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LETTER TO THE EDITOR

Formation and stability of double gyroid in microphase-separated diblock copolymers

Makiko Nonomura[1], **Kohtaro Yamada and Takao Ohta**

Institute for Nonlinear Sciences and Applied Mathematics, Graduate School of Sciences, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

E-mail: nonomura@math.sci.hiroshima-u.ac.jp

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Abstract

We investigate the morphology and kinetics of microphase separation of diblock copolymers by means of a mode expansion method. In a weak segregation limit, we employ two-wavenumber approximation to study the formation and stability of a double gyroid structure and derive the phase diagram of the microphase separated states. We have studied the kinetics of structural transitions due to temperature change by solving the coupled set of amplitude equations for the fundamental modes. We focus our attention on the morphological evolution from a double gyroid to a lamellar structure and to a hexagonal structure.

Microphase separation of block copolymers has been studied both theoretically and experimentally for many years. Various mesoscopic structures in equilibrium have been found, such as a lamellar structure, a double gyroid structure, a hexagonal structure of cylindrical domains, and a body centred cubic (BCC) structure of spherical domains [1, 2]. These investigations have focused mainly, however, on the static properties of each mesophase.

Recently, several experiments have been performed on the structural transitions of mesophases [3–5]. Lamellar–gyroid or cylinder–gyroid transitions have been investigated by using scattering techniques and rheological measurements [6–8]. Similar experiments for lamellar–cylinder transitions have been performed in triblock copolymers [9, 10]. The kinetics and fluctuations of lamellar–gyroid transitions have also been investigated in non-ionic surfactant systems [11–14].

In this letter, we shall report on the dynamics of structural transitions in diblock copolymer melts. We start with the time-evolution equation for the local volume fraction of monomers [15]. In the limit of weak segregation, we apply a mode expansion method [16, 17] to derive a coupled set of equations for the amplitude of each fundamental mode. In the previous

[1] Author to whom any correspondence should be addressed.

studies [16, 18], a single-wavenumber approximation was employed for lamellar, hexagonal and BCC structures. Here, however, we are concerned with a double gyroid structure [19] for which two-wavenumber approximation is necessary. The phase diagram for various mesophases is obtained by evaluating the equilibrium solutions of the amplitude equations. Furthermore, the structural evolution from a double gyroid to a lamellar structure and to a hexagonal structure is investigated by solving numerically the amplitude equations. The stability of mesophases without including a double gyroid has been analysed theoretically [20]. Structural transitions omitting a double gyroid have also been studied [17, 18, 21]. The cylinder-to-gyroid transition has been discussed based on the free-energy surface without solving the dynamics directly [22]. In these aspects, to the authors' knowledge, the kinetics of morphological transitions from a double gyroid to other structures have until now not been studied theoretically.

We start with the free energy functional for A–B type diblock copolymers [23]. Imposing the incompressibility condition $\phi_A(\vec{r}) + \phi_B(\vec{r}) = 1$, where $\phi_A(\phi_B)$ is the local volume fraction of A(B) monomers, the free-energy functional can be written in terms of the local volume fraction difference $\phi = \phi_A - \phi_B$ as

$$F[\phi] = \int \mathrm{d}\vec{r} \left[\frac{1}{2}(\nabla\phi)^2 + W(\phi) \right] + \frac{\alpha}{2} \int \mathrm{d}\vec{r}\, \mathrm{d}\vec{r}\,' G(\vec{r}, \vec{r}\,')(\phi(\vec{r}) - \bar{\phi})(\phi(\vec{r}\,') - \bar{\phi}), \tag{1}$$

where

$$W(\phi) = -\frac{\tau}{2}\phi^2 + \frac{g}{4}\phi^4, \tag{2}$$

$$-\nabla^2 G = \delta(\vec{r} - \vec{r}\,'). \tag{3}$$

The coefficients α and g are positive constants and $\bar{\phi}$ stands for the spatial average of ϕ. The parameter τ is negative for the high-temperature uniform phase, whereas it is positive for the microphase-separated state at low temperature.

