

# Anomalous height increases upon bending for an Alexander–de Gennes polymer brush

E. M. Sevick

*Institute of Advanced Studies, Research School of Chemistry, The Australian National University, Canberra, Australia*

D. R. M. Williams

*Institute of Advanced Studies, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australia*

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We examine the bending of an Alexander–de Gennes polymer brush over a wide range of curvature from weak to strong. Two different models are used, a blob model and a simpler Flory mean field model. In both cases the height change upon bending is anomalous. In the case of a blob model the height increases for weak bending. In the Flory model there is no height change to first order in the curvature. This is in sharp contrast to more sophisticated theories for brushes with free ends, and may have applications to real-life Alexander–de Gennes brushes which have been synthesized recently. © 1996 American Institute of Physics. [S0021-9606(96)50441-1]

## I. INTRODUCTION

A polymer brush is a system of polymers densely end-grafted onto a surface.<sup>1,2</sup> Such brushes are important in a number of applications, most notably surface modification and colloidal stabilization,<sup>3</sup> and occur ubiquitously in the ordered phases of block copolymers.<sup>4,5</sup> The equilibrium structure and attendant properties of these brushes is now very well understood, particularly for brushes grafted onto planar surfaces.<sup>6,4,7–13</sup> Brushes grafted onto curved surfaces have also been investigated<sup>14–19</sup> as they are important in strongly asymmetric block copolymer systems and for chains grafted onto rough surfaces. Other examples of curved brushes include polymers grafted to the interior pores of membranes or to the exterior surface of colloidal particles and hairy-rod polymers or molecular bottlebrushes. In this paper we calculate the effect of bending upon two model polymer brushes. We show that for these brushes the bending behavior is anomalous and that in the more sophisticated blob model swelling takes place.

One of the most fundamental and easily measured properties of a polymer brush is its height. In colloidal stabilization applications, the brush height determines the hydrodynamic radii of the brush-coated particles and increases the range of repulsive interactions between two particles, thereby reducing colloidal aggregation. In a good solvent the brush height is determined by a balance of the osmotic pressure of the monomers, which favors large heights, and the entropic stretching of the polymer chains, which favors small heights. Intuitively one expects that a brush grafted onto a convex surface will have a smaller height than one grafted to a planar surface with the same grafting density. One can understand this by considering that the local accessible volume per chain segment increases from root to brush tip, reducing the local stretching of the chain near the tip, and hence reducing the size of the convex-grafted brush below that of an equivalent planar brush. Indeed theory confirms this idea;<sup>14–16,21</sup> scaling predictions demonstrate a decrease in height with an

increase in grafting surface convexity. For weakly curved surfaces, detailed self-consistent field calculations also show a small decrease in height.

In general there are two theoretical approximations which can be used to model polymer brushes in good solvents. The one which has proven very popular in recent years is to use self-consistent field theory (SCF).<sup>7,8</sup> This uses a local osmotic pressure which is determined from the local polymer concentration. SCF theory provides detailed information about the internal structure of the brush, namely the distribution of monomers and chain ends throughout the brush body<sup>4</sup> as well as the height of the brush; however, it suffers from being complex and difficult to use in all but the simplest geometries. For more complex geometries,<sup>14,15,22–24</sup> for problems involving fluid flows or other non-equilibrium effects<sup>9–13,18,24,25,19,20</sup> and for problems which have not been tackled previously, it is more usual to use an earlier and simpler kind of approach. This second theoretical approximation,<sup>6</sup> the Alexander–de Gennes ansatz, ignores the detailed structure of the brush and assumes that all the chain ends are located at the brush edge. The Alexander–de Gennes approach has the definite advantage of simplicity and usually gives correct answers for “bulk” brush properties such as the brush height and brush modulus. However, as we will show, for our model brushes it produces highly anomalous results for a weakly bent brush, predicting that a brush expands when bent slightly onto the outside of a cylinder or sphere. That the Alexander–de Gennes ansatz predicts a height-convexity relation far different from intuition and SCF calculations is surprising and is contrary to the usual reliance on the ansatz for first-order results.

