**Introduction**

Electric double layers form whenever two conducting phases meet at an interface. Generally, one of the phases acquires a positive excess charge on its surface, which is balanced by a countercharge of the same magnitude and opposite sign on the other phase. Well-known examples are the interfaces between two metals with different work functions, of two semiconductors with n- and p-type conductivities, and of a metal electrode in contact with an electrolyte solution. Here, we consider mainly metal/solution interfaces, because they are of greatest relevance to fuel cells, supercapacitors, and batteries. In addition, carbon is often used in devices, and we will treat this as a special case. Because of its unique band structure, its capacity shows quite an unusual dependence on the electrode potential.

Traditionally, electrochemical double-layer theory has been concerned with the so-called ideally polarizable interfaces, at which no electrochemical reaction takes place and hence no direct current passes through the interface. However, this condition can be relaxed: for double-layer studies, it is sufficient that any electrochemical reaction does not disturb the distribution of the excess charges at the interface, and this is the assumption that we shall make throughout this article. In this case, a potential difference can be applied to the two sides of the interface, which entails a change in the excess charges. Hence, the interface resembles a capacitor, and, indeed, much research has been focused on the capacity of the double layer.

Specific adsorption can have a large effect on the charge distribution near the interface. Since each kind of ion has its specific adsorption behavior, it is not possible to make a general, nontrivial theory for the double layer in the presence of adsorption. Hence, in the major part of this article, we shall assume that specific adsorption is absent or has only a negligible effect on the double-layer properties.

**The Helmholtz Model**

The oldest model for the structure of the double layer at metal electrodes was put forward by Helmholtz (see Figure 1). In the absence of specific adsorption, the electrode surface is covered by a layer of water molecules; the ions can only enter into the second layer, whose center is called the outer Helmholtz plane. Helmholtz assumed that all of the excess charge of the solution resides in this plane. This should be qualitatively correct at high ionic concentrations, where the conductivity of the solution is high, and its excess charge should hence be located at the surface. Thus, in this model, the interface acts like a parallel plate capacitor, and the effective plate separation is given by the distance of the outer Helmholtz plane to the metal surface, which is of the order of 0.4 nm.

---

### Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gouy–Chapman theory</strong></td>
<td>Model for the metal–solution interface valid at low electrolyte concentrations; equivalent to the Debye–Hückel theory.</td>
</tr>
<tr>
<td><strong>Helmholtz capacity</strong></td>
<td>First-order correction to Gouy–Chapman theory.</td>
</tr>
<tr>
<td><strong>Ideally polarizable interface</strong></td>
<td>Electrochemical interface, at which no electrochemical reaction takes place.</td>
</tr>
<tr>
<td><strong>Inner Helmholtz plane</strong></td>
<td>Idealized plane containing the centers of molecules or ions adsorbed on a planar electrode.</td>
</tr>
<tr>
<td><strong>Jellium</strong></td>
<td>Simple model for an unstructured metal, in which the ions are represented by a positive background charge and the electrons as a plasma.</td>
</tr>
<tr>
<td><strong>Outer Helmholtz plane</strong></td>
<td>Idealized plane containing the centers of the first layer of solvent molecules at the interface with a planar electrode.</td>
</tr>
<tr>
<td><strong>Poisson–Boltzmann equation</strong></td>
<td>A combination of the Poisson equation of electrostatics with the Boltzmann distribution. Plays a role in space-charge regions in electrolytes and in semiconductors.</td>
</tr>
</tbody>
</table>
The intervening water layer acts as a dielectric, since it consists of a monolayer of water only and its dielectric constant $\varepsilon$ will be appreciably less than that of bulk water. Assuming an effective value of $\varepsilon = 20–30$, this gives an interfacial capacity per unit area of the order of $0.4–0.5 \ \text{C m}^{-2}$, independent of the electrode potential. For higher charge densities, we may expect dielectric saturation of the water layer, since the field is so high that the solvent dipoles will be largely oriented. So the capacity should decrease at both sides of the potential of zero charge. The resulting picture is, in fact, not a bad average description of the interfacial capacity at high ionic concentrations, as is evidenced by the capacity of Ag(111) in contact with a 0.1 M solution of KClO$_4$ (upper curve in Figure 4).

