PHYSICAL REVIEW E VOLUME 60, NUMBER 3 SEPTEMBER 1999

Debye-Hückel theory for interfacial geometries

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(Received 26 February 1999)

The Debye-Hückel theory for bulk electrolyte solutions is generalized to planar interfacial geometries, including screening effects due to mobile salt ions which are confined to the interface and solutions with in general different salt concentrations and dielectric constants on the two sides of the interface. We calculate the general Debye-Hückel interaction between fixed test charges, and analyze a number of relevant special cases as applicable to charged colloids and charged polymers. Salty interfaces, which are experimentally realized by monolayers or bilayers made of cationic and anionic surfactants or lipids, exert a strong attraction on charged particles of either sign at large separations from the interface; at short distances image-charge repulsion sets in. Likewise, the effective interactions between charged particles are strongly modified in the neighborhood of such a salty interface. On the other hand, charged particles which are immersed in a salt solution are repelled from the air (or a substrate) interface, and the interaction between two charges decays algebraically close to such an interface. These general results have experimentally measurable consequences for the adsorption of charged colloids or charged polymers at monolayers, solid substrates, and interfaces.
[S1063-651X(99)11109-7]

PACS number(s): 61.20.Qg, 68.10.−m, 82.45.+z

I. INTRODUCTION

The Debye-Hückel (DH) theory was introduced some 70 years ago [1]. As was demonstrated, the effective interactions between charges are weakened (i.e., *screened*) due to the presence of mobile ions in the surrounding space. These mobile ions form a highly polarizable background, which reacts to the presence of fixed charges by organizing into loosely bound counterion clouds, thereby partially neutralizing the fixed charges. As a result, the long-ranged Coulomb interaction $v(r)\sim 1/r$ between two charges is reduced and acquires an exponential screening factor, $v(r)\sim e^{-\kappa r}/r$, where κ is the inverse *screening length* which is proportional to the square root of the salt concentration.

The approximations leading to the DH theory are valid as long as the electrostatic potential is small everywhere. This condition is satisfied if the charge density is not too high or if the salt concentration is large enough. In the opposite case, for high electrostatic potentials, nonlinear effects, not captured by DH theory, become important, which can be described, on a mean-field level, by the Poisson-Boltzmann equation [2,3]. The main advantage of the DH theory is that it captures (on a Gaussian level) ion fluctuations and that, since it is a linear theory, the *superposition principle* is valid: Once the electrostatic potential distribution of a single charge has been calculated (which is merely the Green's function), the total potential of an arbitrary charge distribution follows by the summation over the potentials created by each single charge. This also holds for an interfacial geometry, which forms the motivation for the present work in which we calculate the DH Green's function in the presence of an interface.

Interfacial effects in the context of ionic systems have received preliminary attention because it was shown that the surface tension of a salt solution is considerably increased due to a depletion zone of salt ions close to the free surface [4–7]. The electrostatic self-energy of an ion which is moved towards an interface between two different salt solutions has been considered theoretically using approximations which essentially correspond to the DH theory [8,9], showing that it costs energy to move an ion from an electrolyte solution to a substrate surface or the electrolyte-air interface. A salt solution which is confined to a two-dimensional plane has been shown to produce (in the absence of additional salt ions in the surrounding three-dimensional bulk) an effective interaction between two charges, which decays as the inverse cube of the separation [10–13]. Quite recently, it was realized that a two-dimensional salt solution is realized by membranes consisting of cationic and anionic lipids or surfactants, with important consequences for the membrane elastic behavior and the interaction between two such membranes [14,15]. Also, it is clear that the influence of fluctuation effects, such as those captured within DH theory, on the interaction between charges will play a role for a variety of biological phenomena, such as DNA adsorption on charged membranes [16–18]. Finally, the interaction between test charges at a surface of a three-dimensional salt solution has also been shown to decay algebraically [19–22].

In this paper we formulate the DH theory in the presence of an interface, which furnishes a unified description of all phenomena mentioned above. In specific, we consider a planar interface which contains salt ions of a certain fixed concentration, and which separates two half-spaces, each with a fixed (in general different) salt concentration and with different dielectric constants. As a main result, we obtain the effective interaction between two charges located at arbitrary distances from the interface, i.e., the DH Green's function $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$, and we analyze its behavior for various limiting cases. We find strong modifications of the ordinary DH interaction: The self-energy of a single charge, which is given by the equal-point Green's function $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r})$, exhibits a strong attraction towards regions of increased salinity, both for the case of a two-dimensional salt layer or a salty half-

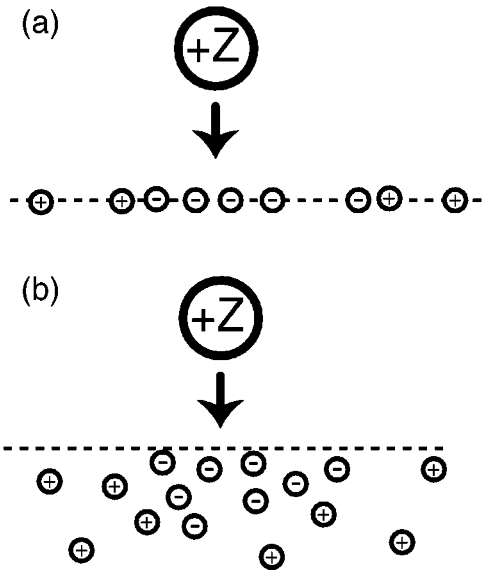

FIG. 1. Charged colloidal particle interacting with (a) a salty plane, and (b) a salty half-space. In both cases, polarization charges of opposite sign gather near the colloidal particle and lead to a strong attraction to the interface.

space (see Fig. 1). The interaction between two charges is modified close to a salty interface or close to a half-space with a different salt concentration and decays algebraically for a wide class of different cases. These results do have some relevance for the adsorption of charged colloids and charged polymers at substrates or the air-water interface.

