# Phase Field Crystal Simulations of Nanostructure Formation

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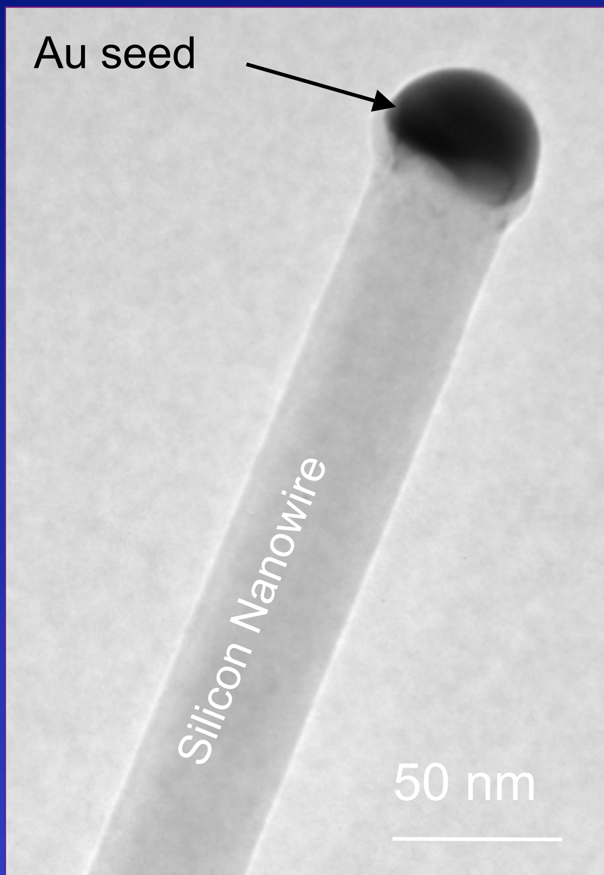
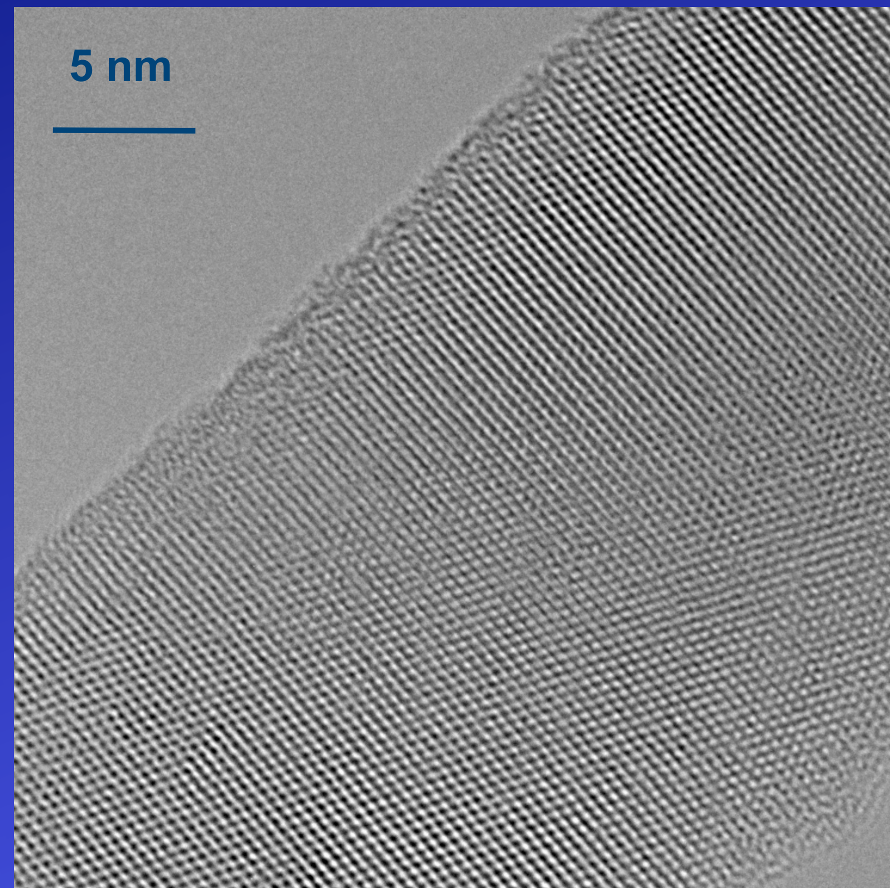
# Outline

- Nanostructure growth processes
- Phase field crystal model
- Quantum dot formation on surfaces
- Nanowire growth
- Conclusions

# Semiconductor Nanowires

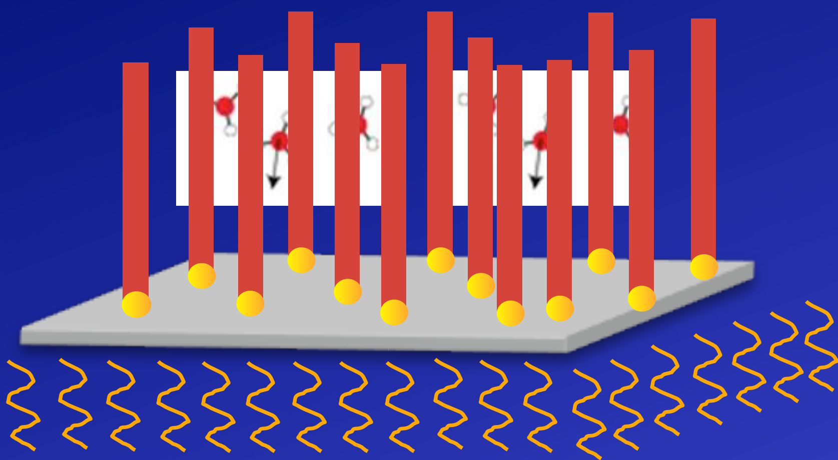


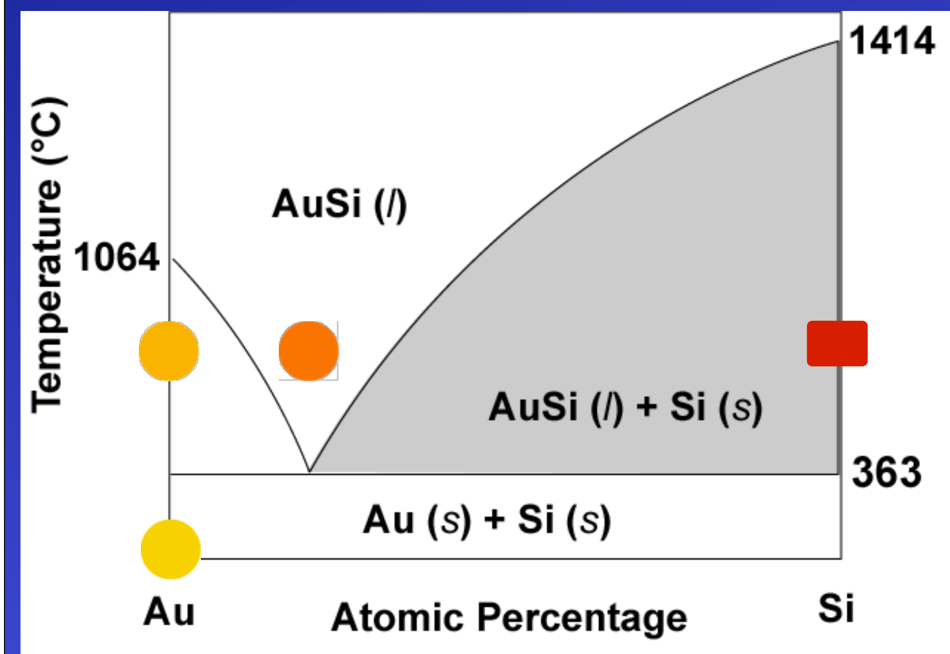



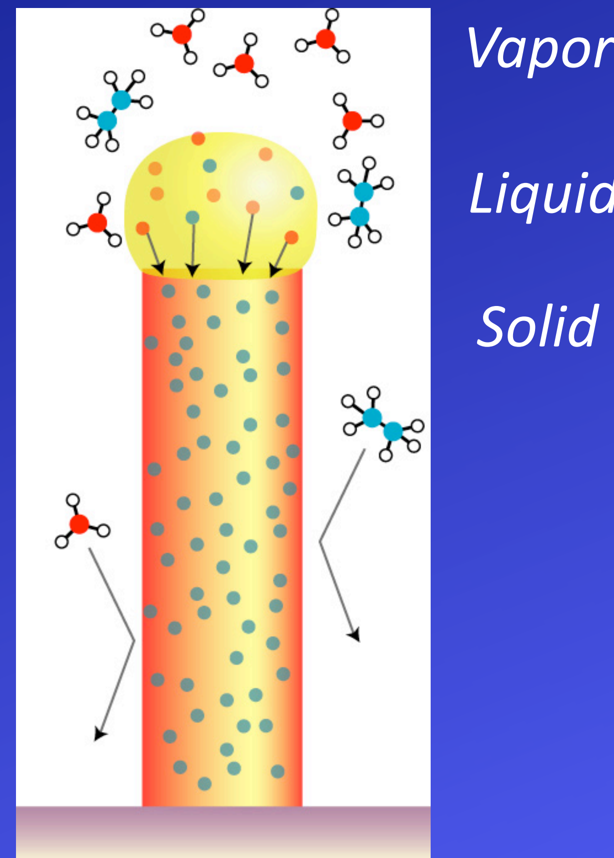

- Single crystal, nanoscale diameters, micron lengths
- Unique properties by virtue of aspect ratio

