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Polymer Brushes

S. T. MILNER

Polymers attached by one end to an interface at relatively high coverage stretch away from the interface to avoid overlapping, forming a polymer "brush." This simple picture may serve as the basis for models in diverse interfacial systems in polymer science, such as polymeric surfactants, stabilized suspensions of colloidal particles, and structures formed by block copolymers. The structure and dynamics of polymer brushes have been the subject of considerable theoretical and experimental activity in recent years. An account is given of recent advances in theoretical understanding of stretched polymers at interfaces, and the diverse experimental probes of systems modeled by brushes are briefly reviewed.

POLYMER "BRUSHES" ARE LONG-CHAIN POLYMER MOLEcules attached by one end to a surface or interface by some means, with a density of attachment points high enough so that the chains are obliged to stretch away from the interface, sometimes much farther than the typical unstretched size of a chain. This situation, in which polymer chains stretch along the direction normal to the grafting surface (like the bristles in a brush, hence the name), is quite different from the typical behavior of flexible polymer chains in a solution, where the long molecules adopt random-walk configurations.

Polymer brushes, with some important variations, are a central model in many important problems in polymer science, and are relevant even in biophysics and surfactant science (where the chains in question are only marginally long enough to be called polymers). One of the most important variations among brushes is the presence or absence of solvent for the polymer chains. With solvent present, the physical reason for the chains stretching away from the interface to which they are attached is their affinity for the solvent (and/or dislike of each other). For melt conditions (no solvent present), the chains must stretch away from the interface to avoid overfilling space (since the matter of which the chains are made is approximately incompressible).

The interface to which the chains in the brush are attached may be a solid substrate or the interface between two solvents, between solvent and air, or between melts or solutions of homopolymers. The mechanism by which the chains are attached to the interface varies with the interface. For solid substrates, the chain end may be chemically bonded to the substrate or the chain may be terminated by a special chemical group that adsorbs onto the surface. This end group may be either a small molecule that is strongly attracted to the surface, or a long copolymer, each monomer of which is only weakly attracted. For interfaces between fluids, the attachment may be achieved by similar adsorption mechanisms in which the end group of the chain prefers one medium and the chain prefers the other. Finally, the chain may be attached to a "substrate" that is the narrow interface between microdomains in a melt or concentrated solution of diblock copolymers (two dissimilar polymers joined end to end) when the two blocks of the copolymer are strongly segregated.

Within these variations in interface and solvents, several important physical systems are contained (see Fig. 1):

1) Colloid stabilization by end-grafted chains. In this case solid particles are maintained in suspension (protected against flocculation due to van der Waals attraction) by attaching a "brush" of grafted chains that prefer the solvent of the suspension; the brushes of two approaching particles resist overlapping, separating the particles to a distance at which the van der Waals interaction is too weak to keep the particles together.

2) Polymeric surfactants. A polar end-group is attached to a hydrocarbon chain, which is insoluble in polar solvents; a polymeric surfactant molecule is formed that is attracted to oil-water interfaces.

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Practical surfactants typically have chains too short to be described as polymers; however, theoretical results are much easier to obtain for long molecules and may yield insights into the behavior of short-chain surfactants.

3) Polymer compatibilizers. A diblock copolymer, formed by chemically joining two dissimilar polymers end to end, adsorbs at interfaces between its constituent polymers. (Here the "solvents" are homopolymer solutions or melts, and may in fact be excluded from the copolymers at the interface.) Chemically different polymers are very difficult to mix into a stable phase because the interaction per molecule may be large compared to k_BT, the relevant scale for entropy of mixing (k_B is Boltzmann's constant and T is absolute temperature). Diblock copolymers may stabilize small (submicrometer) domains of one incompatible homopolymer in another.

4) Copolymer microphases. A great variety of microphases may be obtained from melts or concentrated solutions of diblock copolymers by varying the relative length, bulk, and flexibility of the two dissimilar blocks of the molecule (*1*). When the two blocks are strongly incompatible, the interface between microdomains of the two chains is sharp. Then the local structure of the chains in the microphase is that of a grafted chain in melt conditions.

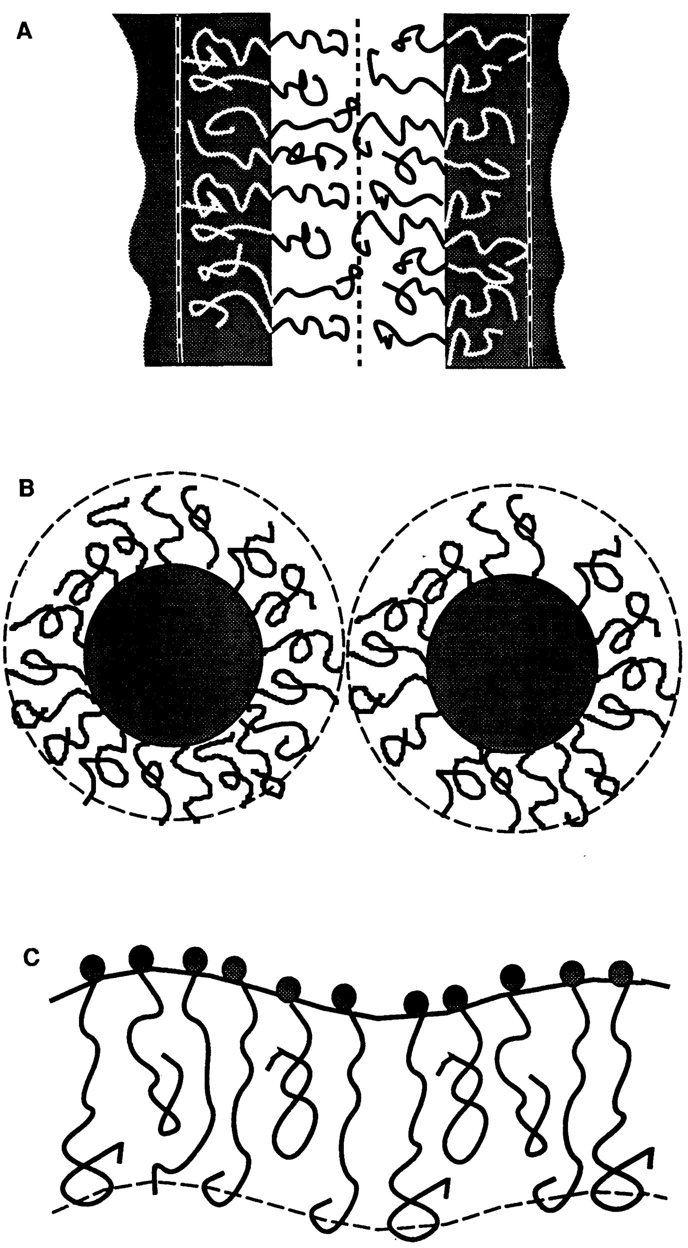

Fig. 1. Cartoons of three physical situations that may lead to stretched polymers at interfaces. (**A**) Strongly segregated diblock copolymers forming a lamellar microphase. (**B**) Colloidal particles stabilized in suspension by "brushes" of end-grafted soluble polymer chains. (**C**) Polymeric surfactant molecules adsorbed on a liquid-liquid, liquid-vapor, or liquid-solid interface.

