

Effective macroion-macroion potentials in asymmetric electrolytes

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Effective macroion-macroion potentials in solutions of macroions carrying 60 elementary charges and either monovalent or divalent counterions have been calculated at different concentrations by means of Monte Carlo simulations with a consequent inversion of radial distribution functions according to Lyubartsev and Laaksonen [Phys. Rev. E **52**, 3730 (1995)]. With monovalent counterions, the effective potentials are essentially of a Yukawa type, whereas with divalent ones, an attractive region appears at short separation. A charge renormalization scheme invoking the cell model and the assumption of a Yukawa-type potential works favorably only in the case of monovalent counterions.

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Charged colloids appear in a wide variety of biological and technological systems, and the physico-chemical properties of these solutions are dominated by electrostatic interactions. The classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [1,2] predicts purely repulsive forces between like-charged colloids. Although this cornerstone of colloidal science is qualitatively correct in most applications, it is presently challenged by recent experimental data indicating the existence of effective attraction between such colloids [3–6]. A more general description of the interaction between charged colloids allowing for attractions is now warranted, and intense theoretical and simulation activities have recently made some progress [7,8].

The primitive asymmetric electrolyte model, where the charged colloids (referred to as macroions) and the small ions are explicitly present, constitutes a firm basis for examining properties of colloidal solutions. Employing this model, attractive forces between like-charged macroions and/or vapor-liquid phase separation arising from electrostatic interactions have been observed in computer simulations [9–16] and proposed by various theories [17–25]. In all of these simulation studies, and in some of the theories [17–19,23,24], the attractive force appears to be of short-range (operating on a nanometer scale), whereas in the other theoretical investigations, a more long-range attraction is present at certain conditions [22] or appears as a collective effect [20,21,25]. So far, in bulk solution, simulations have only confirmed a presence of the short-range attraction, which can be viewed as originating from spatial correlations appearing between ions residing on different macroions. Short-range attraction of the same origin appearing between planar charged surfaces was demonstrated some 15 years ago [9,17] whereas similar progress has been proven to be more difficult for other geometries.

A much simpler view of an asymmetric electrolyte can be obtained by considering a reduced system where an integration over the degrees of freedom of the small ions have been performed. Provided that the N -particle potential of mean force is used for the effective macroion interactions, this is formally an exact way of treating the colloidal system (as it is the case of McMillan-Mayer theory of solutions [26], where solvent degrees of freedom are treated implicitly). In practice, however, the many-body potential is approximated as a sum of effective pair potentials. Once it exists, a set of effective pairwise potentials solving the inverse problem constitutes its unique solution, provided the full system possesses pairwise interactions only [27]. Moreover, the corresponding (pairwise) potentials provide maximum entropy among all other (nonpairwise) potentials, consistent with a given set of radial distribution functions (RDF's) [28,29]. One therefore can hope that the effective potentials represent the optimal choice in the sense that they reproduce the basic structural properties (i.e., the RDF's) of the system and treating other higher-order correlations within the maximum entropy principle.

In this Rapid Communication, we report on effective macroion-macroion potentials in solutions of macroions carrying 60 elementary charges and either monovalent or divalent counterions obtained from Monte Carlo (MC) simulations. In the reduced model with only macroions explicitly present, this effective potential is thus the exact pairwise potential (within the statistical uncertainty) to be operating between the macroions to produce the macroion-macroion RDF of the original primitive asymmetric electrolyte model. We also compare the exact effective potentials with approximate ones as obtained by means of a charge renormalization scheme [30]. Other approximate liquid state theories and approximate methods have been used in the past to address effective interactions between colloids [31–37].

The systems under consideration are asymmetric electrolytes described within the frame-work of the primitive

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model. The model contains two types of spherical charged particles: (i) macroions of diameter $\sigma_M=40$ Å and charge $Z_M=-60$ and (ii) small ions of diameter $\sigma_I=4$ Å and charge $Z_I=+1$ or $+2$, representing the counterions (no extra salt is added), whereas the solvent enters the model only by its relative dielectric permittivity ϵ_r . The system with monovalent counterions (60:1 system) represents an aqueous micellar solution of charged surfactants, and the analogous system with divalent counterions (60:2 system) has been previously found to exhibit macroion pairing due to attraction of electrostatic origin [13,14]. The interaction between the particles is pairwise additive, and for pair ij , where i and j denote either macroion or counterion, it is given by

$$U_{ij}(r) = \begin{cases} \infty, & r < (\sigma_i + \sigma_j)/2 \\ \frac{Z_i Z_j e^2}{4\pi\epsilon_0\epsilon_r} \frac{1}{r}, & r \geq (\sigma_i + \sigma_j)/2, \end{cases} \quad (1)$$

where e is the elementary charge, ϵ_0 the dielectric permittivity of vacuum, and r the center-to-center separation between the particles.

