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Fluctuation Corrections to Mean-Field Theory for Homopolymer–Copolymer Phase Separation: Sequence Distribution Effects

Peter D. Olmsted* and Scott T. Milner†

Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

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ABSTRACT: Mean-field theories (Flory–Huggins, RPA) predict that the critical repulsive interaction parameter (χ_c) for polymer–polymer phase separation is independent of the monomer sequence distribution. In this work, we generalize the RPA to account for sequence distribution effects on the spinodal by including fluctuations in both the composition and its conjugate field. We calculate $\chi_c(p)$ for a blend of homopolymers and regular multiblock copolymers with $2p$ blocks and find an architecture-dependent shift of relative order $N^{-1/2}$. This shift either increases or decreases as p is increased (corresponding to a more evenly distributed copolymer), depending roughly on whether the homopolymer is shorter or longer than the copolymer. Fluctuations also shift the critical *composition* away from the Flory–Huggins value, even in asymmetric homopolymer/homopolymer blends.

Polymer–polymer phase separation is an example of a phase transition which may be reasonably described by mean-field theories based on semimicroscopic models: Flory–Huggins (FH) theory describes liquid–liquid phase separation (macrophase separation)[1] and the random phase approximation (RPA)[2,3] describes both macrophase and *microphase* separations of block–copolymer melts. Despite intense investigations of the architecture dependence of block–copolymer microphase behavior,[3,4] comparatively little attention has been paid to the architecture dependence of the *macrophase* behavior of block–copolymers.[5,6] In this work, we calculate systematic corrections to mean-field theory to calculate the architecture dependence of the critical point for homopolymer–copolymer macrophase separation.

Consider an incompressible blend of a homopolymer of species A and an A/B copolymer, with ϕ being the copolymer volume fraction. This melt has, for a wide range of copolymer architectures, an instability to phase separation into homopolymer-rich and copolymer-rich liquids, driven by the incompatibility (χ) between A and B monomers,[1]

$$\chi = \frac{1}{k_B T}\Big[u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})\Big] \tag{1}$$

where u_{AA}, u_{BB}, and u_{AB} are energetic penalties for monomer contacts. Mean-field theories compute the enthalpy of a given phase by assuming random mixing of the monomers. Thus, they predict that the critical point χ_c is a function only of the chain lengths (in Kuhn steps) N_c and N_h and the average composition of the copolymer (parametrized by f, the B fraction of the copolymer).

However, melts with different copolymer architectures have different composition fluctuations: a "coarse" copolymer (with few blocks) has stronger fluctuations than a "fine" copolymer (with many blocks), with correlation lengths of the order of the radius of gyration ($N_b^{1/2}$) of a block, where N_b is the average block length. Since composition fluctuations typically depress critical temperatures,[9] we might expect a fine copolymer to have a smaller χ_c than a coarse copolymer, for demixing from the same homopolymer. Moreover, we expect fluctuations on the scale of a monomer to yield identical contributions to the shift in χ_c for different architectures, while the relative shift for two architectures depends on larger length scales and is *independent* of the Kuhn step a. We will show that

$$\chi_c(\sigma) = \chi_{MF}[1 + \epsilon + \lambda(\sigma, N_b/N_c, f)N_c^{-1/2}] \tag{2}$$

where ϵ depends on the microscopic parameters (a, u_{AA}, u_{AB}, u_{BB}), $\lambda(\sigma, N_b/N_c, f)$ is independent of the microscopic parameters, σ denotes a particular architecture, and χ_{MF} is the predicted mean-field critical interaction parameter (see eq 7 below).

Unlike previous theoretical studies[5,6] which enlarge the parameter space to include three-body interactions (χ_{AAA}, χ_{AAB}, ...), we show that shifts in the critical point can arise from different architectures and are *independent* of the single parameter χ. While we cannot exclude effects due to distinct monomer triads, our results suggest several experiments to distinguish the two effects: one example is the scaling of the architecture-dependent contribution to χ_c with N_c, eq 2.

