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Thermal fluctuation for the time-dependent Ginzburg-Landau simulation

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Thermal fluctuation for the time-dependent Ginzburg-Landau simulations is considered on the basis of the ensemble theory and the fluctuation-dissipation relation. The treatment for evaluating the thermal fluctuation for a nonconserved system is proposed and the formula for the fluctuation is presented. The magnitude of the fluctuation depends on the coarse-grained volume and the curvature of the free-energy function at thermal equilibrium. The validity of the formula is verified by numerical simulation.

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I. INTRODUCTION

Computer simulations based on the time-dependent Ginzburg-Landau (TDGL) approach (more widely, the phase-field approach) have been frequently made for understanding the formation of microstructures in various kinds of alloys [1–4], and have successfully reproduced the microstructures observed experimentally. Therefore, this approach is regarded as a powerful method for analyzing the transformation processes. However, such an approach involves ambiguity in evaluating the thermal fluctuation. To the authors' knowledge, treatment of the thermal fluctuation has not been reported so far; it has been neglected, in particular, for transformation from an unstable phase, or arbitrary small values have been adopted for that from a metastable phase. Recently, we reported the TDGL-simulation study for explaining the variant-structure formation in the cubic to tetragonal (fcc-$L1_0$) transformation of FePd alloy under stress [5]. As pointed out in the paper, the thermal fluctuation plays an essential role in the transformation kinetics, and the resultant microstructures in the simulations strongly depend on the magnitude of the thermal fluctuation. Therefore, evaluation of the thermal fluctuation is necessary to perform the predictive simulations.

Before taking up the main subject, we shall briefly state the TDGL-simulation method and a problem in the fluctuation below. In the TDGL approach for simulating formation of microstructures, we divide a system into small partial systems as the coarse-grained regions (the volume of each region is denoted as Ω), define the coarse-grained order parameter $\phi(\boldsymbol{r})$ at $\boldsymbol{r}\in\Omega$, and use the Ginzburg-Landau free-energy functional of the following form:

$$\hat{F}\{\phi\}=\int d\boldsymbol{r}\left[f(\phi(\boldsymbol{r}))+\frac{K_{\mathrm{s}}}{2}|\nabla\phi(\boldsymbol{r})|^2\right], \tag{1}$$

where $f(\phi(\boldsymbol{r}))$ is the free-energy function per unit volume of the Landau type and K_{s} is the gradient coefficient which takes account of the excess energy by interfaces. Then, the stochastic TDGL equation for nonconserved system is given by

$$\frac{\partial\phi(\boldsymbol{r},t)}{\partial t}=-L\frac{\delta\hat{F}\{\phi\}}{\delta\phi}+\theta(\boldsymbol{r},t), \tag{2}$$

where t is the time, L is the relaxation rate (coefficient), and θ refers to the thermal fluctuation. The problem is how to actually evaluate the magnitude of the thermal fluctuation θ. In this paper, we present a formula for evaluating the thermal fluctuation for a nonconserved system. Finally, the validity of the formula is verified by solving the Langevin equation.

II. FORMULA FOR THE THERMAL FLUCTUATION

We start from the thermal fluctuation on the basis of the ensemble theory. In thermal equilibrium, the probability for the state with the internal energy E to occur is given by

$$P(E)=Z^{-1}\exp[-\beta\mathcal{F}(E)], \tag{3}$$

with $\beta=(kT)^{-1}$ (k is Boltzmann's constant and T is the temperature) and Z the partition function

$$Z=\sum_i W(E_i)\exp(-\beta E_i)=\sum_i \exp[-\beta\mathcal{F}(E_i)], \tag{4}$$

where $W(E_i)$ is the number of states in which the internal energy equals E_i and the summation is performed over all i. The function $\mathcal{F}(E)$ is defined by $\mathcal{F}(E)=E-TS(E)$, where $S(E)=k\ln W(E)$. $\mathcal{F}(E)$ has a stochastic meaning, and therefore, is different from the so-called *free energy* defined by $F=-kT\ln Z$. Hereafter, the function $\mathcal{F}(E)$ is called *the free-energy function*.

When the size of the system is not extremely small, $\exp[-\beta\mathcal{F}(E)]$ displays a very sharp peak at the ensemble average of the internal energy, $\langle E\rangle$; the summation in Eq. (4) can be approximated by $\exp[-\beta\mathcal{F}(\langle E\rangle)]$. Consequently, the free energy is given by $F\approx\mathcal{F}(\langle E\rangle)=\langle E\rangle-TS(\langle E\rangle)$, where $\mathcal{F}(\langle E\rangle)$ is the minimum among all $\mathcal{F}(E_i)$. Therefore, $\partial\mathcal{F}(E)/\partial E=0$ must be satisfied at $E=\langle E\rangle$, resulting in $\partial S(\langle E\rangle)/\partial\langle E\rangle=1/T$ in thermal equilibrium.

