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LETTER TO THE EDITOR

Fddd structure in AB-type diblock copolymers

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Abstract

It is well known that lamellar structure, hexagonal structure of cylinder domains, gyroid and body-centred cubic structure of spherical domains all exist as equilibrium structures in AB-type diblock copolymers. We shall show in the present letter that, in addition to the above four phases, there is another equilibrium phase, the so-called *Fddd* structure which is an interconnected but uniaxial structure. We confirm this conclusion by two different methods. One is the mode-expansion including a substantial number of modes. The other is direct simulations of the time-evolution equation in three dimensions.

1. Introduction

Block copolymers exhibit various mesoscopic structures due to microphase separation at low temperatures. It is well known that lamellae, hexagonally packed cylinders, body-centred cubic (bcc) spheres and gyroid structures exist as equilibrium structures of AB-type diblock copolymer melts [1, 2]. The relative stability of these equilibrium structures depends on the block ratio, the interaction strength between monomers and temperature.

It has not been fully explored whether there are other equilibrium structures apart from the four basic structures. In ABC-type linear triblock copolymers it has been found experimentally that an *Fddd* structure appears in thermal equilibrium [3]. Tyler and Morse have investigated this problem theoretically by means of a self-consistent field theory (SCFT) and have found that an *Fddd* phase can appear in the phase diagram as the most stable equilibrium structure both in ABC triblock copolymers and in AB diblock copolymers [4].

In our previous paper, we studied the morphological transitions of diblock copolymers by using a mode expansion method [5]. The time evolution of the microphase-separated structures was investigated by solving the amplitude equations of various fundamental modes. An *Fddd* structure was obtained as a stable time-independent solution. However, the free energy of the *Fddd* structure was not the lowest, so this was only a metastable state. In fact, the *Fddd* structure appeared in the process of the structural transitions such as those between lamellar and gyroid structures [5]. Quite recently, Takenaka *et al* have observed an *Fddd* structure during

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the lamellar–gyroid transition process [6] and in thermal equilibrium in AB diblock copolymer melts [7]. The former is consistent with our prediction [5].

The purpose of the present paper is to investigate the *Fddd* structure in thermal equilibrium and clarify the discrepancy between the results of [4] and [5]. We start with the following free energy functional and the time-evolution equation [8–10]

$$F\{\phi\} = \int \mathrm{d}\vec{r}\left[\frac{1}{2}(\nabla\phi)^2 - \frac{\tau}{2}\phi^2 + \frac{g}{4}\phi^4\right] + \frac{\alpha}{2}\int \mathrm{d}\vec{r}\int \mathrm{d}\vec{r}\,' G\left(\vec{r},\vec{r}\,'\right)\left(\phi(\vec{r}) - \bar{\phi}\right)\left(\phi\left(\vec{r}\,'\right) - \bar{\phi}\right), \tag{1}$$

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

where $\phi(\vec{r})$ represents the local concentration difference between A and B monomers. The parameters in the free energy (1), τ, g, and α are positive in the microphase-separated state. Throughout this paper, we shall put $\alpha = g = 1$. The quantity $\bar{\phi}$ represents the spatial average of ϕ. The function $G(\vec{r},\vec{r}\,')$ in the second term of (1) is defined through the following relation:

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

In the present study, we shall employ two computational methods. One is the mode-expansion method. In this method, the local concentration field ϕ is Fourier expanded in terms of the fundamental reciprocal lattice vectors and their higher harmonics and it is valid in the weak-segregation region. As described above, we found a metastable *Fddd* structure and predicted that it appears as an intermediate state in the transitions between gyroid and lamellar structures [5]. In the present paper, we carry out the above analysis in a more precise manner to confirm whether the *Fddd* structure is metastable or stable.

Another method is to solve the time-evolution equation (2) directly in three dimensions. The equilibrium solution ϕ for each structure is substituted into the free energy functional (1) to examine the relative stability of the structures. This method is time consuming, but more reliable compared with the mode expansion truncated up to finite number of modes. In the numerical simulations under the periodic boundary condition, the system size is an important parameter because each structure must be commensurate with the system size to avoid any artefacts. That is, the steady solution of the time-evolution equation is forced to accommodate the periodicity of the system, which is not necessarily a true equilibrium period (times integers). Therefore it is necessary to examine the equilibrium free energy of lamellar, hexagonal, gyroid and *Fddd* structures by changing the system size and searching for the region in the τ–$\bar{\phi}$ plane where the free energy of the *Fddd* structure is lowest.

