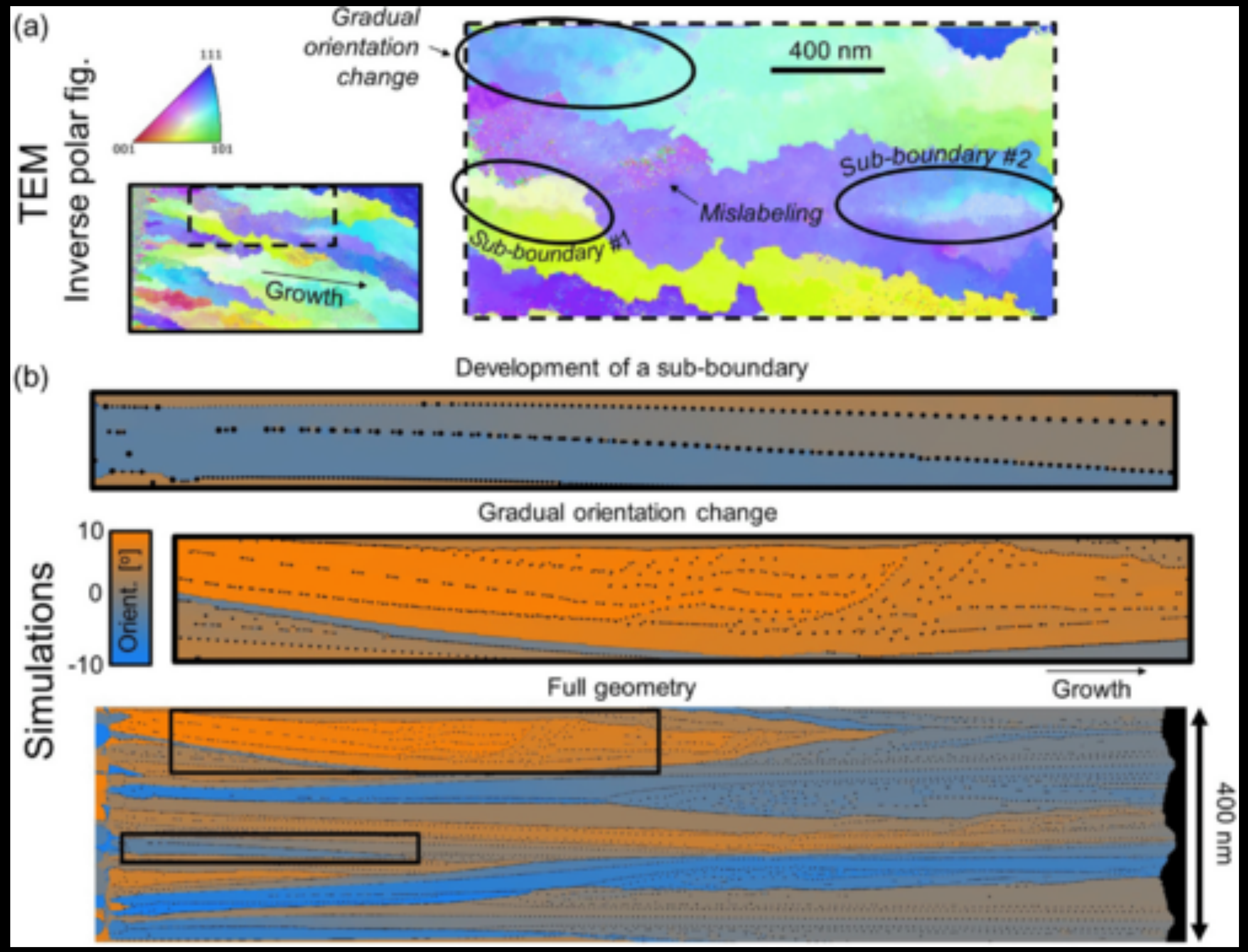
Prelim Exam: Research Proposal

Investigating the role of plasticity in rapid solidification

Sam Nittala
Supervisor: Dr. Nikolas Provatas

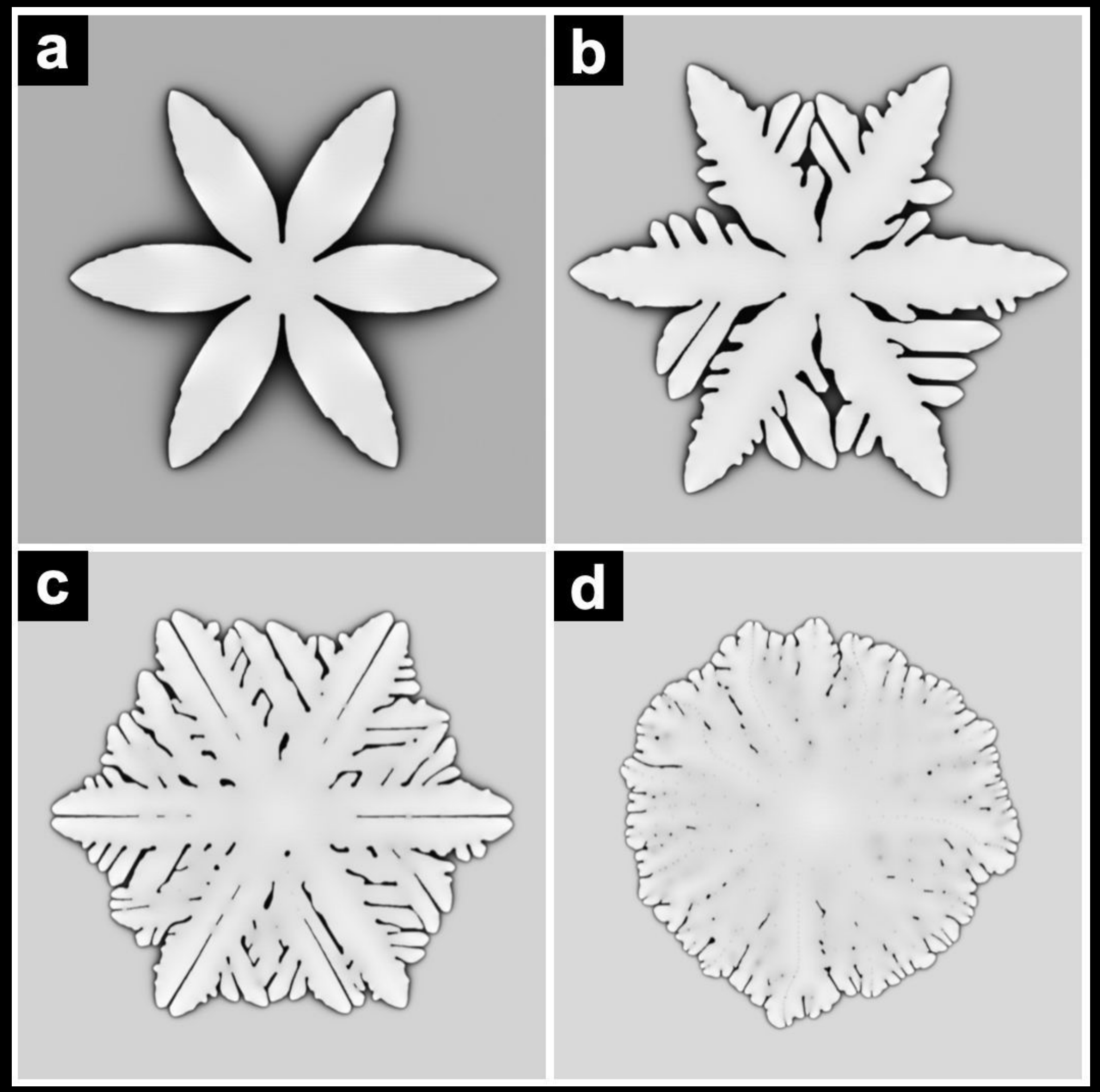
Motivation: Some complicated pictures

Jreidini, Paul, et al. "Orientation gradients in rapidly solidified pure aluminum thin films: Comparison of experiments and phase-field crystal simulations." *Physical Review Letters* (2021). https://doi.org/10.1103/physrevlett.127.205701.



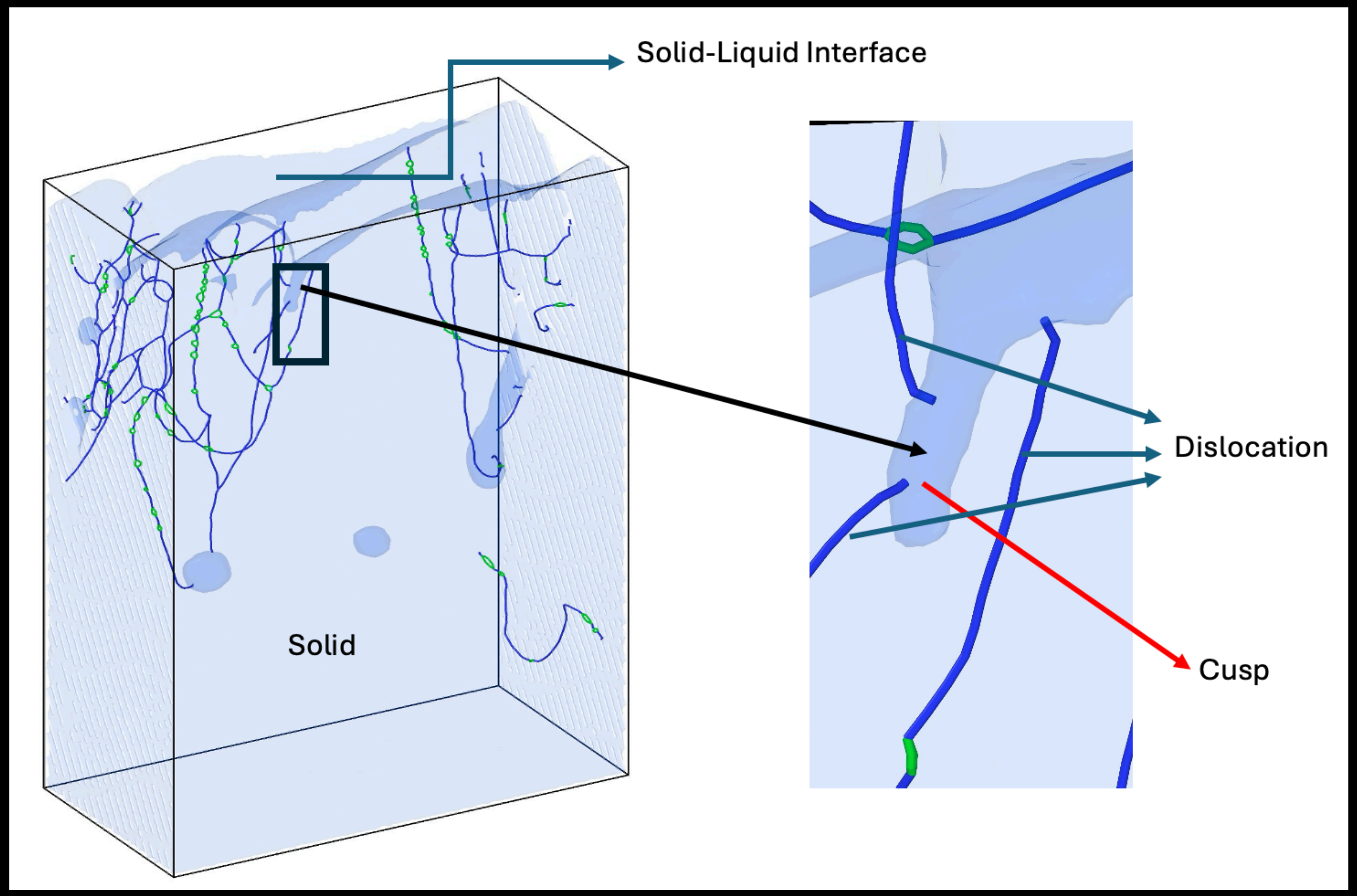
Spontaneous orientation gradients in Rapidly Solidified Aluminum Thin Films

Daniel Coelho, unpublished.



Interface Morphology vs Quench Depth

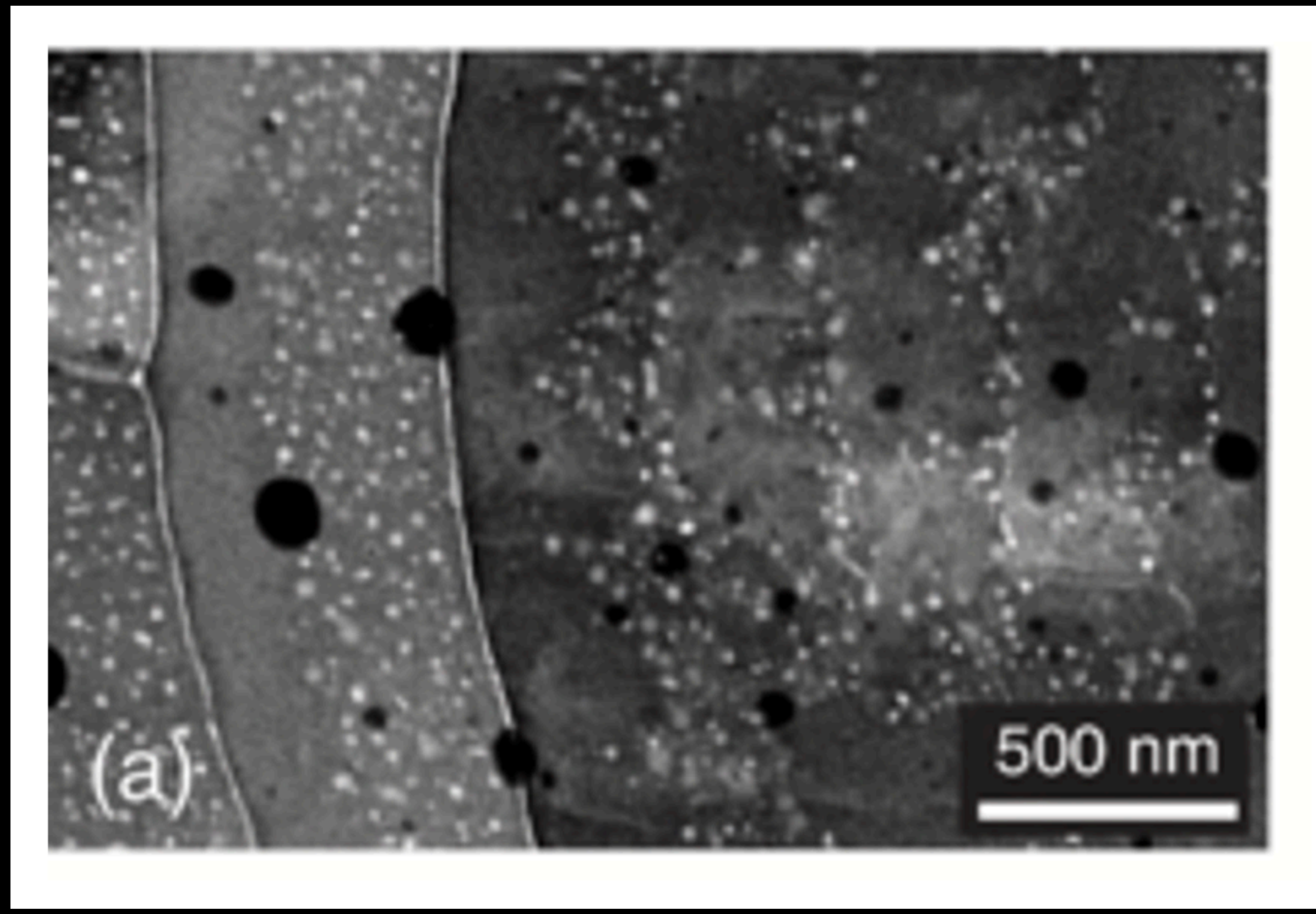
Jaarli Suviranta, unpublished.



