Modelling atomic-scale structure and dynamics at interfaces on diffusive timescales

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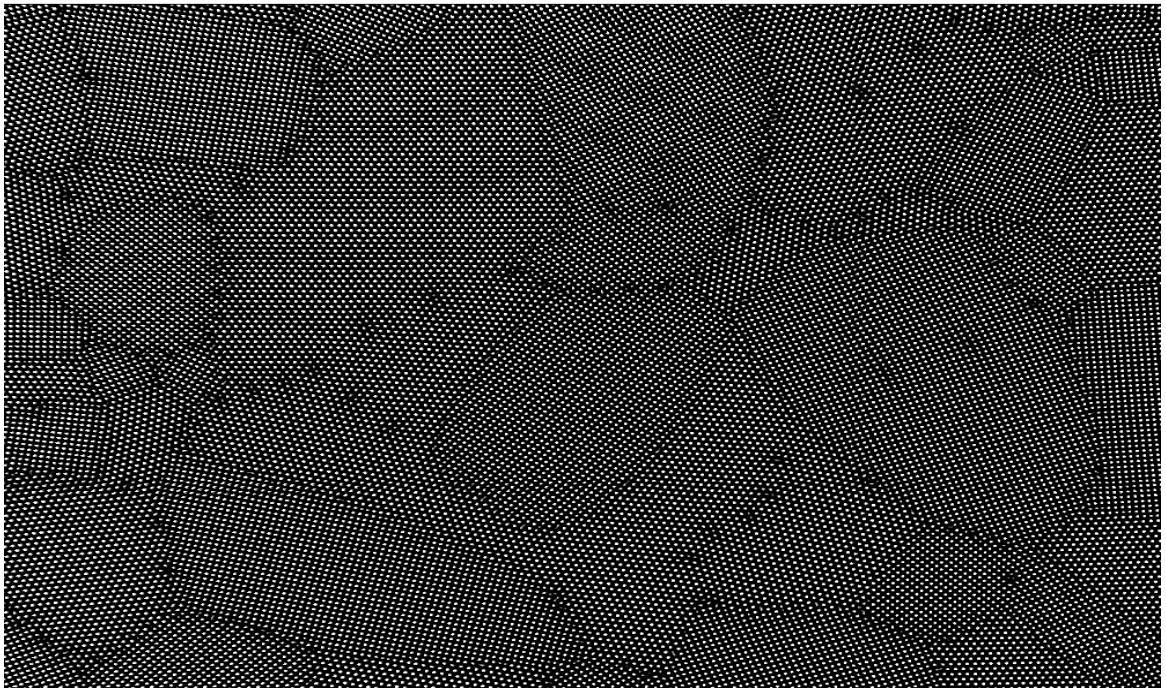


KITP workshop “Physical Principles of Multiscale Modeling”, June 2012

Materials phenomena at interfaces

- Solid-Solid phase transformations (eg. fcc-bcc in iron), grain growth and coarsening
- Crystallization and solidification from the melt
- Thin film epitaxial growth at surfaces

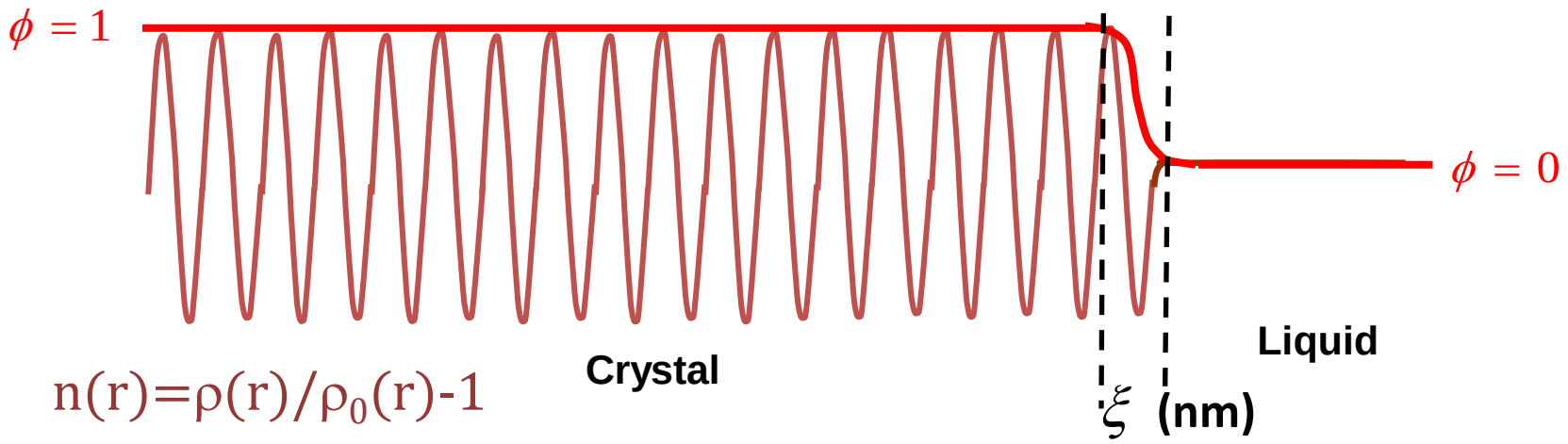
→ Involve complex structural changes that couple elastic and plastic effects with long ranged mass transport on diffusional timescales.

→ Decidedly beyond the reach of traditional molecular dynamics, but atomic level detail is still important.

→ Lattice kinetic Monte Carlo describes diffusion efficiently, but very difficult to include elastic interactions between defects such as dislocations.

→ Continuum Phase Field methods are equally fast, but entirely lacking atomistic features and must be parameterized by hand.

Traditional phase field models



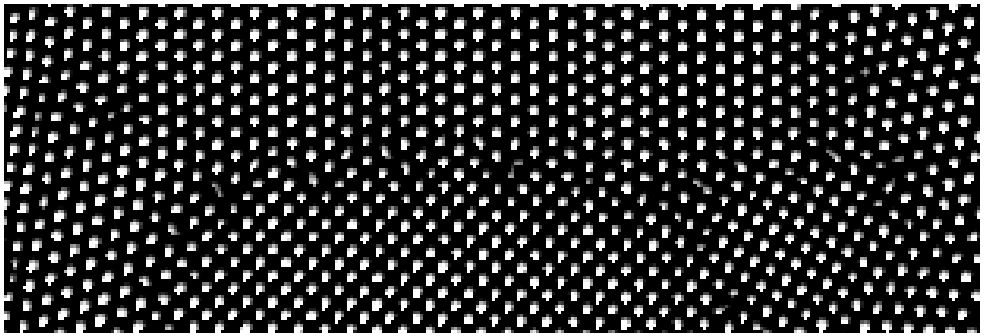
- Order parameter (the "phase field" ϕ) characterizes liquid/solid on μm length scales

- "Ginzburg-Landau" type free energy functional

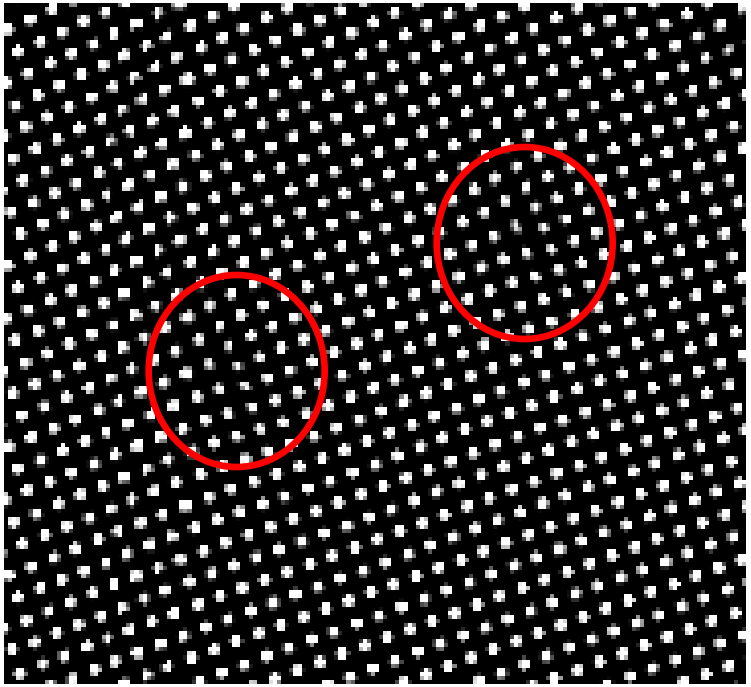
$$F[\phi] \cong \int \frac{\xi^2}{2} \left|\vec{\nabla}\phi\right|^2 dV + \frac{f_0}{4}\left(\phi^2 - 1\right)^2$$

What we need to describe?