II. DEBYE-HÜCKEL THEORY

In this section, we formulate the DH theory within a field-theoretic formalism. We start from the partition function of N test particles which carry an (in general different) charge Q_i each, and which are fixed at positions $\mathbf{R}_i$. These fixed test particles are immersed in a multicomponent electrolyte solution which is confined to a planar interfacial geometry. In specific, we have $M_>$ different types of $n_j^>$ ions with a charge $q_j^>$ $(j=1,\ldots,M_>)$, confined to the upper half-space $(z>0)$, $M_<$ different types of ions confined to the lower half-space $(z<0)$, and $M_=$ types of ions which move in the separating plane $(z=0)$. The partition function, with all ions freely moving and the test particles fixed at their positions, reads

$$Z[\{\mathbf{R}_N\}]=\int\tilde{\mathcal{D}}\exp\left\{-\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\hat{\rho}_c(\mathbf{r})v(\mathbf{r},\mathbf{r}')\hat{\rho}_c(\mathbf{r}')\right\}. \tag{1}$$

In the partition function, the positions of the N fixed test particles are denoted by $\{\mathbf{R}_N\}$ and the symbol $\int\tilde{\mathcal{D}}$ stands for a multiple integral over the positions of all mobile salt ions,

$$\begin{aligned}\int\tilde{\mathcal{D}}\equiv&\prod_{j=1}^{M_>}\left[\frac{1}{n_j^>!}\prod_{k=1}^{n_j^>}\int\frac{d\mathbf{r}_{k,j}^>}{\lambda^3}\Theta[z_{k,j}^>]\right]\\&\times\prod_{j=1}^{M_<}\left[\frac{1}{n_j^<!}\prod_{k=1}^{n_j^<}\int\frac{d\mathbf{r}_{k,j}^<}{\lambda^3}\Theta[-z_{k,j}^<]\right]\\&\times\prod_{j=1}^{M_=}\left[\frac{1}{n_j^=!}\prod_{k=1}^{n_j^=}\int\frac{d\mathbf{r}_{k,j}^=}{\lambda^2}\delta[z_{k,j}^=]\right],\end{aligned} \tag{2}$$

where the length λ is an arbitrary constant, equivalent to the thermal wavelength. The Heavyside function $\Theta(z)=\int_{-\infty}^{z}dz'\,\delta(z')$ is used to restrict the configurational integrals to one of the two half-spaces. We allow for a jump in the dielectric constant, which we denote by ε for $z>0$ and ε' for $z<0$. The Coulomb operator is given by

$$v(\mathbf{r},\mathbf{r}')=\begin{cases}\dfrac{\ell_B}{|\mathbf{r}-\mathbf{r}'|}+\dfrac{\varepsilon-\varepsilon'}{\varepsilon+\varepsilon'}\dfrac{\ell_B}{\sqrt{(\mathbf{r}-\mathbf{r}')^2+4zz'}} & \text{for}\quad z,z'\geqslant 0\\[2ex] \dfrac{2\ell_B\varepsilon}{(\varepsilon+\varepsilon')|\mathbf{r}-\mathbf{r}'|} & \text{for}\quad z\geqslant 0\geqslant z',\end{cases} \tag{3}$$

where the Bjerrum length $\ell_B\equiv e^2/4\pi\varepsilon k_BT$ defines the length at which two unit charges interact with thermal energy k_BT in the positive half-space. In the absence of a jump in the dielectric constant, $\varepsilon=\varepsilon'$, the Coulomb interaction Eq. (3) reduces to $v(\mathbf{r},\mathbf{r}')=\ell_B/|\mathbf{r}-\mathbf{r}'|$; the modifications from this standard form are due to the formation of polarization charges at the interface. The charge-density operator $\hat{\rho}_c$ is defined by

$$\begin{aligned}\hat{\rho}_c(\mathbf{r})\equiv&\sum_{i=1}^{N}Q_i\delta(\mathbf{r}-\mathbf{R}_i)+\sum_{j=1}^{M_>}\sum_{k=1}^{n_j^>}q_j^>\delta(\mathbf{r}-\mathbf{r}_{k,j}^>)\\&+\sum_{j=1}^{M_<}\sum_{k=1}^{n_j^<}q_j^<\delta(\mathbf{r}-\mathbf{r}_{k,j}^<)+\sum_{j=1}^{M_=}\sum_{k=1}^{n_j^=}q_j^=\delta(\mathbf{r}-\mathbf{r}_{k,j}^=)\end{aligned} \tag{4}$$

and contains the fixed test charges (the first term) and the mobile salt ions (the last three terms). We enforce electroneutrality of the mobile salt distributions separately in the two half-spaces and in the plane, which leads to the conditions $\Sigma_{j=1}^{M_>}n_j^>q_j^>=0$, $\Sigma_{j=1}^{M_<}n_j^<q_j^<=0$, and $\Sigma_{j=1}^{M_=}n_j^=q_j^==0$. Noting that the inverse Coulomb operator can be explicitly written as $v^{-1}(\mathbf{r},\mathbf{r}')=-(k_BT/l^2)\nabla\varepsilon(\mathbf{r})\nabla\delta(\mathbf{r}-\mathbf{r}')$, when $\varepsilon(\mathbf{r})$ is the position-dependent dielectric constant, after a Hubbard-Stratonovich transformation, the partition function is up to second order in the fluctuating field ϕ given by

$$\begin{aligned}Z[\{\mathbf{R}_N\}]=\int\frac{\mathcal{D}\phi}{Z_0}\exp\Bigg\{&-\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\phi(\mathbf{r})v_{\mathrm{DH}}^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')\\&-i\sum_{i=1}^{N}Q_i\phi(\mathbf{R}_i)+\mathcal{S}\Bigg\},\end{aligned} \tag{5}$$

where Z_0 is the partition function of the inverse Coulomb operator, $Z_0 \sim \sqrt{\det v}$. This second-order expansion corresponds to the DH theory generalized to an interfacial geometry. The higher-order terms in the fluctuating field ϕ which we neglect contain nonlinear effects (such as those present in the Poisson-Boltzmann theory), but also higher-order correlation effects. These higher-order terms have recently been considered for the bulk situation in a systematic field-theoretic expansion [23]. It is important to note that the DH theory in the present formulation, although it neglects nonlinear effects, goes beyond the mean-field (Poisson-Boltzmann) approach in that correlations and fluctuations are included on a Gaussian level. The entropy of ideal mixing is $\mathcal{S} \equiv -\Sigma_j n_j^{>} \ln(\lambda^3 c_j^{>}) - \Sigma_j n_j^{<} \ln(\lambda^3 c_j^{<}) - \Sigma_j n_j^{=} \ln(\lambda^2 c_j^{=})$ with $c_j^{>} \equiv n_j^{>}/V_{>}$, $c_j^{<} \equiv n_j^{<}/V_{<}$, and $c_j^{=} \equiv n_j^{=}/A$ denoting the concentrations of ion species j in the two half-spaces and at the interface, respectively. The kernel v_{DH}^{-1} is the functional inverse of the DH potential and is defined by

$$v_{\mathrm{DH}}^{-1}(\mathbf{r},\mathbf{r}') \equiv v^{-1}(\mathbf{r},\mathbf{r}') + [\kappa_{>}^2 \Theta(z) + \kappa_{<}^2 \Theta(-z) + \kappa_{=} \delta(z)] \delta(\mathbf{r}-\mathbf{r}')/4\pi \ell_B . \tag{6}$$

