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Phase-Field Crystal Modeling
of
Nucleation and Growth Processes

Ph.D. dissertation pamphlet

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Premise

Crystalline freezing of liquids is a process of great importance in various branches of science, including materials science, atmospheric science, geosciences and biology (the formation of crystalline materials in living organisms via biomineralization: mollusc shells, coral skeletons, bones, teeth, etc.). It is also of crucial importance from a technological point of view.

Ideally, after cooling pure liquids below their melting point, the crystalline phase forms via nucleation, during which nanoscale crystal-like heterophase fluctuations appear. Those, that exceed a critical size grow further with a high probability, whereas the smaller fluctuations decay. This critical size is determined by the interplay of the solid-liquid interface free energy and the grand potential difference between the crystal and the liquid. Although, nucleation happens on the nanoscale, it usually influences the grain-size distribution and the related physical properties on larger scales. Accordingly, crystallization is a multiscale process both in time and space.

A variety of theoretical models have been developed to capture different aspects of solidification. The inventory of modelling tools, which describe crystallization from the melt ranges from ab initio computations and atomistic descriptions such as Monte Carlo/molecular dynamics simulations and particle based cluster dynamics simulations, to the density functional theory of classical particles, coarse-grained phase-field models and large-scale classical continuum models. Each of these theoretical tools have their limitations and their respective domain of validity. Accordingly, often a combination of models is required to address specific problems.

During the past decades, the knowledge gained on crystal nucleation and growth by experiment and molecular simulations grew spectacularly: trajectories of colloidal particles in suspensions can be followed by confocal laser scanning microscopy, providing structural/dynamical information, comparable to the particle scale information from molecular dynamics or Brownian dynamics simulations. For example, it has been established, that two-step nucleation via dense liquid/amorphous/metastable crystalline precursors is rather the rule, than the exception, a finding in accord with a range of experiments. These also indicate the limitations of classical nucleation theory, which does not contain structural information explicitly. Optical experiments on hard-sphere-like colloidal suspensions indicate, that the crystal structure plays an important role in heterogeneous crystal nucleation. To account for such effects, one needs a theory, which contains both crystalline and amorphous structures, anisotropies and elasticity naturally and which also offers a possibility to go beyond overdamped density transport.

In this dissertation, I am going to address on the molecular scale early stages of crystallization, including homogeneous and heterogeneous crystal nucleation, formation of defects at the solidification front and during strained epitaxial growth. I rely on the phase-field crystal (PFC) model, which can be viewed as a simple dynamical density functional theory. It has been proposed in its simplest form by K. R. Elder et al. [1] in 2002. It can be obtained from the density functional theory of classical particles via gradient expansion. Owing to its relative simplicity, especially when numerical simulations are concerned, this approach rapidly became fairly popular and has been employed to model a broad range of physical phenomena, as it is able to address fairly sizeable samples (containing up to several millions of atoms) on a diffusive time scale.

Topics

My dissertation is broken into three main chapters, each consisting of distinct topics of my investigations. Each section below is connected to the chapter with the same title in the dissertation. Here, each topic is briefly exposed, so that the corresponding section in "Theses" will solely *state* my own results.

1 Precursor assisted nucleation

In a variety of experimental and model systems, crystal nucleation seems to progress in a more complex way, than classical nucleation theory (CNT) predicts. The critical heterophase fluctuation does not necessarily posses the configuration of the most stable crystalline solid. The PFC model at large undercoolings follows this pattern: the stable BCC phase appears only after the formation of an initial amorphous cluster.

I perform instantaneous quenches in the diffusive PFC model to study precursor formation. For local structure identification, I use the first neighbor averaged bond orientational order parameters ($\bar{q}_l$) of Lechner and Dellago [2]. I analyse the medium range crystalline order (MRCO) recognized by Tan et al. [3], in terms of these bond order parameters. For a more coarse-grained analysis, I compare the radial distribution functions (RDFs) of the amorphous clusters to molecular dynamics (MD) simulations of BCC metal nanoparticles, conducted by Hoang [4] and Shibuta et al. [5].

In summary, dynamical mean field theories, such as the PFC model are not limited by the assumptions of CNT and predict the non-direct appearance of the thermodynamically most stable solid phase at large undercoolings via an amorphous solid structure.

2 Hydrodynamic EOMs

Dynamical density functional theory (DDFT) and the diffusive phase-field crystal (DPFC) model are appropriate equations of motion (EOMs) for time dependent modeling of crystallization in systems with a carrier fluid, such as colloidal suspensions. The realized diffusive density transport limits the applicability of these theories to overdamped systems. To describe solidification in molecular liquids as well, the coupling of PFC thermodynamics to hydrodynamic density transport is an ongoing effort. I use two of such hydrodynamic models to study crystallization kinetics.

