5

The metal-solution interface

5.1 Ideally polarizable electrodes

The interface between a metal and an electrolyte solution is the most important electrochemical system, and we begin by looking at the simplest case, in which no electrochemical reactions take place. The system we have in mind consists of a metal electrode in contact with a solution containing inert, non-reacting cations and anions. A typical example would be the interface between a silver electrode and an aqueous solution of KF. We further suppose that the electrode potential is kept in a range in which no or only negligible decomposition of the solvent takes place – in the case of an aqueous solution, this means that the electrode potential must be below the oxygen evolution and above the hydrogen evolution region. Such an interface is said to be ideally polarizable, a terminology based on thermodynamic thinking. The potential range over which the system is ideally polarizable is known as the potential window, since in this range electrochemical processes can be studied without interference by solvent decomposition.

As we pointed out in the introduction, a double layer of equal and opposite charges exists at the interface. In the solution this excess charge is concentrated in a space-charge region, whose extension is the greater the lower the ionic concentration. The presence of this space-charge region entails an excess (positive or negative) of ions in the interfacial region. In this chapter we consider the case in which this excess is solely due to electrostatic interactions; in other words, we assume that there is no specific adsorption. This case is often difficult to realize in practice, but is of principal importance for understanding more complicated situations.

5.2 The Gouy-Chapman theory

A simple but surprisingly good model for the metal-solution interface was developed by Gouy [13] and Chapman [14] as early as 1910. The basic ideas are
The solution is modeled as point ions embedded in a dielectric continuum representing the solvent; the metal electrode is considered as a perfect conductor. The distribution of the ions near the interface is calculated from electrostatics and statistical mechanics.

To be specific we consider a planar electrode in contact with a solution of a \( z^- z \) electrolyte (i.e., cations of charge number \( z \) and anions of charge number \( -z \)). We choose our coordinate system such that the electrode surface is situated in the plane at \( x = 0 \). The inner potential \( \phi(x) \) obeys Poisson’s equation:

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

(5.1)

where \( \rho(x) \) is the charge density in the electrolyte, \( \varepsilon \) the dielectric constant of the solvent, and \( \varepsilon_0 \) the permittivity of the vacuum. Let \( n_+(x) \) and \( n_-(x) \) denote the densities of the cations and anions; in the bulk they have the same density \( n_0 \). We have:

\[
\rho(x) = z \varepsilon_0 [n_+(x) - n_-(x)]
\]

(5.2)

The ionic densities must in turn depend on the potential \( \phi(x) \). We choose \( \phi(\infty) = 0 \) as our reference, and apply Boltzmann statistics:

\[
\begin{align*}
n_+(x) &= n_0 \exp \left( -\frac{ze_0 \phi(x)}{kT} \right) \\
n_-(x) &= n_0 \exp \left( -\frac{ze_0 \phi(x)}{kT} \right)
\end{align*}
\]

(5.3)

Strictly speaking the exponents should not contain the inner potential \( \phi \) but the so-called potential of mean force, but this subtlety is only important at high electrolyte concentrations and high potentials, where other weaknesses of this theory also become important. Substituting Eqs. (5.3) and (5.2) into Eq. (5.1) gives:

\[
\frac{d^2 \phi}{dx^2} = -\frac{ze_0 n_0}{\varepsilon \varepsilon_0} \left( \exp \left( -\frac{ze_0 \phi(x)}{kT} \right) - \exp \left( -\frac{ze_0 \phi(x)}{kT} \right) \right)
\]

(5.4)

which is a nonlinear differential equation for the potential \( \phi(x) \) known as the Poisson-Boltzmann equation. We first consider the simple case in which \( ze_0 \phi(x)/kT \ll 1 \) everywhere so that the exponentials can be linearized. This gives the linear Poisson-Boltzmann equation:

\[
\frac{d^2 \phi}{dx^2} = \kappa^2 \phi(x)
\]

(5.5)

where \( \kappa \) is the Debye inverse length:

\[
\kappa = \left( \frac{2(ze_0)^2 n_0}{\varepsilon \varepsilon_0 kT} \right)^{1/2}
\]

