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Polymer Brush in Contact with a Mixture of Solvents

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ABSTRACT: We study a polymer brush, in the strongly-stretched regime, in contact with a binary mixture of low-molecular weight solvents. The height of the polymer brush is found to always scale linearly with polymer chemical length. Depending on the solubility of the monomers in the two solvents, a variety of behaviors are possible as the bulk composition of the mixed solvent is varied. In the case of a mixture of a good and bad solvent, we find that, at intermediate concentrations, a collapse of the brush may occur: the collapsed state is distinguished by a step in monomer density at the brush tip. In a mixture of two good solvents, there may be nonmonotonic dependence of the brush thickness on solvent composition.

I. Introduction

Long polymers grafted to a surface are strongly perturbed from their ideal random-coil state: as molecular weight is increased, the polymer excluded-volume interactions force the chains to stretch. The properties of grafted polymers were first studied by de Gennes[1] and Alexander[2] and later by Semenov.[3] More recent studies[4,5,12] have developed a microscopic statistical–mechanical picture of chain conformations of grafted polymers in the long-chain limit. A central result of all of these studies is that the free energy per chain and the typical chain extension scale *linearly* with molecular weight. The "strong-stretching" theory uses these properties to justify a mean-field approach that ignores conformational fluctuations around a set of "classical" chain configurations.

In experiments it is technically feasible to achieve free energies per chain of several kT, resulting in chain extensions greater than 5 times the unperturbed chain radius.[6] Recent experimental results are in good agreement with the scaling properties predicted by the strong-stretching theories,[7,8] recent simulation results are in good agreement with predicted details of the grafted layer structure, even for rather short chains.[9,10]

Auvray and Auroy have recently carried out an interesting series of experiments on strongly-stretched grafted layers, following naturally from their previous studies concerning layer structure in good and poor solvents.[7] In a good solvent, the polymer layer is rather sparse, as the chains stretch out to contact the solvent. However, in a solvent that is poor for the polymer, the layer collapses in order to escape the solvent: a high density layer of reduced height, with a sharp polymer–solvent interface is obtained. The experiments relevant to this paper are studies of polymer layers immersed in a *mixture* of two solvents.[11] By changing the bulk composition of a mixture of a good and bad solvent, one may drive a layer collapse transition,[12] accompanied by preferential adsorption of one of the two components into the polymer layer.

In this paper we study the structure of a polymer brush in contact with a mixture of two solvents. Section II.A presents the model, which is essentially that of independent flexible chains, subject to a self-consistently determined inhomogeneous chemical potential due to interactions between the different species. The equilibrium requirements that allow us to solve the model are presented in section II.B: central to the analysis is the requirement that the total monomer potential be a parabolic "equal-time" potential.

Section III studies the behavior of the theory in a variety of limits. In section III.A, we check that when the composition dependence is removed from the theory, the proper limiting behavior is observed. Also, we note the recovery of the dilute, strong-stretching limit. Section III.B studies the scaling properties of the general problem. in section III.C, the effect of slight dilution of one solvent by a second is studied: this case may be analytically solved in the limit of low polymer and impurity solvent volume fractions.

Section III.D examines the behavior of the theory when the mixture of solvents is not in a dilute limit: the theory is highly nonlinear, and dramatic reorganizations of the polymer layer may occur. We isolate the location of a "collapse" of the polymer layer,[12] a phenomenon analogous to the collapse of an isolated coil as solvent conditions are changed from good to poor. In section III.E, numerical results illustrating some interesting nonlinear effects including the collapse of the layer in a mixture of a good and bad solvent are presented.

II. Grafted Polymers Immersed in a Two-Component Solvent

A. The Model. 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. Monomers are taken to a distance b in length ($b \approx 5$ Å); a monomer is supposed to displace a volume b^3. The ith chain is described by a space curve $\mathbf{r}_i(n)$, where n runs from 0 at the grafted end to N at the free end; the position of the grafted end is fixed: $\mathbf{r}_i(0) = (x_{0i}, y_{0i}, 0)$. The polymer volume fraction at a position $\mathbf{r}$ is thus

$$\Phi(\mathbf{r}) = b^3 \sum_{\text{chains } i} \int_0^N \mathrm{d}n\, \delta^3(\mathbf{r}-\mathbf{r}_i(n)) \tag{1}$$

The local volume fraction of solvent B is defined to be $\psi(\mathbf{r})$: volume conservation indicates that the volume fraction of solvent A is thus $1 - \psi(\mathbf{r}) - \Phi(\mathbf{r})$. In the bulk, outside the polymer brush, the B concentration is ψ_0, while the A concentration is $1 - \psi_0$; the bulk concentration ψ_0 is taken to be a control parameter. We consider a bulk reservoir of sufficient volume that the shift in ψ_0 due to adsorption in the brush may be neglected.

