Inflation of the screening length induced by Bjerrum pairs

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Abstract
Within a modified Poisson–Boltzmann theory we study the effect of Bjerrum pairs on the
typical length scale $1/\bar{\kappa}$ over which electric fields are screened in electrolyte solutions, taking
into account a simple association–dissociation equilibrium between free ions and Bjerrum pairs.
At low densities of Bjerrum pairs, this length scale is well approximated by the Debye length
$1/\kappa \propto 1/\sqrt{\rho_s}$, with ρ_s the free-ion density. At high densities of Bjerrum pairs, however, we find
$1/\bar{\kappa} \propto \sqrt{\rho_s}$, which is significantly larger than $1/\kappa$ due to the enhanced effective permittivity of
the electrolyte, caused by the polarization of Bjerrum pairs. We argue that this mechanism may
explain the recently observed anomalously large colloid-free zones between an oil-dispersed
colloidal crystal and a colloidal monolayer at the oil–water interface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Phase separation and criticality in electrolyte solutions, following from Debye–Hückel (DH) theory [1], was extensively studied by Fisher and Levin [2, 3]. The calculated critical density and temperature differed by only ∼10% from the results of Monte Carlo simulations by Panagiotopoulos [4], showing DH theory to be a reliable basis to describe some basic features of electrolyte solutions. Fisher and Levin extended the original DH theory by inclusion of *Bjerrum pairs*, following the ideas of Bjerrum [5] that plus and minus ions can form neutral pairs. These Bjerrum pairs or *dipoles* are considered as a separate particle component, and reduce, within the restricted primitive model, the total number of free ions. The results of the extended DH theory agreed remarkably with simulation results, especially when couplings between the dipoles and the ions, as well as hard-core repulsions, were taken into account [2]. Here, we apply the same ideas of Bjerrum to describe screening effects in low-dielectric solvents ('oils') by means of a modified Poisson–Boltzmann theory. In these solutions we expect strong correlations between the ions, since the energy gain of bringing two oppositely charged ions at contact can exceed the thermal energy considerably.

We will consider systems of free ions and dipolar particles, similar to the study of, for example, [6], and find that electric fields are screened over a typical length scale $1/\bar{\kappa}$ that can be significantly larger than the Debye length $1/\kappa$ (based on the ionic strength), at least for large dipole densities. We predict that these densities are to be expected in low-dielectric solvents by considering a simple association–dissociation equilibrium between the free and bound ions [7]. Recently, strong electrostatic repulsions were observed by Leunissen *et al* [10] in low-dielectric solvents ($4 \lesssim \epsilon \lesssim 10$), sometimes extending over a length scale beyond 100 μm. The Debye length $1/\kappa^{-1}$ was found to be only ∼4 μm, calculated from conductivity measurements (the density of free ions). The analysis presented in this paper provides a possible explanation and a reason for the quantitative differences between these experiments [10] and the theory in [11], where Bjerrum pairs were not taken into account.

In section 2 a reaction equilibrium between free and paired ions will be discussed. The parameter space will be divided into regions where bound ions outnumber free ions, and vice versa, by a similar analysis as presented in [3, 7]. In section 3 the effect of the dipole density on the screening length will be analyzed. First we extend Gouy–Chapman theory [12] by including dipoles and calculate the *effective* screening length $1/\bar{\kappa}$, similar to the calculations in [6]. Remarkably, we find $1/\bar{\kappa} \propto \sqrt{\rho_s}$ at high dipole densities, in contrast to $1/\kappa \propto 1/\sqrt{\rho_s}$, where ρ_s is the density of free ions. Finally we review and extend the theory presented in [11] and predict a larger effective screening length due to dipoles. The considered densities of free ions are well below the critical value, i.e. phase equilibrium is not considered, even though the temperatures of interest are close to the critical temperature.

2. Bjerrum pairs

First we consider a three-dimensional bulk electrolyte of monovalent cations and anions, at a total density of $2\rho_{tot}$. The ions may form pairs or remain free; the number density of dipolar Bjerrum pairs is ρ_d and the number densities of free ions are $\rho_+ = \rho_- = \rho_s$. In terms of dimensionless densities $\eta_x = \rho_x \sigma^3$, where σ is the common diameter of the ions, the total density η_{tot} of ions (of one type) is

$$\eta_{tot} = \eta_d + \eta_s. \tag{1}$$

The strength of the electrostatic interactions in the solvent is reflected by the Bjerrum length, which is the length at which the bare Coulomb interaction between two monovalent ions is exactly $k_B T$:

$$\lambda_B = \frac{e^2}{4\pi \epsilon k_B T}, \tag{2}$$

where e is the elementary charge and ϵ is the dielectric constant of the medium. For water at room temperature, this length is only 0.71 nm, for apolar solvents it measures up to several tens of nanometers and in vacuum it is $\sim$57 nm. The Coulomb interaction between two ions can hence be written in terms of the Bjerrum length:

$$\frac{V_C(r)}{k_B T} = \pm\frac{\lambda_B}{r} \equiv \pm\frac{1}{l}, \tag{3}$$

where the $+, -$ refer to equal and oppositely charged particles, respectively, r is the distance between the particles and l is a dimensionless distance. The dimensionless equilibrium constant K of the reaction of free ions that bind into paired ions is defined by

$$K = \frac{\eta_d}{\eta_+ \eta_-} = \frac{\eta_d}{\eta_s^2} = \frac{\Lambda^3}{\sigma^3} \exp\left(-\frac{\Delta G}{k_B T}\right), \tag{4}$$

where Λ is the ionic de Broglie wavelength and where ΔG is the free energy of a bound pair of ions (being separated by a distance $\sigma < r < \lambda_B$), with an associated Coulombic binding energy $V_C = -k_B T/l$. It will be convenient to introduce the dimensionless temperature $T^* = \sigma/\lambda_B$, such that K can be expressed in terms of an internal partition function:

$$K = 4\pi \left(\frac{1}{T^*}\right)^3 \int_{T^*}^1 dl\, l^2 \exp\left(\frac{1}{l}\right), \tag{5}$$

as already postulated by Bjerrum [5]. It can easily be checked that $T^* \simeq 1$ for typical ions such as Na$^+$ and Cl$^-$ in water at room temperature and $T^* \lesssim 0.2$ in oils with $\epsilon \lesssim 15$. Figure 1 shows the relation between the equilibrium constant K and the dimensionless temperature T^*. With increasing temperature K decreases, thereby lowering the tendency to form pairs according to (4). Using (1) this can be further quantified by relating η_s to η_{tot} as

$$\eta_{tot} = \eta_s + K\eta_s^2, \tag{6}$$

which yields η_s and η_d as a function of η_{tot} and $K(T^*)$ as

$$\frac{\eta_s}{\eta_{tot}} = \frac{1}{2K\eta_{tot}}(\sqrt{1 + 4K\eta_{tot}} - 1) = 1 - \frac{\eta_d}{\eta_{tot}}. \tag{7}$$
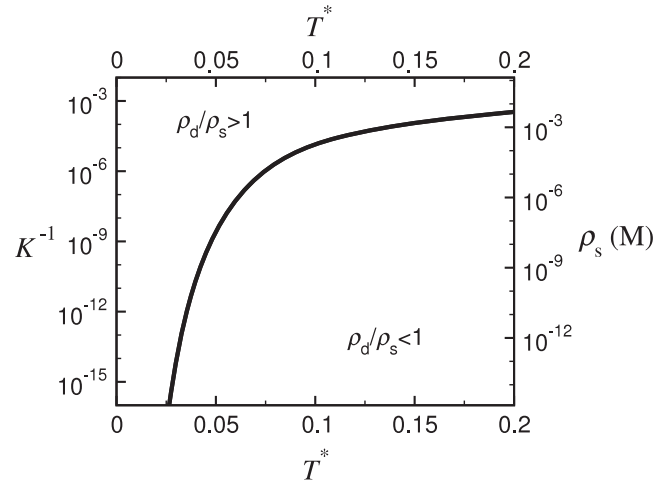
Figure 1. The inverse equilibrium constant K^{-1} as a function of the dimensionless temperature $T^* = \sigma/\lambda_B$. The line also marks the points where the density of paired ions equals the density of free cations/anions for given concentration of free ions (see right vertical axis), for an ionic diameter $\sigma = 0.5$ nm.

From (4) it can be easily seen that, if $K^{-1} = \eta_s$, then $\eta_s = \eta_d$. If the left vertical axis of figure 1 is read as the dimensionless density η_s of free ions, the curve $K(T^*)$ thus separates the parameter regime where dipoles dominate ($\eta_d/\eta_s > 1$) from the regime where free ions dominate ($\eta_d/\eta_s < 1$). The right vertical axis converts the corresponding $\eta_s = K^{-1}(T^*)$ to the molar density ρ_s for the typical choice $\sigma = 0.5$ nm. We have already seen that $T^* \simeq 1$ for typical ions such as Na$^+$ and Cl$^-$ in water at room temperature, and that $T^* \lesssim 0.2$ in oils with $\epsilon \lesssim 15$. Figure 1 therefore illustrates, for instance, that an electrolyte with a millimolar ionic strength, $\rho_s \simeq 1$ mM, is dominated by free ions for $T^* \gtrsim 0.15$ and by dipoles for $T^* \lesssim 0.15$. For nanomolar concentrations, $\rho_s = 1$ nM, the crossover is at $T^* \simeq 0.05$. For later reference we also consider the mean separation $\bar{\sigma}$ between the ions in a pair. Assigning a statistical weight $\propto \exp(\lambda_B/r)$ to a pair at separation r, one finds