The screening lengths in the two half-spaces and at the interface, $\kappa_{>}^{-1}$, $\kappa_{<}^{-1}$, and $\kappa_{=}^{-1}$, are defined by $\kappa_{>}^2 = 4\pi \ell_B \Sigma_j (q_j^{>})^2 c_j^{>}$, $\kappa_{<}^2 = 4\pi \ell_B (\varepsilon/\varepsilon') \Sigma_j (q_j^{<})^2 c_j^{<}$, and $\kappa_{=} = 4\pi \ell_B \Sigma_j (q_j^{=})^2 c_j^{=}$. The linear term in ϕ in Eq. (5) can be removed by a shift of the fluctuating field ϕ, leading to

$$Z[\{\mathbf{R}_N\}] = e^{-\mathcal{F}[\{\mathbf{R}_N\}]} \int \frac{\mathcal{D}\phi}{Z_0} \times \exp\left\{ -\frac{1}{2} \int d\mathbf{r}\, d\mathbf{r}'\, \phi(\mathbf{r}) v_{\mathrm{DH}}^{-1}(\mathbf{r},\mathbf{r}') \phi(\mathbf{r}') + \mathcal{S} \right\}. \tag{7}$$

The effective free energy for the N test particles reads

$$\mathcal{F}[\{\mathbf{R}_N\}] = \frac{1}{2} \sum_i Q_i^2 v_{\mathrm{DH}}(\mathbf{R}_i,\mathbf{R}_i) + \sum_{i>j} Q_i Q_j v_{\mathrm{DH}}(\mathbf{R}_i,\mathbf{R}_j). \tag{8}$$

For a continuous charge distribution $\sigma(\mathbf{r})$ the free energy can in a simple generalization of Eq. (8) be written as

$$\mathcal{F}[\sigma] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}'\, \sigma(\mathbf{r}) v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}') \sigma(\mathbf{r}'). \tag{9}$$

Equations (8) and (9) constitute straightforward but important results, since it means that once the DH potential $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$ has been calculated, the electrostatic energy of an arbitrary fixed charge distribution can be computed, which then takes into account correlations between the counterion distributions. The first term in Eq. (8) corresponds to the test-particle *self-energies*, and the second term in Eq. (8) describes interactions between *different* particles. It remains to actually calculate $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$, which is complicated because of the broken translational invariance in the z direction. Since the system still has translational invariance parallel to the plane, we may write

$$v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}') = \int \frac{d\mathbf{p}}{(2\pi)^2} e^{\imath \mathbf{p}\cdot(\mathbf{r}_\parallel - \mathbf{r}'_\parallel)} v_{\mathrm{DH}}(z,z',\mathbf{p}), \tag{10}$$

with a similar transformation for the inverse potential, v_{DH}^{-1}. Combining the canonical relation between the DH potential v_{DH} and its inverse,

$$\int_{-\infty}^{\infty} d\tilde{z}\, v_{\mathrm{DH}}(z,\tilde{z},\mathbf{p}) v_{\mathrm{DH}}^{-1}(\tilde{z},z',\mathbf{p}) = \delta(z-z'), \tag{11}$$

with the definition of v_{DH}^{-1}, Eq. (6), we obtain the differential equations

$$-4\pi \ell_B \delta(z-z') = \left[\frac{\partial^2}{\partial z^2} - \kappa_{>}^2 - p^2 \right] v_{\mathrm{DH}}(z,z',\mathbf{p}), \tag{12}$$

$$-4\pi \frac{\ell_B}{\eta} \delta(z-z') = \left[\frac{\partial^2}{\partial z^2} - \kappa_{<}^2 - p^2 \right] v_{\mathrm{DH}}(z,z',\mathbf{p}), \tag{13}$$

valid for $z>0$ and $z<0$, respectively. We introduced the dielectric constant ratio $\eta = \varepsilon'/\varepsilon$. In the limit $z \rightarrow 0$, we obtain the boundary condition

$$\kappa_{=} v_{\mathrm{DH}}(0,z',\mathbf{p}) = \frac{\partial}{\partial z} [v_{\mathrm{DH}}(z,z',\mathbf{p}) + \eta v_{\mathrm{DH}}(-z,z',\mathbf{p})].$$

Similar Green's functions occur in the context of surface critical phenomena [24,25]. The solutions can be calculated in a straightforward manner and are given by

$$v_{\mathrm{DH}}(z,z',\mathbf{p}) = \frac{4\pi \ell_B}{\sqrt{\kappa_{>}^2 + p^2} + \eta \sqrt{\kappa_{<}^2 + p^2} + \kappa_{=}} \times e^{-z\sqrt{\kappa_{>}^2+p^2} + z'\sqrt{\kappa_{<}^2+p^2}} \tag{14}$$

for $z \geqslant 0 \geqslant z'$, and

$$v_{\mathrm{DH}}(z,z',\mathbf{p}) = \frac{2\pi \ell_B}{\sqrt{\kappa_{>}^2 + p^2}} \left[e^{-|z-z'|\sqrt{\kappa_{>}^2+p^2}} + \frac{\sqrt{\kappa_{>}^2+p^2} - \eta\sqrt{\kappa_{<}^2+p^2} - \kappa_{=}}{\sqrt{\kappa_{>}^2+p^2} + \eta\sqrt{\kappa_{<}^2+p^2} + \kappa_{=}} \times e^{-(z+z')\sqrt{\kappa_{>}^2+p^2}} \right] \tag{15}$$

for $z \geqslant 0$ and $z' \geqslant 0$. These two equations constitute the main result of this paper, and the remaining sections are devoted to discussions of special cases.

