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Electric double layers near modulated surfaces

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The screened electrostatic potential and free energy of electric double layers near modulated boundaries are computed in terms of the height function h of the surface, as an extension of linearized Gouy-Chapman theory. Two approaches, one perturbative, the other iterative, are explored and compared, both expressing the average electrostatic potential away from the surface as a power series involving n-point correlations of h. When compared order by order in powers of the height function, the two methods are found to be equivalent, but they differ in the degree of differentiability demanded of h for a convergent expansion, the perturbative technique requiring infinite differentiability, and the iterative method needing only twice-differentiable functions. The wider applicability of the iterative method is shown to arise from the summation of certain infinite classes of terms in the perturbative expansion which remove ultraviolet divergences associated with the high-order nondifferentiability of the height function. The electrostatic free energy of interacting double layers is found to depend on height-height correlations both within and between the surfaces, a result that may also be interpreted as expressing the coefficients of capacity and induction of conductors in terms of their surface roughness. For boundaries with a well-defined modulation wavelength, the thermodynamic and electrostatic quantities are computed perturbatively in terms of the ratio of the modulation amplitude to the Debye-Hückel screening length, and the characteristic gradients of the height function. It is suggested that these long-wavelength results may find application in the study of the stability and structure of multilamellar liquid crystals composed of modulated membranes.

I. INTRODUCTION

The mathematical problem of determining the electrostatic potential in an electrolyte near a boundary has traditionally been studied under the simplifying assumption that the boundary has a simple geometrical form.[1] Yet there are many examples of interest in nature of surfaces exhibiting modulations about such simple shapes. Important examples are provided by the "rippled" phases of lipid membranes[2] and by "rough" metallic electrodes in electrochemical systems.[3] In contemplating electric double layers near modulated surfaces, two complementary areas of investigation may be distinguished, dealing, respectively, with the properties associated with individual double layers and with their interactions. How does the electrostatic potential away from the surface depend on the nature of surface corrugations? What features control the dominant decay length of screened Coulomb interactions between opposed double layers? How does the free energy of a double layer depend on the structure of the modulations? How do the forces between double layers depend on the nature of interface distortions?[4] Here we study these issues and others by developing techniques to express the electrostatic potential and free energy of such structures directly in terms of the geometrical properties of the modulation.

While there exists a highly developed microscopic theory of electric double layers with simple geometries,[5] a theory which goes far beyond the "mean-field" level of the classical Gouy-Chapman treatment in recognizing microscopic details such as finite ion size,[6] we suggest that it is of basic interest to investigate first the role of surface modulation even within that simplified approach, particularly in the regime of modulation length scales large compared to the Debye-Hückel screening length. The generalization considered here of Gouy-Chapman theory[1] to modulated geometries is studied within the context of the *linearized* Poisson-Boltzmann equation for the electrostatic potential $\phi(\mathbf{r})$,

$$(\nabla^2-\kappa^2)\phi=0 , \tag{1.1}$$

where $\kappa^{-1}=(\varepsilon k_B T/8\pi c e^2)^{1/2}$ is the Debye-Hückel screening length at temperature T, with c the mean ion concentration, ε the dielectric constant, k_B Boltzmann's constant, and e the charge of the electron. Although the quantitative validity of (1.1) may be rather limited,[1,5] particularly in the low-salt regime in which the interactions are weakly screened,[7] we expect the relationships between long-wavelength features of the modulation and the various electrostatic and thermodynamic properties of double layers to be correct on a qualitative level. We shall see that even the solution of the linearized Poisson-Boltzmann equation with specified boundary conditions on a modulated surface may be rather complex. The goal of understanding the fully nonlinear problem is thus perhaps best reached by way of a concisely formulated linearized theory.

The general statement of the problem may be illustrated in two dimensions with the surface lying on average along the x axis and specified by a height function $h(x)$ [for instance, the lower surface in Fig. (1(a)]. Solve (1.1) subject either to Dirichlet or Neumann boundary conditions (i.e., either the potential or charge on the surface given),

$$\phi(x,h(x))=a(x), \quad \hat{\mathbf{n}}(x)\cdot\nabla\phi(x,h(x))=b(x) \ , \tag{1.2}$$

where $\hat{\mathbf{n}}(x)$ is the unit normal to the surface, and a and b are some prescribed functions of x. We shall assume that the surface is indeed representable by a single-valued height function, that is, that it has no overhangs.

For a periodically modulated interface in an electrolyte, it is readily appreciated that there are two important dimensionless parameters that enter any perturbative treatment which starts from the known properties of the planar interface. Considering the simplest sinusoidal modulation $h(x)=a\cos(qx)$, we see that the amplitude a, the modulation wavelength $\lambda=2\pi/q$, and the Debye-Hückel screening length $\lambda_{\mathrm{DH}}=\kappa^{-1}$ are the only three intrinsic length scales in the problem. From these, two convenient dimensionless combinations are the typical value of the *gradient* g of the height function,

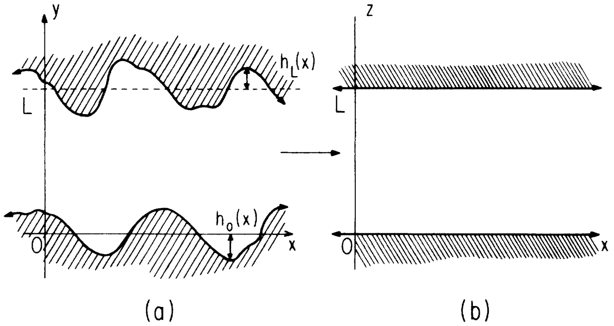
$$g\sim a/\lambda \ , \tag{1.3}$$

and the relative *amplitude* m of the modulation

$$m\sim a/\lambda_{\mathrm{DH}} \ , \tag{1.4}$$

and for small-amplitude long-wavelength modulations, g and m will enter naturally into the analysis here.

Two alternative approaches to the general problem outlined above are explored in Secs. II and III. The first preserves the simplicity of the modified Helmholtz operator in Eq. (1.1) and solves (1.2) by means of a power series in the function $h(x)$, using the eigenfunctions of the original operator in the planar geometry.[8] The second method involves a change of variables which maps the modulated domain onto a planar one [Fig. 1(b)] such that the boundary conditions may be satisfied exactly, but at the expense of changing (1.1) to a more complicated differential equation. We will see below that the first method is essentially *perturbative,* while the second method may be cast in an *iterative* form and is applicable to a wider class of height functions than the former, requiring that h be twice differentiable, rather than infinitely differentiable. For the cases in which $h(x)$ is infinitely differentiable, the two methods are equivalent. Here we focus on single and interacting pairs of electric double layers, and specialize primarily to the case of Dirichlet boundary conditions, with a specified potential at the surface. In Sec. IV we review the computation of the electrostatic free energy of an arrangement of double layers, and carry through the analysis of the previous sections to determine the effects of modulation on the thermodynamics of interacting double layers.



(a) (b)

FIG. 1. Schematic illustration of two modulated boundaries (a) a distance L apart, defined by height functions h_0 and h_L. A change of variables maps the domain in (a) to the simpler one in (b).

The basic result of these analyses is that the electrostatic potential and free energy of electric double layers near modulated boundaries may be expressed in terms of a hierarchy of n-point height-height correlations of the modulation function $h(x)$. When cast in this form, we may treat surfaces specified directly by the modulation function, but also consider situations in which the surface is "random," namely, the undulations arise from some stochastic process whose properties are defined only through these many-point correlations. The discussion in Sec. V summarizes our results and suggests important extensions necessary to treat interacting charged surfaces in a quantitatively realistic way.

