Cylindrical and Spherical Polymer Brushes: Moduli and Force Laws

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I. Introduction

The elastic moduli of any material are among its most important properties. They are essential in understanding deformational behavior. In this paper we are interested in the moduli of polymer brushes grafted to curved surfaces. While the first study of the modulus for a planar brush has appeared,[1] there have been as yet no studies of the moduli of curved brushes. These exhibit novel features, not present in the planar case. Notably, the elastic properties vary both with space and direction; i.e., the local moduli are inhomogeneous and anisotropic.

Densely grafted polymers stretch away from a grafting surface because of excluded-volume effects, forming a polymer brush.[2,3] The properties of such brushes are important for a number of practical reasons, notably in understanding the properties of microphase separation in diblock copolymers. Such copolymers consist of two different homopolymers joined at one end and form a series of microphases somewhat analogous to those of metals and alloys but on a much larger spatial scale. In particular, they can form lamellae, spherical and cylindrical micellar phases. Here we concentrate on the shear moduli of a melt brush. A melt brush consists entirely of polymer; i.e., there is no solvent, and the melt brush is incompressible to a very good approximation.

The shear moduli are of fundamental importance. They control the surface modes on polymer brushes.[1,4] For cylindrical and spherical micelles they determine the micelle–micelle interaction potential. This potential is analogous to the interatomic potential in ordinary solids. This interaction has up to now been ignored in calculating diblock microphases,[5] and one way of including it is to use the moduli calculated here, along with some results from contact mechanics. The interaction will produce some modifications to the phase diagram for such systems. The interaction also controls the dispersion law for phonon and other wave modes in such systems. In a recent paper Fredrickson et al.[1] used three different methods to calculate the shear modulus μ_p for a planar brush with monomer size b, monomer volume v, and grafting density σ. They find $\mu_p(\sigma) = 3kTb^{-2}v\sigma^2$. A simple calculation[6] shows that polymer brushes are easily deformed and μ_p is about 10^{-6} smaller than that of ordinary solids. Here, our interest is in cylindrical and spherical brushes grafted to a convex surface. These exhibit distinctive elastic properties compared to the planar brush. In particular, the effective grafting density σ varies with the distance from the grafting surface, giving a spatially dependent modulus. As we shall see the cylindrical brush is particularly interesting since it can exhibit very anisotropic elastic properties. A cylindrical or spherical polymer brush is thus interesting as a microscopic composite material with well-defined size and variation of modulus.

II. The Planar Brush Revisited

In the calculation for a planar brush[1] the Alexander–de Gennes approximation[7] was used. In this ansatz the chains all terminate on the exterior of the brush. For the planar brush this should provide a modulus which is correct up to a numerical prefactor. For cylindrical and spherical brushes this approximation is even more correct and is known to be exact[8] in the limit $\rho = R/r_0 \to \infty$, where r_0 and R are the internal and external radii of the brush. The inclusion of an arbitrary end distribution[8,9] would provide small corrections to our results but would not change any of the main conclusions. The basic technique of ref 1 is to apply a given deformation to the surface of a brush and calculate the free energy change. This is then compared to the free energy change of an ordinary elastic medium of modulus μ, undergoing the same surface deformation. Equating the free energies gives the modulus of the brush. In the undistorted planar brush the free energy per chain is $(3/2)kT(h^2/Nb^2)$, where h is the brush height and N the degree of polymerization. By incompressibility, $Nv = h/\sigma$, so the free energy per unit area is $(3/2)kTb^{-2}hv\sigma^2$. Now consider a brush that has its surface monomers displaced horizontally and which thus tilts uniformly through some angle α. The free energy of each chain is proportional to the square of its stretched length, which increases by $\tan^2\alpha$. The change in free energy per unit area for the brush upon shearing is thus $(3/2)kTb^{-2}hv\sigma^2\tan^2\alpha$. The expression for an elastic medium undergoing a similar deformation is $(1/2)\mu h\tan^2\alpha$. This gives μ_p, the central result of ref 1.