Although it was first introduced and exploited as a theoretical ansatz, an Alexander–de Gennes brush has been realized in practice<sup>27</sup> using water-soluble polymers with graftable stickers at one end and lipid molecules at the other end. The stickers end-graft the chain forming the root of the brush and the lipids self-assemble into a flat membrane at the edge

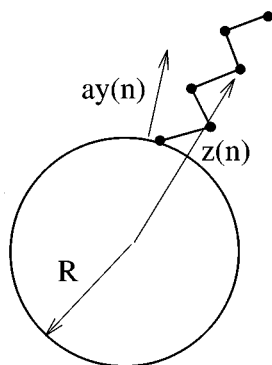


FIG. 1. The geometry used for the calculation for a bent brush.

of the brush, effectively trapping all the chain ends there. This experimentally realized brush should closely adhere to the Alexander–de Gennes model. However, our calculation described here ignores the lipid contribution to the free energy and thus cannot be directly applied to that system. In general such sticky-end brushes show novel phase behavior including lateral inhomogeneities. Here we wish to concentrate on the implications of the Alexander–de Gennes ansatz and we will not discuss sticky brushes any further.

In this note we will discuss two kinds of theories for an Alexander–de Gennes brush grafted to the outside of a curved surface. The first is a free-energy blob model, which is a modification of that used in the planar case by Rabin, Alexander and Barrat.<sup>9,10</sup> The second is a simpler Flory model. In the following section we present the model calculations for the blob model in detail for the case of weak bending for cylindrical and spherical brushes. The intermediate and strongly convex cases are presented in section 3. The dependence of the Alexander–de Gennes brush height upon curvature is also predicted from a simpler Flory model and the results are described in section 4. In the last section, we note the importance of these results in comparison with more sophisticated theories.

## II. WEAK BENDING

We consider first a blob model of the free energy for chains grafted to the outside or convex surface of a cylinder of radius  $R$  (Fig. 1). Each chain is comprised of  $N$  monomers, each monomer having radius  $a$ . None of our conclusions depend on numerical prefactors which we thus ignore; our conclusions are however sensitive to the exponents. The first monomer of each chain is grafted with grafting density (number of chains per unit area of grafting surface)  $\sigma$ . We let  $r(n)$  be the radial position of the  $n$ th monomer measured from the center of the cylinder. The first, tethered monomer is at  $r(1) = R$  and the final, free end of the monomer is at the brush tip,  $r(N) = R + H$ , where  $H$  is the height measured from root to tip of the brush. A flat brush results when the ratio of brush height to cylinder radius is zero,  $H/R \rightarrow 0$ , and weakly-bent brushes correspond to  $H/R \ll 1$ .

In the blob model, the structure of the chain is modeled as a sequence or necklace of blobs.<sup>28,29,9,10</sup> The size of a blob

located at  $r$ ,  $\xi(r)$ , depends upon the local stretching,  $dr/dn$ , according to

$$\xi(r) = a^{5/2} (dn/dr)^{3/2}. \quad (1)$$

The number of blobs along the contour of the chain between  $r$  and  $r + dr$  is  $dn_b = dr/\xi(r)$ . From this structural description, the stretching and excluded volume contributions to the free energy can be constructed. The stretching free energy per chain is then given by the prescription of  $kT$  per blob

$$F_{\text{stretch}} = kT \int_R^{R+H} dr \xi^{-1}(r) = kT a^{-5/2} \int_R^{R+H} dr \left( \frac{dr}{dn} \right)^{3/2}. \quad (2)$$

Each blob acts like a hard sphere of radius  $\xi$  and consequently, we may write the excluded volume energy per unit volume as  $kT \xi^3 c^2$ , where  $c$  is the concentration of blobs. In a length  $L$  of the cylinder there are  $N_c = 2\pi RL\sigma$  chains and in a radial volume element of size  $dV = 2\pi r L dr$  there are  $dr/\xi(r)$  blobs per grafted chain. Hence, the local concentration of blobs is  $c = \sigma R r^{-1} \xi^{-1}$  and the excluded volume energy per chain is

$$F_{ev} = kT \sigma R \int_R^{R+H} dr \xi r^{-1} \\ = kT \sigma R a^{5/2} \int_R^{R+H} dr r^{-1} \left( \frac{dr}{dn} \right)^{-3/2}. \quad (3)$$

The total free energy per chain is then

$$F/kT = \int_0^N dn \left( \frac{dz}{dn} \right)^{5/2} + u \mathcal{R} z^{-1} \left( \frac{dz}{dn} \right)^{-1/2}, \quad (4)$$

where we have defined  $u \equiv \sigma a^2$ ,  $\mathcal{R} \equiv R/a$  and  $z \equiv r/a$  and have changed the integration variable to  $n$  via  $dr = (dr/dn) dn$ .