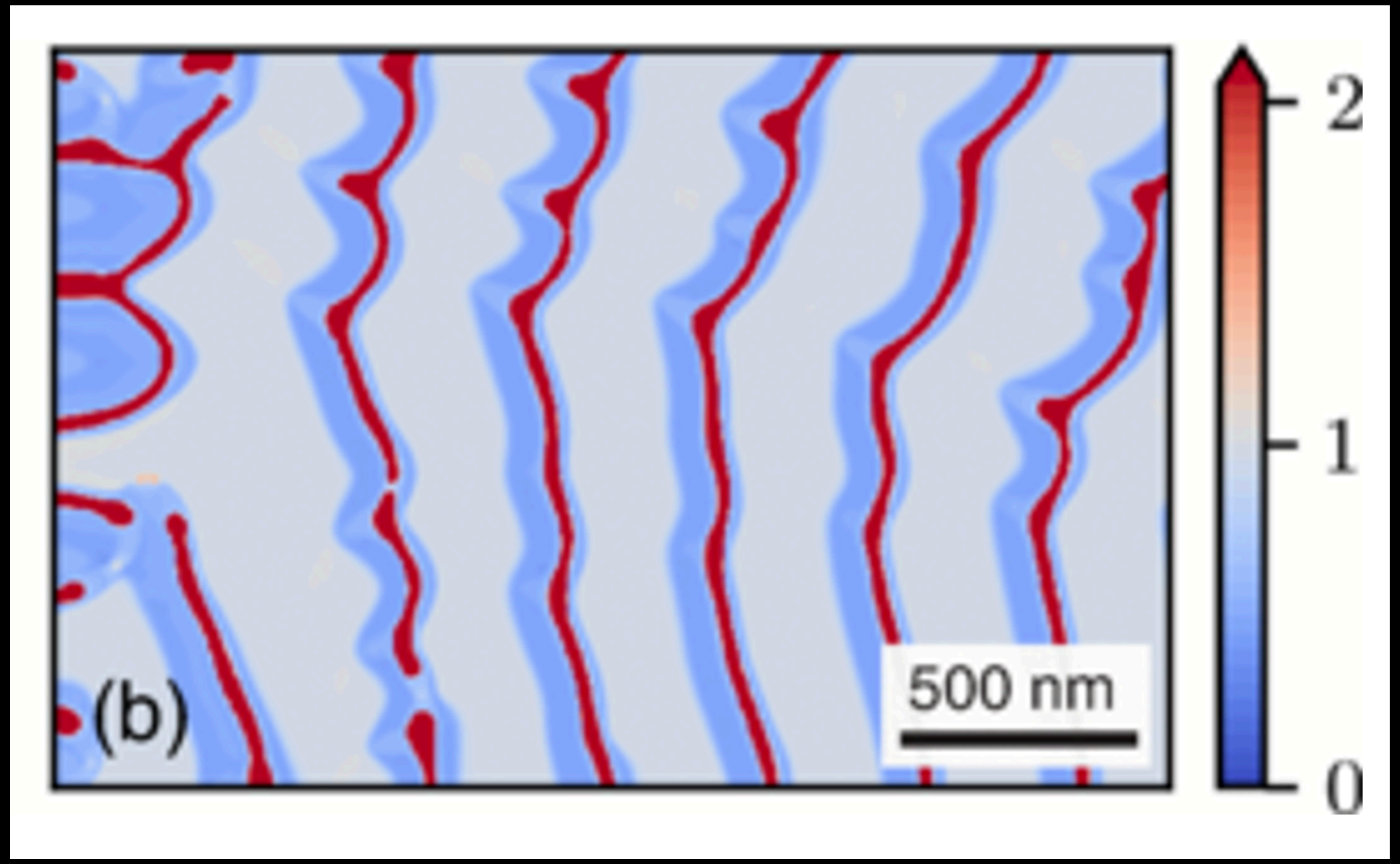
Dislocations during directional solidification

Motivation: More weird pictures

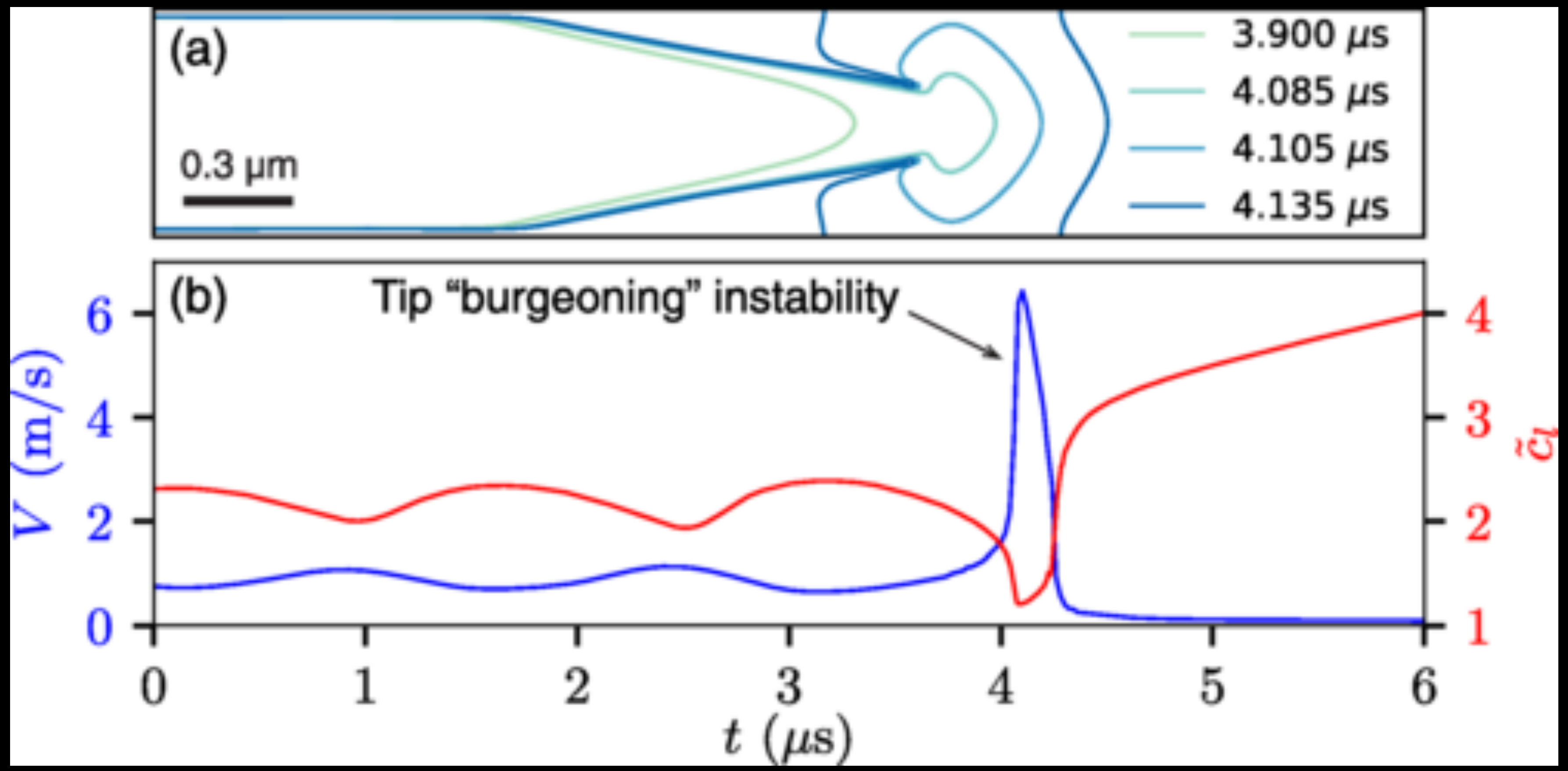
My real motivation is to be able to say I'm into cool bands



Banding: Experiment



Banding: Phase Field



Banding: Burgeoning

Ji, Kaihua, et al. "Microstructural Pattern Formation during Far-from-Equilibrium Alloy Solidification." Physical Review Letters, vol. 130, no. 2, Jan. 2023, p. 026203. DOI.org (Crossref), https://doi.org/10.1103/PhysRevLett.130.026203.

Ok, now let's try explaining what's going on.

... Using what theoretical framework?

What should our theory account for?

1. Equilibrium Thermodynamics

First-Order Phase Transitions

Two-Phase Coexistence (Equilibrium)

General Rule: Temperature, Pressure, Chemical Potential must be uniform in equilibrium.

For simulation reasons, it is convenient to consider Helmholtz Ensemble (T, V, N fixed).

$$\Longrightarrow \boxed{\begin{aligned} &T_1 = T_2 = T \\ &\mu_1 = \mu_2 \\ &-P_1 = f_1 - \mu_1\rho_1 = f_2 - \mu_2\rho_2 = -P_2 \end{aligned}} \Longleftrightarrow \boxed{\text{Common Tangent/Maxwell Equal Area Construction*}}$$

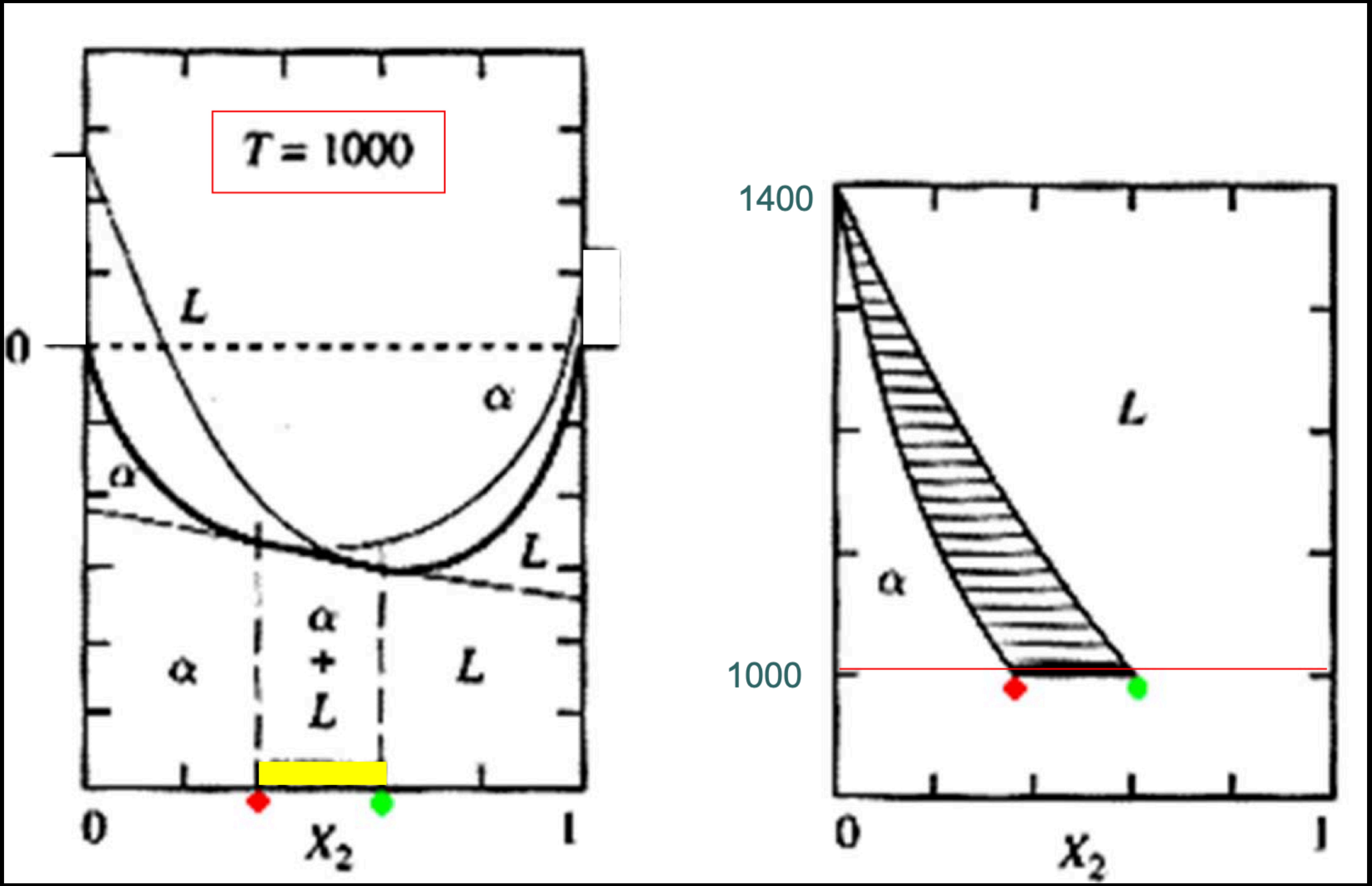
f_i : free energy density of phase i

ρ_i : (conserved) order parameter/number density of phase i

*These constructions are equivalent but this is not trivial to see. I will use the common tangent here but you can ask me about equal areas during question time!

When do phases coexist?

Free Energy Wells and Phase Diagrams



https://nanowires.berkeley.edu/teaching/253a/2016/253A-2016-08.pdf

$$T_1 = T_2 = T$$

$$\mu_1 = \mu_2$$

$$f_1 - \mu_1 \rho_1 = f_2 - \mu_2 \rho_2$$

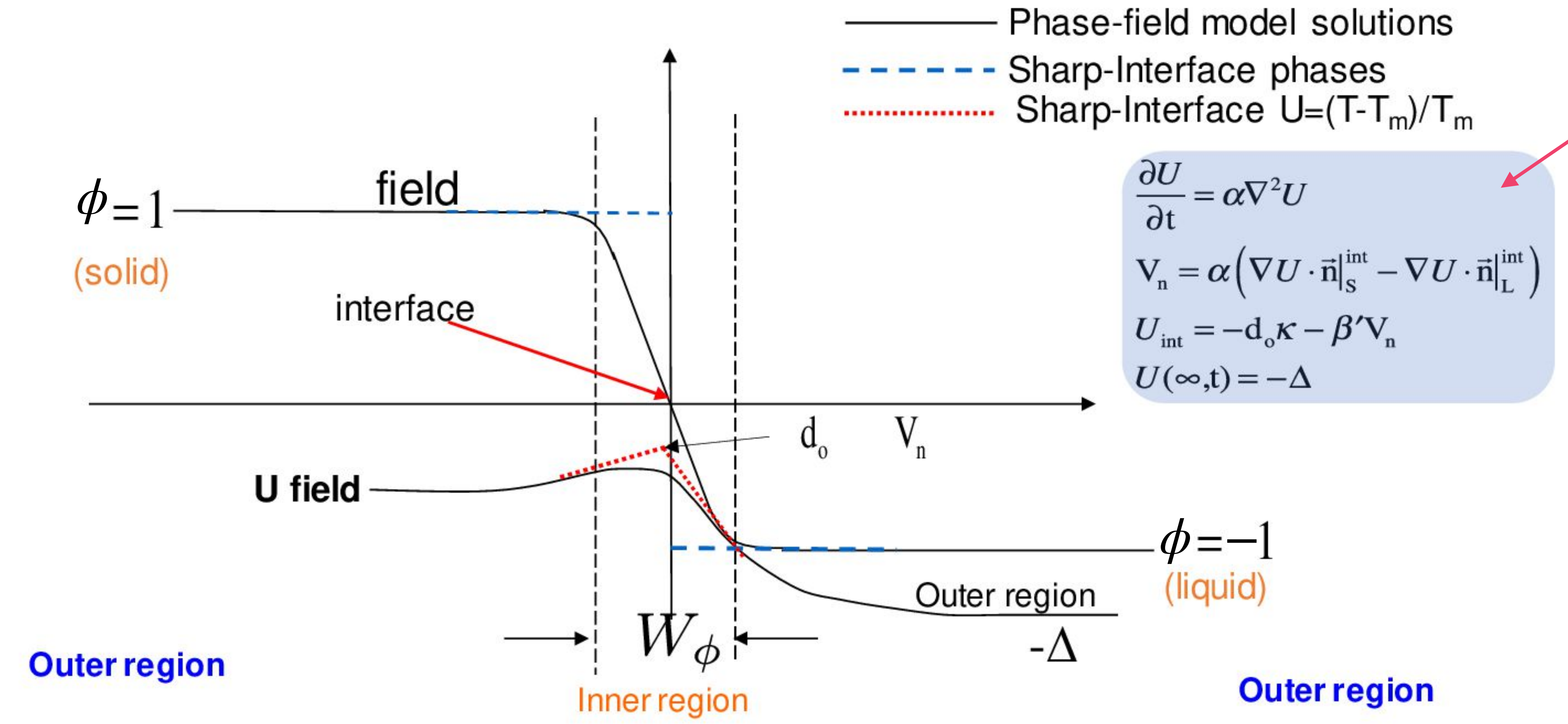
We’re looking for:
a theory that can *make good free energy wells*.

