

The interaction between colloids in polar mixtures above T_c

Sela Samin and Yoav Tsori^{a)}

Department of Chemical Engineering and The Ilse Katz Institute for Nanoscale Science and Technology,
Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel

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We calculate the interaction potential between two charged colloids immersed in an aqueous mixture containing salt near or above the critical temperature. We find an attractive interaction far from the coexistence curve due to the combination of preferential solvent adsorption at the colloids' surface and preferential ion solvation. We show that the ion-specific interaction strongly depends on the amount of salt added as well as on the mixture composition. The calculations are in good agreement with recent experiments. For a highly antagonistic salt of hydrophilic anions and hydrophobic cations, a repulsive interaction at an intermediate inter-colloid distance is predicted even though both the electrostatic and adsorption forces alone are attractive. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4704673>]

I. INTRODUCTION

Charged surfaces in liquid media are ubiquitous in soft matter and the interaction between such surfaces has been studied extensively. In the seminal theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) the total interaction potential is the additive combination of the attractive van der Waals interaction and an electrostatic repulsive screened Coulomb potential.^{1,2} In the DLVO theory the liquid between the surfaces is a homogeneous dielectric medium and only enters the electrostatic potential through its permittivity ϵ . The situation is different in solvent mixtures, where the structure of the solvent may vary in space due to gradients in electric field and ion density. Several authors explored experimentally the interaction between charged surfaces in mixtures.^{3–7} In a homogeneous binary mixture of water and 2,6-lutidine close to the demixing temperature, a reversible flocculation of suspended colloids has been observed.³ The flocculated region in the phase diagram is suppressed by the addition of salt.⁴ These experiments were interpreted in terms of the preferential adsorption of one of the solvents on the colloid surface in accord with wetting theory.^{8,9} More recently, it was suggested that the selective solvation of ions in the two solvents is important in these experiments^{10,11} as well as charge-regulation effects.¹¹

Recently, direct measurement of the interaction potential between a colloid and a charged wall was performed in water–2,6-lutidine mixtures below the lower critical solution temperature (LCST).^{6,7} In these experiments the addition of salt greatly influenced the range and strength of the interaction,⁷ leading to an attractive interaction far from the critical temperature T_c . Addition of salt has a remarkable effect on the flocculation of colloids in a critical mixture of water–3-methylpyridine, where it reduces dramatically the onset temperature of the flocculation.⁵ Preliminary experiments¹² suggest that the variation of the mixture composition also has a pronounced effect on the interaction.

A theoretical effort has been made to incorporate ionic solvation effects in polar mixtures.^{10,11,13–15} The solvation energy of an ion arising from the ion-dipole interaction and sometimes other specific interactions with the polar solvent strongly depends on the solvent and the chemical nature of the ion.^{16–18} The total solvation energy of an ion when it is transferred from one solvent into another (the Gibbs transfer energy) is in many cases much larger than the thermal energy, especially if one solvent is water and the other is an organic solvent.^{17–19} In addition, for a given solvent, the solvation energy of cations and anions is generally different due to their different size and specific chemical interactions with the solvent, such as Lewis acid-base interaction. Thus, the magnitude and sometimes even the sign of the Gibbs transfer energy for cations and anions may differ in various salts and solvents.^{19,20}

In bulk binary mixtures, the addition of salt modifies the coexistence curve.^{21–25} In particular, for strongly hydrophilic or hydrophobic solutes in aqueous mixtures, solvation-induced phase separation is predicted to modify the bulk coexistence curve significantly, leading to the precipitation of water domains enriched with ions.²⁴ When a salt-containing mixture is confined between charged surfaces, the influence of ionic solvation on the surface interaction in miscible solvents has been studied in Ref. 15, while for partially miscible mixtures close to the coexistence curve it was explored in Ref. 10. In the latter case it was shown that preferential solvation alone can qualitatively modify the interaction between similarly charged surfaces, resulting in a strong long-range attraction.

In order to account for the recent experimental findings in critical mixtures,⁷ Bier *et al.*¹³ had employed a linear theory that includes both ion solvation and solvent adsorption on the confining surfaces. However, in their theory preferential solvation is only a small perturbation. Recently, Okamoto and Onuki¹¹ included in the theory solvent dependent charge-regulation whereby the colloid's charge is a fluctuating quantity dependent on the local solvent composition and solute concentration. In their work they found enhanced prewetting

^{a)}Electronic mail: tsori@bgu.ac.il.

and wetting transitions close to the coexistence curve and consequently a substantial modification of the colloid interaction.

In this paper, we theoretically investigate how the interplay between ion solvation and solvent adsorption affects the interaction between surfaces in the nonlinear regime. We show that a strong attraction exists even far from T_c due to the nonlinear coupling between solvation and adsorption. These effects are strongly ion-specific and hence depend on the salt properties and concentration. We highlight the qualitative features of the theory and give several new predictions.

We focus on the regime far from the prewetting and wetting transitions and neglect charge-regulation, assuming large surface ionization. Thus, we do not expect any discontinuities in physical quantities such as pressure and adsorption. We concentrate on electrostatics and ion-solvation forces and hence ignore the van der Waals interaction (which is relatively small in the current range of parameters).

The organization of this paper is as follows. In Sec. II we present a coarse-grained model of a salt-containing binary mixture, taking into account the specific ion-solvent and surface-solvent interactions. In Sec. III we present results for critical and off-critical mixture compositions and show how ion specific effects can be used to tune the inter-colloidal potential. Conclusions are given in Sec. IV.

II. MODEL

The surfaces of the two colloids are modeled as parallel plates of area S separated by a distance D and carrying a uniform charge density $e\sigma_L$ and $e\sigma_R$ per unit area, where e is the elementary charge and the indices L and R denote the left and right plates, respectively. An aqueous binary mixture containing salt is confined between the plates. ϕ is the volume fraction of the water ($0 \leq \phi \leq 1$), while the densities of the positive and negative ion are denoted by n^+ and n^- , respectively. Given their low density and small size, the volume fractions of the ions are neglected.