Grain Boundary Interfaces



Dislocations



These features are important in phase transformations, but captured only implicitly in phase field simulations

The phase field crystal approach

- continuum field theory: 'soft' atoms → modulated density field n(r) minimizes a "free energy" $\Delta F = \Delta F_{id} + \Delta F_{ex}$

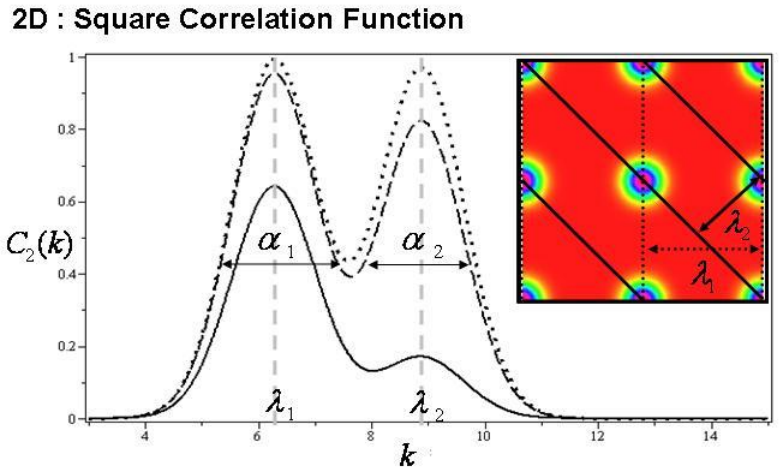
$$\Delta F_{id} = k_B T \int dr \left[\frac{n(r)^2}{2} - \frac{n(r)^3}{6} + \frac{n(r)^4}{12} \right]$$

Local entropy
→ promotes uniform phase

$$\Delta F_{ex} = -\frac{k_B T}{2} \int dr_1 \int dr_2 \left[n(\vec{r}_1) C_2(|\vec{r}_1 - \vec{r}_2|) n(\vec{r}_2) \right]$$

Nonlocal "excess"
→ promotes structured phase

- two-point correlation $C_2(|r|)$ contains info about symmetry of ordered phase: sc, bcc, fcc, hcp
- promote growth of wavelengths corresponding to the magnitude of the shortest reciprocal lattice vectors of the desired structure
- rotationally invariant



M. Greenwood, N. Provatas, J. Rottler, PRL 105, 045702 (2010)

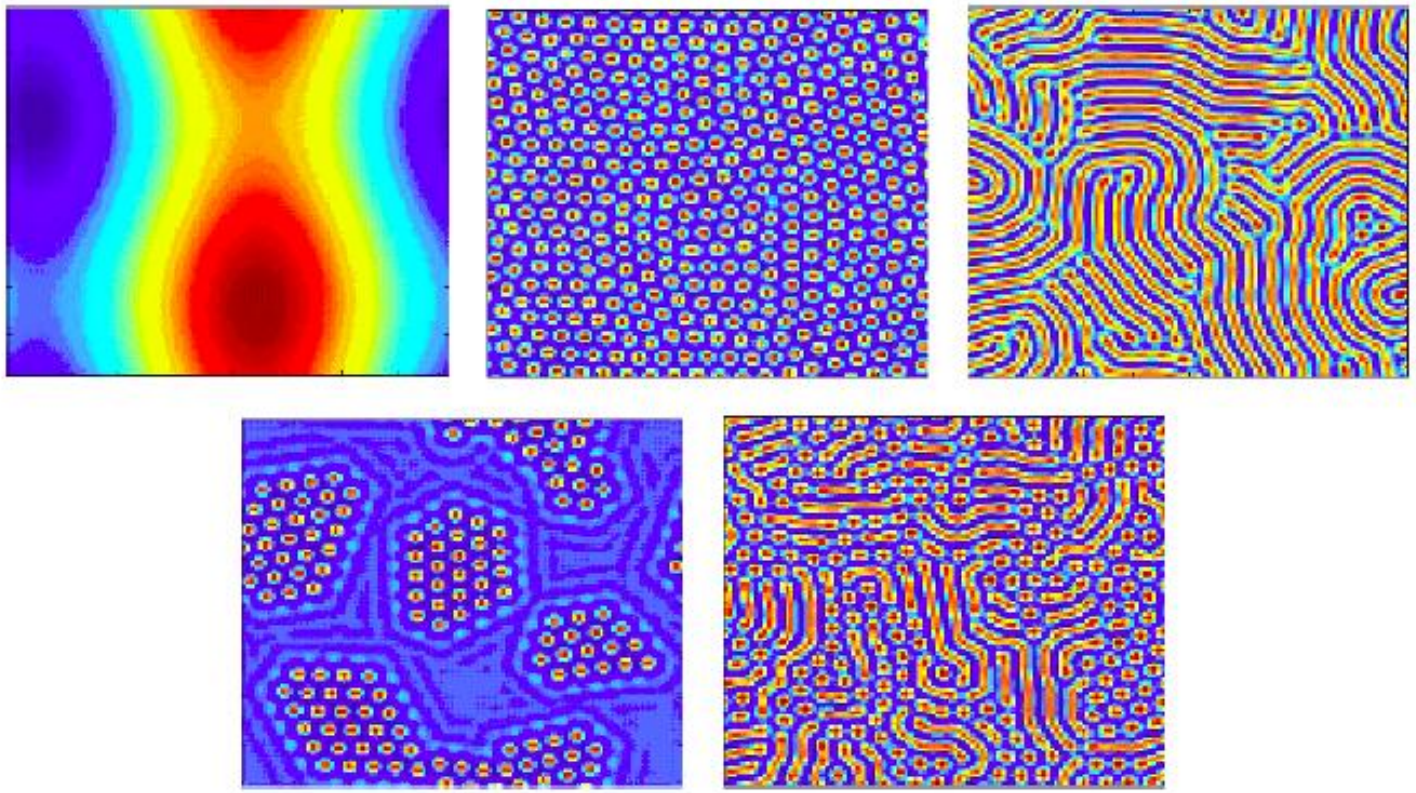
A bit of history

- Essentially based on “Brazovskii” functional (1975):

$$\mathrm{F}[\rho] = \int dr[\rho(\tau + \alpha(k^2{}_0 + \nabla^2)^2)\rho/2 + u\rho^4/4]$$

S. A. Brazovskii,
Zh. Eksp. Teor. Fiz 68, 175 (1975).

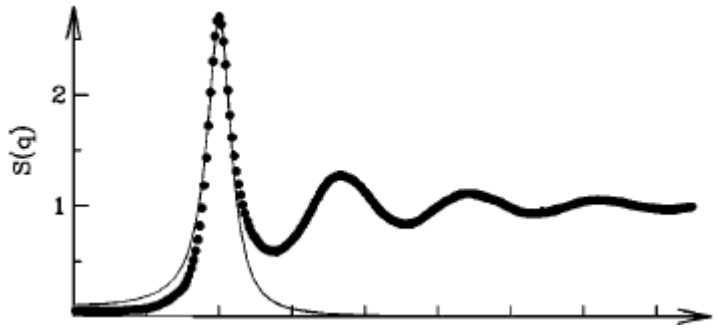
- Minimized by spatially modulated order parameter

