Thermal undulations in salt-free charged lamellar phases: Theory versus experiment

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The interplay between thermal undulations and electrostatic repulsion is investigated theoretically for salt-free lamellar phases of charged fluid membranes. The electrostatics of the undulating charged membranes is dealt with in the nonlinear Poisson-Boltzmann approximation. A harmonic undulation theory is formulated that accounts quantitatively for the shift of the Bragg peak that has recently been observed in light-scattering experiments on the dilute lamellar phase of the nonionic surfactant *n*-dodecyl pentaethylene glycol ether, to which small amounts of the ionic surfactant sodium dodecyl sulphate were added. [S1063-651X(97)13207-X]

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I. INTRODUCTION

The behavior of charged fluid membranes in aqueous solutions is strongly influenced by their electrostatic interactions. For lamellar phases of charged fluid membranes, an important issue is the interplay between the thermally excited undulations of the semiflexible fluid membranes and the electrostatic interactions. Undulations in charged lamellar phases have been studied in x-ray-scattering [1–3], static light-scattering [4], dynamic light-scattering [3,5], and NMR [6] experiments. The experiments clearly show that, if unscreened, the electrostatic interactions lead to small undulation amplitudes. If the electrostatic interactions are screened by the addition of monovalent electrolyte, the undulation amplitudes increase. Statistical-mechanical theories describing the interplay between the electrostatic interactions and the thermal undulations have been proposed [7–13] for charged lamellar phases with excess added monovalent electrolyte, for the important regime in which the typical wavelength of the undulations is much larger than the Debye screening length. In this regime, since they are effectively flat on the scale of the Debye length, the undulating membranes interact as pieces of a flat membrane. Furthermore, an electrostatic contribution to the bending modulus [14–16] can account for the curvature energy of the undulating electric double layers. Unfortunately, statistical-mechanical theories that calculate the electrostatic interaction energy of the undulating membranes in a harmonic approximation, quadratic in the undulation amplitudes [7,8,10], are of very limited validity, due to the simultaneous requirements of typical undulation wavelengths much longer and undulation amplitudes much smaller than the Debye screening length [13]. Undulation amplitudes appreciably larger than the Debye length can be dealt with in a self-consistent field approximation [9,11,13]. For even larger undulation amplitudes, beyond the validity of the self-consistent field approximation [12,13], there is a transition to the limit of Helfrich steric repulsion [17], except for the presence of a boundary layer that prevents the undulating membranes from touching each other, due to the electrostatic repulsion [12].

In the absence of added electrolyte, for salt-free charged lamellar phases, the situation is very different from that with excess added electrolytes. The long-wavelength smectic fluctuations can be described by the usual harmonic continuum model of smectic-A liquid crystals [18]. This has been well documented for salt-free charged lamellar phases [2,5,19]. However, the typical undulations in salt-free charged lamellar phases have wavelengths of the order the electrostatic screening length, which typically is of the order of the distance between the membranes. At these wavelengths, the undulating membranes no longer interact as pieces of flat membrane, and the curvature energy of the undulating electric double layers can no longer be accounted for by an electrostatic bending modulus. In the present work a statistical-mechanical theory of undulations in salt-free lamellar phases is introduced, that also applies to undulations with wavelengths of the order of, and smaller than the electrostatic screening length. The theory, which is harmonic in the undulation amplitudes, is based on an expression for the electrostatic free energy of the undulations that was derived recently by Fogden *et al.* [20], on the basis of the nonlinear Poisson-Boltzmann equation. Predictions of the theory will be compared to experimental results of Schomäcker and Strey [4].

These authors performed a light-scattering study on the effect of adding small amounts of the ionic surfactant sodium dodecyl sulphate (SDS) to dilute lamellar phases of the nonionic surfactant $C_{12}E_5$ (*n*-dodecyl pentaethylene glycol ether) in aqueous solution. They also studied the effect of adding monovalent electrolyte to the weakly charged lamellar phases. The light-scattering experiments were performed at a fixed scattering angle, by varying the wavelength [21]. Upon adding the ionic surfactants, the position of the Bragg peak was found to shift to smaller wavelengths. Subsequently adding monovalent electrolyte, it shifted back again. Similar effects have also been reported elsewhere [22–24]. Schomäcker and Strey assumed that the shift was caused by the effect of the electrostatic interactions on the thermal undulations. More specifically, they assumed that the main effect of adding the ionic surfactants was to cause an increase in the bending modulus of the fluid membranes.

The latter, however, is a rather questionable assumption, since it completely neglects the effect that the electrostatic repulsion between opposite membranes has on the thermal undulations. Furthermore an electrostatic contribution to the bending modulus can only account for the curvature energy

of the undulating electric double layers, if the typical wavelength of the undulations is much larger than the electrostatic screening length. This will indeed be the case if sufficient electrolyte is added, but, for salt-free charged lamellar phases, this is generally not the case. As will be shown below, a more appropriate interpretation of the experimental results can be given using the harmonic theory of undulations in salt-free charged lamellar phases.

