Formation of periodic minimal surface structures in polymeric materials

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We shall review our recent theoretical study of formation of curious mesoscopic structures in soft matter, especially in diblock copolymers. Universality of the mechanism of forming these structures is emphasized in terms of the coarse-grained approach.

A binary mixture of A-B polymer melts undergoes macrophase separation at low temperature if there is an repulsive interaction between A and B monomers. If these different polymer chains are connected chemically at the chain ends macrophase separation is impossible and what happens is microphase separation where A-rich domains and B-rich domains are arrayed alternatively like a lamellar structure with the typical spatial period of the order of $50nm$ comparable to the size of each polymer chain.[1] When the molecular weights of A and B blocks are different, other morphologies appear such as gyroid, hexagonal structures of cylindrical domains and body centered cubic structure of spherical domains. The gyroid structure is an interconnected domain structure with cubic symmetry, whose surface is approximately represented by a minimal surface as shown in Fig. 1(a) together with its Bragg points in Fig. 1(b).

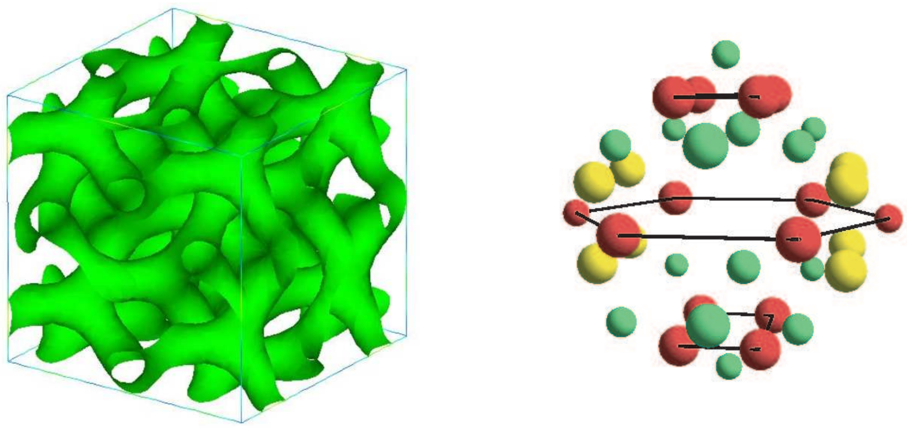

Fig. 1. (a) Gyroid structure and (b) the Bragg points of the gyroid structure. The size of the Bragg point is proportional to the intensity.[2]

The free energy functional for microphase separation of A-B diblock copolymer

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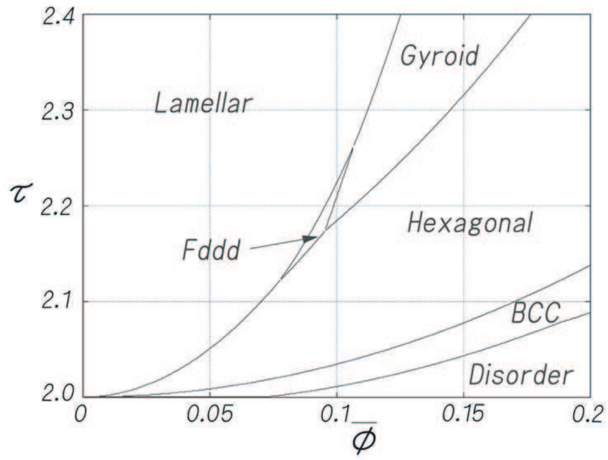

Fig. 2. Phase diagram in the $\tau - \bar{\phi}$ plane.[5] "Disorder" indicates the high temperature uniform phase.

melts is given within a mean filed approximation by[3]

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

where ϕ is the local concentration difference between A monomers and B monomers, $\bar{\phi}$ indicates the spatial average of ϕ and the coefficients τ, α and g are all positive. The function G is defined by

$$-\nabla^2 G(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{2}$$

The free energy functional (1) is applied to a weak segregation regime near the microphase separation temperature. The last term of (1) arises from the osmotic incompressibility. If this term is absent, (1) is the usual Ginzburg-Landau free energy for macrophase separation. The competition of the long range interaction and the short range attractive interaction (the gradient term of (1)) gives us the mesoscopic periodic structures.

Since ϕ is a conserved quantity, the time-evolution equation in its simplest form is given by[4]

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

In order to avoid a difficulty at the system boundary in the direct numerical simulations of eq. (3), we employ the mode expansion method such that

$$\phi(\mathbf{r},t) = \bar{\phi} + [\sum_{n=1}^{N} a_n(t)e^{i\mathbf{q}_n\cdot\mathbf{r}} + c.c.] \tag{4}$$

