

# Membrane Curvature Elasticity in Weakly Charged Lamellar Phases

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We study the effect of electrostatic interactions on the membrane bending energies of weakly charged, swollen, lamellar phases of surfactant solutions. We treat the surface charge density of the lamellae as a constant and consider only situations where it is low enough so that the distance  $2d$  between lamellae is the smallest relevant length scale in the problem. In the presence of salt (the short-distance Debye-Hückel regime) we show that the electrostatic contribution to the bending energy of a membrane is in general small, in disagreement with a previous result, is proportional to  $d^3$ , and is independent of ionic strength. Identical results are obtained for membranes undulating sinusoidally in phase and for concentric cylindrical membranes. The bending constant is also calculated for membranes held at constant electric potential and is compared to the constant charge density case. In the absence of salt, continuity arguments predict an electrostatic contribution to the bending energy that scales as  $d^3$ . Furthermore, a direct calculation for concentric cylindrical membranes gives *exactly* the same scaling behavior (including the numerical prefactor) as in the presence of salt.

## 1. Introduction

Amphiphilic molecules in solution exhibit many self-organizing features.<sup>1,2</sup> Among other mesophases, lamellar phases consisting of alternating layers of amphiphilic and solvent molecules are observed over a wide range of surfactant concentrations. The lamellar structure takes the form of stacks of surfactant bilayers separated by coherent regions of solvent (either polar or nonpolar), and as a function of solvent dilution, intermembrane spacings up to several thousand angstroms have been observed.<sup>3,4</sup> The lamellar phases are stabilized by a variety of repulsive interactions between membranes. In particular, individual membranes have a very low surface tension and may undergo strong thermally induced out-of-plane undulations; Helfrich<sup>5</sup> has argued that a repulsive interaction of entropic origin results from the confinement of each fluctuating membrane between its adjacent neighbors. The strength of this steric repulsion is controlled by the bending elasticity of the membranes and can be described by the bending moduli  $k_c$  and  $\bar{k}_c$  of mean and Gaussian curvature, respectively. Note that  $\bar{k}_c$  is relevant only when the topology of the membranes changes.

In the case of electrically neutral lamellar phases, such as those obtained by oil dilution, the bending moduli are determined by molecular packing considerations in the bilayers and are typically of the order of the thermal excitation energy  $T$  (in units where the Boltzmann constant  $k_B$  is set to unity). This implies very flexible membranes in swollen lamellar phases. For sufficiently high dilutions,

the Helfrich forces dominate over other interactions and are responsible for the very large intermembrane spacings observed.<sup>6</sup>

In the case of water dilution, other interactions become relevant. The short range hydration forces, for instance, prevent membranes from adhering to one another.<sup>7</sup> If the lamellar phase is made of ionic surfactants, the repulsive Coulombic interactions contribute to the stability of the structure. The electrostatic interaction combines with the Helfrich interaction in a nontrivial way: it modifies the bending rigidity of each membrane and can thus change the nature of the out-of-plane fluctuations that drive the steric repulsions. At low ionic strength (in the absence of added salt), if the membranes are highly charged, Coulombic interactions between adjacent membranes are not screened and dominate over the Helfrich interactions.<sup>6,8,9</sup> The lamellar phase is then formed by relatively flat, inflexible membranes with a renormalized bending modulus which can be in general larger than the intrinsic value. Upon addition of salt, the membranes regain their intrinsic flexibility and the intermembrane interactions are once again determined by the repulsive Helfrich interactions. In intermediate conditions of ionic strength and membrane surface charge density, both interactions play a role. Recent X-ray scattering experiments on lamellar phases of surfactant membranes diluted by oil, by pure water, and by brine are in qualitative agreement with this description.<sup>6</sup>

Recent theoretical effort has focused on determining the electrostatic contribution to the bending modulus of mean curvature  $\delta k_c$  in different regimes of membrane surface charge density and aqueous electrolyte strength. It is convenient to characterize these regimes in terms of

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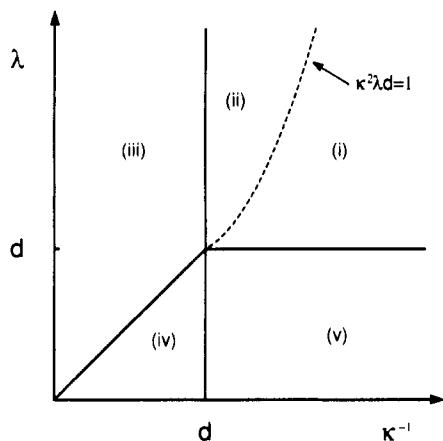
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**Figure 1.** Diagram of membrane bending modulus regimes as a function of  $d$ ,  $\lambda$ , and  $\kappa^{-1}$ . Regions i and ii are the ideal gas and short-distance Debye-Hückel regimes, respectively. We find that, in contrast to previously reported results, the electrostatic contribution to the bending modulus in both these regimes scales as  $\delta k_c \sim Td^3/\lambda^2 l$ . Thus, in terms of the scaling of  $\delta k_c$ , the distinction between the ideal gas and short-distance Debye-Hückel regimes is somewhat arbitrary, as indicated by the dashed boundary separating these regimes. Region iii is the usual Debye-Hückel regime with  $\delta k_c \sim T/\kappa^3 \lambda^2 l$ . For regions i-iii, the electrostatic contribution to  $\delta k_c$  is very weak. Region iv is the intermediate regime with  $\delta k_c \sim T/\kappa l$ , while region v is the Gouy-Chapman regime with  $\delta k_c \sim Td/l$ . In these latter two regimes the electrostatic contribution to  $\delta k_c$  is quite large.

