programmable motion of molecules on a solid surface

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Work with

W. Hong, Harvard University

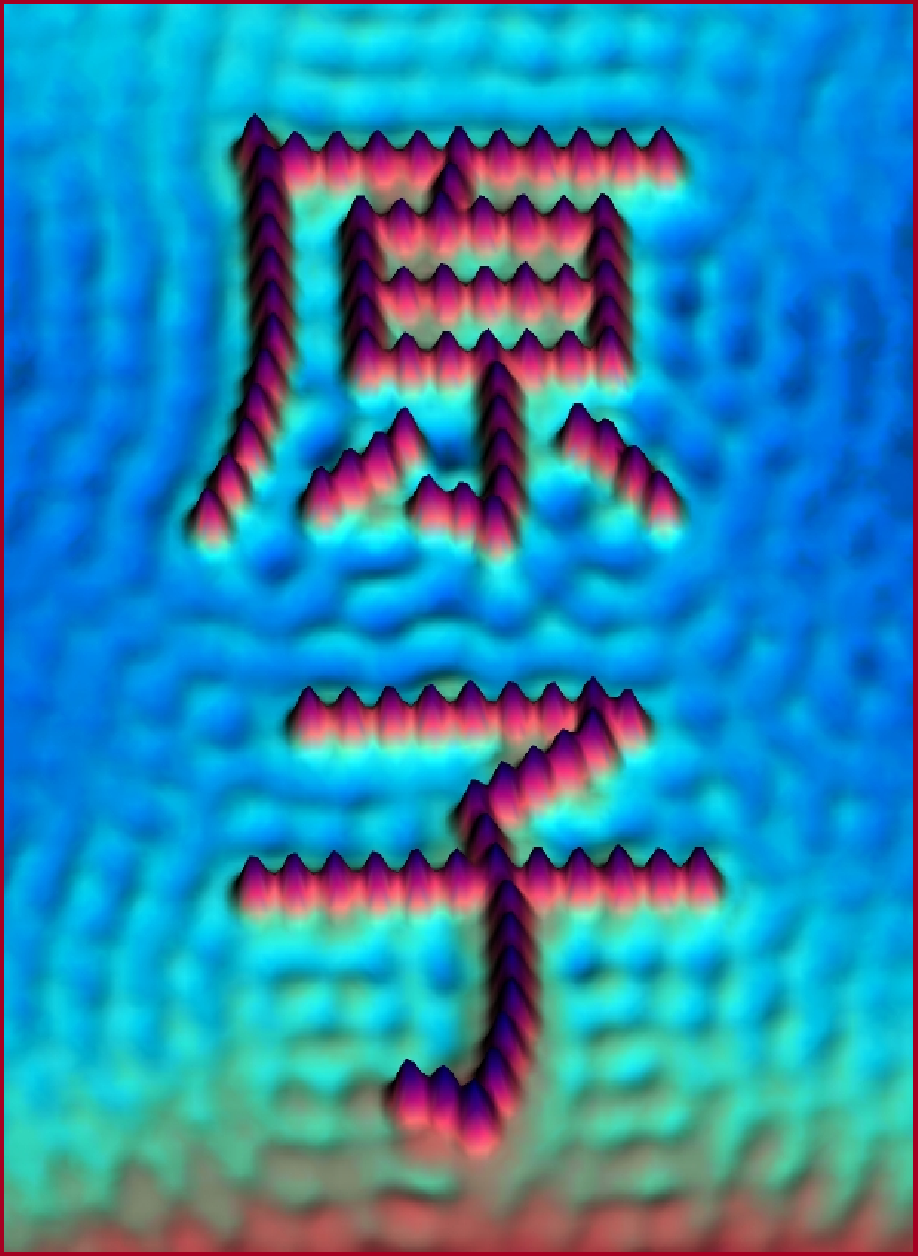
W. Lu, University of Michigan, Ann Arbor

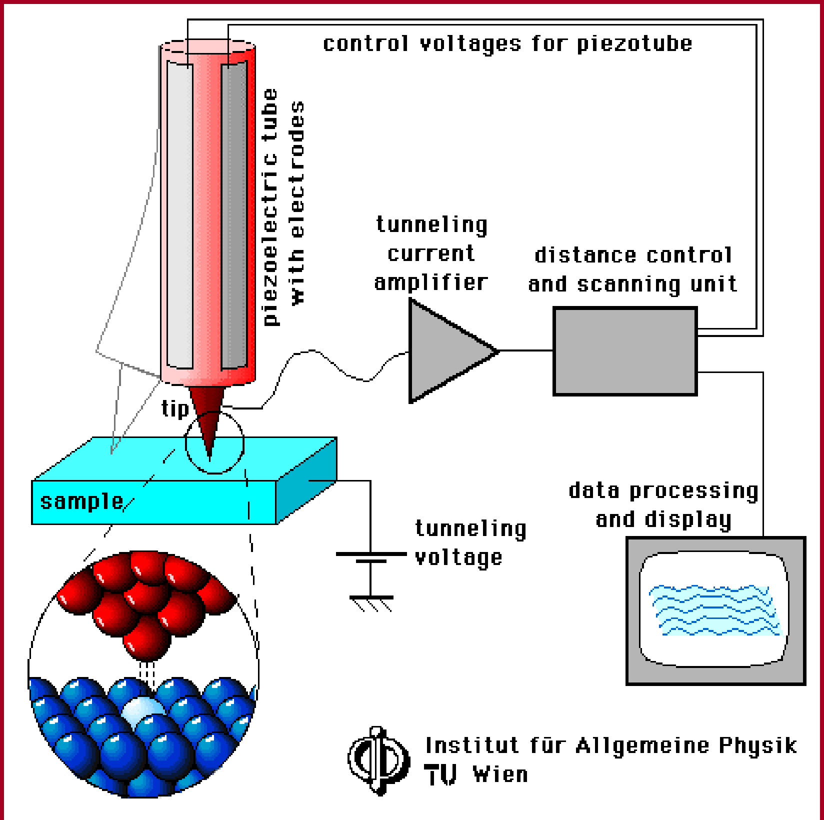
Y.F. Gao, Brown University

G. Scoles, Princeton University

AP298r lecture

18 February 2004





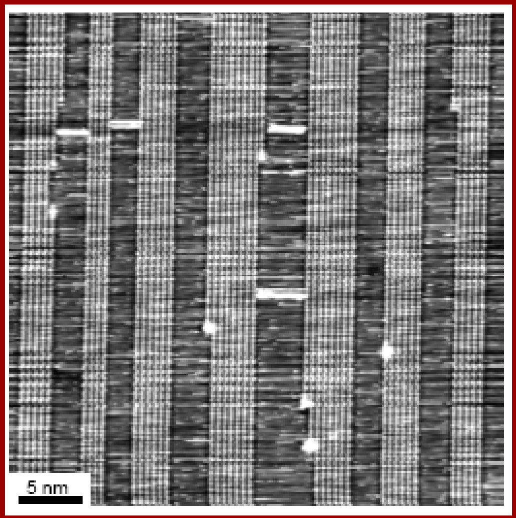
STM

Scanning Tunneling Microscope

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

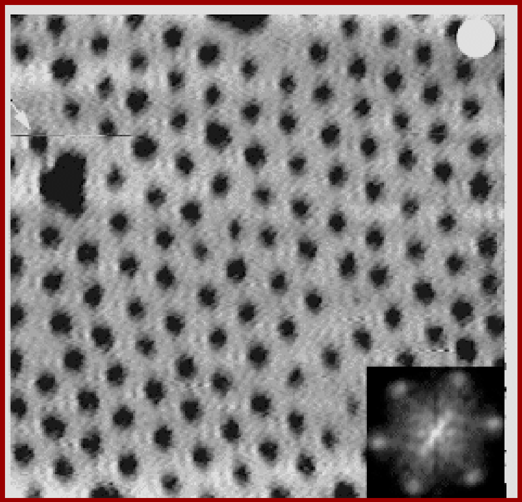
sub-monolayer

O on Cu (011)



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

Ag+S on Ru (0001)



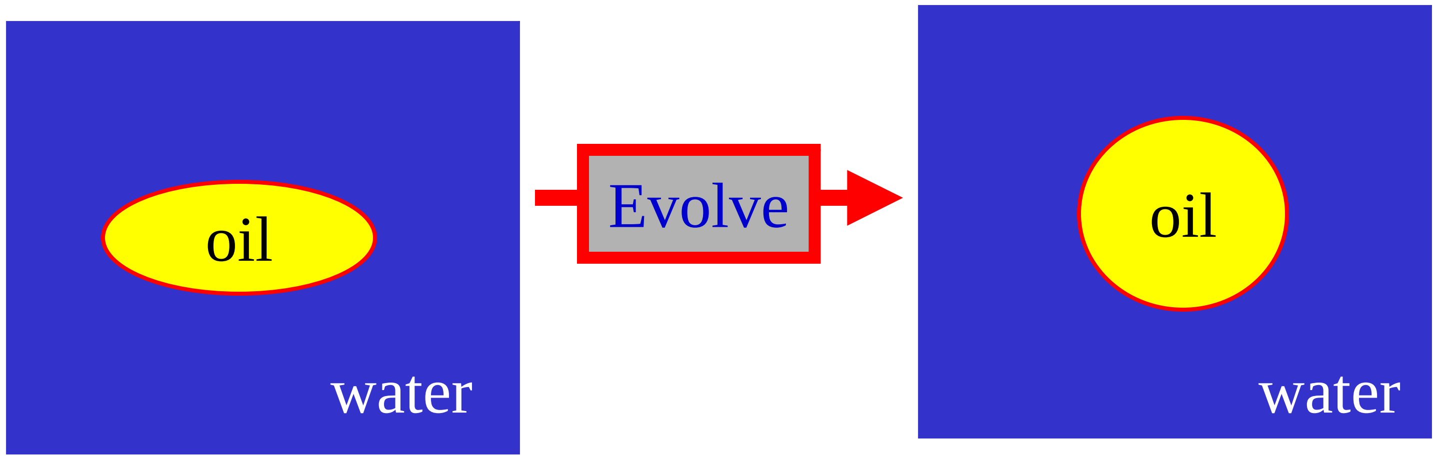
Pohl *et al.*
Nature, **397**, 238 (1999)

- Self-assembled
- Nanoscale
- High mobility
- Stable on annealing

A basic mechanics question:

What are the Forces
that drive self-assembly?

A familiar example



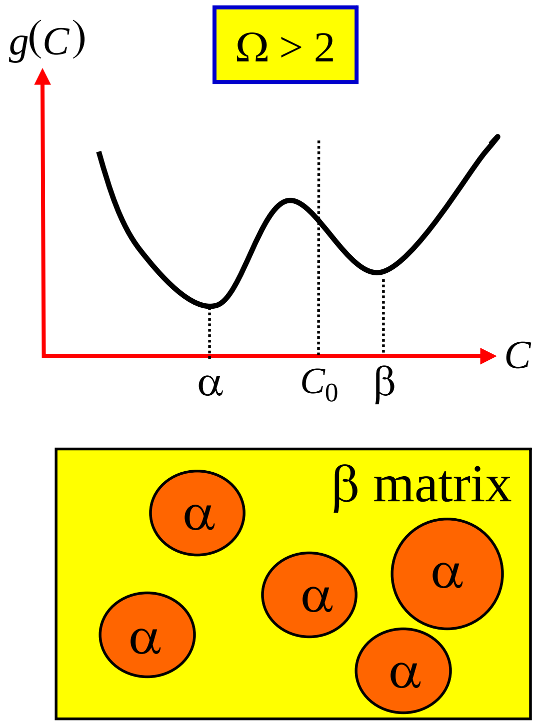
Large surface energy

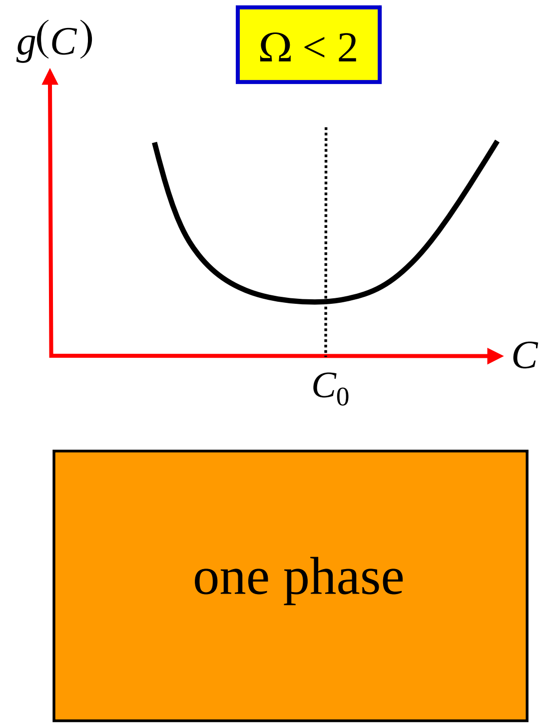
Small surface energy

Free energy $\boxed{G = \gamma A}$

- Free energy depends on geometry
- Geometry changes to reduce free energy—configurational force
- Geometry changes by mass transport—kinetic process

Phase Separation



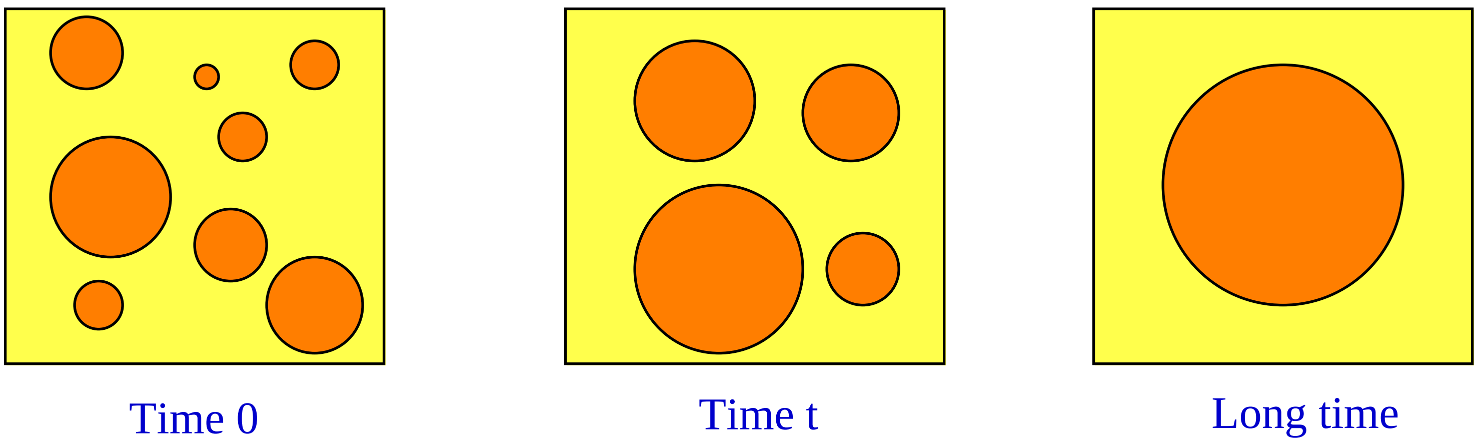


Free energy of mixing $g(C)$

Regular solution

$$\boxed{g(C) = g_A C + g_B (1-C) + \Lambda kT\left[C \ln C + (1-C)\ln(1-C) + \Omega C(1-C)\right]}$$

