Electrostatic correlation forces between surfaces with surface specific ionic interactions

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We have studied some consequences of a generalized theory of electrostatic interactions between two macroscopic surfaces immersed in a dilute electrolyte. The ionic interactions close to the two bounding surfaces were supposed to be specifically affected by the presence of the surfaces, leading to a surface contribution to the total free energy density of the system. A functional integral (sine-Gordon) representation of the grand canonical partition function was derived and evaluated in the saddle-point approximation, leading to the repulsive mean-field and an attractive first-order correlation correction to the interaction free energy. The magnitude of the correlation term was investigated in detail and general conditions on the form of the surface-specific free energy density were derived that would lead to an anomalously large exponentially decaying attractive interactions. We present some arguments in favor of the view that this anomalous long-range attraction could well represent a case for the electrostatic nature of the recently measured long-range "hydrophobic" attraction.

I. INTRODUCTION

The original observation[1] that forces between equally charged surfaces immersed in an electrolyte can under certain conditions become attractive has initiated several new theoretical approaches that try to go beyond the standard Poisson–Boltzmann theory in an attempt to include correlations into the description of electrostatic interactions between charged surfaces[2,4]. The inclusion of bulk correlations into the description of electrostatic forces also stimulated the investigation of models that exhibit special types of surface correlations as is the case in the studies of interactions between neutral surfaces with adsorbed, mobile ions, or dipoles.[3]

In this contribution we shall try to establish a formalism that will connect the surface and the bulk correlations in a theory of electrostatic forces of considerable generality. We shall treat the interaction of two surfaces immersed in an electrolyte, while excluding the complications brought about by the image forces. The surfaces will be described in a general way through a surface contribution to the total free energy of the system that takes into account the direct short-range interaction between the Coulombic charges and the surface as well as the possibility of a short-range interaction among the charges close to or mediated by the surfaces. A representation of the grand canonical partition function[4] will be introduced that allows a rather straightforward decoupling into a mean-field (Poisson–Boltzmann) and a fluctuation contribution to the thermodynamic potential. We will show that the fluctuation (correlation) contribution in general leads to an attractive force between the two surfaces. We shall analyze the magnitude of the correlation term in the asymptotic limit of large intersurface separations and show that it depends on the properties of the surface free energy at or close to the mean-field potential. We will show that there exists a regime of very large attractive forces and describe the type of behavior of the surface free energy that leads to this anomalous attraction.

The outline of the paper is as follows. In Sec. II we shall introduce a special representation, the s.c. sine-Gordon transformation,[5] of the grand canonical partition function in terms of a functional integral over local electrostatic potentials. The "action" of the functional integral will be shown to decouple into a bulk and a surface term, of which only the former can be written in an explicit form. This form of the grand canonical partition function will form the basis of our subsequent analysis.

Sections III and IV deal with an approximate evaluation of the functional integral. It is assumed that the only significant contribution to the functional integral comes from the regions where the action is stationary. This is the essence of the saddle-point method, where the deviations from the stationary point in the function space are dealt with in the harmonic approximation. The saddle-point method[6] will give us an explicit form for the mean and the fluctuation contribution to the thermodynamic potential. The former will be shown to be equivalent to an appropriate Poisson–Boltzmann description.

Though the saddle-point thermodynamic potential will be derived explicitly it still eludes exact evaluation and the WKB method[4] will be introduced in Sec. V to obtain an explicit form amenable to further analysis. It will be shown that it leads to a generalization of the expression for the zero order van der Waals–Lifshitz interaction. The dependence of the correlation part of the free energy on the intersurface separation will be examined in Sec. VI. It will be shown that it leads to an attractive force of approximately exponential decay.

In Sec. VII we shall discuss the magnitude of the correlation interaction and its relation to the analytic properties of the surface free energy. We shall establish two different regimes of the magnitude of the correlation forces. We will show that if there exists a region in the "phase space" defined by the surface free energy density (f) that is not thermodynamically stable, than the attractive correlation forces can

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become anomalously large. The general conditions that have to be satisfied by the form of f will be stated in order that these large attractive forces become a distinct physical possibility.

In the last section we shall assess the evidence in favor of the conclusion that the recently measured very long-range "hydrophobic" interactions[7] can be rationalized in terms of the general enhanced-attraction type of correlation forces hypothesized on theoretic grounds in this work.

II. FUNCTIONAL INTEGRAL REPRESENTATION OF THE GRAND CANONICAL PARTITION FUNCTION

We shall consider two surfaces immersed into an uni–uni valent electrolyte, separated by a distance $2a$ (Fig. 1). Close to each surface we shall assume there is a region of spatial dimension ζ where the ionic species i is perturbed by the surface with energies $E_i^{\pm}$. In the asymptotic regime of large intersurface separations, corresponding to the limit $\zeta \Rightarrow 0$, this will in general contribute an additional term to the interaction energy.[8] It is our aim to investigate the physical consequences of this specific interaction confined to the region near each surface. In order to make the analysis as simple as possible we shall ignore the contribution of image forces while assuming that the electrolyte is distributed on both sides of the interfaces.

The configurational part of the Hamiltonian for the model system defined above can be written in the form

$$U_N = \frac{1}{2}\sum_{i\neq j} e_i e_j u(\mathbf{r}_i,\mathbf{r}_j) + \sum_s E_s^{\pm}\,, \tag{2.1}$$

where the summation in the first term is carried over all the charges e_i of all the ionic species provided that $i \neq j$. The index in the second sum runs over all the charges of those species that interact with the surface. We shall assume that the interaction potential is purely electrostatic and can be obtained as a solution of Poisson equation

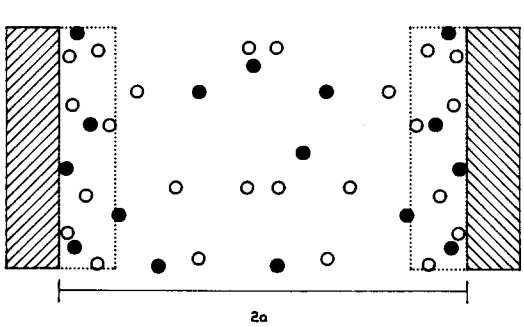

FIG. 1. Two surfaces separated by 2a with uni–uni valent ionic solution in between. The ζ regions close to the two surfaces, where the surfaces influence the energy of the neighboring ions, are indicated by dotted lines. To make the analytical treatment as easy as possible, we have assumed that the ions are distributed on both sides of the surfaces. This assumption considerably simplifies the formal manipulations without altering the general conclusions of our discussion.

