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Origin of epitaxies between ordered phases of block copolymers

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The origin of epitaxial relationships between different ordered phases of diblock copolymers is studied by examining the nucleation barrier of an arbitrarily oriented nucleus. It is found that the orientation-dependence of the nucleation barrier exhibits a very corrugated landscape with a few deep minima, corresponding to preferred crystallographic orientations of the nuclei. These minima are identified as the epitaxies between the ordered phases. Examination of the nucleation pathways reveals that the origin of the epitaxial relationships can be attributed to the matching of the dominant Fourier components of the density distributions. The predicted epitaxial relationships among lamellae, cylinders, spheres and gyroid phases are in excellent agreement with previous experimental and theoretical observations. Furthermore, new expitaxial relationships between the Fddd and lamellar phases are revealed by the theory.

In systems undergoing a first-order phase transition, the nucleation and growth of a new ordered phase frequently proceeds with a preferred crystallographic orientation between the original (mother) and transformed (daughter) phases. These specific symmetry and lattice spacing matching relationships, commonly referred as epitaxies, between two ordered phases have been observed in many physical systems,[1] particularly in the ordered phases of block copolymers.[2,3] Intuitively, epitaxies between two ordered phases must correspond to certain optimized crystallographic orientations which minimize the total interfacial energy between the two phases. However, despite the ubiquitousness of the phenomena, a theoretical description of the origin of epitaxies has been lacking. In this communication we fill this gap by examining the nucleation barrier of ordered phases of diblock copolymers based on a generic free energy functional of weak crystallization.[4,5] The preference of a particular crystallographic orientation of the daughter phase is quantified by the free energy barrier of the critical nucleus. Epitaxial relationships are identified as the orientations of the daughter phase corresponding to the deep minima of the nucleation barrier. Furthermore, the origin of the epitaxies can be traced to the matching of the dominant Fourier components of the density distributions. Although the theory is applied to diblock copolymers, the principles of epitaxy obtained from the study applies to any physical systems undergoing order–order phase transitions.

Diblock copolymers are amphiphilic macromolecules that can self-assemble into a variety of ordered phases, making them an ideal model system for studying the formation of, and transitions between, different ordered phases.[6] Specifically, diblock copolymer melts can assemble into five ordered phases: lamellae (L), hexagonally-packed cylinders (C), body-centrally packed spheres (S), a double gyroid network (G) and an orthorhombic Fddd (O^{70}) network (Fddd). Experimental studies have shown that phase transitions among these ordered phases (L ↔ C, C ↔ S, L ↔ G and C ↔ G) occur epitaxially with matched crystallographic orientations and lattice spacings.[2,7–9] For instance, in the L → C nucleation process, the cylinder and lamella spacings, D_c and D_l, are approximately related by $D_l = \sqrt{3}D_c/2$, and the newly formed cylinders are aligned parallel to the lamellae plane.[7]

The phase transition processes between different ordered phases of block copolymers have been examined by numerical simulations,[10–12] linear stability analysis,[13] self-consistent field theory calculations,[14,15] and nucleation theory.[16,17] For a system undergoing a first-order phase transition, classical nucleation theory has been used to calculate the shape, size and free energy barrier of the critical nuclei.[16] More accurate nucleation theory has also been developed based on the string method, in which the minimum energy path connecting the mother and daughter states can be obtained.[17] In these previous nucleation theory calculations, the mother and daughter states are assumed to follow certain epitaxial relationships, typically obtained in experiments. The essence of the current research is to relax the orientational relationships between the mother and daughter phases and compute the nucleation barrier as a function of the relative orientation of the two phases. Minima of the nucleation barrier are then used to predict the epitaxies between the two ordered phases.

