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Moduli of Polymer Brushes, Contact Mechanics, and Atomic Force Microscope Experiments

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ABSTRACT: We present two new simple derivations of the elastic moduli of planar polymer brushes in the melt regime. We find moduli which are somewhat deformation dependent. We also examine the problem of the penetration of such a brush by the tip of an atomic force microscope for the case of weak deformations.

Introduction

In a recent paper[1] (hereafter referred to as [F]), Fredrickson et al. studied the problem of the surface deformations on a densely grafted "melt" polymer brush. They presented convincing heuristic arguments that the elastic properties of such a brush can be understood in terms of an effective shear modulus

$$\mu_p = \frac{3kT}{b^2} v \sigma^2 \qquad (1)$$

Here b is a monomer length, v is a monomer volume, and σ is the polymer grafting density of the chains. This result is of fundamental importance since it determines the deformational properties of such brushes.[1-3] The result was derived by three separate methods in [F], all of them involving small deformations applied to an equilibrium brush. Our purpose here is 3-fold. We first rederive (1) using two methods different from those of [F]. This allows us to argue that the modulus of a planar brush is, at least weakly, deformation dependent. We then re-examine a problem to which (1) was applied, namely the penetration of a polymer brush by the tip of an atomic force microscope. We limit ourselves to weak tip penetrations and find a result somewhat different from that of the strong penetration regime.[1]

A Simple Derivation of the Modulus

The stretching energy of a uniformly stretched single polymer chain of N monomers, with end-to-end separation H, is[4] $F = (3/2)kTH^2/(Nb^2)$. If we assume the polymer is stretched into a cylinder of crosssectional area A, then by volume conservation, $AH = Nv$ and thus the free energy per unit volume, $F/(AH)$, is $(3/2)kTvb^{-2}A^{-2}$. We now use the fact that for a uniform deformation the modulus is just twice the deformational energy per unit volume[5] to obtain (1). Note this argument is independent of the polymers being part of a brush. The result (1) is a direct consequence of Gaussian elasticity and volume conservation. We can also reverse this argument. Taking the modulus (1) we can say that the energy per unit volume of a brush is $(\mu_p/2)$ and hence the energy per unit area is $3kTb^{-2}\,Hv\sigma^2$—a well-known result.[6,7]

Comparison with Bending Moduli

There exists at least two other calculations of moduli for polymer brushes, that of Leibler[8] and of Milner and Witten[9] of the *bending* moduli of flat polymer brushes in the melt state. For a weakly bent bilayer brush (i.e. one which has no spontaneous curvature) the free energy per unit area can be written

$$F = {}^1/_2 K({R_1}^{-1} + {R_2}^{-1})^2 + \bar{K}{R_1}^{-1}{R_2}^{-1} \qquad (2)$$

where R_1, R_2 are local curvatures and K, $\bar{K}$ are the mean and Gaussian rigidities. The latter are (per monolayer; noting that in ref 9 dimensionless units are used so $3kTvb^{-2} = 1$) $K = {}^3/_{16}\pi^2 kTv^4b^{-2}N^3\sigma^5$ and $\bar{K} = -{}^1/_{20}\pi^2 kTv^4b^{-2}N^3\sigma^5$. This can be compared with a simple mechanics problem, that of the bending of an incompressible thin plate of thickness H and shear modulus μ.[5] In this problem the free energy per unit area is written

$${}^1/_6 \mu H^3[({R_1}^{-1} + {R_2}^{-1})^2 - {R_1}^{-1}{R_2}^{-1}] \qquad (3)$$

Comparing this to (2), we find $K = -\bar{K} = {}^1/_6 \mu H^3$. The first thing to note is that the mean and Gaussian rigidities for the bending plate are equal in magnitude. This is not true for the polymer brush and thus a brush *does not* bend as if it were a simple flat plate of given modulus. It is possible to extract two different shear moduli from this result

$$\mu_1 = {}^9/_8 \pi^2 (kT/b^2) v\sigma^2 \qquad \mu_2 = {}^3/_{10} \pi^2 (kT/b^2) v\sigma^2 \qquad (4)$$

Of course μ_1 and μ_2 have the same scaling structure as (1) and differ only by a prefactor: $\mu_1 = 3.70\mu_p$, $\mu_2 = 0.987\mu_p$, so $\mu_2 < \mu_p < \mu_1$. In fact, one would expect that the results of (4) are better estimates of the modulus than (1) for the following reason. In calculating (1) the Alexander–de Gennes approximation[6,7,10,11] for the chain end distribution was used—i.e. all chain ends were located at the outside edge of the brush. While this gives correct (up to numerical factors) values for many brush properties, it is only an approximation. As shown explicitly by Semenov,[12] the chain ends are distributed throughout the brush. In the derivation of K and $\bar{K}$ [9] the correct chain distribution was used. This creates an effective grafting density $\sigma(z)$, which varies with height, z, above the grafting surface. Thus the modulus (1) of the brush varies with height and a planar brush should be thought of as a microscope composite material made up of layers of different moduli. The modulus gradually decreases toward the outer edge of the brush.

