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Diblock Copolymer Surfactants in Immiscible Homopolymer Blends: Interfacial Bending Elasticity

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ABSTRACT: Self-consistent field theory (SCFT) has been used to calculate the Helfrich bending elastic constants for monolayers of AB diblock copolymers at interfaces between immiscible A and B homopolymer liquids. We focus on the properties of saturated monolayers, with vanishing interfacial tension, considering both symmetric and asymmetric systems. In asymmetric mixtures containing homopolymers with different degrees of polymerization or statistical segment lengths, we calculate the copolymer block compositions required to create balanced surfactants, for which saturated monolayers have vanishing spontaneous curvature.

1. Introduction

Mixtures of two immiscible homopolymers and a diblock copolymer exhibit phase behavior closely analogous to that of mixtures of oil, water, and a small-molecule surfactant. Some such polymer mixtures form equilibrium structures containing domains of nearly pure A and B homopolymer separated by copolymer monolayers. Among these are both swollen ordered phases and disordered microemulsion phases. The interfacial tension within the surfactant monolayers in such phases is generally very low[1,2] for reasons that were first articulated by Schulman.[3] Surfactant-laden interfaces with vanishing interfacial tension are referred to here as saturated interfaces. When the characteristic radii of curvature of the surfactant monolayers are sufficiently large (i.e., significantly larger than the monolayer thickness), the thermodynamic competition between phases that are characterized by different arrangements of interfaces can be described by the Canham−Helfrich theory of interfacial bending elasticity.[4,5]

In both small molecule and polymeric surfactant mixtures, bicontinuous microemulsion phases tend to form under conditions near those for which saturated monolayers have a vanishing spontaneous curvature, i.e., for which the free energy of a monolayer is minimum with respect to its mean curvature for a flat monolayer. Saturated monolayers with vanishing spontaneous curvature are referred to in what follows as balanced monolayers. In mixtures of oil, water, and small nonionic C_iE_j surfactants, in which interaction between water and the hydrophilic polyethylene glycol block is strongly temperature dependent, a bicontinuous microemulsion phase is found to exist only within a relatively narrow range of temperatures around a balance temperature T_b at which the monolayer spontaneous curvature is believed to vanish.[6] In such systems, the minimum of macroscopic interfacial tension between oil- and water-rich phases is obtained at this balance temperature.[6,7] This is also the temperature at which a microemulsion phase that exists in three-phase coexistence with oil- and water-rich phases contains nearly equal volume fractions of oil and water within the microemulsion.

Such balanced bicontinuous microemulsion phases have been created in ternary polymer systems of A and B homopolymers mixed with symmetric AB copolymers[8−10] and with carefully chosen AC[11,12] block copolymers. The identification of copolymers that form balanced monolayers in systems with asymmetric homopolymers is thus potentially useful as a guide to the synthesis of optimal surfactants for either interfacial tension reduction in immiscible blends or for the creation of stable bicontinuous morphologies.

The bending elasticity of a diblock copolymer monolayer has been considered in several previous theoretical studies. The interfacial behavior of diblock copolymer monolayers at a liquid−liquid interface was studied within the Alexander−de Gennes picture by Cantor, who considered both flat and curved monolayers,[13] and by Leibler.[16] The Helfrich elastic constants were calculated by Wang and Safran[14,15] using strong-stretching theory, and by Matsen[17] using numerical SCFT theory, as is also done here. Müller and Gompper have used Matsen's method to examine the behavior of interfacial properties of diblock monolayers very near tricritical and Lifshitz points.[19] Matsen's method has also been used to study mixed diblock copolymer monolayers[18,19] and monolayers containing ABA triblocks.[19]

In his original SCFT study of monolayer bending elasticity,[17] Matsen proposed a general method for calculating the Helfrich elastic constants but gave results only for symmetric systems containing homopolymers of equal molecular weights and a symmetric diblock copolymer. As much attention was devoted in this study to systems with nonzero interfacial tensions as to saturated monolayers. Here, we present results for asymmetric as well as symmetric mixtures, but restrict ourselves to the study of elastic properties of saturated monolayers. There are also technical differences between our method of defining and calculating the free energy of a curved interface and that introduced by Matsen, which are discussed in Section 4.

Throughout this paper, we consider an interface in an incompressible ternary mixture of two immiscible A and B homopolymers and an AB diblock copolymer, in which the copolymer adsorbs to an interface between phases rich in A and B. Monomers of types A and B occupy an equal volume v and have statistical segment lengths b_A and b_B. Let N_A, N_B, and N_C be the degrees of polymerization of the two homopolymers and the copolymer (C), respectively. Let f_A be the volume fraction of the A block within the copolymer, and $f_B = 1 - f_A$. Let $\alpha_A \equiv N_A/N_C$, $\alpha_B \equiv N_B/N_C$, and $\beta \equiv N_A/N_B$.

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2. Interfacial Thermodynamics

This section is devoted to a discussion of some general features of the classical thermodynamics of curved copolymer monolayers. For more general reviews of this subject, see refs 20 and 21. It is convenient to formulate both the classical thermodynamics and the SCFT calculations for a monolayer in the grand-canonical ensemble. We consider a grand-canonical free energy $\Phi = F - \sum_i \mu_i M_i$, where F is the Helmholtz free energy, μ_i is the chemical potential, and M_i the total number of molecules of species i in a system of interest. For any macroscopic phase of volume V and pressure P, $\Phi = -PV$.

The interfacial tension γ of a flat macroscopic interface is the interfacial excess grand-canonical free energy per unit area of interface, defined by taking $\Phi = -PV + A\gamma$ for a system of total volume V with an interface of area A. Here, we consider a system containing a curved interface, in which a curved Gibbs dividing surface of area A divides an exterior A-rich domain (I) of volume V_{I} from an inner B-rich domain (II) of volume V_{II}. We define an interfacial tension γ for such an interface by writing the total free energy Φ as a sum

$$\Phi \equiv -P_{\mathrm{I}}V_{\mathrm{I}} - P_{\mathrm{II}}V_{\mathrm{II}} + A\gamma \tag{1}$$

where P_{I} and P_{II} are the pressures of homogeneous bulk phases I and II at the temperature and chemical potentials of interest. In the special case of a flat interface, for which $P_{\mathrm{I}} = P_{\mathrm{II}} = P$, both the area A of the dividing surface and the interfacial tension γ are independent of the definition chosen for the dividing surface. In the general case of a curved interface, however, P_{I} and P_{II} are generally unequal (for reasons discussed below), and so the values of both A and γ depend on the choice of dividing surface. The thermodynamic relationships among different interfacial excess quantities that are derived in this section are, however, valid for any choice of dividing surface.

2.1. Mechanical Equilibrium. For a curved surface to be in mechanical equilibrium, the total free energy Φ must be minimized with respect to normal displacements of the interface at constant values of all chemical potentials. For a flat surface, this condition reduces to the statement that pressures on either side of the interface must be equal. We consider the mechanical equilibrium condition for a curved interface with an interfacial tension that may depend on curvature. For simplicity, we restrict ourselves to situations in which the inner B-rich domain (II) is either a spherical or cylindrical domain of radius R. Differentiating eq 1 with respect to R while holding temperature and all chemical potentials fixed yields the condition

$$0 = \frac{\partial \Phi}{\partial R} = (P_{\mathrm{I}} - P_{\mathrm{II}})\frac{\partial V_{\mathrm{II}}}{\partial R} + \frac{\partial(\gamma A)}{\partial R} \tag{2}$$

The required derivative of volume V_{II} with respect to radius R is area: $\partial V_{\mathrm{II}}/\partial R = -\partial V_{\mathrm{I}}/\partial R = A$. The derivative of the area is given by $\partial A/\partial R = AC$, where the mean curvature C is defined as

$$C = \frac{d-1}{R} \tag{3}$$

with $d = 3$ for a sphere and $d = 2$ for a cylinder. Substitution in eq 2 then yields a pressure difference

$$P_{\mathrm{II}} - P_{\mathrm{I}} = C\gamma + \frac{\partial \gamma}{\partial R} \tag{4}$$

If we parametrize γ at fixed temperature and chemical potentials as a function of C rather than R, this becomes

$$P_{\mathrm{II}} - P_{\mathrm{I}} = C\gamma - \frac{C^2}{d-1}\frac{\partial \gamma}{\partial C} \tag{5}$$

This mechanical equilibrium condition reduces to the usual Young−Laplace condition for the pressure drop across a curved interface in the limit $\gamma \gg |C(\partial\gamma/\partial C)|$ in which the curvature dependence of γ is negligible. It further reduces to the condition $P_{\mathrm{I}} = P_{\mathrm{II}}$ for macroscopic phase coexistence in the limit $C = 0$ of a flat interface.

