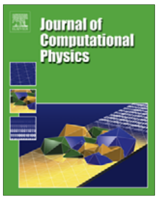
Journal of Computational Physics 229 (2010) 1797–1809

Contents lists available at ScienceDirect

Journal of Computational Physics

journal homepage: www.elsevier.com/locate/jcp



A numerical method for the study of nucleation of ordered phases

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ARTICLE INFO

Article history:
Received 3 June 2009
Received in revised form 4 October 2009
Accepted 6 November 2009
Available online 17 November 2009

Keywords:
Nucleation
Ordered phase
Critical nuclei
Minimum energy path (MEP)
String method
Liquid crystal
Block copolymer

ABSTRACT

A numerical approach based on the *string method* is developed to study nucleation of ordered phases in first-order phase transitions. Among other things, this method allows an efficient computation of the minimum energy path (MEP) during the nucleation process. The MEP provides information about the size, shape and free energy barrier of the critical nucleus. To improve the efficiency of the string method, a special initialization process is proposed. Constraints from physical models are treated using two methods, a generalized coordinates method and a projection method. Strategies for choosing the computational domain and defining the nucleus boundary are also introduced. The validity of our approach is illustrated by two nontrivial examples from soft condensed matter physics, namely the nematic–isotropic transition of liquid crystals and the ordered-to-ordered phase transition of diblock copolymers.

1. Introduction

For a physical system undergoing a first-order phase transition, nucleation occurs when the system becomes metastable against a new stable state. Nucleation refers to the emergence of the new (stable) phase from the old (metastable) phase. In general, nucleation process proceeds via two different routes, often termed homogeneous and heterogeneous nucleation. Homogeneous nucleation refers to the case where clusters of the new phase are in contact only with the old phase, whereas heterogeneous nucleation is aided by foreign objects and/or defects. Both homogeneous and heterogeneous nucleation processes are widely encountered in first-order phase transitions of all types of systems, including materials of small molecules (like liquid–vapor phase transition of water) and macromolecules (like nematic–isotropic transition of liquid crystals). Nucleation, especially that in macromolecular systems (also termed complex fluid/soft material), has attracted wide research interests over the past decades.

Over the past century, three classes of methods have been developed to theoretically understand the nucleation phenomenon [1]. The first family, under the umbrella of *classical nucleation theory*, is developed by Gibbs et al. [2] since 1920s. This approach assumes the existence of sufficiently large nuclei, whose energetics is described by a bulk free energy and a *surface energy*. The size and shape of the critical nucleus are determined by the competition between the bulk free energy reduction and the surface free energy increase. In practical applications, spherical nuclei, or nuclei of other specific simple shapes, have

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doi:10.1016/j.jcp.2009.11.009

often to be assumed. The above assumptions limit this approach to (i) systems near binodal line/phase boundary, where the critical nucleus is macroscopically large, (ii) nuclei with "sharp interface", so that the definition of *surface energy* can be made, and (iii) systems where only isotropic or weakly anisotropic phases are involved. Situation (ii) and (iii) are not always satisfied in a majority of soft condensed matter systems, especially those containing ordered microphases (like block copolymers). When one or both of the phases involved in the phase transition have ordered microdomains, the different symmetries of microphases make the *surface energy* anisotropic, leading to anisotropic nuclei as well as complex phase interface. Assuming large nucleus with sharp interface, one can compute the anisotropic interfacial free energy first, and then obtain the shape of the critical nucleus using the well-known Wulff construction. Such an approach within the content of *classical nucleation theory* has been used by Wickham, Shi and Wang for the study of nucleation of ordered block copolymer phases [3], where non-spherical aspect of nucleus and anisotropic *surface energy* were obtained.

The second family, in the microscopic extreme, is within the scope of *atomistic nucleation theory* [4]. This family of methods, often assisted by molecular dynamics, treat situations involving a small number of molecules. Thus, they are often feasible only for the atomistically small nuclei, This approach is most appropriate when the system is approaching spinodal line.

The third family of theoretical methods for the study of nucleation is based on the *density-functional nucleation theory* [5–7]. The density-functional theory is a framework bridging the microscopic theory with the macroscopic descriptions. The essence of the density functional theory is that the free energy (F) of a statistical mechanical system can be written as a functional of the molecular density ρ. The molecular details of the model are included in the functional form of the free energy. In many cases, the density-functional approach overcomes many shortcomings of the above two families. In practice, the free energy functional may come from density-functional theory or mean-field theory according to the systems studied, or needs to be further approximated by a variety of methods, such as the Landau-type approximation used in our numerical examples. The density-functional approach for the study of nucleation has been applied successfully to phase transitions involving isotropic phases, so it is natural to extend this approach to systems involving anisotropic phases [7]. However, in the density-functional approach the critical nucleus corresponds to a saddle point on the energy landscape, i.e. an unstable stationary solution of the Euler–Lagrange equation

$$\frac{\delta F[\rho]}{\delta \rho} = 0, \tag{1}$$

and solving this variational problem presents a challenge to numerical computation [8]. Using density-functional approach, Wang and co-workers studied both homogeneous and heterogeneous nucleation in macrophase seperation of binary homopolymer blends based on self-consistent field model [9–11]. In their cases no ordered microphase is involved so spherical nuclei can be assumed. On the other hand, the minimax algorithm they used to solve Eq. (1) can not be extended to the anisotropic systems in a simple way. Generally, when ordered microphases are present, the solution of (1) involves a number of different length scales, including the period of the ordered microstructure and the width of the interface between different phases [3]. The purpose of the current study is to develop a new numerical method which is capable of resolving these different length scales.

The *string method*, developed by E, Ren and Vanden-Eijnden [12–15], is a general and efficient method to study thermally activated transitions between metastable states. Since its development, this method has been successfully applied to a variety of problems originated from many disciplines, including nucleation problems in different systems [16,17]. Using an iterative algorithm, to be explained in Section 2, the *string method* can be used to locate the *minimum energy path* in the configuration space, which is the optimal transition pathway in the zero-temperature limit. Each *minimum energy path* contains at least one saddle-point corresponding to a solution of Eq. (1). In this paper we will develop a numerical method which applies *string method* to evaluate anisotropic nucleation in phase transitions involving one or more ordered phases. The advantage of this new approach is illustrated by two nontrivial examples from soft condensed matter systems, i.e. the nematic–isotropic transition of liquid crystals and the order-to-order phase transition of diblock copolymers. For simplicity, Landau-type free energies are used to describe these two classes of phase transitions. However it should be emphasized that our method is independent of the specific free energy functional employed. We will show that, with an efficient initialization procedure and appropriate methods to enforce physical constraints, the *string method* can be used to capture the physical state of critical nucleus and study its many interesting properties.