$$\nabla^2 u(\mathbf{r},\mathbf{r}') = -\delta(\mathbf{r},-\mathbf{r}')/\epsilon\epsilon_0\,, \tag{2.2}$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac function and ϵ is the relative dielectric permittivity, assumed to be the same in all regions of space. Equation (2.1) can be rewritten in a somewhat modified form better suited for further analysis:

$$U_N = \frac{1}{2}\sum_{i,j} e_i e_j u(\mathbf{r}_i,\mathbf{r}_j) - \frac{1}{2}\sum_a N_a e_a^2 u(\mathbf{r}_a,\mathbf{r}_a) + \sum_s E_s^{\pm} \tag{2.3}$$

the first sum now running over all the indices. a in the above equation is the index of the ionic species that has N_a ions of charge e_a. $u(\mathbf{r}_a,\mathbf{r}_a)$ is the self-energy of each ion of the ath ionic species. There are altogether $N = \Sigma N_a$ ions in the system. If we now define the canonical partition function without any restriction on summation indices

$$Q_N = \int \exp\left[-\beta\tfrac{1}{2}\sum_{i,j} e_i e_j u(\mathbf{r}_i,\mathbf{r}_j)\right] d^{3N}\mathbf{r} \tag{2.4}$$

with β the inverse thermal energy, than the grand canonical partition function with configurational part of the Hamiltonian given by Eq. (2.3) can be cast into the following form:

$$\Xi = \prod_a \prod_s \left[\sum_a \left(\frac{z_a^{N_a}}{N_a!}\right)\sum_s \left(\frac{z_s^{N_s}}{N_s!}\right) Q_N\right], \tag{2.5}$$

where the index a again runs over all the ionic species and index s only over those that interact with the surfaces. In the above equation the absolute activities have been transformed into

$$z_a \Rightarrow z_a \exp[\tfrac{1}{2}\beta N_a e_a^2 u(\mathbf{r}_a,\mathbf{r}_a)]\,, \tag{2.6a}$$

$$z_s \Rightarrow z_s \exp(-E_s^{\pm})\,. \tag{2.6b}$$

We shall now proceed by using the Hubbard–Stratonovich[9] transformation to obtain a more convenient expression for Ξ, i.e., we use the following representation:

$$\exp\left[-\beta\tfrac{1}{2}\sum_{i,j} e_i e_j u(\mathbf{r}_i,\mathbf{r}_j)\right] = \left\langle \exp\left[i\beta\sum_i e_i\varphi(\mathbf{r}_i)\right]\right\rangle_{\varphi}\,, \tag{2.7}$$

where i is the imaginary unit with the average over auxiliary fields $\varphi(\mathbf{r})$ defined as

$$\langle\cdots\rangle_{\varphi} = \Delta(\beta)\int_{(N)}(\cdots) \times\exp\left[-\tfrac{1}{2}\beta\sum_{i,j}\varphi(\mathbf{r}_i)u^{-1}(\mathbf{r}_i,\mathbf{r}_j)\varphi(\mathbf{r}_j)\right] \times d\varphi(\mathbf{r}_i)\cdots d\varphi(\mathbf{r}_N) \tag{2.8}$$

with

$$\Delta(\beta) = (2\pi)^{N/2}[\det\beta u^{-1}(\mathbf{r},\mathbf{r}')]^{1/2}\,. \tag{2.9}$$

In the limit of $N \Rightarrow \infty$ we shall use the symbolic designation $d\varphi(\mathbf{r}_1)\cdots d\varphi(\mathbf{r}_N) \Rightarrow \mathcal{D}\varphi(\mathbf{r})$. The auxiliary fields $\varphi(r)$ were introduced above in a rather formal manner but we shall show later that they have a fairly straightforward physical interpretation. Using the Hubbard–Stratonovich representation we can derive the following functional integral form for the grand canonical partition function[5]:

$$\Xi = [\det \beta u(\mathbf{r},\mathbf{r}')\ ]^{-1/2} \int \exp\{S(\varphi(\mathbf{r})\}\, \mathscr{D}\varphi(\mathbf{r})\,, \tag{2.10}$$

where the "action" has been defined as

$$S = -\tfrac{1}{2}\beta \iint \varphi(\mathbf{r}) u^{-1}(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')d^3\mathbf{r}\, d^3\mathbf{r}' + \int \rho(\mathbf{r})d^3\mathbf{r} - \beta \oint f(\mathbf{s})d^2\mathbf{s} \tag{2.11}$$

and can be obtained by executing the summations in Eq. (2.5) explicitly. In the above equation we have also introduced the local density of the ions as

$$\rho(\mathbf{r}) = \sum_a \rho_{0a} \exp[i\beta e_a \varphi(\mathbf{r})]\,, \tag{2.12}$$

where ρ_{0a} is the bulk density of the ath ionic species defined as $\rho_{0a} = z_a/V$, where V is the volume occupied by the ions, the surface part of the free energy is obtained as

$$f[\varphi(\mathbf{s})] = -kT \sum_s n_s \times \ln\left(\sum_{N_s=0}^{M_s} \frac{\{Z_s \exp[i\beta e_s \varphi(\mathbf{s})]\}^{N_s}}{N_s!} \right), \tag{2.13}$$

where n_s is the surface density of the adsorbing ions. If the local ion density is a universal function $\varphi(\mathbf{r})$ depending only on z_a and e_a, the surface free energy density (2.13) depends on the details of the interactions at the surfaces. For example, if we have adsorption sites at the surface where only a single ion can be located, then $M_s = 1$. Other situations can easily be imagined leading to different forms of the surface free energy.

Coulomb system described with the interaction as in Eq. (2.1) is not, in general, thermodynamically stable and is bound to collapse. This is due to the fact that the short-range interactions have not been explicitly included into the configurational part of the Hamiltonian. This difficulty could be overcome in the bulk part of Eq. (2.11) by making the approximate identification[10]

$$\int \rho(\mathbf{r})d^3\mathbf{r} \simeq \beta \int p_0(z_a e^{i\beta e_a \varphi(\mathbf{r})}, \beta)\, d^3\mathbf{r}\,, \tag{2.14}$$

where $p_0(z,\beta)$ denotes the grand canonical pressure of the reference (short-range) system at activity z and temperature T. This modification would, however, greatly complicate further analysis. We will therefore resort to a simpler, more heuristic approach. We shall keep track of the divergent integrals, as they arise, and introduce an appropriate cutoff to make them finite.[4]

There are similar problems with the surface part of Eq. (2.11). The surface free energy density, defined in Eq. (2.13), represents only the ideal (entropic) contribution with no short-range interactions included. We could again make the identification

$$f[\varphi(\mathbf{s})] \simeq f(z_a e^{i\beta e_a \varphi(\mathbf{s})}, \beta)\,, \tag{2.15}$$

where now $f(z,\beta)$ is the total surface free energy density with the short-range interactions included. The form (2.13) would consequently not remain valid in this general case, instead, appropriate Landau expansions could be used in order to obtain an explicit form of f. Without introducing new technical difficulties we shall therefore assume the approximate identity (2.15) when referring to the surface free energy density.