---

**Figure 1** Structure of the double layer in the Helmholtz model without specific adsorption; the excess charge in the outer Helmholtz plane is balanced by a countercharge on the metal, which is not shown.

**Figure 2** Structure of the double layer in the Helmholtz model with specific adsorption; the charge on the metal is not shown.
In the presence of specific adsorption, this model must be modified. The adsorbed ions are in contact with the electrode; their centers form the so-called inner Helmholtz plane. Figure 2 depicts the case in which anions are specifically adsorbed. The total charge at the interface is still zero, so the charge on the adsorbed ions must be balanced by the ions in the outer Helmholtz plane and by the charge on the metal. Specific adsorption increases the capacity, since the distance that separates the charges of opposite sign is shorter.

**Gouy–Chapman and Gouy–Chapman–Stern Models**

While the Helmholtz model gives a reasonable description at high ionic concentrations, it does not explain the behavior at low concentrations. This was achieved by the first statistical double-layer theory presented by Gouy and Chapman at the beginning of the last century. It has much in common with the Debye–Hückel theory, which was developed several decades later.

The Gouy–Chapman theory considers a planar metal electrode in contact with an ionic solution and starts from the following assumptions: (1) The metal is a perfect conductor, and its excess charge is distributed evenly on the surface. (2) The solvent is a dielectric continuum, characterized by a dielectric constant \( e \). (3) The ions are point particles, whose distribution is determined by the Poisson–Boltzmann equation. For the case of an electrolyte containing cations and anions with the same charge number \( z \), explicit expressions for the differential capacity and for the profile of the electrostatic potential can be derived. The quantity that is commonly measured is the differential capacity per unit area:

\[
C = \frac{\partial \sigma}{\partial \phi}
\]

where \( \sigma \) is the charge per unit area of the electrode and \( \phi \) the electrode potential. The Gouy–Chapman theory gives the following expression:

\[
C_{GC} = \frac{d\sigma_M}{d\phi} = \frac{\varepsilon e z_0}{L_D} \cosh \left( \frac{\phi - \phi_{pzc}}{2kT} \right)
\]

where \( \phi \) is the electrode potential and \( \phi_{pzc} \) the potential of zero charge (pzc), at which the charge density \( \sigma_M \) on the electrode vanishes. \( k_B \) is the Boltzmann constant and \( T \) the temperature. The Debye length \( L_D \), which is familiar from the Debye–Hückel theory for electrolyte solutions, is given by

\[
L_D = \left( \frac{\varepsilon e kT}{2(z_0)^2 n_0} \right)^{1/2}
\]

where \( n_0 \) is the concentration of the ions in the bulk of the solution. The Gouy–Chapman capacity has a pronounced minimum at the pzc and rises rapidly on both sides (see Figure 3) and decreases strongly with the ionic concentration of the solution.

For comparison, Figure 4 shows experimental values for the interfacial capacity of a Ag(111) electrode in contact with an aqueous solution of KClO\(_4\) – an electrolyte that adsorbs only weakly. For lower concentrations, the minimum at the pzc predicted by the Gouy–Chapman theory is clearly visible; in fact, for solid electrodes, the observation of this minimum is practically the only way to determine the pzc. For a concentration of 0.1 M, the minimum has disappeared, and a vestige can be seen as a shoulder. At potentials far from the pzc, the capacity drops, while Gouy–Chapman theory predicts a continuous rise to unreasonably large values.