For each of these situations, the brush structure of the polymer chains is responsible for novel behavior. For colloidal dispersions stabilized by end-grafted chains, the repulsive force between brushes arises ultimately from the high osmotic pressure inside the brush. The modification of liquid-liquid interfacial properties (such as surface tension and bending stiffness) by polymeric surfactants depends on the balance between the affinity of the polar head for the interface and the free-energy cost of stretching the chains. The effectiveness of copolymer compatibilizers depends on similar considerations; the strength of the bond between domains depends on the degree to which the copolymer is entangled with the homopolymer domains. The response of a strongly segregated lamellar phase to shear is also expected to depend sensitively on the entanglement of the constituent chains; because of their uniaxial stretching, the shear viscosity may show considerable anisotropy. These are a few examples of the physical consequences of polymer chains end-grafted to interfaces that will be encountered throughout this review.

A Simple Model for Brushes

Polymer chains under conditions of strong stretching may be understood most simply by free-energy–balance arguments. Consider, for example, the case of flexible polymer chains of length N (measured in units of the persistence or Kuhn length a) permanently attached at a grafting density of σ chains per unit area to a flat interface and exposed to a solvent. The polymer chains have two contrary tendencies: first, they maximize their configurational entropy by adopting random-walk configurations (which favors short dense brushes); second, they would prefer to be wet by solvent (which favors tall sparse brushes). If the distance $\sigma^{-1/2}$ between grafting sites is much smaller than the typical chain dimension, $R_g = N^{1/2}a$, both tendencies cannot be met. The chain responds by choosing the height h of the brush to balance two free energy costs—stretching, which reduces the configurational entropy, and overlapping with its neighboring chains, which reduces the energetically favorable contact with solvent molecules.

A very simple estimate of the balance achieved by the stretched chains, first presented by Alexander (*2*) and de Gennes (*3, 4*), is the so-called Flory (*5*) argument. This argument estimates the reduction in configurational entropy from results for an ideal random walk [self-avoidance is neglected; see (*2, 6–8*)] constrained to travel a distance h from the grafting surface to the outer edge of the brush. More physically, the polymer chains of length N can be regarded as entropic "springs" with spring constant $k_BT/R_g{}^2$ (that is, it costs k_BT to double the typical end-end separation) stretched from the grafting surface to the outer fringe of the brush. Consistent with that assumption, the cost of unfavorable contacts between chain units is estimated by assuming that the chain units are distributed randomly with a uniform density equal to the average density in the brush, $\phi \sim N\sigma/h$. (Throughout this article, a tilde ($\sim$) denotes the omission of a constant of order unity.)

This approach leads to a free-energy cost per chain

$$\Delta f \sim k_BT\left[\frac{3h^2}{2Na^2} + wN\left(\frac{N\sigma}{h}\right)\right] \tag{1}$$

in which w is the excluded volume parameter, which measures the strength of the repulsion between chain units. Minimization with respect to the brush height h leads to

$$h \sim N(w\sigma a^2)^{1/3}, f \sim k_B T N(w\sigma a^{-1})^{2/3} \qquad (2)$$

This is a striking result for the following reason, first noted by Alexander (*2*): a sequence of brushes with the same coverage σ and increasingly large N, the height h grows linearly with N, while the unstretched chain dimension R_g only grows as $N^{1/2}$. For long enough chains, h is much larger than R_g—the chains are strongly stretched; their properties may then be expected to be quite different from unstretched chains in solution.

In a brush without solvent (melt brush), the height h is related to the coverage σ by the requirement that the density is fixed: $\rho_0 = N\sigma/h$. In typical instances of melt brushes (such as the chains in a lamellar microphase), the coverage is not fixed but chosen by the system to minimize the free energy. For example (*2*), if there is a surface tension γ between domains of dissimilar A and B chains, surface tension favors a large layer spacing h and a smaller area per chain σ^{-1}, whereas stretching favors the reverse.

The sum of surface and stretching free energy per chain is approximately

$$f = \frac{\gamma}{\sigma} + \frac{(N\sigma/\rho_0)^2}{Na^2} \qquad (3)$$

Minimization with respect to σ gives

$$h \sim \left(\frac{\gamma a^2}{\rho_0}\right)^{1/3} N^{2/3}, f \sim \left(\frac{\gamma}{\rho_0 a^2}\right)^{2/3} N^{1/3} \qquad (4)$$

Hence in principle the melt brush height h again grows faster than the typical chain dimension as N increases (but not very much faster; this must be borne in mind when the limit $h >> R_g$ is considered below).

Results for the simple model. Before discussing more detailed theoretical treatments of the structure of brushes, it is worth outlining what properties of brushes can be adequately represented with the above simple treatment, and what sorts of properties require more detailed information, such as the density profile or chain conformations.

The simple free-energy–balance argument (*2–4*) does not attempt to discuss details of the polymer chain conformations or the density profile of chain units $\phi(z)$ at a distance z from the grafting surface; rather, it estimates a rough balance between the free-energy costs of stretching and chain-chain contact. Many experimental probes and physical properties depend only on some measure of the height h or the free energy per chain f and are thus well described by the simple argument if measurements are not so precise that coefficients of order unity are tested. Some examples are:

1) Rough measurements of the brush height h. If the ubiquitous constants of order unity in the simple argument are not 1/10 or 10 but really are close to 1 (as they turn out to be), then measurements of the height of a brush must be rather accurate to see the details omitted by the simple argument. Hence the approximate range of forces between two brushes, or its thickness as observed by neutron scattering, may be described within the simple Flory picture.

Hydrodynamic properties of brushes, such as the hydrodynamic thickness or permeability of a brush, may also be roughly described by the Flory picture. A brush in solvent with a supposed constant density $\phi = N\sigma/h$ has a characteristic length $\xi \sim a/\phi$ over which hydrodynamic flow is screened. Beyond this (short) length ξ, flow does not penetrate into the brush. The length ξ also plays the role of a pore size in permeative flow (in which a hydrostatic pressure Δp across a brush drives a trickle of fluid of viscosity η at a velocity $v \sim \xi^2 \Delta p/\eta$). These hydrodynamic properties have interesting consequences for the lubrication forces that arise when two brushes (such as the surface of two brush-stabilized colloidal particles) are brought into near contact (*9*).

2) Rough measurements of the free energy per chain f. Likewise, many properties of brushes depend only on a rough estimate of the cost attaching one more chain to the grafting surface; this is the central parameter in studies of brushes in equilibrium with a reservoir of chains that may adsorb onto or desorb from the surface. The Flory argument gives reasonable estimates of the coverage at equilibrium with a solution of end-adsorbing chains of a given concentration and end groups of a given binding energy.

