$\frac{2}{3}$-Power Law for Copolymer Lamellar Thickness Implies a $\frac{1}{3}$-Power Law for Spinodal Decomposition

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We demonstrate the relation $\theta=2\phi$. Here the exponent θ is defined as $D\sim N^{\theta}$, where D is the equilibrium lamellar thickness of the diblock copolymer ordered phase and N is the molecular weight. The exponent ϕ is defined as $l\sim t^{\phi}$, where l is the pattern size of the spinodally decomposing system (say, a binary alloy) and t is the time.

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It is now reasonably well established, by real[1] and numerical experiments,[2] that the form factor $S(k,t)$ at time t for the quenched binary alloy undergoing spinodal decomposition has the following form[3]:

$$S(\mathbf{k},t)=l(t)^{d}F(kl(t)),$$

where $l(t)$ is the representative length scale (e.g., the pattern size) and F is an appropriate master function. Furthermore, it is believed that the length scale obeys a power law $l\sim t^{\phi}$. There is strong evidence for the exponent ϕ to be $\frac{1}{3}$,[1,2,4] although this value is not unanimously accepted.[5] The purpose of the present Letter is to show that there is a simple relation, $\theta=2\phi$, between the exponent ϕ and the lamellar-thickness exponent θ for block copolymers defined by $D\sim N^{\theta}$, where D is the equilibrium lamellar thickness and N is the molecular weight of the copolymer ordered phase. This implies that the experimentally established value $\theta=\frac{2}{3}$ (Ref. 6) is further support for $\phi=\frac{1}{3}$.

A 1:1 diblock copolymer (BCP) is a linear-chain molecule consisting of two equal-length subchains a and b grafted covalently to each other [Fig. 1(a)]. The subchains a and b are made of different monomer units, A and B, respectively. Below some critical temperature T_c these two blocks tend to separate, but because of the covalent bond, they can segregate at best locally to form a lamellar structure [Fig. 1(c)]. To describe the quenching process of the system consisting of many BCP's (i.e., a BCP melt) from above T_c to below it, a simple model was proposed in terms of a cell dynamical system (CDS), and the corresponding partial differential equation model was derived[7]:

$$\partial\psi/\partial t=L\nabla^{2}(-\tau\psi+u\psi^{3}-\nabla^{2}\psi)-B\psi, \qquad (1)$$

where $\psi(\mathbf{r},t)$ is the order parameter describing the local monomer concentration difference between A and B; L, τ, and u are positive phenomenological parameters, τ being a measure of the quench depth; and $B\in(0,1)$. The equation is essentially the Cahn-Hilliard (CH) equation with the subtraction of $B\psi$. The spirit of modeling in Ref. 7 was purely phenomenological, so that, strictly speaking, we can fix parameters only by comparison with real experimental results. Furthermore, the motivation was to have the simplest model to give the spatially nonuniform equilibrium pattern; the equation need not describe the ordering process of the BCP system faithfully. In any case in this Letter what we need is the property of (1) giving the right equilibrium patterns for BCP's when $B\neq0$ (Fig. 2), as will be discussed below. We should point out that Fig. 2(a) and the patterns obtained in the actual BCP film experiments[8] are hardly distinguishable.

When the segregation is weak, i.e., the interface thickness and the thickness of lamellae are of the same order, we can accurately study this equation or the corresponding CDS model[9] numerically without any particular difficulty. We have computed the spherically averaged static form factor $S(k)$ after a sufficiently long time, and calculated the average $\langle k\rangle_{\rm eq}$ of k with respect to $S(k)$. $\langle k\rangle_{\rm eq}^{-1}$ is regarded as the measure of the lamellar thick-

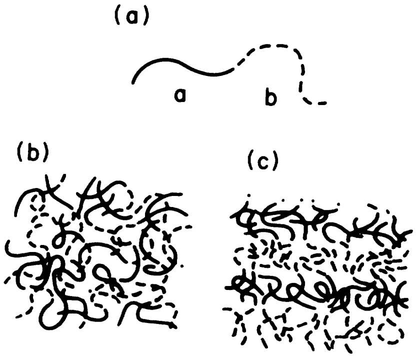

FIG. 1. (a) A diblock copolymer molecule. We consider here only the 1:1 block copolymer which has equal-sized subchains *a* and *b*. (b) Above T_c, *a* and *b* portions mix to make a disordered phase. (c) Below T_c, *a* and *b* tend to segregate, but because of the covalent bonds between subchains, segregation is possible only locally and a lamellar structure forms.

