LETTER TO THE EDITOR

Discrete solvent effects on the effective interaction between charged colloids

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Abstract

We implement a new solvent-bath computer simulation scheme to calculate effective interactions between two charged colloidal spheres with their counterions in a hard-sphere solvent in order to test the primitive model and a solvent-averaged primitive model. We show that the presence of a granular solvent significantly influences the effective colloidal interaction. For divalent counterions, the total effective force can become attractive, generated by counterion hydration, while for monovalent counterions the forces are repulsive and well described by a solvent-induced colloidal charge renormalization. Neither effect is contained in the traditional 'primitive' approaches but both can be accounted for in a solvent-averaged primitive model.

(Some figures in this article are in colour only in the electronic version; see `www.iop.org`)

Supramolecular aggregates, such as colloids, polymers, or biological macromolecules, are typically suspended in a molecular solvent which guarantees their stability and profoundly influences their viscoelastic properties [1]: examples range from paints to dense DNA solutions in biological cells. A full *ab initio* statistical description of supramolecular solutions should start from a molecular scale including the solvent explicitly. Obviously this is a tremendous task due to the large length scale separation between the microscopic solvent and the mesoscopic solute and the enormous number of solvent particles which have to be considered explicitly. Therefore, most of the common statistical approaches are based on so-called 'primitive' models insofar as they disregard the molecular nature of the solvent completely such that solvent properties only enter via a continuous background.

A particular example for such a separation of length scales is furnished by charged colloidal suspensions [2] consisting of highly charged mesoscopic particles (so-called polyions) suspended in water or any other organic solvent together with their oppositely charged microscopic counterions. The key quantity for understanding the stability, structure, and dynamics of such colloidal dispersions is the *effective interaction* between two polyions, as a function of their mutual distance r. Neglecting the discrete solvent, this quantity has been calculated using modelling on different descending levels:

(i) the 'primitive model' (PM) of strongly asymmetric electrolytes which takes the counterions into account explicitly;

(ii) the nonlinear Poisson–Boltzmann approach which is inferior to the PM as it neglects counterion correlations;

(iii) the linearized screening theory resulting in a Yukawa form for the effective interaction potential as given by the electrostatic part of the celebrated Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [3].

The main effects of nonlinear Poisson–Boltzmann theory can be encaptured by a similar Yukawa potential but with 'renormalized' parameters leading to the concept of colloidal charge renormalization [4]. This picture is consistent with experimental data on dilute bulk solutions with monovalent counterions [5, 6]. Very strong correlations between divalent and trivalent counterions, however, may lead to attractive effective forces between like-charge polyions as shown in recent computer simulations of the PM [7–9].

In this letter, we investigate the influence of *solvent granularity* on the effective interactions between charged colloids. We explicitly add to the PM a molecular solvent modelled by a hard-sphere fluid. We study this model by direct computer simulation and use the concept of effective interactions to bridge the gap between microscopic and mesoscopic length scales. Our motivation for doing so is twofold. First, although the dipolar nature of the solvent [10] is not included, the model provides a minimal framework for moving towards a statistical description of hydration forces. Second, the solvent hard-sphere model was considered in earlier studies for the effective interaction between charged plates using liquid integral equations [11], modified Poisson–Boltzmann theory [12], or more sophisticated density functional approaches [13]. All of these descriptions, however, suffer from additional uncontrolled approximations such that 'exact' computer simulation results are highly desirable. Such simulations were performed for two parallel plates [14], which is a geometry different to that of two spheres, and for small neutral particles [15], but have hitherto not been available for spherical charged colloids.

As the primary focus, we implement a new 'solvent-bath' simulation scheme which allows us to simulate many neutral spheres together with the charged species and obtain explicit results for the effective force between nano-sized highly charged colloids. We use these data to test a theory with solvent-averaged effective interactions between the charged particles similar in spirit to the old McMillan–Mayer approach for electrolyte solutions [16]. This solvent-averaged primitive model (SPM), which describes hydration forces in terms of depletion interactions, yields good agreement with the simulation data and can thus be used to obtain the effective interaction between larger colloidal particles. For monovalent counterions and large distances r, our simulation data can be described perfectly within a Yukawa potential with a solvent-induced polyion charge and screening length renormalization. For divalent counterions and nano-sized colloids, we find an attractive force. Neither effect is contained in the PM.

