Title: Kinetics of Microstructural Transitions in Block Copolymer Melts

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Abstract: Soft materials are dynamical by nature and the study of the dynamics of soft materials is an exciting, rich area of current interest. During macromolecular self-assembly, as occurs in block copolymers, long structural relaxation timescales due to collective molecular motion are often seen. How microstructure influences the dynamics, the existence and lifetime of metastable states, and the dynamics of long-lived non-equilibrium structures are all poorly-understood issues. I will discuss our dynamical simulations that address these questions in the context of the nucleation of one microstructured phase out of another in a block copolymer melt.

Kinetics of Microstructural Transitions in Block Copolymers

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Perimeter Institute
April 22, 2010

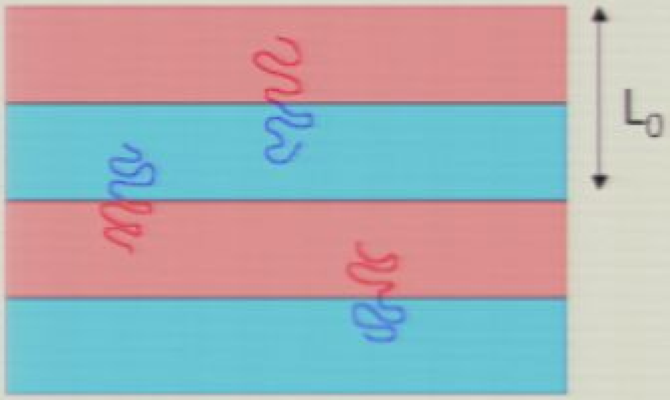
Formation of Microstructures

Competition between entropy (coil) and block repulsion (stretch)

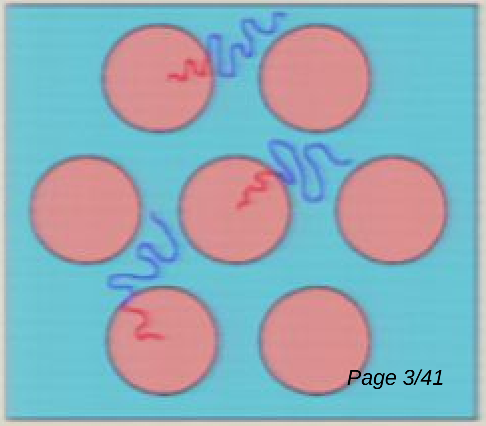
$R_G \sim N^{1/2}$ $\quad T \downarrow \ (\chi \uparrow) \quad$ $d \sim \chi^{1/6} N^{2/3}$

Leads to microphase separation of diblock copolymers

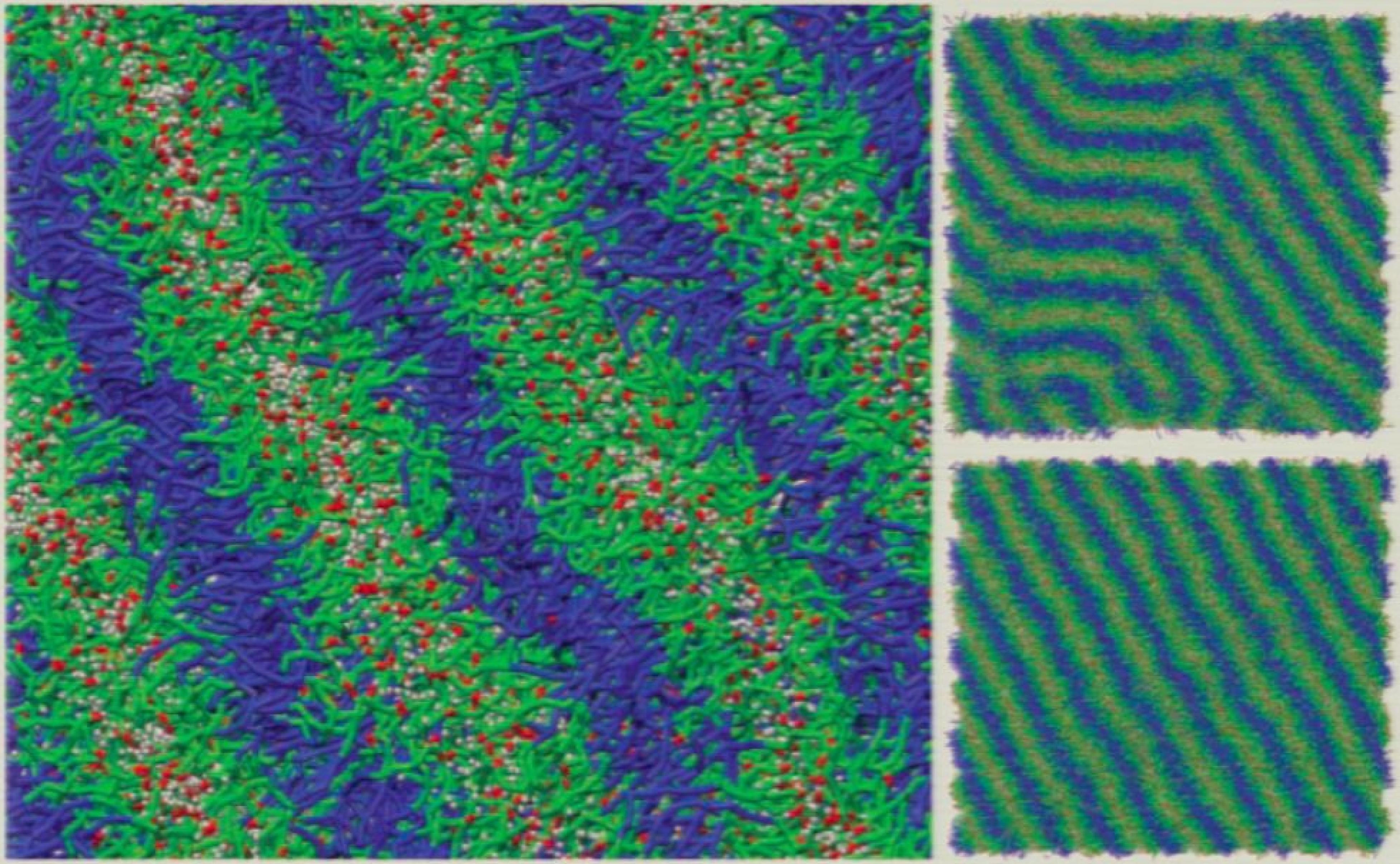
$f_A = 1/2:$



$f_A < 1/2:$



From M. Klein and W. Shinoda, Science (2008)



Molecular dynamics simulation of an aqueous surfactant solution

Bulk diblock copolymer melt phase diagram

Self-consistent mean-field theory (SCMFT) - Matsen and Schick (1994):

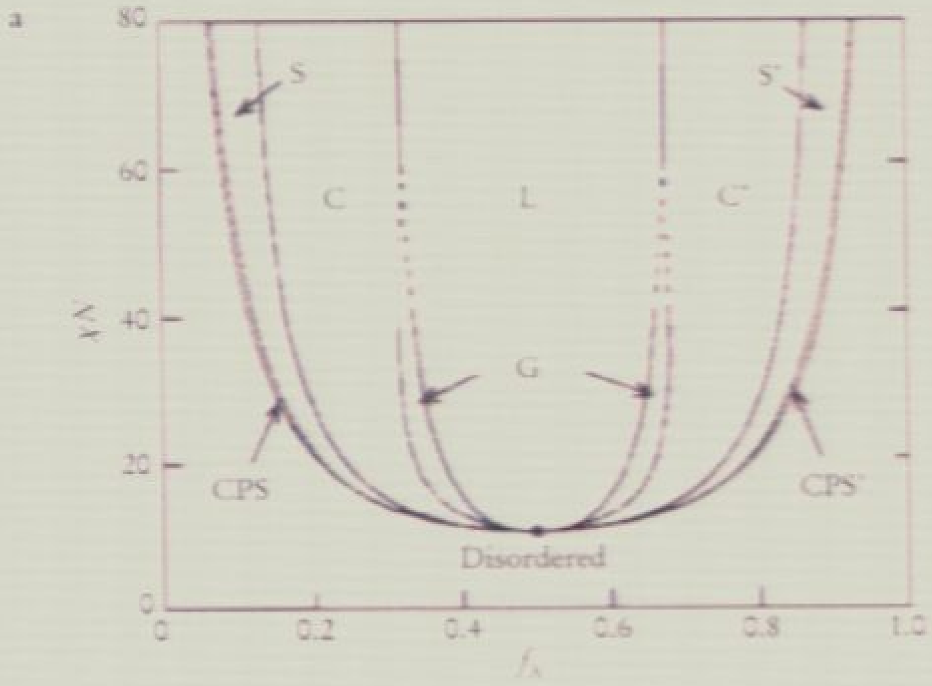
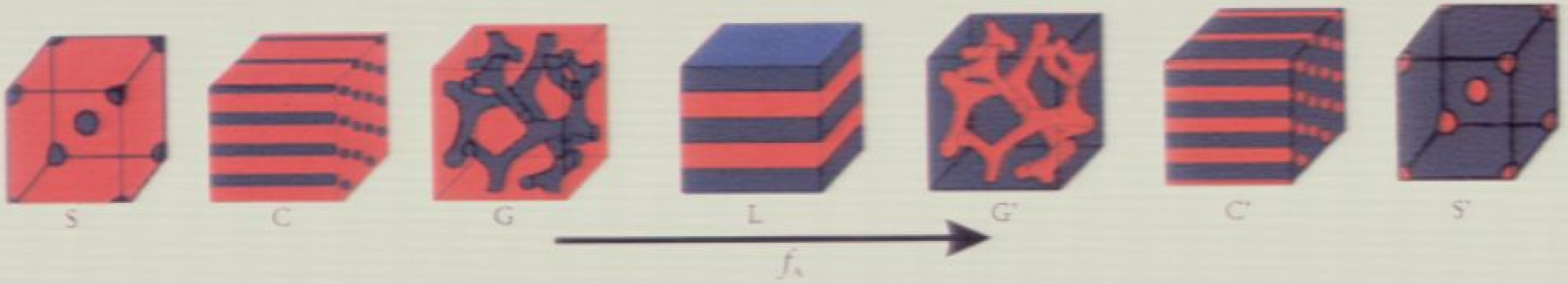
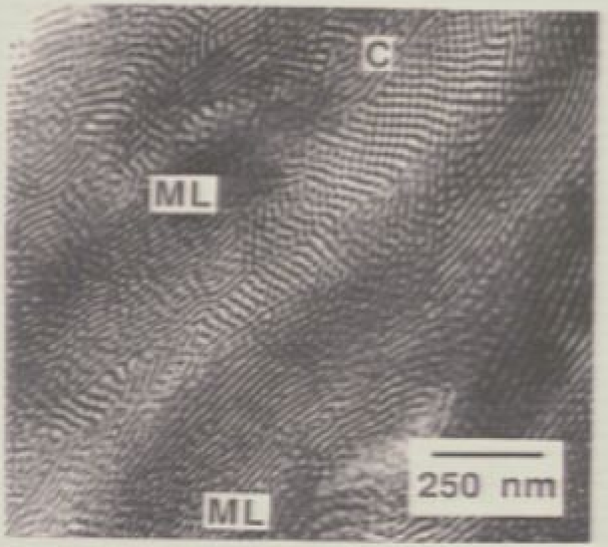


Diagram:
Fredrickson and
Bates (1999)

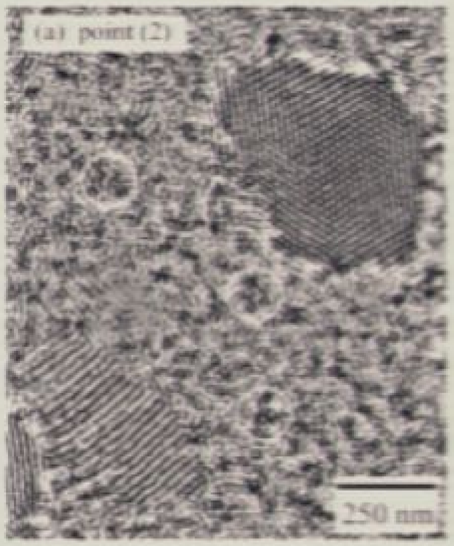


Applications: nanolithographic templates, high-density memory...