# Nanowire Growth

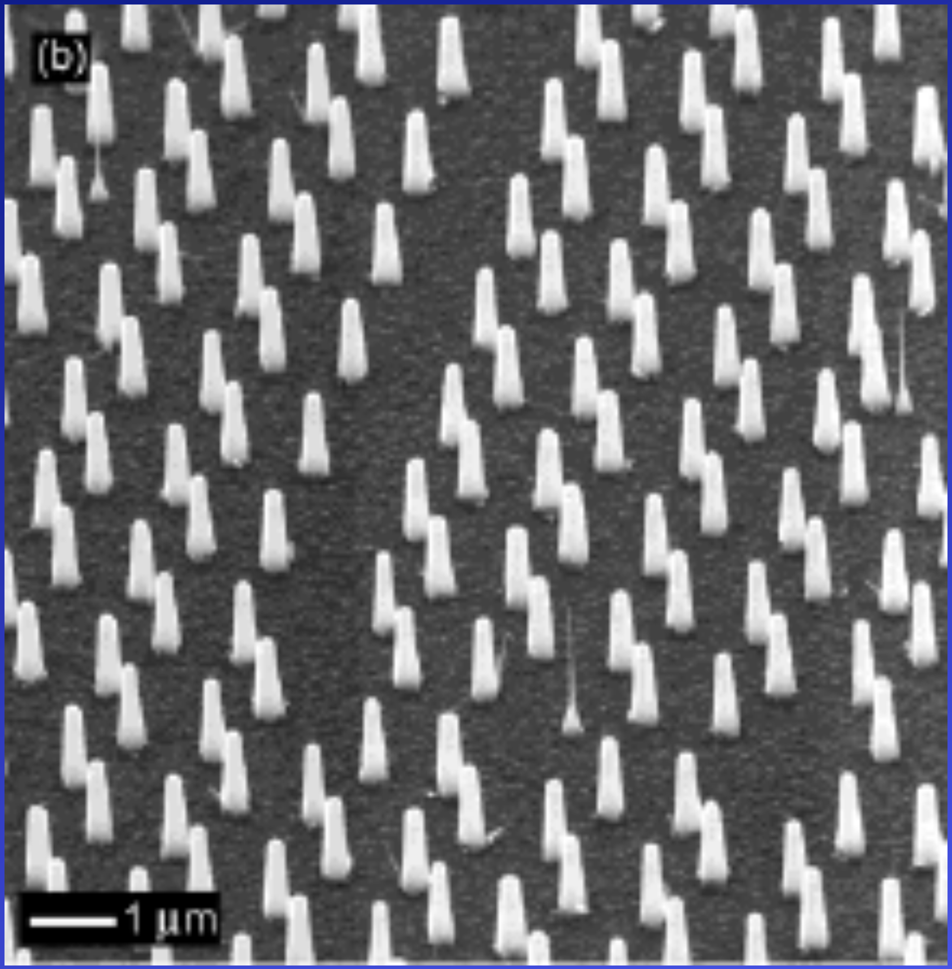
## Vapor-Liquid-Solid Mechanism



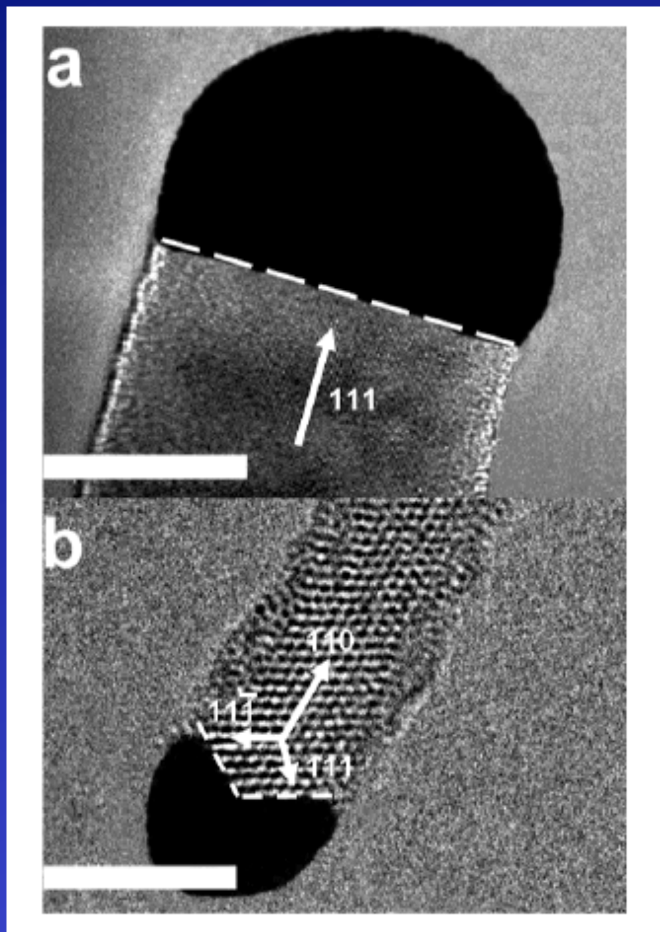



R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).




Martenson et al, Nano letters **4**, 669 (2004)