(5.6)
$L_D = 1/\kappa$ is the Debye length; Table 5.1 shows values for several concentrations of a 1-1 electrolyte in an aqueous solution at room temperature. The solution compatible with the boundary condition $\phi(\infty) = 0$ has the form: $\phi(x) = A \exp(-\kappa x)$, where the constant $A$ is fixed by the charge balance condition:

$$\int_0^\infty \rho(x) \, dx = -\sigma$$ (5.7)

where $\sigma$ is the surface charge density on the metal. $\rho(x)$ is obtained from $\phi(x)$ via Poisson’s equation, and a straightforward calculation gives:

$$\phi(x) = \frac{\sigma}{\epsilon_0 \kappa} \exp(-\kappa x)$$ (5.8)

for the potential and:

$$\rho(x) = -\sigma \kappa \exp(-\kappa x)$$ (5.9)

for the charge density. So the excess charge on the metal is balanced by a space-charge layer, which decays exponentially in the solution. This configuration of charges obviously has a capacity. The electrode potential is: $\phi = \phi(0) = \sigma/\epsilon_0 \kappa -$ dipole potentials are ignored in this simple model. The interfacial capacity per unit area, known as the double-layer capacity, is:

$$C = \epsilon_0 \kappa$$ (5.10)

So the double-layer capacity is the same as that of a parallel-plate capacitor with the plate separation given by the Debye length. Since for high concentrations the latter is of the order of a few Angstroms, these capacities can be quite high.

While Eqs. (5.9) and (5.10) are quite instructive, they are valid for small charge densities on the electrode only. For a $z - z$ electrolyte the nonlinear Poisson-Boltzmann equation (5.4) can be solved explicitly. We are mainly interested in the differential capacity, defined as $C = \partial \sigma / \partial \phi$, which is a measurable quantity. A short calculation, whose details are given in the appendix of this chapter, gives:

$$C = \epsilon_0 \kappa \cosh \left( \frac{\epsilon_0 \phi(0)}{2kT} \right)$$ (5.11)

This is not a useful form since the potential $\phi(0)$ cannot be measured. The electrode potential $\phi$ differs from $\phi(0)$ by a constant; when $\phi(0) = 0$ the
electrode carries no charge, and the corresponding electrode potential $\phi_{pzc}$ is
the potential of zero charge ($pzc$). So we rewrite Eq. (5.11) in the form:

$$C = \epsilon_0 \kappa \cosh \left( \frac{z e_0 (\phi - \phi_{pzc})}{2kT} \right)$$  \hspace{1cm} (5.12)

This differential capacity is known as the Gouy-Chapman capacity. It has a
pronounced minimum at the pzc, and it increases with the square root of
the electrolyte concentration. Figure 5.1 shows the Gouy-Chapman capacity
calculated for several electrolyte concentrations.

Because of the simple model on which it is based, the validity of the Gouy-
Chapman theory is limited to low concentrations and small excess charge
densities. Even at $5 \times 10^{-2}$ M solutions, there are substantial deviations at
potentials away from zero charge. As an example, Fig. 5.2 shows the capacity
of single-crystal silver electrodes in a $5 \times 10^{-2}$ M solution of a weakly adsorbing
electrolyte. All three curves show the characteristic capacity minimum at the
pzc, but the deviations from Gouy-Chapman theory away from the pzc are
quite evident. The plot also illustrates the dependence of the pzc on the crystal
face.

5.3 The Helmholtz capacity

At low electrolyte concentrations, up to about a $10^{-3}$ M solution, the Gouy-
Chapman theory agrees quite well with experimental values of the double layer
capacity for nonadsorbing electrolytes. At higher concentrations systematic
deviations are observed. In fact the experimental values follow an equation of
the form:

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig51.png}
\caption{Gouye-Chapman capacity for various concentrations of a 1-1 electrolyte in
aqueous solution at room temperature.}
\end{figure}
Fig. 5.2. Experimental capacity of single-crystal silver electrodes in a solution of $5 \times 10^{-2}$ M KClO$_4$.

\[ \frac{1}{C} = \frac{1}{C_{GC}} + \frac{1}{C_H} \]  \hspace{1cm} (5.13)

where $C_{GC}$ is the Gouy-Chapman capacity given by Eq. (5.12), and the Helmholtz capacity $C_H$ is independent of the electrolyte concentration.

Fig. 5.3. Parsons and Zobel plot; the intercept gives the inverse Helmholtz capacity.

Experimentally the Helmholtz capacity can be obtained by measuring the interfacial capacity $C$ per unit area for several concentrations, and plotting $1/C$ versus the calculated inverse Gouy-Chapman capacity $1/C_{GC}$ at a constant surface charge density $\sigma$ (Parsons and Zobel plot); the intercept of the resulting straight line gives $1/C_H$ (see Fig. 5.3). If the electrode area is not
known, one plots the capacity instead and obtains the area from the slope of the plot. If a Parsons and Zobel plot does not result in a straight line, this is an indication that specific adsorption occurs.