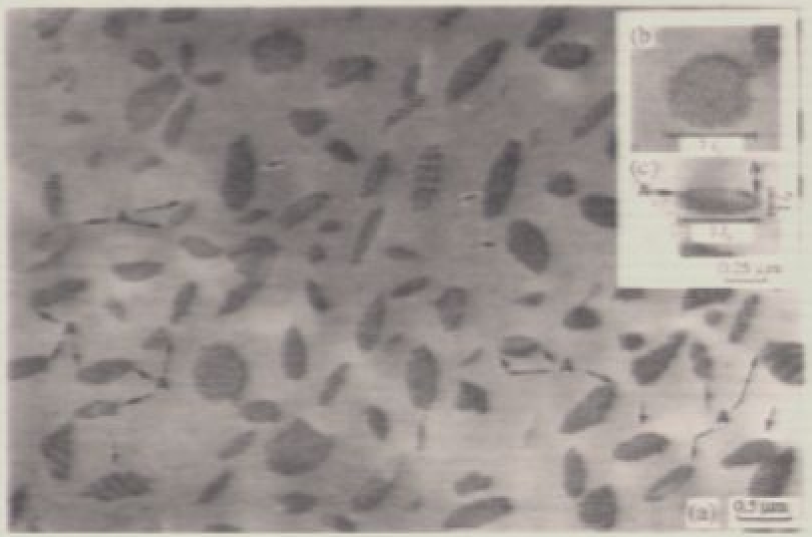
Reality is more complicated…



Hajduk et al. (1994)

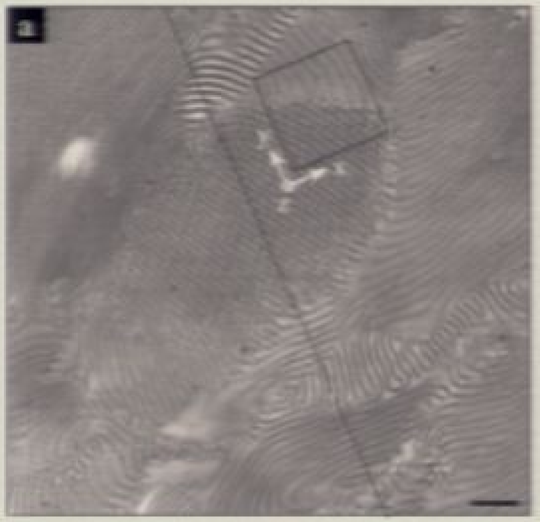


Sota et al. (2003)



Koizumi et al. (1994)

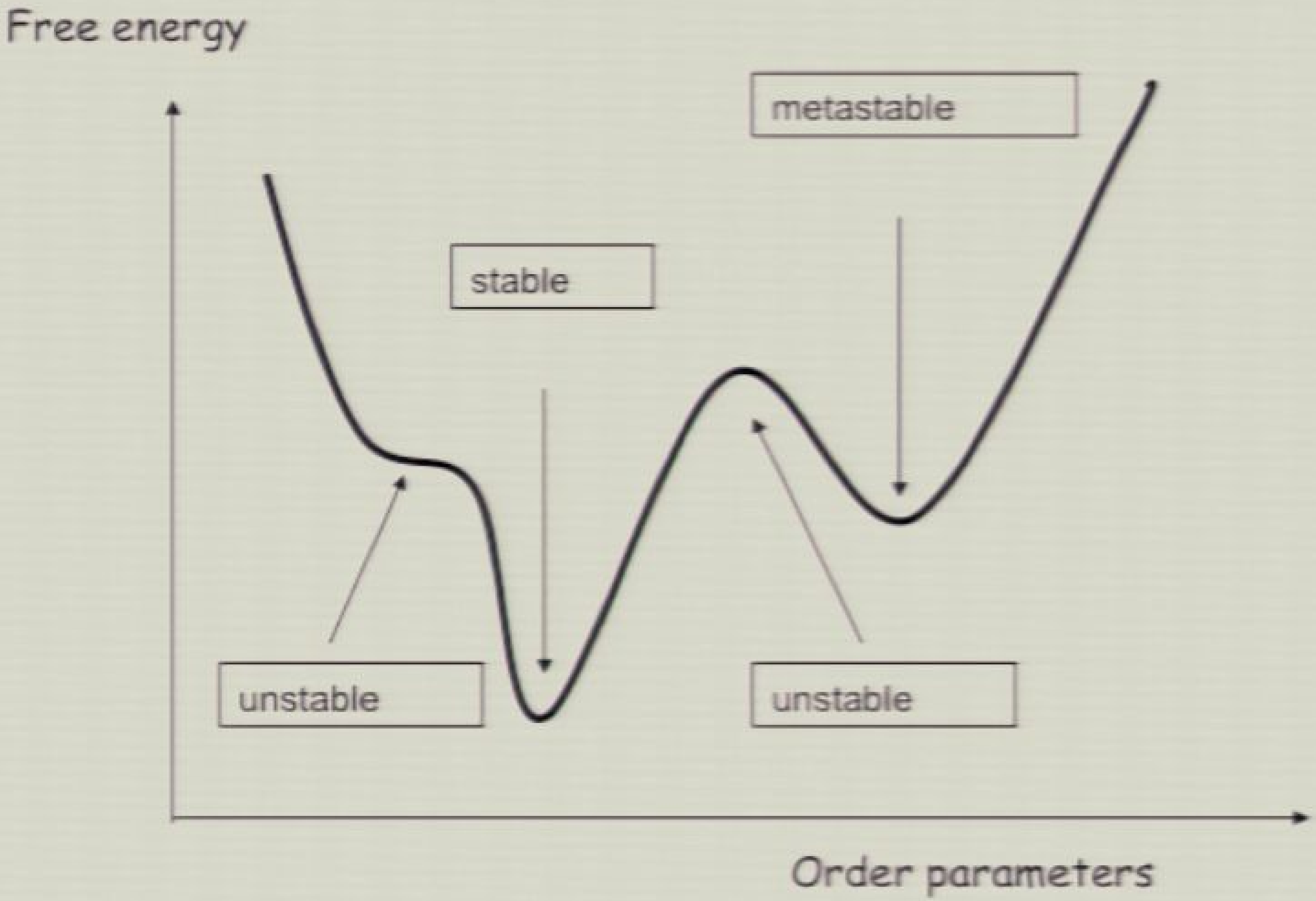
Chastek and
Lodge (2006)



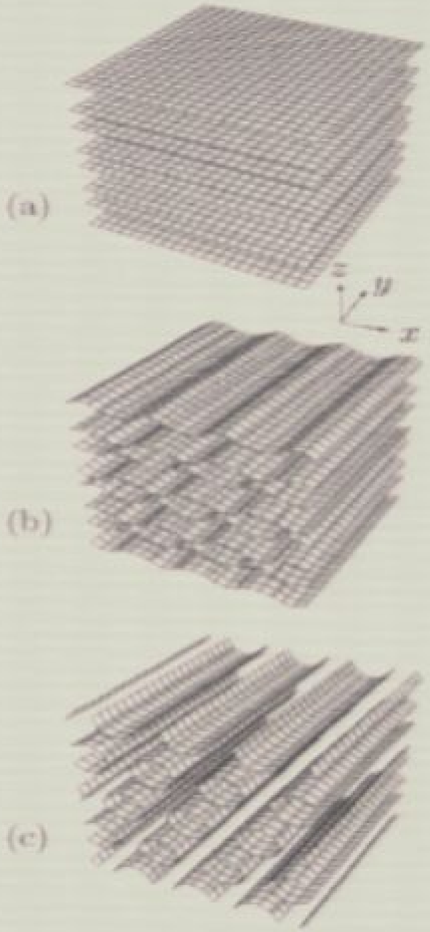
Mareau et al. (2007)

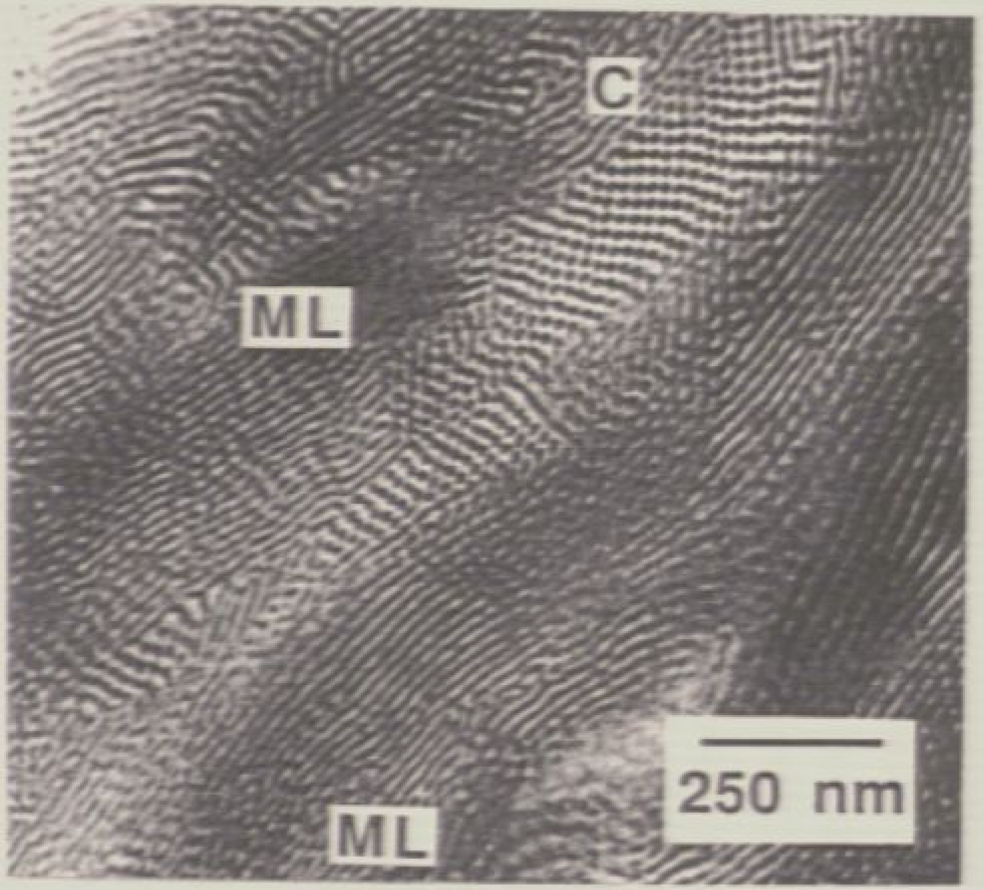
Need to understand these out-of-equilibrium structures, and their dynamics

Free-energy landscape



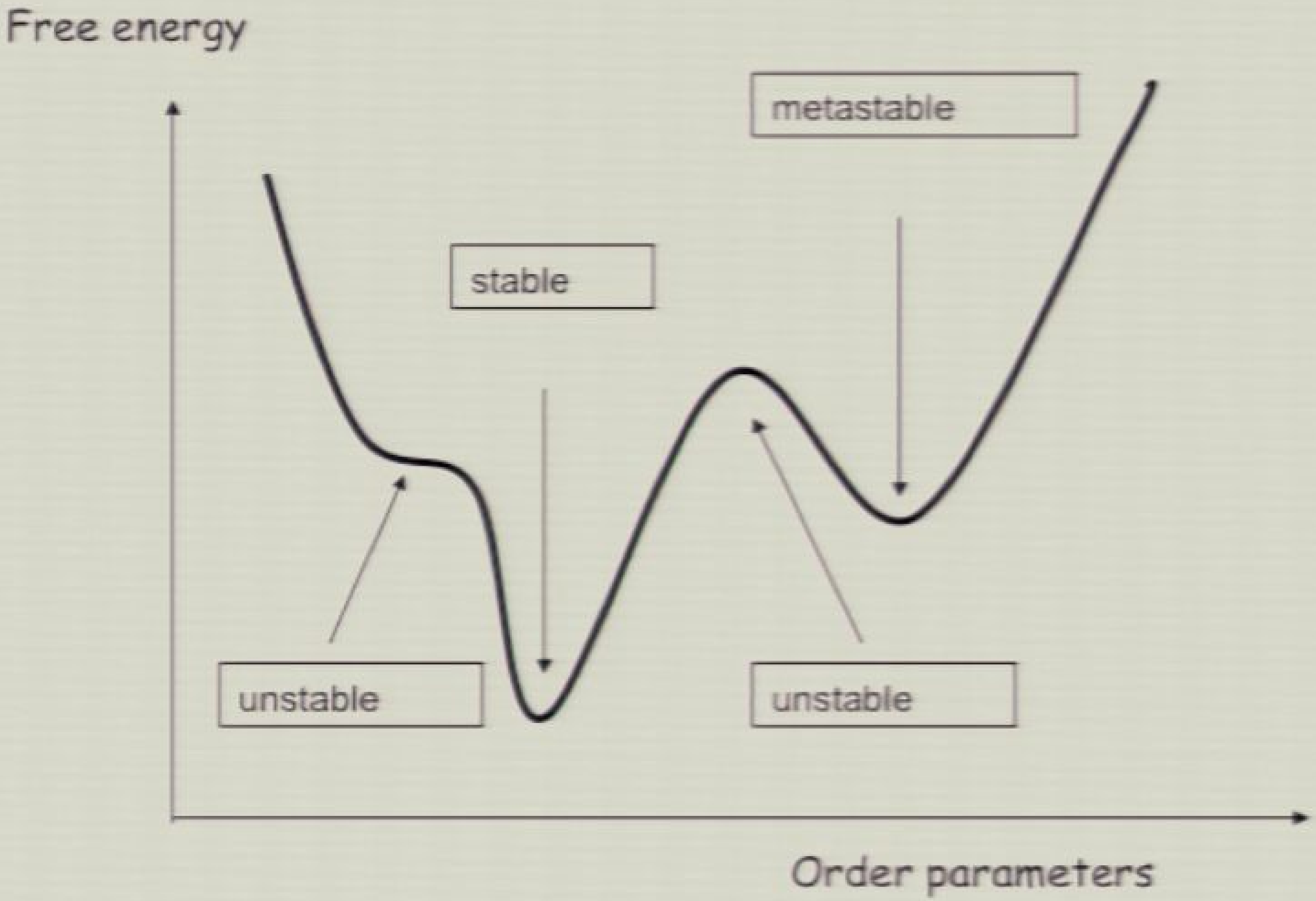
Spinodal decomposition of unstable phase





Stability theory for anisotropic phases: Shi et al. (1996)

