10: Electrostatics in solution

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Announcements

- Video assignment discussion/questions
  - Example: [http://vimeo.com/3315489](http://vimeo.com/3315489)
- PS2 due next Monday (Feb/22)
Recap: small-scale flows

- Wall friction grows nonlinearly as flow scale (e.g., pipe diameter) decreases
- However, when wall friction dominates, we must consider the nature of molecule-wall interactions, called **slip**
- We define flow regimes by Knudsen number,
  \[ \text{Kn} = \frac{\lambda}{L_o} \text{ Gases, } l = \text{mean free path} \]
  \[ \text{Kn} = \frac{b}{L_o} \text{ Liquids, } b = \text{slip length} \]

- We can superimpose slip upon a no-slip model

\[
Q_{i,s} = -\pi \frac{dp}{dz} \left( \frac{R^4}{8\mu} + \frac{sR^3}{2\mu} \right)
\]
What’s the molecular origin of slip?

- Fluid-fluid interactions are stronger than fluid-wall interactions (e.g., hydrophobicity).
- Surface roughness traps gas molecules dissolved in the liquid, creating a lubrication layer at the wall. Here, what happens at high Re?
- Molecules “hop” between minimum-energy sites in the wall lattice; therefore slip is a rate process and slip length depends on temperature.

Measuring gas flows in microchannels

They measured $10^{-12}$ kg/s
$10^{-4}$ cm$^3$/s
Fig. 10. Helium mass flow for 1.33-μm channel (95% confidence intervals indicated). The solid curve is the solution to (21), assuming full tangential momentum accommodation, and the dashed curve is the solution to (21) setting $\kappa = 0$ (no-slip solution).

Flow through CNTs

Fig. 1. (A) Schematic of the fabrication process. Step 1: microscale pit formation (by KOH etching). Step 2: catalyst deposition/annealing. Step 3: nanotube growth. Step 4: gap filling with low-pressure chemical vapor–deposited Si$_3$N$_4$. Step 5: membrane area definition (by XeF$_2$ isotropic Si etching). Step 6: silicon nitride etch to expose nanotubes and remove catalyst nanoparticles (by Ar ion milling); the membrane is still impermeable at this step. Step 7: nanotube uncapping (reactive ion etching); the membrane begins to exhibit gas permeability at this step. (B) SEM cross section of the as-grown DWNTs (CNTs). (C) SEM cross section of the membrane, illustrating the excellent gap filling by silicon nitride. (D) Photograph of the open membrane areas; inset shows a close-up of one membrane. (E) Photograph of the membrane chip that contains 89 open windows; each window is 50 µm in diameter.

Flow through CNTs

Fig. 4. Air (red) and water (blue) permeability as measured for three DWNT membranes (DW#1, 2, and 3) and a polycarbonate membrane (PC). Despite considerably smaller pore sizes, the permeabilities for all DWNT membranes greatly exceed those of the polycarbonate membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore diameter (nm)</th>
<th>Pore density (cm⁻²)</th>
<th>Thickness (μm)</th>
<th>Enhancement over Knudsen model* (minimum)</th>
<th>Enhancement over no-slip, hydrodynamic flow† (minimum)</th>
<th>Calculated minimum slip length‡ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DWNT 1</td>
<td>1.3 to 2.0</td>
<td>≤0.25 × 10¹²</td>
<td>2.0</td>
<td>40 to 120</td>
<td>1500 to 8400</td>
<td>380 to 1400</td>
</tr>
<tr>
<td>DWNT 2</td>
<td>1.3 to 2.0</td>
<td>≤0.25 × 10¹²</td>
<td>3.0</td>
<td>20 to 80</td>
<td>680 to 3800</td>
<td>170 to 600</td>
</tr>
<tr>
<td>DWNT 3</td>
<td>1.3 to 2.0</td>
<td>≤0.25 × 10¹²</td>
<td>2.8</td>
<td>16 to 60</td>
<td>560 to 3100</td>
<td>140 to 500</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>15</td>
<td>6 × 10⁸</td>
<td>6.0</td>
<td>2.1</td>
<td>3.7</td>
<td>5.1</td>
</tr>
</tbody>
</table>

