Electrostatics of a modulated membrane with specific adsorption

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We present a simple model for the electrostatic properties of a modulated membrane separating two different electrolyte solutions. The model is based on an extension to linear Gouy-Chapman theory. Starting from a Hamiltonian which contains a singular part for the surface contributions, we obtain within the mean-field approach a set of equations which allows us to study the equilibrium between the diffuse and singular parts of the charge carriers. It is shown that the interface modulation leads to a higher potential of zero charge compared to the flat system. The value of this effect depends on the interplay between the height and the characteristic length of the interface modulation and the Debye lengths on both sides, even if the adsorption occurs only on one side of the interface. In the latter case, the side where no adsorption occurs locally exihibits a diffuse charge distribution, which averages to zero, but which makes a contribution to the overall potential drop across the interface. We also calculate the electrostatic contribution to the elastic bending modulus of the membrane and show that specific adsorption of ions can destabilize the flat interface.
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I. INTRODUCTION

An interface consisting of a thin boundary which separates two different electrolytes is of great importance, since it is found in various fields such as colloid chemistry and physics, membrane science, electrochemistry, and biology, for example in cell membranes. It is therefore of fundamental interest to understand the electrostatic properties of such a system. If one considers a planar interface geometry, one can make use of electric double layer theories, which are familiar from theoretical electrochemistry and which go far beyond the mean-field level of the widely used Gouy-Chapman theory, taking into account many microscopic details of the system [1]. However, most of these interfaces are not flat, but roughened due to thermal fluctuations of the interface position. It is therefore useful to investigate the effects introduced by a modulation $h(x)$ of the interface position on the electrostatic properties within a simple model, in order to understand some basic physical aspects. With basic physical aspects we mean the interplay between the two Debye lengths of the system and the two new length scales introduced by the surface modulation, namely the height of the modulation and its characteristic length. In addition, there is another length chracterizing the specific adsorption.

If the size of the thermal fluctuations is mainly determined by the surface tension of the system, the modulation of the interface can usually be described within the theory of capillary waves [2,3]. Under neglect of gravitational effects, the mean square height fluctuation of the interface position in Fourier space is given by

$$\langle |\hat{h}(\mathbf{q})|^2 \rangle = \frac{k_B T}{\gamma q^2}, \tag{1}$$

where $\hat{h}(\mathbf{q})$ is the Fourier transform of the function describing the surface modulation, $\mathbf{q}$ is the wave vector, and γ is the surface tension. If, however, the system has a very low surface tension—which is often the case for biological membranes—the fluctuations are very large and controlled by the elastic bending modulus k_c of the interface. For this type of fluctuations the mean height fluctuation is given by [4]

$$\langle |\hat{h}(\mathbf{q})|^2 \rangle = \frac{k_B T}{k_c q^4}. \tag{2}$$

There is a large amount of literature dealing with the electrostatic contribution to the elastic bending modulus (and also the Gaussian modulus in the case of an interface modulated in two dimensions). Since k_c has the dimensions of energy, the electrostatic contribution to it must have the form $f\epsilon(\Delta V)^2/\kappa$, $f\sigma_0^2/\epsilon\kappa^3$, or a mixed form $f\sigma_0\Delta V/\kappa^2$ for a potential drop ΔV across the interface or a surface charge σ_0, respectively. Here, f is a dimensionless constant which is determined by the boundary condition. The exact value and the sign of f are important, since k_c enters for example exponentially into the persistence length [5], which is a measure for the distance over which the normals of the surface become decorrelated, and it can be measured with great precision (for a review see Ref. [6]). Expansion of the linear or nonlinear Poisson-Boltzmann equation in terms of the curvature for highly symmetric interface geometries [7–9] and a sinusoidal modulation of a planar membrane [10], or expansion of the linearized Poisson-Boltzmann equation in the case of arbitrary geometries [11–14] allows the incorporation of the electrostatic effects into the curvature free energy. A peculiarity of highly symmetric interfaces such as planes, cylinders, and spheres is that a uniform normal component of the dielectric displacement at the interface position corresponds also to a constant potential at the interface. For an arbitrary interface geometry no such correspondence exists. This has an important consequence for the boundary condi-

tion of an elctrically transparent membrane between two electrolyte solutions, since in this case neither the dielectric displacement nor the potential at the interface is uniform. In our opinion, this aspect has been overlooked so far in the above cited literature.

In a recent publication we derived an extension to the linear Gouy-Chapman theory, in order to describe the properties of an modulated liquid-liquid interface between two immiscible electrolyte solutions [15]. The same approach is also valid for the description of an idealized infinitesimal thin and electrically transparent membrane which separates two different electrolyte solutions. In this work, we will extend our recent approach, in order to include specific adsorption of ions at the interface. The adsorption or nonelectrostatic interaction of ionic species with a membrane is for example an important preceding step in the delivery of drugs. We will start from an effective Hamiltonian for the system, which consists of a regular and a singular part. The mean-field approach, together with the appropriate boundary condition for the dielectric displacement at the interface, leads to a set of self-consistent equations for the potential and the ionic distribution, which can be solved analytically within the linear Poisson-Boltzmann approximation. This will be shown in Sec. II for the general case of a modulated interface. In Sec. III we describe in more detail the potential profile and the charge distribution for the case of cation adsorption on one side of the interface, and in Sec. IV we turn to the appropriate electrostatic contribution to the elastic bending modulus for this system. Finally, we give a short summary in Sec. V.

II. THEORETICAL APPROACH

A. Mean-field approximation

Recently a field theoretic approach was used to describe electrified interfaces [16,17]. Starting from an effective Hamiltonian it was shown that within the mean-field approximation the Poisson-Boltzmann equation is the result of the competition between the nonlocal electrostatic interaction and the entropy, which was described in terms of an ideal mixing entropy functional [16]. The effect of adsorption was studied by adding an adsorption potential, which was contracted to a delta function, and a squared gradient term of the total density to the Hamiltonian [17]. In this case the mean-field minimization leads to a set of two coupled second-order differential equations, which can be solved analytically in the case of small potential drops across a flat interface [18]. This Hamiltonian has the advantage that one obtains a regular solution for the ionic densities, but from a mathematical point of view this approach would be very difficult for the application to a modulated interface, since in this case one has to apply a complicated boundary condition for the dielectric displacement at the interface (see Sec. II B).

Here, we will start from a different Hamiltonian, which contains a singular part for the description of the adsorbed layer. This corresponds to the introduction of an inner layer, but since the structure of this inner layer is not known, it is contracted to a singular layer in such a way that it makes no contribution to the potential drop across the interface. All the influence of this singular layer on the regular part of the system is taken into account by the boundary condition. This

approach has the advantage that the resulting equations are fairly simple. It is similar to that of Binder [19] for the description of surface phase transitions. The important difference, however, is that in our case the boundary condition is not contained in the Hamiltonian itself, but is imposed by macroscopic electrostatics.

We can write the Hamiltonian for our system as a functional of the bulk (regular) ionic densities $\rho^{\pm}(\mathbf{r})$ and the surface (singular or adsorbed) ionic densities $\Gamma^{\pm}(\mathbf{R})$

$$\beta H^{\mathrm{tot}}[\rho_i^{\pm}(\mathbf{r}),\Gamma_i^{\pm}(\mathbf{R})] = \sum_{i=1,2} \beta\{H_i^{\mathrm{bulk}}[\rho_i^{+}(\mathbf{r}),\rho_i^{-}(\mathbf{r})]$$
$$+ H_i^{\mathrm{surf}}[\Gamma_i^{+}(\mathbf{R}),\Gamma_i^{-}(\mathbf{R})]\}, \quad (3)$$

where β is $1/k_BT$, $\mathbf{r}=(x,y,z)$ is a point in the bulk of the solution, $\mathbf{R}=(x,y,z=h(x,y))$ is a point on the interface, and i denotes the side of the interface. The modulation of the interface position is described by the function $h(x,y)$, and $i=1$ for $z>h(x,y)$ and $i=2$ for $z<h(x,y)$. Furthermore, we require the following condition for the surface modulation function:

$$\int h(x,y)dxdy = 0. \quad (4)$$

If the spontaneous curvature of the interface is zero, this can always be achieved without loss of generality by a suitable choice of the midplane position. The bulk part of the Hamiltonian consists of the nonlocal Coulombic interaction and the local ideal entropy

$$\beta H_i^{\mathrm{bulk}}[\rho_i^{+}(\mathbf{r}),\rho_i^{-}(\mathbf{r})] = \frac{1}{2}\beta e \int [\rho_i^{+}(\mathbf{r}) - \rho_i^{-}(\mathbf{r})]V(\mathbf{r})d\mathbf{r}$$
$$+ \sum_{j=\pm} \int \left[\rho_i^{j}(\mathbf{r})\left(\ln\frac{\rho_i^{j}(\mathbf{r})}{\rho}-1\right)\right]d\mathbf{r}, \quad (5)$$

where e is the elementary charge and ρ is a reference value for the bulk system, which will be eliminated later. The potential $V(\mathbf{r})$ is the total potential of the system, and we can write it in a general form as

$$V(\mathbf{r}) = \int M(\mathbf{r},\mathbf{r}')q^{\mathrm{tot}}(\mathbf{r}')d\mathbf{r}', \quad (6)$$

with

$$q^{\mathrm{tot}}(\mathbf{r}) = e\sum_{i=1,2} \{\rho_i^{+}(\mathbf{r}) - \rho_i^{-}(\mathbf{r}) + [\Gamma_i^{+}(\mathbf{R}) - \Gamma_i^{-}(\mathbf{R})]$$
$$\times \delta(z-h(x,y))\}. \quad (7)$$

