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Bicontinuous Phase in Diblock Copolymer Melts with Added Homopolymer

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ABSTRACT: We compute in the strong-segregation regime the phase diagram of A−B diblock copolymer with added B homopolymer to see if the bicontinuous phase can be stabilized by adding homopolymers. Our work is motivated by the results of Ajdari and Leibler, who showed using a bending expansion that a single copolymer bilayer in excess homopolymer is unstable to Gaussian bends if the copolymers are sufficiently asymmetric. Our methods, which are not limited to a bending expansion, determine the region of homopolymer concentration and copolymer asymmetry for which a bicontinuous phase might be stable.

Diblock copolymers are a fascinating class of blend materials that form spatially periodic structures. The simplest ordered structure is the lamellar phase, in which the A and B monomers separate into periodic A-rich and B-rich layers. Diblock copolymers can also form cylindrical microdomains (which pack in a hexagonal lattice) and spherical microdomains (which pack in a body-centered cubic lattice). In 1986 a new ordered phase of diblock copolymers was discovered,[1,2] only recently identified as space group $Ia3d$ or gyroid.[3] This bicontinuous phase is found at copolymer compositions intermediate between the lamellar and cylindrical phases. The geometry of this bicontinuous phase is intimately related to the Schoen G "minimal surface", one of a class of triply-periodic, zero-mean-curvature surfaces. Such surfaces have been referred to generically as "plumbers' nightmares" (PN).[4] This exotic bicontinuous geometry has fascinated experimenters and theorists over the past few years.

There have been several previous studies to calculate a phase diagram for A−B diblock copolymers in the strong-segregation regime,[5] including the bicontinuous phase.[6−8] Anderson and Thomas estimated the free energy of the bicontinuous structure using the approximation of Ohta and Kawasaki[12] to treat the stretching free energy, but found no stable bicontinuous phases (relative to lamellae and cylinders). Wang and Safran[13] considered bicontinuous (as well as spherical, cylindrical, and lamellar) phases in emulsions of homopolymers A and B with A/B copolymer monolayers residing at the interface, by considering the curvature elastic properties of diblock copolymer layers. Recently, Olmsted and Milner[9] computed the phase diagram for diblock copolymers in the strong-segregation regime without making the Ohta−Kawasaki approximation but again found no stable bicontinuous phase. Likhtman and Semenov[10] used similar methods to compute the free energy of a bicontinuous double-diamond structure in the strong-segregation limit, which was again found not to be stable. Finally, Matsen and Schick[11] have extended numerical self-consistent mean-field techniques for copolymer phase behavior from weak segregation toward intermediate values of χN, which affords a complementary technique as more Fourier modes (describing the concentration profile) are added.

Adjari and Leibler[14] and Wang[15] have studied the stability of the flat lamellar phase to small bending deformations, for which the deformation free energy is of the form[16]

$$F = F_0 + \int\left[\frac{1}{2}K(c_1 + c_2)^2 + \bar{K}c_1c_2\right] \mathrm{d}S \qquad (1)$$

where $\bar{K}$ and K are the mean and Gaussian bending moduli, respectively. They showed that a single copolymer bilayer in excess homopolymer is unstable to Gaussian bends (i.e., $\bar{K} > 0$) if the copolymers are sufficiently asymmetric. In particular, flat lamellae are unstable to saddle-splay deformations if the fraction f of the copolymer which is the inner block exceeds a critical value $f^* \approx 0.56$. For copolymers more asymmetric than this, an initially flat bilayer floating in excess homopolymer can lower its free energy by deforming into a minimal surface, which has zero mean curvature but negative Gaussian curvature.

Suppose that $f > f^*$, and the copolymer bilayer adopted some plumbers' nightmare geometry; what would be the optimum lattice constant? Within the lowest order bending expansion, the free energy would decrease without bound as the dimension of the unit cell decreased. The homopolymer volume fraction, which approaches unity in the limit of large lattice constant, would also decrease as the lattice constant decreased (the homopolymer being rejected into a coexisting phase, at negligible cost in entropy of mixing). This reduction in free energy would be cut off by higher order terms in the bending expansion, which were neglected in the stability analysis. Thus to predict the free energy of the bicontinuous phase at finite deformation, or the optimum amount of homopolymers in the bicontinuous phase, we must go beyond the bending expansion. Also, to compute the range of stability of such a homopolymer-containing bicontinuous phase, we must compute the free energies of competing phases on the same footing. That is, we must consider the free energy of cylindrical phases possibly containing homopolymers.

Thus motivated by the work of Wang, Ajdari, and Leibler, we consider a system of A−B diblock copolymers dissolved in excess B homopolymer in the strong-segregation regime. Our method determines the region of homopolymer concentration ϕ and composition asymmetry f of the copolymer for which a bicontinuous phase might be stable, and is not limited to a bending expansion. Our calculation contains as a limiting case the critical value of composition asymmetry of copolymer found previously.

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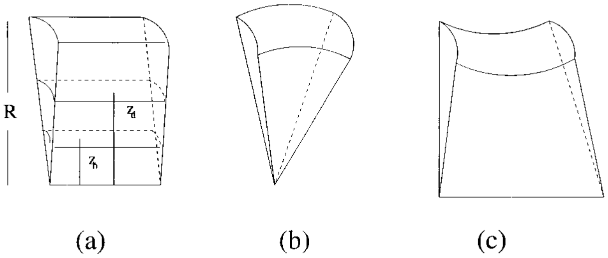

Figure 1. Shapes of an infinitesimal wedge of various structures: (a) cylindrical, (b) spherical, and (c) PN phases. Here R is the radius of the structure, $z = z_d$ is the dividing surface separating A–B diblock copolymer with B in the interior, and $z = z_h$ is the dividing surface separating copolymer A–B from homopolymer B.