We consider two large spherical polyions with diameter σ_p and charge q_p at distance r, together with their counterions of diameter σ_c and charge q_c in a bath of a neutral solvent ($q_s = 0$) with diameter σ_s. In our model, the pair potential between the particles as a function of the mutual distances r is a combination of excluded-volume and Coulomb terms:

$$V_{ij}(r) = \begin{cases} \infty & \text{for } r \leqslant (\sigma_i + \sigma_j)/2 \\ q_i q_j / \epsilon r & \text{otherwise} \end{cases} \tag{1}$$

where ϵ is the smeared background dielectric constant of the solvent and $(ij) = (pp), (pc), (ps), (cc), (cs), (ss)$. Further parameters are the thermal energy $k_B T$ and the partial number densities ρ_i which can be expressed as partial volume fractions $\phi_i = \pi \rho_i \sigma_i^3 / 6$ ($i = p, c, s$). Charge neutrality requires $\rho_p |q_p| = \rho_c |q_c|$. We fix the two polyions along the body diagonal in a cubic simulation box of length L and use periodic boundary

conditions; hence $\rho_p = 2/L^3$. Henceforth, we fix ϕ_s to 0.3 corresponding to a dense fluid solvent with many solvent spheres in the box, such that a direct simulation is impossible. Thus we resort to the following 'solvent-bath' molecular dynamics method: the hard-sphere solvent is confined to a rectangular cell around the colloidal pair which is smaller than the full simulation box but still contains $N_s = 25.000$–30.000 solvent particles while the counterion motion is unrestricted; see figure 1 for the set-up. Periodic boundary conditions for the solvent–solvent interaction in the cell are applied: if a sphere centre is leaving the cell it is entering at the opposite face of the cell while always being affected by its neighbours and their periodically repeated images. The minimal distance $h = 12\sigma_s$ from the colloidal surface to the cell boundary is much larger than the hard-sphere bulk correlation length $\xi = 2.5\sigma_s$, such that the local hard-sphere packing fraction is constant and very close to $\phi_s = 0.3$ near the cell boundary. Furthermore, the typical counterion–counterion separation outside the cell is much larger than ξ, such that the effective counterion–counterion interaction there is very close to $V_{cc}(r)$. As an artifact of the solvent bath, the counterions experience an unphysical difference between their chemical potentials inside and outside the cell, thus artificially preventing the counterions
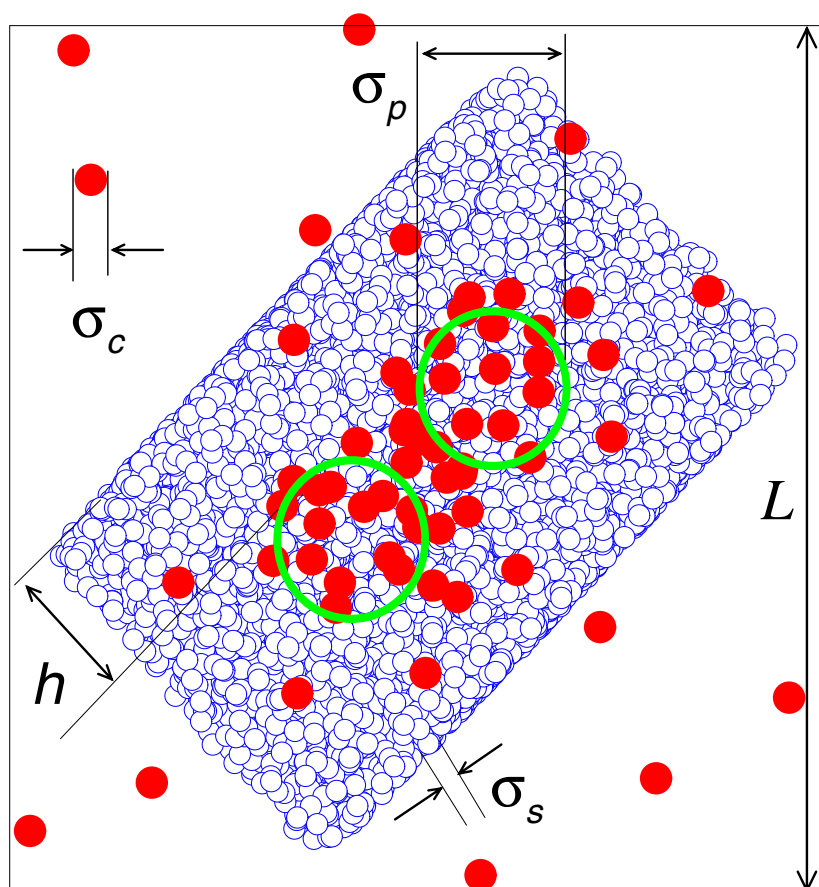

