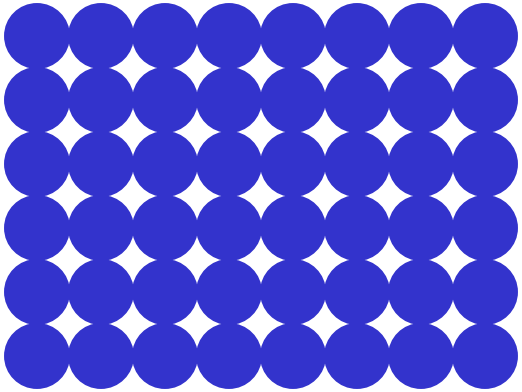
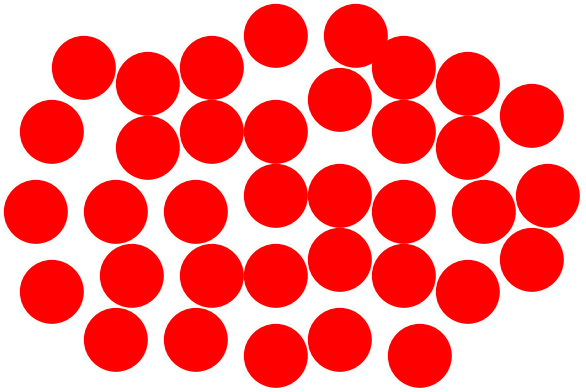
Surface stress-induced self-assembly

Zhigang Suo

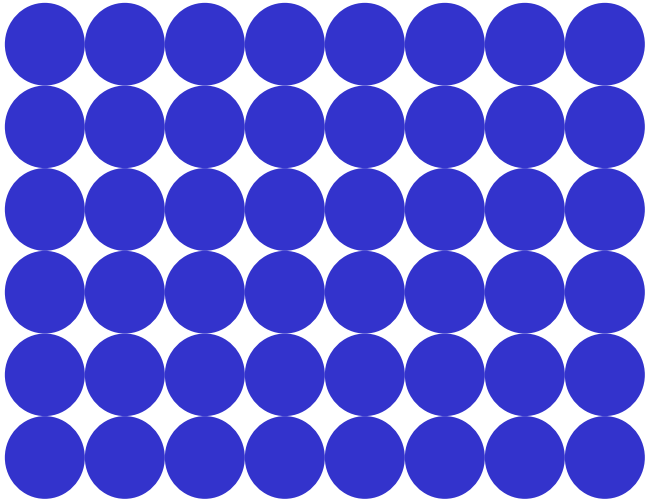
Work with Wei Lu



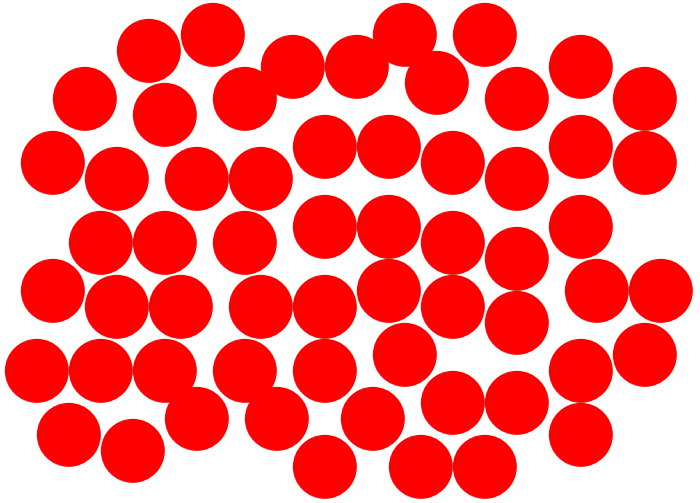
Solid surface



Liquid surface



Stretched solid surface

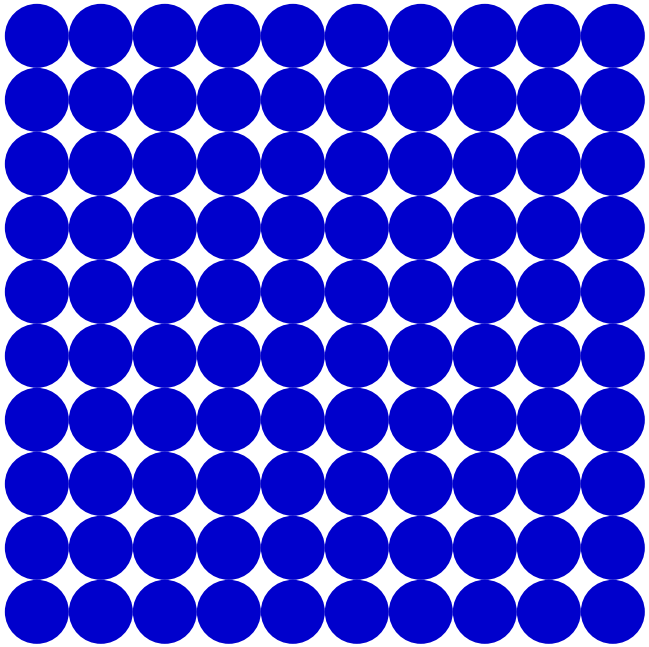


Stretched liquid surface

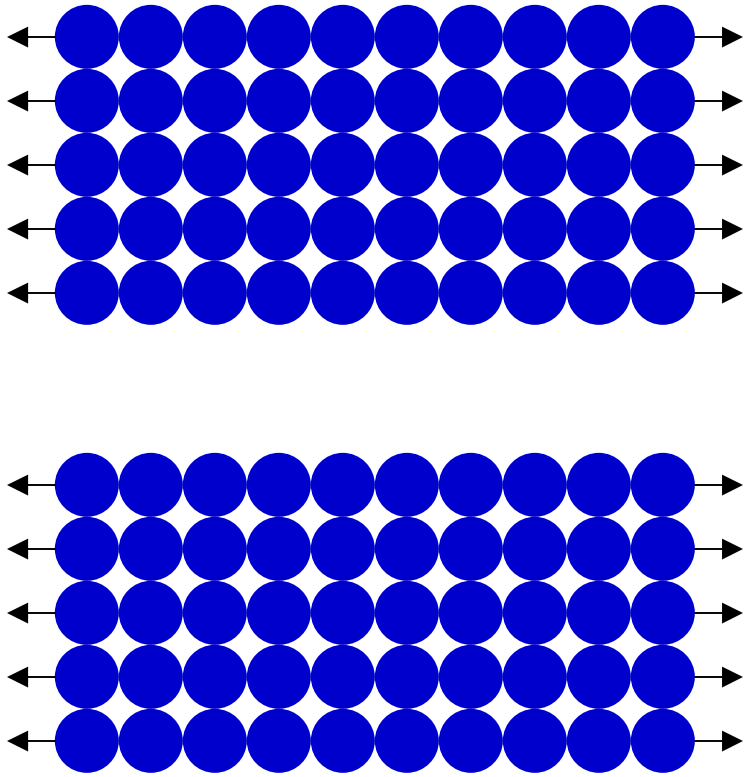
Energy per surface atom depends on stretch

Energy per surface atom is independent of stretch

Surface energy of an elastic solid



Reference state
stress-free, infinite solid



Current State

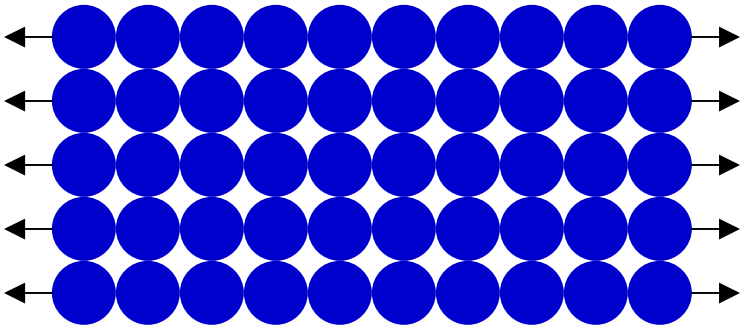
$$G = \Gamma A + WV$$

A = area in reference state. V = volume in reference state

Surface Stress

Current State

$$G = \Gamma A + WV$$



strain $\varepsilon = \dfrac{a - a_0}{a_0}$

Bulk elastic energy $W = \dfrac{1}{2} E\varepsilon^2$

Surface energy $\Gamma = g + f\varepsilon$

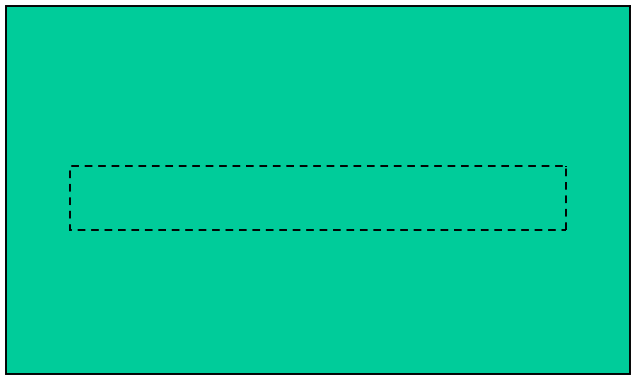
surface stress

- Surface energy depends on elastic strain
- Residual stress field in surface layers
- Surface stress can be either tensile or compressive

$$f \sim (\text{residual stress}) \times (\text{layer thickness})$$

$$\sim \left(10^{10}\,\text{N/m}^2\right) \times \left(10^{-10}\,\text{m}\right) = 1\,\text{N/m}$$

A thin foil



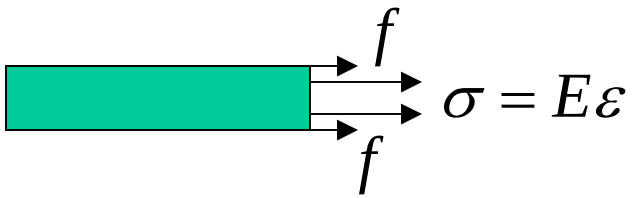
$$W = \frac{1}{2} E\varepsilon^2 \qquad \Gamma = g + f\varepsilon$$

$$G = hW + 2\Gamma \qquad \text{(energy/area)}$$

Reference state
stress-free, infinite solid

$$G(\varepsilon) = \frac{1}{2} hE\varepsilon^2 + 2(g + f\varepsilon)$$

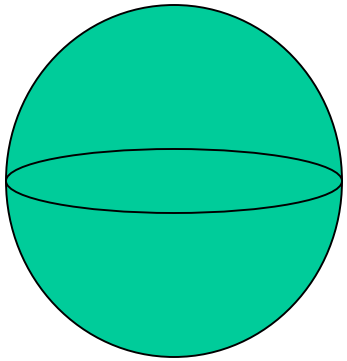
Select strain to minimize G $\qquad \dfrac{dG}{d\varepsilon} = 0 \qquad hE\varepsilon + 2f = 0$

