

Inclusions in Thin Smectic Films

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Abstract. — We study theoretically the behaviour of inclusions in thin films of smectic-A liquid crystal consisting of a stack of regularly spaced membranes. Such membranes are frequently formed in thin diblock copolymer films or in solutions of amphiphilic surfactants. Inclusions, such as colloidal particles or large proteins, couple locally to the smectic and may deform the membranes over a large length scale. Using the Landau-de Gennes description of smectic liquid crystals we obtain the deformation field of the membranes for the two cases of a freely suspended film and a film on a rigid substrate. In the first case we compare and contrast with earlier work on inclusions confined between two membranes and in a lamellar phase of infinite thickness. We show that the existence of an overshoot in the deformation of the layers is intrinsically related to the finite size of the sample. This leads to qualitative differences in the interaction potential between two inclusions for finite and infinite systems. The interaction, monotonically attractive for infinite systems, becomes repulsive at large distance is the sample is finite. We show that the equilibrium position of the particle depends on the surface tension at the film boundary and give quantitative predictions for the particle-induced deformation of the membranes.

1. Introduction

Lamellar phases consisting of stacks of regularly spaced membranes are often found in nature [1]. Typical examples include symmetric bilayers of lipid surfactants, separated by solvent, and certain copolymers melts [2, 3] as well as many others. Membranes play many essential roles in biology too and cell membranes are known to contain a wide spectrum of embedded proteins in a medium rich in various colloidal particles [4, 5].

Recent theoretical work on the physics of membrane inclusions can be divided into two categories: (i) studies of foreign bodies in lamellar systems of finite extent, namely particles embedded in or between one or two fluctuating membranes [6, 7] and (ii) particles embedded in a stack of membranes of infinite thickness [8–10]. In these studies the inclusions are assumed

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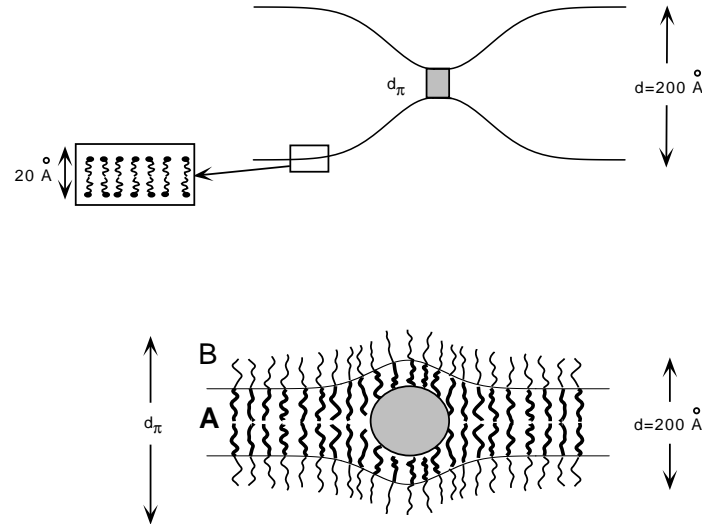


Fig. 1. — Schematic diagram showing the deformation of the lamellae near an inclusion. Two types of inclusions might be typical. **a)** Amphiphilic inclusions suspended in a lyotropic lamellar (L_α) phase. Here the inclusions shown locally pinch the neighbouring membranes together, reducing the intermembrane spacing by $d - d_\pi$. The opposite effect of an increase in the layer spacing is also possible. **b)** Colloidal particles doping a thermotropic, such as a diblock copolymer lamellar phase. Here the layer spacing is locally increased by $d + d_\pi$. In both cases typical dimensions are shown.

to pinch together or push apart neighbouring membranes by locally fixing the spacing between them (see Fig. 1). The deformation is usually assumed to be weak and a linearized version of the smectic hamiltonian is often used. However the case of strong pinches, for which a non-linear treatment is required, has also been investigated [7]. A fundamental difference between the two-membrane and multi-membrane systems is the presence of an “overshoot” in the profile of the layers in the two layer system, while the deformation profile is monotonic in an infinite stack of membranes. When the deformation is weak the amplitude of the overshoot is small, typically of the order of 1% of the maximum amplitude of the deformation. In the opposite case of strong perturbation (pinch) the amplitude of the overshoot can instead be much larger. These features are of considerable importance for, *e.g.* the interaction potential between two inclusions mediated by the fluid membranes, which has been actively studied in both cases [11]. The presence of an overshoot in the layer deformation near an inclusion can usually be traced to non-monotonic two body interactions and associated metastable states.

In this paper, we study the effect of inclusions embedded in a thin lamellar film. This work explains the predicted qualitative difference between two membrane and multimembrane systems. Experimental measurements of inclusions in thin copolymer lamellar films are expected soon [12].

The physics of lamellar films is studied using the so-called Landau-de Gennes Hamiltonian for smectic liquid crystals [1]. In this description, the normal displacement of the membranes with respect to their unperturbed (flat) position is described by a continuous field $u(\mathbf{r}, z)$ where \mathbf{r} and z are the spatial coordinates in the plane and normal to the flat layers respectively.

The bulk hamiltonian reads:

$$\mathcal{H}_{\text{bulk}} = \frac{B}{2} \int d^2\mathbf{r} dz [(\partial_z u)^2 + \lambda^2 (\nabla_{\parallel}^2 u)^2] . \quad (1)$$

In this expression ∇_{\parallel} is the gradient operator in the x - y plane, $\lambda = \sqrt{K/B}$ is a length characteristic of the smectic (typically of the order of the layer spacing d) and B and K are respectively the compression and bending moduli of the smectic.

Most of the calculations presented below will be performed in Fourier space, where the forward and reverse transforms are defined by:

$$f_{\mathbf{q}}(z) = \int d^2\mathbf{r} f(\mathbf{r}, z) e^{i\mathbf{q}\cdot\mathbf{r}} \quad f(\mathbf{r}, z) = \int \frac{d^2\mathbf{q}}{(2\pi)^2} f_{\mathbf{q}}(z) e^{-i\mathbf{q}\cdot\mathbf{r}} . \quad (2)$$

We intend to consider films of finite thickness where the last layer of the film (located in $z = H$) is in contact with some other gas or liquid and, as a result, experiences a surface tension γ . The complete hamiltonian of such a film in $\{\mathbf{q}, z\}$ -space is given by

$$\mathcal{H} = \int \frac{d^2\mathbf{q}}{(2\pi)^2} \mathcal{H}_{\mathbf{q}} \quad (3)$$

where

$$\mathcal{H}_{\mathbf{q}} = \frac{1}{2} \left[\gamma q^2 |u_{\mathbf{q}}(H)|^2 + B \int dz \{ |\partial_z u_{\mathbf{q}}(z)|^2 + \lambda^2 q^4 |u_{\mathbf{q}}|^2 \} \right] . \quad (4)$$

Hence the total Hamiltonian of the smectic slab is obtain by integrating (4) over all possible Fourier modes \mathbf{q} .