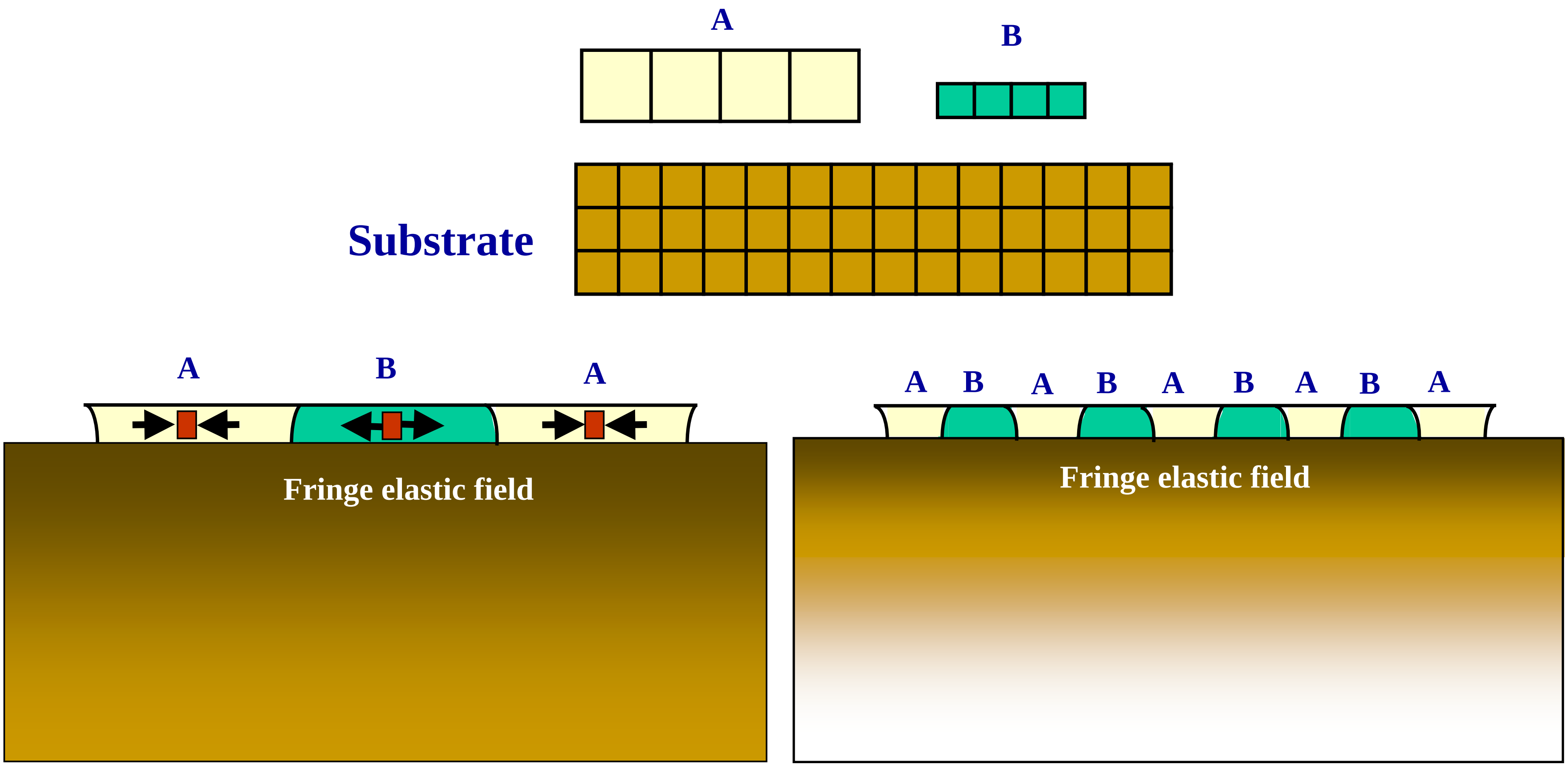
Phase Coarsening

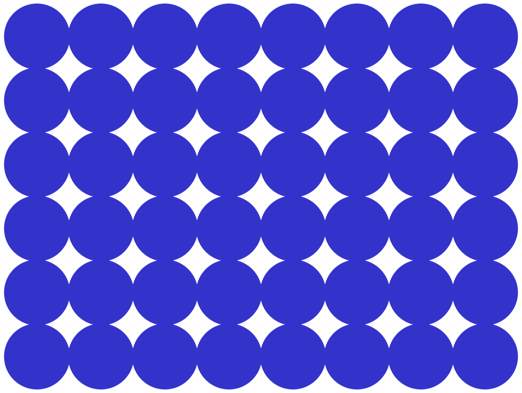


Phase boundary energy

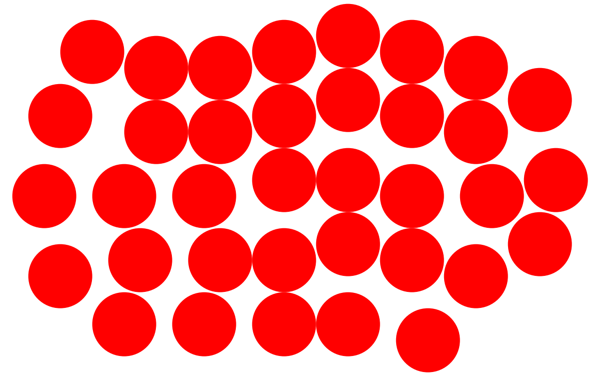
$$\boxed{G = \Sigma \gamma L}$$

Phase Refining

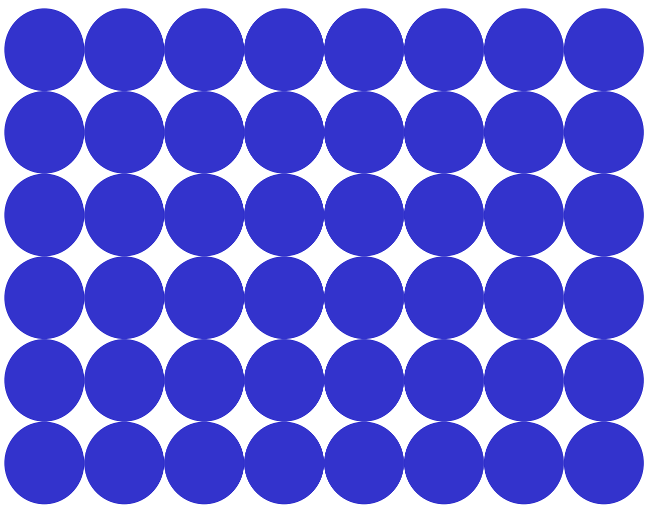




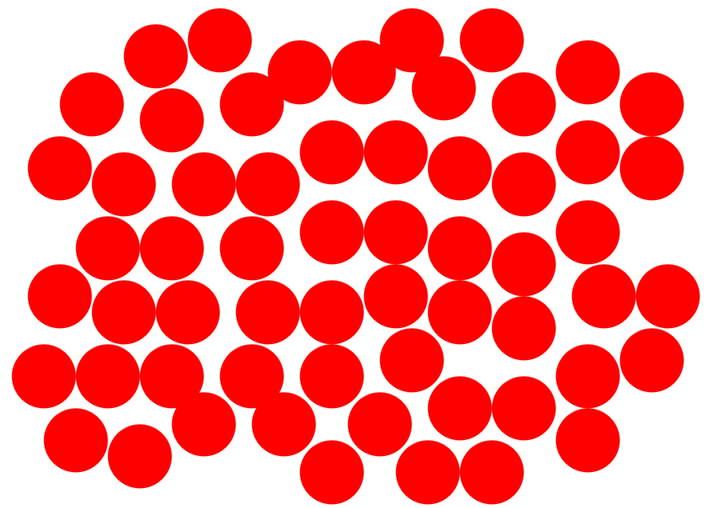
Solid surface



Liquid surface



Stretched solid surface

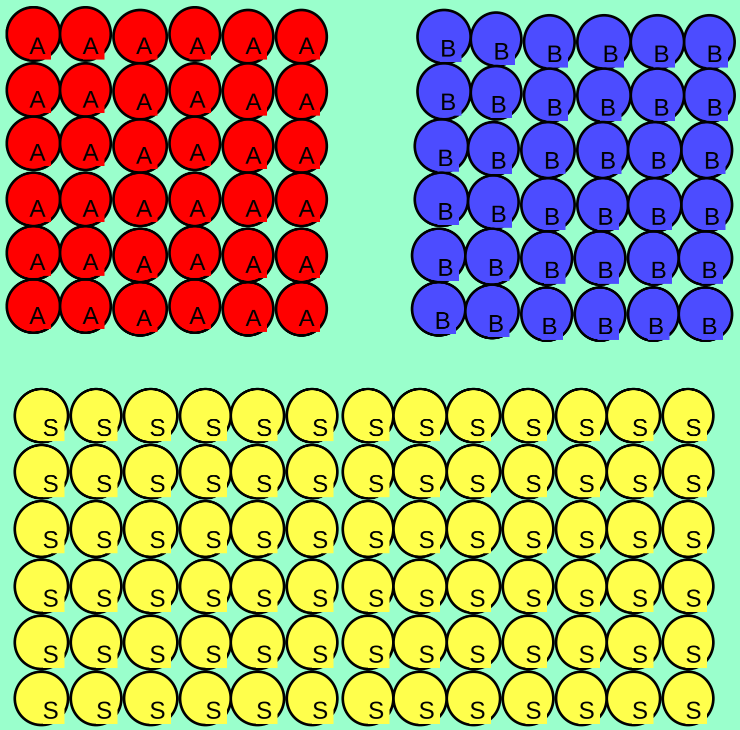


Stretched liquid surface

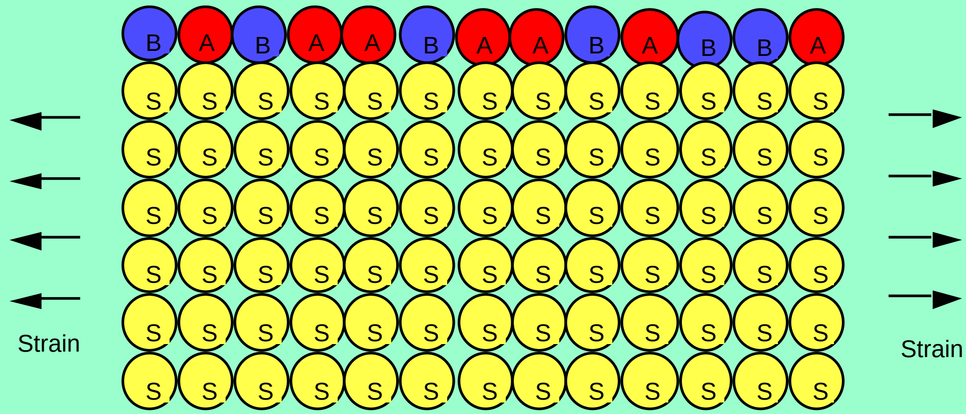
Energy per surface atom depends on stretch

Energy per surface atom is independent of stretch

Reference State:
3 infinite crystals



Current State



$$G = WV + \Gamma A$$

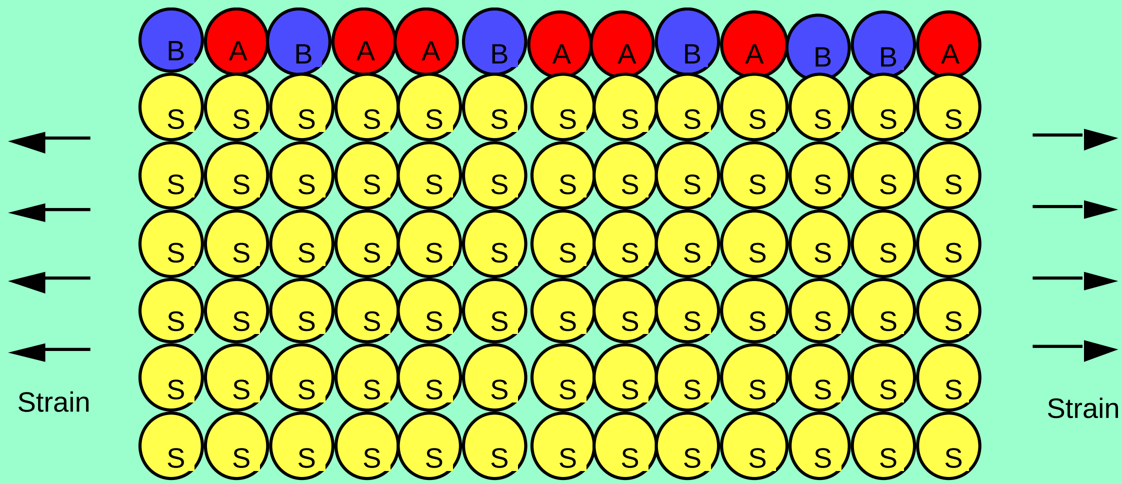
$$W = \frac{\text{elastic energy}}{\text{volume}} \qquad \Gamma = \frac{\text{excess energy}}{\text{area}}$$

Surface Stress

Residual stress field in surface layers

Surface energy depends on elastic strain

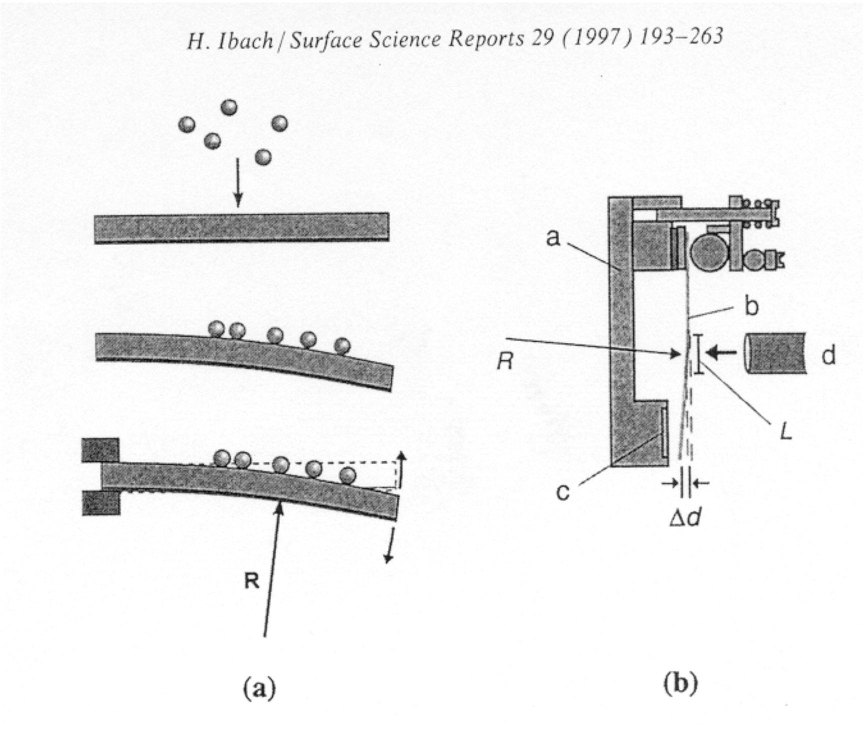
$$\Gamma = g + f\varepsilon$$

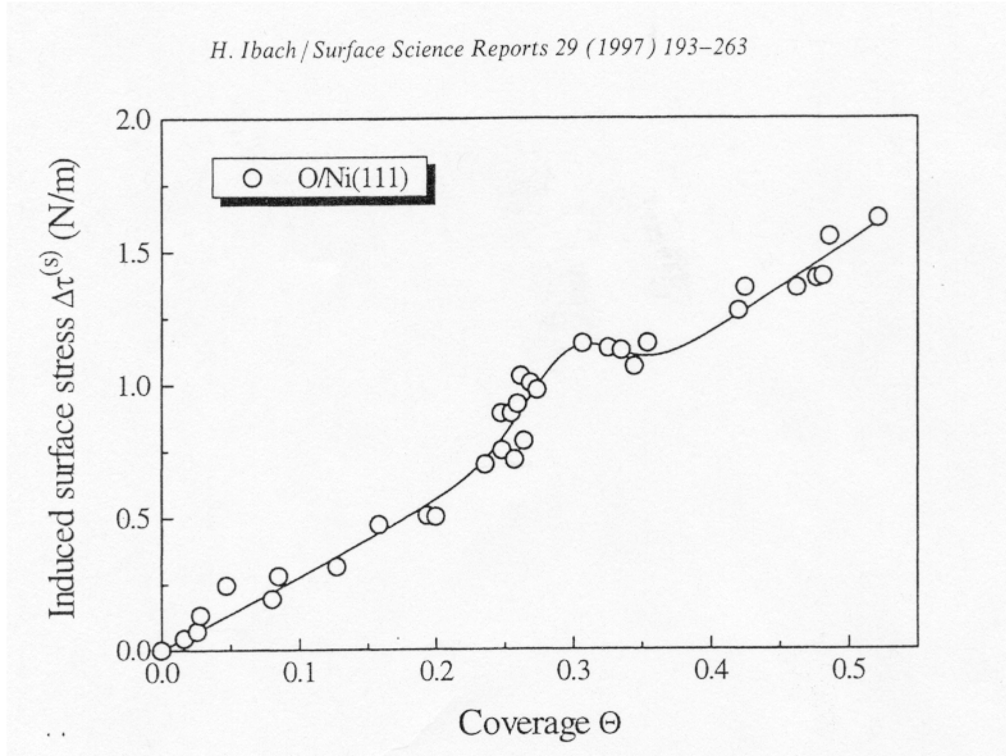


$$f \sim (\text{residual stress}) \times (\text{layer thickness})$$

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

Surface stress depends on concentration



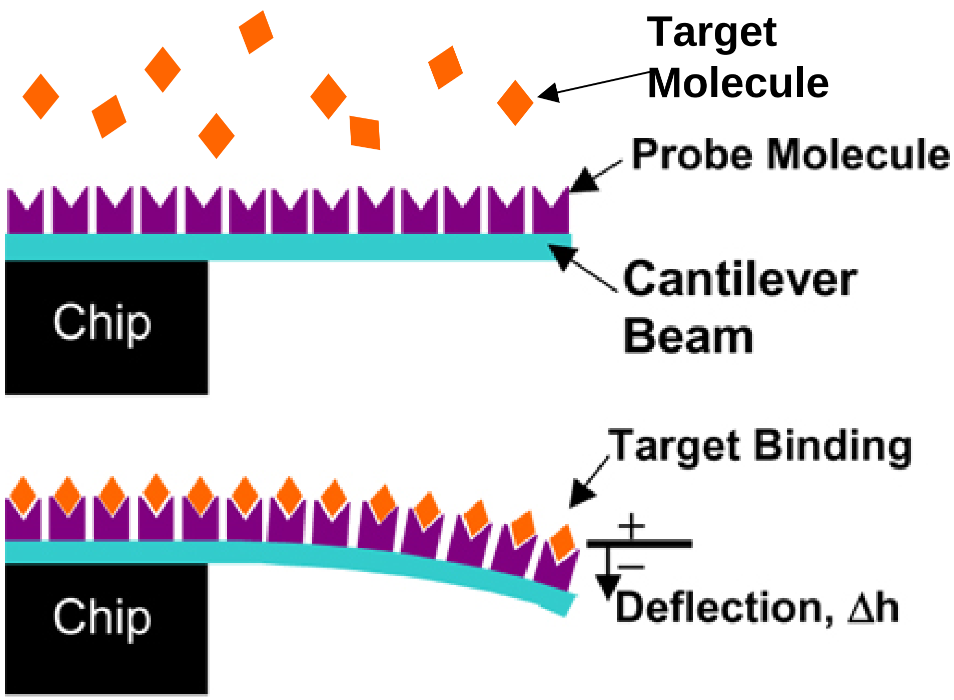


Wafer Curvature Measurement $$\Delta f = \frac{EH^2}{6R}$$

$$\boxed{\Delta f = \phi \Delta C}$$

Translating biomolecular recognition into nanomechanics

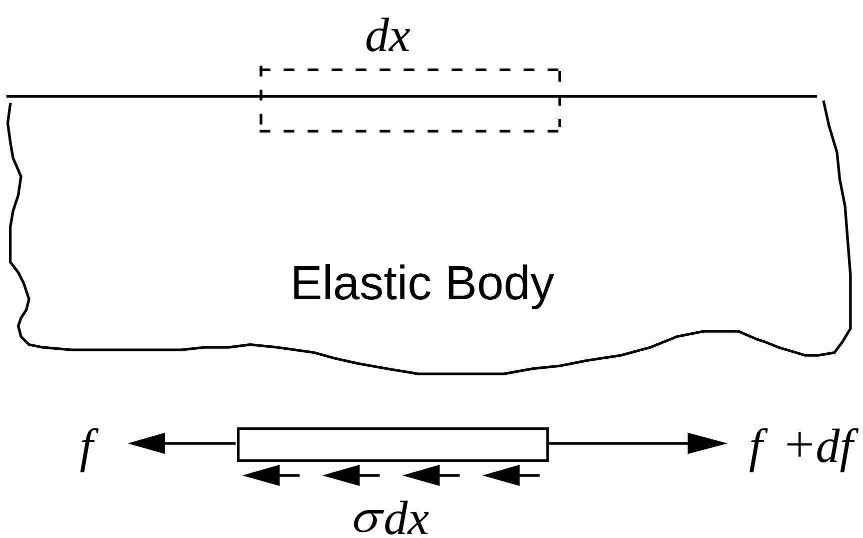
Fritz et al., *Science* **288**, 316 (2000)



