

Grafted polymers under the influence of external fields

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The structure of grafted polymer “brushes” may be profoundly modified by the action of “external fields”—local shifts in chemical potential due to, e.g., interfacial effects at the grafting surface. We discuss the strong-stretching limit of the self-consistent mean-field theory for a brush exposed to an arbitrary external potential, a simple scaling law for the brush height arises in the case where the external field pushes monomers towards the surface. In contrast, repulsive interactions can lead to “exclusion zones” or regions from which polymer ends are repelled, leading to a breakdown of the simple scaling formula. We exactly solve the self-consistent theory of the brush in a repulsive square well where an exclusion zone always appears. Our results describe a brush in the case where a thin layer of one component of a binary solvent that is a worse solvent for the polymer than is the bulk mixture wets the grafting surface. We also discuss the effects of thermal fluctuations and chain polydispersity on our results, and estimate the effects of various interfacial phenomena on the brush structure.

I. INTRODUCTION

Long polymers grafted at one end to a surface are strongly perturbed from their free-chain conformation in bulk solution. As the grafting density (the number of attachments per unit area) or molecular weight is increased, the excluded volume interactions force the chains to stretch away from the surface, to form a “brush.” Interest in brushes is motivated by their application to stabilization of colloidal particles. Coating such particles with grafted polymers introduces repulsive (osmotic) forces between the grafted coronas sufficient to overcome the van der Waals attractions that favor aggregation. Because the strength and the range of these repulsive forces depend on the mass of the polymer and on the grafting density, much experimental effort has been directed toward increasing surface coverages. Surface coverages of order of 8 mg m^{-2} have been recently reported, corresponding to layers as thick as 110 nm and to stretching energies as large as $\sim 10k_B T$.¹

A theory of grafted polymer layers was first proposed by Alexander² and de Gennes³ and later elaborated by Semenov.⁴ More recent work^{5,6} has developed a detailed statistical-mechanical picture of chain conformations in polymer brushes. A central theoretical result—well confirmed by experiments—is that the typical chain extension scales *linearly* with molecular weight.¹

Polymer brushes are not only useful in colloidal stabilization but can also influence, or have their structure influenced by, other interfacial phenomena such as wetting,^{7,8} capillarity,⁹ polymer adsorption, and electrical double layers.^{10,11,12} In each of these examples, the chain conformations are determined not simply by the balance of osmotic and elastic energies, but also by their interplay with a third, interfacial energy. The precise nature of this third contribution to the free energy depends on the sur-

face under study. As an example, if there is wetting of the substrate by the minority component of a two-solvent mixture, there are forces acting on the chain monomers near the wetting layer due to differences in chemical potential of monomers in each of the solvents. In this case, the chains will adopt conformations maximizing the number of monomers in the better solvent.⁷

Given the large amount of free energy ($\sim 10k_B T$) stored per chain under strong-stretching conditions, one might question whether such external fields will be able to significantly alter the brush structure. However, one must remember that for these strongly stretched brushes the polymerization index N is very large ($N > 1000$), and thus the free energy *per monomer* is of order $0.01k_B T$. Substantial responses can thus be expected to external fields, since they can *locally* greatly exceed $0.01k_B T$ per monomer.

This paper is organized as follows. In Sec. II we first review the self-consistent mean-field (SCMF) description of polymer brushes, and then discuss the effect of an arbitrary external field on the chain conformations. If the free ends of the grafted chains remain distributed throughout the layer, the usual theory^{5,6} only requires slight modification to give a closed-form description of brush structure in the presence of an external field. This is usually the case when the external field tends to push the polymers towards the grafting surface. However, in many situations, external fields will tend to stretch the polymers away from the grafting surface. Given sufficiently strong forces of this sort, there may arise “end-exclusion zones”—regions in the layer from which the free ends are expelled. In Sec. III, we discuss the appearance of such an exclusion zone in the treatment of brush response to a wetting layer of a minority solvent that is present on the grafting surface. This problem can be solved exactly in the SCMF theory even in the case where the polymer segments encounter repulsive interactions with the wetting layer leading to forma-

tion of an exclusion zone. Section III ends with a discussion of the effects of thermal fluctuations and chain polydispersity on these results. In Sec. IV we discuss the competition between grafted and adsorbed layers of polymers, a problem of some practical interest since the final properties of the brush can in principle be finely tuned by the adsorption of a (possibly different) polymer. This study also provides some insight into the problem of attractive, pointlike interactions that may exist between the substrate and the chains in the grafted layer. Lastly, in the Discussion, we make some estimates of effects of various sorts of interfacial phenomena on the brush structure.

II. GRAFTED LAYERS UNDER EXTERNAL FIELDS

A. The mean-field model for strongly stretched chains

Identical flexible polymers each of chemical length N are end-grafted to the surface $z=0$; the polymers are restricted to the half-space $z>0$, and the number of chains grafted per unit area is σ . We take the monomers to be of length unity, and we take energy units where $k_B T=1$. The i th chain is described by a space curve $\mathbf{r}_i(n)$, where n runs from 0 at the free end to N at the grafted end; the position of the grafted end is fixed, $\mathbf{r}_i(N)=[x_i(N), y_i(N), 0]$. The free energy of the system for a given set of chain conformations is

$$F = \sum_i \left[\frac{3}{2} \int_0^N dn \left(\frac{d\mathbf{r}_i}{dn} \right)^2 + \int d^3r \left[\frac{w}{2} [\Phi(\mathbf{r})]^2 + \Lambda_S v(z) \Phi(\mathbf{r}) \right] \right], \quad (2.1)$$

where the first term measures the entropy loss due to stretching of the chains, and the second term accounts for interactions; $\Phi(\mathbf{r})$ is the volume fraction occupied by monomer at point \mathbf{r} . Two types of interactions are included in Eq. (2.1) (a) excluded volume interactions of strength w and (b) an external field whose precise form depends on the interactions between the monomers and the interfacial phenomenon of interest, be it a wetting layer, additional adsorbed polymer, van der Waals interactions between monomers and substrate, etc. The potential energy due to this interaction per monomer at \mathbf{r} is $\Lambda_S v(z)$ and the resulting force on a piece of chain of size dn at \mathbf{r} is thus $-\Lambda_S v'(z) dn$ [where $v'(z) \equiv dv/dz$] and is directed in the z direction. We take the potential profile $v(z)$ to be normalized,

$$\int_0^\infty dz v(z) = 1, \quad (2.2)$$

so that Λ_S measures the integral of the external potential. If a uniform monomer solution of volume fraction Φ_0 were in contact with the grafting surface, $\Lambda_S \Phi_0$ would be the surface energy due to the external field. A typical profile $v(z)$ will decay from its peak value at $z=0$, thus, we expect $v'(z) < 0$ under most circumstances. In such cases, $\Lambda_S < 0$ corresponds to an attractive potential between monomers and the surface, while $\Lambda_S > 0$ models a repulsive interaction.

A mean-field theory may be obtained by retaining only the portion of the excluded-volume interaction linear in the fluctuating part of Φ ; the free energy Eq. (2.1) then decouples into a sum of single-chain contributions each of the form

$$f(\mathbf{r}) = \int_0^N dn \left[\frac{3}{2} \left(\frac{d\mathbf{r}}{dn} \right)^2 + p(z) \right] + \text{constant}, \quad (2.3)$$

where $p(z) = w\phi(z) + \Lambda_S v(z)$. Here $\phi(z)$ is the *expectation value* of the microscopically defined $\Phi(\mathbf{r})$; $\phi(z)$ does not fluctuate in the mean-field theory. Symmetry indicates that ϕ is independent of the x - y planar coordinates. The “potential” $p(z)$ is the work required per chain volume to insert a section of chain at a given height z ; the work per unit total volume, $\phi(z)p(z)$, is the osmotic pressure. We will find it useful to express ϕ in terms of p as $\phi(z) = \alpha p(z) - \gamma v(z)$, where $\alpha = 1/w$ and $\gamma = \Lambda_S/w$ is a length characterizing the strength of the surface interactions compared to excluded volume interactions. A mean-field approach will be used throughout this paper. We note this is completely valid only when the solvent has “marginal” quality,¹³ or for weak self avoidance, $w < \sigma^{1/2}$ in $d=3$. The theory could be extended to good solvent conditions by the approach of Milner *et al.*⁶ Effects of the correlations arising in a good solvent on the layer structure at scales beyond the blob size $\sigma^{-1/2}$ are small, except at the outer edge of the brush.

