

Phase-Field Crystal Modeling of Complex Solidification Processes

Theses of PhD Dissertation
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Introduction

Crystalline ordering in colloidal systems is a key process in various practical applications, and serves as a useful analogue to the crystallization of molecular fluids since it can be directly observed, even in real space and real time. Conclusions drawn from observing colloidal crystallization often apply in a more general sense. Most theoretical approaches, that address crystallization are missing important features arising from the microscopic behavior, and can be applied only on mezo and macro scales. Time-dependent, dynamical density functional techniques (DDFT) are the most effective atomic scale theories in addressing real-size crystallization processes on diffusive time scales. Phase-field crystal (PFC) theory, which is derived from the Ramakrishnan-Yussouff type DFT using power series expansions has further two orders of magnitude computational advantage over conventional DDFT techniques. Conserved, diffusive equation of motion, derived from the PFC free energy functional represents a qualitative model of colloidal self-assembly. Concerning the dynamics of crystallization, DDFT and PFC models uniquely provide sub-particle-scale spatial resolution on diffusive timescales.

Research objectives

Although, the PFC theory is effective in merging features of different spatial and time regimes, the mesoscopic description of the ordering process is not feasible using conventional numerical techniques (e.g. explicit finite difference method). I was aiming at setting up a novel numerical scheme to extend the applicable scales to real case crystalline morphologies. The numerical procedure explained in thesis statement No. 1.

Contrary to the DDFT and its variants, in most theories the anisotropies of the crystal are incorporated in an extrinsic way, using parameters controlling them in a direct way. In setting up the tasks, I have considered as a major feature that in DFT theories the anisotropic properties are intrinsic, arising from the local crystalline structure. The anisotropy of the crystal-fluid interfacial energy and the growth anisotropy of kinetic origin are considered as the most important factors affecting crystal growth on mesoscale.

Under free growth conditions, 2D colloidal systems order into a hexagonal lattice. Despite its simplicity, various dynamical growth-patterns are observed in these systems. Using the PFC technique I have explained how the formation of these morphologies can be related to the dynamic properties, and the anisotropies of the interface (thesis statement No. 2.).

In 3D, the PFC model features simple 3D crystalline structures, such as body centered cubic (BCC), face centered cubic

(FCC) and hexagonal close packed (HCP) lattices. In thesis statement No. 3. I am aiming to discuss the growth anisotropies of kinetic origin for BCC, FCC and HCP structures. Dendritic texture is common in crystalline matter, and it is generally acknowledged that growth anisotropy plays crucial role in controlling the morphology. The relation between the measured anisotropy and the formation of primary dendrite arms are discussed in single component colloidal systems. Examining the formation of the secondary arms is computationally more demanding, therefore, it has been done in a 2D binary model system (thesis statement No. 4.).

Thesis statements

1. In the PFC theory, the simplest diffusive equation of motion is a sixth order nonlinear partial differential equation (PDE). When time integrating, using simple explicit method the applicable time-step is very limited. Also, conventional implicit finite difference (FD) and finite element (FE) discretizations lead to large, sparse sets of algebraic equations. I have used a new concept to improve computational efficiency. Using operator splitting I have separated the homogeneous terms from nonlinear and variable coefficient terms. It was shown that the time-stepping with a properly separated variable coefficient term is unconditionally stable. Also, using Fourier spectral discretization, the implicit stepping with the

homogeneous operators ending up with a trivial set of algebraic equation, which can be written in diagonal matrix form. This numerical approach is superior to conventional explicit FD schemes both in terms of accuracy and computational efficiency. Excellent scalability on massively parallel systems has been achieved.

