Surface Modes and Deformation Energy of a Molten Polymer Brush

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ABSTRACT: We report on an analysis of the free energy of distortion of a molten polymer brush, such as a layer of block copolymer at an air interface. Within the Alexander–de Gennes approximation of a delta function distribution of chain ends, but rigorously enforcing incompressibility, we calculate the change in the free energy of a brush associated with a small-amplitude sinusoidal displacement of the free surface about the equilibrium height. Unlike the surface of a liquid, long-wavelength modes in a brush are suppressed due to the lateral chain stretching required to maintain constant density. We demonstrate the existence of a preferred wavelength for the surface modes of a molten brush and estimate the fluctuation amplitude. The energy cost to deform a brush with a blunt object, e.g., the tip of an atomic force microscope, is also discussed.

I. Introduction

Polymer layers that are built up from flexible polymer chains end-grafted to a surface or interface have received widespread attention in recent years.[1-4] At sufficiently high coverage (chains/area of surface), the chains are strongly extended in the direction of the surface normal and a dense layer or so-called *brush* is formed. Such brushes can be produced by selective adsorption of end-functionalized polymers in solution[5,6] but are also self-assembled in melts of block copolymers.[7] A detailed understanding of the equilibrium and nonequilibrium properties of polymer brushes is key to the design of materials with tailored surface properties, improved methods for stabilizing colloidal suspensions, and new co-polymeric alloys.

Most theoretical studies of polymer brushes have focused on average properties at equilibrium, such as layer height, distribution of chain ends, and monomer concentration profile.[1-4] Fewer studies have been concerned with non-equilibrium properties[8] or with the deformation behavior of polymer brushes.[9] The present paper is a contribution on this latter topic.

Here we consider the response of a molten polymer brush (unit volume fraction of polymer within the layer) to a *nonuniform*, volume-conserving deformation. The particular deformation of interest is a small-amplitude sinusoidal displacement of the brush free surface (opposite the grafting surface). As depicted in Figure 1, the brush height $z = h(x)$ is displaced about the equilibrium uniform height h_0 according to

$$h(x) = h_0 + \epsilon \cos (qx) \qquad (1.1)$$

where the amplitude ϵ is assumed to satisfy $\epsilon/h_0 \ll 1$ and $2\pi/q$ represents the characteristic wavelength of the distortion. By calculating the change in free energy of the brush to second order in ϵ, one can investigate which modes of distortion are thermally populated (i.e., have energy of order $k_B T$ or less). By further invoking equipartition of these surface excitations, height–height correlations in the brush can be explored as a function of wavevector q. Such
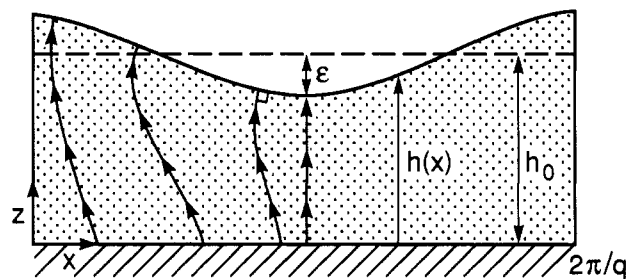

Figure 1. One period of a molten polymer brush deformed according to eq 1.1. The unperturbed equilibrium brush height is h_0, and the perturbation amplitude is ϵ. The wavelength of the surface perturbation is $2\pi/q$.

correlations can in principle be studied in reflectivity experiments on block copolymer interfaces.

Intuitively, one expects that a grafted melt brush will exhibit surface modes that have features in common with, but nevertheless are distinct from, the excitations of liquid/vapor interfaces and elastic solid/vapor interfaces. Surface modes with wavelengths $\lambda = 2\pi/q$ that are much less than the unperturbed radius of gyration of a grafted chain, $R_0 = b(N/6)^{1/2}$ (N is the degree of polymerization and b is the statistical segment length), will require limited stretching of chains in the interface plane. Thus, the grafting constraint should be irrelevant for such short-wavelength excitations, and the free energy cost is expected to be proportional to the additional interfacial area imposed by the distortion, as in the case of capillary waves at a liquid/vapor interface. In contrast, a long-wavelength surface excitation of a brush ($q \ll R_0^{-1}$) requires lateral displacements of chains over a characteristic distance that greatly exceeds R_0 in order to maintain a constant monomer density. Because the chains are attached with (assumed) uniform coverage at the grafting surface, these lateral displacements impose a configurational entropy (stretching) penalty. We demonstrate below that this entropy penalty (per unit area) diverges as q^{-2}, consistent with the deformation free energy of a thin film of an isotropic elastic solid subjected to the same sinusoidal displacement.

The above expectations are borne out in qualitative arguments presented in section II.A and in explicit calculations described in the subsequent sections. In sections II.B and II.C we develop an approximation for the free energy of a weakly deformed brush and explore the connections with an incompressible, isotropic elastic film of comparable thickness. In section III, this free energy expression is used to study the penetration of a molten brush by a blunt object, such as the tip of an atomic force microscope (AFM). We demonstrate in section IV that the competition between the elastic restoring force at long wavelengths and the interfacial tension penalty at short wavelengths leads to an energetically preferred wavelength for thermally excited surface modes on an incompressible brush. This length scale is elucidated, and the consequences for scattering experiments are explored. Extensions and limitations of our work are discussed in section V.

II. Free Energy of a Deformed Melt Brush

A. Model and Qualitative Picture. In the present section we consider an assembly of flexible polymer chains, each of degree of polymerization N, statistical segment length b, and monomer volume v, end-grafted to a surface at uniform density σ (chains/area). The grafting density is assumed to be sufficiently high that a dense molten brush of uniform monomer density is produced. The grafting surface could be a solid substrate (e.g., mica or silicon) or might represent an interface between two microdomains of a block copolymer melt. In the latter case, we require that the microdomain below the grafting surface be semicrystalline or glassy so that the grafting density remains uniform on imposition of a deformation at the free (top) surface. Such a situation could be realized, for example, at the air interface of a styrene–isoprene diblock copolymer melt. Isoprene, having a lower surface tension, is found at the air interface[10] and constitutes the "brush", while the styrene "grafting" blocks are glassy at room temperature.

