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Simulation of Lamellar Phase Transitions in Block Copolymers

R. G. Larson

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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ABSTRACT: Monte Carlo simulations of the lamellar phase transitions for symmetric amphiphilic chains are carried out on a cubic lattice, with the amphiphilic chain length N as large as 192 lattice sites, corresponding to lengths typical of those in experimental systems. We find that there is a qualitative change in the order–disorder transition when N exceeds about 50. For $N \lesssim 50$, the compositional order parameter S at the transition is large; $S \approx 0.8$ on the ordered side of the transition. For $N \gtrsim 50$, the jump is more modest, around 0.50 or less. Also, for $N \lesssim 50$, the dominant compositional fluctuations in the disordered state near the transition have correlation lengths that are less than the lamellar spacing, while for $N \gtrsim 50$, fluctuations with correlation lengths longer than this affect the transition. For $50 \lesssim N \lesssim 200$, which is the range corresponding to many experimental diblocks, the effective value of the interaction parameter χN at the disordering transition is around 15–17, in good agreement with the fluctuation theory of Fredrickson and Helfand but much higher than predicted by the Leibler mean-field theory. Near the disordering transition, dilation or compression of the lamellae can induce lamellar buckling or melting transitions.

I. Introduction

In a previous paper,[1] we showed that the transition to an ordered lamellar state for idealized amphiphilic molecules, including diblock copolymers, could be simulated using a lattice Monte Carlo method for chains of length up to 48 lattice sites. If each lattice site is considered to be an effective segment of a "freely-jointed chain", then molecules composed of 48 lattice sites constitute a molecular weight of around 15 000 for a polymer with the statistical properties of polyisoprene, to take one example. Chains of this length are typical of the shortest polymer molecules used in recent experiments exploring the phase behavior and rheology of lamellar diblock copolymers;[2–5] longer chains studied by Bates and co-workers have molecular weights of around 50 000–80 000, corresponding to about 200 lattice sites.[6,7]

The simulations referred to above show that the transition to the lamellar state for chains as short or shorter than $N = 48$ lattice sites is a rather strong one in that the compositional order parameter on the lamellar side of the transition is high, around 0.8. The compositional order parameter is defined as the amplitude of the one-dimensional compositional wave in the lamellar state, divided by the maximum possible amplitude of this wave. Images of the simulated system show that the lamellar state near the transition consists of well-defined lamellae riddled with fluctuation-induced "hole" and "bridge" defects; the correlation length of these defects appears to be short, of order one lamellar spacing or less. When the temperature is raised, or equivalently the value of χN is decreased, where χ is the Flory "chi" parameter, the transition to the disordered state occurs via multiplication of these defects until the lamellar phase is torn apart, leaving a bicontinuous isotropic phase with appearance similar to that of a spinodally decomposing liquid. In these respects, the phase transitions for all simulated amphiphiles with lengths ranging from $N = 6$ to $N = 48$ were qualitatively similar. Correspondingly, Binder and co-workers[8] have found that the structure factor for melts of simulated diblock chains in the disordered state near the transition is qualitatively similar for all chain lengths from $N = 16$ to $N = 60$. The effective value of χ at the disordering transition, $\chi_{\mathrm{eff,d}}$, for all these amphiphiles was such that $\chi_{\mathrm{eff,d}}N = 17$–21, where a precise definition of $\chi_{\mathrm{eff,d}}$ for our lattice model will be given shortly.

This effective value of χN for $N = 48$ at the transition roughly agrees with that predicted by the Fredrickson–Helfand (FH) theory[9] but is significantly larger (approximately 25% larger) than that predicted by the Barrat–Fredrickson (BF) theory.[10] These theories correct the Leibler[11] mean-field theory for the order–disorder transition of block copolymers by including the effect of weak, but possibly long-ranged, compositional fluctuations. The BF theory should be more accurate than the FH theory because the former allows for "chain stretching", i.e., the tendency of one block, say the A block, to increase its separation from the B block as χN increases. This "chain-stretching" effect is predicted not only to shift downward the value of χN at the transition but also to increase the lamellar spacing, d, at the transition. For the FH theory, d at the transition is given by $d = 3.2R_{g,0}$ where $R_{g,0}$ is the undisturbed radius of gyration of the polymer chain. While for the simulations with chain length $N \leq 48$, χN at the transition shows better agreement with the FH theory than the BF theory, the value of $d/R_{g,0}$ in the lamellar state at the transition is around $4.71R_{g,0}$ for $N = 48$, which is considerably greater than that predicted by the FH theory, at least in part because of chain-stretching effects.[8] In fact, $d/R_{g,0}$ from the simulations is even greater than predicted by the BF theory; see Figure 1.

