

Anisotropic Fluctuations And Kinetics of Order-order And Order-disorder Phase Transitions of Diblock Copolymers

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Abstract

Diblock copolymers (DCP) represent the simplest block copolymers that can microphase separate into a variety of ordered phases. While the equilibrium properties of DCP have been studied extensively, the dynamical aspects have been relatively unexplored. In this work, we study the kinetics of order-disorder and order-order transitions in weakly segregated diblock copolymers using a time-dependent Ginzburg-Landau (TDGL) approach. In particular, we investigate the microstructural change as well as the order parameter evolution after a sudden temperature jump from one phase to another. Direct numerical simulation of the TDGL equations shows that depending on the extent of the temperature jump, these transitions often occur in several stages and can involve nontrivial intermediate states. For example, we find that transition from the lamellar phase to the hexagonal cylinder phase goes through a perforated lamellar state within a certain temperature range. A theory is developed based on the anisotropic fluctuations in the ordered phases. These fluctuations play two crucial roles: first, they determine the stability limit of the initial structure, and second, they are responsible for the emergence of new structures, whether they are the final equilibrium states or transient states during the transition. A linear stability analysis allows us to identify the largest fluctuation modes under both equilibrium and nonequilibrium conditions. By combining the order parameter of the initial structure with the largest fluctuation modes into a simplified multimode model (under the single-wavenumber approximation), we are able to describe qualitatively the full nonlinear evolution of the system after sudden temperature jumps beyond the spinodal of the initial phase. Specifically, the analysis reveals that the geometric characteristics of the free energy surface, particularly saddle points and ridge-like features, are responsible for the nontrivial intermediate states on the kinetic pathways. On the basis of this analysis, a generalized kinetic “phase diagram” is constructed, which is able to account for all the different scenarios observed in the numerical simulation.

Our results are discussed in connection with available experimental observations.

A closely related problem concerns the nature, stability, and mechanism of formation of the so-called perforated lamellar structure, which generates considerable confusion of controversy in recent years. We show that this structure develops from the anisotropic fluctuations of the lamellar phase when it reaches its spinodal. It is proposed that there can be two different perforated lamellar structures, one based on a hcp lattice and one based on a bcc lattice, with nearly degenerate free energy. In the framework of a Leibler-type free energy functional, it is shown that the perforated lamellar structure is only pseudostable (corresponding to a saddle point in the free energy surface) in the weak-segregation limit, but can become metastable in the intermediate-segregation regime. Calculation of the fluctuation spectrum of metastable perforated lamellar structures enables us to explain in a simple and consistent manner several puzzling structural data from small-angle neutron scattering studies.

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Chapter 1 Introduction

1.1 Block Copolymers and Their Applications

Macromolecules, or polymers, are long-chain molecules that are composed of a large number of repeating units called monomers. These materials are widely used in our everyday life[1]. For example, elastomers, such as natural rubber whose main component is polyisoprene, are used in producing tires, hoses and some automotive parts because of their resiliency; fibers, either natural or synthetic, because of their high tenacity, are used in textile and composite applications; biological polymers, such as DNAs and proteins, are essential for life.

While single types of polymer show abundant properties and functionalities, the mixture of two or more types of polymers provide much richer possibilities and better controls on material performances. For example, two or more polymers can be blended together to improve the cost-performance ratio: blending may be used to reduce the cost of an expensive engineering thermoplastic, or to improve the processability of high-temperature or heat-sensitive thermoplastic, or to improve impact resistance. Blending is also very important for recycling industry[2]. Therefore, a critical problem in polymer industry is the compatibility of different types of polymers. When two types of polymers are mixed, the mixing entropy per chain is proportional to $k_B T$, where k_B is the Boltzmann constant and T is the temperature, while the mixing enthalpy is proportional to $N\chi$, where N is the number of monomers in a polymer chain and χ is the so-called Flory-Huggins parameter which characterizes the repulsive interaction between different monomers. When temperature is lowered such that the enthalpy cost is larger than the entropy gain, two polymers will tend to demix. One way to overcome this is to form block copolymers by chemically connecting the different types of polymers. Because of the connectivity of the different blocks, macroscopic phase separation is impossible in block copolymers. Upon decreasing

the temperature, these systems can only microseparate into ordered domains. The temperature at which this happens, however, is considerably lower - by as much as a factor of 2.5 or more - than the temperature for macroscopic phase separation in a polymer blend [3][4][5][6]. In practice, block copolymers are often blended with the corresponding homopolymers because of the relatively low cost of the latter.

On the other hand, block copolymers provide a new class of *soft* materials whose ordered, nanometer-scale microphases have recently been found to be of great importance for material designs. For example, the spheres formed by the minority component in a body-centered-cubic (BCC) structure can become the host lattice sites for synthesizing metal nanocrystals[7]. The size of the metal core can be easily controlled by changing the molecular weights of the blocks. These spheres can also provide the medium for synthesizing other polymers[8] which prefer the minority component to the majority one, again with easy control of the size of the polymer. These ordered nanostructures of block copolymers can also serve as a template for a nanoscale nonlinear optical device[9]. Since these applications are related to the phase behaviors of block copolymers, the study of the stability and kinetics of block copolymers is of great interest.

Block copolymer can exist in many different architectures. In this thesis, we will consider the simplest block copolymer, namely a diblock copolymer. Most experiments have been done on diblocks because of the relative ease in synthesizing and characterizing these systems. The phase behavior of multiblock copolymers made from connecting the A and B blocks is similar to that of the A-B diblock. Therefore, the results we have obtained for the simple A-B diblock copolymers can be used qualitatively to multiblocks.

1.2 Phase Behaviors of Diblock Copolymers

The equilibrium problem of diblock copolymer melts has been thoroughly studied since early 1970s. It is now well-known that their phase behavior is determined by three parameters[10][11] [12]: the polymerization index (the number of monomers in

a polymer molecule) N , the Flory-Huggins interaction parameter χ scaled by $k_B T$ (see below for its definition), and the fraction of one of the components in a diblock copolymer molecule, f . The combined parameter $N\chi$ controls the degree of segregation of different block domains, which can be divided into three regimes: the weak segregation limit (WSL), the strong segregation limit (SSL) and the intermediate segregation region (ISR)[11].

In the WSL ($N\chi \leq 12$ for symmetrical diblock copolymers or $f \sim 0.5$), the microphases can be characterized by small deviations in the local composition from the uniform value. By considering a Landau expansion of the free energy to the fourth order in the composition order parameter (to be defined later), Leibler[4] showed that in the WSL there are three ordered equilibrium phases for diblock copolymers: one-dimensional lamellar (L) phase, two-dimensional hexagonally packed cylindrical (H) phase and three-dimensional body-centered-cubic (BCC) phase. The schematic morphologies are shown in Fig. 1.1. One important result of this mean-field theory is that there is a finite optimal wavenumber for the ordered phase in the vicinity of order-disorder transition (ODT) temperature. Thus, the ordered phases in WSL can be described by the density waves with a single wavenumber. Experiments by Cohen and co-workers showed that the WSL behavior in 1,4-polyisoprene-1,4-polybutadiene[13] and 1,4-polybutadiene-1,2-polybutadiene[14] diblock copolymers melts is qualitatively consistent with Leibler's mean-field theory. Bates *et al.*[15][16], by using small-angle neutron scattering (SANS) in partially deuterated 1,4-polybutadiene-1,2-polybutadiene, and Mori *et al.*[17], by applying small-angle X-ray scattering (SAXS) on polystyrene-polyisoprene diblock copolymers, also demonstrated the temperature dependence of measured structure factor in the disordered state agrees with what Leibler predicted for $f \sim 0.5$.

The strong segregation limit (SSL) is reached as $N\chi$ approaches 50. In this regime, the A-rich and B-rich domains are separated by sharp interfaces and the blocks are highly stretched. Helfand and Wasserman[18][19] developed a self-consistent field theory that enables quantitative calculations of free energies, composition profiles and chain conformations in the regime of $N\chi \gg 10$. They also developed numerical tech-

niques for calculating the phase diagram in SSL, and located the nearly temperature-independent phase boundaries for the L, H and BCC phases, see a schematic in Fig. 1.2. Experiments[20] using TEM clearly showed L, H and BCC structures in this region with well-defined composition ranges. The compositions at the phase boundaries are consistent with what Helfand and Wasserman[19] predicted.

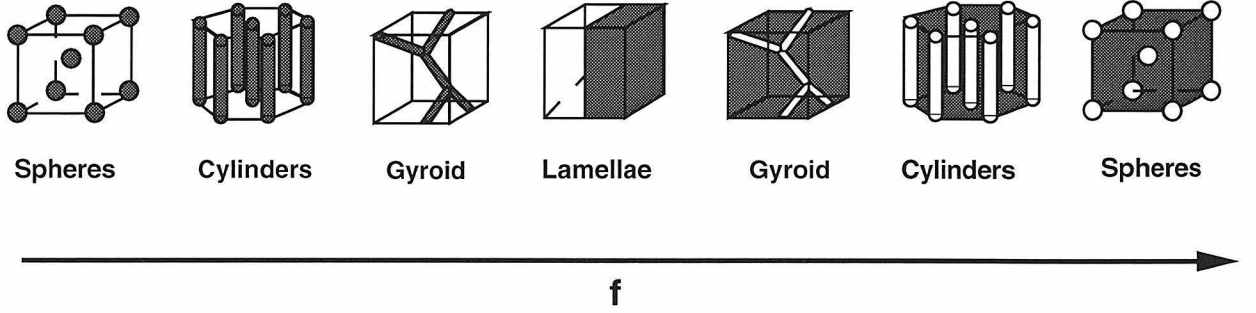


Figure 1.1: Schematic diblock copolymer morphologies. (Reproduce from Ref. [25])

Only in the past several years has the intermediate segregation region (ISR) been distinguished as a separate regime, distinct from the asymptotic WSL and SSL. In this regime, additional Fourier modes are required to accurately model the microphases. Matsen and Schick[21] examined this region by using incompressible Gaussian chain and self-consistent field theory formulated using Bloch waves. Thus, a complete phase diagram in ISR is calculated. Roughly speaking, for $f = 0.5$, the ISR is between $N\chi = 12$ to $N\chi = 50$, but a more precision location is not possible since the progression from the WSL to the ISP and then to the SSL is a gradual one. An interesting discovery within the ISR is a new equilibrium bicontinuous gyroid (G) phase[22][21] [23][24], which starts and ends at two triple points, see the schematic morphology in Fig. 1.1 and phase diagram in Fig. 1.2. This phase requires at least two sets of Fourier modes to describe, and it was not included in the Leibler's mean-field theory.

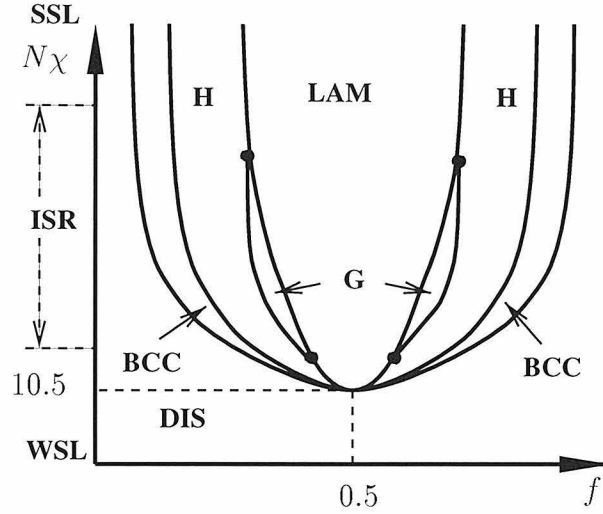


Figure 1.2: The schematic phase diagram of diblock copolymers.

The equilibrium morphological behaviors of such simple diblock copolymers are now well understood. Relevant to the current work is the fact that in the weak-segregation limit (i.e., near the microphase separation transition or MST), phase transitions can be affected by changing the temperature, see the phase diagram in Fig. 1.2. Thus an interesting and natural question is: what are the kinetic pathways during the various order-order and order-disorder transitions after a sudden temperature change? More specifically, how does the system transform from one microstructure to another (of different symmetry)? Are there interesting intermediate states during the transition? If so, what is the nature of these intermediate states? Apart from the fundamental interest in understanding the kinetics of phase transitions involving spatially modulated phases, answers to these questions are also helpful in designing suitable processing routes for obtaining well-ordered structures in self-assembling systems. For example, our results indicate that hexagonal cylinders obtained by a temperature jump from a defect-free lamellar structure do not contain many structural defects, whereas the same structure obtained by a temperature quench from the disordered or even the BCC phase will usually be laden with defects. This in turn raises an interesting question about the role of the initial symmetry in directing the structural evolution of another phase.

In the following chapters, we will address the question of thermally induced microphase transition kinetics by a time-dependent Ginzburg-Landau (TDGL) approach. We will focus on the WSL, since the phase behavior in this regime depend most sensitively on the temperature. Apart from directly addressing the issues outlined above, our study also sheds light on the nature and stability of certain new structures discovered in several recent experiments[26][27] [28][29].

1.3 Theoretical Approach for Weakly Segregated DCP Melts

Our study employs the time-dependent Ginzburg-Landau (TDGL) approach. A key input in this approach is the free energy functional in term of an appropriate order parameter. In this section, we briefly outline the derivation of the order-parameter free energy.

Consider a system of n_p diblock copolymer molecules with N_A monomers of type A and $N_B = N - N_A$ monomers of type B in one chain. For a single noninteracting polymer, the statistical weight for a given configuration $\{\vec{R}(n)\}$ (where $\vec{R}(n)$ is the position of the n th segment which is taken as continuous) is

$$\Psi[\{\vec{R}(n)\}] \sim \exp \left[-\frac{3}{2b^2} \sum_{\alpha=1}^{n_p} \int_0^N dn \left(\frac{\partial \vec{R}^\alpha(n)}{\partial n} \right)^2 - \beta U \right], \quad (1.1)$$

where $\beta = 1/(k_B T)$ and b is the statistical segment length (called Kuhn length). U is the potential which includes interaction between the monomers and the potential coming from external fields. The total Hamiltonian, therefore, is of the form

$$H = \frac{3k_B T}{2b^2} \sum_{\alpha=1}^{n_p} \int_0^N dn \left(\frac{\partial \vec{R}^\alpha(n)}{\partial n} \right)^2 + U. \quad (1.2)$$

Because of the liquid density of the diblock copolymers, the system can be considered incompressible. This is conveniently expressed as a delta-function $-\delta(\hat{\rho}_A(\vec{r}) + \hat{\rho}_B(\vec{r}) - \rho)$ in the statistical weight, where the microscopic local volume fraction $\hat{\rho}_i(\vec{r})$ is defined

as

$$\hat{\rho}_i(\vec{r}) = \frac{V}{n_p N} \sum_{\alpha=1}^{n_p} \sum_{n=1}^{N_i} \delta[\vec{r} - \vec{R}_i^\alpha(n)], (i = A, B). \quad (1.3)$$

Where V is the volume of the sample.

Since we are interested in properties that are on much larger length scales than the monomer size, it is often adequate to write the interaction between monomer as a local pseudopotential

$$U = \frac{n_p N}{V} \sum_{i,j} w_{ij} \int \hat{\rho}_i(\vec{r}) \hat{\rho}_j(\vec{r}) d\vec{r}, \quad (1.4)$$

where $i, j = A$ or B , and w_{ij} are the interaction parameters between monomer type i and type j . Because of the incompressibility condition, U can be written as

$$U = U_0 - \frac{n_p N \chi k_B T}{V} \int \hat{\rho}_A(\vec{r})^2 d\vec{r}. \quad (1.5)$$

Where χ satisfies

$$\chi = \beta w_{AB} - \beta(w_{AA} + w_{BB})/2. \quad (1.6)$$

Since it is more appropriate to describe the microphase behavior by using an order parameter, we define a coarse grained local density $\rho_j(\vec{r})$ ($j = A$ or B) as the thermal average of the microscopic local density $\hat{\rho}_j(\vec{r})$: $\langle \hat{\rho}_j(\vec{r}) \rangle = \rho_j(\vec{r})$. From this, we define the order parameter ψ as $\psi(\vec{r}) = \rho_A(\vec{r}) - f$, here f is the fraction of monomers A in one chain: $f = N_A/N$. Because the problem can be solved more easily in k -space, we shall use the Fourier transform of the order parameter, *i.e.* $\psi(\vec{q})$ as the variable. Thus, the incompressibility condition becomes $\hat{\rho}_A(\vec{q}) + \hat{\rho}_B(\vec{q}) = 0$ for $\vec{q} \neq 0$ and $\hat{\rho}_A(\vec{q}) + \hat{\rho}_B(\vec{q}) = \text{const}$ for $\vec{q} = 0$. Since $\vec{q} = 0$ terms contribute constant prefactor in the statistical weight, we shall ignore it. After these definitions, we introduce the free energy functional $F[\psi(\vec{q})]$ of the diblock copolymer system through

$$\begin{aligned}
Z &= \int D[\psi(\vec{q})] \exp\{-\beta F[\psi(\vec{q})]\} = \int \Pi_{\alpha=1}^{n_p} \left\{ D[\vec{R}_j^\alpha(n)] \delta[\vec{R}_A^\alpha(n) - \vec{R}_B^\alpha(0)] \right\} \\
&\times \exp \left\{ -\frac{3}{2b_A^2} \sum_{\alpha=1}^{n_p} \int_0^{N_A} dn \left(\frac{\partial \vec{R}_A^\alpha(n)}{\partial n} \right)^2 - \frac{3}{2b_B^2} \sum_{\alpha=1}^{n_p} \int_0^{N_B} dn \left(\frac{\partial \vec{R}_B^\alpha(n)}{\partial n} \right)^2 + \frac{n_p N \chi}{V} \int \hat{\rho}_A(\vec{q}) \hat{\rho}_A(-\vec{q}) d\vec{q} \right\} \\
&\times \int D[\rho_A(\vec{q})] D[\rho_B(\vec{q})] \Pi_{\vec{q} \neq 0} \left\{ \delta[\hat{\rho}_A(\vec{q}) + \hat{\rho}_B(\vec{q})] \delta[\hat{\rho}_A(\vec{q}) - \rho_A(\vec{q})] \delta[\hat{\rho}_B(\vec{q}) - \rho_B(\vec{q})] \right\}, \quad (1.7)
\end{aligned}$$

where $D[\vec{R}_j^\alpha(n)] = \Pi_{n=0}^{N_j} d\vec{R}_j^\alpha(n)$, $D[\rho_j(\vec{q})] = \Pi_{\vec{q} \neq 0} d\rho_j(\vec{q})$, $j = A$ or B , and the first delta-function in Eq. 1.7 ensures the connectivity of the A and B blocks.

The free energy functional $F[\psi]$ can be obtained by using the random phase approximation on the above partition function. This was done first by Leibler[4]. The resulting free energy functional has the form of

$$\begin{aligned}
F &= F_0 + \frac{1}{2} \int d\vec{k} \Gamma_2(\vec{k}, -\vec{k}) \psi(\vec{k}) \psi(-\vec{k}) + \frac{1}{3!} \int d\vec{k}_1 d\vec{k}_2 \Gamma_3(\vec{k}_1, \vec{k}_2, -\vec{k}_1 - \vec{k}_2) \psi(\vec{k}_1) \psi(\vec{k}_2) \\
&\times \psi(-\vec{k}_1 - \vec{k}_2) + \frac{1}{4!} \int d\vec{k}_1 d\vec{k}_2 d\vec{k}_3 \Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, -\vec{k}_1 - \vec{k}_2 - \vec{k}_3) \psi(\vec{k}_1) \psi(\vec{k}_2) \psi(\vec{k}_3) \\
&\times \psi(-\vec{k}_1 - \vec{k}_2 - \vec{k}_3) + \dots, \quad (1.8)
\end{aligned}$$

where $\psi(\vec{k})$ is the Fourier transformation of $\psi(\vec{r})$. $\Gamma_2(\vec{k}_1, \vec{k}_2)$, $\Gamma_3(\vec{k}_1, \vec{k}_2, \vec{k}_3)$, and $\Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$ are in general wavevector-dependent coefficients in the expansion. The two-point vertex function has the form of $\Gamma_2(\vec{k}, -\vec{k}) = S_0^{-1}(k) - 2N\chi$, where $S_0(k)$ is the structure factor for noninteracting diblock copolymers and is peaked at a wavenumber k^* . The derivation of Γ_2 is given in Appendix. The derivation of $\Gamma_3(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ and $\Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$ is similar by considering higher order expansion in Eq. A.7. In the weak-segregation regime where the temperature is close to ODT temperature, the density waves are dominated by wavevectors with the optimal wavenumber k^* . Thus we approximate the functions $\Gamma_3(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ and $\Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$ by their values corresponding to wavevectors having the optimal magnitude k^* . In this approximation, $\Gamma_3(\vec{k}_1, \vec{k}_2, \vec{k}_3)$ becomes independent of the wavevectors while $\Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$ has only a weak angular dependence. We further ignore the angular dependence in Γ_4

by the approximation $\Gamma_4(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4) = \Gamma_4(0, 0)$, where $\Gamma_4(0, 0)$ is a function defined in Ref. [4]. We denote these functions as γ_3 and γ_4 , respectively. These approximations are not necessary and are not expected to have any significant effects on the issue we wish to address here, but greatly simplify the calculations and make the results much more transparent. Thus, above free energy functional becomes

$$F = F_0 + \frac{1}{2} \int d\vec{k} [S_0^{-1} - 2N\chi] \psi(\vec{k})\psi(-\vec{k}) + \frac{\gamma_3}{3!} \int d\vec{k}_1 d\vec{k}_2 \psi(\vec{k}_1)\psi(\vec{k}_2)\psi(-\vec{k}_1 - \vec{k}_2) + \frac{\gamma_4}{4!} \int d\vec{k}_1 d\vec{k}_2 d\vec{k}_3 \psi(\vec{k}_1)\psi(\vec{k}_2)\psi(\vec{k}_3)\psi(-\vec{k}_1 - \vec{k}_2 - \vec{k}_3) + \dots \quad (1.9)$$

Based on the free energy in Eq. 1.9, the mean-field phase diagram of diblock copolymers has been depicted, see Fig. 1.3. This phase diagram is valid only when $N\chi$ is close to ODT value, *i.e.*, in WSL. Notice that the phase behavior is related to $N\chi$, instead of N and χ , and for compositional symmetrical diblock copolymers (*i.e.*, $f = 0.5$), only L phase can be formed from disordered phase (DIS) through a second order phase transition.

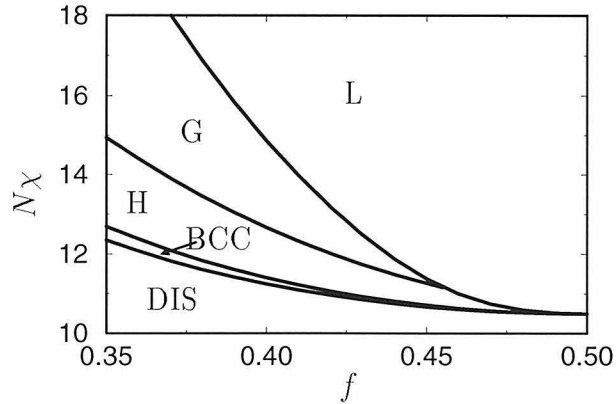


Figure 1.3: The mean-field phase diagram for diblock copolymer melts, calculated using the free energy Eq.1.9.