This letter is organized as follows. In section 2, we investigate the stability focusing on the *Fddd* structure using the mode-expansion method. In section 3, we carry out numerical simulations of the time-evolution equation (2) in three dimensions. From these two independent methods, we conclude that the *Fddd* structure is one of the equilibrium structures. A summary and discussion are given in section 4.

2. Mode expansion method

First, we employ the mode-expansion method and expand ϕ as follows:

$$\phi(\vec{r}) = \bar{\phi} + \left[\sum_{l=1}^{12} a_l(t)\,\mathrm{e}^{\mathrm{i}\vec{q}_l\cdot\vec{r}} + \sum_{m=1}^{6} b_m(t)\,\mathrm{e}^{\mathrm{i}\vec{p}_m\cdot\vec{r}} + \sum_{n=1}^{12} c_n(t)\,\mathrm{e}^{\mathrm{i}\vec{k}_n\cdot\vec{r}} + \sum_{j=1}^{3} d_j(t)\,\mathrm{e}^{\mathrm{i}\vec{s}_j\cdot\vec{r}} + \mathrm{c.c.}\right]. \tag{4}$$

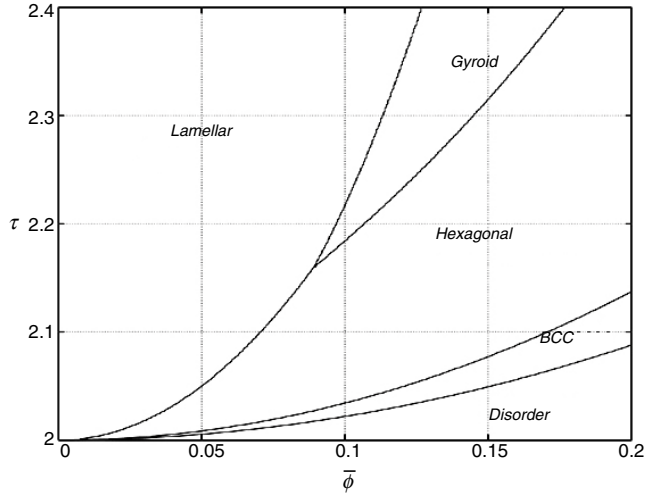

Figure 1. Phase diagram in the τ–$\bar{\phi}$ plane within the two-mode expansion [5].

The reciprocal vectors $\vec{q}_l$ and $\vec{p}_m$ have been introduced in the previous two-mode expansion [5] and are given by

$$\begin{aligned}
&\vec{q}_1 = C_Q\,(2,-1,1)\,, && \vec{q}_2 = C_Q\,(-2,1,1)\,, && \vec{q}_3 = C_Q\,(-2,-1,1)\,,\\
&\vec{q}_4 = C_Q\,(2,1,1)\,, && \vec{q}_5 = C_Q\,(-1,-2,1)\,, && \vec{q}_6 = C_Q\,(1,-2,1)\,,\\
&\vec{q}_7 = C_Q\,(-1,2,1)\,, && \vec{q}_8 = C_Q\,(1,2,1)\,, && \vec{q}_9 = C_Q\,(1,-1,-2)\,,\\
&\vec{q}_{10} = C_Q\,(1,1,-2)\,, && \vec{q}_{11} = C_Q\,(-1,1,-2)\,, && \vec{q}_{12} = C_Q\,(-1,-1,-2)\,,\\
&\vec{p}_1 = C_Q\,(2,2,0)\,, && \vec{p}_2 = C_Q\,(2,-2,0)\,, && \vec{p}_3 = C_Q\,(0,2,2)\,,\\
&\vec{p}_4 = C_Q\,(0,-2,2)\,, && \vec{p}_5 = C_Q\,(2,0,2)\,, && \vec{p}_6 = C_Q\,(-2,0,2)\,,
\end{aligned} \tag{5}$$

where the coefficients are chosen as

$$C_Q \equiv \frac{Q}{\sqrt{6}}. \tag{6}$$

The unknown magnitude Q is to be determined by the minimization of the equilibrium free energy.

