Surface Waves on Polymer Brushes

Hao-Wen Xi and Scott T. Milner*

Exxon Research and Engineering Company, Annandale, New Jersey 08801

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ABSTRACT: We present a simple analytical method to study the deformation behavior of a grafted melt polymer brush. We calculate the change in the free energy associated with (1) small-amplitude deformations of the free surface, (2) nonuniformity in the areal density of grafted chains, and (3) deformations of the grafting surface. We obtain the same results as Fredrickson et al.[4] for long-wavelength surface modes of melt brushes if we make their approximation that all the chain free ends reside at the surface. Our method can be applied to a wide range of problems, such as the deformation of cylindrical or spherical micelles.

Many theoretical and experimental studies on the equilibrium properties of grafted polymer layers in the molten state, known commonly as melt polymer brushes, have been undertaken in recent years.[1] Early models of the equilibrium structure of melt polymer brushes assumed the chains to be uniformly stretched away from the grafting surface, while more recent self-consistent-field (SCF) studies[2,3] yield the nonuniform chain stretching and corresponding parabolic hydrostatic pressure profile without a *priori* assumption. The agreement between scaling theory, self-consistent-field theory, computer simulation and experiments suggests that the basic physics governing the equilibrium properties of polymer brushes is well understood.

Fewer studies have been concerned with deformation behavior of polymer brushes.[4−6] In this paper, we present a simple method to study the behavior of deformed polymer brushes. Our approach is a generalization of the "wedge" methods developed for computing free energies of block copolymer microphases with realistic-shaped unit cells.[9] In this paper, we take the wedges, which describe the local geometry of some "bundle" of chains grafted on a given small patch of grafting surface, to have curved shapes, which are determined by minimizing the stretching free energy. The resulting analytical calculations are quite straightforward for the cases we consider here: (1) small-amplitude surface waves of arbitrary wavelength on a grafted layer; (2) melt brushes with weakly modulated grafting density; and (3) melt brushes attached to weakly corrugated grafting surfaces. The methods we present here can easily be generalized to solvated brushes, and can also serve as the basis for numerical calculations to treat deformations of brushes beyond linear response. As a result, our present approach may be useful for many problems in strongly-stretched block copolymer mesophases.

I. Surface Waves

We first consider surface waves on polymer brushes, assembled from polymers of N monomers per chain, grafted to a flat surface at a density of σ chains per unit area. As shown in Figure 1, the brush is subjected to a sinusoidal displacement of its free surface about the equilibrium layer height h_0 according to

$$h(x) = h_0[1 + \epsilon \cos(qx)] \tag{1}$$

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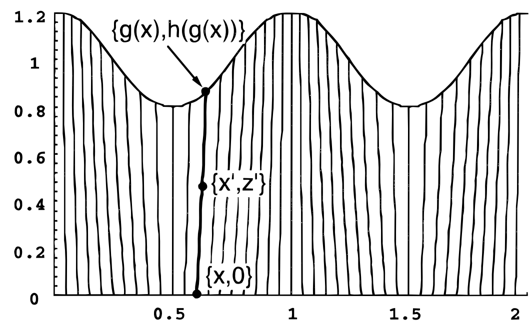

Figure 1. Chain paths in a polymer brush with a surface wave, $h(x) = h_0(1 + \epsilon \cos(qx))$ [amplitude shown $\epsilon = 0.2$]. Vertical scale in units of equilibrium height h_0; horizontal scale in units of wavelength $2\pi/q$.

where $\epsilon \ll 1$ is the small surface modulation amplitude, and $\lambda = 2\pi/q$ is the characteristic wavelength of the deformation at the free surface.

The coordinate system used throughout the paper is $\mathbf{r} = (x',z')$ as shown in Figure 1. The coordinates x' and z' vary over the range $0 \le x' \le 2\pi/q$ and $0 \le z'/h(g) \le 1$. Consider a path (x',z') which starts on the grafting surface at point $(x,0)$ and ends at the upper surface $(q(x),h(g))$ and x' and z' (see Figure 1) related as

$$x' - x = [g(x) - x]f\left(\frac{z'}{h(g)}\right) \tag{2}$$

The chain trajectories in the deformed brush are assumed (see below) to a lie along a set of nonintersecting curvilinear paths extending from the grafting surface to the upper surface. The function $f(y)$: $(0,1) \rightarrow (0,1)$ gives the relative displacement in the x-direction of these paths as a function of height, while $g(x)$ and $h(g)$ give the x- and z-coordinates of the endpoint of the path that begins at $(x,0)$. We impose periodic boundary conditions at $x = 0$ and $x = 2\pi/q$, and assume translational invariance in the third direction.