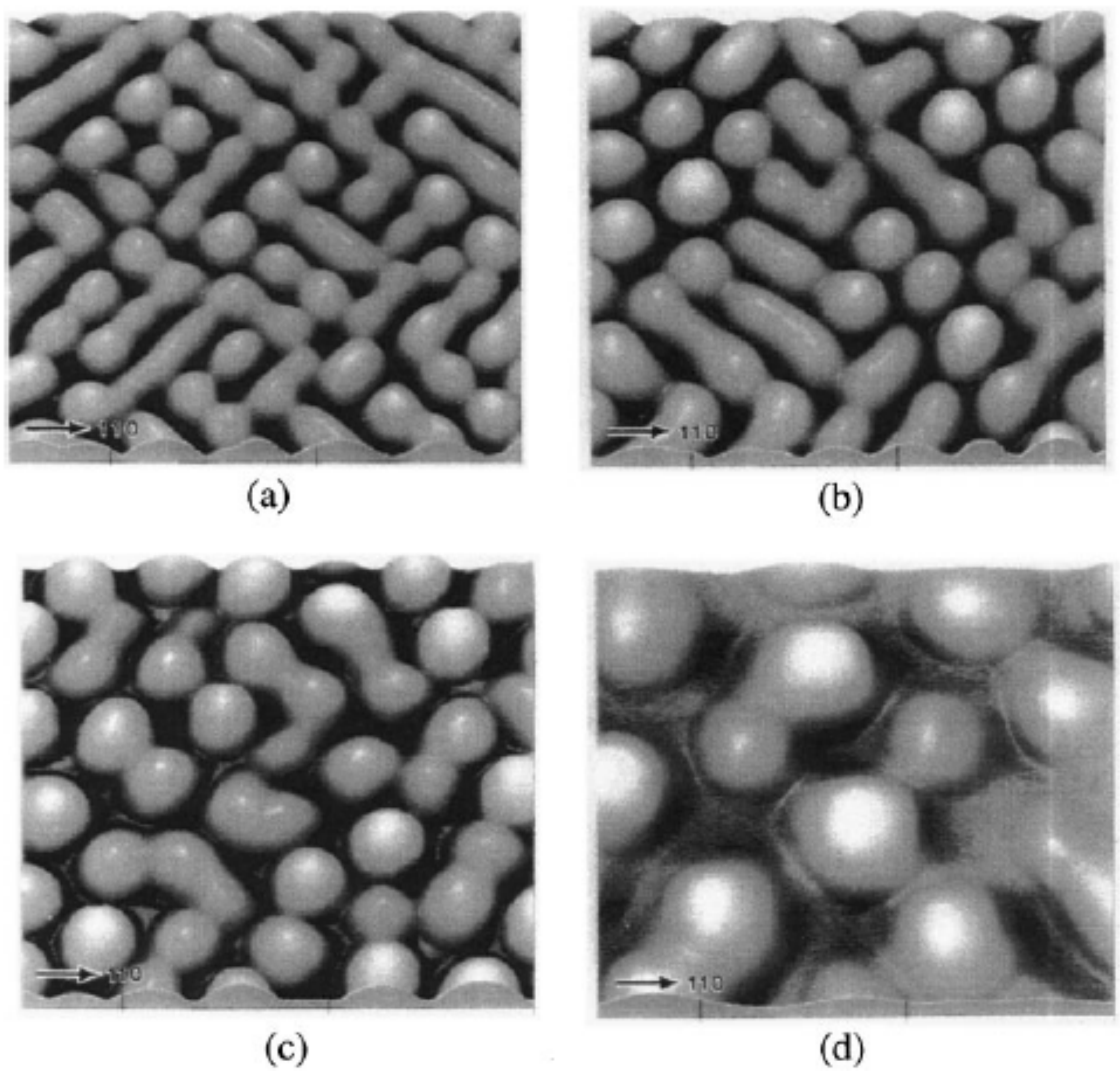



5 nm

Wu et al, Nanoletters, 2004


Ross and Hannon

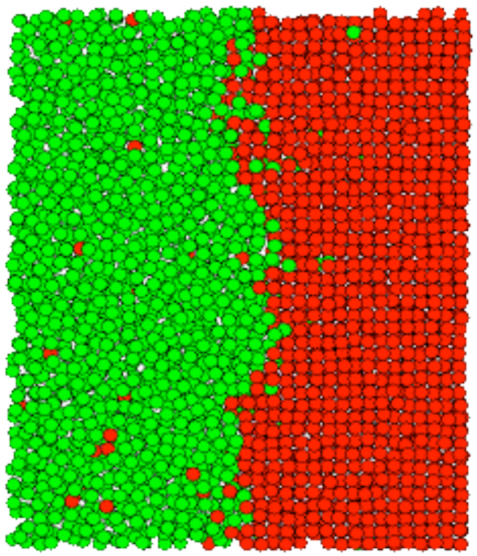
# Heteroepitaxial $Si_{0.82}Ge_{0.18}$/Si films




AFM images for 100Å thick $Si_{0.82}Ge_{0.18}$/Si films annealed at 850°C. (no misfit dislocation)
Ozkan et al., Appl. Phys. Lett., 1997

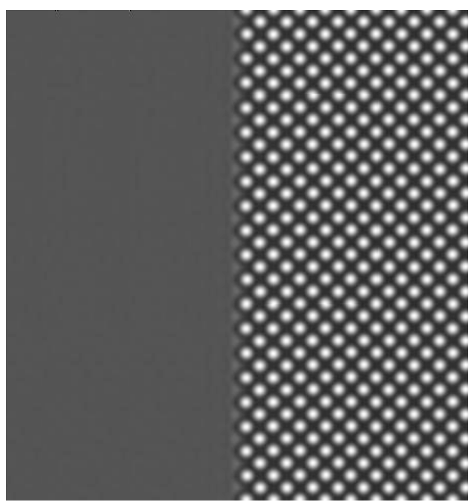
# Atomic-Scale Simulation Methods

MD
simulations



- Lattice vibration (ps)
- Fundamental physics

PFC Model
Elder et al.
(Swift-Hohenberg
type free energy)

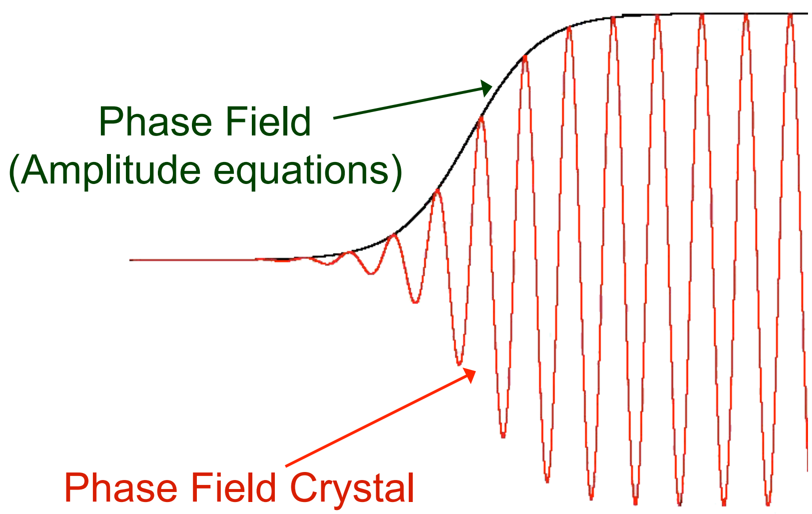


- Mean field theory
  $\phi$ : Time averaged density
- Atomistic length scale
- Diffusive time scale ($\mu$s-ms)
- Multiple crystalline planes
- Elasticity
- Dislocations

$$F[\phi, \nabla\phi] = \int \left( f(\phi) - 2k_o^2 |\nabla\phi|^2 + |\nabla\phi|^4 \right) dV$$

Swift- Hohenberg Free Energy

$$F[\phi, \nabla\phi] = \int \left\{ \frac{\phi}{2} \left[ a + \lambda \left( \nabla^2 + k_o^2 \right) \right] \phi + \frac{g}{4} \phi^4 \right\} dV$$

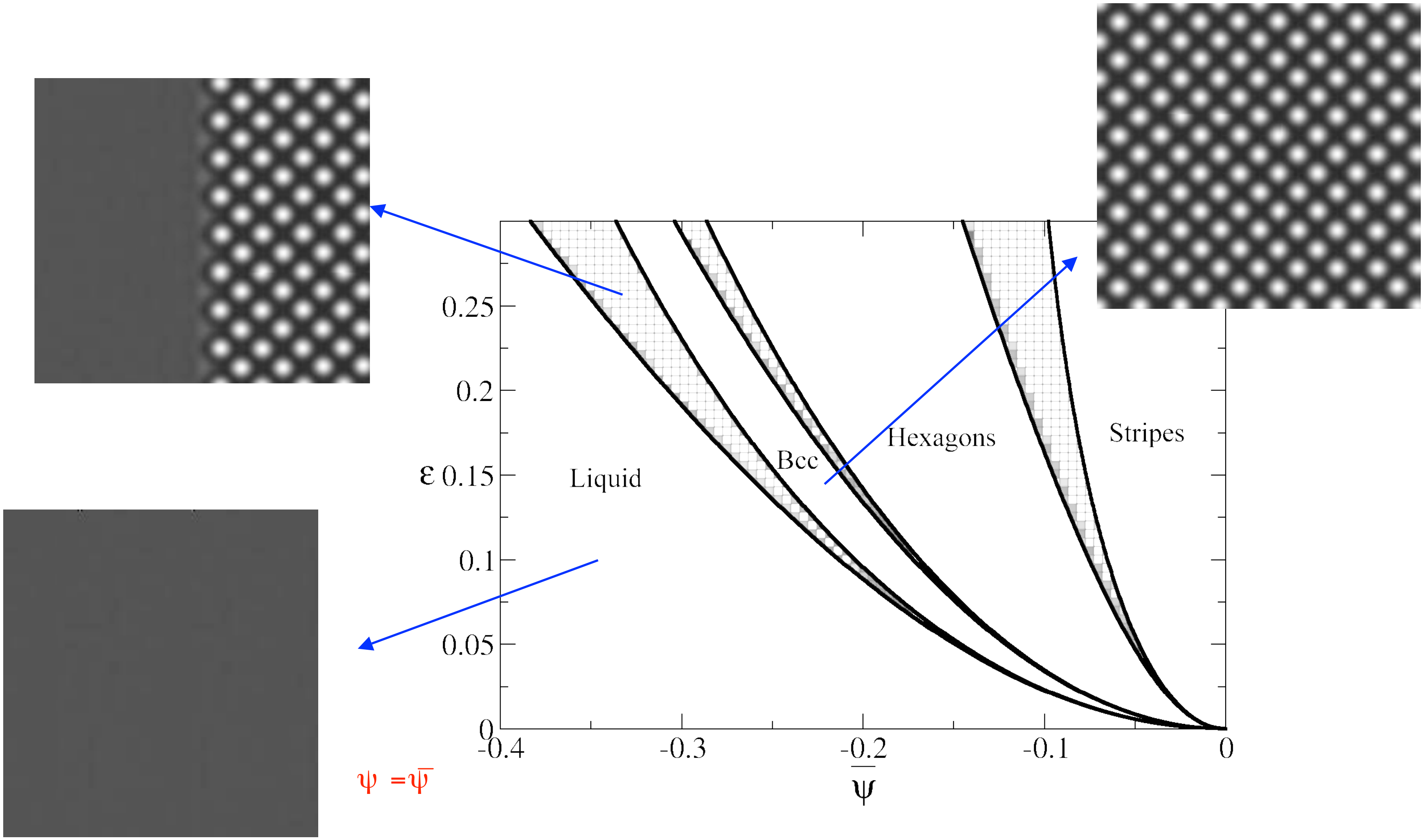



$$\phi(\vec{r}) = \bar{\phi}(\vec{r}) + \sum_{|\vec{k}|=k_0} A_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