![Figure 3](image-url)  
*Figure 3*  
Interfacial capacity for an aqueous solution of a 1–1 electrolyte according to the Gouy–Chapman equation.
Thus, for low concentrations and near the potential of zero charge, the Gouy–Chapman theory works quite well. At high charges and for high concentrations, it significantly overestimates the interfacial capacity. This is not surprising, because under these circumstances, this theory predicts an extension of the space-charge region, which is of the same order of magnitude as the diameters of the solvent or of the ions. The simplest model that accounts for the finite size of the solvent molecules is the introduction of an ion-free layer, or Stern layer, as in the Helmholtz model. This resulting equation for the capacity resembles two capacities in series:

$$\frac{1}{C} = \frac{1}{C_{HC}} + \frac{1}{C_H}$$

where $C_H$ is known as the Helmholtz or inner-layer capacity. If it is caused by the finite size of the ions, it should be independent of the ionic concentration. Equation [4] is best seen as a definition of the Helmholtz capacity; it has little predictive value but is a convenient tool for describing the corrections to the Gouy–Chapman theory.

Specific adsorption has a large effect on the double-layer capacity. As an example, Figure 5 shows the effect that the addition of a small amount of Br$^-$ ions, which adsorb quite strongly, has on the capacity of a Au(210) electrode. With the exception of very high potentials, the capacity is greatly enhanced. The magnitude of the enhancement and the shape of the capacity–potential characteristics depend strongly on the type of ions, and there are no general rules.

Often, it is difficult to decide if a weak specific adsorption occurs or not. For this purpose, a Parsons and Zobel plot is a good method: According to eqn [4], a plot of the inverse measured capacity $1/C$ versus the inverse Gouy–Chapman capacity $1/C_{GC}$.
performed at constant charge density $\sigma$, should result in a straight line with unit slope – the Gouy–Chapman capacity is varied by changing the concentration of the electrolyte. Figure 6 shows such a plot for a mercury electrode in an aqueous solution of NaH$_2$PO$_4$. Actually, this is one of the very few examples where a unit slope has been obtained, indicating that there is no specific adsorption. Generally, on solid metals, nearly all anions show some specific adsorption near the pzc and at higher potentials.

In any case, extrapolating the Parsons and Zobel plot to the intercept corresponds to the limit of infinite ionic concentrations and yields the Helmholtz capacity. Figure 7 shows the corresponding curves for mercury and Ag(111). Notice the large difference between the two curves, which indicates that the metal itself has a considerable influence on the capacity.

The examples presented here have all been from experiments in aqueous solutions. The double-layer capacities of nonaqueous solutions follow the same principles. Since the dielectric constants are usually lower than those of water and the size of the solvent molecules larger, capacities are generally lower than those in aqueous solutions. Unfortunately, there are few systematic studies, and those that do exist are mostly from the last century.

**Hard Sphere Electrolyte and Jellium**

The Helmholtz capacity denotes the deviations from the Gouy–Chapman model at high concentrations and charges. It seems that there are two effects: the finite size of the solvent and the ions, which explains why the real capacity is smaller than the Gouy–Chapman theory predicts, and a contribution of the metal, which would explain why the capacity on Ag(111) is so much higher than that on mercury.

A simple model to describe finite size effects is to regard the solution as an ensemble of hard spheres. There are three types of hard spheres: two types of ions with appropriate charges at the center and spheres with a dipole moment at the center, which model the solvent. The statistical mechanics even of this simple model is quite complicated, and it has been solved only approximately – in the so-called mean-spherical approximation – and only for small excess charges. For this case, it gives an explicit formula for the Helmholtz capacity as the first-order correction to the Gouy–Chapman theory:

![Figure 6](image1.png)

**Figure 6** Parsons and Zobel plot for a mercury electrode in an aqueous solution of NaH$_2$PO$_4$. The line indicates unit slope.