2.2. Thermodynamic Variables. It may be shown by a straightforward extension of the Gibbs phase rule that the interfacial tension γ of a mechanically stable spherical or cylindrical interface in an incompressible ternary two-phase mixture is a function of three variables, which we may take to be temperature T, the copolymer chemical potential μ_{C}, and interfacial curvature C. To see this, we first specify the state of a generally compressible system in terms of five degrees of freedom, which may be taken to be temperature, three chemical potentials (which must be the same in both phases), and interfacial curvature. The requirement that the interface be in mechanical equilibrium removes one degree of freedom, leaving four, one of which is the curvature. The usual Gibbs phase rule, which yields three degrees of freedom for a ternary two-phase system, corresponds to the case $C = 0$ of a flat interface.

The restriction to incompressible fluids reduces the number of physically relevant degrees of freedom by one more: changes in the hydrostatic pressure in an incompressible mixture have no effect upon the state of the system other than to cause trivial shifts in the chemical potentials without changing γ or any other interfacial excess properties. This trivial dependence on pressure is discussed in the context of SCFT in Appendix A.1. The state of a mechanically stable curved interface in an incompressible ternary two phase mixture may thus be specified as a function of three variables. We take these to be T, μ_{C}, and C.

To define an unambiguous relationship between γ and μ_{C}, it is helpful to introduce a standard state for μ_{C}. We use a flat saturated interface, with $\gamma = 0$, at a pressure $P_{\mathrm{I}} = P_{\mathrm{II}} = 0$ as a standard state and denote the copolymer chemical potential in this state by $\mu_{\mathrm{C}}^*(T)$. We thus express γ as a function of T, C, and the chemical potential difference

$$\delta\mu \equiv \mu_{\mathrm{C}} - \mu_{\mathrm{C}}^* \tag{6}$$

To define a function $\gamma(T, \delta\mu, C)$ for a curved interface that separates domains I and II in which the pressure is generally different, it is also necessary to choose an arbitrary convention for either the pressure in one of the two domains or the value of one of the homopolymer chemical potentials. We have chosen to define $\gamma(T, \delta\mu, C)$ for $C \neq 0$ as the interfacial tension in a state in which μ_{A} retains the value obtained for a flat membrane with $P_{\mathrm{I}} = P_{\mathrm{II}} = 0$ at the prescribed values of T and $\delta\mu$, and in which μ_{B} is adjusted so as to produce whatever pressure difference is needed to stabilize an interface with the prescribed curvature C.

A reasonable alternative convention would be to require that μ_{A} and μ_{B} be chosen so yield a pressure $P_{\mathrm{I}} = 0$ in the exterior A-rich phase and satisfy the mechanical equilibrium condition for $P_{\mathrm{I}} - P_{\mathrm{II}}$. With our convention, the pressure P_{I} instead varies slightly with the curvature at fixed values of $\delta\mu$ and T because changes of μ_{B} with changing curvature at fixed μ_{A} and μ_{C} change the osmotic pressure arising from the B homopolymer dissolved within the A-rich phase. These two conventions are, however, expected to yield equivalent results for $\gamma(T, \delta\mu, C)$ for systems containing homopolymers with negligible mutual solubility, and extremely similar results for the conditions of interest here.

2.3. Helfrich Expansion. The Canham−Helfrich theory of bending elasticity is an expansion of the excess interfacial free energy of a curved interface about that of a flat interface to the second order in powers of the principal curvatures of the interface (i.e., the inverse principal radii of curvature). Such expansions can be constructed for either the excess Helmholtz free energy density or the excess grand-canonical free energy density γ. Here, we consider an expansion of γ about the flat saturated state, at fixed temperature T, as a function of the principal curvatures and of the chemical potential deviation $\delta\mu$ defined in eq 6. Expanding γ to quadratic order in curvature and linear order in $\delta\mu$, while respecting symmetries imposed by the assumed in-plane isotropy of the interface, yields an expansion of the form

$$\gamma = -\tau C + \frac{1}{2}\kappa C^2 + \bar{\kappa} K + \Gamma^* \delta\mu + \Lambda \delta\mu C \tag{7}$$

where $C = R_1^{-1} + R_2^{-1}$ is the mean curvature, and $K = 1/(R_1 R_2)$ is the Gaussian curvature of a surface with principal radii of curvature R_1 and R_2. For a sphere, $C = 2/R$ and $K = 1/R^2$, while for a cylinder $C = 1/R$ and $K = 0$. The coefficients κ and $\bar{\kappa}$ are bending rigidity and Gaussian rigidity, respectively, while

$$\tau \equiv \frac{\partial \gamma}{\partial C}\bigg|_{\mu_C = \mu_C^*} \tag{8}$$

is a parameter that controls the asymmetry of the monolayer. The coefficient of the term linear in $\delta\mu$ is given by the Gibbs adsorption equation

$$\Gamma^* = -\frac{\partial \gamma}{\partial \mu_C}\bigg|_{C=0} \tag{9}$$

in which Γ^* is the excess number density (copolymers per area) of copolymers in a flat saturated interface. The coefficient Λ is the second derivative $\Lambda \equiv (\partial^2\gamma/\partial\mu_C\partial C)$. Saturated monolayers for which $\tau = 0$ are referred to here as balanced monolayers.

The interfacial tension γ of a cylindrical or spherical surface at a constant chemical potential $\mu_C = \mu_C^*$ may be expressed as a harmonic function

$$\gamma = -\tau C + \frac{1}{2}\kappa' C^2 \tag{10}$$

where $\kappa' = \kappa$ for a cylindrical surface, or $\kappa' = \kappa_+ \equiv \kappa + \bar{\kappa}/2$ for a spherical surface. The minimum of interfacial tension with respect to C at $\mu_C = \mu_C^*$ is obtained for a cylindrical surface at a curvature $C = \tau/\kappa$. The quantity τ/κ is often referred to as the spontaneous curvature (though "spontaneous cylindrical curvature" might be more appropriate). The corresponding spontaneous curvature for a spherical surface is given by τ/κ_+. The curvatures τ/κ and τ/κ_+ correspond to the thermodynamically preferred radii of swollen cylindrical or spherical micelles, respectively, in the absence of any stoichiometric constraint on the amount of the emulsified B homopolymer.[1,6,24]

3. Lifshitz Point

Consider an incompressible ternary system containing two coexisting phases rich in A and B. For a specified set of three molecules, and a fixed pressure, the behavior of such a system depends on only temperature T and surfactant chemical potential μ_C or activity $z_C = e^{\mu_C/k_BT}$. For simplicity, we assume in the following discussion that χ monotonically decreases with increasing T and ignore the possibility of three-phase coexistence.

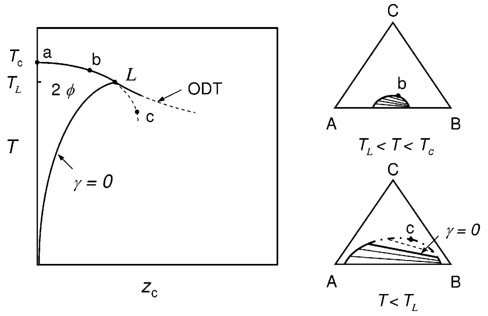

Figure 1. Schematic view of the state of a two-phase system at fixed pressure as a function of T and of a copolymer activity $z_C = e^{\mu_C/kT}$ that is proportional to the concentration of free copolymer dissolved in either of the two coexisting phases. The Lifshitz point L is the intersection of a line of critical points ($a - L$) with the line $z_C^*(T) = e^{\mu_C^*/kT}$ along which $\gamma = 0$ for a flat interface. Saturated monolayers can exist only for $T < T_L$.

