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Comment on the Free Energy Functional of Block Copolymer Melts in the Strong Segregation Limit

TAKAO OHTA*[†] AND KYOZI KAWASAKI[‡]

Department of Physics, Ochanomizu University, Tokyo, 112 Japan, and Department of Physics, Kyushu University, Fukuoka, 812 Japan.

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In a previous study[1] (which will be referred to as I) we have formulated a statistical theory of a microphase separation of block copolymer melts in the strong segregation limit. By ignoring the long-range interaction which appears in the higher order expansion in the free energy functional as shown in ref 2) (which will be referred to as II) we have obtained the equilibrium ordered structures which are in good agreement with the available experiments. An elastic theory has also been developed for gently deformed periodic structures.[3] However the elastic constants obtained are not consistent with those of Wang and Safran[4] calculated recently by a different method. The main difference is the block ratio dependence of the equilibrium period D. Our result shows a rather strong dependence of the block ratio f while Wang and Safran have derived D independent of f.

In this short paper we explore the origin of the above discrepancy. We start with the bilinear free energy functional (3.20) in I:

$$F_2\{\hat{\Psi}\} = \frac{1}{2\rho_0 N}\int_q \left[B(f)q^2 + A(f)\frac{1}{q^2} - \bar{\chi} \right]\hat{\Psi}_q\hat{\Psi}_{-q} \qquad (1)$$

where

$$A(f) = 3/[Nf^2(1-f)^2] \qquad (2)$$

$$B(f) = N/[4f(1-f)] \qquad (3)$$

Under the incompressibility condition $\hat{\Psi}(r)$, the inverse Fourier transform of $\hat{\Psi}_q$, represents the local monomer density of one of the blocks subtracted by its spatial average. N is the molecular weight and ρ_0 the average total monomer density. $\bar{\chi}$ is essentially the Flory–Huggins parameter. In I we used (1) together with the higher order local part $W\{\Psi\}$ in (3.14) in I to study the equilibrium morphology of the microphase-separated state.

The free energy functional (1) gives us the interface width $\xi = (B(f)/\bar{\chi})^{1/2}$. This f-dependent width is valid in a weak segregation near the critical point but is clearly unphysical in the strong segregation limit where ξ is very small compared to the radius of gyration of the blocks and is expected to be insensitive to N and f. In fact this is the origin of the disagreement with the result of Wang and Safran.[4] However one cannot simply ignore the factor $B(f)$ since it arises from the fact that in the limit $f \to 0$ or $f \to 1$, i.e., in a homopolymer melt, the nonuniformity of the local density is inhibited because of the incompressibility condition. It should be mentioned that the above difficulty does not exist in the more general theory put forward in II provided that the surface tension in that theory is chosen to be independent of f.

A similar problem also occurs in a macrophase separation in polymer blends. The short distance part of the free energy functional has been assumed,[5] in the strong segregation limit, to be

$$[\Psi(r)(1-\Psi(r))]^{-1}(\nabla\Psi(r))^2 \qquad (4)$$

where $\Psi(r)$ now denotes the local volume fraction of one of the components of the mixture. If one replaces $\Psi(r)$ in square brackets by the average volume fraction ϕ, it corresponds to the $B(f)$ term in (1). In the strong segregation limit in polymer blends the interface width is proportional to $\chi^{-1/2}$ independent of ϕ.[6] The form of (4) can be made consistent with this fact if Ψ in square brackets in (4) is replaced by $^1/_2$, the value at the center of the interface.

The above consideration suggests that the $B(f)$ term should also be generalized to

$$\frac{N}{4\theta(r)(1-\theta(r))}(\nabla\hat{\Psi}(r))^2 \qquad (5)$$

where

$$\theta(r) = f + \hat{\Psi}(r)/\rho_0 \qquad (6)$$

Note that $\hat{\Psi}(r)$ has been defined to satisfy the condition

$$\int \mathrm{d}r\, \hat{\Psi}(r) = 0 \qquad (7)$$

In the weak segregation the magnitude of $\hat{\Psi}(r)/\rho_0$ is small so that (5) reduces to the original $B(f)$ term. On the other hand since $\theta(r) \approx {}^1/_2$ near the center of the interface in the strong segregation limit, the f dependence does not appear in the interface width. This suggests that in the strong segregation limit $B(f)$, (3) should be replaced by

$$\tilde{B} = N \qquad (8)$$

obtained by replacing f in (7) by $^1/_2$. Thus α defined by (4.8) in I now becomes

$$\tilde{\alpha} = A(f)/\tilde{B} = 3/[Nf(1-f)]^2 \qquad (9)$$

In this way the equilibrium period such as the one in (4.20) of I does not depend on f in accord with that obtained by Wang and Safran. The N dependence of elastic constant obtained by us (B_2 in ref 3) with this new $\tilde{\alpha}$, if B_2 is defined per molecular chain, is now consistent with the elastic constant K in ref 4. However, there is still a discrepancy on the f dependence. That is, our B_2 takes a maximum value at $f = {}^1/_2$ while K becomes a minimum at $f = {}^1/_2$. The reason for this difference is not well understood but may have to do with our truncating the series expansion at low order.[1,2]

It should be emphasized here that in the long-range part of F in (1) the replacement of f by $\theta(r)$ is not necessary since the Fourier component θ_q of $\theta(r)$ is simply given by f in the $q \to 0$ limit because of (7). Furthermore the critical volume fractions for the transitions from a lamellar to a cylindrical structure and from a cylindrical to a spherical (*bcc*) structure given by (4.44) and (4.45), respectively, in I are not altered by this replacement.

In summary we have shown that the generalization of the free energy functional of I in a way suggested here using (5) yields the f-independent period of the microphase-

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[†] Ochanomizu University.

[‡] Kyushu University.

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separated structures as obtained by other treatments.[4] In view of the consistency of the critical volume fractions with the experimental observations,[1,7] our generalized free energy functional is expected to serve as a simple but useful prototype model for studying the morphology of mesophase structures.

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