A Bulk Perturbation in a Grafted Brush

Francisco J. Solis*

The James Franck Institute, The University of Chicago, 5640 S. Ellis Avenue,
Chicago, Illinois 60637

Hai Tang

Departments of Materials Science and Engineering and of Chemistry, and Materials
Research Laboratory, University of Illinois, 1304 West Green Street, Urbana, Illinois 61801

Received December 19, 1995; Revised Manuscript Received June 12, 1996[⊗]

ABSTRACT: We find the response of a grafted polymer brush in a melt state to the insertion of a small, impenetrable object in its bulk. The response is calculated by means of perturbation theory applied to Semenov's self-consistent mean-field theory of polymer brushes. We find that both the induced pressure field and the deformation of the free surface decay exponentially away from the region of insertion. The pressure field exhibits no dependence on the depth at which the object is inserted. The decay length for both quantities is of the order of the thickness of the brush, h_0. We also discuss the induced interaction between two immersed objects.

1. Introduction

Grafted polymer brushes are structures formed by irreversibly attaching polymer chains by one end to a solid surface. If the grafting density is high enough, the chains are forced to stretch in the direction normal to the surface, thus giving the system a "brushlike" appearance. (Halperin et al.[1] have presented an overview of this and related microstructures.) These systems are technologically important for the possibilities of modifying the physical and chemical properties of the covered surfaces.

There are still many interesting features of these systems that need to be explored from both the theoretical and experimental points of view. Witten[2] has posed the following problem: Assume that into a grafted polymer brush (in a melt state) one inserts a small balloon of some extraneous material that displaces a certain number of monomers but does not otherwise interact with them; what is then the pressure field created by the insertion? This pressure response is of fundamental importance since it encodes the mechanical properties of the system.

For the case of a flat brush in a melt (incompressible) state, we provide an answer that is rather simple. The resulting pressure field has no structure in the direction normal to the surface and decays exponentially away from the region of insertion in directions parallel to the surface. We call this a "softness" property of the system.

Our work here makes use of a mean field approach[3] and follows, in particular, the self-consistent field theory of Semenov[4,5] (these and related theoretical works have been reviewed by Milner[6]). Here we extend the approach of Semenov to consider transverse deformation of the average paths of the chains. The form of our solution is basically the same as the one provided by Tang[7] for the structure of the pressure field in the related problem of pure surface deformations in melt state brushes.

Many previous works regarding the mechanical properties of brushes have used the Alexander−de Gennes model as starting point.[8−11] The present treatment should be considered to be a more precise description of the system, providing a more reliable estimation of its moduli. It is important to point out that both in these previous works and in our present approach, there is an implicit condition of high grafting density, or equivalently, strong stretching of the chains. The free energy functional we use is a good approximation only if most of the chains are stretched over distances many times larger than their natural radius of gyration. While many physical systems do present many characteristics similar to those described by these models, we do not know of systems in which the strong stretching limit is actually satisfied. The models proposed, however, do provide us with a reasonable theoretical picture and in many cases qualitative agreement with experiments.

We will use the following description for the brush. The polymer chains are assumed to be monodisperse, with monomer number N. Each chain is attached by one end to the flat base. In addition, in the mean-field approach we are following, an ensemble of chains is considered to be attached to each point of the base surface (physically, the ensemble is attached to small region). The chains in the ensemble can be labeled according to the maximum height they reach within the layer (z_m). The average path of a chain is given as a function of the monomer number t along the chain (running from 0 to N) and written as $\mathbf{X}(t; \mathbf{x}, z_m)$, where $\mathbf{x}$ is the point of attachment of the chain in the base plane (a two-dimensional coordinate). See Figure 1.

In a melt state the system is incompressible and each monomer occupies a definite volume v. For a (uniform) grafting density σ (chains/area), the unperturbed polymer layer will have a well-defined height $h_0 = \sigma v N$.

2. Free Energy for the Variational Formulation

Following Semenov, we will write a variational functional for the free energy of the system. The main contribution to this free energy is the entropic cost of stretching the chains to make them follow a prescribed average path. Locally, we weight the stretching by $^1/_2 m\dot{\mathbf{X}}^2$, where m is a temperature-dependent phenomenological constant and the over-dot indicates differentiation with respect to the monomer number. This contribution is to be integrated over the monomer numbers of all chains.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

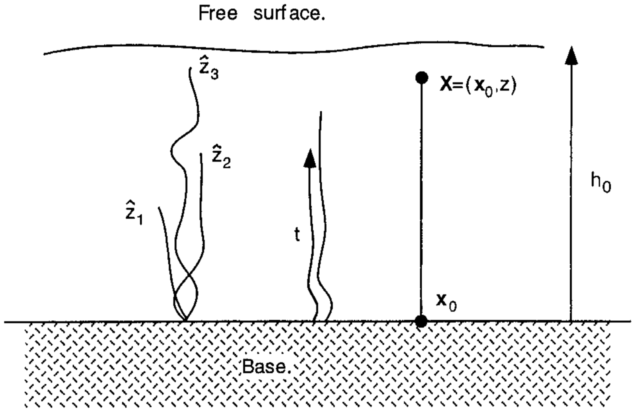

Figure 1. Scheme of the assumed structure of the brush. A group of chains attached to a small area extend to different heights z_m within the layer.

