Pressure-Controlled Dynamic Equation for the Phase-Field Crystal Method

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Abstract. The phase-field crystal (PFC) method is a density-functional-type materials model with atomic resolution on diffusive timescale, and has been shown to be a robust tool for modeling materials phenomena. In this study, a pressure-controlled dynamic equation for the PFC model was developed to describe a system under externally applied hydrostatic pressure. The formulation is based on the established frameworks including the thermodynamics of solids, kinematics of deformation, and non-equilibrium thermodynamics. The proposed equation exhibits the tensile and compressive deformation rates that are different from those from the recently-proposed pressure-controlled dynamic equation. The derivation in this work also provides a framework that can be readily extended to describe a more complex system such as multi-component solid under non-hydrostatic stress.

1. Introduction

With increasing computing performance and availability, computational materials study has become a promising alternative to experimental study in terms of expanding our understanding of materials behavior and providing insight into new phenomena. Among wide ranges of available computational materials techniques, the phase-field crystal (PFC) method [1], has shown to be a robust materials modeling tool. The appeal of the PFC method is that the model exhibits atomic-scale resolution while operating on diffusive timescale, which has advantages over the conventional phase field model in terms of accuracy and self-consistency, and over other atomistic models in terms of computational expense. Such advantages result in numerous applications of the PFC method in describing materials phenomena such as liquid-solid transition, elasticity, plasticity, dislocation dynamics, and crack propagation (see Ref. [2] for comprehensive review in this topic).

The original formulation of the PFC method describes non-equilibrium behavior of a system through the minimization of the free energy under controlled temperature, mass, and volume. Due to the controlled-volume condition, the pressure is naturally not independent and cannot be directly controlled. Although this controlled-volume condition is applicable to many situations, it is often more experimentally relevant to simulate materials behavior under a pressure-controlled condition. Recently, Kocher and Provatas [3] proposed the scheme where the pressure-controlled dynamic equation is added to the PFC formulation to control the (internal) pressure through the specified external pressure. Although this equation can be successfully used to obtain equilibrium

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states of a system, the validity of the non-equilibrium behavior from this equation needs to be investigated due to certain postulations that might not be fully consistent with the established non-equilibrium thermodynamic framework.

Therefore, in this work, we proposed an alternative pressure-controlled dynamic equation that is consistent with the non-equilibrium thermodynamic framework. The equation is based on the thermodynamic description of solids by Larché and Cahn [4], the balance laws and kinematics of deformation from the work by Mishin et al. [5], the balance law from the Reynolds transport theorem [6,7], and the linear relations between driving forces and fluxes from the classical irreversible thermodynamics [7,8]. The result shows that the equation proposed in this work exhibits higher (lower) deformation rate under tensile (compressive) deformation than that exhibited by the equation by Kocher and Provatas [3]. Moreover, the derivation presented in this work provides a framework that can be readily extended to describe a more complex situation such as a multi-component system under non-hydrostatic stress.

The paper is organized as follows. In Section 2, we provide background information on the PFC method and the pressure-controlled dynamic equation recently proposed by Kocher and Provatas [3]. In Section 3, we present the derivation of the alternative pressure-controlled dynamic equation and show the comparison between the proposed and the original equations in Section 4. In Section 5, we provide a summary of our work.

2. PFC Method
The central part of the PFC method is the expression of the Helmholtz free energy which is written in terms of dimensionless quantities [9]:

$$ F = \int_V f \, d\vec{r}, \quad f = \rho \left( -\epsilon + \left( 1 + \nabla^2 \right)^2 \right) \rho + \rho^4. $$

(1)

where $f$ is the free energy density, $\rho$ is the atomic number density field, $\epsilon$ is the model parameter related to temperature. The evolution of $\rho$ is driven by dissipative dynamics through the conserved Cahn-Hilliard equation:

$$ \frac{\partial \rho}{\partial t} = \nabla^2 \mu \equiv \nabla^2 \left( \frac{\delta F}{\delta \rho} \right), $$

