

Effective forces between macroions: a Monte Carlo study

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Received 16 August 1996

Abstract

The effective forces between two spherical highly charged colloidal macroions are calculated within the primitive model of strongly asymmetric electrolytes using Monte Carlo simulations. For typical parameters corresponding to aqueous suspensions of polystyrene spheres, the forces are found to be repulsive over a broad range of distances between the macroions. Our results are in semi-quantitative agreement with different variants of linear screening theory. A recently developed cumulant expansion, however, fails in predicting the correct sign of the effective forces.

PACS: 82.70.Dd

Keywords: Charged colloids; Effective interaction; Counterion screening; Primitive model; Monte Carlo simulation

1. Introduction

Charged colloidal particles suspended in a polar solvent represent an excellent realization of a classical fluid on a mesoscopic length scale and exhibit all kinds of phase transitions as known from microscopic system [1]. The spherical colloidal particles are frequently called *macroions*: they carry a total surface charge Z which is much larger than the charge q of the microscopic counterions. Any statistical theory of the structural correlations and the phase diagram for these macroions requires a detailed knowledge of the effective inter-particle forces between the macroions [2]. These forces, obviously, first contain a part due to the excluded volume of the macroions and another due to long-ranged Coulombic repulsion. The Coulomb part, however, is screened by the counterions resulting in a total effective short-ranged interaction.

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Almost every statistical mechanical theory starts from the so-called “primitive model” (PM) of strongly asymmetric electrolytes involving only the excluded volume and the Coulomb interactions of the charged species (macroions and counterions) while the solvent enters only by its static dielectric constant ϵ screening the Coulomb interaction. However, a direct computer simulation of the PM is only feasible for relatively small charge asymmetries ($Z/q \lesssim 50$) corresponding to the micellar regime [3,4]. The traditional additional approximation is to neglect counterion correlations completely treating them as an ideal gas with a mean-field-like Coulomb potential energy, resulting in the (nonlinear) Poisson–Boltzmann theory or its linearized version, the Debye–Hückel approach [5–7]. The latter predicts an effective macroion pair potential $V(R)$ of Yukawa form

$$V(R) = \frac{Z^{*2} e^2 \exp(-\kappa R)}{\epsilon R} \quad (1)$$

with an inverse screening length

$$\kappa^2 = 4\pi\rho_c q^2 e^2 / k_B T \epsilon \quad (2)$$

and an effective charge

$$Z^* = Z \exp(\kappa\sigma/2) / (1 + \kappa\sigma/2). \quad (3)$$

Here, $k_B T$ is the thermal energy, σ is the macroion diameter and R the center-of-mass distance of two macroions.

In the present paper we simulate the primitive model by the Monte Carlo method for *two* ($N_m = 2$) macroions in a rectangular box at a fixed given distance R . Consequently, we get *exact* (in our case pairwise) results for the effective forces which were up to now only obtained with different levels of approximations [8–10]. From a canonical counterion average, the effective forces acting on the macroions are extracted for different R . One parameter combination is investigated corresponding to typical experimental values for polystyrene spheres in aqueous solution. These parameters were also used in Ref. [11]. We found an effective repulsion which is semi-quantitatively described by standard Yukawa expressions of linear screening theory. Our work is a natural generalization of recent Monte Carlo studies for a single macroion ($N_m = 1$) in a spherical cell [12–16]. Most of the latter studies yield the osmotic pressure of the macroionic solution but, in every case, they are unable to predict the distance-resolved effective forces.

Our paper is organized as follows: In Section 2 we define the primitive model and the statistical expression for the mean force acting on the macroions. The results are presented in Section 3 and finally, Section 4 is devoted to an outlook.

2. Effective macroion forces in the primitive model

We consider $N_m = 2$ macroions with bare charge Ze and diameter σ confined in a cubic volume V of linear size $L = V^{1/3}$ corresponding to a finite number density

$\rho_m = N_m/V$ at a temperature T . The two macroions are placed symmetrically along the body diagonal of the cube such that the centre of the cube coincides with the center-of-mass of the two particles.