Of more significance than these modest quantitative failings of the theories, however, is the qualitatively different picture of the transition itself that is afforded by the simulation vis-à-vis the weak-fluctuation theories. In the theories, as the transition is approached from the ordered side, long wavelength—i.e., multilamellar—fluctuations are predicted to appear, and the amplitude of the lamellar pattern is predicted to diminish continuously (to around 0.35 for $N = 48$), before a discontinuous decrease to zero order parameter occurs at the transition. As noted above, in the simulations for $N \leq 48$, the fluctuations are of short correlation length, and at the transition the order parameter is around 0.80, much higher than predicted by weak segregation theories.

These quantitative and qualitative differences between simulation results and the weak-fluctuation theories are not too surprising; the theories are based on perturbation analyses for small order parameter, which become rigorous only for very large N. However, since the simulations for

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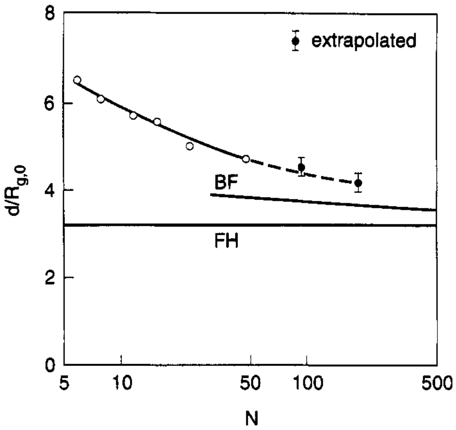

Figure 1. Dimensionless lamellar spacing versus chain length N from the simulations compared to the predictions of the Fredrickson–Helfand (FH) and Barrat–Fredrickson (BF) theories. The two points with error bars are estimated values for $N = 96$ and $N = 192$ based on extrapolations from smaller values of N.

$N \leq 48$ encompass lengths that overlap with the shorter end of experimental systems, it is of interest to determine if the minimum value of N for which the weak-fluctuation picture does become at least qualitatively correct falls within the range of at least some experimental systems. In what follows, results will be presented for simulations with chain lengths up to $N = 192$, i.e., up to lengths that correspond to those of diblock copolymers used in recent experiments of Bates and co-workers.

II. Lattice Model and Simulation Technique

The Monte Carlo lattice model has been discussed elsewhere;[1,12] here we limit ourselves to a brief summary. The simulated block-copolymer "molecule" is a sequence of $N/2$ "A" sites connected to $N/2$ "B" sites on the simple cubic lattice, with periodic boundary conditions. We use the nomenclature A_iB_i to define a copolymer that consists of a string of i head units attached to i tail units. The connection from one polymer site to the next site along the backbone of the chain can be along any of the $z = 26$ nearest or diagonally-nearest neighbors. There is a single dimensionless interaction energy parameter w, which is the interaction energy per A/B contact, divided by k_BT. To make chain movements easier, we include a modest volume fraction, 0.4, of single-site "solvent" molecules in our simulation. The "solvent" molecules are of two types, A and B, taken to be identical, respectively, to the A and B units on the polymer chain. As shown earlier,[1] and confirmed shortly, for long chains with $N \geq 48$, the value of w at the transition is small enough that the solvent molecules distribute themselves nearly randomly on the lattice and act like "holes" that merely dilute the number of A/B polymer/polymer contacts and thus correspondingly reduce the effective χ value.

The parameter χ_{eff} is therefore defined as $\chi_{\text{eff}} = Cz_{\text{eff}}w$. As discussed in ref 1, for long chains ($N \geq 48$), the effective χ value is proportional to the volume fraction $C = 0.6$ of block copolymer. This was confirmed by simulations using a smaller volume fraction of solvent; the quantity $Cz_{\text{eff}}w$ remained nearly the same when C was increased from 0.6 to 0.8[1]. The definition of χ_{eff} also contains the effective coordination number, $z_{\text{eff}} \approx 22$, of the lattice. This value of z_{eff} is less than the actual coordination number $z = 26$, because χ accounts only for interchain contacts and not intrachain contacts in which a chain contacts itself.[1] Obviously, all units of the chain except the ones at the ends automatically have at least two intrachain contacts, because of the connectivity of the chain. One finds out by analysis of the lattice statistics[1] that there are, on average, about two other self-contacts because of the meandering nature of the chain configuration, so that $z_{\text{eff}} \approx z - 4 = 22$. For short chains, such as A_3B_3, the ordering transition occurs at a value of w high enough that the A solvent tends to segregate with the A block, and B solvent segregates with the B block. Hence χ_{eff} must be defined differently, as discussed in ref 1.