three characteristic length scales: the mean membrane separation  $2d$ , the Debye-Hückel screening length  $\kappa^{-1} = (8\pi n_\infty l)^{-1/2}$ , and the Gouy-Chapman length  $\lambda = e/2\pi l\sigma$ , where  $n_\infty$  is the nominal bulk electrolyte concentration,  $\sigma$  is the (negative) surface charge density per membrane side,  $e$  is the electronic unit charge,  $l = e^2/4\pi\epsilon_w T$  is the Bjerrum length, and  $\epsilon_w$  is the dielectric constant of the aqueous solvent (for water,  $\epsilon_w \simeq 80$ , implying  $l \simeq 7 \text{ \AA}$ ). In Figure 1, we present schematically the different electrostatic regimes as function of  $\lambda$  and  $\kappa^{-1}$  for a fixed  $d$ . In the limit of high electrolyte concentration (region iii) ( $\kappa d > 1$  and  $\kappa \lambda > 1$ ), the solution of the linearized Poisson-Boltzmann (PB) equation for several geometries<sup>8,10-12</sup> all indicate that the electrostatic contribution to the bending constant  $\delta k_c$  is independent of  $d$  and given by

$$\delta k_c = \frac{3T}{4\pi\kappa^3 l \lambda^2} \quad (1)$$

An additional linear PB regime at short distances ( $\kappa d < 1$  but  $\kappa^2 d \lambda > 1$ ) has been identified and studied<sup>8</sup> (region ii in Figure 1); in this short-distance Debye-Hückel regime,  $\delta k_c$  was found to scale as

$$\delta k_c \sim \frac{T}{\kappa^3 l \lambda^2 (\kappa d)^3} \quad (2)$$

For somewhat weaker electrolyte or higher surface charge densities ( $\kappa d > 1$  and  $\kappa \lambda < 1$ , called hereafter the "intermediate regime"—region iv) the solution of the non-linear PB equation gives<sup>13-16</sup>

$$\delta k_c = T/\pi\kappa l \quad (3)$$

On the basis of these results for the Debye-Hückel and intermediate regimes quoted above, scaling relations for

**Table I.** Scaling Behavior of  $\delta k_c$  for the Case of Constant Surface Charge Density

regime	region of Figure 1	$\delta k_c$
ideal gas <sup>a</sup>	i	$Td^3/\lambda^2 l$
short distance Debye-Hückel <sup>a</sup>	ii	$Td^3/\lambda^2 l$
Debye-Hückel	iii	$T/\kappa^3 \lambda^2 l$
intermediate	iv	$T/\kappa l$
Gouy-Chapman	v	$Td/l$

<sup>a</sup> New results reported in this work.

the limits of low salt and high surface charge density ( $\lambda < d < \kappa^{-1}$ , called the "Gouy-Chapman" regime—region v), and of low salt and low surface charge density ( $d < \lambda$  and  $\kappa^2 d \lambda < 1$ , called the "ideal gas" regime—region i) were proposed, and a coherent picture of the behavior of charged lamellar phases was presented.<sup>8</sup> Subsequent theoretical calculations<sup>9</sup> confirmed the proposed scaling behavior of  $\delta k_c$  in the Gouy-Chapman regime

$$\delta k_c \sim Td/l \quad (4)$$

In the Gouy-Chapman and intermediate regimes, eqs 3 and 4, the electrostatic contribution to the bending modulus can be in general larger than the intrinsic value and the total bending modulus is larger than  $T$ . Strongly charged membranes thus have small undulations and may be viewed as essentially flat.

There are, however, several puzzling features remaining in the short distance and low charge regimes (regions i and ii). For instance, in the ideal gas regime  $\delta k_c$  was conjectured to scale as  $\delta k_c \sim T\lambda/l$ , i.e., increasing with decreasing membrane surface charge density.<sup>8</sup>

In this paper, we re-examine the short distance and low surface charge limits of swollen lamellar phases. As in our earlier work, this is done at the Poisson-Boltzmann mean field level, and all nonelectrostatic interactions such as van der Waals and hydration interactions are ignored. This is justified for relatively dilute lamellar systems. In section 2, we give a derivation of  $\delta k_c$  in the short-distance Debye-Hückel limit for a stack of undulating membranes and show that our result is identical to that computed for membranes arranged in a concentric cylinder geometry. Then, we briefly compared this result with  $\delta k_c$  obtained for membranes held at constant electric potential. In section 3, we give an estimate of  $\delta k_c$  for the ideal gas regime obtained by an expansion of an exact result for the electrostatic potential between concentric charged cylinders without electrolyte. Finally, in section 4 we discuss our results in relation to previous theories, and their relevance to experiments. The final results for  $\delta k_c$  in all regimes for the case of constant surface charge density are summarized in Table I.