For example, when the concentration of adsorbed chains in solution is not too high (so that solution osmotic pressure may be neglected), the equilibrium coverage is roughly given by a balance between the cost $f - T\log(\phi_s/N)$ to bring a chain from the solution (concentration ϕ_s) to the surface and the binding energy ΔE of the end group (*10, 11*). (Recent work on the dynamics and equilibrium of brush formation is discussed briefly below.) Similar approximations have been made to estimate the free energy of micelle formation in studies of micellization of copolymers in dilute solution (*12*) and equilibrium of such micelles by exchange of single copolymers (*13*).

3) Rough measurements of the stretching-repulsion balance. Many brush properties depend on perturbing the balance between chain stretching and chain-chain repulsion, such as the force per area required to compress a brush (either vertically or laterally) or the bending stiffness of a brush. In some instances, these properties are correctly given (to within the ubiquitous factor of order unity) by Flory arguments.

For example, the surface pressure $\pi(\sigma)$ of an insoluble monolayer forming a brush—which acts to reduce the interfacial tension—may be estimated from

$$\pi(\sigma) = \partial f/\partial(1/\sigma) \sim f\sigma \qquad (5)$$

The mean bending stiffnesses K may likewise be estimated by repeating the simple balance arguments for a brush grafted to a slightly curved interface. Alternatively, one could guess that the bending stiffness (with dimensions of energy) scales as $f\sigma h^2$, the free energy of a brush of area h^2 (*14–16*). This gives

$$K \sim N^3\sigma^{7/3} \text{ (solvent)}, N^3\sigma^5 \text{ (melt)} \qquad (6)$$

Such estimates may be used for gently curved interfaces to compute the free energy of phases of homopolymer A + homopolymer B + copolymer A/B, analogous to surfactant-oil-water microemulsion phases (*17, 18*). Transitions between lamellae, cylinders, and spheres of emulsified homopolymer occur as the asymmetry of the copolymer (and thus the preferred radius of curvature) is varied.

For solvent brushes, the Flory argument can be extended to give compressional force laws. A compressional force may be applied to an imaginary surface to which the chain free ends are attached, with the result that the free energy per chain of a brush compressed to a height $h' < h$ is (*19, 20*)

$$f(u) = \frac{2f}{3}\left(\frac{1}{u} + \frac{1}{2}u^2\right), u \equiv h'/h \qquad (7)$$

For large forces this expression reduces to the osmotic pressure of a solution of concentration $\phi' = N\sigma/h$; the grafting is irrelevant. A "large" force is large compared to the osmotic pressure $\Pi \sim \phi^2$ inside the brush. De Gennes (*4*) noted that brushes exposed to solutions of long-chain homopolymer at concentrations $\phi_h \gtrsim \phi$ will be significantly compressed. (For small forces the simple Flory balance is linearly perturbed with the result that the compressional force $\partial f/\partial h'$ is linear in $h' - h$. This result is incorrect, as is shown below.)

A More Detailed Picture: "Parabolic" Brushes

Some important properties depend more sensitively on details of the brush structure, such as the shape of the chain unit density $\phi(z)$, how the chains are stretched, or where the free ends of the chains are to be found. In general, probes of a brush that are localized in space, or properties of the brush that depend sensitively on chain units far from the interface, are not well represented by calculations based on Flory arguments. Here are some examples of brush properties that require a more detailed theory:

1) Accurate experiments. All of the properties discussed in the previous section depend on a detailed theory to calculate prefactors, which are important if sufficiently accurate measurements are made.

2) Density profiles of chain units [$\phi(z)$], of free ends [$\epsilon(z)$], and of a distinguished chain unit s [$\phi_s(z)$]. Obviously, the simple description presented above makes no prediction about the way that chains are distributed in the brush, other than the estimate of the brush height (*21*). Any experiment that is sensitive to the spatial variation of brush properties requires a more detailed theory.

3) Weak compressional forces. One may expect that if brushes are in fact not homogeneous throughout their thickness, they will have softer and stiffer regions, which will lead to more easily compressible brushes for weak forces. (The reasonable expectation that the outer fringe of a brush is softer is indeed borne out.) Weak compressional forces are perhaps most important in stabilizing colloidal suspensions.

4) Segregation and mixing. An important generalization of brushes is to the case of mixed chains, either of different chain lengths or of different chemical compositions. One may then ask how the chains mix or segregate, either in the case of freely moving or permanently affixed grafting anchors.

5) Hydrodynamic penetration. A shear flow of solvent adjacent to a brush can penetrate into the brush some distance; the answer depends on the details of the density profile at the outer fringe of the brush.

6) Chain interpenetration. Likewise, the penetration of homopolymer molecules in a solution adjacent to a brush, or of another brush brought into contact, depends on the details of the outer fringe. Since the degree of penetration of polymers controls entanglement, and entanglement slows polymer dynamics enormously, penetration effects are important for many instances of the rheological properties of brushes (*22*) (such as in suspensions of brush-stabilized colloidal particles, in micellar solutions of polymeric surfactants, and in lamellar phases of block copolymers).

Strongly stretched "parabolic" brushes. This review is devoted in large part to recent theoretical developments in understanding polymer brushes, beyond the simple free-energy balance estimates. It turns out that under conditions of strong stretching—where polymer chains are extended much farther than their natural dimensions by the need to escape their neighbors attached to the substrate—elegant and relatively simple theoretical results can be obtained for a wide variety of brush properties and situations. Immediately, it must be said that for many physical situations of interest, the criterion of strong stretching is only marginally satisfied (or not at all). In the more general case, there are other theoretical approaches, that rely on extensive computer calculations (*23–27*); these can be quite useful for many purposes. However, because the strong-stretching results are relatively simple (they do not require large numerical calculations or simulations), but not so simple that all of the physics is lost, they are worthy of some attention. It is also possible to investigate the corrections to the limit of strong stretching, both analytically and with the help of the more general computer-intensive theories; this combined approach gives some insight into more physical brushes.

It is evident that the Flory argument may be made exact for a brush in which the chain free ends are attached to a "phantom surface" at an adjustable distance from the interface; this leads to a step-function profile for the density of chain units. The phantom surface restricts the chains in two ways: first, all of the chains are constrained to behave the same way (for example, their ends must be located the same distance from the interface); second, because the chains are all ganged together, fluctuations of a chain away from its most likely path are suppressed. The natural length scale fluctuations is the typical chain dimension R_g; when $h >> R_g$ one may expect fluctuations to be unimportant, except in the outermost fringe of the brush. Discussion of fluctuation effects is deferred until the end of this article.

Requiring that all of the chain ends reside at the outer edge of the brush does not result in the optimum state; one chain end released from the phantom surface can snap back toward the interface, lowering its stretching free energy without suffering more contacts with chain units. For the chains to be stretched away from the interface in a stable and self-consistent way, the osmotic pressure $\mu(z)$ of a chain (the cost to place a chain unit at a distance z from the interface) must decrease as z increases. In a brush with solvent, the cost to add a chain unit is the likelihood of contact with another chain, so $\mu(z) \propto \phi(z)$; in a melt brush (no solvent), μ is the pressure (against which work is done when an extra chain unit is added).