## Swift-Hohenberg Free Energy

$$F[\phi, \nabla\phi] = \int \left\{ \frac{\phi}{2} \left[ a + \lambda \left( \nabla^2 + k_o^2 \right) \right] \phi + \frac{g}{4} \phi^4 \right\} dV$$

+ Conservation gives the following ground-state patterns:



## PFC Free Energy Functional

$$F = \int d\vec{r} \left\{ \frac{\phi}{2}[a + \lambda(\nabla^2 + q_o^2)^2]\phi + \frac{g}{4}\phi^4 \right\}$$

## Dimensionless Form

$$\mathcal{F} = \int d\vec{r} \left\{ \frac{\psi}{2}[-\epsilon + (\nabla^2 + 1)^2]\psi + \frac{1}{4}\psi^4 \right\}$$

## Equation of Motion

$$\frac{\partial \psi}{\partial t} = \nabla \cdot \nabla \frac{\delta \mathcal{F}}{\delta \psi} = \nabla \cdot \nabla \left\{ [-\epsilon + (\nabla^2 + 1)^2]\psi + \psi^3 \right\}$$

## Dimensionless units

$$\epsilon = -\frac{a}{\lambda q_o^4}$$

$$q_o \vec{r} \to \vec{r}$$

$$\sqrt{\frac{g}{\lambda q_o^4}}\phi \to \psi$$

$$\frac{g}{\lambda^2 q_o^5} F \to \mathcal{F}$$

Question :
Is the phase field crystal model
a physical model?

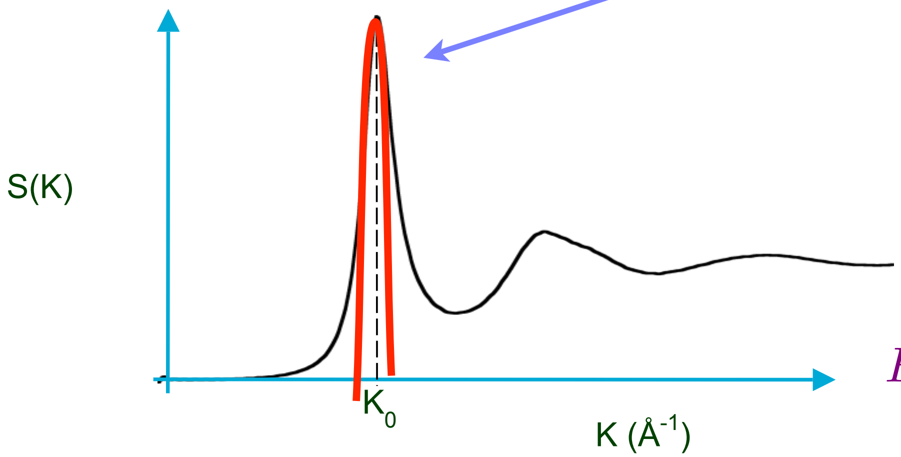
# Connection to density functional theory

From Ramakrishnan and Youssoff, expanding around a liquid of uniform density relative to an ideal gas:

$$\frac{F}{k_B T \rho_o} = \int d\mathbf{r} \left[ (1+n(\mathbf{r})) \ln(1+n(\mathbf{r})) - n(\mathbf{r}) \right] - \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) C(|\mathbf{r}-\mathbf{r}'|) n(\mathbf{r}')$$

where $n(\mathbf{r}) = (\rho(\mathbf{r}) - \rho_o)/\rho_o$

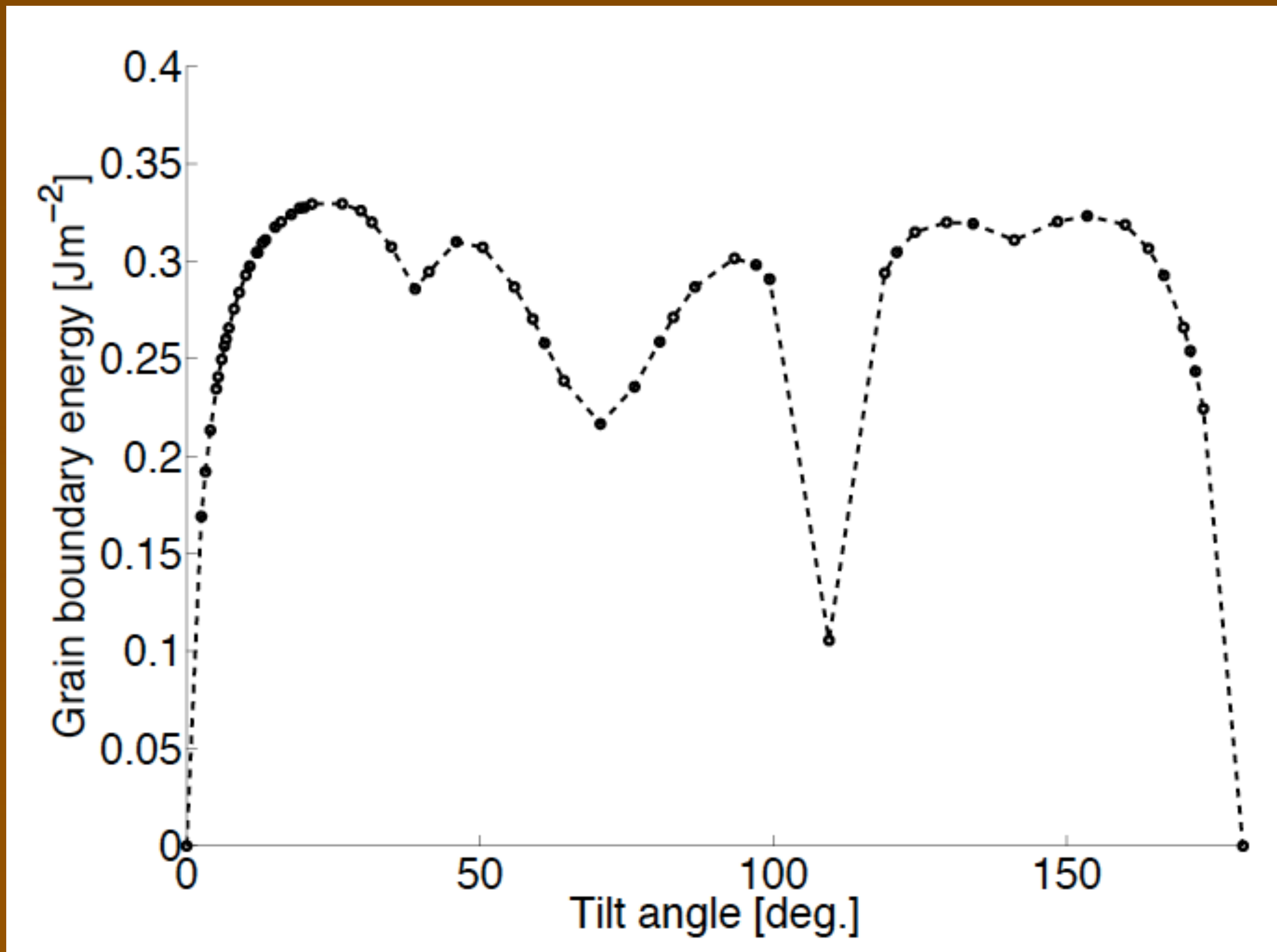
$$C''(K_o) = S''(K_o)/S(K_o)^2$$




$$F = \int d\mathbf{r} \left\{ \frac{\psi}{2} \left[ -\epsilon + \left(\nabla^2 + 1\right)^2 \right] \psi + \frac{1}{4} \psi^4 \right\}$$

$$\epsilon = \frac{8}{(1 - 3\psi_c^2) K_o^2 S(K_o) C''(K_o)}$$

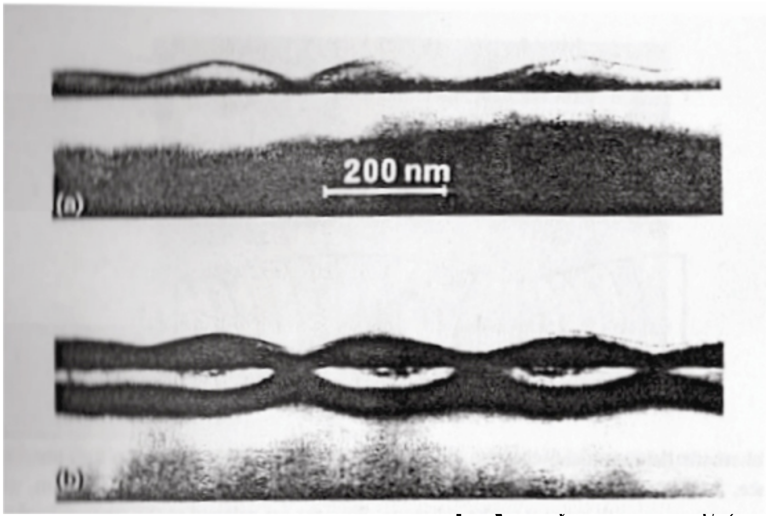
By expanding the structure function of Fe to eighth order, BCC crystal:



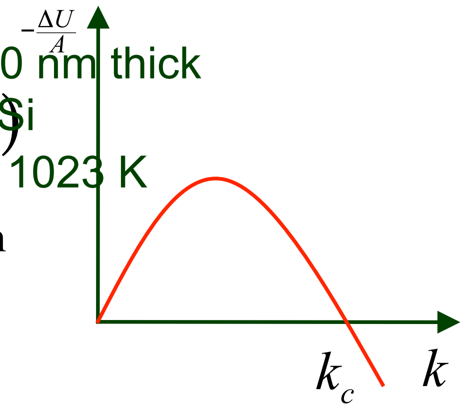

Results agree well with MD simulations using Finnis-Sinclair potential

A. Jaatinen C. V. Achim, K. R. Elder, T. Ala-Nissila

# Stress Induced Instability – Asaro-Tiller-Grinfeld Instability

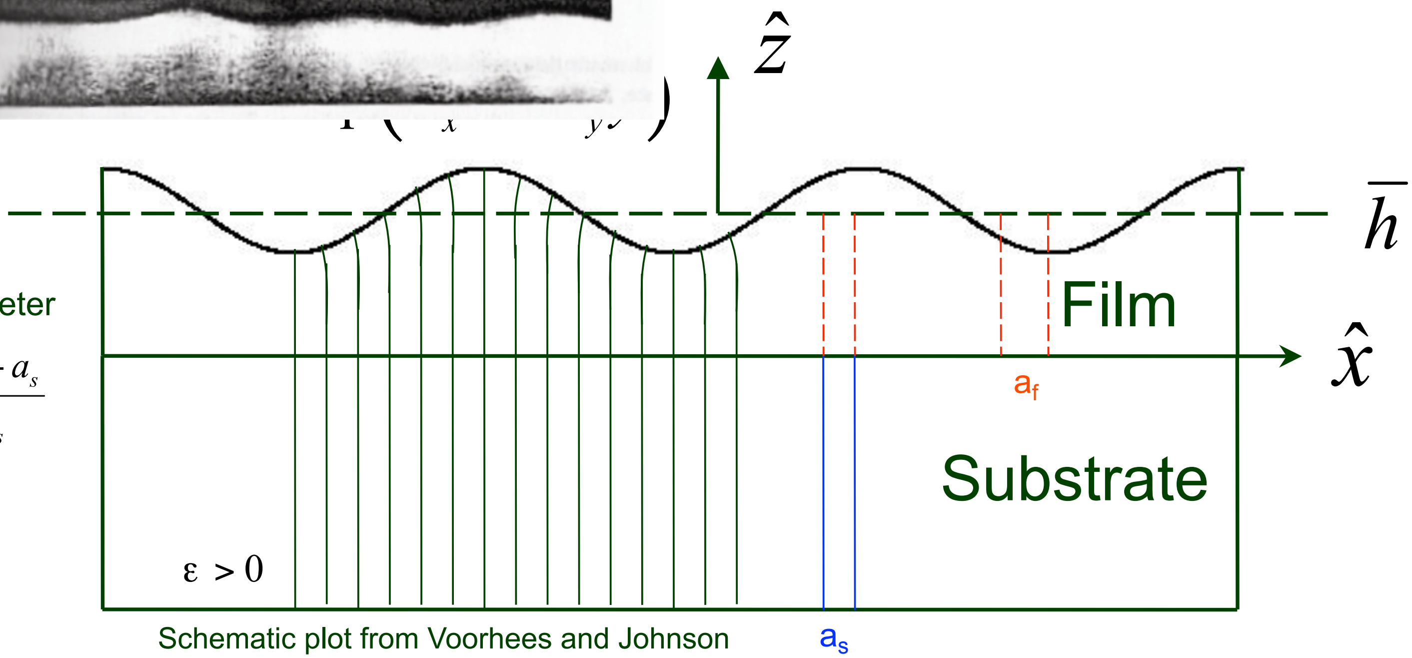


Cullis et al. (1992): 40 nm thick $Si_{0.79}Ge_{0.21}$ on (001) Si substrate - Grown at 1023 K (Defect-free growth)




Misfit Parameter

$$\varepsilon \equiv \frac{a_f - a_s}{a_s}$$



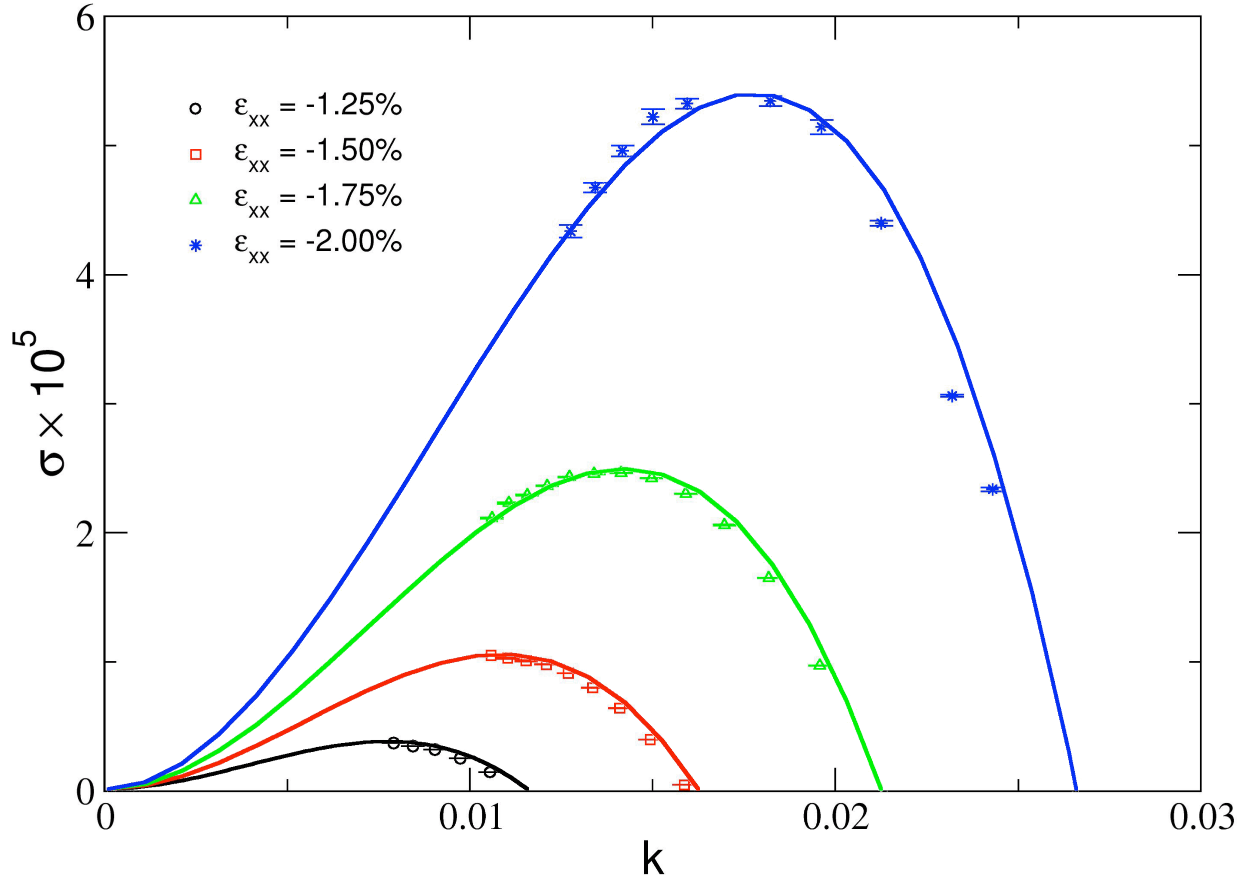

Schematic plot from Voorhees and Johnson
Solid State Physics, **59**

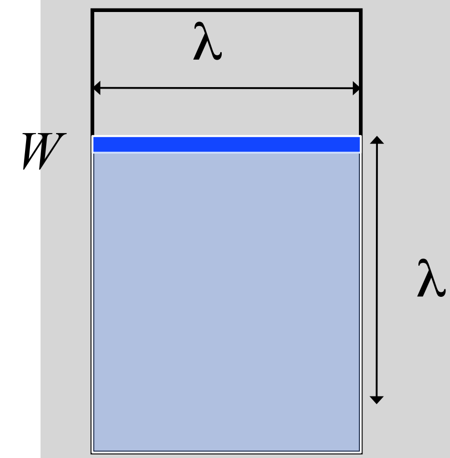
# Growth Rate vs. Wavenumber: Solid–Liquid

