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Bending of ionic surfactant monolayers

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The electrostatic contribution to the bending moduli and spontaneous curvature of monolayers formed by ionic surfactants in solution is calculated for all salt concentrations, ranging from no added salt (counterions only) to excess salt. This is accomplished using a perturbative expansion in curvature of the free energy of the Poisson-Boltzmann cell model, which is shown to give precisely the same results for the moduli as would an alternative calculation employing moments of the transverse pressure profile of the electric double layer. With this treatment, it is possible to quantify the dependence of the moduli and spontaneous curvature on surfactant concentration alone (i.e., with fixed average salt concentration), a point of central importance to the validity of the flexible surface model in the description of ionic surfactant systems. A manifestation of the counterion condensation phenomenon is also observed, as the monolayer rigidity saturates and becomes independent of the surface area per ionic headgroup. [S1063-651X(96)03810-X]

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I. INTRODUCTION

The curvature energy concept, introduced by Helfrich [1], has allowed a significantly deepened understanding of the thermodynamics of surfactant systems. Most germane to its success in capturing the phenomenology of these complex fluids is that it relies on a few parameters that are intuitively appealing, such as the rigidity of membranes formed by the self-assembled amphiphiles. This framework has been applied to a large class of systems, ranging from ‘‘simple’’ binary systems composed of nonionic surfactant and a single solvent, to multicomponent solutions of ionic surfactant, cosurfactant (such as alcohol), added salt, and two solvents. To further this understanding it is always useful, where possible, to describe phenomenological parameters in terms of more fundamental quantities and variables that are experimentally accessible. The current paper is in the tradition of studies that have sought to characterize the coupling constants of the flexible surface model in terms of molecular quantities.

Herein, we constrain ourselves to a partial description of systems containing ionic surfactants, partial in the sense that it is only the electrostatic contribution to the bending moduli that is considered. It is beyond question that intraparticle effects (such as the conformational entropy of the amphiphiles) and interparticle interactions of a nonelectrostatic origin (such as headgroup steric repulsion) may play a significant or seemingly dominating role in these systems. While several worthwhile attempts (which we shall summarize shortly) have been made to incorporate a number of these effects into a comprehensive understanding of the molecular origin of the bending moduli, the problem is that the simplicity that the flexible surface model brought to our understanding of these systems is then confounded by a highly complicated dependence of its phenomenological parameters on other, more fundamental, quantities.

To consider only the electrostatics shows a bias that may be defended in a number of ways of varying justifiability: that the theoretical description of the electrostatics of colloidal systems is (arguably) more highly developed than other aspects, that it is not difficult to prepare systems where electrostatic effects may be significant or dominating (for example, in regimes of low or intermediate added salt concentration), and perhaps most importantly, that the present understanding is that the main effect of adjusting the salt concentration in an ionic system is to change the spontaneous curvature and bending moduli of the surfactant membrane through a variation in the electrostatic screening length. It is the last of these that provides our strongest motivation, as a phenomenological model requires one other important (and related) element to make it truly useful: a connection to experimental tuning parameters. In ionic systems, adjustment of the concentration of added salt can induce phase transitions and is thus often employed as an experimental control parameter, with the link to the flexible surface model alluded to above. One of the main results of this paper is that purely electrostatic effects of at least equal significance may also be induced by simple adjustment of the surfactant concentration, without changing the average salt concentration. This suggests that a decoupling of the surfactant concentration and salt concentration into conjugate experimental variables is not viable for at least some systems. Since the coupling constants themselves are dependent on the surfactant concentration, scaling laws based primarily on surfactant-concentration-induced effects (such as the steric repulsion law of Helfrich [2] for lamellar phases) are thus problematic to invoke for such systems. Not surprisingly, however, in regimes of high concentrations of added salt where the electrostatics is highly screened, the conventional picture is, to all intents, valid. Hence our stated aim will be

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to give a more complete description of the electrostatics, so as to indicate how the flexible surface model may better be applied to ionic systems.

In the flexible surface model, the curvature energy per unit area of the surface g_c expanded to harmonic order is given by

$$g_c = 2k_c(H-H_0)^2 + \bar{k}_c K, \tag{1}$$

where H is the mean curvature, H_0 is the spontaneous mean curvature, K is the Gaussian curvature, the bending modulus is k_c, and the saddle-splay constant is $\bar{k}_c$. We emphasize that in this paper we will be interested in all three bending ''constants'' that appear here: k_c, $\bar{k}_c$, and the product $k_c H_0$, which occurs in the coefficient of the term linear in H above [3]. The discussion is restricted to one of surfactant monolayers (although the results could be generalized to bilayers without difficulty) and to the curvature energy expanded only to harmonic order (although a calculation of the electrostatic contribution to the moduli associated with anharmonic terms could be made, with difficulty). We shall not consider here the surface tension, which in surfactant systems is commonly understood to be vanishingly small. If the calculation is made for a given, fixed geometry (without thermal fluctuations of the surface) then the curvature energy and free energy are one and the same. To make a connection to the electrostatic free energy of an ionic system, the usual method (which we shall follow) is to begin by calculating the electrostatic potential ψ using the Poisson-Boltzmann equation for a 1:1 electrolyte

$$\nabla^2\psi = \frac{4\pi q}{\varepsilon}\left(n_-^c e^{\beta q\psi} - n_+^c e^{-\beta q\psi}\right), \tag{2}$$

where q is the protonic charge, $\beta = 1/k_B T$, $\varepsilon = 4\pi\varepsilon_0\varepsilon_r$ is the dielectric constant of water, and $n_\pm^c$ are the respective number densities of the ionic species of charge ± where $\psi = 0$. (For definiteness, we shall assume the surfactants to be anionic.) In principle, we require the geometries of the plane, cylinder, and sphere to derive the moduli (although, as we will show that, only one of the cylinder and sphere geometries is ultimately needed). We should note at this point that there are many well-known deficiencies in the description offered by Eq. (2), such as the neglect of ion-ion correlations and finite ion size, but these we shall ignore.

Winterhalter and Helfrich [4] calculated the electrostatic contribution to the moduli, linearizing the Poisson-Boltzmann (PB) equation (2) and thus working within the Debye-Hückel approximation. As the solution to the linearized PB equation for all above-mentioned geometries is well known and relatively uncomplicated, quite simple expressions were obtained in this limit, requiring low surface potential (less than around 25 mV) and thus low surface charge density. Another, later, treatment of the linearized problem, for surfaces of arbitrary geometry and topology, is due to Duplantier *et al.* [5]. Further progress for systems with added salt hinged on the development of solutions of the nonlinear PB equation for cylindrical and spherical geometries or for sinusoidal corrugations of the planar geometry. As full analytic solutions for the spherical and cylindrical geometries are still unknown and all that is required for the calculation of the moduli is the free energy expanded to quadratic order in the curvatures, asymptotic analytic solutions given independently (and using complementary methods) by Mitchell and Ninham [6] and Lekkerkerker [7] allowed these authors to evaluate the electrostatic contribution to the moduli using the full nonlinear theory. Lekkerkerker [8] later rederived these results by evaluating moments of the electrostatic pressure profile of the electric double layer. Fogden, Mitchell, and Ninham [9] considered a sinusoidally undulating charged plane and derived the free energy for the full nonlinear theory to quadratic order in the amplitude, also extracting k_c in the harmonic limit. Later, Winterhalter and Helfrich [10] and Fogden and Ninham [11] reexamined the predictions of the above calculations, with a particular emphasis on the coupling of the monolayers constituting a bilayer. What we wish to point out here, and our initial motivation for the current work, is that all of these calculations are in the limit of *excess salt*. In other words, the surfactant concentration is zero and the electrostatic contribution to the moduli is calculated for a single, isolated sheet. This would be a valid approximation to a real system in certain regimes of salt concentration (high) and surfactant concentration (low). However, without allowing for the effect of nonzero surfactant concentration, it is unclear how good an approximation this is, how the moduli behave as the salt concentration is reduced towards the low-salt limit, and how the moduli change as a function of surfactant concentration alone.

An initial study to attempt to cover the broad regime incorporating both the weak and strong electrolyte limits is due to Pincus *et al.* [12], who investigated the undulation spectrum of weakly fluctuating membranes in four regions: the linearized regime, the excess salt nonlinear regime, and in the no-salt limit for both high and low surface charge density (which they labeled the ''Gouy-Chapman'' and ''ideal gas'' regions, respectively). A more detailed investigation of the no-salt (counterions only) limit was given by Higgs and Joanny [13], employing the cylindrical and undulating sheet geometries, and a further exposition and development of the combined results of Refs. [12,13] was given by Harden *et al.* [14]. The scaling of k_c was shown to be determined by the relative sizes of the Debye screening length, the Gouy-Chapman length (both to be defined in Sec. II), and the intermembrane spacing of the lamellar system. The important conclusion reached by these authors was that with excess added salt, the long-range steric repulsion of Helfrich [2] between the lamellae well exceeds the electrostatic contribution to the free energy, whereas in the low-salt limit the unscreened electrostatic repulsion dominates. Recently, two of us, with Mitchell and Ninham [15], have given a further investigation of the no-salt limit using the cylinder and undulating plane geometries. Therein, we develop an expression for the bending modulus valid over all regimes of surface charge density. We also confirm and generalize the original suggestion of Harden *et al.* [14] that a calculation of k_c from different geometries can give the same functional form. This is important, as it indicates that the local nature of Eq. (1) is maintained even in the limit of unscreened electrostatic interactions. To again place the current work in a proper context, Refs. [12–14] actually dealt with the two extremes of excess salt and no salt, in the limits of low and high surface charge density. The aim of the current paper is to allow for intermediate-salt concentrations and finite surfactant concentrations, at any surface charge density. This is more appropriate to many systems, where single phases (such as the lamellar phase) may span a very broad range of salt and surfactant concentrations.