We first summarize the mean-field results and then incorporate fluctuations. We describe the macroscopic phase behavior in terms of the averages $\langle\hat{\phi}_B(\mathbf{r})\rangle$ and $\langle\hat{\phi}_A(\mathbf{r})\rangle$, where $\hat{\phi}_\alpha(\mathbf{r})$ is the microscopic volume fraction of species α (α = A, B).[3,7,8] For an incompressible system, it is sufficient to consider the single degree of freedom

$$\psi(\mathbf{r}) = \delta\phi_A(\mathbf{r}) - \delta\phi_B(\mathbf{r}) \tag{3}$$

where $\delta\phi_A = \langle\hat{\phi}_A(\mathbf{r})\rangle - [(1 - \phi) + (1 - f)\phi]$ and $\delta\phi_B = \langle\hat{\phi}_B(\mathbf{r})\rangle - f\phi$. The RPA yields the following mean-field coarse-grained free energy for the blend:[3,4]

$$\frac{\mathcal{F}_{RPA}}{k_B T} = \sum_{n=2}^{4}\frac{1}{n!}\int_{\mathbf{q}_1\ldots\mathbf{q}_n}^{\Lambda}\gamma_{RPA}^{(n)}(\{\mathbf{q}_i\})\,\psi(\mathbf{q}_1)\ldots\psi(\mathbf{q}_n)\,\delta\Big(\sum_{i=1}^{n}\mathbf{q}_i\Big) \tag{4}$$

where $\int_0^\Lambda \equiv \int_0^\Lambda d^3q/(2\pi)^3$, $\Lambda = 2\pi/a$, and a is the statistical segment size (assumed the same for both species). The vertices are given in terms of single-chain correlation

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* e-mail address: pdo1001@phy.cam.ac.uk.

† e-mail address: stmilne@erenj.com.

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functions.[3,4] For example,

$$\gamma^{(2)}_{\mathrm{RPA}}(\mathbf{q}) = \frac{S_{\mathrm{AA}}(\mathbf{q}) + S_{\mathrm{BB}}(\mathbf{q}) + S_{\mathrm{AB}}(\mathbf{q})}{S_{\mathrm{AA}}(\mathbf{q})S_{\mathrm{BB}}(\mathbf{q}) - S_{\mathrm{AB}}{}^2(\mathbf{q})} - 2\chi a^{-3} \qquad (5)$$

where $S_{\alpha\beta}(\mathbf{q}) = \langle \hat{\phi}_\alpha(\mathbf{q})\hat{\phi}_\beta(-\mathbf{q})\rangle_0/V$ and the average $\langle\cdot\rangle_0$ is over configurations in a noninteracting A–A/B blend. These single-chain correlation functions, and hence the vertex functions $\gamma^{(n)}_{\mathrm{RPA}}$, depend on the detailed architecture of the copolymers. For example, a regular multiblock with period M exhibits enhanced correlations at wavenumbers $q \sim M^{-1/2}$.

The critical point for liquid–liquid phase separation is found by searching for a continuous instability of the homogeneous state at $q = 0$, determined by

$$\langle \psi(0)\,\psi(0)\rangle^{-1} \equiv \gamma^{(2)}(0) = 0 \qquad (6a)$$

$$\langle \psi(0)\,\psi(0)\,\psi(0)\rangle \equiv \gamma^{(3)}(0,0) = 0 \qquad (6b)$$

Within mean-field theory, $\gamma^{(2)}_{\mathrm{RPA}}(0) = 0$ and $\gamma^{(3)}_{\mathrm{RPA}}(0,0) = 0$ determine the critical point:

$$\phi_{\mathrm{MF}} = \frac{N_{\mathrm{h}}^{1/2}}{N_{\mathrm{c}}^{1/2} + N_{\mathrm{h}}^{1/2}} \qquad \chi_{\mathrm{MF}} = \frac{(N_{\mathrm{c}}^{1/2} + N_{\mathrm{h}}^{1/2})^2}{2f^2 N_{\mathrm{c}} N_{\mathrm{h}}} \qquad (7)$$

Note that the predicted demixing is independent of architecture and is as if the A/B copolymer were replaced with a homopolymer made of an "average" monomer C, such that $\chi_{\mathrm{AC}} = f^2\chi_{\mathrm{AB}}$.

