Interaction between Grafted Polymeric Brushes: A Molecular-Dynamics Study

Michael Murat and Gary S. Grest

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

(Received 2 June 1989)

We present a molecular-dynamics study of a system of end-grafted polymers between parallel surfaces. We find that the forces between the surfaces as a function of their separation can be described both by scaling and self-consistent-field theories and agree with the experiments of Taunton *et al.* We quantify the amount of interpenetration of the two brushes and describe it with a simple scaling form. Overall monomer density profiles as well as the contribution from each brush are also presented.

The configuration of end-grafted polymers, the so-called polymeric brushes, and the interactions between such brushes have been the subject of recent interest. Experimental studies of such systems have focused on the direct measurement of the force between two surfaces onto which polymers have been terminally attached.[1-3] The force is found to be purely repulsive. Theoretical treatments have utilized scaling arguments,[4,5] numerical self-consistent-field (SCF) calculations,[6,7] and analytical SCF equations suitable for the limiting case of high molecular weight.[8,9] These studies have produced predictions about the equilibrium configuration of such brushes as well as the force profiles of two such brushes under compression.

Alexander[4] assumed a uniform monomer density from the grafting surface up to a cutoff at a distance $h_{\max}$ and minimized the free energy given by the repulsive interaction between the monomers and the stretching energy of the chains. Then using a simple scaling theory he was able to predict the equilibrium configurations of polymeric brushes as a function of grafting density ρ_a and chain length N. Milner, Witten, and Cates,[8] on the other hand, noted that SCF equations for highly stretched polymers can be solved exactly in the limit of high molecular weight, and obtained a density profile that decays parabolically from the surface. Although these two approaches are very different, both theories produce predictions for various observables that scale almost identically with N and ρ_a. For instance, for a single grafted brush, both predict that the thickness $h_{\max}$ of the brush should scale as $h_{\max} \sim N\rho_a^{1/3}$. Furthermore, the experimental force versus separation profiles for a pair of such brushes have successfully been fitted by the predictions of both theories,[5,9,10] even though the functional forms of the two predictions as well as the scaling of the force with the grafting density are different. It should be emphasized, however, that the fit by SCF is achieved with no adjustable parameters, while for the fit by the scaling theory one needs to take the brush height and the absolute magnitude of the forces from the force profiles themselves.

An important question not addressed by either of the theories is the extent of the interpenetration of the poly-

mers from the two brushes. Both theories assume that there is no interpenetration. Experiments do not provide an answer either, as no measurements have been performed yet to monitor the density of the monomers that originate from one of the grafting surfaces as a function of the distance from that surface. Such questions can, however, be answered by a detailed microscopic simulation that monitors the positions of each monomer and its interactions with the other monomers.

In a recent publication,[11] we presented the results of a molecular-dynamics-simulation study of a single grafted brush. By calculating the overall monomer density, the density of the free ends, and other characteristics of the brushes for several values of N and ρ_a, we checked the detailed predictions of the theory of Milner, Witten, and Cates.[8] In this Letter, we will present the results of a similar study for two brushes separated by a distance D, for several values of N and ρ_a. We find that for a given N and ρ_a, the amount of interpenetration (that will be quantitatively defined later) increases with decreasing separation between the brushes. We propose a scaling form for this quantity using the prediction of Witten, Leibler, and Pincus,[12] who studied the interpenetration depth in lamellar copolymer mesophases. We find that the data from four different cases collapse reasonably well with this scaling form. We also find that the force versus separation curves for the different cases studied have the same form if the separation D is scaled by the *maximum extent* of each brush, suggesting that the brushes interact as soon as their density profiles overlap. For the cases with the lowest ρ_a, the force profiles agree extremely well with the experimental profiles of Taunton *et al.*[10] As the surface coverage increases, we find that the forces exhibit a steeper increase with decreasing separation than is observed experimentally or is predicted by the scaling and the SCF theories since at those grafting densities the overall monomer density between the surfaces is above the semidilute regime.