The nonlocal function $M(\mathbf{r},\mathbf{r}')$ describes the Coulombic coupling between two charges at different locations. Due to the difference of the dielectric constants on both sides of the interface $M(\mathbf{r},\mathbf{r}')$ will have a complicated form. Note, however, that the potential as given in Eq. (6) contains no image terms, but these are also absent in the usual Gouy-Chapman theory. Likewise, the singular part of the total Hamiltonian consists of the electrostatic interaction and a surface entropy

term. In addition, it contains also a nonelectrostatic potential u, which represents the effect of the attractive short-range interaction

$$\beta H_i^{\text{surf}}[\Gamma_i^+(\mathbf{R}), \Gamma_i^-(\mathbf{R})]$$

$$= \frac{1}{2} \beta e \int [\Gamma_i^+(\mathbf{R}) - \Gamma_i^-(\mathbf{R})] V(\mathbf{R}) d\mathbf{R}$$

$$+ \sum_{j=\pm} \int \left\{ \beta u_i^j \Gamma_i^j(\mathbf{R}) + \Gamma_i^j(\mathbf{R}) \left(\ln \frac{\Gamma_i^j(\mathbf{R})}{\Gamma_{0,i}^j} - 1 \right) \right\} d\mathbf{R}. \tag{8}$$

Here, $\Gamma_{0,i}^j$ is the corresponding reference value for the surface part of the system, which in general can be different for anions and cations. The nonelectrostatic potential u has to be understood as an effective potential, where solvation effects are taken into account. Furthermore, we assume that this potential depends on the nature of the ion. This may seem a little artificial, since in the bulk of the solution we describe a symmetric electrolyte. In fact, the asymmetry of the electrolyte in the bulk of the solution, which is caused by the different short-range interactions, can be taken into account by introducing a term of the following form into the Hamiltonian [16,17]:

$$\beta H_i^{as} = \int \{ a_i^{++} [\rho_i^+(\mathbf{r})]^2 + a_i^{+-} \rho_i^+(\mathbf{r}) \rho_i^-(\mathbf{r})$$

$$+ a_i^{--} [\rho_i^-(\mathbf{r})]^2 \} d\mathbf{r}. \tag{9}$$

The coefficients a_i would lead to a renormalization of the inverse Debye length [16], but we will ignore such a term here for simplicity.

In the mean-field approximation the profiles can be calculated by the condition that they minimize the Hamiltonian. Due to the separation into a regular and a singular part we get

$$\frac{\delta}{\delta \rho_i^\pm(\mathbf{r})} \left\{ \beta H_i^{\text{bulk}}[\rho_i^+(\mathbf{r}), \rho_i^-(\mathbf{r})] - \mu_i^\pm \int \rho_i^\pm(\mathbf{r}) d\mathbf{r} \right\} = 0, \tag{10}$$

$$\frac{\delta}{\delta \Gamma_i^\pm(\mathbf{R})} \left\{ \beta H_i^{\text{surf}}[\Gamma_i^+(\mathbf{R}), \Gamma_i^-(\mathbf{R})] - \mu_i^\pm \int \Gamma_i^\pm(\mathbf{R}) d\mathbf{R} \right\} = 0, \tag{11}$$

where the Lagrange multiplier $\mu^\pm$ takes into account the constraint of a fixed number of particles. From the minimization of the bulk part of the Hamiltonian [Eq. (10)] one gets, after elimination of $\mu^\pm$ by applying Eq. (10) at a position far from the interface, the usual Boltzmann equations for the ionic densities

$$\rho_i^\pm(\mathbf{r}) = \frac{\rho_{B_i}}{2} \exp\{\mp \beta e[V(\mathbf{r}) - c_i]\}, \tag{12}$$

where ρ_{B_i} is the total bulk density on side i and c_i is a constant, which is usually set to zero on one side. With the

Poisson equation one obtains in the linear potential regime the linear Poisson-Boltzmann equation

$$(\Delta - \kappa_i^2) V(\mathbf{r}) = c_i. \tag{13}$$

For a 1-1 binary electrolyte the inverse Debye length is $\kappa_i = \lambda_{DB}^{-1} = \sqrt{\beta \rho_{B_i} e^2 / \epsilon_i}$, where $\epsilon_i = \epsilon_{solv,i} \epsilon_0$ is the solvent dielectric constant.

The minimization of the surface part [Eq. (11)] leads to the following two equations on each side:

$$\mu_i^\pm = \pm \beta e V(\mathbf{R}) + \beta u_i^\pm + \ln \frac{\Gamma_i^\pm(\mathbf{R})}{\Gamma_{0,i}^\pm}. \tag{14}$$

If we apply Eq. (10) at the position $\mathbf{r} = \mathbf{R}$ we get

$$\mu_i^\pm = \pm \beta e V(\mathbf{R}) + \ln \frac{\rho_i^\pm(\mathbf{R})}{\rho}, \tag{15}$$

and subtract Eq. (15) from Eq. (14) we obtain

$$\beta u_i^\pm + \ln \frac{\Gamma_i^\pm(\mathbf{R})}{L_i^\pm \rho_i^\pm(\mathbf{R})} = 0, \tag{16}$$

where we have introduced the length $L_i^\pm = \Gamma_{0,i}^\pm / \rho$. This length can be interpreted as the thickness of the adsorbed layer, and it is an additional parameter in our model. The last equation can be rearranged into

$$\Gamma_i^\pm(\mathbf{R}) = L_i^\pm \rho_i^\pm(\mathbf{R}) e^{-\beta u_i^\pm}. \tag{17}$$

This equation has the familiar form of the Henry law of adsorption, but in our model it has a different meaning, since $\rho_i^\pm(\mathbf{R})$ itself depends via the boundary condition for the potential on $\Gamma_i^\pm(\mathbf{R})$. In fact, in the linear potential region we obtain a Langmuir-type adsorption isotherm, as will be shown in Sec. III. If we substitute the linear form of Eq. (12) into Eq. (17) we obtain the following relation between the total surface charge density $q_i^{\text{surf}}(\mathbf{R}) = e[\Gamma_i^+(\mathbf{R}) - \Gamma_i^-(\mathbf{R})]$ and the total bulk charge density at the interface $q_i^{\text{bulk}}(\mathbf{R}) = e[\rho_i^+(\mathbf{R}) - \rho_i^-(\mathbf{R})]$:

$$q_i^{\text{surf}}(\mathbf{R}) = \frac{1}{2} \{ e \rho_{B_i} [L_i^+ e^{-\beta u_i^+} - L_i^- e^{-\beta u_i^-}] + q_i^{\text{bulk}}(\mathbf{R})$$

$$\times [L_i^+ e^{-\beta u_i^+} + L_i^- e^{-\beta u_i^-}] \}. \tag{18}$$

The second term of this equation depends via the Poisson equation on the potential, but the first term is independent of it. If $L_i^+ e^{-\beta u_i^+} \neq L_i^- e^{-\beta u_i^-}$, this term gives rise to a potential of zero charge. Note that the surface charge density $q_i^{\text{surf}}(\mathbf{R})$ is not zero for $u_i^\pm = 0$. This is due to fact that we divided our system from the beginning into a singular and a regular part, and the entropy term in the surface Hamiltonian [Eq. (8)] also makes a contribution to the free energy of the adsorbed layer. Only in the limit of $u_i^\pm \rightarrow +\infty$ the surface charge density would be zero, since then the inner layer is destroyed.

B. The boundary condition

In order to calculate the potential profile, we have to solve Eqs. (13) and (18) for a complicated boundary geometry. For a simplification of the following calculation we restrict ourselves to a two-dimensional system, that is, the surface is modulated in only one spatial direction and is translationally invariant along the orthogonal direction in the midplane of the surface. Note that a two-dimensional modulation of the surface can introduce important additional features due to the possible change of the topology of the surface. The investigation of these effects may be the topic of future work.

Far from the interface position the modulation of the membrane has a negligible effect and we can assume a planar equipotential line. Hence, the second-order differential equation [Eq. (13)] has to be solved with the following two boundary conditions:

$$V(x,-\infty)=c_2\equiv\Delta V_{PZC}, \quad V(x,\infty)=c_1\equiv0, \quad (19)$$

where the potential of zero charge (PZC) ΔV_{PZC} is the total potential drop across the interface, caused by the nonelectrostatic adsorption of ions. However, from macroscopic electrostatics it is known that the dielectric displacement $\mathbf{D}_i = \epsilon_i\nabla V(x,y)$ at the electrically transparent boundary between two different dielectric media has to fulfill the following condition [20]:

$$\mathbf{n}(x)[\mathbf{D}_1(x,y=h(x))-\mathbf{D}_2(x,y=h(x))]=\sigma(x), \quad (20)$$

where $\sigma(x)$ is the total surface charge density on the interface. It is given by

$$\sigma(x)=q_1^{surf}(x,y=h(x))+q_2^{surf}(x,y=h(x)). \quad (21)$$

This means that the adsorbed part of the ionic density has an influence on the boundary condition for the potential and hence on the diffuse part of the ionic density, and vice versa. So Eqs. (13) and (18) together with the boundary condition Eq. (20) form a set of self-consistent equations.