We should also consider the presence of a surface tension γ between the brush free surface and the surrounding media. This contributes to the free energy by

$$F_\gamma = \int \gamma \, \mathrm{d}S \tag{1}$$

Later on, we will write in detail the integral in terms of the variables $\mathbf{X}$.

We also need to deal with the fact that the melt condition imposes a constraint in the accessible configurations of the system. We will enforce this in our variational principle with the aid of a Lagrangian multiplier ϕ, coupled to the local density of monomers so that the expression for the total stretching energy reads

$$F_m = \int \mathrm{d}^2\mathbf{x} \int_0^N \mathrm{d}t \int_0^{h_0} \mathrm{d}z_m \, {}^1/_2 g(z_m) m \dot{\mathbf{X}}^2(t;\, \mathbf{x},\, z_m) + \int \mathrm{d}^3\mathbf{r}\, \phi(\mathbf{r})[\rho(\mathbf{r}) - \rho_p] \tag{2}$$

Here $g(z_m) = \mathrm{d}\sigma/\mathrm{d}z_m$ is the number of chains (attached at some given point) having free ends placed at height z_m. In the second term of this expression the region of integration is the volume occupied by the melt, and $\mathbf{r} = (x,y,z) = (\mathbf{x},z)$ is the space coordinate. We take the z coordinate to measure distance from the base surface while $\mathbf{x} = (x, y)$ defines a point in the base surface. The prescribed density in the absence of external intrusions is $\rho_p = 1/v$.

The monomer density ρ can be written in terms of the trajectories for the chains after noting that, if we invert the path function for chains, for each point $\mathbf{r}$ in the bulk there is a set of chains passing through it, with labels $(\mathbf{x},z_m)$ at a certain value of the parameter t. A natural assumption is that if a point inside the bulk of the brush is reached by a chain that extends up to some height, there is always another chain that reaches the same point but extends farther (up to the maximum height available). Also note that the trajectories passing through one point do not necessarily share a common tangent at such point. We have for the density

$$\rho(\mathbf{r}) = \int_z^{h_0} \mathrm{d}z_m g(z_m)\, J(\mathbf{x},\, t;\, \mathbf{X}) \tag{3}$$

where J is the Jacobian between the coordinates $(\mathbf{x},\, t)$ and $\mathbf{X}$ at constant z_m. Here, the Jacobian has the function of counting the number of monomers, $\sigma\, \mathrm{d}t\, \mathrm{d}\mathbf{x}$ in the volume $\mathrm{d}^3\mathbf{X}$. While we use the chain trajectories as basic variables, in previous works the local stretching field $\dot{\mathbf{X}}$ was taken as the basic variable.

The free energy functional can also be written to stress the interaction of the mean-field ϕ with the trajectory of the individual chains, as

$$F = \int \gamma \, \mathrm{d}S - \int \mathrm{d}\mathbf{r}\, \phi\rho_p + \sum_{\text{all chains}} \int_0^N \mathrm{d}t\, [{}^1/_2 a \dot{\mathbf{X}}^2 + \phi(\mathbf{r})] \tag{4}$$

3. Remarks on the Ground State

Application of the variational principle for solutions that are uniform in the transverse direction gives the following results:[5]

(a) The minimum energy is obtained when we allow the chains to distribute along the layer. This feature is assumed to remain valid at later stages. That is, the introduction of a perturbation will not drive every chain to reach the same extremum position; rather, there will always be chain ends everywhere in the bulk of the brush.

(b) The only potential ϕ consistent with the kind of solution described in (a) is parabolic in the z coordinate:

$$\phi = P_0[1 - (z/h_0)^2] \tag{5}$$

where $P_0 = \pi^2 m h_0^2/8N^2$. The shape of the chain trajectory is given by the solution of

$$m\ddot{\mathbf{X}} = \nabla\phi \tag{6}$$

together with the equilibrium condition at the free end of the chain, $\dot{\mathbf{X}}(t = N) = 0$ (i.e., no force acting in the chain end), and the condition of attachment to the base $\mathbf{X}(t{=}0) = \mathbf{x}_0$. Thus

$$Z = A \sin(\pi t/2N) \tag{7}$$

with possible amplitudes A ranging from 0 to h_0. In the following we will denote this solution as $Z(t;A)$. This last result is better understood by an analogy with the classical mechanics system of a particle of mass m in a potential ϕ: The harmonic oscillator is the only potential that allows for all oscillating solutions to have the same period. In our problem, this is required by the condition of monodispersity.

(c) The distribution of chain ends is obtained by solving the constraint equation of constant density

$$\rho_P(z) = 1/v = \int_z^{h_0} \mathrm{d}\hat{z}\, g(\hat{z})[\dot{Z}(t;\, \hat{z})]^{-1} \tag{8}$$

$$= \int_z^{h_0} \mathrm{d}\hat{z}\, g(\hat{z}) \frac{2N}{\pi(\hat{z}^2 - z^2)^{1/2}} \tag{9}$$

with the result

$$g(z) = \frac{\sigma}{h_0} \frac{z}{(h_0{}^2 - z^2)^{1/2}} \tag{10}$$

(d) The distribution of chain ends can be modified to provide solutions of eq 9 for a more general prescribed density that depends only on the z coordinate (but with identical total volume). This is done using the formula (solution of an Abel integral equation)

$$g(z) = (z/N) \int_z^{h_0} \mathrm{d}\hat{z}\, \frac{\mathrm{d}\rho}{\mathrm{d}\hat{z}} \frac{1}{(h_0{}^2 - \hat{z}^2)^{1/2}} \tag{11}$$

The formula solution given by this formula cannot be used if the required chain-end density is negative at some point. A posteriori, we know that the formal divergences of the result are irrelevant if the perturbation source is smooth and will not turn g negative. Note that there is no need to change the potential to allow the mass redistribution. This fact will be very important later on, and it is the basis of the "softness" property.