![Figure 7](image2.png)

**Figure 7** Helmholtz capacities for mercury and Ag(111) in aqueous solution of a nonadsorbing electrolyte.
where $\sigma_i$ is the diameter of the ions – assumed to be the same for cations and anions – and $\sigma_s$ is that of the solvent molecules. The parameter $\lambda$ describes the dielectric properties at the interface and is obtained from the dielectric constant via $\lambda^2(1+\lambda)^4 = \varepsilon$. The contribution of the solvent is significantly greater than that of the ions. This explains an experimental finding: the values of the Helmholtz capacity depend only very little on the nature of the ions, as long as they are not specifically adsorbed.

For aqueous solutions, eqn [5] predicts Helmholtz capacities of the order of $10^{-2}$ $\mu$F cm$^{-2}$ at the pzc. This is at least of the correct order of magnitude. The next-order correction to the Gouy–Chapman theory can also be calculated explicitly, though the formula is not so simple. It has been successfully employed to explain the small but systematic deviations from the straight line that can be seen in Figure 6 for small values of $1/C_{GC}$.

Experimental values for the Helmholtz capacity lie in the range of $30$–$80$ $\mu$F cm$^{-2}$ and, as discussed earlier in the text, depend on the nature of the metal and, in the case of single crystals, even on the orientation of the surface. This fact has been explained through the response of the metal electrons to the electric field in the double layer. At the surface, the electronic density decays over a distance of about 0.1 nm. The response of this electronic tail to the double-layer field can be viewed as an electronic polarizability of the surface, which increases the capacity. Explicit calculations for this effect have mostly been based on the jellium model, in which the electrons are described as an electronic plasma and the metal ions are represented by a constant positive background charge. This model predicts that the interfacial capacity should increase with the electronic density of the metal, a trend in which the capacities of the sp metals follow at the pzc (see Figure 8). Metals with $d$-bands near the Fermi level are not well described by jellium and do not follow this trend.

There have been various attempts to extend the hard sphere model to higher charges. While certain effects, in particular the decrease of the Helmholtz capacity at high electric fields, have been successfully explained, there is yet no satisfactory quantitative model.

The Double Layer at Graphite Electrodes

Graphite has manifold advantages, which make it an important electrode material both in analytical electrochemistry and in electrochemical devices such as fuel cells, batteries, and supercapacitors. It is cheap, chemically inert, and stable over a wide range of electrode potentials, has a decent conductivity; and shows activity for a number of redox reactions. Electronically, graphite is not a semiconductor, since it has a finite density of electronic states at the Fermi level. It has an indirect bandgap and is better described as a semimetal, which has a minimum of the density of states at the Fermi level. Figure 9 shows the electronic density of states of graphite near the Fermi level.

There are two different surface structures on graphite: basal planes and edge sites. The latter have dangling bonds, which show up as surface states situated at the Fermi level and which are quite reactive. Usually, they are occupied by an adsorbate. Therefore, the electrochemical behavior of graphite electrodes is mostly dominated by the basal planes.

On metal electrodes, an electric field cannot penetrate the surface; because of the slow decay of the electronic density mentioned earlier in the text and the high density of electronic states near the Fermi level (see Figure 9), excess charges are centered somewhat in front of the metal surface. In contrast, because of the low electronic density at the Fermi level, the behavior of graphite electrodes is quite different. An electric field can penetrate the surface over a distance of a few Ångströms, and any excess charge is centered...
inside the graphite. This makes the distance between the charge in the electrolyte and the counter charge larger than on metals, and hence, the capacity is smaller.

The penetration of an external field shifts the Fermi level at the surface with respect to the electronic levels and hence to the density of states at the surface. Since, in the absence of a field, the density of states of graphite has a minimum at the Fermi level (see Figure 9), the application of a field, no matter if it is positive or negative, increases the electronic density at the Fermi level and makes the behavior more metallike. Hence, the capacity increases with the field strength.

