Electric field-induced self-assembly

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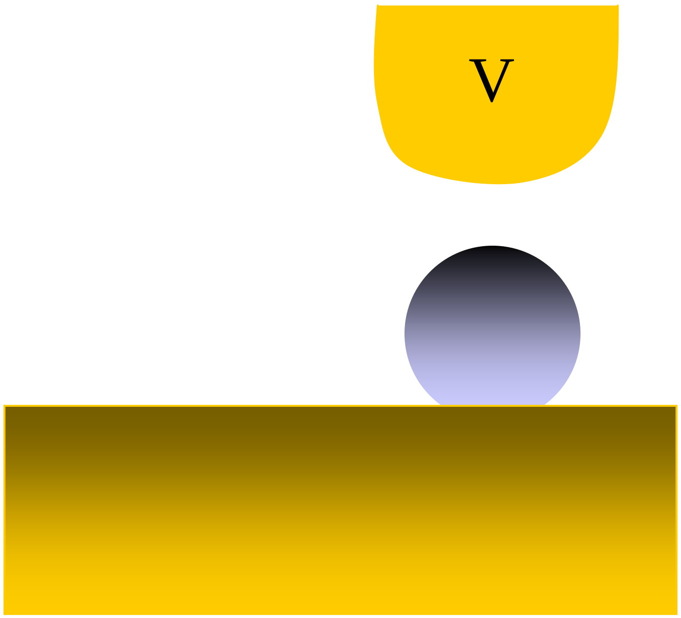
Work with

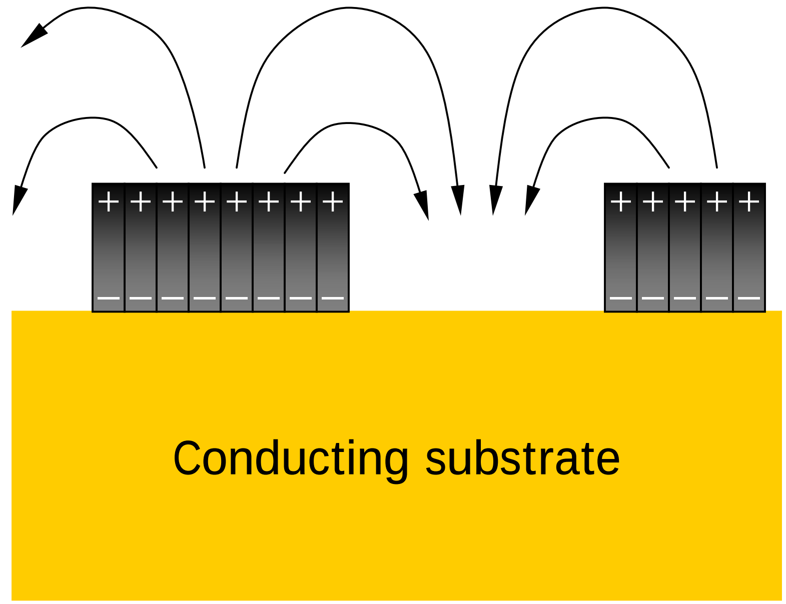
W. Hong, Harvard University

Y.F. Gao, Brown University

G. Scoles, Princeton University

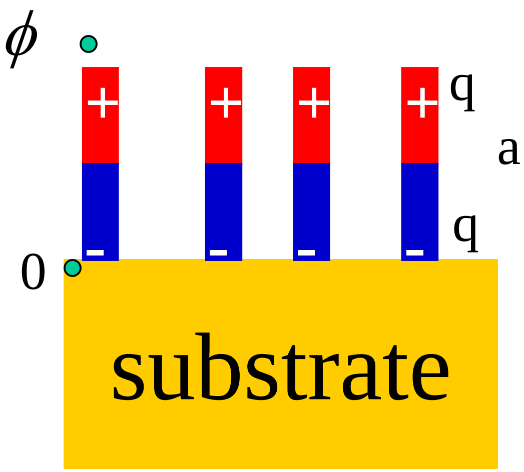
Forces that move adsorbates



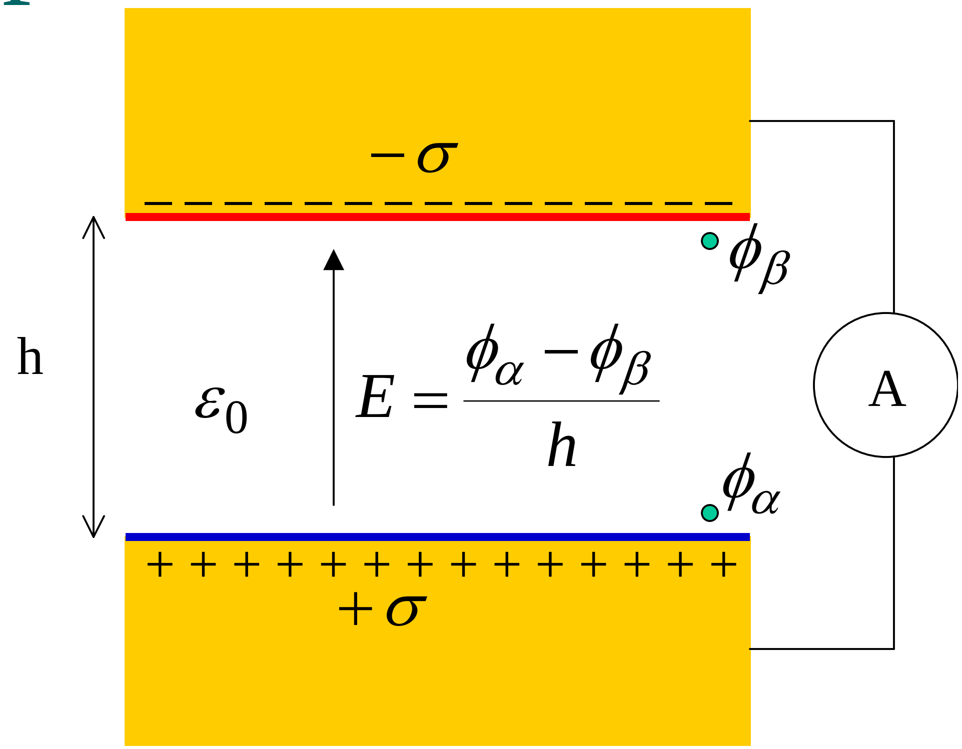


- Entropy
- Inter-adsorbate attraction (phase coarsening)
- Dipole-dipole repulsion (phase refining)
- Dipole-electrode interaction (guiding force)

Surface potential



$a << h$



A molecular capacitor:

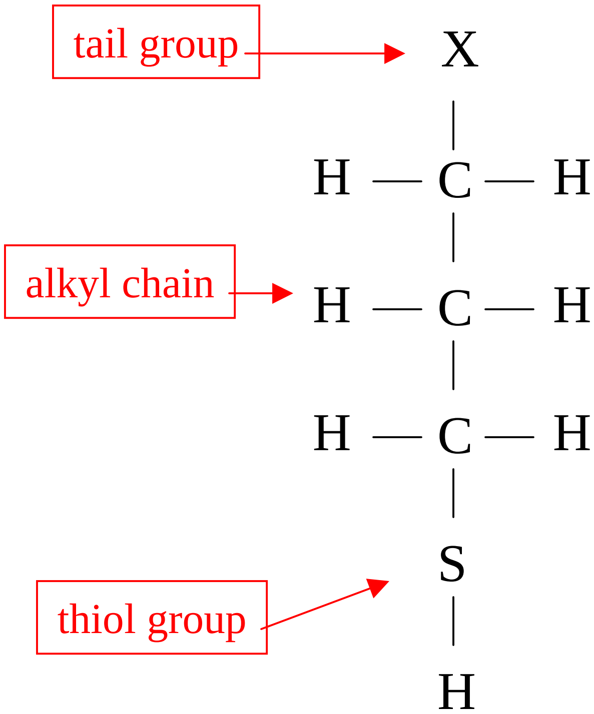
$$\phi \approx \frac{qa}{\varepsilon}$$

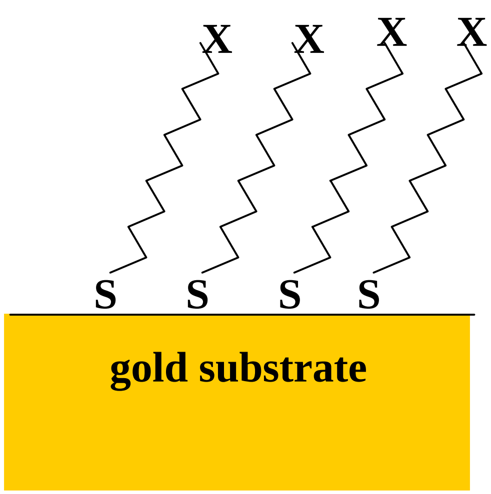
$$\sigma = \varepsilon_0 \frac{\phi_\alpha - \phi_\beta}{h}$$