We are concerned in this paper with the “strong-stretching limit” relevant to long polymers, where the layer thickness h , the typical distance that chains are extended over, is much larger than the ideal chain radius of gyration $R_G = \sqrt{N/6}$, but is much less than the maximum extension of the chain. In this limit^{5,6} one expects that a chain with free end at a height z_0 fluctuates only narrowly about the path $\mathbf{r}(n)$ which minimizes the free energy functional $f(\mathbf{r})$; more precisely, in the x - y plane monomer n fluctuates a distance of order $R_G \ll h$ away from $\mathbf{r}(n)$. Again symmetry indicates that a chain grafted at a position \mathbf{r}_N has a free-energy minimizing conformation of the form $\mathbf{r}(n) = \mathbf{r}_N + z(n)\hat{\mathbf{z}}$.

Since the chains are in mechanical equilibrium, we demand that there is no tension at the free end, $dz/dn|_{n=0} = 0$. Functional minimization of f furthermore indicates that $z(n)$ satisfies “Newton’s law” for the trajectory of a particle when the variable n is interpreted as “time” and p is interpreted as potential energy,

$$\frac{d^2 z}{dn^2} = \frac{dp}{dz} \quad (2.4)$$

with boundary conditions $z(0) = z_0$, $z(N) = 0$, and $dz/dn|_{n=0} = 0$. Integration of this equation leads to the classical relation between the “velocity” dz/dn and the two potentials p and p' reflecting the positions of an observation point, and the free end, respectively,

$$\left[\frac{dz(p)}{dn} \right]_{z_0=z(p')} = -\sqrt{2(p-p')/3}. \quad (2.5)$$

Assuming that ends are distributed throughout the layer, we see that the boundary conditions strongly constrain $p(z)$; it must be an "equal-time" potential with the property that the "time" required to "fall" from rest to $z=0$ is independent of the initial height. For a chain with free end at a height z_0 , this "fall time" is

$$N(z_0) = \int_{z_0}^0 dz \left(\frac{dn}{dz} \right)_{z_0} = \int_0^{z_0} \frac{dz}{\sqrt{2[p(z) - p(z_0)]/3}} \quad (2.6)$$

It is convenient to work in terms of the potential p as a height coordinate; from mechanical stability considerations we know that $p(z)$ is monotonic, decreasing from some value P at $z=0$ to 0 as one moves to the top of the layer. Writing Eq. (2.6) in terms of the potential p and inverting it¹³ leads to

$$\frac{dz}{dp} = \sqrt{\frac{2}{3\pi^2}} \int_p^P \frac{dp'}{\sqrt{(p'-p)}} \frac{dN}{dp'} \quad (2.7)$$

In the case that ends are distributed throughout the layer, we require the equal-time condition $N(p) = N\Theta(P-p)$ [$\Theta(z)$ is the usual Heaviside distribution throughout this paper]. Thus, $dN/dp = -N\delta(p-P)$; Eq. (2.7) then gives $dz/dp = -(2N^2/3\pi^2)^{1/2}(P-p)^{-1/2}$. Integration yields the celebrated parabolic potential

$$p(z) = P \left(1 - \frac{z^2}{h^2} \right), \quad (2.8)$$

where the layer height is $h = (8PN^2/3\pi^2)^{1/2}$.

In the absence of external fields ($\Lambda_S=0$), the value of $P=P_0$ is determined by monomer conservation to be $P_0 = (27\pi^2/32)^{1/3} w^{2/3} \sigma^{2/3}$. The layer height for $\Lambda_S=0$ follows $h_0 = (4w\sigma/\pi^2)^{1/3} N$. Assuming that the free ends are distributed throughout the layer, we can compute the free energy density per unit surface for the brush by integrating the chain chemical potential from the bare surface to the actual surface density σ . Because the chains are in equilibrium they all have the same chemical potential. In particular, we choose those with a free end at the surface for which the chemical potential is easily calculated to be NP_0 .⁶ This leads to an areal free energy density in the $\Lambda_S=0$ case,

$$F_0 = N \int_0^\sigma d\sigma' P_0(\sigma') = \frac{9}{10} \left(\frac{\pi^2}{4} \right)^{1/3} w^{2/3} \sigma^{5/3} N. \quad (2.9)$$

Returning to the general case $\Lambda_S \neq 0$, we introduce a function indicating the number of free ends per unit height, $d\sigma/dz$. This distribution is normalized so that $\int dz (d\sigma/dz) = \sigma$. This quantity is determined by recognizing that the monomer density at height z may be computed by adding up all of the contributions from chains with free ends above z ,

$$\phi(z) = \int_z^h dz' \frac{d\sigma}{dz'} \left(\frac{dn}{dz} \right)_{p(z')} \quad (2.10)$$

This equation may be written in terms of $p(z)$,

$$\phi[z(p)] = \alpha p - \gamma v[z(p)] = \int_0^p dp' \frac{d\sigma}{dp'} \left(\frac{dn}{dz} \right)_{p'} \quad (2.11)$$

where we have introduced the distribution of ends per unit change in p , $d\sigma/dp = (d\sigma/dz) |dz/dp|$. We may invert Eq. (2.11) by Laplace transform to give an integral for the end distribution

$$\sqrt{\frac{3\pi^2}{2}} \frac{d\sigma}{dp} = \int_0^p \frac{dp'}{(p-p')^{1/2}} \left[\alpha - \gamma \frac{dz}{dp'} v'[z(p')] \right]. \quad (2.12)$$

In the event that this $d\sigma/dp$ is everywhere positive, there are no end exclusion zones, and the end distribution may be directly calculated using this equation with dz/dp given by Eq. (2.7).

From Eq. (2.7) it is evident that the end distribution Eq. (2.12) is everywhere positive if the derivative of the external field with height always exceeds the (negative) slope of the parabolic potential [i.e., $\Lambda_S v'(z) > dp/dz$; this condition corresponds to a monomer concentration profile that decreases monotonically as z increases]. For a decaying $v(z)$ with $v'(z) < 0$ everywhere, we see that this condition is satisfied for $\Lambda_S < 0$, or for a wide class of potentials attracting the monomers to the grafting surface.

If this condition is not met for all z , $d\sigma/dp$ may become negative; the self-consistent solution outlined above is nonphysical. To remedy this, one must consider *constrained* self-consistent solutions that introduce "end-exclusion zones," or finite regions of z for which $d\sigma/dz = 0$. We will extensively discuss this point in Sec. II C.

B. Attractive potentials

In the case where $v'(z) < 0$ and $\gamma < 0$ (everywhere attractive forces) Eq. (2.12) leads always to a positive (physical) end distribution. In this case, the potential p has the parabolic form Eq. (2.8), and we may proceed to compute the end distribution using Eq. (2.12). Since dp/dz is known, the end distribution may be explicitly computed once $v(z)$ is specified. However, some aspects of the system are independent of the form of $v(z)$ within the bounds stated above.

An important property of the end distribution is that it is a sum of two contributions. The first, proportional to α , is the end distribution that would arise without surface interactions. The second, proportional to γ , arises solely due to the surface forces, and is only nonzero in regions where $v'(z)$ is nonzero. Thus, if $v(z)$ has a range smaller than the layer height (we expect this under a wide range of circumstances), then at heights above the cutoff of $v(z)$, $d\sigma/dp$ has the same form as that for an unperturbed layer. Since $p(z)$ is parabolic, we find that $d\sigma/dz$ is also of the same form as for the unperturbed layer, above the surface force cutoff. This remark also applies to the monomer density, which is explicitly

$$\phi(z) = \alpha P (1 - z^2/h^2) + |\gamma| v(z). \quad (2.13)$$

Above the cutoff of $v(z)$, the monomer distribution is parabolic, and of the same form as in the case $\gamma=0$. Inside the

range of f , we note an enhancement in monomer density near the surface that is proportional to the coupling γ , physically consistent with the attractive nature of the surface interaction.