The simulations are performed using a molecular-dynamics method[13] in which each monomer is coupled to a heat bath. This method has already been successfully applied to several problems related to static and dynamic properties of polymers.[13,14] The monomers are treated

    © 1989 The American Physical Society

as beads of mass m which interact through a shifted short-range Lennard-Jones potential given by

$$U^0(r) = \begin{cases} 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6 - (\sigma/r_c)^{12} + (\sigma/r_c)^6], & \text{if } r \le r_c, \\ 0, & \text{if } r > r_c, \end{cases} \tag{1}$$

with $r_c = 2^{1/6}\sigma$. As this potential is purely repulsive, our simulations are in the good-solvent regime. In addition, there is an attractive interaction between neighboring monomers along the chains, and a strongly repulsive one of range $\sigma/2$ between the wall and the monomers. The parameters of these potentials are the same as in Ref. 11. Denoting the total potential of monomer i by U_i, the equation of motion for monomer i is given by

$$\frac{d^2\mathbf{r}_i}{dt^2} = -\nabla \cdot \mathbf{U}_i - \Gamma\frac{d\mathbf{r}_i}{dt} + \mathbf{W}_i(t). \tag{2}$$

Here Γ is the bead friction which acts to couple the monomers to the heat bath. $\mathbf{W}_i(t)$ describes the random force acting on each bead. It can be written as a Gaussian white noise with

$$\langle \mathbf{W}_i(t) \cdot \mathbf{W}_j(t') \rangle = \delta_{ij}\delta(t - t')6k_BT\Gamma, \tag{3}$$

where T is the temperature and k_B is the Boltzmann constant. We have used $\Gamma = 0.5\tau^{-1}$ and $k_BT = 1.2\epsilon$. With this choice of parameters, the average bond length between neighboring beads along the chains is found to be 0.97σ. The equations of motion are then solved using a predictor-corrector algorithm with a time step $\Delta t = 0.006\tau$. Here $\tau = \sigma(m/\epsilon)^{1/2}$. Further details of the method can be found elsewhere.[11,13]

Using this method we simulated systems of two parallel plates at a distance D, onto each of which M polymers of $N+1$ monomers are anchored at one end. Each plate has a surface area S in units of σ^2, giving a grafting density of $\rho_a = M/S$. Periodic boundary conditions are used in the two directions parallel to the plane of the plates. We have studied four cases with $(N, \rho_a, M) = (50, 0.03, 25)$, $(50, 0.1, 25)$, $(50, 0.2, 25)$, and $(100, 0.03, 20)$. The simulations were carried out in the following manner: We start with the plates at a separation D slightly above the contact distance $D_c = 2h_{ext}$, where h_{ext} is the maximum extent of a single brush[11] and equilibrate the system. After equilibration, we continue the

simulation while reducing D by a very small amount at each time step. The configurations at several selected values of D are saved. These are then used as starting states for subsequent longer runs at those values of D, from which the quantities of interest are calculated. We run the simulations for times much longer than the configurational relaxation times of the chains to assure that proper averaging is achieved. These times (for a single brush) and the duration of the runs, as well as the maximum extent of the brushes, h_{ext}, and their height from the parabolic fit,[11] h_{par}, for $D \gg D_c$, are listed in Table I. h_{ext} is taken to be the distance from the plate at which the monomer density practically vanishes. These two measures of the brush height are in general not proportional as the finite length of the chains affects each differently. Also shown is $3R_z^2/R_0^2$, which shows the amount of stretch induced in the chains. Here R_z^2 is the mean squared end-to-end height of the chains and R_0^2 is the mean squared end-to-end distance of a free chain of the same length.

Figure 1(a) shows the monomer number density $\rho(z)$ in the region between the two surfaces for three values of D at $\rho_a = 0.03$ for $N = 100$. Here z is the distance from one of the plates. We scale this coordinate by D to place all three curves on the same scale. As D is decreased, the density increases everywhere and becomes almost

TABLE I. The total duration of the runs, T_t, relaxation time of the end-to-end distance of each chain in a single brush, τ_R, the parabolic fit to the brush height, h_{par}, and the maximum extent of each brush, h_{ext}, for the four combinations of chain length N and ρ_a studied. Also shown is the amount of stretch, $3R_z^2/R_0^2$, as described in the text.

