morphology and processing properties of virgin PTFE are not an inherent property of the monomer or the equilibrium chain architecture but are primarily due to a very special polymerization process that produces polymer of an extremely large degree of polymerization and in a highly chain-extended form.

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Note Added in Proof. We have recently recalculated the MWDs from the data reported here using a different least-squares fitting routine. This new fitting routine allows a more objective judgment of the goodness of fit of the calculated curve to the data.[17] For PTFE this procedure gives essentially the same results as reported here, whereas for FEP copolymers the MWDs obtained with the two different procedures are found to be quite different.[17]

Registry No. PTFE, 9002-84-0.

References and Notes

(1) Plunkett, U.S. Patent 2 230 654.
(2) Hanford, W. E.; Joyce, R. M. *J. Am. Chem. Soc.* **1946**, *68*, 2082.
(3) Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encycl. Polym. Sci. Technol.* **1970**, *13*, 623.
(4) Smith, P.; Gardner, K. H. *Macromolecules* **1985**, *18*, 1222.
(5) Wu, C.; Buck, W.; Chu, B. *Macromolecules* **1987**, *20*, 98.
(6) English, A. D.; Garza, O. T. *Macromolecules* **1979**, *12*, 351.
(7) Wu, S. *Macromolecules* **1985**, *18*, 2023.
(8) Tuminello, W. H. *Polym. Eng. Sci.* **1986**, *26*, 1339.
(9) Starkweather, H. W.; Zoller, P.; Jones, G. A.; Vega, A. J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 751.
(10) Suwa, T.; Seguchi, T.; Takehisa, M.; Machi, S. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2183.
(11) Seguchi, T.; Suwa, T.; Tamura, N.; Takehisa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 2567.
(12) Suwa, T.; Takehisa, M.; Machi, S. *J. Appl. Polym. Sci.* **1973**, *17*, 3253.
(13) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(14) (a) Graessley, W. W. *Faraday Symp. Chem. Soc.* **1983**, *18*, 7. (b) Graessley, W. W. "Viscoelasticity and Flow in Polymer Melts and Concentrated Solutions" In *Physical Properties of Polymers*; Mark, J. E., Eisenberg, A., Graessley, W. W., Mandelkern, L., Koenig, J. L., Eds.; American Chemical Society: Washington, D.C., 1984.
(15) Liu, T.; Soong, D. D.; Williams, M. C. *J. Rheology* **1983**, *27*, 7.
(16) (a) Wu, S. *Polym. Mater. Sci.* **1984**, *50*, 43. (b) Wu, S. *Polym. Eng. Sci.* **1985**, *25*, 122.
(17) Tuminello, W. H., submitted for publication in *Polym. Eng. Sci.*
(18) Zoller, P. *J. Appl. Polym. Sci.* **1978**, *22*, 633.
(19) Starkweather, H. W. *J. Polym. Sci., Polym. Phy. Ed.* **1979**, *17*, 73.
(20) Chanzy, H. D.; Smith, P.; Revol, J.-F. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 557.
(21) Tobolsky, A. V.; Takahashi, M. *J. Appl. Polym. Sci.* **1963**, *7*, 1341.
(22) (a) Matsuo, K.; Stockmayer, W. H. *J. Phys. Chem.* **1981**, *85*, 3307. (b) Matsuo, K.; Stockmayer, W. H.; Needham, G. F. *J. Polym. Sci., Polym. Symp.* **1984**, *71*, 95.
(23) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(24) Smith, P.; Chanzy, H. D.; Rotzinger, B. P. *J. Mater. Sci.* **1987**, *22*, 523.
(25) Starkweather, H. W. *Macromolecules* **1977**, *10*, 1161.
(26) Starkweather, H. W. *Macromolecules* **1984**, *17*, 1178.
(27) Starkweather, H. W. *Macromolecules* **1986**, *19*, 1131.
(28) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(29) Schreiber, H. P.; Bagley, E. B.; West, D. C. *Polymer* **1963**, *4*, 355.
(30) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(31) Chu, B.; Wu, C.; Buck, W., submitted for publication in *Macromolecules*.

Theory of the Grafted Polymer Brush

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ABSTRACT: We calculate the free energy of surfaces coated with grafted polymers in a solvent. We use a self-consistent field (SCF) method appropriate for weak excluded-volume interactions and at moderately high surface coverage. We give the exact solution for the "classical limit" of our SCF equations which shows that, at high molecular weight, the concentration profile approaches a parabolic form rather than the step-function suggested by Alexander and de Gennes. Accordingly, the energy required to slightly compress the brush varies as the cube of the compression distance. An extension of the method to the good-solvent, semidilute regime is described.

Introduction

Polymers attached by one end to a substrate and immersed in solvent are a system of practical importance. Colloidal particles may be kept in suspension by grafting polymers onto their surfaces; the attached polymer layers repel each other and may keep the colloidal particles from aggregating. Equilibrium conformations of, and forces between, such polymer "brushes" have thus been the object of both theoretical[1–4] and experimental[5,6] study.

Previous theoretical treatments[1,2] of polymer brushes have employed either Flory arguments of global energy balance or scaling arguments which treat each polymer as a sequence of "blobs". In the former, the equilibrium height at fixed surface coverage is obtained by balancing the pairwise excluded-volume interaction with the free energy to stretch a typical chain away from the grafting

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surface. This balance gives (per unit area, in three dimensions) $w\sigma h^2/N \sim (N\sigma/h)^2$, or $h^* \sim N(w\sigma)^{1/3}$, where h is the brush height ($=h^*$ at equilibrium), N the molecular weight, σ the surface coverage, and w the excluded-volume parameter.

The scaling arguments[2] observe that the radius ξ of correlation blobs in the stretched, semidilute solution must be of the order of the distance between grafting points, in the limit $R_g \sim N^{1/2} \gg \sigma^{-1/2}$, if the solvent is good. The chains are envisioned as a string of blobs of size $\xi \sim \sigma^{-1/2}$ normal to the grafting surface. Each blob contains $g \sim \xi^{1/\nu}$ monomers, where $\nu \approx {}^3/_5$ is the swelling exponent. This gives a height h^* which scales as $(N/g)\xi \sim N\sigma^{1/3}$.

The Flory argument is expected to be valid for a high density of weakly interacting chains; scaling conditions obtain in the opposite limit. Both the Flory and the scaling argument suggest a step-function density profile for the brush: each assumes that any chain behaves in a manner identical with every other.

Repulsive forces between two grafted layers can be estimated[7] in the limit of strong compression ($h \ll h^*$) by ignoring all but the osmotic pressure. Forces in the limit of weak compresiion ($h \sim h^*$) have been estimated by arguing that the balance of stretch and repulsion energies gives rise to a quadratic minimum in the free energy about h^*.[7]

A numerical study of brush conformations and forces within a self-consistent mean-field approximation has also been performed by Hirz;[3] the study seems to confirm the scaling of h^* with σ but suggests a density profile rather different from the step function assumed in the Flory theory and in the scaling picture.

Our analytic treatment of the polymer brush, like that of Hirz, is based on a self-consistent field (SCF) approximation;[8,9] the monomer interactions are replaced by a position-dependent monomer chemical potential arising self-consistently from the calculated monomer density profile. For simplicity, our calculation assumes binary interactions between monomers, whereas that of Hirz uses a Flory–Huggins expression. The two choices of interaction should only differ at very high coverages, when the monomer density in the brush approaches saturation. Our calculation can readily be extended to the saturating case, as is briefly discussed in section 4.

Our method makes no assumption about the monomer density profile, but determines it self-consistently. The mean-field approximation used is realistic when the solvent quality is not too good and when the monomer concentration is sufficiently high (but not high enough to approach saturation). In practice, the signature of this mean-field regime of concentration is that the osmotic pressure of a uniform solution varies as the square of the concentration;[10] it is very likely that real grafted polymer brushes sometimes fall in this concentration range.

As is well-known, the self-consistent field approximation provides a powerful method to treat confined polymers, such as a chain squeezed between two plates.[9] Here the treatment simplifies, in the limit of long chains, because the physics is dominated by the ground state[9,11] of a closely related Schrödinger equation.

The SCF has also been used extensively to treat grafted chains[3,12,13] and other "end-constrained" polymers.[14-17] The latter studies concern block copolymer melts, in which the monomer chemical potential varies with position, but the monomer concentration is constant; the junction point of the block is constrained to lie at the interface between microphases. These end-constrained systems have proven harder to treat than confined polymers; ground-state dominance is not applicable. Thus the results so far have been chiefly numerical, using transfer-matrix methods or eigenfunction expansions of the Schrödinger equation.

