

Journal of Crystal Growth 237-239 (2002) 1813-1817



www.elsevier.com/locate/jcrysgro

Crystal nucleation and growth in binary phase-field theory

László Gránásy^{a,*}, Tamás Börzsönyi^{a,b}, Tamás Pusztai^a

^a Research Institute for Solid State Physics and Optics, POB 49, H-1525 Budapest, Hungary ^b Groupe de Physique des Solides,CNRS UMR 75-88, Universités Paris VI at VII,Tour 23, 2 place Jussieu,75251, Paris Cedex 05, France

Abstract

Nucleation and growth in unary and binary systems is investigated in the framework of the phase-field theory. Evaluating the model parameters from the interfacial free energy and interface thickness, a quantitative agreement is found with computer simulations and experiments on the ice-water system. The critical undercoolings predicted for a simple binary system are close to experiment. Phase-field simulations for isotropic and anisotropic systems show that due to the interacting diffusion fields the Avrami–Kolmogorov exponent varies with transformed fraction and initial concentration. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 81.10.Aj; 82.60.Nh; 64.60.Qb

Keywords: A1. Nucleation; A1. Phase-field theory; A1. Solidification; B1. Alloys

1. Introduction

The physical interface thickness is comparable to the size of critical fluctuation [1]. Accordingly, the diffuse interface models lead to a more accurate description of nucleation than those based on a sharp interface [2,3]. In this paper, the binary phase-field theory developed recently [4,5] is applied for crystal nucleation and growth. Since it is essentially a mean-field type approach, the fluctuations that lead to crystal nucleation need to be introduced artificially. This is done here either by incorporating uncorrelated noise into the governing equations, or by randomly placing slightly supercritical fluctuations into the simulation area.

2. Phase-field theory

Our starting point is a free energy functional developed along the lines described in Refs. [4] and [5]:

$$F = \int \mathrm{dr} \{ 1/2 \,\varepsilon^2 T(\nabla \phi)^2 + f(\phi, c) \},\tag{1}$$

where ϕ and *c* are the phase-field and the solute (B) concentration, $f(\phi, c) = WTg(\phi) + [1 - P(\phi)]g_{\rm S} + P(\phi)g_{\rm L}$ is the local free energy density, $W = (1 - c)W_{\rm A} + cW_{\rm B}$ the free energy scale, $g(\phi) = 1/4\phi^2(1-\phi)^2$, $P(\phi) = \phi^3(10 - 15\phi + 16\phi^2)$, while $g_{\rm S,L}$ are the free energy densities of the solid and liquid phases. We describe here the solidification of an ideal solution, thus $g_{\rm L,S} = (1 - c)g_{\rm L,S}^{\rm A} + cg_{\rm L,S}^{\rm B} + RT/v\{c\ln(c) + (1 - c)\ln(1-c)\}$, *R* the gas constant, and *v* the molar volume. Suband superscripts A and B refer to the pure components.

0022-0248/02/\$ - see front matter \odot 2002 Elsevier Science B.V. All rights reserved. PII: S 0 0 2 2 - 0 2 4 8 (0 1) 0 2 3 5 0 - 8

^{*}Corresponding author. Tel.: +36-1-3922222/3155; fax: +36-1-392-2219.

E-mail address: grana@szfki.hu (L. Gránásy).

In equilibrium, the model parameters, ε , W_A and W_B , are related to the interface free energies $\gamma_{A,B}$, melting points $T_{A,B}$, and interface thickness $\delta_{A,B}$ as $\varepsilon_{A,B}^2 = 6\sqrt{2\gamma_{A,B}\delta_{A,B}}/T_{A,B}$ and $W_{A,B} = 12\gamma_{A,B}/(\sqrt{2\delta_{A,B}T_{A,B}})$ [5]. To fulfill these relationships, we assume that $\varepsilon^2 = \varepsilon_B^2 + (\varepsilon_A^2 - \varepsilon_B^2)(T - T_B)/(T_A - T_B)$.