A simple hypothesis about chain free ends—that they may be located at any distance from the interface—turns out to allow us to guess the form of $\mu(z)$. [This approach was first used by Semenov (*28*) for the case of brushes without solvent; it was developed for brushes with solvent by Milner, Witten, and Cates (*8, 16, 29*) and independently by Skvortsov, Zhulina, Priamitsyn, and collaborators (*30, 31*).] The equation that gives the most favorable configuration of a chain in a prescribed potential $\mu(z)$, is found by minimizing the sum of *local* stretching and repulsion free-energy terms (analogous to the global Flory estimate) with respect to the configuration $Z(s)$ of a chain [only the distance $Z(s)$ of chain unit s from the interface is relevant]:

$$0 = \frac{\delta F[Z(s)]}{\delta Z(s)} = \frac{\delta}{\delta Z(s)} \int ds \left[\frac{3}{2a^2} \left(\frac{\partial Z}{\partial s} \right)^2 + \mu[Z(s)] \right]$$

$$= -\frac{3}{a^2} \frac{\partial^2 Z}{\partial s^2} + \frac{\partial \mu}{\partial Z} \qquad (8)$$

This equation of motion looks like that of a particle with trajectory $Z(s)$ falling in a potential $-\mu(z)$. The chain length N is analogous to the time of flight of the particle. For chains to be in equilibrium with free ends at any distance from the interface, then the potential μ must be such that any starting point (free end position) gives the same time of flight (length of chain to the interface).

That potential is a parabola, the potential of the harmonic oscillator

$$\mu(z) = \text{constant} - \frac{\pi^2}{8N^2} z^2 \qquad (9)$$

The resulting state of affairs for the chains may be likened to the relation between commuting time and quality of life near a major city. Because commuters are approximately identical, and are free to change their lifestyles, the tradeoff between a long commute and a high-pressure life in the city must be roughly even. (Chains with free ends far from the interface have more stretching free energy but less chain-chain repulsion; the situation is reversed for chains with free ends near the interface.)

All of the properties of the more detailed "parabolic" brush description are completely consistent with the scaling analysis of the Flory argument (*8*). In particular, the ratio of equilibrium values of the brush height and free energy per chain in the parabolic calculation and "step-function" estimate are $h/h_{\text{step}} = 1.3$, and $f/f_{\text{step}} = 0.89$ (see Fig. 2).

The distribution of free ends is determined from the requirement that the chain-unit density profile be reproduced, which leads to end density profiles (*8, 28, 30*) (see Fig. 2)

$$\epsilon(z) = \frac{3\sigma}{h^3}z(h^2 - z^2)^{1/2}(\text{solvent}), = \frac{\sigma}{h}z(h^2 - z^2)^{-1/2}(\text{melt}) \quad (10)$$

A brush compressed by an impenetrable surface to a height $h' < h$ still has a parabolic osmotic pressure $\mu(z)$, now with a nonzero value of the concentration at the outer edge (so that the brush osmotic pressure balances the compressional force). Instead of Eq. 7, the free energy of a compressed brush (*8*) is

$$f(u) = \frac{10f}{9}\left(\frac{1}{2u} + \frac{1}{2}u^2 - \frac{1}{10}u^5\right), u \equiv h/h' \quad (11)$$

When $h' << h$, the third term is negligible and the two resulting force laws have the same shape; for small compression the parabolic brush is softer and the compressive force starts as $(h - h')^2$.

Experimental Probes of Brushes

Some of the many experimental probes of brushes that in principle could be sensitive to the details of brush structure beyond the simple Flory-type description are considered below (*32*). (As is often the case, there is considerable distance between theory and experiment which arises from the difference between what theorists and experimenters consider a simple system. The theoretically appealing limit of strongly stretched brushes is difficult to attain in the laboratory, and weakly stretched brushes are difficult to analyze.)

Profiles and equilibration. Many scattering experiments have been used to investigate the structure of end-grafted polymer systems. This is a difficult experimental situation, however, because polymer brushes are (i) small, and in the case of brushes with solvent, (ii) not very dense. Typical end-adsorbed brushes (for example, with $R_g \sim 100$ Å and $E_{\text{bind}} \sim 10\ k_BT$) may only be around 500 Å thick, so that light-scattering probes are not useful for probing the chain unit density profile. Various optical probes [evanescent waves (*33*), ellipsometry (*34*), and multiple-reflection interferometry (*35*)] give information equivalent to the total amount of polymer adsorbed. The total amount adsorbed has also been measured with infrared spectroscopy (*36*), as well as with an elegant method in which the shift in the surface plasmon of a metal substrate (*37*) is used.

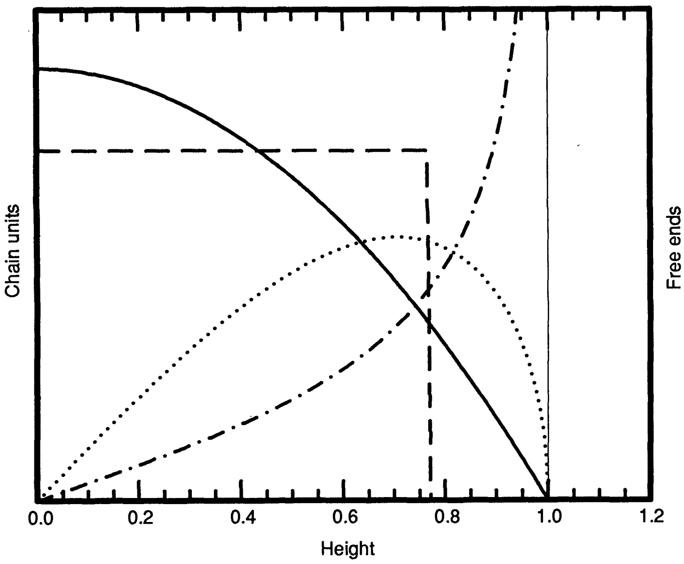

Fig. 2. Chain-unit density profiles $\phi(z)$ for a "parabolic" brush (that is, $\phi << 1$ so $\mu \propto \phi$), and the step-function ansatz at equal coverage σ and chain length N. Also shown are end-density profiles for brushes with (dotted) and without (dot-dashed) solvent.

The experiments of Munch and Gast (*35*) and Tassin *et al.* (*37*) give the amount adsorbed as a function of the time a fresh surface has been exposed to a solution of adsorbed chains. This experiment was considered theoretically by Ligoure and Leibler (*11*), who pointed out that the kinetics of adsorption of chains onto the surface, after an initial rapid increase in coverage, would become very slow because of the barrier to adsorption posed by the brush already present. Their treatment of the adsorption kinetics also predicted that the time to "wash off" an adsorbed brush with fresh solvent would be much longer than even the characteristic time to grow the brush. Both observations are in qualitative agreement with experiment; more detailed comparisons with theory of the coverage as a function of time and chain length appear feasible.

Ausserre *et al.* pushed evanescent-wave fluorescence techniques toward effectively shorter length scales by using a very large, stiff polymer (xanthan) in an experiment on homopolymer-surface repulsion (*38*). They were able to extract some information about the shape of the depletion layer, which was of order 1500 Å thick; perhaps very large, stiff end-adsorbed polymers could be studied in this way.