2. Dynamics

Classical Approaches to Solidification

Sharp Interface and Phase-Field Models

Separation of Length Scales



Classic approach: phase-field (order parameter) and temperature field approach sharp-interface profiles when $W_\phi \rightarrow 0$

Sharp-Interface Model

Phase-Field Model

$$\frac{\partial \phi}{\partial t} = -\frac{\delta F(\phi, T)}{\delta \phi} + \xi(\vec{x}, t)$$

$$\frac{\partial u}{\partial t} = \alpha \nabla^2 u + \frac{1}{2}\frac{\partial P(\phi))}{\partial t}$$

$$F[\phi, T] = \int_V \left(\frac{W_\phi^2}{2}|\nabla \phi|^2 + g(\phi) + \lambda u P(\phi) \right) dV$$

phi-4 potential

$u = \frac{T - T_M}{L / c_p}$ Tilts the wells

$\tau = \frac{1}{MH}$

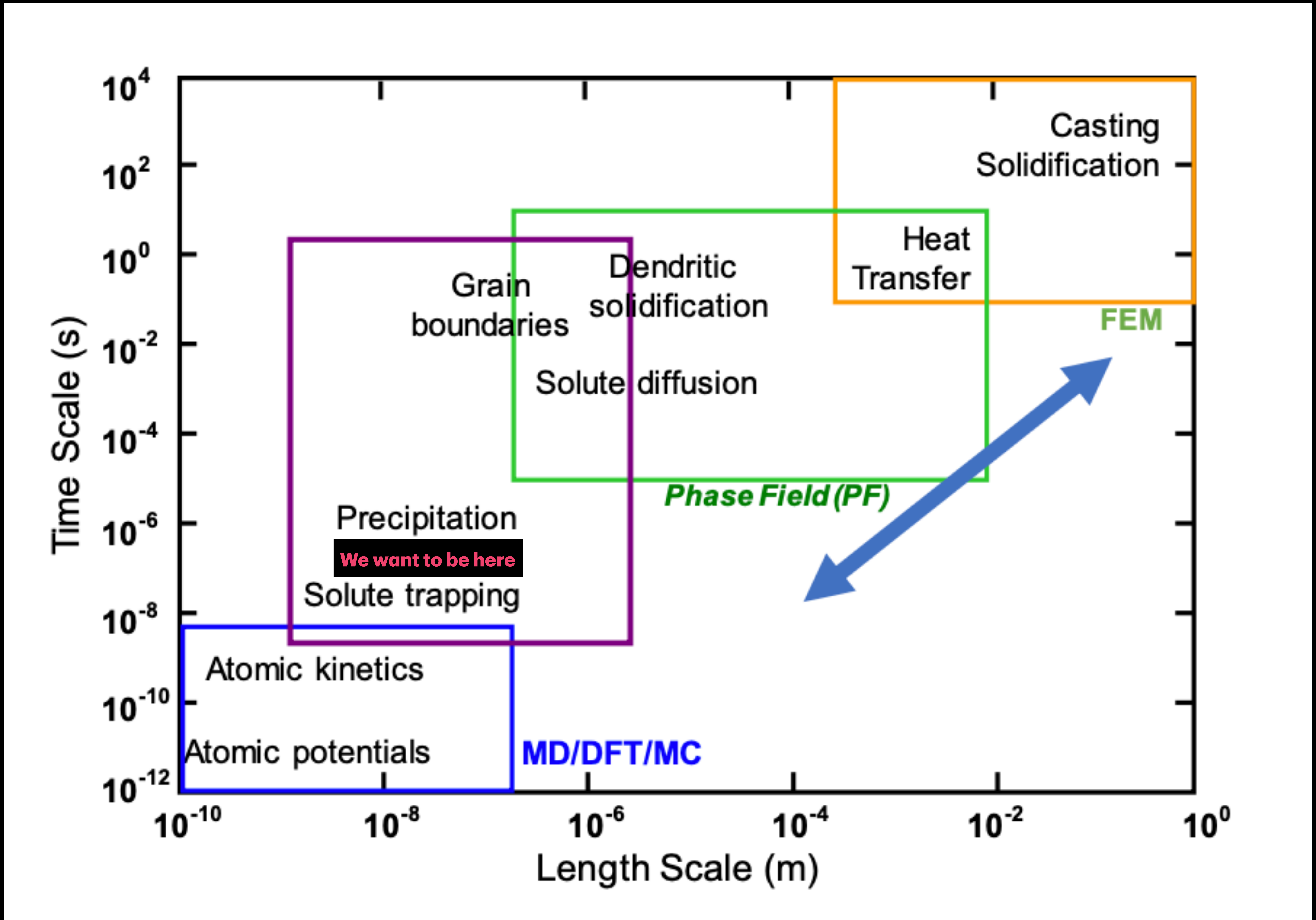
$W_\phi = \frac{\epsilon_\phi}{\sqrt{H}}$

$\lambda = \frac{L^2}{H c_p T_M}$

$\alpha = \frac{k}{\rho c_p}$

Provatas, Nikolas. Modelling Rapid Solidification Kinetics Quantitatively using Phase Field Methods, ChiMAD Spring 2021

3. Length + Time Scales



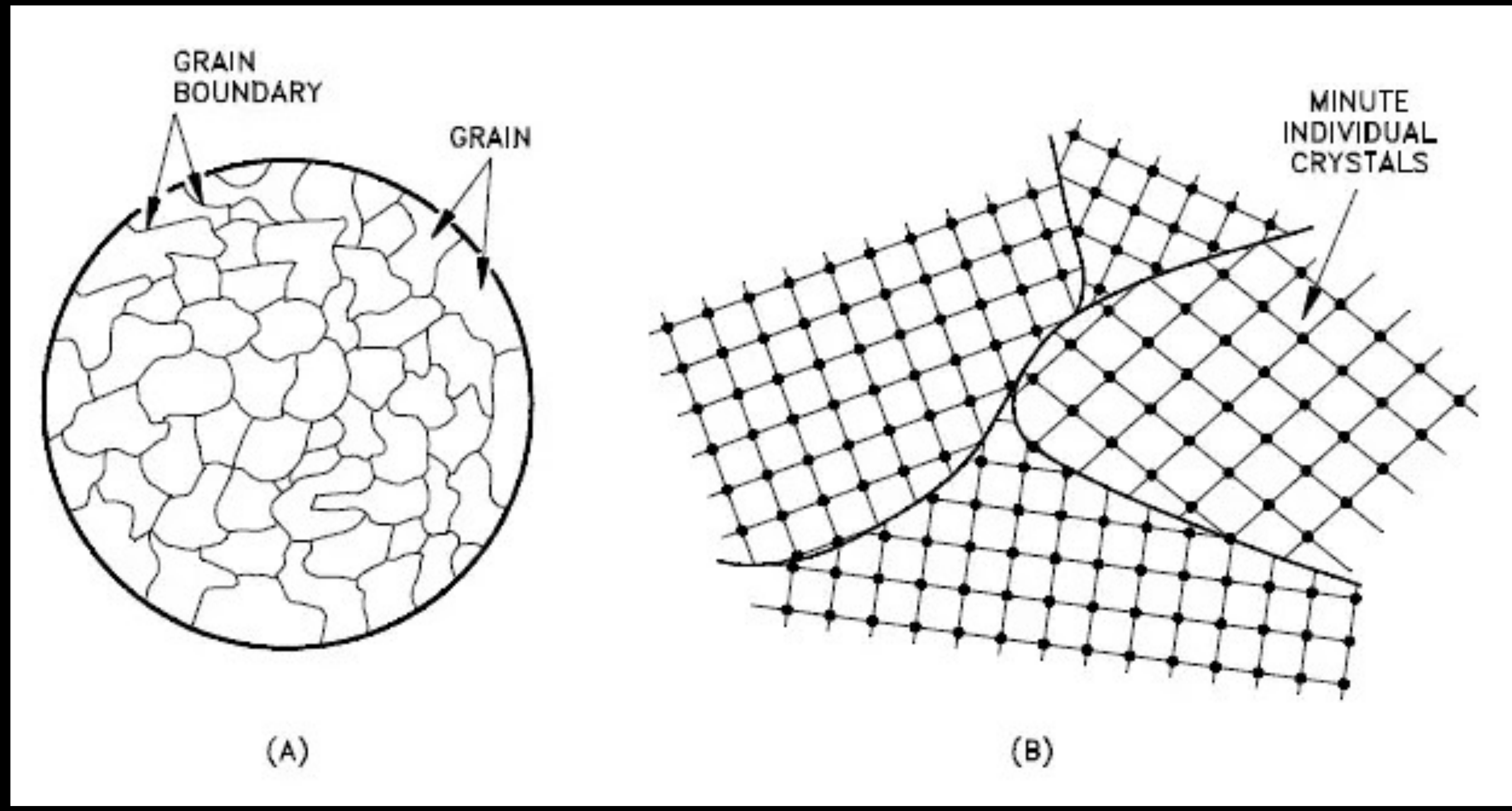
Provatas, Nikolas. Modelling Rapid Solidification Kinetics Quantitatively using Phase Field Methods, ChiMAD Spring 2021

We're looking for:
a *field theory*
with *diffusive(ish) dynamics*
that can *make good free energy wells*.

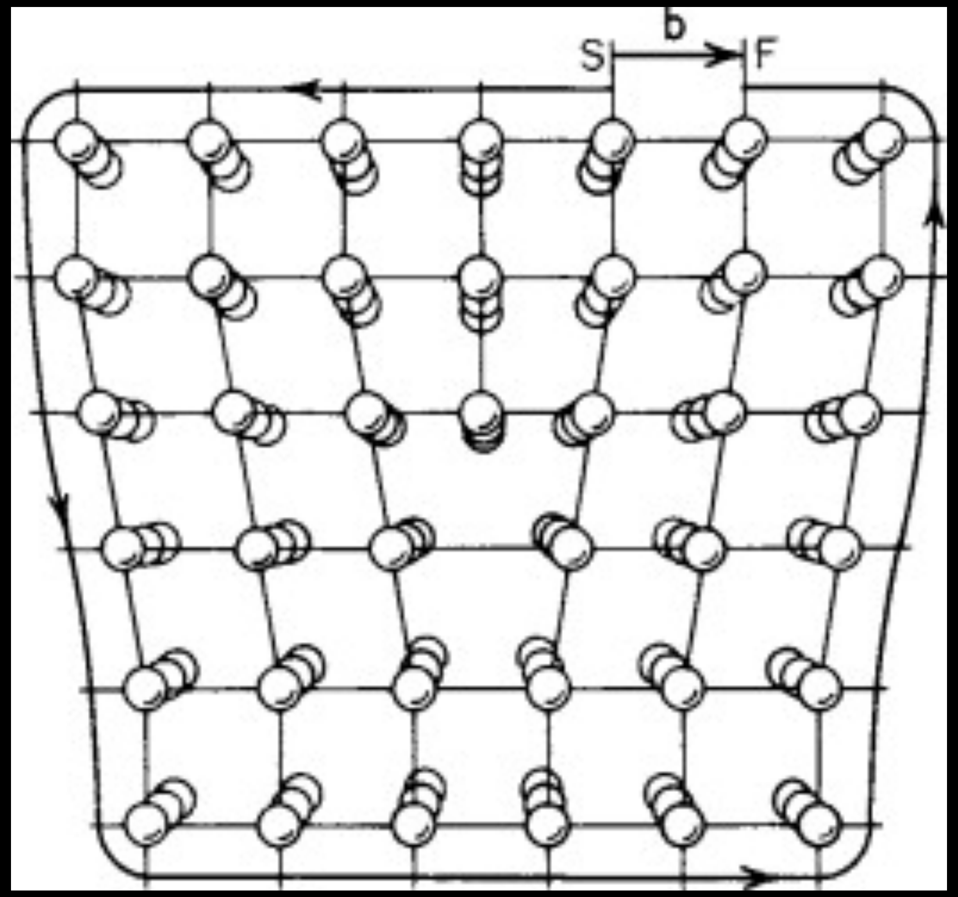
4. Topological Defects

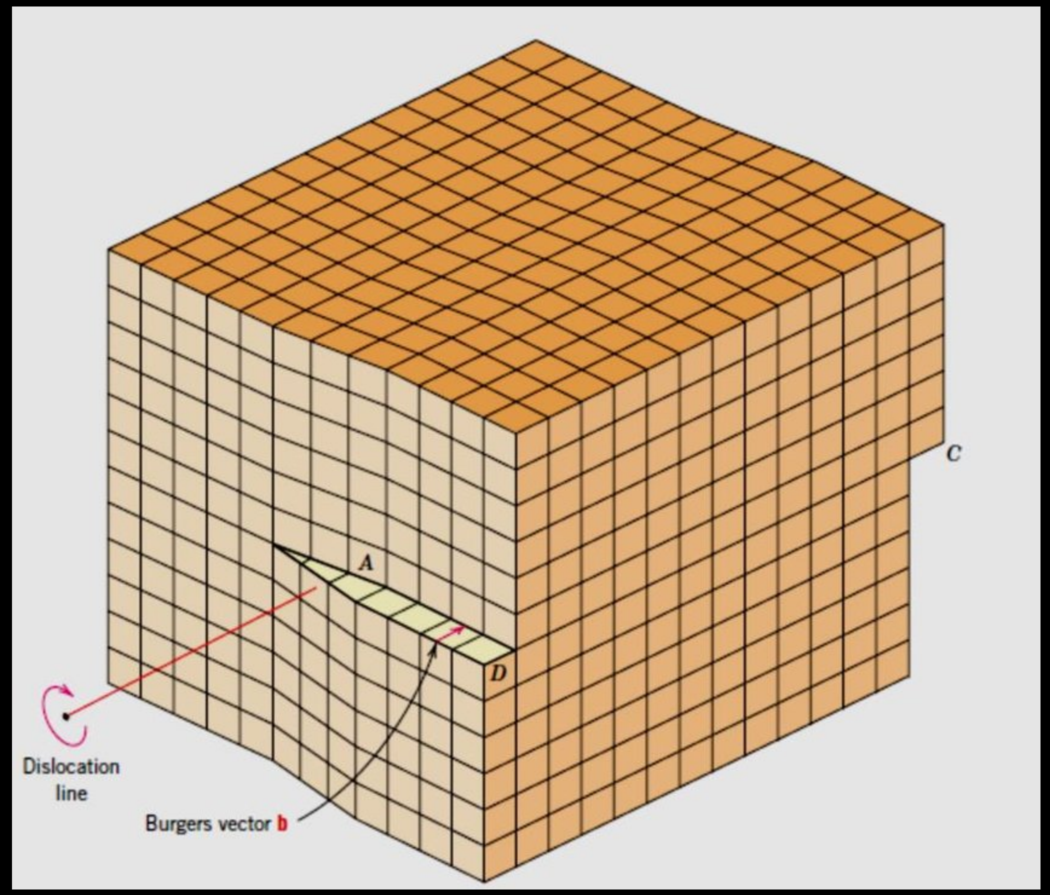
Defects in Solids

Free Energy is always GLOBALLY rotationally and translationally invariant

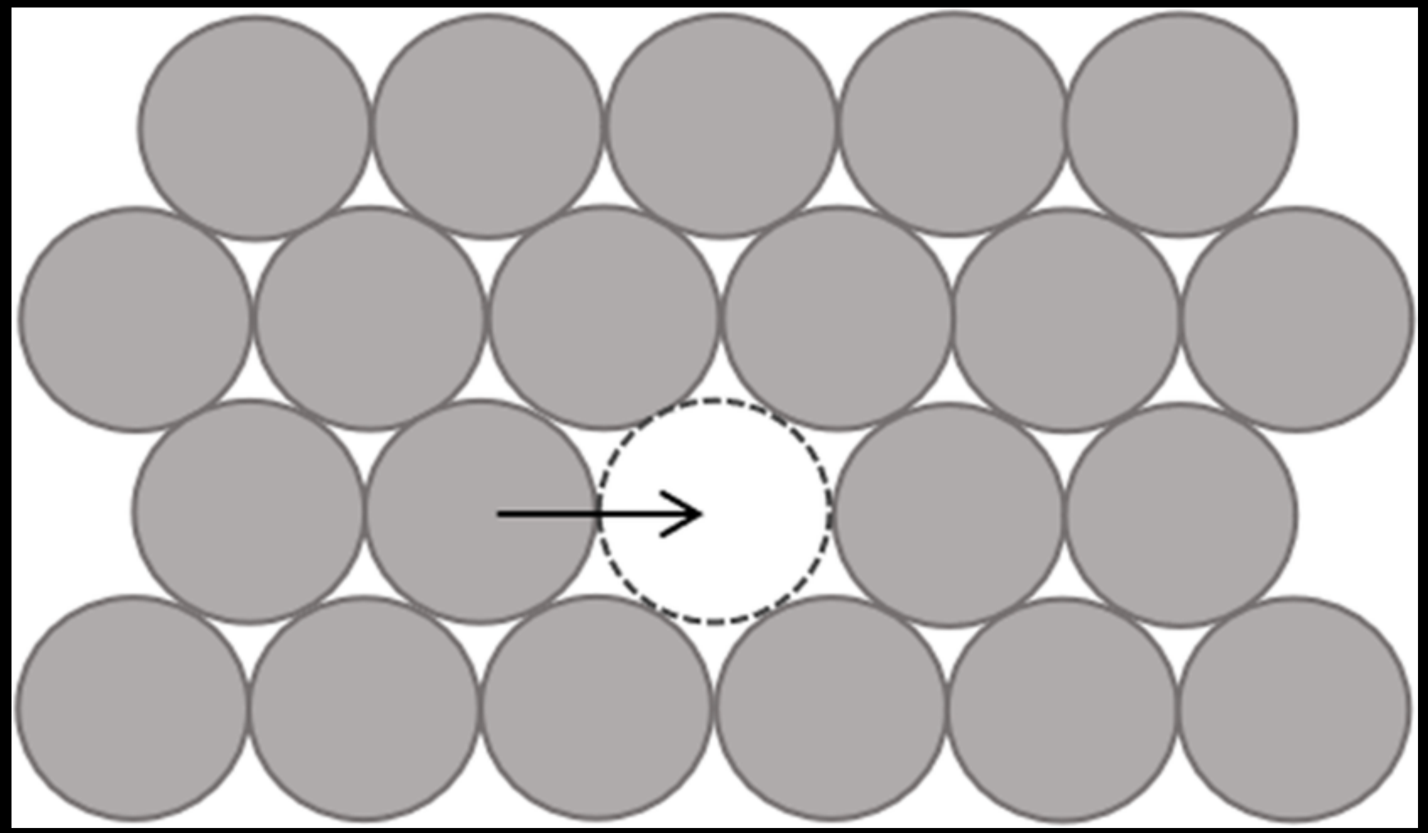


(1) Needs: Orientation dependent order parameter





(2) Needs: <u>Crystallographically periodic order parameter</u>



(3) Needs: A fully atomistic (MD/DFT) treatment. Too expensive for solidification.

