On the Stability of the Alexander Polymer Brush

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ABSTRACT: We present a Lagrangian description of the deformations of flat Alexander polymer brushes. An Alexander brush is one in which all polymer chains are stretched from the base to the free surface of the brush. We analyze the linear stability of a grafted brush and a symmetric diblock lamella in a melt state. Both systems are unstable against plane-wave surface deformations of short wavelengths. Stability can be recovered with the introduction of a small but finite surface tension.

I. Introduction

In the following we will consider some systems formed by polymer chains attached at one end to a surface. At high coverage density the polymers create a layer in which the chains be stretched in the direction normal to the surface. Such layers are referred to as "brushes".

Polymer brushes appear naturally as the local structure formed in several block copolymer microphases. The rich phase structure of these systems and the possibilities of inducing transitions by the application of dynamical stress make them very interesting as a means to produce controlled structures on small length scales. A review on the general theoretical aspects of brushes appears in ref 1. In these microphases the attaching surface is a liquid interface between two homopolymer or solvent species. Brushes are also technologically interesting as coating layers for solids. Particularly interesting are the possibilities of modifying chemical and physical surface properties. A well-known example of this is the stabilization of colloidal particles for which the coating creates an effective repulsion force between particles. Experimental techniques employed to study these layers include force microscopy and neutron scattering.

In real brushes, the chains take diverse configurations and their free ends are present all across the thickness of the layer. We shall consider a model in which all the chains have their free ends at the top surface of the layer. This condition is often used as a theoretical approximation (Alexander−de Gennes model[2]), and it could be possible to realize it in practice.[5] These systems will be referred to as Alexander brushes. We will only consider a brush whose bulk is in a melt (incompressible) state (Figure 1).

The Alexander−de Gennes model uses a mean field approach for the description of the brush configurations. Fluctuations are disregarded, and the chains follow well-defined, nonintersecting, average paths from the base to the top surface of the brush. As usual, the mean field approach should give the correct answer only in the limit of very strong stretching. Given the description of the system in terms of chain trajectories, one looks for the set of these trajectories that minimize the free energy of the system. In refs 3 and 4, this method was used to analyze the energy cost of deformations of the bounding surfaces in two different instances of brushes: a grafted brush[3] and a symmetric diblock lamella.[4] The results presented therein were, however, not complete. Here we carry out a more detailed calculation of these energies. Our main conclusion will be the existence of certain intrinsic instabilities in these systems.

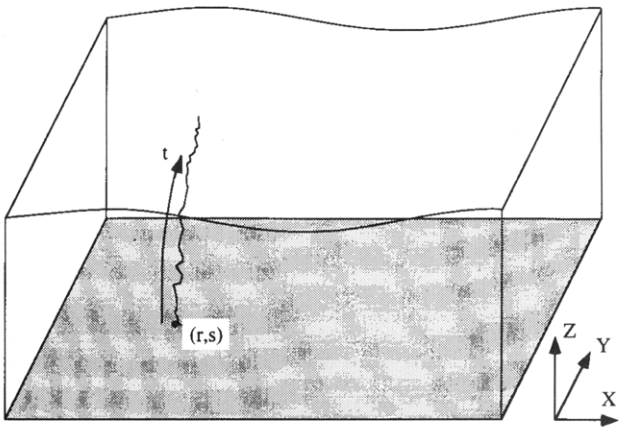

Figure 1. Schematic view of the grafted brush. The chains that form the brush are anchored to a base surface and extend to the (deformed) top surface.

For the description of the configurations we make use of a system of body coordinates, (Lagrangian description), in which considerations concerning the boundaries of the system become straightforward. In an accompanying paper[6] the stability problem is discussed by following closely the formalism of refs 3 and 4 using space coordinates providing the complementary Eulerian description.

We take as reference state the brush with flat horizontal base and top surfaces. The trajectory of a chain is a vertical line from the base to the top surface. The chains are uniformly stretched along their trajectories. The height of the layer is h_0, the uniform chain coverage of the base is σ (chains/area), the monomer number of the chains is N, and the (constant) volume per monomer is v. The incompressibility condition gives us the relation $h_0 = \sigma v N$.