Satija and co-workers attempted to observe solvent-brush structure with neutron reflectivity (*39*), which has given excellent information for lamellar phases (*40*), but the low contrast makes the brush invisible. Earlier studies of homopolymer adsorption (in which each monomer on a chain is weakly attracted to an interface) using synchrotron x-ray fluorescence (*41*) proved effective in probing the relatively low-density adsorbate molecules at length scales of a few tens to a few hundreds of angstroms; similar studies for end-grafted polymers might be successful in observing the density profile.

Cosgrove and Ryan (*42*) have performed neutron scattering experiments from short (average molecular weight $M \approx 5000$) polyethylene oxide chains end-grafted to 100-μm latex spheres in suspension. Neutron scattering has ample spatial resolution to observe features of the density profile; results of this study compare favorably to numerical calculations. The short chain length and the fact that the homopolymer itself adsorbs on latex (*43*) prevent this system from being well described by a "parabolic" brush.

Recently, Auroy and co-workers have performed neutron scattering from chemically end-grafted polymers on porous silica particles (*44*) (which gives a large amount of brush as a scattering target). They were able to extract both the total amount adsorbed and a measure of the brush height, and they verified the scaling of height with coverage (Eq. 4).

Vertical and lateral forces. A powerful method for probing the structure of brushes is the force-balance technique. Several groups (*45–51*) have measured the forces between polymers end-adsorbed onto mica; the adsorption has been achieved with both zwitterionic (*47, 48*) and copolymeric (*45, 46, 49*) anchors.

The onset of detectable force between two brushes gives a rough measure of the brush height; thus, varying molecular weight (and measuring the coverage) would allow a test of the scaling $h \sim N\sigma^{1/3}$. Measurements of the coverage on mica substrates has proved difficult; Taunton *et al.* have shown (*48*) that the height h scales roughly as $N^{0.6}$, which is consistent with a constant free energy per chain (the coverage is *not* fixed) (*6, 10, 11*).

The system of copolymers adsorbed by an insoluble block [polystyrene-polyvinylpyridine (PS-PVP) in toluene] is more complex because the PVP adsorbed layer has some unknown structure that enters into determining the amount adsorbed. Marques, Joanny, and Leibler have analyzed this adsorption mechanism and found many regimes that depend on the relative sizes of PVP and PS blocks and on the strength of the van der Waals interaction between the PVP and the mica substrate (*52*).

The Minnesota group has used radiolabeling techniques to measure accurately coverages for various PS-PVP copolymers on mica (*53*). With fixed PVP block, they found roughly constant coverage over a range of PS chain lengths and found brush heights h scaling as N. For more general PS-PVP length ratios, this group found good agreement with the description of copolymer adsorption of (*52*).

In principle, the differing shapes of the force-balance curve itself for the parabolic brush and the step-function ansatz should be evident in experimental data. There are some practical problems with this. In the range over which forces have been measured, it is possible to fit acceptably either form (Eq. 7 or Eq. 11) if the coverage and overall scale of the force are taken as fitting parameters. One attempt has been made (*10*) to use known material parameters and measured coverage values for the experiment in (*47*) to distinguish the two descriptions (which is possible; for example, the predicted brush heights differ by 30%). This approach gives a value for the free energy per chain f around 10 k_BT for the system of (*47*) [which is reasonable, since f is expected to be roughly (*11*) equal to the binding energy of the zwitterion end-group].

In (*10*) it has been shown that a parabolic brush with only a small polydispersity in chain length could account for the force curves without adjustable parameters, whereas the step-function brush was far too short to agree with the experiment (Fig. 3). The polydispersity in the chain length has the effect of making the force extend farther (*29*); another source of corrections to the parabolic-brush force law that may have the same general effect are "fluctuation corrections," that is, corrections to the limit of large h/R_g. (The latter subject is discussed briefly below.)

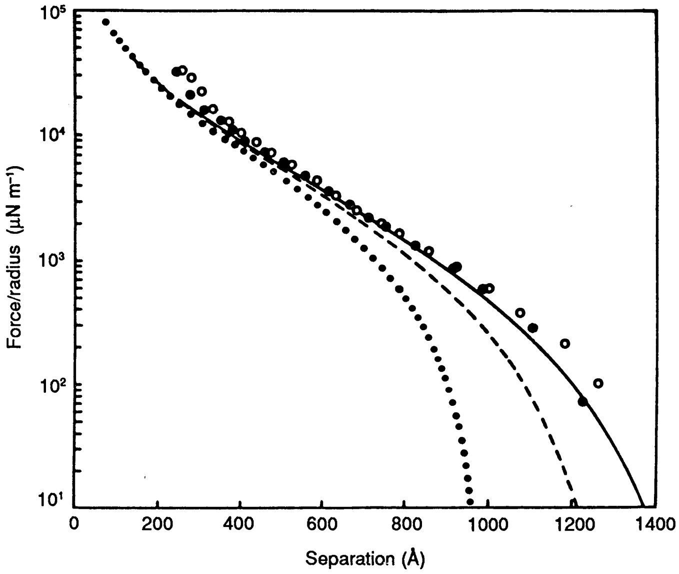

Fig. 3. Force versus height data from (*47*). The curves are theory for a step-function brush (dotted), the equivalent "parabolic" brush (dashed), and a parabolic brush with small (M_W/M_N = 1.02) polydispersity corrections (solid). The dark (open) circles represent data from measurements made with steadily decreasing (increasing) separation between surfaces. [Reprinted from (*10*) with permission ©*Europhysics Letters*.]

Lateral compressive forces in brushes at air-liquid interfaces, which reduce the macroscopic surface tension, may be measured in Langmuir trough experiments. Granick and Herz performed an early study (*54*) on diblock copolymers (one insoluble block anchoring the other soluble block at the surface) and observed the surface pressure $\pi(\sigma)$ due to the adsorbed chains, which showed features in qualitative agreement with Eq. 5.

More recently, Sauer *et al.* have performed similar Wilhelmy-plate studies in conjunction with surface light scattering from capillary waves at air-water and oil-water interfaces at which short (M_N = 4135) polyethylene oxide-polystyrene (PEO-PS) diblock copolymers were adsorbed (*55*). They found excellent agreement between the two methods of extracting $\pi(\sigma)$. The light-scattering method also holds promise of extracting the bending constant K and surface viscosity when these play a significant role in the capillary wave dispersion relation. Further studies with longer copolymers should be useful in checking validity of Eqs. 5 and 6 for the bending constant and the lateral pressure.

Hydrodynamic properties. Hydrodynamic flows have also been used to investigate brush thicknesses. The hydrodynamic thickness of brushes grown on colloidal particles may in principle be determined in many ways (such as by viscosity increase, sedimentation, or dynamic light scattering); but precise measurements are required because the brush height h is typically a small fraction of the particle diameter (*32*).

