Non-equilibrium pattern formation in materials physics

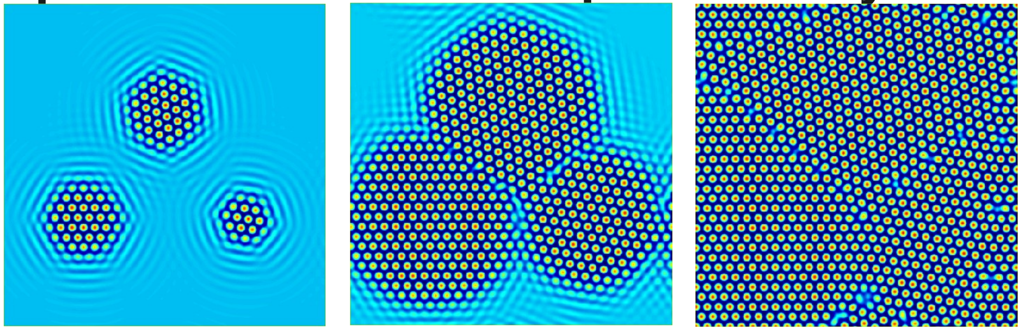
Ken Elder (not Peter Voorhees)

Talk 1 : pattern formation in “uniform” systems

spinodal decomposition
(Cahn Hilliard)
order/disorder transtions
(Allen Cahn)

sharp interface limits
universal scaling

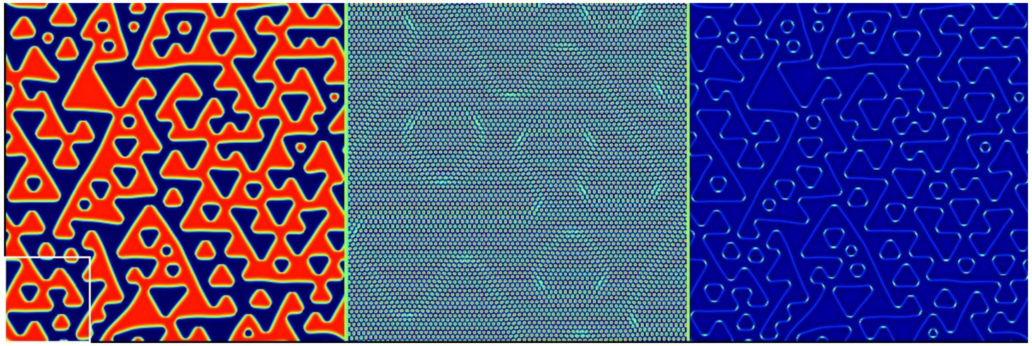
Talk 2 : pattern formation in “periodic” systems



Rayleigh Benard convection
(Swift Hohenberg)
crystal growth
(Phase Field Crystal)

elasticity
dislocations

Talk 3 : pattern formation in “uniform” systems with elasticity



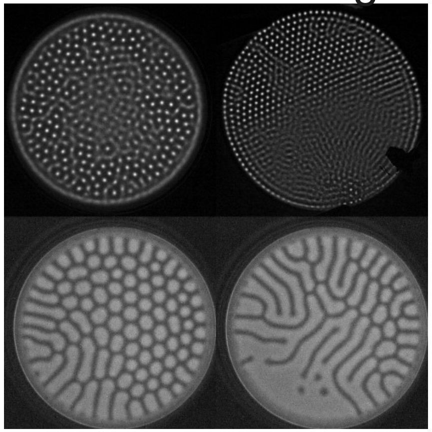
Amplitude expansions
crystal growth

micron simulations
with atomic resolution

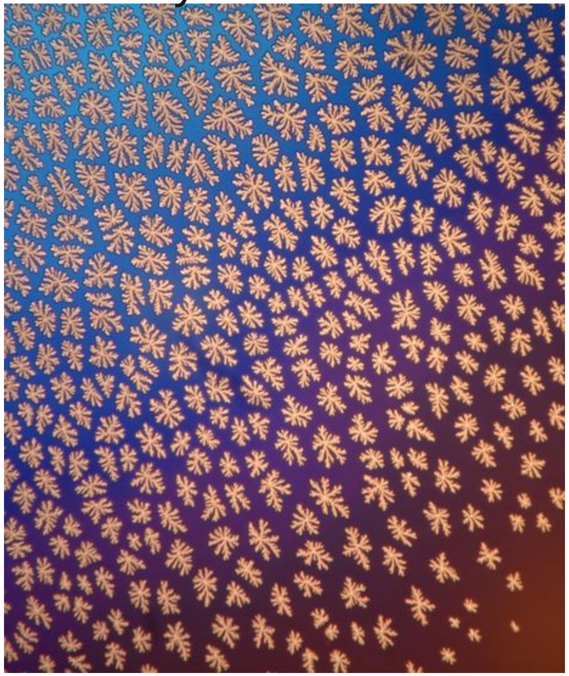
Lightning

$\sim 10^4$ m ~ 10 km

Electric discharge

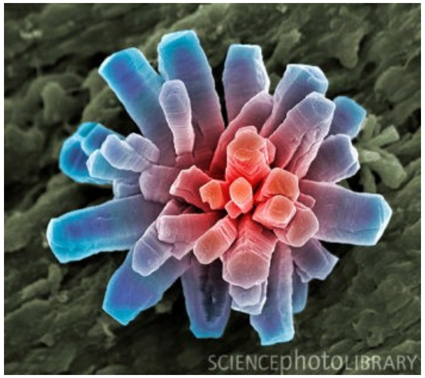


Polymer thin film



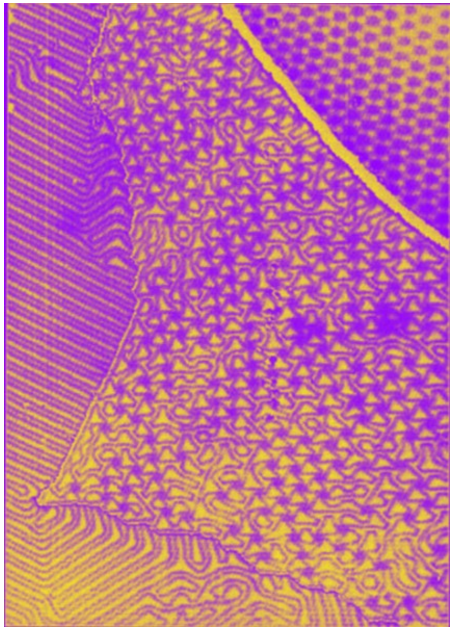
~100µm

Calcium phosphate



~ 100 nm

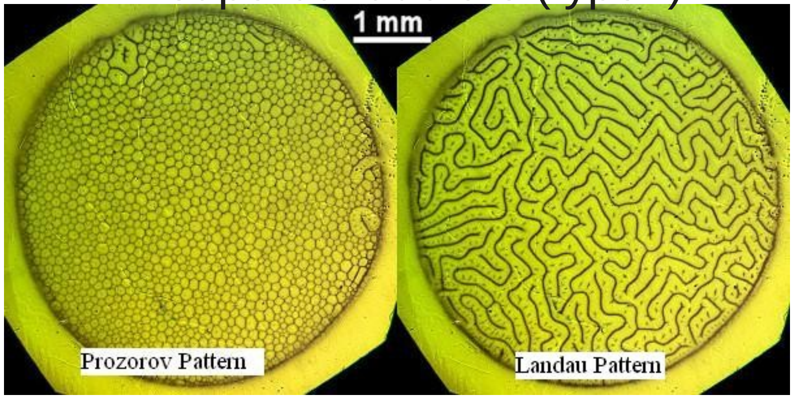
Cu on Ru



~ 100 nm

Bacteria colonies

superconductors (type I)



~ 10 mm

Non-equilibrium pattern formation in materials physics

Why do we care?

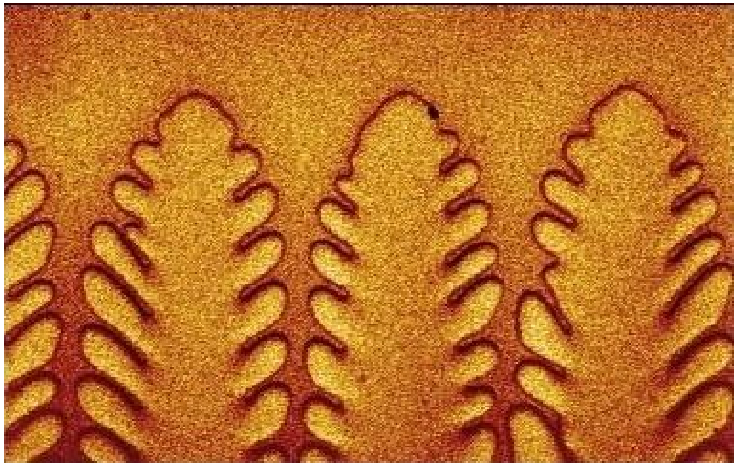
1) very few solids in equilibrium due long lived transients/driving forces

long lived transient states
- never get to equilibrium

eg., polycrystals
-- crystal

http://www-cms.llnl.gov/mstd_page/mchar/microscopy/images/eqx_grains.jpg

driving forces
- always out of equilibrium



eg., directional
solidificaiton

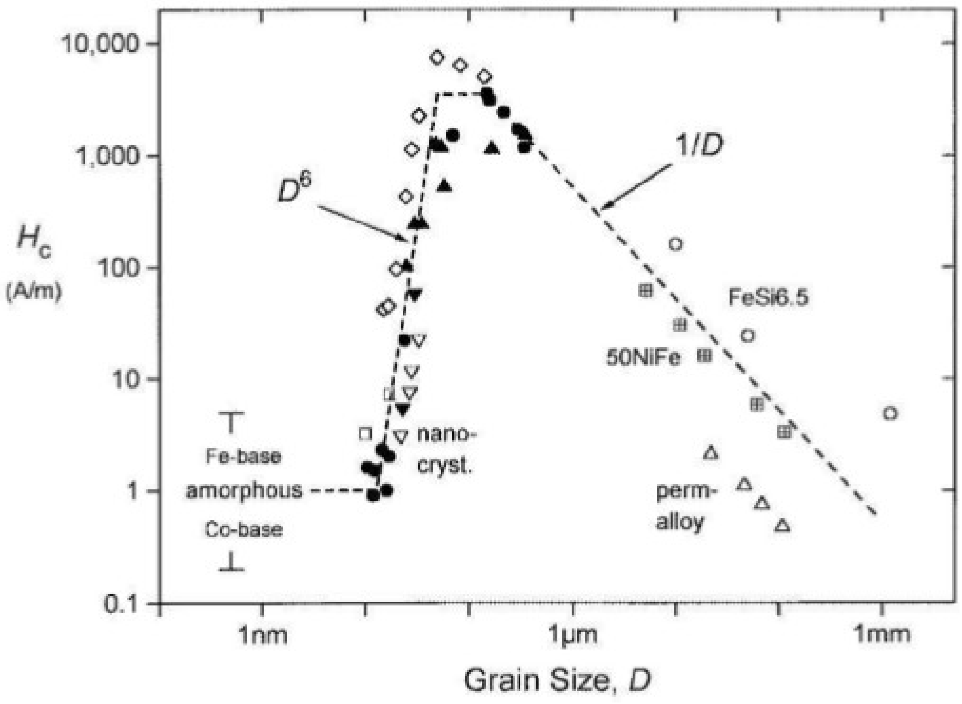
http://milou.msc.cornell.edu/solidification.html

Non-equilibrium pattern formation in materials physics

Why do we care?

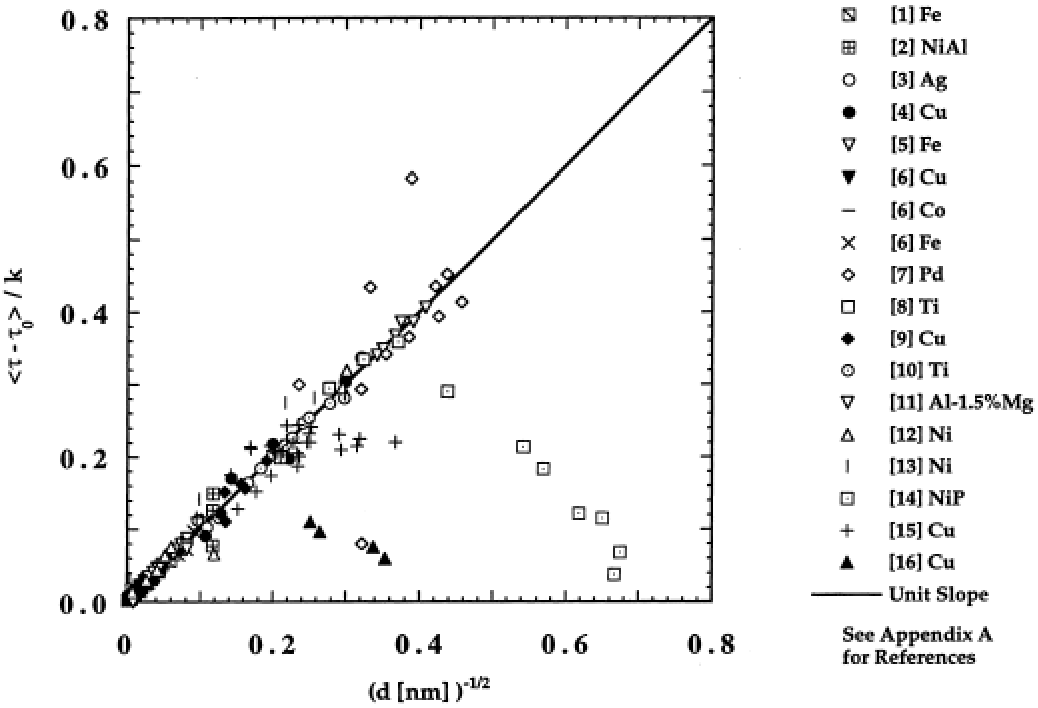
2) Microstructures influences material properties

Magnetic coercivity vs grain size



Herzer in *Handbook of Magnetic Materials*
Ed Buschow, v 10, ch 3 (1997)

Yield stress vs (grain size)$^{-1/2}$



Masumura etal, Acta Mater.
***46**, 4527 (1998)*

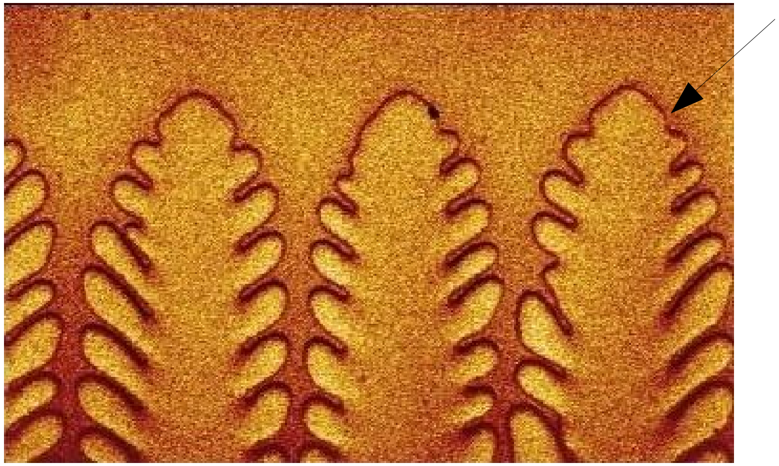
Non-equilibrium pattern formation in materials physics

Basic physics

Patterns formation controlled by

type of defects

Grain boundary



Liquid/solid
interface

interaction of defects

Dislocations – interact through elastic fields

Liquid/solid surface – interact through diffusion

How do we model such patterns using **continuum fields**?

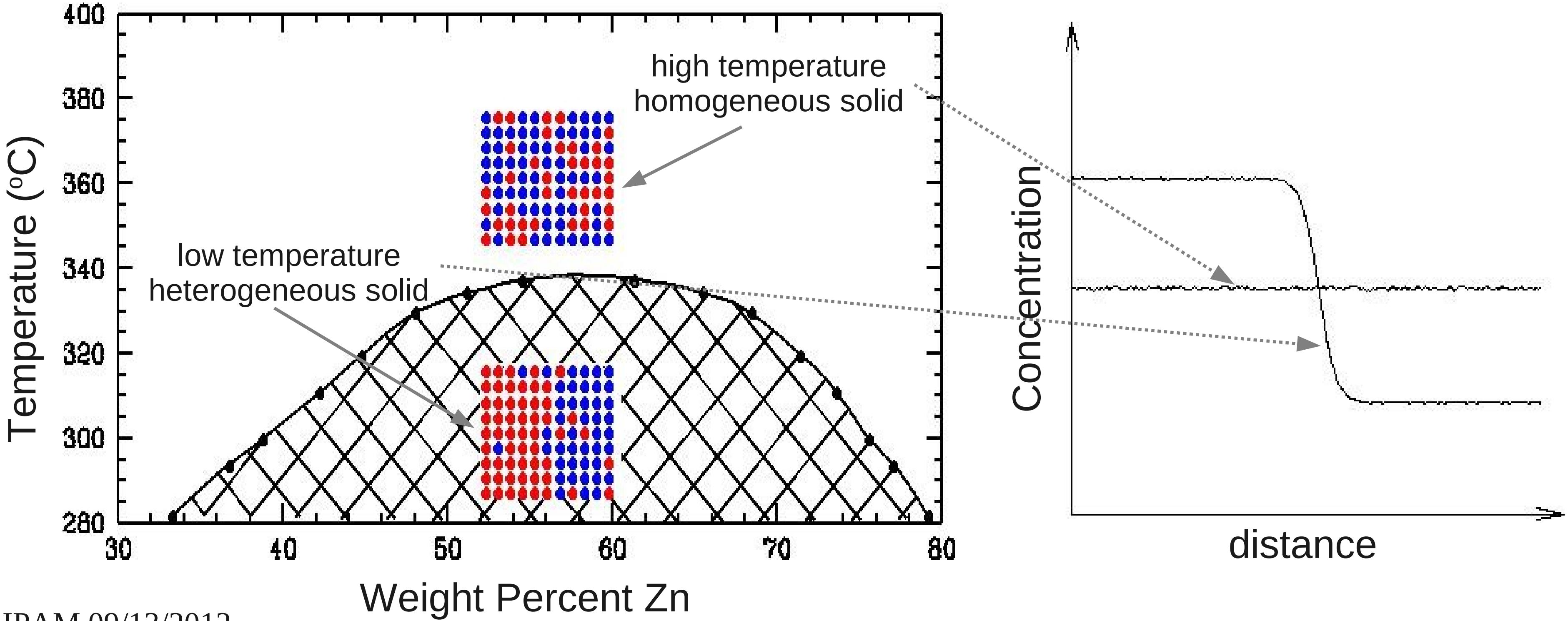
Non-equilibrium pattern formation in materials physics

1st case : systems defined by **uniform scalar real fields**, i.e.,

Cahn/Hilliard (model B)
Allen/Cahn (model A)
Alloy solidification (model C = A + B)
continuum elasticity theory

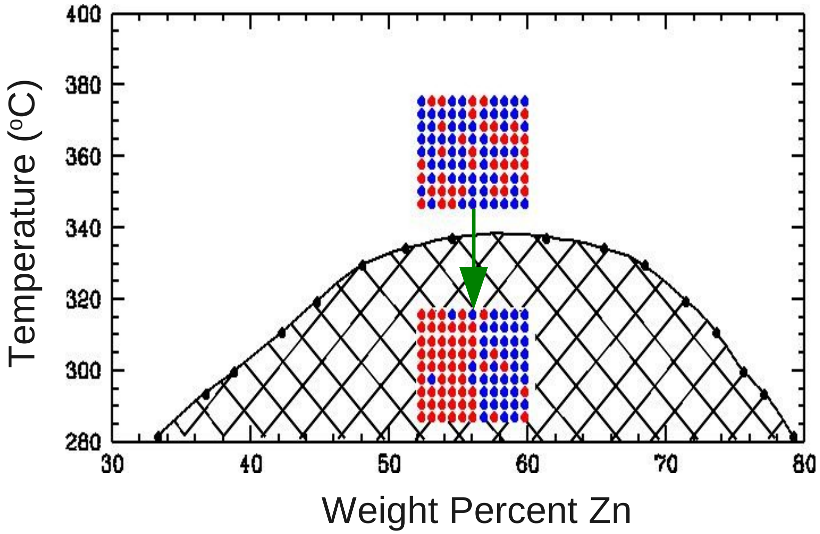
Describe spatially uniform fields (concentration, magnetization, displacement,...)

Example: Binary Alloy
AlZn phase diagram



Example non-equilibrium phenomena: spinodal decomposition

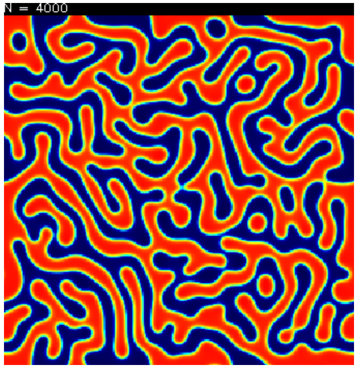
Quench homogenous solid into two phase regime



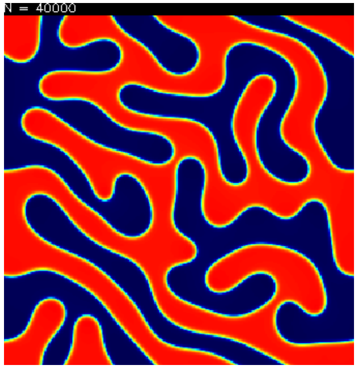
Spontaneous phase separation into
Zn and Al rich domains following quench

Time dependence of domain size?
Spatial distribution of domains?

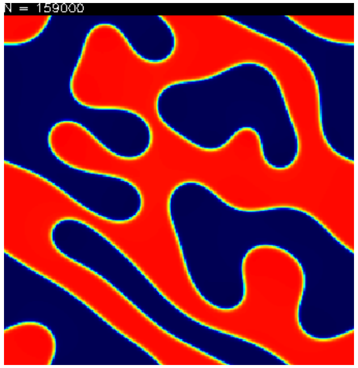
t = 400



t = 4000



t = 16000



How do we model such processes using continuum (phase) fields?

Basic ingredients

1) Identify **field**(s) that characterizes pattern, eg., concentration, sublattice concentration, polarization, magnetization, charge density....

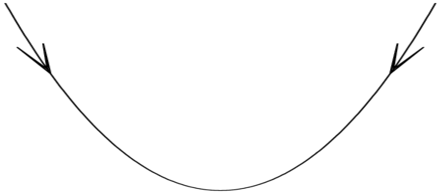
2) Construct **free energy** functional (F) ~ symmetry arguments

$$\text{typically } F \sim \int d\vec{r}\,\left(Bulk + Surface\right)$$

How many phases?
1st order, 2nd order transition?

3) Assume dissipative dynamics driven to **minimize F**

$$\frac{\partial \phi}{\partial t} \sim -\frac{\delta F}{\delta \phi}$$



Goal

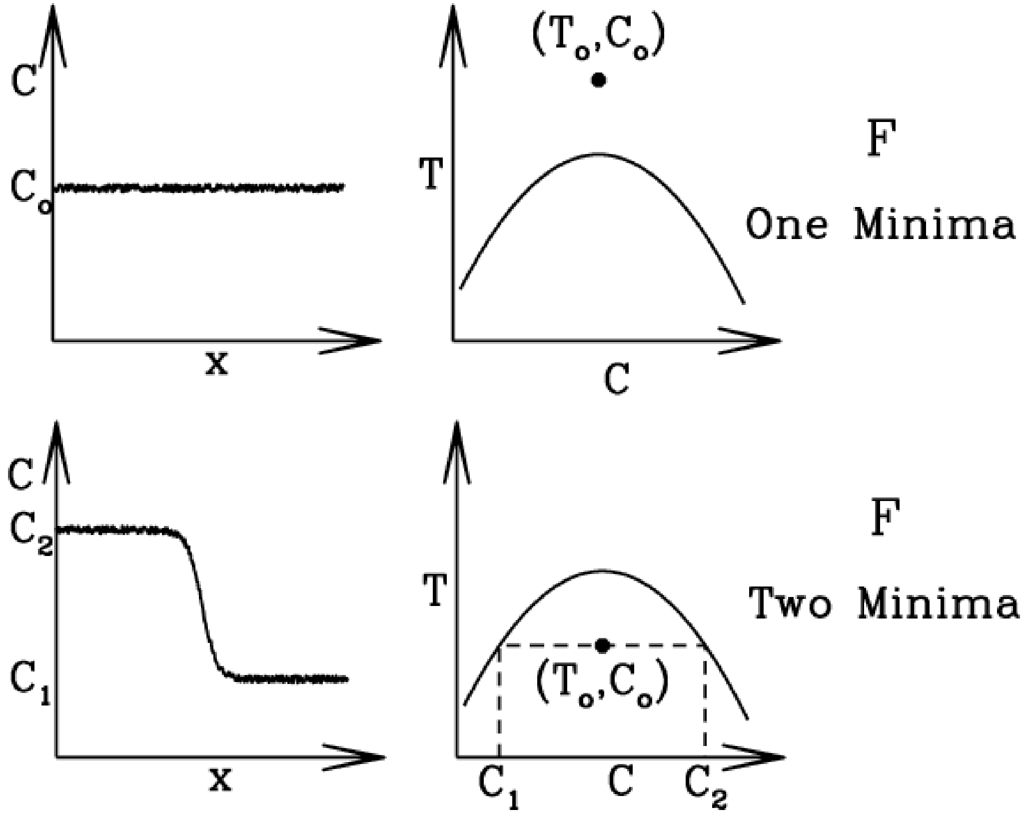
put in equilibrium properties → $\boxed{\dfrac{\partial \phi}{\partial t} \sim -\dfrac{\delta F}{\delta \phi}}$ → **predict non-equilibrium properties**

or derive from scratch ....

Example: Spinodal Decomposition

1) Identify **field**(s) that characterizes pattern, eg., concentration, sublattice concentration, polarization, magnetization, charge density...

2) Construct **free energy** functional (F) ~ symmetry arguments



High Temperature

Low Temperature

Example: Spinodal Decomposition

Free energy functional

$$F = \int d\vec{r}\left(f(C) + g(\vec{\nabla} C)\right)$$

$$\text{where } f(C) \equiv \text{ bulk contribution}$$

$$g(\vec{\nabla} C) \equiv \text{ surface contribution}$$

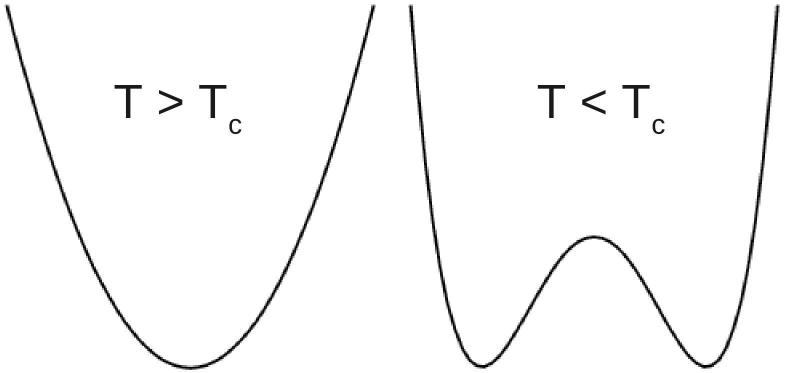
$$f(C) \sim \text{ one minima high temp, two minima low temp}$$

Simplest form

$$\boxed{f(c) = \frac{r}{2}c^2 + \frac{u}{4}c^4}$$

$$\text{where } c \equiv C - 1/2$$

$$\text{and } r \equiv a(T - T_c)$$



Example: Spinodal Decomposition

Free energy functional

$$F = \int d\vec{r}\left(f(C) + g(\vec{\nabla} C)\right)$$

where $f(C) \equiv$ bulk contribution

$g(\vec{\nabla} C) \equiv$ surface contribution

$g(\vec{\nabla} C)$ – surfaces cost energy

$$g(\vec{\nabla} C) = c \sum K_n \nabla^{2\mathrm{n}} c$$

– symmetry: no odd powers (i.e., $c \vec{\nabla} c$)
i.e., direction of gradeint doesn't matter

– long wavelength limit

$$g(\vec{\nabla} c) = -\frac{K_1}{2} c \nabla^2 c = \frac{K_1}{2} \left|\vec{\nabla} c\right|^2$$

(forms ~ equivalent inside integral)

Example: Spinodal Decomposition

Minimal free energy functional

$$F = \int d\vec{r} \left(\frac{r}{2} c^2 + \frac{u}{2} c^4 + \frac{K}{2} |\vec{\nabla} c|^2 \right)$$

Dynamics

- concentration – locally conserved quantity

→ continuity equation: $\frac{\partial c}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0$

where $\vec{J} \equiv$ particle flux

- assume: flux ~ gradient in chemical potential, i.e.,

$$\vec{J} = -M \vec{\nabla} \mu$$

where $M \equiv$ Mobility and $\mu =$ chemical potential $= \frac{\delta F}{\delta c}$

- combine

$$\frac{\partial c}{\partial t} = M \nabla^2 \frac{\delta F}{\delta c}$$

Example: Spinodal Decomposition

Minimal free energy functional

$$F = \int d\vec{r} \left(\frac{r}{2} c^2 + \frac{u}{2} c^4 + \frac{K}{2} \left| \vec{\nabla} c \right|^2 \right)$$

Dynamics

$$\frac{\partial c}{\partial t} = M \nabla^2 \frac{\delta F}{\delta c}$$

So ... minimal model of spinodal decomposition

$$\frac{\partial c}{\partial t} = M \nabla^2 \left(r c + u c^3 - K \nabla^2 c \right)$$

$$r = a\left(T - T_c\right)$$

Cahn-Hilliard Equaton
or
“Model B”

Minimal model of spinodal decomposition

$$\frac{\partial c}{\partial t} = M \nabla^2 \left(r c + u c^3 - K \nabla^2 c \right)$$

Cahn-Hilliard Equation or “Model B”

For non-conserved fields (eg., sublattice concentration)

$$\frac{\partial \phi}{\partial t} = - M \frac{\delta F}{\delta \phi}$$

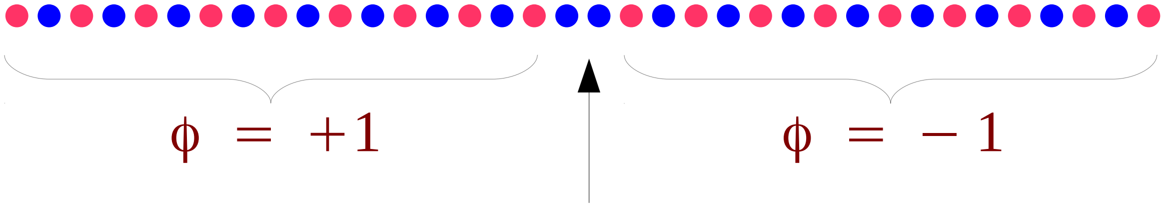
Allen-Cahn Equation or “Model A”

“Model C” – one conserved field, one non-conserved field
- eg., eutectic solidification, liquid/solid field and concentration

“Models D, E, F ...” Halperin and Hohenberg classification scheme
Rev. Mod. Phys. **49**, 435 (1977)
- alphabet soup of models

Model A properties (easier than Model B)

eg., $\phi \equiv$ sublattice concentration



$\phi = +1$

$\phi = -1$

defect
anti-phase
domain wall

$$\frac{\partial \phi}{\partial t} = -M \frac{\delta F}{\delta \phi}$$ with free energy in long wavelength limit,

$$F = \int d\vec{r} \left(f(\phi) + \frac{K}{2} \left| \vec{\nabla} \phi \right|^2 \right)$$

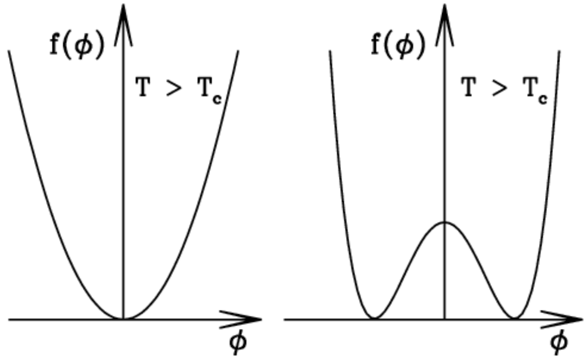
gives

$$\frac{\partial \phi}{\partial t} = M \left(K \nabla^2 \phi - \frac{\partial f}{\partial \phi} \right)$$

Model A properties: Equilibrium

Consider 2nd order phase transition with minimal free energy, i.e.,

$$f(\phi) = r\frac{\phi^2}{2} + u\frac{\phi^4}{4} \text{ where } r \equiv a(T - T_c)$$

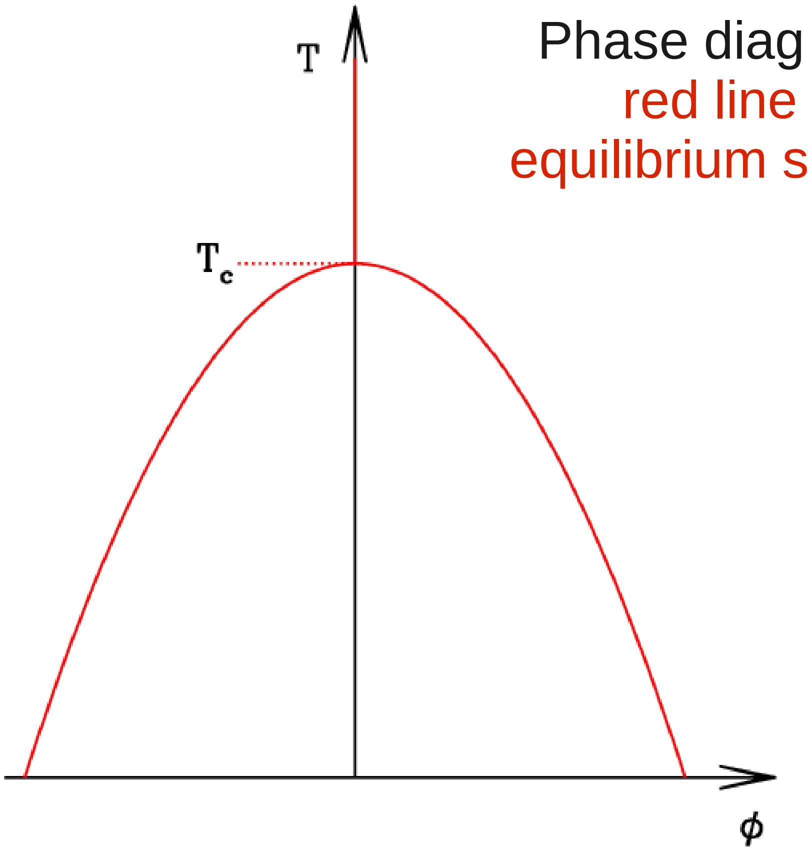


Equilibrium (mean field)

$$T > T_c\text{: minima at } \phi_{eq} = 0$$

$$T < T_c\text{: minima at } \frac{\partial f}{\partial \phi} = 0$$

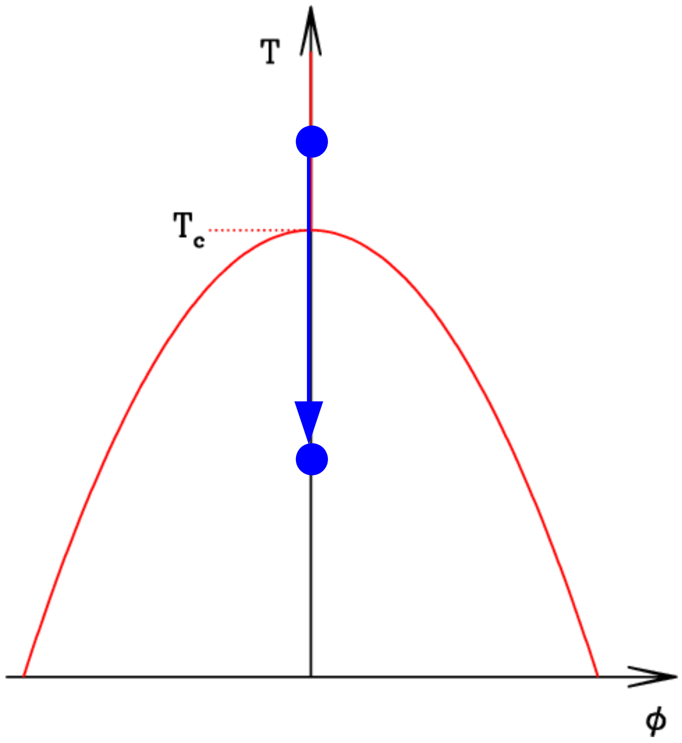
$$\rightarrow \phi_{eq} = \pm\sqrt{|r|/u}$$