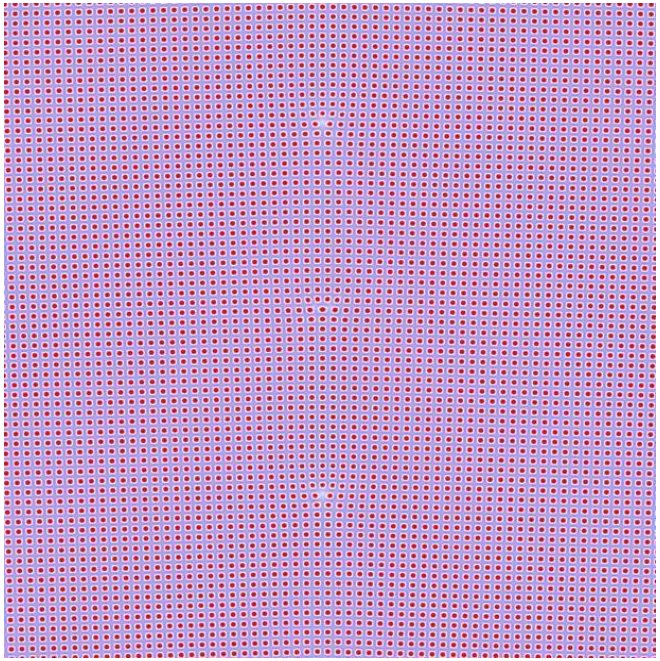


Courtesy of Amy Liu (2007)

A bit of history

- Proposal by Ken Elder & collaborators (2002):
  interpret peaks as “atoms” and troughs as space in between.
  Fit gradient terms to first peak of liquid structure factor





- Selects specific length scale;
  modulated phase emerges as
  “ground state”, defect configurations
  have higher energy

K. Elder, M. Katakowski, M. Haataja, and M. Grant,
Phys Rev Lett 88, 245701 (2002).
K. Elder and M. Grant, Phys Rev E 70, 051605 (2004).

Field dynamics

- purely relaxational, conserved dynamics minimizes free energy functional

$$\frac{\partial n}{\partial t} = \mathrm{M}\nabla^2 \frac{\delta \Delta F}{\delta n} + \eta$$

- propagative if elastic interactions must be faster than density relaxations

$$\frac{\partial^2 n}{\partial t^2} + \beta \frac{\partial n}{\partial t} = \alpha^2 \nabla^2 \frac{\delta \Delta F}{\delta n} + \eta$$

- can add stochastic noise to facilitate nucleation, overcoming of metastable states etc.

Why is this useful?

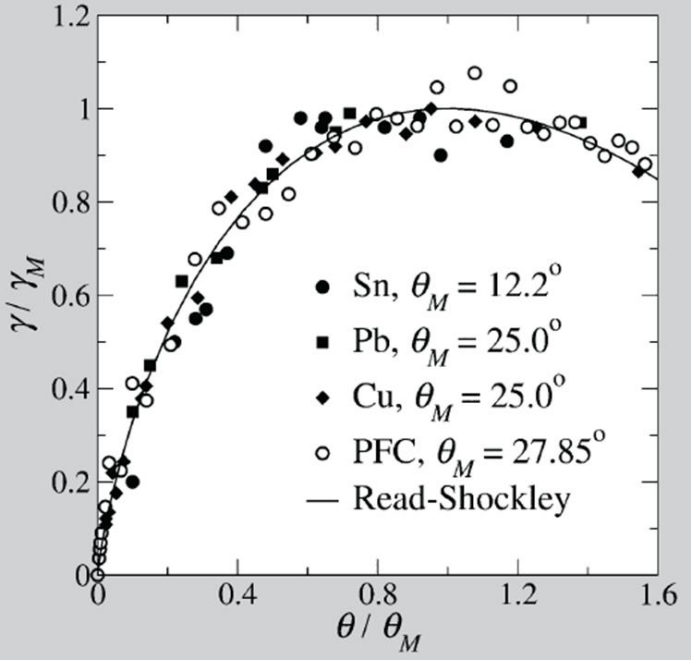
- not slaved to phononic timescales (10^{-13} s) as in molecular dynamics

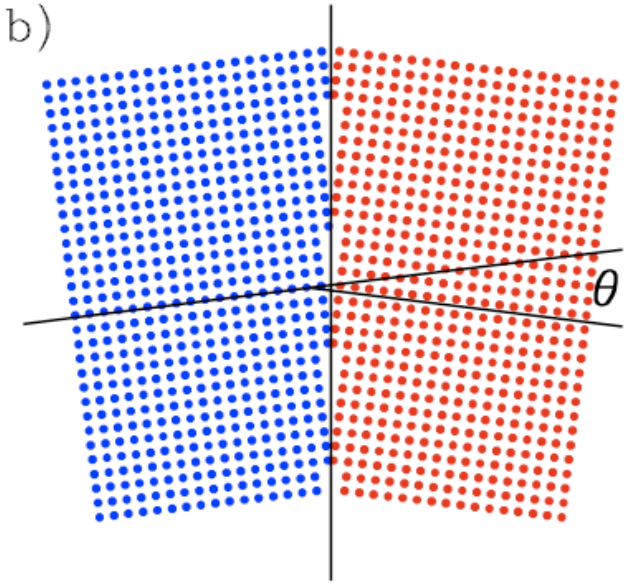
- density fluctuations equilibrate rapidly and do not require explicit microscopic diffusion mechanism (vacancy exchange)

- This implies: there are no vacancies in a PFC crystal!
- And: only total density is conserved, not # of peaks!

- But: deviations from the periodic ground state (eg. dislocations, grain boundaries) emerge naturally
- Nonlinear elasticity is automatically included
- Natural link to traditional phase field models (in fact can be coarse-grained via “amplitude expansions”)

Semiquantitative test I: grain boundary energy

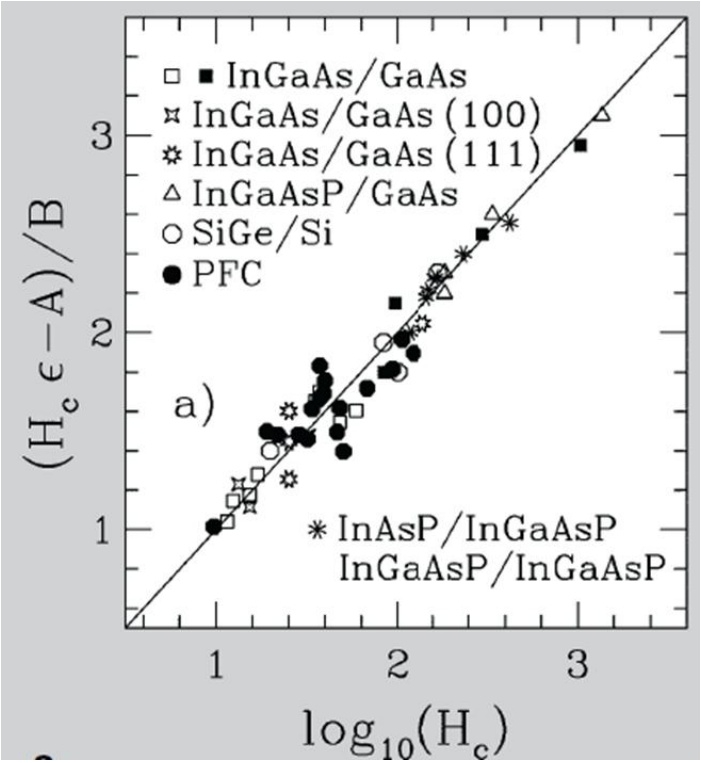




- Grain boundary energy as a function of mismatch angle Θ compared to PFC results and continuum theory.
- Read-Shockley result $$\frac{\gamma}{\gamma_m} = \theta(A - \ln(\theta))$$