We now require the trajectory of the chain,  $r(n)$ ,  $1 < n < N$ , which minimizes the total free energy. This equilibrium trajectory is one for which any small deviation from the trajectory  $z(n) \rightarrow z(n) + \delta(n)$  gives zero change in the free energy to order  $\delta$ . The first order change for such a perturbation is

$$\Delta F/kT = \int_0^N dn \left( -u \mathcal{R} z^{-2} z'^{-1/2} \delta + \frac{5}{2} z'^{3/2} \delta' - \frac{1}{2} u \mathcal{R} z^{-1} z'^{-3/2} \delta' \right), \quad (5)$$

where the prime means  $(d/dn)$ . The above equation can be simplified by noting that the two terms in  $\delta'$  may be integrated by parts

$$\Delta F/kT = - \int_0^N dn \delta \left( u \mathcal{R} z^{-2} z'^{-1/2} + \frac{d}{dn} \left[ \frac{5}{2} z'^{3/2} - \frac{1}{2} u \mathcal{R} z^{-1} z'^{-3/2} \right] \right), \quad (6)$$

where the two boundary terms vanish due to the boundary conditions  $z(0) = R/a$  and  $z'^{3/2}(N) = \mathcal{R} u / (5z(N))$ . The first

boundary condition arises from the fact that the chain end is tethered to the cylinder of radius  $R$ . The second represents a balance between the spring force,  $\frac{5}{2}z'^{3/2}$ , and the osmotic force,  $\frac{1}{2}u\mathcal{R}z^{-1}z'^{-3/2}$  for the final, free monomer. The condition  $\Delta F=0$  for any  $\delta(n)$  applied to (6) yields a differential equation for the equilibrium trajectory

$$\mathcal{R}uz^{-2}z'^{-1/2} + \frac{d}{dn} \left[ \frac{5}{2}z'^{3/2} - \frac{1}{2}u\mathcal{R}z^{-1}z'^{-3/2} \right] = 0. \quad (7)$$

It is convenient to recast this equation with a change variables from  $z(n)$  to  $y(n)$  via  $y(n) \equiv z(n) - \mathcal{R}$ , where  $y(n)$  is the chain trajectory, expressed as a dimensionless radial distance between a monomer and the grafting surface

$$\mathcal{R}u(y + \mathcal{R})^{-2}y'^{-1/2} + \frac{d}{dn} \left[ \frac{5}{2}y'^{3/2} - \frac{1}{2}u\mathcal{R}(y + \mathcal{R})^{-1}y'^{-3/2} \right] = 0. \quad (8)$$

The chain trajectory described by Equation (8) is valid for any curvature. We are interested here in weak curvatures so we expand the solution in powers of  $h \equiv H_0/R$ , where  $H_0$  is the height of the unbent brush. Writing  $y(n) = y_0(n) + y_1(n) + O(h^2)$ , where  $y_0(n)$  is of order  $h^0$  and  $y_1(n)$  is of order  $h^1$ , and collecting the terms of different orders, yields an equation for weakly bent, convex brushes

$$\frac{d}{dn} \left[ \frac{5}{2}y_0'^{3/2} - \frac{1}{2}uy_0'^{-3/2} \right] + \frac{d}{dn} \left[ \frac{15}{4}y_0'^{1/2}y_1' + \frac{3}{4}uy_0'^{-5/2}y_1' + \frac{1}{2}u\mathcal{R}^{-1}y_0y_0'^{-3/2} \right] + u\mathcal{R}^{-1}y_0'^{-1/2} = 0 \quad (9)$$

with boundary conditions  $y_0(0) + y_1(0) = 0$  and  $y_0'^3 - (u/5) + 3y_0'^2y_1' + (u/5)\mathcal{R}^{-1}y_0 = 0$  at  $n=N$ . This equation can be easily solved for the flat brush: up to order  $\mathcal{R}^0$  the solution is  $y_0$  is a constant. Thus the flat brush is uniformly stretched. This constant is found from the boundary condition  $y_0' = (u/5)^{1/3}$ , and thus the solution for the flat brush is  $y_0(n) = n(u/5)^{1/3}$ . The height of the flat brush in dimensional units is then  $H_0 = Na(\sigma a^2/5)^{1/3}$ . This has the correct scaling form expected from Ref. 15.