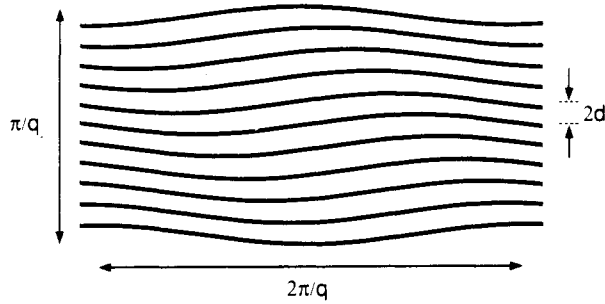
## 2. Short-Distance Debye-Hückel Regime

**2.1. Constant Surface Charge Density.** We consider a stack of membranes of mean separation  $2d$  and with mean orientation parallel to the  $x$ - $y$  plane in a polar solvent of dielectric constant  $\epsilon_w$  (water) and bulk electrolyte concentration  $n_\infty$ . We assume that an individual membrane has thickness  $t$  and consists of a bilayer of negatively charged amphiphilic molecules separated by a thin layer of nonpolar solvent of dielectric constant  $\epsilon_{oil}$ , and that each side of the membrane has a uniform charge density  $-\sigma$ . In the short-distance Debye-Hückel limit,  $\kappa d < 1$  but  $\kappa^2 d \lambda > 1$ , the electrostatic potential between membranes obeys the linearized Poisson-Boltzmann (PB) equation<sup>2,8</sup>

$$\nabla^2 \phi = \kappa^2 \phi \quad (5)$$

where  $\phi(\vec{r})$  is the electrostatic potential at  $\vec{r}$ .

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**Figure 2.** Sketch of a stack of undulating charged membranes. Membranes are assumed to have average intermembrane separation  $2d$ , and undulations of wavelength  $2\pi/q_{\parallel}$  and relative phase  $2dq_{\perp}$ . Undulation amplitudes are shown exaggerated for effect; actual membranes are assumed to have low amplitude ( $u_0 \ll d$ ), long wavelength fluctuations ( $q_{\parallel}d \ll 1$ ) with small intermembrane phase angle ( $q_{\perp}d \ll 1$ ).

This equation is subject to appropriate boundary conditions on each membrane surface. In the linear Debye-Hückel regime, one can show<sup>17</sup> that if the thickness of a membrane  $t$  satisfies  $t \gg (\epsilon_{oil}/\epsilon_w)d$ , the energy stored in the electric field within a membrane is negligible, and the two sides of a membrane may therefore be considered as electrically independent. Typically,  $\epsilon_w/\epsilon_{oil} \approx 40$  and  $t \approx 20$  Å, so this requirement is not unreasonable for the small membrane separations we are considering.<sup>18</sup> In this case, we may solve eq 5 separately in each intermembrane region subject to the boundary condition  $\hat{n} \cdot \vec{\nabla} \phi = \sigma/\epsilon_w$  on either surface of each membrane, where  $\hat{n}$  is the local unit vector normal to the membrane surface.

In order to compute the electrostatic contribution to the membrane bending moduli, we must solve the linearized PB equation with the above boundary conditions for fluctuating membranes. In analogy with the hydrodynamics of smectic liquid crystal phases, we will consider small amplitude, long wavelength membrane undulations about the mean membrane positions of the form

$$u(x, z) = u_0 \cos(q_{\parallel}x + q_{\perp}z) \quad (6)$$

where we restrict our attention for convenience to membrane fluctuations with  $q_{\parallel}$  in the  $x$ -direction and where we assume  $u_0 \ll d$ ,  $q_{\parallel}d \ll 1$ ,  $q_{\perp}d \ll 1$ , and that  $u(x, z)$  is to be evaluated at the mean membrane positions  $z = 2nd$  for all integers  $n$ , as depicted in Figure 2.

In the smectic description,<sup>19</sup> one considers the lamellar phase as a stack of membranes, each having a spatially-averaged free energy per unit volume  $\mathcal{G} \equiv F/V$  of the form<sup>20</sup>

$$\mathcal{G} = \mathcal{G}_0 + \frac{1}{4}K q_{\parallel}^4 u_0^2 + \frac{1}{4}B q_{\perp}^2 u_0^2 + O(u_0^4) \quad (7)$$

where  $K$  and  $B(q_{\parallel})$  are respectively the splay constant and the bulk compressional modulus of the lamellar structure. Rather than the lamellar free energy per unit volume  $\mathcal{G}$ , we use the free energy per unit area of one membrane  $\mathcal{F} = F/A = 2\mathcal{G}d$

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{4}k_c q_{\parallel}^4 u_0^2 + \frac{1}{2}dB(q_{\parallel})q_{\perp}^2 u_0^2 + O(u_0^4) \quad (8)$$

where  $\mathcal{F}_0$  is the  $q$ -independent part of the free energy density and  $k_c = 2dK$  is the modulus of bending rigidity of one membrane. We ignore the effects of Gaussian

curvature and surface tension, as is appropriate for membranes of fixed genus that have self-assembled from solution.

