



# A phase-field model of anisotropic polycrystalline system and computer simulation – Part I: Theory

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## ABSTRACT

A three-dimensional phase field model of anisotropic polycrystalline solids has been developed. In this model the system's free energy is derived in a generalized form based on Ginzburg–Landau's (GL) theory [1], which is a function of lattice's parameters and electron density. A grain boundary in this model is viewed as a discontinuity of periodic atoms array, represented by the Read–Shockley dislocation representation [3]. The Peierls–Nabarro's dislocation potential [84] has been built into the model to characterize grain boundary's adhesion. Therefore, the model establishes the links between lattice's structure, sub-atomic quantum physics, and the evolutions of grains and grain-boundaries, leading to a meso-scopic constitutive law that governs grains' nucleation, growth, and distortion in a polycrystalline system. This also provides a means to pursue analytical solutions of an alloy's micro-structure's evolution and establishes a framework for corresponding numerical analysis.

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## 1. Introduction

### 1.1. Phase field theory

A challenge to modern computational material science is to quantify the relationships between a material's structural parameters and physics properties at micro and nano-scales as well as the evolutions of its structure and properties at micro and macro-scales.

For a polycrystalline solid, phase field model is a well-known theory to describe diffusion-based physical processes associated with migrations of interfaces in a continuous manner [2,11–15,22–37,41–49,102–106]. Obviously, in order to establish the links between structure, process, and properties in alloys' development, it is vital important to understand the links between sub-atomic physics, crystallography, and a microscaled structural evolution such as grains nucleation, coarsening, or distortion when environmental parameters change. This is the purpose of the research reported hereafter, focusing on grain boundary dynamics.

In this paper a grain boundary refers to a discontinuity of atomic array. When the lattices on both side of such a boundary are made of the same atomic arrays but maybe with different lattice orientation, this boundary coincides to the conventional definition of a “grain boundary”. When the lattices at two sides are made of different atomic species, this grain boundary is an interface defined

in conventional metallurgical analysis, for example, that between an alloy matrix' grain and a secondary-phase particle.

Considering a multi-phase system, denoted as a domain  $\Omega$ , which contains multiple grains. According to the convention of phase-field theory, the physical state of the  $k$ th grain is characterized by its order parameter, denoted as  $\eta_k$ . The physical state of the system is characterized by the amplitude of its free energy, denoted as  $F$ , which, therefore, can be expressed as the following integral over the domain  $\Omega$ :

$$F = \int_{\Omega} \sum_k dV [f(\eta_k, T) + \Gamma(|\nabla \eta_k|, T)] \quad (1)$$

where  $f$  is a function related to the free energy density in bulk phase;  $\Gamma$  is a function of the gradient of the order parameter so it characterizes its fluctuation at grain boundary. On the other hand, according to Ginzburg–Landau theory [1,2], in a time-dependent evolution process, the free energy density  $f$  in the  $k$ th phase (or the  $k$ th grain) is governed by the diffusion equation with respect to the order parameter  $\eta_k$ :

$$\frac{\partial \eta_k}{\partial t} = -\lambda \frac{\partial f(\eta_k, T)}{\partial \eta_k} + \kappa \nabla^2 \eta_k \quad (2)$$

where  $\lambda$  and  $\kappa$  are material's constants. Eq. (2) is a degenerated form of the convection–diffusion equation in continuum fluid mechanics when convection vanishes. Theory and numerical methods to solve this class of partial difference equations have been introduced, for examples, in [5–10,16–19,51–53,80,94].

A polycrystalline metal can also be viewed as a network of grain boundaries. The formation and evolution of grain boundaries may

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occur through at least the following three kinds of processes: a regular metallurgical process from liquid to solid, i.e. nucleation and coarsening; a phase transformation in solid state when an environmental parameter, such as temperature or applied force, varies; a formation of new grain boundaries, for examples, new phase nucleation in solid state or recrystallization in a grain. In recent years, significant progresses can be found in the research of phase-field theories from all perspectives. According to the best knowledge of the author, a list of literatures is given in the end of this article. Surely there are more published works beyond the cited publications. By reviewing published literatures in related leading professional journals and books, for examples, [21–61,63,73,77], one can find increasing interests and needs for further developments within the following respects:

- (i) rational formulation of free energy and its evolution law in anisotropic polycrystalline systems,
- (ii) methodology and procedure to link sub-atomic physics with micro and macro-scopic phenomena for phase transformation and material's failure, and
- (iii) numerical algorithm and procedure for three dimensional anisotropic phase transformation, its evolution, and the underlying grain's and grain boundary's dynamics based constitutive representation.

Focused on these challenges, this study develops an anisotropic phase field model and associated numerical scheme of three-dimensional grain growth in polycrystalline system. In this model a grain boundary is represented as a generalized dislocation zone; mathematic formulation of free energy has been derived by applying Fourier expansion of the quantum scaled electron-density distribution in grains based on Ginzburg–Landau's phase transformation theory. This free energy formulation can be used as a framework to establish a continuum mechanics constitutive law including grains' mechanisms. This paper, i.e. the part I, focuses on theoretic model. Numerical analysis will be discussed in the next paper, i.e. part II of this research [108]. Introductions of the fundamental metallurgy can be found, e.g. in [44,50,76], and in [62,66,83,85,86,89–96] of grain boundaries' research; in [4,64,107] of dislocations.

## 1.2. Notations

Standard notation is used throughout. Boldface symbol denote tensor, the order of which is indicated by the context. Plain symbols denote scalars or a component of a tensor when a subscript is attached. Repeated indices are summed. For example, in three-dimensional Cartesian system the three unit coordinate vectors are  $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ . So a vector  $\mathbf{t}$  is defined as:

$$\mathbf{t} = [t_i] = t_1\mathbf{e}_1 + t_2\mathbf{e}_2 + t_3\mathbf{e}_3 \text{ or } \mathbf{t} = t_i\mathbf{e}_i, \quad i = 1, 2(2D) \text{ or } i = 1, 2, 3(3D) \quad (3)$$

