Electrostatic interactions in critical solvents

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Abstract – The subtle interplay between critical phenomena and electrostatics is investigated by considering the effective force acting on two parallel walls confining a near-critical binary liquid mixture with added salt. The ion-solvent coupling can turn a non-critical repulsive electrostatic force into an attractive one upon approaching the critical point. However, the effective force is eventually dominated by the critical Casimir effect, the universal properties of which are not altered by the presence of salt. This observation allows a consistent interpretation of recent experimental data.

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Introduction. – Effective interactions among surfaces in contact with fluid media play a central role for a variety of topical fields in soft- and condensed-matter physics, cell biology, colloid and surface science, and nanotechnology. Since many relevant fluid media contain polar liquids such as water, their confining surfaces acquire an electric charge due to ion association or dissociation. As a result, electrostatic forces are known to contribute significantly to these effective interactions. In addition, a strong and highly temperature-sensitive solvent-mediated effective force arises upon approaching critical points of the solvent. This critical Casimir force has recently been reported for a single colloidal particle close to a wall and immersed in a binary liquid mixture near its critical demixing point [1]; it is expected to play also a role for the aggregation of colloidal suspensions [2,3] and to provide control of the spatial distribution of colloids in the presence of patterned substrates [4].

Motivated by recent experiments, here we investigate the interplay between electrostatic and critical Casimir forces, which turns out to be responsible for rather unexpected effects in binary liquid mixtures with added salt. Colloids dispersed in such a solvent have been reported [2] to aggregate at temperatures further away from the critical demixing point as the ionic strength, i.e. the screening of the electrostatic forces, is increased. This observation has been confirmed experimentally also for a single colloid near a wall [5]. While it was originally argued [2] that the aggregation could be completely explained in terms of a simple superposition of the critical Casimir and screened Coulomb forces (see, however, ref. [3]), subsequent experimental results challenge this picture: an attractive colloid-wall interaction has been observed within a suitable temperature range even though both the electrostatic and the critical Casimir force are expected to be separately repulsive under these experimental conditions [5]. This observation poses a challenge because there is no obvious mechanism explaining the emergence of an attraction as salt is added to the solvent: van der Waals attraction, which is typically rather weak already in the absence of salt [1], is expected to become even weaker upon adding salt due to screening [6] and the formation of aggregates in the solvent, which might serve as depletion agents, has been ruled out experimentally [5]. All this points towards an important and yet unexplored aspect of the coupling between electrostatics and the critical fluctuations of the medium. Certain features of ion-solvent coupling near critical points were investigated in the past, such as the possibility of a micro-heterogeneous phase [7] and the influence of criticality onto the solubility.
The solvent particles are all assumed to be of equal number densities of the solvent components are given at positions coordinatesystem, we consider two parallel walls located ticphenomenawhichsofarhavebeeninthefocusonly of anon-trivialinterplaybetweencriticalandelectrosta-
tricdoublelayersgeneratedbytheunequalpartitioningofdue
totheinteractionofthesurfacechargeswilelec-
tparently.Wehaveverifiednumericallythattheapproxi-
mationstothefulloriginalmodel, the effective interaction potential the theoretical analysis on a suitable extension of standard
solventandthereforeontothecriticalCasimireffecthas notbeenstudiedyet.
In order to infer the mechanism responsible for the unexpected attraction mentioned above, we have based our theoretical analysis on a suitable extension of standard models [8,9]. From this we have derived an approximate Ginzburg-Landau–like description for which, in contrast to the full original model, the effective interaction potential between the confining surfaces can be interpreted transparently. We have verified numerically that the approximations used do not alter the results qualitatively. It turns out that the leading correction to the simple superposition of critical Casimir and screened Coulomb forces is due to the interaction of the surface charges with electric double layers generated by the unequal partitioning of salt ions in a non-uniform solvent. Within this picture the experimental observations mentioned above can be consistently interpreted. The present analysis provides an understanding of the unexpected effective interaction in terms of a non-trivial interplay between critical and electrostatic phenomena which so far have been in the focus only separately.