Phase diagram
red line
equilibrium states

Model A properties: Dynamics

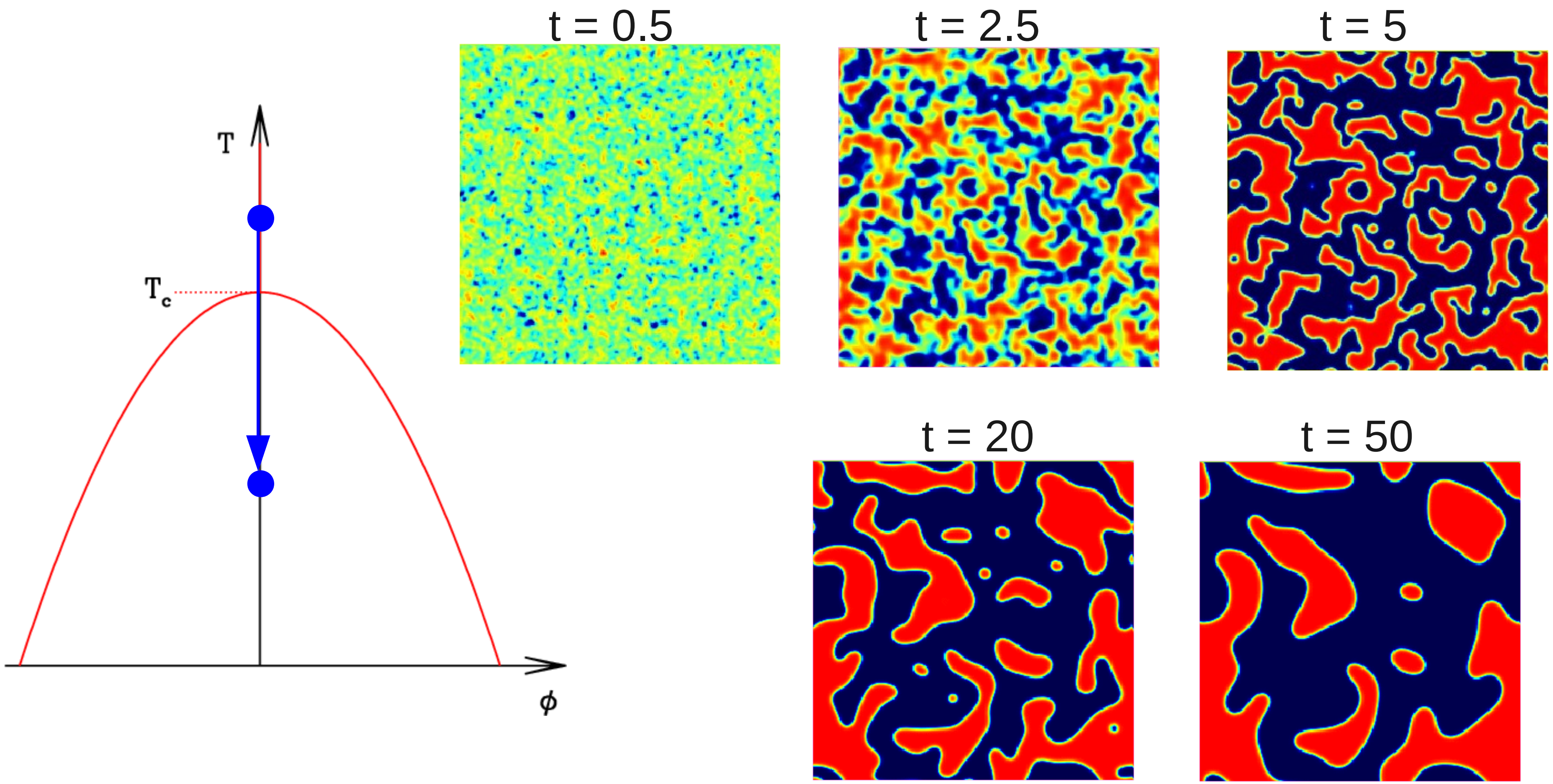
Pattern formation following rapid temperature quench



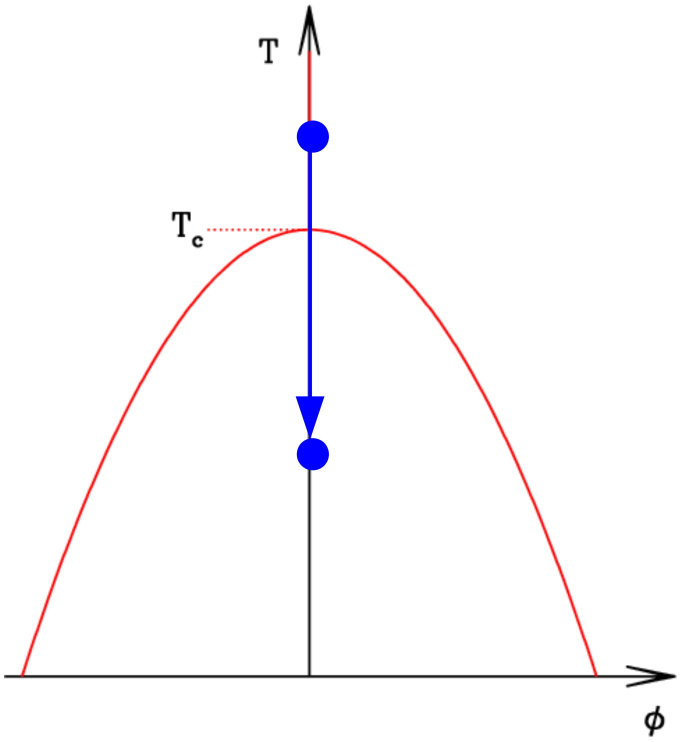
$\Phi = + (|r|/u)^{1/2}$ $\Phi = - (|r|/u)^{1/2}$

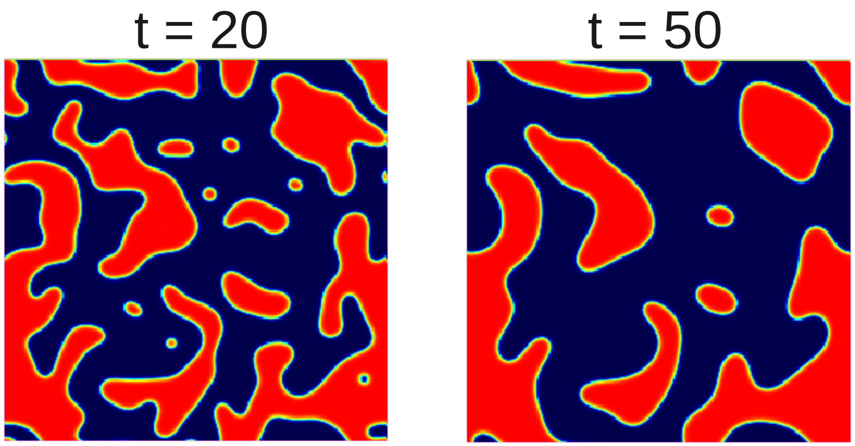
Model A properties: Dynamics

Pattern formation following rapid temperature quench



Pattern formation following rapid temperature quench

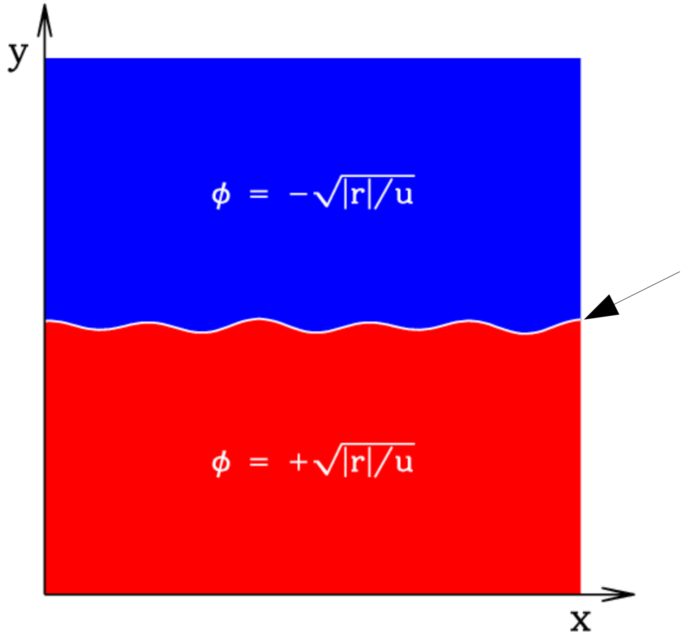



t = 20

t = 50

Late stages – interface dynamics

Simplify – consider slowly varying interface



interface
position
$\equiv h(x,t)$

defect
motion

$h(x,t) = ?$

Late stages – interface dynamics

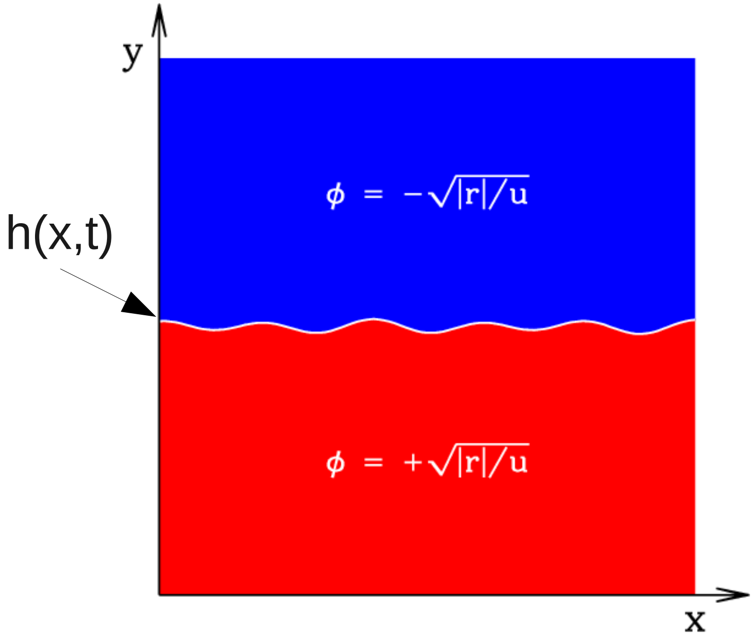
Simplify – consider slowly varying interface

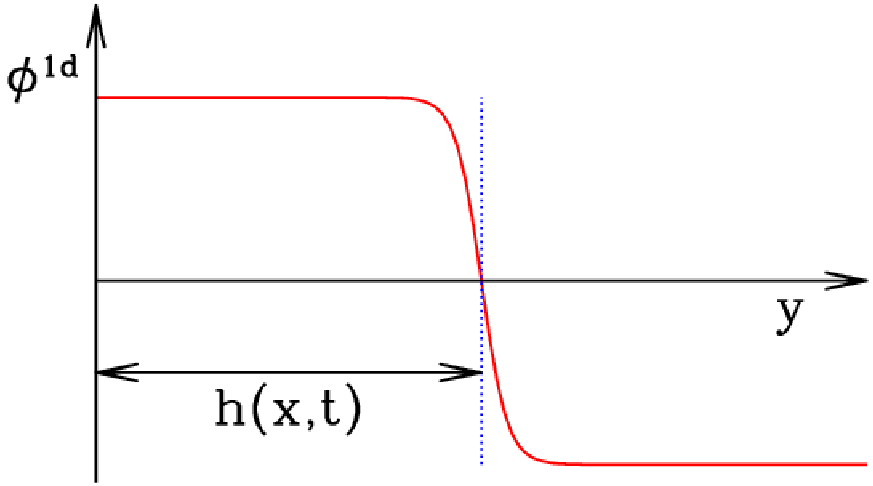
Expand around 1d planar interface,
i.e., assume

$$\phi(x, y, t) = \phi^{1d}(x, y - h(x, t))$$

where ϕ^{1d} defined by equation

$$K \frac{d^2 \phi^{1d}}{dy^2} - \left(\frac{\partial f}{\partial \phi} \right)_{\phi^{1d}} = 0$$





If $f = -|r|\phi^2/2 + u\phi^4/4$, then

$$\phi^{1d}(y) = \sqrt{\frac{|r|}{u}} \tanh\left(\frac{y}{2\zeta} \right)$$

where $\zeta \equiv \sqrt{K/2|r|}$

$=$ correlation length

Late stages – interface dynamics

substitute $\phi(x,y,t) \approx \phi^{1d}(y-h(x,t))$ into $\frac{\partial \phi}{\partial t} = M\left(K\nabla^2\phi - \frac{\partial f}{\partial \phi}\right)$

$$-\frac{\partial \phi^{1d}}{\partial u}\frac{\partial h}{\partial t} = M\Bigl(K\underbrace{\Bigl[\cancel{\frac{\partial^2 \phi^{1d}}{\partial u^2}} - \frac{\partial \phi^{1d}}{\partial u}\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 \phi^{1d}}{\partial u^2}\left(\frac{\partial h}{\partial x}\right)^2\Bigr] - \cancel{\left(\frac{\partial f}{\partial \phi}\right)_{\phi^{1d}}}}_{\text{cancel: by definition of } \Phi^{1d}}\Bigr)$$

$$-\frac{\partial \phi^{1d}}{\partial u}\frac{\partial h}{\partial t} = MK\left[\frac{-\partial \phi^{1d}}{\partial u}\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 \phi^{1d}}{\partial u^2}\left(\frac{\partial h}{\partial x}\right)^2\right]$$

To lowest order in h,

$$\boxed{\frac{\partial h}{\partial t} = D\frac{\partial^2 h}{\partial x^2}}$$

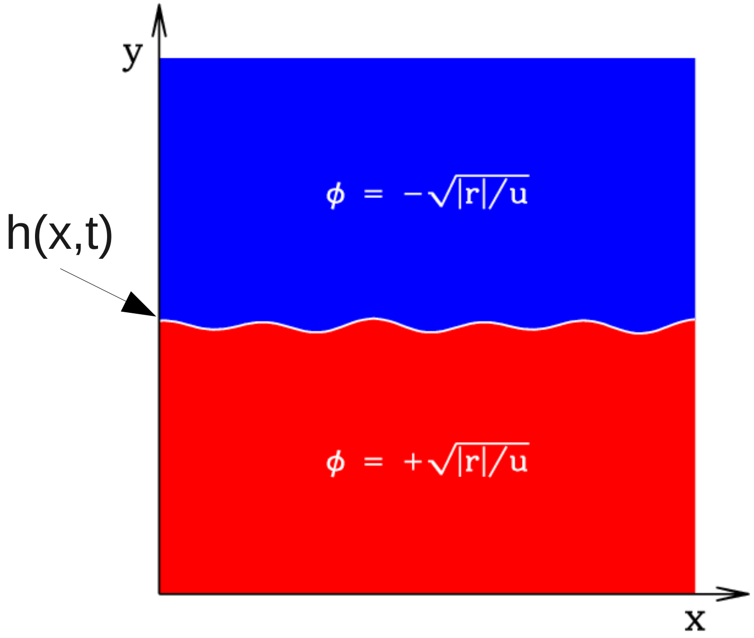
Diffusion Equation!

where D ≡ MK = interface diffusion constant

Late stages – interface dynamics

$$\frac{\partial h}{\partial t} = D \frac{\partial^2 h}{\partial x^2}$$

Diffusion Equation!



Couple of points

1) Result independent of form of f(Φ), i.e., never needed to specify Φ^{1d} --- **universal behavior of interface**

2) Diffusion equation:

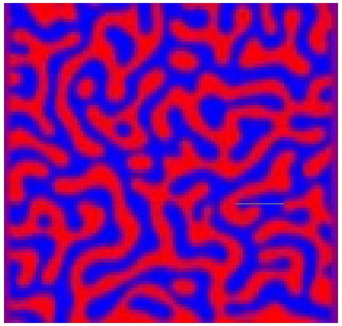
$$\hat{h}(q,t) = \exp(-q^2 t)\hat{h}(q,0)$$

space/time scaling, let $u = qt^{1/2}$ then

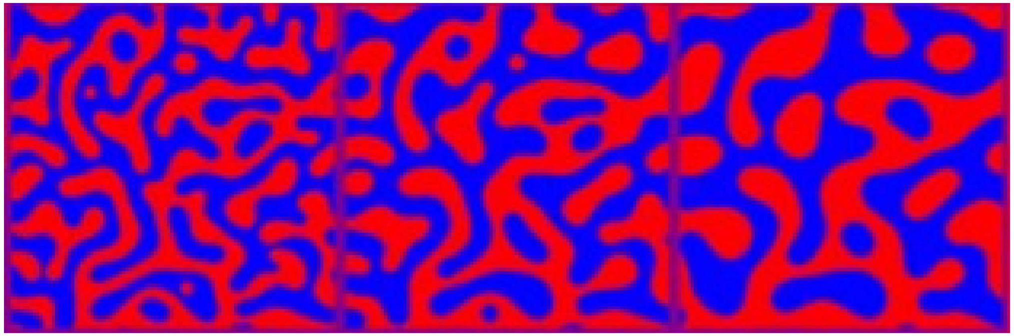
$$\hat{h}(u) = \exp(-u^2)\hat{h}(0)$$

space/time scaling, let $u = qt^{1/2}$ then

$t = t_o$

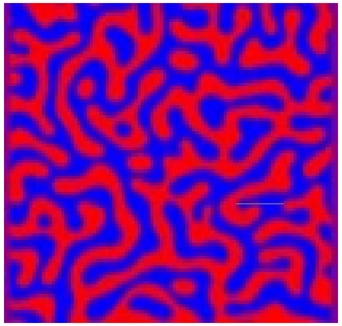


time evolution

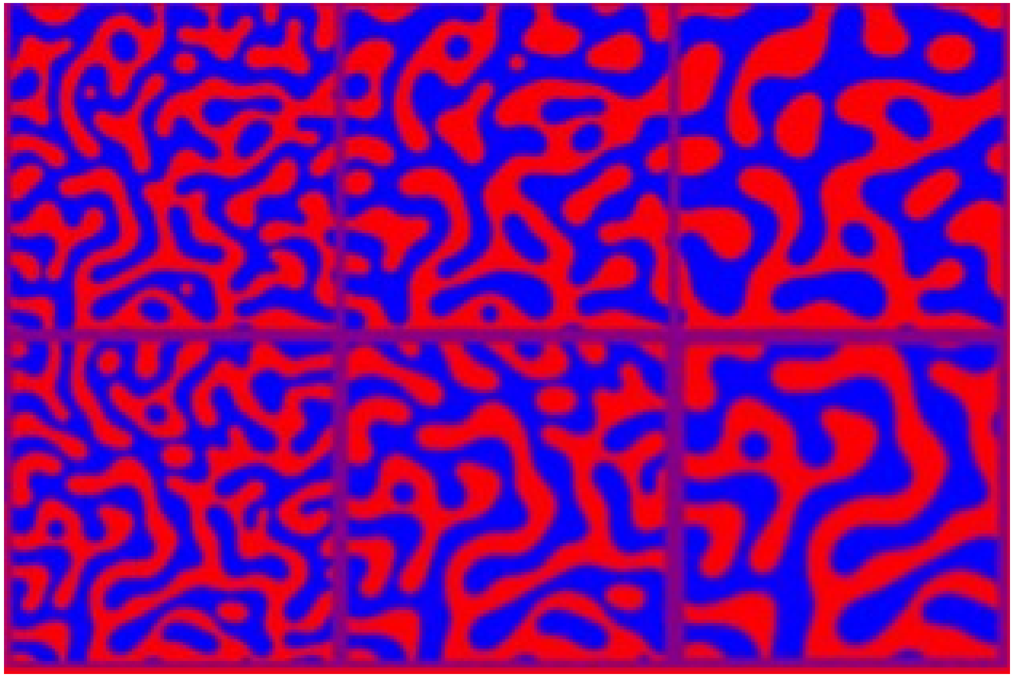


space/time scaling, let $u = qt^{1/2}$ then

$t = t_o$



time evolution



statistically equivalent

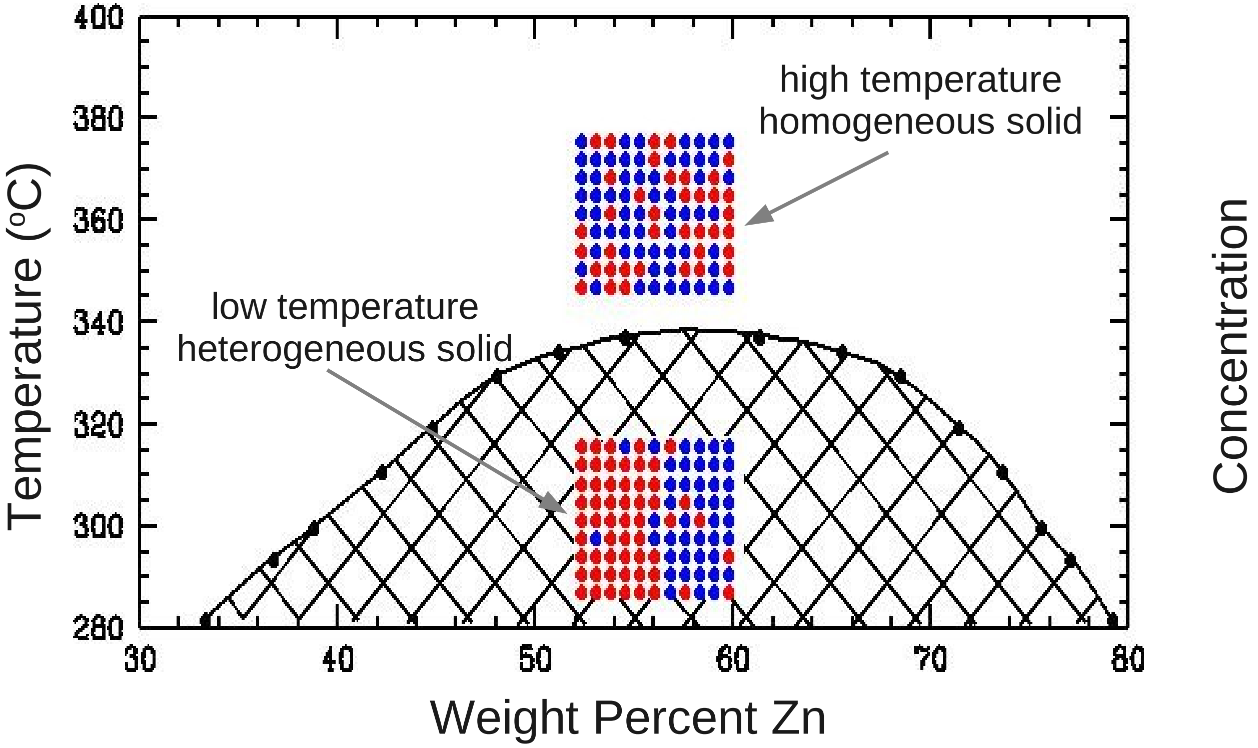
space rescaling

$$\vec{r} \;\rightarrow\; \vec{r}\left(t/t_o\right)^{1/2}$$

Expect average length scale (domain size) to grow ~ $(\text{time})^{1/2}$

Model B properties: conserved field, spinodal decomposition

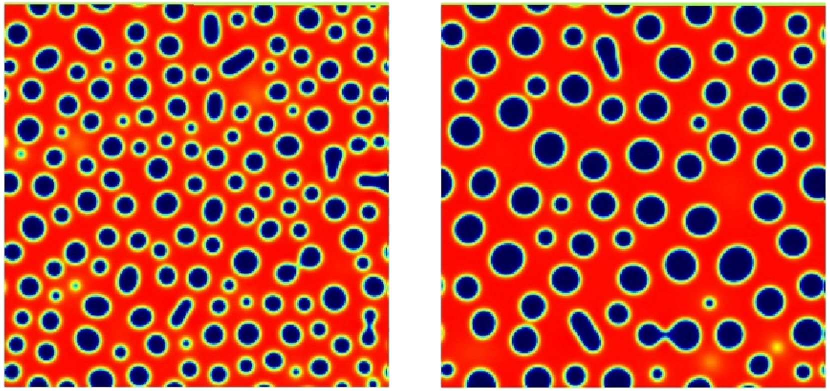
Example: Binary Alloy
AlZn phase diagram



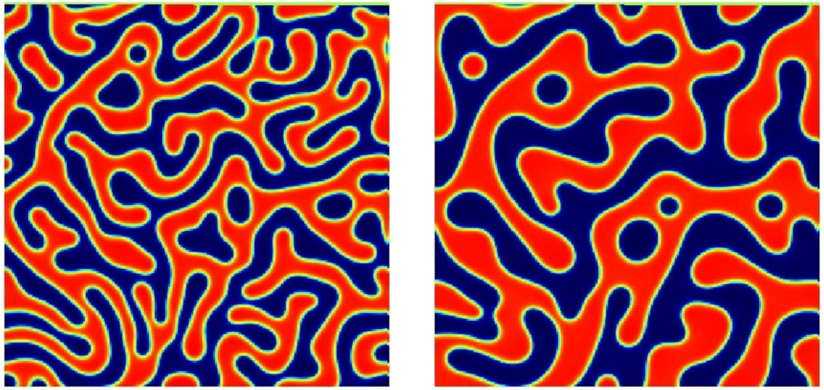
Pattern formation following rapid temperature quench

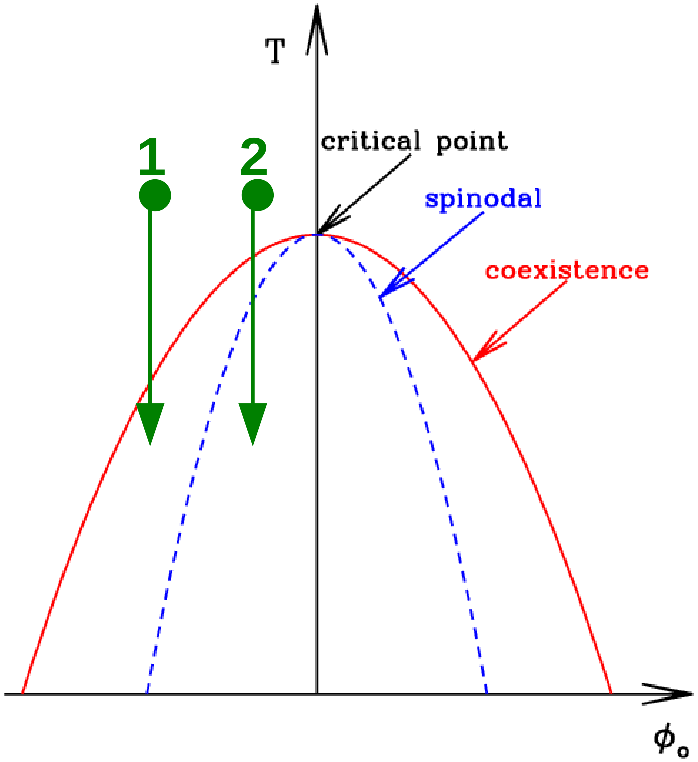
Late stages

1 Ostwald ripening: droplet growth



2 Spinodal decomposition: interface motion

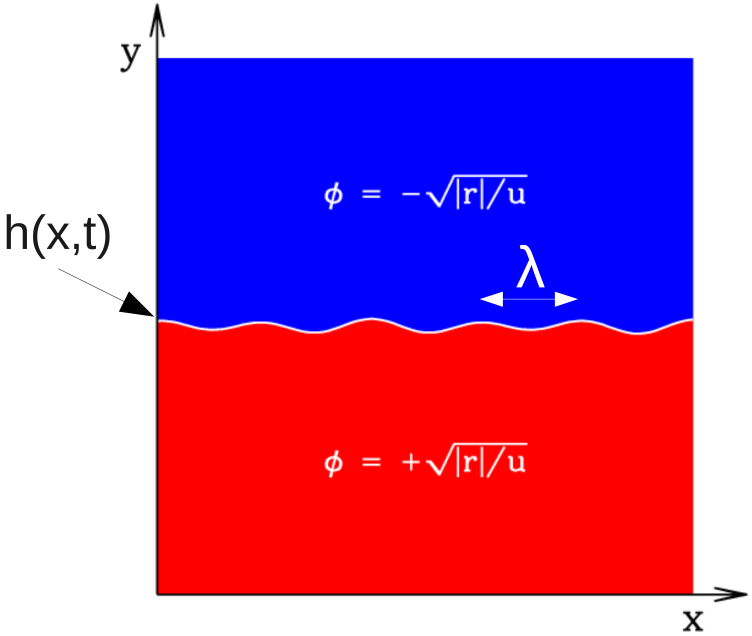




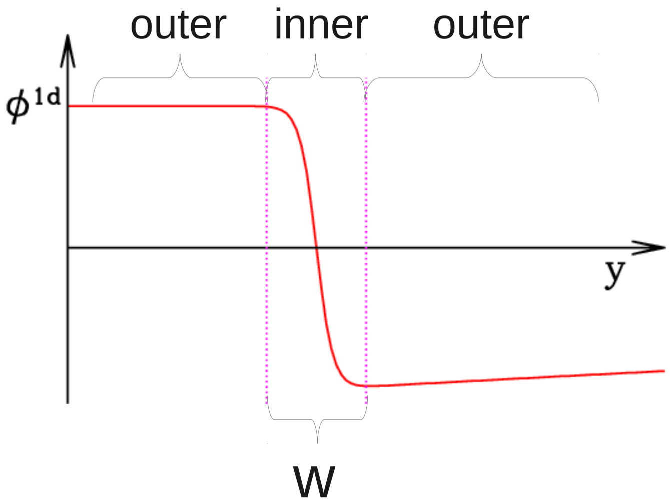
Pattern formation following rapid temperature quench

Late stages: Interface dynamics ~ more complicated than model A

(see for eg., Elder etal PRE **64**, 21604 (2001))



Split problem into “inner” and “outer” regions



introduce small parameter

$$\varepsilon \equiv \frac{w}{\lambda}$$

- solve in “inner” region

$$\phi^{\text{in}}(x,y,t) \approx \phi^{1d}(y-h(x,t)) + \delta\phi$$

- solve in “outer” region (diffusion equation)

$$\phi^{\text{out}}(x,y,t) \approx \delta\phi$$

match solutions at inner/outer boundary

Pattern formation following rapid temperature quench

Late stages: Interface dynamics

(see for eg., Elder etal PRE **64**, 21604 (2001))

Obtain in sharp interface limit (ε << 1)

- mass conservation for normal velocity

$$\Delta\phi V_n \approx \Delta\phi \frac{\partial h}{\partial t} = \left[D\, \hat{n}\cdot\vec{\nabla}\,\delta\phi\right]_{y=h^-} - \left[D\hat{n}\cdot\vec{\nabla}\,\delta\phi\right]_{y=h^+}$$

- Gibb's Thompson (at y = h)

$$\delta\phi/\Delta\phi = d_o\kappa + \beta V_n$$

- diffusion in bulk

$$\frac{\partial\,\delta\phi}{\partial t} = D\frac{\partial^2\,\delta\phi}{\partial x^2}$$

parameters (d_o, β, D, ΔΦ)
~ depend on specific details
of free energy functional

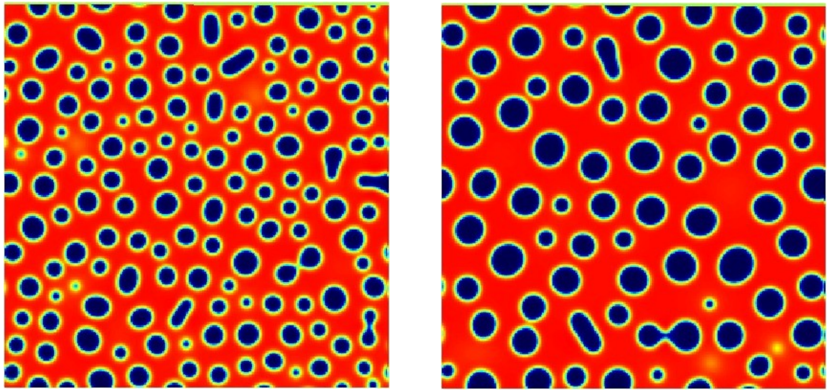
form of equation
~ independent of specific details
of free energy functional

Universal Features

Pattern formation following rapid temperature quench

Late stages: solutions of sharp interface model

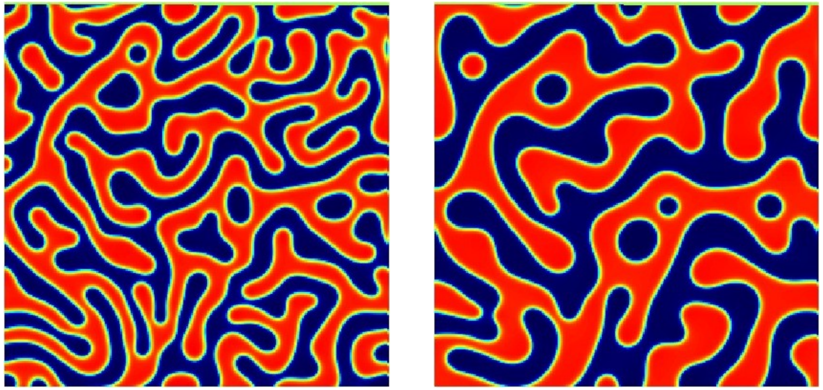
1 Ostwald ripening: droplet growth



Lifshitz Slyozov analysis,
J. Phys. Chem. Solids **19**, 35 (1961)
~ single drop in infinite
supersaturated background

Droplet Radius ~ $(\text{time})^{1/3}$

2 Spinodal decomposition: interface motion



~ slowly varying interface,
$h(x,t) \sim A_q(t)\cos(qx)$

$$A_q(t) \sim f(qt^{1/3})$$

Domain size ~ $(\text{time})^{1/3}$

Non-conserved ordering: Model A, Allen-Cahn Equation

$$\text{Domain size} \sim (time)^{1/2}$$

Conserved ordering: Model B, Cahn-Hilliard Equation

$$\text{Domain size} \sim (time)^{1/3}$$

Dynamic growth exponents, 1/2 and 1/3 thought to be “universal”

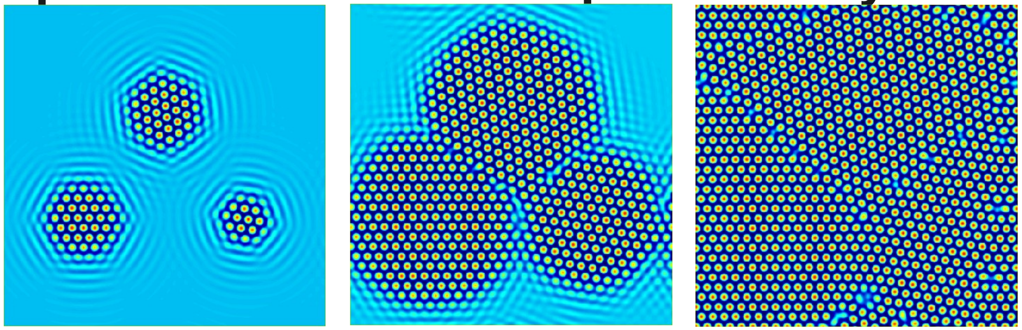
Non-equilibrium pattern formation in materials physics

Talk 1 : pattern formation in “uniform” systems

spinodal decomposition
(Cahn Hilliard)
order/disorder transtions
(Allen Cahn)

sharp interface limits
universal scaling

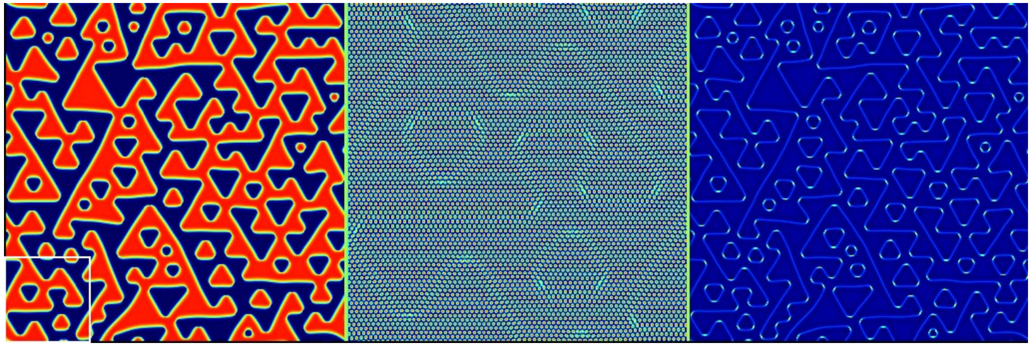
Talk 2 : pattern formation in “periodic” systems



Rayleigh Benard convection
(Swift Hohenberg)
crystal growth
(Phase Field Crystal)

elasticity
dislocations

Talk 3 : pattern formation in “uniform” systems with elasticity

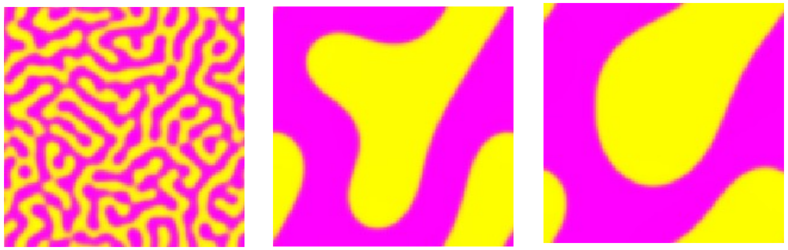


Amplitude expansions
crystal growth

micron simulations
with atomic resolution

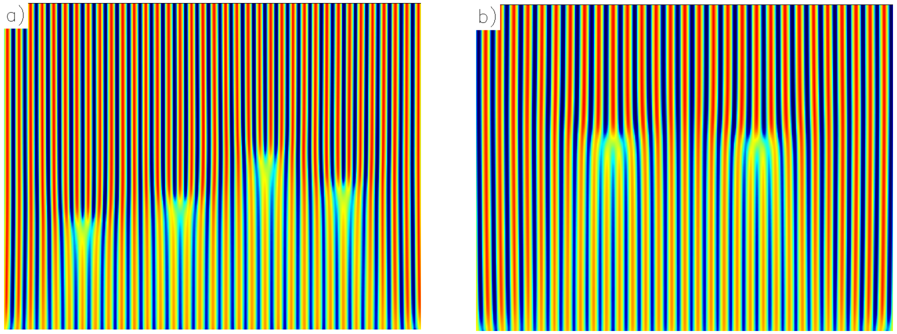
Phase Field Modeling in Periodic Systems

Comparison: uniform versus periodic fields

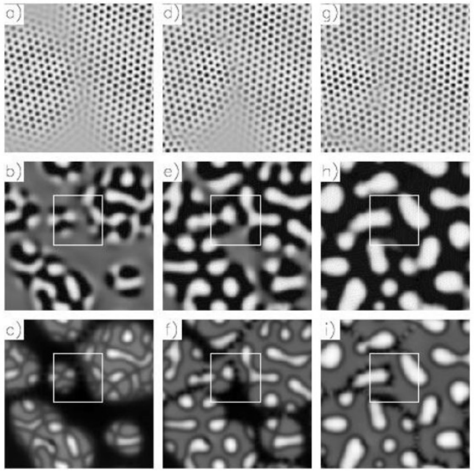


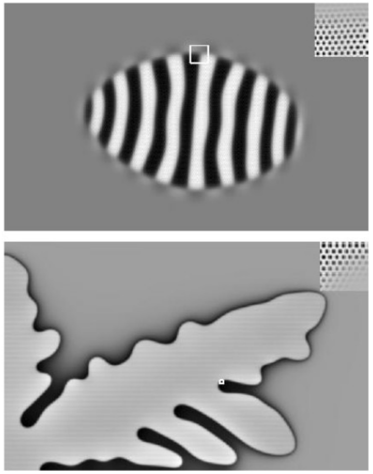
vs

Periodic fields:
non-conserved dynamics
(Swift Hohenberg Equation)



Periodic fields:
conserved dynamics
(Phase field crystal)



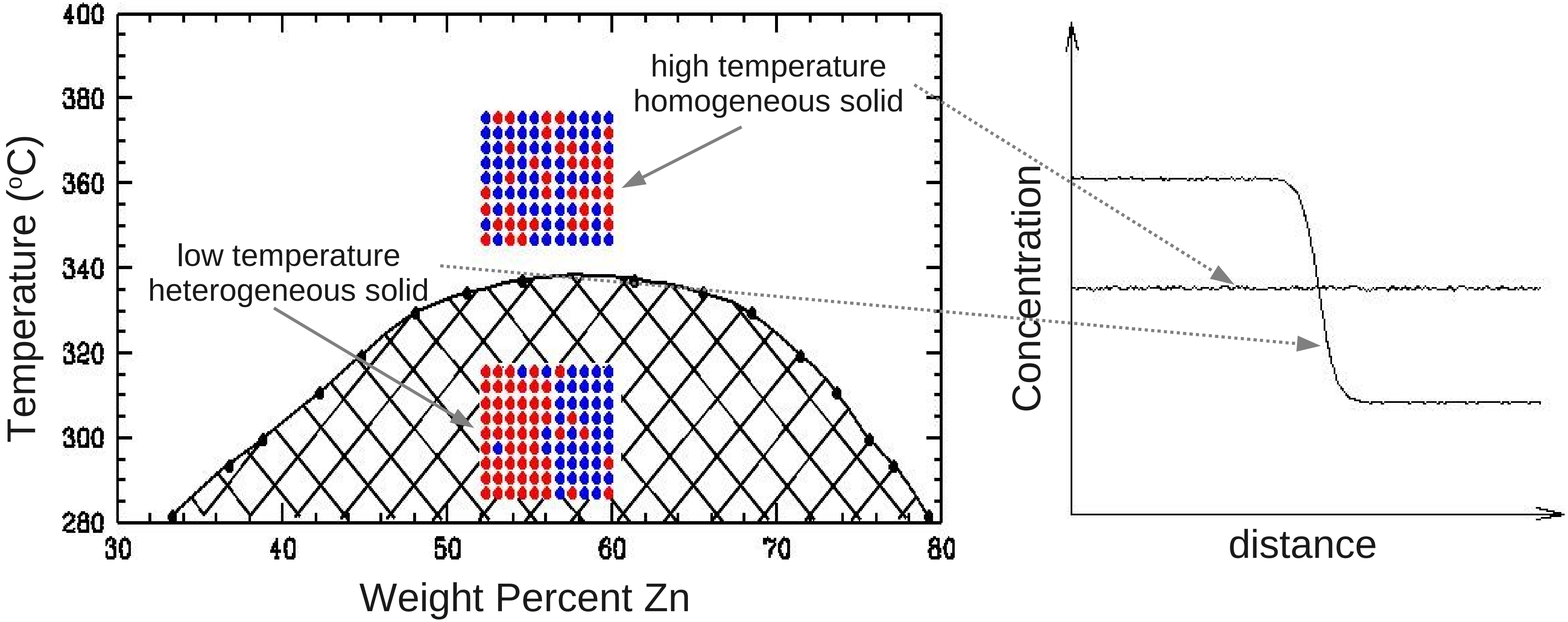


Traditional phase/continuum field theories,

Cahn/Hilliard (model B)
Allen/Cahn (model A)
Alloy solidification (model C = A + B)
continuum elasticity theory

Describe spatially uniform fields (concentration, magnetization, displacement,...)