The free energy (energies throughout this paper will be reported in units of kT) of the system for a given set of chain conformations is

$$F = \sum_i \frac{3}{2b^2}\int_0^N \mathrm{d}n \left(\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}n}\right)^2 + \int \frac{\mathrm{d}^3r}{b^3} f(\psi(\mathbf{r}),\Phi(\mathbf{r})) \tag{2}$$

where the first term measures the entropy loss due to

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extension (stretching) of the chains, and the second term reflects the ideal gas entropy of the solvent and interactions; it is taken to have only local dependence on the field variables Φ and ψ. We thus ignore all correlation effects on scales shorter than the correlation length for polymer volume fraction fluctuations, which is of order $\sigma^{-1/2} \approx 50$ Å. Since the chain dimensions of interest to us are on the order of the layer thickness $h \approx 800$ Å, this assumption is reasonable.

The local part of the free energy is taken to have the following structure:

$$f(\psi,\Phi) = \psi \log \psi + (1-\psi)\log(1-\psi) + \mu\psi + \frac{1}{2}w\Phi^2 + w_{\mathrm{sp}}\psi\Phi + \frac{1}{2}w_{\mathrm{s}}\psi^2 - \frac{1}{2}w_{\mathrm{spp}}\psi\Phi^2 + \frac{1}{3}v\Phi^3 \quad (3)$$

The first two terms are the ideal lattice-gas entropy associated with the two solvents; the third term is the chemical potential of solvent B. For solvent concentration in the bulk of ψ_0, the required chemical potential follows from the equilibrium condition $\partial_\psi f(\psi_0,0) = 0$:

$$\mu(\psi_0) = \log\left(\frac{1-\psi_0}{\psi_0}\right) - w_{\mathrm{s}}\psi_0 \quad (4)$$

The fourth term in (3) is due to polymer–polymer excluded-volume interactions in the absence of B molecules. The fifth term is due to B-polymer interactions with $w_{\mathrm{sp}} > 0$ modeling repulsion of B particles and the monomers: this term is important as it translates changes in the local solvent composition into changes in the local monomer chemical potential. The sixth term is due to A–B interactions, and $w_{\mathrm{s}} > 0$ stabilizes the solvent mixture against phase separation. The seventh term models the change in solvent quality due to changes in solvent composition: for pure A ($\psi = 0$) solvent, we have polymer–polymer excluded-volume interactions of strength w; for pure B ($\psi = 1$) we have excluded-volume interactions of strength $w - w_{\mathrm{spp}}$. Finally, the last term is repulsive ($v > 0$) and models three-body polymer interactions that stabilize a high-polymer-density phase under bad solvent conditions.

The model described thus far is a generalization of that used by various authors,[4,5,12,13] to describe grafted polymers in solvent stretched by their mutual self-avoidance.

We now expand the free energy as a function of the fluctuating monomer density Φ, around its expectation value. We write $\Phi(\mathbf{r}) = \phi(\mathbf{r}) + \delta(\mathbf{r})$, with $\phi(\mathbf{r}) \equiv \langle\Phi(\mathbf{r})\rangle$. The free energy (eq 2), ignoring terms of order δ^2, becomes

$$F = \sum_i \int_0^N \mathrm{d}n \left[\frac{3}{2b^2}\left(\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}n}\right)^2 + U(\mathbf{r})\right] - \int \frac{\mathrm{d}^3r}{b^3}\Pi(\psi,\phi) \quad (5)$$

where the monomer chemical potential is $U = \partial_\phi f(\psi,\phi)$ and where $\Pi = \phi U - f$ is the local monomer osmotic pressure, neglecting contributions from chain stretching. In our model, U is just

$$U = -\log(1-\psi-\phi) - 1 + w\phi + w_{\mathrm{sp}}\psi - w_{\mathrm{spp}}\psi\phi + v\phi^2 \quad (6)$$

Both U and Π are local: they are defined at a given point $\mathbf{r}$ once ψ and ϕ are known at that point. Symmetry allows us to conclude that ϕ, ψ, U, and Π are independent of the x–y planar coordinates.

B. Equilibrium and Self-Consistency Conditions. In this paper, we are concerned 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 end-to-end distance $R = bN^{1/2}$ but is much less than the maximum extension of the chain. Correspondingly, we expect that a chain with a free end at a height z_N fluctuates only narrowly about the path $\mathbf{r}(n)$ which minimizes its total free energy (we expect the monomer at position n to fluctuate only a distance of order R away from $\mathbf{r}(n)$). Again, by symmetry, for a chain grafted at a position $\mathbf{r}_0$, this minimizing conformation has the form $\mathbf{r}(v) = \mathbf{r}_0 + z(v)\hat{\mathbf{z}}$.

Since the chains are in mechanical equilibrium, we demand that there is no tension at the free end: $\mathrm{d}z(N)/\mathrm{d}n = 0$. The conformation function $z(n)$ thus satisfies "Newton's law" for the trajectory of a particle when the variable $N - n$ is interpreted as "time" and U is interpreted as potential energy:

$$\frac{3}{b^2}\frac{\mathrm{d}^2z}{\mathrm{d}n^2} = \frac{\mathrm{d}U}{\mathrm{d}z} \quad (7)$$

where we have boundary conditions $z(0) = 0$, $z(N) = z_N$, and $\mathrm{d}z(N)/\mathrm{d}n = 0$.

