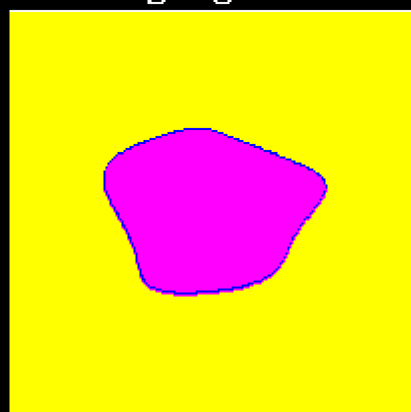
# Phase Field Crystal Modeling of Solidification, Phase Segregation and Elasticity

Ken Elder

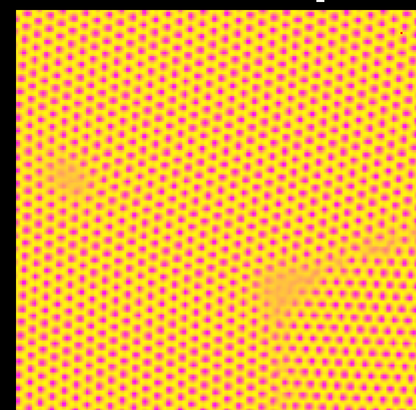
topology of field { nature of defects / nature of interactions

**Segregation**



Uniform Phases
Defects: Surfaces
Interaction: Diffusion

**Elasticity**



Periodic Phases
Defects: Dislocations ..
Interaction: Elastic

CHC equation + SH equation

## Collaborators

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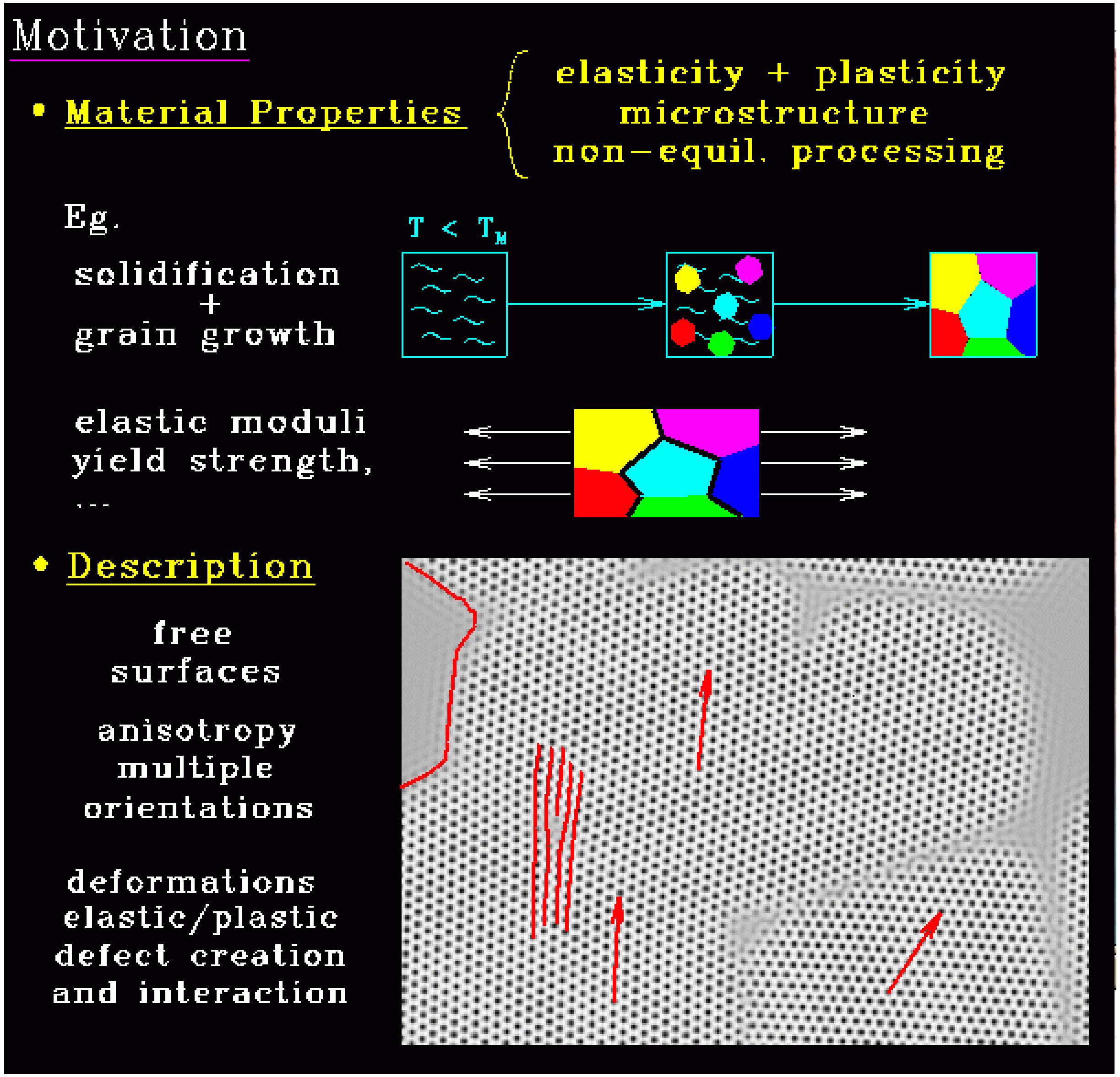
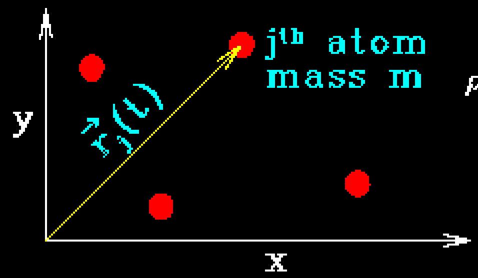
Research Corporation


Motivation
• Material Properties
elasticity + plasticity
microstructure
non-equil. processing
Eg.
solidification
+
grain growth
T < T_M
elastic moduli
yield strength,
...
• Description
free
surfaces
anisotropy
multiple
orientations
deformations
elastic/plastic
defect creation
and interaction

# Phase Field Crystals (pure material)

- **Consider time averaged density** $\rightarrow \rho(\vec{r},t)$




$$\rho(\vec{r},t) \equiv (m/\tau)\int_{t-\tau/2}^{t+\tau/2} dt' \sum_j \delta(\vec{r}-\vec{r}_j(t'))$$

lattice vibrations (ps) $<< \tau <<$ diffusion times ($\mu s$, ms, s, ..)

- **Phase Field Model Ingredients**

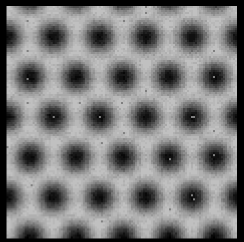
Free energy : $\mathcal{F} = \int d\vec{r}\; H(\rho, \nabla\rho, \ldots)$

Dynamics : $\dfrac{\partial \rho}{\partial t} = \Gamma \nabla^2 \dfrac{\delta \mathcal{F}}{\delta \rho}$

- **Minimal requirements** $\rightarrow H(\rho, \nabla\rho, \ldots) = ?$

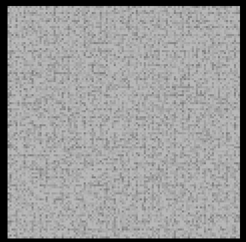
$\mathcal{F}$ minima

low temp. high density



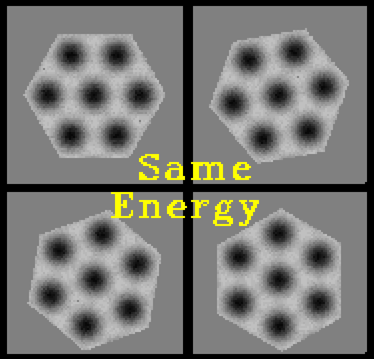
$\rho$ = periodic crystal anisotropic

high temp. low density



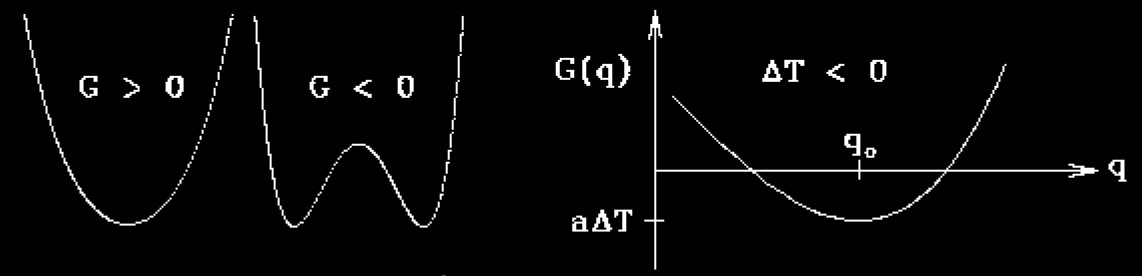
$\rho$ = uniform liquid

$\mathcal{F}$ isotropic

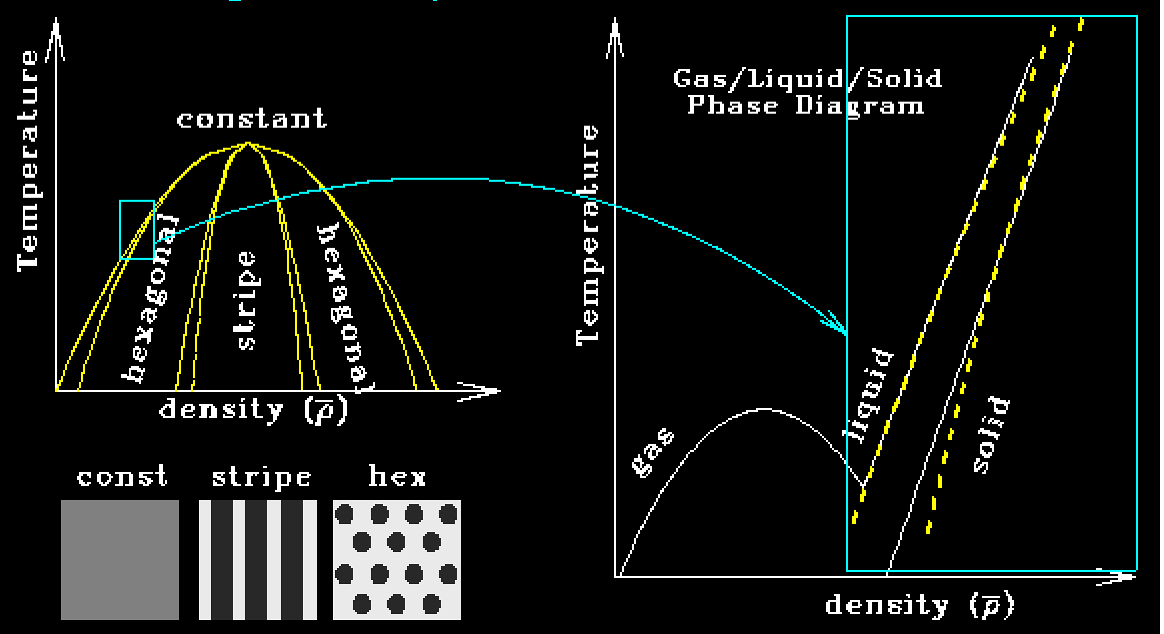


## • Simplest PFC Model

$$H = \frac{1}{2}\rho\, G\, \rho + \frac{u}{4}\rho^4 \quad : \quad G = a\Delta T + \lambda(q_o^2 + \nabla^2)^2$$




### Phase Diagram (2d)



- <u>What do you get?</u>
  - at this level of simplification (i.e., ignorance)

  * Free Surfaces

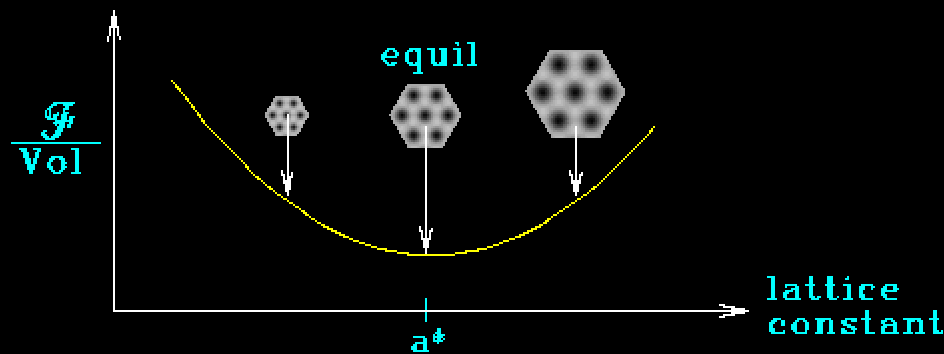
$$\frac{\partial \rho}{\partial t} = \nabla^2 \frac{\delta \mathcal{F}}{\delta \rho} \rightarrow \text{liquid/crystal coexistence}$$

(conservation law – Maxwell equal area const.)