This paper is organized as follows. In Sec. II, the harmonic theory of undulations in salt-free charged lamellar phases is introduced. Then, in Sec. III, the theory is used to give a quantitative interpretation of the experimental results of Schomäcker and Strey. Assuming that the shift in the Bragg peak is indeed caused by the effect of the electrostatic interactions on the undulations, an estimate is deduced for the bending modulus of the uncharged $C_{12}E_5$ bilayers, that is in agreement with a previous estimate [21]. Finally, Sec. IV presents concluding remarks. Elsewhere [25], it will be shown that a quantitative interpretation of the experiment with added monovalent electrolyte, can be given using the self-consistent theory of Odijk [11,26].

II. THEORY

The harmonic theory of undulations in salt-free charged lamellar phases is best understood as an extension of the harmonic theory of long-wavelength undulations in salt-free charged lamellar phases. Therefore this section first reviews the harmonic long-wavelength theory, which applies to undulations of long wavelength and small amplitude, with respect to the electrostatic screening length. Then the more general harmonic theory is introduced, which is valid for small-amplitude undulations of arbitrary wavelength. This section concludes with a discussion of the transition to the regime of very low surface charge densities, where the Helfrich steric repulsion is expected to dominate. An estimate is deduced for the critical surface charge density of the transition.

A. Harmonic long-wavelength theory

For monovalent counterions the ionic profiles and the electrostatic potential ψ of the electric double layers surrounding the charged membranes are accurately described by the nonlinear Poisson-Boltzmann equation. The solution between two parallel plates on a distance D, carrying a uniform surface charge density (of σ elementary charges e per unit area), is

$$\Psi(y)=2\ln[\cos(y/\lambda)], \quad y=-D/2,\ldots,D/2, \tag{1}$$

where $\Psi=e\psi/k_BT$ is the dimensionless potential, k_B is Boltzmann's constant, and T is the absolute temperature. The electrostatic screening length λ is related to the midplane concentration of counterions n_0,

$$\lambda^{-2}=2\pi Q n_0, \tag{2}$$

and, via the boundary conditions, to the surface charge density σ:

$$\lambda=\tfrac{1}{2}D/\varphi, \tag{3}$$

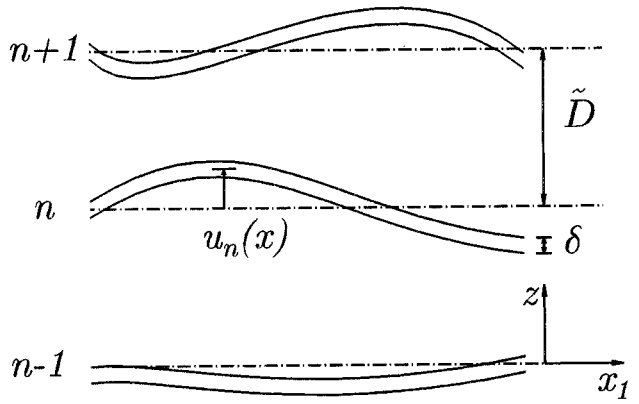

FIG. 1. Geometry of the stack of undulating membranes. The x_2 axis points into the figure.

$$\varphi\tan\varphi=\pi\sigma QD\equiv\Lambda. \tag{4}$$

In these equations $Q=e^2/\epsilon k_BT$ is the Bjerrum length, and ϵ is the solvent permittivity. For low surface charge densities, $\Lambda\ll1$, $\varphi^2\approx\Lambda$, whereas for high surface charge densities, $\Lambda\gg1$, $\varphi\approx\pi/2$. The screening length λ typically is of the order of the distance D between the plates, except for very low surface charge densities, for which it may be appreciably larger than D. Here it will be assumed that the surface charge densities are indeed such that $\lambda\approx D$. For the very low surface charge densities for which the screening length λ is appreciably larger than the distance D between the membranes, a transition is expected to a regime where the Helfrich steric repulsion dominates. This case is considered separately, at the end of this section.