For the fluid free energy we have $F_b = \int f_b d\mathbf{r}$, where f_b is the bulk free energy density:^{23,26}

$$\begin{aligned} \frac{f_b}{T} = & f_m(\phi) + \frac{C}{2} |\nabla\phi|^2 + \frac{1}{2T} \varepsilon(\phi) (\nabla\psi)^2 \\ & + n^+ (\log(v_0 n^+) - 1) + n^- (\log(v_0 n^-) - 1) \\ & - (\Delta u^+ n^+ + \Delta u^- n^-) \phi. \end{aligned} \quad (1)$$

Here the Boltzmann constant is set to unity and T is the thermal energy. $v_0 = a^3$ is the molecular volume of the solvent molecules where a is the linear dimension of the molecules. The first term in Eq. (1) is the mixture free energy:²⁷

$$v_0 f_m = \phi \log(\phi) + (1 - \phi) \log(1 - \phi) + \chi \phi(1 - \phi), \quad (2)$$

where $\chi \sim 1/T$ is the Flory interaction parameter. In this symmetric model the critical composition is given by $\phi_c = 1/2$ and the critical interaction parameter by $\chi_c = 2$. The square-gradient term in Eq. (1) takes into account the free energy increase due to composition inhomogeneities,²⁷ where C is a positive constant. The third term in Eq. (1) is the electrostatic energy density, where ψ is the electrostatic potential. This energy depends on the composition through the constitutive re-

lation for the dielectric constant: $\varepsilon = \varepsilon(\phi)$. For simplicity we use the linear form: $\varepsilon(\phi) = \varepsilon_c + (\varepsilon_w - \varepsilon_c)\phi$, where ε_w and ε_c are the water and cosolvent permittivities, respectively. The second line of Eq. (1) is the ideal-gas entropy of the ions, valid at low densities, while the third line is the ion solvation in the mixture. In the simple bilinear form we employ, the strength of selective solvation is proportional to the coefficients Δu^+ and Δu^- for positive and negative ions, respectively.²⁶ In this form the Gibbs transfer energies of the ions are $T\Delta u^\pm(\phi_2 - \phi_1)$, where ϕ_1 and ϕ_2 are the compositions of two solvents.

In addition to the bulk term, one adds the contribution of the confining surfaces to the free energy: $F_s = \int f_s dS$, where f_s is the surface free energy density given by

$$f_s = e\sigma\psi_s - \Delta\gamma\phi_s, \quad (3)$$

where ψ_s and ϕ_s are the electrostatic potential and mixture composition at the surface, respectively. Equation (3) includes a short range interaction between the surface and liquid which is linear in ϕ , neglecting higher order terms. The surface field $\Delta\gamma$ measures the difference between the surface-water and surface-cosolvent surface tensions.

The fluid is in contact with a matter reservoir having composition ϕ_0 and ion densities n_0^\pm . Hence, the appropriate thermodynamic potential to extremize is the grand potential Ω :

$$\Omega = F_b + F_s - \int [\mu\phi + \lambda^+ n^+ + \lambda^- n^-] d\mathbf{r}, \quad (4)$$

where μ and λ^\pm are the Lagrange multipliers for the composition and ions, respectively. They can be identified as the chemical potentials of the species in the reservoir: $\mu = \mu_0(\phi_0, n_0^\pm)$ and $\lambda^\pm = \lambda_0^\pm(\phi_0, n_0^\pm)$.

The governing equations are obtained by minimization of Ω , leading to the Euler-Lagrange equations

$$\frac{\delta\Omega}{\delta n^\pm} = \frac{\pm e\psi}{T} + \log(v_0 n^\pm) - \Delta u^\pm \phi - \lambda^\pm = 0, \quad (5)$$

$$\frac{\delta\Omega}{\delta\psi} = \nabla \cdot (\varepsilon(\phi)\nabla\psi) + (n^+ - n^-)e = 0, \quad (6)$$

$$\begin{aligned} \frac{\delta\Omega}{\delta\phi} = & -C\nabla^2\phi + \frac{\partial f_m}{\partial\phi} - \frac{1}{2T} \frac{d\varepsilon}{d\phi} (\nabla\psi)^2 \\ & - \Delta u^+ n^+ - \Delta u^- n^- - \mu = 0. \end{aligned} \quad (7)$$

The first equation yields the Boltzmann distribution for the ion density

$$n^\pm = v_0^{-1} e^{\lambda^\pm} e^{\mp e\psi/T + \Delta u^\pm \phi}. \quad (8)$$

Note the dependence on the mixture composition in this equation. The ion distributions are inserted into Eq. (6) to obtain a modified Poisson-Boltzmann equation with the boundary conditions $-\mathbf{n} \cdot \nabla\psi_{L,R} = e\sigma_{L,R}/\varepsilon$. \mathbf{n} is the outward unit vector perpendicular to the surface. The governing equation for the composition [Eq. (7)] is supplemented by the boundary conditions $\mathbf{n} \cdot \nabla\phi_{L,R} = \Delta\gamma_{L,R}$. Assuming that $\psi = 0$ in the reservoir, the Lagrange multipliers for the different species

are

$$\mu_0 = \frac{\partial f_m}{\partial \phi}(\phi_0) - \Delta u^+ n_0^+ - \Delta u^- n_0^-, \quad (9)$$

$$\lambda_0^\pm = \log(v_0 n_0^\pm) - \Delta u^\pm \phi_0. \quad (10)$$

In our effectively one-dimensional system, solution of the Euler-Lagrange equations yields the density profile $\phi(z)$ and potential $\psi(z)$ from which we calculate all relevant quantities. Of particular interest is the pressure P_n exerted on the surfaces by the liquid. $-P_n$ is the normal component of the Maxwell stress tensor and it is given by^{15,28}

$$\begin{aligned} \frac{P_n}{T} = & \frac{C}{2} |\nabla \phi|^2 - C \phi \nabla^2 \phi + \phi \frac{\partial f_m}{\partial \phi} - f_m + n^+(1 - \Delta u^+ \phi) \\ & + n^-(1 - \Delta u^- \phi) - \frac{1}{2T} \left(\phi \frac{d\varepsilon}{d\phi} + \varepsilon \right) (\nabla \psi)^2. \end{aligned} \quad (11)$$

In a planar geometry P_n is the zz component of the stress tensor and is uniform in mechanical equilibrium. The net pressure on the plates is given by the osmotic pressure $\Pi = P_{zz} - P_b$, where P_b is the bulk pressure. The interaction potential between the plates $U(D)$ is calculated from the osmotic pressure through

$$U(D) = -S \int_{-\infty}^D \Pi(D') dD'. \quad (12)$$

The excess surface adsorption in a planar geometry is defined as usual by

$$\Gamma = \frac{1}{D} \int_0^D [\phi(z) - \phi_0] dz. \quad (13)$$

This quantity is measurable experimentally and accounts for the total excess of fluid between the plates relative to the bulk.