$$\bar{\sigma}^2 = \sigma^2 \frac{\langle l^2 \rangle}{T^{*2}} = \sigma^2 \frac{4\pi}{K}\left(\frac{1}{T^*}\right)^5 \int_{T^*}^1 dl\, l^4 \exp\left(\frac{1}{l}\right), \tag{8}$$

which can straightforwardly be evaluated numerically. The result is shown in figure 2, as a function of T^*, for several upper bounds of the integration domain to check the dependence of $\bar{\sigma}$ and K on the definition of a Bjerrum pair, being two oppositely charged particles separated by a distance $\lesssim \lambda_B$. At low temperatures $T^* \lesssim 0.05$ the values do not depend on the precise definition, because the deep potential well of $>20k_B T$ at contact dominates the probability distribution.

3. Effective screening length

We now consider a system of monovalent ions near a charged plate at $z = 0$, where the z axis is perpendicular to the plate and the ion density is ρ_s at $z \to \infty$. We expect that the charge of the plate is screened by an oppositely charged ionic cloud of
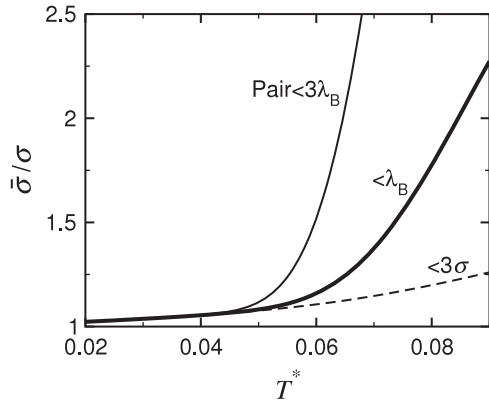
Figure 2. The mean ion separation of the Bjerrum pairs $\bar{\sigma}$ (in units of the ionic diameter σ) as a function of the dimensionless temperature $T^* = \sigma/\lambda_B$ for several definitions of the maximum ion separation that is still called a Bjerrum pair. At low temperatures $T^* \lesssim 0.05$ the separation does not depend on the precise definition, because the deep potential well of $> 20\,k_B T$ at contact dominates the partition sum of the pair.

net charge, generated by the ions. By the Poisson–Boltzmann equation, solved by Gouy and Chapman [12], the typical width of this cloud (the double layer) can be found. This length scale is also known as the Debye length $1/\kappa = 1/\sqrt{8\pi \lambda_B \rho_s}$. We now extend Gouy–Chapman theory [12] by the inclusion of an additional particle species of dipoles with number density ρ_d in the bulk far from the plate. Following the derivation of [6], we find the Poisson–Boltzmann equation for $z > 0$:

$$\phi''(z) = \kappa^2 \sinh\phi(z) - \kappa^2 \frac{\rho_d}{2\rho_s}\bar{\sigma}\frac{d}{dz}[\mathcal{G}(\bar{\sigma}\phi'(z))], \quad (9)$$

where a prime denotes a derivative with respect to z and $k_B T\phi(z)/e$ is the electrostatic potential. The function $\mathcal{G}(u) = \cosh(u)/u - \sinh(u)/u^2$ can be accurately approximated by a first-order expansion $\mathcal{G}(u) = \frac{1}{3}u + \mathcal{O}(u^2)$, since the mean separation $\bar{\sigma} = \mathcal{O}(1)$ nm and the electric field $\phi'(z) = \mathcal{O}(1)\,\mu\text{m}^{-1}$ for the systems of interest. The PB equation then reduces to

$$\phi''(z) = \bar{\kappa}^2 \sinh\phi(z), \quad (10)$$

where

$$\bar{\kappa}^2 = \frac{\kappa^2}{\alpha\kappa^2 + 1}, \quad (11)$$

with $\alpha \equiv \rho_d \bar{\sigma}^2/6\rho_s$. The presence of dipoles thus increases the screening length significantly as soon as $\alpha\kappa^2 = \mathcal{O}(1)$, which can only be obtained at high ionic strength in low-dielectric media, such that ρ_d/ρ_s is large. Equivalently, one can also consider the dielectric constant to be effectively changed by the presence of the dipoles. Writing $\bar{\kappa} = 8\pi e^2\rho_s/(\bar{\epsilon}k_B T)$, with $\bar{\epsilon}$ the effective dielectric constant gives with (11) that

$$\bar{\epsilon} = \epsilon + \frac{4\pi\bar{\sigma}^2\lambda_B^{\text{vac}}\rho_d}{3}, \quad (12)$$

where λ_B^{vac} is the Bjerrum length in vacuum. The molar density of pairs has to be large enough for a significant change in the effective dielectric constant. For typical ion diameters of a few ångström one needs $\rho_d \gtrsim 10$ mM for $\bar{\epsilon} \gtrsim 2\epsilon$.