The general solution to eq 5 between membranes subject to the spatial periodicity imposed by eq 6 may be written as a Fourier series:

$$\phi(x, z) = \sum_{n=-\infty}^{\infty} [A_n \exp(q_n z) + B_n \exp(-q_n z)] \exp(inq_{\parallel}x) \quad (9)$$

where  $q_n^2 = \kappa^2 + (nq_{\parallel})^2$  and  $A_n$  and  $B_n$  are determined in each intermembrane region from the boundary conditions; the dependence of  $\phi$  on  $u_0$ ,  $\sigma$ ,  $d$ , and  $q_{\perp}$  stems from these boundary conditions. The free energy per unit area  $\mathcal{F}$  is the sum of an electrostatic contribution and of the translational entropy of the small ions. It can be shown that this free energy per unit area may be written as<sup>21,22</sup>

$$\mathcal{F} = \frac{1}{2A} \int_{\Sigma_1 \cup \Sigma_2} dS \sigma \phi \quad (10)$$

where  $\Sigma_1$  and  $\Sigma_2$  denote the upper and lower surfaces of an undulating membrane, and  $dS$  is the membrane area element. Only terms of order  $u_0^2$  in eq 10 are relevant for the determination of the membrane bending modulus. Hence, we need only to calculate  $\phi$  to order  $u_0^2$ . Furthermore, only the  $n = 0, \pm 1$  terms in eq 9 are important, and we find

$$\begin{aligned} \phi(x, z) = & \frac{\sigma}{\epsilon_w \kappa} \left\{ \left[ 1 + \frac{1}{4}(q_{\parallel}u_0)^2 \right] \frac{\cosh(\kappa z)}{\sinh(\kappa d)} + \right. \\ & (\kappa u_0) \frac{\kappa}{2q_1} \coth(\kappa d) [\cosh[q_1(z-d)] \cos(q_{\parallel}x) - \\ & \left. \cosh[q_1(z+d)] \cos(q_{\parallel}x + 2q_{\perp}d)] / \{\sinh(q_1 d) \times \right. \\ & \left. \cosh(q_1 d)\} - \frac{(\kappa u_0)^2}{4} \left[ 1 + \frac{\kappa}{q_1} \coth(\kappa d) \times \right. \\ & \left. \left. \left( \frac{\cos(2q_{\perp}d) - \cosh(2q_1 d)}{\sinh(q_1 d) \cosh(q_1 d)} \right) \right] \frac{\cosh(\kappa z)}{\sinh(\kappa d)} \right\} \quad (11) \end{aligned}$$

The desired membrane free energy density is obtained by performing the integral given in eq 10 using  $\phi$  of eq 11 in the limit of  $\kappa d \ll 1$ , and then expanding the result around  $q_{\parallel} = 0$  and  $q_{\perp} = 0$ . The free-energy may be written in the form

$$\begin{aligned} \mathcal{F} = & \frac{\sigma^2}{2\epsilon_w \kappa} \left\{ \frac{2}{\kappa d} + \frac{2\kappa d}{3} - \frac{2(\kappa d)^3}{45} + \right. \\ & \left[ \frac{q_{\parallel}^2}{\kappa d} + \frac{(\kappa d)^3 q_{\parallel}^2}{45} + \frac{2(\kappa d)^3 q_{\parallel}^4}{15\kappa^2} \right] u_0^2 + \\ & \left. \left[ \frac{\kappa^2 - q_{\perp}^2}{(\kappa d)^3} + \frac{q_{\perp}^4}{\kappa^2 (\kappa d)^3} + O(\kappa d)^{-1} \right] d^2 q_{\perp}^2 u_0^2 \right\} \quad (12) \end{aligned}$$

where  $O(\kappa d)^{-1}$  indicates that we have omitted, for the sake of brevity, all but the lowest order  $\kappa d$  terms in the coefficient of  $q_{\perp}^2 u_0^2$ .

The term in the free energy proportional to  $q_{\perp}^2 u_0^2$  gives the electrostatic contribution to the compressional modulus, while the term proportional to  $q_{\parallel}^4 u_0^2$  gives the electrostatic contribution to the bending modulus in the short-distance Debye-Hückel regime

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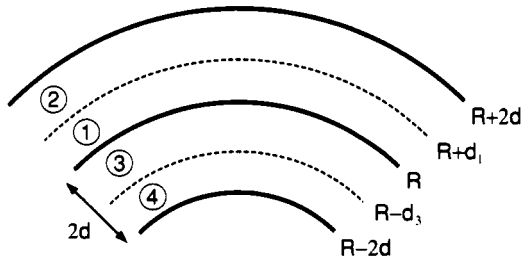
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**Figure 3.** Sketch of a section of concentric cylindrical charged membranes showing three membranes with radii of curvature  $R + 2d$ ,  $R$ , and  $R - 2d$  for  $d \ll R$ . The electric field between membranes vanishes on the dashed curves at  $R + d_1$  and  $R - d_3$ , separating the space between membranes into regions 1 to 4.

$$\delta k_c = \frac{4}{15\pi} \frac{T}{\lambda^2 l} d^3 \quad (13)$$

where  $\lambda = e/2\pi l\sigma$  and  $l = e^2/4\pi\epsilon_w T$  were defined in section 1. Note that this result is independent of the screening length  $\kappa^{-1}$  or equivalently the ionic strength  $n_{\infty}$ . Furthermore, this scaling of  $\delta k_c$  with  $d$ ,  $\delta k_c \sim d^3$ , differs by six powers of  $\kappa d$  from previously reported results,<sup>8</sup>  $\delta k_c \sim d^{-3}$ , quoted in eq 2. This difference is not surprising and can be understood from the essentially different nature of membrane undulations assumed for each calculation. The present calculation treats an entire stack of fluctuating membranes in the limit of long wavelength fluctuations ( $q_{\parallel}d \ll 1$ ) and small intermembrane phases ( $q_{\perp}d \ll 1$ ), whereas in ref 8 the membrane free energy density was obtained for two charged membranes undulating out of phase ( $2q_{\perp}d = \pi$ ). One expects that in the latter geometry the free energy contains contributions from the compressional modulus in addition to the bending terms. Indeed, eq 12 contains the scaling relation of ref 8 as the coefficient of a term in  $q_{\perp}^2 u_0^2$ , indicating that it is a part of a  $q$ -dependent correction  $\delta B(q_{\parallel})$  to the compressional modulus  $B(q_{\parallel}) = B_0 + \delta B(q_{\parallel})$