To extract the architecture dependence, we must include fluctuation corrections to the osmotic modulus $\gamma^{(2)}(0)$.[9–11] Before outlining our calculation, we describe a simple version which omits some important physics but demonstrates the nature of the corrections. We first assume (which we shall correct below) that the RPA free energy serves as an effective Hamiltonian governing fluctuations about mean-field theory; that is, $Z_{\mathrm{RPA}} = \int \mathcal{D}\psi \exp\{-\mathcal{F}_{\mathrm{RPA}}\}$. If we neglect contributions from the cubic vertex $\gamma^{(3)}_{\mathrm{RPA}}$ (valid only when $\gamma^{(3)}_{\mathrm{RPA}}(\mathbf{q}_1, \mathbf{q}_2)$ vanishes for all $\mathbf{q}$, which is only true for certain homopolymer blends), the one-loop correction to $\gamma^{(2)}_{\mathrm{RPA}}$ is given by[9,10]

$$\gamma^{(2)}(0) = \gamma^{(2)}_{\mathrm{RPA}}(0) + \tilde{\Sigma}(\chi,\sigma) \qquad (8)$$

$$\tilde{\Sigma}(\chi,\sigma) = \frac{1}{2}\int_q^\Lambda \frac{\gamma^{(4)}_{\mathrm{RPA}}(0,0,q)}{\gamma^{(2)}_{\mathrm{RPA}}(q)} \qquad (9)$$

Demanding $\gamma^{(2)}(0) = 0$, we find $2\chi_{\mathrm{c}}(\sigma) = 2\chi_{\mathrm{MF}} + \tilde{\Sigma}(\chi_{\mathrm{MF}}, \sigma)$, to first order in $\chi_{\mathrm{c}}(\sigma) - \chi_{\mathrm{MF}}$.

The low-q and high-q limits of $\gamma^{(2)}_{\mathrm{RPA}}(q)$ are[3,11]

$$\gamma^{(2)}_{\mathrm{RPA}}(q) = \begin{cases} 2(\chi_{\mathrm{MF}} - \chi) + g(\sigma)q^2 & q \to 0 \\ \tilde{g}q^2 & q \to \Lambda \end{cases} \qquad (10)$$

where $\tilde{g}$ is independent of architecture; $\gamma^{(4)}_{\mathrm{RPA}}(0,0,q)$ has similar behavior. Hence, χ_{c} has an architecture-independent contribution which depends on the cutoff as Λ^3, and architecture-dependent contributions from the low-q behavior. This cutoff dependence is due to fluctuations on a monomer scale a and yields the same shift for all architectures. However, the architecture-dependent fluctuations on larger length scales introduce a cutoff-independent contribution to $\chi_{\mathrm{c}}(\sigma)$ so that the *difference* $\chi_{\mathrm{c}}(\sigma_1) - \chi_{\mathrm{c}}(\sigma_2)$ is a universal quantity that may be extracted by comparing χ_{c} for two A–A/B blends whose copolymers have the same mean composition but different sequence distributions.

This would appear to determine, the lowest order in perturbation theory, the architecture dependence of the critical temperature. However, there are several features of this calculation that we shall correct below:

(1) The derivation of $\mathcal{F}_{\mathrm{RPA}}$ involves a saddle-point approximation to a functional integral over a two-component constraint field $\boldsymbol{J}$ that maintains given mean composition profiles $\langle\phi_{\mathrm{A}}(\mathbf{r})\rangle$ and $\langle\phi_{\mathrm{B}}(\mathbf{r})\rangle$, where $\langle\phi_{\mathrm{B}}(\mathbf{r})\rangle = 1 - \langle\phi_{\mathrm{A}}(\mathbf{r})\rangle$ in the incompressible limit. Hence, to ensure that composition fluctuations $\delta\phi$ also obey these constraints, we must include fluctuations in these chemical-potential-like fields $\boldsymbol{J}$.

(2) In addition to the renormalization from eq 9, a nonsymmetric system requires additional contributions. This is because the cubic vertex $\gamma^{(3)}_{\mathrm{RPA}}(\mathbf{q}_1, \mathbf{q}_2)$ is adjusted be zero *only* at $q_1 = q_2 = 0$ (see eqs 6a and 6b); only for a blend of two equal length homopolymers does this condition imply that $\gamma^{(3)}_{\mathrm{RPA}}(\mathbf{q}_1, \mathbf{q}_2) = 0$ for *all* $\mathbf{q}$. The structure at nonzero wavenumber induces corrections to χ_{c}.

(3) A further feature of a nonsymmetric theory is a renormalization of $\gamma^{(3)}(0, 0)$. Similar behavior is found for the theory of the liquid–gas transition, which is also a nonsymmetric binary fluid demixing transition.[12] This renormalization shifts the *critical composition* (eq 7) and is cutoff-independent.

