Stretching Polymer Brushes in Poor Solvents

A. Halperin* and E. B. Zhulina

Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500 Mainz, FRG

Received March 13, 1991; Revised Manuscript Received May 11, 1991

ABSTRACT: A scaling analysis of the stretching of collapsed polymer brushes is presented. The stretching is associated with a first-order phase transition involving a coexistence of a collapsed layer and stretched chain segments. The coexistence regime is characterized by a $f \sim L^0$ force law. Linear force laws are found for weaker as well as for stronger deformations.

I. Introduction

Polymer brushes, comprising dense, terminally anchored chains, attract considerable current interest.[1] Most studies focus on unperturbed or compressed brushes.[2-9] Less attention was paid to the behavior of stretched brushes.[10] Such stretching can result from the shear generated by sliding a plate against the brush. It is thus relevant to the understanding of the frictional properties of tethered layers. In turn, these are of practical interest since coating by polymer brushes, such as layers of adsorbed diblock copolymers, may be used to modify the frictional characteristics of surfaces. Experimental study of this problem recently became possible with the development of a force measurement apparatus capable of lateral motion.[11] The first theoretical treatment of this problem was produced by Rabin and Alexander,[10] who considered the stretching of brushes immersed in good solvents. The equilibrium thickness of the layer was obtained by balancing the external force, f_{ex}, with osmotic and elastic forces. The novel aspect of this analysis is the calculation of the interaction free energy of stretched chains and of the associated osmotic force. In the following, we extend this analysis to the case of *stretched brushes in poor solvents*. In particular, we consider a flat tethered layer consisting of monodispersed, flexible grafted chains each comprising N monomers of size a. The average separation between grafting sites d is much smaller than $R_c \approx N^{1/3}a$, the radius of a collapsed free chain. The layer is immersed in a poor solvent ΔT below the Θ temperature.

A full analysis of friction-induced deformation, allowing for dynamics, is beyond the scope of this work. A focus on the thermodynamical facets is possible for a simplified system of a brush tethered to *two* parallel, flat surfaces separated by a distance L and characterized by an identical spacing of grafting sites, d. The deformation may be induced by a combination of lateral and vertical displacements of the upper surface by an appropriate external force. However, in the following we confine the discussion to vertical stretching. Furthermore, we assume that the collapsed polymer wets the lower surface but is repelled by the upper one. Consequently, force exerted on the upper surface acts only on the grafted ends. As we shall discuss later, it is possible to envision a physical realization of this system. In particular, a network obtained by selective cross-linking of a lamellar phase formed by ABA triblock copolymers.

The discussion of brush stretching in a poor solvent, as in a good one, involves a balance of external, osmotic, and elastic forces. However, the poor solvent case exhibits novel features because of the distinctive deformation behavior of collapsed chains. The new features arise because the stretched chains strive to minimize the number of unfavorable monomer–solvent contacts. However, the constraint imposed by the stretching prevents complete collapse. Consequently, certain stretching regimes involve a coexistence of a dense phase and a dilute phase incorporating stretched chain segments. For a single stretched chain it is convenient to describe this regime in terms of the surface energy of the collapsed globule. For a macroscopic grafted layer the coexistence is associated with a proper phase transition. In particular, the stretching of the brush is associated with a first-order phase transition involving the coexistence of a collapsed brush and strongly stretched chain segments. In this regime the external force is independent of L; i.e., $f \sim L^0$. Thus, while the stretched brush in a good solvent is of uniform density, in a poor solvent it can be spatially inhomogeneous. Another difference between the two cases relates to the role of the osmotic force. It counteracts stretching in a poor solvent while favoring it in a good one.

Our scaling type analysis is based on the Alexander model,[1-3] assuming uniform stretching and a steplike concentration profile. This model is known to yield the correct scaling behavior for polymer brushes and is rigorously correct for the twice-grafted chains considered in this work. The structure of the unperturbed brush, in good[1-3] and poor solvents,[7-9] is summarized in section II. The stretching of a polymer brush in a good solvent is discussed in section III following the presentation of Rabin and Alexander.[10] Section IV concerns the stretching behavior of a single collapsed globule.[12] The stretching of a collapsed brush is discussed in section V. In the spirit of scaling arguments numerical prefactors are omitted.

