Phase-Field Modeling of Spiral Eutectic Dendrites

Ph.D. Thesis Booklet

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Introduction and objective

A broad variety of systems show single- or multi-arm spiraling, including spiral galaxies[1], tropical cyclones[2], biological excitable systems[3], seeds in a head of sunflower[4], oscillating chemical reactions[5], helical Liesegang systems[6], certain semiconductor materials grown by molecular beam epitaxy[7], and binary-[8] and ternary eutectic systems[9].

Although the formation mechanism of spiral structures is an actively researched topic for a long time, a general explanation is not available partly due to the diversity of the underlying physical phenomena. While the details differ in various realizations of spiral growth, diffusion and phase separation often play a role in the respective models. Models of spiral growth range from wave theory[10], via the FitzHugh-Nagumo theory for excitable media[11] and reaction-diffusion models[6] to the Ginzburg-Landau/phase-field type models[12].

The main motivation of this work was the experimental results of Akamatsu *et al.* (published in 2010), who discovered two-phase spiraling dendrites in a ternary eutectic alloy during univariant directional solidification[9]. These spiraling structures were exciting new results in the area of eutectic systems that was investigated both experimentally and theoretically for a long time. The spiraling dendrites emerge from the interplay of two-phase eutectic solidification with the Mullins-Sekerka-type diffusional instability caused by a third component, which has different solubility in the solid and liquid phases.

The objective of my work was to develop a simple phase-field model to reproduce and investigate the details of these exotic growth patterns.

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Applied method

In our work we used the Phase-Field Theory, which is a versatile technique for simulating microstructure evolution at the mesoscale. It is widely used for describing different phenomena including many aspects of solidification[13]. The model is a direct descendant of the Ginzburg-Landau/Cahn-Hilliard type classical field theoretical approaches[14] developed to describe phase transitions. In the Phase-Field technique the local state is characterized by fields that are continuous in time and space. The total free energy of the system is formulated as a functional of these variables and their gradients. The time evolution of the field variables is given by a set of coupled partial differential equations, derived from the free energy functional of the system.

In order to model the ternary eutectic alloy with two solid phases, the standard binary Phase-Field Model was extended to ternary systems. Ideal solution model was used for the liquid, and regular solution model for the solid phases. For solving the equations of motion numerically, 3D parallel simulation programs were developed, that can utilize hundreds of CPU cores or graphical cards to allow for sufficiently large simulation boxes. The programs used the finite difference method with the forward Euler time-stepping scheme to solve the equations on uniformly spaced grids. The directional solidification setup used in the experiments was modeled by a temperature gradient that was moved with the pulling speed. In order to save a lot of computational power and reduce the memory requirement, the simulation box followed the solidification front, which greatly decreased the necessary size of the simulation box. The thermal fluctuations were modeled with added concentration noise or by starting the simulations with a random initial configuration of the two solid phases.

The majority of the simulations were run on our CPU or GPU clusters located in Wigner RCP, Budapest. For a few large simulations we used a supercomputer of the Tohoku University, Sendai, Japan.

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Theses

1. To investigate the formation of spiraling two-phase dendrites observed recently during directional solidification of transparent ternary systems, I constructed a simple ternary phase-field model that relies on ideal solution thermodynamics in the liquid and the regular solution model in the solid state. This turned out to be the first model that reproduced spiraling two-phase dendrites. I identified the stability domain of these spiraling structures both in composition and velocity space. With increasing pulling velocity, I observed the following sequence of transitions in growth morphology and eutectic pattern: flat front with disordered lamellae $\rightarrow$ cellular structure built of eutectic colonies $\rightarrow$ two-phase (eutectic) dendrites with a variety of ordered patterns $\rightarrow$ one phase-dendrites without partitioning for two of the three components $\rightarrow$ partitionless solid (due to full solute trapping) growing with a flat front. I have shown furthermore that in the case of two-phase spiraling dendrites the eutectic wavelength follows the Jackson-Hunt scaling law when the pulling velocity changes. [P1, P3]

2. I demonstrated that in addition to the single-spiral surface pattern observed experimentally, which emerges from a helical structure in the volume, the two-phase dendrites may have other eutectic motifs on their surface, such as the target pattern or multi-armed spiraling patterns that are the manifestation of layered two-phase structures or multiple helical structures in their volume. I have determined the growth mechanism of these eutectic patterns: the target pattern is formed by the alternating nucleation of the two solid phases at the tip. In the single spiral case, the two solid phases grow simultaneously via rotating around each other. At the double spirals, the two solid phases grow alternately at the tip region. The growth becomes fairly complex for more than two spiraling arms. Here the formation of eutectic patterns happens in two stages: (a) nucleation of one phase on top of the other in the tip region, (b) when it grows sufficiently large, existing spiral arms of the same phase merge with it. [P1, P2]

