Macromolecules **1992,** *25,* 832–834

A Possible Mechanism for Swelling of Polymer Brushes under Shear

Jean-Louis Barrat*

Department of Chemical and Nuclear Engineering and Materials, University of California, Santa Barbara, California 93106

Received July 19, 1991; Revised Manuscript Received August 29, 1991

ABSTRACT: The behavior of grafted polymer brushes subjected to shear forces is discussed along the lines of a model recently proposed by Rabin and Alexander. The model is shown to predict an increase in the layer height when a shear force is applied. The theory is tentatively applied to the interpretation of recent experimental results.

Introduction

Polymer "brushes", i.e., systems of polymers end-grafted to a flat surface, have been the subject of numerous experimental[1-3] and theoretical[4-6] studies in the past 10 years. Recent reviews of this work can be found in refs 7 and 8. The physical behavior of these systems can be understood in terms of a balance between elastic tensions transmitted along the polymer chains and osmotic pressure resulting from the interactions between monomers. Both under good solvent and melt conditions and for sufficiently dense brushes, this balance results in a characteristic thickness of the brush that varies as $Nd^{-2/3}$, where N is the molecular weight of the polymers and d the typical distance between grafting sites. This law was originally formulated on the basis of scaling arguments (applicable both in good solvent and under melt conditions),[4,5] but was also obtained by more sophisticated calculations[6] and accounts well for experimental observations.[2,3]

The above scaling law gives a satisfactory description of a polymer brush at equilibrium. Recently, Rabin and Alexander (RA)[9] presented a theoretical study of the behavior of polymer brushes subjected to a shearing force in good solvent conditions. One of the main conclusions of their work was that when a polymer layer is sheared against the solvent, its thickness is not affected by the shear, but remains pinned at the equilibrium value. Experiments of this type were carried out by Klein and co-workers using a force measurement apparatus.[10] Their results strongly suggest that the effect of the shear is in fact an increase in the brush thickness. In this article, we revisit the RA calculation and show that their model is actually capable of predicting such a swelling effect. The next section presents the revised theory; we then consider the application of our calculation to the interpretation of the experiment of ref 10. The paper ends with a brief discussion.

Theory

The polymer brush is made of chains of N monomers, and statistical segment length a grafted on a flat surface with a grafting density $1/d^2$ and immersed in a good solvent. Following Rabin and Alexander we adopt the Alexander–de Gennes picture, in which the density profile of the brush is assumed to be a step function. All the chains then have their free ends on the outer surface of the brush. Each chain end is subjected to a force $F_\parallel$ parallel to the grafting surface. As a result, the chains are stretched beyond their equilibrium dimension L_0. The new configuration of the brush under this shear force can be described by the chain end-to-end vector $\mathbf{L} = (h_\perp, h_\parallel)$, where $h_\perp$ is the new brush height (see Figure 1).

To calculate $\mathbf{L}$, the Gibbs free energy per chain is written as

$$U(\mathbf{L}) = U_{\text{stretch}}(L) + U_{\text{int}}(\mathbf{L}) - F_\parallel h_\parallel \tag{1}$$

where $U_{\text{stretch}}(L)$ is the elastic energy stored in a chain with an end-to-end distance L, $U_{\text{int}}(\mathbf{L})$ describes the contribution to the free energy due to the interactions between different chains, and the last term is the contribution from the external force. To obtain $\mathbf{L}$, one has to solve the coupled equations

$$\frac{\partial U}{\partial h_\parallel} = \frac{\partial U}{\partial h_\perp} = 0 \tag{2}$$

To obtain the different contributions to U, we follow the procedure of ref 9: each chain is pictured as a string of N_b blobs of size ξ. Inside a blob, the chain statistics is that of a usual Flory chain so that ξ and N_b are related by $\xi = R_F/N_b^{3/5}$, where $R_F = N^{3/5}a$ is the Flory radius. The blob size is determined by the condition

$$L = N_b\xi \tag{3}$$

which expresses the fact that the chains are strongly stretched. Implicit in eq 3 is the mean-field-type assumption that the configurations the chains adopt inside the brush are identical to the configuration of an isolated chain submitted to a force F_{ext} that gives it an extension L, a situation studied in refs 11 and 12. The interactions between chains are accounted for separately in the term U_{int}.

With this assumption, one obtains for a given L the number of blobs per chain $N_b = (L/R_F)^{5/2}$, the blob size $\xi = R_F^{5/2}/L^{3/2}$, and the elastic energy stored in a chain, which can be computed as if the chain was a Gaussian chain of blobs:

$$U_{\text{stretch}}(L)/(k_BT) = \frac{L^2}{2N_b\xi^2} = \frac{1}{2}\left(\frac{L}{R_F}\right)^{5/2} \tag{4}$$

This particular form of the elastic energy gives rise to the nonlinear relation between force and extension $F_{\text{ext}} \sim L^{3/2}$ first predicted in ref 11.