The basic properties of ordered block copolymer/homopolymer melts in the strong-segregation regime are governed by the competition between (1) the stretching free energy (reduction of conformational entropy) of diblock copolymer chains, which are essentially tethered to the dividing surface separating the A and B monomers, and (2) the interfacial tension resulting from unfavorable A–B contacts along the dividing surface. We assume the B block of the copolymer to be chemically identical to the B homopolymer, so that we may ignore in the strong-segregation limit any interfacial tension along the copolymer–homopolymer interface. We assume also that the homopolymers are sufficiently long that they do not penetrate the copolymers (see eq 2 below). The total free energy is then the sum of the stretching energy and the interfacial tension terms.

The stretching energy of the A–B diblock copolymer, which is the difficult part of the free energy to compute, is obtained using methods developed for polymer brushes. (For simplicity, we assume here that the diblock copolymers are "elastically symmetric", *i.e.*, that the A and B monomers have the same volume and statistical segment length.) For a given geometrical structure (lamellae, cylinders, bicontinuous), the free energy as a function of the fraction f of A monomer on the copolymer is determined by optimizing the stretching plus interfacial free energy per copolymer with respect to (1) the length scale of the structure and (2) the homopolymer volume fraction ϕ. This assumes coexistence with excess homopolymer at essentially zero chemical potential, as described above. Alternately, we can compute the free energy at a particular fixed value of ϕ, assuming a single phase, which would be relevant if for instance the amount of homopolymer were limited.

In the present paper we extend methods developed for neat diblock melts by Olmsted and Milner to include the case of mixtures of A–B diblock copolymer and B homopolymer; we now briefly review this approach. We model the various microphase structures as assembled from many long, thin "wedges" as shown in Figure 1. The unit cells of the various structures are decomposed into such wedges, each of which contain some number of copolymers as well as a region of homopolymer "filler". Because we are considering the strong-segregation limit, the penetration of homopolymer into the region containing copolymer is suppressed and can be neglected.

The copolymer chain trajectories are assumed to lie along the normals of the wedges; this assumption need not be true of the actual minimum free energy configuration, so the free energies we compute will be upper bounds. The reason for making this assumption is that we can then compute the stretching free energy of the copolymers confined to such wedges. The error in this upper bound will certainly be small if the unit cell is nearly "round". For instance, if the hexagonal unit cell of the cylindrical phase were instead circular in shape, then it could indeed be decomposed into thin pie-shaped wedges in which the chain trajectories would be along the wedge normals (*i.e.*, radial) by azimuthal symmetry.

Different structures (lamellar, cylindrical, and spherical) differ qualitatively in the shapes of the wedges necessary to build up the unit cell, which is to say in the local geometry governing the stretching of the chains within the wedges. The shape of the wedges is determined by the shape of the unit cell. Chains in the lamellar phase are described (exactly) by cylindrical or "can-shaped" wedges, *i.e.*, with a cross-section independent of position along the normal. The local geometry in a cylindrical phase is a pie-shaped wedge, with a cross-section that varies linearly with the distance along the normal; within the approximation of a circular unit cell, the wedges are all identical. Likewise, the cross-section of the "conical" wedges in a spherical phase vary quadratically with distance along the normal (see Figure 1).

The shape of the wedges (specifically, the dependence of the cross-section on the distance along the normal) determines the stretching free energy as follows. We imagine assembling the copolymers into a wedge by grafting blocks one by one onto the "dividing surface" that separates the A and B monomers. The height of the dividing surface along the normal is determined beforehand by volume conservation; *i.e.*, we fill the wedge with homopolymer and copolymer of the given asymmetry in the proper proportions. As we add blocks, the height of the brushes composed of copolymer material on each side of the dividing surface increases, in a manner determined by volume conservation and the shape of the wedge. We compute the stretching free energy by summing the work to add each successive block.

The work to add each successive block into the growing layer is determined using methods developed for brushes in the strong-segregation limit, which we now summarize briefly. Under the assumption that free ends of the blocks can be found at all distances from the dividing surface within the growing layer, it can be shown that the hydrostatic pressure required to enforce incompressibility in the layer is a quadratic function of the distance from the dividing surface, with the curvature of this function determined by the block molecular weight[5,9] (separately on each side of the dividing surface). This pressure may be taken to vanish at the outer extremity of the growing layer. Furthermore, it can be shown that the work to add an additional block is independent of where the free end is placed;[17] thus the work to add each block can be found conveniently by considering the addition of the least-stretched conformation at each stage, *i.e.*, a chain with its free end near the dividing surface, for which the work done is entirely against hydrostatic pressure (no work done to stretch the chain for this conformation).