4. Perturbation Theory

We will use perturbation theory to find the response of the system to the insertion. In this section we describe the elements that enter in the calculation. Most of these considerations were treated in detail in a previous paper in Tang.[7]

We need ot represent the fact that the bulk space occupied by monomers is reduced by introduction of an impenetrable object. A general object can be modeled by a profile of displaced volume fraction $\epsilon f(\mathbf{r})$. That is, in a small box of volume dV centered around $\mathbf{r}$, the object occupies a fraction ϵf of the volume of the box. This changes the number of monomers inside the box to $(1/v)(1 - \epsilon f)\,\mathrm{d}V$. Under these circumstances, the incompressibility constraint reads

$$\rho - \rho_P = \rho - (1 - \epsilon f)/v = 0 \tag{12}$$

where ϵ is the small perturbation parameter.

Consider next the effects of perturbations of the potential. If the perturbation is $\epsilon\delta\phi(\mathbf{x},z)$, we can Taylor-expand the potential in the neighborhood of a column $(\mathbf{x}_0,z)$ as

$$\phi(\mathbf{x},z) = \phi_0(z) + \epsilon[\delta\phi(\mathbf{x}_0,z) + \nabla_{\mathbf{x}_0}\delta\phi(\mathbf{x},z)(\mathbf{x} - \mathbf{x}_0)] + ... \tag{13}$$

(Here and in the following, $\nabla_{\mathbf{x}}$ is the two-dimensional gradient operator acting on functions of the attachment point coordinate $\mathbf{x}$.) As a result of the change in the potential, the new chain trajectories will have a transverse component. However, to calculate the change of the trajectory in the normal direction, it is sufficient to consider only the longitudinal changes in the potential given by $\delta\phi(\mathbf{x}_0,z)$. The corrections to the z component of the force $\partial_z\phi$ felt by the chains as a result of their transverse motion are of order ϵ^2.

If we expand the trajectory as

$$\mathbf{X} = \mathbf{X}_0 + \epsilon\mathbf{X}_1 + ... \tag{14}$$

the longitudinal perturbation of the trajectory for a chain that (after the perturbation) extends up to a height A is then

$$m\dot{Z}_0\dot{Z}_1(t) = \delta\phi(Z_0(t)) - \delta\phi(A) \tag{15}$$

This result follows from integrating the trajectory equation (eq 6) in a form equivalent to the statement of energy conservation for a Newtonian particle in a potential,[5] and expanding the quadratic terms up to first order in the perturbation parameter.

The problem that one runs into here is that, for a generic potential perturbation, this new trajectory requires a different "time" and we cannot keep (to first order) the condition of monodispersity. We then have to assume that the modification to the potential is such that it retains the parabolic form of eq 5 (with identical parameter P_0) with respect to the height coordinate z, but with a shift on its maximum value depending only on the base point, i.e.

$$\phi(\mathbf{x}_0,z) = \phi_0(z) + \epsilon\psi(\mathbf{x}_0) + ... \tag{16}$$

with $\psi(\mathbf{x})$ independent of the height in the layer. This is quite an important restriction on the form of the potential, and one may worry that a consistent solution of the problem is not possible within the approximations made, in which case we would be forced to consider the problem in a more general setting, for example, by relaxing the constraint of constant density everywhere, or looking for solutions that have zero chain-end densities over finite regions. We will see, however, that this is not the case.

The perturbed potential presented in eq 16 has the same longitudinal gradient as the unperturbed potential so that the longitudinal trajectories $Z(t)$ remain the same as in the perturbed case, and only the transverse part of the trajectories are modified. This implies that remark (d) of section 3 is still valid, and by modifying the chain-end density to $g_0(z) + \epsilon g_1(\mathbf{x},z)$, we can create any perturbation in the density profile $\epsilon\rho_1(\mathbf{x},z)$ that respects the monomer count $\int\mathrm{d}z\ \rho_1 = 0$. This fact was already pointed out by Witten[2] for the case of a slab of material with no transversal structure ($\rho_1 \approx \delta(z - z_0)$), but our work extends this result to almost arbitrary forms of insertions. We have, then, the relation

$$\rho_1(\mathbf{x},z) - \int_z^h \mathrm{d}\hat{z}\ \frac{2N}{\pi(\hat{z}^2 - z^2)^{1/2}}g_1(\mathbf{x},\hat{z}) \tag{17}$$

The required g_1 can be obtained using solution 11 of the Abel equation. As mentioned before, given the weak singularity of the kernel of this integral equation, $\sim(\hat{z} - z)^{-1/2}$, most smooth densities ρ_1 will integrate to a well-behaved chain-end distribution g_1, but the requirement that the total chain-end distribution $g_0 + \epsilon g_1$ should be nonnegative everywhere may impose a restriction in the region of applicability of the perturbation theory. This requirement can be particularly strict in the region near the base of the brush where the unperturbed distribution is already small and would call for a nonperturbative treatment of the problem. We will, however, not attempt at a more precise quantification of the conditions of convergence of the perturbation theory in this paper.