The body coordinates $\mathbf{r} = (r, s, t)$ label a monomer by the base point of its chain (r, s), and a coordinate t proportional to its monomer number along the chain. The coordinates in physical space, $\mathbf{X} = (X, Y, Z)$, are now fields that depend on the body coordinates. In general, the trajectory of a particular chain is given in parametric form by $\mathbf{X}(t) = \mathbf{X}(r, s, t)$ for a given attaching point (r, s). In the reference state mentioned above we have the defining relation $\mathbf{X}(\mathbf{r}) = \mathbf{r}$.

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In the case of the diblock lamella, we will consider only the symmetric case. The total height will be $2h_0$, and the monomer number for each species will be N.

II. Free Energy

To obtain the equilibrium configurations of the brush when certain external conditions are imposed, we will write the free energy of the system as a functional of the configurations and use a variational principle to look for the minimum of the functional. The deformations imposed on the surfaces of the brush will be treated as small, and the response of the bulk will be calculated by means of perturbation theory. We now derive the form of the terms involved in this functional and later construct it explicitly for each of the cases in consideration.

The most important free energy contribution is of entropic origin. A chain following a highly stretched average path has a large reduction in the number of configurations accessible to it. The free energy for an average path is obtained by weighting the square of the local stretching (measured in length/monomer units) by a phenomenological constant a; so we have a term of the form

$$\frac{1}{2}a(h_0/N)^2\dot{\mathbf{X}}^2 \tag{1}$$

where the dot indicates partial derivation with respect to t. This density should be integrated over the monomer number of each chain.

We should only consider configurations that have the specified constant volume fraction v. Since we assume nonintersecting trajectories, the map from body to space coordinates is one to one and the volume fraction has to equal the Jacobian $J = \det ||\partial\mathbf{X}/\partial\mathbf{r}||$ of this map. This can be enforced in the variational approach by adding a Lagrangian multiplier $P(\mathbf{r})$, coupled to the constraint

$$J(X, Y, Z; r, s, t) - 1 = 0 \tag{2}$$

Upon introduction of this term in the functional for the free energy, the energy cost of increasing the volume of a certain number of monomers n by an amount dV away from vn can be calculated as PdV. We thus identify P as the pressure.

Finally, we need to consider surface terms. The free surfaces of the brush can be put in contact with a bad solvent, and the creation of extra contact area has a free energy cost proportional to the extra area. In the case of the diblock lamella, there is also an effective surface tension for area changes in the surface that separates the two species. In both cases the surfaces in consideration have a constant value of the t coordination. The area of the surfaces is obtained by the integration of

$$[\partial_r\mathbf{X}^2 + \partial_s\mathbf{X}^2 - (\partial_r\mathbf{X}\cdot\partial_s\mathbf{X})^2]^{1/2} \tag{3}$$

along the t plane in question.

III. Stability of the Grafted Brush

The free energy for the variational approach in the case of the grafted brush is

$$F = \int dr\, ds \int_0^{h_0} dt \left[\frac{1}{2}b\dot{\mathbf{X}}^2 - P(|J(\mathbf{X};\mathbf{r})| - 1) + \delta(t - h_0)\gamma_G[(\partial_r\mathbf{X})^2(\partial_s\mathbf{X})^2 - (\partial_r\mathbf{X}\cdot\partial_s\mathbf{X})^2]^{1/2}\right] \tag{4}$$

where γ_G is the surface tension for the polymer–solvent interface, and $b = ah_0^2(vN^2)$.

For simplicity, we will only consider configurations with translational symmetry along one transversal direction r, so that $X = r$ at all times and no other field depends explicitly on the r coordinate. This reduces our previous expression to

$$F = \int ds \int_0^{h_0} dt \left[\frac{1}{2}b(\dot{Y}^2 + \dot{Z}^2) - P(Y'\dot{Z} - Z'\dot{Y} - 1) + \delta(t - h_0)\gamma_G(Y'^2 + Z'^2)^{1/2}\right] \tag{5}$$

where the prime denotes partial derivation with respect to s.