Webber *et al.* studied changes in hydrodynamic diameter of small pores in mica when PS-PVP diblock copolymers were adsorbed (by measuring the pressure drop as a function of flow rate) (*56*). They estimated the total amount of polymer adsorbed by inducing collapse of the (irreversibly) adsorbed layers in a poor solvent and demonstrated that the adsorbed layers had coverage and thickness in good solvents comparable to that observed in force-balance experiments.

The force-balance apparatus can also be used to make hydrodynamic measurements on brushes in close proximity or under compressive contact. Fredrickson and Pincus have investigated the lubrication forces that arise when two brush-coated surfaces are brought into contact at a given rate (*9*). Before contact, the brushes are roughly equivalent to impenetrable surfaces; shear flow is screened out inside the brush (but see below). When brushes are squeezed beyond contact, however, the combination of permeative flow through the brush and shear deformation of the brush itself as material is forced out from between the approaching substrates leads to large lubrication forces and long characteristic times. Experiments of this kind may be performed on force-balance apparatus (*57*).

In the above work a step-function profile was assumed in the analysis, which is reasonable for the precision of experiments performed to date. However, there is an interesting difference between penetration of shear flow (the apparent location of a no-slip boundary) in step-function and parabolic-profile brushes. The Brinkman equation (*58*)

$$\eta\,[\nabla^2 v + \xi(\phi)^{-2} v] = \nabla p \tag{12}$$

describes porous media in terms of a local hydrodynamic penetration length (*59*) $\xi \sim a/\phi$. In a step-function brush this length is constant, leading to exponential decay of shear flow into the brush and an effective no-slip boundary a distance of order ξ inside the brush. For a brush with a parabolic profile, the hydrodynamic penetration length diverges at the outer fringe of the brush; the value of $\xi(\overline{\phi})$ corresponding to the average density $\overline{\phi}$ is only attained well inside the brush where penetration of the flow is not expected. The result is that the no-slip boundary is of order $[\xi(\overline{\phi})h]^{1/2}$ inside the brush, which can be much larger than $\xi(\overline{\phi})$.

Local probes—NMR and fluorescence. A different class of experiments probing brush structure are those which examine the properties of a tagged subset of chain units. One example is the nuclear magnetic resonance (NMR) studies by Blum and co-workers of PS-PVP copolymers ($M_N = 20,000$) in toluene adsorbed on silica (*60*). The soluble PS chains were prepared with either the first or the last half of the monomers deuterated. Measurements of the relaxation time T_1 give an estimate of the local monomer density, which was found to be 0.11 g/ml for the chain half nearest the interface and 0.048 g/ml for the other half. With independent measurement of the coverage as 1.75 mg/m^2, the average density suggests a brush thickness of 4 to 5 R_g.

These results might be compared to the density in the vicinity of the *s*th monomer (averaged over its locations in the brush), which for parabolic brushes at low density ($\mu \propto \phi$) is

$$\phi(s) = \phi(0)\left[1 - \frac{2}{5}\cos^2\left(\frac{s\pi}{2N}\right)\right] \qquad (13)$$

The ratio of the average density seen by the inner and outer half-chains is then $(2\pi + 1)/(2\pi - 1) \approx 1.4$ versus 2.3 from experiment, suggesting that the physical system may have (i) grafting density high enough to require higher order virial coefficients, or (ii) fluctuation effects leading to a lower density for chain units in the extreme outer fringe of the brush, or both. A more tedious synthesis to label the chain by quarters, as well as the use of longer chains, would provide a striking test of the analytical brush theory.

Another experimental technique with considerable promise that has not yet been applied to brushes is fluorescent labeling. Croucher *et al.* have performed an elegant study of solvent-induced flocculation of homopolymer-stabilized colloidal particles (*61*). By controlling the concentration and location of donor and acceptor dye molecules on stabilizing chains, the penetration of chains between colliding or flocculating particles was studied with a spatial resolution of 45 Å (distance over which the dye molecules interact).

Similar experiments would be extremely useful to probe (i) the distribution of chain free ends by labeling them with acceptor and placing quencher on the surface, or (ii) interpenetration of brushes in contact (see below) by experiments similar to those of (*61*).

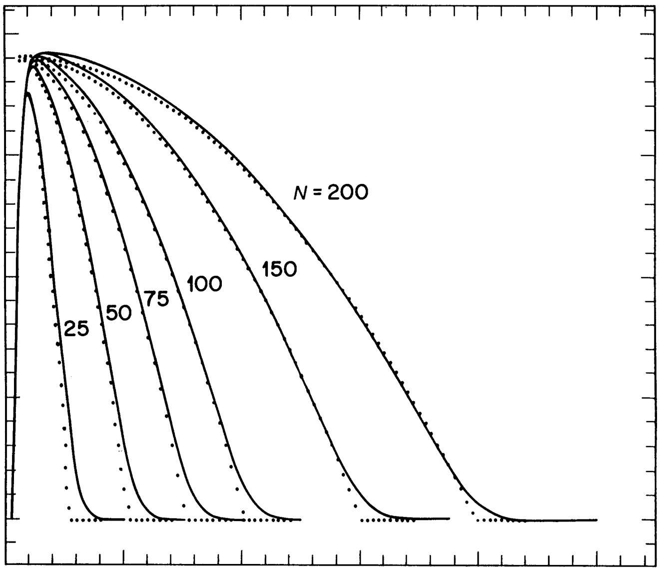

Fig. 4. Chain-unit density profiles for coverage $\sigma = 0.1$ and chain lengths N as indicated. The dotted curves are parabolic profiles predicted by strong-stretching theory; the solid curves are results of Scheutjens-Fleer numerical calculations. Note that the "foot" region at the outer edge of the brush becomes smaller as N increases. [Reprinted from (*65*) with permission ©The Chemical Society.]

Computer "experiments." Two final sorts of "experiment" to test the parabolic brush description are (i) computer simulations and (ii) direct numerical solutions of the mean-field (*7*) equations of Dolan and Edwards (*62*).

Molecular dynamics simulations of Murat and Grest (*25*) examine both chain-unit and free end density profiles, as well as forces between brushes, and find agreement with the analytical theory in the appropriate regime of long chains and moderately high coverage. At increasingly high coverage, flattening of the density profile relative to the simple parabola is observed (*25*), which may be attributed to higher order terms in the virial expansion of the equation of state entering to limit the density to below the melt value (see below).

Monte Carlo simulations have been performed by Chakrabarti and Toral (*26*), who find excellent agreement with the chain-unit and end-density profiles of (*8*) as well as with the results of (*29*) for the behavior of brushes composed of chains of different lengths (see below).

Finally, Scheutjens and Fleer (SF) (*23*) and collaborators (*63*) and other groups (*64, 65*) have performed extensive numerical studies in order to solve directly the mean-field equations (*66*). When fluctuations of a chain about its most likely configurations are not neglected, chain configurations are not limited to those that minimize the free energy (Eq. 8). Rather, the chains are described by a partition function, which is a sum over all chain paths with a Boltzmann weight

$$Z = \sum_{z(s)} \exp\{-F[z(s)]\} \qquad (14)$$

This partition function looks like the path integral representation of quantum mechanics for a particle in a potential $-\mu(z)$, just as Eq. 8 for the most likely chain path was analogous to the classical mechanics of a particle. The potential $\mu(z)$ is determined self-consistently to enforce a constraint on the chain unit density [for example, that $\phi(z) = 1$ for melts, or that $\mu(z)$ is some function of $\phi(z)$ for solutions]. To summarize, the mean-field equation of Dolan and Edwards is the self-consistent Schrodinger equation for this "quantum mechanics."