The Helmholtz capacity $C_H$ dominates at high electrolyte concentrations, when the extension of the space-charge layer is small, and hence its origin must be in a narrow region right at the interface. For a given system $C_H$ generally depends strongly on the charge density $\sigma$ and somewhat more weakly on temperature. The capacity-charge characteristics $C_H$ versus $\sigma$ vary greatly with the nature of the metal and the solvent, and are even somewhat different for different faces of a single crystal. However, they depend only weakly on the nature of the ions in the solution, as long as they are not specifically adsorbed. Figure 5.4 shows capacity-charge characteristics for mercury and for a single crystal silver electrode in contact with an aqueous solution; notice the maximum near the pzc, and how much smaller the capacity of mercury is.

\[ C_H / \mu \text{Cm}^{-2} \]

\[ \sigma / \mu \text{Cm}^{-2} \]

**Fig. 5.4.** Helmholtz capacity for Ag(111) and mercury in aqueous solutions.

Several theories have been proposed to explain the origin and the order of magnitude of the Helmholtz capacity. Though differing in details, recent theories agree that the Helmholtz capacity contains contributions both from the metal and from the solution at the interface:

1. Due to the finite size of the ions and the solvent molecules, the solution shows considerable structure at the interface, which is not accounted for in the simple Gouy-Chapman theory. The occurrence of a decrease of $C$ from the maximum near the pzc is caused by dielectric saturation, which lowers the dielectric constant and hence the capacity for high surface-charge densities.
2. The surface potential $\chi$ of the metal varies with the surface charge. A little thought shows that the change in the surface potential opposes the applied external potential, thus decreasing the total potential drop for a given surface charge and increasing the capacity.

The latter effect can be understood within a simple model for metals: the *jellium model*, which is based on the following ideas: As is generally known, a metal consists of positively charged ions and negatively charged electrons. In the jellium model the ionic charge is smeared out into a constant positive background charge, which drops abruptly to zero at the metal surface. The electrons are modeled as a quantum-mechanical plasma interacting with the background charge and with any external field such as that caused by surface charges. Due to their small mass the electrons can penetrate a little into the solution; typically the electronic density decreases exponentially with a decay length of about 0.5 Å. Since the electronic density of metals is high, this gives rise to an appreciable negative excess charge outside the metal, which for an uncharged surface must be balanced by an equal and opposite positive excess charge within the metal. The resulting electronic charge distribution, plotted as a function of the distance $x$ from the metal surface, is shown in Fig. 5.5; it carries a surface dipole moment which gives rise to a surface potential $\chi$ of the order of several volts.

The electric field in the double layer distorts the electronic distribution and changes the surface potential $\chi$. A negative surface charge creates an excess of electrons on the surface. The resulting electrostatic field pulls the electrons toward the solution, and increases the surface dipole potential. Conversely, a

![Fig. 5.5. Distribution of the electronic density in the jellium model; the metal occupies the region $x \leq 0$. The unmarked curve is for an uncharged surface, the other two curves are for the indicated surface-charge densities. The distance along the $x$ axis is measured in atomic units (a.u.), where 1 a.u. of length = 0.529 Å.](image-url)
positive excess charge gives rise to a deficiency of electrons, and the surface dipole potential becomes smaller. The change in dipole potential opposes the change in the external potential, and hence increases the capacity. In other words, the electrons at the metal surface form a highly polarizable medium, which enhances the double-layer capacity. Since this is an electronic effect, one might expect that its magnitude increases with the electronic density of the metal. This seems indeed to be the case for simple metals, the $sp$ metals of the second and third column of the periodic table (see Fig. 5.6); the Helmholtz capacity of these elements at the pzc correlates with their electronic densities.

**5.4 The potential of zero charge**

The potential of zero charge (pzc) is a characteristic potential for a given interface, and hence is of obvious interest. In the absence of specific adsorption, it can be measured as the potential at which the Gouy-Chapman capacity obtains its minimum; this value must be independent of the electrolyte concentration, otherwise there is specific adsorption. The pzc coincides with the maximum of the surface tension (see Section 4.4), which can be measured directly for liquid metals.