*From (18). †From (26). ‡From (29).
Extreme slip flow through CNTs

### Table 1 | Pressure-driven flow through aligned MWCNT membrane

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Initial permeability*</th>
<th>Observed flow velocity†</th>
<th>Expected flow velocity†</th>
<th>Slip length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.58</td>
<td>25</td>
<td>0.00057</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>1.01</td>
<td>43.9</td>
<td>0.00057</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>9.5</td>
<td>0.00015</td>
<td>39</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.35</td>
<td>4.5</td>
<td>0.00014</td>
<td>28</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>0.088</td>
<td>1.12</td>
<td>0.00077</td>
<td>13</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.44</td>
<td>5.6</td>
<td>0.00052</td>
<td>9.5</td>
</tr>
<tr>
<td>Decane</td>
<td>0.053</td>
<td>0.67</td>
<td>0.00017</td>
<td>3.4</td>
</tr>
</tbody>
</table>

MWCNT, multiwalled carbon nanotube. For details of methods, see supplementary information. *Units, cm$^3$ per cm$^2$ min bar. †Flow velocities in cm s$^{-1}$ at 1 bar. Expected flow velocity is that predicted from conventional flow.

Importance of gas damping in MEMS: DMD micromirrors
Mirror dynamics at various ambient pressures

FIGURE 7.2. Dynamic response of the $DMD^{TM}$ mirrors subject to a step pulse under various air pressures. (The data were obtained by Dr. Larry Hornbeck (1988); Courtesy of Texas Instruments)
Today’s agenda

- How surfaces become charged in solution
- Modeling the electrical “double layer”
- Competition between electrostatic repulsion and VDW attraction forces (DLVO theory) → stability vs. coagulation
- Nanofluidic transistors
- Electrophoresis
Today’s readings (ctools)

Nominal:
- Hiemenz and Rajagopalan, excerpt on “The electrical double layer and double-layer interactions”, from Principles of Colloid and Surface Chemistry
- Karnik et al., “Electrostatic control of ions and molecules in nanofluidic transistors”

Extras:
- Israelachvili, excerpt on “Electrostatic forces between surfaces in liquids”, from Intermolecular and Surface Forces
  → same topics as Hiemenz above
- Bouzigues et al., “Nanofluidics in the Debye layer at hydrophilic and hydrophobic surfaces”
  → measurements of slip length on charged surfaces
Surfaces become charged in solution –WHY?

- Ionization or dissociation of surface groups, e.g., -COOH $\rightarrow$ -COO$^-$ + H$^+$
- Adsorption of ions from solution

$\rightarrow$ Charged surfaces are balanced by counterions in solution, so electrical neutrality is preserved
$\rightarrow$ Some counterions adsorb to the surface, and others are distributed near the surface within the double layer
$\rightarrow$ This is very important for interactions between nanostructures in solution
Ion concentration profiles

Israelachvili, Mulvaney.
total electric neutrality
planar, isolated, constant potential

\[ \nabla^2 \psi = -\frac{\rho^4}{\varepsilon} \]

permittivity

\[ \varepsilon = \varepsilon_r \varepsilon_0 \]

charge density

\[ \frac{e}{H^3} \]

\[ \rho^4(x, y, z) \]

constant

\[ \frac{d^2 \psi}{dx^2} = -\frac{\rho^4(x)}{\varepsilon} \]

\[ \text{Bcs: } \psi(0) = \psi_0, \quad \psi(\infty) = 0 \]
Ions in solution obey Boltzmann distribution

\[
\frac{n_i}{n_i, \infty} = \exp \left( \frac{-z_i e \psi}{k_b T} \right)
\]

charge electron

thermal energy \( \frac{1}{2} \)

valence of ion

\[\text{Na}^+, z = 1\]
\[\text{Na}^+, z = 2\]

\[\rho^+ = z_i \epsilon n_i\]

\[\text{Na}^+, \text{Cl}^-\]

