

## A GENERAL STRATEGY FOR NUMERICAL APPROXIMATIONS OF NON-EQUILIBRIUM MODELS—PART I: THERMODYNAMICAL SYSTEMS

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**Abstract.** We present a general approach to deriving energy stable numerical approximations for thermodynamical consistent models for nonequilibrium phenomena. The central idea behind the systematic numerical approximation is the energy quadratization (EQ) strategy, where the system's free energy is transformed into a quadratic form by introducing new intermediate variables. By applying the EQ strategy, one can develop linear, high order semi-discrete schemes in time that preserve the energy dissipation property of the original thermodynamically consistent model equations. The EQ method is developed for time discretization primarily. When coupled with an appropriate spatial discretization, a fully discrete, high order, linear scheme can be developed to warrant the energy dissipation property of the fully discrete scheme. A host of examples for phase field models are presented to illustrate the effectiveness of the general strategy.

**Key words.** Energy stable schemes, nonequilibrium models, thermodynamic consistent models, energy quadratization.

### 1. Introduction

Time-dependent dynamics or transient dynamics in nonequilibrium phenomena is ubiquitous in science and engineering. One objective of scientific and engineering research is to develop mathematical models to describe the complex dynamics for various nonequilibrium systems. For material systems, especially, flowing materials, the development of a viable models to describe nonequilibrium phenomena at a given degree of freedoms is often not governed by a single physical equation unlike the Maxwell equation in the electromagnetic theory or the Schrodinger equation in quantum mechanics. Namely, universally accepted physical laws do not exist in many material systems once the choice of the variables, time and length scales is made. The Onsager principle has been proven to be an effective tool for one to arrive at a reasonable theory for describing near nonequilibrium dynamics [34, 35, 57, 66, 67, 26]. The Onsager principle is consisted of the linear response theory for kinetics and appropriate choices for describing reversible and irreversible dynamics within the regime of the time and length scale selected. It is equivalent to the GENERIC or the Poisson bracket formalism for non-equilibrium phenomena [2, 36], the energetic variational principle coupled with the minimum dissipation principle [13, 46, 25], and the second law of thermodynamics. But, the Onsager principle is easier to use in practice.

In a nutshell, the Onsager principle [34, 35] simply states that for a matter system, after one has identified the generalized coordinate, flux, and forces, there exists a balance between the frictional force and the totality of the other forces. It provides a specific way to calculate the frictional and the other forces. The Onsager principle was proposed for dissipative systems. It can be extended to yield a generalized Onsager principle to include reversible processes corresponding to

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transport phenomena. A large majority of the thermodynamic and hydrodynamic models, if they are derived correctly, obey the generalized Onsager principle in that the models possess a variational structure and admit energy dissipation laws.

Now that many models can be derived using the generalized Onsager principle, can we develop a systematic approach to fully utilize the variational as well as the dissipative structure in the models? The answer is positive. This paper aims at developing such a systematic approach to obtaining a second order temporal discretization for the thermodynamic model equations. This can form a paradigm for the future development of effective numerical approximations to models that describe non-equilibrium phenomena, enabling one to focus on more fine details or higher order approximations as well as implementation efficiency.

For a given non-equilibrium model consisted of partial differential equations, a high order approximation, computational efficiency as well as property preserving at the discrete level are always the desired properties to attain. For the dissipative system, one of the properties, one would like to preserve firstly, is the positive entropy production rate, or equivalently the second law of thermodynamics. In the isothermal case, it implies energy dissipation, commonly known as the energy law. The type of numerical schemes that retains the energy dissipate property at the discrete level is called the energy stable scheme. When the energy stability property of the scheme is independent of the discrete step size, the scheme is termed unconditionally energy stable. For these schemes, a large step size can be chosen to compute numerical solutions of the model equations.

In the past, two distinct, broadly-used strategies for developing energy stable schemes were proposed, which are the convex splitting approach [17, 53, 39, 52, 24] and the stabilizing approach [32, 69, 73, 31, 42, 45, 44, 70, 74, 54, 7, 68, 43]. The convex-splitting strategy relies on the existence of a pair of convex components that give rise to the free energy as the difference of the two functions. If such a splitting exists, a nonlinear scheme can be devised to render an unconditionally energy stable scheme. The stabilizing approach augments discretized equations by high order terms to turn the scheme into an energy stable scheme. Usually, this is accomplished by adding additional dissipation to the numerical scheme. Both strategies can yield dissipative schemes but do not guarantee to preserve the dissipation rate. Recently, Badia, Guillen-Gonzales, Gutierrez-Santacreu and Tierra explored a new idea of transforming the free energy into a quadratic functional to derive energy stable schemes [1, 23]. Recently, it is amplified and systematically applied to many specific thermodynamic models by Yang, Zhao, Shen and Wang [58, 61, 8, 62, 56, 60, 65, 70, 64, 71, 72, 21, 22]. Yang, Zhao and Wang coined the name Invariant Energy Quadraticization (IEQ) method for this class of methods. Later, we abbreviated the name to simply Energy Quadraticization (EQ) method, which is more appropriate. This strategy bypasses the traditional complicated ones to arrive at semi-discrete, second order or higher order in time linear schemes readily. This strategy is so general that it has little restriction on the specific expression of the free energy.

In this paper, we summarize the works that we have done using the EQ strategy and present a general framework to discretize the thermodynamically consistent models in forms of partial differential equations to arrive at linear, second order, energy stable numerical schemes. Implied by the name of EQ, one introduces new intermediate variables to quadraticize the free energy of the model. Then, one reformulates the thermodynamic model in the new variables. In all cases, the second order in time, numerical scheme based on the linearized, implicit Crank-Nicolson method can be applied to the models to arrive at energy stable schemes. The

thermodynamically consistent models include a wide class of PDE-based models that have intrinsic energy dissipation laws. The Cahn-Hilliard type equation and Allen-Cahn type equation are two prominent examples. The resultant schemes are always linear, second order in time, and unconditionally energy stable, so that they are supposed to be solved more efficiently than the discrete equations resulting from nonlinear schemes. These desired attributes of the schemes make the numerical approximation especially appealing.

We organize the rest of the paper as follows. In section 2, we present some useful lemmas and introduce basic notations. In section 3, we present the derivation of a general thermodynamic model using the generalized Onsager principle; it is followed by a systematic numerical approximation exploiting the mathematical structure in the model equations. In section 4, we present a plethora of phase field models consistent with the thermodynamic derivation and discuss their numerical approximations using EQ methods. Finally, we give a concluding remark in the last section.

## 2. Notations

In this section, we define the necessary notations to be used later in the paper. Denote  $\mathbb{Z}^+$  the set of all the positive integers,  $\mathbb{Z}$  the set of all the non-negative integers,  $\mathbb{R}$  the set of all the real number,  $\mathbb{R}^+$  the set of all the positive real number and  $\mathbb{R}_0^+$  the set of all the non-negative real numbers.

We consider a time domain given by  $[0, T]$  for  $T \in \mathbb{R}^+$ . For a  $N_t \in \mathbb{Z}^+$ , we define the time step as  $\Delta t = T/N_t$ , and the  $n$ -th step  $t_n = n\Delta t, 0 \leq n \leq N_t$ . Consider a spatial domain  $\Omega \subset \mathbb{R}^d$  ( $d = 2, 3$ ) with a smooth boundary  $\partial\Omega$ . We denote the computational domain by  $\Omega_t = \Omega \times (0, T)$ . For simplicity, we assume periodic boundary conditions for all models to be discussed in this paper unless stated otherwise. For physical boundary conditions, a consistent spatial discretization will also give us the desired results. We use normal symbols (such as  $\phi, \psi, c$ ) to represent scalar variables, bold-faced symbols (such as  $\mathbf{v}, \mathbf{p}, \mathbf{h}, \mathbf{g}$ ) to represent vector variables, and bold-faced capital symbols (such as  $\mathbf{F}, \mathbf{G}, \mathbf{M}$ ) to represent second order tensors or matrix variables.

We define the following difference operators

$$(1) \quad \delta_t^+ f^n = \frac{1}{\Delta t}(f^{n+1} - f^n), \quad \delta_t f^{n+1} = \frac{1}{2\Delta t}(3f^{n+1} - 4f^n + f^{n-1}),$$

and the extrapolation operators by overbars

$$(2) \quad \bar{f}^{n+1} = 2f^n - f^{n-1}, \quad \bar{f}^{n+\frac{1}{2}} = \frac{3}{2}f^n - \frac{1}{2}f^{n-1}.$$

We define inner product of two functions  $f, g \in L^2(\Omega)$  as follows  $(f, g) = \int_{\Omega} fg d\mathbf{x}$ , and  $L^2$  norm by  $\|f\| = (f, f)^{\frac{1}{2}}$ . In a similar manner, for  $\mathbf{f}, \mathbf{g} \in (L^2(\Omega))^d$ , we define the inner product  $(\cdot, \cdot)$  and norm  $\|\cdot\|$  for vector functions

$$(3) \quad (\mathbf{f}, \mathbf{g}) = \sum_i (\mathbf{f}_i, \mathbf{g}_i), \quad \|\mathbf{f}\| = (\mathbf{f}, \mathbf{f})^{\frac{1}{2}}.$$

Analogously, we define the inner product and norm for tensor functions

$$(4) \quad (\mathbf{F}, \mathbf{G}) = \sum_{i,j} (\mathbf{F}_{i,j}, \mathbf{G}_{i,j}), \quad \|\mathbf{F}\| = (\mathbf{F}, \mathbf{F})^{\frac{1}{2}}.$$

For any matrix  $\mathbf{M} \in \mathbb{R}^{n \times n}$ , we denote  $\mathbf{M} \leq 0$  as  $\mathbf{M}$  is negative semi-definite, and  $\mathbf{M} \geq 0$  as  $\mathbf{M}$  is positive semi-definite. For any operator  $\mathcal{M} \in \mathcal{B}(H)$ , where  $\mathcal{H}$  is a Hilbert space, say  $\mathcal{H} = L^2(\Omega)$ , we denote  $\mathcal{M} \leq 0$  as  $\mathcal{M}$  is negative semi-definite

operator, i.e.  $\forall f \in \mathcal{H}, (\mathcal{M}f, f) \leq 0$ . Similarly, we denote  $\mathcal{M} \geq 0$  as  $\mathcal{M}$  is positive semi-definite operator, i.e.  $\forall f \in \mathcal{H}, (\mathcal{M}f, f) \geq 0$ .

### 3. Model Derivation Using the Generalized Onsager Principle

**3.1. Model derivation for dissipative thermodynamic systems.** We consider a thermodynamic system whose state is described by a set of thermodynamic variables given in a vector  $\Phi$ . We assume the system's free energy is given by

$$(5) \quad F = \left( f(\Phi, \nabla\Phi, \dots, \nabla^m\Phi), 1 \right),$$

with  $m \in \mathbb{Z}^+$ . Assuming the system is dissipative, the transport equation of the variable  $\Phi$  can be derived systematically.

We begin with a dynamical system for the time evolution of  $\Phi$ :

$$(6) \quad \partial_t \Phi = \mathbf{s}(\Phi, \dots, \nabla^{2m}\Phi),$$

where  $\mathbf{s}$  is a vector functional to be determined below. We calculate the time derivative of the free energy as follows

$$(7) \quad \begin{aligned} \frac{d}{dt} F &= \left( \frac{\delta}{\delta\Phi} F(\Phi, \nabla\Phi, \dots, \nabla^m\Phi), \partial_t \Phi \right) \\ &= \left( \sum_{i=0}^m (-1)^i \nabla^i \frac{\partial f}{\partial \nabla^i \Phi}, \mathbf{s} \right) \\ &\quad + \int_{\partial\Omega} dS \left[ \sum_{i=0}^{m-1} \left( \sum_{k=i+1}^m \mathbf{n} \cdot (-1)^{k-i-1} \nabla^{k-i-1} \frac{\partial f}{\partial \nabla^k \Phi} \right) \nabla^i \partial_t \Phi \right], \end{aligned}$$

where  $\mathbf{n}$  is the unit external normal of  $\partial\Omega$ . If the boundary integral does not contribute to the energy dissipation, the boundary integral should vanish. Otherwise, it must be taken into account. Here, we assume the boundary conditions are chosen in such a way that the boundary integrals resulted during the integration by parts process all vanish, which yield  $m$  boundary conditions. One set of sufficient boundary conditions is given by

$$(8) \quad \sum_{k=i+1}^m \mathbf{n} \cdot (-1)^{k-i-1} \nabla^{k-i-1} \frac{\partial f}{\partial \nabla^k \Phi} = 0, i = 0, \dots, m-1.$$

We note that the periodic boundary condition also makes the boundary integral vanish. There can be other possibilities, which we will not enumerate here. These boundary conditions will be part of the boundary conditions for  $\Phi$  in (6). Additional boundary conditions may be necessary depending on the form of the mobility matrix, which will be introduced below.

We choose  $\mathbf{s}$  as a linearly functional of the chemical potential  $\mu$  using the Generalized Onsager Principle [67]

$$(9) \quad \mathbf{s} = \mathcal{M} \cdot \mu,$$

where  $\mathcal{M}$  is called the mobility matrix or coefficient matrix with elements including possibly differential or integral operator. This dynamical system is known as a gradient system. We decompose  $\mathcal{M}$  into the symmetric ( $\mathcal{M}_s$ ) and antisymmetric part ( $\mathcal{M}_a$ )

$$(10) \quad \mathcal{M} = \mathcal{M}_s + \mathcal{M}_a.$$

Then, the energy dissipation rate is given by

$$(11) \quad \frac{dF}{dt} = \left( \mu, \mathcal{M}_s \cdot \mu \right).$$

The time-dependent transport equation system is dissipative if  $\mathcal{M}_s \leq 0$  while the energy is conserved if  $\mathcal{M}_s = 0$ .

For example, if

$$(12) \quad \mathcal{M}_s = \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \mathbf{M}_i \cdot \nabla^i,$$

where  $\mathbf{M}_i, i = 0, \dots, N'$  (with  $N' \in \mathbb{Z}^+$ ) are non-negative definite tensors, the thermodynamic system is dissipative. This includes the well-known Allen-Cahn and Cahn-Hilliard equations for multiphase materials systems [4, 5]. For a mobility matrix containing differential operators, additional boundary conditions are necessary. These boundary conditions must be introduced based on whether the boundary terms in the energy dissipation rate formula contribute to the energy dissipation or not. For instance, for the mobility given in (12),  $N'$  boundary conditions need to be supplied. These conditions are defined based on the integration by parts during the reduction process to show the energy is dissipative. We will remark on this point wherever we give examples in the following. So, the total number of boundary conditions is  $m + N'$ . Again, the periodic boundary condition is an alternative boundary condition that makes all boundary/surface integrals vanish during the integration by parts process.

We use the fairly general case (12) to illustrate the idea. The transport equation for dynamics of the system is given by

$$(13) \quad \frac{\partial \Phi}{\partial t} = \left[ \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \mathbf{M}_i \cdot \nabla^i + \mathcal{M}_a \right] \mu,$$

with the consistent boundary condition discussed above, and proper initial conditions.

The system is dissipative if  $\mathcal{M}_s \leq 0$  and the energy dissipation rate is given by

$$(14) \quad \frac{d}{dt} F = - \sum_{i=0}^{N'} \left( \nabla^i \mu, \mathbf{M}_i \cdot \nabla^i \mu \right) \leq 0.$$

**3.2. Model reformulation based on energy quadratization method.** We next propose a systematic way to develop semi-discrete numerical schemes which are unconditionally energy stable and linear. The strategy we utilize is called the energy quadratization (EQ) method. We illustrate the idea using the specific form of  $\mathcal{M}_s$  given in (12). For more exotic mobility matrices, analogous results can be obtained on a case-by-case basis.