Our analytical method to determine the conformation and free energy of the deformed chain is based upon two assumptions. First, we assume as described above that the trajectories of chains in the brush do not cross, i.e., that all chains passing through a given point have the same tangent; the trajectories are thus assumed to lie along a set of nonintersecting curvlinear paths. The chain free ends, however, may be at any location along these paths. In an undeformed brush, the paths are straight, and we recover the SCF description of the

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brush. In a deformed brush with an imposed long-wavelength ripple on the upper surface, the paths will be curved.

This first assumption does not result in the lowest free energy state of a deformed brush, as it can be shown that individual chains in the brush are not in equilibrium configurations; the sum of chain tension and osmotic forces on individual monomers do not balance. However, if we consider the entire "bundle" of chains passing through any small region of space, the sum of forces on all the monomers in this small volume can be shown to cancel. Thus the chain trajectories we calculate give the lowest free energy state subject to the imposed constraint that the chain paths do not cross.

With this assumption, a relation exists expressing the fact that a fixed numbe of monomers are contained in all the chains attached to a small length Δx of grafting surface. We can express this "local mass conservation" as

$$N\sigma\Delta x = \int_0^{h(g)} \Delta x'(z')\, \mathrm{d}z', \qquad \Delta x'/\Delta x = \partial x'/\partial x \quad (3)$$

where the melt density has been taken to be unity. The cross-sectional area $\Delta x'$ at point (x',z') along the trajectory and cross-sectional area Δx at the grafting surface $(x,0)$ are related by applying the chain rule to eq 2:

$$\Delta x' = \Delta x[1 + (g'(x) - 1)f(z'/h) - (g(x) - x)f'(z'/h)\,(z'/h(g)^2)h'(g)g'(x)] \quad (4)$$

Our second assumption is that some chain free ends can be found at all distances along the curvilinear path. As in the flat brush case, this has the consequence that the monomer chemical potential V (which in a melt brush is just the hydrostatic pressure) is a parabolic function of the arc length. For the outwardly curved portions of the brush there are in principle "dead zones", in which no chain free ends are located sufficiently close to the grafting surface. However, for a long-wavelength surface wave the brush is very weakly curved, so the dead zones would be extremely thin. Also, it has been shown that even for curvature radii comparable to the brush height, the effect of dead zones on the free energy per chain is very small.[7]

Hence it is an excellent approximation to write the self-consistent potential as a quadratic function of the arc length along the curvilinear path:

$$V(x',z') = B\,[s^2(g,h(g)) - s^2(x',z')] \quad (5)$$

Here $s(g,h(g))$ and $s(x',z')$ are the arc length along the chain trajectory starting from the point $(x,0)$ at the grafting surface and terminating at $(g,h(g))$ and (x',z'), respectively. The coefficient B is still given by the equal-time requirement on the chain conformation, i.e. $B = 3\pi^2/8N^2$.

We use the "mass conservation" relation eq 3 together with the relation between the chain paths and the differential cross-section eq 4 to write a relation between the functions $h(g)$ and $g(x)$,

$$N\sigma = h_0 = h(g) + (g'(x) - 1)h(g)C_1 + (g(x) - x)h'(g)g'(x)(C_1 - 1) \quad (6)$$

where $h_0 = N\sigma$ is the equilibrium flat brush height, and we have defined $C_1 \equiv \int_0^1 \mathrm{d}y\, f(y)$.

We solve eq 6 for the unknown function $g(x)$, with $h(g)$ given by eq 1, perturbatively in ϵ. We expand $g(x)$ as

$$g(x) = x + \epsilon g_1(x) + \epsilon^2 g_2(x) + ... \quad (7)$$

and likewise expand $h(x)$,

$$h(g) = h_0\,[1 + \epsilon\cos(qg)] = h_0\,[1 + \epsilon\cos(qx) - \epsilon^2 g_1(x) q \sin(qx) + ...] \quad (8)$$

Substituting these expressions into eq 6, we obtain

$$g_1(x) = -\frac{\sin(qx)}{qC_1} \quad (9)$$

$$g_2(x) = \frac{\sin(2qx)}{2qC_1} \quad (10)$$

The sign of g_1 indicates that the chains are stretching to transport the monomers from the "valleys" of the surface wave toward the "peaks", in order to satisfy mass conservation.