As shown in Figure 1, the melt brush is subjected to a sinusoidal displacement of its free surface about the equilibrium layer height h_0 (cf. eq 1.1). By volume conservation, h_0 is related to the grafting density, monomer volume, and degree of polymerization by

$$h_0 = \sigma v N \qquad (2.1)$$

Throughout our discussion, we will refer to the coordinate system $\mathbf{r} = (x, z)$ shown in Figure 1. We impose periodic boundary conditions at $x = 0$ and $2\pi/q$ and note the symmetry axis at $x = \pi/q$.

In computing the free energy of the deformed layer we make several simplifying assumptions. First of all, we assume that the chains are sufficiently stretched on average that the passage from a "quantum" to a "classical" description is permissible.[2–4,7] This amounts to the requirement that the characteristic dimensions of a chain parallel and perpendicular to the grafting surface exceed the unperturbed radius R_0. For the perpendicular displacement to satisfy this criterion, it follows from eq 2.1 that the grafting density σ must exceed $1/(b^2 N^{1/2})$. As regards the lateral displacement of chains, the strong stretching condition is met only for $q R_0 \ll 1$; this will be the regime of most interest in the present paper. Besides the description of chain configurations by their classical trajectories, we also make the simplifying (Alexander–de Gennes) assumption that the chain ends are all located at the free surface of the brush. For the flat (undeformed) brush, a more precise calculation shows that while the

chain ends are more concentrated near the free surface, they are distributed with nonvanishing probability throughout the entire layer.[4,7] It turns out, however, that the approximation of replacing the end distribution function with a delta function centered at h_0 recovers the proper scaling of the flat brush free energy[7] and leads to a 20% overestimate of the prefactor. Since only small-amplitude perturbations of the flat brush are considered in the present paper, we assume that the Alexander–de Gennes approximation will be suitable for our purposes as well.

Before turning to a detailed calculation of the free energy of a deformed brush, we present a qualitative argument that yields the result alluded to in the Introduction, namely, that the free energy per area scales as q^{-2} in the small q, i.e., long-wavelength, limit. This implies that long surface waves will be strongly suppressed in molten brushes, such as block copolymer interfaces. The argument is facilitated by reference to Figure 1. Consider first a chain that is grafted along the symmetry axis at $x = \pi/q$. Since the volume occupied by a chain, Nv, is unchanged by the deformation, it follows that, for the chain under consideration, $(h_0 - \epsilon)dd' \approx Nv$, where d is the average distance between grafting points ($\sigma = 1/d^2$) and d' is the increased distance between chains (along x) after the deformation. The increase in the spacing of chains along x (at some average height in the layer) is thus $\Delta d = d' - d \approx \epsilon d/h_0$. Although the lateral spreading of a chain grafted at the symmetry axis is of order Δd, the spreading accumulates for chains that are grafted at points removed from $x = \pi/q$. In particular, for long-wavelength deformations one expects that the lateral extension of a chain that is n chains removed from the central chain will be of order $n\Delta d$. Since the "typical" chain is located a quarter wavelength, $\lambda/4 = \pi/(2q)$, from the symmetry axis, the lateral extension of such a chain can be estimated as $\Delta D = n\Delta d \sim (\lambda/d)\Delta d \sim \epsilon/qh_0$. It thus follows that the stretching free energy per chain can be estimated as $k_B T(\Delta D)^2/(Nb^2)$ and the free energy per area of grafting surface should scale as $k_B T \sigma \epsilon^2/[Nb^2(qh_0)^2]$. As demonstrated below (eq 2.31), this scaling is precisely that obtained from a more rigorous method of calculation.

B. Quantitative Approach. Our analytical method is similar to that employed by Semenov[7] for the purpose of computing the interaction energy between two copolymer micelles. Consider an infinitesimal oriented surface element $d\mathbf{S}$ within the brush and the set of dQ chains that pass through the element. To a good approximation, all of the chains have the same orientation and the same degree of stretching as they pass through the surface element. Hence, if each chain expends ds monomers in making a displacement $d\mathbf{r}$ through the surface element, it follows by local volume conservation that

$$d\mathbf{S} \cdot \mathbf{E} = v \, dQ \qquad (2.2)$$

where $\mathbf{E} = d\mathbf{r}/ds$ is the local rate of stretch of a chain. If eq 2.2 is integrated over a closed surface, we obtain

$$\int_S \mathbf{E} \cdot d\mathbf{S} = v Q_e \qquad (2.3)$$

where Q_e is the number of grafting points minus the number of free chain ends that are enclosed by the surface. From the divergence theorem, it now follows that

$$\nabla \cdot \mathbf{E} = v \rho_e \qquad (2.4)$$

where $\rho_e(\mathbf{r})$ is the difference between the local density of grafting points and the free end density. As pointed out by Semenov,[7] this expression is analogous to electrostatics, with the local stretch $\mathbf{E}$ playing the role of the electric field and ρ_e playing the role of the charge density. In the

present situation we can associate the grafting surface of the brush with the surface of a positively charged conductor and the brush free surface (in the Alexander–de Gennes approximation) with the surface of a negatively charged conductor.

From eq 2.4 and the assumption that all chain ends lie on the upper surface of the deformed brush, the incompressibility constraint amounts to the restriction that the vector field $\mathbf{E}(\mathbf{r})$ be *divergence free* in the brush interior. A second constraint on $\mathbf{E}$ is that, on passing from the grafting surface to the free surface, a chain must expend a total of N monomers. We can use the uniqueness of the chain trajectories to formulate this as an integral constraint, i.e., for a chain that starts on the grafting surface at a point $(x_i, 0)$ there is a unique position of the free end at the upper surface $(x_f, h(x_f))$. The constraint can be written as

$$\int_{C_f} \mathrm{d}l \, |\mathbf{E}|^{-1} = N \qquad (2.5)$$

where $\mathrm{d}l$ is the differential arc length element along the chain trajectory C_f that terminates at a point $(x_f, h(x_f))$ on the free surface. If we define $\mathbf{E}(z;x_f)$ as the local stretch at z contributed by the chain which terminates at x_f, and using $E_z(z;x_f) > 0$, eq 2.5 can be rewritten as

$$\int_0^{h(x_f)} \mathrm{d}z \, [E_z(z;x_f)]^{-1} = N \qquad (2.6)$$

This constraint is to be imposed at all x_f, i.e., for all chains in the layer.