To derive the dynamic equation governing the evolution of the order parameter under nonequilibrium conditions, one should in principle start from the equations of motion at the level of the polymer chains. Formally, this is accomplished by projecting the chain-level dynamics onto the order parameter dynamics[30], or by applying a

dynamic RPA[31]. Implementation of this procedure, however, is extremely involved, and has only been done for some specific systems. Since the focus of our study is not to understand the order-parameter dynamics from the microscopic chain dynamics, we adopt a more phenomenological approach, namely the time-dependent Ginzburg-Landau (TDGL) approach[32]. In this approach, the evolution of the order parameter is driven by the functional derivative of the order-parameter free energy. For conserved order parameter, the TDGL takes the form of

$$\frac{\partial \psi(\vec{r}, t)}{\partial t} = \int d\vec{r}' M(\vec{r} - \vec{r}') \nabla_{\vec{r}'}^2 \left[\frac{\delta F}{\delta \psi(\vec{r}')} \right] + \eta(\vec{r}, t), \quad (1.10)$$

where $M(\vec{r} - \vec{r}')$ is a mobility coefficient which is in general nonlocal[30][31] [33][34][35][36]. $\eta(\vec{r}, t)$ is a random fluctuating force with zero mean and with a variance satisfying the fluctuation-dissipation theorem:

$$\langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle = -2k_B T \nabla^2 M(\vec{r} - \vec{r}') \delta(t - t'). \quad (1.11)$$

Eqs. 1.10 and 1.11 together with the free energy functional Eq. 1.9 form the basis of our study.

1.4 Thesis Perspective

In this thesis, we analyze the various order-order and order-disorder transition kinetics by the time-dependent Ginzburg-Landau (TDGL) approach. In Chapter 2, we investigate the microstructural changes as well as the order parameter evolution after a sudden temperature jump from one phase to another by direct simulation of the TDGL equations. We find that depending on the extent of the temperature jump, these transitions often occur in several stages and can involve nontrivial intermediate states. For example, we find that transition from the lamellar phase to the hexagonal cylinder phase goes through a perforated lamellar (PL) state within a certain temperature range. In Chapter 3, we develop a theoretical framework to elucidate the numerical results of Chapter 2. First, based on the concept of anisotropic fluctu-

ations of the order parameter in the ordered structures, different fluctuation modes (eigenvectors) are obtained. The emergence of the new structure is due to the least stable fluctuation modes. A systematic linear stability analysis is presented both for the equilibrium states (in order to locate the spinodal of the initial structure) and for nonequilibrium states where the thermodynamic driving force is nonvanishing. This allows us to determine the stability of the mean-field kinetic path. By combining the least stable modes and the order parameter of the initial structures into an expanded order-parameter space, we are able to describe qualitatively the full nonlinear evolution of the system during the various transitions. Based on the results of both Chapters 2 and 3, we provide two models for the puzzling modulated lamellar and perforated lamellar phases in Chapter 4. The nature and stability of the suggested models are discussed, and analytically calculated structure factors are compared with available experimental results.

Bibliography

- [1] Fried, J. R. 'Polymer Science and Technology', Prentice Hall PTR, New Jersey, 1995
- [2] Utracki, L. A. 'Polymer Alloys and Blends', Hanser, New York, 1990
- [3] de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell Univ. Press, Ithaca, 1979
- [4] Leibler, L. *Macromolecules* 1980, **13**, 1602
- [5] de la Cruz M. O. and Sanchez, I. C. *Macromolecules* 1986, **19**, 2501
- [6] Matsen, M. W. and Schick, M. *Macromolecules* 1994, **27**, 6761
- [7] Alivisato, A. P. *J. Phys. Chem.* 1996, **100**, 13226
- [8] Antonietti, M. *Macromolecules* 1991, **24**, 6636; 1992, **25**, 1139
- [9] Asher, S. *Macromolecules* 1995, **28**, 6533
- [10] Bates, F. S. and Fredrickson, G. H. *Ann. Rev. Phys. Chem* 1990, **41**, 525
- [11] Fredrickson, G. H. and Bates, F. S. *Ann. Rev. Mater. Sci* 1996, **26**, 501
- [12] Bates, F. S. *Science* 1991, **251**, 898
- [13] Ramos, A. R. and Cohen, R. E. *Polym. Eng. Sci* 1977, **17**, 639; Cohen, R. E. and Ramos, A. R. *Macromolecules* 1979, **12**, 131
- [14] Cohen, R. E. and Wilfong, D. E. *Macromolecules* 1982, **15**, 370
- [15] Bates, F. S. and Hartney, M. A. *Macromolecules* 1985, **18**, 2478; *Macromolecules* 1986, **19**, 2892
- [16] Bates, F. S. *Macromolecules*, 1985, **18**, 525

- [17] Mori, K., Hasegawa, H. and Hashimoto, T. *Poly. J.*, 1985, **17**, 799
- [18] Helfand, E. *Macromolecules* 1975, **8**, 552; Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879
- [19] Helfand, E. and Wasserman, Z. R., p 99 *Developments in Block Copolymers-1*. Goodman, I. ed. New York: Applied Sci.
- [20] Gallot, B. R. M. *Adv. Polym. Sci.* 1978, **29**, 85
- [21] Matsen, M. W. and Schick, M. *Phys. Rev. Lett.* 1994, **72**, 2660
- [22] Matsen, M. W. and Bates, F. S. *Macromolecules* 1996, **29**, 1091
- [23] Hajduk, D. A., Harper, P. E., Gruner, S. M., Honeker, C. C., Kim, G., Thomas, E. L., Fetters, L. J. *Macromolecules* 1994, **27**, 4063
- [24] Schulz, M. F., Bates, F. S., Almdal, K., Mortensen, K. *Phys. Rev. Lett.* 1994, **73**, 86
- [25] Zheng, W. *Ph.D. Thesis*, Caltech, 1996
- [26] Hamley, I. W., Koppi, K. A., Rosedale, J. H., Bates, F. S., Almdal, K. and Mortensen, K. *Macromolecules* 1993, **26**, 5959
- [27] Thomas, E. L., Anderson, D. M., Henkee, C. S. and Hoffman, D. *Nature* 1988, **334**, 598
- [28] Förster, S., Khandpur, A. K., Zhao, J., Bates, F. S., Hamley, I. W., Ryan, A. J. and Bras, W. *Macromolecules* 1994, **27**, 6922
- [29] Khandpur, A. K., Förster, S., Bates, F. S., Hamley, I. W., Ryan, A. J., Bras, W., Almdal, K. and Mortensen, K. *Macromolecules* 1995, **28**, 8796
- [30] Kawasaki, K. and Sekimoto, K. *Physica* 1988, **143A**, 349; *Physica* 1988, **148A**, 361
- [31] Kumaran, V. and Fredrickson, G. H. *Physica* 1994, **204A**, 378

- [32] Gunton, J. D., Miguel, M. S. and Sahni, P. S. 'Phase Transition and Critical Phenomena' **vol18** (edited by Domb, C. and Lebowitz, J. L.), Academic Press, New York, 1983
- [33] de Gennes, P. G. *J. Chem. Phys.* 1980, **72**, 4756
- [34] Pincus, P. *J. Chem. Phys.* 1981, **76**, 1996
- [35] Binder, K. *J. Chem. Phys.* 1983, **79**, 6387
- [36] Fredrickson, G. H. *J. Chem. Phys.* 1986, **85**, 5306

Chapter 2 Simulation of Diblock Copolymer Phase Transition Kinetics

2.1 Introduction

As mentioned in Chapter 1, one of the most fascinating properties of block copolymers is their ability to self-assemble into a variety of ordered microstructures. The simplest block copolymer system is an undiluted diblock copolymer with two incompatible blocks, where upon decreasing the temperature and/or increasing the molecular weight, a variety of ordered microstructures, such as lamellae (LAM), hexagonally packed cylinders (HEX), body-centered-cubic (BCC) spheres, and bicontinuous gyroid (G) structures, have been obtained [1].

In this Chapter, we address the questions of thermally induced phase transitions by a time-dependent Ginzburg-Landau (TDGL) approach. To be concrete, we shall use A-B diblock copolymers as the context, although the same analysis can be easily extended to other systems. For diblock copolymers, the appropriate order-parameter is $\psi(\vec{r}) = \rho_A(\vec{r}) - f$, where $\rho_A(\vec{r})$ is the local volume fractions of A-monomers, and f is the fraction of A-monomers in the diblock. The time evolution of the order parameter ψ is governed, in the spirit of linear irreversible thermodynamics, by the time-dependent Ginzburg-Landau (TDGL) equation[2] shown in Eq. 1.10. As mentioned in Chapter 1, derivation of the TDGL equations from the microscopic chain dynamics generally yield a non-local mobility coefficient[3][4][5]. Here we ignore this non-locality by assuming a constant mobility M ($M(\vec{r} - \vec{r}') = M\delta(\vec{r} - \vec{r}')$). This should not be a serious approximation in the weak-segregation regime since the order parameter in this regime is dominated by a single wavenumber. By the same token, the distinction between conserved and non-conserved order-parameter dynamics is not essential, and therefore most of our results for the case of conserved order param-

eters should be applicable also for nonconserved order parameters. The simplified TDGL thus takes the form of

$$\frac{\partial \psi}{\partial t} = M \nabla^2 \left(\frac{\delta F}{\delta \psi} \right) + \eta(\vec{r}, t), \quad (2.1)$$

where we have used the fact that ψ is a conserved order parameter as is appropriate for diblock copolymers. $\eta(\vec{r}, t)$ is a random force, which for a system in equilibrium at temperature T , satisfies the fluctuation-dissipation relation:

$$\langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle = -2Mk_B T \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t'); \quad (2.2)$$

and $F[\psi(\vec{r})]$ is the free energy functional which we take to be of the form:

$$\begin{aligned} F[\psi(\vec{r})] = & \int d\vec{r} \left\{ \psi(\vec{r}) \left[-\frac{\tau}{2} + \frac{a}{2}(1-2f)^2 - \frac{b}{2}\nabla^2 \right] \psi(\vec{r}) \right. \\ & + \frac{v}{3}(1-2f)\psi(\vec{r})^3 + \frac{u}{4}\psi(\vec{r})^4 \Big\} \\ & + \frac{c}{2} \int d\vec{r}_1 \int d\vec{r}_2 G(\vec{r}_1 - \vec{r}_2) \psi(\vec{r}_1) \psi(\vec{r}_2). \end{aligned} \quad (2.3)$$

This form of the free energy can be considered as an expansion in the order-parameter $\psi(\vec{r})$ and $1-2f$ from the free energy functional in Eq. 1.9 with Fourier transformation. The long-range interaction in the last integral arises from the connectivity of the two blocks and is typical of amphiphilic systems[6] [7][8], where $G(\vec{r}_1 - \vec{r}_2)$ satisfies $\nabla^2 G(\vec{r}_1 - \vec{r}_2) = -\delta(\vec{r}_1 - \vec{r}_2)$. The coefficients a, b, c, u, v can be computed by evaluating the appropriate vertex functions given by Leibler[9] together with the local approximation for the higher (3rd and 4th) vertex functions[7][10]. τ is related to the Flory-Huggins interaction parameter χ (thus the temperature) by relation

$$N\chi = S_0^{-1}(k^*, f)/2 + \frac{3u\gamma_3^2}{4v^2\gamma_4(1-2f)^2} \left[\tau - 2\sqrt{bc} - a(1-2f)^2 \right]. \quad (2.4)$$

We point out that a large class of physical systems with competing short-range and long-range interactions can be described by a free energy functional of the type Eq.

(2.3)[11]. Therefore we believe that the phenomenology we are studying is quite general and hence we allow the freedom of choosing the parameters in Eq. (2.3) as phenomenological constants not specifically limited to diblock copolymers.

Several dynamical aspects of systems that can be described by the free energy functional Eq. (2.3) have been addressed in the literature. Desai and co-workers, using a combination of numerical and analytical approaches, have extensively investigated the kinetics of microstructure formation from the disordered phase [12]. Oono and co-workers [13] [14] developed a cell-dynamics approach for simulating the formation of microstructures in diblock copolymers. Chakrabarti *et al*, using the cell-dynamics approach combined with simulated annealing, showed that large, defect-free lamellar domains can be obtained with sufficiently slow cooling rate [15]. A number of researchers have addressed the rheological properties of block copolymers near the order-disorder transition [16][17] and in the ordered phases[18][19]. In recent years, flow-induced ordering and alignment of microstructures by flow in block copolymers, have attracted much attention both theoretically [20] [21] [22] [23] and experimentally[24]. While these dynamical issues are all important and interesting, we feel that the simpler but no less important question of the kinetics of transitions between different ordered phases and between an ordered and the disordered phase in the quiescent condition need to be addressed. The kinetics turns out to be far from trivial, even in transitions where there is no free energy barrier: as we will demonstrate in this Chapter and Chapter 3, pseudostable and transient states on the kinetic pathway, which are due, respectively, to saddle and ridge-like features on the free energy surface, give rise to interesting intermediate structures during the transition and to non-simple temporal behaviors.

The TDGL equation will be analyzed by two methods: in this Chapter, direct numerical simulation will be applied; in Chapter 3, based on the concept of anisotropic fluctuation, a simplified single-wavenumber mode analysis is used to explain above simulation results by combining the least stable fluctuation and the order parameter of the initial structures into an expanded order parameter space. The temperature change is mimicked by a change in the parameter $N\chi$ from an initial value favoring

one phase $(N\chi)_i$ to a value favoring a different phase $(N\chi)_f$. Broadly speaking, an increase in $N\chi$ corresponds to a decrease in temperature and vice versa. In this work we shall focus on temperature-jump (T-jump) kinetics because in temperature-quench cases, the kinetics usually involves the formation of complicated topological defects accompanying the lowering of symmetry in a system. Inclusion of such defects requires a much larger system in the direct numerical simulation and more sophisticated analytical approaches than those employed here. Also, we avoid the issue of nucleation and consider cases where the T-jumps are beyond the spinodal of the initial phase in question. Thus the transitions we study are barrierless and the microstructural changes are global. Finally, we limit our study to transitions involving the lamellar (L), hexagonal cylinder (H), body-center-cubic (BCC) and disordered (DIS) phases. We omit the gyroid phase[25] since this phase is not stable in the weak segregation limit (WSL)[26][27].

2.2 Direct Numerical Simulation

In this section, we present results from direct numerical simulation of Eq. (2.1). The parameters are chosen to be $u = 0.5, v = 1.5, b = 0.5, c = 0.02$ and $a = 1.5$. To facilitate the numerical procedure, we bring Eq. (2.1) into a cell-dynamics form suggested by Oono and co-workers[13][14]. The numerical simulations are performed on a $48 \times 48 \times 50$ simple cubic lattice. An initial ordered structure (L, H, BCC) is prepared at the initial temperature $(N\chi)_i$; then we change $N\chi$ to $(N\chi)_f$ and follow the subsequent evolution of the system after this sudden change in temperature. To be consistent with the mean-field level mode analysis in Section 3.4, we will ignore the thermal noise term in Eq. (2.1), except to include it as providing an initial randomness (for possible symmetry breaking). We have conducted studies that include the fluctuation during the simulation and do not find its effects to be essential. The effects of fluctuations will be discussed further in Section 2.3.

Two different procedures are used to generate the initial defect-free ordered phases. One is to set a sinusoidal wave with the appropriate symmetry of the state (with the

wavelength determined from the free energy) and then let the system equilibrate for sufficiently long time. Another procedure is to let the ordered phase evolve from the disordered state by adding a random but anisotropic initial perturbation determined by the symmetry of the state. The two schemes lead to the same ordered structures. In both cases, we make sure that the initial ordered phase is the equilibrium structure at the temperature ($N\chi$) from the mean-field diagram.

To quantify the global temporal behavior of the system, we introduce an order parameter $Q = \sqrt{\sum_{sites} \psi(\vec{r})^2} = \sqrt{\sum_k \psi_k \psi_{-k}}$. At the mean-field level, Q is zero in the disordered phase and is positive in the ordered phases. The time evolution of Q is used to demonstrate different stages in the kinetics. Where there involve interesting intermediate states, we also show 3-dimensional gray-level plots of the order parameters or 2-dimensional cross-sections. The different transitions are listed below. Cross references are made between this Section and Section 3.4 in order to corroborate between the numerical findings and results from the simplified mode analyses.

2.2.1 L to H Transition

A transition from L to the hexagonal cylinder (H) phase is possible only for asymmetric diblocks. Here we choose $f = 0.45$. The initial value of the temperature-like parameter $(N\chi)_i = 11.67$ (or $\tau_i = 0.35$). The mean-field equilibrium structure corresponding to this set of parameters is the lamellar structure. The structure is shown in Fig. 2.1(a), with the layer normal along the z-direction. Three temperature jumps are studied with the final $(N\chi)_f$ equal 10.95, 10.80 and 10.74 (or τ_f equal 0.25, 0.23 and 0.22), respectively, all within the H phase in the mean-field phase diagram. On physical grounds, we expect the cylinders to pinch off from the lamellar layers containing the minority blocks, with their axes lying within the initial lamellar layers.

Direct visual inspection of the gray-level plot of the microstructures during the first plateau region does not reveal any specific structure within the lamellar layers. Thus the system remains in the lamellar phase, with a decreased order-parameter.

A multimode analysis using the single wave-number approximation in the Section 3.4 shows that the first plateau in Fig. 2.2 corresponds to a saddle-point in the free energy surface.

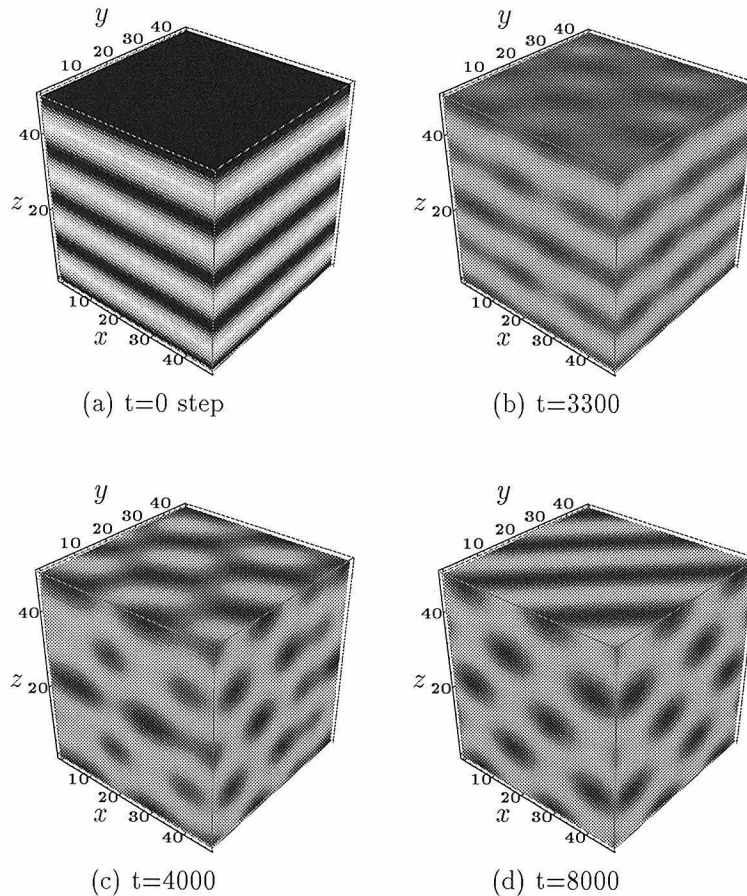


Figure 2.1: Microstructural evolution after a T-jump from L to H at $f = 0.45$ ($(N\chi)_i = 11.67$, $(N\chi)_f = 10.95$ or $\tau_i = 0.35, \tau_f = 0.25$); Data taken at various stages of the simulation.

Fig. 2.2 shows the temporal evolution of the global order parameter Q . For all the three temperature jumps, the order parameter reaches a final steady-state value consistent with the equilibrium H phase. However, in all three cases, the evolution is non-monotonic. In the cases of the two lower temperatures (or larger $(N\chi)_f$ values), there is a clear plateau following the initial rapid decrease in the order parameter,

suggesting that the system reaches some kind of stagnation point. The duration of the plateau is clearly longer for the lower temperature ($(N_\chi)_f = 10.95$) than for the higher temperature ($(N_\chi)_f = 10.80$). For $(N_\chi)_f = 10.74$ the plateau is less pronounced.

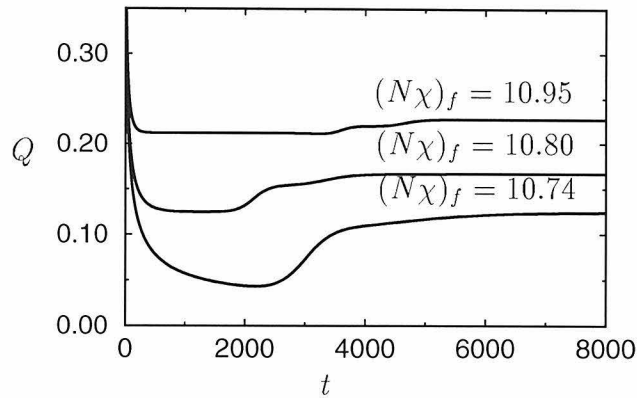


Figure 2.2: Temporal evolution of the global order parameter Q during the L to H transition at $f = 0.45$ for T-jumps from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.95$, 10.80 and 10.74 (or from $\tau_i = 0.35$ to $\tau_f = 0.25$, 0.23 and 0.22), respectively.

Of special interest is the appearance of a second plateau in the two lower temperature cases. A gray-level order-parameter plot (Fig. 2.1(b)) shows that at the end of the first plateau, modulation within the lamellar layers begins to develop. The structure becomes most pronounced in the flat part of the plateau; see Fig. 2.1(c). There seems to be clear correlations between different layers. At the end of the plateau, cylinders evolve by connecting the dark regions in one of the diagonal directions of the xy plane. The final H structure is shown in Fig. 2.1(d). It is remarkable that this structure is nearly perfect, *i.e.*, free of any structural defects, although a symmetry breaking is clearly required to select the orientation of the cylinders within the lamellar layers.

The structural characteristics of the intermediate structure resembles in many respects the so-called perforated or modulated lamellar (PL or ML) phase reported in literature[28][29][30]. One may tentatively identify the structure in Fig. 2.1 (b) as the modulated lamellae (ML) and that in Fig. 2.1(c) as the perforated lamellae (PL) although the evolution from ML to PL is a continuous process. It will be

shown in the Section 3.4 that the second plateau is due to another saddle point in the free energy surface. The PL structure corresponds to this saddle point, whereas the ML is a transient state between L and PL states. Analyses there show that the perforated lamellar plateau exists only when the final temperature is within a certain “phase boundary” in the H part of the phase diagram. This saddle point disappears when the temperature jump is outside of this “phase boundary” as is the case for $(N\chi)_f = 10.74$. In that case, the cylinder phase emerges directly without going through a distinct PL stage, although a short transient ML state is still involved when the plateau L decays.

2.2.2 L to BCC Transition

The initial state is the same as in the L to H transition. The temperature parameter is changed from $(N\chi)_i = 11.67$ to $(N\chi)_f = 10.705$ (or from $\tau_i = 0.35$ to $\tau_f = 0.216$). The temporal evolution of the global order parameter is shown in Fig. 2.3. Notice the large initial decrease in the order parameter. This initial fast decrease is followed by a long valley where the order parameter increases only slightly but overall remains very weak. Gray-level plots (with the same contrast level as in Fig. 2.1(a)) of the spatial distribution of the order parameter shows no specific structure within the lamellar layers at the bottom of the curve, corresponding to $t = 5000$ [31]. However, upon enhancing the contrast in the images, some weak traces of the BCC wave superposed on the lamellar structure can be detected, see Fig. 2.4. The BCC waves appear at an accelerated pace at about $t = 15000$ and the final BCC structure is completed within a short period of time thereafter. It will again be shown that the long valley is due to the existence of saddle regions in the free energy surface. At $t = 20000$, the system reaches a stable BCC microstructure, see Fig. 2.5. Note again the absence of defects in the structure.

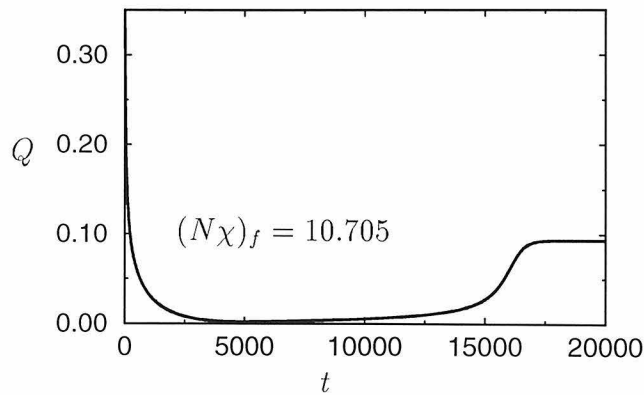


Figure 2.3: Temporal evolution of the global order parameter Q during the L to BCC transition at $f = 0.45$ for a T-jump from $(N\chi)_i = 11.67$ to $(N\chi)_f = 10.705$ (or from $\tau_i = 0.35$ to $\tau_f = 0.216$).