Our new analytic approach to the grafted polymer brush exploits the fact that grafted chains of high molecular weight are increasingly strongly stretched relative to their ideal radius. In the limit of strong stretching, the partition function of the brush is dominated by the "classical paths" of the chains, and random-walk fluctuations about these paths can be neglected. This limit is opposite to one studied analytically by Gerber and Moore[18] (see also ref 4), who considered the case of brushes compressed so strongly that the brush height was smaller than the radius of gyration of a free chain ($h \ll R_g$). In that limit, ground-state dominance[18] is applicable; in contrast, for a free brush ($h = h^* \gg R_g$) or one under less extreme compression ($R_g \ll h < h^*$), the strong stretching assumption is valid instead.

In this "classical" limit of strongly stretched chains, the SCF treatment becomes greatly simplified, as first discussed by Semenov[17] for the copolymer melt case (see also ref 19). Indeed, the classical SCF formalism provides a powerful and elegant description of stretched chains, which is a natural counterpart to the ground-state dominance approach for chains in confined geometries. For the grafted polymer brush with binary interactions, we find that the classical SCF equations yield a simple, analytic solution: the concentration profile is parabolic. At moderate coverage and small w ($w^{(d-1)/(4-d)} \ll \sigma \ll 1$), this result should describe the exact limiting behavior of very long grafted chains.

The outline of our paper is as follows. In the first section, we present our "classical limit" SCF theory for strongly stretched chains. The fact that all the grafted chains have the same molecular weight is used, with general stability arguments, to infer the equilibrium parabolic brush profile. We compute the heights and free energies for the equilibrium brush and compare them with the Alexander–de Gennes Ansatz of a step-function profile, which is here shown to be unstable.

In section 2, we extend our theory to compressed brushes, and compute the free energy as a function of brush height, $F(h)$, for $h < h^*$. Again we compare to the step-function Ansatz; the free energy density for $h \ll h^*$ follows the (mean field) osmotic pressure in both cases, but the force at onset ($h \sim h^*$) between parabolic brushes is "softer" by a factor $h - h^*$ than that previously predicted from the step-function Ansatz. This is because the density at the outer fringe of the parabolic brush vanishes linearly with $h - h^*$, rather than being discontinuous there.

In section 3, we construct an "augmented" SCF theory which incorporates semidilute scaling exponents, appropriate to the description of polymer brushes in good solvents at low converage, in which semidilute conditions prevail. We find that the profile and compressibility are quite similar to those in the concentrated regime. Our approach is related to the scaling functional[20] used previously by de Gennes to discuss interfacial profiles for adsorbed polymers in solution. We solve the resulting model analytically in the uncompressed case and numerically in the compressed case. Finally, in section 4, we discuss some specific experimental consequences of our new predictions and outline further generalizations of the model and directions for future work.

1. The Equilibrium Brush

Our problem concerns the overall statistical properties of polymers on the scale of many monomers. Such properties may be treated by using a structureless model for the chains and their interactions, as discussed in ref 8 and 9.

Each grafted chain i in our system may be represented as a set of N monomer coordinates $\vec{r}_i(n)$, with $n = 0, 1, ..., N$. The free energy $F(K)$ for a surface of area A in the $x-y$ plane, with $K = \sigma A$ chains grafted to it, is given by

$$e^{-F(K)} = \sum_{\{\vec{r}_i(n)\}} e^{-(T+W)} \tag{1}$$

Here the coordinates $\vec{r}_i(n)$ are to be summed over the positive half-space $z > 0$ above the grafting surface. (For definiteness, the reader may imagine that the coordinates $\vec{r}_i(n)$ all lie on a fine-mesh lattice.) The boundary condition for grafted chains is that $z_i(N) = 0$ for each chain i.

The energy $T + W$ consists of the stretch free energy T and an excluded-volume energy W. The stretch energy is a sum of independent energies T_i for the individual chains. Since there are arbitrarily many coordinates n along the chain, it is natural to write T_i in continuum language[8]

$$T_i = \int_0^N \mathrm{d}n \, \frac{1}{2}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2 \tag{2}$$

The excluded-volume energy W, in d dimensions, has the form

$$W = \frac{1}{2}\int \mathrm{d}V \, w\phi^2(\vec{r}) \tag{3}$$

where $\mathrm{d}V = \mathrm{d}^d\vec{r}$ is the volume element, and the local concentration $\phi(\vec{r})$ is given by

$$\phi(\vec{r}) = \sum_{i,n} \delta(\vec{r} - \vec{r}_i(n)) \tag{4}$$

If the interaction strength w is small and the average concentration $\langle\phi\rangle$ is large, the mean-field approximation is valid. The criterion is that the "swelling length" λ (such that $w\lambda^{(4-d)} = 1$) at which single-chain self-avoidance first becomes important[21] must be larger than the distance $\sigma^{-1/(d-1)}$ between chains on the grafting surface. In this case, a chain emerging from the surface encounters many other chains before it noticeably avoids itself; each chain i interacts with itself and the others only through the average concentration $\langle\phi(\vec{r})\rangle$.

Under these conditions, the free energy change $F(K) - F(K - 1)$ to add a chain to the system is given by

$$e^{-(F(K)-F(K-1))} = \sum_{\{\vec{r}(n)\}} e^{-S_k} \tag{5}$$

where

$$S_i = \int \mathrm{d}n \left[\frac{1}{2}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2 - U(\vec{r}(n))\right] \tag{6}$$

and the effective potential $U(\vec{r}) = -w\langle\phi(\vec{r})\rangle$. The concentration $\langle\phi(\vec{r})\rangle$ is to be determined self-consistently. The single-chain partition function of eq 5 and 6 is (to within factors of $i = (-1)^{1/2}$) analogous to the path integral for one-particle quantum mechanics[8,9] in a potential $U(\vec{r})$; S in eq 6 corresponds to the action $\int \mathrm{d}t \, (T - U)$ with T the kinetic energy of the particle, and $\vec{r}(n)$ is in position at "time" n.

1.1. The Classical Limit of the SCF Equations. The scaling and/or Flory analyses of Alexander[1] and de Gennes[2] provides us with an important insight. As noted above, these analyses show that chains in a brush are strongly stretched; for large molecular weight N the brush height, $h \sim N$, becomes much larger than the unperturbed radius, $R_0 \sim N^{1/2}$. A chain whose free end is at $\vec{r}(0) \equiv \vec{\rho}$ fluctuates weakly about some definite path $\vec{r}(\vec{\rho},n) \sim n$ with an amplitude of order $R_0(n) \sim n^{1/2}$. Such fluctuations are unimportant in the overall properties of the polymer brush. Thus these chains approach the "classical limit" of our quantum mechanics, in which the only important paths are those which minimize the action S. That is, a chain beginning at $\vec{\rho}$ follows that path $\vec{r}(\vec{\rho},n)$ which minimizes S (eq 6) for the given potential $U(\vec{r})$, subject to the boundary condition that $z(N) = 0$ (which ensures that the path terminates, at "time" = N monomers, at the grafting surface).

The minimized action, $S_{\min} \equiv s(\vec{\rho})$, is closely related to the free energy F for a set of K chains whose ungrafted (free) ends are held fixed at spatial positions $\vec{\rho}_1, ..., \vec{\rho}_K$. Specifically, the configuration sum in eq 5 is dominated by the path which minimizes S, so that up to an unimportant additive constant, $F(K) - F(K - 1) = s(\vec{\rho}_K)$. Alternatively, the total free energy $F(K)$ can be expressed directly (in the classical limit) by substituting the classical trajectories $\vec{r}_i(n) = \vec{r}(\vec{\rho}_i,n)$ into the following general expression:

$$F = \sum_{i=1}^{K} \int \mathrm{d}n \left[\frac{1}{2}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2\right] + \frac{1}{2}w \int \mathrm{d}V \, \phi^2(\vec{r}) \tag{7}$$

This free energy then becomes simply the sum of Gaussian stretch energies and pairwise excluded volume for chains whose free ends are held at positions $\vec{\rho}_1, ..., \vec{\rho}_K$ and that follow the corresponding classical paths $\vec{r}(\vec{\rho}_i,n)$ in the potential $U(\vec{r}) = -w\phi(\vec{r})$. The monomer density $\phi(\vec{r})$ is to be calculated self-consistently by substitution of the classical trajectories $\vec{r}(\vec{\rho}_i,n)$ into eq 4; the resulting free energy must finally be minimized over the positions $\vec{\rho}_i$ of the free chain ends to determine the equilibrium state of the brush.

