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Attraction between likely charged colloidal macroions?

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Abstract The distance-resolved effective force between two spherical highly charged colloidal macroions is calculated within the primitive model of strongly asymmetric electrolytes using computer simulations. For parameters corresponding to typical experimental samples, a repulsive force is obtained. Possibilities for an effective attraction induced by very high coupling and small distances between the macroionic surfaces. We also discuss briefly the influence of glass plates on the effective interaction.

strong coupling between the macroions or by a geometric confinement of the macroions between glass plates are briefly discussed.

Key words Charged colloids – effective interaction – screening – computer simulation

Introduction

The total effective force between two highly charged colloidal particles ("macroions") in solution with their microscopic counterions is expected intuitively to be repulsive since the screening by the thermal counterions is imperfect, in general. Nevertheless, there is a long debate in the literature about a possible attraction between macroions (or – equivalently – an "overscreening" by the counterions), for recent references and reviews see e.g. [1–3]. Recent measurements [4–7] reveal that the presence of a charged planar glass plate may influence the nature of the effective interactions between macroions drastically: Apparently it is repulsive in the bulk and gets attractive near the glass plates.

The aim of the present paper is to understand and to calculate within a simple microscopic model (the so-called primitive model of strongly asymmetric electrolytes) the nature of these forces theoretically. Using extensive Monte-Carlo simulations, we obtain the distance-resolved forces between the macroions. For parameters typically encountered in experiments, there is no indication for an attractive force. This may change, however, for extremely

Theory of the effective force

We consider N_m macroions with bare charge Ze and diameter σ confined in a volume V corresponding to a finite number density $\rho_m = N_m/V$ at a temperature T. The macroion density can conveniently be expressed in terms of their volume fraction $\phi = \pi\rho_m\sigma^3/6$. The counterions carry an opposite charge $-qe$ and possess a number density $\rho_c + N_c/V$ which is determined by global charge neutrality to be

$$\rho_c = Z\rho_m/q . \tag{1}$$

Since the system is invariant with respect to charge inversion $Z \to -Z$ and $q \to -q$, it is sufficient to consider positive Z and q. Within the "primitive model" one assumes the following pair interaction potentials $V_{mm}(r)$, $V_{mc}(r)$, $V_{cc}(r)$ between macroions and counterions, r denoting the corresponding interparticle distance and ε the dielectric constant of the solvent:

$$V_{mm}(r) = \begin{cases} \infty & \text{for } r \leq \sigma , \\ \frac{Z^2 e^2}{\varepsilon r} & \text{for } r > \sigma , \end{cases} \tag{2}$$

$$V_{mc}(r) = \begin{cases} \infty & \text{for } r \leq \sigma/2 , \\ \frac{Zqe^2}{\varepsilon r} & \text{for } r > \sigma/2 , \end{cases} \tag{3}$$

$$V_{cc}(r) = \frac{q^2 e^2}{\varepsilon r} . \tag{4}$$

The effective macroion forces contain two parts, one stemming from the direct Coulomb repulsion between the macroions (2) and the other from the macroion–counterion interaction (3). This implies that the force $\mathbf{F}_i$ acting on the ith macroion located at $\mathbf{R}_i$ can be written as

$$\mathbf{F}_i = \mathbf{F}_i^{(m)} + \mathbf{F}_i^{(c)} , \tag{5}$$

where the direct macroionic part $\mathbf{F}_i^{(m)}$ is pairwise

$$\mathbf{F}_i^{(m)} = -\nabla_{\mathbf{R}_i} \sum_{j=1;\, j \neq i}^{N_m} V_{mm}(|\mathbf{R}_i - \mathbf{R}_j|) , \tag{6}$$

$\{\mathbf{R}_j;\, j = 1, \ldots, N_m\}$ being the given macroion positions. The second contribution to the total effective force, $\mathbf{F}_i^{(c)}$, is the canonically counterion-averaged force from the macroion–counterion-interaction (3):

$$\mathbf{F}_i^{(c)} = -\left\langle \sum_{j=1}^{N_c} \nabla_{\mathbf{R}_i} V_{mc}(|\mathbf{R}_i - \mathbf{r}_j|) \right\rangle_c . \tag{7}$$