III. RESULTS

In the absence of an interface, i.e., for $\eta = 1$ (no dielectric jump), $\kappa_{=} = 0$ (no surface ions), and $\kappa_{>} = \kappa_{<} = \kappa$ (no jump in salt concentration), we obtain from Eqs. (10) and (14) the classical result

$$v_{\rm DH}(\mathbf{r},\mathbf{r}')=\ell_B\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}. \tag{16}$$

Another example where the Green's function can be solved with ease is for a metallic half-space, characterized by $\eta=\infty$. We obtain

$$v_{\rm DH}(\mathbf{r},\mathbf{r}')=\ell_B\frac{e^{-\kappa_>|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}-\ell_B\frac{e^{-\kappa_>\sqrt{(\mathbf{r}-\mathbf{r}')^2+4zz'}}}{\sqrt{(\mathbf{r}-\mathbf{r}')^2+4zz'}}. \tag{17}$$

One sees that the second term counteracts the first term as one goes closer to the surface, i.e., when z and z' approach zero. Right at the surface, for $z=z'=0$, the interaction vanishes identically. The ionic self-energy is, subtracting off the energy at an infinite distance from the plane, defined as

$$v_{\rm DH}^{\rm self}(z)=\int\frac{d\mathbf{p}}{(2\pi)^2}[v_{\rm DH}(z,z,p)-v_{\rm DH}(\infty,\infty,p)] \tag{18}$$

and measures the free energetic cost of bringing a single ion to the surface. For the metallic substrate, characterized by $\eta=\infty$, we obtain the screened version of the usual image-charge interaction,

$$v_{\rm DH}^{\rm self}(z)=-\ell_B\frac{e^{-2\kappa_>z}}{2z}. \tag{19}$$

The substrate strongly attracts charges of any kind.

On the other hand, setting $\eta=0$, which is a fairly accurate approximation for a substrate with a low dielectric constant (as will be briefly discussed at the end of this section), one obtains in the case when $\kappa_==0$ (no surface ions) the result

$$v_{\rm DH}(\mathbf{r},\mathbf{r}')=\ell_B\frac{e^{-\kappa_>|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}+\ell_B\frac{e^{-\kappa_>\sqrt{(\mathbf{r}-\mathbf{r}')^2+4zz'}}}{\sqrt{(\mathbf{r}-\mathbf{r}')^2+4zz'}}, \tag{20}$$

i.e., the interaction close to the surface is enhanced. Right at the substrate surface, for $z=z'=0$, the Debye Hückel interaction in Eq. (16) is enhanced by a factor of 2. The self energy follows from Eq. (18) as

$$v_{\rm DH}^{\rm self}(z)=\ell_B\frac{e^{-2\kappa_>z}}{2z}, \tag{21}$$

and in this case the ions are repelled from the substrate. In the following we give a comprehensive overview over the self-energies and interaction energies for the more complicated cases.

A. Self energy—Asymptotic results

The general behavior of the self-energy for large separations from the interface follows from Eqs. (15) and (18) as

$$v_{\rm DH}^{\rm self}(z)\simeq\ell_B\frac{\kappa_>-\eta\kappa_<-\kappa_=}{\kappa_>+\eta\kappa_<+\kappa_=}\frac{e^{-2\kappa_>z}}{2z}, \tag{22}$$

and we find an attraction to the interface only if $\eta\kappa_<+\kappa_=>\kappa_>$ holds, i.e., for relatively large concentrations of ions at the interface or for an excess of salt ions in the lower half-space. The asymptotic result for small separations from the interface is

$$v_{\rm DH}^{\rm self}(z)\simeq\frac{\ell_B}{2z}\frac{1-\eta}{1+\eta}, \tag{23}$$

which is just the bare Coulomb interaction, Eq. (3). For $\eta<1$ (lower half-space of low dielectric constant) the interaction is repulsive, for $\eta>1$ (lower half-space of high dielectric constant) the interaction is attractive. For $\eta=1$, i.e., for two half-space which are dielectrically matched, the leading term given in Eq. (23) vanishes; for this interesting case we present results in the following sections. One notes that for the air-water interface one has a dielectric constant ratio of about $\eta=\varepsilon_{\rm air}/\varepsilon_{\rm water}\approx 0.01$, and thus putting the constant η to zero is in many cases a good approximation. In some cases, however, the small deviations from the $\eta=0$ limit are important (see, for example, Sec. III F).

B. Self-energy at a salty interface

The experimental situation we have in mind here is a charged particle (a multivalent ion or a charged colloid) at a membrane or monolayer consisting of cationic and anionic lipids.

We first assume the salt concentrations and the dielectric constants on the two sides of the plane to be the same, i.e., $\kappa_>=\kappa_<=\kappa$ and $\eta=1$, which is a good approximation for the case of a thin lipid bilayer immersed in a salt solution if the distance of the colloidal particle from the bilayer is larger than the bilayer diameter. In this case we obtain for the self-energy

$$v_{\rm DH}^{\rm self}(z)=-\frac{\ell_B\kappa_=}{2}e^{z\kappa_=}\Gamma[0,z(\kappa_=+2\kappa)], \tag{24}$$

where Γ denotes the incomplete Gamma function [26]. Using the asymptotic behavior of the incomplete Gamma function, this leads to

$$v_{\rm DH}^{\rm self}(z)\simeq\frac{\ell_B\kappa_=}{2}\ln[z(\kappa_=+2\kappa)]$$

for $z\ll(\kappa_=+2\kappa)^{-1}$, and, in agreement with the asymptotic result in Eq. (22),

$$v_{\rm DH}^{\rm self}(z)\simeq-\frac{\ell_B\kappa_=e^{-2z\kappa}}{2z(\kappa_=+2\kappa)}$$

for $z\gg(\kappa_=+2\kappa)^{-1}$. We see that an ion is always attracted to the salty plane. In Fig. 2(a) we plot the rescaled self-energy $v_{\rm DH}^{\rm self}/\ell_B\kappa$ as determined by Eq. (24) as a function of the rescaled distance $z\kappa$ from the salty interface for four different values of the ratio $\kappa_=/\kappa=1,5,10,50$ (from top to bottom). As it turns out in a systematic field-theoretic treatment, the density $\rho_j(z)$ of ion species j is given by $\rho_j(z)=c_je^{-q_j^2v_{\rm DH}^{\rm self}(z)/2}$, where c_j is the bulk density. The logarithmic attraction at small separations leads to a self-similar ion-density profile $\rho_j\simeq z^{-\mu}$ with an exponent $\mu=\ell_B\kappa_=q_j^2/4$. The attraction is only physical for separations larger than the ion size [27]. We therefore expect that the self-similar den-