We shall outline our calculation and discuss the results, while the details will appear elsewhere.[11] We first reproduce the exact microscopic theory before the RPA has been performed. The partition function is[4]

$$Z = \int \mathcal{D}\delta\phi\,\mathcal{D}\boldsymbol{J}\,\mathrm{e}^{-\Phi[\delta\phi,\boldsymbol{J}]} \qquad (11)$$

where (truncated to fourth order)

$$\Phi[\delta\phi, \boldsymbol{J}] = \int_{\mathbf{q}}^{\Lambda}\left\{i\boldsymbol{J}(\mathbf{q})\cdot\delta\phi(-\mathbf{q}) + \frac{1}{2}\delta\phi(\mathbf{q})\cdot\chi\cdot\delta\phi(-\mathbf{q})\right\} + \sum_{n=2}^{4}\frac{1}{n!}\int_{\mathbf{q}_1\ldots\mathbf{q}_n}^{\Lambda}\hat{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\{\mathbf{q}_i\})\,J_{\alpha_1}(\mathbf{q}_1)\ldots J_{\alpha_n}(\mathbf{q}_n)\,\delta\Big(\sum_{i=1}^{n}\mathbf{q}_i\Big) \qquad (12)$$

$$\hat{\Gamma}^{(n)}_{\alpha_1\ldots\alpha_n}(\{\mathbf{q}_i\}) = \frac{-i^n}{V}\langle\hat{\phi}_{\alpha_1}(\mathbf{q}_1)\ldots\hat{\phi}_{\alpha_n}(\mathbf{q}_n)\rangle_0^{\mathrm{c}} \qquad (13)$$

Here $\langle\cdot\rangle_0^{\mathrm{c}}$ denotes a cumulant evaluated with the noninteracting Hamiltonian ($\mathcal{H}_0$) for Gaussian polymers.[4] The interaction matrix $\chi_{ij} = U + a^{-3}\chi(1 - \delta_{ij})$ ensures incompressibility in the limit $U \to \infty$. The vector of fields $\boldsymbol{J}$ was introduced to define the order parameter $\delta\phi$, and in the incompressible limit, $J_{\mathrm{A}} - J_{\mathrm{B}}$ plays the role of a chemical potential for exchanging A and B monomers.

The RPA is obtained by evaluating the $\boldsymbol{J}$ functional integral by saddle points to the desired order in $\delta\phi$ and taking the incompressible limit $U \to \infty$. This yields $\mathcal{F}_{\mathrm{RPA}}$, whose minimum over $\psi(\mathbf{r})$ gives mean-field theory. Hence, mean-field theory is given by a saddle-point evaluation of eqs 6a and 6b with respect to the four-component field η:

$$\eta = (\delta\phi, \boldsymbol{J}) \qquad (14)$$

Having cast the theory in terms of η, the natural way to incorporate fluctuation effects is to calculate the one-loop corrections to eqs 6a and 6b, which include both $\boldsymbol{J}$ and $\delta\phi$ fluctuations.

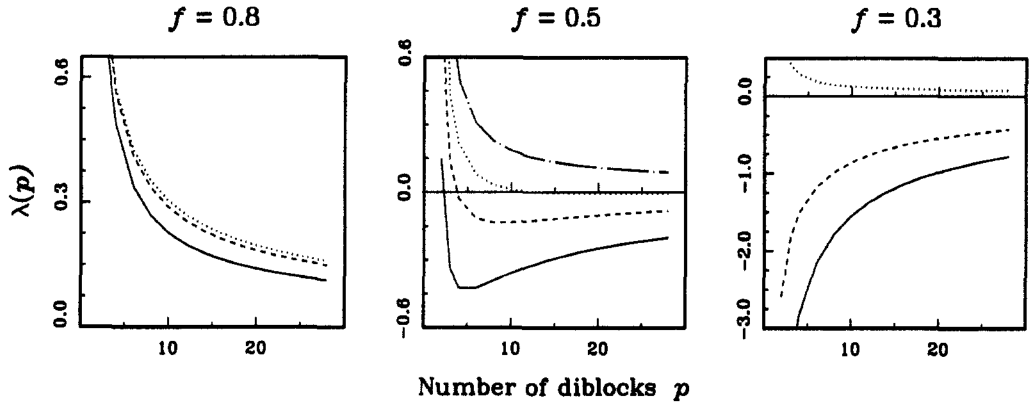

Figure 1. Scaled relative shifts $\lambda(p, N_h/N_c, f)$ as a function of p for (a) $f = 0.8$, $N_h/N_c = 0.4$ (smooth), 0.8 (dash), 1.2 (dot); (b) $f = 0.5$, $N_h/N_c = 0.4$ (smooth), 0.5 (dash), 0.6 (dot), 0.8 (dot-dash); and (c) $f = 0.3$, $N_h/N_c = 0.8$ (smooth), 1.2 (dash), 4.0 (dot).