In (9)–(12) we treated ρ_s and ρ_d as independent densities, whereas in (4) we related them directly through an equilibrium reaction. Using (4) we find $\alpha = K\eta_s\bar{\sigma}^2/6$ such that the limit $\alpha\kappa^2 \gg 1$ gives

$$\bar{\kappa}^{-1} = \sqrt{\alpha} \propto \sqrt{\rho_s}, \quad (13)$$

which is a remarkable dependence, since in the absence of dipoles the Debye length scales as $\kappa^{-1} \propto 1/\sqrt{\rho_s}$. The full dependence of $\bar{\kappa}^{-1}$ on κ^{-1} follows from (11) and (4) as

$$\bar{\kappa}^{-1} = \kappa^{-1}\sqrt{(A\kappa)^4 + 1} \approx \begin{cases} \dfrac{A^2}{\kappa^{-1}}, & \kappa^{-1} \ll A; \\[2mm] \kappa^{-1}, & \kappa^{-1} \gg A, \end{cases} \quad (14)$$

with $A^4 = KT^*\sigma^2\bar{\sigma}^2/(48\pi)$. Relation (14) is plotted, in a conveniently scaled fashion, in figure 3(a), revealing a minimum at $\kappa^{-1} = 2^{\frac{1}{4}}A$ that separates the dilute limit (where $\kappa \simeq \bar{\kappa}$) from the dense limit (where $\bar{\kappa}^{-1} \sim A^2\kappa$). In figure 3(b) the ratio $\bar{\kappa}^{-1}/\kappa^{-1}$, which equals $\sqrt{(A\kappa)^4 + 1}$ from (14), is plotted as a function of T^* for $\rho_d = 0.1$, 1 and 10 M, setting $\bar{\sigma} = \sigma = 0.5$ nm. Figure 3 reveals a strong modification of the effective screening length (by factors of 2–10) provided $\rho_d \gtrsim 1$ M and $T^* \lesssim 0.1$ (or $\epsilon \lesssim 10$). The key question is therefore if such conditions are experimentally attainable; the answer will be provided in section 4.

4. Physically relevant regime

From (14) and figure 3 we conclude that the effective screening length is significantly larger than the Debye length, if the density of dipoles is of the order of 1 M. We do not expect that these densities can be reached in polar solvents (water), where T^* is high, and hence K is low, such that free ions dominate according to (7) and figure 1. The equilibrium constant K can be very high in low-polar solvents (oil), such that there are many more Bjerrum pairs than free ions. However, salt also dissolves worse in oil than in water, and the question is whether or not enough ionic strength is possible to produce the Bjerrum pairs at all. In order to get an estimation of the parameter regime where inflation of the screening length could take place, we calculate the minimal free-ion density $\rho_s^{\text{min}}\sigma^3 = \eta_s^{\text{min}}$ at which $\kappa/\bar{\kappa} > 1$ to a significant degree. From (4) it can be found that $\alpha\kappa^2 \gtrsim 1$ implies