II. Unperturbed Brush

The Alexander model is founded on two related assumptions: (1) All chains are uniformly stretched; that is, their end-to-end distance is equal to the layer thickness, L (in this section the layer's thickness is equal to the spacing between the tethering surfaces). (2) The concentration profile of the layer is steplike. The monomer volume fraction within the layer is thus $\Phi \approx Na^3/d^2L$. These two assumptions enable a simple expression for the free energy per chain, F. F comprises two contributions, an elastic energy, F_{el}, allowing for the deformation of the tethered chains, and an interaction free energy, F_{int}, accounting for monomer–monomer and monomer–solvent interactions. In a good solvent the equilibrium structure is set by the interplay of F_{el} and F_{int} or, equivalently, by a balance of osmotic and elastic forces. In this case F_{int} is dominated by binary interactions. The equilibrium structure of a collapsed layer is determined by F_{int} alone, allowing, however, for ternary as well as for binary interactions.

A brush immersed in a good solvent may be considered as a slab of semidilute polymer solution. As such it comprises close-packed, impenetrable blobs of size $\xi \approx$

0024-9297/91/2224-5393$02.50/0

$\Phi^{-3/4}a$ consisting of $g \approx (\xi/a)^{5/3} \approx \Phi^{-5/4}$ monomers. Each blob exhibits self-avoidance while the string of blobs, as a whole, obeys Gaussian statistics. Since the unperturbed radius of such a string is $(N/g)^{1/2}\xi \approx N^{1/2}a$, F_{el} is given by $F_{el}/kT \approx (L^2/Na^2)\Phi^{1/4}$. The kT per blob ansatz leads to $F_{int}/kT \approx N/g \approx N\Phi^{5/4}$. Altogether we have

$$F/kT \approx N^{9/4}(a/d)^{5/2}(a/L)^{5/4} + N^{-3/4}(a/d)^{1/2}(L/a)^{7/4} \qquad \text{(II-1)}$$

Minimization with respect to L specifies the equilibrium characteristics

$$\xi \approx d \qquad \text{(II-2)}$$

$$L_0 \approx N(a/d)^{2/3}a \approx (N/g)\xi \qquad \text{(II-3)}$$

In other words, the chain, when viewed as a string of blobs, is fully stretched. This strong stretching, $L_0 \sim N$, occurs because the concomitant decrease in Φ lowers F_{int}.

To make for convenient comparison, we describe the collapsed brush in terms of blobs. In this case the blob structure is determined by the solvent quality rather than the above equilibrium condition. The chain may be viewed as a string of N/g_c blobs of size $\xi_c = g_c^{1/2}a$. Each blob incorporates $g_c = (\Theta/\Delta T)^2$ monomers exhibiting Gaussian statistics.[13,14] g_c is set by the requirement that the attractive interactions within the blobs are comparable to kT; i.e., $(v/kT)(g_c^2/\xi_c^3) \approx g_c^{1/2}|\Delta T|/\Theta \approx 1$ where $v/kT = \nu_0(\Delta T/\Theta)$ is the second virial coefficient. In terms of the second and third virial coefficients, v and w, ξ_c is expressed as $\xi_c \approx -aw^{1/2}/v$ where w is a constant of order unity.[15] In the following we limit the discussion to the case $\xi_c < d$. To obtain the equilibrium structure of the layer we write a Flory type free energy for a string of ξ_c blobs accounting also for "three-blob" interactions[16]

$$F/kT \approx L^2/R_0^2 - (\xi_c^3/Ld^2)(N/g_c)^2 + (\xi_c^6/L^2d^4)(N/g_c)^3 \qquad \text{(II-4)}$$

where $R_0 \approx (N/g_c)^{1/2}\xi_c$ is the radius of an ideal string of ξ_c blobs. The first term, L^2/R_0^2, allows for the Gaussian elasticity of an ideal chain of ξ_c blobs. The remaining two terms account for the interaction free energy: blob–blob attraction and three-blob repulsion. Because in this approach ξ_c blobs replace monomers of size a, the coefficients scale as ξ_c^3 and ξ_c^6 rather than a^3 and a^6.[17] Minimization with respect to L yields

$$L_0 \approx N(a/d)^2\xi_c \qquad \text{(II-5)}$$

or equivalently $d^2L_0 \approx (N/g_c)\xi_c^3$. This suggests a simple picture of ξ_c blobs close packed within a cylinder of radius d and height L_0. The density within the collapsed layer, g_ca^3/ξ_c^3, corresponds to the dense phase resulting from polymer precipitation. The interface of the collapsed brush is associated with a surface tension of

$$\gamma \approx kT/\xi_c^2 \qquad \text{(II-6)}$$

identical with that of the dense polymer precipitate.