The rest of the paper is organized as follows: in Section 2 the *string method* and relevant numerical treatments are outlined. The two numerical examples are given in Sections 3 and 4, along with brief introductions to the two soft matter systems. Finally a conclusion of the current method and applications is given in Section 5.

2. Application of the string method to nucleation of ordered phases

2.1. Stable/metastable state, critical nucleus, minimum energy path

In this section we use a generic density-functional model to formulate the nucleation problem. Within this formulation the statistical mechanics of the system is described by a free energy functional $F[\phi]$, which is a functional of the molecular density, or the order parameter, ϕ. The thermodynamic properties of the system corresponds to the minima of this free energy functional. In particular, the equilibrium density is a solution of the Euler–Lagrange equation of the free energy functional. Different solutions of the Euler–Lagrange equation correspond to different phases.

For a given free energy functional, the phase diagram of the system can be constructed by comparing the free energies of the different phases, corresponding to different minimum solutions to the Euler–Lagrange Eq. (1). These solutions can be periodic functions, corresponding to phases with periodically ordered crystalline structures. If a minimum solution is globally minimal, it is the stable state. Otherwise, there is another minimum solution of lower energy and is thus more stable, which makes this solution only metastable. A first-order phase transition is a transition from a metastable state $\phi_m(\vec{r})$ to a stable state $\phi_s(\vec{r})$. In order for a first-order phase transition to occur, a free energy barrier must be overcome via thermal fluctuations and/or external fields such as defects.

The critical nucleus is the *saddle-point transition state* of the phase transition mentioned above. The existence of a critical nucleus is guaranteed by the Mountain Pass Lemma [18]. The critical nucleus acts as the rate-determining process in a first-order phase transition, as the nucleation barrier is exactly the energy needed to form the critical nucleus. The critical nucleus is termed *saddle-point transition state* because it corresponds to a saddle-point solution of the Euler–Lagrange Eq. (1).

The *Minimum Energy Path* (MEP) can be defined as a curve φ in the phase space connecting the metastable ($\phi_m(\vec{r})$) and the stable ($\phi_s(\vec{r})$) solutions. The MEP satisfies the equation,

$$(\nabla F)^{\perp}(\varphi) = 0, \tag{2}$$

where $(\cdot)^{\perp}$ denotes the component of $(\cdot)$ normal to φ. Within the model system, the MEP is the most probable transition pathway in the zero-temperature limit. The *saddle-point transition state*, i.e. the critical nucleus, corresponds to the point on the MEP with the maximum free energy. Thus, once the MEP is found the nucleation barrier can be calculated directly by plotting the free energy along the MEP. The size and shape of the critical nucleus can be computed from the configuration of the order parameter at the maximum of the MEP.

2.2. Outline of the string method

Details of the *string method*, including discussion concerning accuracy and stability, are found in the literature [12–15]. For completeness a brief introduction of the method is given here.

The main idea behind the string method is to represent the transition paths by curves (strings) in the configuration space with intrinsic parameterization. These strings are evolved according to the dynamical equation

$$\varphi_t = -(\nabla F)^{\perp}(\varphi) + r\vec{\tau}, \tag{3}$$

where t is a pseudo-time variable, $\vec{\tau}$ is the unit tangent vector of the string φ. The dynamics is designed such that the strings approach the MEP, as defined in Eq. (2), at the limit $t \to \infty$. The scalar field $r(\alpha, t)$ in Eq. (3) is a Lagrange multiplier uniquely determined by the parameterization of the string φ. The parameterization of the string φ can be arbitrary. In the simplest case φ is parameterized by its normalized arc-length s. In general the parameter α is determined by the equation

$$\begin{cases} \frac{\mathrm{d}}{\mathrm{d}\alpha}\left(M(s)\frac{\mathrm{d}s}{\mathrm{d}\alpha}\right) = 0, \\ s(0) = 0, \ s(1) = 1, \end{cases}$$

where the coefficient $M(s)$ is a monitor function specifying the particular parameterization.

Numerical solution of Eq. (3) is obtained by a two-step scheme. First the string is discretized into a collection of points. These discrete string points are evolved by the force in the normal direction, $\varphi_t = -(\nabla F)^{\perp}(\varphi)$. This step can be accomplished by a suitable difference scheme, such as the forward Euler scheme for the time derivative of the left side. Then a re-parameterization step is applied to enforce the proper parameterization of the string through numerical interpolation. The re-parameterization step is necessary to keep the discrete points representing the string in a specified pattern of distribution along the string, e.g. evenly distributed rather than clustered at the two minima $\phi_m(\vec{r})$ and $\phi_s(\vec{r})$.

2.3. Treatment of constraints

For many physical systems undergoing phase transitions, the order parameter must satisfy certain constraints. Thus, special treatment is needed to confine the strings to a feasible set $\mathcal{M}$ so that the constraints are satisfied at each time step of the evolution algorithm. It can be shown that, within the string method, enforcing the constraints is reduced to the computation of the gradient vector $\nabla_{\mathcal{M}}F$, the derivative of function F with respect to the subspace $\mathcal{M}$. Since the coordinate system can be arbitrarily chosen, we can use two different approaches to enforce the constraints.

The first approach is based on a generalized coordinates method. In this approach a set of new coordinates, $\{q^1, \ldots, q^s\}$, is used for the s-dimensional feasible set

$$\mathcal{M} = \{\vec{x} = (x^1, \ldots, x^n) : f^i(\vec{x}) = 0, \quad i = 1, \ldots, k, k = n - s\}.$$

Here $q^1, \ldots, q^s$ are independent variables, which are termed as the generalized coordinates. The ith coordinate of the gradient vector $\nabla_{\mathcal{M}}F$ is then given by

$$Q^i = \sum_{j=1}^{s} g^{ij} \frac{\partial F}{\partial q^j}, \, i = 1, \ldots, s$$

where (g^{ij}) is the inverse matrix of (g_{ij}), whose elements are specified by

$$g_{ij} = \sum_{l=1}^{n} \frac{\partial x^l}{\partial q^i} \frac{\partial x^l}{\partial q^j}.$$

The second approach is based on a projection method, in which we compute the gradient vector $\nabla_{\mathcal{M}} F$ in the original coordinates, and use the fact that $\nabla_{\mathcal{M}} F$ is the orthogonal projection of ∇F onto the tangent space of $\mathcal{M}$. The orthogonal projection can be performed using Lagrangian multipliers $\lambda_1, \ldots, \lambda_k$. Specifically, the ith coordinate of the gradient vector $\nabla_{\mathcal{M}} F$ is

$$X^i = \frac{\partial F}{\partial x^i} - \sum_{j=1}^{k} \lambda_j \frac{\partial f^j}{\partial x^i}, \quad i = 1, \ldots, n. \tag{4}$$