Note that from eq 7, the change in free energy ΔF_i upon removing the ith chain (keeping all others fixed) is simply the action S_i given by eq 6:

$$\begin{aligned}\Delta F_i &= \frac{1}{2}\int \mathrm{d}n \left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2 + \int \mathrm{d}V \, \frac{\delta F}{\delta\phi}(\vec{r}_i)\delta\phi(\vec{r}_i) \\ &= \frac{1}{2}\int \mathrm{d}n \left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2 + \int \mathrm{d}n \, \frac{\delta F}{\delta\phi}(\vec{r}_i(n))\end{aligned} \tag{8}$$

The second of these expressions reduces to the single-chain action S_i of eq 6 when one substitutes the mean-field expression for the effective potential $U(\vec{r}) = -\delta F/\delta\phi(\vec{r}) = -w\phi(\vec{r})$.

In the classical limit, when the free energy of the system (eq 7) is stationary under variation in the path of any chain, each single-chain action S_i is separately minimized with respect to the path $\vec{r}(\vec{\rho}_i,n)$. This variation may be taken in two parts. If we fix the chain end $\vec{\rho}_i$ and vary the rest of the path, we obtain the "equation of motion" for the chain,

$$\frac{\mathrm{d}^2\vec{r}_i}{\mathrm{d}n^2} = -\nabla_{\vec{r}}U, \qquad U = -\frac{\delta F}{\delta\phi} \tag{9}$$

as would describe the classical mechanics of a particle in the potential U. If we now vary the position $\vec{\rho}_i$ of the chain end, all the while satisfying the equation of motion, we must have at equilibrium

$$\frac{\partial S(\vec{\rho}_i,\vec{r}_i(n))}{\partial\rho_i} = \frac{\partial s}{\partial\rho_i} = 0 \tag{10}$$

where $\vec{r}_i(n)$ satisfies the equation of motion, eq 9.

1.2. The Equal Time Constraint. To proceed further, we make use of the analogy between chain conformation $\vec{r}(n)$ and the path of a fictitious classical particle of unit mass moving in a potential $U(\vec{r})$. From eq 9, we see that the monomer index n is to be identified with time, and the local stretching rate, $d\vec{r}/dn$, with the velocity of the particle. Moreover, each fictitious "particle" starts some distance away from the wall (grafting surface) with zero velocity:

$$\frac{d\vec{r}}{dn}(\vec{\rho}_i,0) = 0 \tag{11}$$

Equation 11 can be simply understood in terms of the mechanical equilibrium of a chain: unless an external force is applied to the end of a chain, the stretch $d\vec{r}/dn$ must vanish there.[22] The starting point $\vec{\rho}$ of a particle corresponds to the position of the free end of a polymer chain. The particle falls toward the wall from $\vec{\rho}$ in the potential $U(\vec{r})$ and reaches it in a time $N(\vec{\rho})$.

For the particular case of a polymer brush, we need only consider a one-dimensional motion, since we expect translational invariance parallel to the grafting surface, so that $U(\vec{r}) = U(z)$.

The condition that all the chains are the same length N turns out to be surprisingly powerful, allowing us to guess the form of $U(z)$ immediately. Because the time integral along the path of a particle is equal to the molecular weight N, all particles must reach the wall in the same time regardless of their starting point. Our potential U is thus an equal-time potential.

If all the free chain ends were at the same distance from the wall, as in the Alexander–de Gennes Ansatz of a step-function profile, this equal-time constraint would tell us nothing. In contrast, if the free ends are distributed with nonzero density over the entire height of the brush, the equal-time requirement forces the effective potential to be that of a harmonic oscillator: $U(z) \propto z^2$ + constant. Such a potential clearly satisfies the equal-time requirement, since the period $N(\rho)$ of a particle moving in it is independent of its amplitude ρ; that it is unique may be seen from a step-by-step construction starting at the wall, requiring throughout that $N(\rho + \delta\rho) = N(\rho)$.

This construction exploits the fact that there are always some chains whose ends are at ρ, wherever ρ lies in the brush. On the other hand, the potential $U(z)$ will not be harmonic if there are one or more intervals in the height coordinate z at which the density of ends vanishes. We will call such intervals "dead zones"; the step-function Ansatz then corresponds to a single dead zone the entire height of the brush. It will be demonstrated below that such brush configurations are, quite generally, not of minimum free energy.

Presuming the effective potential to be parabolic and writing $-U(z) = A - Bz^2$, we can fix B by the equal-time requirement. The angular frequency of a harmonic oscillator with unit mass and "spring constant" $2B$ is $(2B)^{1/2} = 2\pi/\tau$. The path of each of our fictitious particles is a one-quarter cycle, so $\tau = 4N$ and

$$B = \pi^2/8N^2 \tag{12}$$

Since in mean field the effective potential $U(z)$ is related to the monomer density $\phi(z)$ by $U(z) = -w\phi(z)$, our Ansatz for $U(z)$ means that the density profile obeys

$$\phi(z) = w^{-1}(A(h) - Bz^2)\theta(h - z) \tag{13}$$

The constant $A(h)$ is fixed by computing the net amount of material in the brush per unit area of surface and equating this with $N\sigma$, which is the total surface density of grafted chain:

$$N\sigma = \int_0^h dz\ \phi(z) \tag{14}$$

which implies

$$A(h) = \frac{N\sigma w}{h} + \frac{Bh^2}{3} \tag{15}$$

Since $\phi(z)$ cannot be negative, the maximum possible value of the brush height, $h_{\max}$, obeys $h_{\max} = (A(h_{\max})/B)^{1/2}$. From eq 15 we find $h_{\max} = (12/\pi^2)^{1/3}(\sigma w)^{1/3}N$. For the moment, we shall treat the brush height h as a parameter; we will find below that at equilibrium, for a brush under no external forces, $h = h_{\max}$.

1.3. The Parabolic Profile. To check that our parabolic profile, eq 13, is the true equilibrium state (considered for the moment at some imposed brush height h) we must show (1) that the density profile $\phi(z)$ is realizable, i.e., that it arises from a nonnegative density of ends $\epsilon(z)$, and (2) that there is no unbalanced force on the end of any chain, i.e., that $\partial\varsigma/\partial\rho = 0$ over the entire height of the brush ($0 < \rho < h$). These criteria uniquely determine the profile, so long as there are no dead zones; finally, then, we must show (3) that there are no such zones. Last of all, we must determine the equilibrium value $h = h^*$ for a brush under no external forces. By these several stages, a particular parabolic profile shall be shown to be the unique solution of the SCF equations in the classical (long-chain) limit. The reader not interested in the details of steps 1–3 may, at this point, proceed directly to section 1.4.

1.3a. Nonnegativity of $\epsilon(z)$. For a brush configuration to be physically meaningful, the monomer density $\phi(z)$ must arise from a positive density of chain ends $\epsilon(z)$ with the chains obeying the equation of motion (eq 9). The monomer density $\phi(z)$ is a sum of the contribution $dn/dz_i(z)$ (monomers per unit length) that each chain i makes at the position z:

$$\phi(z) = \sum_i |dz_i/dn|^{-1} \tag{16}$$

We may write $\phi(z)$ in terms of $\epsilon(z)$ as

$$\phi(z) = \int_z^h d\rho\ \epsilon(\rho)\left|\frac{dz}{dn}\ (\rho;z)\right|^{-1} \tag{17}$$

where $dz/dn\ (\rho;z)$ is the velocity at z of a particle which began at ρ.

It is clear that any profile $\phi(z)$ which is a decreasing function of z arises from a nonnegative $\epsilon(z)$. The function $|dz/dn\ (\rho;z)|^{-1}$ decreases as z decreases, which means that a chain end produces a profile $d\phi(z)$ which is an increasing function of z. Starting away from the wall (at $z = z_{\max}$), we can in principle construct any decreasing profile $\phi(z)$ by adding new chain ends as they are needed.

Explicitly, using results of Semenov,[17] we find that for the general parabolic profile eq 13, the end density $\epsilon(z)$ obeys

$$\epsilon(z;h) = \frac{4(2^{1/2})B^{3/2}}{\pi w}[2z(h^2 - z^2)^{1/2} + (A/B - h^2)z(h^2 - z^2)^{-1/2}] \tag{18}$$

(Here, the first term is the equilibrium end density in a brush under no external force; for a compressed brush, the second term gives an extra contribution. See Figure 1.)