The zero curvature solution can then be used in (9) to solve for the correction due to curvature. This correction is given by the equation  $y_1'' = -\mathcal{R}^{-1}(u/5)^{2/3}$ , subject to the boundary conditions  $y_1(0) = 0$  and  $y_1'(N) = -(1/3)(N/\mathcal{R}) \times (u/5)^{2/3}$ . The solution is

$$y_1(n) = \left( \frac{u}{5} \right)^{2/3} \frac{N^2}{\mathcal{R}} \left( \frac{2}{3} \frac{n}{N} - \frac{1}{2} \left( \frac{n}{N} \right)^2 \right). \quad (10)$$

Of most interest is the change in height upon bending,  $\Delta H = ay_1(N)$ . This is

$$\Delta H = \left( \frac{u}{5} \right)^{2/3} \frac{N^2}{6R} = \frac{1}{6R} H_0^2 \quad (11)$$

indicating that the brush swells upon bending. This agrees well with a direct numerical minimization of the free energy (4) (Fig. 2). It is interesting to compare this blob prediction of brush swelling with curvature with the prediction of brush

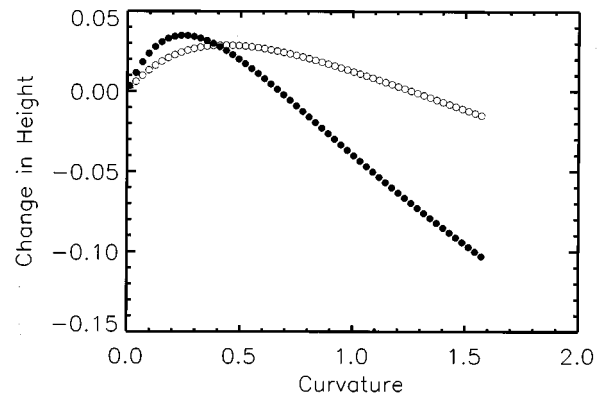


FIG. 2. The change in height  $\Delta H/H_0$  plotted against the curvature  $H_0/R$  for a brush grafted to the outside of a cylindrical brush (open circles) and a spherical brush (filled circles). The results were found by a direct numerical minimization of the free energy (4) using a blob model. Note that in each case the height initially increases upon bending. The increase is however a maximum of a few percent.

shrinkage that is predicted by the SCF theory,<sup>21</sup>  $\Delta H = -\frac{1}{8} H_0^2/R$ . The blob result has the same magnitude (to within a numerical prefactor) as that predicted by the SCF theory, but it is of the opposite sign.

Although the swelling of a brush obeying the Alexander–de Gennes ansatz is both anomalous and surprising it is not totally unexpected and can be “explained” as follows. We examine the volume available to a single chain in its trajectory from the grafting surface to the brush tip. This volume controls the osmotic pressure term in the free energy, i.e., the more the volume that is available the smaller the osmotic pressure (for a given number of monomers). For a planar brush this volume increases linearly with distance from the grafting surface. This implies that the volume available per unit distance along the trajectory is a constant. Consequently, no place in the brush is more favorable as a monomer position than another and a planar brush is uniformly stretched. For a chain grafted to the outside of a cylinder the volume available to the chain increases more rapidly than linearly, i.e., as  $r^2$  where  $r$  is the distance from the centre of the cylinder. The usual argument is that shrinkage will occur with bending as this additional available volume reduces the excluded volume interactions (which promote swelling). However, this argument is inverted in the case of an Alexander–de Gennes brush. An Alexander–de Gennes brush expands with convex curvature because at greater distances from the grafting surface the volume available is significantly larger and by stretching into this volume the osmotic pressure can be reduced. This of course costs some stretching energy, but overall expansion is favorable with energies described as in the blob model. The effect discussed here is clearly related to the undulational instability of an Alexander–de Gennes brush discussed by Solis and Pickett.<sup>30</sup> They found that a melt brush grafted uniformly to a planar surface is unstable to undulations of the surface formed by the free ends. The swelling effect discussed here almost certainly implies a similar instability exists for a

brush in a good solvent. Thus a planar Alexander–de Gennes brush can lower its energy by forming small hemispherical caps on the surface of the planar brush, where some of the chains splay out at the brush surface.

It is possible to extend the above analysis to the case of bending the brush onto the outside (convex surface) of a sphere of radius  $R$ . In that case the free energy per chain is

$$F/kT = \int_0^N dn \left( \frac{dz}{dn} \right)^{5/2} + u \mathcal{R}^2 z^{-2} \left( \frac{dz}{dn} \right)^{-1/2} \quad (12)$$

with boundary conditions  $z(0) = \mathcal{R}$  and  $z'^3(N) = u \mathcal{R}^2 / (5z^2(N))$ . Again the height of the brush increases upon bending (Fig. 2), by an amount

$$\Delta H = \frac{1}{3R} H_0^2. \quad (13)$$

### III. INTERMEDIATE AND STRONG CURVATURES

In the above section we have discussed the weak bending of a brush when  $H_0 \ll R$ . In the strong bending limit  $H_0 \gg R$  the differential Equation (9) can be analyzed using a scaling approach. In this limit we replace  $(d/dn)$  by  $1/N$  and  $z$  by  $H$ . This gives a result for the height of  $H \sim (\sigma a^2)^{1/4} (R/a)^{1/4} N^{3/4}$ . Thus in the strong bending limit we obtain a height which decreases at smaller bend radii and which agrees with previous scaling theories.<sup>15,14</sup> In the strong bending limit the height decreases with increasing curvature, as one would expect. In the intermediate case when  $H_0 \approx R$  we numerically minimize the free energies (4) and (12) (Fig. 2). This yields one important piece of information, i.e., that the magnitude of the height increase is at most a few percent of the planar brush height.