Now consider a stack of undulating charged fluid membranes, for which the average distance between the membranes is D. The geometry of the stack of undulating membranes is indicated in Fig. 1. There are N membranes, with a repeating distance $\tilde{D}=D+\delta$, where $\delta\ll D$ is the membrane thickness. The undulation amplitude of the nth membrane in the $\hat{z}$ direction is $u_n(\mathbf{x})$, where $\mathbf{x}=(x_1,x_2)$ are Cartesian in-plane coordinates, in the directions perpendicular to the $\hat{z}$ axis. Due to the strong electrostatic repulsion between opposite membranes, the amplitude of the undulations is expected to be small with respect to the distance D between the membranes. Concomitantly, the undulation amplitude is also expected to be small with respect to the electrostatic screening length λ, and hence the electrostatic free energy of the undulations can be computed in a harmonic approximation, quadratic in the undulation amplitudes. The electrostatic free energy of undulations with wavelengths much longer than the screening length λ, can be given in terms of a long-wavelength expansion. The leading-order term of the expansion is the compressional energy involved in changing the distance between flat membranes. For undulations that do not change the distance between the membranes, the compressional energy vanishes. The amplitude of these in-phase undulations is limited by their curvature energy rather than by the compressional energy. Therefore it is necessary to include the next-order term of the expansion, which is the electrostatic curvature energy of long-wavelength in-phase undulations. This term involves the in-phase electrostatic bending

modulus $k_{c,\mathrm{el}}$. The harmonic Hamiltonian $\mathcal{H}[u_n(\mathbf{x})]$ for the energy of long-wavelength undulations in salt-free charged lamellar phases thus takes the form [13,27]:

$$\mathcal{H}[u_n(\mathbf{x})]=\tfrac{1}{2}\widetilde{D}\sum_{n=1}^{N}\int d^2\mathbf{x}K_1[\Delta_{\mathbf{x}}u_n(\mathbf{x})]^2 + B\{[u_n(\mathbf{x})-u_{n+1}(\mathbf{x})]/\widetilde{D}\}^2. \tag{5}$$

The bulk modulus B is $B=\widetilde{D}\partial^2V(D)/\partial D^2$, where $V(D)$ is the potential of interaction, per unit area, of two flat membranes on a distance D. From the solution of the Poisson-Boltzmann equation, one has, in units of k_BT,

$$B=\widetilde{D}\frac{4}{\pi QD^3}\frac{\varphi^2(\Lambda^2+\varphi^2)}{\Lambda^2+\Lambda+\varphi^2}\approx\begin{cases}2\sigma/D, & \Lambda\ll 1\\ \pi/QD^2, & \Lambda\gg 1.\end{cases} \tag{6}$$

The splay modulus K_1 is given by $K_1=k_c/\widetilde{D}$, with

$$k_c=k_{c,\mathrm{el}}+k_{c,0}, \tag{7}$$

where $k_{c,0}$ is the bending modulus of the membranes themselves, and $k_{c,\mathrm{el}}$ is the in-phase electrostatic bending modulus. The latter can be calculated either from the electrostatic free energy of charged membranes that undulate in phase, or from the known exact solution of the Poisson-Boltzmann equation between two concentric cylinders in the absence of added electrolyte [28,29]. Neglecting electrostatic coupling between opposite sides of the membranes [30], Fogden *et al.* [20] found, in units of k_BT,

$$k_{c,\mathrm{el}}=\frac{D}{\pi Q}\left\{\frac{\Lambda(2\Lambda+1-\varphi^2)}{\Lambda^2+\varphi^2}-(1+\varphi^2/3)\right\}. \tag{8}$$

This generalizes the expressions derived previously for the limiting cases $\Lambda\ll 1$ [31]and $\Lambda\gg 1$ [32]:

$$k_{c,\mathrm{el}}\approx\begin{cases}(2\pi/15)\sigma^2QD^3, & \Lambda\ll 1\\ (1/\pi-\pi/12)D/Q, & \Lambda\gg 1.\end{cases} \tag{9}$$

In dealing with the problem of undulations in charged lamellar phases with excess added electrolyte, instead of considering all the undulations in the lamellar phase, a number of authors [8–11] considered a single membrane, confined by a self-consistent field, due to the surrounding membranes. Such an approach neglects the long-wavelength in-phase undulations, and leads to slightly different values for the numerical constants, compared to theories [33] that do take into account all the undulations in the lamellar phase.

Next it is convenient to introduce Fourier-transformed undulation amplitudes $u(\mathbf{k})$, along the lines of the analysis of David [27]:

$$u(\mathbf{k})=\widetilde{D}\sum_{n=1}^{N}\int d^2\mathbf{x}u_n(\mathbf{x})\exp(i\mathbf{k}_\perp\cdot\mathbf{x})\exp(ik_znD). \tag{10}$$