The transverse deformations caused by the extra potential are obtained as solutions of the equations of motion

$$m\ddot{\mathbf{X}}_\perp = \partial\phi(\mathbf{X})/\partial\mathbf{X}_\perp = \epsilon\nabla_{\mathbf{x}_0}\psi(\mathbf{x}_0) \tag{18}$$

with the conditions $\dot{\mathbf{X}}_\perp(t = N) = 0$ and $\mathbf{X}_\perp(t = 0) = \mathbf{x}_0$ as stated after eq 6. The solution is simply

$$\mathbf{X}_\perp = \mathbf{x}_0 + (1/m)\epsilon\nabla_{\mathbf{x}_0}\psi(\mathbf{x}_0)\ {}^{1}\!/_{2}\,(t^2 - 2Nt) \tag{19}$$

This transversal displacement will modify the density of monomers inside the columnlike region associated with a generic base point $\mathbf{x}$. The Jacobian that appears in the calculation of the density (3) is easily calculated to be (to first order)

$$\frac{\partial\mathbf{x}}{\partial\mathbf{X}_\perp}(t) = 1 - \epsilon\nabla_{\mathbf{x}}^2\psi(\mathbf{x})\,\frac{1}{2m}\,(t^2 - 2Nt) \tag{20}$$

$$\frac{\partial\mathbf{x}}{\partial\mathbf{X}_\perp}(z;\,\hat{z}) = 1 - \epsilon\nabla_{\mathbf{x}}^2\psi(\mathbf{x})\,\frac{2N^2}{m\pi^2}\Big[\Big(\cos^{-1}\Big(\frac{z}{\hat{z}}\Big)^2 - \Big(\frac{\pi}{2}\Big)^2\Big] \tag{21}$$

The total change in the monomer density induced by the transverse motion is

$$\rho_1\,(\mathbf{x}, z) = -\int_z^h \mathrm{d}\hat{z}\ \sigma g(\hat{z})[\dot{Z}(z,\hat{z})]^{-1}\nabla_{\mathbf{x}}^2\psi(\mathbf{x})\,\frac{2N^2}{m\pi^2}\left[\left(\cos^{-1}\left(\frac{z}{\hat{z}}\right)\right)^2 - \left(\frac{\pi}{2}\right)^2\right] \tag{22}$$

Integration over the column gives the total flux of monomers (per unit area) toward the column:

$$n_1 = \sigma(N^3/3m)\nabla_{\mathbf{x}}^2\psi(\mathbf{x}) \tag{23}$$

The introduction of an object of finite volume into the bulk of the brush requires the deformation of the free surface to create the extra space required for the displaced monomers. We should thus examine the consequences of surface deformations. We describe the new surface as a deformation of the original, flat one:

$$h(\mathbf{x}) = h_0 + \epsilon h_1(\mathbf{x}) + ... \tag{24}$$

For a column based at a point $\mathbf{x}$, of section dS, the number of monomers in the extra volume at the top of the section is ϵh_1 dS/v. These monomers were displaced from the bulk of the column in consideration. The depletion in the bulk should be compensated by a combination of transversal drift and volume exclusion by an external object, i.e.

$$\frac{h_1}{h_0} = \frac{N^2}{3m}\,\nabla_{\mathbf{x}}^2\psi(\mathbf{x}) + \frac{1}{h_0}\int \mathrm{d}z\ f \tag{25}$$

Again, it is important to emphasize that whatever way the depletion is balanced, the chain-end density can always be rearranged so that the density prescription is satisfied.

Upon deformation of the free surface as described above, the expansion for the free energy contribution arising from the surface tension is

$$\int \mathrm{d}^2\mathbf{x}\ \gamma[1 + {}^1/_2(\epsilon\nabla_{\mathbf{x}}h_1)^2 + ...] \tag{26}$$

In the Appendix, we prove that if we require mechanical equilibrium of the new surface, in the absence of surface tension, the potential there vanishes and we obtain a relation between the amplitude of the surface deformation and the perturbation potential. The potential at the surface is

$$\phi(\mathbf{x}, h) = \phi_0(h_0) + \epsilon h_1\phi'(h_0) + \epsilon\psi(\mathbf{x}) = \epsilon(-2P_0h_1/h_0 + \psi) \tag{27}$$

The equilibrium condition $\phi(h) = 0$ is then

$$h_1 = (h_0/2P_0)\psi \tag{28}$$

If there is a surface tension present, the potential should compensate the force derived from the increment of area:

$$-2P_0\frac{h_1}{h_0} + \frac{\psi_1}{P_0} = -\frac{\gamma}{v}\,\nabla_{\mathbf{x}}^2\,\frac{h_1}{h_0} \tag{29}$$

Equations 25 and 29 completely determine all the fields for a given bulk perturbation.