For any viable thermodynamic model, the free energy is normally bounded below. Without loss of generality, we assume the free energy is bounded below in this paper. If the free energy density functional has a lower bound, one can always add a constant  $A$  to it making it positive, without affecting the underlying dynamics. Then the modified free energy can be rewritten into a quadratic form

$$(15) \quad F = \sum_{i=0}^m \frac{1}{2} \beta_i \|\nabla^i \Phi\|^2 + \sum_{i,j=1}^N \alpha_{ij} (q_i, q_j),$$

where  $\beta_i$  are non-negative numbers,  $N \in \mathbb{Z}$ ,  $(\alpha_{ij})_{N \times N} > 0$ , and  $q_i$ 's are scalar functions of  $(\Phi, \nabla \Phi, \dots, \nabla^m \Phi)$ . This process is called energy quadratization (EQ). In principle, any potential functional with lower bound can be rewritten into such a quadratic form. However, the representation is not unique. We will give more

detailed discussions on how to reformulate the potential functional into quadratic forms, and comparing different quadratization approaches in the next section.

Once we reformulate the free energy functional into quadratic forms (15), the generalized chemical potential vector can be rewritten into the following

$$\begin{aligned}
 (16) \quad \mu &= \sum_{i=0}^m (-1)^i \beta_i \Delta^i \phi + \sum_{i,j=1}^N \alpha_{ij} \frac{\delta}{\delta \Phi} (q_i q_j) \\
 &= \sum_{i=0}^m (-1)^i \beta_i \Delta^i \phi + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i \frac{\partial q_j}{\partial \Phi} + q_j \frac{\partial q_i}{\partial \Phi} - \nabla \cdot (q_i \frac{\partial q_j}{\partial \nabla \Phi}) - \nabla \cdot (q_j \frac{\partial q_i}{\partial \nabla \Phi}) \right. \\
 &\quad \left. + \nabla \nabla : (q_i \frac{\partial q_j}{\partial \nabla \nabla \Phi}) + \nabla \nabla : (q_j \frac{\partial q_i}{\partial \nabla \nabla \Phi}) + \dots \right],
 \end{aligned}$$

and the time evolutionary equation of the intermediate variables are given by

$$(17) \quad \frac{\partial q_j}{\partial t} = \frac{\partial q_j}{\partial \Phi} \frac{\partial \Phi}{\partial t} + \frac{\partial q_j}{\partial \nabla \Phi} : \nabla \frac{\partial \Phi}{\partial t} + \frac{\partial q_j}{\partial \nabla \nabla \Phi} : \nabla \nabla \frac{\partial \Phi}{\partial t} + \dots$$

Then, we obtain the equivalent form of the equations given in (13)

$$(18) \quad \left\{ \begin{aligned}
 \frac{\partial \Phi}{\partial t} &= \left[ \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \mathbf{M}_i \cdot \nabla^i + \mathcal{M}_a \right] \mu, \\
 \mu &= \sum_{i=0}^m (-1)^i \beta_i \Delta^i \phi + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i \frac{\partial q_j}{\partial \Phi} + q_j \frac{\partial q_i}{\partial \Phi} - \nabla \cdot (q_i \frac{\partial q_j}{\partial \nabla \Phi}) - \nabla \cdot (q_j \frac{\partial q_i}{\partial \nabla \Phi}) \right. \\
 &\quad \left. + \nabla \nabla : (q_i \frac{\partial q_j}{\partial \nabla \nabla \Phi}) + \nabla \nabla : (q_j \frac{\partial q_i}{\partial \nabla \nabla \Phi}) + \dots \right], \\
 \frac{\partial q_j}{\partial t} &= \frac{\partial q_j}{\partial \Phi} \frac{\partial \Phi}{\partial t} + \frac{\partial q_j}{\partial \nabla \Phi} : \nabla \frac{\partial \Phi}{\partial t} + \frac{\partial q_j}{\partial \nabla \nabla \Phi} : \nabla \nabla \frac{\partial \Phi}{\partial t} + \dots
 \end{aligned} \right.$$

We remark the choice of consistent initial conditions for  $q_i$  ( $1 \leq i \leq N$ ) are essential to keep the reformulation equivalent. More details will be provided in the examples in the following section. The equivalence between the reformulated model given in (18) and the original one (13) could be easily verified, as  $q_i$  are only intermediate variables, and nothing else have been changed.

Next, we will show that the reformulated model given in (18) share the same energy dissipation rate as the original one in (13). In fact,

$$\begin{aligned}
 (19) \quad \frac{dF}{dt} &= \sum_{i=0}^m \beta_i \left( \nabla^i \Phi, \nabla^i \frac{\partial \Phi}{\partial t} \right) + \sum_{i,j=1}^N \alpha_{ij} \left[ \left( q_i, \frac{\partial q_j}{\partial t} \right) + \left( \frac{\partial q_i}{\partial t}, q_j \right) \right] \\
 &= \sum_{i=0}^m (-1)^i \beta_i \left( \Delta^i \Phi, \frac{\partial \Phi}{\partial t} \right) + \sum_{i,j=1}^N \alpha_{ij} \left( q_i \frac{\partial q_j}{\partial \Phi} + q_j \frac{\partial q_i}{\partial \Phi} - \nabla \cdot (q_i \frac{\partial q_j}{\partial \nabla \Phi}) \right. \\
 &\quad \left. - \nabla \cdot (q_j \frac{\partial q_i}{\partial \nabla \Phi}) + \nabla \nabla : (q_i \frac{\partial q_j}{\partial \nabla \nabla \Phi}) + \nabla \nabla : (q_j \frac{\partial q_i}{\partial \nabla \nabla \Phi}) + \dots, \frac{\partial \Phi}{\partial t} \right) \\
 &\quad + \text{boundary terms} \\
 &= \left( \mu, \frac{\partial \Phi}{\partial t} \right) \\
 &= \left( \mu, \left[ \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \mathbf{M}_i \cdot \nabla^i + \mathcal{M}_a \right] \cdot \mu \right) \\
 &= - \sum_{i=0}^{N'} \left( \nabla^i \mu, \mathbf{M}_i \cdot \nabla^i \mu \right) + \text{boundary terms.}
 \end{aligned}$$

We adopt the boundary conditions obtained in the derivation of the transport equation of  $\Phi$  at  $\partial\Omega$  so that the boundary integrals vanish. Thus (19) is equivalent with (14).

This procedure for obtaining the energy dissipation equation serves as the foundation for deriving the energy stable numerical schemes for the system. In the following, we focus on dissipative thermodynamic systems.

#### 4. Energy Stable Numerical Approximations

**4.1. Time discretization using the energy quadratization method.** The energy quadratization method (EQM) provides a systematic way to linearize the governing system of equations when deriving numerical schemes. Using EQM, we discretize the system of equations (18) in time as follows

**Scheme 4.1.** (*Second Order, Linear Crank-Nicolson Scheme*). Given initial conditions  $\Phi^0, q_i^0$ , we first compute  $\Phi^1, q_i^1$  by a first order scheme. Having computed  $\Phi^{n-1}, q_i^{n-1}$ , and  $\Phi^n, q_i^n$ , we compute  $\Phi^{n+1}, q_i^{n+1}$  as follows:

$$(20) \quad \begin{cases} \delta_t^+ \Phi^n = \left[ \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i + \overline{\mathcal{M}}_a^{n+\frac{1}{2}} \right] \mu^{n+\frac{1}{2}}, \\ \mu^{n+\frac{1}{2}} = \sum_{i=0}^m (-1)^i \beta_i \Delta^i \Phi^{n+\frac{1}{2}} + \sum_{i,j=1}^N \alpha_{ij} [q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}} + q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \\ - \nabla \cdot (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \nabla \Phi}^{n+\frac{1}{2}}) - \nabla \cdot (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}) \\ + \nabla \nabla : (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \nabla \nabla \Phi}^{n+\frac{1}{2}}) + \nabla \nabla : (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \nabla \nabla \Phi}^{n+\frac{1}{2}}) + \dots], \\ \delta_t^+ q_i^n = \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \cdot \delta_t^+ \Phi^n + \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}} : \nabla \delta_t^+ \Phi^n + \frac{\partial q_i}{\partial \nabla \nabla \Phi}^{n+\frac{1}{2}} : \nabla \nabla \delta_t^+ \Phi^n + \dots \end{cases}$$

*Remark 4.1.* We note that the initial conditions of  $q_i, i = 1, \dots, N$  are determined by the initial conditions of  $\Phi$  via the definition of the  $q_i$ .

For the scheme, we have the following theorem.

**Theorem 4.1.** *Scheme 4.1 is unconditionally energy stable, in the sense that*

$$(21) \quad F^{n+1} - F^n = -\Delta t \sum_{i=0}^{N'} \left( \nabla^i \mu^{n+\frac{1}{2}}, \overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu^{n+\frac{1}{2}} \right),$$

where  $F^k = \sum_{i=0}^m \frac{1}{2} \beta_i \|\nabla^i \Phi^k\|^2 + \sum_{i,j=1}^N \alpha_{ij} (q_i^k, q_j^k), k \in \mathbb{N}$ , is the semi-discretized free energy. In particular, the numerical scheme is energy decay, i.e.  $F^{n+1} \leq F^n$ , provided  $\mathbf{M}_i \geq 0$ .

*Proof.* Using the integration-by-parts formula, we deduce

$$(22) \quad \sum_{i=0}^m \beta_i (\nabla^i \Phi^{n+\frac{1}{2}}, \nabla^i \delta_t^+ \Phi^n) = \sum_{i=0}^m (-1)^i \beta_i (\Delta^i \Phi^{n+\frac{1}{2}}, \delta_t^+ \Phi^n).$$

Similarly, we have from the third equation of (20)

$$(23) \quad \begin{aligned} & \sum_{i,j=1}^N \alpha_{ij} [(q_i^{n+\frac{1}{2}}, \delta_t^+ q_j^n) + (\delta_t^+ q_i^n, q_j^{n+\frac{1}{2}})] \\ &= \sum_{i,j=1}^N \alpha_{ij} \left( q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}} + q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} - \nabla \cdot (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \nabla \Phi}^{n+\frac{1}{2}}) \right. \\ & \quad \left. - \nabla \cdot (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}) + \nabla \nabla : (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \nabla \nabla \Phi}^{n+\frac{1}{2}}) \right. \\ & \quad \left. + \nabla \nabla : (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \nabla \nabla \Phi}^{n+\frac{1}{2}}) + \dots, \delta_t^+ \Phi^n \right). \end{aligned}$$

Adding (22) and (23) and using the second equation of (20), we obtain

$$(24) \quad \sum_{i=0}^m \beta_i (\nabla^i \Phi^{n+\frac{1}{2}}, \nabla^i \delta_t^+ \Phi^n) + \sum_{i,j=1}^N \alpha_{ij} [(q_i^{n+\frac{1}{2}}, \delta_t^+ q_j^n) + (\delta_t^+ q_i^n, q_j^{n+\frac{1}{2}})] = (\mu^{n+\frac{1}{2}}, \delta_t^+ \Phi^n).$$

Then we take the inner product of the first equation of (20) with  $\mu^{n+\frac{1}{2}}$ , and then perform integration-by-parts to arrive at

$$(25) \quad (\mu^{n+\frac{1}{2}}, \delta_t^+ \Phi^n) = - \sum_{i=0}^{N'} (\nabla^i \mu^{n+\frac{1}{2}}, \overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu^{n+\frac{1}{2}}),$$

where the boundary conditions used in deriving the equations are adopted. According to (24), (25) and the following identity

$$\delta_t^+ (\mathbf{u}^n \cdot \mathbf{v}^n) = \delta_t^+ \mathbf{u}^n \cdot \mathbf{v}^{n+\frac{1}{2}} + \mathbf{u}^{n+\frac{1}{2}} \cdot \delta_t^+ \mathbf{v}^n,$$

we have

$$(26) \quad \begin{aligned} \delta_t^+ F^n &= \sum_{i=0}^m \beta_i (\nabla^i \Phi^{n+\frac{1}{2}}, \nabla^i \delta_t^+ \Phi^n) + \sum_{i,j=1}^N \alpha_{ij} [(q_i^{n+\frac{1}{2}}, \delta_t^+ q_j^n) + (\delta_t^+ q_i^n, q_j^{n+\frac{1}{2}})] \\ &= (\mu^{n+\frac{1}{2}}, \delta_t^+ \Phi^n) = - \sum_{i=0}^{N'} (\nabla^i \mu^{n+\frac{1}{2}}, \overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu^{n+\frac{1}{2}}), \end{aligned}$$

which leads to (21). □

*Remark 4.2.* (i) The linear, second order in time discretization preserves the energy dissipation rate. If we remove the overline in the above numerical scheme, we end up with the Crank-Nicolson scheme which is second order but nonlinear, unconditionally energy stable. (ii) The discrete boundary conditions are either periodic boundary conditions or the consistent physical boundary conditions with respect to the continuous system, discretized at  $n + \frac{1}{2}$ . (iii) If we retain the boundary terms due to inhomogeneous boundary conditions in the energy dissipation rate, a second order in time semidiscrete scheme can be derived as well which preserves the energy dissipation rate. (iv) In practice, when the free energy contains quadratic terms like  $\|\nabla v_i\|^2$ , there is no need to introduce a new intermediate variable  $q_j$  to replace it. The variation of the quadratic term is a linear term  $-\nabla^2 v_i$  in the chemical potential, which is treated semi-implicitly at level  $n + \frac{1}{2}$ . The resulting scheme is unconditionally energy stable.

We note that the second order in time scheme for the general thermodynamic system can also be obtained using the Backward Difference (BDF) method. The linear, second order in time BDF scheme is given as follows.

**Scheme 4.2.** (*Second Order, Linear BDF2 Scheme*). Given initial conditions  $\Phi^0, q_i^0$ , we first compute  $\Phi^1, q_i^1$  by a first order scheme. Having computed  $\Phi^{n-1}, q_i^{n-1}$ ,

and  $\Phi^n, q_i^n$ , we compute  $\Phi^{n+1}, q_i^{n+1}$  as follows:

$$(27) \quad \left\{ \begin{aligned} \delta_t \Phi^{n+1} &= \left[ \sum_{i=0}^{N'} (-1)^{i+1} \nabla^i \cdot \overline{\mathbf{M}}_i^{n+1} \cdot \nabla^i + \overline{\mathcal{M}}_a^{n+1} \right] \mu^{n+1}, \\ \mu^{n+1} &= \sum_{i=0}^m (-1)^i \beta_i \Delta^i \Phi^{n+1} + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i^{n+1} \frac{\partial q_j}{\partial \Phi} \overline{\phantom{q_i^{n+1} \frac{\partial q_j}{\partial \Phi}}}^{n+1} + q_j^{n+1} \frac{\partial q_i}{\partial \Phi} \overline{\phantom{q_i^{n+1} \frac{\partial q_j}{\partial \Phi}}}^{n+1} \right. \\ &\quad \left. - \nabla \cdot (q_i^{n+1} \frac{\partial q_j}{\partial \nabla \Phi} \overline{\phantom{q_i^{n+1} \frac{\partial q_j}{\partial \nabla \Phi}}}^{n+1}) - \nabla \cdot (q_j^{n+1} \frac{\partial q_i}{\partial \nabla \Phi} \overline{\phantom{q_j^{n+1} \frac{\partial q_i}{\partial \nabla \Phi}}}^{n+1}) + \nabla \nabla : (q_i^{n+1} \frac{\partial q_j}{\partial \nabla \nabla \Phi} \overline{\phantom{q_i^{n+1} \frac{\partial q_j}{\partial \nabla \nabla \Phi}}}^{n+1}) \right. \\ &\quad \left. + \nabla \nabla : (q_j^{n+1} \frac{\partial q_i}{\partial \nabla \nabla \Phi} \overline{\phantom{q_j^{n+1} \frac{\partial q_i}{\partial \nabla \nabla \Phi}}}^{n+1}) + \dots \right], \\ \delta_t q_i^{n+1} &= \frac{\partial q_i}{\partial \Phi} \overline{\phantom{\frac{\partial q_i}{\partial \Phi}}}^{n+1} \cdot \delta_t \Phi^{n+1} + \frac{\partial q_i}{\partial \nabla \Phi} \overline{\phantom{\frac{\partial q_i}{\partial \nabla \Phi}}}^{n+1} : \nabla \delta_t \Phi^{n+1} \\ &\quad + \frac{\partial q_i}{\partial \nabla \nabla \Phi} \overline{\phantom{\frac{\partial q_i}{\partial \nabla \nabla \Phi}}}^{n+1} : \nabla \nabla \delta_t \Phi^{n+1} + \dots \end{aligned} \right.$$

