Asymptotic Properties of Higher-Order Vertex Functions for Block Copolymer Melts

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The transition to periodic morphologies observed in block copolymer melts has been the subject of numerous theoretical investigations. In a seminal paper, Leibler first introduced the fourth-order, random-phase approximation (RPA) vertex function expansion to analyze diblock copolymer melts in the weak segregation limit.[1] Following this approach, the free energy of the ordered copolymer phase is written as a perturbation series about a disordered state of total monomer density ρ according to

$$[F(\psi) - F(\rho)]/kT \approx \rho^2/2\sum_q \Gamma_2(q,-q)\ {\psi_q}^2 + \rho^3/6\sum_{q_1}\sum_{q_2}{}^{*}\Gamma_3(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\ \psi_{q_1}\psi_{q_2}\psi_{q_3} + \rho^4/24\sum_{q_1}\sum_{q_2}\sum_{q_3}{}^{*}\Gamma_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)\ \psi_{q_1}\psi_{q_2}\psi_{q_3}\psi_{q_4} \quad (1)$$

The asterisks appearing in eq 1 denote that $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 \equiv \mathbf{0}$ is satisfied for finite third-order contributions, while finite fourth-order terms require that $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{q}_4 \equiv \mathbf{0}$. The vertex functions Γ_n, $n = 2, 3, 4$, are properties of the homogeneous reference state where translational invariance implies these relations between the wave vectors. The density order parameters ψ_q are related to the local excess of, say, A monomers above their fixed average value f by

$$\psi_q = \int \mathbf{dr}\ \exp(i\mathbf{q}\cdot\mathbf{r})\ [f(\mathbf{r}) - f] \quad (2)$$

Conservation of A and B monomers implies $\psi_{q=0} = 0$.

The sums in eq 1 run over an infinite set of reciprocal lattice vectors (RLV's) characteristic of the morphology of interest. For calculations valid in the weak segregation limit, these infinite sums are often approximated by sums over the basis RLV's (associated with the primary Bragg reflection) of the ordered phase. Indeed, recent self-consistent-field (scf) calculations find good agreement with results obtained using a single-harmonic approximation of eq 1 near the continuous transition point ($f = 0.5$).[2,3] However, for highly asymmetric copolymers or for systems well within the ordered phase, this approach breaks down, and higher-order contributions must be included in the free energy expansion. While scf approaches provide better quantitative results for strongly segregated melts, solving the multidimensional, nonlinear partial-differential equations generated in the scf model is difficult in more than one spatial dimension.[4] Thus, the scf technique is not as well-suited for the analysis of complex morphologies (such as bicontinuous double-diamond or lamellar-catenoid structures) as other models which employ the fourth-order, RPA vertex function expansion in eq 1. However, in the strong-segregation limit, where large numbers of RLV's are required to characterize the system, the evaluation of the Γ_3 and Γ_4 functions becomes a limiting factor to performing the calculations in two or more dimensions.

To further illustrate this point, let us consider a typical parametrized variational form for $f(\mathbf{r}) - f$. The specific form chosen does not affect the basic conclusions of our arguments. However, for concreteness, we choose an $f(\mathbf{r})$ applicable to the hexagonal or body-centered-cubic morphologies. This example is also a generalization of the Gaussian window function employed in recent density functional calculations to study the lamellar phase of an incompressible diblock copolymer melt.[5,6] In two or more dimensions, we take

$$f(\mathbf{r}) = \sum_R E(\mathbf{r}-\mathbf{R}) \quad (3)$$

with

$$E(\mathbf{r}) = [1/(2\pi\sigma^2)]^{d/2}\int \mathrm{d}\mathbf{y}\ \exp(-y^2/2\sigma^2)\theta(D - |\mathbf{y} - \mathbf{r}|) \quad (4)$$

where D is the domain size, σ describes the interfacial width of the domains, $\mathbf{R}$ denotes the positions of the domain centers, and θ is the Heaviside step function. Fourier transforming eqs 3 and 4 yields