The three-dimensional wave vector $\mathbf{k}$ has a component $k_z=-\pi/\widetilde{D},\ldots,\pi/\widetilde{D}$ in the $\hat{z}$ direction, as well as components $\mathbf{k}_\perp$ in the perpendicular directions. In terms of $u(\mathbf{k})$, the harmonic long-wavelength Hamiltonian in the limit $N\to\infty$ is

$$\mathcal{H}[u(\mathbf{k})]=\tfrac{1}{2}\int_{\mathbf{k}}(K_1k_\perp^4+\widetilde{D}^{-2}B4\sin^2[(k_z\widetilde{D}/2)]u(\mathbf{k})u(-\mathbf{k}), \tag{11}$$

where

$$\int_{\mathbf{k}}=\int_{-\pi/\widetilde{D}}^{\pi/\widetilde{D}}\frac{dk_z}{2\pi}\int_{-\infty}^{\infty}\frac{d^2\mathbf{k}_\perp}{(2\pi)^2}. \tag{12}$$

From the equipartition theorem it follows that, in the harmonic long-wavelength approximation, the mean-square amplitude of the undulations as a function of their wave vector, or equivalently, the correlation function, is given by

$$\langle u(\mathbf{k})u(-\mathbf{k})\rangle=\frac{1}{K_1k_\perp^4+\widetilde{D}^{-2}B4\sin^2(k_z\widetilde{D}/2)}\equiv S_0(\mathbf{k}). \tag{13}$$

For $|k_z\widetilde{D}|\ll 1$, one recovers the well-known correlation function of a smectic-A liquid crystal in the long-wavelength, harmonic continuum approximation [18]. At high $k_\perp$ the correlation function is dominated by the splay, or bending term, whereas for small $k_\perp$ compression dominates. The inverse of the crossover wave vector, averaged over k_z, is the deflection length of the fluid membranes [11,34], which is the typical wavelength of the undulations in the lamellar phase. This length has also been called the undulation length [17], or in-plane correlation length [8]. The expression for the deflection length ξ_0 in the harmonic long-wavelength approximation is

$$K_1\xi_0^{-4}=\widetilde{D}^{-2}B. \tag{14}$$

B. General harmonic theory

For electrostatic screening lengths λ of the order of the distance D between the membranes, the deflection length ξ_0 in the harmonic long-wavelength approximation is found to be of the order of the screening length λ. Hence the long-wavelength approximation does in fact not apply to the typical undulations in the lamellar phase, which have wavelengths of the order of the screening length λ, rather than much longer. A more general harmonic theory, valid for undulations of all wavelengths, is obtained by replacing the wave-vector-independent moduli B and K_1 of the long-wavelength theory, by wave-vector-dependent moduli $B(k_\perp)$ and $K_1(k_\perp)$ [35–37]. The contribution to the splay modulus of the membranes themselves remains wave vector independent:

$$K_1(k_\perp)=K_{1,el}(k_\perp)+K_{1,0}, \tag{15}$$

where $K_{1,0}=k_{c,0}/\widetilde{D}$. The Poisson-Boltzmann prediction for the wave-vector-dependent moduli, for salt-free charged lamellar phases, can be derived from the results of Fogden *et al.* [20]. These authors calculated the electrostatic free energy of the electric double layers between two charged

monolayers, on an average distance D, undulating respectively in phase, and with opposite phases, with an amplitude $u(x)=a\cos(k_\perp x)$, where x is a one-dimensional in-plane coordinate. The result of Fogden *et al.* for the electrostatic free energy $\mathcal{F}_{el}^{e,o}$ per unit area per monolayer is, in units of k_BT,

$$\mathcal{F}_{el}^{e,o}=\frac{2a^2}{\pi QD^3}f_{e,o}(x,\Lambda),\quad x=k_\perp D/2, \tag{16}$$

$$f_e(x,\Lambda)=\frac{(\Lambda^2+\varphi^2)x(\varphi^2\sinh x-\Lambda x\cosh x)}{(\Lambda^2+\varphi^2+x^2)\cosh x+\Lambda x\sinh x}+x^2(\Lambda-\varphi^2), \tag{17}$$

where the superscripts and subscripts e and o refer, respectively, to the in-phase, or even mode, and to the odd mode, in which the monolayers undulate with opposite phases. The expression for the function $f_o(x,\Lambda)$ pertaining to the odd mode is found by swapping sinh and cosh in the expression for $f_e(x,\Lambda)$. In terms of $K_{1,el}(k_\perp)$ and $B(k_\perp)$, the energy of the odd and even modes, respectively, is,

$$\mathcal{F}_{\rm el}^{e}=\tfrac{1}{8}\widetilde{D}K_{1,\rm el}(k_\perp)k_\perp^4a^2, \tag{18}$$

$$\mathcal{F}_{\rm el}^{o}=\tfrac{1}{8}\widetilde{D}K_{1,\rm el}(k_\perp)k_\perp^4a^2+\tfrac{1}{2}\widetilde{D}^{-1}B(k_\perp)a^2. \tag{19}$$