2.2.3 L to DIS Transition

Using the same initial condition as in Section 2.2.1 and Section 2.2.2 (Fig. 2.1(a)), we studied two temperature jumps, from $(N\chi)_i = 11.67$ to $(N\chi)_f = 10.66$ and $(N\chi)_f = 10.60$ (or from $\tau_i = 0.35$ to $\tau_f = 0.21$ and $\tau_f = 0.202$), respectively. Both $(N\chi)_f$'s correspond to the disordered (DIS) phase. In both cases, the global order parameter decreases monotonically, see Fig. 2.6. However, visualization of the gray-level plots of the order parameter during the melting process reveal that melting proceeds through two different routes for the two cases: while in the case of large temperature jump the lamellae melt directly (*i.e.* the amplitude of the lamellar wave simply decreases), in the case of the smaller temperature jump, the lamellae melt by first developing modulation within the lamellar layers and melt as this three-dimensionally ordered structure. Fig. 2.7 shows the gray-level plot in the xy cross-section (*i.e.*, in the lamellar layers). Although the exact symmetry of this intermediate structure is difficult to ascertain owing to the small system size used in the simulation and the weakness of the structure, it is reasonable to believe that this structure is the same as the intermediate, modulated lamellar structure observed during the transition from lamellae to hexagonal cylinders. Using this assumption, we can show that this transient structure results from a ridge-like landscape in the free energy surface, similar to the transient sphere structure seen during the melting of the hexagonal

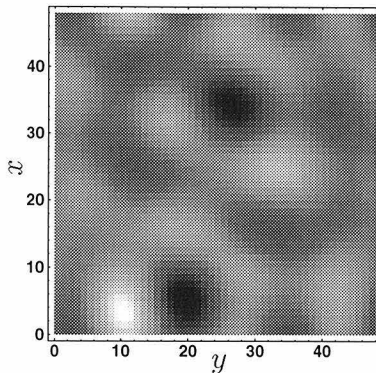


Figure 2.4: Cross-section view of the in-layer (xy plane) structure during the L to BCC transition at $f = 0.45$ for $(N\chi)_f = 10.705$ or $\tau_f = 0.216$ at $t = 5000$, the contrast has been enhanced.

cylinders[32]; see Sections 2.2.5 and 3.4. On the other hand, the melting for the large temperature jump follows a simple down-hill path in a simple parabolic free energy surface.

2.2.4 H to BCC Transition

For the two transitions involving H below, we shall choose $f = 0.4$ instead of $f = 0.45$ used in the previous transitions [33]. An initial equilibrium hexagonal cylinder phase is prepared at $(N\chi)_i = 11.62$ or $\tau_i = 0.30$ (see the initial structure in Fig. 2.9(a)). Two temperature jumps to $(N\chi)_f = 11.27$ and $(N\chi)_f = 11.24$ (or $\tau_f = 0.25$ and 0.246), respectively, are studied. The evolution of the global order-parameter Q is shown for the two cases in Fig. 2.8.

As with temperature jumps from the L phase, a temperature jump from the H phase to the BCC phase leads to a rapid initial decrease in the order parameter. This rapid decrease is followed by a plateau which is again due to a saddle point in the free energy surface. At this saddle point, the system remains a H phase. Thus there is a time lag before the BCC structure appears. The sphere structure begins to emerge from the cylinders at the end of the plateau; see Fig. 2.9(b). The final state is shown in Fig. 2.9(c). Both temperature jumps exhibit the same qualitative

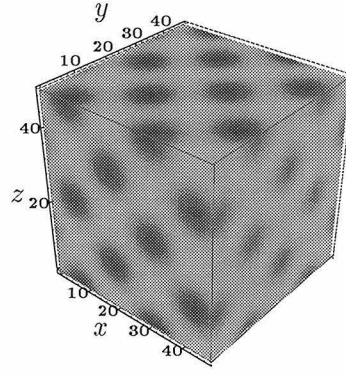


Figure 2.5: Final microstructure after a T-jump from L (same initial state as in Fig.2.1(a)) to BCC at $f = 0.45$ ($(N_\chi)_i = 11.67$, $(N_\chi)_f = 10.705$ or $\tau_i = 0.35$, $\tau_f = 0.216$).

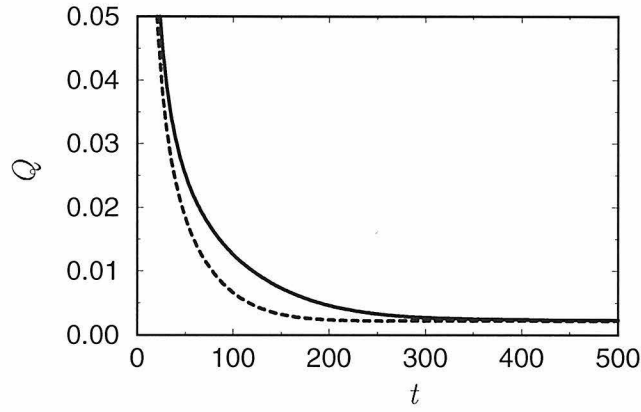


Figure 2.6: Temporal evolution of the global order parameter Q during the L to DIS transition at $f = 0.45$ for a T-jump from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.66$ (solid curve) and 10.60 (dashed curve).

behavior, although the duration of the plateau shortens for the higher temperature (small N_χ). This implies that the saddle point becomes more unstable. Indeed, we have determined that there exists a boundary within the BCC phase, such that the saddle point no longer exists for a temperature jump beyond this boundary. It is interesting to note that, as in the case of L to BCC transition, existence of such a saddle point does not correspond to a new distinct, intermediate structure, but changes the temporal behavior of the kinetics.

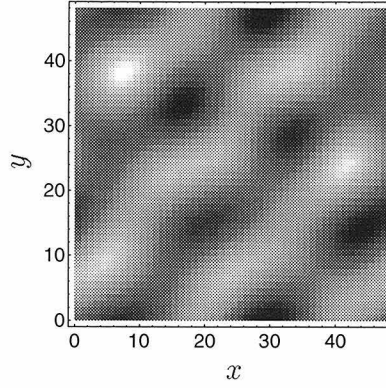


Figure 2.7: Cross-section view of the in-layer (xy plane) structure during the L to DIS transition at $f = 0.45$ for $(N_\chi)_f = 10.66$ or $\tau_f = 0.21$ at $t = 2000$.

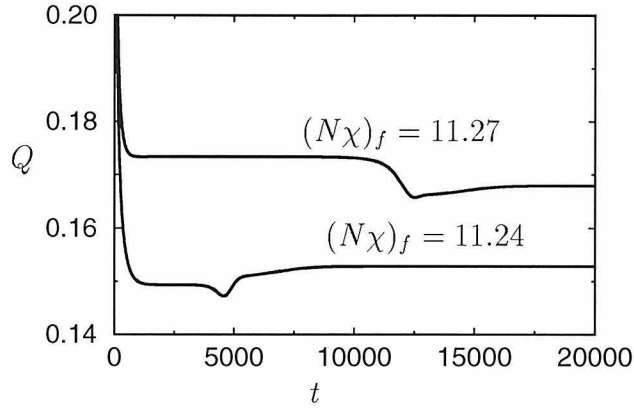


Figure 2.8: Temporal evolution of the global order parameter Q during the H to BCC transition at $f = 0.4$ ($(N_\chi)_i = 11.62$ or $\tau_i = 0.30$).

2.2.5 H to DIS Transition

The same initial state as used in the last subsection is used as the initial state for the H to DIS transition. Two temperature jumps to $(N_\chi)_f = 11.2$ and to $(N_\chi)_f = 11.0$ (or to $\tau_f = 0.24$ and to $\tau_f = 0.21$, respectively, are studied. The evolution of the global order parameter is depicted in Fig. 2.10. For the larger temperature jump to $(N_\chi)_f = 11.0$ (or $\tau_f = 0.21$), the order parameter decays in a simple manner, suggesting direct melting of the cylinders. Gray-level plots of the order-parameter at various times show no structural change as the cylinders melt.

In contrast, the behavior of Q in the case of the smaller temperature jump (to

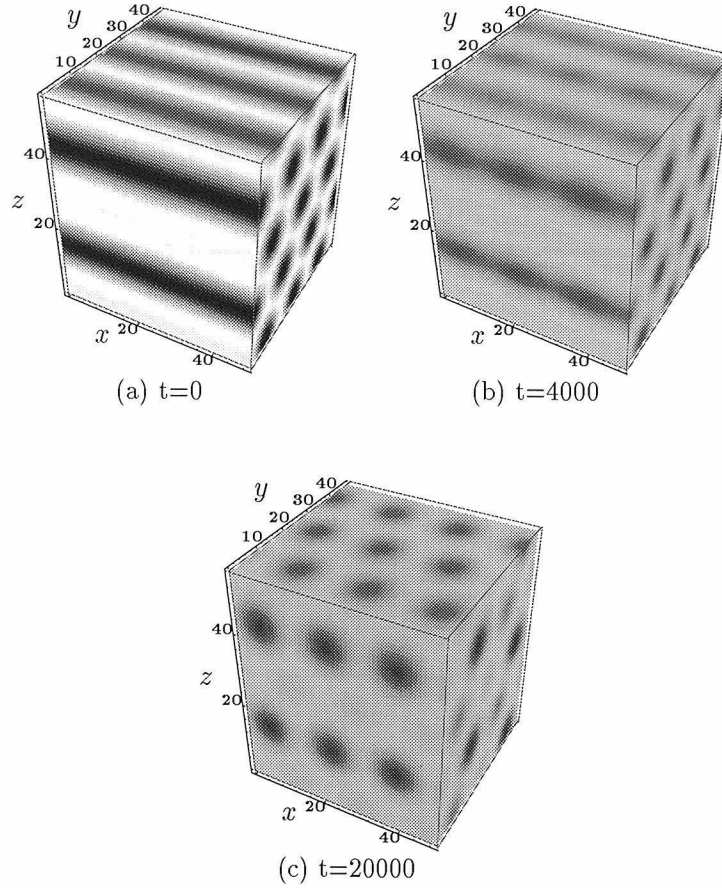


Figure 2.9: Microstructural evolution during the H to BCC transition at $f = 0.4$ with $(N\chi)_i = 11.62$ and $(N\chi)_f = 11.24$ (or $\tau_i = 0.30$, and $\tau_f = 0.246$).

$(N\chi)_f = 11.2$ or $\tau_f = 0.24$) suggests a nontrivial melting process. The slower decay at intermediate times is accompanied by the formation of structures along the cylinders: the cylinders seem to first break into spheres and the melting proceeds via this modulated hexagonal cylinder (MHC) phase. This transient structure is clearest between the two inflection points on the curve in Fig. 2.10, because at long times the structure has all but melted and at short times the structure is dominated by the hexagonal cylindrical structure of the initial state. Fig. 2.11 shows the transient MHC state.

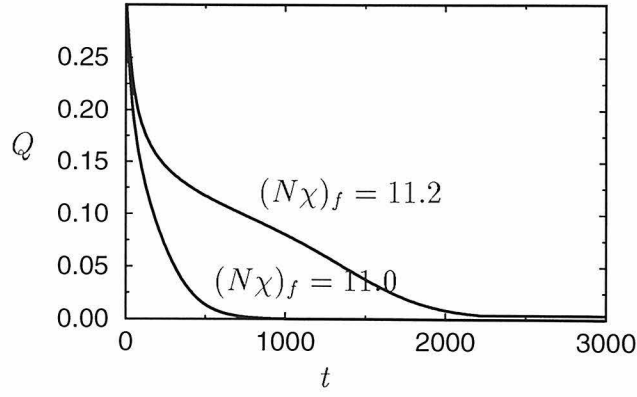


Figure 2.10: Evolution of the global order parameter Q for the T-jump from the H to DIS phase at $f = 0.4$ with $(N\chi)_i = 11.62$ (or $\tau_i = 0.30$).

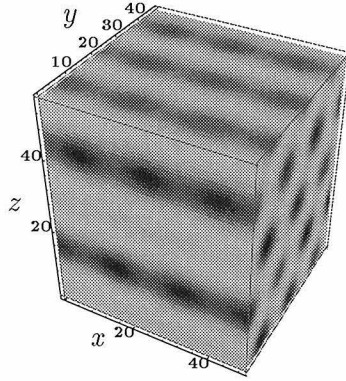


Figure 2.11: Intermediate state during the H to DIS transition at $f = 0.4$ ($(N\chi)_i = 11.62$, $(N\chi)_f = 11.2$ or $\tau_i = 0.30$, $\tau_f = 0.24$), taken at $t=1000$.

To study the effects of *in situ* thermal fluctuations, we have performed simulations both with and without these fluctuations and found that the same qualitative behaviors are observed. (The results presented in this subsection for the smaller temperature jump have been obtained with thermal fluctuations: the final nonvanishing value of Q in Fig. 2.10 is due to these fluctuations.). However, the inclusion of thermal fluctuations in the case of the smaller temperature jump is found to enhance the transient modulated cylinder structure. This point will be discussed further in Section 3.5.

2.2.6 BCC to DIS Transition

For this transition, we choose $f = 0.45$ and use the final BCC structure obtained in the L to BCC transition with $(N\chi)_f = 10.705$ (or $\tau_f = 0.216$) as the initial structure; see Fig. 2.5. Two temperature jumps are studied with $(N\chi)_f = 10.66$ and $(N\chi)_f = 10.60$ (or $\tau_f = 0.21$ and $\tau_f = 0.202$), respectively. The behavior of the global order parameter shows some slight difference for the two temperature jumps, see Fig. 2.12. For the smaller temperature jump ($(N\chi)_f = 10.66$ or $\tau_f = 0.21$), the curve has two inflection points, while for the larger temperature jump ($(N\chi)_f = 10.60$ or $\tau_f = 0.202$), the decay is rather fast and is nearly exponential. This difference for the larger and smaller temperature jumps in this case is rather similar to that in the L to DIS and H to DIS transitions. However, in this case, there is no free energy ridge. In Section 3.4 we will show that there exist two inflection points along the kinetic path on the free energy surface. Although this does not lead to any new intermediate structures (the system melts as a perfect BCC structure), it changes the temporal behavior of the melting process.

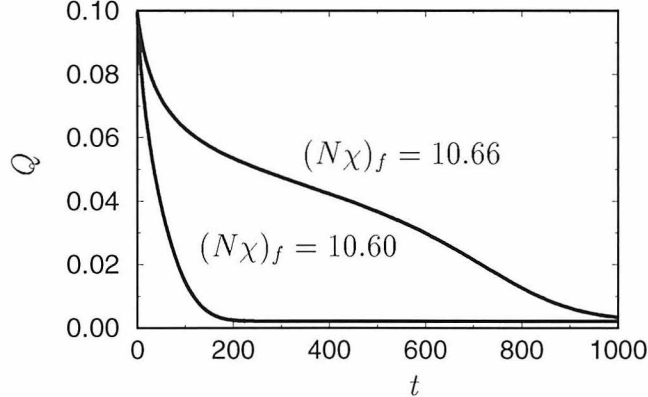


Figure 2.12: Evolution of the global order parameter Q for the T-jump from the BCC to DIS phase at $f = 0.45$ with $(N\chi)_i = 10.705$ (or $\tau_i = 0.216$).

2.3 Discussion

In this Chapter, we have studied the kinetics of several order-order and order-disorder transitions after a T-jump in weakly-segregated block copolymers by a direct numer-

ical simulation of the TDGL equation. The numerical results reveal that the kinetics is far from trivial even in the absence of any free energy barriers. In particular, we propose that the kinetic pathways often involve interesting intermediate states and non-simple temporal evolution. A multitude of novel kinetic scenarios have been identified.

An important result of this study is that the kinetics of the various order-order and order-disorder transitions after temperature jumps depends on the extent of the temperature jump. For example, in the case of H to DIS transition, the cylinders melt uniformly for large temperature jumps, but the melting goes through a modulated cylinder state for small temperature jumps. This dependence will be understood from the temperature dependence of the growth rate of the most unstable mode in the linear stability analysis and the free energy landscape to be studied in the next Chapter.

It will be shown in the next Chapter that the nontrivial kinetic paths can be understood in term of the anisotropic fluctuations around the initial structure. Besides providing driving force for the emergence of new structures, fluctuations (either thermal fluctuations or other externally imposed perturbations) have some systematic quantitative effects on the pseudostable and transient states. Since the pseudostable states correspond to saddle points on the free energy surface, fluctuations will lead to a faster decay from the saddle point and hence the lifetime of these pseudostable structures become shorter with the inclusion of fluctuations. On the other hand, transient structures that are caused by ridge-like landscapes of the free energy will be enhanced since fluctuations help the sideways pushes which are responsible for the appearance of these transient structures in the first place. The opposite effects of fluctuations on the pseudostable states and transient states caused by ridge-like free energy landscapes could conceivably be exploited to experimentally distinguish between these two types of intermediate states.

Bibliography

- [1] See F.S. Bates, *Science* **251**, 898 (1991); F.S. Bates and G.H. Fredrickson, *Ann. Rev. Phys. Chem* **41**, 525 (1990); G.H. Fredrickson and F.S. Bates *Ann. Rev. Mater. Sci* **26**, 501 (1996), and references therein.
- [2] J. D. Gunton, M. S. Miguel & P. S. Sahni *Phase Transition and Critical Phenomena* **vol8**, edited by C. Domb & J. L. Lebowitz, Academic Press, New York (1983).
- [3] K. Kawasaki and K. Sekimoto, *Physica* **143A**, 349 (1988); *Physica* **148A**, 361 (1988).
- [4] V. Kumaran and G. H. Fredrickson, *Physica* **204A**, 378 (1994).
- [5] See also M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford (1986).
- [6] F. H. Stillinger, *J. Chem. Phys.* **78**, 4654 (1982).
- [7] T. Ohta and K. Kawasaki, *Macromolecules* **19**, 2621(1986).
- [8] D. Wu, D. Chandler and B. Smit, *J. Chem. Phys* **96**, 4077 (1992); M. W. Deem and D. Chandler, *Phys. Rev. E* **49**, 4276 and 4268 (1994).
- [9] L. Leibler, *Macromolecules* **13**, 1602 (1980);
- [10] A. M. Mayes, M. O. de la Cruz, and W. E. McMullen, *Macromolecules* **26**, 4050 (1993).
- [11] M. Seul and D. Andelman *Science* **267**, 476(1995); and references therein.
- [12] C. Roland and R. C. Desai, *Phys. Rev. B* **42**, 6658 (1990); C. Sagui and R. C. Desai, *Phys. Rev. Lett.* **71**, 3995 (1993); *Phys. Rev. E.* **49**, 2225 (1994); *Phys.*

- Rev. E.* **52**, 2807 (1995); *Phys. Rev. E.* **52**, 2822 (1995); *Phys. Rev. Lett.* **74**, 1119 (1995).
- [13] S. Puri and Y. Oono, *Phys.Rev.A* **38**, 1542 (1988).
- [14] Y. Oono and Y. Shiwa, *Mod. Phys. Lett. B* **1**, 49 (1987); M. Bahiana and Y. Oono, *Phys.Rev.A* **41**, 6763 (1990).
- [15] A. Chakrabarti, R. Toral and J. D. Gunton, *Phys. Rev. E* **47**, 3025 (1993).
- [16] G. H. Fredrickson and R. G. Larson, *J. Chem. Phys.* **86**, 1553 (1987); R. G. Larson and G. H. Fredrickson, *Macromolecules* **20**, 1897 (1987).
- [17] G. H. Fredrickson and E. Helfand, *J. Chem. Phys.* **89**, 5890 (1988).
- [18] K. Kawasaki and A. Onuki, *Phys. Rev. A* **42**, 3664 (1990).
- [19] M. Rubinstein and S. P. Obukhov, *Macromolecules* **26**, 1740 (1993).
- [20] A. Onuki, *J. Chem. Phys.* **87**, 3692 (1987).
- [21] M. E. Cates and S. T. Milner, *Phys. Rev. Lett.* **62**, 1856 (1989).
- [22] G. H. Fredrickson, *J. Rheol.* **38**, 1045 (1994).
- [23] T. Ohta, Y. Enomoto, J. L. Harden and M. Doi, *Macromolecules* **26**,4928(1993); *Macromolecules* **26**,4935(1993); H. Kodama and M. Doi *Macromolecules* **29**,2652(1996).
- [24] For an excellent review of theoretical and experimental work on the dynamics of block copolymers, see G. H. Fredrickson and F. S. Bates *Ann. Rev. Mater. Sci* **26**, 501 (1996).
- [25] D. A. Hadjuk, P. E. Harper, S. M. Gruner, C. C. Honecker, G. Kim, E. L. Thomas and L. J. Fetters, *Macromolecules* **27**, 4063 (1994).
- [26] M. W. Matsen and M. Schick *Phys. Rev. Lett.* **72**, 2660 (1994); *Macromolecules* **27**, 4014 (1994).

- [27] M. W. Matsen and F. S. Bates *Macromolecules* **29**, 1091 (1996).
- [28] I. W. Hamley, K. A. Koppi, J. H. Rosedale, F. S. Bates, K. Almdal and K. Mortensen, *Macromolecules* **26**, 5959 (1993); S. Förster, A. K. Khandpur, J. Zhao, F. S. Bates, I. W. Hamley, A. J. Ryan and W. Bras, *Macromolecules* **27**, 6922 (1994).
- [29] E. L. Thomas, D. M. Anderson, C. S. Henkee and D. Hoffman, *Nature* **334**, 598 (1988).
- [30] M. M. Disco, K. S. Liang, S. K. Behal, R. J. Roe and K. J. Jeon, *Macromolecules* **26**, 2983 (1993).
- [31] The time unit we use in this Chapter is $d^2/(200Mk_BT)$, where d is the period of the microstructure corresponding to the optimal wavenumber, M is the mobility coefficient, and (MK_BT) can be thought of as the collective, mutual diffusion coefficient.
- [32] S. Y. Qi and Z. -G. Wang, *Phys. Rev. Lett.* **76**, 1679 (1996).
- [33] In general it is desirable to be in the more asymmetric part of the phase diagram since the windows for the different phases get wider. In the temperature jumps involving the lamellar phase, however, increasing the asymmetry also increases the temperature difference between the different phases and too large a temperature difference can sometimes lead to numerical instabilities in the simulation. This is the reason why $f = 0.45$ was used in the cases involving the lamellar phase.

Chapter 3 Anisotropic Fluctuations and Kinetics of Microphase Transitions

3.1 Introduction

In Chapter 2, we studied the kinetics of several order-order and order-disorder transitions after sudden temperature jumps in weakly segregated diblock copolymers using a time-dependent Ginzburg-Landau (TDGL) approach[1][2]. Direct numerical simulation of the TDGL equations shows that depending on the extent of the temperature jumps, these transitions often occur in several stages and can involve nontrivial intermediate states. For example, we find that melting of the hexagonal cylinder phase can involve the transient appearance of density modulations along the cylinders for small temperature jumps (which are nevertheless beyond the spinodal of the initial cylinder phase). Transition from the lamellar phase to the hexagonal cylinder phase goes through a perforated lamellar (PL) state within a certain temperature range.

In this Chapter, we seek a theoretical understanding of the kinetics of order-order and order-disorder transitions. A unified framework is developed based on anisotropic fluctuation in the ordered phases. The fluctuation is shown to play two crucial roles: first, they determine the stability limit of the initial structure, and second, they are responsible for the emergence of new structures, whether they are the final equilibrium states or transient states during the transition. A linear stability analysis allows us to identify the largest fluctuation modes under both equilibrium and nonequilibrium conditions. By combining the order parameter of the initial structure with the largest fluctuation modes into a simplified multimode model, we are able to describe qualitatively the full nonlinear evolution of the system after sudden temperature jumps beyond the spinodal of the initial phase.