Multiple ions add charge densities

\[
\rho^+ = \sum z_i \epsilon n_i = \sum z_i \epsilon n_i, \infty \exp \left( \frac{-z_i e \psi}{k_b T} \right)
\]

up concentration in bulk
Poisson / Boltzmann eqn.

\[ \frac{d^2 \psi}{dx^2} = -\frac{e}{\varepsilon} \sum z_i n_i,\infty \exp \left\{ \frac{-z_i e \psi}{k_b T} \right\} \]

\[ \text{if } z_i e \psi \ll k_b T, \quad \frac{k_b T}{e} e 29 e k = 25.7 \text{ MV} \]

"low surface potential"

\[ \frac{d^2 \psi}{dx^2} = \left( \frac{e^2}{\varepsilon k_b T} \right) \sum z_i^2 n_i,\infty \psi \]

\[ k^{-1} \text{ Debye length} \]

\[ \text{"debye layer thickness"} \]

\[ k^{-1} = \left( \frac{e^2}{\varepsilon k_b T} \right) \sum z_i^2 n_i,\infty, \quad \frac{d^2 \psi}{dx^2} = k^2 \psi \quad [\text{nm}] \]

\[ \psi = \psi_0 e^{-kx}, \quad \gamma = \gamma_0 e^{-kx} \]
\[ K^{-1} = 3.04 \text{ nm}^{-1} \]

Unit conversion:

\[ n_i = 1000 \, M_i \, N_A \]

\[ \text{ions/m}^3 = \left( \frac{L}{M^3} \right) \left( \text{mol/L} \right) \left( \text{ions/mol} \right) \]

\[ K = \left[ \left( \frac{1000 \, e^2 \, N_A}{k_B T} \right) \left( \sum i^2 \, M_i \right) \right]^{1/2} \]
Effect of electrolyte concentration and valence (Debye-Huckel approximation)
Comparison of double layer models

Exact solution (Gouy-Chapman)

Large $\Psi_0$

Debye-Huckel approximation

0.01M solution of 1:1 electrolyte

Hiemenz and Rajagopalan.
## Limiting solutions for small (spherical) and large (locally planar) particles

Hiemenz and Rajagopalan.

<table>
<thead>
<tr>
<th>Small $\kappa a$</th>
<th>Large $\kappa a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi(r) = \psi_0 \frac{a}{r} \exp[-\kappa(r-a)]$</td>
<td>$\psi(x) = \psi_0 \exp(-\kappa x)$</td>
</tr>
<tr>
<td>$\nabla^2 \psi = \frac{2zn^\infty e}{\varepsilon_r \varepsilon_0} \sinh \left( \frac{e\psi}{kT} \right)$</td>
<td>$\tanh \left( \frac{ze\psi(x)}{4kT} \right) = \tanh \left( \frac{ze\psi_0}{4kT} \right) \exp(-\kappa x)$</td>
</tr>
</tbody>
</table>

where $\kappa^2 = \frac{2z^2 e^2 n^\infty}{\varepsilon_r \varepsilon_0 kT}$
Repulsion between overlapping layers

Hiemenz and Rajagopalan.
\[ F = 0 \]
\[ F_x = -\frac{dp}{dx} \]
\[ F_{el} = -\rho^* \frac{d\psi}{dx} \]
\[ F_x + F_{el} = 0 \]
\[ \frac{dp}{dx} + \rho^* \frac{d\psi}{dx} = 0 \]
\[ \frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon} \left( \frac{d\psi}{dx} \right) \left( \frac{d^2\psi}{dx^2} \right) \]
\[ \frac{d}{dx} \left( p - \frac{\varepsilon}{2} \left( \frac{d\psi}{dx} \right)^2 \right) = 0 \]
\[ \frac{d}{dx} \left( \frac{1}{2} \frac{d}{dx} \left( \frac{d\psi}{dx} \right)^2 \right) = 0 \]
\[ = \text{constant} \]
\[ F_K = 64 k_b T n_\infty \Phi_0^2 \exp(-K_h) \]