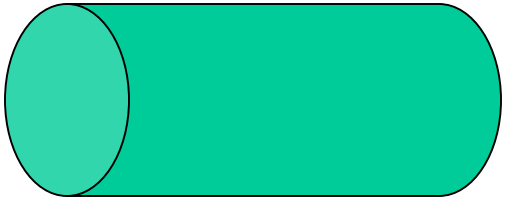


$\sigma = E\varepsilon$

Force balance: $\sigma h + 2f = 0$

Elastic sphere and cylinder



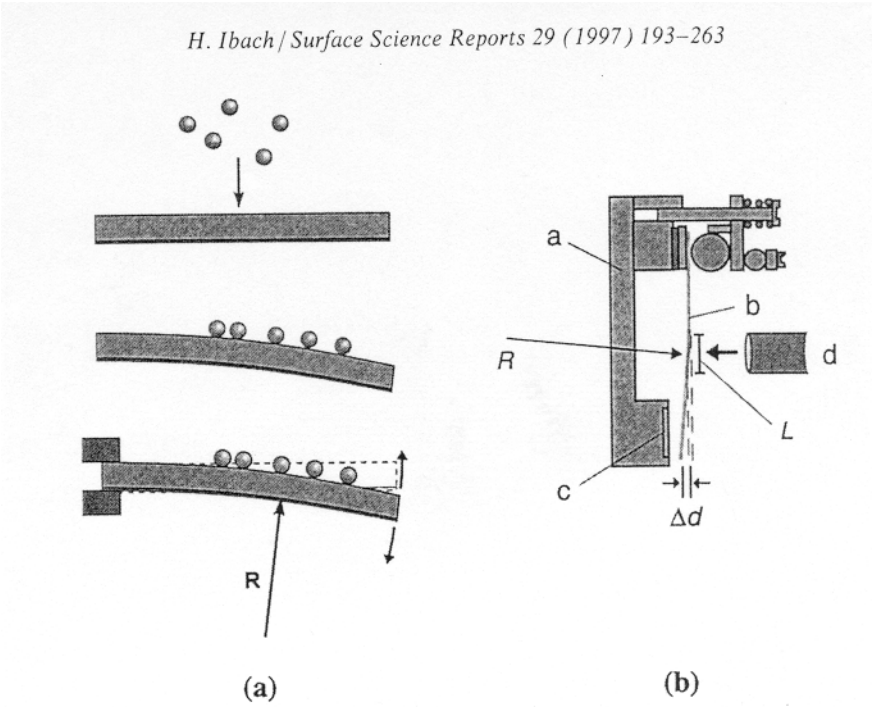


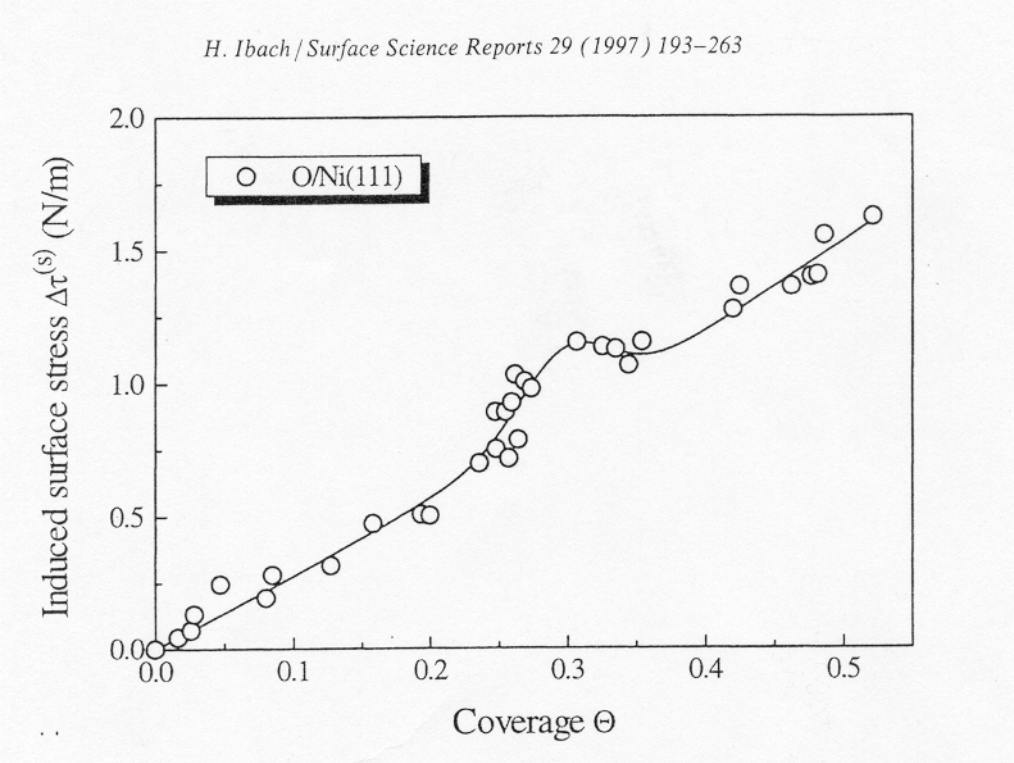
$$\sigma = -\frac{2f}{R}$$

$$\sigma_L = -\frac{2f_L}{R}, \quad \sigma_T = -\frac{f_T}{R}$$

- Surface stress can be either tensile or compressive
- Stress in the crystal can be either compressive or tensile

Surface stress depends on concentration



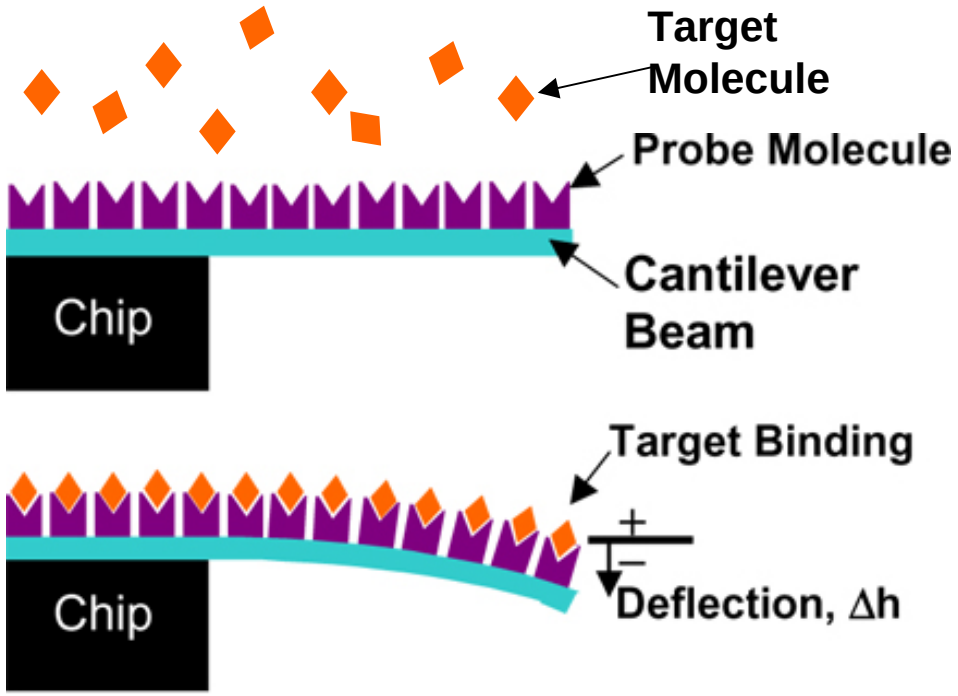


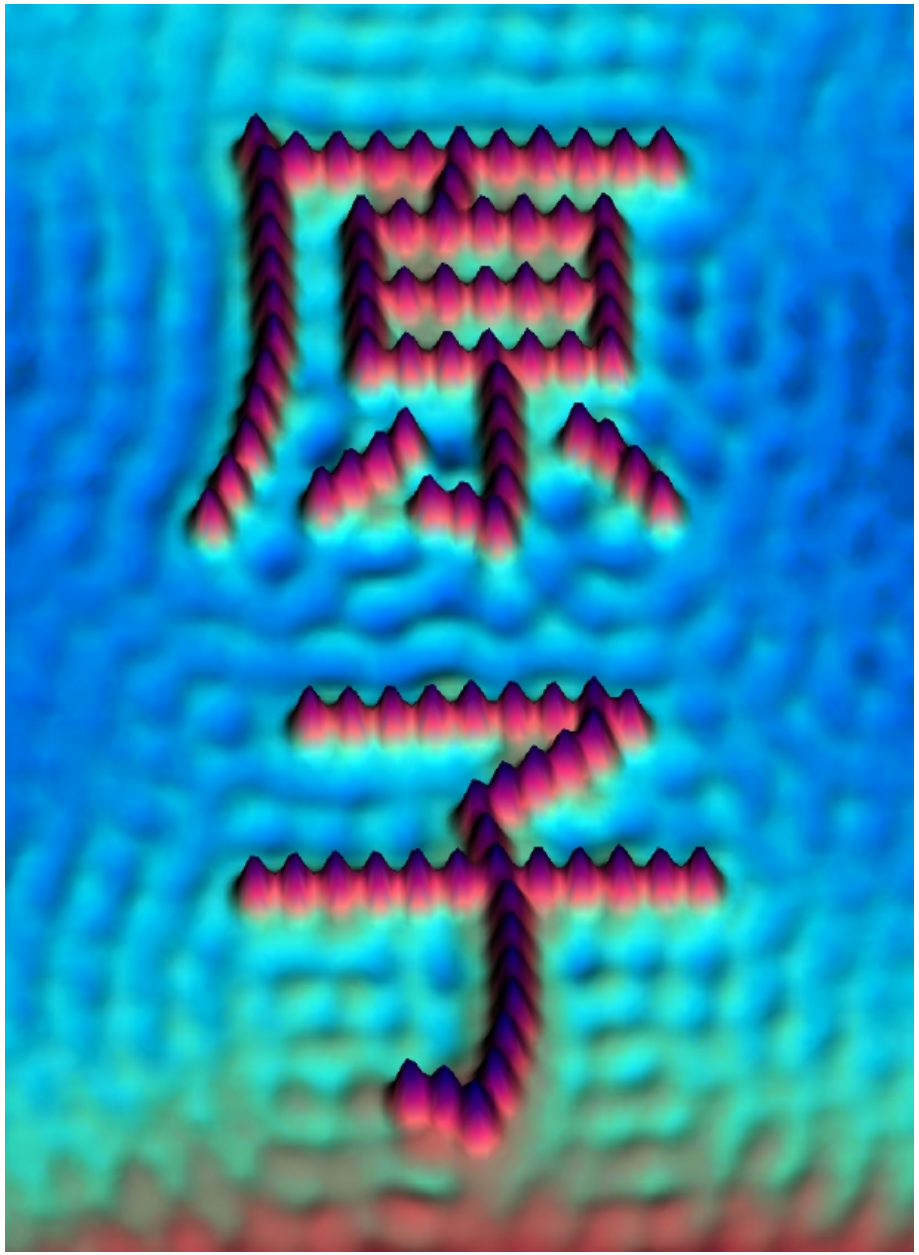
Wafer Curvature Measurement $\Delta f = \frac{EH^2}{6R}$

