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Stochastic kinetic mean field model

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ABSTRACT

This paper introduces a new model for calculating the change in time of three-dimensional atomic configurations. The model is based on the kinetic mean field (KMF) approach, however we have transformed that model into a stochastic approach by introducing dynamic Langevin noise. The result is a stochastic kinetic mean field model (SKMF) which produces results similar to the lattice kinetic Monte Carlo (KMC). SKMF is, however, far more cost-effective and easier to implement the algorithm (open source program code is provided on http://skmf.eu website). We will show that the result of one SKMF run may correspond to the average of several KMC runs. The number of KMC runs is inversely proportional to the amplitude square of the noise in SKMF. This makes SKMF an ideal tool also for statistical purposes.

1. Introduction

Mean field approach to the thermodynamics of phase transformations in solids has been well-known for years [1]. It was developed into Generalized Stochastic Field Kinetic Model by inclusion of the Langevin noise of conserved (composition) and non-conserved order parameters. [2,3]. Noise amplitude satisfied the fluctuation–dissipation theorem and was determined by the temperature and mobility. Among attempts of non-linear generalization to kinetics of diffusion controlled processes—the most well-known now (and self-consistent)—is a quasi-one-dimensional model by George Martin [4]. Martin's kinetic mean field model (KMF) was developed from the very beginning for atomic scale (at the base of master equation) and took into account the dependence of jump frequencies (and corresponding activation energies) on the local surrounding of jumping atoms. Note that in Martin's atomistic model one does not need any additional non-conserved order parameter to describe ordering of alloy—it is fully described by distribution of composition (conserved parameter) at each site. This model did not contain noise and was applied not only to phase transformations but also to initial stages of diffusion. The most interesting results were obtained for systems with a large asymmetry of components (large difference between A–A and B–B pair interaction energies) [5,6]. In particular, asymmetry may lead to sharpening of composition profile instead of its smoothening (of course, simultaneously with its movement due to intermixing). Also, formation of intermediate B2 ordered phase in the contact zone of the couple with sharp asymmetry may start far from stoichiometric composition [7]. In [8] this approach was modified to 3D case.

All systems treated by KMF, may be alternatively treated by KMC [9,10]. The main advantage of algorithms based on the kinetic mean field (KMF) approximation is that they give definite results. We do not need to run the algorithm several times and then average them to predict the most probable scenario of a process. They have, however, a significant drawback: stochastic fluctuations induced processes cannot be simulated. For instance, nucleation of precipitates in a supersaturated solid solution outside of the spinodal will never occur in a mean field model. Moreover, a random solid solution (described in KMF by absolutely the same composition at all sites) quenched into the spinodal region will never decompose. Therefore, if evolution of the system includes overcoming of some barrier via some saddle point with

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further normal decrease of free energy, the KMF method fails. Overcoming of the (nucleation) barrier is an important stage of the first order transformation. Introduction of noise into the kinetic mean field model provides the possibility of first order phase transformations but still keeps the advantages of KMF.

2. Methods

The problem of noise is well-known from Brownian motion. It is important to introduce the stochastic factor into a deterministic scheme keeping the phase trajectories continuous—excluding the possibility of jumps in the phase space. Therefore the noise is prescribed neither to coordinates nor to velocities but to forces (or accelerations). Force acting on the Brownian particle is represented as the sum of two forces: viscous and stochastic. Substituting them into Newton's second law:

$$\frac{d\overrightarrow{v}}{dt} = -\gamma\overrightarrow{v} + \frac{\overrightarrow{F}_{stoch}}{m}$$

where γ is a damping coefficient. Stochastic force $\overrightarrow{F}_{stoch}$ and corresponding stochastic acceleration $\overrightarrow{a}_{stoch} = \overrightarrow{F}_{stoch}/m$ are treated as random variables with zero time correlation. Accordingly, the correlation function has the form of Dirac delta-function:

$$\left\langle \overrightarrow{a}_{stoch}(t), \overrightarrow{a}_{stoch}\left(t'\right)\right\rangle = A_n\delta\left(t-t'\right)$$

where $<>$ means averaging over ensemble or – according to ergodic hypothesis – over time, and A_n is the amplitude of the noise. In numeric solution, when the time is discrete with time step dt:

$$\left\langle \overrightarrow{a}_{stoch}(t_i), \overrightarrow{a}_{stoch}\left(t_j\right)\right\rangle = \frac{A_n}{dt}\delta_{i,j}.$$

In such representation the results (average values) will not depend on the time step. Physically it means that we fix the change of velocity during one time step. Such noise without memory is called a Langevin noise. Noise amplitude is determined from the constraint of thermodynamic equilibrium between the ensemble of Brownian particles and the surrounding fluctuating medium.

We will introduce the noise into mean field kinetic equations taking into account that these equations contain only first time derivative instead of second one (no inertia). Accordingly, one might assume that the noise amplitude should be divided not by dt but by $\sqrt{dt}$. One must also decide the noise of WHAT should be introduced. Noise (random change) of composition in each site at each time moment is not the best idea, since it immediately leads to singularities in the composition change rates. Accordingly, noise must be prescribed to the REASON of change in composition—to the microfluxes between neighboring sites. Actually, it is a noise of jump frequencies. This can be introduced in at least two ways: random addition to deterministic frequencies or random change of activation energy in the expression for jump frequency. In this paper we will demonstrate the first way.

