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Theory for phase transitions in diblock copolymers: The lamellar case

A. Rebei and J. De Pablo
Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706

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A mean-field type theory is proposed to study order-disorder transitions (ODT's) in block copolymers. The theory applies to both the weak segregation and the strong segregation regimes. An energy functional is proposed without appealing to the random phase approximation (RPA). We find additional terms unaccounted for within the RPA. We work out in detail transitions to the lamellar state and compare the method to other existing theories of the ODT and numerical simulations. We find good agreement with recent experimental results and predict that the intermediate segregation regime may have more than one scaling behavior.

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I. INTRODUCTION

Predicting morphologies of block copolymers continues to be a very challenging problem from the computational point of view. To make computation more feasible, appropriate energy functionals are needed, and that is the goal of this paper. For linear copolymers, the self-consistent field theory (SCFT) developed by Helfand and others [1–7] is considered to be the method of choice. It applies quite well to all regimes of segregation. Recently it was successfully used to predict different morphologies of linear triblock copolymers [6]. The method is based on a naive mean-field approximation to the partition function. Fluctuation effects can also be added but at the expense of complicating the method [8].

Around the order-disorder transition point, Leibler's [9] field theory for diblock copolymers is superior to the self-consistent field theory. For this reason there have been attempts to generalize it to all types of segregation, intermediate as well as strong. Ohta and Kawasaki [10–12] proposed a free energy functional of Leibler's form that treats the strong segregation case of a diblock copolymer. It gives comparable results to the self-consistent field method and its predictions are well supported by experiment [13,14]. Fluctuation effects were later added to Leibler's theory by Fredrickson, Helfand, and Barrat [15–19], who showed that the peak of the scattering function depends not only on χN, the Flory-Huggins parameter, but also on the average segment length and volume. The Leibler free energy functional was also shown to be useful in the strong segregation case if the wave vector dependence of the energy functional is fully kept, since higher order spatial harmonics of the order parameter become more and more important as the temperature is lowered in the ordered phase [20,21].

Here, we set out to find a similar, but simpler, energy functional for incompressible diblock copolymers that is valid for both the weak and strong segregation regimes. Our work has the same spirit as the recent work of Stepanow [22], where he used graphical methods to obtain an improved self-consistent expression for the structure factor of a diblock copolymer. He avoided using the random phase approximation (RPA) [23], i.e., Leibler's theory, and instead found an expansion of the partition function in terms of an effective potential [24–26]. Here we adopt the same goal of developing an expression of the free energy based on an effective potential. The random phase approximation will not be used to get our energy functional.

Besides succeeding in finding an expression for the energy of a diblock copolymer, we also find additional ''ideal'' terms that are missed by the RPA and that were already found by Holyst and Vilgis [27] in the polymer mixture case. Unlike other existing theories of the order-disorder transition (ODT) in diblock copolymers, our functional predicts a more complex physics between the fully disordered state and the fully segregated state. We show that the symmetric diblock copolymer goes through at least two different non-Gaussian regimes before reaching the strong segregation (SS) regime. Our results agree favorably with those from experiment and simulation.

Our method is strictly functional; we do not use any graphs. Our results to lowest order are similar to the Stepanow result [22] and our energy functional is qualitatively the same as Leibler's. The quartic term is similar to Leibler's fourth order term but is much simpler to work with.

The paper is organized as follows. In Sec. II, we develop the formalism. The details are left to the Appendixes. In Sec. III, we solve the transition to the lamellar morphology of a symmetric diblock. In Sec. IV, we compare our results with those of the self-consistent method, Leibler's method, and simulations [28].

II. FREE ENERGY OF A BLOCK COPOLYMER

We start by deriving an expression for the free energy of a block copolymer melt. Even though in this paper we are mainly interested in incompressible diblock copolymers, it can be easily generalized to, e.g., triblocks. The method we use bypasses the random phase approximation and the use of virtual sources, as was done originally by Leibler [9]. The Hamiltonian we use for our system is that of Edwards [24] generalized to copolymers and can be taken in the form

$$H = H_0 + V,$$

$$H_0[\mathbf{r}_i] = \frac{3}{2\sigma^2} \sum_{i=1}^{n} \int_0^N ds \left(\frac{d\mathbf{r}_i(s)}{ds} \right)^2$$

$$\mathbf{V}[\mathbf{r}_i]=\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\sum_{i,j=1}^{2}\rho_i(\mathbf{r})\rho_j(\mathbf{r}')\mathbf{V}_{ij}(\mathbf{r},\mathbf{r}'),$$

$$i,j=A,B. \tag{1}$$

$r_i(s)$ is a curve along the ith macromolecule that has two types of monomer A and B with densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$, respectively. We assume both monomers to have the same Kuhn length σ. There are n chains in the melt, each with $N_A(N_A=fN)$ monomers of type A and $(N-N_A)$ of type B. The interaction potential $\mathbf{V}$ is taken to have the simple form

$$\mathbf{V}(\mathbf{r},\mathbf{r}')=\rho_0\begin{pmatrix}0 & \chi\\ \chi & 0\end{pmatrix}\delta(r-r'), \tag{2}$$

where χ is the Flory-Huggins constant and ρ_0 is the total average density of monomers. The partition function of this incompressible system of macromolecules is then given by

$$\mathcal{Z}=\int d(\mathbf{r}_i)\,\delta(1-\rho_A(\mathbf{r})-\rho_B(\mathbf{r}))$$

$$\times\exp\left[-\left(H_0+\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\vec{\boldsymbol{\rho}}^{T}(\mathbf{r})\mathbf{V}(\mathbf{r},\mathbf{r}')\vec{\rho}(\mathbf{r}')\right)\right]. \tag{3}$$

In the above we have set the Boltzmann constant to 1 and used a vector notation for the densities, i.e.,

$$\vec{\rho}(\mathbf{r})=\begin{pmatrix}\rho_A(\mathbf{r})\\ \rho_B(\mathbf{r})\end{pmatrix}. \tag{4}$$