It is this hydrostatic pressure that acts to exclude homopolymer from the copolymer region. The pressure $\Pi(0)$ near the dividing surface turns out[9] to scale such that $\Pi(0)N \sim (\chi N)^{1/3}$; then the work to introduce a homopolymer chain of length M as a random coil near the dividing surface is $M\pi(0)$. Hence the homopolymer chains are long enough to be expelled from the copolymer-containing regions when

$$\frac{M}{N}(\chi N)^{1/3} > 1 \tag{2}$$

The various plumbers' nightmare structures (including the observed gyroid structure as well as the proposed "ordered bicontinuous double diamond" (OBDD) and hypothetical "ordered bicontinuous double cubic" (OBDC) structures) are each related to triply-periodic minimal surfaces. Each of these structures consists of two identical connected interpenetrating regions, separated by a "partitioning surface", for which a minimal surface appears to be a reasonable model experimentally[3] and theoretically, in the sense that it is a smooth surface of the appropriate symmetry. Each of the two identical connected regions is threaded by a bond-lattice; the region of space filled with the B monomer may be visualized as a "fattened-up" version of these two identical bond-lattices. For the case without homopolymer this region contains the shorter B block of the copolymer, whereas with B-homopolymer filler present this region contains the B-homopolymer filler and the outer (shorter) B-block of the diblock copolymer bilayer. The remaining interstitial space is filled with the inner (longer) A block of the copolymer bilayer. The partitioning surface of the gyroid structure (space group *Ia*3*d*) is well represented by the Schoen G minimal surface, the OBDD structure (space group *Pn*3*m*) corresponds to the Schwartz D minimal surface, and the OBDC (space group P432) corresponds to the Schwartz P minimal surface.

In the plumbers' nightmare structures, then, we model the partitioning surface, which is the middle surface of the diblock bilayer (separating the two monolayers), with the corresponding minimal surface. The shapes of the wedges in the PN structures are dictated by the shape of the partitioning surface, as for the simpler structures (lamellae, cylinders, spheres). Taking a small piece of a minimal surface as the top of the wedge and following it along the normal, we generate a "Gaussian wedge", which narrows linearly in one direction and widens linearly in the other direction as we move along the normal until its cross-section degenerates into a line segment, which is part of the bond-lattice (see Figure 1c).

In ref 9, the actual unit cells of the various bicontinuous structures were decomposed into a large number of nonidentical wedges, and a general expression for the stretching free energy in a wedge of general cross-section was summed on a computer over the different wedges to determine the stretching free energy. Rather than pursuing this approach, we will approximate the structure of a generic PN phase with a single "generic wedge", which we take to have an upper surface with equal and opposite curvature radii characteristic of a minimal surface. This approximation is analogous to assuming a circular unit cell for the cylindrical phase. Such an approximation does not correspond to a space-filling unit cell and so does not provide an upper bound to the free energy.

In fact, in the case of cylindrical and spherical structures, such a calculation corresponds to a micellar structure, assuming the interstitial regions to be filled with long homopolymer matching the outer block of the micelles at no free additional energy cost (no stretching, and no interfacial tension between homopolymer and outer block). Thus the "round unit cell" calculations for cylindrical and spherical structures in fact give distinct lower bounds to the free energy of the structures without homopolymer, because work would have to be done on the micelles to deform them to pack space. No such rigorous argument can be made, however, for the "generic wedge" approximation for PN phases, because these wedges cannot be assembled into a stable "plumbers' micelle" even in the presence of interstitial homopolymer: there is no closed minimal surface with constant negative Gaussian curvature.

We now turn to the details of the calculations described above. We shall first present the "round unit cell" approach, generalized from ref 9 to allow for the presence of inert homopolymer filler, in a way that allows us to treat the lamellar, cylindrical, spherical, and PN geometries simultaneously. As described above, the calculation of the free energy depends on the shape of the wedge, as described by its cross-sectional area $S(z)$ (relative to the top of the wedge) as a function of the distance z along the wedge. This function determines both the dividing surface area and the stretching energy as a function of volume fraction. Our calculation of the stretching and interfacial free energies can be given in terms of a general $S(z)$.

Within the "single wedge" approximation (which corresponds to a "round unit cell" for cylinders and spheres, a "generic wedge" for the PN phase, and the exact result for the lamellar phase), we can write for each phase a single function $S(z)$. The function $S(z)$ has the following form for various phase structure,

$$\begin{aligned} S(z) &= 1 && \text{lamellae} \\ S(z) &= z/R && \text{cylinders} \\ S(z) &= (z/R)^2 && \text{spheres} \\ S(z) &= (z/R)(2 - z/R) && \text{PN} \end{aligned} \tag{3}$$

where R is the radius of the structure. Figure 1 illustrates an infinitesimal wedge of radius R of the various structures. The dividing surface separating A–B diblock copolymer with B in the interior is located at $z = z_d$, and the dividing surface separating copolymer A–B from homopolymer B is located at $z = z_h$. Imposing volume conservation, we find that the volume fraction f of block A and the volume fraction ϕ of homopolymer B are determined by

$$f(1 - \phi) = \frac{V(R) - V(z_d)}{V(R)} \tag{4}$$

$$\phi = \frac{V(z_h)}{V(R)} \tag{5}$$

where $V(z)$ is the volume in the wedge up to a height z, and $V(R)$ is the total volume of the wedge per unit top surface area; *i.e.*, $V(z) = \int_0^z dz\ S(z)$.

By volume conservation, the heights h_A and h_B of the growing A and B layers at a partial coverage (diblocks per unit dividing surface area) σ are

$$V(z_d + h_A) - V(z_d) = \sigma S(z_d)\Omega_A \tag{6}$$

$$V(z_d) - V(z_d - h_b) = \sigma S(z_d)\Omega_B \tag{7}$$

Here Ω_A and Ω_B are the volumes displaced by the A and B blocks of the copolymer. As σ approaches the total coverage that fills the wedge, we have $h_A = R - z_d$ and $h_B = z_d - z_h$.

As described above, using arguments developed for brushes,[17] we take the hydrostatic pressure to be a quadratic function of the distance from the dividing surface, *i.e.*

$$U_A(z) = \frac{3\pi^2}{8\Omega_A l_A^{\,2}}(h_A^{\,2} - (z - z_d)^2), \qquad z > z_d \tag{8}$$

$$U_B(z) = \frac{3\pi^2}{8\Omega_B l_B^{\,2}}(h_B^{\,2} - (z - z_d)^2), \qquad z < z_d \tag{9}$$

where l_A^2 and l_B^2 are the mean square end-to-end distances of the A and B blocks of the copolymer.