Finally we comment on the calculation of energies associated with deformations. Small deviations from the value of the density, $\delta\rho$, can be expressed in terms of the volume fraction as $-\delta v/v^2$. The pressure that opposes the changes in the occupied volume can then be read from (4) to be ϕ/v. For a small volume insertion ϵV, the work required for the insertion has an expansion of the form $\epsilon V\ \phi(\mathbf{r})/v$ + ... We are particularly interested in the case in which two objects are immersed in the bulk of the brush. If they are spatially separated, a first insertion modifies the potential by an amount ψ_1 so that a second small insertion, in addition to the zeroth-order pressure, feels the extra pressure ψ/v. The contribution to the total energy of the system from the interaction between the two insertions (of volumes V_1, V_2) is

$$F_{\mathrm{int}} = \epsilon^2\psi_1V_2/v = \epsilon^2\psi_2V_1/v \tag{30}$$

5. Equilibrium Equations and Solutions

Let us write the final equations for the potential and the surface deformation as found in the Appendix:

$$2\frac{h_1}{h_0} - C\lambda^2\nabla_{\mathbf{x}}^2\,\frac{h_1}{h_0} - \frac{\psi_1}{P_0} = 0 \tag{31}$$

$$-\frac{h_1}{h_0} + \frac{\lambda^2}{2}\,\nabla_{\mathbf{x}}^2\,\frac{\psi}{P_0} - \frac{1}{h_0}\int \mathrm{d}z\ f(\mathbf{x},z) = 0 \tag{32}$$

where $C = 12\gamma/\pi^2(P_0h_0)$ and $\lambda^2 = \pi^2h_0{}^2/12$.

We will now consider some solutions to these equations. Any density perturbation can be decomposed by a Fourier transformation into a superposition of density plane waves concentrated at fixed heights within the layer:

$$f = h_0\delta(z - z_0)\cos(\mathbf{k}\cdot\mathbf{x}) \tag{33}$$

$$\rho_P = (1/v)[1 - \epsilon h_0\delta(z - z_0)\cos(\mathbf{k}\cdot\mathbf{x})] \tag{34}$$

Consider one such wave. It is easy to see that the potential field and surface deformations are of the form

$$\psi = \epsilon\psi(k)\cos(\mathbf{k}\cdot\mathbf{x}) \tag{35}$$

$$h_1 = \epsilon h_1(k)\cos(\mathbf{k}\cdot\mathbf{x}) \tag{36}$$

where $k = |\mathbf{k}|$. Solving the equilibrium equations, we obtain

$$\frac{\psi(k)}{P_0} = \frac{2 + C(\lambda k)^2}{1 + (\lambda k)^2(1 + (C/2)(\lambda k)^2)} = \frac{1}{(k\lambda^2) + (k_+\lambda)^2} + \frac{1}{(k\lambda)^2 + (k\_\lambda)^2} \tag{37}$$

$$\frac{h_1(k)}{h_0} = \frac{1}{1 + (\lambda k)^2(1 + (C/2)(\lambda k)^2)} = \frac{1}{(1 - 2C)^{1/2}}\left(\frac{-1}{(k\lambda)^2 + (k_+\lambda)^2} + \frac{1}{(k\lambda)^2 + (k\_\lambda)^2}\right) \tag{38}$$

where

$$(k_\pm\lambda)^2 = [1 \pm (1 - 2C)^{1/2}]/C \tag{39}$$

The four poles of both $\psi(k)$ and $h_1(k)$ are then $\pm ik_\pm$. We choose the signs of the roots so that $k_\pm$ have a positive

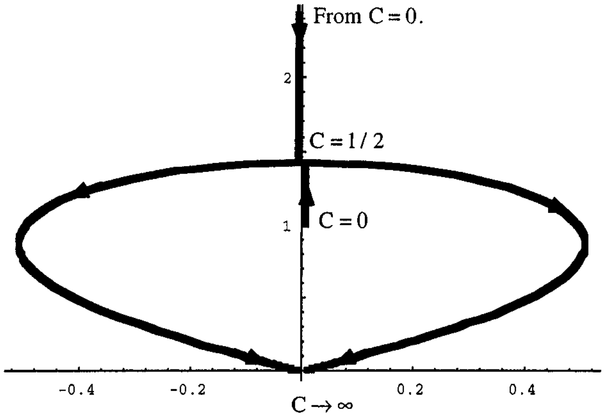

Figure 2. Location of the poles in the upper half-plane, $ik_\pm$, as a function of the parameter C, which measures the relative strength of the surface tension.

real part. A graph of the location of the poles in the complex plane is shown in Figure 2.