Model. – In a three-dimensional (d = 3) Cartesian coordinate system, we consider two parallel walls located at positions \( z = 0 \) and \( z = L > 0 \), respectively, with the space in between being filled by a binary liquid mixture.

In this solvent cations (+) and anions (−) are dissolved. The solvent particles are all assumed to be of equal size with volume \( \tilde{a}^3 > 0 \), whereas the ions are considered point-like. At the dimensionless position \( z := \tilde{z}/\tilde{a} \), the number densities of the solvent components are given by \( \phi(z)\tilde{a}^{-3} \) and \( (1 - \phi(z))\tilde{a}^{-3} < 0 \), whereas the densities of the cations and anions are given by \( \phi_+ \tilde{a}^{-3} \) and \( \phi_- \tilde{a}^{-3} \), respectively. The walls carry surface charge densities \( \sigma_+ \tilde{e} a^{-2} \) at \( z = 0 \) and \( \sigma_- \tilde{e} a^{-2} \) at \( z = L = \tilde{L}/\tilde{a} \), where \( \tilde{e} \) is the elementary charge. The influence of the walls on the solute due to chemical effects is captured by surface fields localised at the walls.

The composition \( \phi(z) \) of the solvent is coupled to surface fields \( h_0 \) at \( z = 0 \) and \( h_L \) at \( z = L \), where \( h_{0,L} > 0 \) \((<0)\) leads to a preferential adsorption of the solvent component with \( \phi = 1 \) \((=0)\). In principle, the surface fields \( h_{0,L} \) can be inferred from, e.g., studies of concentration profiles at a single isolated wall. The equilibrium profiles \( \phi, \phi_+ \), and \( \phi_- \) minimise the approximate grand potential density functional \( k_B T \Omega[\phi, \varrho_{\pm}] / A \),

\[
\Omega[\phi, \varrho_{\pm}] = \int_0^L dz \left\{ \omega_{\text{sol}}(\phi(z)) + \frac{\chi(T)}{6} \phi'(z)^2 + \sum_{i=\pm} [\omega_{\text{ion}}^{(i)}(\varrho_i(z)) + \varrho_i(z) V_i(\phi(z))] \right\} - h_0 \phi(0) - h_L \phi(L),
\]

with \( \omega_{\text{sol}}(\phi) = \phi(\ln \phi - \mu_\phi) + (1 - \phi) \ln(1 - \phi) + \chi(T) \phi(1 - \phi) \) and \( \omega_{\text{ion}}^{(\pm)}(\varrho_{\pm}) = \varrho_{\pm} \ln(\varrho_{\pm} \pm \mu_{\pm}) \) as the grand potential contributions to the surface fields \( h_{0,L} \). However, since the surface fields \( h_{0,L} \) are expected to be dominated by chemical effects, which are difficult to quantify, we refrain from formulating a microscopic model for \( h_{0,L} \); instead we consider \( h_{0,L} \) a priori unknown parameters.

The (temperature-dependent) Flory-Huggins parameter \( \chi(T) > 0 \) describes the solvent-solute interaction, which leads to a phase separation in the range \( \chi(T) > \chi(T_c) \); the gradient term \( \propto \phi'(z)^2 \) accounts for the spatial variation of the solvent composition [11].

The ion-solvent interaction is given by the effective ion potential \( k_B T V_{\pm}(\phi) \) due to the solvent, with \( V_{\pm}(\phi) = -\ln(1 - \phi - 1/\exp(-f_\pm)) \) and where \( f_\pm k_B T \) is the difference of the bulk solvation free energies of a ± ion in solvents with \( \phi = 1 \) and \( \phi = 0 \). This expression of \( V_{\pm}(\phi) \) follows [12] from the limit of low ionic strength, \( \varrho_{\pm} \rightarrow 0 \), of the free energy of a model within which a single site is occupied by one solvent particle and by an arbitrary number of positive and negative ions. \( V_{\pm}(\phi) \) leads to a bulk phase diagram with a critical point which is shifted towards larger values of \( \chi(T_c) \) as the salt concentration increases and the form used here is an improvement of the standard random-phase approximation \( \phi f_{\pm} \) (which it reduces to for \( f_\pm \ll 1 \)) because for \( f_\pm \gtrsim 1 \) the latter leads to multiple critical points [12] which are, however, not observed experimentally. For \( f_\pm \rightarrow \infty \) the ion potentials \( V_{\pm}(\phi) \) reduce to \( -\ln(1 - \phi) \), which describes the entropy loss and thus free energy increase due to the insolubility of ions in the solvent component with \( \phi = 1 \).