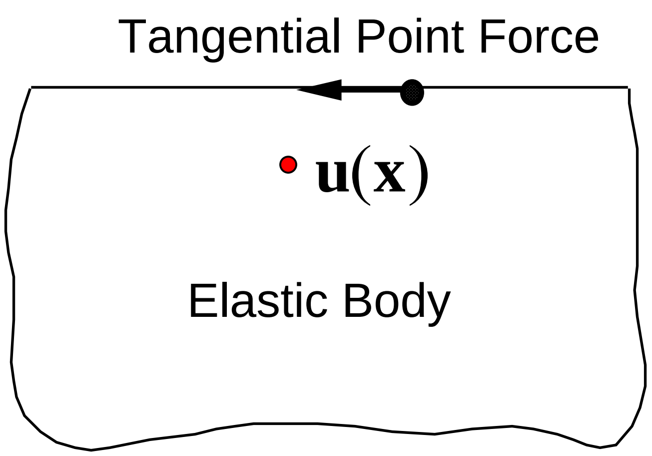
Surface stress couples concentration field and elastic field

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

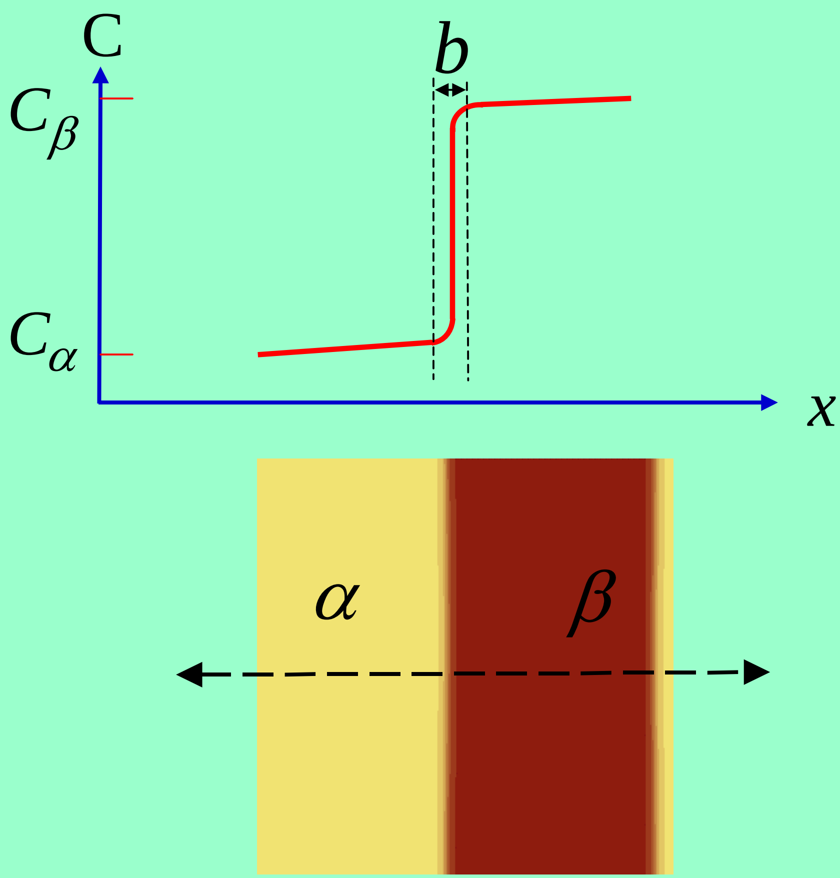
"Marangoni effect" (elastic analog)



Cerruti solution



Phase boundary energy



Diffused boundary

Cahn-Hilliard model

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

Thermodynamic Model

Free energy functional $$\boxed{G = \int \Gamma dA + \int W dV}$$

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

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

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

Chemical potential $$\boxed{\delta G = \int \mu \delta C dA}$$

$$\boxed{\mu = \underbrace{\frac{\partial g}{\partial C}}_{\text{Demixing}} - \underbrace{2h_0 \nabla^2 C}_{\text{coarsening}} + \underbrace{\phi \varepsilon_{\beta\beta}}_{\text{refining}}}$$

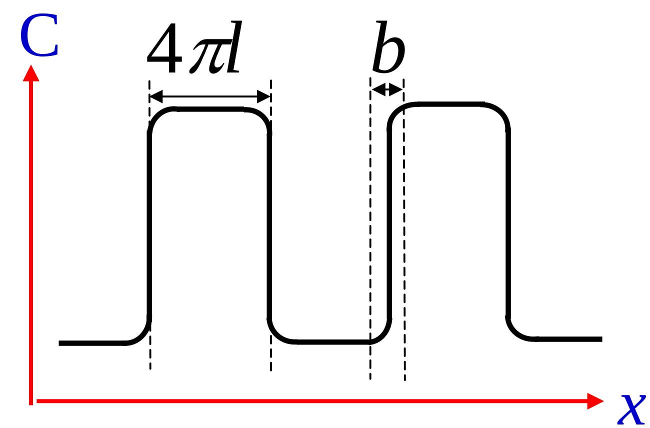
Demixing **coarsening** **refining**

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

Two Length Scales

$$\mu = \frac{\partial g}{\partial C} - 2h_0 \nabla^2 C + \phi \varepsilon_{\beta\beta}$$

Demixing **coarsening** **refining**



Phase Boundary thickness: $b = \left(\dfrac{h_0}{\Lambda kT} \right)^{1/2}$

$h_0 \sim 10^{-19}$ J
$\Lambda \sim 5 \times 10^{19}\ \mathrm{m}^{-2}$
$kT \sim 5 \times 10^{-21}$ J ($T = 400$ K)

$\Rightarrow$ $b \sim 0.3$nm

Phase Size: $l = \dfrac{E h_0}{\phi^2}$

$E \sim 10^{11}\ \mathrm{N/m}^2$
$\phi \sim 4$ N/m

$\Rightarrow$ $4\pi l \sim 4$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

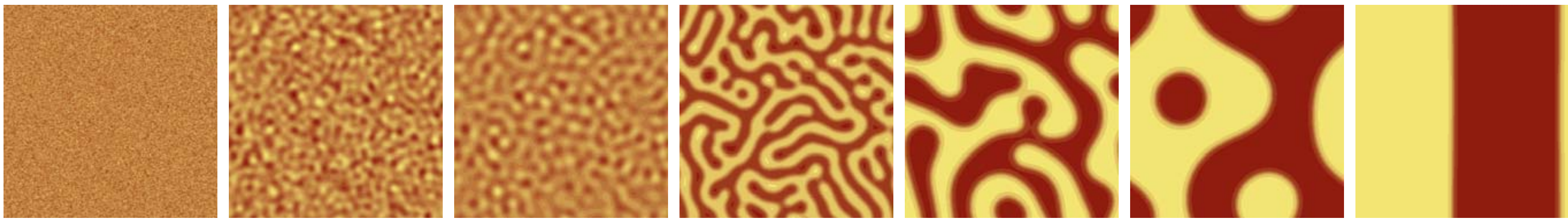
$$\varepsilon_{\beta\beta} = -\frac{\left(1-\nu^2\right)\phi}{\pi E}\iint \frac{(x_1-\xi_1)\frac{\partial C}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2$$

Cerruti solution

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

Simulation Results, C = 0.5

No elasticity refining

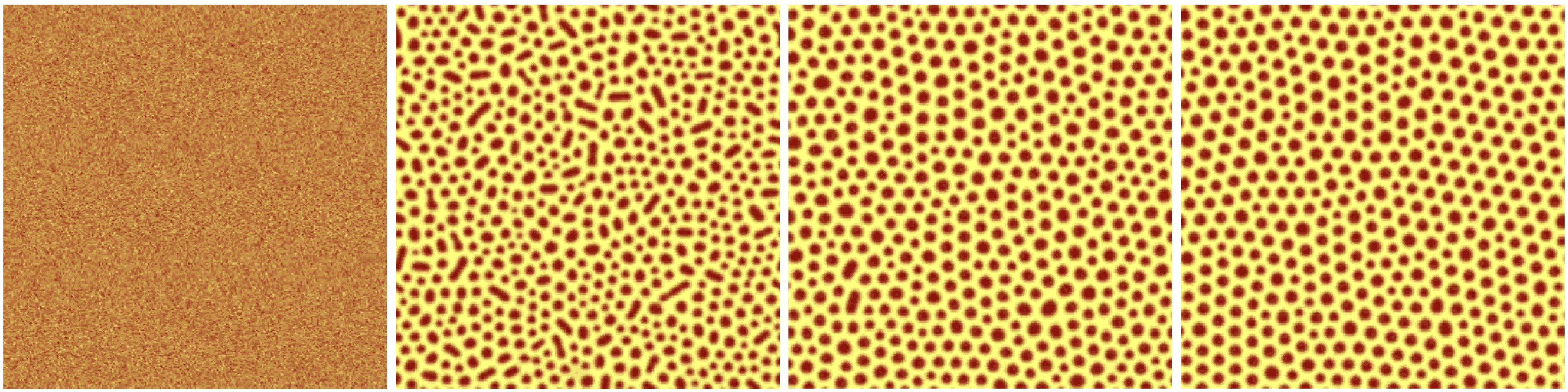


With elasticity refining

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

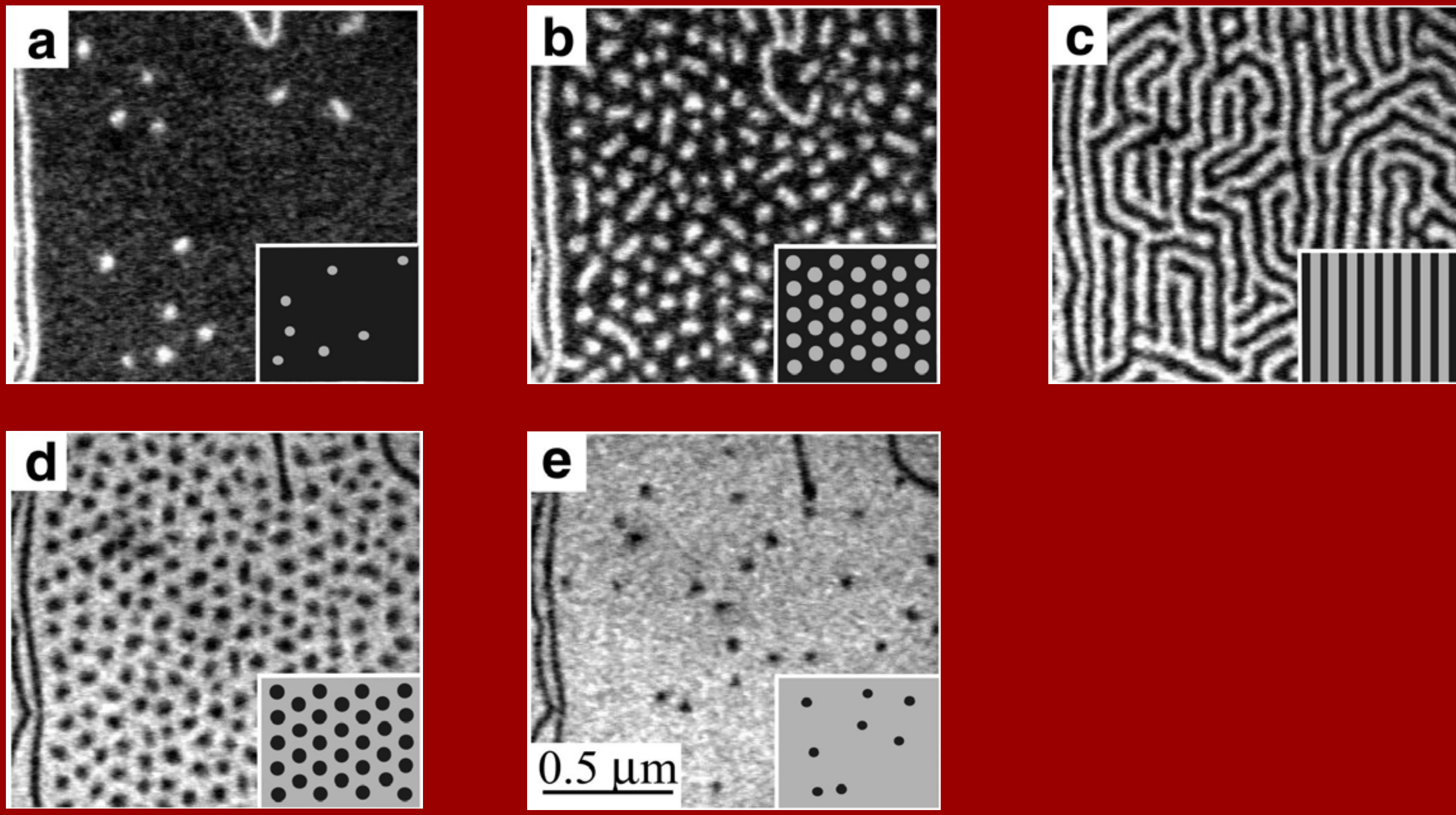
Lu, Suo, *J. Mech. Phys. Solids* **49**, 1937 (2001).

Simulation Results, C = 0.4



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

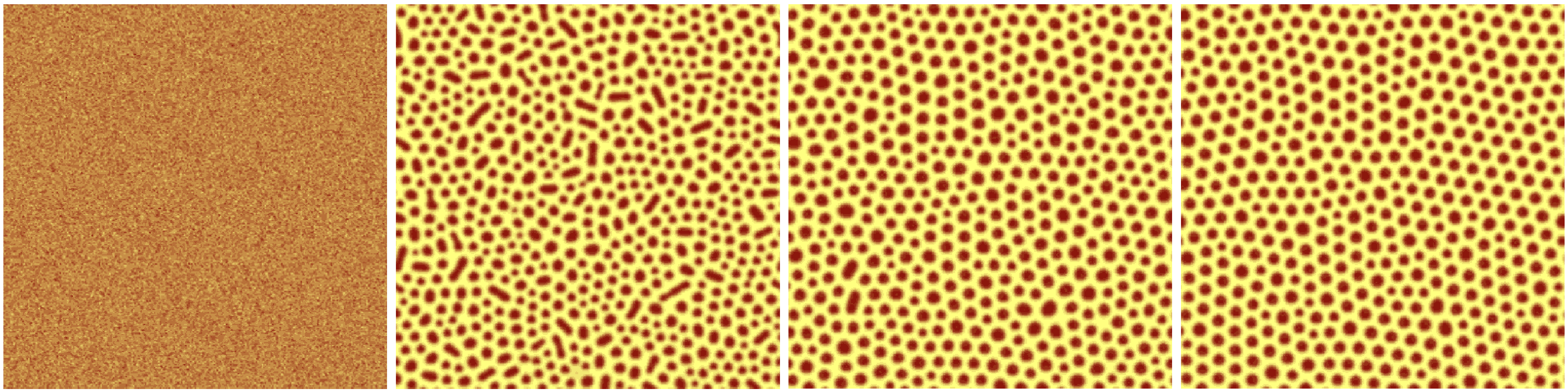
Pb on Cu (111)



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

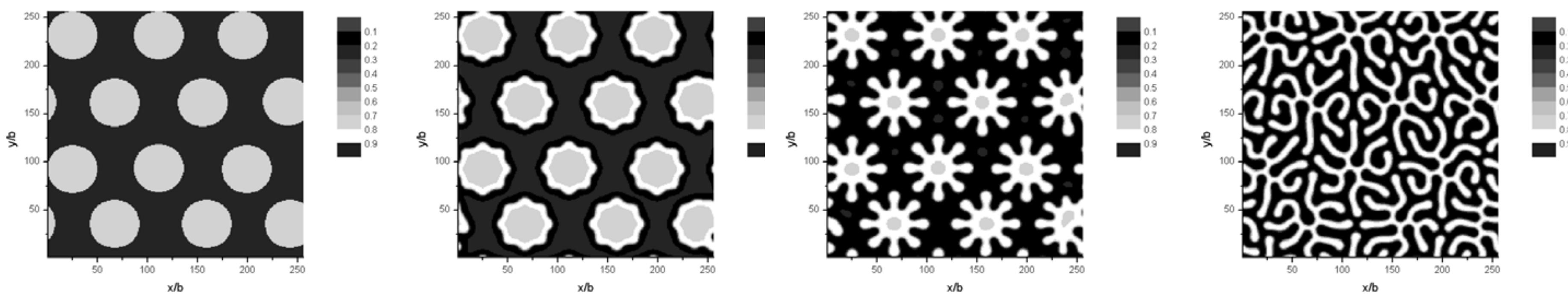
Courtesy of Gary Kellogg, of Sandia National Lab.