The operations of two order tensors  $\mathbf{a}$  and  $\mathbf{b}$ :  $\mathbf{a} = [a_{ij}] = a_{ij} \mathbf{e}_i\mathbf{e}_j$ ,  $\mathbf{b} = [b_{ij}] = b_{ij} \mathbf{e}_i\mathbf{e}_j$ , are defined as

$$\begin{aligned} \mathbf{a} \cdot \mathbf{b} &= [a_{ik}b_{kj}] = a_{ik}b_{ij}\mathbf{e}_i\mathbf{e}_k \cdot \mathbf{e}_j\mathbf{e}_j = a_{ik}b_{ij}\mathbf{e}_i\mathbf{e}_j\delta_{kj} = a_{ik}b_{kj}\mathbf{e}_i\mathbf{e}_j \\ \mathbf{a}\mathbf{b} &= [a_{ij}b_{kl}] = a_{ij}b_{kl}\mathbf{e}_i\mathbf{e}_j\mathbf{e}_k\mathbf{e}_l \\ \mathbf{a} : \mathbf{b} &= \mathbf{a} \cdot \mathbf{b} = [a_{ij}b_{ij}] = a_{ij}b_{ij} \end{aligned} \quad (4)$$

## 2. Proposed model

### 2.1. Grain boundary and generalized dislocations zone

An evolution of a grain boundary can be viewed as a motion of short-range disordered atoms layer between two long-range or-

dered, different orientated, atomic arrays. An alloy's atomic structure and associated mechanical properties, such as energy barrier against dislocations, play crucial role to such a motion that can be characterized averagely by mesoscopic diffusion when an environmental parameter, such as force or temperature, changes.

Hence, grain boundaries essentially are the discontinuities of periodic atomic arrays, which form a network of the interfaces between crystals. Coarsening represents the motions of these discontinuities driven by temperature field, the potential differences caused by the differences in alloy's chemical composition and lattice structures, as well as imposed force and displacement conditions [2,49,50,66,76]. When such an interface separates crystals from two different species, it usually is a coherent or semi-coherent boundary between matrix and second phase particles, such as precipitates and inclusions; when an interface is between crystals of the same specie, it is a conventional grain boundary. In the following analysis, these two geometric "discontinuities" are termed "grain boundary" in general. From structural viewpoint, these heterogeneities can be simply classified into the following categories according their geometric characters: tilt, mis-orientated, misfitted boundaries, and a combination of them with or without segregated impurities (see Fig. 1a–d) [93].

As a grain boundary is a discontinuity in long-range ordered atomic arrays, it can be formed by inconsistent motions of two adjacent grains that breaks an original periodicity; hence, this discontinuity can be viewed as a "generalized dislocations zone". This zone is an accumulation of dislocations with segregated impurities atoms and empties. The grain boundary's dislocation model was first proposed by Read and Shockley [3] for tilted boundaries. As an extent of Read–Shockley model, this "general dislocation zone" contains the complexities demonstrated in Figs. 1, 2. It is a low-ordered structure, i.e. periodically only along the direction parallel to an interface between grains, which can be considered as a "transient" phase from solid to liquid or between two stable solid states.

An immediate consequence enhanced to the formation of such a generalized dislocation zone is the reduction of adhesion energy. Let  $E^{coh}$  be the atomic coherent energy per unit area in a defect-free crystal and  $E^{gb}$  the actual coherent energy of a grain boundary, then according to Fig. 1, this reduction can be approximately expressed as a linear combination below:

$$E^{gb} = E^{coh} - \Delta E^{tilt} - \Delta E^{misore} - \Delta E^{misfit} - \Delta E^{segregate} \quad (5)$$

where  $\Delta E^{tilt}$ ,  $\Delta E^{misore}$ ,  $\Delta E^{misfit}$ , and  $\Delta E^{segregate}$  are the deductions due to grain boundary tilt, misorientation, misfit, and impurities segregations, respectively. Similarly, when a grain boundary becomes a slip plane ( $\gamma$  plane), the corresponding energy barrier against gliding, denoted as  $\gamma_P^{GB}$ , is:

$$\gamma_P^{GB} = \gamma_P \pm \Delta\gamma^{tilt} - \Delta\gamma^{misore} - \Delta\gamma^{misfit} - \Delta\gamma^{segregate} \quad (6)$$

where  $\gamma_P$  is Peierls' energy barrier in bulk crystal; the rest terms on its right hand side have the similar meaning as the corresponding terms in (5). The reason for the " $\pm$ " in the front of  $\Delta\gamma^{tilt}$  is because certain tilt angle, such as an anti-phase boundary like a twin, may elevate the energy barrier. These deductions in adhesion energy result in the changes of magnitude for the order parameter  $\eta_k$  in Eq. (1).

When a grain boundary is formed by multiple atomic layers, the total adhesion energy per unit area can be expressed as

$$\sum_{\text{number of layer}} E^{gb} = E^{gb} \frac{w}{\bar{b}} \quad (7)$$

where  $w$  is the width of the grain boundary,  $\bar{b}$  is the average of the lattice constants for the species on each side of the boundary.

An advantage of this "generalized dislocation zone" model is the convenience to apply the results of plasticity for analyzing

