PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Static and dynamic collective correlations of polymer brushes

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(Received 1 February 1993)

We report the results from a detailed Monte Carlo study of dynamic concentration fluctuations of a two-component grafted polymer "brush." We compute the correlations at long length scales and their associated characteristic relaxation times, which could be measured in a dynamic scattering experiment. We find that the dynamic concentration fluctuations are dominated by *in-plane* contributions due to lateral chain fluctuations.

PACS number(s): 36.20.$-$r, 82.70.$-$y, 87.15.$-$v, 81.60.Jw

I. INTRODUCTION

A polymer "brush" consists of flexible chain molecules of chemical length N, each with one end restricted to a point in the plane $z=0$ and with monomers (of size $a \approx 5$ Å) restricted to the region $z>0$; the resulting assembly is immersed in a good solvent for the polymers [1,2]. If the distance between chains D is less than the "Flory" radius R_F of the chains under dilute good-solvent conditions, then the chains will *stretch* to form a layer of thickness $h \approx (a/D)^{2/3}Na$ to minimize their free energy, as first discussed by Alexander [3] and de Gennes [4]. Current experiments [5] have $D \approx 50$ Å and $N \approx 1000$, yielding $h \approx 1000$ Å. Polymers under such conditions are strongly stretched, and have free energies per chain of $\approx 10kT$.

Under conditions where $R_F \ll h \ll Na$ (Na is the maximum distance that the chains may be extended), fluctuations in the local volume fraction occupied by the monomer $\phi(\mathbf{r})$ are characterized by a correlation length determined by the equilibrium correlation length in a system of overlapping polymers under good solvent conditions (semidilute solution) [6]: $\xi = a\phi_0^{-3/4}$. Since the average volume fraction is $\phi_0 = Na^3/D^2h$, we have $\xi = D$. At scales larger than the distance between grafts, correlations will be screened, and the chains behave like Gaussian polymers, in a nonfluctuating inhomogeneous chemical potential that provides the force to stretch the chains vertically. However, there are two long length scales at which there remain correlations due to the *connectivity* of the chains: these are (i) the typical vertical distance that chains are extended over (h), and (ii) the typical distance for *lateral* chain fluctuations $R=(D/a)^{1/6}N^{1/2}a$ (the size of a random walk of N/n_B steps of distance D, where $n_B = \phi_0 D^3$ is the number of chemical units in a correlation volume).

In this paper, we discuss static and dynamic correlations of grafted polymers. In Sec. II, we discuss how correlations at long length scales may be related to a scattering structure factor for a polymer layer composed of two species of chains. In Sec. III, we present the results from Monte Carlo (MC) simulations of grafted polymers and identify the characteristic distances and times associated with the static and dynamic correlations. The static structure shows scaling behavior in agreement with the theory of Alexander and de Gennes [3,4]. For polymers that are not too strongly overlapped, the relaxation scaling is described by a simple single-chain diffusive relaxation model. This appears to break down for strongly overlapping polymers, and in Sec. IV, we argue that this is due to chain entanglements. We conclude that entanglements prevent the relaxation process in the vertical direction from ever having a longer characteristic time than that of chain fluctuations from side to side.

II. CORRELATIONS IN A TWO-COMPONENT POLYMER LAYER

In a single-component polymer layer, the length scale R cannot be simply revealed since most scattering probes couple to the total density contributed by *all* monomers. However, in a polymer brush composed of *two* species of chains (A and B), the long scales appear naturally as the correlation lengths of the two-point correlation [7] of the *difference* of the local A and B monomer volume fractions: $\psi \equiv \phi_A - \phi_B$. We consider the symmetric case where $\langle \psi(\mathbf{r}) \rangle = 0$ at scales larger than the distance between grafting points D, achieved when the A and B chains are grafted in equal numbers. The static correlations of the $A-B$ concentration fluctuations might be studied by neutron scattering, from A and B polymers with substantially different neutron indices of refraction, immersed in a solvent whose index of refraction was matched to one of the polymers. This might be accomplished by partial deuteration of B chains to obtain the contrast matching condition, combined with a different degree of deuteration of otherwise identical A chains to obtain $A-B$ contrast. In a good solvent, the small demixing tendency due to differing deuteration should be predominantly screened [8].