Eq. (4) can be combined with

$$\sum_{i=1}^{n} \frac{\partial f^j}{\partial x^i} X^i = 0, \quad j = 1, \ldots, k$$

to solve for the ith coordinate X^i and the Lagrangian multipliers $\lambda_1, \ldots, \lambda_k$. It is useful to notice that $(\lambda_1, \ldots, \lambda_k)$ is the solution of the following least square problem:

$$\min_{\vec{v}} |\vec{b} - A\vec{v}|, \quad A = \left(\frac{\partial f^j}{\partial x^i} \right), \quad \vec{b} = \left(\frac{\partial F}{\partial x^i} \right).$$

In order to use the generalized coordinates method, explicit expression of the generalized coordinates are needed. Therefore this method is applicable when explicit form of the generalized coordinates are known or can be easily found. On the other hand, the projection method is general, thus it has much wider applications than the generalized coordinates method. The computational expense associated with these two methods are different. It is proportional to s for the generalized coordinates method and it is proportional to k for the projection method.

2.4. Initialization of the strings

The efficiency of the *string method* is highly dependent on the initialization of the strings. More importantly, the converged MEP solution may depend sensitively on the choice of the initial string. Specifically, different initial strings may converge to different MEP solutions which may have a locally minimal energy barrier as well as a globally minimal one. The *string method* itself does not guarantee a globally minimal barrier. The appropriateness of the MEP solutions should be judged from their physical properties. It should also be noticed that there is no generic method to initialize the strings, thus initialization is a case-by-case problem.

For the nucleation problem, the two ends of the MEP are known. To compute the MEP, i.e. the nucleation pathway, the strings can be initialized by the following construction. For an initial string $\varphi(\alpha)$ parameterized by $\alpha \in [0, 1]$, we take $\varphi(0) = \phi_m$ and $\varphi(1) = \phi_s$. For the intermediate values of α we choose a domain $\mathcal{B}_\alpha$ as the expected domain of the equilibrium phase and let the sequence $\{\mathcal{B}_\alpha\}$ increases as α is increased. The simplest example is to take $\{\mathcal{B}_\alpha\}$ as concentric spheres. The initial string is then defined by

$$\varphi(\alpha)(\vec{r}) = \begin{cases} \phi_m(\vec{r}), \ \vec{r} \notin \mathcal{B}_\alpha \\ \phi_s(\vec{r}), \ \vec{r} \in \mathcal{B}_\alpha \end{cases}$$

where $\vec{r}$ is the position vector.

In the case where constraints are present, the treatment given in Section 2.3 should be applied to the initial strings so that the constraints are enforced in the construction.

2.5. Computational domain and boundary conditions

The nucleation process often presents a computational problem which is unbounded in certain dimensions. For example, when the nucleus is larger than the critical size, it will continue to grow throughout the material. Large computational domain presents a challenge to computations, especially when dealing with 3D problems. Practically, a finite computational domain has to be used, thus boundary conditions must be specified. This spacial truncation may lead to numerical errors as the nucleus approaches the computational boundaries, while the influence is negligible when the nucleus stays well away from the boundaries. In other words, a computational domain large enough will guarantee the calculation of critical nucleus of interest to a desired accuracy, even though the later part of MEP may become inaccurate when the nucleus surpasses the critical size and grows near to the domain boundaries. In principle, one should make the computational domain as large as possible. In practice, it will be a waste of computational effort to choose too big a domain. Therefore there is an optimal choice of domain size. The criterion for choosing a good domain size should be that the truncation effect due to the computational boundary does not affect the accuracy of the calculated critical nucleus.

To illustrate the influence of different computational domain sizes, we compute 2D critical nuclei of lamellar (L) → cylindrical (C) phase transition in diblock copolymer (the three-dimensional calculation is carried out in Section 4). Although the 2D nucleation is an idealization of real physical world, mathematically this example is sufficient to test our choices of 2D computational domains. We do not expect any qualitative difference when dealing with 3D nucleation problems later. We compute the MEP on a series of domains of varying sizes with periodic boundary conditions. For each given domain size, the critical nucleus state and the energy barrier are computed. The critical nucleus states calculated in different domains are compared in Fig. 1, where only parts of the area around the nuclei are illustrated and outlying areas are omitted. The one on the left is calculated in a small domain, where the critical nucleus state obtained is qualitatively inaccurate. The one in the middle is in a median-size domain, and the one on the right a large domain; the two critical nucleus states are almost the same. The nucleation barrier calculated on different domains are shown in Fig. 2, which shows a tendency to converge with the domain size is large enough. We further discover an exponential decay of the calculated nucleation barrier when the domain area increases. The least square fit (dashed curve in Fig. 2) of the data gives

$$\Delta F = F_0 + Ae^{-CS} \tag{5}$$

where $F_0 = 0.446, A = 0.347, C = 0.0242$ and S is the area of domain.

The additional computational effort required by an increase of domain size is considerable. This is due to that a large domain requires $\mathcal{O}(N^2)$ more grid points ($\mathcal{O}(N^3)$ in 3D computing), as well as more points on the string. We compared the results above and found out that the median-size domain (in the middle of Fig. 1) turns out to be a good choice in our 2D computation here.

Based on the 2D computations, we propose a general strategy for choosing a computational domain size as follows: firstly, obtain an estimate of the shape and size of the critical nucleus. To do this, one can choose a domain large enough to prevent the influence of computational boundaries on calculated critical nucleus, and then carry out a trial computation on a coarse grid. One can also obtain this estimate through other approaches, such as an experimental observation or a physical analysis. Secondly, adjust the computational domain to a suitable size: the optimal domain boundaries are, according to our 2D computations, about two times the nuclear radius away from the center of the nucleus.

Since we concentrate on homogeneous nucleation in this paper, we use cubic domains with periodic boundary conditions in all the numerical examples given below in Sections 3 and 4. Similar spacial truncations and other boundary conditions can be employed in other situations, including heterogeneous nucleation, as a variation of our method.

2.6. Matching of the metastable and stable phases

As the MEP is calculated in a fixed computational domain, when initializing the string the metastable and stable phases, $\varphi(0) = \phi_m$ and $\varphi(1) = \phi_s$, should be embedded in the same computational domain. Therefore these two structures must be connected into one larger structure in the domain. When at least one of the two phases is homogeneous/isotropic, the matching of the two structures can be trivially done. However, when both of the structures are anisotropic, the orientation of the two phases should be matched in accordance with certain orientation relationships. Furthermore, when both phases have periodic microstructures, their periods should also be matched as will be done in Section 4. If necessary, these matching relationships can be assumed based on existing theoretical and experimental observations. In the case of copolymer ordered microphases, regular matching patterns termed "epitaxial relations" have been discovered [19] and used in previous studies.