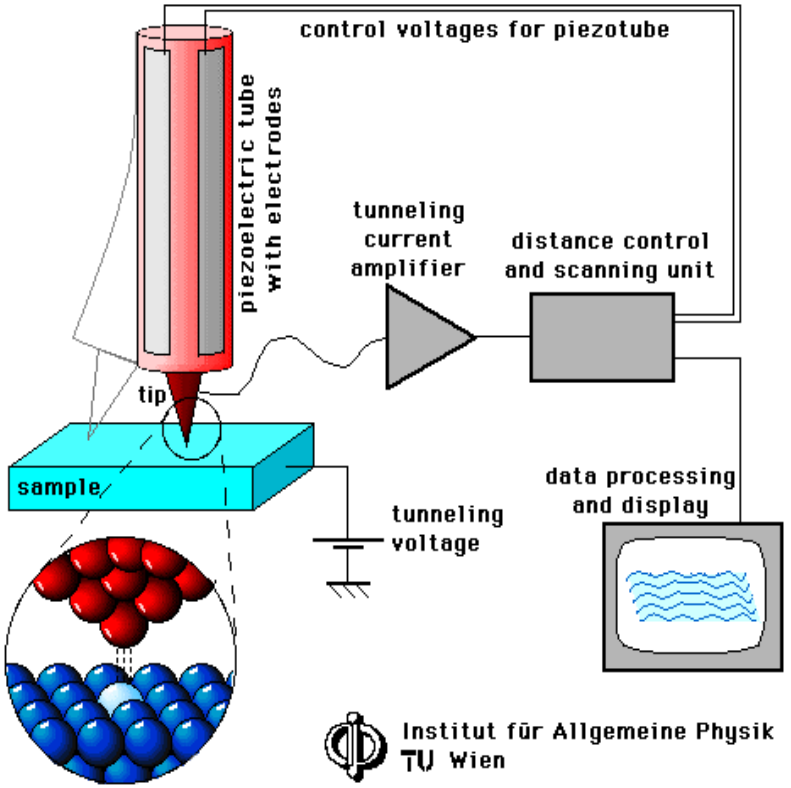
$$\Delta f = \phi C$$

Translating biomolecular recognition into nanomechanics

Fritz et al., *Science* **288**, 316 (2000)







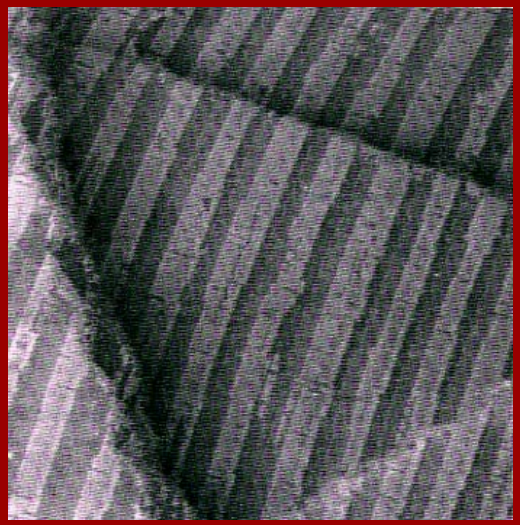
STM

Scanning Tunneling Microscope

Invented by
Gerd Binnig, Heinrich Rohrer
IBM Zurich, 1980s

Self-assembled, nanoscale monolayer patterns

O on Cu (011)

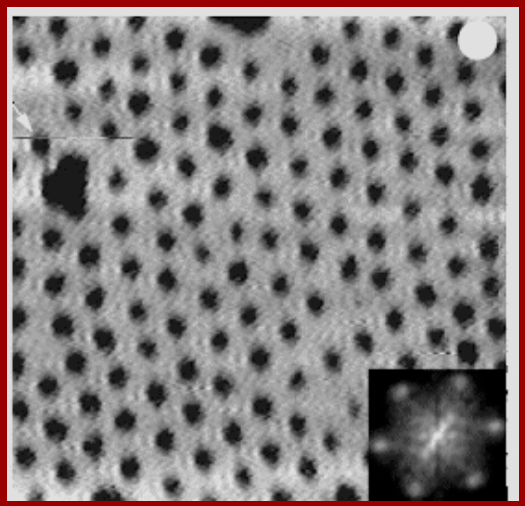


Kern *et al.*
Phys. Rev. Lett., **67**, 855 (1991)

N on Cu (100)

Parker *et al*.
Phys. Rev. B, **56,** 6458 (1997)

Ag+S on Ru (0001)



Pohl *et al*.
Nature, **397**, 238 (1999)

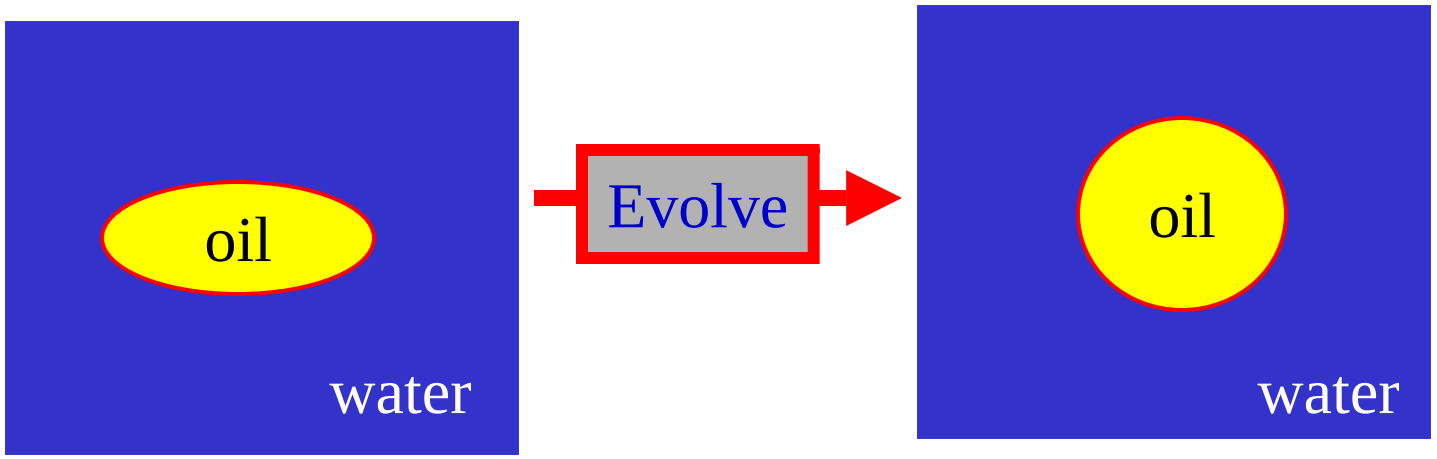
Observations

- Self-assembly at nanoscale
- Size selection
- Pattern selection (sometimes)
- Stable on annealing (seems to be)

A basic question:

What are the Forces that drive self-assembly?

A familiar example



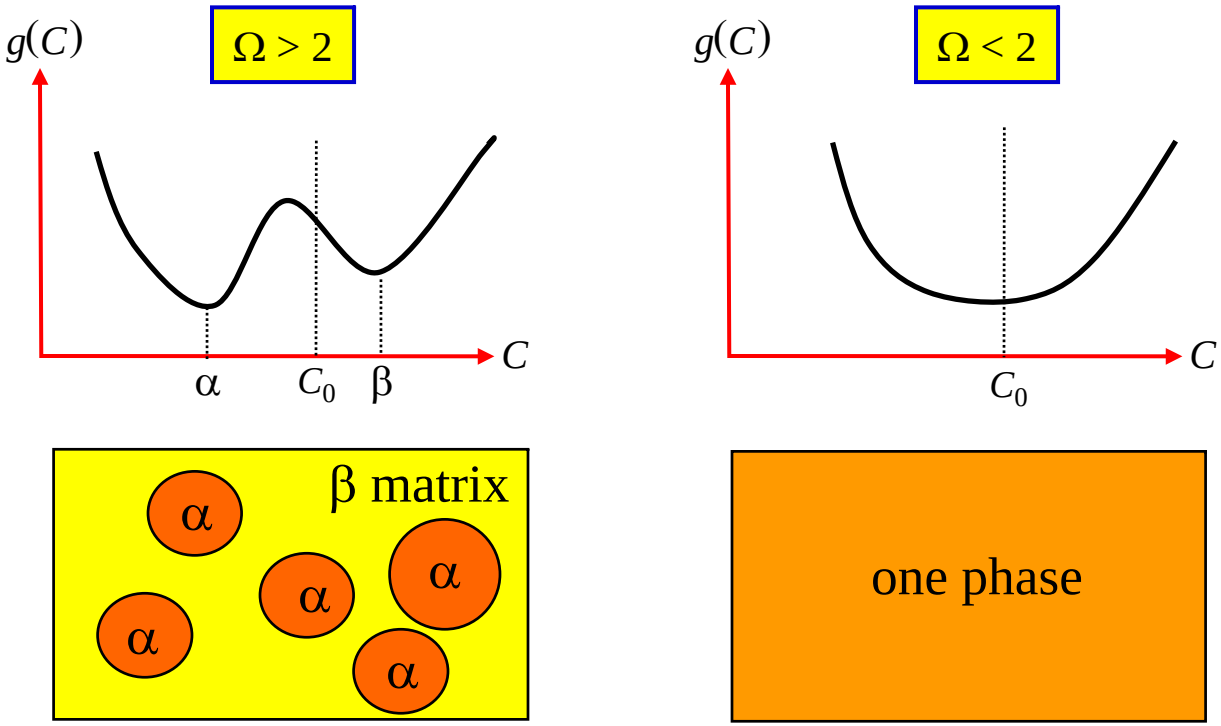
Large surface energy

Small surface energy

Free energy depends on geometry: $G = \gamma A$

- Geometry changes to reduce free energy—configurational force
- Geometry changes by mass transport—kinetic process