Assuming that ends are distributed throughout the layer, we see that the boundary conditions strongly constrain $U(z)$: it must be an "equal-time" potential with the property that the "time" N required to "fall" from rest ($\mathrm{d}z(N)/\mathrm{d}n = 0$) to $z = 0$ is independent of the initial position $z(N)$. The potential must be harmonic: $U(z) = U(\infty) + A - Bz^2$, where $B = 3\pi^2/(8b^2N^2)$ and where we have used $U(\infty) = -\log(1-\psi_0) - 1 + w_{\mathrm{sp}}\psi_0$, the chemical potential of monomers in the bulk, as a reference for $U(z)$. Defining $p = A - Bz^2$, we thus obtain

$$p = \log\frac{1-\psi_0}{1-\psi-\phi} + w\phi + w_{\mathrm{sp}}(\psi-\psi_0) - w_{\mathrm{spp}}\psi\phi + v\phi^2 \quad (8)$$

The value of $A \equiv p(z{=}0)$ must be set using the requirement that each chain be in mechanical equilibrium. A sufficient condition is that the local monomer osmotic pressure ($\Pi \equiv \phi\partial f/\partial\phi - f$) at $z = h^-$ should be equal to the monomer osmotic pressure in the bulk. That this is a suitable equilibrium condition follows from the fact that the monomers at $h = z$ are only at the ends of chains and thus have no stretching forces acting on them. Thus, if we make sure that there is no osmotic pressure due to the local free energy acting on these monomers, we will know that the chains with free ends at $z = h$ are in equilibrium, and in turn (since the chemical potentials of all chains are equal for parabolic $U(z)$) all of the polymers are in equilibrium. Thus, we require

$$[\phi U - f]_{z=h^-} + f(\psi_0,0) = 0 \quad (9)$$

In cases where $\phi(h^-) = 0$ (which occurs when the solvent quality at the tip of the brush is good), $\psi = \psi_0$ and $\phi = 0$ at the brush tip, and thus (9) is satisfied. In this case, $p(z{=}h) = 0$ follows from (8), giving $A = Bh^2$.

The equilibrium solvent concentration is obtained by requiring solvent molecules to have the same free energy regardless of position in the system: this is expressed as the local condition $\partial_\psi f(\psi,\phi) = 0$, which in our case gives

$$0 = \log\frac{\psi}{1-\psi-\phi}\frac{1-\psi_0}{\psi_0} + w_{\mathrm{s}}(\psi-\psi_0) + w_{\mathrm{sp}}\phi - \frac{1}{2}w_{\mathrm{spp}}\phi^2 \quad (10)$$

The layer height h is determined by the sum rule relating the integral of ϕ to the chain chemical length N:

$$\int_0^h \frac{\mathrm{d}z}{\sigma}\phi(z) = Nb^3 \quad (11)$$

This formula simply expresses that, above each region of the surface of area $1/\sigma$, there must be on average N monomers. The equations (8), (10), (9), and (11) must be solved simultaneously to obtain the equilibrium densities ϕ and ψ and the layer thickness h.

Once the structure is solved, one may extract the distribution of free ends using established techniques;[13] in this paper we do not report such calculations. However, we comment that, in all cases considered, the end distribution is positive (i.e., there are no end-exclusion zones).

III. Results for Brush in Mixed Solvent

A. Absence of Solvent Composition-Dependent Interactions. We consider the case where w_s, w_{sp}, and w_{spp} are all zero. In this case, the polymer is insensitive to the local composition of the solvent, and we expect all properties of the polymer field to be independent of ψ_0. In this case, (10) immediately leads to $\psi = \psi_0(1 - \phi)$, indicating that the local volume fraction of solvent A is just its average volume fraction ψ_0, multiplied by the available volume fraction (volume fraction unoccupied by polymer), $1 - \phi$. Plugging this into (8) leads to the relation

$$p = -\log (1 - \phi) + w\phi + v\phi^2 \qquad (12)$$

which is independent of ψ_0 as required. In addition, we note that, for small ϕ, (12) reduces to $p = (1 + w)\phi$, indicating that the "bare" self-avoidance w is shifted to $1 + w$ by a contribution from the solvent entropy. This shift is usually just absorbed into the definition of w in problems where there is a single-component solvent.

In this case where we ignore terms of order ϕ^2 and assume good solvent $(1 + w > 0)$ we find the results of previous treatments for the (unperturbed) layer height h and maximum chemical potential $P_0 \equiv p(z{=}0) = A = B$:

$$h_0 = (4\sigma b^2[1 + w]/\pi^2)^{1/3}Nb$$

$$P_0 = (27\pi^2\sigma^2b^4[1 + w]^2/32)^{1/3} \qquad (13)$$

B. Scaling Properties. The large number of interactions results in a large number of dimensionless parameters required to describe our model. However, there is an important symmetry that may be revealed by noting that N explicitly appears only in the sum rule (11). Thus, if we measure heights in units of the unperturbed brush height $h_0 = (P_0/B)^{1/2}$, all N-dependence disappears from the theory. This indicates that all intensive quantities (ψ, ϕ, and all quantities derived from them) are N-independent and that the brush height must scale linearly with N.

The coupling constants, concentrations, and the grafting density σ are taken to be defined in terms of the lattice scale b and are taken to be dimensionless. Examination of equations (8)–(10) indicates that we must specify the dimensionless quantities P_0 (the unperturbed brush potential scale of section III.A; equivalently one may specify σb^2), bulk composition ψ_0, and coupling constants w, w_s, w_{sp}, w_{spp}, and v.