II. PERTURBATIVE APPROACH

A. Single surface

As a first approach, we use a perturbative technique[9] which consists essentially of proposing for the boundary condition and the function $\phi(x,y)$ itself power series in a small parameter related to the modulation function. This procedure allows us to satisfy order by order in that small parameter the Helmholtz equation (1.1) and the boundary condition (1.2), through a new set of coupled differential equations. In this section, we illustrate the method with two examples, namely, an isolated double layer and a pair of interacting double layers, and specialize first to the simplest case of a double layer satisfying Dirichlet boundary conditions, in particular that the potential on the boundary be a constant. The extension to more complicated boundary conditions is straightforward; we shall discuss briefly the important differences between the results for surfaces with specified surface charge and those with specified potential. A further simplification we introduce is to view the problem as two dimensional, that is, to assume that the boundary itself is modulated in only one spatial direction, say x, with translational invariance along the orthogonal direction within the mean plane of the surface. We remark that this simplifying feature is present in a number of systems, including the modulated lipid membrane phases. The basic equation to solve is then

$$(\partial_{xx}+\partial_{yy}-\kappa^2)\phi(x,y)=0\ , \tag{2.1}$$

subject to the boundary condition

$$\phi(x,h(x))=\phi_0\ . \tag{2.2}$$

It is convenient to introduce a parameter of smallness ϵ into the boundary condition in order to develop a perturbative expansion of (2.2) as

$$\begin{aligned}\phi(x,\epsilon h(x)) \simeq{}& \phi(x,0)+\epsilon h(x)\phi_y(x,0)\\ &+\frac{1}{2!}[\epsilon h(x)]^2\phi_{yy}(x,0)\\ &+\frac{1}{3!}[\epsilon h(x)]^3\phi_{yyy}(x,0)+\dots\ ,\end{aligned} \tag{2.3}$$

where subscripts indicate differentiation. Now, we assume that the function $\phi(x,y)$ itself has an expansion in ϵ of the form

$$\phi(x,y)\simeq\phi^{(0)}(x,y)+\epsilon\phi^{(1)}(x,y)+\epsilon^2\phi^{(2)}(x,y)+\dots\ , \tag{2.4}$$

where the superscripts denote the order in ϵ. Substituting (2.4) into (2.1), we see that each of the $\phi^{(n)}$ satisfies the modified Helmholtz equation,

$$(\partial_{xx}+\partial_{yy}-\kappa^2)\phi^{(n)}(x,y)=0 \quad \forall n\ , \tag{2.5}$$

and using (2.4) in (2.3), we obtain a hierarchy of boundary conditions on the $\phi^{(n)}(x,0)$, the first three of which are

$$\phi^{(0)}(x,0)=\phi_0\ , \tag{2.6a}$$

$$\phi^{(1)}(x,0)=-h(x)\phi_y^{(0)}(x,0)\ , \tag{2.6b}$$

$$\phi^{(2)}(x,0)=-h(x)\phi_y^{(1)}(x,0)-\frac{1}{2!}h^2(x)\phi_{yy}^{(0)}(x,0)\ . \tag{2.6c}$$

Having recast the problem in a domain with a modulated boundary into a series of simpler problems in planar geometry with specified boundary conditions, it proves convenient to introduce the Fourier transform $\hat\phi(k,y)$,

$$\hat\phi(k,y)=\int_{-\infty}^{\infty}dx\, e^{ikx}\phi(x,y)\ , \tag{2.7}$$

and obtain (2.5) in the form

$$(\partial_{yy}-\kappa_q^2)\hat\phi^{(n)}(q,y)=0\ , \tag{2.8}$$

where

$$\kappa_q^2=\kappa^2+q^2\ . \tag{2.9}$$

The functions $\hat\phi^{(n)}(q,y)$ away from the surface are then determined simply by the values they take at $y=0$,

$$\hat\phi^{(n)}(q,y)=\hat\phi^{(n)}(q,0)e^{-\kappa_q y}\ , \tag{2.10}$$

and the perturbative solution of (2.4) is then equivalently one for $\hat\phi(q,0)$. We may now Fourier transform each of the equations of the hierarchy and solve them order by order to obtain the new hierarchy ($\epsilon=1$)

$$\hat\phi(q,y)=\phi_0\left[\sum_{n=0}^{\infty}\hat I^{(n)}(q)\right]e^{-\kappa_q y}\ , \tag{2.11}$$

where

$$\hat I^{(0)}(q)=2\pi\delta(q)\ , \tag{2.12a}$$

$$\hat I^{(1)}(q)=\kappa\hat h(q)\ , \tag{2.12b}$$

$$\hat I^{(2)}(q)=\frac{1}{2!}\kappa^2\int\frac{dk}{2\pi}\hat h(k)\hat h(q-k)(2r_{q-k}-1)\ , \tag{2.12c}$$

$$\begin{aligned}\hat I^{(3)}(q)=\frac{1}{3!}\kappa^3\int\frac{dk}{2\pi}\int\frac{dk'}{2\pi}&\hat h(k)\hat h(k')\hat h(q-k-k')\\ &\times[1-3r_{q-k-k'}^2\\ &\quad+3r_{q-k}(2r_{q-k-k'}-1)]\ ,\end{aligned} \tag{2.12d}$$

etc., and with

$$r_k\equiv\frac{\kappa_k}{\kappa}=\left[1+\frac{k^2}{\kappa^2}\right]^{1/2}\ . \tag{2.13}$$

For the case of constant charge density σ_0, a completely analogous procedure leads to the result

$$\hat\phi(q,y)=\frac{4\pi\sigma_0}{\varepsilon\kappa}\left[\sum_{n=0}^{\infty}\hat J^{(n)}(q)\right]e^{-\kappa_q y}\ , \tag{2.14}$$

where

$$\hat J^{(0)}(q)=2\pi\delta(q)\ , \tag{2.15a}$$

$$\hat J^{(1)}(q)=\frac{1}{r_q}\kappa\hat h(q)\ , \tag{2.15b}$$

$$\begin{aligned}\hat J^{(2)}(q)=\frac{1}{2!r_q}\kappa^2\int\frac{dk}{2\pi}&\hat h(k)\hat h(q-k)\\ &\times\left[2r_{q-k}-1\right.\\ &\quad\left.+\frac{k(q-k)}{\kappa^2}\left[\frac{2}{r_{q-k}}-1\right]\right]\ .\end{aligned} \tag{2.15c}$$

Significantly, the two expansions differ even at the first level of perturbation. The consequences of these differences will become apparent in a later discussion of the thermodynamics of double layers.

Equations (2.11)–(2.15) are the main formal results of this section. It is now apparent the restrictions that must be placed on the class of height functions for which the boundary perturbation method is convergent: Consider the generalization of the boundary conditions in Eq. (2.6) to nth order, where the boundary value $\phi^{(n)}(x,0)$ will involve, among others, the term

$$\frac{1}{(n-1)!}h^{n-1}(x)\phi^{(1)}_{yy\cdots y}(x,0)\ , \tag{2.16}$$

where there are $n-1$ y derivatives. Using the Fourier representation, we obtain

$$\phi^{(1)}_{yy\cdots y}(x,0)=(-1)^{n-1}\kappa\phi_0\int\frac{dq}{2\pi}e^{-iqx}\kappa_q^{n-1}\hat{h}(q)\ . \tag{2.17}$$

At large momentum, the kernel κ_q^{n-1} varies as q^{n-1}, so the integrals are divergent if the associated $(n-1)$th derivative of the height function does not exist. Thus a *necessary* condition for the applicability of this approach to all orders in perturbation theory is that the surface function be *infinitely differentiable.*

While for some problems we may know a particular surface function $\hat{h}(k)$, and hence can compute each of the functions $\hat{I}^{(n)}$, we may imagine situations in which the surface of interest is defined instead through its n-point correlation functions. This situation would pertain if the surface itself were generated by a stochastic random process. In such cases it is of interest to study the properties of the mean value of the electrostatic potential, averaged over those processes.

