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Physics Abstracts

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Crumpling and second sound in lyotropic lamellar phases

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Résumé. — Nous montrons que les fluctuations de concentration dans une phase smectique formée de lamelles de surfactant d'épaisseur w , séparées de couches fluides isotropes, sont dominées par le froissage des lamelles lorsque $(w/\ell)^2 \ll 1$, (ℓ périodicité de la structure). Nos résultats sont fondés sur une généralisation de la théorie d'Helfrich, dans laquelle le taux de froissage k^{-2} , les densités ρ_s et ρ_b du surfactant et du fluide sont susceptibles de varier. Dans la limite « incompressible » où ρ_s , ρ_b et w sont fixés, les fluctuations de concentration à ℓ constant sont déterminées entièrement par k^{-2} , et le rapport du module de compression des couches à concentration constante (mesuré à « haute fréquence ») sur celui à potentiel chimique constant (mesuré à « basse fréquence ») est d'ordre $(\kappa/T)^2 (\ell - w)^2/\ell^2$ où κ est le module de courbure des lamelles et T la température. Nous montrons que les corrections à la limite « incompressible », liées aux fluctuations de w sont d'ordre $(w/\ell)^2 (\kappa/U)$ où U est une énergie moléculaire.

Abstract. — We study relative concentration fluctuations in two component lamellar smectic liquid crystals consisting of surfactant layers of width w separated by a background fluid and show that these fluctuations are dominated by crumpling fluctuations of the surfactant layers when $(w/\ell)^2 \ll 1$ where ℓ is the average layer spacing. Our results are based on generalizations of the Helfrich theory in which the crumpling ratio k^{-2} , densities ρ_s and ρ_b of the surfactant and background fluid, and w as well as ℓ are allowed to vary. In the incompressible limit with ρ_s , ρ_b and w fixed, concentration fluctuations at constant ℓ are determined entirely by fluctuations in k^{-2} . In this limit, the ratio of the high-frequency, constant concentration compressibility modulus B to the low-frequency, constant chemical potential modulus \bar{B} is of order $(\kappa/T)^2 (\ell - w)^2/\ell^2$ where k is the layer bending rigidity and T is the temperature. We show that corrections to the incompressible limit arising from fluctuations in w are of relative order $(w/\ell)^2 (\kappa/U)$ where U is a molecular energy.

1. Introduction.

Lyotropic smectics [1] are lamellar phases consisting of stacks of regularly spaced fluctuating fluid membranes separated by a background fluid of oil (or of water). The separation between membranes can be as large as hundreds or even thousands of angstroms [2-10]. The

membranes consist of bilayers of surfactant molecules, possibly enclosing a thin layer of water (or oil). Thus, unlike thermotropic smectics, lyotropic smectics are necessarily multi-component systems with at least two conserved masses and correspondingly at least one hydrodynamic mass diffusion mode. In this paper, we will generalize Helfrich's theory [11, 12] of sterically stabilized lamellar phases to include density as well as layer fluctuations in a two component smectic. Our principal new result is that changes in the degree of crumpling of membranes (depicted schematically in Fig. 1) at constant density of material in both the background fluid and surfactant layer are the dominant cause of relative density fluctuations at constant layer spacing when the ratio w/ℓ of the width w of the surfactant layer to ℓ is small. Such changes in surfactant volume fraction can be described mathematically in terms of the crumpling ratio [13] specifying the inverse ratio of the area of a membrane surface element to its area projected onto a plane parallel to the average layers.

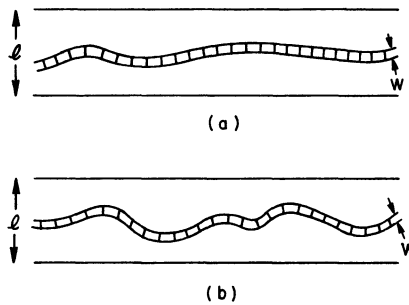


Fig. 1. — Schematic representation of how changes in the degree of crumpling of a surfactant layer lead to changes in the relative surfactant density. The crumpling ratio k^2 equation (2.1) is the ratio A_B/A of the projected area A_B of a membrane to its total area A . (a) shows a surfactant layer with k^2 near one. (b) shows a similar layer but with greater total area and thus smaller k^2 . The relative surfactant concentration in (a) is larger than in (b).