In both cases the chains are, in effect, confined to a virtual capillary of diameter d (Figure 1). However, in the good solvent case d sets the blob size, $\xi \approx d$, while in a poor solvent ξ_c is determined by the solvent quality. Also it is important to note that the chains undergo Gaussian lateral fluctuations. The traverse dimensions of the chains, or actually of their projections on the surface, are given by $(N/g)^{1/2}\xi$ for a good solvent and $(N/g_c)^{1/2}\xi_c$ in a poor one.

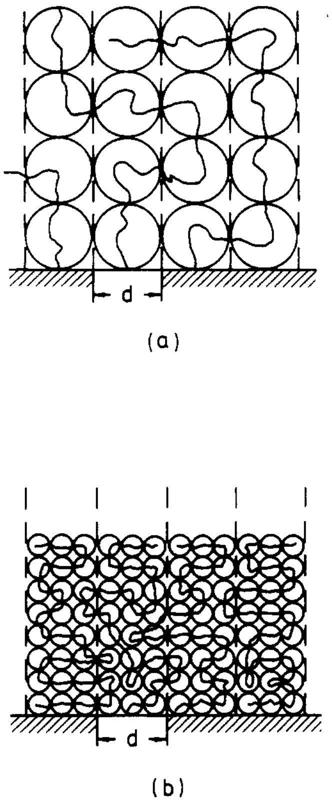

Figure 1. Structure of an unperturbed brush immersed in a good (a) and a poor (b) solvent according to the Alexander model.

III. Stretching of a Brush in a Good Solvent

The stretching of a twice-grafted brush in a good solvent results in a uniform layer of thickness $L > L_0$. As before the free energy per chain includes two contributions, F_{el} and F_{int}. However, the two terms take different forms since it is no longer possible to consider the layer as a slab of semidilute solution. In particular, the blob size is set by the tension in the chain rather than Φ. Furthermore, the resulting blobs are not close packed, and the prescription for the calculation of F_{int} must be modified accordingly.[10] F_{el} used in section II allows for the extension of an ideal string of blobs from $R_0 \approx (N/g)^{1/2}\xi$ to $L \approx (N/g)\xi$. This gives rise to a Gaussian penalty $F_{el}/kT \approx L^2/R_0^2$ and a linear force law $f \sim L$. Since the string of blobs is fully stretched, further extension requires modification of the blob structure. This regime is described by the Pincus prescription.[17,18] The chain is pictured as a stretched string of blobs of size $\xi \approx kT/f$ set by the tension in the chain, f. In a good solvent each Pincus blob comprises g_p monomers exhibiting self-avoidance so that $g_p^{3/5}a \approx \xi_p$ or $g_p \approx (kT/fa)^{5/3}$. Accordingly, the chain elongation is $L \approx (N/g_p)\xi_p$ or $L \approx Na(fa/kT)^{2/3}$. The appropriate force law is thus

$$f \approx \frac{kT}{R_F}\left(\frac{L}{R_F}\right)^{3/2} \qquad \text{(III-1)}$$

where $R_F \approx N^{3/5}a$ is the Flory radius of a free chain in a good solvent. The elastic free energy, using the kT per blob ansatz, is

$$F_{el}/kT \approx N(fa/kT)^{5/3} \approx (L/R_F)^{5/2} \qquad \text{(III-2)}$$

A semidilute solution is viewed as a collection of close-packed blobs of size $\xi \sim \Phi^{-3/4}$. The kT per blob prescription leads to an interaction free energy density, or osmotic pressure, of $kT/\xi^3 \sim \Phi^{9/4}$. A stretched brush is described in terms of Pincus blobs of size $\xi_p \approx Lg_p/N$