The final form of the action can be obtained after taking into account that the electrostatic potential satisfies Eq. (2.2) as

$$S = -\frac{1}{2}\beta\epsilon\epsilon_0 \int [\nabla\varphi(\mathbf{r})]^2 d^3\mathbf{r} + \int \rho[\varphi(\mathbf{r})]d^3\mathbf{r} - \beta \oint f[\varphi(s)]d^2\mathbf{s}\,. \tag{2.16}$$

The above form of the action in the functional integral representation of the grand canonical partition function (2.10) will be the starting point of our further analysis.

III. THE SADDLE-POINT (EXTENDED POISSON–BOLTZMANN) APPROXIMATION

Since the action in the functional integral (2.10) is not Gaussian no exact evaluation of the partition function is at present feasible. Standard approximation schemes, however, can be profitably exploited in order to get a good estimate for all the relevant statistical mechanical quantities. Saddle-point method was shown to yield reasonable results for Coulomb systems[4] without any surface specific interactions and we shall try to extend it to our present case.

If the action (2.16) has a stationary point in the space of functions $\varphi(\mathbf{r})$ than in the weak fluctuations regime one can write to the lowest order

$$S = S_0 + \frac{1}{2}\iint \left[\frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')}\right]_0 \times \delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')d^3\mathbf{r}\, d^3\mathbf{r}'\,, \tag{3.1}$$

where the subscript 0 stands for the value of the auxiliary field $\varphi(\mathbf{r})$ defined by

$$\left[\frac{\delta S}{\delta\varphi(\mathbf{r})}\right]_0 = 0\,. \tag{3.2}$$

In this approximation the grand canonical partition functions is therefore given by the following expression:

$$\Xi = [\det \beta u(\mathbf{r},\mathbf{r}')\ ]^{-1/2} \times \left\{ \det\left(\frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')} \right)_0 \right\}^{-1/2} \exp(S_0) \tag{3.3}$$

and the thermodynamic potential can be obtained as

$$\Omega = -kT \ln \Xi = -kT S_0 + \frac{kT}{2} \times \ln \det\left\{ \int u(\mathbf{r},\mathbf{r}') \left[\frac{\delta^2 S}{\delta\varphi(\mathbf{r}')\delta\varphi(\mathbf{r}'')}\right]_0 d^3\mathbf{r}' \right\}. \tag{3.4}$$

Formally this is the basic result of the saddle-point method. The thermodynamic potential is given by its extremal value plus a contribution due to the fluctuations of the auxiliary fields around this extremum.

Let us first of all analyze the Euler–Lagrange equation

(3.2). Using the action S in the form of Eq. (2.16) we can see that the extremum condition decouples into two equations. First of all we obtain the boundary condition at the two limiting surfaces of the form

$$-\epsilon\epsilon_0 \frac{\partial\varphi(z,\mathbf{s})}{\partial\mathbf{n}}\bigg|_{\pm a} = \frac{\partial f[\varphi(\mathbf{s})]}{\partial\varphi}, \tag{3.5}$$

where $\mathbf{n}$ is the surface normal. If the mean field is distributed on both sides of the boundary surfaces then the appropriate jump across the surface should be taken in Eq. (3.5). The variation in the bulk part of the action gives

$$\int u(\mathbf{r},\mathbf{r}')\varphi(\mathbf{r}')d^3\mathbf{r} = -\epsilon\epsilon_0\nabla^2\varphi(\mathbf{r}) = kT\frac{\partial\rho(\mathbf{r})}{\partial\varphi}. \tag{3.6}$$

Both the above equations show that the saddle-point solution is purely imaginary. Therefore making the substitution $\varphi \Rightarrow i\varphi$ we can recognize Eqs. (3.5) and (3.6) as the Lippmann and Poisson–Boltzmann equation.[11] This is readily verified by taking the form of $\rho(\mathbf{r})$ valid for the uni–uni valent electrolyte, $\rho(\mathbf{r}) = \rho_0 ch[\beta e_0\varphi(\mathbf{r})]$, where ρ_0 is the bulk ionic concentration.

A clear physical interpretation of $\varphi(\mathbf{r})$ therefore emerges from the above discussion, viz. that the auxiliary fields introduced formally through the Hubbard–Stratonovich transformation are just the local electrostatic potentials[5] and the action S of the functional integral (2.10) is just the Poisson–Boltzmann free energy evaluated at imaginary values of the charges $S = F_{\mathrm{PB}}(ie_a)$. Furthermore, in the saddle-point approximation S_0 is nothing but the mean-field free energy and the mean-field thermodynamic potential is given in the standard form

$$\frac{\Omega_0}{S} = -\tfrac{1}{2}\epsilon\epsilon_0\int[\nabla\varphi(\mathbf{r})]^2 d^3\mathbf{r} - kT\int\rho[\varphi(\mathbf{r})]d^3\mathbf{r} + \int f[\varphi(\mathbf{s})]d^2\mathbf{s}, \tag{3.7}$$

where again the substitution valid at the mean-field $\varphi \Rightarrow i\varphi$ has been used. The above equation can be cast into a much simpler form:

$$\frac{\Omega_0}{S} = f(\varphi) - \int_0^{\varphi}\sigma\, d\varphi, \tag{3.8}$$

where σ is the surface charge density and φ is the solution of the boundary condition (3.5). The standard Poisson–Boltzmann result[11] in the case of constant surface charge is now obtained by taking $f(\varphi) = \sigma\varphi$.

A point of notice here is the boundary condition. Should the surface part of the energy density depend linearly on φ, Eq. (3.5) would clearly state the electroneutrality of the system. In general, however, Eq. (3.5) expresses the charge regulation condition at the surface. Let us show this by a simple example. If we assume that there are no short-range interactions between the adsorbing charges [the entropic form of f, viz. Eq. (2.13) is valid] and that the anions adsorb with a very large energy $E^- \Rightarrow \infty$, being therefore basically fixed on the surface, while the cations can adsorb to the same sites one at a time, we get from Eq. (2.13),

$$f[\varphi(\mathbf{s})] = n_s\ln(1 + z_s e^{-\beta e_0\varphi(\mathbf{s})}) + \beta\sigma\varphi(\mathbf{s}), \tag{3.9}$$

where we introduced the surface charge density of the anions as $\sigma = n_s e_0$. It is straightforward to see that in this case the boundary condition (3.5) corresponds exactly to the Ninham–Parsegian[12] charge regulation condition. Other surface free energies are clearly possible leading to different forms of the charging equilibrium at the surface.[13]

We would like to note here that we used the expression "extended Poisson–Boltzmann approximation" for the saddle-point method as applied to an inhomogeneous Coulomb fluid.[14] Simultaneously this terminology has also been used in a similar context by Attard *et al.*[2] with slight but in certain cases nevertheless important differences. We shall address the differences between the two approaches in a forthcoming publication.[14]