(2)

where $\mu = \delta F/\delta \rho$ is the chemical potential and can be obtained from the variational derivative of $F$ with respect to $\rho$. The evolution equation (2) evolves the system along the free-energy-minimizing path under fixed temperature, mass and volume (or computational domain). This indicates that the (internal) pressure, the conjugate variable to the volume, is not independent. To provide a more direct control over the internal pressure, Kocher and Provatas [3] proposed an evolution equation for the volume or the pressure-controlled dynamic equation:

$$ \frac{dV}{dt} = M \left( \bar{P}_{\text{int}} - \bar{P}_{\text{ext}} \right), $$

(3)

where $\bar{P}_{\text{int}} = (1/V) \int_V (-f + \mu \rho) \, d\vec{r}$ is the averaged internal pressure, $\bar{P}_{\text{ext}}$ is the externally applied pressure, and $M$ is the mobility. The above equation provides a driving force for the system to deform (change in $V$) to minimize $\bar{P}_{\text{int}} - \bar{P}_{\text{ext}} \equiv \Delta \bar{P}$. If $\Delta \bar{P} > 0$, the system undergoes tensile deformation while $\Delta \bar{P} < 0$ results in compressive deformation.

3. Derivation of the Alternative Pressure-Controlled Dynamic Equation
3.1. Thermodynamics of Solids
We first introduce the thermodynamic description of solids proposed by Larché and Cahn [4] which considers the solids as networks of lattices occupied by atomic species and vacancies.
For a hydrostatically-stressed, single-component solid, the number of lattices sites \( N_L \) can be written as

\[
N_L = N_A + N_v,
\]

where \( N_A \) and \( N_v \) are the numbers of lattices occupied by the atomic species and vacancies, respectively. The internal energy, \( E \), is then postulated to have the following functional dependence: \( E(S, V, N_A, N_v) \), where \( S \) is the entropy and \( V \) is the volume. We can then write the differential of \( E \) as [10]

\[
dE = Ts dS - P dV + \mu_A dN_A + \mu_v dN_v,
\]

where \( T \) is temperature, \( \mu_A \) and \( \mu_v \) are the chemical potentials. Next, we consider the energy density \( e_V' = E/V' \), where \( V' \) is the volume at the undeformed state. It can be shown using the standard thermodynamic relationships such as the Euler relation and Gibbs-Duhem equation that [10]

\[
de_V' = T ds_V' - P J dJ + \mu_A e d\rho_A,
\]

where \( s_V' = S/V' \), \( \rho_A' = N_A/V' \), \( J = V/V' \), and \( \mu_A' = \mu_A - \mu_v \). In arriving at the expression for \( de_V' \), we use the assumption that the network is conserved or \( \rho_A' + \rho_v' = \rho_L' \equiv \text{Constant} \), where \( \rho_v' = N_v/V' \) and \( \rho_L' = N_L/V' \). Alternative to \( e_V' \) which is defined by the undeformed volume (Lagrangian frame), we can define \( e_V = E/V = e_V'/J \) which is the energy density defined by the deformed volume (Eulerian frame). By using the transformations, \( e_V' = J e_V \), \( \rho_A' = J \rho_A \), and \( s_V' = J s_V \), we obtain the differential of \( e_V' \):

\[
de_V = T ds_V - \left( \frac{P + f_v - \mu_A e}{J} \right) dJ + \mu_A e d\rho_A,
\]

where \( f_v = e_V - T s_V \) is the Helmholtz free energy density (Eulerian frame). Finally, we rearrange the expression of \( de_V' \) to arrive at the differential of \( s_V' \):

\[
T ds_V = de_V + \left( \frac{P + f_v - \mu_A e}{J} \right) dJ - \mu_A e d\rho_A.
\]

3.2. Balance Equations

Here, we introduce the balance equations for mass, internal energy and entropy. We centralize the description of deformation by using a lattice velocity field, \( \vec{v}_L \), which is the velocity of the imaginary network of indestructible sites called “markers” [5]. Consequently, the relationship between the lattice material time derivative and the partial derivative can be written as

\[
\frac{dL}{dt} = \frac{\partial}{\partial t} + \vec{v}_L \cdot \nabla.
\]

Let us first consider the mass balance equation. In the absence of site creation and annihilation, the density of the material species \( i \), where \( i \) can be \( A \) or \( v \), changes through the equation:

\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}_L + J_{i}^L) = 0,
\]

where \( J_{i}^L \) is the flux of the species \( i \) relative to the lattice. Using equation (9), we arrive at [5]

\[
\frac{dL \rho_i}{dt} + \rho_i \nabla \cdot \vec{v}_L + \nabla \cdot \vec{J}_i^L = 0.
\]
For the energy balance equation, we first consider the fact that the total energy of the system comprises of the internal, kinetic, and potential energies; however, the latter two can be neglected if the system is stationary and is not influenced by an external field such as gravity. Therefore, the balance equation for the energy is [5]

$$\frac{\partial e_V}{\partial t} + \nabla \cdot \left( e_V \vec{v}_L + \vec{J}_E^I \right) = \dot{\omega},$$  \hspace{1cm} (12)

where $\dot{\omega}$ is the rate of mechanical work per unit volume and $\vec{J}_E^I$ is the flux of the internal energy relative to the lattice. In the absence of an applied field and the assumption of the mechanical equilibrium, we have $\dot{\omega} = \sigma : \nabla \vec{v}_L$, where $\sigma$ is the Cauchy stress tensor. Furthermore, for a system under hydrostatic pressure, $P_{\text{ext}}$, the stress tensor becomes $\sigma = -P_{\text{ext}}I$, where $I$ is the identity tensor. The mechanical work then reduces to $\dot{\omega} = -P_{\text{ext}} \nabla \cdot \vec{v}_L$. Using the expression for $\dot{\omega}$ and equation (9), the energy balance equation becomes [5]

$$\frac{d L e_V}{d t} + e_V \nabla \cdot \vec{v}_L + \nabla \cdot \vec{J}_L^E = -P_{\text{ext}} \nabla \cdot \vec{v}_L.$$  \hspace{1cm} (13)

Lastly, the entropy balance is postulated to be [5]

$$\frac{\partial s_V}{\partial t} + \nabla \cdot \left( s_V \vec{v}_L + \vec{J}_S^L \right) = \dot{s},$$  \hspace{1cm} (14)

where the entropy change is affected by the entropy flux relative to the lattice, $\vec{J}_S^L$, and entropy generation, $\dot{s}$, due to irreversibility. Using equation (9), we arrive at [5]

$$\frac{d L s_V}{d t} + s_V \nabla \cdot \vec{v}_L + \nabla \cdot \vec{J}_S^L = \dot{s}.$$  \hspace{1cm} (15)

### 3.3. Entropy Production

In this section, we derive the expression for the entropy production, $\dot{s}$, which will be used to identify the corresponding flux and force for the phenomenological relation in the next subsection. We consider the fundamental equation (8) derived earlier and replace the differential with the lattice material time derivative to obtain

$$T \frac{d L s_V}{d t} = \frac{d L e_V}{d t} + \left( \frac{P + f_V - \mu_{Av} \rho_A}{J} \right) \frac{d L J}{d t} - \frac{\mu_{Av} d L \rho_A}{dt}.$$  \hspace{1cm} (16)

Using the balance equations (11) and (13), and the identity $d L J / d t = J \nabla \cdot \vec{v}_L$, we arrive through lengthy but straightforward derivation

$$\frac{d L s_V}{d t} + s_V \nabla \cdot \vec{v}_L + \nabla \cdot \vec{J}_S^L = -\vec{J}_Q^T \cdot \frac{\nabla T}{T^2} - \vec{J}_A^T \cdot \frac{\nabla \mu_{Av}}{T} + \left( P - P_{\text{ext}} \right) \frac{\nabla \cdot \vec{v}_L}{T},$$  \hspace{1cm} (17)

where $\vec{J}_Q^T = T \vec{J}_S^L = \vec{J}_E^I - \mu_{Av} \vec{J}_A^T$ is the heat flux relative to the lattice. Compared the above equation with equation (15), we can identify the entropy production to be

$$T \dot{s} = -\vec{J}_Q^T \cdot \frac{\nabla T}{T} - \vec{J}_A^T \cdot \nabla \mu_{Av} + \nabla \cdot \vec{v}_L (P - P_{\text{ext}}).$$  \hspace{1cm} (18)

Following Ref. [11], the form of the above equation allows us to identify that one of the fluxes is $\nabla \cdot \vec{v}_L$ and the corresponding force is $P - P_{\text{ext}}$. 
3.4 Phenomenological Relations and Pressure-Controlled Dynamic Equation