$$\delta B(q_{\parallel}) = -B_0 \frac{q_{\parallel}^2}{\kappa^2} \left( 1 - \frac{q_{\parallel}^2}{\kappa^2} \right) + O(\kappa d)^{-2} \quad (14)$$

where  $B_0 = \sigma^2/\epsilon_w(\kappa d)^2 = T/\pi\lambda^2 l(\kappa d)^2$  is the average electrostatic contribution to the compressional modulus.

As a check of our result for  $\delta k_c$ , we repeated the calculation for fixed concentric cylindrical membranes of separation  $2d$ , as shown in Figure 3, in the short-distance Debye-Hückel limit. The bending modulus in this case is given by the coefficient of the  $1/2R^2$  term in an expansion in  $d/R$  of the free energy density for a membrane with radius of curvature  $R \gg d$ . Since the calculation is tedious but quite straightforward its details are not given here. The resulting expression for  $\delta k_c$  is, however, identical to the one given in eq 13 for the case of a planar stack of undulating membranes. In fact, one can show that these two geometries give the same bending modulus for any value of  $\kappa d$ .

**2.2. Constant Surface Potential.** Another case of interest where the bending constant can be calculated is the case of two conducting and undulating membranes, in which the membranes are kept at a constant potential  $\phi_0$ . The free energy in the linear Debye-Hückel regime for two such membranes with well-defined wavevector  $q_{\parallel}$ , and amplitude  $u_0$ , and with a relative phase shift  $\theta$  has been given.<sup>11</sup> In terms of our notation,  $\theta = 2q_{\perp}d$  and the undulation profiles of the two membranes are  $u_0 \cos(qx)$  and  $u_0 \cos(qx + 2q_{\perp}d)$ , respectively. Since the phase between the two undulating membranes  $\theta = 2q_{\perp}d$  is kept as a parameter, the electrostatic free-energy and the bending constant depend on this phase angle.

Expanding the free energy to order  $u_0^2$ , the  $q$ -dependent part of the free energy can be written as<sup>11</sup>

$$\mathcal{F} = \mathcal{F}_0 - \frac{1}{2}\epsilon_w\phi_0^2\kappa^2q_{\parallel}^2 \tanh^2(\kappa d) \left( \tanh^{-1}(2q_{\perp}d) + \frac{1}{2} \sinh^{-1}(2q_{\perp}d) \cos(2q_{\perp}d) \right) u_0^2 \quad (15)$$

where  $\mathcal{F}_0$  is the electrostatic free energy for two flat membranes, and  $q_{\perp}^2 = \kappa^2 + q_{\parallel}^2$ . Expanding eq 15 to fourth order in  $q_{\parallel}$  and then looking only at the short-distance Debye-Hückel limit ( $\kappa d \ll 1$ ), we obtain the following electrostatic contribution for the bending modulus  $\delta k_c$

$$\delta k_c = \frac{\epsilon_w\phi_0^2}{90\kappa} (\kappa d)^5 (16 - 7 \cos(2q_{\perp}d)) \quad (16)$$

The above expression for  $\delta k_c$  is positive for any phase  $2q_{\perp}d$ ; i.e., electrostatic interactions always rigidify the membrane. As in the constant charge problem, the maximal rigidity is obtained in the case where  $2q_{\perp}d = \pi$ , corresponding to an out-of-phase mode of the two membranes, whereas the minimal rigidity is obtained for the (in-phase) undulation mode,  $2q_{\perp}d = 0$ .

It is interesting to compare the expression for  $\delta k_c$  for conducting and insulating charged membranes. In the latter, eq 16,  $\delta k_c \sim d^5$ , whereas in the former, eq 13,  $\delta k_c \sim d^3$ . Hence in the short-distance Debye-Hückel regime the bending constant does not scale in a universal way but depends on the specific details of the model. Note, however, that as  $\kappa d$  becomes large, the constant potential and constant surface charge density contributions to  $\delta k_c$  have the same scaling behavior.<sup>23</sup> Furthermore, it should be added that at a given potential  $\phi_0$ , in the short distance Debye-Hückel regime, the average induced charge density is  $\sigma_{\text{ind}} \sim \phi_0\epsilon_w\kappa^2d$ . Hence, the electrostatic contribution to the bending modulus can be written as  $\delta k_c \sim d^3\sigma_{\text{ind}}^2/\epsilon_w$ —to be compared with eq 13 for the constant surface-charge case.