A theory with (2) captures (1) exactly and (3) in a mean-field sense.

(1) U.S. Department of Energy, Material Science. DOE Fundamentals Handbook, Volume 1 and 2. January 1993.

(2) https://www.researchgate.net/publication/340444469_Metallurgy_almadn_Im_Solidification_and_Crystalline_Imperfection_of_Metals +

(3) Li, Rongbin & Chen, Tongtong & Jiang, Chunxia & Zhang, Jing & Zhang, Yong & Liaw, Peter. (2020). Applications of High Diffusion Resistance Multi-component AlCrTaTiZrRu/(AlCrTaTiZrRu)N0.7 Film in Cu Interconnects. Advanced Engineering Materials. 22. 10.1002/adem.202000557.

We're looking for:
a *field theory*
with *diffusive(ish) dynamics*
that can *make good free energy wells*
and *supports a periodic order parameter*.

Classical Density Functional Theory

Has all the right ingredients, but is numerically too stiff.

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

Free Energy change due to density fluctuations in a metastable liquid

Configurational Entropy $\longleftrightarrow$ $k_B T \rho_0 \left(\rho(\mathbf{r}) \log\left(\frac{\rho(\mathbf{r})}{\rho_0}\right) - (\rho(\mathbf{r}) - \rho_0) \right)$

$-k_B T \Gamma_2(\mathbf{r}_1, \mathbf{r}_2)$ $\longleftrightarrow$ 2-point "vertex" function

Dynamics: $$\frac{\partial \rho}{\partial t} = \nabla \cdot \left(M(\rho) \nabla \frac{\delta \Delta F}{\delta \rho} \right)$$

Provatas, Nikolas, and Ken Elder. Phase-Field Methods in Materials Science and Engineering. Wiley-VCH Verlag GmbH & Co. KGaA, 2010., https://doi.org/10.1002/9783527631520.

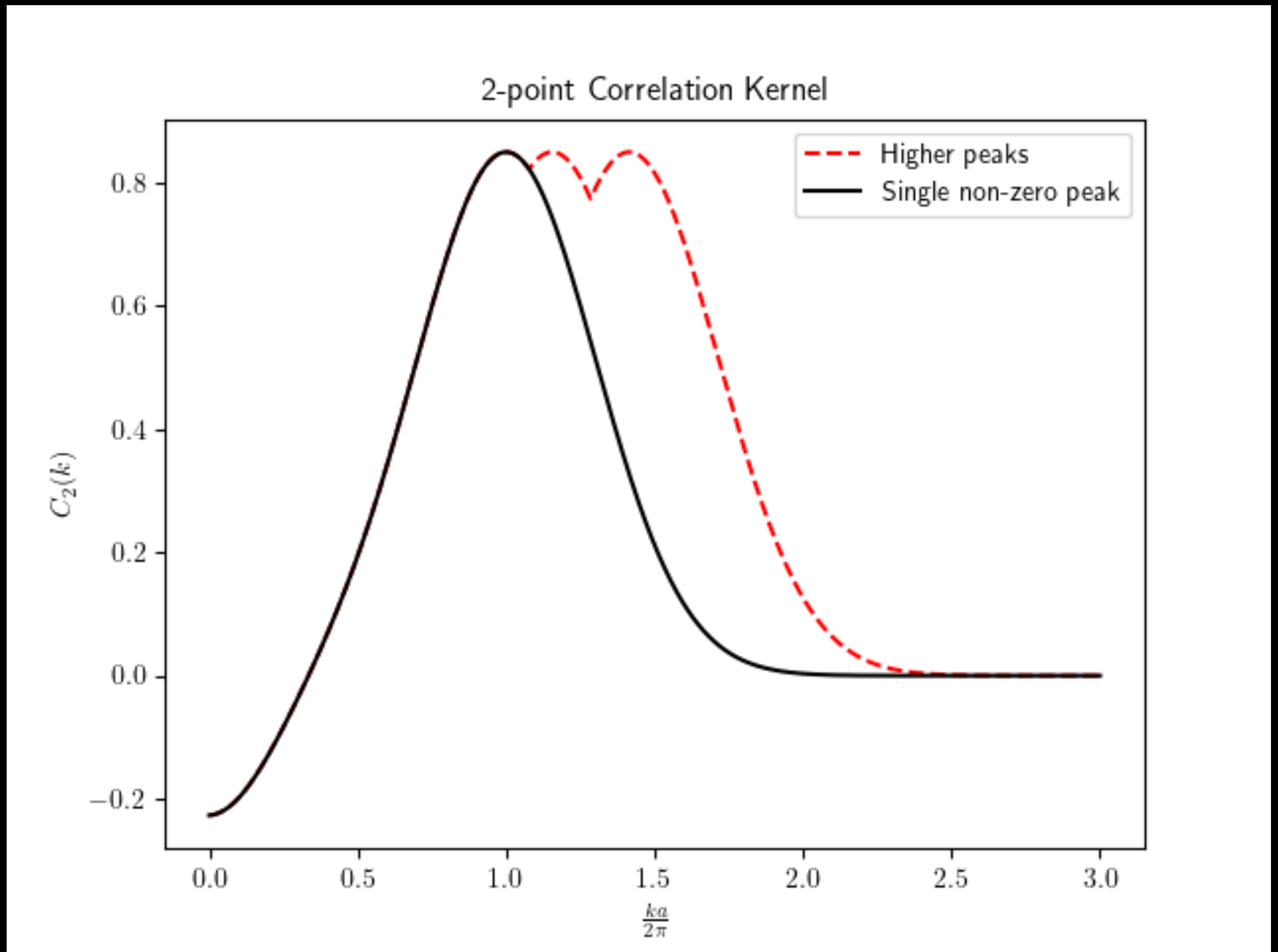
Phase Field Crystal (simplified cDFT)

Landau Theory (wells) + Periodic OP (dislocations)

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

$$\boxed{n = \frac{\rho - \rho_0}{\rho_0}}$$

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



Directional Solidification

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

Provatas, Nikolas, and Ken Elder. Phase-Field Methods in Materials Science and Engineering. Wiley-VCH Verlag GmbH & Co. KGaA, 2010., https://doi.org/10.1002/9783527631520.

PFC Dynamics

Diffusive relaxation

$$\frac{\partial n}{\partial t} = \nabla \cdot \left[M \nabla \frac{\delta \mathcal{F}}{\delta n} \right]$$

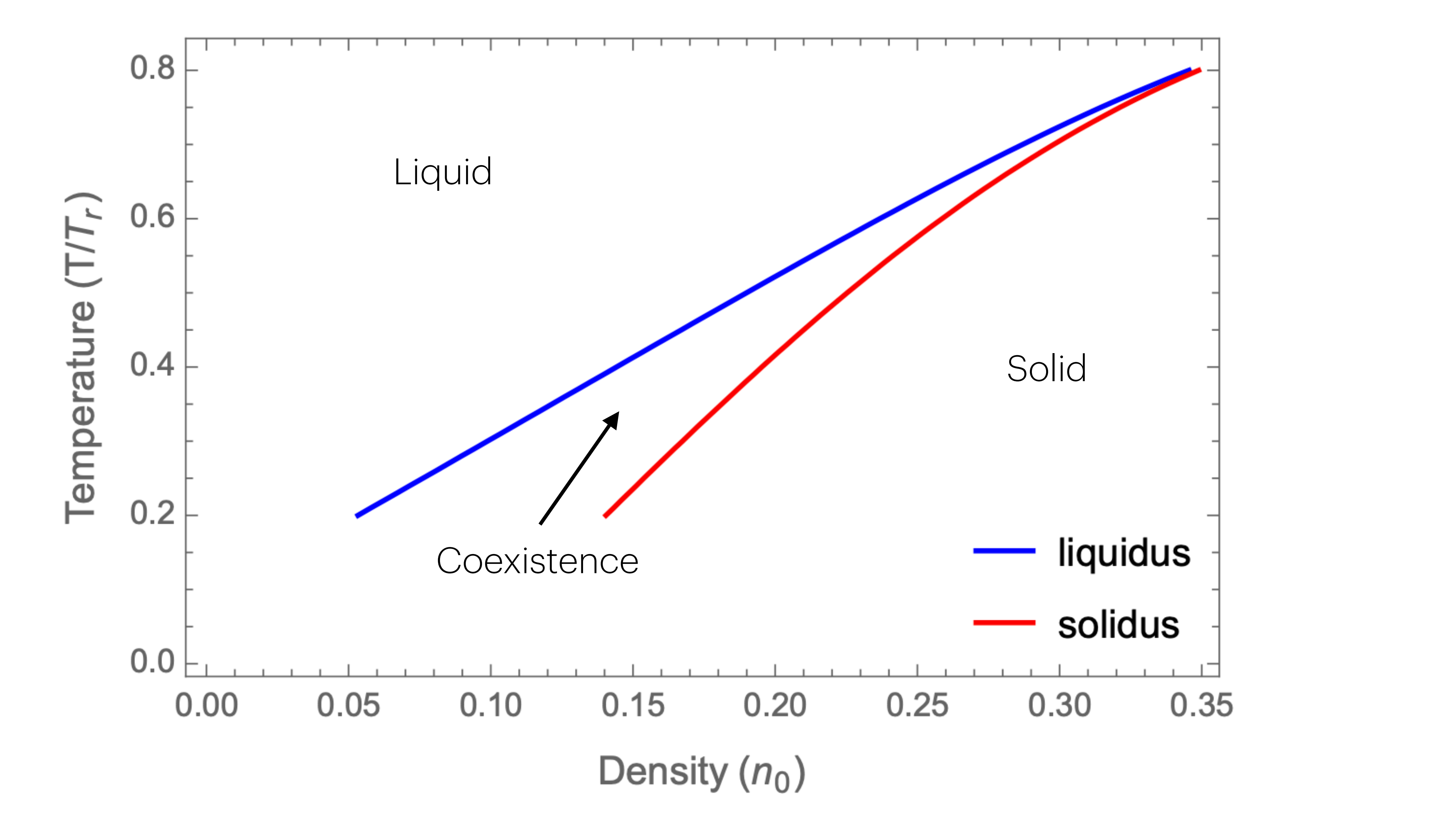
Provatas, Nikolas, and Ken Elder. Phase-Field Methods in Materials Science and Engineering. Wiley-VCH Verlag GmbH & Co. KGaA, 2010., https://doi.org/10.1002/9783527631520.

PFC Equilibrium

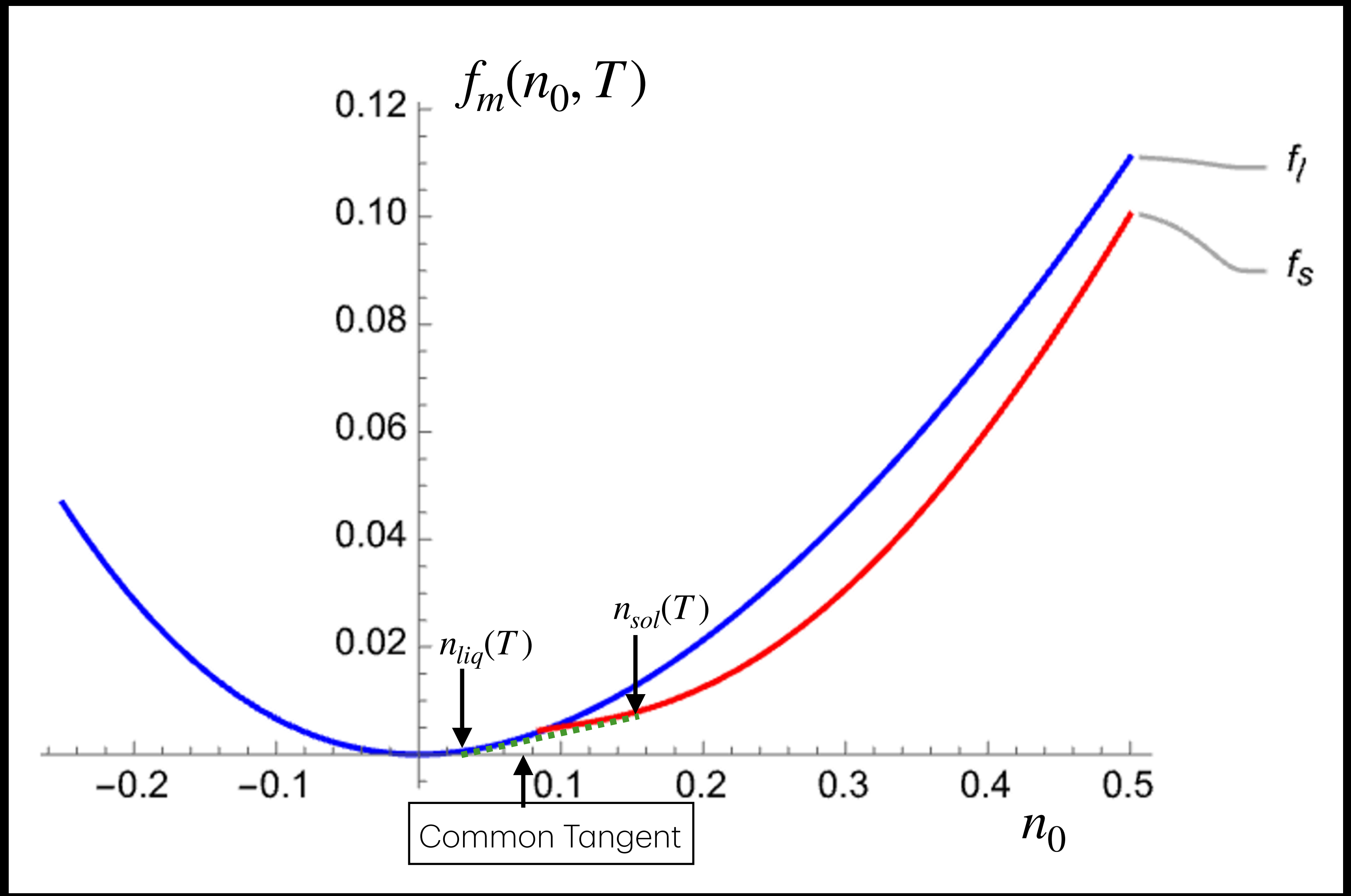
Free Energy Wells and Phase Diagrams

$$n(\mathbf{r}) = n_0 + \sum_j A_j e^{i\mathbf{k}_j\cdot\mathbf{r}} \xrightarrow[\text{Average over unit cell}]{\text{Sub. into } \mathcal{F}} f(n_0, A_j, T) \xrightarrow{\text{Minimize w.r.t. } A_j} f_m(n_0, T)$$