The important point to note here is that Eq. (20) is only a *local* condition for the dielectric displacement. In the framework of Gouy-Chapman theory, which describes the electrolyte as point ions in a dielectric continuum, the charges can move freely and respond to the modulation of the interface in such a way that the total free energy of the interphase is minimized. It would be a gross oversimplification, if we assume a constant dielectric displacement at the interface. This means that at the interface we have neither a uniform normal component of the dielectric displacement nor an equipotential line. Since the x dependence of the dielectric displacement is due to the deviation of the interface from a planar geometry, we can write it in the following general form:

$$\mathbf{n}(x)\mathbf{D}_i(x,h(x))=\sigma_i^{bulk}+\int dx'\,\alpha_i^{bulk}(x-x')h(x')$$

$$+\int dx'\int dx''\beta_i^{bulk}(x-x',x'-x'')$$

$$\times h(x')h(x'')+\cdots. \quad (22)$$

This equations describes the dielectric displacement *at the* boundary as a *nonlinear* and *nonlocal* response of the regular surface charge distribution to the perturbation $h(x)$ and it can be interpreted in the following way: In the case of a modulated interface the dielectric displacement at the boundary is not simply given by the local surface charge density σ_i^{bulk}, but it contains additional contributions from all the other points on the surface. In order to see the first nonvanishing influence on quantities which involve an integration over the lateral dimension, we have to go to the second order in the height function, because, due to the condition of Eq. (4), first order terms vanish. Since in principle the nonelectrostatic adsorption potential u does not restrict the distribution of the charge in the lateral direction of the singular layer, the singular surface charge *on* the interface can also respond to the modulation of the interface and we write a similar perturbative expansion for it

$$q_i^{surf}(x,h(x))=\sigma_i^{surf}+\int dx'\,\alpha_i^{surf}(x-x')h(x')$$

$$+\int dx'\int dx''\beta_i^{surf}(x-x',x'-x'')$$

$$\times h(x')h(x'')+\cdots. \quad (23)$$

Equations (22) and (23) are the basic equations in this work, since the behavior of the system is due to the constants σ_i^{bulk}, σ_i^{surf} and the nonlocal response functions α_i^{bulk}, α_i^{surf}, and β_i^{bulk}, β_i^{surf}, which have to be determined self-consistently.

It is convenient to solve Eq. (13) together with the boundary conditions Eqs. (19) and (20) separately for $y<h(x)$ and $y>h(x)$ and require the continuity of the potential at the interface

$$V_1(x,y=h(x))=V_2(x,y=h(x)). \quad (24)$$

With Eqs. (13), (18) and Eqs. (19)–(24) the problem is now completely defined and the response functions can be determined.

C. The formal solution for the potential

In order to solve the linearized Poisson-Boltzmann equation [Eq. (13)] subject to the boundary conditions Eqs. (19) and (20), we assume that $h(x)$ is a small quantity. In this case we can use standard perturbative techniques for solving differential equations with complicated boundaries [21,11]. A detailed description of this approach was given elsewhere [15]. There is also an approach based on the multiple scattering technique [13], which gives a formally exact solution of the linearized Poisson-Boltzmann equation. But since in this work we introduce a boundary condition, which itself is written as a perturbative expansion in $h(x)$ [see Eq. (22)], the standard perturbative technique for the solution of Eq. (13) is more convenient. The result for the potential up to the second order in the height function can be written for each side as

$$\hat{V}_i(q,y)=\sum_n \hat{V}_i^{(n)}(q,0)\exp[(-1)^i\kappa_{i,q}y], \quad (25)$$

with

$$\hat{V}_i^{(0)}(q,0)=\pm\frac{\sigma_i^{\text{bulk}}}{\epsilon_i\kappa_i}2\pi\delta(q)+c_i,\quad\text{with}\quad c_1=0,\quad c_2=\Delta V,$$

(26)

$$\hat{V}_i^{(1)}(q,0)=\frac{1}{\epsilon_i\kappa_{i,q}}[\sigma_i^{\text{bulk}}\kappa_i\pm\hat{\alpha}_i^{\text{bulk}}(q)]\hat{h}(q),\qquad(27)$$

$$\hat{V}_i^{(2)}(q,0)=\pm\frac{1}{\epsilon_i\kappa_{i,q}}\int\frac{dk}{2\pi}\hat{h}(q-k)\hat{h}(k)$$

$$\times\left\{\frac{1}{2}\sigma_i^{\text{bulk}}\kappa_i^2\left[(2r_{i,k}-1)+\frac{(q-k)k}{\kappa_i^2}\left(\frac{2}{r_{i,k}}-1\right)\right]\right.$$

$$\left.\pm\hat{\alpha}_i^{\text{bulk}}(k)\left[\kappa_{i,k}+\frac{(q-k)k}{\kappa_{i,k}}\right]+\hat{\beta}_i^{\text{bulk}}(q,k)\right\},\quad(28)$$

where the upper sign of $\pm$ refers to $i=1$. Here we have introduced the lateral Fourier transform of the potential

$$\hat{V}(q,y)=\int_{-\infty}^{+\infty}dx e^{iqx}V(x,y)\qquad(29)$$

and the modified Debye length

$$\kappa_q=\kappa r_q\quad\text{and}\quad r_q=\sqrt{1+\frac{q^2}{\kappa^2}}.\qquad(30)$$

This expansion can be stopped at the second order term, if the condition $\kappa h(x)\ll1$ holds. Furthermore, the height function $h(x)$ must be infinitely differentiable, since otherwise the series does not converge [11]. Far from the interface the perturbation from the flat geometry is negligible since $\kappa_q\geq\kappa$, and therefore the higher order terms decay faster than the zeroth order. Care has to be taken, if one uses Eq. (25) for the calculation of the potential at $y=h(x)$, since the exponential has to be expanded, in order to be consistent with a solution up to second order in h.

Having the general form of the solution for the potential, we can calculate the constants σ_i^{bulk}, σ_i^{surf} and the response functions α_i^{bulk}, α_i^{surf} and β_i^{bulk}, β_i^{surf} by satisfying the conditions for the dielectric displacement and the potential at the interface position. This is done in the Appendix.

So far we have assumed that the potential of zero charge ΔV_{PZC} is our independent variable, since it enters directly into the boundary condition. However, it has to be determined from the condition that the total interfacial excess charge Q on one side of the interface is zero. The total charge on each side is simply given by the sum of the diffuse and the adsorbed part of the ionic density

$$Q_1=\int dx\int_{h(x)}^{\infty}dy q_1^{\text{bulk}}(x,y)+\int dS q_1^{\text{surf}}(x,h(x)),$$

(31a)

$$Q_2=\int dx\int_{-\infty}^{h(x)}dy q_2^{\text{bulk}}(x,y)+\int dS q_2^{\text{surf}}(x,h(x)),$$

(31b)

where $dS=[1+\frac{1}{2}h_x^2(x)]dx$ is the metric of a weakly modulated surface. The result up to the second order in the height function is

$$Q_1\equiv-Q=-(\sigma_1^{\text{bulk}}-\sigma_1^{\text{surf}})\int dS-h^2\int\frac{dk}{2\pi}[\hat{\beta}_1^{\text{bulk}}(0,k)$$

$$-\hat{\beta}_1^{\text{surf}}(0,k)]\hat{g}(k),\qquad(32a)$$

$$Q_2\equiv Q=(\sigma_2^{\text{bulk}}+\sigma_2^{\text{surf}})\int dS+h^2\int\frac{dk}{2\pi}[\hat{\beta}_2^{\text{bulk}}(0,k)$$

$$+\hat{\beta}_2^{\text{surf}}(0,k)]\hat{g}(k),\qquad(32b)$$

where we have chosen the charge on side 2 to be positive and introduced the two-point height-height correlation function of the interface

$$\hat{g}(k)\equiv\frac{\hat{h}(-k)\hat{h}(k)}{h^2}.\qquad(33)$$

It is important to note that $\hat{\beta}(0,k)$ depends on $\hat{\alpha}(k)$ and σ. Therefore, even if the terms linear in $h(x)$ are averaged out by integration, they have an influence on the second order terms and must be taken into account. On the other hand, if we only take into account the nonlocal linear response of the dielectric displacement at the surface, we obtain the trivial result that $Q=(\sigma_1^{\text{bulk}}-\sigma_1^{\text{surf}})\int dS=(\sigma_2^{\text{bulk}}+\sigma_2^{\text{surf}})\int dS$. This shows that it is crucial to go beyond the linear response of the dielectric displacement.

III. ION ADSORPTION AT ONE SIDE OF THE MEMBRANE

In this section, we will describe the influence of specific adsorption of cations contained in the electrolyte on side 1 of the interface. The adsorption of ions gives rise to a diffuse charge distribution on the same side of the interface, which, due to the electroneutrality of the total system, exactly counterbalances the adsorbed charge. However, the electroneutrality is only a global condition and as we will see, interesting local behavior can appear, when the interface is perturbed from the flat geometry. In order to study the behavior of our model system as a function of the different parameters like Debye lengths and adsorption potential in more detail, we assume that the modulation of the membrane can be described by a simple deterministic function

$$h(x)=h\cos\frac{2\pi}{l_{\text{min}}}x\quad\text{and}\quad\hat{h}(k)=\frac{hA(\delta_{m,1}+\delta_{m,-1})}{2},$$

(34)

where $k=2\pi m/l_{\text{min}}$ and $m=0,\pm1,\pm2,\ldots$. The integral $\int(dk/2\pi)$ can then be replaced by the summation $(1/A)\Sigma_k$, and we can calculate the response functions very easily for a given set of parameters. The values we use for the height and the wavelength of the interface modulation are based on results from a molecular dynamics simulation of the water-1,2 DCE interface [22]. Liquid-liquid interfaces are commonly used as models for biological membranes. Note, however,
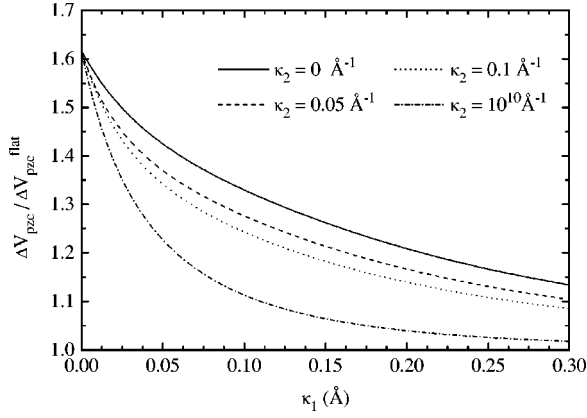
FIG. 1. Ratio of the PZC for a rough and a flat surface as a function of κ_1 with $\epsilon_1 = \epsilon_2 = 80$, $h = 5$ Å, $l_{\min} = 20$ Å, $L_1^+ = 1$ Å, and $u_1^+ = -3$ kT. The geometrical roughness is $A_{\text{real}}/A = 1.62$. If not stated otherwise, these parameters are the same for the following plots.

that our simple model calculations are only intended to illustrate the general behavior of the system.