We remind the reader that this scaling behavior requires the strong-stretching approach to be valid: the layer height h must be much larger than the unperturbed chain radius of order $bN^{1/2}$ and much less than the maximum allowed extension of order bN.

C. Good Solvent with a Small Amount of Added Solvent. Consider the case where the solvent is mostly good solvent A (volume fraction $1 - \psi_0 \approx 1$) mixed with a small amount of solvent B ($\psi_0 \approx 0$). We consider ϕ to be small (this may be achieved under good solvent conditions by taking the limit of long chains and a low grafting density, as usual) so that terms of order ϕ^2 may be ignored. Since we expect $\psi \approx \psi_0$ in this limit, we also neglect terms of order ψ_0^2; the resulting linearized problem may be solved in closed form and is physically relevant. An additional simplification follows from the fact that under good solvent conditions we have $p = B(h^2 - z^2)$, and we do not need to worry about the monomer osmotic pressure equation (eq 9).

We may rewrite (10) as

$$\psi/\psi_0 = 1 - (1 + w_{sp})\phi \qquad (14)$$

where we have dropped all terms of order $(\psi - \psi_0)^2$ and ϕ^2. We note that since $\phi > 0$, we generally have $\psi < \psi_0$, indicating a preferential adsorption of solvent A in the case where there is repulsion of A molecules and monomer ($w_{sp} > 0$). We may compute the amount of solvent B in the brush to first order in ψ_0:

$$\Psi \equiv \int_0^h \frac{\mathrm{d}z}{\mathrm{b}}\psi(z) = \psi_0[h_0/b - N\sigma b^2] - \psi_0 w_{sp} N\sigma b^2 \qquad (15)$$

The first term is the B adsorption in the absence of solvent-selective interactions and is purely geometrical, corresponding to ψ_0 times the volume available for solvent in the brush (total volume minus the volume occupied by polymer). The second term is the excess adsorption of B due to solvent-selective interactions. To lowest order in ψ_0, only the coupling w_{sp} causes excess respulsion (or adsorption, if $w_{sp} < 0$) of B molecules from the interior of the brush. We note that since $N\sigma b^3 \ll h_0$ for a swollen brush ($N\sigma b^3$ is the height of a brush under melt conditions), the excess of solvent B in the brush changes rather slowly with ψ_0 in comparison to the large geometrical term.

Carrying out a similar expansion of (8), we find that the potential p is

$$p = (1 + w - \psi_0[w_{spp} + 2w_{sp} + w_{sp}^2])\phi \qquad (16)$$

Since p is parabolic, the profile of adsorbed solvent ϕ is also parabolic. Both the direct repulsion of polymer and solvent (w_{sp}) and the induced change in the polymer–polymer interactions (w_{spp}) can reduce $\phi(p)$ as ψ_0 is increased from zero.

We may use the sum rule (eq 11) to determine the layer thickness: at lowest order in ψ_0, we find

$$\frac{h}{h_0} = 1 - \frac{w_{spp} + 2w_{sp} + w_{sp}^2}{3[1 + w]}\psi_0 \qquad (17)$$

Thus h depends linearly on ψ_0 for small ψ_0, as has been observed in recent experiments. For any combination of B-polymer repulsion ($w_{sp} > 0$) and reduction of polymer–polymer exclusion due to the presence of B molecules ($w_{spp} > 0$), we see that h is reduced as the fraction of B in the bulk (ψ_0) is increased and that the B solvent fraction is reduced below the bulk concentration inside the brush. One expects this case to hold when A is a good solvent and B is a poor solvent.

We note that already there are some interesting possibilities indicated by these results. We again suppose that solvent A is a good solvent. However, if the minority solvent B is an even better solvent for the polymer, we will likely have the situation that $w_{sp} < 0$ (B-polymer *attraction*) and $w_{spp} < 0$ (presence of B enhances self-avoidance of the polymer). In such a case, we may find *either* an increase *or* a decrease in the overall layer thickness with ψ_0, depending on the sign of $w_{spp} + 2w_{sp} + w_{sp}^2$. In such a case where $w_{sp} < 0$, excess B is adsorbed into the brush.

D. General Case. Solving the general case where ψ_0 is not small is experimentally relevant; however, since the solvent quality may change when ψ_0 becomes of order unity, we no longer can afford the simplification of ignoring nonlinear terms in ϕ. The general case is interesting because the qualitative features of the brush change as the solvent changes from good to bad for the monomers. However, far beyond chain-collapse transitions, stronger nonlinearities than we have included are important in a quantitative description of the high-density polymer brush.

Since we expect a chain-collapse type instability as solvent quality is decreased, our aim is to write the monomer chemical potential (eq 8) as a power series in ϕ. We proceed by rewriting (10) as an expansion in powers of ϕ for $\log(1-\psi_0)/(1-\psi-\phi)$:

$$\log\left(\frac{1-\psi_0}{1-\psi-\phi}\right) = -\log F + \frac{1-w_{sp}E\psi}{F}\phi + \left[\frac{(w_{spp}-w_{sp}{}^2)E\psi}{F} + \frac{(E\psi w_{sp}-1)^2}{F^2}\right]\frac{\phi^2}{2} \quad (18)$$

where $E \equiv \exp[w_s(\psi-\psi_0)]$ and $F \equiv 1 + (E-1)\psi$ and where contributions of order ϕ^3 and higher have been dropped. We will keep ϕ small to make this an accurate approximation; we recall that we have already ignored the terms of this order in the original free energy function. We note that, for $\psi = \psi_0$, $E = F = 1$.