Here, we consider the fluctuation in the free-energy function that is caused by the internal energy fluctuation in thermal equilibrium. When the internal energy is $\langle E\rangle+\delta E$, the free-energy function is expressed as $\mathcal{F}(\langle E\rangle+\delta E)=(\langle E\rangle+\delta E)-TS(\langle E\rangle+\delta E)\equiv\mathcal{F}(\langle E\rangle)+\delta\mathcal{F}$. The entropy S is expanded up to the second-order term:

$$S(\langle E\rangle+\delta E)\approx S(\langle E\rangle)+\frac{\partial S}{\partial\langle E\rangle}\delta E+\frac{\partial^2 S}{\partial\langle E\rangle^2}\frac{(\delta E)^2}{2}. \qquad (5)$$

Using Eq. (5) and $\partial S(\langle E\rangle)/\partial\langle E\rangle=1/T$, the fluctuation in the free-energy function, $\delta\mathcal{F}$, is expressed as

$$\delta\mathcal{F}\approx-\frac{T}{2}\frac{\partial}{\partial\langle E\rangle}\left(\frac{\partial S}{\partial\langle E\rangle}\right)(\delta E)^2=\frac{(TC_{\mathrm{V}})^{-1}}{2}(\delta E)^2, \qquad (6)$$

where C_{V} is the heat capacity, and $(TC_{\mathrm{V}})^{-1}$ indicates the curvature of the free-energy function at $E=\langle E\rangle$. Since the square average of the internal energy fluctuation in the canonical distribution is given by $\langle(\delta E)^2\rangle=kT^2C_{\mathrm{V}}$, the average fluctuation $\langle\delta\mathcal{F}\rangle$ is given by

$$\langle\delta\mathcal{F}\rangle\approx\frac{(TC_{\mathrm{V}})^{-1}}{2}\langle(\delta E)^2\rangle=\frac{kT}{2}. \qquad (7)$$

We apply the above relation to computer simulations based on the TDGL approach. As an example of the Landau free-energy function, we deal with that for the fcc / $L1_0$ order-disorder transition previously reported [5]. Since the transition is first-order, the free-energy function per unit volume is expressed as

$$f(\phi)=\alpha(T-T_0)\phi^2-b\phi^4+c\phi^6, \qquad (8)$$

where α, b, and c are positive constants, and T_0 is the instability temperature of the disordered phase; the details of Eq. (8), e.g., its coefficients are discussed in Sec. III.

Figure 1(a) shows the free-energy function at a temperature (873 K) below the transition temperature T_{t} (923 K). The thermal-equilibrium distribution $P_{\mathrm{eq}}(\phi)$ is calculated using

$$P_{\mathrm{eq}}(\phi)=C\exp[-\beta f(\phi)\Omega], \qquad (9)$$

for $\Omega=1$ and 27 (nm^3) (C is the normalization constant), the results of which are displayed in Fig. 1(b). Obviously, the fluctuation of the order parameter changes depending on the size of the coarse-grained volume Ω, which indicates the necessity to clearly define the volume for evaluating the thermal fluctuation.

At thermal equilibrium, the order parameter ϕ fluctuates around the equilibrium value $\phi_{\mathrm{e}}(\neq 0)$. The curvature of the Landau free-energy function at $\phi=\phi_{\mathrm{e}}$ is denoted as $f''(\phi_{\mathrm{e}})$. Equation (7) indicates that the average magnitude of the fluctuation in the free-energy function $f(\phi)\Omega$ assigned to each region equals $kT/2$; we obtain $\langle\delta(f\Omega)\rangle=(1/2)f''(\phi_{\mathrm{e}})\Omega\langle(\phi-\phi_{\mathrm{e}})^2\rangle_\Omega\approx kT/2$; that is,

$$\langle(\phi-\phi_{\mathrm{e}})^2\rangle_\Omega\approx\frac{kT}{f''(\phi_{\mathrm{e}})\Omega}. \qquad (10)$$

Next, we shall derive a formula for the fluctuation in the kinetic equation such as Eq. (2). As shown in Fig. 1(b), the fluctuation of the physical quantities generally depend on the size of a system. Accordingly, being conscious of the size of a system, we obtain the fluctuation-dissipation (FD) relation [6] from the Fokker-Planck equation [7].