The two systems are considered at macroion number densities $\rho_M = \rho_M^0$, $2\rho_M^0$, $4\rho_M^0$, and $8\rho_M^0$, where $\rho_M^0 = 2.5 \times 10^{-7}$ Å⁻³ corresponds to a macroion volume fraction $\phi_M = 0.0084$. A temperature of $T = 298$ K and a relative dielectric permittivity of $\epsilon_r = 78.4$ were used. The simulated systems were composed of 80 macroions and 4800 (60:1 system) or 2400 (60:2 system) counterions. The macroion-macroion RDF, $g_{MM}(r)$, were sampled employing a grid length of 0.5 Å. The Ewald summation for handling the long-range electrostatic interaction and the cluster move technique for improving the MC sampling were employed; further details of the simulation protocol can be found in Refs. [30,38].

The reconstruction of the effective macroion-macroion potentials, $U_{MM}^{eff}(r)$, from the macroion-macroion RDF's was performed using an inverse Monte Carlo (IMC) technique [28], previously applied to aqueous solutions of small ions [29,39]. For the present system, the procedure involves MC simulations of a system containing macroions only with iterative correction of the trial potential in order to reproduce $g_{MM}(r)$ of the full system using exact statistical-mechanical relations. The grid for the potential was set the same as for the original $g_{MM}(r)$. The macroion-macroion potential of mean force $U_{MM}^{pmf}(r) \equiv -kT \ln g_{MM}(r)$ was taken as the initial potential, and typically, six to seven iterations were required to get $U_{MM}^{eff}(r)$ with appropriate accuracy. The average relative deviation of $g_{MM}(r)$ from the original one did not exceed 0.01.

The (Wigner-Seitz) cell model applied to an asymmetric electrolyte, solved by either the Poisson-Boltzmann (PB) equation [35] or the MC simulation [30], in conjuncture with a charge renormalization (CR) procedure constitutes an approximate and simpler method to obtain effective macroion-macroion potentials. The two variants of this approach will be referred to as the Cell-PB-CR and the Cell-MC-CR approach, respectively. The effective macroion-macroion potential is assumed here to be of the form

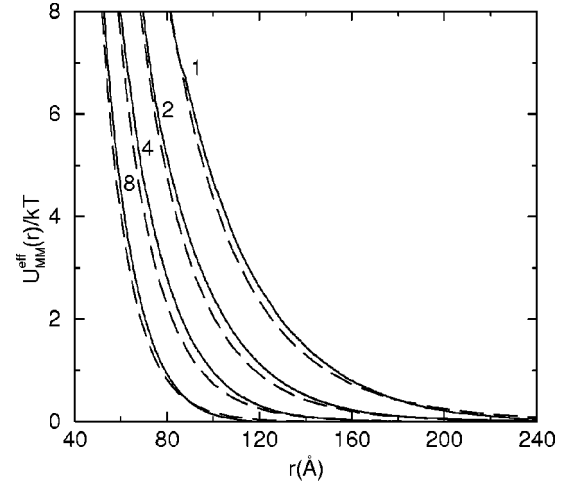


FIG. 1. Effective macroion-macroion potentials for the 60:1 system obtained from the IMC procedure (solid curves) and the Cell-MC-CR approach (dashed curves) at indicated macroion number density given in units of ρ_M^0 .

$$U_{MM}^{eff}(r) = U_0 \frac{\exp(-\kappa r)}{r}, \quad (2)$$

where the prefactor $U_0 = [(eZ_M^{eff})^2 \exp(\kappa\sigma_M) / (4\pi\epsilon_0\epsilon_r kT(1 + \kappa\sigma_M/2)^2)]$ and the inverse screening length $\kappa = (\rho_M |Z_M^{eff}| e^2 / \epsilon_0\epsilon_r kT)^{1/2}$ depend on the effective macroion charge Z_M^{eff} . For the 60:1 system, we previously found that the Cell-MC-CR approach (i) predicted $g_{MM}(r)$ in very close agreement with those of the primitive model, and (ii) gave a more accurate $g_{MM}(r)$ as compared to the Cell-PB-CR approach (see Fig. 7 of Ref. [30]).

