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Particulate inclusions in a lamellar phase

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We study theoretically the effect of colloidal inclusions in a smectic liquid crystal. Our treatment is appropriate for any type of particle that exerts a small force perpendicular to the nearest layers. This force may either be outward, forming a local ''bulge,'' or inwards, pinching the neighboring membranes together. We calculate both the distortion field and associated energy due to one such inclusion, as well as the membrane mediated two body interaction potential. Aggregation of particles to form polydisperse disklike assemblies is treated using a simple Flory-Huggins theory. In this case there exists a characteristic aggregate radius $\sqrt{\lambda d}$, where λ is the usual characteristic smectic penetration length and d is the layer spacing. A novel feature of this system is that ''large'' disklike aggregates of this size may be formed. There is no such length for disklike aggregation in solution, where it is difficult to obtain aggregates much bigger than the particle size. Our treatment of aggregation neglects interaggregate interactions studied in more detail elsewhere. In this approximation, we find that for certain systems, such as strongly segregated copolymer melts and stacks of surfactant bilayers stabilized by electrostatic interactions, some significant aggregation is occurring. On the other hand we predict only weak aggregation in a stack of flexible surfactants bilayers governed by the Helfrich interaction. We use our results, combined with a simplistic mean field theory, to study an inclusion driven binding transition. [S1063-651X(97)14803-6]

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I. INTRODUCTION

Lamellar phases consisting of a stack of regularly spaced membranes are formed by many different classes of amphiphilic molecules. For example, lipid surfactants in solution self-assemble to form bilayer membranes. The hydrophobic tails of the surfactants form the internal part of the membrane and are shielded from the solvent by the hydrophilic head groups found at the outer surfaces [1]. Over a wide range of temperature and concentration, these bilayers stack together to form a lamellar phase [see Fig. 1(a)]. Lamellar phases can also be found in thermotropic systems such as diblock *A*-*B* copolymer melts. At sufficiently low temperatures or high surface tension between the two blocks, mesophases are formed containing regions rich in the *A* and *B* species. If the two blocks are of similar size the most stable phase is a lamellar phase where layers of *A* and *B* blocks alternate [see Fig. 1(b)] [2]. The dilute surfactant lamellar phase is of fundamental interest in the search for simple physical models to describe certain biological processes, such as those involving cell membranes. Biological membranes are extremely complex but are, at the simplest level, a lipid bilayer with many other molecules incorporated [3]. If we are to hope to understand biological membranes we need first to understand the properties of heterogeneous membranes made up of a mixture of different surfactant molecules or containing embedded inclusions, such as proteins. Furthermore, copolymers are commonly used for the blending and the compatibilization of different polymer molecules. The introduction of particles in a diblock lamellar phase might allow us to tune the properties of the phase in order to satisfy specific requirements.

Since a lipid bilayer is a two-dimensional fluid in which the inclusions are free to move one may expect interactions between them to arise, perhaps leading to collective processes such as aggregation of proteins within the membranes. These phenomena have been observed in biological systems and are known to play an important role in controlling exchange between the cell and the external medium [4].

Most of the theoretical work in this field so far has fo-

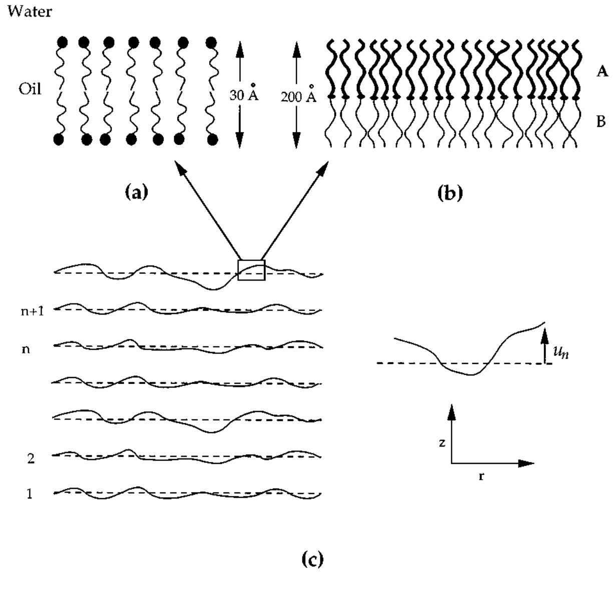

FIG. 1. (a) Smectic liquid crystal in a dilute phase of surfactant molecules. (b) Similar phase in a diblock copolymer melt. (c) The membranes are located using the Monge representation for the displacement field $u(\mathbf{r},z)$.

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cused on particles residing within a single surfactant membrane [5], or on a pair of membranes pinched together either by gap junctions (particles bridging two bilayers together) [6] or by optical tweezers [7]. Hydrophobic colloids, for instance, may reside in the membrane interior, taking advantage of the protective shell formed by the hydrophilic heads of the surfactants. The reorganization of the surfactant molecules due to the presence of a foreign body and the associated cost in deformation energy have been investigated extensively. Such work has yielded several interesting predictions, including the possibility of a nonmonotonic interaction (force) between inclusions in the same layer as a function of their separation. The possibility of ordered phase in such systems has also been suggested [5].

Our aim in the present work is to understand the effect of a general class of heterogeneities in a multilamellar system. These include any heterogeneities that affect the local membrane conformation by either (i) pinching neighboring membranes together, or (ii) pushing them apart. For example, certain proteins are now thought to form bridges or junctions between two neighboring membranes, leading to them being locally pinched together [8]. Recent studies concerning this type of junction in a two layer system have shown the existence of a membrane mediated interaction between the junctions [6]. This is due to the effect that such junctions have on the fluctuation spectrum of the membranes. It is also possible that similar bridging proteins could act to push neighboring membranes apart, if they were larger than the layer spacing. Furthermore any colloidal particle that has a purely steric interaction with the membrane will tend to increase the mean membrane separation locally. Such colloidal particles should include surfactant stabilized ferrite particles, such as those used in ferrosmectic phases [9]. We are able to study the two types of impurities described above within the same framework since, for small deformations, the smectic Hamiltonian is insensitive to the sign of the local deformation. Thus we need only to define the magnitude of the local deformation(s) for our predictions to apply to both cases (i) and (ii) above.

It is convenient to use a continuum theory to describe the behavior of smectic liquid crystals [10]. This description assumes that one can define a continuous deformation field for the mean position of the membranes, neglecting their discrete nature, which is valid for length scales larger than the mean spacing between lamellae. For small deformation fields, the smectic Hamiltonian can be written as an expansion to quadratic order in the deformation field of the lamellae. This involves two parameters that describe the bending and the compression of the lamellar phase (the bending and compression modulii K and B). Such an expansion follows from the symmetries of the lamellar phase and is insensitive to the precise nature of the system. The two modulii K and B can be calculated via molecular parameters such as the bending constant of a single surfactant bilayer κ or the size N of each blocks of a copolymer molecule and the interfacial tension between the two blocks γ_{AB}.

Estimation of the bending and compression modulus can be obtained for the examples cited above. The physical origin of the smectic parameters (especially the compression modulus B) is quite different each case:

(i) In the case of lyotropic smectics [Fig. 1(a)], the surfactant molecules self-organize into bilayers that experience strong thermal fluctuations leading to collisions between membranes. Since the total surface area of each membrane can adjust itself freely the membranes have no surface tension. Instead the shape of the membranes is controlled by their curvature modulus κ [11], which is an energy of the order of a few k_BT in a typical L_α phase. At finite temperatures the fluctuations of the membranes lead to collisions between neighboring layers, yielding an effective repulsive interaction called the Helfrich steric repulsion [12,13]. The interaction energy per unit volume U is a function of the local separation between layers d and is given by

$$U(d)=C_H\,\frac{T^2}{\kappa d^3},\tag{1}$$

where C_H is a numerical constant of order unity associated with the Helfrich theory, T is the temperature, and all energies are written in k_B units throughout. Helfrich's original estimate [12] of this constant is $C_H=3\pi^2/128$. The repulsive interaction described by Eq. (1) tends to swell the lamellar phase or, at fixed volume fraction of surfactant, leads to the effective compressibility of the phase. The compressibility modulus B as well as the global bending modulus per unit length K can be expressed by

$$B_H\simeq T^2/(\kappa d^3),\quad K_H=\kappa/d,\tag{2}$$

where d is the spacing between layers.