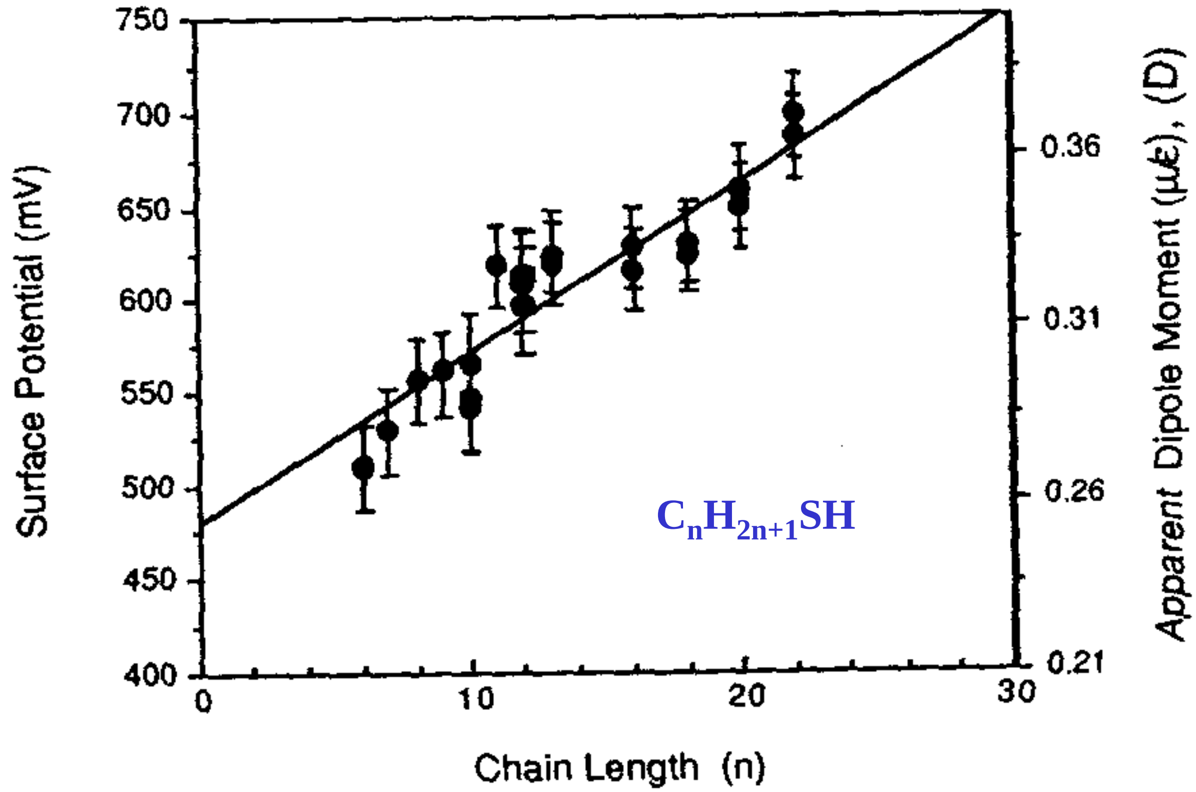
$$\Delta\sigma = \varepsilon_0 (\phi_\alpha - \phi_\beta) \Delta\left(\frac{1}{h}\right)$$

Kelvin method

Adsorbates carry electric dipoles



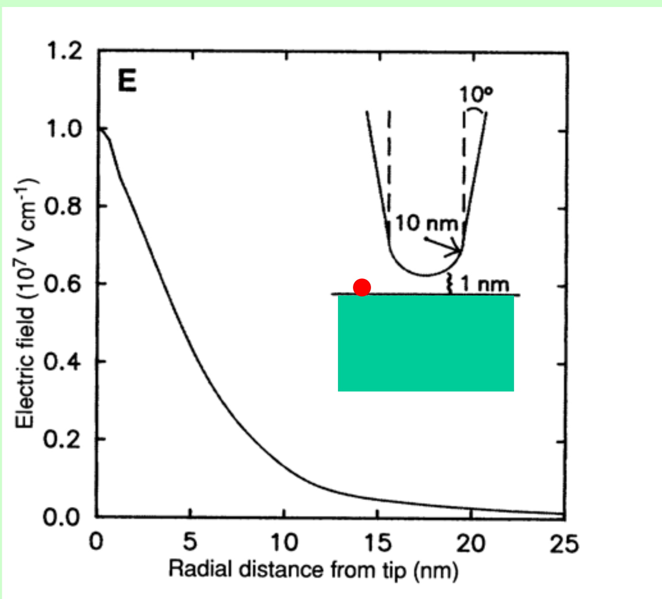


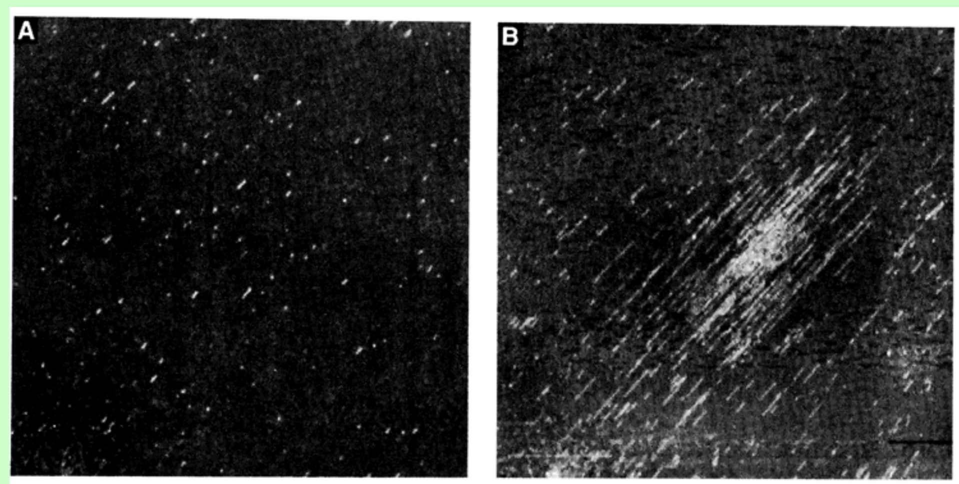


Evans, Ulman, Chem. Phys. Lett. 170, 462 (1990)

Cesium on GaAs

Whitman et al.
Science 251, 1206 (1991)

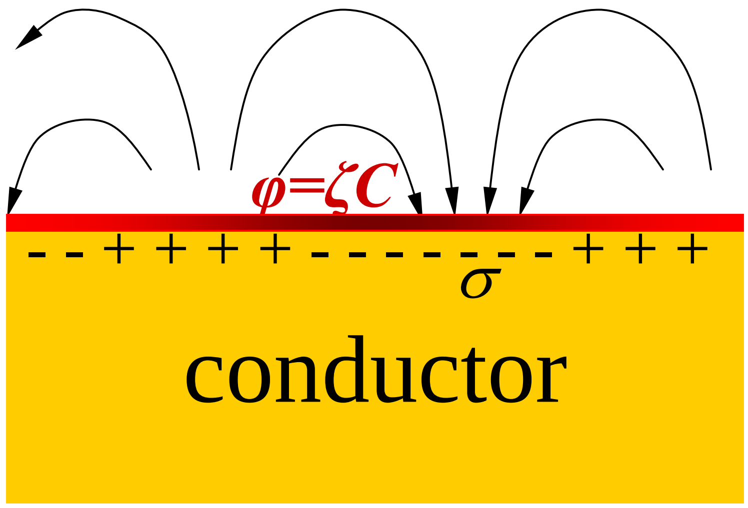




350 nm

3V for 0.1s

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

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

Electrostatic B.V.P.