Here, $\{\mathbf{r}_j;\, j = 1, \ldots, N_c\}$ are the counterion positions and the canonical average $\langle \cdots \rangle_c$ over an $\{\mathbf{r}_j\}$-dependent quantity $\mathscr{A}$ is defined via the classical trace

$$\langle \mathscr{A}(\{\mathbf{r}_k\}) \rangle_c = \frac{1}{Z} \frac{1}{N_c!} \frac{1}{A^{3N_c}} \int_V d^3 r_1 \cdots \int_V d^3 r_{N_c}$$
$$\times \mathscr{A}(\{\mathbf{r}_k\}) \exp\left[-\frac{V_c}{k_B T}\right] , \tag{8}$$

where k_B is the Boltzmann constant, A the de Broglie thermal wavelength of the counterions and

$$V_c = \sum_{n=1}^{N_m} \sum_{j=1}^{N_c} V_{mc}(|\mathbf{R}_n - \mathbf{r}_j|) + \frac{1}{2} \sum_{i,j=1;\, i \neq j}^{N_c} V_{cc}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{9}$$

is the total counterionic part of the potential energy. Furthermore, the classical partition function

$$Z = \frac{1}{N_c!} \frac{1}{A^{3N_c}} \int_V d^3 r_1 \cdots \int_V d^3 r_{N_c} \exp\left[-\frac{V_c}{k_B T}\right] \tag{10}$$

guarantees the correct normalization $\langle 1 \rangle_c = 1$.

At this stage let us emphasize a couple of points.

(i) Since the counterions are averaged out, the effective forces acting on the macroions do not depend on the counterion positions $\{\mathbf{r}_j\}$. They do, however, depend parametrically on the positions of the macroions $\{\mathbf{R}_j\}$. While the repulsive $\mathbf{F}_i^{(m)}$ is explicitly given and clearly a pairwise interaction, the nontrivial part $\mathbf{F}_i^{(c)}$ contains in general *many-body forces* of arbitrary order (triplet, quadruplet, etc.) due to nonlinear counterion screening [8]. It is only in linearized theories (like Debye–Hückel approaches) that these forces are pairwise, too.

(ii) As it can be checked immediately, the effective force $\mathbf{F}_i$ can be derived as a gradient of an effective *potential energy*, i.e. $\mathbf{F}_i = -\nabla_{\mathbf{R}_i} V_{eff}(\{\mathbf{R}_j\})$ with

$$V_{eff}(\{\mathbf{R}_j\}) = \sum_{i,j;\, i<j}^{N_m} V_{mm}(\mathbf{R}_i - \mathbf{R}_j) - k_B T\, Z . \tag{11}$$

This quantity clearly differs from the counterion-averaged total potential energy

$$U(\{\mathbf{R}_j\}) := \sum_{i,j;\, i<j}^{N_m} V_{mm}(|\mathbf{R}_i - \mathbf{R}_j|) + \langle V_c \rangle_c . \tag{12}$$

(iii) An alternative expression for the counterion-induced forces $\mathbf{F}_i^{(c)}$ can be obtained by using the inhomogeneous equilibrium counterion density profile in the field of fixed macroions which is defined via

$$\rho^{(0)}(\mathbf{r};\, \{\mathbf{R}_j\}) = \left\langle \sum_{n=1}^{N_c} \delta(\mathbf{r} - \mathbf{r}_n) \right\rangle_c . \tag{13}$$

Then $\mathbf{F}_i^{(c)}$ can be rewritten as

$$\mathbf{F}_i^{(c)}(\{\mathbf{R}_j\}) = -\int_V d^3 r\, \rho^{(0)}(\mathbf{r};\, \{\mathbf{R}_j\})\, \nabla_{\mathbf{R}_i} V_{mc}(|\mathbf{r} - \mathbf{R}_i|) . \tag{14}$$

(iv) The definition of the effective forces differs from those derived from the potential of mean force. While the effective force represent the full bare interaction, the latter incorporates also correlations between the macroions, see e.g. [9].

Equations (5)–(6) are the exact expressions for the effective forces in the framework of classical statistical mechanics. The counterion average, however, can in general not performed analytically. In principle, there are two different routes to follow: First, one can use (approximative) density functional theory to obtain $\rho^{(0)}(\mathbf{r};\, \{\mathbf{R}_j\})$ and then use (14) to get $\mathbf{F}_i^{(c)}(\{\mathbf{R}_j\})$. This strategy was employed in Ref. [8]. However, since the exact free energy functional is only known approximatively, one gets an uncontrolled error at least if the counterion density profile is strongly inhomogeneous near the macroionic surfaces.

The second route which we shall follow in this paper is to calculate the counterion average (6) by "exact" computer simulation. The drawback here is that – due to the enormous number of counterions – one can only treat relatively small system sizes. In the following we consider only *two* macroions ($N_m \equiv 2$). The two macroions are

placed symmetrically along the room diagonal of a cubic box such that the centre of the cube coincides with the center-of-mass of the two particles. The box length L is determined by the macroion density $L = (N_m/\rho_m)^{1/3}$. The center-of-mass distance between the two macroionic spheres is denoted by $r \equiv |\mathbf{R}_2 - \mathbf{R}_1|$. Periodic boundary conditions resulting in periodically repeated image charges were taken. Hence our macroion configuration corresponds to a body-centered cubic (BCC) crystal distorted in $(1\,1\,1)$ direction. Due to symmetry, $\mathbf{F}_1 = -\mathbf{F}_2$ and the total effective force depends only on the macroion distance r. From symmetry consideration, the direction of $\mathbf{F}_1$ is along the room diagonal, i.e. parallel to $\mathbf{R}_1 - \mathbf{R}_2$. We therefore consider only the magnitude of the force projecting it onto the room diagonal

$$F(r) = \mathbf{F}_1(r)\cdot(\mathbf{R}_1 - \mathbf{R}_2)/r \tag{15}$$

which is the key quantity of the paper. If $F(r)$ is positive, then the effective force is repulsive for the given separation r while it is attractive if $F(r)$ becomes negative.