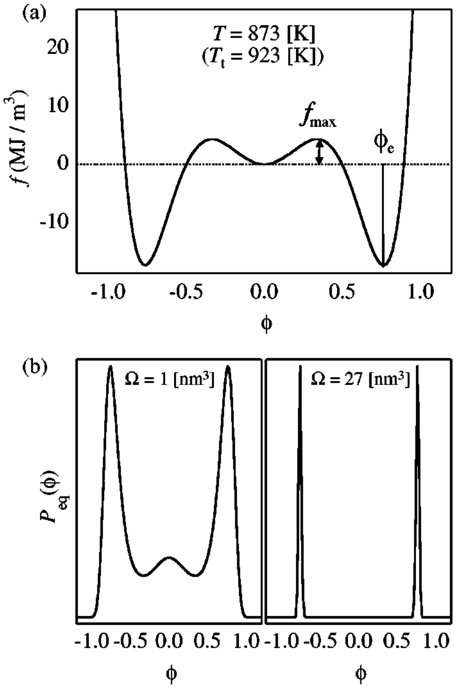

FIG. 1. (a) The free-energy function for a fcc/$L1_0$ ordering system at 873 K. The transition temperature T_{t} is set at 923 K. The sign of the order parameter indicates the types of $L1_0$ variants. (b) Distribution functions for different coarse-grained volume, $\Omega=1$ (nm^3) and 27 (nm^3).

The time variation of a parameter ϕ is assumed to be governed by the Langevin equation,

$$\frac{\partial\phi}{\partial t}=-L_\Omega\frac{\partial\mathcal{F}_\Omega}{\partial\phi}+\theta(t), \qquad (11)$$

where the character of the Gaussian thermal fluctuation θ is expressed as follows: $\langle\theta(t)\rangle=0$, $\langle\theta(t_1)\theta(t_2)\rangle=2D\delta(t_1-t_2)$. $\mathcal{F}_\Omega$ is the free-energy function for the region with the volume Ω in which the parameter ϕ is defined, and L_Ω is the relaxation rate for the region Ω. When the distribution function is expressed as $P(\phi,t)$, the Fokker-Planck equation corresponding to Eq. (11) is given by

$$\frac{\partial P(\phi,t)}{\partial t}=\left(D\frac{\partial^2}{\partial\phi^2}+\frac{L}{\Omega}\frac{\partial}{\partial\phi}\frac{\partial f\Omega}{\partial\phi}\right)P(\phi,t), \qquad (12)$$

where $f\Omega=\mathcal{F}_\Omega$ and $L/\Omega=L_\Omega$. If $D=(L/\Omega)kT$ holds, the thermal-equilibrium distribution, Eq. (9), holds. The FD relation, $D=(L/\Omega)kT$, guarantees a solution of Eq. (12) to lead to the thermal-equilibrium distribution.

Expressing the derivative of the free-energy functional in Eq. (2), we obtain

$$\frac{\partial\phi(\boldsymbol{r},t)}{\partial t}=-\frac{L}{\Omega}\left(\frac{\partial f\Omega}{\partial\phi}-K_{\mathrm{s}}\Omega\nabla^2\phi\right)+\theta(\boldsymbol{r},t). \qquad (13)$$

Note that the volume Ω is explicitly displayed in the TDGL equation. From the FD theorem, the character of the thermal fluctuation is given by

$$\langle \theta(t) \rangle = 0, \quad \langle \theta(t_1)\theta(t_2) \rangle = 2\frac{L}{\Omega} kT \delta(t_1 - t_2). \tag{14}$$

It is emphasized here that Eq. (14) that involves the volume Ω is the appropriate formula for the thermal fluctuation θ in Eqs. (2) or (13).

We shall consider the discrete equation with the time increment Δt next. The discrete equation at $\boldsymbol{r}$ corresponding to Eq. (13) is written as

$$\phi(t+\Delta t) = \phi(t) - \frac{L\Delta t}{\Omega}\frac{\partial f\Omega}{\partial \phi} + \int_t^{t+\Delta t} ds\, \theta(s), \tag{15}$$

where the gradient term is omitted. From Eq. (14), the variance of the integration of the Gaussian thermal fluctuation, $\sigma^2(\Delta t)$, is calculated as

$$\sigma^2(\Delta t) \equiv \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \langle \theta(s)\theta(s') \rangle = 2\frac{L\Delta t}{\Omega} kT. \tag{16}$$

Equation (16), which involves Ω and Δt explicitly, should be adopted in the TDGL simulations. The definitions (or physical limitations) of Δt and Ω shall be stated below.