The electric displacement \( D(z, [\varrho_{\pm}]) \) is defined in eq. (1) fulfills Gauss’ law with fixed surface charges [6]: \( D(z, [\varrho_{\pm}]) = \varrho_+(z) - \varrho_-(z) \) and \( D(0, [\varrho_{\pm}]) = \sigma_0, D(L, [\varrho_{\pm}]) = -\sigma_0 \). Note that \( D(z, [\varrho_{\pm}]) \) is generated by the ±-ions and the surface charges \( \sigma_0 \), independent of \( \phi \). Within the present model, ions interact with the walls only electrostatically.

Approximations. – While the model in eq. (1) proved to be useful in certain previous investigations [8,9], this form is not appropriate for the present purpose of understanding the influence of ion-solvent coupling on the effective wall-wall interaction potential, because its complexity precludes analytical approaches and the corresponding high-dimensional parameter space does not lend itself to numerical scans. Therefore we use eq. (1) as a starting point for systematic approximations which simplify the model and thus allows us to identify the mechanism.
responsible for the leading-order contribution of ion-solvent coupling to the effective wall-wall interaction potential. By analysing the full original model eq. (1) numerically, we have verified that the approximations used do not alter the results qualitatively. Accordingly, we focus on an approximate grand potential functional for the solvent composition alone, which is obtained by expanding $\Omega[\phi, \varphi_\pm]$ in eq. (1) in terms of the order parameter $\varphi := \phi - \bar{\phi}$ and the ion density differences $\Delta \varphi_\pm := \varphi_\pm - I$ retaining quadratic contributions as well as terms proportional to $\varphi^3$ and $\varphi^4$. Here $\bar{\phi}_0$ and $I = \varphi_+ + \varphi_-$ denote the bulk solvent composition and the bulk ionic strength, respectively, corresponding to the chemical potentials $\mu_0$ and $\mu_\pm$. Similar to the Ginzburg-Landau theory for critical phenomena the expanded density functional no longer restricts the solvent composition $\phi_0$ and $\varphi$ and the ion densities $I + \Delta \varphi_\pm$ to the ranges $[0,1]$ and $[0,\infty)$, respectively; however, this feature of the approximate density functional is not expected to influence the resulting effective wall-wall interaction potential qualitatively, because the monotonicity of the profiles, which has been verified numerically for the full original model in eq. (1), is preserved. The minimisation of the expanded density functional with respect to $\Delta \varphi_\pm$ leads to linear, analytically solvable Euler-Lagrange equations for $\Delta \varphi_\pm(\xi, |\varphi|)$, which are functions of $\varphi$. Inserting these solutions into eq. (1) one obtains a Ginzburg-Landau-type functional

$$\frac{\mathcal{H}[\varphi]}{A} = \int_0^L dz \left\{ U(z) \varphi(z) + \frac{t(T)}{2} \varphi(z)^2 + \frac{g}{24} \varphi(z)^4 + \frac{x(T)}{6} \varphi(z)^2 \right\}$$

with the temperature-like variable $t(T) := 1/\phi_0 + 1/(1 - \phi_0) - 2x(T)$. Here we assume that the mixture is at its critical composition such that there is no $\varphi^3$-term. The electrostatic effects are contained in the coupling $g := 2/\phi_0^3 + 2/(1 - \phi_0)^3 + 6I(\gamma_+^2 + \gamma_-^2), \gamma_\pm := V'_\pm(\phi_0)$, as well as in an “external” field generated by the surface charges $\sigma_{0,L}$:

$$U(z) := -\frac{\kappa \Delta \varphi}{2(1 - \exp(-2\kappa L))} \times \left[ (\sigma_0 + \sigma_L \exp(-\kappa L)) \exp(-\kappa z) + (\sigma_L + \sigma_0 \exp(-\kappa L)) \exp(-\kappa(\kappa L - z)) \right]$$

