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Generalization of the Fourier-spectral Eyre scheme for the phase-field equations: Application to self-assembly dynamics in materials

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ABSTRACT

Self-assembly is one of the most promising ways to develop novel materials with high performance. Thanks to the flexibility in treating of the topological changes in systems, the phase-field approach has emerged as a method of choice to study this phenomenon at mesoscale. In recent years, the phase-field equations have also been upgraded to incorporate the atomic scale effects. In this work, we propose an efficient numerical method based on the generalization of the Fourier-spectral Eyre's scheme, to simulate the dynamics of self-assembly, using the phase-field model at different time and length scales. To show its versatility, the method is explicitly implemented, and numerically tested, for three phase-field models describing patterned structure in systems: the modified Cahn-Hilliard equation for irradiation induced patterned microstructures at mesoscale, and the Phase-field Crystal and Continuous Atomic Density Functional methods, to study the formation of complex crystal structures at atomic scale.

1. Introduction

The concept of self-assembly refers to the spontaneous formation of patterns or structures, stemming from the competition between repulsive and attractive interactions in a system [1–3]. Lately, this process has turned into a new paradigm for structure design in nanotechnology [4], material sciences [5], and biophysics [6]. Together with new experimental techniques for the synthesis and characterization of new materials, the theoretical understanding and modeling of their structure are essential to engineering design. At atomic scale, the straightforward approach to simulate the dynamics of a system is Molecular Dynamics (MD) [7]. However, this class of models cannot address pattern formation at mesoscopic and higher space scales. Moreover, even at atomic scale, diffusional processes rooting self-assembly are still beyond reach for MD [8]. Alternatively, the Monte-Carlo (MC) approach is applicable to describe the self-assembly kinetics at diffusion scale [9], but the stochastic sampling in the MC dynamics requires the time consuming generation of a Markov chain [10]. Because it is naturally defined at the time scale of diffusion, the Phase-Field (PF) approach is emerging as a powerful tool to study self-assembly dynamics at mesoscopic scale, but also at atomic scale. Indeed, atomic scale PF models have recently appeared, such as the Phase-field Crystal (PFC) [11–13], and the Continuous Atomic Density Functional (CADF) [14]. Notwithstanding, the constant struggle for accelerated simulations on bigger spatial domains requires the implementation of new fast and light algorithms, especially for PF models. The purpose of this work is to address the need for a fast PF numerical method, prospecting the patterned structures emerging at the late stages of self-assembly kinetics.

The semi-implicit time integration of Eyre [15–18] was shown to guarantee the unconditional gradient-stability of the numerical solutions. This property allows to use high time steps, and reach the late stage of the dynamics swiftly. Based on this general algorithm, a non-linear convex splitting of the free energy functional was proposed in [19,20], resulting in a second order of convergence. However, this class of algorithms requires a linear algebraic solver. In addition, the non-linear splitting is not always compatible with the Fourier-spectral treatment of space discretization, usually used to solve the PF equations. These two features induce an additional computational load, which considerably reduce the efficiency of

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simulations [21]. This shortcoming reveals especially true for PFC and CADF simulations, as it requires very large simulation boxes (typically 256^3 and bigger [22]). In this work, we propose an alternative strategy, by taking the seminal Semi-Implicit Fourier (SIF) numerical scheme [23], as a starting point. Because it is fast, computationally light, and easy to implement, this method has become standard for PF simulations prospecting the steady states of dynamical processes [24–26]. Notwithstanding, it is not unconditionally stable, and the time step is thus limited by the stability of the scheme. In this context, the purpose of this study is to demonstrate that the combination of the Fourier-spectral treatment of space, with the time integration of Eyre, provides a simple and powerful alternative to the SIF scheme for the fast prospecting of various system dynamics. At the root of it, the unconditional stability of the scheme, which allows to decrease the simulation time, by at least one order of magnitude, without weighing the algorithm. Second, following the idea of Galenko et al. [27,28], this study aims at generalizing this procedure to different PF equations, in order to simulate a wide manifold of self-assembly dynamics.

In the present work, the *Spectral-Eyre* (SE) scheme, combining the Fourier-spectral treatment of space, with the time integration of Eyre, is thus reformulated for the general framework of self-assembly kinetics. The SE scheme is proved to be numerically fast, and computationally light. The versatility of the scheme is also demonstrated, through its ready-to-use implementation in three cases of phase field models of self-assembly dynamics. The first example relates to the MCH equation for irradiation induced patterned microstructure in binary alloys [29,30]. The second example is the PFC method, developed by Elder et al. in [13], to simulate the formation of periodic structures. Finally, particular emphasis is put on the CADF method [14], which was alternatively elaborated to simulate the self-assembly of complex crystal structures [31]. The study is organized as follows. First, the general PF equation for self-assembly kinetics is presented, and applied to the MCH, PFC, and CADF models. Then, the sound mathematical basis of the SE scheme established, and the correct parameter setting is demonstrated. After that, the implementation of the SE scheme for the MCH, PFC, and CADF models is written, and the computational properties are numerically proved in two dimensions. In particular, the computation time gain on the SIF scheme is demonstrated. Examples of 2D simulations are then displayed, such as the simulation of graphene monolayer, which is an active field of research, in both experimental and modeling science [32]. Finally, the fast three-dimensional simulation of the FCC structure assembly, and the challenging simulation of grain boundaries between diamond crystallites are presented.