The stretching free energy per chain w_{str} can be computed by the method of summing the work done to add blocks one by one as

$$w_{str} = \frac{3\pi^2}{8l_A^{\,2}}\frac{1}{\sigma\Omega_A S(z_d)}\int_0^{R-z_d} dz\; S(z+z_d)z^2 + \frac{3\pi^2}{8l_B^{\,2}}\frac{1}{\sigma\Omega_B S(z_d)}\int_0^{z_d-z_h} dz\; S(z_d-z)z^2 \tag{10}$$

The interfacial free energy per chain w_{int} is simply a geometrical quantity, a surface tension γ times the interfacial area per chain,

$$w_{int} = \frac{\gamma S(z_d)\Omega}{V(R) - V(z_h)} \tag{11}$$

where $\Omega = \Omega_A + \Omega_B$ is the displaced volume of a copolymer chain.

It is easy to see from eqs 10 and 11 that the stretching free energy per chain scales as R^2 and the interfacial free energy per chain scales as $1/R$ in the strong-segregation limit. After calculating the stretching and interfacial free energies per chain, we optimize over the scale of the structure, *i.e.*, the radius R. After minimization, the free energy is conveniently expressed in terms of copolymer asymmetry f and homopolymer volume fraction ϕ. It turns out that in the strong-segregation limit, the free energy per copolymer of all of the phases scales the same way with the surface tension γ and the total copolymer volume per chain Ω, namely as $(\chi\Omega)^{1/3}$, where we have taken the Helfand result $\gamma \propto \chi^{1/2}$.[18] (This is why the phase boundaries in the strong-segregation limit are independent of χN.)

Thus it is convenient to give the free energies of the various phases in units of the lamellar phase free energy, which is itself independent of both f and ϕ. In this way, our final result for the free energy per chain for the PN phase $F^{pn}(f,\phi)$ and the cylindrical phase $F^{cyl}(f,\phi)$ can be written explicitly as

$$F^{pn} = 3^{1/3}\left[\frac{3\beta(2-\beta)}{2(1-\phi)}\right]^{2/3}\left[\frac{(1-\beta)^3(9+2\beta-\beta^2)}{20f^2(1-\phi)} + \frac{(\beta-\alpha)^3(15\alpha - 6\alpha^2 + 5\beta - 3\alpha\beta - \beta^2)}{20(1-f)^2(1-\phi)}\right]^{1/3} \tag{12}$$

$$F^{cyl} = 3^{1/3}\left[\frac{2\beta}{1-\phi}\right]^{2/3}\left[\frac{(1-\beta)^3(3+\beta)}{6f^2(1-\phi)} + \frac{(\beta-\alpha)^3(3\alpha+\beta)}{6(1-f)^2(1-\phi)}\right]^{1/3} \tag{13}$$

where $\beta = z_d/R$ and $\alpha = z_h/R$ are determined by the given structures using eqs 4 and 5. We find explicit expressions for α and β for the cylindrical phase,

$$1 - \beta^2 = f(1-\phi), \qquad \alpha^2 = \phi; \qquad \text{cylindrical phase}$$

$$1 - (3/2)(\beta^2 - \beta^3/3) = f(1-\phi), \quad 1 - (3/2)(\alpha^2 - \alpha^3/3) = \phi; \ \text{PN phase} \tag{14}$$

Thus the free energy of a given structure is completely specified by f and ϕ.

We now discuss our results for the PN phase. Experimentally, the bicontinuous structure (gyroid) is observed between the lamellar and cylindrical phases as the copolymer asymmetry is varied in the strong-segregated regime. Now we have an additional parameter, namely, the homopolymer concentration ϕ. In Figure 2a, we show a family of curves of the PN phase free energy versus ϕ for different copolymer asymmetries f. Observe that for sufficiently large f, these free energy curves display a minimum: there is an optimum amount of homopolymer for a given f. The free energy per copolymer chain for a given copolymer composition f (Figure 2b) is determined by optimizing with respect to ϕ, under the assumption that the PN phase is in equilibrium with excess homopolymer at essentially zero chemical potential.

The relationship between the optimized value ϕ_{opt} and the copolymer composition f is shown in Figure 2c. For a given microphase structure, ϕ_{opt} and f determine the dividing radii of the A−B block and dividing radii of the copolymer/homopolymer, z_d/R and z_h/R, respectively, in eqs 14 and 15. Note in Figure 2c that for f less than a critical $f^* \approx 0.56$, which Wang, Ajdari, and Leibler found was the threshold for lamellae in excess homopolymer to be unstable to Gaussian bends, we find $\phi_{opt} = 1$. To understand this, consider the Gaussian wedge with the volume fraction of homopolymer approaching unity; the copolymer-filled region shrinks to a thin layer, with its curvature radii large compared to its thickness. Thus the limit of ϕ approaching unity corresponds to a nearby flat bilayer in excess homopolymer, the original case studied by Ajdari and Leibler; the limiting value $\phi_{opt} = 1$ corresponds to a perfectly flat bilayer.

Likewise, having considered cylindrical phases with homopolymer filler contained inside the cylinders, we optimize the cylindrical phase free energy per copolymer chain with respect to the homopolymer volume fraction. Recall that this approximation of the geometry as a “round unit cell” provides a lower bound on the free energy (as in the case without homopolymer filler). The optimized cylindrical phase free energy is shown in Figure 3a. The optimized homopolymer volume fraction ϕ_{opt} as a function of copolymer asymmetry f is shown in Figure 3b.

