Research Proposal: Investigating The Role of Topological Defects during Rapid Solidification

Nittala, S.

1 Executive Summary

As we enter the age of Additive Manufacturing (AM) (or (very) Rapid Solidification (vRS) more generally) (interface velocities $\sim mm/s - m/s$), it is becoming apparent that physics occurring at/beyond the limits of currently experimentally probe-able length and timescales is increasingly important [1, 2]. Of particular interest for this research proposal is the role played by the elastoplastic effects (i.e., by topological defects) in these fast processes. This requires new models/methods (introduced later) that bridge the gap between atomistic and micro-scale physics. Here, I will focus on two situations of experimental interest:

1. It has been experimentally observed that rapidly solidified aluminum thin films display orientation gradients that seemingly develop within a single grain [2]. It is strongly believed that dislocations are the primary culprit. I will present some preliminary results that suggest a possible mechanism for such dislocation-mediated orientation changes. It is based on the **nucleation of dislocations at sharp cusps that form at the (moving) solid-liquid interface** at high solidification rates, a phenomenon which has not been considered thus far in the literature. These dislocations penetrate into the bulk grain to induce intra-grain rotations. The physics of this process is unknown, and will form the heart of the investigation comprising **my first (first author) PhD paper**. The present hypothesis is that in this regime, vacancy trapping (and the stress exerted by the excess vacancies) plays an important role.

2. There is another phenomenon in which an analogue of vacancy trapping in alloys (solute trapping [3]) induces a new microstructure in the vRS regime: banding [4]. The velocity regime where this process occurs is comparable to the regime where vacancy trapping also becomes relevant [5]. Previous investigations did not couple these two effects, and focused only on solute trapping and latent heat effects during banding [6, 7, 8]. However, the preliminary results from project (1) are suggestive of vacancy trapping playing a role in topological defect formation. It is known that topological defects influence the observed precipitate structure in alloys [9, 10]. These observations motivate the **exploration of banding from an atomistic perspective**. The specifics of this investigation, however, will rely crucially on insights to be gained from project (1) and thus only a brief section will be allocated to this topic in this proposal. It is included primarily to show the direction subsequent investigations will focus on for **my second (first author) PhD paper**.

2   General Overview of Solidification

It is well known that several properties of metallic solids (strength, ductility, conductivity, etc.) depend crucially on their *microstructure*. For a pure metal, the microstructure is determined by the structure of a specific type of defect: interfaces (solid-liquid and solid-solid). For alloys, the distribution of solute(s) across the system also plays an important role. The coupling between the microstructure and the solidification process itself (i.e., the thermodynamic conditions under which the solidification process occurred) is of primary concern. The typical situations of interest are: (i) a stable solid growing in an undercooled liquid, and (ii) directional solidification, in which a solid grows into a liquid under an externally imposed (moving) thermal gradient. While situation (i) is more amenable to theoretical analysis, situation (ii) is more representative of experimental conditions. In practice, models are developed for situation (i) and then adapted to situation (ii) by introducing a position dependent temperature field [11].

Most of the early theoretical models ignored structural differences between liquid and solid[1]; thus they captured only the physics of solid-liquid interfaces and of solute segregation. These *Sharp Interface* (SI) models take the form of a classical Stefan problem which involves a solid region and a liquid region separated by a (moving) sharp interface across which certain "matching conditions" must be imposed to make the problem well posed. Due to space restrictions, specific details are omitted here and may be found in Refs. [12, 6]. Manually tracking the interface and imposing the matching conditions "by hand" turns out to be very computationally expensive. In order to facilitate bigger and longer simulations, the diffuse interface/Phase Field (PF) models were developed [13, 14]. In the PF models, in addition to the diffusing fields (solute concentration, temperature, etc.), an additional order parameter field is introduced. It takes different values in the bulk liquid and bulk solid and rapidly (yet continuously) changes from one value to the other across a smeared "interface" region. It has been shown that several PF models can be mapped onto generalized Stefan problems [14, 15], but since PF models are formulated in the language of field theory, there is no need to explicitly impose matching conditions in the interface region(s). The PF approach has another very important advantage over the SI models: PF models are based on free energy functionals that are built based on the principles of the Landau theory of phase transitions. This makes it much easier to first design a PF model for a given system and then to *infer* the corresponding SI model than to go the other way around [16].

At moderate to high solidification rates (interface velocities $\sim mm/s - m/s$), the traditional Stefan problem breaks down, in the sense that local equilibrium at the solid-liquid interface no longer holds, and the matching conditions across the moving boundary need to be modified [6]. The most important correction (for a binary alloy) is due to *solute trapping* [3]. As it turns out, PF models naturally possess the physics of solute trapping [17], and as demonstrated in Refs. [14, 7], they can be matched to experimentally observed solute segregation patterns. Several studies argue that *vacancy trapping* also becomes relevant in the very Rapid Solidification (vRS) regime (interface velocities $\sim$ m/s) [18, 19, 5]. Solidification techniques of modern interest (in particular metallic additive manufacturing) operate in precisely this regime, and the solidified products exhibit a rich variety of (poorly understood) defect structures. I believe that vacancy trapping and the formation of some of these defect structures are closely related, as I explain further in Section 3. These effects lie outside the purview of presently available PF models.