The concentration fields $\phi_I (I=A,B)$ are microscopically defined as a function of space $\mathbf{r}$ and time t, in terms of chain i's monomer positions $\mathbf{r}_i(n,t)$, using single-chain density operators $\gamma_i(\mathbf{r},t) \equiv \int_0^N dn\, a^3 \delta^3(\mathbf{r}-\mathbf{r}_i(n,t))$:

$$\phi_I(\mathbf{r},t) \equiv \sum_{i \in I} \gamma_i(\mathbf{r},t) \ . \tag{1}$$

The observable that we will discuss is just the dynamic structure factor of ψ:

$$S(q,q_z,t) \equiv \frac{1}{V} \int_V dz\, dz' d^2x\, d^2x' e^{2\pi i[q\cdot(x-x')+q_z(z-z')]} \times [\langle \psi(\mathbf{r},t+t')\psi(\mathbf{r}',t') \rangle - \langle \psi(\mathbf{r},t') \rangle \langle \psi(\mathbf{r}',t') \rangle] \ , \tag{2}$$

where z and q_z are the position and corresponding wave number in the normal direction, x and q are two-dimensional in-plane positions and wave numbers, and V is the system volume. Using the *connected* correlator in the definition of the structure factor eliminates time-independent contributions to S due to the quenched graft distribution.

At scales larger than D, we expect different chains to have independent statistics, or $\langle \gamma_i(\mathbf{r},t)\gamma_j(\mathbf{r}',t+t') \rangle = \langle \gamma_i(\mathbf{r},t') \rangle \langle \gamma_j(\mathbf{r}',t') \rangle$ for $|\mathbf{r}-\mathbf{r}'| > D$, and we may write (2) in terms of Fourier-transformed single-chain operators $\hat{\gamma}_i(\mathbf{q},t)$ as

$$S(q,q_z,t) = \frac{1}{V} \sum_{\text{all chains } i} \langle \hat{\gamma}_i(\mathbf{q},t+t')\hat{\gamma}_i(-\mathbf{q},t') \rangle - \langle \hat{\gamma}_i(\mathbf{q},t') \rangle \langle \hat{\gamma}_i(-\mathbf{q},t') \rangle \ , \tag{3}$$

just the sum of single-chain correlations. Thus, $S(q,q_z,t)$ measures averaged single-chain properties at scales beyond D.

III. MONTE CARLO SIMULATIONS AND STRUCTURE FACTOR MEASUREMENTS

We have carried out a direct calculation of $S(q,q_z,t)$ using Monte Carlo simulation. Previous simulation studies of the dynamics of such systems have been those of *single-chain* relaxation. Murat and Grest [9], using molecular dynamics, and Lai and Binder [10], using MC simulation, found that the relaxation time of the polymers in the z direction scales as $D^{-4/3}N^3$. In contrast to these studies we study a collective property: the dynamic scattering from the concentration difference of the two types of monomers present in a two-component grafted layer. In our study monomers occupy sites of a simple-cubic lattice with lattice constant of unit, and the only interaction between monomers is mutual exclusion. One end of each chain is restricted to a particular site in the $z=0$ plane, while all other monomers are restricted to the region $z \geq 0$ [11]. Since the MC moves [12] are local (they occur at a scale $<D$), we expect the dynamics at long scales (e.g., R or h) to not depend on details of the algorithm. We expect relaxation at the scale of the correlation length D to occur in the time for an object of size n_B to diffuse a distance D: this "Rouse" relaxation time is thus of order $\tau_0 \approx D^{11/3}$ in units of MC steps per monomer (MCS/M) [13].

In real grafted polymers (in good solvent), at scales less than D, monomer motions are coupled by hydrodynamic flows of the small solvent molecules. The relaxation time for a correlation volume is $\tau_0 \approx (a^3\eta/kT)(D/a)^{10/3}$, where η is the solvent viscosity [13]. At longer scales, there are no correlations between motions of blobs due to such flows: such hydrodynamic flows are "screened" beyond D, as in semidilute solution. Using these considerations we can translate our simulation time into real time for grafted polymers: for $D/a=5$, $\eta=0.01$ poise and $a \approx 5$ Å, 1 MCS/M corresponds to 1.5 nsec of real time.

All of our studies have been of chains grafted to a 40×40 surface, with periodic xy boundary conditions. We have studied seven cases, with $(N, 1/D^2, T_0)$ listed in Table I, where T_0 is in MCS/M and is much larger than any characteristic relaxation time. These cases cover a range for which previous static studies have shown "brush" scaling behavior, but which can be brought to equilibrium in a reasonable amount of computer time. In particular, it was previously established that the equilibrium layer thickness follows the scaling law $h=0.85D^{-2/3}N$ [11].