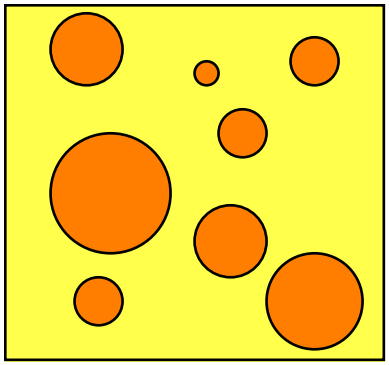
Phase Separation



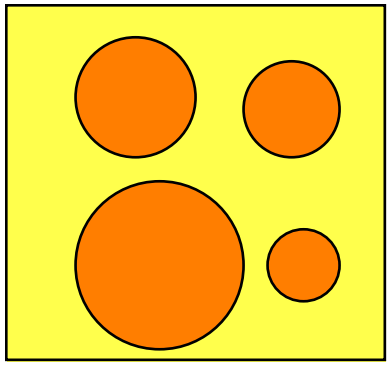
Free energy of mixing $g(C)$

Regular solution $g(C) = \Lambda kT\left[C\ln C + (1-C)\ln(1-C) + \Omega C(1-C)\right]$

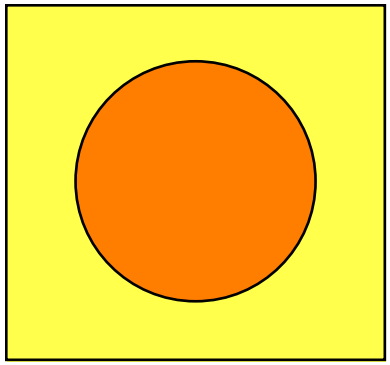
Phase Coarsening



Time 0



Time t

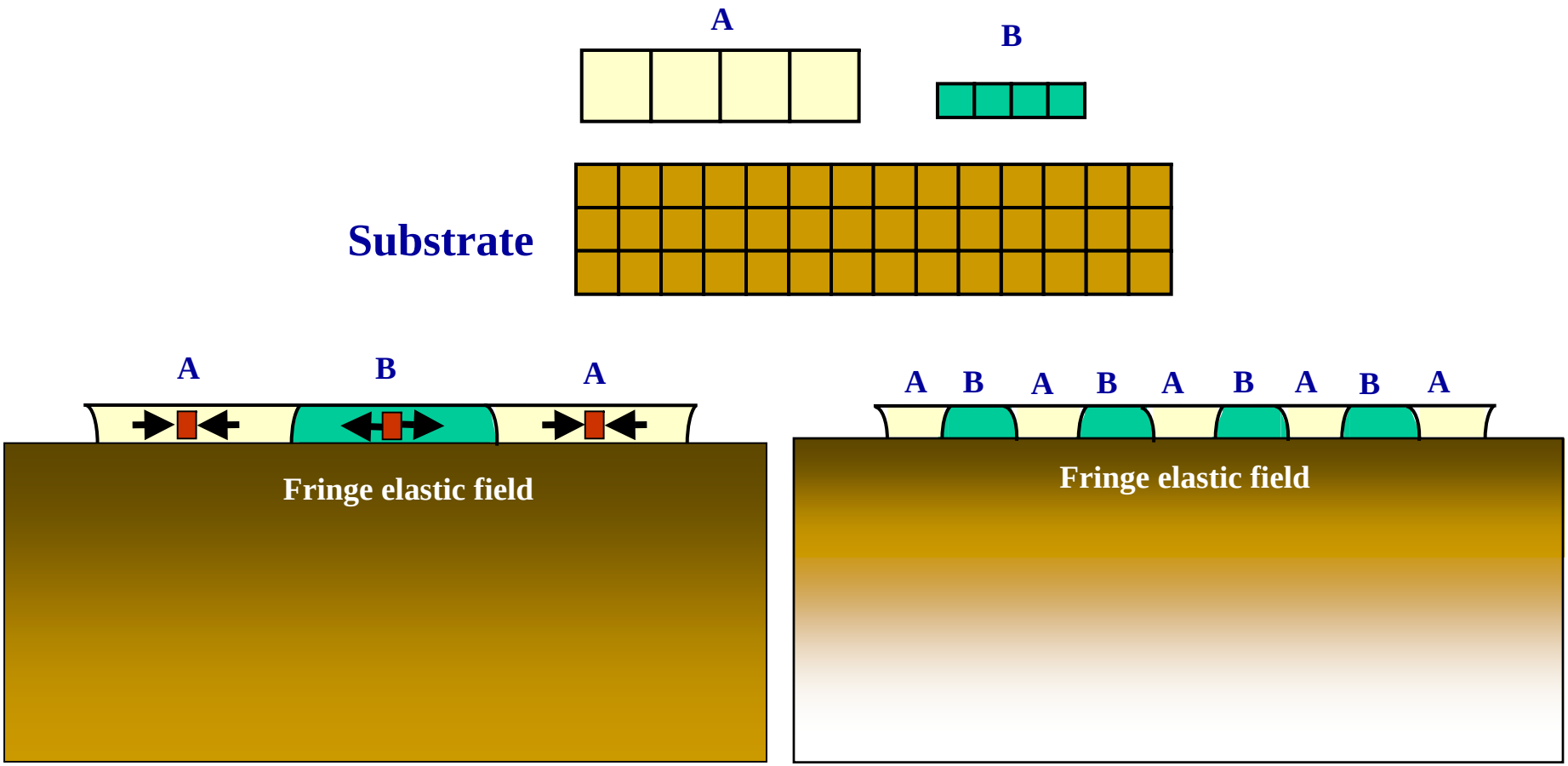


Long time

Phase boundary energy

$$G = \Sigma \gamma L$$

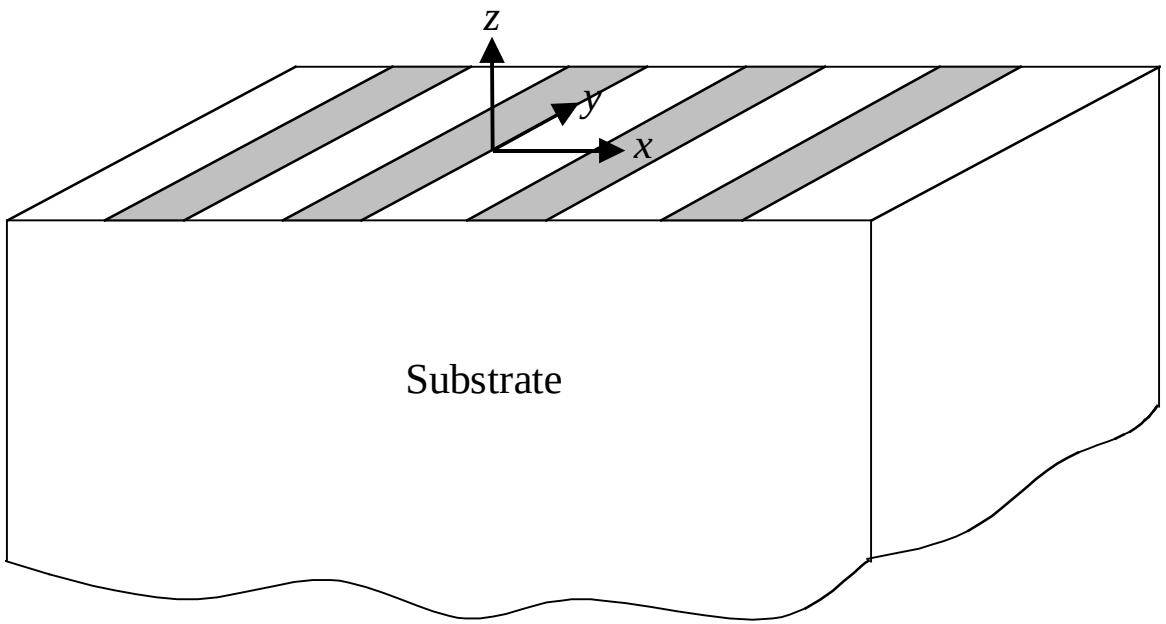
Phase Refining



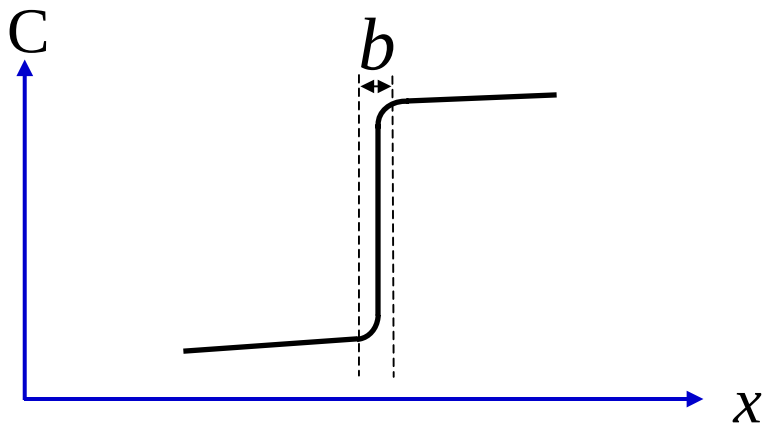
Pompe, Gong, Suo, Speck, *J. Appl. Phys.*, **74**, 6012 (1993).
Lu, Suo, *Zeitschrift fur Metallkunde*, **90**, 956-960 (1999)

Ingredients of the model

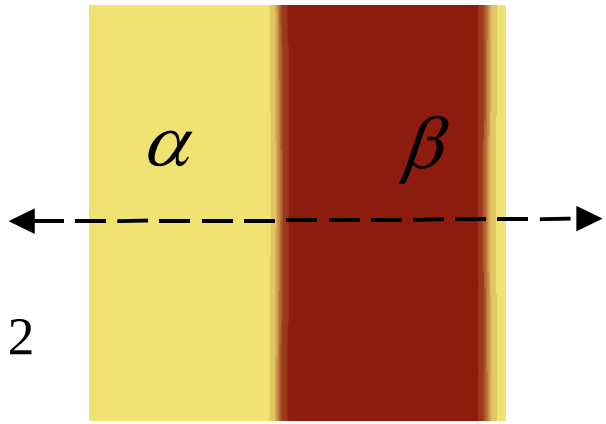
- Phase separation
- Phase coarsening
- Phase refining



Phase boundary energy



Diffused boundary



Cahn-Hilliard model

$$\text{free energy} \propto h_0 \left(\frac{\partial C}{\partial x} \right)^2$$

Free Energy

$$G = \int \Gamma dA + \int W dV$$

Elastic energy density: $W = \frac{E}{2(1+\nu)}\left[\varepsilon_{ij}\varepsilon_{ij} + \frac{\nu}{1-2\nu}(\varepsilon_{kk})^2\right]$

Surface energy is a function of $\left(C, C_{,\alpha}, \varepsilon_{\alpha\beta}\right)$

$$\Gamma = g(C) + h(C)C_{,\alpha}C_{,\alpha} + f(C)\varepsilon_{\alpha\alpha}$$

g: free energy of mixing, **phase separation**

f: surface stress, **phase refining** $f(C) = \psi + \phi C$

h: phase boundary energy, **phase coarsening** $h(C) = h_0$

Suo andLu, *J. Mech. Phys. Solids*. **48**, 211 (2000).