To find the extrema of a functional $S = \int_V L(\phi,\partial_\mu\phi)$, we have the well-known Euler–Lagrange equations $\partial_\mu(\partial L/\partial(\partial_\mu\phi)) - (\partial L/\partial\phi) = 0$ to be satisfied in the interior of V. When no restrictions are put on the boundaries, the boundary terms also have to be extremes.[9] This condition yields the not so frequently used natural boundary conditions $n_\mu(\partial L/\partial(\partial_\mu\phi)) = 0$, where n_μ is the unit vector normal to the surface S bounding V. Such boundary conditions are easily interpreted as the requirement that no external force acts at the boundary of the system.

Taking the variation of the free energy with respect to the fields $\mathbf{X}$ and P without restrictions in the boundaries, we obtain the equilibrium equations satisfied in the bulk of the brush,

$$-b\ddot{Y} + P'\dot{Z} - \dot{P}Z' = 0 \tag{6}$$

$$-b\ddot{Z} - P'\dot{Y} + \dot{P}Y' = 0 \tag{7}$$

$$Y'\dot{Z} - Z'\dot{Y} - 1 = 0 \tag{8}$$

as well as the set of natural force-free boundary conditions associated with the variation of both the Z field

$$\left[b\dot{Z} - PY' - \gamma_G\left(\frac{Z'}{(Y'^2 + Z'^2)^{1/2}}\right)'\right]_{t=h_0} = 0 \tag{9}$$

$$[b\dot{Z} - PY' = 0]_{t=0} = 0 \tag{10}$$

and the Y field

$$\left[b\dot{Y} + PZ' - \gamma_G\left(\frac{Y'}{(Y'^2 + Z'^2)^{1/2}}\right)'\right]_{t=h_0} = 0 \tag{11}$$

$$[b\dot{Y} + PZ']_{t=0} = 0 \tag{12}$$

However, since external forces do act on the lower boundary of the brush, conditions (10) and (12) are inapplicable. Instead, we substitute the condition of constant grafting density as

$$Y'(t = 0) = 1 \tag{13}$$

and

$$Z(t = 0) = 0 \tag{14}$$

It is easy to check that our reference state is indeed a solution of the previous equations, and in doing so we learn that the potential P takes the constant value P_0

$= b$. Also, a simple evaluation gives us the free energy per unit area

$$f_0 = \frac{1}{2}bh_0 + \gamma_G = \frac{1}{2}a\sigma^4 v^3 N + \gamma_G \tag{15}$$

We would like now to discuss the stability of this solution. Introducing a plane-wave deformation on the top surface of amplitude ϵh_0, we calculate in perturbation theory the energy associated with the deformation up to second order in the perturbation. We will find that in some situations the deformed configuration is more favorable energetically than the flat one.

The equation defining the new surface shape is

$$[Z]_{t=h_0} = h_0(1 + \epsilon \sin(qYh_0)) \tag{16}$$

The wavelength λ is thus $\pi h_0/q$.

In view of the form of the perturbation, the expansion for the fields will be written as

$$\mathbf{X} = \mathbf{X}_0 + \epsilon\mathbf{X}_1 + \epsilon^2\mathbf{X}_2 + \ldots = \mathbf{r} + \epsilon\mathbf{X}_1 + \epsilon^2\mathbf{X}_2 + \ldots \tag{17}$$

$$Y = Y_0 + \epsilon Y_1 + \ldots = s + \epsilon h_0 y(t) \cos(qs/h_0) + \ldots \tag{18}$$

$$Z = Z_0 + \epsilon Z_1 + \ldots = t + \epsilon h_0 z(t) \sin(qs/h_0) + \ldots \tag{19}$$

$$P = P_0 + \epsilon P_1 + \ldots = b + \epsilon bp(t) \sin(qs/h_0) + \ldots \tag{20}$$

The consequent linearization of the equilibrium equations (6)−(8) reads

$$b\ddot{\mathbf{X}}_1 = \nabla P_1 \tag{21}$$

$$\nabla\cdot\mathbf{X}_1 = 0 \tag{22}$$

It will also be important for us to write down the second-order term in the expansion of the constraint equation (8),

$$\nabla\cdot X_2 + Y_1'\dot{Z}_1 - Z_1'\dot{Y}_1 = 0 \tag{23}$$

A simple consequence of eqs 21 and 22 is that P_1 is an harmonic function, $\nabla^2 P_1 = 0$. Is also important to note the role of the pressure perturbation P_1 as the potential for the "acceleration" of the chain trajectory.