Although sophisticated free energy functionals for the description of the complex ordered phases have been developed,[18] for simplicity we will employ the Landau–Brazovskii (LB) free energy functional to describe the phases and phase transitions of diblock copolymers. It should be noted that the LB theory can be viewed as a generic model for modulated phases occurring in a variety of physical systems.[5] In the scaled form, the LB free energy density is given by,

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$$f = \frac{1}{V}\int_{\Omega} d\mathbf{r}\left\{\frac{\xi^2}{2}\left[(\nabla^2 + q_0^2)\phi\right]^2 + \frac{\tau}{2}\phi^2 - \frac{\gamma}{3!}\phi^3 + \frac{1}{4!}\phi^4\right\}, \quad (1)$$

where $\phi(\mathbf{r}) = \phi_A(\mathbf{r}) - f_A$ is the order parameter defined as the density deviation of the A-monomer from its uniform state, $q_0 = 1$ is a critical wavevector, and ξ, τ and γ are parameters related to the molecular parameters of the diblock copolymers, χN and f_A. Here N is the degree of polymerization of the diblock copolymers, f_A is the fraction of A-blocks in one copolymer chain, while χ is the Flory–Huggins parameter characterizing the repulsive between the A and B monomers. Despite its simplicity, it has been shown that the LB model can reproduce all the known ordered phases of diblock copolymers.[16] This model is accurate near the order–disorder boundary and it provides an accurate, *albert* approximate, description of the phase behaviour of diblock copolymers.

Within mean-field theory, the stable and metastable phases correspond to global and local minimum of the free energy functional eqn (1). For an ordered phase, the order parameter, $\phi(\mathbf{r})$, is a periodic function, which can be expanded in Fourier space as $\phi(\mathbf{r}) = \sum_{k,l,m}\phi(\mathbf{G}_{klm})\exp[i\mathbf{G}_{klm}\cdot\mathbf{r}/L]$, where the reciprocal lattice vectors are specified by $\mathbf{G}_{klm} = (2\pi k/\beta_1, 2\pi l/\beta_2, 2\pi m/\beta_3)$. Here L and $\vec{\beta} = (\beta_1,\ \beta_2,\ \beta_3)$ specify the size and shape of the unit cell. For a cubic unit cell, $\vec{\beta} = (1,1,1)$ and for the Fddd phase, $\vec{\beta} = (1,2,2\sqrt{3})$. The stable and metastable ordered phases are determined by minimizing the free energy functional with respect to the amplitude $\phi(\mathbf{G})$ and the period. For a given $\phi(\mathbf{G})$, the simplicity of the LB theory allows the minimization with respect to L to be carried out analytically, leading to the relationship,

$$L^* = \sqrt{\frac{\sum_{k,l,m}\phi(\mathbf{G}_{klm})^2|\mathbf{G}_{klm}|^4}{\sum_{k,l,m}\phi(\mathbf{G}_{klm})^2|\mathbf{G}_{klm}|^2}}. \quad (2)$$

On the other hand, the determination of the amplitudes requires numerical techniques in general and an efficient algorithm is available.[19] At the weak segregation regime, numerical results show that the order parameter is dominated by contributions from the first and second modes. In what follows we will use the dominant mode approximation, one mode in the case of L, C, S and Fddd, and two modes in the case of G, to describe the ordered phases[20,21] Within the one mode approximation the period matching among L, C, S and Fddd is perfect. On the other hand, the period of G is slightly larger than the unperturbed one (at $f_A = 0.41$ and $\chi N = 12.6$, the period of G is about 4% larger than those of L and C).

The energetics of a nucleus are examined using the classical nucleation theory.[16] The analysis is divided into two steps, the calculation of the interfacial free energy between two ordered phases and the construction of the minimum-energy nucleus. The interfacial free energy between two ordered phases is obtained using a variational method.[16] Assuming the two ordered phases are described by order parameters ϕ_A and ϕ_B, an ansatz of the interface connecting the two ordered phases can be written as,

$$\phi(\mathbf{r},\mathbf{n},\mathbf{P},\mathbf{b},s_0,w) = \frac{1}{2}\left[1 - g\left(\frac{s-s_0}{w}\right)\right]\phi_A(\mathbf{r}) + \frac{1}{2}\left[1 + g\left(\frac{s-s_0}{w}\right)\right]\phi_B(\mathbf{P}\cdot\mathbf{r}+\mathbf{b}), \quad (3)$$

