Network Model of the Disordered Phase in Symmetric Diblock Copolymer Melts

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Network Model of the Disordered Phase in Symmetric Diblock Copolymer Melts

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We present a model for the order-disorder transition of symmetric A-B diblock copolymer melts in which the disordered phase is treated as bicontinuous network, and in which self-consistent field predictions of properties of an analogous ordered network are used to estimate some properties. Such a model is shown to accurately predict the latent heat of this transition. The dependence of the location of the transition upon the invariant degree of polymerization $\overline{N}$ is shown to be consistent with a simple hypothesis that the disordered bicontinuous structure is stabilized relative to an analogous ordered network by a nearly constant entropy per network junction.

Block copolymer melts can undergo an order-disorder transition (ODT) from a disordered phase to a variety of spatially periodic ordered structures. The ODT of symmetric AB block copolymers, with A and B blocks of equal volume, has long been of particular theoretical interest as an example of a type of fluctuation-induced first order transition that was first considered by Brazovskii [1], and later predicted for symmetric diblock copolymers by Fredrickson and Helfand [2]. The Fredrickson-Helfand (FH) theory of this transition assumes that the lamellar phase remains weakly segregated at the ODT. FH showed that this would occur for sufficiently high molecular weights. Within the experimentally relevant range of molecular weights, however, both experiments and simulations have shown that the ordered and disordered phases are both rather strongly segregated near the ODT, and contain nearly pure domains of A and B monomers [3–5]. In this regime, the disordered phase near the ODT appears to have a disordered bicontinuous network structure qualitatively similar to that of the bicontinuous microemulsion phase of some ternary systems [3, 6–8]. To describe this regime, one should use a theoretical approach that can describe strongly segregated structures. In this paper, we consider a model of the disordered bicontinuous structure near the ODT that is based on a self-consistent field theory (SCFT) description of an analogous periodic structure.

Understanding of the ODT is currently based on a combination of SCFT and the FH theory. SCFT predicts that symmetric diblock copolymer melts should undergo a continuous 2nd order transition between disordered and lamellar phases at a critical value of χN given by $(\chi N)_{ODT}^{SCF} = 10.495$, where χ is an effective Flory-Huggins parameter and N is degree of polymerization [9]. The FH theory instead predicts a first order transition at a higher value of $(\chi N)_{ODT}$ that depends on a dimensionless parameter $\overline{N} = N(cb^3)^2$, in which c is monomer concentration, and b is statistical segment length [2]. The quantity $\overline{N}^{1/2} \equiv cR_{e0}^3/N$ is equal to the ratio of the volume R_{e0}^3 pervaded by a polymer to the occupied steric volume N/c, where $R_{e0} = \sqrt{N}b$.

Simulations [4, 5, 10] have confirmed that various properties of symmetric diblock copolymer melts exhibit a universal dependence on $\overline{N}$, as first predicted by the FH theory. Simulations have also shown, however, that the assumption of weak segregation underlying the FH theory is valid only for $\overline{N} \gg 10^4$ [4, 5]. At typical experimental value of $\overline{N} \simeq 10^2 - 10^4$, both ordered and disordered phases contain rather strongly segregated A and B domains near the ODT. Furthermore, SCFT has been shown to give quite accurate predictions for the free energy and other properties of the lamellar phase in this regime [4, 5]. The inaccuracy of SCFT predictions for $(\chi N)_{ODT}$ is thus primarily the result of the inability of SCFT to describe a strongly correlated disordered phase. Interestingly, comparison to SCFT predictions showed that, over the range $(\chi N)_{ODT}^{SCF} < \chi N < (\chi N)_{ODT}$, the free energy and degree of A/B contact in the disordered phase change with χN in a manner similar to that predicted by SCFT for the ordered lamellar phase. This observation suggests that characteristics of local structure in the disordered phase (*e.g.,* the degree of segregation and typical domain size) are similar to those predicted by SCFT for an ordered phase over this range. Because the disordered phase has a bicontinuous morphology near the ODT, however, we expect it to more closely resemble a periodic network structure than a lamellar phase.