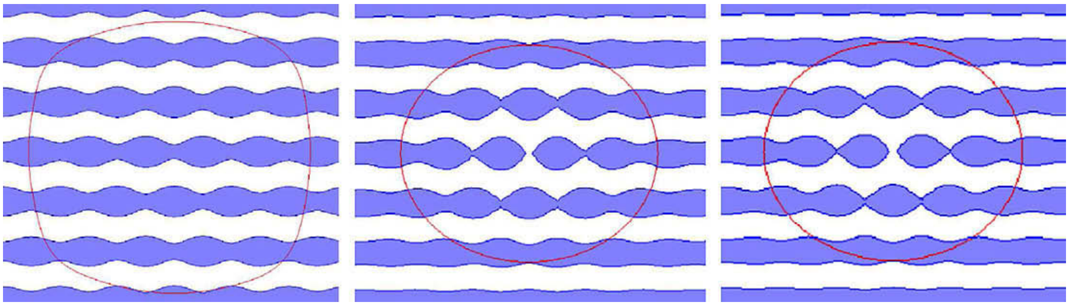

Fig. 1. 2D computation of lamellar (L) → cylindrical (C) phase transition: comparison of critical nucleus states obtained in computational domains of different sizes. The figures may not include the entire computational domain because only the critical nucleus is shown. The red line indicates the nucleus boundary, i.e. the interface of L and C ordered phases, defined according to (6). (Left) an inaccurate critical nucleus state from calculation in a small domain. (Right) an accurate critical nucleus state from calculation in a large domain. (Middle) calculation in a domain of an intermediate size, with the critical nucleus state's accuracy comparable to the one on the right. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

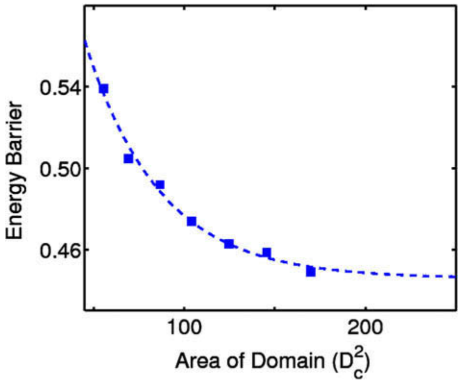

Fig. 2. Nucleation energy barrier (square) plotted as function of sizes of computational domains, measured in units of D_c^2 where D_c is the distance between neighboring cylinders. The dashed curve is an exponential decay function in form of Eq. (5) obtained by least square fitting.

We expect that the widely observed matching patterns correspond to the ones which minimize the nucleation barriers. This can be verified by numerical calculation, possibly using our method.

2.7. Improving the accuracy of the critical nucleus calculation

Within the context of nucleation process, we are specially interested in locating the critical nucleus, which is the saddle point on the MEP. To increase the precision of the saddle-point calculation, there are methods other than simply increasing the number of points N along the string. One method, as presented in [15], is to introduce a special parameterization of the string which makes a certain point $\varphi(\alpha_{i_s})$ move toward the saddle point. Another possibly more convenient method is an interpolation approach, which is proposed here: after the convergence of a string, we have N points along the calculated MEP, $\varphi(\alpha_i), i = 1, \ldots, N$. An MEP on a finer mesh denoted by $\varphi(\alpha_i), i = 1, \ldots, \widehat{N}$ ($\widehat{N} > N$) can be obtained by numerical interpolations, such as cubic spline. We can then locate an interpolated state $\varphi(\alpha_{i^*})$ satisfying

$$F[\varphi(\alpha_{i^*})] = \max_{0 \leqslant i \leqslant \widehat{N}} F[\varphi(\alpha_i)]$$

which is likely to be closer to the saddle point. Further more, if we are only interested in the nucleation barrier $\Delta F = F[\varphi(\alpha_{i^*})] - F[\phi_m]$, we can interpolate the 1D function $F[\varphi(\alpha)](0 \leqslant \alpha \leqslant 1)$ to a finer mesh so as to more precisely locate its maximum, given that $F[\varphi(\alpha_i)], i = 1, \ldots, N$ are known.

2.8. Definition of nucleus boundary

In order to study the size and shape of the nucleus, it is necessary to define the location of the interface between the stable and metastable phases, i.e. the surface/boundary of the nuclei. Within the density-functional approach, the structure of the system is described by a density function $\phi(\vec{r})$. When the two phases involved in the phase transitions are isotropic ones, the density function is a monotonic function. The specification of the interface can then be carried out by specifying a level set at the average density. On the other hand, when ordered phases are involved in the phase transition, the density profile becomes a periodic function. Therefore a simple level set method can not be used to specify the interface between the old and new phases. Therefore new methods to identify the nucleus boundary are needed.

For the cases involving ordered phases, it is useful to construct a scalar order parameter which uniquely specifies the corresponding ordered phases. When the complicated order parameter is reduced to a scalar one, a simple level set method can be used to define the interfaces. For example, in the case of liquid crystals the eigenvalue of a tensor-type order parameter can be extracted as a scalar order parameter, and this idea is used in Section 3 to define the isotropic–nematic nucleus boundary. Another example of such construction, to be used in Section 4 to define nucleus boundary separating two periodic microphases, utilizes the following strategy. Because the two ends of the string, $\phi_m(\vec{r})$ and $\phi_s(\vec{r})$, have been calculated before the start of the MEP computation, we can define a point-wise stable-phase-density function $\Phi_s(\vec{r})$ for any order parameter function ϕ by

$$\begin{aligned} \Phi_s(\vec{r}) &\equiv \frac{|\phi - \phi_m|(\vec{r})}{|\phi - \phi_m|(\vec{r}) + |\phi - \phi_s|(\vec{r})}, \\ |\phi_1 - \phi_2|(\vec{r}) &\equiv \int w(\vec{r}' - \vec{r})(\phi_1(\vec{r}') - \phi_2(\vec{r}'))^2 d\vec{r}', \end{aligned} \tag{6}$$

where the weight function $w(\vec{r})$ is a *mollifier* ($w(\vec{r})$ has the form $Ce^{R^2/(|\vec{r}|^2 - R^2)}$) whose supporting set covers at least one "common period" of the new and the old phases (i.e. the lowest common multiple of their respective periodic structures). The integration takes an L^2 form so as to describe the difference between the "symmetries" of the two periodic microphases.

The *mollifier* $w(\vec{r})$ is utilized to make the Φ_s thus defined more smooth. The supporting set of w is adjusted to a suitable size to balance localization and smoothness. In practice, a low-pass filter may be used for further smoothness of Φ_s. The nucleus boundary is set to be a specific level set, usually at $\Phi_s = 0.5$, of the scalar order parameter Φ_s.