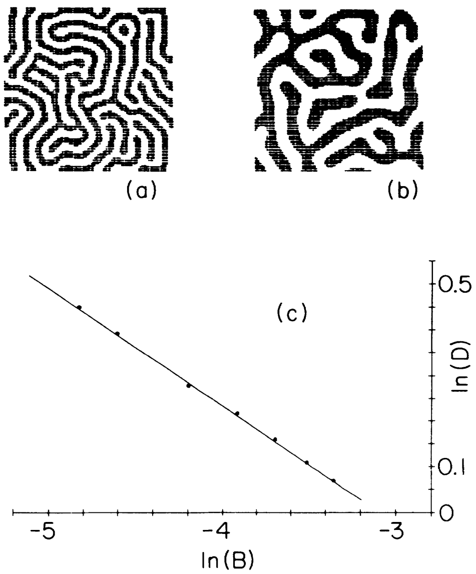

FIG. 2. The pattern after 7000 time steps for (a) $B=0.002$ and (b) $B=0.02$. $\langle k\rangle_{\mathrm{eq}}$ is sufficiently equilibrated by then. (c) The empirical relation between $\langle k\rangle_{\mathrm{eq}}=D$ and B. The line has the slope 0.254 corresponding to the best fit.

ness D. The result is $D \sim B^{\alpha}$ [Fig. 2(c)] with $\alpha = -0.254 \pm 0.005$. In actual experiments for the weak-segregation case, $D \sim N^{1/2}$.[6] Hence we can empirically conclude that B is proportional to N^{-2}. This can also be understood by dimensional analysis. Looking at Eq. (1), we have $[\nabla^4\psi]=[B\psi]$, so that $[B]^{-1}=[l]^4$, where l is the relevant length scale; we have ignored L since it is independent of l. The subtraction term, which makes the final equilibrium pattern spatially nonuniform, should represent the effect of the connectedness of each chain. Hence the relevant length scale due to this effect must be $N^{1/2}$, so that we get $B \sim N^{-2}$. A more direct justification that Eq. (1) exhibits the correct equilibrium behavior can be obtained by the following rewriting of Eq. (1)[7]:

$$\frac{\partial\psi(\mathbf{r},t)}{\partial t} = L\nabla^2 \frac{\delta H[\psi(\mathbf{r},t)]}{\delta\psi(\mathbf{r},t)}, \tag{2}$$

where H happens to be the effective Hamiltonian first derived by Leibler for a BCP system.[10] The comparison of Eq. (2) and the Hamiltonian derived by Ohta and Kawasaki[11] also gives $B \sim N^{-2}$. Since the lamellar thickness is an equilibrium quantity, we should stress again that even if Eq. (1) is a crude model for the actual kinetics, these comparisons tell us that the correct exponent for the thickness can be obtained from (1). In the case of strong segregation, i.e., when the interface thickness is much smaller than the lamellar thickness, to get a reliable numerical result from Eq. (1) or its CDS counterpart is extremely difficult, since we need a huge system to avoid finite-size effects. Ohta and Kawasaki[11] obtained for this case $\theta=\frac{2}{3}$ from the Hamiltonian in (2) using a variational technique.

The equilibrium pattern should obey

$$B\psi = L\nabla^2(-\tau\psi + u\psi^3 - \nabla^2\psi). \tag{3}$$

Comparing this result with the CH equation [Eq. (1) with $B=0$], we realize by dimensional analysis that $[B^{-1}]$ corresponds to $[t]$, i.e., $[N^2]$ corresponds to $[t]$. Hence the asymptotic growth law $l(t) \sim t^{\phi}$ for the CH equation, which is usually the dimensional-analysis result,[4] should imply $l \sim N^{2\phi}$; that is, $\theta = 2\phi$. This argument may seem trivial, but we have used an implicit assumption that the interface thickness is independent of N and sufficiently small compared to the representative pattern size l. Notice that (3) has infinitely many solutions, but the one with the lowest free energy should be with well defined thin interfaces. The hypothesis has been empirically substantiated by a simulation with very small B, say 10^{-4}. A more explicit demonstration of the exponent equality follows.

We expect that in the true equilibrium state stripes would be straight and parallel fairly globally. Although this true equilibrium stripe pattern requires global transport of polymers, the width of the pattern is determined by local rearrangements of polymers. This implies that the lamellar width is essentially determined during the time span when the radius of the interface curvature and the width are comparable; that is, when the dynamics is curvature driven. Therefore, we can proceed more explicitly with the aid of the interface equation of motion[4(a)]: In the strong-segregation case, following Allen and Cahn,[12] we can reduce Eq. (1) in the tubular neighborhood of the interface to

$$\partial\psi(\mathbf{r},t)/\partial t + B\psi(\mathbf{r},t) = -L\nabla^2[\nabla\psi(\mathbf{r},t)\cdot\hat{\mathbf{n}}(\mathbf{r},t)\nabla\cdot\hat{\mathbf{n}}(\mathbf{r},t)], \tag{4}$$

where $\hat{\mathbf{n}}$ is the unit vector locally normal to the interface. Introducing the Green's function $G(\mathbf{r},\mathbf{r}')$, defined as $\nabla^2 G(\mathbf{r},\mathbf{r}') = -\delta(\mathbf{r}-\mathbf{r}')$ with appropriate boundary conditions, we can rewrite (4) as

$$\int d^3r'\, G(\mathbf{r},\mathbf{r}')\left[\frac{\partial\psi(\mathbf{r}',t)}{\partial t} + B\psi(\mathbf{r}',t)\right] = L[\nabla\psi(\mathbf{r},t)\cdot\hat{\mathbf{n}}(\mathbf{r},t)]\nabla\cdot\hat{\mathbf{n}}(\mathbf{r},t). \tag{5}$$