Energy Variation

$$\delta G = \int f \delta u_{\alpha,\alpha} dA + \int \sigma_{ij} \delta u_{i,j} dV$$

$$+ \int \left(\frac{\partial g}{\partial C} - 2h_0 \nabla^2 C + \phi \varepsilon_{\beta\beta} \right) \delta C dA$$

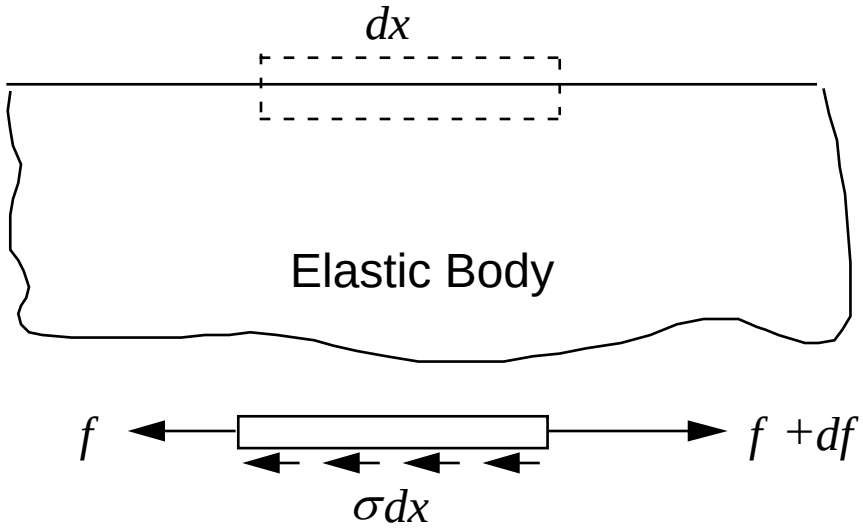
$\delta \boldsymbol{u}$ Elastic displacement. Elastic equilibrium:

$$\int f \delta u_{\alpha,\alpha} dA + \int \sigma_{ij} \delta u_{i,j} dV = 0$$

δC Mass relocation. Driving force for diffusion:

$$F_\alpha = -\frac{\partial}{\Lambda \partial x_\alpha} \left(\frac{\partial g}{\partial C} - 2h_0 \nabla^2 C + \phi \varepsilon_{\beta\beta} \right)$$

Morphology-Elasticity Coupling

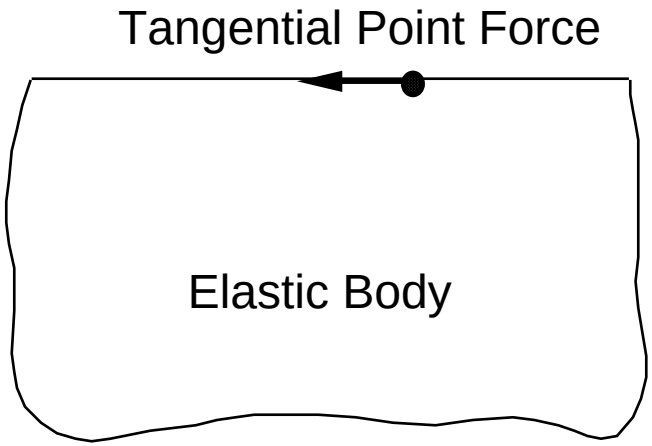


Boundary Conditions:

$$\sigma_{31} = \frac{\partial f}{\partial x_1}, \quad \sigma_{32} = \frac{\partial f}{\partial x_2}$$

Elastic Half-Space

Cerruti Solution: a point force on a half space



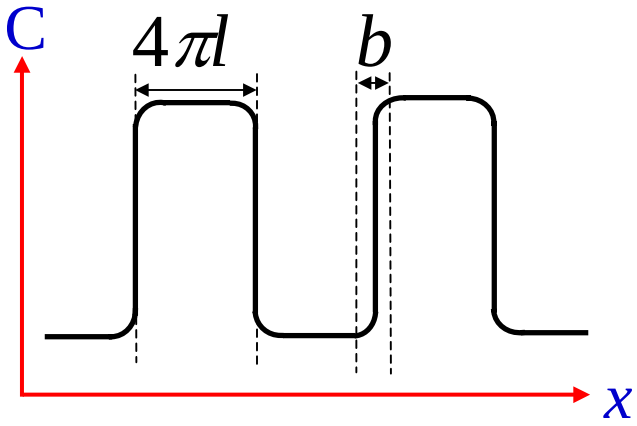
Linear superposition

$$\varepsilon_{\beta\beta} = -\frac{\left(1-\nu^2\right)\phi}{\pi E}\iint \frac{(x_1-\xi_1)\dfrac{\partial C}{\partial \xi_1}+(x_2-\xi_2)\dfrac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2$$

Two Length Scales

$$F_\alpha = \frac{\partial}{\Lambda \partial x_\alpha}\left(\frac{\partial g}{\partial C} - 2h_0\nabla^2 C + \phi\varepsilon_{\beta\beta}\right)$$

Demixing **coarsening** **refining**



Phase Boundary thickness:

$$b = \left(\frac{h_0}{\Lambda kT}\right)^{1/2}$$

$h_0 \sim 10^{-19}$ J

$\Lambda \sim 5 \times 10^{19}\,\mathrm{m}^{-2}$

$kT \sim 5 \times 10^{-21}$ J $\quad (T = 400$ K$)$ → $b \sim 0.3$nm

Phase Size:

$$l = \frac{Eh_0}{\phi^2}$$

$E \sim 10^{11}\,\mathrm{N/m}^2$

$\phi \sim 4\,\mathrm{N/m}$ →

$l \sim 0.3$nm

$4\pi l \sim 4$nm

A Diffusion Equation

$$\frac{\partial C}{\partial t} = \frac{M}{\Lambda^2}\nabla^2\left(\frac{\partial g}{\partial C} - 2h_0\nabla^2 C + \phi\varepsilon_{\beta\beta}\right)$$

Phase separation Coarsening Refining

$$\varepsilon_{\beta\beta} = -\frac{\left(1-\nu^2\right)\phi}{\pi E}\iint \frac{(x_1-\xi_1)\dfrac{\partial C}{\partial \xi_1} + (x_2-\xi_2)\dfrac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2$$

Substrate elasticity

Regular solution $g(C) = \Lambda kT\left[C\log C + (1-C)\log(1-C) + \Omega C(1-C)\right]$

Numerical: Spectral Method

$$\hat{C}(k_1,k_2,t)=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} C(x_1,x_2)e^{-i(k_1x_1+k_2x_2)}dx_1dx_2$$

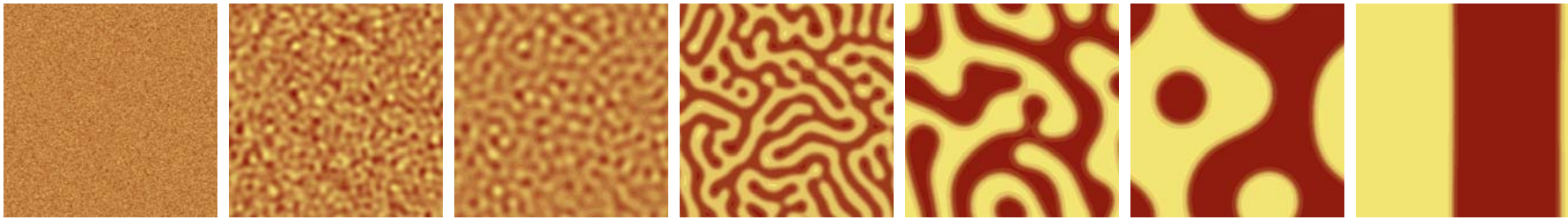
$$\frac{\partial\hat{C}}{\partial t}=-k^2\hat{P}+2\left(-k^4+\frac{b}{l}k^3\right)\hat{C}$$