The conserved variables of a two component smectic [14-16] are the energy density ϵ , the density $\bar{\rho}_b$ of the background fluid (water or oil), the density $\bar{\rho}_s$ of the surfactant, and the momentum density \mathbf{g} . In addition, the strain $\nabla_z u = \delta\ell/\ell$ expressing the change $\delta\ell$ in layer spacing ℓ from equilibrium is a broken symmetry elastic variable. The variables entering naturally into the two-component smectic hydrodynamics are ϵ , $\nabla_z u$, the total mass density,

$$\bar{\rho} = \bar{\rho}_b + \bar{\rho}_s, \quad (1.1)$$

and the relative density,

$$c = \frac{\bar{\rho}_s}{\bar{\rho}}. \quad (1.2)$$

To obtain a complete description of all hydrodynamic modes, one needs to know the free energy to second order in all of these variables. At low frequencies, one may assume that both the background fluid and the surfactant layers are incompressible, i.e., that the local density ρ_b of the background fluid and the local density ρ_s and width w of the surfactant layers are constant. In this case, it is sufficient to consider the free energy density

$$f(\delta c, \nabla_z u) = \frac{1}{2} B (\nabla_z u)^2 + \frac{1}{2} \chi^{-1} (\delta c)^2 - C_c (\nabla_z u) \delta c. \quad (1.3)$$

Here z is the direction normal to the smectic layers, χ is the relative concentration susceptibility, C_c a strain-concentration cross coupling, and B the layer compression modulus at constant relative concentration which determines the velocity of second sound, $c_2 = (B/\bar{\rho})^{1/2}$. In our present thermodynamic analysis, we may assume that $u(\mathbf{x})$ is independent of coordinates \mathbf{x}_\perp perpendicular to the z axis, and we ignore the bending term $K_1(\nabla_\perp u)^2/2$ in f . This term is, of course, needed to describe spatially nonuniform distortions of the smectic. Fluid membranes are characterized [12] by a bending modulus κ with units of energy. All of the coefficients in equation (1.3) can be calculated in a controlled expansion in the ratio T/κ of the temperature T to the bending modulus. To lowest order in T/κ , we find

$$B \sim \frac{w^2}{\ell^2} \chi^{-1} \sim \frac{w}{\ell} C_c \sim \frac{\kappa}{\ell(\ell - w)^2}. \tag{1.4}$$

B is related to the static or constant chemical potential modulus,

$$\bar{B} \sim \frac{T^2 \ell}{\kappa (\ell - w)^4}, \tag{1.5}$$

calculated in the Helfrich theory [6,11-14,17] *via* the thermodynamic identity,

$$B = \bar{B} + C_c^2 \chi. \tag{1.6}$$

Thus $\bar{B} = B - \chi C_c^2$ is determined by corrections to the leading order terms in T/κ in B , χ , and C_c . Equations (1.4) and (1.5) imply

$$\frac{B}{\bar{B}} = A \left(\frac{\kappa}{T} \right)^2 \left(\frac{\ell - w}{\ell} \right)^2 (1 + O(T + \kappa)). \tag{1.7}$$

Our calculations yield $A = 256/[3 - (12/\pi^2)] \sim 100$. B/\bar{B} should be approximately independent of ℓ for $\ell \gg w$. In addition, B/\bar{B} can be quite large (~ 400) even for experimentally realizable values of κ/T of order 1.5 or 2.0.

We have also calculated the contributions to B , χ , and C_c arising from a nonzero compressibility of surfactant layers (i.e., by variations in w considered in Ref. [16]). We find when $w \ll \ell$ that these are smaller than those arising from steric repulsion and crumpling by a factor of order $(w/\ell)^2 (K/U) \ll 1$ where U is a molecular energy that is expected to be of order κ or greater.