We shall consider stochastic processes which are translationally invariant in the lateral coordinate x, and denote averages over the process with an overbar. By a suitable choice of origin and without loss of generality, it may be assumed that the mean height function is zero,

$$\overline{h(x)}=0\ . \tag{2.18}$$

Define the two- and three-point height-height correlation functions

$$\begin{aligned} &C^{(2)}(x-x')\equiv\overline{h(x)h(x')}\ ,\\ &C^{(3)}(x-x'',x'-x'')\equiv\overline{h(x)h(x')h(x'')}\ . \end{aligned} \tag{2.19}$$

The average potential $\Phi(y)$ may then be written as

$$\begin{aligned}\Phi(y)&\equiv\overline{\phi(x,y)}=\phi_0\int\frac{dq}{2\pi}e^{-iqx}\overline{\hat{I}(q)}e^{-\kappa_q y}\\ &=\phi_0\left[1+\frac{1}{2!}\kappa^2\int\frac{dk}{2\pi}\hat{C}^{(2)}(k)\omega^{(2)}(k)+\frac{1}{3!}\kappa^3\int\frac{dk}{2\pi}\int\frac{dk'}{2\pi}\hat{C}^{(3)}(k,k')\omega^{(3)}(k,k')+\cdots\right]e^{-\kappa y}\ ,\end{aligned} \tag{2.20}$$

where the kernels ω are

$$\begin{aligned} &\omega^{(2)}(k)=2r_k-1\\ &\omega^{(3)}(k,k')=1-3r_{k+k'}^2+3r_k(2r_{k+k'}-1)\ . \end{aligned} \tag{2.21}$$

Note that each of the $\omega^{(n)}$ is unity when its momentum arguments vanish, so that were the height function simply to be translated from the original point $y=0$, the series in Eq. (2.20) could be summed exactly to give $\exp(\kappa\bar{h})$, thus simply translating the zero of the usual exponential decay.

Provided the two-point correlation function of the surface modulation decays beyond some correlation length ξ which is larger than the screening length κ^{-1}, we may look at the expansion of the kernel $\omega^{(2)}$ in powers of k/κ, namely, $\omega^{(2)}(k)\simeq1+(k/\kappa)^2-\frac{1}{4}(k/\kappa)^4+\cdots$, and write the average potential in terms of low-order moments of the height-height correlation function, or, in real space,

$$\Phi(y)\simeq\phi_0\left[1+\tfrac{1}{2}\kappa^2\overline{h^2}+\tfrac{1}{2}\overline{(\nabla h)^2}-\frac{1}{8}\frac{1}{\kappa^2}\overline{(\nabla^2 h)^2}+\cdots\right]e^{-\kappa y}\ . \tag{2.22}$$

Thus, in the long-wavelength limit, the mean potential is sensitive to the average *roughness, gradient, curvature,* etc. of the surface modulation.

A particular "deterministic" surface of interest is one which is perfectly periodic, $h(x)=a\cos(px)$, for which $\hat{h}(k)=a\pi[\delta(k-p)+\delta(k+p)]$ and the second-order perturbation result in real space is

$$\begin{aligned}\phi(x,y)\simeq\phi_0\{&[1+\tfrac{1}{2}(a\kappa)^2(r_p-\tfrac{1}{2})]e^{-\kappa y}+(a\kappa)\cos(px)e^{-\kappa_p y}\\ &+\tfrac{1}{2}(a\kappa)^2(r_p-\tfrac{1}{2})\cos(2px)e^{-\kappa_{2p}y}\}\ .\end{aligned} \tag{2.23}$$

As in the case of a stochastic modulation, we may also compute the average potential $\langle\phi(x,y)\rangle$ for this deterministic surface simply by integrating over one period of the modulation. From (2.23) we obtain immediately

$$\langle\phi(x,y)\rangle=\phi_0[1+\tfrac{1}{2}(a\kappa)^2(r_p-\tfrac{1}{2})+O(a^4)]e^{-\kappa y}\ , \tag{2.24}$$

and in the limit of long wavelengths relative to the screening length, the correction to the simple form $\phi_0\exp(-\kappa y)$ involves the factor

$$1+\tfrac{1}{4}(a\kappa)^2+\tfrac{1}{4}(ap)^2-\frac{1}{8}\frac{a^2p^4}{\kappa^2}+\cdots\ , \tag{2.25}$$

expressed, as for the stochastic surface, in terms of the *mean-square amplitude,* the *mean-square gradient,* and *mean-square curvature.*

As a final remark, observe from Eq. (2.23) that the method of perturbation of boundary conditions is effectively an expansion of the potential in the eigenfunctions of the planar geometry, the lateral variation $\cos(npx)$ being associated with the decay $\exp(-\kappa_{np}y)$. There is no "mixing of modes" in the x and y directions.

B. Two surfaces

The generalization of the boundary perturbation technique to two modulated surfaces centered at $y=0$ and L, with height functions $h_0(x)$ and $h_L(x)$ (see Fig. 1) involves the perturbative expansion of the boundary conditions:

$$\begin{aligned}\phi(x,\epsilon_0 h_0(x))=\phi_0 &\simeq \phi(x,0)+\epsilon_0 h_0(x)\phi_y(x,0)\\ &\quad+\frac{1}{2!}[\epsilon_0 h_0(x)]^2\phi_{yy}(x,0)+\cdots ,\\ \phi(x,L+\epsilon_L h_L(x))=\phi_L &\simeq \phi(x,L)+\epsilon_L h_L(x)\phi_y(x,L)\\ &\quad+\frac{1}{2!}[\epsilon_L h_L(x)]^2\phi_{yy}(x,L)\\ &\quad+\cdots ,\end{aligned} \tag{2.26}$$

where we have allowed for different values of the boundary potential on the two surfaces. Similarly, the potential itself is expanded as

$$\begin{aligned}\phi(x,y)&=\phi^{(0,0)}+\epsilon_0\phi^{(1,0)}+\epsilon_L\phi^{(0,1)}+\epsilon_0^2\phi^{(2,0)}\\ &\quad+\epsilon_0\epsilon_L\phi^{(1,1)}+\epsilon_L^2\phi^{(0,2)}+\cdots .\end{aligned} \tag{2.27}$$

The $\phi^{(m,n)}$ then solve the usual modified Helmholtz equation, with the boundary conditions

$$\phi^{(0,0)}(x,0)=\phi_0,\quad \phi^{(0,0)}(x,L)=\phi_L , \tag{2.28a}$$

$$\begin{aligned}&\phi^{(1,0)}(x,0)=-h_0(x)\phi_y^{(0,0)}(x,0) ,\\ &\phi^{(1,0)}(x,L)=0 ,\end{aligned} \tag{2.28b}$$

$$\begin{aligned}&\phi^{(0,1)}(x,L)=-h_L(x)\phi_y^{(0,0)}(x,L),\\ &\phi^{(0,1)}(x,0)=0 ,\end{aligned} \tag{2.28c}$$

$$\begin{aligned}&\phi^{(1,1)}(x,0)=-h_0(x)\phi_y^{(0,1)}(x,0) ,\\ &\phi^{(1,1)}(x,L)=-h_L(x)\phi_y^{(1,0)}(x,L) ,\end{aligned} \tag{2.28d}$$

etc.

