Communications to the Editor

Fluctuation Effects in the Density Functional Theory of Order–Disorder Transitions in Block Copolymers

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The calculation of the phase diagram of diblock copolymer is of tremendous current interest.[1] Many procedures[2–16] have been presented which account for different essential features of the problem. In general, there are two kinds of fluctuations to account for. First is the familiar order parameter fluctuations, which we call composition fluctuations, present in all systems whether small molecular or macromolecular. Proper accounting of these fluctuations leads to non-mean-field results. The second kind of fluctuation is specific to polymers, which we call chain fluctuation, and captures the internal excitations of the chains. These two kinds of fluctuations are coupled, and the coupling is manifest in a wide range of nonuniversal properties of polymeric systems in addition to belonging to the same universality classes if the conditions are just right.

The pioneering work of Helfand[3,4] and the most recent extensions by Shull[5] and Vavasour and Whitmore[6] deal with a self-consistent-field theory by partially accounting for chain fluctuations and ignoring composition fluctuations. The other pioneering work of Leibler[7] starts with more terms of chain fluctuations but ignores composition fluctuations; in addition, a saddle-point approximation is made for the two-point vertex term Γ_2 to enable analytical tractability in determining the stabilities of different morphologies. Thus Leibler's theory is a double mean-field theory. Ohta and Kawasaki[8] and Semenov,[9] using the starting point of Leibler's theory, obtained a description of the strong segregation regime. This work ignores composition fluctuations, in addition to suppressing chain fluctuations in higher vertex terms (Γ_3 and Γ_4). The first work in diblock literature to include composition fluctuations is by Fredrickson and Helfand[10] (FRH) but is confined to the weak segregation limit. In this calculation a saddle-point approximation was made for chain fluctuations. This work was extended by Mayes and Olvera de la Cruz[11] to include the leading wave vector dependence of Γ_3 and Γ_4 but keeping the saddle-point approximation for Γ_2 and confining to the weak segregation limit.

The recent density fluctional theory[12,13] of Melenkevitz, Lescanec, and Muthukumar ignored composition fluctuations. By making the local approximation for Γ_3 and Γ_4 as in Ohta–Kawasaki and FRH but including full chain fluctuations in Γ_2, they found a crossover between the weak and strong segregation limits with a well-pronounced intermediate regime. These calculations are extended in this paper to include composition fluctuations following the random-phase approximation of Brazovskii.[14] This calculation may be called the double random-phase approximation. We find below that the range of dominance of composition fluctuations is extremely narrow near the order–disorder transition (ODT), and we conclude that any quibble about theoretically predicted quantitative details near the ODT is moot as far as experimental data are concerned, except that all ODTs are first order.

Consider a collection of n A–B diblock chains each with N segments, with f being the number of monomers of type A. The free energy F of this system is given by

$$\exp(-F) = Z = \int \prod_{\alpha=1}^{n} \mathcal{D}[\mathbf{R}_\alpha(s)] \exp(-H_\mathrm{E}) \qquad (1)$$

where the Edwards Hamiltonian H_E for the diblock copolymers is

$$H_\mathrm{E} = \frac{1}{2}\sum_{\alpha=1}^{n} \int_0^N \mathrm{d}s \left(\frac{\partial \mathbf{R}\alpha(s)}{\partial s}\right)^2 + \frac{u}{2}\sum_{\alpha,\beta}^{n} \int_0^f \mathrm{d}s \int_0^f \mathrm{d}s' \times \delta[\mathbf{R}_\alpha(s)-\mathbf{R}_\beta(s')] + \frac{v}{2}\sum_{\alpha,\beta}^{n} \int_f^N \mathrm{d}s \int_f^N \mathrm{d}s'\, \delta[\mathbf{R}_\alpha(s)-\mathbf{R}_\beta(s')] + w\sum_{\alpha,\beta}^{n} \int_0^f \mathrm{d}s \int_f^N \mathrm{d}s'\, \delta[\mathbf{R}_\alpha(s)-\mathbf{R}_\beta(s')] \qquad (2)$$