3. The nematic–isotropic transition of liquid crystals

In the following two sections, the string method is applied to two specific examples from soft condensed matter physics, namely the phase transitions of liquid crystals and diblock copolymers. For these two physical systems, a variety of theoretical models have been established. Among the different versions of theoretical models, the Landau-type theory is usually the simplest. It has been well established that Landau theory is capable of the phases and phase transitions in complex soft matter systems. In what follows we will employ Landau theories to describe the phases and phase transitions of liquid crystals and diblock copolymers. Generally speaking, Landau-type free energy functional $F[\phi]$ is often analytical and explicit, thus convenient for numerical calculation. Therefore Landau theories can be used as a test ground for the string method introduced above. We expect that our method will be applicable to more complex thermodynamic models since the method itself is independent of the specific type of free energy functional involved.

3.1. The Landau–de Gennes model of liquid crystals

A liquid crystal (LC) was first reported about 120 years ago by Reinitzer [20]. Since then many different liquid crystalline phases have been identified and characterized. Among the various liquid crystalline phases, the nematic phase is the simplest, which is characterized by a long range molecular orientational order as well as short range positional and bond orientational order. The liquid crystal director $\mathbf{n}$ is used as the order parameter to describe the orientational order of the system. At lower temperatures than the nematic, the smectic phases are found, which possess layered structures.

A variety of models have been developed to study the phase behavior of LCs, including the hard-rod model proposed by Onsager [21], the statistical model by Maier and Saupe [22], etc. Doi and Edwards proposed the molecular theory of LCs [23]. This theory is based on a rigid rod-like model. After integrating the degrees of freedom associated with the molecular conformation out, the free energy of the system is specified by a orientational distribution function $f(\mathbf{m})$, which specifies the probability density that a molecule be found with its orientation at $\mathbf{m}$. The expression of the free energy per unit volume is given by

$$\mathcal{F} = \int_{\|\mathbf{m}\|=1} k_B T f(\mathbf{m}) \ln f(\mathbf{m}) + \frac{1}{2} f(\mathbf{m}) U(\mathbf{m}) d\mathbf{m},$$

where the nematogenic potential $U(\mathbf{m})$ could be given by Onsager theory or Maier–Saupe theory. A very important average is the so-called order parameter tensor $\mathbf{S}$ given by

$$\mathbf{S} = \langle \mathbf{mm} \rangle = \int_{\|\mathbf{m}\|=1} \mathbf{mm} f(\mathbf{m}) d\mathbf{m}$$

which is the second-order moment of the orientational distribution. The tensor $\mathbf{S}$ is obviously symmetric and positive-semi-definite, its geometrical representation is an ellipsoid. In an equilibrium nematic phase, the molecular distribution is uniaxial about the director $\mathbf{n}$; correspondingly, the ellipsoid $\mathbf{S}$ is itself axial symmetric, that is the two principal axes orthogonal to $\mathbf{n}$ have equal length, as strictly proved by Liu et al. [24] and Fatkullin et al. [25]. Under these conditions, $\mathbf{S}$ can be written in the form

$$\mathbf{S} = S\left(\mathbf{nn} - \frac{1}{3}\mathbf{I}\right) + \frac{1}{3}\mathbf{I}$$

where the scalar factor S is called the order parameter of the nematic phase. The most common choice for the order parameter tensor is $\mathbf{Q} = \mathbf{S} - \frac{1}{3}\mathbf{I}$, which is traceless tensor.

Within the description of Landau theory, the free energy can be written as a functional of the order parameter. In what follows we employ the Landau–de Gennes model to describe the phases and phase transitions of liquid crystals. More information concerning the model is found in [26]. In its dimensionless form, the Landau–de Gennes free energy of liquid crystals is given by de Gennes [26],

$$\mathcal{F} = \int d\vec{r} \left[\frac{A}{2} Tr(\mathbf{Q}^2) - \frac{B}{3} Tr(\mathbf{Q}^3) + \frac{1}{4} (Tr(\mathbf{Q}^2))^2 + \frac{D}{2} \frac{\partial \mathbf{Q}_{\alpha\beta}}{\partial x_\gamma} \frac{\partial \mathbf{Q}_{\alpha\beta}}{\partial x_\gamma} + \frac{E}{2} \frac{\partial \mathbf{Q}_{\alpha\beta}}{\partial x_\beta} \frac{\partial \mathbf{Q}_{\alpha\gamma}}{\partial x_\gamma} \right], \tag{7}$$

where A, B, D and E are phenomenological parameters, which can be determined from the related molecular theory. The order parameter tensor must satisfy the constraints

$$\mathbf{Q}_{\alpha\beta}(\vec{r}) = \mathbf{Q}_{\beta\alpha}(\vec{r}), \tag{8}$$

$$\sum_{\alpha=1}^{3} \mathbf{Q}_{\alpha\alpha}(\vec{r}) = 0. \tag{9}$$

3.2. Numerical calculation

In the numerical computations, a unit cube is typically chosen as the computational domain. The mesh number is N^3 with $N = 32$. The discrete points along the string is set to 40. The dimensionless phenomenological parameters in (7) are chosen to be $A = 0.27$, $B = 3.0$, $D = 0.001$, $E = 0.001$, so that the isotropic phase is metastable while the nematic phase is stable. Before evolving the strings, we obtain solutions of the two metastable/stable phases, namely the isotropic and the nematic phases. For the isotropic phase, there is no orientational order and the order parameter tensor **Q** can be set to zero. For the nematic phase, the orientational order leads to a non-zero order parameter, whose value is determined by minimization of the homogeneous part of free energy density (7)

$$\mathcal{F}_H[\mathbf{Q}] = \frac{A}{2} Tr(\mathbf{Q}^2) - \frac{B}{3} Tr(\mathbf{Q}^3) + \frac{1}{4} (Tr(\mathbf{Q}^2))^2$$

under constraints (8) and (9). This minimization can be carried out numerically using a conjugate-gradient algorithm. To enforce the constraints, both the generalized coordinates method and the projection method are used. We carry out the computation by the coordinates $\{\mathbf{Q}_{\alpha\beta}(\vec{r}), \alpha \leqslant \beta\}$, which are the general coordinates with respect to the first constraint (8). The projection method is used to enforce the second constraint (9). Since the metastable phase is isotropic, there is no need to match the two phases here, and we can set the nematic phase to be aligned along the z-axis. The strings are initialized using the method described in Section 2.4, where

$$\mathcal{B}_\alpha = \{\vec{r} : |\vec{r} - \vec{r}_0| \leqslant \alpha R\}, \quad 0 \leqslant \alpha \leqslant 1, \tag{10}$$

where r_0 is the center of the computational domain Ω (which is a unit cube here) and $R = \sup_{\vec{r} \in \Omega} |\vec{r} - \vec{r}_0|$ (which equals $\sqrt{3}/2$ here).

