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Kinetics of rapid crystal growth: phase field theory *versus* atomistic simulations

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Abstract. Kinetics of crystal growth in undercooled melts is analyzed by methods of theoretical modeling. Special attention is paid to rapid growth regimes occurring at deep undercoolings at which non-linearity in crystal velocity appears. A traveling wave solution of the phase field model (PFM) derived from the fast transitions theory is used for a quantitative description of the crystal growth kinetics. The “velocity – undercooling” relationship predicted by the traveling wave solution is compared with the data of molecular dynamics simulation (MDS) which were obtained for the crystal-liquid interfaces growing in the $\langle 100 \rangle$ -direction in the Ni₅₀Al₅₀ alloy melt.

1. Introduction

Interface kinetics at high driving forces of growth/melting of crystals have received special attention due to advanced experimental techniques [1, 2, 3]. In fact, the rapid solidification front may undergo diffusionless (chemically partitionless) transformation which may proceed in wide or narrow intervals of driving forces [1, 3, 4]. In such case, the crystal growth kinetics often exhibit the non-linear behavior [5] which is not predicted by the traditional kinetic theories or phase field models (PFM) based on local thermodynamic equilibrium [6]. Recent attempts to describe non-linearity in the crystal growth velocity by the local equilibrium phase field model with the mobility extracted from molecular dynamics simulation (MDS) are limited so far by a small interval of driving forces [7] in comparison with a wide range of undercooling attained in atomistic simulations for the crystal growth kinetics [8, 9, 10, 11, 12].

The present work extends the kinetic equation formulation presented for description of growth kinetics of Ni-crystal in Refs. [13, 14] to investigation of crystal growth kinetics from the undercooled Ni₅₀Al₅₀ melt. Tang and Harrowell [12] published the data of MDS for the growth of Ni₅₀Al₅₀ crystals growing in the $\langle 100 \rangle$ -direction which are used by us as a reference to check consistency of our kinetic equation and consistency of the well-known Wilson-Frenkel kinetic equation formulated as an outcome of the diffusion limited theory (DLT).

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2. Diffusion Limited Theory

In application to the melting/crystallization, the kinetic rate theory (or thermally activated growth theory [15]) compares two atomic fluxes at the moving crystal-liquid interface: the first one goes from the liquid over to crystal per unit time at a single kink or atomic micro-roughness, and the second one comes from crystal to liquid if the atomic configuration in liquid favors to solid atoms detachment. This results in the non-zero interface velocity [4] which is proportional to the temperature dependent kinetic growth coefficient, $\beta_k(T)$, having various atomistic theories adopted to the concrete growth mechanism of crystals depending of the absolute temperature T and the Gibbs free energy change on transformation ΔG given by

$$\Delta G = G_s(T, C) - G_l(T, C) \begin{cases} < 0, & \text{solidification,} \\ > 0, & \text{melting,} \end{cases} \quad (1)$$

where $G_l(T, C, \phi)$ and $G_s(T, C, \phi)$ are the Gibbs free energies of the liquid and solid phases, respectively.

The diffusion-limited mechanism of growth as was analyzed by Wilson and Frenkel [16, 17], using the approximation $\Delta G \ll k_B T$ and a simplest expression for the driving force [18],

$$\Delta G = \Delta H_f(-\Delta T)/T_m, \quad \Delta T = T_m - T, \quad (2)$$

yields the Wilson-Frenkel equation taking into account the liquid diffusivity and expressing the solid-liquid interface velocity V as

$$V = \beta_k^{(DLT)} \Delta T = \frac{a}{\lambda^2} f_0 D(T) \frac{\Delta H_f}{k_B T_m^2} \Delta T, \quad (3)$$

with $\beta_k^{(DLT)}$ stands for the kinetic coefficient in the framework of DLT, a is the spacing between crystalline layers, λ is the mean free path of atoms, f_0 is the fraction of collisions with the crystal that contributes to the growth of the crystal, ΔH_f is the melting enthalpy, $D(T)$ is the diffusion coefficient taken as [4] $D(T) = D_0 \exp(-\Delta E_B/k_B T)$ with the diffusion prefactor $D_0 = \Lambda^2 \tilde{\nu}/6$, given by [19], where $\tilde{\nu}$ is the frequency of thermal vibrations of an atom in the crystal and the liquid, Λ is an elementary diffusive jump distance of particles in the liquid, E_B is the activation energy for diffusion, T_m is the melting (crystallization) point temperature, k_B is the Boltzmann constant and ΔT is the undercooling which is necessary for non-zero attachment/detachment of atoms in the case of solidification/melting. This undercooling is defined in the dendrite growth models as the ‘‘kinetic undercooling’’ [2, 3, 20, 21].