  * Multiple orientations

$\mathcal{F}$ isotropic -- $\rho$ anisotropic

  * Elasticity



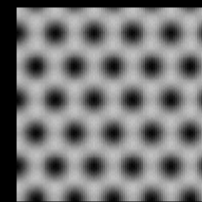

Expand: $$\frac{\mathcal{F}}{\text{Vol}} = \frac{\mathcal{F}^*}{\text{Vol}} + \underbrace{B\ (a-a^*)^2}_{\text{Hooke's Law}} + \ldots$$

## * Elasticity General Case

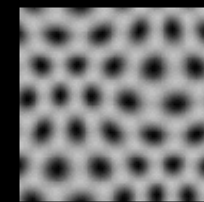
Expand around unstrained state, $\rho_o$

$$\rho(\vec{r}) = \rho_o(\vec{r}+\vec{u})$$

$\vec{u}(\vec{r}) \equiv$ displacement vector



$\rho_o(\vec{r})$



$\rho_o(\vec{r}+\vec{u})$

Expand in strain tensor, $u_{ij} \sim \partial u_i/\partial x_j + \ldots$

$$F(\rho_o(\vec{r}+\vec{u})) = \int dV \Big[ H_o + \left(\frac{\partial H}{\partial u_{ij}}\right)_o u_{ij} + \frac{1}{2}\left(\frac{\partial^2 H}{\partial u_{kl}\partial u_{ij}}\right)_o u_{kl}\, u_{ij} + \cdots$$

(first-order term crossed out: = 0 (def'n))

stress $= K_{ijkl} u_{kl}$

Elastic constants

$$K_{ijkl} = \left[\frac{\partial^2 H}{\partial u_{kl}\, \partial u_{ij}}\right]_o \sim \text{curvature of free energy}$$

Symmetry of Elastic Constants (K) $\equiv$ Symmetry of H $\equiv$ Symmetry of $\rho_o$

**Correct Symmetry relationships for all elastic constants**

## * Length and Time scales

Length Scales (bad news)

$\Delta x <$ atomic spacing $\equiv a$

simulations: $\Delta x = a/10$

Time Scales (good news)

$\Delta t <$ Diffusion time $\equiv \tau_D = a^2/D$

simulations: $\Delta t = 1000\ \tau_D$

---

Comparison with Molecular Dynamics

$N_D \equiv$ (# time steps)/(diffusion time) $= t_D/dt$

$t_D$ = time to diffuse one lattice site $= a^2/D$

dt = time step in numerical simulation

Eg., Copper T = 850°C ~ Billion times faster than MD

| | $N_D$ | |
|---|---|---|
| $t_D$ | This Work | MD |
| 1 $\mu$s | $10^3$ | $10^9$ |
| 1 ms | $10^3$ | $10^{12}$ |
| 1 s | $10^3$ | $10^{15}$ |
| dt | $t_D/1000$ | $10^{-15}$ s |

Copper: $T_{melt}$ = 1083°C

T = 650°C $t_D$ = 0.20 ms
T = 850°C $t_D$ = 2.51 $\mu$s
T = 1030°C $t_D$ = 0.23 $\mu$s

Gold: $T_{melt}$ = 1063°C

T = 800°C $t_D$ = 0.26 ms
T = 900°C $t_D$ = 33.2 $\mu$s
T = 1020°C $t_D$ = 5.53 $\mu$s

## ✵ Defects

### → Kinds (classification)

dislocations – edge, twist
disclinations – wedge, twist

} cubic vs hex

determined by symmetry ✓

### → Interaction

lattice deformation

elastic energy ✓

(core energy?)

### → Creation and Dynamics

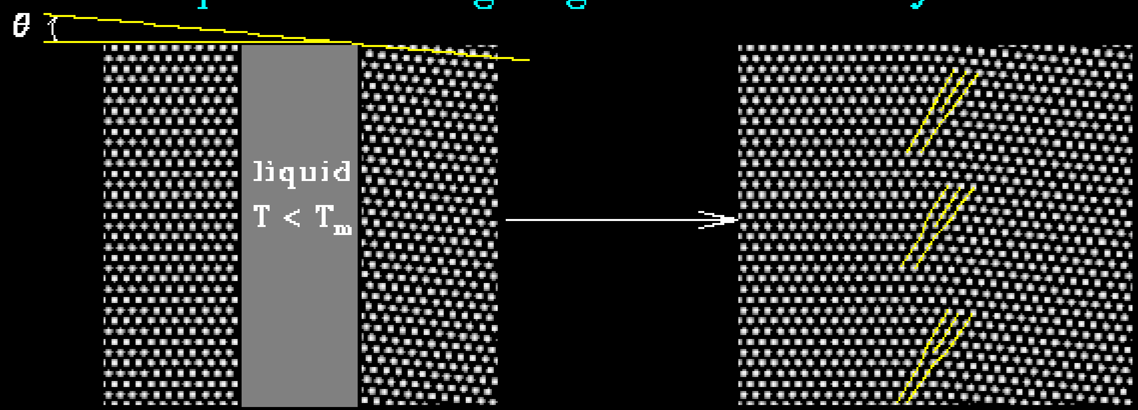
spontaneous, creep, climb, ...

$\partial \rho / \partial t \sim \nabla^2 \delta \mathcal{F} / \delta \rho$

– creates and moves defects if
energetically favorable
+ no local barriers (or fluctuations)

caveat – ~~sound modes~~

# Example: Low angle grain boundary




→ liquid solidifies

kinetics → equilibrium  kinetics $\sim \nabla^2 \delta \mathcal{F} / \delta \rho$

→ defects form and interact

geometrical constraints

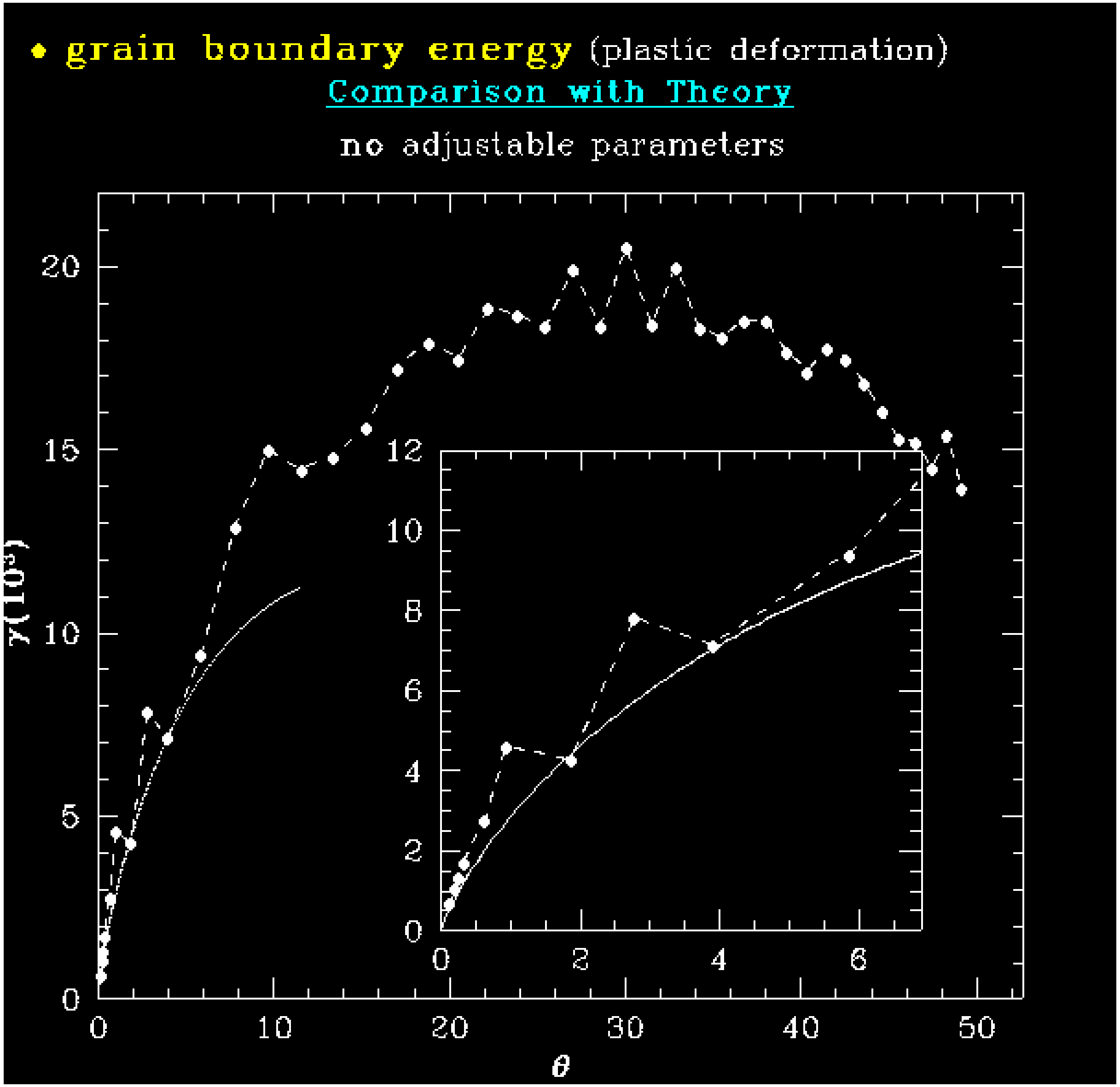
elastic field

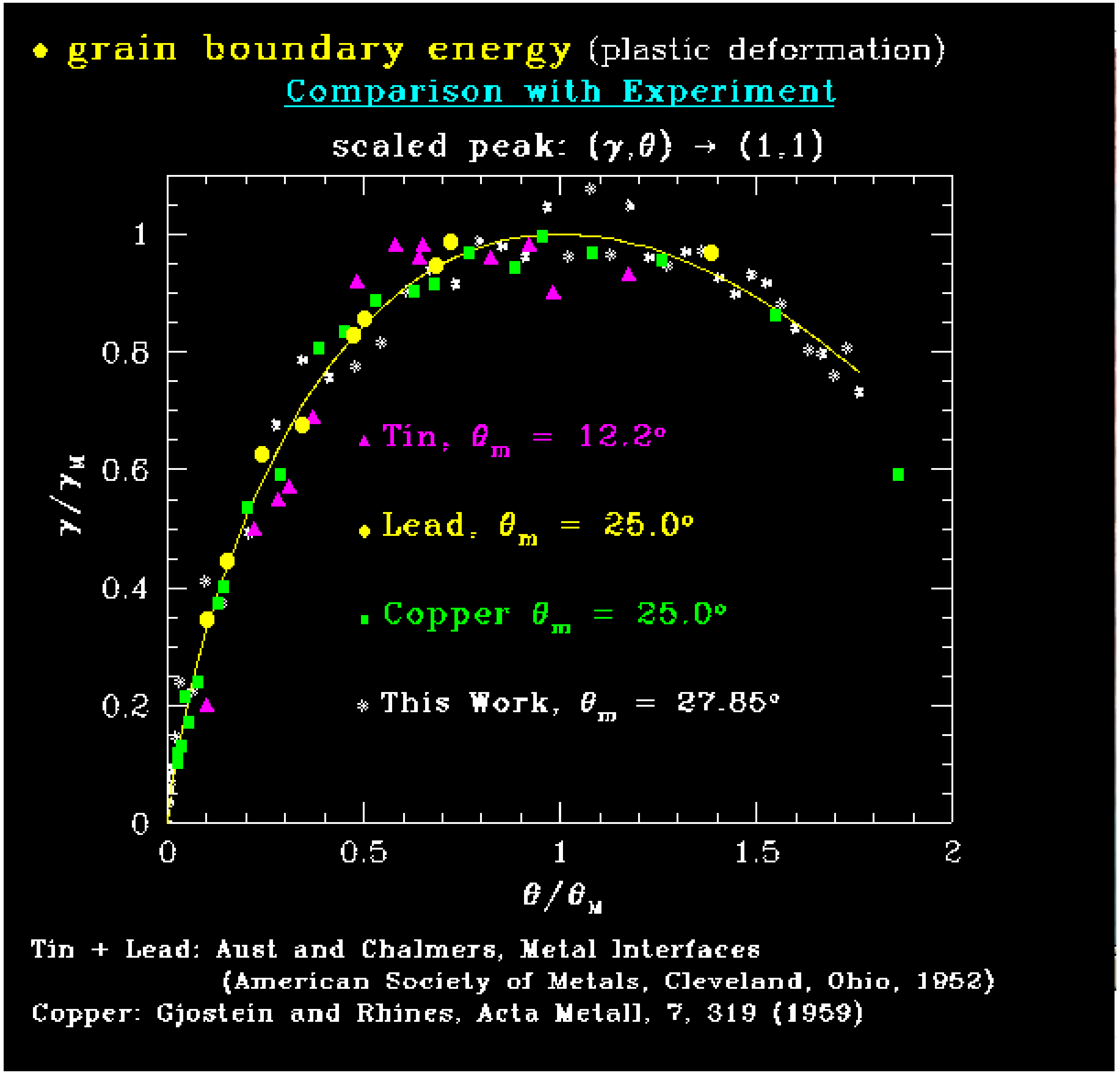
$\mathcal{F} \sim \left\{ \begin{array}{l} \text{periodic solutions} \\ \text{isotropic} \end{array} \right.$

→ grain boundary energy

$$E/L \sim \theta \left[ 1 - \ln(\theta) \right]$$

Read/Shockley Phys. Rev., 78, 275 (1950)


• grain boundary energy (plastic deformation)
Comparison with Theory
no adjustable parameters
γ(10³)
θ
0
5
10
15
20
0
10
20
30
40
50
0
2
4
6
8
10
12
0
2
4
6

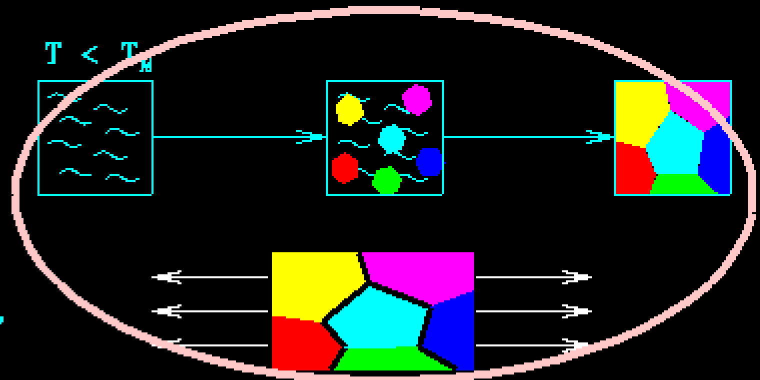

• grain boundary energy (plastic deformation)
Comparison with Experiment
scaled peak: (γ,θ) → (1,1)
γ/γ_M
θ/θ_M
0
0.2
0.4
0.6
0.8
1
0
0.5
1
1.5
2
Tin, θ_m = 12.2°
Lead, θ_m = 25.0°
Copper θ_m = 25.0°
This Work, θ_m = 27.85°
Tin + Lead: Aust and Chalmers, Metal Interfaces
(American Society of Metals, Cleveland, Ohio, 1952)
Copper: Gjostein and Rhines, Acta Metall, 7, 319 (1959)

# Motivation

- **Material Properties** { elasticity + plasticity; microstructure; non-equil. processing

Eg.

solidification
+
grain growth



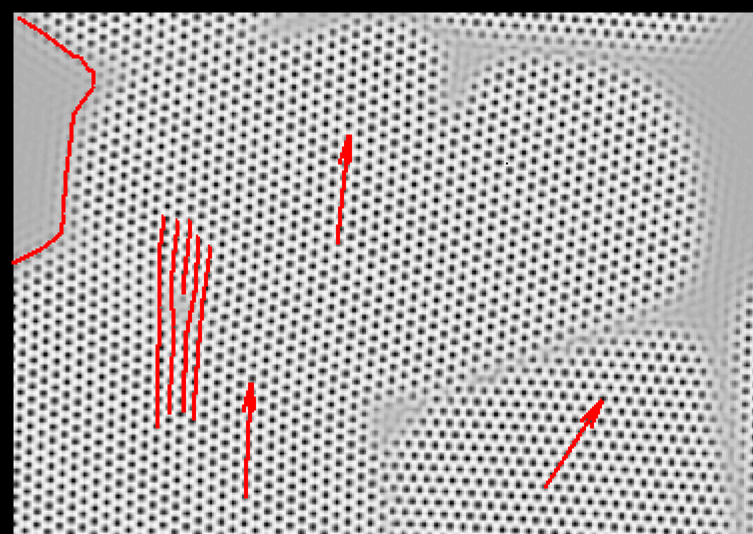

elastic moduli
yield strength,
...

