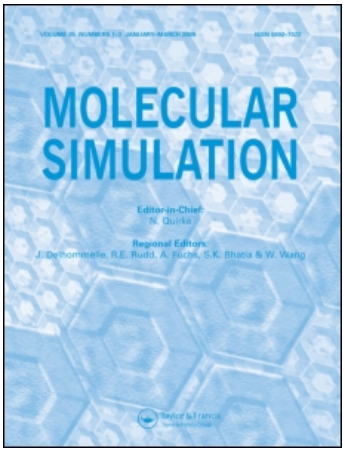

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The Nosé thermostat for the pattern formation dynamics

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The Nosé thermostat for the pattern formation dynamics

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The Nosé thermostat method for pattern formation dynamics is developed by coupling the dynamical equation of the friction coefficient with the Langevin-type equation for diblock copolymer mesophases. It is clarified that the physical value obtained along the trajectory generated by the deterministic system reproduces Gibbs' canonical ensemble by keeping the kinetic energy of the system at a target value. Using this method, one can obtain well-defined three-dimensional ordered morphologies from numerical simulations within a finite small duration of computational time. In particular, we found the double gyroid and the F_{ddd} mesophases in the transition region between layers and column phases from the random initial conditions.

Keywords: Numerical simulation; The Nosé thermostat; Pattern formation; Block copolymer; Double gyroid

1. Model and theory

For about two decades, Professor Shuichi Nosé lectured on computational physics to the graduate students of Keio University, in which he introduced self-consciously about his famous method by using his freehand sketches like figure 1(a) where his thermostat were expressed as an object connected to the original molecular system with a spring. The Nosé thermostat method has been widely applied to various fields of molecular simulations [1,2]. In this study, we apply the Nosé thermostat to a mesoscale system and demonstrate the richness of spatial ordered morphologies of the diblock copolymer mesophases [3]. In a molecular system, the orbits in the phase space are described in terms of **p** and **q**, momentum and coordinate of monomers. In a mesoscale system, on the other hand, those are the scalar field variable of ψ such as the local deviation of the monomer concentration, in other words, the local order parameter which is familiar used in the Ginzburg–Landau theory of phase transition dynamics.

1.1 Pattern formation for block copolymers

Block copolymers are produced by joining several chemically distinct polymer blocks, each linear series of identical monomers. They hate each other like oil and vinegar. The simplest architecture is the linear AB diblock copolymer, consisting of chain of type A monomers covalently bonded to chain of type B monomers. At low temperature, the copolymer mixture undergoes a spatial segregation. In forming an equilibrium morphology, such a material may separate into distinct phases, those create domains of component A and B. However, macro-phase separation does not occur, since the two sequences are chemically connected at a junction point. Segregation of these blocks can produce ordered morphologies on mesoscale [4]. The block copolymer system is an interesting example for which a simple model is proposed to realize the spatially nonuniform mesophases, where the positive values of the ψ field indicate higher concentration of one block monomers and that negative values indicate higher concentration of the other block. Although the specific origins vary from system to system, the formation of ordered morphologies can be attributed to the competing short-range and long-range interactions. For the volume fraction $\bar{\psi}$, the Landau-type free energy functional is given by:

$$F(\psi) = \int_{\Omega} \mathrm{d}\mathbf{r} \left\{ \left[-\frac{\alpha}{2} + \frac{\beta}{2}\bar{\psi}^2 \right] \psi^2 + \frac{\gamma}{3}\bar{\psi}\psi^3 + \frac{\lambda}{4}\psi^4 + \frac{D}{8k_0^2}\left[\left(\Delta + k_0^2\right)\psi \right]^2 \right\}, \tag{1}$$

where $\alpha, \beta, \gamma, \lambda, D$ are positive phenomenological parameters and Ω represents the physical space. Notation k_0

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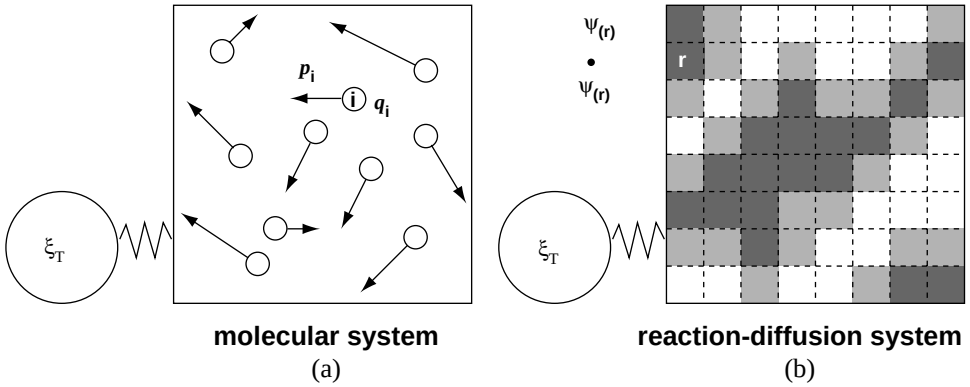