**Theorem 4.2.** *Scheme 4.2 is unconditionally energy stable, and satisfies the following discrete identity leading to an energy decay*

$$(28) \quad F^{n+1} - F^n + \tilde{F}^n = -\Delta t \sum_{i=0}^{N'} \left( \nabla^i \mu^{n+1}, \overline{\mathbf{M}}_i^{n+1} \cdot \nabla^i \mu^{n+1} \right),$$

where

$$(29) \quad \begin{aligned} F^n &= \sum_{i=0}^m \frac{\beta_i}{4} (\|\nabla^i \Phi^n\|^2 + \|\nabla^i (2\Phi^n - \Phi^{n-1})\|^2) \\ &\quad + \sum_{i,j=1}^N \frac{\alpha_{ij}}{2} [(q_i^n, q_j^n) + (2q_i^n - q_i^{n-1}, 2q_j^n - q_j^{n-1})], \\ \tilde{F}^n &= \sum_{i=0}^m \frac{\beta_i}{4} \|\nabla^i (\Phi^{n+1} - 2\Phi^n + \Phi^{n-1})\|^2 \\ &\quad + \sum_{i,j=1}^N \frac{\alpha_{ij}}{2} (q_i^{n+1} - 2q_i^n + q_i^{n-1}, q_j^{n+1} - 2q_j^n + q_j^{n-1}). \end{aligned}$$

In particular (since  $\tilde{F}^n \geq 0$ )

$$(30) \quad F^{n+1} - F^n \leq -\Delta t \sum_{i=0}^{N'} \left( \nabla^i \mu^{n+1}, \overline{\mathbf{M}}_i^{n+1} \cdot \nabla^i \mu^{n+1} \right).$$

*Proof.* Analogous to the proof of Theorem 4.1, we have from (27)

$$(31) \quad \begin{aligned} &\sum_{i=0}^m \beta_i (\nabla^i \Phi^{n+1}, \nabla^i \delta_t \Phi^{n+1}) + \sum_{i,j=1}^N \alpha_{ij} [(q_i^{n+1}, \delta_t q_j^{n+1}) + (\delta_t q_i^{n+1}, q_j^{n+1})] \\ &= -\sum_{i=0}^{N'} \left( \nabla^i \mu^{n+1}, \overline{\mathbf{M}}_i^{n+1} \cdot \nabla^i \mu^{n+1} \right). \end{aligned}$$

Combining the following identity

$$\begin{aligned} f^{n+1} \cdot \delta_t g^{n+1} + \delta_t f^{n+1} \cdot g^{n+1} &= \frac{1}{2\Delta t} \left[ f^{n+1} g^{n+1} + (2f^{n+1} - f^n)(2g^{n+1} - g^n) \right. \\ &\quad \left. - f^n g^n - (2f^n - f^{n-1})(2g^n - g^{n-1}) \right. \\ &\quad \left. + (f^{n+1} - 2f^n + f^{n-1})(g^{n+1} - 2g^n + g^{n-1}) \right], \end{aligned}$$

and (31) leads to (28). □

*Remark 4.3.* The excessive energy dissipation rate in  $\tilde{F}^n$  renders a more dissipative equation system at the discrete level.

**Theorem 4.3.** *There exists a unique solution for linear system resulted from semi-discrete scheme 4.1 and 4.2, respectively.*

*Proof.* Here we show the proof for the Crank-Nicolson scheme, as the proof for the BDF2 scheme is similar. Since the model (18) is rather general, to simplify our proof, we only consider the case  $\beta_i > 0$ ,  $\mathbf{M}_i > 0$ , and  $q = q(\Phi, \nabla\Phi)$ , (which includes the broadly used Allen-Cahn and Cahn-Hilliard type equations). We remark these assumptions are not absolutely necessary, but the detailed proof would be much more complex (such as to use Poincar inequality to prove the coercivity of the bilinear form when some  $\beta_i$  or  $\mathbf{M}_i$  are zero [16]). Here we only illustrate the idea.

The weak form of scheme 4.1 is given as follows: denote  $q = (q_1, q_2, \dots, q_N)$ , and  $r = (r_1, r_2, \dots, r_N)$ . We set initial condition  $(\Phi^0, \mu^0, q^0) \in H^m(\Omega) \times H^{N'}(\Omega) \times (L^2(\Omega))^N$ . Given  $(\Phi^{n-1}, \mu^{n-1}, q^{n-1}) \in H^m(\Omega) \times H^{N'}(\Omega) \times (L^2(\Omega))^N$  and  $(\Phi^n, \mu^n, q^n) \in H^m(\Omega) \times H^{N'}(\Omega) \times (L^2(\Omega))^N$ , we can obtain  $(\Phi^{n+1}, \mu^{n+1}, q^{n+1}) \in H^m(\Omega) \times H^{N'}(\Omega) \times (L^2(\Omega))^N$  from the following system

$$(32) \quad \left\{ \begin{aligned} &(\delta_t^+ \Phi^n, w) + \sum_{i=0}^{N'} (\overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu^{n+\frac{1}{2}}, \nabla^i w) - (\overline{\mathcal{M}}_a^{n+\frac{1}{2}} \mu^{n+\frac{1}{2}}, w) = 0, \\ &(\mu^{n+\frac{1}{2}}, \Psi) - \sum_{i=0}^m \beta_i (\nabla^i \Phi^{n+\frac{1}{2}}, \nabla^i \Psi) \\ &\quad - \sum_{i,j=1}^N \alpha_{ij} \left[ (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}}, \Psi) + (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}}, \Psi) \right. \\ &\quad \left. + (q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Psi) + (q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Psi) \right] = 0, \\ &(\delta_t^+ q_i^n, r_i) - (\frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \cdot \delta_t^+ \Phi^n, r_i) - (r_i \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \delta_t^+ \Phi^n) = 0, \quad i = 1, 2, \dots, N. \end{aligned} \right.$$

The weak form (32) could be rewritten as

$$(33) \quad a\left((\delta_t^+ \Phi^n, \mu^{n+\frac{1}{2}}, q^{n+\frac{1}{2}}), (\Psi, w, r)\right) = l(\Psi, w, r),$$

where the bilinear form  $a$  is given as

$$(34) \quad \begin{aligned} a\left((\Phi, \mu, q), (\Psi, w, r)\right) &= (\Phi, w) + \sum_{i=0}^{N'} (\overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu, \nabla^i w) - (\overline{\mathcal{M}}_a^{n+\frac{1}{2}} \mu, w) - (\mu, \Psi) \\ &+ \sum_{i,j=1}^N \alpha_{ij} \left[ (q_i \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}}, \Psi) + (q_j \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}}, \Psi) + (q_i \frac{\partial q_j}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Psi) + (q_j \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Psi) \right] \\ &+ \sum_{i=0}^m \frac{\Delta t}{2} \beta_i (\nabla^i \Phi, \nabla^i \Psi) + \frac{2}{\Delta t} \sum_{i,j=1}^N \alpha_{ij} [(q_i, r_j) + (q_j, r_i)] \\ &- \sum_{i,j=1}^N \alpha_{ij} \left[ (r_i \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}}, \Phi) + (r_j \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}}, \Phi) + (r_i \frac{\partial q_j}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Phi) + (r_j \frac{\partial q_i}{\partial \nabla \Phi}^{n+\frac{1}{2}}, \nabla \Phi) \right], \end{aligned}$$

and the right-hand-side linear form is given by

$$(35) \quad l(\Psi, w, r) = - \sum_{i=0}^m \beta_i (\nabla^i \Phi^n, \nabla^i \Psi) + \frac{2}{\Delta t} \sum_{i,j=1}^N \alpha_{ij} [(q_i^n, r_j) + (q_j^n, r_i)].$$

Therefore, it is easily seen the bilinear form  $a$  is continuous, i.e.

$$(36) \quad \begin{aligned} a\left((\Phi, \mu, q), (\Psi, w, r)\right) &\leq \alpha_1 \|\Phi\|_{H^m(\Omega)} \|\Psi\|_{H^m(\Omega)} \\ &+ \alpha_2 \|\mu\|_{H^{N'}(\Omega)} \|w\|_{H^{N'}(\Omega)} + \alpha_3 \sum_{i=1}^N \|q_i\| \|r_i\|, \end{aligned}$$

with  $\alpha_1, \alpha_2, \alpha_3 > 0$ . In addition, one can shown

$$(37) \quad \begin{aligned} & a\left((\Phi, \mu, q), (\Phi, \mu, q)\right) \\ &= \sum_{i=0}^N \left(\overline{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \nabla^i \mu, \nabla^i \mu\right) + \sum_{i=0}^m \frac{\Delta t}{2} \beta_i \|\nabla^i \Phi\|^2 + \frac{4}{\Delta t} \sum_{i,j=1}^N \alpha_{ij} (q_i, q_j), \end{aligned}$$

such that

$$(38) \quad a\left((\Phi, \mu, q), (\Phi, \mu, q)\right) \leq C_1 \|\mu\|_{H^{N'}(\Omega)}^2 + C_2 \|\Phi\|_{H^m(\Omega)}^2 + C_3 \sum_{i=1}^N \|q_i\|_{L^2(\Omega)}^2,$$

with  $C_1 > 0, C_2 > 0, C_3 > 0$  (given  $\mathbf{M}_i, \beta_i, (\alpha_{ij})$  are positive definite), i.e. the bilinear form  $a$  is coercive. then the existence and uniqueness of the weak solution  $(\Phi^{n+1}, \mu^{n+1}, q_i^{n+1}) \in H^m(\Omega) \times H^{N'}(\Omega) \times (L^2(\Omega))^N$  directly follows from the Lax-Milgram theorem [16]. □

**4.2. Spatial discretization.** Here for simplicity, we present a spatial discretization in 2D space. We remark that the results obtained in this section also work for 3D space. Following the notations in [20], we consider a rectangular domain  $\Omega = [0, L_x] \times [0, L_y]$  in 2D space, and let  $N_x, N_y$  be positive integers. The domain  $\Omega$  is uniformly partitioned with mesh sizes  $h_x = L_x/N_x, h_y = L_y/N_y$ . The grid points are denoted by

$$(39) \quad \Omega_h = \left\{ (x_i, y_j) \mid x_i = ih_x, y_j = jh_y, \quad 0 \leq i \leq N_x, 0 \leq j \leq N_y \right\}.$$

We define the following finite difference operators

$$(40) \quad \begin{aligned} \delta_x^+ f_{i,j} &= \frac{f_{i+1,j} - f_{i,j}}{h_x}, \delta_x^- f_{i,j} = \frac{f_{i,j} - f_{i-1,j}}{h_x}, \delta_{\bar{x}} f_{i,j} = \frac{\delta_x^+ + \delta_x^-}{2} f_{i,j}, \\ \delta_y^+ f_{i,j} &= \frac{f_{i,j+1} - f_{i,j}}{h_y}, \delta_y^- f_{i,j} = \frac{f_{i,j} - f_{i,j-1}}{h_y}, \delta_{\bar{y}} f_{i,j} = \frac{\delta_y^+ + \delta_y^-}{2} f_{i,j}, \end{aligned}$$

$$(41) \quad \nabla_h^+ = \begin{pmatrix} \delta_x^+ \\ \delta_y^+ \end{pmatrix}, \nabla_h^- = \begin{pmatrix} \delta_x^- \\ \delta_y^- \end{pmatrix}, \bar{\nabla}_h = \frac{1}{2}(\nabla_h^+ + \nabla_h^-), \Delta_h = \delta_x^+ \delta_x^- + \delta_y^+ \delta_y^-.$$

The discrete inner product and norm are defined by

$$(42) \quad (f, g)_h = \sum_{i=0}^{N_x-1} \sum_{j=0}^{N_y-1} f_{i,j} g_{i,j} h_x h_y, \quad \|f\|_h = \sqrt{(f, f)_h}.$$

The following summation-by-part formulas are analogous to the integration-by-part formulas

$$(43) \quad (f, \delta_{\alpha}^+ g)_h + (\delta_{\alpha}^- f, g)_h = 0, \quad (f, \delta_{\bar{\alpha}} g)_h + (\delta_{\bar{\alpha}} f, g)_h = 0,$$

where  $f$  and  $g$  satisfy periodic boundary conditions.

Then, the fully discrete CN scheme is given by the following.

**Scheme 4.3.** (Full Discrete CN Scheme). Given initial conditions  $\Phi^0, q_i^0$ , we first compute  $\Phi^1, q_i^1$  by a first order scheme. Having computed  $\Phi^{n-1}, q_i^{n-1}$ , and  $\Phi^n, q_i^n$ ,

we compute  $\Phi^{n+1}, q_i^{n+1}$  as follows.

$$(44) \quad \left\{ \begin{array}{l} \delta_t^+ \Phi^n = \left[ \sum_{i=0}^{N'} (-1)^{i+1} \bar{\nabla}_h^i \cdot \bar{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \bar{\nabla}_h^i + \bar{\mathcal{M}}_a^{n+\frac{1}{2}} \right] \mu^{n+\frac{1}{2}}, \\ \mu^{n+\frac{1}{2}} = \sum_{i=1}^m (-1)^i \beta_i \Delta_h^i \Phi^{n+\frac{1}{2}} + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}} + q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \right. \\ \quad \left. - \bar{\nabla}_h \cdot \left( q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) - \bar{\nabla}_h \cdot \left( q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) \right. \\ \quad \left. + \bar{\nabla}_h \bar{\nabla}_h : \left( q_i^{n+\frac{1}{2}} \frac{\partial q_j}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) + \bar{\nabla}_h \bar{\nabla}_h : \left( q_j^{n+\frac{1}{2}} \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) + \dots \right], \\ \delta_t^+ q_i^n = \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \cdot \delta_t^+ \Phi^n + \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} : \bar{\nabla}_h \delta_t^+ \Phi^n + \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} : \bar{\nabla}_h \bar{\nabla}_h \delta_t^+ \Phi^n + \dots \end{array} \right.$$

Analogously, we have the fully discrete BDF2 scheme.

**Scheme 4.4.** (Full Discrete BDF2 Scheme). Given initial conditions  $\Phi^0, q_i^0$ , we first compute  $\Phi^1, q_i^1$  by a first order scheme. Having computed  $\Phi^{n-1}, q_i^{n-1}$ , and  $\Phi^n, q_i^n$ , we compute  $\Phi^{n+1}, q_i^{n+1}$  as follows

$$(45) \quad \left\{ \begin{array}{l} \delta_t \Phi^{n+1} = \left[ \sum_{i=0}^{N'} (-1)^{i+1} \bar{\nabla}_h^i \cdot \bar{\mathbf{M}}_i^{n+1} \cdot \bar{\nabla}_h^i + \bar{\mathcal{M}}_a^{n+1} \right] \mu^{n+1}, \\ \mu^{n+1} = \sum_{i=1}^m (-1)^i \beta_i \Delta_h^i \Phi^{n+1} + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i^{n+1} \frac{\partial q_j}{\partial \Phi}^{n+1} + q_j^{n+1} \frac{\partial q_i}{\partial \Phi}^{n+1} \right. \\ \quad \left. - \bar{\nabla}_h \cdot \left( q_i^{n+1} \frac{\partial q_j}{\partial \bar{\nabla}_h \Phi}^{n+1} \right) - \bar{\nabla}_h \cdot \left( q_j^{n+1} \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+1} \right) \right. \\ \quad \left. + \bar{\nabla}_h \bar{\nabla}_h : \left( q_i^{n+1} \frac{\partial q_j}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+1} \right) + \bar{\nabla}_h \bar{\nabla}_h : \left( q_j^{n+1} \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+1} \right) + \dots \right], \\ \delta_t q_i^{n+1} = \frac{\partial q_i}{\partial \Phi}^{n+1} \cdot \delta_t \Phi^{n+1} + \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+1} : \bar{\nabla}_h \delta_t \Phi^{n+1} \\ \quad + \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+1} : \bar{\nabla}_h \bar{\nabla}_h \delta_t \Phi^{n+1} + \dots \end{array} \right.$$

**Theorem 4.4.** The full discrete schemes 4.3 and 4.4 are unconditional energy stable. In particular, Scheme 4.3 satisfies the discrete energy law

$$(46) \quad F_A^{n+1} - F_A^n = -\Delta t \sum_{i=0}^{N'} \left( \bar{\nabla}_h^i \mu^{n+\frac{1}{2}}, \bar{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \bar{\nabla}_h^i \mu^{n+\frac{1}{2}} \right)_h,$$

and Scheme 4.4 satisfies the discrete energy law

$$(47) \quad F_B^{n+1} - F_B^n + \tilde{F}_B^n = -\Delta t \sum_{i=0}^{N'} \left( \bar{\nabla}_h^i \mu^{n+1}, \bar{\mathbf{M}}_i^{n+1} \cdot \bar{\nabla}_h^i \mu^{n+1} \right)_h,$$

where

$$(48) \quad \begin{aligned} F_A^k &= \sum_{i=0}^m \frac{1}{2} \beta_i \|(\nabla_h^+)^i \Phi^k\|_h^2 + \sum_{i,j=1}^N \alpha_{ij} (q_i^k, q_j^k)_h, \quad k \in \mathbb{N}, \\ F_B^n &= \sum_{i=0}^m \frac{\beta_i}{4} (\|(\nabla_h^+)^i \Phi^n\|_h^2 + \|(\nabla_h^+)^i (2\Phi^n - \Phi^{n-1})\|_h^2) \\ &\quad + \sum_{i,j=1}^N \frac{\alpha_{ij}}{2} [(q_i^n, q_j^n)_h + (2q_i^n - q_i^{n-1}, 2q_j^n - q_j^{n-1})_h], \\ \tilde{F}_B^n &= \sum_{i=0}^m \frac{\beta_i}{4} \|(\nabla_h^+)^i (\Phi^{n+1} - 2\Phi^n + \Phi^{n-1})\|_h^2 \\ &\quad + \sum_{i,j=1}^N \frac{\alpha_{ij}}{2} (q_i^{n+1} - 2q_i^n + q_i^{n-1}, q_j^{n+1} - 2q_j^n + q_j^{n-1})_h. \end{aligned}$$

*Proof.* The proof is similar to the proof of the semi-discrete scheme when the discrete integration-by-parts formula are applied. We thus omit it for simplicity.  $\square$

For the linear schemes, we have the following theorem about their solvability.