Figure 1. A view of the set-up as a projection of a simulation snapshot: two polyions (dark open circles) in a bath of solvent particles (small hollow spheres) contained in a rectangular cell of width h. The counterions shown as small dark spheres can move throughout the whole simulation box of size L.

from entering the solvent cell. This can be effectively suppressed by implementing a 'smooth' counterion crossing through the cell boundary. In detail, a counterion is by definition inside the cell if its centre is at least a distance $\Delta = (\sigma_s + \sigma_c)/2 + \delta$ (with a small $\delta = \sigma_s/10$) from the cell boundary—to ensure that it does not 'feel' periodic images of the solvent. If a counterion approaches this distance Δ from inside, we instantaneously turn off the counterion–solvent interaction. For the inverse process, i.e. for a counterion which is penetrating into the solvent cell from outside, the solvent–counterion interaction is kept turned off until the counterion centre has reached the penetration depth Δ from the cell boundary. Then the solvent–counterion interaction is switched on. In the case where the counterion is overlapping with solvent spheres, the positions of the solvent spheres are changed in that the separation vector between the counterion and solvent centre is scaled until the solvent spheres do not overlap with the counterion. If the moved hard spheres overlap with other ones (or with periodic images), their positions are scaled again. This is repeated until an overlap-free configuration is obtained. All velocities remain unchanged during this procedure. Of course, this procedure does not reproduce the true microscopic dynamics of counterions, but it gives the correct statistical sampling of their static equilibrium averages inside and outside the cell[1]. We have carefully tested the solvent-bath scheme against a huge simulation where the whole simulation box was filled with solvent particles (for the same parameters as in figure 2(a) but with a size ratio of σ_p:σ_c:$\sigma_s = 5$:1:1 and $\phi_p = 4.4 \times 10^{-3}$), and found perfect agreement for the effective forces and the inhomogeneous counterion- and solvent-density profiles.

We have also considered a simpler description on the primitive level *with solvent-averaged interactions* between the charged particles. The statistical recipe for getting these interactions from the full solvent model is to integrate out the solvent degrees of freedom [17]. In our case, the solvent-averaged interactions become hard-sphere depletion interactions which have been well studied theoretically [18] and by means of simulation [19]. The solvent-averaged primitive model (SPM) is defined by decomposing the depletion interactions approximately into pairwise parts. The corresponding interactions in the SPM are $\tilde{V}_{ij}(r) = V_{ij}(r) + V_{ij}^{(d)}(r)$ with $(ij) = (pp), (pc), (cc)$, and where $V_{ij}(r)$ is the primitive model interaction taken from equation (1) and $V_{ij}^{(d)}(r)$ is the depletion potential between two spheres of diameters σ_i and σ_j at distance r embedded in a hard-sphere solvent of bulk packing fraction ϕ_s [18]. We determine the set of input potentials for the SPM, $V_{ij}^{(d)}(r)$, in a reference computer simulation following reference [19]. They exhibit an attraction near contact of the order of several $k_B T$ and oscillations on the scale of the molecular solvent diameter σ_s decaying on the scale of the bulk hard-sphere solvent correlation length ξ. The counterion–counterion depletion is masked by the Coulomb part as typically $V_{cc}^{(d)}(r) \ll V_{cc}(r)$. The polyion–counterion depletion interaction $V_{pc}^{(d)}(r)$, on the other hand, adds to the Coulombic attraction and is essential. Counterion hydration is thus described as solvent depletion attraction which pushes counterions towards the colloidal surface.