The densities are given by

$$\rho_A(\mathbf{r})=\frac{N}{\rho_0}\sum_{\alpha=1}^{n}\int_0^f ds\,\delta(r-r_\alpha(s)), \tag{5}$$

and

$$\rho_B(\mathbf{r})=\frac{N}{\rho_0}\sum_{\alpha=1}^{n}\int_f^1 ds\,\delta(r-r_\alpha(s)). \tag{6}$$

In $\mathcal{Z}$, the second term in the exponential has a quadratic symmetric form and hence it can be diagonalized. This diagonalization allows us to deal with a virtual set of monomers that are decoupled. We therefore introduce a new set of variables ρ_1 and ρ_2 such that

$$\rho_1(\mathbf{r})=\frac{1}{2}[\rho_A(\mathbf{r})+\rho_B(\mathbf{r})], \tag{7}$$

$$\rho_2(\mathbf{r})=\frac{1}{2}[\rho_A(\mathbf{r})-\rho_B(\mathbf{r})]. \tag{8}$$

In this set of variables the potential becomes diagonal, with

$$V_{11}=2\chi\rho_0, \tag{9}$$

$$V_{22}=-2\chi\rho_0, \tag{10}$$

$$V_{12}=V_{21}=0. \tag{11}$$

Ignoring the incompressibility condition for now and after isolating the free energy of the disordered state we have

$$\mathcal{Z}=\int\mathcal{D}\mathbf{r}_i\exp\left\{-\frac{1}{2}\Delta\rho_\alpha\mathbf{V}_{\alpha\beta}\Delta\rho_\beta-\rho_\alpha^0\mathbf{V}_{\alpha\beta}\Delta\rho_\beta\right\}$$

$$\times\exp\left\{-\frac{1}{2}\rho_\alpha^0\mathbf{V}_{\alpha\beta}\Delta\rho_\beta^0\right\}, \tag{12}$$

where we have adopted a matrix notation and have chosen not to write the space integrals explicitly. The measure is defined by

$$\mathcal{D}\mathbf{r}_i=d(\mathbf{r}_i)\exp(-H_0),$$

and the new densities are measured with respect to those of the homogeneous state,

$$\Delta\rho_\alpha(\mathbf{r})=\rho_\alpha(\mathbf{r})-\rho_\alpha^0,\quad \alpha=1,2.$$

For a symmetric diblock,

$$\rho^0=\left(\frac{1}{2},0\right). \tag{13}$$

Upon introducing a two-component Hartree type field φ_α with which these virtual molecules are interacting, the partition function becomes

$$\mathcal{Z}=\int\mathcal{D}(\mathbf{r}_i)\mathcal{D}\varphi\exp\left\{-\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\varphi_\alpha(\mathbf{r})V_{\alpha\beta}^{-1}(\mathbf{r},\mathbf{r}')\varphi_\beta(\mathbf{r}')\right.$$

$$\left.+i\int d\mathbf{r}[\varphi_\alpha(\mathbf{r})+i\rho_\beta^0V_{\alpha\beta}]\Delta\boldsymbol{\rho}_\alpha(\mathbf{r})\right\}. \tag{14}$$

We introduce now two more fields, Φ and μ. Since

$$\int\mathcal{D}\Phi_\alpha\delta(\Phi_\alpha(\mathbf{r})-\Delta\rho_\alpha(\mathbf{r}))=1, \tag{15}$$

we have

$$\mathcal{Z}=\exp(-F_0)\int\mathcal{D}\varphi\mathcal{D}\Phi\mathcal{D}\mu\mathcal{D}(\mathbf{r}_i)\exp\{-i\mu_\alpha\Phi_\alpha\}$$

$$\times\exp\left\{-\frac{1}{2}\varphi_\alpha V_{\alpha\beta}^{-1}\rho_\beta+i(\rho_\alpha+\mu_\alpha+i\rho_\beta^0V_{\alpha\beta})\Delta\rho_\alpha\right\}, \tag{16}$$

where

$$F_0=n\chi Nf(1-f) \tag{17}$$

is the energy of the disordered state. Now, we make a change of variables and let

$$\overline{\varphi_\alpha}(\mathbf{r})=\varphi_\alpha(\mathbf{r})+\mu_\alpha(\mathbf{r})+i\int d\mathbf{r}V_{\alpha\beta}(\mathbf{r})\rho_\beta^0(\mathbf{r}). \tag{18}$$

We also define the functional

$$\mathbf{F}[\varphi]\equiv\ln\left\{\int\mathcal{D}(r_i)\exp\left[-\left(\mathbf{H}_0(r_i)+i\int d\mathbf{r}\overline{\varphi}(\mathbf{r})\cdot\rho(\mathbf{r})\right)\right]\right\}. \tag{19}$$

This functional can be expanded in $\overline{\varphi}$ around a homogeneous state

$$\mathbf{F}[\varphi]=\sum_{m=0}^{\infty}\frac{1}{m!}\sum_{\{\alpha\}}\int\int\cdots\int d\mathbf{r}_1 d\mathbf{r}_2\ldots d\mathbf{r}_m \times C_{\alpha 1\alpha 2\ldots\alpha_m}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_m)\varphi_{\alpha_1}(\mathbf{r}_1)\varphi_{\alpha_2}(\mathbf{r}_2)\ldots\varphi_{\alpha_m}(\mathbf{r}_m),$$

$$\alpha_i=1,2. \tag{20}$$

The coefficients $C_{\alpha\beta\ldots}$ are given in Appendix A. In the following we keep only terms up to the fourth order. After some rearrangements and writing φ in place of $\overline{\varphi}$, we have the following expression for the partition function:

$$\mathcal{Z}=\int\mathcal{D}\Phi\mathcal{D}\mu\mathcal{D}\varphi\exp\left\{-\frac{1}{2}\varphi_\alpha(V_{\alpha\beta}^{-1}+C_{\alpha\beta})\varphi_\beta-\frac{1}{4!}C_{\alpha\beta\lambda\gamma}\varphi_\alpha\varphi_\beta\varphi_\lambda\varphi_\gamma+i\Xi_\alpha\varphi_\alpha\right\}\times\int\mathcal{D}\Psi\exp\left\{\frac{1}{4!}C_{\alpha\beta\lambda\gamma}(\Psi_{\alpha\beta}-\varphi_\alpha\varphi_\beta)(\Psi_{\lambda\gamma}-\varphi_\lambda\varphi_\gamma)\right\}. \tag{21}$$