We now briefly summarize some other related literature. As alluded to above, a number of important works have attempted to incorporate nonelectrostatic effects into the calculation of the bending moduli, notably by Szleifer and coworkers [16–18] and by Ennis [19]. Such effects include those of steric head-head interactions, chain packing, and chain-oil interactions. Barneveld *et al.* [20] have presented an alternative approach to the calculation of bending moduli, employing a self-consistent field lattice model, allowing for the finite size of the ions. A simpler, more recent approach by Cantor [21] relies on the high-salt limit to employ a quasi-two-dimensional mean-field approximation, where only the interaction of the surface and the nearest ''layer'' of ions is dealt with, in the context of the stability of bicontinuous microemulsions. On the other hand, Odijk [22] and de Vries [23,24] have investigated the issue of electrostatic forces in lamellar phases. Interestingly, the most recent of these [24] presents a calculation of the free energy of passage formation in lamellar phases, where de Vries concludes that anharmonic terms in the curvature free energy play an important role. There is also a significant body of work by Bedeaux and co-workers [25] dealing with the statistical mechanics and bending constants of curved surfaces. Recently, Andelman [26] has given a review of the literature on electrostatic properties of membranes. On the challenging experimental problem of measuring the electrostatic contribution to the bending moduli, we shall reserve a discussion of this literature to a later section.

The paper is organized as follows. In Sec. II we describe how the electrostatic free energy of the cell model depends on curvature and make a perturbation in the reciprocal aggregate radius. In Sec. III we explicitly solve the PB cell model up to first order in curvature for cylinders and spheres and present the results for the bending moduli. These are compared with existing results in the excess- and no-salt limits. We also show calculations for a specific system, indicating the dependence of the moduli on the salt and surfactant concentrations and surface charge density. We conclude with a discussion of our results in Sec. IV.

Finally, we note that a companion paper by two of us [27] contains a calculation of k_c in the general case of all salt and surfactant concentrations, employing the rippled-plane geometry. We shall make a connection to this work herein whenever appropriate.

II. ELECTROSTATIC FREE ENERGY OF THE CELL MODEL

A. Curvature dependence of the free energy

As stated in the Introduction, some previous calculations of electrostatic contributions to the elastic moduli have dealt with the excess-salt case, where the bending free energy of a single isolated surface may be considered. In order to deal with the situation of a nonzero surfactant concentration at a general salt concentration, an additional length scale must be introduced. This is done by constraining the ions in some way, naturally introducing the new length scale (the width of the water layer). In the case of no added salt, the exact solution of the PB equation is known for the concentric cylindrical geometry [31], allowing the calculation of k_c (and k_cH_0, if desired). However, there is no such exact solution to the PB equation extant for the cylindrical or spherical geometries in the case of added salt.

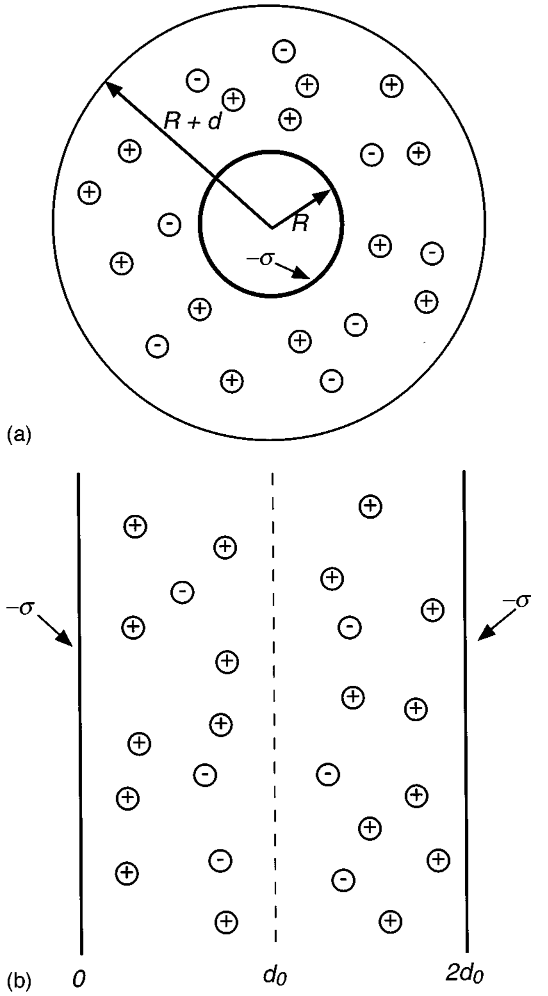

FIG. 1. (a) Cross section of the cylindrical and spherical cell models. (b) Planar reference geometry. Note that in fact it is the subsystem from $r=0$ to d_0 that forms the reference for the perturbed state.

The usual method of introducing nonzero aggregate concentration (or particle concentration, in the case of macroion systems) for charged systems with ionic atmospheres is the *Poisson-Boltzmann cell model*, which has a long history in colloid science [32,33]. In this model, the system is divided into electroneutral cells, each with a macroion or aggregate surrounded by an aqueous region containing the ions. The cell size is directly determined by the macroion or aggregate concentration. A schematic representation of the cross section of such a cell, equally applicable to the cylindrical and spherical geometries, is given in Fig. 1(a). Because of electroneutrality, the electric field vanishes at the cell boundary (i.e., $d\psi/dr=0$) at a distance $R+d$ from the center of the aggregate, where R is the aggregate radius. The surface charge density is $-\sigma$ (where $\sigma > 0$). It will be convenient to conceptualize the interior as being filled by oil in the context of the current problem; we will assume no electrostatic coupling across the interior. All charged groups on the surfactant will be idealized to lie on the surface at R; however, the surfactant concentration will be introduced through a finite hydrocarbon tail length of l, extending into the interior. We also assume that there are no free surfactant monomers in the aqueous solution. The planar geometry at finite concentration is the reference state and is shown as Fig. 1(b). This system has been studied extensively [28], and a treatment with boundary conditions appropriate to the current work has been given by Jönsson and Wennerström [29]. For reference, we recount this briefly in Appendix A.

We seek now a curvature expansion for the electrostatic free energy per unit area of surface $g = G/A$ of the cylindrical and spherical cell models, i.e., an asymptotic series in $1/R$ [30]. At least in principle, we shall need to consider both the cylindrical and spherical geometries in order to calculate all of $k_c H_0$, k_c, and k_c. The free energy is given by the sum of the electrostatic internal energy and entropy contributions

$$G = E_{\mathrm{el}} - TS, \tag{3}$$

where

$$E_{\mathrm{el}} = \frac{\varepsilon}{8\pi}\int_V dV |\nabla\psi|^2. \tag{4}$$

In order to calculate the curvature dependence of g at *fixed total monolayer surface area in the system* A_{tot}, we make the following connection [34] for both the cylindrical and spherical geometries:

$$\begin{aligned}\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\mathrm{tot}}} &= -R^2\left(\frac{\partial V_i}{\partial R}\right)_{A_{\mathrm{tot}}}\left(\frac{\partial g}{\partial V_i}\right)_{A_{\mathrm{tot}}} \\ &= -\frac{R}{A}\left\{E_{\mathrm{el}} + \frac{1}{\beta}\int_V dV \right. \\ &\quad \left. \times [n_-^c e^{\beta q\psi} + n_+^c e^{-\beta q\psi}]_r^{R+d}\right\},\end{aligned} \tag{5}$$

where A is the surface area of a single aggregate and V_i and V are the volumes of the aggregate interior and aqueous region, respectively. In Appendix B 1 we show how the above may be manipulated into the simpler form

$$\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\mathrm{tot}}} = \frac{\chi}{1+\chi}\,\frac{\varepsilon}{4\pi}R\int_R^{R+d} dr\left[\frac{R}{r} - \left(\frac{r}{R}\right)^{\chi}\right]\left(\frac{d\psi}{dr}\right)^2, \tag{6}$$

where $\chi = 1$ for the cylindrical geometry and $\chi = 2$ for the spherical geometry. This last equation is central to our treatment of the problem at hand. No assumption has been made in its development other than the overall electroneutrality of the cell. Although this equation is strictly equivalent to Eq. (5), the cancellations that occur in its derivation allow the negativity of the derivative to be evident and, as will be shown later, permit determination of the curvature energy up to quadratic order using only the first-order perturbations for the potential. We emphasize that keeping A_{tot} fixed while changing R means that the length of the cylinders L and the *number* of spheres in the respective systems will change in compensation [30]. We may for convenience choose $\psi = 0$ at $r = R + d$, although, by gauge invariance, we could take it to be any constant value there (ψ_c, say), so that

$$n_\pm^c = n_c e^{\mp\beta q\psi_c}. \tag{7}$$

It is useful now to switch to dimensionless quantities and to also define quantities associated with the reference planar state. The dimensionless potential is $\phi = \beta q\psi$, and d_0 and $n_{\pm,0}^c$ will be the appropriate planar quantities. It will be also useful to define $\alpha_0 = n_{-,0}^c / n_{+,0}^c$ and to introduce the length [35]

$$\lambda_D \equiv \kappa^{-1} = \left(\frac{\varepsilon}{2\pi n_{+,0}^c \beta q^2}\right)^{1/2}, \tag{8}$$

which we then use to scale other lengths as

$$x \equiv \kappa(r - R), \quad D \equiv \kappa d, \quad b \equiv 1/(\kappa R). \tag{9}$$