$$\hat{h} \sim \exp(\sigma t)$$

$$\sigma = D\left(Ak^2 - Bk^3\right)$$

Bulk Diffusion



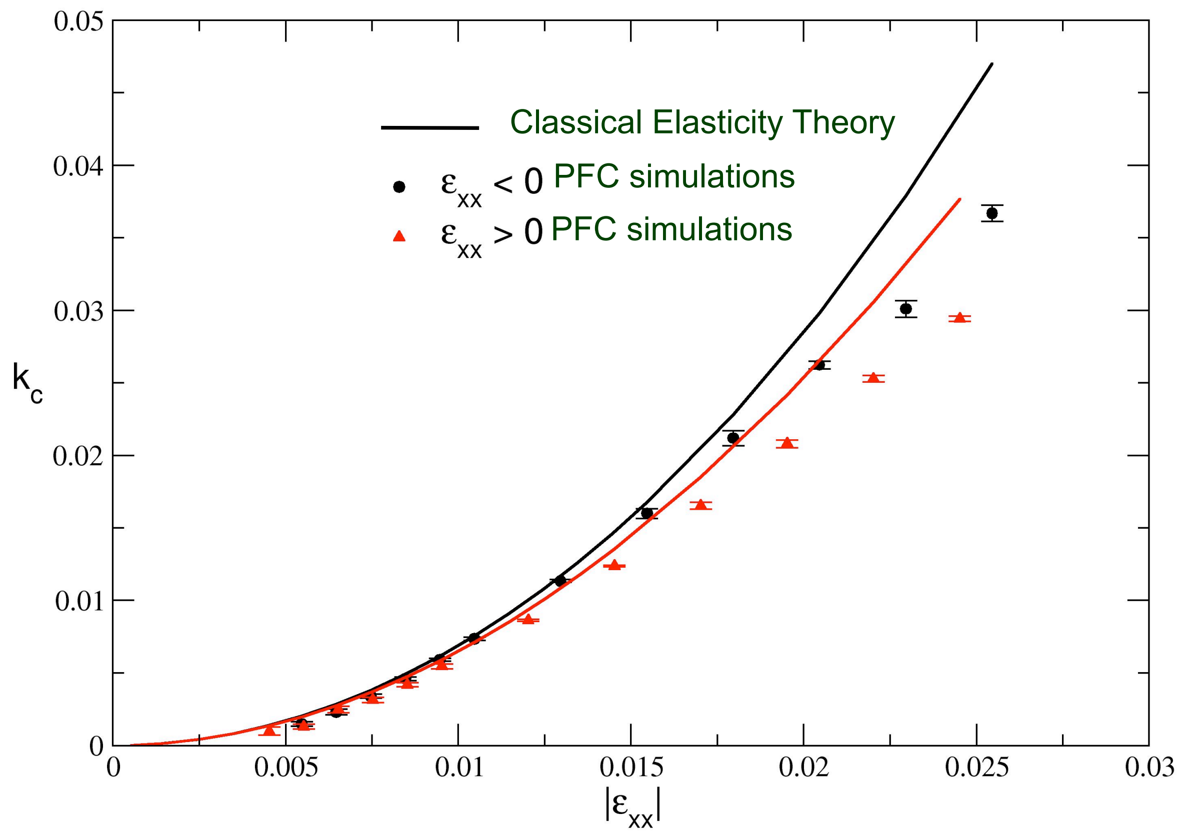
# Critical Wavenumber vs Strain

See also Huang and Elder, PRL 2008

Linear perturbation theory
- Sharp Interface
- Homogeneous Materials

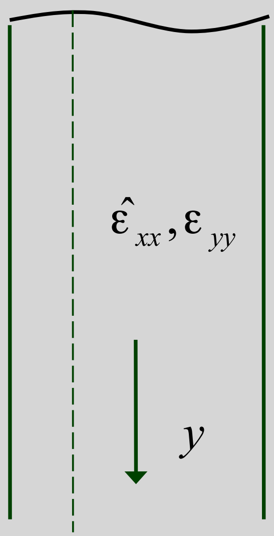
$$k_c = \frac{2E\epsilon_{xx}^2}{\gamma}$$

$k_c \sim \varepsilon_{xx}^2$ for small strains



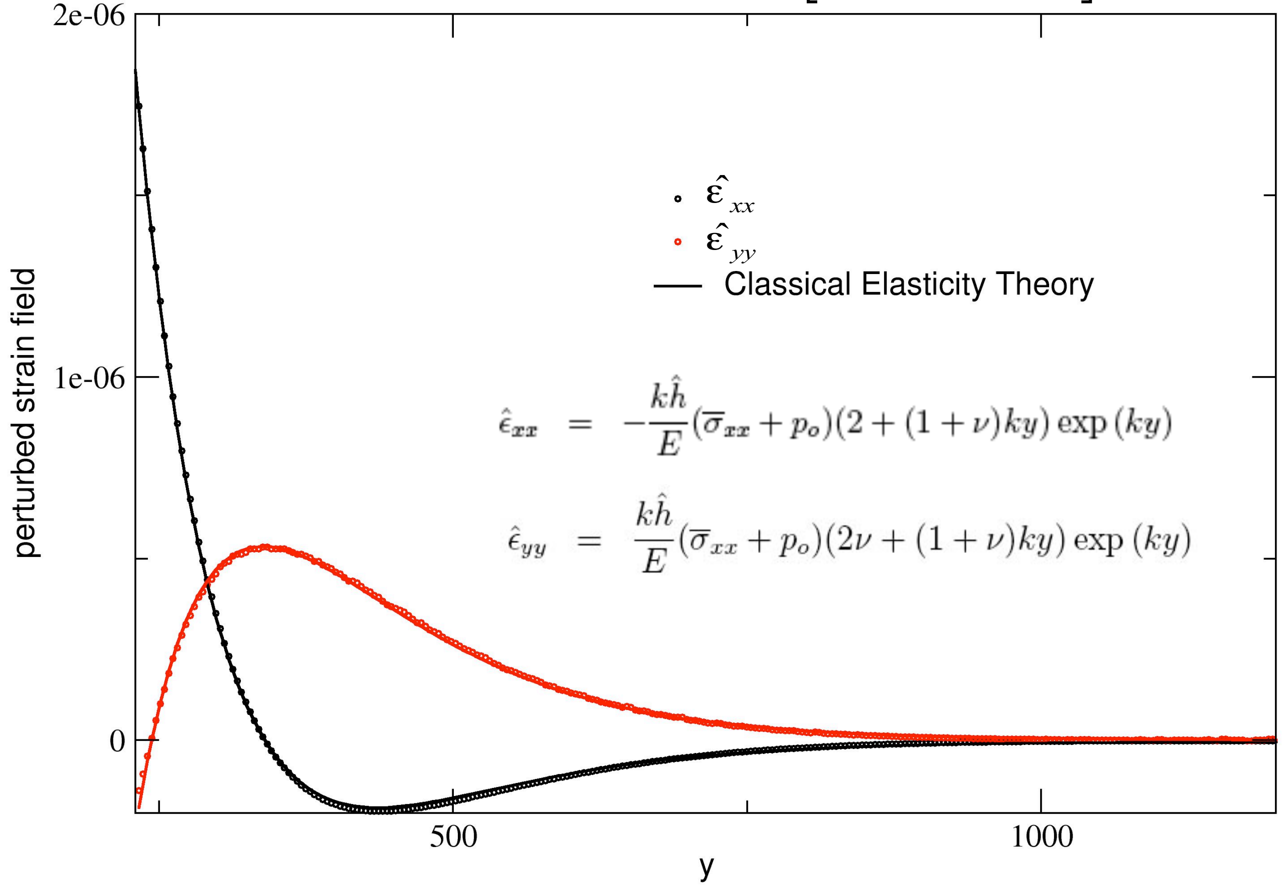
# Quantitative Comparison of Strain Fields