Here we have introduced a pairing field $\Psi_{\alpha\beta}$ so we can cancel the quartic term in φ_α. We have also set

$$i\Xi_\alpha(\mathbf{r})=i\rho_\alpha^0+V_{\alpha\beta}^{-1}\mu_\beta(\mathbf{r}), \tag{22}$$

and again have not written the space integrals explicitly. Thus, we can integrate the φ field and then the μ field exactly. We are left with only two fields Φ and Ψ (see Appendix B),

$$\mathcal{Z}=\int\mathcal{D}\Phi\mathcal{D}\Psi\exp\{-\mathcal{F}(\Phi,\Psi)\}, \tag{23}$$

where

$$\mathcal{F}(\Phi,\Psi)=-\frac{1}{4!}\Psi_{\alpha\beta}C_{\alpha\beta\lambda\gamma}\Psi_{\lambda\gamma}+\frac{1}{2}\rho_\alpha^0A_{\alpha\beta}^{-1}\rho_\beta^0+\tfrac{1}{2}\zeta_\alpha^0B_{\alpha\beta}^{-1}\zeta_\beta^0+\tfrac{1}{2}\ln\det A_{\alpha\beta}+\frac{1}{2}\ln\det B_{\alpha\beta} \tag{24}$$

and

$$\zeta_\alpha(\mathbf{r})=\Phi_\alpha(\mathbf{r})+\rho_\alpha^0-V_{\alpha\beta}^{-1}A_{\beta\lambda}^{-1}\rho_\lambda^0, \tag{25}$$

$$\mathbf{A}=(1+\tfrac{1}{6}\boldsymbol{\Delta}\mathbf{U})\mathbf{U}^{-1},$$

$$\mathbf{B}=\mathbf{V}^{-1}-\mathbf{V}^{-1}\mathbf{A}^{-1}\mathbf{V},$$

$$\Delta_{\alpha\beta}=\Psi_{\lambda\gamma}C_{\lambda\gamma\alpha\beta},$$

$$U_{\alpha\beta}=(V+C)_{\alpha\beta}^{-1}.$$

In the above A, B, Δ, and U are space dependent matrices. $U_{\alpha\beta}$ is the desired effective potential [24]. We expand the logarithmic terms in powers of U. We do the same when we seek an expression for B. In all expansions, we keep only quadratic terms in Ψ. This is consistent with the fact that we originally kept only terms up to order 4 in Eq. (20). The final lowest order expression we get from this expansion is our expression for the energy,

$$H(\Phi)=\frac{1}{2\mathscr{V}}\sum_q\Phi(q)\left(\frac{1}{C_{22}(q)}-2\chi\rho_0\right)\Phi(-q)-\frac{1}{3!}\frac{1}{(\mathscr{V})^2}\sum_p\Phi(q)\frac{C_{2222}(q,-q,p,-p)}{[C_{22}(q)]^2C_{22}(p)}\Phi(-q)-\frac{1}{4!}\frac{1}{(\mathscr{V})^3}\sum_{q_1q_2q_3}\frac{C_{2222}(q_1,q_2,q_3,-q_1-q_2-q_3)}{C_{22}(q_1)C_{22}(q_2)C_{22}(q_3)C_{22}(q_1+q_2+q_3)}\times\Phi(q_1)\Phi(q_2)\Phi(q_3)\Phi(q_1+q_2+q_3). \tag{26}$$

It can be easily shown that $\mathscr{V}/2nC_{22}(q)$ is actually Leibler's structure function. Leibler's structure function $S(q)$ is given by

$$S^{-1}(q)=\frac{S_{AA}(q)+2S_{AB}(q)+S_{BB}(q)}{S_{AA}(q)S_{BB}(q)-S_{AB}^2(q)}. \tag{27}$$

The definitions of these functions are given in Appendix A. This is indeed equivalent to $C_{22}^{-1}(q)$ with the proper normalization. However, it is easier to see this graphically and in Fig. 1 we plot this function. Hence the first and second terms in Eq. (26) are the usual RPA result for the inverse scattering function. The third term is not captured by the RPA approximation. It is not due to fluctuations. It was pointed out by Holyst and Vilgis in their study of polymer blends [27]. This term appeared through the introduction of the pairing field

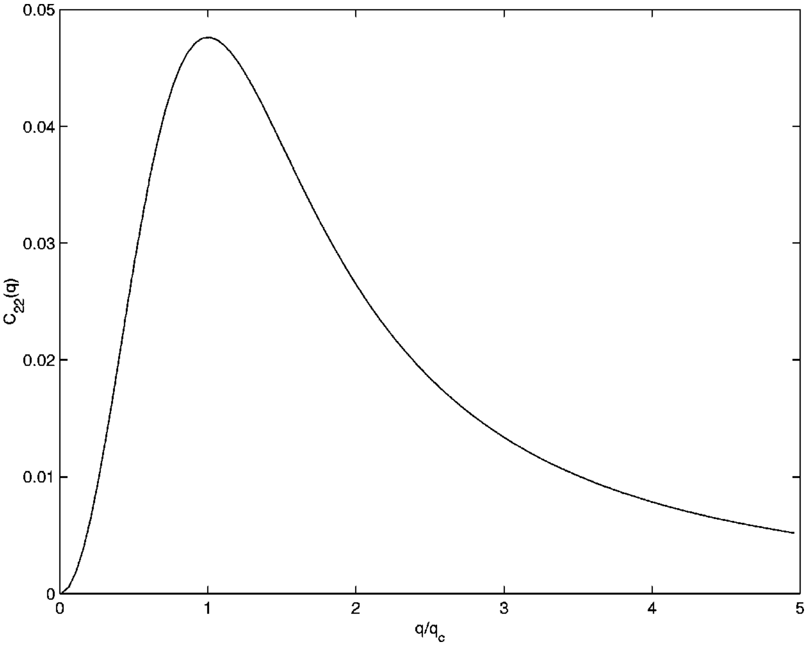

FIG. 1. The two-body correlation function $C_{22}(q)$ in our diagonalized system of collective densities.

