Notes

Polymer Brush at High Coverage

PIK-YIN LAI*

Institut für Physik, Johannes-Gutenberg Universität-Mainz, Postfach 3980, D-6500 Mainz, Germany

AVI HALPERIN

Max Planck Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Germany

Received January 31, 1991; Revised Manuscript Received April 2, 1991

Polymer brushes comprising terminally anchored chains are of practical importance because of their relevance to colloidal stabilization by block copolymers.[1] The more fundamental interest is due to the stretched configurations adopted by such tethered chains in dense brushes. Remarkably, these obtain in equilibrium conditions and give rise to various manifestations in phase behavior and dynamics. Theoretical studies, analytical[2-4] and numerical,[5-7] of these systems often focus on the low-coverage limit; i.e., the chains overlap but the volume fraction, ϕ, in the layer is still low. In this regime the interaction free energy is dominated by binary interaction and the elastic free energy is Gaussian. For denser brushes one must allow for interactions of higher order and for the finite extensibility of the chain. An analytical self-consistent-field[3,4] (SCF) theory of this regime was formulated recently by Shim and Cates.[8] In this theory the binary interaction free energy density, $\sim\phi^2$, was replaced by $(1-\phi)\ln(1-\phi)$ while the Gaussian elastic free energy density, $\dot{z}^2$, was replaced by $\dot{z}^2/(1-|\dot{z}|)$ where $\dot{z} = dz(n)/dn$ and $z(n)$ is the distance of the nth monomer of the chain from the wall. The last choice is reminiscent of the relativistic analogy of Vilgis and Kilian,[9] but the particular form used was chosen because of mathematical convenience. Two important conclusions emerge from this study: (i) The concentration profile becomes more and more steplike as the coverage approaches unity. (ii) At the same time the free ends exhibit a growing tendency to straddle the outer boundary of the layer. Both trends are easily understood if one considers brushes for which the separation between grafting sites, d, approaches the monomer size, a. In other words, the study indicates that dense brushes approach the structure assumed in the Alexander model.[2] This suggests that a properly modified version of the Alexander analysis should prove useful in the discussion of dense brushes. The formulation of such a scheme is of interest because of its mathematical simplicity and in view of its remarkable success in accounting for the properties of dilute brushes.

We consider a flat polymer brush comprising monodispersed, flexible polymers, of polymerization degree N. d is much smaller than $R_F \sim N^{3/5}a$, the Flory radius of the free coils. The polymers stretch out along the normal to the surface so as to lower the concentration within the layer and thus lower the interaction free energy. Within the Alexander model we assume that the volume fraction within the layer is constant, $\phi \simeq Na^3/(d^2L)$, i.e., a steplike concentration profile. We also assume that all chains are uniformly extended; i.e., their end points are constrained to a single surface at a distance L from the wall.

The free energy per chain in this system consists of two terms, the elastic free energy, F_{el}, and the interaction energy, F_{int}

$$F = F_{el} + F_{int} \tag{1}$$

The Flory mixing free energy is used for F_{int}. In particular, F_{int} is given by $F_{int} = f_{mix}d^2L$ where f_{mix} is the mixing free energy per site and d^2L is the volume per chain. Altogether F_{int} is given by

$$\beta F_{int} \simeq d^2L[(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)] \tag{2}$$

where β is the inverse temperature and χ is the Flory interaction parameter. The $N^{-1}\phi\ln\phi$ term, corresponding to the translational entropy of the polymer, is deleted because the chains are grafted. To account for the finite extensibility, the natural choice is to express F_{el} in terms of the inverse Langevin function[10]

$$\beta F_{el} = \frac{1}{a}\int_0^L \mathcal{L}^{-1}\left(\frac{x}{Na}\right)dx \tag{3}$$

where $\mathcal{L}^{-1}$ is the inverse of the Langevin function $\mathcal{L}(x) = \coth(x) - 1/x$. Within this description the stretching of the chain is analogous to the alignment of N noninteracting dipoles by an electrical field. This form reduces to the Gaussian stretching expression in the limit of small deformation ($L \ll Na$). It also has a divergent derivative as $L \to Na$, which enforces the extensibility limit to be Na. These requirements are also met by the expressions used in ref 8 and 9; however, the limits are approached at different rates and may thus lead to different predictions. Denoting the coverage by σ, we have

$$\frac{\beta F}{N} = \int_0^t \mathcal{L}^{-1}(u)\,du + \frac{t}{\sigma}\left(\left(1-\frac{\sigma}{t}\right)\ln\left(1-\frac{\sigma}{t}\right) + \chi\frac{\sigma}{t}\left(1-\frac{\sigma}{t}\right)\right) \tag{4}$$

where $t \equiv L/Na$. Notice that the free energy depends on the scaled variable t but not on L; hence, L scales linearly with N. This is the characteristic property of densely grafted polymer brushes.[2] The equilibrium thickness t^*, obtained by minimizing F, is given by

$$t^* + \mathcal{L}\left(\frac{1}{t^*} + \frac{1}{\sigma}\ln\left(1-\frac{\sigma}{t^*}\right) + \frac{\chi\sigma}{t^{*2}}\right) = 0 \tag{5}$$

At small coverage ($\sigma \ll 1$), eq 5 reduces to $t^* \sim \sigma^{1/3}$, in agreement with known results.[2-7] Near the fully extended limit, $\sigma \to 1$, eq 5 gives

$$t^* \simeq \sigma \tag{6}$$

This result is "universal" in the sense that it is independent of the particular form of F_{el} used provided it has a divergent derivative as the fully extended limit is approached. On the other hand, the free energy does depend on the form of F_{el}. The force of compression, $\Pi(t)$, required to compress the brush from t^* to a thickness $t < t^*$ is

$$\Pi(t) = -\left(\mathcal{L}^{-1}(t) + \frac{1}{t} + \frac{1}{\sigma}\ln\left(1-\frac{\sigma}{t}\right) + \frac{\chi\sigma}{t^2}\right) \tag{7}$$

Π diverges as $1/(1-t)$ as $\sigma \to 1$. We now present the results for the athermal case ($\chi = 0$).