The free energy of the deformed brush is calculated by the method of summing the work to construct the brush.[3] The chains are added one by one to the brush, and the free energy to add each chain is summed. It can be shown that the free energy increment to add a chain to the brush is independent of where the free end of the new chain is placed. There are chains with their free ends at the grafting surface, for which the free energy increment is purely due to the potential $V(0)$ at the grafting surface. As each "curvilinear wedge" of brush volume is filled with chains, the arc length of that wedge grows according to mass conservation. The corresponding value of $V(0)$ is simply $Bs^2(z')$, where z' is the z-coordinate of the top of the growing wedge. Hence we may write the free energy per unit area as

$$F = \lambda^{-1}\int_0^{\lambda} \mathrm{d}x \int_0^{h} \mathrm{d}z'\; NBs^2(z')\,\frac{\mathrm{d}\sigma'}{\mathrm{d}z'} \quad (11)$$

To compute the free energy F, we need the relation between the height z' and partial coverage σ' of the growing wedge. This relation is a differential form of the mass conservation relation:

$$N\,\frac{\mathrm{d}\sigma'}{\mathrm{d}z'} = \frac{\Delta x'}{\Delta x} \quad (12)$$

Likewise, we require the arclength $s(x',z')$ starting from the point $(x,0)$ to the point (x',z'), which is simply

$$s(x',z') = \int_0^{z'} [1 + (\mathrm{d}x''/\mathrm{d}z'')^2]^{1/2}\, \mathrm{d}z'' \quad (13)$$

From eq 2 for the chain paths one easily finds the gradient at point (x',z') as

$$\frac{\mathrm{d}x'}{\mathrm{d}z'} = \left(\frac{g - x}{h(g)}\right) f'(y) \quad (14)$$

The arc length s to order ϵ^2 for chains grafted at the point $(x,0)$ is thus:

$$s^2(x',z') = z'^{\,2} + z'h(g)\left(\frac{g - x}{h}\right)^2 \int_0^{z'/h(g)} \mathrm{d}y\,[f'(y)]^2 \quad (15)$$

The free energy of the deformed brush can then be calculated by using eq 15 and eq 4 in eq 11. After a short calculation, we find the free energy per unit area of the deformed brush as a function of the chain-path function $f(y)$:

$$\frac{F\{f(y)\}}{F_0} = 1 + \frac{3\epsilon^2}{2}\left(1 + \frac{C_2}{(qh_0)^2 C_1^{\,2}}\right) \quad (16)$$

where $F_0 \equiv Bh_0^3/3$ is the free energy per unit area of the undeformed brush, and we have defined $C_2 \equiv (1/2)\int_0^1 dy\,(1 - y^2)\,[f'(y)]^2$.

We now determine the optimum chain-path function $f(y)$ by minimizing the free energy of the deformed brush with respect to $f(y)$, subject to the requirements that $f(0) = 0$ and $f(1) = 1$. We find

$$f(y) = \frac{\log(1+y)}{\log 2},$$
$$\frac{3C_2}{2C_1^{\,2}} = [4(2\log 2 - 1)^2]^{-1} \approx 1.675 \quad (17)$$

Thus we find that the energy for long-wavelength surface waves on a melt brush has the same form as found by Fredrickson *et al.* (who assumed that the chain free ends all reside at the top surface), with a slightly different coefficient (1.675 *versus* 1.5). The $(qh_0)^{-2}$ dependence is a consequence of the grafting; material must be translated a distance of order a wavelength, so the grafted chains must stretch increasingly far as $q \to 0$, as pointed out in ref 4. The corresponding chain paths for a deformation of amplitude $\epsilon = 0.2$ are shown in Figure 1. Since the chain path function $f(y)$ is independent of q, this picture can be scaled horizontally to any desired wavelength. Our results are not limited to $q \to 0$, and may be applied for qh_0 of order unity, breaking down only when $qh_0 \gg 1$.