Combining (18) with (8) allows us to write the monomer equation of state as a power series in ϕ:

$$0 = X + Y\phi + Z\phi^2$$

$$X \equiv w_{sp}(\psi-\psi_0) - p - \log F$$

$$Y \equiv w - w_{spp}\psi + \frac{1-w_{sp}E\psi}{F}$$

$$Z \equiv v + \frac{1}{2}\left[\frac{(w_{spp}-w_{sp}{}^2)E\psi}{F} + \left(\frac{w_{sp}E\psi-1}{F}\right)^2\right] \quad (19)$$

This equation may be combined with (10) to find the values of ψ and ϕ as a function of p.

In this paper, we are primarily interested in possible structural changes driven by a change in solvent quality modeled by a large positive value of w_{spp} and moderate w_{sp} and w_s. In particular, we are interested in studying the profile near the tip of the brush: we wish to know under which circumstances the monomer density goes smoothly to zero and under which circumstances there is a step in ϕ at $z = h$.

We may locate the point at which such a transition takes place by solving (19) and (10) for $p \approx 0$, $\psi \approx \psi_0$, and $\phi \approx 0$. It is straightforward to expand (10) around this point to first order in ϕ:

$$\phi = c(\psi_0 - \psi)$$

$$c \equiv \frac{\psi_0{}^{-1} + [1-\psi_0]^{-1} + w_s}{[1-\psi_0]^{-1} + w_{sp}} \quad (20)$$

Since $c > 0$ for $w_{sp} > 0$ and $w_s > 0$, we see that, for small ϕ, we will have ψ slightly less than the bulk value ψ_0, as is physically reasonable. Insertion of this result into (19) yields

$$p = t\phi + \mathcal{O}(\phi^2)$$

$$t \equiv 1 + w - [w_{spp} + w_{sp}]\psi_0 + (\psi_0 w_s - w_{sp})/c \quad (21)$$

If t is positive, $\phi = p/t$ as $p \to 0$. This will be the case for small w_{sp} if ψ_0 is also small.

If t is negative, if p is to approach zero from positive values (it is a parabolic function of z), the branch of (21) for which $\phi(p=0) = 0$ takes on negative values as $p \to 0$. This solution is physically inadmissable: for $t < 0$ the physical solution to (21) is one which satisfies $\phi(z=h^-) \neq 0$. The monomer density at the brush tip $\phi(z=h^-)$ is determined by the nonlinear terms of the above equations and by the osmotic pressure equation (eq 9); we expect $p(z=h) = P - Bh^2 \neq 0$ in this case. We thus identify $t = 0$ as a special point, at which the qualitative properties of the polymer layer change.

For $w_s = w_{sp} = 0$, the value of ψ_0 at which t changes sign is particularly simple:

$$\psi_0{}^* = (1 + w)/w_{spp} \quad (22)$$

which is simply the point at which the effective solvent quality in the bulk changes from good to poor. For $\psi_0 < \psi_0{}^*$, the layer is "swollen", with $\phi(h^-) = 0$; for $\psi_0 > \psi_0{}^*$, the layer is "collapsed", with a jump in monomer density at $z = h$.

E. Survey of Strongly Nonlinear Regimes. In this section we examine some isolated examples of the global nonlinear behavior of our model. This is necessarily a numerical study. In this section we take $w = 1$; this value for the two-body self-avoidance coupling for $\psi_0 = 0$ is near that for lattice polymers used in Monte Carlo studies of grafted polymers.[9,10] Since we require ϕ to be small and since, in the unperturbed brush, $\phi(z=0) = P_0/(1 + w)$, we take $P_0 \approx 0.1$. This ensures that the monomer density ϕ will be on the order of a few percent. Finally, we take $v = 1$ to be the three-body self-avoidance parameter. This parameter is not crucial and simply sets a scale for the high-density phase below the polymer Θ point. We are left with the three parameters w_s, w_{sp}, and w_{spp}, which control the miscibility of the two solvents, the B-polymer repulsion, and the reduction of the polymer–polymer self-avoidance due to presence of B, respectively.

The first situation that we consider is $P_0 = 0.05$, $w_{sp} = 1$, and $w_{spp} = 0$, with $w_s > 0$. This corresponds to a solvent mixture that is at a temperature above its bulk phase separation point, with a moderately strong direct B-polymer repulsion, and no change of self-avoidance due to the presence of B. In Figure 1, we show the calculated height h, in units of h_0, as a function of $1 - \psi_0$, the bulk volume fraction of solvent A. In the case $w_s = 0.5$, we see a monotonic decrease in h as $1 - \psi_0$ is decreased from 1 (we note that $h(\psi_0=0)$ is slightly larger than h_0 due to the fact that $v > 0$). This effect is simply due to the repulsion between solvent B and the monomers.