In the absence of copolymer, A and B are completely miscible above a binary critical temperature T_c. As T is decreased below T_c, a two-phase region of the Gibbs phase triangle emerges from the binary critical point (a), as shown in Figure 1. Within the two phase region, each tie-line may be characterized by a value of μ_C and a corresponding value of the interfacial tension $\gamma(T, \mu_C)$ for a flat interface, which generally decreases with increasing μ_C. At T slightly below T_c, the two-phase region generally terminates at a critical point (b) that moves to higher surfactant concentration with decreasing T and at which $\gamma(T, \mu_C)$ must vanish because the compositions of the coexisting phases merge.

At T below a Lifshitz temperature T_L, however, the macroscopic interfacial tension may be driven to zero at a saturation chemical potential $\mu_C^*(T)$ lower than the value of μ_C at the critical point (c), allowing the formation of a saturated monolayer. A Lifshitz point is thus the intersection of a line of critical points with the saturation line $\mu_C^*(T)$ along which $\gamma = 0$, as shown in Figure 1. The Lifshitz point can also be identified by examining instabilities of the disordered phase, as the point along the line of critical points ($a - L$) at which the divergence of the structure factor $S(q)$ at wavenumber $q = 0$ is first preempted by a divergence of $S(q)$ at $q \neq 0$, signaling an instability toward the formation of a mesophase. As the Lifshitz point is approached along the saturation line $\mu_C^*(T)$, the compositions of the two coexisting phases must merge, and so the Helfrich constants of a saturated monolayer must vanish at the Lifshitz temperature.

Broseta and Fredrickson[22] have considered thermodynamics of symmetric mixtures, with $f = {}^1/_2$, $\alpha_A = \alpha_B = \alpha$, and $b_A = b_B$. In this case, a stable Lifshitz point occurs at $\phi_A = \phi_B$ and

$$(\chi N_C)_L = \frac{2(1 + 2\alpha^2)}{\alpha} \qquad (\phi_C)_L = \frac{2\alpha^2}{1 + 2\alpha^2} \tag{11}$$

for all $\alpha < 1$.[22,23] For $\alpha > 1$, they found that the appearance of the Lifshitz point is preempted by the appearance of a region of coexistence between three homogeneous phases. The resulting three-phase triangle is predicted to grow continuously from a tricritical point with decreasing temperature for $1 < \alpha < {}^5/_2$ and to appear discontinuously for $\alpha > {}^5/_2$. At exactly $\alpha = 1$, there exists a Lifshitz tricritical point at $\chi N_C = 6$ and $\phi_C = {}^2/_3$, which is the intersection of the line of Lifshitz points that are stable for $\alpha < 1$ and a line of tricritical points that are stable for $1 < \alpha < {}^5/_2$.

A Lifshitz point generally also exists in systems with slightly asymmetric homopolymers and/or an asymmetric copolymer. For each choice of a set of monomers, and values N_A, N_B, and N_C (or $f_B N_C$), however, there will exist a unique value of f_A for which a balanced saturated monolayer can be formed at temperatures infinitesimally below T_L. Fredrickson and Bates[23] have proposed the identification of such *balanced* Lifshitz points as a strategy for the formulation of balanced bicontinuous microemulsions in mixtures with asymmetric homopolymers. Fredrickson and Bates also proposed an approximate criterion for identifying balanced Lifshitz points: They required that the critical fluctuation mode at the Lifshitz point not involve any fluctuation in surfactant concentration. This is equivalent to requiring that tie-lines infinitesimally close to the critical point at $T = T_L$ should be parallel to the binary A−B homopolymer edge of the Gibbs phase triangle. This criterion was shown to be satisfied for systems with $b_A = b_B$ when

$$f_A = \sqrt{\beta}/(1 + \sqrt{\beta}) \tag{12}$$

This criterion does not appear to us to be equivalent to the requirement $\tau = 0$ near the Lifshitz point, but the two criteria are shown in section 5.2 to yield similar results for the balanced composition.

4. SCFT Methodology

SCFT calculations of γ have been carried out for both spherically and cylindrically curved interfaces. The grand-canonical formulation of SCFT that is used here is discussed in the Appendix. Calculation of γ for such a curved interface requires the construction of a spherically or cylindrically symmetric solution to the SCF equations within an annular domain $R_- < r < R_+$, where r is a radial coordinate. R_- and R_+ must be chosen to be far enough from the dividing surface so that the monolayer structure is not affected by proximity to the boundaries. We solve the one-dimensional modified diffusion equation using a finite-difference discretization of r and a Crank−Nicolson scheme for integration of the contour variable s.

To calculate the elastic parameters for an expansion about a saturated flat interface, for a system containing a specified set of molecules at a specified value of χ, the saturation chemical potential μ_C^* is first determined by calculating interfacial tension $\gamma(\mu_C, C = 0)$ of a flat interface for several values of μ_C. In these simulations, the chemical potentials μ_A and μ_B are chosen for each value of μ_C so as to satisfy the condition $P_I = P_{II} = 0$. The required values of μ_A and μ_B for each μ_C are calculated from the Flory−Huggins theory obtained by taking the homogeneous limit of SCFT (as discussed in the Appendix).

Once μ_C^* is known for a specific system, calculations of $\gamma(\mu_C^*, C)$ are conducted for both cylindrical and spherical interfaces at several values of $1/R$. For each calculation, the values of μ_A and μ_C are kept fixed at the values obtained for a saturated flat monolayer at zero bulk pressure, and μ_B is adjusted to whatever value is needed to stabilize a curved interface for which the Gibbs dividing surface has the prescribed radius of curvature. We take the Gibbs dividing surface to be the equimolar surface for either type of monomer, defined so that there is a vanishing interfacial excess of either A or B monomers taken to include contributions from the corresponding homopolymer and one block of the copolymer. Values of κ and κ_+ are obtained for each system of interest by fitting SCFT results of $\gamma(\mu_C^*, C)$ for cylindrical and spherical surfaces, respectively, to eq 10.

A Newton−Raphson iteration scheme is used to solve the grand-canonical SCF equations simultaneously with a constraint requiring that the dividing surface have a specified radial position at $r = R$ in the middle of the simulation cell. The macroscopic chemical potential μ_B must be adjusted so as to satisfy this additional constraint. Each iteration thus involves a simultaneous adjustment of the SCFT chemical potential fields ω_α at all spatial grid points and of μ_B. In the case of a flat interface, the addition of a constraint on the interfacial position is necessary to obtain a unique solution to the SCF equations because the position of a flat interface within the simulation cell is otherwise indeterminate in the grand-canonical ensemble. In the case of a weakly curved interface, the interfacial radius R is a mathematically unique but extremely sensitive function of μ_B, so this procedure is helpful for numerical stability.

4.1. Nondimensionalization. It is shown in Appendix A.3 that, as noted previously by Matsen,[17] the SCF expression for interfacial tension of a spherical or cylindrical surface of radius R may be expressed in the dimensionless form

$$\gamma = \frac{kT\,b}{N^{1/2} v}\,[\gamma] \tag{13}$$

where $[\gamma]$ is a dimensionless function that can depend only upon the dimensionless molecular parameters χN, f_A, α_A, α_B, b_B/b_A, and μ_C/kT, and the dimensionless radius $R/(N^{1/2}b)$, where $N = N_C$ and $b = b_A$. Following Matsen, we express the Helfrich expansion for a membrane with $\mu_C = \mu_C^*$ in the nondimensional form

$$[\gamma] = \frac{1}{2}[\kappa][C]^2 + [\bar{\kappa}][K] - [\tau][C] \tag{14}$$

where $[C] \equiv C\,N^{1/2}b$ and $[K] \equiv KNb^2$ are dimensionless mean and Gaussian curvatures, and

$$\begin{aligned} \kappa &= kT\bar{N}^{1/2}[\kappa] \\ \bar{\kappa} &= kT\bar{N}^{1/2}[\bar{\kappa}] \\ \tau &= kT\frac{\bar{N}^{1/2}}{N^{1/2}b}\,[\tau] \end{aligned} \tag{15}$$

where $\bar{N} \equiv Nb^6/v^2$, and where $[\kappa]$, $[\bar{\kappa}]$, and $[\tau]$ are dimensionless elastic parameters that depend only upon χN, f_A, α_A, α_B, and b_B/b_A.

