Lecture #20 of 26
The Double Layer

Chapter 13
Q: What’s in this set of lectures?
A: B&F Chapter 13 main concepts:

- **Section 1.2.3:** Double layer structure
- **Sections 13.1 & 13.2:** Gibbs adsorption isotherm, Electrocapillar(ity), Surface excess, Lippmann’s equation, Point of Zero Charge
- **Section 13.3:** Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), Gouy–Chapman–Stern
- **Section 13.5:** Specific adsorption
Flat? ... Eh; not really.

Why were both of these measured using fluoride salts?

In order to minimize specific adsorption!

Figure 13.3.1  Differential capacitance vs. potential for NaF solutions in contact with mercury at 25°C. [Reprinted with permission from D. C. Grahame, Chem. Rev., 41, 441 (1947). Copyright 1947, American Chemical Society.]
For the purposes of this class, we want to understand the microscopic origin of the *most prominent features* of these $C_d$ vs. $E$ data:

a) A minimum in $C_d$ exists at the pzc.

b) $C_d$ is quasi-constant at potentials well positive and well negative of the pzc.

c) This quasi-constant $C_d$ is larger when $E$ is (+) of pzc than when it is (−) of pzc.

d) $C_d$ increases with salt concentration at all potentials, and the "dip" near the pzc disappears.
... do you want to understand the details of $C_d$ away from the pzc?
Do you want to understand *the hump*? There is a book for that...

John Bockris

Three traditional models for double layer structure:

1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

... let’s take a look at each of these...
Models of Electrical Double Layer:

1) **The Helmholtz Model**: this is the simplest possible model. It postulates that ions (anions *and* cations) occupy a plane located a distance, $d$, from the electrode surface, and that the effective "dielectric constant" operating in the double layer is potential independent:

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

... for a parallel plate capacitor, $C$ is independent of $E$ because the permittivity of the capacitor, $\varepsilon \varepsilon_0$, and its spacing, $d$, are both independent of applied potential...

$\text{http://www.cartage.org.lb/}$
... the Helmholtz model says that the electrical double layer acts like, and looks like *(rare in *EChem*), a parallel plate capacitor...

\[ C_d = \frac{\varepsilon \varepsilon_0}{d} \]

... \( C_d \) is therefore independent of \( E \) because the permittivity of the capacitor, \( \varepsilon \varepsilon_0 \), and its spacing, \( d \), are both independent of applied potential...

... Question: *What value for \( C_d \) do we calculate by plugging in to this model the known "dielectric constant" (permittivity = IUPAC) of water?*
... recall, here’s what the double layer really looks like...
... and here’s what the double layer looks like in the Helmholtz approximation...

Then, what’s $\varepsilon_r$?

Now, $4\text{Å} = 0.4 \times 10^{-9} \text{ m}$

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$
... first, what’s $\varepsilon_r$ for water? Well, that depends... *can it rotate?*

for water at 20 °C...

78.4

5.9

Scenario is where electric field oscillates too quickly for molecules to reorient.

Scenario is where electric field oscillates slow enough that molecules do reorient.

**Electrochemical impedance spectroscopy range**
... and here’s what the double layer looks like in the Helmholtz approximation...

Answer: $\varepsilon_r \approx 78$

(static relative permittivity)

$C_d = \frac{\varepsilon \varepsilon_0}{d}$

$4\text{Å} = 0.4 \times 10^{-9} \text{ m}$
... and here’s what the double layer looks like in the Helmholtz approximation...

\[ C_d = \frac{\varepsilon \varepsilon_0}{d} \]

\[ C_d = \frac{(78)(8.854 \times 10^{-12} \text{ F/m})}{0.4 \times 10^{-9} \text{ m}} = 1.73 \text{ F/m}^2 \]

\[ 1.73 \text{ F/m} \times \frac{10^6 \mu \text{F}}{F} \times \frac{m^2}{100^2 \text{ cm}} = 172.6 \mu \text{F/cm}^2 \]