\[ \Phi_0 = \left( \frac{\Delta - 1}{\Delta + 1} \right) \]

\[ \Delta = \exp\left( \frac{2eV}{2k_b T} \right) \]

\[ K \propto n_\infty^{-1/2} \]

\[ F_K = c_1 n_\infty \exp\left(-c_2 n_\infty^{1/2}\right) \]

\[ \Delta \text{ separation} \]

\[ \text{Gouy-Chapman solution} \]

\[ 1:1 \text{ electrolyte} \]

\[ \uparrow n_\infty \]

\[ \downarrow \text{dominate} \]
\[ V = \int_{0}^{\infty} dV = \int_{0}^{\infty} -F_{R}(h) \, dh \]

Energy interaction

\[ U(h) = \frac{64 k_{B} T \eta_{o} \beta_{o}^{2}}{E_{S}} k^{-1} \exp(-h k) \]

Total interaction energy: \[ U_{tot} = U_{ES} + U_{vdw} \]

"Equilibrium": \[ \frac{dU_{tot}}{dD} = 0 \]

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Stabilization of colloids: DLVO theory

FIGURE 2.24 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other.\textsuperscript{27}
Net interaction energy governs stability

Fig. 12.12. Schematic energy versus distance profiles of DLVO interaction. (a) Surfaces repel strongly; small colloidal particles remain ‘stable’. (b) Surfaces come into stable equilibrium at secondary minimum if it is deep enough; colloids remain ‘kinetically’ stable. (c) Surfaces come into secondary minimum; colloids coagulate slowly. (d) The ‘critical coagulation concentration’. Surfaces may remain in secondary minimum or adhere; colloids coagulate rapidly. (e) Surfaces and colloids coalesce rapidly.
a) Strong long-range repulsion, fully dispersed
  - highly-charged surface in dilute electrolyte; long Debye length
b) Kinetically stable at secondary minimum or fully dispersed
  - higher electrolyte concentration than (a)
c) Slow aggregation
  - low surface charge density
d) Rapid coagulation
e) Effectively no repulsion
Example: interaction between a pair of Au particles

FIGURE 5.4 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation, for several particle radii. Hamaker constant $= 25 \times 10^{-20} \text{ J}$, $I = 1 \text{ mM}$, $\psi_0 = 0.10 \text{ V}$, $a = 1.0 \text{ nm, } 3.0 \text{ nm, and } 10.0 \text{ nm}$, Debye length $= 10 \text{ nm}$. Note that the secondary minimum is negligible for nanoparticles, but becomes important above 10 nm.
Example: interaction between a pair of Au particles

**FIGURE 5.5** Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation for several surface potentials. Hamaker constant $= 25 \times 10^{-20}$ J, $I = 10$ mM, $a = 10$ nm, Debye length = 3 nm. Note that a zeta potential, $|\zeta| > 50$ mV, is necessary for colloid stability because of the high Hamaker constant.
Zeta potential is typically measured

Think about slip..
Overlapping double layers in a nanogap

Figure 1: Schematic diagram and equivalent circuits of conventional electrode polarization (a) & (b) and nanogap electrodes (c) & (d).

Figure 5: Electric potential between two electrodes for various channel width; the concentration of solution is 0.1mM of 1:1 electrolyte.
Nanofluidic transistors

Electrophoresis: placing particles in gaps

- Motion is diffusive (Brownian) far from gap
- Substrate-particle repulsion dominates at low V
- “Spherical” DEP region grows and dominates at high V
- EP-induced oscillation only important at low frequencies

$V = 1.5 \text{ V} \rightarrow 2\text{ V} \rightarrow 3\text{ V}$

$g = 30 \text{ nm} \rightarrow 80 \text{ nm} \rightarrow 125 \text{ nm}$

Dielectrophoresis for positioning CNTs

Electric field-directed growth of CNTs

(a) Poly-Si

(b) Poly-Si

(c) Poly-Si

(d) Poly-Si

Quartz

Alignment force vs. thermal vibration