IV. FREE ENERGY IN THE SADDLE-POINT APPROXIMATION

We next proceed to the evaluation of the functional determinant in the expression for the thermodynamic potential in the saddle-point approximation (3.4). First of all we note that

$$\left[\frac{\delta^2 S}{\delta\varphi(\mathbf{r})\delta\varphi(\mathbf{r}')}\right]_0 = u^{-1}(\mathbf{r},\mathbf{r}') + \beta\epsilon_0^2\gamma(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \tag{4.1}$$

with

$$\gamma(\mathbf{r}) = \gamma(z) = \frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2} + \frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\delta(z-a) + + \frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\delta(z+a) \tag{4.2}$$

since the mean-field (Poisson–Boltzmann) solution depends only on the transversal coordinate (z). Next we notice the identity

$$\ln\Xi = S_0 - \tfrac{1}{2}\,\mathrm{Tr}\ln[1 + Be_0^2\gamma(z)u(\mathbf{r},\mathbf{r}')], \tag{4.3}$$

where we employed the matrix identity $\ln\det(A) = \mathrm{Tr}\ln(A)$. Furthermore we introduce the resolvent operator defined as

$$R_\mu(\mathbf{r},\mathbf{r}') = \gamma(\mathbf{r}')G_\mu(\mathbf{r},\mathbf{r}') = \gamma(\mathbf{r}')u(\mathbf{r},\mathbf{r}') - \mu\int\gamma(\mathbf{r}'')u(\mathbf{r},\mathbf{r}'')\times R_\mu(\mathbf{r}'',\mathbf{r}')d^3\mathbf{r}'' \tag{4.4}$$

with the help of which we can reduce Eq. (4.3) to an analytically tractable form. This is obtained by noticing Eq. (2.2) of the pair potential and taking the Laplacian of Eq. (4.4). Thereby we are led to the following identity:

$$\mathrm{Tr}\ln[1 + \beta e_0^2\gamma(z)u(\mathbf{r},\mathbf{r}')] = \mathrm{Tr}\int_0^{\beta e_0^2} d\mu\, R_\mu(\mathbf{r},\mathbf{r}'). \tag{4.5}$$

The equation for R_μ is reduced to the one for G_μ of the form

$$\epsilon\epsilon_0\nabla^2 G_\mu(\mathbf{r},\mathbf{r}') - \mu\frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2}G_\mu(\mathbf{r},\mathbf{r}') = -\delta(\mathbf{r},\mathbf{r}') \tag{4.6}$$

with the boundary condition

$$\epsilon\epsilon_0\frac{\partial G_\mu}{\partial z}\bigg|_{\pm a} = \mu\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}. \tag{4.7}$$

Clearly the resolvent operator or, what amounts to the same thing, the function G_μ satisfy a Debye–Hückel type equation with a position (z) dependent screening length. This result has already been obtained in the case of no surface specific interactions.[14] What is new here is the boundary condition satisfied by the resolvent operator (4.7). It depends only on the nonlinearities present in the surface free energy density as a function of the local potential. If f is a linear function of φ the boundary condition is decoupled from the charging (μ) process.

It follows from the approximate form (2.15) that the right-hand side of Eq. (4.7) could depend on the transversal coordinate as well. This would furthermore lead to a transversal wave vector (Q) dependence of $\partial^2 f/\partial(\beta e_0\varphi)^2$. However, this is not really essential for our further arguments. It will become clear later on that in the asymptotic limit only the $Q=0$ component of $\partial^2 f/\partial(\beta e_0\varphi)^2$ makes an appreciable contribution to the interaction free energy.

The calculation of the fluctuation contribution to the free energy now proceeds in a straightforward manner. Since the system is translationally invariant in the (x,y) plane we can introduce the Fourier–Bessel transform

$$G_\mu(\mathbf{r},\mathbf{r}') = \int g_\mu(Q;z,z')e^{i\mathbf{Q}(\mathbf{s}-\mathbf{s}')}\frac{d^2\mathbf{Q}}{(2\pi)^2}, \tag{4.8}$$

where $\mathbf{s}$ is the radius vector in the (x,y) plane. With this definition we can finally obtain a manageable expression for the fluctuation part of the free energy:

$$\begin{aligned}\mathrm{Tr}\int_0^{\beta e_0^2} d\mu\, R_\mu(\mathbf{r},\mathbf{r}') = \frac{S}{(2\pi)^2}\int d^2\mathbf{Q}\int_0^{\beta e_0^2} d\mu \\ \times\Bigg[\int_{-a}^{+a}\frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2}g_\mu(Q;z,z)dz \\ + \frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}g_\mu(Q;a,a) \\ + \frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}g_\mu(Q;-a,a)\Bigg].\end{aligned} \tag{4.9}$$

This is the last general expression that we can derive in the frame of the saddle-point method. To obtain the Green function G_μ [Eq. (4.6)] the mean-field problem should be solved first giving us the form of $\partial^2\rho(z)/\partial\varphi^2$. There is no general solution to Eq. (4.6) and we have to take recourse to additional approximations.[8]

V. THE GREEN FUNCTION IN THE WKB APPROXIMATION AND THE COUPLING CONSTANT INTEGRAL

Recently we have shown[4] that the WKB method gives a fair approximation to the Green function and has the simplifying feature of being exactly solvable for any form of sufficiently slowly variable density profile $\rho(z)$. Using this method to solve Eq. (4.6) with the boundary condition (4.7) we are led to the following form for the Green function:

$$\begin{aligned}g_\mu(Q;z,z') = \frac{1}{2\epsilon\epsilon_0[u(z)u(z')]^{1/2}}\{\exp[-|\Delta(z,z')|] \\ + \frac{2\alpha\exp[-2\Delta(a,-a)]}{\{1-\alpha^2\exp[-2\Delta(a,-a)]\}} \\ \times[\exp[\Delta(a,-a)]ch[\Delta(z,-z')]] \\ + \alpha\, ch[\Delta(z,z')]\},\end{aligned} \tag{5.1}$$

where we have used the following definitions:

$$u^2(z) = Q^2 + \frac{\mu}{\epsilon\epsilon_0}\frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2}, \tag{5.2a}$$

$$\Delta(z,z') = \int_{z'}^{z} u(z'')dz'', \tag{5.2b}$$

$$\alpha = \left[\frac{\mu}{2\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right]\Bigg/\left[2u(a) + \frac{\mu}{2\epsilon\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right]. \tag{5.2c}$$