The perturbation condition (16) is a nonlinear relation between the fields. Substitution of the expansions for the fields gives us, to first order in ϵ, a boundary condition that replaces (9) (but note that they are consistent to zeroth order in ϵ)

$$[Z_1]_{t=h_0} = h_0 \sin(qs/h_0) \tag{24}$$

The rest of the boundary conditions for the linearized problem are

$$[Z_1' + \dot{Y}_1]_{t=h_0} = 0 \tag{25}$$

$$[Z_1]_{t=0} = 0 \tag{26}$$

$$[Y_1']_{t=0} = 0 \tag{27}$$

Equation 25 is easily interpreted as the condition that the chain trajectories have a normal incidence at the top surface; since there is no force acting tangent to the top surface, the chain tension acts normal to it. The same conclusion could also be obtained from (11) and (9) as a nonperturbative result.

To solve our equations, all the fields are rephrased in terms of p alone:

$$h_0\dot{z} = p - p(0) \tag{28}$$

$$z = (h_0/q^2)(\dot{p} - \dot{p}(0)) - p(0) \tag{29}$$

$$y = (p - p(0))/q \tag{30}$$

The solution for the pressure is

$$p(t) = A \cosh(qt/h_0) + B \sinh(qt/h_0) \tag{31}$$

$$A = q(2 \cosh(q) - 1)/(\sinh(q) - q \cosh(q)) \tag{32}$$

$$B = q(q - 2 \sinh(q))/(\sinh(q) - q \cosh(q)) \tag{33}$$

We now evaluate the energy cost of the deformations. From (5), the expression for the second-order part of the free energy is

$$F_2 = \epsilon^2 \int ds \int_0^{h_0} dt \left[\frac{1}{2}b\dot{\mathbf{X}}_1^2 + b\dot{Z}_2 + \frac{1}{2}\delta(t - h_0)\gamma_G Z_1'^2\right] \tag{34}$$

We would like to avoid having to calculate second-order quantities such as $\dot{Z}_2$ and thus express F_2 as a quadratic form in the first-order quantities just obtained. This can be done by noticing that, due to the periodicity (in the s direction) of Y_2, at a constant t the integral of Y_2' over a period vanishes. Then, using (23), we can write

$$\int ds\, dt\, b\dot{Z}_2 = \int ds\, dt\, b(\dot{Z}_2 + Y_2') = \int ds\, dt\, b\nabla\cdot\mathbf{X}_2 = -\int ds\, dt\, b[\dot{Z}_1 Y_1' - \dot{Y}_1 Z_1'] \tag{35}$$

Substitution of this result in (34) gives the desired quadratic form. Further, by an integration by parts we can present F_2 as a surface integral, the bulk integration disappearing in virtue of the equilibrium equations. This final expression is

$$F_2 = \frac{1}{2}b\epsilon^2 \int_{t=h_0} ds\, Z_1[\dot{Z}_1 - X_1' - P_1 - (\gamma_G/b)Z_1'] \tag{36}$$

Per unit area we have

$$f_2 = \frac{1}{4}\epsilon^2 bh_0[h_0\dot{z} + qy - p + (\gamma_G/b)q^2 h_0]_{t=h_0} \tag{37}$$

Evaluation of the free energy per unit area gives

$$f_2 = \frac{1}{4}\epsilon^2 bh_0[(\gamma_G/bh_0)q^2 + q(4 - 5 \cosh(q) + q \sinh(q))/(\sinh(q) - q \cosh(q))] \tag{38}$$

This result is shown in Figure 2 for the case of zero surface tension. The q^{-2} divergence at low q is easily understood in terms of the incompressibility of the system and the condition that the attaching points are fixed. In the region of compression, the chain ends have to displace laterally a distance of order h_0/q and the total stretching energy has the above mentioned dependence.