In our solvent-bath simulations, we fixed $T = 298$ K and $\epsilon = 81$ (water at room temperature) with $\sigma_s = 3$ Å and $\sigma_c = 6$ Å. We varied the polyion size σ_p and charge q_p and calculated the solvent- and counterion-averaged total force acting on a polyion for a given colloidal distance r. The force is projected onto the separation vector of the two colloidal spheres such that a positive sign means repulsion. This effective force $F(r)$ is the sum of four different contributions [7]; two of them are of pure electrostatic origin and two are entropic: the direct Coulomb repulsion as embodied in $V_{pp}(r)$, the counterion screening resulting from

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[1] Details of the counterion motion across the cell boundary cause only small relative corrections to the solvent bulk properties, of the order of the local number-density ratio between counterions and solvent at the cell boundary, which is smaller than 5×10^{-3}.
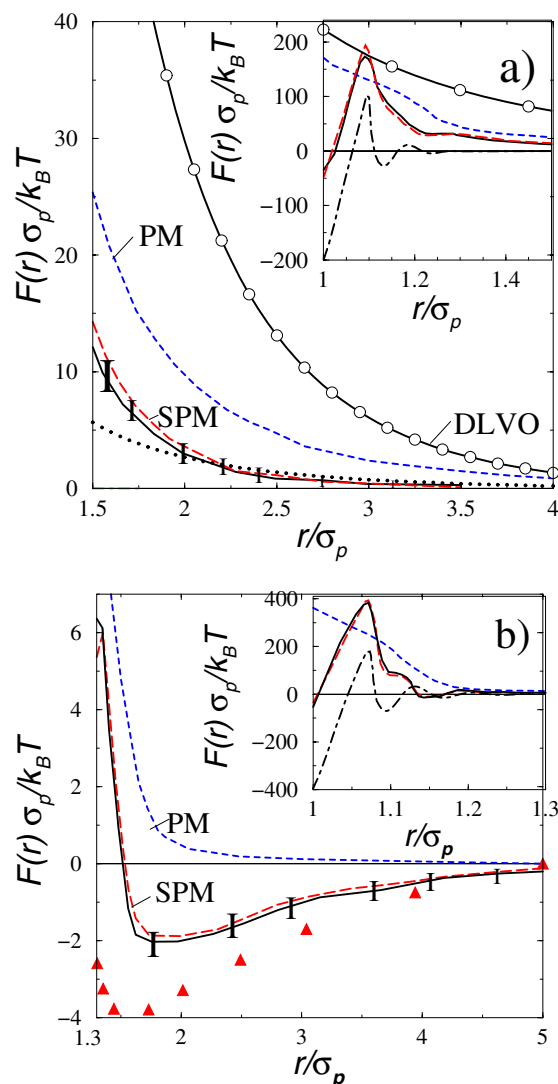
Figure 2. Reduced force $F(r)\sigma_p/k_BT$ versus reduced distance r/σ_p. The inset shows the same for nearly touching polyions at molecular distances (a) for monovalent counterions and $\sigma_p{:}\sigma_c{:}\sigma_s = 10{:}2{:}1$; (b) for divalent counterions and $\sigma_p{:}\sigma_c{:}\sigma_s = 14{:}2{:}1$. The further parameters are $|q_p/q_c| = 32$ and $\phi_p = 5.8 \times 10^{-3}$. Solid line with error bars: full solvent-bath simulation; long-dashed line: SPM; short-dashed line: PM; open circles: DLVO theory; dot–dashed line in inset: solvent depletion force. The dotted line in (a) represents the solvent-renormalized Yukawa model. The triangles in (b) show the electrostatic part of the total force in full solvent-bath simulations.

the averaged Coulomb force of counterions acting on the polyions, the counterion depletion (or contact) term arising from the hard-sphere part of $V_{pc}(r)$, and the solvent depletion force.

For nano-sized colloids, results for $F(r)$ are presented in figures 2(a) and 2(b). For nearly touching polyions (full curves in the insets of figures 2(a) and 2(b)) the force exhibits oscillations on the scale of the solvent diameter due to solvent layering leading to attraction for touching polyions, as the attractive solvent depletion part exceeds the bare Coulomb repulsion. For larger distances and monovalent counterions, the force is repulsive. Simulation data for

the PM using parameters identical to those of the solvent simulations are also included, which overestimate the force. The repulsion is even stronger in DLVO theory as derived from the Yukawa pair potential

$$V(r) = \frac{q_p^2 \exp(-\kappa(r - \sigma_p))}{(1 + \kappa\sigma_p/2)^2 \epsilon r} \tag{2}$$

