



PHASE-FIELD ANALYSIS OF NUCLEATION PHENOMENA

Theses of Ph.D. dissertation

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Budapest

2011

Background

Crystalline materials play an important role in our everyday life. Most of them are polycrystalline, i.e. composed of a large number of individual crystallites. Despite intensive research, the formation of such polycrystalline structures is poorly understood. One of the main sources of difficulty is the process of nucleation: The critical fluctuations (i.e. nuclei) forming on practically accessible time-scales are usually so small ($\sim 1nm$) that they do not show bulk crystal properties even in their center, i.e. their size is comparable to the thickness of the solid-liquid interface (that extends to several molecular layers). Thus, the Classical Nucleation Theory – which assumes sharp solid-liquid interface – predicts the height of the nucleation barrier with a poor accuracy. Apparently, field theoretic models that rely on a diffuse interface, offer a natural way to handle non-bulk crystal properties occurring in small clusters.

A quantitative testing of cluster models is far from being trivial. The primary measurable quantity in nucleation experiments is the nucleation rate [$J_{SS} = J_0 \exp(W^*/kT)$], which can be converted to an estimate of the nucleation barrier height W^* , which in turn can be deduced from an appropriate cluster model and be related to the interfacial free energy and the thermodynamic driving force. Even if the pre-exponential factor J_0 is predicted with a sufficient accuracy, and the experiments refer to homogeneous nucleation (a condition almost impossible to ensure), the interfacial free energy is usually sufficiently unavailable. Therefore, despite the wealth of data available for the nucleation rate in the literature, there is very little hope for a conclusive experimental test of a nucleation theory. In contrast, simple model systems, where the W^* , and all the data needed to fix the model parameters can be evaluated with a high accuracy from atomistic simulations, offer an ideal test ground.

Aims

1. **Quantitative testing of nucleation theories:** The best known simple model system that shows crystallization is the hard-sphere fluid. Extensive studies performed using the Monte-Carlo and molecular dynamics techniques have clarified its main physical properties. Using the equations of state, and the coexistence pressure, the free energy densities of the bulk phases can be calculated. The properties of the solid-liquid interface (e.g., the interfacial free energy and the thickness of the interface) have been determined by molecular dynamics simulations, and an accurate value is available for the nucleation barrier from Monte-Carlo simulation. The existence of these data offers a unique possibility for testing different nucleation theories. While such a test has been performed earlier, a recent substantial downward revision of the interfacial free energy necessitates a re-evaluation of the nucleation models.
2. **Investigation of crystal nucleation in eutectic systems in advanced phase-field theory:** Having validated the Ginzburg-Landau free energy based phase-field approach in the case of the hard-sphere system, I am going to address crystal nucleation in binary systems. Even though atomistic simulation performed for the Cu-Ni system indicate a composition dependent interfacial free energy, little is known about the properties of the crystal-liquid interface in more complex systems, such as the eutectic systems that are of technological importance. Utilizing that the crystal structure is *fcc* for both components, I have chosen the Ag-Cu eutectic system for my study, whose phase diagram incorporates a metastable liquid-liquid miscibility gap in the highly undercooled state. I am going to map the nucleation pathways and composition and temperature dependencies of the nucleation barrier both inside and outside of the miscibility gap. A behavior resembling to the results from classical density functional calculations for globular proteins is expected, however, the nucleation pathways are probably more complex here, as there are two solid phases that can nucleate. Besides its theoretical interest, investigation of nucleation at the metastable critical point in eutectic systems is further emphasized by its practical importance: identification of the possible nucleation pathways may help us to control phase selection and the respective microstructure.

- 3. Advanced phase-field model for describing crystal nucleation in the presence of metastable crystalline phase:** The role played by metastable phases in nucleation is a long standing problem. Alexander and McTague argued that the *bcc* structure is preferred in simple liquids, a finding supported by molecular dynamics simulations. I propose here a Multiphase-Field Theory based on the Ginzburg-Landau free energy for the liquid-*fcc*, liquid-*bcc*, and *fcc-bcc* transitions. I am going to explore the competition between *fcc* and *bcc* nucleation in the Fe-Ni system.

Applied methods

In the present thesis three different levels of modeling are applied to address the nucleation in the hard-sphere, the Ag-Cu, and the Fe-Ni systems.

(i) **The droplet model of the classical nucleation theory** (CNT) extends the concept of macroscopic droplets into the microscopic regime without correction, and relies on the macroscopic interfacial free energy, while assuming bulk crystal properties in the volume of the droplet. This approach is widely used in interpreting the experiments, though it is known to be of very limited accuracy at the small size of nuclei relevant for typical time scales.

(ii) **Phenomenological cluster models**: Two significantly different approaches are considered here. The Self-Consistent Classical Theory tries to remove the evident inconsistency of the CNT that it distinguishes the monomer of the solid phase and the monomer of the liquid phase (which should be, in principle, the same physical object). In contrast, the phenomenological Diffuse Interface Theory (DIT) tries to take into account the diffuseness of the solid-liquid interface. Assuming yet bulk crystal properties at the center of the nuclei, this approach predicts a curvature dependent interfacial free energy, and usually improves significantly the agreement between theory and experiment for nucleation.