The elastic free energy of the polymer brush is simply related to the square of the vector field $\mathbf{E}(\mathbf{r})$, integrated over the layer

$$F_{el} = \frac{3k_B T}{2b^2 v} \int \mathrm{d}\mathbf{r} \, \mathbf{E}^2 \qquad (2.7)$$

The desired free energy of the deformed brush is obtained by minimizing F_{el} with respect to $\mathbf{E}(\mathbf{r})$, subject to the incompressibility constraint $\nabla \cdot \mathbf{E} = 0$ and the chain length constraint eq 2.6. This is most easily accomplished with the use of two Lagrange multiplier fields, $\phi(\mathbf{r})$ and $g(x)$, and the modified free energy functional

$$\frac{F}{k_B T} = \frac{B}{2} \int \mathrm{d}\mathbf{r} \, \mathbf{E}^2 + \int_0^{2\pi/q} \mathrm{d}x \, g(x) \left\{ \int_0^{h(x)} \mathrm{d}z \, [E_z(z;x)]^{-1} - N \right\} - B \int \mathrm{d}\mathbf{r} \, \phi(\mathbf{r}) \, (\nabla \cdot \mathbf{E}) \quad (2.8)$$

Here we have defined $B \equiv 3/(b^2 v)$.

Variation of eq 2.8 with respect to $E_i(\mathbf{r})$ leads to the Euler–Lagrange equations $(\partial_x \equiv \partial/\partial x)$

$$E_x = -\partial_x \phi \qquad (2.9)$$

$$E_z = -\partial_z \phi + B^{-1} E_z^{-2} g(x_f(\mathbf{r})) \qquad (2.10)$$

and the constraint equations in eq 2.6 and $\nabla \cdot \mathbf{E} = 0$. In eq 2.10, $x_f(\mathbf{r})$ denotes the x coordinate at the free surface of a chain that passed through the point $\mathbf{r}$ in the brush interior. Note that ϕ would play the role of the electrostatic potential in the absence of the integral constraint eq 2.6. The latter breaks the strict analogy with electrostatics of conductors.

To complete the specification of the problem, we must impose boundary conditions at the upper and lower surfaces of the brush (recall that periodic boundary conditions are imposed on x). If the surface of integration in eq 2.3 is chosen to be a thin shell that encloses the grafting surface, the lower boundary condition on $\mathbf{E}$ is

easily obtained:

$$E_z(x,0) = v\sigma \qquad (2.11)$$

A similar choice of integration surface in eq 2.3 for the upper surface leads to

$$E_n(x,h(x)) = v\sigma_e(x) \qquad (2.12)$$

where E_n is the component of $\mathbf{E}$ along the (outward) normal at the free surface and $\sigma_e(x)$ is the surface density of ends at the top of the brush. The final boundary condition is that of no tangential stress at the upper surface:

$$E_t(x,h(x)) = 0 \qquad (2.13)$$

C. Perturbative Calculation of the Free Energy.
Having now formulated the variational problem for the free energy of a deformed brush, we proceed to a perturbative solution of the above set of equations, using ϵ as an expansion parameter. This is conveniently carried out by expressing $\mathbf{E}$, ϕ, g, σ_e, and $x_f(\mathbf{r})$ in terms of their contributions at each order in ϵ. We employ the following notation; e.g., for ϕ

$$\phi(\mathbf{r}) = \phi^{(0)}(\mathbf{r}) + \epsilon\phi^{(1)}(\mathbf{r}) + \epsilon^2\phi^{(2)}(\mathbf{r}) + \dots \qquad (2.14)$$

At order ϵ^0, the above equations are easily solved, yielding well-known expressions for a flat brush in the Alexander–de Gennes approximation. We obtain

$$E_x^{(0)} = g^{(0)} = 0$$

$$E_z^{(0)} = v\sigma$$

$$\phi^{(0)} = -v\sigma z$$

$$\sigma_e^{(0)} = \sigma$$

$$x_f^{(0)} = x \qquad (2.15)$$

Substituting these results into eq 2.8, a simple expression is obtained for the free energy per area of grafting surface, $f^{(0)}$:

$$\frac{f^{(0)}}{k_B T} = \frac{B}{2}(v\sigma)^2 h_0 = \frac{3v^2\sigma^3 N}{2b^2} \qquad (2.16)$$

At order ϵ it is apparent that we can replace $g^{(1)}(x_f(\mathbf{r}))$ with $g^{(1)}(x)$. The equations to be solved at this order are thus

$$E_x^{(1)} = -\partial_x \phi^{(1)}$$

$$E_z^{(1)} = -\partial_z \phi^{(1)} + B^{-1}(v\sigma)^{-2} g^{(1)}(x)$$

$$\nabla^2 \phi^{(1)} = 0$$

$$\int_0^{h_0} \mathrm{d}z \, E_z^{(1)}(x,z) = v\sigma \cos(qx) \qquad (2.17)$$

The boundary condition 2.11 at $z = 0$ translates at first order in ϵ to

$$\partial_z \phi^{(1)} = B^{-1}(v\sigma)^{-2} g^{(1)}(x) \qquad (2.18)$$

while the free surface conditions 2.12 and 2.13 can be written at $O(\epsilon)$ as

$$\sigma_e^{(1)}(x) = v^{-1}E_z^{(1)}(x,h_0) \tag{2.19}$$

$$\partial_x\phi^{(1)} + qv\sigma\sin(qx) = 0 \tag{2.20}$$

These equations have the following unique solution:

$$E_x^{(1)} = v\sigma q \sin(qx)[2C(qh_0)\cosh(qz) - G(qh_0)e^{-qz}] \tag{2.21}$$

$$E_z^{(1)} = v\sigma q \cos(qx)[-2C(qh_0)\sinh(qz) + G(qh_0)(1 - e^{-qz})] \tag{2.22}$$

$$\phi^{(1)} = v\sigma\cos(qx)[2C(qh_0)\cosh(qz) - G(qh_0)e^{-qz}] \tag{2.23}$$

$$g^{(1)} = B(v\sigma)^3 q \cos(qx)G(qh_0) \tag{2.24}$$

$$\sigma_e^{(1)} = \sigma q \cos(qx)[-2C(qh_0)\sinh(qh_0) + G(qh_0)(1 - e^{-qh_0})] \tag{2.25}$$