The effective macroion-macroion potentials for the 60:1 system as obtained from (i) the IMC procedure using $g_{MM}(r)$ of the primitive model as input and (ii) the Cell-MC-CR approach are given in Fig. 1. We found that $U_{MM}^{eff}(r)$ obtained from the IMC procedure can well be fitted by a Yukawa potential of the form given by Eq. (2). Parameters of the fit as well as of $U_{MM}^{eff}(r)$ of the Cell-MC-CR approach are collected in Table I. We note that the prefactor U_0 obtained from the Cell-MC-CR approach is higher than those obtained from the Yukawa fit to the IMC results, whereas the opposite holds for the screening length κ^{-1} . Hence, the Cell-MC-CR approach underestimates the effective macroion-macroion repulsion at short separations and overestimate it at longer ones, the intercept appearing approximately at the mean interparticle distance $\rho_M^{-1/3}$ [30,36]. Nevertheless, the accuracy of the Cell-MC-CR results for the 60:1 system is satisfactory. The effective macroion charge Z_M^{eff} varies between -21 and -24 (cf. $Z_M = -60$) and grows negative as ρ_M increases.

The corresponding effective macroion-macroion potentials for the 60:2 system are displayed in Fig. 2. In this case, however, $U_{MM}^{eff}(r)$ possesses an additional attraction at short separations, and hence predictions based on the cell model are qualitatively incorrect. The long-range tail of $U_{MM}^{eff}(r)$

TABLE I. Parameters of Yukawa fits to the effective macroion-macroion potentials from the IMC procedure and of the effective macroion-macroion potentials predicted by the Cell-MC-CR approach for the 60:1 and 60:2 systems at different macroion number densities.

ρ_M/ρ_M^0 ^a	IMC		Cell-MC-CR		
	U_0/kT	$\kappa^{-1}/\text{\AA}$	U_0/kT	$\kappa^{-1}/\text{\AA}$	Z_M^{eff}
	60:1				
1	3070	52	3880	46	-21.3
2	3820	36	4580	32	-21.5
4	5170	25	6550	22	-22.4
8	12 220	16	12 120	15	-23.8
	60:2				
1	298	63	379	57	-6.9
2	308	42	347	42	-6.3
4	286	29	342	31	-5.8
8	220	23	356	23	-5.3

$$^a \rho_M^0 = 2.5 \times 10^{-7} \text{ \AA}^{-3}.$$

can still be well fitted by the Yukawa potential (Fig. 3) with a weakly density dependent prefactor and a decay length proportional to the square root of the density (Table I). The parameters of the Yukawa fit are compared with results of the Cell-MC-CR approach in Table I. Despite the failure at short distances, the Cell-MC-CR approach describes reasonably the true effective potential at large separations. The effective macroion charge lies in the range -5.3 and -6.9 and becomes less negative as ρ_M increases.

Figure 3 displays that after a subtraction of the Yukawa tail, the residual part of $U_{MM}^{\text{eff}}(r)$ is repulsive at $r < 44.5 \text{ \AA}$ and attractive in the interval $44.5 \text{ \AA} < r < 55 \text{ \AA}$ with a minimum of about -1.5 kT . Moreover, this additional attraction is practically independent on ρ_M , which is related to the very weak density dependence of the ion accumulation at the macroion surfaces [14]. The lower end of the attraction region corroborates well with $\sigma_M + \sigma_I$ and the upper one with

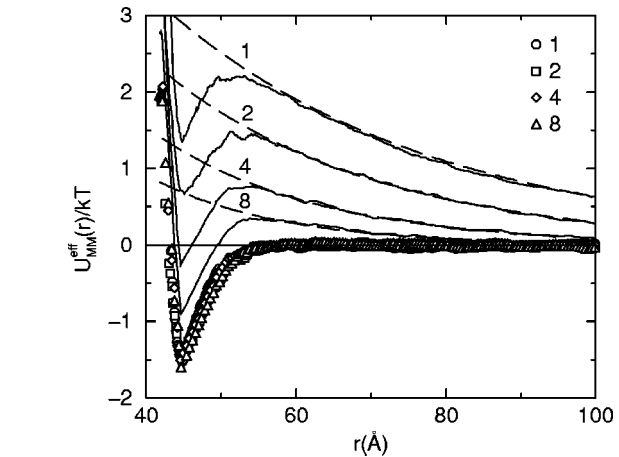


FIG. 3. Effective macroion-macroion potentials for the 60:2 system: full potentials are obtained from the IMC procedure (solid curves), Yukawa fit of the long-range repulsive tails (dashed curves), and the residual part of the potential (symbols) at indicated macroion number density given in units of ρ_M^0 .