Ψ. This field is in fact the propagator of our theory. The fourth term is familiar but the coefficient is much simpler to calculate and behaves differently from Leibler's term for large wave vectors. In Fig. 2, we plot both terms for a subset of wave numbers. Our fourth order coefficient is given by

$$C^{(4)}(q_1,q_2,q_{3,}-q_1-q_2-q_3)$$
$$=\frac{C_{2222}(q_1,q_2,q_{3,}-q_1-q_2-q_3)}{C_{22}(q_1)C_{22}(q_2)C_{22}(q_3)C_{22}(q_1+q_2+q_3)}. \tag{28}$$

This term is independent of any three-body correlation functions. Leibler's $\Gamma^{(4)}$ term does depend on three-body correlation terms, however, and this greatly complicates computations involving it; it is given by [9]

$$\Gamma^{(4)}(q_1,q_2,q_{3,}-q_1-q_2-q_3)$$
$$=\gamma_{ijkl}(q_1,q_2,q_{3,}-q_1-q_2-q_3)$$
$$\times[S_{iA}^{-1}(q_1)-S_{iB}^{-1}(q_1)][S_{jA}^{-1}(q_2)-S_{jB}^{-1}(q_2)]$$
$$\times[S_{kA}^{-1}(q_3)-S_{kB}^{-1}(q_3)][S_{lA}^{-1}(q_4)-S_{lB}^{-1}(q_4)] \tag{29}$$

with $i,j,k,l=A,B$. γ_{ijkl} is a function of two-point, three-point, and four-point correlation functions. In Fig. 2, we plot both coefficients for $q_1=-q_2=q_3=-q_4$.

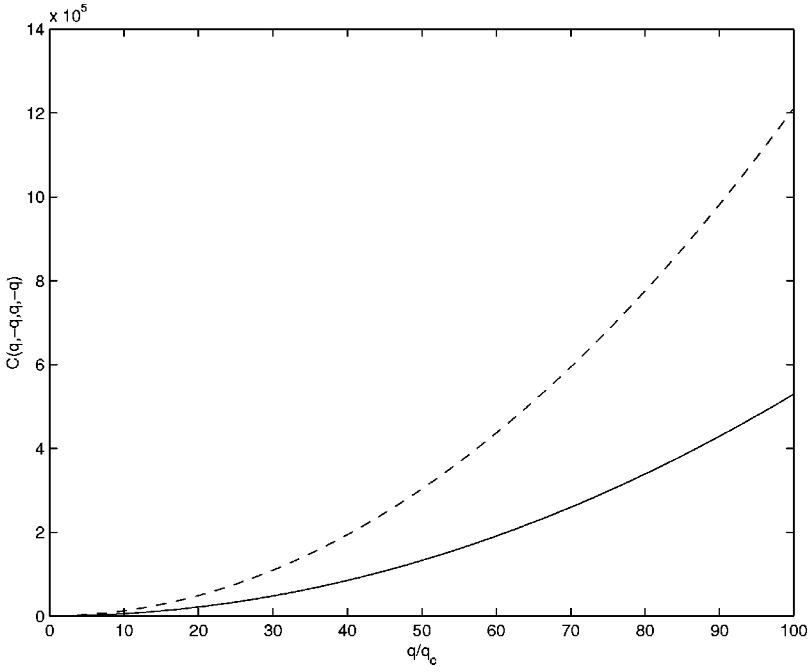

FIG. 2. Comparison of the fourth order coefficient $C^{(4)}$ of this theory with that of Leibler's RPA theory, $\Gamma^{(4)}$. $C=C^{(4)}$, Eq. (28), for the continuous curve and $C=\Gamma^{(4)}$ for the discontinuous curve.

To lowest order, the propagator of this theory also agrees with that of Stepanow [22], except that our self-energy term has additional contributions from the fourth term $\mathrm{Tr}(\Lambda U)$ of the free energy in Eq. (B5). Even though RPA [16] and non-RPA [22] calculations of the properties of the scattering function give qualitatively similar results, the physical origin of the observed behavior is entirely different in the two cases. Hence, before considering any fluctuations, the contribution of this quadratic term must first be studied. In the next section, where we use our functional to study transitions from a disordered state to a lamellar state, we will not include the quadratic non-RPA term in order to compare our functional with that of Leibler.

III. THE LAMELLAR SOLUTION

Following Melenkevitz and Muthukumar [20], we conjecture a solution that minimizes the energy functional. Knowing that in the SCFT the densities are found by solving a modified heat equation, we choose a function of the form

$$\Phi(x)=\sum_{l=1,3,\ldots}\frac{2}{\pi l}\exp[-\tfrac{1}{2}(q_l\lambda)^2]\sin(q_l x). \tag{30}$$