In Eq. (3), DLT introduces the diffusion transport coefficient $D(T)$ of the supercooled liquid and, therefore, the kinetic coefficient exhibits the strong temperature dependence associated with an activated process. Quantitative estimations of kinetic growth coefficients for various crystal growth models can be found in Refs. [8, 11] as obtained from atomistic simulations and in Ref. [20] as obtained from experimental measurements. However, DLT has difficulties to quantitatively describe the growth kinetics for a wide range of temperatures [8, 9]. The results of calculations by Eq. (3) for pure Ni in comparison with data of MDS [5, 11] are given in Ref. [14] from which follows that (i) in the relatively small range of undercooling and overheating, the MDS-data exhibits linear behavior for the interface velocity, both in melting and in crystallization that is well described by DLT; (ii) for the large range of undercooling, the predictions of DLT behaves inconsistently in comparison with MDS-data qualitatively and, as a consequence, quantitatively.

3. Phase Field Model

Consider a binary mixture consisting of solvent and solute undergoing phase transition, solidification/melting, from the undercooled/overheated state for which the free energy is described by

$$\mathcal{G} = \int_{v_0} \left[\frac{\varepsilon_\phi^2}{2} |\vec{\nabla}\phi|^2 + G(T, C, \phi, \partial\phi/\partial t) \right] dv_0, \quad (4)$$

where v_0 is the volume of the mixture, ε_ϕ is the gradient energy coefficient related to the interface energy γ , ϕ is the phase field variable defined as $\phi = 0$ in the liquid phase and $\phi = 1$ in the solid phase, $\partial\phi/\partial t$ is the gradient flow for the phase field, and C is the solute concentration.

Introducing the phase field ϕ and gradient flow $\partial\phi/\partial t$ as independent thermodynamic variables in the Gibbs potential $G(T, C, \phi, \partial\phi/\partial t)$ can be considered in the full analogy with Newtonian mechanics, where the initial position and velocity of a particle must be specified to determine their evolution and velocity. Indeed, if inertial effects are sufficiently low in comparison with dissipative effects during phase field propagation, $\partial\phi/\partial t$ will be determined directly by a dynamical equation in terms of ϕ and its gradient. Otherwise, ϕ and $\partial\phi/\partial t$ will be independent and an equation for $\partial^2\phi/\partial t^2$ must be found [22, 23]. Therefore, the Gibbs potential $G(T, C, \phi, \partial\phi/\partial t)$ which is a combination of local equilibrium contribution, $G_{eq}(T, C, \phi)$, and local non-equilibrium contribution, $G_{neq}(T, \partial\phi/\partial t)$, takes the following form,

$$G(T, C, \phi, \partial\phi/\partial t) = [1-p(\phi)]G_l(T, C) + p(\phi)G_s(T, C) + W_\phi(T, C)g(\phi) + (\alpha_\phi(T)/2) (\partial\phi/\partial t)^2, \quad (5)$$

where $p(\phi)$ is the interpolation function $p(\phi) = (3 - 2\phi)\phi^2$, $g(\phi)$ is the double-well function $g(\phi) = (1 - \phi)^2\phi^2$ [24], $W_\phi(T, C)$ is the barrier between phases, $\alpha_\phi(T)$ is phenomenological coefficient being proportional to the relaxation time τ_ϕ of the gradient flow $\partial\phi/\partial t$ which is introduced as independent thermodynamic variable [25]. The latter term in Eq. (5), which is proportional to $(\partial\phi/\partial t)^2$, is considered as the kinetic energy term added to Gibbs potential [26].

A stable evolution of the entire system is given by the Lyapunov condition of non-positive change of the total Gibbs free energy in time [27]. Application of this condition to the functional (4) yields the following phase field equation [13]

$$\tau_\phi \frac{\partial^2\phi}{\partial t^2} + \frac{\partial\phi}{\partial t} = D_\phi \nabla^2\phi - M_\phi \left[\Delta G \frac{dp(\phi)}{d\phi} + W_\phi(T, C) \frac{dg(\phi)}{d\phi} \right], \quad (6)$$

where the Gibbs free energy difference ΔG is defined by Eq. (1) and the diffusion coefficient of the phase field $D_\phi(T) = \varepsilon_\phi^2 M_\phi(T)$ is essentially depends on the temperature if the phase transition is considered in a wide temperature range [28].