- **Description**

free surfaces

anisotropy
multiple orientations

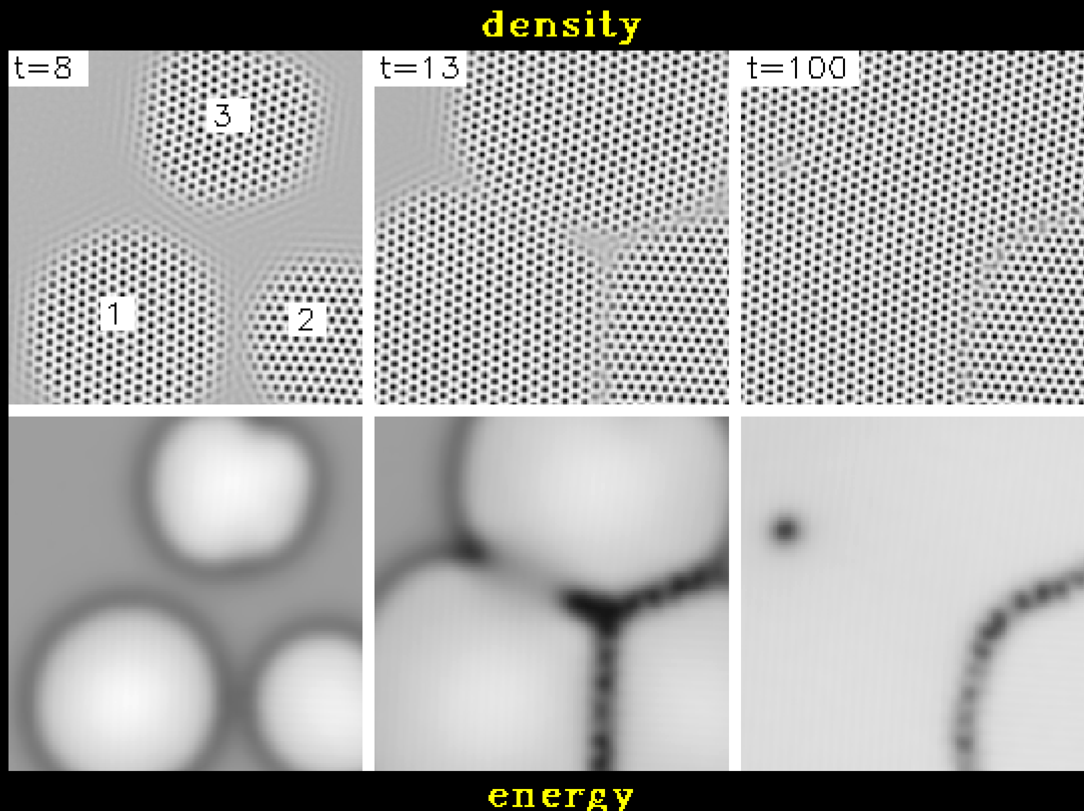
deformations
elastic/plastic
defect creation
and interaction



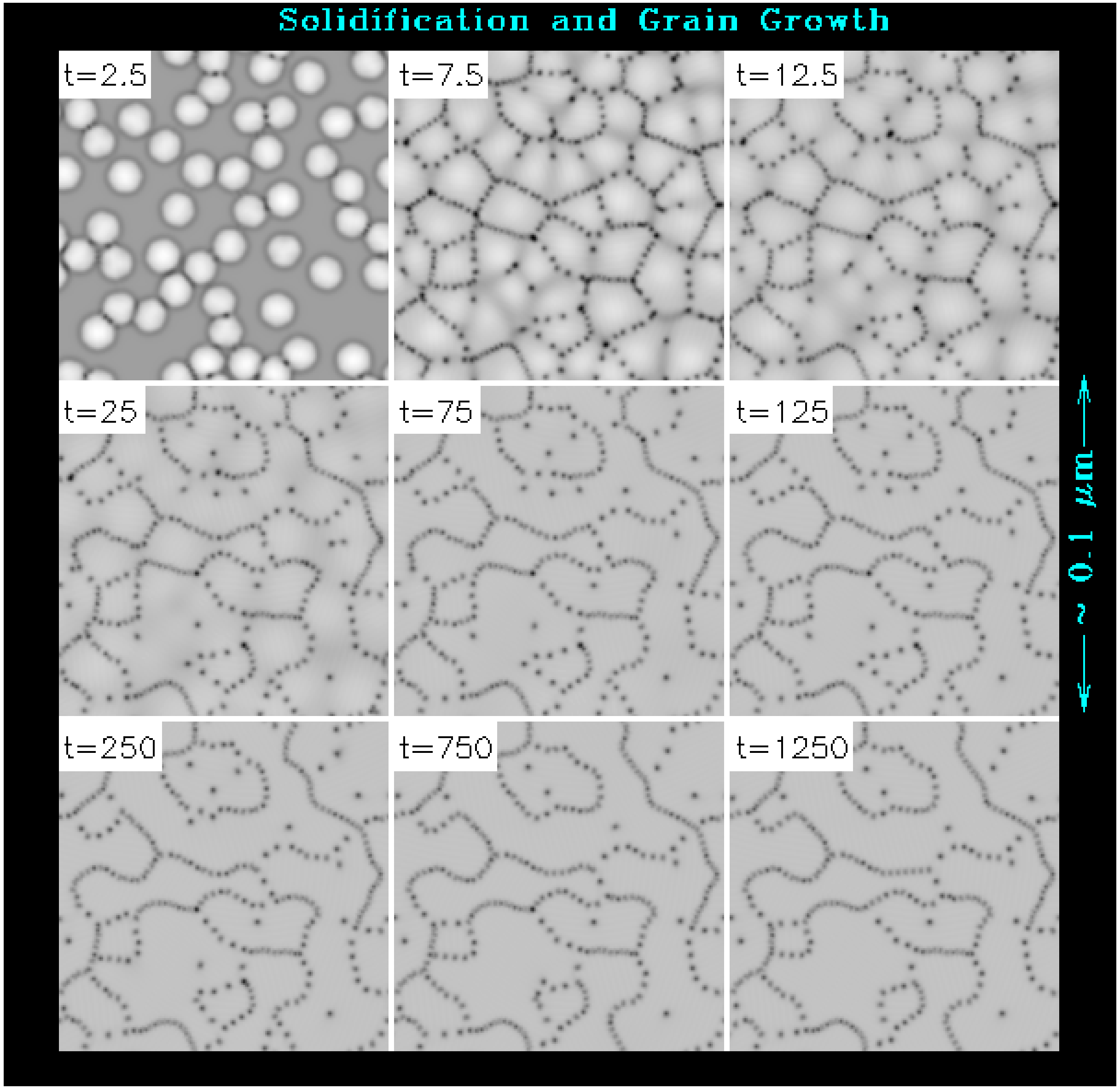
## Solidification and Grain Growth

→ free surface, multiple orientations

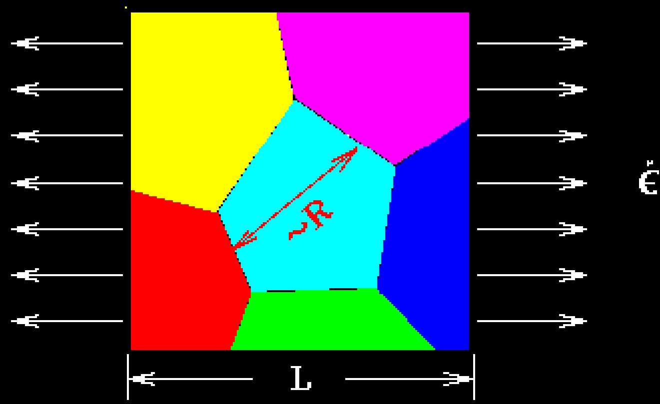
→ grain grain boundaries, elastic + plastic



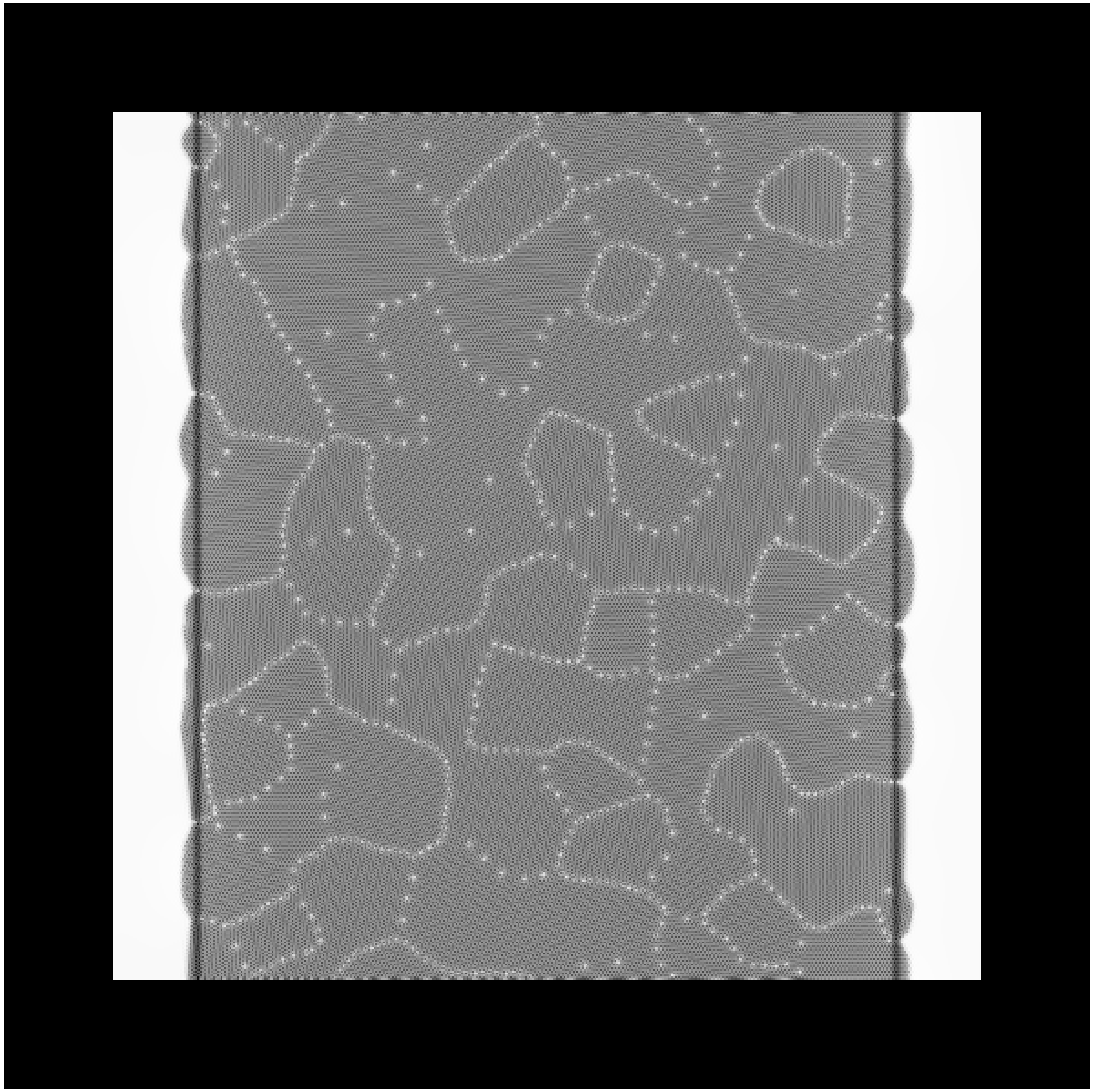

Time units → diffusion time ≡ $t_D = D/a^2$

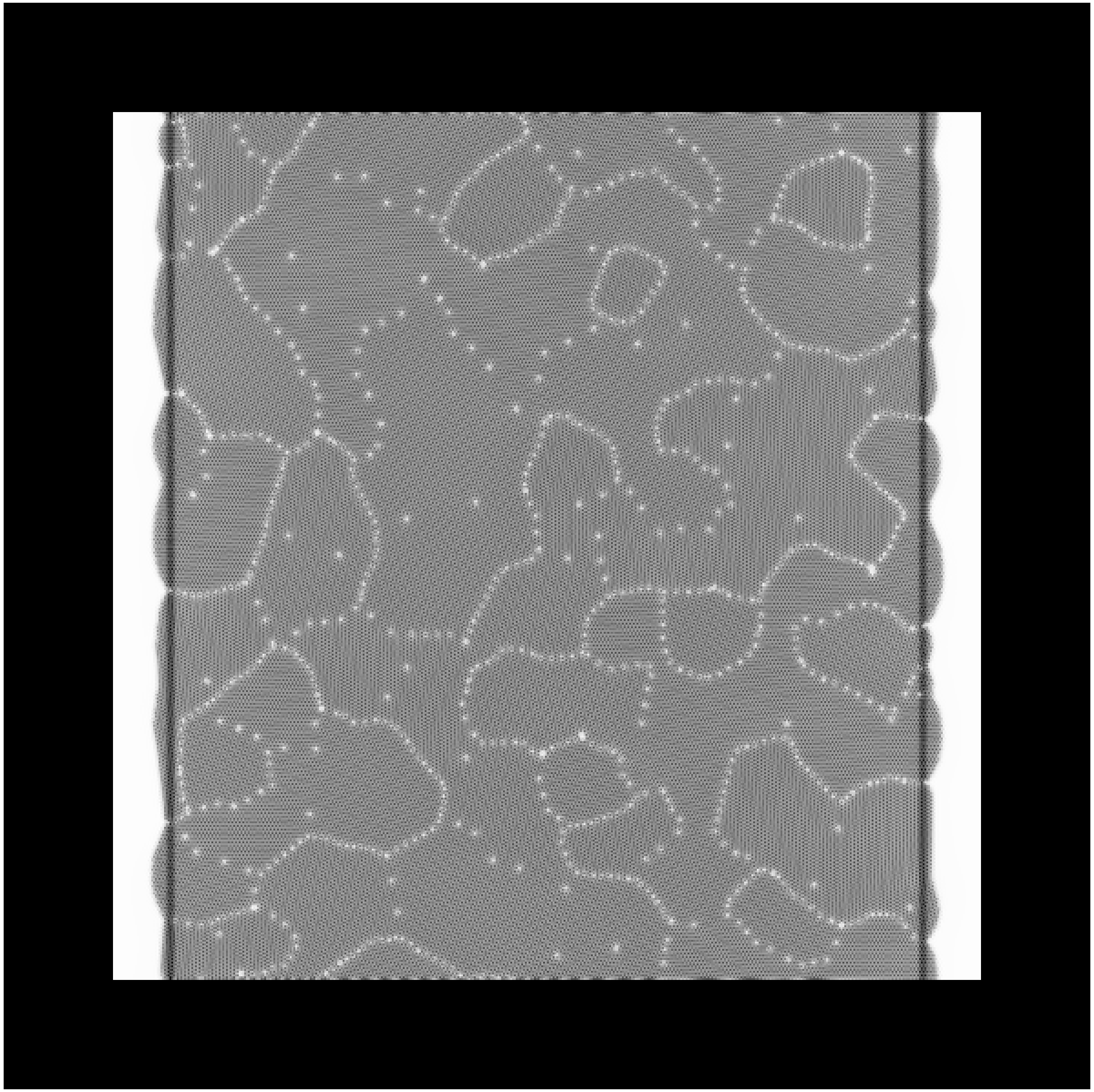

Solidification and Grain Growth
t=2.5
t=7.5
t=12.5
t=25
t=75
t=125
t=250
t=750
t=1250
~ 0.1 μm