The remainder of this paper is organized as follows. In Section 2 we consider the deformation caused by a single inclusion in a freely suspended smectic film. We find a qualitative difference between our results and the deformation in an infinite slab, namely an overshoot appears in the deformation profile. In Section 3 we investigate the special case of a film on a rigid substrate, where the free surface has an interfacial tension γ . We see that at low surface tension the inclusion resides close to the interface and migrates toward the center of the film as the surface tension increases. The interactions between two inclusions in a freely suspended film are investigated in Section 4. Because of the overshoot in the deformation profile the potential exhibits a repulsive region which is not observed in a slab of infinite thickness. The last section contains remarks on possible experiments to check our predictions as well as concluding comments. We have confined much of the non-essential algebra to an appendix in the interest of readability.

2. Freely Suspended Film

We consider a symmetric smectic film with two free surfaces, both having surface tension γ , which contains a single inclusion. As shown in Figure 2 the position of the inclusion defines the origin of the coordinate system (\mathbf{r}, z) , and we denote h^{up} and h^{down} the position of the interface above ($z > 0$) and below ($z < 0$) the inclusion respectively (hereafter we use the notation X^i where i is either up or down to designate the value of the variable X in the upper or lower region of the film). The total thickness of the film is then given by $H = h^{\text{up}} + h^{\text{down}}$.

We are only interested in the equilibrium position (deviation from flatness) of the membranes due to the inclusions. Averaging over the fluctuations of the membranes, we obtain this

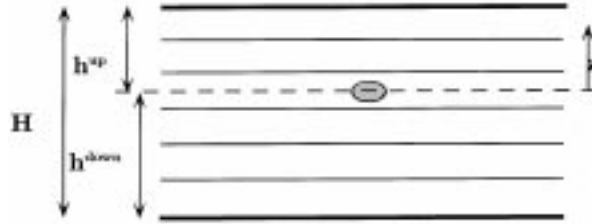


Fig. 2. — Schematic diagram representing a thin lamellar film bearing a single inclusion. The parameters defined in the text are shown.

equilibrium position by minimizing the hamiltonian in Fourier space (4) with respect to the field $u(\mathbf{q}, z)$. The corresponding Euler-Lagrange equations and their solutions are:

$$\partial_z^2 u_{\mathbf{q}}^i = \lambda^2 q^4 u_{\mathbf{q}}^i \quad \Rightarrow \quad u_{\mathbf{q}}^i(z) = \frac{u_{\mathbf{q}}^i(0) \sinh q^2 \lambda (h^i - z) + u_{\mathbf{q}}^i(h^i) \sinh q^2 \lambda z}{\sinh q^2 \lambda h^i} \quad (5)$$

where $u_{\mathbf{q}}^i(0)$ and $u_{\mathbf{q}}^i(h^i)$ are the Fourier transforms of the deformation of the layers immediately in contact with the inclusion ($z = 0$) and of the interfaces surface layer ($z = h^i$) respectively. Following the work of Turner *et al.* [13] for a dislocation in copolymer lamellar phase, the function $u_{\mathbf{q}}^i(0)$ is chosen to mimic the effect of the inclusion on the first layers, located at $z = \pm d/2$. The boundary conditions for $z = 0$ are written:

$$u_{\mathbf{q}}^{\text{up}}(0) = \hat{u} + \frac{\Delta u}{2} \quad u_{\mathbf{q}}^{\text{down}}(0) = -\hat{u} + \frac{\Delta u}{2} \quad (6)$$

where Δu is the Fourier transform of the deformation at the inclusion, and \hat{u} is the Fourier transform of the layer deformation once the actual contribution of the inclusion has been subtracted. In the following, the choice of Δu depends on the type of inclusion we wish to study. The function \hat{u} is fixed by the minimization of the smectic energy in \mathbf{q} -space (Eq.(4)).

In the appendix, we show how to calculate the deformation field of the membranes and the free energy of the smectic as a function of the deformation Δu induced by the inclusion only.

2.1. EQUILIBRIUM POSITION OF THE INCLUSION. — The equilibrium position of the inclusion is the one which minimizes the total energy for a given deformation Δu . As shown in the appendix, the distance from the inclusion to the upper surface of the film h^{up} can be obtained from the integral equation

$$\int_0^\infty dq q^5 |\Delta u|^2 \frac{(1 - \Gamma^2) \sinh q^2 \lambda (H - 2h^{\text{up}})}{(1 + \Gamma^2) \sinh q^2 \lambda H + 2\Gamma \cosh q^2 \lambda H} = 0 \quad (7)$$

where

$$\Gamma \equiv \frac{\gamma}{\sqrt{KB}} \quad (8)$$

is the normalized surface tension of the film, discussed in more details in Section 5. In the following we will use a point-particle approximation, which corresponds to choosing a delta function for Δu (or a constant for $\Delta u(\mathbf{q})$). This is appropriate for small inclusions and is equivalent to assuming that the lateral size of the inclusion is not an important length in the problem. The resulting approximate solution (to $u(\mathbf{r})$, say) is asymptotically exact in the far field limit. The reader might be reassured to know that the solutions of equation (7) are

quite insensitive to the precise choice of Δu . Solving (7) for $\Gamma > 1$ gives $h^{\text{up}} = H/2$. This solution is a minimum of the energy. For $\Gamma < 1$, the same solution is obtained, but this time it is a maximum of the energy, and for $\Gamma = 1$, the energy is independent of the position of the inclusion. This means that if the surface tension is lower than the intrinsic interfacial tension of the film \sqrt{KB} , the inclusion will reside at the interface, $h^{\text{up}} = 0$ or $h^{\text{down}} = 0$, while the equilibrium position is in the middle of the film if the surface tension is higher than the interfacial tension between lamellae. When the two tensions are exactly equal, the inclusion can reside anywhere in the film. The reason for which $\Gamma = 1$ is such a special value is discussed in the next section.

2.2. INCLUSION IN THE CENTER OF A FREELY SUSPENDED FILM. — In this section, we study the case where the inclusion is located in the middle of the film $h^{\text{up}} = h^{\text{down}} = H/2$, for any value of the surface tension of the film. We have seen in the previous section that this position does not correspond to the equilibrium position of the inclusion if $\Gamma < 1$. Nevertheless, we choose to examine this situation for all Γ for two main reasons. First of all as mentioned in the introduction, we wish to check the present study against the two known limits of an inclusion in a lamellar phase of infinite thickness and of an inclusion between two membranes. The second reason is that in experiments the inclusion may be found away from its equilibrium position for dynamical reasons. In many cases, it is difficult for the inclusion to travel through the membranes.