This Chapter is organized as follows. In Section 3.2, we discuss anisotropic fluc-

tuation in a stationary ordered phase. This study allows us to obtain the fluctuation spectrum from which we can identify the least stable modes (or the largest fluctuation modes). The vanishing of the eigenvalue associated with the least stable modes signals the limit of stability of the structure. A key result in this section is that the least stable modes are generally located on reciprocal lattice positions that are different from those constituting the initial ordered structure. This is the very reason for the emergence of new structures. In Section 3.3, we discuss the kinetics of order-order and order-disorder transitions under nonequilibrium conditions. We perform a linear stability analysis on the dynamic equation. A key step here is the separation of the free energy driving force into a mean-field, deterministic part and a fluctuating part. The deterministic contribution serves primarily to change the amplitudes of the density waves of the initial ordered phase. The fluctuating part determines the stability of the mean-field trajectory, the deviation from which leads to the emergence of new structures. The most unstable modes give the directions of deviation from the mean-field path. In Section 3.4, evolution beyond the linear regime is studied by a multimode analysis which composes the most unstable modes together with the mean-field order parameter associated with the initial structure. Combining the linear stability analysis with the simplified multimode analysis, we arrive at a fairly complete picture of the various kinetic scenarios. We highlight two types of intermediate states in this section: the pseudostable state[3] and the transient state which correspond respectively to saddle and ridge-like features in the free energy surface. A generalized phase diagram which includes the various metastability and pseudostability limits as well as regions in which other interesting intermediate structures are to be observed, is constructed. Section 3.5 is a summary of our main results, together with discussions of relevant experiments.

3.2 Anisotropic Fluctuation and Stability of Ordered Phases

In this section, we discuss anisotropic fluctuation in a stationary ordered structure. The purpose of this section is two-fold: first, the analysis allows us to identify the high temperature spinodal and the largest fluctuation modes in an ordered structure, and second and more relevant to the transition kinetics, the method of analysis can be easily extended to nonequilibrium conditions.

At a stationary state (stable, metastable, or state corresponding to a saddle point on the free energy surface), the first derivatives of the free energy with respect to the order parameters (to be specified later) vanish. The stability of the structure is determined by the matrix of the second derivatives. A stable structure, either locally or globally, is characterized by the positive definiteness of the matrix of the second derivatives. The system reaches its spinodal when the lowest eigenvalue of the matrix of the second derivatives vanishes.

The stability of a structure is intimately related to the spontaneous, thermal fluctuation in that structure. A structure is stable if the mean-square fluctuation of the order parameter is finite, and becomes unstable when any mean-square fluctuation diverges. In an ordered diblock copolymer phase, the fluctuation is generally anisotropic because of the anisotropy of the ordered structure. The structure reaches its spinodal when the largest fluctuation becomes divergent. These largest, or most unstable, modes dictate the potential direction for the spontaneous emergence of new structures.

A rigorous approach for studying anisotropic fluctuation based on the exact self-consistent solutions has been developed by Shi *et al.*[4]. Here, we provide a simpler, approximate approach based on an order-parameter free energy functional. Although not accurately enough for quantitative purposes, the current approach is simpler to implement and is mathematically more transparent than the rigorous one. The order parameter approach is also more suitable for studying kinetics. Since the issues addressed in this paper do not depend on quantitative accuracy, we choose this simpler

approach.

We start with the standard Leibler free energy functional [5] for incompressible diblock copolymers, *i.e.*, Eq. 1.9. To be convenient, we rewrite it here:

$$\begin{aligned}
F[\psi(\vec{k})] &= \frac{1}{2} \int d\vec{k} [S_0^{-1}(k) - 2N\chi] \psi(\vec{k})\psi(-\vec{k}) \\
&+ \frac{\gamma_3}{3!} \int d(\vec{k}_1\vec{k}_2) \psi(\vec{k}_1)\psi(\vec{k}_2)\psi(-\vec{k}_1 - \vec{k}_2) \\
&+ \frac{\gamma_4}{4!} \int d(\vec{k}_1\vec{k}_2\vec{k}_3) \psi(\vec{k}_1)\psi(\vec{k}_2)\psi(\vec{k}_3)\psi(-\vec{k}_1 - \vec{k}_2 - \vec{k}_3),
\end{aligned} \tag{3.1}$$

where $\psi(\vec{k}) = \rho_A(\vec{k}) - f$, $\rho(\vec{k})$ is the Fourier transform of local density $\rho_A(\vec{r})$ of monomers A and f is the fraction of monomers A in a diblock copolymer molecule.

The mean-field order parameter $\psi_0(\vec{k})$ for a given morphology can be written as:

$$\psi_0(\vec{k}) = \sum_{\vec{G}} A_{\vec{G}} \delta(\vec{k} - \vec{G}), \tag{3.2}$$

where $\vec{G}$ is the set of reciprocal lattice wavevectors of the morphology, and the $A_{\vec{G}}$'s are obtained by minimizing the free energy Eq. 3.1 by substituting Eq. 3.2 into the free energy.

To study the fluctuation around the mean-field structure, we write

$$\psi(\vec{k}) = \psi_0(\vec{k}) + \Delta\psi(\vec{k}). \tag{3.3}$$

Substituting this into Eq. 3.1, keeping terms only up to quadratic order in $\Delta\psi(\vec{k})$ and noting the stationary condition for $\psi_0(\vec{k})$, we obtain

$$\begin{aligned}
F[\psi(\vec{k})] &= F[\psi_0(\vec{k})] + \frac{1}{2} \int d\vec{k} [S_0^{-1}(k) - 2N\chi] \\
&\times \Delta\psi(\vec{k})\Delta\psi(-\vec{k}) + \frac{\gamma_3}{2} \sum_{\vec{G}} \int d\vec{k} A_{\vec{G}} \Delta\psi(\vec{k})\Delta\psi(-\vec{k} - \vec{G}) \\
&+ \frac{\gamma_4}{4} \sum_{\vec{G}} \sum_{\vec{G}'} \int d\vec{k} A_{\vec{G}} A_{\vec{G}'} \Delta\psi(\vec{k})\Delta\psi(-\vec{k} - \vec{G} - \vec{G}').
\end{aligned} \tag{3.4}$$

The presence of periodic order makes the fluctuation in $\vec{k}$ -space non-diagonal. To study the anisotropic fluctuation and the stability of the ordered phases, the quadratic term of free energy needs to be diagonalized. This generally requires diagonalization of a infinite-large matrix. In this work, we make the simplifying approximation that the dominant fluctuation arises from modes with wavevectors $|\vec{k}| \approx k^*$. This approximation is justified in the weak segregation regime where fluctuations are mainly determined by the leading quadratic coefficient $S_0^{-1}(k) - 2N\chi$ which has a minimum at $k = k^*$, see Fig. A.1. Using this approximation, the matrix can be truncated to a smaller matrix involving $\vec{k}$ and $\vec{k} \pm \vec{G}$, and can then be diagonalized analytically; the eigenvalues of this matrix determine the stability of an ordered structure. The structure is stable or metastable if all the eigenvalues are positive. The spinodal of a structure is reached when the lowest eigenvalue turns negative.

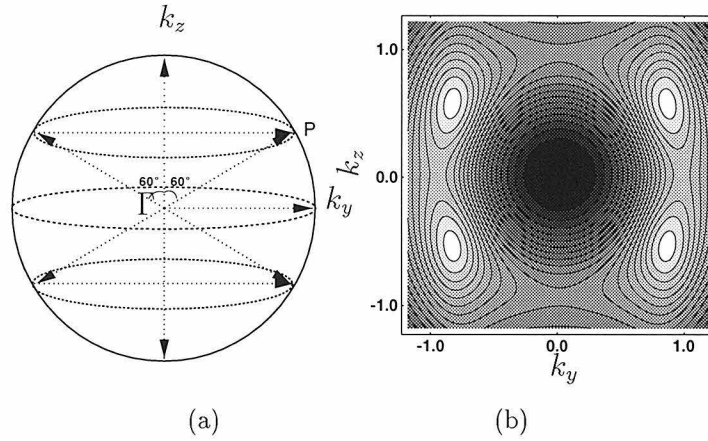


Figure 3.1: (a) A schematic showing the two rings in the k -space at $k_z = \pm \frac{1}{2}k^*$ corresponding to the least stable fluctuation modes in a lamellar structure of wavevector $\vec{k} = k^*\hat{e}_z$. (b) The fluctuation part of the scattering pattern of the L phase with $N\chi = 18.0$ for $f = 0.35$ in $k_x = 0$ plane in unit of k^* . The two Bragg spots at $k_z = \pm k^*$, $k_y = 0$ due to the mean-field lamellar wave are not shown.

The structure factor of an ordered phase when it is stable or metastable is given by

$$\langle \psi(\vec{k})\psi(-\vec{k}) \rangle = \psi_0(\vec{k})\psi_0(-\vec{k}) + \langle \Delta\psi(\vec{k})\Delta\psi(-\vec{k}) \rangle. \quad (3.5)$$

$\langle \Delta\psi(\vec{k})\Delta\psi(-\vec{k}) \rangle$, which is the fluctuation part of the structure factor, is obtained by taking the diagonal element of the inverse matrix of the quadratic coefficient in Eq. 3.4.

We now illustrate the theory by applying it to the lamellar and hexagonal cylinder phases.

3.2.1 Anisotropic Fluctuations in L Phase

For the mean-field lamellar structure, we assume a sinusoidal wave in the z-direction for the order parameter, with $\vec{k} = k^* \hat{e}_z$. The amplitude of the mean-field lamellar wave is obtained by minimizing the free energy Eq. 3.1.

To study the fluctuation spectrum and the stability of the lamellar phase, we consider a small perturbation of the form given by Eq. 3.3. The diagonalization of the matrix in Eq. 3.4 can be easily performed with the result that the lowest eigenvalues lie on two rings at $k_z = \pm(1/2)k^*$ and $|\vec{k}| = k^*$, as shown in Fig. 3.1 (a). Thus the dominant fluctuations, *i.e.*, the least stable fluctuation modes will come from wavevectors on these rings.

Fig. 3.1 shows the fluctuation contribution to the structure factor in the $k_x = 0$ plane of the L phase with $f = 0.35$ in the metastable state near the spinodal. The scattering due to fluctuations at $k_z = \pm\frac{1}{2}k^*$ and $k_y = \pm\frac{\sqrt{3}}{2}k^*$ is a result of the intersection of the rings with $k_x = 0$ plane. The same scattering pattern was obtained earlier by Yeung *et al.* [4] using a more rigorous approach.

As $N\chi$ decreases, fluctuations on the two rings in Fig. 3.1 will increase. The vanishing of the eigenvalue corresponding to these least stable modes, or equivalently, the divergence of the fluctuations of these modes, signals the spinodal of the lamellar phase.

Although the scattering pattern resulting from the linear stability analysis lacks any in-layer structure (in the x-y plane), the finding that the dominant fluctuations occur at $k_z = \pm\frac{1}{2}k^*$ leads to the important conclusion that any structures that form as a result of instability of the L phase will have a periodicity of two layers.

The location of the largest fluctuation modes in k -space can be understood with a simple geometric argument. In the presence of a periodic structure, the fluctuations interact with the mean-field order parameter associated with the ordered structure, and become anisotropic as a result. Such interactions satisfy a momentum conservation law as manifested in the forms of the last two terms in Eq. 3.4. In the weak-segregation regime, the mean-field order parameter is dominated by Fourier modes with reciprocal lattice wavevectors $|\vec{G}| = k^*$. The dominant fluctuations are also from modes with wavevectors $|\vec{k}| \approx k^*$. Thus we focus on fluctuations with $|\vec{k}| = k^*$. Take the γ_3 -term first. The restriction that the wavevectors of the fluctuations be on a sphere with $k = k^*$ means $|\vec{k}| = k^*$ and $|\vec{k} \pm \vec{G}| = k^*$. Since $|\vec{G}| = k^*$, it follows that the dominant fluctuations, as a result of interacting with the mean-field order parameter with a wavevector $\vec{G}$, are on the ring formed by the intersection between the sphere $|\vec{k}| = k^*$ and the plane $\vec{k} = \pm(1/2)\vec{G}$. A similar analysis of the γ_4 -term yields two types of contributions: an isotropic contribution when $\vec{G}' = -\vec{G}$ and an anisotropic contribution when $\vec{G} + \vec{G}' = \vec{G}''$ where $\vec{G}'$ and $\vec{G}''$ are other reciprocal lattice wavevectors. For the lamellar phase in the weak-segregation limit, the second contribution will be small since either $\vec{G}$ or $\vec{G}'$ or $\vec{G}''$ will have to be outside the spherical shell $|\vec{k}| = k^*$. For nonlamellar structure, *e.g.* for hexagonal cylinders, it is possible to satisfy $\vec{G} + \vec{G}' = \vec{G}''$ while still having $|\vec{G}| = |\vec{G}'| = |\vec{G}''| = k^*$. In that case the analysis becomes identical to that for the γ_3 -term.

3.2.2 Anisotropic Fluctuations in H Phase

The hexagonal cylinder (H) structure in the weak-segregation limit can be represented as a superposition of six co-planer density waves with wavevectors that are 60 degrees apart from each other. The positions of these wavevectors in k -space are indicated by the six large black dots at $\pm\vec{G}_1, \pm\vec{G}_2, \pm\vec{G}_3$ in Fig. 3.2. The amplitudes of the density waves are obtained by minimizing the free energy, and the fluctuation spectrum can be obtained using the method described earlier.

To locate the positions of the largest fluctuation modes in k -space, we use the

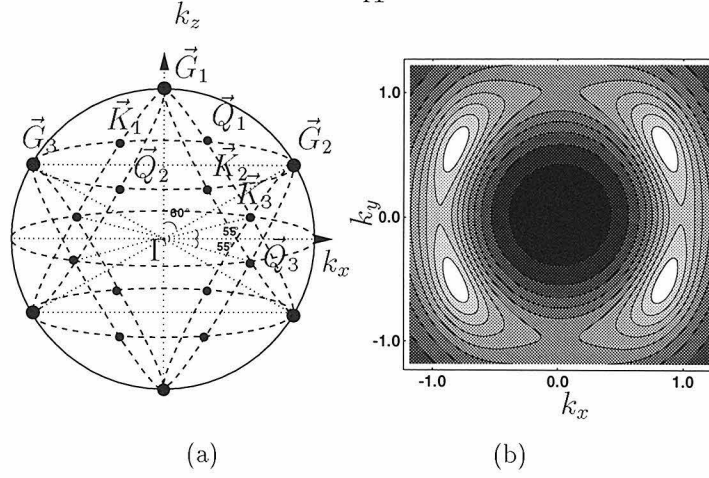


Figure 3.2: (a) Locations of the largest fluctuation modes of the H phase in k -space. The 18 spots constitute the set of the smallest wavevectors of a twinning-bcc structure. (b) Calculated structure factor for the H phase in the $k_z = 0$ plane for $N_\chi = 13.0$ with $f = 0.35$.

simple geometric construction outlined above in Section 3.2.1. For each of the six reciprocal lattice wavevectors, we form a plane that is perpendicular to the wavevector and that cuts the wavevector at a half. The intersection of this plane with the spherical shell $|\vec{k}| = k^*$ forms a ring. This construction results in six rings associated with the six reciprocal lattice wavevectors. Fluctuations modes will be larger on these rings than elsewhere, and will be the largest at points where two rings intersect. There are 18 such points, 6 of which coincide with the positions of the original H waves, and the other 12 are shown by the dots at $\pm\vec{K}_1, \pm\vec{K}_2, \pm\vec{K}_3$ and $\pm\vec{Q}_1, \pm\vec{Q}_2, \pm\vec{Q}_3$ in Fig. 3.2. These 18 spots constitute the reciprocal lattice of a twinning-bcc structure. Therefore, the anisotropic fluctuations in the H phase are on a twinning-bcc structure. The twinning-bcc structure was observed in the experiment by Almdal *et al.*[6] by dynamically shearing the BCC phase of poly(ethylenepropylene)-poly(ethylethylene) diblock copolymers. Their scattering pattern agrees well with our Fig. 3.2(b). They interpreted the twinning-bcc structure as arising from the shear deformation of the initial structure. An alternative interpretation is that shear destroys the bcc structure and turns it into the cylinder phase with large fluctuations. What they observed could be the fluctuation from the H phase rather than Bragg peaks from a twinning-bcc

structure.

The analysis in this section identifies the least stable fluctuation modes in an ordered block copolymer structure. These modes provide hints of the potential evolution of the system when the spinodal is reached. However, to address the kinetics of phase transition, we need to study the nature of anisotropic fluctuation under general non-equilibrium condition where there is a nonvanishing thermodynamic driving force. This task is undertaken in the next section.

3.3 Fluctuation vs. Deterministic Driving Forces: Linear Stability Analysis

We describe the dynamic evolution of the order parameter by TDGL equation, see Eq. 1.10. It is convenient to work with the Fourier modes of the order parameter. In the Fourier representation, Eq. 1.10 becomes

$$\frac{\partial \psi(\vec{k})}{\partial t} = -k^2 M(\vec{k}) \left[\frac{\delta F}{\delta \psi(-\vec{k})} \right] + \eta(\vec{k}, t), \quad (3.6)$$

while Eq. 1.11 becomes

$$\langle \eta(\vec{k}, t) \eta(\vec{k}', t') \rangle = 2(2\pi)^3 k_B T k^2 M(\vec{k}) \delta(\vec{k} + \vec{k}') \delta(t - t'). \quad (3.7)$$

A general expression for the mobility coefficient $M(k)$ has been derived by Kumaran and Fredrickson[7]; it is:

$$M(k) = D S_0(k), \quad (3.8)$$

where $S_0(k)$ is the structure factor for the same diblock copolymer in the absence of enthalpic interaction (*i.e.* with $N\chi = 0$), see Appendix. D is the diffusivity of the polymer chains whose scaling behavior depends on whether the chains are entangled or not. We define an effective kinetic coefficient $\lambda(\vec{k}) = k^2 M(\vec{k})$. In the weak-segregation limit (WSL), the order parameter as well as fluctuations are dominated by wavevectors

with $|\vec{k}| = k^*$ (This is valid when temperature is close to MST temperature). Thus it is reasonable to replace the k -dependent $\lambda(\vec{k})$ by $\lambda(k^*)$. $\lambda(\vec{k})$ also becomes independent of $\vec{k}$ in the limit of large $|\vec{k}|$. Therefore henceforth we will take $\lambda(\vec{k})$ to be a constant λ , and Eq. 3.6 simplifies to

$$\frac{\partial \psi(\vec{k})}{\partial t} = -\lambda \left[\frac{\delta F}{\delta \psi(-\vec{k})} \right] + \eta(\vec{k}, t). \quad (3.9)$$

Eq. 3.7 also simplifies correspondingly.

In Eq. 3.9, the order parameter $\psi(\vec{k})$ includes both a part that represents the structure of the initial phase and a part due to fluctuations. To gain insights and to make use of the concept of anisotropic fluctuations, it is instructive to write the order parameter as a sum of a mean-field part $\psi_0(\vec{k})$ and a fluctuating part $\Delta\psi(\vec{k})$, in the same form in Eq. 3.3, but now allowing both $\psi_0(\vec{k})$ and $\Delta\psi(\vec{k})$ to be time-dependent. Substituting Eq. 3.3 into Eq. 3.9, we obtain, to linear order in $\Delta\psi(\vec{k})$ (to be consistent with the level of treatment of equilibrium fluctuations in the last section):

$$\frac{\partial \psi_0(\vec{k})}{\partial t} = -\lambda \left[\frac{\delta F}{\delta \psi(-\vec{k})} \right]_0, \quad (3.10)$$

and

$$\frac{\partial \Delta\psi(\vec{k})}{\partial t} = -\lambda \int d\vec{k}' \left[\frac{\delta^2 F}{\delta \psi(-\vec{k}) \delta \psi(\vec{k}')} \right]_0 \Delta\psi(\vec{k}') + \eta(\vec{k}, t), \quad (3.11)$$

where the subscript “0” indicates that the derivatives are taken at $\psi(\vec{k}) = \psi_0(\vec{k})$. More explicitly, using Eq. 3.1 for the free energy, Eq. 3.10 and Eq. 3.11 become, respectively,

$$\begin{aligned} \frac{\partial A_{\vec{G}}}{\partial t} = & -\lambda \left\{ \left[S_0^{-1}(k^*) - 2N\chi \right] A_{\vec{G}} + \frac{\gamma_3}{2} \sum_{\vec{G}'} A_{\vec{G}'} A_{\vec{G}-\vec{G}'} \right. \\ & \left. + \frac{\gamma_4}{6} \sum_{\vec{G}'} \sum_{\vec{G}''} A_{\vec{G}'} A_{\vec{G}''} A_{\vec{G}-\vec{G}'+\vec{G}''} \right\}, \end{aligned} \quad (3.12)$$

and

$$\begin{aligned} \frac{\partial \Delta\psi(\vec{k})}{\partial t} = & -\lambda \left\{ [S_0^{-1}(k) - 2N\chi] \Delta\psi(\vec{k}) + \gamma_3 \sum_{\vec{G}} A_{\vec{G}} \Delta\psi(\vec{k} - \vec{G}) \right. \\ & \left. + \frac{\gamma_4}{2} \sum_{\vec{G}} \sum_{\vec{G}'} A_{\vec{G}} A_{\vec{G}'} \Delta\psi(\vec{k} - \vec{G} - \vec{G}') \right\} + \eta(\vec{k}, t). \end{aligned} \quad (3.13)$$

where we have used our ansatz Eq. 3.2 for the mean-field order parameter.

The equation for the mean-field order parameter, *i.e.*, Eq. 3.12, describes a steepest descent path along the gradient of the (mean-field) free energy. Thus, if the system finds itself in a nonequilibrium condition, as after a temperature jump, the mean-field order parameter will follow a downhill path until the gradient vanishes. It is clear from Eq. 3.12, that if we start with a structure described by the mean-field order parameters $\{A_{\vec{G}}\}$, the system will remain in the frame of that structure; only the magnitude of the order parameter changes. Thus the mean-field path corresponds to a trivial dynamics. Deviation from such trivial, mean-field dynamics is due to anisotropic fluctuations. As we showed in the last section, fluctuations in ordered structures are anisotropic and generally the largest fluctuations are located at different positions in Fourier space than the reciprocal lattice positions of the original structure. Thus the emergence of new structures on the kinetic pathway is a result of anisotropic fluctuations: these fluctuations determine whether the mean-field deterministic path is stable.

The coefficient of the linear term on the right-hand side of Eq. 3.13 has the same form as the quadratic coefficient in Eq. 3.4. However, in Eq. 3.4, the mean-field order parameters are those that minimize the free energy, and are hence time independent, whereas in Eq. 3.13 the order parameters in general do not correspond to an equilibrium condition and are time dependent. This makes the analysis of Eq. 3.13 difficult. However, our main concern here is to determine the local, instantaneous stability of Eq. 3.12, for which we only need to know if a certain fluctuation around an instantaneous value of $A_{\vec{G}}$ will grow or decay. For this purpose, it suffices to analyze

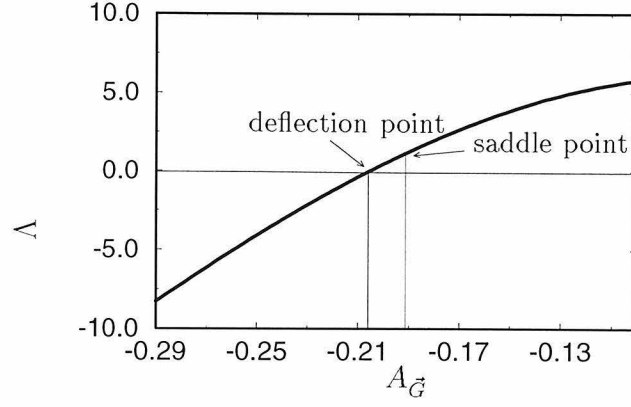


Figure 3.3: Growth rate of the least stable fluctuation modes Λ (in unit of λ) as a function of the L order parameter at $f = 0.35$ and $(N_\chi)_f = 15.0$. After a temperature jump, $A_{\vec{G}}$ evolves in the direction of decreasing $|A_{\vec{G}}|$. The saddle point of the L at this N_χ value is at $A_{\vec{G}} = -0.1911$.

the growth rate matrix on the right hand side of Eq. 3.13. This is the same matrix as the quadratic coefficient in Eq. 3.4 multiplied by -2λ , and its analysis thus can be performed following the same procedure as outlined in Section 3.2. In particular, the locations of the least stable fluctuation modes in k -space remain the same; but the stability of these modes now depends on the instantaneous value of $A_{\vec{G}}$. When all eigenvalues of the matrix are negative, the mean-field path is stable, and when one or more eigenvalues turn positive, the mean-field path becomes unstable, signaling the emergence of new structure. The new structure should now be represented by adding the most unstable modes to the mean-field order parameter.

