Electric field-induced self-assembly

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Forces that move adsorbates

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

A molecular capacitor:

\[ \phi \approx \frac{q a}{\varepsilon} \]

Kelvin method

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

\[ \Delta \sigma = \varepsilon_0 (\phi_\alpha - \phi_\beta) \Delta \left( \frac{1}{h} \right) \]
Adsorbates carry electric dipoles


C\textsubscript{n}H\textsubscript{2n+1}SH

Cesium on GaAs

Whitman et al.
Science 251, 1206 (1991)
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

\[
g(C) = \Lambda k T \left[ C \ln C + (1-C) \ln(1-C) + \Omega \mathcal{O}(1-C) \right]
\]

Electrostatic B.V.P.

\[
\nabla^2 \Psi = 0
\]

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

\(\Psi\) 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
Pattern on the mask

Write one book, print many copies

Gao & Suo, JAP, 93, 4276-4282 (2003).
Field-Directed Assembly
Re-Configurable Assembly (RCA)

W. Hong
The molecular car
electrodes  Dielectric
Turning
Splitting (or merging)
Speeding

\[ \nu = 0.02 \]

\[ \nu = 0.05 \]

\[ \nu = 0.1 \]
Modular architecture

receptor → dipole → binder → on-chip infrastructure

passenger → pavement
Add a dipole to a molecule

\[ p = 0.9 \times 10^{-29} \text{ Cm} \]

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, $E_b \gg kT$

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

The Authority of Electrode

\[ U = -pE \]

\[ kT = 0.025 \text{eV} \]

\[ E \sim \frac{V}{d} \sim \frac{(1 \text{V})}{(10^{-9} \text{m})} = 10^9 \text{V/m} \]

\[ p \sim ea \sim (10^{-19} \text{C})(10^{-10} \text{m}) = 10^{-29} \text{Cm} \]
More numbers

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

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

<table>
<thead>
<tr>
<th>( E_m )</th>
<th>0.1 eV</th>
<th>0.5 eV</th>
<th>1.0 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D )</td>
<td>( 10^{-9} \text{ m}^2/\text{s} )</td>
<td>( 10^{-16} \text{ m}^2/\text{s} )</td>
<td>( 10^{-25} \text{ m}^2/\text{s} )</td>
</tr>
<tr>
<td>( X = \sqrt{2Dt} )</td>
<td>( 10^{-5} \text{ m} )</td>
<td>( 10^{-8} \text{ m} )</td>
<td>( 10^{-13} \text{ m} )</td>
</tr>
<tr>
<td>( u = \frac{D}{kT} f )</td>
<td>( 10^{-1} \text{ m/s} )</td>
<td>( 10^{-8} \text{ m/s} )</td>
<td>( 10^{-17} \text{ m/s} )</td>
</tr>
</tbody>
</table>
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.
In search of engines, wheels, and pavements

Car molecule

Pavement molecules

Substrate

Scanning probe: an imaging tool and a loading tool

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

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

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