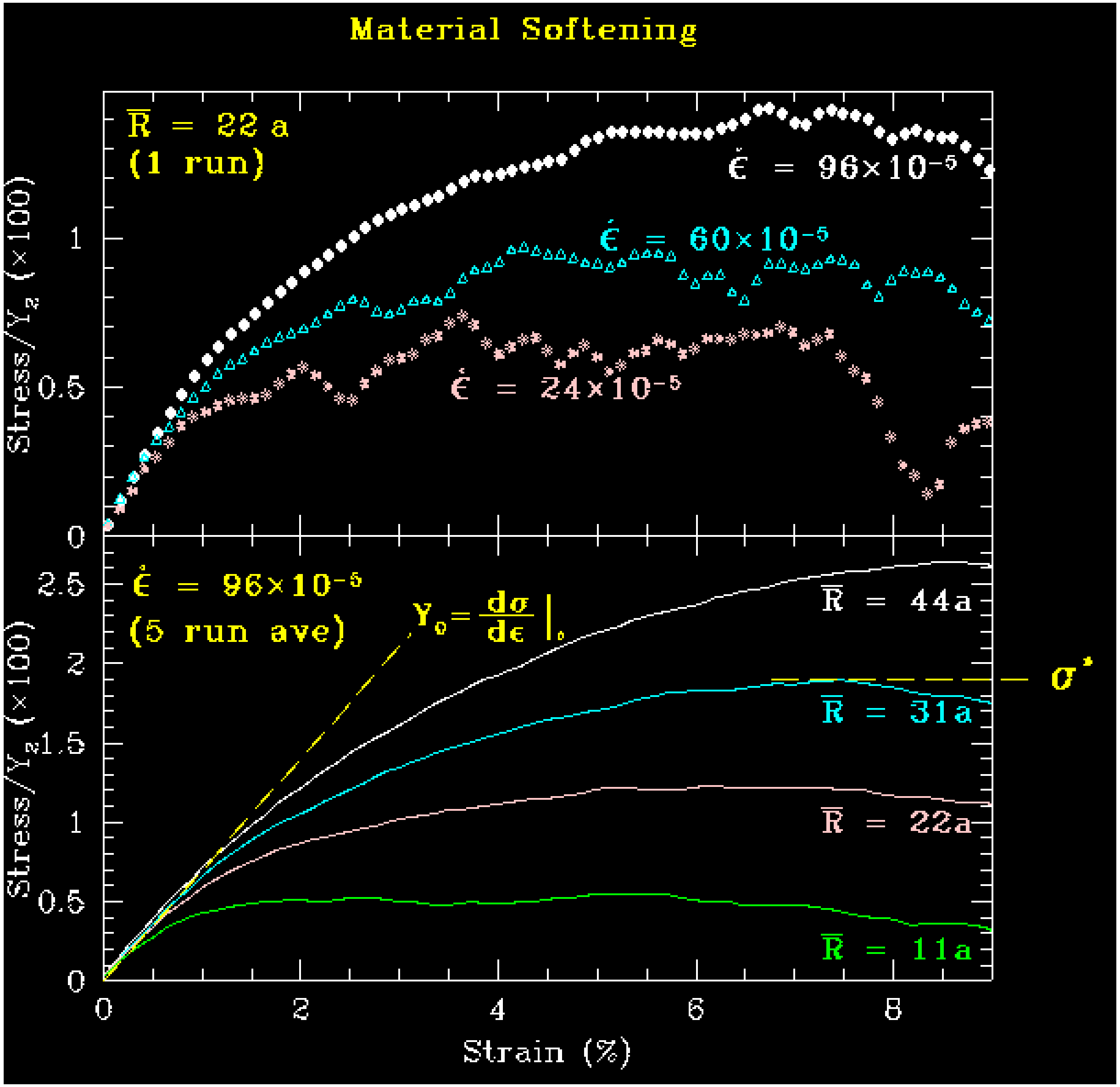
# Yield Strength



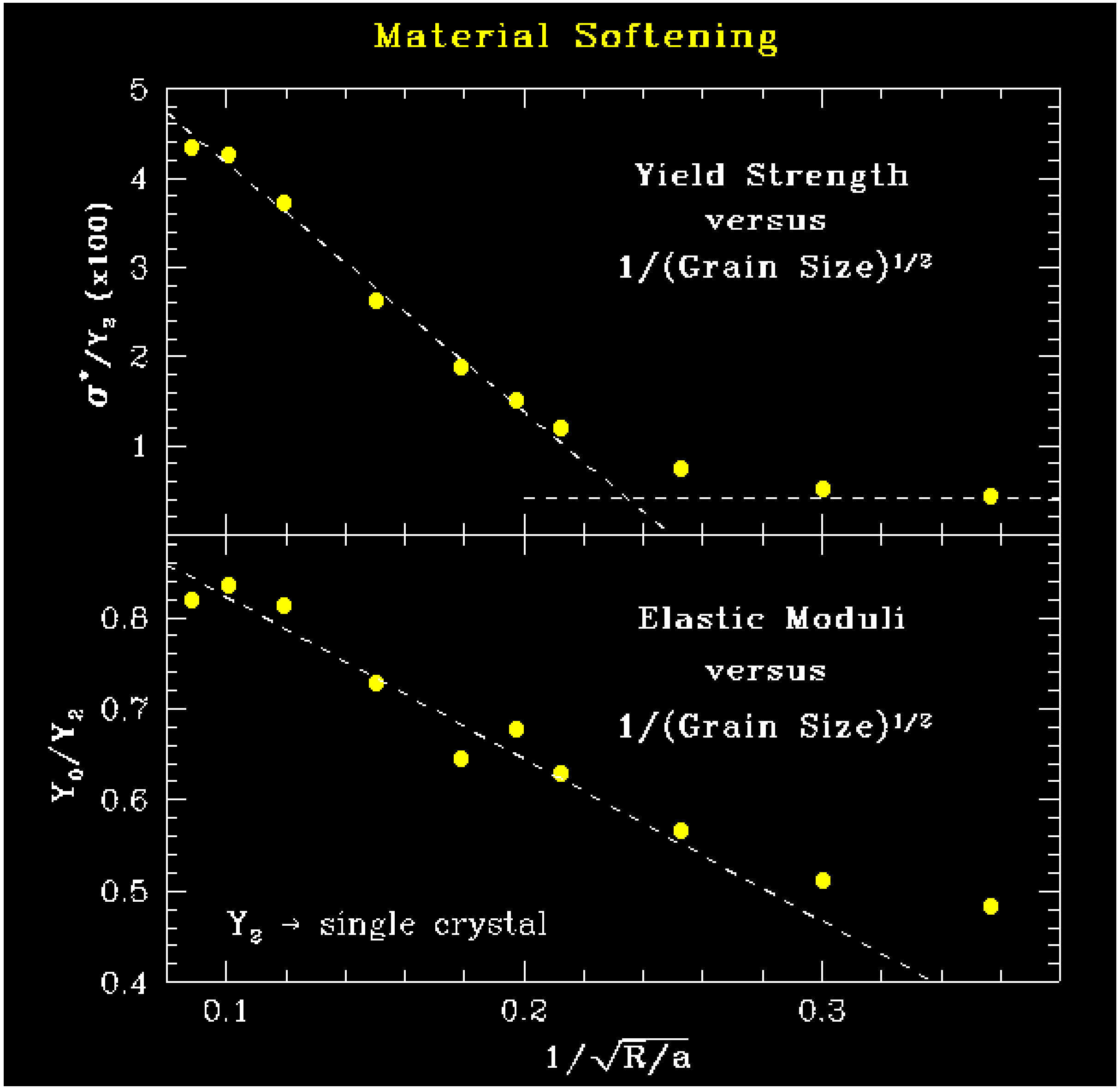

| Simulation | Example (Cu, 650°C) |
|---|---|
| a = lattice constant | a ≈ 0.4 nm |
| $t_D$ = diffusion time | $t_D$ ≈ 0.2 ms |
| $\overline{R}$ = average domain size | |
| 8 a – 128 a | 3 nm – 51 nm |
| ( 800 – 3 grains) | |
| L = system size | |
| 180 a × 220 a | 72 nm × 88 nm |
| $\dot{\epsilon}$ = strain rate = $\frac{1}{L}\frac{dL}{dt}$ | |
| $24\times10^{-6} - 96\times10^{-6}/t_D$ | $0.12\ s^{-1} \times 0.48\ s^{-1}$ |