The time-evolution equation for ϕ is given by [15]

$$\frac{\partial\phi}{\partial t} = \nabla^2 \frac{\delta F}{\delta\phi} = \nabla^2(-\nabla^2\phi - \tau\phi + g\phi^3) - \alpha(\phi - \bar{\phi}), \tag{4}$$

where we have ignored the possible non-local effect in the mobility and it has been set to unity. This equation has been used for numerical simulations to study the kinetics of microphase separation in two dimensions [15]. Quite recently, Teramoto and Nishiura [24] have shown, by using three-dimensional simulations, that equation (4) has a double gyroid structure as a stable equilibrium solution in a certain parameter region. In their study, however, the simulations were carried out in a small system where the system size was the equilibrium period of a double gyroid.

In this letter, we do not perform direct simulations of equation (4). Since morphological transitions of a double gyroid to other structures are generally accompanied by a change of equilibrium period, one has to provide a sufficiently large system to eliminate the finite size effects. However, this is technically demanding in three dimensions. Therefore, we use the mode expansion approach to derive the time-evolution equations for the amplitude of the relevant modes.

It is well known that a double gyroid structure can be approximated by the following level set equation:

$$\begin{aligned} 0 = {} & 8(1-s)[\sin 2x \sin z \cos y + \sin 2y \sin x \cos z + \sin 2z \sin y \cos x] \\ & - 4s[\cos 2x \cos 2y + \cos 2y \cos 2z + \cos 2z \cos 2x] - t, \end{aligned} \tag{5}$$

where s and t are the parameters [25]. The relations with the physical quantities will be given

below equation (8). Using equation (5), we expand ϕ as

$$\phi(\vec{r},t) = \bar{\phi} + \left[\sum_{i=1}^{12} a_i(t)\mathrm{e}^{\mathrm{i}\vec{q}_i\cdot\vec{r}} + \sum_{i=1}^{6} b_i(t)\mathrm{e}^{\mathrm{i}\vec{p}_i\cdot\vec{r}} + \text{c.c.}\right], \tag{6}$$

where a_i and b_i are real amplitudes, c.c. means complex conjugate, and the fundamental reciprocal vectors $\vec{q}_i$ and $\vec{p}_j$ for a double gyroid are defined by

$$\begin{array}{lll}
\vec{q}_1 = C_Q(2,-1,1) & \vec{q}_2 = C_Q(-2,1,1) & \vec{q}_3 = C_Q(2,1,-1) \\
\vec{q}_4 = C_Q(2,1,1) & \vec{q}_5 = C_Q(1,2,-1) & \vec{q}_6 = C_Q(1,-2,1) \\
\vec{q}_7 = C_Q(-1,2,1) & \vec{q}_8 = C_Q(1,2,1) & \vec{q}_9 = C_Q(-1,1,2) \\
\vec{q}_{10} = C_Q(1,1,-2) & \vec{q}_{11} = C_Q(1,-1,2) & \vec{q}_{12} = C_Q(1,1,2) \\
\vec{p}_1 = C_P(2,2,0) & \vec{p}_2 = C_P(2,-2,0) & \vec{p}_3 = C_P(0,2,2) \\
\vec{p}_4 = C_P(0,2,-2) & \vec{p}_5 = C_P(2,0,2) & \vec{p}_6 = C_P(-2,0,2),
\end{array} \tag{7}$$

with $C_Q = Q/\sqrt{6}$ and $C_P = P/(2\sqrt{2})$. To make equation (6) identical with equation (5) for a double gyroid, we note the relation

$$Q^2 = \tfrac{3}{4}P^2. \tag{8}$$

In the spirit of the mode expansion, we shall impose this not only in equilibrium but also during the structural transition. A gyroid structure is expressed as $|a_i| = a_g \neq 0$ and $|b_j| = b_g \neq 0$ ($i = 1,\ldots,12$; $j = 1,\ldots,6$). If one defines the iso-surface given by $\phi = 0$, the constants a_g, b_g and $\bar{\phi}$ are related to s and t in equation (5) as $a_g = c(1-s)$, $b_g = -cs$ and $\bar{\phi} = -ct$ with an arbitrary constant c. A lamellar structure and a hexagonal structure can be obtained as a special case. For example, if only a_1 is finite, then it expresses a lamellar structure and if only a_2, a_6 and a_{10} are finite with the same magnitude, then it expresses a hexagonal structure. A BCC structure cannot be expressed by the 12 modes of a_i. (It can be represented by using the b_i modes.) However, since we are not concerned with the transition from a double gyroid to a BCC structure, we do not go into the further details of this.