$\approx L(kT/fR_F)^{5/3}$; i.e., $\xi_p \sim L$ as opposed to $\xi \sim L^{3/4}$ expected from $\xi \sim \Phi^{-3/4}$. The kT per blob contribution is reflected in F_{el} while F_{int} is due to blob–blob interactions occurring because the blobs are not space filling. Since the chains are strongly stretched, the relevant interactions involve different chains. These occur because the chains experience Gaussian lateral fluctuations of amplitude $\langle r_\perp{}^2\rangle \approx (N/g_p)\xi_p{}^2 \approx Na^2(\xi_p/a)^{1/3}$ larger than d^2. Following Rabin and Alexander, one may argue that each blob interacts with neighboring blobs at the same altitude. A Flory type argument suggests that each blob experiences interaction energy of, approximately $kT\Phi_p$ where Φ_p is the blob volume fraction. Since $\Phi_p \approx (N/g_p)\xi_p{}^3/Ld^2 \approx \xi_p{}^2/d^2$, the interaction free energy per chain, $kT(N/g_p)\Phi_p$, is given by

$$F_{int}/kT \approx N(a/d)^2(\xi_p/a)^{1/3} \approx (N^2a^3/V)(a/\xi_p)^{1/3} \qquad \text{(III-3)}$$

F_{int} scales as $F_{int} \sim \Phi$, as opposed to $F_{int} \sim \Phi^{5/4}$ found in semidilute solutions. The osmotic pressure, $\pi \approx F_{int}/V$, is given by $\pi/kT \approx (N^2a^3/V^2)(a/\xi_p)^{1/3} \approx (kTa/d^4)(Na/L)^{3/2}$. Accordingly the osmotic force per chain, $f_{os} \approx \pi d^2$, is

$$f_{os} \approx (kTa/d^2)(Na/L)^{3/2} \qquad \text{(III-4)}$$

f_{os} is always directed along the normal to the layer. In good solvents f_{os} favors stretching. Consequently, for simple extension by an external force, f_{ex}, acting along the normal to the layer, we have $f_{ex} = f - f_{os}$ or

$$f_{ex} \sim (L/L_0)^{3/2} - (L/L_0)^{-3/2} \qquad \text{(III-5)}$$

The restoring force for simple extension is thus dominated by the Pincus force $f \sim L^{3/2}$.

IV. Stretching of a Single Collapsed Coil

Before we proceed to consider the stretching of a brush immersed in a poor solvent, it is helpful to summarize the relevant aspects of the deformation behavior of a single collapsed coil.[12] The imagined experimental set up comprises two plates connected by dilute, nonoverlapping coils in a poor solvent. In its unperturbed state each of the twice-grafted chains forms a spherical globule of close-packed ξ_c blobs. The radius of the globule is $r_c \approx (N/g_c)^{1/3}\xi_c$ and its volume is $V_c \approx (N/g_c)\xi_c{}^3$. We deform the globule by adjusting the spacing of the plates, L. Since we are now interested in the stretching regime, we confine ourselves to $L \geq r_c$. The surface energy of the globule plays an important role in this process. This is in marked distinction to the deformation behavior in good and Θ solvents where the distortion of the coils is dominated by the configurational entropy. The interplay of configurational entropy and surface energy gives rise to three deformation regimes (Figure 2). The weakly deformed globule is associated with a linear restoring force, $f \sim L$, due to surface energy. For intermediate deformations f is weakly dependent on L. This regime is associated with a configurational transition involving a coexistence of the globule and a stretched string of Pincus blobs. Apart from finite size corrections, this regime is characterized by an $f \sim L^0$ force law. Finally, for strong stretching we recover the $f \sim L$ behavior of a Gaussian chain.

We initially assume that the deformation occurs continuously, thereby detecting the signatures of the configurational transition. A continuous deformation of the collapsed globule produces prolate ellipsoids of increasing eccentricity. Eventually the coil is transformed into a stretched string of Pincus blobs. For weak deformations the ellipsoid is nearly spherical. Its long semiaxis, L, is only slightly longer than $r_c \approx (N/g_c)^{1/3}\xi_c$, the radius of the collapsed coil. The deformation is associated with an increase in the surface area, $\Delta A \approx (L - r_c)^2$. This gives rise to a surface energy penalty of $\gamma\Delta A$, which, in turn, results in a linear restoring force