In this paper, we discuss a phenomenological model of the disordered phase near the ODT that is based on the use of SCFT to predict properties of an analogous ordered bicontinuous network. The motivation for this approach is analogous to the motivation for the study of cell models of simple liquids [11–13], which rely on the observation that local environments in a strongly correlated liquid often closely resemble those in an analogous ordered structure.

The first step in developing such a model is to choose one of the many possible network structures of a diblock copolymer melt [14] as an optimal "surrogate" for the structure of the disordered phase. Our proposed choice is based on the following criterion: Because we focus here on symmetric AB copolymers, we seek a structure in which the A and B domains are geometrically equivalent bicontinuous regions. The skeleton of either domain

in such a bicontinuous structure can be described as a network of "tubes" that meet at junctions, with three or more tubes meeting at each junction. Prior work [14, 15] indicates that the most favorable network structures in melts of monodisperse diblock copolymers contain only three-fold junctions. We thus seek a network with only 3 fold junctions. The only periodic network that we know of that meets these two criteria is the single gyroid (SG) cubic structure, with space group $I4_132$. We thus choose this structure as our surrogate for the disordered phase. The SG structure is distinct from both the double gyroid (DG) structure of space group $Ia\bar{3}d$, which contains two disconnected networks of one component in a matrix of the other, and the $Fddd$ network [16, 17], both of which are equilibrium phases of slightly asymmetric copolymers that have topologically inequivalent A and B domains.

A good surrogate structure should also have a comparatively low SCFT free energy. Let g denote free energy per chain divided by the thermal energy k_BT. For each phase other than the lamellar (L) phase, let $\Delta g = g - g_L$ denote the difference between the value of g in that phase and the value g_L in the lamellar phase. Figure 1 shows SCFT predictions for Δg for symmetric copolymers, denoted by Δg_{SCF}, for the SG and DG networks and the disordered (D) phase. No $Fddd$ solution to SCFT was found for symmetric copolymers. Because SCFT predicts that the lamellar phase is stable for all $\chi N > (\chi N)_{ODT}^{SCF}$, $\Delta g > 0$ for all other phase over this range. Note that the free energies of the DG and SG networks are similar and significantly lower than that of the disordered phase, indicating close competition among candidate network structures. The SG structure is, however, slightly preferred over the DG structure over a range $(\chi N)_{ODT}^{SCF} < \chi N < 24$ that includes the entire range of values of $(\chi N)_{ODT}$ observed in simulations on systems with $\overline{N} > 200$. The single gyroid is thus the lowest free energy network we have found in the regime of interest.

Because the ODT is a first order transition, it has a nonzero latent heat. The enthalpy in each phase of interest and the degree of contact between A and B monomers can both be related to the value of the dimensionless derivative $g' \equiv \partial g/\partial(\chi N)$ [4, 5]. In SCFT, the value of g' in each phase is equal to the overlap integral $g' = \int d\mathbf{r}\ \phi_A(\mathbf{r})\phi_B(\mathbf{r})/V$, where $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are local volume fractions of A and B monomers at point $\mathbf{r}$, and V is the volume of the region over which the integral is evaluated. Hence, g' measures the extent of contact between A and B monomers. In an experimental system in which $\chi(T)$ is a function of absolute temperature T, it can be shown [5] that g' is related to enthalpy h per chain by the relation

$$g' = h\left[N\frac{d\chi(T)}{d(1/k_BT)}\right]^{-1} \quad . \qquad (1)$$

Let $\Delta g' = g'_D - g'_L$ denote the difference between values of g' in the disordered and lamellar phases. Eq. (1) implies that the latent heat of the transition (*i.e.,* change in enthalpy) is proportional to the value of the difference $\Delta g'$ at the ODT. In a strongly segregated structure, A and B monomers come into contact primarily along interfaces between A and B domains, and the change $\Delta g'$ arises primarily from the change in the amount of A/B interfacial area per volume upon transformation from a bicontinuous to a layered structure.