The vectors shown in (7) are obtained easily by comparing (5) with (6). It is noted that they are not independent but satisfy some relations. Several examples are listed as

$$\begin{array}{ll}
\vec{q}_1 - \vec{q}_4 - \vec{q}_{11} + \vec{q}_{12} = 0 & \vec{q}_5 + \vec{q}_6 + \vec{q}_7 - \vec{q}_8 = 0 \\
\vec{q}_2 + \vec{q}_7 - \vec{q}_9 + \vec{p}_2 = 0 & \vec{q}_3 + \vec{q}_6 + \vec{q}_9 - \vec{p}_5 = 0 \\
\vec{p}_1 - \vec{p}_2 - \vec{p}_3 - \vec{p}_4 = 0 & \vec{q}_1 + \vec{q}_3 - \vec{p}_1 - \vec{p}_2 = 0 \\
\vec{q}_2 + \vec{q}_4 - \vec{p}_3 = 0 \qquad \vec{q}_1 + \vec{q}_7 - \vec{q}_{12} = 0 & \vec{p}_2 + \vec{p}_3 - \vec{p}_5 = 0.
\end{array} \tag{9}$$

The expansion (6) neither takes account of the spatial variation of the amplitudes nor contains the phase variable, since the amplitudes are assumed to be real. In the present approach, therefore, nucleation and growth of localized new structures cannot be investigated. However, our main concern is the domain evolution in the transitions from a double gyroid. Such a study, although it would clarify the fundamental mechanism of structural evolutions, has so far not been carried out intensively. If one considers the elastic effect of the mesoscopic structures, then the phase variable must be introduced. However, when there are 18 modes, as in the present method, this generalization is not easy and is left for a future study.

Substituting equation (6) into equation (4) and ignoring the higher harmonics, which is justified in the weak segregation limit, we obtain a set of coupled equations for the amplitudes. For instance, equation for a_1 is given by

$$\frac{\mathrm{d}a_1}{\mathrm{d}t} = (-Q^4 + \tau Q^2 - \alpha)a_1 - 3gQ^2\left[(\bar{\phi}^2 - {a_1}^2)a_1 + 2\left(\sum_{i=1}^{12} {a_i}^2 + \sum_{j=1}^{6} {b_j}^2\right)a_1\right.$$

$$+ 2(\bar{\phi}a_3b_4 + \bar{\phi}a_7a_{12} + a_1b_2b_5 + a_2a_3a_4 + a_2a_5a_8 + a_2a_6a_7 + a_3b_1b_2 + a_3b_1b_5 + a_3b_2b_6 + a_3b_5b_6 + a_4a_9a_{10} + a_4a_{11}a_{12} + a_5a_{10}b_2 + a_5a_{10}b_5 + a_5a_{12}b_6 + a_6a_9b_3 + a_6a_9b_6 + a_6a_{11}b_2 + a_6a_{11}b_4 + a_6a_{11}b_5 + a_7a_{10}b_1 + a_8a_9b_4 + a_8a_{11}b_1 + a_8a_{11}b_3)\Big]. \tag{10}$$

Similarly, the free energy (1) can also be written in terms of a_i, b_i and P as

$$F_{amp} = F(\{a_i\}, \{b_i\}, P). \tag{11}$$

Since it is lengthy, we do not write down its whole expression. The part which depends on P is given by

$$F_{nl} = \left(\frac{3}{4}P^2 + \frac{4\alpha}{3P^2}\right)\sum_{i=1}^{12} {a_i}^2 + \left(P^2 + \frac{\alpha}{P^2}\right)\sum_{i=1}^{6} {b_i}^2, \tag{12}$$

where we have used the relation (8). The equilibrium value of P is obtained by the variation of (12) with respect to P. To see the time evolution of the period, we employ relaxation dynamics for the wavenumber:

$$\frac{\mathrm{d}P^2}{\mathrm{d}t} = -h\frac{\partial F_{amp}}{\partial P^2} = -h\left[\left(\frac{3}{4} - \frac{4\alpha}{3P^4}\right)\sum_{i=1}^{12} {a_i}^2 + \left(1 - \frac{\alpha}{P^4}\right)\sum_{j=1}^{6} {b_j}^2\right], \tag{13}$$

where h is a positive constant.