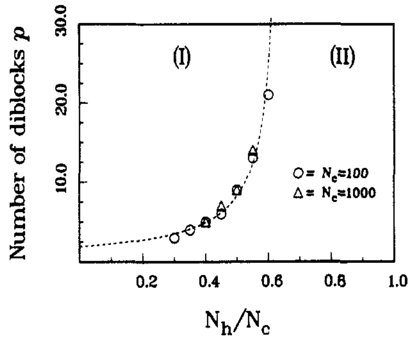

Figure 2. Qualitative behavior of $\chi_c(p)$ for $f = 0.5$. In region I, $\partial\chi_c(p)/\partial p > 0$, and in region II, $\partial\chi_c(p)/\partial p < 0$. The dashed line is a guide for the eye. For smaller f, the asymptote moves to larger N_h/N_c (for $f = 0.3$, the asymptote is at $N_h/N_c \simeq 3.5$).

This procedure differs from previous fluctuation calculations of the isotropic–lamellar transition in block-copolymers at $f = {}^1/_2$,[10,13] which included one-loop corrections to Z_{RPA} and thus neglected $\boldsymbol{J}$ fluctuations. This transition, to a lamellar phase with a wavevector $q^* \sim N_c^{1/2}$, is predicted by mean-field theory to be a continuous transition. The incipient fluctuations on the wavevector shell $|\mathbf{q}| = q^*$ lead to composition fluctuations of diverging *amplitude* in real space at the mean-field critical point,[14] which overwhelm any other fluctuation effects, including $\boldsymbol{J}$ fluctuations. For this unusual transition, one must self-consistently solve for the fluctuation corrections to mean-field critical behavior.[13,14] In contrast, the incipient fluctuations for liquid–liquid phase separation occur at the single wavevector $q = 0$ and do not lead to large-amplitude fluctuations at the mean-field critical point. Hence, in the present calculation, we must include fluctuations of both the composition *and* the chemical-potential-like field $\boldsymbol{J}$.

Explicitly, we calculate the (4 × 4) matrix of self-energies for the η propagator, which vanishes except for the (2 × 2) matrix Σ in the $\boldsymbol{J} - \boldsymbol{J}$ sector. From this self-energy matrix, we evaluate the correlation functions (eqs 6a and 6b) in the incompressible limit, obtaining[11]

$$\gamma^{(2)}(0) = \gamma^{(2)}_{\mathrm{RPA}}(0) + a^3\Sigma(\chi, \sigma, \phi) \qquad (15a)$$

$$\gamma^{(3)}(0,0) = \gamma^{(3)}_{\mathrm{RPA}}(0, 0; \phi) + a^3\frac{\partial}{\partial\phi}\Sigma(\chi, \sigma, \phi) \qquad (15b)$$

where $\Sigma(\chi, \sigma, \phi) = \xi\cdot\mathbf{S}^{-1}(0)\cdot\Sigma(0)\cdot\mathbf{S}^{-1}(0)\cdot\xi$ and $\xi = (1, -1)$. The simple derivative in eq 15b follows because the vertices at $q = 0$ compose a Taylor expansion of the effective potential with respect to ϕ.[9] Hence, the higher order vertices at $q = 0$ may be calculated once the quadratic vertex is known for general ϕ.

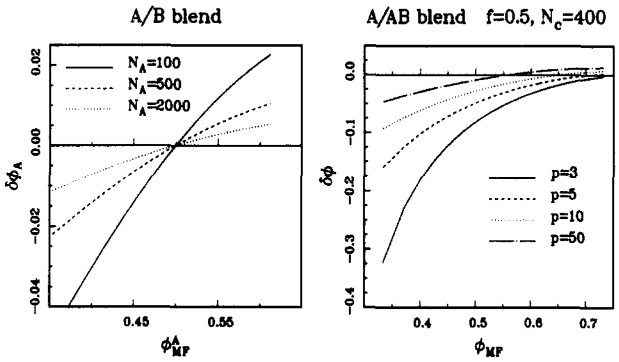

Figure 3. (a) Composition shift $\delta\phi_A$ for an $A = B$ homopolymer–homopolymer blend as a function of the mean-field critical composition ϕ^A_{MF}. (b) Shift in copolymer fraction ϕ for an A–A/B blend with $N_c = 400$ and $f = 0.5$.