An interesting effect results from increasing w_s: this corresponds to an increase in the miscibility of the two solvents. Figure 1 also shows $h(\psi_0)$ for $w_s = 1$, 2, and 4. In the latter two cases, as w_s increases, we find that, although h initially decreases as $1 - \psi_0$ decreases from 1, the (large) free energy cost of pulling the solvent composition inside the brush away from its bulk composition overwhelms the stretching energy of the polymers. As a result, for sufficiently large w_s, the brush actually swells for smaller values of $1 - \psi_0$. We note that all of the states for which h is plotted in Figure 1 have nearly parabolic monomer profiles $\phi(z)$ with $\phi(h^-) = 0$.

We now present an example of a collapse of the polymer layer due to the introduction of a sufficient bulk concentration of a poor solvent. A simple example of this effect is provided by the case $P_0 = 0.1$, $w = 1$, $v = 1$, $w_s = 0$, $w_{sp} = 0$, and $w_{spp} = 8$. According to (22), there should be a collapse of the layer at a bulk good solvent volume fraction of $1 - \psi_0{}^* = 0.75$. In this case, pure A, with $\psi_0 = 0$, is a

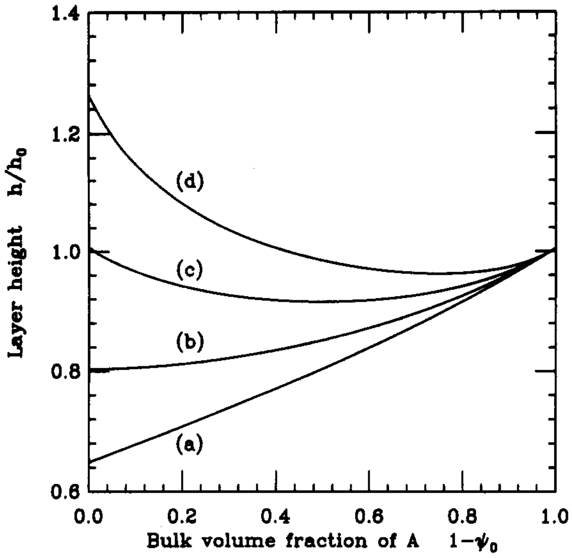

Figure 1. Layer height h as a function of the bulk volume fraction of solvent A, $1 - \psi_0$, for $P_0 = 0.05$, $w = 1$, $w_{sp} = 1$, $w_{spp} = 0$, and $v = 1$. Curves (a)–(d) indicate $w_s = 0.5$, 1, 2, and 4, respectively. For small w_s, the B-polymer repulsion results in a decrease of h with ψ_0. As w_s increases, the free energy cost of pulling the solvent composition away from that of the bulk begins to dominate the polymer stretch energy and the B-polymer repulsion, and the layer height eventually begins to increase with B concentration for large ψ_0.

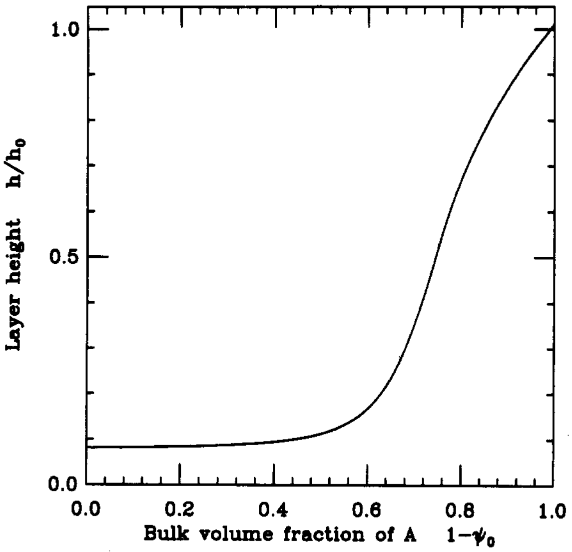

Figure 2. Layer height h as a function of the good solvent fraction $1 - \psi_0$, for $P_0 = 0.1$, $w = 1$, $w_s = 0$, $w_{sp} = 0$, $v = 1$, and $w_{spp} = 8$. Note the smooth evolution from the "swollen" state with $h \approx h_0$ at $1 - \psi_0 = 0$ to the "collapsed" state with h substantially less than h_0.

good solvent for the chains, while pure B, obtained for $\psi_0 = 1$, is a bad solvent.

In Figure 2, we plot the layer height as a function of the bulk concentration for this combined good–bad solvent system: we observe a strong reduction of h as $1 - \psi_0$ decreases past 0.75 although there is no apparent singularity in the layer height near $1 - \psi_0^*$. We note the similarity of this curve to recent experimental results obtained from the study of a polymer brush in a mixture of a good and bad solvent.[11]

There is an obvious singularity in the evolution of the monomer density profile. In Figure 3 we plot $\phi(z)$: for $1 - \psi_0 < 0.75$, there is a step in monomer density at $z = h$. Figure 4 shows the density at the layer tip ($\phi(h^-)$) as a function of $1 - \psi_0$: at $1 - \psi_0^* = 0.75$, it starts to increase from zero linearly in $\psi_0 - \psi_0^*$. Figure 5 shows the bad