Furthermore, $N_c = 2|Z/q|$ point-like counterions are in the box carrying an opposite charge $-qe$. Within the PM 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:

$$V_{mm}(r) = \begin{cases} \infty & \text{for } r < \sigma, \\ \frac{Z^2 e^2}{\epsilon r} & \text{for } r \geq \sigma, \end{cases} \quad (4)$$

$$V_{mc}(r) = \begin{cases} \infty & \text{for } r < \sigma/2, \\ -\frac{Z^2 e^2}{\epsilon r} & \text{for } r \geq \sigma/2, \end{cases} \quad (5)$$

$$V_{cc}(r) = \frac{q^2 e^2}{\epsilon r}. \quad (6)$$

The counterions represent a one-component classical plasma (OCP) with the Coulomb repulsion (6) containing a further length scale, the so-called Bjerrum length $\ell = e^2/\epsilon k_B T$. For water at room temperature ($T = 293$ K) $\ell = 7.29$ Å.

The effective forces $\mathbf{F}_1, \mathbf{F}_2$ acting onto the two macroions have the same magnitude but an opposite sign due to symmetry reasons, i.e., $\mathbf{F}_1 = -\mathbf{F}_2$. With $\{\mathbf{R}_i; i = 1, 2\}$ being the positions of the two macroions we define the magnitude of the forces as follows:

$$F(R) = \mathbf{F}_1(R) \cdot (\mathbf{R}_1 - \mathbf{R}_2)/R, \quad (7)$$

where $R = |\mathbf{R}_2 - \mathbf{R}_1|$. Hence $F(R)$ is positive for repulsion and negative for attraction. Obviously, $F(R)$ consists of a trivial positive part $Z^2 e^2/\epsilon R^2$ stemming from the direct Coulomb repulsion (4). The non-trivial additional term results from nonlinear counterion screening and can exactly be expressed [17] as a counterion-averaged force from the macroion-counterion-interaction (5):

$$F(R) = \frac{Z^2 e^2}{\epsilon R^2} \left\langle \sum_{i=1}^{N_c} \nabla_{\mathbf{R}_1} V_{mc}(|\mathbf{R}_1 - \mathbf{r}_i|) \right\rangle_c \cdot (\mathbf{R}_1 - \mathbf{R}_2)/R. \quad (8)$$

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

$$\langle \mathcal{A}(\{\mathbf{r}_k\}) \rangle_c = \frac{1}{\mathcal{Z}} \frac{1}{N_c!} \frac{1}{\Lambda^3 N_c} \int_V d^3 r_1 \dots \int_V d^3 r_{N_c} \mathcal{A}(\{\mathbf{r}_k\}) \exp \left[-\frac{V_c}{k_B T} \right], \quad (9)$$

where Λ is the de Broglie thermal wavelength of the counterions and

$$V_c = \sum_{j=1}^2 \sum_{i=1}^{N_c} V_{mc}(|\mathbf{R}_j - \mathbf{r}_i|) + \frac{1}{2} \sum_{i,j=1; i \neq j}^{N_c} V_{cc}(|\mathbf{r}_i - \mathbf{r}_j|) \quad (10)$$

is the total counterionic part of the potential energy. Furthermore, the classical partition function \mathcal{Z} guarantees the correct normalization $\langle 1 \rangle_c = 1$.

In linear screening theory (1), we get the following approximation for $F(R)$

$$F(R) \approx |\nabla_{\mathbf{R}} V(R)| = V(R) \left(\frac{1}{R} + \kappa \right). \quad (11)$$

We finally mention that there are modified Yukawa expression in the literature with screening constants κ and effective charges Z^* differing from (1), see e.g. [18,19]. These theories yield quantitatively different but still repulsive results for $F(R)$.

3. Results of the Monte Carlo simulation

In our simulations we use the standard Monte Carlo scheme [20]. Note that we can avoid Ewald sums in the present set-up since there are no image charges. We start with an arbitrary counterion configuration which does not penetrate into the two fixed macroion cores. Typically 1.5×10^4 Monte Carlo steps per counterion are used to equilibrate the counterions and then the canonical average (8) is performed from 2×10^4 Monte Carlo steps per particle. By comparing the results with that corresponding to a periodically repeated cubic box containing two macroions with the same distance R , we have checked that effects due to the finite box are not relevant, at least for the range of R explored in our work.