$$P(C)=\ln\left(\frac{C}{1-C}\right)+\Omega(1-2C)$$

$$k=\left(k_1^2+k_2^2\right)^{1/2}$$

Simulation Results, C = 0.5

No elasticity refining

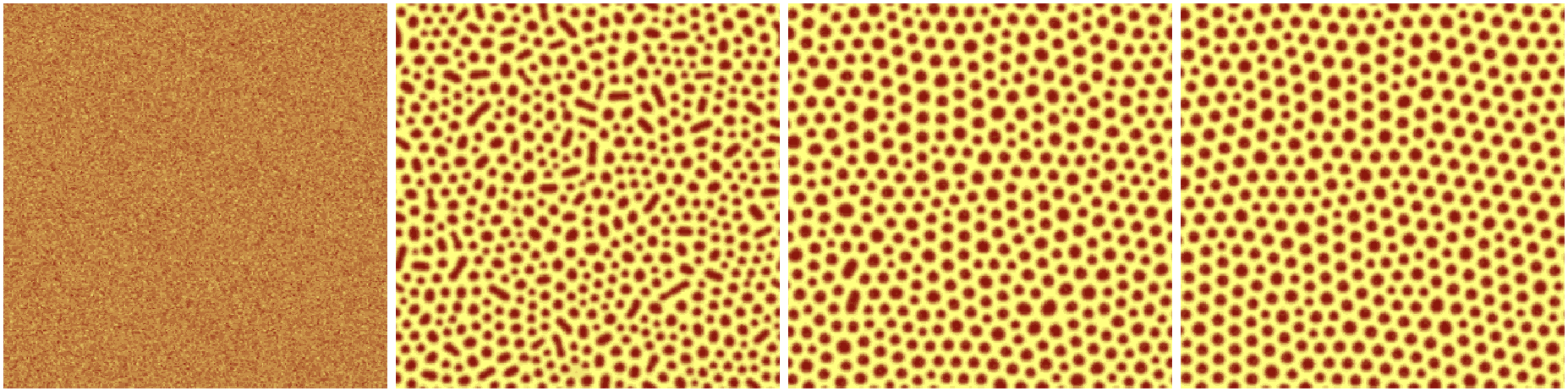


With elasticity refining

$t = 0$ $t = 10$ $t = 10^2$ $t = 10^3$ $t = 10^4$ $t = 10^5$ $t = 10^6$

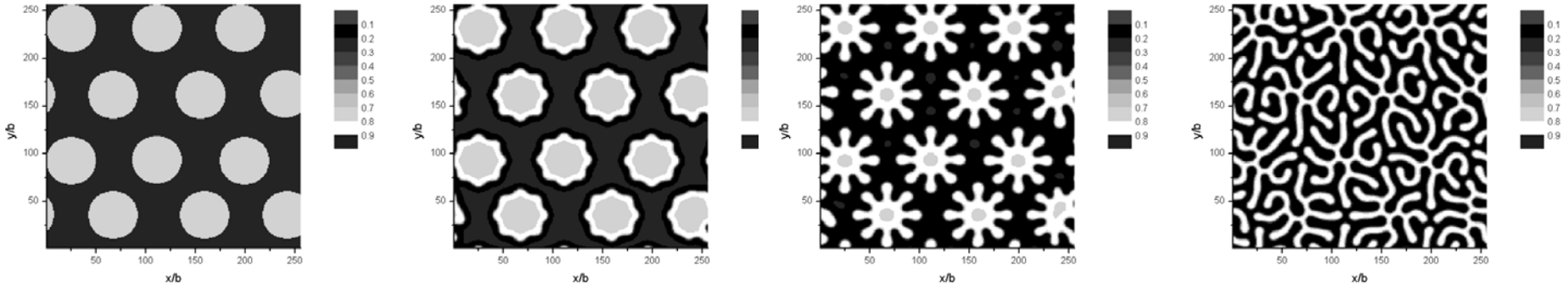
Lu, Suo, *J. Mech. Phys. Solids* **49**, 1937 (2001).

Simulation Results, C = 0.4



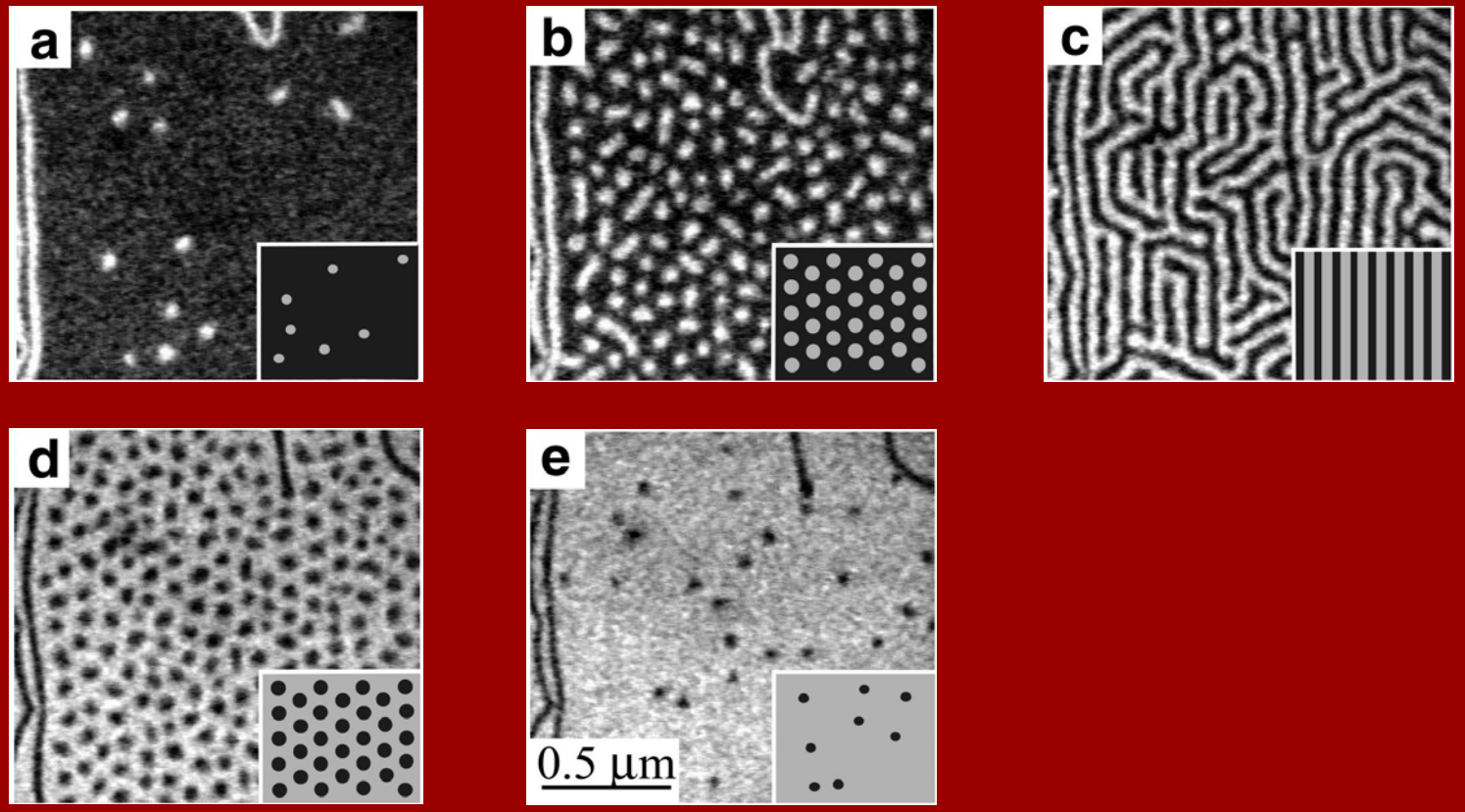
$t = 0$ $t = 10^2$ $t = 10^3$ $t = 8 \times 10^6$

Suo, Lu, *J. Nanoparticles Res.* **2**, 333 (2000).



W. Hong

Pb on Cu (111)



The bright region is the Pb phase. The dark region is the Pb-Cu surface alloy. The average concentration increases from (a) to (e).

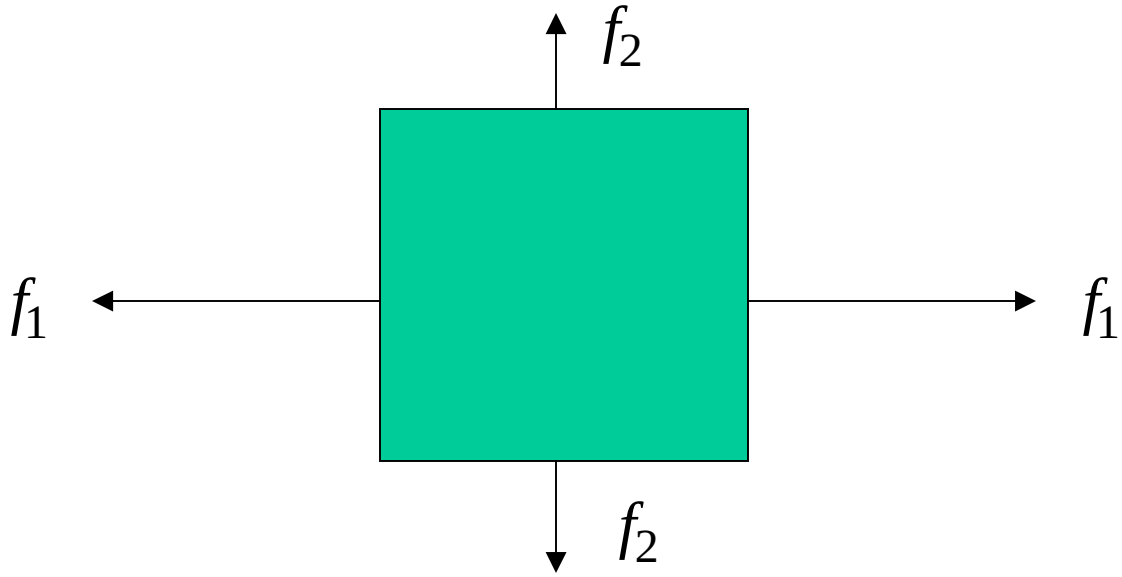
Courtesy of Gary Kellogg, of Sandia National Lab.

Break the symmetry!

Anisotropy in

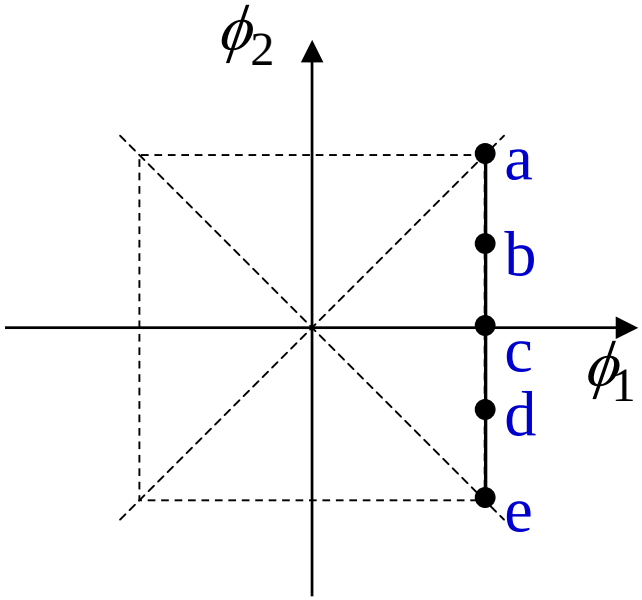
- Substrate elasticity
- Phase boundary energy
- Surface stress

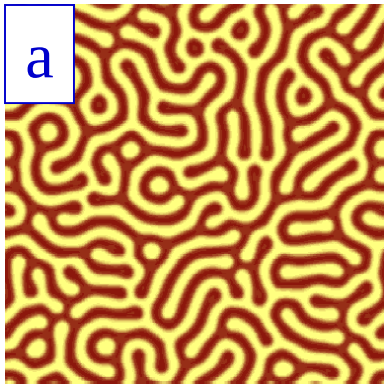
Anisotropic Surface Stress

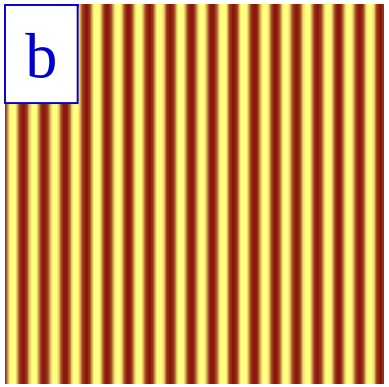


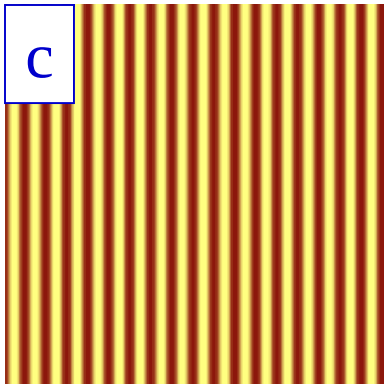
$$f_1 = \phi_1 C \qquad f_2 = \phi_2 C$$

