Charged Polymers

**Introduction and Terminology:**

“Charged” polymers are common in both nature and technology, often in solutions, gels, or swellable solids. Such polymers contain ionizable units that, according to the properties of their surroundings, may or may not dissociate, a process that releases and distributes “counterions” across the surroundings in a relatively disordered manner. (One occasionally encounters the term “polysalt”, suggesting that a charged polymer is able to crystallize as a salt. Actually, crystallization of charged polymers is extremely rare.) When undissociated, each counterion resides against one of the polymer’s “fixed” charges, maintaining a small charge separation and thereby creating an “ion pair”; in water, undissociated ionic species are not fully hydrated. Even fully dissociated (i.e., fully solvated) and thus with the counterions able to explore their environment, the average polymer-counterion separation remains finite, the counterions collectively creating a “counterion cloud” that surrounds the polymer polymer. To a distant observer, the dissociated polymer and its surrounding counterions appear a single, neutral entity. Of course, counterions can exchange with free ions of the surroundings, essentially redefining the species denoted by the term counterion. The spatial disposition of counterions is crucial to all understanding of charged polymer properties.

When the dipole-dipole (or multipole-multipole) attractions generated by undissociated ions dictate a polymer’s interactions and properties, the polymer is termed an “ionomer”. In technology, ionomers are usually employed as neat solids or as solids swollen with a small amount of a polar solvent, usually water. If the counterions have mobility, these solids display a measurable ion conductivity generated by a “counterion-hopping” migration mechanism. Ionomers traditionally have their ionizable units positioned sparsely along uncharged hydrophobic sequences. The ionizable units facilitate swelling by a polar solvent but the poor quality of such solvents for the hydrophobic sequences prevents polymer dissolution, maintaining solid-like mechanical integrity. Neat ionomers frame one category of thermoplastic elastomer, reversible elastic polymeric solids that flow at high temperature, a condition necessary to disrupt aggregated ion pairs, as feature sketched below. Ionomers typically dissolve in less polar organic liquids, although attractive dipole-dipole interactions of undissociated ionizable units may cause aggregation or gelation.
When electrostatic interactions among ionized units and/or released counterions dominate, a polymer is termed a “polyelectrolyte”. A charged polymer behave alternately as an ionomer and a polyelectrolyte, the disposition of its counterions in the environment affecting which description is appropriate. Polyelectrolytes typically are found in nature and technology at a state of high solvation with a polar solvent, most often water. Counterions have much freedom to move about within the solvent, although long-range electrostatic interactions limit the extent to which they do so.

Direct electrostatic interactions make enthalpic contributions to system free energy for both ionomers and polyelectrolytes. The contribution from ion dissociation For polyelectrolytes, the release (dissociation) of small ions makes a positive entropy contribution. Indeed, as the degree of dissociation falls, polyelectrolytes often become insoluble in polar solvents due to the lowering of the entropy gain; each counterion dissociation adds ~kT to system entropy.

Lightly charged hydrophilic biopolymers, such as numerous proteins and polysaccharides, are conventionally not grouped with either polyelectrolytes or ionomers. However, their charge interactions are the same as those described above. Since these macromolecules typically dissolve in polar solvents with their ionizable units fully or mostly dissociated, I refer to them as “weak” polyelectrolytes even if their electrostatic interactions don’t significantly influence overall polymer behavior.

“Pseudo-polyelectrolytes” are neutral polymers that gain charge through physical association with small ions such as ionic surfactants. If the association is strong compared to ~kT, these materials are virtually indistinguishable from polyelectrolytes. [Amine-containing polymers such as polylysine are protonated in water at low enough pH; although their charge is gained by association, these polymers are considered true polyelectrolytes. Poly(ethylene glycol) can gain charge in water by association of protons or small anions with its electronegative oxygens; such charging is so weak that the polymers are typically not considered polyelectrolytes.]
“Block polyelectrolytes” are block copolymers with at least one block that has a substantial density of ionizable units. The uncharged block can be either hydrophobic or hydrophilic.

“Polyampholytes” are copolymers that dissociate to form positive and negative charges simultaneously, the net charge often controlled by pH. The protein gelatin is one example.

“Polyzwitterions” are polymers that contain functional groups pairing positive and negative charge, both usually present in each repeat unit.

Examples:

- polystyrene sulfonate –

  ![Polystyrene sulfonate structure](image)

  *inks, ion exchange resins*

- polyacrylic acid –

  ![Polyacrylic acid structure](image)

  *floculants, crystallization inhibitors*

- quaternized poly(4-vinyl pyridine) –

  ![Quaternized poly(4-vinyl pyridine) structure](image)
ds-DNA -

heparin -
(highly sulfated glycosaminoglycan)

Nafion -

Ionenes -
(polymer with ionized backbone units)

Illustration of a Few Phenomena Particular to Charged Polymers:

Electrostatic packaging of DNA into the cell nucleous by histones -
The “polyelectrolyte effect” -

Volume phase transitions of polyelectrolyte gels -

Layer-by-layer polyelectrolyte deposition -

Empirical Fuoss law: \( \eta \sim c^{1/2} \)

Cohen and Priel

T. Tanaka

Decher
I. A Primer on Electrostatics in Vacuum, Dielectric Media, and Electrolyte Solutions: Fundamentals for Charged Polymers

Electrostatics in Vacuum:

In vacuum, a point charge of magnitude \( q_1 \) defines an isotropic electrostatic potential field \( \psi \) that decays inversely with radial distance \( r \) from the charge,

\[
\psi = \frac{q_1}{4\pi\varepsilon_0 r}
\]

where \( \varepsilon_0 \) is the permittivity of vacuum (8.854x10\(^{-12}\) C\(^2\)/N m\(^2\)). SI units are chosen for this and subsequent equations, so \( \psi \) is in units of volts and charge is in the units of coulombs.