**Theorem 4.5.** *The linear systems resulted from fully discrete schemes given by 4.3 and 4.4, respectively, are uniquely solvable.*

*Proof.* To proof the existence and uniqueness of the linear system of equations, we only need to show that for the corresponding homogeneous linear system, there exists only a zero solution. For simplicity, we present the proof for the CN scheme only. The proof for the other schemes are similar.

The system (44) corresponds to the homogeneous linear equation system

$$(49) \quad \begin{cases} \frac{2}{\Delta t} \Phi = \left[ \sum_{i=0}^{N'} (-1)^{i+1} \bar{\nabla}_h^i \cdot \bar{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \bar{\nabla}_h^i + \bar{\mathcal{M}}_a^{n+\frac{1}{2}} \right] \mu, \\ \mu = \sum_{i=0}^m (-1)^i \beta_i \Delta_h^i \Phi + \sum_{i,j=1}^N \alpha_{ij} \left[ q_i \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} + q_j \frac{\partial q_j}{\partial \Phi}^{n+\frac{1}{2}} \right. \\ \quad \left. - \bar{\nabla}_h \cdot \left( q_i \frac{\partial q_j}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) - \bar{\nabla}_h \cdot \left( q_j \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) \right. \\ \quad \left. + \bar{\nabla}_h \bar{\nabla}_h : \left( q_i \frac{\partial q_j}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) + \bar{\nabla}_h \bar{\nabla}_h : \left( q_j \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} \right) + \dots \right], \\ q_i = \frac{\partial q_i}{\partial \Phi}^{n+\frac{1}{2}} \cdot \Phi + \frac{\partial q_i}{\partial \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} : \bar{\nabla}_h \Phi + \frac{\partial q_i}{\partial \bar{\nabla}_h \bar{\nabla}_h \Phi}^{n+\frac{1}{2}} : \bar{\nabla}_h \bar{\nabla}_h \Phi + \dots, \end{cases}$$

where  $\Phi, \mu, q_i$  are unknowns. Analogous to the proof of Theorem 4.1, we can deduce from (49) that

$$(50) \quad \sum_{i=0}^m \beta_i \|(\bar{\nabla}_h^+)^i \Phi\|_h^2 + \sum_{i,j=1}^N 2\alpha_{ij} (q_i, q_j)_h + \frac{\Delta t}{2} (\bar{\nabla}_h^i \mu, \bar{\mathbf{M}}_i^{n+\frac{1}{2}} \cdot \bar{\nabla}_h^i \mu)_h = 0.$$

If  $\beta_i > 0$  and  $(\alpha_{i,j})_{N \times N}$  is positive definite, then we have from (49) and (50) that

$$q_i = 0, \quad \mu = 0, \quad \Phi = 0.$$

This completes the proof.  $\square$

## 5. Energy Stable Schemes of Dissipative Thermodynamic Systems

In previous two sections, we have presented a general framework to derive general thermodynamic systems and develop second order energy stable numerical schemes for a broad class of dissipative thermodynamic systems. In this section, we present several specific examples, relating numerical approximations based on EQM, to demonstrate the effective utility of the new approach. We focus on two widely used models: the Allen-Cahn and the Cahn-Hilliard equation. The Allen-Cahn equation and the Cahn-Hilliard equation both describe relaxation dynamics of a thermodynamic process. The Cahn-Hilliard equation conserves a first integral of the thermodynamic variable while the Allen-Cahn does not. This is a main feature that separates these two models.

**5.1. Allen-Cahn equations.** Given the expression of the free energy  $F[\phi]$ , where  $\phi$  is the phase variable. The Allen-Cahn equation is given by

$$(51) \quad \partial_t \phi = -\lambda(\phi) \mu, \quad \mu = \frac{\delta F}{\delta \phi}.$$

where  $\lambda(\phi) \geq 0$  is the motility matrix, and  $\mu = \frac{\delta F}{\delta \phi}$  is the variation of the free energy with respect to  $\phi$ , named generalized chemical potential. Here, the boundary condition can be either a periodic or the Neumann boundary condition. The Allen-Cahn equation has been used to model various multi-phasic material systems.

**5.1.1. Phase field models for binary fluids.** Consider a free energy with a double well bulk potential

$$(52) \quad F = \int_{\Omega} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{4} (1 - \phi^2)^2 \right] d\mathbf{x}.$$

The corresponding Allen-Cahn equation for the immiscible binary fluid is given by

$$(53) \quad \begin{cases} \partial_t \phi = \varepsilon^2 \Delta \phi - (\phi^3 - \phi), & \text{in } \Omega_t \\ \nabla \phi \cdot \mathbf{n} = 0, & \text{on } \partial \Omega_t, \\ \phi|_{t=0} = \phi_0, & \text{in } \Omega. \end{cases}$$

It has an energy dissipation law given below

$$(54) \quad \frac{dF}{dt} = \int_{\Omega} \frac{\delta F}{\delta \phi} \frac{\partial \phi}{\partial t} d\mathbf{x} = - \int_{\Omega} \left( \varepsilon^2 \Delta \phi - (\phi^3 - \phi) \right)^2 d\mathbf{x}.$$

Here, we introduce an intermediate variable  $q = \sqrt{\frac{1}{2}(1 - \phi^2)}$ , and take time derivative  $q_t = g(\phi)\phi_t$  with  $g(\phi) = \frac{\partial q}{\partial \phi} = -\sqrt{2}\phi$  to reformulate the equation in new variables as follows

$$(55) \quad \begin{cases} \partial_t \phi = \varepsilon^2 \Delta \phi - qg(\phi), & \text{in } \Omega_t \\ \partial_t q = g(\phi)\partial_t \phi, & \text{in } \Omega_t, \\ \nabla \phi \cdot \mathbf{n} = 0, & \text{on } \partial \Omega_t, \\ \phi|_{t=0} = \phi_0, q|_{t=0} = \sqrt{\frac{1}{2}(1 - \phi_0^2)}, & \text{in } \Omega. \end{cases}$$

Notice that equation (53) is equivalent to (55) with the energy law:

$$(56) \quad \frac{dF}{dt} = - \int_{\Omega} (\varepsilon^2 \Delta \phi - qg(\phi))^2 d\mathbf{x}, \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{2} q^2 \right].$$

We next present two linear, second order schemes to solve this system of equations. The second order numerical scheme based on the Crank-Nicolson method in time is given by

**Scheme 5.1.** Set  $\phi^0 = \phi|_{t=0}$ , and  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ . After obtained  $(\phi^n, q^n)$ , and  $(\phi^{n-1}, q^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1})$  via

$$(57) \quad \begin{cases} \delta_t^+ \phi^n = \varepsilon^2 \Delta \phi^{n+\frac{1}{2}} - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), & \text{in } \Omega_t, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, & \text{in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, & \text{on } \partial \Omega_t. \end{cases}$$

Notice that the intermediate variable  $q$  can be eliminated. In fact, it follows from  $q^{n+1} = q^0 + \sum_{k=0}^n g(\bar{\phi}^{k+\frac{1}{2}}) \delta_t^+ \phi^k$  and  $q^n = q^0 + \sum_{k=0}^{n-1} g(\bar{\phi}^{k+\frac{1}{2}}) \delta_t^+ \phi^k$ , such that

$$(58) \quad q^{n+\frac{1}{2}} = q^0 + g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n + \sum_{k=0}^{n-1} g(\bar{\phi}^{k+\frac{1}{2}}) \delta_t^+ \phi^k.$$

Thus, substituting (58) into (57), we actually solve the following equation with only  $\phi$ .

**Scheme 5.2.** Set  $\phi^0 = \phi|_{t=0}$ , and  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ . After obtained  $\phi^n$ , and  $\phi^{n-1}$ , we calculate  $\phi^{n+1}$  via

$$(59) \quad \begin{cases} \delta_t^+ \phi^n = \varepsilon^2 \Delta \phi^{n+\frac{1}{2}} - g(\bar{\phi}^{n+\frac{1}{2}}) \left[ q^0 + \frac{1}{2} g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n + \sum_{k=0}^{n-1} g(\bar{\phi}^{k+\frac{1}{2}}) \delta_t^+ \phi^k \right] \text{ in } \Omega_t \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t. \end{cases}$$

A second order numerical scheme based on BDF2 is given by the following scheme.

**Scheme 5.3.** Set  $\phi^0 = \phi|_{t=0}$ , and  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ . After obtaining  $(\phi^n, q^n)$  and  $(\phi^{n-1}, q^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1})$  via

$$(60) \quad \begin{cases} \delta_t \phi^{n+1} = \varepsilon^2 \Delta \phi^{n+1} - q^{n+1} g(\bar{\phi}^{n+1}), \text{ in } \Omega_t, \\ \delta_t q^{n+1} = g(\bar{\phi}^{n+1}) \delta_t \phi^{n+1}, \text{ in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t. \end{cases}$$

Similarly, by eliminating intermediate variable  $q$  and from

$$(61) \quad q^{n+1} - q^n = \frac{1}{3}(q^n - q^{n-1}) + 2\delta t g(\bar{\phi}^{n+1}) \delta_t \phi^{n+1},$$

we obtain

$$(62) \quad q^{n+1} = q^0 + \sum_{i=0}^n \left(\frac{1}{3}\right)^i (q^1 - q^0) + 2\delta t \sum_{i=0}^n \sum_{k=1}^i \left(\frac{1}{3}\right)^{i-k} g(\bar{\phi}^{k+1}) \delta_t \phi^{k+1}.$$

Then, the BDF2 scheme is essentially equivalent to the following.

**Scheme 5.4.** Set  $\phi^0 = \phi|_{t=0}$ , and  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ ,  $q^1 = \frac{1}{\sqrt{2}}(1 - (\phi^1)^2)$ . After obtaining  $\phi^n$  and  $\phi^{n-1}$ , we calculate  $\phi^{n+1}$  via

$$(63) \quad \begin{cases} \delta_t \phi^{n+1} = \varepsilon^2 \Delta \phi^{n+1} - g(\bar{\phi}^{n+1}) \left[ q^0 + \sum_{i=0}^n \left(\frac{1}{3}\right)^i (q^1 - q^0) + 2\delta t \sum_{i=0}^n \sum_{k=1}^i \left(\frac{1}{3}\right)^{i-k} g(\bar{\phi}^{k+1}) \delta_t \phi^{k+1} \right], \text{ in } \Omega_t \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t. \end{cases}$$

As alluded to in the previous section, the choice of intermediate variables is not unique; some may be more proper than the others. For instance, for the Allen-Cahn equation with the free energy containing the double-well potential, we can rewrite it as

$$(64) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{2} \gamma \phi^2 + \left( \frac{1}{4} (\phi^2 - 1)^2 - \frac{1}{2} \gamma \phi^2 + A \right) - A \right],$$

where  $A$  is a (large enough) constant, such that  $\frac{1}{4}(\phi^2 - 1)^2 - \gamma \phi^2 + A > 0$ . We introduce the intermediate variable  $q$

$$(65) \quad q = \frac{\sqrt{2}}{2}((1 + \gamma) - \phi^2), \quad A = \frac{1}{4}(1 - (1 + \gamma)^2), \quad g(\phi) = q' = -\sqrt{2}\phi.$$

Then, the equivalent equation is given by

$$(66) \quad \begin{cases} \partial_t \phi = \varepsilon^2 \Delta \phi - \gamma \phi - qg(\phi), \text{ in } \Omega_t, \\ \partial_t q = g(\phi) \partial_t \phi, \text{ in } \Omega_t, \\ \nabla \phi \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t, \\ \phi|_{t=0} = \phi_0, q|_{t=0} = q(\phi_0), \text{ in } \Omega. \end{cases}$$

An energy stable scheme based on this formulation using the CN method is given by the following.

**Scheme 5.5.** Set  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \frac{1}{\sqrt{2}}(1 + \gamma - (\phi^0)^2)$ . After obtaining  $(\phi^n, q^n)$  and  $(\phi^{n-1}, q^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1})$  via

$$(67) \quad \begin{cases} \delta_t^+ \phi^n = \varepsilon^2 \Delta \phi^{n+\frac{1}{2}} - \gamma \phi^{n+\frac{1}{2}} - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), \text{ in } \Omega_t, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t. \end{cases}$$

*Remark 5.1.* The basic idea of the EQ approach is to transform the free energy into a quadratic form. Since the variation of the quadratic form is linear, we then obtain a linear scheme. The EQ method is essentially a linearization method.

Another choice of the intermediate variables is to use

$$(68) \quad \mathbf{p} = \varepsilon \nabla \phi, \quad q = \frac{1}{\sqrt{2}}(1 - \phi^2) \quad g(\phi) = -\sqrt{2}\phi,$$

to transform the free energy into

$$(69) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{1}{2} |\mathbf{p}|^2 + \frac{1}{2} q^2 \right].$$

Then, following the EQ strategy, we end up with a new scheme.

**Scheme 5.6.** Set  $\phi^0 = \phi|_{t=0}$   $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ ,  $\mathbf{p}^0 = \varepsilon \nabla \phi^0$ , . For all  $n \geq 0$ , given  $(\phi^n, q^n, \mathbf{p}^n)$  and  $(\phi^{n-1}, q^{n-1}, \mathbf{p}^{n-1})$ , we compute  $(\phi^{n+1}, q^{n+1}, \mathbf{p}^{n+1})$  using the following scheme

$$(70) \quad \begin{cases} \delta_t^+ \phi^n = \nabla \cdot (\varepsilon \mathbf{p}^{n+\frac{1}{2}}) - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), \text{ in } \Omega_t, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \delta_t^+ \mathbf{p}^n = \varepsilon \nabla \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \Omega_t. \end{cases}$$

Given the consistent initial condition  $\mathbf{p}^0 = \varepsilon \nabla \phi^0$ ,  $\mathbf{p}^{-1} = \varepsilon \nabla \phi^{-1}$ , we easily obtain  $\mathbf{p}^{n+\frac{1}{2}} = \varepsilon \nabla \phi^{n+\frac{1}{2}}$ . We note that this scheme is equivalent to scheme 5.1.