The reciprocal lattice vectors listed above have been obtained from the level surface representation of a gyroid structure [11]:

$$\begin{aligned}
0 = {} & 8\,(1-s)\left[\sin 2x \sin z \cos y + \sin 2y \sin x \cos z + \sin 2z \sin y \cos x\right]\\
& - 4s\left[\cos 2x \cos 2y + \cos 2y \cos 2z + \cos 2z \cos 2x\right] - u,
\end{aligned} \tag{7}$$

where s and u are the parameters. It is noted that these 18 modes of $\vec{q}_l$ ($l = 1, \ldots, 12$) and $\vec{p}_m$ ($m = 1, \ldots, 6$) are the minimal modes to represent lamellar, hexagonal, bcc, gyroid and *Fddd* structures. The phase diagram obtained by using these 18 modes [5] is shown in figure 1.

In the present letter, we employ more accurate mode expansion by taking account of higher modes $\vec{k}_n$ and $\vec{s}_j$ defined by

$$\begin{aligned}
&\vec{k}_1 = C_Q\,(1,3,0)\,, && \vec{k}_2 = C_Q\,(-1,3,0)\,, && \vec{k}_3 = C_Q\,(3,1,0)\,,\\
&\vec{k}_4 = C_Q\,(-3,1,0)\,, && \vec{k}_5 = C_Q\,(0,1,3)\,, && \vec{k}_6 = C_Q\,(0,-1,3)\,,\\
&\vec{k}_7 = C_Q\,(0,3,1)\,, && \vec{k}_8 = C_Q\,(0,-3,1)\,, && \vec{k}_9 = C_Q\,(3,0,1)\,,\\
&\vec{k}_{10} = C_Q\,(3,0,-1)\,, && \vec{k}_{11} = C_Q\,(1,0,3)\,, && \vec{k}_{12} = C_Q\,(1,0,-3)\,,\\
&\vec{s}_1 = C_Q\,(4,0,0)\,, && \vec{s}_2 = C_Q\,(0,4,0)\,, && \vec{s}_3 = C_Q\,(0,0,4)\,.
\end{aligned} \tag{8}$$

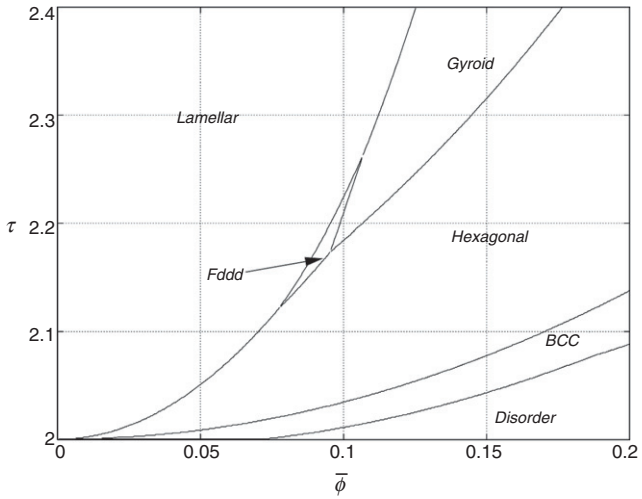

Figure 2. New phase diagram in the τ–$\bar{\phi}$ plane.

We have chosen these modes by the following consideration. First, we solve the time-evolution equation (2) in three dimensions, tuning the system size carefully to obtain an *Fddd* solution as a time-independent solution. Next, we carry out the Fourier transformation of this *Fddd* solution to identify the Bragg peaks. In this way, the new modes $\vec{k}_n$ and $\vec{s}_j$ are obtained as the next higher harmonics (see table 1).

It is noted that the 33 reciprocal vectors given by (5) and (8) are not necessarily independent but satisfy some relations such as

$$\begin{aligned} &\vec{q}_1+\vec{q}_2-\vec{q}_3-\vec{q}_4=0, \qquad \vec{q}_1-\vec{q}_3-\vec{p}_1-\vec{p}_2=0,\\ &\vec{q}_1-\vec{k}_2-\vec{k}_9+\vec{s}_2=0, \qquad \vec{p}_1-\vec{k}_3+\vec{k}_6+\vec{k}_{12}=0,\\ &\vec{q}_1+\vec{q}_7+\vec{q}_{12}=0, \qquad \vec{q}_1+\vec{p}_6-\vec{k}_6=0, \qquad \vec{p}_5+\vec{p}_6-\vec{s}_3=0. \end{aligned} \tag{9}$$

Substituting equation (4) into (2) and ignoring the higher harmonics, we can obtain a closed set of the amplitude equations. Similarly, substituting equation (4) into (1), the free energy is given in terms of the amplitudes a_l, b_m, c_n and d_j and the wavenumber Q. However, we do not write them down here because they are too lengthy.