1.3b. Local Stability of the Parabolic Profile. For our parabolic profile (eq 13) to be valid, the free energy must be stationary with respect to a change in the end positions ρ_i (eq 10). We now show that this holds, i.e., that $\partial\varsigma(\rho)/\partial\rho = 0$ for any chain in the brush (for all ρ, $0 < \rho < h$). In polymer language the change $\Delta\varsigma$ in energy under a displacement $\Delta\rho$ of the end is the work done against the end tension, $d\vec{r}/dn|_{n=0}\ \Delta\vec{\rho}$. Since our solution was con-

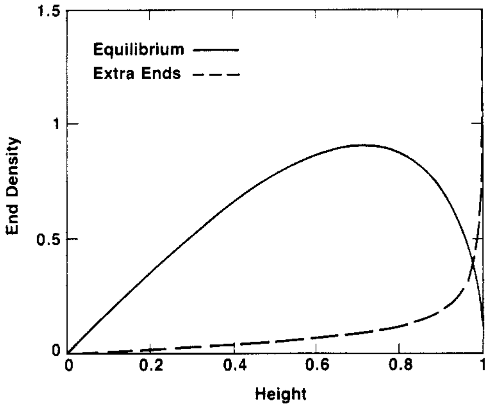

Figure 1. End density $\epsilon(z;h)$ from eq 18. The two terms of eq 18 are plotted separately. The divergent term is absent for the uncompressed brush.

structed with $\mathrm{d}\vec{r}/\mathrm{d}n = 0$ at the ends, we expect $\partial s/\partial \rho$ to vanish as required.

To demonstrate this, we show that an equal-time potential $U(z)$ implies $\partial s(\rho)/\partial \rho = 0$ for paths $z(n)$ satisfying the equation of motion. Consider the action of a particle in an equal-time potential,

$$\mathcal{S} = \int_0^N \mathrm{d}n \left[\frac{1}{2}\dot{z}^2(n) - U(z(n)) \right] \tag{19}$$

where $\dot{z} = \mathrm{d}z/\mathrm{d}n$ and $z(n)$ is a solution of the equation of motion, $\ddot{z} + \partial U/\partial z = 0$. The functions $\dot{z}(\rho,n)$ and $z(\rho,n)$ depend on the starting point $\rho = z(0)$. The time interval $(0,N)$ is constant for ρ in some interval, because $U(z)$ is an equal-time potential.

Consider varying the action with respect to ρ:

$$\frac{\partial s}{\partial \rho} = \int_0^N \mathrm{d}n \left[\dot{z}(n)\frac{\partial \dot{z}}{\partial \rho}(n) - \frac{\partial U}{\partial z}\frac{\partial z}{\partial \rho}(n) \right] \tag{20}$$

$$= \int_0^N \mathrm{d}n \left[\dot{z}(n)\frac{\partial \dot{z}}{\partial \rho}(n) + \ddot{z}\frac{\partial z}{\partial \rho}(n) \right] \tag{21}$$

$$= \dot{z}(n)\frac{\partial z}{\partial \rho}(n)\Big|_0^N \tag{22}$$

If the particles start at rest, $\dot{z}(0) = 0$; if the particles all end at the wall, $\partial z(N)/\partial \rho = 0$. Hence $\partial s/\partial \rho = 0$ and s is constant in any interval where ends are found.

1.3c. Absence of Dead Zones. Our discussion above shows that the parabolic brush, eq 13, is a local minimum in free energy. We now show that it is a global minimum. We do this by ruling out the other possible solutions mentioned at the outset—namely, those with "dead zones" from which chain ends are excluded. We show that these are unstable: an end may be displaced slightly in a way which lowers its action s.

For example, we may reduce s in the step-function brush by moving one end slightly into the brush. Now an external force is needed to hold this end in place (i.e., a nonzero initial velocity is required for it to reach the surface in the required tine N). And now S is no longer stationary with respect to movements of the chain end; as the end moves closer to the wall, the chain lowers its stretch energy but pays no higher price in excluded-volume interaction (since the density profile is flat). Such a chain would, when released, snap back to the wall, lowering its free energy. (The next chain allowed to move its end will snap back to the wall until it encounters the slightly higher monomer density produced by the first chain, and so forth; thus a parabola may be constructed.)

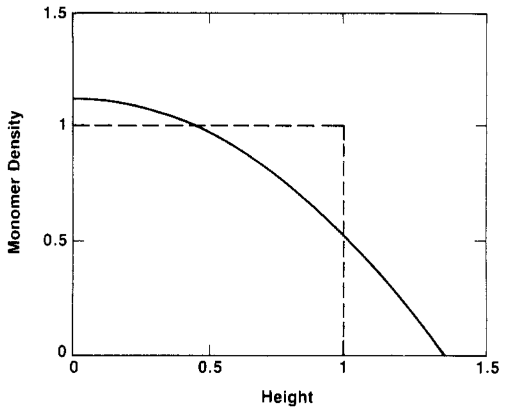

Figure 2. Density profiles $\phi(z)$ of the parabolic brush and the step-function Ansatz at equal coverage σ and molecular weight N.

In general, a dead zone could be of arbitrary width and could occur at an arbitrary position in the brush. But in any such zone the concentration $\phi(z)$ must be constant. This is clear if we rewrite eq 17 for $\phi(z)$ in terms of the potential $U = -w\phi$. Using conservation of energy for our fictitious particles, $^1/_2(\mathrm{d}z/\mathrm{d}n)^2 + U(z) = U(\rho)$, we obtain

$$\phi(z) = \int_{z_\mathrm{b}}^h \mathrm{d}\rho\ \epsilon(\rho)(2w(\phi(\rho) - \phi(z)))^{-1/2} \tag{23}$$

where z_b is the outer edge of the dead zone. This is the same equation for all z in the dead zone, since the same set of chains contributes throughout the zone. Thus a constant $\phi(z)$ is a solution, and, since this equation determines $\phi(z)$ uniquely, $\phi(z)$ must be a constant. Next, we note that the potential $U(z)$ must jump up discontinuously at z_b, because particles starting just beyond z_b need a finite initial velocity to reach the wall in the same time as particles starting from rest at the opposite border of the zone.

Now it is clear that a dead zone is unstable, just as the full step-function brush was. Any end drawn into the dead zone from just beyond requires an external force to keep it in its new position. As before, its free energy s must be lowered by allowing this end to withdraw across the zone. This is clear from eq 22; if we relax the requirement that $\dot{z}(0) = 0$, we obtain $\partial s/\partial \rho = -\dot{z}(0)$. If a chain is drawn into the zone, $\dot{z}(0) < 0$ (initial velocity of particle is toward the wall), then reducing ρ reduces s. Since dead zones are locally unstable, the equilibrium configuration is the parabolic potential, without dead zones.

1.4. The Equilibrium Brush Height; Free Energy Calculation. The above analyses complete our demonstration that the equilibrium brush profile, in the classical SCF limit, is a parabola. We must now specify the equilibrium brush height h^*; with eq 15, this determines A. The equilibrium height $h = h^*$ may in fact be determined by demanding that the density profile $\phi(z)$ has no discontinuity at $z = h$ but vanishes smoothly there.[23] This fact will be explicitly confirmed in section 2, when we compute the free energy $F(h)$ for $h < h^*$ in our discussion of brushes under external compression. Hence $h^* = h_{\max}$ as defined under eq 15:

$$h^* = h_{\max} = (12/\pi^2)^{1/3}(\sigma w)^{1/3}N \tag{24}$$

This corresponds to a profile

$$\phi(z) = (B/w)((h^*)^2 - z^2) \tag{25}$$

which vanishes smoothly at the outer edge of the brush. (See Figure 2.)

We shall now compute the free energy of this parabolic brush. We may construct the brush by progressively adding chains; the change in system free energy upon adding a chain is $s(\sigma)$ for that chain. Since $s(\sigma)$ is independent of where the chain end lies (see section 1.3b), we may evaluate the change in free energy to add a chain by considering one which starts very near the wall. Such a chain has no stretch energy; its potential energy is just $U(0)N$, so that $s = AN$. We may simply integrate to get the free energy per chain, $F/\sigma \equiv \mathcal{F}$:

$$\mathcal{F} = \frac{1}{\sigma}\int_0^\sigma \mathrm{d}\sigma'\; s(\sigma') \qquad (26)$$

Using $(h^*)^2 = A/B$, eq 12 for B, and eq 24 for $h^*(\sigma)$, we find for $A^*(\sigma)$ the expression

$$A^*(\sigma) = (3/2)(\pi^2/12)^{1/3}(w\sigma)^{2/3}$$

and so the equilibrium free energy per chain is

$$\mathcal{F}^* = 9/10(\pi^2/12)^{1/3}(w\sigma)^{2/3}N \qquad (27)$$

We can compare this free energy with that of the step-function profile postulated by Alexander and de Gennes. To compute the latter we must minimize the sum of stretch and repulsion energies to find h^*. The results are

$$\mathcal{F}_{\text{step}} = \frac{h^2}{2N} + \frac{wN^2\sigma}{2h} \qquad (28)$$

$$h^*_{\text{step}} = N(w\sigma/2)^{1/3} \qquad (29)$$

$$\mathcal{F}^*_{\text{step}} = 3(2^{-5/3})(w\sigma)^{2/3}N \qquad (30)$$

We note that ratio of the parabolic to step-function brush free energy is about 0.89; the ratio of the parabolic to step-function equilibrium height is about 1.3.