The first one is the hydrodynamic PFC (HPFC) model developed by Tóth et al. [6], which was the first model, that demonstrated steady growth and a correct capillary wave spectrum. I study two-dimensional crystallization kinetics in the HPFC model. By changing the driving force, I take a look at the corresponding change in growth forms. I study the interaction between nucleation and growth by way of the Johnson-Mehl-Avrami-Kolmogorov [7] model. I also explore the microscopic aspects of the athermal nucleation model of Greer et al. [8].

The interaction of nucleation and the growth front plays the determining role in the structure of polycrystalline growth forms, such as disordered dendrites and spherulites. The mechanism behind the creation of these complex polycrystalline growth forms, has been identified [9] as growth front nucleation (GFN). It describes the formation of grains of new orientation at the propagating solid-liquid interface, the growth front. While this approach, relying on a coarse-grained orientation field proved to be quite successful in capturing rather complex solidification patterns, the microscopic kinetics of the GFN phenomenon remained largely hidden in such coarse-grained models. Due to the fact, that in the HPFC model I observe a change in growth

forms with changing undercooling, it seems promising to study the microscopic origins of GFN in the HPFC model. I find mechanisms, which are not present in the DPFC model and manage to gain insight, under what conditions a single crystal develops into a polycrystalline growth form.

A drawback of the HPFC model surfaced in the meantime, namely, that the velocity field was not able to transport the atomic density pattern of the crystalline domains. Thus, the development of another hydrodynamic model, the incompressibly advected hydrodynamic PFC model (INCA-HPFC) became necessary, to study such phenomena, in which the displacement of solid clusters in fluid flow is important. I develop such a model and study a complex solidification problem in forced convection.

3 Epitaxial studies

The properties of epitaxial films depend on their structural integrity. It is recognized, that if the lattice mismatch between a substrate and the growing epilayers is sufficiently small, the initial atomic layers deposited will be strained to conform to the substrate, resulting in the formation of a coherent interface. Beyond a certain number of layers, however, the most stable configuration might contain dislocations present in the substrate-epilayer interface. I perform systematic investigations of the critical thickness h_c, in heteroepitaxial PFC simulations in two dimensions under well controlled conditions, where a square lattice substrate - represented by a suitable periodic potential - is used.

I study the epitaxial growth process under various circumstances in the two-dimensional DPFC model, in the section perpendicular to the substrate-epilayer interface. I show, that h_c increases with decreasing strain. This is in qualitative agreement with experiments, static energy-balance based approaches, such as the van der Merwe (VDM) [10], the Matthews-Blakeslee (MB) [11] and People-Bean (PB) [12] models.

However, I find large discrepancies when the simulation data from the h_c vs. strain relationship is analyzed in terms of the theoretical results from the VDM, MB and PB models. For the resolution of this issue, I investigate the reasons behind defect formation from the kinetic perspective, based on the Asaro-Tiller-Grinfeld (ATG) [13, 14] instability. I finally conclude, that the dynamic theory of the ATG instability is a more appropriate approach to the study of the formation of misfit dislocations during growth, than the previous, energy-balance based static approaches.

Theses

1 Precursor assisted nucleation

(a) [**P1**] Following the analysis of Tan et al., I segment the solid domains into amorphous, MRCO and BCC atomic neighborhoods. By analyzing the solid fractions of these species in time, I show, that the first solid clusters are definitely amorphous and MRCO, whereas BCC ordering appears later, as a consequence. MRCO regions are present mostly on the surfaces of the amorphous clusters and facilitate the appearance of the BCC crystal.

(b) [**P1**] I present structural analysis of the non-crystalline precursor clusters in terms of the bond order parameters by Lechner and Dellago, which places them at the same region in the two-dimensional $\bar{q}_6$ vs. $\bar{q}_4$ histograms as the Lennard-Jones (LJ) liquid in Ref. [2], implying a structural similarity between the amorphous PFC precursor and the LJ liquid.

(c) [**P1,P5**] When employing refined thermodynamics for iron in the eight-order fitting PFC model, I obtain a remarkable similarity between the RDF of the amorphous state in the PFC model and those from MD simulations of undercooled iron. The RDF of the BCC domains is virtually identical to those from MD simulations of crystalline BCC iron.

2 Hydrodynamic EOMs

(a) [**P2**] Using the HPFC model I document a transition of growth forms, from an isotropic one at low undercoolings, to a highly anisotropic hexagonal one, at high undercoolings, which resembles a faceted shape. I fit the Johnson-Mehl-Avrami-Kolmogorov model to the time development of solid fraction. The Avrami exponent turns out to be $p = 3.31$, which is larger than the expected value of 3, indicating linear growth and an increasing nucleation rate in time. I study athermal nucleation on a solid substrate. I observe a critical undercooling, whereby the heterogeneously nucleated stable crystalline phase on the wetting surface starts to grow unconditionally. I thus demonstrate, that the free growth limited model of particle induced crystallization by Greer et al. remains valid down to the nanoscale in simple liquids.