The model parameters are related to measurable quantities as $W_i \cong 16A \alpha \Delta S_f^i / v_i$ and $\varepsilon_i^2 \cong 4.5 \alpha A^{-1} \Delta S_f^i N_0^{-2/3} v_i^{-1/3}$, where *i* stands for components A or B, $A = \operatorname{atanh}(0.8), \Delta S_f^i$ is the melting entropy, and N_0 the Avogadro number. Here, we utilize that according to experiment [6] and the density functional theory [7] the interfacial free energy can be expressed as $\gamma_i = \alpha \Delta S_f^i T_i N_0^{-1/3} v_i^{-2/3}$, where $\alpha = 0.36$ for the modified Lennard–Jones system (mLJ) from computer simulations [8] and $\alpha \cong 0.6$ for metals (emerging from dihedral angle measurements [9]). While the 10-90% interface thickness $d_{10-90,\phi}$ for the phase-field is unavailable, studies on other systems indicate that for structural changes it should be close to $d_{10-90,D}$ of the diffusion coefficient profile [10]. Thus, $d_{10-90,\phi} \cong d_{10-90,D} = 3\sigma$ [8] is adopted, where σ is the length parameter of the LJ potential. For pure substances we take $d_{10-90,\phi}^i \cong 3(v_i/N_0)^{1/3}$. (Note that $d_{10-90,\phi}^i = 4\sqrt{2} \operatorname{atanh}(0.8)\delta_{i.}$)

We apply here the isothermal approximation. The equations for time evolution read as

$$\partial_{\rm t}\phi = -M_{\phi}\delta F/\delta\phi + \zeta_{\phi},$$
 (2a)

$$\partial_t c = \nabla [M_c \nabla \delta F / \delta c] + \zeta_c, \tag{2b}$$

where $\delta F/\delta x$ stand for the functional derivatives $(x = \phi, c)$, M_x are mobilities, and $\zeta_x = \zeta_{x,0} P(\phi)$ represent uncorrelated noise of amplitude $\zeta_{x,0}$ added to RHS to mimic the fluctuations. The properties of the critical fluctuations (nuclei) can be found as stationary solutions of Eqs. (2).

For spherical symmetry (a reasonable assumption), Eqs. (2a) reduces to:

$$\phi'' + 2/r\phi' = \Delta\mu(\phi, c)/(\varepsilon^2 T), \tag{3}$$

while $c(\phi) = c_{\infty} e^{-y}/(1 - c_{\infty} + c_{\infty} e^{-y})$, where $\phi \to 1$, and $c \to c_{\infty}$ for $r \to \infty$, and $\phi', c' = 0$ for r = 0. Here ' stands for differentiation with respect to the argument, $\Delta \mu(\phi, c) = WTg'(\phi) + [(1 - c)\Delta g_{\rm A} + c\Delta g_{\rm B}]P'(\phi), y = v(W_{\rm B} - W_{\rm A})g(\phi)/R + c$

 $v(\Delta g_{\rm B} - \Delta g_{\rm A})[P(\phi) - 1]/RT$, while Δg_i are the volumetric Gibbs free energy differences between the pure liquid and solid phases. The phase-field/ concentration profiles are determined by solving Eq. (3) numerically. The work of formation of critical fluctuation is $W^* = F - F_0$. F is computed via numerically evaluating Eq. (1) after inserting the solutions of Eq. (3), while F_0 is the free energy of the initial liquid. This is compared with $W_{\rm CNT}^* = (16\pi/3)\gamma_{\rm f}^3/\Delta g^2$ from the droplet model of the classical nucleation theory (CNT) [11] that assumes a sharp interface. (γ_f is the value at the melting point $T_{\rm f}$.) It is useful to evaluate the "interfacial free energy of critical fluctuations", $\gamma = (3W^*\Delta g^2/16\pi)^{1/3}$, that reproduces the phasefield result for W^* when inserted into the CNT, a quantity that is directly comparable with $\gamma(T)$ from nucleation experiment.

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, that proved consistent with experiments on various substances [11].

The Gibbs free energy difference of components has been calculated considering the difference $\Delta C_p(T)$ of the specific heats. Exceptions are the simulations performed in two dimensions (2D), where the simplified dataset and $\Delta C_p = 0$ used by Conti for Cu–Ni [12] has been adopted.

Simulations for nucleation and growth interacting via diffusion fields are performed on a 1000×1000 grid using periodic boundary conditions. Eqs. (2) are solved by an explicit finite difference scheme.

Nucleation is incorporated into the simulations as follows: (a) by increasing the amplitude of noise in Eqs. (2); (b) the simulation area is divided into domains according to the local composition. Eq. (3) is solved for these compositions. Slightly supercritical fluctuations of statistically correct numbers are placed into these areas in every time step.