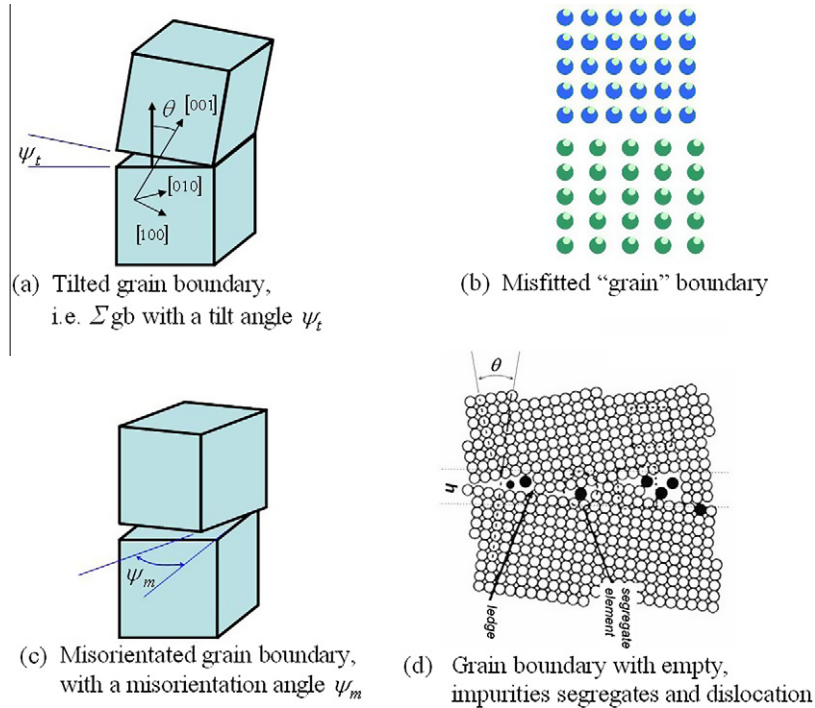
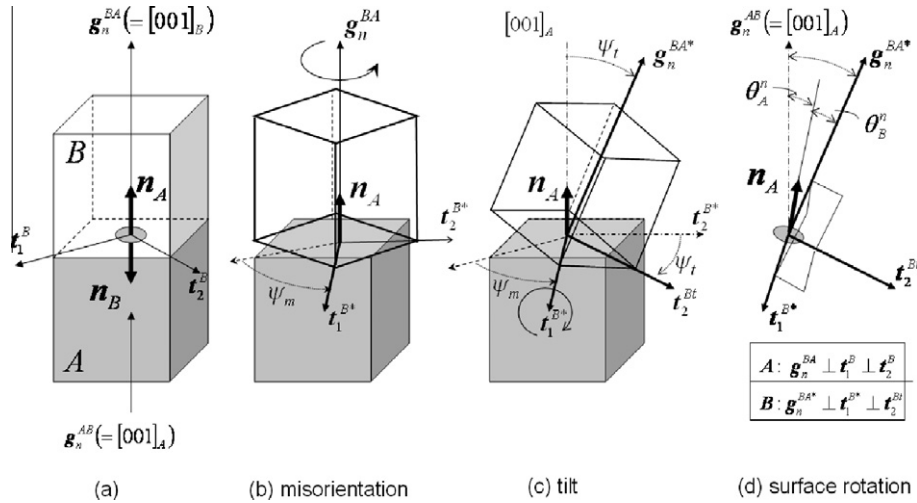


Fig. 1. Grain boundary heterogeneities.



**Fig. 2.** A grain boundary with tilt angle  $\psi_t$  and misorientation  $\psi_m$  can be represented as a superposition of three virtual motions: (a) two grains with coincided crystal orientation initially; (b) an anticlockwise misorientation rotation  $\psi_m$  of the grain  $B$  around  $[001]_A$ ; (c) a clockwise rotation  $\psi_t$  tilted to the vector  $\mathbf{t}_1^B$  orthogonal to  $[001]_B$ ; (d) a rotation of grain boundary surface to its actual orientation. Two Cartesian coordinate systems:  $\{\mathbf{t}_1^B, \mathbf{t}_2^B, \mathbf{g}_n^{BA}\}$  and  $\{\mathbf{t}_1^A, \mathbf{t}_2^A, \mathbf{g}_n^{AB}\}$  are embedded in grain  $B$  and  $A$ , respectively. The  $[001]_B$  is chosen to be the lattice vector with the minimum angle to the grain boundary normal  $\mathbf{n}_A$ . All vectors in (a)–(d) have the same unit length; however, they are plotted with different sizes for easy views.

grain boundary's motion. This is because, according to historical development of solid mechanics, "plasticity" is a theory that describes the average behavior of dislocations-induced atomistic motions by analogy to fluid dynamic theory [79]. The ideally-perfect plasticity, an extreme case of solid, is also an extreme case of viscous flow. This implies an underlying intrinsic connection between these two classes of phenomena, leading to a new avenue to combine well-established dislocation-based plasticity theories and mechanics-based crystallographic analysis, for examples, those listed in [65,78,79,88–92,97–103,107], for the purpose of modeling and simulation of anisotropic grains coarsening.

## 2.2. Geometric representations of grain boundary: Misorientation and tilt

For simplification this paper focuses on single specie polycrystalline system with cubic crystal structure.

A key-issue in grain boundary analysis is to establish an ambiguity-free geometric representation. A three-step superposition model is introduced for this purpose. It starts with two adjacent grains  $A$  and  $B$  with the same lattice orientation, see Fig. 2a. The final position of the grain boundary is obtained by the superposition of the following three virtual motions: (i) an anticlockwise rotation

of the grain B around [001] to obtain misorientation angle  $\psi_m$ , Fig. 2b; (ii) a clockwise rotation  $\psi_t$  around the actual position of  $\mathbf{t}_1^{B*}$  of B to define the tilt, Fig. 2c; (iii) a rotation of the interface surface with normal  $\mathbf{n}_A$  from  $(001)_A$  to its actual position when the angle between  $\mathbf{n}_A$  and  $\mathbf{g}_n^{BA*}$  to be  $\theta_B^n$ , Figs. 2d, where  $\theta_B^n$  is the angle with the minimum value among these between  $\mathbf{n}_A$  and all lattice orientations of grain B.

Similarly, the grain boundary representation can also be obtained through fixing B while performing the virtual motions to the grain A, by which  $\theta_A^n$  is the angle with the minimum value among these between  $\mathbf{n}_B$  and all lattice's orientations of the grain A.

### 3. Electron density-based expression of order parameter and Ginzburg–Landau theory

In phase field theories a challenge is to establish quantitative relationship between the order parameter  $\eta_k$  introduced in (1) and the atomic-electronic structure-based intrinsic energy. To this end, the density-functional theory [68,69] and Ginzburg–Landau's formulation have been applied to derive a governing equation of anisotropic phase-field system. Introduction of Ginzburg–Landau's theory can be found, e.g. in [1,50]; analysis of phase field models can be found in [40,82].

#### 3.1. Electron density and general dislocation zone

According to density functional theory, the physical state of a material is determined by the core structure of atoms and the statistic distribution of electrons' spin and orbits, which can be described by the density distribution of electrons, denoted as  $\rho(\mathbf{r})$ . The associated energy is the integration of  $\rho(\mathbf{r})$  over the system. Therefore, this electron density essentially determines the order of the atomic system. As a long-range ordered crystal can be approximated as an infinite large bulk crystal A, thus the periodic distributed electron density in such a lattice can be expressed in the form of three-dimensional Fourier expansion in the form of Bloch's theorem [81], also, see [68–72,74]

$$\rho^A(\mathbf{r}) = \sum_{\mathbf{K}^A} \bar{u}_{\mathbf{K}^A}^A \exp(i\mathbf{K}^A \cdot \mathbf{r}) \quad (8)$$

where  $\mathbf{K}^A$  are 3-D frequencies-vectors, represented as the reciprocal-lattice basis vectors in bulk crystal;  $\bar{u}_{\mathbf{K}^A}^A$  are the (Fourier) coefficients and  $\mathbf{r}$  is position vector; the superscript “A” denotes the quantities associated with a grain A. The sum in (8) is over all  $\mathbf{K}^A$  including  $\mathbf{K}^A = \mathbf{0}$  because both side of (8) should be the functions of  $\mathbf{r}$ .