u, v, and w are the two-body interaction strengths and $\int\prod_\alpha \mathcal{D}[\mathbf{R}_\alpha(s)]$ denotes the sum over all configurations of the polymer chains. After imposing a prescribed spatial variation of a field variable at position $\mathbf{r}$, say $\psi(\mathbf{r})$, which may be determined experimentally, this sum is performed in two steps: first, sum over all chain configurations which are compatible with the prescribed ψ; second, sum over all possibilities of ψ. Taking ψ to be $\psi(\mathbf{r}) = \rho_\mathrm{A}(\mathbf{r})/\rho - f/N$ (where ρ_A and ρ are respectively the local density of monomers of type A and the density of the system), this procedure was carried out by Ohta and Kawasaki to obtain

$$Z = \int \mathcal{D}[\psi] \exp(-H_\mathrm{LOK}[\psi]) \qquad (3)$$

where $H_\mathrm{LOK}[\psi]$ is the Leibler–Ohta–Kawasaki Hamiltonian given by

$$H_\mathrm{LOK}[\psi] = \frac{1}{2!}\int_\mathbf{k} \Gamma_2(\mathbf{k},-\mathbf{k})\, \psi(\mathbf{k})\, \psi(-\mathbf{k}) + \frac{1}{3!}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2} \Gamma_3(\mathbf{k}_1,\mathbf{k}_2,-\mathbf{k}_1-\mathbf{k}_2)\, \psi(\mathbf{k}_1)\, \psi(\mathbf{k}_2)\, \psi(-\mathbf{k}_1-\mathbf{k}_2) + \frac{1}{4!}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3} \Gamma_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3) \times \psi(\mathbf{k}_1)\, \psi(\mathbf{k}_2)\, \psi(\mathbf{k}_3)\, \psi(-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3) + \dots \qquad (4)$$

The explicit forms of the vertex terms are well-known in the literature as obtained using the random-phase approximation in the incompressibility limit, $\rho_\mathrm{A}(\mathbf{r}) + \rho_\mathrm{B}(\mathbf{r}) = \rho$. This is the Landau expression for the present problem where the coefficients are wavevector dependent. The chain fluctuations and the specificity of a particular system appear through the vertex terms. The parameters u, v, and w of chemical mismatch appear as the interaction parameter χ $(=w-(u+v)/2)$. Among all vertex terms, only

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Γ_2 depends on χ. Near the ODT Γ_2^{-1} is sharply peaked at k^* which enabled Leibler and others to perform a saddle-point approximation in the weak segregation limit.

Since the order parameter ψ is a fluctuating quantity, we write

$$\psi = \psi_0 + \tilde{\psi} \tag{5}$$

where ψ_0 is the mean and $\tilde{\psi}$ is the fluctuating part. Substituting this in eq 3, we get

$$Z = \exp(-H_{\mathrm{LOK}}[\psi_0]) \int \mathcal{D}[\tilde{\psi}] \exp(-\tilde{H}[\psi_0,\tilde{\psi}]) \tag{6}$$

where $\tilde{H}$ is given by

$$\tilde{H}[\psi_0,\tilde{\psi}] = \frac{1}{2!}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\tilde{\Gamma}_2(\mathbf{k}_1,\mathbf{k}_2)\, \tilde{\psi}(\mathbf{k}_1)\, \tilde{\psi}(\mathbf{k}_2) + \frac{1}{3!}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\tilde{\Gamma}_3(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\, \tilde{\psi}(\mathbf{k}_1)\, \tilde{\psi}(\mathbf{k}_2)\, \tilde{\psi}(\mathbf{k}_3) + \frac{1}{4!}\int_{\mathbf{k}_1}\int_{\mathbf{k}_2}\int_{\mathbf{k}_3}\int_{\mathbf{k}_4}\tilde{\Gamma}_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)\, \tilde{\psi}(\mathbf{k}_1)\, \tilde{\psi}(\mathbf{k}_2)\, \tilde{\psi}(\mathbf{k}_3)\, \tilde{\psi}(\mathbf{k}_4) + \dots \tag{7}$$