In scaled form, the PB equation then becomes

$$\phi'' + \chi\frac{b}{1+bx}\phi' = 2\left(\frac{n_-^c}{n_{+,0}^c}e^{\phi} - \frac{n_+^c}{n_{+,0}^c}e^{-\phi}\right), \tag{10}$$

where $\chi = 0$ corresponds to the planar case and the derivative of the scaled potential $\phi(x)$ with respect to x is indicated by the prime. The boundary conditions are then

$$\phi(D) = 0, \tag{11a}$$

$$\phi'(D) = 0, \tag{11b}$$

$$\phi'(0) = 2\frac{\lambda_D}{\lambda_{\mathrm{GC}}}, \tag{11c}$$

where in the last equation

$$\lambda_{\mathrm{GC}} = \frac{\varepsilon}{2\pi\beta q\sigma} \tag{12}$$

is the Gouy-Chapman length. Finally, it will be convenient to give in scaled form Eq. (6), which is, for the cylindrical case,

$$\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\mathrm{tot}}} = -\frac{\varepsilon}{8\pi\beta^2 q^2}\int_0^D dx\, x\left(\frac{2+bx}{1+bx}\right)(\phi')^2, \tag{13}$$

and in the spherical case

$$\begin{aligned}\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\mathrm{tot}}} &= -\frac{\varepsilon}{8\pi\beta^2 q^2}\int_0^D dx \\ &\quad \times x\left[\frac{\frac{4}{3}b^2x^2 + 4(1+bx)}{1+bx}\right](\phi')^2.\end{aligned} \tag{14}$$

B. Perturbation scheme for the electrostatic potential

The planar state ($b=0$) is taken as the reference, and we make the perturbation of the free energy in powers of b, up to harmonic order. It is sufficient for our purposes that the expansion be asymptotic, as the curvature expansion is itself only sensible in the asymptotic limit $b \rightarrow 0$. Over the past ten years or so, there have been several works dealing with the perturbative solutions of the cylindrical cell model, developing bounds on exact solutions of the PB equation [36], for the counterions-only case [37], or perturbations around this solution [38]. The following differs from these in the sense that it makes no assumption regarding the surface charge density and provides exact solutions to the given order in b. We simultaneously deal with the spherical geometry. We also note that the utility of the following treatment of the potential and free energy of the cell model is not restricted to the current problem of monolayer bending elasticity, but could be applied to other systems where the solution of the PB equation in cylindrical or spherical geometry is required.

As stated, we impose that the total area A_{tot} of surface is held fixed on bending and for the present, we also impose a fixed surface charge density $-\sigma$, returning later to the issue of alternative boundary conditions at the surface (such as constant surface potential or mixed conditions). The boundary densities $n_{\pm}^{c}$ are also, in general, allowed to deviate from their planar values. As it happens, it is sufficient to expand the potential and boundary quantities up to linear order in the curvatures to calculate the moduli. We then have

$$\phi=\phi_0+\phi_1 b+\cdots, \tag{15a}$$

$$D=D_0+D_1 b+\cdots, \tag{15b}$$

$$n_{\pm}^{c}=n_{\pm,0}^{c}+n_{\pm,1}^{c} b+\ldots, \tag{15c}$$

and for convenience we will write $\alpha_i=n_{-,i}^{c}/n_{+,0}^{c}$ and $\gamma_i=n_{+,i}^{c}/n_{+,0}^{c}$. Thus the PB equation, as given in (10), becomes to zeroth and first orders

$$\phi_0''=2(\alpha_0 e^{\phi_0}-e^{-\phi_0}), \tag{16a}$$

and

$$\phi_1''-2(\alpha_0 e^{\phi_0}+e^{-\phi_0})\phi_1=-\chi\phi_0'+2(\alpha_1 e^{\phi_0}-\gamma_1 e^{-\phi_0}). \tag{16b}$$

It is also useful to expand the n_c and $\phi_c=\beta q\psi_c$ that appear in (7) in the fashion of Eq. (15), and for later convenience to assign $\eta_i \equiv \phi_{c,i}$ and $\nu_i \equiv n_{c,i}/2n_{c,0}$. The boundary conditions of Eq. (11) imply

$$\phi_0(D_0)=0, \quad \phi_0'(D_0)=0, \tag{17a}$$

$$\phi_1(D_0)=0, \quad \phi_1'(D_0)=-D_1\phi_0''(D_0), \tag{17b}$$

and

$$\phi_0'(0)=2\frac{\lambda_D}{\lambda_{\text{GC}}}, \quad \phi_j'(0)=0 \quad (j=1,2,\ldots). \tag{17c}$$

C. Constraints

In order to close the problem, two additional constraints must be imposed, which may be chosen in any physically reasonable fashion. Here, we consider three possibilities of interest.

1. Fixed water and salt chemical potentials

Marcus [39] originally showed the relationship between the boundary values of the ion densities and electrostatic potential, and the chemical potentials of salt (μ_s) and water (μ_w). These are (ignoring standard chemical potential terms)

$$\beta\mu_s=2\ln n_c \tag{18}$$

and

$$\beta\mu_w=-2v_w n_c(\cosh\phi_c-1), \tag{19}$$

where v_w is the molecular volume of water. Thus, fixing both μ_s and μ_w on bending the surface requires that n_c and ϕ_c remain constant, which simply means that $\eta_j=0$ and $\nu_j=0$ for $j=1,2,\ldots$. So, for this case, it is only the chemical potential of amphiphile μ_a that changes with curvature.

2. Fixed salt chemical potential and amount of water

Alternatively, we may choose to relax the constraint on the osmotic pressure and only keep μ_s fixed, so that $\nu_j=0$. This then allows the freedom to satisfy another requirement, such as conservation of the total amount of water in the cell, i.e., the volume V, on bending the surface. With A_{tot} also fixed, it is straightforward to show that we require

$$\kappa V/A=D\left(1+\frac{\chi}{2}Db+\frac{\chi-1}{\chi+1}D^2b^2\right), \tag{20}$$

which in terms of the perturbation means

$$D_1=-\frac{\chi}{2}D_0^2. \tag{21}$$

3. Fixed amounts of water and ions

Relaxing totally the constraint on all chemical potentials allows us to fix both the total number of water molecules and total number of ions N in a cell, where

$$N=\int_V dV(n_-^c e^{\phi}+n_+^c e^{-\phi}). \tag{22}$$

Hence, in this case the amounts of all of the components and their concentrations are preserved on bending. Using Eqs. (16) and (17), it is possible to show that Eq. (22) is equivalent to stipulating that

$$\int_0^{D_0} dx[\chi x(\phi_0')^2-2\phi_0'\phi_1']=4(\alpha_1+\gamma_1)D_0. \tag{23}$$

This is the most challenging case, of the three that we consider, to solve. We note also that an interesting fourth possibility is the case of fixed μ_w and N; however, we leave that for a future study.

III. BENDING MODULI

A. Connection to the curvature free energy and moduli

We now employ the perturbation scheme outlined above to determine the bending moduli. Expanding Eqs. (13) and (14) to first order gives

$$\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\rm tot}}=-\frac{\varepsilon}{8\pi\beta^2q^2}\int_0^{D_0}dx\{2\chi x(\phi_0')^2+x[4\chi\phi_0'\phi_1'+(\chi-2)x(\phi_0')^2]b+\cdots\}. \tag{24}$$

Comparing with the curvature free energy of Eq. (1) yields

$$k_cH_0=\frac{\varepsilon}{8\pi\beta^2q^2}\int_0^{D_0}dxx(\phi_0')^2, \tag{25a}$$

$$k_c=-\frac{\varepsilon}{8\pi\kappa\beta^2q^2}\int_0^{D_0}dxx[4\phi_0'\phi_1'^{(\rm cyl)}-x(\phi_0')^2], \tag{25b}$$

and

$$\overline{k}_c=-\frac{\varepsilon}{4\pi\kappa\beta^2q^2}\int_0^{D_0}dxx^2(\phi_0')^2, \tag{25c}$$

where in (25b), $\phi_1'^{(\rm cyl)}$ indicates the appropriate quantity for the cylindrical case. In fact, the derivation of the last formula is interesting, and Appendix B 2 is devoted to it. There we also show that $\phi_1^{(\rm sph)}=2\phi_1^{(\rm cyl)}$ (for all of the cases considered in Sec. II C). Hence it becomes clear that we require *either* the cylindrical or spherical geometry in order to solve the current problem, but not both, a point not at all obvious at the outset. Note also that, generally, k_cH_0 and $\overline{k}_c$ are independent of the perturbation on the planar solution and hence are *totally insensitive to the constraints imposed on bending the surface.*

B. Comparison to moments of the transverse pressure profile

An alternative method for calculation of the bending moduli is the evaluation of moments of the transverse pressure profile. It was initially introduced by Kirkwood and Buff [40] in the context of the surface tension of the liquid-vapor interface, and much later Helfrich [41] made the connection to the bending moduli. This was later extended by Szleifer *et al.* [18]. Winterhalter and Helfrich [4,10] and Lekkerkerker [8] have also employed this method in the calculation of ionic surfactant bending moduli.