### IV. FLORY MODEL

In the above we have used a blob model for the free energy. There is an even more primitive model which is based on a simple Flory theory.<sup>6,1,29</sup> In this case the stretching energy per chain is that expected for a simple Gaussian model, and the excluded volume energy per unit volume is  $kT a^3 c^2$  where  $c$  is the concentration of monomers. In the Flory model the free energy per chain is

$$F/kT = \int_0^N dn \left( \frac{dz}{dn} \right)^2 + u \mathcal{R}^\alpha z^{-\alpha} \left( \frac{dz}{dn} \right)^{-1}, \quad (14)$$

where  $\alpha = 1$  for cylinders and  $\alpha = 2$  for spheres. The boundary conditions are  $z(0) = \mathcal{R}$  and  $z'^3(N) = \frac{1}{2} u \mathcal{R}^\alpha z^{-\alpha}(N)$ . In this case the solution for the perturbation caused by curvature is

$$y_1(n) = \frac{\alpha}{3aR} H_0^2 \left( \frac{n}{N} - \left( \frac{n}{N} \right)^2 \right). \quad (15)$$

Thus since  $y(N) = 0$  there is no change in height to first order in the curvature. Again, the results using the Alexander–de Gennes ansatz are anomalous. However, a nu-

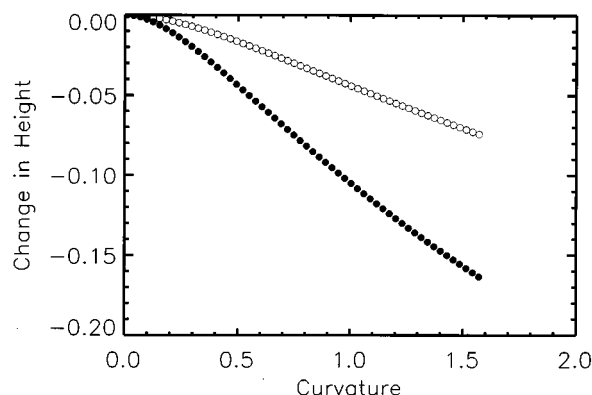


FIG. 3. The same graph as Fig. 2, but for the Flory model. Note that in this case the brush height always decreases upon bending, but that the decrease is very small for weak bending indicating that the coefficient of the first order term is zero.

merical minimization of the free energy (Fig. 3) shows that higher order terms in the curvature always produce a decrease in height upon bending.

### V. CONCLUSION

In this note we have discussed the weak convex, bending of polymer brushes in good solvents. In particular we have given the results for the case when the Alexander–de Gennes ansatz is used, i.e., all the chain ends are located at the far edge of the brush. Four separate cases have been considered. First a blob model for both cylinders and spheres, and then a Flory model for the same geometry. In the former cases to order  $H_0/R$  the brush expands, whilst in the latter cases there is no change in the brush height to that order. In all cases the behavior is anomalous since one expects, and more sophisticated theories confirm, that the brush should shrink. Thus although in general the Alexander–de Gennes ansatz provides reasonable results for many brush properties, here in combination with two model free energies, it gets either the sign of the effect wrong, or fails to predict any effect at all. However, as noted above, systems which do behave as Alexander–de Gennes brushes have been manufactured and may well exhibit the anomalous behavior described here.

In this paper we have calculated the bending behavior of polymer brushes for two different free energy models and for two different geometries using the Alexander–de Gennes ansatz. Our calculations have shown anomalous height changes as a function of curvature. These calculations do not show that the Alexander–de Gennes ansatz always fails, but rather that it fails for the two most commonly used free energy models. Ultimately it remains a useful approximation for many brush properties but must be treated with caution if detailed brush properties are to be examined. For such detailed properties the more sophisticated SCF theories are needed. These allow for a distribution of chain ends within the brush and more freedom in selecting the chain stretching profile. These theories lead to a more physically reasonable brush shrinkage upon curvature.

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