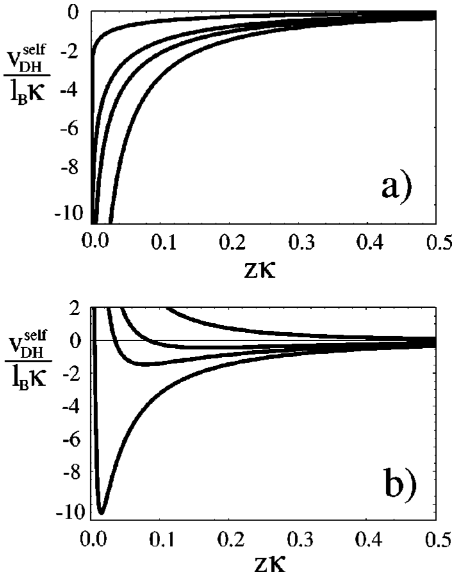

FIG. 2. Rescaled self-energy of a charged particle as a function of the rescaled distance from the salty interface. κ is the inverse screening length in the bulk, and $\kappa_=$ is the in-plane screening length. Shown are results for (a) matching dielectric constants on both sides of the interface, $\varepsilon=\varepsilon'$, and (b) vanishing dielectric constant on the other side of the interface, $\varepsilon'=0$. The screening length ratios are $\kappa_=/\kappa=1$, 5, 10, and 50, from top to bottom.

sity profile is cut off for distances smaller than the ion size. In experiments on membranes it is easy to achieve a situation where one has $\kappa_= \gg \kappa$. In this case one has an intermediate range $\kappa_=^{-1}<z<\kappa^{-1}$ for which the attraction decays as $v_{\rm DH}^{\rm self}(z)\simeq -\ell_B/2z$ and thus behaves like the unscreened Coulomb attraction between the ion and its mirror image.

We next assume that $\eta=0$, which means that the dielectric constant of the lower half-space is infinitely smaller than that of the upper half-space. This is a good approximation for a monolayer at the air-water interface or for a lipid bilayer immersed in a salt solution if the distance of the colloidal particle from the bilayer is much smaller than the bilayer diameter. In this case the results are independent of the salt concentration in the lower half-space, $\kappa_<$, and we obtain for the self-energy

$$v_{\rm DH}^{\rm self}(z)=\frac{\ell_B e^{-2\kappa z}}{2z}-2\ell_B\kappa_= e^{2z\kappa_=}\Gamma[0,2z(\kappa_=+\kappa)]. \tag{25}$$

The asymptotic behavior of this expression is in agreement with the asymptotic formulas (22) and (23). In Fig. 2(b) we plot the rescaled self-energy $v_{\rm DH}^{\rm self}/\ell_B\kappa$ as a function of the rescaled distance $z\kappa$ from the substrate for four different values of the ratio $\kappa_=/\kappa=1,5,10,50$. We see that an ion is attracted to the salty plane for $\kappa_=>\kappa$. The minimum moves towards the substrate as the interfacial ion density increases. The minimum is deep enough to bind multivalent ions or macroions.

C. Self-energy at an interface between two different salt solutions

The experimental situation we envision here is a thin membrane (or a film) which separates two aqueous solutions with different salt concentrations. For the case of an interface between two immiscible liquids, with in general different dielectric constants, it turns out that the self energy is dominated by the dielectric-constant jump at small separations and the asymptotic expressions given in Eqs. (22) and (23) are sufficient to describe the situation. In this section, we therefore consider the case of matching dielectric constants at both sides of the interface, $\eta=1$, and set the salt concentration at the interface to zero, $\kappa_==0$.

The ionic self energy in the positive half space (for $z>0$) follows from Eq. (18) as

$$v_{\rm DH}^{\rm self}(z)=\ell_B\int_{\kappa_>}^{\infty}dt\,\frac{t-\sqrt{t^2+\kappa_<^2-\kappa_>^2}}{t+\sqrt{t^2+\kappa_<^2-\kappa_>^2}}e^{-2zt}. \tag{26}$$

For small separations, $z\ll(\kappa_>+\kappa_<)^{-1}$, the limiting behavior of Eq. (26) is

$$v_{\rm DH}^{\rm self}(z)\simeq v_{\rm DH}^{\rm self}(0)+\ell_B(\kappa_>^2-\kappa_<^2)z\ln[z(\kappa_>+\kappa_<)]/2,$$

and for large separations, $z\gg(\kappa_>+\kappa_<)^{-1}$, the asymptotic expression in Eq. (23) with $\eta=1$ and $\kappa_==0$ is valid. The interaction at contact is finite in this case and reads

$$v_{\rm DH}^{\rm self}(0)=\ell_B\frac{\kappa_>^3-3\kappa_<^2\kappa_>+2\kappa_<^3}{3(\kappa_>^2-\kappa_<^2)}.$$

For $\kappa_>\gg\kappa_<$, here the ion is located in the salt-rich half-space, the ion is *repelled* from the interface, and the interaction is for $z>\kappa_>^{-1}$ given by $v_{\rm DH}^{\rm self}(z)\simeq\ell_B e^{-z\kappa_>}/2z$; the repulsion at contact is $v_{\rm DH}^{\rm self}(0)\simeq\ell_B\kappa_>/3$. For $\kappa_>\ll\kappa_<$, here the ion is located in the salt-poor half-space; the ion is *attracted* to the interface. The interaction is for $\kappa_<^{-1}<z<\kappa_>^{-1}$ given by $v_{\rm DH}^{\rm self}(z)\simeq-\ell_B/2z$, and crosses to an exponentially damped form $v_{\rm DH}^{\rm self}(z)\simeq-\ell_B e^{-z\kappa_>}/2z$ for $z>\kappa_>^{-1}$; the attraction at contact is $v_{\rm DH}^{\rm self}(0)\simeq-2\ell_B\kappa_</3$. We therefore expect an ionic depletion layer in the salt-rich half, and an ionic enhancement layer in the salt-poor half, each layer with a thickness of the respective screening length.

D. Interactions at a salty interface

We next turn to ionic *interactions* as determined by Eq. (10) and start with two charged particles located in a salty plane, i.e., $z=z'=0$, in which case the interaction depends only on the lateral particle spacing $r_\parallel$. We first assume both half-spaces to be free of salt, i.e., $\kappa_>=\kappa_<=0$, and obtain from Eqs. (10) and (14)

$$v_{\rm DH}(r_\parallel)=\frac{2\ell_B}{r_\parallel(1+\eta)}\int_0^\infty dp\,\frac{p}{p+r_\parallel\kappa_=/(1+\eta)}\mathcal{J}_0[p],$$

where $\mathcal{J}_0$ is the Bessel function of the first kind [26]. The integral can be calculated in closed form and leads to [11]

$$v_{\rm DH}(r_\parallel)=\frac{2\ell_B}{r_\parallel(1+\eta)}+\frac{\pi\ell_B\kappa_=}{(1+\eta)^2}\left(N_0\left[\frac{r_\parallel\kappa_=}{1+\eta}\right]-\mathbf{H}_0\left[\frac{r_\parallel\kappa_=}{1+\eta}\right]\right), \tag{27}$$

where N_0 and $\mathbf{H}_0$ denote the Neumann and the Struve functions, respectively [26]. The asymptotic behavior is