The negative of the gradient of \( \psi \) defines the electric field \( E \), the force vector experienced per unit of positive charge. For an isolated point charge in vacuum, \( E \) is directed radially inward or outward, depending on the sign of central charge,

\[
E = -\frac{d\psi}{dr} = \frac{q_1 r}{4\pi\varepsilon_0 r^3}
\]

where \( r \) is a radial vector. A second charge of magnitude \( q_2 \) brought to the vicinity of the first experiences a force \( F \),

\[
F = q_2 E
\]

To bring a like charge from infinity to position \( r \) thus requires work, given as the electrostatic interaction energy \( U \) of the two charges,

\[
U = -\int_{\infty}^{r} F \cdot dr = \frac{q_1 q_2}{4\pi\varepsilon_0 r}
\]

Bringing multiple charges from infinity into a defined spatial arrangement – essentially the process of creating a charged polymer – requires generalization of the preceding formulae. Again, in this first discussion, the medium supporting the charges is considered to be vacuum. The arranged charges are represented through a spatial distribution \( \rho(r) \), where \( r \) now denotes position relative to the origin of an arbitrary coordinate system; \( \rho(r) \) thus has units of charge per volume and the product \( \rho(r)dr \) has units of charge itself, i.e., this product represents the charge \( dq \) contained within the volume \( dr \). (In this notation, \( dr \) is not a differential vector; if spherical coordinates are chosen, for example, \( dr = 4\pi r^2 dr \), where \( r \) is the distance from the coordinate system origin.)
For a discrete point charge, $\rho(r)$ can be written as the product of the charge magnitude $q$ with a three-dimensional delta function $\delta(r-r')$ placed at the charge’s location $r'$. The delta function is defined as zero everywhere except where its argument is zero, where the amplitude is infinite. The volume integral of the delta function is defined as unity, giving the function itself units of inverse volume.

By linear superposition of contributions from all of the distributed charges, the electrostatic potential $\psi(r)$ at any point $r$ in space is given as a volume integral,

$$\psi(r) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|r-r'|} \, dr'$$

Similarly, the electrostatic potential energy $U$ can be written as a double volume integral,

$$U = \frac{1}{4\pi\varepsilon_0} \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr'$$

For an assembly of spatially discrete charges, $\psi(r)$ simply sums individual potentials, and $U$ sums pair-wise interactions energies. For a distribution of charge, $E$ can again be calculated as the negative of the gradient of $\psi(r)$,

$$E(r) = -\nabla \psi(r)$$

All classical electrostatic phenomena can be understood through Maxwell’s equations, and deriving the preceding results from them is a useful exercise. Simplified for electrostatics (i.e., with time derivatives and equations for the magnetic field eliminated), Maxwell’s set if 4 equations reduces to the following two differential equations:

$$\varepsilon_0 \nabla \cdot E = \rho^{(e)}$$

$$\nabla \times E = 0$$

The variable $\rho^{(e)}$, the total charge per unit volume, is generally a function of $r$. The first equation is the important one, as the second one merely ensures that $E$ can be written as the gradient of a potential function, as already done in preceding equations through definition of $\psi(r)$. In terms of $\psi(r)$, the first of Maxwell’s equations can be rewritten

$$\varepsilon_0 \nabla^2 \psi = -\rho^{(e)}$$

Applied to a isolated point charge $q$ positioned at $r=0$, this equation states in spherical coordinates,

$$\varepsilon_0 \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d\psi}{dr} = -q \delta(r)$$

Multiplying by $4\pi r^2$ and integrating from 0 to $r$,

$$\int_0^r 4\pi\varepsilon_0 \frac{d}{dr} r^2 \frac{d\psi}{dr} \, dr = -\int_0^r q \delta(r) 4\pi r^2 \, dr$$

The definition of $\delta(r)$ makes the integral on the right-hand-side equal to $-q$. Integrating the left-hand-side,
\[ 4\pi\varepsilon_0 r^2 \frac{d\psi}{dr} = -q \]

Finally, after dividing through by \(4\pi\varepsilon_0 r^2\) and then integrating with respect to \(r\) once again, now from \(r\) to \(r=\infty\) (where \(d\psi/dr=0\)), provides the first equation of this handout.

**Electrostatics in a Dielectric Medium:**

Instead of a point charge, suppose a single conducting sphere of charge \(q_1\) and radius \(a\) is placed in vacuum. The electrostatic potential at the sphere surface, denoted \(\psi_s\), is found from the first equation of the preceding section by equating \(r\) to \(a\).

\[ \psi_s = \frac{q_1}{4\pi\varepsilon_0 a} \]

The factor \(4\pi\varepsilon_0 a\) is termed the “capacitance” \(C\) of the sphere in the vacuum. More generally, for any situation with a separation of positive and negative charge, \(C\) is defined as the proportionality between the magnitude \(q\) of the separated charges and the potential difference \(\Delta\psi\) established between these charges,

\[ C = \frac{q}{\Delta\psi} \]

The familiar case is a parallel plate capacitor, which separates two conducting plates by a planar gap. When placed at different electrostatic potentials, equal and opposite charges \(+q\) and \(-q\) accumulate on the two plates in proportion to the potential difference \(\Delta\psi\) applied.

Substituting a real material, but one that is not a conductor, for the vacuum in the gap between plates of a capacitor raises \(C\), i.e., the same potential difference produces a larger charge difference. The origin of the additional charge is the bulk polarization of the material, associated with orientation of the material’s permanent dipoles (if present) and/or the creation in the material of induced dipoles by the field. Both effects cause a net charge to accumulate in the material where it contacts the plates. An insulating real material is called a “dielectric”.

For a dielectric material, the bulk polarization vector \(P\) reflects the volume density of dipoles \(N\) and their individual dipole magnitudes \(qd\),

\[ P = Nqd \]

where \(q\) is the magnitude of charge separated to create an average dipole, and \(d\) is a vector capturing the effective average charge separation and orientation. \(P\) for a linear dielectric material is a linear function of the field \(E\) existing inside the material,

\[ P = N\alpha E \]

where \(\alpha\) is the polarizability of the individual atoms or molecules comprising the material; \(\alpha\) has units of volume. Only in a dilute gas will \(E\) be equal to the externally applied field. The product \(N\alpha\) defines the material’s electric susceptibility \(\chi\).
In analogy to $\rho^{(e)}$, the previous equation allows definition of a polarization charge density 
$\rho^{(p)}$, which also has units of charge per volume,

$$
\varepsilon_0 \nabla \cdot P = -\rho^{(p)}
$$

In a spatially uniform material or phase, the case of most interest, polarization charge
appears only at interfaces, where this charge increases $C$ from its value in vacuum.