The transverse pressure profile of the double layer is given by

$$\Pi(x)=\frac{\varepsilon\kappa^2}{8\pi\beta^2q^2}(\phi')^2-\frac{1}{\beta}[n_-^ce^{\phi}+n_+^ce^{-\phi}]_x^D. \tag{26}$$

The bending moduli are then

$$k_cH_0=\frac{1}{2\kappa^2}\int_0^{D_0}dxx\Pi_0, \tag{27a}$$

$$k_c=-\frac{1}{\kappa^2}\int_0^{D_0}dxx\frac{\partial\Pi^{(\rm sph)}}{\partial(2/R)}\bigg|_{R\to\infty}, \tag{27b}$$

and

$$\overline{k}_c=-\frac{1}{\kappa^3}\int_0^{D_0}dxx^2\Pi_0, \tag{27c}$$

where Π_0 and $\Pi^{(\rm sph)}$ are the planar and spherical pressure profiles, respectively. Now, with Eq. (A2), we have that

$$\Pi_0(x)=\frac{\varepsilon\kappa^2}{4\pi\beta^2q^2}(\phi_0')^2. \tag{28}$$

It is then by inspection that we see that Eqs. (27a) and (27c) are identical to (25a) and (25c), respectively, for all of the constraints that we consider. The proof that the isomorphism holds also in the case of k_c is more involved. The explicit prediction of Eq. (27b) is

$$k_c=-\frac{\varepsilon}{8\pi\kappa\beta^2q^2}\int_0^{D_0}dxx(\phi_0'\phi_1'+2\{-[\alpha_1e^{\phi_0}+\nu_1e^{-\phi_0}]_x^{D_0}+(\alpha_0e^{\phi_0}-e^{-\phi_0})\phi_1\}), \tag{29}$$

in which all symbols with subscript 1 refer to the spherical case. This can be expressed most simply, for the purposes of the later calculations, in terms of the variables η_1 and ν_1 as

$$k_c=\frac{\varepsilon}{8\pi\kappa\beta^2q^2}\int_0^{D_0}dx\{\phi_0'\phi_1+x(\eta_1[\phi_0'']_x^{D_0}-\nu_1[\phi_0']^2)\}. \tag{30}$$

However, Eq. (29) could also be reexpressed using the fact that

$$-[\alpha_1e^{\phi_0}+\nu_1e^{-\phi_0}]_x^{D_0}+(\alpha_0e^{\phi_0}-e^{-\phi_0})\phi_1=\frac{1}{2}\phi_0'\phi_1'-\int_x^{D_0}dx(\phi_0')^2, \tag{31}$$

again with all subscripts 1 in Eqs. (30) and (31) related to the sphere. From the fact that $\phi_1^{(\rm sph)}=2\phi_1^{(\rm cyl)}$, Eq. (25b) follows in a straightforward manner. So the predictions for the bending moduli of moments of the transverse pressure profile and a curvature expansion for the electrostatic free energy will be identical for all cases that we consider.

C. General solution for ϕ_1

In order to fully express k_c in terms of planar quantities, we need to find a general solution for ϕ_1 in terms of ϕ_0. As detailed above and in Appendix B 2, with $\phi_1^{(\rm sph)}=2\phi_1^{(\rm cyl)}$ we may choose to evaluate k_c using either the cylindrical or spherical geometry: we choose the latter and substitute into Eq. (30). The other two moduli rely only on the well-known planar solution summarized in Appendix A. We describe now the analytic solution for ϕ_1 in the spherical cell model.

Equations (16a) and (16b) may be combined to give

$$\frac{d}{dx}\left[(\phi_0')^2\frac{d}{dx}(\phi_1/\phi_0')\right]=-2(\phi_0')^2+2\frac{d}{dx}(\alpha_1 e^{\phi_0}+\gamma_1 e^{-\phi_0}). \tag{32}$$

Applying appropriate boundary conditions from (17a) and (17b), two integrations then give the general solution for ϕ_1 in terms of the planar solution ϕ_0:

$$\phi_1=-2\phi_0'\int_x^{D_0}dx(\phi_0')^{-2}\mathcal{E}(x)+\eta_1\phi_0'\int_x^{D_0}dx(\phi_0')^{-2}[\phi_0'']_x^{D_0}-\nu_1(D_0-x)\phi_0'+\mathcal{C}\phi_0', \tag{33}$$

where we have newly defined $\mathcal{C}\equiv\phi_1'(D_0)/\phi_0''(D_0)$ and $\mathcal{E}(x)$, where

$$\mathcal{E}(x)=\int_x^{D_0}dx(\phi_0')^2. \tag{34}$$

We note that $\mathcal{C}$ is unconstrained by any boundary condition at $x=D_0$ in the case of constant μ_s and μ_w (Sec. II C 1), but that we must set $\mathcal{C}=D_0^2$ for the other two cases. We also bear in mind the other boundary conditions and constraints previously laid out in Sec. II above.

D. Formal expression for the bending modulus

It is useful now to provide formal expressions for k_c in terms of planar quantities, valid for all cases discussed in Sec. II C. This is given by substitution of Eq. (33) into the expression (30) and also using $\phi_1'(0)=0$. The resulting expressions are naturally phrased in terms of the integrals

$$\mathcal{W}^{(n)}=\int_0^{D_0}dx(\phi_0')^{-1}\frac{d}{dx}[(\phi_0'')^{-1}\mathcal{E}^n(x)]. \tag{35}$$

For convenience, we write Eq. (30) as

$$k_c\equiv\frac{\varepsilon}{8\pi\kappa\beta^2q^2}\mathcal{I}. \tag{36}$$

The integral $\mathcal{I}$ is then broken up into the sum of three parts

$$\mathcal{I}=\mathcal{I}_1+\eta_1\mathcal{J}_2+\nu_1\mathcal{J}_3, \tag{37}$$

where

$$\mathcal{I}_1=2\mathcal{W}^{(2)}, \tag{38a}$$

$$\mathcal{J}_2=\phi_0''(D_0)(D_0^2/2-\mathcal{W}^{(1)}), \tag{38b}$$

and

$$\mathcal{J}_3=-\phi_0'(0)[\phi_0''(0)]^{-1}\mathcal{E}(0). \tag{38c}$$

We must eliminate the two variables η_1 and ν_1 from $\mathcal{I}$ in terms of the applied constraints. In the case of constant μ_s and μ_w, with $\eta_1=\nu_1=0$, we have that $\mathcal{I}=\mathcal{I}_1$. In the other two cases, we use the constraint $\mathcal{C}=D_0^2$ to eliminate η_1. This then gives

$$\mathcal{I}=\mathcal{I}_1+\mathcal{I}_2+\nu_1\mathcal{K}_3, \tag{39}$$

with

$$\mathcal{I}_2=-\frac{2}{\mathcal{W}^{(0)}}(D_0^2/2-\mathcal{W}^{(1)})^2 \tag{40}$$

and

$$\mathcal{K}_3=-[\phi_0''(0)]^{-1}\left\{\frac{\mathcal{Y}}{\mathcal{W}^{(0)}}[D_0^2/2-\mathcal{W}^{(1)}]+\phi_0'(0)\mathcal{E}(0)\right\}, \tag{41}$$

where

$$\mathcal{Y}=\phi_0'(0)-D_0\phi_0''(0). \tag{42}$$

So, for the case of fixed μ_s and V, $\nu_1=0$ and the modulus is given by Eq. (36) with $\mathcal{I}=\mathcal{I}_1+\mathcal{I}_2$. We note that $\mathcal{I}_2$ is strictly non-negative, as its denominator is negative. This indicates that the constraint of fixing V leads to an increase in k_c and thus to an *increase in the curvature free energy*. This important point indicates that indeed the fixed μ_s and μ_w case has a natural meaning in the definition of a bending modulus, as the imposition of, for example, a volume-fixing constraint gives a higher free energy. Therefore, in an unconstrained real system, thermodynamics dictates that maintaining constant μ_s and μ_w on bending will be preferential to the combination of constant μ_s and V.

For the fixed N and V case, we must eliminate ν_1 using Eq. (23). This ultimately leads to

$$\mathcal{I}=\mathcal{I}_1+\mathcal{I}_2+\mathcal{I}_3, \tag{43}$$

with the extra contribution $\mathcal{I}_3$ now given by

$$\mathcal{I}_3=\frac{2\left\{\frac{\mathcal{Y}}{\mathcal{W}^{(0)}}[D_0^2/2-\mathcal{W}^{(1)}]+\phi_0'(0)\mathcal{E}(0)\right\}^2}{\frac{\mathcal{Y}^2}{\mathcal{W}^{(0)}}+\mathcal{Z}}, \tag{44}$$

where

$$\mathcal{Z}=[\phi_0''(0)]^2\{\mathcal{E}(0)+[\phi_0''(0)]^{-1}[\phi_0'(0)]^3+8(\alpha_0+1)D_0\}. \tag{45}$$

We also note that $\mathcal{I}_3\geqslant 0$, so that the constraint of fixed composition gives the largest k_c and thus the highest-energy penalty for bending the surface. So, to summarize, $k_c=(\varepsilon/8\pi\kappa\beta^2q^2)(\mathcal{I}_1+\mathcal{I}_2+\mathcal{I}_3)$, with the appropriate combination of the $\mathcal{I}_i$ determined by the imposed constraints. Specifically, $\mathcal{I}_3=0$ for the fixed μ_s and μ_w and fixed μ_s and V cases, and also $\mathcal{I}_2=0$ in the former case.