Since we are in the linear potential regime, the charge Q is just proportional to the potential drop ΔV and contains a potential independent part due to the adsorption

$$Q(\Delta V) = C \Delta V + Q(\Delta V = 0), \qquad (35)$$

where the proportionality constant $C = dQ/d\Delta V$ is just the differential capacity and the PZC can be easily determined from Eq. (32a) or Eq. (32b) by the relation

$$\Delta V_{\text{PZC}} = - \frac{Q(\Delta V = 0)}{C}. \qquad (36)$$

At this value the of the PZC the total charge of the system is zero up to the second order in $h(x)$. Note that both the capacity C and the total charge Q contain the information about the real area of surface and hence the PZC is independent of it. Figure 1 shows the ratio of $\Delta V_{\text{PZC}}/\Delta V_{\text{PZC}}^{\text{flat}}$ as a function of κ_1 for different values of κ_2. This ratio starts from the geometrical roughness A_{real}/A for $\kappa_1 = 0$ and decreases with increasing κ_1 towards a limiting value of 1. At a first glance this seems to be surprising, but the reason is the following: In the limit of zero Debye length ($\kappa_1 \to \infty$) the diffuse part of the charge is located directly at the interface and compensates the adsorbed part of the charge. Apart from the different area the situation is exactly the same as for a flat interface, but since the potential drop across the interface does not depend on the area, the PZC is independent of the geometrical roughness. In contrast, for infinite Debye length ($\kappa_1 \to 0$) the adsorbed charge goes to zero for the flat and the rough surface, but the ratio of it differs just by the geometrical roughness. Since the capacity for infinite Debye length is the same for the flat and the rough interface [15,23], the geometrical roughness is also reflected in the ratio of the PZC. This is a very interesting behavior, since it implies that from measurement of the PZC for various concentrations the geometrical roughness can be determined in the limit of zero concentration, if the adsorption parameters are known.

The above explanation for the behavior of the ratio of the PZC as a function of κ_1 is only a "geometrical" argument. However, in order to explain also the dependence on the concentration of that side where no adsorption occurs, one has to investigate the origin of the additional potential drop for the rough interface in more detail. To this end we need to express the PZC as an expansion in $\varepsilon h(x)$, where ε is a parameter of smallness. Instead of expanding Eq. (36) up to $\varepsilon^2 h^2$, it is more convenient to assume that the total charge $Q = 0$ is the external variable. Then we can formally write the PZC as an expansion in terms of εh

$$\Delta V_{\text{PZC}}(Q=0) = \varepsilon^0 \Delta V_{\text{PZC}}^{(0)} + \varepsilon^2 \Delta V_{\text{PZC}}^{(2)}, \qquad (37)$$

where the term linear in εh is zero due to the condition of Eq. (4). If we insert Eq. (37) into Eqs. (A2), (A6), and (A12), we obtain also an expansion of the response functions, which now are inserted into the expression for the total charge in side 2 [Eq. (32b)]. Collecting terms with the same order of ε gives the expression for each order of the PZC. The zeroth order is just the PZC for the flat surface, and it is given by

$$\beta e \Delta V_{\text{PZC}}^{(0)} = \frac{\kappa_1 \lambda_1}{1 + \kappa_1 \lambda_1} = \beta e \frac{\sigma_1^{\text{surf}}(\Delta V_{\text{PZC}}^{(0)})}{\epsilon_1 \kappa_1}, \qquad (38)$$

with a length characterizing the adsorption

$$\lambda_1 = \frac{1}{2} L_1^+ e^{-\beta u_1^+}. \qquad (39)$$

Note that due to the linearization of the Poisson-Boltzmann equation the expression for $\Delta V_{\text{PZC}}^{(0)}$ is only valid for $\kappa_1 \lambda_1 < 1$, since otherwise the high surface charge leads to nonlinearities in the potential profile. The isotherm in Eq. (38) has the form of a Langmuir isotherm; however, this form is only obtained in the linear Poisson-Boltzmann regime, since in the nonlinear regime the expression for σ_1^{surf} in Eq. (A17) and the resulting isotherm is much more complicated.

As expected, on the level of the mean-field approach, the PZC for a flat interface depends only on the properties of side 1. This is no longer true if the interface is perturbed from a flat geometry. The correction to the PZC due to the interface modulation can be written as

$$\Delta V_{\text{PZC}}^{(2)} = \frac{1}{C_{\text{flat}}} h^2 \int \frac{dk}{2\pi} \hat{g}(k) [\hat{\beta}_1^{\text{surf}}(0,k;\Delta V_{\text{PZC}}^{(0)})$$

$$- \hat{\beta}_1^{\text{bulk}}(0,k;\Delta V_{\text{PZC}}^{(0)})]$$

$$= -\frac{1}{C_{\text{flat}}} h^2 \int \frac{dk}{2\pi} \hat{g}(k) \hat{\beta}_2^{\text{bulk}}(0,k;\Delta V_{\text{PZC}}^{(0)}), \quad (40)$$

where C_{flat} is the total differential capacity of the corresponding flat interface

$$\frac{1}{C_{\text{flat}}} = \frac{d(\Delta V^{(0)})}{dQ} = \left(\frac{1}{\epsilon_1 \kappa_1 (1 + \kappa_1 \lambda_1)} + \frac{1}{\epsilon_2 \kappa_2} \right). \qquad (41)$$

The response functions $\hat{\beta}_1^{\text{bulk}}$, $\hat{\beta}_1^{\text{surf}}$, and $\hat{\beta}_2^{\text{bulk}}$ depend on the properties of both sides [see Eqs. (A12) and (A26)]. So Eq. (40) shows that a perturbation from the planar interface geometry leads to an additional potential drop across the inter-
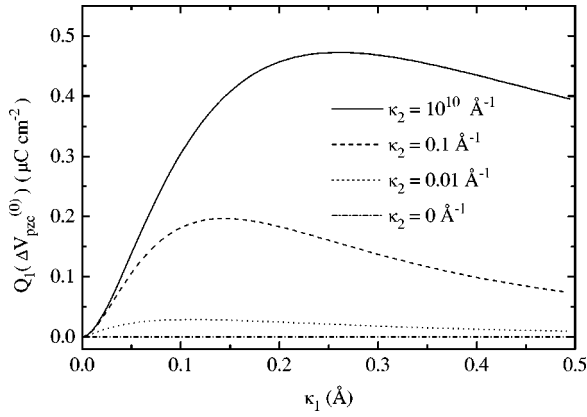
FIG. 2. Effective total charge $Q_1(\Delta V_{PZC}^{(0)})$ induced by the roughening of the membrane as a function of κ_1.

FIG. 3. Induced surface charge and the diffuse counter charge on the same side as a function of κ_2 for $\kappa_1 = 0.1$ Å.

face. This is also true, if one considers perturbations from other highly symmetric geometries (sphere, cylinder). Using again Eq. (32a) one can express the second-order contribution to the PZC also through the total charge on side 1 calculated at the PZC for the flat surface

$$\Delta V_{PZC}^{(2)} = \frac{Q_1(\Delta V_{PZC}^{(0)})}{C_{flat}}. \tag{42}$$

This is an useful equation, since it relates the additional potential drop for the rough surface to an effective charge—effective, because $Q_1(\Delta V_{PZC})$ is zero—and the capacity for the flat system. It can be interpreted as follows: An initially flat interface is kept at $\Delta V_{PZC}^{(0)}$ and hence the adsorbed charge is exactly balanced by the diffuse charge on the same side. Then the interface is roughened, but the potential drop across it is still kept at $\Delta V_{PZC}^{(0)}$. The roughening leads to an increase of the positive surface charge on side 1, since due to the greater surface area more cations are adsorbed. The electroneutrality condition implies that this additional positive surface charge has to be balanced by a negative diffuse charge. However, since the response function β introduces a coupling between the diffuse charges on both sides, the diffuse counter charge can now be located on both sides of the interface. Therefore, the effective charge on side 1, $Q_1(\Delta V_{PZC}^{(0)})$, and hence also the second-order contribution to the PZC is always positive or equals zero in some limiting cases. The effective charge $Q_1(\Delta V_{PZC}^{(0)})$ as a function of κ_1 is shown in Fig. 2. If $\kappa_1 = 0$ the effective charge is of course also zero, since no ions are adsorbed. In the limit of $\kappa_1 \to \infty$ the diffuse charge on side 1 is located at the interface. In this case, it is most favorable for the system to balance the induced adsorbed charge completely on the same side and hence the charge $Q_1(\Delta V_{PZC}^{(0)})$ is zero. The situation is different for a finite Debye length. Now the induced surface charge can be partly balanced by a diffuse charge on the other side, and therefore the induced surface charge is higher the higher the concentration on side 2. This can be seen from Fig. 3. In addition to the increase of the surface charge, the diffuse charge decreases and this results in an overall increase of $Q_1(\Delta V_{PZC}^{(0)})$ with increasing κ_2 (see Fig. 2). However, in the limit of $\kappa_2 \to 0$ it is not possible to balance a net charge on side 1, and therefore $Q_1(\Delta V_{PZC}^{(0)})$ is zero for every