Figure 1. The Nosé-thermostat method is applied into the reaction-diffusion system (the corresponding coupled map lattice system). (a) The $\mathbf{p}_i$ and $\mathbf{q}_i$ are the momentum and coordinate of particle i in a molecular system. (b) The phase space point in our system, on the other hand, is expressed as the scalar field variables of $\psi(\mathbf{r})$ and its time derivative $\dot{\psi}(\mathbf{r})$ at position $\mathbf{r}$.

is the characteristic wave number of the morphology and and Δ is the Laplace operator. The essential physics of the ordered morphologies is captured by this model and the equilibrium patterns are obtained as the energy local minima. The decreasing Helmholtz free-energy $F(\psi)$ is the driving force behind the relaxation to the equilibrium. The gradient system which satisfies the condition of $\mathrm{d}F/\mathrm{d}t \leq 0$ for any value of the ψ field is written by:

$$\tau \frac{\partial \psi}{\partial t} = -\frac{\delta F}{\delta \psi}, \tag{2}$$

where τ is the phenomenological parameter [5]. The gradient form of equation (2) accurately describes the motion of relaxation along the path on the free-energy surface in the vicinity of the global and local minima. As frequently studied such as the references of [4–6], the ragged landscape of the free-energy surface makes it difficult to obtain a well-defined ordered morphology as the global minimizer. The situation is more difficult in three-dimensional systems and this will be mentioned in a later section.

1.2 The Nosé thermostat for pattern formation dynamics

We extend the dynamical equation of the familiar form of equation (2) to the Langevin equation with two variables, the ψ field and its time derivative $\dot{\psi}$, in order to describe the states far from equilibrium [3].

$$\frac{\partial \dot{\psi}}{\partial t} = -\xi \dot{\psi} - \frac{1}{\tau}\left(\frac{\delta F}{\delta \psi}\right), \tag{3}$$

where ξ is the friction coefficient. Then we have

$$\dot{\psi}(t) = -\frac{1}{\tau \xi}\left(\frac{\delta F}{\delta \psi}\right)(1 - \mathrm{e}^{-\xi t}) + \dot{\psi}(0)\mathrm{e}^{-\xi t}. \tag{4}$$

Within the limits of the stationary state, we derive the equilibrium velocity $\dot{\psi}_{\mathrm{eq}}$ as

$$\dot{\psi}_{\mathrm{eq}} = -\frac{1}{\tau \xi}\left(\frac{\delta F}{\delta \psi}\right) \equiv -\mu\left(\frac{\delta F}{\delta \psi}\right), \tag{5}$$

where μ is the mobility. Consequently, from the far-from-equilibrium dynamics of equation (3), we obtain the familiar gradient form of equation (2) at equilibrium. We assert that a far-from-equilibrium system including ψ and $\dot{\psi}$ approaches to an equilibrium system in a sufficiently late stage of the dynamics. In fact, we find that time-reversible dynamics leads the systems to the free-energy minimum for the suitable choice of the value of ξ.

However, there exists minimal work as well as kinetic energy, which are given as the initial distribution of the ψ and $\dot{\psi}$ field, respectively. The kinetic energy $\langle \dot{\psi}^2 \rangle \equiv |\Omega|^{-1} \int_\Omega \mathrm{d}\mathbf{r} \dot{\psi}^2/2$ is described as the heat caused by irregular motions of the constituents ψ in a system, where the $|\Omega|$ corresponds to the total number of cells in our simulations. In order to regulate the dissipation of heat efficiently, the dynamical equation of the friction coefficient ξ is coupled to the equation of motion of equation (3):

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = Q(\langle \dot{\psi}^2 \rangle - T), \tag{6}$$

where Q is the coupling parameter which determines the speed of the kinetic energy control and T is the target kinetic energy.

Figure 2 (a)–(d) shows the time-evolutions of the spatial pattern in a two-dimensional system, in which the formation of a well-defined layered pattern is realized as the well-known equilibrium pattern in the even case. Numerical simulations are carried out by using the coupled map lattice system method, which is composed of computationally efficient discrete space-time model [6]. In particular, we employ the Verlet's algorithm in the every time step procedure in our simulations. As shown in figure 2(e), the dissipation of the kinetic energy progresses smoothly with time, while the value of ξ is zero at $t = 0$ and continues to increase monotonically. At last, it converges to an equilibrium value ξ_{eq}. From the analysis of equation (3), the time evolution of the total kinetic energy can be asymptotically written by $\langle \dot{\psi}^2 \rangle \propto \exp[-2\xi_{\mathrm{eq}} t]$.