We thus now have all of k_cH_0, k_c, and k_c in terms of the known planar solution of the PB equation and the problem is formally solved. If we wished to give these solutions in terms of known functions, it would be a matter of substituting the expressions for x and ϕ_0', given as Eqs. (A3) and (A4), respectively, into the above formulas, and then performing the appropriate integrations. However, this leads to unwieldy expressions that are of marginal value. It is more useful, in our view, to proceed from this point on by numeri-

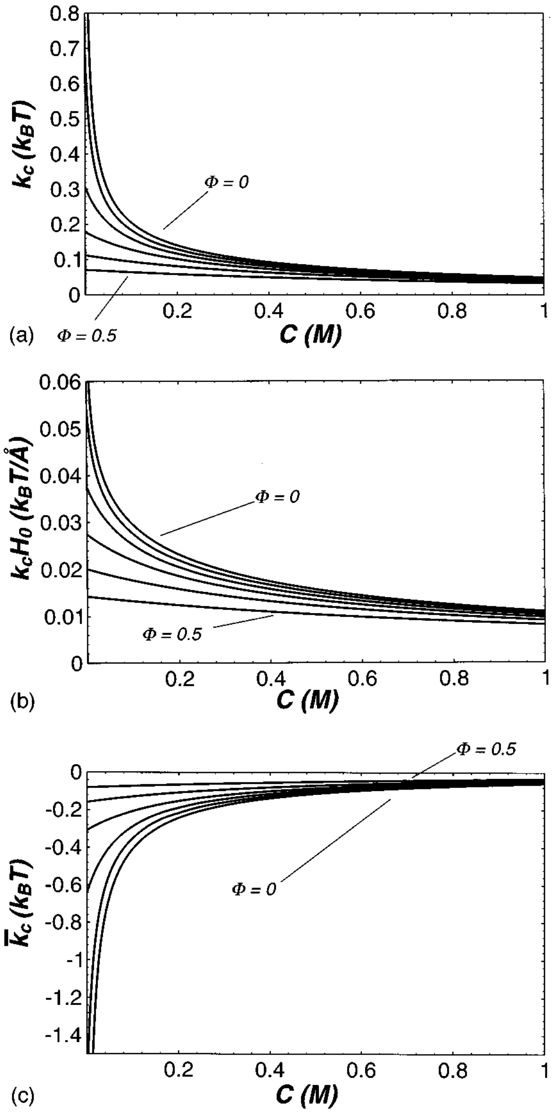

FIG. 2. Bending moduli as a function of average salt concentration C, for fixed values of surfactant volume fraction $\Phi=0$, 0.1, 0.2, 0.3, 0.4, and 0.5. (a) k_c. (b) k_cH_0. (c) $\bar{k}_c$.

cal evaluation of, or alternatively by using analytical approximations to, the expressions that we have developed.

We also point out that we have checked our expressions in the limits of excess salt ($\alpha_0=1$) and counterions only ($\alpha_0=0$) and they do in fact recover the correct limiting forms, which may be found in Refs. [6–15]. We note here though that both $\mathcal{I}_2$ and $\mathcal{I}_3$ above vanish in the excess salt limit (as they must). In fact, $\mathcal{W}^{(0)} \sim \exp(\mathrm{const}/\Phi)$ and $\mathcal{W}^{(1)} \sim 1/\Phi$ in the $\Phi \rightarrow 0$ limit (where Φ is the surfactant volume fraction), allowing one to explicitly deduce the asymptotic behavior of $\mathcal{I}_2$ and $\mathcal{I}_3$ in the excess-salt limit, if desired. In the zero-salt limit, $\mathcal{I}_3$ vanishes and the two cases that fix V become degenerate, as they should for counterions only. Finally, we note that we have also obtained an expression for k_c in the case of constant chemical potentials of salt and water using the rippled-plane geometry, the calculational details of which are given in Ref. [27]. The result agrees precisely with that which we obtain in the current paper for this case.

E. Evaluation of the moduli

The formulas for k_cH_0 and $\bar{k}_c$ given by Eqs. (25a) and (25c), and the expressions for k_c given in Sec. III D are, via substitution of Eq. (A3), functions of the three state variables λ_D, d_0, and α_0. We eliminate these in terms of the planar-state characteristics relevant to our purposes: λ_{GC}, defined in Eq. (12) and given by combining Eqs. (A4) and (17c), the volume fraction of surfactant $\Phi=l/(l+d_0)$, and the average concentration of salt C in molar (M), which is given by

$$C=10^{-3}\frac{n^{c}_{-,0}}{N_A D_0}\int_0^{D_0} dx e^{\phi_0}, \tag{46}$$

where N_A is the Avogadro number. We must also choose numerical values for the system parameters. We take $l=9.5$ Å, the area per charged surfactant headgroup as 67 Å^2, and $T=298$ K. These numbers are relevant to an AOT [sodium bis(2-ethylhexyl) sulfosuccinate] salt-water system [43].

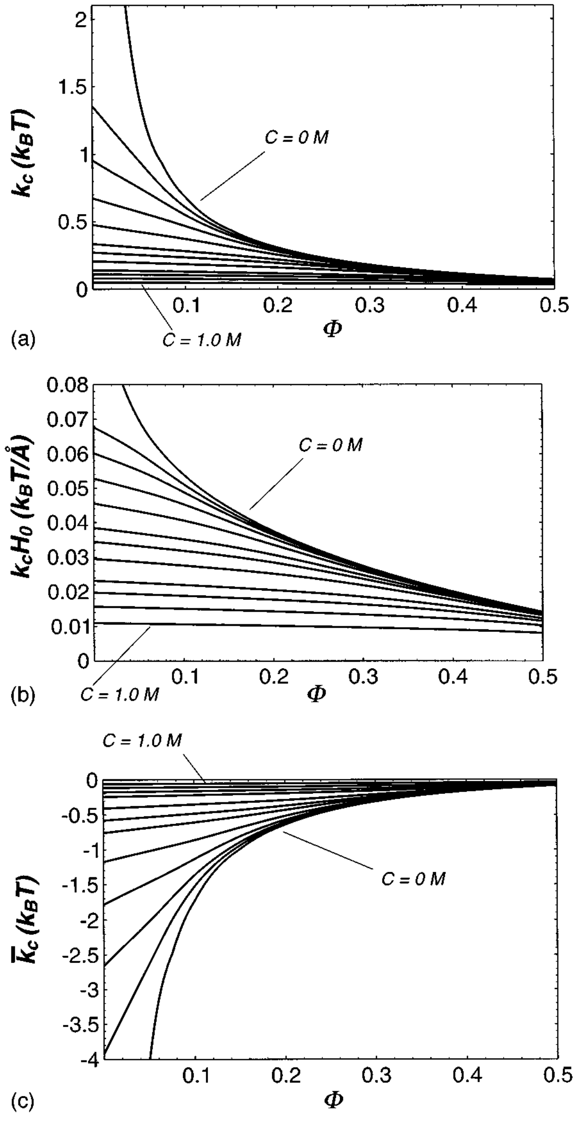

FIG. 3. Bending moduli as a function of surfactant volume fraction Φ, for fixed values of average salt concentration C=0, 0.0025, 0.005, 0.01, 0.02, 0.04, 0.06, 0.1, 0.2, 0.3, 0.5, and 1.0M. (a) k_c. (b) k_cH_0. (c) $\bar{k}_c$.

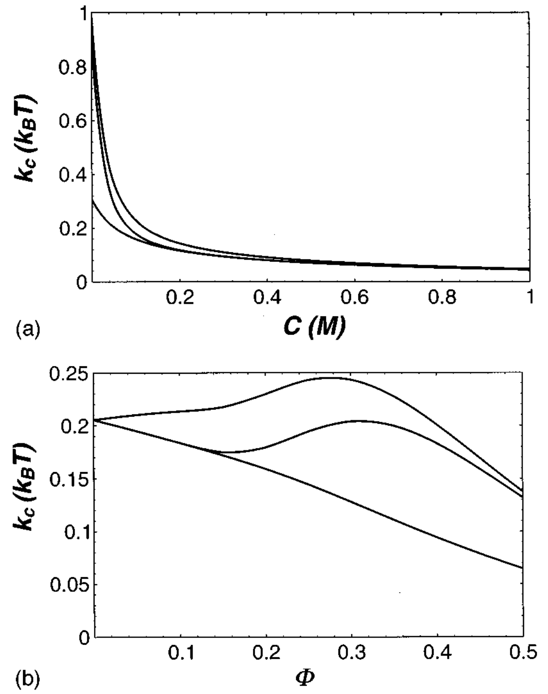

FIG. 4. Comparison of the bending modulus under different constraints for (a) $\Phi=0.2$ and (b) $C=0.1M$. On both graphs, the lower curve corresponds to fixed μ_s and μ_w, the middle curve to fixed μ_s and V, and the upper curve to fixed V and N.

However, we emphasize that our aim here is not to make specific predictions regarding a given system, but rather to indicate the general characteristic behavior of the moduli, and thus these values should be regarded as nominal.

