

Interaction between charged colloids in a low dielectric constant solvent

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Abstract – Based on computer simulations of the primitive model of electrolytes, we show that the effective interaction between low-charge colloids in solvents of low or moderate dielectric constant depends crucially on the salt concentration. While in the absence of salt the interaction is repulsive in agreement with Derjaguin-Landau-Verwey-Overbeek theory, depletion of salt Bjerrum pairs around the colloids leads to an attraction between like-charge colloids even at small salt concentrations.

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Colloidal suspensions are important soft matter systems for many practical applications as they are omnipresent in paints, inks [1] and are used to probe and stretch biomolecules by optical tweezers [2–4]. Charged colloidal dispersions, such as mesoscopic polystyrene spheres, are typically suspended in water. The strong polar character of the aqueous solvent as embodied in the high dielectric constant of $\epsilon = 80$ at room temperature induces counterion dissociation from the colloidal surfaces which keeps the charged suspension stable [5]. The amplitude of the resulting effective repulsion between the colloids can be controlled by the addition of salt into the suspension. Additional counter- and coions enhance the screening of the electrostatic interaction and reduce the repulsion.

Recently, charged colloidal spheres in less polar solvents [6–9] ($\epsilon \approx 6$) have been prepared, well characterized and exploited as valuable model system for phase transitions [10]. From an applicative point of view, low-dielectric solvents are crucial for electronic ink devices [11]. In deionized samples, typically much less impurity ions are contained in the suspension such that the added salt concentration can be kept extremely small (typically 10^{-9} mol/liter). Low-charge colloids have been used together with nonadsorbing polymers in order to observe an equilibrium clustering which is governed by a

short-ranged interaction due to the depletion of polymers and a long-ranged interaction due to the screened electrostatics [12–15]. In oppositely charged binary mixtures, a low-dielectric solvent drastically increases the mutual attraction between oppositely charged species. Thus they have been used to study the formation of ionic crystals [7,16] and lane formation in nonequilibrium [7,17] under the action of an electric driving field.

A reduction of the solvent dielectric constant ϵ drastically increases the Coulomb coupling between the charged species. A convenient measure of this coupling is the interaction energy at contact between charged microions in units of the thermal energy $k_B T$, namely $\Gamma = e^2 / \epsilon \sigma_c k_B T$, where e is the charge and σ_c the hard core of the microions. Switching from aqueous to less polar solvents increases the Coulomb coupling by one order of magnitude. For typical ion radii $\sigma_c = 8 \text{ \AA}$, the Coulomb coupling is about 10 for $\epsilon = 8$ at room temperature. This implies that oppositely charged microions will tend to pair, a clear trend which is well known in the context of the so-called “restricted primitive model” (RPM) [18,19] of equimolar oppositely charged hard sphere mixtures. In fact, these pairing effects lead to a critical point in the RPM and one may expect new phenomena like Casimir forces [20] if two colloids are immersed in a salt solution close to criticality.

In this letter we study the effective interaction between micron-sized low-charge colloids in non-aqueous solution with a strongly reduced dielectric constant at small salt concentrations. The parameters correspond to recent experiments [8]. In the salt-free case, the interaction is repulsive and in quantitative agreement with Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [21]. However, we show that even a small addition of salt of about 10^{-10} molar, leads to a breakdown of the traditional DLVO theory¹ and induces an *attraction* between the colloids. While such a small salt concentration is impossible to achieve in aqueous solution, it is no problem to get to these extremely low concentrations in low dielectric constant solvent. The mechanism of the attraction is traced back to a pairing of co- and counterion which form highly fluctuating dipoles in the solvent. These dipoles have less possibility to correlate and fluctuate near a system boundary and therefore the colloid surface is depleted from them. This gives an effective depletion attraction mechanism in terms of the dipoles which can—for low colloidal charges—beat the electrostatic repulsion.

The depletion attraction clearly is triggered by the salt concentration: in the absence of salt, there is repulsion in good agreement with DLVO theory. Therefore the mechanism of attraction proposed here is different from others proposed earlier also for the salt-free case, such as Coulomb depletion [22] and ionization [23]. Furthermore the effect only occurs for strong co- and counterion coupling in moderate dielectric solvents. In aqueous suspensions, the effective colloid-colloid forces are repulsive. Furthermore we remark that for higher colloidal charges typically used in experiments of ref. [6] the total force is still repulsive. In the experiments, the uncertainty in the bare charge and salt concentration is usually rather large, since only indirect information can be gained by measuring the conductivity and electrophoretic mobility [8]. However, results of the present work are relevant to individuate different regimes of colloid-colloid interaction upon small variations of the experimental conditions.