II. Modulated Coverage

For our second example, we consider a melt polymer brush with a modulated grafting density,

$$\sigma(x) = \sigma_0(1 + \epsilon\cos(qx)) \quad (18)$$

The top surface of the brush will modulate in response, with an amplitude that will vary with qh_0. For long-wavelength coverage modulations, the brush height will perfectly track the coverage variation, $h(x) = N\sigma(x)$, because of the large penalty for transverse stretching. But for larger values of qh_0 (shorter wavelength modulations), the brush surface will become flatter as the chains stretch sideways more easily than vertically.

We write a variational form for the height of the brush,

$$h(x) = h_0(1 + \beta(qh_0)\epsilon\cos(qx)) \quad (19)$$

with the coefficient $\beta(hq_0)$ to be determined by minimizing the free energy. Replacing σ by $\sigma(x)$ in the relation eq 6 between the functions $h(g)$ and $g(x)$ and expanding $g(x)$ and $h(g(x))$ as in eqs 7 and 8, we obtain

$$g_1(x) = \frac{(1 - \beta(qh_0))\sin(qx)}{qC_1} \quad (20)$$

$$g_2(x) = \frac{-\beta(qh_0)(1 - \beta(qh_0))\sin(2qx)}{2qC_1} \quad (21)$$

We expect $\beta(qh_0)$ to approach unity from below in the limit of long wavelengths, so that $g_1 = g_2 = 0$ and the chain paths become vertical. For finite wavenumber, we expect $0 < \beta < 1$, which for $g_1(x)$ corresponds to chain paths bending out of the high-coverage regions.

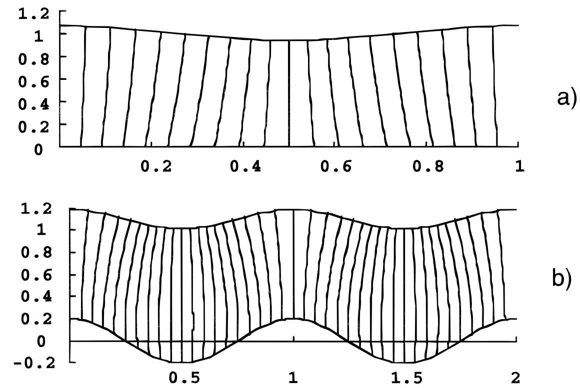

Figure 2. (a) Chain paths in a polymer brush with a modulation of the coverage, $\sigma(x) = \sigma_0(1 + \epsilon\cos(qx))$ [amplitude $\epsilon = 0.2$, wavenumber $qh_0 = \pi/2$]. (b) A polymer brush with a modulated grafting surface, $z(x) = \epsilon\cos(qx)$ [amplitude $\epsilon = 0.2$, wavenumber $qh_0 = \pi/2$].

We evaluate the free energy as before, using eq 11 expanded to second order in ϵ. After some arithmetic we obtain,

$$\frac{F\{f(y)\}}{F_0} = 1 + \frac{3\epsilon^2}{2}\left(\beta^2 + \frac{(1-\beta)^2 C_2}{(qh_0)^2 C_1^{\,2}}\right) \quad (22)$$

where C_1 and C_2 are defined as before in terms of integrals over the chain-path function $f(y)$.

We minimize this expression with respect to the coefficient β and the function $f(y)$. Evidently, since $f(y)$ appears in the same combination C_2/C_1^2 as before, the chain-path function is once again given by eq 17; the value of β is

$$\beta(qh_0) = 1/(1 + (qh_0)^2 C_1^{\,2}/C_2) \approx 1/(1 + 0.895(qh_0)^2) \quad (23)$$

As anticipated, β approaches unity in the long-wavelength limit, and zero in the short-wavelength limit. Note that we have not included the effect of a surface tension γ on the top of the brush, but it is straightforward to do so, as this would simply add a term of the form $\gamma/(2F_0)\epsilon^2\beta^2$ to eq 22.

The corresponding chain paths for the values $\epsilon = 0.2$, $qh_0 = \pi/2$ are shown in Figure 2a. Note that the surface wave amplitude is considerably smaller than 20% (as it would be if the height tracked the coverage perfectly), and the chains deviate sideways to avoid stretching vertically. We remark also that since $\beta(qh_0)$ gives the linear response of the brush surface to the coverage inhomogeneity, an arbitrary (nonperiodic) coverage inhomogeneity $\delta\sigma(x)$ of small amplitude with Fourier transform $\delta\sigma(q)$ gives rise to a height variation

$$h(x) = h_0 + \int d^2q\,\beta(qh_0)\delta\sigma(q)e^{iq\cdot x} \quad (24)$$

III. Corrugated Grafting Surface

Our third example is a melt brush with a modulated grafting surface, and immobile grafted chains at constant coverage. The grafting surface is located at

$$z(x) = h_0\epsilon\cos(qx) \quad (25)$$

The chain paths are now written (compare to eq 2) as

$$x' - x = [g(x) - x]f\left(\frac{z' - z(x)}{h(g) - z(x)}\right) \quad (26)$$

so that the topmost point of a bundle of chain paths grafted at $(x,z(x))$ is still located at $(g(x),h(g(x)))$.

