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Elastic Properties of an Interface of Diblock Copolymer. 2

M. W. Matsen* and M. Schick

Department of Physics, FM-15, University of Washington, Seattle, Washington 98195

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Ternary mixtures of incompatible A and B homopolymers of equal polymerization, N, and a symmetric AB diblock copolymer of smaller index, N/α ($\alpha > 1$), behave similarly to mixtures of water, oil, and amphiphile.[1] In particular, they both exhibit three-phase coexistence between two uniform phases which are rich in one of the two incompatible species and a third, disordered phase in which these two incompatible species are brought together by the third component, copolymer or amphiphile.[2–5] The disordered phases from both systems have regions in their respective phase diagrams where they exhibit pronounced short-range structure. In the amphiphilic system, this region is denoted a microemulsion.

According to mean-field theory, the line of three-phase coexistence extends from a tricritical point to a critical end point at which the disordered (D) phase makes a continuous transition to the lamellar (L) phase. This phase is bounded on the high diblock concentration side by a line of critical transitions to the disordered phase and on the low side by a line of three-phase coexistence with the A- and B-rich homopolymer (A + B) phases. Fluctuations drive the continuous transition between the D and L phases first-order.[6,7] As a consequence, the A + B + D triple line terminates at a A + B + D + L four-phase point.

In the vicinity of the tricritical point, the disordered phase is nearly structureless and it wets the A/B interface between the two homopolymer-rich phases.[5] As one approaches the other end of the A + B + D triple line, a disorder line is encountered, beyond which the asymptotic behavior of a general correlation function develops an oscillatory, as opposed to monotonic, decay.[4,5] This oscillatory behavior reflects the structure of the disordered phase in which microscopic, coherent A-rich regions are separated from coherent B-rich regions by sheets of copolymer. As a consequence of this structure, a wetting transition occurs beyond which it is favorable to form only a microscopically thin layer, rich in copolymer, at the A/B interface.

When the A- and B-rich regions are, in fact, well-separated by well-defined interfaces of diblock, then it should be possible to describe the phase in terms of the elastic properties of the these interfaces, and from them predict the internal structure of the disordered phase.[8] These elastic properties are defined in terms of a free energy per unit area[9,10]

$$f_{\mathrm{el}} = \sigma_{\mathrm{el}} + \lambda\left(\frac{c_1 + c_2}{2}\right) + 2\kappa\left(\frac{c_1 + c_2}{2}\right)^2 + \bar{\kappa}c_1c_2 \qquad (1)$$

where σ_{el} is the free energy per unit area of a flat interface, κ is the bending modulus, $\bar{\kappa}$ is the saddle-splay modulus, c_1 and c_2 are the two local principal curvatures, and $\lambda = -4\kappa c_0$ where c_0 is a preferred or spontaneous curvature. As the internal interfaces separate coherent regions of A- and B-rich polymer regions, we expect them to be similar to the interface between the bulk A- and B-rich phases with which the disordered phase coexists.

We calculated the elastic properties of this interface in a previous paper.[5] Our approach involved the generation of a Landau–Ginzburg free energy functional,

$$\frac{NF[\eta(\vec{r}),\mu]}{k_{\mathrm{B}}T\rho_0} = \int\{h(\eta)\,[R_{\mathrm{AB}}{}^2\nabla^2\eta]^2 + g(\eta)\,[R_{\mathrm{AB}}\nabla\eta]^2 + f(\eta)\}\,\mathrm{d}^3r \quad (2)$$

in terms of the order parameter, $\eta(\vec{r})$, which is the local normalized difference between the A and B homopolymer densities at $\vec{r}$. It varies from -1 in regions of pure B homopolymer to 1 for pure A homopolymer. The system is assumed to be incompressible with a monomer concentration of ρ_0. The chemical potential, μ, controls the copolymer concentration. The function, $f(\eta)$, is the usual Flory–Huggins free energy density for the system. The functions, $g(\eta)$ and $h(\eta)$, were obtained from the η–η structure function, $S_{\eta\eta}(q)$, by expanding its inverse in powers of q about $q = 0$[11]

$$\frac{N}{2\rho_0}S_{\eta\eta}{}^{-1}(q) = \frac{1}{2}f''(\eta) + g(\eta)\,[qR_{\mathrm{AB}}]^2 + h(\eta)\,[qR_{\mathrm{AB}}]^4 + O([qR_{\mathrm{AB}}]^6) \quad (3)$$