2. The PF model for self-assembly kinetics

2.1. General formulation of the kinetic equation

The Phase-Field model has been extensively used to simulate microstructure, and complex atomic structure formation, because of its ability to reproduce a manifold of patterns, without any a priori assumptions. In this method, each phase, or domain in a periodic structure, is characterized by a set of field variables (compositions and/or order parameters). In this work, one scalar field ϕ is considered. The temporal evolution of the variable ϕ is governed by the Landau-Khalatnikov equation of motion [33], which subjects the variations of the field, to the thermodynamic driving force:

$$\frac{\partial\phi}{\partial t} = M\left[\nabla_\phi \mathcal{L}(\phi)\right]. \tag{1}$$

Here, $\nabla_\phi[\cdot]$ is the functional derivative, and M is the Onsager kinetic matrix. In this work, the phase-field variable ϕ is conserved, and M is the Laplacian operator Δ. In the most general case, the effective energy functional $\mathcal{L}(\phi)$ can be expressed as a sum of the local contribution F, and the non-local contribution W:

$$\mathcal{L}(\phi(\boldsymbol{x}-\boldsymbol{x}')) \equiv F(\phi(\boldsymbol{x})) + W(\phi(\boldsymbol{x}-\boldsymbol{x}')), \tag{2}$$

where $\boldsymbol{x}$ and $\boldsymbol{x}'$ are space vectors, belonging to the cubic domain $\Omega =]0, L[^d$ of edge length L, in dimension $d = 1, 2, 3$. The first term $F(\phi)$ sums all local contributions of the free energy density $f(\phi)$. In the formalism of Landau [34], the function f takes the form of a polynomial of the variable ϕ:

$$f(\phi) = -\epsilon\frac{\phi^2}{2} + \frac{\phi^4}{4}, \quad F(\phi) = \int_\Omega f(\phi)\mathrm{d}\boldsymbol{x}. \tag{3}$$

For $\epsilon > 0$, f displays two wells of equal depth, thereby ensuring the stability of two coexisting phases ($\phi < 0$ and $\phi > 0$). The second term $W(\phi)$ is the effective internal energy of the system. In the Cahn-Hilliard (CH) equation [35], it can be related to the interfacial energy between phases [36], the elastic energy of coherent inclusions [37], and external forcings [38]. For the PFC and CADF models, it can be associated with the interatomic interactions [39]. To address the issue of self-assembly, $W(\phi)$ embodies both repulsive and attractive interactions, whose interplay is at the root of patterning [40]. In this work, a quadratic form, corresponding to a two points correlation function is used for $W(\phi)$:

$$W(\phi) = \frac{1}{2}(w\cdot\phi, \phi)_{L^2}, \tag{4}$$

where $(\cdot,\cdot)_{L^2}$ is the scalar product on $L^2(\Omega)$, of corresponding norm $\|\cdot\|_2$. Consequently, the functional derivative of $W(\phi)$ is linear in $\phi : \nabla_\phi W(\phi) \equiv w\cdot\phi$. We also require that the presence of the term W in Eq. (1) is compatible with the gradient system framework [15]:

$$\begin{cases} W(\phi) \to +\infty \iff \|\phi\|_h \to \infty \\ \exists\lambda_0 \in \mathbb{R}, \quad \text{such as} \quad W(\phi) \geqslant \frac{\lambda_0}{2}\|\phi\|_2^2, \end{cases} \tag{5}$$

where $\|u\|_h = \|u\|_2 + \|\nabla u\|_2$ is the norm on the space $H^1(\Omega)$ of functions $u \in L^2(\Omega)$, such that $\int_\Omega |\nabla u|^2 \mathrm{d}\boldsymbol{x} < \infty$, and $\int_\Omega u\mathrm{d}\boldsymbol{x} = \bar{u}$. The strong formulation of Eq. (1) with Neumann boundary (NB) conditions follows:

$$\frac{\partial\phi}{\partial t} = \Delta\left[f'(\phi) + w\cdot\phi\right], \tag{6}$$

for any smooth solution ϕ, mapped to an initial condition ϕ_0. Noteworthy, other boundary conditions can be applied, such as periodic boundary conditions. However, this modifies slightly the Fourier-spectral analysis, as mentioned in the following. The Eq. (6) satisfies three central properties, on which the numerical scheme is built. For a solution ϕ of Eq. (6), the mass is conserved and the effective energy is dissipated:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\int_\Omega \phi\mathrm{d}\boldsymbol{x}\right] = 0, \quad \frac{\mathrm{d}\mathcal{L}(\phi)}{\mathrm{d}t}(t) \leqslant 0. \tag{7}$$

Also, the Eq. (6) belongs to the framework of differential gradient systems [15]:

$$\begin{cases} \frac{\partial\phi}{\partial t} = -\Delta\left[-\nabla_\phi\mathcal{L}(\phi)\right] \\ \mathcal{L}(\phi) \to +\infty \iff \|\phi\|_h \to \infty \\ \left(H_\phi\mathcal{L}(\psi)\frac{\phi}{\|\phi\|_2}, \frac{\phi}{\|\phi\|_2}\right)_{L^2} \geqslant \beta, \quad \beta \in \mathbb{R}. \end{cases} \tag{8}$$

Here, $H_\phi\mathcal{L}(\psi)$ is the Hessian function of $\mathcal{L}$, given by $H_\phi\mathcal{L}(\psi) : \phi \mapsto f''(\psi)\times\phi + w\cdot\phi$. This property stems from the complete definition of $\mathcal{L}(\phi)$, (Eqs. (2)–(4)), and the property $\lim_{\pm\infty} f = +\infty$ for $\epsilon > 0$:

$$\left(H_\phi\mathcal{L}(\psi)\phi, \phi\right)_{L^2} = \left(f''(\psi)\phi, \phi\right)_{L^2} + 2W(\phi) \geqslant (\lambda_0 + \min_{\mathbb{R}} f'')\|\phi\|_2^2.$$