Free-energy landscape



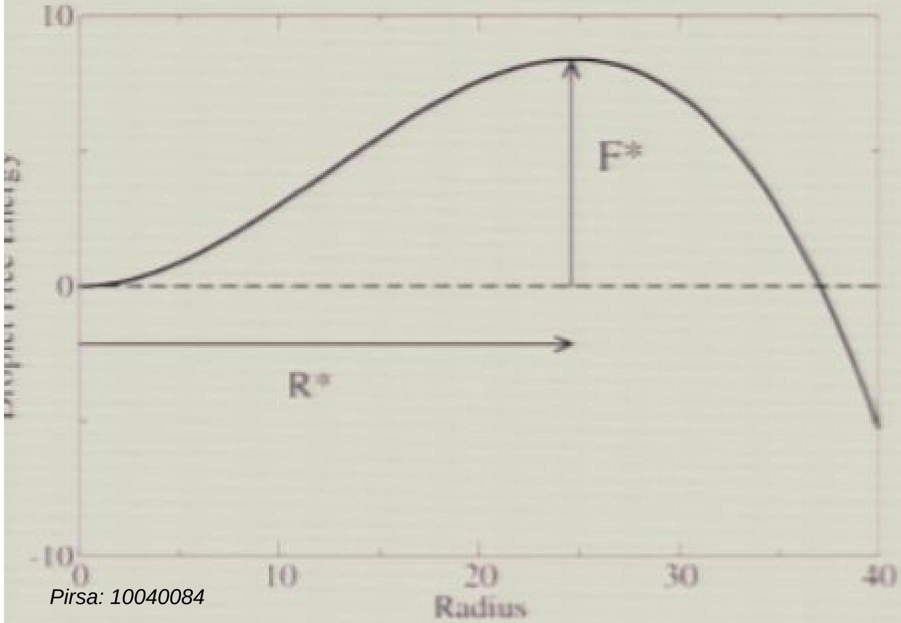
Classical Theory of Droplet Nucleation (CNT)

e.g. nucleation of liquid droplet from supersaturated vapour

$$F(r) = \frac{4}{3}\pi R^3 \times \Delta f + 4\pi R^2 \times \sigma$$

$\Delta f = f_{\mathrm{liquid}} - f_{\mathrm{vapour}} < 0$

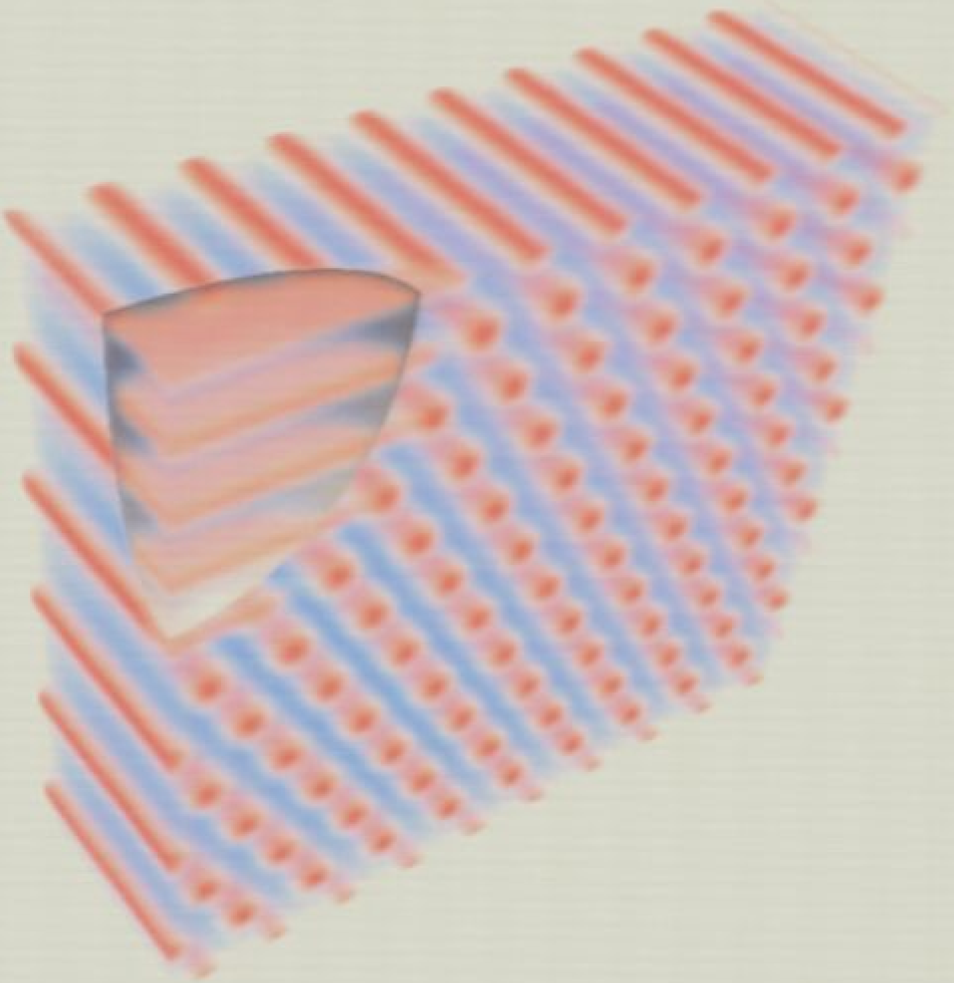
σ = liquid/vapour interfacial tension



$R^* \sim \sigma / |\Delta f|$

Nucleation rate ~ exp(-F*/kT)

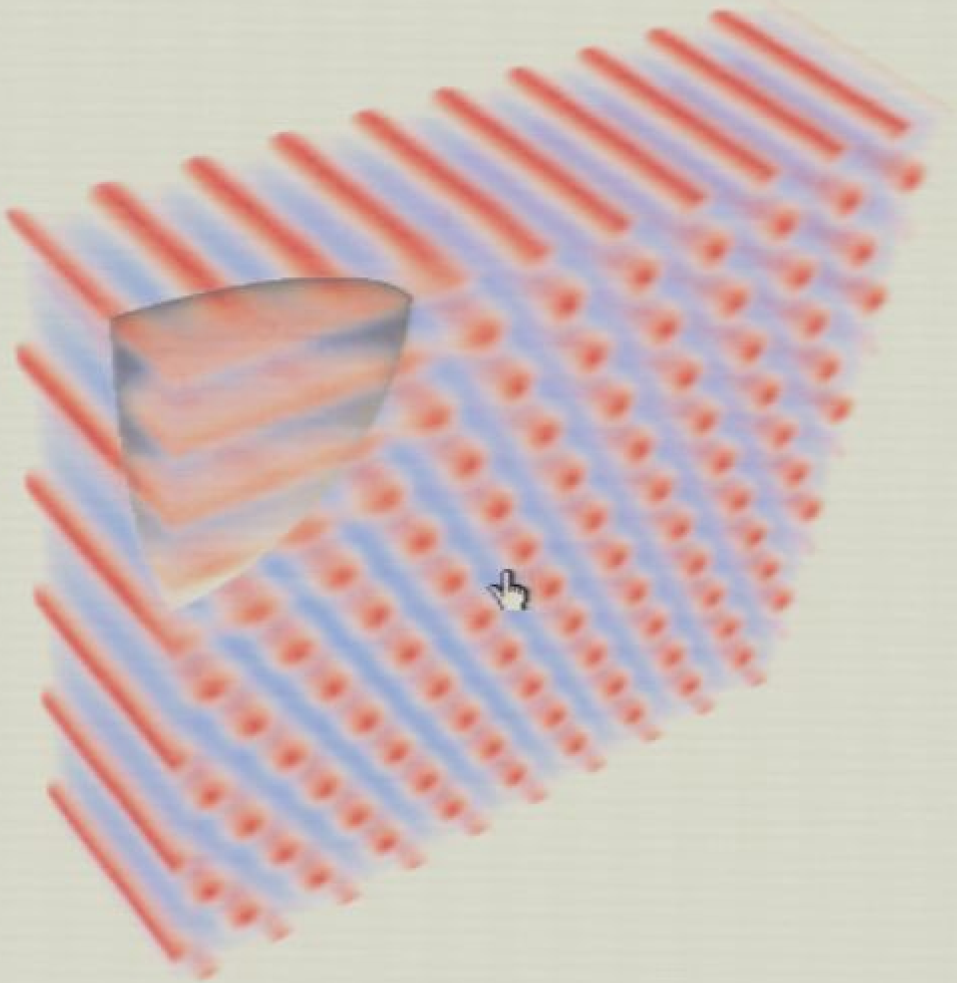
Nucleation and growth from a metastable phase



- Inhomogeneous problem (droplet)
- Multiple length-scales
- Microstructure:
  - structure of interface?
  - anisotropic surface free-energy
  - non-spherical nucleus

Studying nucleation and growth when microstructure is present is challenging

Nucleation and growth from a metastable phase



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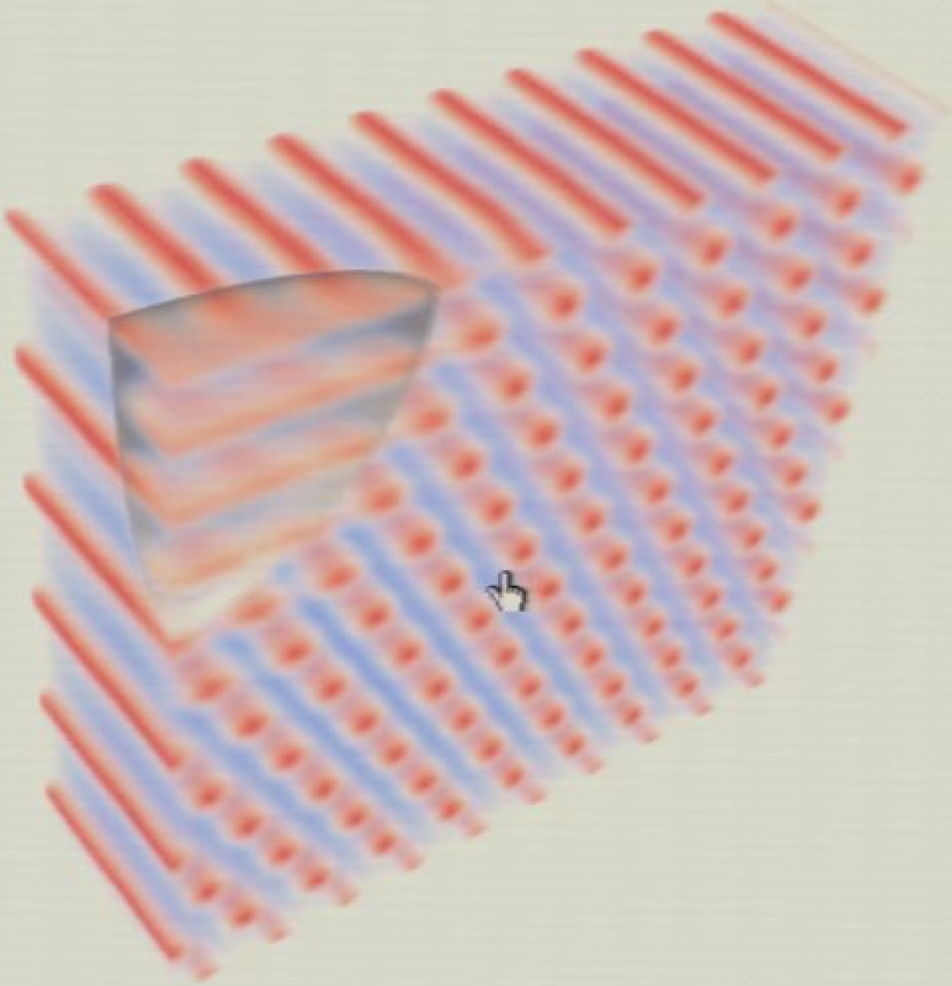

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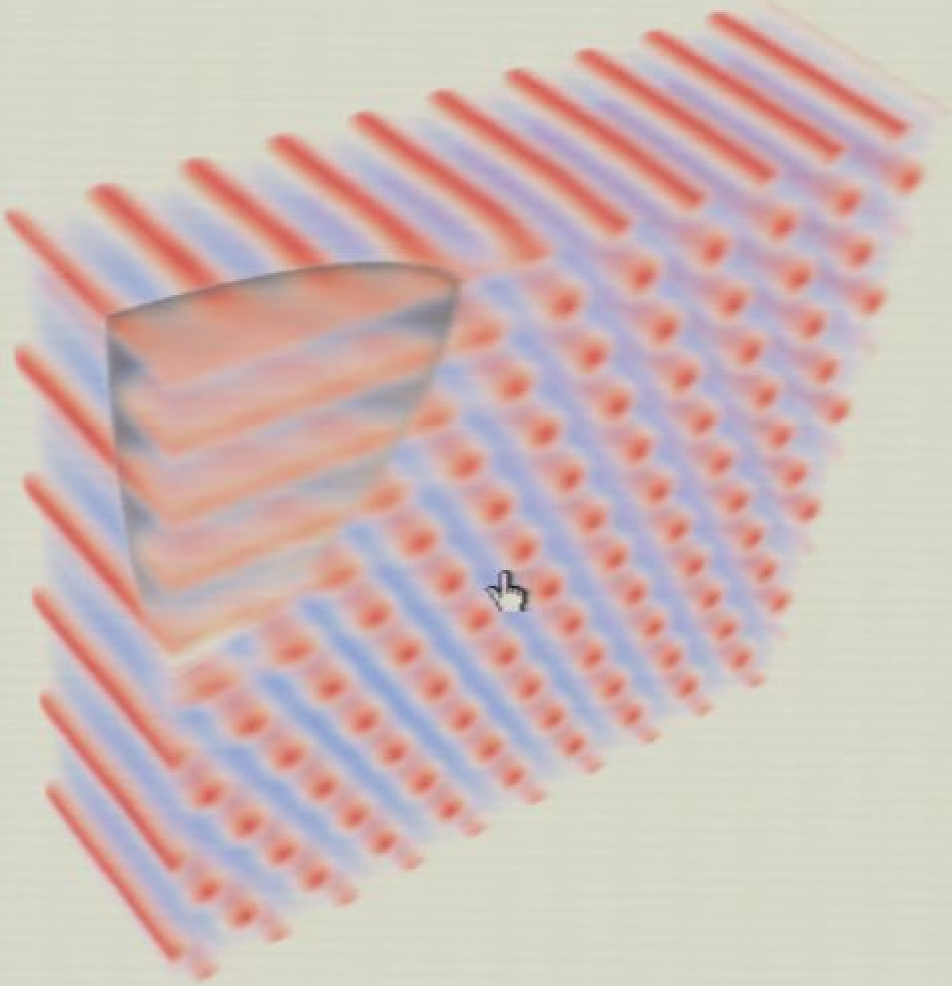