We are now ready to evaluate the coupling constant integral in Eq. (4.9). We shall not go through the algebraically extremely involving but nevertheless straightforward computation. Let us just merely quote the final result. By introducing a function $T(Q,\mu)$ defined as

$$\begin{aligned}T(Q,\mu) = \Delta(a,-a) + \ln\{1-\alpha^2\exp[-2\Delta(a,-a)]\} \\ - \ln(1-\alpha^2) + \ln\left[1 + \frac{\mu}{2\epsilon\epsilon_0 u(a)}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right]\end{aligned} \tag{5.3}$$

with $\Delta=\Delta(\mu)$ and $\alpha=\alpha(\mu)$, we can derive the following identity:

$$\mathrm{Tr}\, R_\mu(\mathbf{r},\mathbf{r}') = \frac{S}{(2\pi)^2}\int d^2\mathbf{Q}\frac{\partial T(Q,\mu)}{\partial\mu}, \tag{5.4}$$

wherefrom it follows that the fluctuation part of the free energy can be obtained in a simple closed form:

$$\begin{aligned}\mathrm{Tr}\int_0^{\beta e_0^2} d\mu\, R_\mu(\mathbf{r},\mathbf{r}') = \frac{S}{(2\pi)^2}\int d^2\mathbf{Q} \\ \times\{T(Q,\mu=\beta e_0^2) - T(Q,\mu=0)\}.\end{aligned} \tag{5.5}$$

The free energy thus derived as a function of the transformed chemical potential defined in Eq. (2.6a). We have argued before[4] that in order to obtain the thermodynamic potential as a function of the bare chemical potential a Legendre transformation has to be applied leading to an additional term in Eq. (4.3) of the form

$$-\frac{1}{2}kT\,\mathrm{Tr}\left[\frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2}u(\mathbf{r},\mathbf{r}')\right]. \tag{5.6}$$

The above expression is nothing but the self-energy of the ions that has to be subtracted from the thermodynamic potential.[5] Combining all these results into the final formula for the fluctuation free energy that can be derived in the combined saddle-point WKB approximation scheme we obtain after some rearrangements and partial integrations

$$\frac{\Omega}{S}=\frac{kT}{12\pi}\int_{-a}^{+a}\left[\frac{\beta e_0^2}{\epsilon\epsilon_0}\frac{\partial^2\rho(z)}{\partial(\beta e_0\varphi)^2}\right]^{3/2}dz$$
$$+\frac{kT}{4\pi}\int_0^\infty Q\,dQ\ln\{1-\alpha^2\exp[-2\Delta(a,-a)]\}$$
$$+\frac{kT}{2\pi}\int_0^\infty Q\,dQ\ln\left[1+\frac{\beta e_0^2}{4\epsilon\epsilon_0 u(a)}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right]. \quad (5.7)$$

Different terms in the above equation have different provenience and different meaning.[4] The first term corresponds to the contribution of the fluctuations in the bulk and is a generalization of the Debye–Hückel expression. The second one corresponds to the fluctuations coupled across the region $|z|<a$ and is a generalization of the van der Waals–Lifshitz term. The last term is a consequence of the fluctuation contributions to the surface free energy of the system. It can be computed exactly, if we set the upper bound of the Q inegration equal to $1/b$, where b is the adsorption site dimension or any general short range interaction characteristic length. Equation (5.7) represents the general solution to our problem in the frame of the approximations that we used to derive them. We shall next try to establish the physical consequences of our model for the interactions between the two surfaces.

VI. THE INTERACTION FREE ENERGY

We shall now investigate the behavior of the free energy (5.7) as a function of the intersurface separation. Clearly, the dependence of $f(\mathbf{s})$ on $\varphi(\mathbf{s})$ is needed in order to solve this problem self-consistently. This knowledge is in general not available, except for some relatively simple models as, e.g., Ninham–Parsegian model[12] (3.9) or the constant charge model [the last term in Eq. (3.9)]. We shall, however, try to establish some general features of $\Omega(a)$ that do not require a detailed knowledge of the function $f[\varphi(\mathbf{s})]$.

First of all let us note that the most substantial contribution to the dependence of Ω on a comes from the second term in Eq. (5.7). This is the "real" interaction term, the other two represent perturbations of the bulk and the surface free energy. Therefore[8]

$$\frac{\Omega}{S}(a)\simeq\frac{kT}{4\pi}\int_0^\infty Q\,dQ\ln\{1-\alpha^2\exp[-2\Delta(a,-a)]\}$$
$$\simeq-\frac{kT}{4\pi}\int_0^\infty Q\,dQ\,\alpha^2(Q,a)e^{-2\Delta(a,-a)}, \quad (6.1)$$

where α as a function of Q and a is implicitly given by Eq. (5.2c). The above equation is valid in the asymptotic limit $a\Rightarrow\infty$. The next simplifying assumption will be that in all the integrals over z the major contribution comes from the region of unperturbed density. This assumption will allow us to write

$$\Delta(a,-a)=\int_{-a}^{+a}u(z'')dz''\simeq 2a\sqrt{Q^2+\kappa^2}, \quad (6.2)$$

where κ^2 is the inverse square of the bulk Debye decay length in the case of a uni–uni valent electrolyte. Again this approximation is exact in the asymptotic limit. It is also clear that in this limit the first term in Eq. (5.7) is not important for the a dependence of Ω.

From Eq. (5.2c) it follows that α depends on $u(a)$. Setting $u^2(a)=Q^2+\kappa_s^2$ it is easy to establish the physical meaning of κ_s. To that purpose let us investigate the dependence of the Green function (5.1) on the transversal coordinate $|\mathbf{s}-\mathbf{s}'|$ right next to the surface $z,z'\Rightarrow a$. After some algebra and straightforward integrations (see Appendix B) we obtain

$$G_\mu(a,a;u=|\mathbf{s}-\mathbf{s};|)$$
$$\simeq\frac{1}{4\pi\epsilon\epsilon_0}\left(2\frac{e^{-\kappa_s u}}{u}-\text{const}\frac{e^{-\kappa_s u}}{(K_f u/2)^2}\right). \quad (6.3)$$

Clearly we can now state that K_s is nothing but the surface screening length. The exponential form of the decay of the transversal part of the correlation function along the surface is a consequence of the fact that we allowed the screening medium to be on both sides of the surface. The general theorem of Jancovici[15] on the long-range nature of the transversal correlation function does not apply to this case.

Proceeding now with the evaluation of Eq. (6.1) we shall first of all investigate the small surface coupling limit, i.e., $\partial^2 f/\partial(\beta e_0\varphi)^2\ll 1$. In this limit we can write

$$\frac{\Omega}{S}(a)\simeq\frac{kT}{4\pi}\left(\frac{\beta e_0^2}{2\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right)^2\int_0^\infty\frac{Q\,dQ\,e^{-2\Delta(a,-a)}}{u(a)}. \quad (6.4)$$

The last integral in the above equation is still a complex function of $\kappa\simeq\kappa_s$. This limit corresponds to the case of vanishing net surface charge and the interaction free energy is purely flutuational in origin. From Eq. (6.4) we can easily derive in this limit

$$\frac{\Omega}{S}(a)\simeq-\frac{kT}{4\pi}\left(\frac{\beta e_0^2}{2\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right)^2\text{Ei}(-4a\kappa) \quad (6.5)$$

with $\text{Ei}(x)$ being the standard exponential integral function. From the form of Eq. (6.5) it is evident that it corresponds to monopolar fluctuations at the two surfaces coupled accross the solution region with a correlation length of κ^{-1}. The other results that we derive in Appendix A are variations on this basic limiting form.

