



Numerical analysis of energy-minimizing wavelengths of equilibrium states for diblock copolymers



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ABSTRACT

We present a robust and accurate numerical algorithm for calculating energy-minimizing wavelengths of equilibrium states for diblock copolymers. The phase-field model for diblock copolymers is based on the nonlocal Cahn–Hilliard equation. The model consists of local and nonlocal terms associated with short- and long-range interactions, respectively. To solve the phase-field model efficiently and accurately, we use a linearly stabilized splitting-type scheme with a semi-implicit Fourier spectral method. To find energy-minimizing wavelengths of equilibrium states, we take two approaches. One is to obtain an equilibrium state from a long time simulation of the time-dependent partial differential equation with varying periodicity and choosing the energy-minimizing wavelength. The other is to directly solve the ordinary differential equation for the steady state. The results from these two methods are identical, which confirms the accuracy of the proposed algorithm. We also propose a simple and powerful formula: $h = L^*/m$, where h is the space grid size, L^* is the energy-minimizing wavelength, and m is the number of the numerical grid steps in one period of a wave. Two- and three-dimensional numerical results are presented validating the usefulness of the formula without trial and error or ad hoc processes.

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1. Introduction

A diblock copolymer is a polymer consisting of a block of one type of monomer, A , joined chemically to a block of another type of monomer, B [1]. Below a critical temperature, the two sequences are incompatible and the copolymer melt undergoes phase separation [2]. This occurs on the mesoscopic scale and the observed mesoscopic domains show periodic structures including lamellae, spheres, cylinders, and gyroids [3]. These phase separations have been observed experimentally [4–16], studied mathematically [3,17–26], and simulated numerically [27–39]. For the mathematical approach to phase separation, dynamic mean field theory, based on the self-consistent field theory [40,41], has been widely studied. In this work, we use the density functional theory proposed by Ohta and Kawasaki [24]. This is dependent on the monomer density [42], which is the minimization of a nonlocal

Cahn–Hilliard (CH) free energy defined by an order parameter. Here, a diblock copolymer is described by the order parameter ϕ , which represents the relative local density difference between two monomers constituting the copolymer. The standard CH free energy, generally used for the modeling of phase separation [43], is supplemented with a nonlocal term [44].

Numerical experiments are useful to predict self-assembly structures of the diblock copolymer, containing lamellae, spheres, and cylindrical tubes. However, because of the non-convexity of the Ohta–Kawasaki functional, the numerical results can draw the metastable state and local minimizer. We would like to refer [45] for the study on assessing the lowest energy state and escaping from certain metastable states by using a spectral weighting. Although there have been a number of numerical studies on diblock copolymer phase separation, there has been little investigation of the accurate calculation of the energy-minimizing wavelengths of equilibrium states. Therefore, the main purpose of this paper is to develop a robust and accurate numerical algorithm for calculating the energy-minimizing wavelengths of equilibrium states in diblock copolymers. We also propose a simple and powerful

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formula for the space grid size. This controllability of the space step size is essential in the computational simulations for the physical experiments.

This paper is organized as follows. In Section 2, we briefly describe a phase field model of diblock copolymer. In Section 3, we present a linearly stabilized splitting-type scheme with a semi-implicit Fourier spectral method to solve the phase-field model efficiently and accurately. In Section 4, we perform a series of numerical experiments. Finally, our conclusion and discussion are given in Section 5.

2. Mathematical model

We consider a diblock copolymer consisting of two homopolymer blocks A and B. The governing equation is the Ohta–Kawasaki model [24]. Let the order parameter $\phi(\mathbf{x}) = \rho_A(\mathbf{x}) - \rho_B(\mathbf{x})$ be defined as the difference between the local volume fractions of A and B at the point \mathbf{x} . The governing equation is the following partial differential equation (PDE),

$$\frac{\partial \phi(\mathbf{x}, t)}{\partial t} = \Delta \left(F'(\phi(\mathbf{x}, t)) - \varepsilon^2 \Delta \phi(\mathbf{x}, t) \right) - \alpha(\phi(\mathbf{x}, t) - \bar{\phi}), \quad (1)$$

where $\mathbf{x} \in \Omega \subset \mathbf{R}^d$ ($d = 1, 2, 3$) is the domain, $F(\phi) = 0.25(\phi^2 - 1)^2$ is the Helmholtz free energy, ε is the gradient energy coefficient, α is inversely proportional to the square of the total chain length of the copolymer [46], and $\bar{\phi} = \int_{\Omega} \phi(\mathbf{x}, 0) d\mathbf{x} / \int_{\Omega} d\mathbf{x}$ is the total mass. We now briefly review the derivation of Eq. (1). The free energy functional is represented as the sum of two parts as $\varepsilon_{\text{total}} = \varepsilon_{\text{short}} + \varepsilon_{\text{long}}$. First, $\varepsilon_{\text{short}}(\phi)$ denotes the short-range part of the free energy functional,

$$\varepsilon_{\text{short}}(\phi) := \int_{\Omega} \left(F(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right) d\mathbf{x}.$$