In the above expressions we have introduced the dimensionless functions $C(y)$ and $G(y)$, defined by

$$C(y) = \frac{2 + e^y(y - 1)}{2[1 + \cosh(y)e^y(y - 1)]} \tag{2.26}$$

$$G(y) = e^y[2C(y)\cosh(y) - 1] \tag{2.27}$$

For future reference, we note that the functions C and G have the following asymptotic properties:

$$C(y) \approx 3/2y^3, \quad y \to 0$$
$$\approx e^{-y}(1 + (2/y)e^{-y} + ...), \quad y \to \infty \tag{2.28}$$

$$G(y) \approx 3/y^3, \quad y \to 0$$
$$\approx 2/y, \quad y \to \infty \tag{2.29}$$

The above results at first order in ϵ are consistent with the basic physics alluded to in the previous sections. In particular, we find a nonuniform distribution of ends on the free surface that, according to eq 2.25, describes an excess of chain ends at the crests of the brush ($x = 0, 2\pi/q$) and a dearth of ends at the troughs ($x = \pi/q$). Consistent with this is the presence of lateral chain stretching, $E_x^{(1)}$, the sign of which indicates that chains are stretched to transport monomers from the troughs to the crests. A nontrivial Lagrange multiplier field $\phi^{(1)}$ given in eq 2.23 serves to maintain constant monomer density in the layer and $g^{(1)}$ enforces constant degree of polymerization at order ϵ. Also apparent from eqs 2.21–2.25 is the existence of a characteristic penetration depth ξ of the surface perturbation. In cases where $qh_0 \gg 1$, the surface distortion modifies the chain configurations only to depths of order $\xi \sim q^{-1}$ from the free surface. For $qh_0 \ll 1$, however, the perturbation influences configurations throughout the entire height of the brush, $\xi \sim h_0$.

Of particular interest is the free energy per area of the grafting surface, which follows from eq 2.8:

$$\frac{f}{k_BT} = \frac{Bq}{4\pi}\int_0^{2\pi/q}dx\int_0^{h(x)}dz\,(E_x^2 + E_z^2)$$
$$\equiv (f_x + f_z)/(k_BT) \tag{2.30}$$

Here, f_x denotes the contribution from E_x^2 and f_z is the E_z^2

contribution. The transverse component f_x is explicitly $O(\epsilon^2)$ for small ϵ, while $f_z = f^{(0)} + O(\epsilon^2)$, with $f^{(0)}$ given in eq 2.16. All terms odd in ϵ give vanishing contributions to f, as can be argued by invariance under sign inversion of the perturbation.

For the purpose of computing f to $O(\epsilon^2)$ at arbitrary q, it proves necessary to carry out the perturbation theory one additional order, i.e., to obtain $E_z^{(2)}$. Fortunately, however, this can be avoided if we confine our interest to the important case of long-wavelength modes of the brush, $qh_0 \ll 1$. In this regime, $(f_z - f^{(0)})/f^{(0)}$ is of order $(\epsilon/h_0)^2$, while $f_x/f^{(0)}$ is much larger—of order $(\epsilon/h_0)^2(qh_0)^{-2}$. This difference is again due to transverse stretching, which is manifested as a singular contribution of E_x to the free energy per area for $qh_0 \to 0$.

Explicitly, this singular contribution to f is computed by inserting eq 2.21 into eq 2.30, expanding for small qh_0, and performing the integrals with the aid of eqs 2.28 and 2.29. We obtain

$$\frac{f_x}{k_BT} \approx \frac{9\sigma^2 v}{4b^2 h_0}\frac{\epsilon^2}{(qh_0)^2}, \quad qh_0 \ll 1 \tag{2.31}$$

or relative to the flat brush free energy

$$\frac{f_x}{f^{(0)}} \approx \frac{3}{2}\frac{\epsilon^2}{q^2 h_0^4} \tag{2.32}$$

Another means of expressing eq 2.31 makes use of a perturbation calculation for the deformation energy of an *incompressible, isotropic elastic film* of thickness h_0. As described in the appendix, we have computed the free energy associated with distorting such a film according to eq 1.1. In the long-wavelength limit, $qh_0 \ll 1$, the change in free energy per unit area of film can be written as

$$\Delta f \approx \frac{3}{4}\frac{\mu\epsilon^2}{q^2 h_0^3} \tag{2.33}$$

where μ is the shear modulus of the incompressible medium.[11] Comparison of eqs 2.32 and 2.33 yields an explicit expression for the *shear modulus of a melt brush*:

$$\mu_0 = 3k_BT\frac{v\sigma^2}{b^2} \tag{2.34}$$

This same result can be obtained by a simple argument as follows. Suppose we shear a flat brush by imposing a displacement u_x (along x) at the upper surface, producing a uniform shear strain (see eq A.1) $u_{xz} = u_x/(2h_0)$. Each chain, originally with end-to-end separation h_0, is extended to a new length L given by $L^2 = h_0^2 + u_x^2$. The increase in free energy (loss of configurational entropy) per chain is given by $\Delta F_c = 3k_BT(L^2 - h_0^2)/(2b^2N)$ and the corresponding increase in the free energy density is simply $\Delta F_c\sigma/h_0$. By equating this free energy density to $2\mu u_{xz}^2$ (cf. eq A.13), the free energy density of an incompressible elastic film, expression 2.34 is exactly recovered with $\mu = \mu_0$.

If the grafting density σ is determined by the equilibrium conditions for a strongly segregated block copolymer (i.e., the "brush" is a copolymer layer at an air interface),[7] then it follows that μ_0 scales as $k_BT\chi^{1/3}/(vN^{2/3})$. ($\chi$ is the Flory interaction parameter between the monomers of the two dissimilar blocks.) This modulus is generally much smaller than the plateau modulus of a polymer melt, $\mu_\infty \sim k_BT/(vN_e)$, provided that $\chi^{1/3}N^{-2/3} \ll N_e^{-1}$. ($N_e$ is the number of monomers between entanglements.) It is important to note, however, that μ_0 given in eq 2.34 is a *zero-frequency* modulus and reflects the limiting shear modulus after all chains in the brush have had sufficient

time to equilibrate their configurations with the imposed deformation. As will be discussed in more detail below, recent theoretical studies suggest that this equilibration time may be very long for highly entangled chains.[12]