(ii) In the case of ionic surfactants, which are most commonly used in polar solvent, the repulsive Coulombic interactions play an important role in the repulsion between layers and can dramatically increase the compression modulus B, as well as renormalize the bending constant κ [14]. In the absence of added salt, the membranes are stiffened due to electrostatic repulsion and their fluctuations are highly reduced. In this case the Helfrich repulsion is completely dominated by the electrostatic repulsion between membranes and for high surface density of charges, the compression and bending moduli can be expressed by

$$B_{\rm io}\simeq T/(d^2 l),\quad K_{\rm io}\simeq T/l,\tag{3}$$

where l is the Bjerrum length of order 7 Å in water [15] (thus $l\ll d$ and $B_{\rm io},K_{\rm io}\gg B_H,K_H$). Some recent experiments [16] have cast doubt on the above predictions for the bending and compressional moduli of charged surfactant lamellae. These experiments suggest that the bending constant of one lamellae κ may not be as high as predicted. Note, however, that the exact dependence of these constants is not important here.

(iii) In a lamellar phase of diblock copolymer [Fig. 1(b)] the bending and compression moduli arise from a balance between the stretching of the polymer chains (an entropic effect) and the incompatibility of the two different blocks. The smectic parameters B and K can attain much larger values than in the case of dilute surfactant phase, and depend on the surface tension γ_{AB} between the two blocks and on the size N of the blocks [17]:

$$K_c\simeq\gamma_{AB}h,\quad B_c\simeq\gamma_{AB}/h,$$

with

$$h\simeq N^{2/3}\left(\frac{\gamma a}{T}\right)^{1/3}a,\tag{4}$$

where h is the distance between two lamellae, which is equivalent to the thickness of the lamellae, and a a microscopical size (monomer size).

In the following, the fluctuations of the membrane around their equilibrium position are integrated out and we will focus on the mean scalar displacement of the membrane $u(\mathbf{r},z)$ in the z direction, normal to the equilibrium (flat) layers. This is the so-called Monge representation for the displacement field [18]. In this representation u is zero everywhere at equilibrium in the absence of any heterogeneities (or defects in the crystal structure which we neglect throughout). The spatial variation of the field u is parametrized by a vector in the plane of the equilibrium position of the membrane (the x-y plane) $\mathbf{r}$ and a coordinate normal to this plane z [see Fig. 1(c)]. In a discrete representation $u(\mathbf{r},z)$ would be replaced by the displacement of the nth membrane $u_n(\mathbf{r})$. In Sec. II below we will calculate the equilibrium value of $u(\mathbf{r},z)$ in the presence of heterogeneities.

The Hamiltonian of the lamellar phase is obtain by symmetry considerations. It is the so-called Landau–de Gennes Hamiltonian for smectic liquid crystals [10], where all the terms compatible with the symmetry of the sample under translation and rotation have been kept up to the quadratic order in the displacement and the lowest order in its derivatives:

$$\mathcal{H}_0=\int d^2r\int dz\,\frac{B}{2}\,[(\partial_z u)^2+\lambda^2(\nabla_r^2 u)^2] \tag{5}$$

with

$$\lambda\equiv\sqrt{\frac{K}{B}},$$

where λ is the smectic penetration length.

The remainder of the paper is organized as follows: In Sec. II A we consider the influence of a single particle on the lamellar phase. We calculate the smectic deformation field u, which is found to be significant inside a parabola defined by $r^2\simeq\lambda z$. We calculate as well the total energy associated with this deformation. We extend this work in Sec. II B to derive the indirect interactions between two particles mediated by the deformation of the lamellae. This interaction is nonmonotonic, and is characterized by the same parabola as the deformation field. It is repulsive inside the parabola and attractive outside. For two particles within the same interlayer region, the interaction is always attractive and may result in aggregation of particles in the lamellar phase. This is discussed in Sec. III where we calculate the energy of an aggregate as a function of its aggregation number and develop a simple Flory-Huggins theory to describe the aggregation process. We then focus on the case of a dilute lamellar phase of nonionic surfactants. Solvent can be expelled fairly easily from this type of phase, and in the particular case of particles that pinch the membranes together, one can expect a ''binding transition'' to occur at high enough concentration of particles. By assuming that the particles are noninteracting we predict in Sec. IV A how the mean spacing between membranes, as can be measured by scattering experiments, varies with particle concentration. To do this we employ a mean-field theory in which d adopts a mean (constant) value throughout the sample. While it is not clear that this kind of mean-field treatment is entirely consistent with the noninteracting assumption (as discussed in more detail later on) it is nonetheless interesting to compare this result with the one of Sec. IV B, where the formation of aggregates is taken into account, and leads to qualitatively different dependence of d with particle volume fraction Φ.

II. POINTLIKE INCLUSIONS IN A LAMELLAR PHASE

We consider pointlike particles, or inclusions in a lamellar phase, that fix the local spacing between two membranes at some value d_π. This value would depend on, e.g., the size of the bridging protein or colloidal particle discussed in Sec. I. We approximate the spatial distribution (density) of particles $\rho(\mathbf{r})$ by a sum of Dirac delta functions $\rho(\mathbf{r},z)=\Sigma_{i=1}^{\mathcal{N}}\delta(\mathbf{r}-\mathbf{r}_i)\delta(z-z_i)$, where $(\mathbf{r}_i,z_i)$ is the position of the ith particle and $\mathcal{N}$ the total number of particles in the sample. The constraint introduced by the particles can be written in the continuous limit: $\partial_z u|_{(\mathbf{r}_i,z_i)}=(d-d_\pi)/d$. With a view to including this constraint in the Hamiltonian we first integrate $\rho\partial_z u$ over the sample:

$$\int d^2r\int dz\rho(\mathbf{r},z)\,\frac{\partial u}{\partial z}=\mathcal{N}\,\frac{(d-d_\pi)}{d}=\text{const.} \tag{6}$$

Hence this constraint can be introduced in the smectic Hamiltonian Eq. (5) via a Lagrange multiplier β:

$$\mathcal{H}=\int d^2r\int dz\,\frac{B}{2}\,[(\partial_z u)^2+\lambda^2(\nabla_r^2 u)^2+\beta\rho(\mathbf{r},z)\partial_z u]. \tag{7}$$

The last term in the Hamiltonian expresses the coupling between the membranes and the particles. Since the Hamiltonian is written only up to quadratic order, the effect of the inclusion, as expressed by the coupling term, is similar to the effect of a spring between two adjacent membranes. The coupling constant β is related to the spring constant, and will be chosen later on in order to satisfy the constraint on the layer spacing [Eq. (6)]. It should be mentioned that our constraint is somewhat arbitrary. The parameter β can be viewed as free parameter dependent on the microscopical details of the particle-membrane coupling. The mean displacement field due to the particles can be calculated by minimizing the Hamiltonian Eq. (7) with the constraint Eq. (6) (which corresponds to an integration over the fluctuations of the membranes).

The derivation is performed in Fourier space with the transform defined by

$$f(\mathbf{r},z)=\int\frac{d^2\mathbf{q}_r dq_z}{(2\pi)^3}\,f_q e^{i(\mathbf{q}_r\cdot\mathbf{r}+q_z z)}, \tag{8}$$

where $\mathbf{q}_r$ and q_z are the Fourier conjugates of $\mathbf{r}$ and z, respectively. The Euler-Lagrange equation for the minimization of the Hamiltonian Eq. (7) yields

$$u_q=\frac{\beta}{2}\,\frac{iq_z}{q_z^2+\lambda^2 q_r^4}\,\rho_q, \tag{9}$$

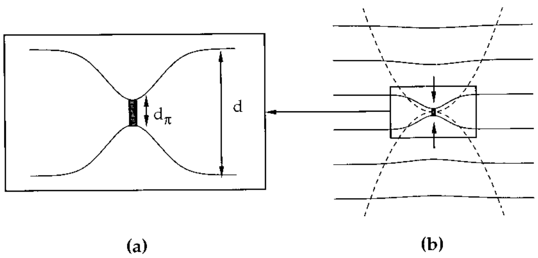


FIG. 2. Deformation of the layers due to an inclusion in the membrane. In this sketch, the particle is smaller than the layer spacing and pinches two membranes together. The lateral extension of the deformation is characterized by the parabola $r^2 \simeq \lambda z$ represented by a dotted line.