A better description of the interplay between solidification kinetics and topological defects is afforded through models which expand the PF approach to include atomic structure in the solid

---

[1]In technical parlance, they ignored the symmetry-breaking variables in the solid, and consequently, they did not possess the physics of lower dimensional topological defects like dislocations and vacancies.

phase. Such models are called *Phase Field Crystal* models[2] [15]. They operate on atomic length scales but on diffusive timescales. PFC models naturally account for anisotropy, arbitrary crystal orientation and grain-boundaries (i.e. PF-type physics) as well as elastoplastic effects and defects making them the ideal candidates to study problems related to lower dimensional defects occurring during directional solidification (where the relevant length scale is several hundreds of nanometers and the relevant timescale is a few microseconds-milliseconds) [15, 21]. It is worth noting that in-situ measurements of these phenomena are still outside the scope of present day technology, *necessitating* numerical models like PFC that can help us understand what happens between the initial set-up and the post-mortem observations [1, 2]. In the next subsection, I introduce the particular Phase Field Crystal model that will be relevant for this proposal. I will then expand a little on trapping (of solute and vacancies) to set the stage for my proposed PhD projects.

2.1   Phase Field Crystal Modelling

Phase Field Crystal (PFC) models are atomistic models of solidification that operate on diffusive timescales. Such models are very useful for studying phenomena involving the interplay between solidification and elastoplasticity [22]. The first step to building a PFC model is to start from classical density functional theory by expanding the free energy of the (undercooled) system about a reference density (ρ_0) [23, 24, 25]. In other words, we are interested in the free energy change caused by inhomogenous density *fluctuations* in an undercooled liquid. The change in free energy (now a functional of the density field $\rho(\mathbf{r})$) is expressed as

$$\Delta F[\rho(\mathbf{r})] = \int d\mathbf{r} \left. \frac{\delta F}{\delta \rho(\mathbf{r})} \right|_{\rho_0} \delta\rho(\mathbf{r}) + \frac{1}{2!} \int d\mathbf{r} \, d\mathbf{r}' \left. \frac{\delta^2 F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right|_{\rho_0} \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') + ... \quad (1)$$

by the ordinary rules of functional calculus, with $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$. It was shown in Ref. [26] that:

$$\left. \frac{\delta F}{\delta\rho(\mathbf{r})} \right|_{\rho_0} = k_B T \left(\rho(\mathbf{r}) \log\left(\frac{\rho(\mathbf{r})}{\rho_0}\right) - (\rho(\mathbf{r}) - \rho_0) \right) \quad (2)$$

$$\left. \frac{\delta^N F}{\delta\rho(\mathbf{r}_1)...\delta\rho(\mathbf{r}_N)} \right|_{\rho_0} = -k_B T \Gamma_N(\mathbf{r}_1, ...\mathbf{r}_N) \quad (\text{for } N > 1) \quad (3)$$

where Γ_N denotes the N-point correlation function/vertex function in the reference liquid and $T < T_m$ (the melting point). For typical solid-liquid transitions (in the absence of vapor phases), truncating at second order is sufficient [15]. To arrive at the PFC model, one introduces the fluctuation field $n(\mathbf{r}) = \frac{\rho(\mathbf{r}) - \rho_0}{\rho_0}$ and further expands the logarithm above to fourth order in n (in the spirit of the Landau "ϕ^4" theory). This gives

$$\mathcal{F} \equiv \frac{\Delta F}{k_B T \rho_0} = \int d\mathbf{r} \left[\frac{n(\mathbf{r})^2}{2} + p_3 \frac{n(\mathbf{r})^3}{3} + p_4 \frac{n(\mathbf{r})^4}{4} - \frac{n(\mathbf{r})}{2} \int d\mathbf{r}' C_2(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') \right] \quad (4)$$

where the p_i are treated as phenomenological constants that provide additional parameters for fitting a material's phase diagram [11]. They can formally be related to the infinite-wavelength part of the 3- and 4-point correlation functions respectively [27]. $C_2(\mathbf{r}_1, \mathbf{r}_2)$ (which is a rescaled

---

[2]Technically, classical Density Functional Theory and Molecular Dynamics (MD) can also serve this purpose, but due to the timescales involved, they would be too computationally expensive for current computers to handle. A PFC simulation can be interpreted as an MD simulation that has been coarse-grained in time [20].

version of Γ_2) inherits the symmetries of the reference liquid, and only depends on $|\mathbf{r}_1 - \mathbf{r}_2|$. It is simpler to model the functional form of its Fourier Transform (that likewise only depends on $|\mathbf{k}| = |\mathbf{k}_1 - \mathbf{k}_2|$) and for my purposes, it will be given by an envelope of Gaussian peaks (a pointwise maximum of a sequence of Gaussians):

$$C_2(\mathbf{k}) = \max_j \left\{ B_x^j \exp\left[-\frac{T}{T_r} \right] \exp\left[-\frac{(|\mathbf{k}| - |\mathbf{k}_j|)^2}{2\sigma_j^2} \right] \right\} \qquad (5)$$

Here, T_r is a temperature-scale parameter that can be used to fit the model to a material's phase diagram, and $B_x^j, |\mathbf{k}_j|, \sigma_j$ specify the (reference) height, position, and width of the jth peak respectively [11]. The exponential of the temperature is akin to a Debye-Waller factor for the scattering intensity of a lattice [28].