In Fig. 1 we show a configuration from the data-taking portion of our simulation of $N=80$ chains with average intergraft distance $D=5$. Figure 1(a) shows only 4 of the 64 chains, which allows us to see typical single-chain configurations. We see that some chains are concentrated near the surface, while others are quite extended. However, the extended chains are still able to wander appreciably from side to side, as they are not near their full extension distance of N. On the other hand, the chains are not so long that they fluctuate across the width of the system, indicating that we should not expect spurious correlations due to the finite area of the grafting surface. In each case we have studied, we have chosen N and D so that the chains are not too stretched for the scaling theory [1] to be appropriate. In Fig. 1(b) we show all 64 chains: this picture is consistent with the notion that there are no appreciable total density fluctuations at scales larger than the "blob" size of order $D=5$ [4]. One must choose D and L sensibly so that the separation of scales $1 < D < L$ holds.

The field ψ is constructed according to the prescription described above, with continuum δ-functions converted to Kronecker deltas, and continuum Fourier transforms converted to fast Fourier transforms (FFT's). Half of the

TABLE I. Characteristic lengths (in lattice units) λ^* and λ_z^* given by inverses of peak positions of scattering function scans $S(q,0,0)$ and $S(0,q_z,0)$, and characteristic times (in MCS/M) t^* and t_z^* corresponding to $1/e$ times of the correlation functions $C(t)$ and $C_z(t)$, respectively.

Run	N	$1/D^2$	T_0	λ^*	λ_z^*	t^*	t_z^*
(a)	50	0.04	1×10^5	16.57	17.32	2135	1266
(b)	50	0.08	2×10^5	15.41	19.55	2982	1820
(c)	50	0.12	4×10^5	15.12	22.03	4558	3669
(d)	60	0.04	2×10^5	18.38	19.44	4026	1723
(e)	80	0.04	2×10^5	22.90	25.76	8254	4723
(f)	100	0.02	2×10^5	25.13	25.57	11359	5640
(g)	100	0.04	2×10^5	25.78	28.30	15022	7147

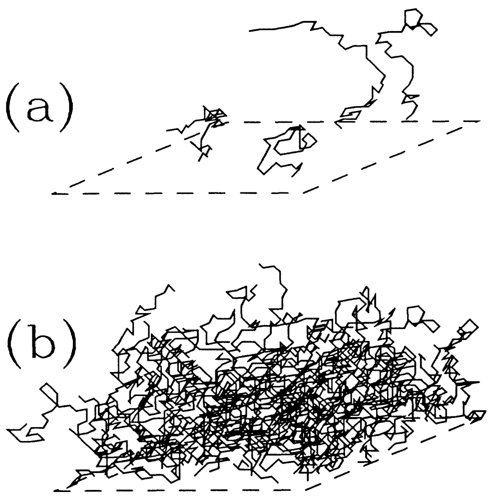

FIG. 1. Configurations of $N=80$, $D=5$ grafted polymers after equilibration. The dashed line indicates the 40×40 grafting surface. In (a), only 4 of the 64 chains are shown in order to better see a few single-chain configurations. In (b), all 64 chains are shown.

chains (chosen randomly) are type A; the other half are type B [14]. The correlation function S can then be computed according to (2): we have then averaged S over 30 such random species assignments.

At equal times, $S(q,q_z,t=0)$ is just the static structure factor. As $q\rightarrow 0$, $q_z\rightarrow 0$, $S(q,q_z,t=0)\rightarrow 0$ because of the attachment of the chains to the surface: large-wavelength fluctuations are prohibited by the large free-energy cost of stretching the polymers more than a vertical distance h or a transverse distance R from their grafting positions. At large momentum, again $S(q,q_z,0)$ tends to zero due to the relative inflexibility of the polymers on short length scales. We thus expect peaks in $S(q,q_z,0)$ at $(q^*\approx 1/R,\ q_z=0)$, and $(q=0,\ q_z^*\approx 1/h)$ corresponding to the characteristic distances for single-chain fluctuations in the xy plane, and in the z direction, respectively. The vertical fluctuations are in fact appreciable because in equilibrium, the brush in good solvent has a rather broad free-end distribution: the same number of free ends is expected above and below $z/h\approx 0.6$.