Rearrangements of the molecules and methods of preparing equilibrium structures are discussed elsewhere.[1,12] In the earlier work, we obtained equilibrium lamellar patterns on $L \times L \times L$ lattices, where L is an integer large enough that the lattice contained at least two lamellar repeat spacings. By starting at infinite temperature ($w = 0$) and "cooling" the system by increasing w in small increments, a lamellar pattern spontaneously appears at the ordering transition. We showed that the orientation of these lamellae on the lattice is self-selected such that the lamellar spacing is nearly independent of L and is therefore characteristic of a bulk, or infinite, system. In this way, the dependence of lamellar spacing d on chain length N shown in Figure 1 was determined. As N gets larger, $R_{g,0}$ increases and $d/R_{g,0}$ decreases only modestly, so that d increases with increasing N. Hence with increasing N the box size L used in the simulations must be made larger. The larger box size and the slower equilibration that is characteristic of longer chains increase the required computer time to such an extent that simulation of the ordering transition for N greater than 48 becomes prohibitively time-consuming for single-processor workstation computers.

However, the *disordering* transition from the lamellar phase to the disordered state is much faster. Thus, *provided we can estimate the correct lamellar spacing closely enough*, the characteristics of the disordering transition for much longer chains can be simulated in the following way. First, we choose a lattice size L exactly equal to the estimated repeat spacing d of the block copolymer of interst. Then we set w equal to a value about twice the estimated value of w required for an ordering transition. On this small lattice, for w much larger than the minimum required to produce ordering, the ordering transition to a lamellar state occurs quickly, and the simulation box then contains one lamella oriented parallel to a face of the box. Then we *replicate* this ordered phase by making eight identical copies of this lamellar state and combining them to form a lamellar state on a $2d \times 2d \times 2d$ lattice. Then w is reduced to a value above, but close to, the expected value of w at the disordering transition (w_d), and the system is equilibrated. Small decreases in w, followed by re-equilibration, then allow the disordering transition to be determined on the $2d \times 2d \times 2d$ lattice. We showed earlier[1] that for chains with $N = 48$ or smaller, a cubic box big enough to hold two lamellar repeat spacings gives a "bulk" value for w_d, i.e., a value that does not change on larger lattices. We will shortly explore the possibility that boxes bigger than $2d \times 2d \times 2d$ might be needed when $N > 48$.

To obtain the lamellar spacings for N greater than 48, we extrapolate the dependence of $d/R_{g,0}$ on N to N as large as 192; see Figure 1. Fortunately, this extrapolation is guided by the Leibler and especially the BF predictions, which should become asymptotically valid at large enough N. (The predictions of the BF theory were obtained using Figure 3 of ref 9 and the correspondence $\bar{N} = 3.24N$, established in ref 1.) We believe that our extrapolated lamellar spacings for $N \geq 48$ near the disordering transition

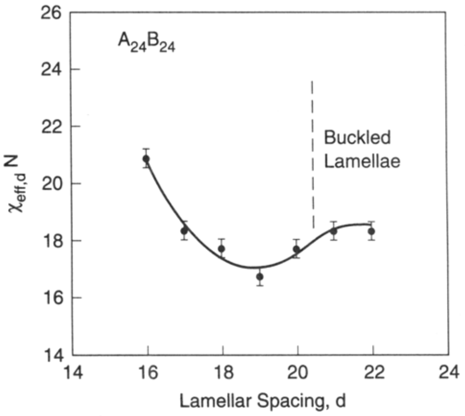

Figure 2. $\chi_{eff,d}N$ versus lamellar spacing for $A_{24}B_{24}$.

are accurate to within ±5%, as shown by the error bars in Figure 1. This estimation of the accuracy of d is reinforced not only by the BF predictions, which can perhaps be viewed as a lower bound, but also by the lack of any *buckling transition* on the $2d \times 2d \times 2d$ lattice, which provides an effective upper bound (see Results). We have repeatedly observed that when the lamellar spacing is as little as 10% thicker than the preferred spacing, the lamellae *buckle*—i.e., form a wavy lamellar structure—to reduce the lamellar spacing toward the desired value. Buckling transitions have been predicted by theory[13] and are frequently observed in layered patterns.[14] The lack of such buckling transitions for our assumed lamellar spacings shows that our estimates of the spacings cannot be much more than 5% higher than the true values.