Both F and h for the two configurations scale in the same way with N, σ, and w. They must, because in both cases the height is proportional to N, and there is only one relevant length scale in the mean-field problem. That scale is the Edwards correlation length ξ_{E}; it may be taken as the radius of a Gaussian random walk which has interaction energy of order unity ($kT = 1$) with the background concentration of other chains, i.e., $w\phi\xi_{\text{E}}^2 \sim 1$. (The grafting distance $\sigma^{-1/(d-1)}$ is irrelevant in a mean-field problem except as it enters the concentration; the length λ is not pertinent because it is essentially ξ_{E} for a chain interacting only with its own mean field.) Monomer conservation implies $\phi \sim N\sigma/h$; then $h \sim N$, together with the requirement that N only enter as R_g^2, implies $h \sim N/\xi_{\text{E}}$ (by dimensional analysis). These three relations together give $\xi_{\text{E}} \sim (w\sigma)^{-1/3}$; thus $h \sim N/\xi_{\text{E}}$ scales as $N(w\sigma)^{1/3}$ and $F^* \sim w\phi^2h/\sigma \sim h^2/N$ scales as $N(w\sigma)^{2/3}$.

In section 3, we will consider the case where $\lambda < \sigma^{-1/(d-1)}$, so that the chains are swollen on length scales smaller than the distance $\sigma^{-1/(d-1)}$ between grafting sites; in that case, $\sigma^{-1/(d-1)}$ between grafting sites; in that case, $\sigma^{-1/(d-1)}$ replaces ξ_{E} as the length scale in the problem. (The mean-field arguments giving rise to ξ_{E} no longer apply, and λ itself only pertains to intrablob properties.)

Though our self-consistent description of the brush has the same scaling as the step-function Ansatz, its detailed predictions are substantially different. In particular, the parabolic brush has a density which gradually falls to zero from its maximum near the wall over the entire height of the brush. The Alexander–de Gennes Ansatz would predict instead a flat density profile that falls abruptly to zero over a narrow region at the outer edge of the brush, the width of this region becoming negligible compared to the total brush height, in the large-N limit. Another major difference is in the distribution of chain ends, which we predict to be spread through the entire height of the brush, rather than restricted to a similarly narrow region. (See Figures 1 and 2.)

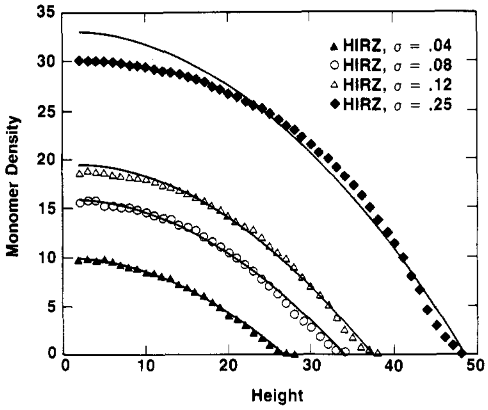

Figure 3. Density profiles $\phi(z)$ of the present theory (solid lines) with numerical mean-field results of Hirz[3] for indicated values of coverage σ.

We may make some comparisons with numerical results of Hirz,[3] based on theories of Scheutjens and Fleer.[12] Hirz solved numerically within self-consistent mean-field theory on a lattice for the probabilities of finding the jth monomer in a grafted chain at the kth site above the grafting surface. She found monomer–density profiles at various values of σ for $N = 200$ which scale by coverage into a single curve well fit by our parabolic profile. In particular, for values of σ ranging over a factor of 6, for which the brush height scales as $\sigma^{1/3}$,[3] the same value of B/w (which we predict to be independent of σ) in $\phi(z) = w^{-1}(A - Bz^2)$ fits all of Hirz' curves. (See Figure 3.)

The difference seen at high coverage between our profile and Hirz' calculation is presumably due in large part to the different treatment of the excluded-volume repulsions. Recall that while our calculation is based on binary monomer interactions, that of Hirz uses a Flory–Huggins expression, which partially incorporates saturation effects. (These saturation effects will be discussed further in section 4.) As is evident from Figure 3, the two descriptions are in very good agreement at lower coverages.

2. Compressed Brushes

We next consider the case of two brushes compressed together so that the separation l between grafting surfaces or "plates" is $l < 2h^*$. We expect a density profile with a minimum halfway between the two plates. In the classical limit, this means that there can be no "interdigitation" of chains from the two surfaces. This corresponds to the fact that a fictitious classical particle falling from rest in the potential $U = -w\phi$ (which has a symmetric maximum between the plates) will always travel to the nearer of the two plates.

Since there is no interdigitation, we may consider each of the two brushes separately, with only $l/2 = h < h^*$ as a parameter. Each brush will have a parabolic density profile; the two profiles meet at a cusp midway between the two grafting surfaces. The arguments of the previous section about equal time and equal action still apply; correspondingly, the profile $\phi(z)$ is given by eq 13 with $h < h^*$. We may use eq 15 for $A(h,\sigma)$, eq 24 for $h(\sigma)$, and eq 26 for $F(\sigma)$. We must integrate eq 26 in two steps, as we build the brushes up until they first touch (during which $h(\sigma)$ increases) and then add the remaining chains (during which h is fixed, while A continues to increase). The result is ($u \equiv h/h^*$)

$$\mathcal{F} = N(\sigma w)^{2/3}(\pi^2/12)^{1/3}\left[\frac{1}{2u} + \frac{1}{2}u^2 - \frac{1}{10}u^5\right] \qquad (31)$$

The functional form of $\mathcal{F}(h)$ for the equilibrium parabolic brush differs from that of a postulated step-function brush, which has (with $u \equiv h/h^*_{\text{step}}$)

$$\mathcal{F}_{\text{step}} = N(w\sigma/2)^{2/3}\left[\frac{1}{u} + \frac{1}{2}u^2\right] \tag{32}$$

We expect our parabolic brush to be "softer" than the postulated step-function brush[7] for small compressions, because $\phi(z)$ vanishes linearly as $z \to h^*$, rather than jumping discontinuously to zero there. Indeed, expanding in $\Delta \equiv 1 - u$, we find, in lowest nontrivial order

$$\mathcal{F} \approx N(\sigma w)^{2/3}(\pi^2/12)^{1/3}\left[\frac{9}{10} + \frac{3}{2}\Delta^3\right] \tag{33}$$

whereas in contrast (from eq 32)

$$\mathcal{F}_{\text{step}} \approx N(w\sigma/2)^{2/3}\left[\frac{3}{2} + \frac{3}{2}\Delta^2\right] \tag{34}$$

Our result (eq 33) for the free energy increment $\delta\mathcal{F} \sim \delta h^3$ can be simply understood by considering the force needed to compress a brush to some $h < h^*$, by replacing one of the brushes with an impenetrable barrier at $z = h$. Because the chain ends are not under tension, the force on the barrier is purely the osmotic pressure, $\Pi = w\phi^2/2$. When the brush is compressed, the profile $\phi(z) = (A - Bz^2)/w$ changes only in that A increases to incorporate the monomers in a shorter brush (see eq 15). We have $\delta A = w\delta\phi(0)$ of order $B\delta h^2$ (this results from taking a small wedge from the end of the equilibrium brush and spreading it uniformly over the height). Hence the monomer density near the end of the brush is simply $\phi(h^* - \delta h) \sim Bh^*\delta h/w$, where we estimate $\phi(h^* - \delta h)$ from the equilibrium profile, neglecting the change in A upon compression. Using $\delta\mathcal{F} = \Pi\delta h$, $h^* \sim n(w\sigma)^{1/3}$, and the expression for Π above, we derive $\delta\mathcal{F} \sim N(w\sigma)^{2/3}(\delta h/h^*)^3$.

In the opposite limit of strong compression, $h \ll h^*$, both the step-function Ansatz (eq 32) and the formula for the parabolic profile (eq 31) predict a free energy $F(h)$ that is dominated by the excluded-volume interaction. This equivalence is not surprising, since one normally expects Flory-type arguments to reproduce correctly the asymptotic power laws obtained from a full SCF calculation. We emphasize, however, that in applications such as colloidal stabilization it is the opposite limit of small compression that is more relevant; in this limit, our results differ significantly from those obtained using the step-function Ansatz.