Writing first of all Eq. (6.4) in the form

$$\frac{\Omega}{S}(a)\simeq-\frac{kT}{4\pi}\left(\frac{\beta e_0^2}{2\epsilon\epsilon_{0\partial}}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right)^2F(a) \quad (6.6)$$

we can derive different limiting forms for the function F. In the case that $2\kappa a,\ 2\kappa_s a\gtrsim 1$ we obtain

$$F(a)\simeq\sqrt{\frac{\pi}{2}}\frac{\kappa^2}{\kappa_s^2}\frac{e^{-4a\kappa}}{(2a\kappa)}. \quad (6.7)$$

A different limiting form is obtained in the case of $2\kappa a\gtrsim 1$ but $2\kappa_s a\lesssim 1$, we derive in this case

$$F(a)\simeq\text{const}\frac{e^{-(2a\kappa_s)^2}}{(2a\kappa)^2}. \quad (6.8)$$

In this limiting case the interaction therefore decays more swiftly with separation than in the former case, but eventually again approaches the decay law exhibited by Eq. (6.5). Equations (6.4) and (6.5) are of course linearizations of the basic form (6.1) valid for small values of $\partial^2 f/\partial\varphi^2$. If this quantity is large the interaction free energy saturates and

reverts to the form characteristic for the screened van der Waals interaction between ideally polarizable half-spaces.

VII. MAGNITUDE OF THE CORRELATION TERM

The result of our analysis is that the properties of the surface free energy determine the nature of the interaction free energy in a very complex manner. First of all the mean-field solution depends on the derivative of the surface free energy, viz. Eq. (3.5). The physical meaning of this equation is simple. The surface free energy exhibits a minimum at the point of zero charge, i.e., at a point, where the right-hand side of Eq. (3.5) equals zero. On the contrary, the mean-field solution has a minimum at a constant value (equal to zero) of the mean potential, i.e., at a point of zero potential. The solution of Eq. (3.5) is therefore obtained as an equilibrium between the electrostatic free energy trying to maintain a zero potential and the surface free energy trying to maintain a zero charge. Where exactly this equilibrium is located depends on all the parameters describing the system.

The fluctuation part of the free energy (5.7) is a complex functional of the mean density profile and of the surface response function, being proportional to the second derivative of the surface free energy at the mean value of the surface potential. We could say, by paraphrasing the fluctuation–dissipation theorem, that the fluctuation free energy depends on the magnitude of the surface potential fluctuations around the equilibrium value determined by Eq. (3.5). There arise several possibilities at this point of our analysis.

Let us first of all suppose that we are close to the surface free energy equilibrium state. Thus (since we are close to an equilibrium state) we must have by the general theory of thermodynamic stability[16]:

$$K_f = \frac{\beta e_0^2}{2\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2} > 0 . \tag{7.1}$$

In this case the fluctuation part of the free energy is fairly limited in magnitude as one can convince oneself by examining the general form (6.1). It is always found between the screened van der Waals free energy of two interacting ideally polarizable half-spaces and the small coupling limit (6.4).

There exists, however, a more interesting case.[8] It is obtained if we assume that the solution of the mean-field equations, notably Eq. (3.5), drives the system far away from the surface equilibrium state, viz. the p.z.c. In this case the surface "state" of the system can be driven towards a thermodynamically unstable region of f where the surface susceptibility becomes negative. In the asymptotic limit of large a this would lead to the following form of Eq. (6.1):

$$\frac{\Omega}{S}(a) \simeq \frac{kT}{4\pi}\left(\frac{\beta e_0^2}{2\epsilon\epsilon_0}\frac{\partial^2 f}{\partial(\beta e_0\varphi)^2}\right)^2 \Gamma(\varphi)\frac{e^{-4a\kappa}}{4a\kappa}, \tag{7.2}$$

where the prefactor is

$$\Gamma(\varphi) = \left(\frac{\kappa}{\Delta(\varphi)}\right)^2 \tag{7.3}$$

with

$$\Delta(\varphi) = \sqrt{\frac{\beta e_0^2}{\epsilon\epsilon_0}\frac{\partial^2\rho(a)}{\partial(\beta e_0\varphi)^2}} - \tfrac{1}{2}|K_f| . \tag{7.4}$$

Clearly expression Eq. (7.2) can become very large for a sufficiently high value of $|K_f|$ and would eventually diverge. This divergence is, however, not physical. It merely signifies that additional, higher order, terms would have to be kept while evaluating the fluctuation contribution to the free energy. The interaction free energy would nevertheless, though remaining finite, still be very large.

A word of caution is needed at this point. The change of sign in the surface sesceptibility K_f does not signify that the whole mean-field solution becomes unstable. It is straightforward [compare Appendix B and the last term of Eq. (5.7)] to show that in the asymptotic regime the stability condition on the mean-field solution itself, which is also a necessary condition for the validity of the saddle-point approximation, reduces to $\Delta(\varphi) > 0$. The sign of K_f is therefore not of immediate importance for the global stability of the mean-field solution.

We can state the condition for the emergence of anomalously high $\Gamma(\varphi)$ in a more elaborated form. First of all we note that in the case of uni–uni valent bulk electrolyte we have

$$\frac{\partial^2\rho(a)}{\partial(\beta e_0\varphi)^2} = \rho(a) . \tag{7.5}$$

Now we can use the contact condition for the mean-field solution[4] that connects the value of the surface charge obtained from Eq. (3.6) and the charge density at the surface $\rho(a)$. Therefore we establish a connection between $\rho(a)$, the density at the midpoint ($\simeq$ bulk density) and the first derivative of the surface free energy density. After a little bit of algebra we obtain

$$\Delta(\varphi) \simeq \sqrt{\frac{\beta e_0^2}{\epsilon\epsilon_0}\rho_0 + \frac{1}{2}\left(\frac{\beta e_0}{\epsilon\epsilon_0}\right)^2\left(\frac{\partial f}{\partial\varphi}\right)^2} - \frac{1}{4\epsilon\epsilon_0}\left|\frac{\partial^2 f}{\partial^2\varphi}\right| . \tag{7.6}$$

Some further statements can now be made on the conditions that have to be fulfilled in order that $\Delta(\varphi)$ be close but larger than zero. First of all ρ_0 should be small. If this condition is not fulfilled, clearly, the first term under the root sign in the above equation would dominate Δ making it large. Furthermore, in order that Δ be as small as possible the surface should be close to an extremum and should exhibit a negative curvature at that point. In order to satisfy this requirements it is unavoidable that the mean potential should be displaced from the thermodynamically stable regions of f. Though we do not possess the relevant information on the detailed form of f, we can, nevertheless, extract the behavior of f that satisfies the above requirements. The two most obvious possibilities are drawn in Fig. 2.