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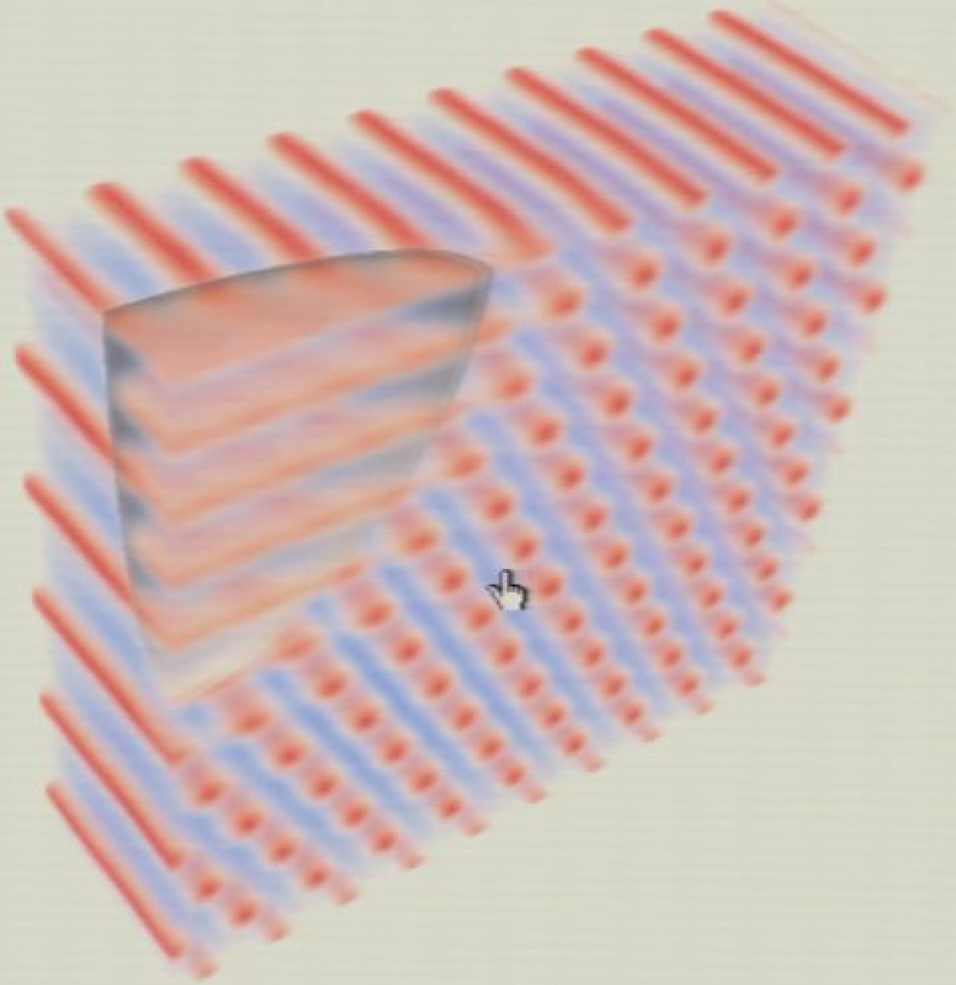

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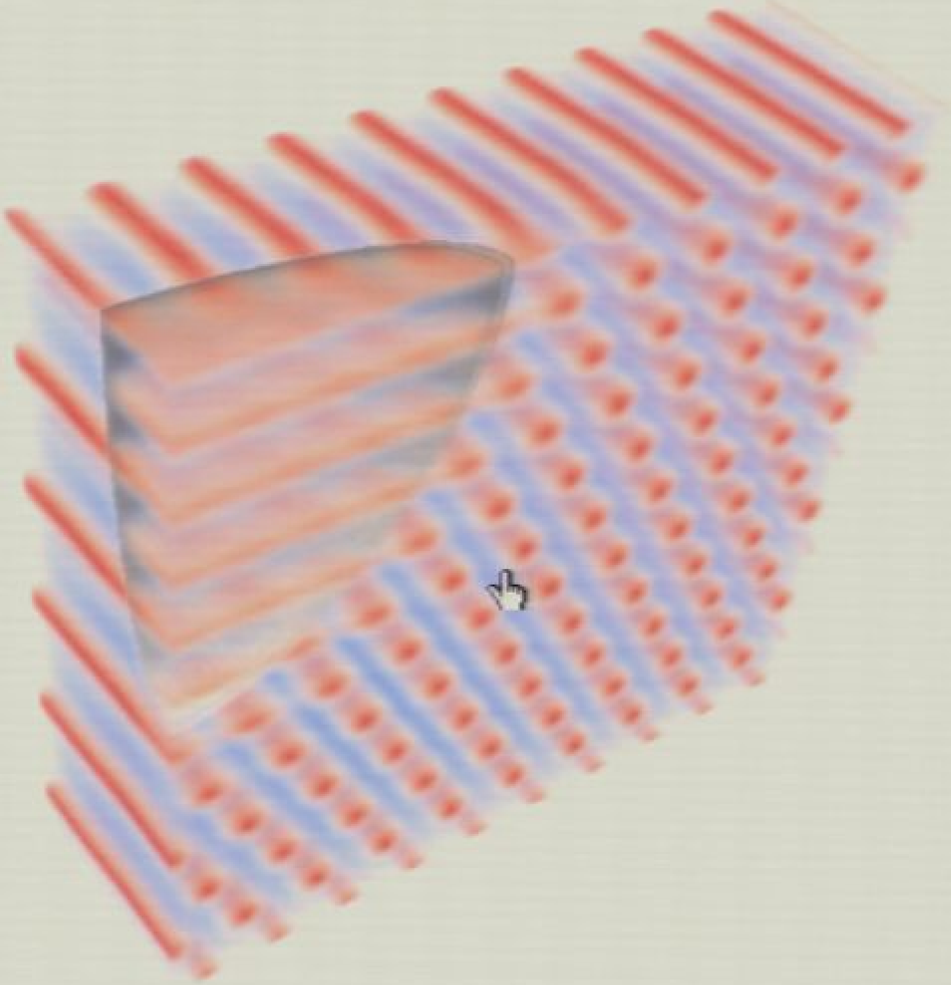

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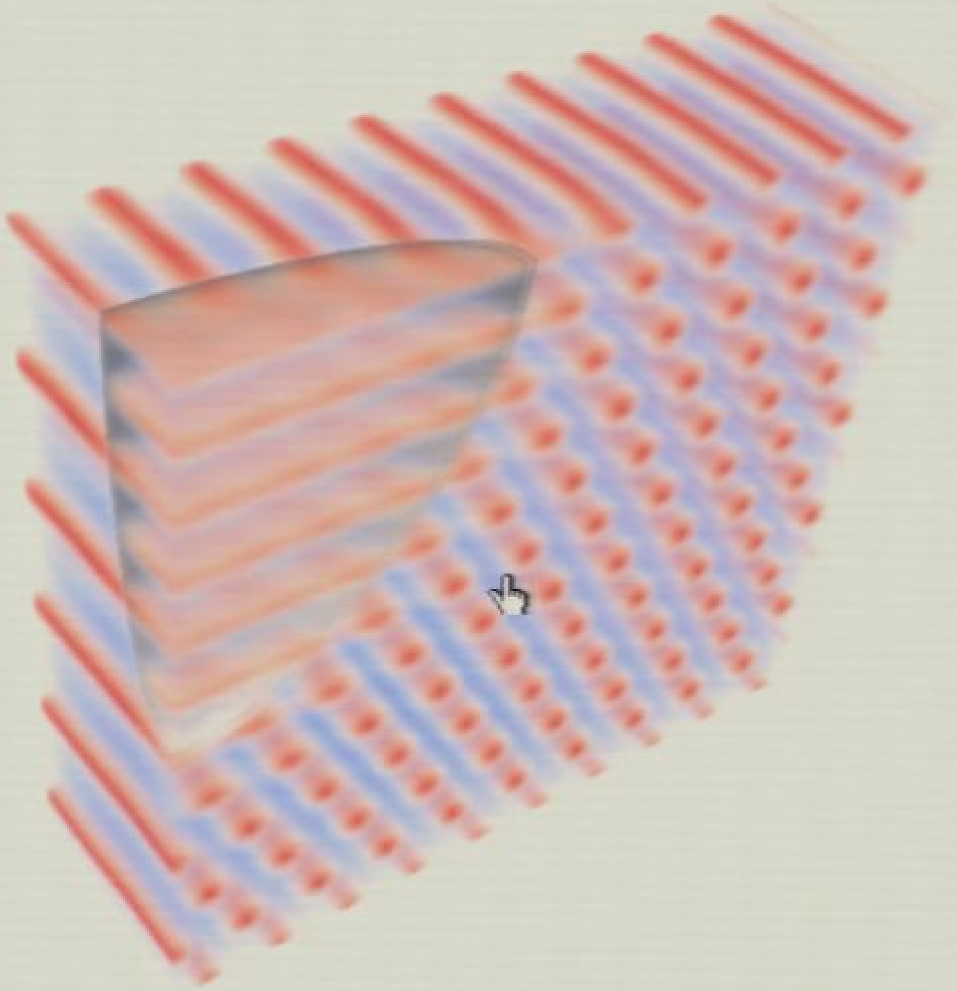

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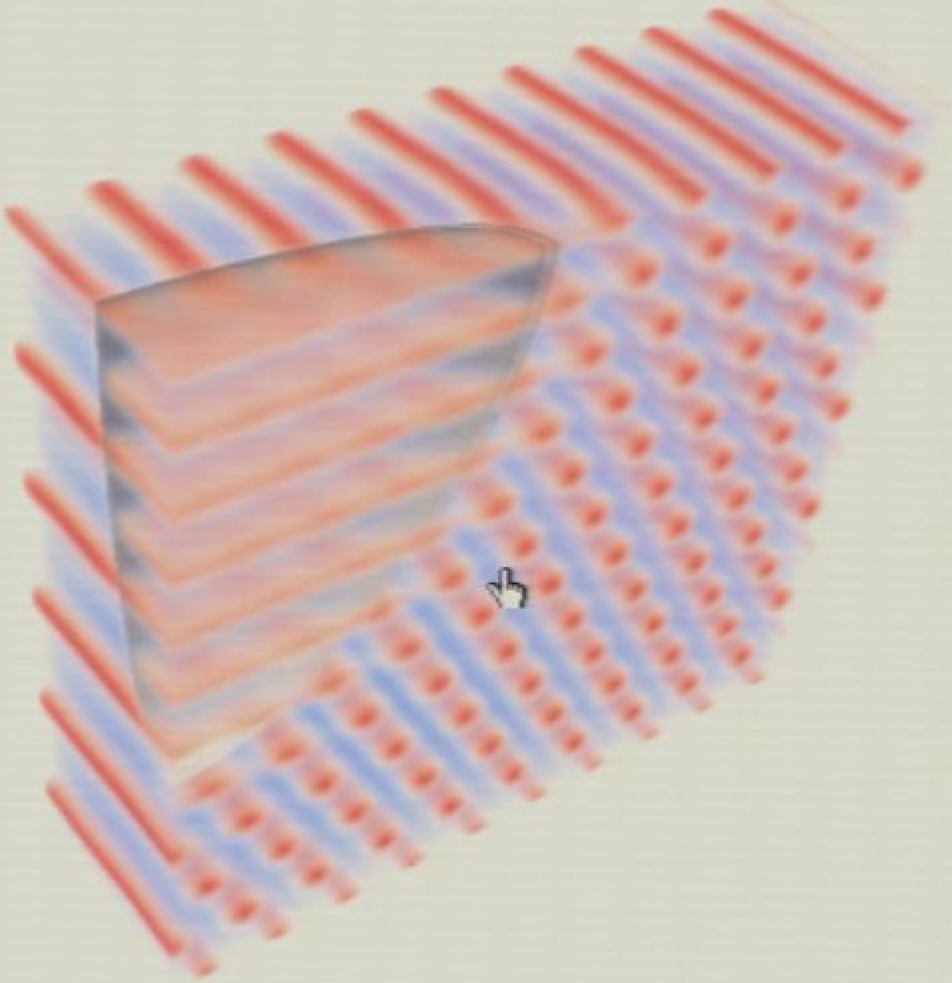

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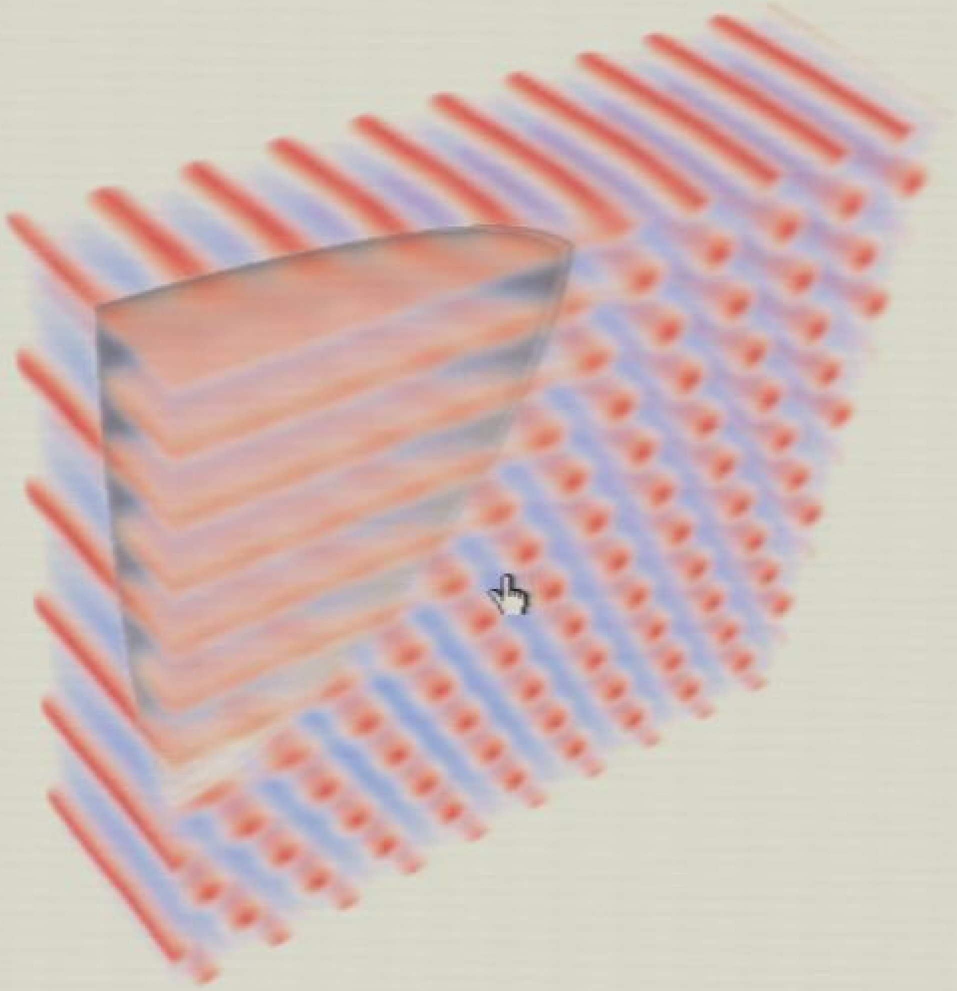