Having said this, even in the Alexander–de Gennes approximation, $K \neq -\bar{K}$.[8] To show this we take an originally flat brush and bend it slightly keeping the grafting density and total grafting area fixed. If we bend

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it into a sphere of radius R, the new free energy per unit area is[12]

$$F_s(\epsilon) = {}^3/_2 kTvb^{-2}\sigma^2 H(1/\epsilon)(1 - (1 + 3\epsilon)^{-1/3}) \qquad (5)$$

and for a cylinder

$$F_s(\epsilon) = {}^3/_2 kTvb^{-2}\sigma^2 H(1/2\epsilon) \ln(1 + 2\epsilon) \qquad (6)$$

where $\epsilon = H/R$. From ref 9 the ratio of the two curvatures is

$$\frac{\bar{K}}{K} = \lim_{\epsilon \to 0} \frac{(F_s(\epsilon) + F_s(-\epsilon) - 2F_s(0))}{2(F_c(\epsilon) + F_c(-\epsilon) - 2F_c(0))} - 2 \qquad (7)$$

This gives $\bar{K}K^{-1} = -{}^1/_4$. Therefore even in the Alexander–de Gennes approximation a melt brush does not always behave like a simple elastic plate.

We thus have some different estimates (eq 4) of the shear modulus of a polymer brush. Unlike in [F] where the moduli were calculated by shear we have used the results obtained by bend. The bending results depend somewhat on the type of bend and thus the effective shear modulus of a polymer brush depends on the deformation involved. We note however that the difference is only in a numerical prefactor. Thus for many applications the variation of the modulus with deformation may prove insignificant.

Application to the AFM

Before proceeding further, we look closely at the case of a lamellar diblock in the strong segregation limit. In the bulk phase the height of the brush formed by one block (of N monomers) of the diblock is[12]

$$H = 2^{2/3}(3/\pi^2)^{1/3}(b/\sqrt{6})N^{2/3}\chi^{1/6} \qquad (8)$$

where χ is the usual Flory parameter describing the interaction between the two blocks. Since $\sigma = H/(Nv)$ the modulus (1) can be written

$$\mu_p = (3/2\pi^2)^{2/3}kTv^{-1}\chi^{1/3}N^{-2/3} \qquad (9)$$

As a typical numerical example, we take the data in [F]: $v^{1/3} = 5 \times 10^{-10}$ m, $\chi = 0.1$, $T = 300$ K, and $N = 500$. This gives a Young's modulus ($=3\mu_p$) of $E \approx 10^5$ N m^{-2}. This modulus is very small compared to that of ordinary solids; in particular, metals have $E \approx 10^{11}$ N m^{-2}. Moreover the modulus gets weaker as the degree of polymerization is increased.

The applications of the modulus (1) are rather numerous. In particular the authors of [F] apply it to the problem of an atomic force microscope (AFM) tip impinging on a planar brush. This is a problem of some practical importance, since AFMs are often used to study the properties of such diblock copolymer lamellae. The AFM tip is modeled as a solid sphere of radius R, and the interest is mainly in the force f needed to push the sphere into the brush a given distance ϵ. In [F] it is claimed that this problem is too difficult to solve exactly, and the authors obtain the following approximate result:

$$f_1 = (192/\pi^2)\mu_p\epsilon^3R^2H^{-3} \qquad (10)$$

This is valid in the regime of strong penetrations, $\epsilon > H^2/R$. In AFM experiments one usually interested in perturbing the system as little as possible. It is thus of some interest to look at the case of weak penetrations $\epsilon < H^2/R$. To do this we use an approach totally different from that of [F]. Since we know the modulus of the brush (eq 1), the problem becomes one of an infinitely hard sphere pushing against a plane of modulus μ_p. This is a well-known Hertzian contact problem, and the answer for the force can be written down at once:[5,13]