Merging the preceding equation with the first of Maxwell’s equations (page 7) provides
an equation governing $E$ in the context of real materials developing polarization charge
(i.e., dielectric materials),

$$
\varepsilon_0 \nabla \cdot (1 + \chi) E = \rho^{(e)} - \rho^{(p)} = \rho^{(f)}
$$

where $\rho^{(f)}$ can be regarded as the volume density of “free” charges in the material, i.e.,
the density of charges developed by mechanisms different than polarization; free charges
are ascribed to the dissociated ions discussed in this handout’s Introduction section. The
quantity $1 + \chi$ becomes a fundamental material constant termed the dielectric constant $\varepsilon$.
The final governing equation, the traditional basis for understanding electrostatic effects
in real materials, is written in terms this constant

$$
\varepsilon \varepsilon_0 \nabla^2 \psi = -\rho^{(f)}
$$

This is known as the Poisson equation. Note that $\varepsilon$ is unitless. Typical values for $\varepsilon$ are
given below (J. Israelachvili, Intermolecular and Surface Forces, 1985):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen-bonding</td>
<td></td>
</tr>
<tr>
<td>methyl-formamide</td>
<td>182.4</td>
</tr>
<tr>
<td>Formamide</td>
<td>109.5</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>84</td>
</tr>
<tr>
<td>Water</td>
<td>78.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>58.5</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>40.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.6</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>20.2</td>
</tr>
<tr>
<td>Ammonia</td>
<td>16.9</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>6.2</td>
</tr>
<tr>
<td>Non–hydrogen bonding</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>(CH$_3$)$_2$CO</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>Benzene</td>
<td>C$_6$H$_6$</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>Dodecane</td>
<td>C$<em>{12}$H$</em>{26}$</td>
</tr>
<tr>
<td>Hexane</td>
<td>C$<em>6$H$</em>{14}$</td>
</tr>
<tr>
<td>Crystals</td>
<td></td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
</tr>
<tr>
<td>Diamond</td>
<td>C</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
</tr>
</tbody>
</table>

*The dielectric constant is a measure of the extent of reduction of electric fields and consequently of the reduced strengths of electrostatic interactions in a medium.

* Value at 0°C.

* Value at 16°C.

The dielectric constant $\varepsilon$ should not be regarded as an abstract quantity: it captures the
ability of an electric field to polarize a material. The difference between a “polar” and
“nonpolar” solvent, descriptions used throughout the field of chemistry, is quantified in $\varepsilon$. The above table shows that $\varepsilon$ varies widely, from close to unity (hexane) to almost 200 (methyl formamide). Water is highly polar ($\varepsilon=78.5$), but it is certainly not the most polar of solvents; electrostatic effects in solvents such as ethylene glycol, methanol, acetonitrile ($\varepsilon=30-40$), all polar organic solvents, are comparable to those in water.

The behavior of a dielectric material is most easily visualized in the context of a parallel plate capacitor, two metal plates of area $A$ separated across a gap of thickness $d$ by a dielectric material:

Negative and positive polarization charges build, respectively, at $x=0$ and $x=d$ due to the electrostatic potential difference, $\Delta \psi = \psi_o - \psi_d$, applied between the plates. Intuitively, we expect the potential across the gap to drop linearly, as sketched. In the bulk of the dielectric material filling the gap, where no excess charge is present (i.e., $\rho(f)=0$), the preceding equation reduces to

$$\varepsilon_0 \varepsilon \frac{d^2 \psi}{dx^2} = 0$$

which after two integrations, confirms this intuition,

$$\psi = ax + b$$

where $a$ and $b$ are constants of integration. To go further, we focus on the region extremely close to $x=0$, the region where negative polarization charge accumulates. Here, letting $q$ be the magnitude of the charge,

$$\varepsilon_0 \varepsilon \frac{d^2 \psi}{dx^2} = -\rho(f) = - \frac{q \delta(x)}{A}$$

Multiplying both sides by $dx$ and integrating,

$$\varepsilon_0 \varepsilon \frac{d\psi}{dx} = - \frac{q}{A}$$

This fact establishes that constant $a = - \frac{q}{A \varepsilon_0 \varepsilon}$, and from this result, we quickly can find

$$\Delta \psi = - ad = \frac{qd}{A \varepsilon_0 \varepsilon}$$
The parallel plate capacitance is thereby \( C = \varepsilon_0 \varepsilon_\text{A} \). This well-known formula illustrates that more polarization charge accumulates in more polar dielectric media. And, with more polarization charge, external applied electric fields are weakened within these media. As discussed in more detail shortly, the high solubility of ionic species in polar solvents such as water simply reflects a reduction in the attraction between positive and negative ions due to the orientation of the solvent molecule around these ions.

For an isolated charged sphere immersed in a dielectric medium, it is not hard to apply the same sort of analysis to find \( C \),

\[
C = 4\pi\varepsilon_0 a
\]

Again, \( C \) accounts not just for the fixed charge of the sphere but also for the polarization charge accumulated in the medium against the sphere surface. The two are typically considered together, residing inside a fictitious “Gaussian” surface encasing the sphere. With this convention, electrostatic problems involving homogeneous dielectric media can be solved by simple replacement of the factor \( \varepsilon_0 \) in the vacuum solution with the factor \( \varepsilon\varepsilon_0 \) in the dielectric solution. For example, the electrostatic potential established by an isolated point charge in a dielectric medium can be written,

\[
\psi = \frac{q_1}{4\pi\varepsilon\varepsilon_0 r}
\]

Note that the potential is lowered by the presence of the dielectric.

This method for solving electrostatic problems by analogy breaks down when there are free charges present in the medium, i.e., when \( \rho^{(f)} \) is nonzero. This important case will be dealt with separately.