This choice is also dictated by the fact that

$$\int dx\Phi(x)=0, \tag{31}$$

and the solution must be periodic. The wave vector q is given by

$$q_l=\frac{2\pi l}{D}, \tag{32}$$

where D is the lamellar periodicity. λ is another parameter besides D that is related to the wall thickness of the interface region between the two components of the diblock copolymer. Both parameters are to be found by minimizing the energy H with respect to them. Actually, we solve for λ for a given D and then calculate the corresponding energy and choose the solution with the lowest energy. We rescale dimensions in terms of the radius of gyration so the energy per chain is given by

$$\begin{aligned}H/n=&\frac{1}{2}\sum_{m=1,3,..}b_m^2\left(\frac{V}{2nC_{22}(m)}-\chi N\right)\\&-\frac{1}{384}\sum_{m,p,r,s=\pm1,\pm3\ldots}\frac{b_m b_p b_r b_s C_{2222}(m,p,r,s)}{C_{22}(m)C_{22}(p)C_{22}(r)C_{22}(s)}\\&\times\delta(s+m+p+r),\end{aligned} \tag{33}$$

where

$$b_m=\frac{2}{\pi m}\exp[-\tfrac{1}{2}(2\pi m\lambda/D)^2]. \tag{34}$$

Figures 3–8 summarize all the results from this particular solution. In particular, we observe that this solution predicts that the order-disorder transition occurs for χN immediately below 10.5. Immediately below the transition temperature, our energy functional shows that the behavior of the polymer chains is no longer Gaussian. For Gaussian chains, the scaling factor δ between $\ln(D)$ and $\ln(\chi N)$ is zero. In our case, we find that for χN less than 13 δ is approximately equal to 0.26. For χN between 13 and 30, $\delta=0.52$, and, for χN above 30, δ becomes about 0.19. Hence the 2/3 power law between D and N in the SSL is also verified by this solution. So far only one intermediate region has been observed [13]. Here, this solution suggests that the intermediate region is really more than one phase. Since the behavior below the ODT is believed to be nonuniversal, it will be interesting to see if this predicted behavior is also observed in some symmetric diblock copolymers other than the one treated in [13]. The inclusion of the non-RPA term that we omitted in this solution will not change this overall picture. It has only a moderate effect at high values of χN where higher and higher wave numbers are needed for an accurate calculation of the energy.

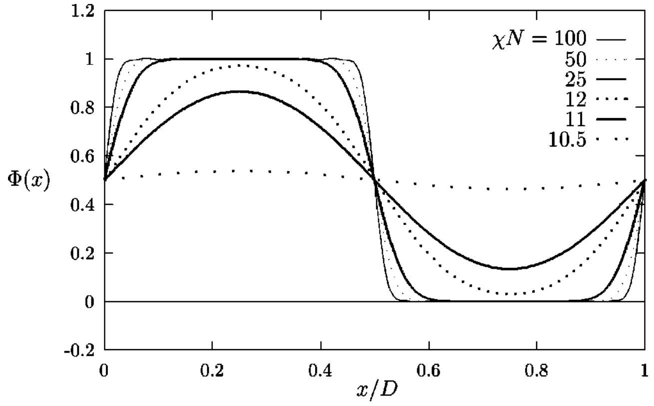

FIG. 3. Density profiles for the lamellar morphology given by Eq. (30) for different values of $\chi N=10.5,11,12,25,50,100$.

IV. COMPARISON AND DISCUSSION

In Fig. 3, we plot density profiles for different χN's. We observe that the order-disorder transition occurs below $\chi N=10.5$. The segregation amplitude grows much faster for χN

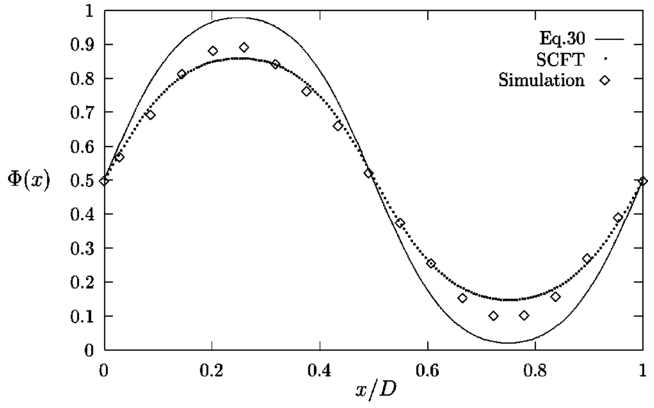

FIG. 4. Density profiles of the symmetric lamellar solution for $\chi N=12.5$. The simulation is done for $\chi N/\chi N_c=1.2$.

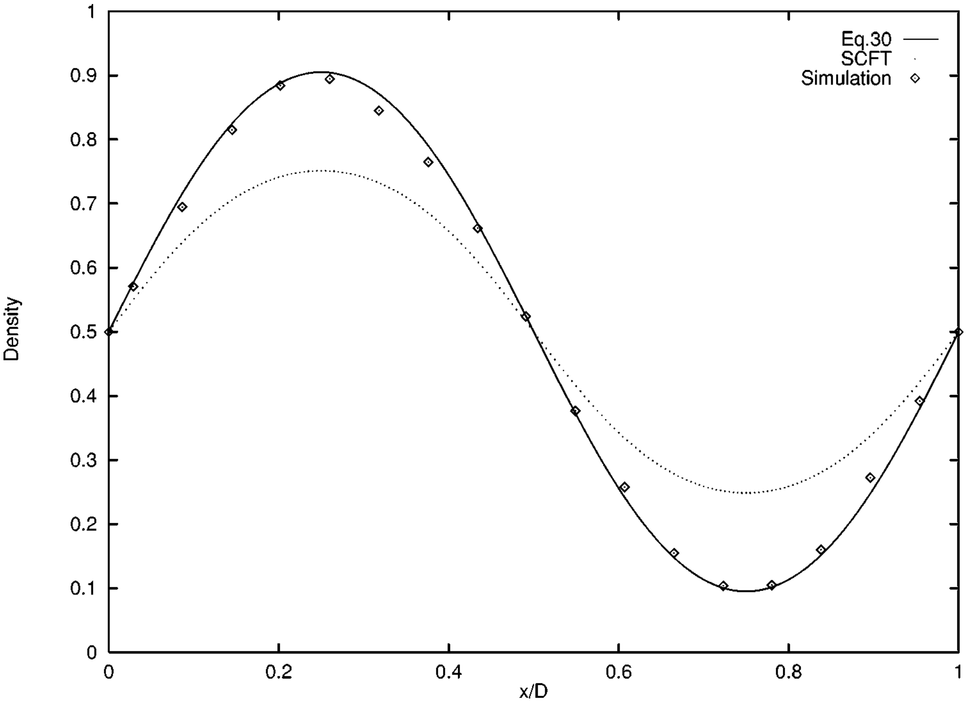

FIG. 5. Comparison of density profiles for $\chi N = 11.15$. The simulation curve is at $\chi N/\chi N_c = 1.2$.