The polynomial terms in the Free Energy promote the higher entropy uniform phase at high temperatures, while at low temperatures the excess term, which favors periodic states, dominates. The dynamical equation for density relaxation takes the form[3][11]

$$\tau \frac{\partial^2 n}{\partial t^2} + \frac{\partial n}{\partial t} = \nabla \cdot \left[M \nabla \frac{\delta \mathcal{F}}{\delta n} \right]. \qquad (6)$$

with τ and M being constants that set the relative timescales of diffusive and wavelike relaxation. In order to adapt the above model for directional solidification, we merely need to make the temperature T a spatially dependent function. For simplicity, I consider the *Frozen Temperature Approximation* (FTA) where

$$T(\mathbf{r}, t) = T_L + \mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_L - \mathbf{V}t) \qquad (7)$$

and $\mathbf{G}$ is the thermal gradient, $|\mathbf{V}|$ is the "pull speed" and $T_L, \mathbf{r}_L$ are related to the initial conditions [6]. This neglects contributions due to latent heat. It has been demonstrated to be a viable model for studying the type of problem considered in Section 3 [2, 29].

2.2 Trapping and Microstructure during Rapid Solidification

In equilibrium, the density field in the bulk solid phase is very well approximated by the "amplitude" expansion

$$n(\mathbf{r}) = n_0 + \sum_j A_j e^{i\mathbf{k}_j \cdot \mathbf{r}} \qquad (8)$$

with $\mathbf{k}_j$ denoting the various reciprocal lattice vectors of the solid and A_j the corresponding density amplitudes (note that they are zero in the liquid). It is often sufficient to only include a single mode in Equation 5 and to only consider those reciprocal lattice vectors with the shortest length in the expansion above. By substituting this expression into Equation 4 and averaging over a unit cell, one obtains a "bulk" free energy $\mathcal{F}(n_0, A_j, T)$ [15]. The amplitudes represent internal degrees of freedom and the free energy must be minimized with respect to them. Then, the common tangent construction may be applied to obtain a density-temperature phase diagram as shown in Figure 1. At slow solidification rates, the solid/liquid bulks on either side of the interface follow the phase diagram reasonably well. When it is assumed that the phase diagram is

---

[3]The work presented in this proposal has been done with $\tau = 0$, but the general case is also of interest for the project.
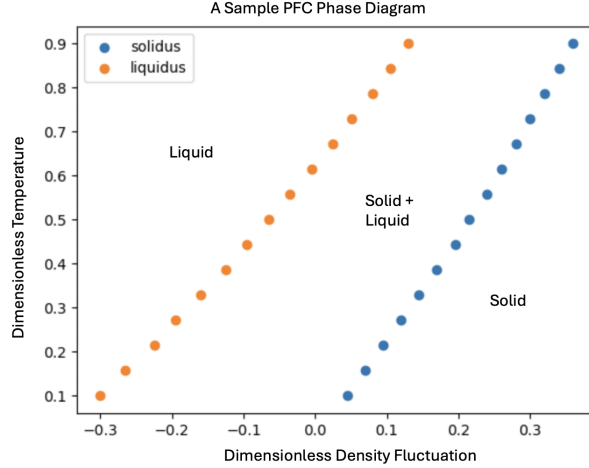
Figure 1: A sample phase diagram for a pure material made using the procedure described in Section 2.2. The y-axis is scaled by the scale parameter T_r (Equation 5), and the x-axis is the average density fluctuation variable n_0 (Equation 8).

followed exactly, there is a well known progression of interface morphologies (for a given thermal gradient G) with increasing pull speeds V: planar $\rightarrow$ cellular/dendritic $\rightarrow$ planar [6]. A similar progression was also theoretically predicted for the dilute binary alloys. However, in the case of the alloy, it was experimentally found that this picture is incomplete. In the high-V regime, it was necessary to consider departures from equilibrium, whereby the solid and liquid bulks on either side of the interface no longer follow the phase diagram (solute is *trapped* in the solid). This consideration leads to a new (experimentally verified) morphology, called the banded structure, which occurs in between the cellular/dendritic and high-speed planar morphologies. As mentioned earlier, vacancies in pure metals also occur in excess concentrations (i.e. more than the equilibrium amount) under rapid solidification conditions. In analogy with the solutes, this is called *vacancy trapping* [5, 18]. Recent molecular dynamics (MD) work has demonstrated that vacancy trapping becomes significant at modest velocities ($\sim 1m/s$, the same regime where solute trapping also becomes significant in most alloys) [19] where we expect the cellular morphology to transition into the planar morphology in a pure metal. However, there has only been one (indirect) exploration of this velocity regime in pure materials (in a large enough system to obtain non-planar morphologies) [2]. When I conducted PFC simulations probing this regime, I found that there is a range of velocities (for given thermal gradient and model parameters) where there is significantly increased nucleation of dislocations at the solid/liquid interface, as will be discussed in detail in Section 3, where I go over my plan for my first PhD paper. This is suggestive of a possible connection between vacancy trapping and defect formation at the solid-liquid interface. If true, this would also suggest that dislocations might play an important role in studying banding, which forms the working premise of my second PhD paper.