4.2. Relation to Matsen's Procedure. The definition of the excess free energy density γ of a curved interface that is used here is somewhat different from that used by Matsen.[17] Because solutions to the SCF equations are extrema of a corresponding SCF free energy functional, and the mechanical equilibrium condition may be obtained by minimization of this functional with respect to normal displacements of the interface, solutions to the SCF equations necessarily satisfy the mechanical equilibrium condition. To impose an arbitrary curvature upon an interface in the SCFT simulation, it is thus generally necessary to exert a force upon the interface so as to maintain mechanical equilibrium.

In the method used here, the required force is supplied by a pressure difference, which may be controlled by adjusting μ_A and/or μ_B. Matsen instead fixed μ_A and μ_B to values obtained for coexisting macroscopic phases with $P_I = P_{II} = 0$ at the prescribed value of μ_C, but added an additional term to the SCF free energy functional whose sole purpose is to exert a stabilizing force upon the interface. This additional term is of the form

$$\delta\Phi = -\psi \int d\mathbf{r}\, \delta(r - R)\, [\phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \tag{16}$$

Here, $r = |\mathbf{r}|$ is a radial coordinate, $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are local monomer volume fractions, and ψ is a parameter whose value can be adjusted so as to stabilize an interface with a specified radius of curvature R. The magnitude of this parameter must vanish in the limit $C = 0$ of a flat interface because Matsen used chemical potentials chosen to give $P_I = P_{II}$, but must become nonzero for any nonzero curvature. When ψ is nonzero, this addition to the free energy functional can apply a localized force on the monolayer along the surface $r = R$ and introduces δ-function spikes in the SCF chemical potential fields $\omega_A(r)$ and $\omega_B(r)$ along this surface. It appears to us that the addition of such δ-function contributions to the SCF chemical potential fields along this surface must perturb the structure calculated for any curved interface. Specifically, we would expect a nonzero value of ψ to produce a discontinuity in the derivatives of $\phi_A(r)$ and $\phi_B(r)$ with respect to r along that surface. This construction seems somewhat artificial to us because there exists no such "magic finger", and no such localized force, in any physical situation.

Our use of a pressure difference to stabilize a curved membrane (and this paper) is an outgrowth of a related study of the thermodynamics of a microemulsion phase. In another paper,[24] we consider a microemulsion of spherical surfactant-coated droplets (or swollen micelles) containing B homopolymer dispersed in a matrix of A. In this morphology, the pressure in the core of each swollen droplet is generally different from that in the surrounding matrix, the pressure difference being whatever is necessary to establish a force balance across the curved surfactant layer surrounding a particular drop. A similar microscopic pressure difference presumably exists between the two interpenetrating domains of a bicontinuous microemulsion and between the A and B domains of various ordered phases of an A/B/A−B ternary system. The use of a pressure difference to stabilize curved monolayers mimics a pressure difference that is present in the equilibrium structures of interest. It is thus the most physically appropriate way of defining excess interfacial free energies for the purpose of calculating free energies of mechanical equilibrium interface configurations (which correspond to local minima in the interfacial free energy landscape) within either microemulsion or swollen ordered phases. The main limitation of the method is that it is restricted to mechanical equilibria interfacial configurations such as spheres, cylinders, and periodic surfaces of constant mean curvature. Conversely, the potential advantage of Matsen's method is its flexibility, because it allows for the application of a normal force that varies over the interfacial surface, which could be used to stabilize arbitrary interfacial shapes.

Despite this difference in methods, our numerical results for the bending rigidities of saturated monolayers in symmetric mixtures appear to agree within our numerical accuracy with those published by Matsen. The precision of the agreement leads us to suspect that the two methods actually yield mathematically equivalent results for the bending rigidities of symmetric mixtures, but we have not proven this analytically. We do not know if this apparent equivalence is a special feature of symmetric mixtures or also applies to the Helfrich constants of arbitrary asymmetric mixtures.

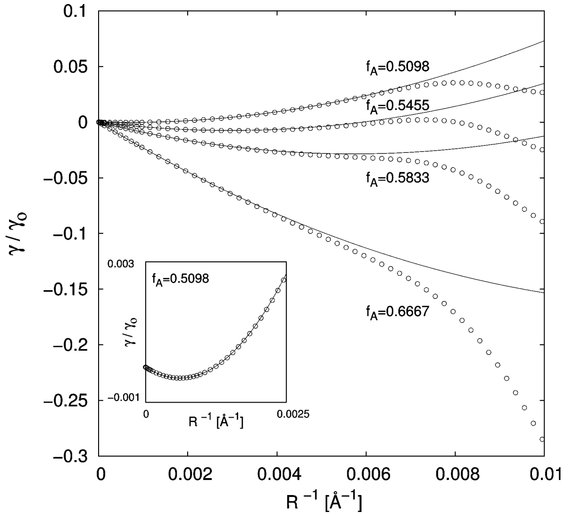

Figure 2. SCFT results for interfacial tension γ vs $1/R = C/2$ for spherical interfaces with $R \geq 100$ Å for systems in which the copolymer has a B block of fixed size $f_B\chi N_C = 10$, and symmetric homopolymers of fixed lengths equal to that of the copolymer B block, so that $\alpha_A = \alpha_B = f_B$, with $b_A = b_B$. Results are shown for several values of f_A, corresponding to copolymer A block of different lengths. Solid lines are parabolic fits of the curvature dependence of γ at small curvatures to membrane1, from which κ_+ and τ are extracted.

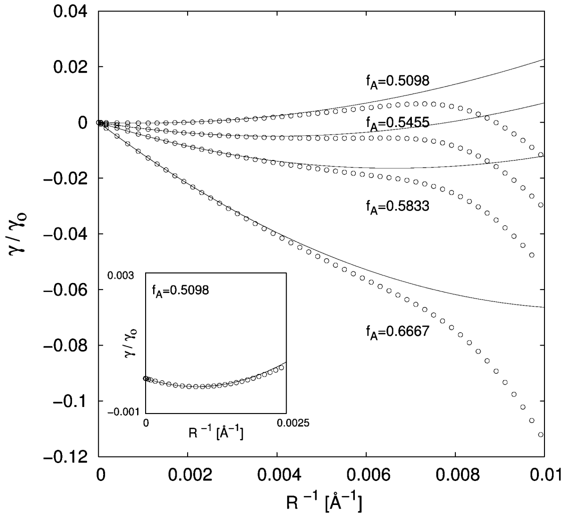

Figure 3. SCFT results for interfacial tension γ vs curvature $1/R = C$ for cylindrical interfaces with $R \geq 100$ Å for the same mixtures as those studied in the previous figure. κ can be obtained from the parabolic fits to γ shown in this plot.

5. Results

5.1. Curvature Dependence. We first consider the curvature dependence of γ at fixed $\mu_C = \mu_C^*$, from which the Helfrich elastic constants are extracted. Figures 2 and 3 show plots of γ vs $1/R$ at $\mu_C = \mu_C^*$ for spherical and cylindrical geometries, respectively, for a series of systems in which $N_A = N_B = f_BN_C = 100$ and $f_B\chi N_C = 10$, and in which the size of the A block of the copolymer is varied to change f_A. These calculations use a monomer volume $v = 135$ Å^3, statistical segment lengths $b_1 = b_2 = 6$ Å, and $N_A = N_B = 100$.