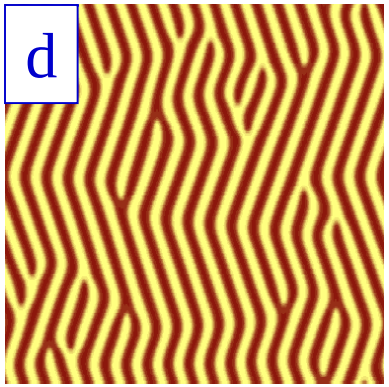
Patterns due to anisotropic surface stress (t = 2.0E5)

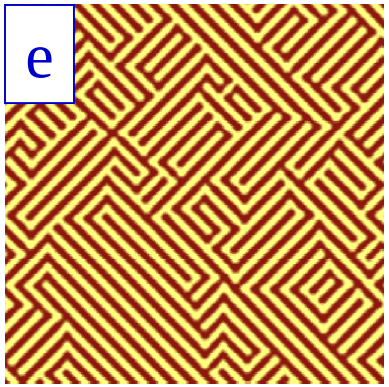












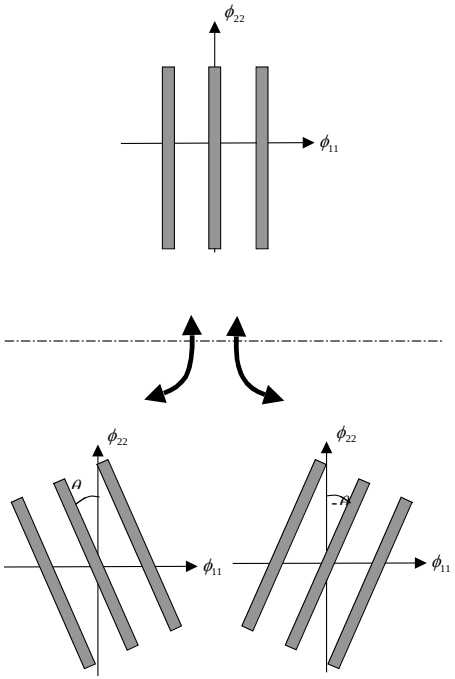
Lu and Suo, *Phys. Rev*. B, **65**, 085401 (2002).

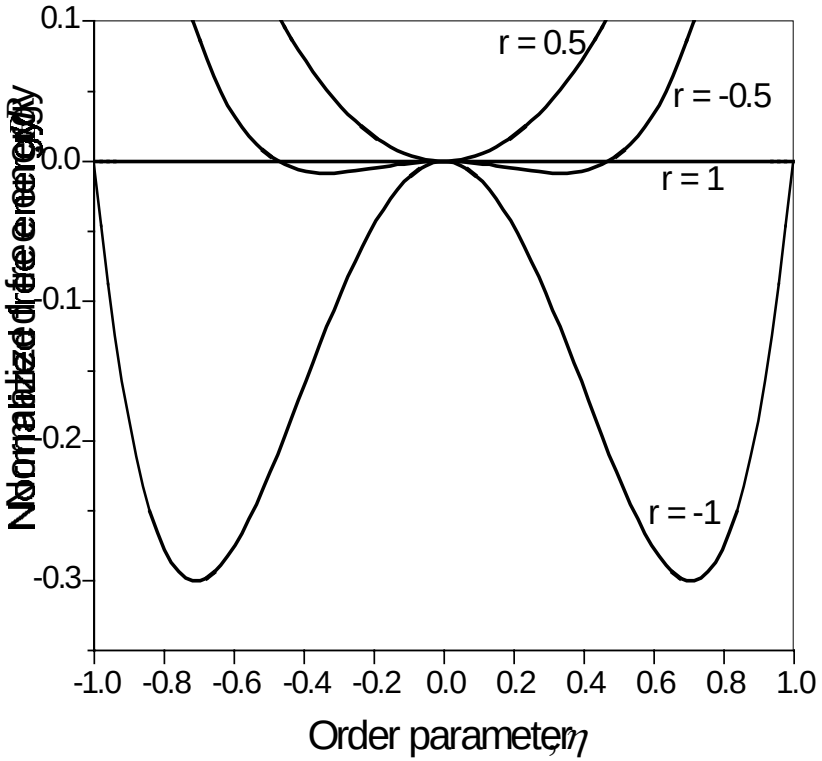
Mesophase transition by symmetry breaking

Normalized free energy

$$R(\eta) = (1-r)\left[r - r_c\right]\eta^2 + \nu(1-r)^2\,\eta^4$$

Critical point $r_c = -(1-2\nu)$





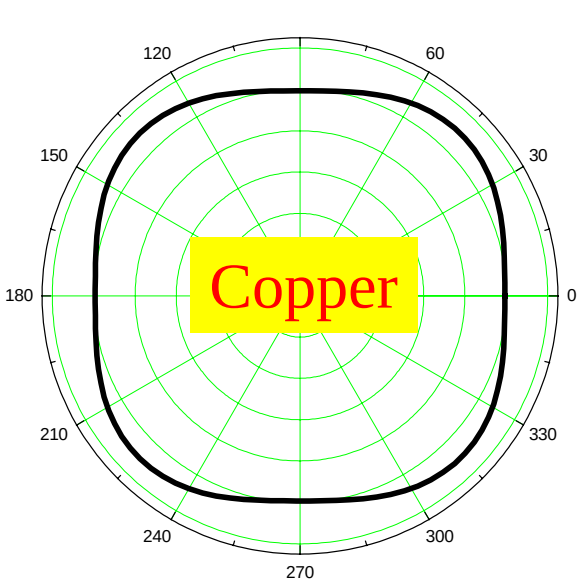
Control parameter $r = \phi_2 / \phi_1$

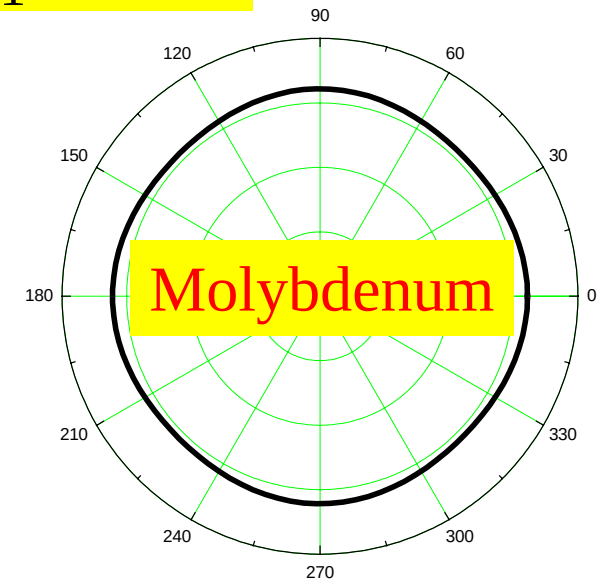
Order parameter $\eta = \sin\theta$

Cubic Elastic Substrate

$$\frac{C(\theta)}{C_{11}} = 1 + 2\left(\frac{C_{12} + 2C_{44}}{C_{11}} - 1\right)\sin^2\theta\cos^2\theta$$

Isotropy: $\dfrac{C_{12} + 2C_{44}}{C_{11}} = 1$

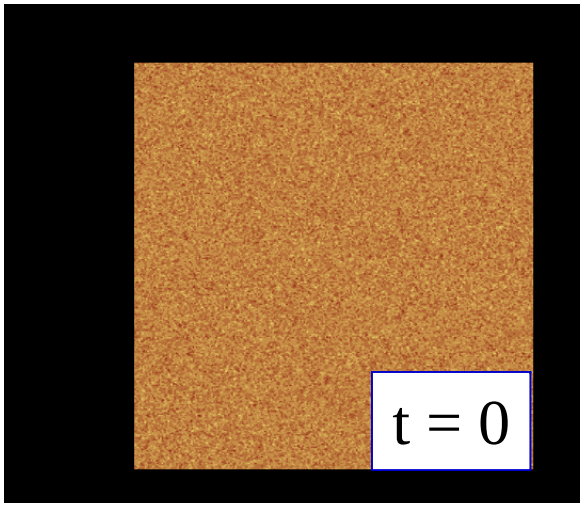


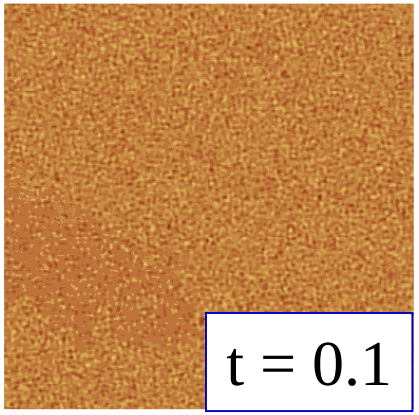


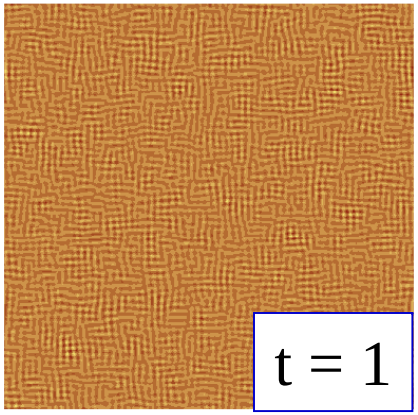
$$\frac{C_{12} + 2C_{44}}{C_{11}} = 1.61$$

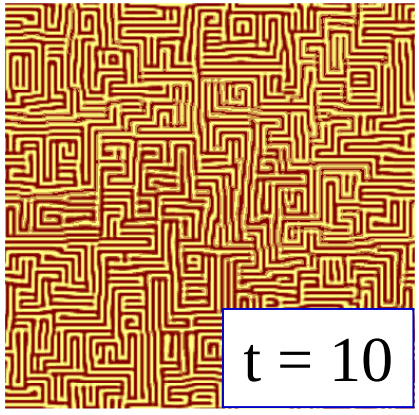
$$\frac{C_{12} + 2C_{44}}{C_{11}} = 0.86$$