III. RESULTS

In the following, we examine the interaction potential $U(D)$ for a binary mixture containing 10 mM of salt at temperatures larger than the critical temperature, $T > T_c$.

A. Colloidal interaction in a mixture at a critical composition

We start with a reservoir at a critical composition, $\phi_0 = \phi_c$, confined by two hydrophilic ($\Delta\gamma_{R,L} > 0$) colloids. We first consider the symmetric case where both colloids are identical: $\Delta\gamma_L = \Delta\gamma_R$ and $\sigma_L = \sigma_R$. We set $\sigma_{L,R} = -\sigma_{sat}$, where $\sigma_{sat} = \sqrt{8n_0/(\pi l_B)}$ and $l_B = e^2/(4\pi\varepsilon(\phi_0)T)$ is the Bjerrum length. σ_{sat} is used because the effective surface charge saturates to this value in the high bare charge limit.²⁹ Furthermore, we assume symmetric preferential solvation, i.e., $\Delta u^+ = \Delta u^-$, and in this case the solvation asymmetry parameter, defined as $\Delta u^d \equiv \Delta u^+ - \Delta u^-$, vanishes: $\Delta u^d = 0$.

The profiles $\phi(z)$ and $n^\pm(z)$ are not uniform due to the presence of a gradient of the electric field (dielectrophoretic force) even in the absence of ions.^{30,31} In polar mixtures, this force is augmented by a more important solvation-related

force occurring when the ions migrating toward the electrodes “drag” with them the solvent in which they are better solvated. The parameters we use are such that in the profiles $\psi(z)$ and $\phi(z)$ the conditions $e\psi(z)/T \ll 1$ and $\Delta u^\pm \cdot (\phi(z) - \phi_0) \ll 1$ do not hold and hence a linearization of Eq. (5) is not expected to be accurate.^{11,13} In fact, we show below that it is the nonlinear coupling between the governing equations that is responsible to an attractive interaction far from T_c .

The solid curves of Fig. 1(a) show $U(D)$ as a function of the reduced temperature $\tau \equiv T/T_c - 1 = \chi_c/\chi - 1$ for $T > T_c$. Far above T_c $U(D)$ is purely repulsive; as the temperature is decreased toward T_c the interaction becomes attractive. The change in the shape of $U(D)$ originates from the interplay between the surface field, the solvation induced attraction, and the electrostatic repulsion between the plates. The attraction between the plates is stronger down to $\tau = 0.003$ and then becomes less attractive for $\tau = 0.002$. The attraction range of a few tenths of nm, its strength of a few T , as well as the temperature dependence are similar to those observed in recent experiments.^{7,12}

The dashed and dashed-dotted curves in Fig. 1(a) are the same as the solid curve for $\tau = 0.008$ except for one parameter. The effect of charge asymmetry is shown by the dashed-dotted curve, where the total charge was kept constant, but $\sigma_L = 3\sigma_R$. Here the attraction is stronger, as in the classic Poisson-Boltzmann theory,³² since the electrostatic repulsion between surfaces is weaker for the asymmetric case. The dashed curve shows that increasing Δu^- by 4 ($\Delta u^d = -4$) results in a slightly weaker interaction. In the linear theory,^{11,13} solvation coupling only enters as a term $\propto \Delta u^d$. Thus, by comparison to the solid curve in Fig. 1(a) where $\Delta u^d = 0$, it is clear that in the nonlinear regime this type of contribution is smaller than contributions proportional to Δu^\pm .

The Gibbs adsorption Γ corresponding to the curves in Fig. 1(a) is shown in Fig. 1(b). When the surface separation decreases Γ increases as the adsorbed fluid layers near the walls merge. Furthermore, since the density of the ions also increases, more fluid is drawn to the walls because of the solvation interaction. Γ increases as the adsorbed fluid layer thickness, which is comparable to the bulk correlation length, increases closer to T_c .

The parameters we use are close to those used in experiments in a salt containing water–2,6-lutidine mixture below the LCST.^{7,12} In these experiments it is reasonable to assume that the surfaces have different charge densities because of their different chemical nature. Therefore, below we use $\sigma_L = 3\sigma_R = -1.5\sigma_{sat}$ for hydrophilic surfaces. The value of $\Delta\gamma$ was chosen arbitrarily since there is no molecular theory to predict it accurately. Furthermore, in water–2,6-lutidine mixtures the anions are expected to favor the water environment more than the cations, since 2,6-lutidine is a Lewis base. This is supported by data of Gibbs transfer energies of ions in water-pyridine mixtures.¹⁹ 2,6-lutidine is a structural analog of pyridine and hence on the basis of Ref. 19 we took $\Delta u^+ = 4$ and $\Delta u^- = 8$. We stress that over a wide range of values for $\sigma_{L,R}$ and positive $\Delta\gamma_{L,R}$, the results do not change qualitatively. This is also true for the solvation parameters as long as the ions are hydrophilic, $\Delta u^\pm > 0$. Note that the molecular volumes of the two components differ substantially in