When the grain A is defined within a domain  $\Omega_A$ , this study proposes a Bloch-type expression scaled by order parameter  $\eta^A(\mathbf{r})$ :

$$\begin{aligned} \rho^A(\mathbf{r}) &= \sum_{\mathbf{K}^A} \bar{u}_{\mathbf{K}^A}^A(\mathbf{r}) \exp(i\mathbf{K}^A \cdot \mathbf{r}) \\ &= \eta^A(\mathbf{r}) \rho_0 \left( \sum_{\mathbf{K}^A} u_{\mathbf{K}^A}^A \exp(i\mathbf{K}^A \cdot \mathbf{r}) \right) \quad \mathbf{r} \in \Omega_A \end{aligned} \quad (9)$$

where  $\rho_0$  is a constant;  $\eta^A(\mathbf{r})$ , the order parameter associated with grain A, is constant inside the grain but varies at its boundary, see Fig. 3; and  $\bar{u}_{\mathbf{K}^A}^A = \eta^A \rho_0 u_{\mathbf{K}^A}^A$ .

Considering the bicrystal system illustrated in Fig. 3:  $\Omega_{AB} = \Omega_A + \Omega_B$  and  $\Omega_A \cap \Omega_B = \emptyset$ . For simplification, it is presumed that both A and B are the same cubic crystals but with different orientations, corresponding to two built-in Cartesian coordinates  $\{\mathbf{t}_1^B, \mathbf{t}_2^B, \mathbf{g}_n^{BA*}\}$  and  $\{\mathbf{t}_1^A, \mathbf{t}_2^A, \mathbf{g}_n^{AB*}\}$ , respectively, as illustrated in Fig. 2. In the analysis thereafter a “crystal” refers a “grain” and vice versa.

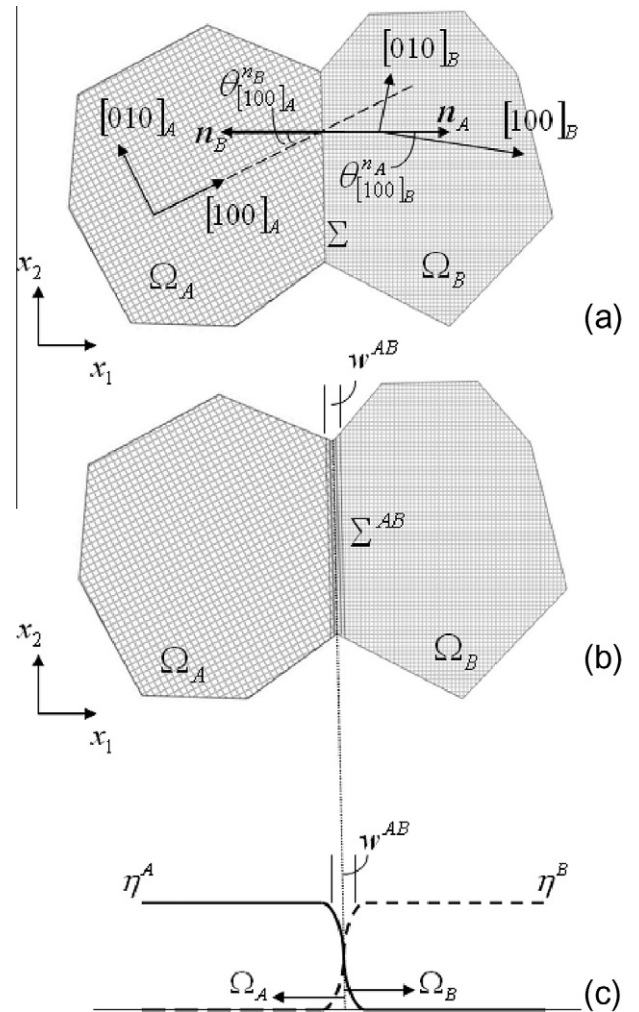


Fig. 3. A bicrystal system with the order parameters  $\eta^A$  and  $\eta^B$ .

Similarly to (9), for the grain B its electron density can also be expressed as:

$$\rho^B(\mathbf{r}) = \eta^B(\mathbf{r}) \rho_0 \sum_{\mathbf{K}^B} u_{\mathbf{K}^B}^B \exp(i\mathbf{K}^B \cdot \mathbf{r}) \quad \mathbf{r} \in \Omega_B \quad (10)$$

Hence, the reciprocal-lattice basis vector  $\mathbf{K}^A$  defined in grain A can be expressed as  $\mathbf{K}^B$  in the coordinate defined in grain B through a two-order rotation tensor  $\mathbf{Q}^{AB}$ :

$$\mathbf{K}^A = \mathbf{Q}^{AB} \cdot \mathbf{K}^B \quad (11)$$

and

$$\mathbf{K}^B = \mathbf{Q}^{BA} \cdot \mathbf{K}^A \quad \text{where } (\mathbf{Q}^{AB})^{-1} = \mathbf{Q}^{BA} \quad (12)$$

$\mathbf{Q}^{AB}$  is determined by the misorientation and tilt angles between two adjacent grains; which, therefore, defines the transformation between two Cartesian systems  $\{\mathbf{t}_1^{B*}, \mathbf{t}_2^{B*}, \mathbf{g}_n^{BA*}\}$  and  $\{\mathbf{t}_1^B, \mathbf{t}_2^B, \mathbf{g}_n^{BA}\}$  in Fig. 2:

$$\mathbf{K}^B = \mathbf{Q}^{BA} \cdot \mathbf{K}^A = (\mathbf{t}_1^{B*} \cdot \mathbf{K}^A) \mathbf{t}_1^{B*} + (\mathbf{t}_2^{B*} \cdot \mathbf{K}^A) \mathbf{t}_2^{B*} + (\mathbf{g}_n^{BA*} \cdot \mathbf{K}^A) \mathbf{g}_n^{BA*} \quad (13)$$

