

Phase Field Theory of Nucleation and Growth in Binary Alloys

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Abstract. We present a phase field theory for binary crystal nucleation. Using the physical interface thickness, we achieve quantitative agreement with computer simulations and experiments for unary and binary substances. Large-scale numerical simulations are performed for multi-particle freezing in alloys. We deduce the Kolmogorov exponents for dendritic solidification and for the "soft-impingement" of crystallites interacting via diffusion fields.

1 Introduction: Diffuse Interface and Nucleation

The solid-liquid interface is known to extend to several molecular layers, as indicated by experiment [1], computer simulations [2], and statistical mechanical treatments based on the density functional theory [3]. This plays an essential role in modeling nucleation, as the typical size of critical fluctuations is comparable to the physical thickness of the interface. Modern nucleation theories, which consider the molecular scale diffuseness of the interface, removed the many orders of magnitude difference seen between nucleation rates from the classical sharp interface approach and experiment [4].

The phase field theory (PFT) predicts a diffuse interface. In conventional applications for solidification at small undercoolings, the diffuse interface is both an advantage and a disadvantage: Advantage, since all mesh points can be handled uniformly (no need for front tracking), and a disadvantage, as the physical interface thickness is by orders of magnitude smaller than the size of the modeled particles, thus due to computational limitations, the true interface thickness cannot be realized. Therefore, one is compelled to use an artificially broad interface, which is accompanied with artifacts. Imaginative work by Karma and coworkers (see [5] and references therein) established operations, such as the introduction of interface currents and specific choice of the phase field parameters, which remove these artifacts and ensure the convergence of the diffuse interface results to the sharp interface solution.

In modeling nucleation, we face a different situation. Here, we are able to choose the model parameters so that the true interface thickness is recovered. We demonstrate that under such conditions the PFT is quantitative for nucleation in unary and binary systems. Note that convergence to the

sharp interface model is not a requirement, as the sharp interface model is inaccurate for nucleation [4].

2 Phase Field Theory of Nucleation

We adopt the standard binary phase field theory (for review see [6,7]). Our starting point is the free energy functional

$$F = \int d\mathbf{r} \left\{ \frac{\epsilon^2 T}{2} (\nabla\phi)^2 + f(\phi, c) \right\}, \quad (1)$$

where ϕ and c are the phase and concentration fields, $f(\phi, c) = WTg(\phi) + [1 - P(\phi)]f_S + P(\phi)f_L$ is the local free energy density, $W = (1 - c)W_A + cW_B$ the free energy scale, the quartic function $g(\phi) = \phi^2(1 - \phi)^2/4$ ensures the double-well form of f , while the function $P(\phi) = \phi^3(10 - 15\phi + 6\phi^2)$ switches on and off the solid and liquid contributions $f_{S,L}$, taken from the ideal solution model. (A and B indicate the constituents.)

For binaries the model contains three parameters ϵ , W_A and W_B that reduce to two (ϵ and W) in the one-component limit. They can be fixed if the respective interface free energy γ , melting point T_f , and interface thickness δ are known. Such information is available for the Lennard-Jones, ice-water, and Cu-Ni systems [8–10].

2.1 Nucleation in 3D

The critical fluctuation (nucleus) is a non-trivial time-independent solution of the governing equations:

$$\frac{\partial\phi}{\partial t} = -M_\phi \frac{\delta F}{\delta\phi}, \quad (2)$$

$$\frac{\partial c}{\partial t} = \nabla M_c \nabla \frac{\delta F}{\delta c}, \quad (3)$$

where $(\delta F/\delta x)$ stands for the functional derivatives ($x = \phi, c$), M_x are mobilities. For spherical symmetry (a reasonable assumption), the phase field equation reduces to $\nabla^2\phi = \Delta\mu(\phi, c)/(\epsilon^2 T)$. Here $\Delta\mu(\phi, c) = WTg'(\phi) + [(1 - c)\Delta f_A + c\Delta f_B]P'(\phi)$ is the local chemical potential difference relative to the initial liquid, prime stands for differentiation with respect to the argument, the local concentration is related to the phase-field as $c(\phi) = c_\infty e^{-y}/(1 - c_\infty + c_\infty e^{-y})$, where $y = v(W_B - W_A)g(\phi)/R + v(\Delta f_B - \Delta f_A)[P(\phi) - 1]/RT$, while Δf_i are the volumetric free energy differences between the pure liquid and solid phases. Solving these equations numerically under boundary conditions that prescribe bulk liquid properties far from the fluctuations ($\phi \rightarrow 1$, and $c \rightarrow c_\infty$ for $r \rightarrow \infty$), and zero field-gradients at the center, one obtains the free energy of critical fluctuation as $W^* = F - F_0$. Here F is obtained

by numerically evaluating (1) after having the time-independent solutions inserted, while F_0 is the free energy of the initial liquid. This is compared with $W^* = (16\pi/3)\gamma_f^3/\Delta f^2$ from the sharp interface “droplet” model of the classical nucleation theory, where $\gamma_f = \gamma(T_f)$.