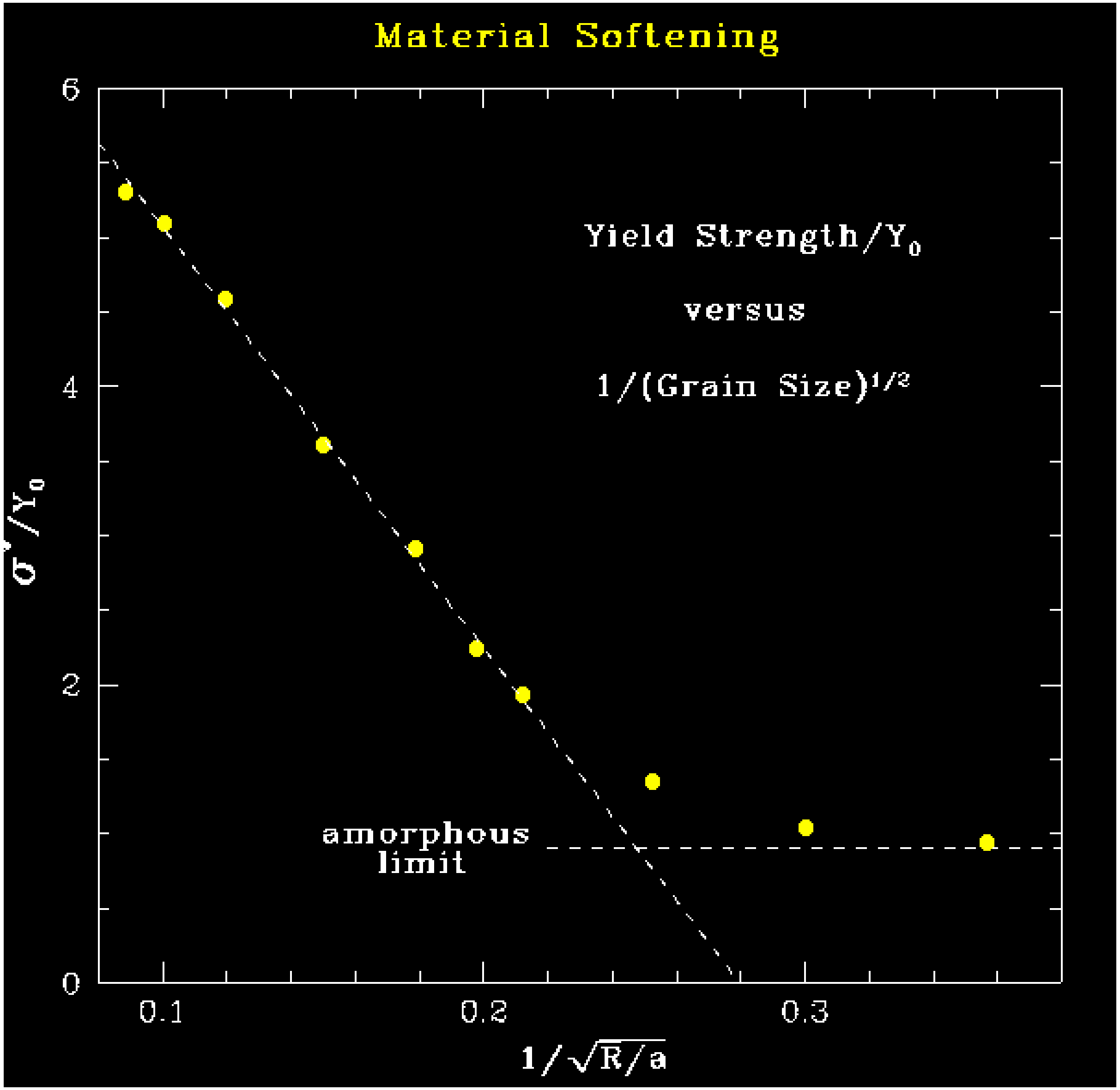




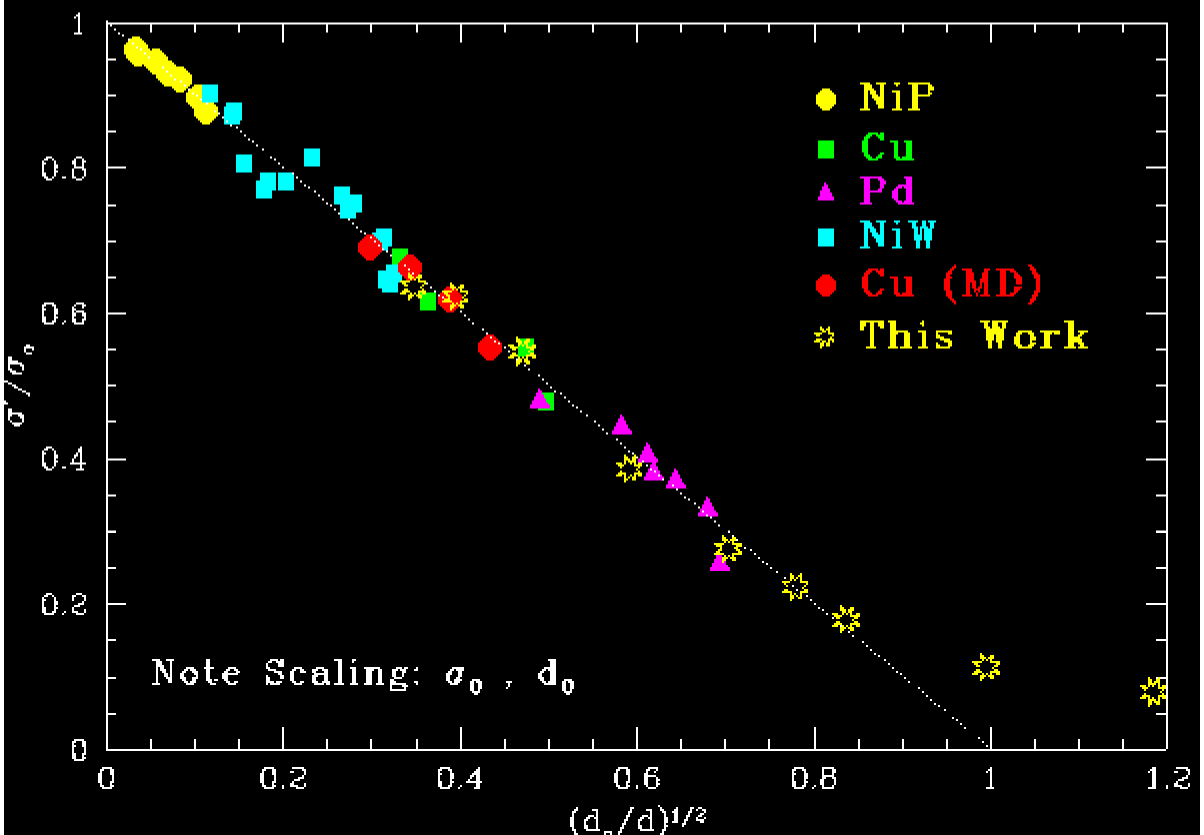
Material Softening
R̄ = 22 a
(1 run)
ε̇ = 96×10⁻⁵
ε̇ = 60×10⁻⁵
ε̇ = 24×10⁻⁵
Stress/Y₂ (×100)
0
0.5
1
ε̇ = 96×10⁻⁵
(5 run ave)
Y₀ = dσ/dε |₀
R̄ = 44a
σ*
R̄ = 31a
R̄ = 22a
R̄ = 11a
Stress/Y₂ (×100)
0
0.5
1
1.5
2
2.5
0
2
4
6
8
Strain (%)



Material Softening
Yield Strength
versus
1/(Grain Size)^1/2
$\sigma^*/Y_2$ (x100)
Elastic Moduli
versus
1/(Grain Size)^1/2
$Y_0/Y_2$
$Y_2 \rightarrow$ single crystal
$1/\sqrt{R/a}$


Material Softening
Yield Strength/$Y_0$
versus
1/(Grain Size)$^{1/2}$
amorphous limit
$\sigma^*/Y_0$
$1/\sqrt{R/a}$
0
2
4
6
0.1
0.2
0.3

## Comparison with Experiment



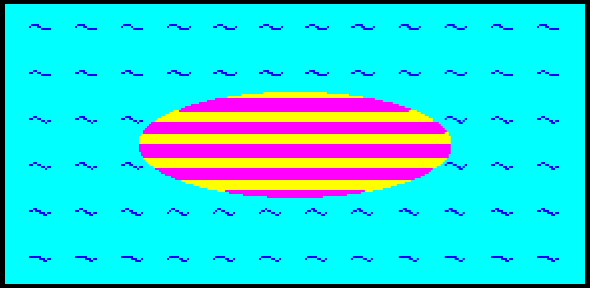

NiP Lu, Wei + Wang, Scripta Metall. Mater., 24, 2319 (1990).

Cu, Pd Chokshi, Rosen, Karch + Gleiter, Scripta Metall. Mater., 23, 1679 (1989).

NiW Yamasaki, Schloßmacher, Ehrlich + Ogino, Nanostruc. Mater., 10, 375 (1998)

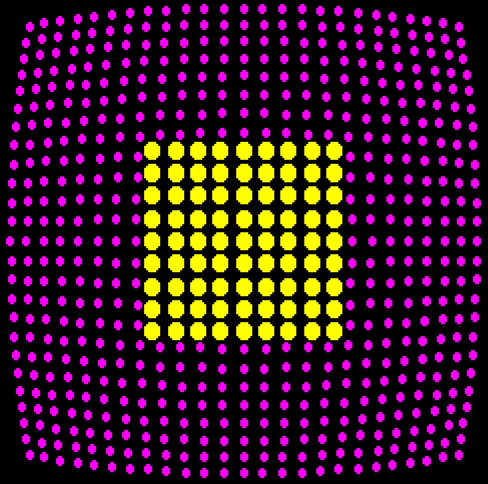
Cu(MD) Schiotz, Vegge, Di Tolla + Jacobsen, Phys. Rev. B, 60, 11971 (1999

## Binary Alloys



Solidification
+
Segregation

+



Elasticity
+
Plasticity

lattice constants
elastic constants ~ f(concentration)
crystal structure
⋮

# Eutectic Phase Field Crystals

→ two fields

$C \equiv$ concentration
uniform, domain walls,...

$\rho \equiv$ density (liquid/solid)
periodic, dislocations,...

→ or – two densities

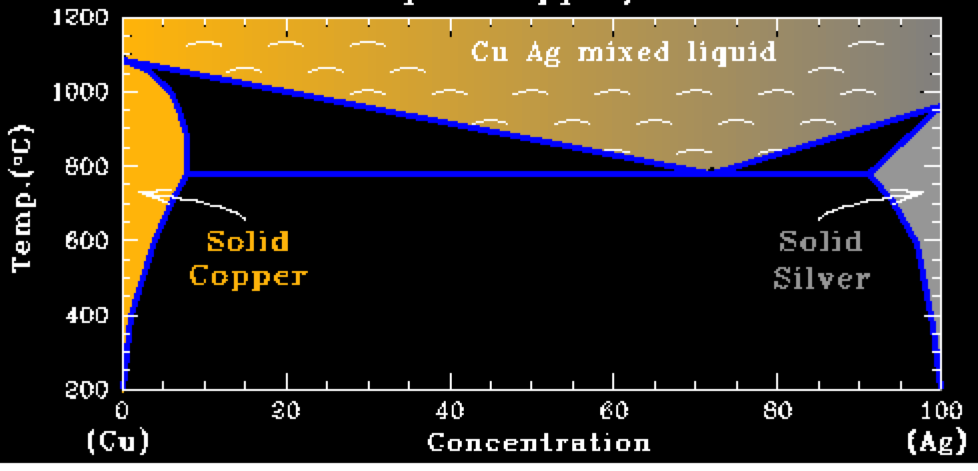
$\rho_A \equiv$ density of A atoms
$\rho_B \equiv$ density of B atoms

→ connection between descriptions

$$\rho = \rho_A + \rho_B$$

$$C \sim \frac{\rho_A - \mu\rho_B}{\rho_A + \mu\rho_B} \qquad \mu \equiv m_A/m_B$$

Example: Copper/Silver



# Eutectics Phase Field Crystals

→ **in principle**

$F_A \equiv$ periodic free energy for A atoms

$F_B \equiv$ periodic free energy for B atoms

$F_{AB} \equiv$ coupling between A and B

→ **in practice**

$F_\rho \equiv$ periodic free energy for $\rho = \rho_A + \rho_B$

$F_C \equiv$ model B free energy for $C = \rho_A - \rho_B$

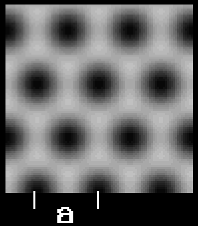
$F_{C,\rho} \equiv$ coupling between $\rho$ and C

**Details**

$$F_\rho = \int d\vec{r}\left[ -R^2|\vec{\nabla}\rho|^2 + \frac{R^4}{2}|\nabla^2\rho|^2 + \Delta T\,\frac{\rho^2}{2} + \frac{\rho^4}{4} \right]$$

One Mode, constant C approximation

$$\rho = A\left[\cos(qx)\cos(qy/\sqrt{3}) - \cos(2qy/\sqrt{3})/2\right] + \rho_o$$




**Lattice constant, a**

$$a = \frac{4\pi}{\sqrt{3}} R(C,T,\ldots)$$

$$a = \frac{4\pi}{\sqrt{3}} \left(R_o + \alpha_C\, C + \alpha_T\, T + \ldots\right.$$

**solute expansion coefficient**

$$\eta = \frac{\alpha_C}{R_o} = \frac{1}{R_o}\frac{\partial R}{\partial C}$$

$$F = F_\rho + F_c + F_{c,\rho}$$

Usual $C^4$ model – allow for phase segregation

$$F_c = \int d\vec{r}\left[ w\frac{C^2}{2} + u\frac{C^4}{4} + \frac{K}{2}\ |\vec{\nabla}C|^2 \right]$$

Coupling

$$F_{\rho,c} = \int d\vec{r}\left[ -A\ C^2\ \rho^2 + S\ C\ \rho^2 \right]$$

"Eutectic Coupling"

$C^2$ term

$(w - 2A\rho^2)\ C^2$

single phase: $w < 2A\rho^2$

two phase: $w > 2A\rho^2$

$\rho^2_{solid} > \rho^2_{liquid} = \rho^2_o$

Liquid favors single phase

Solid favors two phase

"Elastic Coupling"

1–mode, constant C

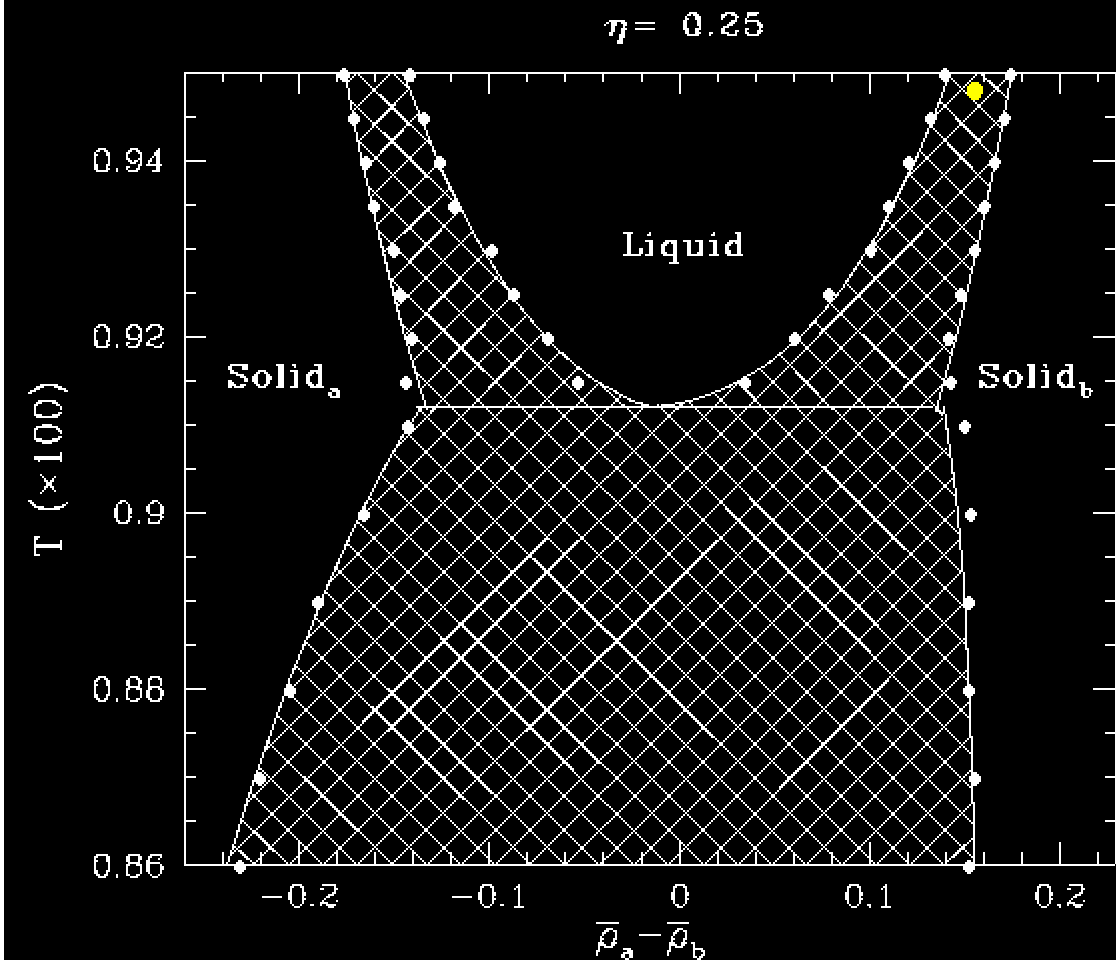
$$C_{11} = \frac{3}{75}\left(3\rho_o + \beta\right)^2 - \frac{8}{5}\left(\frac{3\rho_o + \beta}{\beta}\right) S\ C + \ldots$$