Maxwell’s equations provide an exact treatment of classical electrostatic phenomena at all length scales. Introducing \( \varepsilon \), as done here, renders approximate the equations of electrostatics, the media modeled as continua at all length scales down to the molecular.

The use of a macroscopic continuum property, \( \varepsilon \), at molecular length scales raises questions. Is the dielectric constant of water near a protein surface, for example, really the same as in bulk water? The answer would seem to be no, as \( \varepsilon \) captures the polarizability of the aqueous medium, ultimately reflecting the orientation and creation of dipoles. Certainly we expect the orientation and polarization of water molecules to be different when the molecules are held against a protein surface. To address this problem, Maxwell’s equations can be solved more rigorously, forgoing the introduction of \( \varepsilon \), by solving the equations at the molecular scale. However, following this approach, explicit geometric descriptions of each molecule in the system – including protein, solvent, and ions - and their polarizabilities are needed. The magnitude of the analysis/computation becomes enormous. Fortunately, computer simulations, though not yet sophisticated enough to be regarded as exact, have returned descriptions reasonably consistent with the approach described here.
Ion Self-Energy and Solubility -
(J. Israelachvili, Intermolecular and Surface Forces, 1985, chapter 3)

An ion in vacuum or a dielectric material possesses an electrostatic energy equal to the
work needed to form the ion. In vacuum, this work is known as the self-energy, while in
a dielectric material, it is known as the Born energy. Quantifying these and related
quantities is important to understanding how/when ions dissociate/dissolve into various
materials.

Imagine charging a small neutral sphere of radius a by gradually increasing its charge
from zero. At any intermediate stage, the charge is designated q, and in the final state, Q.
Each charge increment dq must be brought from infinity to r=a, expending work as this
increment is driven against the rising electrostatic potential. The differential amount of
work dw associated with dq can be written

$$dw = \psi_{r=a}(q) dq = \frac{q dq}{4\pi\varepsilon\varepsilon_o a}$$

The net electrostatic or free energy of charging can be obtained by integrating to Q.

$$\mu^i = \int dw = \int_0^Q \frac{q dq}{4\pi\varepsilon\varepsilon_o a} = \frac{Q^2}{8\pi\varepsilon\varepsilon_o a}$$

Transfer of an ion from a medium of low \(\varepsilon\) to one of high \(\varepsilon\) is therefore energetically
favorable. Letting two such media be designated “1” and “2”, the free energy change
associated with the transfer is given

$$\Delta\mu^i = \frac{Q^2}{8\pi\varepsilon\varepsilon_o a} \left( \frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2} \right)$$

There is an additional small contribution to the free energy change arising from the
opening of cavities to accommodate the ions.

To illustrate the importance of the preceding formula for a biological system, consider a
lipid membrane, modeled as a medium of \(\varepsilon=3\) separating two aqueous phases of \(\varepsilon=80\).
For a sodium ion (Q=e, a=0.2 nm) in the aqueous phase to partition into the membrane at
room temperature, the previous formula shows that the ion must surmount an energy
barrier of approximate height \(\Delta\mu_i=44kT\). The associated partition coefficient, given
\(\exp(-44)=10^{-19}\), suggests that such partitioning can ignored to good approximation. Ions
do not dissolve or form in nonpolar environment, so sodium ions cannot directly move in
and out of a cell through its membrane. This sort of calculation is accurate to within a
factor of about 50%.

From the electrostatic interaction energy of two point charges, one can reasonably
estimate the free energy needed to separate (equivalently, to dissociate or dissolve)
monovalent salts such as sodium chloride in various solvent media,
\[ \Delta \mu^i = e^2 \left( \frac{1}{4\pi \varepsilon_0 (a_+ + a_-)} \right) \]

where the sum \( a_+ + a_- \) is of the two ion radii. The calculation ignores both the lattice energy of the ions in their crystal and their Born energies in the solvent, effects which approximately compensate each other when a further small hydration correction is made. The calculated energy change is always positive, favoring ion association, but the entropy of dilution always favors dissolution. The molar solubility \( X_s \), calculated by balancing the two tendencies, is given

\[ X_s = \exp(-\Delta \mu^i/kT) \]

Using values for NaCl in water at room temperature, this formula predicts \( X_s = 0.075 \), a value close to the measured value of 0.10. This calculation’s illustrates that the solubilizing power of water for ions manifests water’s large value of \( \varepsilon \) and not any other special solvating property or specific interaction. As the following figure indicates (J. Israelachvili, Intermolecular and Surface Forces, 1985), varying \( \varepsilon \) predictably varies \( X_s \).

(Some complications are mentioned in the caption.)
Electrostatic interactions are of long range; note that the preceding derivation assumes that the energy of two associated ions, possibly with no solvent molecules between them, can be derived via a formula invoking the bulk dielectric constant of the surrounding fluid. The approach succeeds because the electrostatic energy $\Delta \mu^i$ depends not simply on the properties of the intervening space but by the entire medium bathing the two ions.

**Bjerrum Length** -
A real material experiences some temperature $T$, and the product $kT$ defines a natural energy scale. Normalized by $kT$, the interaction energy $U$ of two unit charges is expressed, 

$$\frac{U}{kT} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT} \frac{1}{r}$$

where a unit charge has the charge magnitude $e$ of an electron. The first factor on the right-hand-side, containing parameters characterizing only the medium and its temperature, has units of length. This material length scale is known as the Bjerrum length $l_b$, 

$$l_b = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT}$$

Fundamentally, $l_b$ is the separation at which two unit charges in a dielectric medium interact with an electrostatic energy equal to their thermal energy. Electrostatic interactions in dielectric materials can always be written using this parameter to collapse dependence on $\varepsilon$ and $T$. Note that the product $\varepsilon T$ is approximately independent of $T$ for most polar liquids.

**Electrostatics in an Electrolyte Medium:**

**Governing Equation** -
Electrolyte media are distinguished by the presence of dissolved charges, contributed by an added low molecular weight electrolyte or dissociation of ionizable units of a charged polymer or interface. While the dielectric properties of the solvating medium remain important, dissolved charges add important new features such as conductivity.