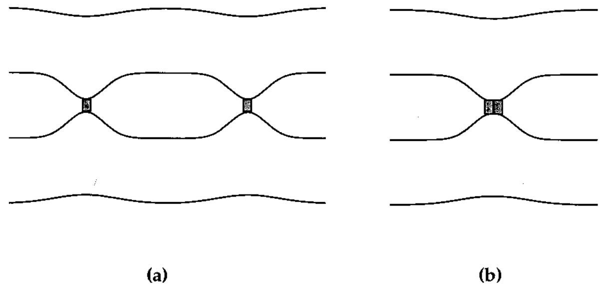


FIG. 3. Attractive interactions between two particles embedded within the same layer. (a) Far apart, the cost in energy is twice the cost of a single particle. (b) In close contact, the deformation is similar to the effect of a single particle.

where ρ_q is the Fourier transform of the particle distribution function.

This is a powerful relation. With it we can calculate the deformation (and deformation energy) of the membranes for a given distribution of inclusions in the smectic.

A. Deformation due to a single particle

We first evaluate the smectic deformation field due to a single pointlike particle at the origin. In this case $\rho(\mathbf{r},z) = \delta(\mathbf{r},z)$ and its transform $\rho_q = 1$. Using Eqs. (8) and (9) we can calculate the deformation due to a single particle:

$$u(r,z) = \int \frac{d^2\mathbf{q}_r dq_z}{(2\pi)^3} \frac{\beta i q_z}{2(q_z^2+\lambda^2 q_r^4)} e^{i\mathbf{q}\cdot\mathbf{r}} = -\frac{(d-d_\pi)d}{4z} \exp\frac{-r^2}{4\lambda|z|}, \tag{10}$$

where the Lagrange multiplier $\beta = 4\pi(d-d_\pi)d\lambda$ is chosen to satisfy the constraint Eq. (6) with $\mathcal{N}=1$.

The deformation $u(\mathbf{r},z)$ is sketched in Fig. 2. One can see that it is quickly damped in the radial direction and propagates over a long range in the z direction. The effect of the particle is significant within a parabola defined by $r^2 = 4\lambda z$. A similar parabolic region for the deformation field is known to exist near an edge dislocation in a smectic liquid crystal. However, the precise form of u is rather different for an edge dislocation [10] (which decays only as $u \sim 1/\sqrt{z}$ in the z direction). One can also remark that the overshoot characteristic of the deformation profile of a two membrane system [5] is not observed here. The difference between the two membrane and multimembrane systems is studied elsewhere [19].

The deformation of the membranes due to the inclusion costs a certain elastic energy, which is obtained by inserting Eq. (10) into the smectic Hamiltonian Eq. (5). The integral over $\mathbf{r}$ converges but the integral over z diverges unless we introduce a microscopic lower cutoff z_c. We choose $z_c \simeq d$, which is the length scale at which the continuum smectic theory breaks down. Furthermore, since the coordinate z corresponds to the position of the membrane, a particle at $z=0$ interacts via two membranes at $z = \pm d/2$. As usual [10] we necessarily neglect the contribution to the energy from material very close to the inclusion $|z| < z_c$ (the so-called ''core'' energy). With this cutoff included the deformation energy takes the form

$$\mathcal{F}_1 = \alpha\sqrt{KB}(d-d_\pi)^2, \tag{11}$$

where α is a numerical factor of order unity, the value of which depends on the precise choice of the cutoff [$\alpha = \pi^3/(2\iota^2)$, where the ratio $z_c/d = \iota$]. This energy is quadratic in the deformation $d - d_\pi$, which means that the same amount of energy is required either to pinch the membranes or to swell them (if the particle is larger than the layer spacing).

Note that in the case of membranes formed by neutral surfactants for which the repulsion between layers is dominated by the Helfrich repulsion, the deformation energy is of order $k_B T$ [see Eq. (2)] and may be of the order of the core energy.

B. Interaction between particles embedded in a lamellar phase

Even for particles with no direct interactions the coupling between the particles position and the membrane deformation field introduces an effective interaction between the particles. This can be easily understood, at least for the special case of two particles in the same layer, as shown in Fig. 3. Two particles far apart [Fig. 3(a)] each create deformation fields and this costs roughly twice the deformation energy of when they are very close together [Fig. 3(b)]. One can thus expect an attractive interaction between particles, as predicted in previous work [6]. We study the interaction in a three-dimensional stack of membranes below.

The Hamiltonian of a lamellar phase containing many particles [Eq. (7)] can be rewritten to emphasize the coupling between particles:

$$\mathcal{H} = \int \frac{d^2\mathbf{q}_r dq_z}{(2\pi)^3} \frac{B}{2} (q_z^2+\lambda^2 q_r^4) \left| \left(u_q - i\,\frac{\beta}{2} \frac{q_z}{q_z^2+\lambda^2 q_r^4} \rho_q \right) \right|^2 - \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{B}{2} \frac{\beta^2 q_z^2}{4(q_z^2+\lambda^2 q_r^4)} \rho_q \rho_{-q}. \tag{12}$$

The first integral is similar to the unperturbed smectic Hamiltonian (the change of variable from u_q to $u_q - i\beta[q_z/(q_z^2+\lambda^2 q_r^4)]\rho_q$ does not affect the calculation of the partition function of the system, for example). This inte-

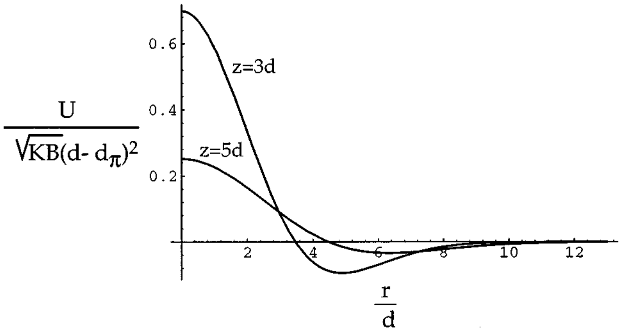


FIG. 4. Interaction energy between two particles [in unit $\sqrt{KB}(d-d_\pi)^2$] as a function of their radial separation (in unit of the layer spacing d) for two numbers of layers separating them (third and fifth layers). The interaction is nonmonotonic, attractive at large distances. The transition between attraction and repulsion is located on a parabola ($r^2 \simeq \lambda z$) characteristic of smectic liquid crystals.

gral vanishes if we neglect fluctuations and are only interested in the equilibrium position of the membranes (9). The second integral describes the membrane-mediated interactions between proteins and can be written in the space as a convolution integral:

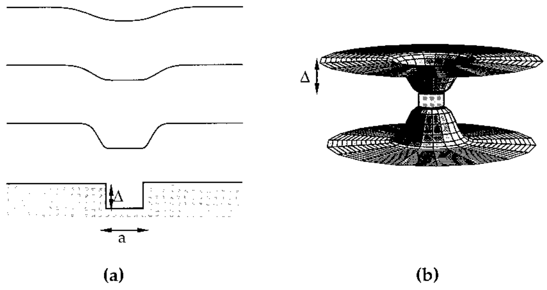
$$\Delta\mathcal{H} = \int\int d^2\mathbf{r}\, dz\, d^2\mathbf{r}'\, dz'\, \rho(\mathbf{r},z) \times G(\mathbf{r}-\mathbf{r}',z-z')\rho(\mathbf{r}',z'), \tag{13}$$

where $G(\mathbf{r}-\mathbf{r}',z-z')$ is the real space Green's function describing the interactions between particles with positions $(\mathbf{r},z)$ and $(\mathbf{r}',z')$. The Green's function can be evaluated exactly:

$$G(\delta r,\delta z) = \frac{\pi}{4}\sqrt{KB}(d-d_\pi)^2 \frac{d^2}{(\delta z)^2}\left(1-\frac{(\delta r)^2}{4\lambda|\delta z|}\right) \times \exp - \frac{(\delta r)^2}{4\lambda|\delta z|}, \tag{14}$$

where $\delta r = |\mathbf{r}-\mathbf{r}'|$ and $\delta z = |z-z'|$ define the distance between particles in the radial and the z direction. The fact that Eq. (14) is poorly behaved in the limit $\delta z \to 0$ is again a feature of our continuous description in which we invoke a microscopic cutoff size of the order of the layer spacing d in the z direction. Two particles in the same layer can be thought of as interacting via membranes located at $z=\pm d/2$. One should remark that the total energy of a system of two particles includes as well the self-energy per particle $\mathcal{F}_1$ calculated previously. Note that the energy scale for the interactions, given by the factor $(\pi/4)\sqrt{KB}(d-d_\pi)^2$ and the energy of an isolated particle, given by Eq. (11), are of the same order of magnitude.

The interaction between particles is clearly nonmonotonic (see Fig. 4), nonetheless its behavior is still characterized by the same parabola that we observed for the deformation of the membranes in the presence of a single inclusion: $r^2 = 4\lambda z$ (see Fig. 2). Not surprisingly the interaction is also similar to the interaction between two dislocations in a smectic liquid crystal [20]. It is attractive outside the parabola and becomes repulsive inside.



(a) (b)

FIG. 5. (a) Deformation field caused by a disklike particle of lateral size $a \gg \sqrt{\lambda d}$ and of thickness Δ. (b) 3D representation of the deformation of the first layer.

The result (14) becomes unreliable for $\delta r \lesssim \lambda d$ because of the singular nature of the particle distribution. A more refined approach, which involves a smoother particle distribution [21] slightly modifies the details of the short-range interaction. For example, two particles in the same layer experience monotonic attraction; see Fig. 3. Although the form of the Green function [Eq. (14)] is obtained by using the parameter β associated to the deformation due to a single particle. A more refined approach would use the calculation of $\beta(\delta r,\delta z)$ for two particles, but would modify the Green function only when the two particles are really close to each other. These details are discussed elsewhere [21].

The two-body interactions in the smectic have been studied in more detail elsewhere [21]. We notice that the attractive nature of the interaction between particles within the same layer is likely to induce aggregation of particles if the strength of the interaction is large enough to overcome the loss of entropy resulting form the aggregation.

III. AGGREGATION OF INCLUSIONS IN A LAMELLAR PHASE

We seek to describe the aggregation of particles in a lamellar phase using a Flory-Huggins theory. We assume that these particles can reside in dense disklike aggregates of any size. We first determine the deformation energy of such an aggregate as a function of its size (the number of particles in the aggregate). Then we calculate the distribution of aggregate sizes and their influence on the smectic phase as a function of the concentration of particles.

A. The deformation energy of a disklike aggregate of *n* particles

Each aggregate is treated as a dense disklike object of radius $a = b\sqrt{n}$, where n is the number of particles in the aggregate and b the lateral size of the particle. This disk imposes a vertical deformation on the neighboring membranes parametrized by a length Δ [see Fig. 5(a)]. Specifically for a disk located at $z=0$ we impose the following boundary condition for $u(r,z=0)$:

$$u(r,z=0)=\Delta,\ r<a \quad \text{and} \quad u(r,z=0)=0,\ r>a. \tag{15}$$

The parameter Δ will be chosen so that the perturbation of the closest layers (located at $z=\pm d/2$) is correctly related to the particle size d_π. Note that the boundary condition in Eq. (15) imposes a boundary condition on the layer spacing $\partial_z u$ and is thus of the same kind as the boundary condition Eq. (6). For large enough aggregates $a \gtrsim \sqrt{\lambda d}$ the parameter Δ is merely given by $\Delta=(d-d_\pi)/2$ where the factor 1/2 arises from the symmetry in the plane $z=0$. For smaller aggregates a larger value of Δ is required, as discussed below.

The displacement field and the energy of an aggregate are calculated using a two-dimensional Fourier transform

$$u(r,z)=\int_0^\infty \frac{d^2\mathbf{q}}{(2\pi)^2}\, u_q(z)e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{16}$$

The Euler-Lagrange equation associated with the smectic Hamiltonian Eq. (5) becomes

$$\frac{\partial^2 u_q(z)}{\partial z^2}=\lambda^2 q^4 u_q(z) \tag{17a}$$

the convergent solution of which is, for $z>0$,

$$u_q(z)=u_q(0)e^{-\lambda q^2 z}. \tag{17b}$$

The smectic energy depends on the Fourier transform of the boundary condition $u_q(0)$ according to

$$\begin{aligned}\mathcal{F}\simeq B\int d^2\mathbf{q}\int_{z_c}^\infty dz\lambda^2 q^4|u_q(0)|^2 e^{-\lambda q^2 z}\\ =\sqrt{KB}\int d^2\mathbf{q}q^2|u_q(0)|^2 e^{-\lambda q^2 z_c},\end{aligned} \tag{18}$$

where $z_c \simeq d$ represents the microscopic cutoff in z, below which the continuum elastic description of the smectic liquid crystal breaks down. The contribution due to deformation on still smaller length scales contributes to the usual ‘‘core energy’’ [10], which we do not attempt to include here.

The boundary condition on the disk possesses cylindrical symmetry and the Fourier transform therefore naturally involves Bessel functions. The boundary condition in Fourier space $u_q(0)$ may be calculated from the real space condition (16) using the inverse transform

$$\begin{aligned}u_q(z)=\int_0^\infty r dr\int_0^{2\pi} d\theta u(r,z)e^{-iqr\cos\theta}\\ =\int_0^\infty 2\pi r\ dr\ J_0(qr)u(r,z),\end{aligned} \tag{19}$$

where J_0 is the Bessel function of the first kind of order 0. The Fourier transform of the boundary condition is given by

$$u_q(0)=\Delta\int_0^a 2\pi r\ dr\ J_0(qr)=2\pi\Delta a^2\,\frac{J_1(qa)}{qa}, \tag{20}$$

where J_1 is the Bessel function of the first kind of order 1. A 3D representation in the real space of the deformation of the first layers is shown in Fig. 5(b).

The energy of the disklike aggregate then follows from Eq. (18) with $x\equiv qa$ a new dimensionless variable and $x_c=a/\sqrt{\lambda z_c}$.

$$\mathcal{F}\simeq\sqrt{KB}\Delta^2\int_0^\infty x dx[J_1(x)]^2 e^{-(x/x_c)^2}. \tag{21}$$

Roughly speaking the Gaussian exponential factor $e^{-(x/x_c)^2}$ in the integral introduces a cutoff at $x=x_c$. This high-q cutoff corresponds to small values of $r\lesssim r_c=\sqrt{\lambda z_c}$. Thus the r cutoff arises as a direct consequence of the one in z, to which it is related by the parabola of Fig. 2. Equation (21) can be evaluated exactly [22]:

$$\mathcal{F}\simeq\frac{x_c^2}{2}\,e^{-x_c^2/2}I_1(x_c^2/2), \tag{22}$$

where I_1 is the modified Bessel function of the first kind of order 1. We now expand this result in the two limits (i) $x_c \ll 1$ and (ii) $x_c \gg 1$, corresponding to aggregates (i) much smaller (ii) much larger than r_c, by an expansion of the Bessel function [22]

$$I_1(x)=\begin{cases}x/2+O(x^3), & \text{for } x\ll 1\\ (2\pi x)^{-1/2}e^x[1+O(1/x)] & \text{for } x\gg 1.\end{cases} \tag{23}$$