$$\psi_q \sim \exp[-{}^1/_2 q^2 D^2 (\sigma/D)^2] \quad (5)$$

where $q \propto 1/D$ so that the product qD is independent of σ and D and proportional to the magnitude of $\mathbf{q}$. The ratio of σ to D determines the number of RLV's that must appear in each sum of eq 1 in order to achieve convergence. The vertex functions generally increase with the magnitude of their arguments, but much more slowly than the ψ_q's decay. Hence, the sums always converge for nonzero values of σ/D. However, as the degree of segregation increases, σ/D decreases dramatically, requiring many more RLV's in the sums. To better appreciate the significance of this, consider the number of RLV's $\Omega(q)\ \mathrm{d}q$ in d dimensions having a magnitude between q and $q + \mathrm{d}q$. Since the dimensionality of the reciprocal space is the same as that of the direct space, we find

$$\Omega(q) \sim q^{d-1} \quad (6)$$

for large enough q. The last term in eq 1 involves a triple sum over RLV's so that a 50% decrease in σ/D requires that we double the size of the largest-magnitude RLV's we include in the calculation. Integrating eq 6 three times shows that this implies $(2^d - 1)^3$ as many terms in the fourth sum. Such a calculation, in three dimensions, would require over 300 times the CPU time as that for the original value of σ/D.

Γ_4 is an extremely complicated function of its arguments, making its functional evaluation unacceptably slow to permit strong-segregation calculations in $d > 1$ dimensions. The same objections apply to Γ_3, though the problem is less critical in this case because the third-order term in eq 1 only involves a double sum over RLV's. We thus propose the following simple, highly accurate forms for Γ_3 and Γ_4, applicable when the arguments of these vertex functions are large. For convenience, we define $|\mathbf{q}_1| = \alpha q^*$, $|\mathbf{q}_2| = \beta q^*$, $|\mathbf{q}_3| = \gamma q^*$, and $|\mathbf{q}_4| = \eta q^*$, where q^* denotes the wave vector which maximizes the disordered phase scattering function,

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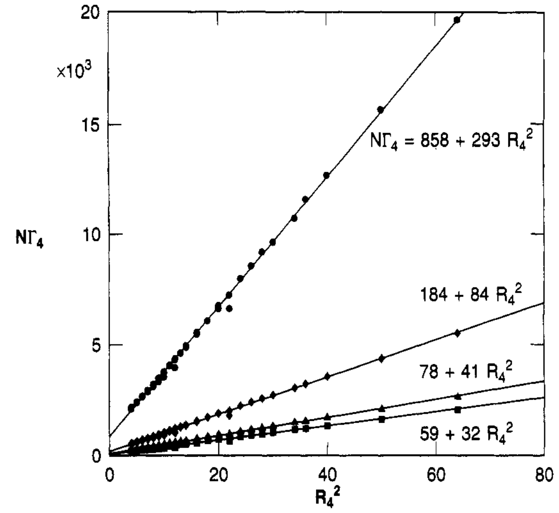

Figure 1. $N\Gamma_4$ vs R_4^2 for $f = 0.2$ (●), 0.3 (♦), 0.4 (▲), and 0.5 (■). Calculated using the disordered state values for $x^* = q^{*2}R_G^2$.

$S(q) = 1/\Gamma_2(q,-q)$, and α, β, γ, and η are greater than or equal to 1. We have calculated Γ_4 as a function of its arguments $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$, and $\mathbf{q}_4$ for the body-centered-cubic, hexagonal cylinder, and double-diamond morphologies using RLV's up to $3q^*$ in magnitude and for the lamellar morphology up to $4q^*$.[7] We find numerically over a hypersphere defined by the surface

$$\alpha^2 + \beta^2 + \gamma^2 + \eta^2 = \text{constant} \tag{7}$$

that Γ_4 is nearly constant. That is, the angular dependence of the Γ_4 function is relatively weak. As a typical example, consider the hypersphere $\alpha^2 + \beta^2 + \gamma^2 + \eta^2 = 8$ for which 14 sets of vectors were sampled. At $f = 0.5$ the calculated values of $N\Gamma_4$ (N is the number of segments per copolymer chain) range between 286 and 319, with an average value of 310 ± 8. At $f = 0.2$ the values fall between 3121 and 3211, with an average of 3196 ± 22. Thus the error in approximating Γ_4 as constant for a given value of $\alpha^2 + \beta^2 + \gamma^2 + \eta^2$ is a few percent or less for most sets of vectors considered. This result is consistent with previous analyses[8] of the Γ_4 angular dependence in a single-harmonic free energy functional ($\alpha^2 + \beta^2 + \gamma^2 + \eta^2 = 4$) and suggests that the angular dependence can generally be neglected in the calculation of the ordered phase free energy.