For both spherical and cylindrical deformations, the Helfrich expansion is found to be accurate for this choice of parameters for surfaces with radii $R \gtrsim 150$ Å, below which γ starts to deviate significantly from eq 7. The radii at which this deviation becomes significant are comparable to those of "dry" binary micelles of the copolymers of interest, in which there is no B homopolymer within the core.[24] The radius for which γ reaches

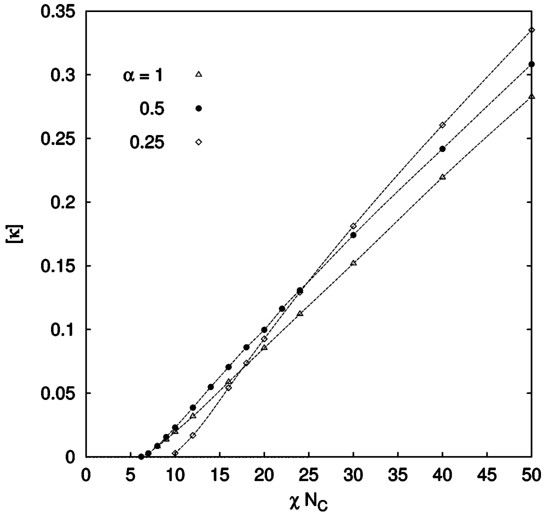

Figure 4. Dimensionless bending rigidity $[\kappa]$ vs χN_C for symmetric systems with several values of α. All values extrapolate to zero at the Lifshitz points analytically predicted by eq 11.

the minimum with respect to $1/R$ for nearly symmetric copolymers is shown elsewhere[24] to correspond within the context of the Helfrich theory to the thermodynamically preferred radius for a highly swollen cylindrical or spherical micelle in a micellar phase that coexists with an excess phase of nearly pure B. This preferred curvature varies rapidly with f_A and moves outside the range of validity of the Helfrich theory for $f_A \geq 0.58$. The Helfrich theory is thus found to be valid over a rather wide range of curvatures, as noted previously by Matsen,[17] but to be useful for describing equilibrium structures of asymmetric monolayers only over a rather limited range of copolymer composition, $|f_A - 0.5| \lesssim 0.1$ because of the rapid variation of spontaneous curvature with f_A.

It is apparent in Figures 2 and 3 that, even for values of f_A very near 0.5, γ decreases with decreasing radius for $R^{-1} \gtrsim 0.008$ Å. We have confirmed that this does not lead to an overall micelle free energy as a function of core radius with two minima or to a very small optimal micelle radius. The excess grand-canonical free energy of a micelle, relative to that of a homogeneous matrix, may be expressed as a sum $\gamma A + (P_I - P_{II})V_{II}$, which includes a core contribution $(P_I - P_{II})V_{II}$ that becomes large and positive in the limit of a nearly dry micelle. Here, P_{II} is the pressure in a hypothetical B-rich phase with the same value of μ_B as that required to stabilize the specified micelle core radius. The decrease in γ with increasing R^{-1} is an artifact of the way we decompose the free energy into bulk and interfacial terms, which becomes meaningless when applied to a micelle that contains little or no B homopolymer within its core.

5.2. Symmetric Mixtures. We next consider the parameter dependence of the bending rigidities for saturated monolayers in symmetric mixtures, with $f_A = {}^1/_2$, $\alpha_A = \alpha_B = \alpha$, and $b_A = b_B = b$.

Figures 4 and 5 show variation of the dimensionless elastic constants $[\kappa]$ and $[\bar{\kappa}]$ as functions of χN_C for several values of α. Here, we show data only for values of $\alpha \leq 1$, which is the range in which there exists a stable Lifshitz point. Within this range, $[\kappa]$ and $[\bar{\kappa}]$ both extrapolate to zero at the value of $(\chi N_C)_L$ given in eq 11. Note that the Gaussian rigidity $\bar{\kappa}$ is negative for all $\chi N_C > (\chi N_C)_L$, as required for flat membranes (as in a lamellar phase) to be stable against the formation of a multiply connected minimal surface structure.

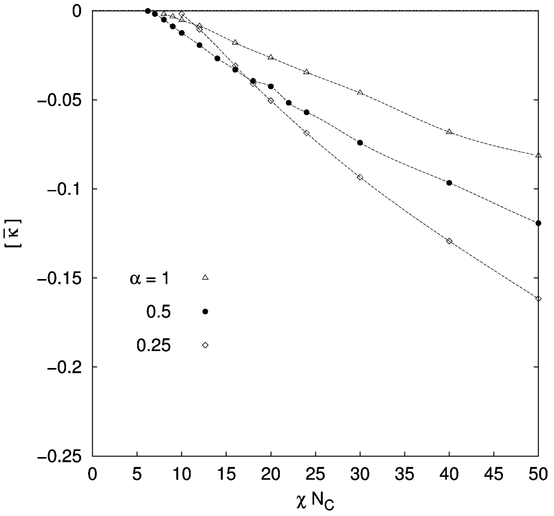

Figure 5. Dimensionless Gaussian rigidity $[\bar{\kappa}]$ vs χN_C for symmetric mixtures with several values of α.

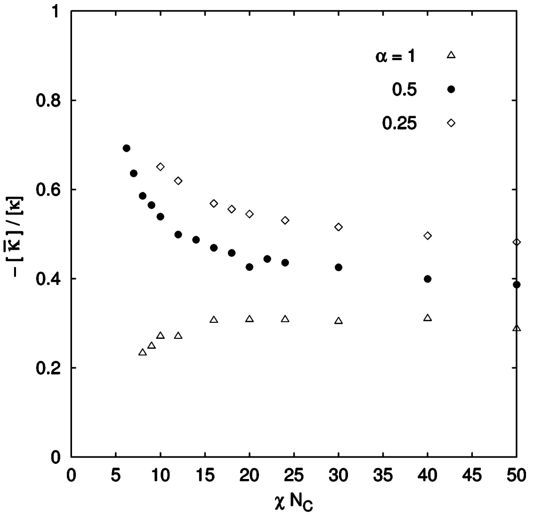

Figure 6. Ratio of the Gaussian rigidity to bending rigidity $-[\bar{\kappa}]/[\kappa]$ vs χN_C for symmetric mixtures with several values of α.

Within the accuracy of our data, both κ and $\bar{\kappa}$ appear to vary roughly linearly with $t \equiv \chi N_C - (\chi N_C)_L$ near the Lifshitz point when the Lifshitz point is approached along a path of vanishing interfacial tension $\gamma = 0$. A much more careful SCFT study by Müller and Gompper[19] of behavior near the Lifshitz point in a symmetric mixture with $\alpha = 0.5$ found $\kappa \propto \bar{\kappa} \propto t^{5/4}$ when the Lifshitz point is approached along a path of constant chemical potentials.

Figure 6 shows the ratio $-[\bar{\kappa}]/[\kappa]$ for saturated monolayers with $\alpha \leq 1$. In the strong stretching limit, Wang and Safran predict a value of $-[\bar{\kappa}]/[\kappa] = 4/14 = 0.266$ for the bending rigidity of a monolayer in the dry brush (melt state) limit,[14,15] and $-[\bar{\kappa}]/[\kappa] = 17/30 = 0.5667$ in the limit of a strongly stretched but fully solvated brush with a parabolic concentration profile. Our numerical results for moderately segregated monolayers appear to be qualitatively consistent with these strong stretching predictions: For $\chi N_C > 20$, we obtain values in the range $0.2 < -[\bar{\kappa}]/[\kappa] < 0.6$, with higher values of $-[\bar{\kappa}]/[\kappa]$ in systems with lower values of α, for which the monolayer is more swollen. For all $\alpha \leq 1$ and $\chi N_C > 20$, the ratio $-[\bar{\kappa}]/[\kappa]$ also satisfies the condition $-[\bar{\kappa}]/[\kappa] < 10/9$. This condition has been proposed[25,26] as a criterion for systems in which, upon swelling, a lamellar phase of balanced membranes will ultimately melt into a bicontinuous microemulsion phase rather than a dispersion of spheres.

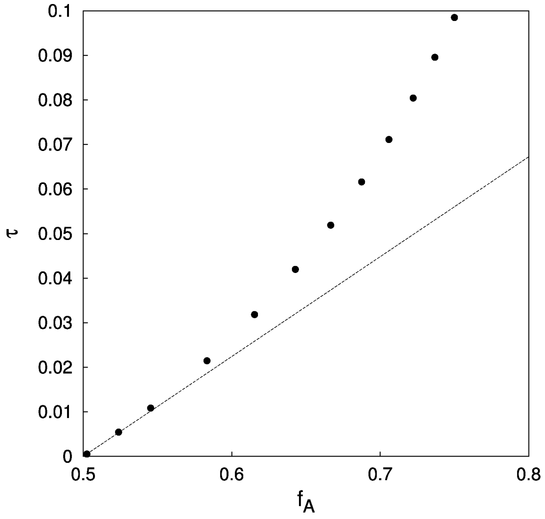

Figure 7. Bending parameter τ of block copolymer monolayer vs f_A for systems in f_A is varied by varying the length of the copolymer A block, while the length of the B block is kept constant with a length equal to that of either homopolymer, so that $f_BN_C = N_A = N_B$, with $f_B\chi N_C = 10$, as in Figures 2 and 3.