An interesting correlation exists between the work function of a metal and its pzc in a particular solvent. Consider a metal $M$ at the pzc in contact with a solution of an inert, nonadsorbing electrolyte containing a standard platinum/hydrogen reference electrode. We connect a platinum wire (label I) to the metal, and label the platinum reference electrode with II. This setup
is very similar to that considered in Section 4.3, but this time the metal-solution interface is not in electronic equilibrium. The derivation is simplified if we assume that the two platinum wires have the same work function, so that their surface potentials are equal. The electrode potential is then:

$$\phi_{\text{pzc}} = \phi_I - \phi_{\text{II}} = \psi_I - \psi_{\text{II}} = \left(\psi_I - \psi_M\right) + \left(\psi_M - \psi_{\text{sol}}\right) + \left(\psi_{\text{sol}} - \psi_{\text{II}}\right) \quad (5.14)$$

The first and the last term can again be expressed through the work function differences, but not the second term, since this interface is not in electronic equilibrium:

$$\phi_{\text{pzc}} = \frac{1}{\varepsilon_0} \left[\left(\Phi_M - \Phi_{\text{Pt}}\right) + \left(\Phi_{\text{Pt}} - \Phi_{\text{ref}}\right)\right] + \left(\psi_M - \psi_{\text{sol}}\right)$$

$$= \frac{1}{\varepsilon_0} \left(\Phi_M - \Phi_{\text{ref}}\right) + \left(\psi_M - \psi_{\text{sol}}\right) \quad (5.15)$$

To evaluate the last term we go through a cycle taking a test charge (not an electron!) from outside the metal first into the bulk of the metal, then through the metal-solution interface, then to a position just outside the solution, and finally back to outside the metal. This gives:

$$\psi_M - \psi_{\text{sol}} = -\chi_M + \chi_{\text{int}} + \chi_{\text{sol}} \quad (5.16)$$

where $\chi_{\text{int}}$ is the surface potential at the metal-solution interface. If the metal and the solvent did not interact, $\chi_{\text{int}}$ would simply be $\chi_M - \chi_{\text{sol}}$, and the outer potential difference would vanish at the pzc. However, the metal-solvent interaction modifies the surface potentials; the presence of the solvent changes the distribution of the electrons at the surface, and the interaction of the solvent with the metal surface can lead to a small net orientation of the

![Diagram](image.png)

**Fig. 5.7.** The potential of zero charge (vs. SHE) of metals in aqueous solution; the upper line is for $sp$ metals, the lower for $sd$ metals [16].
solvent dipoles. Denoting these changes in the surface potentials by \( \delta \chi_M \) and \( \delta \chi_{\text{sol}} \), we have: 
\[
\psi_M - \psi_{\text{sol}} = \delta \chi_M - \delta \chi_{\text{sol}},
\]
so that we obtain for the pzcl potential:
\[
\phi_{\text{pzc}} = \frac{1}{\epsilon_0} (\Phi_M - \Phi_{\text{ref}}) + \delta \chi_M - \delta \chi_{\text{sol}} \tag{5.17}
\]

The changes in the dipole potentials are typically small, of the order of a few tenths of a volt, while work functions are of the order of a few volts. If we keep the solvent, and hence \( \Phi_{\text{ref}} \), fixed and vary the metal, the potential of zero charge will be roughly proportional to the work function of the metal. This is illustrated in Fig. 5.7. A more detailed consideration of the dipole potentials leads to a subdivision into separate correlations for sp, sd, and transition metals [16].

Problems

1. For a z-z electrolyte define the excess distribution of the cations and anions through: \( \delta n_+ (x) = n_+ (x) - n_0 \) and \( \delta n_- (x) = n_- (x) - n_0 \). Show that \( |\delta n_+ (x)| = |\delta n_- (x)| \) holds for the linear Gouy-Chapman theory, but not for the nonlinear version.

2. Consider a point dipole with dipole moment \( m \) in an external electric field \( E \) oriented along the z axis. Choosing a suitable coordinate system, show that the average value of the dipole moment along the direction of the field is:
\[
\langle m_z \rangle = \frac{\int_{-\pi}^{\pi} \sin \theta \ d\theta \ \int_{-\pi}^{\pi} \ d\phi \ \sin \theta \ \cos \theta \ \exp \left( \frac{mE \cos \theta}{kT} \right)}{\int_{-\pi}^{\pi} \ \sin \theta \ d\theta \ \int_{-\pi}^{\pi} \ d\phi \ \exp \left( \frac{mE \cos \theta}{kT} \right)}
\]
For \( mE \ll kT \) the exponentials can be expanded. Show that in this limit:
\[
\langle m_z \rangle = \frac{m^2 E}{3kT}
\]