Introducing the Fourier transforms of the $\phi^{(m,n)}$, we obtain

$$\hat\phi^{(m,n)}(q,y)=\hat\phi^{(m,n)}(q,0)f_0(q,y)+\hat\phi^{(m,n)}(q,L)f_L(q,y) , \tag{2.29}$$

where $f_0(q,y)=\sinh[\kappa_q(L-y)]/\sinh(\kappa_q L)$ and $f_L(q,y)=\sinh(\kappa_q y)/\sinh(\kappa_q L)$. For the simple case in which $\phi_L=\phi_0$, and setting $\epsilon_0=\epsilon_L=1$, (2.27)–(2.29) yield

$$\begin{aligned}\hat\phi(q,y)=\phi_0\Bigg[&\left[\sum_{m,n}\hat I_0^{(m,n)}(q)\right]f_0(q,y)\\ &+\left[\sum_{m,n}\hat I_L^{(m,n)}(q)\right]f_L(q,y)\Bigg] ,\end{aligned} \tag{2.30}$$

where the nonvanishing functions $\hat I^{(m,n)}$ are

$$\hat I_0^{(0,0)}(q)=\hat I_L^{(0,0)}(q)=2\pi\delta(q) , \tag{2.31a}$$

$$\hat I_0^{(1,0)}(q)=\tanh(\kappa L/2)\kappa\hat h_0(q) , \tag{2.31b}$$

$$\begin{aligned}\hat I_0^{(1,1)}(q)=\tanh(\kappa L/2)\kappa^2\int\frac{dk}{2\pi}&r_{q-k}\operatorname{csch}(\kappa_{q-k}L)\\ &\times\hat h_0(k)\hat h_L(q-k) ,\end{aligned} \tag{2.31c}$$

$$\begin{aligned}\hat I_0^{(2,0)}(q)=\kappa^2\int\frac{dk}{2\pi}&[r_{q-k}\tanh(\kappa L/2)\coth(\kappa_{q-k}L)\\ &-\tfrac{1}{2}]\hat h_0(k)\hat h_0(q-k) .\end{aligned} \tag{2.31d}$$

$\hat I_L^{(0,1)}$ is obtained from $\hat I_0^{(1,0)}$ by the replacement $\hat h_0\to-\hat h_L$ and $\hat I_L^{(1,1)}$ is obtained from $\hat I_0^{(1,1)}$ and $\hat I_L^{(0,2)}$ from $\hat I_0^{(2,0)}$ by interchange of the functions $\hat h_0$ and $\hat h_L$.

Generalizing now to a statistical surface, and defining the inter- and intralayer n-point functions

$$C_{\alpha\beta}^{(2)}(x-x')\equiv\overline{h_\alpha(x)h_\beta(x')}\quad[\alpha,\beta=(0,L)] , \tag{2.32}$$

and again assuming vanishing mean height function and a common value of ϕ_0 on the two surfaces, the average electrostatic potential is given to leading nontrivial order as

$$\begin{aligned}\Phi(y)=\phi_0\Bigg[&1+\tanh(\kappa L/2)\kappa^2\int\frac{dk}{2\pi}r_k\operatorname{csch}(\kappa_k L)[\hat C_{0L}^{(2)}(k)+\hat C_{L0}^{(2)}(k)]\\ &+\kappa^2\int\frac{dk}{2\pi}\left[r_k\frac{\tanh(\kappa L/2)}{\tanh(\kappa_k L)}-\frac{1}{2}\right][\hat C_{00}^{(2)}(k)+\hat C_{LL}^{(2)}(k)]\Bigg]f(y) ,\end{aligned} \tag{2.33}$$

where

$$f(y)=f_0(y)+f_L(y)=\cosh[\kappa(y-L/2)]/\cosh(\kappa L/2) .$$

Thus the potential determined by the two surfaces depends not only on the individual correlations of the two boundaries, but also on their cross correlations. We return to the consequences of this result in Sec. IV.

III. GEOMETRICAL TRANSFORMATION

A. Single surface

Though the boundary perturbation method is straightforward to implement, it has an important limitation, namely, that the height functions be infinitely differentiable. This restriction excludes a whole range of surfaces that may be of interest; in particular certain membrane systems and rough electrodes may not satisfy this requirement. In this section we present an alternative way to address such systems by means of a geometrical transformation that maps the original domain onto a new flat one [see Fig. 1(b)]. This transformation, though involving lengthier calculations, allows us to deal with a much wider range of boundaries, namely, those which need only possess two derivatives, as shown below.

For a single layer, the change of variables of interest is

$$\phi(x,y)\rightarrow\phi(t,z),\quad t=x,\quad z=y-h(x)\ . \tag{3.1}$$

The potential $\phi(t,z)$ then satisfies

$$[\partial_{tt}+(1+h_t^2)\partial_{zz}-2h_t\partial_{tz}-h_{tt}\partial_z-\kappa^2]\phi(t,z)=0\ , \tag{3.2}$$

where subscripts indicate differentiation, the boundary condition being

$$\phi(t,0)=\phi_0\ . \tag{3.3}$$

Now define the differential operators $\mathcal{L}$ and $\mathcal{D}$ as

$$\begin{aligned}&\mathcal{L}=\partial_{tt}+\partial_{zz}-\kappa^2\ ,\\&\mathcal{D}(t,z)=h_t^2\partial_{zz}-2h_t\partial_{tz}-h_{tt}\partial_z\ ,\end{aligned} \tag{3.4}$$

in terms of which the full differential equation (3.2) may be written as $\mathcal{L}\phi=-\mathcal{D}\phi$, or, as an integral equation

$$\begin{aligned}\phi(t,z)&=G_0\circ\mathcal{D}\phi\\&\equiv\int_{-\infty}^{\infty}d\xi\int_0^{\infty}d\eta\, G_0(t,z;\xi,\eta)\mathcal{D}(\xi,\eta)\phi(\xi,\eta)\ ,\end{aligned} \tag{3.5}$$

where G_0 is the Green's function of $\mathcal{L}$; $\mathcal{L}G_0(t,z;\xi,\eta)=-\delta(t-\xi)\delta(z-\eta)$, and vanishing on the boundary $z=0$,

$$\begin{aligned}G_0(t,z;\xi,\eta)=-\frac{1}{2\pi}(K_0\{\kappa[(t-\xi)^2+(z-\eta)^2]^{1/2}\}\\-K_0\{\kappa[(t-\xi)^2+(z+\eta)^2]^{1/2}\})\ .\end{aligned} \tag{3.6}$$

Here, K_0 is the modified Bessel function. It may be verified that the change of variables (3.1) preserves the ellipticity of the differential operator $\mathcal{L}+\mathcal{D}$.[10]

The fundamental principle underlying the present technique is that an iterative solution to (3.5) may be developed by writing (3.5) as

$$\phi^{(n+1)}=G_0\circ\mathcal{D}\phi^{(n)}\ , \tag{3.7}$$

where n denotes the order of iteration, and where the boundary condition on the iterates is

$$\phi^{(n+1)}(t,0)=\phi_0\quad\forall n\ . \tag{3.8}$$

From the form of (3.7), with $\mathcal{D}\phi^{(n)}$ acting as an inhomogeneity, we know that the general solution of $\phi^{(n+1)}$ is of the form

$$\phi^{(n+1)}(t,z)=\phi_h^{(n+1)}(t,z)+\phi_p^{(n+1)}(t,z)\ , \tag{3.9}$$

where ϕ_h is the general solution of the homogeneous equation and ϕ_p is a particular solution of the inhomogeneous equation. Note that such a partitioning of the solution will only be possible within the context of the *linearized* Poisson-Boltzmann equation, since for a nonlinear differential equation the superposition principle no longer holds.