Fixed T



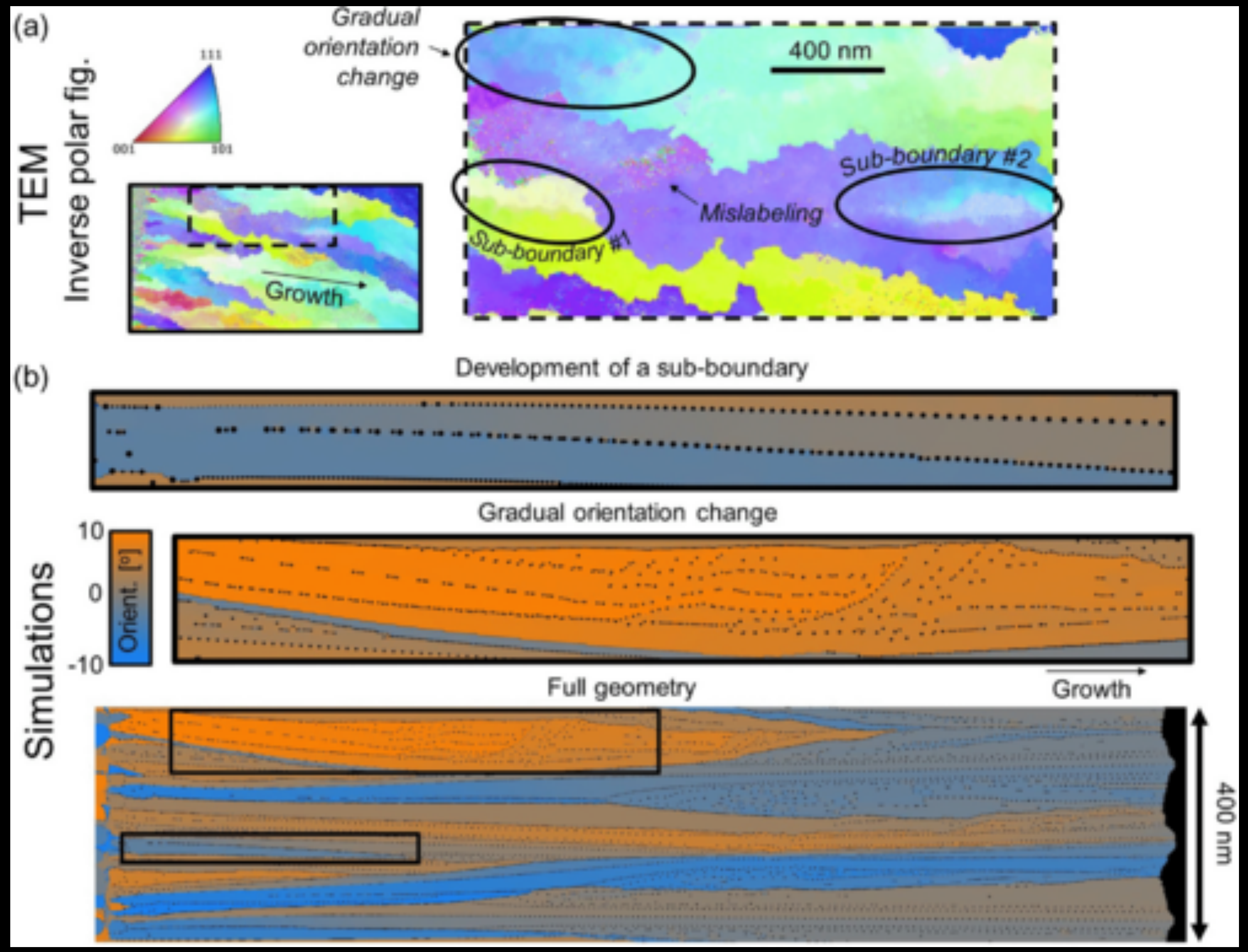
Repeat for various T



Motivation: Paper 1

What do these images have in common (other than being pretty)?

Jreidini, Paul, et al. "Orientation gradients in rapidly solidified pure aluminum thin films: Comparison of experiments and phase-field crystal simulations." *Physical Review Letters* (2021). https://doi.org/10.1103/physrevlett.127.205701.



Spontaneous orientation gradients in Rapidly Solidified Aluminum Thin Films

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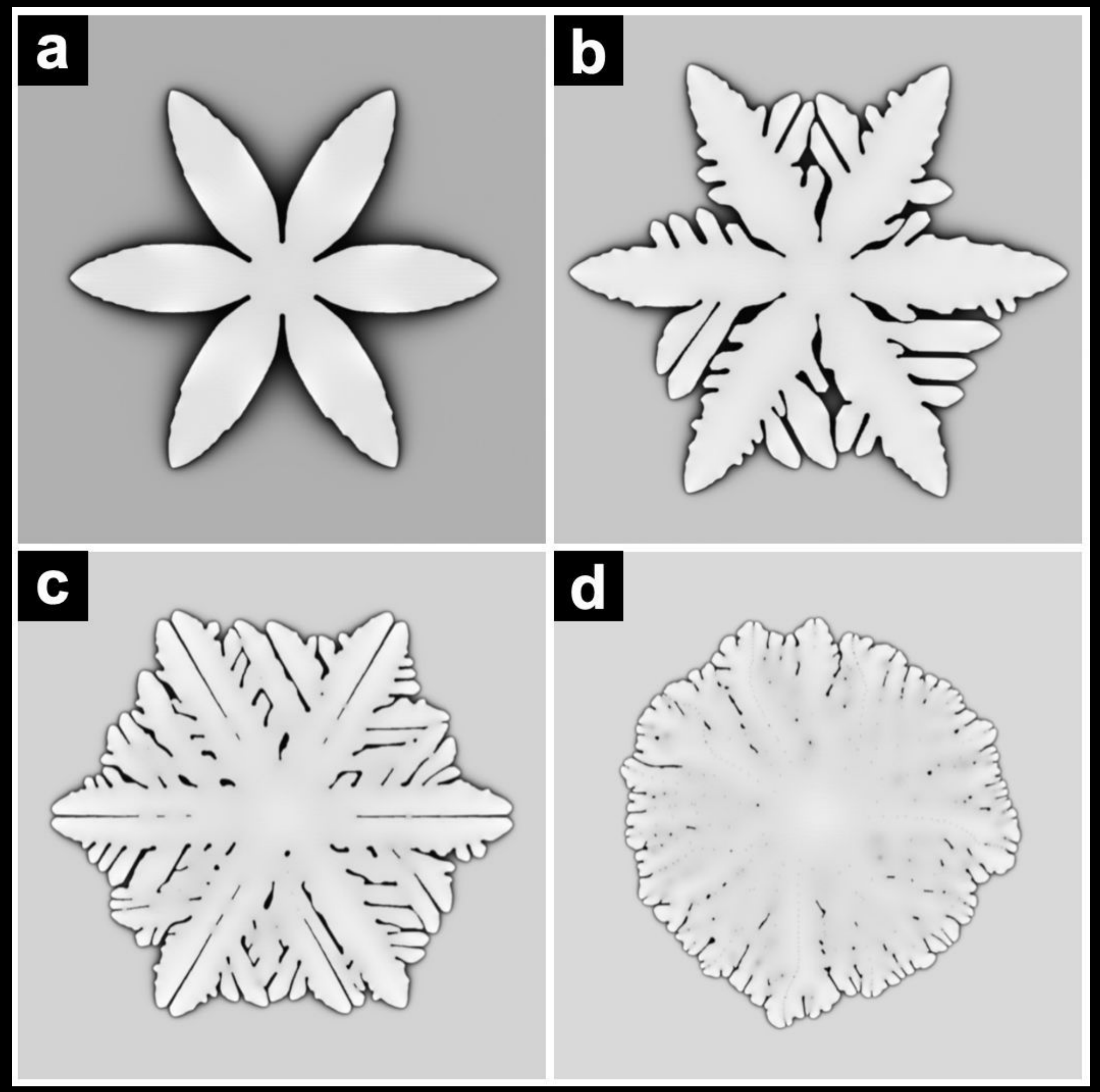

Interface Morphology vs Quench Depth

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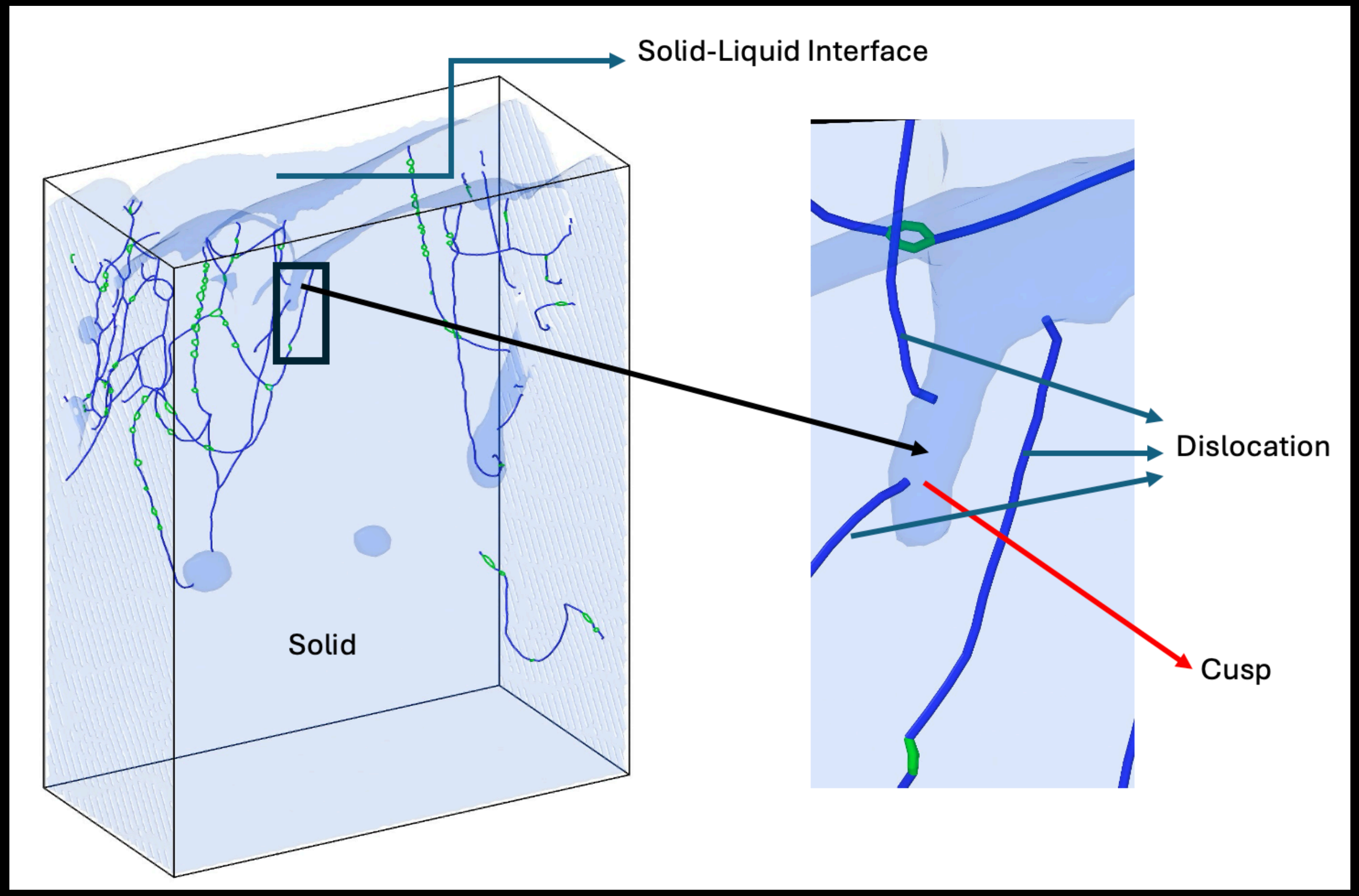
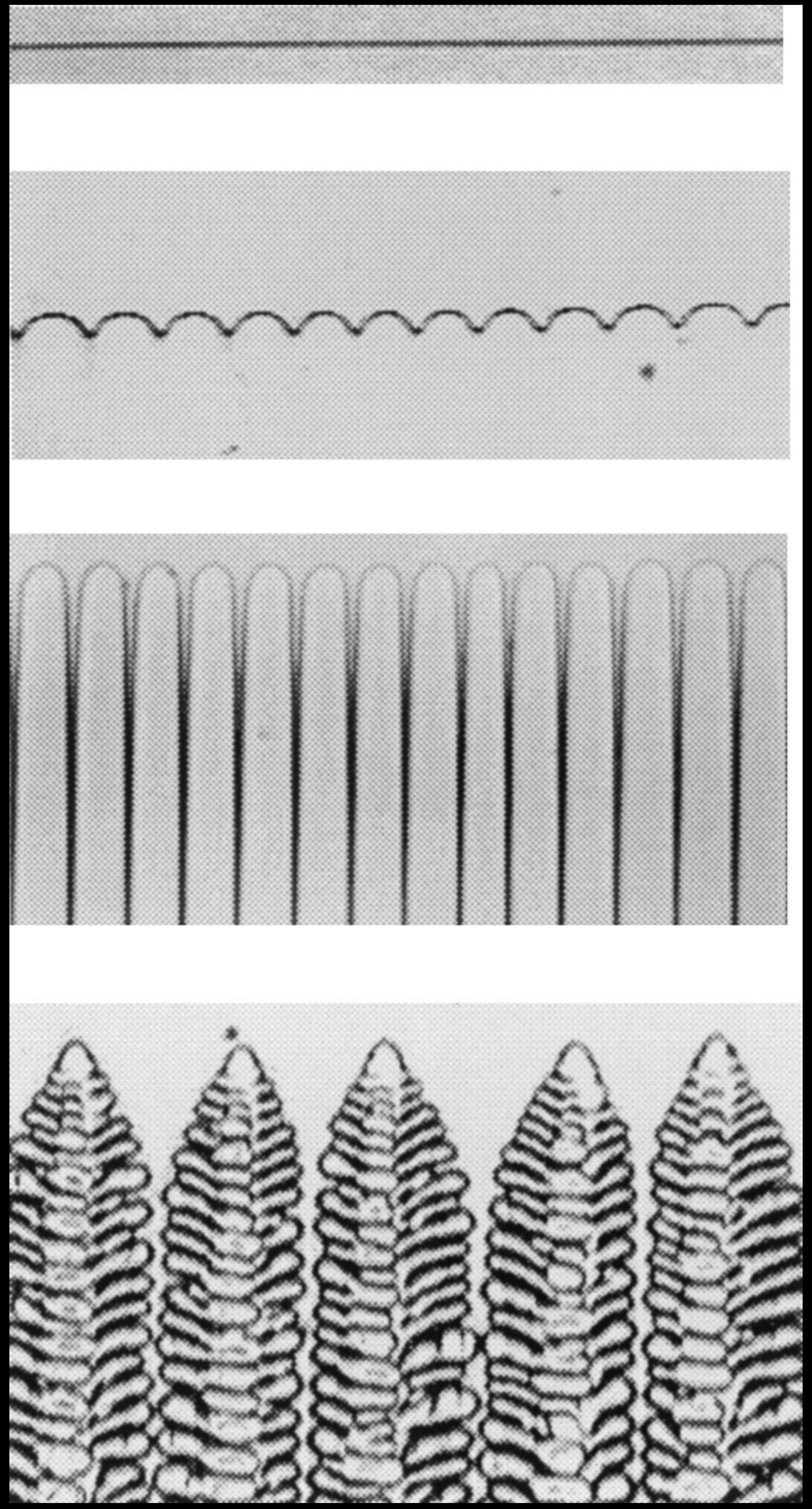


Dislocations during directional solidification

Dislocations keep showing up during rapid solidification. **Where are they coming from?**