with

$$\tilde{\Gamma}_2(\mathbf{k}_1,\mathbf{k}_2) = \Gamma_2(\mathbf{k}_1,\mathbf{k}_2)\, \delta(\mathbf{k}_1+\mathbf{k}_2) + \frac{1}{2}\int_{\mathbf{k}_3}\Gamma_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3)\, \psi_0(\mathbf{k}_3)\, \psi_0(-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3) + \dots \tag{8}$$

$$\tilde{\Gamma}_3(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3) = \Gamma_3(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\, \delta\, (\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3) + \Gamma_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3)\, \psi_0(-\mathbf{k}_1-\mathbf{k}_2-\mathbf{k}_3) + \dots \tag{9}$$

$$\tilde{\Gamma}_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4) = \Gamma_4(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4)\, \delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4) + \dots \tag{10}$$

In fact ψ_0 minimizes $H_{\mathrm{LOK}}[\psi]$ and leads to the absence of any linear term of $\tilde{\psi}$ in $\tilde{H}$, and $H_{\mathrm{LOK}}[\psi]_0$ is the mean-field result. Combining eqs 1 and 6, the free energy becomes

$$F = H_{\mathrm{LOK}}[\psi_0] + F_f \tag{11}$$

where $H_{\mathrm{LOK}}[\psi_0]$ is given by eq 4 with ψ replaced by ψ_0 and F_f is the fluctuation part,

$$F_f = -\ln \int \mathcal{D}[\tilde{\psi}] \exp(-\tilde{H}[\psi_0,\tilde{\psi}]) \tag{12}$$

The two-point correlation function

$$S(\mathbf{k}) = \langle \tilde{\psi}(\mathbf{k})\, \tilde{\psi}(-\mathbf{k}) \rangle \tag{13}$$

can be expressed as an infinite series using the Hamiltonian given in eq 7. Applying the random-phase approximation to enable a truncation in this series yields

$$\frac{1}{S(\mathbf{k})} = \Gamma_2(\mathbf{k},-\mathbf{k}) + \frac{1}{2}\int_{\mathbf{k}_1}\Gamma_4(\mathbf{k},-\mathbf{k},-\mathbf{k}_1,\mathbf{k}_1)\, \{\psi_0(\mathbf{k}_1)\, \psi_0(-\mathbf{k}_1) + \mathbf{S}(\mathbf{k}_1)\} \tag{14}$$

which is an approximate closure. Near the ODT, the exact expression of Leibler for $\Gamma_2(\mathbf{k},-\mathbf{k})$ can be written[10] in the Brazovskii form[14]

$$\Gamma_2 \simeq c^2\left[\frac{\tau}{N} + (\mathbf{k}-\mathbf{k}^*)^2\right] \tag{15}$$

where

$$\tau = 2[(\chi N)_s - \chi N]/c^2$$

$$c^2 = \left[\frac{1}{3}x\frac{\partial^2 F(x,f)}{\partial x^2}\right]_{x=x^*} \tag{16}$$

where $F(x,f)$, with $x = k^2N/6$, is defined in ref 10. In the following calculation we use the local approximation of Ohta and Kawasaki for Γ_3 and Γ_4.

Now we take $\psi_0(\mathbf{r})$ to be a superposition of n plane waves in the weak segregation limit,

$$\psi_0(\mathbf{r}) = \frac{1}{c}\sum_{i=-n,\neq 0}^{n} a_n \exp(i\mathbf{K}_i\cdot\mathbf{r}) \tag{17}$$

The sphere, cylinder, and lamellar morphologies correspond to $n = 1$, 3, and 6, respectively. Near the spinodal the $2n$ wave vectors have magnitude $|\mathbf{K}_i| = k^*$. Following the procedure of Brazovskii and seeking a solution of the form $c^2[(r/N) + (k - k^*)^2]$ for $S^{-1}(k)$, eqs 14 and 17 yield at equilibrium