3 Paper I: Dislocation Nucleation from Atomically Rough Solid-Liquid Interfaces

In this section, I present some preliminary results, a refined version of which will constitute my first (first author) PhD paper as well as a second author paper in collaboration with Jaarli Suviranta,
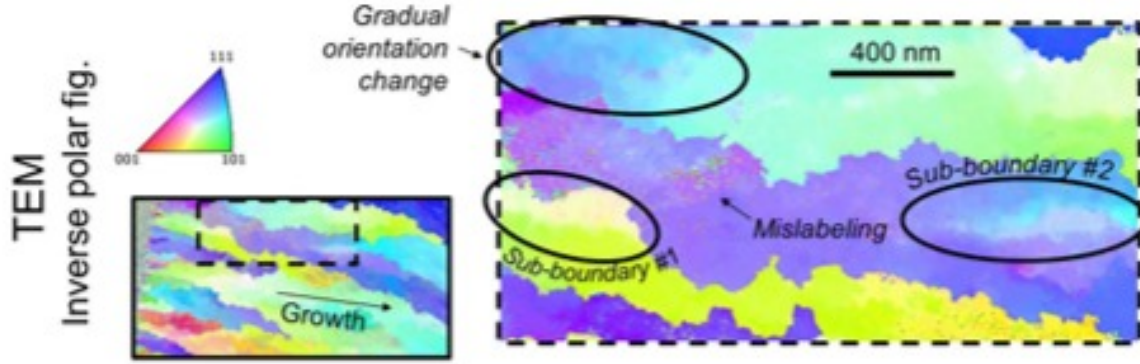
Figure 2: Orientation distribution in a laser thin-film experiment, from Ref. [2]. The color indicates the crystallographic plane oriented with the plane of the image. The thin black arrow in the smaller figure indicates the overall growth direction - the larger image is an inset of the smaller. A gradual orientation change is indicated, as well as two regions where misoriented regions inside a single grain are separated by a sub-grain boundary.

that highlight the fact that defects play a pivotal role in the domain of rapid solidification. At this stage, the exact mechanisms behind the results to be shown below are not very well understood. Of particular interest will be the nucleation of dislocations from a moving solid-liquid interface, which has not received any theoretical treatment thus far. I will begin by setting up the problem and showing some initial results. Since this is a research proposal, I will then list (in my opinion) the most interesting questions that I intend to explore for this project.

3.1   Set-Up and Scientific Relevance

Recent experiments [2] strongly indicate that in some metallic systems (particularly Aluminum) as the solidification rate approaches, or exceeds, absolute stability (this is the speed past which the high-V cellular structure becomes unstable and the interface is supposed to become planar again), each of the directionally solidified cells appear to rotate internally, i.e., there appears to be an orientation gradient that develops within each cell (Figure 2). The exact mechanism for this is currently up for debate. It was originally postulated that voiding[4] was the primary driver of these rotations [2]. However, the experimentalists believe that the effect is in fact primarily dislocation mediated. Through simulations, Jaarli and I found that a mechanism causing spontaneous intra-grain rotation mediated exclusively by dislocations does exist. Figure 3 illustrates a typical simulation done for that project. As highlighted in the image, dislocations spawn at certain "cusps" on the solid-liquid interface. At later stages, the dislocations form dense networks whose geometries make their analysis very complicated[5]. Fortunately, a conceptually similar (yet topologically *much* simpler) effect in which dislocations are emitted from the solid-liquid interface into the bulk solid also occurs in a two-dimensional system that is rapidly solidified (this is a novel result as well). This is illustrated in Figure 4, where a thermal gradient pulls the solid-liquid interface at a speed so fast that the front *should be* planar. However, there appear to be "atomic scale" cusps that remain on the solid-liquid interface. Such an interface would appear "flat" at experi-

---

[4]Voids are experimentally measurable liquid or vapor pockets that appear because certain regions in the solidified product favor melting or sublimation, respectively.