The transfer matrix methods of DiMarzio and Rubin (*67*) allow the evolution of the Boltzmann weight for any chain in a given $\mu(z)$; the chain unit density may be found as a sum over chain configurations of the contribution to the density of each configuration, and $\mu(z)$ can be adjusted to give consistency.

The SF method is a powerful alternative to analytical methods: it has been generalized to curved geometries, polydisperse chains, brushes in presence of homopolymer, adsorbing copolymers, and other problems (*23*). It is thus ideal for studies of small-to-moderate–sized chains where analytical results are difficult to obtain. Alternatively, it can be used as a tool to examine the validity of the analytical approaches. Early observations of parabolic profiles in the appropriate regime of N and σ were made in such numerical calculations (*63, 68*). A subsequent study (*65*) of these numerical methods compared without free parameters to analytical results found excellent agreement of chain-unit and free-end density profiles for moderate chain lengths ($N = 200$) and coverage ($\sigma = 0.1$) for athermal chains (Fig. 4).

Extensions of the "Parabolic" Brush

Several important extensions of the simplest parabolic brush ideas have been made, which increase the range and variety of systems described.

Better equations of state. The SF numerical results and simulations show directly that as the coverage is increased, realistic equations of state or interparticle potentials cannot be represented by the lowest term in a virial expression (implying $\mu \propto \phi$ and a parabolic density profile). Two approaches have been taken to introduce more realistic equations of state analytically. The first approach (*8, 30*) equates the parabolic $\mu(z)$ to the chemical potential of a Flory-Huggins solution, which for athermal solvents ($\chi = 0$) is $\mu_{FH}(\phi) = \log(1 - \phi) + 1$; this gives immediately

$$\phi(z) = 1 - \exp[-\text{constant} + \pi^2 z^2/(8N^2)] \qquad (15)$$

which flattens for large coverage [the constant is fixed by normalization, $\int dz\phi(z) = \sigma$].

A very elegant approach by Zhulina, Borisov, and Priamitsyn (*31*) replaces $\mu \propto \phi$ with $\mu \propto a\phi + b\phi^2$ and recovers closed-form analytic expressions for density profiles and other quantities. As a (which measures the strength of two-body repulsions between chain units) varies, and in particular becomes negative, crossover is observed between swollen brushes ($h \sim N\sigma^{1/3}$ and parabolic ϕ) and collapsed brushes ($h \sim N\sigma$ and flat ϕ).

Shim and Cates considered both Flory-Huggins equation of state (with a nonzero χ parameter) and another important correction at high coverage; namely, finite chain extensibility (*69*). As coverage increases in a brush, chains eventually become highly extended, at which point the expression for stretching free energy of Eq. 1 and Eq. 8—which assumes the polymer is a flexible chain far from full extension ($h << Na$)—breaks down. They find qualitative agreement with SF numerical studies at high coverage.

Mixed chains. New and interesting behavior is encountered in brushes made of mixed chains; both chemically identical chains of different length and chemically dissimilar chains of the same length have been considered.

First, consider a brush made of chains of two different lengths. The shorter chains are harder to stretch; the curvature of $\mu(z)$ is larger for a brush made of shorter chains. Recalling the analogy to commuters, short chains are dedicated urbanites who find a long commute intolerable.

If chains of two different lengths are grafted randomly onto an interface, a vertical segregation of chain free ends occurs, with the short-chain free ends closest to the interface. [The case of general chain length distributions is solved analytically in (*29*).] If the total number of short and long chains at an interface is fixed, mixing of the chains is favored by the brush free energy. It turns out that the short chains act as spacers between longer chains, reducing the need for the long chains to stretch away from the interface.

This remarkable behavior might lead to the mixing in an insoluble monolayer of chemically dissimilar chains of different molecular weight, which would not mix in solution. Another consequence of short chains added to a long-chain brush to reduce the interactions between long chains is the drastic reduction of the bending stiffness of a mixed polymer-surfactant bilayer or copolymer layer relative to a linear mixing law (*16*). This behavior, reminiscent of the effect of short cosurfactants in reducing the bending constant of layers of longer tailed surfactant molecules, has been obtained theoretically by Szleifer, Ben-Shaul, Roux, and Gelbart using self-consistent configuration enumeration techniques appropriate for small molecules (*15*).

Another fascinating segregation effect occurs in brushes made of chemically dissimilar chains of the same length, which have been studied by Marko and Witten (*70*). Consider a brush made of a mixture of A and B chains randomly and irreversibly grafted to an interface. If the A-B interaction per chain in the mixed state is of order $k_B T$, perturbing the overall brush structure is unfavorable (assuming many $k_B T$ of stretching energy per chain), but breaking the degeneracy of free-end locations is favorable.

For example, A-chain ends may be confined to the portion of the end-density distribution nearest the interface, reducing the entropy per chain by order $k_B T$. This gives a region of pure B density far from the interface, so the A-B interactions are reduced by a factor of order unity. However, note that while the most likely chain configurations are various paths normal to the interface, there are random transverse fluctuations in these paths on the scale of R_g. These fluctuations could be perturbed to give an A-B concentration variation *along* the layers, at a cost also of order $k_B T$ per chain, with a reduction in A-B interactions again of order unity. A detailed calculation indicates that the transverse separation occurs first, for $\chi_{AB}N = 4.6$; such a transverse microphase separation would be very interesting to study experimentally.

Curved interfaces. Brushes grafted to interfaces that are not flat are an important and somewhat challenging subject for theorists. A wide variety of mesophases of diblock copolymer melts [micellar or ordered phases of spheres or cylinders, lamellar phases, and more exotic possibilities—see (*1*)], or possible phases of diblock copolymer-homopolymer mixtures analogous to microemulsions, all involve copolymer domains or layers in a curved geometry.

Further, finding the bending stiffness of a flat layer amounts to finding the increase in free energy of the flat layer when the layer is slightly curved. If the layer is uniformly curved (for example, is spherical or cylindrical), the problem of locating the chains is still one dimensional and may be tractable.

If it remains true that chain free ends can be located anywhere within a curved brush, then the osmotic pressure $\mu(z)$ must still be parabolic (the arguments given previously still apply); density profiles, bending stiffnesses, and so forth have been calculated with this assumption. Such results have been used by Wang and Safran to compute phase diagrams for the emulsification of homopolymers by nearly symmetric copolymers as a function of concentration and copolymer asymmetry (*17*). They find a series of transitions (sphere-cylinder-lamellae) and an "emulsification failure" instability analogous to short-chain surfactant systems (*71*).