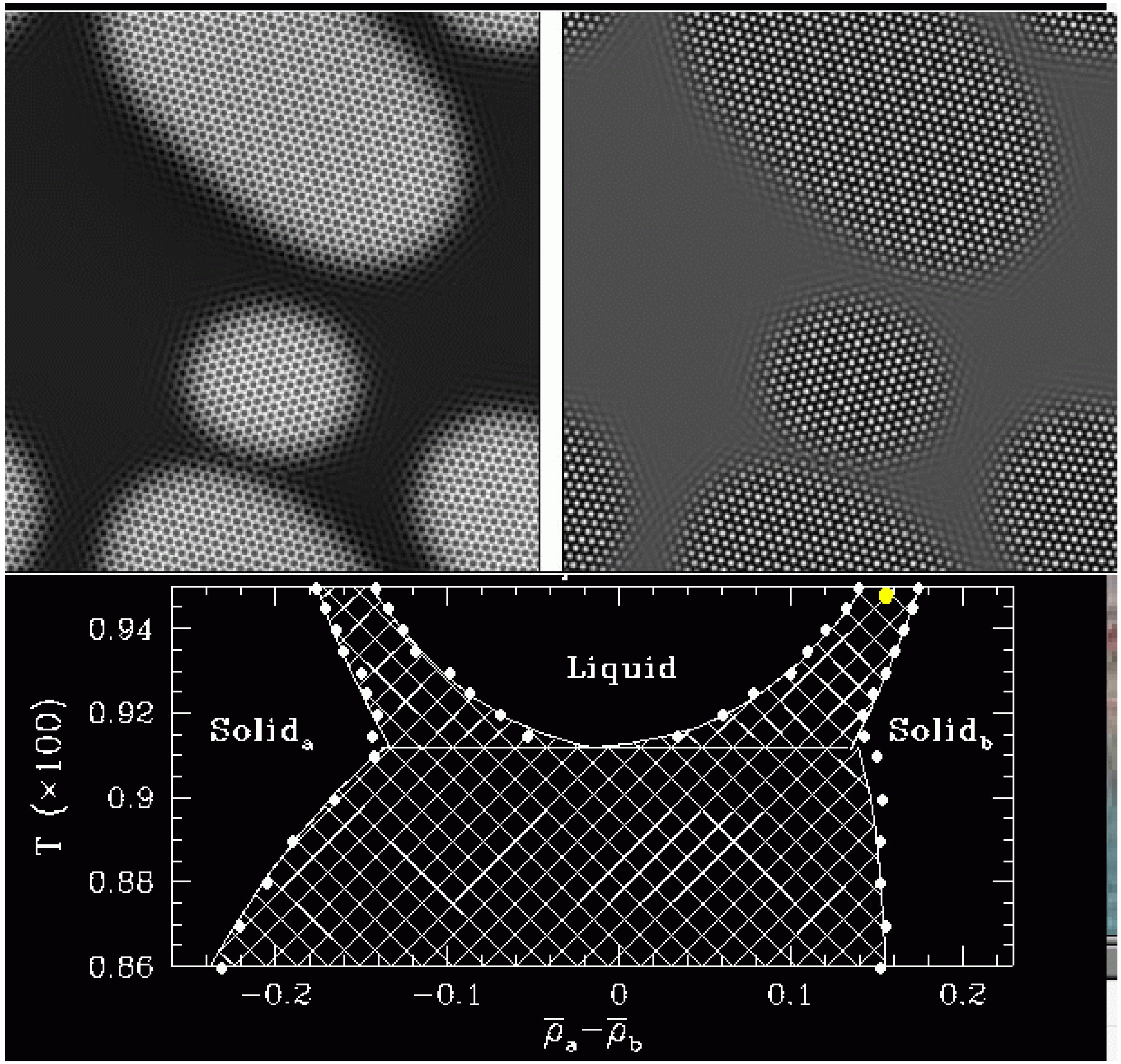
$C_{44} = C_{12} = C_{11}/3$

$\beta = \sqrt{15(1-\Delta T) - 36\rho_o^2}$

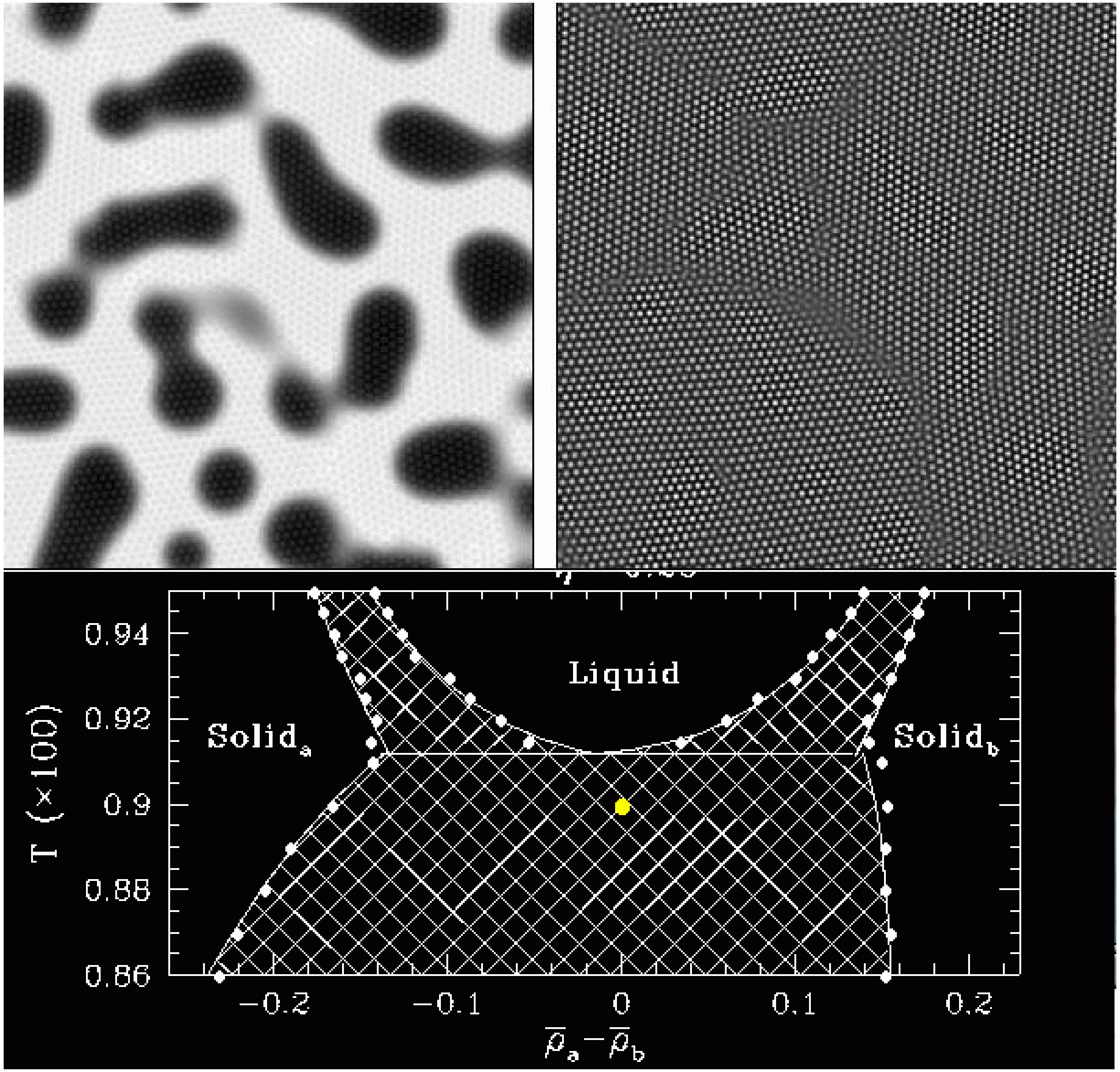
S controls concentration dependence of elastic moduli

# Eutectics Phase Field Crystals





Liquid
Solid$_a$
Solid$_b$
T (×100)
0.94
0.92
0.9
0.88
0.86
−0.2
−0.1
0
0.1
0.2
$\bar{\rho}_a - \bar{\rho}_b$


Liquid
Solid$_a$
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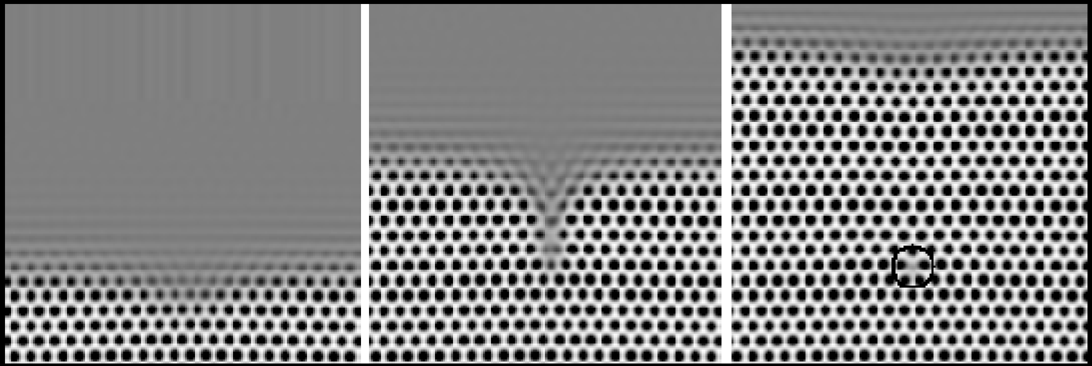
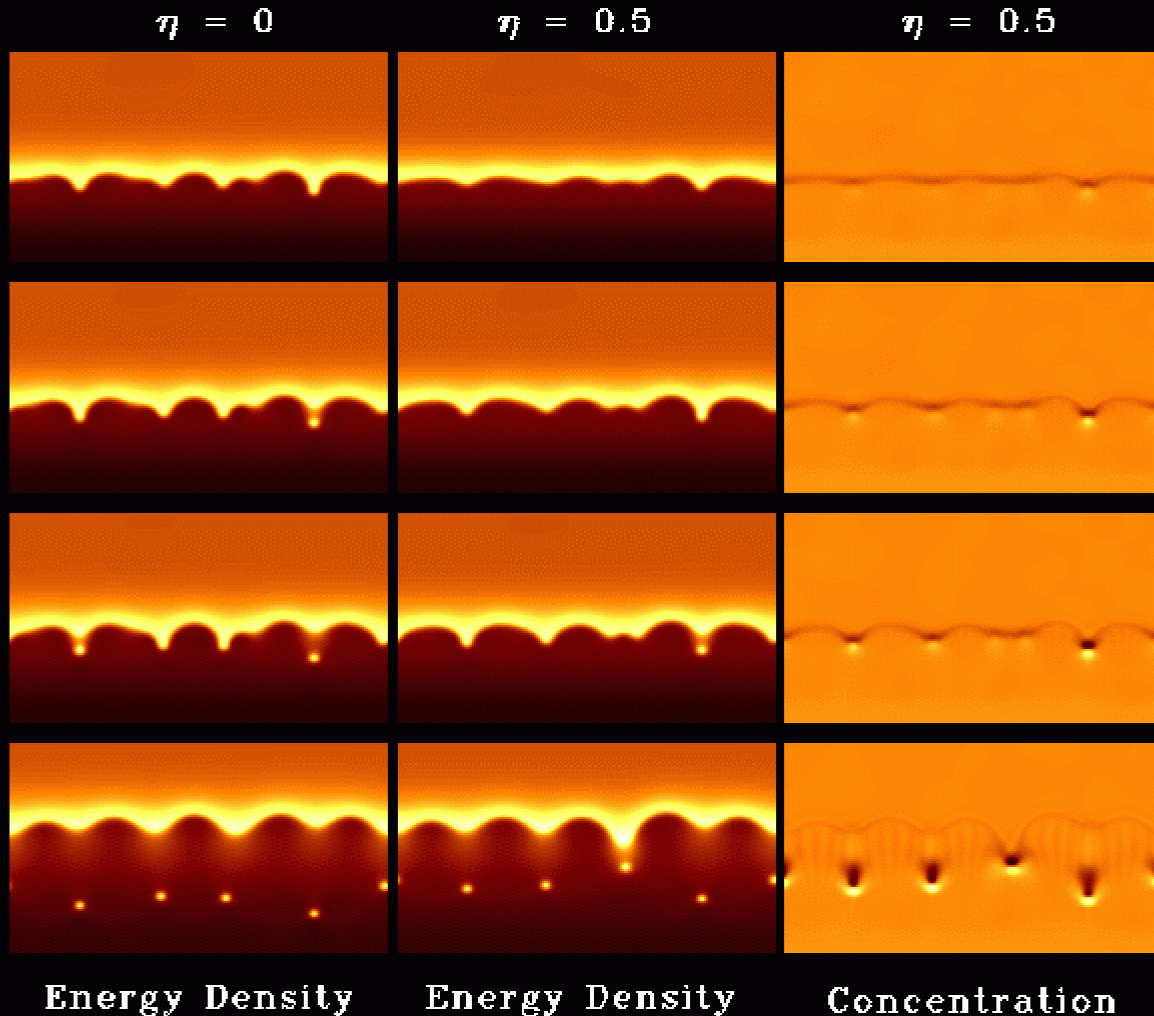
T (×100)
0.94
0.92
0.9
0.88
0.86
−0.2
−0.1
0
0.1
0.2
$\bar{\rho}_a - \bar{\rho}_b$