K. Elder and M. Grant, Phys Rev E 70, 051605 (2004).

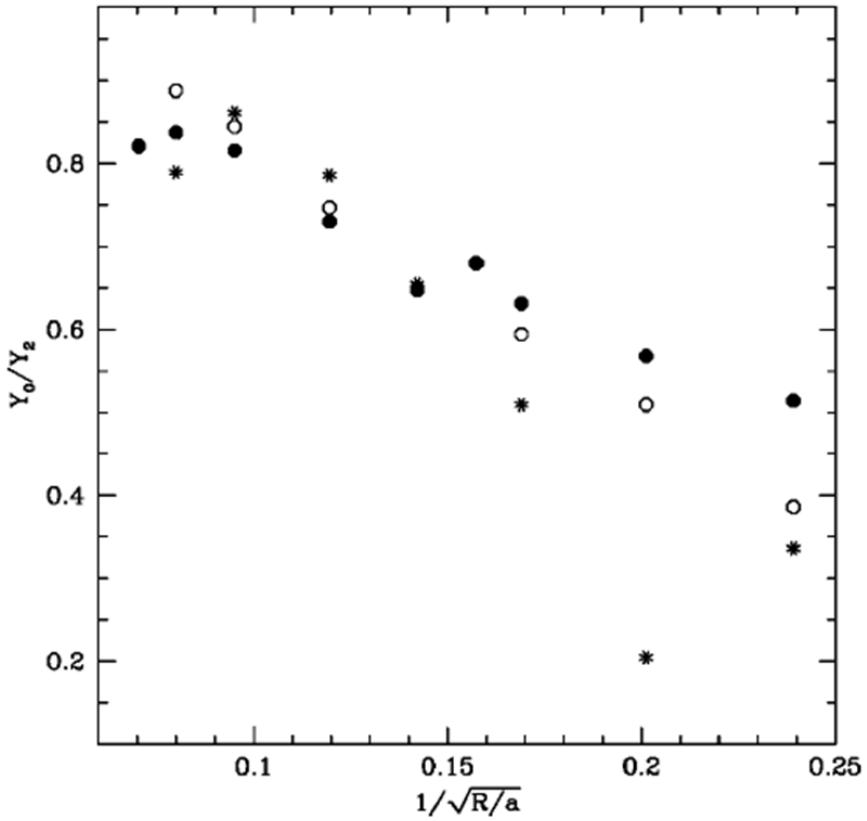
Semiquantitative test II: misfit dislocations



- Strained epitaxial film nucleates dislocations at critical height H_c.
- Matthews-Blakeslee result: $H_c \propto \frac{1}{\varepsilon}(1 + \log[\frac{H_c}{a}])$

K. Elder and M. Grant, Phys Rev E 70, 051605 (2004).

Semiquantitative test III: polycrystal



Elastic modulus of polycrystalline solid

Softening of nanocrystalline materials: $Y_0 \propto 1/\sqrt{grain\ size}$

K. Elder and M. Grant, Phys Rev E 70, 051605 (2004).

Application example I: dislocation dynamics

PRL 105, 015502 (2010) PHYSICAL REVIEW LETTERS week ending 2 JULY 2010

Plasticity and Dislocation Dynamics in a Phase Field Crystal Model

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(Received 26 April 2010; published 28 June 2010)

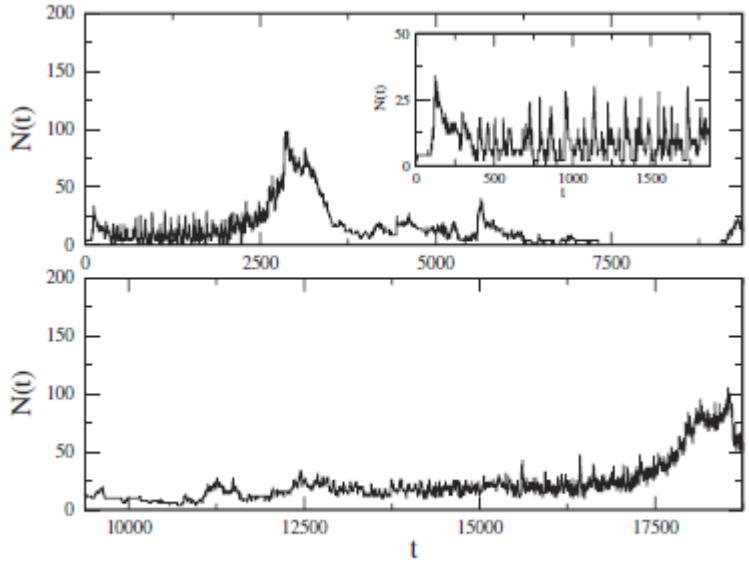

FIG. 1. The number of dislocations in a sheared PFC crystal.

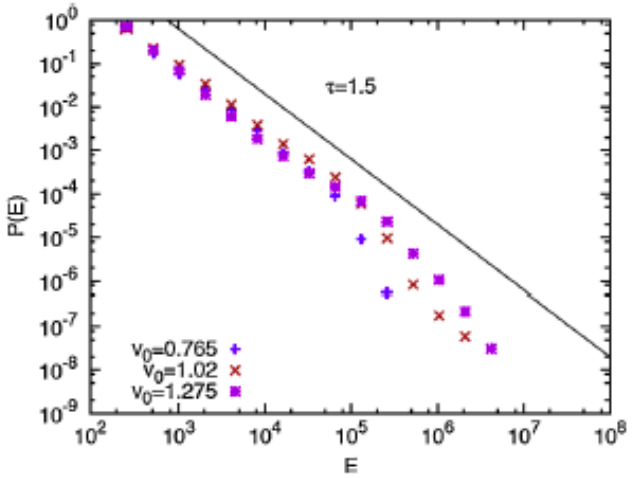

FIG. 3 (color online). The probability distribution of the event energy during dislocation avalanches, for different values of the shearing rates.

Nonequilibrium critical behavior: dislocation avalanches in a 2D PFC model with propagative field dynamics

Application example II: surface physics

PRL 105, 126101 (2010) PHYSICAL REVIEW LETTERS week ending 17 SEPTEMBER 2010

Phase-Field Crystal Modeling of Compositional Domain Formation in Ultrathin Films

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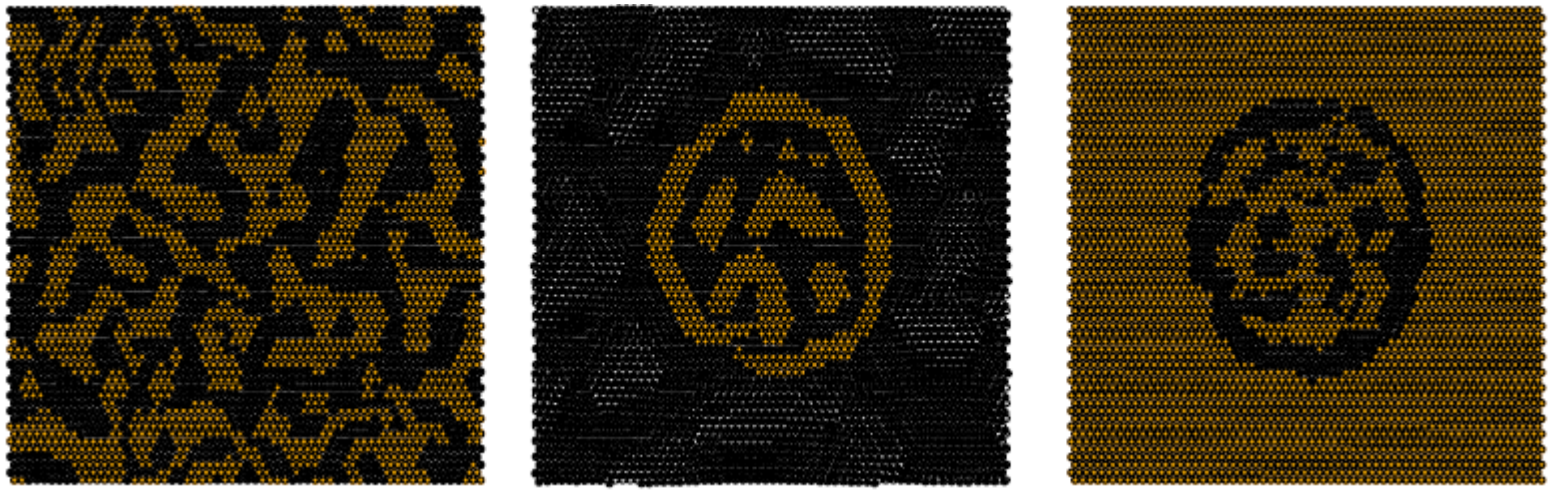
(Received 22 June 2010; published 17 September 2010)