3. The Thomas-Fermi model of a metal is similar to the Gouy-Chapman theory for electrolytes. In this model the surface-charge density \( \sigma \) is spread over a thin boundary layer. If the metal occupies the region \( x \leq h \), the distribution of the charge density is given by:

\[
\rho (x) = A \exp \left( \frac{x}{L_{\text{TF}}} \right)
\]
where \( A \) is a constant to be determined by charge balance, and \( L_{\text{TF}} \) is the Thomas-Fermi length, which is mainly determined by the electronic density of the metal. Combine this model with the linear Gouy-Chapman theory and derive:
\[
\frac{1}{C} = \frac{1}{\epsilon_0 \kappa} + \frac{L_{\text{TF}}}{\epsilon_0}
\]
Compare this result with Eq. (5.13). For most metals \( L_{\text{TF}} \approx 0.5 \text{ Å} \). By examining the experimental data in Fig. 5.6, show that this model cannot explain the origin of the Helmholtz capacity.
Appendix: The nonlinear Gouy-Chapman theory

We rewrite the nonlinear Poisson Boltzmann Eq. (5.4) in the form:
\[
\frac{d^2 \phi}{dx^2} = -\frac{2\varepsilon_0 \sigma_0}{\varepsilon_0} \sinh \frac{ze_0 \phi(x)}{kT}
\]
and multiply both sides by \(2d\phi/dx\). Using
\[
\frac{d}{dx} \left( \frac{d\phi}{dx} \right)^2 = 2 \frac{d^2 \phi}{dx^2} \frac{d\phi}{dx}
\]
we can integrate both sides:
\[
2 \int_0^\infty \frac{d^2 \phi}{dx^2} \frac{d\phi}{dx} \ dx = \left( \frac{d\phi}{dx} \right)^2 \bigg|_0^\infty
\]
\[
= -\int_0^\infty 4\varepsilon_0 \sigma_0 \sinh \left( \frac{ze_0 \phi}{kT} \right) \frac{d\phi}{dx} \ dx
\]
Both the field \(E\) and the potential \(\phi\) vanish at \(\infty\); so we obtain:
\[
E(0)^2 = \frac{4\varepsilon_0 \sigma_0}{\varepsilon_0} \left( \cosh \frac{ze_0 \phi(0)}{kT} - 1 \right)
\]
According to Gauss’s theorem, \(E(0) = \sigma/\varepsilon_0\); using the identity \(\cosh x - 1 = 2 \sinh^2 x/2\) gives:
\[
\sigma = (8\varepsilon_0 \sigma_0 \varepsilon_0) \left( \frac{ze_0 \phi(0)}{kT} \right)^{1/2} \sinh \frac{ze_0 \phi(0)}{2kT}
\]
Differentiation then gives the Gouy-Chapman expression Eq. (5.11).

Sometimes one requires not only the capacity but the potential \(\phi(x)\); we sketch the derivation. If we integrate Eq. (5.18) from \(x\) to \(\infty\), we obtain by the same arguments for the derivative \(\phi'(x)\):
\[
\phi'(x) = -\left( \frac{8\varepsilon_0 \sigma_0 \varepsilon_0}{\varepsilon_0} \right)^{1/2} \sinh \frac{ze_0 \phi(x)}{2kT}
\]
Substituting \(\psi(x) = [ze_0 \phi(x)]/2kT\) gives:
\[
\frac{\psi'(x)}{\sin \psi(x)} = -\kappa
\]
where \(\kappa\) is the inverse Debye length. Integration gives:
\[
\ln \tanh \frac{\psi}{2} = -\kappa x + \ln C
\]
where \(\ln C\) is the constant of integration, which can be expressed through the value of the potential at the origin:
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\[ C = \tanh \frac{z \epsilon_0 \phi(0)}{4kT} \quad (5.26) \]

Equation (5.22) relates \( \phi(0) \) to the charge density \( \sigma \):

\[ \frac{z \epsilon_0 \phi(0)}{2kT} = \arcsinh \alpha \sigma, \text{ where } \alpha = (8kT \epsilon_0 e_0)^{-1/2} \quad (5.27) \]

Using the identity:

\[ \tanh \left( \frac{1}{2} \arcsinh x \right) = \frac{\sqrt{1 + x^2} - 1}{x} \quad (5.28) \]

gives finally:

\[ \tanh \frac{z \epsilon_0 \phi(x)}{4kT} = \frac{\sqrt{1 + \alpha^2 \sigma^2} - 1}{\alpha \sigma} \exp(-\kappa x) \quad (5.29) \]

for the potential.