The structure function was calculated within the random-phase approximation (RPA).[2] From $f(\eta)$, the free energy of the uniform phases was calculated and the location of the triple line determined. Once this was done, we examined the A/B interface. We oriented the interface orthogonal to the z-direction, so that η varied only with z, and minimized the free energy functional with respect to $\eta(z)$ subject to the constraints, $\eta(-\infty) = \eta_{\mathrm{A}}$ and $\eta(\infty) = \eta_{\mathrm{B}}$, where η_{A} and η_{B} are the values of the order parameter in the A- and B-rich phases. Once the order parameter across the profile, $\eta(z)$, was known, the elastic coefficients were calculated using formulas derived by Gompper and Zschocke.[12,13]

The above approach is adequate when the disordered phase is not strongly structured but fails as the lamellar phase is approached because the truncation of the Taylor series at fourth order in q becomes inaccurate shortly after crossing the Lifshitz line (LL). This is the line at which the structure in the disordered phase becomes sufficient to produce a peak in the structure function at a nonzero wave vector, whose inverse is characteristic of the distance between sheets of copolymer in the disordered phase.[4,5] When the peak in the structure function is at $q = 0$, the Taylor series expansion about $q = 0$ is adequate, but when the peak moves off of zero, it becomes increasingly inaccurate.

In this paper, we circumvent this problem by choosing $g(\eta)$ and $h(\eta)$ such that the peak from the RPA structure function matches the peak in the Teubner–Strey form[14]

$$S_{\mathrm{ts}}(q) = \frac{1}{A + Bq^2 + Cq^4} \qquad (4)$$

Figure 1 shows how such a fit does at several points along the triple line. Even close to the four-phase point it is not too bad, whereas the Taylor series approximation would bear no resemblance to the RPA structure function. At the values of χN shown (with χ the usual Flory–Huggins parameter), the transition from the disordered phase to the A- and B-rich phases is no longer weakly first-order. The discontinuity in the order parameter at the transition,

* To whom correspondence should be addressed.

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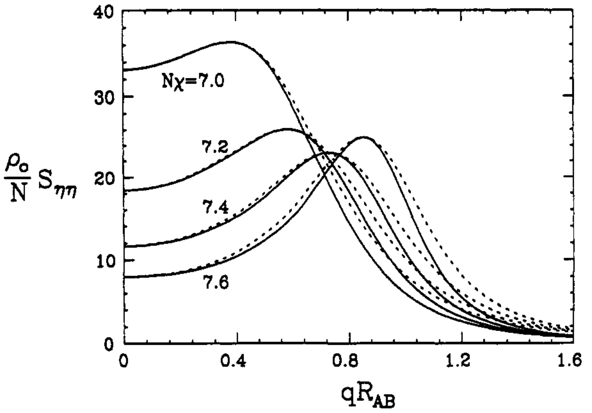

Figure 1. η–η structure function shown along the triple line for several values of $N\chi$. The solid lines are obtained using the RPA, and the dashed lines are fits to the Teubner–Strey form (eq 4).

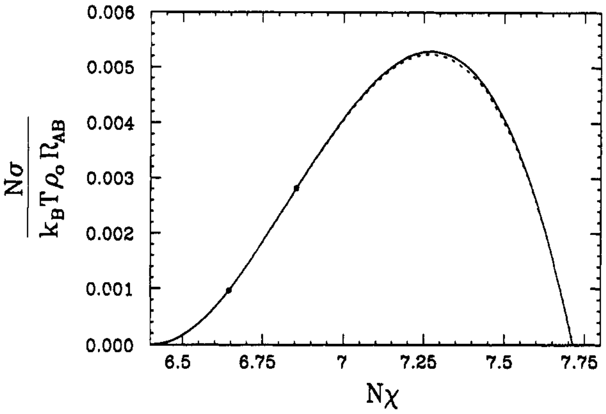

Figure 2. A/B interfacial tension along the A + B + D triple line at $\alpha = 1.1$. The solid and dashed lines correspond to $\gamma = 0$ and $\gamma = \pm 1$, respectively. The dots show the locations of the disorder and Lifshitz lines. The disorder line does shift as γ is varied but not sufficiently to be noticed on the scale of this plot.

normalized to its maximum possible value, is 0.45, 0.51, 0.56, and 0.60 for the four increasing values of χN in Figure 1. Thus, if the disordered phase does resemble a mixture of coherent A- and B-rich regions, it is not a weakly-segregated one. From the fit to the Teubner–Strey form of the structure function, we can extract a comparison of the correlation length ξ, with which the interfacial thickness scales, to the typical distance, d, between internal interfaces. For the ratio $2\pi\xi/d$, we find for the same χN as above the four values 1.35, 1.83, 2.40, and 3.24. These are comparable to values characterizing well-defined microemulsions of amphiphilic systems.[14] For these reasons, the description of the disordered phase of the polymer system in terms of internal interfaces should be sensible.