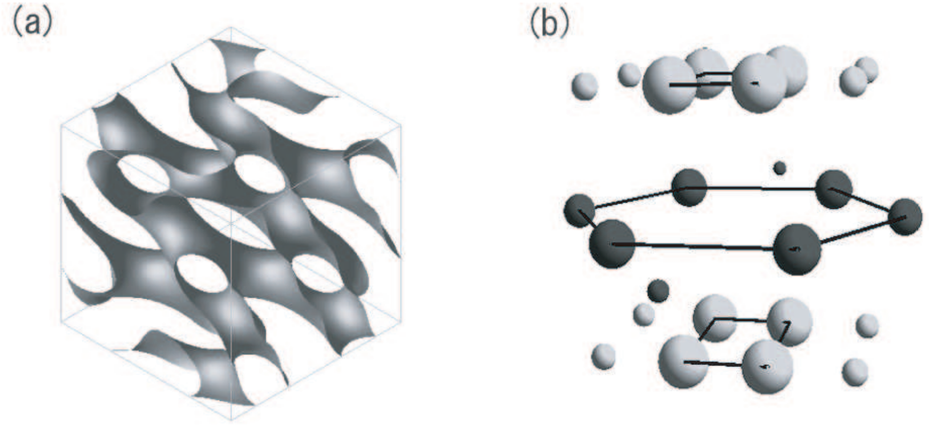

Fig. 3. (a) Fddd structure and (b) its Bragg points.[5)]

where the amplitude a_n is a real value and their time-evolution equation is derived from eq. (3) ignoring the higher harmonics. Here we consider 33 reciprocal lattice vectors $\mathbf{q}_n$ but the details are not presented.[5)]

The equilibrium solution of the coupled amplitude equations and the evaluation of the free energy for each solution give us the phase diagram in Fig. 2. The basic four mesoscopic structures appear in the τ-$\bar{\phi}$ plane. It should be noted that there is a new phase in Fig. 2 indicated by Fddd. This is an interconnected structure with uniaxial symmetry as Fig. 3(a) with the Bragg points in Fig. 3(b). The present result for Fddd structure is in agreement with the one obtained by a self-consistent functional theory.[6)]

The morphological transitions can be investigated by solving the set of amplitude equations. Since the transition is first order, we need to add random forces to avoid trapping at a metastable state. An example of the transition is shown in Fig. 4 where a gyroid structure is provided for $\tau = 2.2$ and $\bar{\phi} = -0.1$ and then the value of τ is changed abruptly to $\tau = 2.5$ at $t = 0$. It is clearly seen that Fddd structure appears at around $t = 14400$ as an intermediate structure.[2)] Quite recently experiments consistent with this prediction have been carried out.[7)]

In summary, we have studied formation and dynamics of mesoscopic structures in diblock copolymers. It is emphasized here that a similar problem has been studied in an entirely different field. That is, various periodic structures have been predicted in nuclear matter.[8)] In particular, those structures expected to exist in a neutron star are called pasta phase.[9)] The Coulomb interaction of protons and the interfacial energy between nuclear matter and the electron-rich phase are responsible for the structure formation. Note that this is essentially identical with the mechanism in the free energy functional (1) extended to the strong segregation regime and that this mathematical equivalence would not have been noticed if one did not have employed the coarse-grained theory like the present one in terms of the local volume fraction in the polymeric systems. Finally it should be mentioned that only BCC, hexagonal and lamellar structures have been predicted in the pasta phase.[8)] However the phase

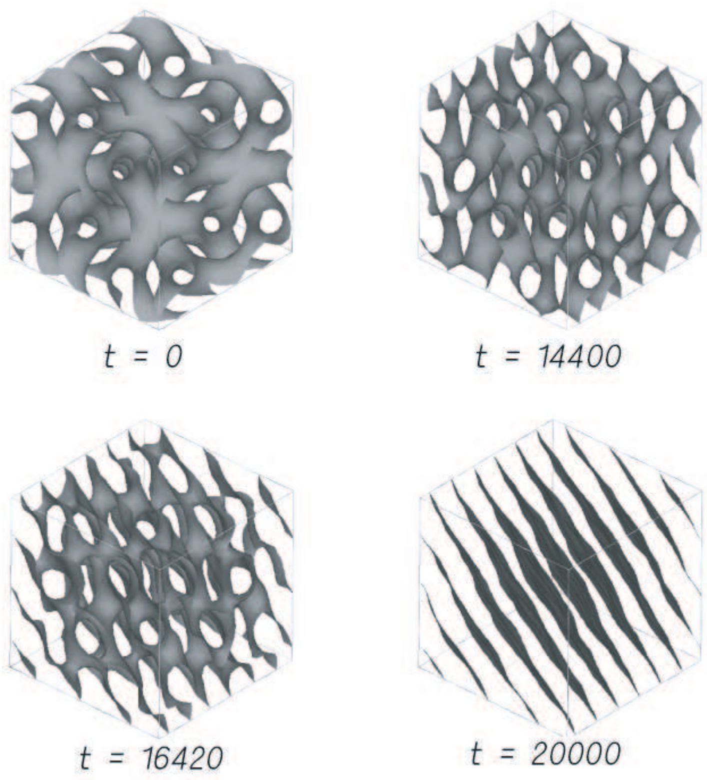

Fig. 4. Time-evolution from Gyroid structure to lamellar structure via the intermediate Fddd structure.[2)]

diagram in Fig. 2 indicates that there must be interconnected periodic structures. Verification of this property in nuclear matter[10)] would be quite interesting.

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