### 3. Ideal Gas Regime

The limit of low electrolyte concentration and low surface charge density is called the ideal gas regime since the main contribution to the free energy is dominated by the counterion entropy and hence follows an ideal gas law. Previous conjectures for the scaling form of  $\delta k_c$  in the ideal gas regime were made on the basis of consistency with known scaling relations: one simply requires the ideal gas result to agree with the Gouy-Chapman and the short distance Debye-Hückel results at the crossover boundaries  $\lambda = d$  and  $\kappa^2\lambda d = 1$ , respectively. The proposed scaling form for  $\delta k_c$  in the Gouy-Chapman regime has been verified in a recent calculation.<sup>9</sup> However, as argued in section 2, the form of  $\delta k_c$  in the short-distance Debye-Hückel regime should be that given by eq 13. A consistency argument now indicates that the bending modulus in the ideal gas limit should scale as

$$\delta k_c \sim T \frac{d^3}{\lambda^2 l} \quad (17)$$

i.e., the same scaling form as in the short-distance Debye-Hückel regime ( $\delta k_c$  being independent of the ionic strength in this regime). One can check this conjecture by considering once again the concentric cylinder geometry. The exact solution of the full PB equation between two concentric charged cylinders *in the absence of added electrolyte* has been known for some time.<sup>24</sup> This solution

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can be used to obtain the free energy per unit area and bending modulus of a charged membrane in a concentric array of membranes in conditions of low surface-charge density,  $\lambda > d$ , and zero salt concentration,  $\kappa \rightarrow 0$ . The calculation closely follows that of ref 9 for the Gouy-Chapman regime, and hence an abbreviated derivation is given in the following.

Consider three membranes of radii of curvature  $R + 2d$ ,  $R$ , and  $R - 2d$ , respectively, selected from a concentric array of weakly charged membranes as shown in Figure 3. The region between membranes contains only dissolved counterions. The potential between two such cylinders is radially symmetric, and the electric field vanishes somewhere near the mid-point between the cylinders. We designate the radii at which the field vanishes by  $R + d_1$  and  $R - d_3$ . The positions of the membranes and of the zeros of electric field divide the space between the membranes into four regions, as indicated in Figure 3. In each region, the solution to the full PB equation for cylindrically symmetric potentials is given by

$$y(r) = \log \left[ \left( \frac{\kappa_1^2 r^2}{2\beta^2} \right) \sin^2 (\beta \log Ar) \right] \quad (18)$$

where  $y = e\phi/T$  is the dimensionless electrostatic potential,  $A$  and  $\beta$  are arbitrary constants to be determined by the boundary conditions, and  $\kappa_1^2 = n_1 e^2 / \epsilon_w T$ , where  $n_1$  is set by the choice of zero of potential. In accordance with the convention of ref 24,  $n_1$  is taken to be the average concentration of counterions between two membranes,  $n_1 = 2\sigma R / e[(R + d_1)^2 - R^2]$ .

The boundary conditions on the potential in each region require the electric field to vanish at  $r = R + d_1$  and  $r = R - d_3$ , and the normal component of the electric field on the surface of each membrane to be given by  $\vec{E} \cdot \hat{n} = -\sigma / \epsilon_w$ , where  $\sigma$  denotes the *magnitude* of the negative surface-charge density. In terms of  $y(r)$ , these conditions are  $|\nabla y| = 0$  on  $r = R + d_1$  and  $r = R - d_3$ , and  $\nabla y \cdot \hat{n} = 2/\lambda$  on each side of the membranes at  $r = R$ ,  $R - 2d$ , and  $R + 2d$ . Consider, for instance, region 1 of Figure 3. Application of these boundary conditions on  $y(r)$  from eq 18 to the counterion distribution in region 1 yields

$$1 + \beta_1 \cot [\beta_1 \log A_1(R + d_1)] = 0 \quad (19)$$

$$1 + \beta_1 \cot [\beta_1 \log A_1 R] = R/\lambda \quad (20)$$

In principle, these transcendental equations give  $\beta_1$  and  $A_1$  for any  $\lambda$ ,  $R$ , and  $d_1$ . However, we are only interested in their behavior in the limit of small  $d_1/\lambda$  and  $d_1/R$ , where an expansion can reduce these to simple algebraic equations. As we want to calculate the membrane bending constant, we must expand to order  $R^{-2}$ . The expansion of eq 19, along with eq 20, gives the value of  $\beta_1$

$$\beta_1 = \frac{R}{(d_1 \lambda)^{1/2}} \left[ 1 - \frac{d_1}{6\lambda} + \frac{11d_1^2}{360\lambda^2} + \frac{3d_1}{4R} \left( 1 - \frac{d_1}{18\lambda} - \frac{d_1^2}{40\lambda^2} \right) - \frac{d_1 \lambda}{2R^2} \left( 1 + \frac{23d_1}{48\lambda} - \frac{163d_1^2}{1440\lambda^2} \right) \right] + O(d_1/\lambda)^3 + O(d_1/R)^3 \quad (21)$$

Application of the same procedure in regions 2–4 gives analogous expressions for  $\beta_2$ ,  $\beta_3$ , and  $\beta_4$ . The expression for  $\beta_3$ , for instance, can be obtained from eq 21 by replacing  $d_1$  and  $\lambda$  with  $-d_3$  and  $-\lambda$ , respectively. The expressions for  $\beta_2$  and  $\beta_4$  are used to determine the values of  $d_1$  and  $d_3$ . The requirement of continuity in the counterion concentration at the zero field radii ( $r = R - d_3$  and  $r = R + d_1$ ) is satisfied if  $\beta_1 = \beta_2$  and  $\beta_3 = \beta_4$ ; the solutions to these equations give

$$d_1 = d \left( 1 - c \frac{d}{R} + c \left( \frac{d}{R} \right)^2 \right) \quad (22)$$

$$d_3 = d \left( 1 + c \frac{d}{R} + c \left( \frac{d}{R} \right)^2 \right) \quad (23)$$

where  $c = 1/2 - d/3\lambda + d^2/5\lambda^2$ .