We now use these theoretical ideas to discuss the kinetics of phase transitions after a sudden temperature jump, using the L to H and H to DIS transition as concrete examples.

Consider the L to H transition first. We start from a well-ordered L structure in equilibrium at $(N_\chi)_i$ in the L region of the phase diagram characterized by a one-dimensional sinusoidal wave with wavevector $\vec{G}$ and amplitude $A_{\vec{G}}$. Now imagine making a temperature jump, *i.e.*, decreasing N_χ to $(N_\chi)_f$ in the H region of the phase diagram, beyond the spinodal limit of the L phase. Due to the deviation from equilibrium, $A_{\vec{G}}$ will evolve according to Eq. 3.12. However, even though $(N_\chi)_f$ is

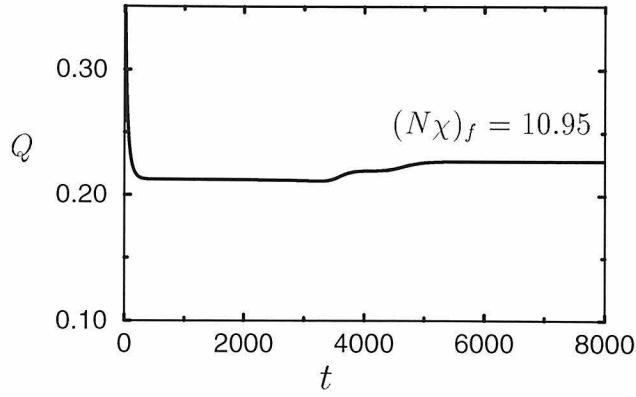


Figure 3.4: Temporal evolution of the global order parameter Q during the L to H transition at $f = 0.45$ for T-jump from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.95$.

now beyond the spinodal of the L phase, the initial stage of the evolution is a simple decay of the L order parameter, *i.e.*, the evolution is well described by Eq. 3.12 and the fluctuations, the largest of which are located on the rings in Fig. 3.1, are still stable, due to the large value of $|A_{\vec{G}}|$. This is shown in Fig. 3.3 where we plot the growth exponent of the least stable fluctuation mode (the largest eigenvalue of the matrix of linear coefficient in Eq. 3.12) as a function of the lamellar order parameter $A_{\vec{G}}$ ($A_{\vec{G}}$ is chosen to be negative to satisfy the correct phase relationship.) For large, negative values of $A_{\vec{G}}$, the exponent is negative. As $A_{\vec{G}}$ decays (according to Eq. 3.12) the deterministic driving force decreases, and at some point, the least stable fluctuation becomes unstable, and new structure corresponding to the two rings in Fig. 3.1 begins to emerge. Note that the onset of the instability, *i.e.*, deflection from the mean-field path, occurs before the system reaches a saddle point.

The above described scenario is in agreement with the result obtained from direct numerical simulation of the Ginzburg-Landau equation. Fig. 3.4 shows the simulation result for the temporal behavior of a global order parameter defined as $Q = \sqrt{\sum_{\vec{r}} \psi(\vec{r})^2} = \sqrt{\sum_{\vec{k}} \psi_{\vec{k}} \psi_{-\vec{k}}}$ for a temperature jump from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.95$ (see also Fig. 2.2). The initial rapid decrease in the order parameter as well as the plateau that follows are well described by the mean-field equation, Eq. 3.12. Direct visual inspection of the gray level plot of the microstructure during this stage does not reveal any specific structure within the lamellar layers. Thus the sys-

tem remains in the lamellar phase, but with a decreased order parameter. At the end of the plateau, however, the global order parameter increases, and at the same time in-layer density undulations begin to emerge as shown in Fig. 2.1(b). This signals the instability of the mean-field path and the growth of the fluctuation mode. Note that the fluctuations have a periodicity in the z -direction of twice the lamellar spacing; this is in excellent agreement with the prediction that the most unstable modes are on the rings at $k_z = \pm \frac{1}{2}k^*$; see Fig. 3.1.

We now discuss the H to DIS transition, this time starting with the simulation results. Fig. 2.10 shows the evolution of the global order parameter for two temperature jumps. For the large temperature jump to $(N\chi)_f = 10.97$, the order parameter decays in a simple manner, suggesting direct melting of the cylinders. Gray level plots of the order parameter at various times show no structure change as the cylinders melt.

In contrast, the behavior of Q in the case of the smaller temperature jump (to $(N\chi)_f = 11.15$) suggests a nontrivial melting process. The slower decay at intermediate times is accompanied by the formation of structures along the cylinders: the cylinders seem to first break into spheres and the melting proceeds via this modulated hexagonal cylinder (MHC) phase. This transient structure is clearest between the two inflection points on the curve. Fig. 2.11 shows the transient MHC state during this stage.

These two qualitatively different behaviors can be understood by analyzing the stability of the mean-field equation Eq. 3.12. For the large temperature jump, fluctuations are stable along the entire path. On the other hand, for the small temperature jump, fluctuations become unstable on certain part of the mean-field path. These two different behaviors are shown by plotting the growth rate of the least stable modes as a function of the order parameter of the H wave; see Fig. 3.5. Since the least stable fluctuations form a twinning-bcc structure (or bcc structure if we restrict to perfect periodic structure), the growth of the fluctuation modes leads to the appearance of a modulated hexagonal cylinder (MHC) structure which is the superposition of the H and bcc waves. The critical value of the final $N\chi$ that separates these two different

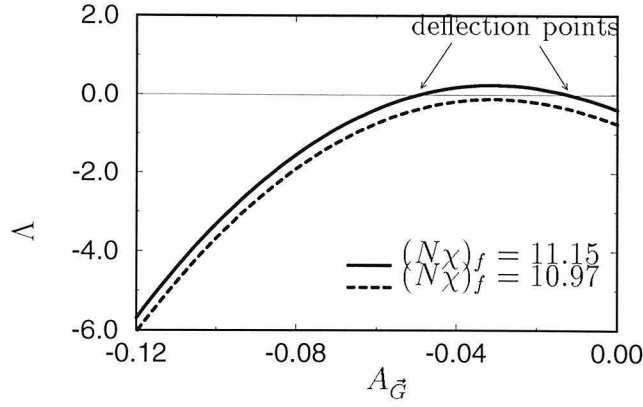


Figure 3.5: Growth rate of the least stable fluctuation modes Λ (in unit of λ) as a function of the H order parameter at $f = 0.4$ for two final values of N_{χ} . After a temperature jump $A_{\tilde{G}}$ evolves in the direction of decreasing $|A_{\tilde{G}}|$. For the smaller temperature jump ($(N_{\chi})_f = 11.15$), the mean-field kinetic path becomes unstable at the first deflection point, and between the two deflection points, the free energy surface has a ridgelike feature.

kinetic behaviors is also calculated, for $f = 0.4$, this critical value is $(N_{\chi})_c = 11.03$. For $(N_{\chi})_f > (N_{\chi})_c$, a nontrivial pathway for the H to DIS transition is expected, where the cylinders will first go through a MHC structure before melting; whereas if $(N_{\chi})_f < (N_{\chi})_c$, a direct featureless melting is expected. These behaviors are captured in Fig. 3.5: the curve for the smaller temperature jump to $(N_{\chi})_f = 11.15$ has two deflection points suggesting a ridgelike structure on the free energy surface between these two points (also see Fig. 3.18) while the curve for the larger temperature jump to $(N_{\chi})_f = 10.97$ indicates that the fluctuations are stable, consistent with a simple melting of the H structure.

3.4 Beyond the Linear Regime: a Simplified Multimode Analysis

The linear stability analysis in Section 3.3 yields information about whether the mean-field path is stable, when it becomes unstable, and if it does become unstable in which direction the system will evolve. However, further evolution of these fluctuation into a three-dimensional structure cannot be predicted by such a linear stability analysis.

In this section, we describe a simplified multimode analysis, which, although lacking in mathematical rigor, has the merit of being physically intuitive, and captures essentially all the qualitative dynamical behaviors revealed by our computer simulation studies. This analysis was first proposed by us in Refs.[1][2], based on symmetry and physical intuition. Here we provide a more rigorous justification.

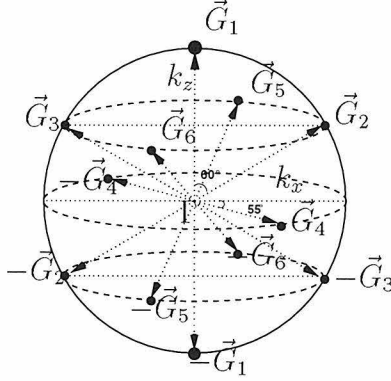


Figure 3.6: The 12 first-order wavevectors for a bcc structure.

We have shown in Section 3.2 that the largest fluctuation modes of an ordered phase are located at positions in k -space usually different from those corresponding to the mean-field order parameter of the initial structure. When the mean-field kinetic path becomes unstable, these fluctuations will grow and will become part of the new order parameter. This suggests that one can construct an expanded order parameter space that includes both the original order parameter and the dominant fluctuation modes. In the weak-segregation limit, both the order parameter and the fluctuations are dominated by modes with $|\vec{k}| = k^*$. Thus we choose a set of waves $A_{\vec{G}}$ with wavevectors $|\vec{G}| = k^*$. If we restrict our consideration to spatially periodic structures, a minimal set of wavevectors that can represent the L, H, BCC, as well as intermediate states during the transitions are the 12 first-order reciprocal lattice wavevectors of a bcc lattice. We set our coordinate system such that

$$\begin{aligned}\vec{G}_1 &= k^*(0, 0, 1), \quad \vec{G}_4 = \frac{k^*}{3}(\sqrt{3}, -\sqrt{6}, 0), \\ \vec{G}_2 &= \frac{k^*}{2}(\sqrt{3}, 0, 1), \quad \vec{G}_5 = \frac{k^*}{2\sqrt{6}}(\sqrt{2}, 4, \sqrt{6}),\end{aligned}$$

$$\vec{G}_3 = \frac{k^*}{2}(-\sqrt{3}, 0, 1), \quad \vec{G}_6 = \frac{k^*}{2\sqrt{6}}(-\sqrt{2}, -4, \sqrt{6}). \quad (3.14)$$

These wavevectors and their inverse wavevectors are shown in Fig. 3.6. The order parameter is then represented by

$$\psi(\vec{r}) = \sum_{\vec{G}} A_{\vec{G}} \exp(i\vec{G} \cdot \vec{r}), \quad (3.15)$$

where $A_{\vec{G}}$'s are the amplitudes associated with the wavevectors $\vec{G}$'s (we use the same notation $A_{\vec{G}}$ for both the order parameter of the initial structure and the dominate fluctuation modes). By considering only periodic structures, we may choose $A_{\vec{G}}$ to be real; then $A_{-\vec{G}} = A_{\vec{G}}$. In this construction, the L phase is represented by a nonzero $A_{\vec{G}_1}$ ($= A_{-\vec{G}_1}$) with all other amplitudes being zero; the H phase is obtained by either the wavevectors $\vec{G}_1, \vec{G}_2, \vec{G}_3$, or $\vec{G}_1, \vec{G}_5, \vec{G}_6$; the BCC phase requires all the six wavevectors with equal amplitudes. Evolution of the order parameter is then described by

$$\begin{aligned} \frac{\partial A_{\vec{G}}}{\partial t} = & -\lambda \left\{ \left[S_0^{-1}(k^*) - 2N\chi \right] A_{\vec{G}} + \frac{\gamma_3}{2} \sum_{\vec{G}'} A_{\vec{G}'} A_{\vec{G}-\vec{G}'} \right. \\ & \left. + \frac{\gamma_4}{6} \sum_{\vec{G}'} \sum_{\vec{G}''} A_{\vec{G}'} A_{\vec{G}''} A_{\vec{G}-\vec{G}'-\vec{G}''} \right\} + \eta_{\vec{G}}(t). \end{aligned} \quad (3.16)$$

This is the same equation as Eq. 3.12, except that $\{A_{\vec{G}}\}$ includes both the order parameter of the original structure and the dominate fluctuation modes.

Note that in this representation, the locations of the fluctuation modes are consistent with the result of anisotropic fluctuation. For example, fluctuations on the lamellar phase with a wavevector $\vec{G}_1$ are captured by the wavevectors $\pm\vec{G}_2, \pm\vec{G}_3, \pm\vec{G}_5, \pm\vec{G}_6$, which reside on the rings identified in Fig. 3.1. The fact that here we have a discrete modes of fluctuation modes instead of the continuum of modes on the rings from the previous analysis, is of little consequence at the linear order of the fluctuation. For example, the same spinodal is predicted independent of the number

of modes used. (This is generally true in any linear stability analysis). Thus the simplified mode analysis is consistent with the full analysis in Section 3.2 and Section 3.3 at the level of linear stability analysis, but has the advantage of allowing a simple qualitative description of the system in the nonlinear regime.

Further symmetry considerations require that $A_{\vec{G}_2} = A_{\vec{G}_3}$ and $A_{\vec{G}_5} = A_{\vec{G}_6}$. Thus we group the six waves into four subsets:

- $A = A_{\vec{G}_1}$;
- $B = A_{\vec{G}_2} = A_{\vec{G}_3}$;
- $C = A_{\vec{G}_5} = A_{\vec{G}_6}$;
- $D = A_{\vec{G}_4}$.

Therefore, the various transient structures can be obtained by the appropriate superposition of these four subsets of waves.

The perforated/modulated lamellar (PL/ML) structure shown in Section 2.2.1 deserves some further remarks. Within the bcc-based, single-wavenumber approximation, periodic density modulations in the lamellar layers can be represented by a structure with $|A| > B = C > |D|$. Such a structure does not have perfect in-layer six-fold symmetry which is believed to be associated with the PL/ML structure[8]. In Chapter 4, we also use a hcp(hexagonal-close-packing)-based wavevector set to describe the L to H transition and we find the same qualitative behavior as we did using the bcc-based lattice. Because bcc structure enables us to treat all the structures considered in a unified framework, we will adhere to the bcc-based representation in most part of this Chapter. In fact, there is reason to believe that experimentally observed PL/ML structures may be either hcp or bcc-based[9].

3.4.1 L to H Transition: Pseudostable L and PL

In this phase transition, all the six groups of waves from $A_{\vec{G}_1}$ to $A_{\vec{G}_6}$ are involved, where as mentioned above, $A = A_{\vec{G}_1}$ is the amplitude of the initial lamellar wave.

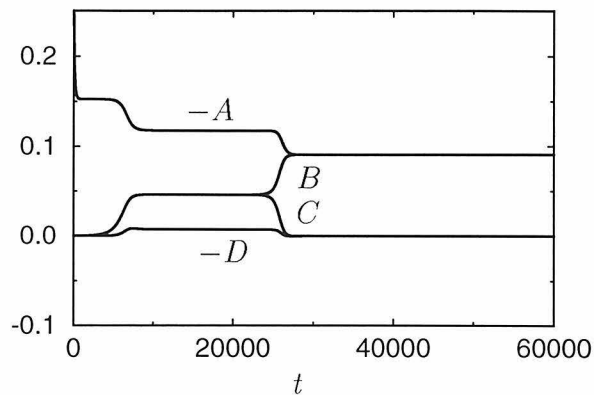


Figure 3.7: Evolution of the wave amplitudes during the L to H transition at $f = 0.45$ ($(N\chi)_i = 11.67$, $(N\chi)_f = 10.95$). Note the appearance of two plateaus beside the final H state.

Either $-A = B = A_{\vec{G}_2} = A_{\vec{G}_3}$ or $-A = C = A_{\vec{G}_5} = A_{\vec{G}_6}$ (where the minus sign ensures the proper phase relationship) can form a H structure given that the other parameters are zero, and when all the $A_{\vec{G}_i}$ ($i = 1$ to 6) are non-zero, a three-dimensional periodic structure is obtained. In Fig. 3.7 we show the temporal evolution of the various modes for the L to H transition after a sudden temperature jump, obtained by a direct numerical integration of Eq. 3.16. (For simplicity, we included the random noise term in the initial conditions for the various modes, but did not keep it during the simulation; this turned out not to have qualitative effects on the dynamical behaviors.) The kinetic path starts with a rapid decrease of the lamellar order parameter which then quickly turns to a plateau. During this initial phase, the amplitudes of the other modes remain small. Thus the system remains in a lamellar state. At the end of the first plateau, the other modes (which in the case of L represent the anisotropic fluctuations) begin to grow and at the same time the amplitude of the lamellar wave undergoes another drop. The system then reaches another plateau. On this plateau, the amplitudes B and C are degenerate; they bifurcate towards the end of this plateau when B merges with the lamellar wave A while C and D decrease to zero to form the hexagonal cylinder structure. This stagewise behavior is consistent with the full simulation results in Fig. 2.2 or Fig. 3.4. (The durations of the plateau are subject to the specific realization of the noise terms and hence are not particularly meaningful.)

Evolution of the microstructure is well captured by superposing the various modes. In particular, the structure corresponding to the second plateau is shown in Fig. 3.8. It is rather reminiscent of the perforated lamellar structure Fig. 2.1(c) observed in the numerical simulation. The results in Section 2.2.1, including the behavior of the global order parameter and the microstructural features during the transition, are all consistent with the foregoing analysis.

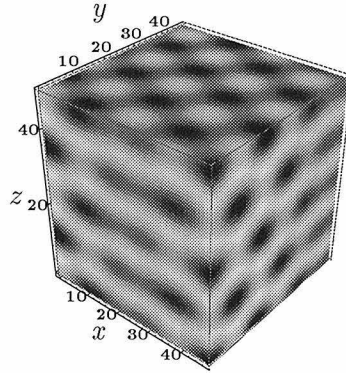


Figure 3.8: Microstructure generated using the six wave amplitudes with values corresponding to the second plateau in Fig. 3.7.

The plateaus in Fig. 3.7 suggest that the system passes near saddle points on the free energy surface. Using the free energy Eq. (3.1), we can locate these saddle points and the region of the phase diagram in which they exist. We find that the first saddle point evolves from the local free energy minimum corresponding to the L phase, i.e., the metastability limit of the L phase is reached by turning the local minimum into a saddle point. This scenario is shown in the reduced parameter space of A (the lamellar wave) and B (which, together with A , constitutes the H wave) in Fig. 3.9(a) and (b) with $C = D = 0$. The value of $N\chi$ where this happens marks the spinodal of the lamellar phase. We shall term states corresponding to saddle points in the free energy surface pseudostable states[3]. The range of $N\chi$ in which this saddle point exists is shown schematically in Fig. 3.20. Because of the positive curvature along the A axis in Fig. 3.9(b), the decay of the initial L structure (with A more

negative than its saddle point value) in this temperature range will follow a path that drives the system to the saddle point. This saddle point is responsible for the first stagnation (plateau) in both Fig. 2.2 and Fig. 3.7. As the temperature increases (N_χ decreases), the negative curvature in the B direction increases and the positive curvature in the A direction decreases, thus the time spent by the system near the saddle point gets shorter. This is indeed the case; see Fig. 2.2.

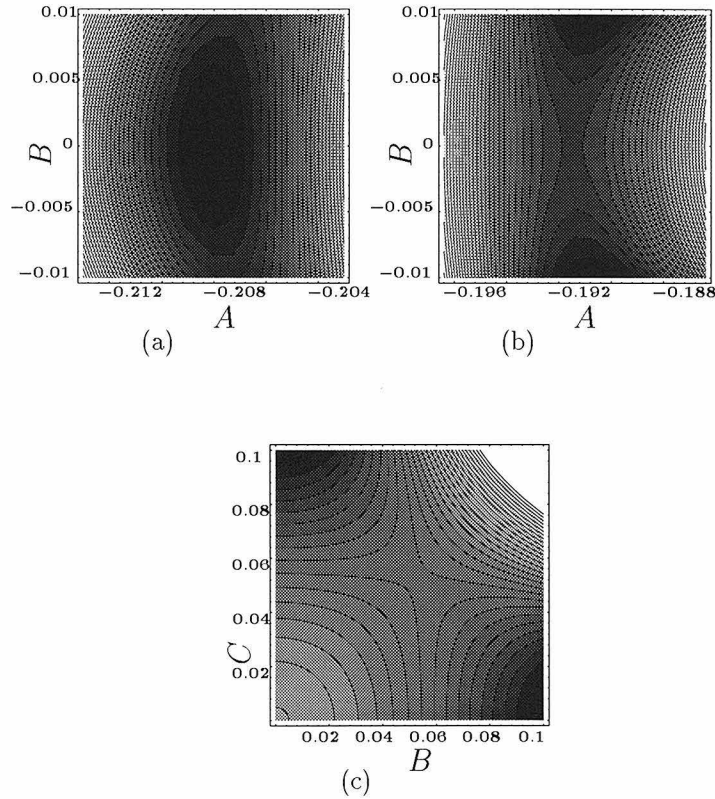


Figure 3.9: Free energy contour plot in reduced order parameter space illustrating (a) the metastable L ($(N_\chi)_f = 11.17$), (b) the pseudostable L ($\tau_f = 11.10$), and (c) the pseudostable PL ($(N_\chi)_f = 10.96$) states. In (a) and (b) C and D are both set to zero whereas in (c) A and D are set to the saddle point values ($A = -0.11781$, $D = 0.00706$). $f = 0.45$ for all three figures.

A similar saddle point is responsible for the appearance of the second plateau in Fig. 3.7. At this saddle point, however, all the three amplitudes B , C , and D are non-zero, but $B = C$. Therefore the structure has three-dimensional rather than

one-dimensional order. The saddle point is unstable with respect to bifurcation from $B = C$. This is shown in Fig. 3.9(c) where we set $A = -0.117808$ and $D = 0.007061$ at their respective saddle point values. The system eventually leaves this saddle point following the unstable direction which leads to either $-A = B, C = D = 0$, or $-A = C, B = D = 0$, both representing a perfect H structure with the cylinder axes lying within the original lamellar layers. The range of $N\chi$ where this saddle point exists is shown schematically in Fig. 3.20, which lies within the H part of the equilibrium phase diagram.

Although the pseudostable L structure itself has no interesting structural features, the decay from this structure is nontrivial. It turns out the most unstable direction is the direction of increasing B and C with $B = C$. This implies that when the system leaves the pseudostable L, it does so by going through a transient ML state. If a pseudostable PL state exists, the ML will evolve to the PL state which eventually decays to the H. If the temperature is outside of the pseudostable PL region, the ML will evolve continuously to the H structure without a distinct intermediate stage, see Fig. 3.10. These conclusions are indeed consistent with the results in Section 2.2.1.

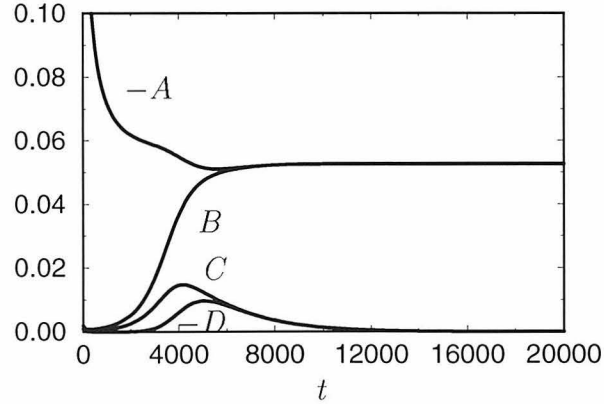


Figure 3.10: Evolution of the wave amplitudes during the L to H transition at $f = 0.45$ ($(N\chi)_i = 11.67$, $(N\chi)_f = 10.74$). A transient ML phase appears around $t = 4000$. We have chosen a more anisotropic fluctuations for the initial value of B and C , to prevent the system to go to the metastable BCC phase.