#### 3.2. Free energy and Landau–Ginzburg expansion

The Bloch's expressions (8–10) are under the approximation of “infinite” large periodic structure; whereby an issue is to find the



expression of electron density at a geometrical discontinuity and the corresponding free energy; for example, a grain boundary. The density function theory [68,69] implies that at ground state the system energy is proportional to the square of electron density. On the other hand, in Ginzburg–Landau’s theory [1], the system free energy at a “transient” state between different phases can be expressed in the form as:

$$F = F_0 + \Phi_2 + \Phi_4 + \dots \quad (14)$$

where  $F_0 = F_0(T)$  is a function only depending upon temperature  $T$ . According to [1], the  $\Phi_n$  in (14) can be expressed as the product of electron densities  $\rho^A(\mathbf{r})$ ,  $\rho^B(\mathbf{r})$  satisfying the following restrictions, i.e. when  $\mathbf{r} \in \Omega_A$ :

$$\Phi_n = \sum_{l=1}^n [\rho^A(\mathbf{r})]^l [\rho^B(\mathbf{r})]^{n-l} = \sum_{l=1}^n [\eta^A(\mathbf{r})]^l [\eta^B(\mathbf{r})]^{n-l} \times \sum_{\mathbf{K}^A, \mathbf{K}^B} \left\{ \exp \left\{ i \left[ \sum_{j=1}^l \mathbf{K}_j^A + \sum_{j=l+1}^n (\mathbf{K}_j^B)^T \cdot \mathbf{Q}^{BA} \right] \cdot \mathbf{r} \right\} \right\} \quad (15)$$

where  $\sum_{\mathbf{K}^A, \mathbf{K}^B}$  means the sum of all reciprocal vectors  $\mathbf{K}_l^A, \mathbf{K}_j^B$  in grains  $A$  and  $B$ ; a restriction to (15) is that this summation has to form closed polygons, i.e.

$$\sum_{j=1}^l \mathbf{K}_j^A + \sum_{j=l+1}^n (\mathbf{K}_j^B)^T \cdot \mathbf{Q}^{BA} = 0 \quad (16)$$

In this analysis, the following sufficient conditions of (16) are applied:

$$\sum_{j=1}^l \mathbf{K}_j^A = 0; \quad \sum_{j=l+1}^n (\mathbf{K}_j^B)^T \cdot \mathbf{Q}^{BA} = 0, \quad (17)$$

which ensures the free energy to be invariant when  $\mathbf{r}$  varies inside a grain or moves from one grain to another, allowing the periodic Bloch wave function to fit the discontinuity at grain boundary through the order parameter  $\eta$ . Therefore, (15), hence (14), is in fact a generalized expressions of (1) including the effects of crystal structure and grain boundary through reciprocal vectors under the restriction (16).

### 3.3. Functional Taylor’s expansion

Obviously, on a grain boundary the electron density (9) or (10) deviates from its original periodic distribution in bulk phase. The corresponding change of free energy should be related to the energy barrier against the atomic motion from long-ranged periodic distribution to “dislocated” heterogeneity zone. As suggested in [68,69], functional analysis is an effective way to obtain the free energy with the best accuracy. By this methodology a fluctuation from a reference state of the free energy is treated as functional variation that has the maximum gradient along the direction normal to grain boundary. The stationary solution provides the conditions to determine the coefficients in (15). Analogy to the analysis in [38,39], the functional Taylor’s expansion of (14) over a domain  $\Omega$  is

$$\Delta F = \Delta F_2 + \dots \quad (18)$$

where

$$\Delta F_2 = \frac{1}{2} \int_{\Omega} \int_{\Omega} d\mathbf{r}^3 d\tilde{\mathbf{r}}^3 \frac{\partial^2 F[\rho]}{\partial \rho(\mathbf{r}) \partial \rho(\tilde{\mathbf{r}})} \delta \rho(\mathbf{r}) \delta \rho(\tilde{\mathbf{r}}) \quad (19)$$

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where  $\rho(\mathbf{r})$  can be either  $\rho^A(\mathbf{r})$  or  $\rho^B(\mathbf{r})$  or both of them. The functional variation of  $\rho(\mathbf{r})$  in (9) or (10) can be expressed as a fluctuation from a reference state characterized by  $\tilde{\eta}_0(\mathbf{r})$ :

$$\begin{aligned} \delta \rho(\mathbf{r}) &= \delta \eta(\mathbf{r}) \rho_0 \sum_{\mathbf{K}} u_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{r}) \\ &= (\eta(\mathbf{r}) - \tilde{\eta}_0(\mathbf{r})) \rho_0 \sum_{\mathbf{K}} u_{\mathbf{K}} \exp(i\mathbf{K} \cdot \mathbf{r}) \end{aligned} \quad (20)$$

which means, as presumed, at grain boundary the Bloch’s wave is scaled by the variation of order parameter  $\eta(\mathbf{r})$ .

By choosing the reference state  $\tilde{\eta}_0(\mathbf{r})$  in (20) be the “zero” state, i.e.  $\tilde{\eta}_0(\mathbf{r}) = 0$ , and omitting the terms with the order of  $\mathbf{K}$  higher than 4 in (18), after tedious derivation it can be proven that the secondary variation, i.e. (19), can be expressed as [21,38,40]:

$$\begin{aligned} \Delta F_2 &\approx \frac{k_B T \rho_0}{2} \sum_{\mathbf{K}, \mathbf{K}'} u_{\mathbf{K}} u_{\mathbf{K}'} \delta_{0, \mathbf{K} + \mathbf{K}'} \\ &\times \int_{\Omega} d\mathbf{r}^3 \left[ \frac{\eta_{\mathbf{K}}(\mathbf{r}) \eta_{\mathbf{K}'}(\mathbf{r})}{S[\mathbf{K}]} + \frac{1}{2} \frac{\partial^2 \hat{C}[\mathbf{K}]}{\partial \mathbf{K}^2} \frac{\mathbf{K}^2}{|\mathbf{K}|^2} : (\nabla(\eta_{\mathbf{K}}(\mathbf{r}) \nabla \eta_{\mathbf{K}'}(\mathbf{r}))) \right] \end{aligned} \quad (21)$$

where “ $\nabla$ ” is the gradient operator and the structure factor “ $S(\mathbf{K})$ ”, following the terminology in fluid dynamics, is defined by

$$S(\mathbf{K}) = [1 - \hat{C}[\mathbf{K}]]^{-1} \quad (22)$$

So  $\hat{C}[\mathbf{K}]$ , the Fourier transformation of the “direct correlation function”  $C(\rho_0; \mathbf{r} - \mathbf{r}')$  [38,39], is the only term to be determined.