This paper contains four sections in addition to this one. Section 2 reviews the thermodynamics of stacks of membranes. Section 3 presents the calculations of B , χ , and C_c using the Helfrich theory. Section 4 outlines how the Helfrich theory can be generalized to include variations of parameters such as the densities of the surfactant and of the background fluid and calculates the corrections to B , χ , and C_c arising from a nonzero layer compressibility. Section 5 reviews our results and discusses their relevance to the hydrodynamic mode structure discussed and measured in reference [16].

2. Thermodynamic potentials.

In the Helfrich [11, 12] theory of lamellar phases, fluid membranes are sterically confined by their neighbors to fluctuate about some average surface. One can, therefore, model the smectic as a stack of identical, hard-walled cells of height ℓ and base area A_B in which a single fluid membrane fluctuates. The total area A of a membrane is in general greater than

A_B (as shown in Fig. 1). A measure of the degree to which a membrane is crumpled is provided by the crumpling parameter [13]

$$k^2 = \frac{A_B}{A} \leq 1. \quad (2.1)$$

The surfactant and background volume fractions are respectively $w(k^{-2}/\ell)$ and $[1 - w(k^{-2}/\ell)]$ so that the mass density of the surfactant and the background fluid are, respectively,

$$\begin{aligned} \bar{\rho}_s &= \rho_s k^{-2} \frac{w}{\ell}, \\ \bar{\rho}_b &= \left(1 - k^{-2} \frac{w}{\ell}\right) \rho_b. \end{aligned} \quad (2.2)$$

Note that the average mass densities $\bar{\rho}_s$ and $\bar{\rho}_b$ differ from the local densities ρ_s and ρ_b , and they can change at constant ρ_s , ρ_b , and w in response to changes in k^{-2} and ℓ . The relative concentration is

$$c = \frac{\bar{\rho}_s}{\bar{\rho}_s + \bar{\rho}_b} = \rho_s k^{-2} \frac{w}{\ell} \left[\left(1 - \frac{w}{\ell} k^{-2}\right) \rho_b + \frac{w}{\ell} k^{-2} \rho_s \right]^{-1} \quad (2.3)$$

so that

$$\delta c = \frac{\rho_s \rho_b}{\bar{\rho}^2} \delta \left(w \frac{k^{-2}}{\ell} \right) \equiv a w \delta \left(\frac{k^{-2}}{\ell} \right) \quad (2.4)$$

at constant ρ_s , ρ_b , and w where $a = \rho_s \rho_b / \bar{\rho}^2$. Thus, in this limit, changes in c are determined entirely by the ratio,

$$c' = \frac{k^{-2}}{\ell}, \quad (2.5)$$

of the inverse crumpling ratio to the layer spacing.

The function $f(\nabla_z u, c)$ is most directly obtained by calculating first the thermodynamic potential that is a function of the variable σ conjugate to c' and then Legendre transforming. We begin by reviewing definitions of the various thermodynamic potentials [13] that can be used to describe a fluctuating nearly flat membrane. A nearly flat membrane is characterized by two extensive parameters: its total area A and its projected area A_B . The thermodynamic potential

$$\Phi_1(A, A_B, \ell) = A_B \phi_1(\ell, k^{-2}) \quad (2.6)$$

satisfies (at constant ℓ)

$$d\Phi_1 = -\sigma dA + h dA_B \quad (2.7)$$

where

$$\sigma = - \left. \frac{\partial \Phi_1}{\partial A} \right|_{A_B, \ell} \quad (2.8)$$

is the surface tension and h is the field conjugate to A_B . The energy per unit volume of a stack of membranes separated by a distance ℓ is simply

$$f_1(\ell, c') = \frac{\phi_1(\ell - w, k^{-2})}{\ell}. \quad (2.9)$$

The free energy f (Eq. (1.3)) is the part of f_1 harmonic in $\delta \ell$ and $\delta c = aw\delta c'$. Note the effects of a finite width of the membrane are described by replacing ℓ by $\ell - w$ in ϕ_1 . Other membrane potentials can be obtained from Φ_1 via Legendre transformation. In particular,

$$\Phi_2(A_B, \ell, \sigma) = \Phi_1 + \sigma A \equiv A_B \phi_2(\sigma, \ell), \tag{2.10a}$$