Rate of change of composition in each site i of a three-dimensional grid is defined according to conservation of matter and the corresponding local flux balance at each site (in the case of the exchange mechanism of diffusion):

$$\frac{dc_i}{dt} = -\sum_{j=1}^{Z}\left[c_i\left(1-c_j\right)\left(\Gamma_{i,j}^{mean\text{-}field} + \delta\Gamma_{i,j}^{Lang}\right) - \left(1-c_i\right)c_j\left(\Gamma_{j,i}^{mean\text{-}field} + \delta\Gamma_{j,i}^{Lang}\right)\right] \quad (1)$$

where c_i is the atomic fraction of A atoms at site i, c_j is the atomic fraction of A atoms on a neighboring site j, and the total number of nearest neighbors is Z. $c_i\left(1-c_j\right)$ is in fact the probability that the site i is occupied by an A atom and a neighboring j site by a B atom; i.e. an A–B exchange is possible. (In mean field approximation the correlations are neglected.) $\Gamma_{i,j}^{mean\text{-}field}$ is the probability of such an exchange per unit time in mean field approximation, i.e. the jump rate of A atoms from site i to a neighboring site j and backward jumps of B atoms ($\Gamma_{j,i}^{mean\text{-}field}$ is for an exchange of an A and a B atoms being on site j and i, respectively):

$$\Gamma_{i,j}^{mean\text{-}field} = \nu\ \exp\left(\frac{-Q_{i,j}}{kT}\right) = \nu\ \exp\left(-\frac{E_0 - E_{i,j}}{kT}\right).$$

Here k is Boltzmann's constant, T is the absolute temperature, $Q_{i,j} = E_0 - E_{i,j}$, E_0 is the saddle point energy, considered constant in this work, and $E_{i,j} = E_i^A + E_j^B$ where $E_i^A = \sum_{l=1}^{Z}[c_l V_{AA} + (1-c_l)V_{AB}]$ and $E_j^B = \sum_{n=1}^{Z}[c_n V_{AB} + (1-c_n)V_{BB}]$ are the interaction energies of an A and a B atom on site i and j, respectively; $V_{\alpha\beta}$ $(\alpha, \beta = A, B)$ are the pair interaction energies. On introducing $M = (V_{AA} - V_{BB})/2$, $V = V_{AB} - (V_{AA} + V_{BB})/2$ and $\Gamma_0 = \nu \exp\{[-E_0 + Z(V_{AB} + V_{BB})]/kT\}$, $\Gamma_{i,j}^{mean\text{-}field}$ can also be written as:

$$\Gamma_{i,j}^{mean\text{-}field} = \Gamma_0 \exp\left(\frac{\hat{E}_{i,j}}{kT}\right) \quad (2)$$

where

$$\hat{E}_{i,j} = (M-V)\sum_{l=1}^{Z} c_l + (M+V)\sum_{n=1}^{Z} c_n. \quad (3)$$

Note that V is the regular solid solution parameter – proportional to the heat of mixing – and M determines the strength of the composition dependence of the tracer diffusion coefficient (diffusion asymmetry). Last but not least, $\delta\Gamma^{Lang}$ in Eq. (1) are the noise terms, which are random additions to the mean field exchange rates:

$$\delta\Gamma_{i,j}^{Lang} = \frac{A_n}{\sqrt{dt}}\sqrt{3}\,(2random - 1) \quad (4)$$

where random is a uniform random number between 0 and 1. It is easy to check that the random expression $\sqrt{3}\,(2random - 1)$ has the mean squared value equal to 1. Note that thanks to the $\sqrt{dt}$ in denominator of Eq. (4) the asymptotic dispersion of concentration at fixed A_n does not depend on dt.

Actually, Eqs. (1)–(4) have to be used to calculate the time evolution of the composition at each site of a 3D lattice (see open source code). With $A_n = 0$, we perform a fully mean field calculation, whereas with increasing A_n the calculation becomes more and more stochastic, that is the dispersion of composition becomes higher.

Formally, it is possible to rewrite the master equations for the vacancy mechanism:

$$\frac{dc_A(i)}{dt} = -c_A(i)\sum_{j=1}^{Z} c_v(k)\Gamma_{ij}^{AV} + c_v(i)\sum_{j=1}^{Z} c_A(k)\Gamma_{ji}^{AV}$$

$$\frac{dc_B(i)}{dt} = -c_B(i)\sum_{j=1}^{Z} c_v(j)\Gamma_{ij}^{BV} + c_v(i)\sum_{j=1}^{Z} c_B(j)\Gamma_{ji}^{BV},$$

$$\frac{dc_v(i)}{dt} = -c_v(i)\sum_{j=1}^{Z} c_A(j)\Gamma_{ji}^{AV} - c_v(i)\sum_{j=1}^{Z} c_B(j)\Gamma_{ji}^{BV} + c_A(i)\sum_{j=1}^{Z} c_v(j)\Gamma_{ij}^{AV} + c_B(i)\sum_{j=1}^{Z} c_v(j)\Gamma_{ij}^{BV}.$$

Here

$$\Gamma_{ij}^{AV} = \nu_A \exp\left(-\frac{E_0 - E_i^A}{kT}\right),$$