By analogy with the theory of plasticity, in (19) the functional variation of the electron density plays the similar role as strain whereas the secondary functional variation in (19), or, alternatively, the “direct correlation function”  $C(\rho_0; \mathbf{r} - \mathbf{r}')$  with the Fourier transformation in (21) and (22), is somewhat like a material’s stiffness matrix. This analogy will be discussed further in next subsection.

Applying (16)–(19) from (14) and (15), then dropping the terms with the order of  $\mathbf{K}$  higher than four:

$$\Delta F \approx 2\Phi_2 + 4\Phi_4 \quad (23)$$

### 3.4. Structure factor and direct correlation function

In the fluid dynamic analysis [38,39] the direct correlation function  $C(\rho_0; \mathbf{r} - \mathbf{r}')$  is originally employed to establish the connection between particles based on their positions and the bonding energy in-between, representing “stiffness” against motions of particles in such a system. Thus, an approximation has been made in this study is that, in the area near or on the interface surface between two grains,  $\hat{C}(\mathbf{K})$  can be expressed as a dimensionless Peierls–Nabarro’ potential [84] in the form of Bloch’s wave function as below [64]

$$\hat{C}(\mathbf{K}) = \frac{h_0}{h_p} + \text{Re}\{i \exp[i2\pi b \mathbf{K}]\} \quad (24)$$

where  $b$  is Burger’s vector;  $h_p$  and  $h_0$  are the amplitude of the Peierls’ energy barrier and its mean value, respectively; both  $h_p$  and  $h_0$  are defined as the energy per unit area;  $\text{Re}(f)$  denotes the real part of a complex function  $f$  inside the blanket. For simplification one may take, e.g.

$$h_0 = \frac{h_p}{2} \quad (24a)$$

In (21)  $\hat{C}(\mathbf{K})$  is the Fourier transformation of  $C(\rho_0; \mathbf{r} - \mathbf{r}')$  whereas  $\mathbf{K}$  is the reciprocal vector corresponding to  $\mathbf{r}$ . In cubic crystals there is no essential difference between coordinates and reciprocal coordinates. The second term of (21) has the same structure as its two-order derivatives (or integrals), which actually is the stiffness against edge-like dislocation. The first term of (21), in conjunction with the constant term in the blanket on the right hand of (22), represents the “stiffness” relevant to the change of “dilatation” energy.

By substituting (24) into (22) and (21), applying (17) and omitting the terms with the power higher than the fourth orders of  $\mathbf{K}$ ; then applying (13), the resulted equation, together with (23a), leads to:

$$\Delta F \approx \frac{\rho_0 k_B T}{2} \int F_\eta d\mathbf{x}^3 \quad (25)$$

and

$$F_\eta = \left\{ 2 \sum_{A=A,B} \sum_{K^A} u_{K_\alpha}^A u_{K_\beta}^A \delta_{0,K_\alpha+K_\beta} (\eta^A)^2 + 4 \sum_{A,A_1=A,B} \sum_{K^A} u_{K_\alpha}^A u_{K_\beta}^A \sum_{K^A} u_{K_\gamma}^{A_1} u_{K_\chi}^{A_1} \delta_{0,K_\alpha+K_\beta+K_\gamma+K_\chi} (\eta^A)^2 (\eta^{A_1})^2 + \sum_{A=A,B} \sum_{K^A} u_{K_\alpha}^A u_{K_\beta}^A \delta_{0,K_\alpha+K_\beta} \left( a_{\alpha\beta} (\eta^A)^2 + b_{\alpha\beta} \left( \cos \theta_\alpha^A \cos \theta_\beta^A |\nabla \eta^A|^2 + \mathbf{K}_\alpha \mathbf{K}_\beta : \eta^A \nabla \nabla \eta^A \right) \right) \right\} \quad (25a)$$

where  $u_{K_\alpha}^A$  are the coefficients in (9) or (10) whereas the superscript  $A (=A, B)$  indicates the adjacent grain  $A$  or  $B$ , respectively. The first two rows of (25) are corresponding to the terms in (23a) and the third row to (21); in the latter, after applying (24), the coefficients  $a_{\alpha\beta}$ ,  $b_{\alpha\beta}$  yield:

$$\begin{aligned} a_{\alpha\beta} &= 1 - \frac{h_0}{h_p} - \sin(2\pi b|K_\alpha|) \sin(2\pi b|K_\beta|) \\ b_{\alpha\beta} &= 2\pi^2 b^2 \cos(2\pi b|K_\alpha|) \cos(2\pi b|K_\beta|) \\ \cos \theta_\alpha^A &= \frac{\mathbf{K}_\alpha^A}{|\mathbf{K}_\alpha^A|} \cdot \frac{\nabla \eta^A}{|\nabla \eta^A|} = \frac{\mathbf{K}_\alpha^A}{|\mathbf{K}_\alpha^A|} \cdot \mathbf{n}_A, \quad \cos \theta_\beta^A = \frac{\mathbf{K}_\beta^A}{|\mathbf{K}_\beta^A|} \cdot \mathbf{n}_A \end{aligned} \quad (25b)$$

Notice that  $\nabla \eta^A$  is parallel to  $\mathbf{n}_A$  and

$$\nabla \nabla \eta^A = \nabla \left( \frac{\nabla \eta^A}{|\nabla \eta^A|} |\nabla \eta^A| \right) = \nabla \mathbf{n}_A |\nabla \eta^A| + \mathbf{n}_A \nabla |\nabla \eta^A|$$