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Theoretical approach to incorporate anisotropy in surface free-energy

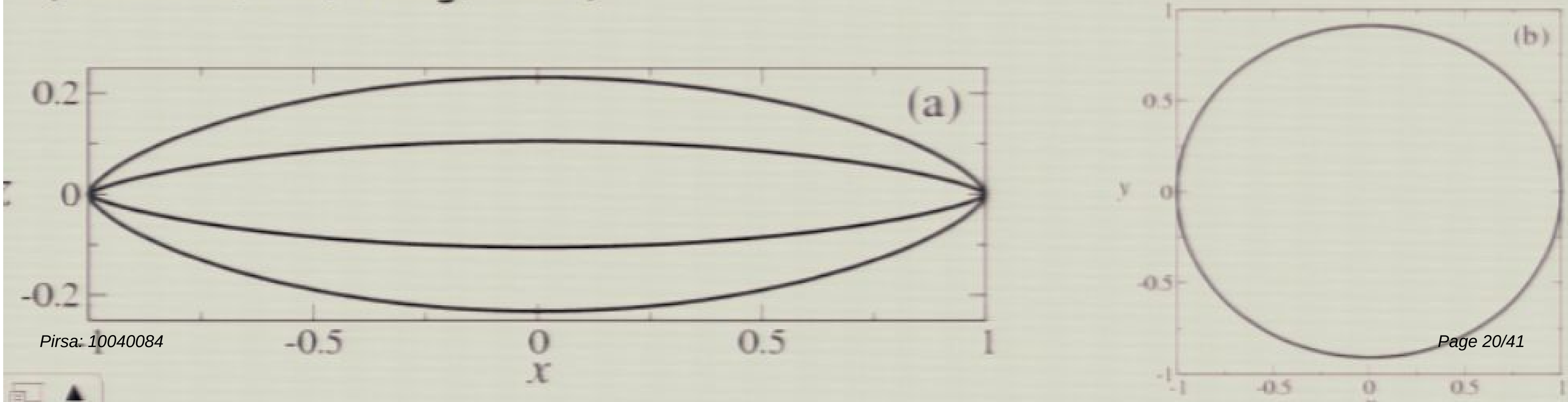
Wickham, Shi and Wang (2003)

Landau-Brazovskii free-energy in terms of order parameter $\phi(\vec{r}) = \rho_A(\vec{r}) - \langle \rho_A \rangle$:

$$F = \int d^3 r \left\{ \frac{\xi^2}{2} [(\nabla^2 + q_0^2)\phi]^2 + \frac{\tau}{2}\phi^2 - \frac{\gamma}{3}\phi^3 + \frac{1}{4}\phi^4 \right\}$$

Exhibits all equilibrium phases for diblock copolymers

Basis of classical nucleation theory for anisotropic droplets
(Wickham, Shi, Wang, 2003)



Time-dependent Landau-Brazovskii model

Spencer, Wickham (2010)

$$F = \int d^3 r \left\{ \frac{\xi^2}{2} [(\nabla^2 + q_0^2)\phi]^2 + \frac{\tau}{2}\phi^2 - \frac{\gamma}{3}\phi^3 + \frac{1}{4}\phi^4 \right\}$$

Add dynamics:

$$\frac{\partial \phi}{\partial t} = \Gamma \nabla^2 \frac{\delta F}{\delta \phi}$$

(conserved order-parameter, model B dynamics)

$$\frac{\partial \phi}{\partial t} = \Gamma \nabla^2 \left[\xi^2 (\nabla^2 + q_0^2)^2 \phi + \tau\phi - \gamma\phi^2 + \phi^3 \right]$$

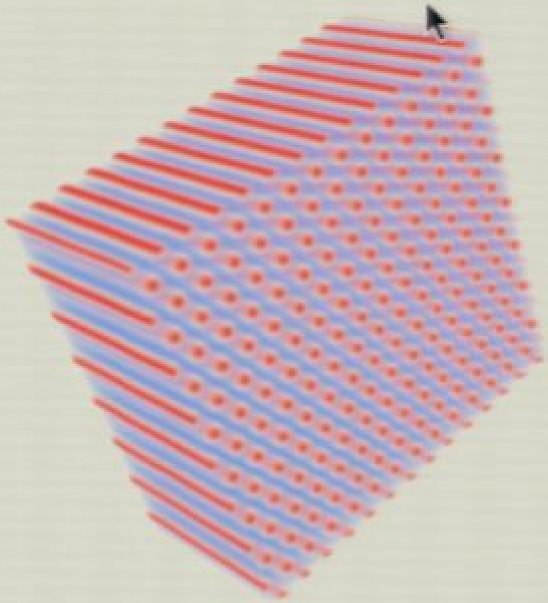
Note that there is no noise term in the model

Numerical Implementation

- Finite difference scheme on cubic lattice
- Largest run: 512x580x200 on 64 core (using MPI) for 1 week (1 million time steps)

Initial state:

Single nucleus of stable lamellar phase in background of metastable cylindrical phase



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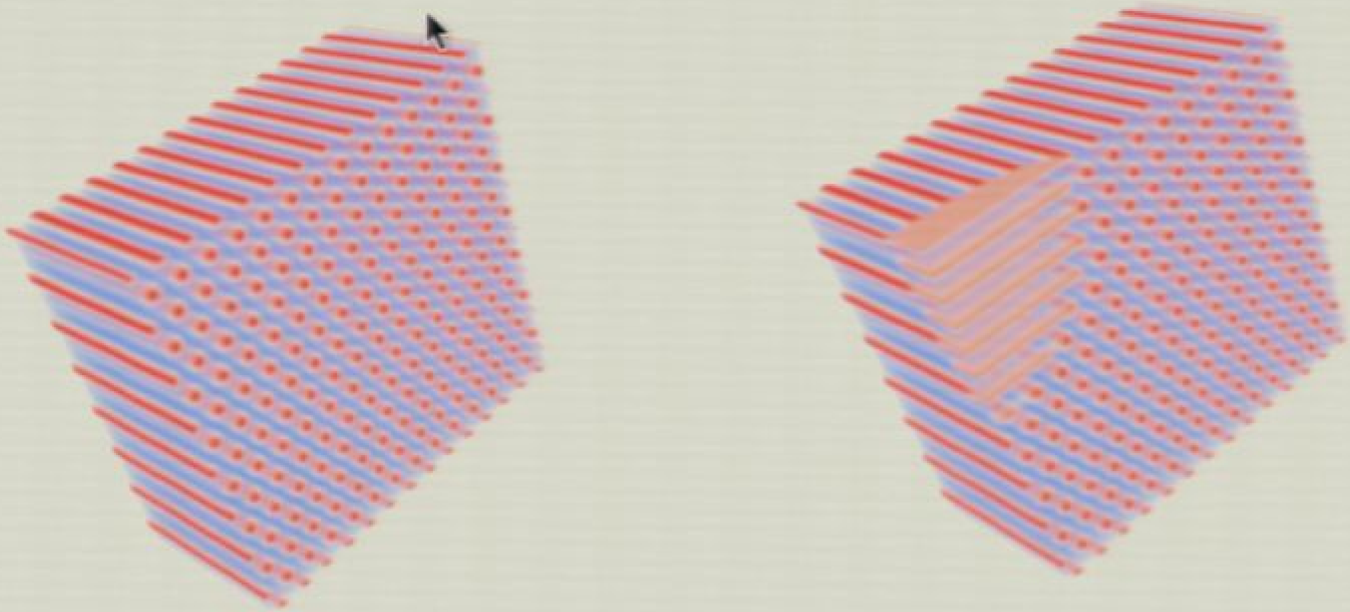
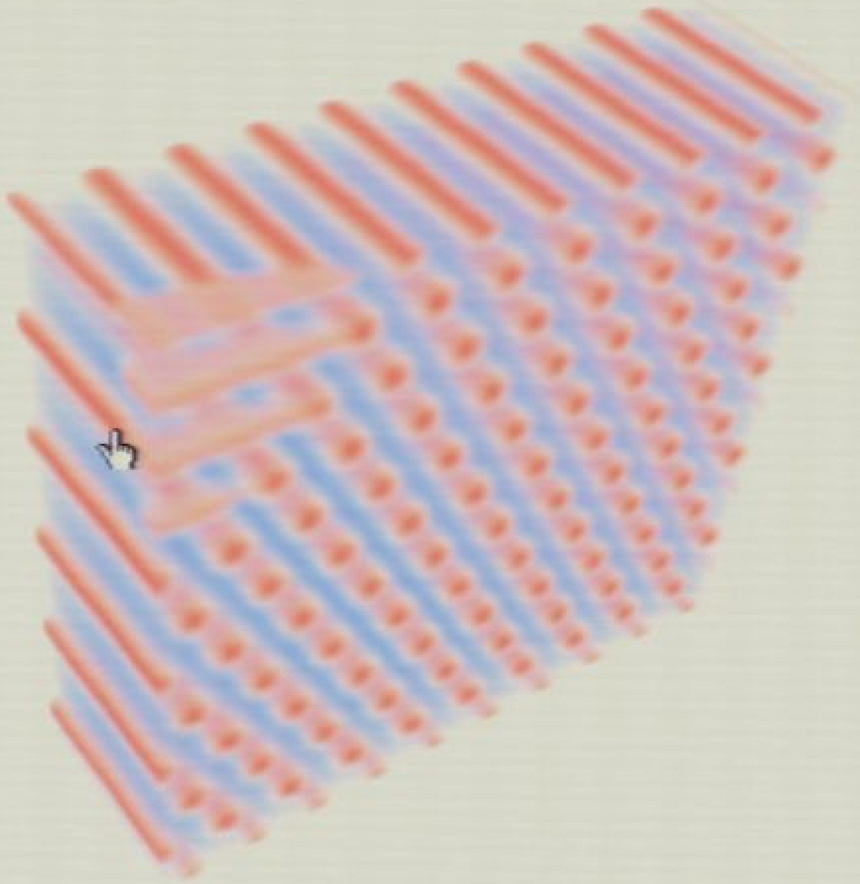


Identifying the critical nucleus size

Fix undercooling: $\tau_{coexist} - \tau = 0.0026$



Nuclei with an initial size below a certain threshold will shrink

Identifying the critical nucleus size

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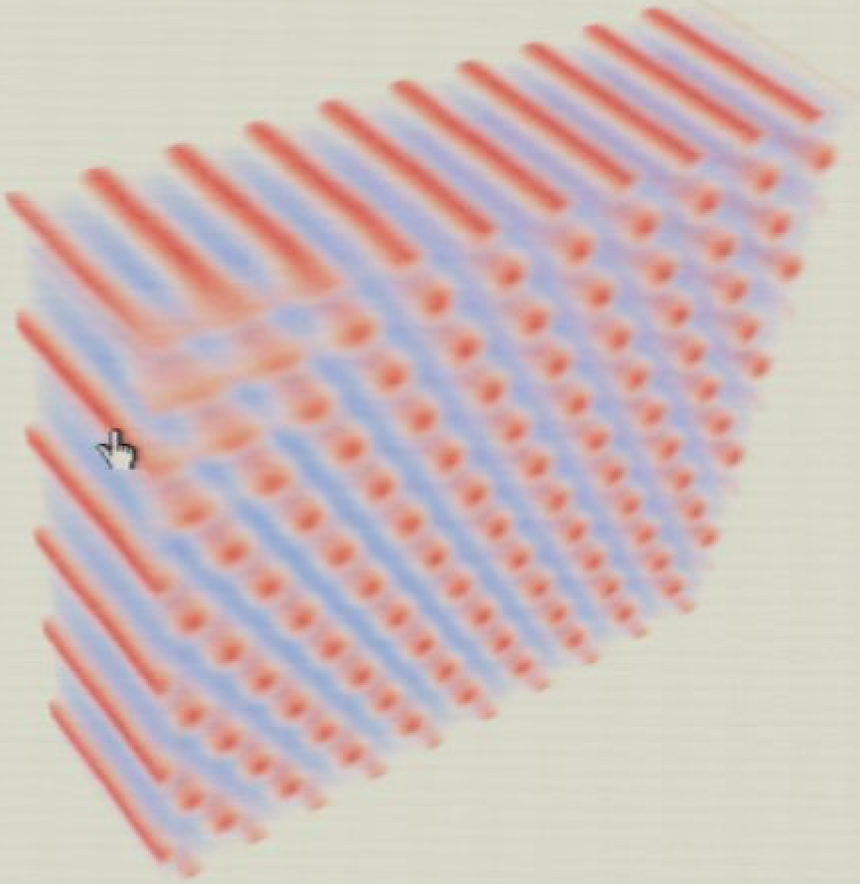