In the limit of short-wavelength deformations, i.e, $1/R_0 \gg q \gg 1/h_0$, f_x and f_z give contributions (Δf) to the brush free energy of comparable order. From eqs 2.30, 2.21 and 2.22, it follows that

$$\frac{\Delta f}{f^{(0)}} = K\left(\frac{\epsilon}{h_0}\right)^2 qh_0, \quad qh_0 \gg 1 \qquad (2.35)$$

where K is an $O(1)$ proportionality constant. (Evaluation of K requires that $E_z^{(2)}$ be calculated; this will prove unnecessary for our purposes, however.) Equation 2.35 indicates the presence of an elastic stabilization of the brush against distortion modes with wavelengths shorter than h_0. Such modes lead to a modification of the lateral and perpendicular chain configurations (described by E_z and E_x) only in a boundary layer of thickness $\xi \sim q^{-1}$ near the free surface. The free energy per area is thus expected to be independent of h_0, as can be seen by rewriting eq 2.35 with use of eq 2.34:

$$\Delta f = \frac{1}{2}\mu_0 K\epsilon^2 q, \quad qh_0 \gg 1 \qquad (2.36)$$

The regime $qh_0 \gg 1$ is also of interest in the context of an incompressible, isotropic elastic film with shear modulus μ. In the appendix we show that such a film when subjected to the same deformation as the brush, has an excess free energy per area of

$$\Delta f = \frac{1}{2}\mu\epsilon^2 q \qquad (2.37)$$

which is identical to eq 2.36 if we make the replacements $K \rightarrow 1$ and $\mu_0 \rightarrow \mu$. Thus, as regards low-amplitude surface perturbations, it is clear that we can think of a melt brush as a thin, incompressible elastic film at all wavevectors $q \ll R_0^{-1}$.

At shorter wavelengths, i.e., $q > R_0^{-1}$, the lateral chain stretching is insufficient to justify the classical method of calculation; other methods are required.[13] Moreover, the increased interfacial energy associated with the deformed free surface becomes relevant and ultimately dominates at large q. For the surface described by eq 1.1, this amounts to a penalty per unit area of

$$\Delta f_i = \frac{1}{4}\gamma(q\epsilon)^2 + O(\epsilon^4) \qquad (2.38)$$

where γ is the interfacial tension of the free surface of the brush (e.g., air/polymer). The total brush free energy per area of grafting surface can thus be written as

$$f_t = f^{(0)} + \gamma + \frac{1}{4}\left(\frac{\epsilon}{h_0}\right)^2\{\gamma(qh_0)^2 + \mu_0 h_0[3(qh_0)^{-2} +$$

$$2qh_0]\} + O(\epsilon^4) \qquad (2.39)$$

where we have approximated the internal brush contribution by the sum of the two asymptotic forms, eqs 2.32 and 2.36 (the latter with $K = 1$; cf. eq 2.37).

It is useful to generalize eq 2.39 to the case of an arbitrary two-dimensional, low-amplitude distortion of the brush height described by $z = h(x,y)$. By invoking equipartition, it follows that the total free energy cost of such a distortion is given by the functional (effective Hamiltonian)

$$F[h] = \frac{1}{2}\int\frac{d^2q}{(2\pi)^2}P(q)\,h(\mathbf{q})\,h(-\mathbf{q}) \qquad (2.40)$$

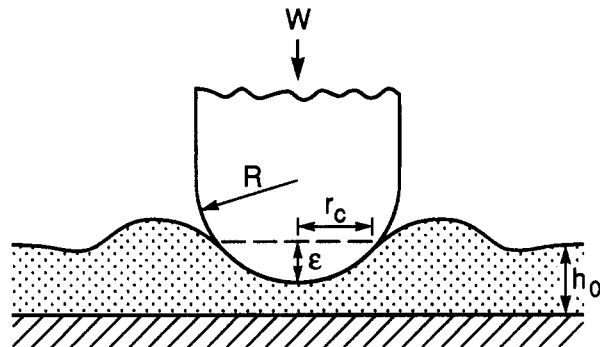where $h(\mathbf{q})$ is the two-dimensional Fourier transform of

Figure 2. Deformation of a molten polymer brush by a spherical tip of radius R. The applied load W is sufficient to deform the brush a center-line displacement of ϵ below its equilibrium height h_0. For $R \gg \epsilon$, the lateral displacement of chains from the center line is $r_c \approx (2\epsilon R)^{1/2}$.

$h(x,y) - h_0$ and $\mathbf{q}$ is the associated wavevector. The susceptibility $P^{-1}(q)$ is given by

$$P(q) = (h_0)^{-2}\{\gamma(qh_0)^2 + \mu_0 h_0[3(qh_0)^{-2} + 2qh_0]\} \qquad (2.41)$$

As will be discussed in section IV, $P^{-1}(q)$ is related to the pair correlation function of height fluctuations at the surface of a brush.

III. Force of a Localized Deformation

Equation 2.40 has a number of useful applications. In the present section we use it to estimate the force required to deform a melt brush with a blunt object, such as the tip of an atomic force microscope (AFM), or with a curved surface, as in measurements with the surface force apparatus (SFA). To illustrate the method, we consider the simple geometry depicted in Figure 2. A spherical tip of radius R is pressed into a molten brush to effect a center-line displacement of ϵ below the equilibrium height h_0. For simplicity, we consider cases where $\epsilon \ll h_0 \ll R$ (weak distortion) and where the lateral displacement of chains $r_c \approx (2\epsilon R)^{1/2}$ exceeds the brush height h_0 (broad tips).