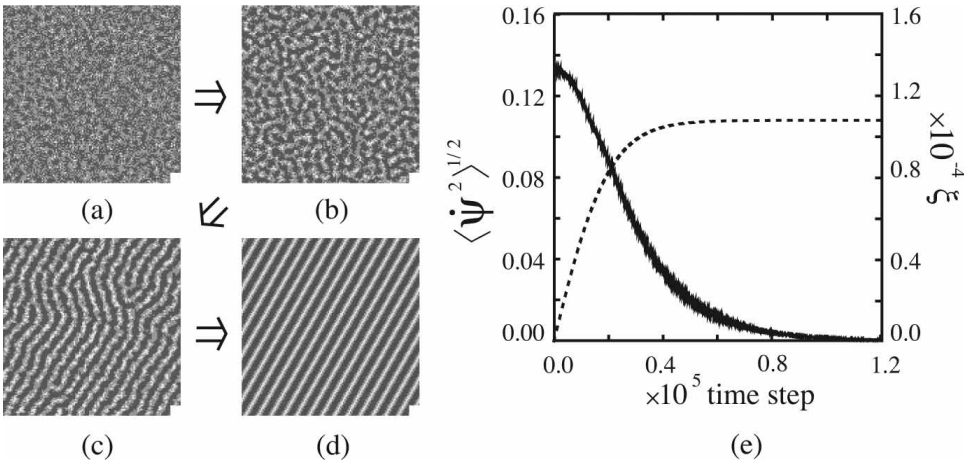

Figure 2. Time evolution of the spatial pattern for $\bar{\psi} = 0$, where dark area denotes the region of high values of the ψ field. $\tau = 1.0, Q = 5.0 \times 10^{-3}/128^2, v_0 = 1.0$ and $T = 0.0$. (a) Initial condition, (b) after 2.0×10^3 steps, (c) after 2.0×10^4 steps, (d) after 1.2×10^5 steps, and (e) time evolution of the kinetic energy $\langle \dot{\psi}^2 \rangle^{1/2}$ and the friction coefficient ξ. Solid and broken lines correspond to $\langle \dot{\psi}^2 \rangle^{1/2}$ and ξ, respectively.

2. Application and numerical results

In the fashion similar to that employed in the Ref [1], we can easily prove that the time evolution of distribution function $\rho(\{\psi\}, \{\dot{\psi}\}, \xi)$ following the deterministic system composed of equations (3) and (6) satisfies the requirement of the equilibrium distribution in the phase space. The time derivative of ρ becomes

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{1}{T}\frac{\mathrm{d}(K+F)}{\mathrm{d}t}\rho, \tag{7}$$

where we define the total kinetic energy as $K \equiv \int_\Omega \mathrm{d}\mathbf{r}\dot{\psi}^2/2 + \xi^2|\Omega|/2Q$. Therefore, the equilibrium distribution with T is realized as $\rho(\{\psi\}, \{\dot{\psi}\}, \xi) \propto \exp[-(K+F)/T]$ [7]. This result does not contradict our intuitive perception of temperature, which is related to the average kinetic energy of a system. In addition, as shown in figure 3(a), there exists a conservation law for the Nosé pseudo Hamiltonian of

$$H_{\text{Nosé}} = K + F + |\Omega|T\Lambda, \tag{8}$$

where the added variable Λ is determined as $\mathrm{d}\Lambda/\mathrm{d}t = \xi$. The negative feedback mechanism of ξ works to keep the total energy $K + F$ of our system around the constant value. Therefore, we can control over the fluctuations around the equilibrium patterns in the presence of heat.