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

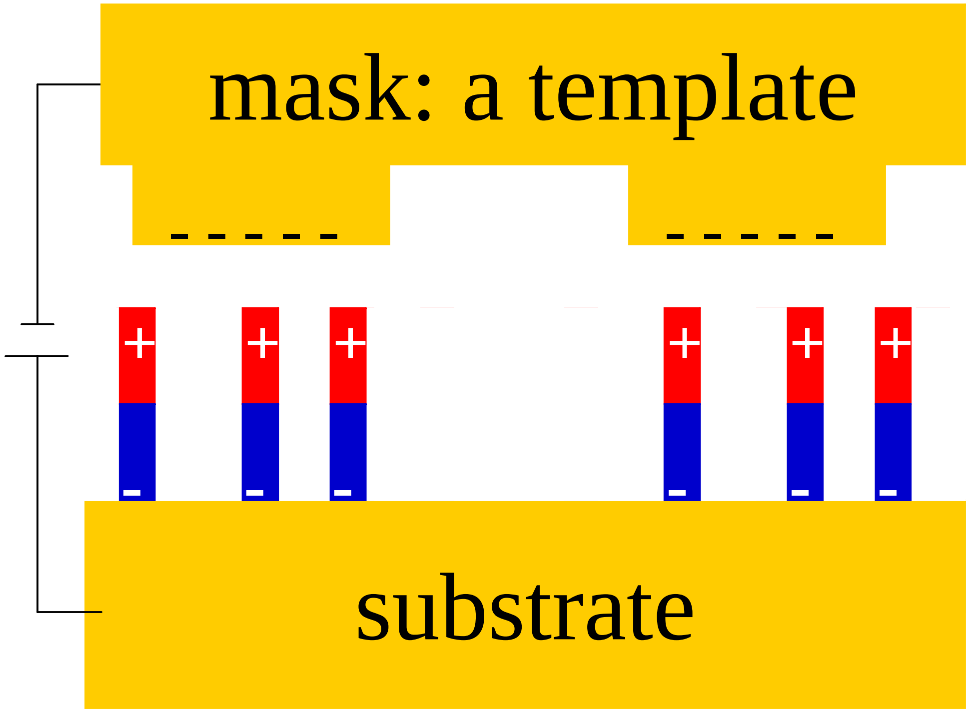
$$\Psi(x_1, x_2, 0) = \varphi(x_1, x_2) = \zeta C(x_1, x_2)$$

Ψ is prescribed at electrodes

Charge at the surface

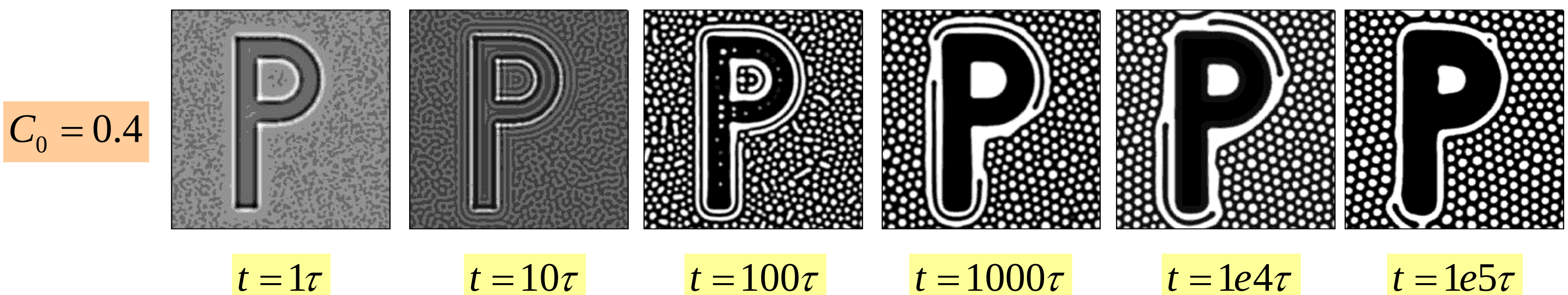
$$\sigma(x_1, x_2) = -\varepsilon\frac{\partial\Psi}{\partial x_3}, \quad x_3 = 0$$

Suo, Gao, Scoles, JAM, in press



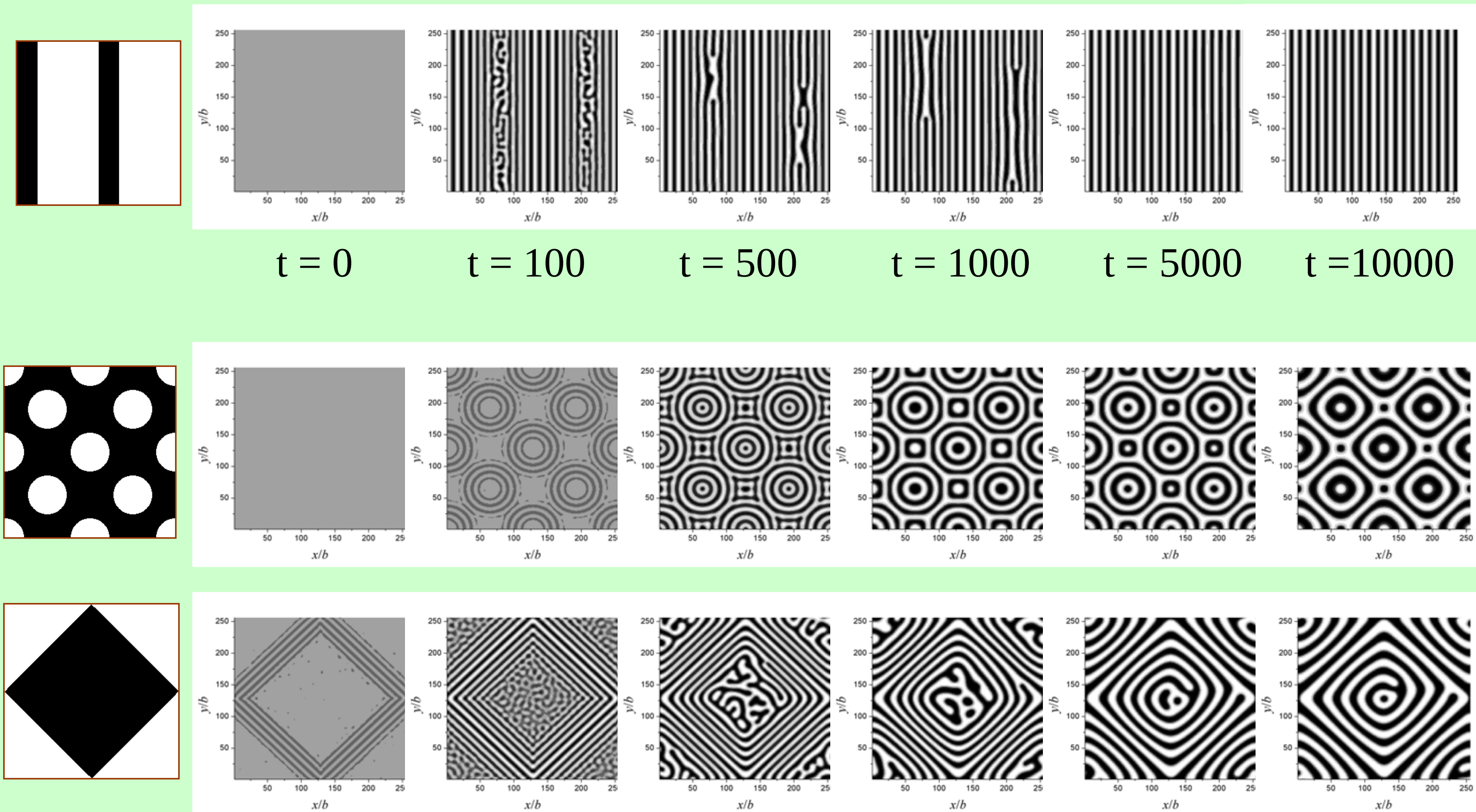
Gao & Suo, JAP, **93,** 4276-4282 (2003).