In our simulations, we model all ions as uniformly charged hard spheres such that they are interacting via excluded volume and Coulomb forces which are reduced by the dielectric constant ϵ of the solvent. The charged colloids have a mesoscopic hard-core diameter σ and a total charge Ze while all microions are monovalent with a charge e (e denoting the proton charge) and a microscopic hard-core diameter σ_c . A microscopic core of the microions is needed to prevent the system from the Coulomb collapse of oppositely charged ions. The averaged concentration of added salt is denoted with n_s . The system is kept at room temperature T such that the Bjerrum length for the microions is $\lambda_B = e^2/\epsilon k_B T$. Constant temperature molecular dynamics of all microions

¹The total interaction also comprises the van der Waals forces but those are typically much smaller than the electrostatic ones.

are used² to calculate canonical averages of the total force acting on the fixed colloidal particles for different colloidal configurations, *e.g.* for a given separation distance R between two colloids [22,24]. By integrating the distance-depending forces, the effective potential $U(R)$ is gained. A finite-size cubic simulation box of length L is used with periodic boundary conditions in the three different directions. For zero salt, the box length $L = (2/\rho)^{1/3}$ is fixed by a given macroion number density ρ . For finite salt concentration the results are independent of L provided L is large enough. We consider either a single macroion or a pair of macroions, placed along the body diagonal of the cube. The distance r between the two macroions is then varied for fixed simulation box size (respectively, macroion number density)³. It was checked that the simulation box is large enough to avoid spurious periodic image effects. Simulations involve up to about 11000 charged particles.

Two different parameter sets were simulated, one for low and another for high colloidal charge. In detail, the parameters for the system I are: $Z = -30$, $\sigma = 15000 \text{ \AA}$, $\sigma_c = 5 \text{ \AA}$, $\epsilon = 8$, $T = 293 \text{ K}$ such that $\lambda_B = 70 \text{ \AA}$. The second set of system II is: $Z = -650$, $\sigma = 20000 \text{ \AA}$, $\sigma_c = 5 \text{ \AA}$, $\epsilon = 6$, $T = 293 \text{ K}$ such that $\lambda_B = 92 \text{ \AA}$. The salt concentration is varied from $n_s = 0$ to $n_s = 11.4 \times 10^{-9} \text{ mol/l}$. For zero salt, the macroion density is chosen to be $7.41 \times 10^7 \text{ cm}^{-3}$, or the macroion packing fraction is 1.309×10^{-4} . For these system parameters the coupling between the oppositely charged salt ions at the contact is $\Gamma_{+-} = e^2/\epsilon k_B T \sigma_c = 15$ for the system I and $\Gamma_{+-} = 18$ for the system II. The inverted coupling parameter is usually referred to as an effective temperature T^* . In our cases, $T^* = 1/\Gamma_{+-} = 0.067$ for system I and $T^* = 0.056$ for system II. It is interesting to compare these effective temperatures to the critical effective temperature for the RPM which is [25] $T^* = T_c^* = 0.05$. The critical point in the RPM occurs at a critical number density of $n\sigma_c^3 = 0.08$. Thus both systems I and II are near-critical electrolytes. Indeed, as it is clearly seen from the snapshot picture of system I in fig. 1, a strong pairing (association) between oppositely charged ions in the system occurs. Still critical fluctuations (like the Casimir effect) are not strong enough to play any significant role for our system parameters.

We define the number of Bjerrum pairs in an actual snapshot by the number of oppositely charged pairs which are closer than a Bjerrum length. In fig. 2 the concentration of Bjerrum pairs n_p for each simulation run is shown. As the salt concentration increases, more and more

²We applied a cluster move to salt ions considered as Bjerrum pairs in order to speed up the simulation. The system then consists of dumbbell particles with a bond length drawn from the Boltzmann distribution of the $+-$ -interaction. The dumbbell concentration n_p and the concentration of the remaining free ions of both signs $n_s - n_p$ were obtained within a full molecular dynamics simulations. By comparing the results of the new system against full molecular dynamics simulations, we confirmed that the results do not change.

³Strictly speaking, the two-body pair potential is defined in the limit of infinite dilution $\rho \rightarrow 0$. Our simulations are carried out at finite albeit small densities.