Since $\nabla\psi\cdot\hat{\mathbf{n}} = \partial\psi/\partial n$ is sharply peaked about the interface, we can integrate both sides of (5) over the local coordinate n, perpendicular to the interface, to get

$$\int dn \int da'\, G(\mathbf{r}(\mathbf{a},n),\mathbf{r}_i(\mathbf{a}',t))\,v(\mathbf{r}_i(\mathbf{a}',t)) + (2\psi_0)^{-1} B \int dn \int d^3r'\, G(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}',t) = LK(\mathbf{r}_i(\mathbf{a},t)), \tag{6}$$

where **a** collectively denotes the coordinates along the interface, K is essentially the mean curvature of the interface, and ψ_0 is the modulus of the equilibrium value of the order parameter far away from the interface. Let us assume that there is only one relevant length scale, l. A simple dimensional analysis gives us $[d\mathbf{a}]=[l]^{d-1}$, $[G]=[l]^{2-d}$, $[v]=[l]/[t]$, $[K]=[l]^{-1}$, and $[dn]=1$. Hence we can reduce Eq. (6) to the following formal relation:

$$\frac{[l]^2}{[t]}+\frac{[l]^2}{[N^2]}=\frac{1}{[l]}. \tag{7}$$

Notice that the terms on the left-hand side of the formal equation (7) do not occur at the same time. For the ordinary spinodal decomposition the second term is absent since $B=0$ in this case, and we obtain $l\sim t^{1/3}$, as found by Kawasaki and Ohta.[4a] For the BCP microphase separation, on the other hand, we do not have the first term which originated from the interface displacement. Consequently, we find that $l\sim N^{2/3}$ in agreement with experimental results. Thus actually, $\frac{2}{3}$ is twice the growth exponent for the spinodal decomposition. The derivation of $2\phi=\theta$ from the comparison with the CH equation suggests that this relation should hold even if the thin-interface condition is not satisfied. The derivation implies that $2\phi=\theta$ if the interface structure in spinodally decomposing and BCP systems is similar. By dimensional analysis, when the interface thickness is significant and the surface diffusion dominates the coarsening process, $l(t)\sim t^{1/4}$ is expected.[13] This region corresponds to the weak-segregation case for BCP's, in which $\phi=\frac{1}{2}$, as mentioned above. Thus, indeed $\theta=2\phi$ holds.

In summary, we have demonstrated that there is a direct relation between the equilibrium lamellar thickness for the block copolymer system and the asymptotic growth law for spinodal decomposition of, e.g., binary alloys.

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[9] We have solved the following CDS model:

$$\psi(t+1,n)=\psi(t,n)-B\psi(t,n)+\mathcal{J}(t,n)-\langle\langle\mathcal{J}(t,n)\rangle\rangle,$$

where $\mathcal{J}=1.3\tanh\psi-\psi+0.5(\langle\langle\psi\rangle\rangle-\psi)$ for $0.01\leq B\leq 0.035$ in a 100×100 square lattice with a uniform random initial condition $-0.125\leq\psi\leq 0.125$. $\langle\langle\cdots\rangle\rangle$ is defined as $\langle\langle\psi(t,n)\rangle\rangle=\frac{1}{6}\sum(\psi$ in the nearest-neighbor cells$)+\frac{1}{12}\sum(\psi$ in the next-nearest-neighbor cells$)$. Thirty samples were used for averaging. For a more general account of CDS see Y. Oono and S. Puri, Phys. Rev. Lett. **58**, 863 (1987), and Phys. Rev. A **38**, 434 (1988).

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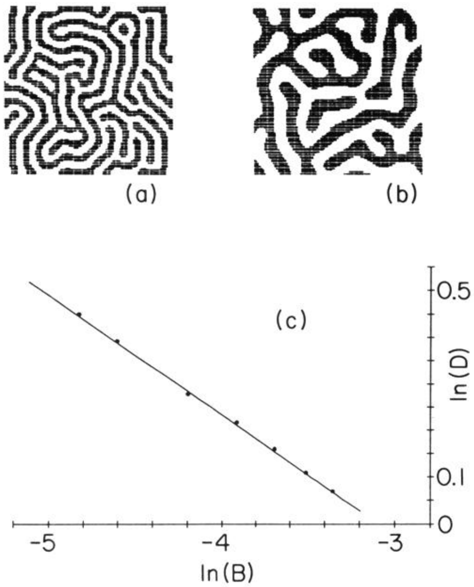

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