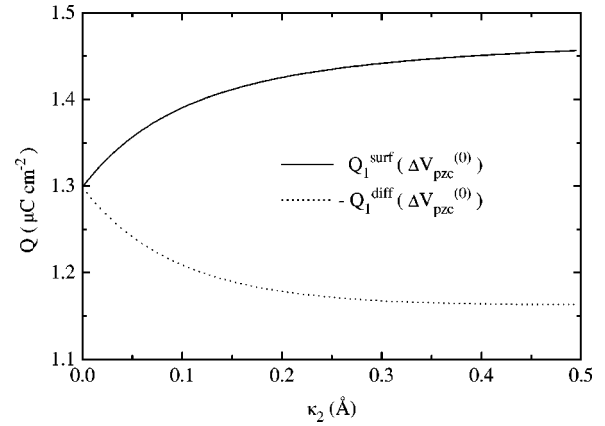value of κ_1, since the additional surface charge is now again completely balanced by a diffuse charge on the same side (see Fig. 3). According to Eq. (42) the additional potential drop is determined by the ratio of the effective charge and the capacity of the flat surface. Since C_{flat} increases much stronger with increasing κ_2 than $Q_1(\Delta V_{PZC}^{(0)})$, the additional potential drop for a rough surface is the smaller the higher κ_2 and the order in Fig. 1 can be explained.

The reason for the coupling between both sides is due to the electrostatic boundary condition Eq. (20). For highly symmetric interface geometries (plane, sphere and cylinder) the normal component of the dielectric displacement on side 2 is zero at each point of the surface, because the normal component of the electric field caused by the surface charge is at each point exactly balanced by the normal component of the field due to the diffuse charge distribution. For an arbitrary interface geometry this symmetry is broken and only the global condition

$$\int \mathbf{n}(x)\mathbf{D}_2(x,y=h(x))dS = Q \equiv 0 \tag{43}$$

holds. Therefore $\mathbf{n}(x)\mathbf{D}_2(x)$ can be nonzero at the interface position. In Fig. 4 we show two examples for the lateral variation of the dielectric displacement and the surface charge. Due to the height-height correlation function, which is a second-order contribution, the dielectric displacement does not follow the surface modulation. In the case of $\kappa_2 \to \infty$ the system corresponds to an ideal metal-solution interface with an equipotential line, and therefore the surface charge is independent of the surface modulation. However, somewhat surprising, also in the case of $\kappa_2 \to 0$ the variation of the surface charge is more than two orders of magnitude smaller than the variation of the dielectric displacement. Hence, the assumption of a modulation-independent surface charge would be a good approximation. Note that this is only true at the PZC. Applying an additional potential drop can lead to variations of the surface charge which are of the same order as the variations of the dielectric displacement. A direct consequence of the nonzero dielectric displacement $\mathbf{n}(x)\mathbf{D}_2(x)$ is that even at the PZC there is a local diffuse charge distribution on that side where no ion adsorption occurs. Furthermore, a part of the PZC falls also off on the side without ion adsorption. This means that the diffuse charge
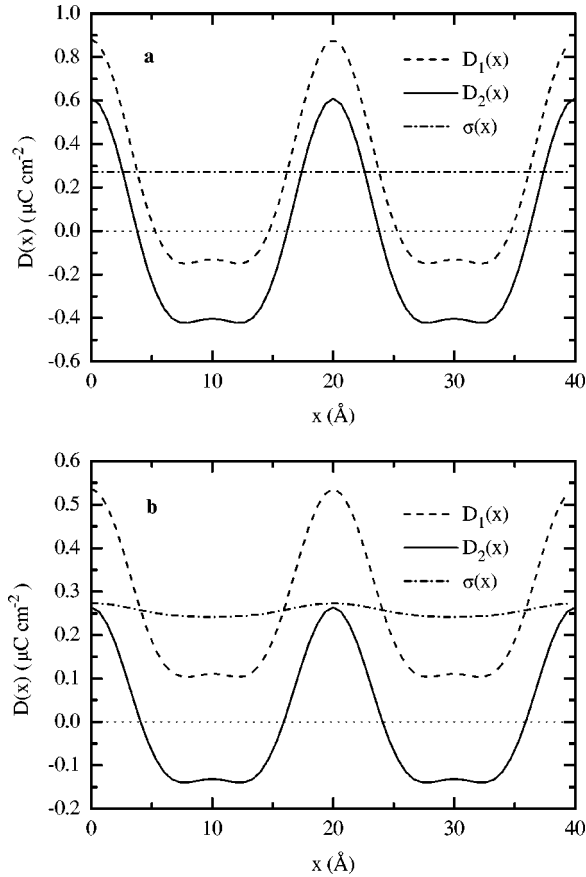
FIG. 4. Dielectric displacement and surface charge at the PZC for a rough interface with cation adsorption on side 1 as a function of the lateral position. The parameters are $\kappa_1 = 0.05$ Å^{-1}, $\kappa_2 \to \infty$ (a) and $\kappa_2 \to 0$ (b).

distribution on side 2 makes no net contribution to the charge, but a net contribution to the potential drop. Therefore, the physical situation differs fundamentally from that for interfaces with highly symmetric geometries.

Locally the potential at the surface can be very different and it depends strongly on the concentration of side 2. This is shown in Fig. 5, where we have plotted the potential distribution at the interface $V(x, h(x))$, which is also the local potential drop across side 1 [see Eq. (25)]. A value above
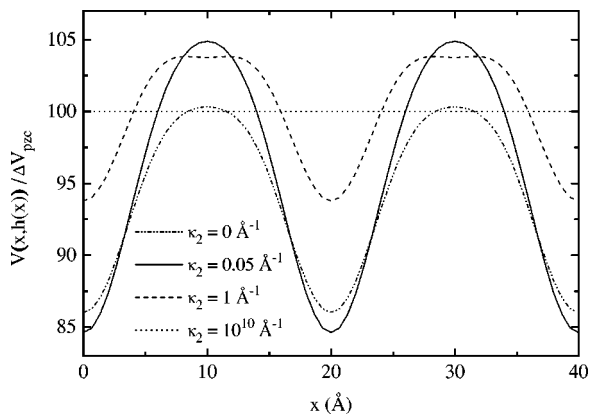

FIG. 5. Lateral distribution of the potential at the interface, which is equal to the potential drop across side 1, normalized by the overall potential drop ΔV_{PZC} with $\kappa_1 = 0.05$ Å^{-1}.

100 means that the local potential drop across side 1 at this lateral position is larger than the overall potential drop. Accordingly, a value below 100 corresponds to a potential drop on side 1 which is lower than the overall potential drop. As can be seen, the behavior changes drastically with a change of κ_2. In the limit of $\kappa_2 \to \infty$ the potential drop occurs of course completely on side 1, similar to an ideal metal-solution interface, but for a finite value of κ_2 the potential oscillates. The amplitude of the variation of the potential drop is the largest for $\kappa_1 = \kappa_2$. This local behavior of the potential drop is of great importance, if an ion or electron transfer reactions across the membrane follows after the ion is adsorbed. From the total potential drop across the interface one cannot conclude, if the necessary overpotential for the transfer is reached at each position, since at some positions the potential has the appropriate value, whereas at other positions it has not. This means that there are preferred positions for the ion or electron transfer. The average potential drop across side 1 is then simple given by the integration over x. For $\kappa_2 \to \infty$ the potential drop occurs completely on side 1, whereas for $\kappa_2 \to 0$ about 94% of it falls off on side 1 and the remaining 6% falls off on side 2. Although the average potential drop on side 2 is not large, the local potential drop can be about 14%.