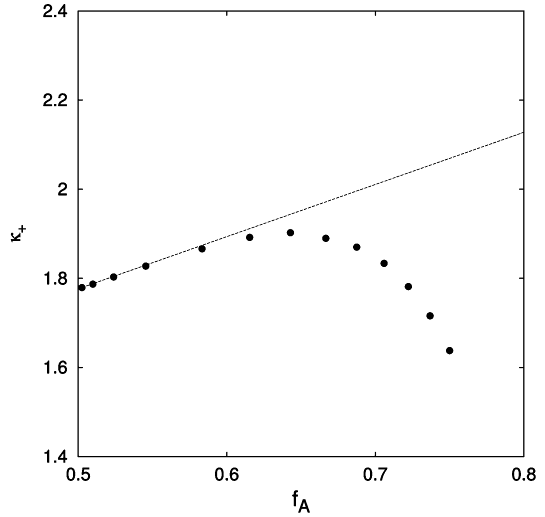

Figure 8. Bending rigidity κ_+ of sphere vs a block ratio f_A of the A block for systems with $f_BN_C = N_A = N_B$ and $f_B\chi N_C = 10$.

5.3. Asymmetric Mixtures. In this subsection, we switch our attention to asymmetric blends, in which $\alpha_A \neq \alpha_B$, $f_A \neq {}^1/_2$, and/or $b_A \neq b_B$. Figures 7 and 8 show how the elastic parameters τ and κ_+ vary with f_A when f_A is varied, changing only the A block length of the copolymer in a series of systems with $N_A = N_B = f_BN_C$, as in Figures 2 and 3. A linear dependence between τ and f_A holds over approximately the same range of $f_A \lesssim 0.58$ as that for which the spontaneous curvature was found to lie within the range of validity of the Helfrich expansion.

Figure 9 shows how the derivative $[\tau'] = \partial[\tau]/\partial f_A$, corresponding to the slope in Figure 7, varies with changes in χN_C. The derivative is evaluated with f_BN_C, N_A, and N_B held constant for symmetric systems with $0.25 \leq \alpha \leq 2$. For $\alpha < 1$, all values approach zero at the Lifshitz point. For $\alpha = 2$, for which the Lifshitz point is unstable, it appears that $[\tau']$ diverges near the Lifshitz point. For $\alpha = 1$, the value at which the Lifshitz point is marginally stable, the results suggest that $[\tau']$ may approach a nonzero limit at the Lifshitz point.

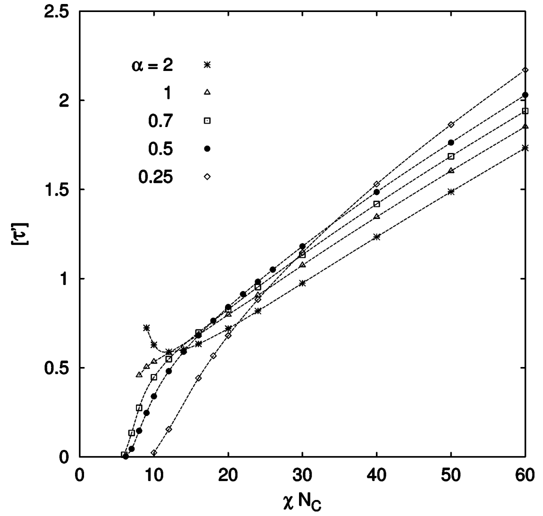

Figure 9. Derivative $[\tau'] \equiv \partial[\tau]/\partial f_A$ that corresponds to the slope in Figure 7 as a function of χN_C for symmetric systems with $N_A = N_B$ and several values of α.

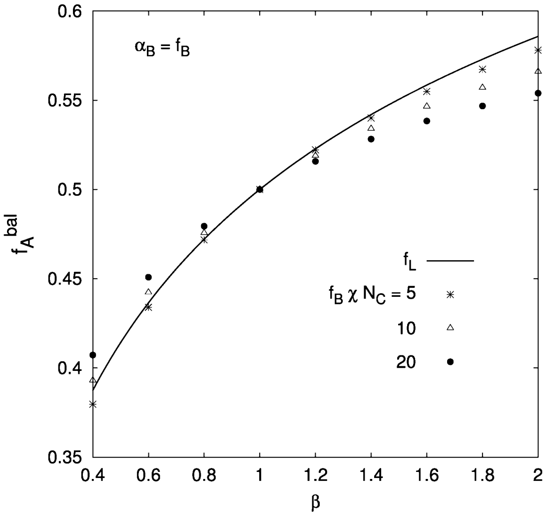

Figure 10. Variation of the balance point f_A^{bal} vs β with fixed $\alpha_B = f_B$. The solid line is eq 12.

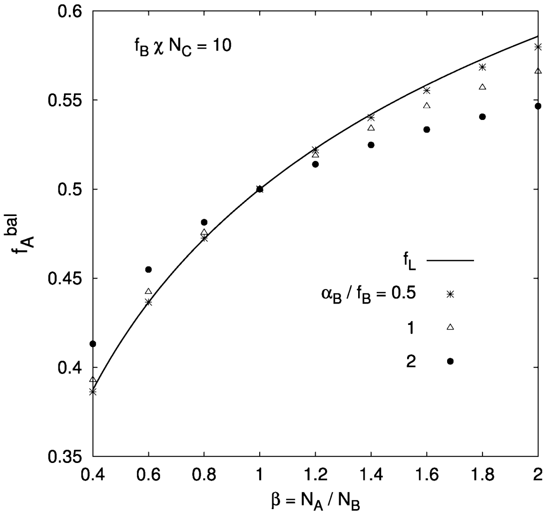

Figure 11. Variation of the balance point f_A^{bal} for asymmetric mixtures with a fixed B block size $f_B\chi N_C = 10$. The solid line is eq 12.

Figures 10 and 11 show the balance point f_A^{bal} at which $\tau = 0$ as a function of the ratio $\beta = \alpha_A/\alpha_B$ for several different sets of systems with $b_A = b_B$. Figure 10 shows the results for a set of systems for which the size of the B homopolymer and the B block of the copolymer are equal ($\alpha_B = f_B$), with several values

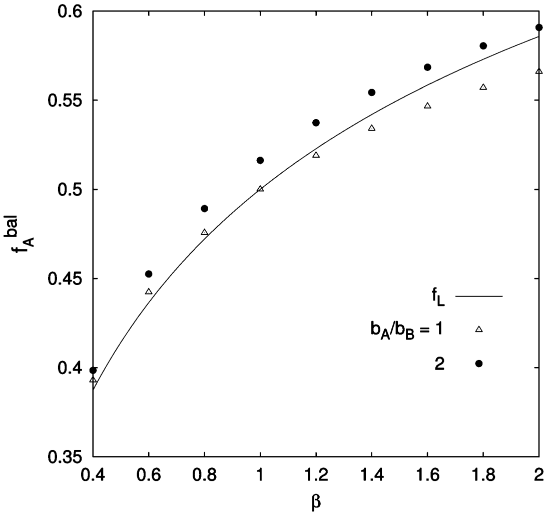

Figure 12. Variation of the balance point f_A^{bal} for asymmetric statistical segment length $b_A/b_B = 1$ and 2 with fixed $\alpha_B\chi N_C = f_B\chi N_C = 10$.

of $f_B N_C \chi$. In this plot, we have varied N_A to vary β and the size of the A block of the copolymer to vary f_A. Figure 11 presents f_A^{bal} vs β for several values of the ratio α_B/f_B for systems in which the B block of the copolymer has a fixed size $f_B\chi N_C = 10$. In both cases, increasing β by increasing N_A leads to an increase in f_A^{bal}. This is because increasing N_A decreases the tendency of the A homopolymer to swell the A brush, which must be compensated by an increase in the size of the A block. The sensitivity of f_A^{bal} to changes in β decreases as the brush is made dryer by increasing either χN_C or α_B. In the limit of a completely dry brush, we would expect f_A^{bal} to approach ($^1/_2$), independent of β.

Equation 12 for the value of f_A at which the balanced Lifshitz point is obtained is shown as a solid line in Figures 10 and 11. It appears to provide a reasonably accurate approximation to the balance point obtained here by setting $\tau = 0$, which remains useful over the entire range of values of χN_C and α_B explored here.