The case of the introduction of a localized intrusion is solved by modeling the small object as a δ-function distribution of strength ϵV:

$$f = V\delta^3(\mathbf{r} - \mathbf{r}_0) = (V/4\pi^2)\int d^2k\ \delta(z - z_0)e^{i\mathbf{k}\cdot\mathbf{x}} \qquad (40)$$

where we have taken $\mathbf{r}_0 = (0,0,z_0)$. The required potential is then

$$\psi(\mathbf{x}) = \frac{V}{4\pi^2 h_0}\int d^2\,k\ e^{i\mathbf{k}\cdot\mathbf{x}}\ \psi(k) \qquad (41)$$

$$= \frac{P_0 V}{2\pi h_0}\frac{1}{\lambda^2}[K_0(k_+r) + K_0(k_-r)] \qquad (42)$$

where $r = |\mathbf{x}|$ and K_0 is a modified Bessel function. In addition we have, for the surface deformation

$$h_1(\mathbf{x}) = \frac{V}{2\pi h_0}\frac{1}{\lambda^2(1 - 2C)^{1/2}}[-K_0(k_+r) + K_0(k_-r)] \qquad (43)$$

These expressions for the potential and the deformation have different characteristics depending on the importance of the surface tension term. For small surface tensions, $C < {}^1/_2$, the poles of the pressure response $\psi(k)$ are purely imaginary, and the pressure and deformation decay exponentially with decay length:

$$l = \lambda\left[\frac{1}{1 - (1 - 2C)^{1/2}}\right]^{1/2} \qquad (44)$$

We should further point out that under this condition the pressure is always positive away from the source, giving the interaction between two insertions a repulsive character.

For large surface tensions, $C > {}^1/_2$, on the other hand, the poles of the susceptibility are complex and create oscillatory behavior superimposed to the exponential decay on the physical-space response. In this case the decay length is

$$l = \lambda\left[\frac{1}{2C} + \left(\frac{1}{2C}\right)^{1/2}\right]^{-1/2} \qquad (45)$$

We note also that, rather naturally, the surface deformation is suppressed as $h_1 \sim 1/C$. Finally, in the limit of very large surface tension, the top surface remains flat, and the pressure field inside the bulk develops a logarithmic behavior, $\psi \sim \ln(r)$.

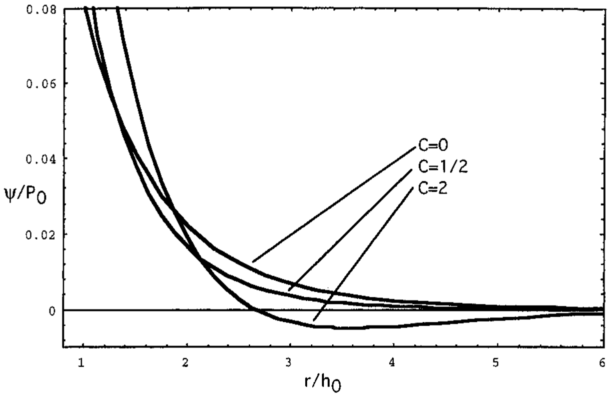

Figure 3. Plot of the potential induced by a concentrated insertion as a function of the transverse distance r for three values of the parameter C. The insertion is such that $V/h_0^3 = 1$.

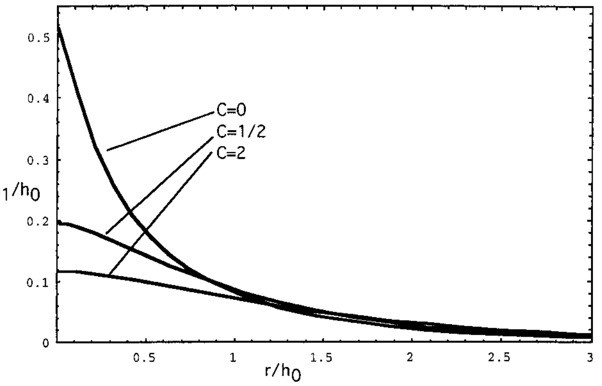

Figure 4. Plot of the surface deformation induced by a concentrated insertion as a function of the transverse distance r for three values of the parameter C. The insertion is such that $V/h_0^3 = 1$.

Plots of the potential and the deformation for different values of the surface tension are presented in Figures 3 and 4.

6. Discussion

As we have seen, the potential does not depend on the height of the insertion. One may ask what the physical reason is for the response to have this simple form. Most of the assumptions in the model are fairly natural, and even after considering higher order corrections, the final picture should be one in which the response is dominated by its transverse structure. We would like to address this as the result of a symmetry-breaking-like mechanism.

It is a simple physical requirement that the chains be able to take different configurations inside the brush and, in particular, to extend to different heights. The alternative is that all the chains have an average configuration with uniform stretching and extend their free ends to the top of the layer, as in the Alexander–de Gennes model.[12] Both the Alexander–de Gennes and Semenov models evaluate the free energy of the system in the same way, but as is well-known, the true ground state is given by Semenov's solution. The Alexander–de Gennes model assumes a nondegenerate ground state where all the chains behave identically. In Semenov's solution, the chain ends are distributed across the layer. To further elaborate this point, we look at the particulars of the model. We note that the longitudinal trajectories are solutions degenerate with respect to their individual contributions, to the total energy, as expressed in eq 4. The chains can then easily interchange positions (up to dynamical and topological constraints). This means that the distribution of chain ends does not arise from the thermal broadening of a concentrated distribution; rather, it appears as a result of the combination of the energy degeneracy with the constraints of constant density. (The effects of the thermal broadening have been discussed previously in a similar context by Marko and Witten.[13])

On physical grounds, we do not expect the introduction of a small perturbation to drive all chain ends away from a region of the layer. The degeneracy property should then be a robust characteristic of the system even in the presence of the perturbation. We can check this in our solution by looking at the extra energy contribution that comes from the transverse displacements. The form of the potential forces all chains in a column to have identical transverse displacements (as a function of the monomer number t) which pick up the same extra energy and thus maintains the degeneracy.