Thus the expressions for the moduli are

$$\widetilde{D}^{-1}B(k_\perp)=\frac{4}{\pi QD^3}[f_o(k_\perp D/2,\Lambda)-f_e(k_\perp D/2,\Lambda)] \tag{20}$$

$$\widetilde{D}K_{1,\rm el}(k_\perp)k_\perp^4=\frac{16}{\pi QD^3}f_e(k_\perp D/2,\Lambda). \tag{21}$$

These expressions neglect any electrostatic coupling between opposite sides of the membranes [31]. The scaling behavior of the bulk modulus is, for weakly charged membranes, $\Lambda\ll 1$,

$$B(k_\perp)\sim\begin{cases}\sigma/D, & k_\perp\ll\lambda^{-1}\\ \sigma^2Q/k_\perp^2D^2, & \lambda^{-1}\ll k_\perp\ll D^{-1}\\ \sigma^2Q\exp(-k_\perp D)/k_\perp D, & k_\perp\gg D^{-1}.\end{cases} \tag{22}$$

Note that for the surface charge densities considered in this section, which are such that $\lambda\approx D$, the intermediate regime is only of very limited extent. For highly charged membranes, $\Lambda\gg 1$,

$$B(k_\perp)\sim\begin{cases}1/QD^2, & k_\perp\ll D^{-1}\\ k_\perp^3D\exp(-k_\perp D)/Q, & D^{-1}\ll k_\perp\ll\Lambda D^{-1}.\end{cases} \tag{23}$$

There is an additional scaling regime $k_\perp\gg\Lambda D^{-1}$, but, for wave vectors in this regime, the bulk modulus is vanishingly small. The scaling behavior of the electrostatic free energy of the in-phase undulations was discussed by Fogden *et al.* [20]. The resulting scaling behavior of the splay modulus is, for weakly charged membranes, $\Lambda\ll 1$,

$$K_{1,\rm el}(k_\perp)\sim\begin{cases}\sigma^2QD^2, & k_\perp\ll D^{-1}\\ \sigma^2Q/k_\perp^2, & k_\perp\gg D^{-1}.\end{cases} \tag{24}$$

And, for highly charged membranes, $\Lambda\gg 1$,

$$K_{1,\rm el}(k_\perp)\sim\begin{cases}1/Q, & k_\perp\ll D^{-1}\\ 1/Qk_\perp D, & D^{-1}\ll k_\perp\ll\Lambda D^{-1}\\ \sigma/k_\perp^2D, & k_\perp\gg\Lambda D^{-1}.\end{cases} \tag{25}$$

In terms of the wave-vector-dependent moduli, again using the equipartition theorem, the expression for the correlation function $S(\mathbf{k})$ is

$$S(\mathbf{k})=\frac{1}{K_1(k_\perp)k_\perp^4+\widetilde{D}^{-2}B(k_\perp)4\sin^2(k_z\widetilde{D}/2)}. \tag{26}$$

This is expected to be valid for all wavelengths, provided steric repulsion can be neglected. In the long-wavelength limit $k_\perp\ll\lambda^{-1}\approx D^{-1}$, $S(\mathbf{k})$ reduces to the correlation function $S_0(\mathbf{k})$ of the long-wavelength theory. In the short-wavelength limit, $k_\perp\gg\lambda^{-1}\approx D^{-1}$, the bulk modulus is essentially zero, and the electrostatic contribution to the splay modulus is much smaller than the contribution $K_{1,0}=k_{c,0}/\widetilde{D}$ due to the membranes themselves. Therefore, at these wavelengths, the undulations are almost unperturbed by the electrostatic interactions, and the expression for the correlation function reduces to

$$S(\mathbf{k})\approx\frac{1}{K_{1,0}k_\perp^4}, \tag{27}$$

which is the expression pertaining to a freely undulating, uncharged membrane. The most important regime, however, is the intermediate regime, $k_\perp=\mathcal{O}(\lambda^{-1}\approx D^{-1})$, since this is the regime that covers the typical undulations in the lamellar phase, which have wavelengths of the order of the deflection length, which is of the order of λ. In this regime, the electrostatic contributions to the moduli are complicated decreasing functions of the wave vector $k_\perp$.

C. Transition to the Helfrich regime

As usual for smectic-A liquid crystals, the total mean-square amplitude of the undulations, $\langle u_n^2(\mathbf{x})\rangle$ diverges logarithmically with system size. On the other hand, the relative mean-square undulation amplitude $d^2\equiv\langle[u_n(\mathbf{x})-u_{n+1}(\mathbf{x})]^2\rangle$ is perfectly finite. In terms of $S(\mathbf{k})$,

$$d^2=\int_{\mathbf{k}}S(\mathbf{k})4\sin^2(k_z\widetilde{D}/2) \tag{28}$$

$$=\tfrac{1}{2}QD\int_0^\infty xdx\frac{1}{f_o(x,\Lambda)-f_e(x,\Lambda)}\times\left[1-\left(\frac{f_e(x,\Lambda)/x^4+\pi Qk_{c,0}/D}{f_o(x,\Lambda)/x^4+\pi Qk_{c,0}/D}\right)^{1/2}\right]. \tag{29}$$