A convenient choice of general and particular solutions leads us to the equivalent system of equations

$$\mathcal{L}\phi_h^{(n+1)}(t,z)=0,\quad \phi_h^{(n+1)}(t,0)=\phi_0\ , \tag{3.10}$$

and

$$\begin{aligned}&\mathcal{L}\phi_p^{(n+1)}(t,z)=-\mathcal{D}\phi^{(n)}(t,z)\ ,\\&\phi_p^{(n+1)}(t,0)=0\ .\end{aligned} \tag{3.11}$$

It is now apparent that the particular solutions $\phi_p^{(n)}$ are not simply the familiar eigenfunctions of the modified Helmholtz operator, for those functions do not vanish on the boundary; the iterative approach is not an eigenfunction expansion. We return to this point below. From (3.10) we immediately obtain

$$\phi_h^{(n)}(t,z)=\phi_0 e^{-\kappa z}\quad\forall n\ , \tag{3.12}$$

and

$$\phi_p^{(n+1)}(t,z)=G_0\circ\mathcal{D}\phi^{(n)}\ . \tag{3.13}$$

For brevity, adopt the notation $\mathbf{s}\equiv(\xi,\eta)$ and $\mathbf{r}\equiv(t,z)$. Then iteration of (3.7) yields a Dyson-like equation,

$$\begin{aligned}\phi(\mathbf{r})=\phi_h(\mathbf{r})+\int d\mathbf{s}\,G_0(\mathbf{r};\mathbf{s})\mathcal{D}(\mathbf{s})\phi_h(\mathbf{s})\\+\int\int d\mathbf{s}\,d\mathbf{s}'G_0(\mathbf{r};\mathbf{s})\mathcal{D}(\mathbf{s})G_0(\mathbf{s};\mathbf{s}')\\\times\mathcal{D}(\mathbf{s}')\phi_h(\mathbf{s}')+\cdots\ .\end{aligned} \tag{3.14}$$

In contrast to the boundary perturbation method, the iterative procedure requires only a twice-differentiable surface function, for reasons that may be seen from the forms of Eqs. (3.13) and (3.14). While the differential operator $\mathcal{D}$ is of second order, at each stage of the iteration there are two spatial integrals, so the order of differentiability required for convergent integrals does not increase with the number of iterations. It is only required that $\mathcal{D}$ itself exist, and this simply means that $d^2h(x)/dx^2$ exist as well.

We may remark parenthetically that the Green's function of the full operator $\mathcal{L}+\mathcal{D}$ also may be written as an integral equation analogous to (3.14). Observing that the full Green's function G satisfies

$$(\mathcal{L}+\mathcal{D})(t,z)G(t,z;\xi,\eta)=-\delta(t-\xi)\delta(z-\eta)\ ,$$

and that $\mathcal{L}^{-1}=-G_0$, we obtain

$$\begin{aligned}G(\mathbf{r};\mathbf{s})=G_0(\mathbf{r};\mathbf{s})+\int d\mathbf{p}\,G_0(\mathbf{r};\mathbf{p})\mathcal{D}(\mathbf{p})G_0(\mathbf{p};\mathbf{s})\\+\int\int d\mathbf{p}\,d\mathbf{p}'G_0(\mathbf{r};\mathbf{p})\mathcal{D}(\mathbf{p})G_0(\mathbf{p};\mathbf{p}')\\\times\mathcal{D}(\mathbf{p}')G_0(\mathbf{p}';\mathbf{s})+\cdots\ .\end{aligned} \tag{3.15}$$

The lack of translational symmetry in the direction normal to the mean surface, as well as, in general, the lack of translational invariance of the modulation function, has the consequence that the integrals in Eq. (3.14) are not convolutions. In addition, $\mathcal{D}$ is a differential operator rather than simply a function. Thus the usual

Fourier or Laplace transform techniques do not render the right-hand side of (3.14) as simply a sum of products of transformed Green's functions and operators. Nevertheless, as with the boundary perturbation method, it is convenient to study the Fourier transform of the electrostatic potential $\hat{\phi}(k,z)$. In order to cast (3.14) into a useful form, note first that the two-dimensional Green's function has the transform

$$\begin{aligned}\hat{G}_0(k,z;\xi,\eta) &\equiv \int_{-\infty}^{\infty} dt\, e^{ikt} G_0(t,z;\xi,\eta) \\ &= \frac{1}{2\kappa_k} e^{ik\xi}\left(e^{-\kappa_k|z-\eta|} - e^{-\kappa_k|z+\eta|}\right) \\ &\equiv e^{ik\xi} H_k(z,\eta) \ , \end{aligned} \tag{3.16}$$

thereby defining the function H_k. It is also necessary to cast into Fourier space the differential operator $\mathcal{D}$, and this is facilitated by use of the identity

$$\mathcal{D}(\xi,\eta) f(\xi,\eta) = \int d\chi\, \mathcal{D}(\xi,\eta)\delta(\chi-\xi) f(\chi,\eta) \ , \tag{3.17}$$

for any function f. The action of $\mathcal{D}$ may then be written as

$$\begin{aligned}\mathcal{D}(\xi,\eta)\delta(\chi-\xi) &= -h_\xi^2 \partial_{\eta\eta}\delta(\chi-\xi) - 2h_\xi \partial_\eta \delta'(\chi-\xi) \\ &\quad + h_{\xi\xi}\partial_\eta \delta(\chi-\xi) \\ &\equiv \mathbf{V}(\xi,\eta)\cdot\mathbf{D}(\chi-\xi) \ , \end{aligned} \tag{3.18}$$

where δ' is the derivative of a delta function, and we have used a convenient vector notation,

$$\begin{aligned}\mathbf{V}(\xi,\eta) &= (h_\xi^2 \partial_{\eta\eta}, -2h_\xi \partial_\eta, -h_{\xi\xi}\partial_\eta) \ , \\ \mathbf{D} &= (\delta(\chi-\xi), \delta'(\chi-\xi), \delta(\chi-\xi)) \ . \end{aligned} \tag{3.19}$$

The iterative expression for the Fourier transform of the electrostatic potential then becomes

$$\begin{aligned}\hat{\phi}(k,z) &= \hat{\phi}_h(k,z) + \int d\eta\, H_k(z,\eta)[\hat{\mathbf{V}}(k,\eta)\cdot\hat{\mathbf{D}}(0)] f_h(\eta) \\ &\quad + \int d\eta \int d\eta' \int \frac{dq}{2\pi} H_k(z,\eta)[\hat{\mathbf{V}}(q,\eta)\cdot\hat{\mathbf{D}}(q-k)] H_{k-q}(\eta,\eta')[\hat{\mathbf{V}}(k-q,\eta')\cdot\hat{\mathbf{D}}(0)] f_h(\eta') + \cdots \ , \end{aligned} \tag{3.20}$$

with

$$\hat{\mathbf{V}}(k,\eta) = \left[\int \frac{dq}{2\pi} q(k-q)\hat{h}(q)\hat{h}(k-q)\partial_{\eta\eta}, 2ik\hat{h}(k)\partial_\eta, -k^2\hat{h}(k)\partial_\eta \right] \ , \tag{3.21}$$

and $\hat{\mathbf{D}}(k) = (1, -ik, 1)$. The explicit form of the homogeneous solution ϕ_h has been used to define the function $f_h(\eta)$ as $\hat{\phi}_h(q,\eta) = 2\pi\delta(q) f_h(\eta)$.