3. Swollen Brushes

The results of the previous section are applicable to brushes at moderately high surface coverage and/or small excluded-volume parameter w, for which the chain density near the surface lies in the regime described by concentrated solution theory ($\Pi \sim \phi^2$). We now extend some of these results to the case of brushes in better solvents and/or at lower surface coverages σ. In this semidilute regime, correlations between and within chains are important, and so we will need a different expression for the free energy. We envision the chains as composed of correlation blobs which fill space and the chains of blobs as performing Gaussian random walks which are weakly perturbed locally (although strongly stretched on a larger scale). The validity of this assumption is discussed in section 3.2. For concentration ϕ, the radius $\xi(\phi)$ and number of monomers $g(\phi)$ of a blob in spatial dimension d satisfy $\phi \sim g(\phi)/(\xi(\phi))^d$ and $\xi(\phi) \sim g(\phi)^\nu$, where ν ($\approx {}^3/_5$ for $d = 3$) is the Flory swelling exponent. The elastic energy T_i needed to stretch a chain weakly is the same as if each blob were undistorted. Thus T_i of eq 2 is replaced by

$$T_i \approx \sum_{\text{blobs}}\left(\frac{\Delta\vec{r}_{\text{blob}}}{\xi}\right)^2 = \frac{\upsilon}{2}\int \mathrm{d}n \left(\frac{\mathrm{d}\vec{r}}{\mathrm{d}n}\right)^2 \phi^\alpha(\vec{r}(n)) \tag{35}$$

where the sum is over blobs in chain i, $\alpha = (2\nu - 1)/(d\nu - 1)$ and υ is a dimensioned constant which is nonuniversal (i.e., it depends on microscopic parameters such as the persistence length of the chains).

The pairwise excluded-volume interaction of eq 3 is replaced by an excluded-volume energy of order unity per blob (expressed in units of kT), giving a system free energy of

$$F = \upsilon\sum_i \int \mathrm{d}n \left[\frac{1}{2}\left(\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}n}\right)^2 \phi^\alpha(\vec{r}(n))\right] + s\int \phi^{\beta+1}(\vec{r})\ \mathrm{d}V \tag{36}$$

where as before the sum i runs over all chains. Here $\beta \equiv 1/(d\nu - 1)$ and s is another nonuniversal dimensioned constant. Alternatively, F may be expressed as a volume integral $\int f\ \mathrm{d}V$, where $f = \Sigma + P$ is the sum of a stretch contribution Σ and an excluded-volume contribution $P = s\phi^{\beta+1}$.

The stretch contribution Σ has a simple form when all the chains are stretched in a common direction $\hat{z}$, as in the case of a grafted brush. We write $\mathrm{d}n\ (\mathrm{d}z_i/\mathrm{d}n)^2$ as $\mathrm{d}z_i \times (\mathrm{d}z_i/\mathrm{d}n)$, and define $\eta(z)$ as the number of chains per unit area at height z above the grafting surface. Then

$$\Sigma = (\upsilon/2)\eta(z)\phi^\alpha(z)\langle \mathrm{d}z/\mathrm{d}n\rangle$$

where $\langle \mathrm{d}z/\mathrm{d}n\rangle$ is the average over the chains at the point in question.

In fact, this Σ is proportional to the average tensile stress in the chains at height z. The tension on the chain i at height z_i is $\upsilon\phi^\alpha\ \mathrm{d}z_i/\mathrm{d}n$, as one may verify from eq 35 by taking $\mathrm{d}T_i/\mathrm{d}z(n)$ with $z(0)...z(n-1)$ fixed. Adding the force on the $\eta \mathrm{d}A$ chains in a small area $\mathrm{d}A$, we obtain the tensile stress or force per unit area $\upsilon\eta\phi^\alpha\langle \mathrm{d}z/\mathrm{d}n\rangle = 2\Sigma$.

Were one to assume conditions of ground-state dominance, the free energy, (36), that we have written down could be used to derive the scaling functional used by de Gennes[21,20] to discuss various polymer adsorption phenomena. For the grafted brush, however, it is appropriate to make the opposite assumption, that the chains are strongly stretched at large length scales, as has already been described in section 1.1.

3.1. Classical SCF Treatment for the Semidilute Brush. As in eq 8 for the concentrated brush, we write the effective single-chain free energy S as the sum of its stretch energy and a potential $-U = \delta F/\delta\phi(\vec{r}) = \partial f/\partial\phi$. In contrast to the mean-field case, $\delta F/\delta\phi$ now contains two terms:

$$(\delta F/\delta\phi)(\vec{r}) = (\beta + 1)P/\phi + \alpha\Sigma/\phi \tag{37}$$

This expression shows the two effects on the system free energy of adding a monomer at $\vec{r}$. First, the monomer feels the usual osmotic compressibility $\sim\phi^\beta$ ($\beta \approx {}^5/_4$ for $d = 3$ and $\nu \approx {}^3/_5$) of the semidilute solution. Second, adding a monomer increases the stretch energy of other chains passing through $\vec{r}$. This is because adding a monomer at $\vec{r}$ reduces the size of the blobs there. Other stretched chains passing through the region have more blobs, and hence larger stretch energy.

A quantity closely related to $\delta F/\delta\phi$ is the osmotic pressure $\Pi(z)$. For a uniform system $\Pi = -\mathrm{d}F/\mathrm{d}V$. For the present system $\Pi(z)$ is the pressure against a semipermeable membrane at z perpendicular to the grafting plane and parallel to the chains. In terms of the free energy f per unit volume, $\Pi(z) = -f + \phi\partial f/\partial\phi + \eta\partial f/\partial\eta$. Using $f = \Sigma + P$ yields

$$\Pi = \beta P + \alpha\Sigma \tag{38}$$

Evidently $\beta P(\phi)$ is the osmotic pressure of a homogeneous solution at concentration ϕ.[24]

We may eliminate the stretch-energy contribution Σ from our effective potential U by exploiting the mechanical equilibrium of the brush. We consider forces on the part of the brush above height z. The tensions transmitted along the chain backbones contribute a force 2Σ per unit area, as discussed above. Opposing this is the osmotic pressure Π. Finally, there may be an externally applied compression p. These three forces must add to zero, so that

$$2\Sigma + p = \Pi = \beta P + \alpha\Sigma \tag{39}$$

Solving for Σ, we may write U as

$$U = ((\gamma + 1)/\gamma)P/\phi - \alpha/(2 - \alpha)p/\phi \tag{40}$$

We have defined the constant $\gamma \equiv 1/\beta - \alpha/2\beta = (d - 1)\nu - 1/2$; hence $\gamma \approx {}^{7}/_{10}$ and $(\gamma + 1)/\gamma \approx {}^{17}/_{7}$ in three dimensions.

In the absence of an external pressure p, the effective potential U is proportional to P and is thus an explicit function of ϕ; namely, $U = ((\gamma + 1)/\gamma)s\phi^{\beta} \equiv q\phi^{\beta}$. For this case we may readily find the equilibrium free energy F and the equilibrium height h^*. The single-chain free energy is

$$\mathcal{S} = \int \mathrm{d}n \left[\frac{\upsilon}{2}\left(\frac{\mathrm{d}z}{\mathrm{d}n}\right)^2 \phi^{\alpha}(z(n)) + q\phi^{\beta}(z(n))\right] \tag{41}$$

It is now convenient to change spatial variables to make the chain stretch energy correspond to that of an equivalent Gaussian chain:

$$\mathrm{d}y \equiv \upsilon^{1/2}\phi^{\alpha/2}(z)\ \mathrm{d}z, \qquad \tilde{\phi}(y) \equiv \phi(z) \tag{42}$$

We may once again make the equal-time arguments (now in y-space); this leads to

$$U(y) = q\tilde{\phi}^{\beta} = A - By^2 \tag{43}$$

where $B = \pi^2/(8N^2)$ as in eq 12.

We may find the coefficient A by using monomer conservation (eq 14 written in y space) and the relation $y^2(h^*) = A/B$; then we use eq 26 to get the following expression for the free energy per chain of the equilibrium brush:

$$\mathcal{F}^* = C_1 N\sigma^{1/(d-1)\nu} \tag{44}$$

with the constants C_1 and n_γ defined by

$$C_1 \equiv \upsilon\frac{(d - 1)\nu}{(d - 1)\nu + 1}\left[\frac{\pi}{2(2^{1/2})n_\gamma}\left(\frac{s(\gamma + 1)}{\upsilon\gamma}\right)^{\gamma}\right]^{1/[(d-1)\nu]}$$

$$n_\gamma \equiv \frac{\Gamma(\gamma + 1)\Gamma(1/2)}{2\Gamma(\gamma + 3/2)}$$

Integrating eq 42 to relate h and $y(h)$ gives us

$$h^* = C_2 N\sigma^{(1-\nu)/((d-1)\nu)} \tag{45}$$

with the constant C_2 given by

$$C_2 = n_{(1/2-\nu)}(n_\gamma)^{(\nu-1)/[(d-1)\nu]}\left(\frac{8s(\gamma + 1)}{\pi^2\upsilon\gamma}\right)^{(d\nu-1)/[2(d-1)\nu]}$$

and $n_{(1/2-\nu)}$ defined as n_γ above.