Previously, mean-field theory [7] has been the only source of information about $S(q,q_z,0)$, and under a variety of solvent conditions, it is found that $S(q^*,0,0)>S(0,q_z^*,0)$. This is due to the static structure being that of *directed* random walks: consider a contribution to the two-point function for a particular chain density γ_i. At one point **r** a monomer is found; the contribution at surrounding points **r**′ depends on the relative *orientation* of **r** and **r**′. We expect the correlation to monotonically decay with $\mathbf{r}-\mathbf{r}'$ in the z direction, over a distance h. However, for $\mathbf{r}-\mathbf{r}'$ in the xy plane, the chain directedness leads to a *depletion* of monomer at **r**′ if the chain passes through **r**. This depletion occurs at a scale of the transverse radius R, and gives rise to extra spectral power in $S(q^*,0,0)$ compared to $S(0,q_z^*,0)$. This peak for transverse fluctuations indicates that the two-component grafted system will have an instability toward the formation of "microdomains" if there is a repulsive interaction between the two species of chains; the strength of such interactions necessary to drive a phase transition is inversely proportional to the structure factor peak value [7].

In Fig. 2, we show momentum scans for the static correlations $[S(q,0,0)$ and $S(0,q_z,0)]$ for the seven systems studied. As can be seen, there are peaks for the $(0,q_z)$ scan, but larger peaks along $(q,0)$, in agreement with the argument presented above. The data are plotted versus wave number rescaled by the characteristic transverse and vertical wave numbers $1/R$ and $1/h$; the coincidence of the peak positions indicates that the characteristic lengths for single-chain fluctuations indeed scale with R and h in the lateral and vertical cases, respectively. The characteristic lengths corresponding to the peak positions of the static scattering are listed in Table I. The ratios of the peak heights of the q and q_z scans are similar to the values obtained in the mean-field theory, where $S(q^*,0,0)/S(0,q_z^*,0)=1.78$ and 1.54 for melt and mean-field ("marginal") good solvent conditions [7]. The peak heights $S(q,0,0)$ are empirically well described by the scaling $S_0=N^{1.85}D^{-1.86}$.

As $t\rightarrow\infty$, $S(q,q_z,t)$ will decay to zero for q and q_z less than $1/D$. We can define time correlation functions for the static peaks at q^* and q_z^*: $C(t)\equiv S(q^*,0,t)/S(q^*,0,0)$ and $C_z(t)\equiv S(0,q_z^*,t)/S(0,q_z^*,0)$. A central issue concerning the dynamics of grafted polymers is what shape these decays take. If entanglements are not important, the decay times τ and τ_z

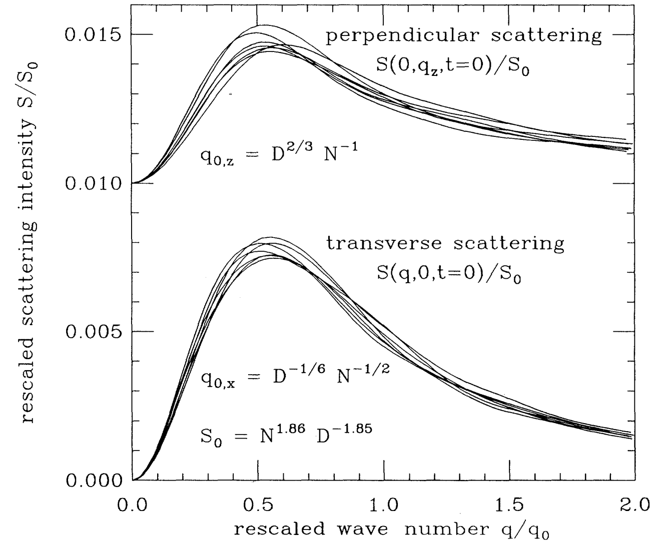

FIG. 2. Static scattering observed from concentration fluctuations in a two-component polymer brush, (i) along $q=0$ $[S(0,q_z,t=0)$, upper curves, vertically shifted by 0.01 for clarity], and (ii) along $q_z=0$ $[S(q,0,t=0)$, lower curves]. In the two cases, S has been scaled by $S_0=N^{1.85}D^{-1.86}$; wave number has been scaled by a characteristic wave number (i) $q_{0,z}=0.5D^{2/3}N^{-1}$ and (ii) $q_{0,x}=D^{-1/6}N^{-1/2}$.