Integrating the end distribution yields an expression for the total end density. A bit of algebra yields

$$\begin{aligned} \sigma &= \int_0^P dp \frac{d\sigma}{dp} \\ &= \frac{4\alpha}{3} \left(\frac{2P^3}{3\pi^2} \right)^{1/2} + \frac{|\gamma|}{N} \left[\int_0^h dz v(z) - \left|_0^h zv(z) \right. \right]. \end{aligned} \quad (2.14)$$

If the layer height h is larger than the range of $v(z)$, this reduces to

$$\sigma = \frac{4\alpha}{3} \left(\frac{2P^3}{3\pi^2} \right)^{1/2} + \frac{|\gamma|}{N}. \quad (2.15)$$

The fraction of ends "bound" to the surface is $|\gamma|/(\sigma N)$, independent of the form of $v(z)$.

Since these free ends are bound inside the range of the potential, and since the unperturbed end distribution goes to zero at $z=0$, in the case that the range of f is small compared to the layer height, these bound ends will contribute with a peak to the end distribution at the grafting surface.

The layer height may be computed by combining the expression for the grafting density Eq. (2.15) with the relation $P=3\pi^2 ah^2/8N^2$,

$$h = h_0 \left(1 - \frac{|\gamma|}{\sigma N} \right)^{1/3}, \quad (2.16)$$

where $h_0 = h(\gamma=0)$ is the unperturbed brush thickness. The expression for h is formally identical to the case where no extra interaction is present if one replaces the density σ by the effective "unbound" end density $\sigma - |\gamma|/N$. An interesting point is that for $|\gamma|/\sigma N \ll 1$, the correction to the brush height (which is independent of N) is indefinitely smaller than h_0 in the $N \rightarrow \infty$ limit.

The preceding results only apply for bound fractions smaller than unity. For sufficiently strong interaction strength (or long range of interaction), low grafting density, or short chains, the polymers are fully bound inside the range of $v(z)$. Under such circumstances, the thickness of the layer is equal to the range of the external field. This tells us that computation of the free-energy cannot be directly made using the above results. There will always be some portion of the integral in Eq. (2.9) near $\sigma=0$ over a regime of totally bound chains. This is further discussed in Sec. III.

C. Repulsive potentials

In the cases where the forces act to push the chains away from the grafting surface [e.g., $v'(z) < 0$ and $\gamma > 0$] the integral contribution to the end distribution Eq. (2.12) can be negative (an unphysical result) if the hypothesis that free ends are distributed throughout the layer, and therefore the parabolic potential Eq. (2.8), is assumed.

There must be, in such circumstances, finite intervals in height where no free ends are found. In the following, we assume that the external potential is monotonically decreasing from the surface, which implies that there will be only one single exclusion zone extending from the wall up to a distance z^* . Let $Q = p(z^*)$ be the value of the potential at the edge of the exclusion zone, and $P = p(z=0)$ to be its value at the wall. It is convenient to use the following dimensionless variables for the potentials and distances in the problem:

$$\begin{aligned} X &= \frac{p-Q}{Q} \quad \text{for } p > Q; \\ Y &= \frac{Q-p}{Q} \quad \text{for } p < Q; \\ V &= \frac{\Lambda_S v}{Q}; \quad x = \frac{z}{h(Q)}. \end{aligned} \quad (2.17)$$

Integration of Eq. (2.11) for the concentration, over the range where chain ends exist ($0 < p < Q$), and integration of the equal-time constraint Eq. (2.6) leads to the two following integrodifferential equations:

$$\frac{dx}{dY} = \frac{1}{\pi Y^{1/2}} \left(\frac{\pi}{2} + \int_0^{X_s} \frac{X^{1/2} dx}{X+Y} dX \right), \quad (2.18)$$

$$\begin{aligned} \frac{dV}{dX} &= \frac{2}{\pi} (\arctan X^{1/2} + X^{-1/2}) \\ &+ \frac{1}{\pi} \frac{1}{X^{1/2}} \int_0^1 \frac{Y^{1/2} dV}{X+Y} dY, \end{aligned} \quad (2.19)$$

which determine the form of the total potential inside and outside the exclusion zone for a given external potential V . The value of the total potential at the wall X_s (or equivalently the value of P), is given by $X[V(x=0)]$. Note that when the derivative dV/dx is a function of V only (i.e., V is piecewise linear), then the preceding equations determine V in the two regions of the brush, which by inversion would give the values of the total potential, $X[V(x)]$ and $Y[V(x)]$ in these regions. Equations (2.18) and (2.19) need to be complemented by the two limiting equations

$$\int_0^{X_s} \frac{1}{X^{1/2}} \frac{dx}{dX} dX = -\frac{\pi}{2}, \quad (2.20)$$

$$\int_0^1 \frac{1}{Y^{1/2}} \frac{dV}{dY} dY = -2. \quad (2.21)$$

The first of these expressions accounts for the flight time of the chains with ends just at the edge of the exclusion zone. The second equation, obtained by combining Eqs. (2.19) and (2.20), states that the end-distribution vanishes at z^* . The value Q of the potential at the edge of the exclusion zone is fixed by the normalization condition

$$\left(\frac{P_0}{Q} \right)^{3/2} = 1 + \frac{3}{2} \int_0^1 Y^{1/2} \frac{dV}{dY} dY. \quad (2.22)$$

Equations (2.18)–(2.22) completely determine the solutions of the problem of the grafted polymer brush under a repulsive, continuous, and monotonically decreasing potential.

Now, we discuss the asymptotic behavior of the solutions for two limiting situations. The first is the limit of a strong potential close to the wall, $V \gg 1$ for $x \approx 0$. For small x one has

$$V - V(x^*) = X \left[1 - \frac{4}{3\pi} \left(\frac{P_0}{XQ} \right)^{3/2} + O(X^{-5/2}) \right]. \quad (2.23)$$

In this region the total potential is dominated by V , and the chains of the brush are very stretched.

A second interesting limit corresponds to weak external potentials linear in x , $V = V_0(1 - x/D)\Theta(D - x)$. Let β be the value of the total potential at the point where the external potential vanishes, $\beta = Y(D)$. The integrals over Y on the right-hand side of Eqs. (2.19) and (2.21) thus have limits 0 and β . The four Eqs. (2.18)–(2.21) determine the four unknown variables of the problem X_s , β , $dx/dY(x^*) = dx/dX(x^*)$, and x^* . We have

$$D - x^* = \frac{X_s^{1/2}}{2} \left[\left(\frac{\beta}{X_s} \right)^{1/2} - \frac{\pi}{2} + \left(1 + \frac{\beta}{X_s} \right) \arctan \left(\frac{X_s}{\beta} \right)^{1/2} \right],$$

$$\frac{V_0 x^*}{D} = \frac{4}{\pi} - \frac{V_0 X_s^{1/2}}{\pi D} \left\{ \left(1 + \frac{\beta}{X_s} \right) \left[\arctan \left(\frac{X_s}{\beta} \right)^{1/2} \right]^2 - \frac{\pi^2}{4} + 2 \left(\frac{\beta}{X_s} \right)^{1/2} \arctan \left(\frac{X_s}{\beta} \right)^{1/2} + \log \left(1 + \frac{\beta}{X_s} \right) \right\},$$

$$\left. \frac{dx}{dX} \right|_{x=0} = -\frac{\pi}{4X_s^{1/2}}, \quad (2.24)$$

$$\frac{2D}{V_0} = \left(\frac{\beta}{X_s} \right)^{1/2} \arctan \left(\frac{X_s}{\beta} \right)^{1/2} + \frac{1}{2} \log \left(1 + \frac{\beta}{X_s} \right),$$

determining the four parameters, and

$$x - x^* = \frac{1}{2X_s^{1/2}} \left[(X_s Y)^{1/2} - \frac{\pi}{2} X_s + (Y + X_s) \arctan \left(\frac{X_s}{Y} \right)^{1/2} \right], \quad (2.25)$$

$$V(x) = V(x^*) + \frac{2}{\pi} [(1+X) \arctan X^{1/2} + X^{1/2}] - \frac{V_0}{\pi X_s^{1/2} D} \int_0^\beta \arctan \left(\frac{X_s}{Y} \right)^{1/2} \arctan \left(\frac{X}{Y} \right)^{1/2} dY$$

for the potential profiles outside and inside the exclusion zone, respectively. The ratio V_0/D governs the position of the edge of the end exclusion zone. For small values of this ratio the position of x^* diverges from the wall with an essential singularity

$$x^* = \left(\frac{\pi^2 - 4}{4\pi} \right) D \exp \left\{ -\frac{2D}{V_0} \right\}; \quad X_s = D^2 \exp \left\{ -\frac{4D}{V_0} \right\},$$

$$\beta = D^2. \quad (2.26)$$

This behavior echoes that encountered in the theory of a molten brush attached to a convex surface;¹³ in that case, a linear “potential” appears due to the Jacobian of, e.g., cylindrical coordinates. An *effective repulsion* of monomer occurs in that case because of chain crowding as one approaches the convex grafting surface.