The homogeneous nucleation rate is calculated as $J = J_0 \exp\{-W^*/kT\}$, where the nucleation prefactor J_0 of the classical kinetic approach is used, which proved consistent with experiments [11].

2.2 Multi-particle solidification in 2D

To treat nucleation and growth of particles on equal footing, we extend the standard binary phase field theory [6,7] via incorporating a non-conservative orientational field θ , which assumes a constant value between 0 and 1 in the crystal that determines crystal orientation in the laboratory frame as done recently by Kobayashi, Warren, and Carter [12]. We assume, however, that θ is defined in the liquid as well, where it fluctuates. Via this, we capture the feature that the short-range order in the solid and liquid are usually similar, with the obvious difference that the building units have a uniform orientation in the crystal, while their orientation fluctuates in the liquid. Following [12], we assume that the grain boundary energy acts in the solid and is proportional to $|\nabla\theta|$. We realize this by adding $f_{ori} = \mathcal{M}|\nabla\theta|$ to f_S , where \mathcal{M} is taken composition independent. The governing equation is

$$\frac{\partial\theta}{\partial t} = -M_\theta \frac{\delta F}{\delta\theta}. \quad (4)$$

For $\phi < 1$, equation (4) switches in orientational ordering, and chooses the value of θ that survives as the orientation of the particle relative to which the anisotropy of γ is measured. Unlike previous work, in our approach the orientation field θ is coupled to the phase field, and extends to the liquid phase where crystallographic orientation develops from orientational fluctuations. While our model incorporates grain boundary dynamics, M_θ is set so in the solid that grain rotation is negligible on the time scale of freezing.

Since PFT is a mean field type approach, nucleation is introduced as follows. Method I.: By including noise into (2)–(4). Method II.: The simulation area is divided into domains according to the local composition. The time-independent solution is found for these compositions. Critical fluctuations of statistically correct numbers following Poisson distribution are placed into these areas in every time step. The added small-amplitude noise makes these fluctuations either grow or shrink.

In nucleation-growth processes the transformed fraction often follows the Kolmogorov scaling, $X(t) = 1 - \exp\{-(t/t_0)^p\}$, where the “Kolmogorov exponent” p is representative of the mechanism of the phase transformation, and is evaluated from the slope of the plot $\ln[-\ln(1 - X)]$ vs. $\ln t$. We define the crystalline fraction via $\phi < 0.5$.

Simultaneous modeling of nucleation and growth raises the question of interface thickness: When using the nanometer size physical interface thickness, growth of large objects cannot be treated. If, in turn, we use a broad interface for large particles, relying on methods for quantitative description of dendritic solidification [5], we face with difficulties when addressing nucleation and particle impingement. Therefore, following previous work [10], we perform the calculations for a hypothetical system of a broader interface ($\delta = 41.6$ nm), a reduced interfacial free energy ($\gamma/6$), and an increased diffusion coefficient ($\sim 100 \times D_L$). The consistent treatment of nucleation and growth in our model, in which both processes emerge from the same governing equations, allows us to describe the life of particles from birth to impingement on other particles, a feature essential for understanding the variation of Kolmogorov exponent with transformed fraction during "soft-impingement".

Equations (2)–(4) were solved numerically on 2000×2000 and 7000×7000 grids, using parallel processing (MPI protocol) on a computer cluster consisting of 36 PCs of 1.0 – 1.6 GHz Athlon processors.

3 Results and Discussion

First we compare the phase-field predictions for the nucleation rate with computer simulations and experimental results for unary systems. In the Lennard–Jones system all relevant properties are known from molecular dynamics simulations [8]. The phase field profiles indicate that for typical undercoolings the critical fluctuations are ramified, and do not show bulk crystal properties. While the phase-field predictions for the nucleation rate agree with results from computer simulations [13], those from the classical sharp interface theory are too low by eight to ten orders of magnitude (Fig. 1a). Similar relationships are observed between predictions and experiment [14] for the ice–water system (Fig. 1b). While the input data are less reliable for the Cu–Ni system, the critical undercoolings computed for the realistic range of nucleation rates ($J = 10^{-4}$ to $1 \text{ drop}^{-1}\text{s}^{-1}$ for electromagnetically levitated droplets of 6 mm diameter) are also in a reasonable agreement with experiment [15] (Fig. 1c). Note that without adjustable parameters, a quantitative agreement has been achieved with simulations and experiment, indicating that the phase-field theory is a powerful tool to attack nucleation problems, provided that the physical interface thickness is used.