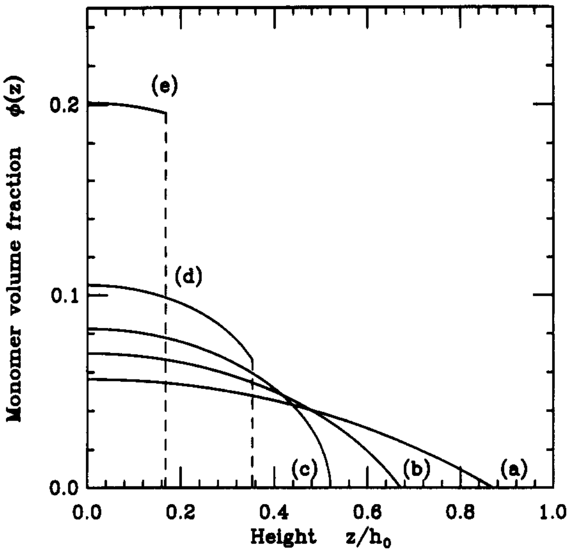

Figure 3. Monomer density ϕ as a function of height z for the parameters of Figure 2: curves (a)–(e) correspond to $1 - \psi_0 = 0.9$, 0.8, 0.75, 0.7, and 0.6, respectively. For $1 - \psi_0 < 0.75$, the monomer density has a step at the layer tip.

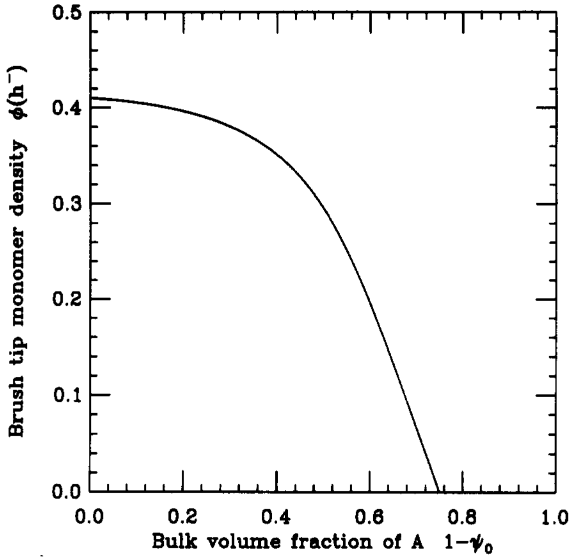

Figure 4. Brush tip monomer density $\phi(h^-)$ as a function of the bulk good solvent concentration $1 - \psi_0$ for the parameters of Figure 2. At $1 - \psi_0 = 1 - \psi_0^* = 0.75$, the tip develops a step in monomer density: the magnitude of this density increases linearly in $\psi_0 - \psi_0^*$.

solvent (B) volume fraction $\psi(z)$: a step is also observed in this quantity at $z = h$ for $1 - \psi_0 < 0.75$.

The profiles shown in Figure 3 are qualitatively similar to those encountered in the theory of the brush in a single solvent of variable quality.[12] In the present model, we may set $\psi_0 = 0$ and $v = 1$ and then vary w to drive a single-solvent collapse transition. In Figure 6 we compare the monomer densities $\phi(z)$ for single- and double-solvent cases at the collapse threshold. The curve labeled "mixed" displays the result from Figure 3 (part c), while the "pure theta" curve is the result using $\psi_0 = 0$, $v = 1$, $w = -1$, and $P_0 = 0.1$ (h_0 is calculated using $w = 1$ for both curves).

The shapes of the curves are almost indistinguishable: the "pure theta" $\phi(z)$ is a quarter-ellipse,[12] and the "mixed" result is only slightly different in shape. However, the values of h are significantly different in the two cases: $h_{\mathrm{mixed}} > h_{\mathrm{pure}}$. This is due to the fact that, in the "mixed" case, the solvent is Θ quality only at the tip: inside the brush, depletion of B leads to an improvement in solvent quality. Thus the "mixed" case is swollen in comparison

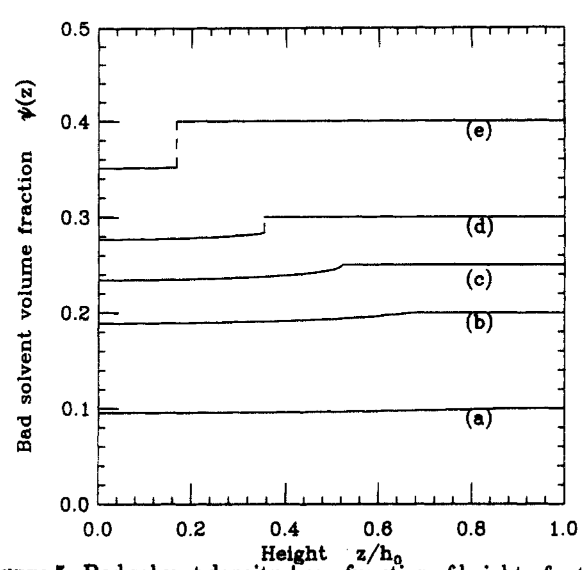

Figure 5. Bad solvent density ψ as a function of height z for the parameters of Figure 2: curves (a)–(e) correspond to bulk good solvent fraction $1 - \psi_0 = 0.9, 0.8, 0.75, 0.7$, and 0.6, respectively. For $1 - \psi_0 < 0.75$, the bad solvent density has a step at the layer tip.