(of C and C_z, respectively) may be estimated using a Rouse [6] or free-draining diffusion approach. As mentioned above, the polymers relax at a scale D after a time τ_0, but at larger distances there are no correlations in the total density, and hydrodynamic interactions are screened. Each polymer can thus be divided into N/n_B correlation "blobs" of size D. An isolated blob moves by diffusion, with diffusion constant D^2/τ_0. The Rouse result, namely that conformational relaxation times are N/n_B times squares of distances that the chain must move to decorrelate, divided by the blob diffusion constant, may be applied to the in-plane and z-relaxation processes. The distance that the coil must move to relax in the xy plane is R, while in the z direction, a distance h must be covered, indicating that $\tau=\tau_0(N/n_B)(R/D)^2$, and $\tau_z=\tau_0(N/n_B)(h/D)^2$. In the MC case, these time scales are $\tau=D^{1/3}N^2$ and $\tau_z=D^{-4/3}N^3$, and are the time scales (in MCS/M) for a chain to relax in the xy plane, and in the z direction, respectively [13].

In Fig. 3 we plot the correlators C_z and C versus rescaled times t/τ_z and t/τ, respectively, using $\tau=D^{1/3}N^2$ and $\tau_z=D^{-4/3}N^3$. The z relaxation collapses well for all the data except for case (c), which decays much more slowly than the Rouse prediction. Similarly, the relaxation of the transverse peak collapses well for all cases except (c); again, this case relaxes much more slowly than the others. We conclude that the six lower-density runs are in the regime described by the Rouse-scaling model. The six lower-density $1/e$ decay times of C_z are $(0.07\pm0.01)\tau_z$; for C, the decay times are in the range $(0.7\pm0.1)\tau$.

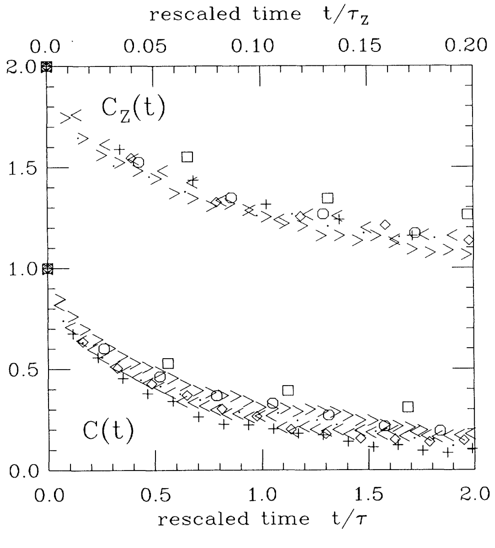

FIG. 3. Decays in time of dynamic scattering function at the peak positions $[(q,q_z)=(0,q_z^*)$ and $(q^*,0)$ for the z and xy scattering, respectively] of the $t=0$ scattering function: $C_Z(t)=S(0,q_z^*,t)/S(0,q_z^*,0)$ (upper curve, upper x axis) and $C(t)=S(q^*,0,t)/S(q^*,0,0)$ (lower curve, lower x axis). Data for C_Z have been shifted upward by 1 to separate the two curves. Symbols $+$, $\circ$, $\square$, $\diamond$, $\bullet$, $<$, and $>$ represent cases (a), (b), (c), (d), (e), (f), and (g) of the text, respectively. Times in MCS/M have been rescaled by the Rouse time scales, which for MC dynamics and lengths corresponding to the z and xy scattering peaks are $\tau_z=D^{-4/3}N^3$ and $\tau=D^{1/3}N^2$, respectively.

IV. ENTANGLEMENT EFFECTS

Entanglements, or "topological" barriers to relaxation due to the impossibility of chain crossing, greatly affect the terminal relaxation of long, interacting polymers. Previous workers [15] have argued that for a brush with quenched grafts, the chains will have relaxation times at least *exponential* in a number of entanglements. In this regime, the x and z relaxation times will be the *same* due to the requirement that relaxation must occur by diffusion of the free end along a specific path to the grafting point, as in relaxation of arms of star polymers [16]. A simple criterion for entanglement [17] is simply that the number of monomers in the volume occupied by a single chain, $\phi hR^2=D^{-5/3}N^2$, is much larger than N, the number of monomers on one chain. This condition $\alpha\equiv D^{-5/3}N\gg1$ holds when a single chain is interacting with many other chains, rather than mainly with itself.

