Streams and Droplets

Fawwaz Habbal
School of Engineering and Applied Sciences
Harvard University
Basic Principles
Field Driven Fluids
Domain of Studies

Fick’s law of diffusion
Concentration \( c \)
- Osmosis
- Convection
- (aqueous) medium, Flow velocity \( v_m \)

Maxwell’s equation
- Electrophoresis
- \( \rho, J \) : source
- E and B field
- Streaming potential

Navier-Stokes’ equation
Electro-Driven Fluids

- Electroosmotic (EO)
- Magnetohydrodynamic (MHD)
- Electrohydrodynamic (EHD)
- Electrowetting
Stokes Radius:

Is the radius of a hard sphere that diffuses at the same rate as the molecule.
A Particle in an Electric Field

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Extended molecule have a larger Stokes' radius than the more compact molecule.
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Stokes Radius
A Particle in an Electric Field

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In liquids the Stokes' radius (of a perfect sphere) is

\[ r = \frac{K_B T}{6\pi \eta D} \]

The frictional coefficient is determined by the size and shape of the molecule under consideration.
Apply a voltage on ions of different charges. They move in different directions.
Assume that no slip at walls, and no shear though out the volume.
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Rate of flow is linear with driving force (electric field $E$), Velocity ($U$) of free charges:

$$U = \mu E \quad qE = (6\pi \eta r)U$$

Mobility $\mu = \frac{q}{6\pi \eta r}$

This is a simplistic view - incorrect, E field is distorted around the particle.
ELECTRICAL DOUBLE LAYER

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: every ion is surrounded by a k^{-1} wide ionic atmosphere.
Fluids

Charges and Electric Fields
SURFACE CHARGES

Fixed Charge Groups on Surface:
1. **Direct ionization or dissociation** of surface chemical groups
2. **Adsorption**
   van der Waals, hydrophobic, or ionic interactions, e.g. lipids, polyelectrolytes (charged polymers)
Net Surface Charge - Fixed Charge Groups on Surface:

1. Direct ionization or dissociation of surface chemical groups
   - weak acid: $\text{COOH} \rightarrow \text{COO}^- + \text{H}^+$ (dependent on pH)
     
     ![Carboxylic Acid Structure](image)

   - strong acid: sulfate $\text{SO}_4^{2-}$ (independent of pH)
     cartilage glycoaminoglycan (chondroitin-6-sulfate)
SURFACE CHARGES

Net Surface Charge - Fixed Charge Groups on Surface:
2- **Adsorption** via:
   - van der Waals,
   - hydrophobic,
   - ionic interactions, e.g. lipids, polyelectrolytes (charged polymers)
Electronic neutrality is maintained:

\[
\text{# of counter ions} = \text{# of surface charge groups} + \text{# of bulk ions}
\]
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1923 **Debye** and **Huckel** [Phys. Z. 1923, 185-206]: every ion is surrounded by a $k^{-1}$ wide ionic atmosphere.

1924 **Stern** [Elektrochem. 1924, 508-516] followed Helmholtz and Gouy-Chapman:
some of the counter-ions are fixed to the charged surface, building a $D$ wide adsorption layer, while the rest form a diffuse layer.
Electrostatic Double Layer Repulsion

- Layer thickness is a few Å, reflects the size of the charged surface groups and bound counter ions.
- When two similarly charged electrical double layers are compressed together and overlap (D1<D2), repulsive force occurs.
• Mobile counter ions are in rapid motion,
• Attractive ionic forces pulling them to the surface create concentration gradient
• They gain translational /rotational entropy by moving away from surface
• Diffusion down the concentration gradient $\rightarrow$ these effects are balanced so their is no net flux of any ionic species
For charged particles, this force arises from a diffuse, highly mobile surface layer of counter ions.

An exponential repulsion exists on compression since the counter ions want to retain their translational mobility.
Electrostatic Double Layer Repulsion

- Helmholtz model (1853)
- Guoy-Chapman model (1910-1913)
- Stern model (1924)

\[ \Phi_0 \quad \kappa^{-1} \quad X \]
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(zeta potential)
Zeta Potential

- Electrokinetic potential in a colloidal system
- It is a measure of the stability of the fluid

<table>
<thead>
<tr>
<th>Zeta Potential [mV]</th>
<th>Stability behavior of the colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>from 0 to ±5</td>
<td>Rapid coagulation or flocculation</td>
</tr>
<tr>
<td>from ±10 to ±30</td>
<td>Incipient instability</td>
</tr>
<tr>
<td>from ±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>from ±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>more than ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>
Debye Length

\[ W(D) = C e^{-\kappa D} \]

Range of the electrostatic interaction \( \sim 5 \kappa^{-1} \)
Debye Length

In pure water (pH=7), screening from H\(^+\) and OH\(^-\)

\[ L_D = 1 \, \mu m \]

In KCl (1 mole) in water,

\[ L_D = 0.3 \, \text{nm} \]
Electroosmotic Flow

Results is a plug flow

Types of Flow

- Electroosmotic flow velocity is independent of the size, and shape of the channel.

\[ V_{EO} = -\frac{\varepsilon \zeta}{\mu} E_z \]

- In a pressure-driven flow, the flow velocity is a function of \( R^2 \).

\[ V_{Poi} = -\frac{R^2}{4 \mu L} \Delta P \]
Pressure-driven Flow and Electroosmotic Flow

Applied: Pressure gradient

Applied: Electric Field
Pressure-driven Flow and Electroosmotic Flow

DNA Gel Electrophoresis
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- DNA has phosphate backbone which is negatively charged – hence DNA drifts in an E-field
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- The field stretches the molecules and they move in a snake-like fashion through the pores of the gel.
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- Separation $\partial L = \partial \mu E t$
- Resolution of separation $N,$ $N = \mu V/2D$
  - $D$ is the diffusion coefficient.
<table>
<thead>
<tr>
<th>MW</th>
<th>Protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>Myosin</td>
</tr>
<tr>
<td>116</td>
<td>β-galactosidase</td>
</tr>
<tr>
<td></td>
<td>Phosphorylase-B</td>
</tr>
<tr>
<td>97</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>Albumin, bovine serum</td>
</tr>
<tr>
<td>55</td>
<td>Glutamic dehydrogenase</td>
</tr>
<tr>
<td>45</td>
<td>Ovalbumin, chicken egg</td>
</tr>
<tr>
<td>36</td>
<td>Glyceraldehyde 3-phosphate dehydrogenase</td>
</tr>
<tr>
<td>29</td>
<td>Carbonic anhydrase</td>
</tr>
<tr>
<td>24</td>
<td>Trypsinogen</td>
</tr>
<tr>
<td>20</td>
<td>Soybean trypsin inhibitor</td>
</tr>
<tr>
<td>14</td>
<td>α-lactalbumin</td>
</tr>
<tr>
<td>6.5</td>
<td>Aprotinin</td>
</tr>
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