$$\Phi_3(A, \ell, h) = \Phi_1 - hA_B. \tag{2.10b}$$

Changes in Φ_2 at constant ℓ satisfy

$$\begin{aligned} d\Phi_2 &= A d\sigma + h dA_B \\ &= A_B \left. \frac{\partial \phi_2}{\partial \sigma} \right|_{\ell} d\sigma + \phi_2 dA_B \end{aligned} \tag{2.11}$$

so that

$$\phi_2(\ell, \sigma) = h, \quad \left. \frac{\partial \phi_2}{\partial \sigma} \right|_{\ell} = \frac{A}{A_B} = k^{-2}. \tag{2.12}$$

Thus, the surface tension σ , is the variable conjugate to k^{-2} . In analogy with equation (2.9), we introduce the free energy density,

$$f_2(\ell, \sigma) = \frac{\phi_2(\ell - w, \sigma)}{\ell}, \tag{2.13}$$

which satisfies

$$df_2 = \alpha_{\ell} \delta \ell + \frac{k^{-2}}{\ell} d\sigma = \alpha_{\ell} \delta \ell + c' d\sigma, \tag{2.14}$$

where α_{ℓ} is the force conjugate to the layer spacing which is zero in equilibrium. Thus, $f_1(\ell, c')$ is the Legendre transform of f_2 :

$$f_1(\ell, c') = f_2(\ell, \sigma) - \sigma c'. \tag{2.15}$$

$f(\nabla_2 u, \delta c)$ is easily obtained from equations (2.15) and (2.5).

In the next section, we will calculate $f_2(\ell, \sigma)$ to lowest order in T/κ using the Monge gauge for the fluid surface. As discussed in reference [13], the short length cutoff is treated more consistently in a gauge in which A rather than A_B is fixed. This leads more naturally to the potential $f_3(\ell, h) = \Phi_3/(\ell A)$ rather than $f_2(\ell, \sigma)$. The latter is, however, easier to calculate and suffices for our purposes.

3. The harmonic free energy.

In order to calculate $\phi_2(\sigma, \ell)$, we follow references [18] and [13] and replace the hard wall constraint by a global constraint on ℓ . In the Monge gauge where the membrane position is $\mathbf{R} = (\mathbf{x}_{\perp}, h(\mathbf{x}_{\perp}))$ where $\mathbf{x}_{\perp} = (x, y)$, the membrane Hamiltonian is

$$H = \int d^2x_{\perp} \left[\sigma \sqrt{g} + \frac{1}{2} \kappa \sqrt{g} (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} \sqrt{g} \gamma h^2 \right], \tag{3.1}$$

where $\sqrt{g} = \sqrt{1 + (\nabla_{\perp} h)^2}$ and $\mathbf{n} = g^{-1/2}(-\nabla_{\perp} h, 1)$ is the unit normal to the surface. The projected area of the membrane is the area of the domain of integration in the

xy plane and remains fixed in this calculation. The free energy density associated with H is, therefore,

$$\bar{\phi}_2(\sigma, \gamma) = -\frac{T}{A_B} \ln \int Dh e^{-H/T}. \quad (3.2)$$

The mean square height is

$$\frac{1}{2} \langle h^2 \rangle = \frac{\partial \bar{\phi}_2}{\partial \gamma} = \frac{1}{2} \mu \ell^2, \quad (3.3)$$

where μ is a phenomenological parameter introduced by Helfrich [1]. The free energy $\phi_2(\sigma, \ell)$ is the Legendre transform of $\bar{\phi}_2$:

$$\phi_2(\sigma, \ell) = \bar{\phi}_2 - \frac{1}{2} \mu \gamma \ell^2. \quad (3.4)$$