with the Debye screening length $\kappa^{-1} = (8\pi \epsilon_B I)^{-1/2}$ and $\Delta \varphi := \gamma_+ - \gamma_-$. The “direct”, i.e. solely ion-mediated, electrostatic interaction between the walls is given by $W(L) := (4\pi \epsilon_B/\kappa)P(\kappa L, \sigma_0, \sigma_L)$, where

$$P(x, y_0, y_L) := \frac{2y_0 y_L + (y_0^2 + y_L^2) \exp(-x)}{2 \sinh(x)}.$$  

The ion-solvent coupling affects the critical point only at order $O((\Delta \varphi)^2)$ [12].

Upon approaching the critical point the dimensionless bulk correlation length $\xi = \xi/\tilde{a} = \sqrt{\chi(T)/(3\tilde{H}(T))}$, which characterises the exponential decay of the two-point correlation function, diverges. Accordingly, on the scale $\xi$, $U(z)$ is localised at the boundaries and, therefore, it merely modifies the surface fields $h_{0,L}$. Consequently $\mathcal{H}$ turns into a standard $\varphi^4$-theory, which describes the critical behaviour of the Ising universality class [13]. Thus, within the present model, electrostatic interactions do not affect the universal critical behaviour of the solvent.

The effective wall-wall interaction potential is defined by $\bar{\mathcal{H}}(L) := \omega(L)k_BT\tilde{a}^{-2}$ with $\omega(L) := (\mathcal{H}(L) - \mathcal{H}(\infty))/A$, where $\mathcal{H}(L)/A$ is the minimum of eq. (2). In general, for the critical contribution one has $\omega(L) = \vartheta(L/\xi)/L^{d-1}$, with a universal scaling function $\vartheta(x)$, which depends only on the relative signs of $h_{0,L}$ [14], with $\vartheta(x = 0) = \text{const}$ and $\vartheta(x \to \infty) = Cx^{d-1}\exp(-x)$, where $C$ is a universal, boundary-condition-dependent constant [14].

For a sufficiently small bulk correlation length, i.e. if $\xi \ln \xi \ll L$, the term $\propto \varphi^2$ in eq. (2) can be neglected relative to the term $\propto \varphi^4$. The resulting quadratic functional can be readily minimised and leads to the approximate effective wall-wall interaction,

$$\omega(L) = -\frac{3\xi}{\chi(T)}P(L/\xi, h_0, h_L) + 4\frac{\pi \epsilon_B}{\kappa}P(\kappa L, \sigma_0, \sigma_L)$$

$$-\Delta \varphi \frac{3k\xi^2}{\chi(T)}Q_1(\kappa L, \kappa \xi)(h_0 \sigma_L + h_L \sigma_0)$$

$$+Q_2(\kappa L, \kappa \xi)(h_0 \sigma_0 + h_L \sigma_L)$$

$$+O((\Delta \varphi)^2)$$  

with the function, which is analytical for $y > 0$,

$$Q_k(x, y) := \frac{1}{y^2 - 1} \left( \frac{y \exp(-2kx/y) - 1}{1 - \exp(-2kx/y)} \right).$$

The approximate effective wall-wall interaction potential $\omega(L)$ in eq. (5) has been found to agree qualitatively with that obtained numerically from the full original model in eq. (1).

In eq. (5) the term $\propto P(L/\xi, h_0, h_L)$ corresponds to the contribution of the surface fields to the wall-wall interaction in the absence of ion-solvent coupling ($\Delta \varphi = 0$), whereas the term $\propto P(\kappa L, \sigma_0, \sigma_L)$ is the direct electrostatic wall-wall interaction. The term $\propto (h_0 \sigma_L + h_L \sigma_0)$ is the dominant correction to the effective wall-wall interaction potential, whereas the term $\propto (h_0 \sigma_0 + h_L \sigma_L)$ is small. This dominant correction can be interpreted as the interaction of the electric double layer due to the unequal partitioning of ions ($\propto \Delta \varphi$) in the non-uniform order parameter close to one wall ($\propto h_{0,L}$) with the electric double layer due to the surface charge on the opposite wall ($\propto \sigma_{1,0}$).