If either of the cylindrical or PN microphases were “starved” of homopolymer, in the sense that not enough homopolymer was available to bring the microstructure to its optimum volume fraction of homopolymer, then the phase behavior is more complicated than the simple rule that the microphase with the lowest free energy is preferred. In that case, there can in principle be coexistence along the cylindrical−PN phase boundary in the f−ϕ plane, as the two phases compete for the available homopolymer. There would not be coexistence regions along the phase boundaries with the lamellar phase, since the lamellar phase does not take up copolymer. We leave this subject for future work.

Observe that within the “round unit cell” approximation, as the volume fraction of homopolymer ϕ_{opt} in-

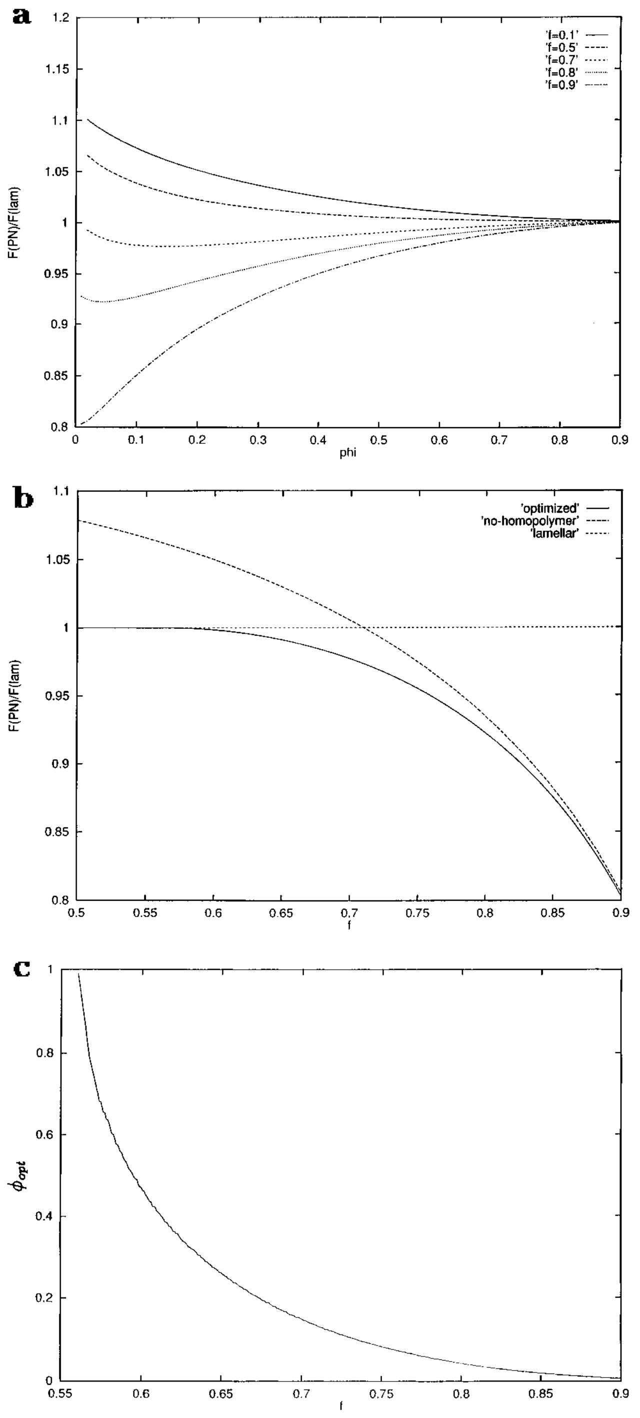

Figure 2. (a) Family of curves of the PN phase free energy versus volume fraction of homopolymer ϕ for different copolymer asymmetries *f*. Note that for sufficiently large *f*, these free energy curves display a minimum: there is an optimum amount of homopolymer for a given *f*. (b) Optimized free energy of the PN phase for a given copolymer composition *f* (solid). Also shown are the free energy of the PN phase without homopolymer (dashed) and the free energy of the lamellar phase (dotted). (c) Optimized value $\phi_{\rm opt}$ versus the copolymer composition *f* for the PN phase. Note that there exists a critical value $f^* \approx 0.56$ beyond which a lamella in excess homopolymer is unstable to Gaussian bends.