where $g(x)$ is a transition function satisfying $g(x) \rightarrow \pm 1$ as $x \rightarrow \pm\infty$ and $g(0) = 0$. The parameter w characterizes the interface width, s_0 denotes the location of the interface, $\mathbf{n}$ is the interface normal, $s = \mathbf{r}\cdot\mathbf{n}$ so that $s - s_0$ is the perpendicular distance to the interface. Rotation and translation of the B-phase relative to the A-phase are described by an orthogonal matrix $\mathbf{P}$ and a vector $\mathbf{b}$, respectively. By substituting eqn (3) into eqn (1) and minimizing the free energy with respect to interfacial width w, the interfacial free-energy per unit area or interfacial tension, σ, is obtained. In general, σ is a 9-dimensional function of the normal vector of the interface $\mathbf{n}$, the relative position and orientation of the B-phase described by $\mathbf{b}$ and $\mathbf{P}$, and the interface location s_0, $\sigma(\mathbf{n}, \mathbf{b}, \mathbf{P}, s_0)$. In practice, by adopting a slow variational approximation[16] and minimization with respect to $\mathbf{b}$, σ is reduced to a function of 5 variables $\sigma(\mathbf{n}, \mathbf{P})$. Once the interfacial tension $\sigma(\mathbf{n}, \mathbf{P})$ is obtained, the shape of the nucleus is determined by Wulff construction, which minimizes the total interfacial free energy, $\sigma_0 = \int\sigma(\varphi,\theta)\mathrm{d}S$, subject to the constraint of constant droplet volume. The solution of this constrained minimization problem is the well-known Wulff construction. After the determination of the nucleus shape, the reaction coordinate becomes the size of the nucleus. The critical nucleus corresponds to the maximum along the reaction coordinate and the nucleation barrier, $\Delta F(\mathbf{P})$, is then determined from this maximum. The value of the nucleation barrier is used to quantify the energetics of the relative orientation of the critical nucleus with respect to the mother phase.

The above procedure has been applied to the different ordered phases of diblock copolymers. As a first example, the C → L nucleation is examined at $f_A = 0.45$, $\chi N = 11.4$. Because of the simple one-dimensional nature of the lamellar phase, the relative orientation of the daughter L-phase is determined by two angles as illustrated in Fig. 1. The landscape of the nucleation barrier $\Delta F(\mathbf{P})$ is a very corrugated surface in the (θ, ϕ)-space (Fig. 1, where ΔF is in unit of $\rho_0 b^3 N^{1/2} k_B T$). The most striking feature of this energy landscape is the existence of a very deep and unique minimum at $\phi = 90°$ and $\theta = 30°$, which corresponds precisely to the epitaxy between the lamellae and cylinders observed in experiments.[7] Assuming $\rho_0 = b^{-3}$ and $N = 1000$,

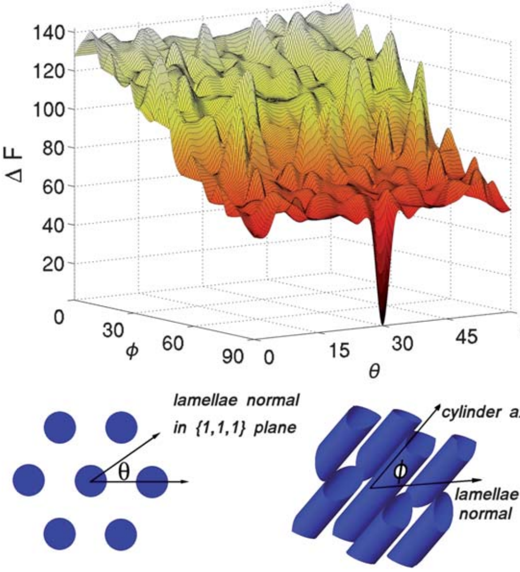

Fig. 1 Plot of the C → L nucleation barrier as a function of the L-orientation. The parameters are $f_A = 0.45$ and $\chi N = 11.4$. Because of the symmetry of the L and C phases, the surface is drawn in region $0° \le \phi \le 90°$, $0° \le \theta \le 60°$, where ϕ and θ are defined in the lower part of the figure.