$$r = \tau + \frac{d\lambda}{(rN)^{1/2}} + n\lambda a_n^{\,2} \tag{18a}$$

$$r = \alpha_n \mu a_n - \frac{1}{2}\beta_n \lambda a_n^{\,2} \tag{18b}$$

where $d = 3x^*/2\pi$, $\lambda = N\gamma_4(0,0)/c^4$, and $\mu = N\gamma_3/c^3$. The coefficients α_n and β_n for $n = (1, 3, 6)$ are $(0, -1, -2)$ and $(-1, -1, 3)$, respectively, as shown by Leibler and FRH. The coefficient of the second term on the right-hand side of eq 18a is given by an integral[17] with an ultraviolet divergence. The cut-off momentum Λ is taken to be such that $\Lambda\sqrt{r}$ approaches zero in order to recover the coefficient of FRH. Alternatively, the coefficient of FRH is the finite part and the divergent part is ignored by the regularization procedure. But for finite r, a different choice of Λ (which is related to the Kuhn length) will result in a slightly different result. Now care must be exercised in any quantitative comparison between experimental data and the fluctuation theory. Using a Legendre transform, F_{f} can be obtained in this limit, as shown by FRH, to be

$$F_{\mathrm{f}} = \frac{1}{2\lambda}(r^2 - r_0^{\,2}) + \frac{d}{\sqrt{N}}(\sqrt{r} - \sqrt{r_0}) - \frac{2}{3}n\alpha_n\mu a_n^{\,3} + \frac{1}{4}n\beta_n\lambda a_n^{\,4} \tag{19}$$

where r_0 is the inverse susceptibility of the disordered phase given by eq 18a where $a_n = 0$.

Near the spinodal, the amplitudes of the density profile $\psi_0(\mathbf{r})$ are very weak. In this limit, the procedure of Brazovskii is repeated to obtain the phase diagram and the nature of the various ODTs. The conclusions are exactly the same as those of FRH. For example, at $f = 1/2$, there is a weak first-order transition from the disordered state to the lamellar state. At this transition the value of χN is

$$(\chi N)_t = 10.495 + 41.0N^{-1/3} \tag{20}$$

and the jump in the order parameter is

$$a_1 = 0.815N^{-1/6} \tag{21}$$

By approximating the functional integration of eq 12 by the functional Gaussian integral,

$$\int \mathcal{D}[\tilde{\psi}] \exp(-\tilde{H}[\psi_0,\tilde{\psi}]) \sim \int \mathcal{D}[\tilde{\psi}] \exp\left\{-\frac{1}{2}\int_{\mathbf{k}} S^{-1}(\mathbf{k})\, \tilde{\psi}(\mathbf{k})\, \tilde{\psi}(-\mathbf{k})\right\}$$

where S is given by eq 14, F_f becomes near the spinodal at $f = 1/2$,

$$F_f = 2d\sqrt{r}N^{-3/2} \tag{22}$$

Overall we see that the effect of fluctuations becomes increasingly negligible as N increases.

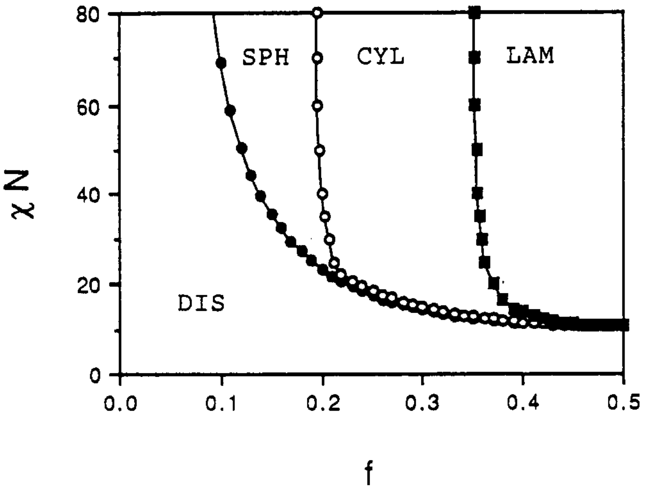

Figure 1. Phase diagram from the present calculation. The lamellar, cylinder, sphere, and disordered phases are denoted by LAM, CYL, SPH, and DIS, respectively.