IV. THE STABILITY OF A MEMBRANE WITH SPECIFIC ADSORBTION

It is of fundamental interest to understand the electrostatic contributions to the elastic bending constants of a membrane, since they determine the stability of the interface. Phenomenologically the total free energy of a two-dimensional modulated surface can be written as [24,4]

$$F_{\text{surf}} = \gamma_0 \int dS + 2k_c \int dS (H - c_0)^2 + \tilde{k} \int dS K, \quad (44)$$

where c_0 is the spontaneous curvature and $\tilde{k}$ the Gaussian bending modulus. The mean curvature H and the Gaussian curvature K are given by [4]

$$H = \text{div}\left(\frac{\nabla h(x,y)}{2\sqrt{1 + [\nabla h(x,y)]^2}} \right), \quad (45)$$

$$K = \frac{h_{xx}h_{yy} - h_{xy}^2}{\{1 + [\nabla \mathbf{h}(\mathbf{x},\mathbf{y})]^2\}^2}, \quad (46)$$

and the metric dS is

$$dS = dx \, dy \sqrt{1 + [\nabla h(x,y)]^2}. \quad (47)$$

As before, we confine ourselves here to a weakly one-dimensional modulation of an interface with zero spontaneous curvature. In this case the curvature free energy simplifies to

$$F_{\text{surf}} = \gamma_0 \int dx \left(1 + \frac{1}{2} h_x^2(x) \right) + \frac{1}{2} k_c \int dx \, h_{xx}^2(x). \quad (48)$$

The easiest way to calculate the electrostatic free energy of our system is to start with the Lippmann equation

$$\left(\frac{\partial \gamma}{\partial (\Delta V)}\right)_{\mu_1, \mu_2} = -\frac{Q}{A_{\text{real}}}. \tag{49}$$

Integration on both sides leads to the expression

$$A_{\text{real}}(\gamma - \gamma_0) = \Delta F = -\int_0^{\Delta V} Q(\Delta V') d(\Delta V'). \tag{50}$$

Here, γ_0 is the surface tension in the absence of a potential drop, and ΔF is the change in free energy due to the formation of the diffuse double layers. The interfacial excess charge Q can be expressed through Eqs. (32a) or (32b). This is a closed expression for the electrostatic free energy of the modulated interface in terms of the height-height correlation function, which is valid for every value of the Debye lengths. However, our aim here is to compare it only to the curvature free energy of Eq. (48), where the bending modulus is independent of the wavelength.

If the height-height correlation function has a smallest correlation length l_{min} and the condition $\kappa_i l_{\text{min}} \gg 1$ holds, we can expand the terms of the response functions which contain the quantity $r_{i,k}$ up to $(k/\kappa_i)^4$ and write the free energy [Eq. (50)] in the case of equal dielectric constants as

$$F = (\gamma_0 + \gamma_{\text{corr}}) \int dx \left(1 + \frac{1}{2} h_x^2(x)\right)$$
$$+ \frac{1}{2}(k^{\text{el}} + k_1^{\text{ad}} + k_2^{\text{ad}} + k_3^{\text{ad}}) \int dx h_{xx}^2(x), \tag{51}$$

where the contribution to the surface tension is

$$\gamma_{\text{corr}} = -\frac{1}{2}\left[\epsilon\left(\frac{\kappa_1 \kappa_2}{\kappa_1 + \kappa_2}\right)(\Delta V)^2 + \Theta_1^{\text{surf}}(\Delta V)\right]. \tag{52}$$

The contributions to the elastic bending modulus are given by

$$k^{\text{el}} = k_c(\Delta V) = \frac{1}{8}\epsilon(\Delta V)^2 \left[3\left(\frac{\kappa_1 \kappa_2}{\kappa_1 + \kappa_2}\right)^2 \left(\frac{1}{\kappa_1^3} + \frac{1}{\kappa_2^3}\right)\right.$$
$$\left. -2\left(\frac{\kappa_1 \kappa_2}{\kappa_1 + \kappa_2}\right)^3 \left(\frac{1}{\kappa_1^2} - \frac{1}{\kappa_2^2}\right)^2\right], \tag{53}$$

$$k_1^{\text{ad}} = \frac{1}{4}\frac{\Theta_1^{\text{surf}}(\Delta V)}{(\kappa_1 + \kappa_2)^2}\left(\frac{\kappa_2^2 - \kappa_1^2}{\kappa_1 \kappa_2}\right), \tag{54}$$

$$k_2^{\text{ad}} = -\frac{1}{4}\left(\frac{\Theta_1^{\text{bulk}}(\Delta V)}{\kappa_1^2} - \frac{\Theta_2^{\text{bulk}}(\Delta V)}{\kappa_2^2}\right)\frac{\kappa_1 \kappa_2}{(\kappa_1 + \kappa_2)^2}\frac{\kappa_1 \lambda_1}{M}, \tag{55}$$

$$k_3^{\text{ad}} = -\frac{1}{2}\left(\frac{\Theta_1^{\text{bulk}}(\Delta V)}{\kappa_1^2} + \frac{\Theta_2^{\text{bulk}}(\Delta V)}{\kappa_2^2}\right.$$
$$\left. + \frac{\Theta_1^{\text{bulk}}(\Delta V) + \Theta_2^{\text{bulk}}(\Delta V)}{\kappa_1 \kappa_2}\right)\frac{\kappa_1 \kappa_2}{(\kappa_1 + \kappa_2)^2}\frac{M-1}{M}, \tag{56}$$

where M is defined in the Appendix and

$$\Theta(\Delta V) = \int_0^{\Delta V} \sigma(\Delta V') d(\Delta V'). \tag{57}$$

The pure electrostatic contribution k^{el} to the bending modulus is always positive. This means that a diffuse layer which is not influenced by a surface charge (for example, if one applies an external potential drop across the interface) leads always to a stabilization of the membrane. The precise value of k^{el} depends on the combination of the Debye lengths given in the parentheses of Eq. (53), which can vary between 1.5 for $\kappa_1 = \kappa_2$ or 1 for $\kappa_1 \gg \kappa_2$ or $\kappa_1 \ll \kappa_2$.

In contrast to the pure electrostatic contribution k^{el}, the contribution arising from the adsorbed charge can also be negative. This is an important result, since it means that due to the adsorption the membrane can be destabilized. Note that in our model this stems only from the electrostatic contributions of the adsorbate and not from the nonelectrostatic effects of the ions themselves. The contribution k_1^{ad} is due to the response of the dielectric displacement to the modulation of the interface in the presence of a modulation-independent surface charge. If the inverse Debye length on the side where no adsorption occurs is higher than on the side with adsorbing ions, this contribution is positive. It vanishes for equal Debye lengths and becomes negative for $\kappa_1 > \kappa_2$. This shows that the usual assumption of equal Debye lengths on both sides of the membrane describes only a very special situation, which is rarely observed in a real system. If the surface charge itself can also respond to the perturbation from the flat interface geometry, one obtains two additional contributions to the bending modulus. The direct second-order response of the surface charge leads to k_2^{ad}, and k_3^{ad} is due to the response of the dielectric displacement in the presence of a modulation-dependant surface charge.

The bending modulus at the PZC of the interface is obtained, if one calculates it at $\Delta V = \Delta V_{\text{PZC}}^{(0)}$, since the terms proportional to the bending modulus give already a second-order contribution to the free energy. The pure electrostatic contribution is shown in Fig. 6(a) for different values of the adsorption potential u_1^+. This contribution is the higher the higher κ_1 and the more attractive the adsorption, because both parameters increase the potential drop and hence the diffuse charge. The total contribution from k^{ad} is shown in Fig. 6(b). This contribution becomes negative in the region $\kappa_1 \approx \kappa_2$. The precise intersection value with $y = 0$ depends also on u_1^+. The different contributions to k^{ad} are shown in Fig. 7. The dominating part is k_1^{ad}, the contributions k_2^{ad} and k_3^{ad} are much smaller, apart from the range where $\kappa_1 \approx \kappa_2$. This shows again, as expected from Fig. 4, that the main effect is the response of the dielectric displacement in the presence of a surface charge and not the response of the surface charge itself. Therefore a modulation independent surface charge would be a good approximation. Figure 8 shows the ratio of the total contribution to bending modulus and the pure electrostatic contribution as a function of κ_1. For very low concentrations of the adsorbing ions the bending modulus is positive and can be even greater than the pure electrostatic contribution, but for higher concentrations it is lower than the pure electrostatic contribution and becomes
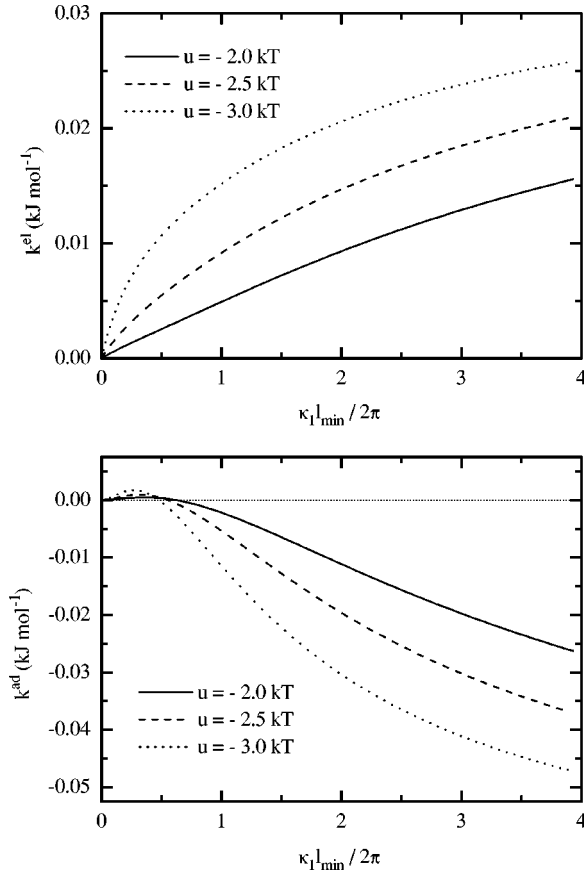
FIG. 6. (a) Pure electrostatic contribution to the bending modulus k^{el}, (b) contribution of the adsorbed charge to the bending modulus. The parameters for this and the following plots are $\kappa_2 = 0.1$ Å^{-1} and $l = 50$ Å.

negative for high concentrations. This means that a membrane that specifically adsorbs one kind of ions is destabilized due to the electrostatic contribution of the adsorbed charge to the bending modulus, if the bulk concentration of the adsorbed ion exceeds a certain value. With increasing strength of the adsorption potential u_1^+ the destabilization is shifted to lower concentrations. The expression for the curvature free energy [Eq. (51)] is only valid for $\kappa_i l_{min}/2\pi > 1$, but for large l_{min} and large κ_2 the region where the bending modulus is greater than the pure electrostatic contribution k^{el}