In lamellar phases stabilized by Helfrich steric repulsion [17], one has $d^2=\mu_1D^2$, with $\mu_1\approx\frac{1}{5}$ [38]. Presumably then, the transition to a regime dominated by Helfrich steric repul-

sion takes place for a critical surface charge density σ_c, such that $d^2=\mu_2 D^2$, with μ_2 slightly smaller than or equal to μ_1. Undoubtedly, there will be corrections to the harmonic theory upon approaching the Helfrich limit, but these are not expected to change the order of magnitude of σ_c. Since the explicit expression (29) for the undulation amplitude is rather complicated, a scaling analysis is used to estimate σ_c. As in the harmonic long-wavelength approximation, the deflection length ξ is the inverse of the crossover wave vector:

$$K_1(\xi^{-1})\xi^{-4}=\tilde{D}^{-2}B(\xi^{-1}). \tag{30}$$

For d of order D, the crossover wave vector is expected to be in the regime $\lambda^{-1}\ll k_\perp \ll D^{-1}$. According to Eq. (22), the scaling of the bulk modulus in this regime is

$$B(k_\perp)\sim \frac{\sigma^2 Q}{k_\perp^2 D^2}. \tag{31}$$

Assuming that at these surface charge densities, the intrinsic contribution to the splay modulus dominates over the electrostatic contribution, and, using expressions (30) and (31), the following estimate for the correlation length ξ is found:

$$\xi^6\sim \frac{k_{c,0}D^3}{\sigma^2 Q}. \tag{32}$$

At the critical surface charge density one has $\xi^2\sim k_{c,0}D^2$. Equating the two estimates, one finds an expression for the critical surface charge density,

$$\sigma_c\approx \frac{\mu_3}{k_{c,0}Q^{1/2}D^{3/2}}, \tag{33}$$

where μ_3 is some numerical constant, of order 1. Numerical calculations using the explicit expression (29) for the undulation amplitude indicate that, for $k_{c,0}$ of order 1, $\mu_3\approx 0.1$. From estimate (33) for σ_c it is very clear that, especially in very dilute lamellar phases, extremely small amounts of charge, if unscreened, can cause a transition from a regime in which the Helfrich steric repulsion dominates, into a regime where electrostatic repulsion dominates. For example, any small amount of free charges may indeed be responsible for the increased orientational order at high dilution found by Appel *et al.* [39] in extremely dilute lamellar phases swollen by a mixture of decane and pentanol.

III. COMPARISON WITH EXPERIMENT

The order of magnitude of the excess area stored in thermal undulations of fluid membranes was first considered theoretically by Helfrich [40]. For lamellar phases, the important quantity is the ratio $\Delta A/A$, where A is the area of undulating membrane projected on the (x_1,x_2) plane, and $A+\Delta A$ is the average of the true area of the undulating membrane. This quantity can be extracted from an experiment that measures the repeating distance $\tilde{D}$ as a function of the volume fraction Φ of the membranes:

$$\frac{\Phi\tilde{D}}{\delta}=1+\frac{\Delta A}{A}. \tag{34}$$

In turn, $\Delta A/A$ is related to the average amplitude of the undulations as a function of their wave vector:

$$\frac{\Delta A}{A}=\tfrac{1}{2}\int_{\mathbf{k}} S(\mathbf{k})k_\perp^2 . \tag{35}$$

This is valid provided $\Delta A/A\ll 1$, which is usually the case. In general however, the absolute value of $\Delta A/A$ is also sensitive to the behavior of undulations of very short wavelengths, for which an accurate description is lacking. Therefore it is better to consider only differences or derivatives of this quantity, since these do not depend on the behavior of the very short-wavelength undulations. For dilute lamellar phases stabilized by Helfrich steric repulsion, one expects [21,41]

$$\frac{\Phi\tilde{D}}{\delta}=-\frac{1}{4\pi k_{c,0}}\ln\Phi+\text{ const.} \tag{36}$$

The constant does not depend on Φ, but it may depend, among other things, on the precise behavior of the very short-wavelength undulations. The value of the bending modulus $k_{c,0}$ can be extracted from a plot of $\Phi\tilde{D}/\delta$ versus $\ln\Phi$. From the results of a light-scattering experiment on the dilute lamellar phase of the nonionic surfactant $C_{12}E_5$ in aqueous solution, Strey *et al.* [21] thus found a bending modulus of $k_{c,0}\approx 1.3$ for the uncharged $C_{12}E_5$ bilayers.