III. Results

With the above method of estimating the lamellar spacing, we are in a position to extend the results obtained earlier for symmetric diblocks with $N \leq 48$ to N values of 96 and 192. First, however, let us estimate the error in the ordering transition that might be incurred because of a 5% error in the lamellar spacing. To do this, we create lamellar spacings for $A_{24}B_{24}$ that are deliberately too small or too large, by preparing single-lamellar patterns on boxes small enough for only one lamellar repeat distance, and choose that repeat distance to be larger or smaller than the "true" value of $d = 19$ determined in ref 1. We then *replicate* these lamellar patterns to create corresponding patterns on a $2d \times 2d \times 2d$ lattice as discussed above. Then, by reducing w in small increments and re-equilibrating between each increment, we obtain the disordering transition as a function of lamellar spacing d; see Figure 2. These results show that a 5% error in the lamellar spacing leads to only a 5% error in $\chi_{eff,d}N$, where $\chi_{eff,d} \equiv Cz_{eff}w_d$. Thus our method of determining the value of w_d by using estimated values of d would seem to be justified. Also, the lamellae with spacings more than 5% larger than their preferred size show the buckling transition discussed above; see Figure 3, for example. The lamellae become thinner when they buckle and so come closer to their equilibrium thickness. Hence, the disordering transition for the thinner buckled lamellae occurs at a lower value of $\chi_{eff}N$ than would be the case if the lamellae had remained unbuckled and thicker. For lamellae that are initially thinner than the equilibrium spacing, buckling cannot increase the spacing and so does not occur. This argument accounts for the asymmetric effect of changing the box size from the optimal one; see Figure 2.

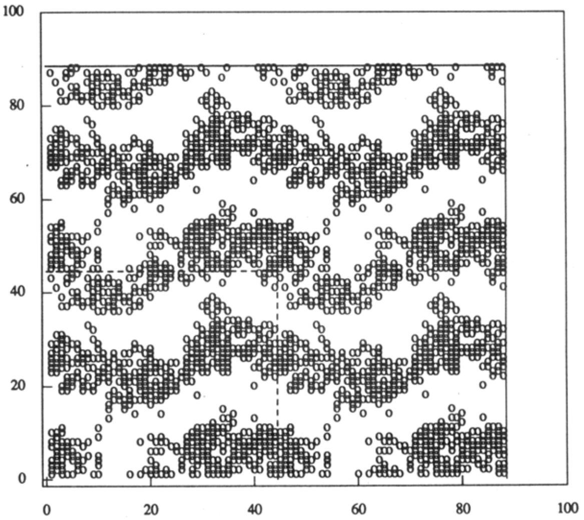

Figure 3. Slice of a lamellar system containing 60% $A_{24}B_{24}$ at $w = 0.030$ on a 44 × 44 × 44 lattice. The lamellae are severely buckled because the lattice dimension is 15% larger than twice the preferred spacing. The circles represent A units on the polymers. This image contains four periodic copies of the simulated system, which is enclosed in dashed lines.

When d is smaller than the equilibrium value, the lamellae melt rather than buckle. After melting, lamellae may re-form if there is an orientation in the box that would permit the newly formed lamellae to have spacing close to the equilibrium value. Thus when $d = 16$, the lamellae melt at $w = 0.033$ but then quickly regrow with normal oriented along a body diagonal so that $d = 18.5$, close to the equilibrium value, $d = 19$. These processes of lamellar buckling, melting, and regrowing in new orientations probably occur in block copolymers whose layer thicknesses have been changed by a flow field. The results presented in Figure 2 can therefore be used to estimate, for a given χN, the degree of lamellar distortion required to melt lamellae. Distortion-induced melting of lamellae can also occur near defects under static conditions.[15]

We now determine the values of w and $\chi_{eff,d}$ for $A_{48}B_{48}$ (i.e., $N = 96$) and $A_{96}B_{96}$ ($N = 192$) by "heating" lamellar patterns on boxes large enough to contain two lamellar repeat distances to the disordering point. These lamellar patterns were prepared as discussed in section II. For $A_{48}B_{48}$, we estimate $d \approx 26$, while for $A_{96}B_{96}$, $d \approx 34$; see Figure 1. Thus, lamellar patterns on boxes of dimension $2d \times 2d \times 2d$, or 52 × 52 × 52 for $A_{48}B_{48}$ and 68 × 68 × 68 for $A_{48}B_{48}$, were prepared. Shortly, we will consider patterns on even bigger boxes.

Figure 4 shows the compositional profiles normal to the lamellae for $A_{48}B_{48}$ at $w = 0.016$, 0.014, and 0.013. These profiles are obtained from the simulation by averaging the concentration of unit A over the two directions that are parallel to the lamellae. The profiles for $w = 0.014$ and $w = 0.013$ were also averaged over two Monte Carlo realizations obtained by extended Monte Carlo runs,[1] since with only one realization the profiles are excessively noisy because of composition fluctuations. Figure 4 shows that the amplitude of the compositional wave decreases as w decreases, reaching zero (to within statistical fluctuations) when $w = 0.013$. Figure 5 shows the averaged composition profiles in each of the three directions on the lattice at $w = 0.014$. As expected, a nonzero compositional variation only exists in the direction orthogonal to the lamellae. At $w = 0.013$, there is no statistically significant variation in any direction, showing that $A_{48}B_{48}$ is disordered at this value of w. The disordering transition is therefore $w_d \approx 0.013$ for $A_{48}B_{48}$. A similar analysis for $A_{96}B_{96}$ shows that an ordered state is obtained for $w = 0.0065$ and a disordered one for $w = 0.0060$; thus for $A_{96}B_{96}$ we take $w_d \approx 0.006$.