- Binary PFC alloy modeling CoAg monolayer adsorbed on Ru(0001) surface
- Competition between thermodynamics and strain relaxation leads to nanoscale domain formation



Equal composition Ag-rich Co-rich

"Informing" the field theory

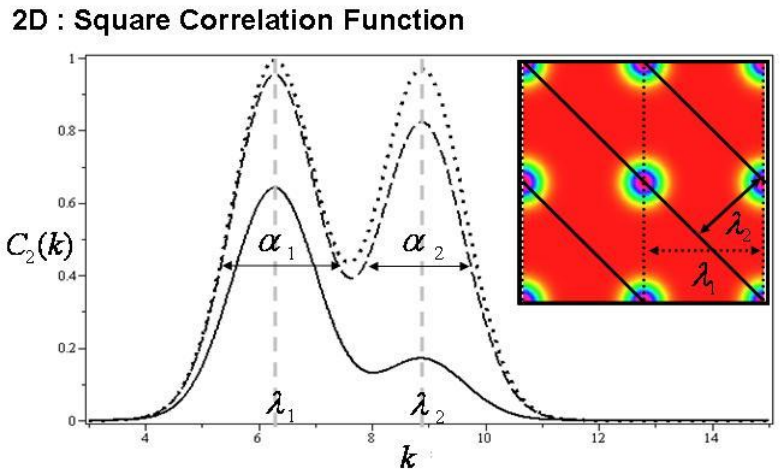
- Brazovskii functional is simple to implement, but it is difficult to get crystal symmetries other than triangular (2D) or bcc (3D)

- Our approach (2010) provides more flexibility and introduces physically motivated "control parameters"

$$\Delta F_{ex} = -\frac{k_B T}{2}\int dr_1 \int dr_2 \left[n(\vec{r}_1) C_2(|\vec{r}_1 - \vec{r}_2|) n(\vec{r}_2) \right]$$

Nonlocal "excess"
→ promotes structured phase

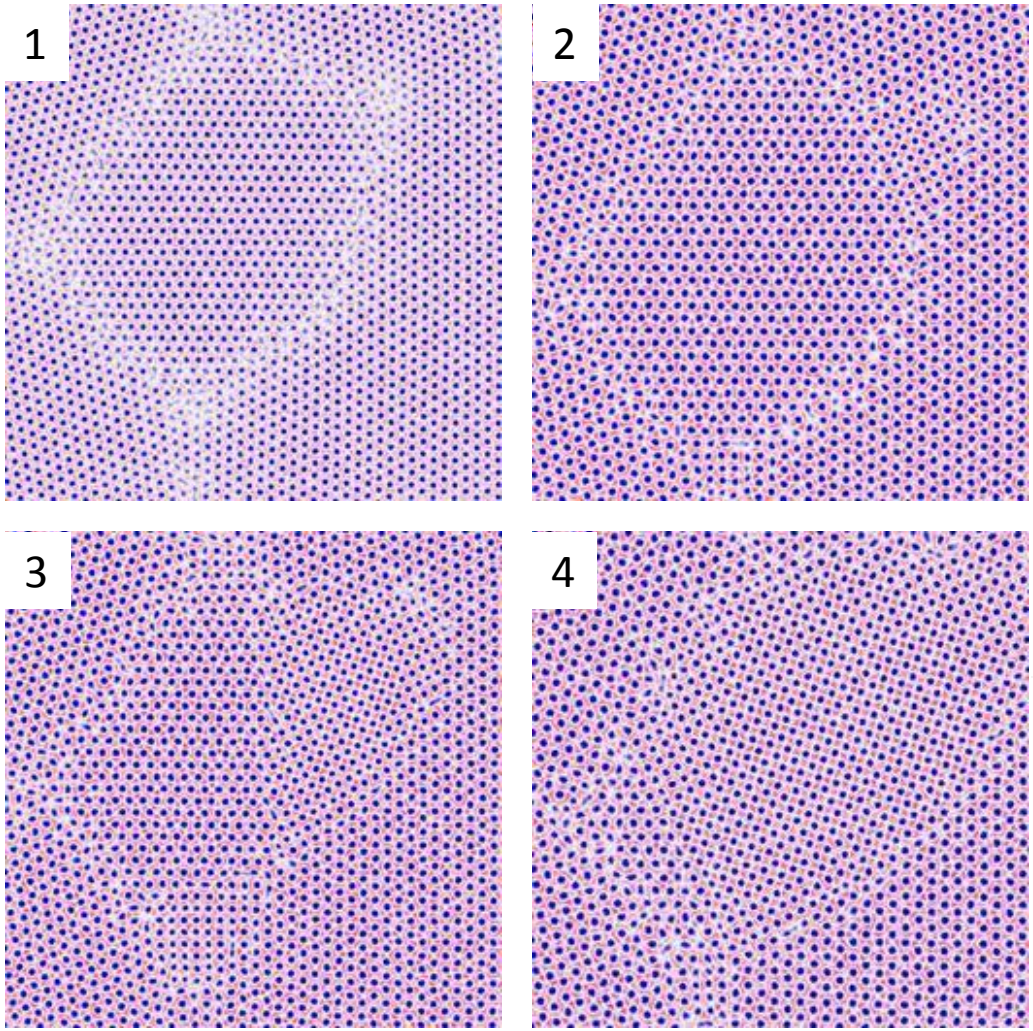
→ stabilizes lattices other than bcc through higher order peaks
→ peak width α_i controls elastic constants and energy penalty for defects
→ relative peak height modulated by a Debye-Waller like prefactor $\exp(-\sigma^2 k^2/2)$ provides a "temperature" control parameter