Example: Binary Alloy
AlZn phase diagram



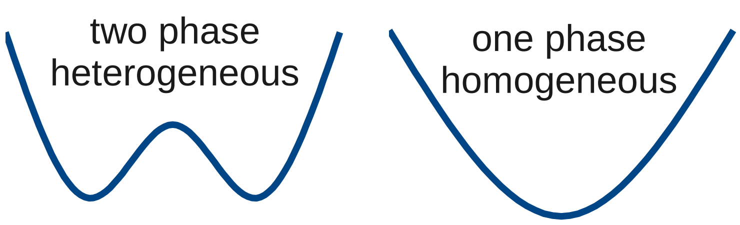
Traditional phase/continuum field theories,

Example: Cahn/Hilliard model of spinodal decomposition

Free energy functional: uniform fields

$$F = \int d\vec{r} \left(f(c) + \frac{K}{2} \left| \vec{\nabla} c \right|^2 \right) \qquad \text{where } c = \text{concentration}$$

bulk



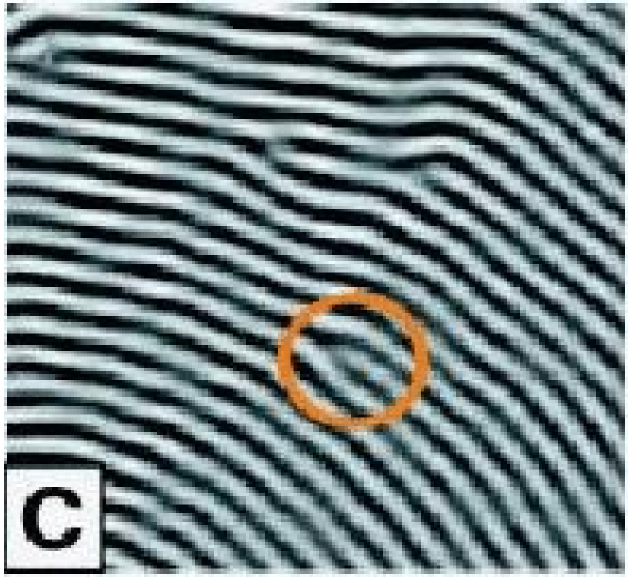
surface

* surface cost energy (K > 0)

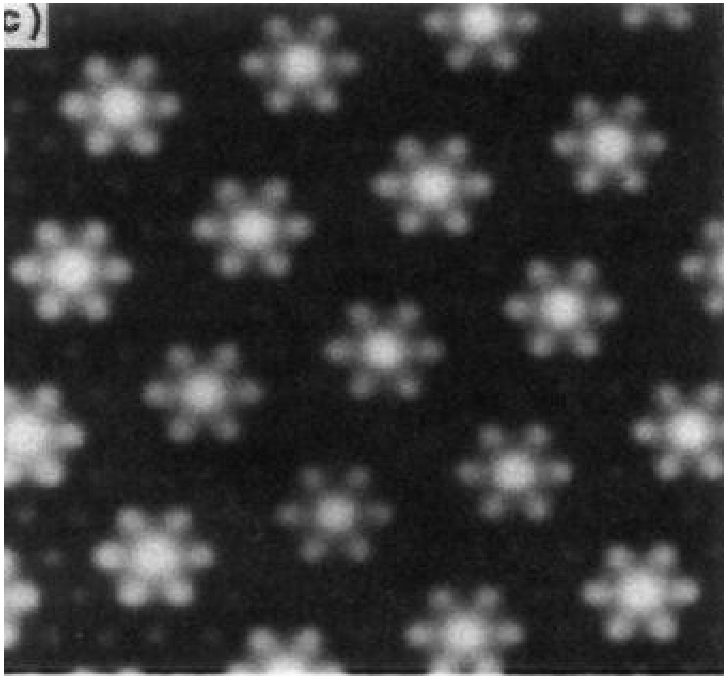
* dynamics driven to minimize F
– eliminate gradients in c

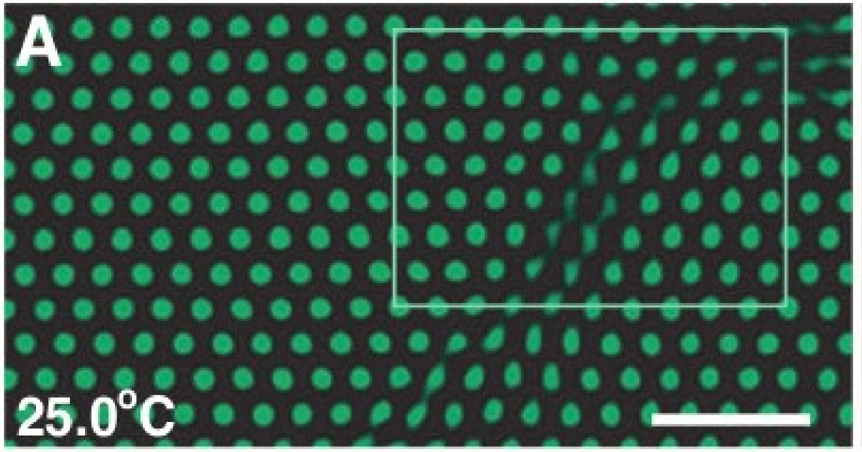
Periodic systems – many in nature

Block copolymer
Harrison etal
Science **290**, 1558 (2000)



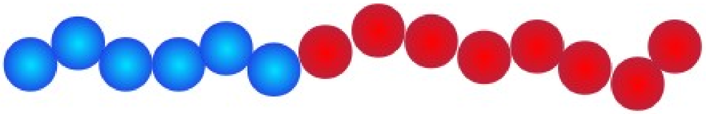
Charge Density Wave
Thomson etal,
PRB **49**, 16899 (1994)

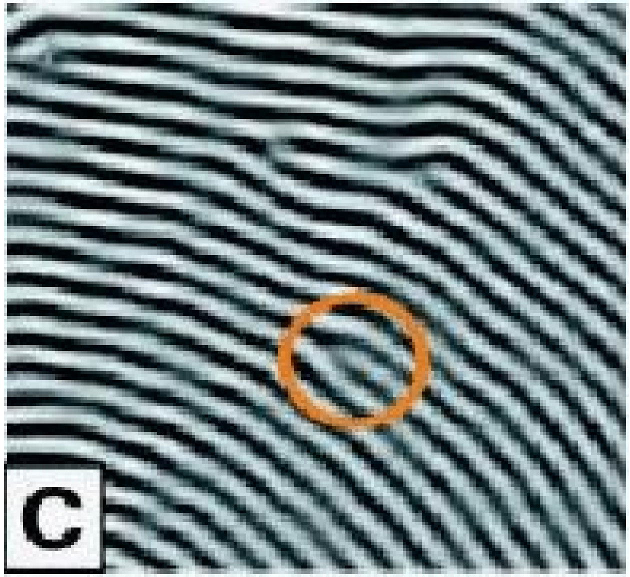




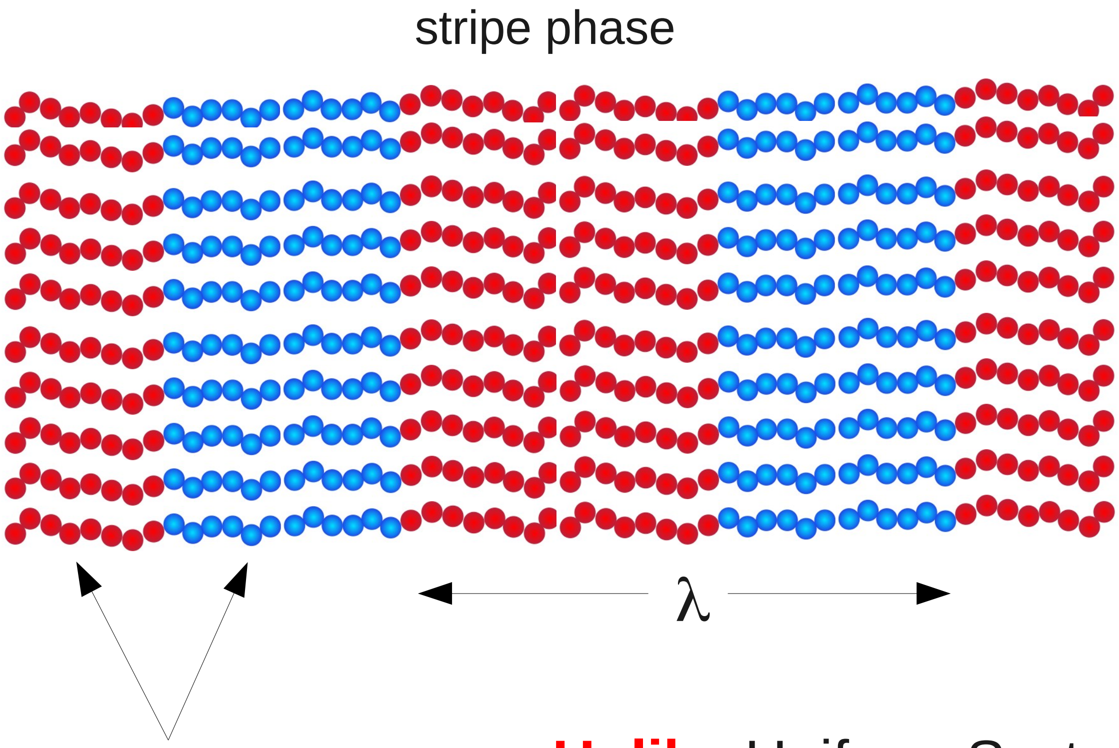
Colloidal Crystals (premelting)
Alsayed, etal
Science **309**, 1207 (2005)

Periodic systems – Eg. Block copolymer





Harrison etal
Sci, **290**, 1558 (2000)

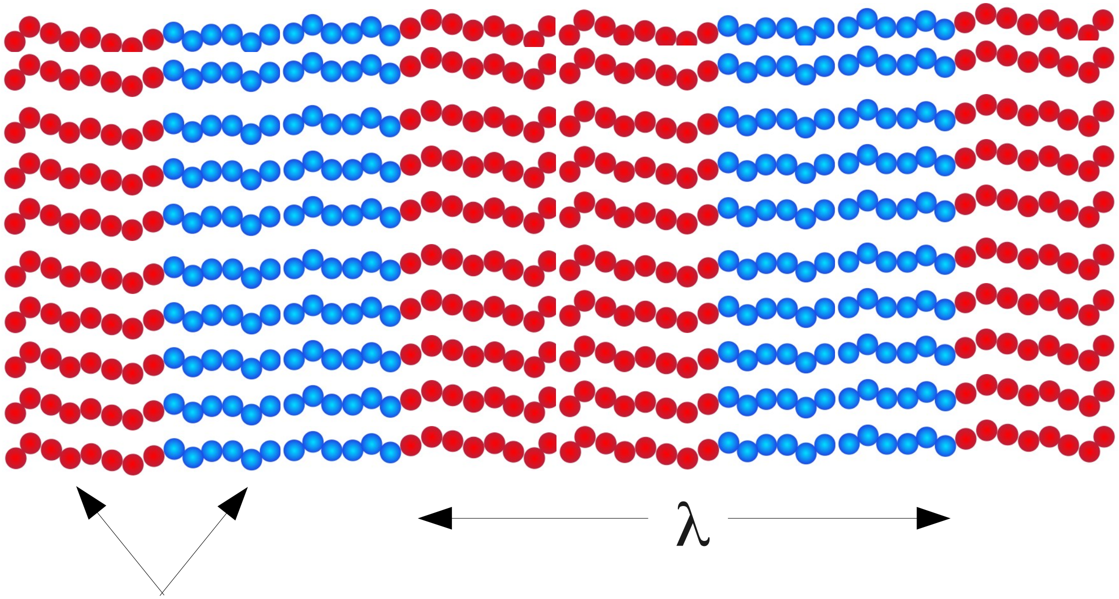


Like Uniform System
- two phases

Unlike Uniform System
- length scale selected

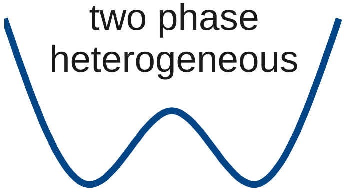
Periodic systems – minimalist free energy

stripe phase



Like Uniform System
- two phases

Unlike Uniform System
- length scale selected



$$-\frac{\varepsilon}{2}\psi^2 + \frac{\psi^4}{4}$$

$$\psi\left(q_o^2+\nabla^2\right)^2\psi$$

Minimalist free energy

Consider $\psi = A\cos(qx) \rightarrow \nabla^2\psi = -q^2\psi$

Periodic systems

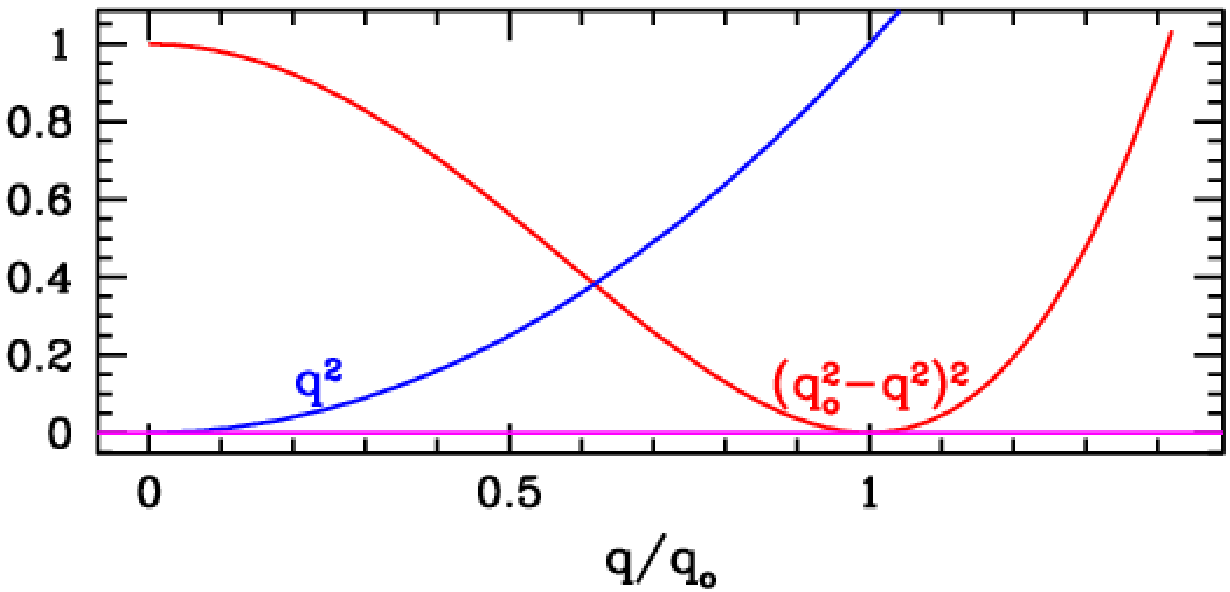
$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \underbrace{\frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2\psi}_{\longrightarrow\; +\left(q_o^2 - q^2\right)^2\left[A\cos(qx)\right]^2}\right)$$

F minima when $q = q_o$

Uniform systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 \underbrace{- \frac{\psi}{2}\nabla^2\psi}_{\longrightarrow\; +q^2\left[A\cos(qx)\right]^2}\right)$$

F minima when $q = 0$



Minimalist free energy

Periodic systems

$$F = \int d\vec{r} \left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

Equilibrium in a one mode approximation

Consider $\underline{\psi = A\cos(qx)}$, then the free energy/length is

$$\frac{F}{a} = \frac{1}{a}\int_0^a d\vec{r} \left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

$$= -\frac{\varepsilon}{4}A^2 + \frac{3}{32}A^4 + \frac{1}{4}\left(q_o^2 - q^2\right)^2 A^2$$

Minimize wrt A, i.e. solve $\frac{dF/a}{dA} = 0$ for A

$$\boxed{A = \frac{2}{\sqrt{3}}\sqrt{\varepsilon - \left(q_o^2 - q^2\right)^2}} \longrightarrow \boxed{\frac{F}{a} = -\frac{1}{6}\sqrt{\varepsilon - \left(q_o^2 - q^2\right)^2}}$$

Minimalist free energy

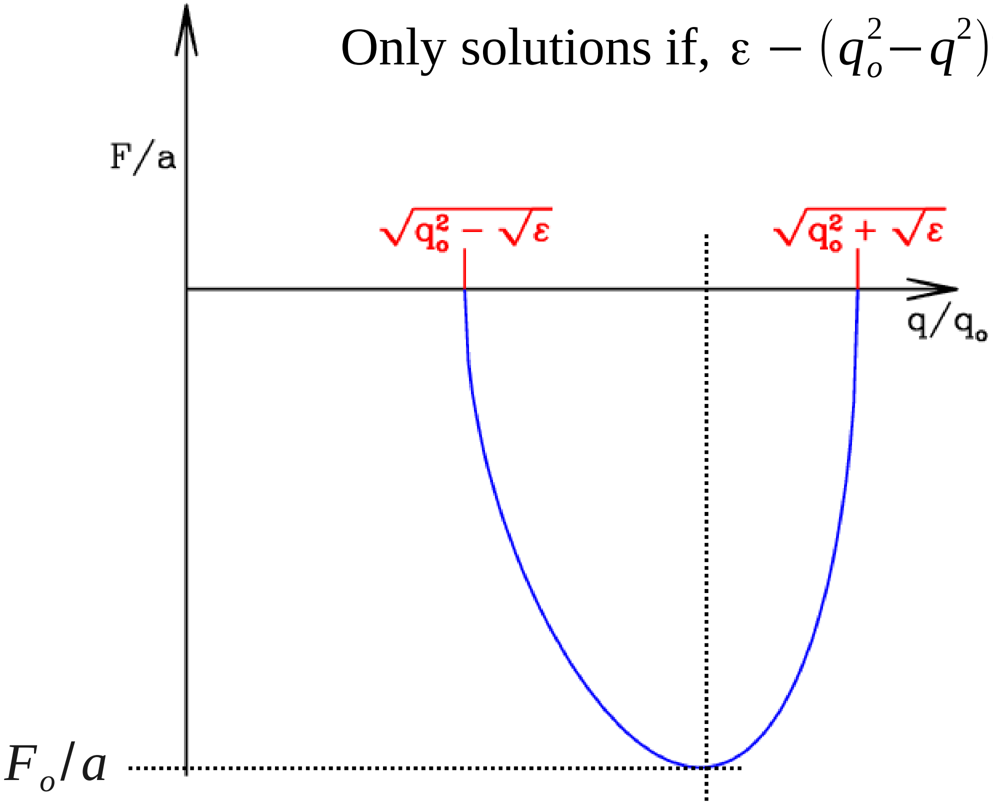
Periodic systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2+\nabla^2\right)^2\psi\right)$$

Equilibrium in a one mode approximation

$$\psi = A\cos(qx) \qquad A = \frac{2}{\sqrt{3}}\sqrt{\varepsilon-\left(q_o^2-q^2\right)^2} \qquad \frac{F}{a} = -\frac{1}{6}\sqrt{\varepsilon-\left(q_o^2-q^2\right)^2}$$

Only solutions if, $\varepsilon - \left(q_o^2-q^2\right)^2 > 0$



$$q_1 < q < q_2$$

$$q_1 = \sqrt{q_o^2-\sqrt{\varepsilon}}$$

$$q_2 = \sqrt{q_o^2+\sqrt{\varepsilon}}$$

Minima occurs
At **finite** q, i.e., $q = q_o$

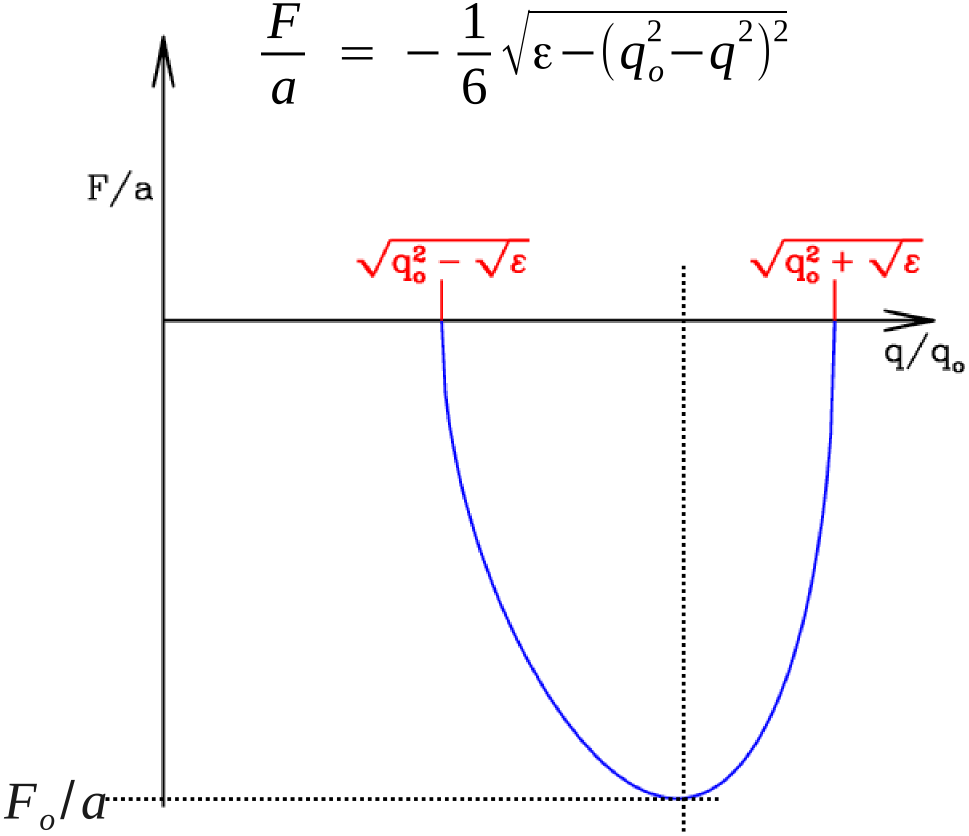
Minimalist free energy

Periodic systems

$$F = \int d\vec{r} \left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

Equilibrium in a one mode approximation

$$\frac{F}{a} = -\frac{1}{6}\sqrt{\varepsilon - \left(q_o^2 - q^2\right)^2}$$



Expand free energy around minima

Let $a = \dfrac{2\pi}{q}$ and $a_o = \dfrac{2\pi}{q_o}$

$$\boxed{\frac{F}{a} = \frac{F_o}{a} + \frac{K}{2}\frac{\left(a - a_o\right)^2}{a_o^2} + \ldots}$$

where $K \equiv 32 A_o^2 q_o^4,\ A_o^2 \equiv 4\varepsilon/3$

Hooke's Law!!

Minimalist free energy

Periodic systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2\psi\right)$$

Two simple points

a) free energy selects wavelength - periodicity

b) deviations from selected periodicity – costs energy – Hooke's Law

Minimalist free energy

Periodic systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2\psi\right)$$

Now consider dynamics

Non-conserved: Swift-Hohenberg Equation

- Rayleigh Benard convection

$$\frac{\partial\psi}{\partial t} = -\frac{\delta F}{\delta\psi} = \varepsilon\psi - \psi^3 - \left(q_o^2 + \nabla^2\right)^2\psi$$

Conserved: Phase Field Crystal

- crystal solidification

$$\frac{\partial\psi}{\partial t} = \nabla^2\frac{\delta F}{\delta\psi} = -\nabla^2\left[\varepsilon\psi - \psi^3 - \left(q_o^2 + \nabla^2\right)^2\psi\right]$$

Non-conserved: Swift-Hohenberg Equation

- Rayleigh Benard convection

$$\frac{\partial \psi}{\partial t} = \varepsilon \psi - \psi^3 - \left(q_o^2 + \nabla^2\right)^2 \psi$$

Non-linear partial differential equation: difficult to solve

Consider linearizing around state Ψ_o, i.e.,

$$\psi = \psi_o + \delta \psi$$

$$\frac{\partial \delta \psi}{\partial t} = \left(\varepsilon - \left(q_o^2 + \nabla^2\right)^2 - 3\psi_o^2\right) \delta \psi + \ldots$$

a) expand around $\Psi_o = 0$

b) expand around $\Psi_o = A \sin(qx)$

Non-conserved: Swift-Hohenberg Equation

- Rayleigh Benard convection

$$\frac{\partial \psi}{\partial t} = \varepsilon \psi - \psi^3 - \left(q_o^2 + \nabla^2\right)^2 \psi$$

a) linearize around ψ_o = 0 state, i.e.,

$$\frac{\partial \psi}{\partial t} \approx \varepsilon \psi - \left(q_o^2 + \nabla^2\right)^2 \psi$$

Fourier transform and solve

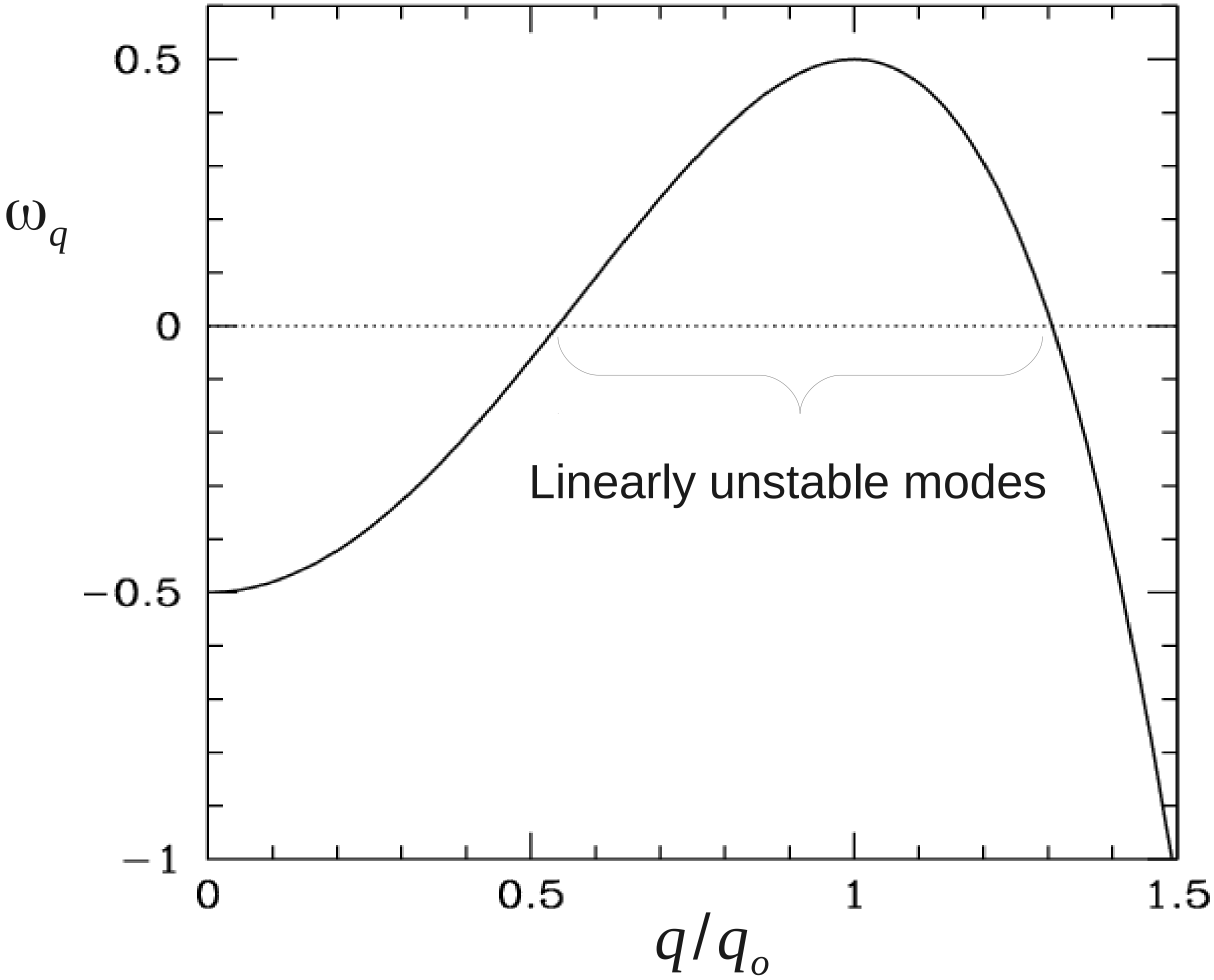
$$\frac{\partial \hat{\psi}_q}{\partial t} = \omega_q \hat{\psi}_q \qquad \hat{\psi}_q(t) = e^{\omega_q t} \hat{\psi}_q(t=0)$$

$$\text{where } \omega_q \equiv \varepsilon - (q_o^2 - q^2)^2$$

a) linearize around ψ = 0 state, i.e.,

$$\hat{\psi}_q(t) = e^{\omega_q t}\hat{\psi}_q(t=0)$$

where $\omega_q \equiv \varepsilon - (q_o^2 - q^2)^2$



Most unstable mode
(largest ω_q)
$q = q_o$

Dynamics: non-conserved

$$\frac{\partial\psi}{\partial t} = -\frac{\delta F}{\delta\psi} = \varepsilon\psi - \psi^3 - \left(q_o^2+\nabla^2\right)^2\psi$$

b) linearize around periodic state

$$\psi = \psi_o + \delta\psi \qquad \psi_o = A\cos(qx) \qquad A = 2\omega_q/\sqrt{3}$$

$$\frac{\partial\delta\psi}{\partial t} = \left(\varepsilon - \left(q_o^2+\nabla^2\right)^2 - 3\psi_o^2\right)\delta\psi$$

→ Problem – ψ_o depends on 'x'

Bloch/Floquet theory

Write

$$\delta\psi = \sum_{n=-N}^{N} b_n(t)\, e^{i(qn+Q)x} \qquad \psi_o = \sum_{n=-N}^{N} a_n e^{inqx}$$

Solve for $b_n(t)$ ....