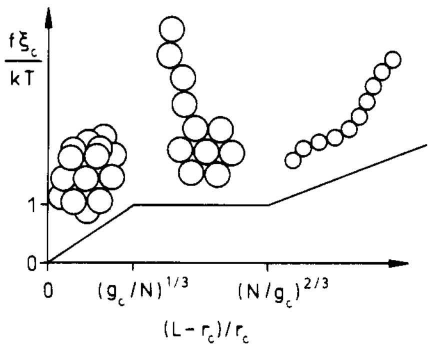

Figure 2. fL diagram for the stretching of an isolated collapsed coil ignoring finite size effects. The insets show the configurations corresponding to the various regimes. Note that for finite systems the "tadpole" configuration occurs only when L (and not f) is varied.

$$f = -\gamma(L - r_c) \qquad \text{(IV-1)}$$

This linear response regime is only found for small deformations. For stronger deformations we may approximate the ellipsoid as a cylinder of height L and diameter D. In this regime the lateral surface area, LD, is much larger than the basal area, D^2. Because of volume conservation, $V_c \approx r_c{}^3 \approx LD^2$, we have $D \approx (V_c/L)^{1/2}$. Accordingly, the surface area of the cylinder is approximately $A \approx DL \approx V_c{}^{1/2}L^{1/2}$. The associated surface energy, $\gamma V_c{}^{1/2}L^{1/2}$, gives rise to the following restoring force:

$$f \approx -\gamma V_c{}^{1/2}L^{-1/2} \qquad \text{(IV-2)}$$

This stage ends when a stretched string of ξ_c blobs is obtained. From this point onward further increase in the applied force can be accommodated only by restructuring of the blobs. The chain forms a stretched string of Pincus blobs of size $\xi_p \approx kT/f$ comprising g_p monomers such that $\xi_p \approx g_p{}^{1/2}a$. As noted before, the Pincus blobs in a poor solvent exhibit Gaussian statistics as opposed to the self-avoidance found in good solvents. Consequently the Gaussian behavior of an extended coil is recovered

$$L \approx (N/g_p)\xi_p \approx fNa^2/kT \approx fR_0{}^2/kT \qquad \text{(IV-3)}$$

Thus, if the stretching is assumed to take place continuously, the fL diagram exhibits $f \sim L$ behavior for weak and strong deformations and an $f \sim L^{-1/2}$ behavior for intermediate extensions. This sequence describes a van der Waals loop in the fL diagram, signaling the instability of the cylindrical structure. For an infinite system this is the signature of a first-order phase transition. However, the system considered here is finite and thus incapable of undergoing a proper phase transition. Nevertheless, it is helpful to interpret the fL diagram by means of the Maxwell equal area construction. This suggests that the instability of the cylindrical state results in a configurational transition involving a coexistence of a weakly deformed globule and a stretched string of ξ_c blobs. Since the tension in such a string is kT/ξ_c, it coexists with a weakly deformed globule characterized by $L = r_c + \xi_c$. Thus, the coexistence region, neglecting finite size corrections, is specified by

$$f \approx kT/\xi_c \qquad (N/g_c)^{1/3} + 1 < L/\xi_c < N/g_c \qquad \text{(IV-4)}$$

Finite size corrections take simple form in this case. Their origin is in the change of the globule surface area when monomers are redistributed between the two