We can now extend our previous calculation of the bending moduli to encompass the entire triple line. We allow for an asymmetry between the Kuhn lengths of the A and B monomers, a_A and a_B, respectively. This asymmetry is expressed with the parameter, $\gamma \equiv (a_A^2 - a_B^2)/(a_A^2 + a_B^2)$. Our previous results are unchanged up to the LL. The A + B + D triple line ends at a critical end point at $\chi N = 7.975$. In Figure 2, one sees that the calculated surface tension drops to zero somewhat before this. We expect the surface tension to become small as the end of the triple line is approached, but it must remain positive. We believe the reason it becomes negative is due to the approximation of expanding the free energy of eq 2 only to second order in gradients of the order parameter η. We plot our results only up to the point where the calculated surface tension vanishes.

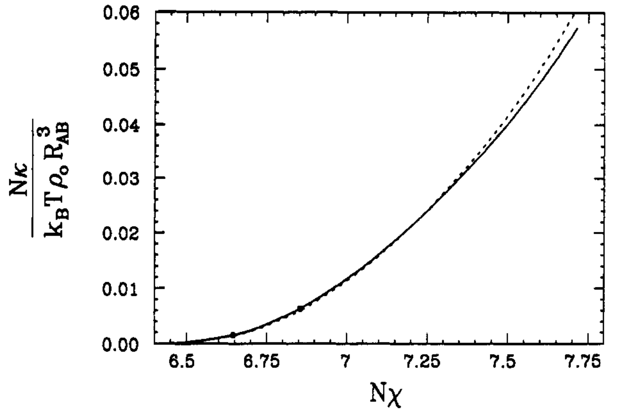

Figure 3. Bending rigidity of the A/B interface along the triple line. The solid and dashed lines correspond to $\gamma = 0$ and $\gamma = \pm 1$, respectively. The dots show the locations of the disorder and Lifshitz lines.

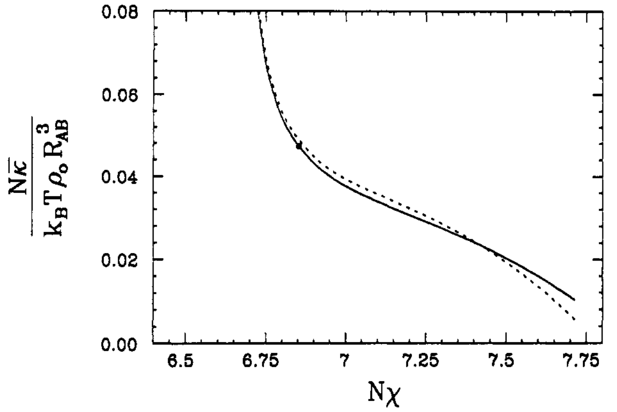

Figure 4. Saddle-splay modulus of the A/B interface along the triple line. The solid and dashed lines correspond to $\gamma = 0$ and $\gamma = \pm 1$, respectively. The dot shows the location of the Lifshitz line.

The spontaneous-curvature modulus λ (not shown) remains nearly linear with γ over the entire triple line and is the only quantity substantially affected by γ. Our previous result for $N\lambda/\gamma k_B T \rho_0 R_{AB}^2$ now smoothly extends to 0.042 as χN increases to 7.72. In Figure 3, one sees that κ increases as the lamellar phase is approached, just as it did in our previous calculation. The major difference between the results from this improved approximation and the former one is that $\bar{\kappa}$ now continues to decrease as the lamellar phase is approached, instead of leveling off. Still, $\bar{\kappa}$ remains positive, indicating that the coexisting microemulsion will be bicontinuous.[8] The effect of increasing γ, when χN is less than about 7.4, is to increase the ratio, $\bar{\kappa}/\kappa$ favoring a bicontinuous microemulsion. For the larger χN that we can now investigate, we find that increasing γ for values of χN beyond 7.4 decreases this ratio and therefore disfavors the bicontinuous microemulsion.

As before, this approach encounters problems for larger α because $S_{\eta\eta}^{-1}(q)$ is no longer well described by a fourth-order polynomial in q. The correct structure function exhibits two peaks, for which one would need at least terms of order q^6. In addition, the triple line starts to extend into the strong-segregation region in which interfaces are sharp, invalidating the gradient expansion in the order parameter. We are in the process of extending the calculation to larger α by using the self-consistent-field theory approach. From the results in Figure 4 and those of Milner and Witten[15] that $\bar{\kappa}$ is negative in the strong-segregation limit, it is likely that this quantity changes sign somewhere along the triple line. The leading term in the elastic free energy of an internal interface, σ_{el}, is presumed to be comparable to the interfacial tension σ between A- and B-rich homopolymer phases and, therefore, to be quite small. In this case, the effects of the bending moduli are large, and such a change in sign of $\bar{\kappa}$ would be expected to cause profound changes in the structure of the disordered phase.

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