When the inclusion is located in the center of the film, one can argue on symmetry ground that the function \hat{u} vanishes, since the deformation of the first layer at $z = 0$ has to be symmetric in z . The deformation due to the inclusion is modeled by a delta function, such that its Fourier transform is simply a constant: $u_{\mathbf{q}}(0) = \pi\alpha$ (α has the dimensions of a volume). The amplitude α depends on the strength of the coupling between the membranes and the inclusion.

From the results of the appendix (Eqs. (A.2a), (A.3)), the deformation of the layers can be written in the following simple scaling form

$$u(\mathbf{r}, z) = \frac{\alpha}{\lambda H} I_{\Gamma}(\bar{\mathbf{r}}, \bar{z}) \quad (9)$$

with scaled (dimensionless) variables $\bar{\mathbf{r}} = \mathbf{r}/\sqrt{\lambda H/2}$ and $\bar{z} = 2z/H$ and

$$I_{\Gamma}(\mathbf{r}, z) \equiv \int_0^{\infty} q dq J_0(qr) \frac{\cosh q^2(1-z) + \Gamma \sinh q^2(1-z)}{\cosh q^2 + \Gamma \sinh q^2}. \quad (10)$$

The function I_{Γ} is plotted in Figure 3 for different values of the rescaled surface tension Γ . The numerical factor α in (9) is chosen to satisfy some boundary condition for the layers in contact with the inclusion ($z = d/2$). This boundary condition can be imposed in two different ways, corresponding to different microscopic physics. One can assume that an inclusion of thickness d_{π} fixes the lamellar spacing locally at d_{π} . This would correspond to an inclusion that rigidly holds the membranes. In this case the constant α is chosen so that $u(\mathbf{r} = 0, d/2) = (d_{\pi} - d)/2$ (see Fig. 1). In this case the layer displacement becomes

$$u(\mathbf{r}, z) = \frac{(d_{\pi} - d)}{2} \frac{I_{\Gamma}(\bar{\mathbf{r}}, \bar{z})}{I_{\Gamma}(0, d/H)}. \quad (11)$$

On the other hand, α can be thought of as an independent parameter which corresponds to applying a constant point force to the bilayers at $\mathbf{r} = 0, z = 0$. Such a representation might be relevant for inclusions which act like springs, coupling two neighbouring membranes, rather than like rigid objects.

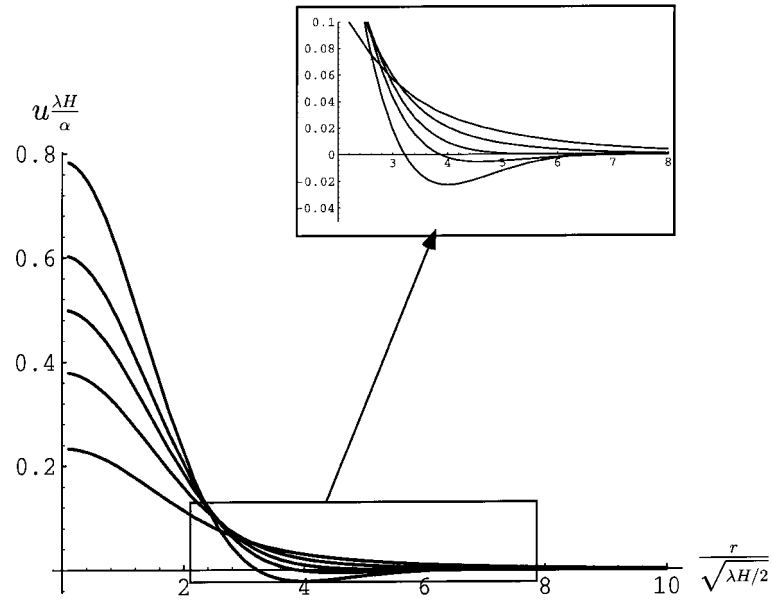


Fig. 3. — The variation of the deformation of the film surface with radial distance r from an inclusion in the center of a symmetric film, at $r = 0$. Five different values of the surface tension $\Gamma = 0, 0.5, 1, 2, 5$ are shown. Increasing values of Γ correspond to decreasing amplitudes immediately above the inclusion. The region of the overshoot is shown magnified.

By evaluating the integral $I_{\Gamma}(0, \bar{z})$ for $\bar{z} \ll 1$ ($d \ll H$), one can prove that these two results coincide for a film containing many layers. In this limit, the integral is dominated by the large wave vectors and is independent of the surface tension at leading order. For the first layer, located at $z = d/2$, the integral is: $I_{\Gamma}(0, d/H) \simeq H/d$. Upon re-insertion of this relation into equation (9) one sees that the two boundary conditions are equivalent for films with many layers where $\alpha = (d_{\pi} - d)d\lambda/2$.

2.2.1. Profile of the Interfaces. — This section is devoted to the study of the shape of the last layer of the film ($\bar{z} = 1$) which might be measurable experimentally by surface probes such as Atomic Force Microscopy. The profile of the last layer is shown in Figure 3 for different values of the surface tension. Several remarks should be made concerning these plots.

◇ The profile exhibits an overshoot which is clearly related to the finite thickness of the slab — no overshoot is observed in an infinite lamellar phase [8]. The position r_{ov} and the amplitude u_{ov} of the overshoot cannot be calculated analytically, but one can see from equation (9) that r_{ov} increases with the thickness of the slab as $\sqrt{\lambda H}$, as does any radial lengthscale, and that the amplitude u_{ov} decreases as the inverse of the slab thickness.

◇ The overshoot disappears completely when the reduced surface tension Γ is equal to unity. In fact the case $\Gamma = 1$ is the only one soluble analytically. From equations (9, 10) we find

$$u(\mathbf{r}, z) = \frac{\alpha}{2\lambda H} e^{-r^2/(4\lambda z)} \quad \text{for } \Gamma = 1. \quad (12)$$

Surprisingly enough, this profile is exactly the same as the profile for a layer located at height z in an infinite slab [8] and is independent of the film thickness. As discussed in Section 5,

the value $\Gamma = 1$ corresponds to, *e.g.* a diblock copolymer film of the architecture B-A-...-A-B in contact with a melt of homopolymer-A.