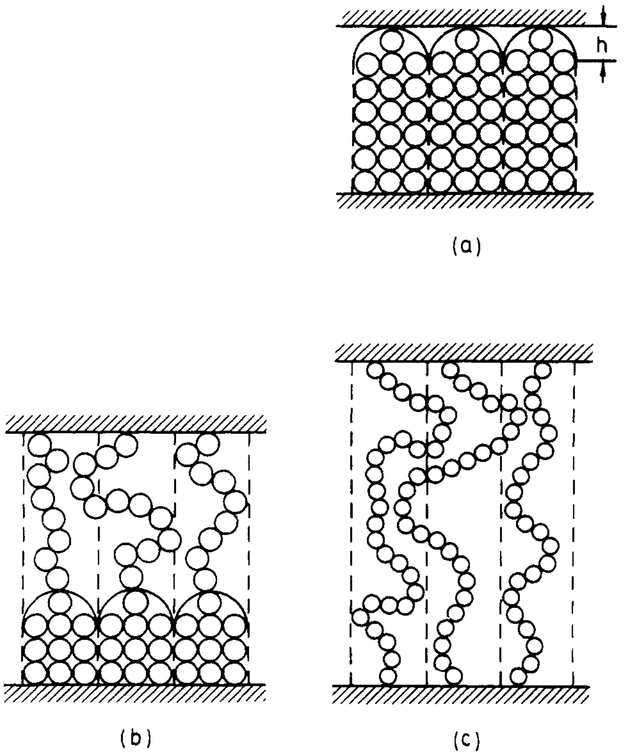

Figure 3. Schematic cross sections of a stretched brush in a poor solvent. Weak stretching results in slight surface deformation (a). Further stretching gives rise to a coexistence of a collapsed brush and a brush of stretched chain segments (b). Finally, for a strong stretching the brush is comprised wholly of stretched chains (c).

"phases". A simple analysis of these corrections is possible when the stretched string is sufficiently extended, i.e., when the string consists of N_s monomers such that $1 \ll N_s \ll N$ and the globule's diameter is negligible in comparison to the length of the string, L. The free energy of the chain, F, may be written as $F/kT \approx (N - N_s)^{2/3} g_c^{-2/3} + N_s/g_p$. The first term accounts for the surface energy of the globule, γr_g^2, whose radius is $r_g \approx (N - N_s)^{1/3} g_c^{-1/3} \xi_c$. The second term reflects the deformation free energy of a stretched string of Pincus blobs. Assuming, and later confirming, that g_p is weakly dependent on N_s, we approximate g_p, ξ_p, and dL as g_c, ξ_c, and $dL \approx (\xi_c/g_c)dN_s$, respectively. The restoring force, $f = -\partial F/\partial L$, may than be expressed as

$$|f_\infty| - |f| \approx kT/r_g \approx \gamma \xi_c^2/r_g \qquad \text{(IV-5)}$$

where $f_\infty \approx kT/\xi_c$ is the force required to stretch an ideal coil of N_s/g_c ξ_c blobs. In other words, the tension in the chain, $|f|$, diminishes when r_g approaches ξ_c. The system is unstable: When a force of kT/ξ_c is applied to the globule, it unravels completely, yielding a stretched chain of ξ_c blobs. A similar effect was considered by Higgs and Ball in biopolymer gels.[19] A globule–string coexistence is nevertheless expected at constant L. Finally, note that eq IV-5 is reminiscent of the Laplace equation.

V. Stretching of a Collapsed Brush

Surface energy plays a role in the stretching behavior of a collapsed brush as in the deformation of a collapsed globule. This is in distinction to the good solvent case when configurational entropy and interaction free energy dominate. Also, the single-chain behavior alerts us to the possibility of a phase transition associated with the stretching of the collapsed brush. In this case the system is infinite and thus capable of undergoing a proper phase transition. In particular, redistribution of monomers between the two phases does not cause a change in the surface energy of the dense phase. As opposed to the single-globule case, the analysis of the brush must also allow for interaction between the stretched segments. These osmotic corrections were considered for the stretching of a brush in a good solvent. However, in a poor solvent blob–blob interactions are attractive. Consequently, in this case the osmotic pressure counteracts the stretching rather than favoring it.

As in the stretching of a collapsed globule it is possible to distinguish between three stages (Figure 3). Initially the brush is weakly deformed. At this stage the penalty is due to an increased surface energy. The next stage involves a coexistence between the weakly deformed, collapsed brush and a brush comprising stretched strings of Pincus blobs. As we shall see, this stage occurs as a first-order transition. Finally when the stretched brush incorporates all the monomers, the layer enters a regime of the type considered in section III. In this regime the system consists of a uniform brush comprising stretched strings of Pincus blobs.

To analyze the initial stage, we describe the chains in the collapsed brush as strings of ξ_c blobs close packed within cylinders of radius d. In the absence of a stretching force the bases of the cylinders are flat. The application of a stretching force deforms the bases into roughly spherical caps. The excess surface created is of area $\Delta A \approx h^2$ where h is the maximal deviation from the flat surface. In this regime $L = L_0 + h$. The excess surface energy, γh^2, gives rise to a linear restoring force

$$f \approx -\gamma h \qquad \text{(V-1)}$$

This linear response regime is analogous to the regime described by eq IV-1.