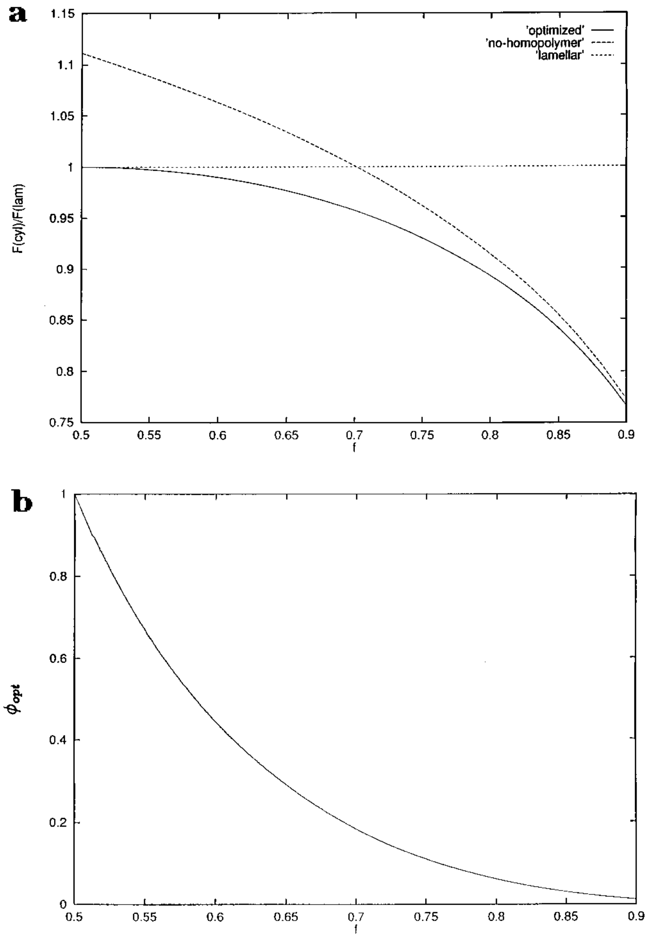

Figure 3. (a) Optimized free energy of cylindrical phase (round-unit-cell approximation) for a given copolymer composition *f* (solid). Also shown are the free energy of the cylindrical phase without homopolymer (dashed) and the free energy of the lamellar phase (dotted). (b) Optimized value $\phi_{\rm opt}$ versus the copolymer composition *f* for the cylindrical phase (round-unit-cell approximation).

creases, the copolymer layer becomes a thin layer near the top surface of the wedge, and its curvature radius becomes large compared to the layer thickness. This leads in the limit $\phi \rightarrow 1$ to a structure essentially identical to a flat lamellar layer floating in excess homopolymer—which is an unrealistic feature of the "round unit cell" model. In fact, in the limit $\phi \rightarrow 1$ the copolymer layer must follow the unit cell boundary, which has vertices at the corners of the hexagons, at which the copolymer layer cannot be flat. Thus the free energy in the "round unit cell" approximation approaches the lamellar-phase free energy in an unrealistic way for $\phi \rightarrow 1$.

We have considered two other model assumptions for the packing of copolymer chains into the cylindrical phase. By analogy with the case of neat copolymer,[9] we may also assume that the dividing surfaces between A and B monomers and between the copolymer and homopolymer regions are both hexagonal. This provides a space-filling structure, and thus an upper bound to the free energy. This structure is convenient because, as for the case without homopolymer, such a unit cell can be assembled from pie-shaped wedges cut from cylinders of different radii. In each wedge, the paths of the copolymer chains are straight and run along the wedge axis. Thus the results of eq 11 for the free energy per copolymer chain can be averaged over the radii of the wedges (weighted by the number of copolymer chains in each wedge). It turns out that the ratio of these upper and lower bounds for the free energy of the cylindrical phase is independent of the asymmetry *f* and the volume fraction ϕ and is given by $(10/9)^{1/3} = 1.036$. Thus we need only multiply our "round unit cell" results by 1.036 to obtain an upper bound. We refer to this

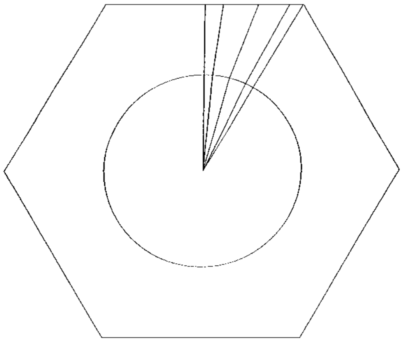

Figure 4. The chain path mapping in a hexagonal unit cell with the dividing surface separating A and B monomers is circular. A chain path of B block which starts at point (0, 0) and ends at the dividing surface, and a chain path of A block starts at the dividing surface and ends on the upper surface.

upper bound result from this model as the "straight-path" bound.

Another upper bound can be computed for the cylindrical phase based on the assumption that the dividing surface separating A and B monomers is circular within a hexagonal unit cell. First consider the case without homopolymer. The inner blocks are assumed to be confined to identical pie-shaped wedges. The paths of the outer blocks are assumed to be straight; however, they cannot be taken to be exactly parallel to the inner blocks to which they are connected. This is because then the wedges so constructed would not all have the correct volume fraction of copolymer blocks; the paths to the face centers are shorter than those to the unit cell corners. To remedy this, we force the copolymer paths to have a slight "kink" at the dividing surface. By symmetry, the paths to the face center and to the unit cell corner have no kink; in general, the outer block path bends slightly toward the nearest unit cell corner (see Figure 4). We refer to this ansatz for the unit-cell geometry as the "kinked-path" ansatz.

Imposing the requirement that each wedge have the proper proportionality of inner and outer block areas f:(1 − f) and assuming the paths of each block are straight as described above, we can work out the mapping to determine the path of each bundle of chains. We assume that unit cell is hexagonal and the dividing surface separating A and B monomers is circular as described above. Consider a chain path for the B block which starts at point (0, 0) and ends at the dividing surface ($r \sin \theta$, $r \cos \theta$). Let the corresponding path of the A block be a straight line from ($r \sin \theta$, $r \cos \theta$) to a point ($x(\theta)$, $3^{1/2}/2$) on the upper surface of the hexagonal unit cell, the function $x(\theta)$ to be determined. We impose boundary conditions with $x(\theta{=}0) = 0$ and $x(\theta{=}\pi/6) = 1/2$ (see Figure 5). By imposing the relation of inner and outer block areas f:(1 − f), we have

$$x(\theta) = \left[\frac{r\theta}{(1-f)} - \frac{3^{1/2}}{2}\sin\theta\right] \Big/ \left[\frac{3^{1/2}}{2r} - \cos\theta\right] \quad (15)$$

Because the chain paths are straight in each half of the wedge, we can still work out the stretching free energy per chain using our general methods. We then compute the appropriately weighted average over the different wedges of the stretching free energy per chain. The resulting upper bound is not merely a constant multiple of the "round unit cell" lower bound, and is in fact a tighter upper bound than the previous "straight-path" ansatz over the range of copolymer asymmetries for which the cylindrical phase is stable. In particular, the ratio of this new upper bound to the lower bound at the lamellar−cylindrical phase boundary in neat copolymer is 1.01.