◇ Finally, we observe from Figure 3 that the surface tension acts to flatten and broaden the deformation of the last layer (and as a consequence all the layers below it). This broadening can be understood if one identifies that the total volume displaced by the membrane: $\int 2\pi r dr u(\mathbf{r})$ is equal to the $\mathbf{q} = 0$ Fourier mode of the layer profile $u_{\mathbf{q}}(0)$. According to equation (A.2a), the $\mathbf{q} = 0$ mode is independent of the surface tension and of the thickness of the film. In the limit of high surface tension ($\Gamma \gg 1$), one can estimate the variation of the amplitude of the deformation (at $\mathbf{r} = 0$ say), which is: $u(\mathbf{r} = 0, \bar{z} = 1) \simeq \alpha/(2\lambda H) \log \Gamma/\Gamma$. Since the total volume of the deformation is conserved, a good definition of the characteristic length δ is $u(\mathbf{r} = 0, \bar{z} = 1)\delta^2 = u_{\mathbf{q}}(0)$, which leads to the following expression for the characteristic length of the deformation in the large surface tension limit:

$$\delta \simeq \sqrt{\frac{\lambda H \Gamma}{\log \Gamma}}. \quad (13)$$

This result is similar to a result obtained in the case of an edge dislocation in a copolymer lamellar film ($\sqrt{\lambda H \Gamma}$ [13]) to within a logarithmic correction. The reader might notice that another characteristic length may be constructed from the curvature of the deformation at the origin: $\partial^2(u(\mathbf{r})/u(0))/\partial \mathbf{r}^2|_{\mathbf{r}=0} = (\delta')^{-2}$. This gives a length $\delta' \propto \sqrt{\lambda H \log \Gamma}$ which is slowly varying with Γ and does not describe correctly the broadening of the deformation with the surface tension.

2.2.2. Variation of the Layer Profile with the Distance from the Interface. — In this section we describe the variation of the profile with z for the internal layers of the film $\bar{z} < 1$. For simplicity we consider only the case when the surface tension at the film surface vanishes ($\Gamma = 0$). This is expected to be appropriate for surfactants in solutions and for diblock copolymers films where the component presented at the surface is in contact with a homopolymer melt of the same species. Corresponding results for $\Gamma \neq 0$ may also be derived from the results of Section 2.

The layer deformation in the film interior is shown in Figure 4. Notice that:

◇ The amplitude of the maximum of the deformation at $\mathbf{r} = 0$ decreases with z , while the amplitude of the overshoot increases with z , and reaches its maximum at the interface. If the first result is natural, the second result is more surprising. However, it can be related to the fact that the amplitude u does not enter the hamiltonian directly. The profile can (and does) actually become smoother by increasing u , but decreasing its derivatives.

◇ More quantitatively, one can evaluate the amplitude of the maxima as a function of z for small z . The evaluation of the integral (10) gives $I(\Gamma = 0, \mathbf{r} = 0, z) \simeq 2/z$ for small z . Figure 4b shows that this scaling law is valid roughly until $\bar{z} \simeq 0.6$. We see on the same figure that the amplitude of the overshoot increase linearly with z for small z .

◇ The curvature of the deformation at $\mathbf{r} = 0$ depends on z . The lateral extent of the deformation increases with z as $\delta \simeq \sqrt{\lambda z}$ for small z . This result is expected, see *e.g.* equation (13), and is similar to that predicted for an infinite lamellar phase.

2.2.3. Two Dimensional Case - Long Rodlike Inclusions. — In this section we briefly overview the main differences between the three dimensional case, discussed above, and the two dimensional case, where there is translational symmetry in the y direction (say). This case is appropriate for very long rod-like inclusions, of length l , embedded in a smectic film. One expects that near the inclusion $r \ll l$ the deformation will be close to that of an infinite rod while in the other limit $r \gg l$ the distortion field will resemble that of a point-like inclusion [14].

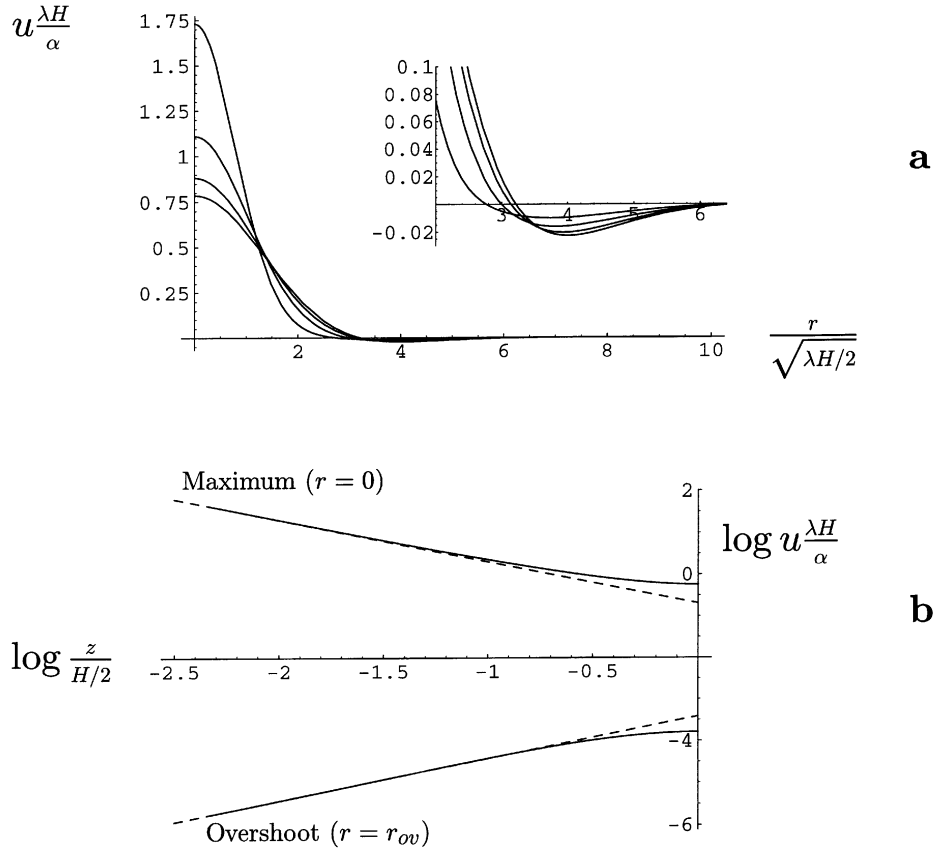


Fig. 4. — a) Variation of the layer profile with distance to the inclusion z for a film with no surface tension ($\Gamma = 0$). The deformation is shown for four values of $\bar{z} = 2z/H$: $\bar{z} = 0.3, 0.5, 0.7, 1$. Increasing values of z correspond to the curves with decreasing amplitude. The region of the overshoot is shown magnified. b) Variation of the amplitude of the maximum of the deformation at $r = 0$ (upper curve) and of the amplitude of the overshoot (lower curve) with z . The two dashed lines correspond to the slopes 1 (overshoot) and -1 (maximum)

The main difference with the three dimensional case is the definition of the integral (10), which becomes

$$I_{\Gamma}^{2D}(x, z) \equiv \int_{-\infty}^{\infty} dq e^{iqx} \frac{\cosh q^2(1-z) + \Gamma \sinh q^2(1-z)}{\cosh q^2 + \Gamma \sinh q^2}. \quad (14)$$

This modifies the scaling of equation (9) to give $u(x, z) = \frac{\alpha}{\sqrt{\lambda H}} I_{\Gamma}^{2D}(\bar{x}, \bar{z})$. As follows from calculations similar to the 3-D case, the characteristic radial length at the film surface varies as a function of the surface tension like $\delta \simeq \sqrt{\lambda H \Gamma}$. As in the 3-D case, the length $\delta' = \Gamma^{1/4} \sqrt{\lambda H}$ associated with the curvature at the origin depends less strongly on the surface tension.