$$f_2 = {}^{16}/_3\mu_p\epsilon^{3/2}R^{1/2} \qquad (11)$$

The two expressions (10) and (11) are very different; in particular, the force versus displacement dependence is much weaker in (11). It should be possible to test the $^3/_2$ power in (11) experimentally. This would indirectly also test the idea that a brush can be treated as an elastic medium. The authors of [F] give a numerical example of an AFM tip with $R = 500 \times 10^{-10}$ m and a tip force 10^{-8} N penetrating into the same polymer mentioned above. They find a penetration of 10^{-8} m, which is of the order of the brush height. The tip thus penetrates through the brush. The same problem is present using (11); in fact the penetration, $\approx 10^{-7}$ m, is even worse. Of course both (10) and (11) break down well before such large penetrations. Both (11) and (10) show that the force on an AFM tip should be very weak to avoid disturbing the brush. In fact, (11) provides a more accurate estimate of the relevant force since AFM tips should perturb the system as little as possible. (11) is the result for a sphere penetrating a semi-infinite half-space. In the case of a brush on a *solid* substrate it ceases to be valid whenever the stresses caused by the tip penetrate down to the substrate. The penetration depth is of the order of the contact width $a = (\epsilon/R)^{1/2}$, and thus $a < H$ gives $\epsilon < H^2/R$. The condition $\epsilon = H^2/R$ defines where (11) becomes inaccurate and one must use (10). For the specific example considered above this means $\epsilon < 2.4 \times 10^{-9}$ m, i.e. only about 5 monomers. Since H^2 increases with chain length like $N^{4/3}$, this will be less of a problem with long chains, but it should be born in mind when dealing with very short polymers. In AFM experiments one is usually interested in penetrating as little as possible, in which case (11) will provide a reasonable estimate of the likely penetration for a given force.

Conclusion and the Effect of Surface Tension

The two expressions for tip penetration, (10) and (11), provide a complete description of both penetration regimes. The first equation was derived assuming strong penetration, $\epsilon > H^2/R$, while the second result assumes weak penetration $\epsilon < H^2/R$. The two results thus complement each other and are valid in different regimes. As expected, when $\epsilon \approx H^2/R$, they give the same result $\sim\mu_pH^3/R$ (up to a numerical prefactor). Since we have argued that the modulus is somewhat deformation dependent, even (10) and (11) may need to be corrected.

In our derivation of the weak penetration force we have ignored surface tension effects. While this is reasonable for the strong penetration regime considered earlier in [F], it can be a bad approximation for our case.[14] The correction made by surface tension is given by a standard result[13]

$$(f - f_2)^2 = 64\pi\gamma\mu_p(\epsilon R)^{3/2} \qquad (12)$$

where f_2 is given by (11). Here $\gamma = \gamma_{pa} + \gamma_{ba} - \gamma_{pb}$, where the γ's are surface tensions and p = probe, b = brush, and a = air. We assume here that $\gamma > 0$ so that the brush wets the probe. The force can be written in dimensionless form

$$f(16\mu_pR^2/3)^{-1} = x^{3/2}[1 \pm x^{-3/4}\sqrt{9\pi\gamma/16\mu_pR}] \qquad (13)$$

where $x \equiv \epsilon/R$. Surface tension introduces hysteresis into the system,[13] so there are now two possible forces associated with a given displacement. For surface tension effects to be negligible we require $x^{-3/4}(9\pi\gamma/16\mu_p R)^{1/2}$ to be small compared to unity. This implies the displacement satisfies $\epsilon > \gamma^{2/3}R^{1/3}\mu_p{}^{-2/3}$. Since we also require $\epsilon < H^2/R$, we must have $\gamma < kT\beta^5 N^{1/2} R^{-2}$. Here we have written $H = \beta N^{1/2}$ where $\beta > 1$ is a "stretching factor", which must be greater than unity for a strongly-stretched brush, and can be at least as high as 5 for practical systems. In general $\gamma < kT/a^2$ so we require $(R/a)^2 < \beta^5\sqrt{N}$. For brushes with high β or large degree of polymerization this condition can be readily satisfied. There are thus in general three regimes. For very weak penetration $\epsilon < \gamma^{2/3}R^{1/3}\mu_p{}^{-2/3}$ surface tension effects are dominant. For $\gamma^{2/3}R^{1/3}\mu_p{}^{-2/3} < \epsilon < H^2/R$ we have weak penetration with perturbations caused by surface tension. For $\epsilon > H^2/R$ there is the strong penetration regime of [F].

If a brush can be treated as an elastic medium with an effective modulus μ, then contact mechanics[13] is the natural way to treat problems of brush–brush and brush–solid interactions. The fact that the modulus is deformation dependent implies that such calculations will never be exact. Nevertheless, for planar brushes the deformation dependence is encouragingly weak, so the concept of *the* modulus of a brush is a reasonable one.

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References and Notes

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