The previous section placed an important constraint on $\varepsilon$ for electrolyte media: $\varepsilon$ must be large enough to allow dissociation of ion pairs to create dissolved charges. Most electrolyte media are liquids, so small dissolved ions have significant mobility, moving with thermal motion and responding to electric and flow fields. Small ions also have finite solubilities in many uncharged polar polymers (PEO, PMMA, etc.)

An equation central to the understanding of electrostatic interactions in electrolyte media, the Poisson equation, has already been written. In such media, the fluctuating thermal rearrangement of dissolved ions makes $\rho^{(f)}$ locally nonzero. Writing the Poisson equation again, we must now consider impact from the right-hand-side 

$$\varepsilon \varepsilon_0 \nabla^2 \psi = -\rho^{(f)}$$
Origin and Behavior of Dissolved Charges -

In addition to dissociation of fixed ionizable units, additional mechanisms can provide a local charge imbalance near a polymer or interface:

1. Differences in electron affinities
2. Differences in ion affinities (mentioned previously for pseudo-polyelectrolytes)
3. Entrapment of ions

Because of its greater importance, focus here will lie on ion dissociation.

Suppose, as is commonly the case, that a polymer or interface bears ionizable acid groups that dissociate according to

\[ \text{AH} \leftrightarrow \text{A}^- + \text{H}^+ \]

At equilibrium,

\[ K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} \]

The simplest approximation (to be more fully explored later) is that the dissociated H\(^+\) ions near polymer or interface, at local concentration \([\text{H}^+]_s\), rearrange (equilibrate) in the local electrostatic potential \(\psi_s\) according to the Boltzmann law, i.e.,

\[ [\text{H}^+]_s = [\text{H}^+]_b \exp(-e\psi_s/kT) \]

Note that dissociation of a positive species such as H\(^+\) leaves the nearby polymer or surface with negative \(\psi_s\); the sign of this potential implies that H\(^+\) at/near the surface is enhanced from the bulk value \([\text{H}^+]_b\) as measured, by say, a pH meter.

Substituting the expression for \([\text{H}^+]_s\) into the immediately preceding equation and taking the negative base 10 logarithm of both sides,

\[ pK_a = \text{pH} - \log \frac{[\text{A}^-]}{[\text{AH}]} + \frac{0.4343 e\psi_s}{kT} \]

where \(pK_a = -\log_{10} K_a\). This form is more often written in terms of the degree of dissociation \(\alpha\),

\[ \text{pH} = pK_a - \log \frac{(1 - \alpha)}{\alpha} - \frac{0.4343 e\psi_s}{kT} \]

facilitating a comparison to the standard Henderson-Hasselbalch (H-H) equation for dissociation of monomer HA. (The H-H equation is identical to the one given above except it lacks the last term.) Localization of \([\text{H}^+]\) near polymer or surface effectively increases \(pK_a\) by the final term on the right-hand-side (remember that \(\psi_s\) is negative). Thus, dissociation of H\(^+\) from poly(AH) is suppressed compared to the analogous
dissociation of monomer AH. To evaluate the shift in $pK_a$, we would next need to relate $\psi_s$ to $\alpha$, a step too complicated to attempt at this point.

The lesson here is that the apparently straightforward charging of a polymer or interface by ionization may be complex, and ionization criteria for the analogous small molecule are not immediately relevant; ionizable units on charged polymers or interfaces effectively dissociate to much lesser extent than predicted from the dissociation constant of the single ionizable unit.

**Double Layer (Counterion Cloud)-**

In study of charged polymers, one often considers the whole polymer, or perhaps just a polymer segment, to be surrounded by a perturbed solution region containing thermally equilibrated small ions. The polymer itself is considered fixed (not thermally equilibrated). The perturbed region collects a sufficient excess of oppositely charged small ions to neutralize the ionized units of polymer. The excess ions are said to form a “counterion cloud”, and the central charged species together with its counterion cloud defines a “double layer”.

In the Gouy-Chapman model of the counterion cloud, the dissolved ions in the cloud are considered to equilibrate in the presence of two opposing forces, respectively associated with localized gradients in the electrostatic and chemical potentials.

In the classical (and simplest) treatments, chemical potentials are calculated by treating all dissolved ions as thermodynamically ideal, and the chemical and electrical potentials experienced by these ions are analyzed at the mean field level, smearing out correlations parallel to the polymer backbone or interface. Some charged polymer phenomena cannot be explained under these approximations, but comment about these matters will be reserved for later.

The term “counterion” deserves clarification: by convention, any dissolved ion of charge opposite to the polymer or interface may be termed a counterion. Thus, if the contacting medium contains added low molecular weight electrolyte, reference by this term is made to both dissociated ions AND added electrolyte ions of similar charge.

Distinguishing different ionic species through index “i” and indicating ion valence by $z$ (which can be negative or positive), under the approximations mentioned above, the force balance on species i reduces to

$$kT \nabla (\ln n_i) + e z_i \nabla \psi = 0$$

where $n_i$ is the number density of species i. The Boltzmann distribution law satisfies this balance,

$$n_i = n_b^i \exp(-e z_i \psi / kT)$$

The parameter $n_b^i$ is the bulk volume density of the ith species; a large reservoir at this density is assumed to remain in equilibrium with the medium near the polymer or
interface. Note that the potential chosen in the Boltzmann factor is the local electrostatic potential. In principal, the correct potential to use here is the potential of mean force, which accounts for the steric and electrostatic interactions among all ions.

The function $\rho^{(f)}$ is calculated from the local imbalance of charge in the contacting medium, obtained as the sum of the volume charge density contributed by each dissolved ion species,

$$\rho^{(f)} = \sum_i ez_i n_i$$

Inserting the two previous expressions into the Poisson equation generates the Poisson-Boltzmann equation,

$$\varepsilon \varepsilon_o \nabla^2 \psi = -e \sum_i z_i n_i \exp(-ez_i \psi / kT)$$

a celebrated nonlinear differential equation for $\psi$ in electrolyte media.