Figure 12 explores the effect of changes in statistical segment length upon the variation of the balance point f_A^{bal} for a system containing a B block of fixed size $f_B N_C \chi = 10$ and $\alpha_B = f_B$. Increasing b_A/b_B by a factor of 2 is found to cause a rather slight increase in f_A^{bal}. The sign of the change may be understood by noting that an increase in b_A decreases the free energy cost of stretching the A block of the copolymer by decreasing the spring constant $kT/b_A{}^2$ in the Gaussian stretching energy. Thus, it causes a tendency for the monolayer to curve around the A block, which may be compensated by increasing f_A.

Results for κ, $\bar{\kappa}$, and κ_+ are shown in Figure 13 as a function of β for a series of asymmetric systems with a fixed size of the B block $f_B\chi N_C = 10$, $\alpha_B = f_B$, and $b_A = b_B$. Note that all three rigidities seem to extrapolate to zero at a value of β slightly below the lower limit of the range shown in this plot (beyond which the simulations become difficult to converge), indicating the existence of a Lifshitz point at this value of χN_C for a system with $\beta \simeq 0.2$.

6. Conclusions

We have used numerical SCFT to investigate the bending elasticity of block copolymer monolayers in melts of immiscible homopolymers. The method used to calculate the free energy of an interface as a function of an imposed curvature is somewhat different from that employed previously by Matsen. In both methods, a force must be exerted upon an interface in order to impose an arbitrary curvature. Here, the required force is provided by a pressure difference.

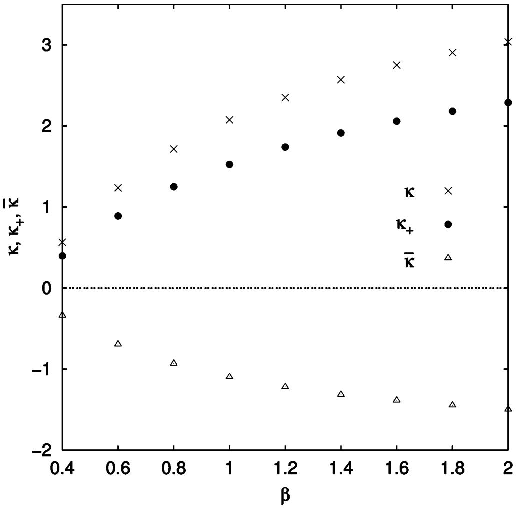

Figure 13. Rigidities κ_+, κ, and $\tilde{\kappa}$ vs β for systems with a fixed B block of size $f_B\chi N_C = 10$, a B homopolymer of length $\alpha_B = f_B$, and $b_A = b_B$. The results are given in units with $kT = 1$.

The Helfrich expression for the free energy of a curved interface is a Taylor expansion about a flat reference state. This expansion is useful for describing equilibrium structures only if it remains accurate at curvatures comparable to the spontaneous curvature. The Helfrich expansion is found to be accurate over a surprisingly wide range of imposed curvatures, extending almost to the curvature of a "dry" micelle, with no homopolymer in its core. However, this expansion appears to be valid only over a rather limited range of values of the copolymer block ratio f_A because of a rapid variation of spontaneous curvature with f_A. For the moderately segregated systems considered here, with $\chi N_C \simeq 20$, the spontaneous radius of curvature of a spherical micelle is significantly greater than the core radius of a dry micelle only for $0.5 \lesssim f_A \lesssim 0.6$ (for micelles in an A matrix). This limits the usefulness of the Helfrich expansion to roughly the same range of values.

The three elastic constants κ, $\bar{\kappa}$, and τ were shown to all continuously approach zero at the analytically predicted Lifshitz point for symmetric systems with $\alpha \le 1$. The Gaussian rigidity for moderately segregated symmetric systems was found to always lie with the range $0 < -\bar{\kappa} < (10/9)\kappa$, with $\kappa > 0$. In this range of parameters, the lamellar phase is mechanically stable but has been predicted to be susceptible to melting into a bicontinuous microemulsion if swollen sufficiently,[25,26] as the results of effects of interfacial fluctuation that are not captured by SCFT.

The value f_A^{bal} of the copolymer block ratio at which the spontaneous curvature vanishes has been determined for a variety of systems with asymmetric homopolymers. Knowledge of this "balance point" is potentially useful for the design of optimal polymeric surfactants. The sensitivity of f_A^{bal} to changes in the ratio β of homopolymer lengths decreases as the brush becomes dryer. This is true whether the brush is made dryer by increasing χN_C or by increasing homopolymer molecular weight. The analytical approximation for f_A^{bal} proposed by Fredrickson and Bates,[23] which was obtained from an analysis of the critical mode at the Lifshitz point, is found to provide a reasonably accurate estimate even far from the Lifshitz point.

Acknowledgment. We acknowledge support for this work by the University of Minnesota Industrial Partnership for Research in Interfacial and Materials Engineering (IPRIME), the RTP company, and the Minnesota Supercomputing Institute.

Appendix A: Self-Consistent Field Theory

In this appendix, we review the SCFT for polymer blends and discuss conventions and numerical methods used in this work. For generality, we consider a mixture of polymer species labeled by indices i and j that are constructed from monomers that are labeled by indices α or β. Polymers of type i contain a total of N_i monomers, whose position within the chain is parametrized by a variable $0 < s < N_i$.

A.1. Field Equations. SCFT requires the calculation of a statistical weight $q_i(\mathbf{r}, s)$ for each species that is proportional to the constrained partition function of the subchain containing monomers 0 to s of species i, when monomer s is constrained to point $\mathbf{r}$, in a self-consistently determined chemical potential field. This function satisfies a modified diffusion equation

$$\frac{\partial q_i(\mathbf{r}, s)}{\partial s} = -\left[-\frac{b_{\alpha(s)}^{\;2}}{6}\nabla^2 + \omega_{\alpha(s)}(\mathbf{r})\right]q_i(\mathbf{r}, s) \tag{17}$$

with an initial condition $q_i(\mathbf{r}, 0) = 1$ for all $\mathbf{r}$. Here, b_α is a statistical segment length and $\omega_\alpha(\mathbf{r})$ is a chemical potential field for α monomers, and $\alpha(s)$ is the type index for monomer s, which has different values within different blocks. An analogous function $q_i^\dagger(\mathbf{r}, s)$ for the subchain containing monomers s to N_i satisfies a corresponding equation with the left-hand side multiplied by -1, with a final condition $q_i^\dagger(\mathbf{r}, N) = 1$. In the case of an immiscible homopolymer blend, we assume no flux at a unit cell boundary such as $\partial q_i(\mathbf{r}, s)/\partial\mathbf{r} = 0$. The chemical potential field $\omega_\alpha(\mathbf{r})$ is given

$$\omega_\alpha(\mathbf{r}) = \sum_\beta \chi_{\alpha\beta}\phi_\beta(\mathbf{r}) + \xi(\mathbf{r}) \tag{18}$$

where $\chi_{\alpha\beta}$ is a binary Flory–Huggins interaction parameter, for which $\chi_{\alpha\beta} = \chi_{\beta\alpha}$ and $\chi_{\alpha\alpha} = \chi_{\beta\beta} = 0$, $\phi_\alpha(\mathbf{r})$ is a local volume fraction of α monomers, and $\xi(\mathbf{r})$ is a Lagrange multiplier field, which is chosen so as to satisfy the incompressibility constraint,

$$\sum_\alpha \phi_\alpha(\mathbf{r}) = 1 \tag{19}$$

The local volume fraction $\phi_\beta(\mathbf{r})$ is given by

$$\phi_\beta(\mathbf{r}) = \sum_i \frac{\bar{\phi}_i}{Q_i}\int_0^{N_i}\frac{\mathrm{d}s}{N_i}\, q_i(\mathbf{r}, s)\, q_i^\dagger(\mathbf{r}, s)\, \delta_{\beta,\alpha(s)} \tag{20}$$

where $\bar{\phi}_i = M_i N_i v/V$ is the overall volume fraction of i molecules, M_i is the total number of i molecules, v is a monomer reference volume, and

$$Q_i \equiv \frac{1}{V}\int \mathrm{d}\mathbf{r}\; q_i(\mathbf{r}, N_i) \tag{21}$$

The s integral in eq 20 is constrained to blocks of monomer type β by the Kronecker δ function $\delta_{\beta,\alpha(s)}$.