Multi-particle freezing has been studied in 2D using the thermodynamic properties of Cu–Ni, and a large anisotropy for the interface free energy ($\gamma_0 \{1 + s_0 \cos[4\vartheta]\}$ with $s_0 = 0.25$). With appropriate choices of M_θ and \mathcal{M} single orientation nucleates per particle. The freezing morphologies and the variation of exponent p with crystalline fraction are shown as a function of liquid composition in Fig. 2. Here the particles were nucleated by Method II. (Method I yields less regular shapes.) At small dimensionless nucleation rates $\tilde{J} = 0.49$ dendritic particles evolve, yielding $p \approx 3$, that obeys the

relationship $p = 1 + d$ (constant nucleation and growth rates in d -dimensions), which follows from the steady-state traveling tip solution of the diffusion equation. At large \tilde{J} pillow-shaped particles form. The variation of p with transformed fraction depends on the liquid composition. Similar behavior has been observed during the formation of nanocrystalline alloys.

At reduced M_θ , different orientations nucleate at the perimeter, of which those with their fastest growth direction perpendicular to the interface survive, yielding spherulitic growth morphology (Fig. 3).

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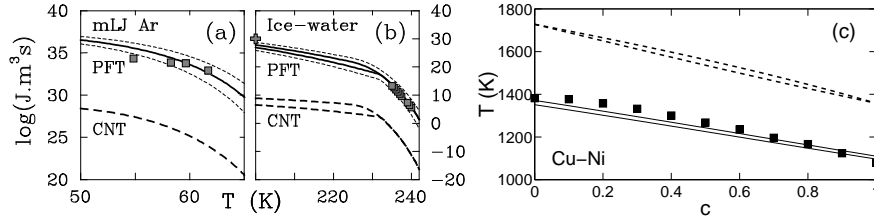


Fig. 1. Comparison of the predicted 3D nucleation rates with computer simulations and experiment (squares) on unary and binary systems. (PFT – phase field theory; CNT – classical sharp interface theory; dotted lines – limits due to the error of γ_f .)

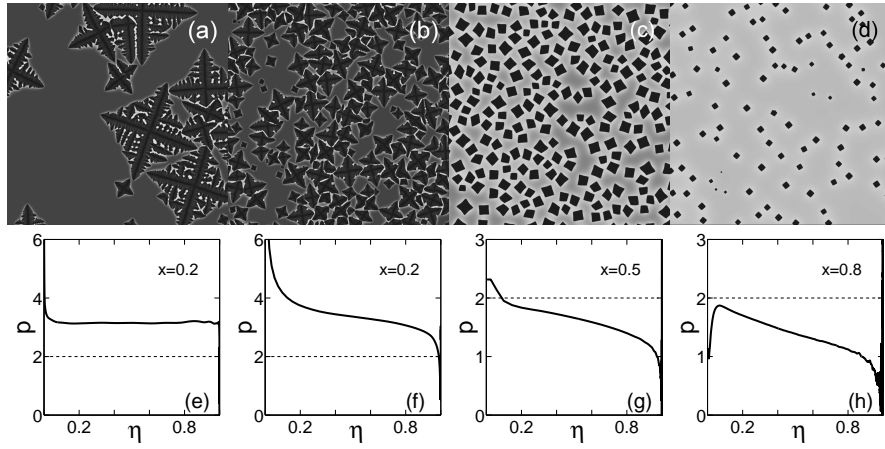


Fig. 2. Transformation kinetics in 2D vs. composition in the Cu-Ni system at 1574 K ($x = (C - C_l)/(C_s - C_l)$, where C_l and C_s are the solidus and liquidus compositions). (a)–(d) Snapshots of concentration distributions (black – solidus; light grey – liquidus); (e)–(f) Kolmogorov exponent vs. normalized transformed fraction $\eta = X/X_{max}$, where X_{max} is the maximum crystalline fraction.

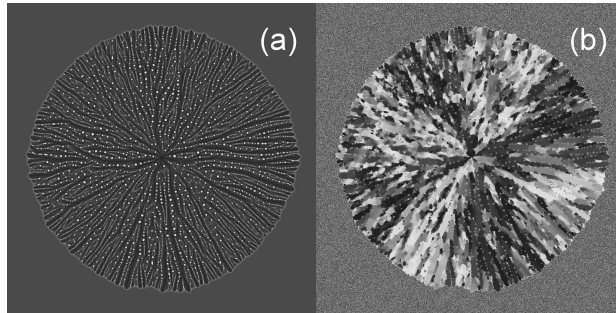


Fig. 3. Spherulitic growth at $x = 0.23$: (a) Composition and (b) orientation maps. Note the self-organized radial grain structure.