III. Cylindrical and Spherical Brushes

We first look at the case of a cylinder, of effectively infinite length L. Here, there are many differences with the planar case. There are two fundamentally different kinds of deformation, with associated moduli μ_θ and μ_z. We use cylindrical coordinates (r, θ, z). μ_θ corresponds to a deformation where there is no variation along the z direction, while μ_z is associated with the opposite case. Because of incompressibility pure deformations along the radical direction are forbidden for cylinders of fixed length. To calculate μ_θ, consider the twist deformation caused by holding the inner cylinder fixed and rotating the ends on the outer cylinder through an angle β (Figure 1). We introduce a local tilt angle $\alpha(r)$ which is the tilt with respect to the local radial direction. In the planar case this tilt had no r dependence, but in a general geometry this will not be true. To calculate the free energy, we divide the brush into infinitesimal concentric cylinders. A cylinder at radius r of thickness δr may be treated as a planar brush as $\delta r/r \to 0$ and hence contributes $(1/2)\mu(r)\,2\pi r\,L\tan^2\alpha(r)\,dr$ to the free energy. To obtain $\mu(r)$, we need the radially dependent effective grafting density $\sigma(r)$. For the undistorted brush, by conservation of chains we have $2\pi r\sigma(r) = 2\pi r_0\sigma_0$, where σ_0 is the grafting density on the inner cylinder. This relation is still valid even for strong distortions, provided they are symmetrical about the axis. The shear modulus thus varies as $\mu(r) = \mu_p r_0^2/r^2$, where $\mu_p \equiv \mu_p(\sigma_0)$ is the modulus of a planar brush of grafting density σ_0. The total free energy of the cylinder is thus $F = L\pi\mu_p r_0^2\int_{r_0}^{R} dr\, r^{-1}\tan^2\alpha(r)$. This free energy is obviously minimized for no distortion, $\alpha(r) = 0$. However, we have imposed an external angular displacement β, so each chain must travel from the central cylinder to the outer cylinder and in so doing rotate through an angle β. We can calculate $\alpha(r)$ by considering the torque acting on the inner and outer radii of an infinitesimal shell. These two torques must be equal and opposite for the shell to remain in equilibrium. The torque on the inner radius is $2\pi rL \times r \times \mu(r)\tan\alpha(r)$ and that on the outer radius $2\pi(r + dr)L \times (r + dr) \times \mu(r + dr)\tan\alpha(r + dr)$. Equating these gives $d[r^2\mu(r)\tan\alpha(r)]/dr = 0$ and hence in this case $\alpha(r)$ is a

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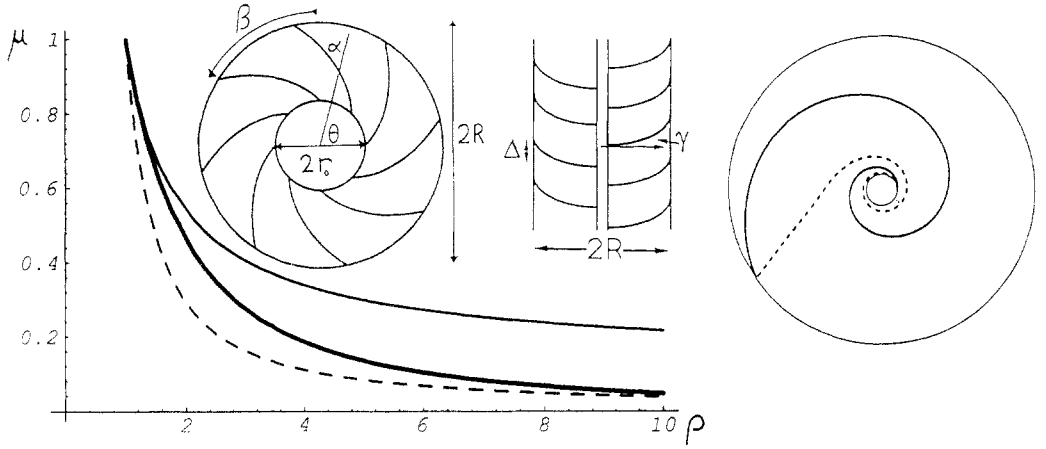

Figure 1. (Left) Plot of the moduli (scaled with respect to the planar modulus) versus $\rho \equiv R/r_0$. Thin line = μ_θ; heavy line = μ_z; dashed line = μ_s. The insets show the coordinate systems used in the cylindrical case: left = twist; right = shear in the z direction. (Right) Plot of the chain trajectories for an extreme twist deformation of a cylinder with $\beta = 10$ and $\rho = 10$. The heavy line is a polymer trajectory. The dashed line is for an ordinary elastic medium. For the latter such large deformations are unrealistic, but for a polymer chain they are certainly possible. Note that at large radii the polymer chain is still bending as much as it is at small radii; i.e., the spiral is equiangular.

constant. The total free energy of the cylinder is $F = \pi L \mu_p r_0^2 \beta^2 (\ln \rho)^{-1}$.