[5]I will be second author on the paper concerning the 3D work, where we showcase the effect but make no attempt at a physical explanation.
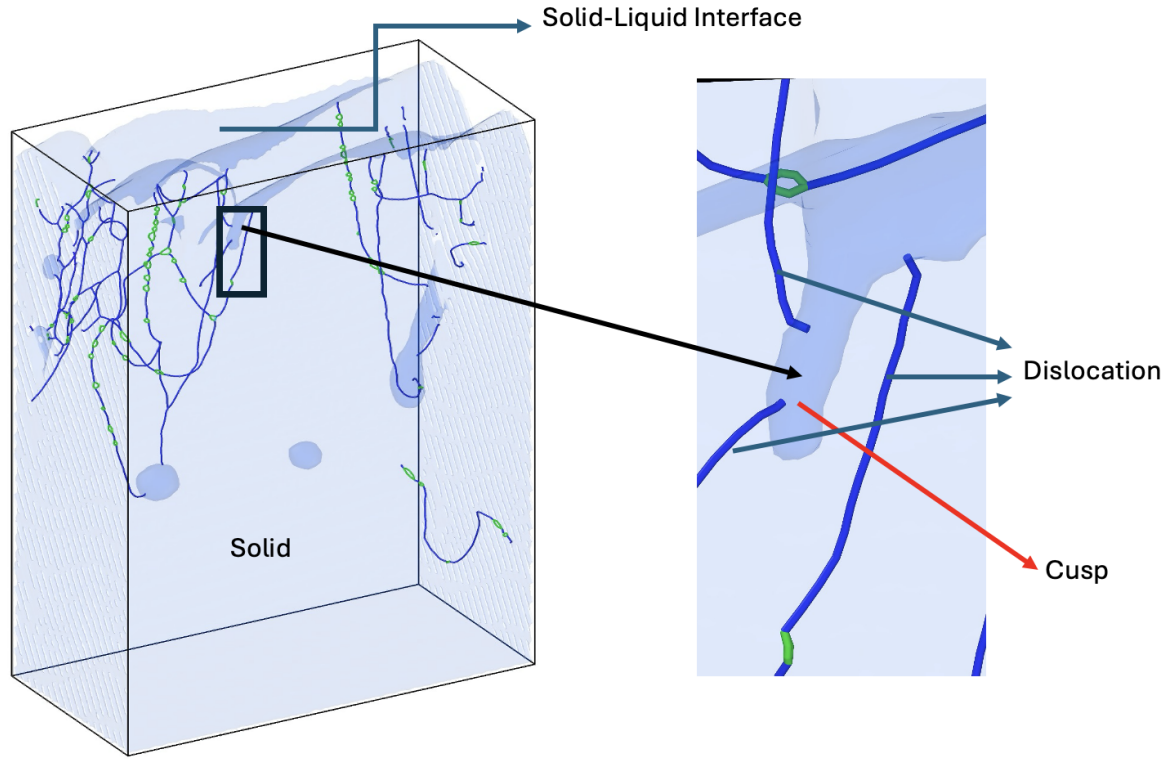
Figure 3: Early stages of a 3D directional solidification simulation showing dislocations forming at a sharp cusp on the solid-liquid interface. At later times these dislocations form complex networks that cause intra-grain rotations. The networks have complex geometries making them difficult to analyze.
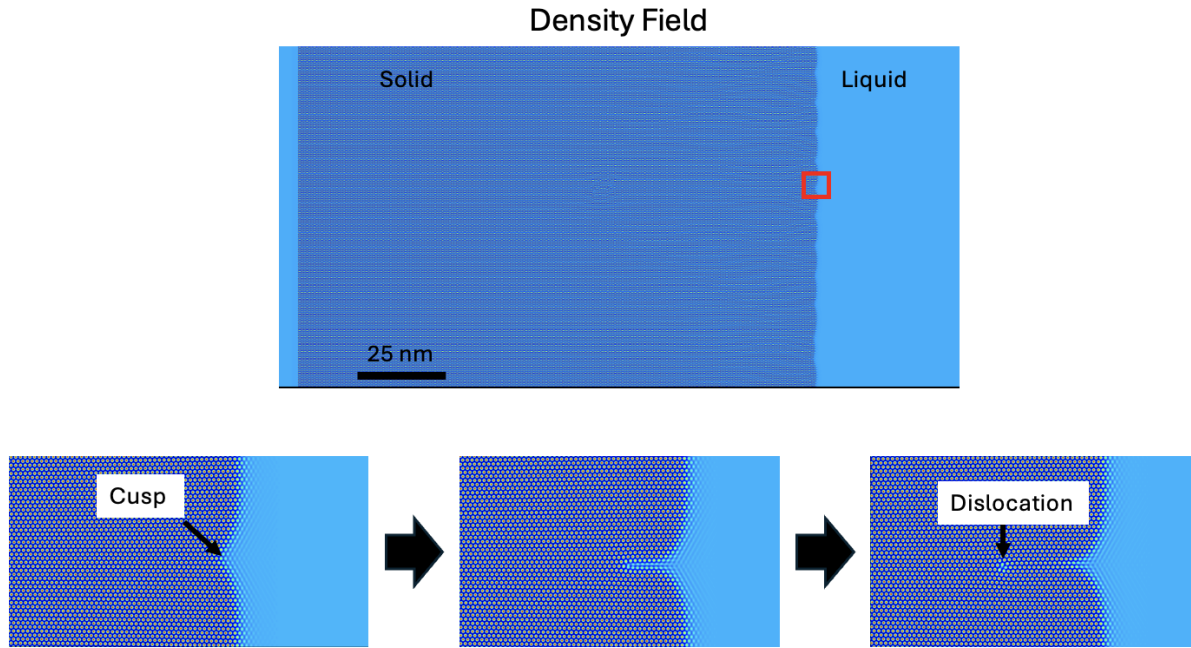

Figure 4: Atomic-scale cusps at a rapidly moving solid liquid interface nucleating a dislocation in 2D. The lower images are a time-sequence of the region corresponding to the red box in the top image. This phenomenon has not been studied thus far. It can help explain the intra-grain orientation gradients observed in rapidly solidified thin films.

mentally observable scales. Nonetheless, these cusps stochastically produce dislocations. In 2D, the nucleation is stochastic because dislocation networks are impossible. In 3D, once a dislocation nucleates, its subsequent growth requires significantly less energy and this leads to the formation of continuous networks within each grain. However, the cusps and the subsequent nucleation of dislocations from these cusps appear to be a universal features that have not received sufficient (if any) explanation. Analysis of this 2D system will comprise my first (first author) PhD paper.

3.2   Research Questions

The questions of current interest are as follows:

1. **Why do cusps remain even past absolute stablity?**
   It is unclear whether the cusps remain on the interface past absolute stability because:

   (a) There is a "supply" of stress from the trapping of excess vacancies at the moving interface. This is motivated by the fact that these cusps occur in the same velocity regime where vacancy trapping *should be* important. There is a proposed connection between the PFC density field (Equation 8) and the vacancy concentration [30]. It is also known that both n_0 and the A_j in Equation 8 differ from their equilibrium values in a way that depends on the interface speed [31]. Thus, it is reasonable to expect that at least some aspects of vacancy trapping are contained within the PFC model, much like how solute trapping is contained in binary PFC models [32]. I would like to explore the connection between vacancy trapping at the interface and dislocation nucleation through this investigation.

   (b) There is a build-up of stress within the bulk of the solid[6] due to either the initial transient dynamics[7] or due to a mismatch between the fastest growth direction of the solid and the thermal gradient. This stress might require the interface to maintain these cusps as a relaxation mechanism.

   It is hypothesized that both effects play a role. Quantifying the various stresses in the system during its dynamical evolution, and attributing them to appropriate sources is currently underway.