This degeneracy among the chains attached to a small base area is what gives the layer its "softness" property. The degeneracy allows the smearing of the interaction with the insertion, requiring only that the potential change locally by a constant. In this regard we may compare our results with those based in the Alexander−de Gennes approximation models.[10,11] There, the pressure field induced by the external object has, at short distances, a divergent behavior similar to that of the potential field of an electric quadrupole, but that away from the source decays exponentially. We can also compare, on the other hand, this response with that of a layer of an ideal liquid in a container: the insertion will raise the level of the fluid, and the hydrostatic pressure will increase uniformly everywhere in the layer. Thus, our results present the brush as closer to a liquidlike behavior than to the rubberlike elasticity picture of the Alexander−de Gennes approximation.

An important characteristic of the solution we have obtained is its dependence on the relative magnitude of the surface tension. As we have seen, the interaction between the insertions turns out to have an oscillatory behavior in the separation between the insertions when the surface tension is large enough as was also found in the Alexander−de Gennes approximation.[10] Among other things, this effect suggests the possibility of the creation of a stable lattice of objects immersed in the brush. The first minimum in the interaction energy occurs at a separation of the order

$$l = \frac{\pi\gamma}{2}\left[\left(\frac{1}{2C}\right)^{1/2} - \frac{1}{2C}\right]^{-1/2} \tag{46}$$

We must point out, nevertheless, that while the relative magnitude of the surface tension required to produce such effects is small, namely, $C = {}^{1}/_{2}$, the actual absolute magnitude for this surface tension may be rather high. This energy should be comparable with the minimum energy required to irreversibly attach the polymer chains. Such situations may arise when the free surface of the brush is in contact with a bad solvent.

A gold−copolymer system with characteristics similar to those described by our model was recently studied by Morkved et al.[14] A copolymer lamella is roughly equivalent to our model with a small surface tension. We can then estimate the interaction between gold spheres induced by the diblock lamella of their experiment. The lamella are symmetric diblocks of polystyrene and poly(methyl methacrylate) containing 300 monomers/block. They were observed to have a layer thickness h of about 10 nm at a temperature of 430 K. In these conditions, $P_0h^2 \approx 10^2kT$. The gold spheres had diameters ≈4 nm. If the spheres were separated by a distance of twice their diameters, the estimated interaction energy would be $F_{\text{int}} \approx 10^{-1}kT$. This is a somewhat small effect, particularly for such large spheres. The available diblocks, however, do not present a case of strong stretching. If strongly stretched brushes are constructed, the effects can become more important. The numerical result of this estimation is essentially the same as that obtained using the Alexander−de Gennes model.[10] Although the different approximations give very different short distance behaviors, the size of the gold spheres in this example cannot probe such differences.

7. Conclusions

Our central result is the evaluation of the response function of the brush to an insertion of a small, extraneous object. The final answer has a very simple form. It does not depend on the depth of the insertion and has a simple exponential decay away from the object with a characteristic length on the order of the brush's thickness. Although these characteristics were present in the solution of the problem of pure surface deformations solved by Tang,[7] it is interesting that the same form of the solution is available for this problem.

In addition, the strength of the interaction between two objects immersed in different regions of the brush is simply given by a multiple of the potential ψ. For small surface tensions, the interaction is of a repulsive nature. At larger values of the surface tension, the interaction still decays away from the source but also presents an oscillatory behavior.

We have argued that the simplicity of the result depends crucially on the fact of the existence of a highly degenerate ground-state configuration. We expect to further exploit this characteristic of the system in dealing with other static and dynamical problems of brush structures. We also plan to more carefully incorporate the effects of the statistical broadening of the distribution of trajectories, i.e., improving the theory to include the contributions of trajectories that do not satisfy the "classical" equations of motion. We expect the statistical broadening to modify our results for short distances but retain the long-wavelength behavior described here.

Finally, we compare these results with those obtained using the Alexander−de Gennes approximation.[10,11] The exponential decay of interactions and deformations has been obtained there too, but the form of the interaction at short distances is clearly distinct. In that case it was found that the interaction could be attractive or repulsive depending on the relative height of the particles. As expected, substantial differences between the models appear whenever the internal structure of the brush becomes relevant to the problem at hand. Of particular importance is to note that the short wavelength surface rippling instability found in the Alexander−de Gennes model[9] does not appear in the model considered here nor in the previous discussion of surface deformations by Tang.[7] Such instability is therefore an artifact of the Alexander−de Gennes model, rather than a physical feature.

Acknowledgment. We have had many useful discussions with Tom Witten and Hao Li. F.J.S. acknowledges support from the National Science Foundation under contract DMR-9208527.

Appendix

In this Appendix we derive the equilibrium conditions for the brush from our variational principle.

First, using all the considered constraints and properties of the trajectories and fields, our aim is to write an expansion of the free energy functional that involves only the fields ψ and h_1. This can be done since we already know the form of the chain trajectories, so they can be integrated over within the functional. From the variation of the resulting functional, we will obtain equations for the determination of the potential and the deformation.