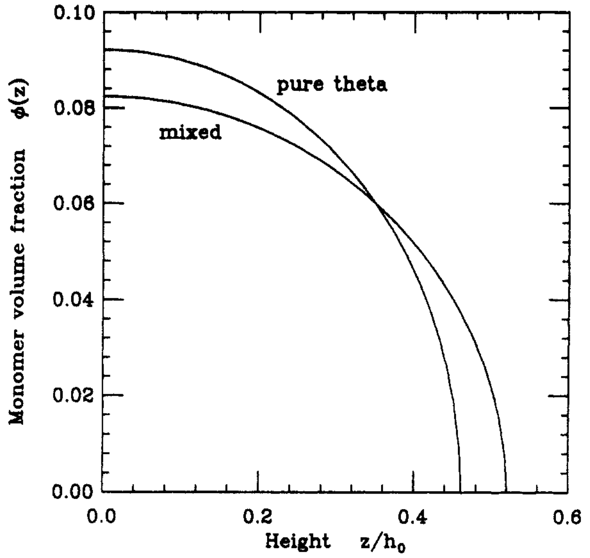

Figure 6. Comparison of monomer densities $\phi(z)$ in the two-solvent case ("mixed") with parameters of Figure 3c ($w = 1$, $v = 1$, $P_0 = 0.1$, $w_s = 0$, $w_{sp} = 0$, $w_{spp} = 8$, and $\psi_0 = 0.25$), and in the one-solvent case ("pure theta") at bulk Θ conditions ($w = -1$, $v = 1$, $P_0 = 0.1$, $\psi_0 = 0$). Both cases are at the layer collapse threshold.

to the "pure" case, where Θ conditions prevail throughout the brush.

IV. Discussion

In this paper, we have presented some basic results concerning the application of established mean-field methods to the equilibrium structure of a strongly-stretched polymer brush immersed in a mixture of two solvents. An important result is that the layer height h always scales linearly with N. This is the only length scale in the problem, so consequently all integrated quantities (amount of adsorbed solvent, total free energy, etc.) scale linearly with N, although they in general have some complicated dependence on other parameters. This result is a consequence of the assumption that the interactions may be treated as purely local on the scale that our description of chain stretching is valid. Experiments should be able to check this basic scaling property.[11]

Other important results of this treatment include the asymptotic behavior of the layer height for small amounts of added solvent B. This may be directly measured in experiments[11] and may allow one to learn something about the parameters w_{sp} and w_{spp}. This coupled with the adsorption properties and the value of w from other experiments may allow all of these parameters to be uniquely determined. Once these parameters are known, a strong test of the assumptions of our self-consistent approach is to see how well the structural properties predicted by the theory match those observed experimentally.

We have also found that there may be a collapse transition similar to that studied in the case of a single solvent,[12] the major difference in this case being that the solvent quality is continuously varying inside the layer. We have found that the gross features of this collapse are similar to the behavior reported by Auroy and Auvray in experiments on brushes in mixtures of good and bad solvents. Neutron reflectivity experiments should be able to determine whether a brush is in a collapsed state with a discontinuity in ϕ at the tip, or if it has a "parabolic" $\phi(z)$ that goes to zero at the brush edge.

The current model has many parameters: although our description is complete (in the sense of a density expansion) for small ψ_0 and ϕ, even more coefficients may be required to accurately describe the properties of dense, collapsed polymers. We have not fully explored the phase diagram of the current model, and it is possible that there are new states of the polymer brush buried in it. For example, if there is a strong A-polymer attraction, with B a poor solvent, it may be possible to have states where near the tip of the brush (where the B concentration is high) the polymers are collapsed, but deeper in the brush (where there is more of the better solvent A) the solvent conditions may change back to being good! This may result in nonmonotonic behavior of $\phi(z)$: in the lower, good solvent region of the brush, the density may end up *lower* than in the high-density region near the tip. If this nonmonotonicity can be made strong enough, it is known that there will be a "dead zone" in the brush from which polymer free ends are expelled.[13,14] Under such conditions, the chemical potential ceases to have a parabolic shape, and the layer structure may change drastically. In the present model, we have not found such states, but they may exist somewhere in parameter space.

There are some interesting related problems that might be treated using this general approach. A simple variation on the problem presented here is the case where space is almost entirely filled with polymer brush, so that adsorption of one component into the brush actually affects the composition of the solvent in the exterior reservior. The adsorption properties under such conditions may suggest applications of this type of system to solvent separation applications. Suitable polymer brushes might act as smart sponges that strongly selectively adsorb one component of a mixture.

In the present paper, we have presumed that the correlation length for solvent concentration fluctuations is much less than the length scale h. This is the case for any $w_s > 1$. However, this may not be the case in short-surfactant systems or in solvent mixtures close to their consolute critical points. In order to study competition between the brush height and the solvent composition correlation length, one may include a $(\nabla\psi)^2$ term in the free energy. However, one must start to consider fluctuations in ψ in this case, which may induce large fluctuations in ϕ near the brush edge if the two solvents have differing affinity for the polymers.

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