2.1 Canonical ensemble average of fluctuations around equilibrium pattern

In our simulations with the finite temperature, to keep the kinetic energy around the target T value, the thermostat variable ξ needs to oscillate slightly around a zero value. The negative feedback oscillation of ξ causes the flow of

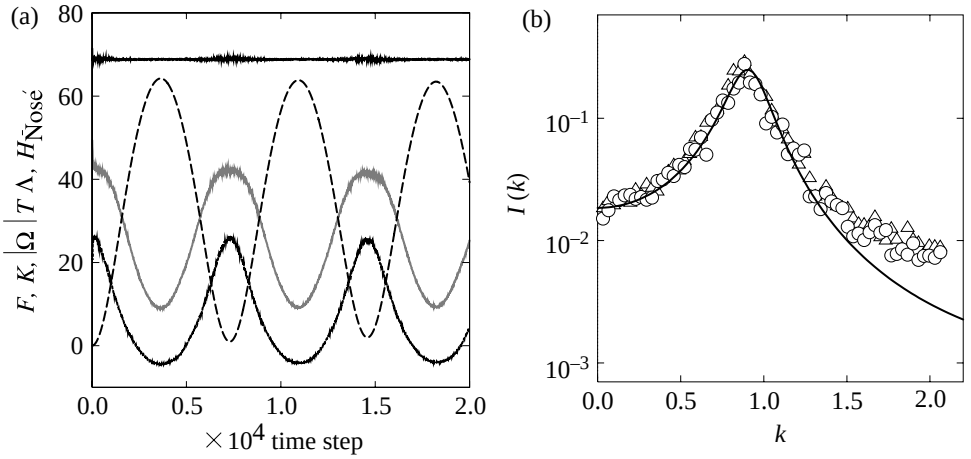

Figure 3. (a) Time evolution of the energy values for $\alpha = 0.05, \beta = 1.50, \gamma = 1.50, \lambda = 0.50, D = 1.00, k_0 = 0.75, \bar{\psi} = 0.00$ and $Q = 5.0/128^2$. The sets of (v_0, T) are chosen as $(0.25, 0.05^2)$. Dotted line: free energy F, gray line: kinetic energy K, broken line: $|\Omega|T\Lambda$, solid line: Nosé pseudo Hamiltonian $H_{\text{Nosé}}$. (b) The scattering form factors $I(k)$ for $\alpha = -0.01$; The parameters are set to $\gamma = 0.00, \lambda = 0.00, Q = 10.0/128^2$ and $T = 0.10$. The circles and triangles correspond to the results of the deterministic and stochastic system simulations, respectively. The solid line indicates the mean-field analysis of (7), where the ψ^2-correlations in the k space is explicitly written by $I(k) = T/[-\alpha + \beta\bar{\psi}^2 + (D/4k_0^2)(k^2 - k_0^2)^2]$.

energy between a heat bath and our system. We have considered that such fluctuations far from equilibrium should be different from the thermal fluctuations around the equilibrium state. It means that the trajectory of ψ generated by deterministic system differs from that of the stochastic system based on the following Langevin equation,

$$\tau\frac{\partial\psi}{\partial t} = -\frac{\delta F}{\delta\psi} + \eta, \tag{9}$$

where $\langle\eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle = 2T\tau\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$.

To make a numerical comparison quantitatively between the deterministic system and the stochastic forcing system, we calculate the circular averaged scattering form factors $I(k) \equiv N_{\mathbf{k}}^{-1}\sum I(\mathbf{k})$ for the homogeneous state, where $I(\mathbf{k}) \equiv \left\langle \int_\Omega d\mathbf{r}\exp(-i\mathbf{k}\cdot\mathbf{r})\psi(\mathbf{r},t) \int_\Omega d\mathbf{r}'\exp(-i\mathbf{k}\cdot\mathbf{r}')\psi(\mathbf{r}',t)\right\rangle$. Notation $N_{\mathbf{k}}$ denote the number points in the $\mathbf{k}$ space. The $\dot{\psi}$ fields are uniformly distributed between $\pm v_0$ to satisfy the relation of $v_0^2/12 = 2T$ [7]. As depicted in figure 3(b), numerical results of $I(k)$ correspond to each other and they are in agreement with the functional form obtained from the mean-field analysis. In this way, it is reasonable that the kinetic energy of our system is related to the thermal fluctuation.

2.2 *Formation of the three-dimensional morphology for diblock copolymers*

In the rest of this paper, we will present the three-dimensional morphology of AB diblock copolymer melts [8]. Here we consider the following deterministic system which satisfies the two following requirements; (i) there exists an equation of continuity, and (ii) the minimization of free energy occurs, as the case for the familiar Cahn–Hilliard equation [6].

$$\begin{cases} \frac{\partial\dot{\psi}}{\partial t} = -\xi\dot{\psi} + \triangle\left(\frac{\delta F}{\delta\dot{\psi}}\right), \\ \frac{\mathrm{d}\xi}{\mathrm{d}t} = Q(\langle\dot{\psi}^2\rangle - T) \end{cases} \tag{10}$$

with the free-energy form

$$F(\psi) = \int_\Omega \mathrm{d}\mathbf{r}\left(\frac{D}{2}|\nabla\psi|^2 + \frac{(\psi^2-1)^2}{4} + \frac{\sigma}{2}|(-\Delta)^{-1/2}(\psi-\bar{\psi})|^2\right), \tag{11}$$

where σ and D are phenomenological parameters [9]. The first term minimizes the interface area and the third term avoids the over-stretching of the copolymer blocks. As