The hyperbolic equation (6) describes relaxation of two variables: relaxation of the slow ϕ -field by the first time derivative and relaxation of the gradient flow, $\partial\phi/\partial t$, by the second time derivative. In this sense, due to introducing relaxation of $\partial\phi/\partial t$, Eq. (6) describes the evolution of the local non-equilibrium system. Further we show how it is important to use of the gradient flow relaxation and, consequently, what is the role the local non-equilibrium in fast crystal growth kinetics. On one hand, Eq. (6) admits, in the equilibrium state $\Delta G = 0$, $G_s(T, C) = G_l(T, C)$, one dimensional steady solution $\phi(x) = (1/2) [1 - \tanh(x/\delta_I)]$, at $\partial\phi/\partial t = 0$ along the spatial x -axis with the stationary width of diffuse interface $\delta_I = \varepsilon_\phi \sqrt{2/W_\phi(T, C)}$ and the surface energy of the crystal-liquid interface $\gamma = \delta_I W_\phi(T, C)/6$. On the other hand, Eq. (6) has, in the dynamic state $\Delta G = G_s(T, C) - G_l(T, C) \neq 0$, one dimensional traveling-wave solution $\phi(x, t) = (1/2) [1 - \tanh((x - Vt)/\ell)]$ [13, 29]. This particular solution with the hyperbolic tangent function follows from the general set of analytical solutions of Allen-Cahn-type equations [30] which is given in the present model by Eq. (6). In this solution, the crystal

growth velocity V is limited by a maximum speed of phase field propagation, V_ϕ because the phase field itself dictates the interface shape and its velocity, i.e. $V < V_\phi$, [13]. In the simplest approximation $\Delta G \ll k_B T$ (see Eq. (2)) the velocity has the following form [31]

$$V = \beta_k^{(PFM)} \Delta T = \frac{D_\phi(\Delta T) \Delta H_f}{\gamma T_m \sqrt{1 + \left[\frac{D_\phi(\Delta T) \Delta H_f}{\gamma T_m V_\phi(\Delta T)} \Delta T \right]^2}} \Delta T, \quad (7)$$

which is consistent with the approximation of kinetic equation (3) and for which the kinetic coefficient, $\beta_k^{(PFM)}$, depends on the undercooling ΔT . The maximum speed V_ϕ of phase field propagation in Eq. (7) is defined by the diffusion of the phase field as

$$V_\phi(\Delta T) = \sqrt{D_\phi(\Delta T) / \tau_\phi}, \quad (8)$$

where the relaxation time τ_ϕ is taken as a constant independent from the temperature in the present analysis.

The diffusion coefficient of phase field in Eqs. (7) and (8) is given by

$$D_\phi(\Delta T) = D_\phi^0 \exp\left(-\frac{E_A}{T_m - \Delta T - T_A}\right), \quad (9)$$

where the diffusion factor D_ϕ^0 , the energetic barrier E_A and the pseudo-glass transition temperature T_A are parameters of the phase field propagation. The form of Eq. (9) is similar to the form of phase field mobility $M_\phi(T)$ given in Ref. [28] and it shows that, as soon as the undercooling approaches its critical value, the phase field diffusion begins its steep decrease down to its zero value.

Table 1: Material parameters for Ni₅₀Al₅₀ used in calculations

Parameter	Set 1	Set 2	Reference
Melting temperature, T_m (K)	1520	1520	[9, 12]
Enthalpy of melting, ΔH_f (J · m ⁻³)	1.74×10^9	1.74×10^9	[21]
Interface energy, γ (J · m ⁻²)	0.24	0.24	[21]
Pseudo-glass transition temperature, T_A (K)	950	950	present work
Relaxation time, τ_ϕ (s)	8.22×10^{-11}	→ 0	present work
Diffusion factor, D_ϕ^0 (m ² · s ⁻¹)	1.10×10^{-8}	1.06×10^{-8}	present work
Energetic barrier, E_A (K)	368.19	403.07	present work

4. Predictions of DLT and PFM in comparison with MDS-data

Previously, the nonlinearity in the growth kinetics having a form of the velocity with saturation has been described for pure Ni [13, 14]. However, there are other type of non-linearity in the “velocity – undercooling” relationship which is presented by the crystal growth velocity curve having a maximum at fixed undercooling [8, 9, 10, 12]. Such curves are typical for glass forming metals and alloys. PFM-solutions summarized by Eqs. (7)-(9) shall now be tested against MDS-data found in growth kinetics of Ni₅₀Al₅₀ crystals [12]. Note that Ni₅₀Al₅₀ belongs to congruently melting alloys which are solidifying without chemical segregation. Therefore we do not need to introduce constitutional effects in consideration and Eqs. (7)-(9) can be used to describe the growth of Ni₅₀Al₅₀ crystals without chemical contributions. All calculations have