just above the ODT temperature χN_c and less than 30. Hence, in this theory, the strong segregation regime is attained much faster than the self-consistent field method predicts [5]. This is also confirmed by recent experiments on symmetric diblock copolymers [13]. Figure 4 compares our results to those of SCFT calculations at $\chi N = 12.5$ and simulations [28]. The simulation was done with chains of 48 segments. Assuming that the critical temperature χN_c for these chains is close to 10.495, as is the case for infinite chains, we find that the simulation gives a result that falls between our result and the SCFT result. However, the ODT temperature for these short chains is expected to be lower than in the ideal case. The SCFT curves were found by solving Eqs. (3)–(7) in [5], using a finite difference method and with a random configuration as input. Our results agree well with those given in [7]. In Fig. 5, we instead predict the χN value for which our theory coincides with the simulation results. We find a χN value of approximately 11.15. Assuming now that $\chi N/\chi N_c = 1.2$ corresponds to $\chi N = 11.15$ in our theory, we plot in Fig. 6 and Fig. 7 the density profiles for $\chi N = 22.3$ and $\chi N = 44.5$ and compare our results with those of the simulation. We find relatively good agreement between

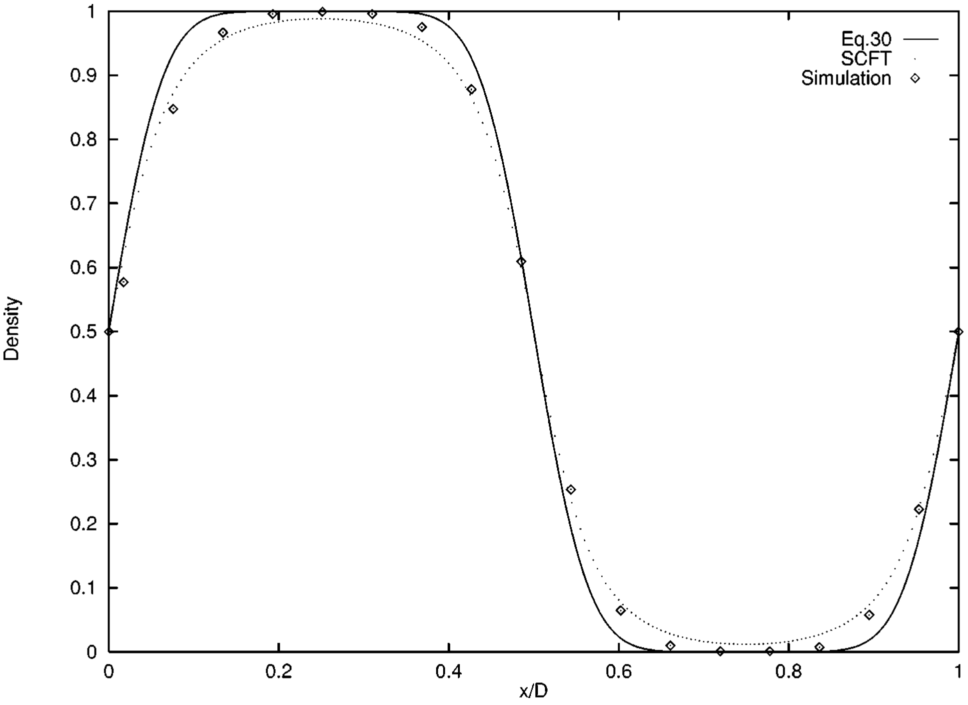

FIG. 6. Comparison of density profiles for $\chi N = 22.3$. The simulation curve is at $\chi N/\chi N_c = 2.4$.

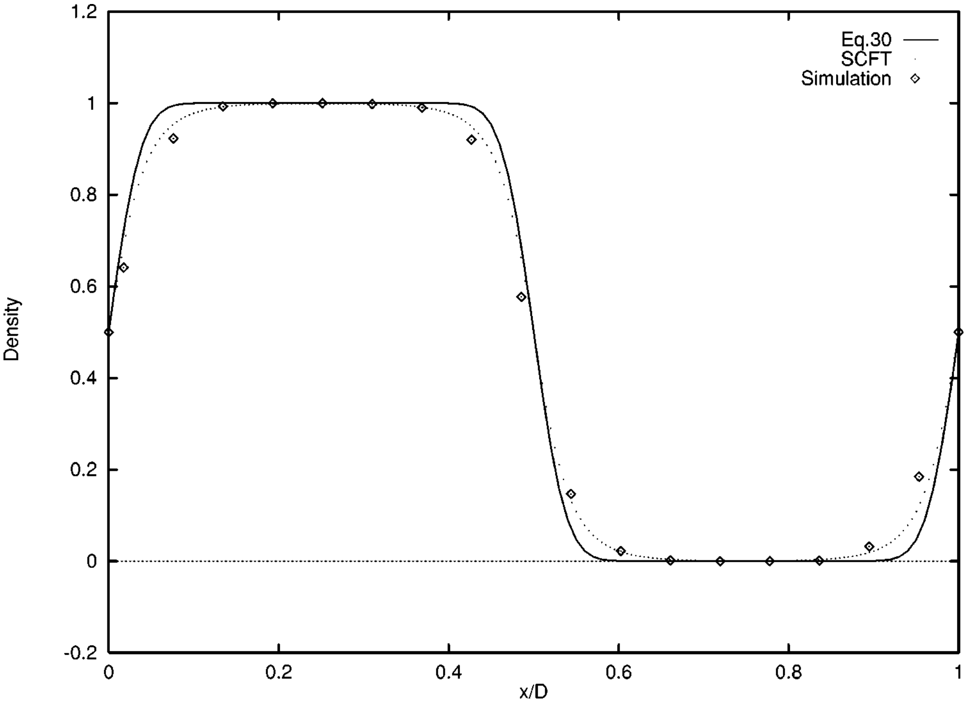

FIG. 7. Comparison of density profiles for $\chi N=44.5$. The simulation curve is at $\chi N/\chi N_c=4.8$.