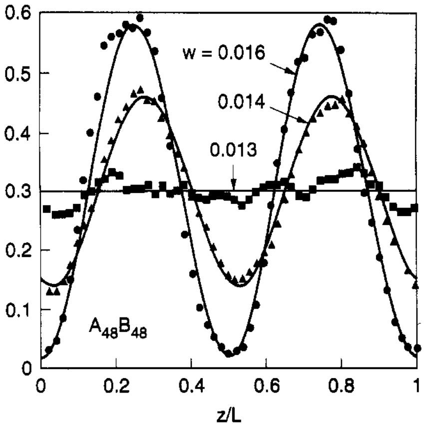

Figure 4. Averaged composition profile normal to the lamellae of block A for 60% $A_{48}B_{48}$ on a 52 × 52 × 52 lattice at $w = 0.016$, 0.014, and 0.013. The compositional order parameters are $S = 0.93$ at $w = 0.016$, $S = 0.53$ at $w = 0.014$, and $S \approx 0$ at $w = 0.013$.

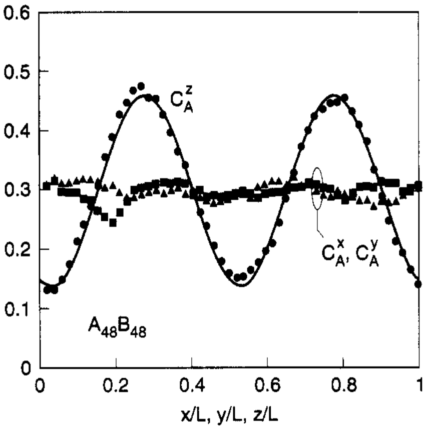

Figure 5. Averaged composition profiles of block A for 60% $A_{48}B_{48}$ on a 52 × 52 × 52 lattice at $w = 0.014$ in each of three nutually perpendicular directions.

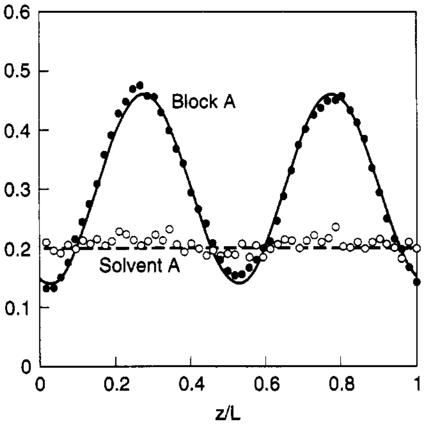

Figure 6. Averaged composition profiles of block A and solvent A for 60% $A_{48}B_{48}$ on a 52 × 52 × 52 lattice at $w = 0.014$.

Figure 6 shows that the A solvent is indeed distributed uniformly on the lattice near the disordering transition for $A_{48}B_{48}$. By symmetry, the B solvent is also distributed uniformly, and both A and B solvents can be regarded as simple diluents that reduce the effective value of χ, as discussed in section II.

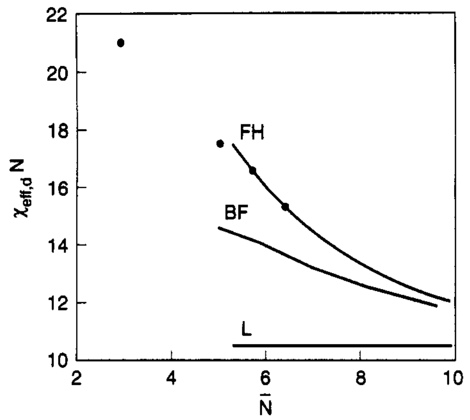

Figure 7. Symbols are values of $\chi_{\mathrm{eff,d}}N$ versus rescaled chain length $\bar{N}$ from simulations for chains of length $N = 6$, 48, 96, and 192 on boxes containing two lamellar repeats; these are compared to the predictions of the Leibler (L), Fredrickson–Helfand (FH), and Barrat–Fredrickson (BF) theories. For our lattice model, $\bar{N} = 3.24N$. For $N = 6$, $\chi_{\mathrm{eff,d}}$ is defined somewhat differently, as discussed in ref 1.