$$\eta_s^{\text{min}} = \sqrt{\frac{3T^*}{4\pi K}}, \quad (15)$$

where the dimensionless η_s, T^* and K were defined in section 3. This condition provides a lower bound for the ion concentrations in oil where a significant effect from pairs can be expected. We consider the oil to be in contact with a water reservoir, and assume the ions to partition between the two phases due to a difference in Born self-energy [15–17, 20]. Given the maximum ionic strength in water of about 10 M, we find an estimate for the maximum ionic strength ρ_s^{max} in the oil: $\rho_s^{\text{max}}[\text{M}] = 10 \times \exp(\frac{\lambda_B^{\text{water}}}{\sigma} - \frac{1}{T^*})$, where the Born energy $k_B T/T^*$ in oil is used, with σ the effective ionic diameter in oil. A significant increase of $\bar{\kappa}^{-1}$ due to Bjerrum pairs thus requires the existence of a regime where $\rho_s^{\text{min}} < \rho_s < \rho_s^{\text{max}}$.
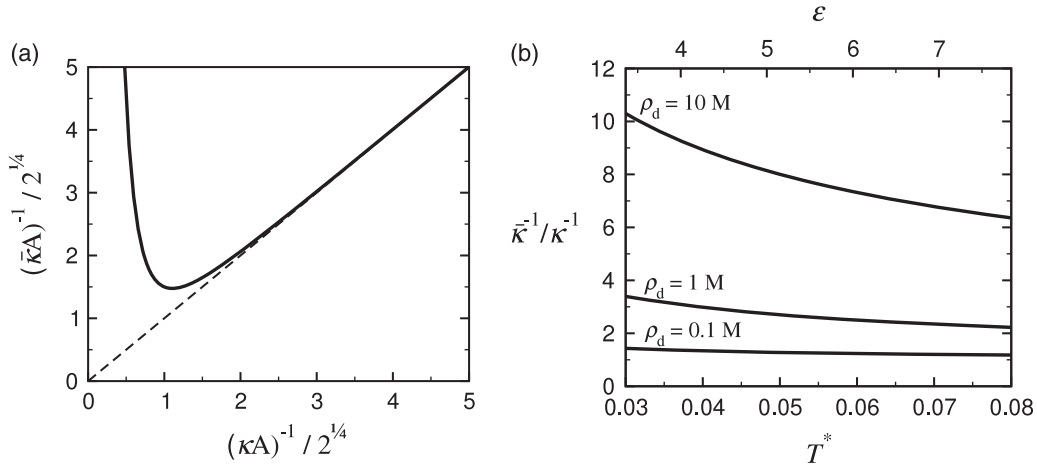
Figure 3. (a) The (dimensionless) effective screening length as a function of the Debye length $\kappa^{-1} = (8\pi\lambda_B\rho_s)^{-\frac{1}{2}}$ on the basis of (14) showing the asymptotic regimes $\bar\kappa^{-1} = \kappa^{-1}$ and $\bar\kappa^{-1} = \kappa A^2$, separated by a minimum at $\kappa^{-1} = 2^{\frac{1}{4}}A$ (see text). (b) The effective screening length (in units of the Debye length) as a function of dimensionless temperature T^* on the basis of (14) for several dipole densities $\rho_d = 0.1, 1$ and 10 M, at a mean separation and particle diameter $\bar\sigma = \sigma = 0.5$ nm. The upper axis shows the conversion from T^* to ϵ at $\sigma = 0.5$ nm. The effective screening length can be up to a factor of $\mathcal{O}(10)$ higher than the Debye length κ^{-1}, at high dipole densities.

From a numerical analysis, however, we find that $\rho_s^{\max} < \rho_s^{\min}$ for all T^* using reasonable values for σ. In other words, the required high density of dipoles cannot be reached according to the equilibrium constant K defined in (5).

In order to make some further progress, we treat solvation effects in a slightly less naive fashion. So far we considered the ions to have an effective radius $a_\pm$ of a few ångström, connected to a Born self-energy of several tens of $k_B T$ in oil and less than 1 $k_B T$ in water. The bare radius of $\sim$1 Å for small ions such as Na$^+$ or Cl$^-$ would overestimate the self-energies and underestimate the solvation of the ions in low-polar solvents, as found for example in experiments [10]. The actual effective radius is thus larger due to hydration shells of water molecules that form a cage around the ion [18]. By assuming now that two ions can approach each other up to the *bare* diameter $\xi\sigma$ of the ions, where $0 < \xi < 1$, instead of σ, the effective diameter of the ions, the equilibrium constant K is found to be much higher. This is visualized by the breaking and forming of the structure of water molecules around the ions. Within this speculative picture the equilibrium constant of (5) is redefined by

$$K_\xi = 4\pi \left(\frac{1}{\xi T^*}\right)^3 \int_{\xi T^*}^1 \mathrm{d}l\, l^2\, \exp\left(\frac{1}{l}\right), \qquad (16)$$

where an explicit energetic and entropic cost of restructuring the layer of surrounding water molecules is ignored. A small ξ can lead to much higher densities of dipoles, by orders of magnitude, compared to $\xi = 1$. Intuitively one could expect higher-order clusters to form at such densities. We expect, however, that higher-order clusters are increasingly unfavorable. The energy gain by electrostatic arguments has to compensate for both the loss of entropy and the energy needed to restructure the surrounding water molecules [19].

In figure 4(a) we plot K_ξ^{-1} as a function of T^* for several ξ; for $\xi = 1$ the curve is identical to the curve of figure 1.