The contribution of the interactions between chains is then computed in a mean-field approximation: the system is pictured as a fluid of blobs of size ξ, the blob concentration is $N_b/h_\perp d^2$, and the corresponding energy per chain of N_b blobs is approximately expressed by the viral expression for hard spheres of diameter ξ:

$$U_{\text{int}}(\mathbf{L})/(k_BT) = \xi^3 N_b \frac{N_b}{d^2 h_\perp} = \frac{L^{1/2}R_F^{5/2}}{d^2 h_\perp} \tag{5}$$

Using expressions 4 and 5, and minimizing the total energy

---

[*] Permanent address: Laboratoire de Physique, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, Lyon, France.

0024-9297/92/2225-0832$03.00/0

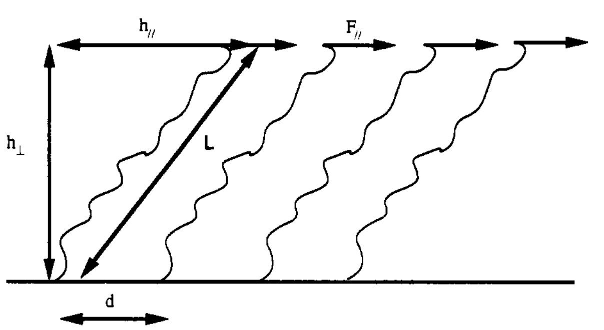

Figure 1. Schematic representation of the sheared polymer brush.

(eq 1) in the particular case $F_\| = 0$, one obtains the equilibrium height of the brush:

$$L_0 = (2/5)^{1/3} N a^{5/3} d^{-2/3} \tag{6}$$

It must be remembered, however, that eqs 4 and 5 are valid only if the blob volume fraction, $\phi = (N_b\xi^3)/(d^2h_\perp)$, is smaller than 1. If ϕ reaches 1, the correct picture for the system becomes that of a semidilute polymer solution: the blob size is now given by $\xi \simeq c^{-3/4}$, where $c = N/(d^2h_\perp)$ is the monomer concentration. The interaction energy per unit volume is as usual $k_BT\xi^{-3}$.[12] In the absence of a shearing force, $F_\| = 0$, the equilibrium thickness L_0 of eq 6 precisely corresponds to the crossover between the two different regimes of a semidilute solution (where the volume fraction of blobs is unity) and of a fluid of blobs with volume fraction smaller than 1. Therefore, the correct L_0 can be obtained by using the free energy function appropriate for either of these two regimes. In general, however, one will have to assume one of the two situations $\phi = 1$ or $\phi < 1$ to carry out the minimization of the appropriate free energy and to check the validity of the original assumption at the end of the calculation.

In the following, we shall assume that we are in the regime $\phi < 1$ correctly described by eqs 4 and 5. This is reasonable since we only consider the application of a shearing force, without compression of the brush. Using eqs 4 and 5, the minimization with respect to $h_\|$ and $h_\perp$ gives

$$F_\|(k_BT) = \frac{5h_\|L^{1/2}}{4R_F^{5/2}}\left(1 + \frac{2L_0^3}{h_\perp L^2}\right) \tag{7a}$$

$$h_\perp^3 = 2L_0^3(1 - h_\perp^2/2L^2) \tag{7b}$$

These equations still have to be solved numerically for L, and the result of such a numerical solution is presented in Figure 2. Even without considering this numerical solution, it is clear from eq 7b that $2^{1/3}L_0 > h_\perp > L_0$; i.e., the brush thickness increases when a shear force is applied, with a maximum increase of ~25%. Note that since eq 7b is expressed in terms of the equilibrium thickness L_0, the latter result is independent of any numerical prefactor that might appear in eqs 4 and 5. Finally, the finding that the brush volume increases when the shear force is applied justifies our original assumption that the blob fraction ϕ is smaller than 1 in this situation.

Our result is different from the RA prediction, $h_\perp$ = constant, even though we used the same expressions for the stretching and interaction free energies. However, we obtain the "osmotic" contribution to the forces not by dividing the interaction energy by the volume, but by taking a derivative with respect to the displacement vector **L**. This latter procedure is more rigorous: the free energy, which is a function of the configuration, can be computed *for a given configuration* by assuming a certain representation in terms of blobs of a given size ξ. Rabin and Alexander then obtain the pressure by dividing the energy by the volume, or equivalently by writing the interaction energy as $U_{\text{int}}(\mathbf{L})/(k_BT) = \xi^3N_b(N_b/d^2h_\perp)$, where ξ is assumed to be a fixed quantity. This would be justified if the system was a collection of hard spheres of diameter ξ independent of L. Here, however, the size ξ depends on L, so taking the derivative with respect to **L** and dividing by V gives different results.