Interlude: Interface Morphology

Dependence on cooling rate/pull speed

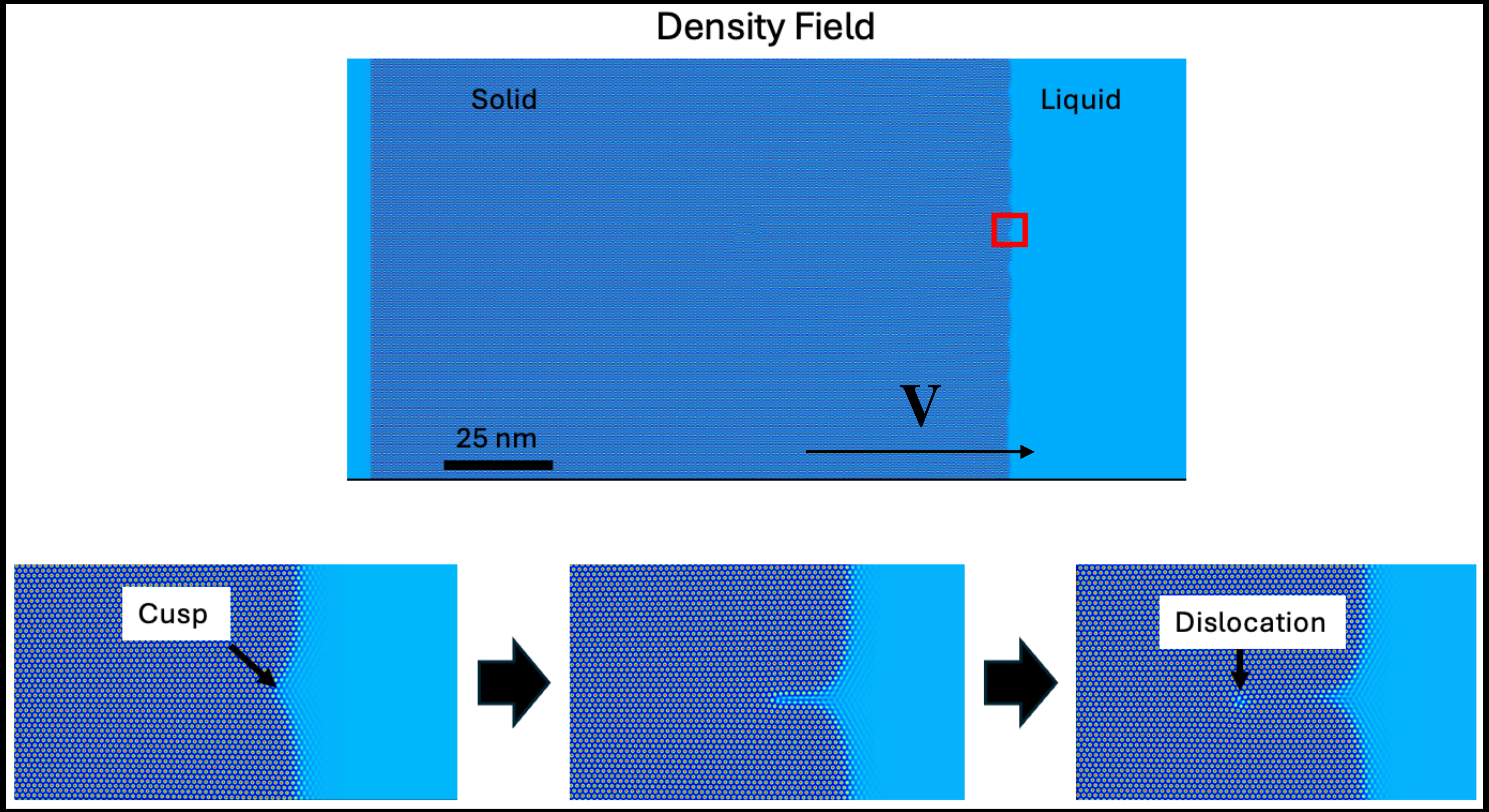


W. Losert, B.Q. Shi, H.Z. Cummins, Evolution of dendritic patterns during alloy solidification: Onset of the initial instability, Proc. Natl. Acad. Sci. U.S.A. 95 (2) 431-438, https://doi.org/10.1073/pnas.95.2.431 (1998).

Paper 1: Dislocation Nucleation from Atomically Rough Solid-Liquid Interfaces

Directional Solidification

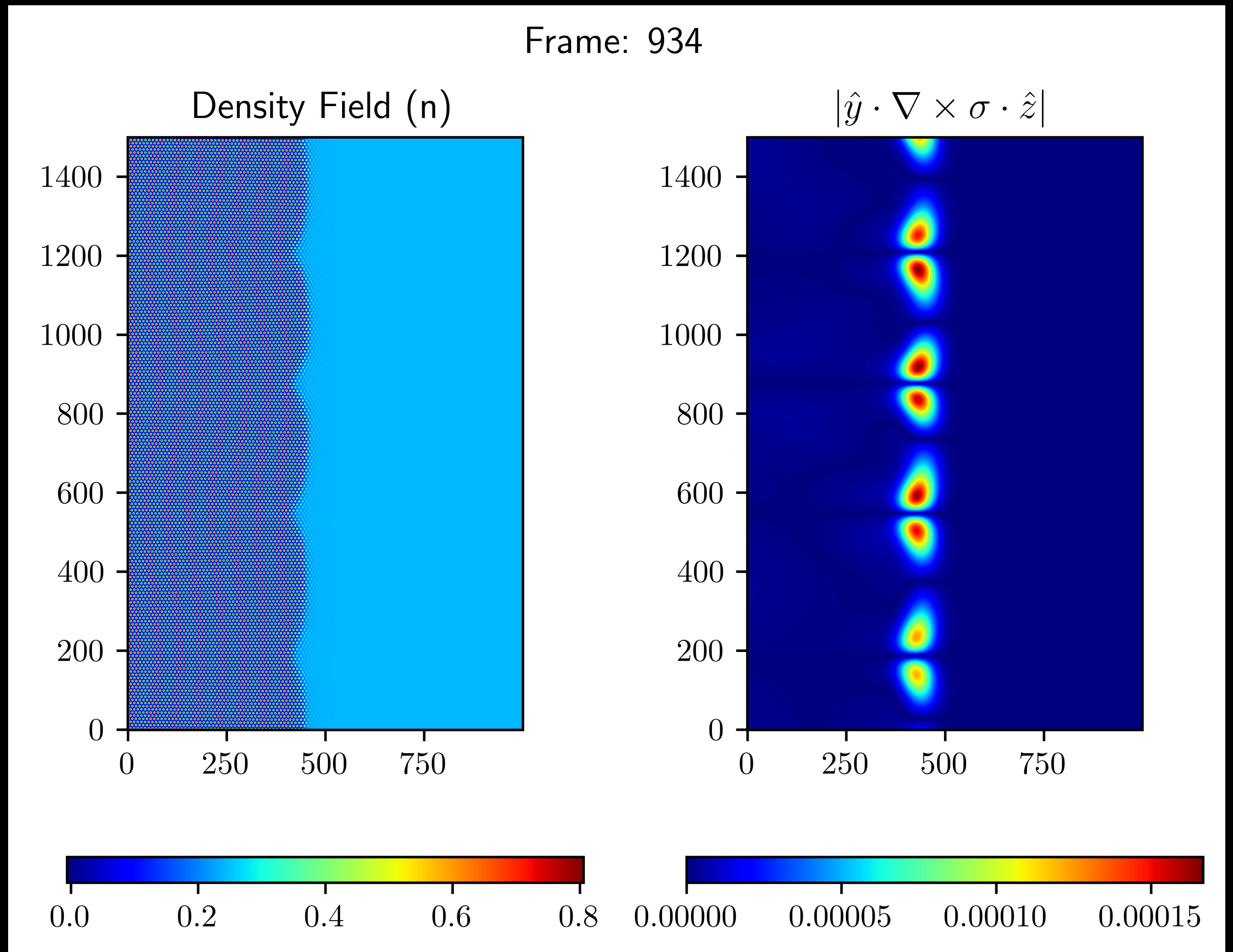
$$T(\mathbf{r}, t) = T_L + \mathbf{G} \cdot (\mathbf{r} - \mathbf{r}_L - \mathbf{V}t)$$

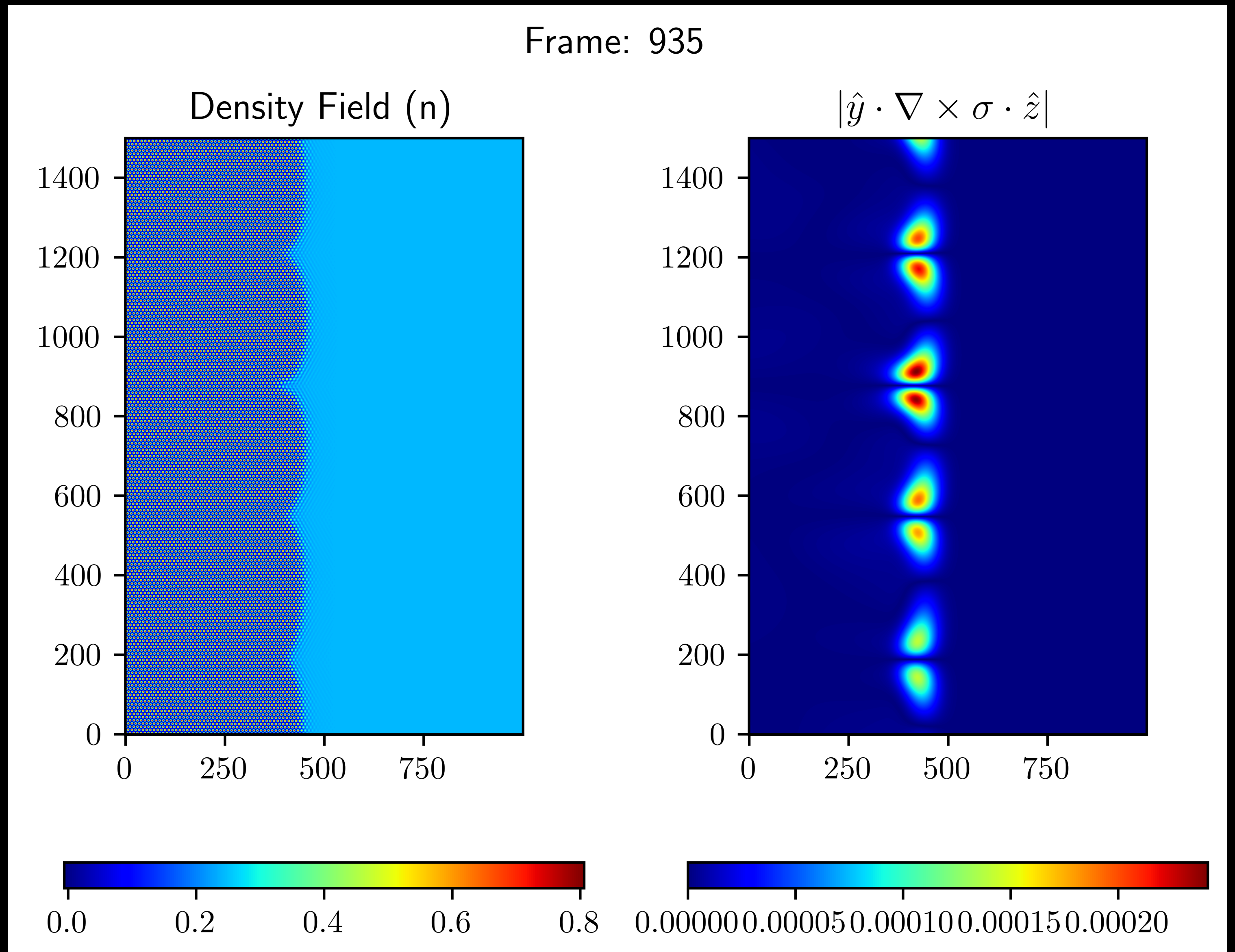


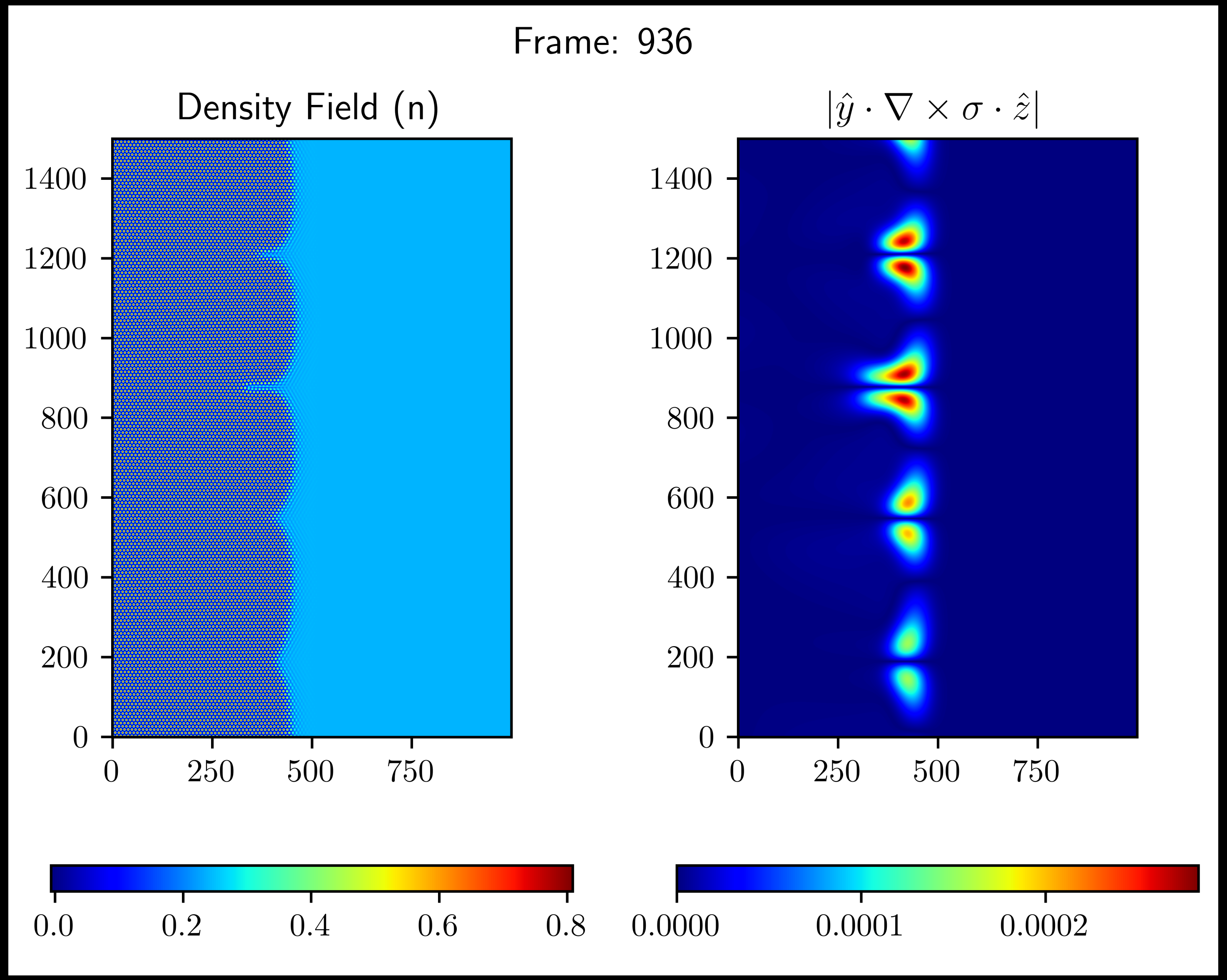
<u>Research Questions</u>

1. When/Why does a given cusp nucleate a dislocation?
2. Why do cusps remain past absolute stability?
3. How do (statistical) properties of the cusps relate to experimental parameters?