(cf. Stefanovic, Haataja and Provatas, PRL, 2006)

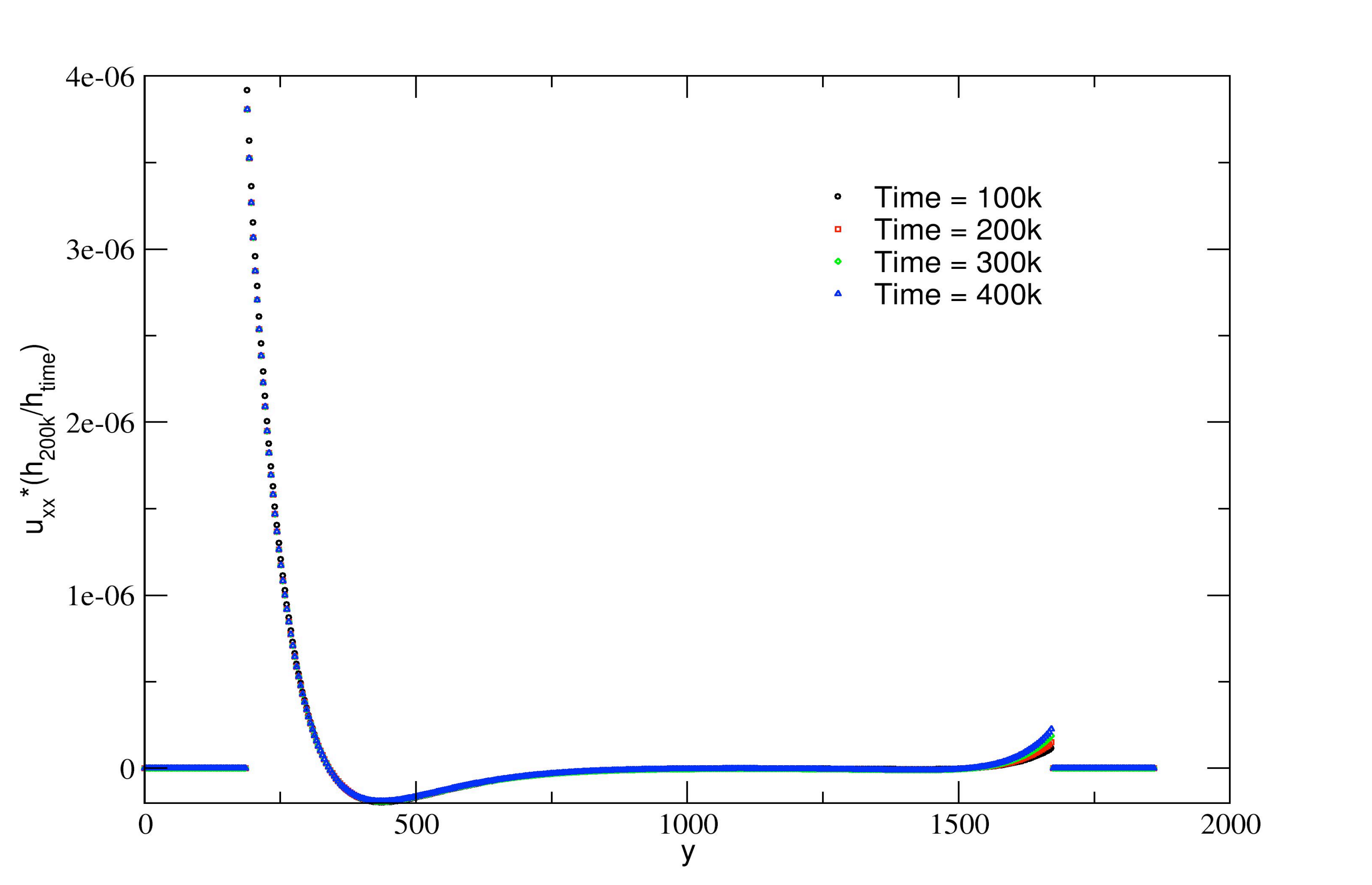



$\bar{\varepsilon}_{xx} = -1\%$

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

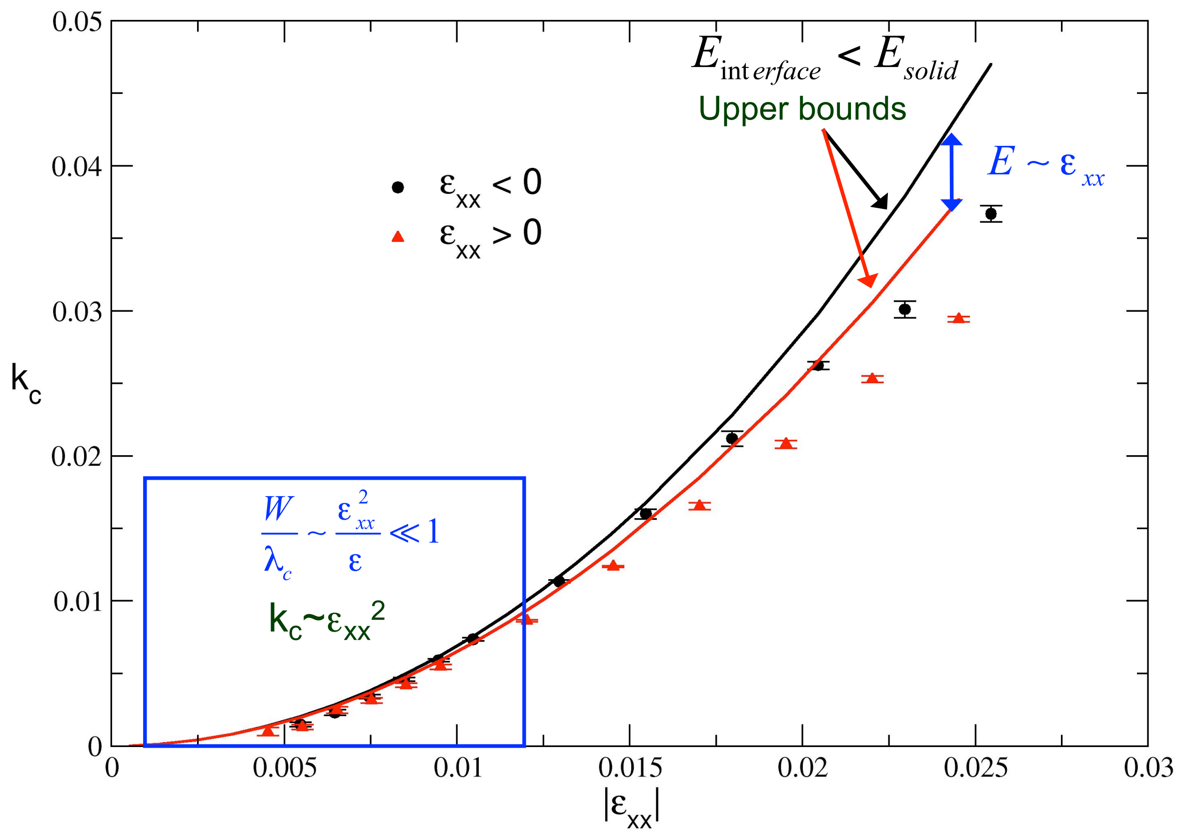


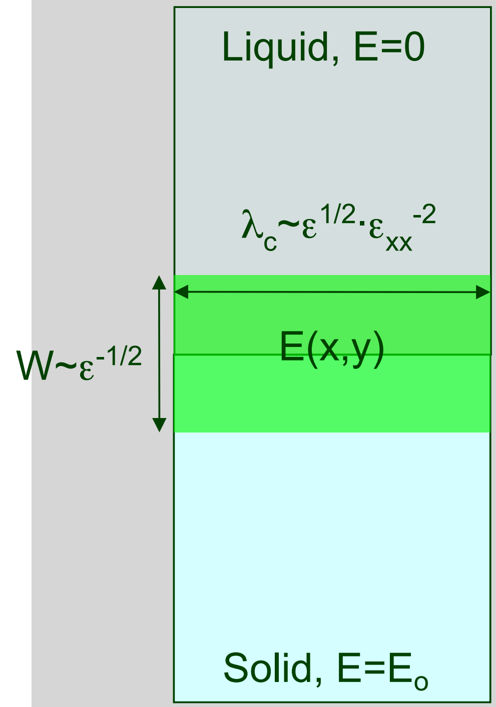
# Strain Field as a Function of Time




Elastic field completely relaxed on the time scale of interface evolution

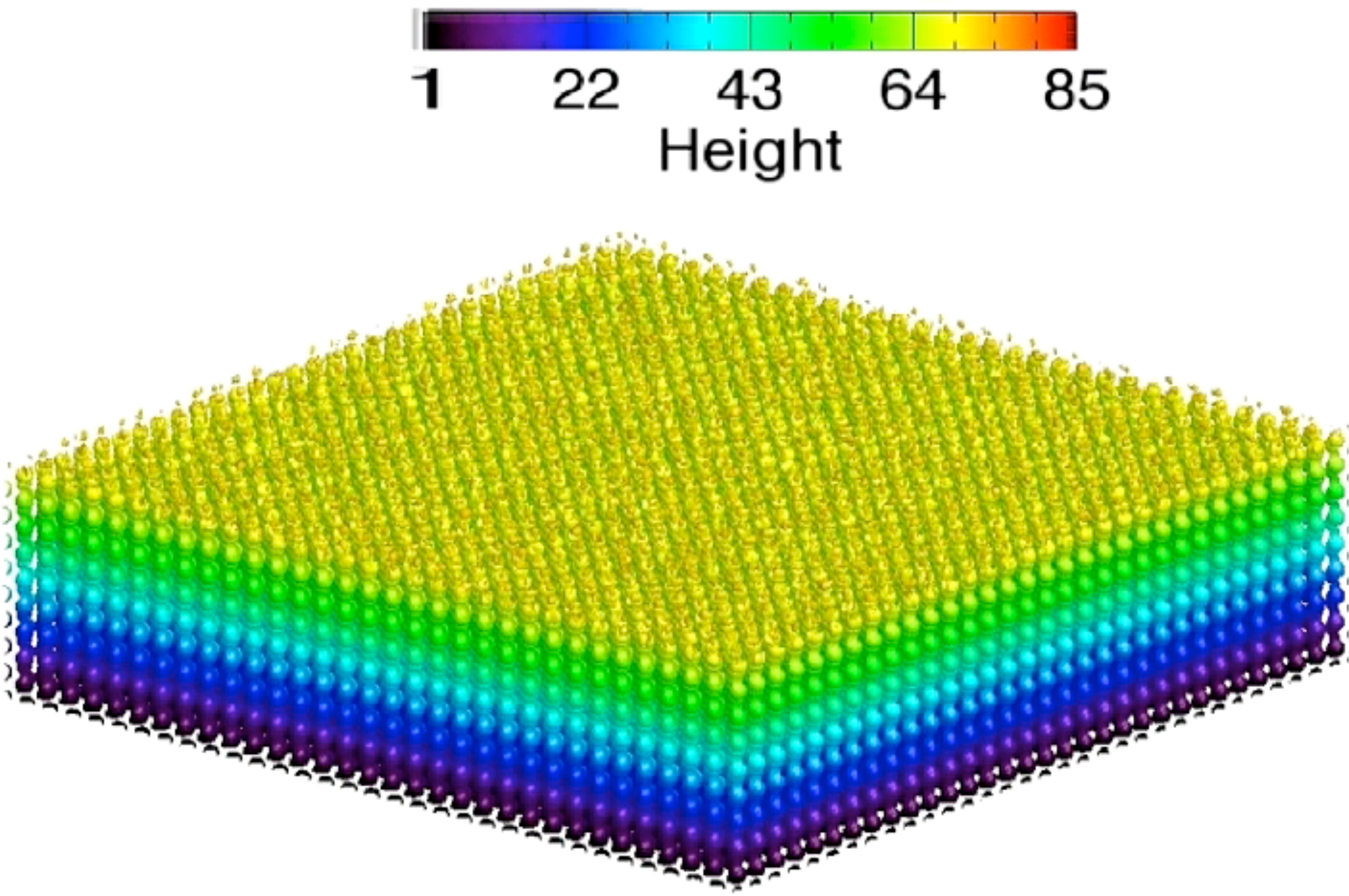
# Finite Interface Thickness and Nonlinear Elasticity



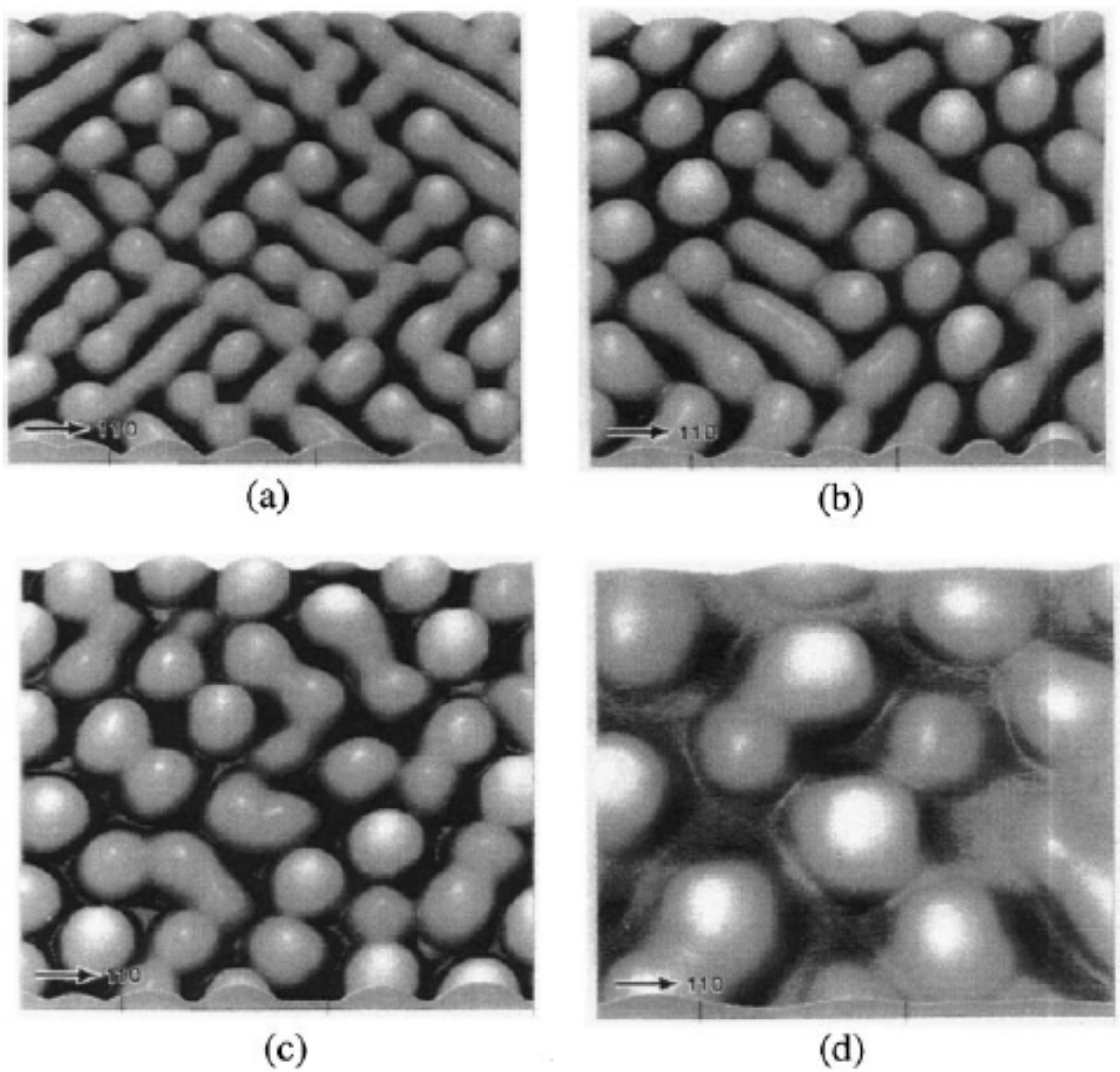




Finite interface thickness *W*
Elastic constants vary smoothly across the Interface region

# 3D Island – BCC Systems



# Heteroepitaxial $Si_{0.82}Ge_{0.18}$/Si films




AFM images for 100Å thick $Si_{0.82}Ge_{0.18}$/Si films annealed at 850°C. (no misfit dislocation)
Ozkan et al., Appl. Phys. Lett., 1997

# Conclusions

- Stress driven instability:
  - Phase field crystal method can be used for quantitative simulations: critical wavelength
  - Captures the effects of a finite interface thickness and nonlinear elasticity associated with the large strains in semiconductor systems
  - Critical wave number can be linearly related to strain, as observed experimentally
- Solid-vapor PFC model has been developed:
  - Density oscillations at a liquid-vapor interface
  - Definable step energy
  - Facet formation during nanowire growth
  - Importance of the solid-vapor-liquid triple line