Based on the classical irreversible thermodynamics framework, it is postulated that the forces and fluxes are related by the phenomenological (linear) law [12]:

\[ J_\alpha = \sum_\beta L_{\alpha\beta} X_\beta, \] (19)

where \( J_\alpha \) represents thermodynamic fluxes, \( X_\beta \) represents thermodynamic forces and \( L_{\alpha\beta} \) represents phenomenological coefficients. Using the assumption of symmetry properties of materials [5], the linear law reduces to

\[ J_\alpha = L_{\alpha\alpha} X_\alpha. \] (20)

Considering the flux and force identified in the previous subsection, we can write the phenomenological relation as

\[ \nabla \cdot \bar{v}_L = L_P \cdot (P - \bar{P}_{ext}). \] (21)

where \( L_P \) is the phenomenological coefficient. From the Reynolds transport theorem [6, 7], we can write the balance law as

\[ \frac{dV}{dt} = \int_V (\nabla \cdot \bar{v}_L) d\vec{r}. \] (22)

Substituting equation (21) into equation (22), we finally arrive at the pressure-controlled dynamic equation:

\[ \frac{dV}{dt} = L_P \int_V (P - \bar{P}_{ext}) d\vec{r}. \] (23)

4. Numerical Results

To highlight the difference between equation (3) (referred to as the KP equation) and equation (23) (referred to as the EP equation), we set \( M = L_p V' \) (time scaling) and rearrange the KP equation to obtain \( dJ/dt = L_P \left( \bar{P}_{int} - \bar{P}_{ext} \right) = L_P \Delta \bar{P}, \) where \( J = V/V' \) and \( V' \) is the volume at the initial state. For the EP equation, we assume that \( P = -f + \mu \rho \) and thus the EP equation becomes \( dJ/dt = J L_P \left( \bar{P}_{int} - \bar{P}_{ext} \right) = J L_P \Delta \bar{P}. \) From these alternative expressions of the KP and EP equations, one can see the extra \( J \) factor in the right-hand side of the EP equation. This extra factor causes the rate of deformation \( (dJ/dt) \) from the EP equation to be different from that of the KP equation. For tensile deformation from the initial state \( (J(0) = 1) \), one can see that \( J(t) > 1 \) and the deformation rate from the EP equation will be higher than that from the KP equation. On the other hand, for compressive deformation, \( J(t) < 1 \) and the deformation rate from the EP equation will be lower than that from the KP equation. This behavior can also be shown from numerical calculations in figure 1. In figure 1(a), the system undergoes tensile deformation \( (\Delta \bar{P} > 0) \) and the rate of increase in \( J \) from the EP equation is greater than that from the KP equation. In figure 1(b), the system is subjected to compressive deformation \( (\Delta \bar{P} < 0) \) and the rate of decrease in \( J \) from the EP equation is now less than that from the KP equation.

\[ ^4 \text{See Ref. [13] for a more rigorous definition of the pressure of the solid phase.} \]
5. Summary
In this work, we developed the pressure-controlled dynamic equation for a single-component solid under applied hydrostatic pressure. The derivation is based on the established theories such as the thermodynamics of solids, kinematics of deformation, and non-equilibrium thermodynamics. The resulting equation (EP equation) exhibits non-equilibrium behavior that is different from that from the previously proposed pressure-controlled dynamics equation (KP equation). The deformation rate from the EP equation is higher (lower) than that from the KP equation for the tensile (compressive) deformation. The derivation presented in this work also provides a platform for further extension to describe a more complex system such as multi-component solid under non-hydrostatic stress.

Acknowledgments
This research was supported by the NSTDA-University-Industry Research Collaboration (NUI-RC) program under grant No. NUI-RC-M33-22-59-001D, King Mongkut’s Institute of Technology Ladkrabang (KMITL) Research Fund under Grant No. KREF 015803, Thailand Research Fund (TRF) under Grant No. TRG5880008, and High Performance Computing Services from NECTEC (Thailand). The authors are indebted to Assoc.Prof.Wicharn Techidheera and Dr.Sasawat Mahabunphachai for their helpful discussion and support.

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