3. Films on Rigid Flat Substrates

In this section we discuss the case of a lamellar film on a flat rigid substrate. This geometry may be particularly relevant to experiments on thin copolymer lamellar films doped with colloidal inclusions. Unfortunately quantitative estimates require numerical computation. This can be traced to the loss of up/down symmetry for the film. The equilibrium position of the inclusion varies continuously with z and may be calculated for a given surface tension by minimising the free energy. In this paper we will merely discuss the general method for solving the problem and mention a few typical numerical results. A more specific study might become appropriate should suitable experimental results become available.

3.1. EQUILIBRIUM POSITION OF THE INCLUSION. — The equilibrium position of an inclusion in a lamellar film on a rigid substrate can be derived using the same formalism as the one discussed in Section 2.1. A rigid substrate is introduced merely by setting the interfacial tension of the lower interface to infinity. In this way we suppress any deformation of the lower interface thereby correctly modeling a rigid substrate. An integral equation equivalent to equation (7) for the thickness h^{up} is derived in the appendix:

$$\int_0^\infty dq q^5 \frac{\cosh q^2(1-2\bar{h}) - \Gamma \sinh q^2(1-2\bar{h})}{\cosh q^2 + \Gamma \sinh q^2} = 0 \quad (15)$$

where $\bar{h} = h^{\text{up}}/H$. The results of numerical analysis of this equation are shown in Figure 5a and share similarities with those obtained for an edge dislocation in a copolymer lamellar phase [13]. The asymptotic solutions are $\bar{h} = 1/2$ when $\Gamma \rightarrow \infty$ since the film is symmetrical in this limit. When $\Gamma < 1$, equation (15) has no solution and the inclusion is located on the last layer of the film $\bar{h} = 0$. One can also expand the integral for $\Gamma \simeq 1$. The integral (15) can be performed analytically to lowest order in $\Gamma - 1$. Assuming that $h^{\text{up}} = \epsilon H$ with $\epsilon \ll 1$ one can expand the result of the integration to lowest order in ϵ . In this limit we find the scaling behaviour for the position of the inclusion as a function of the surface tension $\bar{h} = \left(\frac{\Gamma-1}{2}\right)^{1/3}$. The validity of this scaling law is shown on Figure 5a, together with the position of the inclusion for any surface tension. The power law derived above seems to hold only for Γ *extremely* close to 1 (see inset in Fig. 5a) and is probably of limited experimental relevance. Note also that the equilibrium position of the inclusion quickly approaches the center of the film for surface tensions $\Gamma \gtrsim 2$.

3.2. DEFORMATION OF THE INTERFACE. — Once the position of the inclusion is known, the deformation of the interface, or of any layer inside the film, can be determined numerically using the result of the appendix. The shape of the interface is found to be determined by the integral

$$u(\mathbf{r}, z = H) = \frac{\alpha}{\lambda H} \int_0^\infty dq q J_0 \left(\frac{qr}{\sqrt{\lambda H}} \right) \frac{\cosh q^2 \lambda (H - h^{\text{up}}(\Gamma))}{\cosh q^2 \lambda H + \Gamma \sinh q^2 \lambda H} \quad (16)$$

where $h^{\text{up}}(\Gamma)$ is shown in Figure 5a and the interface profile is shown in Figure 5b. Notice that for $\Gamma \approx 1$ the deformation is highly peaked, since the inclusion is quite close to the interface. As the surface tension is increased the profile is rapidly smoothed out partly because the inclusion itself moves down, away from the film surface.

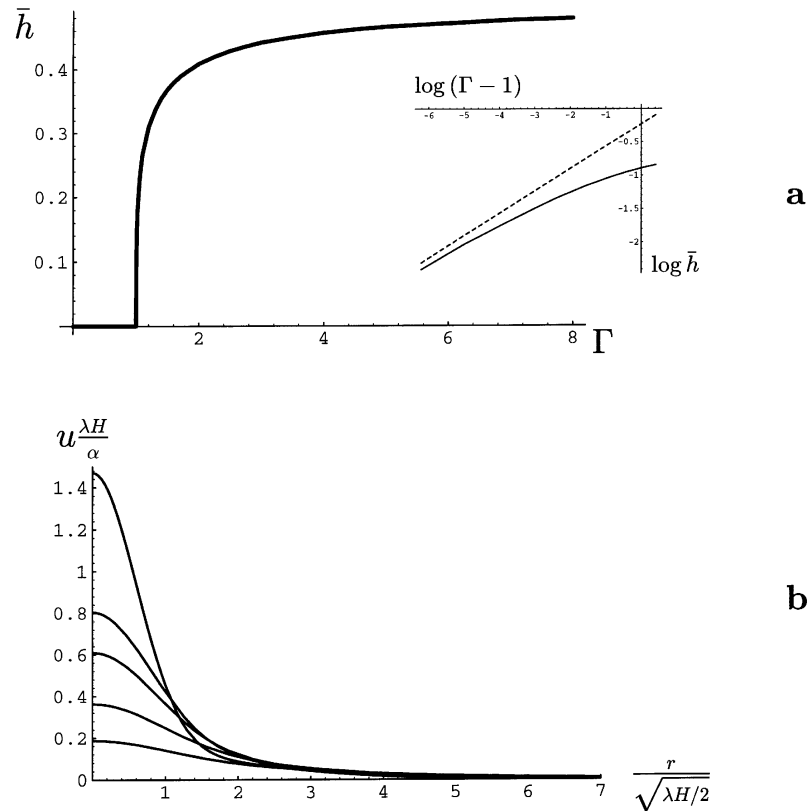


Fig. 5. — Smectic film on a rigid substrate. **a)** Variation of the equilibrium position of an inclusion in the film with the renormalized surface tension of the interface. The position is given by the variable $\bar{h} = h^{\text{up}}/H$ where h^{up} is the distance at the upper interface and H the total thickness of the film. The inclusion lays at the interface if $\gamma < 1$ and goes toward the middle of the film ($\bar{h} = 1/2$) as the surface tension is increased. Inserted is shown a Log-Log plot of the same function for Γ close to unity. The dashed line shows the power law $\bar{h} = (\frac{\Gamma-1}{2})^{1/3}$ derived in Section 3.1. **b)** Deformation of the film surface for different values of the surface tension $\Gamma = 1.1, 1.5, 2, 4, 10$. Increasing values of Γ correspond to curves with decreasing amplitude. The position of the inclusion may be obtained from Figure 5a