the nucleation barrier at epitaxy is estimated as $39.82k_BT$, which could produce an observable rate of nucleation. In contrast, the nucleation barriers along the non-epitaxial orientations are beyond $1000k_BT$. The origin of the predicted epitaxial relationships can be traced to the relationship between the order parameters of the two ordered phases. Epitaxy or barrier minimum occurs when the dominant mode of the daughter (L) phase is one of the three dominant modes of the mother (C) phase. This mode-matching leads to a smooth transition between the two phases, thus the lowest free energy barrier. The condition of epitaxy derived from the C ↔ L case is further verified in the transitions between the other ordered phases.[15] In the case of S ↔ C, one epitaxy is found, in which the C-axis is along the (1, 1, 1) direction of the BCC spheres. This epitaxial relationship is due to the fact that the three dominant modes of the C-phase are a subset of the six dominant modes of the BCC spherical phase. It should be noticed that the location of the nucleation barrier minima does not depend on the specific values of f_A and χN.

Due to the complexity of the gyroid phase, the order–order transitions involving the G-phase (G ↔ C and G ↔ L) are more interesting. Besides the intricate structure, it is well-known that the description of the G-phase requires at least two dominant modes,[20] thus providing more matching conditions for the L and C phases. For example, the three dominant modes of the G-phase, (1, −2, 1), (1, 1, −2) and (−2, 1, 1), can be matched to a C-phase with a regular hexagonal symmetry. On the other hand, three other dominant modes of the G-phase, (1, 1, −2), (1, 1, 2) and (2, 2, 0), could be matched to a C-phase with a slightly deformed arrangement (Fig. 2). These different mode-matching conditions lead to different epitaxies between the gyroidal and cylindrical phases. The nucleation energy barriers of the G → C phase transitions are plotted in Fig. 2, which again exhibit one sharp minimum at epitaxy. It should be noticed that the nucleation barrier depends on three angular variables and only two-dimensional cross sections are shown. These results lead to the prediction of two possible epitaxial relationships in the case of G ↔ C transitions. For the G ↔ L transitions, there are also two possible matching conditions, corresponding to lamellae matching to the (1, 1, −2) and (2, 2, 0) modes of the gyroid phase. The second epitaxy would correspond to a slightly stretched structure from the equilibrium lamellae. Because for the G-phase with amplitudes ϕ_G, the amplitude of {2, 2, 0} is relatively smaller than the amplitude of {1, 1, 2}, the second epitaxy is less preferred than the first one. Experimentally, cylinders with axis along the (1, 1, 1) directions and lamellae with normal along the (1, 1, −2) directions are classical epitaxies.[2,3,10–12,14] On the other hand, slightly deformed cylinders along the (2, 2, 0) of the G-phase have been observed recently.[9] The current theoretical predictions are in excellent agreement with these experimental observations.

The Fddd phase is a networked structure resembling the gyroid phase.[21,22] The complexity of this phase implies that interesting epitaxial relationships are expected for phase transitions involving the Fddd phase. Although the Fddd phase has a more complex topological structure and an orthorhombic unit cell, the variational method presented above can be applied to this phase directly. For the L ↔ Fddd transitions, the nucleation barrier landscape is shown in Fig. 3. It is striking that the theory predicts three possible epitaxial relationships between the L and Fddd phases, corresponding to the formation of the lamellae from the A (1, 1, −1), B (0, 2, −2) and C (0, 0, 4) planes. Among these three minima, the first one has the lowest barrier and the (1, 1, −1)-mode of the Fddd phase also has the largest amplitude. For the C ↔ Fddd transitions (not shown), two epitaxial relationships are predicted by the theory, corresponding to the matching of the cylinder axis with the (0, 1, 1) and (1, 0, 0) directions of the Fddd unit cell. These theoretical results on epitaxies involving the Fddd phase provide clear predictions which should be tested in future experiments and simulations.