- Liquid phase epitaxial growth

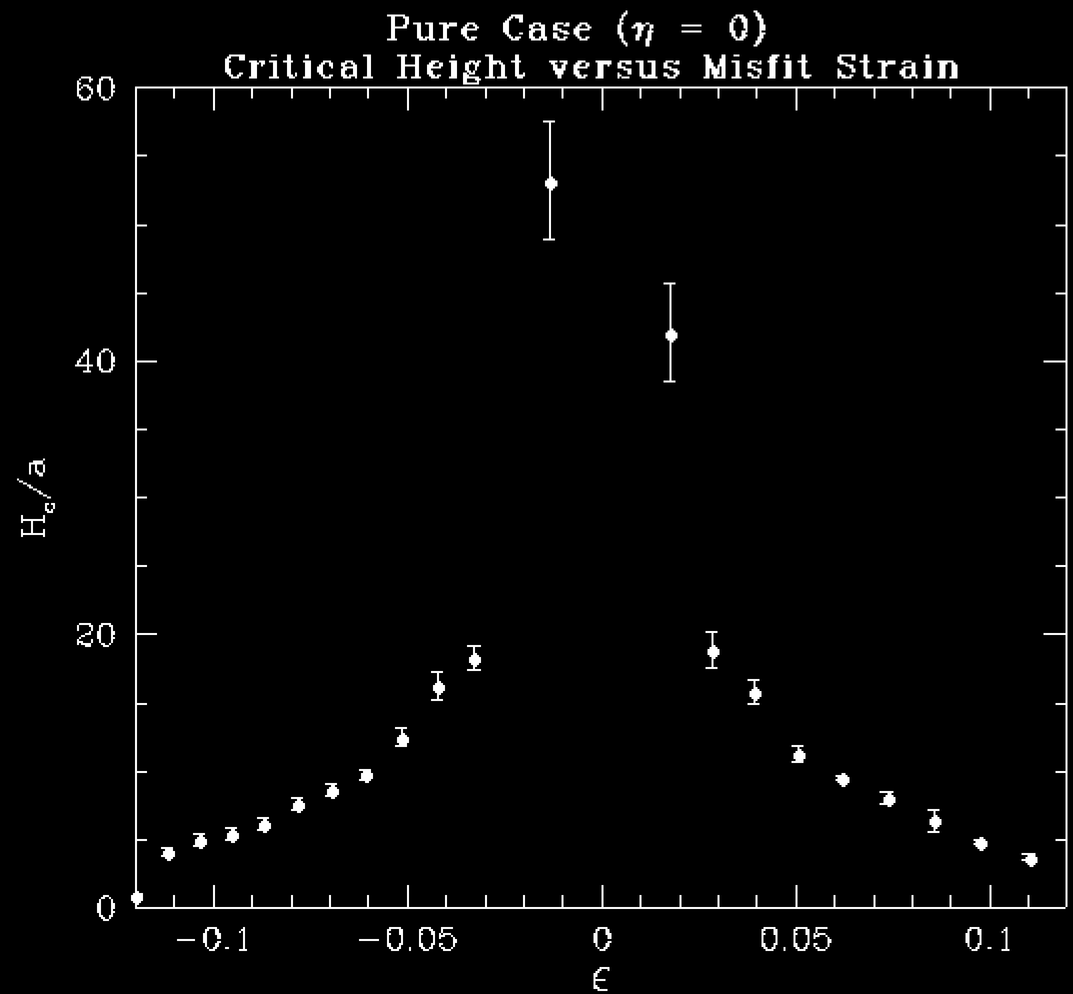


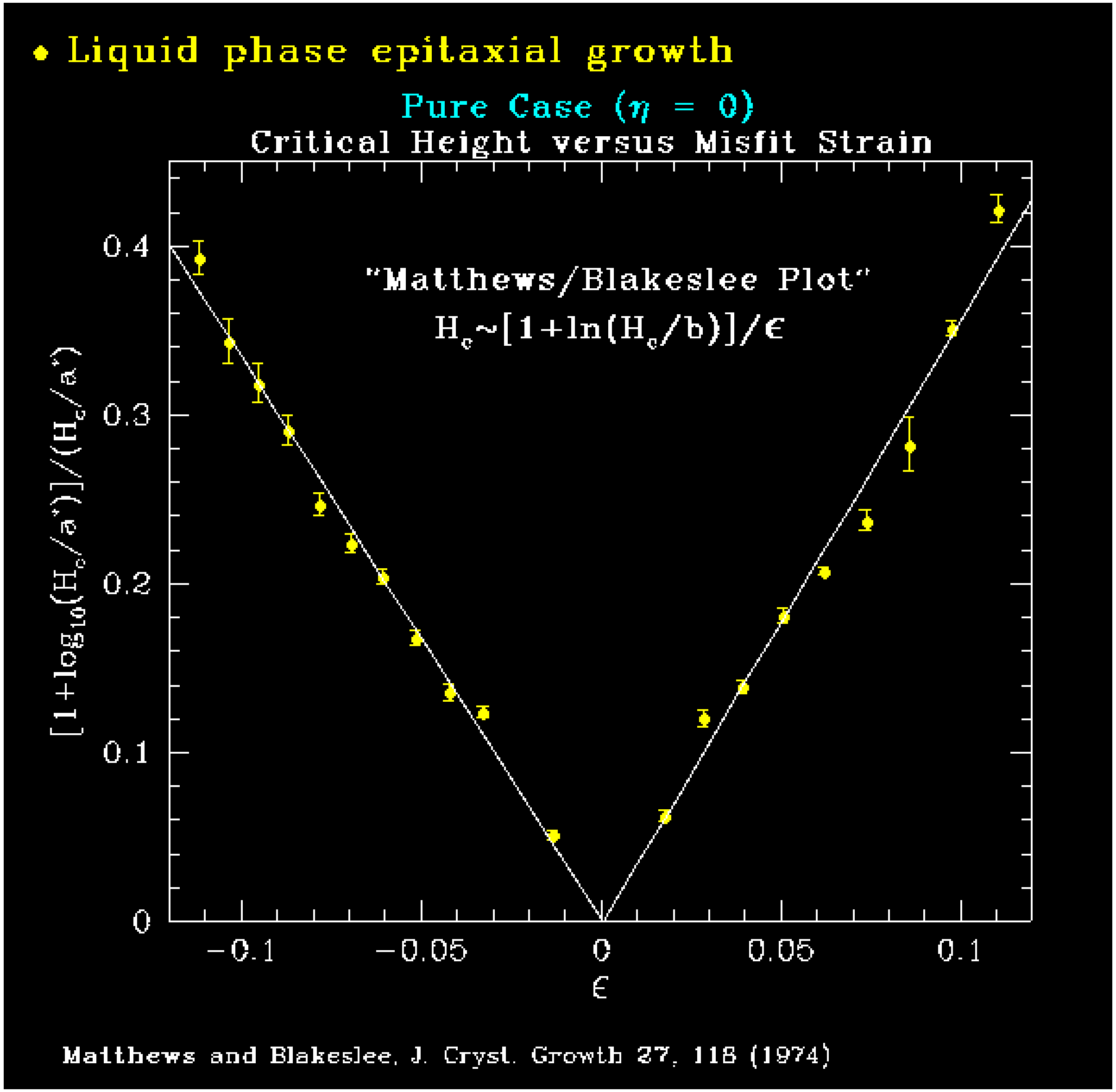
- Liquid phase epitaxial growth

Example: Misfit Strain $\epsilon = 2.4\ \%$ (tensile)

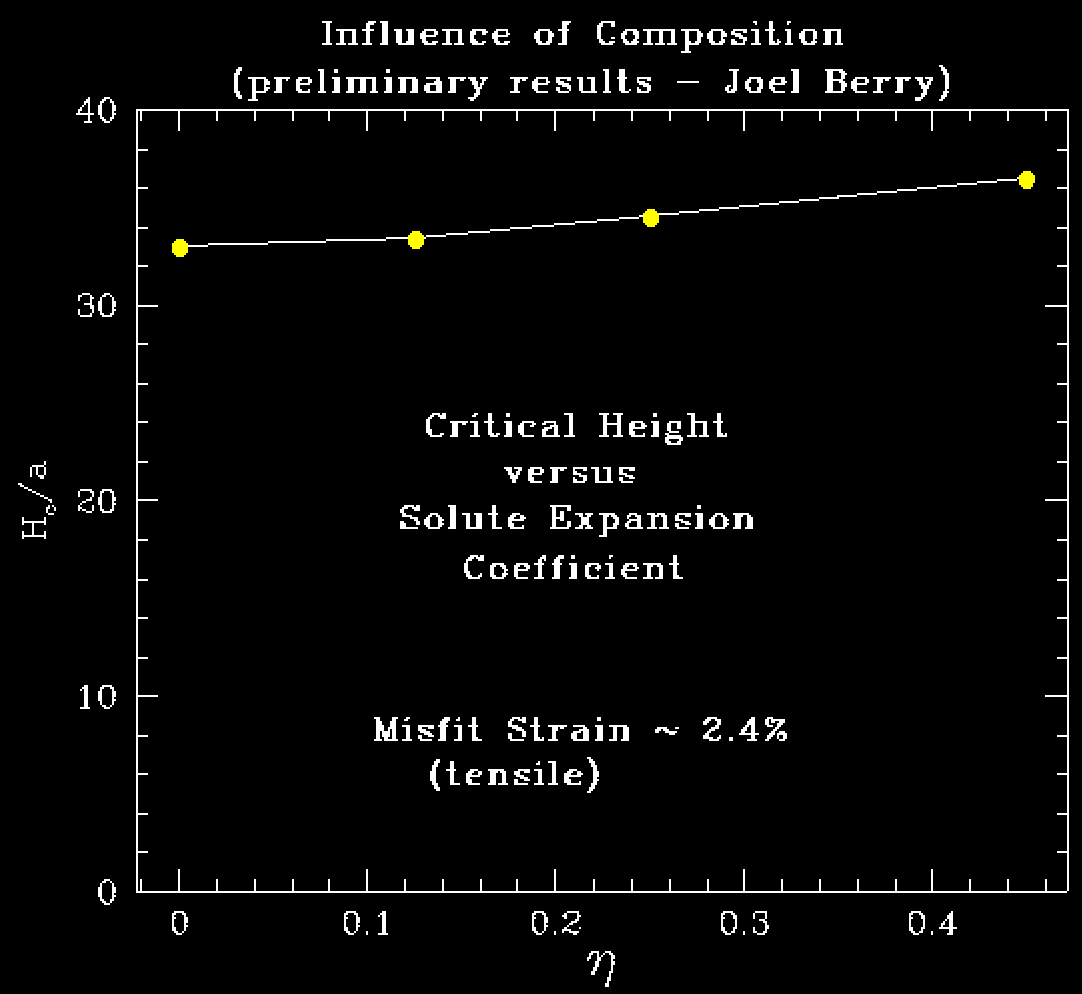


• Liquid phase epitaxial growth




• Liquid phase epitaxial growth
Pure Case (η = 0)
Critical Height versus Misfit Strain
"Matthews/Blakeslee Plot"
H_c~[1+ln(H_c/b)]/ε
[1+log_10(H_c/a')]/(H_c/a')
0.4
0.3
0.2
0.1
0
−0.1
−0.05
0
0.05
0.1
ε
Matthews and Blakeslee, J. Cryst. Growth 27, 118 (1974)