4. Interaction between Inclusions

In this section, we study the interactions between inclusions induced by their coupling with the membranes. If two inclusions are located close enough to one another, their deformation fields interfere and as a result, the inclusions may experience a force. These interactions have been studied in detailed in several cases [8,9,11], and it is our aim here to study the effect of the finite film thickness on the interaction potential. For the sake of simplicity, we will study the interaction only for the special case of a freely suspended lamellar film in which both particles are located within the same layer at the mid-plane ($z = 0$). As mentioned previously [9], the interactions when the two inclusions are in the same layer are rather subtle, due to the breakdown of the continuum approximation at length scales smaller than the layer spacing,

as well as to the point-like nature of the inclusions. A naive derivation of the interaction potential for two-point like inclusions leads to an unphysical divergence when the inclusions are within the same layer, which can be avoided by smoothing out the distribution function of the inclusions. If a gaussian shape of width b is assumed for the distribution function, a reasonable interaction potential is obtained provided the width of the gaussian distribution is chosen to be $b \simeq \sqrt{\lambda d}$, which is the range of the deformation of the layers in contact with the inclusion [9].

We use this method to study the interaction potential between two particles embedded in a smectic film of finite thickness. We assume a density distribution function at $z = 0$ of the form

$$\rho(r) \sim \left(e^{-\frac{r^2}{2b^2}} + e^{-\frac{(r-\mathbf{R})^2}{2b^2}} \right) \quad (17)$$

where \mathbf{R} is the in-plane distance between inclusions. The Fourier transform of the shape of the layer at $z = 0$ is given by

$$u_{\mathbf{q}}(0) = 2\pi b^2 \beta e^{-\frac{b^2 \mathbf{q}^2}{2}} (1 + e^{-i\mathbf{q} \cdot \mathbf{R}}) \quad (18)$$

where β is a normalization factor depending on the strength of the coupling with the membranes. In the following, we will consider the case where the deformation at the inclusions is fixed to a given value. In this case, the parameter β is a function of the distance \mathbf{R} (see appendix): $\beta(\mathbf{R}) = \Delta(1/(1 + e^{-\mathbf{R}^2/(2b^2)}))$.

The interaction energy, along with the self energy of an isolated particle in the film, are shown in Figure 6. It should be noted that these energies are dependent upon three parameters, namely the normalised separation between the two inclusions $\mathbf{X} = \mathbf{R}/b$, the number of layers in the film $N \simeq \lambda H/b^2$, and the normalised surface tension Γ . As expected, we can see in Figure 6a that both for $\Gamma = 1$ and for $N \gg 1$, the self energy of a single particle reaches the value of the infinite film limit. In Figure 6b we display the normalised interaction energy \bar{F}_{int} for different values of the film thickness. We display only the case where the surface tension $\Gamma = 0$, for which the effect of the finite thickness of the film is the most striking. We see that when the film contains of the order of 20 layers or more the interaction is almost indistinguishable from that of an infinite film. For thin films, of only 4 layers or so, the interaction is repulsive at large distances (in fact, it oscillates very weakly at even larger distances, as does the deformation of the layers). This can be thought of as a consequence of the overshoot in the deformation profile. Although one could argue that for such a small number of layers the continuum approximation may be starting to break down, the repulsive interaction itself can be traced to the presence of an overshoot in the deformation profile and is therefore unlikely to be an artifact of the continuum model. To see this note that near the overshoot the spacing between the first two membranes ($z = \pm d/2$) is *larger* than the asymptotic layer spacing for inclusions which pinch the membranes and *vice versa*. It is energetically unfavorable for the second inclusion to reside in this region.

As a final comment, we would like to stress that the shape of the interaction potential for small distances of the order of $\sqrt{\lambda d}$ is very sensitive to the choice of the boundary conditions and is not something that we wish to focus on here. On the other hand we claim that the repulsive regime at large distances is a much more universal feature and is directly related to the finite thickness of the film.

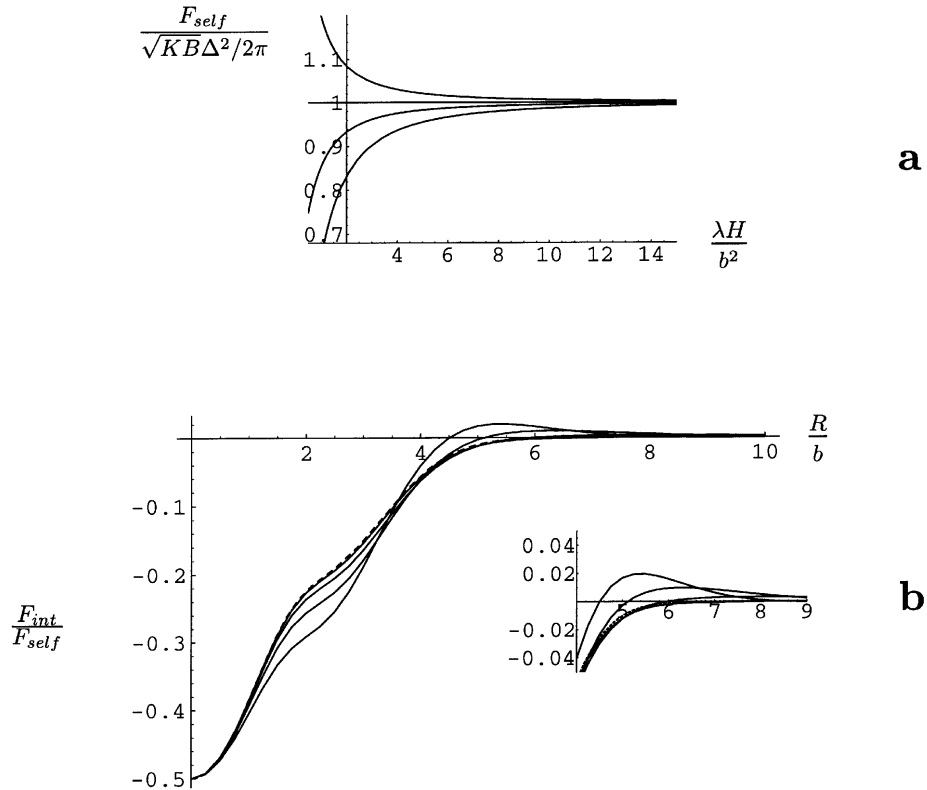


Fig. 6. — **a)** Self energy of a particle in a thin film as a function of the film thickness for 4 values of the surface tension: $\Gamma = 0$ (lowest curve), 0.5, 1, 2 (highest curve). For $\Gamma = 1$ the self energy is the one in an infinite film. **b)** Interaction energy as a function of the distance between two inclusions for $\Gamma = 0$ and for different values of the number of layers in the film: $N \simeq \lambda H/(b^2) = 2, 4, 8, 20$. The dashed curve represents the interaction energy in an infinite smectic phase. The region where the interaction changes sign is shown magnified. The features around $R/b \approx 2$ are not thought to be universal but rather depend delicately on the choice of boundary conditions, as discussed in the text.