To obtain $\bar{\phi}_2$ at low temperature (small T/κ), we can expand H to harmonic order in h . Higher order terms in h give rise to subdominant corrections in T/κ , which for example lead to a softening of the effective bending modulus [19-23]. They will not concern us here. In this case,

$$H = \sigma A_B + \frac{1}{2} \int d^2x_{\perp} [\gamma h^2 + \sigma (\nabla_{\perp} h)^2 + \kappa (\nabla_{\perp}^2 h)^2] \quad (3.5)$$

and

$$\bar{\phi}_2 = \sigma + \frac{1}{2} T \int \frac{d^2q}{(2\pi)^2} \ln \left(\frac{\gamma + \sigma q^2 + \kappa q^4}{T} \right) \quad (3.6)$$

$$= \sigma \left[1 + \frac{T}{16\pi\kappa} \ln(\Lambda^4 \gamma/\kappa) \right] - \frac{T\sigma^2}{64\kappa^2} \left(\frac{\kappa}{\gamma} \right)^{1/2} + \frac{1}{8} T \left(\frac{\gamma}{\kappa} \right)^{1/2} + \bar{\phi}_2(\sigma=0, \gamma=0) \quad (3.7)$$

where Λ is the ultraviolet wavenumber cutoff and where $K\Lambda^4 \gg \gamma$, $\sigma\Lambda^2$ and $K\gamma \gg \sigma^2$. Using equations (3.7), (3.3), and (3.4), it is straightforward to derive (apart from an irrelevant constant)

$$\Phi_2(\sigma, \ell) = \frac{T^2}{128\mu\kappa\ell^2} + \sigma r(\ell) - \frac{1}{2} b\mu\ell^2 \frac{\sigma^2}{\kappa} \quad (3.8)$$

where $b = \frac{1}{4} [1 - (4/\pi^2)]$,

$$\mu\ell^2 = \frac{T}{8\sqrt{\gamma\kappa}}, \quad (3.9)$$

and

$$r(\ell) = 1 + \frac{T}{8\pi\kappa} \ln(8\kappa\Lambda^2\mu\ell^2/T). \quad (3.10)$$

Then using equations (2.13) and (2.15), we find

$$f_1(\ell, c') = \frac{T^2}{128\mu\kappa\ell(\ell-w)^2} + \frac{1}{2} \frac{\kappa}{b\mu} \frac{\ell}{(\ell-w)^2} \left(\frac{r[(\ell-w)]}{\ell} - c' \right)^2. \quad (3.11)$$

In the absence of external stresses, $\partial f_1 / \delta \ell = 0$, and we find

$$\frac{r}{\ell} - c' = -\frac{b}{128} \frac{1}{\ell} \left(\frac{T}{\kappa} \right)^2 \left(1 + \frac{2\ell}{\ell - w} \right) \left(r(\ell - w) - \frac{T}{4\pi\kappa} \frac{\ell}{\ell - w} \right)^{-1} + O\left(\frac{T^4}{\kappa^4} \right). \quad (3.12)$$

Using equations (3.10), (3.12), and (1.3), we obtain

$$B = \frac{\kappa}{b\mu\ell(\ell - w)^2} \left(r - \frac{T}{4\pi\kappa} \frac{\ell}{\ell - w} \right)^2 + \frac{T^2}{64\mu\kappa} \frac{1}{\ell(\ell - w)^2} \left(1 - \frac{\ell^2}{(\ell - w)^2} \right), \quad (3.13a)$$

$$\chi^{-1} = \frac{1}{a^2 w^2} \frac{\kappa}{b\mu} \frac{\ell}{(\ell - w)^2}, \quad (3.13b)$$

$$C_c = -\frac{1}{aw} \frac{\kappa}{b\mu(\ell - w)^2} \left[r - \frac{T}{4\pi\kappa} \frac{\ell}{\ell - w} - \frac{b}{128} \frac{T^2}{\kappa^2} \left(4 \frac{\ell^2}{(\ell - w)^2} - 1 \right) \right]. \quad (3.13c)$$

It is straightforward to verify using equation (1.6) that

$$\bar{B} = \frac{3T^2}{64\mu\kappa} \frac{\ell}{(\ell - w)^4} \quad (3.14)$$

in agreement with references [6] and [11]. Equations (3.14) and (3.13a) yield equation (1.7) for B/\bar{B} . Note that B/\bar{B} is independent of the phenomenological parameter μ . Note also that $B\chi = a^2 w^2 (r/\ell)^2$ to lowest order in T/κ . Thus, to this order, $B\chi = c^2$ if $w \ll \ell$.