In general, an expansion up to second order in the perturbation parameter will contain quadratic terms in the fields of the form $h_1{}^2$, as well as linear terms in second-order quantities ($\mathbf{X}_2$, etc.). For the purpose of obtaining the equilibrium equations for the fields, however, we will need only the quadratic terms.

We start by rewriting the functional (5) as

$$F = \sigma\int \mathrm{d}^2\mathbf{x}\int_0^N \mathrm{d}t \left[\frac{m}{2}\dot{Z}^2 + \phi_0 + \epsilon\psi(\mathbf{x}) + \frac{\gamma}{\sigma}(1 + {}^1\!/_2(\nabla_{\mathbf{x}}\epsilon h_1)^2)\right] + \sigma\int \mathrm{d}^3\,\mathbf{x}\int_0^N \mathrm{d}t\left(\frac{m}{2}\,\dot{\mathbf{X}}_\perp{}^2 + \mathbf{X}_\perp\cdot\epsilon\nabla_{\mathbf{x}}\psi\right) - \int \mathrm{d}^2\,\mathbf{x}\int_0^{h_0+\epsilon h_1}\mathrm{d}z\,(1/v)\,(\phi 0 + \epsilon\psi)(1-\epsilon f) + \ldots \quad \text{(A1)}$$

Integration over the trajectories (eqs 7 and 19) and expansion of the last integral gives

$$F = \int \mathrm{d}^2\mathbf{x}\left\{\frac{\pi^2}{24N}m\sigma h_0{}^2 + \gamma[1 + {}^1\!/_2(\nabla_{\mathbf{x}}\epsilon h_1)^2] + \int_0^{h_0}\mathrm{d}z\,\epsilon\frac{f}{v}\phi_0 + \epsilon^2\psi\int_0^{h_0}\mathrm{d}z\,\frac{f}{v} + \epsilon^2\,\frac{\pi^2}{8N}m\sigma h_1{}^2 - \epsilon^2\,\frac{N^3\sigma}{6m}(\nabla_{\mathbf{x}}\psi)^2 - \epsilon^2\,\frac{\sigma N}{h_0}\,h_1\psi\right\} \quad \text{(A2)}$$

We have not included here terms containing second-order quantities.

Variation of the effective free energy for the potential and deformation fields gives the equilibrium equations (eqs 32 and 31):

$$2\frac{h_1}{h_0} - C\lambda^2\nabla_{\mathbf{x}}^2\,\frac{h_1}{h_0} - \frac{\psi_1}{P_0} = 0 \qquad \text{(A3)}$$

$$-\frac{h_1}{h_0} + \frac{\lambda^2}{2}\,\nabla_{\mathbf{x}}^2\,\frac{\psi}{P_0} - \frac{1}{0}\int \mathrm{d}z\; f(\mathbf{x},z) = 0 \qquad \text{(A4)}$$

where $C = 12\gamma v/\pi^2(P_0h_0)$ and $\lambda^2 = \pi^2h_0{}^2/12$.

We note that this variational procedure recovers the anticipated relation between the potential and the surface deformation. In addition, as can be expected from the original introduction of the ϕ field to enforce incompressibility, the resultant equation for the variation of the free energy with respect to ψ (eq A4) is equivalent to the requirement of balance between monomer displacements and external insertion eq 25.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 1.
(2) Witten, T. *Macromol. Rep.* **1992**, *A29*, 87.
(3) Muthukumar, M.; Ho, J. S. *Macromolecules* **1989**, *22*, 965. Helfand, E. *Macromolecules* **1975**, *8*, 552. Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *9*, 879; **1978**, *11*, 960; **1980**, *13*, 994.
(4) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733 (*Zh. Eksp. Teor. Fiz.* **1988**, *88*, 1242).
(5) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1990**, *5*, 413; *Macromolecules* **1990**, *21*, 2610.
(6) Milner, S. T. *Science* **1991**, *251*, 845.
(7) Tang, H. Laterally Inhomogeneous Polymer Melt Brushes: I. Free Energy Expansion, Height Profile, and Fluctuation Modes. *Macromolecules*, in press.
(8) Fredrikson, G. H.; Ajdari, A.; Leibler, L.; Carton, J.-P. *Macromolecules* **1992**, *25*, 2882.
(9) Turner, M. S.; Joanny, J.-F. *Macromolecules* **1992**, *25*, 6681. Solis, F. J.; Pickett, G. T. *Macromolecules* **1995**, *28*, 4307.
(10) Solis, F. J. A Bulk Perturbation in an Alexander Brush. *Macromolecules*, submitted.
(11) Williams, D. R. M.; Pincus, P. A. *Europhys. Lett.* **1993**, *24*, 29.
(12) Alexander, S. J. *J. Phys. (Paris)* **1977**, *38*, 983. de Gennes, P.-G. *J. Phys. (Paris)* **1976**, *37*, 1435; *C. R. Acad Sci. (Paris)* **1977**, *300*, 983; *Macromolecules* **1980**, *13*, 1069.
(13) Marko, J. F.; Witten, T. A. *Phys. Rev. Lett.* **1991**, *66*, 1541.
(14) Morkved, T. L.; Wiltzius, P.; Jaeger, H. M.; Grier, D. G.; Witten, T. A. *Appl. Phys. Lett.* **1994**, *64*, 422.

MA951874M