Second, $\varepsilon_{\text{long}}(\phi)$ denotes the long-range part of the free energy functional,

$$\varepsilon_{\text{long}}(\phi) := \frac{\alpha}{2} \int_{\Omega} \int_{\Omega} G(\mathbf{x} - \mathbf{y}) (\phi(\mathbf{x}) - \bar{\phi}) (\phi(\mathbf{y}) - \bar{\phi}) d\mathbf{y} d\mathbf{x},$$

where G is the Green's function having the following property: $\Delta G(\mathbf{x} - \mathbf{y}) = -\delta(\mathbf{x} - \mathbf{y})$. Here, periodic boundary conditions are assumed and δ is Dirac delta function. By taking a variational derivative and letting $f = F$, we have,

$$\frac{\delta \varepsilon_{\text{short}}(\phi)}{\delta \phi} = f(\phi) - \varepsilon^2 \Delta \phi, \quad (2)$$

$$\frac{\delta \varepsilon_{\text{long}}(\phi)}{\delta \phi} = \alpha \int_{\Omega} G(\mathbf{x} - \mathbf{y}) (\phi(\mathbf{y}) - \bar{\phi}) d\mathbf{y}. \quad (3)$$

Next, we deduce Eq. (1) by substituting Eqs. (2) and (3) into the evolution equation.

$$\phi_t = \Delta \left(\frac{\delta \varepsilon_{\text{short}}(\phi)}{\delta \phi} + \frac{\delta \varepsilon_{\text{long}}(\phi)}{\delta \phi} \right) = \Delta \left(f(\phi) - \varepsilon^2 \Delta \phi \right) - \alpha(\phi - \bar{\phi}).$$

Note that if ψ satisfies $-\Delta \psi = \phi - \bar{\phi}$ with the periodic boundary condition [3], then we can represent $\varepsilon_{\text{long}}(\phi)$ as,

$$\varepsilon_{\text{long}}(\phi) = \frac{\alpha}{2} \int_{\Omega} \Delta \mathbf{x} \psi(\mathbf{x}) \left[\int_{\Omega} \Delta \mathbf{y} G(\mathbf{x} - \mathbf{y}) \psi(\mathbf{y}) d\mathbf{y} \right] d\mathbf{x} = \frac{\alpha}{2} \int_{\Omega} |\nabla \psi(\mathbf{x})|^2 d\mathbf{x}.$$

Therefore, an alternative form of the total system energy is given as,

$$\varepsilon_{\text{total}}(\phi) = \int_{\Omega} \left(F(\phi) + \frac{\varepsilon^2}{2} |\nabla \phi|^2 \right) d\mathbf{x} + \frac{\alpha}{2} \int_{\Omega} |\nabla \psi|^2 d\mathbf{x},$$

which we will use for the numerical evaluation of the total energy. Differentiate the energy $\varepsilon_{\text{total}}$ and the total mass $\int_{\Omega} \phi d\mathbf{x}$ with respect to time, and using the periodic boundary condition, we have,

$$\frac{d}{dt} \varepsilon_{\text{total}}(t) = - \int_{\Omega} |\nabla(\mu + \alpha \psi)|^2 d\mathbf{x} \leq 0 \quad \text{and} \quad \frac{d}{dt} \int_{\Omega} \phi d\mathbf{x} = 0,$$

where $\mu = f(\phi) - \varepsilon^2 \Delta \phi$. Therefore, the total energy is non-increasing and the total mass is conserved in time.

3. Numerical solution

In this section, we present a fully discrete scheme for the following one-dimensional nonlocal CH equation with the periodic boundary condition on $\Omega = (0, L)$:

$$\frac{\partial \phi(x, t)}{\partial t} = \frac{\partial^2 f(\phi(x, t))}{\partial x^2} - \varepsilon^2 \frac{\partial^4 \phi(x, t)}{\partial x^4} - \alpha(\phi(x, t) - \bar{\phi}). \quad (4)$$

We use the equidistant grid $x_m = (m - 1)h$ for $m = 1, \dots, M$ where M is an even number and $h = L/M$. Let ϕ_m^n be an approximation of $\phi(x_m, n\Delta t)$, where Δt is the temporal step size. We define the grid function $\phi^n = (\phi_1^n, \dots, \phi_M^n)$ as a vector of grid point values. In particular, we denote the constant vector as $1 = (1, \dots, 1)$. The discrete Fourier transform and its inverse transform are defined by,

$$\hat{\phi}_p^n = \sum_{m=1}^M \phi_m^n e^{-ix_m \xi_p}, \quad (5)$$

$$\phi_m^n = \frac{1}{M} \sum_{p=1-M/2}^{M/2} \hat{\phi}_p^n e^{ix_m \xi_p}, \quad (6)$$

where $\xi_p = 2\pi(p-1)/L$. The second- and fourth-order partial derivatives are,

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{M} \sum_{p=1-M/2}^{M/2} \xi_p^2 \hat{\phi}_p^n e^{ix \xi_p}, \quad \frac{\partial^4 \phi}{\partial x^4} = \frac{1}{M} \sum_{p=1-M/2}^{M/2} \xi_p^4 \hat{\phi}_p^n e^{ix \xi_p}.$$

To solve Eq. (4), we use the linearly stabilized splitting-type scheme [47] with a semi-implicit Fourier spectral method [33,48–50]. The linear terms are treated implicitly and the nonlinear term is treated explicitly,

$$\frac{\phi_m^{n+1} - \phi_m^n}{\Delta t} = 2 \frac{\partial^2 \phi_m^{n+1}}{\partial x^2} - \varepsilon^2 \frac{\partial^4 \phi_m^{n+1}}{\partial x^4} + \frac{\partial^2 g_m^n}{\partial x^2} - \alpha(\phi_m^{n+1} - \bar{\phi}), \quad (7)$$

where $g_m^n = f(\phi_m^n) - 2\phi_m^n$ and $\bar{\phi} = \sum_{m=1}^M \phi_m^0 / M$. If $\alpha = 0$, then Eq. (7) becomes the linear stabilized scheme for the CH equation [47]. For the higher temporal order spectral scheme of the nonlocal CH

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