Yet, another choice of free energy quadratization is to introduce intermediate variables  $p$  and  $q$  as follows:

$$(71) \quad p = \sqrt{\varepsilon^2 |\nabla \phi|^2 + A}, \quad \partial_t p = \mathbf{h}(\phi) \cdot \nabla \partial_t \phi, \quad \mathbf{h}(\phi) = \frac{\varepsilon^2 \nabla \phi}{\sqrt{\varepsilon^2 |\nabla \phi|^2 + A}},$$

$$(72) \quad q = \frac{1}{\sqrt{2}}(1 - \phi^2), \quad \partial_t q = g(\phi) \partial_t \phi, \quad g(\phi) = -\sqrt{2}\phi.$$

The free energy is expressed as follows

$$(73) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{1}{2} p^2 + \frac{1}{2} q^2 - \frac{1}{2} A \right].$$

Then, the corresponding numerical scheme resulted from applying EQ method is given by the following.

**Scheme 5.7.** Set  $\phi^0 = \phi|_{t=0}$ ,  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ ,  $p^0 = \sqrt{\varepsilon^2|\nabla\phi^0|^2 + A}$ . For all  $n \geq 0$ , given  $(\phi^n, q^n, p^n)$  and  $(\phi^{n-1}, q^{n-1}, p^{n-1})$ , we obtain  $(\phi^{n+1}, q^{n+1}, p^{n+1})$  by the following scheme

$$(74) \quad \left\{ \begin{array}{l} \delta_t^+ \phi^n = \nabla \cdot (p^{n+\frac{1}{2}} \mathbf{h}(\bar{\phi}^{n+\frac{1}{2}})) - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), \text{ in } \Omega_t, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \delta_t^+ p^n = \mathbf{h}(\bar{\phi}^{n+\frac{1}{2}}) \cdot \nabla \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \Omega_t. \end{array} \right.$$

One can easily verify that if we propose proper initial conditions and time extrapolation for  $\mathbf{h}$ , namely  $p^0 = \sqrt{\varepsilon^2|\nabla\phi^0|^2 + A}$ ,  $p^{-1} = \sqrt{\varepsilon^2|\nabla\phi^{-1}|^2 + A}$ , and  $\mathbf{h}^{n+\frac{1}{2}} = \frac{\varepsilon^2 \nabla \phi^{n+\frac{1}{2}}}{\frac{1}{2} \left( \sqrt{\varepsilon^2|\nabla\phi^n|^2 + A} + \sqrt{\varepsilon^2|\nabla\phi^{n+1}|^2 + A} \right)}$ , the new scheme is equivalent to the previous one. However, in order to linearize it, we have to use a second order approximation  $\mathbf{h}^{n+\frac{1}{2}} = \frac{\varepsilon^2 \nabla \bar{\phi}^{n+\frac{1}{2}}}{\sqrt{\varepsilon^2|\nabla\bar{\phi}^{n+\frac{1}{2}}|^2 + A}}$ .

Another energy stable method can be derived [41, 40], if we introduce a scalar variable

$q = \sqrt{2[\int_{\Omega} f(\phi) d\mathbf{x} + C_0]}$ ,  $C_0 > 0$ ,  $g(\phi) = \frac{\delta q}{\delta \phi} = \frac{\frac{\delta f}{\delta \phi}}{\sqrt{2[\int_{\Omega} f(\phi) d\mathbf{x} + C_0]}}$ . Then, the free energy is transformed as

$$(75) \quad F = \int_{\Omega} \frac{\varepsilon^2}{2} |\nabla\phi|^2 d\mathbf{x} + \frac{q^2}{2}.$$

and the chemical potential is  $\mu = -\nabla^2\phi + 2q\frac{\delta q}{\delta \phi}$ . A second order energy stable scheme is given by the following.

**Scheme 5.8.** Set  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \sqrt{2[\int_{\Omega} f(\phi^0) d\mathbf{x} + C_0]}$ . After obtaining  $(\phi^n, q^n)$  and  $(\phi^{n-1}, q^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1})$  via

$$(76) \quad \left\{ \begin{array}{l} \delta_t^+ \phi^n = \varepsilon^2 \Delta \phi^{n+\frac{1}{2}} - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), \text{ in } \Omega_t, \\ \delta_t^+ q^n = \int_{\Omega} g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n d\mathbf{x}, \text{ in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t. \end{array} \right.$$

**5.1.2. Allen-Cahn equations subject to a volume constraint.** As mentioned earlier, the Allen-Cahn equation does not conserve the "total volume" if  $\phi$  is identified as the volume fraction. To enforce the constraint, we augment the free energy by a penalizing term as follows

$$(77) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla\phi|^2 + \frac{1}{4} (1 - \phi^2)^2 \right] + \frac{\eta}{2} \left( \int_{\Omega} \phi(t) d\mathbf{x} - V_0 \right)^2,$$

where  $V_0$  is the initial volume and  $\eta > 0$  is a prescribed constant. With the modified free energy, the Allen-Cahn equation is given by

$$(78) \quad \left\{ \begin{array}{l} \partial_t \phi = \varepsilon^2 \Delta \phi - (\phi^3 - \phi) - \eta \left( \int_{\Omega} \phi(t) d\mathbf{x} - V_0 \right), \text{ in } \Omega_t, \\ \nabla \phi \cdot \mathbf{n} = 0, \text{ on } \partial\Omega_t, \\ \phi|_{t=0} = \phi_0, \text{ in } \Omega. \end{array} \right.$$

We introduce  $q = \sqrt{\frac{1}{2}(1 - \phi^2)}$  and  $\zeta = \sqrt{\eta} \left( \int_{\Omega} \phi(t) d\mathbf{x} - V_0 \right)$ . Then, the free energy is reformulated into

$$(79) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{2} q^2 \right] + \frac{1}{2} \zeta^2.$$

Then the equivalent equations are given by

$$(80) \quad \begin{cases} \partial_t \phi = \varepsilon^2 \Delta \phi - qg(\phi) - \sqrt{\eta} \zeta, & \text{in } \Omega_t, \\ \partial_t q = g_1(\phi) \partial_t \phi, \quad g_1(\phi) = -\sqrt{2} \phi, & \text{in } \Omega_t, \\ \partial_t \zeta = \sqrt{\eta} \int_{\Omega} \partial_t \phi d\mathbf{x}, & \text{in } \Omega_t, \\ \nabla \phi \cdot \mathbf{n} = 0, & \text{on } \partial \Omega_t, \\ \phi|_{t=0} = \phi_0, \quad q|_{t=0} = q(\phi_0), & \text{in } \Omega. \end{cases}$$

The corresponding linear, second order, energy stable numerical scheme is given by the following.

**Scheme 5.9.** Set  $\phi^0 = \phi|_{t=0}$ ,  $q^0 = \frac{1}{\sqrt{2}}(1 - (\phi^0)^2)$ ,  $\zeta^0 = \sqrt{\eta}(\int_{\Omega} \phi^0 d\mathbf{x} - V_0)$ . For all  $n \geq 0$ , given  $(\phi^n, q^n, \zeta^n)$  and  $(\phi^{n-1}, q^{n-1}, \zeta^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1}, \zeta^{n+1})$  by the following scheme

$$(81) \quad \begin{cases} \delta_t^+ \phi^n = \varepsilon^2 \Delta \phi^{n+\frac{1}{2}} - q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}) - \sqrt{\eta} \zeta^{n+\frac{1}{2}}, & \text{in } \Omega_t, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, & \text{in } \Omega_t, \\ \delta_t^+ \zeta^n = \sqrt{\eta} \int_{\Omega} \delta_t^+ \phi^n d\mathbf{x}, & \text{in } \Omega_t, \\ \nabla \phi^{n+1} \cdot \mathbf{n} = 0, & \text{on } \Omega_t. \end{cases}$$

Notice that  $\zeta$  is a time dependent function and  $q$  is a time as well as space dependent function after the quadratized reformulation. We discretize the equations in Scheme 5.9 using finite difference method in space. Figure 1 depicts a numerical simulation of a reshaping of a cross under Allen-Cahn dynamics involving a binary fluid. Here we choose  $L_x = L_y = 1$ ,  $N_x = N_y = 128$ , the initial condition  $\phi = \max(a, b)$ , with  $a = \min(\tanh \frac{0.1 - |x - 0.5|}{\varepsilon}, \tanh \frac{0.2 - |y - 0.5|}{\varepsilon})$  and  $b = \min(\tanh \frac{0.2 - |x - 0.5|}{\varepsilon}, \tanh \frac{0.1 - |y - 0.5|}{\varepsilon})$ , and time step  $\delta t = 10^{-3}$ , and  $\varepsilon = 10^{-2}$ ,  $\eta = 20$ . Figure 2(a) shows the volume ratio between the initial volume and the volume at time  $0 \leq t \leq 500$ . Figure 2(b) demonstrates the total energy decay as a function of time. The energy settles down after  $t = 150$ .

**5.1.3. Phase field model with an elastic bending energy.** We briefly discuss a phase field model for an elastic membrane with the bending energy and then demonstrate how the EQ method can be applied to yield energy stable, linear schemes. Here, the free energy  $F$  is consisted of three parts:

$$(82) \quad F = F_b + F_{surf} + F_{vol},$$

where  $F_b$  is the Helfrich elastic or bending energy given by

$$(83) \quad F_b = \int_{\Omega} \frac{\gamma_b}{2} \left( \nabla^2 \phi - f_b(\phi) \right)^2 d\mathbf{x}, \quad f_b(\phi) = \frac{2}{\varepsilon^2} \phi(\phi - 1) \left( 2\phi - 1 - \frac{\varepsilon}{\sqrt{2}} C_0 \right),$$

$C_0$  is the spontaneous curvature;  $F_{vol}$  is the volume constraint, given by

$$(84) \quad F_{vol} = \frac{\lambda_V}{2} (V(t) - V_0)^2, \quad V(t) = \int_{\Omega} \phi(\mathbf{x}, t) d\mathbf{x}, \quad V_0 = V(0);$$

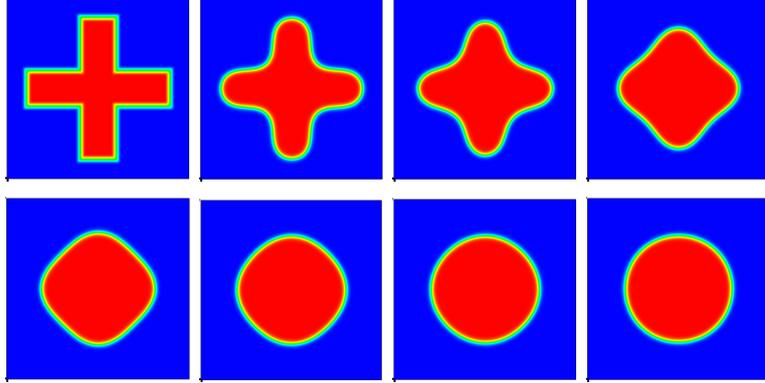


FIGURE 1. Coarsening dynamics with the volume-constraint Allen-Cahn equation. The snapshots of  $\phi$  (with red representing 1, and blue representing -1) at times  $t = 0, 5, 10, 20, 30, 40, 50, 100$  are shown respectively.

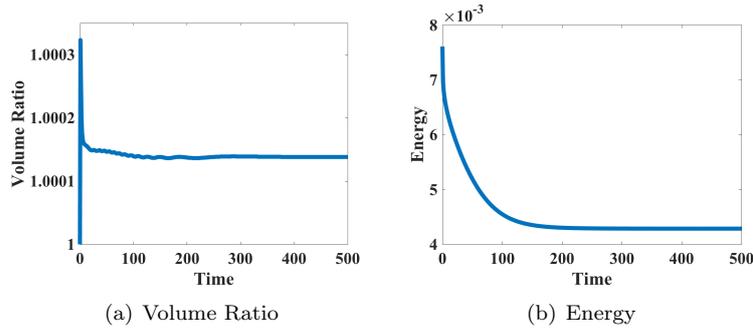


FIGURE 2. Volume ratio and energy function at different times of the simulation shown in Figure 1. The volume is conserved up to the error tolerance and the free energy reaches a near steady state at the end of the simulation.

and  $F_{surf}$  is the constraint for the surface area,  
 (85)

$$F_{surf} = \frac{\lambda_S}{2}(S(t) - S_0)^2, \quad S(t) = \int_{\Omega} \left[ \frac{\varepsilon}{2} |\nabla \phi(t)|^2 + \frac{1}{\varepsilon} \phi^2(t)(1 - \phi(t))^2 \right] dx, \quad S_0 = S(0).$$

The chemical potential  $\mu$  is given by

$$(86) \quad \mu = \frac{\delta F}{\delta \phi} = \gamma(\nabla^2 - f_b(\phi))(\nabla^2 \phi - f'_b(\phi)) + \lambda_V(V(t) - V_0) + \lambda_S(S(t) - S_0)$$

The Allen-Cahn model for relaxation dynamics of the membrane is given by

$$(87) \quad \tau \partial_t \phi = -\frac{\delta F}{\delta \phi},$$

where  $\tau$  is the relaxation time. Specifically,

$$(88) \quad \tau \partial_t \phi = -\gamma \left( \nabla^4 \phi - f'_b(\phi) \nabla^2 \phi - \nabla^2 f_b(\phi) + f_b(\phi) f'_b(\phi) \right) - \lambda_V(V(t) - V_0) - \lambda_S(S(t) - S_0).$$

We introduce the following intermediate variables to quadratize the free energy density function  $f$ :

$$(89) \quad q = \sqrt{\frac{\gamma_b}{2}} (\nabla^2 \phi - f_b(\phi)), \quad \zeta = \sqrt{\frac{\lambda_V}{2}} (V(t) - V_0), \quad \xi = \sqrt{\frac{\lambda_S}{2}} (S(t) - S_0).$$

The time evolutionary equations for the intermediate variables are given by

$$(90) \quad \begin{cases} \partial_t q &= \nabla^2 \partial_t \phi - f'_b(\phi) \partial_t \phi, \text{ in } \Omega_t, \\ \partial_t \zeta &= \int_{\Omega} \partial_t \phi d\mathbf{x}, \text{ in } \Omega_t, \\ \partial_t \xi &= \int_{\Omega} (-\gamma \Delta \phi + f'(\phi)) \partial_t \phi d\mathbf{x}, \text{ in } \Omega_t. \end{cases}$$

The free energy of the system is given by

$$(91) \quad F = \int_{\Omega} \frac{1}{2} q^2 d\mathbf{x} + \frac{1}{2} \zeta^2 + \frac{1}{2} \xi^2.$$

The transport equations of the variables are summarized as follows

$$(92) \quad \begin{cases} \partial_t \phi &= -\gamma \nabla^2 q + \gamma f'_b(\phi) q - \zeta - g(\phi) \xi, \text{ in } \Omega_t, \\ \partial_t q &= \nabla^2 \partial_t \phi - f'_b(\phi) \partial_t \phi, \text{ in } \Omega_t, \\ \partial_t \zeta &= \int_{\Omega} \partial_t \phi d\mathbf{x}, \text{ in } \Omega_t, \\ \partial_t \xi &= \int_{\Omega} g(\phi) \partial_t \phi d\mathbf{x}, \quad g(\phi) = -\gamma \Delta \phi + f'(\phi), \text{ in } \Omega_t. \end{cases}$$

A second order, energy stable numerical scheme is given by the following.

**Scheme 5.10.** Set  $\phi^0 = \phi|_{t=0}$ ,  $q^0 = \sqrt{\frac{\gamma_b}{2}} (\Delta \phi^0 - f_b(\phi^0))$ ,  $\zeta^0 = \xi^0 = 0$ . For all  $n \geq 0$ , given  $(\phi^n, q^n, \zeta^n, \xi^n)$  and  $(\phi^{n-1}, q^{n-1}, \zeta^{n-1}, \xi^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1}, \zeta^{n+1}, \xi^{n+1})$  by the following scheme

$$(93) \quad \begin{cases} \delta_t^+ \phi^n &= -\gamma \nabla^2 q^{n+\frac{1}{2}} + \gamma f'_b(\bar{\phi}^{n+\frac{1}{2}}) q^{n+\frac{1}{2}} - \zeta^{n+\frac{1}{2}} - g(\bar{\phi}^{n+\frac{1}{2}}) \xi^{n+\frac{1}{2}}, \text{ in } \Omega_t, \\ \delta_t^+ q^n &= \left( \Delta - f'_b(\bar{\phi}^{n+\frac{1}{2}}) \right) \delta_t^+ \phi^n, \text{ in } \Omega_t, \\ \delta_t^+ \zeta^n &= \int_{\Omega} \delta_t^+ \phi^n d\mathbf{x}, \text{ in } \Omega_t, \\ \delta_t^+ \xi^n &= \int_{\Omega} g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n d\mathbf{x}, \text{ in } \Omega_t, \end{cases}$$

This scheme has been developed and investigated by Yang and Ju in [59].