Our result, eq 44, for the free energy of the self-consistent scaling profile may again be compared with that for a hypothetical step-function profile.[1,2] Evaluating the system free energy for the step-function brush (eq 36, with $\phi = N\sigma/h$ and $\mathrm{d}x/\mathrm{d}n = h/n$) and minimizing F_{step} with respect to h give

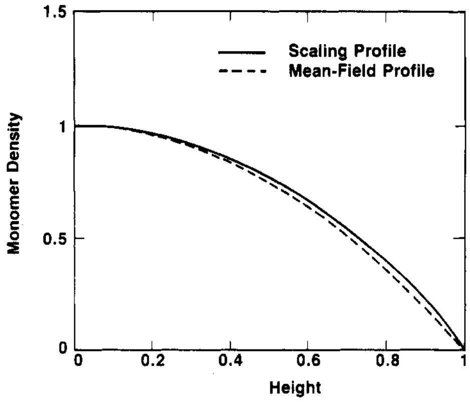

Figure 4. Comparison of the brush density profile for the self-consistent mean-field theory (eq 13) with that of the swollen brush model ($d = 3$, $\nu = {}^{3}/_{5}$) obtained by integrating eq 42 and 43 numerically. (Each profile is normalized by its equilibrium brush height, h^*, and the density at the origin, $\phi(0)$.)

$$\mathcal{F}^*_{\text{step}} = C_3 N\sigma^{1/((d-1)\nu)} \tag{46}$$

$$h^*_{\text{step}} = C_4 N\sigma^{(1-\nu)/((d-1)\nu)} \tag{47}$$

with the constants C_3 and C_4 given by

$$C_3 = \upsilon(d - 1)\nu\left(\frac{s}{\upsilon\gamma}\right)^{\gamma/[(d-1)\nu]}, \qquad C_4 = \left(\frac{s}{\upsilon\gamma}\right)^{(d\nu-1)/[2(d-1)\nu]}$$

The ratios of the free energies, F/F_{step}, are brush heights, h^*/h^*_{step}, for the two types of profile are independent of the nonuniversal constants υ and s. However, they depend on the values of d and ν; setting $d = 3$ and $\nu = {}^{3}/_{5}$, we find $F/F_{\text{step}} \approx 0.88$ and $h^*/h^*_{\text{step}} \approx 1.3$. To describe the case $d = 4$, in which the mean-field theory of section 1 is correct even at low coverages, we can set $d = 4$, $\nu = {}^{1}/_{2}$, $s = w/2$, and $\upsilon = 1$ in the above expressions; the results check precisely with the predictions (eq 24, 27–30) that were obtained with our mean-field analysis, as they should.

To see how the equilibrium profile $\phi(z)$ differs from the mean-field case, eq 25, we examine the function $y(z)$. We know $\mathrm{d}y/\mathrm{d}z = \tilde{\phi}^{\alpha/2}(y)$ and $q\tilde{\phi}^{\beta}(y) = B(y^2(h^*) - y^2)$. From this we find that y is proportional to z for small y and z, while $y(h^*) - y$ varies as $(h^* - z)^{2\beta/(2\beta-\alpha)}$ for z near h^*. Hence the monotonic function $y(z)$ begins linearly and ends in a weak singularity, since $2\beta/(2\beta - \alpha) = 2/(3 - 2\nu) = {}^{10}/_{9}$ for $\nu = {}^{3}/_{5}$.

Substituting $y(z)$ into the expression for $\tilde{\phi}(y)$ results in $\phi(z) = \phi(0) + \mathcal{O}(z^2)$ for small z; for z near h^*, $\phi(z)$ is proportional to $(h^* - z)^{2/(2\beta-\alpha)}$. The exponent $2/(2\beta - \alpha) = 2(d\nu - 1)/(3 - 2\nu)$ is about ${}^{8}/_{9}$ for $d = 3$, $\nu = {}^{3}/_{5}$. Thus $\phi(z)$ at the outer edge of the brush vanishes with an exponent slightly less than unity (see Figure 4).

Computation of the free energy as a function of height, $F(h)$, for compressed brushes in the semidilute regime, requires that we solve eq 40 for $\tilde{\phi}(y)$ in general, which we are unable to do analytically. However, we may still compute the force $\partial F(h)/\partial h$ in the limits of $h \ll h^*$ and $h \sim h^*$. In the case $h \ll h^*$, the osmotic pressure dominates the free energy and we expect that monomer density ϕ to scale as $N\sigma/h$, while the osmotic pressure $\Pi \sim \partial F(h)/\partial h$ scales as ϕ^{β}, or $(N\sigma/h)^{1/(d\nu-1)}$. This result is the same as the Alexander–de Gennes step-function profile.[7]

For small compressions of the semidilute brush, we can apply an argument exactly analogous to that used in sec-

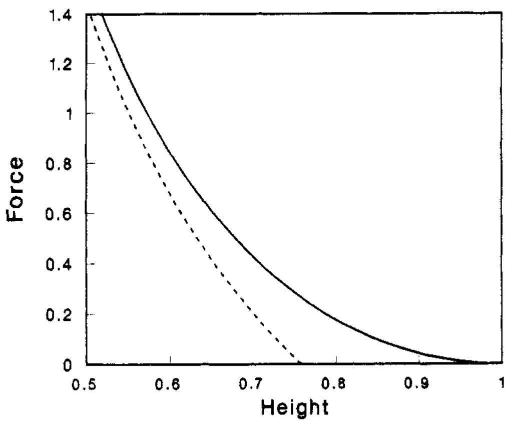

Figure 5. Force $p(h)$ (arbitrary units) required to compress a semidilute brush to a height $h < h^*$ (solid curve) is compared to the force $p_{\mathrm{step}}(h)$ calculated from the step-function Ansatz. The x-axis for both curves is h/h^*, where h^* is the equilibrium height of the fully self-consistent brush.

tion 2 for the mean-field case. We find $\delta F \sim \Pi(h^* - \delta h)\delta h \sim (\phi(h^* - \delta h))^{\beta+1}\delta h \sim \delta h^{\mu}$, where $\mu = (2(d-1)\nu + 3)/(3 - 2\nu)$. Remarkably, taking the Flory estimate[21] $\nu = 3/(d + 2)$ gives $\mu = 3$ for any dimension d, exactly as in mean-field theory (eq 33). However, use of a more accurate value of ν would yield a small correction to this exponent in three dimensions.

In fact, we can compute numerically the force p needed to compress a brush to a height $h < h^*$. This is done as follows. We fix arbitrarily a value of the coefficient A, solving eq 40 numerically for $\tilde{\phi}(y;A,p)$. Equation 14 (monomer conservation) and eq 42 (relation of y and z) are then integrated numerically to give the coverage σ and height h corresponding to a range of values of the applied pressure p. We may write a scaling form for h,

$$h(p;\sigma) = f(p/\Pi_0(\sigma))\sigma^{(1-\nu)/((d-1)\nu)}$$

where $\Pi_0(\sigma) \sim \sigma^{d/(d-1)}$ is, for example, the osmotic pressure at the wall of an equilibrium brush of coverage σ. Now we may scale the values of $h(p;\sigma)$ we generated onto a single curve at constant σ. The resulting $p(h)$ curve, which displays the features we deduced above, is shown (together with $p_{\mathrm{step}}(h)$) in Figure 5.

Thus, while the specific exponents differ, the brush in the semidilute regime is qualitatively similar to our parabolic mean-field brush. In particular, the density profile is still flat near the wall and decreases over the entire brush height, approaching zero "nearly linearly" (i.e., with an exponent close to unity) at the outer extremity of the brush (see Figure 4). The force for small compressions δh is still softer by roughly one power of δh than that of the proposed step-function model, while for large compressions the force is dominated by osmotic pressure as before.