Finally, we mention that the equilibrium period of microphase-separated structures should be determined by the minimization of the free energy [5]

$$\frac{\partial F(a_l, b_m, c_n, d_j, Q)}{\partial Q} = 0. \tag{10}$$

We have solved the set of the amplitude equations together with equation (10) and obtained the equilibrium solutions corresponding to lamellar, hexagonal, bcc, gyroid, *Fddd* and perforated lamellar structures. The last one will be discussed separately elsewhere. By using these solutions, the equilibrium free energy $F(a_l, b_m, c_n, d_j, Q)$ for each structure is evaluated. The phase diagram in figure 2 has been obtained in this way.

We emphasize that there is a small but finite area near the intersection point of lamellar, hexagonal and gyroid phases where the *Fddd* structure is the mostly stable equilibrium structure. The real space image of the *Fddd* structure is shown in figure 3(a), whereas the Bragg points are shown in figure 3(b). This phase diagram is consistent with that obtained by Tyler and Morse by SCFT [4].

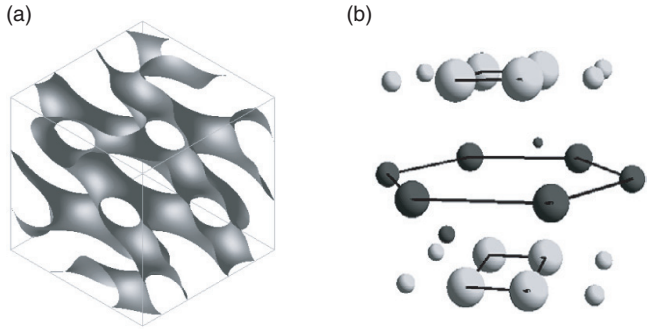

Figure 3. (a) *Fddd* structure and (b) the Bragg points. The Bragg points on the same plane are drawn by the same grey scale and the size of spheres indicates the relative strength of Bragg peaks. The Bragg points for the modes with the amplitudes a_i and b_j are indicated by the spots connected by the lines (a hexagon and two squares) whereas the new modes considered in the present study are shown by the tiny isolated $(8 + 2)$ spots.

Table 1. Representative values of the amplitudes of a gyroid and an *Fddd* structure for $\tau = 2.3$ and $\bar{\phi} = 0.13$.

Gyroid		*Fddd*	
Amplitudes	Absolute value	Amplitudes	Absolute value
$a_i (i = 1, \ldots, 12)$	0.078 816	a_5, a_6, a_{10}, a_{11}	0.132 386
$b_j (j = 1, \ldots, 6)$	0.033 577	a_2, a_4	0.068 444
$d_k (k = 1, 2, 3)$	0.001 795	b_3	0.039 548
		c_1, c_2, c_{11}, c_{12}	0.008 913
		d_1	0.006 094

3. Direct simulations of the time-evolution equation

In this section we carry out direct numerical simulations of equation (2) in three dimensions to confirm the results obtained by the mode expansion method in the preceding section.

It should be noted that the equilibrium period of the structures is unknown before solving the equation. Therefore we have to repeat simulations by changing the system size to find the optimal system size which gives us the lowest free energy for each structure. Because this is time consuming, simulations are performed in a small system such that only one period of the structure is contained. The cubic system is divided into $64 \times 64 \times 64$ cells by varying the cell size and the periodic boundary conditions are imposed.

We obtain the four equilibrium solutions of lamellar, hexagonal, gyroid and *Fddd* structures as asymptotic time-independent solutions. Substituting these solutions into the free energy functional (1), the equilibrium free energy of each structure can be calculated. Figures 4(a)–(c) display the results, respectively, for $\tau = 2.15$, $\tau = 2.19$ and $\tau = 2.2$ and for $\bar{\phi} = 0.097$. The horizontal axis and the vertical axis are the system size and the free energy per unit volume, respectively. Note that the scale of the vertical axis is quite small. Nevertheless, it is evident from these figures that the free energy per unit volume of the *Fddd* structure is lowest for $\tau = 2.19$ and $\bar{\phi} = 0.097$, whereas the free energy of a hexagonal structure is lowest for $\tau = 2.15$ and that of a lamellar structure is lowest for $\tau = 2.2$.