We ran an MPI parallel program with 8 processes (for spatial decomposition) to finish thousands of iterations in hours. After convergence of the string, a definition of the interfaces between the two phases needs to be identified, as mentioned in Section 2.8. Because the nematic phase can be quantified by a scalar order parameter S, which corresponds to the largest eigenvalue of $\mathbf{Q}_{\alpha\beta}$, the nematic–isotropic interface is simply defined as the 0.4 level set of S. Once the nucleus is defined, the volume of the nucleus can be used as the reaction coordinate. The free energy of the nucleus is plotted as a function of the nuclear volume in Fig. 3. The existence of a critical nucleus (the state of maximal energy) is clearly shown in this result. The shape of the critical nucleus is found to be elliptic (egg-shape), elongated along the director of the nematic director, as depicted in Fig. 4. The aspect ratio of the critical nucleus is about 1.27. Inside the nucleus a uniform direct field is found. These results are consistent with those from previous theoretical studies and simulations [27,28].

4. The order-to-order phase transition of diblock copolymers

In this section the string method is applied to a more a more complex nucleation problem where ordered microphases are involved. Specifically, the numerical method is used to study the nucleation process in a simple model, the Landau–Brazovskii model, for the microphases of diblock copolymer melts in the weak-segregation limit.

4.1. Landau–Brasovskii model for diblock copolymers

Ordered microphases are widely encountered in macromolecular materials. One imminent example is the formation of complex ordered phases in diblock copolymers. Diblock copolymers are macromolecules composed to two chemically dis-

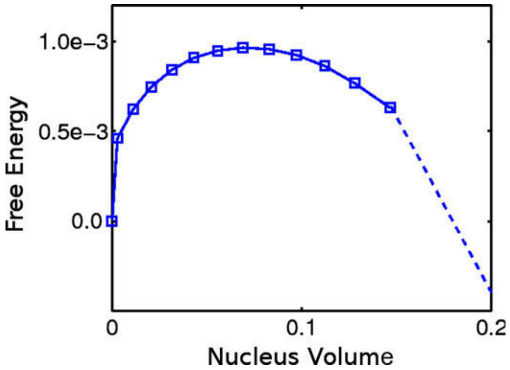

Fig. 3. Free energy plotted as a function of the nuclear volume, calculated at $A = 0.27, B = 3.0, D = 0.001, E = 0.001$. Here free energy of isotropic phase has been subtracted to let the curve start from zero. The later part of the curve is omitted as being far from the critical nucleus and inaccurate due to the influence of computational boundary (see Section 2.5).

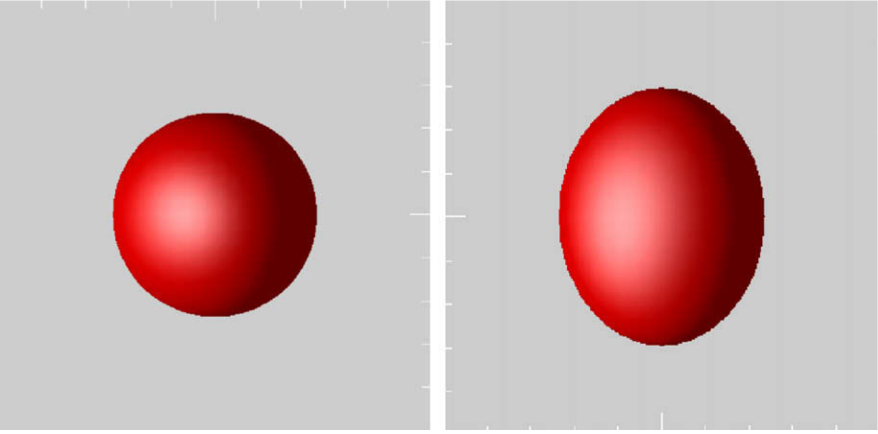

Fig. 4. Critical nuclei of isotropic → nematic phase transition in liquid crystals, calculated at $A = 0.27, B = 3.0, D = 0.001, E = 0.001$. (left) View from the z-axis. (right) View from the y-axis.

tinct polymers linked at their ends. The repulsive interaction between the different polymers drives the system to phase separate, whereas the connectivity of the block copolymers prevents a macroscopic phase separation. As a result of this competition between the two opposing trends, diblock copolymers can self-assemble into a number of ordered microphases, including Lamellar (L), hexagonally packed cylinder (C), body-centered-cubic sphere (S) and bicontinuous gyroid (G) phases [19]. We consider an incompressible melt of n AB diblock copolymers in a fixed volume V_0 at a fixed temperature T, with degree of polymerization N, *Kuhn segment lengths* $b_A = b_B = b$, and *volume fraction* of A-type segment f_A $(0 \leqslant f_A \leqslant 1)$. The A-type and B-type segment density functions are $\phi_A(\vec{r})$ and $\phi_B(\vec{r})$, respectively. These density functions satisfy the incompressible condition

$$\phi_A(\vec{r}) + \phi_B(\vec{r}) = \rho_0 \tag{11}$$

where $\rho_0 = \frac{nN}{V_0}$ is the average copolymer segment density. For ordered phases, $\phi_A(\vec{r})$ and equivalently $\phi_B(\vec{r})$ are periodic spatial functions.

The equilibrium phase behaviors of this system are well described by a number of theories, including the famous self-consistent mean-field theory (SCFT) [29–31,19]. Based on the Gaussian chain model (Edwards model), the SCFT energy functional of an equilibrium state is controlled by the parameters N, f_A, χ_{AB} and R_g, where χ_{AB} is the Flory–Huggins interaction parameter of A and B segments and $R_g^2 = Nb^2/6$ is the *unperturbed radius of gyration* of the diblock copolymer. Besides the SCFT, which is a highly non-local and non-linear theory, other simpler theoretical models have been proposed for the study of phases and phase transitions of block copolymers. Among the many variations of theories, the Landau–Brazovskii (LB) model provides a particularly simple framework for the understanding of block copolymers. In what follows we will use this simple model to examine the nucleation of block copolymers.