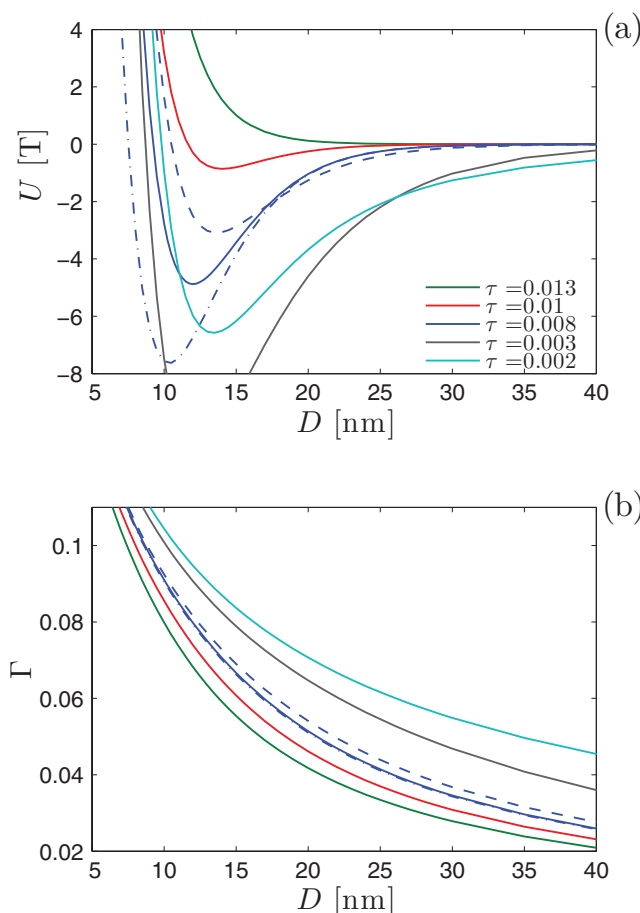


FIG. 1. (a) The interaction potential $U(D)$ between two colloids at a distance D at different temperatures $\tau \equiv T/T_c - 1 > 0$ immersed in a mixture at a critical composition ($\phi_0 = \phi_c$). $U(D)$ becomes attractive as τ decreases. Here $n_0 = 10$ mM and $\Delta\gamma_{R,L} = 0.1 \text{ T a}^2$, corresponding to about 3.4 mN/m. For the solid curves, $\Delta u^\pm = 4$ and the surfaces have the same charge $\sigma_{L,R} = -\sigma_{sat}$. Dashed-dotted curve: the same as the solid curve for $\tau = 0.008$ except that $\sigma_L = 3\sigma_R = -1.5\sigma_{sat}$. Dashed curve: the same as for $\tau = 0.008$ except that $\Delta u^- = 8$. (b) The corresponding excess surface adsorption Γ . In this and in other figures, as an approximation of a water-2,6-lutidine mixture we used $T_c = 307.2$ K, $v_0 = 3.9 \times 10^{-29} \text{ m}^3$, $C = \chi/a$,²⁷ $\varepsilon_{2,6\text{-lutidine}} = 6.9$, and $\varepsilon_{\text{water}} = 79.5$, and the surface area is taken to be $S = 0.01 \mu\text{m}^2$.

the real mixture leading to $\phi_c \neq 1/2$. Furthermore, our simplified model mixture has an upper critical solution temperature, whereas experiments are performed below the LCST in water-2,6-lutidine mixtures. Thus, one should interpret results in terms of the absolute distance from T_c .

$U(D)$ can be attractive when only surface fields are present ($\Delta u^\pm = 0$, $\Delta\gamma_{L,R} \neq 0$) due to critical adsorption.³³⁻³⁷ When only preferential solvation exists ($\Delta u^\pm \neq 0$, $\Delta\gamma_{L,R} = 0$), we have shown recently¹⁰ that fluid enrichment near the surface, induced by solvation, leads to an attractive interaction near T_c . Interestingly, as is shown in Fig. 2, the attraction between the surfaces is significantly altered by the coupling of solvation and surface fields.

In part (a) we highlight this idea by choosing parameters such that far from T_c , removing either the surface tension (dashed curve) or preferential solvation (dashed-dotted curve) the interaction is purely repulsive. When both forces are present the result is surprisingly a strong attractive interaction between the colloids (solid curve). Fig. 2(b) shows that

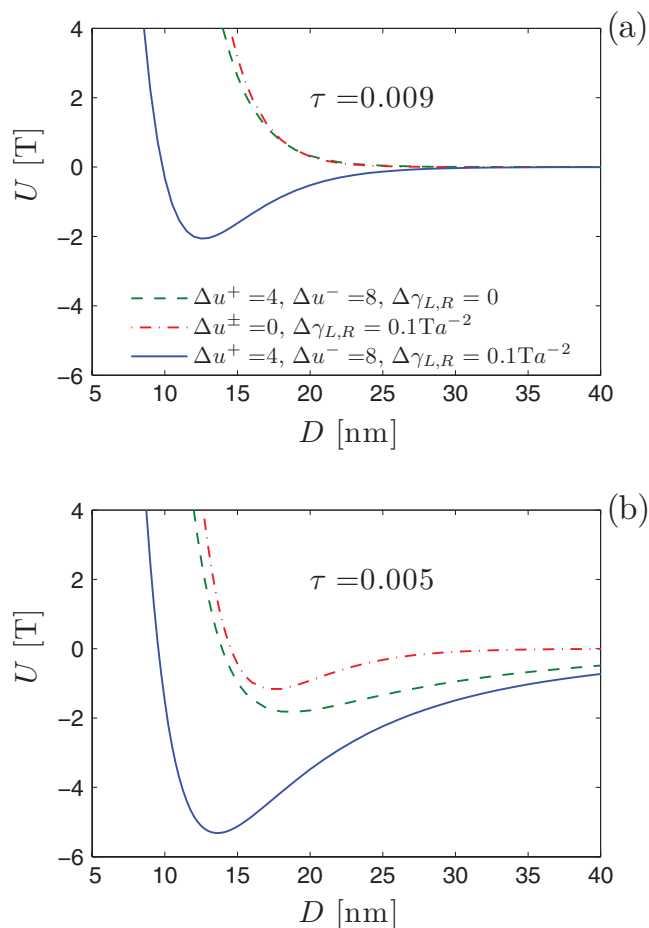


FIG. 2. The effect of removing preferential solvation or short-range chemical interactions on the potential $U(D)$ between the colloids at temperatures given by (a) $\tau = 0.009$ and (b) $\tau = 0.005$. The dashed and dashed-dotted curves show $U(D)$ when either the surface chemical affinity or preferential solvation parameters are zero, respectively. In the solid curves both short-range chemical preference and solvation are included. These two interactions are clearly nonadditive as the solid curve is not the sum of the dashed and dashed-dotted lines.

closer to T_c , an attractive interaction of similar magnitude exists when either force is missing, but the interaction is unexpectedly much stronger when both are present. Thus, in the nonlinear regime, solvation and adsorption forces are nonadditive and their coupling can account for attractive interactions far from T_c .