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{2\ell_B}{r_\parallel(1+\eta)}+\frac{2\ell_B\kappa_=}{(1+\eta)^2}\ln[r_\parallel\kappa_=] \qquad (28)$$

for $r_\parallel \ll \kappa_=^{-1}$, and

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{2\ell_B(1+\eta)}{\kappa_=^2 r_\parallel^3} \qquad (29)$$

for $r_\parallel \gg \kappa_=^{-1}$. We see that screening is much weaker for large separations than in the case of a three-dimensional salt solution, resulting in a DH interaction which is in fact long ranged. In the presence of salt ions in the embedding space (in the following we assume $\kappa_< = \kappa_> = \kappa$) the behavior is modified at large separations. The behavior now depends on the relative salt concentration in the interface and in the bulk: for $\kappa > \kappa_=$, that means that for large bulk salt concentration, one has a behavior described by Eq. (28) for short separations $r_\parallel < \kappa^{-1}$ and the regular DH interaction,

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{2\ell_B e^{-\kappa r_\parallel}}{r_\parallel(1+\eta)} \qquad (30)$$

for $r_\parallel > \kappa^{-1}$; in this case the salt ions in the plane are relatively unimportant. In the opposite limit, $\kappa < \kappa_=$, for small bulk salt concentration, one obtains Eq. (28) for short separations $r_\parallel < \kappa_=^{-1}$, Eq. (29) for $r_\parallel > \kappa_=^{-1}$, and a crossover between Eq. (29) and Eq. (30) at $r_\parallel^* \sim \kappa^{-1}\ln[\kappa_=/\kappa]$. For two charges which are both a distance z apart from the plane, the interaction depends on z and the lateral separation $r_\parallel$ and is defined by

$$v_{\mathrm{DH}}(r_\parallel,z)=\ell_B\int_0^\infty dp\left[1+\frac{p(1-\eta)-\kappa_=}{p(1+\eta)+\kappa_=}e^{-2zp}\right]\mathcal{J}_0[pr_\parallel].$$

For $z < \kappa_=^{-1}$ the fact that the charges are a finite distance away from the salty plane only leads to subfluent corrections and Eqs. (28) and (29) are valid. For intermediate separations from the interface, for $\kappa_=^{-1} < z < r_\parallel$, we find

$$v_{\mathrm{DH}}(r_\parallel,z)\simeq\frac{2\ell_B z^2}{r_\parallel^3}. \qquad (31)$$

If the two particles are far apart from the surface, $\kappa_=^{-1} < z$, but relatively close to each other, $r_\parallel < z$, screening effects can be neglected and we obtain $v_{\mathrm{DH}}(r_\parallel,z)\simeq \ell_B/r_\parallel$. In the case of a finite salt concentration in the external space, all interactions are replaced by the ordinary DH potential (30) if any of the length scales, z or $r_\parallel$, becomes larger than the screening length κ^{-1}.

E. Interactions through a salty interface

We discuss the interaction of two charges through a salty membrane for the symmetric case $\kappa_> = \kappa_< = \kappa$ and also assume the dielectric constants are the same, i.e., $\eta = 1$. For simplicity, we assume both particles share the same lateral position. The interaction only depends on the distance $\delta z = |z - z'|$ between the particles,

$$v_{\mathrm{DH}}(\delta z)=\frac{\ell_B}{\delta z}e^{-\kappa\delta z}\left(1-\left[1+2\frac{\kappa}{\kappa_\parallel}\right]^{-1}xe^x\Gamma[0,x]\right),$$

where we have used the short-hand notation $x = \delta z(\kappa_\parallel/2 + \kappa)$. The function $xe^x\Gamma[0,x]$ is negative for $x < 1$, with a minimum of ≈ -0.4 at $x \approx 0.1$; for this range of particle separations, the DH interaction is *enhanced* by the presence of the salty membrane. For $x > 1$, the function $xe^x\Gamma[0,x]$ is positive, with a maximum of ≈ 0.1 at $x \approx 1.9$; for this range of particle separations the DH interaction is *weakened* by the presence of the salty membrane. Since the prefactor $1/(1+2\kappa/\kappa_\parallel)$ is smaller than unity, it follows that the effective interaction for separations $x > 1$ is weakened due to polarization charges on the membrane, but never changes sign. The repulsion between two similarly charged spheres is thus enhanced for small *trans*-membrane separations, and weakened for larger separations, but never turns into an attraction.

F. Interactions at an interface between two different salt solutions

Here we describe the experimental situation where two charged objects which are immersed in a salt solution approach each other close to the water-air interface or a substrate. The air or the substrate contain no salt. We therefore set $\kappa_< = 0$. The dielectric constant ratio η is an important parameter. We also set the interfacial ion concentration to zero, $\kappa_= = 0$. For two ions which are located right at the interface, $z = z' = 0$, the interaction energy follows from Eqs. (10) and (15) as

$$v_{\mathrm{DH}}(r_\parallel)=\ell_B\int_0^\infty dp\left[1+\frac{\sqrt{\kappa_>^2+p^2}-\eta p}{\sqrt{\kappa_>^2+p^2}+\eta p}\right]\frac{p\,\mathcal{J}_0[pr_\parallel]}{\sqrt{\kappa_>^2+p^2}}.$$

For small values of η it is permitted to expand in powers of η. We obtain for small separations, $r_\parallel < \kappa_>^{-1}$,

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{2\ell_B(1-\eta)}{r_\parallel},$$

and for large separations, $r_\parallel > \kappa_>^{-1}$,

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{2\ell_B}{r_\parallel}\left(e^{-\kappa_> r_\parallel}+\frac{\eta}{\kappa_>^2 r_\parallel^2}\right).$$

We see that for very large separations the algebraic decay dominates the interaction [19–21]. The crossover from exponential to algebraic decay occurs at $r_\parallel^* \sim \kappa_>^{-1}\ln(1/\eta)$, which can for small values of η be a large number. The algebraic decay comes about since the charges form, together with their associated counterion clouds, dipoles, which interact without screening effects through the lower half-space. If we now consider the interaction between two charges which are both a distance z away from the salty interface, we obtain for small values of η and for large separations, $r_\parallel > \kappa_>^{-1}$,

$$v_{\mathrm{DH}}(r_\parallel)\simeq\frac{\ell_B e^{-\kappa_> r_\parallel}}{r_\parallel}+\frac{\ell_B e^{-\kappa_>\sqrt{r_\parallel^2+4z^2}}}{r_\parallel}+\frac{2\eta\ell_B}{\kappa_>^2 r_\parallel^3}e^{-2\kappa_> z}.$$

The algebraic decay is exponentially weakened as the distance from the interface z increases, but it is always relevant for large lateral distances. The crossover distance is shifted to higher values as the distance from the interface increases and reads $r_\parallel^* \simeq 2z + \kappa_>^{-1} \ln(1/2\eta)$.