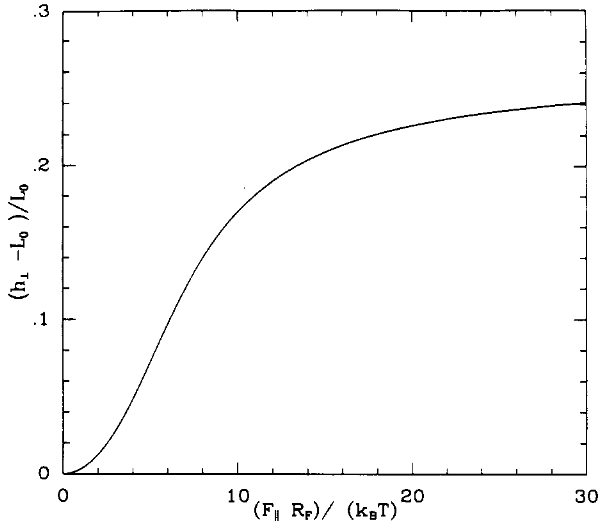

Figure 2. Relative increase in the brush thickness, $(h_\perp - L_0)/L_0$ as a function of the reduced shear force per chain, $F_\|R_F/k_BT$. The solution of eqs 7a and 7b was carried out for $L_0/R_F = 1.95$, which corresponds to the brushes studied in ref 10.

Comparison with Experimental Results

Recently, experiments involving the shearing of polymer brushes were reported by Klein and co-workers.[10] In these experiments, a force measurement apparatus is used to obtain the normal force between two mica surfaces bearing grafted polymers (in a good solvent) as they slide past each other. The equilibrium properties of the polymer–solvent system used in the experiments had been extensively studied in previous experiments[2] and are well understood.

The calculation presented in the preceding section was limited to the case of uncompressed brushes and therefore is relevant only to the situation designated as experiment b in ref 10: in this experiment, two brushes of height $L_0 \simeq 625$ Å are sheared past each other while being maintained at a fixed distance $D = 1550$ Å. Above some critical velocitiy v_c, a repulsive force between the two plates is measured. According to the theory, this velocity would correspond to a shear force per chain $F_\|$ (i.e., the drag force exerted by the flowing solvent on the polymer chain), satisfying eqs 7a and 7b with $h_\perp = D/2 = 775$ Å.

To compute $F_\|$, one needs the Flory radius of the chains, which is taken from ref 2: $R_F \simeq 320$ Å. If the values of R_F and L_0 are used in eq 6, one finds that the grafting distance is $d \simeq 77$ Å, in agreement with the estimate in ref 2.

Using eqs 7b and 7a, we find that when the two brushes come in contact, one has

$$L = 2536\ \text{Å} \qquad h_\| = 2414\ \text{Å} \qquad F_\|/k_BT = 0.089\ \text{Å}^{-1}$$
$$F_\| = 3.7 \times 10^{-12}\ \text{N} \tag{8}$$

The resulting shear stress should be of order $F_\|/d^2 \simeq 6 \times 10^4\ \text{N·m}^{-2}$.

The problem is now to compare the theoretical estimate for the shear force per chain, or equivalently the shear stress, to the experimentally measured critical velocity v_c. Such a comparison would require a self-consistent solution of the coupled problems of hydrodynamic flow inside the brush and chain conformation. This clearly goes far beyond the oversimplified theory presented in the preceding section and would in particular imply a reconsideration of the basic assumptions of a step profile and of a shear force applied at the chain end. We shall therefore content ourselves with an order of magnitude estimate of the relationship between velocity and stress in two limiting situations:

(i) The hydrodynamic flow is screened inside the brush on the scale ξ of one blob. The drag force on one chain will then be of order $6\pi\eta\xi v$, which with $\xi = R_F^{5/2}/L^{3/2} \simeq 17$ Å and $\eta = 5.5 \times 10^{-4}$ P a·s (for toluene) gives $F_\parallel = 1.76 \times 10^{-11} v$. The velocity required to produce a force $F_\parallel = 3.7 \times 10^{-12}$ N is then 0.2 m·s^{-1}, 2 orders of magnitude larger than what is measured by Klein et al.

(ii) The blob volume fraction ϕ (which can be estimated from the figures in eq 8 to be of order 0.15) is so low that the solvent flow completely penetrates the brush. The above estimate for the drag force has then to be multiplied by the number of blobs, $N_b \simeq 170$. This means that the critical velocity is about 10^{-3} m·s^{-1}, in agreement with the experimental results.