First, we address the definition of Δt. Comparing Eqs. (10) and (16), we obtain the following significant relation,

$$\sigma^2(\Delta t) = 2 f''(\phi_e) L \Delta t \langle (\phi - \phi_e)^2 \rangle_\Omega, \tag{17}$$

which presents a criterion for defining Δt. Suppose that Δt is set at a value much larger than the relaxation time $\tau \sim 1/Lf''(\phi_e)$, the relaxation process that should occur naturally during Δt is inevitably neglected in the simulation, so that $\phi(t)$ becomes out of physically meaningful range, e.g., the range shown in the abscissa of Fig. 1(a). As found from Eq. (17), such a matter can be avoided necessarily when the time increment is chosen so as to satisfy $\Delta t \leqslant 1/2Lf''(\phi_e)$. On the other hand, when Δt is quite small, the simulation is not performed effectively; a lot of iterative calculations are needed for completing a simulation run. Therefore, it is appropriate that Δt is defined so as to satisfy the relation $2f''(\phi_e)L\Delta t \sim 1$, i.e., for $\sigma^2(\Delta t)$ to be of the same order as $\langle (\phi - \phi_e)^2 \rangle_\Omega$. Thus, in the TDGL simulations for nonconserved systems, we can adopt the following formulas:

$$\Delta t \sim \frac{1}{2Lf''(\phi_e)}, \quad \sigma^2(\Delta t) \sim \frac{kT}{f''(\phi_e)\Omega}. \tag{18}$$

There exists arbitrariness in the determination of the coarse-grained volume Ω, but at least, we should take notice that the volume Ω is to be smaller than a typical domain size, for example, the specific wave length in the spinodal decomposition or the critical nucleation size, etc. In the case of nucleation process, the critical radius of a spherical nucleus is given by $r_c = -2\gamma_s / f(\phi_e)$, where γ_s is the surface energy given by $\gamma_s \approx K_s \phi_e^2 / 2\Delta d$ and $(\Delta d)^3 = \Omega$, with Δd the grid distance of the divided partial systems. If the nucleation process is simulated, the coarse-grained volume should be defined so as to satisfy a condition $\Omega \ll (4/3)\pi r_c^3$.

III. VALIDITY OF THE FORMULA FOR THE THERMAL FLUCTUATION

In this section, we examine the validity of Eq. (18) by solving Eq. (15) numerically. The term of the gradient energy is not considered here (i.e., $K_s = 0$); we observe not the nucleation process, but the process of overcoming the saddlepoint energy $f_{\max}$ shown in Fig. 1 (a). Note that $f_{\max}$ is the free-energy maximum characterizing the first-order transition and is essentially different from the work required for the formation of a nucleus. Since the gradient energy is zero (i.e., there is no shrink effect by surface tension) in this model, even a infinitesimally small domain can stably exist once it changes into an equilibrium state via the saddlepoint from a metastable state. What is checked here is whether such an activation process can be simulated *physically correctly*, that is, the activation (saddlepoint) energy for a region with the volume Ω becomes equal to $f_{\max}\Omega$. The activation process is analyzed in the light of the conventional theory on the thermal fluctuation.

We use the free-energy function [in the form of Eq. (8)] per unit volume for the fcc/$L1_0$ transition: $f(\phi) = (RT/V_m)[0.746(kT/v - 0.708)\phi^2 - 0.497\phi^4 + 0.475\phi^6]$, where ϕ represents the tetragonality of the $L1_0$ phase, V_m is the volume per unit mole, and R is the gas constant [5]. In this phase transition, the reduced transition temperature has been calculated to be $kT_t/v \approx 0.882$ (v is the effective atomic interaction energy) from Monte Carlo simulations [8]. We set the parameters: $T_t = 923$ (K) and $V_m = 8.32 \times 10^{-6}$ [m^3/mol]. Temperature for the simulation is set at $T = 823$ (K), i.e., $kT/v \approx 0.786$. At this temperature, the saddlepoint energy is $f_{\max} \approx 1.51 \times 10^6$ (J/m^3), i.e., $\beta f_{\max} = 0.133$ [nm^{-3}], and the curvature of the free-energy function is $f''(\phi_e) \approx 1.68 \times 10^9$ (J/m^3). On the basis of Eq. (18), we use $L\Delta t \approx 1/2f''(\phi_e) \approx 2.97 \times 10^{-10}$ (m^3/J) and assign the Gaussian random number with the variance $\sigma^2(\Delta t) \approx 6.75 \times 10^{-30}/\Omega$ to the thermal fluctuation. The time increment is set at $\Delta t = 1$ (s') (s' denotes the unit of time used in the simulation).