To describe multi-particle solidification in the presence of *anisotropy*, we introduce a nonconservative orientational field θ (normalized orientational angle), which is random in the liquid, and has a definite value between 0 and 1 in the crystal that determines crystal orientation in the laboratory frame. Following [13], we assume that the grain boundary energy acts in the solid and is proportional with $|\nabla \theta|$. We realize this by adding $g_{\rm ori} = M |\nabla \theta|$ to $g_{\rm S}$, where coefficient M is assumed to be independent of c. The respective equation of motion has the form $\partial_t \theta = -M_\theta \delta F / \delta \theta + \zeta_\theta$, where $\zeta_{\theta} = \zeta_{\theta,0} P(\phi)$. Owing to the $P(\phi)[1 - P(\phi)]$ multiplier, this correction does not influence the free energy difference between the bulk solid and liquid, however, contributes to γ , making the original solution of Eq. (3) subcritical. After placing down the original solution (made supercritical by increasing $1 - \phi(r)$ a few percent), the equation of motion chooses from the local fluctuating orientations the one that survives as the orientation of the particle, and serves as the direction relative to which the anisotropy of $\gamma(=$ $\gamma_0[1 + s_0 \cos(m\vartheta)/2]$ for *m*-fold symmetry) is measured.

For isothermal nucleation and growth, the transformed fraction often scales with time as $X(t) = 1 - \exp\{-(t/\tau)^p\}$, where the "Avrami-Kolmogorov exponent" p is representative to the mechanism of the phase transformation, and is evaluated from the slope of the "Avrami-plot" $\ln[-\ln(1-X)]$ vs. $\ln t$. Standard references [14] present p = 3 for steady-state nucleation and interface controlled growth in 2D, while p = 2 is expected for nucleation and diffusion controlled growth. However, the latter is valid so far as the diffusion fields of the growing particles do not overlap. In the phase-field theory the evaluation of X(t) is straightforward. $\phi < 0.5$ is used to define the transformed fraction.

3. Nucleation in 3D

A simple one-component model system for which sufficiently detailed information is available from molecular dynamics simulations is the modified Lennard–Jones system by Broughton and Gilmer. Besides nucleation rate [15] and interfacial free energy [8], all relevant physical properties are known [8,16]. The predicted interfacial free energy of critical fluctuations (Fig. 1) is in a good agreement with that from computer simulation [15].



Fig. 1. Phase-field theory for the modified Lennard–Jones system: (a) order parameter profiles for the critical fluctuations at several reduced temperatures; (b) relative interfacial free energy of critical fluctuations as a function of reduced temperature. The value evaluated from the nucleation rate data from computer simulations [15] is also shown.



Fig. 2. Comparison of the predicted interfacial free energy with data evaluated from nucleation experiments [19–21].

A unique case, where reasonably accurate experimental values are available for the crystalliquid interfacial free energy is the ice-water system $\gamma_f = 29.1 \pm 0.8 \text{ mJ}^{-1} \text{ m}^{-2}$ ($\alpha = 0.297$) [17]. The other relevant parameters were taken from Ref. [18]. The estimate $d_{10-90,\phi} \cong 3(v/N_0)^{1/3}$ = 0.96 nm for the structural order parameter profile falls close to that of the translational order profile of the basal interface (0.99 nm) for hexagonal ice [10], that is isostructural to the (1111) face of metastable cubic ice, expected to nucleate. The temperature dependence predicted for the interfacial free energy of critical fluctuations accords well with that from nucleation experiments [19-21] (Fig. 2).

The binary calculations were performed for the nearly ideal Cu–Ni system. The thermodynamic properties of Cu and Ni were taken from [22]. While the predicted critical undercoolings for the nucleation rates $J = 10^{-4}$ and $1 \text{ drop}^{-1} \text{ s}^{-1}$ are fairly close to the experimental ones, the model

does not reproduce the slight curvature displayed by the experiments [23] (Fig. 3). Work is underway



Fig. 3. Nucleation temperature vs. composition as predicted by the phase-field theory for Cu–Ni. (Upper lower solid lines correspond to nucleation rates of 10^{-4} and $1 \, drop^{-1} s^{-1}$ for droplets of 6 mm diameter.) The experimental data (squares) refer to electromagnetically levitated droplets [23]. The calculated liquidus and solidus lines (dashed) are also shown.

to clarify the origin of this shortcoming of the model.

4. Crystallization in 2D

Owing to the different time and length scales of the coupled fields, we are compelled to use an enhanced interface thickness (41.6 nm) and a reduced interfacial free energy ($\alpha = 0.1$) in the simulations, as done by Conti [12]. Accordingly, no quantitative predictions can be made for the Cu–Ni system, although the proper (2D) scaling behavior is expected.