In summary, the nucleation of an arbitrarily oriented ordered daughter phase from a metastable ordered mother phase is studied by applying the classical nucleation theory to the Landau–Brazovskii model of diblock copolymers. The free energy barrier of the critical nucleus is used to quantify the structural relationships between different ordered phases. It is shown that the landscape of the nucleation barrier is very complex and corrugated, with some very deep and narrow minima at particular orientations of the daughter phase. These minima correspond to special symmetry and lattice space matching

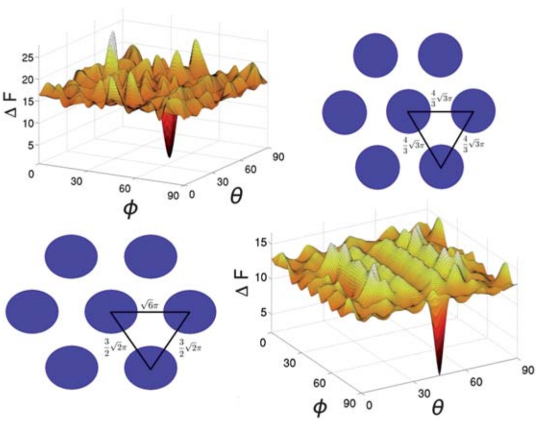

Fig. 2 G → regular C (upper) and G → distorted C (lower) nucleation barrier in terms of C's orientations. θ and ϕ are polar coordinate parameters for cylinder axis, and the rotation dimension of cylinders is not shown. The barriers are calculated at $\chi N = 11.25$ and $f_A = 0.44$. Distances in the sketches of cylinders are in unit of q_0^{-1}.

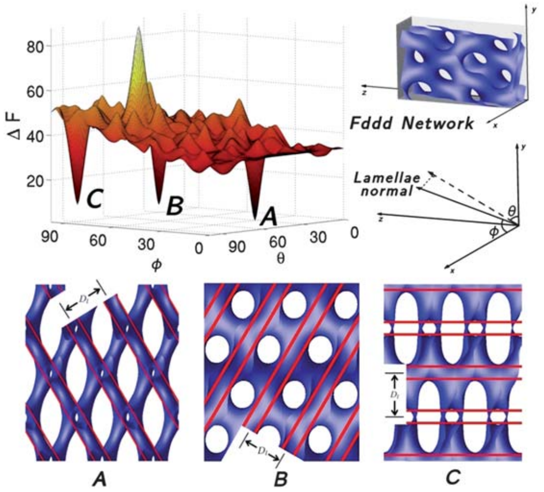

Fig. 3 Fddd → L nucleation barrier in terms of L's orientations. The orientation is described by θ and ϕ, which are defined in the upper right part of the figure. The barriers are calculated at $\chi N = 12.0$ and $f_A = 0.45$. Only the regions $0° \le \phi \le 90°$ and $0° \le \theta \le 90°$ are shown because of the symmetry.

relationships between the daughter and mother phase, which are identified as the epitaxial relationships often observed in experiments. For the different ordered phases of diblock copolymers, our theory gives unambiguous predictions of epitaxial relationships among the different ordered phases of diblock copolymers, which are in excellent agreement with available experimental observation.

The origin of the predicted epitaxies between different ordered phases is revealed by examining the condition for the occurrence of the deep minima in the nucleation barrier landscape. These deep minima correspond to the matching of the dominant modes between the two ordered phases. These modes determine the matched symmetry and lattice spacing of the two phases. This observation provides a clear physical understanding of the occurrence of epitaxies between two ordered phases. When the daughter and mother phases share some common dominant modes, the density profile connecting the two ordered phases transforms from one phase to the other smoothly, thus resulting in a smaller interfacial energy. On the other hand, when there are no common shared modes between the two ordered phases, the interfacial structures between the two ordered phases must possess complicated deformations, resulting in a high interfacial energy. This mode matching condition has been observed in a previous experiment.[2] Finally it should be noticed that, although the theoretical study is carried out within the context of diblock copolymers, the principles of epitaxies obtained from the study should apply to any physical systems undergoing order–order phase transitions.

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