Simulation Results



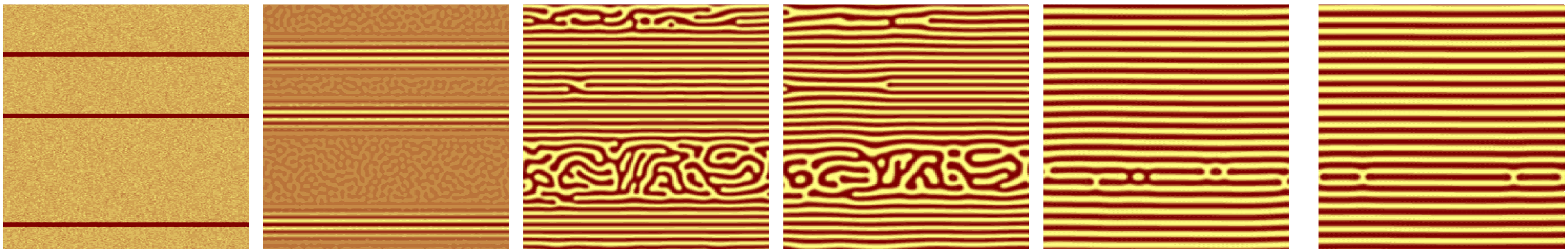
$t = 0$ $t = 10^2$ $t = 10^3$ $t = 8 \times 10^6$

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



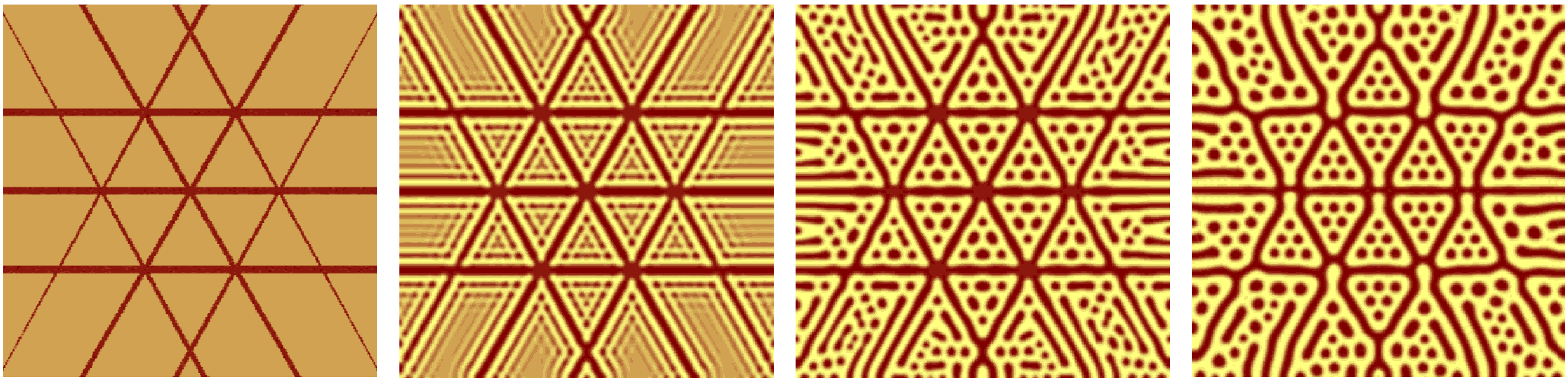
W. Hong

“Crystal Seeds”



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

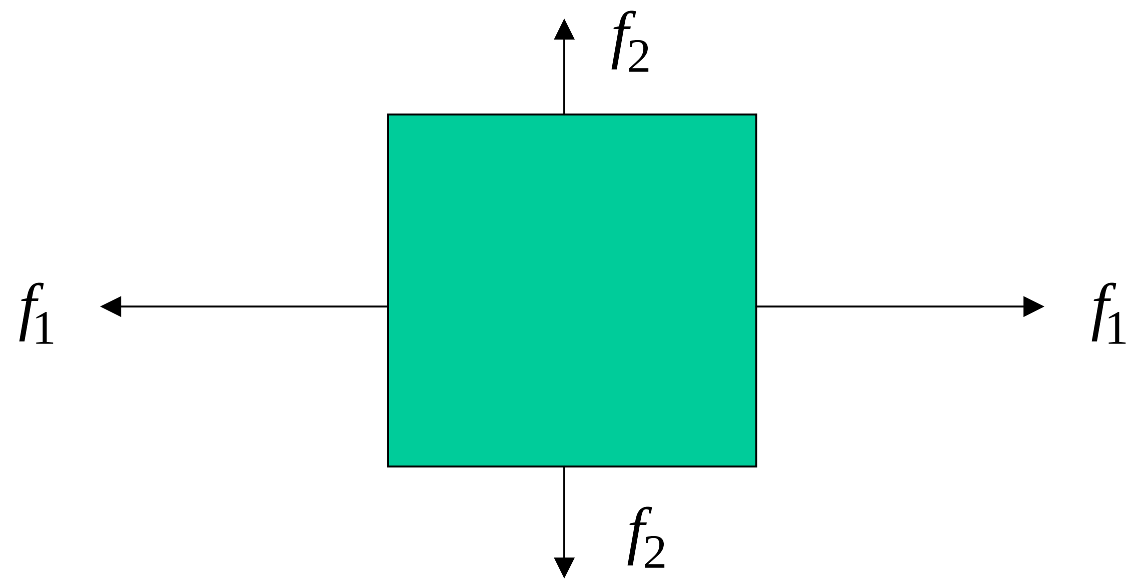
Guide self-assembly with a coarse pattern



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

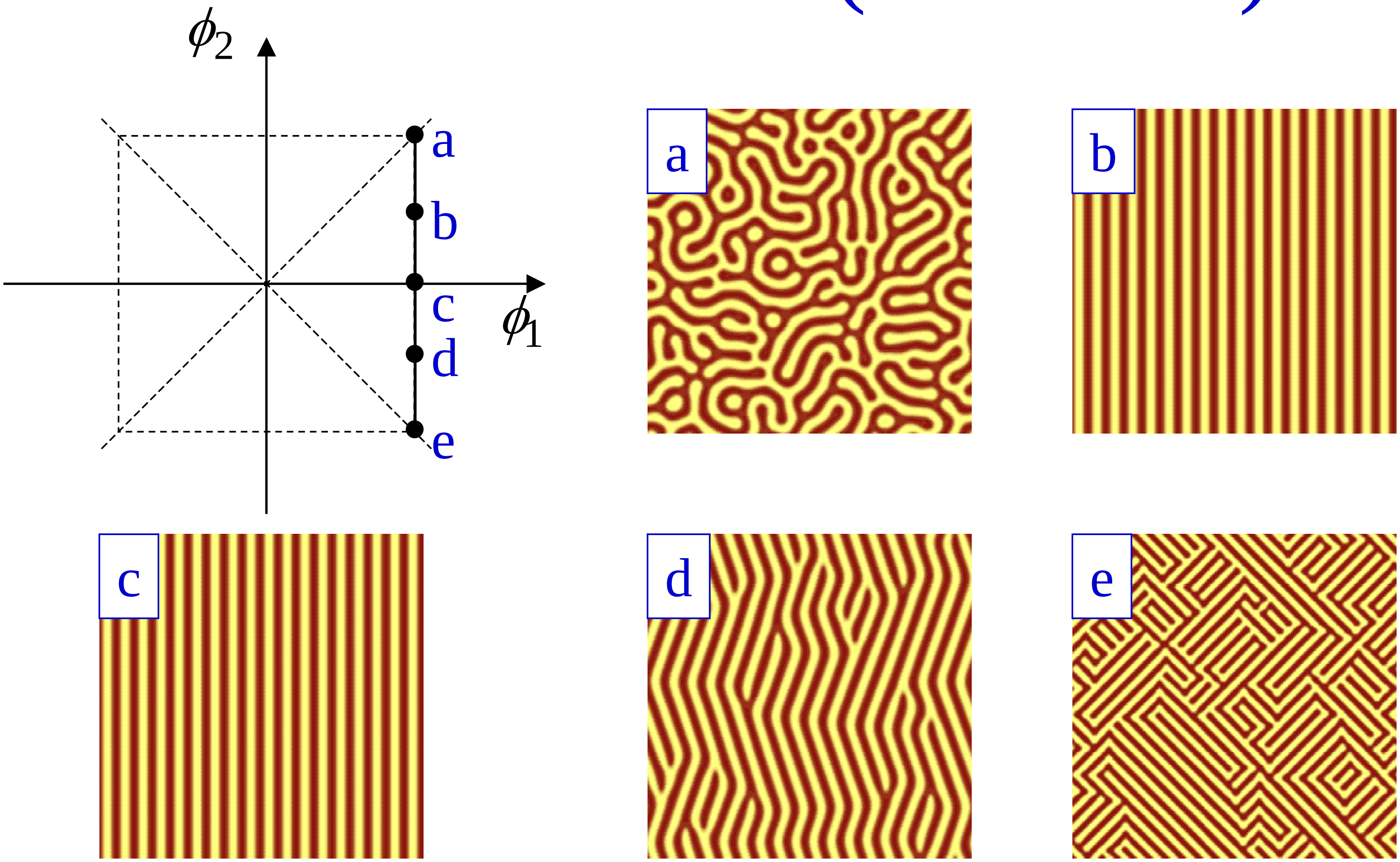
Suo and Lu,. J. Nanoparticles Research **2**, 333 (2000).

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).

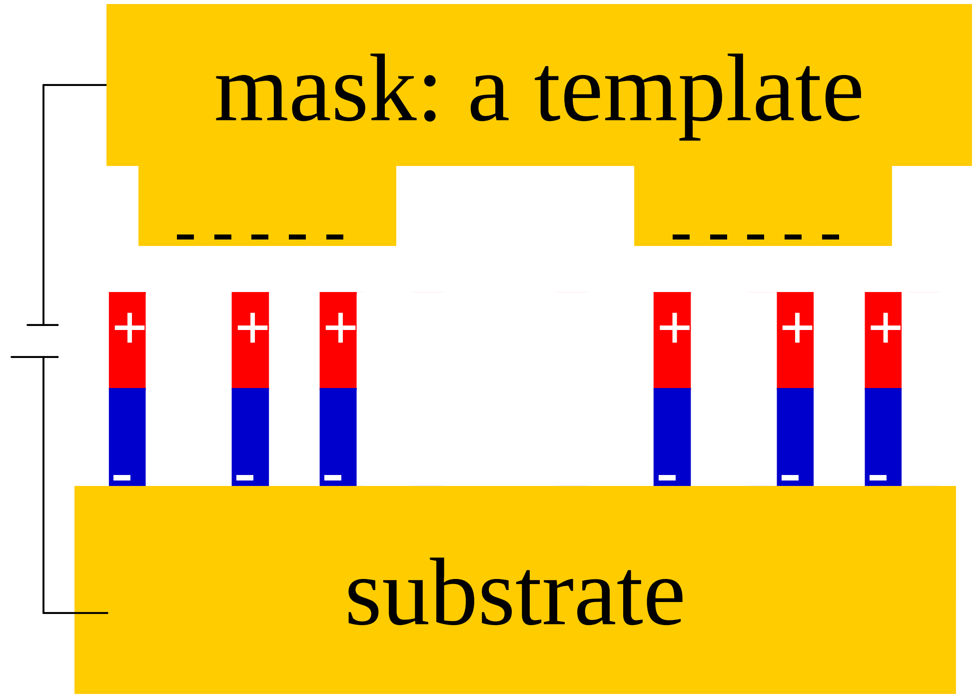
Molecules are more versatile than atoms.

Electrostatics is more versatile than elasticity.

Can electric field direct molecular motion?

Gao & Suo, JAP, **93,** 4276-4282 (2003).

Pattern on the mask

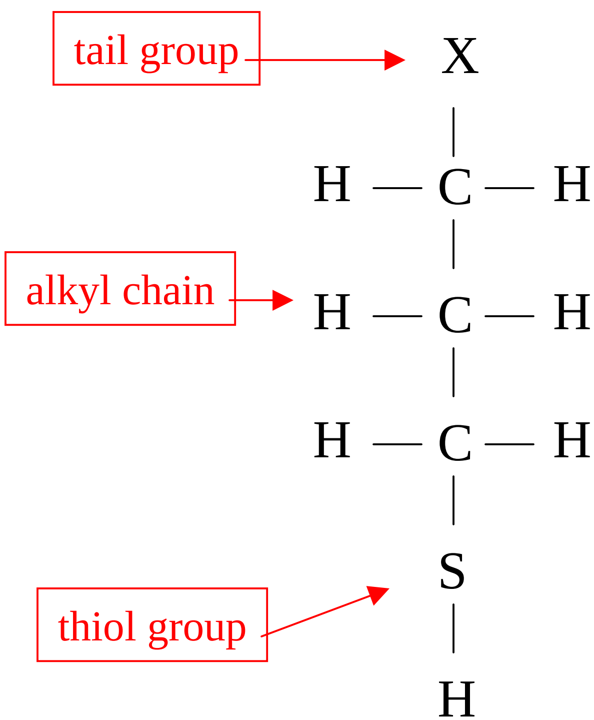


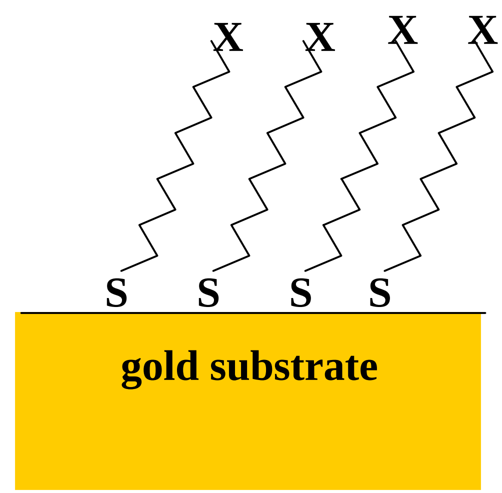
$C_0 = 0.4$

$t = 1\tau$ | $t = 10\tau$ | $t = 100\tau$ | $t = 1000\tau$ | $t = 1e4\tau$ | $t = 1e5\tau$