B. Surface interaction in an off-critical mixture

The interaction potential between two surfaces for off-critical mixture compositions at different temperatures is shown in Fig. 3. The legend also shows the dimensionless parameter $\kappa\xi_b$ corresponding to τ , where $\kappa = \sqrt{8\pi l_B n_0}$ is the Debye wave number and ξ_b is the bulk correlation length in the absence of ions, defined as $\xi_b(\tau) = \sqrt{\chi a^2 / (\partial^2 f_m(\phi_c) / \partial \phi^2)}$. The combination $\kappa\xi_b$ is useful for comparison with experimental results. Experimentally, it was found that ions do not modify the correlation length significantly.⁷

As is seen in Fig. 3 for $\phi_0 \neq \phi_c$, the curve $U(D)$ becomes attractive closer to T_c , similar to the $\phi_0 = \phi_c$ case, but the

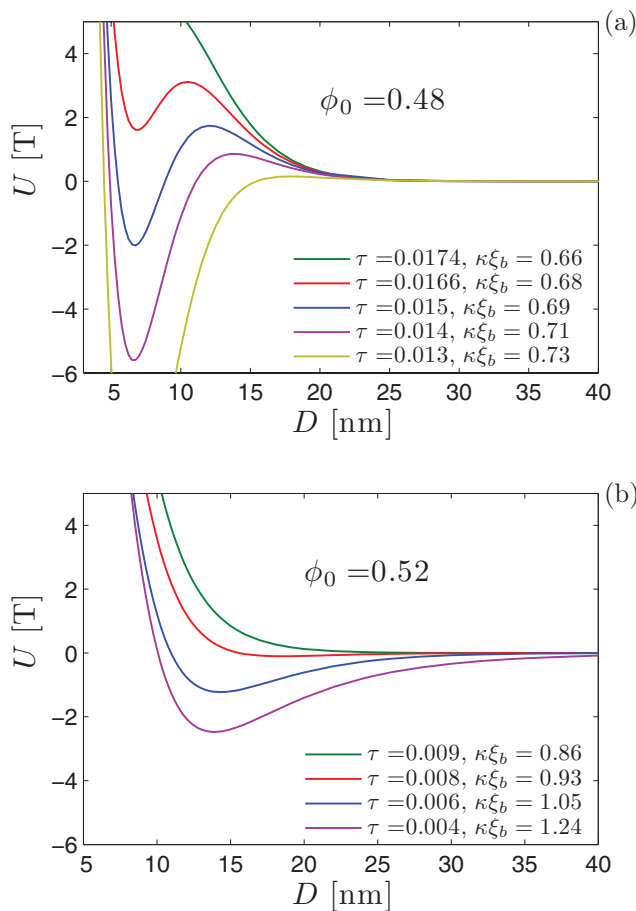


FIG. 3. Interaction potentials at different temperatures τ , (a) for $\phi_0 = 0.48 < \phi_c$ with $\Delta\gamma_{R,L} = 0.1T/a^2$ and (b) for $\phi_0 = 0.52 > \phi_c$ with $\Delta\gamma_{R,L} = 0.4T/a^2$. The onset temperature for attraction is higher for $\phi_0 < \phi_c$ due to preferential solvation. In (a), at intermediate temperatures the potential has metastable states. Here we used $\Delta u^+ = 4$, $\Delta u^- = 8$, and $\sigma_L = 3\sigma_R = -1.5\sigma_{sat}$. We took the average ion density to be $n_0 = 10$ mM leading to κ values of $\kappa \approx 2.69$ nm.

temperature range at which this occurs is different. The attractive interaction is stronger for $\phi_0 < \phi_c$ [Fig. 3(a)] and thus the temperature range above T_c at which it occurs is larger; compare with τ values in Fig. 2. Note that in Fig. 3(a) several curves have metastable states and that the interaction is repulsive at long range. The attractive interaction is weaker for $\phi_0 > \phi_c$ [Fig. 3(b)]. Here, we had to use a larger value of water-surface interaction in order to obtain a potential depth similar to the one which can be resolved in experiments (few T 's).⁷

In order to understand the dependence on reservoir composition we insert Eq. (10) for λ_0^\pm into the Boltzmann distribution Eq. (8) to obtain

$$n^\pm = n_0 e^{\mp e\psi/T + \Delta u^\pm(\phi - \phi_0)}. \quad (14)$$

This equation suggests that the ion density near the plates increases when ϕ_0 is reduced, which is verified numerically. This leads to a decrease of the osmotic pressure in the system since when $\Delta u^\pm \phi > 1$ the solvation contribution to Π overcomes the ions entropic repulsion [cf. Eq. (11)]. Thus, the coupling between the mixture composition and the ion density is important for the interaction between the surfaces. Due to the ion-solvent coupling the attraction is increased when salt

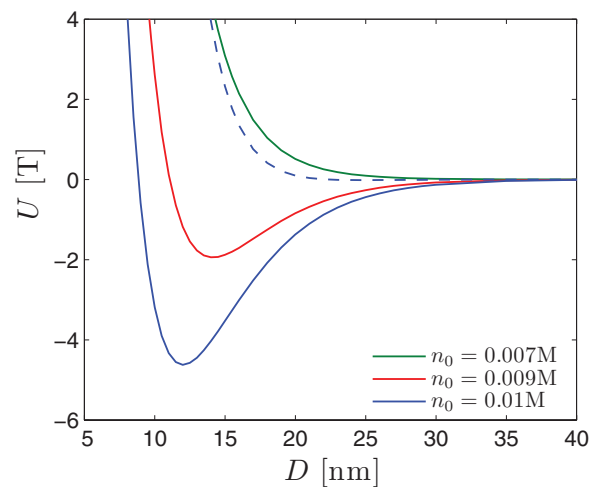


FIG. 4. Solid curves show the dependence of $U(D)$ on the mixture salt concentration n_0 with $\Delta u^+ = 4$ and $\Delta u^- = 8$; colloidal attraction increases with the addition of salt. The attraction is weak for a salt concentration of $n_0 = 0.01$ M but with $\Delta u^\pm = 0$ (dashed curve). Here $\phi_0 = \phi_c$, $\tau = 0.008$, $\Delta\gamma_{L,R} = 0.17T/a^2$, and $\sigma_L = 3\sigma_R = -1.5\sigma_{sat}$.