2. a) It has been shown in a two dimensional, single component PFC model that varying the supersaturation may lead to two distinct crystallization modes. At low driving force the moving crystal-fluid interface is diffusion controlled, contrary to the steady, diffusionless mode at high supersaturations. The existence of these modes is consistent with colloid experiments and with the predictions of the Wilson-Frenkel theory [W.B. Russel, Langmuir 1997].
- b) Dynamical properties characterizing the crystallization mode are distinctive. Bulk densities are different for the two cases: when the crystallization is diffusionless, hardly any change can be observed compared to the liquid density while in the diffusion controlled case the crystal density at the interface governed by the thermodynamic driving force, and depends on the local liquid density. As a consequence of dynamical broadening or kinetic roughening, the interface is broader at high supersaturations, than the sharp faceted interfaces at low supersaturation. This dynamical broadening can also be identified as the main re-

ason behind the reducing growth anisotropy as interface velocity increasing.

- c) As supersaturation is increasing, *compact hexagonal - dendritic - fractal-like - porous compact* multi-step morphological transition is observed. This sequence of morphologies shows striking similarity to 2D colloidal textures when varying the area fraction in the suspension. Simulations unveil, that fluctuation-driven random selection of the solidification modes along the interface yields fractal-like shape at intermediate driving forces.
3. a) In 3D systems the kinetic anisotropy has been measured for planar growth of BCC, FCC and HCP phases. The reduced anisotropy of the FCC-fluid interface is in good agreement with optical measurements performed on ^3He crystal [V. Tsepelin, Phys. Rev. Lett. 2002]. As for the 2D cases, the kinetic anisotropy depends on the driving force, decreases as the supersaturation increasing. The change is not uniform, it differs for the particular crystal faces.
- b) Supersaturation dependent growth anisotropy, observed in planar growth, contributes to the formation of mesoscale textures. In my PhD work this is demonstrated via the morphological change of single crystal dendrites. As the anisotropy decreases a transition from a compact octahedral shape to a faceted needle-like dendrite is ob-

served. Beside the above general trend, atypical dendritic growth: hyper-branching, and formation of extra primary arms occur.

- c) On atomic scale the dynamics of planar growth shows layer-wise growth of the crystal faces. It is also found, that the 2D nucleation process plays crucial role in the formation of a new layer. Different nucleation rate on crystal faces identified as a major factor that defines the growth anisotropy of kinetic origin.
4. a) The dynamical behavior of the dendrite tip and the formation of secondary arms have also been discussed in the framework of a two component PFC model. Besides colloidal systems, it can also be applied to binary molecular fluids since diffusion controlled dynamics apply. In the presence of thermal fluctuations, which represented by adding colored noise to the equations of motion, fluctuating dendrite tip radius is observed. Positions of the secondary dendrite arms correlate with the tip fluctuations, which is conform with the selective amplification theory (SAT). In SAT some surface fluctuations at the tip are amplified, and evolve to secondary dendrite arms. Larger scale computations are needed to quantify the correlation.
- b) Macroscopic kinetics of polycrystalline growth has been analyzed in terms of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model. The Avrami exponent (p) varies in time

between 1.5 and 3, respectively. Exponents are in agreement with values expected in a 2D system, at early stage it shows interface controlled kinetics, which turns to be diffusion controlled at late stages.

Supporting publications

- [1] G. Tegze, G. Bansel, G. I. Tóth, T. Pusztai, Z. Fan és L. Gránásy, „Advanced operator splitting-based semi-implicit spectral method to solve the binary phase-field crystal equations with variable coefficients”, *J. Comput. Phys.* **228**, 1612–1623 (2009).
- [2] G. Tegze, L. Gránásy, G. I. Tóth, F. Podmaniczky, A. Jantinen, T. Ala-Nissila és T. Pusztai, „Diffusion-Controlled Anisotropic Growth of Stable, Metastable Crystal Polymorphs in the Phase-Field Crystal Model”, *Phys. Rev. Lett.* **103**, 035702 (2009).
- [3] T. Pusztai, G. Tegze, G. I. Tóth, L. Környei, G. Bansel, Z. Fan és L. Gránásy, „Phase-field approach to polycrystalline solidification including heterogeneous and homogeneous nucleation”, *J. Phys. Cond. Matter* **20**, 404205 (2008).