Hydrodynamic Penetration into Parabolic Brushes

S. T. MILNER

Exxon Research and Engineering,
Annandale, New Jersey 08801

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A polymer "brush" is formed when long-chain molecules are attached by some means to an impenetrable surface at moderately high grafting density and exposed to a solvent. The polymer chains stretch away from the surface to avoid unfavorable monomer–monomer contacts; they sacrifice configurational entropy ("stretching free energy") to do so.

Such a brush may be formed either at a solid–liquid interface or at a liquid–liquid interface, with polymers either chemically bonded to a substrate or adsorbed to a solid or liquid surface. Brushes may be used to stabilize colloidal particles against aggregation or to change wetting or lubrication properties of surfaces.

Mean-field scaling arguments[1] show that the height h of such a brush scales as $N\sigma^{1/3}$, with N being the molecular weight and σ the coverage (chains per unit area). Thus, for large molecules and moderately high attachment density, chains in a brush are extended far beyond their dimensions in free solution, as R_g scales only as $N^{1/2}$.[2]

In light of this strong stretching of chains in a brush, self-consistent-field treatments of brushes in the strong-stretching limit have been employed[3,4] to compute the structure of the chains in the brush. In the limit of long chains, analytic results have been obtained for the density of monomers and of chain free ends, as well as other properties of the chain configurations. A central result is that, for moderate grafting densities (avoiding monomer volume fractions ϕ approaching unity), the monomer density is *parabolic.*

Many gross features of brushes are somewhat insensitive to the details of the parabolic structure. The scaling of the SCF results is entirely consistent with the arguments of ref 1, which may be said to assume a "step-function" brush in which all chains are uniformly stretched from the grafting surface to the outer extremity of the brush. Hence, any property that depends mostly on scaling properties of the brush, such as the mean brush height (defined by the first moment of the monomer density), will be qualitatively described by the step-function brush.

Because the parabolic density profile vanishes linearly at the outer brush extremity, one might expect properties that depend in detail on the monomer density in the "fringe" of the brush to be sensitive to the parabolic structure. (The step-function brush density rises abruptly from zero, while at the outer edge the parabolic density has slope $-2\phi_0/h$.) One such property already explored is the force required to compress a brush; it was shown[3] that the force required to compress a brush vertically a small amount δh is $\delta h/h$ times smaller for the parabolic brush than for the step-function ansatz.

Another striking physical property of brushes that is strongly affected by the parabolic profile is the hydrodynamic penetration length l_p. Consider a simple shear flow in a region alongside a brush. If the monomer density profile were a step function, one would expect that the hydrodynamic penetration length would be essentially the "mesh size" ξ of a semidilute polymer solution of the same concentration: $l_p = \xi = a/\phi$, with a being a coefficient of the order of the monomer size.[5,6] However, if the brush has a parabolic profile, the hydrodynamic penetration length varies from place to place in the brush and diverges at the outer extremity. We may anticipate that the flow will penetrate *much farther* than e.g., the correlation length at the grafting surface ξ_0 (where the density is highest and ξ smallest).

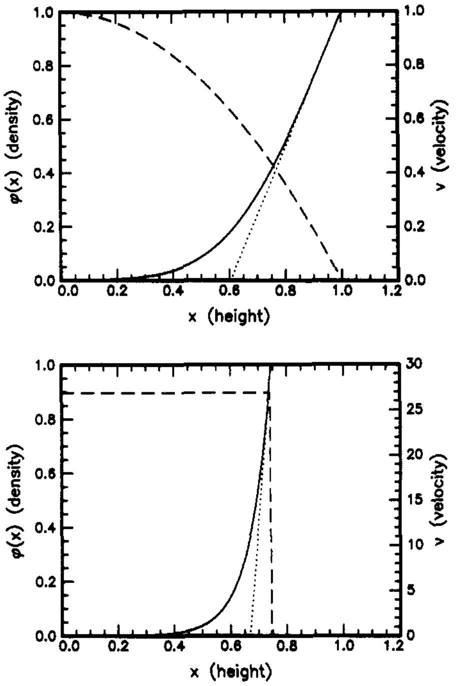

Figure 1. Penetration of the velocity field (solid line) in a simple shear flow adjacent to a surface to which a polymer brush has been attached. (The monomer density is the dashed curve.) The velocity profile outside the brush extrapolates to zero at the penetration depth (dotted curve). a, top, illustrates the parabolic brush and b, bottom, the corresponding step-function ansatz. Here $h/\xi_0 = 30$.

To answer this question quantitatively, we suppose that the brush structure is undistorted by the flow. We consider a parabolic density profile as in ref 3; we compare below to results for a "comparable" step-function brush, i.e., one made of identical chains at the same coverage but in which chains ends are attached to a phantom surface. With the density profile a known function, and screening length $\xi(\phi) = a/\phi$ as above, we invoke the Brinkman equation[7] for flow in a porous medium:

$$0 = \eta\nabla^2\vec{v} - \frac{\eta}{\xi^2(\phi)}\vec{v} - \vec{\nabla}p \tag{1}$$

We define x to be the distance into the brush from the point at which the density vanishes and z the distance from the grafting surface; the parabolic profile $\phi(z) = \phi_0(h^2 - z^2)$ for small $x = h - z$ is $\phi(x) \approx 2\phi_0 x/h$. We anticipate that although the flow of solvent will penetrate much farther than ξ_0 into the parabolic brush, it will penetrate much less than the entire brush height h; thus, approximating the monomer density profile by a wedge is appropriate.