The coverage, which we take to be constant in the sense that each small area of grafting surface has the same number of chains attached, is not constant in the x-coordinate because the grafting surface is modulated. We have to second order in ϵ

$$\sigma(x) = \sigma_0(1 + (1/2)\epsilon^2(qh_0)^2[\sin(qx)]^2) \qquad (27)$$

We take a variational form similar to eq 19 for the surface wave on the top of the brush, except now the average brush height increases to second order in ϵ because the average coverage along x has increased due to the modulation (see eq 27):

$$h(x) = (1 + \beta(qh_0)\epsilon\cos(qx) + (qh_0)^2\epsilon^2/4) \qquad (28)$$

The "mass conservation" relation is now

$$N\sigma(x)\Delta x = \int_{z(x)}^{h(g)} \Delta x'(z')\, dz', \qquad \Delta x'/\Delta x = \partial x'/\partial x \quad (29)$$

Using the new expression for chain paths eq 26 to compare $\partial x'/\partial x$ (compare eq 4), the modulated grafting surface eq 25, the modulated surface eq 28, and the expansion eq 7 for $g(x)$, we find one again the results eqs 20 and 21 for $g_1(x)$ and $g_2(x)$.

Once again, we compute the free energy of the brush with modulated grafting surface by the now-familiar eq 11, expanded to second order in ϵ. We obtain (after a bit more arithmetic)

$$\frac{F\{f(y)\}}{F_x} = 1 + \frac{3\epsilon^2}{2}\left((1-\beta)^2 + \frac{(1-\beta)^2 C_2}{(qh_0)^2 C_1^{\,2}} - \frac{2(1-\beta)C_4}{C_1} + \frac{(qh_0)^2}{3}\right) \qquad (30)$$

where we have defined $C_4 \equiv \int_0^1 dy\, yf(y)$, and $F_x \equiv F_0(1 + \epsilon^2(qh_0)^2/4)$. Note that we want to compare the average free energy per unit x-length $\lambda^{-1}\int_0^\lambda F\, dx$ not with F_0 (the equilibrium free energy per unit grafting surface area), but instead with F_x, because there is a factor of $(1 + \epsilon^2(qh_0)^2/4)$ more grafting surface per x-length due to the modulation.

Minimizing first over $1 - \beta$ gives

$$1 - \beta(qh_0) = C_4C_1(qh_0)^2/(C_2 + (qh_0)^2C_1^{\,2}) \qquad (31)$$

which when substituted into eq 30 gives

$$\frac{F\{f(y)\}}{F_x} = 1 + \frac{3\epsilon^2}{2}\left(\frac{-C_4^{\,2}(qh_0)^2}{C_2 + (qh_0)^2C_1^{\,2}} + \frac{(qh_0)^2}{3}\right) \qquad (32)$$

Minimizing this expression with respect to the chain-path function $f(y)$ gives a result that now depends on qh_0,

$$f(y;qh_0) = y + 2(qh_0)^2C_1(qh_0)(y\log 2 - \log(1+y)) \qquad (33)$$

with the integral $C_1(qh_0)$ given by

$$C_1(qh_0) = [2 + (qh_0)^2(6\log 2 - 4)]^{-1} \qquad (34)$$

Finally we obtain explicit expressions for $\beta(qh_0)$ and the free energy,

$$1 - \beta(qh_0) = \frac{(qh_0)^2}{2 + (qh_0)^2(8\log 2 - 4)}$$

$$\frac{F\{f(y)\}}{F_x} = 1 + \frac{3\epsilon^2(qh_0)^4}{8(1 + (qh_0)^2(4\log 2 - 2))} \qquad (35)$$