In these limits the energy becomes

$$\mathcal{F}\simeq\begin{cases}\sqrt{KB}\Delta^2 x_c^4 & \text{for } x_c\ll 1\\ \sqrt{KB}\Delta^2 x_c & \text{for } x_c\gg 1.\end{cases} \tag{24}$$

This expression implies that the energy is quadratic in the volume Δa^2 for small disks and scales like the circumference of the disk for large disks. The first of these results is understandable: The total distortion energy should scale with the perturbation volume Δa^2 for small enough inclusions. Furthermore the lowest order contribution must be quadratic in this volume by symmetry. The second result is also to be expected: For large enough disks there should be a contribution per unit length of edge (it locally resembles a dislocation). In order to fully understand the result Eq. (24) we need to choose Δ so that the perturbation of the closest layers (located at $z=d/2$) is related to the particle size according to $u(z=d/2,r=0)=(d-d_\pi)/2$. Using Eqs. (16), (17), and (20) the deformation is given by

$$u(r,z)=\Delta\int dx J_0\left(x\,\frac{r}{a}\right)J_1(x)e^{-(x/x_z)^2}, \tag{25}$$

where $x_z\equiv a/\sqrt{\lambda z}$. Evaluating this at $r=0$, $z=d/2$ we find

$$u(0,d/2)=\Delta(1-e^{-a^2/2\lambda d})\times\begin{cases}\Delta a^2/(2\lambda d) & \text{for } a/\sqrt{\lambda d}\ll 1\\ \Delta & \text{for } a/\sqrt{\lambda d}\gg 1.\end{cases} \tag{26}$$

Hence Δ is chosen as follows:

$$\Delta=\begin{cases}(d-d_\pi)\lambda d/a^2 & \text{for } a/\sqrt{\lambda d}\ll 1\\ (d-d_\pi)/2 & \text{for } a/\sqrt{\lambda d}\gg 1.\end{cases} \tag{27}$$

For small disks we need to choose the amplitude Δ in such a way that the volume Δa^2 is constant. It is reassuring that in

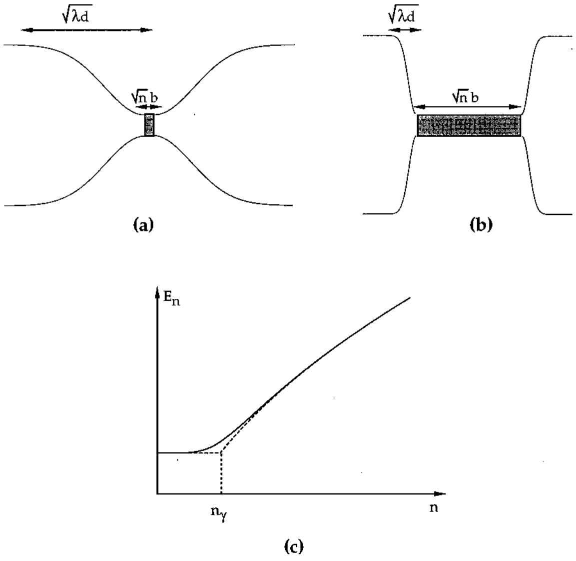


FIG. 6. Energy of the aggregates as a function of their size. (a) For a small aggregate, the deformation is insensitive to the size of the aggregate. (b) For a large aggregate, the deformation is linear with the size of the aggregate. (c) Schematic representation of the deformation energy with the aggregation number. The dashed line corresponds to the approximate expression used in the text.

the limit $a\to 0$ we recover the delta function representation of Sec. II A. Substituting Eq. (27) into (24) we finally obtain

$$\mathcal{F}\simeq\begin{cases}\sqrt{KB}(d-d_\pi)^2 & \text{for } a/\sqrt{\lambda d}\ll 1\\ \sqrt{KB}(d-d_\pi)^2 a/\sqrt{\lambda d} & \text{for } a/\sqrt{\lambda d}\gg 1.\end{cases}\tag{28}$$

This result gives the energy E_n of an aggregate containing n individual particles

$$E_n=\begin{cases}E_\gamma\sqrt{\dfrac{n}{n_\gamma}} & \text{for} \quad n\gg n_\gamma=\lambda d/b^2\\ E_\gamma \quad \text{for} & n\ll n_\gamma\end{cases}\tag{29}$$

[with $E_\gamma\simeq\sqrt{KB}(d-d_\pi)^2$], where b is the lateral radius of one particle.

This expression may be understood with the aid of Fig. 6: the layers in contact with the aggregate are deformed over a length $\sqrt{\lambda d}$, even if the aggregate is much smaller than this size ($n\ll n_\gamma$); see Fig. 6(a). In this case the far field distortion, and associated energy, are insensitive to the size of the aggregate. If, on the other hand, the lateral size of the aggregate is much larger than $\sqrt{\lambda d}$ ($n\gg n_\gamma$), the energy is linear in the size of the aggregate; see Fig. 6(b). The resulting variation of the deformation energy with the aggregation number is shown in Fig. 6(c).

B. Aggregation of inclusions in the lamellar phase

In this section we will construct a simple model to describe the aggregation of inclusions in the smectic phase. Interactions between inclusions will be included only by way of the aggregation process itself and we will neglect interactions between aggregates. We first assume that the characteristics of the L_α phase (layer spacing, compressibility, etc.) are not affected by the presence of inclusions. The possible variation of the layer spacing d with the concentration of particles (compaction of the lamellar phase) will be discussed below. We will use a Flory-Huggins theory [23] to model the aggregation process. The concentration of particles in the smectic phase is $C=\mathcal{N}/V$ where V is the total volume of the phase and $\mathcal{N}$ the total number of particle.

The global concentration of aggregates containing n particles is written c_n (for all integer n). The conservation of the total number of particles leads to

$$\sum_{n=1}^{\infty} nc_n=C.\tag{30}$$

The two-dimensional entropy of mixing of these aggregates is calculated via a lattice theory with an elementary lattice area on the membranes of δ^2. We can employ a three-dimensional treatment by defining the lattice volume in the smectic to be a slab of height d and area δ^2 with volume $v=\delta^2 d$, which ultimately corresponds to the volume of one inclusion times the ratio d/d_π. The free energy of the lamellar phase per unit volume is given by

$$F=\sum_{n=1}^{\infty} c_n\left[T\ln\frac{c_n v}{e}+E_n\right],\tag{31}$$

where we assume that the system is dilute so that the volume fraction $\Phi\equiv Cv\ll 1$. The total free energy density F is composed of two terms including the entropy of mixing of aggregates of all sizes and the smectic deformation energy of aggregates of all sizes. Note that since the entropy of the particles is effectively a two-dimensional entropy the term in the logarithm $c_n v/e$ is independent of the layer spacing. This consideration will be important in the next paragraph.

The total particle concentration is fixed by a Lagrange multiplier μ. By considering the system to be in contact with a reservoir of particles, μ may be thought of as the chemical potential for exchange of particles between the reservoir and the system itself. This must be chosen so that the constraint Eq. (30) is satisfied. The chemical potential is defined through the grand, or Gibbs, potential G [24],

$$G=F+\sum_{n=1}^{\infty} nc_n\mu.\tag{32}$$

Minimizing G with respect to c_n gives the concentration of aggregates of size n as a function of the chemical potential μ,

$$c_n=\frac{1}{v}\,e^{-E_n-\mu n},\tag{33}$$

where here and below we adopt units in which $k_BT=1$. Note that the sign of μ is unusual. It is positive at low concentration of particles and decreases as the concentration increases. As mentioned above μ can then be determined by the conservation relation Eq. (30). Low inclusion concentrations correspond to high values of the chemical potential. The chemical potential decreases as the concentration increases, with the concentration C eventually reaching a saturation value C_{sat}, for which $\mu=0$. If yet more particles were to be added to the system we envisage these residing in a second phase of dense particles (‘‘infinite’’ disklike aggregates); if μ were ever to become negative the concentration of the largest aggregates would diverge as $n \rightarrow \infty$; see Eq. (33).