Now consider the same problem for an ordinary elastic medium. In such a material the modulus is constant and the free energy is $F = \pi \mu L \int_{r_0}^{R} dr\ r \tan^2 \alpha(r)$. Torque balance yields $\tan \alpha(r) = 2\beta r_0^2 r^{-2}(1-\rho^{-2})^{-1}$ so that $\tan \alpha(r)$ is no longer a constant. The free energy is then $F = 2\pi \mu L \beta^2 r_0^2 (1-\rho^{-2})^{-1}$. Equating this to the brush free energy gives at once the effective modulus of a cylindrical brush (Figure 1)

$$\mu_\theta = \frac{1}{2}\mu_p (1-\rho^{-2})(\ln \rho)^{-1} \tag{1}$$

First, note that this reduces to the planar result when $\rho \to 1$, i.e., when the brush is very thin. Second, the effective modulus is weaker than in the planar case and grows weaker as $\rho = R/r_0$ increases. Third, the decrease is only logarithmically weak. Thus even for a rather extreme brush $\rho = 100$, the modulus is roughly a tenth of the planar brush modulus. This implies that for many applications use of the planar brush modulus would prove reasonable.

It is of some interest to compute and compare the polymer trajectories in the brush and elastic medium cases. By elementary geometry we have $\tan \alpha(r)\ dr/d\theta = r$. This equation is easily integrated in both cases to yield $r(\theta) = r_0 \rho^{\theta/\beta}$ for the brush and $r(\theta) = r_0(1 - (\theta/\beta)(1-\rho^{-2}))^{-1/2}$ for the elastic medium. Both curves are spirals (Figure 1). The brush trajectory is known as a logarithmic or equiangular spiral. In the elastic medium case most of the curvature or tilt (specified by α) is limited to small radii, where curvature, while being penalized by a free energy penalty, provides large angular displacements, $d\theta = \tan \alpha\ dr/r$. In the brush case, curvature, while inefficient at large radii, costs less free energy there, since $\sigma(r)$ and hence $\mu(r)$ is small. Effectively the brush deforms the most where it is softest.

We now turn to the calculation of μ_z (Figure 1). We again fix the inner cylinder and displace the chain ends at radius R a distance Δ along the z axis. Again the chains undergo some local tilt, $\gamma(r)$, to accomodate this displacement. We have $\Delta = \int_{r_0}^{R} dr \tan \gamma(r)$. The free energy is given by $F = L\pi \mu_p r_0^2 \int_{r_0}^{R} dr\ r^{-1} \tan^2 \gamma(r)$, and a force balance argument gives $d[r\mu(r) \tan \gamma(r)]/dr = 0$. Hence $\tan \gamma(r) = 2r\Delta r_0^{-2}(\rho^2 - 1)^{-1}$, and the free energy is $F = 2\pi L \mu_p \Delta^2 (\rho^2 - 1)^{-1}$. The equivalent elastic medium problem gives $\tan \gamma(r) = \Delta r^{-1}(\ln \rho)^{-1}$ and a free energy of $\pi \mu L \int_{r_0}^{R} dr\ r \tan^2 \gamma(r) = \pi \mu L \Delta^2 (\ln \rho)^{-1}$. Comparing the free energies gives an effective modulus

$$\mu_z = 2\mu_p (\rho^2 - 1)^{-1} \ln \rho \tag{2}$$

As $\rho \to 1$ we have $\mu_z \to \mu_p$, as expected. Note that μ_z is different from the twisting modulus μ_θ; in fact it is always smaller (Figure 1). This is particularly noticeable as $\rho \to \infty$ when $\mu_z \sim \mu_p \rho^{-2}$. For example, at $\rho = 100$ we have $\mu_z \approx 10^{-3}\ \mu_p$.