The numerical evaluation was done using a program written for the MATHEMATICA package, which performs the above change of variables and evaluates the integral expressions for the moduli in a straightforward manner. First, in Fig. 2, we show how the moduli depend on the salt concentration C, at fixed surfactant volume fraction, in the range $\Phi=0$ (the excess-salt case) to $\Phi=0.5$. In Fig. 3 we show how the moduli change with Φ at fixed average salt concentration, in the range $C=0$ (counterions only) to $C=1.0M$. Note the dramatic effect as the salt concentration is reduced: we shall shortly return to this point in our forthcoming discussion in Sec. IV. We note here that we have used the definition of k_c for fixed μ_s and μ_w in Figs. 2 and 3. In Fig. 4, we make a comparison between the three alternative definitions of the bending modulus, indicating that indeed the fixed μ_s,μ_w alternative will give the lowest mean curvature penalty. In Fig. 5 plots are given for $2k_c+\overline{k_c}$ (with k_c again taken for the case of constant chemical potentials of salt and water). This quantity is important, as it indicates whether the electrostatics acts to stabilize ($2k_c+\overline{k_c}>0$) or destabilize ($2k_c+\overline{k_c}<0$) the monolayer at harmonic order in the curvatures. Clearly, our results indicate that either situation is a possibility, depending on the regime of salt and surfactant concentration: again, we return to this important point later, in Sec. IV.

F. Approximate formulas at low volume fraction

For practical applications, it may sometimes be preferable to use analytical approximations rather than evaluation of the full integrals. This is particularly so near the limit of excess salt, where many phases of interest are commonly found. It may then suffice to consider the existing excess-salt formulas [6–9], embellished by their first-order correction in Φ. Such expansions may be found from our integral expressions above. Without giving any details of their development, we exhibit these below. In order to harmonize these with the existing excess-salt formulas, we now take the following definitions: $\tilde{\kappa}=[8\pi\beta q^2(10^3N_AC)/\varepsilon]^{1/2}$ gives the "usual" definition of the inverse Debye length in the excess salt limit and $s=2/(\tilde{\kappa}\lambda_{\mathrm{GC}})$ is the dimensionless variable used by Mitchell and Ninham [6] and $w=(1+s^2/4)^{1/2}$ that by Lekkerkerker [7,8] (which he denotes as q) in their derivations of the excess-salt formulas. We obtain

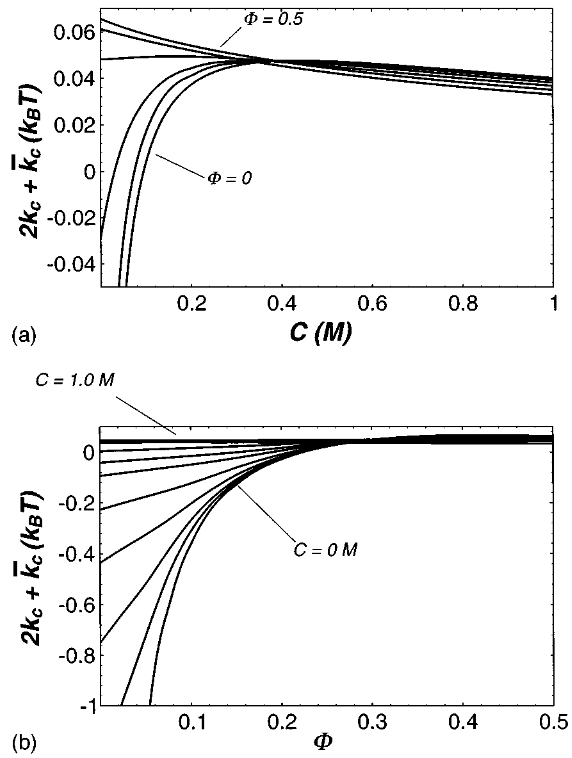

FIG. 5. Behavior of the "stability parameter" $2k_c+\overline{k_c}$, given as a function of (a) the average salt concentration (for fixed $\Phi=0$, 0.1, 0.2, 0.3, 0.4, 0.5), and (b) the surfactant concentration (for fixed $C=0$, 0.0025, 0.005, 0.01, 0.02, 0.04, 0.06, 0.1, 0.2, 0.3, 0.5, and $1.0M$).

$$k_cH_0=\frac{\varepsilon}{4\pi\beta^2q^2}\left\{2\ln[(1+w)/2]-\frac{(s/2)^4}{w(s/2+w)^{1/2}[(1+w)/2]^{3/2}}\left(\frac{\lambda_{\mathrm{GC}}}{l}\right)\Phi+\cdots\right\},\tag{47}$$

$$\overline{k_c}=-\frac{\varepsilon}{\pi\tilde{\kappa}\beta^2q^2}\left\{f(w)+s(w-s/2-1)\times\left(\frac{1}{2}f(w)+\frac{1}{w}\ln[(1+w)/2]\right)\left(\frac{\lambda_{\mathrm{GC}}}{l}\right)\Phi+\cdots\right\},\tag{48}$$

where

$$f(w)=D_1(\ln[(1+w)/2])=\int_0^{\ln[(1+w)/2]} dt \frac{t}{e^t-1} \tag{49}$$

and $D_1(x)$ is a Debye function (related to the dilogarithm).

For k_c, we find that the fixed μ_s,μ_w and μ_s,V cases reduce to the same Taylor expansion, as terms arising from $\mathcal{I}_2$ above are subdominant when expanded for low volume fraction [i.e., the expansion contains terms of the form $\exp(-\text{const}/\Phi)$]. For these two cases, we obtain

$$\begin{aligned} k_c=\frac{\varepsilon}{2\pi\widetilde{\kappa}\beta^2 q^2}\Bigg\{ & \frac{(w-1)(w+2)}{w(w+1)} \\ & -\frac{s^2(w-s/2)^{1/2}(w-1)[w+2+2(2w+1)/w^2]}{2\sqrt{2}w(1+w)^{3/2}} \\ & \times\left(\frac{\lambda_{\mathrm{GC}}}{l}\right)\Phi+\cdots\Bigg\}. \end{aligned} \tag{50}$$

In the case of fixed N and V, it happens that $\mathcal{I}_3$ does in fact have a Taylor expansion. Writing for this case $k_c=\widetilde{k}_c+\delta k_c$, where $\widetilde{k}_c$ is the right-hand side of (50), we have that

$$\delta k_c=\frac{\varepsilon}{\pi\widetilde{\kappa}\beta^2 q^2}\frac{(s/2)^5}{w^2(1+w)^2}\left(\frac{\lambda_{\mathrm{GC}}}{l}\right)\Phi+\cdots. \tag{51}$$

G. Counterion condensation

We now investigate the effect of changing the surface charge density. This we do in relation to the phenomenon of *counterion condensation* and the associated concept of the *effective charge*, a theory attributed to Manning [44] and well known in the polyelectrolyte literature [33,37,38,45]. It has also been discussed in regard to lamellar liquid crystals previously by Jönsson and Wennerström [29] and also by Alexander *et al.* [46] in the context of charged colloidal fluids. Recently, Gisler *et al.* [47] have made measurements on latex suspensions that confirm the concept for these systems. The basic notion is that the nonlinear PB equation obtains, at large distances from the surface (near the cell boundary), an asymptotic solution that is that of the linearized PB equation, with an *effective surface charge density* that takes into account the fact that near the surface there is a high density of accumulated counterions. As the surface charge density is increased, the effective charge saturates and becomes independent of the ''bare'' charge on the surface: this is the signature of counterion condensation.

Here we investigate whether the surfactant bending moduli also display such a saturation phenomenon. If so, then this would lead to a significant simplification of their dependence on the governing molecular parameters and thus make the understanding of ionic surfactant systems relatively straightforward. To this end, in Fig. 6 we plot the moduli as a function of σ (in a physically reasonable range, with k_c for fixed μ_s,μ_w), for both fixed Φ and C. The immediate conclusion is that the three moduli behave in a remarkably different fashion and it is only k_c that demonstrates a true saturation. We shall discuss this interesting phenomenon in the following section.

IV. DISCUSSION

The introduction of nonzero surfactant concentration into the calculation of the electrostatic contribution to the bending moduli has been seen to be significant, from the results presented above, in two ways. First, increasing the surfactant concentration reduces the dependence of the moduli on salt concentration: this is clear from Fig. 2. Second, at fixed-salt concentration *the bending moduli change significantly with surfactant concentration*, as shown in Fig. 3. Furthermore, the notion that it is $k_c H_0$ that is more sensitive to system changes than k_c or k_c is seen to be true, if ever, only in certain regimes: low-salt concentration with high surfactant concentration and low surfactant concentration with high-salt concentration; in all other regimes the two other moduli are as least as sensitive as $k_c H_0$.

All of these results point towards a caveat in applying the flexible surface model to ionic surfactant systems. First, the surfactant concentration dependence of the moduli is problematic, as a considerable amount of knowledge regarding these systems is based on scaling laws where the bending moduli are explicitly assumed to be independent of the surfactant concentration. The undulation free energy of Helfrich [2] for lamellar phases and the ideal scaling law of Porte *et al.* [48] for sponge phases are prominent examples of this. To see the bending moduli and Φ coupled therefore calls for caution in the application of such laws. Second, it is often argued (indeed, as by some of us [49]) that the monolayer spontaneous curvature plays a dominating role as a controlling parameter in surfactant systems, by determining the stability of the competing phases. We see here that apart from in certain special limits, the other moduli are as least as sensitive to changes in system parameters. This complicates the picture for ionic systems; for example, changes in monolayer topology may be induced through changes in either salt or surfactant concentration, judging by our results for k_c, as this couples to the Gaussian curvature K.