As seen in Fig. 2(a), the parameter ϕ fluctuates around $\phi = 0$ in the early stage, and it evolves rapidly at a certain time. It can be judged that the region with the volume Ω overcomes the activation energy $f_{\max}\Omega$ at the transition time. Such a *time delay* in the evolution process is denoted as t_s. The dependence on Ω of t_s is investigated through several simulation runs for various coarse-grained volume. Figure 2(b) shows the $\ln t_s$ versus Ω plots. These points are obviously aligned, and the slope is $\Lambda \approx 0.137 \pm 0.007$ (nm^{-3}). According to the conventional theory on fluctuation, the probability p to overcome the activation energy $f_{\max}\Omega$ is proportional to $\exp(-\beta f_{\max}\Omega)$, so that t_s is considered to be proportional to p^{-1}, that is, $\ln t_s \propto \beta f_{\max}\Omega$. Therefore, the relation $\Lambda = \beta f_{\max}$, is expected to be obtained theoretically.

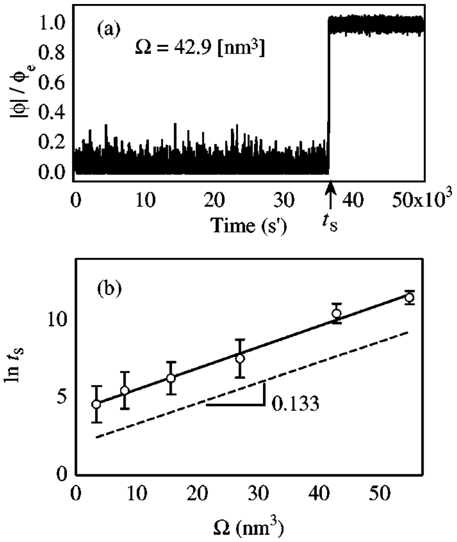

FIG. 2. (a) Time evolution of the order parameter ϕ for $\Omega = 42.9\ (\mathrm{nm}^3)$. t_s denotes the time delay in the evolution process of ϕ. (b) The $\ln t_s$ vs Ω plots. The slope of the dashed line is based on the conventional theory on fluctuation.

The result of the present simulation well satisfies the relation.

The simulation in which Eq. (18) is adopted has yielded two significant results, which are summarized as follows:

(i) The quantity $\ln t_s$ depends linearly on Ω. This indicates that the saddlepoint energy per unit volume remains constant regardless of the definition of Ω.

(ii) The theoretical relation $\Lambda = \beta f_{\mathrm{max}}$ is well satisfied when $L\Delta t \approx 1/2f''(\phi_e)$ is employed. This indicates that the relation, $2f''(\phi_e)L\Delta t \sim 1$, is an appropriate relation to simulate the activation processes correctly. If $L\Delta t \approx 10.0 \times 10^{-10}\ (\mathrm{m}^3/\mathrm{J})$, i.e., $2f''(\phi_e)L\Delta t \approx 3.37$, is arbitrarily used, Λ is computed to be $0.113 \pm 0.003\ (\mathrm{nm}^{-3})$; this value differs from the theoretical value ($\Lambda = 0.133$). Furthermore, when $L\Delta t \rightarrow \infty$, it is expected that $\Lambda \rightarrow 0$, being increasingly far from the theoretical value. On the contrary, when $L\Delta t \approx 0.297 \times 10^{-10}\ [\mathrm{m}^3/\mathrm{J}]$, i.e., $2f''(\phi_e)L\Delta t = 0.1$, is adopted, $\Lambda \approx 0.146 \pm 0.013$. Thus, even if $L\Delta t$ is set at a value smaller than $1/2f''(\phi_e)$, the theoretical relation $\Lambda = \beta f_{\mathrm{max}}$ is virtually satisfied.

The above two facts indicate that the presented formula is valid and can be adopted in the TDGL simulations. As far as we use the formula, we can arbitrarily define the size of a coarse-grained region under some constraints that does not affect the results of the simulations.

IV. CONCLUSIONS

We have presented the formula, Eq. (18), for the thermal fluctuation to be used in the time-dependent Ginzburg-Landau simulations and have examined the validity of the presented formula. By using the formula, the results that are yielded by the simulations would be independent of the definition of the coarse-grained volume, so that nucleation processes (which are barely addressed in this paper) would be simulated successfully and typical domain sizes in microstructures would also be obtained without a proper scaling.

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