Due to the incompressible condition (11), we can choose $\phi(\vec{r})$, defined as

$$\phi(\vec{r}) = \phi_A(\vec{r}) - f_A, \tag{12}$$

to be the order parameter. In the weak-segregation, i.e. assuming that $\phi(\vec{r})$ is small, the SCFT free energy functional can be approximated by an expansion in terms of $\phi(\vec{r})$ [32]

$$f_0[\phi] = \frac{1}{V_0}\int d\vec{r}_0 \left\{ \frac{\xi_0^2}{8q_0^2}[(\nabla^2 + q_0^2)\phi(\vec{r}_0)]^2 + \frac{\tau_0}{2}[\phi(\vec{r}_0)]^2 - \frac{\gamma_0}{3!}[\phi(\vec{r}_0)]^3 + \frac{\lambda_0}{4!}[\phi(\vec{r}_0)]^4 \right\}. \tag{13}$$

This Landau-like free energy functional is usually termed the Landau–Brazovskii (LB) energy. In (13), f_0 is the free energy density per copolymer in units of k_BT, and the parameters $\xi_0, q_0, \tau_0, \gamma_0$ and $\lambda_0 > 0$ can be expressed in terms of SCFT parameters N, f_A, χ_{AB} and R_g [3]. Following the same rescalings as in Ref. [3]

$$\vec{r} = q_0\vec{r}_0, \quad V = q_0^3 V_0, \quad f = \frac{f_0}{\lambda_0}, \quad \xi^2 = \frac{(q_0\xi_0)^2}{4\lambda_0}, \quad \tau = \frac{\tau_0}{\lambda_0}, \quad \gamma = \frac{\gamma_0}{\lambda_0},$$

we can rewrite the LB free energy density in its dimensionless form as

$$f[\phi] = \frac{1}{V}\int d\vec{r} \left\{ \frac{\xi^2}{2}[(\nabla^2 + 1)\phi(\vec{r})]^2 + \frac{\tau}{2}[\phi(\vec{r})]^2 - \frac{\gamma}{3!}[\phi(\vec{r})]^3 + \frac{1}{4!}[\phi(\vec{r})]^4 \right\}. \tag{14}$$

The dimensionless parameters ξ, τ, γ in (14) can be interpreted as such: ξ is the correlation length, τ is the reduced temperature, and γ is related to the asymmetry of the block copolymers. At the same time, as defined in (12) the order parameter $\phi(\vec{r})$ is a conserved one satisfying the constraint

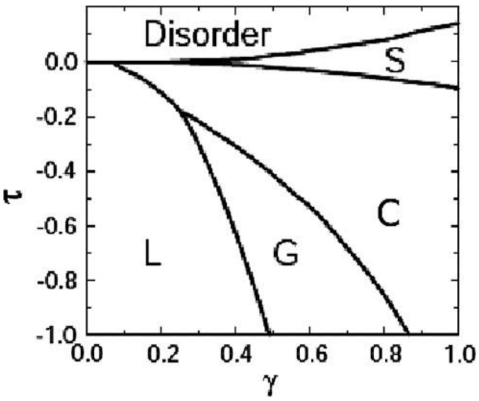

Fig. 5. The phase diagram of diblock copolymer melts given by the LB model for $\xi = 1$. The structures are as follows: disordered phase (disorder), lamellar phase (L), hexagonally packed cylinders (C), body-centered-cubic spheres (S), and gyroid phase with space group *Ia3d* (G). Adopted from Ref. [33].

$$\int \phi(\vec{r})\mathrm{d}\vec{r} = 0. \tag{15}$$

Obviously, the projection method is a reasonable choice to enforce this constraint.

Within the mean-field approximation, it has been shown that the LB model is capable of reproducing the phase diagram of diblock copolymers [33]. The corresponding phase diagram from [33] is reproduced in Fig. 5. To study the nucleation in order-to-order phase transitions, we choose the parameters τ and γ between the phase boundary and the spinodal line of the old phase so as to render the old phase metastable. For example, for the study of Lamellar (L) → Cylinder (C) transition we choose $\tau = -0.03$ and γ around 0.25.

4.2. Numerical calculations

We will compute the Lamellar (L) → Cylinder (C) transition and the Cylinder (C) → Sphere (S) transition to test our method. The first step of the study is the calculation of the two metastable/stable phases $\phi_m(\vec{r})$ and $\phi_s(\vec{r})$. These two solutions are the two ends of the string. These equilibrium solutions are obtained by numerically minimizing (14) under the constraint (15) using a conjugate-gradient algorithm assisted by the projection method. The conjugate-gradient iteration starts from a suitable initial value ϕ_0, which describes the specific periodic symmetries belonging to the target ordered phase.

The second step is to initialize the string. Before that, the symmetries and periods of the two ordered microphases engaged have to be matched. We take the advantage that it has been observed experimentally and theoretically that the ordered phases of diblock copolymers are related epitaxially [19]. Specifically, for the Lamellar–Cylinder transition, the cylinders are aligned along the z-axis while the lamellar normal is directed along the y-axis. The distance between cylinders D_c is related to the lamellar period D_l by $D_c = 2D_l/\sqrt{3}$. For the Cylinder–Sphere transition, the cylinders are aligned along the [1 1 1] direction of the body-center-cubic (BBC) structure of the spherical phase. The ratio of $D_\parallel$ (the spacing of spheres along the [1 1 1] direction) and $D_\perp$ (the distance between cylinders) is equal to $3/\sqrt{8}$. The string is then initialized using the method in Section 2.4, and the choice of $\mathcal{B}_\alpha$ is same to Eq. (10).

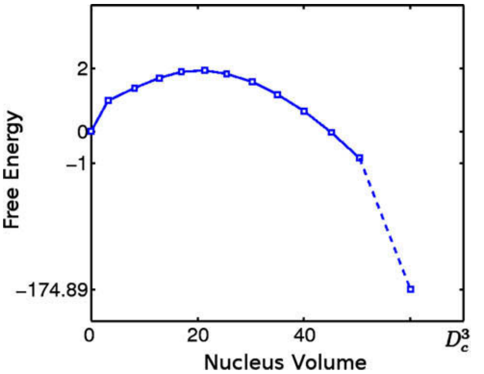

Fig. 6. Free energy as a function of the nuclear volume (D_c^3) in nucleation in L→C order-to-order phase transition of diblock copolymer at $\xi = 1, \tau = -0.03, \gamma = 0.26$. The later part of the curve is omitted (dashed line) for same reason as in Fig. 3.