As in figure 1, the present curves also separate the high-T^* regime dominated by free ions from a low-T^* regime dominated by dipoles. Reducing the contact distance from σ to $\xi\sigma$ is immediately seen to reduce the free-ion regime: dipoles form already at higher T^*. The right vertical axis denotes, again in analogy with figure 1, the free-ion concentration at the crossover $\rho_s = \rho_d$ (using $\sigma = 0.5$ nm to convert to molar concentrations). Figure 4(a) thus reveals a lowering of the free-ion concentration at which dipole formation sets in by orders of magnitude when ξ is reduced from 1 to 0.2. Figure 4(b) shows the (dimensionless and molar) maximum and minimum free-ion concentrations $\rho_s^{\max}$ and $\rho_s^{\min}(\xi)$, respectively, as a function of T^* and several ξ. Consistent with our earlier observations we see that $\rho_s^{\min} > \rho_s^{\max}$ for $\xi \gtrsim 0.6$ in the T^* regime of interest. Interestingly, for $\xi \lesssim 0.6$ a physically attainable regime of $\rho_s^{\min} < \rho_s < \rho_s^{\max}$ opens up in which significant dipolar effects are to be expected to increase the effective screening length beyond the bare one. For the choice of $\sigma = 0.5$ nm used in figure 4(b), this implies that Bjerrum pairs play an important role provided the bare ion diameter $\xi\sigma \lesssim 0.3$ nm. This seems physically reasonable.

5. Possible observations

We will now consider the system of [10], consisting of micrometer-sized, strongly hydrophobic PMMA particles, dispersed in an oily mixture of cyclohexylbromide and *cis*-decalin in contact with water, containing monovalent ions. A densely packed monolayer of colloidal particles was observed at the oil–water interface and a dilute bulk crystal separated by a large colloid-free zone of $\sim$100 μm between the bulk crystal and the interface. The system was theoretically described in [11] with a model that will be extended here by the introduction of Bjerrum pairs. We consider strongly hydrophobic colloidal particles in oil near a planar oil–water interface, in the presence of monovalent ions. We focus
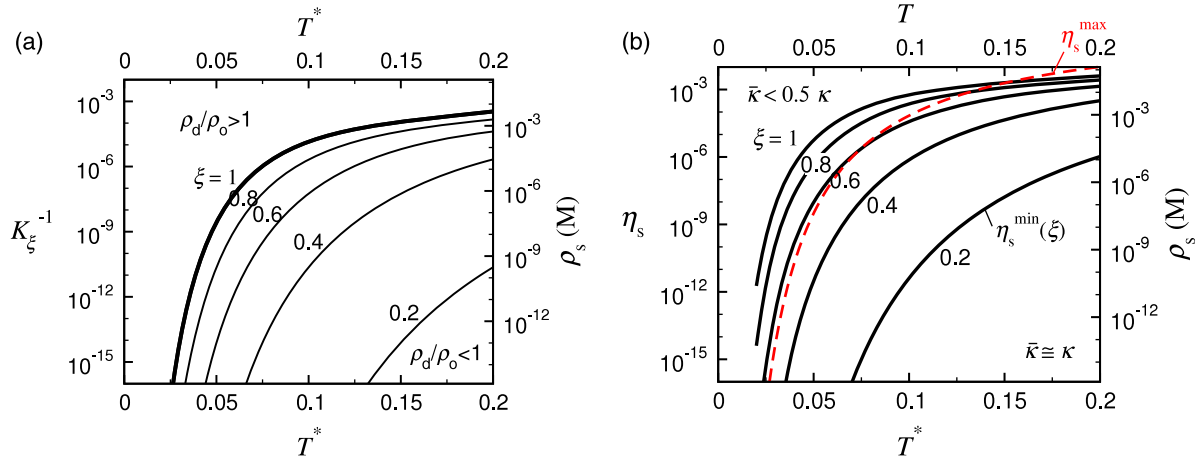
Figure 4. (a) The equilibrium constant K_ξ^{-1} related to the dimensionless temperature $T^* = \sigma/\lambda_B$ for several values of ξ. When one focuses on the left vertical axis, the lines also mark the points where the density of paired ions equals the density of free cations/anions for a given concentration of free ions (see right vertical axis for the molar density, given an ionic diameter of $\sigma = 0.5$ nm). For decreasing ξ the parameter regime where the dipoles dominate increases. (b) The ion densities at which $\alpha\kappa^2 = 1$, i.e. where the effective screening length $\bar{\kappa}^{-1} = \sqrt{2}\kappa^{-1}$ for several values of ξ. For small ξ, i.e. a small bare radius compared to the effective radius, the screening length is increased by the presence of the dipoles, already at low salt concentrations. The red dashed line denotes the ion density at which the salt concentration in water is 10 M, i.e. higher salt concentrations are not physical in oil (in contact with water).