One mode approximation: let N = 1

b) linearize around periodic state “Bloch/Floquet theory”

$$\frac{\partial \delta\psi}{\partial t} = \left(\varepsilon - \left(q_o^2 + \nabla^2\right)^2 - 3\psi_o^2\right)\delta\psi \qquad (1)$$

One mode approximation: let N = 1

$$\delta\psi = \sum_{n=-1}^{1} b_n(t)\, e^{i(qn+Q)x} \qquad\qquad \psi_o = \sum_{n=-1}^{1} a_n e^{inqx}$$

$$\text{where } a_1 = a_{-1} = \omega_q/\sqrt{3},\ a_0 = 0 \rightarrow \psi_o = 2\omega/\sqrt{3}\cos(qx)$$

Substitute $\delta\Psi$ and Ψ_o into (1) and multiply by e^{-imqx} and integrate ...

$$m = 1: \quad \frac{\partial b_1}{\partial t} = \left(\omega_{Q+q} - 2\omega_q\right)b_1 - \omega_q b_{-1}$$

$$m = 0: \quad \frac{\partial b_0}{\partial t} = \left(\omega_{Q} - 2\omega_q\right)b_0 \quad \longleftarrow$$

$$m = -1: \quad \frac{\partial b_{-1}}{\partial t} = \left(\omega_{Q-q} - 2\omega_q\right)b_{-1} - \omega_q b_1$$

for q's of interest:

$$0 < \omega_Q - 2\omega_q$$

$$b_0(t) = e^{-|\omega_Q - 2\omega_q|t}\, b_0(0)$$

→ 0 ... boring

b) linearize around periodic state “Bloch/Floquet theory”

$$\left.\begin{aligned}\frac{\partial b_1}{\partial t} &= (\omega_{Q+q} - 2\omega_q) b_1 - \omega_q b_{-1} \\ \frac{\partial b_{-1}}{\partial t} &= (\omega_{Q-q} - 2\omega_q) b_{-1} - \omega_q b_1\end{aligned}\right\}$$

Eigenvalue problem

two eigenvalues

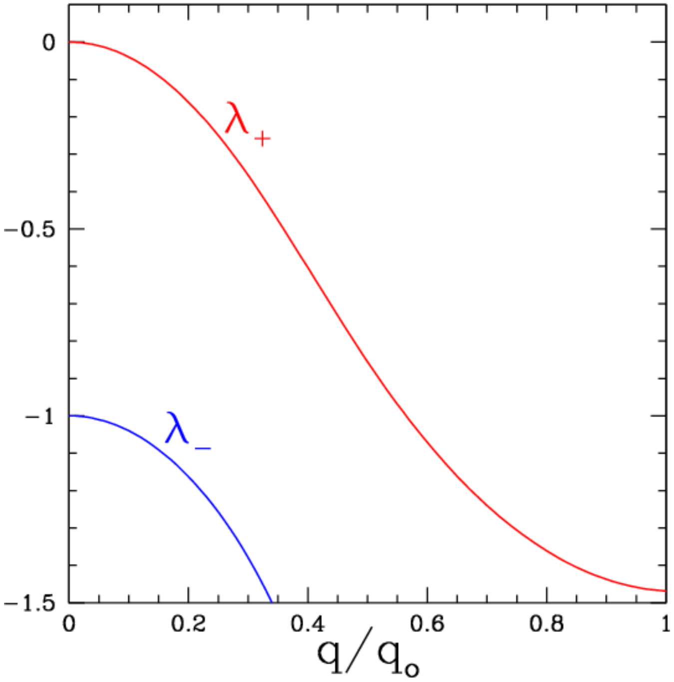
$$\lambda_{\pm} = \frac{1}{2}\left(\omega_{Q+q} + \omega_{Q-q} - 4\omega_q \pm \sqrt{(\omega_{Q+q} - \omega_{Q-q})^2 + 4\omega_q^2}\right)$$

Example

$\varepsilon = 1/2, \; q = q_o$

$\lambda_{\pm} \leqslant 0$

stable



small Q limit
- diffusion

$\lambda_+ \approx -|D(q)|Q^2$

b) linearize around periodic state "Bloch/Floquet theory"

$$\left.\begin{aligned}\frac{\partial b_1}{\partial t} &= (\omega_{Q+q} - 2\omega_q) b_1 - \omega_q b_{-1} \\ \frac{\partial b_{-1}}{\partial t} &= (\omega_{Q-q} - 2\omega_q) b_{-1} - \omega_q b_1\end{aligned}\right\}$$

Eigenvalue problem

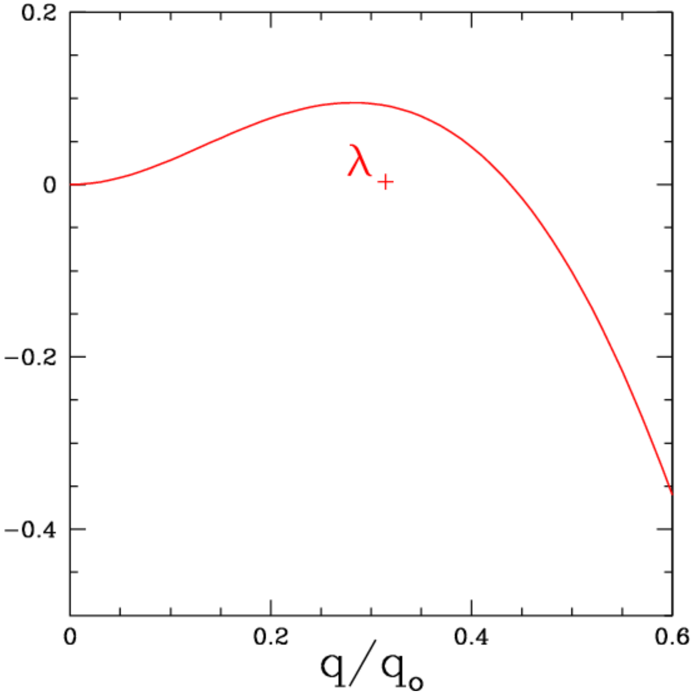
two eigenvalues

$$\lambda_\pm = \frac{1}{2}\left(\omega_{Q+q} + \omega_{Q-q} - 4\omega_q \pm \sqrt{(\omega_{Q+q} - \omega_{Q-q})^2 + 4\omega_q^2}\right)$$

Example

$\varepsilon = 1/2, \ q = 0.7\ q_o$

$\lambda_+ > 0$



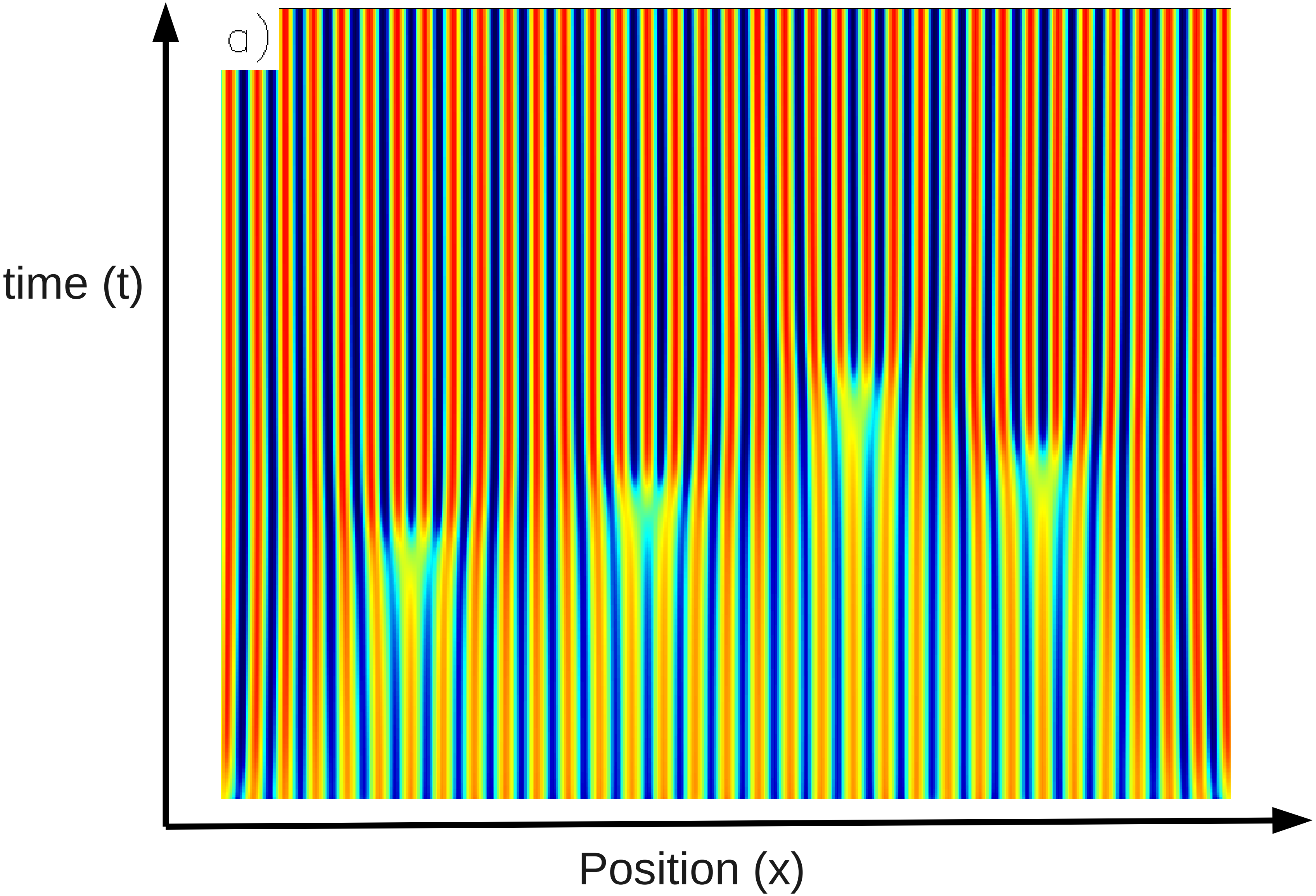
small Q limit
- unstable

$$\lambda_+ \approx +|D(q)|Q^2$$

"Eckhaus" instability

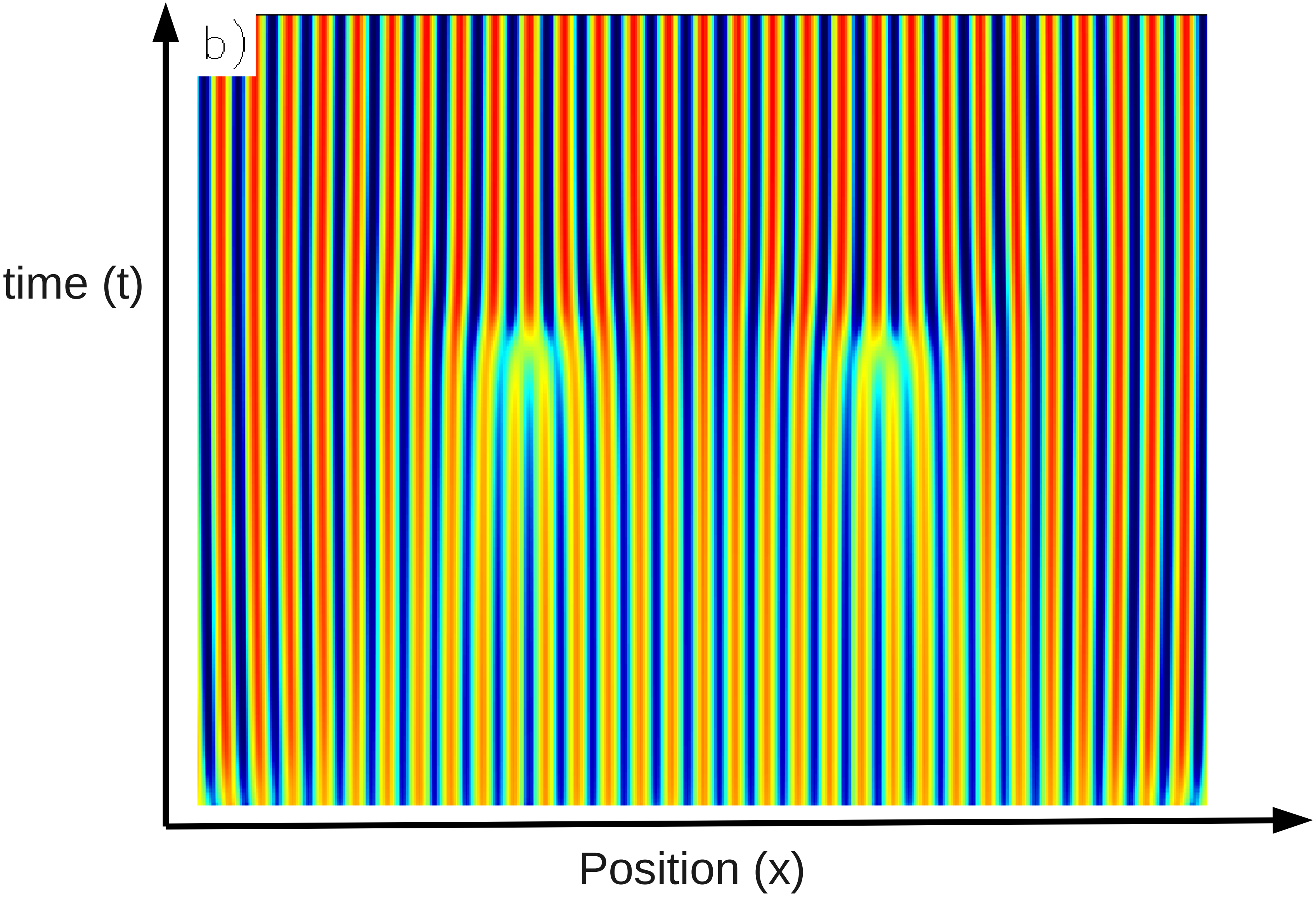
“Eckhaus” instability

a) initial periodicity too large -- split



“Eckhaus” instability

b) initial periodicity too small -- join

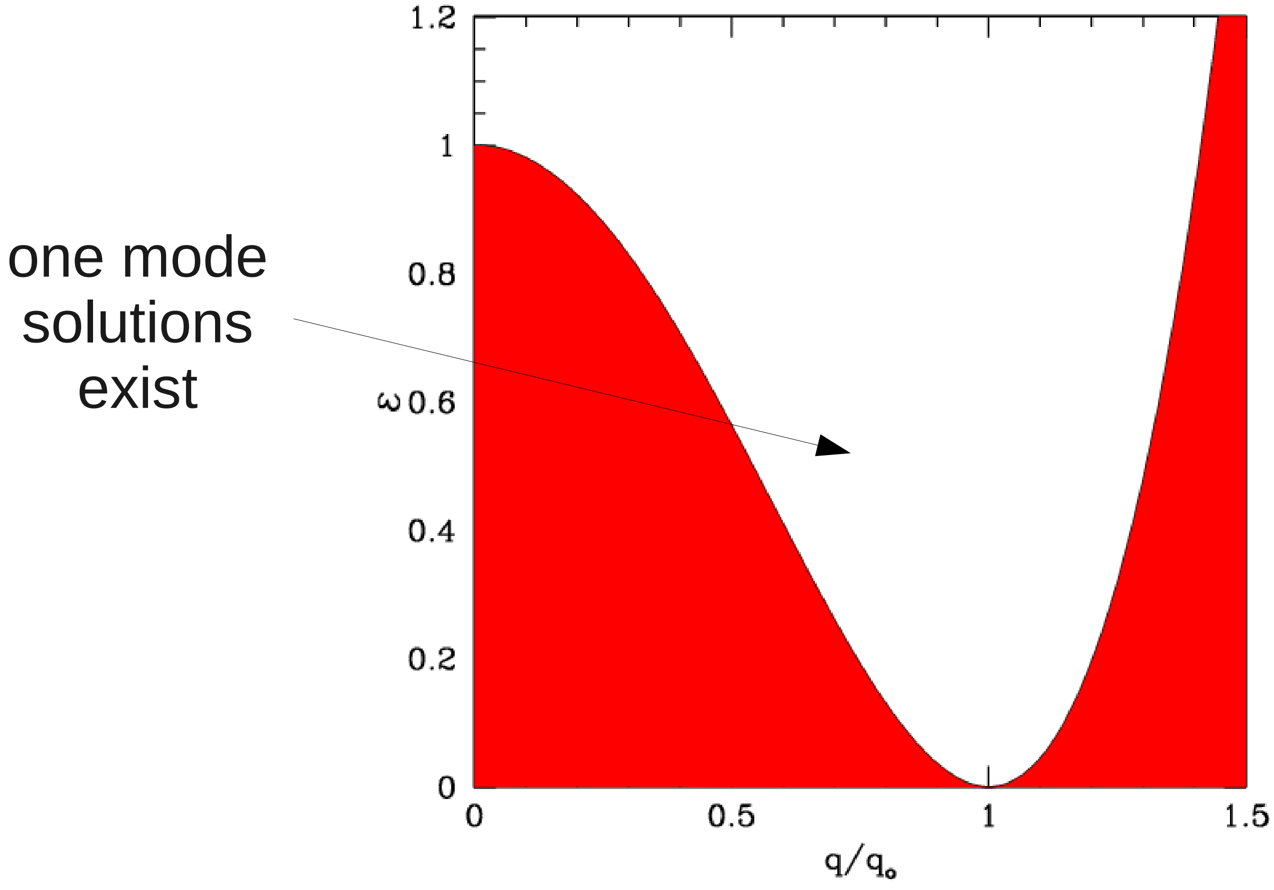


Minimalist free energy

Periodic systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2\psi\right)$$

One mode summary: Ψ = A cos(qx) $A = \frac{2}{\sqrt{3}}\sqrt{\varepsilon-\left(q_o^2-q^2\right)^2}$

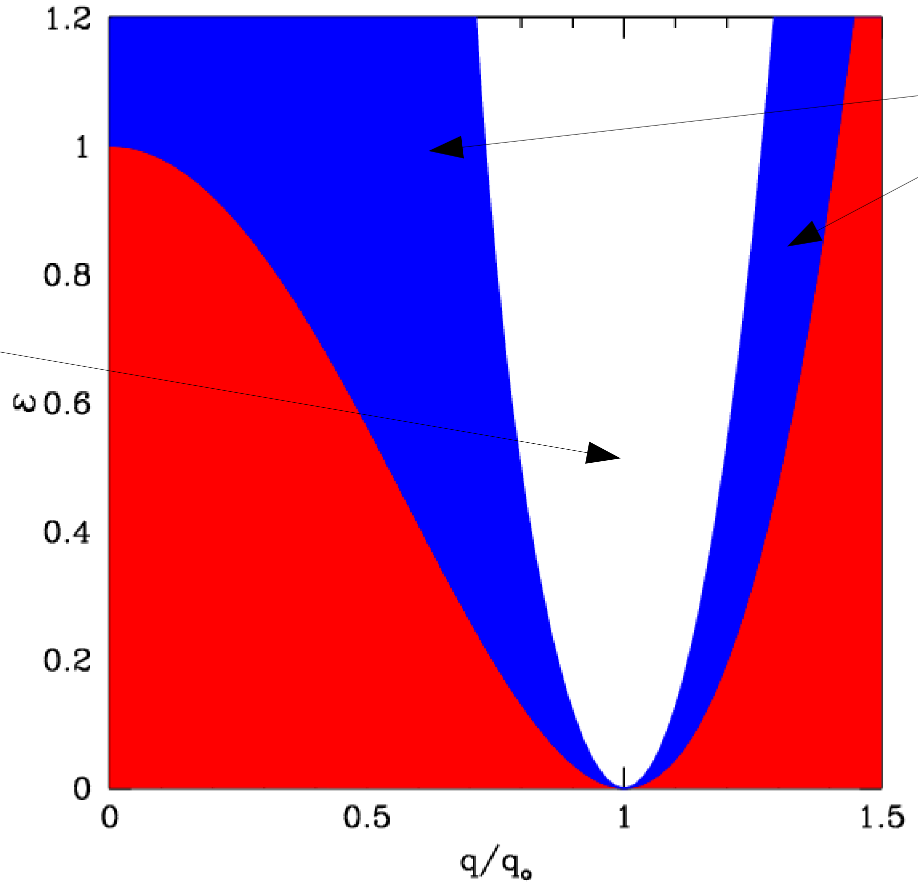


Minimalist free energy

Periodic systems

$$F = \int d\vec{r} \left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

One mode summary: Ψ = A cos(qx) $A = \frac{2}{\sqrt{3}}\sqrt{\varepsilon - \left(q_o^2 - q^2\right)^2}$



unstable
one mode
solutions

stable
one mode
solutions

Minimalist free energy

Periodic systems

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

Three simple points

a) free energy selects wavelength - periodicity

b) deviations from selected periodicity – costs energy – Hooke's Law

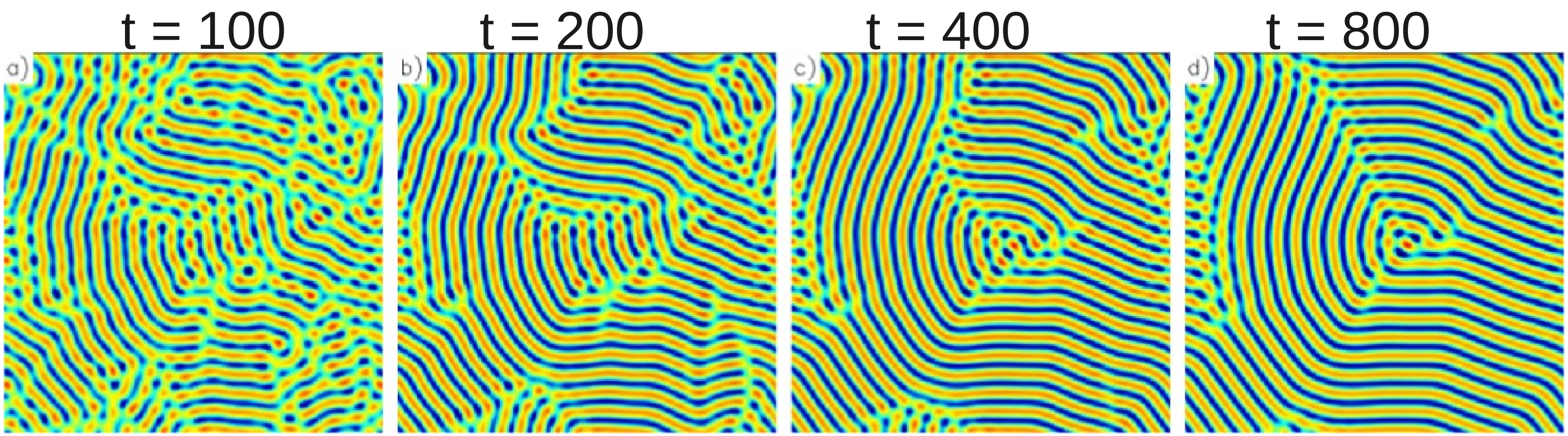
c) spontaneous creation/deletion of wavelengths
(epitaxial growth)

Minimalist free energy

Periodic systems

$$F = \int d\vec{r} \left(-\frac{\varepsilon}{2}\psi^2 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2 \psi \right)$$

Final note: so far one-dimensional solutions
- two-dimensions stripes



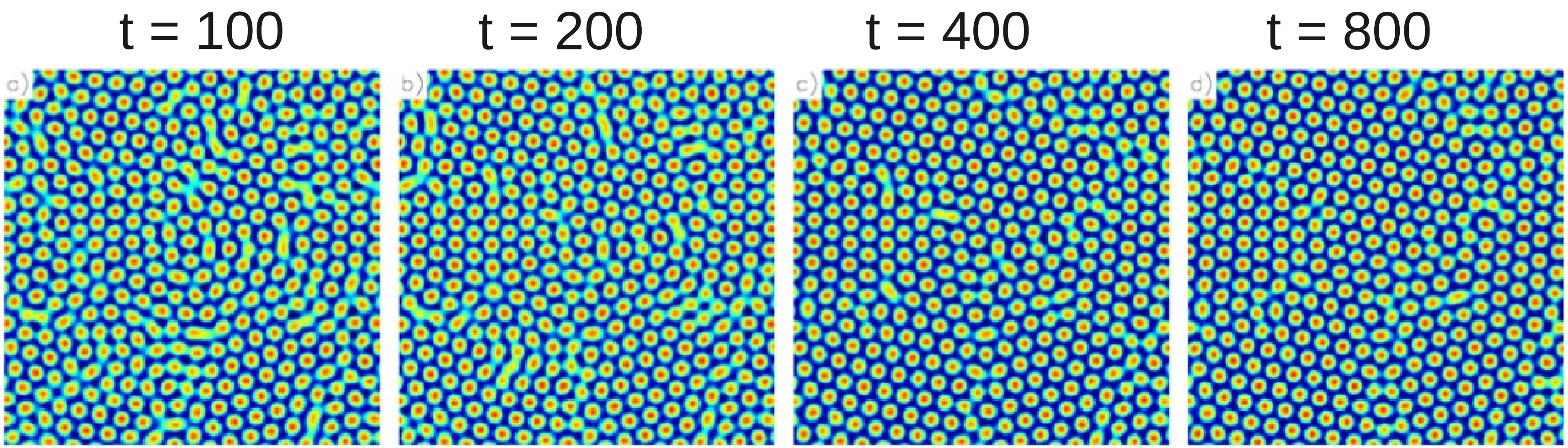
Reason for stripes : F even function of Ψ

Minimalist free energy

Periodic systems with broken symmetry, eg,

$$F = \int d\vec{r}\left(-\frac{\varepsilon}{2}\psi^2 + \frac{\alpha}{3}\psi^3 + \frac{1}{4}\psi^4 + \frac{\psi}{2}\left(q_o^2 + \nabla^2\right)^2\psi \right)$$

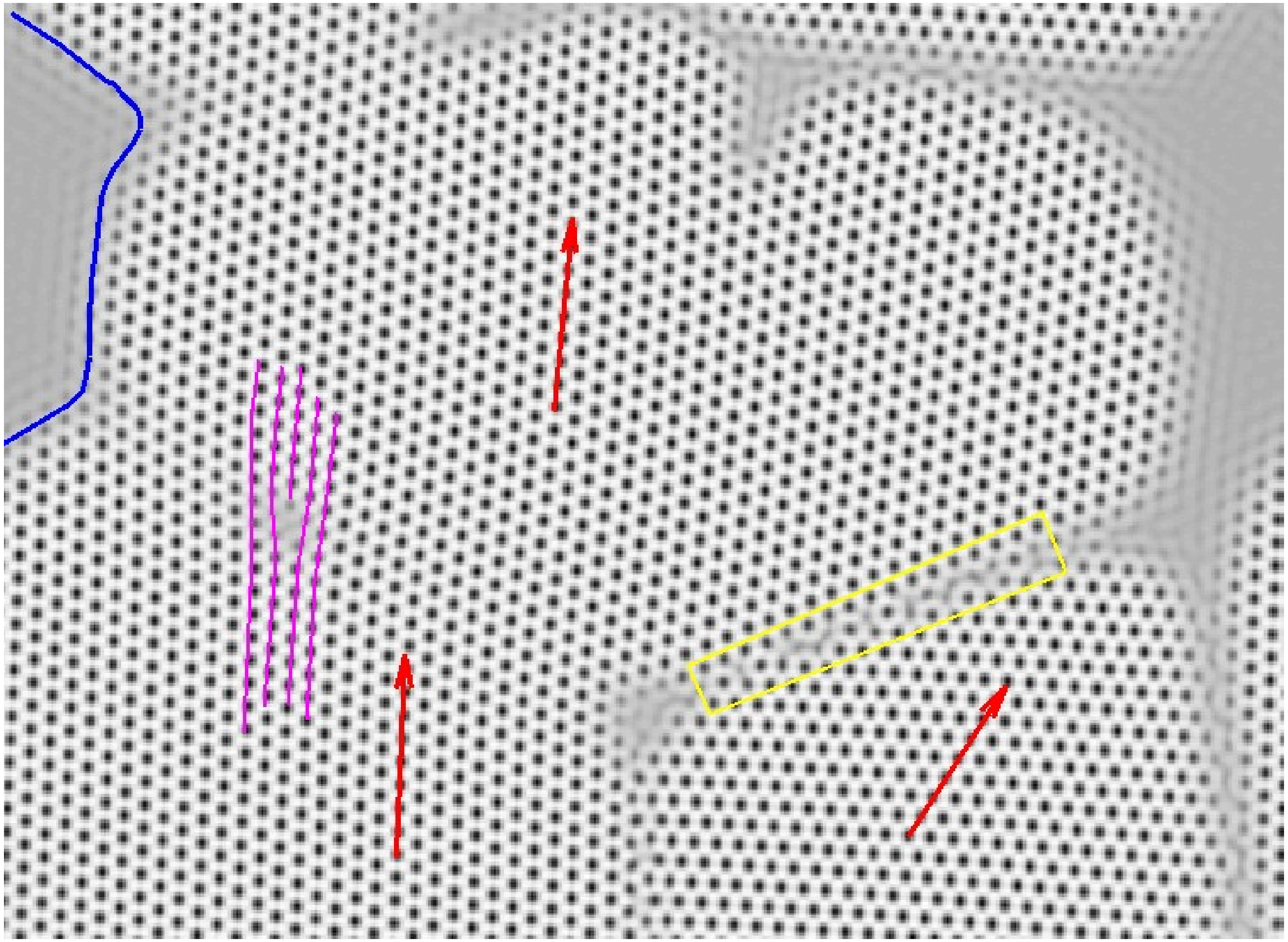
Favor Ψ < 0 states --- can lead to other patterns....
eg. in 2-dimensions - triangular states


t = 100 t = 200 t = 400 t = 800

Modeling Crystal Growth

Physics: liquid/solid interfaces, multiple crystal orientations
dislocations, grain boundaries, elasticity, ...

Field: model **n(r,t)** ~ atomic number density **– periodic field**

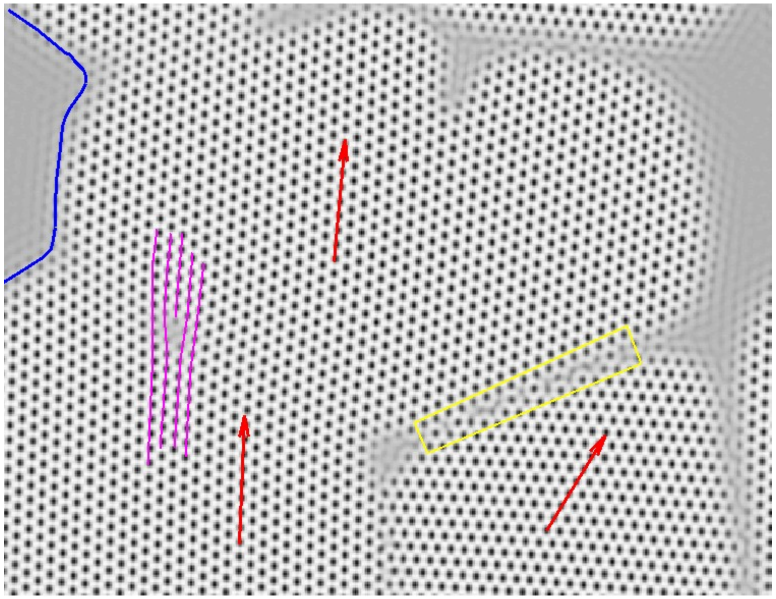


Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)
~ conserved Swift-Hohenberg Eq.

$$\boxed{F = \int d\vec{r}\left[\Delta B \frac{n^2}{2} + \frac{B^x}{2} n \underbrace{\left(1 + \nabla^2\right)^2} n - \frac{t}{3} n^3 + \frac{v}{4} n^4\right]}$$

rotationally invariant periodic solutions



Dynamics

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

$$\boxed{\frac{\partial n}{\partial t} = \Gamma \nabla^2 \left[\left(\Delta B + B^x \left(1 + \nabla^2\right)^2\right) n - t n^2 + v n^3\right]}$$

ensures density conservation

Modeling Crystal Growth

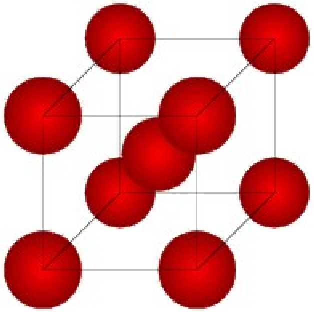
minimalist model : Phase Field Crystal (PFC)

$$\boxed{F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1+\nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]}$$

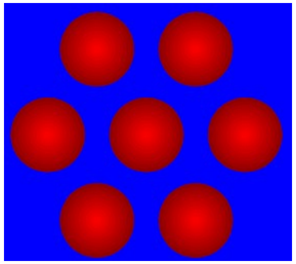
$$\Delta B = B^l - B^x$$

Equilibrium States :

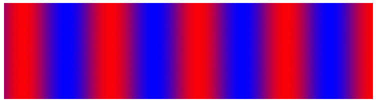
Three dimensions
BCC



Two dimensions:
triangular



One dimension:
stripes



Zero dimensions:
“liquid” constant

Phase Diagram:

1) **Evaluate free energy** of each state
   - use one-mode approx.
2) **Determine coexistence** regions
   - Maxwell's equal area

1) Minimum energy states

$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1+\nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

Liquid state: n = constant = n_o

🟥 $$\frac{\text{free energy}}{\text{volume}} \equiv F_{liq}/a^d = \left(\Delta B + B^x\right)\frac{n_o^2}{2} - \frac{t}{3}n_o^3 + \frac{v}{4}n_o^4$$

Higher dimensions:

$$n = n_o + \sum_{klm}\eta_{klm}\exp\left(i\vec{G}_{klm}\cdot\vec{r}\right) + \text{C.C.}$$

$$\vec{G}_{klm} \equiv k\vec{q}_1 + l\vec{q}_2 + m\vec{q}_3$$

$$\left(\vec{q}_{1,}\vec{q}_{2,}\vec{q}_3\right) \equiv \text{principle reciprocal lattice vectors}$$

$$\left(k,l,m\right) = \text{integers, Miller indices}$$

One mode approximation:

retain smallest $|\vec{G}_{klm}|'s$ and set $\eta_{klm} = \text{constant} = \phi$

solve: $\dfrac{\partial F/a^d}{\partial \phi} = 0$ and $\dfrac{\partial F/a^d}{\partial q} = 0$ where $q = 2\pi/a$

Summary

state	principle reciprocal lattice vectors	modes required	free energy density difference ($\Delta F/a^d$)	amplitude (ϕ)
1d Stripe	$\vec{q}_1 = q\hat{x}$	100	$-\gamma\phi^2 + \dfrac{3v}{2}\phi^4$	$\sqrt{\dfrac{\gamma}{3v}}$
2d Triang.	$\vec{q}_1 = -\dfrac{q}{2}\left(\sqrt{3}\hat{x} + \hat{y}\right)$ $\vec{q}_2 = q\hat{y}$	100, 010 $\bar{1}\bar{1}0$	$-3\gamma\phi^2 - 4\beta\phi^3 + \dfrac{45v}{2}\phi^4$	$\dfrac{\beta}{15v} + \sqrt{\left(\dfrac{\beta}{15v}\right)^2 + \dfrac{\gamma}{15v}}$
3d BCC	$\vec{q}_1 = \dfrac{q}{\sqrt{2}}(\hat{x} + \hat{y})$ $\vec{q}_2 = \dfrac{q}{\sqrt{2}}(\hat{x} + \hat{z})$ $\vec{q}_3 = \dfrac{q}{\sqrt{2}}(\hat{y} + \hat{z})$	100, 010 001, $1\bar{1}0$ $01\bar{1}$, $\bar{1}01$	$-6\gamma\phi^2 - 16\beta\phi^3 + 135v\phi^4$	$\dfrac{2\beta}{45v} + \sqrt{\left(\dfrac{2\beta}{45v}\right)^2 + \dfrac{\gamma}{45v}}$

$\dfrac{\partial F/a^d}{\partial q} = 0$

gives $q = 1$

notation $(01\bar{1})$

$k=0,\ l=1,\ m=-1$

$\Delta F \equiv F - F_c$

$\gamma \equiv 2tn_o - 3vn_o^2 - \Delta B$

$\beta \equiv t - 3vn_o$

Free energy density – versus amplitude

$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1+\nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