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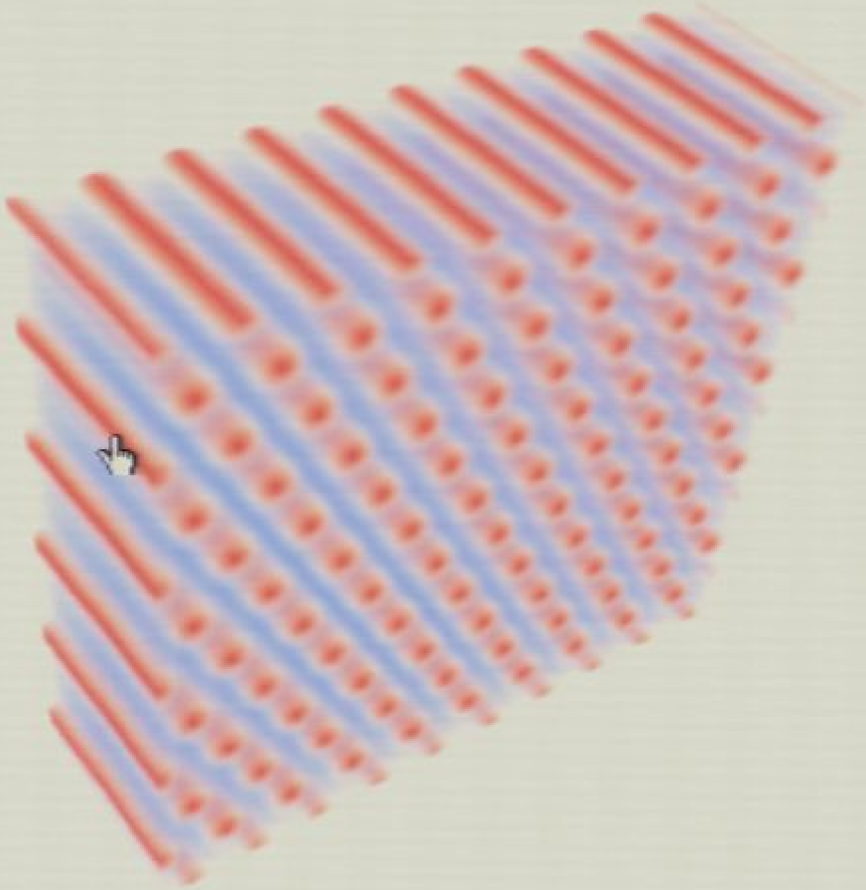

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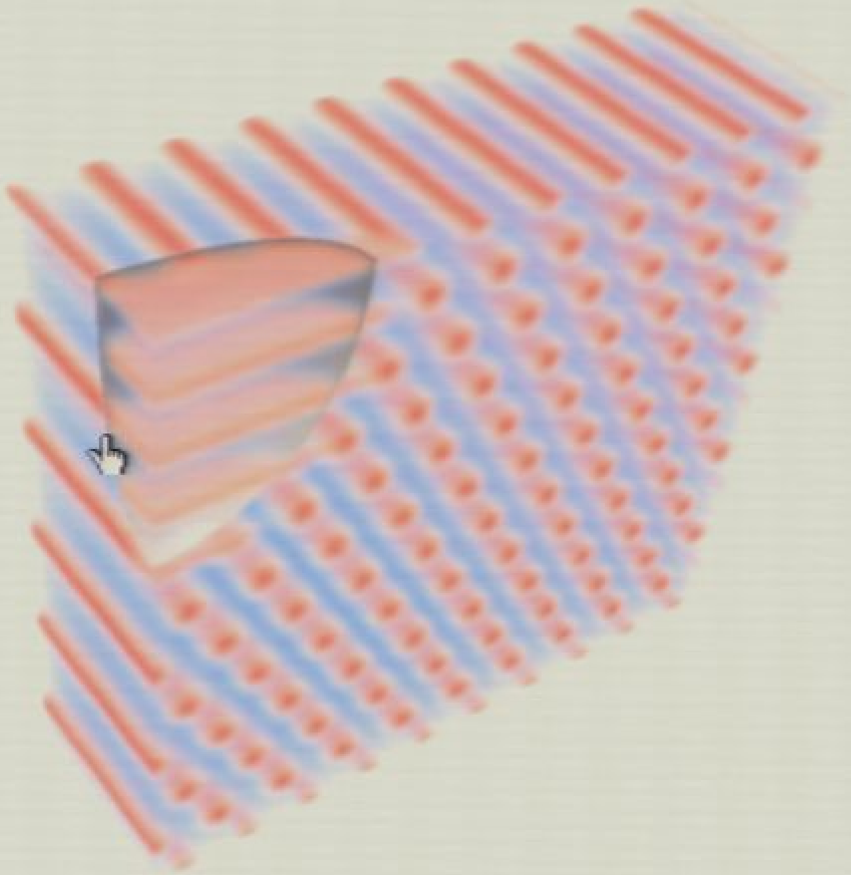
Identifying the critical nucleus size

Nuclei with an initial size above a certain threshold will grow



Find $\frac{L_{crit}}{L_0} = 6.0 \pm 0.5$ in this case

Identifying the critical nucleus size

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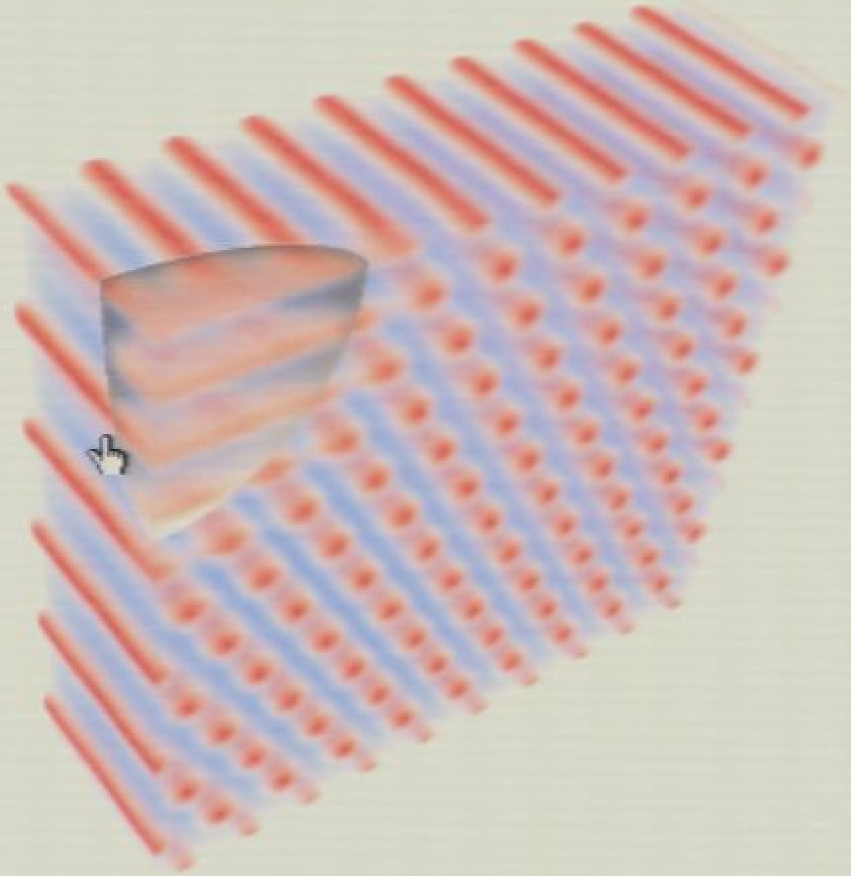

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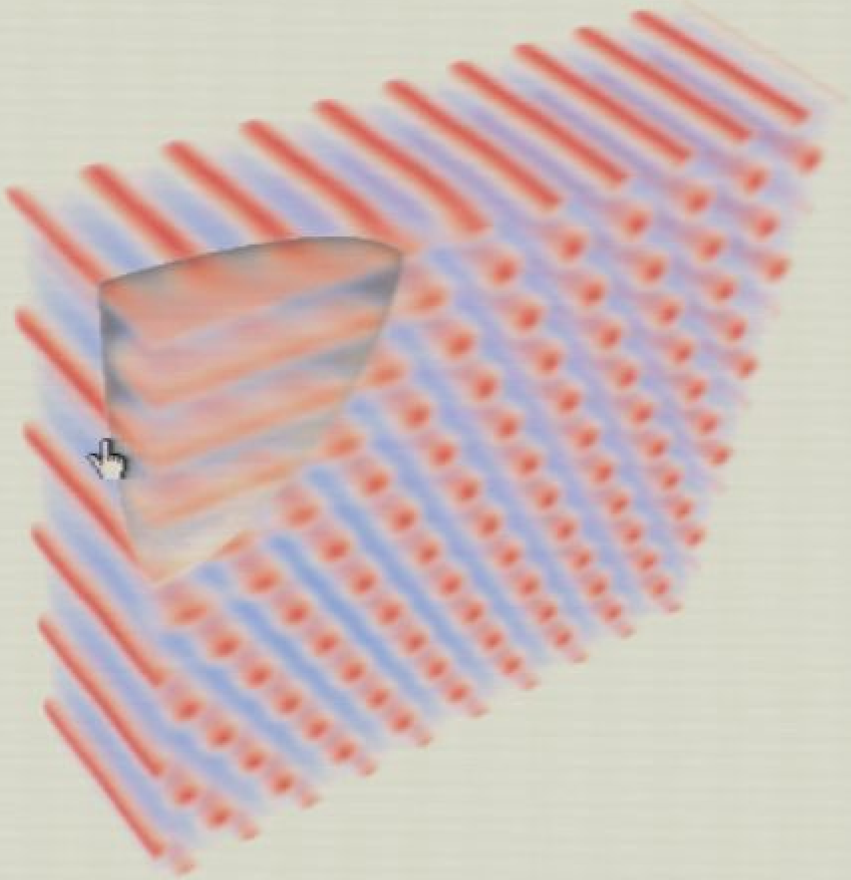

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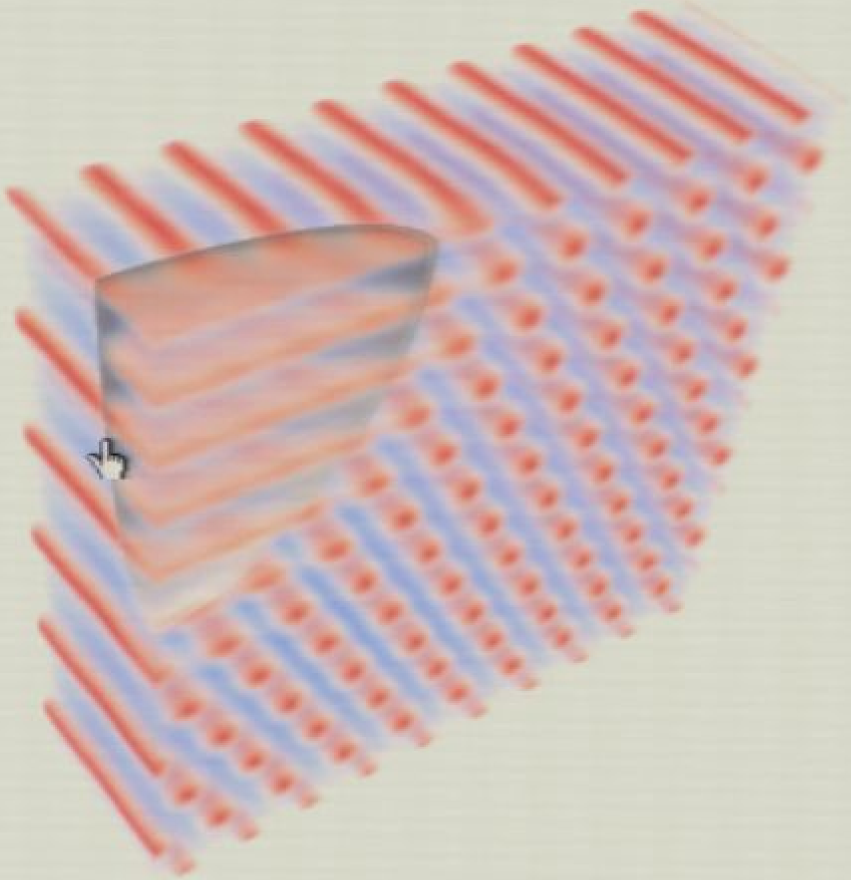

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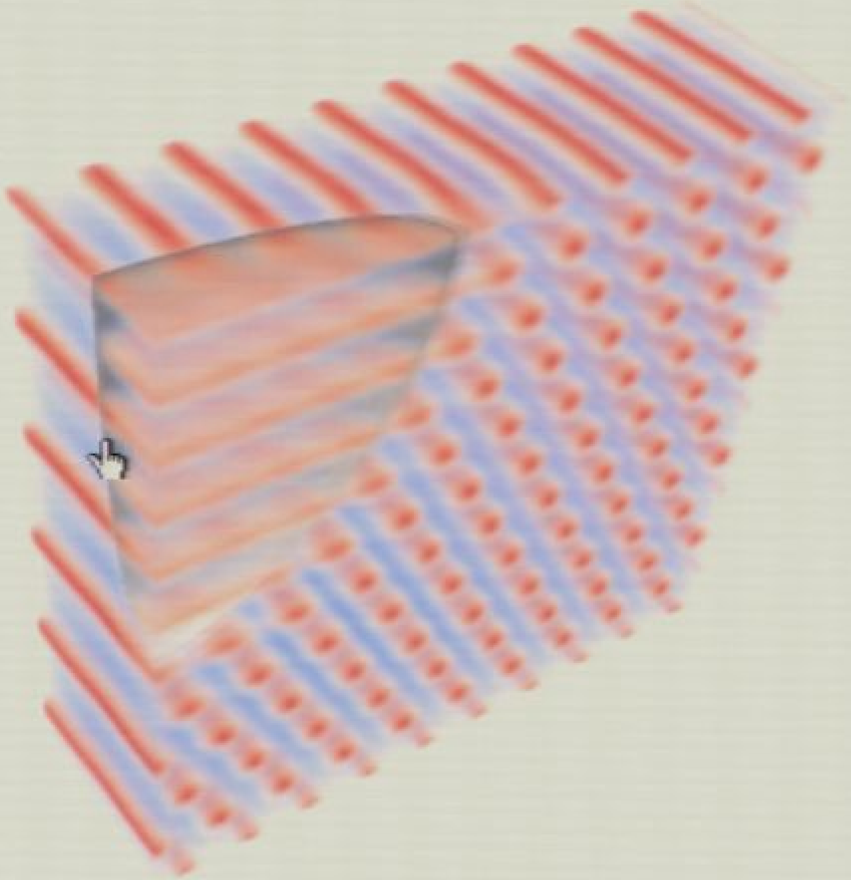