The most important corollary from our solution is the fact that the energy of the reference state, the flat brush,

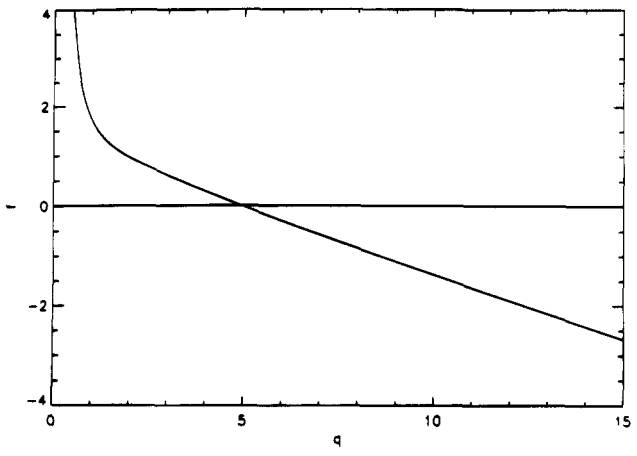

Figure 2. Deformation energy f of the grafted brush (for zero surface tension) as a function of the wave vector q of the surface modulation. The energy scale is such that $\epsilon^2 b h_0 = 1$.

can be lowered by creating surface modulations with wavelengths in the range

$$\lambda < 2\pi h_0/q_c \tag{39}$$

$$q_c = 4.94 \tag{40}$$

The flat brush is then spontaneously rippled for wavelengths $\lambda \leq 0.79 h_0$.

At this point we should look for a way to understand this instability. We have presented several equivalent expressions for the calculation of the deformation energy. We can best argue by starting from (34) and disregard for a moment the stabilizing surface tension. The small perturbations $\mathbf{X}_1$ clearly give a positive definite contribution, but the second-order terms, being linear, can change the final result. It is easy to see that the second-order term is associated with the total average height of the chain ends. Thus, to reduce the energy, we need to put many chains reaching the valley of the surface wave and fewer reaching the crest, all this while trying not to create too much of a distortion in the original straight trajectory. The way to do this is to create the distortions at small wavelengths. The average first-order stretching in the z direction will be similar at all wavelengths, giving always a contribution of order $\epsilon^2 b h_0$ per unit area. The amplitude of the transversal deformations is limited by the wavelength, so that for very small wavelengths it will go to zero as λ^2. We see then that at short wavelengths the chains can move transversally rather easily and pur their ends at the valley of the wave. In this case, the density of chains at the valley has changes of order ϵ while the total height for these chains is reduced by an amount ϵh_0, possibly lowering the energy by an amount of order $\epsilon^2 b h_0$. Since this becomes increasingly easier at small wavelengths one can, as shown by the explicit calculation, have a regime of instability.

As is well-known, more detailed models for the study of brush systems that drop the Alexander approximation (that is, the chain end does not have to reside on the surface) predict a finite density of chain ends at all heights in the ground state of the system (see ref 8 for a review). Our result, that the energy of the brush can be lowered by allowing chain ends to be distributed within a finite neighborhood of the original boundary, can be considered as a hint toward the mentioned results.

The presence of surface tension can, however, stabilize the flat layer. Evaluation of (38) for different values of γ_G shows that when

$$\gamma_G > 0.056 b h_0 \tag{41}$$

the energy cost f_2 is positive for all wavelengths.

IV. Stability of a Flat Diblock Lamella

We write down the free energy functional for the flat lamella (again with the assumption of homogeneity in the r direction) as

$$F = \int ds \int_{-h_0}^{h_0} dt \left[\frac{1}{2}a(\dot{Y}^2 + \dot{Z}^2) - P(Y'\dot{Z} - Z'\dot{Y} - 1) + \delta(t)\gamma_L(Y'^2 + Z'^2)^{1/2}\right] \tag{42}$$

in which the surface tension γ_L acts at the interface between the two species, the $t = 0$ plane. For simplicity we postpone to the end of this section the inclusion of an extra surface tension γ_S between the bounding surfaces and the surrounding medium. The height and the chain density of the flat lamella are not given a priori and should be obtained from minimizing the functional.