$\sigma_M + a$, where $a = [\pi(\sigma_M + \sigma_I)^2 Z_I/Z_M]^{1/2} \approx 14 \text{ \AA}$ corresponds to the characteristic spacing between neighboring ions adsorbed on the macroion surface [19].

Figure 4 shows the effective macroion-macroion potential for the 60:2 system and for the corresponding system with point counterions, $\sigma_I = 0$, at $\rho_M = \rho_M^0$. We observe that the reduction of the counterion size leads to a stronger long-range screening, and a deeper minimum appearing at shorter separation. The minimum appears still at finite macroion separation, owing to the resistance of the counterion layer to be compressed.

We previously favored explaining the short-range attraction appearing in the 60:2 system by spatial correlations between the counterions residing on neighboring macroions [13], a picture advocated by Kjellander for charged planar surfaces [17]. Our calculated effective macroion-macroion potentials support this view in several aspects: (i) the attractive component is virtually density independent, (ii) the dis-

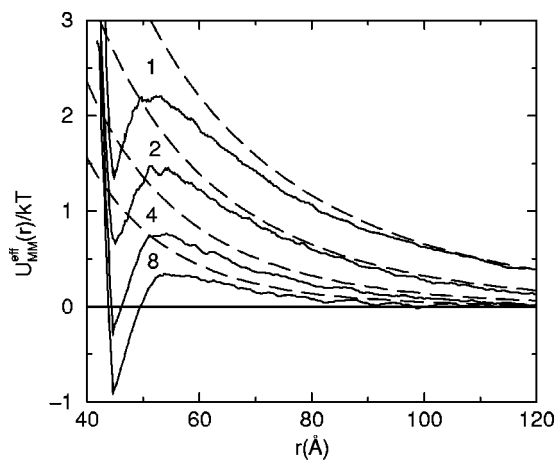


FIG. 2. Effective macroion-macroion potentials for the 60:2 system obtained from the IMC procedure (solid curves) and the Cell-MC-CR approach (dashed curves) at indicated macroion number density given in units of ρ_M^0 .

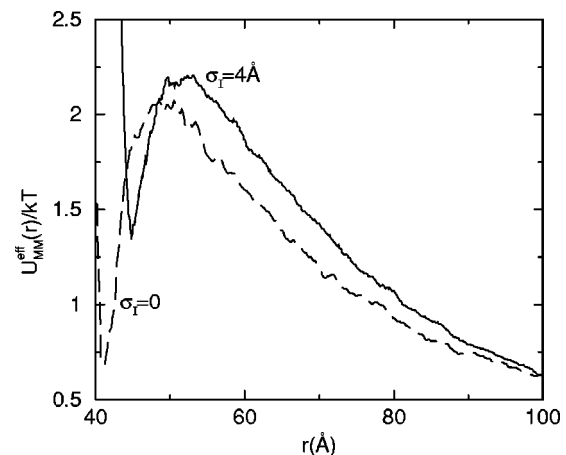


FIG. 4. Effective macroion-macroion potentials for the 60:2 system obtained from the IMC procedure at indicated counterion diameter and at macroion number density $\rho_M = \rho_M^0$.

tance range of the attractive component agrees with the typical spacing between the adsorbed counterions, and (iii) the attraction becomes stronger as the counterion size becomes smaller through a reduced macroion-counterion contact separation. It should be mentioned that the correlation effects are also present in the 60:1 system, although completely masked by the dominating double layer repulsion. Moreover, since (i) the short-range attraction is similar for $\sigma_I=0$ and 4 Å and (ii) depletion attraction is excluded in the case of $\sigma_I=0$, we conclude that depletion contribution to the attraction is negligible for the finite-sized counterions [10]. Finally, we emphasize that the expected long-range Yukawa tail appearing at sufficiently small density and counterion size for finite-sized counterions [37] is demonstrated here by the essentially exact IMC technique.

To conclude, we have successfully calculated effective macroion-macroion potentials appearing in the primitive asymmetric electrolyte model and shed new light on the short-range attraction appearing in solutions of charged colloids. The approach used requires accurate determination of the macroion-macroion RDF within the primitive model, and the effective potential of the reduced system is constructed to

precisely recover the macroion-macroion RDF of the full system. With common computational tools, one is now able to simulate accurate structural properties of primitive asymmetric electrolyte models with macroions carrying up to circa 100 elementary charges [16]. Therefore, the application of these techniques will be of great value for studying large-scale spatial or temporal properties of such systems, when the direct simulation using the primitive model is unfeasible or not necessary. Hence, we can more efficiently study a wide range of charge stabilized colloidal systems, including ionic micellar solutions, microemulsions, silica particles, etc., once their distribution functions are known.

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