Two boundary conditions are needed to solve the Poisson-Boltzmann equation. First, far from polymer or surface, where ion concentrations reach their bulk values, $d\psi/dz \rightarrow 0$. Second, at a uniformly charged interface,

$$-\varepsilon \varepsilon_o \nabla \psi \cdot n = q$$

where $n$ is the surface normal and $q$ is the areal density of charge, i.e., the average number of charges per unit area. (One example of this boundary condition is given by the formula at the top of page 8.)

**Debye Length**

The Poisson-Boltzman equation introduces one new parameter to electrostatics, the Debye length $\kappa^{-1}$, which is sensitive to the overall volume density of dissolved ions. For an electrolyte containing a number of ionic species of different valence, $\kappa^{-1}$ is given

$$\frac{1}{\kappa} = \left( \frac{\varepsilon \varepsilon_o kT}{\sum_i (z_i e)^2 n_i} \right)^{1/2}$$

For a $z:z$ electrolyte, this formula reduces to

$$\frac{1}{\kappa} = \left( \frac{\varepsilon \varepsilon_o kT}{2 z^2 e^2 n_b} \right)^{1/2}$$

which, in terms of the Bjerrum length $l_b$, can be written

$$\frac{1}{\kappa} = \left( \frac{1}{8\pi l_b^2 z^2 n_b} \right)^{1/2}$$
For water at room temperature with only a 1:1 added electrolyte, \( \kappa^{-1} \approx 0.3/\sqrt{c_b} \) nm, where \( c_b \) is the electrolyte molarity. If \( c_b \) is 0.1 M, \( \kappa^{-1} \approx 1 \) nm, while if \( c_b \) is 0.001 M, \( \kappa^{-1} \approx 10 \) nm. Note that \( \kappa^{-1} \) values are not much different than polymer segment sizes.

\( \kappa^{-1} \) can be interpreted as the characteristic length over which a charged surface/solute perturbs the electrolyte environment of an otherwise homogeneous contacting solution. Alternatively, one can view that thermal motions maintain charge neutrality in such solutions only over length scales much greater than \( \kappa^{-1} \).

The Debye length is fundamentally connected to the Poisson-Boltzmann description of electrolyte, as seen shortly.

**Improvements to the Gouy-Chapman model**

The Gouy-Chapman model, described through the Poisson-Boltzmann equation, has been much criticized because of its gross approximation in treatment of dissolved ions. Improvements are regularly postulated, but most of these accomplish little at much cost.

Two corrections are the most common. The first recognizes that the Gouy-Chapman model treats the counterion cloud as an ideal gas of small, point-like charges. If a finite size is assigned to each ion, such a “gas” becomes nonideal. Treatments in analogy to those for a nonideal gas can be implemented. The Restricted Primitive Model (RPM), for example, describes the counterion cloud as a symmetrically charged, hard sphere fluid.

The second correction includes electrostatically induced correlations between the ions. The Poisson-Boltzmann equation can be viewed as asymptotically correct in the limit of weak charges, low counterion valence, and high temperature, conditions defining the “weak coupling” regime. As coupling becomes stronger, electrostatic interactions create correlated ion-density fluctuations about the mean ion distribution. In the limit of “strong coupling”, counterions might compress, for example, against an oppositely charged surface, form a highly correlated layers defining a Wigner crystal.
Salt-free Systems
When the only small dissolved ions are those released by the charged polymer or surface, the system is termed “salt-free”. Here, just a single ion “1” contributes to the counterion cloud, and $n_1$ of the preceding analysis must be reinterpreted as a normalization constant maintaining the system at overall charge neutrality, i.e., the total number of ions in the counterion cloud must exactly compensate for the opposite charge of the polymer or surface. The Poisson-Boltzmann equation still describes the counterion cloud, with the “Gouy-Chapman length” replacing the Debye length in describing the spatial extent of the cloud.

Linearization: the Debye-Hückel Approximation
Because the Poisson-Boltzmann equation is difficult to solve for realistic solute/surface geometries, investigators often obtain approximate solutions by linearizing the equation, i.e., by expanding the exponentials on the equation’s right-hand side and retaining only linear terms,

$$-e \sum_i z_i n_i^b \exp(-ez_i^i \psi / kT) = -e \sum_i z_i n_i^b \left(1 - \frac{ez_i^i \psi}{kT} + ...\right)$$

where the first factor in parenthesis, after weighting by the appropriate prefactors, sums to zero in going to the second line because the bulk solution is charge neutral.

Linearization of the Poisson-Boltzmann equation is known as the Debye-Hückel approximation. Substituting the linearized term of the preceding equation into the Poisson-Boltzmann equation yields a simplified and linear governing equation,

$$\nabla^2 \psi = \kappa^2 \psi$$

that is easily solved.

For a planar charged interface in contact with electrolyte, the Debye-Hückel solution for $\psi(z)$ has the form

$$\psi(z) = \psi_s \exp(-\kappa z)$$

where $z$ measures distance from interface into electrolyte. A linear $q-\psi_s$ relationship,

$$q = \varepsilon \varepsilon_0 \kappa \psi_s$$

now governs $C$ for the double layer. Indeed, this expression for $C$ is analogous to the one that applies to a parallel plate capacitor when the gap separation is $\kappa^{-1}$ and the gap is filled with a medium of dielectric constant $\varepsilon$.

The Debye-Hückel approximation holds when arguments of all exponential terms in the Poisson-Boltzmann equation are small enough to justify linearization, i.e.,

$$\frac{ez_i^i \psi}{kT} \ll 1$$
One recognizes this inequality as a statement that the electrostatic forces exerted on small ions must be weak compared to the thermal forces they experience. If the absolute value of \( z' \) is unity, the inequality specifies that \( \psi \) is everywhere less than \( \sim 25 \text{ mV} \). Rarely does this constraint rigorously apply in charged polymer systems.

From the formula for \( \psi(z) \), one sees that dissolved ions cause \( \psi \) to drop with distance from a charged interface against bulk electrolyte; absent the electrolyte, \( \psi \) would be a constant independent of \( z \). This \( \psi \) drop causes “screening”, the weakening of electrostatic interactions with distance. The Debye length is thus sometime called the “screening” length.