2. **When will a given cusp nucleate a dislocation?**
   Visual examination of the solid-liquid interface makes it appear as if all of the cusps are more of less identical, and yet not all of them nucleate dislocations at the same time. Thus there is a need to identify a criterion (an indicator function) that will predict when a cusp is going to generate a dislocation. It has been shown that in a bulk solid, when the quantity

$$N_{\mathbf{b}} = \frac{|\mathbf{b} \cdot \mathbf{curl}(\sigma) \cdot \hat{\mathbf{l}}|}{|\mathbf{b}|} \tag{9}$$

(σ is the stress tensor) exceeds a certain threshold value that depends on the system under consideration, a dislocation with Burger's vector $\mathbf{b}$ with line direction $\hat{\mathbf{l}}$ will nucleate [36].

---

[6]In the sense of the stress-induced instabilities: a stressed solid in contact with its melt will unevenly solidify at the interface causing undulations, and eventually, cusps [33, 34, 35].

[7]The solid-liquid interface starts from rest, undergoes some morphological transitions as it accelerates and eventually reaches the steady state determined by the speed of the thermal gradient.

Building upon Ref. [37], I derived an approximate formula to compute the stress tensor for a general PFC model[8]. I then used this in Equation 9 and found that the corresponding criterion also works at the solid-liquid interface. I will need to characterize this quantity more thoroughly to test its robustness, but it appears to be adequate for my purposes. Both the computation of the stress tensor, and the demonstration of a criterion for dislocation nucleation at the solid-liquid interface would be useful as general tools for future PFC studies. The goal is to try to isolate various contributions to the stress tensor to come up with the most likely explanation of the dislocation nucleation mechanism.

3. **What are the properties of the cusps and how do they relate to experimental conditions and model parameters?**
Thus far in this section, the focus has been on quantities that are satisfactory for the theoretical physicist. It is also necessary to characterize the role of the elastic constants, the thermal gradient, the pull speed, and other experimental numbers on dynamical quantities like: the spacing between cusps, the average depth of the cusps, the frequency of dislocation nucleation, the rate of grain rotation, etc. Since this is unexplored territory, the plan is to do the things from Q1 and Q2 above, and to see what the dominant physical sources of stress are. This will then facilitate the building of a simple model that would help *explain* these relationships (as opposed to simply *simulate* them). The idea is to use the so-called amplitude formulation [38] of the model to identify the relationship between cusp properties (particularly spacing and depth) and the external conditions. Such a characterization will also be helpful for understanding vacancy trapping in PFC models. I am working with Dr. Provatas on such an analysis. This, in combination with the simulation analysis highlighted above, should yield experimentally testable results.

4 Paper II: Atomistic Perspectives on the Phenomenon of Banding

From the results presented in relation to Paper I (Section 3), it is apparent that defects play an important role in the transition from cellular to planar morphology. There is another known effect that has been experimentally observed in metallic alloys in this transition regime as well: banding [4]. This microstructure is particularly relevant today since it commonly occurs during powder metal additive manufactring (particularly laser melting) [39]. The banded structure is comprised of alternating bands each of which has a distinct microstructure as shown in Figure 5. In this section, I will introduce the necessary ingredients of banding, and highlight what is currently not understood about it (and for which PFC would be the ideal technique). This will be a very brief section[9] since this project is scheduled for after I'm done with the project from Section 3.
The main idea is that at the mesoscopic level, banding occurs because of a competition between interface attachment kinetic effects and solute trapping effects (i.e. between the timescale for atoms to stick to the moving interface with the right structure and the timescale for the solute to diffuse out of the interface into the liquid) [40]. Binary PFC models have already been shown

---

[8]This is a lengthy calculation that is too technical for the purposes of this proposal. I would be happy to share my notes upon request.

[9]Comprehensive accounts of what is currently understood about banding can be found in Refs. [6, 7, 40].
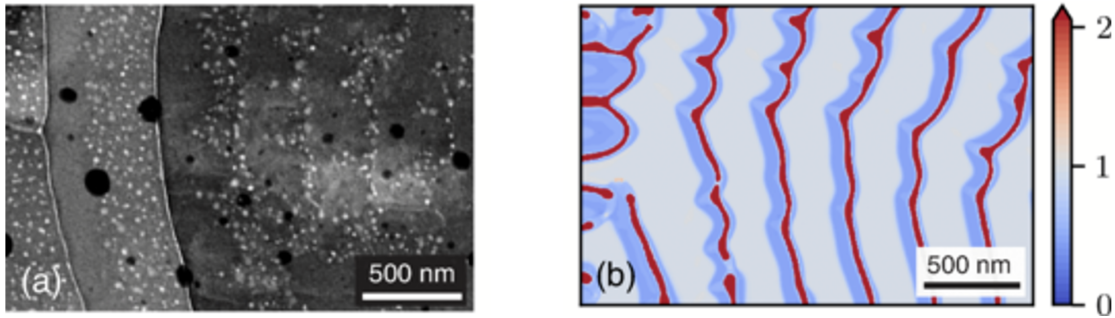
Figure 5: (a) An experimental image of the banded microstructure. (b) A Phase Field Simulation of banding. The PF simulation is capable of correctly predicting the spacing but is unable to accurately describe the precipitation pattern. Phase Field Crystal simulations would be able to provide insight into the precipitation and defect structures. Figure reproduced from Ref. [7].