Is this what is observed? **Nope!**... OK, now what?

\[ 4 \text{Å} = 0.4 \times 10^{-9} \text{ m} \]
... now, what if the water dielectric is saturated, and thus fixed? ... so that water cannot rotate...

\[ C_d = \frac{\varepsilon \varepsilon_0}{d} \]

\[ C = \frac{(6)(8.854 \times 10^{-12} \text{ F/m})}{0.4 \times 10^{-9} \text{ m}} = 0.133 \text{ F/m}^2 \]

\[ 0.133 \text{ F/m} \times \frac{10^6 \mu\text{F}}{F} \times \frac{m^2}{100^2 \text{ cm}} = 13.3 \mu\text{F/cm}^2 \]

... much more reasonable!

4Å = 0.4 \times 10^{-9} \text{ m}
... if the Helmholtz model is correct, we’d get this *exactly*:

\[
\sigma^M = -\left(\frac{d\gamma}{dE}\right)_{\mu_i} \quad C_d = \left(\frac{\partial\sigma^M}{\partial E}\right)
\]
... here are electrocapillary data for various electrolytes...
... hey, you can already see that the Helmholtz Model fails a little...
... mostly on the left...

**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. Grahame, *Chem. Rev.*, 41, 441 (1947). Copyright 1947, American Chemical Society.]
Notwithstanding, notice particularly the following:

a) the \( \gamma \) vs. \( E \) parabola is independent of salt...
   ... at potentials negative of the pzc...

b) ... but strongly dependent on salt positive of pzc...

c) ... and pzc itself depends on the electrolyte...
   ... we’ll get to this shortly...
... if $C$ is dependent on potential, then the $\gamma$ vs. $E$ parabola will be asymmetric...

... for example...

differentiate

differentiate
... and a flat $C_d$ is in no way observed... we need a more sophisticated model...

Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433$V) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].

H.H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press, 2004, Figure 5.13
... and specifically one where the model of the double layer captures these elements?

these $C_d$’s are not constant

... and there is a minimum in the $C_d$ at the pzc...

Fig. 5.13 Capacity of a mercury electrode in a KF solution ($pzc = -0.433\,\text{V}$) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].
Three traditional models for double layer structure:

1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

... let’s take a look at each of these...
Models of Electrical Double Layer:

2) **The Gouy–Chapman Model**: this model adopts all the same assumptions used in Debye–Hückel Theory, which are the following:

a) ions are considered to be point charges; their polarizability is neglected

b) interactions between ions, and between ions and the electrode are purely electrostatic (i.e. no specific (chemical) adsorption); thus, the IHP and OHP will *not* exist in this model since these planes explicitly require finite ion size = polarizability)

c) the metal is considered a planar surface with a surface charge density, $\sigma^M$

d) ions are distributed according to Maxwell–Boltzmann statistics...
RECALL: Debye–Hückel equation

*(in water at 25 °C)*

\[-\log \gamma_x = \frac{0.51 z_x^2 \sqrt{I}}{1 + 3.3 \alpha_x \sqrt{I}}\]

\[\alpha = \text{effective diameter of hydrated ion (nm)}\]

... the derivation is long... but the main idea is that you balance thermal motion (Boltzmann) with electrostatics (Poisson/Gauss)...

Physicist & P-Chemist

Peter Joseph William Debye
(1884–1966)

Erich Armand Arthur Joseph Hückel
(1896–1980)

from Wiki
... d) ions are distributed according to Maxwell–Boltzmann statistics...

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

where \( e \) is the elementary charge, and \( \phi \) is the electric potential relative to the bulk solution.