Pattern on the mask

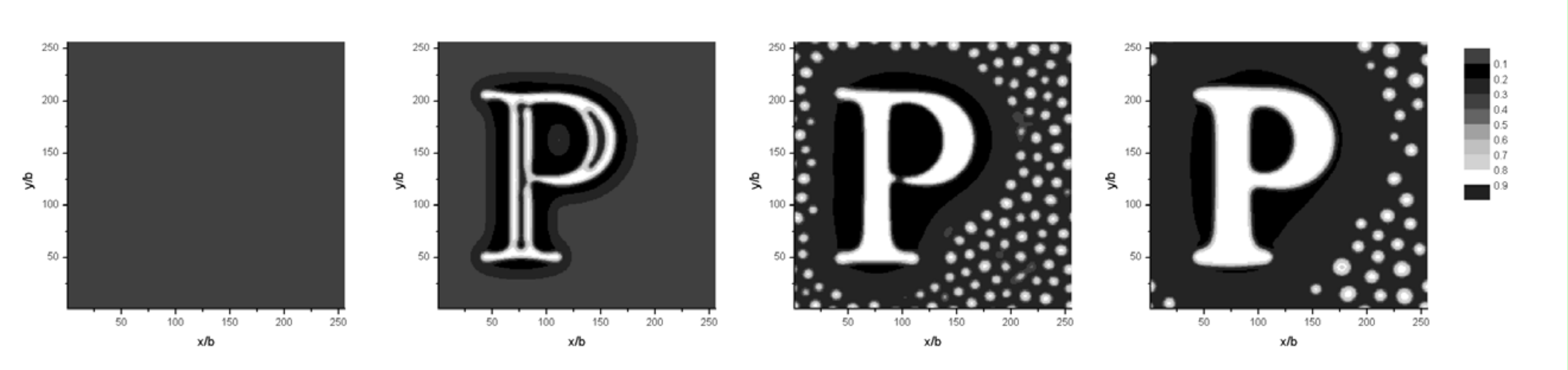


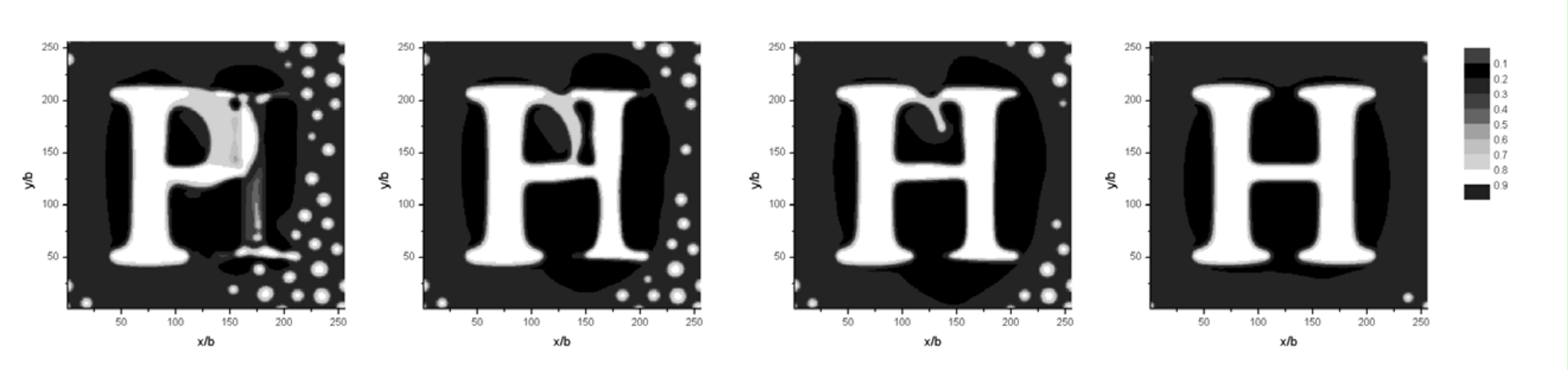
Write one book, print many copies

Field-Directed Assembly



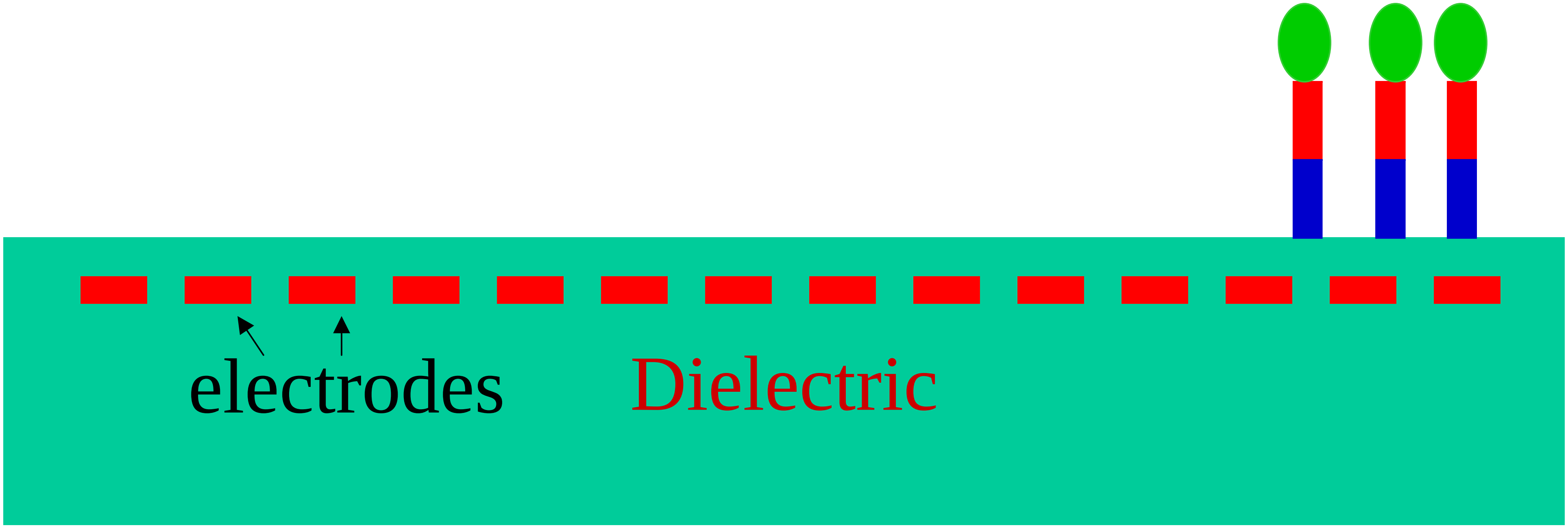
Re-Configurable Assembly (RCA)

