131 Phase-Field Crystalモデルを用いたパターン形成における2つのおどろき

Two Surprises in Phase-Field Crystal Modeling of Pattern Formation

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Two surprises that we have encountered in the numerical analysis of spontaneous pattern formation in the phase-field crystal (PFC) model are reported. One is the appearance of hexagonal patterns in a parameter regime where previously only rolls (lamellae) were known to be stable. We theoretically attribute the physical origin of this novel pattern to the hydrodynamic flow and the conservation law, the latter being inherent in the PFC equation. The other is the outcome of our attempt to control a self-assembling PFC system with as little fine-tuning as possible to create a very long range order of the straight roll or equilateral hexagon domains without defects.

Key Words : Phase-Field Crystal Model, Periodic Pattern Formation, Zero Mode, Patterning

1 Hexagons in Double Phase Separation

In the first half of the talk, we present a study on a generalized version of the phase-field crystal (PFC) model⁽¹⁾ for hydrodynamic systems developing spatially periodic patterns. Specifically, we consider the case where the velocity field $\mathbf{v}$ is driven by distortions of the order-parameter field ψ , and the length scales of the generated flow are large compared to the spatial periodicity of patterns.

The model reads⁽²⁾

$$\partial_t \psi = (i\nabla)^p [\varepsilon \psi - \tilde{\xi}_0^4 (\nabla^2 + k_0^2) \psi - u \psi^3] - \mathbf{v} \cdot \nabla \psi, \quad (1)$$

$$\tau \partial_t \mathbf{v} = \nu (\nabla^2 - c^2) \mathbf{v} - \frac{1}{2} g_0 \nabla (\nabla \psi)^2. \quad (2)$$

Here $p = 0$ for a nonconserved order parameter (NCOP), whereas for a conserved order parameter (COP) $p = 2$. The ε is the control parameter with the transition to, e.g., stripes (also called rolls or lamellae) of a finite wavenumber k_0 occurring for $\varepsilon > 0$. The positive quantities $\tilde{\xi}_0$ and u are phenomenological parameters. The coefficient g_0 of the second term on the right-hand side of Eq. (2) represents the strength of the hydrodynamics coupling between $\mathbf{v}$ and ψ , while the first term represents the viscous dissipation; τ , ν and c are other phenomenological parameters of the velocity field. In the following, assuming a slowly varying vorticity, we neglect the inertial effect and take $\tau = 0$ (the so-called passive vorticity case). The main task in what follows is to discuss the COP case regarding spatial patterns that may be induced by this dynamical model.

The terms inside the square brackets in Eq. (1) are just those of the much-studied Swift-Hohenberg (SH) equation⁽³⁾. In particular, in the NCOP case the above model equations (1) and (2) are equivalent to the model⁽⁴⁾ proposed to describe the mean-flow effect in Rayleigh-Bénard convection. It has been shown by analytical and numerical studies to reproduce complex pattern formation of convective fluids near onset. Among others, spiral-defect chaos was found to be re-

produced by numerically simulating these generalized SH equations⁽⁵⁾.

One of the most intriguing recent discoveries in hydrodynamic coarsening of binary fluid mixtures is the observation of phenomena called spontaneous double phase separation (DPS)⁽⁶⁾. When the hydrodynamic flow is strong enough, the hydrodynamic coarsening can be too quick for the order parameter in each domain to attain its equilibrium value. With domains rendered metastable or unstable in this way, this effectively causes a kind of further quench effect, and the secondary spinodal decomposition can take place within each domain. The resulting pattern is a nested circular droplet formation within the large bicontinuous domains. This scenario for DSP seems to be quite universal for any hydrodynamic coarsening systems, including not only the fluid mixtures (for which $k_0 \equiv 0$) but also systems in which the forming pattern is a spatially periodic state.

Given all the facts mentioned above, we now pose the following questions. (1) Can spirals, which appear for parameter values where the stripe state is known to be stable in the system described by the NCOP model, survive the presence of the conservation law? (2) What is the outcome (pattern morphology) of the two competing growth mechanisms, i.e., the spontaneous DPS and the spiral-defect generation, which may be operative in hydrodynamic systems developing spatially periodic patterns?

In pursuing these goals, we performed numerical study of the COP Eqs. (1) and (2). Instead of using the conventional discretization algorithm to the partial differential equations, we employ the numerically efficient cell-dynamical-system (CDS) method⁽⁷⁾ on a square lattice.

In the absence of hydrodynamic interactions, we only observed the stripes that became more labyrinthine with increasing ε . A spiral defect pattern or a concentric striped (target) pattern solely arises from the hydrodynamic coupling effect. These observations are some-

what similar to the phase behavior in the NCO case where the hydrodynamic coupling is added. The most spectacular qualitative difference from the NCO system was that at strong hydrodynamic couplings the spiral/target pattern gives way to the hexagonal planform in which hexagons of the type H0 and H π coexist (Fig. 1). Furthermore, we observed that patches of coexisting hexagonal patterns underwent slow evolution in time and showed no tendency to reach any stationary state.

Fig. 1 Coexisting up- and down-flow (often called, respectively, H0 and H π type) hexagonal patterns; the white regions denote positive values of the order parameter and the gray ones negative values.

Fig. 2 The growth rate of infinitesimal perturbations of the trivial solution $\psi = 0$, where k is the perturbation wave number. For $0 < \varepsilon \ll 1$, there is a narrow band of unstable wave numbers near $k = k_0$. Furthermore, for small k the conservation law generates a neutrally stable zero-mode.

This unusual appearance of the symmetry-degenerate hexagons can be explained by the following simple argument. In systems in which short wavelength ($\propto k_0^{-1}$) modes are the only mode that is unstable at threshold (such a mode is referred to as critical mode; see Fig. 2), the hexagonal structure is built on wavevectors $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3$ of length k_0 which meet the resonance condition $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = \mathbf{0}$. In the evolution equation of ψ , this resonance condition is maintained only if a quadratic term ψ^2 is present that breaks the ‘up-down’ symmetry $\psi \rightarrow -\psi$. However, in our present situation there is a zero mode which is marginally stable and may be coupled to the critical modes. As a result, the cubic

term ψ^3 of the governing equation provides a quadratic coupling of the critical modes (which themselves couple to the zero mode), thus leading to the formation of equilateral hexagonal patterns without breaking the up-down symmetry of the system (1) and (2).

2 Patterning

A thin film consisting of a fully-ordered (defect-free) lamellae or hexagons is potentially useful in designing nanostructural materials and nanodevices in diverse fields ranging from semiconductor devices to polymer electronics. Unfortunately, it is difficult to produce large, 2D arrays of high uniformity and order. Therefore there has been substantial work⁽⁸⁾ on enhancing order in thin film systems. Possible techniques for inducing order include applied external fields (e.g., electric, shear) and lateral confinement (via photolithographic or chemical patterning).

Although the latter template-directed patterning represents a promising technological tool, the periodicity of lamellar or hexagonal patterns thus generated is slaved to the externally imposed one, and hence deviates from its equilibrium bulk value. There then arises a natural question: is it possible that the systems organize themselves into perfectly periodic pattern with seemingly little external manipulation?

In the latter half of the talk, we will report the unanticipated achievement of *equilibrium* near single-crystal texture in PFC simulations of a thermally driven microphase separation process, as illustrated in Fig. 3.

Fig. 3 Representative order-parameter profiles that are almost perfectly self-organized in numerical simulations of Eq. (1) with $v = 0$.

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