0024-9297/91/2224-4981$02.50/0

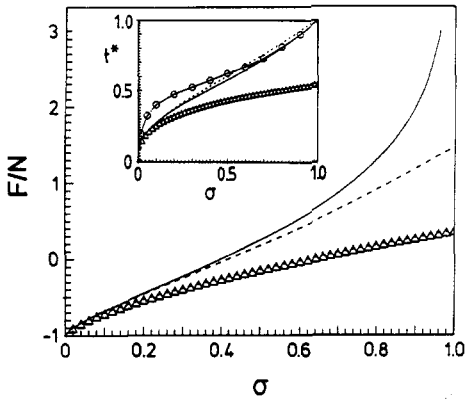

Figure 1. Equilibrium free energy vs coverage. The inset shows t^* vs σ. The solid curves are the results with F_{el} given by eq 3. The dashed curves are obtained with $F_{el} \sim L^2/Na^2$. Δ corresponds to a Gaussian F_{el} and $f_{mix} \sim \phi^2$. The curve with ○ in the inset denotes the result in ref 8.

The equilibrium free energy and the thickness, obtained numerically from eqs 4 and 5, are plotted as a function of σ in Figure 1. Scaling behavior in the semidilute regime ($f_{mix} \sim \phi^2$ and $F_{el} \sim L^2/Na^2$), $F/N \sim \sigma^{2/3}$ and $t^* \sim \sigma^{1/3}$, is shown for comparison. As expected, close agreement with our results is found for low coverages. Significant deviations occur for $\sigma > 0.2$. To demonstrate the effect of finite extensibility, we also present results of t^* and F obtained with Gaussian F_{el} ($\sim L^2/Na^2$) and f_{mix} as given in eq 2. The resulting equilibrium thickness is only a few percent larger; however, the equilibrium thickness exceeds the fully stretched length near $\sigma = 1$, an unphysical result. On the other hand, the difference between the equilibrium free energies for $\sigma > 0.6$ is rather significant. t^* as found by Shim and Cates is also shown for comparison purposes. The two schemes yield nearly identical results at high and low coverages. For intermediate values of σ, a qualitative agreement is found. The agreement at low σ is due to the cancellation of errors in F_{el} and F_{int} when the equilibrium condition is calculated. The agreement at high coverage is due to the validity of the basic assumption of the Alexander model; i.e., a steplike concentration profile is actually obtained in this regime. Figure 2 displays $\Pi(t)$ as given by eq 7 for various values of σ. Results with $F_{el} \sim L^2/Na^2$ replacing eq 3 are presented as well. In the latter case, a softer brush is predicted. The two results essentially coincide at low coverage; however, at higher coverage ($\sigma \gtrsim 0.5$), a significant deviation is observed. The agreement with $\Pi(t)$ obtained

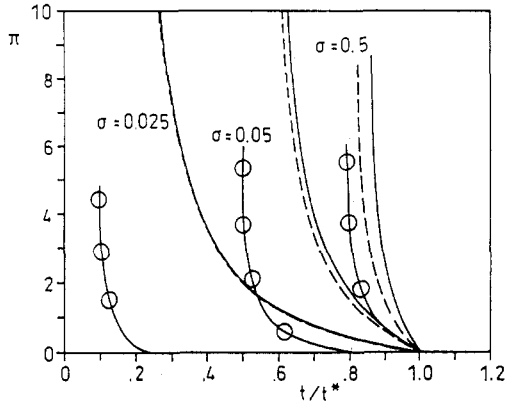

Figure 2. Π vs t/t^* with various values of σ. The symbols used are as in Figure 1.

by Shim and Cates is mediocre. For low coverages, this may be attributed to the breakdown of the basic assumptions of the Alexander model. The discrepency at high coverage ($\sigma \lesssim 1$) is due to the different forms of F_{el} used. In particular, F_{el} used by Shim and Cates implies that the total free energy diverges as $1/(1 - \sigma)$, whereas F_{el} given by eq 3 leads to a weaker divergence $F/N \sim -\ln(1 - \sigma)$. These differences notwithstanding, the Alexander approach described in this paper is useful because of its great simplicity. Furthermore, for high coverages, it is expected to be quite realistic.

Acknowledgment. P.-Y.L. acknowledges support from the Bundesminsterium für Forschung und Technologie (BMFT), Grant No. 03M4040A3. A.H. acknowledges the hospitality of Prof. E. W. Fischer and the Max Planck Institut für Polymerforschung.

References and Notes

(1) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1983.
(2) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.
(3) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413; *Macromolecules* **1988**, *21*, 2610.
(4) Zhulina, E. B.; Pryamitsin, V. A.; Borisov, O. V. *Polym. Sci. U.S.S.R.* **1989**, *31*, 205.
(5) Muthukumar, M.; Ho, J. S. *Macromolecules* **1989**, *22*, 956.
(6) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. *Macromolecules* **1987**, *20*, 1692.
(7) Murat, M.; Grest, G. S. *Macromolecules* **1989**, *22*, 4054.
(8) Shim, D. F. K.; Cates, M. E. *J. Phys. Fr.* **1989**, *50*, 3535.
(9) Vilgis, T.; Kilian, V. *Colloid Polym. Sci.* **1986**, *264*, 131.
(10) Flory, P. J. *Statistical Mechanics of Chain Molecules*; John Wiley & Sons: New York, 1969; p 307.