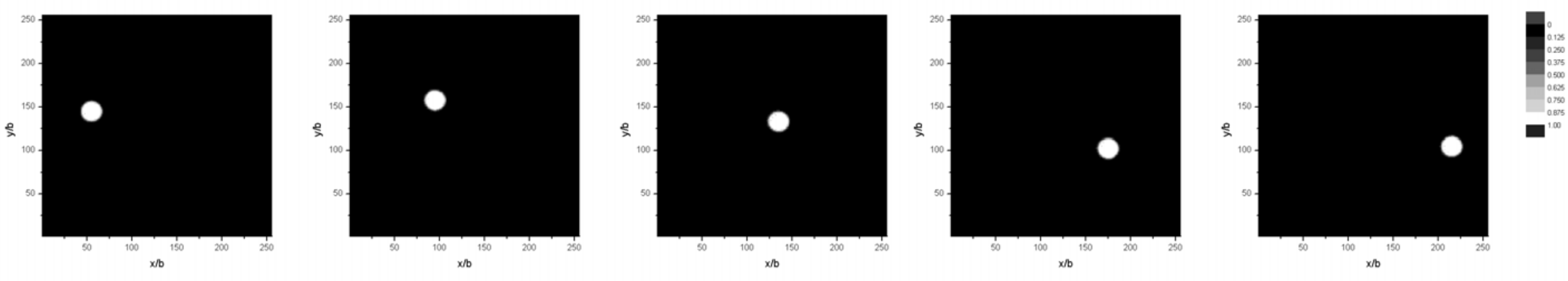




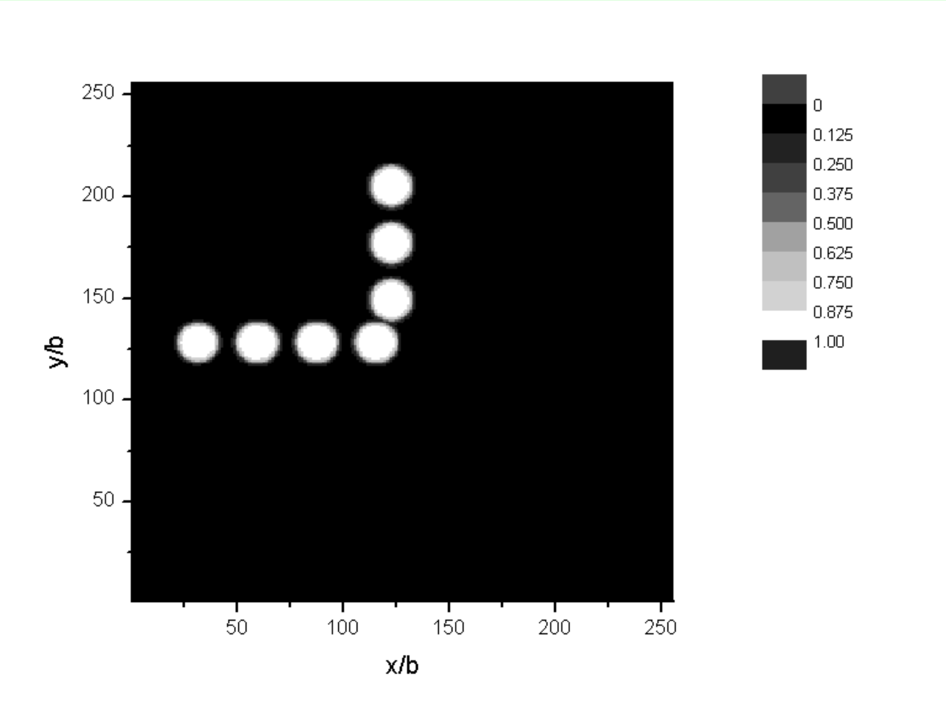
W. Hong

The molecular car



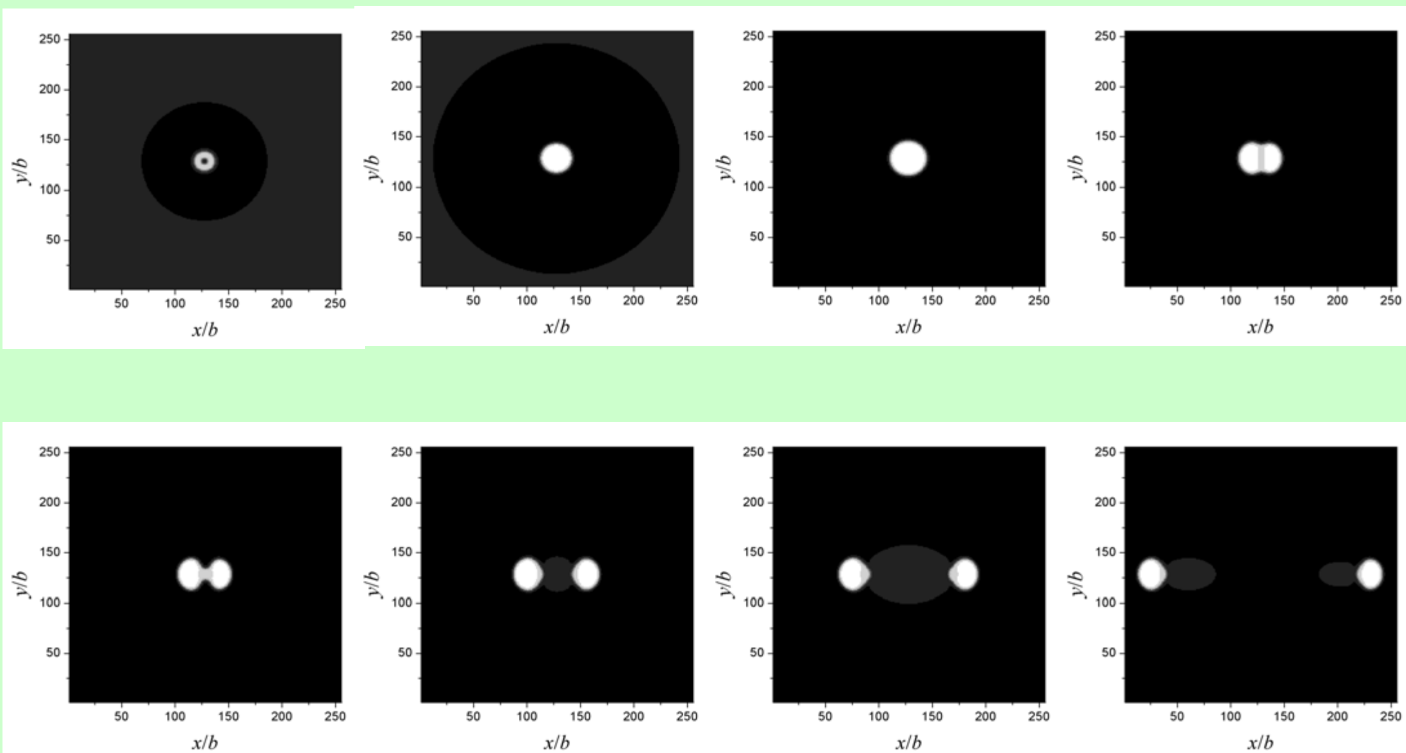


Turning



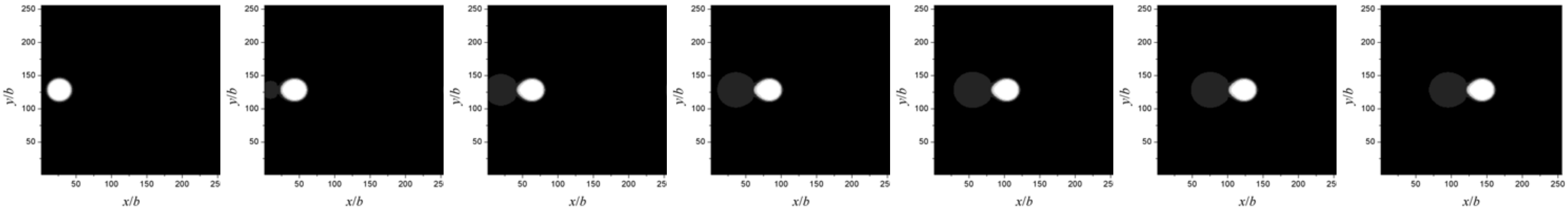
250
200
150
100
50
y/b
50
100
150
200
250
x/b
0
0.125
0.250
0.375
0.500
0.625
0.750
0.875
1.00

Splitting (or merging)