*Figure 13.3.2* View of the solution near the electrode surface as a series of laminae.
the charge density, i.e. charge per unit volume, \( \rho(x) \), is defined as:

\[
\rho(x) = \sum_i n_i z_i e
\]

... so substituting from the last slide...

\[
\rho(x) = \sum_i z_i e n_i^0 \exp\left(\frac{-z_i e \phi}{kT}\right)
\]

... and now the Poisson Equation gives us another expression for \( \rho(x) \):

\[
\rho(x) = -\varepsilon \varepsilon_0 \frac{d^2 \phi}{dx^2}
\]

... substituting, we get the Poisson–Boltzmann Equation (no Maxwell)...

\[
\frac{d^2 \phi}{dx^2} = -\frac{e}{\varepsilon \varepsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \phi}{kT}\right)
\]
... if we apply the Poisson–Boltzmann Equation to a 1:1 electrolyte, we obtain the following (see B&F, pp. 547–548):

\[ \frac{d\phi}{dx} = -\left(\frac{8kTn^0}{\varepsilon\varepsilon_0}\right)^{1/2} \sinh\left(\frac{ze\phi}{2kT}\right) \]

... and if we further assume that \( \phi^0 \) is small, we get...

\[ \phi = \phi^0 \exp(-\kappa x) \]

... where

\[ \kappa = \left(\frac{2n^0 z^2 e^2}{\varepsilon\varepsilon_0 kT}\right)^{1/2} \]

... here, \( \kappa \) has units of 1/distance... we commonly refer to \( \kappa^{-1} \) as \( \lambda_D \), the "Debye (screening) length" characterizing the solution
... Does a more sophisticated model of the double layer better capture features observed experimental?

... the electric potential variation near the electrode under the Gouy–Chapman Model (compare with Helmholtz Model...)

\[ \phi = \phi^0 \exp(-\kappa x) \]

\[ \lambda_D = \frac{1}{K} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2n^0 z^2 e^2}} \]

Figure 13.3.3 Potential profiles through the diffuse layer in the Gouy–Chapman model.

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.3
... how does the Gouy–Chapman Model do in terms of predicting the correct value of $C_d$?

$$C_d = \frac{d\sigma^M}{d\phi_0} = \left(\frac{2z^2e^2\varepsilon\varepsilon_0n^0}{kT}\right)^{1/2} \cosh\left(\frac{ze\phi_0}{2kT}\right)$$

**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 $E_z$.  

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 13.3.5
About Gouy–Chapman Theory we can say the following:

a) it predicts a “dip” in $C_d$, that becomes more capacitive with increased ionic strength = \textit{Good!}

b) but it predicts a $C_d$ that is WAY too high as the potential becomes far from the pzc = \textit{Bad!}...

c) and the $C_d$ is symmetrical about the pzc (\textit{why?}); this is not what is observed experimentally...
Getting close?

... Notably, near the pzc?

---

**Fig. 5.13** Capacity of a mercury electrode in a KF solution ($pzc = -0.433V$) with the respective Gouy-Chapman capacity [Paolo Galleto, EPFL thesis].
**Example:** How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO₄ solution?

**Answer:** The diffuse layer thickness is approximated by \( \lambda_D \). Let’s calculate it.

\[
\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2n^0 z^2 e^2}}
\]

\[
= \sqrt{(78)(8.854 \times 10^{-12} \ C^2 / Jm)(1.381 \times 10^{-23} J / K)(298 K)}
\]

\[
= \sqrt{2(100(6.022 \times 10^{23}) / m^3)(1)^2 (1.602 \times 10^{-19} \ C)^2}
\]

\[
n^0 = \frac{0.1 \text{ moles}}{dm^3} \frac{10^3 \text{ dm}^3}{m^3} \frac{6.022 \times 10^{23} \text{ ions}}{\text{mole}} = 6.022 \times 10^{25} \text{ ions} / m^3
\]
Answer: The diffuse layer thickness is approximated by $\lambda_D$. Let’s calculate it.

$$
\lambda_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon \varepsilon_0 kT}{2n^0 z^2 e^2}}
$$

$$
= \sqrt{(78)(8.854 \times 10^{-12} \text{ C}^2 / \text{Jm})(1.381 \times 10^{-23} \text{ J/K})(298 \text{ K})}
\frac{2(100(6.022 \times 10^{23}) / \text{m}^3)(1)^2 (1.602 \times 10^{-19} \text{ C})^2}{2(100(6.022 \times 10^{23}) / \text{m}^3)(1)^2 (1.602 \times 10^{-19} \text{ C})^2}
$$

$$
= 9.589 \times 10^{-10} \text{ m} = 9.6 \text{ Å}
$$

$\approx 1 \text{ nm}$... about the same thickness as the compact layer...