theory and simulation especially far from the interfaces. Finally, in Fig. 8, we check if our theory predicts the observed scaling behavior. Clearly, we can distinguish three regimes from the plot. The intermediate regime extends from about $\chi N=13$ to about $\chi N=27$ and has a scaling factor δ of about 0.52. Above $\chi N=30$, the scaling factor is about 0.19, in agreement with observations [13]. Compared to Leibler's energy functional [21], our results are much closer to the SCF results. This is due to the fourth order term, which is smaller than Leibler's fourth order term for large wave numbers. For large χN, our energy functional gives periods closer to those of the SCFT method than does the full Leibler Hamiltonian [21], which overestimates periods by as much as 30%. Moreover, our theory predicts that transition to the strong segregation regime occurs at $\chi N\approx 30$, in complete agreement with the experimental results in [13]. In the SCFT, SS is believed to occur around $\chi N=50$. Reference [20] suggests that the SS starts to occur for χN larger than 90.

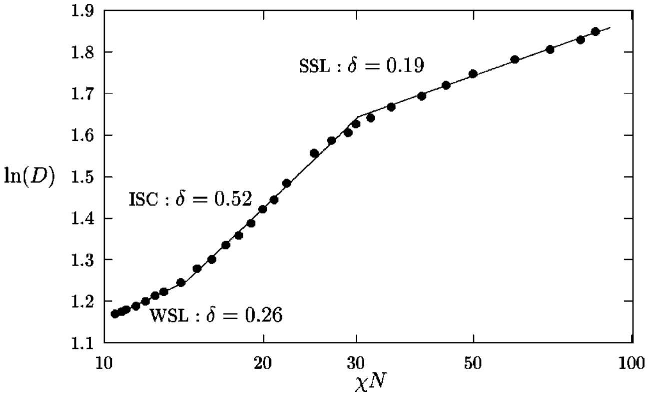

FIG. 8. Plot of $\ln D$ vs $\ln(\chi N)$ for a symmetric lamellar morphology. For high χN, the scaling factor is approximately 0.69. δ is the slope of the best fit segment to the data in three different regions, the weak segregation limit (WSL), the intermediate segregation configuration (ISC), and the strong segregation limit (SSL).

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APPENDIX A

Let Q be a partition function of a melt of polymer chains in external fields φ_1 and φ_1,

$$Q[\varphi_i]=\int \mathcal{D}(\mathbf{r})\exp\{-i\varphi_1\Sigma\phi-i\varphi_2\Delta\phi\}, \tag{A1}$$

where

$$\Delta\phi=(1-f_A)\phi_A-f_A\phi_B, \tag{A2}$$

$$\Sigma\phi=\phi_A+\phi_B-1,$$

and ϕ_A and ϕ_B represent the respective densities of component A and component B. We next expand $\ln Q$ in terms of φ_1 and φ_2. Since Q should be invariant under $\Delta\phi\rightarrow-\Delta\phi$ and $\Sigma\phi\rightarrow-\Sigma\phi$, only even powers of φ_i are present; hence we write

$$\ln Q = \frac{-1}{2!}\int dx_1 dx_2 C_{\alpha\beta}(x_1,x_2)\varphi_\alpha(x_1)\varphi_\beta(x_2) + \frac{1}{4!}\int dx_1\cdots dx_4 C_{\alpha\beta\gamma\delta}(x_1,\cdots,x_4)\varphi_\alpha(x_1)\cdots\varphi_\delta(x_4)+\cdots, \tag{A3}$$

where, e.g.,

$$C_{22}(x_1,x_2)=\langle\Delta\varphi(x_1)\Delta\varphi(x_2)\rangle_0, \tag{A4}$$

$$\begin{aligned} C_{2222}(x_1\ldots x_4) = {} & \langle\Delta\varphi(x_1)\ldots\Delta\varphi(x_4)\rangle_0 \\ & - C_{22}(x_1,x_2)C_{22}(x_3,x_4) \\ & - C_{22}(x_1,x_3)C_{22}(x_2,x_4) \\ & - C_{22}(x_1,x_4)C_{22}(x_2,x_3). \end{aligned} \tag{A5}$$

The statistical averages $\langle\cdots\rangle_0$ are evaluated with a Gaussian distribution. Hence we find

$$C_{22}(q)=S_{AA}(q)-2S_{AB}(q)+S_{BB}(q)$$

with

$$S_{AA}(x)=\frac{2}{x^2}[f_A x+\exp(-f_A x-1)], \tag{A6}$$

$$S_{AB}(x)=\frac{-1}{x^2}[\exp(-f_B x)-1-\exp(-x)+\exp(-f_A x)], \tag{A7}$$

and $x=q^2\sigma^2N/6$. Similar expressions for the other correlation functions, such as C_{2222}, can be derived straightforwardly, but with much more labor. This amounts to calculating all correlation functions $G_{\alpha\beta\gamma\delta}(x_1,x_2,x_3,x_4)$ in a Gaussian distribution of the form

$$\begin{aligned} G_{\alpha\beta\gamma\delta}(x_1,x_2,x_3,x_4) = {} & \int ds_{1,\alpha}\int ds_{2,\beta}\int ds_{3,\gamma}\int ds_{4,\delta} \\ & \times\langle\delta(x_1-x(s_{1,\alpha}))\delta(x_2-x(s_{2,\beta})) \\ & \times\delta(x_3-x(s_{3,\gamma}))\delta(x_4-x(s_{4,\delta}))\rangle_0, \end{aligned} \tag{A8}$$

where $\alpha,\beta,\gamma,\delta=1,2$. Hence C_{2222} will be a linear combination of all these functions.