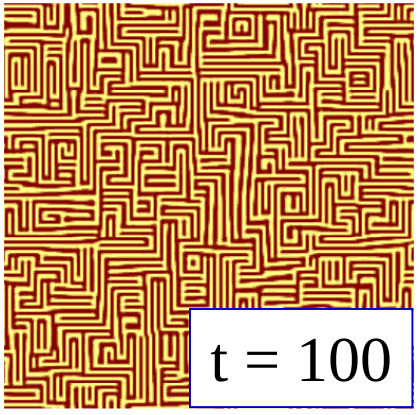
Copper
compliant direction [100]

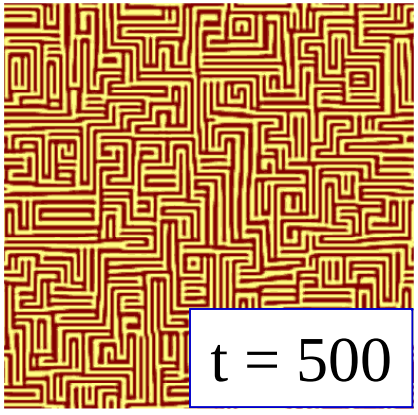






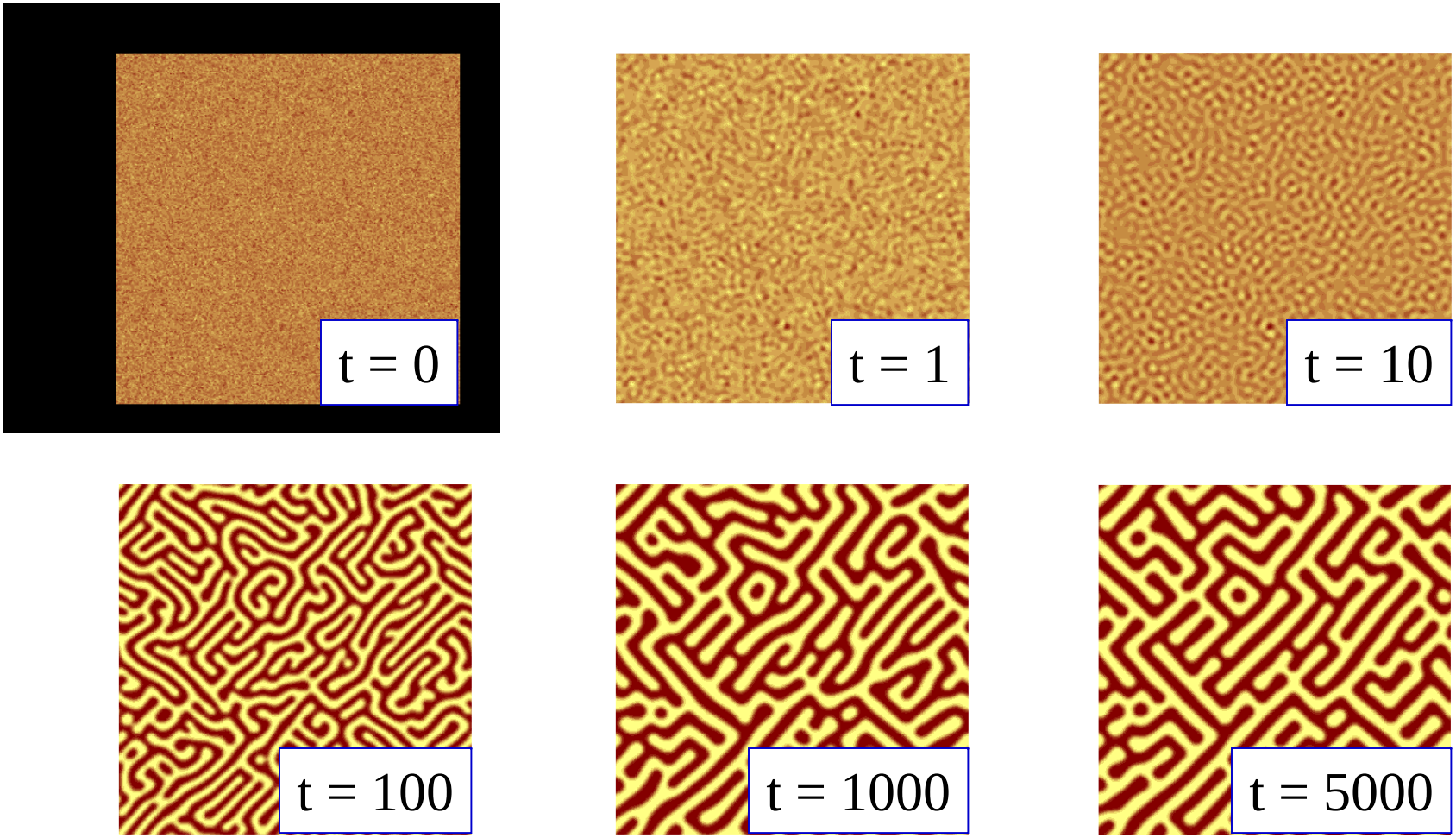






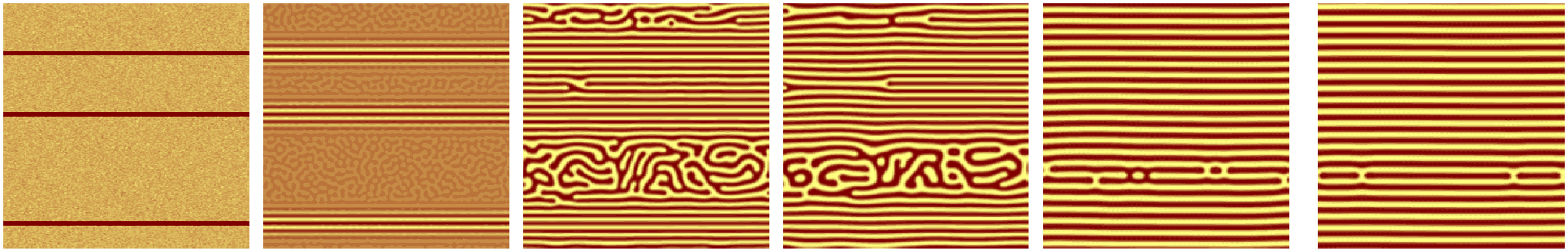
Lu and Suo, Phys. Rev. B, In press.
Gao and Suo, Mech. Phys. Solids. In press.

Molybdenum
compliant direction [110]



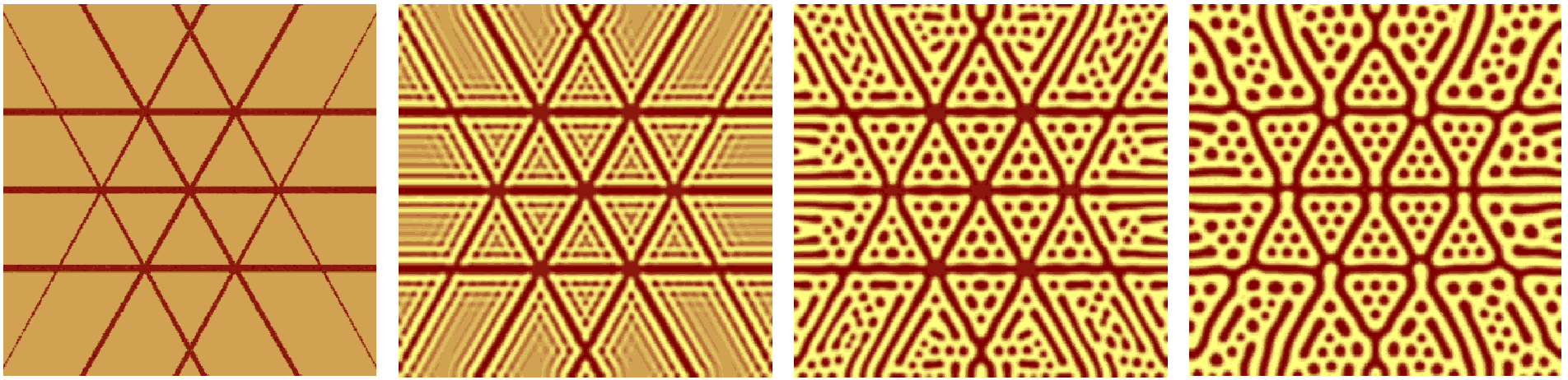
To assemble
a *specific*, *aperiodic* structure,
use a **template**.

“Crystal Seeds”



t = 0 t = 10 t = 100 t = 500 t = 1.0E4 t = 4.0E4

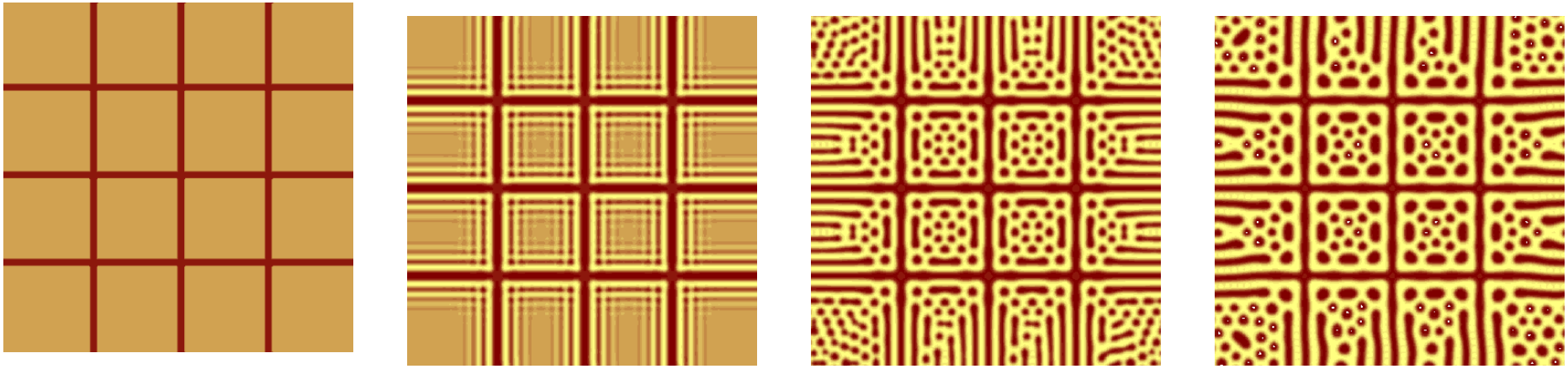
Guide assembly with a coarse pattern



t = 0 t = 10 t = 100 t = 1000

Suo and Lu,. J. Nanoparticles Research **2**, 333 (2000).

Effect of Initial Condition



t = 0 t = 10 t = 100 t = 1000

Summary

- Size selection—**coarsening** and **refining**
- Long-range order—**symmetry breaking**
- Aperiodic structure — **Templating**