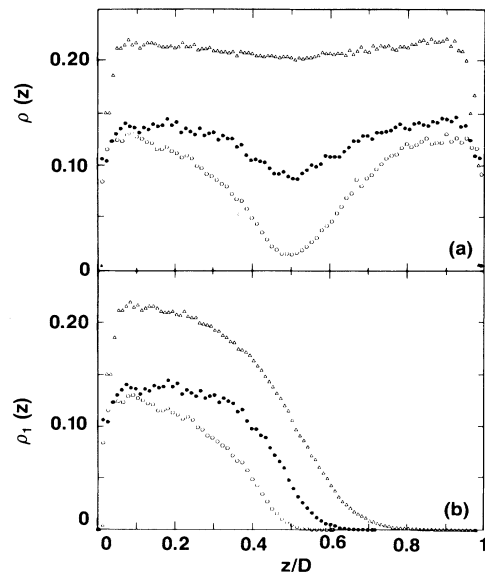| N	ρ_a	T_t/τ	τ_R/τ	h_{par}	h_{ext}	$3R_z^2/R_0^2$
50	0.03	1500	135	18.0	21	3.4
50	0.1	4500	450	25.1	28	7.0
50	0.2	9000	1100	30.7	33	18.8
100	0.03	1100	850	33.9	42	4.1

FIG. 1. (a) Monomer density profile $\rho(z)$ for polymers of length $N = 100$ at $\rho_a = 0.03$. (b) The contribution to $\rho(z)$ from one of the brushes. (O) $D = 70$, (●) $D = 50$, (△) $D = 30$.

uniform for $D < 30$. These results resemble that obtained by Muthukumar and Ho[7] using a numerical SCF calculation. At even higher compressions (not shown in the figure), when this uniform density approaches unity, we find that the monomers tend to form well-defined layers a distance σ apart. For the moderate compressions shown, separation of the contribution of each brush, $\rho_1(z)$, to the overall density reveals [Fig. 1(b)] that the parabolic profile of each brush is largely conserved. However, one can also see that as D is decreased, the number of monomers from each brush found at $z > D/2$ increases, indicating larger interpenetration. To quantify the amount of interpenetration at separation D, we determine $I(D)$, given by

$$I(D) = \int_0^{D/2} \rho_1(z)dz \Big/ \int_0^D \rho_1(z)dz .$$ (4)

We can use the results of the SCF theory of Milner, Witten, and Cates[8] in order to develop a scaling form for $I(D)$ with N and ρ_a. For a brush compressed to a height $h = D/2 < h_{par}$, the monomer density profile is still a parabolic one up to $z = h$ and vanishes abruptly for larger values of z. The density at h is then given by

$$\rho(h) = \frac{\rho_a N}{h}\left[1 - \left[\frac{h}{h_{par}}\right]^3\right] .$$ (5)

Assuming that the bulk of the monomers is at $z < h$ with an exponentially decaying tail of length δ beyond h and noting that the integration over the whole density profile of a single brush yields $\rho_a N$, we find that the amount of interpenetration can be approximated as $I(D) \simeq \delta\rho(h)/\rho_a N$. Recently, Witten, Liebler, and Pincus[12] suggested an estimate for δ in the context of lamellar copolymer phases. Their estimate is applicable to our problem since in both cases the polymers are in identical configurations. Equating the gain in translational entropy as a result of interpenetration with the accompanying penalty of interaction energy, they obtained $\delta \sim (h/N^2)^{-1/3}$. Using this relation in the estimate for $I(D)$, we obtain

$$I(D)N^{-2/3}h_{par}^{4/3} \sim x^{-4/3}(1 - x^3) ,$$ (6)