**5.1.4. Molecular beam epitaxial growth model.** We next discuss another Allen-Cahn type phase field model for molecular beam epitaxial(MBE) growth and its energy stable numerical approximation. Let  $\phi(x, t)$  be the epitaxy surface height with  $x \in \Omega$ , where  $\Omega$  is the material's domain  $\in R^d, d = 2, 3$ . Under typical conditions for the MBE growth, the height evolution equation is given by a phase field model of relaxation dynamics (see, e.g., [33]):

$$(94) \quad \phi_t = -M\mu,$$

where  $M$  is the mobility coefficient and chemical potential  $\mu = \frac{\delta E}{\delta \phi}$  is the variational derivative of the Ehrlich-Schwobel energy  $E$  (cf. [38, 12]), given by

$$(95) \quad E(\phi) = \int_{\Omega} \left( \frac{\varepsilon^2}{2} (\Delta \phi)^2 + F(\nabla \phi) \right) dx,$$

$F(\mathbf{s})$  is a nonlinear, smooth function of its argument  $\mathbf{s} \in R^d$  and  $\varepsilon$  is a constant (inversely proportional to the size of the system).

For the case of slope selection model, the second term in the free energy is given by

$$(96) \quad F(\nabla\phi) = \frac{1}{4}(|\nabla\phi|^2 - 1)^2.$$

Then, the governing equation for  $\phi$  is given by

$$(97) \quad \phi_t = -M \frac{\delta E(\phi)}{\delta\phi} = -M \left( \varepsilon^2 \Delta^2 \phi - \nabla \cdot ( (|\nabla\phi|^2 - 1) \nabla\phi ) \right).$$

With the periodic boundary condition or any other proper boundary conditions that satisfy the flux-free conditions at the boundary  $\partial_{\mathbf{n}}\phi|_{\partial\Omega} = 0$  and  $\partial_{\mathbf{n}}\Delta\phi|_{\partial\Omega} = 0$ , the model conserves the "total mass"

$$(98) \quad \frac{d}{dt} \int_{\Omega} \phi(\mathbf{x}, t) d\mathbf{x} = 0.$$

where  $\mathbf{n}$  is the outward normal on the boundary.

We introduce the intermediate variable  $q(\phi)$  in terms of  $\phi$ ,

$$(99) \quad q(\phi) = \frac{\sqrt{2}}{2} (|\nabla\phi|^2 - 1), \quad \mathbf{g}(\nabla\phi) = \sqrt{2} \nabla\phi.$$

Then, the free energy for  $F(\nabla\phi)$  is transformed into a quadratic function of  $\phi$  and  $q$ :

$$(100) \quad E_A(\phi, q) = \int_{\Omega} \left( \frac{\varepsilon^2}{2} (\Delta\phi)^2 + \frac{1}{2} q^2 \right) d\mathbf{x},$$

We take the time derivative for the new variable  $q$  to obtain an equivalent governing system of equations:

$$(101) \quad \begin{cases} \phi_t = -M \left[ -\varepsilon \Delta^2 \phi + \nabla \cdot (q \mathbf{g}(\nabla\phi)) \right], \text{ in } \Omega_t, \\ q_t = \mathbf{g}(\nabla\phi) \cdot \nabla\phi_t, \text{ in } \Omega_t, \\ \phi|_{t=0} = \phi_0, \quad q|_{t=0} = \frac{\sqrt{2}}{2} (|\nabla\phi_0|^2 - 1). \end{cases}$$

Applying the EQ method, we obtain an energy stable scheme.

**Scheme 5.11.** Set  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \frac{\sqrt{2}}{2} (|\nabla\phi^0|^2 - 1)$ . Assuming that  $\phi^n, q^n$  are already calculated, we compute  $\phi^{n+1}$  and  $q^{n+1}$  from the following temporal discrete system:

$$(102) \quad \begin{cases} \delta_t^+ \phi^n = -M \left( \varepsilon^2 \Delta^2 \phi^{n+\frac{1}{2}} - \nabla \cdot (q^{n+\frac{1}{2}} \mathbf{g}(\bar{\phi}^{n+\frac{1}{2}})) \right), \\ \delta_t^+ q^n = \mathbf{g}(\bar{\phi}^{n+\frac{1}{2}}) \cdot \nabla \delta_t^+ \phi^n. \end{cases}$$

This model was investigated in [64].

Another commonly used phase field model is the Cahn-Hilliard equation. We next discuss how to discretize it systematically using EQ to arrive at energy stable numerical schemes.

**5.2. Cahn-Hilliard equations.** Given the expression of the free energy  $F(\phi)$ , where  $\phi$  is the phase variable. The Cahn-Hilliard equation is given as follows

$$(103) \quad \partial_t \phi = \nabla \cdot (M(\phi) \nabla \mu),$$

where  $M(\phi)$  is the motility matrix and  $\mu = \frac{\delta F}{\delta\phi}$  is the chemical potential. Here, boundary conditions are either periodic or Neumann boundary conditions

$$(104) \quad \nabla\phi \cdot \mathbf{n} = 0, \quad \nabla \frac{\delta F}{\delta\phi} \cdot \mathbf{n} = 0.$$

The Cahn-Hilliard equation preserves the integral  $\int_{\Omega} \phi d\mathbf{x}$ , where  $\Omega$  is the domain of  $\phi$  in question.

**5.2.1. Phase field model for immiscible binary mixtures.** The phase field model for the binary fluid mixture is given by a Cahn-Hilliard equation, in which the free energy is given by

$$(105) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{4} (1 - \phi^2)^2 \right].$$

The governing equation in the model together with the boundary condition is given by

$$(106) \quad \begin{cases} \partial_t \phi = \nabla \cdot (M(\phi) \nabla \mu), & \text{in } \Omega_t, \\ \mu = -\varepsilon^2 \Delta \phi + \phi^3 - \phi, & \text{in } \Omega_t, \\ \nabla \phi \cdot \mathbf{n} = 0, \quad \nabla \mu \cdot \mathbf{n} = 0, & \text{on } \Omega_t. \end{cases}$$

Using the strategy of EQ, we introduce an intermediate variable

$$(107) \quad q = \frac{1}{\sqrt{2}} (1 - \phi^2), \quad \partial_t q = g(\phi) \partial_t \phi, \quad g(\phi) = -\sqrt{2} \phi$$

to reformulate the Cahn-Hilliard system. The following numerical scheme then follows, which was studied by Guillen and Tierra in [23],

**Scheme 5.12.** Set  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \frac{1}{\sqrt{2}} (1 - (\phi^0)^2)$ , For all  $n \geq 0$ , given  $(\phi^n, q^n)$  and  $(\phi^{n-1}, q^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1})$  via the following scheme

$$(108) \quad \begin{cases} \delta_t^+ \phi^n = \nabla \cdot (M(\bar{\phi}^{n+\frac{1}{2}}) \nabla \mu^{n+\frac{1}{2}}), \\ \mu^{n+\frac{1}{2}} = -\varepsilon^2 \Delta \phi^{n+\frac{1}{2}} + q^{n+\frac{1}{2}} g(\bar{\phi}^{n+\frac{1}{2}}), \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n. \end{cases}$$

**5.2.2. Phase field model with the Flory-Huggins free energy for polymer solutions.** For a polymer solution, the Flory-Huggins free energy is given as follows

$$(109) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\gamma_1}{2} |\nabla \phi|^2 + \gamma_2 \left( \frac{1}{N} \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right) \right],$$

where  $\phi$  is the polymer volume fraction,  $\gamma_1$  controls the strength of the conformational entropy, and  $\gamma_2$  measures the strength of mixing free energy,  $N$  is the polymerization index for the polymer phase ( $\phi = 1$ ), and  $\chi$  the mixing parameter. The transport equation of  $\phi$  is given by

$$(110) \quad \begin{cases} \partial_t \phi = \lambda \Delta \mu, \\ \mu = -\gamma_1 \Delta \phi + \gamma_2 \left( \frac{1}{N} \ln \phi - \ln(1 - \phi) + \frac{1-N}{N} + \chi(1 - 2\phi) \right), \end{cases}$$

where  $\lambda$  is the mobility coefficient.

Following the work in [9], we regularize the logarithmic bulk potential by a  $C^2$  piecewise function. More precisely, for any  $0 < \sigma \ll 1$ , the regularized the bulk free energy density is given by

$$(111) \quad \hat{f}(\phi) = \begin{cases} \frac{\phi}{N} \ln \phi + \frac{(1-\phi)^2}{2\sigma} + (1 - \phi) \ln \sigma - \frac{\sigma}{2} + \chi(\phi - \phi^2), & \text{if } \phi \geq 1 - \sigma, \\ \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi(\phi - \phi^2), & \text{if } \sigma \leq \phi \leq 1 - \sigma, \\ (1 - \phi) \ln(1 - \phi) + \frac{\phi^2}{2\sigma} + \frac{\phi}{N} \ln \sigma - \frac{\sigma}{2} + \chi(\phi - \phi^2), & \text{if } \phi \leq \sigma. \end{cases}$$

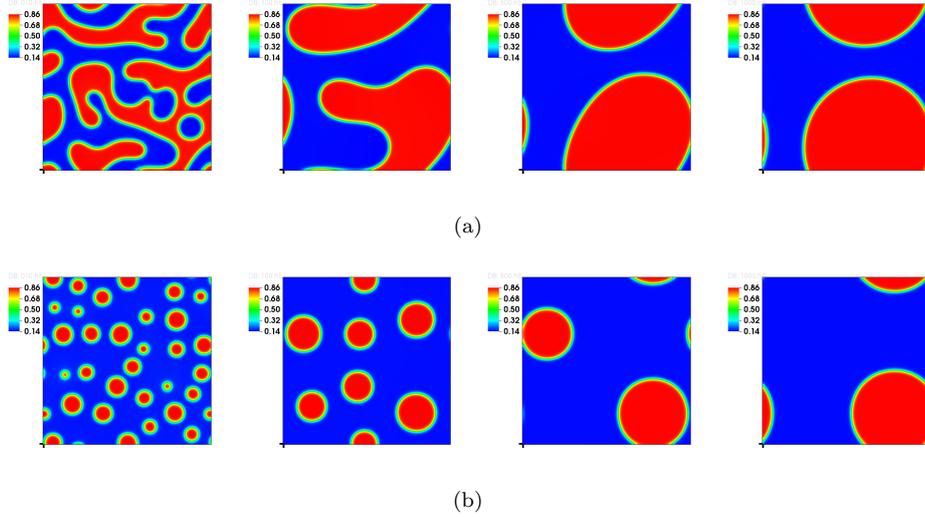


FIGURE 3. Comparison of coarsening and de-mixing dynamics using two different initial profiles. Here, the initial profiles are (A)  $\phi|_{t=0} = 0.5 + 10^{-3}rand(-1, 1)$  and (B)  $\phi|_{t=0} = 0.3 + 10^{-3}rand(-1, 1)$ , where  $rand(-1, 1)$  is random number generated between  $-1$  and  $1$ . The snapshots at time  $t = 1, 10, 50, 100$  are shown respectively.

This effective bulk free energy density is used in numerical simulations in lieu of the Flory-Huggins energy density. To derive the energy stable, linear scheme, We introduce an intermediate variable to quadratize the free energy density

$$(112) \quad q = \sqrt{2(\gamma_2 \hat{f} + A)},$$

where  $A > 0$  is a constant large enough to ensure  $q$  is real valued. Then, we define  $g(\phi) = q'(\phi)$ . Scheme 5.12 gives the second order, linear, energy stable scheme for the Cahn-Hilliard system. A numerical simulation of model (110) using Scheme 5.12 is shown in Figure 3, where we observe coarsening and de-mixing dynamics with respect to different initial profiles of  $\phi$ . For more details, readers are referred to our paper [63, 21].

**5.2.3. Phase-field crystal model.** The phase field crystal model was introduced in [14, 15] in the form of a Cahn-Hilliard equation, in which the free energy is defined by

$$(113) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{1}{4} \phi^4 + \frac{a - \eta}{2} \phi^2 - a |\nabla \phi|^2 + \frac{1}{2} (\Delta \phi)^2 \right],$$

where  $a$  and  $\eta$  are two parameters. The transport equation for  $\phi$  is given by

$$(114) \quad \begin{cases} \partial_t \phi = \nabla \cdot (M_\phi \nabla \mu), \\ \mu = \phi^3 + (a - \eta) \phi + 2a \Delta \phi + \Delta^2 \phi. \end{cases}$$

One can design an energy stable numerical scheme for this model as its free energy only contains an extra quartic term, in addition to the quadratic terms. The bulk energy density can be quadratized using an intermediate variable  $q = \frac{\phi^2}{2}$ . For more details about the energy stable scheme, please refer to the paper by Yang and Han

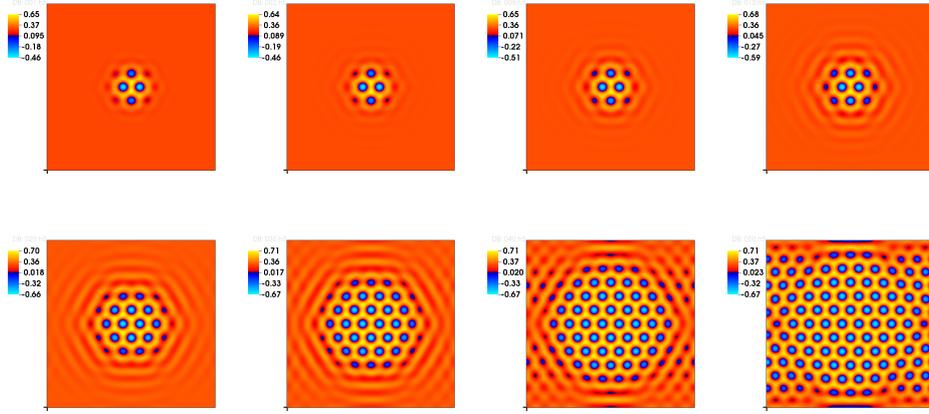


FIGURE 4. Microstructure evolution predicted by the phase field crystal model. Snapshots of the numerical simulation at time  $t = 1, 2, 5, 10, 20, 30, 40, 50$  are shown respectively. Here we use  $256 \times 256$  numerical meshes, and time step  $\delta t = 10^{-3}$ .

in [58]. Using the energy stable linear scheme, we conduct a numerical simulation of crystal growth dynamics. Here we following the initial conditions and parameter choices in [51], i.e.

$$(115) \quad \phi_0(\mathbf{x}) = \bar{\phi} + \omega(\mathbf{x})(A\phi_s(\mathbf{x})), \quad \phi_s(\mathbf{x}) = \cos\left(\frac{q}{\sqrt{3}}y\right)\cos(qx) - \frac{1}{2}\cos\left(\frac{2q}{\sqrt{3}}y\right),$$

where  $q$  represents a wavelength related to the lattice constant,  $A$  represents an amplitude of the fluctuations in density, and the scaling function  $\omega(\mathbf{x})$  is defined as

$$(116) \quad \omega(\mathbf{x}) = \begin{cases} \left(1 - \left(\frac{\|\mathbf{x} - \mathbf{x}_0\|^2}{d_0}\right)^2\right)^2, & \text{if } \|\mathbf{x} - \mathbf{x}_0\| \leq d_0, \\ 0, & \text{otherwise} \end{cases}$$

In the simulation, we choose  $\Omega = [0, \frac{2\pi}{q}a] \times [0, \frac{\sqrt{3}\pi}{q}b]$ ,  $a = 10, b = 12$ ,  $\varepsilon = 0.325$ ,  $\bar{\phi} = \frac{\sqrt{\varepsilon}}{2}$ ,  $A = \frac{4}{5}\left(\bar{\phi} + \frac{\sqrt{15\varepsilon - 36\bar{\phi}^2}}{3}\right)$ ,  $q = \frac{\sqrt{3}}{2}$ .