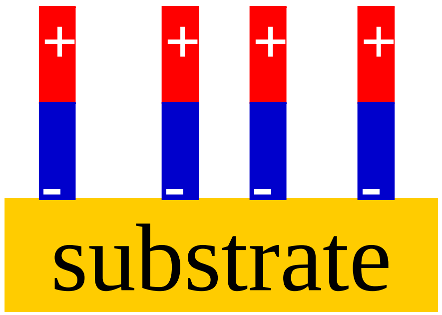
Write one book, print many copies

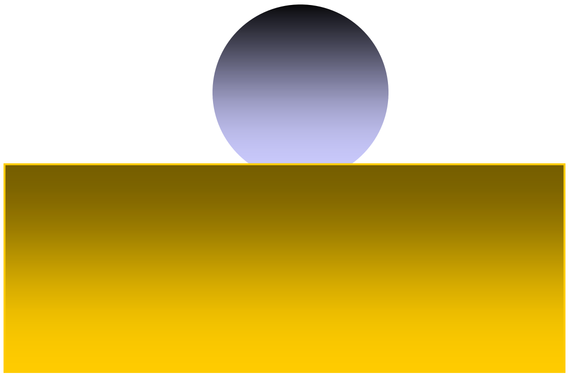
An example: alkanthiol on gold

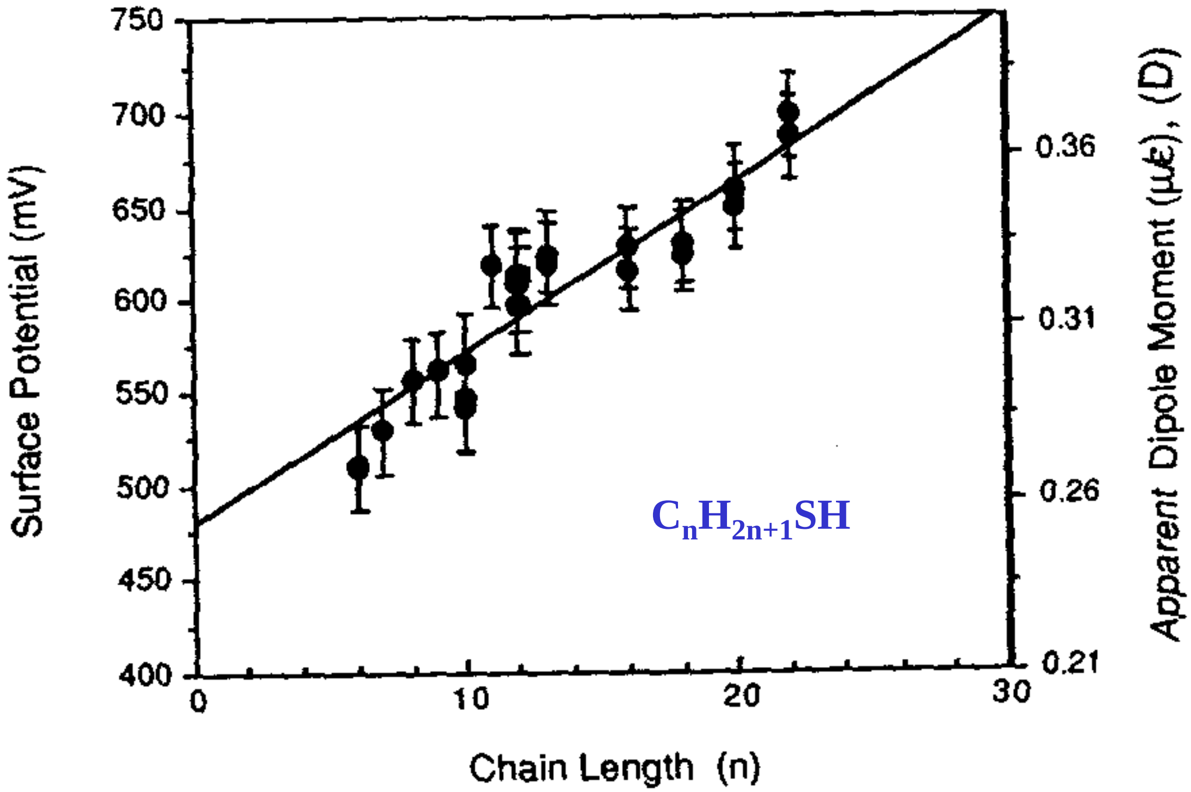




Adsorbates carry electric dipoles

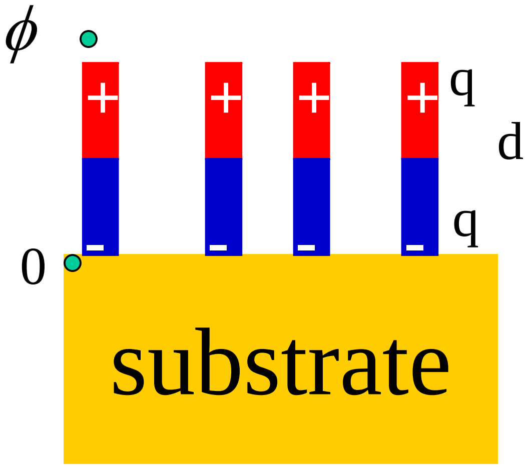




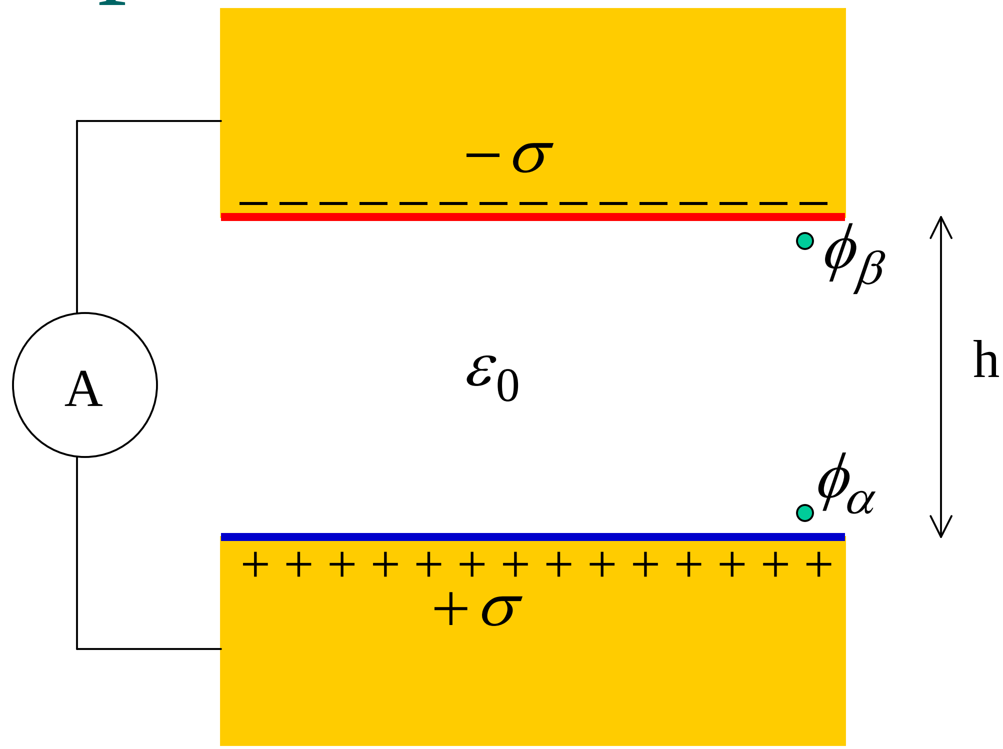


Evans, Ulman, Chem. Phys. Lett. 170, 462 (1990)

Surface potential



$d << h$



A molecular capacitor:

$$\phi \approx \frac{qd}{\varepsilon}$$

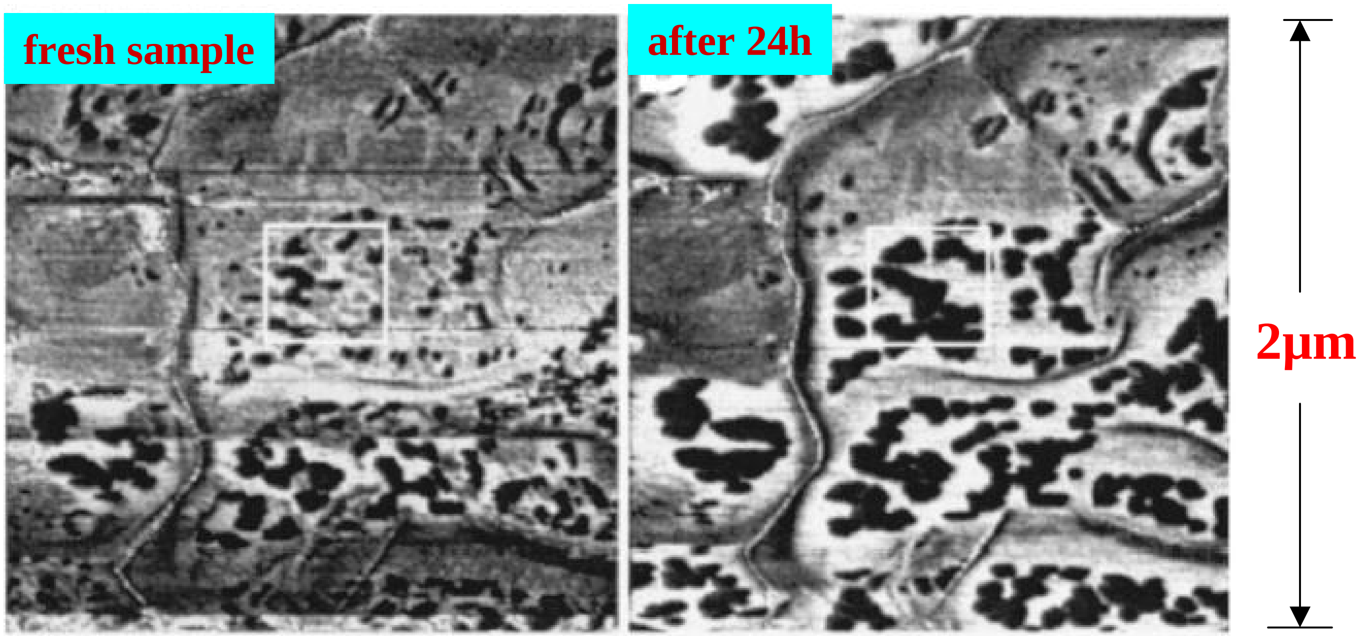
$$\sigma = \varepsilon_0 \frac{\phi_\alpha - \phi_\beta}{h}$$

Kelvin method to measure surface potential

$$\Delta\sigma = \varepsilon_0 (\phi_\alpha - \phi_\beta) \Delta\left(\frac{1}{h}\right)$$

Adsorbates move

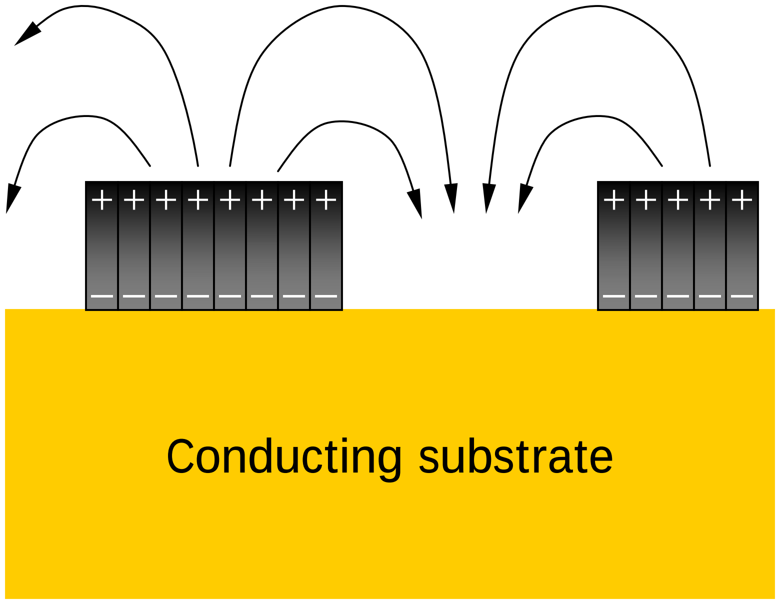
AFM lateral force images: $C_{16}H_{33}SH$ islands on Au(111).



diffusivity ~ 10^{-21} m^2/s

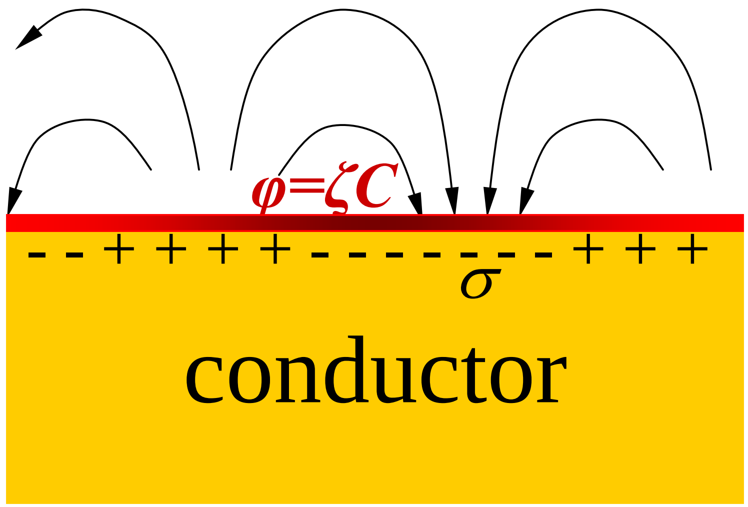
Barrena *et al*., J. Chem. Phys. 111, 9797 (1999); 113, 2413 (2000)

Forces that move molecules



- Entropy
- Intermolecular attraction (van der Waals)
- Dipole-dipole repulsion
- Dipole-electrode interaction

Equation of motion



$$\frac{\partial C}{\partial t} = \frac{M}{\Lambda^2}\nabla^2\left(\frac{\partial g}{\partial C} - 2h\nabla^2 C - \zeta\sigma\right)$$

Regular solution

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

Electrostatic B.V.P.

$$\nabla^2\Psi = 0$$

$$\Psi(x_1, x_2, 0) = \varphi(x_1, x_2) = \zeta C(x_1, x_2)$$

Ψ is prescribed at electrodes

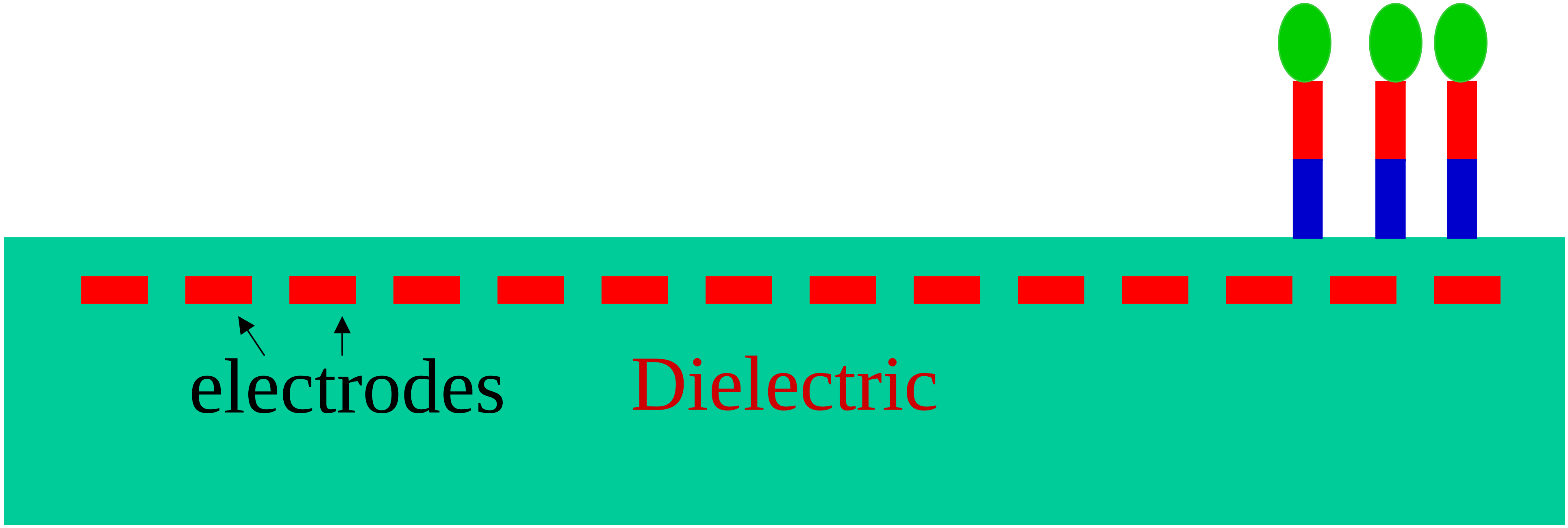
Charge at the surface

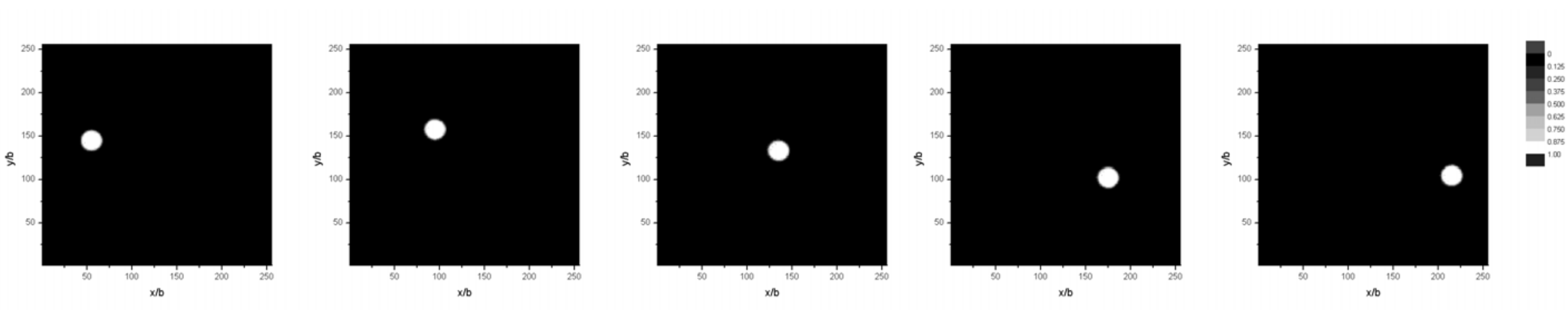
$$\sigma(x_1, x_2) = -\varepsilon\frac{\partial\Psi}{\partial x_3}, \quad x_3 = 0$$

Suo, Gao, Scoles, JAM, in press

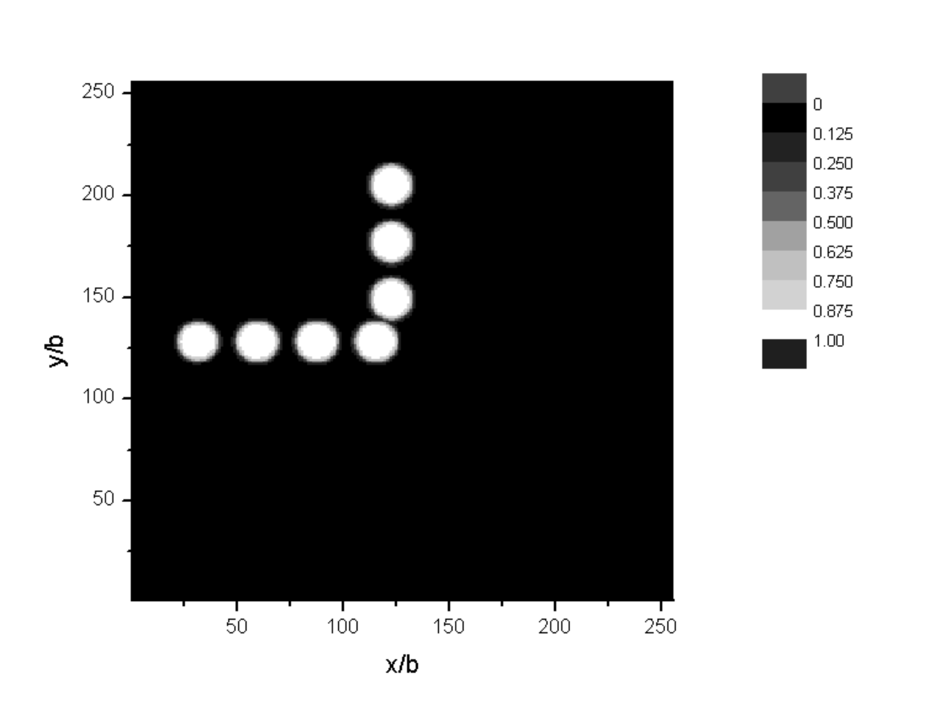
A mechanic has a new dream:

The molecular car



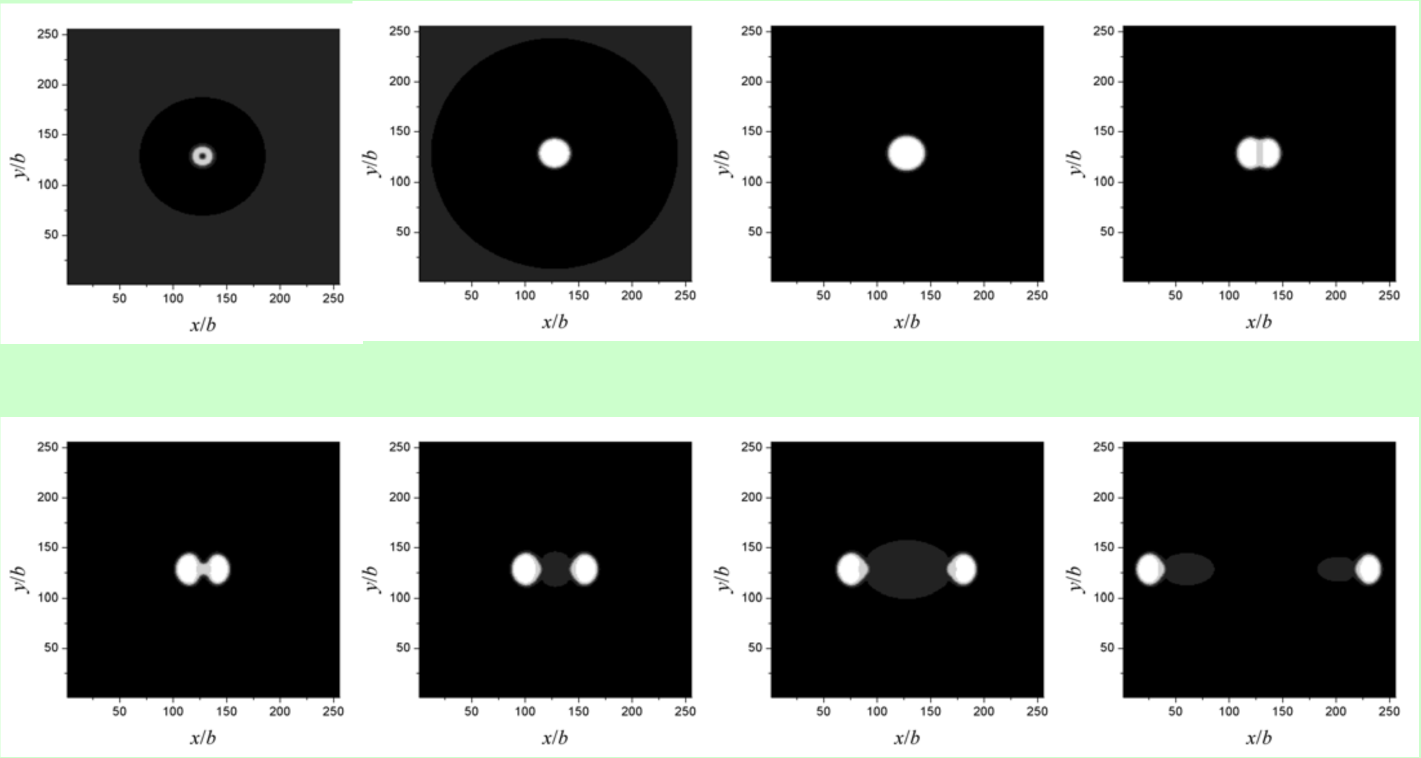


Turning



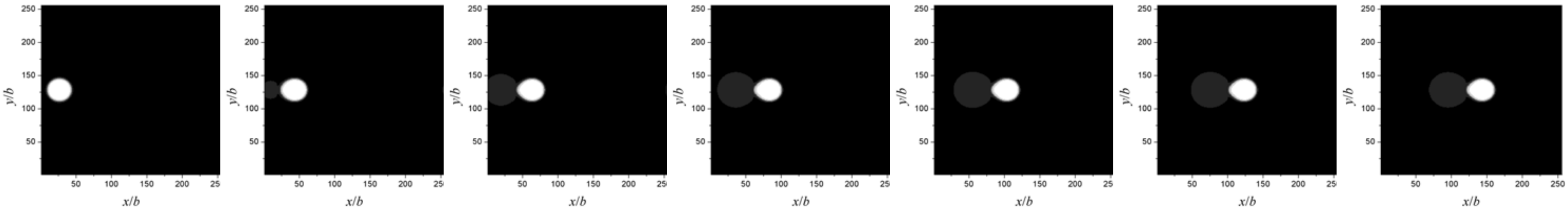
250
200
150
100
50
y/b
50
100
150
200
250
x/b
0
0.125
0.250
0.375
0.500
0.625
0.750
0.875
1.00

Splitting (or merging)

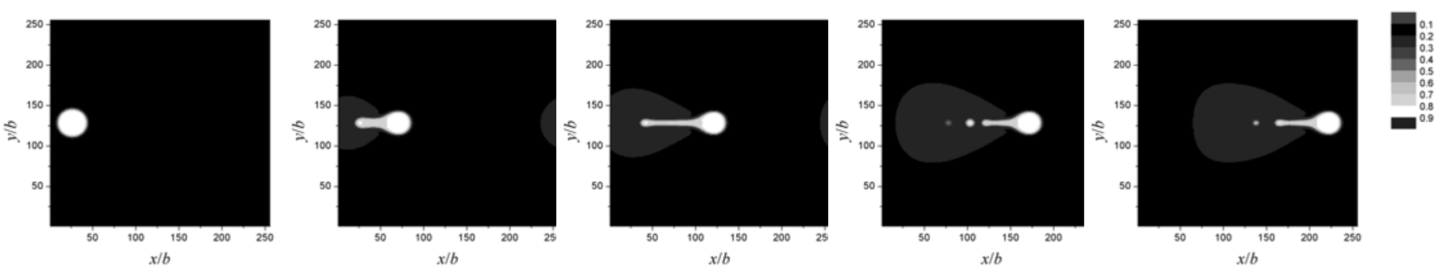


Speeding

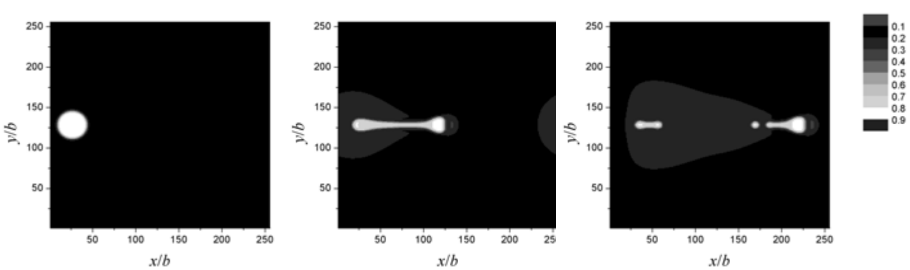
$v = 0.02$



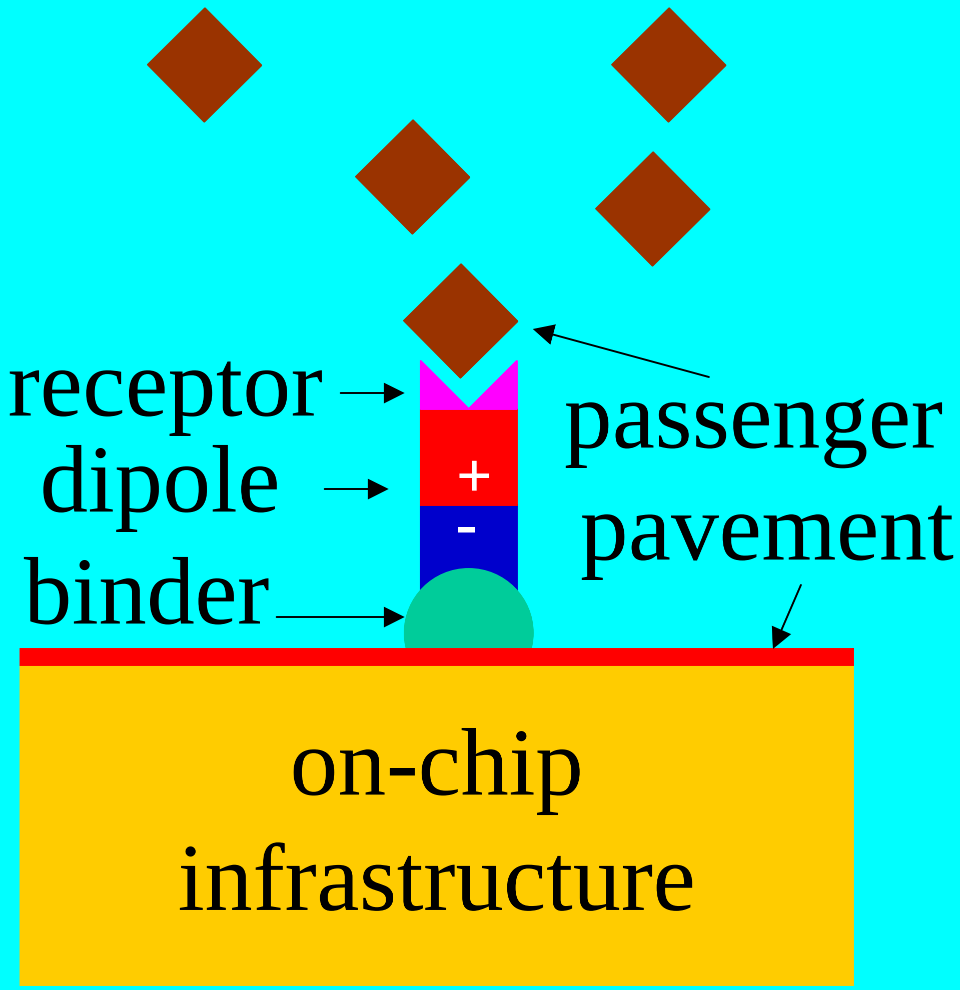
$v = 0.05$



$v = 0.1$

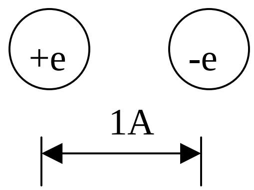


Division of labor: modular architecture

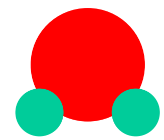


Add a dipole to a molecule

$$p = 1.6 \times 10^{-29}\,\mathrm{Cm}$$

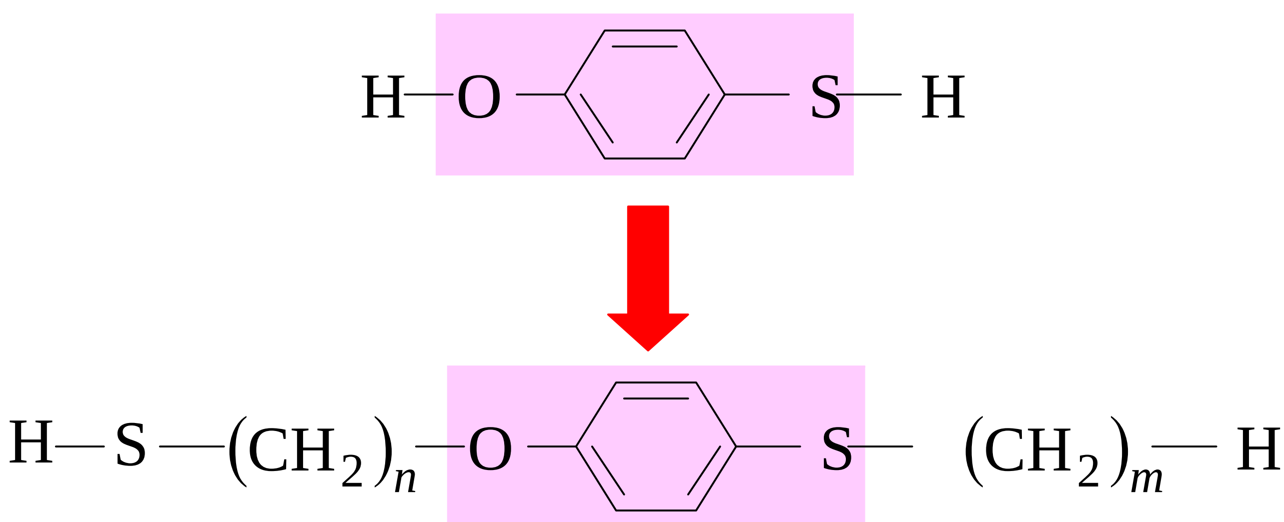


$$p = 0.617 \times 10^{-29}\,\mathrm{Cm}$$



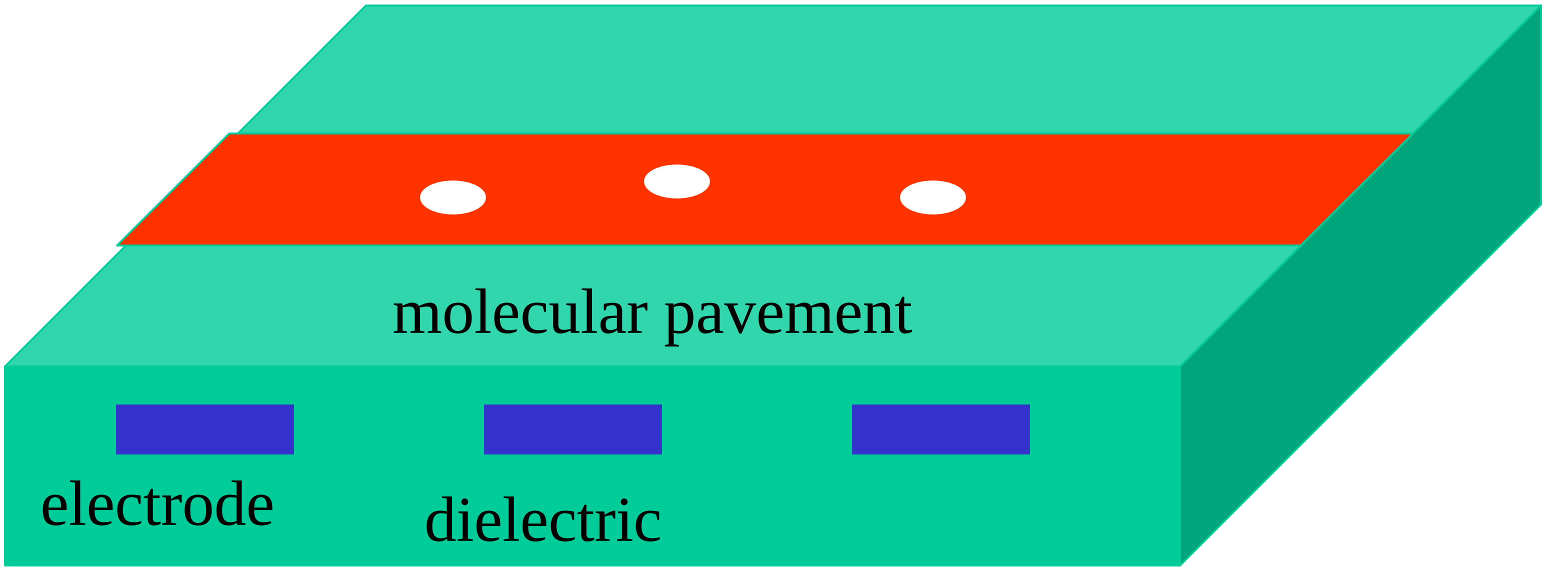
H_2O

$$p = 0.9 \times 10^{-29}\,\mathrm{Cm}$$



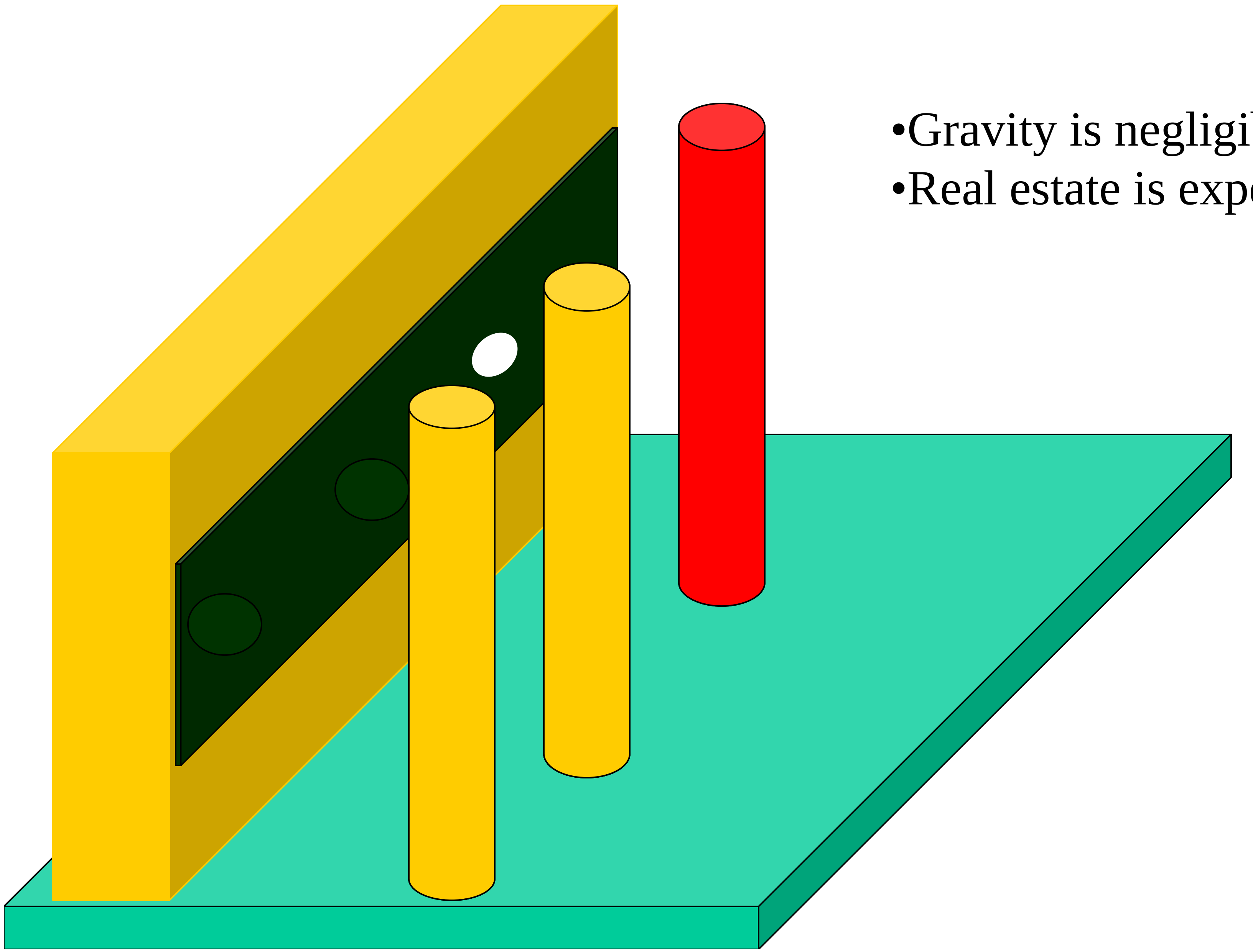
Evans, Urankar, Ulman, Ferris, J. Am. Chem. Soc., 113 4121 (1991)