Although appearing rather complex, this form allows the successive orders of iteration to be expressed simply in terms of powers of the transform of the modulation $\hat{h}$, in a way analogous to that in the perturbative approach. All of the integrals over η, η', etc., in (3.20) may be computed knowing only the simple result

$$\int d\eta\, H_k(z,\eta) e^{-\kappa_{k'}\eta} = \frac{e^{-\kappa_{k'}z} - e^{-\kappa_k z}}{k^2 - k'^2} \ . \tag{3.22}$$

The result of two iterations, keeping only terms up to second order in the height function, is

$$\begin{aligned}\hat{\phi}_{hh}^{(2)}(q,z) &= 2\pi\phi_0\delta(q)e^{-\kappa z} - \phi_0\kappa\hat{h}(q)(e^{-\kappa z} - e^{-\kappa_q z}) + \phi_0\kappa^2(e^{-\kappa z} - e^{-\kappa_q z}) \int \frac{dk}{2\pi} \frac{(q-k)}{q} \hat{h}(k)\hat{h}(q-k) \\ &\quad - \phi_0\kappa^2 \int \frac{dk}{2\pi} \hat{h}(k)\hat{h}(q-k) r_k (e^{-\kappa_k z} - e^{-\kappa_q z}) \ . \end{aligned} \tag{3.23}$$

It is readily verified that (3.23) is consistent with the analogous results (2.10)–(2.12) from boundary perturbation theory when due account is taken of the exponential dependence on $h(x)$ implicitly present in the argument z above. This is not surprising, since the solution of an elliptic linear partial differential equation for a given set of boundary conditions is unique, and both the original and transformed operators are elliptic.[10] Note also that, unlike in the perturbation method, the functions generated in the iterative method are not restricted to the eigenfunctions of the bare Helmholtz operator, as can be seen in the particularly simple example of the height function $h(x) = a\cos(px)$, for which (3.23) becomes

$$\begin{aligned}\phi_{hh}^{(2)}(t,z) &\simeq \phi_0 \{ e^{-\kappa z} - (a\kappa)\cos(pt)(e^{-\kappa z} - e^{-\kappa_p z}) + \tfrac{1}{2}(ap)^2 r_p (e^{-\kappa z} - e^{-\kappa_p z}) \\ &\quad - \tfrac{1}{2}(a\kappa)^2 \cos(2pt)[r_p(e^{-\kappa_p z} - e^{-\kappa_{2p} z}) - \tfrac{1}{2}(e^{-\kappa z} - e^{-\kappa_{2p} z})] \} \ . \end{aligned} \tag{3.24}$$

We see clearly the "off-diagonal" nature of the expansion, in the way it mixes functions of the form $\cos(mpx)$ with $\exp(-\kappa_{np}z)$, with $m \neq n$.

It is now possible to see how the iterative method implicitly sums an infinite class of terms in the perturbative approach, and thereby avoids divergences associated with high-order nondifferentiability of the modulation function. Consider, for example, the second term on the right-hand side of Eq. (3.23). Expanding $\exp(-\kappa_q z)$ generates terms of order $\kappa_q^l \hat{h}(q)$, for all positive l, and these are precisely the ones which at large momentum q behave as the lth derivatives of h, as discussed after Eqs. (2.16) and (2.17).

B. Two surfaces

Here we outline the application of the geometrical transformation to the case of two parallel bilayers. To the extent that the approach for two surfaces is analogous to that of one surface, the main difference being the precise form of the transformation used, we refrain from presenting a number of details of the calculation. As we mentioned in Sec. II, the objective of the change of variables is to map the modulated domain into a flat one where the boundary conditions are easily satisfied. Unlike the case of a single layer for which the change of variables is essentially trivial and *linear,* this is not so for two surfaces.

The change of variables is now

$$\phi(x,y) \to \phi(t,z), \quad t = x, \qquad z = L\frac{y-h_0(x)}{L+h_L(x)-h_0(x)} , \tag{3.25}$$

where $h_0(x)$ and $h_L(x)$ are the height functions that modulate the surfaces at $y=0$ and L, respectively. The domain with modulated boundaries has thus been mapped to a strip with flat boundaries, as shown in Fig. 1(b). As can be easily verified, $z=0$ for $y=h_0(x)$ and $z=L$ when $y=L+h_L(x)$. Note that denominator of the transformation function in (3.25), $L+h_L(x)-h_0(x)$, is positive definite, *provided* that the surfaces do not cross or touch each other, which is what we suppose here.

We are faced again with a problem completely analogous to that in Sec. II, since now the full expression for the linearized Poisson-Boltzmann equation after the change of variables is, as before,

$$\mathcal{L}\phi = -\mathcal{T}\phi , \tag{3.26}$$

with the difference that the boundary conditions to be fulfilled are now

$$\phi(t,0) = \phi_0, \quad \phi(t,L) = \phi_L . \tag{3.27}$$

The differential operator $\mathcal{T}(t,z)$ is

$$\begin{aligned}\mathcal{T} = {} & \mu^2(t,z)\partial_{zz} + \frac{1}{L^2}\Gamma(t)[2L+\Gamma(t)](\partial_{tt}-\kappa^2) \\ & -\frac{1}{L}\{2\Gamma(t)\mu(t,z)-[L+\Gamma(t)]\mu'(t,z)\}\partial_z \\ & -\frac{2}{L}[L+\Gamma(t)]\mu(t,z)\partial_{tz} ,\end{aligned} \tag{3.28}$$

where $\Gamma(t) = h_L(t) - h_0(t)$ and the functions $\mu(t,z)$ and $\mu'(t,z)$ are given by

$$\mu(t,z) = zh_{L,t}(t) + (L-z)h_{0,t}(t) , \tag{3.29}$$

and

$$\mu'(t,z) = zh_{L,tt}(t) + (L-z)h_{0,tt}(t) . \tag{3.30}$$

The formal solution to (3.26), analogous to (3.5) for this case, is

$$\phi = \mathcal{G}_0 \circ \mathcal{T}\phi , \tag{3.31}$$

where $\mathcal{G}_0$ is in this case the Green's function for the operator $\mathcal{L} = \partial_{xx} + \partial_{zz} - \kappa^2$ vanishing on the new boundaries $z=0$ and L,

$$\begin{aligned}\mathcal{G}_0(t,z;\xi,\eta) = G_0(t,z;\xi,\eta) - \frac{1}{2\pi}\Bigg[& \sum_{n=1}^{\infty} \{K_0(\kappa[(t-\xi)^2+(z-\eta+2nL)^2]^{1/2}) - K_0(\kappa[(t-\xi)^2+(z+\eta+2nL)^2]^{1/2}) \\ & + K_0(\kappa[(t-\xi)^2-(z-\eta-2nL)^2]^{1/2}) - K_0(\kappa[(t-\xi)^2-(z+\eta-2nL)^2]^{1/2}\})\Bigg] ,\end{aligned} \tag{3.32}$$

and G_0 is the Green's function for the single-layer problem. As can be readily seen, the problem is now stated in the same terms that those for the single layer, then we can proceed to iterate Eq. (3.26) in the same way as in (3.14).