For larger values of the ratio V_0/D the position of the border tends to D ,

$$\frac{D - x^*}{D} = \frac{D}{V_0};$$

$$X_s = \frac{\pi^2}{16} V_0^2; \quad (2.27)$$

$$\beta = D^2.$$

We may calculate the ratio P_0/Q from Eq. (2.22),

$$\frac{P_0}{Q} = 1 - \frac{X_s V_0}{4D} \left[\frac{\beta}{X_s} + 2 \left(\frac{\beta}{X_s} \right)^{3/2} \arctan \left(\frac{X_s}{\beta} \right)^{1/2} - \log \left(1 + \frac{\beta}{X_s} \right) \right]. \quad (2.28)$$

The value of the total potential at the edge of the exclusion zone is thus slightly larger than P_0 , the maximum value of the unperturbed profile. We have, for small and large values of the ratio V_0/D ,

$$\begin{cases} Q \approx P_0 \left(1 + \frac{3}{2} \frac{DV_0}{2} \right) & \text{if } \frac{V_0}{D} \ll 1 \\ Q \approx P_0 (1 + D^2) & \text{if } \frac{V_0}{D} \gg 1 \end{cases} \quad (2.29)$$

We note that these results have been obtained under the assumption that the slope of the total potential at the edge of the exclusion zone is finite. It can be seen from Eqs. (2.18)–(2.21) that if a power-law is assumed for the variation of the slope, one gets a 0 exponent. Thus, the preceding perturbative results may overlook factors in the potential of the form $\log|z - z^*|$.

III. STRUCTURE OF THE BRUSH IN A SQUARE POTENTIAL

In this section we present detailed calculations for the brush in an external square potential $\Lambda_S v(z) = \epsilon[\Theta(z) - \Theta(z - z^*)]$. We note that $\epsilon = \Lambda_S v/z^*$ is the potential well height/depth. This potential may be used to describe many important situations where the applied external potential is constant over some range and then dies off in a distance much smaller than the brush thickness. Examples of this are the wetting of the polymer grafted substrate by a second minority solvent or the adsorption of a second polymer, for which the brush solvent is a poor solvent. We study both the attractive ($\epsilon < 0$) and the repulsive ($\epsilon > 0$) cases.

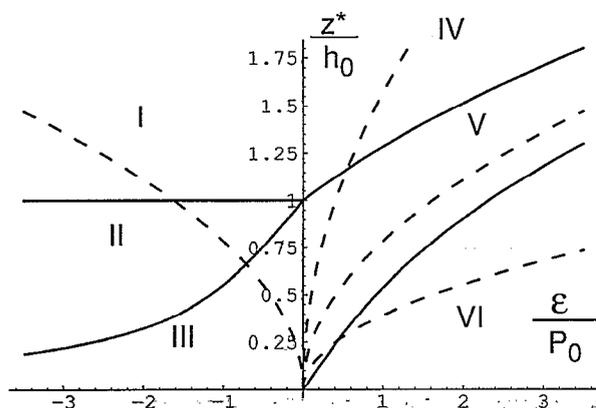


FIG. 1. State diagram for the brush immersed in an external step potential. The coordinates are the potential range z^*/h_0 and the potential strength ϵ/P_0 , where h_0 and P_0 are the brush height and monomer chemical potential at $z=0$ in the absence of the external field. I and IV Unperturbed regime. II Total confinement of chain ends. III Partial confinement. V Partial exclusion of chain ends. VI Total exclusion of chain ends. The dashed lines correspond to different construction paths for the brush.

A. The attractive square well

When the external potential is attractive the free ends are distributed over the whole layer thickness, and the total potential retains its parabolic shape, as discussed in Sec. II B. The concentration profile is then given by Eq. (2.13).

When z^* , the range of the attractive well, is larger than h_0 , the unperturbed brush size, the brush shape and thickness are not modified by the presence of the external field. For values of z^* smaller than h_0 the monomer concentration inside the well increases, causing the layer to shrink. If the attraction is weak, only a finite fraction of the chain ends is confined inside the well (we will refer below to this situation as the regime of partial confinement). The brush thickness is then given by Eq. (2.16) which we rewrite as

$$h = h_0 \left(1 - \frac{3}{2} \frac{|\epsilon| z^*}{P_0 h_0} \right)^{1/3} \quad (3.1)$$

by making use of the equality $w\sigma N = 2P_0 h_0/3$. By increasing the interaction strength ϵ at constant interaction range z^* we reach a critical strength

$$\frac{|\epsilon_c|}{P_0} = \frac{2}{3} \left[\frac{h_0}{z^*} - \left(\frac{z^*}{h_0} \right)^2 \right] \quad (3.2)$$

above which all the chain ends are confined inside the range of the potential; we will refer to this as the regime of total confinement. In this regime the brush thickness is equal to the interaction range z^* and the profile discontinuity at z^* is fixed to its critical value ϵ_c . It is convenient to summarize the preceding results in a “phase diagram” (see Fig. 1) of the two dimensionless parameters of the problem, the reduced interaction strength ϵ/P_0 and the reduced interaction range z^*/h_0 . The three regimes described above correspond to the negative- ϵ/P_0 part of the $(\epsilon/P_0, z^*/h_0)$ plane in Fig. 1 (attractive interaction).

In order to compute the excess free-energy $\Delta F = F - F_0$ we must compute the integral Eq. (2.9). In doing so, for a given value of ϵ and z^* , we may cross the three

regions I–III in the phase diagram, following the construction line $[\epsilon/P_0(\sigma), z^*/h_0(\sigma)]$. Note that the reference potential and length scale as $P_0 \sim \sigma^{2/3}$ and $h_0 \sim \sigma^{1/3}$. The construction path for the brush starts therefore at infinity in the phase diagram ($\sigma=0$) and proceeds from there following a square-root curve, as shown by the dashed line in Fig. 1.

The excess free-energy of a brush in the unperturbed regime is just $-N\sigma|\epsilon|$. A progressive increase of the coverage leads first to a brush in the total confinement regime, with free energy excess

$$\frac{\Delta F}{F_0} = \frac{5}{9} \frac{h_0}{z^*} + \frac{5}{9} \left(\frac{z^*}{h_0} \right)^2 - \frac{1}{9} \left(\frac{z^*}{h_0} \right)^5 - \frac{N\sigma|\epsilon|}{F_0} - 1. \quad (3.3)$$

On the transition line between the partial and total confinement regimes the free energy is given by Eq. (3.3) with the interaction strength is replaced by its critical value Eq. (3.2). Further integration over the partial confinement regime leads to the free energy excess of the partially confined brush

$$\frac{\Delta F}{F_0} = \left(1 - \frac{9}{10} \frac{N\sigma|\epsilon| z^*}{F_0 h_0} \right)^{5/3} + \frac{1}{2} \frac{N\sigma|\epsilon|}{F_0} \left[\left(\frac{z^*}{h_0} \right)^3 - \frac{9}{10} \frac{N\sigma|\epsilon| z^*}{F_0 h_0} \right] - 1. \quad (3.4)$$

B. The repulsive step

For positive values of interaction strength ϵ (repulsion of monomer from the region $z < z^*$) there is always an exclusion zone in the brush. This is a consequence of the infinite slope (discontinuity) at the edge of the external potential. However this exclusion zone, which propagates from z^* inwards, does not always reach the grafting surface. If the discontinuity in the potential is not too strong, the free energy is reduced if a few of the chains place all of their monomers fully inside the range of the external field. This balance leads again to three distinct regions in the positive half-space of the $[\epsilon/P_0, z^*/h_0]$ phase diagram of Fig. 1. For large ranges of the potential the brush size and profiles remain unperturbed, as in the attractive case. By decreasing the potential range at fixed strength one reaches a point where in equilibrium a few of the chains stretch beyond z^* in order to avoid the repulsive field. Below this point, a further decrease of the potential range increases the number of chain ends in the outer part of the potential. This is the repulsive partial exclusion regime. For a small enough z^* all the ends are excluded from the region where the external potential acts, and the size of the exclusion zone is equal to the range of the potential. This is the regime of total exclusion.