3.4.2 L to BCC Transition: Pseudostable L States

As in the L to H transition, all the six waves represented by four parameters A, B, C and D are required to describe this transition. The kinetic pathway displays two different behaviors depending on the extent of the temperature jump. For the smaller temperature jump from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.71$, the kinetic pathway shows a plateau similar to the first plateau in the L to H transition, see Fig. 3.11. At this plateau the structure is again lamellar with a reduced wave amplitude. The other three waves emerge almost equally at the end of this plateau while A continues to decrease, reaching the final value $-A = B = C = -D = 0.02824$ corresponding to the equilibrium BCC structure at this temperature.

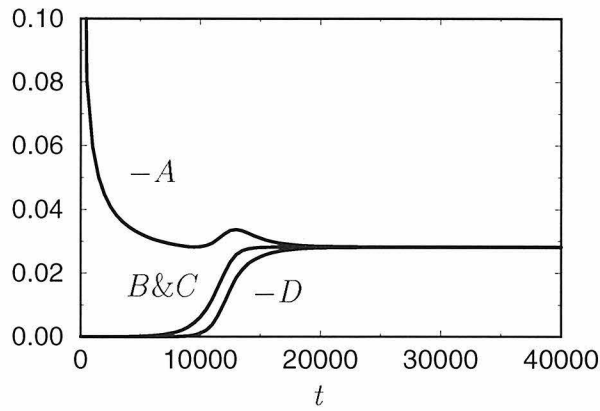


Figure 3.11: Evolution of the wave amplitudes during the L to BCC transition at $f = 0.45$ ($(N_\chi)_i = 11.67$, $(N_\chi)_f = 10.71$). Note the appearance of the first plateau indicates pseudostable L phase.

For the larger temperature jump from $(N_\chi)_i = 11.67$ to $(N_\chi)_f = 10.68$, the pathway is more smooth for $-A$, see Fig. 3.12. The difference between Fig. 3.11 and Fig. 3.12 is small. But the place for $-A$ to turn around in Fig. 3.12 corresponds to nonzero B , C and $-D$ values, and no saddle point is found at this temperature. The four curves finally reach a common steady-state value of 0.02488. Notice that the initial values of B , C and $-D$ come from fluctuations. If the initial fluctuations is not strong enough, L phase will go to DIS phase: This is because the final temperature is quite close to the metastable DIS phase.

The L saddle point for the smaller T-jump in the L to BCC transition has the

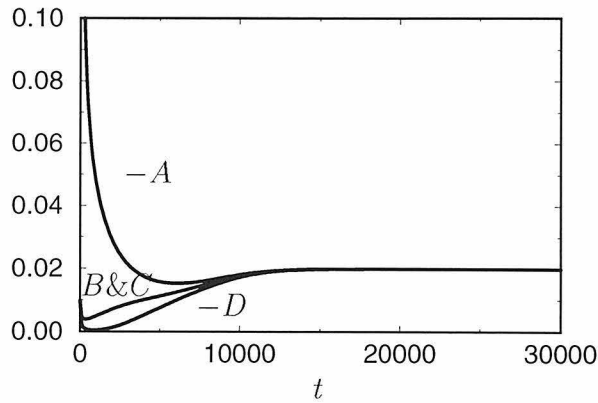


Figure 3.12: Evolution of the wave amplitudes during the L to BCC transition at $f = 0.45$ ($(N\chi)_i = 11.67$, $(N\chi)_f = 10.68$). Note the appearance of the U-turn of $-A$ comes from the overdrive in the direction of A . The initial values for B , C and D come from fluctuations.

same origin as the L saddle point in the L to H transition. Beyond the spinodal of the L phase, the L saddle point (stable with respect to variation in the lamellar wave amplitude A but unstable with respect to perturbations in at least one of the other amplitudes) persists over a rather wide region in the phase diagram; this region has overlap with the lower temperature part of the equilibrium BCC phase. Thus if the T-jump is into this region, transition from the L to the BCC phase will proceed by first going through the L saddle point with the consequence of a time lag in the growth of the BCC structure. Beyond this region, transition will be a more smooth one. The scenario described in this section is fully consistent with the simulation results of Section 2.2.2.

3.4.3 L to DIS Transition: Transient ML State

We again start with the equilibrium L structure at $(N\chi)_i = 11.67$ with $A = -0.3$. Two T-jumps to $(N\chi)_f = 10.66$ and $(N\chi)_f = 10.60$ are studied by numerically solving the four coupled amplitude equations with small perturbations in B , C and D of the order of 0.3 percent of the initial value of A . The evolution of A , B , C and D at $(N\chi)_f = 10.66$ is shown in Fig. 3.13. All these four amplitudes eventually decay to zero as the equilibrium phase at this τ is the DIS phase. However, note the

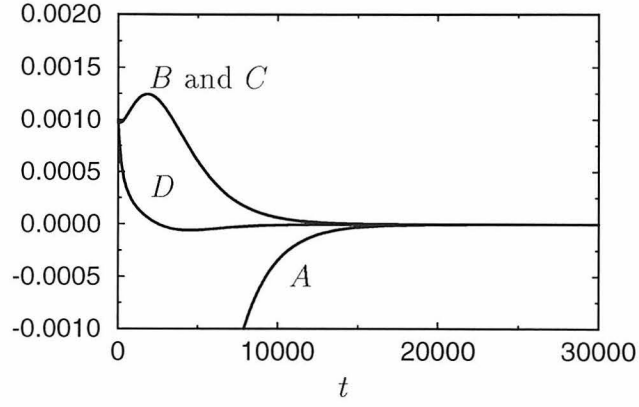


Figure 3.13: Temporal evolution of the different modes during the transition at $f = 0.45$ from L to DIS ($(N\chi)_i = 11.67$, $(N\chi)_f = 10.66$).

transient increase in B and C . At the maximum of B and C , the structural feature is similar to that obtained during the transition from L to H, although the density modulation within the layer (as measured, for example by $|B/A|$ or $|C/A|$) is much weaker here (and this is why the global order parameter Q decreases monotonically for both large and small temperature jump, see Fig. 2.6 compared with Fig. 2.10). For this reason we term this transient structure also ML. Although the structural features between this ML and the ML observed in the L to H transition are the same, the mechanisms which give rise to this structure in the two cases are different. Recall that in the case of the L to H transition, the ML is due to a saddle point on the kinetic path: it is the most unstable mode for the pseudostable L to decay, and if a pseudostable PL state exists, it will further evolve into such a state. Here, however, no such saddle points exist. Rather, the transient growth of the amplitude B or C is due to deflection from the path along the axis $B = C = D = 0$ caused by a ridge-like feature in the free energy landscape. This is shown by a contour plot of the free energy in the reduced parameter space A, B , see Fig. 3.14. We have found analytically that there exists a small finite window $(N\chi)_l < N\chi < (N\chi)_u$ in the phase diagram for this transient state to exist. The upper boundary $(N\chi)_u$ coincides with the BCC/DIS phase boundary. For $f = 0.45$, $(N\chi)_l = 10.64$. Therefore, when $(N\chi)_f = 10.60 < (N\chi)_l$, all four amplitudes decrease monotonically, and melting of the L will proceed directly without involving a transient ML state. This compares

well with the simulation results.

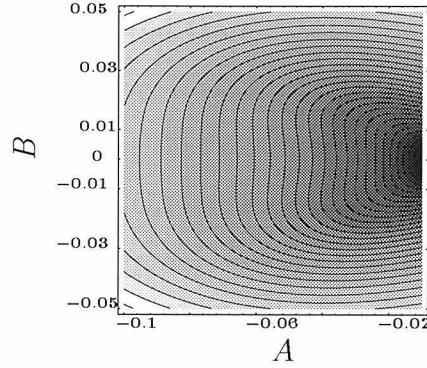


Figure 3.14: Free energy contour plot in the reduced order parameter space showing the ridge-like feature during the L to DIS transition at $f = 0.45$ ($(N\chi)_f = 10.66$). B and C are set to be equal while D is set zero.

3.4.4 H to BCC Transition: Pseudostable H State

Assuming that this transition involves only the initial H waves and another set of waves which are part of the BCC structure, the four groups of waves can be further reduced to two, denoted by $A(=B)$ and $C(=D)$, respectively, where A constitutes the H density wave, with $A = A_{\vec{G}_1} = A_{\vec{G}_2} = A_{\vec{G}_3}$, and $C = A_{\vec{G}_4} = A_{\vec{G}_5} = A_{\vec{G}_6}$.

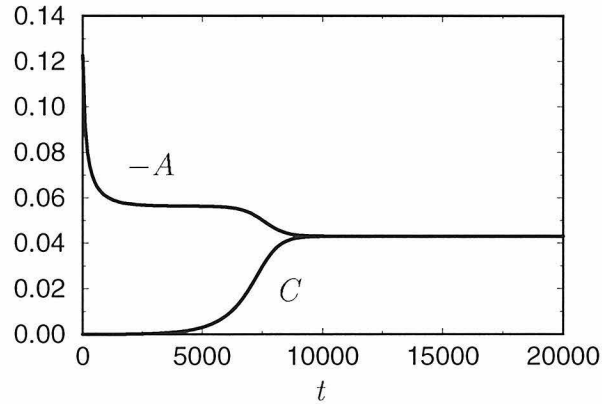


Figure 3.15: Evolution of the wave amplitudes during the H to BCC transition at $f = 0.4$ ($(N\chi)_i = 11.62$, $(N\chi)_f = 11.27$). Note the appearance of the first plateau indicates a pseudostable H state.

The temporal evolution of A and C for a T-jump from $(N\chi)_i = 11.62$ to $(N\chi)_f = 11.27$ at $f = 0.4$ was shown in Fig. 3.15. Note that there is a long plateau after the rapid decrease in A from its initial value. Within the duration of this plateau, C remains close to zero. Thus there is a time lag for the BCC structure to appear, and when it does, the structure becomes that of a modulated hexagonal cylinder (MHC) with a continuous growth of the BCC component, reaching the final equilibrium state with $A = -C$. The plateau arises from a saddle point which lies on the $C = 0$ axis. Thus we have a pseudostable H structure in the H to BCC transition, whose origin is similar to the pseudostable L state. Once again, there is a region in the phase diagram for the pseudostability. The lower temperature (larger $N\chi$) side of the boundary is the spinodal of the H phase, *i.e.*, when the H reaches its metastability limit, it does so by turning the local minimum of free energy into a saddle point. The situation is similar to how the L phase loses its metastability, see Section 3.4.1. The high-T (lower $N\chi$) boundary lies within the BCC part of the phase diagram: for $f = 0.4$, $(N\chi)_c = 11.26$. Therefore a T-jump to a $(N\chi)_f$ value beyond this boundary, *i.e.*, $(N\chi)_f < (N\chi)_c$, but still in the BCC part of the phase diagram leads to a direct transition from the H to the BCC, see Fig. 3.16. This explains the observations in Section 2.2.4.

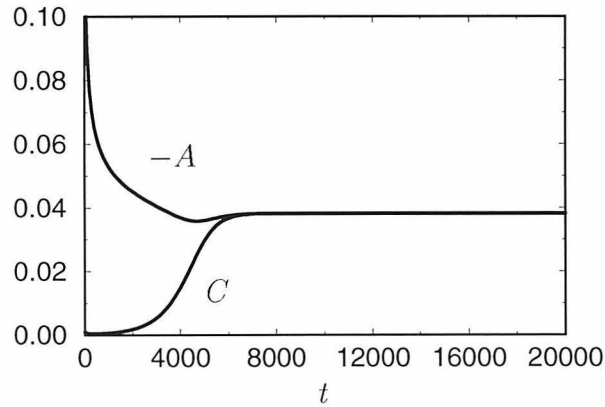


Figure 3.16: Evolution of the wave amplitudes during the H to BCC transition at $f = 0.4$ ($(N\chi)_i = 11.62$, $(N\chi)_f = 11.25$). There is no plateau of $-A$ which has zero-value C parameter.

3.4.5 H to DIS Transition: Transient MHC State

In this case, the kinetics is again described by the two order parameters A and C , as defined in the last subsection. For a large T-jump ($(N\chi)_i = 11.62$ to $(N\chi)_f = 11.0$), A decreases monotonically to zero; also any initial perturbation from $C = 0$ is rapidly damped. This corresponds to a direct melting of the H phase.

For a smaller T-jump ($(N\chi)_i = 11.62$ to $(N\chi)_f = 11.236$), while A still decreases monotonically, an initial perturbation from $C = 0$ first grows before it decays again to zero. Thus there is a transient growth of the BCC component of the density wave. This wave, superposed on the dominant H wave, results in a modulated hexagonal cylinder (MHC) state. These results are in full agreement with the simulation results.

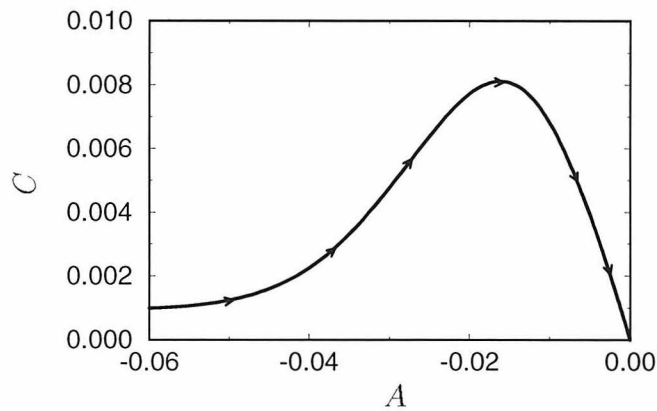


Figure 3.17: Phase portrait for the H to DIS transition for a temperature jump from $(N\chi)_i = 11.62$ to $(N\chi)_f = 11.236$ at $f = 0.4$. The nonzero initial C is due to the initial perturbation.

In Fig. 3.17, we show a phase portrait in terms of A and C for the H to DIS transition in the case of a shallow temperature jump. The transient growth of C is the result of the instability discussed in Section 3.3. While the linear analysis there predicted that the fluctuation modes (which are part of a bcc or twinning-bcc lattice) would grow at some point along the kinetic path, the nonlinear analysis presented here allows us to predict the full trajectory of the system. Fig. 3.17 depicts the full pathway of the system starting from a H structure, going through a transient bcc-modulated hexagonal state, and eventually melting to the DIS state.

A study of the free energy shows that the landscape (in the parameter space of

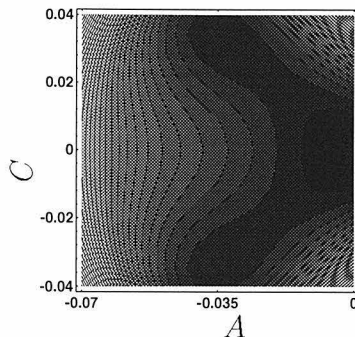


Figure 3.18: The ridgelike structure of the free energy surface for $(N\chi)_f = 11.236$ and $f = 0.4$.

A and C) has two qualitatively different appearances depending on the final temperature. For $(N\chi)_f = 11.0$ corresponding to the larger temperature jump, the free energy surface is parabolic with a simple minimum at $A = 0$ and $C = 0$. However, for $(N\chi)_f = 11.236$, the free energy surface has a ridgelike feature as shown in Fig. 3.18. The transient appearance of the bcc-modulation during the melting of the hexagonal cylinders is thus a result of deflection from the direct downhill path, $C = 0$. By studying the free energy landscape, we also find that there exists a window in the phase diagram in which the landscape exhibits a ridge-like feature, this has been shown schematically in Fig. 3.20.

The degree of the deflection from the ridge, and hence the strength of the modulation and the length of its duration, is closely related to the magnitude of the fluctuations. In the absence of any fluctuations (including initial noise), a path that starts with $C = 0$ will keep $C = 0$ even though the $C = 0$ axis is a ridge. Deviation from $C = 0$ is caused by perturbations (either given initially or included *in situ*). The same considerations apply to other transient phenomena caused by ridge-like free energy landscapes. This issue will be discussed more fully in Section 3.5.

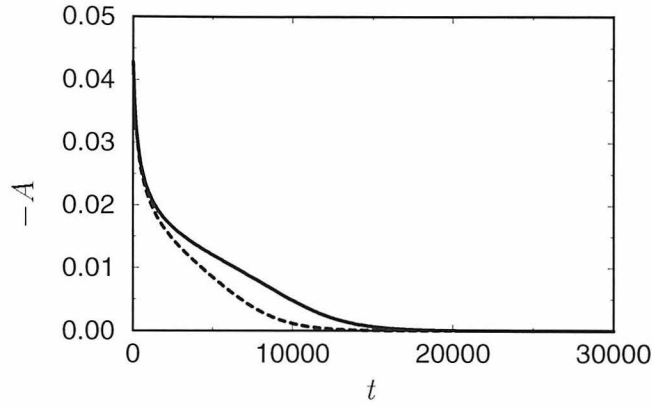


Figure 3.19: Evolution of the wave amplitudes during the BCC to DIS transition at $f = 0.45$ with $(N\chi)_i = 10.71$. Solid line is for $(N\chi)_f = 10.6620$ and dashed line is for $(N\chi)_f = 10.6545$. Note the appearance of two inflection points on the solid curve.

3.4.6 BCC to DIS Transition

The transition from BCC to DIS is relatively featureless. Here, we do not find saddle or ridge-like features in the free energy landscape. The numerical simulation in Section 2.2.6 does not show any distinctive intermediate structure. However, upon closer investigation of the free energy, we find two inflection points (see Fig. 3.19 for $-A = B = C = -D$ curve. The two inflection points are defined as where the second derivatives of free energy with respect to A is zero) on the otherwise downhill path in a temperature window beyond the spinodal limit of the BCC phase. The high-T (low $N\chi$) boundary of this window corresponds to $(N\chi)_l = 10.6615$ at $f = 0.45$. For $(N\chi)_f < (N\chi)_l$ the order parameter will decay as a simple exponential, whereas for $(N\chi)_f > (N\chi)_l$ the melting will be somewhat slowed down between the two inflection points. We believe this is the reason for the non-simple decay of the order parameter seen at the larger $(N\chi)_f$ in Section 2.2.6.

3.4.7 Generalized Phase Diagram

The different scenarios described in the previous sections can be summarized in a generalized phase diagram. This phase diagram is obtained by a detailed study of the free energy landscape in the four order parameters A , B , C and D , because under the

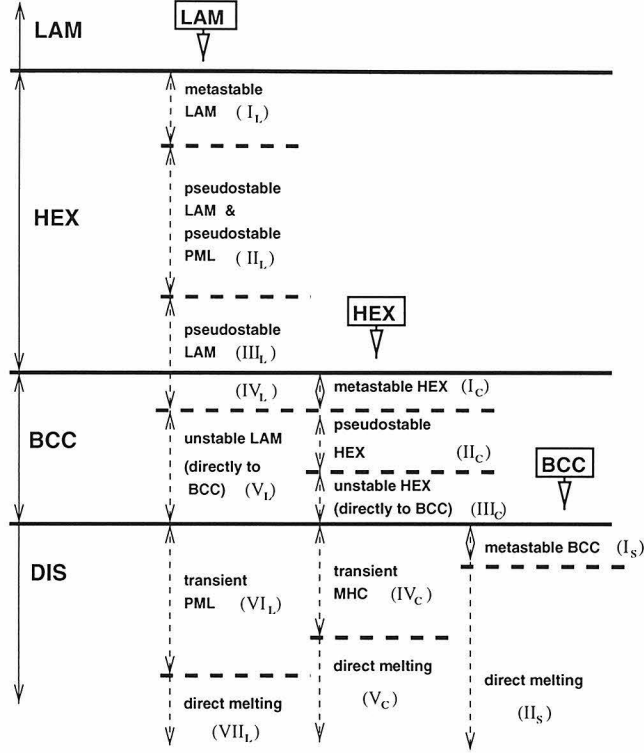


Figure 3.20: Generalized phase diagram: the different regions indicate different transition scenarios and the intermediate states involved, starting (from left to right) from the L, H and BCC phases, respectively.

assumption that the kinetics of the various order-order and order-disorder transitions can be described by a few dominant modes with a single wavenumber, the kinetics reduces to a steepest descent path on the free energy surface. We have calculated analytically all the mean-field “phase boundaries” for the transitions studied in this Chapter and Chapter 2 in terms of $N\chi$ and f . However, there are too many curves in this phase diagram to leave any space for labeling the different scenarios. Therefore, we choose to show only the different behaviors at a single $f = 0.45$. The qualitative behavior is the same for other values of f . The diagram is not drawn to scale; only the correct sequence of these phase boundaries in $N\chi$ is maintained.

We now illustrate the richness of the phase diagram by following a T-jump sequence from the equilibrium L phase. Seven different kinetic scenarios can be identified, depending on the final temperature $((N\chi)_f)$. If $(N\chi)_f$ lies in region I_L (the subscript L refers to the initial L phase), the lamellar phase is metastable. Transition to the H phase can only occur via nucleation of the H within the L phase. The dotted line indicates the spinodal of the L phase. In region II_L , the L phase first becomes pseudostable, then passes through another pseudostable state (which we identify as the PL), and finally reaches the H state. In region III_L , the L state again first becomes pseudostable. However, after some time lag spent at this pseudostable state, the H phase will emerge gradually (via a short transient ML) but directly from the L structure without another clear intermediate stage. In Region IV_L , the L will spend some time at the pseudostable L state, and then transform continually to the BCC structure. This transition will again necessarily involve a short transient ML structure, but no distinct stages can be identified. It is interesting, and not coincidental, that the lower boundary of the pseudostable L is identical to the spinodal limit of the H phase. In Region V_L , the transition from L to BCC will be a direct one. Again, the transition will involve the ML state, but the process is a continuous one with no distinguishable stages. If the final $(N\chi)_f$ lies in Region VI_L , the L phase will melt by going through a transient ML state, caused by a ridge-like feature in the free energy landscape which deflects melting of the L from following a direct path. Finally, in Region VII_L , the L phase will melt directly without involving any other structures.

The different kinetic scenarios for transitions starting from the H or BCC phases can be similarly identified from reading the generalized phase diagram.

Whereas equilibrium states correspond only to the global free energy minimum, the kinetics of the various transitions involves states that are caused by other features of the free energy surface. Besides the thermodynamically stable structures, there are metastable states corresponding to local free energy minima, pseudostable states corresponding to saddle points, and transient states either arising from deflection of a more direct path or serving to connect two distinct states. Finally, unstable states in our study refer to those which possess a non-zero thermodynamic driving force

and decays uniformly and monotonically. Clearly, inclusion of these states greatly broadens the phase diagram.

3.5 Discussion

In this Chapter, we have described a unified approach to understanding the various order-order and order-disorder transitions in weakly segregated diblock copolymers. Our theory is based on the concept of anisotropic fluctuations of the order parameter in the ordered structures. The emergence of new structures, whether they are the final equilibrium structures, or transient structures on the kinetic pathways, is due to the growth of the most unstable fluctuation modes. A systematic linear stability analysis is presented both for the equilibrium states — in order to locate the spinodal of the initial structure and identify the least stable fluctuation modes — and for nonequilibrium states where the thermodynamic driving force is nonvanishing. In the latter case, it is shown that the thermodynamic driving force can be separated into a mean-field, deterministic contribution that governs the evolution of the mean-field order parameter associated with the initial structure, and a fluctuating contribution that determines the stability of the mean-field path and is responsible for the emergence of new structures. The linear stability analysis allows us to determine the stability of the mean-field path for any given value of the mean-field order parameter of the kinetic path. By combining the largest fluctuation modes and the order parameter of the initial structure into an expanded order parameter space, we are able to describe qualitatively the full nonlinear evolution of the system during the various transitions.