is added. This effect is shown by the solid curves in Fig. 4 and is seen in experiment.^{5,12} The dashed curve in Fig. 4 shows $U(D)$ for the highest salt concentration but in the absence of ion-solvent coupling ($\Delta u^\pm = 0$). In this case the attraction is very weak, indicating that the decrease in Debye length when salt is added is not significant for the potential at the given parameters.

In general, attraction occurs up to a temperature window $\Delta T \equiv T - T_c \approx 5$ K above T_c , quite far from T_c but not as large as $\Delta T \approx 10$ K recently observed in experiments. This is reasonable given the simplified mixture model, difference in geometry and many approximations of unknown quantities, e.g., σ , $\Delta\gamma$, and S . Also, in experiments the asymmetric binodal curve of water–2,6-lutidine mixtures is much “flatter” near T_c compared to the binodal in the symmetric Flory-Huggins model we use.

Better agreement with experiments is achieved when the values of $\kappa\xi_b$ are compared. Attraction is observed experimentally when $\kappa\xi_b$ is in the range $\kappa\xi_b \approx 0.85 - 1$ for $\phi_0 = \phi_c$.⁷ In preliminary experimental data¹² we find $\kappa\xi_b \approx 0.65 - 0.8$ for $\phi_0 < \phi_c$ and $\kappa\xi_b \approx 1.1 - 1.8$ for $\phi_0 > \phi_c$. These values are in the range of those in Figs. 2 and 3. The difference in temperature range between the experiments and our theory can be explained by the different scaling of $\xi_b = \xi_0|\tau|^{-\nu}$. The experimental value of ξ_0 and the critical exponent $\nu = 0.61$ ⁷ are quite different from the mean field values of ξ_0 and $\nu = 0.5$. Thus, the adsorbed liquid layers in experiments are thicker, leading to attraction at temperatures higher above T_c . Nevertheless, our results qualitatively show that including ion solvation in the theory accounts for colloid-surface attraction far from T_c in salt containing mixtures.

It is worth noting that in the temperature range we explore $\xi_b \ll D$ and thus composition fluctuations are not expected to affect the interaction significantly. However, close enough to T_c one has $\xi_b \sim D$ and hence a complete treatment of the interaction must go beyond the mean field level. The interaction in this case is also influenced by the confinement of

composition fluctuations that give rise to the so called critical Casimir force.^{6,34–36}

C. Interaction between hydrophilic and hydrophobic colloids

Another physically relevant scenario is that of hydrophilic and hydrophobic colloids, i.e., antisymmetric short-range chemical boundary conditions. For this case the adsorption force in the absence of salt is repulsive.^{34–36} However, experimentally it was observed that in the presence of salt the interaction potential becomes attractive when the temperature is decreased toward T_c , but then repulsive again as T_c is further approached.⁷ In order to explain this phenomenon, Pousaneh and Ciach¹⁴ assumed ions that are insoluble in the cosolvent and suggested that the attraction is due to the hydration of ions and is of entropic origin. Another explanation was given by Bier *et al.*,¹³ who attributed the attraction to the difference in preferential solvation of ions Δu^d . In their theory the attraction is linear in Δu^d .

Fig. 5(a) shows the non-monotonous behavior of $U(D)$ for antisymmetric surface fields within our theoretical framework. Here we assumed the ions have different solubilities, $\Delta u^d = -4$, and the surface charge of the hydrophobic surface is much smaller than that of the hydrophilic surface, as is usually the case. For these parameters the linear theory, relying on the asymmetry in the solvation energy of ions, reproduces surprisingly well the non-monotonous behavior.¹³ In the non-linear regime $\Delta u^d \neq 0$ is a requisite for this trend but the interaction depends on the nominal values of Δu^\pm as is shown below.

The onset of the repulsive force is at a surface distance $D \approx 4\xi_b$, occurring when the two adsorbed solvent layers begin to overlap.³⁷ At larger surface separations, the depletion of the more hydrophilic anions close to the hydrophobic surface gives rise also to an enhanced and energetically favorable hydrophilic solvent depletion. The net result is an attractive interaction at $D \gtrsim 4\xi_b$. As the critical temperature is approached and ξ_b increases the repulsive adsorption force dominates this relatively small attraction.

Fig. 5(b) demonstrates the influence of the value of Δu^+ , Δu^- , and their difference Δu^d on the interaction profile $U(D)$. In the solid blue curve we plot $U(D)$ for $\Delta u^d = -4$ where $\Delta u^+ = 4$ as in Fig. 5(a). Reduction of Δu^d from -4 to -2 (dashed curve) diminishes the strength of interaction by an order of magnitude, a strong nonlinear response. For $\Delta u^d = 0$ (dashed-dotted curve) the interaction is repulsive. Fig. 5(b) shows that the nominal values of Δu^+ and Δu^- are important, not just their difference. The solid curves in this figure all have $\Delta u^d = -4$ but different values of Δu^\pm . For a more hydrophilic salt (purple curve, $\Delta u^+ = 6$) the attraction is weaker while for an antagonistic salt where the cations are hydrophobic and the anions are hydrophilic (yellow curve, $\Delta u^+ = -2$) the attraction is much stronger. The reason for this is that hydrophobic cations reduce the water adsorption on the highly charged hydrophilic surface, thus reducing the repulsive adsorption force and amplifying the asymmetric solvation effect. The antisymmetric case is an example of the del-