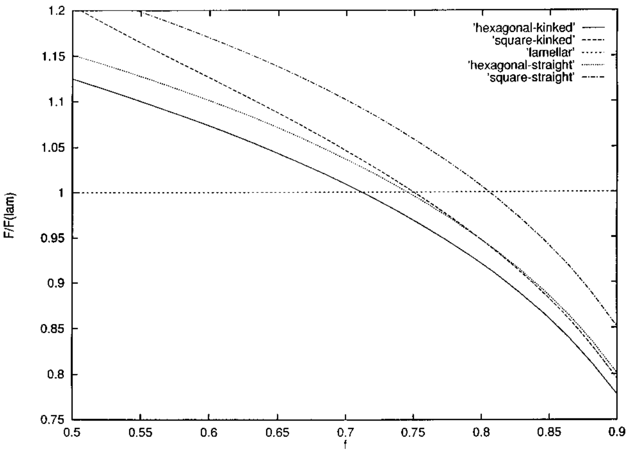

Figure 5. Free energy of the cylindrical phase without homopolymer ("straight-path, hexagonal unit cell") and the free energy of the cylindrical phase without homopolymer ("straight-path", square unit cell"). Also shown are the free energy of the cylindrical phase without homopolymer ("kinked-path, hexagonal unit cell"), the free energy of the cylindrical phase without homopolymer ("kinked-path, square unit cell"), and the free energy of the lamellar phase.

Upper bounds analogous to the "straight-path" and "kinked-path" ansatzes for a hypothetical square packing of cylindrical diblock copolymer domains can also be calculated. For the square-packing "straight-path" ansatz, for which the dividing surface is taken to be square, the upper bound is again a constant multiple of the "round unit cell" lower bound; this time, the ratio is $(4/3)^{1/3} = 1.101$. Thus the "straight-path" upper bound for a square packing of cylinders is higher than that for a hexagonal packing, in agreement with the experimental observation of hexagonal packing. The "kinked-path" ansatz for square packing, again not merely a constant multiple of the lower bound, provides a tighter upper bound than the "straight-path" bound for square packings for the relevant range of copolymer asymmetry. Comparing the lowest of the upper bounds (see Figure 5), we find again that hexagonal packings of cylinders are preferred over square packings, even when the tighter "kinked-path" bounds are used.

By analogy to the "kinked-path" ansatz for the cylindrical phase unit cell for neat copolymer, we can construct a hexagonal unit cell for the case with homopolymer filler in which the dividing surfaces between A and B monomers and between the copolymer and homopolymer regions are both circular. Figure 6a shows the optimized free energy of a such a structure as a function of volume fraction of B block. A similar result for the optimization value of ϕ_{opt} versus the volume fraction of block A is shown in Figure 6b.

Naturally, we take our lowest upper bound at any given copolymer asymmetry as our best estimate of the cylindrical phase free energy. We expect that in the limit of no homopolymer, the "straight-path" estimate does better for relatively symmetric chains (for which the dividing surface must echo the shape of the unit cell) and the "kinked-path" estimate does better for more asymmetric chains (for which minimizing the surface area of the dividing surface determines its shape). In the presence of homopolymer, we expect a similar result: as the volume fraction of homopolymer plus B block increases, the "straight-path" estimate should do

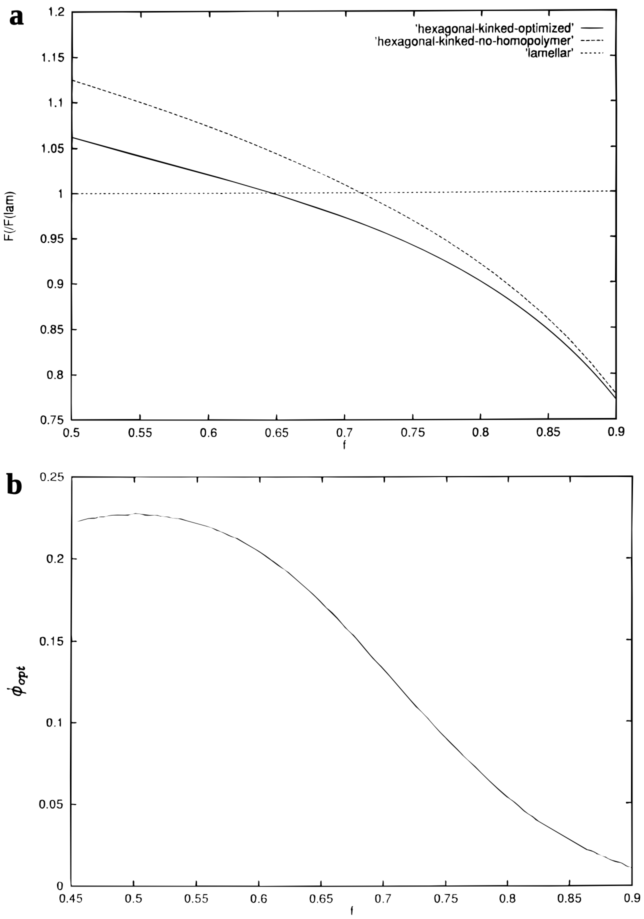

Figure 6. (a) Optimized free energy of the hexagonally-packed cylindrical phase ("kinked path") for a given copolymer composition f (solid). Also shown are the free energy of the cylindrical phase without homopolymer ("kinked path") (dashed) and the free energy of the lamellar phase (dotted). (b) Optimized value ϕ_{opt} versus the copolymer composition f for the cylindrical phase ("kinked path, hexagonal unit cell").