The free energy per unit area  $\mathcal{F}_1$  of side 1 of the membrane at  $r = R$  is given in terms of the integral of the counterion free energy density in region 1. One can show that  $\mathcal{F}_1$  is given in terms of  $y_1$  by<sup>9</sup>

$$\mathcal{F}_1 = \frac{\sigma T}{e} \left[ \log \left( \frac{n_1}{n_*} \right) - y(R) \right] - \frac{\epsilon_w T^2}{2Re^2} \int_R^{R+d_1} dr r \left( \frac{dy}{dr} \right)^2 \quad (24)$$

where  $n_*$  is an arbitrary reference counterion density. An analogous expression may be given for  $\mathcal{F}_3$ . After some simple manipulations  $\mathcal{F}_1$  may be written in terms of  $\beta_1$  as follows:

$$\mathcal{F}_1 = -\frac{2\epsilon_w T^2}{Re^2} \left[ (1 - \beta_1^2) \log \left( 1 + \frac{d_1}{R} \right) + \log \left( \frac{\beta_1^2 + \left( 1 - \frac{R}{\lambda} \right)^2}{\beta_1^2 + 1} \right) + \frac{R}{\lambda} \right] + \frac{\sigma T}{e} \log \left( \frac{1}{R^2} \left[ \beta_1^2 + \left( 1 - \frac{R}{\lambda} \right)^2 \right] \right) \quad (25)$$

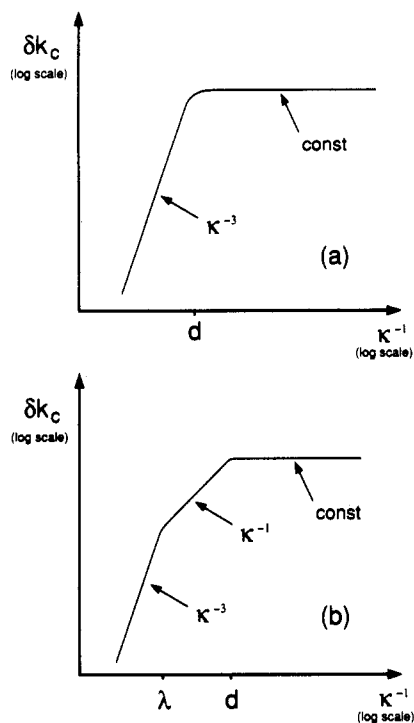
The expression for  $\mathcal{F}_3$  can also be derived from eq 25 by replacing  $d_1$  and  $\lambda$  with  $-d_3$  and  $-\lambda$ . Using the expressions for  $\beta_1$ ,  $\beta_3$ ,  $d_1$ , and  $d_3$  and expanding the logarithmic terms, we obtain an expression for  $\mathcal{F} = \mathcal{F}_1 + \mathcal{F}_3$ , the total free energy per unit area of the membrane. The coefficient of the leading order term in  $\mathcal{F}$  proportional to  $R^{-2}$  gives the electrostatic contribution to the bending modulus; we find

$$\delta k_c = \frac{4}{15\pi} \frac{T}{\lambda^2} d^3 \quad (26)$$

As expected from the scaling analysis,  $\delta k_c \sim d^3$  in the ideal gas regime. Furthermore, this expression for  $\delta k_c$  is identical to that given in eq 13 for the short-distance Debye-Hückel regime; this will be discussed in the next section.

#### 4. Discussion

We have studied in detail the electrostatic contribution to the bending modulus of surfactant membranes in the limit of small separation between membranes and low surface-charge density. Two situations were considered: (i) stacks of lamellae undulating in-phase in the presence of electrolyte (the short distance Debye-Hückel regime); (ii) membranes arranged in concentric cylindrical geometry, both with added electrolyte (the short distance Debye-Hückel regime) and without added electrolyte (the ideal gas regime). In these two regimes, where the distance between membranes  $2d$  is smaller than the Debye-Hückel screening length  $\kappa^{-1}$  and the Gouy-Chapman length  $\lambda$ , the electrostatic contribution to the bending modulus is small and can in general be smaller than the intrinsic value of the bending modulus. Furthermore,  $\delta k_c$  has been found to be independent of ionic strength in these two regimes. This is because in these low charge-density limits the free energy density of the membrane is dominated by the translational entropy of the counterions. However, the electrostatic contribution to the bending modulus varies strongly with the dilution (measured here by the distance between the membranes):  $\delta k_c \sim d^3/\lambda^2$ . In fact, we find the same prefactor in both the short distance Debye-Hückel and the ideal gas limits.



**Figure 4.** Sketch of electrostatic contribution to the membrane bending modulus  $\delta k_c$  as a function of the Debye-Hückel screening length  $\kappa^{-1}$  at fixed  $d$  and  $\lambda$ . In (a), we show the case of weakly charged membranes,  $\lambda < d$ . With increasing  $\kappa^{-1}$ ,  $\delta k_c$  first scales as  $\kappa^{-3}$  and then crosses over to a constant value for  $\kappa^{-1} > d$ . In (b) we show the analogous plot for strongly charged membranes. In this case after an initial regime of  $\delta k_c \sim \kappa^{-3}$ ,  $\delta k_c$  first crosses over to a linear regime,  $\delta k_c \sim \kappa^{-1}$  at  $\kappa^{-1} > \lambda$  followed by a second crossover to a constant value for  $\kappa^{-1} > d$ .