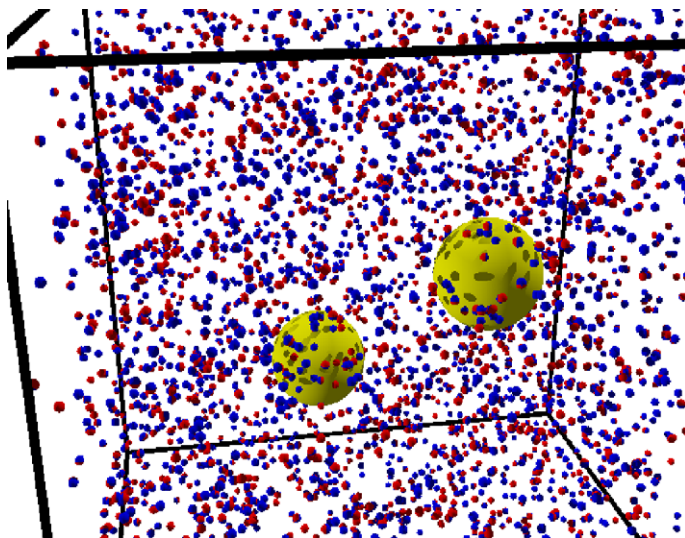


Fig. 1: (Colour on-line) Typical snapshot picture of the system I for $n_s = 7.55 \times 10^{-9}$ mol/l: two colloids (two big yellow spheres) are embedded into a near-critical electrolyte. Most of the positive (blue balls) and negative (red balls) are associated Bjerrum pairs. The size of the simulation box is also indicated. Note that the size of microions is increased one hundred times to make them visible.

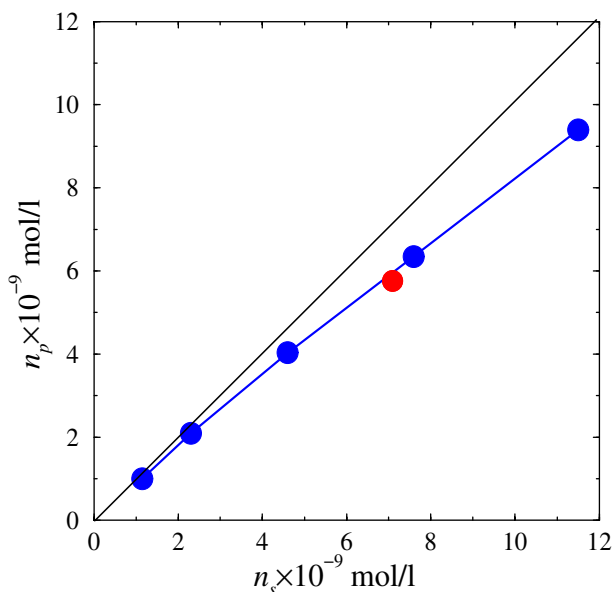


Fig. 2: (Colour on-line) Concentration of associated ion pairs n_p against the bulk salt concentration n_s . Blue line with symbols: results for the system I. Red point: result for the system II.

number of opposite microions are associated but the relative fraction n_p/n_s decreases with increasing salt concentration; for the highest salt concentration considered, 80 percent of the salt ion occur in Bjerrum pairs on average while these are 90 percent for very small salt concentrations. For the sequel, it is important to keep in mind that the major part of electrolyte occurs in pairs.

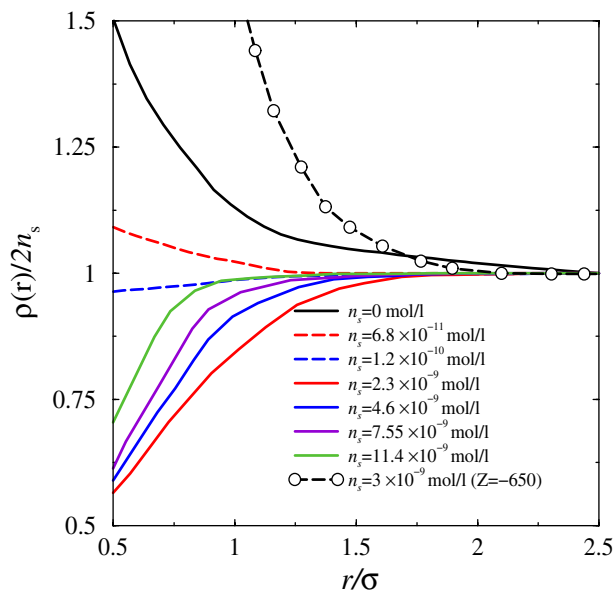


Fig. 3: Total ion number density around the macroion for different added salt concentration for system I. The data are scaled on the bulk total number density $2n_s$. Simulation results for system II are shown as a dashed line with symbols. Note that at higher salt densities there is a depletion zone close to the macroion surface in system I.

The total number density of ions around one single macroion is shown in fig. 3 as a function of their distance to the macroion. A depletion zone is clearly visible in system I except in the salt-free case. The reason for this depletion zone is that Bjerrum pairs tend to be in the bulk. It is known [26] that the internal energy of a salt pair decreases with increasing salt density. Therefore upon increasing the bulk density more salt pairs prefer to stay in the bulk than at the surface. The range of the resulting depletion is comparable with the mean distance $n_s^{-1/3}$ between ions in the electrolyte which roughly corresponds to the correlation length in the bulk. In particular, the range is getting smaller for increasing salt concentration. The depth roughly scales with the bulk concentration $2n_s$.