In order to compare the results of Schomäcker and Strey, for the shift of the Bragg peak, with the harmonic theory of undulations in salt-free charged lamellar phases, some assumptions have to be made. First, Schomäcker and Strey observed that adding more than a certain amount of SDS to the dilute $C_{12}E_5$ lamellar phases caused a transition to an isotropic phase, presumably consisting of vesicles [4]. It is possible that structural changes, to some extent, already take place before the transition to the isotropic phase. Nevertheless it will be assumed here that adding the ionic surfactants only affects the thermal undulations and does not lead to any structural changes in the lamellar phase. Second, it is assumed that corrections due to electrostatic coupling between opposite sides of the membranes, which in the present case will presumably not be completely negligible [30], are nevertheless small enough to allow for a meaningful comparison between theory and experiment. Third, and finally, the amounts of added SDS in the experiment of Schomäcker and Strey correspond to surface charge densities appreciably larger than the critical surface charge density σ_c, as given by Eq. (33). Hence it will be assumed that the surface charge densities are indeed high enough, and the undulation amplitudes small enough, for the harmonic theory to be valid, and for the effects of steric repulsion to be neglected.

Consider the position of the Bragg peaks λ_1 and λ_2 of two lamellar phases with the same volume fraction Φ of membrane, but with different concentrations of added SDS. For $(\Delta A/A)_{1,2}\ll 1$, one has

$$\frac{\lambda_1}{\lambda_2}-1=\left(\frac{\Delta A}{A}\right)_1-\left(\frac{\Delta A}{A}\right)_2 \tag{37}$$

$$= \tfrac{1}{2}\int_{\mathbf{k}} [S_1(\mathbf{k}) - S_2(\mathbf{k})] k_\perp^2 \,. \tag{38}$$

The dominant contribution to $\lambda_1/\lambda_2 - 1$ is due to undulations with wavelengths of the order of the deflection length, which is of the order of the electrostatic screening length λ. These are also exactly the wavelengths for which the wave-vector dependence of the electrostatic contribution to the elastic moduli is most pronounced. Hence the theoretical prediction (38) for $\lambda_1/\lambda_2 - 1$ sensitively depends on the wave vector dependence of the moduli. For wave vectors $k_\perp \ll \lambda^{-1} \approx D^{-1}$, the electrostatics no longer significantly affects the thermal undulations, and both $S_1(\mathbf{k})$ and $S_2(\mathbf{k})$ in Eq. (38) reduce to the correlation function (27) of a freely undulating, uncharged membrane. Therefore, provided the small amount of added SDS does not affect the elasticity of the membranes themselves (for example, it does not affect the value of $k_{c,0}$), the theoretical prediction (38) for $\lambda_1/\lambda_2 - 1$ does not involve the behavior of the very short wavelength undulations, for which an accurate description is lacking.

After performing the k_z integration in Eq. (38) and using the expressions (20) and (21), one finds

$$\tfrac{1}{2}\int_{\mathbf{k}} S(\mathbf{k}) k_\perp^2 = \frac{1}{4\pi k_{c,0}} \int \frac{dx}{x} \left(1 + \frac{D}{\pi Q k_{c,0}} \frac{f_e(x,\Lambda)}{x^4}\right)^{-1/2} \times \left(1 + \frac{D}{\pi Q k_{c,0}} \frac{f_o(x,\Lambda)}{x^4}\right)^{-1/2}, \tag{39}$$

where $x = k_\perp D/2$. The integration over the dimensionless variable x is done numerically. In the experiments of Schomäcker and Strey the position of the Bragg peak was measured as a function of the concentration of added SDS, for four different concentrations of $C_{12}E_5$. For every concentration of $C_{12}E_5$, the lowest concentration of added SDS was 10^{-5} M. The results of the experiment are shown in Fig. 2, together with the theoretical predictions. For every concentration of $C_{12}E_5$ the quantity $\lambda_1/\lambda_2 - 1$ has been plotted as a function of the concentration of added SDS, where λ_2 is the position of the Bragg peak as a function of the concentration of added SDS, and λ_1 is the position of the Bragg peak at the lowest concentration of added SDS, 10^{-5} M. The theoretical prediction for this quantity is given by Eq. (38), which can be evaluated numerically using Eq. (39). In comparing the experimental results with the theoretical prediction, there is only one adjustable parameter [42]: the bending modulus $k_{c,0}$ of the uncharged $C_{12}E_5$ bilayers. A value for $k_{c,0}$ was deduced for each of the four concentrations of $C_{12}E_5$ that were used in the experiment. It was found that the theoretical predictions were very sensitive to small changes of the value of $k_{c,0}$, even of order $0.1 k_B T$. As is indicated in Fig. 2, the values of $k_{c,0}$ deduced from the experimental data are in the range $(1.6\text{–}2.1) k_B T$. Given the present accuracy of experimental determinations of bending moduli, as well as the various assumptions that have been made, this should be considered to be in reasonable agreement with the estimate of Strey *et al.* [21], who found $k_{c,0} \approx 1.3$ for the uncharged $C_{12}E_5$ bilayers.