3. I have characterized the shape of the two-phase dendrites by two quantities: (a) I determined the tip radius from shape of the solid-liquid interface in the vicinity of the tip, (b) I used the exponent of a power-law fit in the fin direction for larger distances from the tip. I have shown that similarly to the single-phase dendrites, the

tip radius of the two-phase dendrites shows a square root dependence on the solid-liquid interface energy, and both the tip radius and the exponent that characterizes the shape decreases with increasing kinetic anisotropy. I have also found, that these parameters are essentially independent of the underlying eutectic pattern. [P1, P3]

4. I have shown that a variety of eutectic patterns (target and spiraling as specified under the second thesis point) form under nominally the same physical conditions. Pattern selection is a stochastic process determined by fluctuations of the system. I have quantified pattern selection via the probability distribution of the structures with different number of spiral arms. I have found that the number of spiral arms tend to increase with increasing tip radius. [P1]

5. Using large scale simulations, I have demonstrated that anisotropy is a precondition for the formation of steady-state spiraling dendrites. In the isotropic system, the growing structures undergo dynamic tip-splitting and tip-elimination phenomena similar to the behavior observed in the case of one-phase cellular structures in experiment and phase-field simulations. Apparently, without a stable dendritic structure no steady-state spiraling pattern can form. [P1]

6. I have investigated the formation of two-phase spiraling dendrites with unequal solid phase ratio by using off-eutectic (asymmetric) composition. Two approaches were used. In the first one, I started from a steady-state single-spiral dendrite, and then gradually changed the ratio of the two major components of the incoming liquid, which eventually resulted in a spiraling structure, where the majority phase formed a homogeneous channel along the axis of the dendrite. In the second method, the composition was set from the beginning to an off-eutectic value, and the simulation was started with a homogeneous grain. Steady-state spiraling dendrites were obtained using this approach as well, where changing the phase ratio resulted in different width of the lamellae of the solid phases until a critical value. I have shown that, when the volume fractions of the two solid phases differ substantially, the regular lamellar spiraling structure is replaced by a complex shape, where the lamellae of the minority phase broke up, the holes are filled by the majority phase, yet the spiraling pattern remained. This phenomenon can be viewed as an analogy of the well-known rod to lamellar transition in binary eutectic systems, realized now in a complex helical environment. [P3]

List of publications

Publications related to the theses in peer reviewed scientific journals:

[P1] L. Rátkai, A. Szállás, T. Pusztai, T. Mohri, L. Gránásy, “Ternary eutectic dendrites: Pattern formation and scaling properties”, *Journal of Chemical Physics*, **142**:154501, 2015

[P2] L. Gránásy, L. Rátkai, A. Szállás, B. Korbuly, Gy. Tóth, L. Környei, T. Pusztai, “Phase-Field Modeling of Polycrystalline Solidification: From Needle Crystals to Spherulites – A Review”, *Metallurgical and Materials Transactions A*, **45**:1694-1719, 2014

[P3] T. Pusztai, L. Rátkai, A. Szállás, L. Gránásy, “Spiraling eutectic dendrites”, *Physical Review E*, **87**:032401, 2013

Publication in Hungarian:

[P4] Szállás A., Rátkai L., Pusztai T., Gránásy L., “Helikális mintázat eutektikus ötvözetekben”, [Helical patterns in eutectic alloys], *Fizikai Szemle*, **63**(10):333-337, 2013

Further publications not included in this disseration:

- L. Rátkai Gy. I. Tóth, T. Pusztai, L. Gránásy, “Phase-field modeling of eutectic structures on the nanoscale: the effect of anisotropy”, *Journal of Materials Science*, **52**:5544, 2017
- T. Pusztai, L. Rátkai, A. Szállás, L. Gránásy, “Phase-Field Modeling of Solidification in Light-Metal Matrix Nanocomposites”, *Magnesium Technology*, 2014
- L. Rátkai, I Kaban, T Wágner, J Kolár, S Valková, Iva Voleská, B Beuneu, P Jóvári, “Silver environment and covalent network rearrangement in GeS3–Ag glasses”, *Journal of Physics: Condensed Matter*, **25**:454210, 2013
- L. Rátkai, C. Conseil, V. Nazabal, B. Bureau, I. Kaban, J. Bednarcik, B. Beuneu, P. Jóvári, “Microscopic origin of demixing in $Ge_{20}Se_xTe_{80-x}$ alloys”, *Journal of Alloys and Compounds*, **509**:5190-5194, 2011
- L. Rátkai, A.P. Gonçalves, G. Delaizir, C. Godart, I. Kaban, B. Beuneu, P. Jóvári, “The Cu and Te coordination environments in Cu-doped Ge-Te glasses”, *Solid State Communications*, **151**:1524-1527, 2011

A figure from the latest publication ([P1]: L. Rátkai, A. Szállás, T. Pusztai, T. Mohri, L. Gránásy, "Ternary eutectic dendrites: Pattern formation and scaling properties", *Journal of Chemical Physics*, **142**:154501, 2015) has been chosen as the journal cover.