To explore the equilibrium structures and kinetics of transitions between the different structures, we have carried out numerical simulations of the coupled set of equations for a_i, b_i and equation (13). The stable equilibrium structures are obtained, starting with a disordered state where $a_i = b_i = 0$ with small random numbers imposed. The time increment is set as 0.01. We have fixed the parameters as $\alpha = g = h = 1$. An example of the domain evolution is shown in figure 1 for $\tau = 2.2$ and $\bar{\phi} = -0.1$, where a double gyroid structure is formed asymptotically. The final values of the amplitudes are given by $a_1 = a_2 = a_5 = a_6 = a_{11} = a_{12} = -0.064\,56$, $a_3 = a_4 = a_7 = a_8 = a_9 = a_{10} = 0.064\,56$ and $b_i = -0.023\,53$ ($i = 1, \ldots, 6$). We have performed simulations by changing the parameters τ and $\bar{\phi}$ to evaluate the free energy (11) for each structure. In this way, we obtain the phase diagram in τ–$\bar{\phi}$ plane displayed in figure 2. The full, dotted and broken curves in this figure indicate the phase boundaries between lamellae and hexagons, between hexagons and BCC, and between BCC and the disordered state, respectively, which were obtained analytically by means of the single-wavenumber expansion [18]. We have found that there are several other stable solutions in the amplitude equations. The free energies for such structures are higher than those in figure 2 and therefore they are only metastable. The phase diagram, including the double gyroid phase shown in figure 2, is consistent with the previous ones [2, 26, 27].

Now we study the kinetics of the morphological transitions. Since these structural transitions are first order, we must add random forces to the amplitude equations for a_i and b_i to initiate the transitions. The random force is not added to equation (13). Figure 3 shows the structural evolution from the double gyroid to a hexagonal structure. Initially we provide a double gyroid structure for $\tau = 2.4$ and $\bar{\phi} = -0.17$ and then change the value of τ to $\tau = 2.1$. The initial values of the amplitudes are $a_1 = a_4 = a_5 = a_8 = a_9 = a_{12} = -0.090\,38$, $a_2 = a_3 = a_6 = a_7 = a_{10} = a_{11} = 0.090\,38$ and $b_i = -0.040\,49$ ($i = 1, \ldots, 6$). The magnitude of the random forces is chosen to be 0.05. Deformation and rupture of domains are clearly seen in figure 3. The final nonzero amplitudes for the hexagonal structure are given by

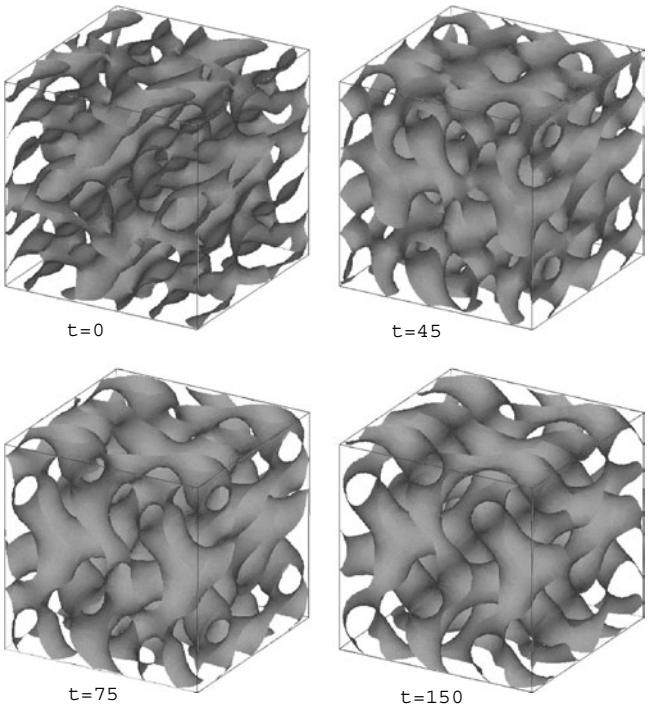

Figure 1. The formation of a double gyroid for $\tau = 2.2$ and $\bar{\phi} = -0.1$, starting from the disordered state.