In the next stage, stretched strings of Pincus blobs emanate from the collapse brush. The associated phase transition involves a coexistence of a dense, collapsed brush and a brush of stretched segments. Each chain consists of a segment building up the collapsed layer and a stretched segment. We denote the number of monomers in the segment embedded in the collapsed layer by N_c and the number of monomers in the stretched segment by $N_s = N - N_c$. The layer thickness is accordingly $(N_c/g_c)(\xi_c/d)^2\xi_c + (N_s/g_s)\xi_s$ where g_s and ξ_s denote the number of monomers in a Pincus blob and its size. The free energy per chain due to the embedded segment is

$$F_c/kT \approx -N_c/g_c + (d^2 + h^2)\xi_c^{-2} \qquad \text{(V-2)}$$

The first term assigns an energy of kT to each ξ_c blob while the second accounts for the surface energy per chain. The chemical potential of an embedded monomer, $\mu_c = \partial F_c/\partial N_c$ is

$$\mu_c/kT \approx -g_c^{-1} \qquad \text{(V-3)}$$

The contribution of the stretched segment to the free energy per chain, F_s, is

$$F_s/kT \approx L^2/N_s - (N_s/g_s)(\xi_s/d)^2 \qquad \text{(V-4)}$$

$L^2/N_s \approx N_s/g_s$ is the stretching energy as obtained by the kT per blob ansatz. The second term is the interaction free energy due to blob–blob interactions, of the type described by eq III-3. $(\xi_s/d)^2$ is the blob volume fraction, and since the solvent is poor, each blob experiences an interaction free energy of $-kT(\xi_s/d)^2$. The chemical potential of a monomer in a stretched segment at constant

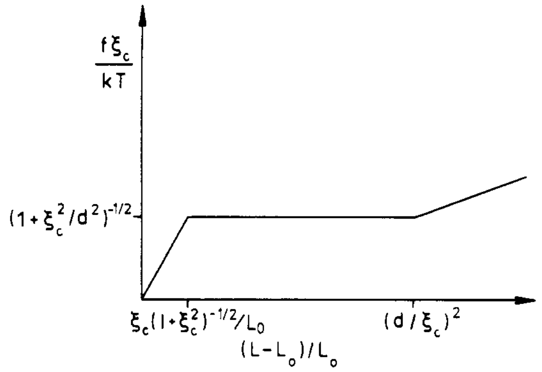

Figure 4. *fL* diagram of a stretched brush immersed in a poor solvent.

L, $\mu_s = \partial F_s/\partial N_s$, is

$$\mu_s/kT \approx -L^2/N_s^2 - g_s^{-1}(\xi_s/d)^2 \approx -g_s^{-1} - (a/d)^2 \qquad \text{(V-5)}$$

By equating the chemical potentials, $\mu_s = \mu_c = \mu$, we specify the size of the Pincus blobs in the stretched brush as

$$g_s^{-1} = g_c^{-1} - (a/d)^2 \qquad \text{(V-6)}$$

and, because $\xi_s = g_s^{1/2}a$, we obtain

$$\xi_s \approx \xi_c(1 - \xi_c^2/d^2)^{-1/2} \qquad \text{(V-7)}$$

Because of the attractive blob–blob interactions, the Pincus blobs are bigger than ξ_c. Their size, ξ_s, sets the tension in the stretched segment

$$f \approx \frac{kT}{\xi_c}(1 - \xi_c^2/d^2)^{1/2} \qquad \text{(V-8)}$$

The onset of the coexistence plateau is obtained by equation f as given by eqs V-7 and V-1, leading to

$$h_m \approx \xi_c(1 - \xi_c^2/d^2)^{-1/2} \qquad \text{(V-9)}$$

The phase transition is completed when all monomers are incorporated into the stretched brush. This occurs for

$$L_m \approx (N/g_s)\xi_s \approx N(a/\xi_c)(1 - \xi_c^2/d^2)^{1/2}a \qquad \text{(V-10)}$$

Thus, the coexistence plateau $h_m < L < L_m$ is characterized by $f \sim L^0$ (Figure 4).

Further stretching requires modification of the blob structure, thus giving rise to behavior of the type discussed in section III. The Gaussian restoring force found for an isolated, strongly stretched chain, $f \approx -(kT/R_0^2)L$, is supplemented by an osmotic restoring force. Since the interaction free energy per chain is $-kT(N/g_p)(\xi_p/d)^2 \approx -kT(R_0/d)^2$ and the osmotic pressure is $\pi = F_{int}/Ld^2$, the osmotic force per chain is $f_{os}/kT \approx -(R_0/d)^2/L$. Altogether the restoring force is

$$f/kT \approx L/R_0^2 + (R_0/d)^2L^{-1} \qquad \text{(V-11)}$$

As in the good solvent case, the osmotic correction is small for simple extension.