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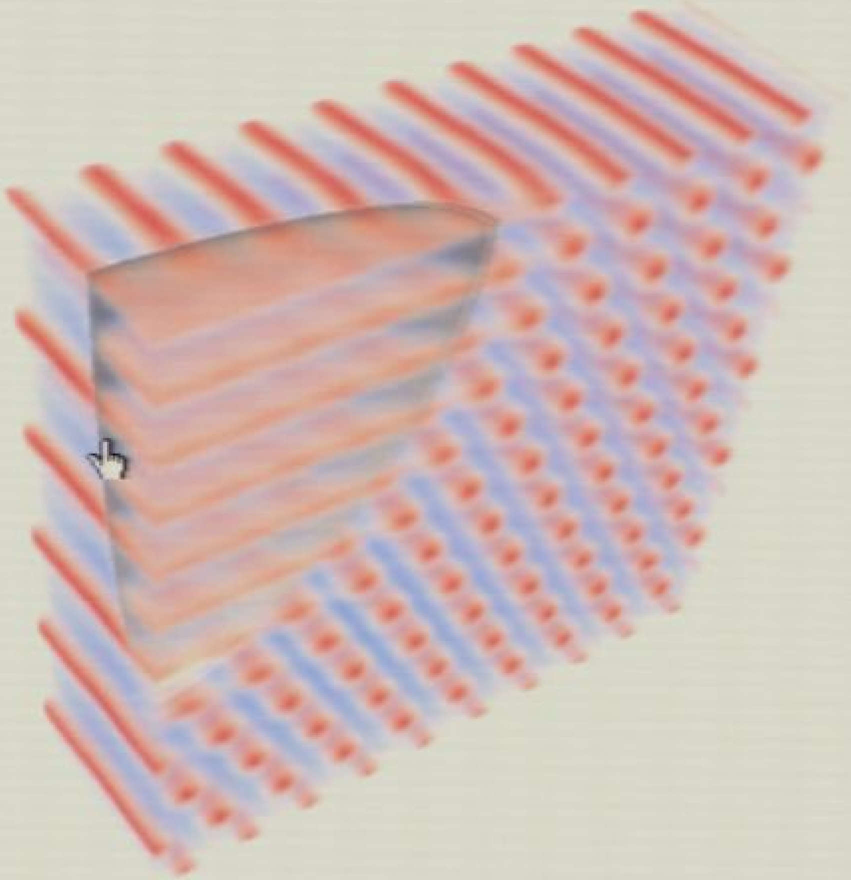

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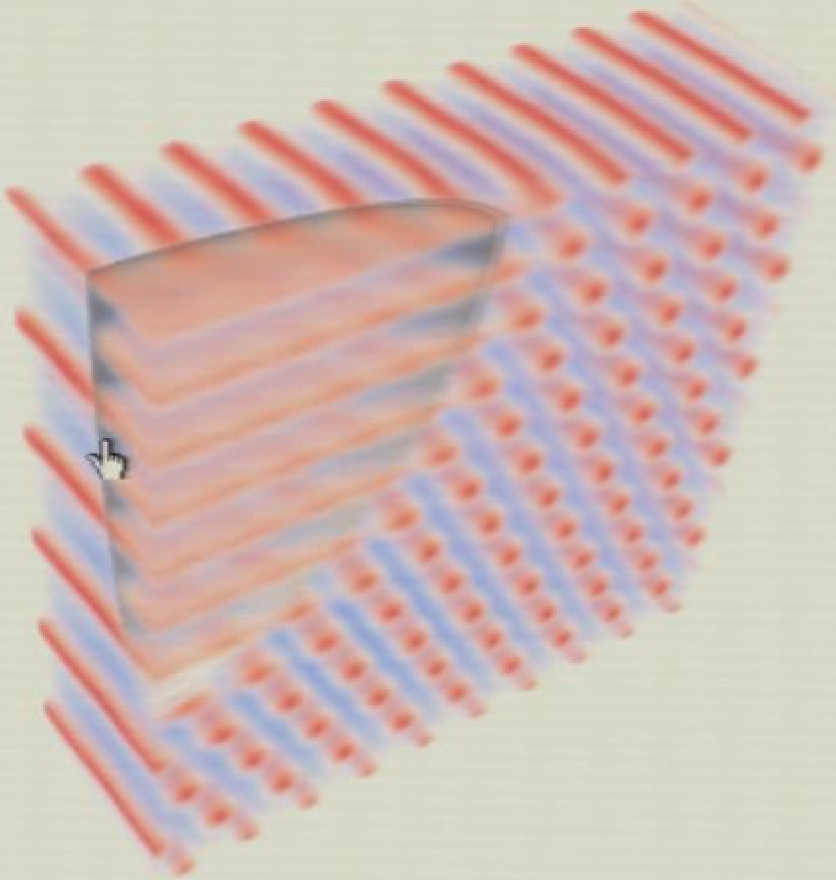

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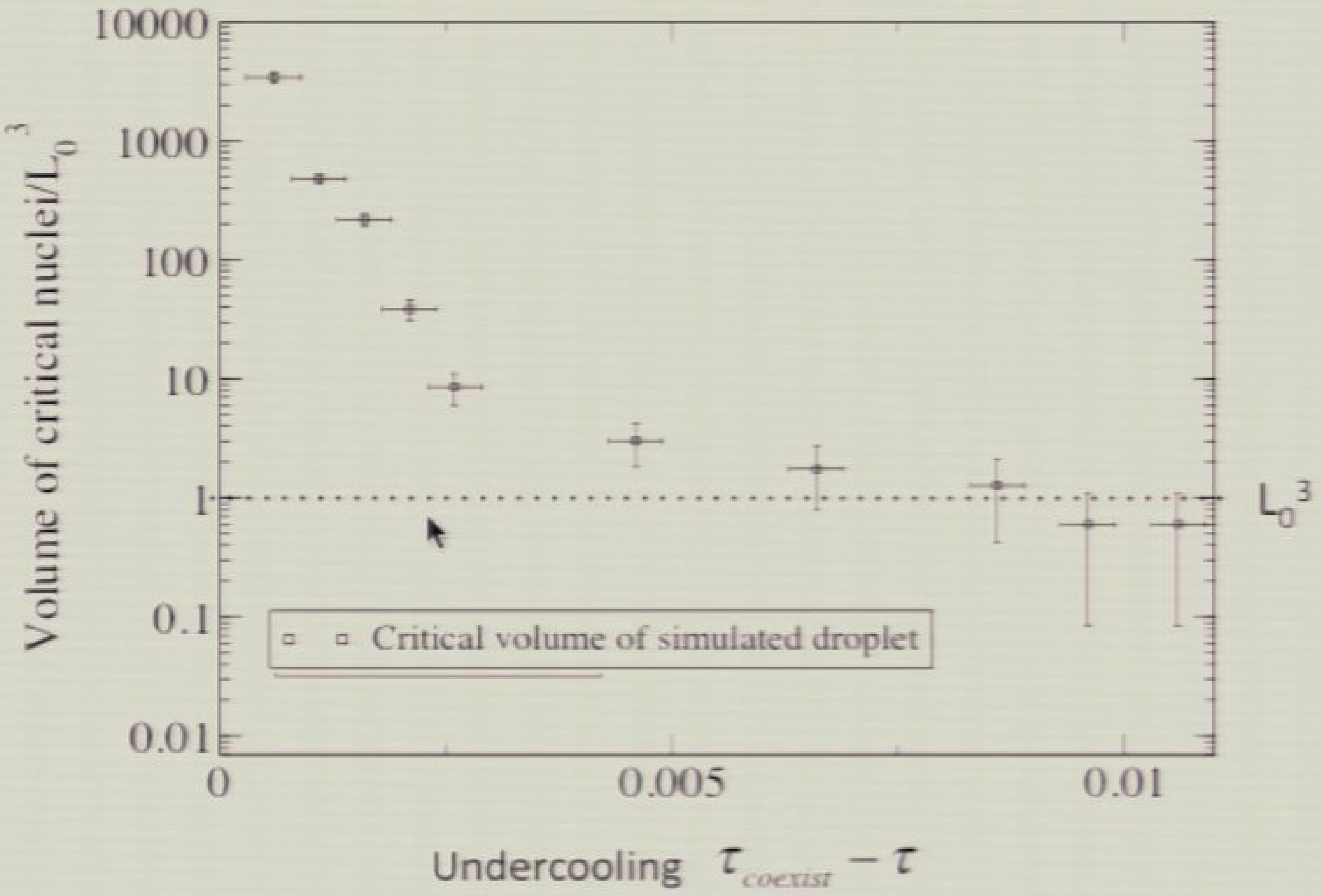
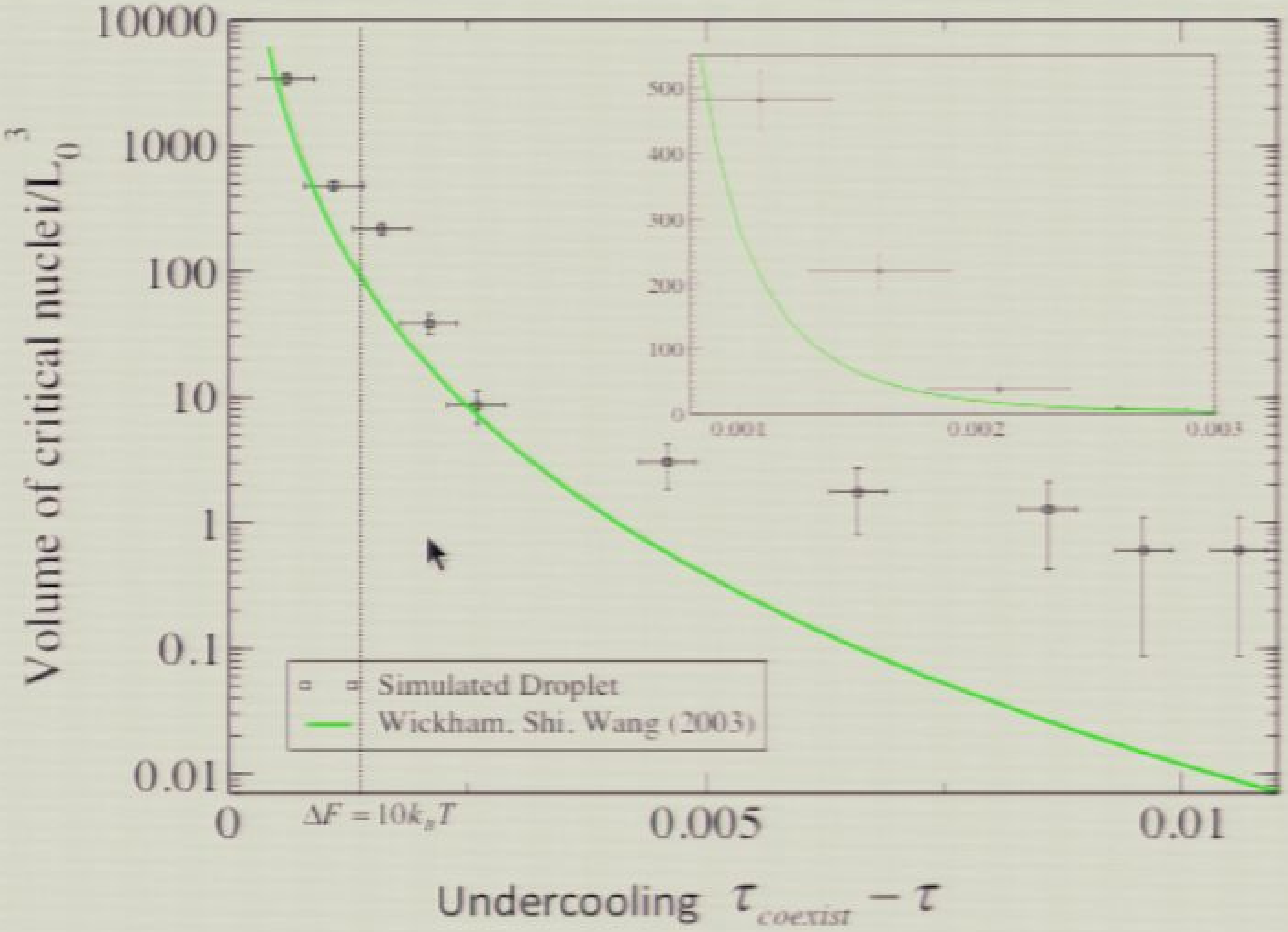
Critical nucleus volume vs. undercooling



Size of critical nucleus increases as coexistence is approached

Test of the approximate (2003) theory



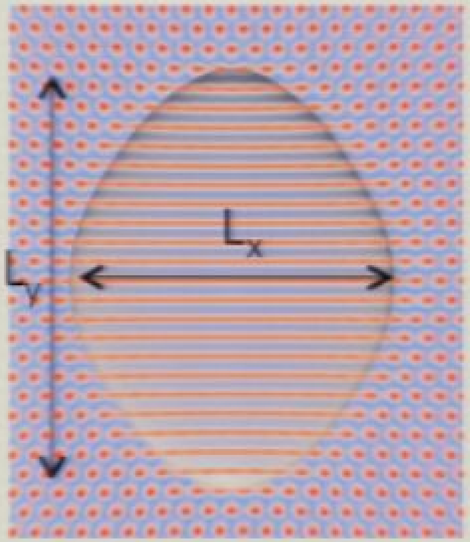
Theory:

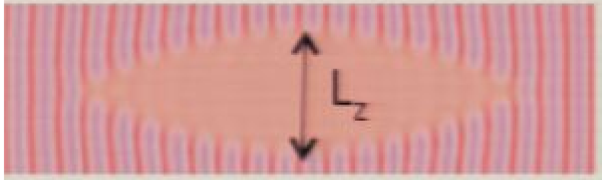
$$V_{crit} \sim \left(\frac{\sigma}{|\Delta f|} \right)^3$$