In the present case of a simple shear flow, the pressure is constant; in terms of the above definitions, we have for the transverse component of velocity

$$\frac{\partial^2 v}{\partial x^2} = \frac{4}{{\xi_0}^2}\left(\frac{x}{h}\right)^2 v \tag{2}$$

Rescaling lengths according to $x^2 = y^2\xi_0 h/2$, we arrive at $v'' = y^2 v$. This equation may be transformed to a modified Bessel equation, with solution

$$v(y) \propto y^{1/2}K_{1/4}(y^2/2) \tag{3}$$

At small y, $v(y)$ is proportional to $1 - 0.68y$; at large y, $v(y)$ decays as a Gaussian $0.69 \exp(-y^2/2)$. Note that the functional form of the decaying velocity field deep in the brush is not exponential; because the mesh size ξ is increasingly smaller deep in the brush, a more rapid decay results.

The hydrodynamic penetration depth l_p is the apparent location within the brush of a no-slip boundary, as observed from far outside the brush. That is, it is the point at which the velocity field would vanish based on the velocity gradient outside the brush:

$$l_p = v(0)\left(\frac{\partial v}{\partial x}(0)\right)^{-1} \tag{4}$$

For the parabolic brush, we find $l_p = 1.04(h\xi_0)^{1/2}$, proportional to the geometric mean[8] of the brush height and smallest mesh size. This justifies our assumption that only the linear behavior of the profile near the outer extremity is important in the calculation. We note that, near the brush extremity, the mesh size is varying rapidly in space; $\xi^{-1}\, \partial\xi/\partial x$ diverges at $x = 0$ and is of the order of unity for $x \sim l_p$. The Brinkman equation may be incomplete for a rapidly varying ξ; however, the term depending on ξ in eq 1 is unimportant when ξ is large, so our results should be reliable.

Because the ratio h/ξ_0 is typically large in brushes, l_p is a factor $(h/\xi_0)^{1/2} \gg 1$ larger than the smallest mesh size ξ_0. Using results from ref 3 for the brush height $h = (12\sigma w/\pi^2)^{1/3}N$ and the density at the grafting surface $\phi_0 = \pi^2h^2/(8N^2w)$, we find $l_p/\xi_0 = 1.27(N\sigma a^2)^{1/2}$. (Here w is the excluded volume parameter.)

We may compare to an "equivalent" step-function brush, in which the free ends of a formerly parabolic brush are attached to a phantom surface. The distance from the phantom surface to the grafting surface is then adjusted to minimize the brush free energy. This leads[3] to a brush height h_s equal to $0.74h$ and a uniform monomer density ϕ_s equal to $0.90\phi_0$.

The step-function brush has constant mesh size ξ_s, equal to a/ϕ_s; this leads to a simple Brinkman equation $v'' = \xi_s^{-2}v$, which has exponential solutions $v \propto \exp(-x/\xi_s)$. Thus, the step-function penetration depth is simply ξ_s. Since ξ_s and ξ_0 only differ by constant factors, the ratio of relative penetration depths $r \equiv (l_p/h)/(\xi_s/h_s)$ scales as $(h/\xi_0)^{1/2}$. Using ref 3, we obtain

$$\frac{l_p/h}{\xi_s/h_s} = 0.69\left(\frac{h}{\xi_0}\right)^{1/2} \tag{5}$$

A comparison of flow penetration into the parabolic and equivalent step-function brushes for $h/\xi_0 = 30$ is shown in Figure 1.

The surprisingly deep penetration of solvent flow into a brush may be observable by comparison of two experiments performed on the force-balance apparatus. First, compressional force measurements[9,10] in conjunction with an independent measurement of surface coverage gives one determination of the brush height.[11] Then, a measurement of lubrication forces, which oppose the approach of two slightly curved brushes separated by a small distance, may give the apparent location of a no-slip boundary.[12] Comparison of the two results would give the hydrodynamic penetration depth for the brush.

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References and Notes

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(2) We will ignore swelling effects here, taking $\nu = {}^1/_2$.

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(6) Again we employ relations that ignore swelling effects.

(7) Brinkman, H. C. *Appl. Sci. Res.* **1947**, *A1*, 27.

(8) If swelling effects are retained, the mesh size scales as $\xi \sim \phi^{-3/4}$ and the brush extremity obeys a power law[3] $\phi \sim x^{8/9}$, with the result that $l_p \sim \xi_0{}^{3/5}h^{2/5}$.

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(10) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

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(12) Fredrickson and Pincus recently obtained results (*Langmuir*, submitted) on lubrication forces between brushes either slightly separated or compressed together, assuming step-function profiles. Their results for separated brushes would be modified by the present work.