4. Summary and discussion

To summarize, we have investigated the stability of the *Fddd* structure in AB diblock copolymers by means of two alternative methods. One is the mode expansion, taking account

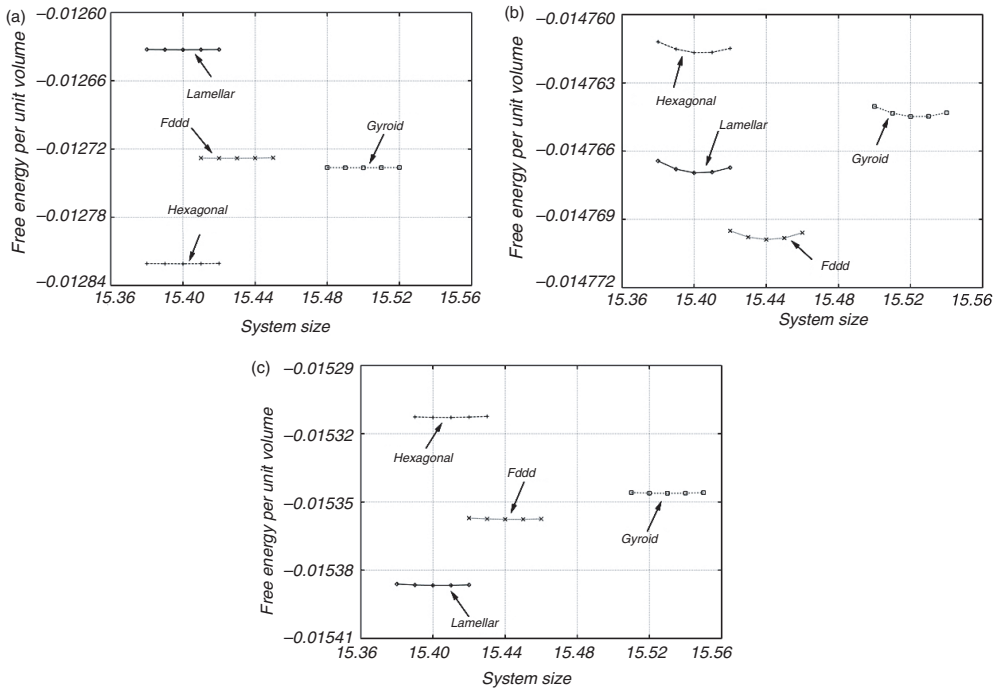

Figure 4. The free energy per unit volume of lamellar, hexagonal, gyroid and *Fddd* structures for (a) $\tau = 2.15$ (b) $\tau = 2.19$ and (c) $\tau = 2.2$ and for $\bar{\phi} = 0.097$. The scale of the vertical axis of (b) is smaller than those of (a) and (c) by the factor of one order of magnitude.

of some higher harmonics. We have found that the *Fddd* structure is most stable in some parameters as shown in figure 2. This result agrees with that obtained by SCFT [4] although the area for the *Fddd* structure is somewhat smaller compared to that obtained in [4].

The amplitudes for the *Fddd* structure are compared with those of the gyroid in table 1. Note that the amplitudes for the *Fddd* structure decrease more slowly for higher harmonics than those of the gyroid, where the magnitudes of d_j in equation (4) are negligible. In our previous paper, we did not consider the modes with the amplitudes c_i and d_j to evaluate the equilibrium free energy of the *Fddd* structure so that it did not appear in the equilibrium phase diagram.

In order to confirm the results obtained by the mode-expansion method we have carried out direct three-dimensional simulations of the time-evolution equation (2). The free energy for each structure is evaluated by substituting the obtained data into equation (1). We have found that there is a definite parameter regime where an *Fddd* structure is most stable. The exact values of τ and $\bar{\phi}$ are not completely consistent with the phase diagram shown in figure 2 obtained by the mode expansion. This is due to the approximation of the mode expansion truncated up to a finite number of modes and the fact that the convergence of the expansion is especially slow for the *Fddd* structure, as shown in table 1.

Finally we make a remark about the present methods. The mode expansion as well as the self-consistent theory [4] reply on the symmetry of the structures, and hence are unable to predict any new structures which are not presupposed. However, the direct simulations of the time-evolution equation with random noises are, in principle, free from this restriction. In fact, the *Fddd* structure was obtained in [12] in three-dimensional simulations although we were unable to identify it with the *Fddd* structure at that time.

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