Recently, Laradji *et al.*[10], using an RPA theory of anisotropic fluctuations developed by this group of researchers [4], have addressed the stability of ordered phases. By expanding the free energy around the exact mean-field solutions to second order, these authors examined the anisotropic fluctuations in the various ordered phases. The most unstable fluctuation modes are used to infer the kinetic pathways of the order-order transitions. While it is true that the most unstable modes in an ordered phase are closely related to the transition kinetics, this information is inadequate to

determine the actual pathways of the transitions for two reasons: first, the stability analysis by Laradji *et al.* is a linear one and can only predict the fastest growing modes when an ordered structure reaches its spinodal but cannot predict the subsequent evolution of the system. Secondly and more importantly, their stability analysis is on a stationary structure where the first derivatives of the free energy vanish, but usually the various order-order and order-disorder transitions are caused by large deviations from equilibrium conditions which result in a large deterministic driving force given by nonvanishing first derivatives of the free energy. This is important, for example, for explaining why hexagonal cylinders melt uniformly for large temperature jumps but proceed through a bcc-modulated hexagonal cylinder state when the temperature jump is small[1][2]. In our theory, the anisotropic fluctuations are studied under both equilibrium and nonequilibrium conditions. The nonlinear dynamics for the evolution of a new structure, whether it is a (meta)stable state or a transient state, is constructed by combining the order parameter of the original structure and the least stable fluctuations. Therefore, our theory enables a complete description of the kinetics of order-order and order-disorder transitions in diblock copolymers.

3.5.1 Comparison with Experiments

In recent years, there have been a number of experiments aimed at probing various dynamical aspects of the order-order and order-disorder transitions in block copolymers[11][12][13][14][15][16][17][18][19][20]. However, experiments that directly address the kinetic pathways after temperature jumps are few and are perhaps difficult. Nevertheless, some tentative comparisons can be made between theory and experiments where such comparisons are appropriate.

We start with the shear cessation experiments of Bates and co-workers[18]. In one of these experiments, an initially disordered phase of asymmetric poly(ethylenepropylene-b-ethylethylene) (PEP-PEE) diblock copolymer close to the order-disorder boundary is subjected to a constant shear which induces a transition to the H phase (with the cylinders aligned along the shear direction). The shear is suddenly stopped, and the

system is now in a condition favoring the DIS phase. These authors observed that the cylinders first break into spheres before melting to the DIS phase, much akin to what we find after a temperature jump. Insofar as a H phase is created and then the condition is changed to favoring the DIS phase, the shear-cessation experiment can be likened to a temperature jump experiment. We believe the mechanism described in this paper is responsible for their observations.

The H to BCC transition has also been studied by Bates and co-workers[17]. These authors showed that BCC spheres pinch off from the H cylinders such that the cylinder axis is the (111) direction of the resulting BCC structure which they term the “epitaxial” relationship. They also suggested that the BCC phase forms by way of an undulating cylinder structure. These are in agreement with our mechanism[1][2].

Thermally induced L to H transition has been studied by Hajduk *et al.*[16] for the poly(styrene-*b*-ethene-co-butene) diblock copolymers. However, these authors did not observe the appearance of the intermediate modulated/perforated lamellar structure predicted by our theory and simulation (see Fig. 2.1). We have shown earlier (Ref.[2]) that a distinct intermediate PL structure appears only in a certain temperature window in the L to H transition; see Fig. 3.20. It is possible that the temperature jump in the experiment is too large for a distinct intermediate PL to appear, but further studies are needed to fully resolve the discrepancy between theory and experiment.

On the other hand, the perforated lamellar (PL) structures have been observed in several experiments by Bates’ group[8] [22][23] in regions of the phase transitions between L and H or the G phase. In a very recent paper by Hajduk *et al.*[21], an extensive series of new experiments demonstrate quite convincingly that the PL is a kinetic state *en route* from the L phase to the H or G phase, thus providing indirect evidence of our proposed L to H transition mechanism. Through both direct computer simulation and theoretical analysis, we found that the PL state during the transition from L to H after a temperature jump can be made metastable by a sudden temperature quench back to the initial temperature: instead of going back to the L phase, the system gets trapped in a metastable PL state. It is possible that the PL

structures reported by Bates and co-workers that had been initially thought to be equilibrium phases, were in fact kinetically trapped states due to a combination of thermal and shear operations used in the experiments. This topic will be discussed in Chapter 4.

Bibliography

- [1] Qi, S. Y. and Wang, Z. -G. *Phys. Rev. Lett.* 1996, **76**, 1679
- [2] Qi, S. Y. and Wang, Z. -G. *Phys. Rev. E.* 1997, **55**, 1682
- [3] Kikuchi, R., Mohri, T. and Fultz, B. *MRS Symposium Proceedings* **205**, 387 (1992); Fultz, B. *Phil. Mag. B* **67**, 253 (1993).
- [4] Yeung, C., Shi, A. -C., Noolandi, J. and Desai, R. C. *Macromol. Theory Simul.* 1996, **5**, 291; Shi, A.-C., Noolandi, J. and Desai, R. C. *Macromolecules* 1996, **29**, 6487
- [5] Leibler, L. *Macromolecules* 1980, **13**, 1602
- [6] Almdal, K., Koppi, K. A. and Bates, F. S. *Macromolecules* 1993, **26**, 4058
- [7] Kumaran, V. and Fredrickson, G. H. *Physica* 1994, **204A**, 378
- [8] Hamley, I. W., Koppi, K. A., Rosedale, J. H., Bates, F. S., Almdal, K. and Mortensen, K. *Macromolecules* 1993, **26**, 5959
- [9] Qi, S. Y. and Wang, Z. -G. *Macromolecules*, 1997, **30**, 4491
- [10] Laradji, M., Shi, A.-C., Desai, R. C. and Noolandi, J., *Phys. Rev. Lett.* 1997, **78**, 2577; *Macromolecule*, 1997, **30**, 3242
- [11] Hashimoto, T., Kowsaka, K., Shibayama, M. and Suehiro, S. *Macromolecules* 1986, **19**, 750; Hashimoto, T., Kowsaka, K., Shibayama, M. and Kawai, H. *Macromolecules* 1986, **19**, 754
- [12] Singh, M. A., Harkless, C. R., Nagler, S. E., Shannon, R. F. and Ghosh, S. *Phys. Rev. B* 1993, **47**, 8425; Harkless, C. R. Singh, M. A., Nagler, S. E., Stepheson, G. B. and Jordan-Sweet, J. L. *Phys. Rev. Lett.* 1990, **64**, 2285

- [13] Sakurai, S., Momii, T., Taie, K., Shibayama, M., Nomura, S. and Hashimoto, T. *Macromolecules* 1993, **26**, 485
- [14] Sakurai, S., Kawada, K., Hashimoto, T. and Fetters, L. J. *Macromolecules* 1993, **26**, 5796
- [15] Floudas, G., Hadjichristidis, N., Iatrou, H., Pakula, T. and Fischer, E. W. *Macromolecules* 1994, **27**, 7735; Floudas, G., Vlassopoulos, D., Pitsikalis, M., Hadjichristidis, N. and Stamm, M. *J. Chem. Phys.* 1996, **104**, 2083; Floudas, G., Hadjichristidis, N., Stamm, M., Likhtman, A. E. and Semenov, A. N. *J. Chem. Phys.* 1997, **106**, 3318
- [16] Hajduk, D. A., Gruner, S. M., Rangarajan, P., Register, R. A., Fetters, L. J., Honeker, C., Albalak, R. J. and Thomas, E. L. *Macromolecules* 1994, **27**, 490
- [17] Schulz, M. F., Bates, F. S., Almdal, K. and Mortensen, K. *Phys. Rev. Lett* 1994, **73**, 86; Koppi, K. A., Tirrell, M., Bates, F. S., Almdal, K. and Mortensen, K. *J. Rheol.* 1994, **38**, 999
- [18] Koppi, K. A. *Ph.D. Thesis*, The University of Minnesota, 1994; Bates, F. S., Koppi, K. A. and Tirrell, M. *Macromolecules* 1994, **27**, 5934; Almdal, K., Mortensen, K., Koppi, K. A., Tirrell, M. and Bates, F. S. *J. Phys. II* 1996, **6**, 617
- [19] Dai, H. J., Balsara, N. P., Garetz, B. A. and Newstein, M. C. *Phys. Rev. Lett.* 1996, **77**, 3677
- [20] Ryu, C. Y., Lee, M. S., Hajduk, D. A. and Lodge, T. P. submitted to *J. Poly. Sci* (Poly. Phys. Ed.)
- [21] Hajduk, D. A., Takenouchi, H., Hillmyer, M. A., Bates, F. S., Vigild, M. E. and Almdal, K. *Macromolecules* 1997, **30**, 3788
- [22] Förster, S., Khandpur, A. K., Zhao, J., Bates, F. S., Hamley, I. W., Ryan, A. J. and Bras, W. *Macromolecules* 1994, **27**, 6922

- [23] Khandpur, A. K., Förster, S., Bates, F. S., Hamley, I. W., Ryan, A. J., Bras, W., Almdal, K. and Mortensen, K. *Macromolecules* 1995, **28**, 8796

Chapter 4 The Nature of Perforated Lamellar Phase

4.1 Introduction

Undiluted diblock copolymers represent the simplest system for studying the various aspects of microphase transitions and hence have been the subject of extensive experimental and theoretical investigations for the past two decades[1]. Earlier theories predicted only three stable ordered phases[2][3]: lamellar (L), hexagonally ordered cylinders (H) and bcc ordered spheres (BCC). More recent experiments have revealed three additional “complex” morphologies: hexagonally modulated lamellar (HML)[4], hexagonally perforated lamellar (HPL)[4] [5] and the bicontinuous double gyroid (G)[6][7]. The structure of the G phase has been well characterized through a combination of x-ray diffraction and transmission electron microscopy (TEM) studies [6]. Also, state-of-the-art mean-field calculations predict that the G phase is stable between the L and H phases, ending at a triple point on the high temperature end of the phase diagram [8][9], see Fig.4.4 for the mean-field calculated phase diagram.

The status of the HML and HPL phases is much less satisfactory. From small-angle neutron scattering (SANS) and TEM studies[4] [10][11], it is believed that the HML phase consists of alternating minority and majority component layers in which the thickness of the minority component domains is modulated with a hexagonal in-layer symmetry. In the HPL phase the majority component is envisioned to form hexagonally ordered channels that extend through the minority component and connect the layers formed by the majority component. However, the three-dimensional stacking of the HML modulations and the HPL perforations is still not known, and this lack of structural information has led several theoretical calculations[12][13][14] to assume different structures, which resulted in conflicting conclusions with regard

to their thermodynamic stability.

Of foremost importance in resolving the structural nature of the HML and HPL phases is a consistent interpretation of the SANS data of Bates and co-workers. There are two outstanding puzzles from these scattering data: the in-layer scattering pattern exhibits six weak broad peaks at wavevectors whose magnitudes are slightly less than that corresponding to the reciprocal of the layer spacing[4], and in samples where the perforations were assumed to be stacked in the *abcabc...* pattern (in order to explain other features of the data), two distinct scattering peaks were missing at positions where they were expected to appear[10]. Bates and co-workers have proposed some rather elaborate structural mechanisms that offer partial explanations for their scattering data, but these two puzzling observations have never been satisfactorily explained.

In the last two Chapters, using a time-dependent Ginzburg-Landau (TDGL) approach, we addressed the kinetics of microphase transitions in diblock copolymers (see also Refs.[15] and [16]). In particular, our numerical simulations show that transition from the L phase to the H phase involves intermediate states whose structural features are strongly reminiscent of the HML and HPL phases[15]. Using a multimode analysis under the single wavenumber approximation, we argued that the perforated lamellar (PL) structure is a saddle point that lies on the pathway between the L and the H phases while the modulated lamellar (ML) structure is simply the incipient PL and results from the most unstable mode of the L phase when the L phase reaches its spinodal. Since the ML and PL structures do not differ in symmetry but only differ in the degree of density modulation, we shall refer to both as the PL phase in the remainder of this chapter. Also, we shall refer to the perforated lamellar as PL rather than HPL, because we believe that the in-plane structure is not necessarily of hexagonal symmetry. Yeung et al.[17] and Laradji et al.[18], based on a theory of anisotropic fluctuations in ordered diblock copolymers recently developed by Shi et al.[19] have also suggested that the modulated or perforated lamellar states are due to fluctuation modes of the lamellar phase; however, they did not address the 3-dimensional structures.

In this Chapter, we present a unified description of the nature, stability, and possible mechanism of formation of the PL structure in undiluted diblock copolymers. Using a simple, Leibler free energy functional, we show that the PL develops from anisotropic fluctuations of the lamellar phase when it reaches its limit of metastability. Specifically, we propose two different PL structures, one based on a hcp lattice, and one based on a bcc lattice, with nearly degenerate free energies. In the framework of this free energy, we find that the PL structure is pseudostable (corresponding to a saddle point in the free energy surface) in the weak-segregation limit, but can become metastable in the intermediate-segregation regime. Our proposed structures produce features that are consistent with all known structural data on the PL structure. In particular, by studying the fluctuation spectrum of the metastable PL structures, we are able to explain in a simple and consistent manner the two puzzles mentioned earlier. In addition, our study provides important insights to the experimental conditions that produce the PL structures.

4.2 Structure and Stability of the PL Phase

In Section 3.2.1 we showed that the least stable fluctuations of L phase appear on the two rings, see Fig. 3.1. It is thus reasonable to assume that PL phase develops from these least stable modes when the L phase reaches its spinodal. Further evolution of these fluctuations into a three-dimensional structure cannot be predicted by such a linear stability analysis. The question of pattern selection due to nonlinear interactions at present is still not fully resolved [20] and is thus beyond the scope of the present work. However, our time-dependent Ginzburg-Landau (TDGL) simulation of the structural evolution beyond the spinodal of the L phase, shows unambiguously a well-defined *abab...* stacking pattern of perforated layers with clear periodic in-layer structures[15], although the exact symmetry of the in-layer structures is difficult to ascertain because of the small system size used in the simulation.

Given that the PL phase is a three-dimensional periodic structure that forms out of the least stable mode of the L phase as discussed in the last Chapter, it follows that the

first-order reciprocal lattice points that are responsible for the structure must reside on the two rings shown in Fig. 3.4. Symmetry considerations limit their distribution on the ring to two choices within the simple space group with reflection symmetry[21]. In the first choice, there are six reciprocal lattice points equally spaced on each ring. The in-layer structure thus has hexagonal symmetry. The set of wavevectors for the three-dimensional structure is shown in Fig. 4.1. Note that the differences formed among the six wavevectors $\vec{G}_1 \dots \vec{G}_6$ give rise to three other sets of wavevectors that lie in the $k_z = 0$ plane, the smallest of which coincide with the projections of $\vec{G}_1$ through $\vec{G}_6$ in that plane. The next two sets are outside the sphere in the Figure. Because these wavevectors have magnitudes that are different from k^* , the amplitudes of these waves are quite small and can be neglected for most purposes. We shall name the PL phase of this structure the hcp-based PL.

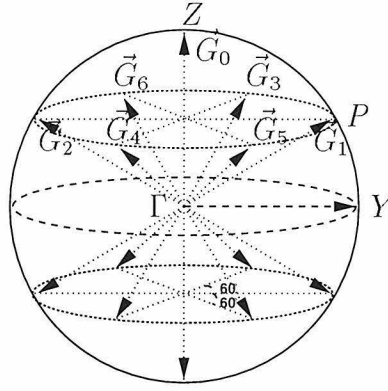


Figure 4.1: The first-order reciprocal lattice wavevectors of a hcp-based PL.

The second choice has four spots on each ring at $k_z = \pm \frac{1}{2}k^*$ and $|\vec{k}| = k^*$. The most symmetric arrangement is into a square; this would give rise to an in-layer square lattice. More generally, the four spots can be arranged into a rectangle. Although symmetry considerations alone are incapable of predicting the angles between these spots, based on the fact that density waves in the weak-segregation regime are dominated by those having the optimal wavenumber k^* , we expect that the optimal arrangement will be such that some of the in-plane wavevectors formed by the difference between the four wavevectors $\vec{G}_1$ through $\vec{G}_4$ have a magnitude of k^* . This consideration leads to a reciprocal lattice shown in Fig. 4.2. In the one wavenumber

approximation, this reciprocal lattice is that of the bcc structure. Thus we name the PL phase of this structure the bcc-based PL.

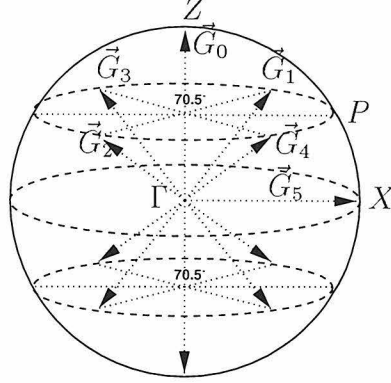


Figure 4.2: The first-order reciprocal lattice wavevectors of a bcc-based PL.

The real space structure of the PL phase corresponding to the two reciprocal-space structures in Fig. 4.1 and Fig. 4.2 are shown in Fig. 4.3 (a) and (b); both structures have the *abab...* stacking.

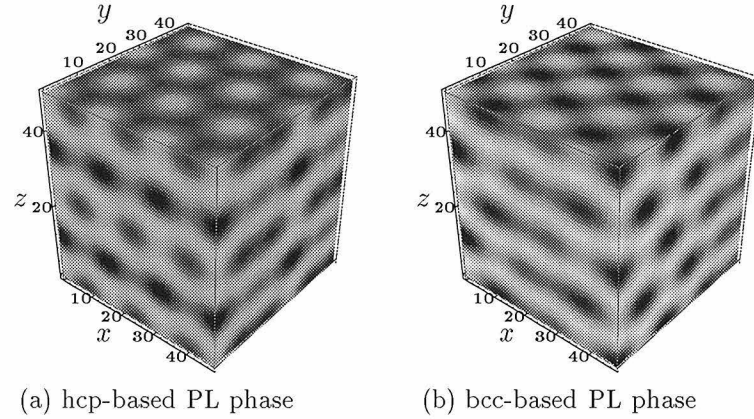


Figure 4.3: Microstructure generated using the wavevectors in (a) Fig.4.1 and (b) Fig.4.2. The wave amplitudes are obtained at the stationary point of the corresponding PL phase.

Using the representation of the PL structure in Fig. 4.1 and Fig. 4.2, we have calculated the stability of the two PL models using the free energy functional, Eq.

3.1. Within the framework of this free energy, we find that neither the hcp-based nor the bcc-based PL is the lowest free energy state when compared with the L, G, H and BCC phases. However, they can exist as metastable states in the region of the phase diagram where the G phase is thermodynamically stable. The bcc-based PL phase has a slightly lower free energy than the hcp-based PL phase, but given the approximations in the theory, such a small difference should not be taken to be of significance. At smaller N_χ and/or f , the PL structure loses its local stability characterized by one or more of the eigenvalues of the matrix turning negative. It should be pointed out that because of the multidimensionality of the order parameter (due to the multitude of the reciprocal lattice wavevectors), some eigenvalues remain positive. Therefore in general the structure beyond the spinodal limit corresponds to a saddle point in the free energy surface, which we termed pseudostable structure in last Chapter, see also ref. [15]. We comment here that allowing $\vec{G}$ to be different from k^* will generally lead to a lower free energy and a slight modification of the structure. However, the effect is quantitative rather than qualitative, and in the weak-segregation regime, the effect is negligible.

The high temperature spinodals of the two PL structures are shown in a restricted part of the phase diagram in Fig. 4.4. Shown there also is the spinodal of the L phase. These three spinodal lines are quite close. Given the approximations in the theory, their relative position in the phase diagram is probably not very meaningful. That they are quite close, however, is significant in understanding the experimental conditions which produce the observed PL structures, as will be discussed in Section 4.3.

In the metastable PL state, it is meaningful to define a (quasi)equilibrium structure factor. The procedure for calculating the fluctuation part of the structure factor is described in Section 3.2. Again for simplicity of calculation, we assume that the dominant fluctuations arise from modes with wavevectors $|\vec{k}| \approx k^*$, although higher order reciprocal lattice wavevectors are used in the representation of the structure as well as in the calculation of the free energy.

Of particular interest is the in-layer scattering pattern (the intensity plot of the

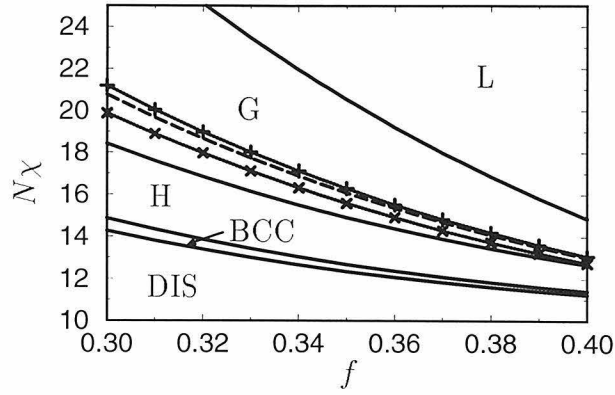


Figure 4.4: The phase diagram for a diblock copolymer system. The solid lines are conventional phase boundaries for L, G, H, BCC, and DIS (the disordered phase); the long dashed line is the spinodal line for L; the dotted line with “+” is the spinodal line for the metastable hcp-based PL, while the dotted line with “x” is the spinodal line for the metastable bcc-based PL.

structure factor in the $k_z = 0$ plane). Fig. 4.5 shows the fluctuation part of the scattering pattern for the hcp-based PL for diblock copolymers with $f = 0.35$ and $N\chi = 17$. The six-fold symmetry compares well with the SANS pattern obtained by Bates and co-workers [4][11]. Though not obvious from the figure, each peak in Fig. 4.5 is actually a combination of two peaks positioned 10° degree apart. Thus the combined peak has a rather wide angular spread. The positions of the two peaks can be understood by the same geometric construction used to understand the fluctuation spectrum in the L phase. For each of the 12 wavevectors ($\vec{G}_1$ through $\vec{G}_6$ and their inverse) we form a plane perpendicular to the wavevector by cutting through the middle of the vector. The intersection of this plane with the sphere $k = k^*$ forms a ring. The intersection of this ring with the scattering plane (in this case the $k_z = 0$ plane) yields the peak positions of the scattering intensity due to fluctuation. This is illustrated in Fig. 4.6. Note that each wavevector is responsible for two scattering spots in the $k_z = 0$ plane. Thus the six wavevectors $\vec{G}_1$ through $\vec{G}_6$ yields 12 scattering spots in the $k_z = 0$ plane. The inverse vectors of $\vec{G}_1$ through $\vec{G}_6$ lead to scattering spots in the $k_z = 0$ plane that are identical in their location to the 12 spots from $\vec{G}_1$ through $\vec{G}_6$. Therefore, this construction leads to 12 distinct points on the ring at $k_z = 0$ and $|\vec{k}| = k^*$. Strictly speaking, the above geometric procedure is valid

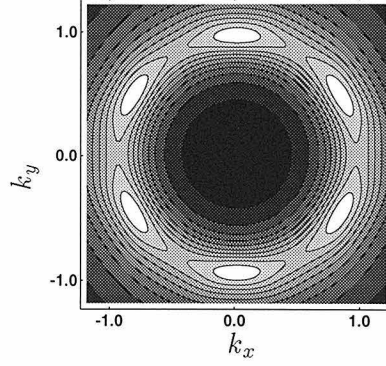


Figure 4.5: The fluctuation part of the scattering pattern in the $k_z = 0$ plane for a metastable hcp-based PL. The parameters are chosen at $N_\chi = 17$ and $f = 0.35$.

for weak sinusoidal periodic potentials. In the metastable PL state, the amplitude of the order parameters are not very small and there are now higher order harmonics contributions. These effects lead to the result that the peaks shift slightly inward from the ring at $|\vec{k}| = k^*$, as shown in Fig. 4.5.