The distorted surface of the brush has cylindrical symmetry; hence, $h(\mathbf{r}) = h(r)$ ($r^2 = x^2 + y^2$). Precise determination of the surface profile $h(r)$ is a difficult free boundary problem that could in principle be solved by the methods of the previous section, or by continuum elasticity theory.[11] For the present purpose of estimating the scaling properties of the force law, however, only the gross features of the profile are required. In particular, we expect that $h(r)$ is an overdamped oscillatory function as sketched in Figure 2, with a characteristic wavelength of order $4r_c$ and a comparable decay length. The two-dimensional Fourier transform of $h(r) - h_0$ is given by

$$h(\mathbf{q}) = h(q) = 2\pi\int_0^\infty dr\, r\, J_0(qr)\,[h(r) - h_0] \qquad (3.1)$$

and must vanish at $q = 0$ due to the assumed incompressibility of the brush. At large q, $h(q)$ also decays due to rapid oscillations of the Bessel function in the integrand. Hence, $h(q)$ is peaked at a value of q that is of order $q_c = \pi/(2r_c)$ and has an integrated strength

$$\frac{1}{2\pi}\int_0^\infty dq\, q\, h(q) = -\epsilon \qquad (3.2)$$

To a first approximation, we can take $h(q)$ to be a Gaussian function centered at q_c, with a variance of order q_c^2 and with an amplitude that satisfies eq 3.2. By using this ansatz in eq 2.40, the free energy of distortion can be

estimated to be of order

$$F \approx (\epsilon r_c)^2 P(q_c) \qquad (3.3)$$

For the assumed case of $q_c h_0 \lesssim 1$ (which is typically met in both AFM and SFM experiments), the second term in eq 2.41 gives the dominant contribution to $P(q_c)$ and we can estimate eq 3.3 as

$$F \approx \frac{12\epsilon^2 r_c{}^4 \mu_0}{\pi^2 h_0{}^3} = \frac{48\epsilon^4 R^2 \mu_0}{\pi^2 h_0{}^3} \qquad (3.4)$$

Note that any modification of the surface energy due to polymer–tip interactions (e.g., van der Waals) should be negligible for $q_c h_0 \lesssim 1$. Finally, the force W required to produce the deformation shown in Figure 2 is given by

$$W = -\frac{dF}{d\epsilon} \approx -\frac{192\epsilon^3 R^2 \mu_0}{\pi^2 h_0{}^3} \qquad (3.5)$$

Equation 3.5 can be used in various ways. In AFM experiments on block copolymer surfaces,[14] for example, one might be interested in calculating the tip penetration depth ϵ for a given tip radius R and normal force W. If this depth were found to be too large, it could be reduced according to eq 3.5 by either increasing the tip radius or decreasing the force. For the case of a diblock copolymer under conditions of complete segregation of the two blocks [the so-called strong segregation limit (SSL) where $\chi N \gg 10$], one can estimate the material-dependent factor $\mu_0/h_0{}^3$ by using eq 2.34 and the SSL estimates[7] for σ and h_0:

$$\frac{\mu_0}{h_0{}^3} \approx \frac{3\sqrt{6}k_B T}{v b^3 \chi^{1/6} N^{8/3}} \qquad (3.6)$$

Hence, for broad tip distortions of a copolymer surface $[h_0/(\epsilon R)^{1/2} \lesssim 1]$ we expect a force given by

$$W \approx -142.0 \frac{k_B T \epsilon^3 R^2}{v b^3 \chi^{1/6} N^{8/3}} \qquad (3.7)$$

It is important to note, however, that this expression is based on the zero-frequency shear modulus given in eq 2.34 and hence is appropriate only for *static* measurements. For high-frequency dynamic force measurements on strongly entangled polymers, eq 3.5 might be better estimated by replacing μ_0 with the plateau modulus μ_∞ (see also section IV). Finally, we should emphasize that the expression 3.7 relies on the anchoring block below the surface being nondeformable, e.g., glassy.

As an example of the application of eq 3.7, we consider a typical diblock copolymer, e.g., styrene/isoprene, at an air interface, with $\chi = 0.1$, $T = 300$ K, $b = v^{1/3} = 5.0$ Å, and isoprene degree of polymerization $N = 500$. For such a system the SSL prediction for the equilibrium height is $h_0 = (b/\sqrt{6})\chi^{1/6} N^{2/3} \approx 87$ Å. A typical normal force in an AFM experiment is 10^{-8} N (e.g., see ref 14); hence, the relationship between the penetration depth ϵ and the tip radius R under such conditions is $\epsilon \approx 6580 R^{-2/3}$ (ϵ and R are in angstroms). For a usual tip of radius $R \sim 500$ Å, this leads to a predicted penetration depth of order 100 Å, i.e., on the order of the layer height! Thus, significantly lower forces must be imposed in AFM experiments if the objective is to leave the brush unperturbed by the tip. (We should note, however, that these estimates are inapplicable to systems where the surface block is below its glass transition at the measurement temperature; such was the case in the experiments of ref 14.) In contrast, SFA experiments typically employ weakly curved surfaces with $R \sim 10^8$ Å. According to the above formula, the

same normal force on our model copolymer system would produce essentially no penetration, $\epsilon \sim 0.01$ Å. It is our hope that the present results may be of some assistance in designing future AFM and SFA experiments on copolymer surfaces.

IV. Surface Modes on a Melt Brush

Another application of the free energy expression 2.40 is to explore the fluctuation spectrum of thermally excited modes on the surface of a melt brush. Due to the elastic film analogy identified in section II.C, it is clear that such modes are properly classified as Rayleigh waves.[11,15,16] Usually, however, Rayleigh waves are analyzed near the surfaces of semiinfinite elastic solids, where the elastic strains associated with the waves penetrate only to depths of order q^{-1}. We have seen in section II.C that such modes have a free energy cost per unit area proportional to q, i.e., diminishing with increasing wavelength. For the present case of a melt brush with characteristic thickness $h_0 \sim 100$ Å, however, the free energy cost of long waves is much larger, scaling as q^{-2} when the penetration depth q^{-1} exceeds the brush height. Thus, we expect a wavelength selection mechanism to be operative, with the preferred wavelength being dictated by a balance of interfacial and elastic energies.

A. Static Fluctuations. The fluctuation spectrum of surface waves can be conveniently studied in various types of radiation scattering experiments, but X-ray and neutron reflectivity[17] measurements are likely to be the most useful for the waves considered here. Such experiments provide access to the equal-time pair correlation function of vertical displacements at the surface of a brush, a thermodynamic quantity that can be obtained from the effective Hamiltonian eq 2.40 without the need to explicitly consider wave dynamics. The two-dimensional Fourier transform of this correlation function, which we shall refer to as the structure factor $S(q)$, is related to $P(q)$ in eq 2.41 by the simple expression

$$S(q) = A^{-1}\langle h(\mathbf{q}) h(-\mathbf{q})\rangle = k_B T/P(q) \qquad (4.1)$$

where A denotes the total area of the grafting surface. The structure factor has a broad peak at a wavenumber q^* that corresponds to the minimum of $P(q)$, indicating that $2\pi/q^*$ is the wavelength of the most probable thermally excited mode of a melt brush. From eq 2.41 it is apparent that this wavelength depends on the value of a dimensionless surface tension, Γ, defined by

