Advantages
1. Atomically smooth
2. Repeatable
3. Clean

An electrofluid interface found at Hg

![Graph](image)

Figure 13.2.1
Electrocapillary curve of drop time vs. potential at a DME in 0.1 M KCl. [Data of L. Meites, J. Am. Chem. Soc., 73, 2035 (1951).]

$t_{max} = \frac{2\pi e \gamma}{mg}$

$\gamma = \text{surface tension}$

Cohesive forces between liquid molecules are responsible for phenomena known as surface tension. Molecules at surface adhere more strongly than ones in bulk so they do not have contacting molecules on the surface.

$\gamma = \frac{\Delta G}{\Delta A} = \text{surface tension}$
Imagine for \( k^+ \):

\[
\Gamma_{k^+(K^+)} = -\left( \frac{2RT}{d\mu_{K^+}} \right)_{E_0, \mu^M}
\]

\[
\mu_{K^+} = \mu_{K^+}^0 + RT \ln a_{K^+}
\]

\[
\Gamma_{k^+(K^+)} = \frac{-1}{RT} \left( \frac{d\mu}{d\ln a_{K^+}} \right)_{E_0, \mu^M}
\]

\[-\sigma^M = \sigma^S = F (\Gamma_{k^+} - \Gamma_{\text{cl}^-}) = (z_i F \Gamma_{K^+} + z_i F \Gamma_{K^-})
\]

**Figure 13.2.5** Surface excesses vs. potential for mercury in 0.1 M KF. Potentials are referenced both to a NCE and the potential of zero charge, \( E_0 \). (From data in D. C. Grahame and B. A. Soderberg, *J. Chem. Phys.*, 22, 449 (1954).)
Figure 13.2.2 Electrocapillary curves of surface tension vs. potential for mercury in contact with solutions of the indicated electrolytes at 18°C. The potential is plotted with respect to the PZC for NaF. [Reprinted with permission from D. C. Graham, Chem. Rev., 48, 441 (1947). Copyright 1947, American Chemical Society.]

Point of zero charge = curve pt. where slope is zero. \((E_{CZT})\)

\[
\sigma^M = \sigma^S = 0 \quad \text{no extra}
\]

\[
\sigma^M = -\left( \frac{2\pi}{3E} \right) \mu_{KCl}, \mu_{Na}
\]

\[
-\frac{d\sigma^M}{dE} = \frac{5}{2} \int \sigma^M d\phi
\]

\[
C_d = \left( \frac{\partial \sigma^M}{\partial E} \right) \quad \text{differential capacitance (slope) } \sigma^M \text{ vs. } E_{CZT}
\]

\[
C_i = \frac{\sigma^M}{E - E_{CZT}} \quad \text{integral capacitance (ratio) total charge density at potential, } E, \text{ to total potential difference}
\]
Remember: \( \sigma^M = - \left( \frac{\partial \psi}{\partial \xi} \right) \) (slope) T vs. E plot = excess charge on metal.

\[ \sigma^M = -F \Gamma_e \quad \text{and} \quad \Gamma_e = \text{excess surface concentration} \]

\[ \sigma^S = -\sigma^M = F \left( \Gamma_{e^+} - \Gamma_{e^-} \right) = - \left[ \varepsilon_i F \Gamma_{e^+} + 2 \varepsilon_i F \Gamma_{e^-} \right] \]

These units of any excess equal each other, hence they counteract the tendency of the surface to contract, and they weaken the surface tension.
Cony-Chapman Theory

* Developed independently - proposed diffuse layer
* Layer of finite thickness containing countervailing charge, electrostatic forces vs. thermal randomization

\[ \eta_i = \eta_i^0 \exp \left( -\frac{z_i e \phi}{RT} \right) \]

\[ \phi = \phi_0 e^{-kx} \]

Figure 13.3.3 Potential profiles through the diffuse layer in the Cony-Chapman model. Calculated for a 10^{-2} M aqueous solution of a 1:1 electrolyte at 25°C. 1/\kappa = 30.4 Å. See equations 13.3.14 to 13.3.16.
\[
\frac{2\Phi}{\partial x} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right) \tanh\left(\frac{z\epsilon\Phi}{2kT}\right)
\]

\[
\frac{\tanh\left(\frac{z\epsilon\Phi}{4kT}\right)}{\tanh\left(\frac{z\epsilon\Phi_0}{4kT}\right)} = e^{-xx}
\]

**Measured** \( \chi = \left(\frac{2n^0e^2\varepsilon^2}{3\varepsilon_0kT}\right)^{1/2} \)

**Diffuse Layer**

**Thickness** (cm)

For dilute solutions, Z:Z electrolyte, 25°C, \( \varepsilon = 78.49 \)

\( \chi = (3.29 \times 10^{-7}) \times C^*^{1/2} \)

\( C^* = \text{mol/L} \)