Stripe

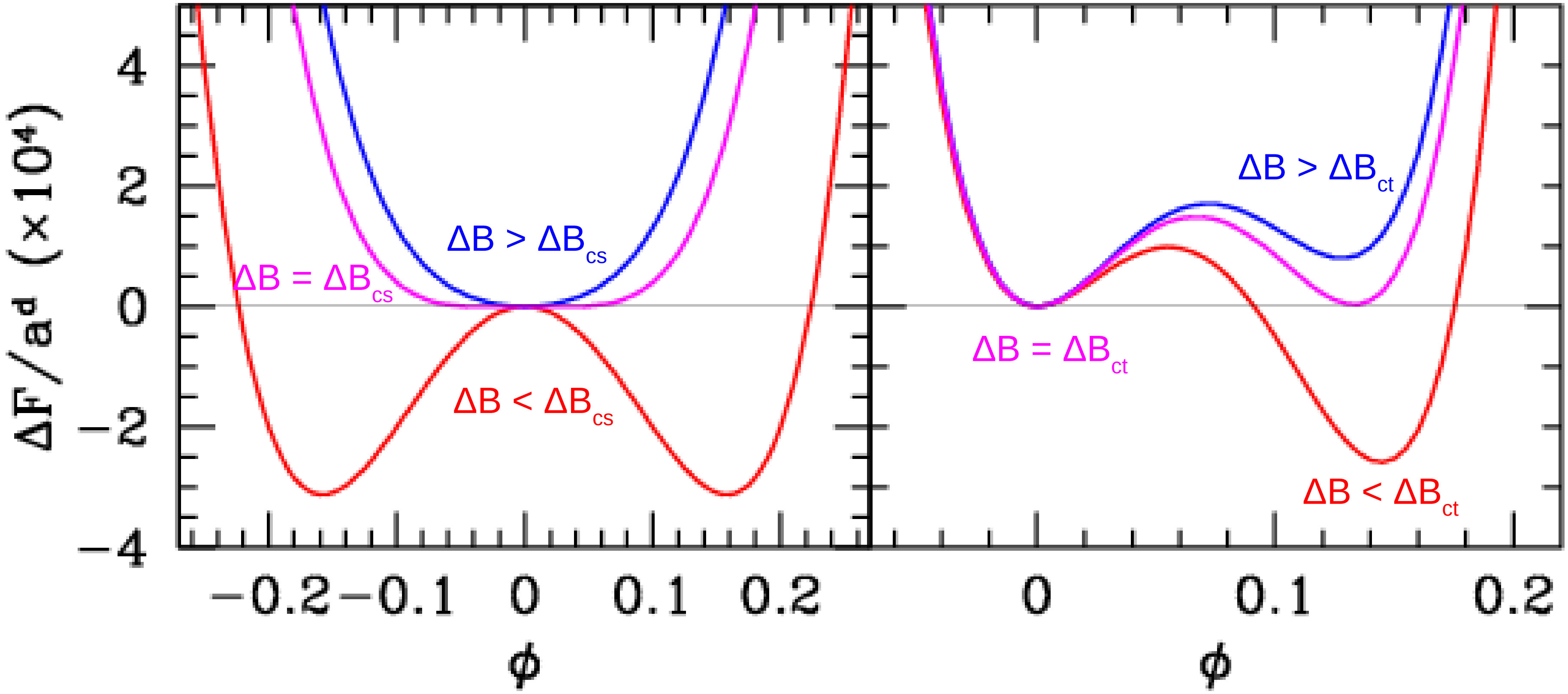
ΔB_{cs} = stripe/constant transition

2nd order transition

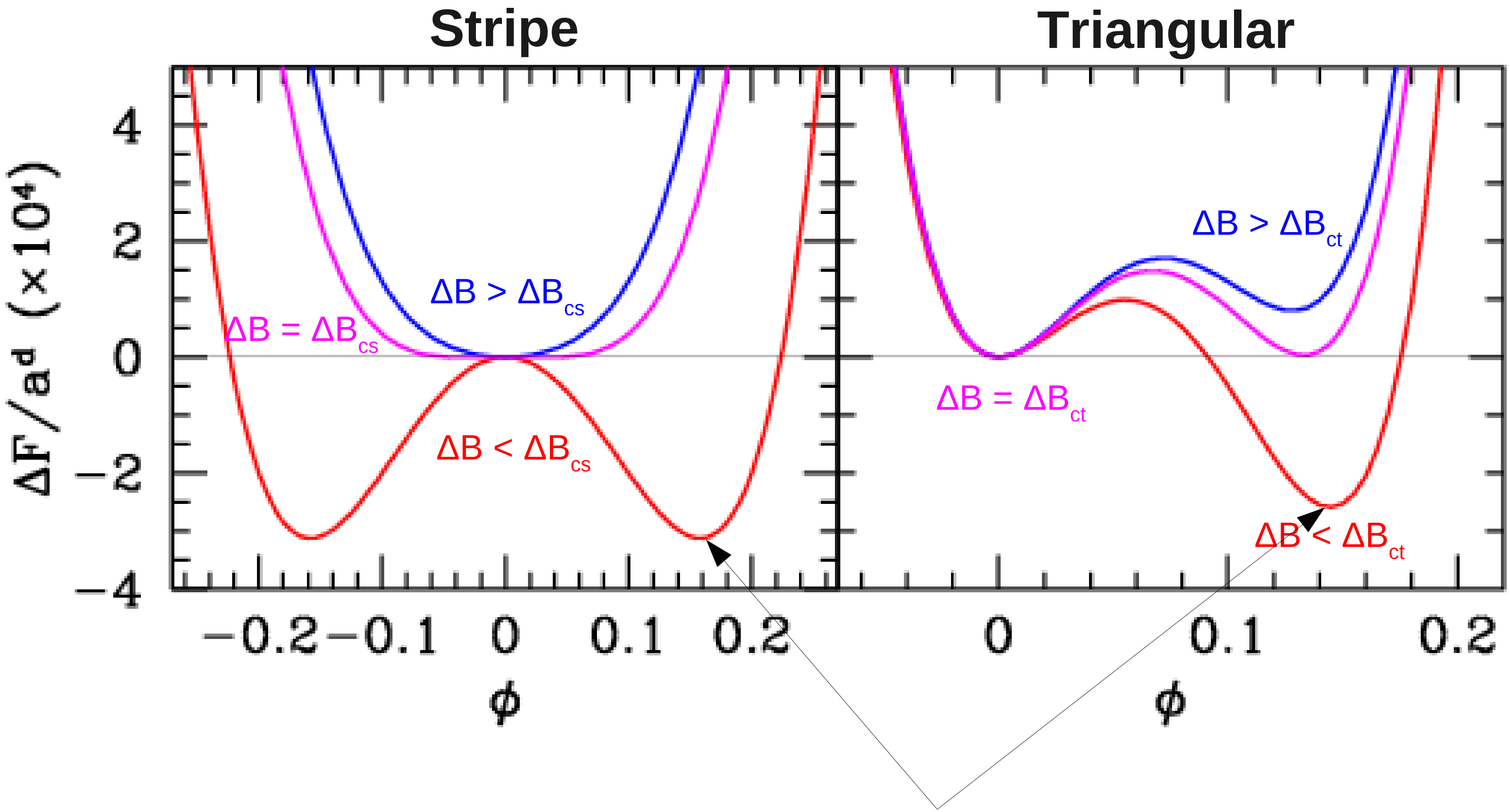
Triangular

ΔB_{ct} = triangular/constant transition

1st order transition



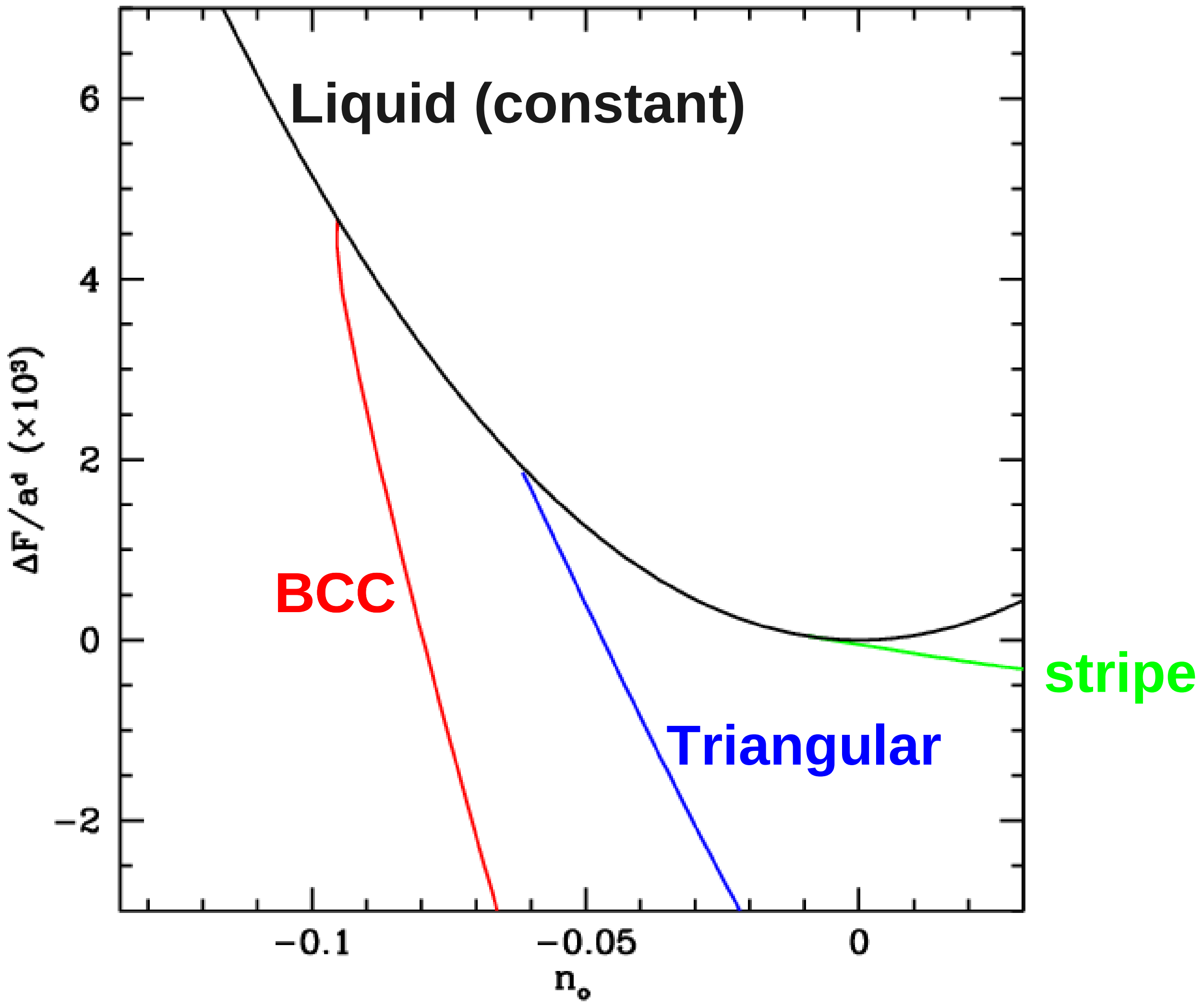
1) Minimum energy states ~ function of n_o



Minimum energy density $\Delta F(n_o)/a^d$
~ function of average density n_o

2) Determine coexistence regions

Free energy density versus n_o



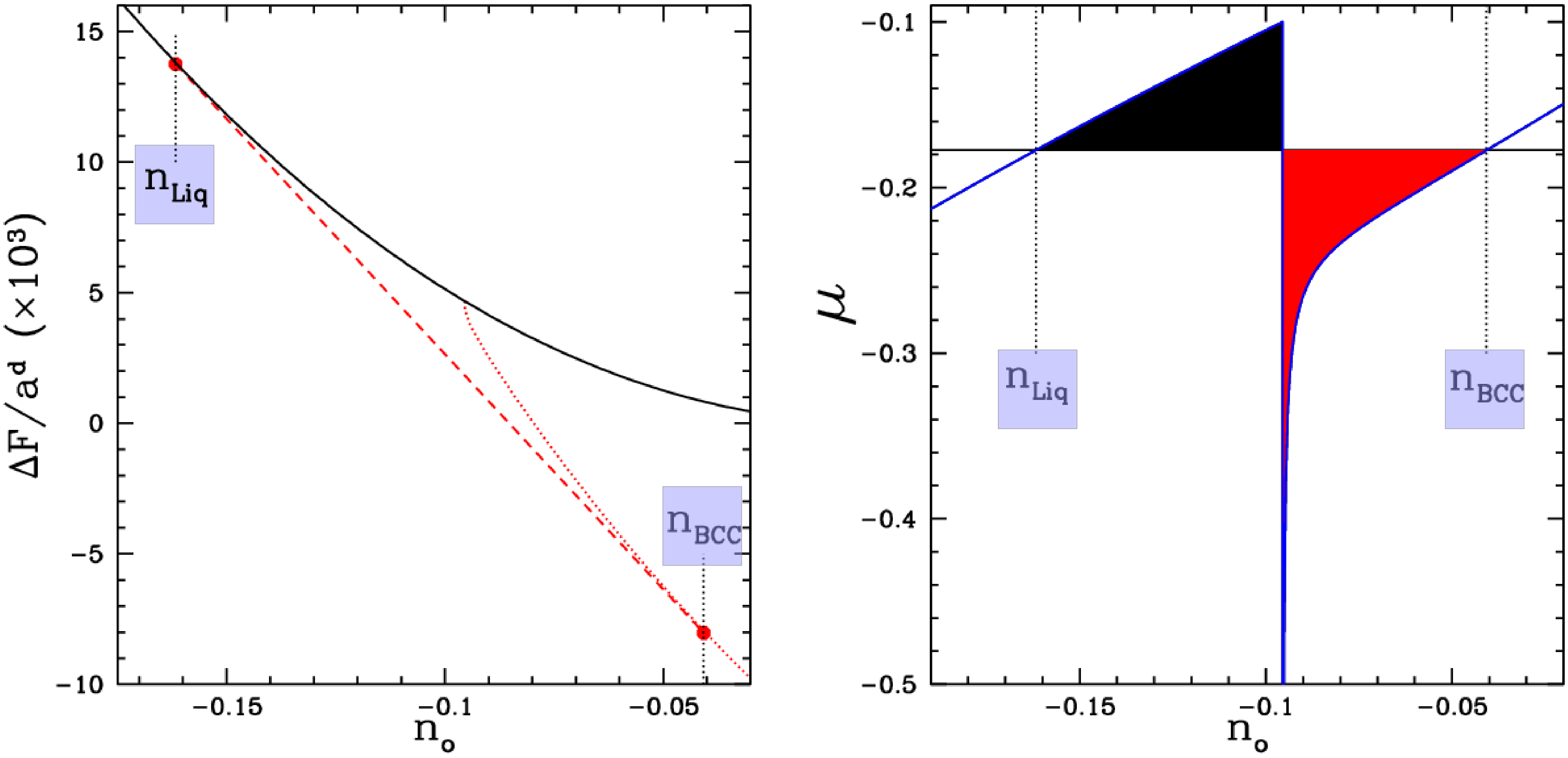
2) Determine coexistence regions: determine n_{Liq} and n_{BCC} such that

$n < n_{Liq}$ liquid phase $n > n_{BCC}$ BCC phase

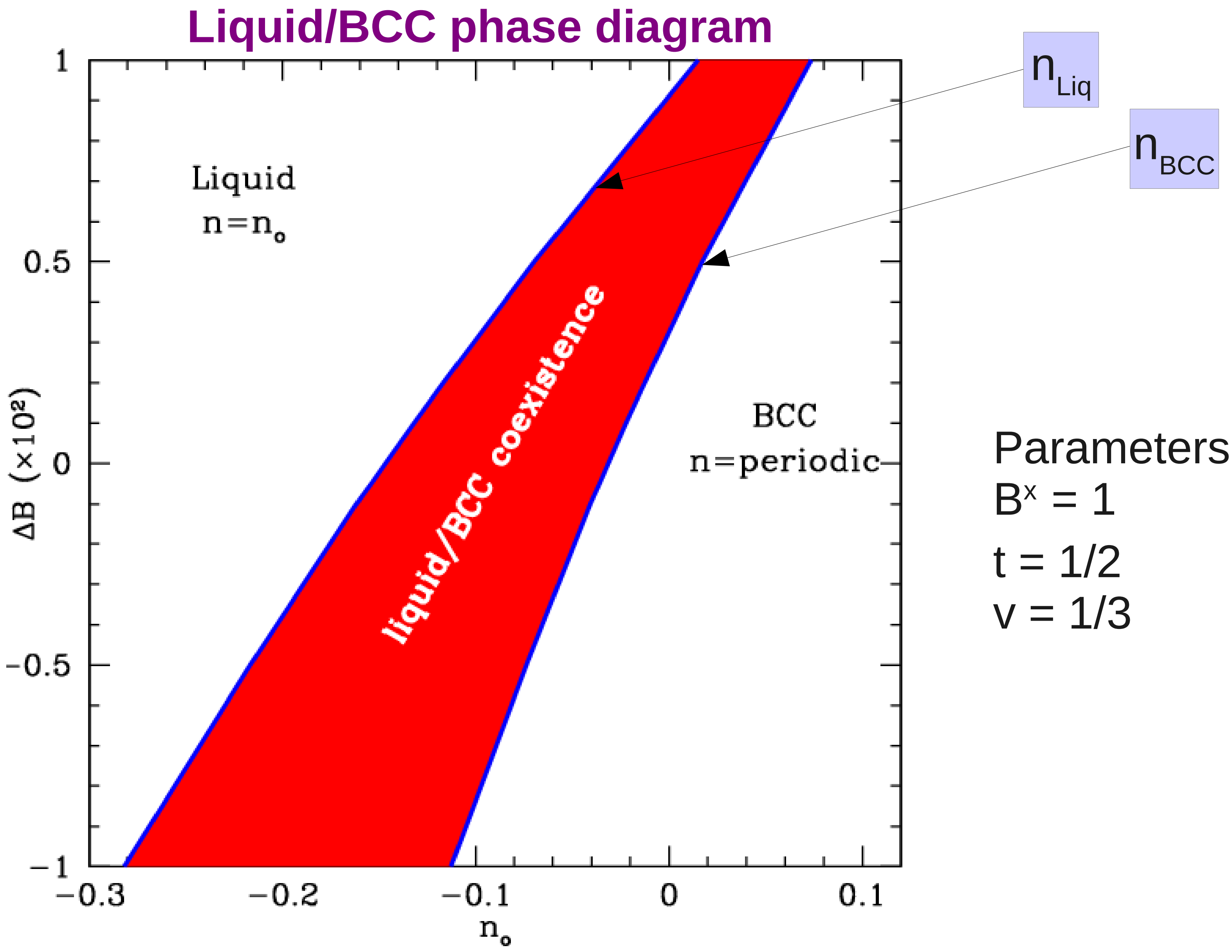
$n_{liq} < n < n_{BCC}$ liquid/BCC coexistence

Example: Liquid/BCC coexistance

equal tangent rule **or** **equal area construction**



Sample phase Diagram:



Parameters

$B^x = 1$

$t = 1/2$

$v = 1/3$

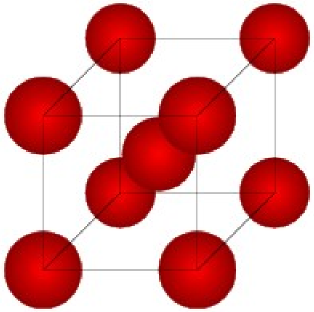
Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)

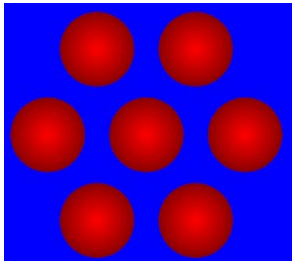
$$\boxed{F = \int d\vec{r}\left[\Delta B \frac{n^2}{2} + \frac{B^x}{2} n\left(1 + \nabla^2\right)^2 n + \frac{t}{3} n^3 + \frac{v}{4} n^4\right]}$$

Equilibrium States :

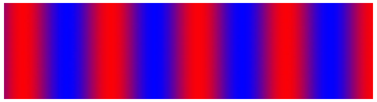
Three dimensions
BCC



Two dimensions:
triangular



One dimension:
stripes



Zero dimensions:
“liquid” constant

Elastic Constants

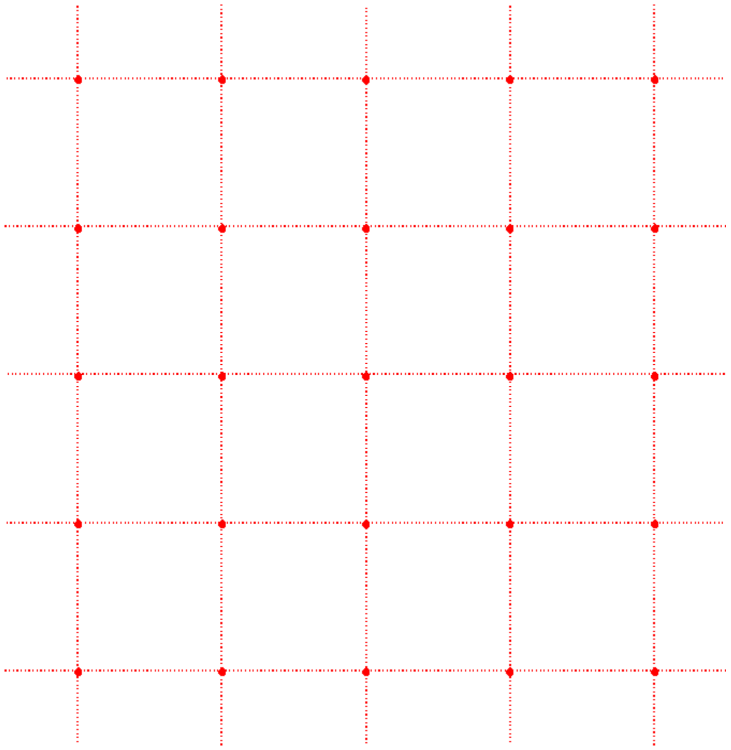
consider energy cost for arbitrary (but small) deformations

Elastic Constants

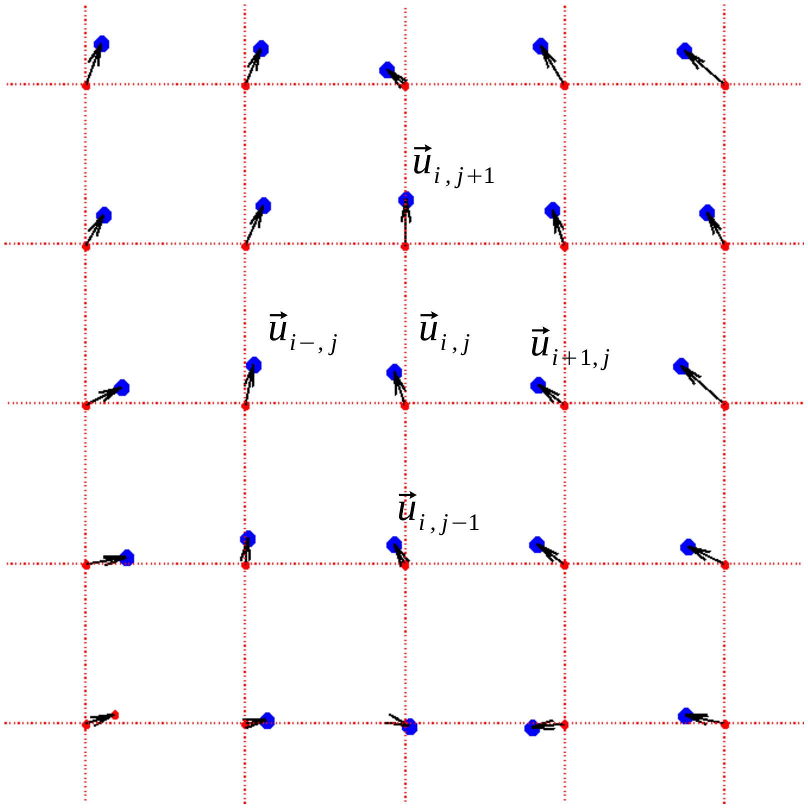
Arbitrary (but small) deformations

Continuum elasticity theory - consider deviations from perfect lattice

perfect lattice



deformed lattice



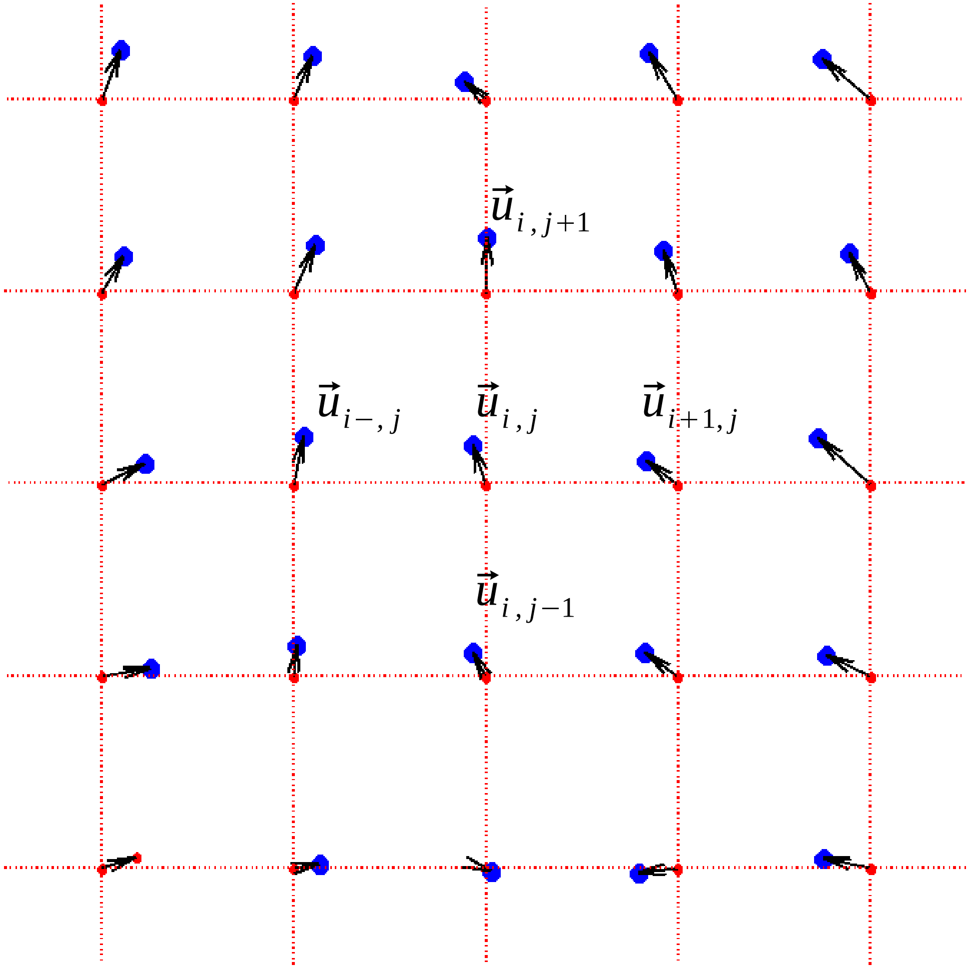
- ● atomic positions

$\vec{u}_{ij} \equiv$ displacement vector

Elastic Constants

Arbitrary (but small) deformations

Continuum elasticity theory: $\vec{u} \;\equiv\;$ diplacement from perfect lattice, i.e.,



Elastic energy (think springs)

$\sim\;$ difference in atomic positions

$$\sim\; \left|\vec{u}_{i,j}-\vec{u}_{i+1,j}\right|^{2,} \;\; \left|\vec{u}_{i,j}-\vec{u}_{i,j+1}\right|^{2}$$

etc.

Continuum limit

$$\vec{u}_{i,j} \;\rightarrow\; \vec{u}(\vec{r})$$

Elastic energy ~ (strain tensor)^2

$$U_{xx} \approx \frac{\partial u_x}{\partial x_j},$$

$$U_{xy} \approx \frac{1}{2}\left(\frac{\partial u_x}{\partial y}+\frac{\partial u_y}{\partial x}\right)$$

etc.

Elastic Constants

Arbitrary (but small) deformations

Deformation starting from continuum density field

consider deformation $n(\vec{r}) \rightarrow n(\vec{r}+\vec{u})$: $\vec{u}=$displacement vector

$$n = \sum_j \eta_j e^{i\vec{G}_j\cdot\vec{r}} + c.c. \rightarrow \sum_j \eta_j e^{i\vec{G}_j\cdot(\vec{r}+\vec{u})} + c.c. \quad : \quad \eta_j \rightarrow \eta_j e^{i\vec{G}_j\cdot\vec{u}}$$

Write η_j as a real amplitude and phase, i.e.,

$$\boxed{\eta_j = \phi \exp\left(i\vec{G}_j\cdot\vec{u}(\vec{r})\right)}$$

Elastic Constants

$$n = n_o + \sum_j \eta_j e^{i\vec{G}_j\cdot\vec{r}} + c.c. \qquad \eta_j = \phi \exp\left(i\vec{G}_j\cdot\vec{u}(\vec{r})\right)$$

Substitute n into free energy

$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \boxed{\frac{B^x}{2}n\left(1+\nabla^2\right)^2 n} - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

only contribution to elastic energy reduces to

$$F_{elas} = 4B^x\phi^2\sum_{klm}\int d\vec{r}\left(\vec{G}_{klm}\cdot\vec{\nabla}\left[\vec{G}_{klm}\cdot\vec{u}\right]\right)^2$$

to lowest order in $\vec{u}$ and gradients in $\vec{u}$

Elastic Constants: Summary

$$\text{1d stripe } \; F_{elas} \;=\; 4\,B^{x}\,\phi^{2}\;U_{11}^{2}$$

$$\text{2d triangular } \; F_{elas} \;=\; B^{x}\,\phi^{2}\left(\frac{9}{2}\sum_{i=1}^{2}U_{ii}^{2} + 3\,U_{11}U_{22} + 6\mathrm{U}_{12}^{2}\right)$$

$$\text{3d BCC } \; F_{elas} \;=\; B^{x}\,\phi^{2}\left(2\sum_{i=1}^{3}\left(2\,U_{ii}^{2} + \sum_{j\neq i}^{3}U_{ii}U_{jj}\right) \;+\; 8\sum_{i=4}^{6}U_{ii}^{2}\right)$$

where $\quad U_{ij} \;\equiv\; \text{strain tensor}$

$$\boxed{\text{Note: in all cases } \; F_{elas} \;\sim\; \phi^{2} \;\rightarrow\; 0 \text{ in liquid}}$$

Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)

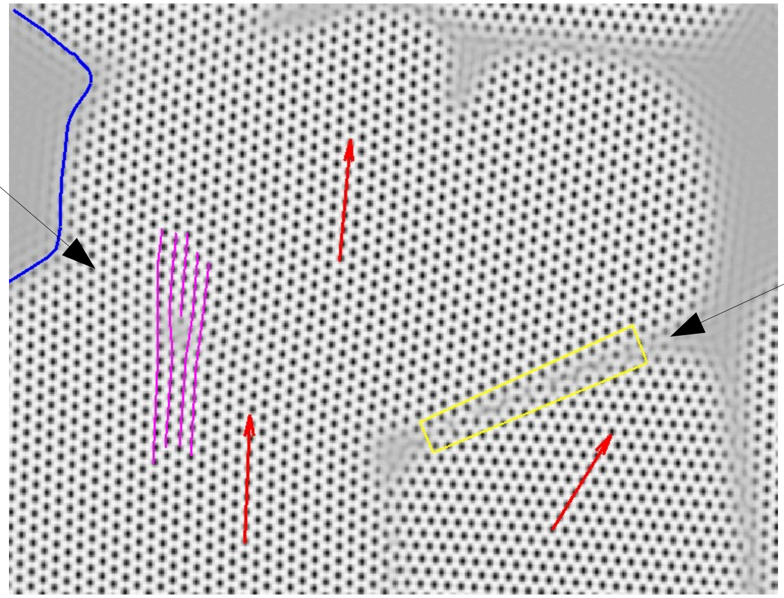
$$\boxed{F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1 + \nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]}$$

Done:

Phase diagram: liquid/solid phase transition (1st order in 2 and 3 dimensions)
Elastic constants: turned of in liquid (Φ = 0)

Now:

Polycrystals/grain boundaries, etc. :



small angle grain boundary

large angle grain boundary

Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)

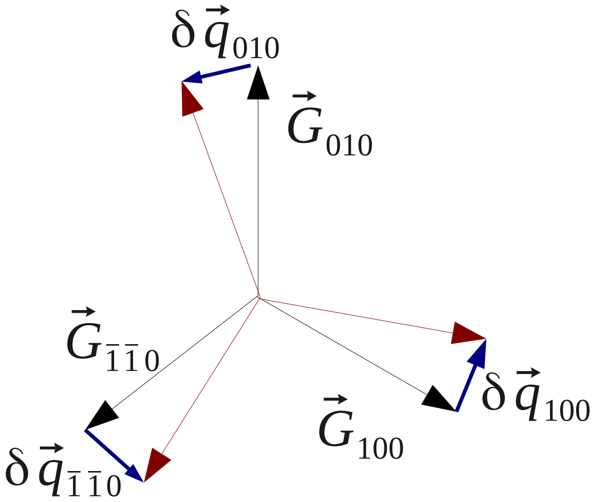
$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1 + \nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

rotationally invariant operator

Polycrystals : rotational invariance

i.e., consider simple rotation in terms of amplitudes

$$n = n_o + \sum_{klm}\eta_{klm}\exp\left(i\vec{G}_{klm}\cdot\vec{r}\right) + \text{C.C.}$$



No rotation $\eta_{klm} = \phi$

$$\nabla^2\exp\left(i\left(\vec{G}_{klm}\right)\cdot\vec{r}\right) = -\left|\vec{G}_{klm}\right|^2$$

With rotation $\eta_{klm} = \phi\exp\left(i\,\delta\vec{q}_{klm}\cdot\vec{r}\right)$

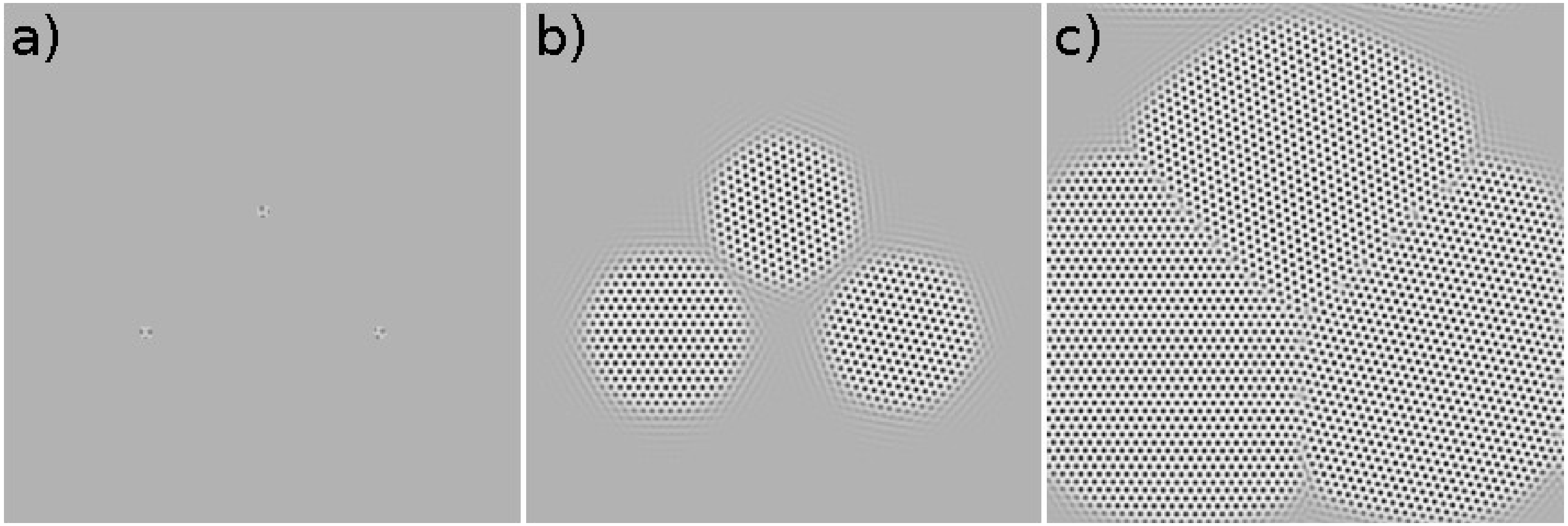
$$\nabla^2\exp\left(i\left(\vec{G}_{klm}+\delta\vec{q}_{klm}\right)\cdot\vec{r}\right) = -\left|\vec{G}_{klm}+\delta\vec{q}_{klm}\right|^2$$

For pure rotation $\left|\vec{G}_{klm}\right|^2 = \left|\vec{G}_{klm}+\delta\vec{q}_{klm}\right|^2$

Polycrystals : **rotational invariance**

natural consequence - grain boundaries

three small grains of different orientations growing in supercooled melt

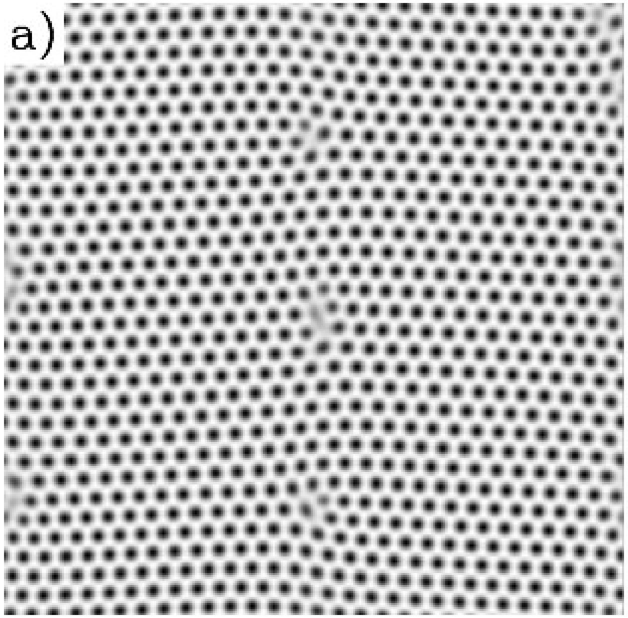


on impingement grain boundaries naturally form

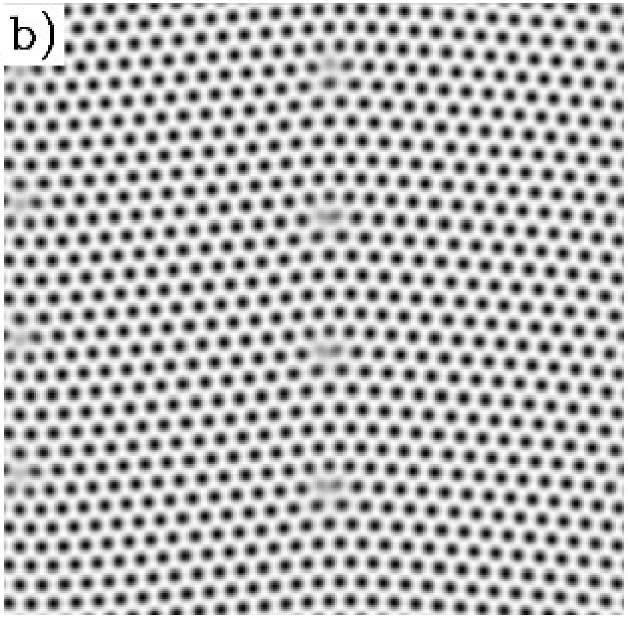
nature of boundary depends on crystal structure/relative orientation
--- geometry

Grain boundaries

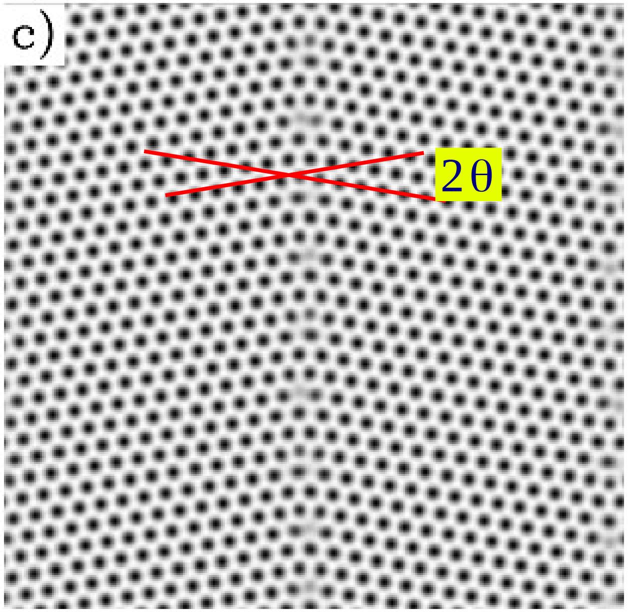
Example: symmetric tilt boundary



$\theta = 2.9^o$



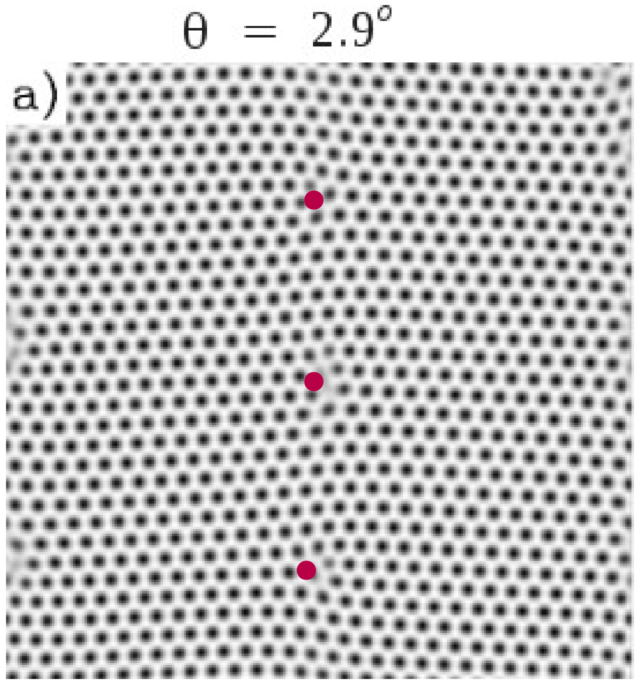
$\theta = 4.7^o$



$\theta = 9.3^o$

Grain boundary energy: small angle limit

Energy/unit length = γ



Small angle limit - row of dislocations
→ elastic deformation

“Read Shockley Equation”