The bulk equilibrium equations for the fields are similar to those for the grafted brush but the midplane surface tension term modifies them to

$$-b\ddot{Y} + P'\dot{Z} - \dot{P}Z' - \gamma_L\left(\frac{Y'}{(Y'^2 + Z'^2)^{1/2}}\delta(t)\right)' = 0 \tag{43}$$

$$-b\ddot{Z} - P'\dot{Y} + \dot{P}Y' - \gamma_L\left(\frac{Z'}{(Y'^2 + Z'^2)^{1/2}}\delta(t)\right)' = 0 \tag{44}$$

$$Y'\dot{Z} - Z'\dot{Y} - 1 = 0 \tag{45}$$

These equations can be solved rather simply for $t \neq 0$ and when integrated around the midplane lead to boundary conditions for the fields at the interface. The force-free boundary conditions for the top and bottom surfaces are similar to (9) and (11).

To obtain the initial values of σ and h_0 we substitute the flat brush solution $P = b$ in (42) with unspecified values for h_0. Evaluation of F, followed by minimization with respect to h_0 gives the following results for the flat state:

$$2bh_0 = \gamma_L \tag{46}$$

$$h_0 = \left(\frac{N^2 v \gamma_L}{2a}\right)^{1/3} \tag{47}$$

$$\sigma = \left(\frac{\gamma_L}{2Nav^2}\right)^{1/3} \tag{48}$$

Evaluation of the free energy in this stage gives us, per unit area,

$$f_0 = bh_0 + \gamma_L = \frac{3}{2}\gamma_L \tag{49}$$

We consider now simultaneous deformations of both surfaces $t = -h_0$, $t = h_0$. Due to the symmetry of the system, there are only two basic independent deformations: the "acoustic" mode, in which the top and bottom surfaces have the same deformation, and the "optic" mode, in which the middle plane is not deformed

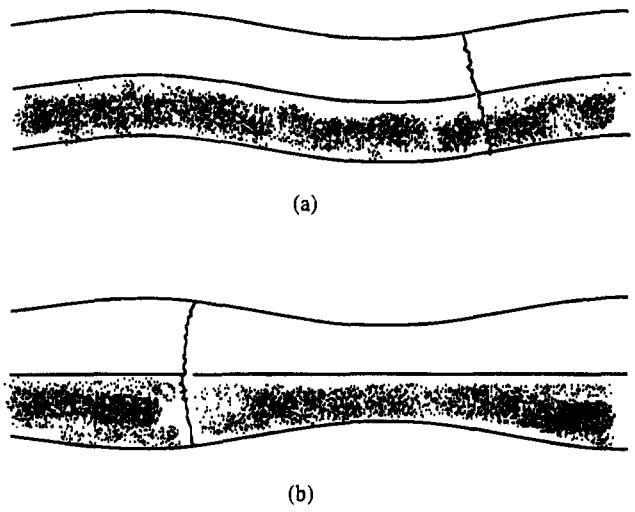

Figure 3. Schemes of the (a) acoustic and (b) optical modes of the symmetric lamella.

and the top and bottom surfaces have a relative half-wave phase (Figure 3). In the acoustic mode, we write the surface deformations as

$$[Z_1]_{t=\pm h_0} = \epsilon h_0 \sin(qs/h_0) \tag{50}$$

In the optic mode, the deformations are taken as

$$[Z_1]_{t=\pm h_0} = \pm\epsilon h_0 \sin(qs/h_0) \tag{51}$$

In both cases, the complementary boundary conditions at both surfaces have the same form of eq 25, which implies normal incidence of the chains at the surfaces.

Given the form of the equations at the interface $t = 0$, it is easier to deal independently with each half of the layer and introduce boundary conditions for each half at $t = 0$. The resulting boundary conditions from (43) and (44) are the continuity of Y_1' and a discontinuity in P_1 of magnitude

$$b\Delta P_1 = \gamma_L Z_1'' \tag{52}$$

The surface tension force on the curved interface has to be compensated for by a Laplace pressure.

We should point out here that the flaw in the previous calculation by Turner and Joanny[4] was the lack of proper consideration of this condition. In their approach, this surface was treated in the same way as the rest of the bulk. Once the deformations of the bulk were obtained, the total energy was calculated using the correct free energy functional. The energy thus calculated overestimated the equilibrium energy of the system.