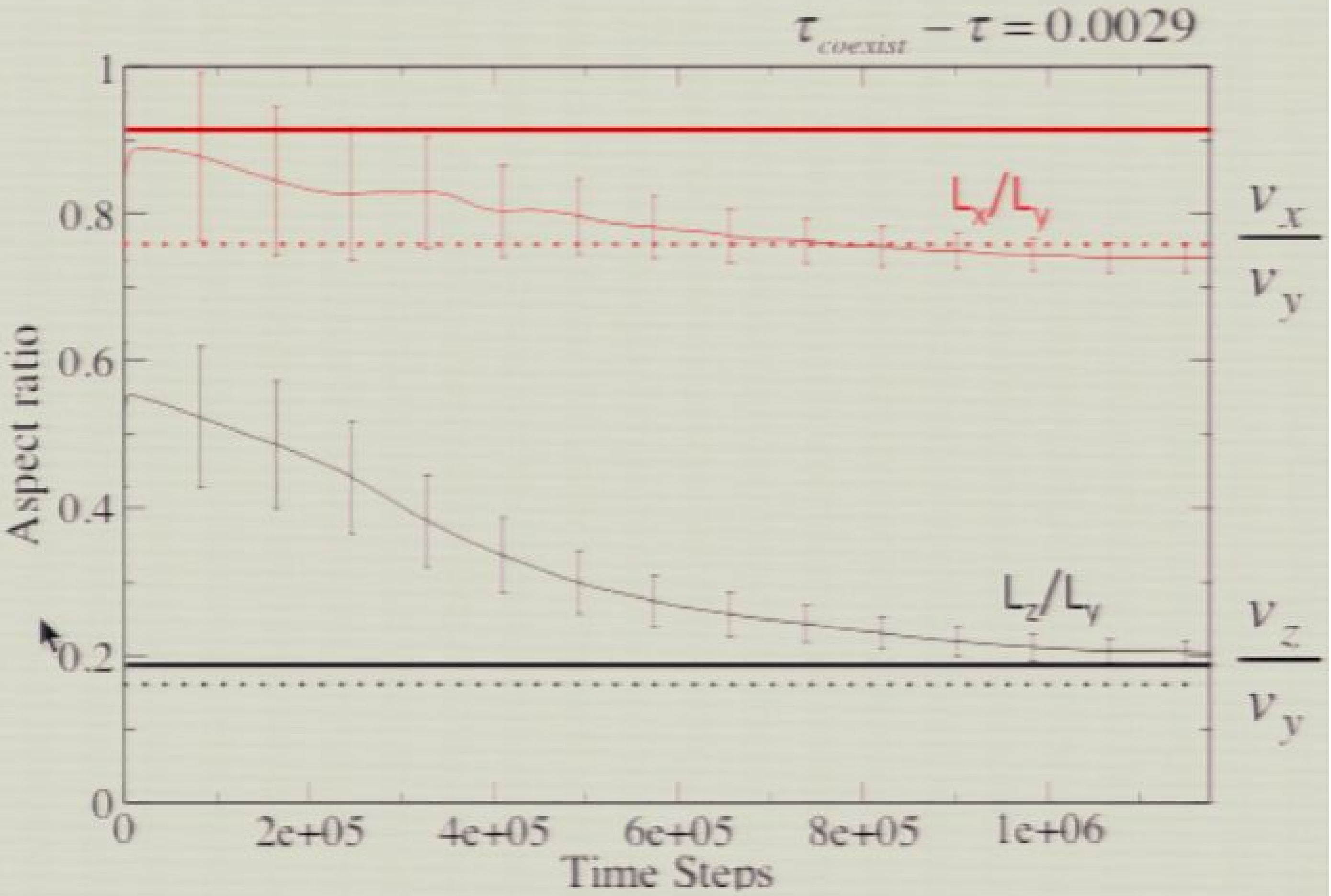
No adjustable parameters

Approximate theory reasonably describes simulation near coexistence

Time-evolution of nucleus shape



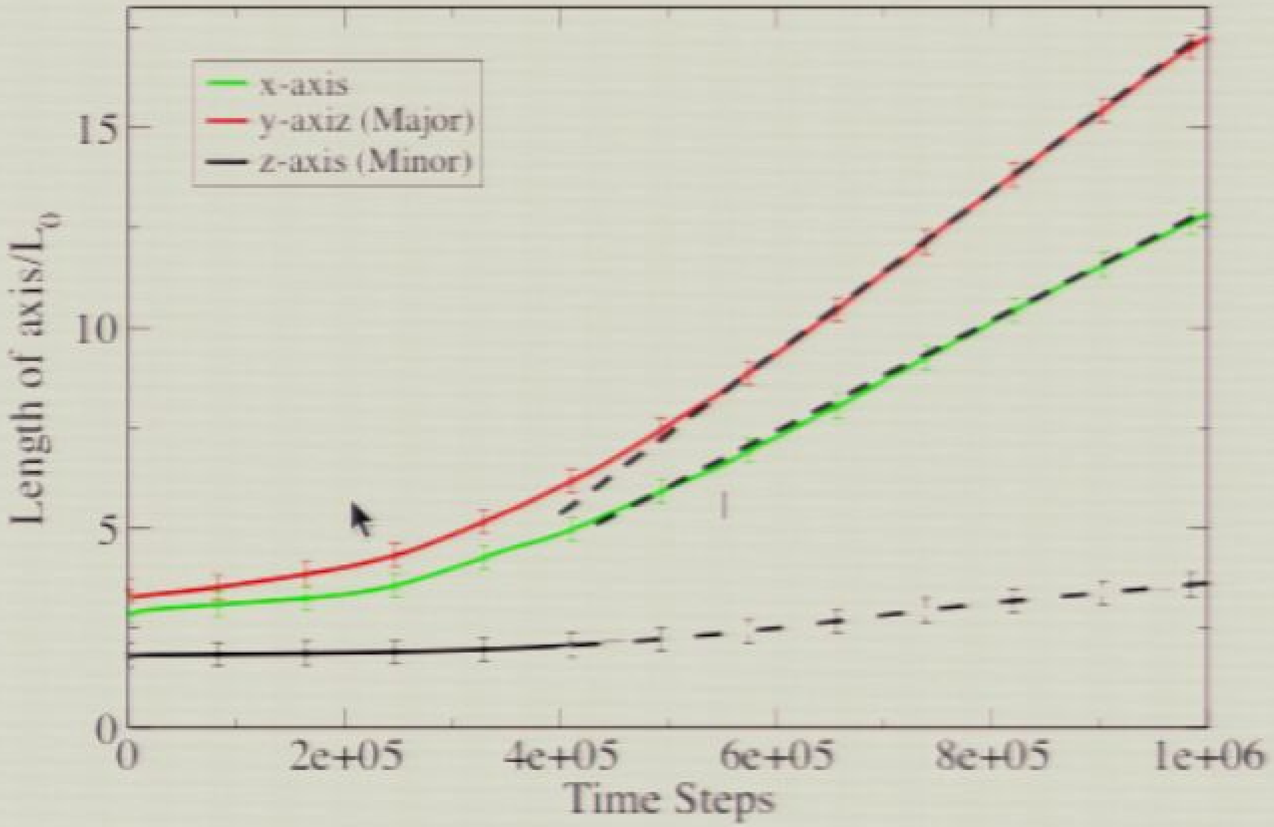




- Observe lens-like nucleus predicted by approximate theory
- Shape becomes constant
- Long-time shape determined by kinetics, rather than equilibrium

Kinetics: Growth of the droplet

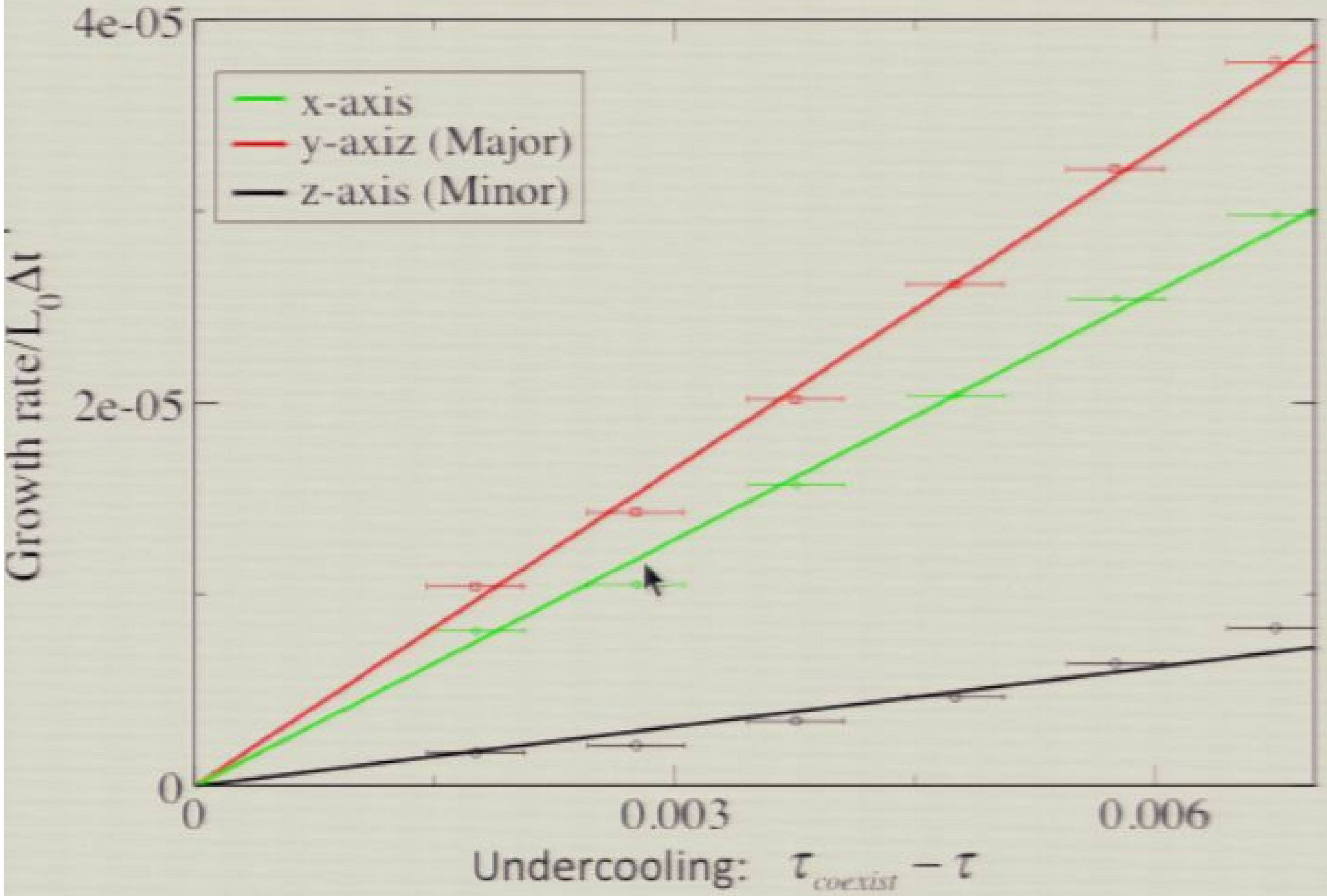
$$\tau_{coexist} - \tau = 0.0029$$



Growth enters linear regime where interface velocity is constant

Supports common assumption of constant-velocity [e.g. Goveas
d Milner (1997)]

Interface velocity as a function of undercooling

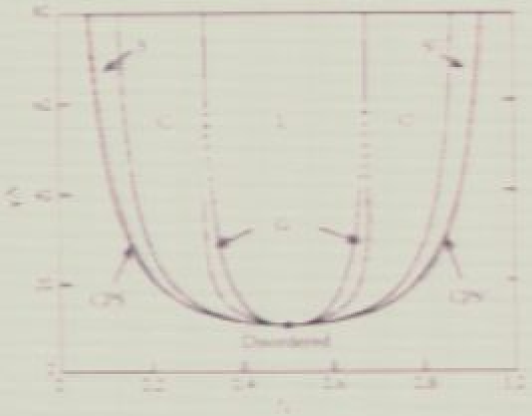


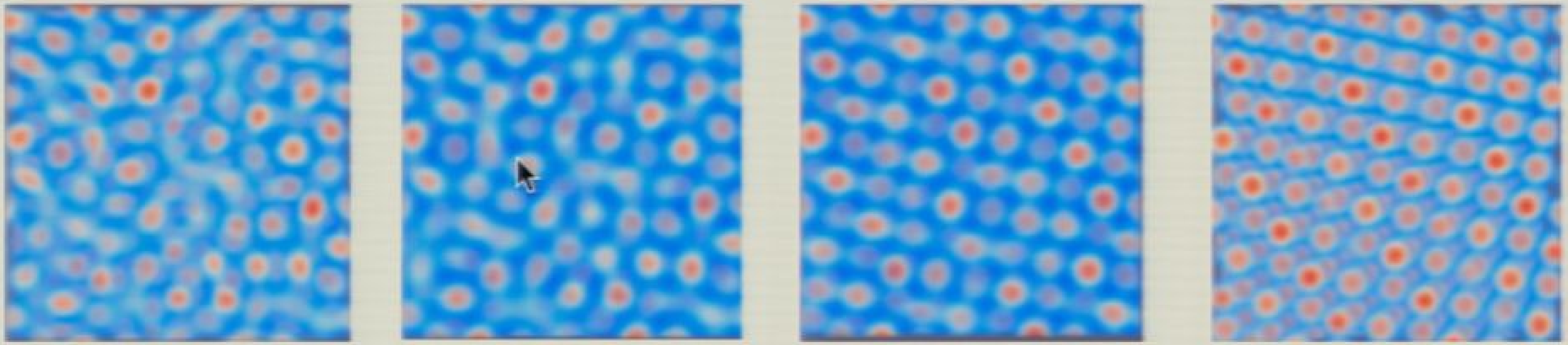
$$v \sim \frac{R_z}{T}\left(\tau_{coexist} - \tau\right)$$

Interface velocity is proportional to undercooling

Agrees with result of Goveas and Milner (1997)

Other dynamical scenarios: Crystalization





1.1 million
time steps

1.3 million
time steps

1.6 million
time steps

2 million
time steps

- Nature of disordered phase
- Kinetic pathways to forming the equilibrium BCC sphere phase

Summary

- Simulating nucleation and growth when microstructure is present is challenging
- We were able to identify a critical nucleus size
- The nucleus size increases as coexistence is approached, consistent with theory of Wickham, Shi and Wang (2003)
- The nucleus is lens-shaped, consistent with theory, but detailed comparison suggests kinetic effects are important
- Observed behaviour of interfacial velocity is consistent with theory of Goveas and Milner (1997)

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