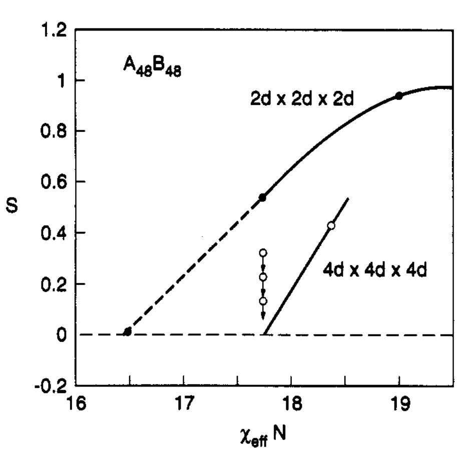

Figure 8. Order parameter S as a function of $\chi_{\mathrm{eff}}N$ for $A_{48}B_{48}$ on 52 × 52 × 52 (2d × 2d × 2d) and 104 × 104 × 104 (4d × 4d × 4d) lattices. On the 104 × 104 × 104 lattice, at $w = 0.014$ (or $\chi_{\mathrm{eff}} = 17.7$), S gradually decreases over a long run; the three points correspond to 7 × 10^5, 14 × 10^5, and 20 × 10^5 attempted Monte Carlo moves per lattice site.

Figure 7 shows that the dependence of $\chi_{\mathrm{eff,d}} = Cz_{\mathrm{eff}}w_{\mathrm{d}}$ on N for $N \geq 48$ is in rough agreement with the prediction of the Fredrickson–Helfand theory. For the longest diblock copolymer considered here, with $N = 192$, $\chi_{\mathrm{eff,d}} \approx$ 15–16, much higher than the mean-field Leibler value of 10.5. Evidently, the Leibler theory is not valid except for chains much longer than those for which experimental data are available.

The lines in Figures 4 and 5 are sinusoidal curves with amplitudes adjusted to fit the profiles given by the simulation. Since the volume fraction of polymer is 60%, the maximum possible peak-to-peak amplitude of the sine wave is 0.6, and the compositional order parameter S is then the actual peak-to-peak amplitude divided by 0.6. For $A_{48}B_{48}$, this gives $S = 0.93$ at $w = 0.016$, $S = 0.53$ at $w = 0.014$, and $S = 0$ at $w = 0.013$; see Figure 8. For $A_{96}B_{96}$, the order parameter at $w = 0.0065$ is $S = 0.57$, and $S = 0$ at $w = 0.0060$. (In ref 1, we found that the order parameter is not significantly affected by the solvent; for $A_{24}B_{24}$, nearly the same order parameter was obtained when the solvent volume fraction was reduced from 0.4 to 0.2.) Since w is changed in discrete increments of 0.0005 or 0.001 and S continues to decrease as the transition is approached, we conclude that for both $A_{48}B_{48}$ and $A_{96}B_{96}$, the order parameter S at the ordered side of the transition is ≈ 0.5 on 2d × 2d × 2d lattices, while for all $N \leq 48$, we found $S \approx 0.80$.[1] Thus, there appears to be a change in the strength of the transition when N exceeds about 50 or so; see Figure 9.

An even more important change occurs in the *effect of the box size on the transition.* By considering the effect

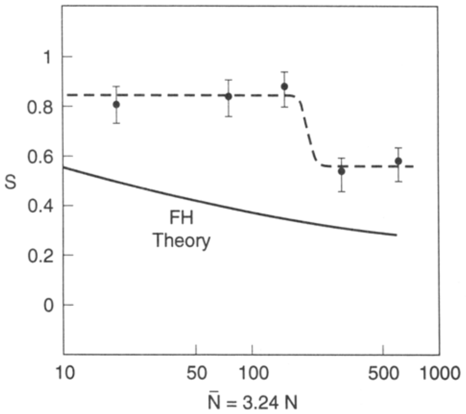

Figure 9. Order parameter S in the ordered state near the disordering transition as a function of $\bar{N}$, from $2d \times 2d \times 2d$ lattices.

of box size for cubic boxes containing as many as eight lamellae, we showed for $A_{12}B_{12}$ that a cubic box large enough to include only two lamellar spacings gives the correct value of w_d to within 1%! For $A_{24}B_{24}$, a box that contains only two lamellae gives a value of w_d that is perhaps 4% too low.[1] Even larger errors in w_d are likely for $A_{48}B_{48}$ and $A_{96}B_{96}$ when the box contains only two lamellae. We find evidence that this is the case by replicating the ordered lamellar pattern containing two lamellar spacings for $A_{48}B_{48}$ at $w = 0.014$; the replicated system is a 104 × 104 × 104 box containing four lamellar spacings. This replicated system is then relaxed through a long "annealing" run at $w = 0.014$. We find that the order parameter decreases during this run to a value at least as low as 0.17; see Figure 8. We suspect that S would drop to zero if the run could be continued long enough. Figure 8 also shows the order parameter on the large lattice for $w = 0.0145$. Thus, the order parameter obtained from the compositional profile is lower on the box containing four lamellae than it is for the box containing only two, and the transition to the disordered state presumably occurs at a higher value of $\chi_{\mathrm{eff,d}}N$ on the large lattice than on the small one. For chains shorter than 48 units, essentially no effect of box size on order parameter can be detected as long as the box contains at least two lamellae.