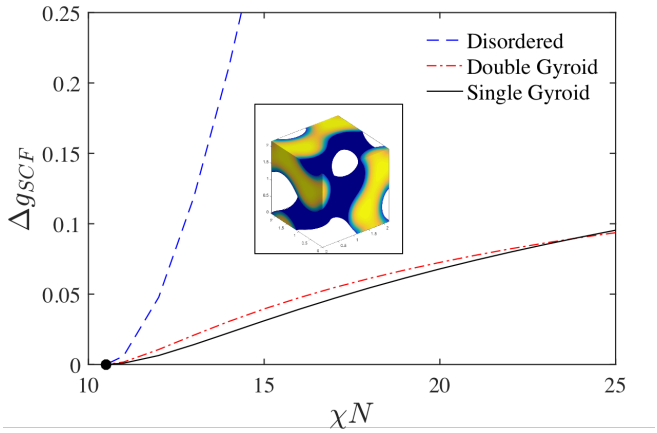

FIG. 1. Plot of Δg_{SCF} vs. χN for the single gyroid, double gyroid and the disordered phases, where Δg_{SCF} is the difference between the free energy per chain and that in the lamellar phase, divided by k_BT. Inset : A cubic unit cell of the single gyroid (SG) phase.

Both experiments and simulations have recently quantified the latent heat of this transition, and been shown to agree [18, 19]. As a simple model for the latent heat, we propose approximating $\Delta g'$ at the ODT by the difference between SCFT predictions for g' in the single gyroid and lamellar phases, evaluated at the value $(\chi N)_{ODT}$ observed in simulations. A test of this approximation is shown in Fig. 2. There, the solid line shows SCFT predictions for the ratio $\Delta g'/g'_L$ as a function of χN, where $\Delta g' = g'_{SG} - g'_L$ is the difference between the SCFT predictions for values of g' in the SG and L phases. Symbols instead show values of $\Delta g'/g'_L$ obtained by analyzing order-disorder transitions in MD simulations [5]. The abscissa of each symbol is equal to the value of $(\chi N)_{ODT}$ observed in the corresponding simulation. Because $(\chi N)_{ODT}$ is a decreasing function of $\overline{N}$, lower values of $(\chi N)_{ODT}$ correspond to larger values of $\overline{N}$. Simulations yield a relatively narrow range of values $\Delta g'/g_L \simeq 0.06$ - 0.08 for systems $\overline{N} \simeq 200 - 8000$, corresponding to a decrease of 6-8 % in the amount of interfacial area per volume upon transformation to a lamellar phase. SCFT predictions for $g'_{SG} - g'_L$ approach zero at $(\chi N)_{ODT}^{SCF}$ because SCFT predictions for g' become the same in all phases at this critical value. Over the range of values $(\chi N)_{ODT} \simeq 13 - 23$ over which $\Delta g'$ has been measured in simulations, however, SCFT yields predictions

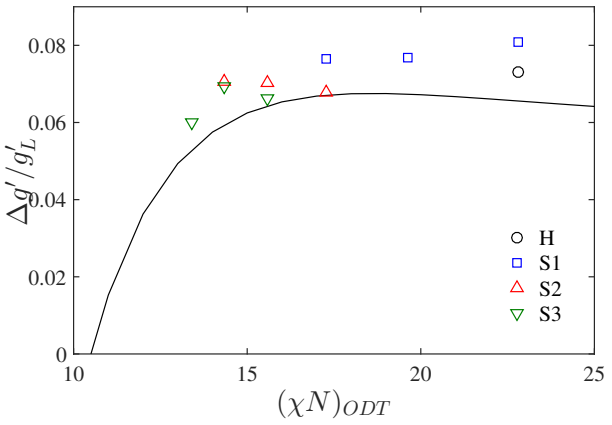

FIG. 2. Fractional change in g' at the ODT *vs.* χN, from MD simulations (symbols) and SCFT (line). Symbols show values of $\Delta g'/g'_L$ from MD simulations vs. the observed value $(\chi N)_{ODT}$. Different symbols indicate results of different simulation models, indicated by the labels H, S1, S2, and S3 used in Ref. [5]. For the SCFT prediction (line), $\Delta g'(\chi N) = g'_{SG}(\chi N) - g'_L(\chi N)$.