The free energy density F of the entire system in k_BT units is given by substituting Eq. (33) into Eq. (31):

$$F = -(\mu C + C_{\rm agg}), \tag{34}$$

where $C_{\rm agg}$ is the total concentration of aggregates of all sizes. Both $C_{\rm agg}$ and the average number of particle per aggregate, written as $\overline{n}$, are fixed by c_n according to

$$C_{\rm agg} = \sum_{n=1}^{\infty} c_n \tag{35}$$

and

$$\overline{n} = \frac{C}{C_{\rm agg}}, \tag{36}$$

respectively. If the average aggregation number is large enough ($\overline{n} \gg 1$) a continuum representation may also be used, in which the sums are replaced by integrals. However, we choose to retain the discrete description in Sec. III B 2 in order to be able to treat correctly the onset of aggregation.

1. Saturation of the lamellar phase

The saturation values of C, $C_{\rm agg}$, and $\overline{n}$ can be calculated from Eqs. (30), (35), and (36) within a continuum approximation by setting $\mu = 0$ in Eq. (33) and by using Eq. (29) for the energy E_n of the aggregates:

$$C_{\rm sat} = \frac{n_\gamma^2}{v} e^{-E_\gamma} f_1(E_\gamma) \quad C_{\rm agg,sat} = \frac{n_\gamma}{v} e^{-E_\gamma} f_2(E_\gamma),$$

$$\overline{n}_{\rm sat} = n_\gamma f_1(E_\gamma)/f_2(E_\gamma), \tag{37}$$

where f_1 and f_2 are polynomials in $1/E_\gamma$:

$$f_1(E_\gamma) = \frac{12}{E_\gamma^4} + \frac{12}{E_\gamma^3} + \frac{6}{E_\gamma^2} + \frac{2}{E_\gamma} + \frac{1}{2}, \tag{38a}$$

$$f_2(E_\gamma) = \frac{2}{E_\gamma^2} + \frac{2}{E_\gamma} + 1. \tag{38b}$$

In deriving Eq. (37) we have also implicitly assumed that the volume fraction $\Phi_{\rm sat} \equiv C_{\rm sat} v \ll 1$, i.e., that saturation occurs before the volume fraction of occupied sites approaches its close packing value. The continuum approximation used above is a good one provided that the characteristic aggregation number n_γ is much larger than unity. This needs not correspond to a particularly strong experimental constraint. For example, the Floch-Π protein [25], which is a typical bridging inclusion, has a lateral (projected) area of 500 Å^2. In a phase of membranes with a bending modulus κ of the order of a few k_BT this leads to characteristic aggregation numbers $n_\gamma \gtrsim 100$. The same typical numbers are found for a lamellar phase of diblock copolymers and of ionic surfactants. The reference energy E_γ [Eq. (11)] is rarely bigger than a few k_BT for nonionic surfactant systems, in which case the saturation concentration $C \simeq C_{\rm sat}$ may often be preceded by the high concentration limit $\Phi \approx 1$. On the other hand $\Phi_{\rm sat} = C_{\rm sat} v$ may be smaller than unity in the case of ionic surfactant and of copolymer lamellae.

2. Low particle concentrations

Here we are interested in the limit where the particle concentration is small enough so that there are very few aggregates larger than n_γ. This corresponds to $\mu > 1/n_\gamma$ (with $n_\gamma \gg 1$) and probably covers the major range of concentration accessible experimentally. While we are interested in the regime where there are very few aggregates larger than n_γ we make no assumptions concerning the mean aggregation number $\overline{n}$ and avoid making the continuum approximation. In this case we evaluate the summations in Eqs. (30) and (35) using the result (33) and obtain the relations

$$\hat{\Phi} \equiv \Phi e^{E_\gamma} = \frac{e^{-\mu}}{(1-e^{-\mu})^2}, \quad \hat{\Phi}_{\rm agg} \equiv C_{\rm agg} v e^{E_\gamma} = \frac{e^{-\mu}}{1-e^{-\mu}},$$

$$\overline{n} = \frac{\hat{\Phi}}{\hat{\Phi}_{\rm agg}} = \frac{1}{1-e^{-\mu}}. \tag{39}$$

We can invert the relation $\hat{\Phi}(\mu)$ to find the chemical potential μ

$$\mu = -\ln R(\hat{\Phi}) = \begin{cases} \hat{\Phi}^{-1/2} + O(\hat{\Phi}^{-3/2}) & \text{for } \hat{\Phi} \gg 1 \\ -\ln\hat{\Phi} + O(\hat{\Phi}) & \text{for } \hat{\Phi} \ll 1, \end{cases} \tag{40}$$

where

$$R(x) = \frac{1 + 2x - \sqrt{1+4x}}{2x}. \tag{41}$$

In the limit of very low concentration $\hat{\Phi} \ll 1$ there is essentially no aggregation, the particles are independent and the chemical potential satisfies the ideal gas law: $\mu = -E_\gamma - \ln\Phi$. The aggregates are instead large $1 \ll \overline{n} \ll n_\gamma$ for intermediate concentrations $1 \ll \hat{\Phi} \ll n_\gamma^2$. In this case our results are identical to those describing the size distribution of wormlike micelles, where E_γ corresponds to the scission energy (the cost of creating two end caps on the worm) [26]. The wormlike and disklike descriptions only diverge when $\hat{\Phi} \simeq n_\gamma^2$ and disks with sizes $n \gtrsim n_\gamma$ start to appear. At this point the energy per disk E_n is no longer constant; see Eq. (29).

As a first approximation, we assume that the inclusions do not affect the characteristics of the lamellar phase, the layer spacing d is kept constant as the concentration C increases. Significant aggregation can occur if the variable $\hat{\Phi} = \Phi e^{E_\gamma}$ is bigger than 1. For this to occur with $\Phi \ll 1$, the energy $E_\gamma = E_0(d - d_\pi)^2/d^2$ has to reach several k_BT. The energy $E_0 = \alpha\sqrt{K_0 B_0} d^2$ can be evaluated in the typical cases considered so far. In the case of a dilute L_α phase of nonionic surfactants stabilized by the Helfrich steric interaction, $E_0 = \alpha\sqrt{C_H} T$ is independent of the bending modulus of the membranes κ and depends mainly on the numerical factor introduced in Eq. (11). This energy is of order a few k_BT and only weak aggregation is to be expected in this case. In the case of a diblock copolymer lamellar phase, the energy E_0 is proportional to the surface tension between the two blocks γ_{AB} [Eq. (4)] and can easily reach $30 k_BT$. In this case, significant aggregation may occur for low volume fraction of inclusions. In the case of highly charged membranes, formed by ionic surfactants, the energy is large $E_0 \simeq (d/l)T$ and aggregation is to be expected.

Finally, let us remark that the so-called core energy associated, for instance, to a possible reorganization of the surfactants around the inclusion, may renormalize the chemical potential. This effect tends to favor aggregation (the self-energy of each particle being increased by the core energy) but is not expected to be a sufficiently important effect to alter our conclusions.

IV. "BINDING TRANSITION" IN A LAMELLAR PHASE CONTAINING JUNCTION PARTICLES

A lyotropic lamellar phase formed from a dilute solution of surfactant can be found in both a bound and an unbound phase [27]. The transition between the two phases is usually driven by the Van der Waals interaction. Below a critical value of the Hamaker constant, the lamellar phase is unbounded and the layer spacing is fixed only by the global concentration of surfactants. If the Hamaker constant is above the critical value, a bound lamellar phase can be observed. The value of the layer spacing is then fixed by the balance between the Van der Waals attraction and, for example, the Helfrich repulsion between the layers in the case of nonionic surfactants. In the case of charged bilayers in the absence of salt (unscreened electrostatic interactions) discussed in the Introduction, the repulsion between the layers is much stronger than in the Helfrich regime. For layer spacing larger than the bilayer thickness, the Van der Waals attraction cannot overcome the repulsion and the lamellar phase is always in the unbound state. In the case of a dense lamellar phase of diblock copolymer, the compaction effect should be negligible because of the absence of solvent.