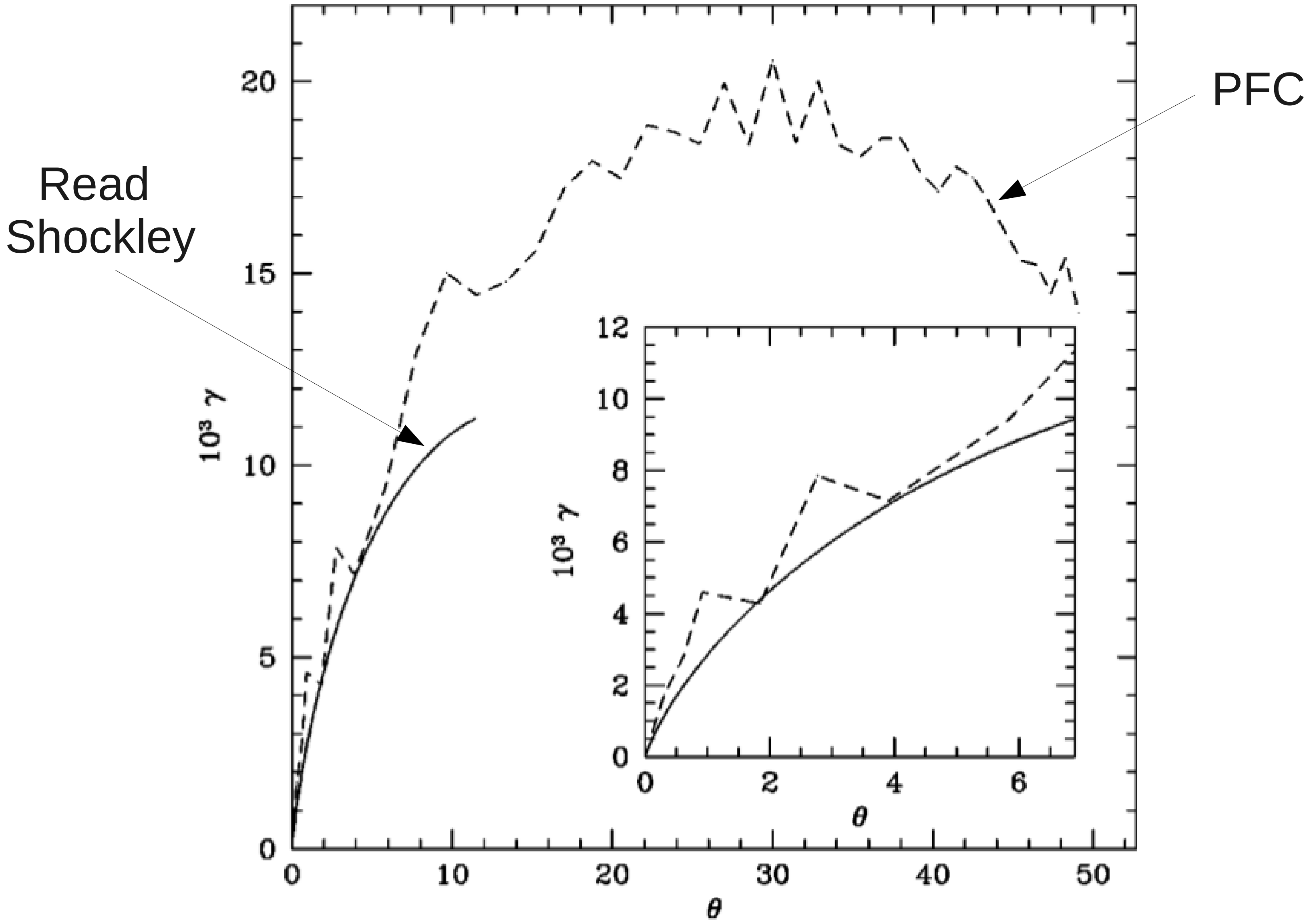
$$\gamma \equiv \frac{F}{L} = \frac{bY_2}{8\pi} \left(\frac{3}{2} - \ln(2\pi\theta) \right) \theta$$

where L = grain boundary length ,
Y_2 = 2d Young's modulus
a = lattice constant

Read Shockley, Phys. Rev. **78**, 275 (1950)
Chaiken and Lubensky, *“Principles of Condensed Matter Physics”*
Elder Grant, PRE **70**, 051605 (2004)

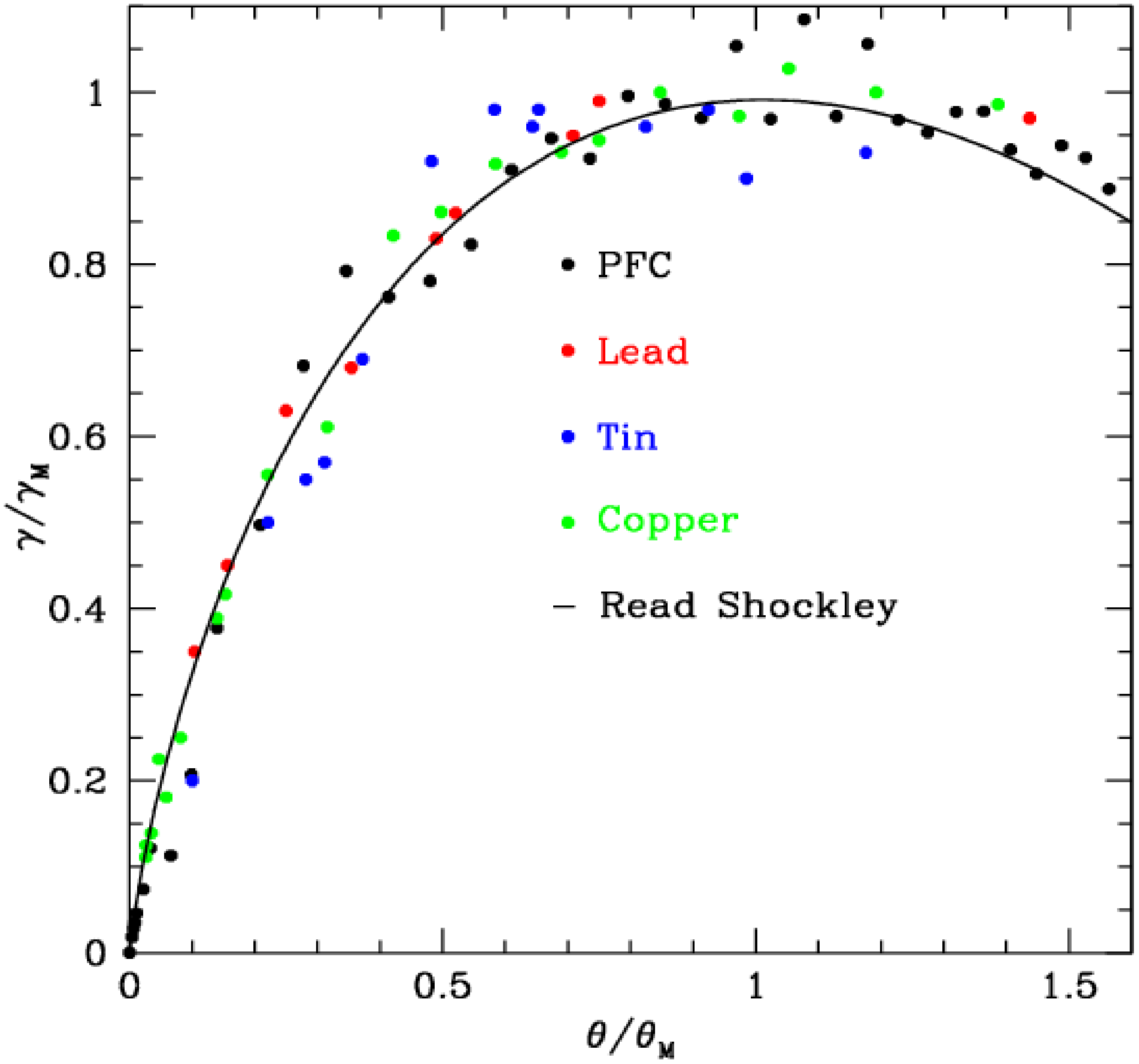
Grain boundary energy: small angle limit

Comparison PFC versus Read Shockley Equation
no adjustable parameters



Grain boundary energy: all angles

Comparison with experiment
In scaled units



scale γ and θ
by values at maximum
γ_M and θ_M

Modeling Crystal Growth

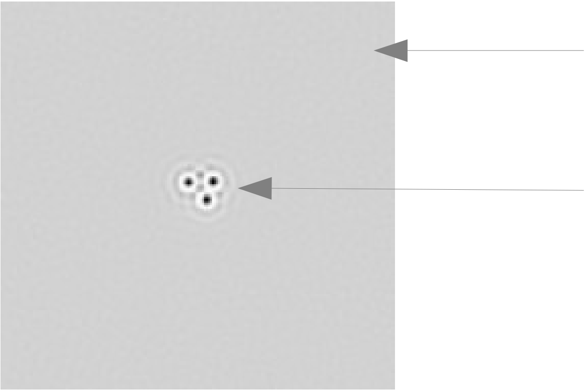
minimalist model : Phase Field Crystal (PFC)

$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2} n\left(1 + \nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

Done: static behavior

Phase diagram: liquid/solid phase transition (1st order in 2 and 3 dimensions)
Elastic constants: turned of in liquid (Φ = 0)
Polycrystals: rotational invariance of free energy functional
Grain boundaries: energy as a function of orientation

Now: dynamic behavior



supercooled liquid
n = constant

crystal seed
n = varying ~ lattice constant

Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)

$$\boxed{F = \int d\vec{r}\left[\Delta B \frac{n^2}{2} + \frac{B^x}{2} n\left(1 + \nabla^2\right)^2 n - \frac{t}{3} n^3 + \frac{v}{4} n^4\right]}$$

Now: dynamic behavior

pull ←

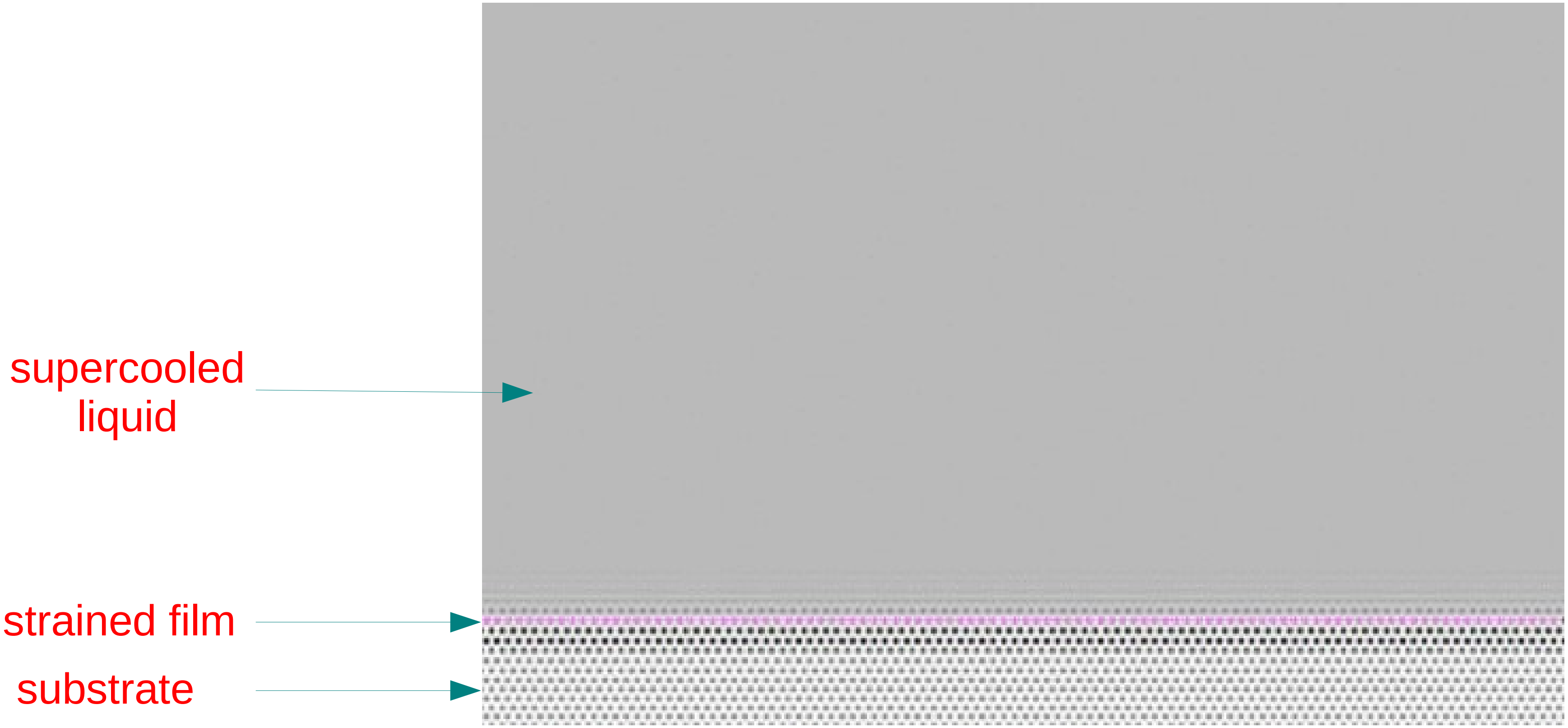
→ pull

Modeling Crystal Growth

minimalist model : Phase Field Crystal (PFC)

$$F = \int d\vec{r}\left[\Delta B\frac{n^2}{2} + \frac{B^x}{2}n\left(1+\nabla^2\right)^2 n - \frac{t}{3}n^3 + \frac{v}{4}n^4\right]$$

Now: dynamic behavior



Dynamic behavior

- assume dynamics dissipative and conserved, i.e.,

$$\frac{\partial n}{\partial t} = \nabla^2 \frac{\delta F}{\delta n} = \nabla^2\left[\left(\Delta B + B^x\left(1+\nabla^2\right)^2\right)n - t n^2 + v n^3\right]$$

Non-linear equation – difficult to solve

Linear PFC: Let $n = n_s + \delta n$ and linearize in δn

$$\frac{\partial \delta n}{\partial t} = \nabla^2\left[\Delta B - 2 t n_s + 3 v n_s^2 + B^x\left(1+\nabla^2\right)^2\right]\delta n$$

a) linearize around liquid state n_s = constant in space = n_o

$n =$ 

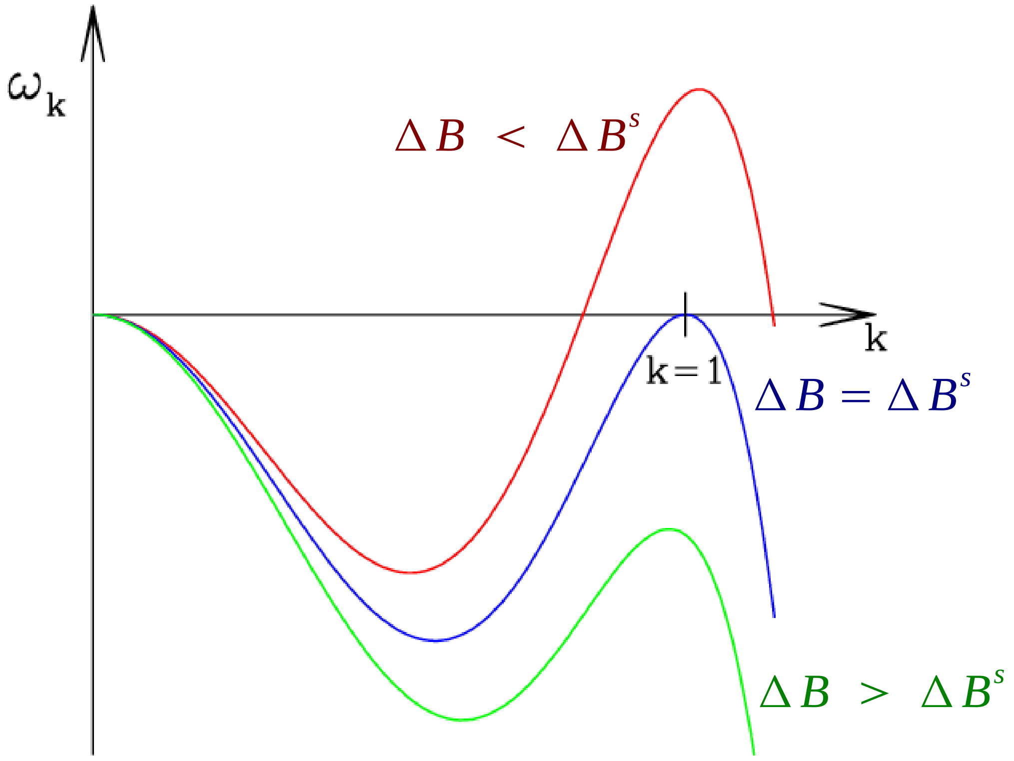
b) linearize around solid state n_s = periodic in space $\sim n_o + A\cos(qx)$

$n =$ 

a) linearize around liquid state n_o = constant in space

$$n = n_o + \delta n$$

$$\delta\hat{n}(k,t) = e^{\omega_k t}\,\delta\hat{n}(k,0) \qquad \omega_k = -k^2\left[\Delta B - 2t\,n_o + 3v\,n_o^2 + B^x(1-k^2)^2\right]$$



$$\omega_{k=1} = -k^2\left[\Delta B - 2t\,n_o + 3v\,n_o^2\right]$$

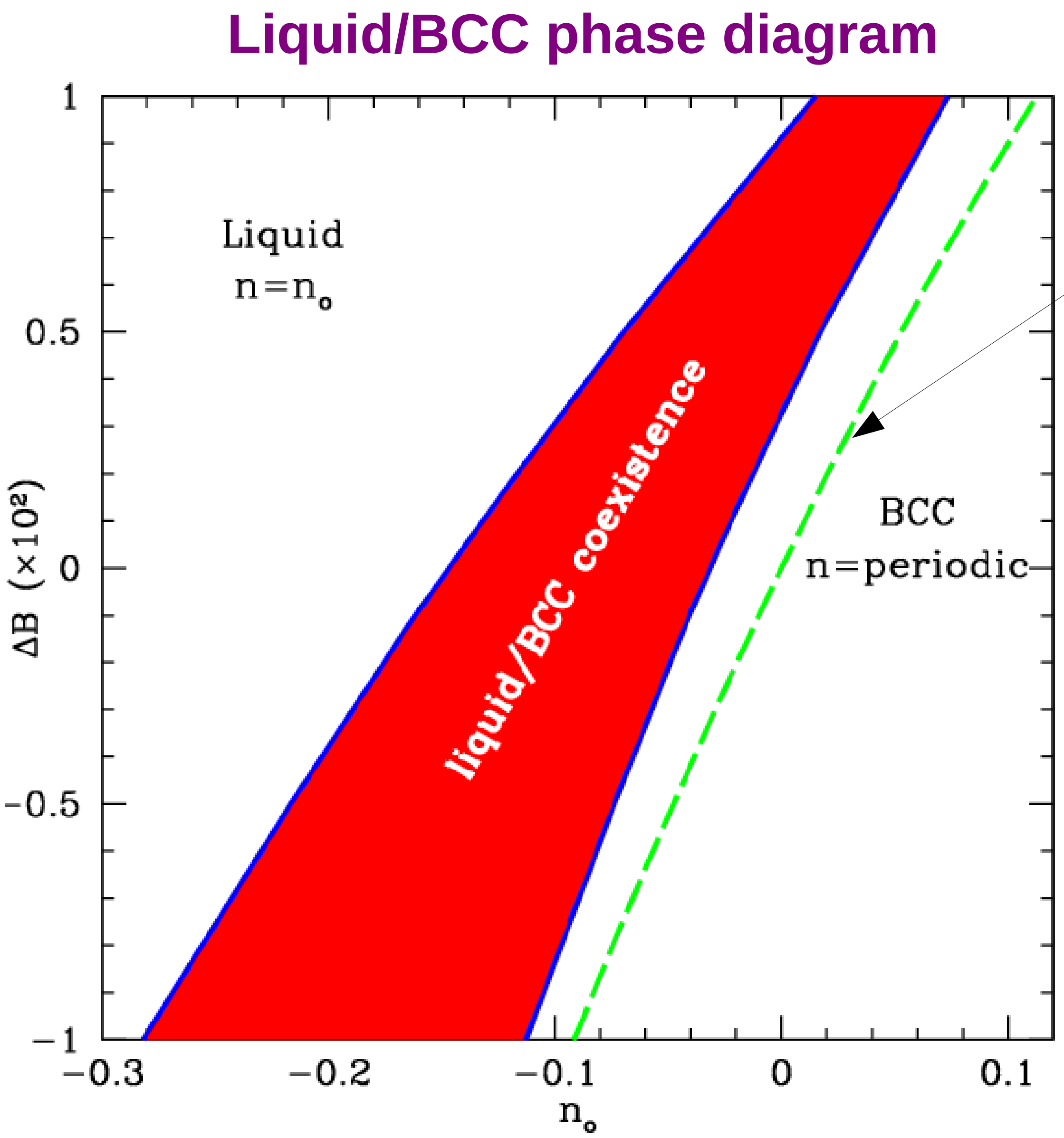
$\omega_{k=1} > 0$ liquid linearly unstable

$\omega_{k=1} < 0$ liquid linearly stable

$\omega_{k=1} = 0$ spinodal line

$$\Delta B^s = 2t\,n_o - 3v\,n_o^2$$

Sample phase diagram: with spinodal line

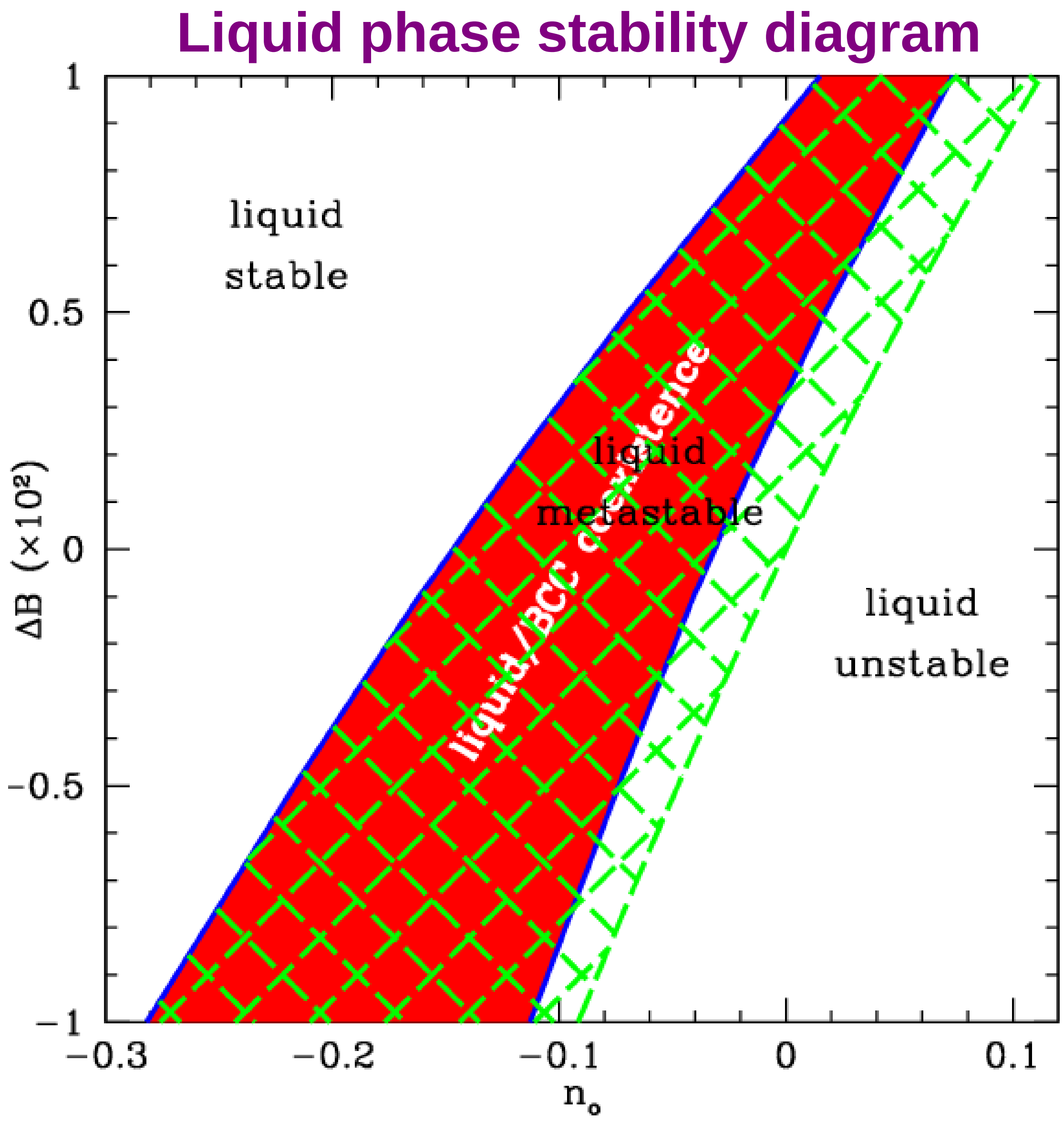


“spinodal line”

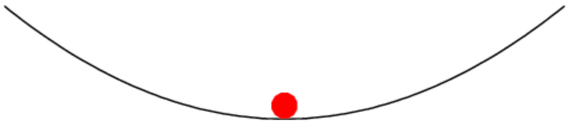
Parameters
$B^x = 1$

$t = 1/2$
$v = 1/3$

Sample phase diagram: with spinodal line


Liquid phase stability diagram

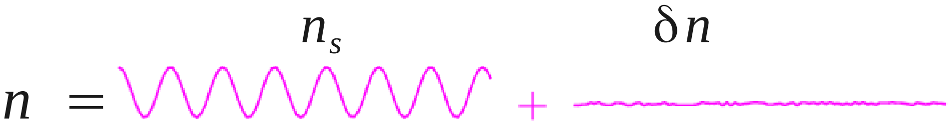
<u>Stable</u>
fluctuations decay



<u>Metastable</u>
small fluctuations decay
large enough ones grow

<u>Unstable</u>
fluctuations grow

b) linearize around solid state n_s = periodic in space



where $n_s = n_o + \sum \eta_{klm} e^{i\vec{G}_{klm}\cdot\vec{r}} + C.C.$

Use Bloch/Floquet analysis since n_s periodic function, i.e.,

$$\delta n = \sum_{n=-N}^{N} b_n(t) e^{i(qn+Q)x}$$

Recall in SH equation, b_o was boring - not so here - consider $\delta n = b_0(t)$

Linear PFC: $$\frac{\partial \delta n}{\partial t} = \nabla^2\left[\Delta B - 2t\, n_s + 3v\, n_s^2 + B^x\left(1+\nabla^2\right)^2\right]\delta n$$

Integrate over unit cell to obtain

$$\frac{\partial b_0}{\partial t} = -Q^2\left[\Delta B - 2t\, n_o + 3v\, n_o^2 + 6v(2d-1)\phi^2 + B^x\left(1-Q^2\right)^2\right] b_0$$
$$\approx -D\, Q^2 b_0$$

where , $d \equiv$ dimension, ϕ is the equilibrium amplitude and

$$D \equiv \Delta B + B^x - 2t\, n_o + 3v\, n_o^2 + 6v(2d-1)\phi^{2,}$$

b) linearize around solid state n_s = periodic in space

$$\frac{\partial b_0}{\partial t} \approx -D\,Q^2 b_0$$

Diffusion Equation!

vacancy diffusion constant

<u>Time scales</u>: Define vacancy diffusion time

$$t_{diff} \equiv \frac{a^2}{D}$$, where a = atomic spacing

Depending on numerical method $\frac{t_{diff}}{\Delta t} = 10-100$

MD: $\frac{t_{diff}}{\Delta t} \sim$ very temperature dependent

Gold at $800^o C$ $\frac{t_{diff}}{\Delta t} \sim 10^{11}$

Phase field crystal model

$$\frac{\partial n}{\partial t} = \Gamma \nabla^2 \left[\left(\Delta B + B^x \left(1 + \nabla^2 \right)^2 \right) n - t\, n^2 + v\, n^3 \right]$$

Basic features

a) selects *smooth* periodic pattern

b) deviations from periodic pattern
   – costs energy – Elasticity, dislocations ...

c) equilibrium solutions rotationally invariant
   – polycrystals, grain boundaries

d) dynamics on diffusive not phonon time scales
   - good fast
   - bad – mechanical equilibrium

Connection to classical DFT?
Connection to traditional continuum (phase) field theories?

* Connection to CDFT

CDFT free energy functional

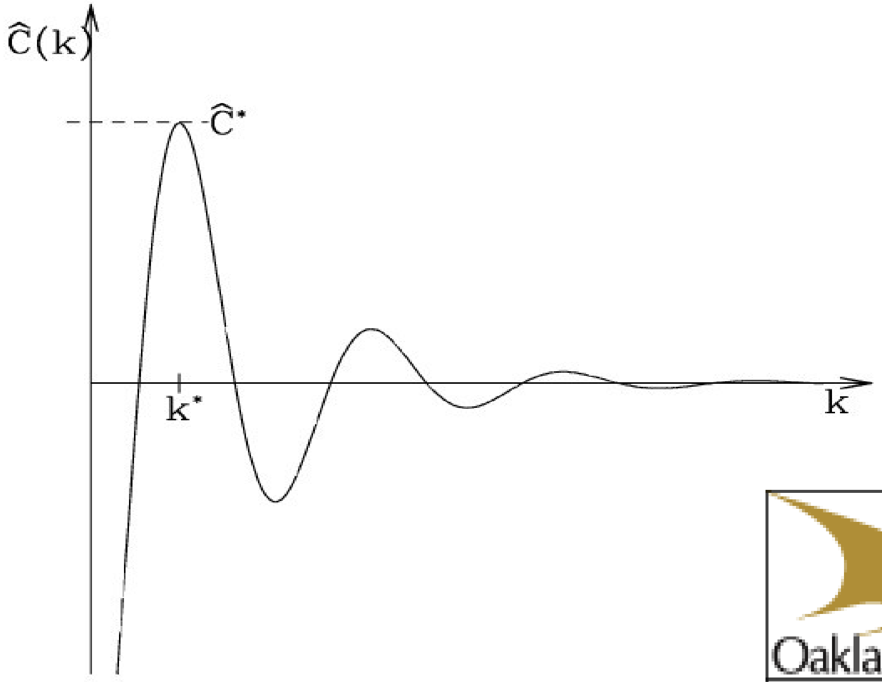
Ramakrishnan and Yussouff, PRB **19**, 2775 (1979)
Singh Phys. Rep. **207**, 351 (1991)

$$\frac{\Delta F}{k_B T} = \int d\vec{r}\left[\rho \ln\left(\frac{\rho}{\rho_l}\right) - \delta\rho\right] - \frac{1}{2!}\int d\vec{r}_1\, d\vec{r}_2\, C_2(\vec{r}_1,\vec{r}_2,)\,\delta\rho_1\,\delta\rho_2$$
$$- \frac{1}{3!}\int d\vec{r}_1\, d\vec{r}_2\, d\vec{r}_3\, C_3(\vec{r}_1,\vec{r}_2,\vec{r}_3)\,\delta\rho_1\,\delta\rho_2\,\delta\rho_3 + \ldots$$

Where ρ = atomic number density
$\delta\rho = \rho - \rho_l$
ρ_l = reference (liquid density)
C_n = direct correlation functions

Note in liquid state
– rotational invariance, i.e.,

$$C_2(\vec{r}_1,\vec{r}_2) = C_2(|\vec{r}_1 - \vec{r}_2|) \equiv C(r)$$



* Hankshake to CDFT

Expand CDFT free energy functional ....

1) Expand in $n \equiv (\rho - \bar{\rho})/\bar{\rho}$ to order n^4

2) truncate at C_2

3) expand C_2 in fourier space up to k^4, $\hat{C} = -\hat{C}_0 + \hat{C}_2 k^2 - \hat{C}_4 k^4$

Result (in dimensionless units $\vec{r} \equiv \vec{x}/R$, $R \equiv \sqrt{2\left|\hat{C}_4\right|/\hat{C}_2}$)

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - \frac{n^3}{6} + \frac{n^4}{12} \right]$$

Very simple model, three (two) parameters

$B^l \equiv 1 - \bar{\rho}\,\hat{C}_0 =$ liquid bulk modulus (dimensionless units)

$B^x \equiv \bar{\rho}\left(\hat{C}_2\right)^2/4\hat{C}_4 \sim$ crystal bulk moduli (dimensionless units)

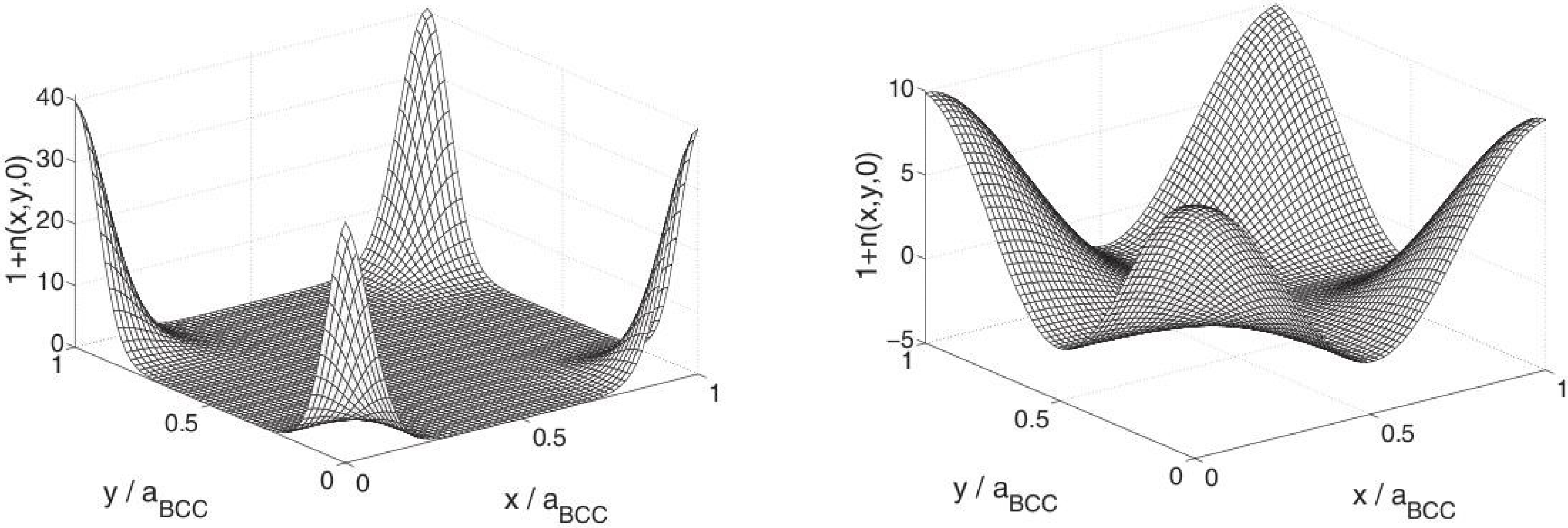
$R \equiv \sqrt{2\left|\hat{C}_2\right|/\hat{C}_2}$ ~ lattice constant

* Handshake to CDFT

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - \frac{n^3}{6} + \frac{n^4}{12} \right]$$

Very simple model, too simple?

Density Profiles Iron, 1833 K



CDFT order C_2

PFC

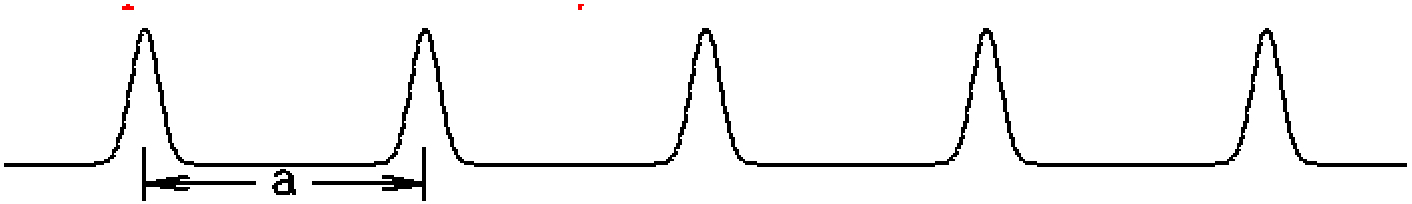
Jaatinen, Achim, Elder, Ala-Nissilä, PRE **80**, 031602 (2009)

* Handshake to CDFT

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - \frac{n^3}{6} + \frac{n^4}{12} \right]$$

Very inaccurate – why bother?