A special case which can be solved in closed form is for $\eta = 1$, in which case we obtain

$$v_{\rm DH}(r_\parallel) = \frac{2\ell_B}{\kappa_>^2 r_\parallel^3}(1 - e^{-\kappa_> r_\parallel}[1 + \kappa_> r_\parallel]).$$

For large separations, $r_\parallel > \kappa_>^{-1}$, we again find an algebraic decay $v_{\rm DH}(r_\parallel) \simeq 2\ell_B/\kappa_>^2 r_\parallel^3$, and for small separations, $r_\parallel < \kappa_>^{-1}$, we recover the bare Coulomb interaction $v_{\rm DH}(r_\parallel) \simeq \ell_B/r_\parallel$.

G. Charged polymers

In this section we give some results for the self-energy of a charged straight line, parallel to the substrate, and for the interaction between two parallel charged lines close to an interface. This is a very simple model for the adsorption of synthetic polyelectrolytes on charged substrates, and should give an acceptable estimate for the electrostatic adsorption energy if (i) the polymer is strongly adsorbed and thus lies flat on the substrate, and (ii) the polymer is locally straight. Both conditions are in fact met over a wide range of parameters for fully charged synthetic polymers, as shown theoretically [28] and experimentally [29]. For the adsorption of DNA on charged substrates, a straight-line model has been used in various theoretical approaches [17,18], and it is in fact expected to be a good approximation, since DNA is very stiff and in the adsorbed state the DNA is flat, straight, and parallel to the substrate [16]. In the following, we assume the lower half-space contains no salt, as is appropriate for the adsorption of a charged polymer at a solid substrate or at the water-air interface.

Denoting the line or polymer charge density by τ, the self-energy per polymer unit length as a function of the distance z from the interface is

$$f_{\rm DH}^{\rm self}(z) = \frac{\tau^2}{2}\int_{-\infty}^{\infty}\frac{dp}{2\pi}[v_{\rm DH}(z,z,p) - v_{\rm DH}(\infty,\infty,p)] \qquad (32)$$

with $v_{\rm DH}(z,z,p)$ given in Eq. (15). The asymptotic result for large distances from the wall is

$$f_{\rm DH}^{\rm self}(z) \simeq \frac{\ell_B \tau^2}{2}\left(\frac{\kappa_> - \kappa_=}{\kappa_> + \kappa_=}\right)\sqrt{\frac{\pi}{\kappa_> z}}e^{-2z\kappa_>}. \qquad (33)$$

The polymer is attracted to the interface only if the salt concentration in the surface is higher than the bulk concentration of salt. In the absence of surface ions, there is an exponential repulsion from the interface which has to do with the missing screening effects in the lower half-space. In the limit of small separations, the asymptotic result is

$$f_{\rm DH}^{\rm self}(z) \simeq \ell_B \tau^2 \frac{1-\eta}{1+\eta}\ln(1/\kappa_> z). \qquad (34)$$

For values of η smaller than unity, the polymer is logarithmically repelled from the substrate, which is due to image-charge effects. For $\eta = 1$ the logarithmic term vanishes.

Setting $\eta = 1$ and $\kappa_= = 0$, we can solve the integral in Eq. (32) exactly and obtain for the self-energy

$$f_{\rm DH}^{\rm self}(z) = \frac{\ell_B \tau^2}{2}\left(K_0[2\kappa_> z] + K_2[2\kappa_> z] + \frac{K_1[2\kappa_> z]}{z\kappa_>} - \frac{1 + 2\kappa_> z}{z^2\kappa_>^2}e^{-2\kappa_> z}\right). \qquad (35)$$

For small separation, $z < \kappa_>$, we obtain from Eq. (35) the asymptotic expansion $f_{\rm DH}^{\rm self}(z) \simeq \ell_B \tau^2 (1/2 - 4z\kappa_>/3)$; for large separations the result is $f_{\rm DH}^{\rm self}(z) \simeq \ell_B \tau^2 e^{-2z\kappa_>}\sqrt{\pi/4z\kappa_>}$ and thus agrees with the general asymptotic result Eq. (33). There is therefore a strong repulsion from the wall, which for small separations is of the order of $\ell_B \tau^2$ per polymer unit length, and which is due to the fact that there are no mobile ions inside the substrate. This repulsion is therefore solely due to the absence of screening in one half-space. It is this term which is contributing to the strong repulsion of a charged rod from an oppositely charged substrate which has been seen in MD simulations at short separations [18].

In the limit $\eta = 0$, which corresponds to a substrate with a very small dielectric constant, and $\kappa_= = 0$, the integral Eq. (32) gives

$$f_{\rm DH}^{\rm self}(z) = \ell_B \tau^2 K_0[2\kappa z]. \qquad (36)$$

For small arguments the Bessel function goes like $K_0[x] \sim -\ln(x)$ and for large arguments it goes like $K_0[x] \sim \sqrt{\pi/2x}e^{-x}$, and we thus recover the general asymptotic results Eqs. (33) and (34). The strong repulsion from the low-dielectric substrate has recently been shown theoretically to induce a polymer desorption transition for strongly charged polymers, and therefore cannot be neglected in a theoretical modeling of polyelectrolyte adsorption [28]. In the limit $\eta = \infty$, corresponding to adsorption on a metal substrate, we obtain the same result as in Eq. (36) but with a negative sign. In this case, there is an overall attraction to the substrate, even in the absence of charges on the substrate surface.