We have also seen, in Fig. 4, that the choice of constraints on bending the surface will significantly affect the value of the bending modulus. As we have argued throughout, it appears as though curvature changes with the salt and water chemical potentials fixed are least penalized. Note the interesting behavior, in Fig. 4, of the upper two curves at the extremes of both vanishing and excess salt.

Another point of interest is as to whether the system is stabilized or destabilized, at harmonic order in the curvatures, by electrostatic effects. Referring to our results presented in Fig. 5, we deduce that electrostatics acts to stabilize the system at high salt and surfactant concentrations, but at low concentrations can play a destabilizing role. In the latter case, higher-order (anharmonic) terms in the curvature energy are required to stabilize the system, a point to which we shall return shortly.

The effect of tuning the surface charge density, as depicted in Fig. 6, does give an interesting indication that the three moduli do behave distinctly. The bending modulus k_c does seem to saturate and thus behaves like a ''far-field'' quantity. In the spirit of Manning's theory, it could well be calculated from the formula of Winterhalter and Helfrich [4] developed in the Debye-Hückel limit, but with an effective surface charge density. In contrast, k_c appears to not be fully

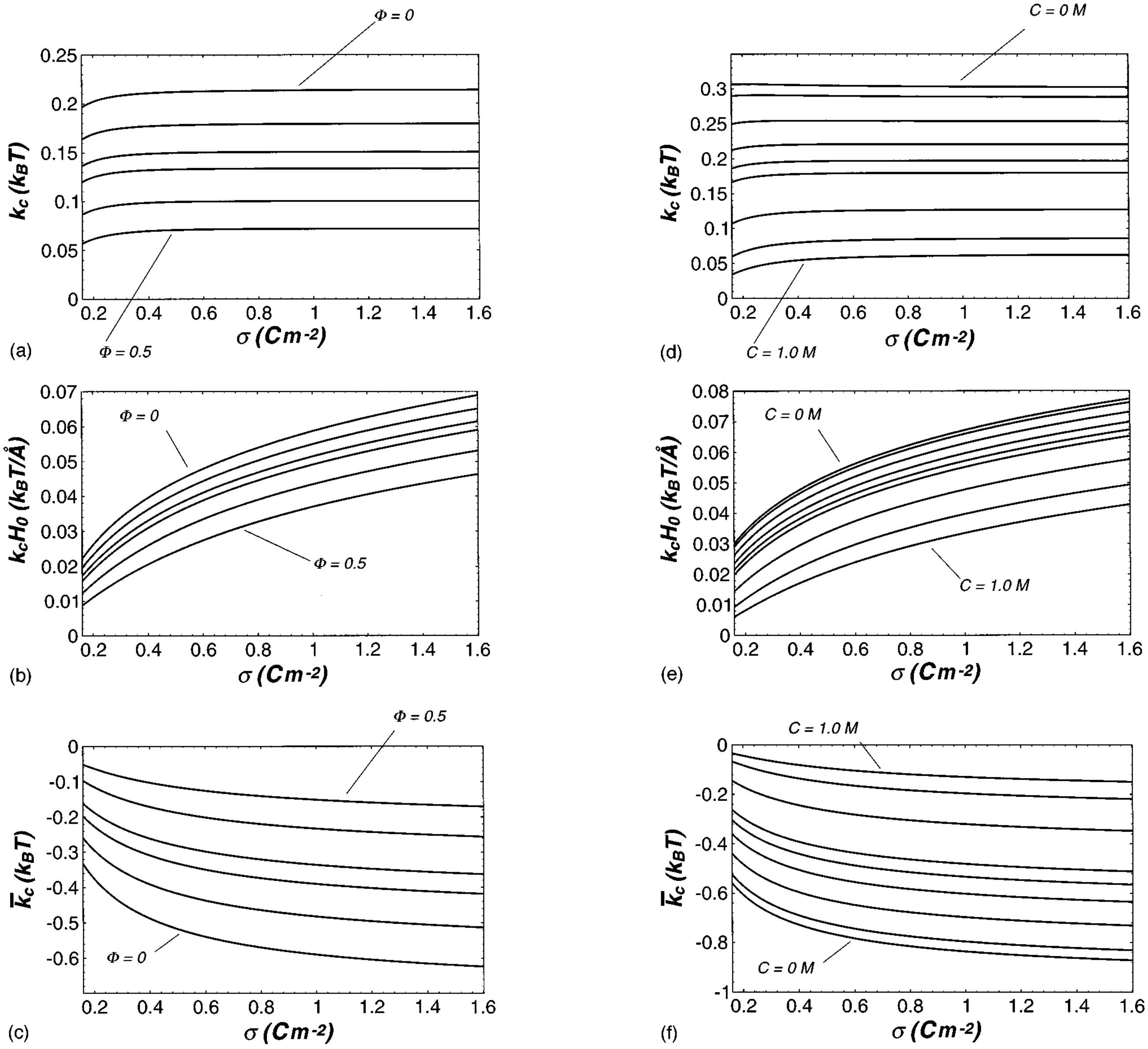

FIG. 6. Dependence of the moduli on the magnitude of the surface charge density σ. Plots (a)–(c) are for C fixed at $0.1M$, and $\Phi = 0$, 0.15, 0.25, 0.3, 0.4, and 0.5; (d)–(f) for Φ fixed at 0.2 and $C = 0$, 0.005, 0.02, 0.04, 0.06, 0.08, 0.2, 0.5, and $1.0M$.

saturated, even for $\sigma = 1.6\ \mathrm{Cm}^{-2}$, and saturation for $k_c H_0$ seems far off. This hierarchy can in some way be understood from the expressions for the moduli given as Eq. (25). It is clear that $k_c H_0$ is "more" of a near-field quantity than k_c, as the former is the first, while the latter is the second, moment of the same quantity (essentially the square of the electric field). Thus there is a relatively heavy weighting in $k_c H_0$ for the near-field (condensed) counterions, but this is reduced for k_c. It is not so clear why k_c behaves as the "farthest-field" quantity, as it depends in a more complicated way on the planar potential. However, our results clearly show this to be the case, indicating a subtlety in the consideration of the condensation phenomenon for quantities, such as the bending moduli, which involve integration over the ionic atmosphere.

A question that we have only partially answered so far is an important one: In terms of the electrostatic contribution, how valid is the harmonic approximation to the curvature energy? We have indicated above that anharmonic terms might well be necessary to stabilize certain systems, supporting the suggestion of de Vries [24] in regard to passages in lamellar phases, and also that made previously by some of us in the context of microemulsions and sponge phases [50]. In order to rectify this, we show in Fig. 7 plots for $\partial g/\partial(1/R)$ for the cylindrical geometry, calculated from Eq. (6) using a full numerical solution of the Poisson-Boltzmann equation. In Fig. 7(a), we give such plots for the three constraints, for $\Phi = 0.372$ and $C = 0.363M$. Plotted also are the predictions of the harmonic approximation, which appear as tangent lines at the point $1/R = 0$. Note the deviation as the radius is decreased, but also that even at $R = 10$ Å, there is only approximately a 10% difference between the full curves and the corresponding harmonic approximations. The difference is more dramatic for the case of Fig. 7(b), where we have made a similar plot, but for $\Phi = 0.5$ and $C = 0.05M$. The deviations are much sharper and the harmonic approximation

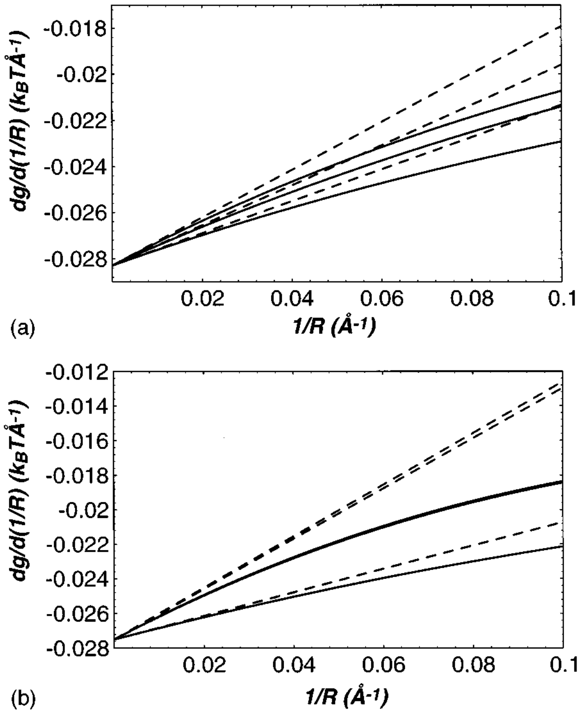

FIG. 7. Plot of the curvature dependence of the full free-energy density of the cylindrical geometry (a) for $\Phi=0.372$ and $C=0.363M$ and (b) $\Phi=0.5$ and $C=0.05M$. In both cases, the full curves, from top to bottom, correspond to the cases of a fixed amount of salt and water, a fixed amount of water and salt chemical potential, and fixed chemical potentials of both salt and water. The dashed lines are the harmonic approximations to these curves.

soon breaks down as the radius of curvature is decreased, other than for the case of both salt and water chemical potentials being fixed, where it remains quite reasonable. Note also that the full curves for the other two constraints effectively collapse onto one another.