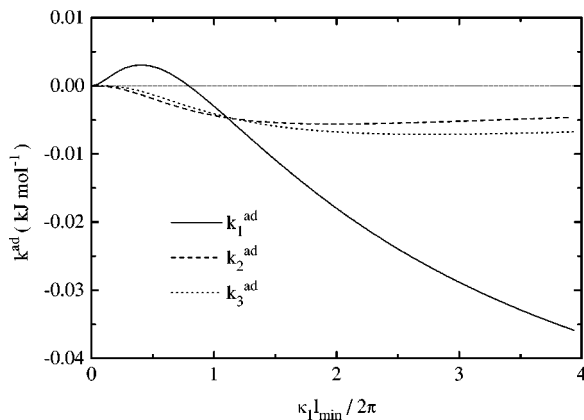FIG. 7. Different contributions to k^{ad}.
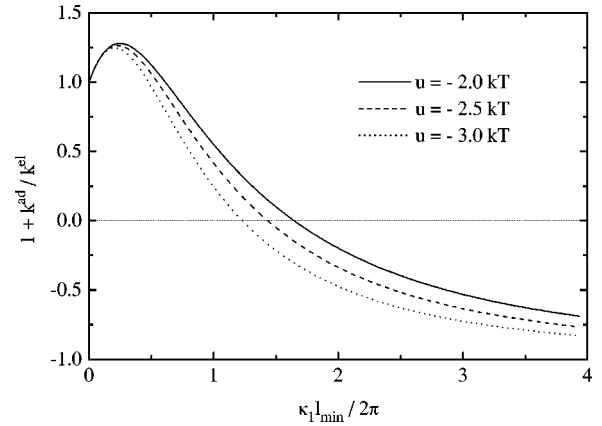

FIG. 8. Ratio of the total electrostatic contribution to the bending modulus $k^{el} + k^{ad}$ and the pure electrostatic contribution k^{el}.

can be reached. Note that due to the coupling between both sides the bending modulus is not a universal function of $\kappa_1 l_{min}$.

Finally, we consider the special case of a modulation-independent surface charge and $\kappa_1 = \kappa_2 = \kappa$. In this case the only contribution to the bending modulus is k^{el}, which we can write as

$$k^{el} = \frac{3}{16} \frac{(\sigma_1^{surf})^2}{\epsilon \kappa^3}. \qquad (58)$$

This result is three times greater than that obtained in Refs. [12–14] for a transparent membrane with an arbitrary surface. The value for k_{el} found in Refs. [12–14] is in accordance with the bending modulus for highly symmetric interface geometries [7–9]. The difference to our result is due to the nonlocal response of the dielectric displacement to a perturbation from a flat surface, which has not been taken into account in Refs. [12–14]. However, the response of the dielectric displacement is crucial, whenever the interface geometry deviates from a highly symmetric one (plane, sphere, or cylinder), since then neither the normal component of the dielectric displacement nor the potential at the interface position can be fixed. In contrast, it is interesting to note that our value is the same as found in Ref. [12] in the case of an electrically insulating (opaque) membrane.

V. CONCLUSION

In this work, we studied the electrostatic properties of a modulated membrane, which adsorbs one sort of ions on one side of the interface. The investigation was based on a model Hamiltonian, which consists of a bulk part and a singular part describing the adsorbed layer. Within the mean-field theory the minimization of the bulk part leads to the usual Boltzmann equations for the ionic densities, whereas the minimization of the singular part leads to an adsorption isotherm. Using the Poisson equation and the linearized Boltzmann equation we derived a solution for the two-dimensional charge profiles, which allows us to study the equilibrium between the diffuse and the adsorbed charge.

The result of this calculation will strongly depend on the applied boundary condition. We investigated the case of an electrically transparent membrane. In this case both sides of

the interface are coupled and the dielectric displacement at the interface position can respond to the perturbation from a flat geometry. This was accounted for by writing it as a non-local and nonlinear response to the interface modulation function.

We have shown that the interface modulation leads to a higher potential of zero charge compared to the flat interface. In the limit of zero concentration on that side where the ions are adsorbed, the ratio of the potential of zero charge for the rough and the flat surface is just given by the geometrical roughness, whereas in the limit of infinite concentration the potential of zero charge is the same as for the flat surface. However, for finite concentrations it depends on the interplay of the Debye lengths of both sides of the membrane, since the second-order response function of the dielectric displacement introduces a coupling between the two diffuse layers. The origin of this coupling lies in the boundary condition [Eq. (20)]. Due to the perturbation from a highly symmetric interface geometry the normal component of the dielectric displacement on that side where no adsorption occurs has not to be zero at each point of the interface. This leads to a complicated local diffuse charge distribution on that side, which averages to zero, but which makes a contribution to the overall potential drop across the interface. Although globally the main part of the potential drop falls off on that side, where the adsorption occurs, the local variation can be quite large, and at some position the potential drop across this side can be even higher than the overall potential drop. This is important for ion and electron transfer reactions across the interface, which follow after the ion has adsorbed, since only at some positions the potential conditions for a transfer will be matched.

For the stability of membranes it is of crucial importance to know the electrostatic contribution to the elastic bending modulus of the membrane. We calculated the appropriate contribution and have shown that the value strongly depends on the ionic concentrations on both sides of the interface. If the Debye lengths are equal for both sides, the electrostatic contribution to the bending modulus is always positive, independent of the amount of adsorbed charge. However, if the Debye length of that side where the adsorption occurs is larger than on the side without adsorption, the electrostatic contribution can become negative and thus leads to a destabilization of the flat interface. Our results differ from previous ones [12–14], since we took into account the response of the dielectric displacement to the perturbation from a flat geometry. Furthermore, we treated the case of different Debye lengths on both sides of the membrane and showed that the condition of equal Debye lengths on both sides of the interface is a very special situation, which is hardly met in a real system.

A simple model for membranes is an interface between two immiscible electrolyte solutions. If we calculate the capacity for such systems within our theory [15], the agreement with experimental results [25,26] is very good. However, we are not aware of systematic measurements of the potential of zero charge, which allow a comparison with the findings of this work. A detailed discussion of the influence of specific adsorption at liquid-liquid interfaces will be given elsewhere [23].

The major drawback of our model is the limitation introduced by the linearization of the Poisson-Boltzmann equation. This limits our approach to a small potential of zero charge and hence to a parameter range, where $\kappa_1 \lambda_1$ is not much greater than 1 [see Eq. (38)], since otherwise the adsorption leads to nonlinearities in the potential profile near the interface. Due to this linearization also the electrostatic contribution to the bending modulus is quite small compared to experimental values of the total bending modulus [6]. In future work, it will therefore be necessary to extend this model to the nonlinear Poisson-Boltzmann regime.

APPENDIX: THE RESPONSE FUNCTIONS

We can calculate the constants σ_i^{bulk}, σ_i^{surf} and the response functions α_i^{bulk}, α_i^{surf} and β_i^{bulk}, β_i^{surf} by satisfying the conditions for the dielectric displacement and the potential at the interface. From Eqs. (20) and (24) we get after some tedious algebra for each order of the perturbative expansion a set of two equations

for zeroth-order terms

$$\begin{pmatrix} 1 & -1 \\ 1/\epsilon_1\kappa_1 & 1/\epsilon_2\kappa_2 \end{pmatrix} \begin{pmatrix} \sigma_1^{\text{bulk}} \\ \sigma_2^{\text{bulk}} \end{pmatrix} = \begin{pmatrix} \sigma^{\text{surf}} \\ \Delta V \end{pmatrix}, \qquad (A1)$$

and the solution

$$\sigma_1^{\text{bulk}} = C_{GC}\left(\Delta V + \frac{\sum_i \sigma_i^{\text{surf}}}{\epsilon_2\kappa_2} \right), \qquad (A2a)$$

$$\sigma_2^{\text{bulk}} = C_{GC}\left(\Delta V - \frac{\sum_i \sigma_i^{\text{surf}}}{\epsilon_1\kappa_1} \right), \qquad (A2b)$$

with

$$C_{GC} = \left(\frac{1}{\epsilon_1\kappa_1} + \frac{1}{\epsilon_2\kappa_2} \right)^{-1}. \qquad (A3)$$

For first-order terms

$$\begin{pmatrix} 1 & -1 \\ 1/\epsilon_1\kappa_{1,q} & 1/\epsilon_2\kappa_{2,q} \end{pmatrix} \begin{pmatrix} \hat{\alpha}_1^{\text{bulk}}(q) \\ \hat{\alpha}_2^{\text{bulk}}(q) \end{pmatrix} = \begin{pmatrix} \hat{\alpha}^{\text{surf}}(q) \\ A^{\text{bulk}}(q) \end{pmatrix}, \quad (A4)$$

with

$$A^{\text{bulk}}(q) = \frac{\sigma_2^{\text{bulk}}}{\epsilon_2}\left(\frac{1}{r_{2,q}} - 1 \right) - \frac{\sigma_1^{\text{bulk}}}{\epsilon_1}\left(\frac{1}{r_{1,q}} - 1 \right), \quad (A5)$$

and the solution

$$\hat{\alpha}_1^{\text{bulk}}(q) = C_{GC,q}\left(A^{\text{bulk}}(q) + \frac{\sum_i \hat{\alpha}_i^{\text{surf}}(q)}{\epsilon_2\kappa_{2,q}} \right), \quad (A6a)$$

$$\hat{\alpha}_2^{\text{bulk}}(q) = C_{GC,q}\left(A^{\text{bulk}}(q) - \frac{\sum_i \hat{\alpha}_i^{\text{surf}}(q)}{\epsilon_1 \kappa_{1,q}}\right), \quad \text{(A6b)}$$

with

$$C_{GC,q} = \left(\frac{1}{\epsilon_1 \kappa_{1,q}} + \frac{1}{\epsilon_2 \kappa_{2,q}}\right)^{-1}. \quad \text{(A7)}$$