VII. DISCUSSION

In this contribution we have achieved a generalization of the standard Poisson–Boltzmann in two directions. We have included a surface contribution to the total free energy of the system and we have simultaneously estimated the contribution of the fluctuations of the local electrostatic potential around its mean field profile to the energy of interaction of two opposed surfaces described by the surface free energy

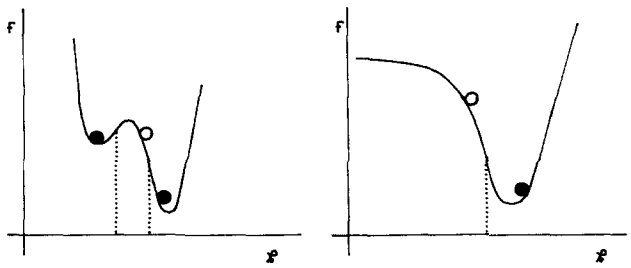

FIG. 2. The two most obvious cases of the surface free energy density as a function of the surface potential (φ_0) are presented that lead to surface unstable states. The unstable regions, where the local curvature (surface response function) is negative, are indicated by open circles. Whenever the mean-field solution drives the surface potential into an unstable region of f that is close enough to the local extremum [*vide* discussion following Eq. (7.6)], the correlation interactions between the two surfaces become anomalously large.

f. On the way we had to make a number of approximations, notably the saddle–point approximation, that allowed us to evaluate the most significant contributions to the partition function. However, even this approximate solution had to be approached through further simplifications as exemplified by the use of the WKB ansatz. Since our discussion will be limited to the cases of small bulk ionic activities and to asymptotic intersurface separation regime, the approximate methods can be supposed to work fairly accurately.

Our formal analysis of the grand canonical partition function (2.5) made it possible to describe the thermodynamics of our model system in terms of a mean-field solution and fluctuations around it. All the thermodynamic functions decouple according to this scheme.

The main result of our paper is the asymptotic formula for the correlation interaction (6.1) between two surfaces, immersed in an electrolyte, described with the surface free energy density (2.15). Clearly this interaction is always attractive, its magnitude, however, depends on the bulk and the surface response functions of the system. In this connection the surface response function is crucial [the bulk one (7.5) is rather trivial]. If the surface part of the system is close to the thermodynamic equilibrium (defined as an extremum of f with positive curvature) the interaction free energy is always below or at most equal to the screened van der Waals interaction free energy of two ideally polarizable surfaces.

Another interesting regime of the correlation attraction is obtained if the mean-field solution drives the two surfaces towards thermodynamically unstable regions of f. This is, in principle, possible since the existence of the double layer at the interface displaces the surfaces away from their thermodynamic stable state in the phase space of f. If the surface mean potential obtained as a solution of Eqs. (3.5) and (3.6) is close to a local maximum of f the correlation attraction can become anomalously large. Closeness to the thermodynamically unstable region of f does not mean that the mean-field solution itself (and, therefore, the saddle-point approximation) becomes unstable. We showed that in general there exists a region characterized by a negative surface susceptibility that, nevertheless, does not affect the global stability of the mean-field solution. The anomalously large intersurface attraction would be a direct consequence of the situation where the surfaces are close to or in their unstable regions.

The interaction of high energy hydrophobic surfaces immersed in aqueous solution has recently received a lot of experimental attention.[7] The conclusions of different studies using surfaces that have been hydrophobized in a different way or the measurement itself done in a different manner are clearly unequivocal: strongly hydrophobic surfaces (with contact angles larger than 90°) in extremely dilute electrolyte solutions show large attractive forces that decay approximately exponentially with intersurface spacing. Furthermore, the nonequilibrium aspect of this anomalous attraction has been repeatedly stressed especially by Claesson[7] who also observed hysteresis phenomena on close approach of the two surfaces.

Due to the anomalously large value of this forces it is tempting to associate them with the type of correlation forces hypothesized on theoretic grounds in this work. There are several arguments for this step:

(i) If the decay length from Eq. (7.2), being equal to half the Debye length, is compared to the measured values we can calculate the effective concentration of the ions that are involved in screening. The number is close to 10^{-5} M and could be due to ionic impurities that are present even in deionized water at this concentration.[17] On the other hand if the ionic concentration is known the computed values are consistent with it.

(ii) From the point of view presented in this paper the magnitude of the anomalous attraction should depend also on the amount of ions (impurities) present in the region between the surfaces (ρ_0), *vide* Eq. (7.3). This is also what one sees experimentally by changing the bulk ionic concentration.[17]

(iii) Our analysis is strictly valid in the asymptotic regime. If we venture to assume its validity at smaller separations one would first have $\kappa \simeq \kappa_s$ in Eqs. (7.2) and (7.3). As we push the surfaces together κ_s goes up, and so should the force. However, pushing the surfaces together makes the coupling between the surfaces larger, making the surface states of smaller energy (if they exist, see Fig. 2) more probable. Eventually, at small enough separations the system would surmount the energy barrier in f and fall into a lower energy state [Fig. 2(a)]. [This lower energy state has a very complicated structure, as revealed in experiments done by Claesson (Ref.7). It is associated with cavitation with bubbles spanning the whole space between the interacting surfaces. Our present formalism, aside from making a possible connection between the existence of lower energy surface states and anomalously large attractive interaction, cannot be presumed to be an adequate description of these states. Cavitation and bubble formation do not enter our analysis at any point.]

We may add that there have recently been several attempts to give a theoretical foundation to the very long-range hydrophobic attraction. The first of them[18] is based on the solvent perturbation idea and leads to water correlation lengths of $\simeq 10$ nm, which we deem to be untenable. The second contribution, due to Attard and Parker,[19] is close to our way of thinking about the problem. They argue that the

anomalously large attraction is due to an anomalously large electrostatic response in the fluid adjacent to the hydrophobic surfaces. This is also the impression created by their formalism that basically leads to an equation of the form of Eq. (6.6). However, as we showed above, large surface dielectric response would merely lead to the screened van der Waals forces between ideally polarizable half-spaces, that are still a couple of orders of magnitude away from what is observed experimentally. We believe that the magnitude of the response is not an issue, the nonequilibrium surface states are. The surfaces are driven away from their thermodynamically stable states due to the presence of charge inhomogeneities close to them. If the coupling is strong enough they can approach a region of f that is thermodynamically unstable. We showed that this can lead to an anomalously high attractive interaction bearing several distinctive features of the very long-range hydrophobic attraction. Finally, a heuristic derivation of the theory proposed here in detail was presented in Ref. 17, where extensive comparison with experimental data on very long range hydrophobic attraction gave ample support to the view that these experimental observatins can be rationalized in terms of anomalous electrostatic correlation forces.

Though a more quantitative theory would clearly have to supplement our formalism in several ways, we think, that the basic physical mechanisms responsible for occurrence of anomalous attraction and described in this work are essentially correct.