IV. FREE ENERGY OF MODULATED DOUBLE LAYERS

We recall first the computation of the electrostatic and configurational free energy of an electric double layer within the context of the Poisson-Boltzmann equation.[1] The contribution to the total free energy coming from the configurational part is given by the usual ideal-mixing expression obtained for a binary mixture, and the electrostatic contribution is simply proportional to the square of the electric field. Thus the excess *bulk* free energy over that of the homogeneous system is

$$\mathcal{F}=\int dV\left\{k_BT\left[c_+\ln\left[\frac{c_+}{c}\right]+c_-\ln\left[\frac{c_-}{c}\right]-(c_++c_--2c)\right]+\frac{\varepsilon\mathbf{E}^2}{8\pi}\right\} . \tag{4.1}$$

The functions c_+ and c_- that extremize the functional $\mathcal{F}$ and are consistent with the Poisson equation $\nabla^2\phi=-4\pi e(c_+-c_-)/\varepsilon$ are

$$c_+=ce^{-\beta e\phi},\quad c_-=ce^{\beta e\phi} , \tag{4.2}$$

where $\beta=1/k_BT$. The expression for $\mathcal{F}$ in terms of electrostatic properties at the surface is already known,[1] however, it will be useful to review the derivation in more strict mathematical terms. Starting from Eq. (4.1) we replace the values of c_+ and c_- given by (4.2), and use the Poisson-Boltzmann equation

$$\nabla^2\phi=\frac{8\pi ce}{\varepsilon}\sinh(\beta e\phi) \tag{4.3}$$

to obtain

$$\mathcal{F}=\int dV\left[\frac{\epsilon}{4\pi}\phi\nabla^2\phi-2ck_BT[\cosh(\beta e\phi)-1]+\frac{\varepsilon\nabla\phi^2}{8\pi}\right] , \tag{4.4}$$

with $\mathbf{E}=-\nabla\phi$. Calculating the variation of $\mathcal{F}$ and using the Poisson-Boltzmann equation, we obtain

$$\delta\mathcal{F}=\frac{\epsilon}{4\pi}\int dV[\nabla\phi\cdot\nabla(\delta\phi)+\phi\nabla^2(\delta\phi)] . \tag{4.5}$$

Through one of Green's identities this may be rewritten as

$$\delta\mathcal{F}=\frac{\epsilon}{4\pi}\sum_i\int_{\mathcal{S}_i}\phi_i\frac{\partial(\delta\phi)}{\partial\hat{\mathbf{n}}_i}\cdot d\mathcal{S}_i , \tag{4.6}$$

where the sum runs over the surfaces in the system: Note that $\hat{\mathbf{n}}_i$ points *into* the ith surface. The quantity $\partial(\delta\phi)/\partial\hat{\mathbf{n}}$ is of course the variation of the normal component of the differential of the electric field δE_n, which is in turn related directly to the charge density through $E_n=4\pi\sigma/\varepsilon$. Thus, integrating Eq. (4.6), we may express the excess bulk free energy as a surface term,

$$\mathcal{F}[\{\sigma_i\}]=\sum_i\int_{\mathcal{S}_i}\int_0^{\sigma_i}\phi_i d\sigma_i' d\mathcal{S}_i , \tag{4.7}$$

as a functional of the charge densities $\{\sigma_i\}$. The full free energy $\tilde{\mathcal{F}}(\{\phi_i\})$ accounting for surface terms omitted in Eq. (4.1), as a function of the potentials, is obtained as a Legendre transform of $\mathcal{F}$ in (4.7),[1,11]

$$\begin{aligned}\tilde{\mathcal{F}}[\{\phi_i\}]&=\mathcal{F}[\{\sigma_i\}]-\sum_i\phi_i\int_{\mathcal{S}_i}d\mathcal{S}_i\sigma_i\\&=-\sum_i\int_{\mathcal{S}_i}dS_i\int_0^{\phi_i}\sigma_i d\phi_i' .\end{aligned} \tag{4.8}$$

The general results in (4.7) and (4.8), valid for the nonlinear theory, simplify considerably in the Debye-Hückel limit, where, due to the linearity of the governing Helmholtz equation, we know that there exist linear relationships between the induced charge densities and potentials of the conductors in the system. This implies in turn that the total free energy of the system may be written as[11]

$$\tilde{\mathcal{F}}(\{\phi_i\})=-\tfrac{1}{2}\sum_{i,j}\mathcal{C}_{ij}\phi_i\phi_j , \tag{4.9}$$

the diagonal and off-diagonal matrix elements of $\mathcal{C}$ being the coefficients of capacitance and mutual induction, respectively. A computation of the free energy of interacting modulated surfaces is thus equivalently one of their capacitances and mutual inductances.

Turning now to the computation of the free energy of a modulated double layer for the case of fixed potential, we express σ as a function of ϕ,

$$\sigma(x)=-\frac{\varepsilon}{4\pi}\nabla\phi(x,h(x))\cdot\hat{\mathbf{n}}'(x) , \tag{4.10}$$

with $\hat{\mathbf{n}}'$ the unit normal to the modulated surface, pointing *into* the solvent,

$$\hat{\mathbf{n}}'(x)=-\frac{h_x}{(1+h_x^2)^{1/2}}\hat{\mathbf{i}}+\frac{1}{(1+h_x^2)^{1/2}}\hat{\mathbf{j}} . \tag{4.11}$$

Using the expansion of the potential given in (2.11) and (2.12), and expressing the integral over the modulated surface in terms of the coordinate x by introducing the metric,

$$\int d\mathcal{S}=\int dx(1+h_x^2)^{1/2} , \tag{4.12}$$

we obtain the total free energy of a single surface as

$$\begin{aligned}\tilde{\mathcal{F}}(\phi_0)=-\frac{\varepsilon\phi_0^2\kappa}{8\pi}\int dx\Bigg[&1+\kappa\int\frac{dq}{2\pi}e^{-iqx}(r_q-1)\hat{h}(q)\\&+\kappa^2\int\frac{dq}{2\pi}e^{-iqx}\int\frac{dk}{2\pi}e^{-ikx}\left[\tfrac{1}{2}+r_{q+k}r_k-\tfrac{1}{2}r_{q+k}-r_k^2-\frac{qk}{\kappa^2}\right]\hat{h}(q)\hat{h}(k)+\cdots\Bigg] .\end{aligned} \tag{4.13}$$

In the case of fixed charge, the expansion to second order yields

$$\mathcal{F}(\sigma_0)=\frac{2\pi\sigma_0^2}{\varepsilon\kappa}\int dx\left\{1+\kappa\int\frac{dq}{2\pi}e^{-iqx}\left[\frac{1}{r_q}-1\right]\hat{h}(q)\right.$$
$$-\frac{\kappa^2}{2}\int\frac{dq}{2\pi}e^{-iqx}\int\frac{dk}{2\pi}e^{-ikx}\left[\frac{qk}{\kappa^2}\left[1+\frac{1}{r_{q+k}}-\frac{2}{r_q r_{q+k}}\right]+\frac{1}{r_{q+k}}(1-2r_q)+1\right]$$
$$\left.\times\hat{h}(q)\hat{h}(k)+\cdots\right\}. \tag{4.14}$$

As with the electrostatic potential itself, it proves informative to examine the "long-wavelength" behavior of the free energy, and so to expand the kernels of the above integrals. Observe first that at zero momenta each of the kernels vanishes, so that the free energy is invariant under uniform translations of the boundary, as must be the case on physical grounds for an *isolated* double layer. Up to terms second order in the height function, the free energies are

$$\tilde{\mathcal{F}}(\phi_0)\simeq-\frac{\varepsilon\phi_0^2\kappa}{8\pi}\int dx\left\{1+\tfrac{1}{2}[\nabla h(x)]^2-\frac{1}{2\kappa}\nabla^2 h(x)\right.$$
$$\left.-\frac{1}{8\kappa^2}[\nabla^2 h(x)]^2+\cdots\right\}, \tag{4.15}$$

and

$$\mathcal{F}(\sigma_0)\simeq\frac{2\pi\sigma_0^2}{\varepsilon\kappa}\int dx\left\{1+\tfrac{1}{2}[\nabla h(x)]^2+\frac{1}{2\kappa}\nabla^2 h(x)\right.$$
$$\left.+\frac{3}{8\kappa^2}[\nabla^2 h(x)]^2+\cdots\right\}. \tag{4.16}$$

We may recognize the first two terms in each of these expressions as expansions of the arc-length factor [Eq. (4.12)].