Since the electric field at the surface is directly proportional to the surface charge density, this entails a peculiar shape of the capacity curves, which have a pronounced minimum at zero charge and rise steeply on either side (see Figure 10). Note how low the capacities are compared with those of silver or mercury (see Figure 4).

The response of the graphite surface to an external field, in particular the penetration of the field, shift of the Fermi level, and position of the center of the excess charge, can be calculated by modern quantum chemical methods such as density functional theory (DFT). This can be complemented by a suitable model for the solution side of the double in order to obtain a model for the whole interface. The simplest version is a combination of the DFT results with the hard sphere model for the electrolyte. The results of this model are also shown in Figure 10. Considering that this is a model without any adjustable parameter, the agreement between the theoretical and the experimental values is very good. The capacity of these electrodes is dominated by the electronic properties of graphite, which can be obtained quite well by DFT. In contrast, the complicated capacity curves of metal–solution interfaces are governed by the complex behavior of the solution, which is much more difficult to model. Hence, the theory for the double layer at graphite works much better than theories for the interface between metals and aqueous solutions.

**Computer Simulations**

The statistical mechanics of more realistic models than hard sphere is intractable by analytical methods; they have therefore been treated by computer simulations, mostly by molecular dynamics. Such simulations require interaction potentials between all the
particles concerned, solvent, ions, and electrode. Usually, these potentials are assumed to have a plausible form with parameters that are determined by ab initio calculations. For pure water in contact with a metal, there have been a few simulations based entirely on density functional theory, but for relatively small ensemble sizes and short times.

Practically all simulations for pure water in contact with a metal agree that water is structured at the electrode surface. The distribution functions for the water molecules show a distinct peak at the surface and a weaker secondary peak (see Figure 11); obviously, this is a packing effect. At uncharged electrodes, the dipole moment of water is mostly parallel to the surface, but with a small preference for the oxygen end to be closer to the metal. The magnitude of the latter effect depends on the metal and on the details of the interaction potentials that are used. It gives rise to a dipole potential drop at the interface, which is typically of the order of several hundred millivolts (see Figure 11).

There have also been a fair number of simulations of water with ions. While these have not been able to explain capacity curves for specific systems, they have produced some interesting results that are useful for understanding the double-layer structure and its influence on electrode reactions. A useful information is the potential of mean force (pmf) that an ion experiences as it approaches the electrode surface. During this approach, its solvation sphere becomes smaller, and this should diminish its energy of solvation. Therefore, the pmf obtained from simulations as shown in Figure 12, which do not include the electronic interaction with the electrode, should rise as close to the surface. However, the resulting curves depend very much on the type of ion, on its size, and on how well it fits into the structure of water. Small univalent metal ions like Ag⁺, Cu⁺, and Li⁺ fit very well into the structure of water and can get very close to the electrode without losing solvation energy; in the figure, this is illustrated by the Ag⁺ ion. The OH⁻ also fits quite well into the water structure, but not quite as well as Ag⁺, and the large I⁻ ion loses about half its solvation energy ($\delta G_{\text{sol}} \approx 2.67 \text{ eV}$) when it goes to the surface. The divalent Zn²⁺ ion can get to about 4.5 Å from the surface without losing energy, and then, it loses its solvation shell in two steps: first the secondary and then the primary shell. The oscillations seen in the pmf’s can be related to the structure of water.

![Figure 11](image1.png)  
**Figure 11**  Particle densities for hydrogen (full line), oxygen (dashed line), and the electrostatic potential (dotted line) for water in contact with a silver electrode. The densities for oxygen and hydrogen have been normalized to unity and two, respectively, in the bulk.