5. Discussion and Conclusion

In this section, we outline the main results of the paper, and discuss possible experimental investigations.

We have studied the influence of inclusions in thin smectic films, both freely suspended in air or in some solvent, and deposited on a rigid substrate. Our formalism is appropriate for both lyotropic and thermotropic smectic films, provided that they contain a sufficient number of layers to justify the use of a continuum description. In practice this may be a rather weak restriction. This calculation assumes a pre-average over the fluctuations in the smectic film, and considers only the average position of the membranes, as given by the minimization of the film energy. This approach is expected to be valid for “rigid” systems such as copolymer melts or highly charged surfactant solutions, for which the repulsive interactions between the lamellae at the molecular level are strong and thus prevent important fluctuations. For “softer” systems where the repulsive interaction is itself induced by the fluctuations of the membranes

(Helfrich interaction), a more adequate treatment of the fluctuations is probably needed. We have presented results for the equilibrium position of a single inclusion in the film, for the evolution of the deformation profile with the distance z from the inclusion, and for the variation of the deformation of the surface of the film with a normalized surface tension Γ . At least two of these might soon be measured experimentally: the equilibrium position of the inclusion can be investigated by Freeze Fracture Electron Microscopy and the shape of the surface of the film by Atomic Force Microscopy.

We use the dimensionless parameter $\Gamma = \gamma/\sqrt{KB}$ (where γ is the actual surface tension of the last layer of the film, and K and B are the bending and compression moduli in the film) to characterize the surface tension of the film. This normalized surface tension deserves a few comments. In the case of a (A-B) diblock copolymer smectic film, the bending and compression moduli are approximately given by $B = 3\gamma_{AB}/d$ and $K = d\gamma_{AB}/3$ [15] where γ_{AB} is the interfacial tension between the monomers A and B, and d is the spacing between layers. Hence, the normalised surface tension $\Gamma = \gamma/\gamma_{AB}$ is roughly zero if the last layer is in contact with a melt of chemically identical polymer (B-chains for a film presenting B at its surface), and is unity if the film is in contact with a melt of the other species (A in the previous example). Note that the latter situation could lead to the swelling of the smectic film, with pure A homopolymer in between the copolymer layers, with a modification the smectic parameter of the film. For a typical polymer-air interface, Γ is simply the ratio of the interfacial tension of a melt of B (say) with air to the interfacial tension between A and B. It might typically be as high as $\Gamma \simeq 20 - 30$. For surfactant membranes, such as those making up surfactant vesicles or biological cell membranes, the surfactant bilayer is usually an equilibrium system in contact with a solution containing surfactant and the surface tension vanishes almost exactly [16].

The main results of the paper are as follows. For a freely suspended film the equilibrium position of the inclusion is either at the interface or in the center of the film, depending on whether the surface tension is smaller or larger than the interfacial tension between the lamellae in the film ($\Gamma = 1$ in our units). In many cases the inclusion might be trapped in a metastable position deep inside the film, even for values $\Gamma < 1$, since large activation energies may prevent it from reaching its equilibrium position. In such cases, we predict an overshoot in the layer deformation which can be directly traced to the finite thickness of the film. When the surface tension is exactly unity, this overshoot disappears and the deformation field coincides exactly with that predicted for a film of infinite thickness. If $\Gamma > 1$, the amplitude of the deformation decreases and its width increases with the surface tension as $1/\Gamma$ and $\sqrt{\Gamma}$ respectively. Furthermore, the amplitude of the overshoot increases linearly with z for membranes further away from the inclusion, while the amplitude of the maximum deformation (at $\mathbf{r} = 0$) decreases linearly with z .

For the case of a film residing on a rigid substrate the equilibrium position of the inclusion is shown (see Fig. 5a) to vary continuously with the surface tension Γ between the free surface (for $\Gamma < 1$) and the middle of the film (as $\Gamma \rightarrow \infty$). The deformation of the free surface may be calculated numerically (from Eq. (16)) given only the surface tension Γ and the smectic length λ . For diblock copolymers one might use the estimate [15], $\lambda = d/3$ where d is the thickness of a layer).

Finally, we have investigated the interaction between two inclusions located within the center layer of a freely suspended smectic film. For high surface tension $\Gamma \geq 1$, the interaction is attractive and monotonically decreasing with \mathbf{r} . It is qualitatively similar to the interaction in an infinite smectic phase. For $\Gamma < 1$ and thin enough films the interaction becomes repulsive for separations of the order of a few $\sqrt{\lambda d}$ due to the presence of an overshoot in the deformation profile. This feature will be important for particle aggregation, and could perhaps be studied *via* scattering experiments.

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Appendix

In this appendix we present the derivation of the mathematical results referred to in the main text. They are confined to this appendix merely to improve overall readability.

Throughout the deformation field in the film is determined by the Euler Lagrange equation (Eq. (5)) given in Section 2 with the boundary conditions (Eq. (6)).

A.1. FREELY SUSPENDED FILM. — The minimization of the smectic energy with respect to the profile of the surface layer $u_{\mathbf{q}}^i(h^i)$ yields:

$$u_{\mathbf{q}}^i(H) = \frac{u_{\mathbf{q}}^i(0)}{\sinh q^2 \lambda h^i (\Gamma + \coth q^2 \lambda H)} \quad (\text{A.1})$$

which involves the dimensionless surface tension $\Gamma \equiv \frac{\gamma}{\sqrt{KB}}$ (see Sect. 5). The deformation profile in the film, as well as the free energy of each Fourier mode can now be written as a function of the shape of the layer in contact with the inclusion ($z = 0$) only:

$$u_{\mathbf{q}}^i(z) = u_{\mathbf{q}}^i(0) \frac{\cosh q^2 \lambda (h^i - z) + \Gamma \sinh q^2 \lambda (h^i - z)}{\cosh q^2 \lambda h^i + \Gamma \sinh q^2 \lambda h^i} \quad (\text{A.2a})$$

$$\mathcal{F}_{\mathbf{q}}^i = \frac{1}{2} \sqrt{KB} q^2 |u_{\mathbf{q}}^i(0)|^2 \Lambda^i \quad \text{with}$$

$$\Lambda^i = \frac{\sinh q^2 \lambda h^i + \Gamma^i \cosh q^2 \lambda h^i}{\cosh q^2 \lambda h^i + \Gamma^i \sinh q^2 \lambda h^i} \quad i = \text{up, down.} \quad (\text{A.2b})$$