The modulus  $\delta k_c$  is much smaller than the value calculated in a previous work for two membranes having an out-of-phase periodic modulation (peristaltic mode):  $\delta k_c \sim 1/d^3\lambda^2$  in the presence of salt (the short distance Debye-Hückel regime) and  $\delta k_c \sim \lambda$  in the absence of salt (the ideal gas regime). The peristaltic mode involves not only the bending of the membranes but also the nonuniform compression of the ionic solution between the membranes. The compression dominates the free energy of the peristaltic mode leading to very high values of the apparent bending constant  $\delta k_c$ . The undulation mode corresponds to the usual short wavelength excitations of lamellar phases and should thus be used to calculate the membrane bending constant  $\delta k_c$ .

With these results, summarized in Table I, a complete theoretical picture of the electrostatic contribution to the bending rigidity of charged surfactant membranes may be given in terms of three relevant experimental length scales:  $d$  (determined by dilution),  $\kappa^{-1}$  (determined by electrolyte strength), and  $\lambda$  (determined by the membrane surface charge density). In the usual Debye-Hückel regime when  $\kappa^{-1}$  is the smallest length (region iii of Figure 1),  $\delta k_c \sim \kappa^{-3}\lambda^{-2}$ . On the other hand, in the weakly charged regimes for which  $d$  is the smallest of these lengths (regions i and ii of Figure 1),  $\delta k_c \sim d^3$ . In each of these regimes, the electrostatic contribution to the bending energy is small. We summarize schematically the dependence of  $\delta k_c$  on  $\kappa^{-1}$  with  $d$  and  $\lambda$  held fixed in Figure 4. The case of weakly charged membranes ( $d < \lambda$ ) is shown in Figure 4a where one crossover in the scaling behavior of  $\delta k_c$  as a function of  $\kappa^{-1}$  is seen. In the other limit of high charge density (regimes iii, iv, and v of Figure 1), the electrostatic contribution to the bending modulus varies as  $\delta k_c \sim \kappa^{-3}$  if  $\kappa d > 1$  and  $\kappa \lambda > 1$  (Debye-Hückel regime),  $\delta k_c \sim T/\kappa$  if  $\kappa d > 1$  (intermediate regime), and  $\delta k_c \sim Td$  if  $\kappa d < 1$

(Gouy-Chapman regime). In Figure 4b we show the dependence of  $\delta k_c$  on  $\kappa^{-1}$  for the high charge density regimes. Two successive crossovers in the scaling behavior of  $\delta k_c$  are noted at  $\kappa^{-1} = \lambda$  and  $\kappa^{-1} = d$ .

In this paper we have considered membranes either with constant charge density or at constant electric potential. If the membranes are far apart (in the regimes where the electrostatic interactions are dominant), constant charge and constant potential boundary conditions lead to the same scaling laws for the bending modulus as a function of the three relevant length scales. In the short distance regimes, the scaling of  $\delta k_c$  with  $d$  depends on the choice of boundary conditions, i.e., constant charge density or constant potential. However, in real systems the situation is always intermediate between constant charge and constant potential and one should certainly include in the theory the coupling between charge density fluctuations and membrane undulations. In these short distance regimes, we have considered only the case of electrostatic interactions within the Poisson-Boltzmann mean field approximation. When the interlamellar spacing  $2d$  is sufficiently small, other types of interactions, such as van der Waals or hydration interactions, must be considered. One must then go beyond the Poisson-Boltzmann approximation and include fluctuations around the average concentration profile.<sup>25</sup> We do not, however, expect these complications to be relevant for swollen lamellar phases when  $d$  is large, even if  $d < \lambda$ .

The theory of the bending elasticity of membranes involves two elastic constants,  $k_c$  and  $\bar{k}_c$ . We have focused on the electrostatic contribution to the bending modulus of mean curvature  $\delta k_c$  in this paper since it is most easily accessible experimentally. However, the electrostatic contribution to the Gaussian bending constant  $\delta \bar{k}_c$  can be directly calculated following an argument of Helfrich<sup>26</sup> from an integral of the stress distribution between flat, parallel surfaces. Some physical insight into the nature of  $\delta k_c$  may be obtained by considering the properties of  $\delta \bar{k}_c$ . Simple dimensional considerations indicate that the scaling of  $\delta \bar{k}_c$  with  $d$ ,  $\lambda$ , and  $\kappa^{-1}$  is the same as that for  $\delta k_c$  in all regimes, including the short distance regimes discussed in this paper. Moreover, we find that  $\delta \bar{k}_c$  is negative, favoring the formation of disconnected vesicles.

No systematic experimental verification of these scaling laws for  $\delta k_c$  exists. Experimentally, predicted scaling laws such as the ones shown in Figure 4 can be checked by solvent dilution (at constant electrolyte strength) or by varying the electrolyte concentration. In particular, the small charge density and short distance regimes can be probed by studying mixtures of charged and uncharged surfactants with a small fraction of charged constituents.<sup>27</sup> The Gouy-Chapman length  $\lambda$  can then be very large (perhaps a thousand angstroms) and hence even with swollen lamellar phases one can have  $d < \lambda$ .

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