![Figure 12](image2.png)  
**Figure 12**  Potential of mean force (pmf) for several ions approaching an electrode surface. Ag⁺ to a Ag(100) electrode, I⁻ and OH⁻ to Pt(111), and Zn²⁺ to Zn. These potentials do not include the electronic interaction with the electrode.
The steady increase in computing power has made it possible to treat the electrochemical interface by DFT. While the representation of a realistic system, including electrode, solvent, and ions, is still impossible, certain aspects can be investigated in this way. Much attention has been paid to the structure of the water layer that is in close contact with a metal electrode. For metal surfaces in the vacuum, the bilayer model proposed by Doering and Maday explains many experimental data well, and it has also been confirmed by DFT calculations with only minor modifications. The basic unit of the bilayer is a ring of six water molecules. Three molecules are bonded to the metal surface with their oxygen ends (see Figure 13); their hydrogen atoms are directed towards a secondary layer of three water molecules, which is situated a little further away from the surface. Thus, in the hexagon, three molecules are bonded to the surface; the other three are held by hydrogen bonds that connect them to the first layer. Two different conformations exist: In one conformation (H-up), one of the hydrogen atoms of the water in the second layer is directed away from the surface; in the other (H-down), these atoms point towards the surface. While this bilayer is often evoked in DFT-based models of the electrochemical interface, extended simulations at room temperature suggest that it is not stable under electrochemical conditions.

Molten Salts and Ionic Liquids

The capacities of interfaces between metal electrodes and molten salts are of the same order of magnitude as those for aqueous solutions. Capacity curves for simple molten salts like the alkali halides usually have a U-type shape, with the minimum near the pzc; an example is shown in Figure 14. Various models have been proposed for the interfacial structure, but no agreement has been reached yet. Computer simulations for alkali halide melts are hampered by the strong Coulomb forces, which make it difficult to reach the equilibrium states.

At present, room-temperature ionic liquids, which have much larger ions than the alkali halides and which are liquid at ambient temperatures, are a very active area of research. They typically consist of large organic cations with similar organic or smaller

![Figure 13](image1.png)  
**Figure 13**  H-down bilayer of water on the surface of Pt(111). Courtesy of Axel Groß, Ulm University.

![Figure 14](image2.png)  
**Figure 14**  Interfacial capacity of a Pb electrode in contact with molten alkali halides at 800 °C.
inorganic anions. Thousands of such liquids have been synthesized, so they offer a large variety of electrolytes. For practical applications, their principal virtues are a low vapor pressure and a large electrochemical window, that is, they can withstand voltages up to 4–6 V without decomposition. They hold promise as electrolytes for supercapacitors, batteries, and solar cells.

The capacity curves of ionic liquids in contact with a metal or graphite electrode display a variety of forms; in a crude phenomenology, they are often classified as bell-like, U-like, or camel-like; the latter form indicates a minimum somewhere in the center with a maximum on each side (see Figure 15). Based on simple theoretical arguments, an extremum near the center is often interpreted as the potential of zero charge, but there seems to be no experimental evidence for this. Somewhat surprisingly, not only the magnitude but also the overall shape of the capacity curves depends on the electrode material. The field is presently undergoing a rapid development, and at the moment, there are no established theory, but a few promising ideas.

Conclusions

Qualitatively, the double layer at the interface between a metal and an aqueous solution is quite well understood, but a quantitative theory is lacking. Thus, after decades of research, it is still not possible to calculate the double-layer capacity of such a basic system like a Ag(1 1 1) electrode in contact with a 0.1 M aqueous solution of KF. Further progress in understanding can be expected from a combination of computer simulations and ab initio calculations. For molten salts, the situation is worse, because there is not even a basic theory on the Gouy–Chapman level. Nevertheless, experimentally all electrochemical double layers are well investigated.

Since at the interface between a metal and a concentrated electrolyte solution, the effective charge distribution is exceedingly small, of the order of a few tenths of a nanometer, the capacity is very high. This makes such interfaces interesting for technological applications as the so-called supercapacitors: A high charge density can be stored at these interfaces and discharged during a very short time. They can therefore react faster to a change in power demand than either batteries or fuel cells and can provide short boosts of power when needed.

Further Reading