$$\Gamma = \gamma/(\mu_0 h_0) \qquad (4.2)$$

In particular, it follows that

$$q^* h_0 = 3^{1/3} \approx 1.44, \quad \Gamma \ll 1 \qquad (4.3)$$

$$q^* h_0 = (3/\Gamma)^{1/4}, \quad \Gamma \gg 1 \qquad (4.4)$$

For the particular case of a strongly segregated block copolymer at an air interface, Γ can be estimated from eq 2.34 as $\Gamma \sim \gamma/\gamma_{AB}$, where $\gamma_{AB} \sim v^{-1} b \chi^{1/2}$ is the interfacial tension of the internal block copolymer interfaces between A and B microdomains.[7,18] Normally this ratio is of order unity or greater, implying that eq 4.4 is applicable. However, if we replace the air with a homopolymer of the surface block, then $\Gamma \sim \gamma/\gamma_{AB} \ll 1$ and it follows from eq 4.3 that q^* is strictly of order $h_0{}^{-1}$.

For the purpose of estimating the characteristic amplitude of the surface waves, we assume $\Gamma \gtrsim 1$ and approximate $P(q)$ by dropping the term proportional to

q in eq 2.41. (Note that eq 4.4 crosses over smoothly to eq 4.3 for $\Gamma \sim 1$.) The mean-squared fluctuation in surface height is thus given by

$$\langle (\delta h)^2 \rangle = \frac{k_B T}{(2\pi)^2} \int d^2 q \, [P(q)]^{-1} = \frac{k_B T}{2\pi \gamma} \ln \, (q_c/q^*) \quad (4.5)$$

where q_c is an ultraviolet cutoff that should scale as the reciprocal monomer size, $q_c \sim b^{-1}$. Since $k_B T/\gamma$ is typically of order b^2 for most air/polymer interfaces and $q_c/q^* \sim 20$, we expect root-mean-square fluctuations in surface height that are of order 10 Å. Of course, much larger amplitude fluctuations could be observed if the air were replaced by a homopolymer melt with the same chemical composition as the brush, thereby dramatically lowering the interfacial tension. Finally, we note that in situations where the fluctuations are large enough to be detected, the unusual peak in $S(q)$ should have a signature in off-specular neutron reflectivity measurements.[17]

B. Fluctuation Dynamics. Although the fluctuation spectrum of *equal-time* correlations is governed only by thermodynamics, the observables in time-resolved scattering measurements are very sensitive to the dynamics of the surface elastic waves. Moreover, we expect that the wave dynamics in a melt brush of very high molecular weight polymers (i.e., entangled) should be quite peculiar due to a large separation in time scales within the brush. One such time scale is determined by the wave frequency ω of the Rayleigh-like surface modes. A second scale is the time τ_r for entanglements in a melt brush to relax. Recent theoretical work by Obukhov and Rubinstein[12] suggests that τ_r is a very large time that grows at least exponentially with N.

To estimate the characteristic wave frequency, we again exploit the elastic film analogy identified in section II and make use of the dispersion relationship[11] appropriate for Rayleigh waves at the surface of an incompressible elastic medium with mass density ρ:

$$\omega \approx (\mu/\rho)^{1/2} q \quad (4.6)$$

(Although this expression is strictly valid only for $q h_0 \gg 1$, we assume that it still provides a reasonable estimate of ω for the wavelengths of primary interest, i.e., $q \sim q^* \sim h_0^{-1}$). Applying eq 4.6 to a melt copolymer brush, we estimate $\mu \sim \mu_0 \sim N^{-2/3}$ from eq 2.34 and $q \sim q^* \sim h_0^{-1} \sim N^{-2/3}$. Thus, a scaling estimate of the characteristic wave frequency is $\omega \sim N^{-1}$. As discussed above, however, τ_r^{-1} is expected to be exponentially small for large N. Hence, we conclude that in many practical circumstances, $\omega \gg \tau_r^{-1}$, and the chain entanglements are unable to relax during the time required for a wave to travel a distance of order $2\pi/q^*$.

An important implication of this conclusion is that a high-frequency shear modulus should be used for the propose of computing the wave speed $c = (\mu/\rho)^{1/2}$, *not* the zero-frequency modulus μ_0 given in eq 2.34. This (larger) high-frequency modulus, μ_∞, is governed by the nature of chain entanglements in the brush and can be roughly approximated by the plateau modulus of the corresponding (ungrafted) homopolymer melt, $\mu_\infty \sim k_B T/v N_e$. Thus, the dispersion relationship for the thermally populated (i.e., $q \sim q^*$) Rayleigh waves on a melt brush of high molecular weight should correspond to $\omega \approx (\mu_\infty/\rho)^{1/2} q$. Of course, for unentangled (Rouse) chains of low molecular weight, eq 4.6 remains applicable with μ replaced by μ_0.

Although μ_∞ determines the wave speed in highly entangled brushes, it is μ_0 that controls the observed fluctuation amplitude, *provided* that experimental intensity measurements are averaged over time intervals that exceed τ_r (or, by the ergodic hypothesis, over sufficiently large areas of an equilibrated brush surface). It is useful to note that a similar situation occurs in supercooled liquids near their glass transition temperature.[19] In such systems there is a huge separation between the time scales of structural rearrangement and molecular vibration (phonons). In spite of this dynamical complexity, the static structure factors of supercooled liquids are very similar to those of normal liquids with Debye relaxation behavior (i.e., no dramatic separation of time scales). For the present case of melt brush dynamics, the elastic waves have fast dynamics and play the role of phonons in the liquid, while the slow disentanglement of chains in the brush is controlled by *entropic barriers*, as in the case of structural relaxation in supercooled liquids.[19] By exploiting this analogy, the static structure factor of the brush (eq 4.1) is expected to be insensitive to the separation of time scales (provided one can average over sufficiently long times or large areas in the laboratory to obtain it) and thus should be the same for entangled as for unentangled chains.