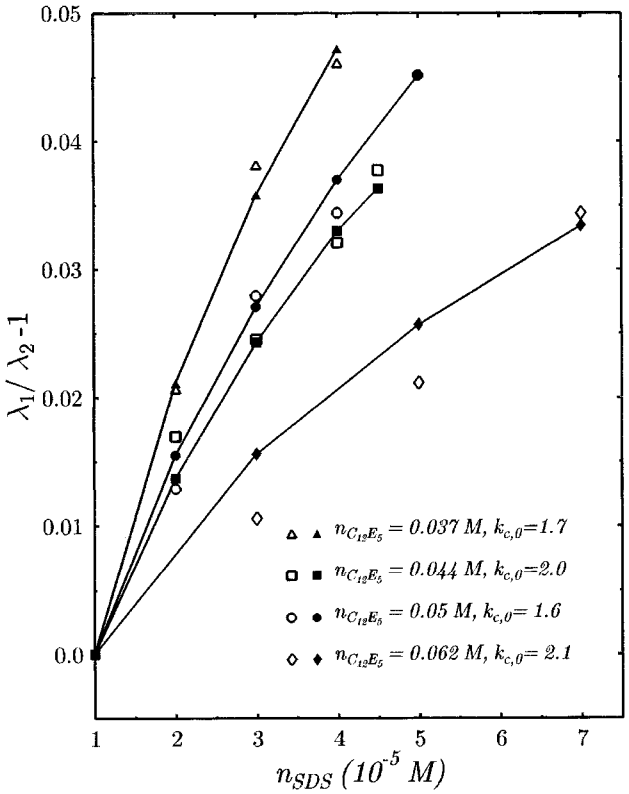

FIG. 2. A plot of $\lambda_1/\lambda_2 - 1$ vs the concentration of added SDS. λ_2 is the position of the Bragg peak as a function of the concentration of added SDS, λ_1 is the position of the Bragg peak at $n_{SDS} = 10^{-5}$ M. The open symbols are the experimental results of Schomäcker and Strey [4], and the filled symbols are the theoretical predictions, assuming values of $k_{c,0}$ as indicated. The lines through the filled symbols are drawn to guide the eye.

IV. CONCLUDING REMARKS

It has been shown that the present theory, which combines undulation theory with the Poisson-Boltzmann predictions of Fogden *et al.* [20], accounts quantitatively for the shift of the Bragg peak that was observed by Schomäcker and Strey [4]. Also, the magnitude of the shift of the Bragg peak has been shown to depend sensitively on the wave-vector dependence of the electrostatic contribution to the elastic moduli.

Provided it can be demonstrated more clearly that the shift in the Bragg peak is indeed due to the effects of thermal undulations, and not so much due to a change in the large-scale organization of the lamellar phase, it provides an experimentally very accessible quantity to test theories of undulations in charged lamellar phases. Moreover the shift of the Bragg peak is very sensitive to the value of the bending modulus $k_{c,0}$ of the uncharged membranes. Further systematic experiments on the shift of the Bragg peak would therefore be very useful, especially if these can be performed in conjunction with experiments that test for changes in the large scale organization of the lamellar phases, such as freeze-fracture microscopy.

From the results of NMR experiments on salt-free charged lamellar phases, Auguste *et al.* [6] concluded that there was no noticeable dependence of the bending modulus on the thickness of the water layers between the membranes. This is surprising, since in the Poisson-Boltzmann approxi-

mation the electrostatic contribution to the bending modulus in salt-free, highly charged lamellar phases is a linearly increasing function of the distance between the membranes. In the experiments, the thickness of the water layers was varied between 2 and 16 nm, implying a variation of the electrostatic contribution to the bending modulus with dilution, of order k_BT. However, the harmonic long-wavelength theory that was used by these authors presumably gives a rather poor description of the undulations, since it assumes that the typical undulation wavelengths are much larger than the electrostatic screening length, whereas in fact they are of the order of the electrostatic screening length.

Another experimental study investigating the effect of unscreened electrostatic forces on thermal undulations was published very recently by Freyssingeas, Roux, and Nallet [43]. These authors studied oil swollen lamellar phases of inverted bilayers. The thickness of the water layer in the membranes was very small (a few nm), implying only a very small contribution of the electrostatic interactions to the bending modulus, of order $0.1k_BT$. Upon increasing the thickness of the water layers, the bending modulus was found to decrease appreciably. Thus in this case other effects presumably dominate over the effects of electrostatic interactions.

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