Numerical simulations of crystal growth at different times are shown in Figure 4.

**5.2.4. Phase-field model for diblock copolymers.** The block copolymer is a linear molecular chain, composed of two or more submolecular chains linked to create a polymer chain. When the sub-chain is made of two (or three) distinct monomer blocks, it is called a diblock (or triblock) copolymer. The phenomenological free energy of a diblock copolymer system is given as follows

$$(117) \quad F(\phi) = \int_{\Omega} \frac{\varepsilon^2}{2} |\nabla\phi|^2 + \frac{1}{4}(\phi^2 - 1)^2 dx + \frac{\alpha}{2} \int_{\Omega} \int_{\Omega} G(\mathbf{x} - \mathbf{y})(\phi(\mathbf{x}) - \bar{\phi})(\phi(\mathbf{y}) - \bar{\phi}) dx dy,$$

where  $G$  is the Green's function, i.e.  $\Delta G = -\delta(\mathbf{x} - \mathbf{y})$  with the periodic boundary condition,  $\bar{\phi}$  is the critical volume fraction of polymer A in the copolymer and  $\delta$  is the Dirac delta function.

The phase variable  $\phi = 1$  denotes polymer A and  $\phi = 0$  polymer B. The transport equation of the phase variable is the Cahn-Hilliard equation given by

$$(118) \quad \begin{aligned} \partial_t \phi &= \lambda \left( \Delta \mu - \alpha(\phi - \bar{\phi}) \right), \\ \mu &= -\varepsilon^2 \Delta \phi + \phi(\phi^2 - 1), \end{aligned}$$

where  $\lambda$  is the motility parameter. Following the EQ approach, we introduce  $q = \frac{1}{2}(\phi^2 - 1)$  and then devise the following second order in time energy stable numerical scheme.

**Scheme 5.13.** *Set the initial condition  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \frac{1}{2}((\phi^0)^2 - 1)$ . Once  $(\phi^n, q^n)$  and  $(\phi^{n-1}, q^{n-1})$  are given, we calculate  $(\phi^{n+1}, q^{n+1})$  via*

$$(119) \quad \begin{cases} \delta_t^+ \phi^n = \lambda(\mu^{n+\frac{1}{2}} + \alpha(\phi^{n+\frac{1}{2}} - \bar{\phi})), \\ \mu^{n+\frac{1}{2}} = -\varepsilon^2 \Delta \phi^{n+\frac{1}{2}} + g(\bar{\phi}^{n+\frac{1}{2}})q^{n+\frac{1}{2}}, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}})\delta_t^+ \phi^n, \quad g(\bar{\phi}^{n+\frac{1}{2}}) = \bar{\phi}^{n+\frac{1}{2}}. \end{cases}$$

The model and its coupled version with hydrodynamics has been studied by Yang and Shen in [8].

**5.2.5. Phase field models of polymer blends.** In this section, we discuss a phase field model describing dynamics of fluctuations and spinodal decomposition in polymer blends of two polymers of equal polymerization indices. The free energy was proposed by De Gennes in 1980 [10],

$$(120) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{a^2}{36\phi(1-\phi)} |\nabla \phi|^2 + \frac{1}{N} (\phi \ln \phi + (1-\phi) \ln(1-\phi)) + \chi \phi(1-\phi) \right],$$

where  $Na^2$  is the mean square end-to-end distance of a polymer chain and  $N$  is the polymerization index, both of which are constants in the model.

We denote

$$(121) \quad \kappa = \frac{a^2}{18\phi(1-\phi)}, \quad f(\phi) = \frac{1}{N} (\phi \ln \phi + (1-\phi) \ln(1-\phi)) + \chi \phi(1-\phi).$$

Then,

$$(122) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\kappa}{2} |\nabla \phi|^2 + f(\phi) \right].$$

The governing system in the phase field model is rewritten into

$$(123) \quad \begin{aligned} \partial_t \phi &= \lambda \Delta \mu, \\ \mu &= -\nabla \cdot (\kappa(\phi) \nabla \phi) + \kappa'(\phi) |\nabla \phi|^2 + f'(\phi). \end{aligned}$$

Following the idea of EQ, we introduce intermediate variables

$$(124) \quad \mathbf{p} = \sqrt{\kappa(\phi)} \nabla \phi, \quad q = \sqrt{2(f+A)},$$

where  $A$  is a constant such that  $f(\phi) + A > 0$  for all feasible  $\phi$ . The new free energy is rewritten into

$$(125) \quad F = \int_{\Omega} \left( \frac{1}{2} \mathbf{p}^2 + \frac{1}{2} q^2 \right) d\mathbf{x}.$$

For simplicity, we denote

$$(126) \quad \mathbf{h}(\phi) = \frac{\partial \mathbf{p}}{\partial \phi} = \frac{\kappa'(\phi)}{2\sqrt{\kappa(\phi)}} \nabla \phi, \quad h(\phi) = \frac{\partial \mathbf{p}}{\partial \nabla \phi} = \sqrt{\kappa(\phi)}, \quad g(\phi) = \frac{\partial q}{\partial \phi} = \frac{f'(\phi)}{\sqrt{2(f(\phi) + A)}}.$$

Then, we obtain the reformulated model

$$(127) \quad \begin{cases} \phi_t = \lambda \Delta \mu, \\ \mu = -\nabla \cdot (h(\phi) \mathbf{p}) + \mathbf{h}(\phi) \cdot \mathbf{p} + g(\phi) q, \\ \partial_t q = g(\phi) \partial_t \phi \\ \partial_t \mathbf{p} = \mathbf{h}(\phi) \partial_t \phi + h(\phi) \nabla \partial_t \phi. \end{cases}$$

Using EQ strategy, we derive a linear, second order in time Crank-Nicolson scheme

**Scheme 5.14.** Set the initial condition  $\phi^0 = \phi|_{t=0}$  and  $q^0 = \sqrt{2(f(\phi^0) + A)}$ ,  $\mathbf{p}^0 = \sqrt{\kappa(\phi^0)} \nabla \phi^0$ . After we have calculated  $(\phi^n, q^n, \mathbf{p}^n)$  and  $(\phi^{n-1}, q^{n-1}, \mathbf{p}^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1}, \mathbf{p}^{n+1})$  via

$$(128) \quad \begin{cases} \delta_t^+ \phi^n = \lambda \Delta \mu^{n+\frac{1}{2}}, \\ \mu^{n+\frac{1}{2}} = -\nabla \cdot (\sqrt{\kappa(\bar{\phi}^{n+\frac{1}{2}})} \mathbf{p}^{n+\frac{1}{2}}) + g_2(\bar{\phi}^{n+\frac{1}{2}}) \nabla \bar{\phi}^{n+\frac{1}{2}} \cdot \mathbf{p}^{n+\frac{1}{2}} + g_1(\bar{\phi}^{n+\frac{1}{2}}) q^{n+\frac{1}{2}}, \\ \delta_t^+ q^n = g_1(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^{n+\frac{1}{2}}, \\ \delta_t^+ \mathbf{p}^n = g_2(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n \nabla \bar{\phi}^{n+\frac{1}{2}} + \sqrt{\kappa(\bar{\phi}^{n+\frac{1}{2}})} \nabla \delta_t^+ \phi^n. \end{cases}$$

This model was initially investigated in [29] and later the EQ approach was applied to it by Yang [55].

**5.2.6. Anisotropic Cahn-Hilliard equation.** There are many classes of free energies in the literature used to study coarsening in anisotropic fluid mixtures. For example, one case is when the surface tension parameter depends on the concentration of the phase volume fraction, instead of being a constant; other cases include anisotropic crystal growth due to anisotropic interactions with the substrate. To these models, the EQ method can be readily applied to yield energy stable, linear schemes [71]. Here, we focus on an example studied in [6] using other numerical approaches.

Consider the free energy density of the following form

$$(129) \quad F = \int_{\Omega} d\mathbf{x} \left[ \gamma(\mathbf{n}) \left( \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{4} (1 - \phi^2)^2 \right) + \frac{\varepsilon \beta}{2} |\Delta \phi|^2 \right],$$

where  $\mathbf{n}$  is the interface normal defined by

$$(130) \quad \mathbf{n} = \frac{\nabla \phi}{|\nabla \phi|}$$

and  $\gamma(\mathbf{n})$  is the anisotropic surface tension coefficient. In two space dimension, a fourfold symmetric anisotropic function is defined by

$$(131) \quad \gamma(\mathbf{n}) = 1 + \alpha \cos(4\theta),$$

where  $\theta$  is the angle formed between  $\mathbf{n}$  and the x-axis. We remark that the last term in the free energy density is a regularization term [6].

The transport equation of the phase variable  $\phi$  is the Cahn-Hilliard equation

$$(132) \quad \begin{aligned} \partial_t \phi &= \lambda \Delta \mu, \\ \mu &= \gamma(\mathbf{n}) f'(\phi) + \gamma'(\mathbf{n}) f(\phi) - \varepsilon^2 \nabla \cdot (\gamma(\mathbf{n}) \nabla \phi) + \gamma'(\mathbf{n}) \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \varepsilon \beta \Delta^2 \phi, \end{aligned}$$

where  $\lambda$  is the constant motility coefficient. Following the EQ strategy, we introduce

$$(133) \quad \mathbf{p} = \varepsilon h(\phi) \nabla \phi, \quad h(\phi) = \sqrt{\gamma(\mathbf{n})}, \quad \partial_t \mathbf{p} = \varepsilon h(\phi) \nabla \partial_t \phi + \varepsilon h'(\phi) \partial_t \phi \nabla \phi$$

and

$$(134) \quad q = \sqrt{\gamma(\mathbf{n})} \frac{\sqrt{2}}{2} (1 - \phi^2), \quad \partial_t q = g(\phi) \partial_t \phi, \quad g(\phi) = \left( -\sqrt{2} \phi h(\phi) + \frac{\sqrt{2}}{2} (1 - \phi^2) h'(\phi) \right).$$

The reformulated Cahn-Hilliard equation is given by

$$(135) \quad \begin{cases} \partial_t \phi = \lambda \Delta \mu, \\ \mu = \varepsilon \eta \Delta^2 \phi + g(\phi) q + \nabla \cdot (\varepsilon h(\phi) \mathbf{p}) + \varepsilon h'(\phi) \nabla \phi \cdot \mathbf{p}, \\ \partial_t q = g(\phi) \partial_t \phi, \\ \partial_t \mathbf{p} = \varepsilon h(\phi) \nabla \partial_t \phi + \varepsilon h'(\phi) \partial_t \phi \nabla \phi. \end{cases}$$

Based on the reformulated equations, we present the linear, second order, energy stable scheme in the following.

**Scheme 5.15.** *Set the initial condition  $\phi^0 = \phi|_{t=0}$ ,  $q^0 = \sqrt{\gamma(\mathbf{n})} \frac{1}{\sqrt{2}} (1 - \phi^0)$ , and  $\mathbf{p}^0 = \varepsilon h(\phi^0) \nabla \phi^0$ . Given  $(\phi^n, q^n, \mathbf{p}^n)$  and  $(\phi^{n-1}, q^{n-1}, \mathbf{p}^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1}, \mathbf{p}^{n+1})$  via*

$$(136) \quad \begin{cases} \delta_t^+ \phi^n = \lambda \Delta \mu^{n+\frac{1}{2}}, \\ \mu^{n+\frac{1}{2}} = \varepsilon \eta \Delta^2 \phi^{n+\frac{1}{2}} + g(\bar{\phi}^{n+\frac{1}{2}}) q^{n+\frac{1}{2}} \\ \quad + \nabla \cdot (\varepsilon h(\bar{\phi}^{n+\frac{1}{2}}) \mathbf{p}^{n+\frac{1}{2}}) + \varepsilon h'(\bar{\phi}^{n+\frac{1}{2}}) \nabla \bar{\phi}^{n+\frac{1}{2}} \cdot \mathbf{p}^{n+\frac{1}{2}}, \\ \delta_t^+ q^n = g(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, \\ \delta_t^+ \mathbf{p}^n = \varepsilon h(\bar{\phi}^{n+\frac{1}{2}}) \nabla \delta_t^+ \phi^n + \varepsilon h'(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n \nabla \bar{\phi}^{n+\frac{1}{2}}. \end{cases}$$

This scheme has not been studied before. We have used a similar approach to investigate the dendritic growth model in [71], which differs from this one in some details.

**5.2.7. Functionalized Cahn-Hilliard equation.** The functionalized Cahn Hilliard model has been used to describe phase separation of an amphiphilic mixture, later several papers have been published to extend the model to study lipid bilayer membrane and pearling bifurcation, formation of pore-like, micelles network structures etc [19, 37, 11]. The free energy in the model is given by

$$(137) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^{-2}}{2} \left( \frac{\delta F_0}{\delta \phi} \right)^2 - \eta F_0 \right],$$

where  $\eta$  is a parameter and  $F_0$  is the surface energy expressed in the bulk free energy form:

$$(138) \quad F_0 = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^2}{2} |\nabla \phi|^2 + \frac{1}{4} (\phi^2 - 1)^2 \right].$$

This free energy quantifies the competition between the surface tension and the surface energy. The governing equation in the Cahn-Hilliard model is given by

$$(139) \quad \begin{cases} \partial_t \phi = \nabla \cdot (M(\phi) \nabla \mu), \\ \mu = 3\varepsilon^{-2} \phi^5 - (4\varepsilon^{-2} + \eta) \phi^3 + (\varepsilon^{-2} + \eta) \phi \\ \quad + \varepsilon^2 \Delta^2 \phi + (2 + \eta \varepsilon^2) \Delta \phi + 6\phi |\nabla \phi|^2 - 6\nabla \cdot (\phi^2 \nabla \phi). \end{cases}$$

Expanding F, we have

$$(140) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon^{-2}}{2} \phi^6 - (\varepsilon^2 + \frac{\eta}{4}) \phi^4 + (\frac{\varepsilon^{-2}}{2} + \frac{\eta}{2}) \phi^2 + \frac{\varepsilon^2}{2} (\Delta \phi)^2 - (1 + \frac{\eta \varepsilon^2}{2}) |\nabla \phi|^2 + 3\phi^2 |\nabla \phi|^2 \right]$$

We rewrite it as follows

$$(141) \quad F = \int_V d\mathbf{x} \left[ \frac{\varepsilon^{-2}}{2} \left( \phi^3 - \left(1 + \frac{\eta\varepsilon^2}{4}\right)\phi \right)^2 + \left( \frac{\varepsilon^{-2}}{2} + \frac{\eta}{2} - \frac{\varepsilon^{-2}}{2} \left(1 + \frac{\eta\varepsilon^2}{4}\right)^2 \right) \phi^2 + \frac{\varepsilon^2}{2} (\Delta\phi)^2 - \left(1 + \frac{\eta\varepsilon^2}{2}\right) |\nabla\phi|^2 + 3\phi^2 |\nabla\phi|^2 \right].$$

Following the EQ strategy, we introduce  $q = \varepsilon^{-1} \left( \phi^3 - \left(1 + \frac{\eta\varepsilon^2}{4}\right)\phi \right)$ ,  $\mathbf{p} = \sqrt{6}\phi\nabla\phi$  to reformulate the Cahn-Hilliard equation into an equivalent system with a quadratic energy density. Then, we derive the linear, energy stable numerical scheme as follows.