For second-order terms

$$\begin{pmatrix} 1 & -1 \\ 1/\epsilon_1\kappa_{1,q} & 1/\epsilon_2\kappa_{2,q} \end{pmatrix}\begin{pmatrix} \hat{\beta}_1^{\text{bulk}}(q,k) \\ \hat{\beta}_2^{\text{bulk}}(q,k) \end{pmatrix} = \begin{pmatrix} \hat{\beta}^{\text{surf}}(q,k) \\ B^{\text{bulk}}(q,k) \end{pmatrix} \quad \text{(A8)}$$

with

$$B^{\text{bulk}}(q,k) = \frac{1}{2}\frac{\sigma_1^{\text{bulk}}\kappa_1}{\epsilon_1}f_1^\sigma(q,k) + \frac{1}{2}\frac{\sigma_2^{\text{bulk}}\kappa_2}{\epsilon_2}f_2^\sigma(q,k)$$
$$+ \frac{\hat{\alpha}_1^{\text{bulk}}(k)}{\epsilon_1}f_1^\alpha(q,k) - \frac{\hat{\alpha}_2^{\text{bulk}}(k)}{\epsilon_2}f_2^\alpha(q,k), \quad \text{(A9)}$$

and

$$f_i^\sigma(q,k) = 1 - \frac{1}{r_{i,q}}\left\{(2r_{i,k}-1) + \frac{(q-k)k}{\kappa_i^2}\left(\frac{2}{r_{i,k}}-1\right)\right\}, \quad \text{(A10)}$$

$$f_i^\alpha(q,k) = 1 - \frac{1}{r_{i,q}}\left\{r_{i,k} + \frac{(q-k)k}{\kappa_i^2 r_{i,k}}\right\}, \quad \text{(A11)}$$

and the solution

$$\hat{\beta}_1^{\text{bulk}}(q,k) = C_{GC,q}\left(B^{\text{bulk}}(q,k) + \frac{\sum_i \hat{\beta}_i^{\text{surf}}(q,k)}{\epsilon_2 \kappa_{2,q}}\right), \quad \text{(A12a)}$$

$$\hat{\beta}_2^{\text{bulk}}(q,k) = C_{GC,q}\left(B^{\text{bulk}}(q,k) - \frac{\sum_i \hat{\beta}_i^{\text{surf}}(q,k)}{\epsilon_1 \kappa_{1,q}}\right). \quad \text{(A12b)}$$

Inserting Eqs. (A2), (A6), and (A12) into Eq. (25), and performing the back transformation into real space, the two dimensional potential profile is determined in terms of the solution parameters ϵ_i and κ_i, the potential drop ΔV across the interface, the height function $h(x)$ and the surface charge response functions σ^{surf}, α^{surf}, and β^{surf}, which depend themselves on the potential at the boundary.

According to Eq. (18) the adsorbed charge density *on the* interface depends on the diffuse charge density *at the* interface, which has also to be calculated from a perturbative expansion in $h(x)$ [15]. If one compares this expansion with Eq. (23) and uses Eqs. (A2)–(A12), one obtains for each order of the perturbative expansion again a set of two equations

For zeroth-order terms

$$\begin{pmatrix} 1+x_1\kappa_1\lambda_1 & x_1\kappa_1\lambda_1 \\ x_2\kappa_2\lambda_2 & 1+x_2\kappa_2\lambda_2 \end{pmatrix}\begin{pmatrix} \sigma_1^{\text{surf}} \\ \sigma_2^{\text{surf}} \end{pmatrix} = \begin{pmatrix} c_1 - C_{GC}\Delta V\kappa_1\lambda_1 \\ c_2 + C_{GC}\Delta V\kappa_2\lambda_2 \end{pmatrix}, \quad \text{(A13)}$$

with

$$x_i = \frac{\epsilon_i \kappa_i}{\epsilon_1 \kappa_1 + \epsilon_2 \kappa_2}, \quad \text{(A14)}$$

$$\lambda_i = \frac{1}{2}(L_i^+ e^{-\beta u_i^+} + L_i^- e^{-\beta u_i^-}), \quad \text{(A15)}$$

$$c_i = \frac{1}{2}(e\rho_{Bi}L_i^+ e^{-\beta u_i^+} - L_i^- e^{-\beta u_i^-}), \quad \text{(A16)}$$

and the solution

$$\sigma_1^{\text{surf}} = \frac{1}{M}\{c_1(1+x_2\kappa_2\lambda_2) - x_1\kappa_1\lambda_1 c_2 - C_{GC}\Delta V\kappa_1\lambda_1(1+\kappa_2\lambda_2)\}, \quad \text{(A17a)}$$

$$\sigma_2^{\text{surf}} = \frac{1}{M}\{c_2(1+x_1\kappa_1\lambda_1) - x_2\kappa_2\lambda_2 c_1 + C_{GC}\Delta V\kappa_2\lambda_2(1+\kappa_1\lambda_1)\}, \quad \text{(A17b)}$$

with

$$M = 1 + x_1\kappa_1\lambda_1 + x_2\kappa_2\lambda_2. \quad \text{(A18)}$$

For first-order terms

$$\begin{pmatrix} 1+x_{1,q}\kappa_1\lambda_1 & x_{1,q}\kappa_1\lambda_1 \\ x_{2,q}\kappa_2\lambda_2 & 1+x_{2,q}\kappa_2\lambda_2 \end{pmatrix}\begin{pmatrix} \hat{\alpha}_1^{\text{surf}}(q) \\ \hat{\alpha}_2^{\text{surf}}(q) \end{pmatrix}$$
$$= \begin{pmatrix} -x_{1,q}\kappa_1\lambda_1 A^{\text{surf}}(q) \\ -x_{2,q}\kappa_2\lambda_2 A^{\text{surf}}(q) \end{pmatrix}, \quad \text{(A19)}$$

with

$$x_{i,q} = \frac{\epsilon_i \kappa_i}{\epsilon_1 \kappa_{1,q} + \epsilon_2 \kappa_{2,q}}, \quad \text{(A20)}$$

$$A^{\text{surf}}(q) = \sigma_1^{\text{bulk}}\kappa_1(1-r_{1,q}) + \sigma_2^{\text{bulk}}\kappa_2(1-r_{2,q}) \quad \text{(A21)}$$

and the solution

$$\hat{\alpha}_1^{\text{surf}}(q) = -x_{1,q}\kappa_1\lambda_1 \frac{A^{\text{surf}}(q)}{M_q}, \quad \text{(A22a)}$$

$$\hat{\alpha}_2^{\text{surf}}(q) = -x_{2,q}\kappa_2\lambda_2 \frac{A^{\text{surf}}(q)}{M_q}, \quad \text{(A22b)}$$

with

$$M_q = 1 + x_{1,q}\kappa_1\lambda_1 + x_{2,q}\kappa_2\lambda_2. \quad \text{(A23)}$$

For second-order terms

$$\begin{pmatrix} 1+x_{1,q}\kappa_1\lambda_1 & x_{1,q}\kappa_1\lambda_1 \\ x_{2,q}\kappa_2\lambda_2 & 1+x_{2,q}\kappa_2\lambda_2 \end{pmatrix} \begin{pmatrix} \hat{\beta}_1^{\text{surf}}(q,k) \\ \hat{\beta}_2^{\text{surf}}(q,k) \end{pmatrix}$$

$$= \begin{pmatrix} -x_{1,q}\kappa_1\lambda_1 B^{\text{surf}}(q,k) \\ -x_{2,q}\kappa_2\lambda_2 B^{\text{surf}}(q,k) \end{pmatrix} \qquad (A24)$$

with

$$B^{\text{surf}}(q,k) = -\frac{1}{2}[\sigma_1^{\text{bulk}}\kappa_1^2 r_{1,q} f_1^{\sigma}(q,k) - \sigma_2^{\text{bulk}}\kappa_2^2 r_{2,q} f_2^{\sigma}(q,k)]$$

$$- \hat{\alpha}_1^{\text{bulk}}(k)\kappa_1 r_{1,q} f_1^{\alpha}(q,k)$$

$$- \hat{\alpha}_2^{\text{bulk}}(k)\kappa_2 r_{2,q} f_2^{\alpha}(q,k), \qquad (A25)$$

and the solution

$$\hat{\beta}_1^{\text{surf}}(q,k) = -x_{1,q}\kappa_1\lambda_1 \frac{B^{\text{surf}}(q,k)}{M_q}, \qquad (A26a)$$

$$\hat{\beta}_2^{\text{surf}}(q,k) = -x_{2,q}\kappa_2\lambda_2 \frac{B^{\text{surf}}(q,k)}{M_q}. \qquad (A26b)$$

If we now substitute Eqs. (A17), (A22), and (A26) into Eq. (25) and perform the back transformation into real space, the two dimensional potential profile is completely determined in terms of the solution parameters ϵ_i and κ_i, the potential drop ΔV across the interface, the external adsorption parameters $u_i^{\pm}$, $L_i^{\pm}$ and the height function $h(x)$.

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