Molecular pavement



- cover steps
- confine the Brownian movement
- fast car
- repel trash
- chemical gradient

Highway-on-a-wall



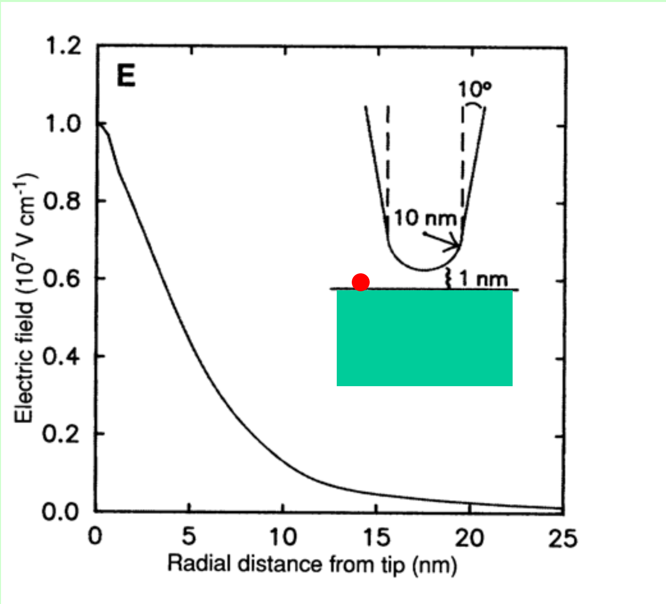
- Gravity is negligible
- Real estate is expensive

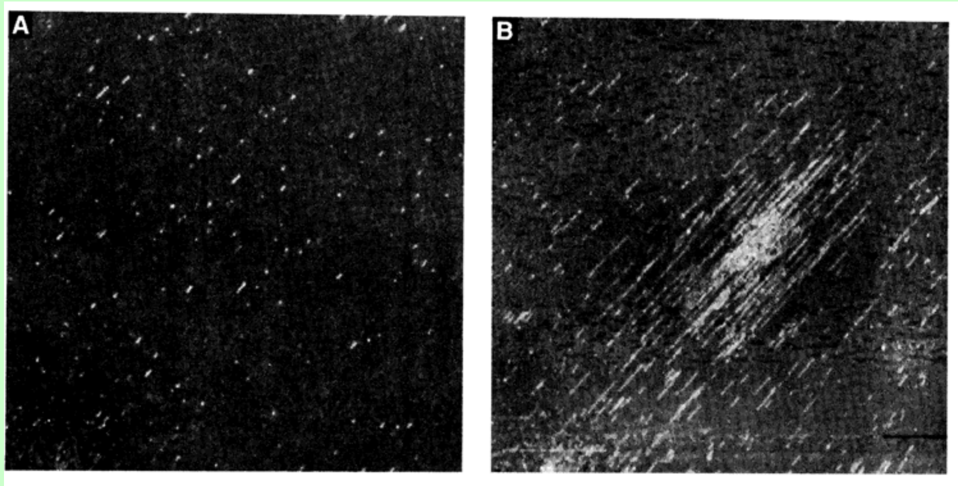
Questions from a mechanic

- Can we find a wheel/pavement pair so that the car runs rapidly on the surface, but does not fly away?
- Can we drive the car against thermal motion?

Cesium on GaAs

Whitman et al.
Science 251, 1206 (1991)

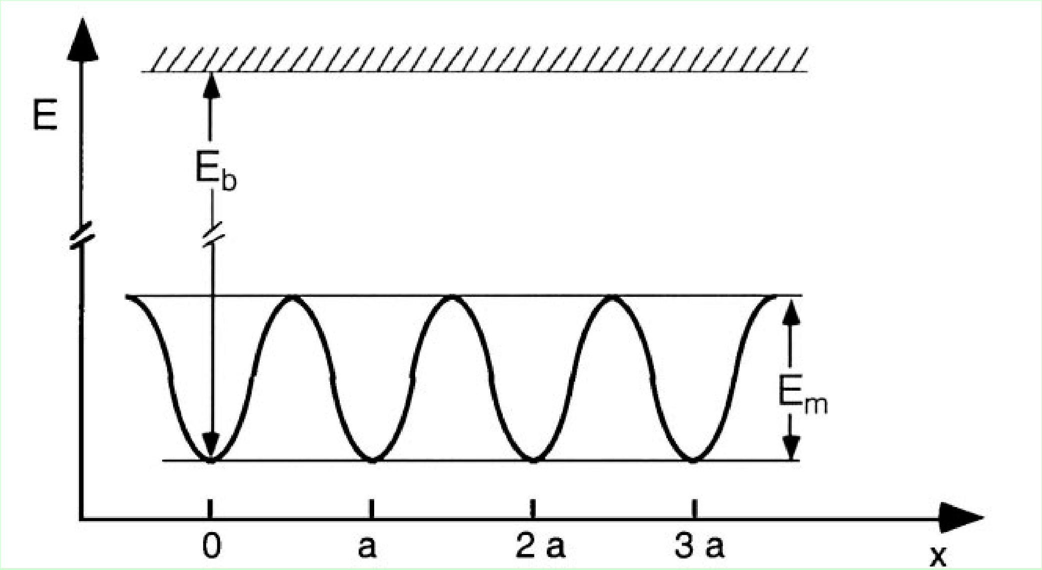




350 nm

3V for 0.1s

Binding energy, migration energy



$E_b \sim 1\text{eV}$

$E_m \sim 0.1\text{eV}$

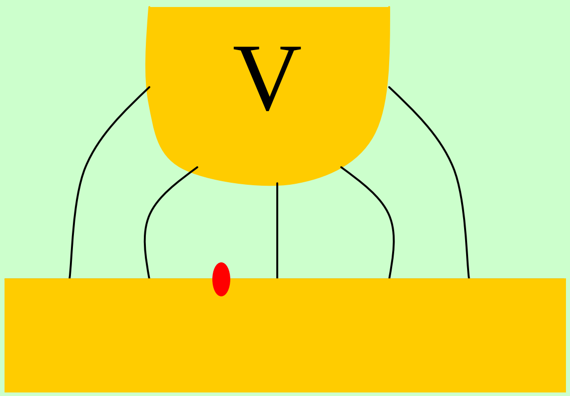
$kT = 0.025\text{eV}$

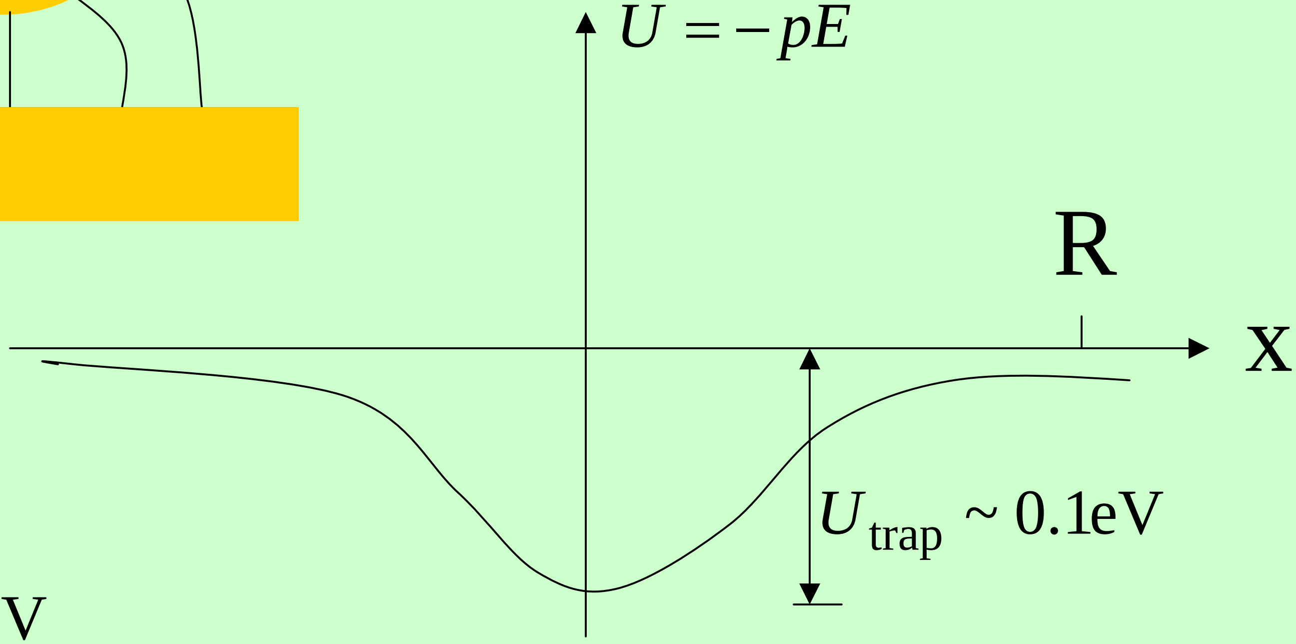
No desorption: $E_b >> kT$

Rapid migration: $D \sim \nu a^2 \exp\left(-\frac{E_m}{kT}\right)$

Barth, Surface Sci. Rep. 40, 75 (2000).

Electrode creates an energy trap





$$kT = 0.025\text{eV}$$

$$E \sim V/d \sim (1\text{V})/\left(10^{-9}\,\text{m}\right) = 10^{9}\,\text{V/m}$$

$$p \sim ea \sim \left(10^{-19}\,\text{C}\right)\left(10^{-10}\,\text{m}\right) = 10^{-29}\,\text{Cm}$$

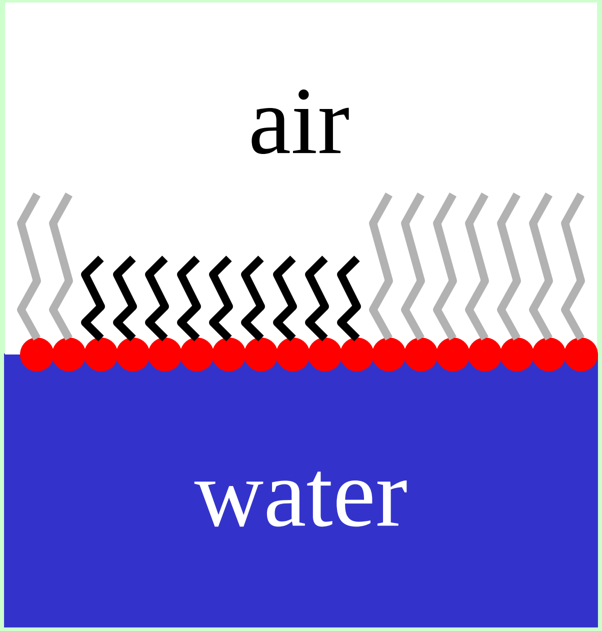
More numbers

$$D \sim \nu a^2 \exp\left(-\frac{E_m}{kT}\right) \sim \left(10^{13}/\mathrm{s}\right)\left(10^{-10}\,\mathrm{m}\right)^2 \exp\left(-\frac{E_m}{0.025\mathrm{eV}}\right)$$
$$= \left(10^{-7}\,\mathrm{m}^2/\mathrm{s}\right)\exp(-40E_m)$$

$$f = \nabla(\mathbf{p}\cdot\mathbf{E}) \sim p(V/d)/R \sim \left(10^{-29}\,\mathrm{Cm}\right)\left(10^{9}\,\mathrm{V/m}\right)/\left(10^{-8}\,\mathrm{m}\right) = 1\mathrm{pN}$$

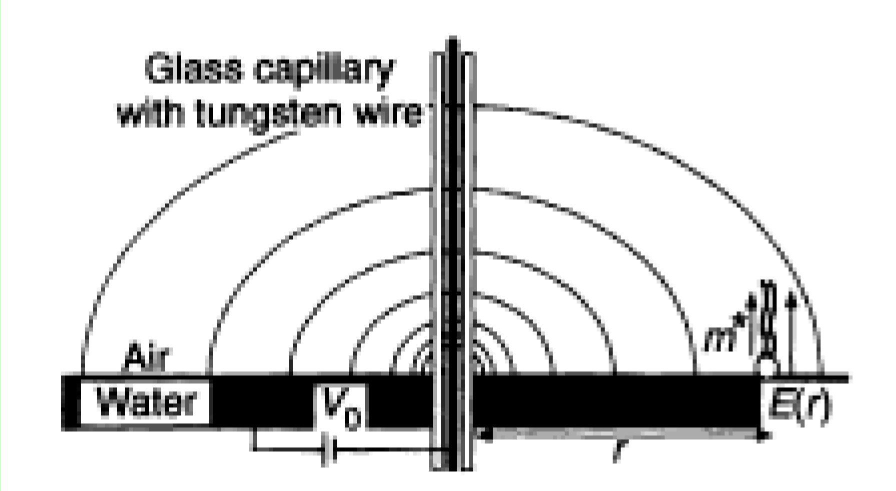
E_m	0.1 eV	0.5 eV	1.0 eV
D	$10^{-9}\,\mathrm{m}^2/\mathrm{s}$	$10^{-16}\,\mathrm{m}^2/\mathrm{s}$	$10^{-25}\,\mathrm{m}^2/\mathrm{s}$
$X = \sqrt{2Dt}$	$10^{-5}\,\mathrm{m}$	$10^{-8}\,\mathrm{m}$	$10^{-13}\,\mathrm{m}$
$u = \frac{D}{kT}f$	$10^{-1}\,\mathrm{m/s}$	$10^{-8}\,\mathrm{m/s}$	$10^{-17}\,\mathrm{m/s}$

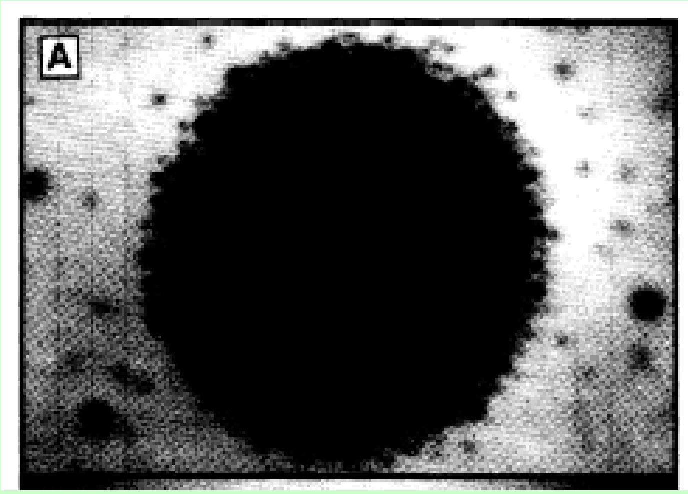
Molecular boat?



Lipids on air/water interface

Lee, Klingler, McConnell.
Science 263, 655 (1994)



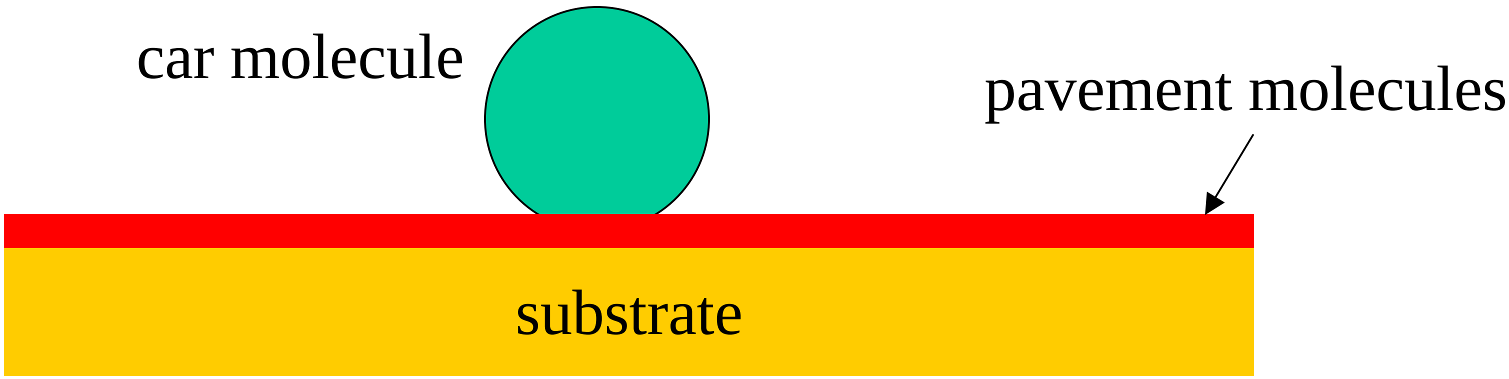


Why the molecular car now?