Figure 10 plots the compositional correlation function $g(t)$ in the isotropic state just below w_d for $A_{12}B_{12}$ simulated on a box large enough to contain exactly four lamellar spacings in the ordered state. We define the correlation function $g(i')$ as

$$g(i') \equiv \frac{1}{L^3} \sum_{i,j,k} \langle x(i,j,k)\, x(i-i',j,k) \rangle \qquad (1)$$

where $x(i,j,k) = 1$ if the lattice site at lattice coordinates $\{i,j,k\}$ is occupied by a A unit and is -1 if it is occupied by a B unit. The angular brackets denote an average over multiple system realizations. Analogous correlation functions $g(j')$ and $g(k')$ can be computed for the other two directions. In the disordered state, these three correlation functions differ only because of noise, which we reduce by averaging the three together to obtain $g(t)$. $g(t)$ approaches unity both when $t \to 0$ and when $t \to L$, because of the periodic boundary conditions. As t moves away from these limits toward $L/2$, however, the correlation function decays in an oscillatory manner because of coherent compositional fluctuations in the disordered state. For $A_{12}B_{12}$, the decay is nearly complete when $t = L/2$, showing that the correlations in composition fluctuations do not span the box. This readily accounts for the lack of any influence of box size on the transition or on the order parameter. For $A_{48}B_{48}$ the fluctuations are apparently correlated over a longer distance; accurate determination of $g(t)$ for $A_{48}B_{48}$ is not available at present because of slow equilibration times and the large box sizes required.

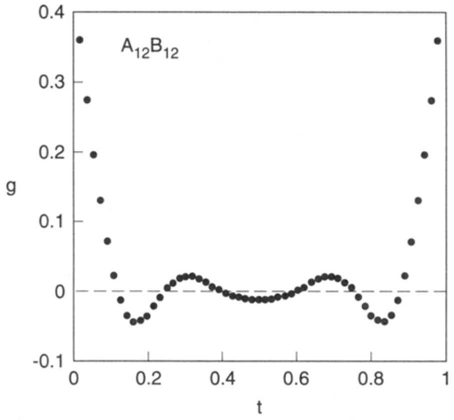

Figure 10. Correlation function $g(t)$ for $A_{12}B_{12}$ on a 56 × 56 × 56 lattice on the disordered side of the transition at $w = 0.049$.

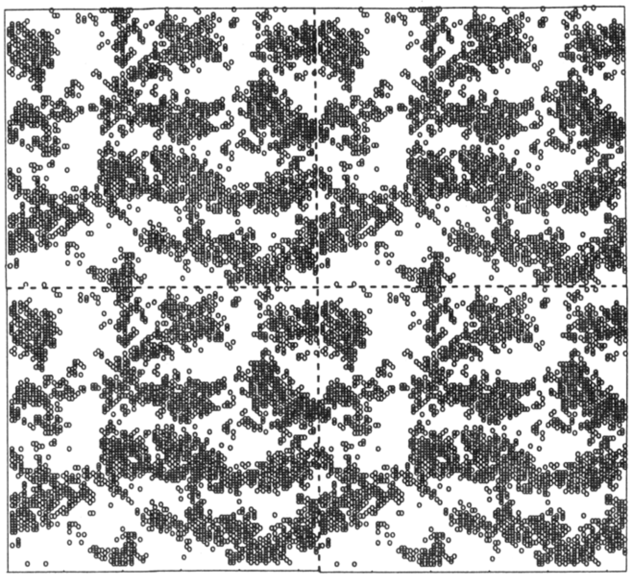

Figure 11. Slice from a 104 × 104 × 104 lattice containing 60% $A_{48}B_{48}$ in the fluctuating lamellar state near the transition at $w = 0.0145$. This image contains four periodic copies of the simulated system.

Figure 11 shows a slice from the 104 × 104 × 104 box containing the ordered phase near the transition at $w = 0.0145$ for $A_{48}B_{48}$. The order parameter is around 0.43, and the lamellae are highly disrupted by fluctuations, much more so than the ordered phase near the transition for $A_{12}B_{12}$; see Figure 12, which reproduces a figure from ref 1. This image reinforces our impression that near the transition for "long" block copolymers, with $N > 50$, there are significant fluctuations with correlation length greater than one or two lamellar repeat spacings, while for short block copolymers with $N < 50$, the fluctuation correlation length is less than roughly one repeat spacing.