to capture both attachment kinetics and solute trapping well [32, 41]. Thus, computational difficulties notwithstanding, the mesoscopic physics of banding must be contained in any binary PFC model[10]. The interesting missing piece is this: *how does banding occur*? Ref. [7] identified a brand new interface instability (called "tip burgeoning") that occurs (in simulation) during the onset of banding (see Figure 3 in Ref. [7]). In principle, this occurs at speeds comparable to those where the dislocation nucleation at the solid-liquid interface increased significantly in Section 3. Thus, it is my hypothesis that there must be an interplay between these two effects, i.e., dislocations play an important role in banding. In particular, the defects would greatly influence the precipitation patterns that will be experimentally observable post-mortem [9, 10]. In Figure 5, it is seen that while the band spacing seems to be reasonably captured in the PF models, the precipitation pattern is not. PFC simulations can help relate the morphology and precipitation patterns by including the physics of defects. While running a PFC simulation covering the entire process is computationally unfeasible, an approach that uses PFC to study the tip burgeoning instability and dislocation behavior coupled with an amplitude model [38] to study the mesoscale physics is possible. Such a multi-scale approach will provide a comprehensive understanding that couples plasticity, precipitation and morphology.

5 PhD Timeline

2024	2025			2026		
Fall	Winter	Summer	Fall	Winter	Summer	Fall
Prelim Exam						
Explore various stress sources, characterize cusps and dislocations	Develop and Implement a directional solidification PFC model for a binary alloy		Explore three varieties of models: ``rhoA-rhoB", "n,c", "Amplitude"	Start writing thesis, prepare to wrap up, apply to jobs, etc.		Hopefully have a thesis to defend
Work with Nik on amplitude calculations and on developing a "simple" model to help understanding the physics	Try to incorporate long-wavelength enthalpy effects		Gather data on banding and prepare manuscript for Paper II			
	Get manuscript for Paper I ready for publication					

Figure 6: A naive and hopeful timeline for my PhD.

---

[10]I also briefly note here that enthalpy effects are important for a quantitative description of banding [6, 7], although it is not clear if any new qualitative features (i.e. new physical mechanisms) arise due to them.

References

[1] Tatu Pinomaa, Matti Lindroos, Paul Jreidini, Matias Haapalehto, Kais Ammar, Lei Wang, Samuel Forest, Nikolas Provatas, and Anssi Laukkanen. Multiscale analysis of crystalline defect formation in rapid solidification of pure aluminium and aluminium–copper alloys. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 380(2217):20200319, February 2022.

[2] Paul Jreidini, Tatu Pinomaa, Jörg M. K. Wiezorek, Joseph T. McKeown, Anssi Laukkanen, and Nikolas Provatas. Orientation Gradients in Rapidly Solidified Pure Aluminum Thin Films: Comparison of Experiments and Phase-Field Crystal Simulations. *Physical Review Letters*, 127(20):205701, November 2021.

[3] Tatu Pinomaa, Anssi Laukkanen, and Nikolas Provatas. Solute trapping in rapid solidification. *MRS Bulletin*, 45(11):910–915, November 2020.

[4] W. Kurz and R. Trivedi. Banded solidification microstructures. *Metallurgical and Materials Transactions A*, 27(3):625–634, March 1996.

[5] Mats Hillert, Martin Schwind, and Malin Selleby. Trapping of vacancies by rapid solidification. *Acta Materialia*, 50(12):3285–3293, July 2002.

[6] Alain Karma and Armand Sarkissian. Interface dynamics and banding in rapid solidification. *Physical Review E*, 47(1):513–533, January 1993.

[7] Kaihua Ji, Elaheh Dorari, Amy J. Clarke, and Alain Karma. Microstructural Pattern Formation during Far-from-Equilibrium Alloy Solidification. *Physical Review Letters*, 130(2):026203, January 2023.

[8] Massimo Conti. Heat diffusion and banding in rapid solidification. *Physical Review E*, 58(5):6166–6172, November 1998.

[9] John W Cahn. Nucleation on dislocations. *Acta Metallurgica*, 5(3):169–172, March 1957.

[10] R. Bullough, R. C. Newman, J. Wakefield, and J. B. Willis. Precipitation on a Dislocation. *Nature*, 183(4653):34–35, January 1959.

[11] Paul Jreidini. Novel developments in phase-field crystal modeling for the solidification of complex materials.

[12] J. S. Langer. Instabilities and pattern formation in crystal growth. *Reviews of Modern Physics*, 52(1):1–28, January 1980.

[13] Alain Karma. Phase-Field Formulation for Quantitative Modeling of Alloy Solidification. *Physical Review Letters*, 87(11):115701, August 2001.

[14] Blas Echebarria, Roger Folch, Alain Karma, and Mathis Plapp. Quantitative phase-field model of alloy solidification. *Physical Review E*, 70(6):061604, December 2004.

[15] Nikolas Provatas and Ken Elder. *Phase-Field Methods in Materials Science and Engineering*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, October 2010.

[16] Klaus Kassner, Chaouqi Misbah, Judith Müller, Jens Kappey, and Peter Kohlert. Phase-field modeling of stress-induced instabilities. *Physical Review E*, 63(3):036117, February 2001.

[17] N. A. Ahmad, A. A. Wheeler, W. J. Boettinger, and G. B. McFadden. Solute trapping and solute drag in a phase-field model of rapid solidification. *Physical Review E*, 58(3):3436–3450, September 1998.

[18] C. DeW. Van Siclen and W. G. Wolfer. Vacancy supersaturation in rapidly solidified metal droplets. *Physical Review A*, 43(10):5344–5354, May 1991.