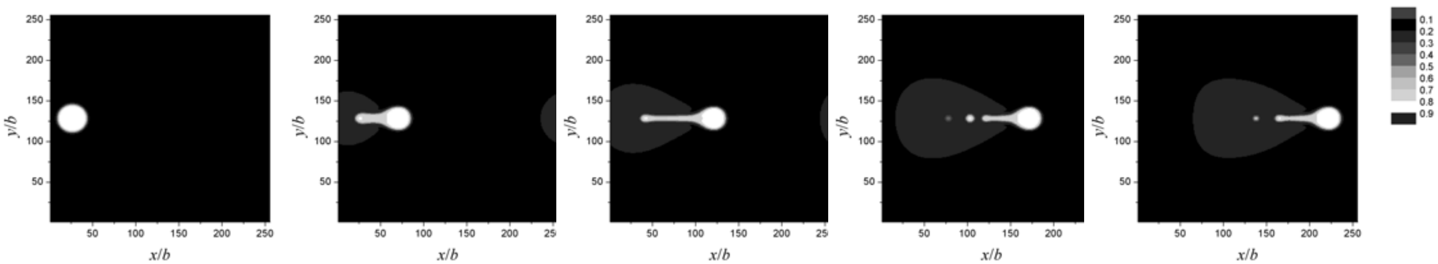


Speeding

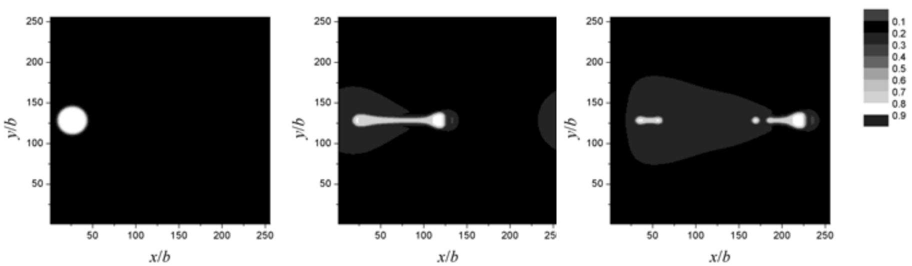
$v = 0.02$



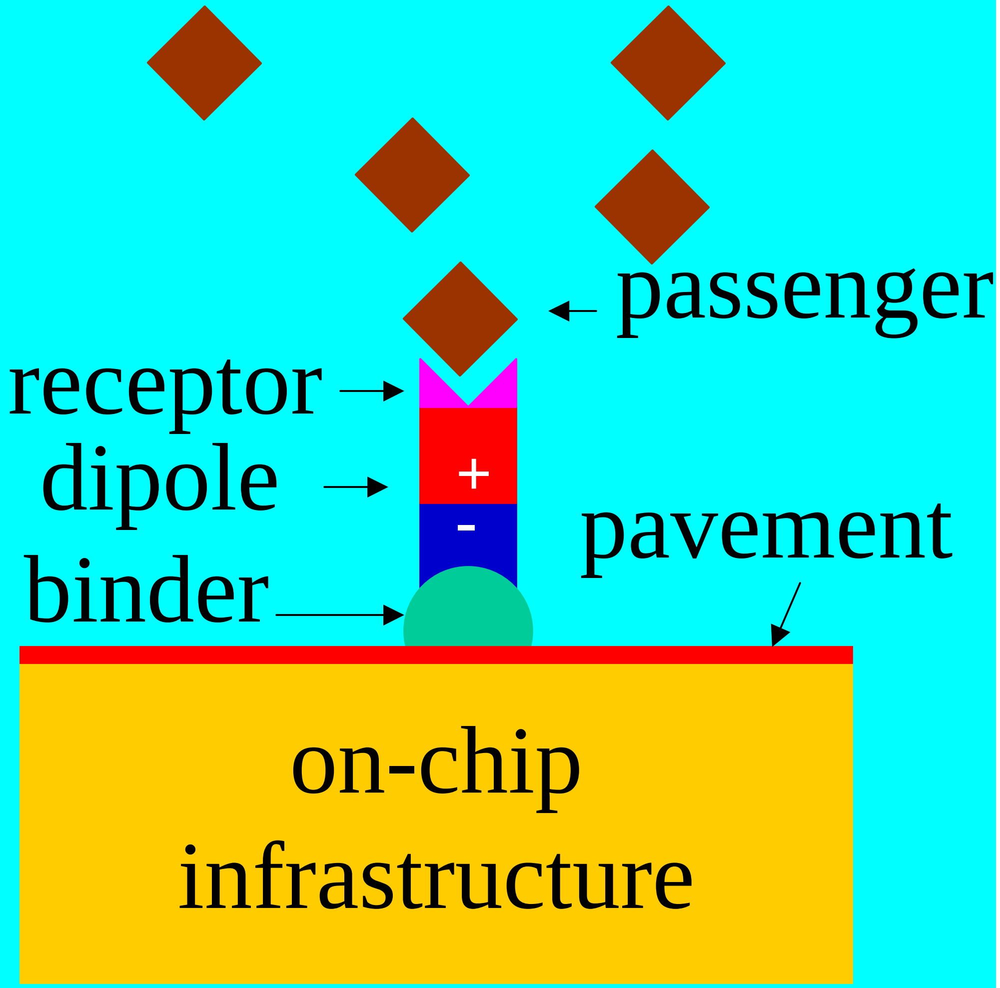
$v = 0.05$



$v = 0.1$

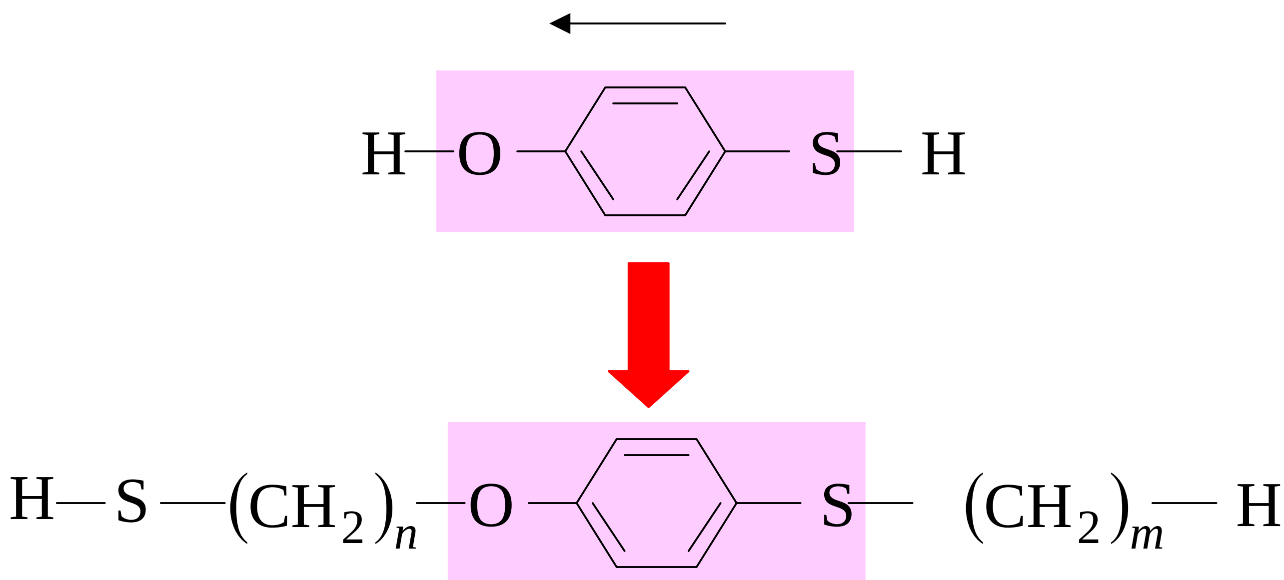


Modular architecture



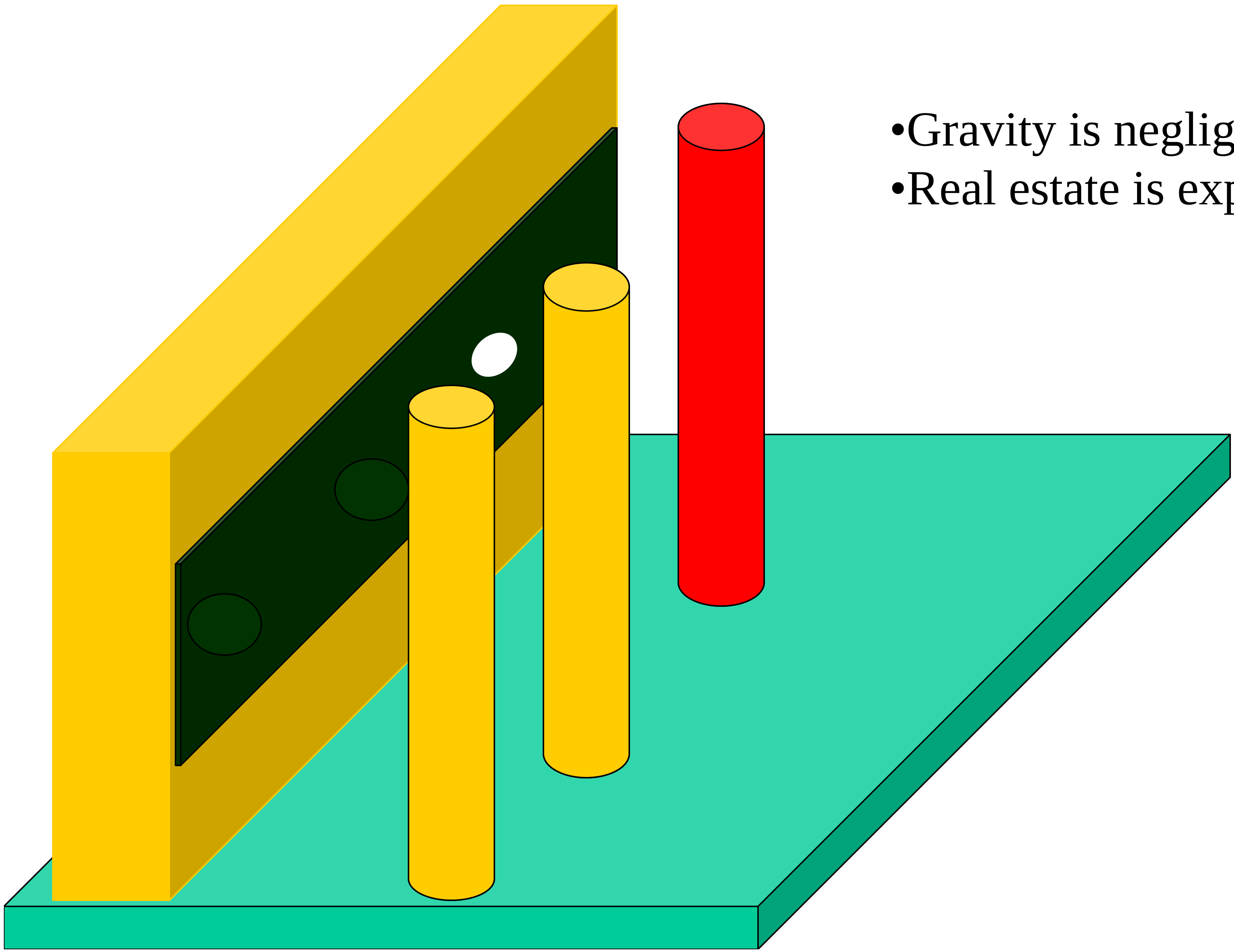
Add a dipole to a molecule

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



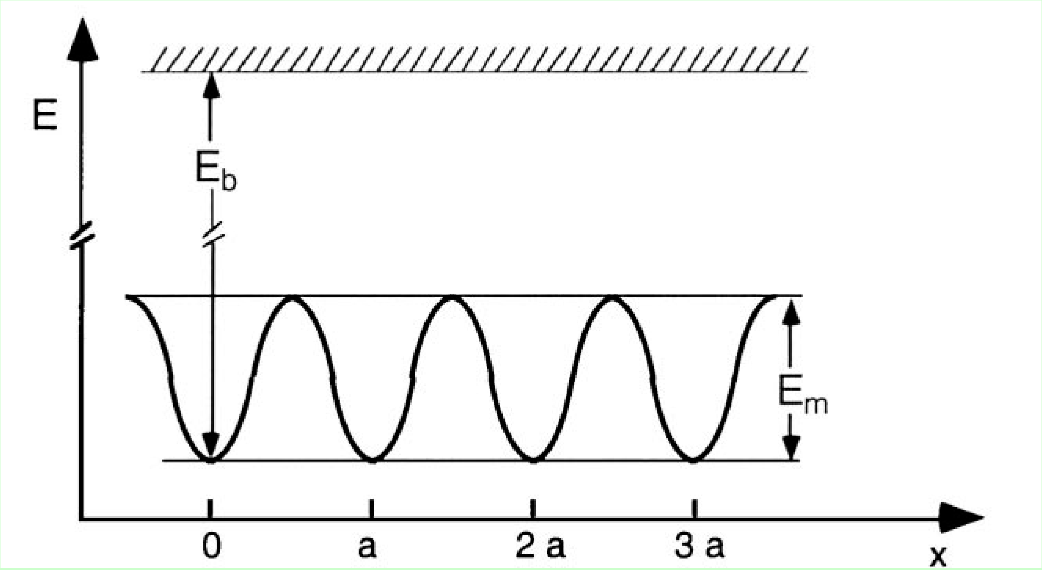
Evans, Urankar, Ulman, Ferris, J. Am. Chem. Soc., 113 4121 (1991)