We present now the solutions for the pressure. For the acoustic mode we have

$$p(t) = A \sinh(qt/h_0) + (\Theta(t) - \Theta(-t))B \cosh(qt/h_0) \tag{53}$$

$$A = q(2q \sinh(q) - q^2 - 1)/(\cosh(q) + q^2 \cosh(q) - q \sinh(q)) \tag{54}$$

$$B = -q^2(2 \cosh(q) - 1)/(\cosh(q) + q^2 \cosh(q) - q \sinh(q)) \tag{55}$$

And, for the optic mode,

$$p(t) = B \cosh(qt/h_0) \tag{56}$$

$$B = -q/\sinh(q) \tag{57}$$

By an argument similar to the one presented in the preceding section, the contributions to the second-order term of the free energy coming from the integration of second-order quantities like Y_2' and $\dot{Z}_2$ can be written in terms of bilinear terms on the first-order quantities. The energy can then be calculated by inserting the solutions to the equilibrium equations in

$$F_2 = \epsilon^2 \int ds \int_{-h_0}^{h_0} dt \left[\frac{1}{2} b \dot{\mathbf{X}}_1^2 + b\dot{Z}_2 + \delta(t)\gamma_L\left(\frac{1}{2}Z_1'^2 + Y_2'\right)\right] \tag{58}$$

Again, with some manipuatlions we arrive at an expression in terms of fields evaluated at the top and bottom surfaces,

$$F_2 = \frac{1}{2} b\epsilon^2 \int_{t=h_0} ds\, Z_1[\dot{Z}_1 - Y_1' - P_1/b] - \frac{1}{2} b\epsilon^2 \int_{t=-h_0} ds\, Z_1[\dot{Z}_1 - Y_1' - P_1/b]\, ds \tag{59}$$

Using the conventions of the previous section we finally write

$$f_2 = \frac{1}{4}\epsilon^2 b h_0([z(h_0\dot{z} + qy - p)]_{t=h_0} - [z(h_0\dot{z} + qy - p)]_{t=-h_0}) \tag{60}$$

Here it is important to note that the energy per unit area obtained from this expression refers to the unit area in the unperturbed state. Since these brushes are not grafted, the area covered per chain at, for example, the midplane, is subject to changes, and further, the overall average density of chain changes has correction terms of order ϵ^2. Calculation of this correction does require solution of the second-order equations. We note, however, that our result is correct if interpreted as an (up to a constant) energy per chain and therefore it gives the correct criteria for the stability of the system.

The evaluation of the energies for both modes gives

$$f_A = \frac{1}{4}\epsilon^2\gamma_L\left[q\frac{4q - 5q \cosh(q) + \sinh(q) + q^2 \sinh(q)}{q \sinh(q) - \cosh(q) - q^2 \cosh(q)}\right] \tag{61}$$

$$f_O = \frac{1}{4}\epsilon^2\gamma_L[4 - q \coth(q)] \tag{62}$$

A plot of these energies for a range of wave vectors is presented in Figure 4.

For large wavelength deformations the optic mode has a finite energy cost while for the acoustic mode the deformation energy has an expansion of the form $f_2 = (1/3)\epsilon^2\gamma_L h_0^2 q^4 + \ldots$. The deformation of the lamella at the top of the wave corresponds (for long wavelengths) to the deformation caused by bending it into a cylindrical shape with radius of curvature $h_0/(\epsilon q^2)$. From evaluating the energy density in that region (twice the result in (61)), we can read the bending modulus,