1. The total exclusion regime

We first consider the case where chain ends are excluded from the whole interaction range $0 < z < z^*$.

In the outer part of the brush $v(z)=0$ for $z > z^*$, and $p(z)$ reduces to $w\phi(z)$; therefore, the free end distribution Eq. (2.12) as a function of total potential retains its unperturbed form. This is valid for values of the total poten-

tial ranging from 0 at $z=h$ to $Q=p(z=z_+^*)$. Because all the chain ends lie outside the interaction range, we also have (by normalization) $Q=P_0$. Integrating Eq. (2.11) for the concentration profile in the inner part of the layer leads to

$$R-\epsilon=\frac{2}{\pi}\left[R\arcsin\sqrt{\frac{Q}{R}}-\sqrt{Q(R-Q)}\right]. \quad (3.5)$$

The potential is constant [$R=p(z<z^*)$] inside the range of the external potential, and has a discontinuity at z^* . We measure the discontinuity with the parameter η defined as $\eta=R-P_0$. For small interaction strength ($\epsilon\ll P_0$) Eq. (3.5) reduces to

$$\eta=\frac{\pi^2\epsilon^2}{16P_0}+O(\epsilon^3). \quad (3.6)$$

For large potential strengths ($\epsilon\ll P_0$), we have $\eta\approx\epsilon$, a result also valid for continuous but large applied-fields observed earlier in Eq. (2.23).

The concentration profile in the outer region ($z>z^*$) can now be calculated from the equal time constraint Eq. (2.6). Taking care to incorporate the discontinuity in the monomer density, we obtain

$$\frac{z-z^*}{h_0}=\left(\frac{P_0-p}{P_0}\right)^{1/2}-\frac{2z^*}{\pi h_0}\arctan\sqrt{\frac{P_0-p}{\eta}}. \quad (3.7)$$

For a weak external potential ($\eta\ll P_0$) the exterior profile is only modified in the region near to the potential well. For large external potentials ($\eta\gg P-P_0$), the shape of the concentration profile outside the external potential is again a parabola with its maximum at z^* , but with (slightly) larger curvature than in the weak-potential limit. The total layer height follows

$$h=h_0+\frac{2z^*}{\pi}\arctan\sqrt{\frac{\eta}{P_0}}, \quad (3.8)$$

and varies between $h(\epsilon=0)=h_0$ and $h(\epsilon\rightarrow\infty)=h_0+z^*$.

We now calculate the transition line between the total and partially excluded regimes. To locate the partial-total transition line, we consider a chain with free end at z_+^* , just outside the exclusion zone. Across the discontinuity its tension dz/dn jumps from zero to the constant value $\sqrt{2\eta/3}$. This chain needs $z^*/\sqrt{2\eta/3}$ steps to cross the exclusion zone and has thus $N-z^*\sqrt{3/2\eta}$ monomers dangling just behind z^* . Chains with different end locations are in equilibrium with each other (they have equal single-chain chemical potentials). The chains dangling behind z_+^* have a chemical potential $\mu=\mu_0+z^*\sqrt{6\eta}$, where $\mu_0=P_0N$ is the chemical potential of the chains in the unperturbed brush. At the transition, the (very few) chains which have all their monomers inside the potential have a chemical potential $\mu=\mu_0+N\eta$. Equating the chemical potentials for both populations leads then to an equation for the transition line between the total and partial exclusion regimes

$$\frac{z_c^*}{h_0}=\frac{\pi}{4}\sqrt{\frac{\eta}{P_0}}. \quad (3.9)$$

It can be checked from Eq. (3.9) that as σ is increased from zero (as is considered for free energy calculation), if one is in the total exclusion regime for $\sigma=0$, one remains in the total exclusion regime for larger σ . This follows from the fact that h_0^2/P_0 is σ -independent, and since η increases as σ increases [see Eq. (3.5)], if the condition for total exclusion ($z^*<(\pi/4)\sqrt{\eta h_0^2/P_0}$) holds for $\sigma=0$, it holds for all larger σ . For $\sigma=0$, Eq. (3.5) indicates that $R=\epsilon$, and thus, we can write this condition as $z^*<N\sqrt{\epsilon/6}$ —given sufficiently long chains, small z^* , or strong ϵ , one has total exclusion at $\sigma=0$. Under such circumstances, a single grafted chain has lower free energy if it is stretched so that some of its end monomers “float” on top of the potential well, than if it stays near $z=0$. In this case, the free energy excess can be computed by integration of the chemical potential

$$\Delta F=z^*\int_0^\sigma d\sigma'\sqrt{6\eta}. \quad (3.10)$$

Setting $\epsilon/P_0=g(\eta/P_0)$ with $g(y)$ given by Eq. (3.5), we have,

$$\Delta F=\sqrt{6\epsilon\sigma z^*}f\left(\frac{\epsilon}{P_0}\right), \quad (3.11)$$

where

$$f(x)=\frac{3x^{3/2}}{2}\int_{g^{-1}(x)}^\infty dy\frac{\sqrt{y}}{g^3(y)}\frac{dg}{dy}. \quad (3.12)$$

For large x , $f(x)\rightarrow 1$, whereas for small x , $g(y)\approx 4\sqrt{y/\pi}$ so that the integral in Eq. (3.12) is dominated by its lower bound and $\Delta F\approx\frac{3}{2}\sqrt{192/(3\pi^3)}\sigma N\epsilon z^*/h_0$.

2. The partial exclusion regime

The partial exclusion regime—the region in the phase diagram of Fig. 1, located above the transition line given by Eq. (3.9), corresponds to a situation where only a fraction of the brush chains have their ends excluded from the interaction range. By increasing the range of the potential at fixed interaction strength, we increase also the stretching energy of the chains. There must thus be a point where it is energetically less expensive for the chains to have all their monomers inside the repulsive well than to stretch. At this critical range value z_s^* , the last few external, excluded chains, are in equilibrium with the “parabolic” ones extending between $z=0$ and h_0 . Equating again the chemical potentials of the two populations leads to the critical line separating the partially excluded and unperturbed regimes

$$\frac{z_s^*}{h_0}=\frac{1}{2}\left(1+\frac{\epsilon}{P_0}\right)\sqrt{\frac{P_0}{\epsilon}}\arctan\sqrt{\frac{\epsilon}{P_0}+\frac{1}{2}}. \quad (3.13)$$

We now give a detailed description of the partial exclusion regime corresponding, for a given interaction strength ϵ , to the region delimited by the two critical range values, $z_c^*<z^*<z_s^*$. In this regime the brush consists of three different, distinct regions (a) the external region

$h > z > z^*$, or $0 < p < Q$; (b) the exclusion zone $z^* > z > z^* - \delta$, or $p = R$; (c) the parabolic zone $z^* - \delta > z > 0$, or $R < p < P$.

Here $P = p(0)$, $R = p(z^* - \delta < z < z^*)$, and $Q = p(z^*_+)$ are the total potential at the grafting surface, in the exclusion zone, and just above the exclusion zone, respectively. Equation (3.5) still holds for the exclusion zone, but now the external zone does not contain all the chain ends so that Q (to be determined) is smaller than the unperturbed value P_0 . The parameters to be determined are thus P , Q , $\eta = R - Q$ and δ .