**Scheme 5.16.** Set the initial condition  $\phi^0 = \phi|_{t=0}$ ,  $q^0 = \sqrt{\gamma(\mathbf{n})} \frac{1}{\sqrt{2}} (1 - \phi^0)$ , and  $\mathbf{p}^0 = \varepsilon h(\phi^0) \nabla\phi^0$ . Given  $(\phi^n, q^n, \mathbf{p}^n)$  and  $(\phi^{n-1}, q^{n-1}, \mathbf{p}^{n-1})$ , we calculate  $(\phi^{n+1}, q^{n+1}, \mathbf{p}^{n+1})$  via

$$(142) \quad \begin{cases} \delta_t^+ \phi^n = \nabla \cdot (M(\bar{\phi}^{n+\frac{1}{2}}) \nabla \mu^{n+\frac{1}{2}}), \\ \mu = \varepsilon^2 \Delta \bar{\phi}^{n+\frac{1}{2}} + (2 + \eta\varepsilon) \Delta \phi^{n+\frac{1}{2}} + 2a\phi^{n+\frac{1}{2}} + q^{n+\frac{1}{2}} g_1(\bar{\phi}^{n+\frac{1}{2}}) \\ \quad + \sqrt{6} \nabla \bar{\phi}^{n+\frac{1}{2}} \cdot \mathbf{p}^{n+\frac{1}{2}} + \nabla \cdot (\sqrt{6} \bar{\phi}^{n+\frac{1}{2}} \mathbf{p}^{n+\frac{1}{2}}), \\ \delta_t^+ q^n = g_1(\bar{\phi}^{n+\frac{1}{2}}) \delta_t^+ \phi^n, \quad g_1(\phi) = \varepsilon^{-1} (3\phi^2 - 1 - \frac{\eta\varepsilon^2}{4}), \\ \delta_t^+ \mathbf{p}^n = \sqrt{6} \nabla \bar{\phi}^{n+\frac{1}{2}} \delta_t^+ \phi^n + \sqrt{6} \bar{\phi}^{n+\frac{1}{2}} \nabla \delta_t^+ \phi^n. \end{cases}$$

This linear scheme has never been studied. However, we note that some non-linear, convex splitting schemes for this Cahn-Hilliard model have been proposed [18].

**5.3. Phase field models for multi-component material systems.** For phase field models of multiphase materials, there are a few versions. Here, we discuss the one proposed by Boyer [3]. For simplicity, we focus on the three-component model.

**5.3.1. Ternary phase field models.** Here, we use phase variables  $\phi_1, \phi_2, \phi_3$  to label the three distinct phases. The free energy of the multiphase system is defined as follows

$$(143) \quad F = \int_{\Omega} d\mathbf{x} \left[ \sum_{i=1}^3 \frac{3}{8} \Sigma_i \varepsilon |\nabla\phi_i|^2 + \frac{12}{\varepsilon} f(\phi_1, \phi_2, \phi_3) \right],$$

where  $f(\phi_1, \phi_2, \phi_3) = \sum_{i=1}^3 \frac{\Sigma_i}{2} \phi_i^2 (1 - \phi_i)^2 + 3\Lambda \phi_1^2 \phi_2^2 \phi_3^2$ ,  $\Sigma_i$  and  $\Lambda$  are model parameters.

The transport equations of the phase variables are given by

$$(144) \quad \begin{cases} \partial_t \phi_i = \frac{M_0}{\Sigma_i} \Delta \mu_i, \\ \mu_i = -\frac{3}{4} \varepsilon \Sigma_i \Delta \phi_i + \frac{12}{\varepsilon} \frac{\partial f}{\partial \phi_i} + \beta, \quad i = 1, 2, 3, \\ \beta = -\frac{4\Sigma_T}{\varepsilon} \sum_{i=1}^3 \frac{1}{\Sigma_i} \frac{\partial f}{\partial \phi_i}, \quad \frac{3}{\Sigma_T} = \sum_{i=1}^3 \frac{1}{\Sigma_i}. \end{cases}$$

Using the EQ strategy, we introduce

$$(145) \quad q = \sqrt{2(f + A)},$$

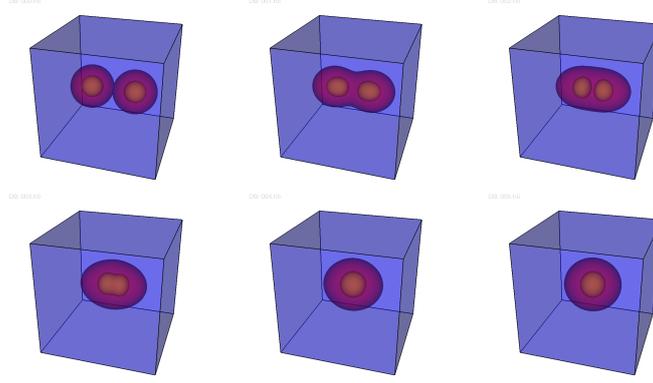


FIGURE 5. Dynamical evolution of a pair of biphasic drops merging in a third fluid matrix. The time step is  $\delta t = 10^{-3}$  and  $128^3$  grid points are used. Snapshots of the numerical approximation are taken at  $t = 0, 1, 2, 3, 4, 5$ . The color in yellow, red, and blue represents the three phases  $\phi_1, \phi_2, \phi_3$ , respectively.

where  $A$  is a nonnegative constant such that  $f(\phi) + A > 0$  for all  $\phi \in \mathbb{R}$ , which is feasible since  $f$  has a lower bound [3]. Then, the model is rewritten into

$$(146) \quad \begin{cases} \partial_t \phi_i = \frac{M_0}{\Sigma_i} \Delta \mu_i, \\ \mu_i = -\frac{3}{4} \varepsilon \Sigma_i \Delta \phi_i + q \frac{\partial q}{\partial \phi_i} + \beta, \quad i = 1, 2, 3, \\ \beta = -\frac{4\Sigma_T}{\varepsilon} \sum_{i=1}^3 q \frac{\partial q}{\partial \phi_i}, \quad \frac{3}{\Sigma_T} = \sum_{i=1}^3 \frac{1}{\Sigma_i}, \\ q_t = \sum_{i=1}^3 g_i(\phi_1, \phi_2, \phi_3) \phi_{i,t}, \quad g_j(\phi_1, \phi_2, \phi_3) = \frac{\partial q}{\partial \phi_j}, \quad j = 1, 2, 3. \end{cases}$$

With the reformulated model, we derive a second order, linear, energy stable numerical scheme as follows

**Scheme 5.17.** Set the initial condition  $\phi_i^0 = \phi_i|_{t=0}$  and  $q^0 = \sqrt{2(f(\phi^0) + A)}$ . Once we have obtained  $(\phi_i^n, q^n)$  and  $(\phi_i^{n-1}, q^{n-1})$ , we calculate  $(\phi_i^{n+1}, q^{n+1})$  via

$$(147) \quad \begin{cases} \delta_t^+ \phi_i^n = \frac{M_0}{\Sigma_i} \Delta \mu_i^{n+\frac{1}{2}}, \\ \mu_i = -\frac{3}{4} \varepsilon \Sigma_i \Delta c_i^{n+\frac{1}{2}} + g_i(\bar{\phi}_i^{n+\frac{1}{2}}) q_i^{n+\frac{1}{2}} + \beta, \quad i = 1, 2, 3, \\ \beta = -\frac{4\Sigma_T}{\varepsilon} \sum_{i=1}^3 q_i^{n+\frac{1}{2}} g_i(\bar{\phi}_i^{n+\frac{1}{2}}), \quad \frac{3}{\Sigma_T} = \sum_{i=1}^3 \frac{1}{\Sigma_i}. \end{cases}$$

This scheme has been investigated in [65]. Here we conduct a new 3D simulation shown in Figure 5. We choose  $L_x = L_y = L_z = 1$  with mesh  $128^3$ , and use the initial condition  $\phi_1 = \frac{1}{2} \left( 1 + \max(\tanh \frac{0.1-R_1}{\varepsilon}, \tanh \frac{0.1-R_2}{\varepsilon}) \right)$ ,  $\phi_2 = \frac{1}{2} \left( 1 + \max(\tanh \frac{0.2-R_1}{\varepsilon}, \tanh \frac{0.2-R_2}{\varepsilon}) \right) (1 - \phi_1)$ ,  $\phi_3 = 1 - \phi_1 - \phi_2$ , where  $R_1 = \sqrt{(x-0.5)^2 + (y-0.6)^2 + (z-0.5)^2}$ ,  $R_2 = \sqrt{(x-0.5)^2 + (y-0.4)^2 + (z-0.5)^2}$ . The parameters are chosen as  $\Sigma_1 = \Sigma_2 = \Sigma_3 = 1$ ,  $\varepsilon = 10^{-2}$ . Figure 5 depicts the 3D numerical simulation of drop fusion dynamics of three phasic material system.

**5.3.2. Cahn-Morral model.** Next, we consider the phase field model for general multiphase fluids. Consider a fluid with  $n$  components and let  $0 \leq \phi(t, \mathbf{x}) \leq 1$

represent the volume fraction of the  $i$ -th component at time  $t$  and location  $\mathbf{x} \in \Omega$ . We denote  $\Phi = (\phi_1, \phi_2, \dots, \phi_n)$  and define the Gibbs simplex as

$$(148) \quad \mathcal{S} = \left\{ \Phi \in \mathbb{R}^n : \sum_{i=1}^n \phi_i = 1, \quad \phi_i \geq 0, i = 1, 2, \dots, n \right\}.$$

The general Cahn-Morral free energy functional is given as follows [47]

$$(149) \quad F(\phi_1, \phi_2, \dots, \phi_n) = \int_{\Omega} \sum_{i=1}^n \frac{\varepsilon}{2} |\nabla \phi_i|^2 d\mathbf{x} + \int_{\Omega} f(\phi_1, \phi_2, \dots, \phi_n) d\mathbf{x}.$$

There are many choices of  $f$ . For instance, one choice is

$$(150) \quad f = -\frac{1}{2} \Phi^T \mathbf{A} \Phi + \theta \sum_{i=1}^n \phi_i \ln \phi_i,$$

where  $\theta$  is a positive constant and  $\mathbf{A} \in \mathbb{R}^{n,n}$  is a symmetric, non-negative definite matrix describing the interaction among the different phases. Another choice is

$$(151) \quad f = \frac{1}{4} \sum_{i=1}^n \phi_i^2 (\phi_i - 1)^2.$$

For instance,

$$(152) \quad \mathbf{A} = -\theta_c (\mathbf{1}\mathbf{1}^T - \mathbf{I}), \quad \theta_c \in \mathbb{R}^+, \mathbf{1} = (1, \dots, 1)^T \in \mathbb{R}^n.$$

When  $n = 3$ , the coefficient matrix is given by

$$(153) \quad \mathbf{A} = -\theta_c \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}$$

The governing equation is derived and given in [28, 47]

$$(154) \quad \begin{cases} \partial_t \phi_i = \Delta \mu_i, & i = 1, 2, \dots, n-1, & \text{in } \Omega_t, \\ \mu_i = -\varepsilon \Delta \phi_i + f_i(\Phi) + \varepsilon \Delta \phi_n - f_n(\Phi), & \text{in } \Omega_t, \\ \nabla \phi_i \cdot \mathbf{n} = 0, \quad \nabla(-\varepsilon \Delta \phi_i + f_i(\Phi)) \cdot \mathbf{n} = 0, & \text{on } \Omega_t. \end{cases}$$

An alternative form of the transport equation system in the phase field model is given by the following when  $n \geq 3$ :

$$(155) \quad \begin{cases} \partial_t \phi_i = \Delta \mu_i, & i = 1, 2, \dots, n, & \text{in } \Omega_t \\ \mu_i = -\varepsilon \Delta \phi_i + f_i(\Phi) - \frac{1}{n} \sum_{j=1}^n \left( -\varepsilon \Delta \phi_j + f_j(\Phi) \right), & \text{in } \Omega_t \\ \nabla \phi_i \cdot \mathbf{n} = 0, \quad \nabla(-\varepsilon \Delta \phi_i + f_i(\Phi)) \cdot \mathbf{n} = 0, & \text{on } \Omega_t. \end{cases}$$

We note that these are two different phase field models which are not equivalent when number of phases exceeds 2. Using the EQ method, we can develop linear, second order, energy stable schemes for these phase models [22]. We will not elaborate further for this class of phase field models.

**5.3.3. Phase field models involving surfactant at fluid interfaces.** Insoluble surfactant is the type of materials that attaches at the interface of two immiscible fluids to reduce the interfacial tension. There are many diffuse interface models for immiscible binary fluid mixtures accounting for surfactant [48, 49, 27]. An overview about this topic can be found in [30]. Here we give a brief introduction of some models in this class and present some energy stable numerical schemes.

When one ignores the hydrodynamic effect, a reduced model to study the phase transition with surfactant emerges, given by

$$(156) \quad \begin{cases} \partial_t \phi + \nabla \cdot (\phi \mathbf{v}) = \nabla \cdot (M_\phi \nabla \mu_\phi), \\ \partial_t \psi + \nabla \cdot (\psi \mathbf{v}) = \nabla \cdot (M_\psi \nabla \mu_\psi), \end{cases}$$

where  $\phi$  is the volume fraction of a fluid and  $\psi$  is the concentration of the surfactant.

The free energy for the material system is consisted of two parts and given by

$$(157) \quad F = \int_{\Omega} d\mathbf{x} \left[ \frac{\varepsilon}{2} |\nabla \phi|^2 + \frac{1}{4} (\phi^2 - 1)^2 + G(\phi, \psi) \right],$$

where the first part is the interfacial energy of the two immiscible fluid mixture, and the second part is the free energy due to the surfactant. There are a couple choices for the surfactant contribution to the free energy  $G(\phi, \psi)$ .

- The following free energy part was proposed in [48]

$$(158) \quad G(\phi, \psi) = -\frac{s\psi}{2} |\nabla \phi|^2 + \frac{\varepsilon\psi}{2} |\nabla \psi|^2 + \frac{w}{2} \psi \phi^2 + \frac{\lambda}{2} \psi^2 + \frac{v\psi}{2} (\Delta \phi)^2.$$

where  $s, \varepsilon, w, \lambda, v$  are model parameters.  $s$  is a parameter measuring the reduction of surface tension at the presence of the surfactant;  $\varepsilon$  is the strength of conformation entropy for the surfactant;  $v$  measures the surfactant induced regularization; and  $\omega$  and  $\lambda$  are two model parameters for the bulk part of free energy of the surfactant.

- In [50], another form of  $G$  was proposed as follows

$$(159) \quad G(\psi, \phi) = -\frac{s\psi}{2} |\nabla \phi|^2 + \frac{w}{2} \psi \phi^2 + \lambda \left[ \psi \ln \psi + (1 - \psi) \ln(1 - \psi) \right],$$

where the first term represents that reduction of surface tension at the presence of surfactant, the second term is to avoid the surfactant from colliding, and the last term denotes the entropy of the surfactant.

- In [49], a different form of  $G$  was proposed as

$$(160) \quad G(\phi, \psi) = \frac{s}{2} (\psi - |\nabla \phi|)^2 + \lambda \left[ \psi \ln \psi + (1 - \psi) \ln(1 - \psi) \right],$$

where the first term makes the surfactant to concentrate on the interface and the second term is the entropy of surfactant.

- In [27], yet another  $G$  was proposed as

$$(161) \quad G(\psi, \phi) = -\frac{s\psi}{2} |\nabla \phi|^2 + \frac{d}{2} (\Delta \phi)^2 + \frac{w}{2} \psi^2 (\psi - \psi_0)^2,$$

where the first term represents the reduction of surface tension by surfactant, the second term is a stabilizing term, and the last term controls the coarsening of surfactant using a double well potential.

We remark that Yang and Ju studied (160) in [60], and Yang studied (161) partially in [56]. Both studies focused on thermodynamics effects for simplicity. Applying the EQ strategy, one can design linear schemes for the models. For instance, for the free energy given in (160), we introduce

$$(162) \quad q_1 = \psi - |\nabla \phi|, \quad q_2 = \sqrt{\psi \ln \psi + (1 - \psi) \ln(1 - \psi) + A},$$

such that the free energy is reformulated into a quadratic form. We omit the details of the numerical development, which can be readily derived following the general framework discussed in this paper. Interested readers are referred to the references [56, 60] for details.

## 6. Conclusions

We have presented the energy quadratization method as a general and systematic strategy for developing numerical approximations to thermodynamically consistent model, especially, the dissipative models. This approach is closely related to the variational and dissipative property of the governing system of equations in the models. It exploits the mathematical structure of the models to arrive at linear, second order, energy stable numerical schemes. After discussing the strategy of applying EQ method for general thermodynamically consistent models, we apply it to numerically approximate a plethora of thermodynamically consistent phase field models. Through the examples, we have demonstrated that the EQ strategy is so general and easy-to-learn that it can become a general practice for everyone who would like to develop efficient numerical approximations to thermodynamically consistent models.

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