on the distribution of particles in the direction perpendicular to the interface. By employing the framework of density functional theory we write the grand potential as a functional $\Omega[\rho, \rho_+, \rho_-, \rho_d]$ of the variational density profiles of the colloidal particles $\rho(\mathbf{r})$, the cations $\rho_+(\mathbf{r})$, the anions $\rho_-(\mathbf{r})$ and the dipoles $\rho_d(\mathbf{r}, \mathbf{s})$, with $\mathbf{s}$ the vector of the dipole orientation. The functional is also given in [11] except for the dipole contributions (with a subscript d), and is

$$
\Omega = \sum_{\alpha=\pm} \int d\mathbf{r}\, \rho_\alpha(\mathbf{r})(k_B T (\ln \rho_\alpha(\mathbf{r})\Lambda^3 - 1) + V_\alpha(\mathbf{r}))
$$
$$
+ \int d\mathbf{r}\, \rho(\mathbf{r})\left(k_B T \left(\ln \frac{\eta(\mathbf{r})}{\eta_0} - 1\right) + V(\mathbf{r})\right)
$$
$$
+ \int d\mathbf{r}\, d\mathbf{s}\, \rho_d(\mathbf{r}, \mathbf{s})(k_B T (\ln \rho_d(\mathbf{r}, \mathbf{s})\Lambda^3 - 1)
$$
$$
+ V_+(\mathbf{r}) + V_-(\mathbf{r}) + \Delta G(\mathbf{r}))
$$
$$
- \sum_{\alpha=\pm} \mu_\alpha \int d\mathbf{r}\left(\rho_\alpha(\mathbf{r}) + \int d\mathbf{s}\, \rho_d(\mathbf{r}, \mathbf{s})\right)
$$
$$
+ k_B T \int d\mathbf{r}\, (\rho(\mathbf{r})\Psi(\bar{\eta}(\mathbf{r})) + \tfrac{1}{2}Q(\mathbf{r})\phi(\mathbf{r})), \qquad (17)
$$

where $\eta(\mathbf{r}) = 4\pi a^3 \rho(\mathbf{r})/3$ is the colloidal packing fraction, and where the first and second lines are the ideal gas grand-potential functionals of the ions and the colloidal particles in their external fields, respectively, the third and fourth lines are the ideal gas free energy of the dipoles and the binding free energy, the fifth line a grand canonical contribution (for fixed chemical potentials) and the last line describes the hard-core and Coulomb interactions [11]. The electrostatic interactions between ion–ion, ion–dipole and dipole–dipole are taken into account on a mean-field level, similarly to [6]. For reasons of simplicity we do not include the correlation effects presented in [2, 3, 8, 9]. The chemical potential of the colloidal particles is represented in terms of a reference colloid packing fraction η_0, to be discussed below. The total local charge number

density $Q(\mathbf{r}) = Z\rho(\mathbf{r}) + \rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) + \int d\mathbf{s}\, [\rho_d(\mathbf{r} + \mathbf{s}\frac{\bar{\sigma}}{2}, \mathbf{s}) - \rho_d(\mathbf{r} - \mathbf{s}\frac{\bar{\sigma}}{2}, \mathbf{s})]$, with $\mathbf{s}$ the unit vector denoting the direction of the dipole and $\bar{\sigma}$ the mean distance between the centers of the ions of a pair (previously found to be $\bar{\sigma} \simeq \sigma$ in low-dielectric media, see (8) and figure 2). For small $\bar{\sigma}$ the last term in the expression for $Q(\mathbf{r})$ reduces to

$$
\int d\mathbf{s}\, \bar{\sigma}\nabla\rho_d(\mathbf{r}, \mathbf{s}) \cdot \mathbf{s}. \qquad (18)
$$

We obtain the equilibrium distribution of colloidal particles by minimization of the functional (17) with respect to $\eta(\mathbf{r})$, which reduces to $\eta(z)$ due to the symmetry of the system. Minimizations with respect to the densities $\rho_\pm(z)$ yield the Boltzmann distributions for the free ions, also given in [11] (only we use the slightly different notation $\rho(\infty) \equiv \rho_s$ here) and dipole density $\rho_d(\mathbf{r}, \mathbf{s})$:

$$
\rho_d(z) = \rho_d \frac{\sinh(\bar{\sigma}|\phi'(z)|)}{\bar{\sigma}|\phi'(z)|}, \qquad (19)
$$

where the expression is integrated over $\mathbf{s}$ and where we used the relations between K, ρ_d and ρ_s given in earlier sections. Combining these with the Poisson equation yields a Poisson–Boltzmann equation (9) from which we can find the electrostatic potential $\phi(z)$, for the boundary conditions

$$
\lim_{z\uparrow 0} \epsilon_w \phi'(z) = \lim_{z\downarrow 0} \epsilon_o \phi'(z); \qquad \lim_{z\to\pm\infty} \phi'(z) = 0,
$$

where ϵ_w is the relative permittivity of water and ϵ_o that of oil. The five equations of the five unknowns (the particle densities and the electrostatic potential) are solved numerically.