We present below a study of the compaction of an unbound lamellar phase driven by bridging inclusions.

A. Nonaggregating particles

We first consider $\mathcal{N}$ independent particles. The deformation energy due to each particle is expressed by the energy $\mathcal{F}_1$ derived in Sec. II [Eq. (11)]. The energy is of course minimal if the layer spacing is d_π, however, such a global compression of the sample would lead to a large increase in collisions between membranes and thus to a large cost in compression energy. We account for this fact by writing the total energy of the L_α phase as follows:

$$\mathcal{F} = \nu B V + \mathcal{N}\mathcal{F}_1, \tag{42}$$

where the first term of the right hand side is the energy of a global compression and where ν is a numerical factor of order 1 [28].

The layer spacing of the phase without inclusions d_0 is fixed by the total volume of the sample V_0. The balance between the Helfrich repulsive force and the particle induced attraction leads to a binding transition at some particle concentration $\hat{C}$. For $C > \hat{C}$ the equilibrium spacing in the smectic phase d is smaller than d_0 and varies with the particle concentration. We employ a mean-field treatment in which d adopts a constant mean value throughout the smectic. This assumption is rather crude in that it probably requires that the particles' deformation fields are at least starting to overlap significantly, in which case the noninteracting assumption is already starting to break down. However, a treatment based on this kind of mean field assumption does seem a natural choice for a preliminary study of these systems. We will also make a simplifying assumption regarding the phase behavior. We assume that when $d < d_0$ two phases exist and they correspond to a smectic, with layer spacing d occupying a volume V, and pure solvent in the remaining volume $V_0 - V$. Reassuringly recent experiments [25] on just such a system report a separation into a dense lamellar phase and an almost pure solvent phase. A calculation of the full phase behavior probably also requires an improvement of the mean-field treatment and is beyond the scope of this work. Within this model the free energy of $\mathcal{N}$ independent particles is given by

$$\mathcal{F} = \nu B_0 V_0 \left(\frac{d_0}{d}\right)^2 + \alpha \mathcal{N} \sqrt{K_0 B_0}\, d_0^2 \left(\frac{d - d_\pi}{d}\right)^2. \tag{43}$$

In this expression, we have expressed explicitly the d dependence of the various terms by using the relations Eq. (2). The length d_0 represents the layer spacing in the smectic free of particles, and X_0 designates the value of X when $d = d_0$. For example, the volume of the smectic-rich phase can be written as $V = V_0(d/d_0)$ if the number of layers in the lamellar phase is kept constant during the compression. The first term in Eq. (43) represents the pressure resisting a global reduction in the layer spacing. In the absence of any attractive interaction between the membranes the layer spacing d_0 is fixed by the finite surfactant concentration in the sample. The second term is quadratic in the difference between the layer spacing d and the relevant particle dimension d_π. It is attractive if $d_\pi < d$, i.e., for the bridging inclusions discussed in Sec. I, and in this case acts to lower the spacing d. The d spacing is obtained by simple minimization of Eq. (43):

$$d(C_0) - d_\pi = \frac{\nu}{\alpha \lambda_0 d_\pi} \frac{1}{C_0}, \tag{44}$$

where $C_0 = \mathcal{N}/V_0$ is the concentration of particles in the sample and where the penetration length $\lambda \equiv \sqrt{K/B}$ can be determined with Eqs. (2) and (5). This result only gives the correct layer spacing if $d(C_0) < d_0$ where d_0 is the maximum layer spacing set by the surfactant concentration. Setting $d(C_0) = d_0$ we calculate the smallest concentration $\tilde{C}_0$ for which the layer spacing can be expected to vary with C_0 according to Eq. (44). This concentration defines an average in-plane particle separation $\tilde{L}$ according to $\tilde{C}_0 \tilde{L}^2 d_0 = 1$. We find $\tilde{L} = \sqrt{\alpha/\nu (d_0 - d_\pi) d_\pi C_H^{-1/2} \kappa/T}$. For typical values of the parameters, $\alpha = 8$, $\nu = 1/12$, $C_H = 3\pi^2/128$, $d_0 = 200$ Å, $d_\pi = 50$ Å, and $\kappa = 10$ T, the lateral separation of particles is $\tilde{L} \approx 4000$ Å $\simeq 4\sqrt{\lambda_0 d_0}$. At these separations interactions may start to become significant.

B. Aggregating particles

We now include the results concerning the particle aggregation (Sec. III) in our treatment of compaction of the lamellar phase.

Using Eq. (34), we can write the free energy density of the entire system in k_BT units as

$$F=\nu B_0\left(\frac{d_0}{d}\right)^2-(\mu C+C_{\mathrm{agg}}). \tag{45}$$

For low concentrations ($\hat{\Phi}\ll 1$) there is little aggregation and the relation Eq. (44) must be recovered. For higher concentrations the layer spacing d is obtained by minimization of the total free energy density Eq. (45) using the results of Eq. (39).

$$F=\nu B_0\left(\frac{d_0}{d}\right)^2+C[\ln R(\hat{\Phi})-1+R(\hat{\Phi})], \tag{46}$$

where the reference energy E_γ is itself a function of the layer spacing

$$E_\gamma=\alpha\sqrt{KB}(d-d_\pi)^2=E_0\left(\frac{d-d_\pi}{d}\right)^2,$$

with (47)

$$E_0=\alpha\sqrt{K_0B_0}d_0^2.$$

The equilibrium layer spacing in the smectic phase is therefore given by the solution of the following transcendental equation:

$$\Theta(d-d_\pi)Q(\hat{\Phi})e^{-E_\gamma(d)}=1, \quad \text{with} \quad \Theta=\frac{\alpha\lambda_0 d_\pi}{\nu v_0}, \tag{48}$$

where

$$Q(\hat{\Phi})=\frac{1}{2}\left(\sqrt{1+4\hat{\Phi}}-1\right)=\begin{cases}\hat{\Phi}^{1/2}+O(1) & \text{for } \hat{\Phi}\gg 1\\ \hat{\Phi}+O(\hat{\Phi}^2) & \text{for } \hat{\Phi}\ll 1.\end{cases} \tag{49}$$

In general Eq. (48) must be solved numerically to obtain the layer spacing as a function of the concentration of inclusions. However, the inverse function has an analytical solution:

$$\Phi=\frac{1}{\Theta(d-d_\pi)}\left(1+\frac{e^{E_\gamma}}{\Theta(d-d_\pi)}\right). \tag{50}$$

If $\hat{\Phi}\ll 1$, which corresponds to $e^{E_\gamma}\ll\Theta(d-d_\pi)$, no aggregates are formed and Eq. (44) is recovered. In the opposite case where $\hat{\Phi}\gg 1$, the inclusions form aggregates and the dependence of the layer spacing on the concentration of inclusions is no longer a power law: $\Phi\simeq e^{E_\gamma}/(\Theta^2(d-d_\pi)^2)$. In the two limits of high and low concentration of inclusions this relation can be approximated by $\Phi\simeq e^{E_0}/(\Theta^2d^2)$ for $d\gg d_\pi$ and $\Phi\simeq 1/(\Theta^2(d-d_\pi)^2)$ for $d\to d_\pi$. It is interesting to compare these scaling results with the corresponding result for independent particles (no aggregation) Eq. (44). The different scaling can be attributed to the fact that the aggregation reduces the influence per particle because the mean aggregation number varies with the concentration.

As in Sec. III B 2, aggregation is predicted only if the variable $\hat{\Phi}$ is bigger than 1. The condition $\hat{\Phi}\gg 1$ with $\Phi\ll 1$ requires the typical energy E_0 to be several k_BT. With typical values of $E_0\simeq 8k_BT$, only weak aggregation is observed in the lamellar phase (the mean aggregation number $\overline{n}\simeq 2$ for $d_0=200$, $d_\pi=50$, and $\Phi=2\%$). If E_0 is significantly bigger than this value aggregation is stronger. Numerical analysis of Eqs. (46) and (50) shows regions of negative curvature in the free energy as a function of the layer spacing in a certain range of concentration of inclusions. As usual [29], this indicates a phase separation into a dilute and a more concentrated lamellar phase. This phenomenon is studied in more detail elsewhere [30].