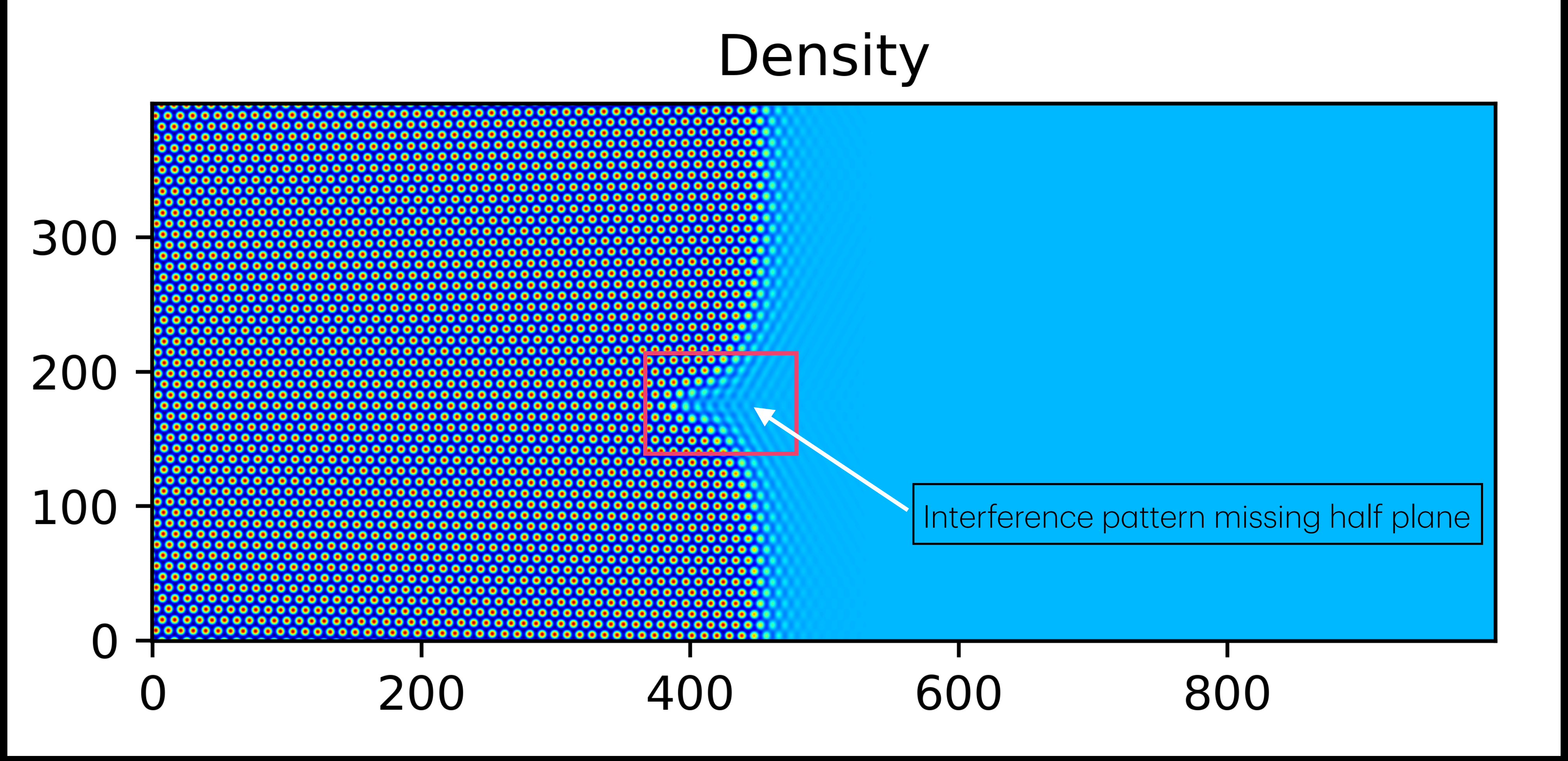
When/Why does a given cusp nucleate a dislocation?







$$N_{\mathbf{b}} = \hat{b} \cdot (\nabla \times \sigma) \cdot \hat{l}$$



Why cusps past absolute stability?

Experimental Conditions, Coarse-Graining

Coarse-Graining (and asymptotics) can relate interface morphology to model and experimental parameters.

Unfortunately, it is a difficult analysis -> Nik and I are working on it.

This will likely be the key piece to having a coherent story for a paper.

Why cusps past absolute stability?

Connections with Vacancy Trapping

1. Experiments: Vacancy trapping is important at these speeds.

2. PFC:

   - Vacancies are embedded in the theory via n_0 and A_j (exact details are not yet known)

   - Both n_0 and A_j change according to interface speed -> Vacancy trapping?

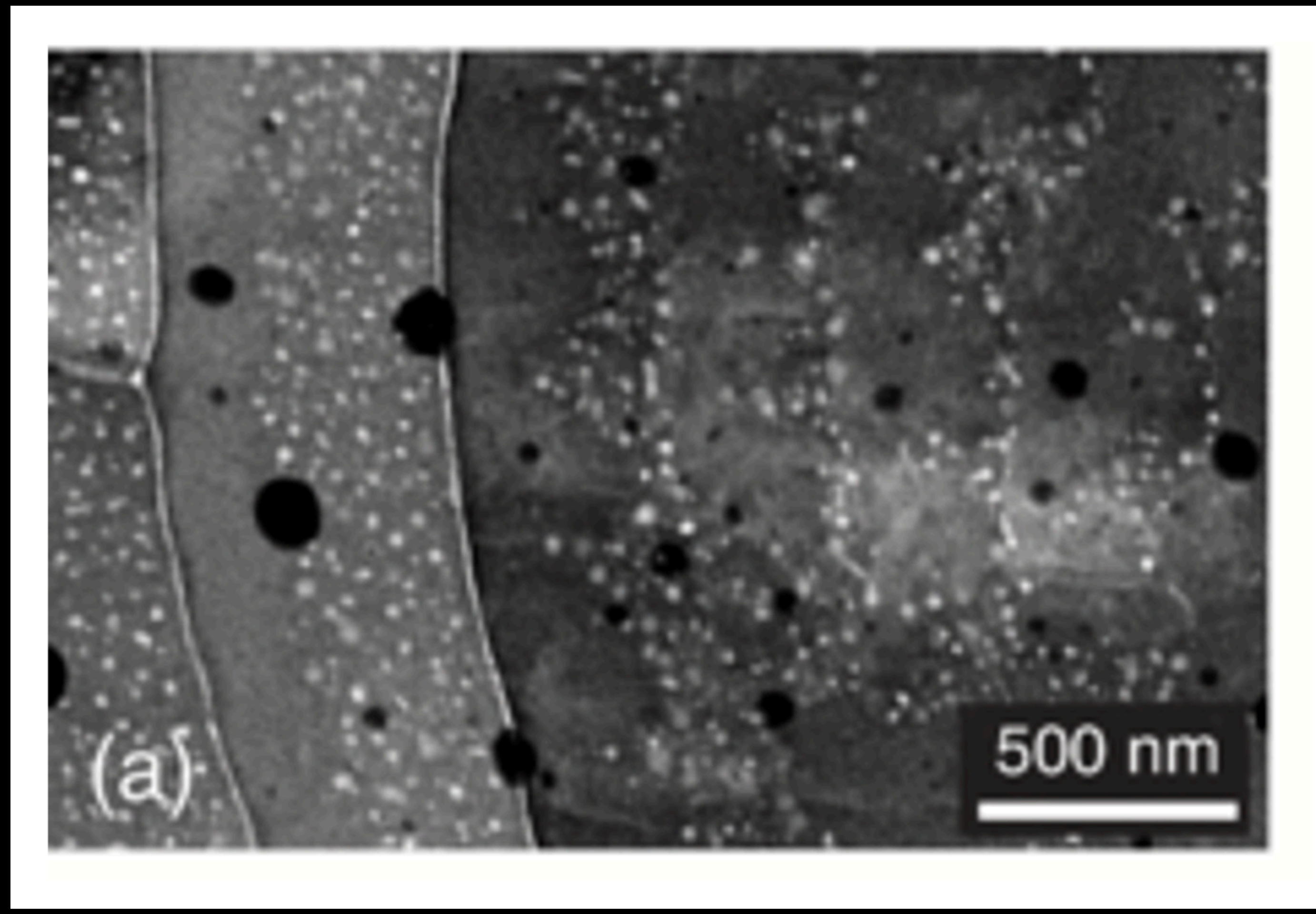
Is vacancy trapping responsible for the cusps and dislocations? Are there any other possible sources of stress?

Is there a length-scale to the cusps that can be obtained from coarse-graining?

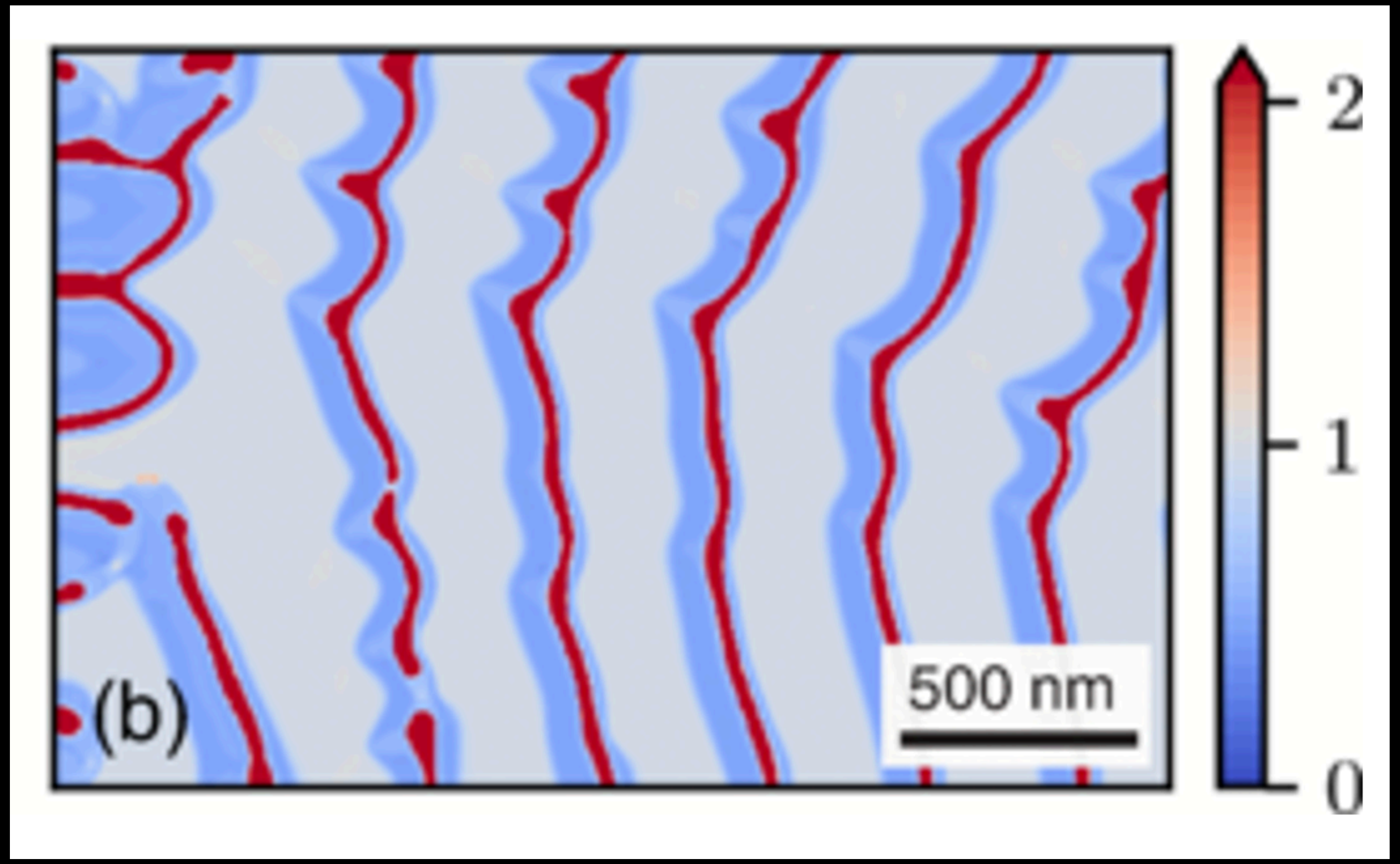
Like Dr. Guo suggested: Is this also a time-scale issue?

Motivation: Paper 2

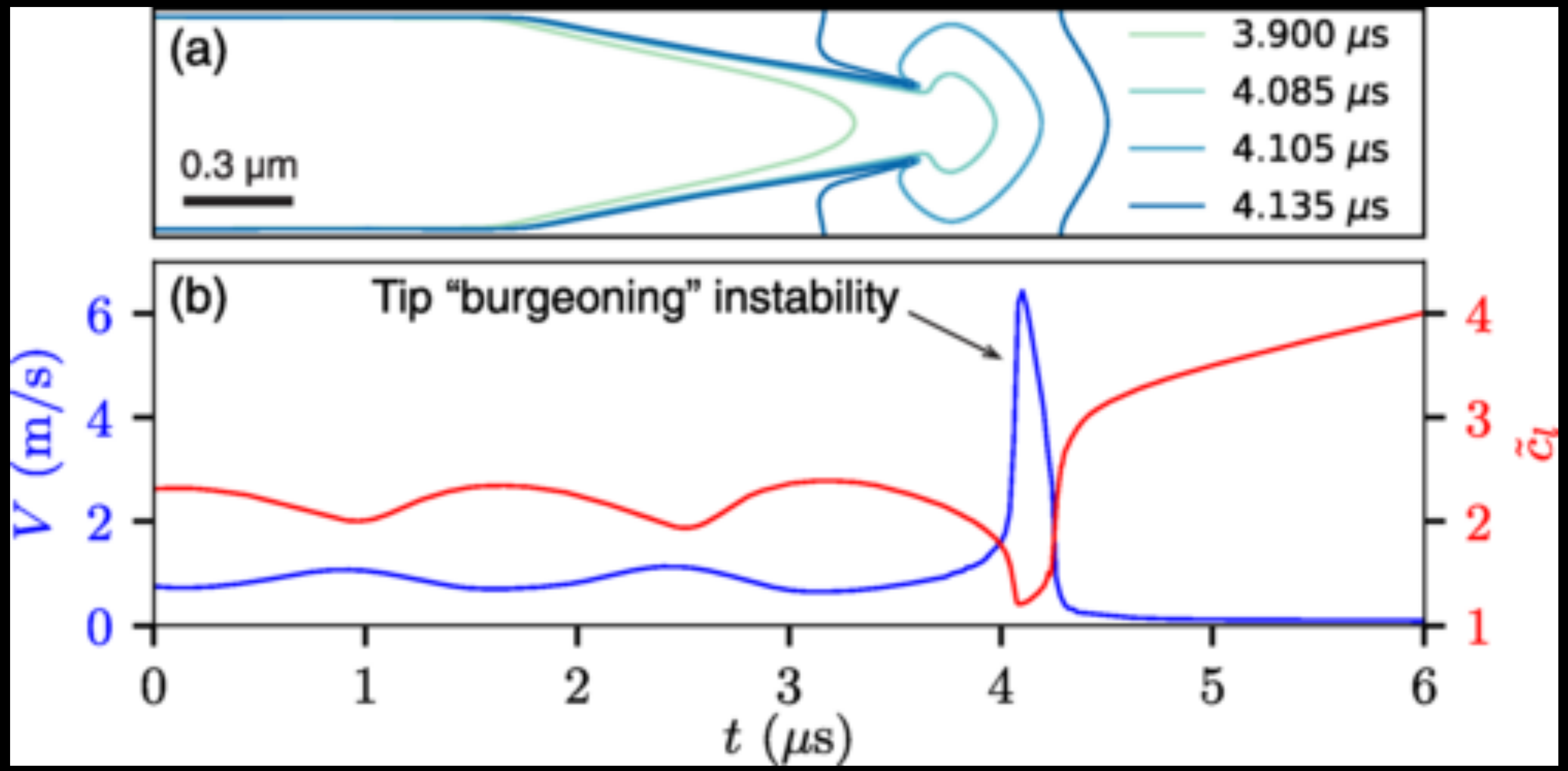
My real motivation is to be able to say I'm into cool bands