**Electrostatics in Different Geometries - Points, Lines, and Cylinders:**

Electrostatics near a planar charged surface have little immediate relevance to the study of charged polymers. Solutions of the Poisson-Boltzmann equation in spherical or cylindrical coordinates, on the other hand, play a great role. Unfortunately, except under the Debye-Hückel approximation, analytical solutions are difficult.

**Debye-Hückel Solutions**

a) *Single, isolated point charge*

\[
\psi = \frac{Q}{4\pi\varepsilon\varepsilon_0 r} \exp(-\kappa r)
\]

The presence of the ‘extra’ exponential decay is the only difference from the result for a point charge immersed in a dielectric medium.

As a linear equation governs the Debye-Hückel potential function, potentials from individual point charges located at different positions in a homogenous electrolyte medium can be summed to construct the net potential created by a charged assembly such a polyelectrolyte. We must be careful, however, to make certain that the summing of many small potentials does not produce a potential so large as to violate the validity of the underlying Debye-Hückel approximation.

b) *Single, isolated sphere of radius a*

\[
\psi = \frac{Q}{4\pi\varepsilon\varepsilon_0} \frac{\exp(\kappa a) \exp(-\kappa r)}{1 + \kappa a r}
\]

From this formula, \( C=4\pi\varepsilon\varepsilon_0 a(1+a\kappa) \), which is larger by a factor \( 1+a\kappa \) than \( C \) achieved in the absence of electrolyte. This ‘extra’ capacitance arises from the charge separation maintained by counterions across the double layer.

c) *Isolated, infinite line charge*

Letting \( p \) be the linear density of charge (\( = e/b \), where \( b \) is the average separation between dissociated unit charges along the line):
\[ \psi = \frac{\rho}{2\pi\varepsilon\varepsilon_0} K_0(\alpha \kappa) \]

\( K_0 \) is a modified Bessel Function (widely tabulated in math handbooks).

d) *Isolated cylinder of uniformly smeared surface charge*

\[ \psi = \frac{\rho}{2\pi\varepsilon\varepsilon_0} \frac{K_0(\alpha \kappa)}{\alpha \kappa K_1(\alpha \kappa)} \]

where \( \alpha \) is the cylinder radius and \( \rho \) is the projection of the surface charge onto the cylinder axis, a parameter with units of charge per length. The product \( \alpha \kappa K_1(\alpha \kappa) \) asymptotes to unity as \( \alpha \kappa \) goes to zero, properly replicating the outcome for a line charge (case c).

**Solutions of the Nonlinear Poisson-Boltzmann Equation**

a) *Infinite Line Charge in Salt-Free Solution*

A closed-form analytical solution to the full nonlinear Poisson-Boltzmann equation for an infinite cylinder in salt-free solution is available, although its form is complex.

b) *Poisson-Boltzmann Cell Model*

The “Poisson-Boltzmann Cell Model” solves the full nonlinear Poisson-Boltzmann equation for a single extended charged line or cylinder aligned inside a larger cylindrical cell. By imagining parallel, space-filling cells, electrostatic effects for charged polymers are predicted as a function of polymer concentration simply by changing the cell radius.

c) *Numerical Solutions*

Numerous papers describe numerical solutions of the Poisson-Boltzmann equation for particular geometries and boundary conditions. The most important case is an infinite cylinder of uniformly smeared surface charge, a situation much cited in discussion of counterion condensation on polyelectrolytes.

**Polar Interactions:**
(J. Israelachvili, Intermolecular and Surface Forces, 1985, chapter 4)

Molecules need not bear charge to undergo electrostatic interactions, and the interactions of ionomers are dominated by the dipole interactions of their undissociated ionizable units. Such units are characterized by displacement of finite charge over finite distance. The dipole moment \( p \) in such cases is defined

\[ p = ql \]

where \( l \) is the distance between two charges \( +q \) and \(-q\). Polar molecules are those having a net dipole. Most bonds are themselves asymmetric, and the dipole moment of a molecule can be roughly estimated by doing a vectorial summation of individual bond moments, which are tabulated. For example, the dipole moment of water may be
computed using the O-H bond moment $p_{OH}$ of 1.51 D (D is the abbreviation of Debye, equal to 3.336 C m) and the H-O-H bond angle of 104°.

\[ p = 2\cos(\frac{\theta}{2})p_{OH} = 1.85 \text{ D} \]

**Self and Interaction Energies of Dipoles**

**Dipole Self-Energy**

The self energy of a dipole in a dielectric media sums the Born energies of two isolated charges $\pm q$ with their mutual electrostatic interaction energy,

\[ \mu^i = \frac{1}{4\pi \varepsilon \varepsilon_0} \left[ \frac{q^2}{2a} + \frac{q^2}{2a} - \frac{q^2}{r} \right] \]

At contact of two ions of radius $a$ (l=r=2a), the dipole self-energy is close to the self-energy of each of the two ions. The solubility of polar molecules as a function of $\varepsilon$ might be expected to follow the same trends as for an ion, i.e., increased solubility at larger $\varepsilon$, but the preceding equation doesn’t quantitatively follow the experimental trend as well as it does for an ion, principally because the value of $p$ varies from solvent to solvent.

**Ion-Dipole Interaction Energy**

Ions and dipoles interact in a manner explained through the following sketch:

Charges $+q$ and $-q$ define the dipole, and $Q$ is a charge brought into the dipole’s vicinity. The ion-dipole interaction energy $w(r,\theta)$ is simply the sum of the two charge-charge electrostatic interaction energies,

\[ w(r,\theta) = -\frac{Qq}{4\pi \varepsilon \varepsilon_0} \left[ \frac{1}{A} - \frac{1}{B} \right] \]

For $r>>l$ (providing a relatively good approximation even for $r=2l$)

\[ w(r,\theta) = -\frac{Q(ql) \cos \theta}{4\pi \varepsilon \varepsilon_0} \frac{1}{r^2} \]

which, after recognizing that ion’s electric field at the dipole is given $E(r) = Q/(4\pi \varepsilon \varepsilon_0 r^2)$, can be rewritten,

\[ w(r,\theta) = -pE(r) \cos \theta \]

This expression can be viewed as general for the ion-point dipole interaction energy.