Wow!
example: How thick is the diffuse layer from an electrode in, say, aqueous 0.1 M NaClO$_4$ solution?

**TABLE 13.3.1  Characteristic Thickness of the Diffuse Layer$^a$**

<table>
<thead>
<tr>
<th>C* (M)$^b$</th>
<th>1/κ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
</tr>
<tr>
<td>10$^{-1}$</td>
<td>9.6</td>
</tr>
<tr>
<td>10$^{-2}$</td>
<td>30.4</td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>96.2</td>
</tr>
<tr>
<td>10$^{-4}$</td>
<td>304</td>
</tr>
</tbody>
</table>

$^a$For a 1:1 electrolyte at 25°C in water.

$^b$C* = $n^0/N_A$ where $N_A$ is Avogadro’s number.
... and related, this means that the electrostatic repulsion between charged colloid particles, for example, is very short range at high electrolyte concentrations... suspensions of these particles frequently precipitate
Three traditional models for double layer structure:

1) Helmholtz

2) Gouy–Chapman (GC)

3) Gouy–Chapman–Stern (GCS)

... let’s take a look at each of these...
3) **The Gouy–Chapman–Stern Model**: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

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

Parallel plate capacitance of the compact layer from the (H)elmholtz model

Potential-dependent non-parallel-plate capacitance of the (D)iffuse layer from the GC model

Potential-dependent non-parallel-plate capacitance of the (d)ouble layer from the GCS model
Models of Electrical Double Layer:

3) **The Gouy–Chapman–Stern Model**: basically, the idea is to use both the Helmholtz Model and the Gouy–Chapman Model in series:

Parallel plate capacitance of the compact layer from the (H)elmholtz model

Potential-dependent non-parallel-plate capacitance of the (D)iffuse layer from the GC model

\[ C_H \quad C_{D}(E) \quad = \quad C_{d}(E) \]

But, wait a minute! This is modeling just one interface with two sides, but there are two capacitors (and thus in total seemingly four sides)... what gives?

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

If it barks like a dog, and smells like a dog, then maybe we should call it a dog... **What are the units?**

This means that the electric potential drop across the Helmholtz Layer (inside of the OHP) will be linear, and a quasi-exponential potential drop will extend from this point and into the bulk solution...
... our three models for the potential distribution near a charged electrode immersed in an electrolyte solution...

Helmholtz (H)  Gouy–Chapman (GC)  Gouy–Chapman–Stern (GCS)

http://electrochem.cwru.edu/
Hermann Ludwig Ferdinand von Helmholtz
(1821–1894)

Physician & Physicist

Louis Georges Gouy
(1854–1926)

Physicist

David Leonard Chapman
(1869–1958)
P-Chemist

Otto Stern
(1888–1926)
Nobel Prize (Physics, 1943)

Physicist

from Wiki
splice a Helmholtz capacitor to a GC capacitor, right here... and then thank Stern!

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 (13.3.23) for $10^{-2} M$ 1:1 electrolyte in water at 25°C.
... the mathematical details are in B&F, pp. 551 – 552, but qualitatively, what GCS does is it uses the smaller capacitance of either $C_H$ or $C_{D(GC)}$...

$$\frac{1}{C_d} = \frac{1}{C_H} + \frac{1}{C_D}$$

**Figure 13.3.7** Expected behavior of $C_d$ according to GCS theory as the electrolyte concentration changes.