Highway-on-a-wall



- Gravity is negligible
- Real estate is expensive

Adsorption and Mobility



$E_b \sim 1\text{eV}$

$E_m \sim 0.1\text{eV}$

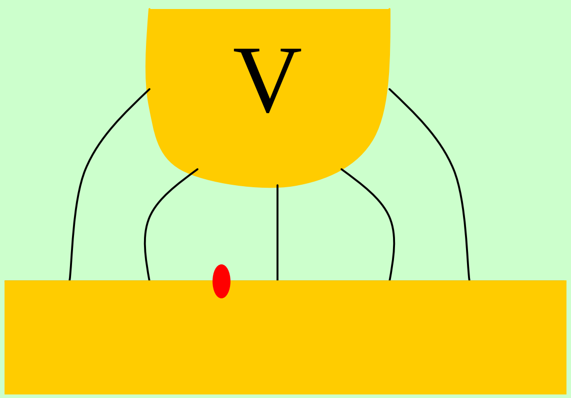
$kT = 0.025\text{eV}$

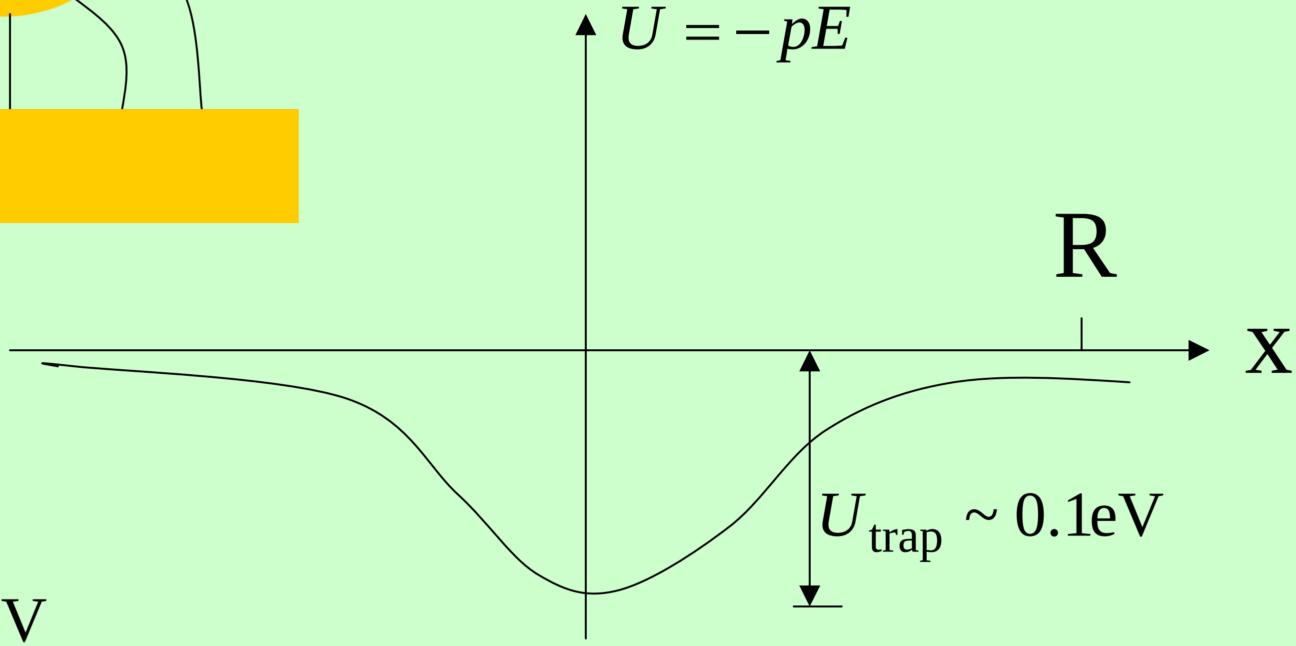
Strong adsorption: deep well, $E_b >> kT$

High mobility: small E_m, $D \sim \nu a^2 \exp\left(-\frac{E_m}{kT}\right)$

Barth, Surface Science Report 40, 75 (2000).