We first equate the chemical potential of the chains with ends at z^*_+ with the chemical potential from those with ends at $z=0$,

$$\frac{P-Q}{P_0} \arctan \sqrt{\frac{\eta}{P-Q-\eta}} = \sqrt{\frac{\eta}{P_0}} \frac{\delta + z^*}{h_0}. \quad (3.14)$$

The chains with ends inside the range of the external potential move on a constant potential field over all their trajectory. The corresponding profile has thus a parabolic shape, with the unperturbed brush curvature, and P , the value of the total potential at the wall, is given by

$$P = Q + \eta + \frac{3\pi^2}{8N^2} (z^* - \delta)^2. \quad (3.15)$$

Since the potential in the parabolic zone is known, the chain-end distribution can also be calculated and then the conservation of chain number imposed. This leads to a fourth equation for the four unknown parameters,

$$\begin{aligned} 2(P^{3/2} - P_0^{3/2}) &= \sqrt{P-Q-\eta} \left(3\epsilon - \frac{2}{\pi} \sqrt{Q\eta} \right) \\ &\quad - \frac{2}{\pi} (2P+Q+\eta) \\ &\quad \times \sqrt{P-Q-\eta} \arctan \sqrt{\frac{\eta}{Q}} \\ &\quad - \frac{4}{\pi} Q^{3/2} \arctan \sqrt{\frac{\eta}{P-Q-\eta}} \\ &\quad + \frac{4}{\pi} R^{3/2} \arctan \sqrt{\frac{\eta P}{Q(P-Q-\eta)}}. \end{aligned} \quad (3.16)$$

Equations (3.5) and (3.14)–(3.16) allow for the determination of η , P , Q , and δ . An instructive limiting case arises for weak values of the interaction strength. In this limit the total potential discontinuity η is small compared both to the absolute value of the potential p^* and to the potential difference between the wall and the edge of the external field, $R - p^* - \eta$. The four parameters assume then the limiting forms

$$\begin{aligned} \frac{\delta}{h_0} &= \frac{\pi^2 (\epsilon/P_0)^2}{48(1 - z^{*2}/h_0^2)(z^*/h_0)}, \\ P &= P_0 \left(1 + \frac{\epsilon}{P_0} \frac{z^*}{h_0} \right), \end{aligned} \quad (3.17)$$

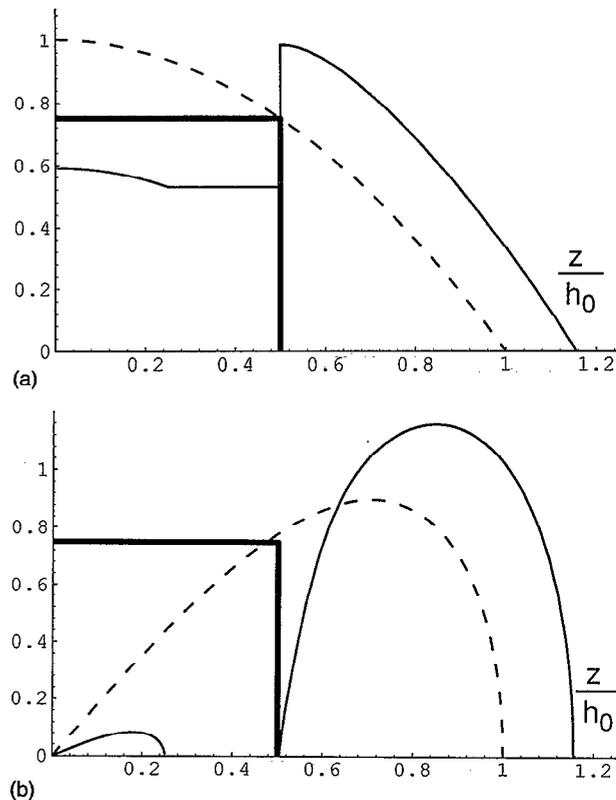


FIG. 2. (a) Monomer density $\phi(z)$ for a polymer brush immersed in a repulsive step potential (the thick bold line) for the case $z_0/h_0=0.5$, $\epsilon/P_0=0.75$. The dashed line corresponds to the monomer density of the unperturbed profile. (b) Free end distribution $d\sigma/dz$ for a polymer brush immersed in the same repulsive step potential. The dashed line corresponds to the end distribution of the unperturbed profile. Distances are in units of h_0 , monomer density is normalized to $\phi(0) = P_0/w$ for the brush without surface field, and the end distribution is in units of σ/h_0 .

$$\begin{aligned} Q &= P_0 \left[1 - \left(\frac{z^*}{h_0} \right)^2 + (\epsilon/P_0) \frac{z^*}{h_0} \right], \\ \eta &= \frac{\pi^2}{16} \frac{\epsilon^2/P_0}{(1 - z^{*2}/h_0^2)}. \end{aligned}$$

The above expansions apply for small values of ϵ/P_0 , except in two small regions of size $(\epsilon/P_0)^2$ close to the border lines in the phase diagram of Fig. 1. In the general case Eqs. (3.5) and (3.14)–(3.16) need to be solved numerically, for each case $(z^*/h_0, \epsilon/P_0)$. We present in Fig. 2 the concentration and free-ends profiles for a typical situation corresponding to the point (0.5, 0.75) in the phase diagram. The external part of the profile has been obtained by inverting the equal flight time Eq. (2.6),

$$\begin{aligned} \frac{z(p)}{h_0} &= \sqrt{\frac{P-p}{P_0}} + \frac{2}{\pi} \sqrt{\frac{Q-p}{P_0}} \arctan \sqrt{\frac{\eta}{P-Q-\eta}} \\ &\quad - \frac{2}{\pi} \sqrt{\frac{P-p}{P_0}} \arctan \sqrt{\frac{\eta(P-p)}{(P-Q-\eta)(Q-p)}} \\ &\quad + \frac{z^*}{h_0} \frac{2}{\pi} \arctan \sqrt{\frac{\eta}{Q-p}}. \end{aligned} \quad (3.18)$$

The brush size follows from this equation by setting $h = z(p=0)$.

C. Effect of fluctuations and polydispersity

We have so far neglected the effects of conformational fluctuations on the chains (which lead to finite corrections for $N < \infty$) and of polydispersity. As explained below, these contributions can both reduce the range of parameters over which an excluded zone is well defined.

1. Fluctuations due to finite N

Consider a chain starting at the tip of the exclusion zone, with some of its monomers dangling just behind z^* . Some of these monomers can penetrate the exclusion zone by fluctuations. A configuration with n monomers penetrating the exclusion zone requires a free energy of order ηn . Since chain fluctuations have an energy $k_B T$ and will have Gaussian conformation, the typical penetration depth is of order $\sqrt{n} \approx h_0 \sqrt{P_0/\eta} (R_G/h_0)^2$. In order for it to be well defined, the exclusion zone should be larger than this penetration depth! For small values of the interaction strength ϵ (for which the penetration depth is largest) we find a criterion for a well defined exclusion zone, $\epsilon/P_0 \gg (R_G/h_0)^{2/3}$, which can be easily satisfied for even a rather small ϵ , since as mentioned in the introduction, P_0 is typically of order $0.01 k_B T$, while R_G/h_0 is as small as $1/5$ in current experiments.

This criterion can also be written in terms of the exclusion zone depth [of order $\delta/h_0 \approx (h_0/z^*)(\epsilon/P_0)^2$ for small ϵ] as $\delta/h_0 \gg (h_0/z^*) (R_G/h_0)^{4/3}$, which will likely be satisfied if z^*/h_0 is not much less than 1. The distance $h_0 (R_G/h_0)^{4/3}$ has been previously identified as the typical distance that chain ends will fluctuate vertically in an unperturbed brush.¹⁴ This criterion can be interpreted by saying that the exclusion zone will be destroyed by fluctuations if its width δ is smaller than this characteristic fluctuation distance.

In the regime of total exclusion ($z^* < z_c^*$), we must use the relation $\eta \approx \epsilon^2/P_0$ to obtain $z^* \gg P_0^{1/2}/\epsilon$, which is reasonably easily satisfied (we can expect $\epsilon \approx 0.1 k_B T$ and $P_0 \approx 0.01 k_B T$, which gives a fluctuation length of order one monomer length). We may alternately write this condition in terms of the potential range z_c^* at which the complete-partial exclusion transition occurs; $z^* z_c^* \gg R_G^2$. For practical values of the interaction range and strength, the effect of fluctuations only reduce the exclusion zone by a negligible amount.