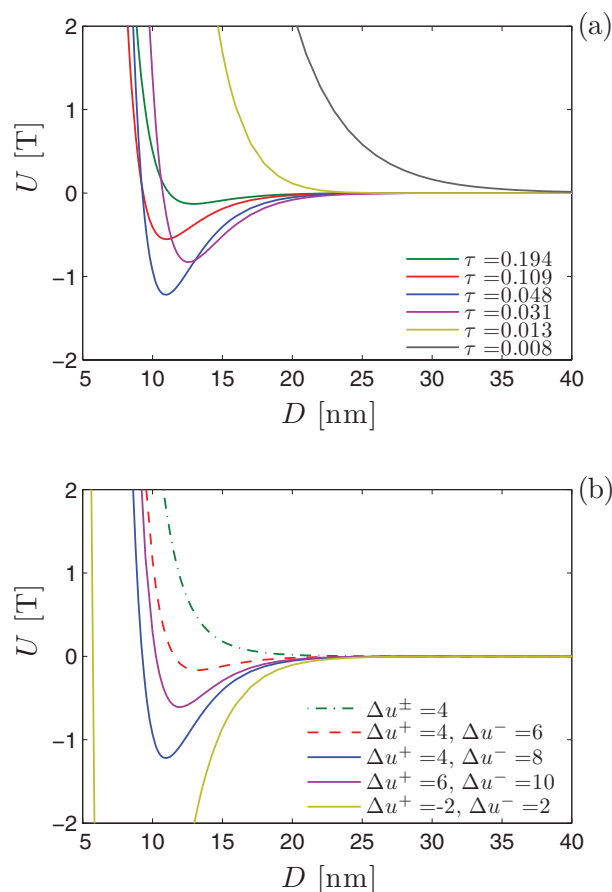


FIG. 5. Inter colloid potentials $U(D)$ for hydrophilic and hydrophobic colloids (antisymmetric boundary conditions). For the surface on the right we used $\Delta\gamma_R = 0.1T/a^2$ and $\sigma_R = -\sigma_{sat}$. For the surface on the left we used $\Delta\gamma_L = -0.4T/a^2$ and $\sigma_L = -0.01\sigma_{sat} \ll \sigma_{sat}$. (a) The interaction potential $U(D)$ at different temperatures τ showing that U becomes attractive when τ decreases, but repulsive close to T_c . Here we took for the ions $\Delta u^+ = 4$ and $\Delta u^- = 8$. (b) $U(D)$ at $\tau = 0.048$ and different values of Δu^\pm . The interaction is purely repulsive for $\Delta u^d = \Delta u^+ - \Delta u^- = 0$ (dashed-dotted curve) and weakly attractive for $\Delta u^d = 2$ (dashed curve). The attraction is much stronger in the solid curves, all having different values of Δu^\pm but the same difference $\Delta u^d = -4$. Among these curves, the attraction is strongest for the antagonistic salt ($\Delta u^- = -\Delta u^+ = 2$).

icate and complex interplay between solvent adsorption and electrostatic interactions in confined salty mixtures.

D. Ion specific effects

In this section we discuss some consequences of the specific nature of the ion solvation. The ion solvation energy can vary greatly depending on the chemical nature of the ion and solvent, its value being typically of the order $O(1)$ or $O(10)$. Large values of Δu^\pm are not uncommon, for example, in water-pyridine mixtures¹⁹ $\Delta u^+ \approx -25$ for Ag^+ and $\Delta u^- \approx 15$ for Cl^- . Hence, selective solvation can greatly modify the phase behavior and properties of the mixture. We refer the interested reader to the book by Marcus²⁰ and the more recent review of Onuki.²⁵

As a consequence, the influence of the ion-solvent coupling on the interaction potential is highly ion-specific. In Fig. 6(a) we plot $U(D)$ for hydrophilic ions and surfaces, Δu^+

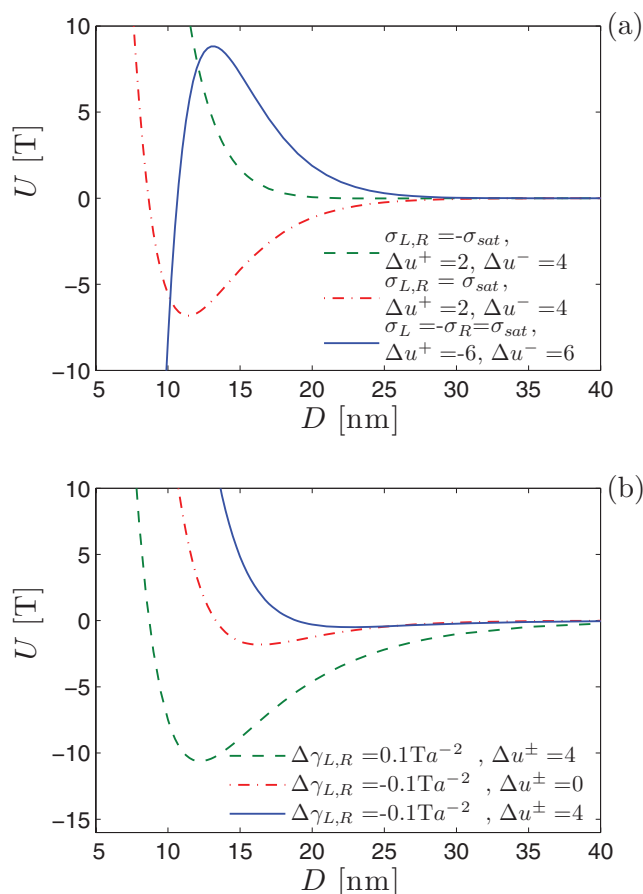


FIG. 6. (a) The effect of the sign of the colloids' charge on the inter-colloid potential $U(D)$. The interaction is attractive for two positively charged surfaces and is repulsive for two negatively charged surfaces; compare the dashed-dotted and dashed curves. We used $\Delta u^+ = 2$, $\Delta u^- = 4$, $\Delta\gamma_{R,L} = 0.1T/a^2$, and $\tau = 0.008$. In the solid curve the surfaces are both hydrophilic ($\Delta\gamma_{R,L} = 0.1T/a^2$) but oppositely charged. For an antagonistic salt with $\Delta u^- = -\Delta u^+ = 6$ there is a repulsive regime at an intermediate range. (b) The effect of the hydrophilicity or hydrophobicity of the colloid's surface. In the absence of preferential solvation ($\Delta u^\pm = 0$) two hydrophobic (and hydrophilic, not shown) surfaces weakly attract (dashed-dotted curve). For a hydrophilic salt ($\Delta u^\pm = 4$), hydrophobic surfaces repel (solid curve) whereas hydrophilic surfaces attract (dashed curve). We used $\tau = 0.003$ and $\sigma_{L,R} = -\sigma_{sat}$.