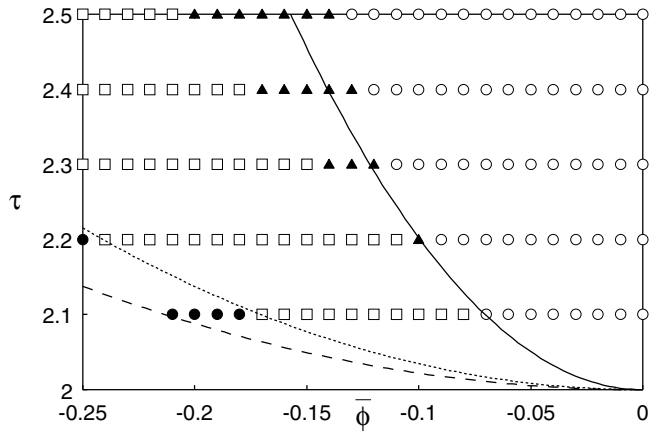

Figure 2. Phase diagram. The region indicated by white circles, black triangles, white squares and black circles is the stable phase of lamellae, hexagons, double gyroid and BCC, respectively.

$a_4 = a_5 = -a_{11} = -0.079\,20$. This means that the cylindrical axis of the hexagons is parallel to the $(-1, 1, 1)$ direction.

The morphological transition from a double gyroid to a lamellar structure is shown in figure 4, where $\bar{\phi} = -0.1$ and τ is changed from $\tau = 2.2$ to 2.5. The magnitude of the random forces is chosen in this case to be 0.26. This fairly large random force is necessary,

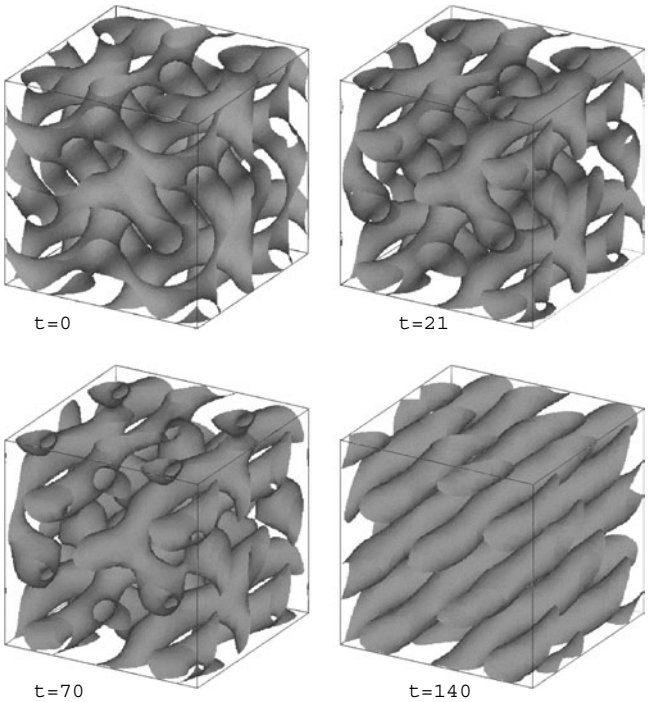

Figure 3. The structural evolution from a double gyroid to a hexagonal structure for $\bar{\phi} = -0.17$ and $\tau = 2.1$.