where $x = D/2h_{par}$. Figure 2 shows the left-hand side of this equation as a function of x for all the cases studied. The data from the four different cases collapse reasonably well, as predicted. We also observe that the points for $\rho_a = 0.2$ start to deviate from this curve first (at the lowest values of compression), followed by those for $\rho_a = 0.1$. This can be qualitatively understood by noting that when the overall monomer density approaches unity, the density profile is almost uniform and further decrease of D causes a uniform compression rather than an increase in the interpenetration. The scaling results for $I(D)$ deviate sooner for higher values of the surface coverage since a smaller compression is needed to reach such high densities. As such high densities are achieved
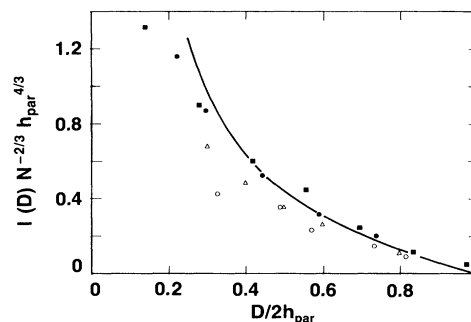

FIG. 2. The interpenetration $I(D)$ scaled as explained in the text for the four cases studied. ($\bullet$) $N = 100$, $\rho_a = 0.03$; ($\blacksquare$) $N = 50$, $\rho_a = 0.03$; ($\triangle$) $N = 50$, $\rho_a = 0.1$; ($\circ$) $N = 50$, $\rho_a = 0.2$. The full curve shows the functional form predicted in Eq. (6).

at smaller compressions for increasing surface coverage, $I(D)$ curves for those cases saturate first.

At each separation we also calculated the force between the plates. This is done by calculating the pressure from the virial.[15] The force per unit area, $f(D)$, between the two plates is then found by subtracting from this pressure the pressure at $D = D_c$. We find that this force relaxes very rapidly; runs of lengths of only a few τ are sufficient to obtain $f(D)$ quite accurately. In order to compare our result with recent experiments, which measure the interaction energy per unit area, we calculated

$$E(D) = \int_{D_c}^D f(D')dD' .$$ (7)

Both scaling arguments[5] and SCF theory[9] predict that this energy should scale as $E(D) \sim h_{max}\rho_a^x \tilde{E}(D/2h_{max})$, with $x = \frac{3}{2}$ and $\frac{4}{3}$, respectively. The difference originates from the dependence of the osmotic pressure on the monomer density in the two theories. The two theories also predict different scaling functions $\tilde{E}(x)$. We show in Fig. 3 $E(D)$ scaled as suggested by the scaling theory. We find that the scaling works much better when we substitute h_{ext} rather than h_{par} for h_{max}. The energies for the two different values of N at $\rho_a = 0.03$ collapse to a single curve. The two other cases converge to this curve only for $D/2h_{ext} \rightarrow 1$, although all four curves have the same basic form. The inset in Fig. 3 shows the experimental results of Taunton et al.[10] from experiments with terminally attached polystyrene chains of various molecular weight. The solid line is a smooth curve passing through our data points for $\rho_a = 0.03$. Since our energy scale is arbitrary, this line is vertically shifted to lie on the experimental points for comparison. The overall agreement between the simulation and the experimental results is excellent. We emphasize that the fit is achieved using no adjustable parameters, except the vertical shift due to the arbitrary energy scale of our simulations. The length scale used in the scaling of D is taken from an independent simulation.
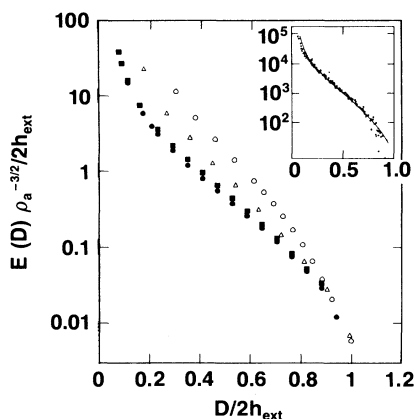
FIG. 3. The energy per unit area of the interaction between the plates for all the cases studied. (●) $N = 100$, $\rho_a = 0.03$; (■) $N = 50$, $\rho_a = 0.03$; (△) $N = 50$, $\rho_a = 0.1$; (○) $N = 50$, $\rho_a = 0.2$. Inset: A comparison between the experimental results of Taunton et al. (Ref. 10) (data points) and our results (full line obtained by joining our data points for $N = 100$, $\rho_a = 0.03$; it is vertically shifted by an arbitrary amount). The experimental points include results from measurements with polymers of various molecular weight at corresponding grafting densities.