The simulations performed at 1574 K for different compositions and anisotropies are shown in Fig. 4. The Avrami–Kolmogorov exponent was found to vary with composition and transformed fraction. For example, due to diminishing



Fig. 4. Snapshots (composition maps) of nucleation and growth in binary phase-field theory: Upper row is for isotropic system, the central and lower ones are for extremely anisotropic interfacial free energy ($s_0 = 0.5$, yielding excluded orientations). The compositions from left to right are $x = (c_{\infty} - c_S)/(c_L - c_S) = 0.2$, 0.5, and 0.8, where c_L (light gray) and c_S (black) are the compositions at the solidus and the liquidus. The initial nucleation rate is 10 times smaller for the 3rd row.



Fig. 5. Avrami–Kolmogorov exponent, *p* vs. normalized transformed fraction, $f = X/X_{\text{max}}$, for nucleation and isotropic growth at x = 0.5 (solid line). The normalized number of nuclei $n = N/N_{\text{max}}$ is also shown (dotted line). X_{max} and $N_{\text{max}} (\cong 203)$ are the maximum crystalline fraction and particle number reached during solidification. The curves are averages over six runs.

nucleation rate and diffusional coupling between growing particles at x = 0.5, p approaches 1 as solidification proceeds, a value that corresponds to diffusion controlled growth of fixed number of nuclei (Fig. 5).

The particles formed by introducing noise into Eqs. (3) have more irregular shapes. Due to numerical stability problems emerging at large noise amplitudes, this approach can only be applied far from equilibrium, where nucleation occurs in a reasonable simulation time and area.

5. Summary

It has been demonstrated that the phase-field theory is an appropriate tool (i) to describe *quantitatively* crystal nucleation in 3D, and (ii) to model complex morphologies formed during equaxial solidification.

Acknowledgements

This work has been supported by the ESA Prodex Contract No. 14613/00/NL/SFe, by the Hungarian Academy of Sciences under contract No. OTKA-T-025139, the EU grant EU HPMF-CT-1999-00132, and the ESA MAP Project No. AO-99-101.

References

- P.R. ten Wolde, M.J. Ruiz-Montero, D. Frenkel, Phys. Rev. Lett. 75 (1995) 2714.
- [2] L. Gránásy, F. Iglói, J. Chem. Phys. 107 (1997) 3624.
- [3] L. Gránásy, D.W. Oxtoby, J. Chem. Phys. 113 (2000) 2399.
- [4] G. Caginalp, J. Jones, Ann. Phys. 237 (1995) 66.
- [5] M. Conti, Phys. Rev. E 61 (2000) 642.
- [6] D. Turnbull, J. Appl. Phys. 24 (1950) 1022.
- [7] W.H. Shih, Z.Q. Wang, X.C. Zeng, D. Stroud, Phys. Rev. A 35 (1987) 2611.
- [8] J.Q. Broughton, G.H. Gilmer, J. Chem. Phys. 84 (1986) 5749.
- [9] J. Waseda, W.A. Miller, Trans. JIM 19 (1978) 546.
- [10] J.A. Hayward, A.D.J. Haymet, J. Chem. Phys. 114 (2001) 3713.
- [11] K.F. Kelton, Solid State Phys. 45 (1995) 75.
- [12] M. Conti, Phys. Rev. E 56 (1997) 3197.
- [13] J.A. Warren, R. Kobayashi, W.C. Carter, J. Crystal Growth 211 (2000) 18.
- [14] J.W. Christian, The Theory of Transformations in Metals and Alloys, Pergamon, Oxford, 1981.
- [15] L.A. Báez, P. Clancy, J. Chem. Phys. 96 (1992) 4655.
- [16] J.Q. Broughton, G.H. Gilmer, J. Chem. Phys. 79 (1983) 5095.
- [17] S.C. Hardy, Philos. Mag. 35 (1977) 471.
- [18] L. Gránásy, J. Mol. Str. 485-486 (1999) 523.
- [19] P. Taborek, Phys. Rev. B 32 (1985) 5902.
- [20] G.T. Butorin, V.P. Skripov, Kristallographie 17 (1972) 379.
- [21] J. Huang, L.S. Bartell, J. Phys. Chem. 99 (1995) 3924.
- [22] J. Wachter, F. Sommer, J. Non-Cryst. Solids 117/118 (1990) 890.
- [23] R. Willnecker, D.M. Herlach, B. Feuerbacher, Mater. Sci. Eng. 98 (1988) 85.