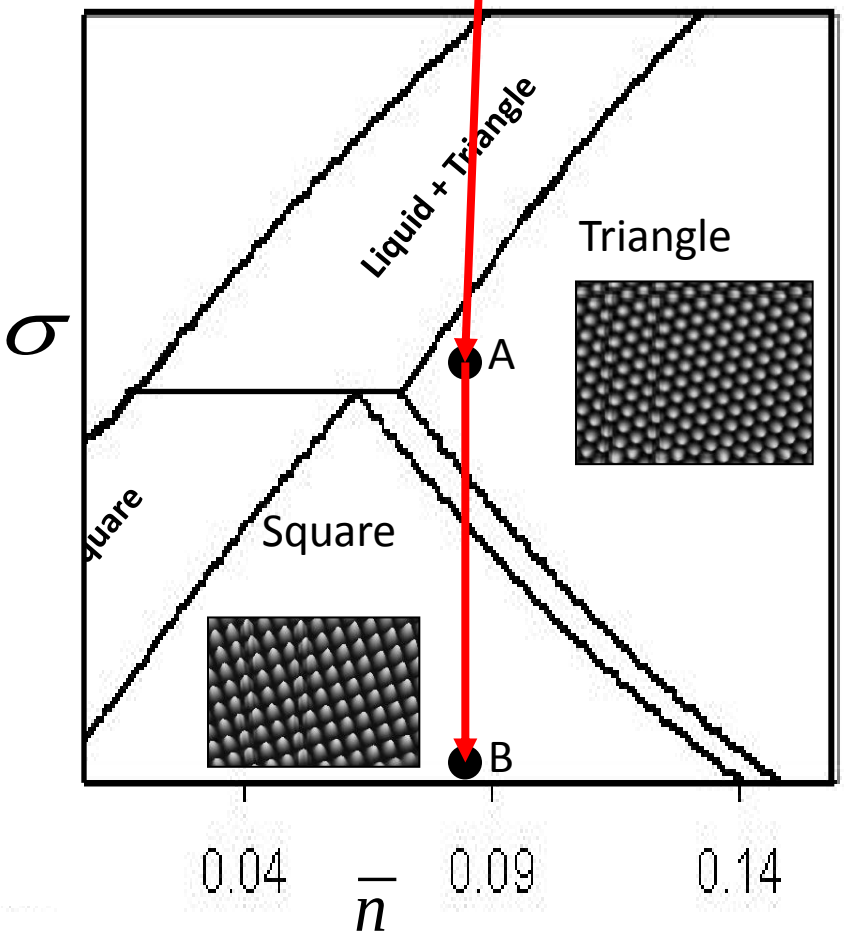


M. Greenwood, N. Provatas, J. Rottler, PRL 105, 045702 (2010)

Nucleation and coarsening after quench

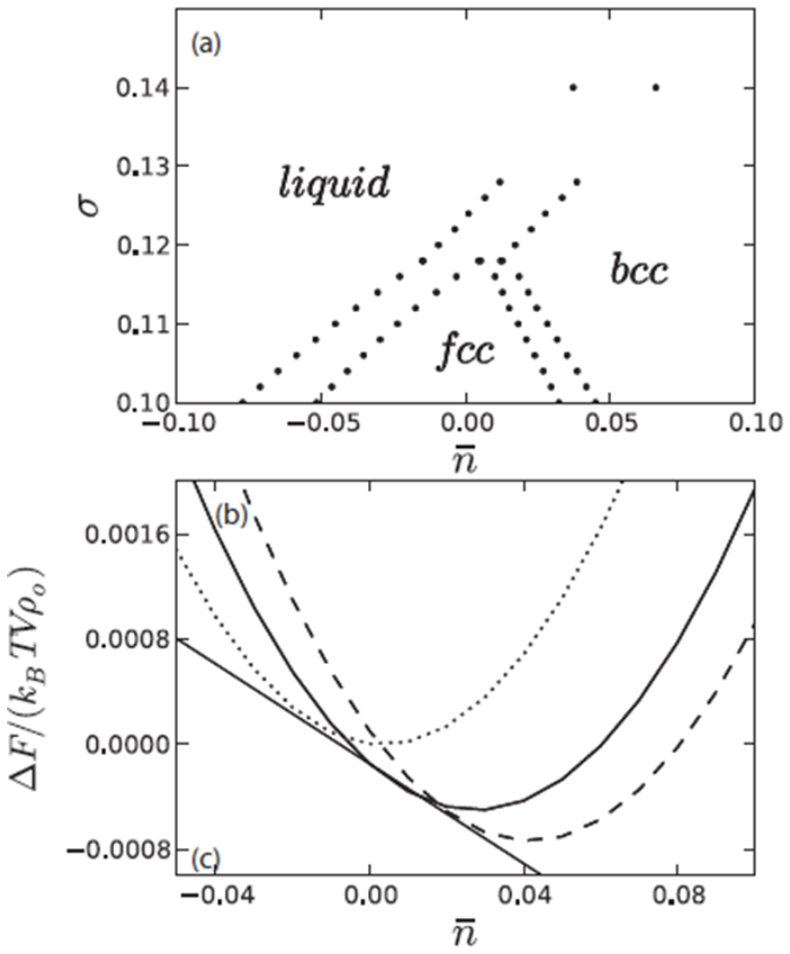
Quench liquid → Point A: triangular grains
Quench Point A → Point B in square phase





- Square phase nucleates from the higher energy triple points.
- Seeds grow, coarsen and merge eventually

Phase diagram for cubic systems



M. Greenwood, J. Rottler, N. Provatas, Phys Rev E **105**, 031601 (2011)

- Equilibrium phase determined from "double tangent "construction
- Excess free energy with only one frequency is always minimized by bcc
- fcc is stabilized by including two frequencies at $k_1 = 2\pi\sqrt{3}/a$ and $k_2 = 4\pi/a$.
- Relative height of 2nd peak controls equilibrium structure.
- Elastic constants C_{11}, C_{12} and C_{44} $\propto \alpha_i^{-2}$ and $\propto -\sigma^2$
- Elastic anisotropy can be tuned by the ratio α_2/α_1

Binary alloys

Assume solute concentration c varies slowly relative to density fields

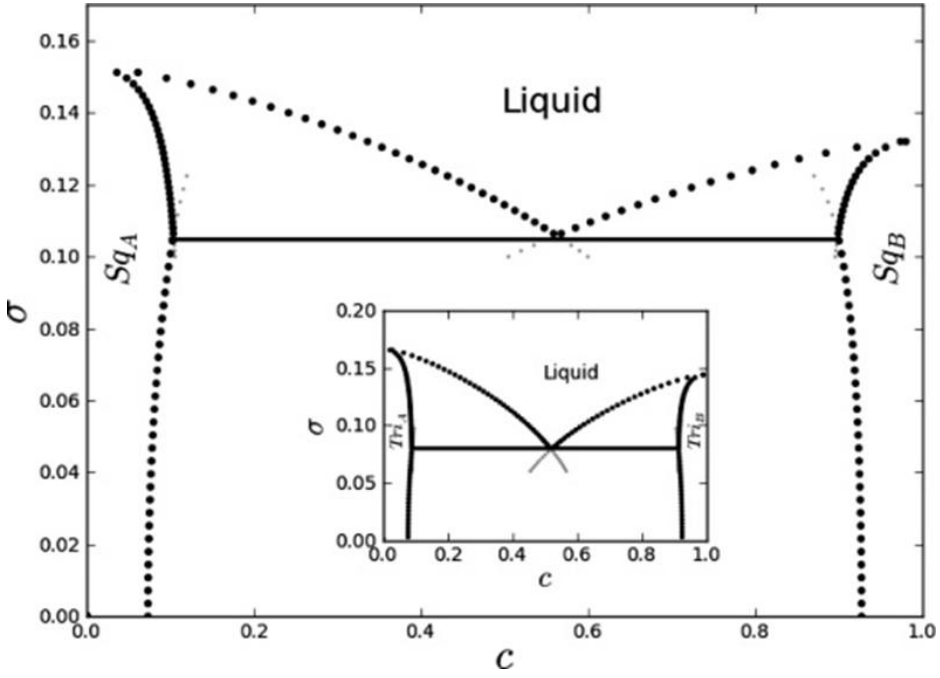
$$\frac{\Delta F}{k_B T} = \Delta F_{id} + (n+1)\Delta F_{mix} - \frac{1}{2}\int dr_1 \int dr_2 n(r_1) C_{eff}(|r_1 - r_2|) n(r_2) + \alpha|\nabla c|^2$$

Entropy of mixing

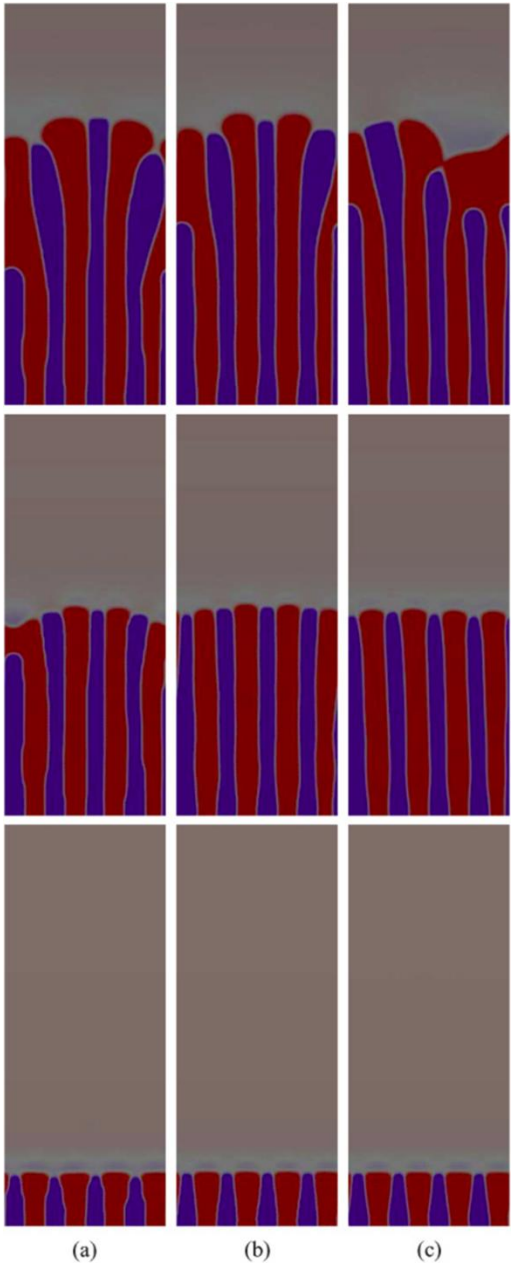
Composition-dependent interpolating correlations

$$C_{eff} = X_1(c)C^{AA} + X_2(c)C^{BB}$$

Eutectic phase diagram:

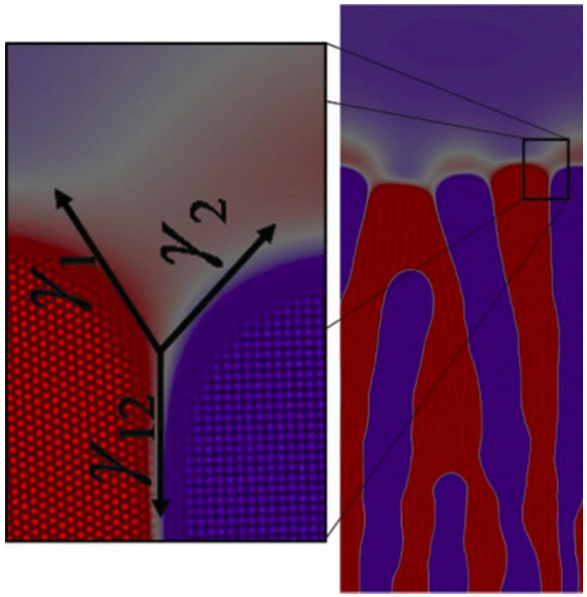


Lamellae growth



Growth channels with different misorientations
(a) 0, (b) 4, (c) 20 degrees.

Growth of structurally dissimilar phases



M. Greenwood, N. Ofori-Opoku, J. Rottler, and N. Provatas, Phys. Rev. B **84**, 064104 (2011)

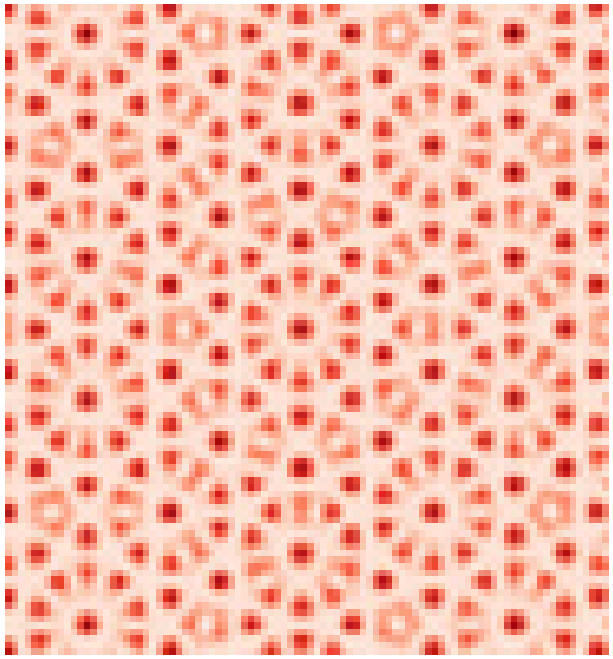
Phase field quasicrystals

- many useful properties: low friction, resistance to oxidation, catalysis
- widely studied in thin film epitaxy due to potential for pseudomorphic growth of adsorbates
- most common surfaces: icosahedral Al-Pd-Mn or Al-Cu-Fe with 5-fold symmetric surfaces, wide range of adsorbates: Sb, Bi, Ag, Cu, Au

- quasicrystals still have sharp diffraction peaks (unlike disordered solids)

- for a 5-fold symmetry the ratio of wavevectors of two lowest order peaks is the golden ratio

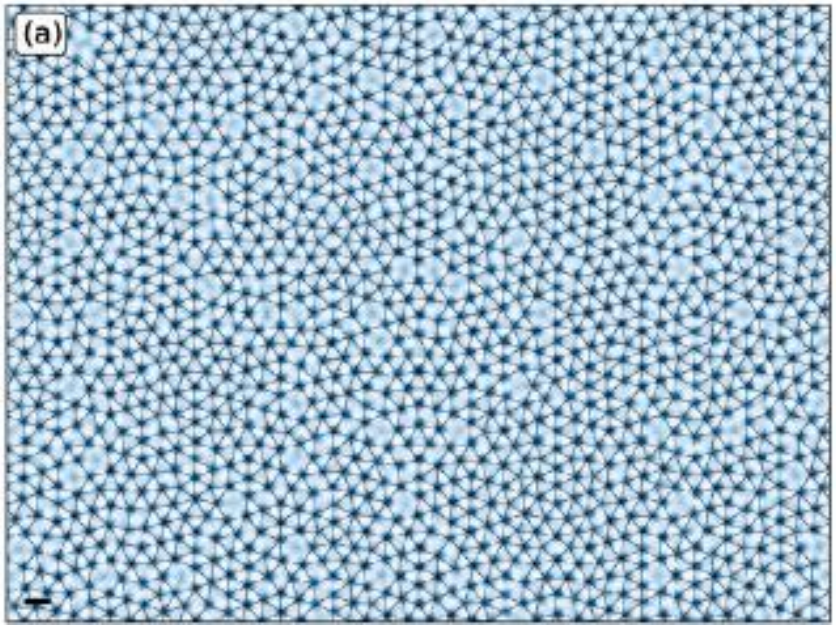
$$\tau = (1+\sqrt{5})/2 \approx 1.618...$$



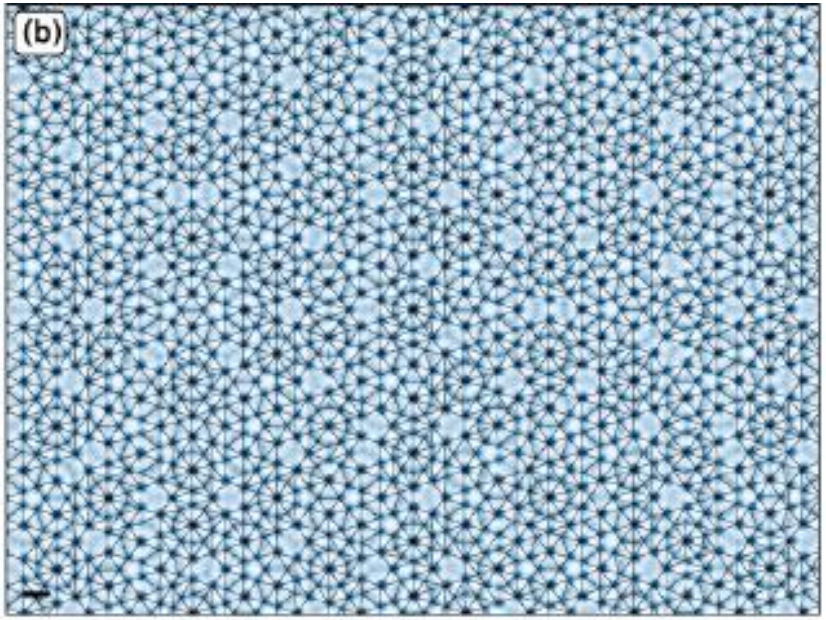
2D film on 5-fold surface

Elastic Substrate-adsorbate interaction: $\Delta F_{\text{int}} = -\gamma k_B T \int d\vec{r} n_{qc}(\vec{r}) n(\vec{r})$

Competes against ΔF which favors triangular symmetry
→ similar to Frenkel-Kontorova model, but allows for defects