**Thickness of Diffuse Layer**

<table>
<thead>
<tr>
<th>( C^* (\text{mol}) )</th>
<th>( \frac{1}{\chi} (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>10^{-1}</td>
<td>10</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>30</td>
</tr>
<tr>
<td>10^{-3}</td>
<td>94</td>
</tr>
<tr>
<td>10^{-4}</td>
<td>301</td>
</tr>
</tbody>
</table>

At large \( \Phi_0 \) (highly charged electrode), the drop is precipitous because the diffuse layer is relatively compact.
**Figure 13.3.5** Predicted differential capacitances from the Gouy–Chapman theory. Calculated from (13.3.21) for the indicated concentrations of a 1:1 electrolyte in water at 25°C. Note the very restricted potential scale. The predicted capacitance rises very rapidly at more extreme potentials relative to $E_c$.

\[
\frac{Q}{A} = \sigma^M = 2 \varepsilon_0 \left( \frac{d \sigma}{d \phi} \right)_{\phi=0}
\]

\[
\sigma^M = -\sigma^S = (8 \pi T \varepsilon_0 n)^{1/2} \sinh \left( \frac{z e \phi_0}{2 kT} \right)
\]

\[
\sigma^M = 11.7 C^{1/2} \sinh(19.5 z \phi_0)
\]

\[
\frac{d \sigma^M}{d \phi_0} = \left( \frac{2 \pi^2 e^2 \varepsilon_0 n^2}{6 T} \right)^{1/2} \cosh \left( \frac{z e \phi_0}{2 kT} \right)
\]

\[
C_d = 228 \varepsilon C^{1/2} \cosh(19.5 z \phi_0)
\]
Figure 13.3.6 (a) A view of the differential capacitance in the Gouy-Chapman-Stern (GCS) model as a series network of Helmholtz-layer and diffuse-layer capacitances. (b) Potential profile through the solution side of the double layer, according to GCS theory. Calculated from (3.3.23) for $10^{-2} M$ 1:1 electrolyte in water at 25°C.

$$\Phi_0 (\text{potential relative to bulk}) = \Phi_2 - \left( \frac{d\Phi}{dx} \right)_{x=x_2}$$

$$\sigma^M = -\sigma^S = -\varepsilon \varepsilon_0 \frac{d\Phi}{dx} \bigg|_{x=x_2} = 8\varepsilon \varepsilon_0 n_0 \left( \frac{Q}{2} \right)^{1/2} \sinh \left( \frac{z e \phi_2}{2kT} \right)$$

$$C_d = \frac{d\sigma^M}{d\Phi_0} = \frac{(2\varepsilon \varepsilon_0 e^2 n_0^0 kT)^{1/2} \cosh(ze\phi_2/2kT)}{1 + (x_2 \varepsilon \varepsilon_0 e^2 n_0^0 kT)^{1/2} \cosh(ze\phi_2/2kT)}$$
\[
\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}
\]

*Independent of E (assumed to be)*

*Varies in V-shape with E*

Figure 13.3.7 Expected behavior of \( C_d \) according to GCS theory as the electrolyte concentration changes.

\[
\frac{1}{C_d} = \frac{x_2}{\varepsilon \varepsilon_0} + \frac{1}{\left(2\varepsilon\varepsilon_0 \varepsilon^2 n^2 (2\pi T)^{1/2} \cosh\left(\frac{2\pi}{kT}\right)\right)}
\]

\( C_d \) governed by the smaller of the two components \( C_H \) or \( C_D \).

\[
C_d = \frac{1}{\frac{1}{C_H}} + \frac{1}{\frac{1}{C_D}}
\]
Specific Adsorption

\[ \sigma^+ M = - \sigma^+ S = - [Z_i F \Gamma_{kH_2O} + Z_i F \Gamma_{aB/H_2}] \]

In this case, potential must shift to more negative potential to counterbalance the "extra" negative surface charge by charge in diffuse layer.

\[
\frac{1}{RT} \left( \frac{\partial E_x}{\partial \ln a_{zalt}} \right)_{\sigma^+} = \frac{\partial E_x}{\partial \mu_{zalt}} \left( \frac{\partial \mu_{zalt}}{\partial \sigma^+} \right)
\]

Esin-Markov Coefficient

When \( \frac{\partial E_x}{\partial \mu} = 0 \), no specific adsorption.

---

**TABLE 13.3.2 Potentials of Zero Charge in Various Electrolytes**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration, M</th>
<th>( E_x ), V vs. NCE(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>1.0</td>
<td>-0.472</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.472</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>-0.480</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>-0.482</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.0</td>
<td>-0.556</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>-0.524</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.505</td>
</tr>
<tr>
<td>KBr</td>
<td>1.0</td>
<td>-0.65</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.58</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>-0.54</td>
</tr>
<tr>
<td>KI</td>
<td>1.0</td>
<td>-0.82</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-0.72</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>-0.66</td>
</tr>
<tr>
<td></td>
<td>0.001</td>
<td>-0.59</td>
</tr>
</tbody>
</table>


\(^b\)NCE = normal calomel electrode.

---

PZC shifts with change in electrolyte concentration = evidence for specific adsorption.