Many groups (*12, 72, 73*) have made calculations of phase behavior for structures with *sharply* curved brushes present (the bending radius R is comparable to the brush height h). The use of the parabolic $\mu(z)$ here is problematic, as pointed out by Semenov in (*28*); for outwardly curved brushes (such as the outside of a sphere), the assumption of parabolic $\mu(z)$ leads to a contradiction: the density of free ends required to reproduce the chain-unit density turns out to be negative near the interface.

Thus a "dead zone," or region free of chain ends, must appear near the interface; then the argument that $\mu(z)$ is parabolic fails. The size of this dead zone is exponentially small when h/R is small, so calculations for nearly flat layers are unaffected (*16*). For sharply curved interfaces ($h \sim R$), parabolic estimates might be expected to be no improvement on simple Flory arguments.

However, for the specific case of a melt brush bent into a cylinder, Ball *et al.* have found an analytic solution for $\mu(z)$, for arbitrary radius of curvature, under strong-stretching conditions (*74*). They find that the dead zone in the limit of $R \to 0$ (chains grafted to a very small sphere) is still only a finite fraction of the brush volume. Furthermore, they show that even when $h/R = 1$, an estimate of the brush free energy in which a parabolic $\mu(z)$ is used is off by only a few percent. Thus, calculations baesd on a parabolic $\mu(z)$ for strongly curved brushes may be useful in practice.

There is another more serious concern about the use of strong-stretching descriptions in highly curved geometries; it is evident that for cylindrical or spherical substrates, increasing the chain length at fixed coverage does not lead to layer thicknesses large compared to unstretched chain dimensions. In fact, for spherical substrates, increasing N makes stretching smaller—much more volume is available in which chains may avoid each other. The only way to attain strong stretching in such cases is to increase the coverage (that is, in copolymer melts, to increase the tension between components). Thus, fluctuation effects may actually dominate in long-chain spherical micelles; this situation is described by the scaling arguments of Daoud and Cotton (*75*).

Fluctuation effects. Fluctuation effects lead to corrections in the strong-stretching limit that can narrow the gap between elegant analytic descriptions of brushes in the limit of infinite chain length and real brushes (or at least numerical calculations for finite N).

In the strong-stretching limit, many features of brushes may strike one as unphysical:

1) The density probe $\phi(z)$ has a discontinuous slope where it vanishes at $z = h$.

2) Although the free end locations can be found anywhere in the brush, once the free end location is known, the location of all other monomers in the chain is specified by the path of lowest free energy.

3) Brushes brought into contact do not interpenetrate (because a chain configuration that meanders into the opposite brush is more stretched and encounters more chain units than necessary).

All of these results are violated for finite h/R_g; some important properties of brushes depend crucially on the failure of these results. For example, Witten, Leibler, and Pincus (WLP) considered the viscosity of a strongly segregated lamellar phase of block copolymers when layers are sheared against each other (*22*). If the chains do not interpenetrate, there is no entanglement, and hence a small shear viscosity independent of chain length is found.

In fact, chains do interpenetrate in brushes brought into contact; to estimate this, WLP computed the work required (and thus the probability) for a "demon" to pull a chain end from one brush into the other. This method may also be used to estimate the size and shape of rounding of the sharp edge of the parabolic density profile by considering a brush chain pulled into the solvent. Similarly, the penetration of a solution of long homopolymers into a brush proceeds by one end of the homopolymer stretching into the brush against $\mu(z)$, as if pulled by a demon (*11*).

These arguments lead to a characteristic length l_p for penetration and a density profile well beyond $z = h$

$$l_p \sim N^{2/3}h^{-1/3}, \quad \phi(z) \sim \exp\{-\text{ constant } [(z - h)/l_p]^{3/2}\} \qquad (16)$$

This result was combined in (*22*) with an estimate of the time τ required to relax shear stress by retracting the overlapping (and thus entangled) chain, with the result

$$\tau \sim N^{25/9} \exp[\text{constant } N^{7/9}] \qquad (17)$$

The viscosity when a strong segregated lamellar phase is sheared within each layer may be larger still, again because of fluctuation effects. The transverse random fluctuations in chain paths can lead to entanglement of chains in a brush. Because the joint between dissimilar chains is localized at a narrow interface by segregation energy, the chains cannot freely reptate. Instead, stress must be relaxed by some combination of chain retraction and activated escapes of the chain from the interface, both of which lead to stress relaxation times that are exponential in chain length N (*76*).

The natural way to check such ideas about fluctuation corrections to the strongly stretched limit is by comparison to results from SF numerical methods. One such study showed that the scale and shape of the corrections to the chain-unity density profile and the free energy per chain were in accord with the arguments sketched above (*65*). Furthermore, the numerical prefactor in the corrections to the free energy per chain was extracted from the SF calculations for athermal chains and turns out to be small—which indicates that strong-stretching limit may be well attained for moderate values of h/R_g.

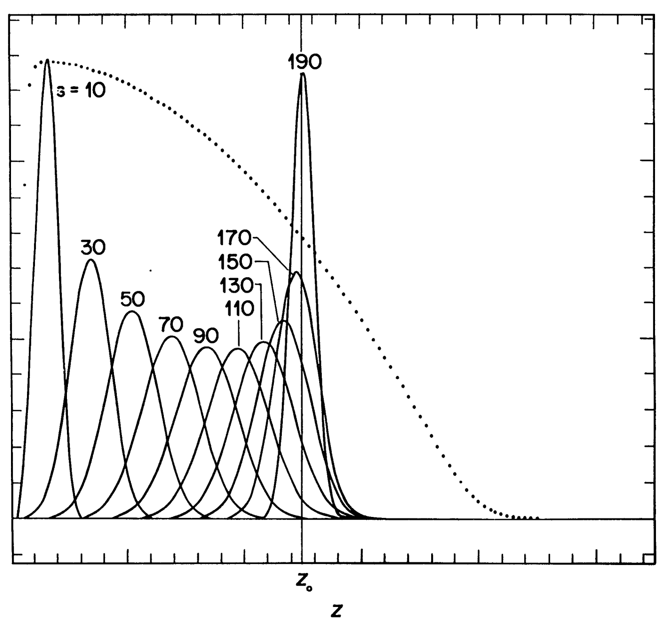

Fig. 5. Scheutjens-Fleer numerical results for the probability of finding the sth chain unit at z if the free end is located at z_0, for the indicated values of $s(N = 200)$. The dotted curve is the chain-unit density profile for reference. The mean chain-unit position is given by the most probable chain path; the widths of the peaks indicate fluctuations, analogous to quantum-mechanical broadening of wave packets. [Reprinted from (*65*) with permission ©The Chemical Society.]

Finally, SF studies may be used to inquire about the fluctuations in position of the sth chain unit of a chain with given end position, that is, fluctuations about the most likely chain path. The expected result may be found by making an analogy to a quantum-mechanical harmonic oscillator (*65*). If a parabolic potential is assumed, a narrow wave packet constrained to travel from the end location to the grafting surface broadens along the way; the SF results show precisely this behavior for fluctuations of a chain unit about its most probable path (Fig. 5).

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