[19] H. Y. Zhang, F. Liu, Y. Yang, and D. Y. Sun. The Molecular Dynamics Study of Vacancy Formation During Solidification of Pure Metals. *Scientific Reports*, 7(1):10241, August 2017.

[20] P. F. Tupper and M. Grant. Phase field crystals as a coarse-graining in time of molecular dynamics. *Europhysics Letters*, 81(4):40007, January 2008.

[21] K. R. Elder and Martin Grant. Modeling elastic and plastic deformations in nonequilibrium processing using phase field crystals. *Physical Review E*, 70(5):051605, November 2004.

[22] Duncan Burns, Nikolas Provatas, and Martin Grant. Time-scale investigation with the modified phase field crystal method. *Modelling and Simulation in Materials Science and Engineering*, 30(6):064001, July 2022.

[23] K. Elder, Nikolas Provatas, Joel Berry, Peter Stefanovic, and Martin Grant. Phase-field crystal modeling and classical density functional theory of freezing. *Physical Review B - PHYS REV B*, 75, February 2007.

[24] Andrew J. Archer, Daniel J. Ratliff, Alastair M. Rucklidge, and Priya Subramanian. Deriving phase field crystal theory from dynamical density functional theory: Consequences of the approximations. *Physical Review E*, 100(2):022140, August 2019.

[25] Michael te Vrugt, Hartmut Löwen, and Raphael Wittkowski. Classical dynamical density functional theory: From fundamentals to applications. *Advances in Physics*, 69(2):121–247, April 2020.

[26] T. V. Ramakrishnan and M. Yussouff. First-principles order-parameter theory of freezing. *Physical Review B*, 19(5):2775–2794, March 1979.

[27] Daniel L. Coelho, Duncan Burns, Emily Wilson, and Nikolas Provatas. Generalizing the structural phase field crystal approach for modeling solid-liquid-vapor phase transformations in pure materials. *Physical Review Materials*, 8(9):093402, September 2024.

[28] Neil W. Ashcroft and N. David Mermin. *Solid State Physics*. Brooks/Cole Thomson Learning, South Melbourne, repr edition, 2012.

[29] Tatu Pinomaa, Jukka Aho, Jaarli Suviranta, Paul Jreidini, Nikolas Provatas, and Anssi Laukkanen. OpenPFC: An open-source framework for high performance 3D phase field crystal simulations. *Modelling and Simulation in Materials Science and Engineering*, 32(4):045002, June 2024.

[30] Duncan Burns, Nikolas Provatas, and Martin Grant. Two dimensional phase field crystal study of thermo-density coupling: Thermal expansion, recalescence, and plasticity. *Acta Materialia*, 267:119712, April 2024.

[31] P. K. Galenko and D. Jou. Rapid solidification as non-ergodic phenomenon. *Physics Reports*, 818:1–70, July 2019.

[32] Harith Humadi, Jeffrey J. Hoyt, and Nikolas Provatas. Phase-field-crystal study of solute trapping. *Physical Review E*, 87(2):022404, February 2013.

[33] Jiangwei Li, Cheng-hsin Chiu, and Huajian Gao. Dislocation Nucleation from a Surface CUSP. *MRS Proceedings*, 317:303, 1993.

[34] M. P. Gururajan and Arka Lahiri. Elastic stress effects on microstructural instabilities, July 2016.

[35] Frigyes Podmaniczky, Gyula I. Tóth, György Tegze, Tamás Pusztai, and László Gránásy. Phase-field crystal modeling of heteroepitaxy and exotic modes of crystal nucleation. *Journal of Crystal Growth*, 457:24–31, January 2017.

[36] Ronald E. Miller and Amit Acharya. A stress-gradient based criterion for dislocation nucleation in crystals. *Journal of the Mechanics and Physics of Solids*, 52(7):1507–1525, July 2004.

[37] Audun Skaugen, Luiza Angheluta, and Jorge Viñals. Dislocation dynamics and crystal plasticity in the phase-field crystal model. *Physical Review B*, 97(5):054113, February 2018.

[38] Marco Salvalaglio and Ken R Elder. Coarse-grained modeling of crystals by the amplitude expansion of the phase-field crystal model: An overview. *Modelling and Simulation in Materials Science and Engineering*, 30(5):053001, July 2022.

[39] B. Vishwanadh, J. T. McKeown, and J. M. K. Wiezorek. Microstructural evolution of rapidly solidified hypoeutectic Al10Cu alloy during non-isothermal annealing transients induced by nano-second laser pulses. *Materials Characterization*, 207:113608, January 2024.

[40] M. Carrard, M. Gremaud, M. Zimmermann, and W. Kurz. About the banded structure in rapidly solidified dendritic and eutectic alloys. *Acta Metallurgica et Materialia*, 40(5):983–996, May 1992.

[41] Zhi-Feng Huang, K. R. Elder, and Nikolas Provatas. Phase-field-crystal dynamics for binary systems: Derivation from dynamical density functional theory, amplitude equation formalism, and applications to alloy heterostructures. *Physical Review E*, 82(2):021605, August 2010.

A General Textbooks

Below is a short list of books that should help guide the examiner in terms of the broader subject matter and context of this research (particularly for giving me a list of resources and questions to prepare for the oral exam).

1. Statistical Physics (Volume I), Landau and Lifshitz

2. Phase Field Methods for Materials Science and Engineering, Provatas and Elder

3. Solidification, Dantzig

4. Principles of Condensed Matter Physics, Chaikin and Lubensky