The interaction between two parallel polymers at a mutual separation d, which are both at a distance z from the substrate, is defined as

$$f_{\rm DH}(z,d) = \tau^2 \int_{-\infty}^{\infty}\frac{dp}{2\pi}v_{\rm DH}(z,z,p)\cos[pd] \qquad (37)$$

with $v_{\rm DH}(z,z,p)$ given in Eq. (15). The asymptotic result for large distances between the polymers is obtained from Eq. (37) by partial integration and reads

$$f_{\rm DH}(z,d) \simeq 2\ell_B \tau^2 K_0[d\kappa_>] + \frac{4\ell_B \tau^2 \eta}{d^2(\kappa_> + \kappa_=)^2}e^{-2z\kappa_>} \qquad (38)$$

and we see that for large lateral separations d the repulsion decays as an inverse square of d. This is a direct consequence of the fact that the interaction between two charges decays as an inverse cube of the lateral distance between them; see Sec. III F. We note that for small values of η the algebraic decay of the repulsive energy only dominates the exponential decay from the Bessel function for lateral separations much larger than the screening length. For small separations the repulsion goes as

$$f_{\mathrm{DH}}(z,d) \simeq \frac{4\ell_B \tau^2}{1+\eta} \ln(1/d\kappa_>), \tag{39}$$

that is, we find a small increase of the repulsion in the case of a low-dielectric substrate. The algebraic decay of polymer-polymer interactions at large separation has been recently shown to lead to an enhancement of the electrostatic persistence length of a polyelectrolyte close to a substrate [28].

IV. DISCUSSION

In this paper we consider the generalized DH theory for planar interfaces which contain mobile salt ions and which divide half-spaces with different salt concentrations and different dielectric constants. We explicitly calculate the DH Green's function, $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$, for several special cases. The equal-point Green's function, $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r})$, corresponds to the self-energy of a charged particle. We find charged particles to be strongly attracted to salty layers, which could be experimentally tested with complexation experiments on charged colloids and membranes containing anionic and cationic lipids. Similarly, for an interface dividing salt solutions of two different concentrations, a charged particle residing in the salt-poor half-space is attracted to the salt-rich half-space. This could be checked experimentally with vesicles which have a high intravesicular salt concentration, osmotically matched with a nonelectrolyte extravesicular solution: charged colloids should strongly bind to these salty vesicles. We also analyze $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$, the interaction between two charges. Close to salty interfaces and close to an interface to a salt-free half-space, we find the interaction to decay algebraically with the lateral distance between the two charges.

Our calculations are restricted to—on average—neutral planes and half-spaces. The potential distribution $\phi(\mathbf{r})$ of an arbitrary charge distribution $\sigma(\mathbf{r})$ can be calculated within the framework of DH theory by convoluting $\sigma(\mathbf{r})$ with the Green's function,

$$\phi(\mathbf{r}) = \int d\mathbf{r}' \sigma(\mathbf{r}') v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}'). \tag{40}$$

For a homogeneously charged interface with surface charge density σ we obtain from Eqs. (14) and (40) the reduced electrostatic potential

$$\phi(z) = \frac{4\pi\ell_B \sigma \mathrm{e}^{-z\kappa_>}}{\kappa_> + \eta\kappa_< + \kappa_=}. \tag{41}$$

The potential is reduced for interfaces containing surface ions ($\kappa_= > 0$), which is a pure correlation effect between surface ions and counterions. The total electrostatic potential of a charged colloidal particle at a charged interface follows by adding the electrostatic potential, Eq. (41), and the electrostatic self-energy, which has been calculated in Secs. III B and III C.

As is well known, DH theory neglects nonlinear effects, which become important when the electrostatic potential is larger than the thermal energy. These nonlinear effects are equivalent to effective multipoint interactions and can be treated in a systematic field theory by including higher-loop corrections [23].

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[1] P. W. Debye and E. Hückel, Z. Phys. **24**, 185 (1923).

[2] D. Fennel Evans and H. Wennerström, *The Colloidal Domain* (VCH Publishers, New York, 1994).

[3] D. Andelman, in *Handbook of Biological Physics*, edited by R. Lipowsky and E. Sackmann (Elsevier, Amsterdam, 1995), Vol. I, p. 603.

[4] C. Wagner, Phys. Z. **25**, 474 (1924).

[5] L. Onsager and N. T. Samaras, J. Chem. Phys. **2**, 528 (1934).

[6] E. Schmutzer, Z. Phys. Chem. (Leipzig) **204**, 131 (1955).

[7] F. P. Buff and F. H. Stillinger, J. Chem. Phys. **25**, 312 (1956).

[8] F. H. Stillinger and J. G. Kirkwood, J. Chem. Phys. **33**, 1282 (1960).

[9] F. H. Stillinger, J. Chem. Phys. **35**, 1584 (1961).

[10] H. Totsuji, J. Phys. Soc. Jpn. **40**, 857 (1976).

[11] V. M. Muller and B. V. Derjaguin, J. Colloid Interface Sci. **61**, 361 (1977).

[12] V. M. Muller and B. V. Derjaguin, Colloids Surface **6**, 205 (1983).

[13] E. S. Velázquez and L. Blum, Physica A **244**, 453 (1997).

[14] P. A. Pincus and S. A. Safran, Europhys. Lett. **42**, 103 (1998).

[15] A. W. C. Lau and P. Pincus, Phys. Rev. Lett. **81**, 1338 (1998).

[16] J. O. Rädler, I. Koltover, T. Salditt, and C. R. Safinya, Science **275**, 810 (1997); R. Zantl, F. Artzner, G. Rapp, and J. O. Rädler, Europhys. Lett. **45**, 90 (1998); B. Maier and J. O. Rädler, Phys. Rev. Lett. **823**, 1911 (1999).

[17] R. Menes, P. Pincus, R. Pittman, and N. Dan, Europhys. Lett. **44**, 393 (1998).

[18] R. J. Mashl, N. Grønbech-Jensen, M. R. Fitzsimmons, M. Lütt, and DeQuan Li, J. Chem. Phys. **110**, 2219 (1999).

[19] B. Jancovici, J. Stat. Phys. **28**, 43 (1982).

[20] S. L. Carnie and D. Y. C. Chan, Mol. Phys. **51**, 1047 (1984).

[21] P. Attard, R. Kjellander, D. J. Mitchell, and B. Jönsson, J. Chem. Phys. **89**, 1664 (1988).

[22] D. Goulding and J.-P. Hansen, Mol. Phys. **95**, 649 (1998).

[23] R. R. Netz and H. Orland, Europhys. Lett. **45**, 726 (1999).

[24] T. C. Lubensky and M. H. Rubin, Phys. Rev. B **12**, 3885 (1975).

[25] H. W. Diehl, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic Press, London, 1983), Vol. 8, p.1.

[26] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover Publications, New York,

1972).
[27] The hard-core radius a can be implemented by using a large-momentum cutoff π/a in the integral Eq. (18). Since our results are only affected at short length scale by this, we use the limit $a=0$ for the sake of clarity.
[28] R. R. Netz and J.-F. Joanny (unpublished).
[29] K. de Meijere, R. R. Netz, G. Brezesinski, and H. Möhwald (unpublished).