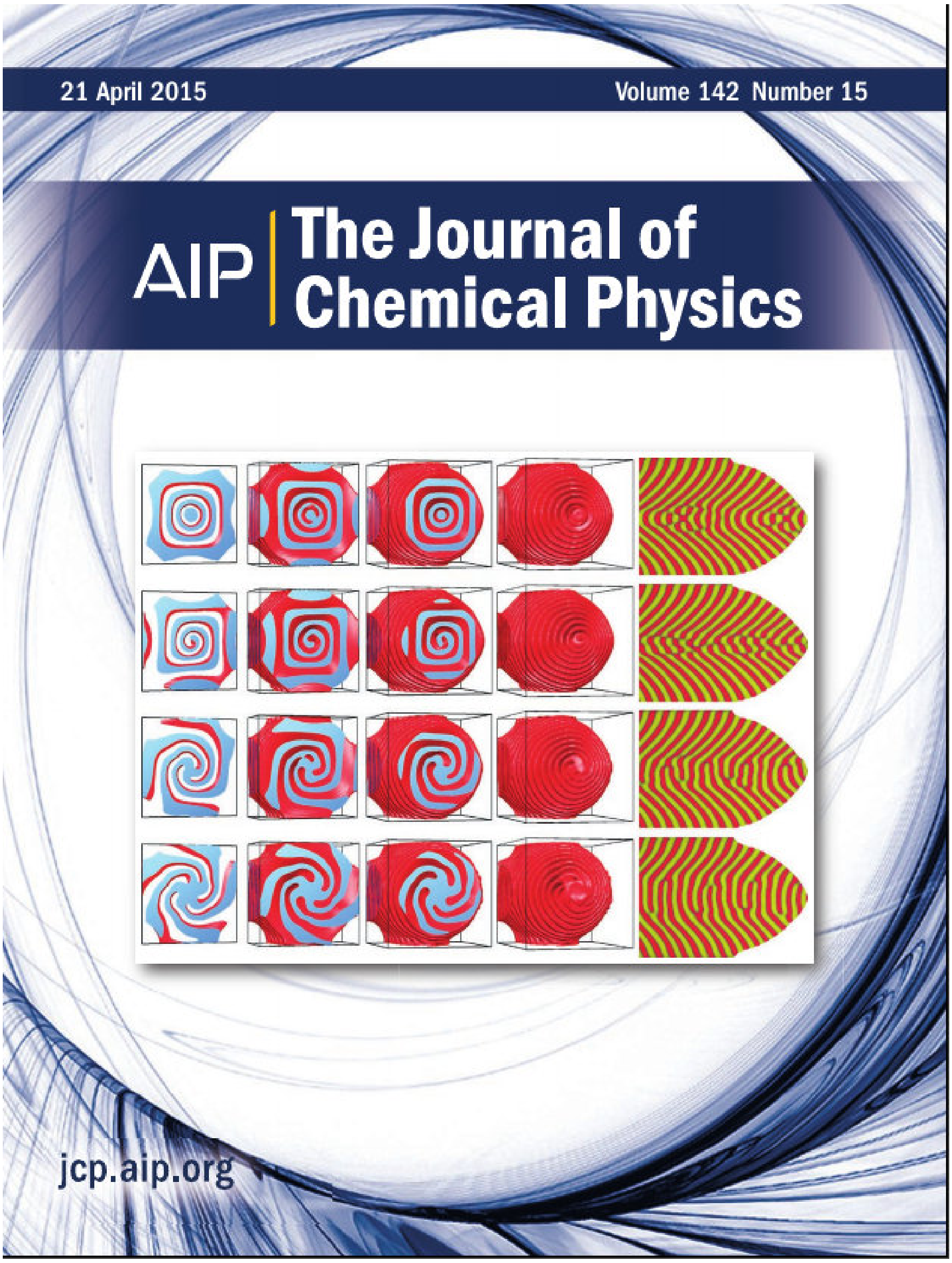

Figure 1: Dendrite cross-sections for the target pattern and single-, triple-, and five-arm spiral cases. Cover page of *Journal of Chemical Physics* Volume 142, Issue 15, 2015. `http://aip.scitation.org/toc/jcp/142/15`