For a calculation consistent to one-loop order, we replace χ and ϕ in Σ by their mean-field critical values (eq 7), equate eqs 15a and 15b to zero, and expand to linear order in the deviation $\delta\phi = \phi_c - \phi_{MF}$, to obtain

$$2\chi_c(\sigma) = 2\chi_{MF} + \Sigma(\chi_{MF}, \sigma, \phi_{MF}) \qquad (16)$$

$$\delta\phi_c = -\frac{1}{2}f^2(N_hN_c)^{3/2}\frac{\partial}{\partial\phi}\Sigma(\chi_{MF}, \sigma, \phi_{MF}) \qquad (17)$$

where we have used eq 7. Explicit evaluation reduces eq 16 to the form of eq 2.[11]

As a simple illustrative example of the architecture-induced shifts in the critical behavior of copolymer–homopolymer blends, we have calculated the corrections to mean-field theory for melts containing (2p)-block copolymers. This choice allows us to interpolate smoothly between a diblock and a very fine multiblock which approaches the equivalent homopolymer C as $p \rightarrow \infty$. The architecture dependence $\lambda(p, N_h/N_c, f)$ may then be extracted by subtracting the shift for the A/C blend from that for a finite p and is shown in Figure 1. For example, for $N_c = N_h = 100$ and $f = {}^1/_2$, we find $(\chi_c(3) - \chi_c(\infty))/\chi_{MF} \simeq 10.7\%$.

Surprisingly, $\lambda(p, N_h/N_c, f)$ is not always a monotonically decreasing function with increasing p, as might be expected from the simple argument that increasing the number of block (p), thereby reducing the block size and hence the fluctuations, increases the critical temperature (or reduces χ_c). For copolymers with $f \lesssim {}^1/_2$, we find that $\lambda(p, N_h/N_c, f)$ decreases with increasing p for large N_h/N_c but crosses over to an *increasing* function of p for small enough homopolymers. This behavior is summarized in Figure 2.

How do we account for this nonmonatonic behavior? Our simple argument appears to hold unless the homopolymer is small and solventlike [the smaller component has the greater volume fraction at ϕ_c; see eq 7] or B block on the copolymer is small. In these cases, the fluctuations near the critical point might reasonably be expected to be micellelike structures, in which long loops of A block extend outward from aggregated groups of short B blocks. Such a micelle is more easily constructed, with less stretching free energy, if there are fewer blocks; hence, a larger χ is required to induce phase separation for larger p. The nonmonotonic behavior may then emerge as a crossover between the two extremes.

Finally, Figure 3 shows a plot of the critical composition shifts. For an A–B homopolymer–homopolymer blend, the shifts roughly collapse onto the form

$$\delta\phi_c^A \simeq \alpha\frac{\log(N_B/N_A)}{(N_AN_B)^{1/4}} \tag{18}$$

where $\alpha \simeq 3.2$ is weakly N-dependent. The critical composition is shifted away from the symmetry point $\phi = {}^1/_2$, scales as $N^{-1/2}$, and vanishes for a symmetric blend ($N_A = N_B$). The shift for a homopolymer blend is virtually immeasurable ($\delta\phi_c^A \simeq -0.03$ for $N_A \simeq 100$, $N_B \simeq 45$) but is predicted to be much larger for an A–A/B blend with a coarse copolymer ($\delta\phi_c \simeq -0.1$ for $N_c \simeq 400$, $N_h \simeq 180$, $p = 10$).

In conclusion, we have shown how to systematically correct mean-field theories for polymer phase separation and have calculated the first-order corrections to the critical point (χ_c, ϕ_c) for an A–A/B homopolymer–multiblock/copolymer blend. The critical interaction parameter $\chi_c(p)$ contains a universal architecture-dependent contribution which may be extracted by comparing $\chi_c(p)$ for different copolymer architectures (p). The departures from mean-field predictions are most pronounced for smaller chains, and suggest both experimental and numerical[15] tests on blends of different architecture for which Flory–Huggins theory predicts identical critical points.

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