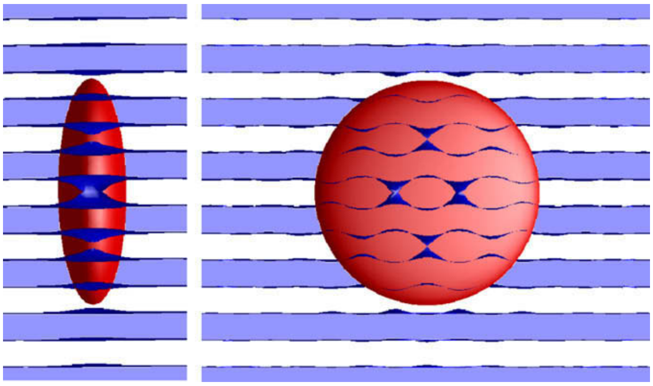

Fig. 7. The critical nuclei in nucleation in L→C order-to-order phase transition of diblock copolymer at $\xi = 1, \tau = -0.03, \gamma = 0.26$. (left) View from the *x*-axis. (right) View from the *z*-axis. Dark area indicate A-rich domains and the blue surface is the AB interface. Red surface is the nucleus boundary defined according to (6). Not all of the computational domain is included in the figures so as to display the nucleus more clearly. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

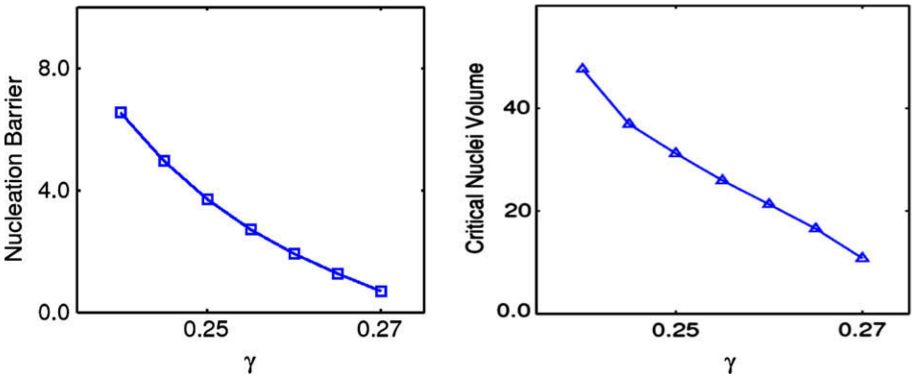

Fig. 8. Free energy barrier (left) and critical nuclear volume (right) as a function of the parameter γ ($\xi = 1, \tau = -0.03$ are fixed) in L→C nucleation of diblock copolymers.

In the study of the L→C transition, the computation domain is set to be $\left[0, \frac{32\pi}{\sqrt{3}}\right] \times [0, 16\pi] \times [0, 8\pi]$, with the total number of mesh points equals to $64 \times 64 \times 32$. 50 discrete points are used along the string. The parameters ξ and τ are fixed as $\xi = 1$ and $\tau = -0.15$, with parameter γ varying around 0.24–0.27, an area in which the cylindrical phase is stable and the lamellar phase metastable. After convergence of the strings, we define the nucleus boundary according to (6).

To illustrate the MEP obtained, the volume of the nucleus of the cylindrical phase can be used as the reaction coordinate. The free energy of the points along MEP (with $\gamma = 0.26$) is plotted in Fig. 6. The nuclear volume is in units of (D_c^3), and the free energy plotted is the dimensionless free energy per copolymer $f\widehat{V}$, where f is defined in (14) and $\widehat{V}$ is the volume of the computational domain. The maximum of the free energy curve indicates the critical nucleus, whose shape is illustrated in Fig. 7. It can be seen that the shape of the critical nucleus is lens-like with cylinders parallel to the short axis. A similar shape of critical droplets has been obtained at other values of γ. This shape anisotropy can be characterized as the ratio of the half-lengths along the three principal axes, l_x, l_y and l_z, based on the definition of the nucleus boundary (Eq. (6)). For these critical droplets thus obtained, the aspect ratios are $\frac{l_y}{l_z} \approx 4$ and $\frac{l_y}{l_x} \approx 1$. There are about 15–30 cylinders across the critical droplets, with a tendency of larger critical nucleus for smaller γ. The free energy barrier and critical nuclear volume are plotted as functions of γ in Fig. 8. The above results are in good agreement with a previous study using classical nucleation theory [3].[1]

For the study of nucleation of spheres from a cylindrical phase, the computational domain is taken as a cube with side length $L = 8\sqrt{2}\pi$ and the mesh number is set to be N^3 with $N = 64$. Forty discrete points are used along the string. The parameters are fixed as $\xi = 1, \tau = -0.03, \gamma = 1$, so that the spherical phase is stable while the cylindrical phase is metastable. It is found that the critical nucleus is egg-shaped with long axis along the cylinders. The aspect ratio of the critical nucleus is found to be $\frac{l_\parallel}{l_\perp} \approx 1.4$, where $l_\parallel$ and $l_\perp$ are the half-length along and perpendicular to the [1 1 1] direction of the BCC structure. There are about 7 cylinders across the critical droplets.

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[1] In this previous study the L→C critical nucleus obtained is of a lens-like shape, with aspect ratios $l_y/l_z, l_y/l_x$ of close values to our results.

For the L→C problem, we used 8 processes and the program ran for 1 day before convergence. For C→S, it is 64 processes and about the same length of computation time.

5. Conclusion

An efficient numerical method based on the *string method* is developed for the study of nucleation of ordered phases. The essential idea of this method is that the minimum energy path (MEP) of a free energy functional can be obtained by evolving a set of strings in the configuration space. Two techniques are proposed to enforce constraints of physical systems. In order to increase the efficiency of the iteration procedure, a special initialization method is employed, which takes the advantage of the known stable and metastable solutions. Special care is paid to the choice of computational domain and the matching relationship of the stable and metastable phases. Once the MEP is obtained, the properties of nucleation process, including the size and shape of critical nucleus and the free energy barrier of the nucleation, can be computed, utilizing a suitable definition of the nucleus boundary.

The usefulness of our based approach is demonstrated in two examples from soft condensed matter systems. For the case of nucleation of nematic nucleus from an isotropic phase of liquid crystal, MEP solutions of the Landau–de Gennes free energy functional is obtained. The critical nucleus is found to be of an elliptic shape with a uniform director field, in agreement with previous studies. For the case of diblock copolymers, a simple free energy functional, the Landau–Brazovskii model, is used. The MEP between cylindrical and lamellar, and between spherical and cylindrical phases, are calculated. The sizes and shapes of critical nuclei are obtained, along with energy barriers. These results are also in good agreement with previous studies.

The 2D computations are carried out on a serial computer using C, and the 3D computations are accomplished by MPI parallel programs written in C++.

Acknowledgments

All the computing was carried out on the HP Linux Cluster CCSE-I (HP DL360 G4). We would like to express our deepest gratitude to the substantial help of computer center and CCSE. A.-C. Shi would like to thank Peking University and Prof. Pingwen Zhang for their hospitality, and NSERC for financial support. The work of E is partially supported by ONR under Contract No. N00014-01-1-0674. PWZ would like to thank the financial support by the special funds for Major State Research Projects (2005CB321704), and National Natural Science Foundation of China (50930003).

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