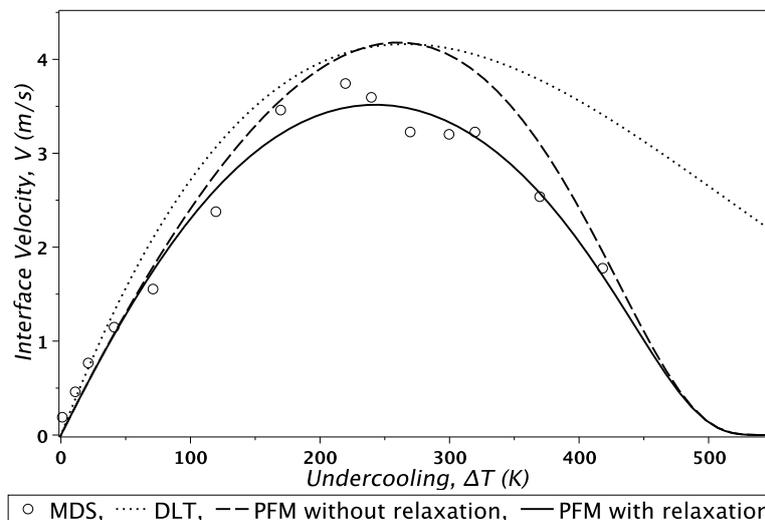


Figure 1: Comparison of growth kinetic equations based on Diffusion Limited Theory (DLT)- and Phase Field Model (PFM) (curves) with data kinetics of molecular dynamics simulations (MDS) of Tang and Harrowell [12] for $\text{Ni}_{50}\text{Al}_{50}$ -crystals in the $\langle 100 \rangle$ direction (\circ). Calculations are given by: (i) DLT (\cdots), Eq. (3) with $\lambda \approx 2.25a$, $\Lambda \approx 4a$ and the other constants from [9, 12]; (ii) PFM without relaxation ($---$), Eqs. (7)-(9) with $\tau_\phi \rightarrow 0$, $V_\phi \rightarrow \infty$ and all other parameters are given by Set 2 from Table 1; (iii) PFM with relaxation ($—$), Eqs. (7)-(9) with $\tau_\phi \neq 0$, finite V_ϕ and other parameters given by Set 1 from Table 1.

been made using material parameters for $\text{Ni}_{50}\text{Al}_{50}$ from Table 1, where the relaxation time, τ_ϕ , the diffusion factor, D_ϕ^0 , and the energetic barrier, E_A , are considered as free parameters at a fixed pseudo-glass transition temperature, T_A . They can be obtained from molecular dynamics simulation (e.g., τ_ϕ) and from phase field simulations (e.g., D_ϕ^0 and E_A).

Figure 1 shows that Wilson-Frenkel equation (3) based on DLT (dotted curve) describes well the molecular dynamics data for the growth of $\text{Ni}_{50}\text{Al}_{50}$ crystals (open circle) only for smallest values of undercoolings. Beyond the small undercooling, Wilson-Frenkel equation (3) disagrees with MDS-data despite its tendency to reach the maximum value of growth velocity.

Two cases for solution of Eqs. (7)-(9) have been considered and plotted in Figure 1: with the local non-equilibrium effect ($\tau_\phi \neq 0$, V_ϕ is finite) and without it ($\tau_\phi \rightarrow 0$, $V_\phi \rightarrow \infty$). With no local non-equilibrium effects, the predicted velocity well describes data of atomistic modeling only at very small and very high undercooling (see dashed curve which is obtained with the new parameters of E_A and D_ϕ^0 from Table 1 providing the better fit to data of simulations). If, however, the local non-equilibrium effect is included, we recover perfectly the atomistic simulation data in the entire undercooling range and the growth rate (solid curve). The solidification kinetics of glass forming alloys is well described by the theory which includes local non-equilibrium effects in the form of relaxation of the gradient flow in the phase field. Therefore, good comparison with MSD-data confirms our initial theoretical assumption in PFM about the predominant influence of local non-equilibrium effects in crystal growth under large driving forces.

5. Conclusions

- The non-linearity in the “interface velocity – kinetic undercooling” behavior was described by the traveling wave solution of the PFM for $\text{Ni}_{50}\text{Al}_{50}$ crystals growing in the $\langle 100 \rangle$ -direction. This non-linearity was found for the velocity with maximum at the fixed value of undercooling.

- Predictions of the developed PFM and DLT have been compared with the data of MDS for Ni₅₀Al₅₀-crystals growing in a wide range of undercoolings.
- The Wilson-Frenkel equation based on DLT describes the data of MDS only for limited range of undercoolings and disagrees elsewhere despite its tendency to reach the maximum velocity at fixed undercooling.
- Using the traveling wave solution of PFM the MDS-data are predicted perfectly if the deviation from local thermodynamic equilibrium is taken into account in the form of local relaxation of the gradient flow of the phase field. Such good prediction of MSD-data confirms an existence of the local non-equilibrium effect on the growth kinetics of crystals under large driving forces.

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