APPENDIX B

We start from

$$\begin{aligned} \mathcal{Z} = {} & \int \mathcal{D}\Phi\mathcal{D}\Psi\, \exp\{-i\mu_\alpha\Phi_\alpha-\tfrac{1}{2}\mu_\alpha V^{-1}_{\alpha\beta}\mu_\beta-i\rho^0_\alpha\mu_\alpha\} \\ & \times\int\mathcal{D}\varphi\,\exp\{-\tfrac{1}{2}\varphi_\alpha(V^{-1}_{\alpha\beta}+C_{\alpha\beta})\varphi_\beta+i\Xi_\alpha\varphi_\alpha \\ & -\tfrac{1}{12}\Psi_{\alpha\beta}C_{\alpha\beta\lambda\delta}\varphi_\lambda\varphi_\delta\}. \end{aligned} \tag{B1}$$

The integral over φ is Gaussian and can be performed exactly. If we set

$$A_{\alpha\beta}=V^{-1}_{\alpha\beta}+C_{\alpha\beta}+\frac{1}{6}\Psi_{\lambda\delta}C_{\alpha\beta\lambda\delta}, \tag{B2}$$

we have

$$\begin{aligned} \mathcal{Z} = {} & \int \mathcal{D}\Phi\mathcal{D}\Psi\,\exp\left\{\frac{-1}{4!}\Psi_{\alpha\beta}C_{\alpha\beta\lambda\gamma}\Psi_{\lambda\gamma}-\frac{1}{2}\rho^0_\alpha A^{-1}_{\alpha\beta}\rho^0_\beta \right. \\ & \left. -\frac{1}{2}\mathrm{Tr}\ln A_{\alpha\beta}\right\}\int\mathcal{D}\mu\,\exp\left\{-\frac{1}{2}\mu_\alpha V^{-1}_{\alpha\beta}\mu_\beta-i\mu_\alpha\Phi_\alpha \right. \\ & \left. -i\rho^0_\alpha\mu_\alpha+\frac{1}{2}\mu_\alpha V^{-1}_{\alpha\beta}A^{-1}_{\beta\lambda}V^{-1}_{\lambda\gamma}\mu_\gamma+i\mu_\alpha V^{-1}_{\alpha\beta}A^{-1}_{\beta\lambda}\rho^0_\lambda\right\} \end{aligned} \tag{B3}$$

Again the μ integral is Gaussian. After integrating out μ, we have

$$\begin{aligned} \mathcal{Z} = {} & \int \mathcal{D}\Phi\mathcal{D}\Psi\,\exp\left\{\frac{-1}{4!}\Psi_{\alpha\beta}C_{\alpha\beta\lambda\gamma}\Psi_{\lambda\gamma}-\frac{1}{2}\rho^0_\alpha A^{-1}_{\alpha\beta}\rho^0_\beta \right. \\ & \left. -\frac{1}{2}\mathrm{Tr}\ln A_{\alpha\beta}-\frac{1}{2}\zeta_\alpha B^{-1}_{\alpha\beta}\zeta_\beta-\frac{1}{2}\mathrm{Tr}\ln B_{\alpha\beta}\right\} \\ := {} & \int\mathcal{D}\Phi\mathcal{D}\Psi\,\exp\{-\mathcal{F}(\Phi,\Psi)\}. \end{aligned} \tag{B4}$$

If we set

$$T^{-1}=V^{-1}-V^{-1}UV^{-1}, \tag{B5}$$

leave out terms of order $(C_{\alpha\beta\lambda\gamma})^2$, and use the incompressibility constraint, i.e.,

$$\rho^0_2=0, \tag{B6}$$

$$\Phi_1=0,$$

we get after some quite heavy but simple algebra the following form:

$$\begin{aligned} \mathcal{F}(\Phi,\Lambda) = {} & \frac{1}{2}\int dx_1dx_2\Phi(1)T(1,2)\Phi(2) \\ & -\frac{1}{4!}\int dx_1\cdots dx_4\Lambda(1,2)C^{-1}_{2222}(1,2,3,4)\Lambda(3,4) \\ & -\frac{1}{2}\int dx_1\cdots dx_8\Phi(1)(TV^{-1}U)(1,3)\Lambda(4,5) \\ & \times(UV^{-1}T)(5,8)\Phi(8) \\ & +\frac{1}{12}\int dx_1dx_2\Lambda(1,2)U(2,1) \\ & +\frac{1}{12}\int dx_1\cdots dx_6(TV^{-1}U)(1,4)\Lambda(4,5) \\ & \times(UV^{-1}T)(6,1). \end{aligned} \tag{B7}$$

Here

$$\Lambda(x_1,x_2)=\int dx_3 dx_4 C_{2222}(1,2,3,4)\Psi(3,4) \qquad \text{(B8)}$$

and

$$\Phi(x)=\Phi_2(x).$$

Now we can integrate over Λ since the integral is only Gaussian, and we find that

$$\mathcal{Z}=\int \mathcal{D}\Phi \exp\{-\mathcal{F}(\Phi)\}, \qquad \text{(B9)}$$

where

$$\begin{aligned}\Delta\mathcal{F}(\Phi)&=\mathcal{F}(\Phi)-\mathcal{F}_0\\ &=\frac{1}{2\mathscr{V}}\sum_q \Phi(q)\Bigg(T(q)-\frac{1}{6}\frac{1}{\mathscr{V}}\\ &\quad\times\sum_p \frac{C_{2222}(q,-q,p,-p)}{[C_{22}(q)]^2 C_{22}(p)}\Bigg)\Phi(-q)-\frac{1}{24}\frac{1}{(\mathscr{V})^3}\\ &\quad\times\sum_{qpk}\frac{C_{2222}[q,p,k,-(q+p+k)]}{C_{22}(q)C_{22}(p)C_{22}(k)C_{22}(q+p+k)}\\ &\quad\times\Phi(q)\Phi(p)\Phi(k)\Phi(-p-q-k),\end{aligned} \qquad \text{(B10)}$$

and

$$T(q)=\frac{1}{C_{22}(q)}+V_{22}(q) \qquad \text{(B11)}$$

is now, within our approximation, the effective potential for the two-component incompressible copolymer melt.

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