2. Effects of polydispersity

If there is in the brush some distribution of chemical lengths N , the end of a chain with a given length will be associated with a given position in the brush; the grafted polymer layer segregates the chain ends according to the polymer contour length to which they belong.¹⁵ As a consequence, if one considers a polydisperse brush in the absence of an external field, it is possible to associate some contour length N^* to the interaction range z^* . When the repulsive field is switched on, chains with a mass slightly smaller than N^* will stretch to escape the potential and an

exclusion zone is expected. To build up a large exclusion zone the shorter chains have to stretch up to z^* ; polydispersity thus induces an extra energy cost if the exclusion zone is to be sustained. In order to estimate the effect of introducing polydispersity we consider now some (arbitrary) length distribution of average size N and a lower cutoff N_{\min} . A simple estimate of how much larger a potential discontinuity at the exclusion zone edge (accomplished by, e.g., larger external field strength ϵ) will be needed to achieve total exclusion follows from Eq. (3.9),

$$\eta_{c,\text{poly}}/\eta_{c,\text{mono}} \approx \left(\frac{N}{N_{\min}} \right)^2 \quad (3.19)$$

while relations (3.5), (3.6) between η and ϵ still hold. The polydispersity shifts to larger ϵ/P_0 the border line between the total and the partial exclusion regimes in the phase diagram (Fig. 1) by a numerical factor which might be of order unity for fairly polydisperse samples.

IV. COMPETITION BETWEEN ADSORBED AND GRAFTED POLYMERS

An alternative route to colloidal stabilization is provided by polymer adsorption, which arises when all monomers are equally attracted by the surface. The interfacial layer formed via adsorption is a diffuse polymer "atmosphere," which extends over a distance of the order of the correlation length in the bulk solution.¹⁶ In contrast to end-grafted polymers, adsorbed chains are not strongly stretched, and the behavior of the polymers in the adsorbed layer is dominated by fluctuations. Pictorially, the adsorbed layer can be described as a semidilute polymer solution with a z -dependent correlation length which must be just the distance to the wall, $\xi[\phi(z)] = z$. The exact dependence of the concentration profile with the distance from the wall is therefore fixed by the statistics assumed for the semidilute solution. For Gaussian chains ("mean field," or marginal solvent conditions) $\xi \approx \phi^{-1/2}$, giving $\phi \approx z^{-2}$, while in a good solvent, once concentration fluctuations are accounted for, $\xi \approx \phi^{-3/4}$, giving $\phi \approx z^{-4/3}$. This self-similar (i.e., power-law) profile holds out to distances comparable to the chain radius for layers adsorbed from a dilute solution, and out to a distance comparable to the bulk screening length for chains adsorbed from a semidilute solution.

In this section, we discuss the behavior of such an adsorbed layer in the case where a polymer brush is attached to the surface; there will thus be competition between adsorption energy, and brush elastic energy. There are two apparent reasons for which this is important. First, it may be useful to finely tune properties of a polymer brush by adsorbing at the same time another (typically shorter) polymer. Second, even without an ungrafted, adsorbing species present, there may be attractive interactions between the wall and monomers of the chains in a brush, causing some degree of adsorption of the grafted chains. We wish to describe such a hybrid system of grafted/adsorbed chains. We take some steps in this direction, using the Cahn-de Gennes description of a polymer solution.¹⁷ In Secs. IV A and IV B, we study these two

problems, assuming “marginal solvent” conditions in order to use mean-field theory. In Sec. IV C we briefly outline the extension of the results to the case of good solvent.

A. Adsorption of free chains with a grafted layer present

In order to study the interfacial structure resulting from the competition between an adsorbed layer of chains A and a grafted layer of chains B , we need to minimize the total free energy with respect to the two concentration profiles ϕ_A and ϕ_B . At a mean-field level, minimization with respect to the grafted profile is equivalent to the determination of the brush structure under the external field $w_{AB}\phi_A$, where w_{AB} is the Flory interaction parameter between the monomers on the A and B chains. For infinite chains, mean-field theory predicts segregation of A and B chains if $w_{AB}^2 \gg w_A w_B$, where w_A and w_B are the A and B chain Flory excluded volume interactions, respectively.

The grand-potential functional relevant for the adsorbed polymer layer is

$$\Omega = \int d^3r \left[\frac{1}{6} (\nabla\psi_A)^2 + \frac{1}{2} w_A \psi_A^4 + (w_{AB}\phi_B - \mu) \psi_A^2 \right], \quad (4.1)$$

where $\psi_A^2 = \phi_A$ and μ is the chemical potential associated either with (a) the bulk chemical potential $\mu = w_A \phi_{AB} = w_A \phi_A(\infty)$ when the adsorbed layer is taken to be in equilibrium with a bulk solution [in this case an extra pressure term needs to be added to Eq. (4.1)], or with (b) a Lagrange multiplier used to enforce monomer conservation when the polymer layer is taken to be irreversibly adsorbed.

Functional minimization of Eq. (4.1) with respect to ψ_A leads to

$$\frac{1}{6} \frac{d^2\psi_A}{dz^2} = w_A \psi_A^3 + (w_{AB}\phi_B - \mu) \psi_A. \quad (4.2)$$

This equation needs to be solved subject to the two boundary conditions

$$\left. \frac{1}{\psi_A} \frac{d\psi_A}{dz} \right|_{z=0} = -\frac{1}{D}, \quad (4.3)$$

$$\lim_{z \rightarrow \infty} \psi_A(z) = 0.$$

The first of these conditions relates the logarithmic slope of the potential to the strength of the attraction, represented here by an extrapolation length D . For strong attractions, D is of order unity. The second condition only holds exactly for irreversibly adsorbed chains, but it is also a good approximation for chains in equilibrium with a not too concentrated polymer solution—how small the concentration needs to be will become clear shortly.

The solution to Eq. (4.2) possesses two main regimes. First, close to the wall (where the first term on the right-hand side dominates) we find an unperturbed (mean-field) adsorbed layer profile, $\phi_A \approx 1/z^2$. Further away from $z=0$, we observe a second regime where there is a roughly exponential decay of ϕ_A with a decay length ξ

$= 1/\sqrt{w_{AB}P_0 - \mu}$ which is of order of the mean-field brush “blob” size $\sigma^{-1/3}$ when $\mu \ll w_{AB}P_0$. This decay is not precisely exponential as the brush concentration profile will vary somewhat over the adsorption region. However, the results of Sec. II B indicate that ϕ_B will be small in the region where the external field $w_{AB}\phi_A$ exceeds the scale of the brush chemical potential $P_0 \approx (w_B\sigma)^{2/3}$, which will be true at $z=0$ for $D^{-1} \gg w_{AB}^{-1/2} (w_B\sigma)^{1/3}$. Beyond the range of the absorption layer, the brush profile will extend a distance of order $h_0 \approx (w_B\sigma)^{1/3} N$. For long grafted polymers at low coverages, the brush profile will be approximately constant over the region where the second term in the right-hand side of Eq. (4.2) dominates.

Qualitatively the adsorption of a polymer inside the brush can be thus viewed as adsorption from a semidilute solution with a correlation length of the order of the brush blob size. Comparison of the last two terms on the right-hand side of Eq. (4.2) indicates that the $z \rightarrow \infty$ boundary condition presuming a vanishing tail of the adsorbed profile is valid for an equilibrium situation where the adsorption is from semidilute solution, as long as the concentration of the solution remains smaller than the average concentration of polymers B in the brush. Geometrically, this is equivalent to recognizing that this boundary condition is appropriate when the screening length for bulk polymer concentration fluctuations is large compared to the brush blob size. If the bulk concentration is larger than the brush concentration, the adsorption is insensitive to the presence of the grafted layer; the self-similar profile holds over a distance of the order of the bulk blob size, which is then smaller than the distance between grafting points.

B. Adsorption of grafted chains

We now use the preceding ideas to describe a brush whose monomers are attracted by the surface. In order to do so, we first note that the attraction will create a zone close to the wall of higher density than the average density in the brush. The monomers in this zone will belong to chain loops which have at least one of their monomers in contact with the wall; in these regions, monomers feel the influence of the adsorbing wall. By contrast, monomers close to the outer edge of the brush do not experience any effect of the adsorption. Chains in the adsorbed-grafted layer may be divided into two classes. The first class, making up σ_1 of the total coverage σ , are “adsorbed” chains, with free ends in the zone where attraction from the wall is important (a criterion to be developed below). The second class, “nonadsorbed chains” of graft density σ_2 , is made up of the remaining chains that have free ends outside this zone. The chains in this latter class may be regarded as making up a brush immersed in an “external potential” near the grafting surface that is due to interactions with the dense portion adsorption layer near $z=0$. Naturally, $\sigma_1 + \sigma_2 = \sigma$, the total brush graft density.