VI. Discussion: On Lamellar Gels

The stretching of collapsed brushes immersed in poor solvents reveals a novel feature: a first-order phase transition giving rise to a distinctive $f \sim L^0$ force law. This behavior may be probed by use of a force measurement apparatus capable of shearing two brushes. A more direct observation may be possible in lamellar gels. Such gels may be obtained from lamellar phases formed be ABA triblock copolymers by selective cross-linking of the A layers. Such selectivity may be attained, for example, by irradiating lamellar phases containing A blocks susceptible to radiation. The gel state of the final product depends on the existence of a significant number of bridges between adjacent lamellas. The superior mechanical properties of lamellar phases of triblock copolymers, as compared with those formed by diblock copolymers, suggest that this is indeed the case. At this point one should note that the precise nature of the bridges, whether by loop entanglement or by direct bridging, is an open and interesting question. The novel features of lamellar gels and other ordered gels obtainable from mesophases of block copolymers will be discussed in a forthcoming publication. However, the stretching of lamellar gels immersed in a poor solvent is expected to exhibit the *fL* diagram predicted by our analysis. To test for this behavior, it is necessary to obtain a well-aligned lamellar gel of sufficient size. This may be accomplished by repetitive cycles of spin coating, healing, and cross-linking.

Finally, a brief comment on the stretching of a brush immersed in a Θ solvent: clearly, a Gaussian restoring force is expected. The osmotic force is expected to favor stretching. It is, however, much weaker since it is due to ternary, rather than binary, interactions.

Acknowledgment. The hospitality of Prof. E. W. Fischer and Prof. G. Wegner is gratefully acknowledged. E.B.Z. acknowledges the financial support provided by the A. v. Humboldt Foundation. We benefited from useful discussions with Dr. L. Klushin, Prof. P. Pincus, Prof. S. Alexander, and Prof. H. Benoit. R. C. Ball brought ref 19 to our attention and pointed out that the tension is a decreasing function of length in the "tadpole" regime.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.*, in press.
(2) Alexander, S. *J. Phys. Fr.* **1976**, *38*, 1443.
(3) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(4) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610; *Europhys. Lett.* **1988**, *5*, 413.
(5) Birshtein, T. M.; Borisov, O. V.; Zhulina, E. B. *Vysokomol. Soedin.* **1988**, *A30*, 767.
(6) Muthukumar, M.; Ho, J. S. *Macromolecules* **1989**, *22*, 956.
(7) Halperin, A. *J. Phys. Fr.* **1988**, *49*, 547.
(8) Shim, D. F. K.; Cates, M. E. *J. Phys. Fr.* **1989**, *50*, 3535.
(9) Birshtein, T. M.; Zhulina, E. B. *Polym. Sci. USSR* **1983**, *25*, 2165.
(10) Rabin, Y.; Alexander, S. *Europhys. Lett.* **1990**, *13*, 49.
(11) (a) Kelin, J., private communication. (b) Israelaschvili, J., private communication.
(12) Halperin, A.; Zhulina, E. B. *Europhys. Lett.* **1991**, *15*, 417.
(13) Lifshits, I. M.; Grosberg, A. Y.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.
(14) Williams, C.; Brochard, F.; Frisch, H. L. *Annu. Rev. Phys. Chem.* **1981**, *32*, 433.
(15) (a) Joanny, J. F. Theèse de 3eme cycle, Université Paris VI, 1978. (b) Johner, A.; Joanny, J. F. *J. Phys. Fr.*, in press.
(16) This treatment incorporates the essential physics used in other presentations[7,9] and recovers the results contained therein. It is however somewhat questionable because the final state comprises close-packed ξ_c blobs and the associated blob volume fraction is unity.
(17) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University, Ithaca, NY, 1979.
(18) Pincus, P. *Macromolecules* **1976**, *9*, 386.
(19) Higgs, P. G.; Ball, R. C. *Macromolecules* **1989**, *22*, 2432.