**Discussion.** In the following we discuss the experiments with colloids alluded to in the introduction. The predictions of the present model for two walls can be readily translated into those for the wall-sphere and

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sphere-sphere geometry by means of the Derjaguin approximation, which is applicable at separations much smaller than the sphere radii [6]. It turns out that assuming additivity of Casimir and screened Coulomb forces, i.e. independence of the order parameter from electrostatics, is in general insufficient to explain the experimental observations, whereas the present model, which includes ion-solvent coupling, leads to a consistent picture.

First we consider symmetric boundary conditions, \((h_0, h_L) = (-, -)\), for which the ion-solvent coupling is masked by the strong direct electrostatic repulsion. This situation has been investigated experimentally with a suspension of hydrophilic spherical colloids in a water-oil mixture [2] as well as with a single hydrophilic colloidal sphere in a similar water-oil mixture near a hydrophilic glass wall [5]. In the presence of salt aggregation [2] or strong wall-sphere attraction [5] has been observed upon approaching the critical point of the binary mixture already several kelvins away from the critical point. Within the present model, this setting is described by \(h_0 = h_L < 0\) and \(\sigma_0 = \sigma_L < 0\) with the composition \(\phi\) expressed as the mole fraction of the non-aqueous component. For a certain choice of parameters fig. 1(a) displays the effective wall-wall interaction potential \(\tilde{\omega}(L)\). Since \(\Delta \gamma \geq 0\) corresponds to \(f_+ \geq f_-\), a negative ion-solvent coupling strength \(\Delta \gamma < 0\) describes a salt the cations of which are slightly better soluble in oil than the anions, which is expected because the oils used in the experiments, 3-methylpyridine and 2,6-dimethylpyridine (2,6-lutidine), are Lewis bases [15]. The parameters used in fig. 1 correspond to a critical water-2,6-lutidine mixture (\(\bar{a} = 0.34 \text{ nm}, \ell_B = 2.82\)) with 10 mM salt \((1/\kappa = 7.73)\). The value \(\Delta \gamma = -0.2\) corresponds to conditions \(f_- \gg f_+\), which are reasonable for Gibbs free energies of transfer [16]. Taking the renormalised surface charges \(\sigma_0 = \sigma_L\) of the approximate, linearised electrostatics to be equal to the saturation value \(\pm \sigma_{\text{sat}}\) corresponds to having large bare surface charges. Finally, due to the lack of a reliable microscopic theory, the values of the surface fields \(h_{0, L}\) have been chosen without further analyses. It has been verified, however, that the shapes of the curves \(\omega(L)\) do not change qualitatively over a wide range of choices for \(h_{0, L}\). Far away from \(T_c\) the effective wall-wall potential \(\omega(L)\) exhibits a repulsion due to the direct electrostatic wall-wall interaction. Upon approaching \(T_c\), \(\omega(L)\) starts to develop an increasing attraction due to the critical Casimir effect. Since the change from repulsion to attraction occurs at \(\kappa \xi \approx 1\), the attraction sets in only very close to the critical point if the ionic strength is small, whereas this change occurs already considerably far away from the critical point if the ionic strength is large. Due to the strong direct electrostatic wall-wall interaction between hydrophilic walls, the ion-solvent coupling does not qualitatively influence the effective wall-wall potential, so that the assumption of additivity of critical Casimir and screened Coulomb forces [2,3] is justified.

The situation is different for antisymmetric boundary conditions, \((h_0, h_L) = (+, -)\), as studied experimentally in ref. [5] using a single hydrophilic colloid near a hydrophobic glass plate. Repulsion is observed far away from as well as close to the critical point, whereas within an intermediate temperature range a strong attraction is found. The near-critical repulsion is readily understood in terms of the critical Casimir effect for antisymmetric boundary conditions and the repulsion far away from the critical point is of electrostatic origin. However, the attraction occurring in the intermediate temperature range due to the ion-solvent coupling induced by the difference between the solubility contrasts of cations and anions in the binary solvent.