**Remark.** In cubic system

$$|\nabla \mathbf{n}_A| = |\nabla \theta| \quad (26a)$$

where  $\theta$  is the angle between  $\mathbf{n}_A$  and a reference direction, e.g., one specified lattice direction, so it can be the tilt angle. Hence, the term  $\eta \nabla \nabla \eta$  in (25) represents the effect of variation in tilt angle, in other word, the change of grain boundary curvature. By substituting (26a) into (25), one can find that the latter has the similar expression as the following free energy expression obtained in [11] but with  $\varepsilon = 0$ :

$$F = \int dV \left[ f(\eta, T) + \frac{\alpha^2}{2} \Gamma^2 (|\nabla \eta|, \theta - \psi) + sg(\eta) |\nabla \theta| + \frac{\varepsilon^2}{2} h(\eta) |\nabla \theta|^2 \right] \quad (26b)$$

where  $\psi$  is the angle between grain boundary surface (originally defined as solid–liquid interface) normal and a specified direction, e.g. the  $x$ -coordinate in Cartesian system;  $\theta$  is a specified orientation of crystalline so  $\nabla \theta$  is the “misfit” angle at grain boundary between grains;  $\Gamma$ ,  $g$ , and  $h$  are functions of  $\eta$  and  $\theta$ , respectively;  $\alpha$ ,  $s$ , and  $\varepsilon$  are coefficients to be determined. The Eq. (26) is termed “WKC model” in this paper since it first systemically presents the free energy as a function of tilt angle  $\psi$ , orientation angle  $\theta$ , and the gradient of  $\theta$ . We will discuss this point again in next section.

Also, the grain boundary (surface) energy per unit area  $A$  can be calculated approximately by applying of (25):

$$\gamma = \frac{\Delta F}{A} \approx \frac{\rho_0 k_B T}{2} \int_w F_\eta dr \quad (27)$$

where the one-dimensional integration  $dr$  is along the direction perpendicular to grain boundary over the length scale “ $w$ ” that represents the thickness of surface layer.

#### 4. Short range interaction: the effects of crystallography

Since in this study a grain boundary is viewed as a disordered generalized dislocation zone between two long-range ordered atoms arrays, the short-ranged atomic interaction may dominate its diffusion and mechanical behavior. Hence, in the expansion (25) the part constructed by the reciprocal vectors that span primitive cell (the first Brillouin zone) may provide satisfactory precision for computing the fluctuation of the free energy. This postulation is termed the “approximation of short-range interaction” in this paper. On other hand, by performing a rotate or a translate operation to the Cartesian’s coordinate in a crystal, i.e. choosing  $\mathbf{K}_\alpha$ ,  $\mathbf{K}_\beta$  from different coordinates, the free energy (14) and its fluctuation (18,25) must be invariant, which leads to the normalization principle suggested by Karma et al.. (Ref. [31] in [26], also see [40]):

$$\begin{aligned} \sum_{K^A} \{ u_{K_\alpha}^A u_{K_\beta}^A \delta_{0,K_\alpha+K_\beta} \} &= \sum_{I_K \in K^A} \frac{u_{2I_K}^A}{\bar{u}_2^A}; \\ u_{2I_K}^A &= \bar{u}_2^A \left( u_{K_\alpha}^A u_{K_\beta}^A \delta_{0,K_\alpha+K_\beta} \right) \end{aligned} \quad (28a)$$

$$\begin{aligned} \sum_{K^A} u_{K_\alpha}^A u_{K_\beta}^A \sum_{K^{A_1}} u_{K_\gamma}^{A_1} u_{K_\chi}^{A_1} \delta_{0,K_\alpha+K_\beta+K_\gamma+K_\chi} &= \sum_{I_K \in K^A} \frac{u_{4I_K}^A}{\bar{u}_4^A}; \\ u_{4I_K}^A &= u_{2I_K}^A \sum_{J_K \in K^{A_1}} \frac{u_{2J_K}^{A_1}}{\bar{u}_2^{A_1}} \end{aligned} \quad (28b)$$

and

$$\bar{u}_2^A = \sum_{I_K \in K^A} u_{2I_K}^A, \quad \bar{u}_4^A = \sum_{I_K \in K^A} \sum_{J_K \in K^{A_1}} \frac{u_{2I_K}^A u_{2J_K}^{A_1}}{\bar{u}_2^{A_1}} \quad (29)$$

whereby an natural choice is to let each coefficients on the right hand side of (28a), (28b) proportional to the projection of the corresponding reciprocal vector onto the outer normal vector of grain boundary surface. This is because the functional Taylor’s expansion (18,19) describes the fluctuation of free energy; the gradient of this fluctuation is the outer normal vector that defines a grain boundary.

As examples, the BCC and FCC crystals, respectively, are picked to compute the coefficients in the proposed free energy formulation. The correlated alloys can be, for examples, iron, and many others [20,66,76].

##### 4.1. BCC crystal

For BCC crystal, the reciprocal vectors corresponding to the lattice vectors that span its primitive cell form a FCC crystal cell. They belong to the group of vectors  $\langle \frac{1}{2b}, \frac{1}{2b}, 0 \rangle$  that contains the following six pairs satisfying (17):

$$\begin{aligned} &\left[ \frac{1}{2b}, \frac{1}{2b}, 0 \right] \text{ and } \left[ -\frac{1}{2b}, -\frac{1}{2b}, 0 \right], \left[ \frac{1}{2b}, 0, \frac{1}{2b} \right] \text{ and } \left[ -\frac{1}{2b}, 0, -\frac{1}{2b} \right] \\ &\left[ 0, \frac{1}{2b}, \frac{1}{2b} \right] \text{ and } \left[ 0, -\frac{1}{2b}, -\frac{1}{2b} \right], \left[ \frac{1}{2b}, -\frac{1}{2b}, 0 \right] \text{ and } \left[ -\frac{1}{2b}, \frac{1}{2b}, 0 \right] \\ &\left[ \frac{1}{2b}, 0, -\frac{1}{2b} \right] \text{ and } \left[ -\frac{1}{2b}, 0, \frac{1}{2b} \right], \left[ 0, \frac{1}{2b}, -\frac{1}{2b} \right] \text{ and } \left[ 0, -\frac{1}{2b}, \frac{1}{2b} \right] \end{aligned} \quad (30)$$