The full phase diagram is constructed by calculating F of eq 11 for different morphologies and comparing their relative stabilities. In obtaining this phase diagram, we generalized the density functional theory to include the composition fluctuations. The mean-field part is treated by the variationally optimized parametrization of the density profile, and the fluctuation part is treated by the same procedure as in FRH. The results are given in Figure 1 for $N = 10^6$. Near the spinodal, the order parameter is weak so that the mean-field contribution to the free energy is negligible in comparison with F_f obtained from eq 19. In view of this it is sufficient to take the parametrization of ψ_0 to be the same as in eq 17. In this regime where composition fluctuations $\tilde{\psi}$ dominate over mean field ψ_0, there is a direct first-order transition from the disordered state to the lamellar state for $0.47 \leq f \leq 0.53$; a direct transition from the disordered state to the cylinder state for $0.42 \leq f \leq 0.47$ and $0.53 \leq f \leq 0.58$; and a direct transition from the disordered state to the sphere morphology for $f < 0.42$ and $f > 0.58$. At $f = {}^1/_2$, $(\chi N)_t$ is ~10.9. There is a weak effect of N on these features.

However, as χN deviates from $(\chi N)_t$, the magnitude of ψ_0 becomes nonnegligible and $H_{\mathrm{LOK}}[\psi_0]$ becomes increasingly significant and eventually dominates over F_f. We numerically find that, for $\chi N \geq (\chi N)_t + 1$, F_f is negligible in comparison with $H_{\mathrm{LOK}}[\psi_0]$. For such values of χN, we recover the phase diagram of Lescanec and Muthukumar (LM) calculated using the density functional theory with H_{LOK} only.

The results may be summarized as follows. Near the spinodal, composition fluctuations dominate only over a narrow range of χN, $(\chi N)_t \leq \chi N \leq (\chi N)_t + 1$, although these fluctuations are essential in changing the nature of ODT at $f = {}^1/_2$ to first order and in opening up windows in f for direct ODTs to lamellar and cylinder morphologies. The small range of χN for the validity of composition fluctuation dominance becomes even smaller as f deviates away from ${}^1/_2$. In this weak segregation regime, eq 18 is valid and the domain spacing D is proportional to $\sqrt{N}$. As $\chi N > (\chi N)_t + 1$, $H_{\mathrm{LOK}}[\psi_0]$ dominates over F_f in eq 11 and the mean-field phase diagram of LM is obtained for such χN values. The sphere–cylinder and cylinder–lamellar transition lines in χN versus f graphs are essentially vertical for $\chi N \geq 20$. The locations of these transitions are at f ~0.195 and ~0.345 respectively. When the phase diagram of LM is valid, different morphologies will exhibit the characteristic features of weak, intermediate, and strong segregation behaviors for different values of χN as reported earlier. The occurrence of the intermediate regime can be directly attributed to the chain fluctuations captured by keeping the full k-dependence of $\Gamma_2(k)$ in the expression of $H_{\mathrm{LOK}}[\psi_0]$. The range of intermediate segregation is $(\chi N)_t + 1 \leq \chi N \leq 100$ and $D \sim N^{\alpha}$, with $\alpha = 0.72$–0.82 depending on f. For $\chi N \geq$ ~100, strong segregation prevails where $D \sim N^{2/3}$. This regime corresponds to the zero temperature limit where both the composition and chain fluctuations have died out.

The present extension of the previous density functional theory of diblock copolymers to include composition fluctuations is only the simplest attempt to obtain a comprehensive theory of phase behavior of diblock copolymers at all levels of segregation. It is hoped that this paper will stimulate more detailed calculations to include refinements[15] of the vertex terms and wave-vector dependencies[11,15,16] of higher order vertex terms.

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(17) The value of the integral $\int_0^{\Lambda} \mathrm{d}k\, k^2/(r + (k - k^*)^2)$, where Λ is a cutoff, is

$$\Lambda + k^* \ln\left[\frac{(\Lambda - k^*)^2 + r}{(k^*)^2 + r}\right] + \frac{(k^*)^2 - r}{\sqrt{r}}\left[\arctan\left(\frac{\Lambda - k^*}{\sqrt{r}}\right) + \arctan\left(\frac{k^*}{\sqrt{r}}\right)\right]$$

The value of the integral is Λ-dependent. It becomes $\pi k^{*2}/\sqrt{r}$ if Λ is chosen such that $\Lambda < k^{*2}/\sqrt{r}$ and $r \rightarrow 0$.