(iii) *Phase-field type models* (PFT): These are *van der Waals / Cahn-Hilliard / Landau* type classical field theoretical descriptions, in which the transition between the solid and liquid phases is monitored by a coarse-grained structural order parameter. The spatial change of the order parameter is penalized by a square-gradient term, and has a skewed double-well contribution to the free energy density, whose minima represent the newly forming and the parent phase. Accordingly, they predict a diffuse interface, and are inherently capable of describing small clusters composed entirely of interface. Their accuracy, however, depends critically on the accuracy of the double-well free energy used in the model. In this work, different PFT approaches are compared: one with conventional choices for the double-well and interpolation functions, and a version, in which a Ginzburg-Landau type free energy is used that considers the structure of the crystal.

Results

1 I have performed a quantitative test of a range of nucleation theories in the hard-sphere system using the recently updated value of the solid-liquid interfacial free energy [P3,P4]. It has been found that after fixing all model parameters to interfacial properties evaluated from atomistic simulations, only a Phase-Field Theory relying on a Ginzburg-Landau free energy (PFT/GL) and the phenomenological Diffuse Interface Theory predicted the height of the nucleation barrier with reasonable accuracy. In contrast, phase-field models using the standard double-well and interpolation functions (PFT/S) significantly underestimate the nucleation barrier. A comparable underestimation is observed for the sharp interface models, such as droplet models of the Classical Nucleation Theory and the Self-Consistent Classical Theory.

2 I have investigated the properties of the solid-liquid and solid-solid interfaces and the possible nucleation pathways for the *fcc* crystalline phase in the eutectic alloy Ag-Cu using a phase-field theory based on a single-order parameter Ginzburg-Landau theory. Outside of the metastable liquid-liquid immiscibility region I have observed the following [P1].

- The interfacial free energy of the equilibrium planar *fcc*-liquid interface shows a complex behavior as a function of both temperature and composition. In contrast, the interface thickness is roughly independent of temperature.
- Two types of *fcc* nuclei compete: a Ag rich and a Cu rich. For the terminal compositions, the effective interfacial free energy of critical fluctuations increases with increasing temperature at large undercoolings and levels off at the melting point. At $c = 0.5$ the interfacial free energy shows a maximum. The interface thickness decreases with temperature for all compositions.
- While the DIT predictions for the interfacial free energy of nuclei fall reasonably close to those from the PFT/GL, the CNT with an interfacial free energy from Spaepen's model, and the PFT/S model underestimate the undercooling necessary for homogeneous nucleation.

3 I have investigated possible nucleation pathways in the metastable liquid-liquid immiscibility region of the eutectic Ag-Cu system [P2]. In this region of the phase diagram I have found the following.

- Three pairs of nuclei may occur inside the liquid-liquid coexistence region: liquid-liquid nuclei; normal crystal-liquid nuclei that are the continuation of the nuclei observed outside the immiscibility region; and the "composite" nuclei in which the solid core is surrounded by a well-defined liquid "skirt" resembling to the liquid-liquid nucleus forming at the initial liquid composition.
- Four types of these nuclei may occur on both side of the spinodal line. These are (a) a liquid phase nucleus rich in the minority component of the initial liquid and three kinds of *fcc*-type nuclei. Two solutions of the latter have an *fcc* core rich in the minority component of the initial liquid: (b) one that is the continuation of nuclei observed outside the immiscibility region and (c) a composite nucleus, in which the *fcc* core appears inside a well-defined liquid droplet forming in the initial liquid. The last one (d) is the continuation of that *fcc* nucleus observed outside the immiscibility region whose crystal core is rich in the majority component of the initial liquid. Remarkably, moving toward the spinodal line from outside solutions (b) and (c) converge to each other at a bifurcation line. Between this line and the spinodal line only solutions (a) and (d) may exist.
- An enhanced nucleation rate has been observed near the critical point for both the Ag and Cu rich crystal nuclei along the constant driving force lines. This is in agreement with previous results from density functional calculations, atomistic simulations and experiments performed on globular proteins.

4 I have proposed a microscopic Multiphase-Field Theory relying on a Ginzburg-Landau expanded free energy. By anchoring the model parameters to measurable physical properties I have studied competing nucleation of *fcc* and *bcc* structures in the peritectic Fe-Ni system.

- I have shown that composite nuclei - where both the *fcc* and *bcc* structures are present at the interface - are preferable to single-phase nuclei.
- With a reasonable choice of free energy of the *fcc-bcc* interface, the proposed model predicts well the *fcc-bcc* phase-selection boundary in the Fe-Ni alloys.

Scientific publications related to the theses

[P1] G. I. Tóth and L. Gránásy. phase-field theory of interfaces and crystal nucleation in a eutectic system of *fcc* structure. I. Transitions in the one-phase liquid region. *J. Chem. Phys.* **127**, 074709 (2007).

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- [P12] G. Tegze, T. Pusztai, G. Tóth, L. Gránásy, A. Svandal, T. Buanes, T. Kuznetsova, B. Kvamme: Multi-scale approach to CO₂-hydrate formation in aqueous solution: Phase field theory and molecular dynamics. Nucleation and growth. *J. Chem. Phys.* **124**, 234710 (2006).

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