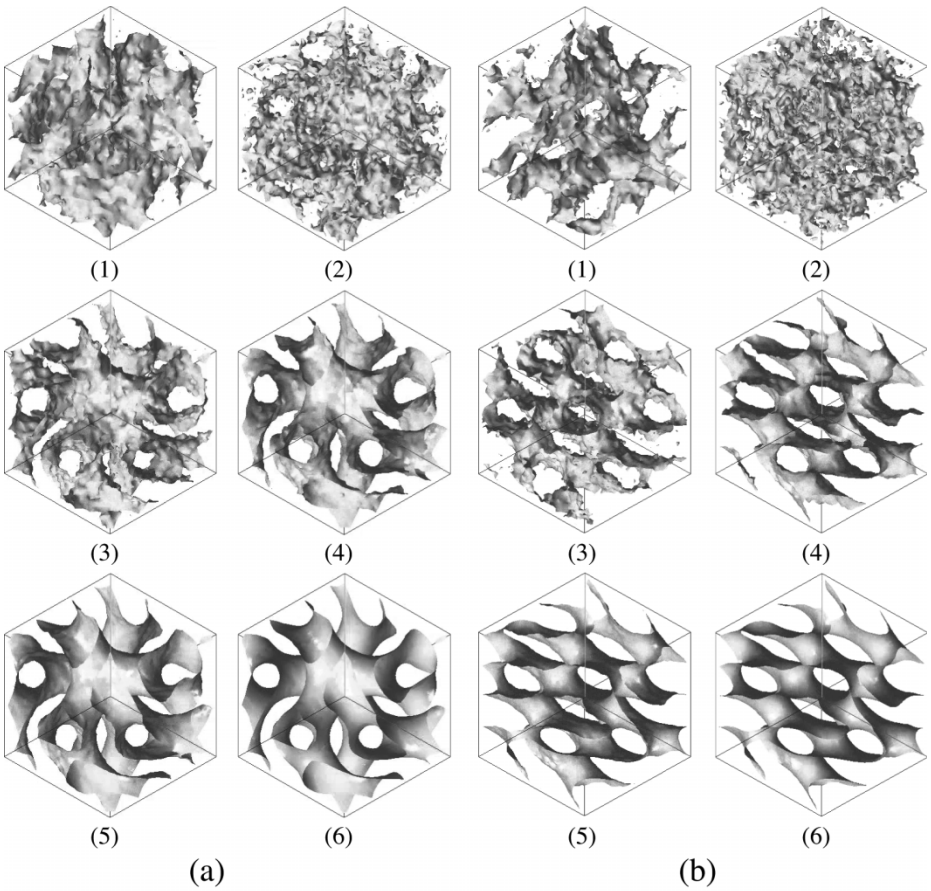

Figure 4. The formation processes of (a) the double gyroid and (b) the F_{ddd} morphologies from the disordered state for $D = 0.60, \sigma = 5.0\times10^{-4}, \bar{\psi} = 0.10, Q = 1.0\times10^{-3}/32^3$ and $T = 0$. (1) initial condition, (2) after 4.0×10^4 steps, (3) after 8.0×10^4 steps, (4) after 1.2×10^5 steps, (5) after 1.6×10^5 steps, (6) after 2.0×10^5 steps. The figures show the isosurfaces at $\psi = \bar{\psi}$.

a result of compromising between these opposite tendencies.

The composition of the diblock controls the geometry of the morphology. For nearly symmetric diblocks, layers appear. At higher asymmetries, the minority component forms hexagonal columns and spheres arranged on a body-centered cubic lattice. For the parameter region between layers and columns, as depicted in figure 4, a complex bicontinuous state, known as the double gyroid phase, is obtained in which the minority blocks from domains consisting of two interweaving threefold-coordinated lattice. Likewise, the F_{ddd} morphology of appears from the random initial distribution. Computing those free energy values and then comparing them to the free energy of other candidate morphologies, we identify that the F_{ddd} as well as double gyroid morphologies play a role as the global minimizer of the free energy of equation (11) within the framework of all morphologies [8].

Overall, we demonstrate that the Nosé-thermostat method for pattern formation dynamics is successful in finding the interconnected ordered mesophases such as double gyroid and F_{ddd} morphologies. This work was supported by the Grant-in-Aid for Young Scientists (B)18740238 from the Japan Society for the Promotion of Science.

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