γ=0.1: "melting", first pentagons appear



γ=0.4: fully pseudomorphic, peaks line up with qc motifs

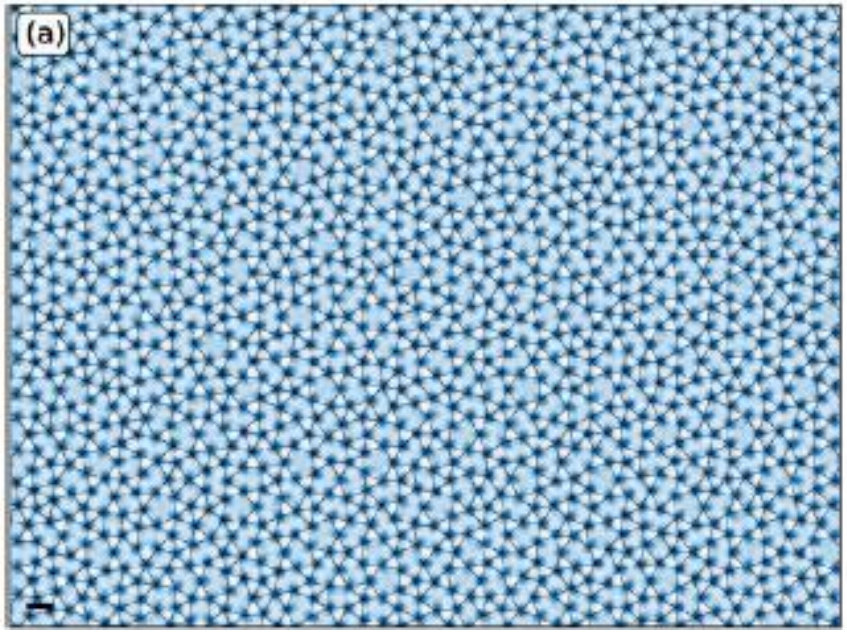
J. Rottler, M. Greenwood, and B. Ziebarth ,
J. Phys.: Condens. Matter **24**, 135002 (2012)

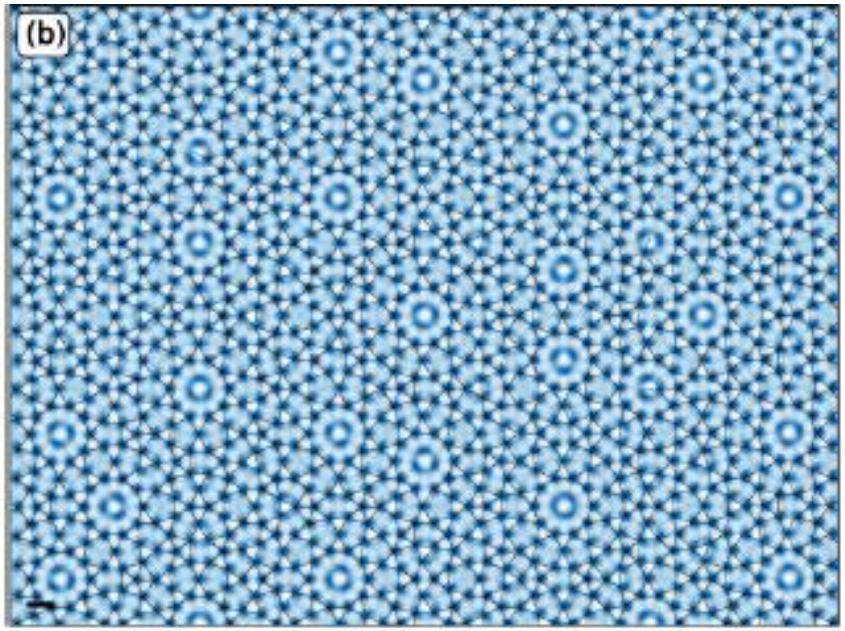
2D film on 5-fold surface: reversed coupling

$$\Delta F_{\text{int}} = -\gamma k_B T \int d\vec{r} n_{qc}(\vec{r}) n(\vec{r})$$

γ= - 0.15: triangles form on top of 10-fold symmetry centers

γ= - 0.4: trend increases, but no qualitative change

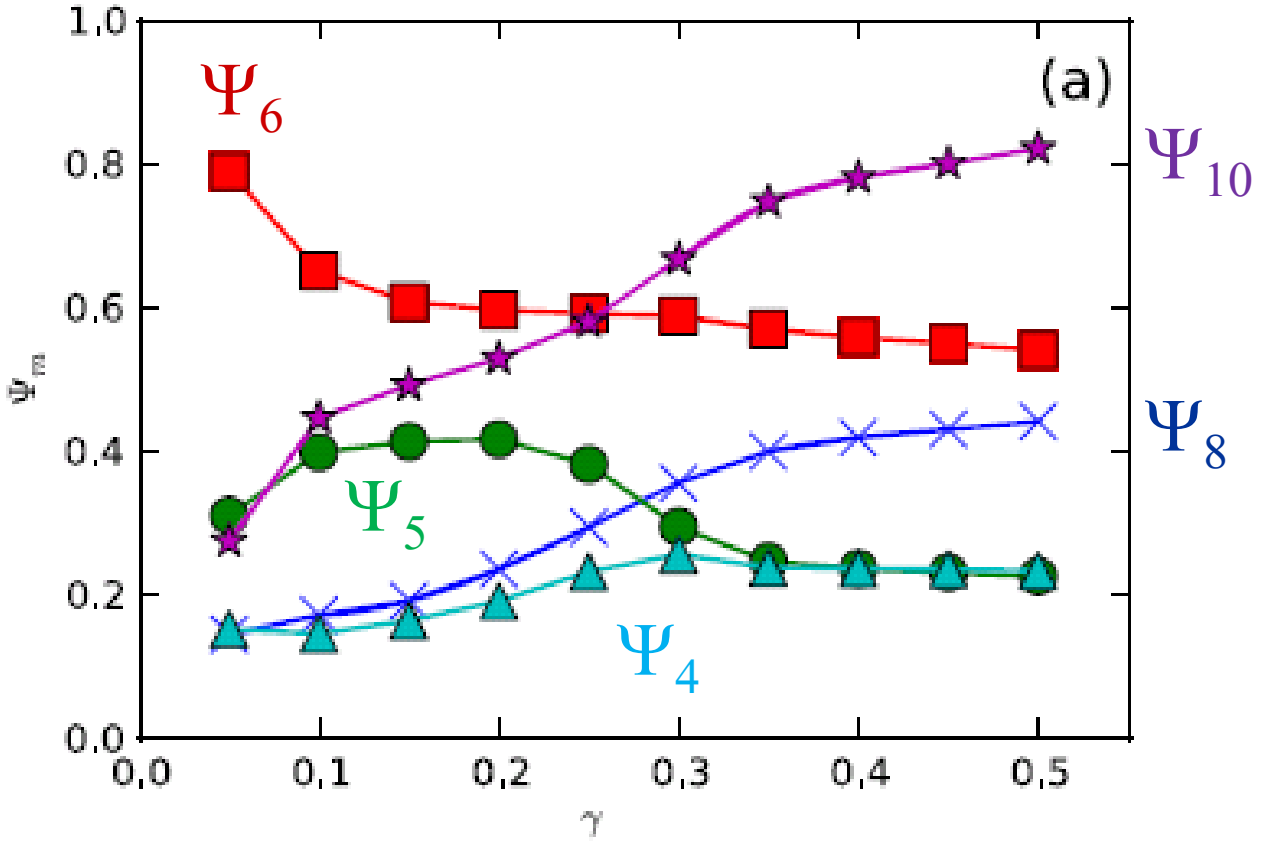




2D film on 5-fold surface – order parameters

m-fold order parameter:

$$\Psi_m = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{n_i}\left|\sum_{j=1}^{n_i} e^{im\Theta_{ij}}\right|$$



Summary

- The Phase Field Crystal: a new simulation technique that describes the emergent properties of complex materials on atomic length and diffusive time scales

- Averages over explicit transport mechanism → many orders of magnitude faster than MD

- Captures a wide range of materials phenomena on semiquantitative level: grain boundary energies, defect energetics, grain growth, epitaxial growth, dislocation dynamics and plasticity

- Provides new insights: on 5-fold quasicrystalline surfaces, transition from freely floating film to fully pseudomorphic phase occurs via a distinct intermediate phase with dominant 5-fold symmetry

- Future challenges: connect quantitatively to atomistics, characterize defect structures (especially in 3D)