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APPENDIX A

We have to investigate the properties of the integral

$$F(a)=\int_{4\kappa_s a}^{\infty}\frac{du}{u}\exp\{-[u^2+16a^2(\kappa^2-\kappa_s^2)]^{1/2}\}. \tag{A.1}$$

After several changes of variables we can derive the following expression that we shall use in deriving the properties of the integral (A1),

$$F(a)=\frac{1}{2}\int_{-\infty}^{+\infty}d\varphi\, e^{-S}, \tag{A2}$$

where S is obtained as

$$S=4\kappa a\sqrt{1+e^{2\varphi}\frac{\kappa^2}{\kappa_s^2}}+\ln(ch\varphi)-\varphi. \tag{A3}$$

Using now the Laplace method[20] we can approximate the integral (A3) by its saddle-point value, viz.

$$F(a)\simeq\frac{1}{2}\int_{-\infty}^{+\infty}d\varphi\exp\left(-S_0-\frac{1}{2}\frac{\partial^2 S}{\partial\varphi^2}\bigg|_0(\varphi-\varphi_0)^2\right)$$
$$=\frac{e^{-S_0}}{2}\sqrt{\frac{2\pi}{\partial^2 S/\partial\varphi^2|_0}}, \tag{A4}$$

where φ_0 is given as the solution of the minimization condition

$$\frac{\partial S}{\partial\varphi}\bigg|_0=4\kappa a\frac{e^{2\varphi}(\kappa_s^2/\kappa^2)}{\sqrt{1+e^{2\varphi}(\kappa_s^2/\kappa^2)}}+th\varphi-1=0. \tag{A5}$$

This equation has several solutions depending on the values of the parameters. In the case $e^{\varphi}\kappa_s/\kappa\gg 1$, or what amounts to the same thing $4a\kappa,\kappa_s\gg 1$, we can obtain an approximate solution of Eq. (A5),

$$e^{2\varphi}\kappa_s^2/\kappa^2\simeq\tfrac{1}{2}\kappa a \tag{A6}$$

that leads to the asymptotic form (6.7). Another limiting case is obtained for $e^{\varphi}\kappa_s/\kappa\ll 1$ but $e^{\varphi}\gg 1$, what amounts to $2a\kappa\gg 1$ but $2a\kappa_s\ll 1$, where the approximate solutions are given as

$$e^{\varphi}\simeq 2\kappa_s a, \tag{A7}$$

$$e^{-\varphi}\kappa/\kappa_s\simeq 2\kappa a, \tag{A8}$$

and leads to the asymptotic form given in Eq. (6.8).

APPENDIX B

We investigate the properties of the correlation function $G_\mu(\mathbf{r},\mathbf{r}')$ near each surface ($z=\pm a$) in the asymptotic regime of large intersurface separations. We obtain form (4.8),

$$G_\mu(a,a;\mathbf{s},\mathbf{s}')=\frac{1}{2\pi}\int_0^{\infty}g_\mu(Q;a,a)\times J_0(Q|\mathbf{s}-\mathbf{s}'|)Q\,dQ, \tag{B1}$$

where $J_0(x)$ is the zero order Bessel function. In the asymptotic limit the correlation function (5.1) assumes the form

$$g_\mu(Q;a,a)=\frac{[1+\alpha(Q,a)]}{2\epsilon\epsilon_0 u(a)}=\frac{1}{2\epsilon\epsilon_0}\left[\frac{2}{u(a)}-\frac{1}{u(a)+K_f/2}\right], \tag{B2}$$

where the definition of K_f is the same as in Eq. (7.1). Taking now into account the definition (5.2a), viz. $u^2(a)=Q^2+\kappa_s^2$, we are led to two integrals of the zero order Bessel function. The first one is elementary, giving

$$\int_0^{\infty}\frac{J_0(Q|\mathbf{s},\mathbf{s}'|)Q\,dQ}{\sqrt{Q^2+\kappa_s^2}}=\sqrt{\frac{2\kappa_s}{\pi|\mathbf{s}-\mathbf{s}'|}}K_{1/2}(\kappa_s|\mathbf{s}-\mathbf{s}'|), \tag{B3}$$

where $K_{1/2}(x)$ is the modified Bessel function of the second kind. The second integral is more tricky. First of all we note the identity

$$\int_0^{\infty}\frac{J_0(Q|\mathbf{s}-\mathbf{s}'|)Q\,dQ}{\sqrt{Q^2+\kappa_s^2}+K_f/2}=\int_0^{\infty}F(\zeta)d\zeta, \tag{B4}$$

where

$$F(\zeta)=\int_0^{\infty}\exp(-\zeta\sqrt{Q^2+\kappa_s^2}-\zeta K_f/2\times J_0(Q|\mathbf{s}-\mathbf{s}'|)Q\,dQ. \tag{B5}$$

The above integral can be computed exactly and leads to

$$F(\zeta) = \sqrt{\frac{2}{\pi}} \frac{\zeta \kappa_s^{3/2}}{(\zeta^2 + u^2)^{3/4}} K_{3/2}(\kappa_s \sqrt{\zeta^2 + u^2}) \times e^{-\zeta K_f/2}, \quad \text{(B6)}$$

where we introduced an abbreviation $u = |\mathbf{s} - \mathbf{s}'|$. We can now limit ourselves to the asymptotic regime $u \Rightarrow \infty$ and after introducing a new variable t, defined by $\zeta^2 + u^2 = u^2 ch^2 t$ we end up with

$$\int_0^\infty F(\zeta) d\zeta \simeq \kappa_s \int_0^\infty dt \exp[-\kappa_s u) cht - (K_f u/2) sht + \ln(th\, t)] . \quad \text{(B7)}$$

First of all let us note that the above integral exists only if the following condition is satisfied:

$$\kappa_s + K_f/2 > 0 . \quad \text{(B8)}$$

Clearly this is the same as $\Delta(\varphi) > 0$ defined in Eq. (7.4). The inequality (B.8) is the asymptotic stability condition on the mean-field solution obtained by the saddle-point approximation. It can also be derived by inspection of the last term in Eq. (5.9).

The integral Eq. (B.7) can again be estimated in asymptotic limit by the Laplace method. We shall not go through all the details that closely follow the development in Appendix A. Let us just write down the final result:

$$\int_0^\infty F(\zeta) d\zeta \simeq \kappa_s e^{-1} \sqrt{2\pi} \exp(-\kappa_s u) (K_f u/2)^{-2} . \quad \text{(B9)}$$

Combining now Eqs. (B3) and (B9) we are led to the following asymptotic form of the correlation function near the two surfaces:

$$G_\mu(a,a;u = |\mathbf{s} - \mathbf{s};|) \simeq \frac{1}{4\pi\epsilon\epsilon_0} \left(2\frac{e^{-\kappa_s u}}{u} - \text{const} \frac{e^{-\kappa_s u}}{(K_f u/2)^2} \right) . \quad \text{(B10)}$$

This is the result that we use in the main text, Eq. (6.3).

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