We now turn to discuss some recent experimental studies that have attempted to measure the bending moduli of ionic surfactant layers. The measurement of the rigidity of surfactant layers presents considerable difficulties, but recently progress has been made using various experimental methods. Kellay *et al.* [51] give an extensive review of such measurements, in particular cataloging in some detail recent measurements of k_c for AOT systems, and we refer the reader to their list of references. The methods used include neutron scattering, the Kerr effect, laser T-jump experiments, and time-resolved flourescence quenching. Kellay *et al.* themselves employ ellipsometry to measure the moduli of AOT droplet systems. However, as shown in the comparison of results given in Ref. [51], the range of reported values for k_c, even for exactly the same system, can differ by an order of magnitude and are therefore problematic to analyze. An interesting recent development has been the use of quadrupole splittings in NMR spectra in the measurement of k_c for lamellar phases of ionic surfactant [52,53]; however, these measurements as presented are mainly concerned with nonelectrostatic effects, such as the chain length of added cosurfactant [53]. Kegel *et al.* [54] have recently used ellipsometry to measure such effects. In contrast, recent papers have appeared that deal with systems where a small amount of ionic surfactant is added to a nonionic system and thus the aim is to directly measure electrostatic effects. Schomäcker and Strey [55] have made measurements, using light scattering, of the Bragg-peak shift of a nonionic lamellar phase upon the addition of ionic surfactant. These results are in a regime (small amount of added salt, low surfactant concentration) where our results would be useful for a full analysis [56]. Also, we note that Rajagopalan *et al.* [57] have investigated the effect of adding a small amount of ionic surfactant to a nonionic system; however, these authors offer the alternative interpretation of electrostatic effects as a curvature stress on the nonionic monolayer and hence electrostatics and elasticity are effectively decoupled in their treatment.

So we await further progress on the experimental front. There is also more that can be done at the theoretical level. Some extensions are relatively straightforward, such as the allowance for a change in the surface charge density on bending (corresponding to constant surface potential or mixed boundary conditions), while others, such as the explicit calculation of the moduli associated with anharmonic curvature terms [27], are much more involved.

V. CONCLUDING REMARKS

We have, herein, presented results that extend our knowledge of the dependence of the phenomenological parameters of the flexible surface model on the fundamental quantities relevant to ionic surfactant systems. The important conclusion that we have drawn is that the electrostatic contribution to the moduli is significantly dependent upon the surfactant concentration, even for systems with added salt. We have also provided perturbative solutions to the Poisson-Boltzmann cell model for cylindrical and spherical systems, investigated the effect of counterion condensation on the moduli, and considered the validity of the harmonic approximation to the electrostatic curvature free energy. All of these results point to yet another manifestation of the subtlety of electrostatic effects in colloidal systems; despite this we conclude that the flexible surface model remains an attractive approach in rationalizing the behavior of surfactants in solution.

ACKNOWLEDGMENTS

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APPENDIX A: PLANAR SOLUTION

Here we briefly recount the solution of the PB equation for the geometry of two charged planes with intervening salt solution. The treatment here is based on that by Jönsson and Wennerström [29], where (unlike other studies) it was not assumed that an equilibrium existed between the system and a reference salt solution, so that the system is self-contained: this is the situation most relevant to the current problem. All symbols (unless stated otherwise) are as defined in Sec. II of the main text. The boundary conditions are those given in Eqs. (17a) and (17c).

The PB equation for planar geometry is

$$\phi_0''=2(\alpha_0 e^{\phi_0}-e^{-\phi_0}), \tag{A1}$$

where the scaled planar potential ϕ_0 is zeroed at the midplane [see Fig. 1(b)]. By symmetry, we need treat only one-half of the geometry. (This subsystem is in fact the reference state for the bending perturbation using the cell model, to be precise.) The first integration of (A1) gives

$$(\phi_0')^2=4[e^{-\phi_0}-1+\alpha_0(e^{\phi_0}-1)]. \tag{A2}$$

With the substitution $\sin^2\rho=e^{\phi_0}$, the next integration becomes possible and yields

$$x=u-u(0), \tag{A3}$$

where $u\equiv F(\rho,\alpha_0^{1/2})$ is the incomplete elliptic integral of the first kind of modulus $\alpha_0^{1/2}$ [42] and $u(0)$ indicates its value at the surface. It will also be useful to rewrite Eq. (A2) in terms of Jacobi elliptic functions [42]

$$(\phi_0')^2=4\,\mathrm{cs}^2u\,\mathrm{dn}^2u. \tag{A4}$$

APPENDIX B: DEVELOPMENTS OF THE CURVATURE EXPANSION AND MODULI FORMULAS

1. Development of the free-energy *R* dependence integral

Further simplification of Eq. (5) may be achieved as follows. Consider multiplication of Eq. (2) by $r(d\psi/dr)$ and then integration over V; thus

$$\int_V dV r\frac{d\psi}{dr}\nabla^2\psi=\frac{4\pi q}{\varepsilon}\int_V dV r\frac{d\psi}{dr}(n_-^c e^{\beta q\psi}-n_+^c e^{-\beta q\psi}). \tag{B1}$$

Evaluation in the cylindrical case gives

$$\int_V dV(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi}) =\left[\pi r^2 L\left\{(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi})-\beta\frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dr}\right)^2\right\}\right]_R^{R+d} \tag{B2}$$

and in the case of the spherical geometry

$$\int_V dV(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi}) =-\frac{1}{3}\beta E_{\rm el}+\left[\frac{4}{3}\pi r^3\left\{(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi})-\beta\frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dr}\right)^2\right\}\right]_R^{R+d}. \tag{B3}$$

This then allows elimination of this term, i.e., the total number of ions N, from the right-hand side of Eq. (5), yielding in the case of the cylinder (of length L)

$$\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\rm tot}}=\frac{1}{2\pi L}\left\{-E_{\rm el}+\left[-\pi r^2 L\frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dr}\right)^2+\beta^{-1}\pi R^2 L(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi})\right]_R^{R+d}\right\} \tag{B4}$$

and in the case of the sphere

$$\left(\frac{\partial g}{\partial(1/R)}\right)_{A_{\rm tot}}=\frac{1}{3\pi R}\left\{-E_{\rm el}+\left[-\pi r^3\frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dr}\right)^2+\beta^{-1}\pi R^3(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi})\right]_R^{R+d}\right\}. \tag{B5}$$

The final step may be achieved by multiplication of Eq. (2) by $d\psi/dr$, followed by one-dimensional integration in r

$$\int_R^{R+d} dr\frac{d\psi}{dr}\nabla^2\psi=\frac{4\pi q}{\varepsilon}\int_R^{R+d} dr\frac{d\psi}{dr}(n_-^c e^{\beta q\psi}-n_+^c e^{-\beta q\psi}), \tag{B6}$$

so that

$$\chi\int_R^{R+d} dr\frac{1}{r}\left(\frac{d\psi}{dr}\right)^2 =\frac{4\pi}{\varepsilon}\left[-\frac{\varepsilon}{8\pi}\left(\frac{d\psi}{dr}\right)^2+\beta^{-1}(n_-^c e^{\beta q\psi}+n_+^c e^{-\beta q\psi})\right]_R^{R+d} \tag{B7}$$

(where $\chi=1$ for the cylinder and $\chi=2$ for the sphere). This is then used to eliminate all of the boundary terms from Eqs. (B4) and (B5), thus yielding Eq. (6).

2. Development of the integral form for $\overline{k_c}$

In order to obtain Eq. (25c) we proceed as follows. Equation (24) gives initially for k_c

$$\overline{k_c}=-\frac{\varepsilon}{4\pi\kappa\beta^2q^2}\times\int_0^{D_0}dx\,x\{x(\phi_0')^2+2\phi_0'(\phi_1'^{(\rm sph)}-2\phi_1'^{(\rm cyl)})\}. \tag{B8}$$

Now, it is clear from (16b) that if one replaces ϕ_1, α_1, and γ_1 by $\chi\phi_1$, $\chi\alpha_1$, and $\chi\gamma_1$, then χ cancels from the defining differential equation for ϕ_1. Similarly, the boundary conditions $\phi_1(D_0)=0$ and $\phi_j'(0)=0$ remain unaltered by such a change. Now, we discuss the constraints. In the case considered in Sec. II C 1 of constant salt and water chemical potentials, there is *ab initio* no problem as α_1 and ν_1 are zero then. In the constant μ_s and V case, a combination of Eqs. (17b) and (21) to eliminate D_1 gives

$$\phi_1'(D_0) = \frac{\chi}{2} D_0^2 \phi_0''(D_0), \tag{B9}$$

which is again insensitive to the above replacements. Finally, in the third case of fixed V and N, this last equation also applies, along with Eq. (23), which is also patently insensitive to the above reassignment. Hence the differential equation, all boundary conditions, and constraints considered being insensitive to this transformation mean that $\phi_1^{(\mathrm{sph})} \equiv 2\phi_1^{(\mathrm{cyl})}$. This gives Eq. (25c). We note that Bedeaux and co-workers [25] have made related observations regarding the independence of k_c on perturbations of the planar state.

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