Banding: Experiment



Banding: Phase Field



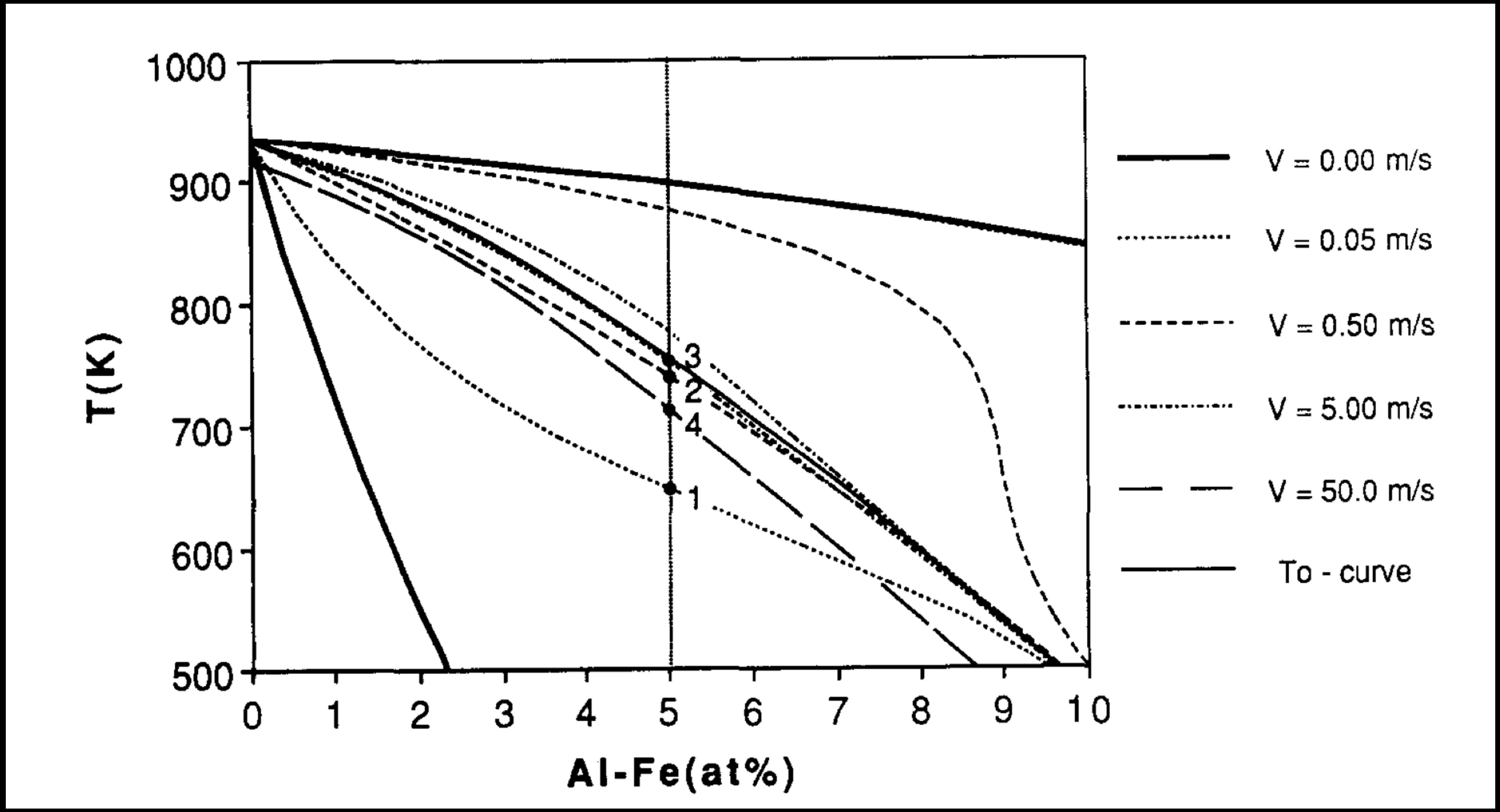
Banding: Burgeoning

Focus on the **precipitates** and the **burgeoning**.

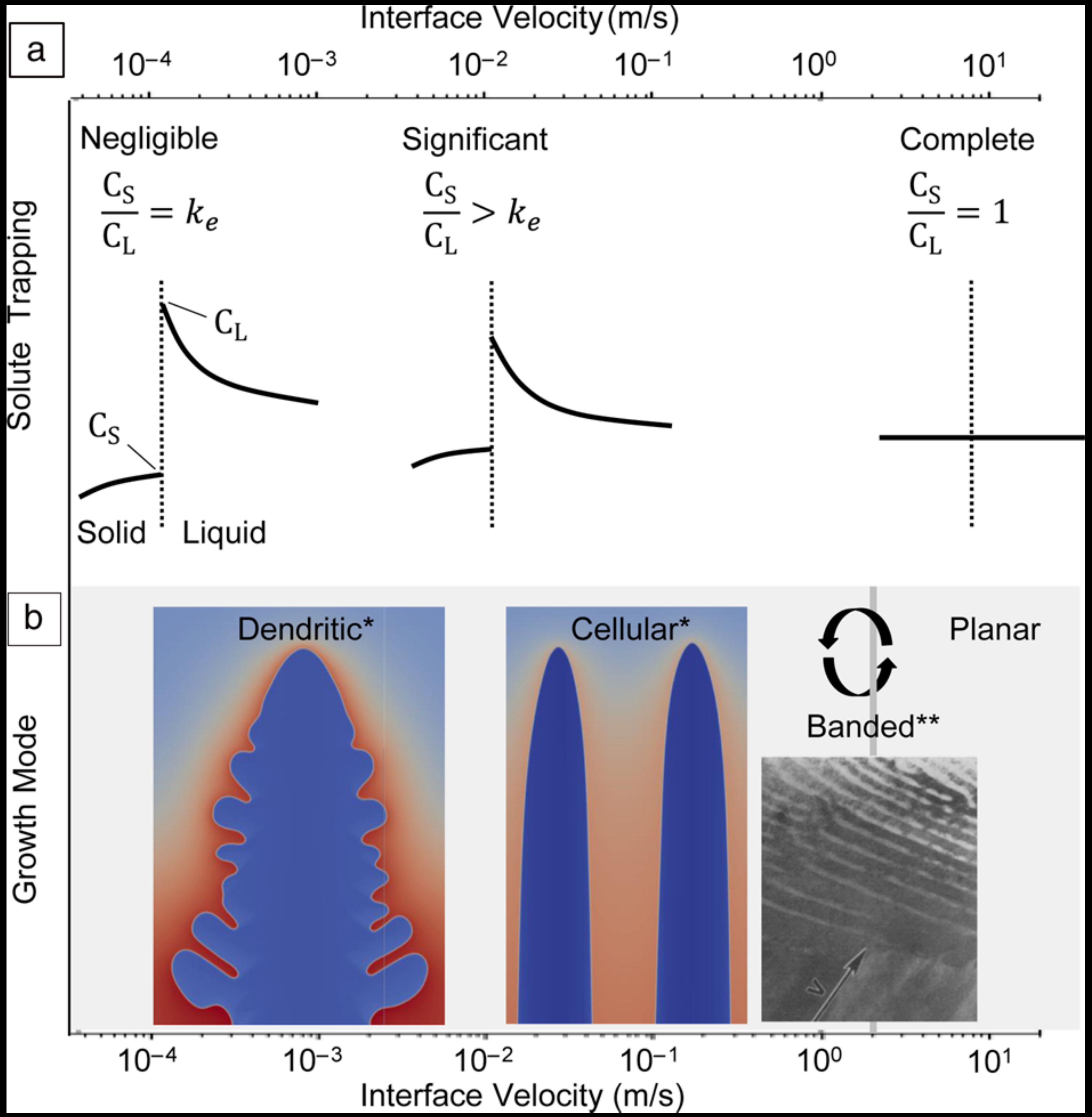
Ji, Kaihua, et al. "Microstructural Pattern Formation during Far-from-Equilibrium Alloy Solidification." Physical Review Letters, vol. 130, no. 2, Jan. 2023, p. 026203. DOI.org (Crossref), https://doi.org/10.1103/PhysRevLett.130.026203.

Interlude: Solute Trapping

How does it influences morphology?



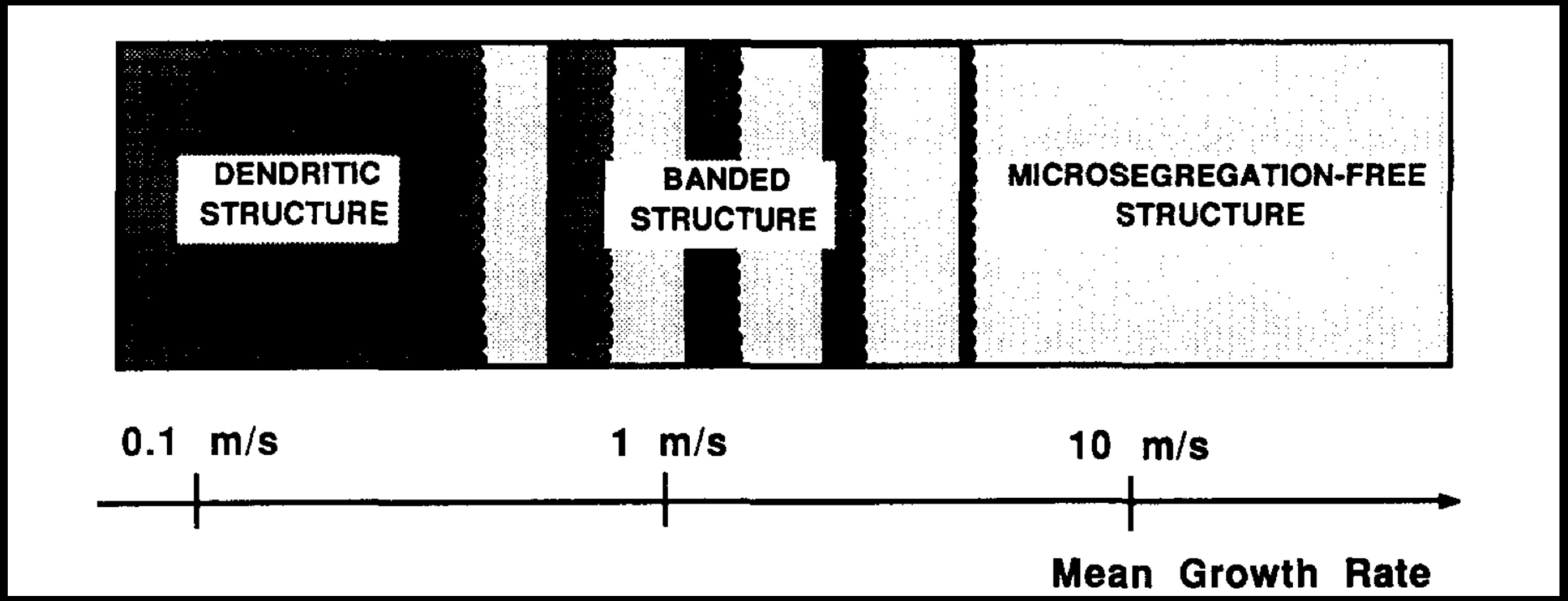
Carrard, M., et al. "About the Banded Structure in Rapidly Solidified Dendritic and Eutectic Alloys." Acta Metallurgica et Materialia, vol. 40, no. 5, May 1992, pp. 983–96. DOI.org (Crossref), https://doi.org/10.1016/0956-7151(92)90076-Q.



Pinomaa T, Laukkanen A, Provatas N. Solute trapping in rapid solidification. MRS Bulletin. 2020;45(11):910-915. doi:10.1557/mrs.2020.274

Paper 2: Atomistic Perspectives on Banding

Background: How/Why does Banding occur?



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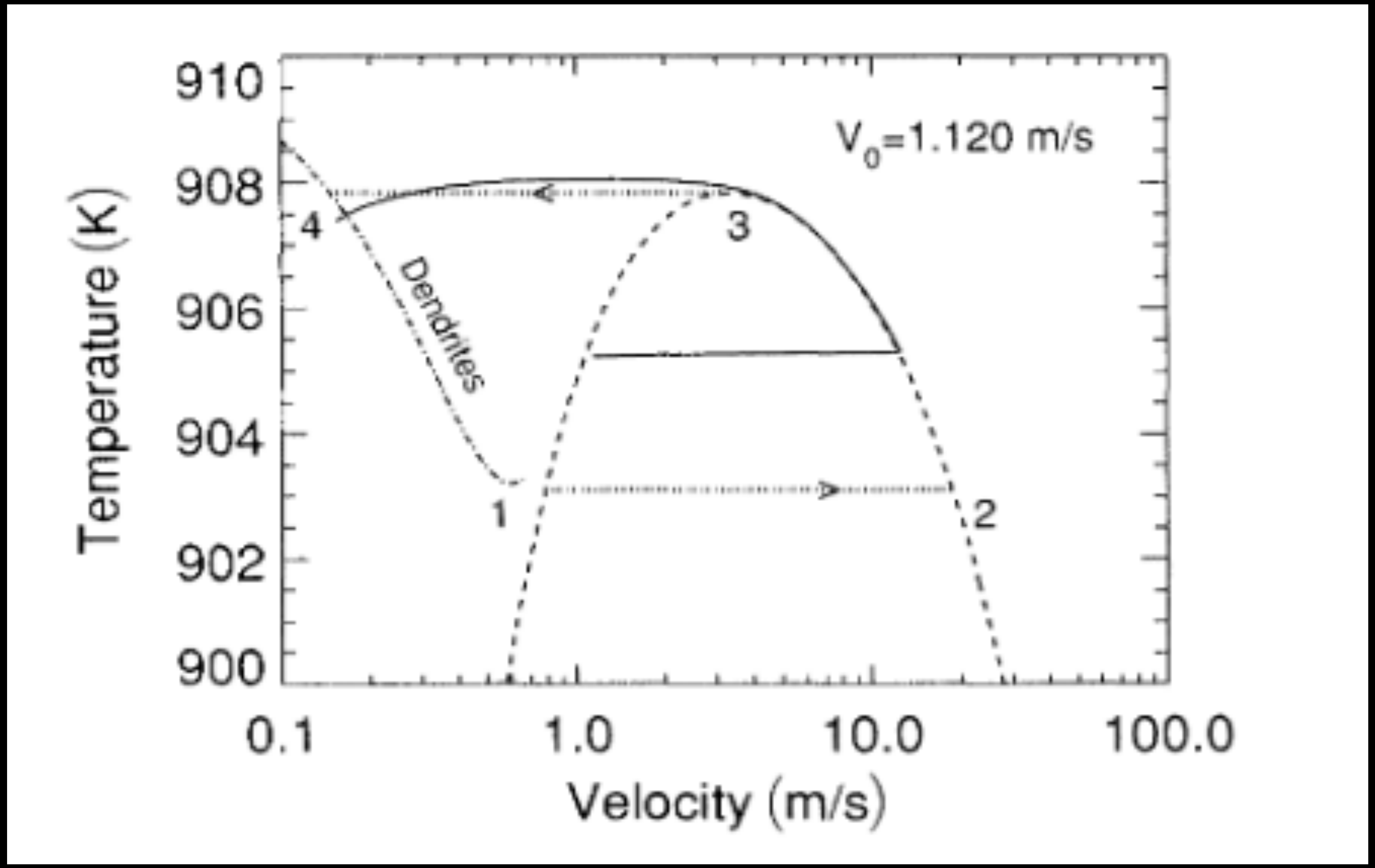

<u>Band spacing</u>

W/o latent heat:

$$\lambda \approx \frac{T_3 - T_2}{G}$$

W latent heat:

$$\lambda' \approx \sqrt{l_C l_T}$$

Competition between attachment kinetics and solute rejection

PFC already has both features!

Karma, Alain, and Armand Sarkissian. "Interface Dynamics and Banding in Rapid Solidification." Physical Review E, vol. 47, no. 1, Jan. 1993, pp. 513–33. DOI.org (Crossref), https://doi.org/10.1103/PhysRevE.47.513.

I don't yet have any data of my own to show here! We are currently conceptualizing the scope of this project.

Thank You!

2024	2025			2026		
Fall	Winter	Summer	Fall	Winter	Summer	Fall
Prelim Exam						Hopefully have a thesis to defend
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.		
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					

Stress Tensor in PFC

$$\frac{\sigma_{ij}}{k_B T \rho_0} = \left\{ -\frac{1}{2} n(C_2 \circledast n) + \frac{p_2 - A_0}{2} n^2 + \frac{p_3}{3} n^3 + \frac{p_4}{4} n^4 \right\} \delta_{ij} + \left\{ A_4 \left[(\nabla^2 n)(\partial_{ij} n) - (\partial_i (\nabla^2 n))(\partial_j n) \right] - A_2 \right\}$$

$$A_0 = -B_x^0 e^{-\frac{1}{2\sigma_0^2}} - \frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{8\sigma_0^4} + \frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{8\sigma_0^2} + B_x^1 e^{-\frac{T}{T_r}} - \frac{B_x^1 e^{-\frac{T}{T_r}}}{8\sigma_1^2}$$

$$A_2 = \frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{4\sigma_0^4} - \frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{4\sigma_0^2} + \frac{B_x^1 e^{-\frac{T}{T_r}}}{4\sigma_1^2}$$

$$A_4 = \frac{1}{2} \left\{ -\frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{4\sigma_0^4} + \frac{B_x^0 e^{-\frac{1}{2\sigma_0^2}}}{4\sigma_0^2} - \frac{B_x^1 e^{-\frac{T}{T_r}}}{4\sigma_1^2} \right\}$$

Obtained from curve-fitting $C_2(k)$ to $A_0 + A_2 k^2 + A_4 k^4$