Finally, notice that in the case of ionic surfactants, the energy scale is much larger and the onset of the aggregation process may show up in the concentration dependence of the layer spacing. Nonetheless, the relation between the layer spacing and the concentration of inclusions is quite different in the case of electrostatic repulsion, as can be derived from Eq. (3).

IV. CONCLUSION

We have studied theoretically the behavior of particles embedded in a lyotropic smectic phase. The particles exert a force on two adjacent membranes, inducing a local change in the layer spacing (pinching or swelling depending on the boundary conditions near the particles). This pinch creates a deformation field in the surrounding membranes, and hence interactions between inclusions. Our treatment of this deformation involves a continuous description of the lamellar phase based on the Landau–de Gennes smectic Hamiltonian. This is appropriate to describe any type of smectic-*A* lamellar phase over length scales much larger than the layer spacing. We have focused on three common molecular structures for the lamellar phases: a dilute lamellar phase in a binary mixture of solvent and neutral or ionic surfactants, and a lamellar phase formed in a melt of symmetric diblock copolymers. The lamellae formed by the surfactants are known to be highly flexible and the stability of such a phase is insured either by the Helfrich steric repulsion in the case of nonionic surfactants or by electrostatic repulsion between the bilayers in the case of ionic surfactants. In the copolymer case, the characteristics of the phase are dictated by the interplay of the stretching of the polymer chains and the chemical incompatibility of the two blocks. In the case of nonionic surfactants, the bending modulus arises only from the steric repulsion between fluctuating membranes and is generally quite low. Large compression moduli are observed in both ionic surfactant and diblock copolymer lamellar phases.

The deformation field around each particle turns out to be similar to the deformation field due to a dislocation in a smectic liquid crystal. The deformation field is exponentially damped along the membranes (the decay length being the characteristic smectic penetration length λ) and decays slowly ($1/z$) in the direction normal to the lamellae. The smectic energy associated to the deformation is a quadratic function of the magnitude of the deformation induced by the particles. The membrane-mediated interaction between particles is characterized by the parabola $r^2=4\lambda z$. The interaction is repulsive inside the parabola, and becomes attractive outside.

The stored elastic energy of two particles close to each other in the same layer is almost the same as the energy associated to one particle (Fig. 3). Since it is twice as much for two particles far apart, aggregation reduces the total elastic energy. A balance between this and the entropy of the particles leads to the formation of aggregates at sufficiently high concentration of particles. For small aggregates the elastic energy associated with the deformation of the membranes is almost insensitive to the aggregation number. For larger aggregates, the energy increases with the perimeter of the aggregates, i.e., as the square root of the aggregation number. The transition between these two behaviors occurs for an aggregation number n_γ, which may easily be of the order of 100. This behavior leads to an aggregation process reminiscent of the formation of wormlike micelles in a surfactant solution. At very low concentration the particles are independent and no aggregates are observed. As the concentration increases, the chemical potential of the particles μ decreases and aggregation starts. When μ reaches the value $1/n_\gamma$, the aggregates are of size close to n_γ. One can theoretically increase the concentration to the critical value $\mu=0$ where the size of the aggregates diverges discontinuously. At this point very large disks of particles are formed in the lamellar phase and phase separate. However, this critical concentration is often much higher than the concentrated limit and may thus often be inaccessible. The aggregation occurs at volume fractions Φ for which $\hat{\Phi}$ [$=\Phi e^{E_\gamma}$; see Eq. (39)] reaches values significantly higher than 1. Thus for aggregation to be observed in the physically relevant regime where $\Phi<1$, one needs the energy scale E_γ to be several k_BT. Only weak aggregation is predicted in sterically stabilized lamellar phases where E_γ is of order a few k_BT, but aggregation may be expected to be much stronger in a copolymer lamellar phase as well as in lamellar phases stabilized by electrostatics.

We have studied the influence of the particles on the free smectic free energy. The elastic energy [$\propto(d-d_\pi)^2$] tends to change the layer spacing while the compressibility of the smectic due to the repulsion between membranes opposes this effect. The balance of these two interactions leads to an equilibrium thickness that depends on the concentration of particles. For independent particles with $d_0-d_\pi>0$, this dependence is found to be $d-d_\pi\sim 1/C$ in the Helfrich regime [Eq. (44)]. We suggest that the inclusion of proteins in the phase may lead to phase separation into a more dense lamellar phase and pure solvent.

The formation of aggregates has a strong influence on the behavior of the lamellar phase. If aggregates of a well-defined size are formed the inclusions could still be considered as independent particles by a simple renormalization of the size and concentration. But since the mean size of the aggregates in the lamellar phase is a function of the concentration of inclusions, the relation between the layer spacing and the concentration gives information on the aggregation process.

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APPENDIX

In Secs. II and III we found it necessary to include a microscopic cutoff when evaluating certain integrals over z. We used throughout the cutoff $z_c\simeq d$, which naturally arises as a result of the breakdown of the continuum theory at this length scale. We call this the ‘‘continuum’’ cutoff. However, one should also check to see if other aspects of the theory break down before this one. In particular the smectic Hamiltonian (5) contains only the leading order terms in an expansion of derivatives of u. In general higher order terms [such as $(\partial_z^2 u)^2$] start to become significant when the lowest order terms $\partial_z u$ or $\lambda\nabla_r^2 u$ are of the order of unity. Thus there is another ‘‘smectic’’ cutoff that corresponds to the value of z when these lowest order terms are of the order of unity. If the the inclusions only weakly deform the membrane, by which we mean $|d-d_\pi|\lesssim d$, then the smectic cutoff is always smaller than, or of the order of, the continuum cutoff. This validates our use of the continuum cutoff $z_c\simeq d$ throughout.

For a single pointlike particle the deformation field was calculated in Sec. II A and is given by Eq. (10). It is a simple task to calculate the maximum values of $\partial_z u$ and $\lambda\nabla_r^2 u$, which depend on the z cutoff. We find that in the weak deformation regime $d_\pi/d\lesssim 1$ the smectic cutoff is small, $z_c\simeq[|(d-d_\pi)|/d]^{1/3}d\lesssim d$. For completeness we also calculate the smectic cutoff in the opposite regime $d_\pi/d\gg 1$, which would correspond to, e.g., colloidal particles with a radius much bigger than the layer spacing. In this case the smectic cutoff is *more* restrictive than the continuum one and is given by $z_c\simeq[(d-d_\pi)/d]^{1/2}d$. Systems for which $d_\pi/d\gg 1$ are not considered in the present work.

We can also check the case of a disklike aggregate. We instead use Eqs. (25) and (20) and find

$$\epsilon=\frac{\partial u(r,z)}{\partial z}=\lambda\nabla_r^2 u(r,z)=\Delta\partial_z\int dx J_0\left(x\,\frac{r}{a}\right)J_1(x)e^{-(x/x_z)^2}$$

$$\simeq\frac{\Delta\lambda}{a^2}\int_0^{x_z}x^2J_0(x)J_1(x)dx, \tag{51}$$

where $x_z\equiv a/\sqrt{\lambda z}$. The integral is evaluated at the edge of the aggregate ($r\simeq a$) where the deformation is the largest. In the physically important limit of large aggregates $x(z)\gg 1\,\epsilon\simeq|(d-d_\pi)/z|$. The smectic theory breaks down for $\epsilon\gtrsim 1$ corresponding to a cutoff $z_c\simeq d-d_\pi$. This is of the same order as the continuum cutoff in the weak perturbation regime $d_\pi/d\lesssim 1$. Although the smectic cutoff can be larger in the opposite case $d_\pi/d\gg 1$ such systems are again not considered in the present work.

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