$$\kappa = \frac{4}{3}\gamma_L h_0^2 \tag{63}$$

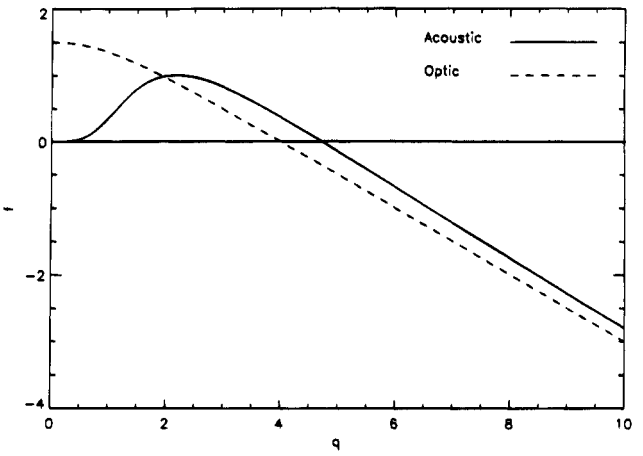

Figure 4. Deformation energy f in the acoustic and optical modes of the symmetric lamella as a function of the wave vector q of the deformation. The energy scale is such that $\epsilon^2 b h_0 = \epsilon^2 \gamma_L/2 = 1$.

which is, up to a factor of 2, the result of Ajdari and Leibler.[7]

For large q the energies for both modes take the asymptotic form $f_2 \sim -q$. More precisely, by looking at the change on the energy sign, we conclude the flat lamella is stable against perturbations in the region

$$\lambda > 2\pi h_0/q_c \tag{64}$$

$$q_c = 3.997 \tag{65}$$

For larger values of q, the energy can be lowered by rippling (preferably) in the optic mode.

Finally, we consider the introduction of a surface tension γ_S at the top and bottom surfaces. In this case, all quantities with an explicit dependence on γ_L are altered by the replacement of γ_L by $\gamma_L + 2\gamma_S$. Further, the energies (61) and (62) get an extra contribution of $\epsilon^2 \gamma_S q^2$. Since, as pointed out before, the energy of both modes behaves asymptotically as $-q$ while the surface tension term has the form q^2, there exists a finite minimum value of γ_S above which all perturbations have a positive energy cost. By numerical evaluation we find this value to be

$$\gamma_S = 0.031\gamma_L \tag{66}$$

V. Conclusions

The picture resulting from our analysis shows that, in the absence of the stabilizing surface tension, these brushes are unstable at short wavlengths. This result bridges the Alexander–deGennes model with more detailed calculations by showing that to lower the energy of the system it is convenient to distribute the chain ends along the layer.

As mentioned in the Introduction, two previous calculations of the properties of this model are closely related to our work. The calculation of Fredrickson et al.[3] for the grafted brush gave results for some specific deformations with large characteristic lengths: plane waves and a large round tip pressing against the surface. Their results are essentially correct but could be refined by the use of the formalism presented here. As we have shown, the second-order energy can be calculated in full for all wavelengths, and the surface tension contribution can be explicitly incorporated in the calculation.

Although not completely correct (by inadequate consideration of the lamella interface), the calculation of Turner and Joanny[4] correctly pointed at the possibility of an instability in the case of a diblock lamella. Their description of the instability involves the enforcement of the deformation in only one of the surfaces of the lamella, leaving the other one free. They found that at small wavelengths the free surface has a deformation amplitude larger than that of the forced surface; i.e. the modulation is amplified. Their main concern was the scenario in which a stack of lamellae is put on top of a rough substrate with appreciable roughness at small wavelengths. The distortions created on the lamella in contact with the substrate will then be amplified by each layer. This process would then bring about the destruction of such a phase. The corrected version of this result that follows from our work is even more drastic. The amplification factor for the roughness is easily written in terms of the energies (for deformation amplitudes of 1) of the the optical and acoustical modes:

$$A = \frac{f_O - f_A}{f_O + f_A} \tag{67}$$

After the first mode becomes unstable, the lamella will amplify the roughness ($|A| > 1$). Further, there is a point at which the amplification becomes infinite and, after that, the amplification remains infinite (the solution given by our equation will refer to a maximum, instead of a minimum, energy state). It is not clear, however, that the instability will be present in other more realistic models that do not relay in the Alexander approximation. Since the instability occurs at short wavelengths, it seems more likely to indicate the preference of the system for a configuration with chain ends distributed along the layer. At long wavelengths the system should maintain a lamella configuration.

Finally, the fact that the stabilizing surface tensions are small compared to the energy scale of the system indicates that the physical realization of a stable Alexander brush can be reasonably easily obtained.

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