Fig. 1: Effective wall-wall interaction potential \(\tilde{\omega}\) as a function of the scaled wall separation \(\kappa L\) and the scaled bulk correlation length \(\kappa \xi\) for (a) \((-\,-)\) and (b) \((+\,-)\) boundary conditions; \(\sigma_{\text{sat}} = \kappa/(\pi \ell_B)\) is the saturation surface charge density. For symmetric \((-\,-)\) boundary conditions, \(\tilde{\omega}\) is repulsive far away from the critical point due to the direct electrostatic interaction between the like-charged walls, whereas the Casimir force gives rise to an increasing attraction upon approaching the critical point. For antisymmetric \((+\,-)\) boundary conditions, \(\tilde{\omega}\) is repulsive far away from as well as close to the critical point. Attraction \((\propto \Delta \gamma)\) occurs in an intermediate temperature range due to the ion-solvent coupling induced by the difference between the solubility contrasts of cations and anions in the binary solvent.
range cannot be explained within a picture without ion-solvent coupling. Figure 1(b) shows $\tilde{\omega}(L)$ for a particular choice of non-symmetric surface fields $h_0 > 0, h_L < 0$ and surface charge densities $\sigma_0, \sigma_L < 0, |\sigma_0| < |\sigma_L|$ corresponding to a weakly charged hydrophobic wall, in accordance with the experimentally observed trend of hydrophobic walls being weakly charged [17]. Far from $(\kappa \xi \leq 0.28)$ and close to $(\kappa \xi \geq 0.82)$ the critical point $\tilde{\omega}(L)$ is repulsive because in eq. (5) the terms $\propto P$ dominate. Upon increasing $\kappa \xi$ beyond 0.28, i.e. en route towards $T_c$, attraction occurs (see $\kappa \xi = 0.39$), which for the chosen parameters is strongest around $\kappa \xi = 0.46$ and which weakens again closer to $T_c$ (see $\kappa \xi = 0.59$). This attraction is caused by the interaction of the electric double layer due to the unequal partitioning of ions ($\propto \Delta \gamma$) in the non-uniform order parameter close to the hydrophobic wall ($\propto h_0 > 0$) with the electric double layer due to the surface charge on the opposite, hydrophilic wall ($\propto \sigma_L < 0$). For the attraction to occur it is essential that the hydrophobic wall is sufficiently weakly charged ($|\sigma_0| \ll |\sigma_L|$).

Ionsolvent coupling manifests itself in yet another experiment described in ref. [5], in which the surface preference of the solvent has been measured by surface plasmon resonance. It is reported that a hydrophilic surface ($h_0 < 0$) becomes less hydrophilic upon adding salt, whereas no changes have been detected for a hydrophobic surface ($h_0 > 0$). According to eq. (2) the “external” field $U$ for a semi-infinite system ($L \to \infty$) acts like an additional, hydrophobic surface field $\delta h_0 = - \int_0^\infty dz U(z) \exp(-z/\xi) = \Delta \gamma \sigma_0 \kappa \xi / (2(1+\kappa \xi)) > 0$ if $\Delta \gamma, \sigma_0 < 0$. A hydrophilic surface becomes less hydrophilic by adding salt or for $T \to T_c$, whereas a hydrophobic surface is influenced only weakly as $|\sigma_0|$ is small.

Conclusion. – We have demonstrated that even though electrolytes do not alter the universal critical behaviour of polar solvents close to their critical point, the ion-solvent coupling is relevant further away, provided the direct electrostatic interaction is sufficiently weak. The crossover from an electrostatics- to a critical Casimir-dominated behaviour is expected to occur near that temperature at which the bulk correlation length becomes comparable with the Debye screening length. Several experiments with monovalent ions in binary liquid mixtures can be consistently interpreted in terms of the present model, according to which the influence of the ions on the order parameter can be described by an effective “external” field proportional to a coupling parameter which measures the difference between the solubility contrasts of cations and anions in a binary solvent. Our analysis makes it transparent how the coupling of critical phenomena and electrostatics can generate counterintuitive effects without violating the asymptotic universal behaviour.

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