As is the case with the experiments,[10] our data for $\rho_a = 0.03$ agree equally well with the scaling functions predicted by both theories. We expect the agreement to break down at high compressions when Φ, the average number density of the monomers between the surfaces, approaches unity. At this limit, the osmotic pressure, which is the leading contribution to the force, diverges logarithmically with $1 - \Phi$, rather than increasing as a power of Φ, as predicted by both theories. In Fig. 3 we indeed see this deviation for $\rho_a = 0.1$ and 0.2 at $D/2h_{ext} \approx 0.6$ and 0.8, respectively, as this dense regime is already reached at these compressions. Such a trend, however, is not seen in the experiments. Systems with polymers of various lengths (and consequently at different surface coverages as these two are not varied independently in the experiments[10]) yield profiles which collapse on the same scaling curve. This difference between the simulations and the experiments can be explained by observing that in the experiments the average monomer number density in the uncompressed system for all the cases (except possibly those with the lowest N) is well within the semidilute regime. Densities of order unity are achieved only at the lowest separation values. Any possible deviation from the theoretical behavior would be hidden in the experimental noise. The predicted deviation from the scaling (or SCF) behavior could be seen experimentally if one used an anchoring unit which attaches to the surface with a much higher sticking energy, which would increase the average density. It can easily be shown that if the sticking energy is ak_BT, then the average density scales with a at constant

N as $a^{4/5}$. Thus if a is increased by a factor of 3-5, one should observe these systematic deviations at intermediate compressions.

In conclusion, we have performed a molecular-dynamics study of the system of two parallel surfaces with end-grafted polymers using a simple bead-spring model for the polymers. We find that the interaction is purely repulsive and that it sets in as soon as the brushes touch each other before any interpenetration occurs. The interaction versus separation profiles agree extremely well with the experimental curves. We also find that these profiles for intermediate values of surface coverage are satisfactorily described by both scaling and SCF theories if one scales the separation by the maximum extent of the brushes. We attribute the deviations from the theoretical behavior at higher surface coverages to the fact that the resulting monomer density is much higher than the regime of validity of both theories. We also monitor the amount of interpenetration in the compressed brushes and show that it can be described by a simple scaling form.

[1]H. J. Taunton, C. Toprakcioglu, and J. Klein, Macromolecules 21, 3336 (1988).

[2]H. J. Taunton, C. Toprakcioglu, L. J. Fetters, and J. Klein, Nature (London) 332, 712 (1988).

[3]G. Hadziioannou, S. Patel, S. Granick, and M. Tirrell, J. Am. Chem. Soc. 108, 2869 (1986).

[4]S. Alexander, J. Phys. (Paris) 38, 983 (1977).

[5]P.-G. de Gennes, C. R. Acad. Sci. Paris 300, 839 (1985).

[6]T. Cosgrove, T. Heath, B. van Lent, F. Leermakers, and J. Scheutjens, Macromolecules 20, 1692 (1987).

[7]M. Muthukumar and J.-S. Ho, Macromolecules 22, 965 (1989).

[8]S. T. Milner, T. A. Witten, and M. E. Cates, Macromolecules 21, 2610 (1988). See also A. N. Semenov, Zh. Eksp. Teor. Fiz. 88, 1242 (1985) [Sov. Phys. JETP 61, 733 (1985)].

[9]S. T. Milner, Europhys. Lett. 7, 695 (1988).

[10]H. J. Taunton, C. Toprakcioglu, L. J. Fetters, and J. Klein, report, 1989 (to be published).

[11]M. Murat and G. S. Grest, Macromolecules (to be published).

[12]T. A. Witten, L. Leibler, and P. A. Pincus, report, 1989 (to be published).

[13]G. S. Grest and K. Kremer, Phys. Rev. A 33, 3628 (1986).

[14]K. Kremer, G. S. Grest, and I. Carmesin, Phys. Rev. Lett. 61, 566 (1988).

[15]M. P. Allen and D. J. Tildesley, Computer Simulation of Liquids (Clarendon, Oxford, 1987), p. 47.