Again we can find the chain trajectories for this problem. These are found by integrating $dz/dr = \tan \gamma(r)$. For the brush case $z(r) = \Delta((r/r_0)^2 - 1)(\rho^2 - 1)^{-1}$; i.e., the trajectory is parabolic. For the elastic medium we get a logarithmic trajectory $z(r) = \Delta \ln(r/r_0)(\ln \rho)^{-1}$. The effect of varying the modulus is again evident. The brush prefers to wait until large radii before displacing the chains.

We now turn to the spherical case. Here, the difficulty is in imagining a reasonable deformation. We proceed as follows. We freeze the whole sphere, apart from a thin circular wedge around the equator, of width $d\theta$, and radii between r_0 and R. We then twist the chains on the outside of this wedge through an angle β. Torque balance gives $r^3 \mu(r) \tan \gamma(r) = \text{const}$, where $\gamma(r)$ is the local twist angle measured with respect to the radial vector. In this case, since $\sigma \propto r^{-2}$, we have $\mu(r) = \mu_p (r_0/r)^4$ and a free energy of $F = d\theta\ \pi \mu_p r_0^3 \beta^2 (1-\rho)^{-1}$. Comparing this with the ordinary elastic case, we find an effective modulus of

$$\mu_s = \frac{1}{3}\mu_p (1-\rho^{-3})(\rho - 1)^{-1} \tag{3}$$

Note $\mu_s(\rho)$ is always smaller than $\mu_\theta(\rho)$ and is also smaller than $\mu_z(\rho)$ provided $\rho < 15.42$.

IV. Applications and Conclusion

The applications of the moduli (1)–(3) are rather numerous. Here we discuss just two. First, consider two diblock copolymer spherical micelles which are brought into close contact. In a melt of diblock copolymers such micelles are always in contact with their neighbors and have their coronas deformed. Provided the deformation is not too great, we can use μ_s and the standard theory of Hertzian contact[10,11] to estimate the micelle–micelle potential, yielding $U(x) = [(16\sqrt{2})/9]\ \mu_p (1-\rho^{-3})(\rho - 1)^{-1} R^{1/2}(2R - x)^{5/2}$. This is the "interatomic" potential between two spherical micelles with center to center

separation distance x and is analogous both to the corresponding potential in ordinary solids and to the Witten–Pincus law for polymer grafted colloidal particles in good solvents.[12,13] It can be used, for instance, to calculate the modified phase diagram for diblock copolymers caused by micelle–micelle interactions.[5] It complements an earlier "electrostatic" result derived by Semenov[9] for the case of very strong compressions. This potential is subject to at least one caveat. The local moduli for a sphere have a radial variation. We have replaced this by a global modulus and used this modulus to calculate the force. Such a caveat is also applicable to the calculations in ref 1 since the end distribution inside a planar brush implies a spatially varying modulus. Similar results could be obtained for two cylinders, where the potential is orientation dependent. A second application is to the surface modes on cylindrical brushes with large ρ. Qualitatively, we expect the peristaltic mode to be more important in brushes than in ordinary elastic media since $\mu_z \ll \mu_\theta$.

It is important to note the limitations of our results. We have considered the simplest and most fundamental of deformations. These deformations and the deformations in ref 1 would be difficult to achieve in practice. Their importance lies in providing a calculation of the moduli. In general, the measured modulus will be somewhat deformation dependent. This is rather obvious in the case of the cylinder, where μ_z can be very different from μ_θ. However, even for deformations which have no z variation we expect some deformation dependence, particularly at wavelengths much shorter than the radius. This is because the brush is a composite material composed of elements with different moduli and cannot be described exactly in terms of a single modulus. This problem is also present in the case of a planar brush, since the chain end distribution[9] within such a brush implies a variation of σ and hence of μ throughout the brush. Despite this caveat, we expect that the moduli for a planar brush presented previously[1] and for cylindrical and spherical brushes presented here will have a number of interesting fundamental and practical applications.

In conclusion, we have found the long-wavelength moduli for spherical and cylindrical melt polymer brushes. These are always weaker than for a planar brush of the same grafting density, sometimes drastically so, and for the case of a cylinder the elastic properties can be very anisotropic.

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