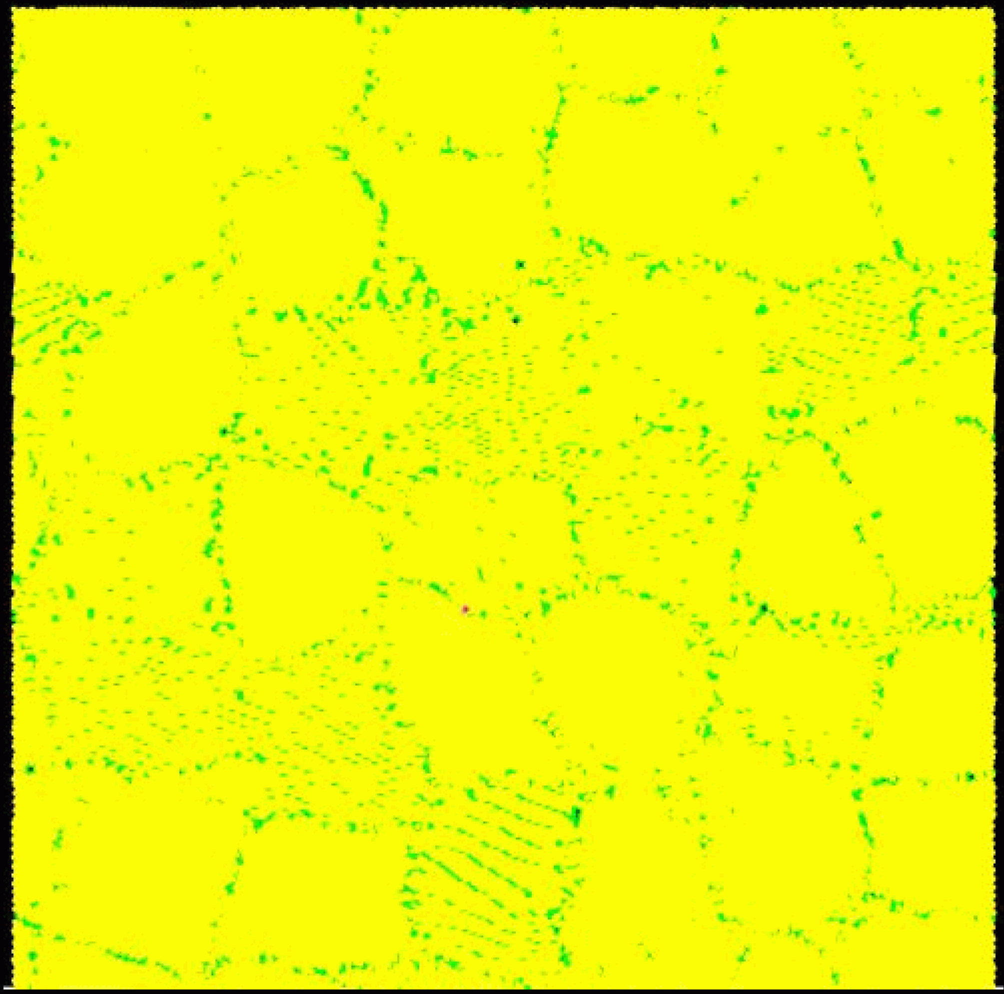
• Liquid phase epitaxial growth



# Other Applications

Structural Phase Transitions: eg. square – triangular

• 4 neighbors • 6 neighbors • other



# Other Applications

Structural Phase Transitions: eg. square – triangular

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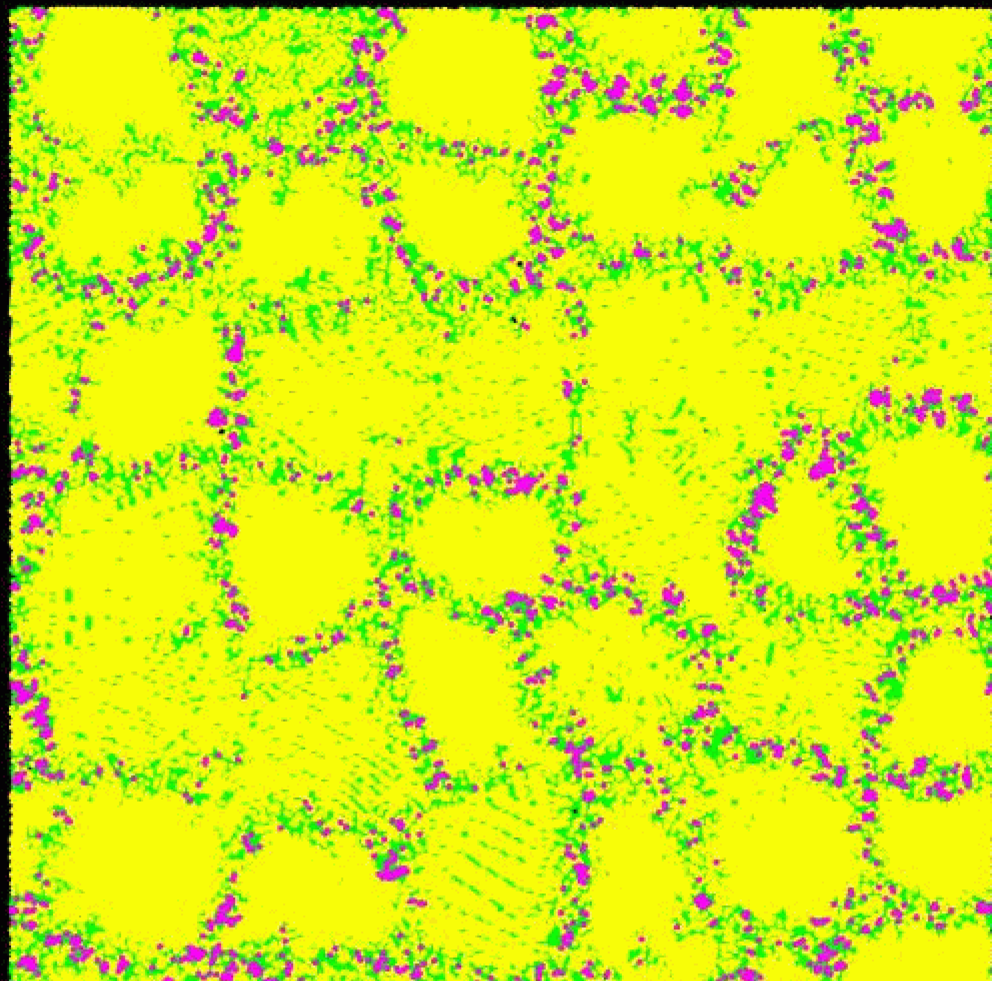
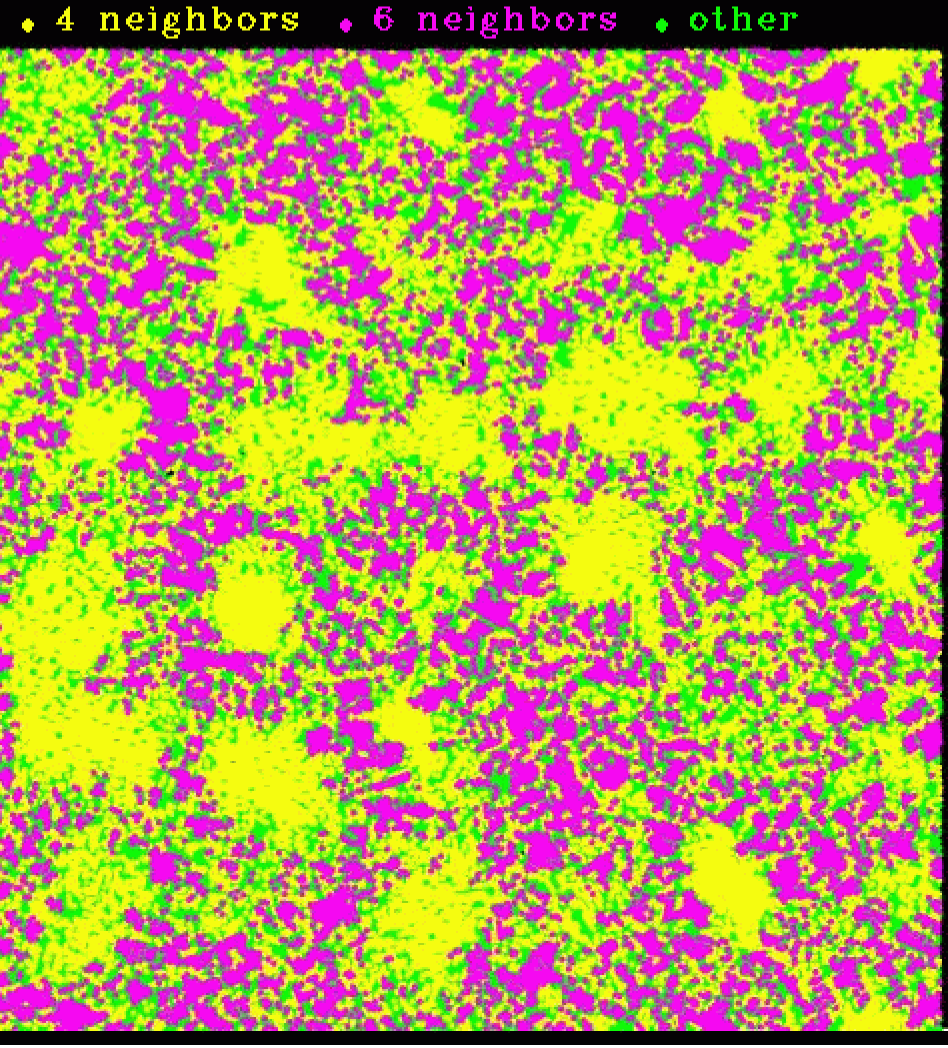


# Other Applications

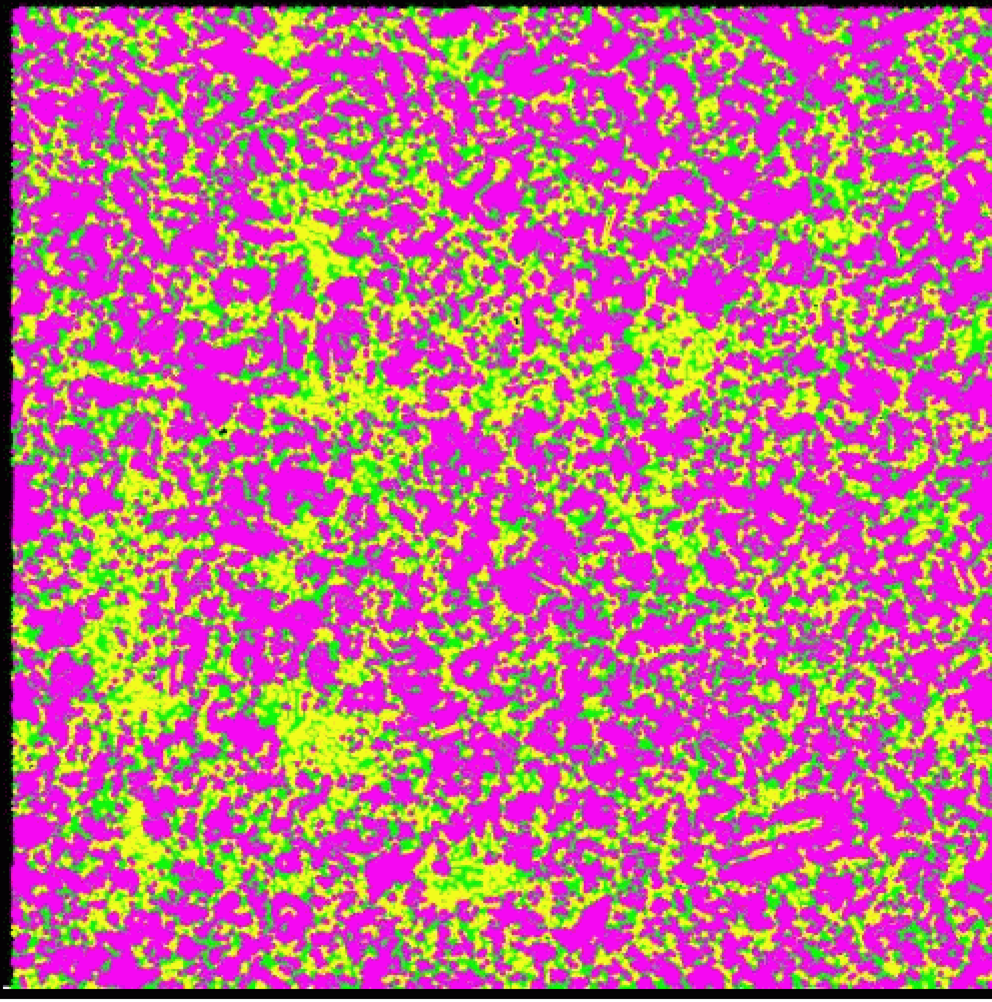
Structural Phase Transitions: eg. square – triangular



# Other Applications

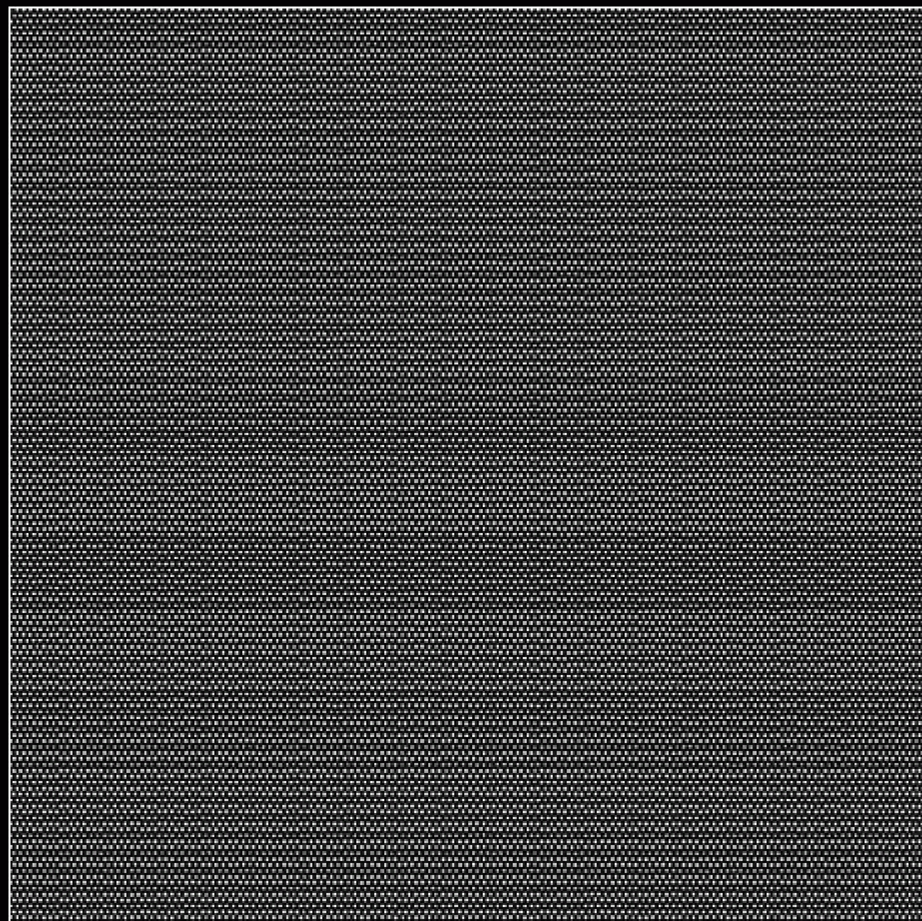
**Structural Phase Transitions: eg. square – triangular**

• 4 neighbors • 6 neighbors • other



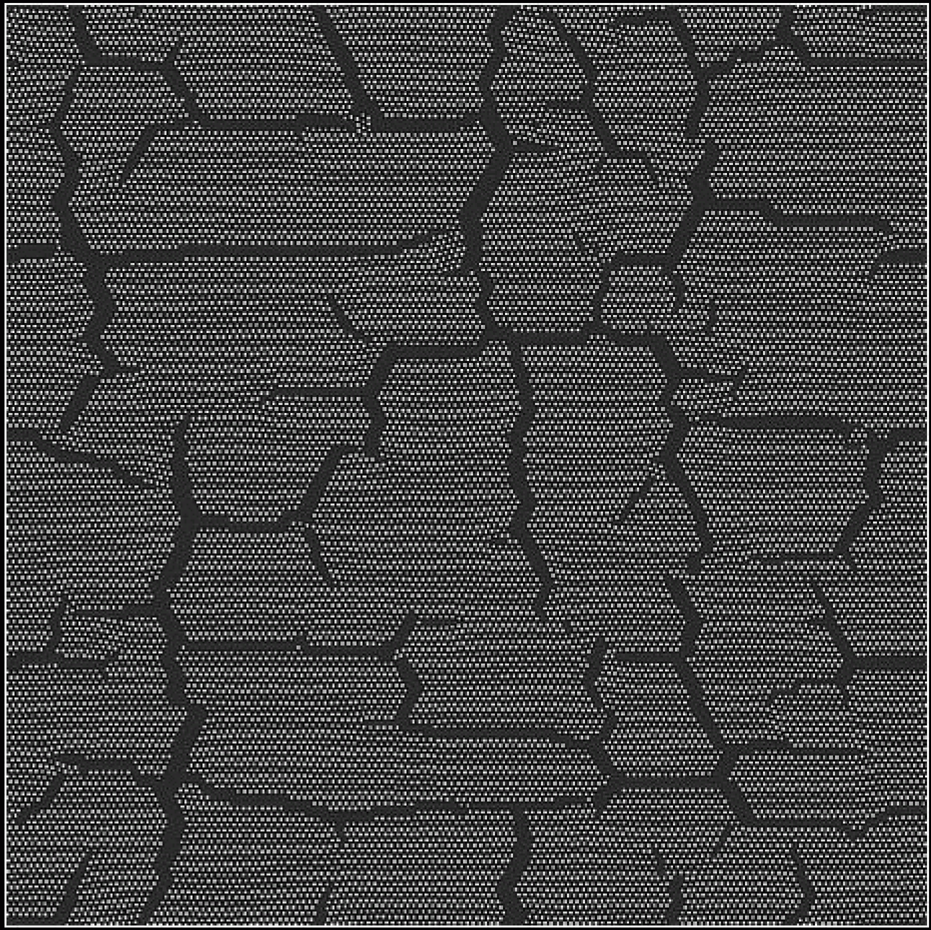
# Other Applications

## Crack Propagation



# Other Applications

## Crack Propagation



# Summary

**Periodic Fields** →
- Elastic + Plastic deformations
- Atomic length scales
- Diffusive time scales

**Applications (current)** →
- Yield Strength
- Epitaxial Growth
- Grain Growth
- Crack Propagation
- Structural Phase Transitions

friction, sintering
spinodal decomposition
step edge growth, ...

**Applications (other)** →
- Charge Density Waves
- Liquid Crystals
- Polymers, Colloids
- Ferroelectrics