At this stage, it is not clear from a theoretical viewpoint which of the two hypothesis should provide a good description of the experimental situation. A theoretical calculation[13] indicates that due to the fact that the density profile of a brush is a parabola rather than a step function, the penetration of the flow inside the brush can be substantial. This calculation, however, assumes that the density profile is not perturbed by the flow and therefore does not apply to the present situation. It is nevertheless a hint that hypothesis i strongly underestimates the drag coefficient. Obviously, a direct measurement of the shear stress rather than the shear velocity would be desirable in order to avoid the ambiguity associated with the determination of the drag coefficient. Such measurements should become feasible in the future.[14]

It must be noted that if the theory is correct and if the effect reported in ref 10 actually constitutes an experimental measurement of the predicted effect, the experimental situation is a rather extreme one: according to the figures in eq 8, the length of the chains would be $\sim {}^2/_3$ of their fully extended length, which can be estimated to be $\sim$3500 Å. The number of blobs per chain in the sheared brush, $N_b \simeq 170$, is $\sim$20 times larger than its equilibrium value. The size of the corresponding "blobs" would be $\sim$20 Å, with no more than 10 monomers per blob. This obviously makes the use of the theoretical scaling laws somewhat hazardous. Another caveat is associated with the use of asymptotically good solvent scaling laws, such as eq 4. In a mean-field approach, the force–displacement relationship for a single chain would be linear and the coupling between the parallel and orthogonal directions that gives rise to the predicted effect would therefore disappear.

Finally, we briefly discuss some other possible interpretations of the experimental results. First, it must be remembered that the experiments involve an oscillatory rather than a steady shear. In the particular experiment we are considering, only one frequency ($v = 400$ s^{-1}) was used, and the velocity was changed by varying the amplitude of the oscillatory motion. Therefore one cannot rule out the possibility that the observed swelling effect is of dynamical origin and takes place only at frequencies higher than some typical relaxation frequency of the brush. Such an explanation would of course be essentially different from the purely static one we are proposing. Another explanation that comes to mind is the possibility that the chains would be pulled off the surface by the shear force. Indeed, the chains are attached to the surface by a single zwitterionic group, and the corresponding binding energy is quite weak, probably of order $5k_BT$.[2] The quantity one should consider in order to assess the possibility of chains being teared out of the brush, however, is not this sticking energy, but rather the maximum force the zwitterionic bond is capable of sustaining. This force can be very roughly calculated by dividing the sticking energy by a typical molecular interaction range of $\sim$10 Å. The resulting force is of order 10^{-11} N, much larger than any possible drag force. Therefore, we think that the chain pulloff mechanism is rather unlikely. The same conclusion was arrived at experimentally in ref 10 by monitoring the integrity of the grafted polymer layers during the course of the shear experiments.

Conclusion

In this article, we have revisited a model originally proposed by Rabin and Alexander for polymer brushes subjected to shear forces. We have shown that a correct interpretation of their model yields the surprising prediction that the thickness of the polymer layer increases when a shear force is applied. We have attempted an interpretation of the experimental results reported by Klein and co-workers within the framework of this theoretical model. At present, this comparison is not conclusive due to the lack of information on the drag coefficient of the polymer brush. Direct measurements of the shear stresses should in the future allow a quantitative assessment of the theory. Another interesting prediction of the theory which could be rather easily tested experimentally is the existence of a limiting value for the brush thickness at large shear rates, as illustrated in Figure 2. In the experiments, this would imply that if the distance between the two plates exceeds a threshold value of $\sim 2.5L_0$, no repulsion between the plates should be observed.

Acknowledgment. Stimulating discussions with G. Fredrickson, F. Pincus, Y. Rabin, and especially J. Klein are acknowledged.

References and Notes

(1) Hadziioannou, G.; Patel, S., Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

(2) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.

(3) Auroy, P.; Auvray, L.; Leger, L. *Macromolecules* **1991**, *24*, 2523.

(4) Alexander, S. *J. Phys.* **1977**, *38*, 983.

(5) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.

(6) Milner, S. T.; Witten, T. A.; Cates, M. C. *Macromolecules* **1988**, *21*, 2610.

(7) Milner, S. T. *Science* **1991**, *251*, 905.

(8) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.*, in press.

(9) Rabin, Y.; Alexander, S. *Europhys. Lett.* **1990**, *13*, 49.

(10) Klein, J.; Perahia, D.; Warburg, S. *Nature* **1991**, *143*, 352.

(11) Pincus, P. *Macromolecules* **1976**, *9*, 386.

(12) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(13) Milner, S. *Macromolecules* **1991**, *24*, 3704.

(14) Klein, J., private communication.