(b) [**P1**] In the presence of momentum fluctuations at large undercoolings, I observe, that an initially single crystal develops new crystallographic orientations, which I identify as GFN. I find two distinct microscopic mechanisms behind this: (1) dislocations enter the hexagonal crystal along its perimeter, which appear to be misfit dislocations, (2) small crystallites nucleate in the neighborhood of the solid-liquid interface, which emerge from the interaction of the density fluctuations in the liquid and the solid-liquid interface. The HPFC appears to be the first atomic scale model, which yields growth front nucleation in the metastable liquid regime. By analyzing single crystal growth without thermal fluctuations, I show clear evidence, that strain is present near the perimeter of the anisotropic growth form. While the direct cause of this change in lattice constant is not clear at the moment, the first mechanism of GFN is clearly a result from internal stresses in the growing interface, which result in misfit dislocations captured during growth.

(c) [**P3**] I develop the so-called INCA-HPFC model to address the interaction of the undercooled melt with a foreign substrate under forced convection and to specifically overcome the limitations of the HPFC model. Using the INCA-HPFC model, I simulate forced convection around a substrate in an undercooled melt. I observe the heterogeneous nucleation of crystalline clusters on the downwind side of the substrate. When the crystal reaches a certain large size, the shearing forces from the fluid parcels tear the crystal off of the substrate, which is then transported away. Afterwards, the substrate is able to facilitate further nucleation events. I so demonstrate, that it is indeed possible to address in a *single order parameter* model stochastic nucleation of crystals on foreign particles, elastic cohesion of crystalline particles, plastic deformation when elastic forces are overcome, interaction between fluid and solid parcels due to shearing forces and free advective transport.

3 Epitaxial studies

(a) [**P1,P4**] I apply the theoretical expressions of the static energy-balance based h_c vs. strain relationships to the simulation data. The correct model should, in principle, transform the data into straight lines intersecting the origin. The worst result is produced by the VDM model. The MB model results in close to straight lines of the data from the continuous cooling studies, both at low and at high anisotropies. However, the lines miss the origin.

For the other cases it shows an overall poor fit quality. The simulation results are fit better by the PB model, especially the isothermal studies. These lines, however, still fail to go through the origin.

(b) By simulating open systems in equilibrium in PFC simulations, I show, that the formation of misfit dislocations is governed by the growth factor of the ATG instability and not by the number of epitaxial layers, indicating, that the dynamics of defect formation and solidification velocity does play a decisive role in the determination of h_c. I show, that basing the estimation of h_c on the ATG growth factor, leads to the divergence of h_c for *non-zero* values of strain, this important fact being the reason, that expressions of the static models when applied to the simulation data miss the origin. Positive and negative values of strain lead to distinct values of h_c, this can be observed experimentally as well as in my simulations. Static theories, however, are symmetric in the sign of strain. Thus, I recover the asymmetry, due to the assumption of total stress elimination, since this leads to distinct values of the periodicity of the appearance of defects for positive and negative strains. I use the ATG growth scenario to recover the logarithmic noise strength dependence of h_c, which I have observed in my numerical simulations [P4]. This suggests, that h_c is more than likely determined by the ATG mechanism, thus defect formation *kinetics* cannot be neglected.

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Supporting publications

P1 **Podmaniczky, F.**; Tóth, Gy. I.; Tegze, Gy.; Pusztai, T.; Gránásy, L. "Phase-field crystal modeling of heteroepitaxy and exotic modes of crystal nucleation" JOURNAL OF CRYSTAL GROWTH 457, 24 (2017)

P2 **Podmaniczky, F.**; Tóth, Gy. I.; Tegze, Gy.; Gránásy, L. "Hydrodynamic theory of freezing: Nucleation and polycrystalline growth" PHYSICAL REVIEW E 95, 052801 (2017)

P3 **Podmaniczky, F.**; Gránásy, L. "Molecular scale hydrodynamic theory of crystal nucleation and polycrystalline growth" JOURNAL OF CRYSTAL GROWTH 597, 126854 (2022)

P4 **Podmaniczky, F.**; Tóth, Gy. I.; Tegze, Gy.; Gránásy, L. "Recent Developments in Modeling Heteroepitaxy/Heterogeneous Nucleation by Dynamical Density Functional Theory" METALLURGICAL AND MATERIALS TRANSACTIONS A 46, 4908 (2015)

P5 Gránásy, L.; Tóth, Gy. I.; Warren, J. A.; **Podmaniczky, F.**; Tegze, Gy.; Rátkai, L.; Pusztai, T. "Phase-field modeling of crystal nucleation in undercooled liquids – A review" PROGRESS IN MATERIALS SCIENCE 106, 100569 (2019)