for $\Delta g'/g_L \simeq 0.06$ - 0.07 that depend very weakly on $\overline{N}$ and that are only slightly less than the values obtained from simulations.

We now consider the thermodynamics of the ODT. Let Δg denote the difference $\Delta g = g_D - g_L$ between the free energy per chain in the disordered and lamellar phases, normalized by k_BT. At the ODT, $\Delta g = 0$. Let $\Delta g_{SCF} = g_{SG} - g_L$ instead denote the corresponding difference between SCFT predictions for the free energies of the SG and L phases.

We picture the disordered phase near the ODT as a statistical ensemble of bicontinuous morphologies of different topology. To make this more precise, imagine dividing the set of molecular microstates in the disordered phase into subsets such that the topology of the A/B interface is the same for microstates in the same subset. Each such subset thus defines a subensemble of microstates with the same network topology, corresponding to a single local minimum in the free energy surface, or a single "inherent" structure [20, 21]. Let $\Delta\overline{g}$ denote the average of the difference between the free energy per chain in such a subensemble and that in a lamellar phase, normalized by k_BT and averaged over the distribution of topologies found in the disordered phase. The typical environment of a molecule in a disordered network of predominantly three-fold junctions is presumably similar to that in an ordered SG network. As a first step, it is thus natural to try approximating $\Delta\overline{g}$ near the ODT by the SCFT prediction Δg_{SCF} for a SG phase. Because SCFT predicts a stable lamellar phase for $\chi N > (\chi N)^{SCF}_{ODT}$, and thus predicts $\Delta g_{SCF} > 0$, SCFT alone cannot explain why the disordered phase remains stable at $\chi N > (\chi N)^{SCF}_{ODT}$. The *disordered* bicontinuous phase is, however, also stabilized relative to the average free energy of a network of fixed topology by a topological entropy that arises from the existence of many possible network topologies. At a formal level, we may take this into account be writing $\Delta g = \Delta\overline{g} - \Delta s$ in which Δs is a dimensionless structural entropy per chain (*i.e.,* entropy divided by k_B).

A picture of the disordered phase as an ensemble of random networks suggests that the structural entropy per junction should be a number of order unity. Let $\Delta S = M\Delta s$ denote the dimensionless topological entropy per junction, where M denotes the average number of chains per network junction. Let ΔG_{SCF} be the corresponding difference between SCFT predictions of gyroid and lamellar free energy, per junction of the SG phase, normalized by k_BT. A minimal phenomenological model of the ODT may be constructed by: (a) Approximating $\Delta\overline{g}$ by Δg_{SCF}, thus mimicking properties of typical disordered network by those of a periodic SG network, and (b) assuming that the value of ΔS at the ODT is of order unity and almost independent of $\overline{N}$. Setting $\Delta g = 0$ at the ODT yields a prediction that the ODT should occur at a value of χN at which $\Delta G_{SCF}(\chi N, \overline{N}) = \Delta S$, in which ΔS is an order unity dimensionless number that depends very weakly on $\overline{N}$.