The Authority of Electrode





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

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

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

More numbers

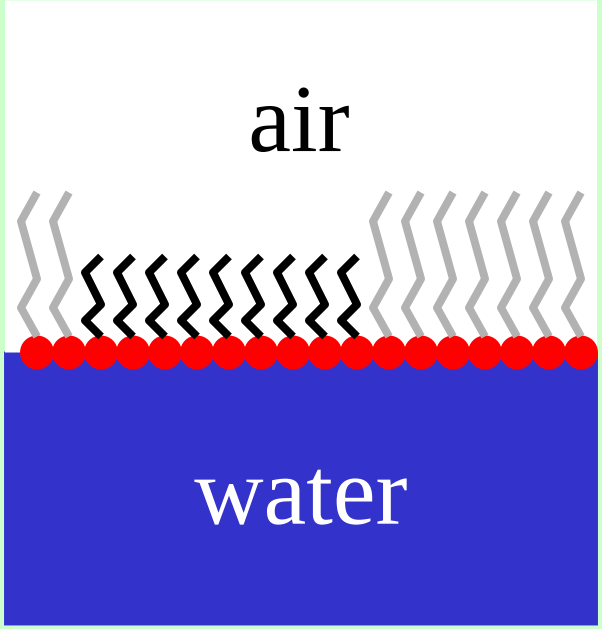
$$D \sim \nu a^2 \exp\left(-\frac{E_m}{kT}\right) \sim \left(10^{13}\,/\,\mathrm{s}\right)\left(10^{-10}\,\mathrm{m}\right)^2 \exp\left(-\frac{E_m}{0.025\mathrm{eV}}\right)$$

$$= \left(10^{-7}\,\mathrm{m}^2/\mathrm{s}\right)\exp\left(-40E_m\right)$$

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

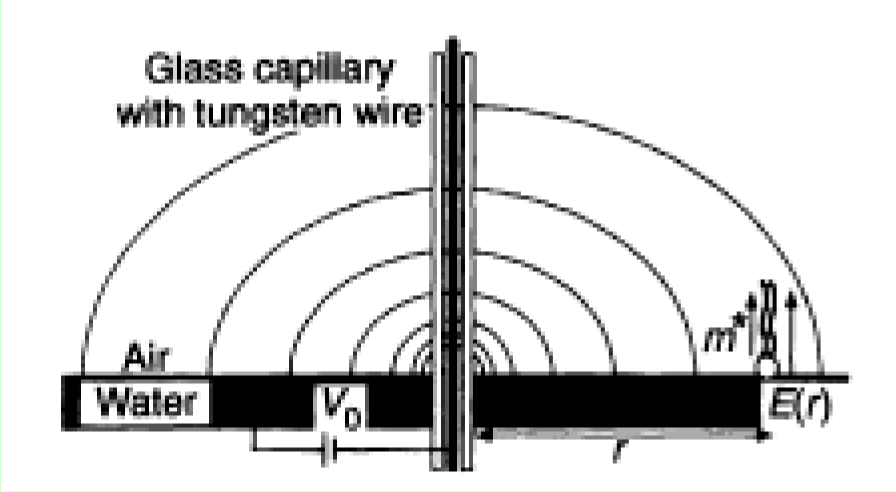
E_m	0.1 eV	0.5 eV	1.0 eV
D	$10^{-9}\,\mathrm{m}^2/\mathrm{s}$	$10^{-16}\,\mathrm{m}^2/\mathrm{s}$	$10^{-25}\,\mathrm{m}^2/\mathrm{s}$
$X = \sqrt{2Dt}$	$10^{-5}\,\mathrm{m}$	$10^{-8}\,\mathrm{m}$	$10^{-13}\,\mathrm{m}$
$u = \frac{D}{kT} f$	$10^{-1}\,\mathrm{m/s}$	$10^{-8}\,\mathrm{m/s}$	$10^{-17}\,\mathrm{m/s}$

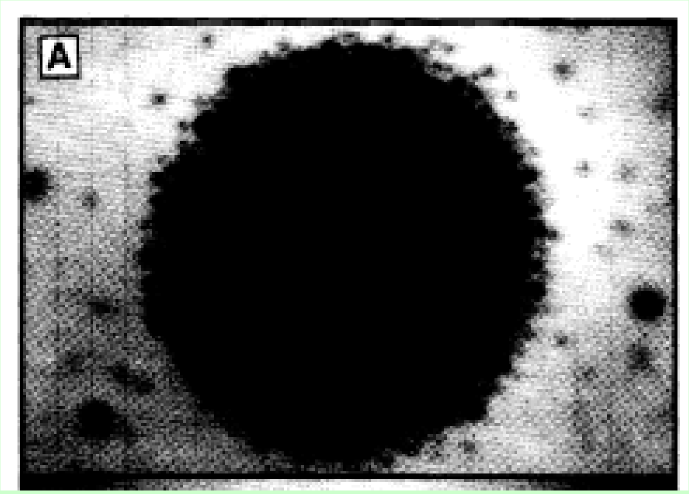
Molecular boat?



Lipids on air/water interface

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



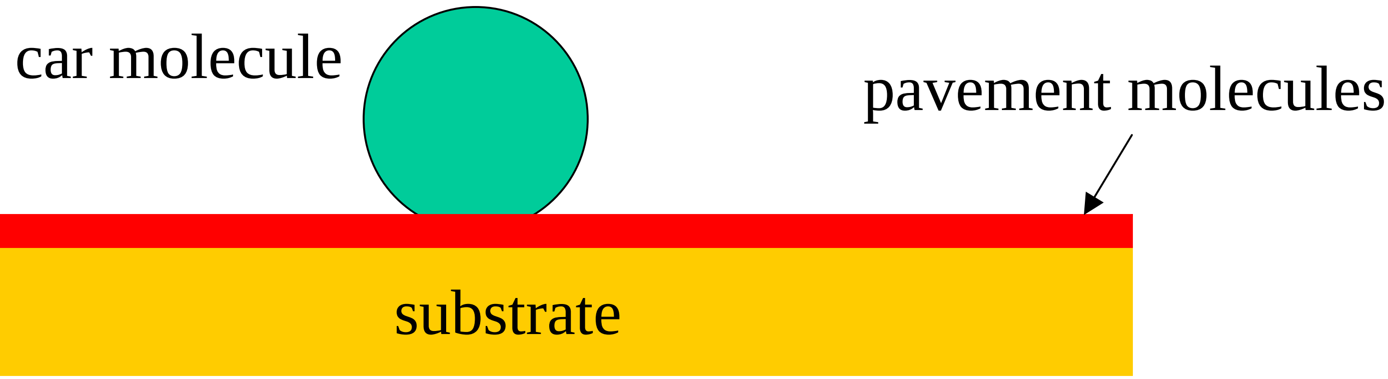


Why the molecular car now?

- **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.

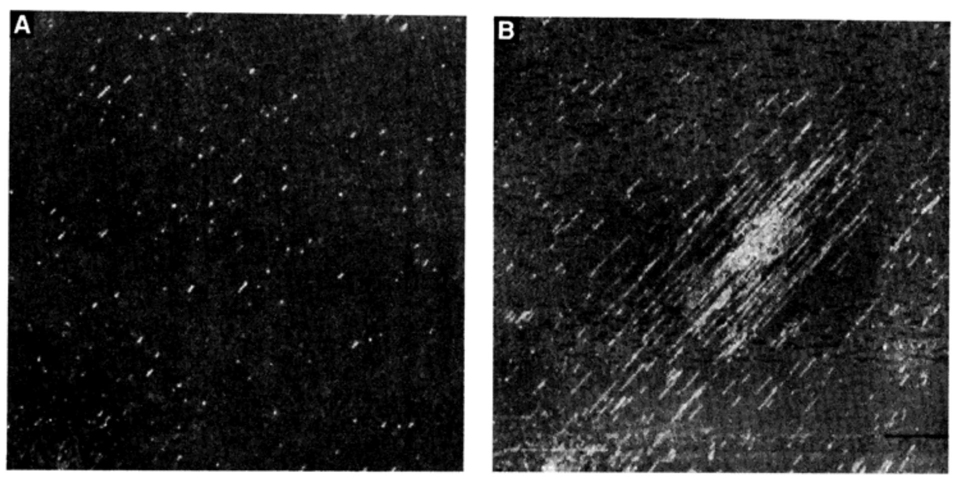
Suo, Chen, Maynard, Saif, Sehitoglu

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).

Summary

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

- Self-assembly.
- Guided assembly.
- Molecular car.

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