4. Generalization to more variables.

In the last two sections, we treated changes in relative concentration brought about by changes in layer spacing and the crumpling ratio. In this section, we will outline a generalization of Helfrich's theory which can take into account the effects of variations in ρ_s , ρ_b , w , ℓ , and temperature T . This theory can be used to calculate all thermodynamic derivatives appearing in the linearized hydrodynamics of the lamellar phase. As a particular application of this approach, we will outline how the results of the previous sections can be corrected for a nonzero layer compressibility. When $w \ll \ell$, these corrections are of relative order $(\kappa/U)(w/\ell)^2$ to lowest order in (T/κ) , where U is a molecular energy which is of order κ or larger. They are thus subdominant compared to already neglected corrections of relative order $(T/\kappa)^2$ when $(w/\ell)^2 \ll (T/\kappa)^2$. They may, however, become important when $(w/\ell) \approx (T/\kappa)$ as may be the case in systems such as those studied by Safinya *et al.* [6] in which the Helfrich theory appears to be valid for ratios w/ℓ as large as $2.9/5.8 = 0.5$.

There are four hydrodynamic variables, $\bar{\rho}_b$, $\bar{\rho}_s$, ε , and ℓ , that are even under time reversal. The susceptibility matrix involving all of these variables can be obtained from a free energy density g that is a function of the background fluid and surfactant chemical potentials, α_b and α_s , the temperature T , and the force α_ℓ conjugate to ℓ . To construct g , we first construct the layer free energy density,

$$f_L(\rho_b, \rho_s, w, c', \ell, T) = wc' f_s(\rho_s, w, T) + (1 - wc') f_b(\rho_b, T) + f_1(\ell, w, c', T). \quad (4.1)$$

Here f_b is the free energy density of the bulk background fluid and wf_s is the free energy per unit area of the surfactant layer. f_1 is the Helfrich free energy, calculated in the last section (Eq. (2.9)) but with variations in w and temperature dependence of κ permitted. The free energy $g(\alpha_b, \alpha_s, \alpha_\ell, T)$ is obtained by minimizing

$$\bar{f}_L(\rho_b, \rho_s, w, c', \ell, \alpha_b, \alpha_s, \alpha_\ell) = f_L - \alpha'_s \bar{\rho}_s - \alpha_b \bar{\rho}_b - \alpha_\ell \ell \equiv \bar{g} - \sigma_\ell \ell \quad (4.2)$$

over $\rho_b, \rho_s, w, c',$ and ℓ .

As an application of the above development, we consider incompressible surfactant and background fluids (ρ_s and ρ_b fixed) at constant temperature and calculate corrections to χ, B and C_c arising from variations in w . For each T, ρ_b, ρ_s , there is a preferred layer width w_0 , and we can expand [16] wf_s as

$$wf_s(\rho_s, T) = w_0 f_s^0(\rho_s, T) + \frac{1}{2} D(w - w_0)^2. \tag{4.3}$$

The parameter D has units of (energy)/(length) [4] and should, thus, be of order U/w^4 where U is a molecular energy that should be of order or greater than κ . To calculate $\chi, B,$ and C_c , we consider the function

$$\tilde{g}(\alpha) = [\bar{g}(\eta) - \alpha_c c - \alpha_\ell \ell]_{\min(\eta)} \tag{4.4}$$

where $\alpha = (\alpha_c, \alpha_\ell), \eta = (w, c', \ell)$ and \bar{g} is defined in equation (4.2). Let $\xi = (c, \ell)$. Then the susceptibility matrix is

$$\chi_{ij} = \frac{\partial^2 \tilde{g}}{\partial \alpha_i \partial \alpha_j} = \frac{\partial \xi_i}{\partial \eta_\mu} \bar{\chi}_{\mu\nu} \frac{\partial \xi_j}{\partial \eta_\nu}, \tag{4.5}$$

where summation over $\mu, \nu = 1, 2, 3$ is understood and where

$$\bar{\chi}_{\mu\nu} = \frac{\partial^2 \bar{g}}{\partial \eta_\mu \partial \eta_\nu}. \tag{4.6}$$