IV. Discussion and Summary

The results presented above suggest that there is a qualitative change in the lamellar order–disorder transition in block copolymers when the number of segments in the molecule exceeds about 50 or so. For chains shorter than 50 or so, fluctuations near the transition are short ranged, roughly a lamellar spacing or less, the order parameter on

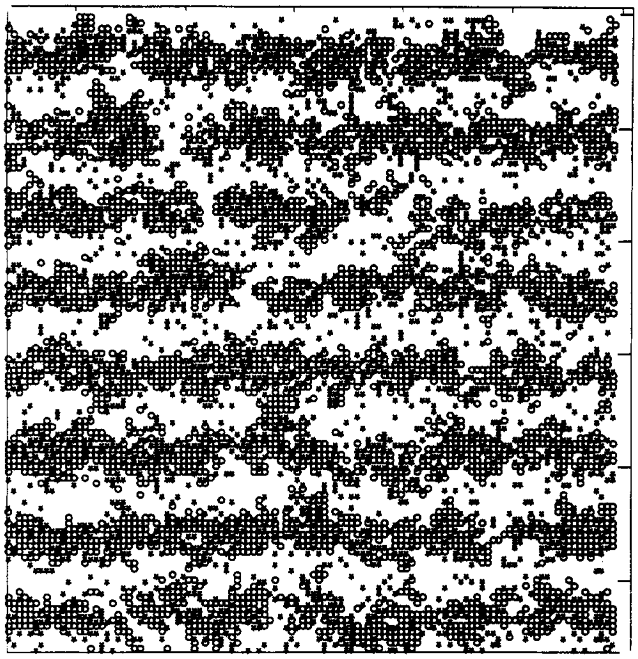

Figure 12. Slice from a 112 × 112 × 112 lattice containing 60% $A_{12}B_{12}$ in the fluctuating lamellar state near the transition at $w = 0.050$.[1] Here, the A solvent units are shown as asterisks.

the ordered side of the transition is high, around 0.80, and boxes large enough to contain only two lamellar spacings are large enough to simulate the characteristics of the transition, including the value of w at the transition. For chains longer than 50 segments or so, fluctuations that are correlated over multiple lamellae become important, the order parameter on the ordered edge of the transition is smaller, around 0.5 or less, and boxes larger than two lamellar spacings are required to represent accurately the structures present in the ordered and disordered phases near the transition. It would thus appear that weak-fluctuation theories might become reasonable for chains longer than 50 units.

There is experimental evidence to suggest that there are qualitative changes in the influence of fluctuation near the order–disorder transition when N exceeds about 50. Rheological measurements by Bates and co-workers[7,16] on relatively long ($N > 100$) poly(ethylenepropylene)–poly(ethylethylene), or PEP–PEE, and 1,4-polybutadiene-1,2-polybutadiene diblock copolymers show a low-frequency fluctuation contribution to the complex modulus G^* in the disordered state near the transition. This anomalous contribution to G^* is absent, however, in measurements of the modulus of shorter ($N \approx 50$) polystyrene–polyisoprene, or PS–PI, diblock copolymers.[4,17] This difference is readily explained if the anomalous contribution is produced by multilamellar fluctuations near the transition. The existence of multilamellar fluctuations in long ($N > 100$) diblock copolymers can be inferred from neutron reflectometry experiments of Foster et al.[18] on thin diblock copolymer layers contacting a solid surface that is preferentially wetted by one of the blocks. In the disordered sate near the transition, ordering induced by the surface propagates several lamellar spacings into the film, which implies that the fluctuation correlation length exceeds the lamellar spacing. The simulation results reported here suggest that for shorter chains ($N < 50$) near the transition similar experiments would show correlation lengths that are less than one lamellar repeat.

The short PS–PI diblock copolymers also differ from the longer PEP–PEE diblocks in the frequency and temperature dependence of the orientation that is induced by large-amplitude oscillatory shearing.[2-4] The orientation behavior of the longer PEP–PEE lamellae seems to be explained qualitatively by a recent theory of Fredrickson[19] that relies on weak-fluctuation theories; this theory seems unable to account for the orientation behavior of shorter PS–PI diblocks. The simulation results, combined with these recent experimental and theoretical findings, suggest that weak segregation theories may be qualitatively valid only for molecular lengths greater than about 50 statistical segment lengths.

Finally, the results presented here show that for values of N characteristic of most experimental systems, the true value of χN at the transition is $\sim 50\%$ higher than the Leibler prediction, $\chi N = 10.5$. This suggests that the temperature dependence of χ for block copolymers *cannot* be obtained by matching the experimental order–disorder transition temperatures to the Leibler prediction. Binder and co-workers have shown[8] that even when χN at the transition is far from the Leibler prediction, the simulated scattering function can be fit reasonably well to that of the Leibler theory; hence successful fitting of experimental scattering data to the Leibler prediction does *not* justify the conclusion that $\chi N = 10.5$ at the transition. Some values of χ reported in the literature may therefore need to be revised.

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