CDFT profiles: **Δx ≈ a/100**



PFC profiles: **Δx ≈ a/10**

Computationally – <u>3d PFC ~ 1000 x faster</u>

Computations – simple is good – but … Fitting to experiment?

* PFC parameter fitting

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \int d\vec{r}\left[\frac{n}{2}\left(B^l + B^x\left(2\nabla^2 + \nabla^4\right)\right)n - \frac{n^3}{6} + \frac{n^4}{12}\right]$$

Physics: elasticity, dislocations,
Multiple crystal orientations

3 (2) parameters

* PFC parameter fitting

$$\frac{\Delta \tilde{F}}{k_b T V \bar{\rho}} \approx \int d\vec{r} \left[\frac{n}{2} \left(B^l + B^x \left(2\nabla^2 + \nabla^4 \right) \right) n - t \frac{n^3}{6} + v \frac{n^4}{12} \right]$$

Physics: elasticity, dislocations,
Multiple crystal orientations

3 (2) parameters

Fitting : **5 parameters** , Iron
Wu, Karma, PRB, **76**, 184107 (2007) (t,v)
liquid/solid surface energy + anisotropy

6 parameters, Iron
Jaatinen, Achim, Elder, Ala-Nissilä, PRE, **80**, 031602 (2009)
liquid/solid surface energy + anisotropy
Miscibility gap, bulk moduli,
Liquid state isothermal compressibility

Fitting : **4 parameters**, Colloids
Van Teeffelen, Backofen, Voigt, Löwen, PRE **79**, 051404 (2009)
Solidification rates - dynamics

* PFC parameter fitting

Fitting to Iron, T = 1772 K

Quantity	Experiment/ MD	5 parameter [1]	6 parameter [2]
surface energy (100) (ergs/cm^2)	177.0 [1]	207.1	165.7
surface energy (110) (ergs/cm^2)	173.5 [1]	201.7	161.5
surface energy (111) (ergs/cm^2)	173.4 [1]	194.8	157.2
Anisotropy (%)	1.0 [1]	1.3	1.3
Expansion upon melting (Å^3/atom)	**0.38 [3]**	**2.07**	**0.43**
Solid bulk modulus (GPa)	**105.0 [4]**	**22.2**	**94.5**
Liquid bulk modulus (GPa)	**96.2 [5]**	**18.6**	**93.2**

[1] Wu, Karma, PRB, **76**, 174107 (2007)
[2] Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009).
[3] Mendelev, Han, Srolovitz, Ackland, Sun, Asta, Phil. Mag. **83**, 3977 (2003)
[4] Dever, J. Appl. Phys., **43**, 3293 (1972):
Adams, Agosta, Leisure, Ledbetter, J. Appl. Phys. **100**, 113530 (2006)
[5] Tsu, Takano, 88th Spring Conference (Japan Institute of Metals, Sendai 1981), **88**, p. 86:
Itami, Shimoji, J. Phys. F: Met. Phys, **14**, L15 (1984).

* PFC parameter fitting

Fitting to Iron, T = 1772 K

Quantity	Experiment/ MD	5 parameter [1]	6 parameter [2]
surface energy (100) (ergs/cm^2)	177.0 [1]	207.1 17%	165.7 6%
surface energy (110) (ergs/cm^2)	173.5 [1]	201.7 16%	161.5 7%
surface energy (111) (ergs/cm^2)	173.4 [1]	194.8 12%	157.2 9%
Anisotropy (%)	1.0 [1]	1.3 30%	1.3 30%
Expansion upon melting (Å^3/atom)	0.38 [3]	2.07	0.43
Solid bulk modulus (GPa)	105.0 [4]	22.2	94.5
Liquid bulk modulus (GPa)	96.2 [5]	18.6	93.2

percent error

[1] Wu, Karma, PRB, **76**, 174107 (2007)
[2] Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009).
[3] Mendelev, Han, Srolovitz, Ackland, Sun, Asta, Phil. Mag. **83**, 3977 (2003)
[4] Dever, J. Appl. Phys., **43**, 3293 (1972):
Adams, Agosta, Leisure, Ledbetter, J. Appl. Phys. **100**, 113530 (2006)
[5] Tsu, Takano, 88th Spring Conference (Japan Institute of Metals, Sendai 1981), **88**, p. 86:
Itami, Shimoji, J. Phys. F: Met. Phys, **14**, L15 (1984).

Oakland UNIVERSITY

* PFC parameter fitting

Fitting to Iron, T = 1772 K

Quantity	Experiment/ MD	5 parameter [1]	6 parameter [2]
surface energy (100) (ergs/cm^2)	177.0 [1]	207.1	165.7
surface energy (110) (ergs/cm^2)	173.5 [1]	201.7	161.5
surface energy (111) (ergs/cm^2)	173.4 [1]	194.8	157.2
Anisotropy (%)	1.0 [1]	1.3	1.3
Expansion upon melting (Å^3/atom)	**0.38 [3]**	**2.07** 440%	**0.43** 13%
Solid bulk modulus (GPa)	**105.0 [4]**	**22.2** 79%	**94.5** 10%
Liquid bulk modulus (GPa)	**96.2 [5]**	**18.6** 81%	**93.2** 3%

percent error

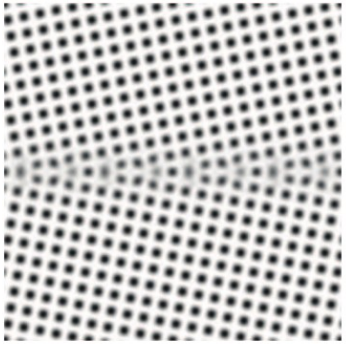
[1] Wu, Karma, PRB, **76**, 174107 (2007)
[2] Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009).
[3] Mendelev, Han, Srolovitz, Ackland, Sun, Asta, Phil. Mag. **83**, 3977 (2003)
[4] Dever, J. Appl. Phys., **43**, 3293 (1972):
Adams, Agosta, Leisure, Ledbetter, J. Appl. Phys. **100**, 113530 (2006)
[5] Tsu, Takano, 88th Spring Conference (Japan Institute of Metals, Sendai 1981), **88**, p. 86:
Itami, Shimoji, J. Phys. F: Met. Phys, **14**, L15 (1984).

Iron grain boundary energy <100> symmetric tilt boundary

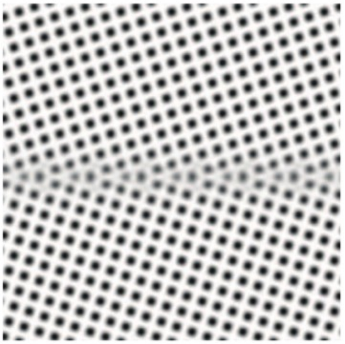
Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

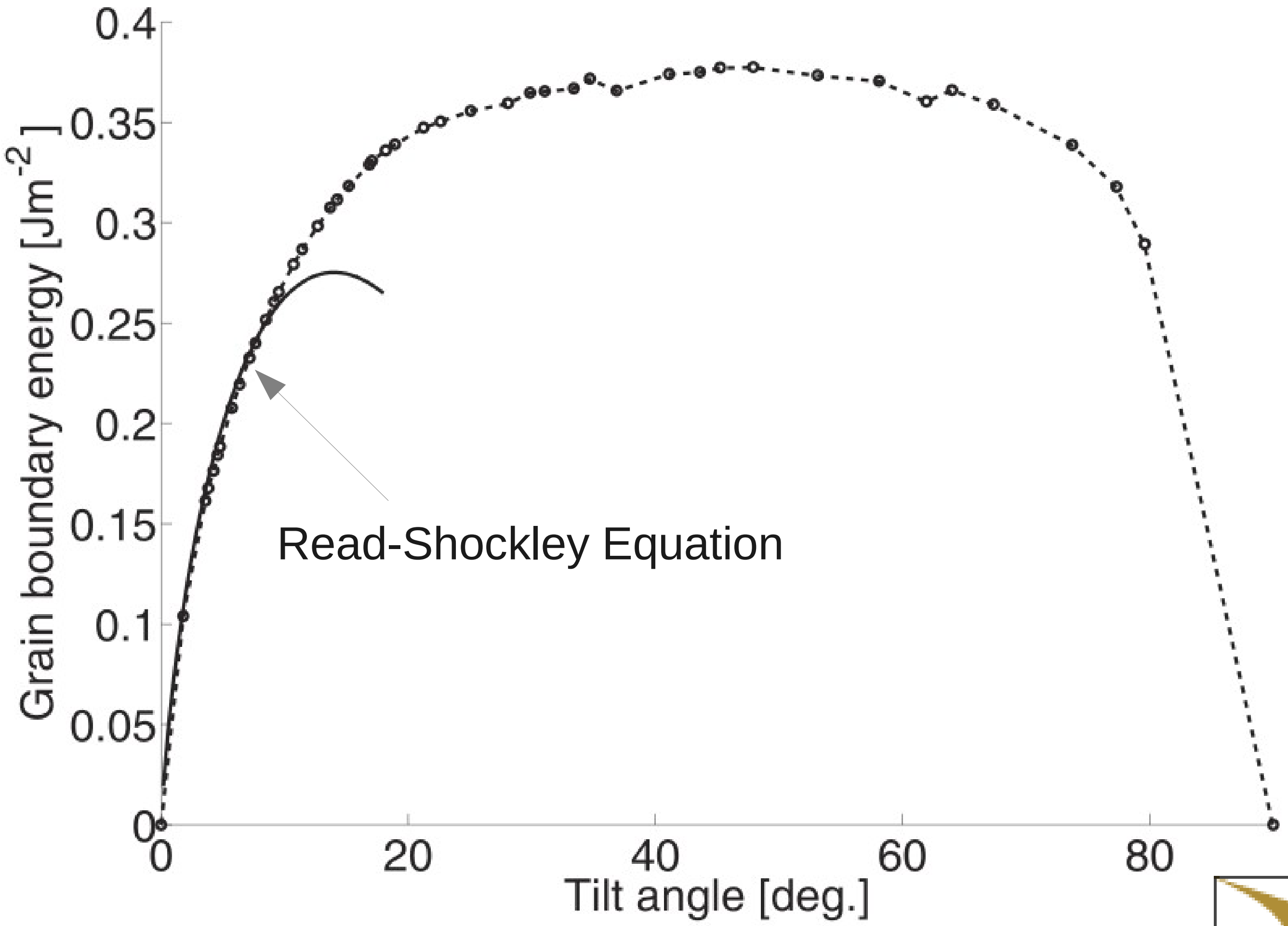
mismatch, θ=1.79°

mismatch, θ=22.62°



mismatch, θ=36.87°



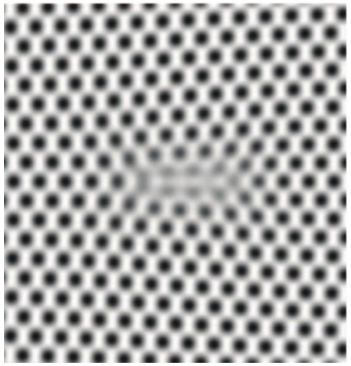


Read-Shockley Equation

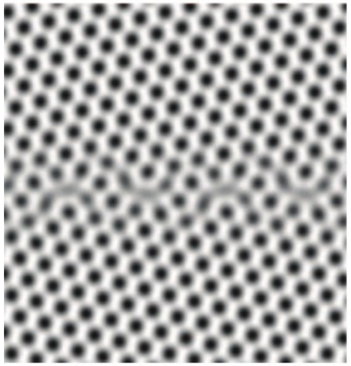
Iron grain boundary energy <110> symmetric tilt boundary

Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

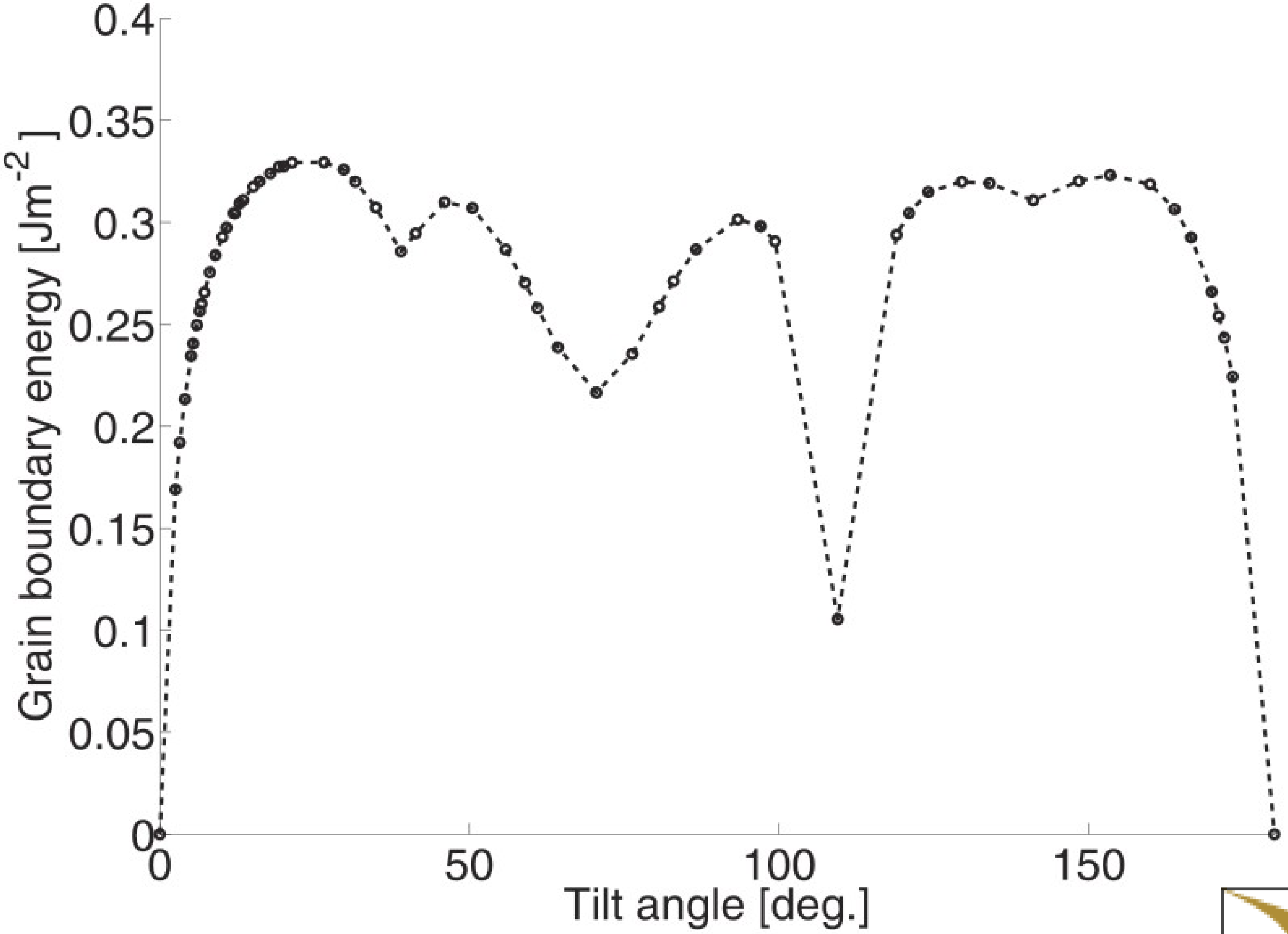
mismatch, θ=2.53°



mismatch, θ=26.52°



mismatch, θ=50.47°

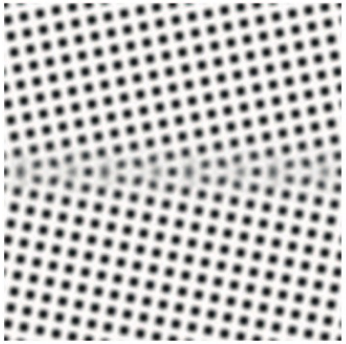


Iron grain boundary energy <100> symmetric tilt boundary

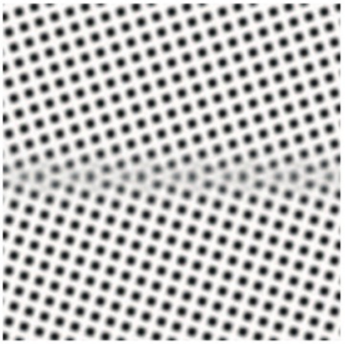
Jaatinen, Achim, Elder, Ala-Nissilä, PRB **80**, 031602 (2009): Tech. Mech, **30**, 169 (2010)

mismatch, θ=1.79°

mismatch, θ=22.62°



mismatch, θ=36.87°



Comparison with other work

Method	Maximum GB energy	Ratio : GB energy to Liq/Sol energy
Current work	0.37 Jm^{-2}	2.2
Experiment[1]	0.46 Jm^{-2}	2.6
Embedded atom (T=0)[2]	10.0 Jm^{-2}	
MD[3]	1.6 Jm^{-2}	

[1] Muir *Interfacial Phenomena in Metals and Alloys*
Addison Wesley, New York (1975)
[2] Zhang, Huang, Wu, Xu, Appl. Surf. Sci. 252, 4936 (2005)
[3] Shibuta, Takamoto, Suzuki, ISIJ Int. 48 1582 (2008)

Phase field crystal model

$$\frac{\partial n}{\partial t} = \Gamma \nabla^2 \left[\left(\Delta B + B^x \left(1 + \nabla^2 \right)^2 \right) n - t\, n^2 + v\, n^3 \right]$$

Connection to classical DFT? → dubious → Colloids...

n_{pfc} ~ convolution of n_{cdft}?

$$n_{PFC} = \int d\vec{r}\,'\, W\left(|\vec{r} - \vec{r}\,'|\right) n_{CDFT}\left(\vec{r}\,'\right)$$

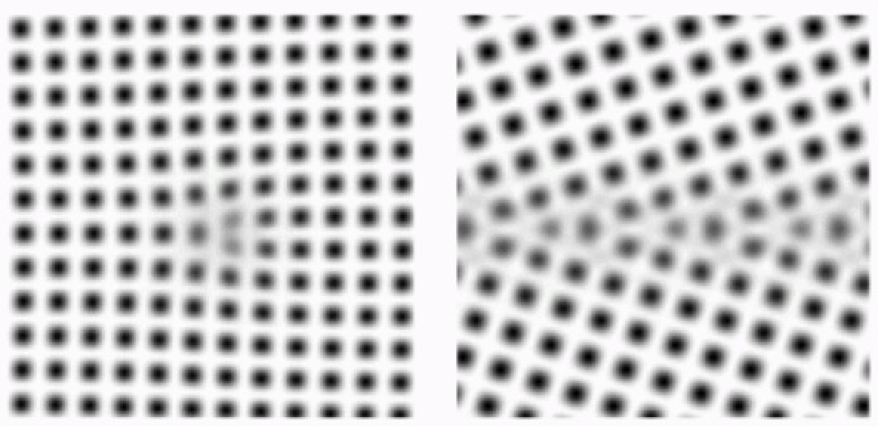
Jaatinen, Ala Nissila PRE 82, 061602 (2010)

or

n ~ fictitious field to introduces elasticity, dislocations, ...

- connection with traditional continuum (phase) field theories: next

Applications

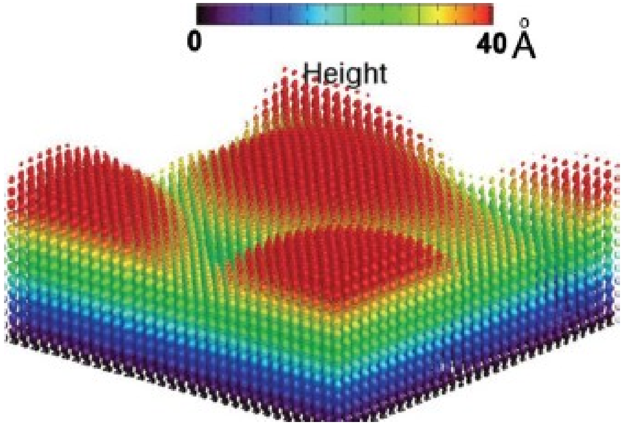


Grain boundaries
– energy, premelting

Berry etal PRB (2008),
Mellenthin etal RPB (2008)
Jaatinen etal PRE (2009)

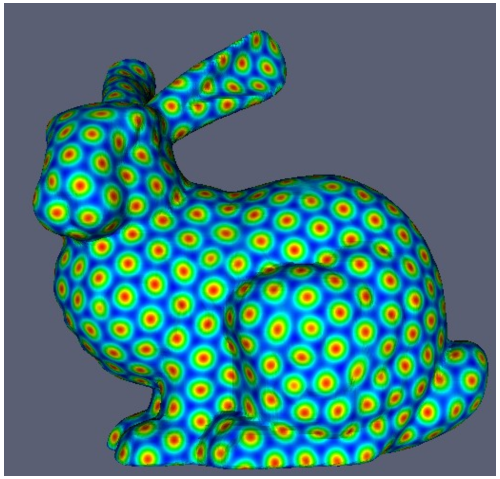
Strained films
-epitaxial growth

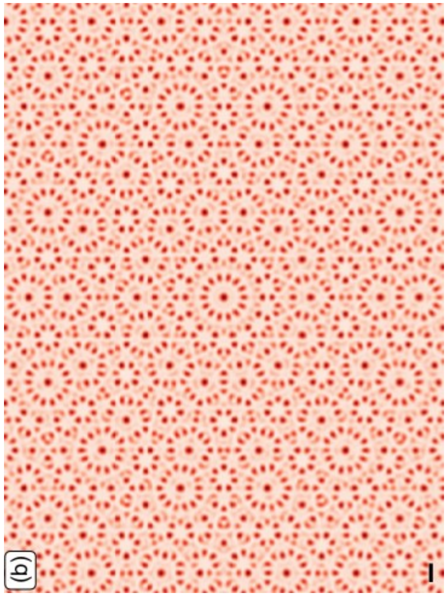
Huang Elder PRL (2008), PRB (2010)
Wu Voorhees PRB (2009)



Surface ordering

Achim etal PRE (2006)
Ramoseal PRE (2008), PRE (2009)
Backofen etal PRE (2010)
Muralidharan Haataja PRL (2010)
Rottler etal J Phys: Cond Mat (2012)

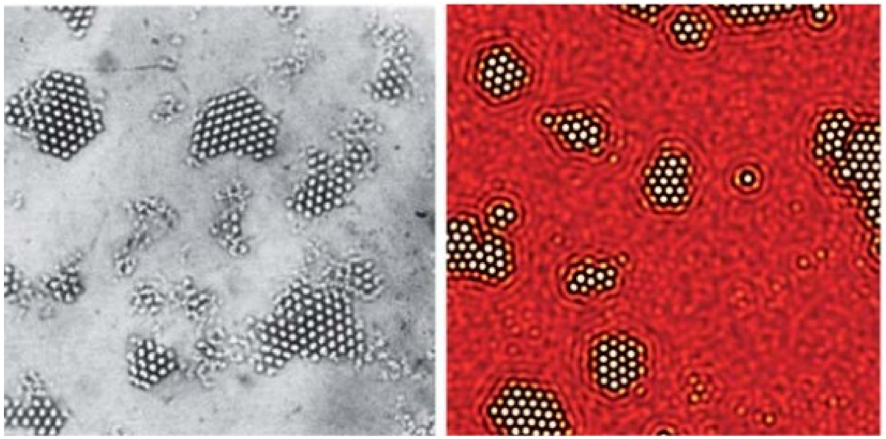




Applications

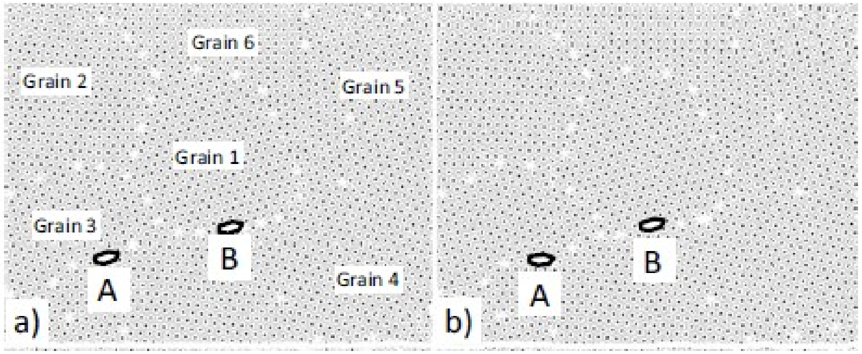
Solidification/nucleation

Backofen etal Phil Mag (2007)
Prieler etal J. Phys. Cond Mat (2009)
Galenko etal PRE (2009)
Tegze etal Soft Matter (2010)
Tegze etal PRL (2011),
Granasy etali (2011)



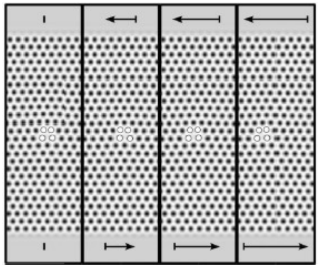
Material strength ~ polycrystals

Hirouchi, etal
Comput Mater Sci (2009)
Stefanovic, etal
PRL (2006), PRE (2009)



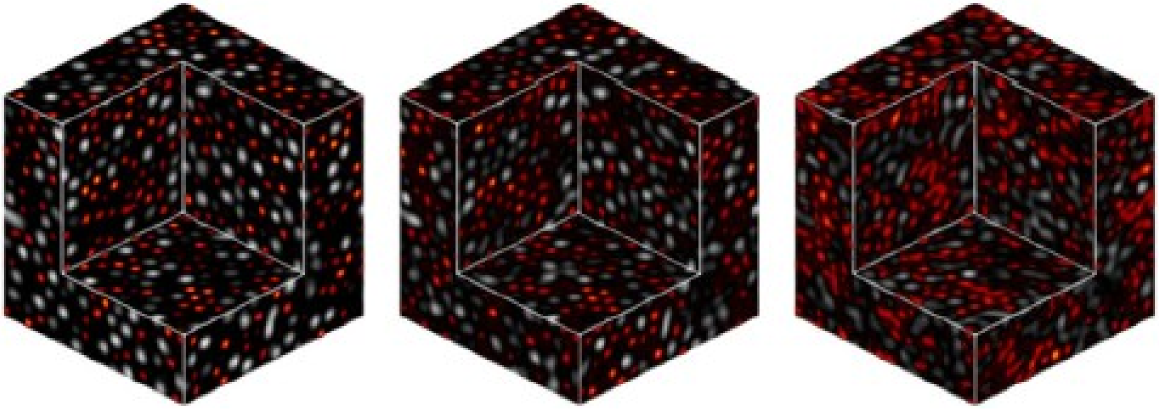
Dislocation dynamics - plasticity

Berry etal PRE (2006)
Chan etal PRL (2010)



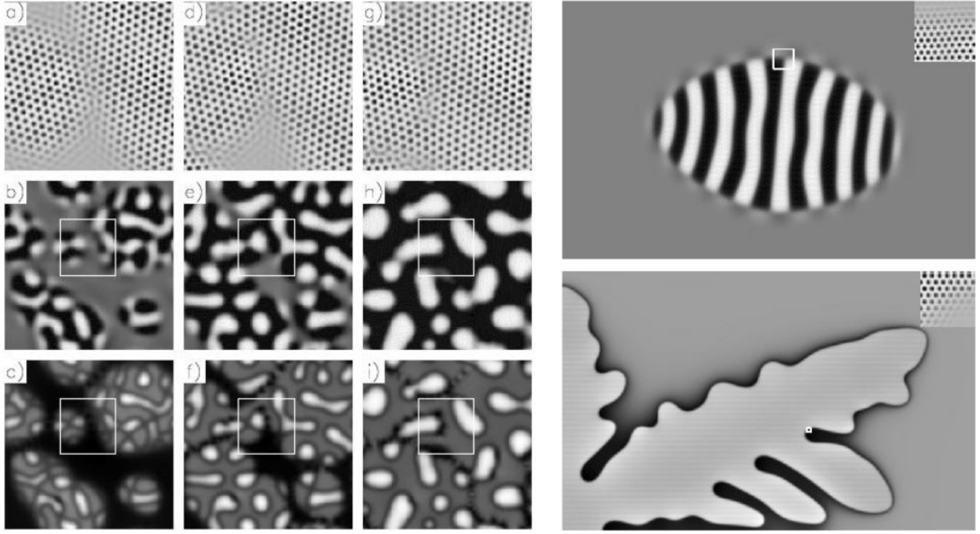
Glass formation

Berry etal PRE (2008),
Berry Grant PRL (2011)



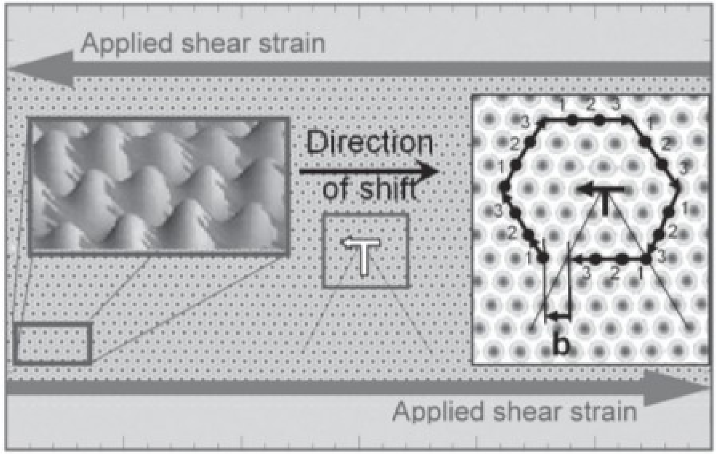
Extensions

Binary Alloys



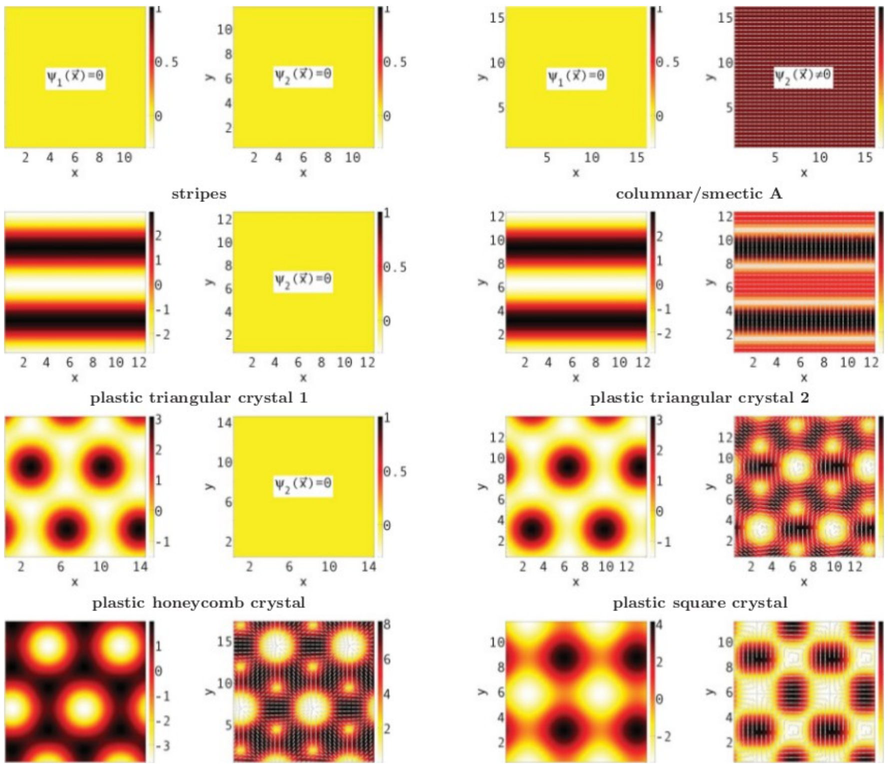
Elder etal PRB, **75**, 064107 (2007)

“sound” modes



Stefanovic etal PRE, **80**, 046107 (2009), PRL, **96**, 225504 (2006)
Majaniemi etal PRB, **75**, 054301 (2007),

Liquid crystals

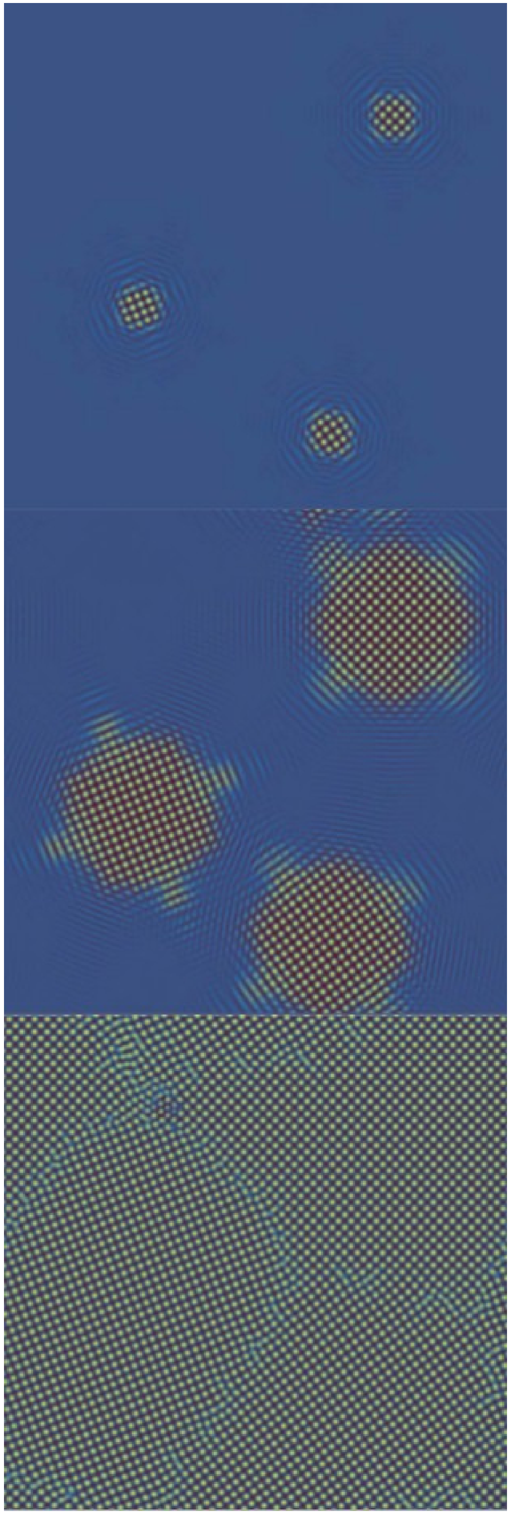


Achim etal PRE, **83**, 061712 (2011)
Wittkowski etal PRE, **82**, 031708 (2010)
Loewen J. Phys-Cond Mat **22**, 364105 (2010)

Extensions

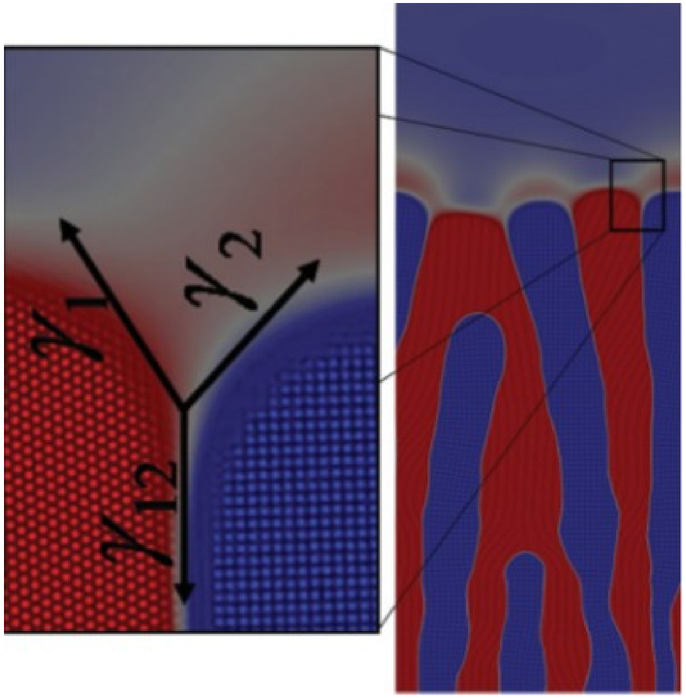
Anisotropic particles

Choudhary etal
J. Phys.: Cond. Mat. **23**, 265005 (2011)
Prieler etal
J. Phys.: Cond. Mat. **21** 464110 (2009)



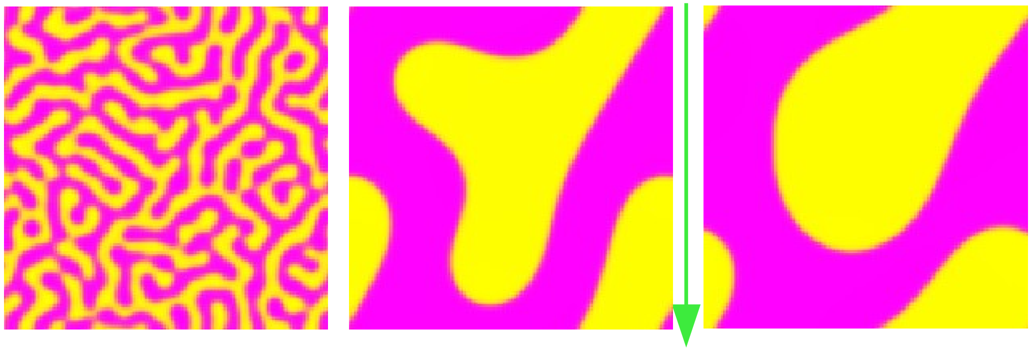
Different crystal symmetries

Greenwood etal
PRB, **84**, 064104 (2011)
PRL, **105**, 045702 (2010)
Wu+Karma,
PRE, **81**, 061601 (2010)