If we identify the Laplacian of the height function with the curvature of the surface, then these expressions may be seen as expansions in the ratio of the Debye-Hückel screening length to the local radius of curvature of the surface. In particular, the terms proportional to the square of the Laplacian are equivalent to a modification of the bending modulus k_c of the surface.[12,13] For a weakly modulated surface the bending energy may be written as

$$F_b=\tfrac{1}{2}k_c\int dS(\nabla^2 h)^2\;, \tag{4.17}$$

so the electrostatic contribution to the bending modulus for the two types of boundary conditions are

$$k_c(\phi_0)=\frac{\varepsilon\phi_0^2}{32\pi\kappa},\quad k_c(\sigma_0)=\frac{3\pi\sigma_0^2}{2\varepsilon\kappa^3}\;. \tag{4.18}$$

It is interesting to note the differences between the two ensembles in the particular coefficients of the expansion of the free energy in powers of the curvature. We emphasize that σ_0 and ϕ_0 in the above equations are independent given quantities. For highly symmetric geometries such as planes, cylinders, and spheres, a correspondence between them exists in the sense that uniform charge density and constant potential are compatible. However, this is not the case for an arbitrary surface. Previous studies of curved double layers[7,12] have mainly focused on the case of specified charge density. Within the present two-dimensional calculation, an appropriate comparison is with the expansion of the exact solution for cylindrical geometry, and the agreement is precise. One may easily verify that the same agreement holds for the cylindrical Dirichlet problem.

Once again, we may consider the very simple case in which there is only one layer modulated according to the periodic height function $h(x)=a\cos(px)$ and lying on the plane (x,z) perpendicular to y. Focusing on the case of fixed potential, and integrating (4.13) over one full period, we obtain the average free energy for a single surface,

$$\tilde{\mathcal{F}}\simeq-\frac{\varepsilon\phi_0^2\kappa}{8\pi}\left[1+\frac{(a\kappa)^2}{2}(r_p-1)\right]+O(h_0^3)\;. \tag{4.19}$$

From the general result (4.15) and this particular case, we conclude that the electrostatic self-energy becomes more negative with increasing amplitude of modulation, thus stabilizing rippled structures. Consequently, in the study of phase transitions between different structures we might expect to find systematic changes in the transition temperatures with varying ionic strength.

In the case of two layers, again assuming zero mean for both height functions and equal potentials, the second-order contribution to the free energy is

$$\tilde{\mathcal{F}}=-\frac{\varepsilon\phi_0^2\kappa}{8\pi}\left[\tanh(\kappa L/2)\kappa^2\int\frac{dk}{2\pi}[\hat{h}_0(k)\hat{h}_0(-k)+\hat{h}_L(k)\hat{h}_L(-k)]\left[r_k\frac{\tanh(\kappa L/2)}{\tanh(\kappa_k L)}-1\right]\right.$$
$$\left.+\tanh^2(\kappa L/2)\kappa^2\int\frac{dk}{2\pi}\hat{h}_0(k)\hat{h}_L(-k)\kappa_k\operatorname{csch}(\kappa_k L)\right], \tag{4.20}$$

showing clearly the role of both self- and cross-correlations between modulation functions of the two surfaces.

An interesting example of a pair of interacting boundaries is that of two sinusoidal surfaces with a *relative phase shift* Θ,

$$h_0(x)=a\cos(px),\quad h_L(x)=a\cos(px+\Theta)\ , \tag{4.21}$$

with $\Theta=0$ implying the two modulations are nested together, and $\Theta=\pi/2$ corresponding to layers with peaks in direct opposition. From (4.20), the average free energy per unit area is

$$\tilde{\mathcal{F}}=-\frac{\varepsilon\phi_0^2\kappa}{2}\Bigg\{2\tanh(\kappa L/2)+(\kappa a)^2\Bigg[\tanh(\kappa L/2)\Bigg[r_p\frac{\tanh(\kappa L/2)}{\tanh(\kappa_p L)}-1\Bigg]+\frac{1}{2}\frac{\tanh^2(\kappa L/2)}{\sinh(\kappa_p L)}r_p\cos(\Theta)\Bigg]\Bigg]\Bigg\}\ . \tag{4.22}$$

Asymptotically for $\kappa L \gg 1$ and for large wavelength modulations ($p \ll \kappa$), the difference in free energy $V(L)\equiv\tilde{\mathcal{F}}(L)-\mathcal{F}(\infty)$, i.e., the *interaction* free energy, is

$$V(L)\simeq\varepsilon\phi_0^2\kappa\{1+(\kappa a)^2[2r_p-1-\tfrac{1}{2}r_p\cos(\Theta)]\}e^{-\kappa L}\ . \tag{4.23}$$

At fixed mean intermembrane spacing, this free energy is minimized when the phase shift $\Theta=0$; i.e., when the two modulated surfaces are in registry. The barrier for relative lateral translations of the surfaces, that is, for changes in the phase shift, is proportional to the relative roughness $(\kappa a)^2$, and decreases exponentially in the intermembrane spacing L. This leads us to predict that in scattering experiments that probe the relative translational order of a multilamellar stack of membranes there should be an exponential decrease in order with progressive hydration.

When the two layers are in registry, the asymptotic behavior of the net repulsive potential between them has the form

$$V(L)\simeq\varepsilon\phi_0^2\kappa\{1+[\tfrac{1}{2}(\kappa a)^2+\tfrac{3}{4}(ap)^2]\}e^{-\kappa L}\ . \tag{4.24}$$

Thus modulation of the membrane surface leads to an increase of the repulsive interaction from that of planar layers. This would be expected to have consequences on the stability of charged membranes in multilamellar arrays, in particular, tending to destabilize modulated structures upon decrease of the intermembrane distance.

V. DISCUSSION

The relationship between boundary modulations and the electrostatic and thermodynamic properties of nearby electric double layers have been explored within linearized Gouy-Chapman theory. Systematic expansions of the electrostatic potential and free energy of double layers, either isolated or interacting in pairs, have been developed in terms of powers of the height function describing modulation, or, in the case of random surfaces, in terms of n-point correlation functions of the modulation. In the long-wavelength limit it is possible to express these quantities directly in terms of the surface roughness, gradients, and curvature.

The analysis presented here suggests some important directions for future study. First, note that the two approaches explored here are fundamentally expansions around the properties of the *planar* membrane systems, and as such are not able to address the regime in which the modulation amplitude is comparable to or larger than the Debye-Hückel screening length. It would appear that a fundamentally different approach is necessary to deal with such systems. The present method is not well suited to the study of closed surfaces of arbitrary shape and topology. Elsewhere,[14] we discuss a formalism appropriate to such geometries. Further, in application to real systems it may likely be the case that the linearized Debye-Hückel approximation studied here will be only qualitatively correct, the more appropriate starting point being the full Poisson-Boltzmann equation.[7] As mentioned earlier, the inherent nonlinearity of this equation complicates the use of an iterative scheme, and suggests the boundary perturbation method as more appropriate starting point, but a careful analysis is necessary to determine if a consistent formalism is possible.

Finally, it should be noted that the formalism for solving the Helmholtz equation in a domain with modulated boundaries finds application also in the study of so-called "hydration" forces,[15] which are known to play an important role in the interactions between neutral, dipolar membranes. Recent experimental[16] and theoretical[17] work has suggested that modulation of the membrane surfaces effects the hydration force in important ways, and vice versa.[18] It is thus of interest to extend the present calculation to treat phenomenological models of hydration forces between modulated membranes.[19] Experiments have also shown that the stability[20-22] and structure[16] of neutral membrane phases depend sensitively on the ionic strength of the surrounding aqueous medium and the activity of the water, as modified by membrane interactions. A natural extension of our results would be a fully *self-consistent* treatment of the modulated phases, with an interplay between, on the one hand, the driving forces that produce membrane modulation in isolated bilayers and, on the other hand, the effects of membrane interactions on the stability of the system.

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