Figure 5 shows the resulting packing fraction profile $\eta(z)$, as well as the electrostatic potential $\phi(z)$ in the inset, for $\xi = 1$ and 0.37. The parameters are the colloidal radius $a = 1\ \mu$m, the colloidal charge $Z = 450$, the relative
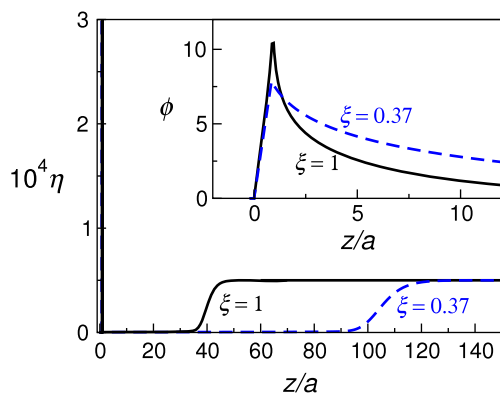
Figure 5. The packing fraction profile $\eta(z)$ of strongly hydrophobic, oil-dispersed colloidal spheres (radius $a = 1\ \mu$m, charge $Z = 450$) in the vicinity of a planar interface at $z = 0$ between water ($z < 0$, dielectric constant $\epsilon_w = 80$) and oil ($z > 0$, $\epsilon_o = 5.2$) for a colloidal bulk packing fraction $\eta_b = \eta(\infty) = 5 \times 10^{-5}$ of weakly wetting colloidal particles ($\cos\theta = 0.987°$) and screening length in oil $\kappa^{-1}/a = 8$. The curves show the influence of Bjerrum pairs on the depletion zone. For $\xi = 1$ the effect of Bjerrum pairs can be ignored ($\bar{\kappa}^{-1}/a = \kappa^{-1}/a = 8$). For $\xi = 0.37$ Bjerrum pairs cannot be ignored and the screening length effectively increases up to $\bar{\kappa}^{-1}/a = 20$, due to an effective increase of the permittivity, resulting in a long range repulsion between the monolayer and the bulk crystal over 100 μm.

permittivity of water $\epsilon_w = 80$ and that of oil $\epsilon_o = 5.2$, and also the external potentials $V(z)$ and $V_\pm(z)$ are identical to those in [11], i.e. $V(z)$ is a Pieranski potential [21] with contact angle $\cos\theta = 0.987°$ and an oil–water interfacial tension of $\gamma_{ow} = 9$ mN m^{-1}, and $V_\pm(z)$ is based on Born self-energy differences in oil and water with ionic radii $a_\pm = 0.3$ nm (i.e. $\sigma = 0.6$ nm).

The curve $\eta(z)$ for $\xi = 1$ is virtually identical to the one published in [11] (i.e. the effect of the Bjerrum pairs can be ignored completely) and reveals a strong monolayer adsorption at $z \simeq a$, a colloid-free zone for $1 \lesssim z/a \lesssim 30$, and a colloidal crystal [14] with a packing fraction $\eta(\infty) = \eta_b = 5 \times 10^{-5}$ at $z \gtrsim 30$. Experimentally, however, a colloid-free zone that extends to $z \simeq 100\ \mu$m was observed [10] for these parameters. Comparing this with the curve for $\xi = 0.37$ in figure 5 yields a much better agreement with the experimental observation. We speculate, therefore, that Bjerrum pairing is an interesting feature for further study in these oily solvents.

6. Conclusion

In this paper we considered the effect of Bjerrum pairs on the screening length and concluded that it can be significantly larger in low-polar media than the Debye length that is calculated from the free-ion concentration (for example, obtained by conductivity measurements) and the bare solvent dielectric constant. Due to the coupling of free ions and dipoles through an association–dissociation equilibrium, we predict the effective screening length to scale as $\bar{\kappa}^{-1} \propto \sqrt{\rho_s}$ at relatively high salt concentrations, in contrast to the scaling $\kappa^{-1} \propto 1/\sqrt{\rho_s}$ for the Debye length, where ρ_s is the free-ion concentration. A large concentration of Bjerrum pairs was found to change the dielectric constant of the medium effectively. By a naive treatment of solvation effects of the ions, the required dipole concentrations seem to be unattainable for physical parameters, such that the effect of Bjerrum pairs could be neglected completely. After making the distinction between an *effective* ionic diameter, due to hydration shells that lower the self-energy, and a *bare* ionic diameter, determining the closest distance between two ions, a regime of physical parameters was found where inflation of the screening length could be expected. Our results provide a possible explanation for the extremely large colloid-free zone that was observed in recent experiments [10]. Clearly, however, more research is needed to investigate this effect.

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