Results from computer simulation

Let us now summarize and discuss computer simulation results, some of them are published in Refs. [10–12].

(i) Monte Carlo results for $F(r)$ are shown in Fig. 1. The parameters are typical for experimental samples and chosen as in Ref. [8]: $q = 1$, $T = 300\,K$, $\varepsilon = 78$, $\sigma = 106\,nm$. As is clear from Fig. 1, the forces are always *repulsive* (i.e. $F(r) > 0$) over the broad range of distances explored. Of course, in an undistorted configuration the forces are exactly zero due to symmetry of the macroionic configuration.

(ii) For extremely high couplings, the computer simulation data exhibit large fluctuations in the force and the corresponding statistical error is huge [13]. Nevertheless, the force becomes much less repulsive if the distance between the macroions is of the order of few Bjerrum lengths. It is still unclear whether the net force gets attractive but in principle large fluctuations in the counterionic Stern-layer around the macroionic surfaces can give rise to an attraction [14]. At this stage let us discuss and compare the effective forces in a different geometric set-up, namely that between rigid rod-like polyelectrolytes and that between charged planar plates. In the first case, a counterionic attraction was found recently [15, 16] if the rod-radius is microscopic. Although this is realistic for DNA-strands, it does not seem to be important for charged macroionic spheres since their radius is much larger. In the second case (charged plates), an effective attraction was found for
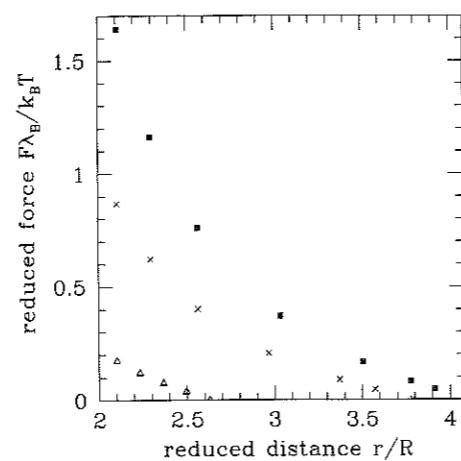

Fig. 1 Effective macroion force $F(r)$ in units of $k_B T/\lambda_B$ versus reduced distance r/R. $\lambda_B = e^2/\varepsilon k_B T$ is the Bjerrum length and $R \equiv \sigma/2$ is the macroion radius. The statistical error of the Monte-Carlo data is smaller than the size of the symbols. The parameters are as follows: (a) crosses: $Z = 200$, $\phi = 0.1$. (b) open triangles: $Z = 100$, $\phi = 0.3$. (c) full squares: $Z = 300$, $\phi = 0.08$

large couplings [17–19]. One may argue that the case of spheres and planes is simply related performing a Derjaguin-like approximation for nearly touching spheres. This is not that simple, however, since the interaction is still long-ranged and the topology of two spheres is different from that of two planes.

(iii) For suspensions with added salt and asymmetric macroions (i.e. macroions of different radii and different charges) there is again repulsion for moderate couplings [12]. However, in the presence of a small neutral cage, the interaction between a particle and a neutral plane can become attractive. This is expected due to counterion exclusion by the neutral cage [12].

Experiments and discussion

As regards recent experiments discussed already in the Introduction, one carefully has to distiguish whether the experimental samples considered were in the bulk or confined between plates. It now seems to be established that there is no direct hint towards a macroionic attraction in bulk systems which is in agreement with our theoretical findings. In a confined system, however, Kepler and Fraden [4] observed a peak in the pair correlation function for high dilution revealing an attraction. Grier and coworkers [5–7, 20] systematically investigated the effect of confinement on the interaction. While the interaction appears to be repulsive in a multilayer system far away from the plates, it becomes attractive for two macroions close to the plates. This becomes apparent by

the observation of metastable crystallites near the charged surfaces but also from dynamical measurements of the diffusion of two nearby particles pinned by tweezers.

Theoretically, it is still unclear whether there is any mechanism leading to attraction near the plates. A possible explanation is the presence of additional counterions stemming from the highly charged plates which give rise to strong fluctuations and correlations absent in the bulk system. More theoretical work is needed to explore this interesting question further.

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