a single macroion. Our most important conclusion is that the attractive force will result in two-dimensional colloidal layers on top of the plates. As the depth of the attractive potential is larger than $k_B T$, these layers possess a large life-time with respect to thermal fluctuations. The layers should be crystalline as the interparticle interaction is also attractive. This can explain at least qualitatively the long-lived metastable crystalline layers found in recent experiments on confined samples of charge colloidal suspensions [6, 7].

We remark that our parameters are actually different from those describing the experiments. The main difference is the high surface charge of the glass plates within an area spanned by a typical macroion separation distance. The mechanism of our attraction is similar to that proposed recently by us in the bulk case [11]. A general simple physical picture explaining the attraction is still missing. It only occurs for strong coupling with divalent counterions and is short-ranged. In this respect, it behaves different than in experiment where the attraction was long-ranged. It can be speculated that the attractive part leads to new phenomena relevant, e.g. for adhesion of red blood cells.

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