$= 2$, $\Delta u^- = 4$ and $\Delta\gamma_{R,L} = 0.1T/a^2$. When the surfaces are both positively charged (dashed-dotted curve), the anions are in excess between the plates and $U(D)$ is attractive since $\Delta u^- = 4$ is large enough and the solvation-related force overcomes electrostatic repulsion. However, this is not the case for negatively charged surfaces (dashed curve) where $U(D)$ is repulsive. In this case the cations are in excess between the plates and $\Delta u^+ = 2$ is not large enough to overcome the repulsion. Thus, the difference in the preferential solvation of cations and anions can produce a selective interaction with respect to the sign of the surface charge.

An even more intriguing scenario is that of oppositely charged surfaces, where for hydrophilic surfaces the interaction is expected to be purely attractive since both adsorption and electrostatic forces are attractive. Nonetheless, if the mixture contains a strongly antagonistic salt ($\Delta u^+ \Delta u^- < 0$, $|\Delta u^d| \gg 1$), $U(D)$ has a repulsive region, as is seen in the solid curve in Fig. 6(a) for which $\Delta u^- = -\Delta u^+ = 6$. In this curve,

since $\sigma_R = -\sigma_L$ the adsorption of both anions and cations is significant and similar in magnitude. Hence, since $\Delta u^- = -\Delta u^+$ the contribution of the solvation energy to the interaction is small. In addition, at separations $D \gtrsim 4\xi_b$, prior to the merging of the adsorbed solvent layers,³⁷ there is significant solvent depletion near a positively charged wall due to hydrophobic anions. This depletion reduces the adsorption force and the overall result is a repulsive interaction. At small separations the adsorption layers merge, Γ increases, and combined with the electrostatic attraction the potential is strongly attractive as expected.

Similar to the effect of the sign of the surface charge, the ion-solvent coupling renders the interaction specific also relative to the sign of the surface field. In the absence of salt, if both surfaces are hydrophobic or hydrophilic they attract.^{33–36} As we saw before, for hydrophilic surfaces the preferential solvation of hydrophilic ions greatly enhances the interaction far from T_c , see the dashed curve in Fig. 6(b) for $\Delta u^\pm = 4$ and $\Delta\gamma_{R,L} = 0.1T/a^2$. By reversing the sign of $\Delta\gamma_{R,L}$ [solid curve in Fig. 6(b)] the interaction becomes repulsive for hydrophobic surfaces and hydrophilic ions. The dashed-dotted curve in Fig. 6(b) shows that for hydrophobic surfaces in the absence of preferential solvation ($\Delta u^\pm = 0$) the interaction is weakly attractive. Here, the addition of hydrophilic ions renders the interaction repulsive by reducing the adsorption of the solvent on the hydrophobic surface while greatly increasing the adsorption and attraction for hydrophilic surfaces.

IV. CONCLUSIONS

In summary, we calculated the interaction potential $U(D)$ between two charged colloids in salt-containing binary mixtures. The preferential adsorption of one of the solvents on the colloid's surface combined with the preferential solvation of the ions gives rise to a strong attraction between the colloids far from the coexistence curve of the mixture. For surfaces with symmetric chemical affinity, the interaction is governed by the nominal ion solvation ($\propto \Delta u^\pm$) and to a lesser extent by the difference in solvation energies of cations and anions. This is true also for the attraction for antisymmetric boundary conditions albeit here $\Delta u^+ \neq \Delta u^-$ is a requisite for an attractive potential.

The ion and solvent densities near the surface of the colloid are highly sensitive to the ion solvation energy. Thus, the bulk mixture composition ϕ_0 and salt concentration n_0 play an important role in determining the inter-colloid potential (Figs. 3 and 4) and this suggests the possibility of fine-tuning the potential with these readily controllable parameters. In addition, the ion specific nature of the solvation energy renders the interaction potential sensitive to the sign of the surface charge or surface fields, as is shown in Fig. 6. We show that the interplay between surface and ion-specific interactions may lead to nontrivial effects whereby (i) two repulsive interactions combine to an attraction [Fig. 2(a)], (ii) for a hydrophilic salt, hydrophobic surfaces repel whereas hydrophilic surfaces attract [Fig. 6(b)], (iii) two oppositely charged colloids repel down to distances ~ 10 nm and have a high repulsive barrier of 5–10 T [Fig. 6(a)], or (iv) two similarly charged colloids

repel when they are negatively charged and attract when they are both positive [Fig. 6(a)].

Our mean-field theory allows the semi-quantitative interpretation of recent experiments performed in salty mixtures not too close to the critical temperature.^{7,12} We do not look at the influence of the critical fluctuations on the interaction between surfaces^{6,33–36} although it has been argued that the addition of a weakly solvating salt does not alter the universal critical behavior of the solvent¹³ However, the addition of a strongly antagonistic salt can change the mixture critical behavior drastically. In this case, a large change in the mixture critical exponents and even a complete suppression of the LCST were observed by Sadakane *et al.*^{38,39}

Recently, multilamellar structures were observed in a bulk binary mixture upon the addition of an antagonistic salt.⁴⁰ We believe that the effect of antagonistic salts on the interaction between *surfaces* is intriguing and deserves similar experimental attention. In addition, for temperatures below the critical temperature and/or near the wetting and prewetting transitions, first order capillary condensation¹⁰ and bridging transitions¹¹ have been predicted. In light of the current work and these recent findings we stress the importance of preferential solvation in salty mixtures. Since the Gibbs transfer energy of ions is usually larger than the thermal energy, the solvation-related force can either induce large composition perturbations by itself¹⁰ or amplify them significantly if already present, as in this work.

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