V. Discussion

In the present paper we have seen that a molten polymer brush, such as a surface layer of block copolymer, has the linear deformation properties of an incompressible, continuum elastic film of comparable thickness and shear modulus. However, due to the fact that such layers are macroscopically thin, the deformation energy and fluctuation spectrum of surface modes are dramatically different than at the surface of a semiinfinite elastic body. In particular, we find that surface modes with wavelengths greater than the film thickness are strongly suppressed, as are very short wavelength modes due to the action of surface tension. Hence, a preferred fluctuation wavelength is selected that will typically be on the order of the equilibrium brush height. We are hopeful that these findings will prove useful in the interpretation of neutron and X-ray reflectivity experiments on copolymer surfaces. Our predictions of section III for the force required to locally deform a melt brush may also have some applications to atomic force microscopy and to surface force apparatus measurements.

The most serious deficiency of the present analysis is probably the assumption that all chain ends reach the top surface of the brush, the so-called Alexander–de Gennes approximation. However, it is known from calculations on weakly curved copolymer layers and bulk copolymer melts[7,20] that this generally produces only small numerical errors in the free energy; we expect that the present situation is similar. The simplification that arises from making the Alexander–de Gennes approximation, however, is considerable. We expect that the method of calculation outlined in section II and the elastic film analogy identified there should have applications to a number of other problems, including thermodynamic calculations for bulk copolymers and surface modes on brushes swollen with solvent.

Prost, and J. F. Joanny.

Appendix: Free Energy of a Distorted Elastic Film

In this appendix we outline our calculation of the free energy for an isotropic elastic film deformed according to eq 1.1. We employ the conventional notation of Landau and Lifshitz[11] and refer to the film geometry shown in Figure 1. For ease of presentation, we rename the coordinates (x, z) as (x_1, x_2) and employ the Einstein summation convention for repeated indices. The problem of interest is to compute the strain field u_{ij} in the deformed film shown in Figure 1 and to use this solution to calculate the free energy of deformation. The (linear) strain field is related to the displacement field u_i (defined with reference to the flat film) by the usual relation

$$u_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right) \tag{A.1}$$

and Hooke's law provides the relationship between the stress σ_{ij} and the strain:

$$\sigma_{ik} = K u_{ll}\delta_{ik} + 2\mu\left(u_{ik} - \frac{1}{3}\delta_{ik}u_{ll}\right) \tag{A.2}$$

Here, K and μ are the bulk and shear moduli, respectively, and K can be related to the Lame coefficient λ by the expression $K = \lambda + 2\mu/3$. The strain fields are obtained by solving

$$\partial\sigma_{ik}/\partial x_k = 0 \tag{A.3}$$

subject to no-displacement boundary conditions at the lower surface, $u_i(x_1,0) = 0$, periodic boundary conditions in the x_1 direction, and top surface boundary conditions of no tangential stress and prescribed vertical displacement:

$$[\sigma_{12} + h'(\sigma_{22} - \sigma_{11}) - (h')^2\sigma_{21}]_{x_2=h(x_1)} = 0 \tag{A.4}$$

$$u_2(x_1,h(x_1)) = \epsilon\cos(qx_1) \tag{A.5}$$

In eq A.4 we have used the shorthand notation $h' = dh(x_1)/dx_1 = -\epsilon q\sin(qx_1)$.

As in section II, we seek a perturbative solution of the above equations to first order in ϵ. The boundary condition A.4 reduces in this case to $\sigma_{12}(x_1,h_0) = 0$. At first order in ϵ, the solutions for the displacement field can be written in the form

$$u_1 = \epsilon\Psi_1(x_2)\sin(qx_1) \tag{A.6}$$

$$u_2 = \epsilon\Psi_2(x_2)\cos(qx_1) \tag{A.7}$$

where the $\Psi_i(x_2)$ are given by

$$\Psi_1(x_2) = C_1[\sinh(qx_2) + \beta qx_2\cosh(qx_2)] + C_2 qx_2\sinh(qx_2) \tag{A.8}$$

$$\Psi_2(x_2) = C_2[\beta^{-1}\sinh(qx_2) - qx_2\cosh(qx_2)] - C_1\beta qx_2\sinh(qx_2) \tag{A.9}$$

and

$$\beta \equiv \frac{\lambda + \mu}{\lambda + 3\mu} \tag{A.10}$$

In eqs A.8 and A.9, the coefficients C_i are complicated functions of the dimensionless variables qh_0 and β. Here, we shall only be concerned with the limit of an incompressible medium for which, according to eq A.10, $\beta \to 1$.

In this limit, the expressions for $C_1(qh_0)$ and $C_2(qh_0)$ simplify to

$$C_1(x) = \frac{x\cosh(x)}{x - \sinh(x)\cosh(x)} \tag{A.11}$$

$$C_2(x) = -C_1(x)\frac{[\cosh(x) + x\sinh(x)]}{x\cosh(x)} \tag{A.12}$$

The free energy per unit area in excess of the flat film can be written in the form

$$\Delta f = \frac{q}{2\pi}\int_0^{2\pi/q}dx_1\int_0^{h_0}dx_2\,\mu(u_{11}^2 + u_{22}^2 + 2u_{12}^2) \tag{A.13}$$

where the strain fields u_{ij} are obtained by forming the appropriate derivatives of eqs A.6 and A.7. The integrals in eq A.13 can be carried out analytically with the result

$$\Delta f = \frac{\mu\epsilon^2 q e^{-2\kappa}}{8}\{C_1^2(-1 + e^{4\kappa} + 2\kappa + 2\kappa e^{4\kappa} - 2\kappa^2 + 2\kappa^2 e^{4\kappa}) + C_2^2(-1 + e^{4\kappa} - 2\kappa - 2\kappa e^{4\kappa} - 2\kappa^2 + 2\kappa^2 e^{4\kappa}) + 4C_1C_2\kappa^2(1 + e^{4\kappa})\} \tag{A.14}$$

where we have introduced $\kappa \equiv qh_0$ and used the shorthand notation $C_i \equiv C_i(\kappa)$.

In the long-wavelength limit, $qh_0 = \kappa \ll 1$, this free energy expression reduces to

$$\Delta f = \frac{3\mu\epsilon^2}{4q^2h_0^3} \tag{A.15}$$

which recovers eq 2.33 in the text. In the opposite limit of $qh_0 \gg 1$, eq A.14 reduces to

$$\Delta f = \frac{1}{2}\mu\epsilon^2 q \tag{A.16}$$

which agrees with eq 2.37 in the text. For values of qh_0 intermediate between these limits, eqs A.11, A.12, and A.14 give an explicit crossover formula for the free energy.

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