When $\ell \gg w$, it is straightforward to show that

$$\bar{\chi}_{\mu\nu}^{-1} = \begin{pmatrix} c' D(1 + \zeta \delta) & TL/(4 \pi b \mu \ell^3) & TRM/(4 \pi b \mu \ell^5) \\ TL/(4 \pi b \mu \ell^3) & \kappa/(b \mu \ell) & \kappa Q/(b \mu \ell^3) \\ TRM/(4 \pi b \mu \ell^5) & \kappa Q/(b \mu \ell^3) & \kappa R^2/(b \mu \ell^5) \end{pmatrix}, \tag{4.7}$$

where

$$\begin{aligned} \zeta &= (6/A) + 1/(4^2 \pi^2 b \mu), \quad \delta = T^2/(\kappa \ell^5 c' D), \\ R &= r - [T/(4 \pi \kappa)], \quad Q = R - (3 b \mu/128)(T/\kappa)^2, \\ L &= 1 + (16 \pi b \mu T)/(AR \kappa) - [b \mu/(AR^2)](T/\kappa)^2, \\ M &= 1 - (8 \pi b \mu T)/(AR \kappa) - [(9 b \mu)/(AR^2)](T/\kappa)^2. \end{aligned} \tag{4.8}$$

The coefficients $\chi, C_c,$ and B are obtained from χ_{ij} calculated according to the above prescription from

$$\chi_{ij}^{-1} = \begin{pmatrix} \chi^{-1} & \ell^{-1} C_c \\ \ell^{-1} C_c & \ell^{-2} B \end{pmatrix}.$$

After some very tedious algebra, we find

$$B = B(D = \infty)(1 - \varepsilon) \tag{4.9a}$$

$$C_c = C_c(D = \infty)(1 - \varepsilon) \tag{4.9b}$$

$$\chi^{-1} = \chi^{-1}(D = \infty)(1 - \varepsilon) \tag{4.9c}$$

where the quantities at $D = \infty$ are those evaluated at fixed w in the preceding section and where

$$\varepsilon = \frac{1}{6 b \mu} \frac{\kappa}{c' D w^2 \ell^3} \sim \frac{1}{6 b \mu} \frac{w^2 \kappa}{\ell^2 U}. \tag{4.10}$$

We have retained only the lowest order terms in T/κ in both equations (4.9) and (4.10). The molecular energy U should be of order T so that $\varepsilon \ll 1$ if $w/\ell \ll 1$ even if T/κ approaches one.

5. Summary.

In this paper, we have considered coupling between fluctuations in relative surfactant concentration $c = \bar{\rho}_s/\bar{\rho}$ and the strain $\nabla_z u$ in lamellar lyotropic liquid crystals stabilized by the Helfrich steric repulsion between surfactant layers when the densities ρ_s and ρ_b of the surfactant and background fluid and the width w of the surfactant layers are fixed. In this incompressible approximation, relative concentration changes are controlled by changes in k^{-2}/ℓ , the inverse crumpling ratio divided by the layer spacing. We generalized the Helfrich theory to treat fluctuations in both k^{-2} and ℓ , and we calculated both the low-frequency, constant chemical potential and the high-frequency, constant relative concentration compression moduli, \bar{B} and B . The ratio B/\bar{B} is proportional to $(\kappa/T)^2(\ell - w)^2/\ell^2$ with a proportionality constant of order 100. Thus, in this incompressible limit, B/\bar{B} is much greater than one and depends only weakly on ℓ when $w \ll \ell$. We also generalized the Helfrich theory to allow for changes in ρ_s , ρ_b , and w as well as in k^{-2} and ℓ . We then fixed ρ_s and ρ_b and calculated the contributions to B and \bar{B} arising from the finite compressibility of w . We found these contributions to provide corrections to the incompressible theory of relative order $(w/\ell)^2 (\kappa/U)$ where U is a molecular energy. Thus, crumpling fluctuations are the dominant source of concentration fluctuations at constant ℓ so long as $(w/\ell)^2 \ll 1$ if $U \sim \kappa$. Layer compression can become important, however, when $(w/\ell)^2$ is not small compared to one. The Helfrich theory provides a good description of the systems studied by Safinya *et al.* [6] for values of $(w/\ell)^2$ as large as 1/4. Such systems may, therefore, be in a crossover region between crumpling dominated and layer compressibility dominated concentration fluctuations. Layer compressibility should be unimportant in large layer spacing systems such as those studied by Porte *et al.* [6].