- **Scanning probes** (imaging, electrode). Tools to search for the engines, wheels, pavements.
- **Nanofabrication** (~100 nm in fabs, ~10 nm in labs). Tools to make on-chip infrastructure.
- **Molecular synthesis.** Tools to make the car.
- **Computation.** Tools to design the car and its on-chip infrastructure.

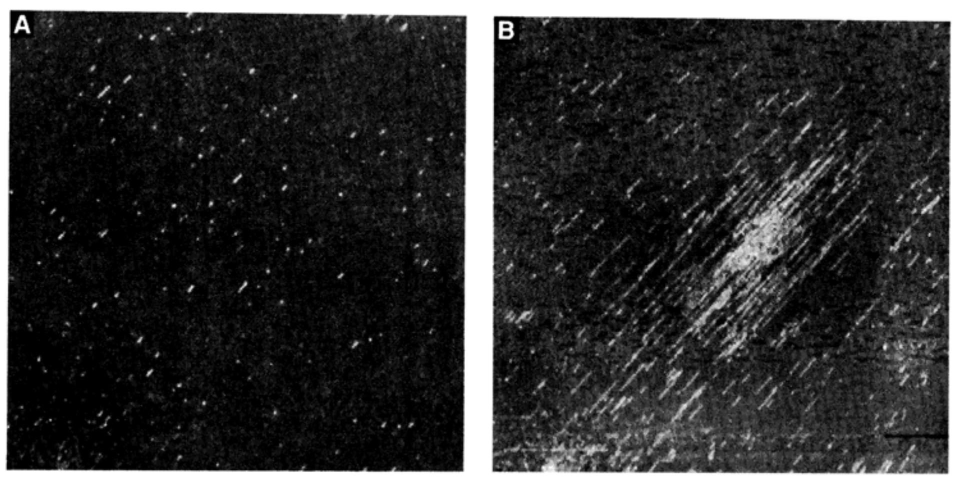
Suo, Chen, Maynard, Saif, Sehitoglu

In search of engines, wheels, and pavements



Scanning probe: an imaging tool *and* a loading tool

$$X = \sqrt{2Dt}$$



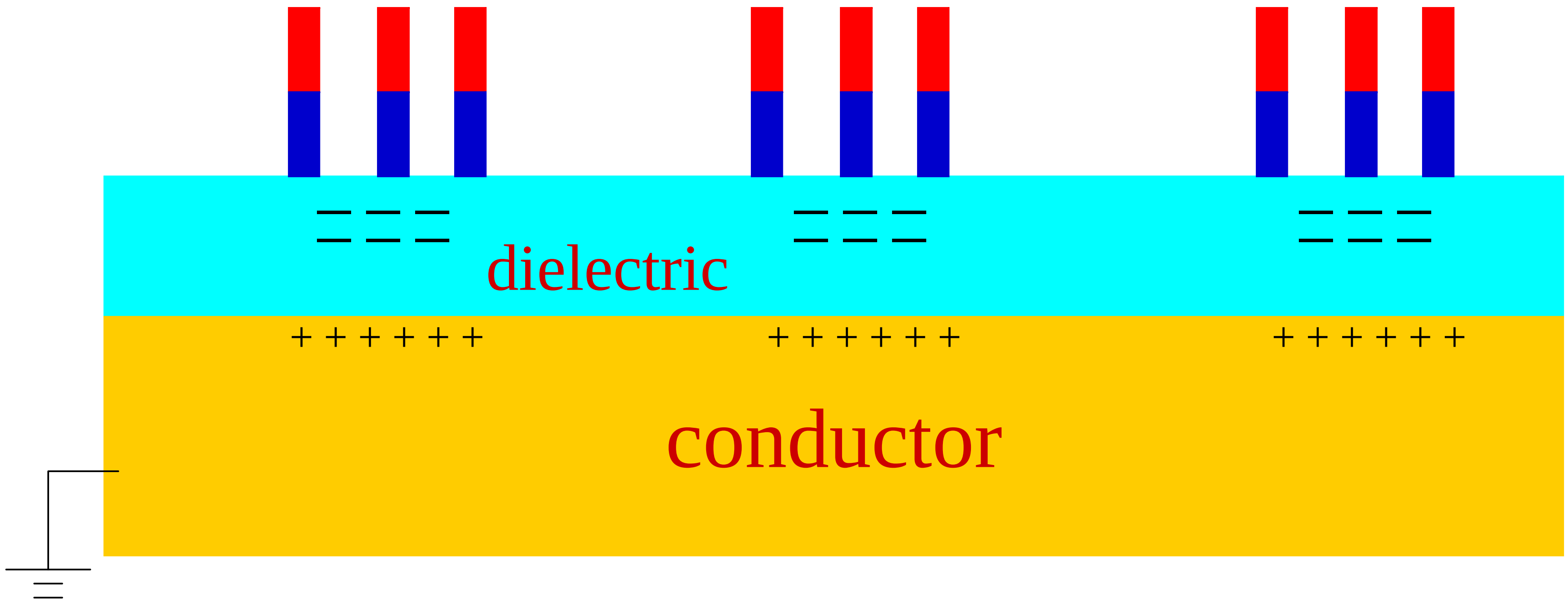
$$U = -pE - \frac{1}{2}\alpha E^2$$

$$\mathrm{Prob} \propto \exp\left(-\frac{U}{kT}\right)$$

What is the molecular car good for?

- **Microfluidics, nanofluidics, molecular cars** (ultimate frontier of matter-transport-on-a-chip).
- **Drug discovery** (combinatorial chemistry).
- **Cancer detection** (medical diagnostics).
- **Proteomics** (identity and function).

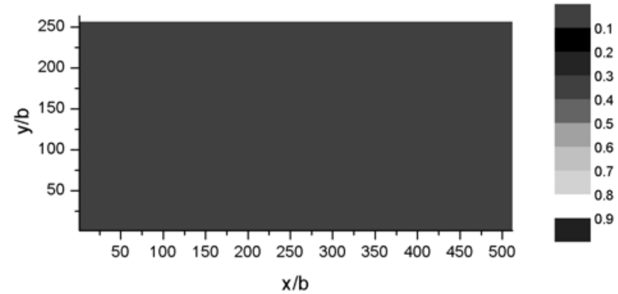
Molecular Xerography



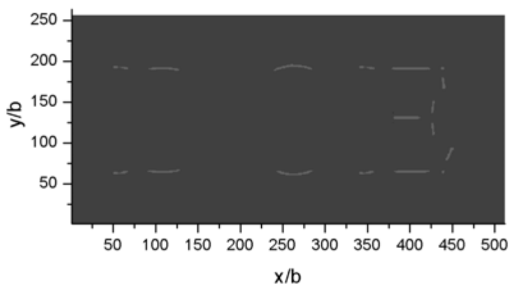
transcirbe a charge pattern into a molecular pattern

Transcribe a charge pattern to molecular pattern

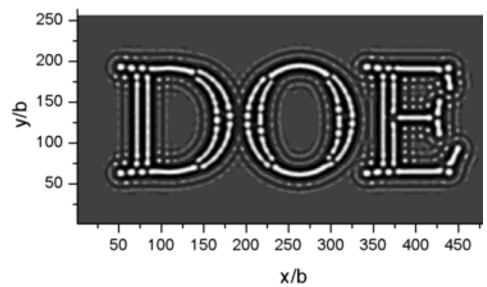
Charge Pattern



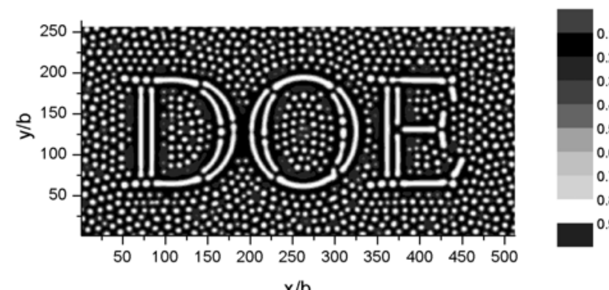
Initial molecular pattern (t = 0)



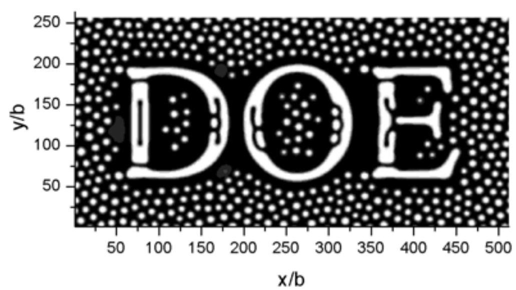
$t = 10\tau$



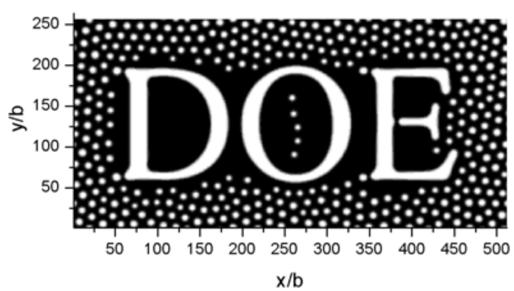
$t = 50\tau$



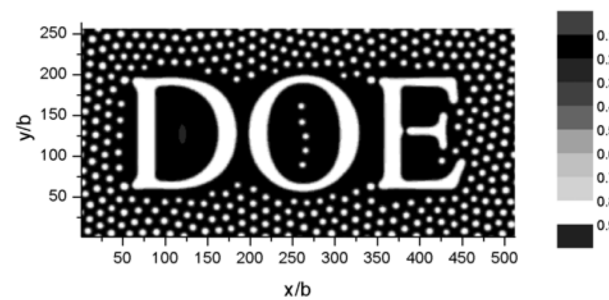
$t = 100\tau$



$t = 1000\tau$



$t = 5000\tau$



$t = 10000\tau$

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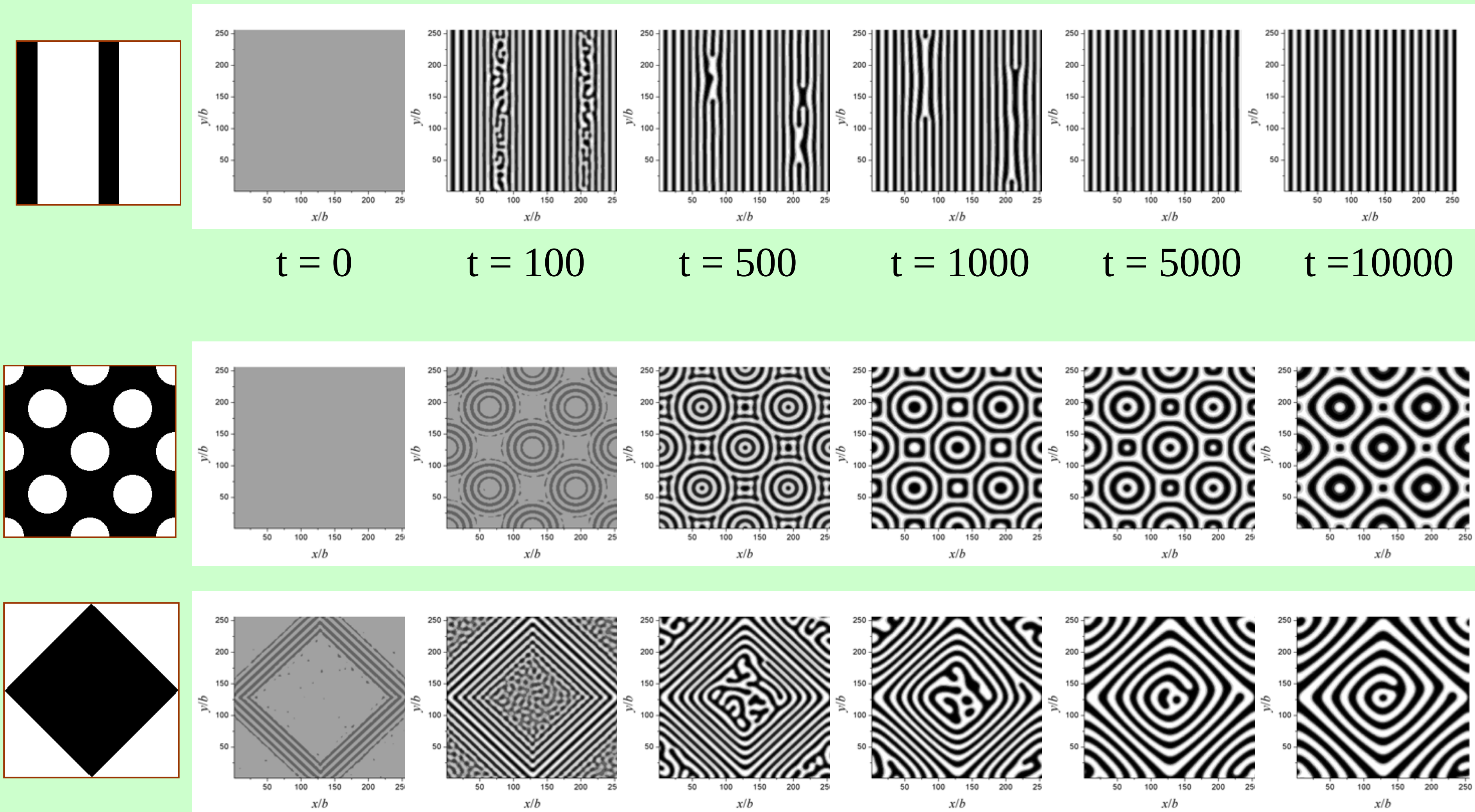
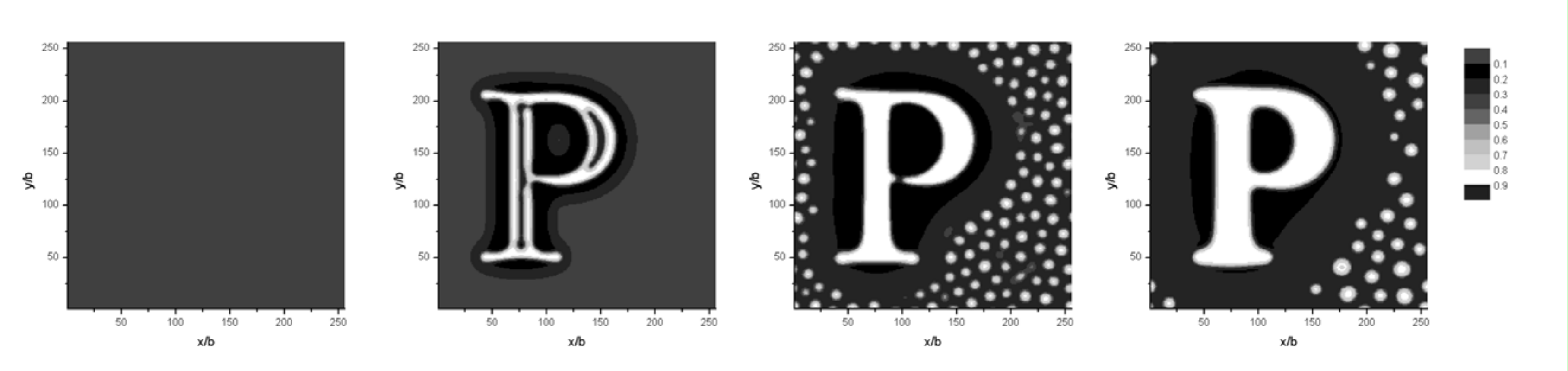
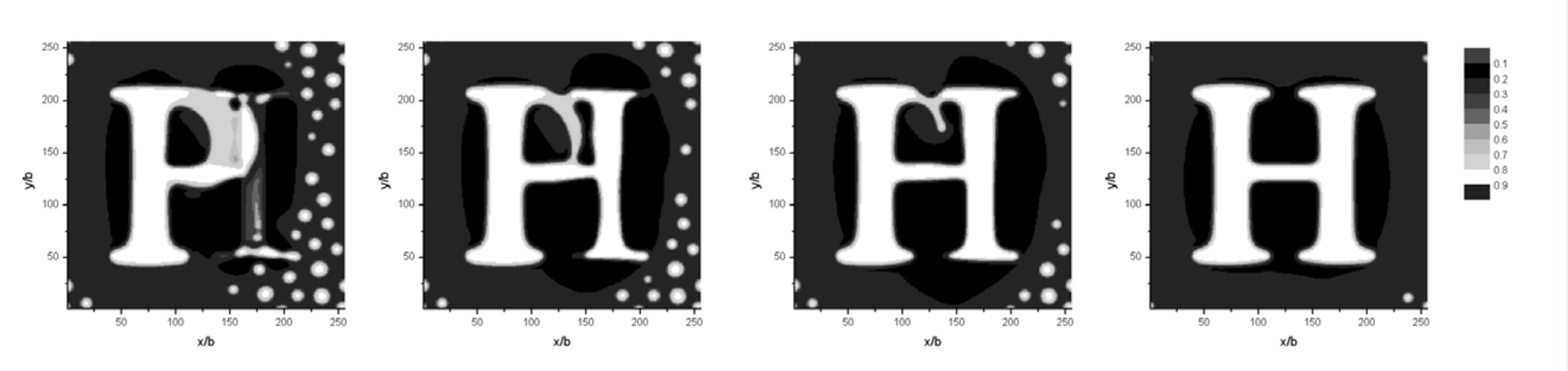
Field-Directed Assembly (FDA)



Re-Configurable Assembly (RCA)





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Summary

- Adsorbates carry electric dipoles.
- Adsorbates move.
- Electric field directs their motion.

- Modular car: wheel, engine, passenger seat.
- On-chip infrastructure: electrodes, pavements.

- Re-configurable assembly.

www.deas.harvard.edu/suo
This lecture
Publications 130, 140, 150