The SCFT free energy difference per junction ΔG_{SCF} is given by a product $\Delta G_{SCF} = M\Delta g_{SCF}(\chi N)$, where M is the SCFT prediction for the number of chains per network junction in the SG phase. The unit cell of the SG phases is a cube of length a that contains 8 junctions in the A or B network. The number of chains of volume N/c per junction is thus $M = a^3c/(8N) = \overline{N}^{1/2}\hat{M}(\chi N)$, where $\hat{M} = (a/R_{e0})^3/8$ is a function of χN alone. The difference ΔG_{SCF} per junction can then also be expressed as a product

$$\Delta G_{SCF}(\chi N, \overline{N}) = \overline{N}^{1/2}\hat{G}(\chi N) \qquad (2)$$

in which $\hat{G}(\chi N) = \hat{M}(\chi N)\Delta g_{SCF}(\chi N)$ is a function of χN alone. Because ΔG_{SCF} is proportional to $\overline{N}^{1/2}$, and $\hat{G}(\chi N)$ is an increasing function of χN that vanishes as χN approaches $(\chi N)^{SCF}_{ODT}$, the requirement that the value of ΔG_{SCF} at the ODT be almost independent of $\overline{N}$ naturally yields a prediction for $(\chi N)_{ODT}$ that is a monotonically decreasing function of $\overline{N}$ that approaches the SCFT prediction $(\chi N)_{ODT} = (\chi N)^{SCF}_{ODT}$ as $\overline{N} \to \infty$.

The most important qualitative prediction of this model is simply that the ODT occurs when ΔG_{SCF} reaches an order unity value that is almost independent of $\overline{N}$. This can be directly tested by comparing SCFT predictions to MD simulations. It has been shown [4, 5] that the value of $(\chi N)_{ODT}$ in a variety of coarse-grained simulation vary with $\overline{N}$ as approximately $(\chi N)_{ODT} = 10.495 + 41.0\overline{N}^{-1/3} + 123\overline{N}^{-0.56}$. By using this empirical formula for $(\chi N)_{ODT}(\overline{N})$ to determine

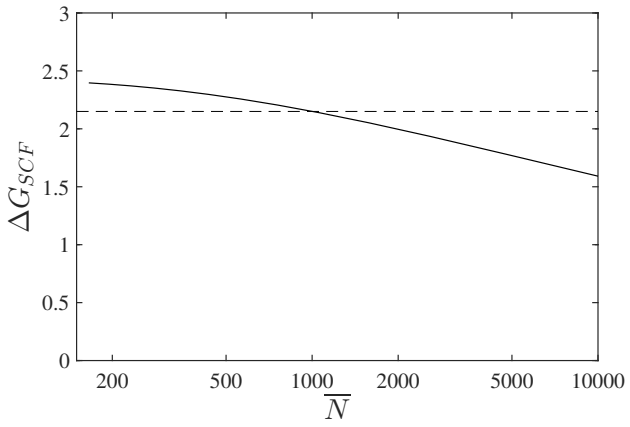

FIG. 3. SCFT prediction $\Delta G_{SCF}(\chi N, \overline{N})$ of the difference between the free energy of the SG and L phases, per junction of the SG phase and normalized by $k_B T$, measured at the value $\chi N = (\chi N)_{ODT}(\overline{N})$ observed in simulations. The horizontal dashed line shows a best fit value of $\Delta G_{SCF} = 2.15$

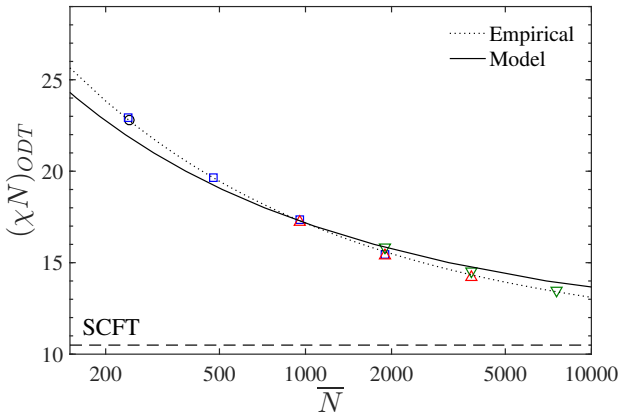

FIG. 4. Comparison of measured and predicted values of $(\chi N)_{ODT}$ vs. $\overline{N}$. Symbols are values measured in simulations. Solid line is a model that assumes ΔG_{SCF} has a constant value at the ODT, for which we take $\Delta G_{SCF} = 2.15$. Dotted line is the empirical formula of Ref [4].