The total charge density $\rho_z(r) = |e|(\rho_+(r) - \rho_-(r))$, where ρ_{\pm} is the radial density of all \pm microions, around a single colloidal particle is shown in fig. 4. As in linear screening theory, the charge density piles up at the macroion surfaces and decays faster to zero as the salt concentration is increased. The building-up of charges mainly comes from the unpaired microions. The continuous decay of the charge density as a function of distance r , however, indicates that there is no charge inversion.

The averaged colloid-colloid effective potentials are shown in fig. 5. There is a well-defined attraction between macroions stemming from the depletion of Bjerrum pairs in the system I. No attraction is present in the salt-free case, where the forces match perfectly with the screened Coulomb prediction of the DLVO theory, which is also shown in fig. 5. Though such an ion association is also

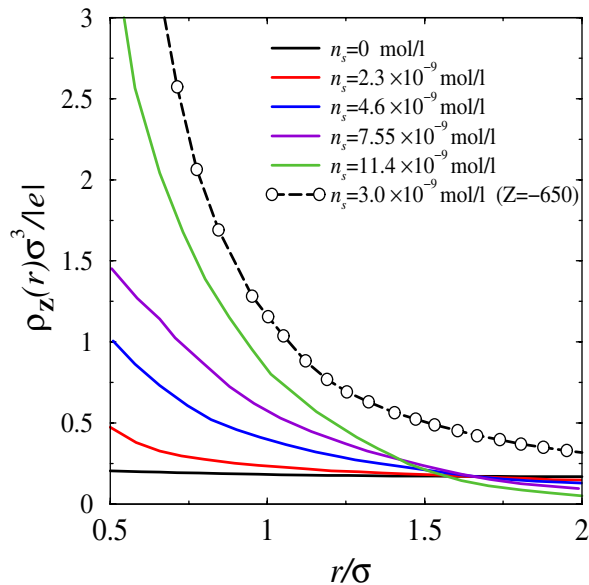


Fig. 4: Ion charge densities $\rho_z(r)$ around the macroion for different added salt concentrations n_s for system I. The charge density for system II is decreased 20 times and shown as a dashed line with symbols.

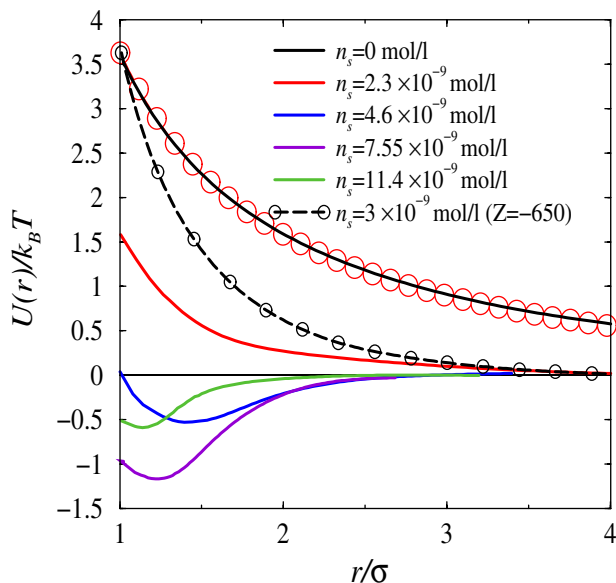


Fig. 5: (Colour on-line) Distance-resolved effective macroion-macroion interaction potential for different salt concentrations. Red circles: DLVO result for salt-free case. The result for the system II is decreased 200 times and shown as a dashed line with symbols.

present in the system II, the electrostatic potential of a highly charged macroion inhibits the creation of a similar depletion zone in the system II resulting in a total repulsive force. We remark that the attraction stays even for zero charge of the macroion ($Z = 0$). The strength of the Bjerrum pair depletion is in qualitative accordance with the general depletion picture [27] as far as the range

and depth are concerned. The depth is of the order of $k_B T$ and the range is in line with the width of the depleted layer around a single macroion. For high colloidal charges (system II), however, the depletion attraction is masked by the strong electrostatic repulsion. This might explain why the experimental samples of ref. [6] were observed to be stable and could be described by a screened Coulomb potential.

In conclusion, we have identified a new mechanism of attraction between like-charge mesoscopic colloids. It is salt-driven and occurs only for low or moderate dielectric constants ϵ of the solvent such that the salt ions form pairs which are depleted around the colloidal surface. This result in a depletion attraction which can overcome the electrostatic repulsion for low colloid charges. The mechanism is clearly different from other mechanisms [28,29] such as high counterion correlations (where attraction already occurs at zero salt concentration) and colloid overcharging. In principle, the interaction forces can be measured in experiments. One immediate consequence of our results concerns colloidal cluster formation. Here the message is to take high enough colloid charge in order to obtain long-ranged repulsion. It would be interesting to study full critical fluctuations by approaching closer the critical point of the salt.

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