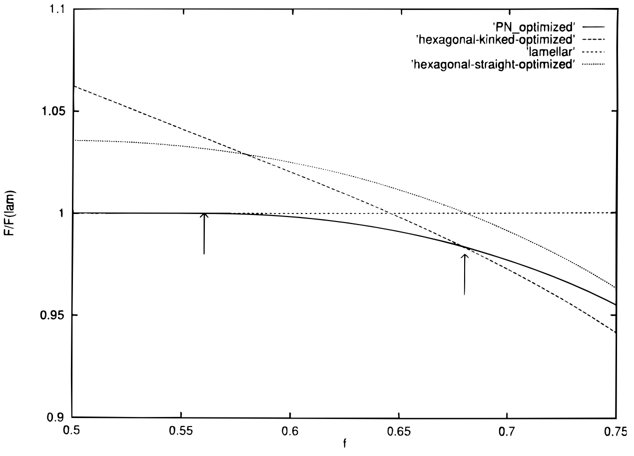

Figure 7. Optimized free energy of hexagonally-packed cylindrical phase estimated by the "straight-path" and "kinked-path" constructions, and the optimized free energy of the PN phase for a given copolymer composition f. Also shown is the free energy of lamellar phase. The arrows denote free energy crossings that limit the stability of the PN phase.

better than the "kinked-path" estimate. This is borne out in Figure 7 (see below).

Figure 7 shows the optimized free energies for the various microdomain structures (lamellar, PN, and cylindrical treated by the "straight-path" and "kinked-path" approximations) versus diblock copolymer composition f in the strong-segregation limit. We conclude based on these estimates that the lamellar phase is the lowest in free energy in the composition range $0.5 < f < 0.56$, while the generic plumbers' nightmare phase is lower in free energy for $0.56 < f < 0.68$, the cylindrical phase being stable for $f > 0.68$ (we have not treated the spherical phase here). The corresponding optimum values of homopolymer volume fraction ϕ in the PN phase can be read off from Figure 2c and are $0.18 < \phi_{\mathrm{opt}} < 1.0$ at the boundaries of stability of the PN phase.

We have computed the free energy of various microdomain structures neglecting the attractive van der Waals force between like domains (e.g., adjacent A-rich cylinders in the cylindrical phase). We now make a simple estimate of the ratio of the van der Waals energy to the sum of the stretching free energy and interfacial tension in the lamellar phase. Our estimate can be applied to all diblock copolymer ordered phase structures inasmuch as only the characteristic dimension of the repeating structure enters the estimate. The total free energy of A–B diblock copolymer in the lamellar phase is the sum of the stretching energy of chain grafted to the interfaces, the interfacial energy between domains of dissimilar A and B chains, and the van der Waals energy. The interfacial contribution is simply the interfacial tension, $\gamma \sim \chi^{1/2}/a^2$. The sum of surface and stretching free energy per chain is roughly

$$f^{\mathrm{e}} = \frac{\gamma}{\sigma} + \frac{h^2}{Na^2} \tag{16}$$

in which σ is the coverage, a is the statistical segment length, and $h = N\sigma a^3$ is the brush height. Optimizing with respect to h makes these two terms of the same order, $f \sim \chi^{1/2}/(a^2\sigma)$. The van der Waals attractive energy per chain between adjacent A domains in the lamellar structure may be estimated as

$$f^{\mathrm{w}} \approx \frac{\chi}{h^2\sigma} \tag{17}$$

where we have assumed that the Hamaker constant is of order χ. The ratio of van der Waals energy per chain to the sum of the stretching and the interfacial tension energy per chain estimate is thus

$$\frac{f^{\mathrm{w}}}{f^{\mathrm{e}}} \approx \chi^{1/2}\left(\frac{a}{h}\right)^2 \ll 1 \tag{18}$$

Clearly the van der Waals energy can be ignored in the estimations of total energy in the strong-segregation regime.

In the present paper we have extended methods developed by Olmsted and Milner for neat diblock melts in the strong-segregation regime to include the case of mixtures of A–B diblock copolymer and B homopolymer. We consider the homopolymer as not penetrating the copolymer, because we are in the strong-segregation limit. Our methods, which are not limited to a bending expansion, determine the region over which a bicontinuous phase might be stable. In the limit of homopolymer volume fraction ϕ nearly unity, which corresponds to a nearly flat bilayer in excess homopolymer, we recover the bilayer instability studied by Wang[15] and Ajdari and Leibler.[14] We have shown that the free minimization of the diblock copolymer ordered structures depends strongly on the overall copolymer asymmetry and homopolymer concentration. We know from the study of bilayer instability that flat lamellae are unstable to saddle-splay deformations if the fraction f of the copolymer exceeds a critical value $f^* \approx 0.56$. For copolymers more asymmetric than this, the flat bilayer floating in excess homopolymer can lower its free energy by deforming into a minimal surface. It is clear that there must therefore be a region in which the homopolymer bicontinuous phase is stable with respect to the lamellar phase. We compare the free energy of bicontinuous "plumbers' nightmare (PN)" phase with homopolymer-containing cylindrical phases to determine the region over which the PN phase is stable. We find that the PN phase is stable for copolymer compositions f ranging from 0.68 to 0.56, with corresponding optimum values of homopolymer volume fraction ϕ_{opt} of 0.18 to 1.0.

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