Nallet *et al.* [16] have derived the dispersion relations for the low frequency modes of an incompressible lyotropic smectic and measured the frequency of one of these modes. The nature of this mode depends on the orientation of its wave vector $\mathbf{q} = (q_x, q_y, q_z)$ relative the layer normal along the z -axis. Assuming temperature fluctuations relax quickly, there are four other low frequency modes. If $\mathbf{q} = (q_x, 0, 0)$, the four modes are two shear modes with frequency $\omega_s = -i(\eta/\bar{\rho}) q_x^2$, an undulation mode with frequency $\omega_u = -i(K/\eta) q_x^2$ and a relative density mode with frequency $\omega_c = -i(\alpha_\perp/\bar{\rho}^2 \chi) q_x^2$ where η is a viscosity, $K = \kappa/\ell$ is the splay elastic constant, and α_\perp is a dissipative coefficient. In the relative density mode, variations in c are decoupled completely from those of u and the transverse velocity. The structure of these modes is independent of any detailed model for the smectic. Nallet *et al.* identify the relative density mode as a membrane peristaltic mode [24] in which the thickness of the surfactant bilayer is modulated in time. We find, however, that relative density variations are dominated by variations in k^{-2}/ℓ rather than by bilayer thickness variations. Since at $q_z = 0$, there are no variations in $\nabla_z u = \delta\ell/\ell$ in the relative density mode, we believe it would be more appropriate to refer to this mode as a crumpling mode in which

density fluctuations relax *via* modulation of the local crumpling ratio. When both q_x and q_z are nonzero, there is a second sound mode with positive and negative frequencies $\pm (B/\bar{\rho})^{1/2} q_x q_z$ and a density or baroclinic mode with frequency $\omega_b = -i(\alpha_{\perp}/\bar{\rho}^2)(\bar{B}/\chi B) q_x^2$ when $q_x \ll q_z$. Again these dispersion relations are independent of any particular model for the lamellar phase. In the model presented in reference [16] in which density fluctuations are dominated by fluctuations in bilayer thickness, $\chi B = c^2$. The same relations applies to the crumpling ratio dominated theory presented here when $(w/\ell) \ll 1$ and $T/(4\pi\kappa) \ll 1$ as discussed after equation (3.14). The experiments presented in reference [16] verify that both ω_u and ω_b are proportional to q_x^2 . In addition, they show that both ω_u and ω_b vary as ℓ^{-1} at fixed q . The first result is in accord with an ℓ -independent viscosity and $K = \kappa/\ell$. The second follows from $B\chi = c^2$, the Helfrich expression for \bar{B} , and the prediction by Brochard and de Gennes [15] that $\alpha_{\perp}/(\bar{\rho}c)^2 \sim (\ell - w)^2$. Thus the experimental results of reference [16] are in agreement with the theory presented here, which predicts $B\chi = c^2$ to a good approximation. They do not, however, provide independent measurements of B , χ , and C_c which would be needed for a verification of our predictions.

It would be of some interest to carry out further experiments to verify the predictions made here. Perhaps the most direct check would be provided by a measurement of the frequency $\omega_c = -i(\alpha_{\perp}/\bar{\rho}^2 \chi) q_x^2$ of the density mode at $q_z = 0$. Then the ratio of the coefficients of q_x^2 in the density mode at $q_z = 0$ and the baroclinic mode at $q_x^2 \ll q_z^2$ is simply the ratio, B/\bar{B} , which in the present theory is given by equation (1.7). Alternatively, of course, second sound measurements with q of order 10^2 cm^{-1} should provide a direct measurement of B .

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