For the seven cases that we have studied, this entanglement index is $\alpha=$(a) 3.4, (b) 6.1, (c) 8.5, (d) 4.1, (e) 5.5, (f) 3.8, (g) 6.8. By this measure, case (c) is the most entangled case that we have examined, and thus we attribute the slowing down in Fig. 3 in this case to entanglements. We adopt the criterion $\alpha>8$ to describe the regime where the Rouse-scaling model fails due to the chains being entangled. Roughly speaking, this indicates that when there are greater than about eight chains in sharing the same volume with a "test" chain, the test chain will suffer at least one entanglement. This criterion agrees very well with that corresponding to measured entanglement molecular weights for entangled polymer melts and solutions [17].

It is interesting to note that for grafted chains, the ratio of the Rouse relaxation times is $\tau_z/\tau=\alpha$: this holds in the case of both MC and real dynamics due to cancellation of all factors of τ_0. It follows that the criterion for the Rouse estimate of the z correlation decay time to exceed that for the x-y correlation decay time is (including the prefactors reported above) $\alpha>10$. However, we have seen that for $\alpha>8$, we expect entanglement and identical x-y and z relaxation. This suggests that for brushes with quenched grafts, the characteristic time associated with transverse fluctuations is always greater than or equal to that of vertical fluctuations. In Table I we list the $1/e$ times of C and C_z, and we note that this inequality is observed by our data.

V. CONCLUSION

In this paper we have presented Monte Carlo calculations of static and dynamic structure factors for a polymer brush composed of two species of chains, with nonmobile, mixed grafts. We have seen that the static structure factor of the difference in concentration of the two species agrees well with results of a self-consistent mean-field theory [7]. This agreement follows from the scaling result that correlations in the total density, which is responsible for the chemical potential gradient that stretches the chains, are screened at scales beyond D, the mean distance between grafts on the surface. Since we are measuring properties at scales beyond D, we expect the results of the mean-field theory to be valid.

The structure factor peaks that we observe as a function of wave number for transverse and vertical momentum transfers are due to correlations of ranges of the chain radius, and the brush height, respectively. These correlations arise from the connectivity of the chains, and from the rich ensemble of chain conformations in a grafted layer. Chains may fluctuate between states of different vertical extension, leading to correlations in z over a scale of the layer height h. However, there are also transverse fluctuations of the chains, leading to correlations in xy over a scale of the transverse chain radius R. The strength of these transverse correlations exceeds that of the vertical correlations, in agreement with mean-field calculations [7].

We have also studied the temporal decay of these correlations by calculation of the two-time structure factor for the volume fraction difference between the two species. We find that for a brush with sufficiently short and sparsely grafted chains, the scaling of the characteristic decay times for the transverse and vertical correlations agree with estimates using scaling arguments of Johner and Marques [13] which assume no entanglement of the polymers. However, we observe that for our densest simulation, there is very slow relaxation which ceases to agree with the nonentangled scaling model: application of a criterion adapted from the study of entanglement of bulk polymers indicates that the polymers in that case should have about one entanglement per chain.

For entangled polymers, one expects the transverse and vertical relaxation times to be the same since the polymers must “reptate” along their contours to relax. For a polymer brush under good solvent conditions, we find that our entanglement criterion coincides exactly with the point at which the nonentangled vertical and horizontal relaxation times are equal. Consequently, the horizontal chain relaxation time always is greater than or equal to the vertical relaxation time.

Thus, since the static scattering from the transverse fluctuations is larger than that observed from vertical chain fluctuations, and since the decay time of the transverse peak is always at least as large as that of the vertical peak, we conclude that $S(q,q_z,t)$ for the two-component brush is always dominated by scattering from the in-plane chain fluctuations, in both the unentangled and entangled cases. We are currently collecting data [18] for $\alpha > 10$ to study the relaxation of chains in more entangled brushes, and also to determine the effect of repulsion of the A and B chains.

Note added in proof. We have recently observed the in-plane microphase separation predicted in Ref. [7] in dense systems ($1/D^2=0.3$ and 0.5, $N=100$) with repulsions between A and B monomers [18].

ACKNOWLEDGMENTS

We thank S. T. Milner and T. A. Witten for many useful comments, and especially A. Johner and C. Marques for communicating much unpublished work. Work at Cornell University was supported by the MRL Program of the NSF under Grant No. DMR-9121654. This material is also based upon work supported by the National Science Foundation under Grant No. OSR-9255223 (NSF-EPSCoR). This work also received matching support from the State of Kansas.

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