otherwise the transition from double gyroid is not triggered within an accessible simulation time. The initial amplitudes are set to be $a_1 = a_4 = a_5 = a_8 = a_9 = a_{12} = -0.064\,56$, $a_2 = a_3 = a_6 = a_7 = a_{10} = a_{11} = 0.064\,56$ and $b_i = -0.023\,53$ ($i = 1, \ldots, 6$). The final nonzero amplitude is $a_{11} = 0.3958$. Comparing with figure 3, one finds that the transition from a double gyroid to a lamellar structure is quite slow. The initial double gyroid structure persists for a long period up to about $t = 26\,400$ and then changes to a transient structure given by $a_2 = -a_4 = 0.079\,18$, $a_5 = -a_6 = -a_{10} = -a_{11} = -0.1730$, $b_3 = 0.059\,70$ and the other vanishing amplitudes. After spending time in the intermediate state of the transition process, it changes to the final lamellar structure. It is found that this transient structure is close to one of the metastable solutions of the amplitude equations and that this is different from the so-called perforated lamellar structure [6, 28]. Note that the gyroid-to-cylinder transition shown in figure 3 does not exhibit any apparent intermediate structure.

In summary, we have studied the morphological transitions in microphase separation in diblock copolymer melts. Despite its simplicity, we have confirmed that the free energy (1) admits a double gyroid solution which is indeed the most stable structure in a finite parameter regime among the solutions of the amplitude equations found numerically. In order to verify its absolute stability, we need to look for all the stationary solutions of the amplitude equation. However, this is a difficult task and is not explored here. By extending the mode expansion method to take account of two kinds of fundamental wavevectors, we have shown—for the first time—the dynamics of the transition from a double gyroid to a lamellar structure as well as to a hexagonal structure. Since the double gyroid does not exist in the strong segregation region [2], this mode expansion valid in the weak segregation limit is a consistent approximation in the present theory.

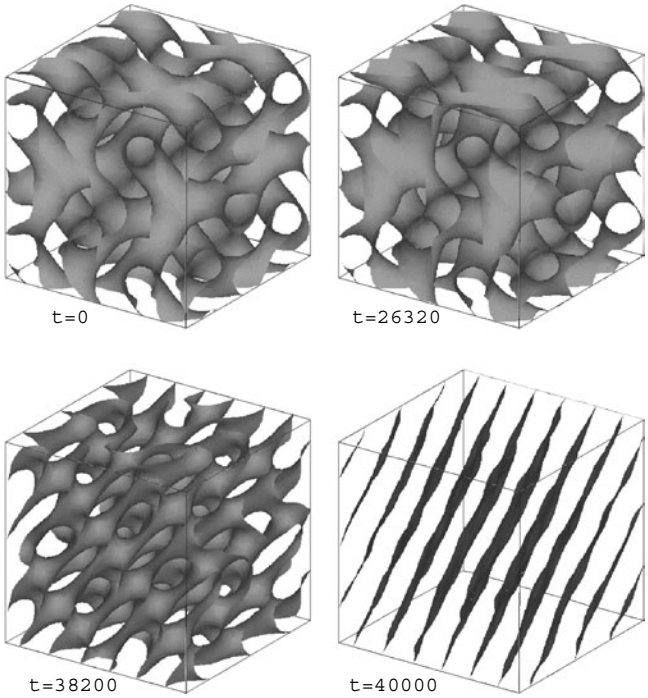

Figure 4. The structural evolution from a double gyroid to a lamellar structure for $\bar{\phi} = -0.1$ and $\tau = 2.5$.

It is emphasized that the equilibrium value of $P^2 = 4/3$ for $\alpha = 1$ in the single-wavenumber approximation cannot be used for a double gyroid structure. This approximation makes the stable region of a double gyroid structure vanish in the phase diagram. Therefore, although the difference from $P^2 = 4/3$ is quite small, we must use the proper equilibrium value $P^2 \approx 1.30$, which is given by the solution of equation (13) and is insensitive to the values of τ and $\bar{\phi}$. This implies that, when one studies the transition between a double gyroid and other structures, the change of the period must be taken properly into account.

An insufficient aspect of the present method is that we have no systematic way of deriving the equation for P. In the theory described above, we have used equation (13) simply given by the variation of the free energy. We have verified at least that the kinetics and the domain morphology during the transitions are not altered qualitatively by changing the magnitude of the coefficient h. Since the phase diagram tells us the parameters where a double gyroid exists, we may carry out simulations of equation (4) directly for the kinetics of transitions. These results, together with further systematic study of morphological transitions, will be given elsewhere in the near future.

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