For example, considering the coefficients related to the grain  $A$  in Fig. 3, where  $\theta_{[a,b,c]_A}^{\mathbf{n}_A}$  is the angle between the outer normal vector  $\mathbf{n}_A$  of the grain boundary and  $[a,b,c]$  direction of the crystal  $A$ ; then the coefficients in (25) or (28a) yield

$$\sum_{K^A} \{ u_{K_\alpha}^A u_{K_\beta}^A \delta_{0,K_\alpha+K_\beta} \} = \sum_{I=1}^6 \frac{u_{2I}^A}{\bar{u}_2^A} \text{ for } A = A, B \quad (31a)$$

where

$$\begin{aligned} u_{21}^A &= \left| \cos\left(\theta_{\left[-\frac{1}{2}, -\frac{1}{2}, 0\right]_A}^{n_A}\right) \cos\left(\theta_{\left[\frac{1}{2}, \frac{1}{2}, 0\right]_A}^{n_A}\right) \right|, & u_{22}^A &= \left| \cos\left(\theta_{\left[-\frac{1}{2}, 0, -\frac{1}{2}\right]_A}^{n_A}\right) \cos\left(\theta_{\left[\frac{1}{2}, 0, \frac{1}{2}\right]_A}^{n_A}\right) \right| \\ u_{23}^A &= \left| \cos\left(\theta_{\left[0, -\frac{1}{2}, -\frac{1}{2}\right]_A}^{n_A}\right) \cos\left(\theta_{\left[0, \frac{1}{2}, \frac{1}{2}\right]_A}^{n_A}\right) \right|, & u_{24}^A &= \left| \cos\left(\theta_{\left[\frac{1}{2}, -\frac{1}{2}, 0\right]_A}^{n_A}\right) \cos\left(\theta_{\left[-\frac{1}{2}, \frac{1}{2}, 0\right]_A}^{n_A}\right) \right| \\ u_{25}^A &= \left| \cos\left(\theta_{\left[\frac{1}{2}, 0, -\frac{1}{2}\right]_A}^{n_A}\right) \cos\left(\theta_{\left[-\frac{1}{2}, 0, \frac{1}{2}\right]_A}^{n_A}\right) \right|, & u_{26}^A &= \left| \cos\left(\theta_{\left[0, \frac{1}{2}, -\frac{1}{2}\right]_A}^{n_A}\right) \cos\left(\theta_{\left[0, -\frac{1}{2}, \frac{1}{2}\right]_A}^{n_A}\right) \right| \end{aligned} \quad (31b)$$

and

$$u_{4j}^A = \sum_{l=1}^6 u_{2l}^A u_{2l}^A \quad (31c)$$

#### 4.2. FCC crystal

For FCC crystal, the reciprocal vectors from the vectors that span its primitive cell form a BCC structure; which is a group of vector  $\langle \frac{1}{2b}, \frac{1}{2b}, \frac{1}{2b} \rangle$  where the following four pairs satisfy (17):

$$\begin{aligned} & \left[ \frac{1}{2b}, \frac{1}{2b}, \frac{1}{2b} \right] \text{ and } \left[ -\frac{1}{2b}, -\frac{1}{2b}, -\frac{1}{2b} \right], \left[ \frac{1}{2b}, -\frac{1}{2b}, \frac{1}{2b} \right] \text{ and } \left[ -\frac{1}{2b}, \frac{1}{2b}, -\frac{1}{2b} \right] \\ & \left[ -\frac{1}{2b}, \frac{1}{2b}, \frac{1}{2b} \right] \text{ and } \left[ \frac{1}{2b}, -\frac{1}{2b}, -\frac{1}{2b} \right], \left[ \frac{1}{2b}, \frac{1}{2b}, -\frac{1}{2b} \right] \text{ and } \\ & \left[ -\frac{1}{2b}, -\frac{1}{2b}, \frac{1}{2b} \right] \end{aligned} \quad (32)$$

**Remark.** In [87] the in-plane grain boundary motion between two hexagonal crystals has been studied. By choosing the order parameter in the form of  $\rho = \sum_{i=1}^6 A_i \exp(ikr)$ , the free energy for the separation of grains with coincided [0001] axes has been derived and it has the similar coefficients as these in (30–31).

#### 5. An alternative expression of the free energy (25)

To be consistent with the general expression (1), the free energy (25) can be rewritten in a simplified form as:

$$\Delta F = \frac{\rho_0 k_B T}{2} \int d\mathbf{x}^3 \left\{ f_0(\eta, \theta) + 2\pi^2 b^2 \Gamma(\nabla\eta, \nabla^2\eta, \theta, \psi) \right\} \quad (33)$$

where  $f_0(\eta, \theta)$  and  $\Gamma(\nabla\eta, \nabla^2\eta, \theta, \psi)$  are the functions that have been determined by (25a) up to the difference in constants, after substituting (25b), (26–31) into this formulation; whereby the undetermined constants are the scaling constant  $\rho_0$  and the interval of the integration, i.e. the width of the grain boundary, denoted as “ $w$ ”.

#### 6. Conclusions

This research has derived a mathematic expression of free energy in a developed three-dimensional phase-field model for polycrystalline systems based on Ginzburg–Landau theory, by which the order parameter, introduced in conventional phase-field theory, is utilized as a scaling factor of the electron density of atoms array in a crystal whereas a grain boundary is represented by a “generalized dislocations zone”, see Fig. 2. The difference in lattices’ orientations at a boundary between two adjacent grains is represented as a superposition of individual motion of each grain from an original state that the two grains’ lattice orientations coincide to each other, see Fig. 3, providing a concise representation of the geometric complicity at grain boundaries.

At sub-micro scale, the Peierls–Nabarro’s energy potential (24) has been built into the free energy formulation to determine a “direct structure factor”, which characterizes the orders of atomic ar-

ray in each grain. A variation of this factor’s amplitude represents the amount of dislocations in an originally periodically distributed atom array; so this factor essentially determines the amplitude of free energy and, thus, the energy barrier and associated adhesion at grain boundary.

Thus, for the anisotropic polycrystalline system considered, the free energy is essentially a function of a crystal’s atomistic-electronic structure and lattice’s symmetry; consequently, its fluctuation at grain boundary is determined by the degree of atoms’ disorder from periodic array and the energy barrier against such atomistic motions toward dislocation. Hence, this energy barrier can be utilized to calibrate free energy in either bulk phase or grain boundary, determining the coefficients in its mathematic expression. As examples, the bulk phase of BCC and FCC lattices, respectively, have been analyzed. For grain boundary, the determinations of the two key-coefficients for this model’s free energy will be introduced in a separated paper – the part II of this research [108], in which the mathematic formulations derived in this paper are implemented into computer program and the examples of numerical computation are given.

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