The scattering pattern in Fig. 4.5 shows only contributions due to fluctuation in the order parameter. The full scattering function includes also contributions due to Bragg scattering from six in-plane wavevectors that are formed from the difference between two adjacent wavevectors in the set $\vec{G}_1$ through $\vec{G}_6$. The six spots are at the same angular position as the six peaks in Fig. 4.5, but at a distance $\frac{\sqrt{3}}{2}k^*$ from the origin. Because of the weakness of these Bragg peaks and the unavoidable broadening of Bragg peaks in the experiments, these peaks will be combined with the scattering peaks due to fluctuation to give the appearance of six broad peaks with the apparent peak position somewhere between $0.866k^*$ and k^* . This is in excellent agreement with experiment[4][11][22].

The fluctuation part of the scattering function for the bcc-based PL can be obtained in a similar manner, with the resulting scattering pattern shown in Fig. 4.7. Note now that the six scattering peaks are no longer six-fold symmetric. The two peaks at $k_x = 0$ are much stronger than the other four. The four weak peaks are situated at angles 19.47° from the k_x axis, on the ring $|\vec{k}| = k^*$. In addition to the six scattering peaks due to fluctuation, there are also two Bragg spots (not shown in

the figure) from the mean-field structure that are located at the same positions at the two bright spots; thus the total scattering intensity at the two bright spots will be even stronger.

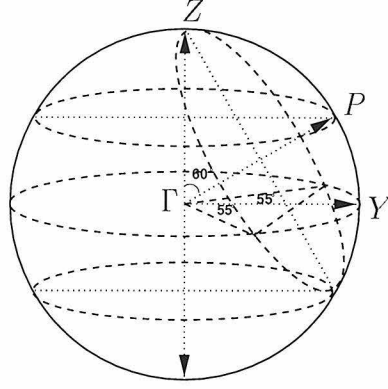


Figure 4.6: Geometric construction for obtaining the locations of the strongest scattering spots in the $k_z = 0$ plane.

The scattering pattern Fig. 4.7 was observed in the work of Förster **et al.**[10]. These authors attributed the scattering pattern as arising from perforated layers with *abcabc...* stacking with the layer normal in the x -direction. Although capable of accounting for the location of the four weak peaks, their model would predict, as noted by these authors, two additional Bragg peaks in the $k_z = 0$ plane at $\pm 35.26^\circ$ with respect to the x -axis, which were not observed in their SANS pattern. Also, the weakness of the four weak peaks was never satisfactorily explained. Our model based on anisotropic fluctuation in a bcc-based PL, on the other hand, predicts the correct position of all the peaks observed in the experiment. The predicted disparity in the intensity between the two groups of peaks is also in excellent qualitative agreement with experiments. As pointed out at the end of Section 3.2, if we assume that the PL phase results from the least stable fluctuation mode of the L phase, then the perforations will be stacked in the *abab...* pattern. Our bcc-based PL model satisfies this requirement and gives a fully consistent explanation of all the features observed in the puzzling SANS data.

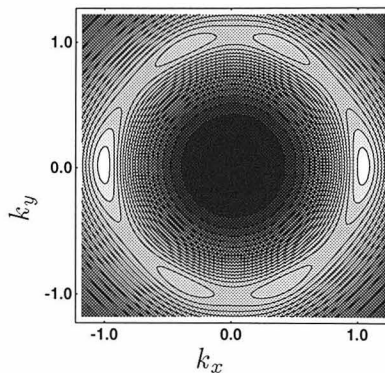


Figure 4.7: The fluctuation part of the scattering pattern in the $k_z = 0$ plane for a metastable bcc-based PL. The parameters are chosen at $N\chi = 17$ and $f = 0.35$.

4.3 Discussion

In this Chapter, we have proposed a consistent theoretical explanation of the nature of the perforated lamellar (PL) phases that were experimentally observed for a number of diblock copolymer samples. Arguing that the PL phase arises from the least stable fluctuation mode of the lamellar (L) phase, we proposed two structural models for the PL phase, an hcp-based PL and a bcc-based PL, both having *abab...* stacking. Within a Leibler-type mean-field theory, we find that these structures are not thermodynamically stable phases but are only pseudostable in the weak-segregation limit and metastable in the intermediate-segregation regime. This last conclusion is consistent with more recent experiments by Hajduk *et al.*[23].

Perhaps the most significant result of this study is a consistent interpretation of the in-plane small-angle neutron scattering patterns for the PL phases obtained by Bates and co-workers[4][7] [10][11][24] . Whereas previous attempts have tried to explain the peaks in the scattering patterns in terms of the crystal symmetry of the reciprocal lattice of the structure, *i.e.*, as Bragg scattering, we propose that the experimentally observed scattering peaks arise from anisotropic fluctuations instead of, and in some cases in addition to, Bragg scattering from the mean-field periodic structure. Our calculated scattering patterns using the two structural models are in excellent agreement with the experimental data. The weakness of some of these

in-plane scattering peaks can be explained by the fact that these peaks are not the primary Bragg peaks associated with the structures, but are either peaks arising from anisotropic fluctuations or secondary Bragg peaks which are generally much weaker in the weak-segregation regime. Thus we are able to explain in a simple and consistent manner both the intensity and the location of the in-plane scattering peaks, particularly with regard to the puzzling non-six-fold scattering patterns in the work of Förster et al[10], which we associate with the bcc-based PL structure.

In contrast to the classical phases (L, C, and BCC) and the bicontinuous G phase, experimentally the PL phases are not easily obtainable by thermal annealing of the samples. Frequently, a combination of temperature change and shear flow is employed to obtain the PL phases [4][10] [11][23]. Although the study of shear flow effects is beyond the scope of this work, our results can be used to qualitatively understand the elusiveness of the PL phase in experiments, as explained in the following.

From our calculated phase diagram, the spinodal of the PL phase (for both models) is very close to that of the L phase. Thus, when the L phase becomes unstable as $N\chi$ decreases (or as the temperature increases), so does the PL phase. If we assume, as we did in this paper, that the PL phase arises from the least stable fluctuation mode of the L phase as the L phase reaches its spinodal, then one cannot obtain a (meta)stable PL by increasing the temperature. Increasing the temperature beyond the spinodal of the L phase results in a pseudostable PL which should subsequently decay to the stable H phase through a continuous symmetry breaking. This is in agreement with our previous computer simulation study of the kinetic pathway of the L to C transitions [15], and also in agreement with experiments [4][23]. However, a metastable PL phase can be obtained by quenching the temperature from the pseudostable PL [25]. This offers a plausible explanation as to why shear is often used in obtaining a (meta)stable PL, because shear has the effect of decreasing the fluctuations[26][27] (albeit anisotropically) and thus is similar to decreasing the temperature. Shear may also help select one PL structure from the other PL structure. In the absence of shear, the near degeneracy in the free energy between the hcp-based and bcc-based PL structures may result in both structures being formed in the same

sample, thus leading to PL structures with apparently poor spatial order[23].

The region of metastable PL overlaps with that of the G phase. Thus over a sufficiently long time the metastable PL will anneal to the more stable G phase. However, we find that the mechanism of this transformation cannot be described by some unstable modes of the PL phase. Such a transition likely involves structural rearrangement in real space, based on spacing and topological requirements. Since both the G phase and the bcc-based PL structure have a cubic underlying lattice, the transition from PL to G is likely to involve the bcc-based rather than the hcp-based PL.

Bibliography

- [1] Bates, F. S.; Fredrickson, G. H. *Ann. Rev. Phys. Chem* **1990**, *41*, 525; Fredrickson, G. H.; Bates, F. S. *Ann. Rev. Mater. Sci* **1996**, *26*, 501, and references therein.
- [2] Leibler, L. *Macromolecules* **1980**, *13*, 1602.
- [3] Vavasour, J. D.; Whitmore, M. D. *Macromolecules* **1992**, *25*, 5477.
- [4] Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almdal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959.
- [5] Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598.
- [6] Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.
- [7] Schulz, M.F.; Bates, F. S.; Almdal, K.; Mortensen, K. *Phys. Rev. Lett.* **1994**, *73*, 86.
- [8] Matsen, M. W.; Schick, M. *Phys. Rev. Lett.* **1994**, *72*, 2660.
- [9] Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1091.
- [10] Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922.
- [11] Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
- [12] de la Cruz, M. O.; Mayes, A. M.; Swift, B. W. *Macromolecules* **1991**, *25*, 944.
- [13] Fredrickson, G. H.; *Macromolecules* **1991**, *24*, 3456.

- [14] Hamley, I. W.; Bates, F. S.; *J. Chem. Phys* **1994**, *100*, 6813.
- [15] Qi, S. Y.; and Wang, Z. -G. *Phys. Rev. E*. **1997**, *55*, 1682.
- [16] Qi, S. Y.; and Wang, Z. -G. *Phys. Rev. Lett.* **1996**, *76*, 1679.
- [17] Yeung, C.; Shi, A. -C.; Noolandi, J.; Desai, R. C. *Macromol. Theory Simul.* **1996**, *5*, 291.
- [18] Laradji, M.; Shi, A. -C.; Desai, R. C.; Noolandi, J., *Phys. Rev. Lett.* **1997**, *78*, 2577; *Macromolecule*, in press.
- [19] Shi, A. -C.; Noolandi, J.; Desai, R. C. *Macromolecules* **1996**, *29*, 6487.
- [20] Cross, M. C.; Hohenberg, P. C. *Rev. Mod. Phys.* **1993**, *65*, 851.
- [21] A third and trivial choice has two spots 180° from each other on each ring; this corresponds simply to hexagonally ordered cylinder phase with the cylinder axis perpendicular to the layer normal of the original L phase.
- [22] The predicted wide angular spread of the in-plane scattering peaks is consistent with the experimental data in Refs [4] and [11]. However, in another paper (Hamley, I. W.; Gehlsen, M. D.; khandpur, A. k.; Koppi, K. A.; Rosedale, J. H.; Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K.J. *Phys. France II* **1994**, *4*, 2161) narrower angular spread for the six peaks was observed. These sharper peaks are probably due to deviation from the weak-segregation regime. Such deviation would enhance the secondary Bragg peaks and suppress the anisotropic fluctuations.
- [23] Hajduk, D. A.; Takenouchi, H.; Hillmyer, M. A.; Bates, F. S.; Vigild, M. E.; Almdal, K. *Macromolecules* **1997**, *30*, 3788.
- [24] Almdal, K.; Koppi, K. A.; Bates, F. S. *Macromolecules* **1993**, *26*, 4058.
- [25] Qi, S. Y.; Wang, Z. -G., unpublished.
- [26] Cates M. E.; Milner, S. T. *Phys. Rev. Lett* **1989**, *62*, 1856.

- [27] Fredrickson, G. H. *J. Rheol.* **1994**, *38*, 1045.

Chapter 5 Conclusion

In this thesis, we studied the kinetics of various order-order and order-disorder transitions in weakly segregated diblock copolymers by using a time-dependent Ginzburg-Landau (TDGL) approach. Our study reveals that the transition kinetics in these systems is considerably richer and more complex than in simple, phase-separating systems, such as binary fluids[1]. Since many microstructured systems, such as ferrofluids and Langmuir films, share the same qualitative behaviors as diblock copolymers, our results should be applicable to a broader class of systems.

One of the key concepts that emerges from our study is that of the anisotropic fluctuation. These fluctuations play two crucial roles: first, they determine the stability limit of the initial structure, and second, they are responsible for the emergence of new structures, whether they are the final equilibrium states, or transient states during the transition. Besides the direct relevance to microphase transition kinetics, anisotropic fluctuations are essential for interpreting small-angle neutron or X-ray scattering data. Since these fluctuations are in general peaked at positions different from those constituting the reciprocal lattice of the ordered structures, it is important to distinguish them from the Bragg peaks in the scattering data.

The kinetic issues investigated in this thesis deals with systems in quiescent state. Experimentally, however, it is much more convenient to cross phase boundaries by applying a flow field than by changing the temperature. Changes in the small-angle neutron scattering patterns of ordered block copolymer phases due to shear have been demonstrated in several experiments by the Bates' group[2] [3][4]. These results reflect the distortion of the spectrum of anisotropic fluctuations. However, no theory is currently available. The distortion of the fluctuation spectrum generally leads to a shift in the spinodal of the original structure and can break the degeneracy in the most unstable modes. For example, under steady shear flow conditions, the hexagonal cylinders that emerge as a result of increasing the temperature from the lamellar phase

will be oriented in the flow direction. Thus understanding the effects of flow on the anisotropic fluctuations will enable us to understand the mechanism of flow alignment of microphase separated block copolymers[5].

Bibliography

- [1] Seul, M. and Andelman, D. *Science* **1995**, *267*, 476, and references therein.
- [2] Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almdal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959.
- [3] Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922.
- [4] Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.
- [5] Gupta, V. K.; Krishnamoorti, R.; Chen, Z. R.; Kornfield, J. A.; Smith, S. D.; Satkowski, M. M.; Grothaus, J. T. *Macromolecules* **1996**, *29*, 875.

Appendix A Derivation of Structure Factor of Diblock Copolymers by the Random Phase Approximation

In this appendix, we outline the derivation of the free energy functional from the partition function Eq. 1.7 and provide an explicit expression for Γ_2 in Eq. 1.8. In a compact form, we rewrite the partition function as:

$$\begin{aligned}
Z &= \int D[\psi(\vec{q})] \exp[-\beta F] \\
&= \int \Pi_{\alpha=1}^{n_p} \left\{ D[\vec{R}_A^\alpha(s)] D[\vec{R}_B^\alpha(s)] P_0[\vec{R}_A^\alpha(s)] P_0[\vec{R}_B^\alpha(s)] \delta[\vec{R}_A^\alpha(N_A) - \vec{R}_B^\alpha(0)] \right\} \\
&\quad \times \exp \left[\frac{n_p N \chi}{V} \int \hat{\rho}_A(\vec{q}) \hat{\rho}_A(-\vec{q}) d\vec{q} \right] \int D[\rho_A(\vec{q})] D[\rho_B(\vec{q})] \Pi_{\vec{q} \neq 0} \delta[\hat{\rho}_A(\vec{q}) + \hat{\rho}_B(\vec{q})] \\
&\quad \times \delta[\rho_A(\vec{q}) - \hat{\rho}_A(\vec{q})] \delta[\rho_B(\vec{q}) - \hat{\rho}_B(\vec{q})]
\end{aligned} \tag{A.1}$$

where $D[\vec{R}_j^\alpha(s)] = \Pi_{s=0}^{N_j} d\vec{R}_j^\alpha(s)$, $D[\rho_j(\vec{q})] = \Pi_{\vec{q} \neq 0} d\rho_j(\vec{q})$, $j = A$ or B , and P_0 is defined as

$$P_0[\vec{R}_j^\alpha(s)] = C_N^{-1} \exp \left[-\frac{3}{2b^2} \int_0^{N_j} dn \left(\frac{\partial R_j^\alpha}{\partial n} \right)^2 \right]. \tag{A.2}$$

$C_{N_j} = (2\pi b^2/3)^{3N_j/2}$ is the normalization constant. To obtain the free energy as a functional of $\rho_j(\vec{q})$ instead of configurational variables $\vec{R}_j^\alpha$, we use the Fourier transform of Eq. 1.3 to rewrite the delta-function

$$\delta[\rho_j(\vec{q}) - \hat{\rho}_j(\vec{q})] = \delta \left[\rho_j(\vec{q}) - \frac{V}{(2\pi)^{3/2} n_p N} \sum_{\alpha=1}^{n_p} \sum_{s=0}^{N_j} \exp \left\{ -i\vec{q} \cdot \vec{R}_j^\alpha(s) \right\} \right]$$

$$= \int d\lambda_j(\vec{q}) \exp \left\{ i\lambda_j(\vec{q}) \left[\rho_j(\vec{q}) - \frac{V}{(2\pi)^{3/2}n_p N} \sum_{\alpha=1}^{n_p} \sum_{s=0}^{N_j} \exp(-i\vec{q} \cdot \vec{R}_j^\alpha(s)) \right] \right\} \quad (\text{A.3})$$

Where we introduce field $\lambda_j(\vec{q})$, thus the coupling imposed by the delta-function in the first step can be divided into configurational dependent and configurational independent part:

$$\begin{aligned} Z &= \int D[\rho_A(\vec{q})] D[\rho_B(\vec{q})] D[\lambda_A(\vec{q})] D[\lambda_B(\vec{q})] \delta[\rho_A(\vec{q}) + \rho_B(\vec{q})] \\ &\times \left\{ \int D[\vec{R}_A(s)] D[\vec{R}_B(s)] P[\vec{R}_A(s)] P[\vec{R}_B(s)] \delta[\vec{R}_A(N_A) - \vec{R}_B(0)] \right\}^{n_p} \\ &\times \exp \left\{ \int d\vec{q} \left[\sum_{j=A,B} iV\lambda_j(\vec{q})\rho_j(\vec{q}) + \frac{n_p N \chi}{V} \rho_A(\vec{q})\rho_A(-\vec{q}) \right] \right\}, \quad (\text{A.4}) \end{aligned}$$

where $D[\rho_j(\vec{q})] = \Pi_{\vec{q} \neq 0} d\rho_j(\vec{q})$, $D[\lambda_j(\vec{q})] = \Pi_{\vec{q} \neq 0} d\lambda_j(\vec{q})$ with $j = A$ or B . Since $\vec{q} = 0$ terms contribute only constant prefactors, we shall ignore them. In the following, all the $\sum_{\vec{q}}$ and $\int d\vec{q}$ mean with $\vec{q} \neq 0$. In the above equation, $P[\vec{R}_j^\alpha(s)]$ is defined as

$$P[\vec{R}_j^\alpha(s)] = P_0[\vec{R}_j^\alpha(s)] \exp \left[-i \frac{V}{n_p N} \sum_{s=0}^{N_j} \Lambda_j(\vec{R}_j(s)) \right], \quad (j = A, B), \quad (\text{A.5})$$

and $\Lambda_j(\vec{R}_j(s))$ is the Fourier transform of $\lambda_j(\vec{q})$:

$$\Lambda_j(\vec{R}_j(s)) = \frac{V}{(2\pi)^{3/2}} \int d\vec{q} \lambda_j(\vec{q}) \exp[-i\vec{q} \cdot \vec{R}_j(s)], \quad (j = A, B). \quad (\text{A.6})$$

The term inside the curve bracket of Eq. A.4 which is the only term of configuration dependence, thus can be calculated by expanding with respect to Λ_j . If we only want to derive the structure factor, *i.e.*, the two-point vertex function this expansion can be cut off at the second order. Higher order vertex functions can be similarly obtained by the expansion of Λ_j to higher order. The result up to the second order is:

$$\begin{aligned}
& \left\{ \int D[\vec{R}_A(s)] D[\vec{R}_B(s)] P[\vec{R}_A(s)] P[\vec{R}_B(s)] \delta[\vec{R}_A(N_A) - \vec{R}_B(0)] \right\} \\
& = V \left[1 - \frac{V^3}{2n_p^2} \int d\vec{q} \vec{\lambda}(\vec{q}) \mathbf{M} \vec{\lambda}^T(-\vec{q}) \right], \tag{A.7}
\end{aligned}$$

where the vector $\vec{\lambda}(\vec{q}) = (\lambda_A(\vec{q}), \lambda_B(\vec{q}))$. The matrix $\mathbf{M}$ is defined as

$$\mathbf{M} = \begin{bmatrix} g(Ny, f) & \frac{1}{2}[g(Ny, 1) - g(Ny, f) - g(Ny, 1 - f)] \\ \frac{1}{2}[g(Ny, 1) - g(Ny, f) - g(Ny, 1 - f)] & g(Ny, 1 - f) \end{bmatrix}. \tag{A.8}$$

In deriving Eq. A.7, we have used the following results:

$$\int_0^{N_j} ds_1 \int_0^{N_j} ds_2 \exp\{-y|s_1 - s_2|\} = N^2 g(Ny, f_j) \tag{A.9}$$

and

$$\sum_{s_1=0}^{N_A} \exp(-ys_1) \sum_{s_2=0}^{N_B} \exp(-ys_2) = \frac{1}{2} N^2 [g(Ny, 1) - g(Ny, f) - g(Ny, 1 - f)]. \tag{A.10}$$

In the above equations $y = b^2 q^2 / 6$, $f_j = N_j / (N_A + N_B) = N_j / N$ and $g(x, f)$ is the Debye function:

$$g(x, f) = 2[f x + \exp(-f x) - 1] / x^2. \tag{A.11}$$

Thus, the partition function Z , in the limit of $n_p \rightarrow \infty$, becomes:

$$\begin{aligned}
Z &= \int D[\rho_A(\vec{q})] D[\rho_B(\vec{q})] D[\lambda_A(\vec{q})] D[\lambda_B(\vec{q})] \delta[\rho_A(\vec{q}) + \rho_B(\vec{q})] \\
&\quad \times \exp \left\{ -\frac{V^3}{2n_p} \int d\vec{q} \vec{\lambda}(\vec{q}) \mathbf{M}(\vec{q}) \vec{\lambda}^T(-\vec{q}) \right\}
\end{aligned}$$

$$\times \exp \left\{ \int d\vec{q} \left[i(V\lambda_A(\vec{q})\rho_A(\vec{q}) + V\lambda_B(\vec{q})\rho_B(\vec{q})) + \frac{n_p N \chi}{V} \rho_A(\vec{q})\rho_A(-\vec{q}) \right] \right\} \quad (\text{A.12})$$

Using

$$\int \exp \left[i\vec{\lambda} \cdot \vec{\rho}^T - 1/2 \vec{\lambda} \mathbf{M} \vec{\lambda}^T \right] d\vec{\lambda} = 2\pi (\text{Det} \mathbf{M})^{-1/2} \exp \left[-1/2 \vec{\rho} \mathbf{M}^{-1} \vec{\rho}^T \right]. \quad (\text{A.13})$$

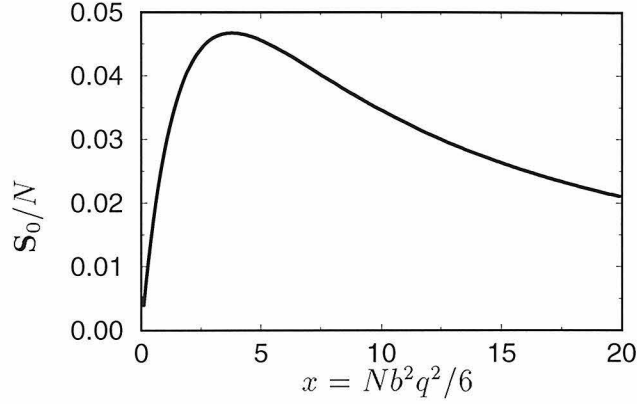


Figure A.1: The structure factor for $f = 0.45$ and $\chi = 0$. The maximum of the curve corresponds to the optimal wavenumber.

we further obtain

$$\begin{aligned} Z &= \int D[\rho_A(\vec{q})] D[\rho_B(\vec{q})] \delta[\rho_A(\vec{q}) + \rho_B(\vec{q})] \\ &\times \exp \left[-\frac{n_p}{2V^2} \sum_{\vec{q}} \vec{\rho}(\vec{q}) \mathbf{M}^{-1} \vec{\rho}^T(-\vec{q}) + \frac{n_p N \chi}{V^2} \sum_{\vec{q}} \rho_A(\vec{q}) \rho_A(-\vec{q}) \right] \\ &= \int D[\rho_A(\vec{q})] \\ &\times \exp \left[-\frac{n_p N}{2V^2} \sum_{\vec{q}} \rho_A(\vec{q}) \rho_A(-\vec{q}) \left(\sum_{i,j=1}^2 \mathbf{M}_{ij} / (N \text{Det} \mathbf{M}) - 2\chi \right) \right]. \quad (\text{A.14}) \end{aligned}$$

Therefore, the structure factor $\mathbf{S}_0(\vec{q})$ is:

$$\mathbf{S}_0^{-1} = \frac{1}{N} \sum_{i,j=1}^2 \mathbf{M}_{ij} / (\text{Det} \mathbf{M}) - 2\chi. \quad (\text{A.15})$$

This function has a maximum which is only related to f . This maximum will be divergent when χ is equal to the critical value. For $f = 0.45$ and $\chi = 0$, the structure factor $\mathbf{S}_0/N$ is shown in Fig. A.1.