The monomer coverage Γ due to the “adsorbed” chains is determined by the attraction strength D , and in mean-field theory is $\Gamma = \sigma_1 N \approx 1/D$. For strong adsorption one has $\Gamma \approx 1$. There is thus a relative fraction $\sigma_1/\sigma \approx \Gamma/$

$N\sigma$ of chains in the adsorbed zone, the brush thickness being now given by $h \approx h_0(1 - \Gamma/N\sigma)^{1/3} + \sigma^{-1/3}$ or for small Γ , $h \approx h_0 - \Gamma/\sigma^{2/3}$; the attraction reduces the overall brush thickness.

One may wonder about the accuracy of our partition of the grafted-adsorbed layer into two different classes. To observe the validity of this idea, consider (as before) the total layer to be a grafted layer immersed in an adsorbed layer, but now allow each chain to contribute an arbitrary number ($< N$) of its monomers to the brush layer, and the remainder of its monomers to the adsorbed region. This picture allows for polydispersity of the chain lengths in the brush portion of the system. In the strong adsorption limit the total surface coverage in the adsorbed layer is imposed by the adsorption strength, $\Gamma = 1/D \approx 1$; the remaining material is stored in the brush. In this limit the energy of the adsorbed layer is also fairly independent of the polydispersity (neither the chain length nor the chain tension should be important since the adsorption energy scale dominates). The polydispersity can be determined by the minimization of the free energy F_{br} of a polydisperse brush¹⁵ with a fixed surface coverage $N\sigma - \Gamma$,

$$F_{br} = A \int_0^N dn [\sigma^+(n)]^{5/3}, \quad (4.4)$$

where $\sigma^+(n)$ is the density of chains of contour lengths larger than n and A is a numerical constant. For simplicity, the upper bound of the distribution is set to the total chain length N . Minimization of the free-energy with total coverage constrained [$\int_0^N dn \sigma^+(n) = \sigma - \Gamma/N$] yields $\sigma^+(n) = \text{constant}$. This shows that the only allowed values for the mass distribution are either 0 or N . The chains are therefore either "fully stretched" or "fully adsorbed," justifying the assumption of a two-class layer.

C. Good solvent conditions

The preceding description for the competition between adsorbed and grafted chains can be simply extended to good-solvent, by replacing the mean-field blob size $\sigma^{-1/3}$ with the corresponding good-solvent value of $\sigma^{-1/2}$, and the mean-field brush chemical potential $w_B \phi_B$ by the good-solvent chemical potential $\phi_B^{5/4}$. The geometrical picture explained above still holds. The structure of the adsorbed layer inside the brush is given, close to the wall, by the unperturbed concentration profile in good-solvent $\phi_A \approx z^{-4/3}$; for distances larger than $\sigma^{-1/2}$ the profile then decays to a very small value, with the characteristic decay length $\sigma^{-1/2}$. The only difference, which is a small one for strong adsorptions, is that the total coverage now depends on the extrapolation length as $\Gamma \approx D^{1/3}$.

V. DISCUSSION

We have developed a mean-field description of polymer brushes subjected to external potentials. In this section we discuss recent simulation results relevant to our conclusions, and estimate the typical parameters for brushes

perturbed by monomer-surface interactions or by a thin wetting layer of some sort that forms at the grafting surface.

Chakrabarti, Nelson, and Toral¹⁸ have recently carried out computer simulations of self- and mutually-avoiding lattice polymers in external potential fields; they chose to study the repulsive and attractive step potentials discussed in Sec. III. In the attractive case, they found that the scaling formula Eq. (2.16) quantitatively describes the layer height. Since the self-avoidance parameter w was previously measured for this type of simulation, there are no adjustable parameters.

The same authors studied a brush in a wide (half the brush height) repulsive square potential barrier, with a strength well into the total exclusion regime. They observe complete exclusion of polymer free ends from the potential region, with only a small depression in the monomer density inside the well, all in good quantitative agreement with the theory. This result is the first unequivocal observation of a free-end-exclusion zone in a simulation of a polymer brush. It is very encouraging that the mean-field theory describes these rather subtle aspects of the full many-body statistical mechanics. It would be interesting to simulate weaker repulsive wells in order to study chain fluctuations into the exclusion zone.

We conclude from the above that many-body effects (correlations due to good solvent) do not change the basic conclusions of our analysis of brush response to an external field. Now we wish to estimate the effects of potentials due to various sorts of interfacial phenomena at the grafting surface, on a brush. Milner⁶ has discussed typical brush experiments of Taunton *et al.*¹⁹ on PS chains in toluene (good solvent) anchored to a mica surface. The chains had a molecular weight of 1.4×10^5 , corresponding to $N \approx 1000$. The graft density was $\sigma = 1.3 \times 10^{-4} \text{ \AA}^{-2}$, and the observed layer thickness was $h_0 = 600 \text{ \AA}$. Assuming a monomer size of 5 \AA , we have a dimensionless grafting density of $\sigma = 0.0033$, and we estimate a dimensionless excluded volume of $w \approx 1.3$. We thus expect a volume fraction near the grafting surface of $\phi_0 = (27\pi^2/32)^{1/3} w^{-1/3} \sigma^{2/3} \approx 0.04$, consistent with the experimental results. The free energy per monomer was of order $0.01 k_B T$.

We now can estimate the characteristic surface energy Λ_S needed to appreciably perturb the brush using Eq. (2.16); we find that there will be a brush height change of order $\Delta h \approx h_0 \Lambda_S / (3w\sigma N)$. If $\Lambda_S \approx 0.5$ (corresponding to a surface energy difference between pure monomer and pure solvent of 8 dyn/cm) we have $\Delta h \approx 2 \text{ nm}$. This kind of shift might be expected in the case that there are chemical differences between solvent and monomer favoring adsorption of monomer at the grafting surface. One expects in this case to observe a strong enhancement of the monomer density profile near the grafting surface, since such surface interactions correspond to contact energies per monomer greatly in excess of $0.01 k_B T$. For this example, we expect a fraction $\Lambda_S / (w\sigma N) \approx 0.12$ of the ends to be found near the surface. Since in the absence of such interactions, the end distribution is strongly quenched near the grafting sur-

face, a peak in $d\sigma/dz$ near $z=0$ would suggest attraction of the monomers to the surface.

For a repulsive surface energy originating from short-range interactions, the layer height will not be appreciably altered, but strong depletion of the monomer density profile near the grafting surface would be expected whenever monomer-surface contact energies exceed $0.01k_B T$.

In the event that a wetting layer of a minority solvent is adsorbed at the grafting surface these effects can be amplified due to the potential long-range nature of the effective surface field. We suppose a 10 nm thick wetting layer (20 monomer lengths) that is adsorbed onto the grafting surface, with a weak chemical potential difference of $0.1k_B T$ between monomers immersed in the two solvents. Clearly the monomer potential (and the monomer density) will be strongly modified by the wetting layer potential. In the attractive case, we now estimate a dimensionless parameter $\Lambda_S \approx 2$. As a result (using the parameters from above), $\Lambda_S/(w\sigma N) \approx 0.5$ of the ends are confined inside the wetting layer; the layer height will be reduced by $\approx 20\%$.

In the repulsive case we have $z^*/h_0 = 0.16$ and $\sqrt{\eta/P_0} \approx 3$; we thus expect to be far into the total exclusion regime. One might keep in mind that the repulsive energy per chain might exceed the tethering energy—or even the backbone bond energy—in our prototype example, we imagine of order 100 monomers to be immersed in our $0.1k_B T$ potential, leading to a $10k_B T$ of repulsive energy, while energies of chemical bonds are of order $50k_B T$.

The exclusion zones that arise in response to such external fields will be robust compared to those that arise in the theory of brushes on curved surfaces¹³ because the discontinuity in the potential at the zone boundary is an externally controlled, typically large energy scale. Without careful tuning, we have argued (e.g., wetting layer discussed above) that external potentials will be of order $0.1k_B T \gg P_0 \approx 0.01k_B T$; fluctuation of chain segments into

this potential will thus be strongly suppressed. By comparison, in the curved surface problem, the potentials that maintain the exclusion zone are only of order P_0 (they arise from monomer-monomer interactions); fluctuations are only suppressed for $N \rightarrow \infty$.

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