values of χN used in a series of SCFT calculations, we have computed $\Delta G_{SCF}(\chi N, \overline{N})$ at $\chi N = (\chi N)_{ODT}$ as a function of $\overline{N}$. Fig. 3 shows results of this computation for $\overline{N} = 200 - 10,000$. This comparison show that SCFT prediction for the free energy of the SG phase exceeds that of the L phase by approximately $2k_B T$ per junction at the ODT, with rather little dependence on $\overline{N}$, consistent with our hypothesis of a nearly constant structural entropy per junction. Fig. 4 demonstrates the same idea in a different form, by comparing simulation results for $(\chi N)_{ODT}$ to predictions of a model in which we assume that ΔG_{SCF} reaches a constant value $\Delta G_{SCF} = 2.15$ at the ODT.

The model discussed above is intended to describe only the strong-segregation regime $\overline{N} \lesssim 10^4$ in which the FH theory fails. If applied to much larger values of $\overline{N}$, this model would predict a shift $(\chi N)_{ODT} - (\chi N)_{ODT}^{SCF} \propto \overline{N}^{-1/4}$, which is different from the $\overline{N}^{-1/3}$ scaling predicted by the FH theory. This $\overline{N}^{-1/4}$ asymptotic scaling follows from the fact that $\Delta G_{SCF} \propto \overline{N}^{1/2}[(\chi N) - (\chi N)_{ODT}^{SCF}]^2$ for χN very near $(\chi N)_{ODT}^{SCF}$. Because the FH theory is expected to be valid for large $\overline{N}$, we assume that the model proposed here breaks down in the weak-segregation regime $\overline{N} \gg 10^4$ in which the FH theory is valid, and vice versa.

The view of the disordered phase underlying this analysis is somewhat similar to that underlying our understanding of the bicontinuous microemulsion phase of surfactant/oil/water systems [22–24] or the bilayer sponge phase of binary surfactant/water systems [25–28]. A bicontinuous microemulsion or sponge phase is stabilized in part by a structural entropy of order k_B per network junction, as suggested above. In these swollen surfactant systems, however, bicontinuous structures are also favored over layered structures by differences in the entropy arising from undulations about the average membrane conformation in a system of constrained topology. This undulation entropy is known to be greater for topologies that impose an average curvature. This effect lowers the free energy cost of curvature, and so has been described as a renormalization of membrane bending rigidities [28–30]. Our analysis of the ODT in block copolymer melts suggests that the disordered phase is stabilized by a free energy of order $k_B T$ per network junction that is not captured by SCFT, but does not tell us the physical origin of this difference. The missing free energy could, for example, arise in part from subtle differences in undulation entropy, as well as topological entropy.

This work explores a proposed analogy between a strongly correlated disordered phase of a symmetric diblock copolymer melt near its ODT and a periodic bicontinuous structure. We argue that the periodic single-gyroid (SG) structure is a natural surrogate for the disordered phase. By comparing simulation results for the latent heat to SCFT predictions, we show that the amount of A/B contact along interfaces in the disordered phase near the ODT is very close to that predicted by SCFT for the SG structure. The observed dependence of $(\chi N)_{ODT}$ on $\overline{N}$ is shown to be consistent with a simple hypothesis that the disordered bicontinuous phase remains stable at values of $\chi N > (\chi N)_{ODT}^{SCF}$ only where the SCFT free energy of the SG phase exceeds that of the lamellar phase by less than a critical value of order $k_B T$ per junction. This suggests a view of the disordered phase near the ODT in systems of relatively short chains analogous to our view of the bicontinuous microemulsion phase, and complementary to the weak-segregation picture of Fredrickson and Helfand.

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