Non-equilibrium pattern formation in materials physics

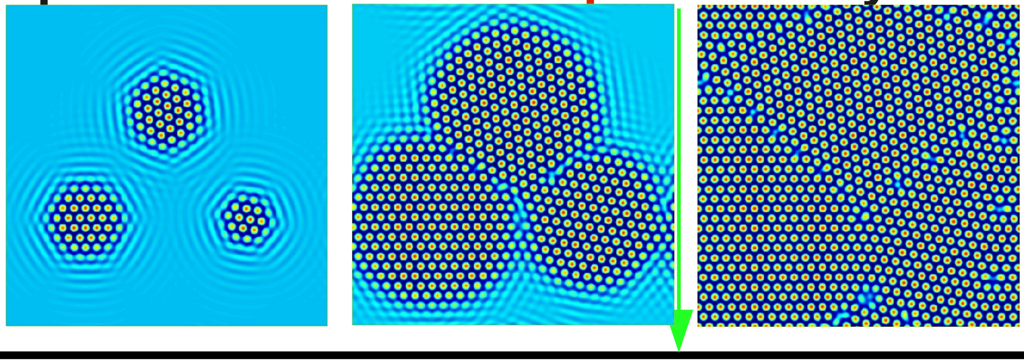
Talk 1 : pattern formation in “uniform” systems



spinodal decomposition
(Cahn Hilliard)
order/disorder transtions
(Allen Cahn)

sharp interface limits
universal scaling

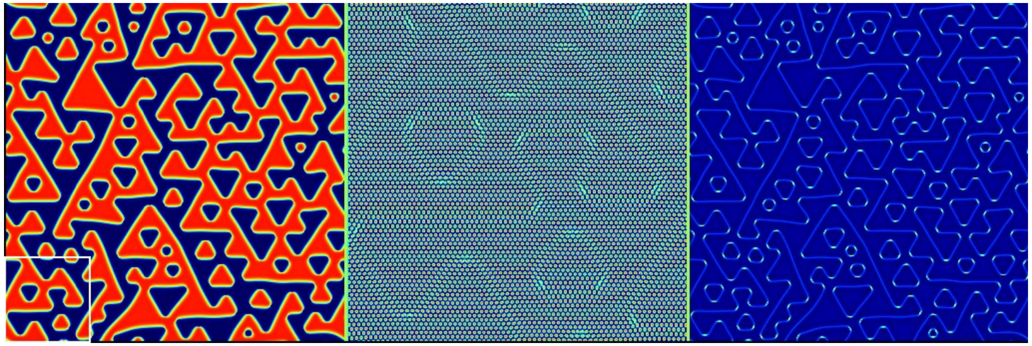
Talk 2 : pattern formation in “periodic” systems



Rayleigh Benard convection
(Swift Hohenberg)
crystal growth
(Phase Field Crystal)

elasticity
dislocations

Talk 3 : pattern formation in “uniform” systems with elasticity



Amplitude expansions
crystal growth

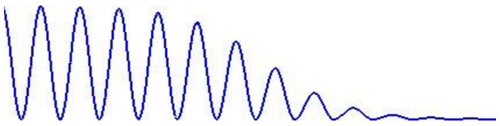
micron simulations
with atomic resolution

Overview

Multiscale modeling

mechanical properties - elasticity, dislocations,
grain boundaries, polycrystals, …

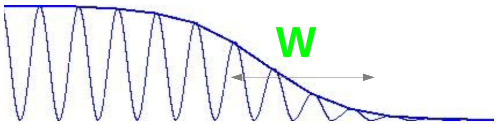
Phase field crystal



$\Delta x \sim a/10$ **~0.1 Å**

→

Amplitude



$\Delta x \sim W/10$ **~1 Å**

→

Continuum

$\Delta x \sim W/10$ **~1 Å**

References

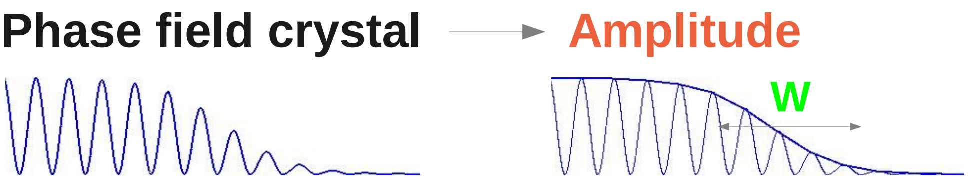
pure systems

Goldenfeld, Athreya, Dantzig, PRE (2005)
Athreya, Goldenfeld, Dantzig, PRE (2006)
Athreya, Goldenfeld, Dantzig, Greenwood, Provatas PRE (2007)
Chan, Goldenfeld PRE (2009)
Yeon, Huang, Elder, Thornton, Phil Mag (2010)

binary systems

Elder, Huang, Provatas PRE (2010)
Huang, Elder, Provatas PRE (2010)
Spatschek, Karma PRB (2010)

PFC to Amplitude expansions


Phase field crystal → Amplitude

PFC free equation of motion

$$\frac{\partial n}{\partial t} = \Gamma \nabla^2 \left[\left(\Delta B + B^x \left(1 + \nabla^2\right)^2 \right) n - t\, n^2 + v\, n^3 \right]$$

Amplitude formulation:

$$\boxed{n = \sum_{\vec{G}} \left(\eta_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}} + \eta^*_{\vec{G}}\, e^{-i\vec{G}\cdot\vec{r}} \right)}$$

$$\vec{G} \equiv l\vec{q}_1 + m\vec{q}_2 + n\vec{q}_3$$

$$\left(\vec{q}_1, \vec{q}_2, \vec{q}_3\right) \equiv \text{principle reciprocal lattice vectors}$$

$$\left(l, m, n\right) \equiv \text{Miller indices}$$

Goal – derive $\boxed{\frac{\partial \eta_{\vec{G}}}{\partial t} = ?}$

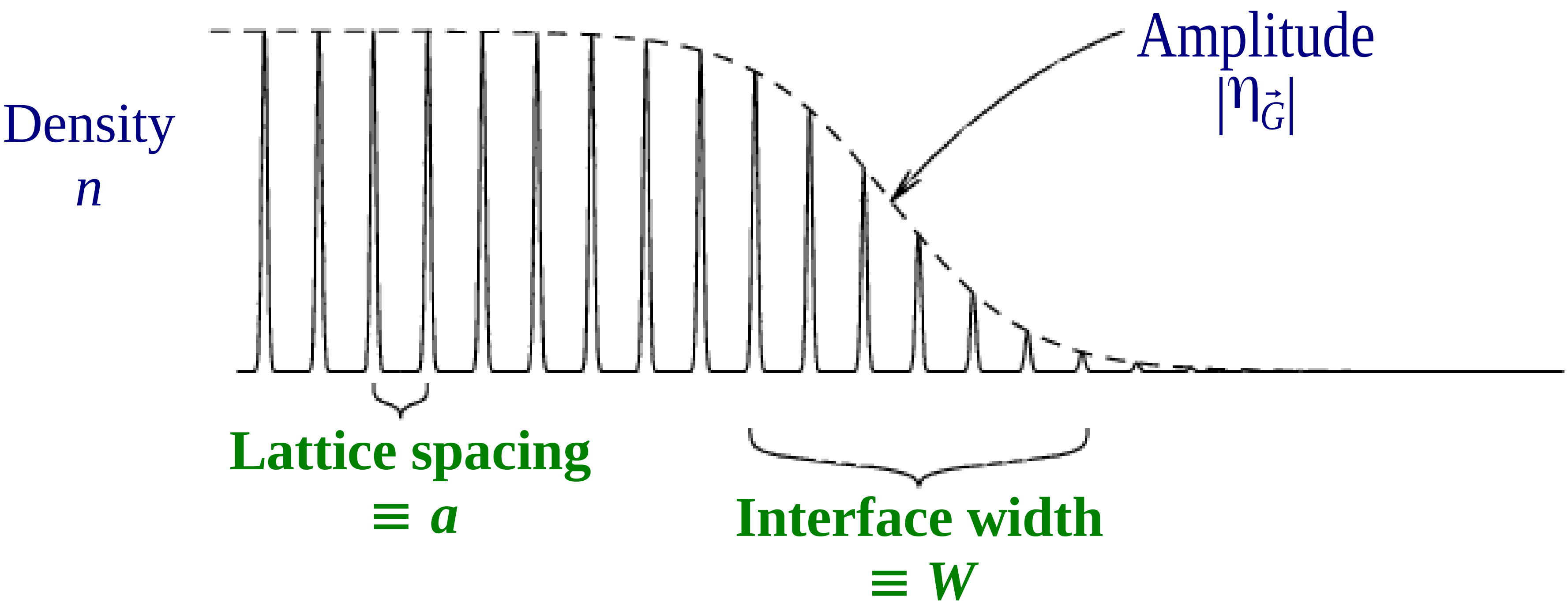
* Amplitude expansion: multiple scales approximation

$$n = \sum_{\vec{G}} \left(\eta_{\vec{G}} \, e^{i\vec{G}\cdot\vec{r}} + \eta^{*}_{\vec{G}} \, e^{-i\vec{G}\cdot\vec{r}} \right)$$

$$\frac{\partial \eta_{\vec{G}}}{\partial t} = ?$$

2 fields *(n, η_G)* – **2 length scales (*a,W*)**

Consider schematic of liquid/solid interface



Multiple scales approximation

$$W \gg a$$ → Phase field limit

* Amplitude expansion: multiple scales approximation

$$n = \sum_{\vec{G}} \left(\eta_{\vec{G}} \, e^{i\vec{G}\cdot\vec{r}} + \eta^{*}_{\vec{G}} \, e^{-i\vec{G}\cdot\vec{r}} \right)$$

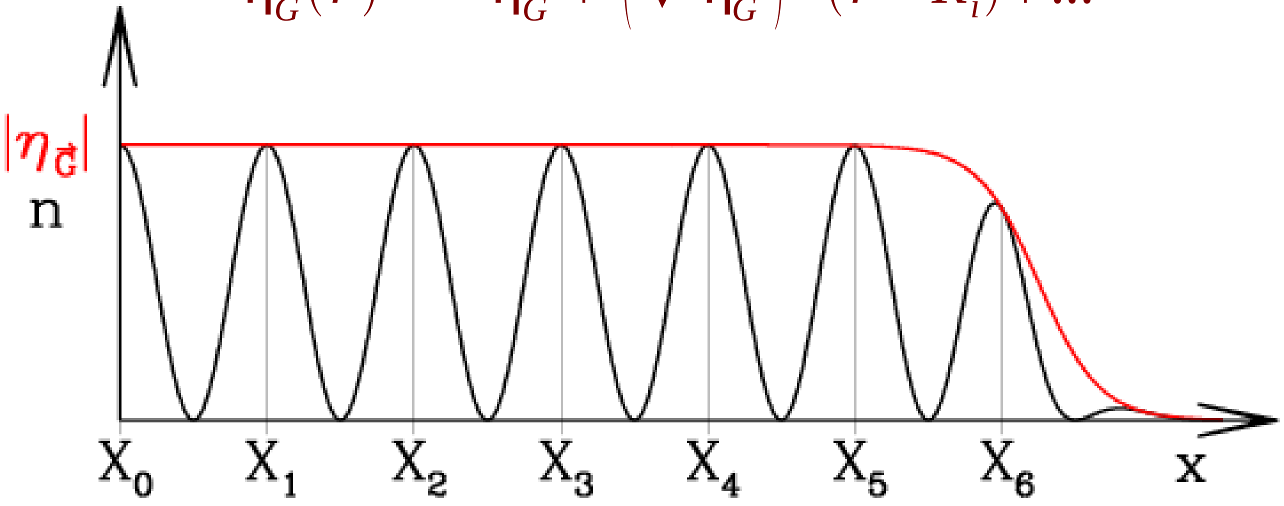
$$\frac{\partial \eta_{\vec{G}}}{\partial t} = ?$$

Multiple scales approximation

$W \gg a$ → Phase field limit

Expand amplitudes (η) around lattice sites, i.e.,

$$\eta_{\vec{G}}(\vec{r}) \approx \eta^{i}_{\vec{G}} + \left(\vec{\nabla} \eta^{i}_{\vec{G}} \right) \cdot \left(\vec{r} - \vec{R}_i \right) + \ldots$$



* Amplitude expansion: multiple scales approximation

$$n = \sum_{\vec{G}} \left(\eta_{\vec{G}}\, e^{i\vec{G}\cdot\vec{r}} + \eta^{*}_{\vec{G}}\, e^{-i\vec{G}\cdot\vec{r}} \right)$$

$$\frac{\partial \eta_{\vec{G}}}{\partial t} = ?$$

Expand amplitudes (η) around lattice sites, i.e.,

$$\eta_{\vec{G}}(\vec{r}) \approx \eta^{i}_{\vec{G}} + \left(\vec{\nabla}\, \eta^{i}_{\vec{G}} \right) \cdot (\vec{r} - \vec{R}_i) + \ldots$$

Multiply equation of motion by $e^{-i\vec{Q}_{\vec{G}}\cdot\vec{r}}$ and average over one unit cell eg., in one dimension

$$\frac{1}{a} \int_{x_i - a/2}^{x_i + a/2} dx\; e^{-iQ_G x} \left[\frac{\partial n}{\partial t} = \Gamma \nabla^2 \left[\left(\Delta B + B^x \left(1 + \nabla^2 \right)^2 \right) n - t\, n^2 + v\, n^3 \right] \right]$$

Eg, left hand side

$$\frac{1}{a} \int_{x_i - a/2}^{x_i + a/2} dx\; e^{-iQx} \left[\frac{\partial}{\partial t} \left(\eta^{i} + \left(\vec{\nabla}\, \eta^{i} \right) \cdot (\vec{r} - \vec{R}_i) + \ldots \right) e^{iQx} \right]$$

$$\approx \frac{\partial \eta^{i}}{\partial t} \left(\frac{1}{a} \int_{x_i - a/2}^{x_i + a/2} dx \right) + \frac{\partial \vec{\nabla} \cdot \eta^{i}}{\partial t} \left(\frac{1}{a} \int_{x_i - a/2}^{x_i + a/2} dx\, (x - x_i) \right) + \ldots$$

* Amplitude expansion: Two dimensions to lowest order

2d: triangular lattice, principle reciprocal lattice vectors ¿

$$\vec{q}_1 = -\frac{1}{2}\left(\sqrt{3}\,\hat{x} + \hat{y}\right) \;\; ; \;\; \vec{q}_2 = \hat{y}$$

$$\frac{\partial \eta_j}{\partial t} = \Im_j \frac{\delta F_{2d}}{\delta \eta_j^*} \approx -\left[\left(\Delta B + B^x \Im_j^2 + 3v\left(A^2 - |\eta_j|^2\right)\right)\eta_j - 2t\prod_{i\neq j}\eta_i^*\right]$$

$$\boxed{F_{2d} = \int d\vec{r}\left[\frac{\Delta B}{2}A^2 + \frac{3v}{4}A^4 + \sum_{j=1}^{3}\left\{B^x|\Im_j\eta_j|^2 - \frac{3v}{2}|\eta_j|^4\right\} - 2t\left\{\prod_{j=1}^{3}\eta_j + c.c.\right\}\right]}$$

where $A^2 \equiv 2\sum|\eta_j|^2$, $\Im_j \equiv \nabla^2 + 2i\vec{q}_j\cdot\vec{\nabla}$

→ **Now 6 equations (3 complex)**

→ **Still includes elasticity, dislocations, multiple crystal orientations**

* Amplitude expansion: applications

Polycrystals – (Φ,u) – adaptive mesh refinement

Athreya, Goldenfeld, Dantzig, Greenwood, Provatas, PRE **76**, 056706 (2007)

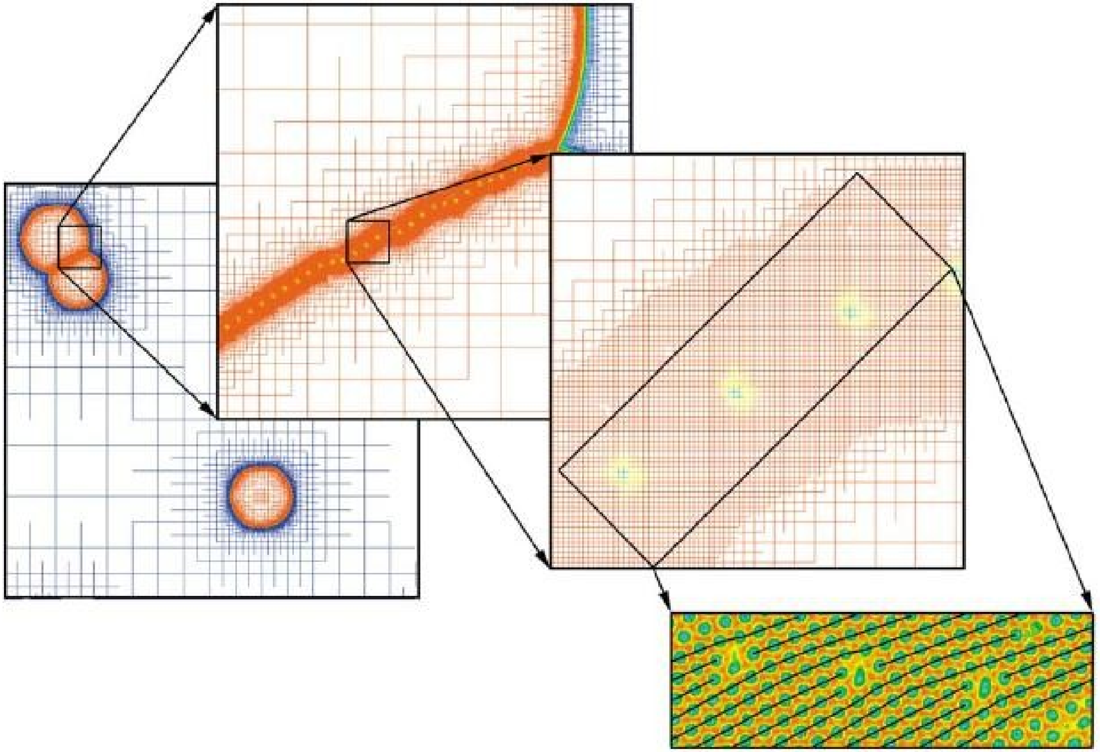


FIG. 12. (Color online) The above grid spans roughly three orders of magnitude in length scales, from a nanometer up to a micrometer. The leftmost box resolves the entire computational domain whereas the rightmost resolves dislocations at the atomic scale.

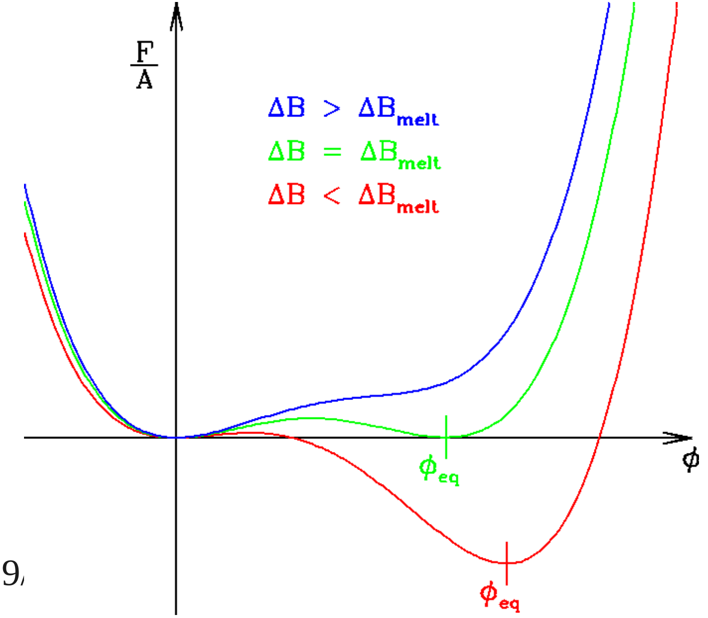
* Continuum limit of amplitude equations

Limiting case: $\eta_j = \phi\, e^{i\vec{G}_j\cdot\vec{u}}$, where, $\vec{u}=$ displacement field

Small deformation limit

$\phi \rightarrow 1^{st}$ order liquid/solid transition, $\vec{u} \rightarrow$ continuum elasticity theory ¿

$$F_{2d} = \int d\vec{r}\left[\underbrace{3\Delta B\phi^2 - 4t\phi^3 + \frac{45}{2}v\phi^4}_{\text{1st order Liquid/Solid phase transition}} + \underbrace{6B^x\left|\vec{\nabla}\phi\right|^2}_{\text{surface energy}} + \underbrace{3B^x\phi^2\left\{\frac{3}{2}\sum_{i=1}^{2}U_{ii}^2 + U_{xx}U_{yy} + 2U_{xy}^2\right\}}_{\text{continuum elastic energy}}\right]$$



Where $U_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{1}{2}\frac{\partial u_k}{\partial x_i}\frac{\partial u_k}{\partial x_j}\right)$

elastic constants

$$C_{11} = 9B^x\phi^2$$
$$C_{12} = C_{44} = C_{11}/3$$

Again note:

liquid: $\phi = 0$, elastic energy $= 0$

solid: $\phi \neq 0$, elastic energy > 0

* Continuum limit of amplitude equations

Limiting case: $\eta_j = \phi$ no deformations

$$F_{2d} = \int d\vec{r} \left[3\Delta B \phi^2 - 4t\phi^3 + \frac{45}{2} v \phi^4 + 6 B^x \left| \vec{\nabla} \phi \right|^2 \right]$$

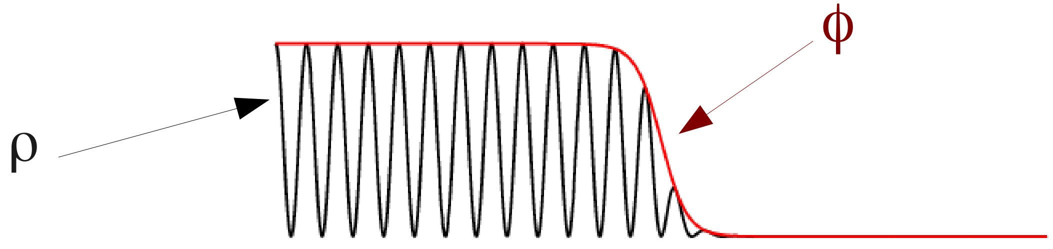
Dynamics

$$\frac{\partial \phi}{\partial t} = -\frac{M}{6} \frac{\delta F}{\delta \phi}$$

$$= M \left[2 B^x \nabla^2 \phi - \Delta B \phi + 2 t \phi^2 - 15 v \phi^3 \right]$$

$\sim$ Model A

Phase field model of liquid/solid transition
order parameter - ϕ - amplitude of density fluctuations



* Continuum limit of amplitude equations

Repeat for binary alloy model:

- substitutional binary alloy A and B atoms, densities ρ_A and ρ_B define two fields,

$$\psi \;=\; 2c-1\,,\; n \;=\; (\rho-\rho_l)/\rho_l, \quad \text{where}\;\; \rho\equiv\rho_A+\rho_B, \quad c\equiv\rho_A/\rho$$

- free energy (see Elder, Provatas, Berry, Stefanovic, Grant, PRB **75**, 064107 (2007))

$$\boxed{\frac{\Delta F}{k_B T\,\rho_l} = \int d\vec{r}\left[\underbrace{\frac{B^l}{2}n^2 + B^x\frac{n}{2}\left(2R^2\nabla^2+R^4\nabla^4\right)n - \frac{t}{3}n^3 + \frac{v}{4}n^4}_{\text{usual PFC model}} + \underbrace{\frac{\omega}{2}\psi^2 + \frac{u}{4}\psi^4 + \frac{K}{2}\left|\vec{\nabla}\psi\right|^2}_{\text{Model B/Cahn Hilliard}}\right]}$$

$$\begin{aligned}
\text{where}\;\; B^l &= B^l_0 + B^l_1\psi + B^l_2\psi^2 + \ldots &&\rightarrow \text{eutectics phase diagrams etc.}\\
B^x &= B^x_0 + B^x_1\psi + B^x_2\psi^2 + \ldots &&\rightarrow \text{elastic moduli} \sim \text{function of } \psi\\
R &= R_0 + R_1\psi + R_2\psi^2 + \ldots &&\rightarrow \text{lattice constant} \sim \text{function of } \psi
\end{aligned}$$

- dynamics, for mobilities M_A and M_B

$$\frac{\partial n}{\partial t} = M_1\nabla^2\frac{\delta F}{\delta n} + M_2\nabla^2\frac{\delta F}{\delta\psi}$$

$$\frac{\partial \psi}{\partial t} = M_2\nabla^2\frac{\delta F}{\delta n} + M_1\nabla^2\frac{\delta F}{\delta\psi}$$

where

$$M_1 \equiv (M_A + M_B)/\rho_l^2$$

$$M_2 \equiv (M_A - M_B)/\rho_l^2$$

* Amplitude expansion: Binary alloys, statics

Small deformation limit $\eta_j = \phi \exp\left(i \vec{G}_j \cdot \vec{u}\right)$

$\psi \equiv$ concentration difference, $\phi \equiv$ liquid/solid order parameter

Elder, Huang, Provatas, PRE, **81**, 011602 (2010)

$$F_{2d} = \int d\vec{r} \left[3\Delta B \phi^2 - 4t\phi^3 + \frac{45}{2} v \phi^4 + 6B^x \left|\vec{\nabla}\phi\right|^2 + 3B^x \phi^2 \left\{ \frac{3}{2} \sum_{i=1}^{2} U_{ii}^2 + U_{xx} U_{yy} + 2U_{xy}^2 \right\} \right.$$

$$\left. + \left(\omega + 6B_2^l \phi^2\right) \frac{\psi^2}{2} + \frac{u}{4} \psi^4 + \frac{K}{2} \left|\vec{\nabla}\psi\right|^2 + 12 \alpha B_0^x \left(-\phi \nabla^2 \phi + \sum_{i=1} 2U_{ii} \phi^2 \right) \psi \right]$$

First Order Liquid/Solid transition with surface energy

Elastic energy

Phase Segregation, eutectic solidification, spindodal decomposition, etc.. with surface energy cost

Vegard's Law
$a = a_o(1+\alpha\Psi)$

Segregation at surfaces, dislocations, etc.

* Amplitude expansion: Binary alloys, dynamics

Small deformation limit $\eta_j = \phi \exp(i\vec{G}_j \cdot \vec{u})$

$\psi \equiv$ concentration difference, $\phi \equiv$ liquid/solid order parameter

Elder, Huang, Provatas, PRE, **81**, 011602 (2010)

$$F_{2\mathrm{d}} = \int d\vec{r} \left[3\Delta B \phi^2 - 4\mathrm{t}\phi^3 + \frac{45}{2} v \phi^4 + 6B^x \left|\vec{\nabla}\phi\right|^2 + 3\mathrm{B}^x \phi^2 \left\{ \frac{3}{2} \sum_{i=1}^{2} U_{ii}^2 + U_{xx} U_{yy} + 2\mathrm{U}_{xy}^2 \right\} \right.$$
$$\left. + \left(\omega + 6\mathrm{B}_2^l \phi^2\right) \frac{\psi^2}{2} + \frac{u}{4}\psi^4 + \frac{K}{2}\left|\vec{\nabla}\psi\right|^2 + 12\alpha B_0^x \left(-\phi\nabla^2\phi + \sum_{i=1} 2U_{ii}\phi^2\right)\psi \right]$$

$$\frac{\partial\phi}{\partial t} = -\frac{\delta F}{\delta\phi}$$

Model **A**
Allen/Cahn

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

Model **B**
Cahn/Hilliard
Hillert

Model **C**

ABC's of pattern formation

$$\sum_i \frac{\partial}{\partial x_i} \frac{\delta F}{\delta U_{ij}} \approx 0$$

Mechanical
Equilibrium

Liquid/solid transition with solute trapping in small deformation limit

$$\frac{\partial \phi}{\partial t} \;=\; \left[-\Delta B_o + B_2^l \psi^2 + B^x \left(2\nabla^2\right)\right] \phi + 2t\phi^2 - 15v\phi^3 - \frac{f_{elas}}{3\phi}$$

$$\frac{\partial \psi}{\partial t} = \nabla^2 \left[\left(\omega + 6B_2^l \phi^2 - K\nabla^2\right) \psi + u\psi^3 - 12\phi^2 B_o^x \alpha \left(U_{xx} + U_{yy}\right)\right]$$

$$\vec{\nabla} \cdot \vec{\vec{\sigma}} = 0$$

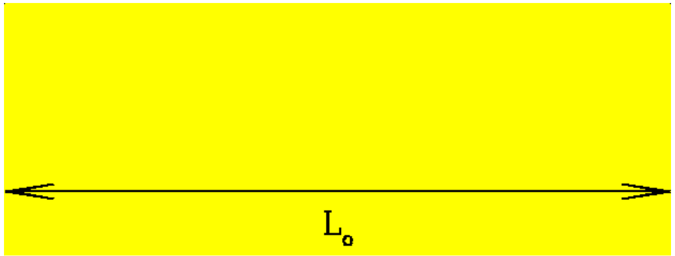
$$\frac{f_{elas}}{3\phi} = B_o^x \phi \left[\frac{3}{2}(U_{xx}^2 + U_{yy}^2) + U_{xx}U_{yy} + 2U_{xy}^2 + 4\alpha\psi \left(U_{xx} + U_{yy}\right)\right]$$

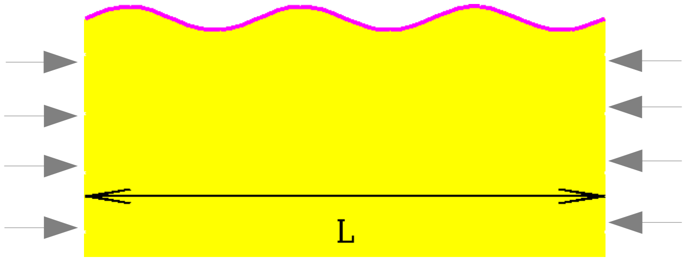
$$\begin{aligned}
\sigma_{xx} \;&=\; \frac{\partial F}{\partial U_{xx}} = 3B^x \phi^2 (3U_{xx} + U_{yy}) + 12\alpha B^x \phi^2 \psi \\
\sigma_{yy} \;&=\; \frac{\partial F}{\partial U_{yy}} = 3B^x \phi^2 (3U_{yy} + U_{xx}) + 12\alpha B^x \phi^2 \psi \\
\sigma_{xy} \;&=\; \frac{1}{2}\frac{\partial F}{\partial U_{xy}} = 6B^x \phi^2 U_{xy}
\end{aligned}$$

* Amplitude expansion: applications – workshop II

Epitaxial growth: stability of strained surface

Huang and Elder, PRL **101**, 158701 (2008), PRB **81**, 165421 (2010)



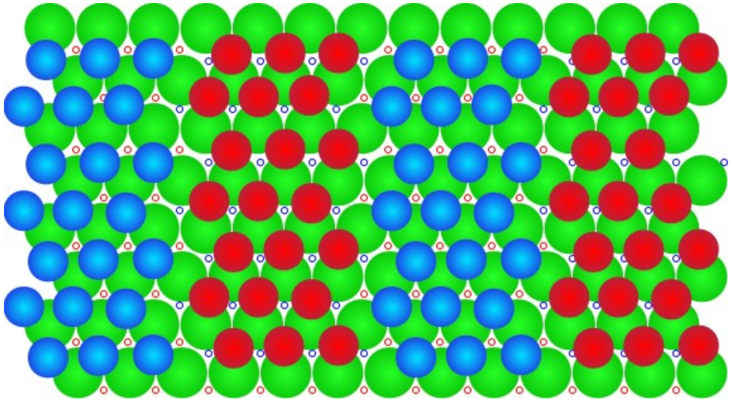


Misfit strain $\varepsilon_M \equiv (a_o - a)/a$

Monolayer(s) ordering: Cu on Ru (0001)

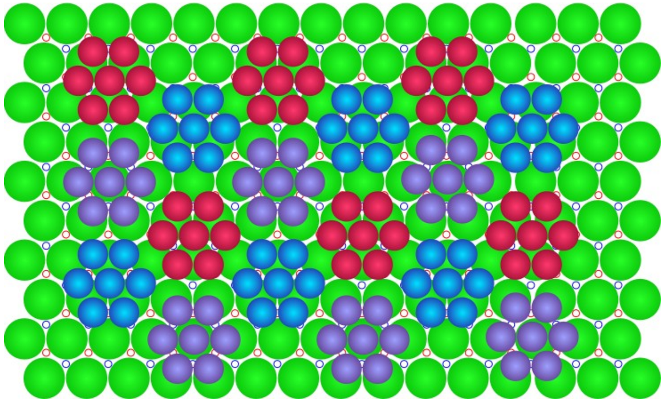
Elder, Rossi, Kanerva, Sanches,Ying, Granato, Achim and Ala Nissila
PRL, **108**, 226102 (2012)

stripes



intermediate V_o

honeycomb



small V_o

🟢 substrate

🔵

🔴 FCC sublattice

🟣

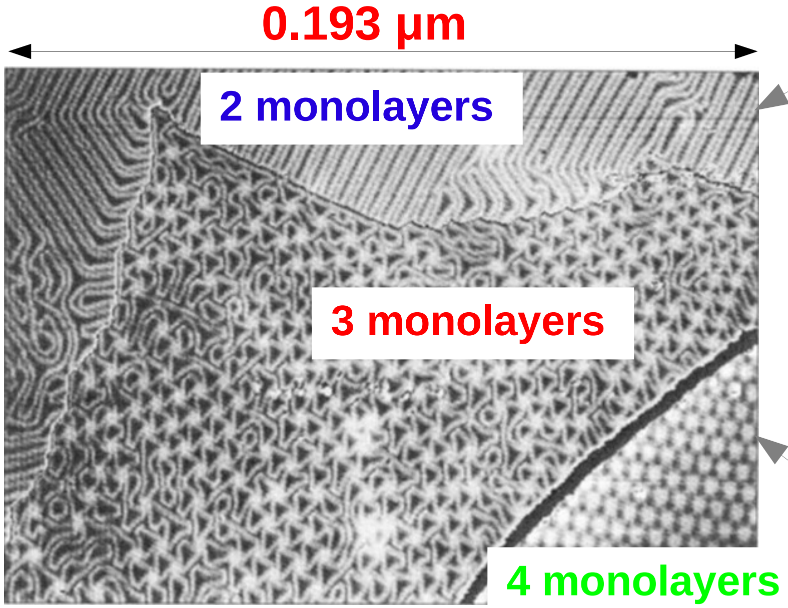
incommensurate

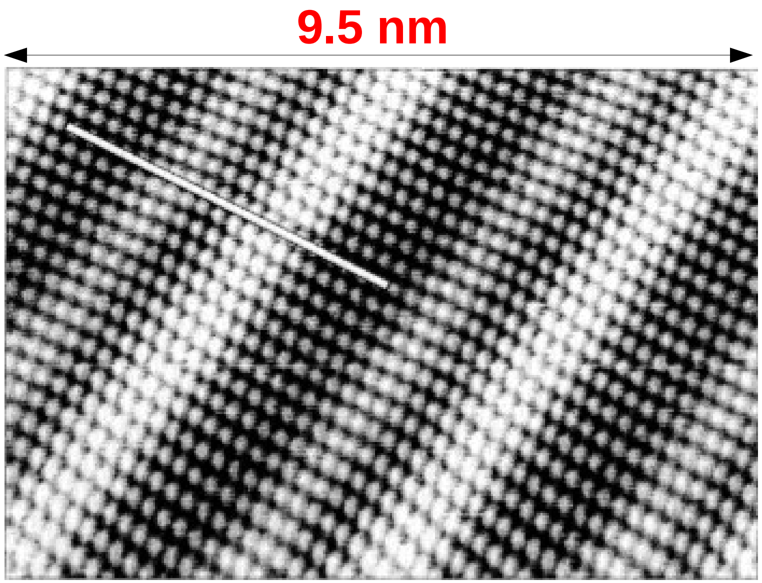
* Amplitude expansion: applications

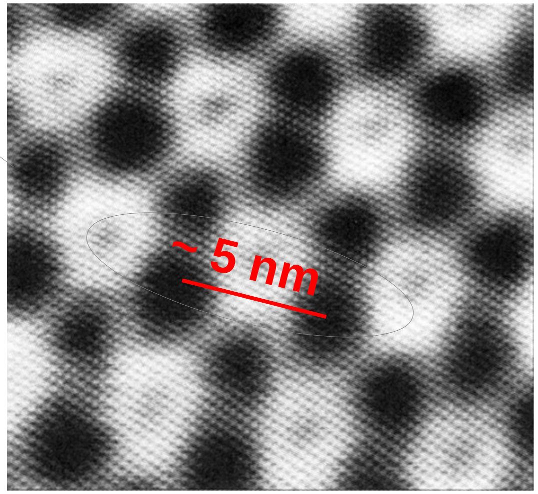
Patterning in Ultrathin Films

Example: **Cu on Ru (0001) surface**
Misfit strain 5.6%

top
view







angstrom sized atoms forming
nanometer sized objects
ordering on **micron** scales

Oakland
UNIVERSITY

Non-equilibrium pattern formation in materials physics

Hamiltonian

↓

DFT: sharply peaked periodic field

↓

PFC: smooth periodic field

↓

Amplitude expansions: uniform complex field

↓

Phase/Continuum field theory: uniform scalar fields

↓

Sharp Interface theory: boundary conditions etc

**“done”
in large
length scales
limit**

**Predictions
large λ good
small λ bad**