The displacement in real space and the free energy of the phase are obtained *via* equation (2):

$$u^i(\mathbf{r}, z) = \int_0^\infty \frac{q dq}{2\pi} u_{\mathbf{q}}^i(z) J_0(qr) \quad \mathcal{F}^i = \int_0^\infty \frac{d^2 \mathbf{q}}{(2\pi)^2} \mathcal{F}_{\mathbf{q}}^i \quad (\text{A.3})$$

where $J_0(x)$ is the Bessel function of the first kind and where the integration over the polar angle has been performed using the relation $\int_0^{2\pi} d\theta \exp(iqx \cos \theta) = 2\pi J_0(qr)$ [17].

To obtain the equilibrium position of the inclusion, we derive the function \hat{u} of equation (6) by minimizing the total energy in Fourier space $F_{\mathbf{q}}^{\text{tot}} = F_{\mathbf{q}}^{\text{up}} + F_{\mathbf{q}}^{\text{down}}$ with respect to \hat{u} . Reinserting it into equation (6), one obtains the new boundary conditions:

$$u_{\mathbf{q}}^{\text{up}}(0) = \frac{\Lambda^{\text{down}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} \Delta u \quad u_{\mathbf{q}}^{\text{down}}(0) = \frac{\Lambda^{\text{up}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} \Delta u \quad (\text{A.4})$$

where Λ^i is defined in equation (A.2b). The total free energy in Fourier space can now be written as a function of the distance from the upper surface h^{up} only:

$$F_{\mathbf{q}}^{\text{tot}} = \frac{\sqrt{KB}}{2} |\Delta u|^2 q^2 \frac{\Lambda^{\text{up}} \Lambda^{\text{down}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} = \frac{\Lambda^{\text{up}} \Lambda^{\text{down}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} = \frac{\Gamma^2 \cosh q^2 \lambda h^{\text{up}} \cosh q^2 \lambda (H - h^{\text{up}}) + \Gamma \sinh q^2 \lambda H + \sinh q^2 \lambda h^{\text{up}} \sinh q^2 \lambda (H - h^{\text{up}})}{(1 + \Gamma^2) \sinh q^2 \lambda H + 2\Gamma \cosh q^2 \lambda H}. \quad (\text{A.5})$$

The equilibrium position of the inclusion is found by minimizing the total free energy (the integral of the previous equation over all \mathbf{q} -modes) with respect to h^{up} . This minimization leads to the integral equation (7) for the thickness h^{up} .

A.2. FILM ON A RIGID SUBSTRATE. — In the case of a film on a rigid substrate, the surface tension of the lower interface is set to infinity: the total free energy in Fourier space is now given by a relation similar to equation (A.5)

$$\begin{aligned} F_{\mathbf{q}}^{\text{tot}} &= \frac{\sqrt{KB}}{2} |\Delta u|^2 q^2 \frac{\Lambda^{\text{up}} \Lambda^{\text{down}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} \\ \frac{\Lambda^{\text{up}} \Lambda^{\text{down}}}{\Lambda^{\text{up}} + \Lambda^{\text{down}}} &= \frac{\cosh q^2 \lambda (H - h^{\text{up}}) (\sinh q^2 \lambda h^{\text{up}} + \Gamma \cosh q^2 \lambda h^{\text{up}})}{\cosh q^2 \lambda H + \Gamma \sinh q^2 \lambda H}. \end{aligned} \quad (\text{A.6})$$

This integral is minimized to obtain the equilibrium position of the inclusion and leads to the integral equation (Eq. (15)).

A.3. INTERACTION BETWEEN TWO INCLUSIONS. — We consider the interaction energy between two particles in the center layer of a symmetrical film for the case where the deformation at the inclusion is fixed to the value Δ . This is perhaps the most natural choice of boundary conditions and is also probably the most appropriate for diblock copolymer lamellae doped with colloidal particles. The deformation of the first layer in real space is obtained by an inverse Fourier transform of equation (18)

$$u(\mathbf{r}, z = 0) = \beta \left(e^{-\frac{r^2}{2b^2}} + e^{-\frac{(\mathbf{r}-\mathbf{R})^2}{2b^2}} \right). \quad (\text{A.7})$$

If we impose a fixed deformation $u(\mathbf{r}, z = 0) = \Delta$ at $\mathbf{r} = 0$ and $\mathbf{r} = \mathbf{R}$, the parameter β is a function of \mathbf{R} :

$$\beta(\mathbf{R}) = \Delta \frac{1}{1 + e^{-\frac{\mathbf{R}^2}{2b^2}}}. \quad (\text{A.8})$$

The energy in a symmetric film simplifies from equation (A.5) and reads:

$$F(q) = \frac{1}{2} \sqrt{KB} q^2 |u_{\mathbf{q}}(0)|^2 \Lambda(q^2 \lambda \frac{H}{2}) \quad \Lambda(\alpha) = \frac{\sinh \alpha + \Gamma \cosh \alpha}{\cosh \alpha + \Gamma \sinh \alpha} \quad (\text{A.9})$$

where $u_{\mathbf{q}}(0)$ is given by equation (18) and H is the thickness of the film. After a transformation of variables, the interaction energy per particle can be written:

$$F_{\text{int}} = E_0 2b'^4 \int dk k^3 \Lambda(k^2) e^{-b'^2 k^2} \left(\frac{1 + J_0(kb'X)}{(1 + e^{-X^2/2})^2 - 1} \right) \quad (\text{A.10})$$

where $k^2 = q^2 \lambda H / 2$, $b'^2 = 2b^2 / (\lambda H)$ and $E_0 = (\pi/2) \sqrt{KB} \Delta^2$ is the self energy of a single particle in an infinite film. The interaction energy is more naturally expressed with respect to the self energy F_{self} of an inclusion in the film. We write this normalised interaction energy as $\bar{F}_{\text{int}} = F_{\text{int}} / F_{\text{self}}$ with:

$$F_{\text{self}} = E_0 2b'^4 \int dk k^3 \Lambda(k^2) e^{-b'^2 k^2}. \quad (\text{A.11})$$

The self energy is shown in Figure 6a as a function of the number of layers in the film $2/b'^2 = \lambda H / b^2$ for several values of the surface tension Γ . The interaction energy is shown in Figure 6b for several values of the film thickness and for $\Gamma = 0$.

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