We recover in the long-wavelength limit the result for the mean bending stiffness of a melt brush[8] and find at finite wavenumber a softening of the dispersion relation for modulations of the grafting surface. Our dispersion relation remains well-defined (positive) for all q. This contrasts with results derived for melt brushes with the additional approximation that all the free ends reside at the surface, for which various instabilities to free-surface or grafting-surface modulation are found.[5,6]

The corresponding chain paths for grafting-surface modulation, for the values $\epsilon = 0.2$, $qh_0 = \pi$, are shown in Figure 2b. Note again that the surface wave amplitude is smaller than 20% (as it would be if the height tracked the grafting surface perfectly), and the chains deviate sideways to avoid stretching vertically. Again, since $\beta(qh_0)$ gives the linear response of the brush surface to the grafting-surface modulation, an arbitrary grafting surface modulation of small amplitude with Fourier transform $z(q)$ give srise to a height variation which is the sum of the responses to each Fourier component separately (as in eq 24).

As one final check of our methods, we now make the approximation of chain free ends confined to the upper surface, in order to compare to the results of Fredrickson et al.[4] The free energy in this case takes the form

$$F = \lambda^{-1}\int_0^\lambda dx \int_0^h dz' \frac{3}{2}\left(\frac{ds}{dn}\right)^2 = \lambda^{-1}\int_0^\lambda dx \int_0^h dz' \frac{3}{2}\left(\frac{dz'}{dn}\right)^2\left(1 + \left(\frac{dx'}{dz'}\right)^2\right) \qquad (36)$$

Here ds/dn is the local stretching of chains passing through the point (x',z'). With all the chain ends confined to the surface, there is only one chain path for each grafting site, and the "mass conservation" relation takes the simple form

$$\Delta x'\, dz' = \Delta x\sigma\, dn \qquad (37)$$

(to be compared to eq 3).

Using eq 37, eq 4 relating $\Delta x'$ and Δx, and eq 14 for the chain-path slope in eq 36 for the free energy, we find after a short calculation

$$\frac{F\{f(y)\}}{F_0} = 1 + \frac{3\epsilon^2}{2}\left(\frac{1}{C_1} + \frac{\int_0^1 dy\,[f(y)]^2}{C_1^{\,2}} + \frac{\int_0^1 dy\,[f'(y)]^2}{3(h_0q)^2C_1^{\,2}}\right) \qquad (38)$$

where now $F\{f(y)\}$ and $F_0 = (3/2)h_0\sigma^2$ are the deformed and undeformed free energies per unit area of this "step-function" brush, i.e., under the assumption that all free ends reside at the surface. Note that with this assumption, the undeformed free energy is a factor of $12/\pi^2$ larger than for the case of free ends everywhere.[2,3]

For simplicity, we only retain the term of order $\epsilon^2/(hq_0)^2$, which is dominant in the long-wavelength limit. (Finding the optimum chain-path function $f(y)$ for the full functional of eq 38 turns out to be more difficult than when the ends are not restricted to the free surface.) Minimizing $\int_0^1 dy\,[f'(y)]^2/C_1^{\,2}$ with respect to the trajectory $f(y)$, we find,

$$f(y) = 2y - y^2, \qquad \frac{F}{F_0} \approx 1 + \frac{3\epsilon^2}{2(qh_0)^2} \tag{39}$$

Thus we obtain the same result for the chain trajectory and the free energy associated with the long-wavelength modes as ref 4 under the constraint that the chain free ends all reside at the upper surface.

Summary

We have presented a new approach to study the deformation behavior of strongly-stretched polymer brushes, which relies on the approximation that the chain paths are locally parallel (i.e., chain paths do not cross). Our method provides a simple analytical calculation of both the chain conformations and the free energy associated with small-amplitude surface modes, variations in the grafting density, and undulations of the grafting surface. Though the examples in this paper have been limited to brushes in the melt state, the method can be easily extended to consider deformations of solvated brushes. Our method yields the same results as Fredrickson et al.[4] if we make their additional approximation, that all chain free ends reside at the top of the brush. Our method, which is an extension of the "wedge" calculations of refs 9 and 10 to curvilinear bundles of chains, can be applied to brush deformations in many different geometries, such as deformation of spherical and cylindrical micelles. We close by noting that except for grafting surfaces of high symmetry (spheres, cylinders, planes), different grafted chain paths do cross in general. How to relax the assumption that chains do not cross, and the nature of the errors this assumption brings, are subjects for future study.

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