SCFT may be implemented either in the canonical ensemble, in which one specifies a value of M_i or $\bar{\phi}_i$ for each species,[27] or in the grand-canonical ensemble, in which one specifies a chemical potential μ_i for each species.[28,29] The chemical potential and molecular volume fraction of a species i are related by the identity

$$\bar{\phi}_i = Q_i\, e^{\mu_i/kT} \tag{22}$$

Equation 22 implicitly introduces a convention for the chemical potential in which μ_i vanishes in a hypothetical standard state consisting of pure species i, with $\bar{\phi}_i = 1$, in a vanishing potential field $\omega_\alpha(\mathbf{r}) = 0$ for all α, for which $q_i(\mathbf{r}, N_i) = 1$ and $Q_i = 1$. In the grand-canonical implementation of SCFT, local monomer densities are thus calculated by replacing the factor of $\bar{\phi}_i/Q_i$ in eq 20 by the activity $e^{\mu_i/kT}$. The total grand-canonical free energy is given by

$$\frac{\Phi}{kT} = -V\sum_i \frac{\bar{\phi}_i}{N_i v} - \sum_\alpha \int \frac{\mathrm{d}\mathbf{r}}{v}\,\omega_\alpha(\mathbf{r})\phi_\alpha(\mathbf{r}) + \frac{1}{2}\sum_{\alpha\beta}\int\frac{\mathrm{d}\mathbf{r}}{v}\,\chi_{\alpha\beta}\,\phi_\alpha(\mathbf{r})\,\phi_\beta(\mathbf{r}) \tag{23}$$

where $\bar{\phi}_i$ is given by eq 22.

In an incompressible liquid, SCFT predictions for the volume fraction fields $\phi_{i,\alpha}(\mathbf{r})$ and Helmholtz free energy $F = \Phi + \sum_i \mu_i M_i$ are invariant under a spatially homogeneous shift

$$\xi(\mathbf{r}) \rightarrow \xi(\mathbf{r}) + \frac{v\delta P}{kT} \tag{24}$$

of the Lagrange multiplier field, which corresponds to a shift δP in hydrostatic pressure. Such a shift causes corresponding trivial shifts

$$\begin{gathered}\omega_\alpha(\mathbf{r}) \rightarrow \omega_\alpha(\mathbf{r}) + \frac{v\delta P}{kT}\\ \mu_i \rightarrow \mu_i + N_i v\,\delta P\end{gathered} \tag{25}$$

in chemical potentials. The solution of the SCFT equations for a two-phase system is thus unique only to within such homogeneous shifts in $\xi(\mathbf{r})$, unless a value is specified for either ξ or for the corresponding macroscopic pressure P in one of the two bulk phases.

A.2. Homogeneous Mixtures. Calculation of an interfacial excess free energy γ requires knowledge of the pressures in the surrounding homogeneous phases as functions of chemical potential. In homogeneous mixtures, SCFT reduces to a form of Flory–Huggins theory. The chemical potential in a homogeneous mixture, in the convention used here, is given by

$$\frac{\mu_i}{kT} = \ln(\phi_i) + N_i\sum_\alpha f_{i,\alpha}\omega_\alpha \tag{26}$$

where $f_{i,\alpha}$ is the fraction of monomers of type α on a chain of species i, and ϕ_i and ω_α are homogeneous values of the fields. The macroscopic pressure $P = -\Phi/V$ for a homogeneous phase may be obtained from eq 23, which yields

$$\frac{Pv}{kT} = \xi + \sum_i \frac{\phi_i}{N_i} + \frac{1}{2}\sum_{\alpha\beta}\chi_{\alpha\beta}\phi_\alpha\phi_\beta \tag{27}$$

By using eq 27 to express μ_i as a function of P, rather than ξ, noting that $M_i = \phi_i V/N_i v$ and $\phi_\alpha = \sum_i \phi_i f_{i,\alpha}$, and evaluating the sum $G = \sum_i M_i\mu_i$, we may confirm that the corresponding Gibbs free energy per monomer is given by an expression

$$\frac{Gv}{VkT} = \sum_i \frac{\phi_i}{N_i}\ln\left(\frac{\phi_i}{e}\right) + \frac{1}{2}\sum_{\alpha\beta}\chi_{\alpha\beta}\phi_\alpha\phi_\beta + \frac{Pv}{kT} \tag{28}$$

which is consistent with Flory–Huggins theory.

A.3. Nondimensionalization. The modified diffusion equation can be nondimensionalized by introducing reduced variables $t \equiv s/N$ and $\tilde{\mathbf{r}} = \mathbf{r}/R_o$, with $R_o^2 = Nb^2$, where N is a reference degree of polymerization, for which we take $N = N_C$, and b is a reference statistical segment length, for which we take $b = b_B$ in this work. This yields the nondimensionalized diffusion equation

$$\frac{\partial q_i(\tilde{\mathbf{r}}, t)}{\partial t} = -\left[-\frac{1}{6}\left(\frac{b_\alpha}{b}\right)^2 \tilde{\nabla}^2 + \tilde{\omega}_\alpha(\tilde{\mathbf{r}})\right] q_i(\tilde{\mathbf{r}}, t) \qquad (29)$$

with $\tilde{\nabla}^2 \equiv R_o^2\nabla^2$ and

$$\tilde{\omega}_\alpha(\tilde{\mathbf{r}}) \equiv N\omega_\alpha(\tilde{\mathbf{r}}) = \sum_\beta \tilde{\chi}_{\alpha\beta}\phi_\beta(\tilde{\mathbf{r}}) + \tilde{\xi}(\tilde{\mathbf{r}}) \qquad (30)$$

where $\tilde{\chi}_{\alpha\beta} \equiv N\chi_{\alpha\beta}$ and $\tilde{\xi}(\tilde{\mathbf{r}}) \equiv N\xi(\tilde{\mathbf{r}})$. By nondimensionalizing the self-consistency conditions in terms of the same variables, it may be shown that the self-consistent solution for q_i near a curved interface is a function of t, $\tilde{\mathbf{r}}$, the chemical potentials μ_A, μ_B, and μ_C, and the dimensionless parameters α_A, α_B, f_A, b_B/b_A, $\tilde{\chi}_{\alpha\beta}$, and $C\sqrt{N}b$ alone.

The grand-canonical free energy per interfacial area may be expressed in nondimensional form as an integral

$$\frac{\Phi}{AkT} = \frac{b}{N^{1/2}v}\int \mathrm{d}\hat{z}\left\{-\sum_i \frac{e^{\mu_i/kT}}{\alpha_i} q_i(\tilde{\mathbf{r}}, \alpha_i) - \sum_\alpha \tilde{\omega}_\alpha(\tilde{\mathbf{r}})\phi_\alpha(\tilde{\mathbf{r}})\right\} + \frac{b}{N^{1/2}v}\int \mathrm{d}\hat{z}\sum_{\alpha\beta}\tilde{\chi}_{\alpha\beta}\,\phi_\alpha(\tilde{\mathbf{r}})\phi_\beta(\tilde{\mathbf{r}}) \qquad (31)$$

where the integrand is a function of dimensionless distance $\hat{z}$ from the interface given by

$$\mathrm{d}\hat{z} = \left(1 + \frac{z}{R}\right)^{d-1}\frac{\mathrm{d}z}{N^{1/2}b} \qquad (32)$$

A and R is the area and radius of the Gibbs dividing surface, and $\alpha_i = N_i/N$, so that $\alpha_C = 1$ with our convention $N = N_C$. To obtain the excess free energy density γ, we must subtract from Φ the bulk pressure of a given phase throughout the domain on the corresponding side of the Gibbs dividing surface and thus cancel contributions to Φ from points far from the interface. This yields an interfacial tension of the form

$$\frac{\gamma}{kT} = \frac{b}{N^{1/2}v}[\gamma]\left(\alpha_A, \alpha_B, \frac{b_A}{b_B}, f_A, \chi N, [C], \frac{\mu_C}{kT}\right) \qquad (33)$$

in which $[\gamma]$ is a dimensionless interfacial tension, and $[C] \equiv CN^{1/2}b$ is a dimensionless curvature.

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