The results for four different macroion distances R are summarized in Fig. 1. The parameters are chosen as in Ref. [11]: $Z = 280$, $q = 1$, $T = 293$ K, $\epsilon = 78$, $\sigma = 1108$ Å, $\rho_m = 3.3 \times 10^{-12}$ Å⁻³. As is clear from Fig. 1, the forces are *repulsive* over the broad range of distances explored. A comparison with linear screening (dashed line) shows that linear screening gives the correct sign of the force, but overestimates its magnitude a bit. If the theory of Alexander et al. [18] as developed for strongly interacting charged colloids is invoked (dotted line), the results become better. In this theory $V(R) = Z_{PB}^2 e^2 \exp(-\kappa_{PB} R) / \epsilon R$ with $Z_{PB} = 264$ and $\kappa_{PB} \sigma = 0.294$. The data agree surprisingly well near macroion contact but again overestimate the forces for larger macroion separation R . Thus, one can conclude that these two variants of linear screening theory provide at least a semi-quantitative description of counterion screening. We finally note that any size correction, as embodied in the factor $\exp(\kappa\sigma)/(1+\kappa\sigma/2)^2$, is practically of no importance here since $\kappa\sigma$ is small both in DLVO and in Alexander's theory.

Recently, a theory was proposed by Allahyarov et al. [11] based upon a cumulant expansion of the primitive model. For the same combination of parameters and in the same range of R , they found an effective attraction between macroions. In the light of our exact data, however, the attraction has to be an artifact of the approximations made.

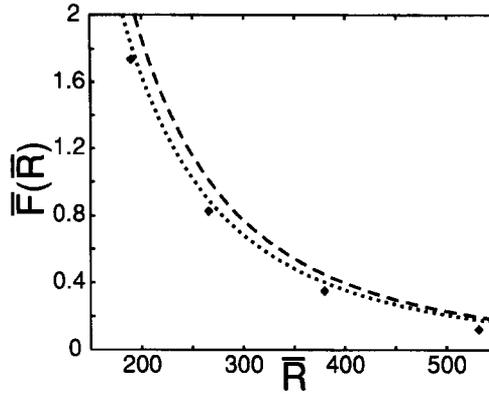


Fig. 1. Reduced total effective force $\bar{F}(\bar{R}) = F(R)\ell/k_B T$ between two macroions versus their reduced distance $\bar{R} = R/\ell$. The parameters are $Z = 280$, $q = 1$, $T = 293$ K, $\varepsilon = 78$, $\sigma = 1108 \text{ \AA}$, $\rho_m = 3.3 \times 10^{-12} \text{ \AA}^{-3}$. Macroion contact is at $\bar{R} = 152$ while the mean macroion distance at $\bar{R} = \rho_m^{-1/3} \ell = 920$. The diamonds are the exact Monte Carlo data; the absolute statistical error in \bar{F} is of the order of 0.003, i.e., it is much smaller than the size of the symbol. The dashed line is the result from DLVO theory (Eq. (1)), the dotted line is from the theory of Alexander et al.

4. Outlook

In conclusion, we have calculated the effective macroion forces starting from the primitive model within a Monte Carlo computer simulation. While a cumulant expansion fails in predicting the correct sign of the force, our result is in semi-quantitative agreement with linear screening theory and variants of it. Our future activities will be in the following directions: First, we plan to investigate, in more detail, a slightly changed set-up by adopting a cubic box with periodic boundary conditions. The advantage one gains here is that the macroionic configuration then really corresponds to a many-body configuration of a distorted bcc crystal and effects due to the finite size of the counterion box are avoided. Also more parameter combinations should be addressed which should be related to a strongly-coupled case where an attraction was found between two parallel plates [21–26]. It would be interesting to check whether such an attraction is also present for other topologically different situations involving two spheres. Third, the forces can be compared to the results of Car–Parrinello-type simulations [19,17] in order to check the validity of the pseudo-potential assumption. Finally, a finite counterion core should be also considered and incorporated in the simulations.

Acknowledgements

We thank S.A. Trigger, A. Bohle, G. Senatore, G. Pastore, M. Schmidt and A. Denton for helpful remarks.

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