3.2. The Weak Local Stretching Assumption. These results for the statistics of the semidilute brush depend on our assumption, in writing eq 35, that stretching forces are weak on the scale of a single blob. (This does not necessarily contradict the assumption that the large-scale structure of each chain is governed by the classical, strong-stretch equations of motion.) However, if the stretching energy of a chain exceeds the order of kT per blob, the structure within a blob is perturbed[25] and our expression (35) for the stretching energy is no longer correct. The stretch energy per blob then grows as the displacement to the larger power $1/(1 - \nu)$; the chains become anharmonic.[25]

In fact, the chains of interest in the semidilute polymer brush lie at the limit of validity of eq 35: the stretching energy is of the order of kT per blob. To see this, we observe that the local stretching energy of a section of chain is of the same order as its osmotic energy (eq 39 with $p = 0$). Thus the stretch energy may differ from eq 35 by a factor on the order of unity as a result of anharmonic effects.

The trajectories of different chains in the brush are affected differently by anharmonic corrections. The least-extended chains are completely harmonic, so their paths in a given potential are unchanged. Chains of intermediate extension have negligible anharmonicity near their free ends and appreciable anharmonicity near the grafting surface. It is probable, then, that the brush profile and free energy including anharmonic effects differ somewhat from that calculated above. Nevertheless, since the anharmonic effects change the stretch energy by at worst a factor on the order of unity (in a given potential), we do not expect these effects to alter our scaling results. Specifically, the density profile near the tip and the force under weak compression should vary with the powers deduced above, despite anharmonic effects.

4. Conclusions. Future Work

The nature of the grafted polymer brush, in both the concentrated and semidilute regimes, is in many respects that anticipated by the step-function picture of Alexander[1] and de Gennes.[2] As we have seen, the energy and height of the brush scale with molecular weight and coverage as they predicted. Nonetheless, our more comprehensive analysis has revealed a number of important departures from this picture.

In studying the concentrated brush, for which the mean-field treatment of section 1 is valid, we have exploited the fact that the chains are strongly stretched to find the exact asymptotic density profile in the limit of long chains. This profile is parabolic (see section 1.2), rather than a step function; moreover, the free ends of the chains are distributed through the entire height of the brush (eq 18), rather than confined to a narrow zone at the outer extremity. Our prediction of a parabola for the asymptotic profile is in excellent agreement with the numerical mean-field calculations of Hirz[3] for moderate coverages σ. Similar qualitative results were found in section 3 for the semidilute brush, although the profile in that case shows a small departure for the parabolic form (see Figure 4).

Another major difference between our results and the earlier predictions[1,2] concerns the free energy required to compress the brush, in the case when this energy is small. (This regime is an important one for understanding the interactions between colloidal particles coated with grafted polymer.) The step-function picture implies that the energy increases as the compression squared; our more detailed treatment shows that it is qualitatively weaker.

One way to test our predictions experimentally, therefore, might be to measure this compression energy directly by a force balance technique. Unfortunately, though, the small-compression regime is harder to probe than that of strong compression,[6] and the results could be rather easily disrupted by polydispersity effects. A more robust test of our theory would be to measure directly the density profile, and particularly the end-density profile, within the brush. The latter might be probed directly by attaching fluorescent labels to the free chain ends and exciting these labels by evanescent waves from the substrate. Fluorescence quenching of those labels that touch the substrate also tests the present theory: the step-function picture predicts an exponentially small contact probability between a free end and the wall, whereas our end density profile (see Figure 2 and eq 18) suggests a contact probability which decreases as the inverse square of the molecular weight.

Finally, we note that the classical-limit SCF approach developed here can readily be extended, in principle, to treat a number of further problems concerning grafted chains in solution under conditions of strong stretch. We mention these in turn.

(i) Saturation Effects. We may extend the present work in the direction of higher coverages σ by adopting a more general expression for the osmotic free energy density as a function of concentration ϕ. Our equal-time arguments suggest that whatever the form of this function, the potential $U(z) = \delta F(\phi)/\delta\phi$ will be parabolic as before. For example, consider the Flory–Huggins form for the osmotic free energy of a polymer solution near saturation ($\phi \sim 1$) in an athermal solvent:

$$F(\phi) = (\phi - 1)\log(1 - \phi)$$

Equating $\partial F(\phi)/\partial\phi(z)$ with $U(z) = A - Bz^2$ (where $B = \pi^2/(8N^2)$) yields immediately

$$\phi(z) = 1 - \exp(-A + Bz^2)$$

where the constant A is again determined by the normalization requirement, $\int dz\ \phi(z) = N\sigma$.

This form of $\phi(z)$ remains approximately constant over an increasingly wide plateau as coverage σ increases but approaches a parabolic profile in the outer region of the brush where the density is low. The analogous expression with a nonzero χ parameter is more cumbersome but may be easily evaluated numerically. These results should be treated with some caution, however, as we have not considered corrections to the Gaussian elasticity of the chains which may arise when the brush height approaches the fully extended length of a chain.

(ii) Polydispersity Effects. While our equal-time arguments are crucially dependent upon the monodispersity of the grafted chains, the formalism is readily extended in principle to the case of general polydispersity. We find that in the limit of strong stretching, the ends of chains having different lengths are never found at the same distance from the grafting surface. (Longer chains always end further from the surface.) For a narrow polydispersity about a mean chain length, corrections to the parabolic profile are small. For the case of a bimodal distribution, however, there can be large departures from the parabola. We hope to discuss these effects further in a future publication.

(iii) Other Geometries. An extension of the present work to the case of curved surfaces would allow one to describe the bending of a liquid–liquid interface saturated with amphiphilic copolymer, for example. It would also allow one to study the density profile of a thick brush coating a small colloidal particle,[26] or indeed that of a star polymer. In the latter case, we may find modifications of the simple scaling picture of Daoud and Cotton.[27]

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References and Notes

(1) Alexander, S. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 983.
(2) de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 1443. de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(3) Hirz, S., unpublished thesis, University of Minnesota. For similar calculations, see also: Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. *Macromolecules* **1987**, *20*, 1692.
(4) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London, A* **1974**, *337*, 509; *Proc. R. Soc. London, A* **1975**, *343*, 427.
(5) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869 and references therein.
(6) Taunton, H.; Toprakcioglu, C.; Fetters, L.; Klein, J., submitted for pubication to *Nature (London)*.
(7) de Gennes, P.-G. *C. R. Acad. Sci. Paris* **1985**, *300*, 839.
(8) Edwards, S. F. *Proc. Phys. Soc., London* **1965**, *93*, 605.
(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; Section VI.2.1.
(10) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering and Velocimetry: Application of Photon Correlation Spectroscopy*; Pecora, R., Ed.; Plenum: New York, 1984.
(11) Moore, M. A. *J. Phys. A: Math. Gen.* **1977**, *10*, 305.
(12) Scheutjens, J.; Fleer, G. *J. Phys. Chem.* **1979**, *83*, 1619.
(13) Ben-Shaul, A.; Szleifer, I.; Gelbart, W. M. *J. Chem. Phys.* **1985**, *83*, 3597. Viouvy, J. L.; Gelbart, W. M.; Ben-Shaul, A. *J. Chem. Phys.*, in press.
(14) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1978**, *5*, 960; *Polym. Eng. Sci.* **1977**, *17*, 582.
(15) Noolandi, J.; Hong, K. M. *Macromolecules* **1982**, *15*, 482.
(16) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(17) Semenov, A. N. *Sov. Phys.—JETP (Engl. Transl.)* **1985**, *61*, 733 [*Zh. Eksp. Teor. Fiz.* **1985**, *88*, 1242].
(18) Gerber, P. R.; Moore, M. A. *Macromolecules* **1977**, *10*, 476.
(19) Nagel, S.; Witten, T. A., unpublished results.
(20) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637; *Macromolecules* **1982**, *15*, 492.
(21) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; p 45.
(22) In principle, there is a nonzero force (arising from the gradient in the density profile) on the "last monomer" of a chain; however, this vanishes in the continuum limit.
(23) To see this, consider starting with a parabolic profile which has a discontinuity at $z = h$ and transferring chains to reduce the discontinuity and extend the height. The density at the origin A decreases; as $S = AN$ is the change in free energy to add a chain, trading a chain from a configuration with $A = A_0$ for one in a configuration $A = A_0 - \delta A$ leads to a reduction in F.
(24) Note that in the limit of $d \to 4$, $\nu \to {}^1/_2$ (in which case mean-field theory is valid even at low concentration), we have $\alpha = 0$ and the osmotic pressure becomes independent of stretch, as adding monomers has no effect on the stretch energy of other chains.
(25) Pincus, P. *Macromolecules* **1976**, *6*, 386.
(26) Witten, T. A.; Pincus, P. *Macromolecules* **1986**, *19*, 2509.
(27) Daoud, M.; Cotton, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 531.