Moreover, the value of Γ_4 is found to increase linearly as a function of the area of the hypersphere $R_4^2 = \alpha^2 + \beta^2 + \gamma^2 + \eta^2$. This is shown in Figure 1 where we have plotted all calculated values[7] of Γ_4 for $R_4^2 \geq 4$ for the four morphologies considered. Analogous results are obtained for Γ_3, except that $\alpha^2 + \beta^2 + \gamma^2 = \textit{constant}$ replaces eq 7. Figure 2 plots Γ_3 as a function of $R_3^2 = \alpha^2 + \beta^2 + \gamma^2$, for values of $R_3^2 \geq 3$. (Note that Γ_4 and Γ_3 in Figures 1 and 2 are scaled by N.)

These observations facilitate highly accurate, almost instantaneous estimates of Γ_4 and Γ_3 when the RLV's are large and the space of wave vectors becomes dense. For example, if we calculate $\Gamma_4(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$ with $\mathbf{q}_1 = \mathbf{q}_2 = 10q^*\hat{i}$ and $\mathbf{q}_3 = \mathbf{q}_4 = -10q^*\hat{i}$ ($R_4^2 = 400$) for $f = 0.2$, we obtain 1.15×10^5, compared with 1.18×10^5 from the linear form in Figure 1, giving an error of less than 3%. Excellent approximations of Γ_4 and Γ_3 for any wave vector combinations may be obtained from the results in Figures 1 and 2, or alternatively, by substituting $R_3^2x^*/3$ for x^* ($x^* = q^{*2}R_G^2$, $R_G^2 \sim N$) in $\Gamma_3(x^*)$ and $R_4^2x^*/4$ for x^* in $\Gamma_4(0,0)$ of ref 1.[9] Density functional calculations of hexagonal, body-centered-cubic, bicontinuous-double-diamond, and lamellar-catenoid phases will depend on such approximations, because the complexity of the higher-order vertex functions precludes brute-force numerical evaluation of these quantities for large numbers of RLV's.

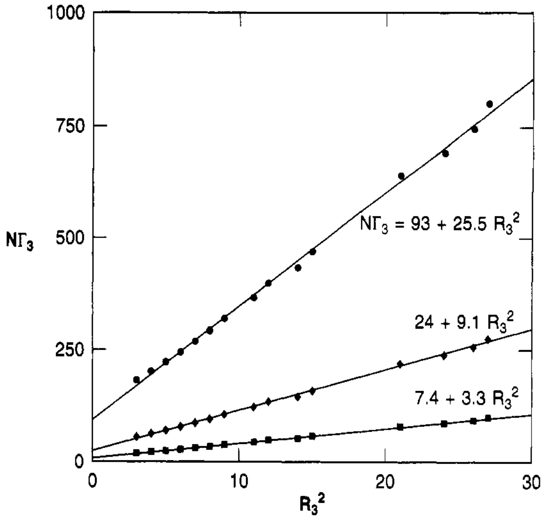

Figure 2. $N\Gamma_3$ vs R_3^2 for $f = 0.2$ (●), 0.3 (♦), and 0.4 (■). Calculated using the disordered state values for $x^* = q^{*2}R_G^2$.

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(9) A word of precaution in applying these substitutions: while x^* depends only on f in the disordered phase, in the ordered phase q^* decreases with decreasing temperature (Mayes, A. M.; Olvera de la Cruz, M. *Macromolecules* **1991**, *24*, 3975). Thus the approximation is only valid for $R_n^2/n \geq x^*_{\text{dis}}/x^*_{\text{ord}}$.