with $\kappa = \sqrt{4\pi\rho_c q_c^2/\epsilon k_B T}$. For divalent counterions, on the other hand, there is attraction within a range of several polyion diameters. While the counterion depletion is repulsive, the attraction originates from the pure electrostatic parts of the force also shown in figure 2(b). It is thus qualitatively different from other mechanisms for attraction proposed recently [7,9]. As a result of solvent depletion, all counterions are pushed towards the colloidal surface, resulting in a strong counterion accumulation which strongly screens the colloidal charge. The attraction is then obtained via counterionic correlations in this electric double layer. We emphasize that the presence of the solvent is crucial for the attraction: simulation data for the pure PM with the same input parameters but without solvent yield repulsive forces as the counterion layer around the polyion is much more diffuse. Furthermore, the SPM describes the solvent-bath data extremely well, yielding results that lie within the statistical error of the full simulation over the whole range of distances. This can be understood from the fact that—except for nearly touching polyions with 'squeezed' counterions—typical distances between triplets of charged particles are larger than ξ. Consequently solvent-induced triplet and higher-order many-body forces between the charged particles are small, such that the SPM is justified.

We finally use the SPM to investigate solvent effects for polyion sizes in the colloidal domain. Distance-resolved colloidal forces $F(r)$ for monovalent counterions are presented in figure 3. These forces are repulsive but again much smaller than those from PM simulations or DLVO theory. They can, however, be quantitatively described by a Yukawa cell model [4]. In fact, we have performed additional solvent-bath simulations for a single polyion in a spherical cell of radius $R = (4\pi\rho_p/3)^{-1/3}$, calculating the counterion density $\tilde{\rho}_c$ at the cell boundary.
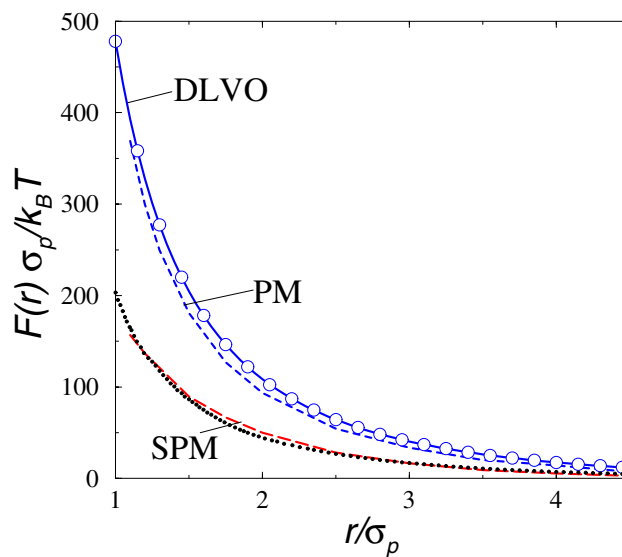

Figure 3. As figure 2(a), but now for larger polyions: $\sigma_p{:}\sigma_c{:}\sigma_s = 370{:}2{:}1$, $|q_p/q_c| = 280$, $\phi_p = 2.3 \times 10^{-3}$.

The corresponding effective Yukawa potential [4] has the same form as in equation (2) but with a solvent-renormalized screening length $\kappa^* = \kappa\sqrt{\tilde{\rho}_c/\rho_c}$ and a solvent-renormalized charge $q_p^* = q_p\tilde{\rho}_c/\rho_c$ which is considerably smaller than the bare charge. The actual value of q_p^*, however, differs strongly from the charge renormalization according to the PM or Poisson–Boltzmann theory [4]. The force resulting from the solvent-renormalized Yukawa model fits our full simulation data for nano-sized colloids for large distances and monovalent counterions (see figure 2(a)) and perfectly describes the SPM data for larger colloids except for molecular distances (see figure 3).

In conclusion, on the basis of a unified statistical description of counterion hydration and screening, we have shown that hydration forces profoundly influence the colloidal interaction. For divalent counterions, there is solvent-induced *attraction* which is not contained in the traditional primitive model but can be encaptured within a solvent-averaged primitive model. For monovalent counterions, the forces can be described by a *charge renormalization* induced by counterion hydration forces. This picture is in agreement with experiments on strongly deionized samples where a Yukawa picture can still be employed, provided that the colloidal charge is renormalized towards a value smaller than the bare charge [5, 20]. The general concept of charge renormalization should be transferable to other situations where screening by a few remaining 'free' counterions dominates the interaction as, e.g., for a polar solvent, for different polyionic surface charge patterns, and for explicit surface chemistry.

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