With an ion placed against the dipole of a water molecule, a contact energy of order several kT is calculated, depending on the size and valence of the ion. Since the
interaction is angle dependent, the size of this interaction will be more than sufficient to orient the dipole relative to the ion. For a cation, $\theta=0^\circ$ is favored, and for an anion, $\theta=180^\circ$ is favored.

Ions orientationally bound by solvent molecules are termed “solvated” or “hydrated” (if water is the solvent). Typically a first shell of solvent molecules, containing 4–6 molecules (“the hydration number”), constitutes the primary solvation shell. The displacement of this shell, and more distant solvent layers, is responsible for the structural or solvation forces between ions.

Agitated by thermal motions, the averaged interaction between an ion and a dipole will become temperature $T$ dependent. As seen by the preceding formula, if the dipole assumes all orientations equally, corresponding to very high $T$, the interaction energy falls to zero. At finite $T$, the appropriate average interaction energy corresponds to a Boltzmann distribution over $\theta$. For strong thermal motion $[w(r,\theta) < kT]$, this distribution leads to

$$w(r) = -\frac{Q^2 p^2}{3(4\pi\varepsilon_0)^2 kT^4}$$

which is attractive, as expected. This interaction drops sharply with $r$, so the ion only strongly perturbs only the first solvation shell. $[w(r)$ is an internal energy and not a free energy. An entropic contribution, associated with dipole alignment, must be subtracted from the above expression to get the free energy.]

Hydrated radii of other properties of various ions are given in the following table (Israelachvili, *Intermolecular and Surface Forces*, Academic Press, 1985)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Bare Ion Radius (nm)</th>
<th>Hydrated Radius (nm)</th>
<th>Hydration Number ($\pm 1$)</th>
<th>Lifetime (Exchange Rate) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$O$^+$</td>
<td>0.068</td>
<td>0.38</td>
<td>5–6</td>
<td>$10^{-9}$–$10^{-8}$</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.095</td>
<td>0.36</td>
<td>4–5</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.133</td>
<td>0.33</td>
<td>3–4</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.169</td>
<td>0.33</td>
<td>1–2</td>
<td>$10^{-9}$–$10^{-8}$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>0.031</td>
<td>0.46</td>
<td>4$^*$</td>
<td>$10^{-7}$–$10^{-2}$</td>
</tr>
<tr>
<td>Be$^{2+}$</td>
<td>0.065</td>
<td>0.43</td>
<td>6$^*$</td>
<td>$10^{-7}$–$10^{-3}$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.099</td>
<td>0.41</td>
<td>6$^*$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0.050</td>
<td>0.48</td>
<td>6$^*$</td>
<td>$10^{-7}$–1</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.176</td>
<td>0.30</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.181</td>
<td>0.35</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.185</td>
<td>0.33</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Br$^-$</td>
<td>0.216</td>
<td>0.33</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>I$^-$</td>
<td>0.264</td>
<td>0.34</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.347</td>
<td>0.37</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Number of water molecules forming a stoichiometric complex with the ion (e.g., [Be(H$_2$O)$_4$]$^{2+}$).

The hydration number gives the number of water molecules in the primary hydration shell, though the total number of water molecules affected is much larger and depends on the method of measurement. Similarly, the hydrated radius depends on how it is measured. Different methods can yield radii that can be as much as 0.1 nm smaller or larger than those shown. Table compiled from data given by Nightingale (1959), Amis (1975), Saluja (1976), Bockris and Reddy (1970), Cotton and Wilkinson (1980).
**Dipole-Dipole Interaction Energy**

The interaction of two dipoles is more complicated than that for ion and dipole but the corresponding interaction expressions are also more familiar to the chemistry field. After Boltzmann averaging of orientations for two dipoles, $p_1$ and $p_2$,

$$w(r) \approx -\frac{2p_1^2 p_2^2}{3(4\pi\varepsilon_0)^2 kT r^6}$$

at $r>>1$. The $r$-dependence is even stronger than for the ion-dipole case.

**Image Charges:**

Except for charges derived from added salt ions, which distribute thermally across their environment, charges within a medium typically are confined near a boundary, making the space surrounding the charges inhomogeneous, the medium across the boundary possessing properties distinct from those surrounding the charge. In such situations, the “image charge” method for calculating electrostatic interactions is a useful tool.

*a) Charge in vacuum near a conducting plate*

This situation is sketched below for a positive point charge $+q$ located a distance $d$ above the plate, which is grounded (i.e., held at zero potential). The potential field of the positive charge will induce a local buildup of negative charge on the surface of the plate, and this induced charge will then interact electrostatically with the point charge, creating an attractive force between charge and plate. An image force of this type, for example, can cause the adsorption of charged molecules onto bare metals.

To address the charge-plate interaction, the conducting plate is replaced by an artificial “image” charge $-q$ positioned a distance $-d$ below the plate surface. The symmetry of the two charges about $z=0$ dictates that the plate surface is everywhere at exactly zero potential, duplicating the actual potential at this surface when the plate is present. Thus, the right depiction produces the same electric field as the left depiction for the domain $z>0$. The two depictions are best analyzed in a cylindrical coordinate system $(r,z)$ with its origin at a position on the plate surface exactly between the charges. The potential for $z>0$ is immediately written as the sum of potentials for the two opposite charges,
\[ \psi(r, z) = \frac{1}{4\pi \varepsilon_0} \left( \frac{q}{\sqrt{r^2 + (z-d)^2}} + \frac{-q}{\sqrt{r^2 + (z+d)^2}} \right) \]

The associated electrical field lines are sketched below; note that the lines are perpendicular to the conductor surface at \( z=0 \), assuring a uniform potential across this surface.

From the form of the potential field, the charge induced at the plate surface can be derived by a small modification of a formula derived on page 10,

\[ \varepsilon_0 \left. \frac{d\psi}{dz} \right|_{z=0} = -\sigma(r) \]

where \( \sigma(r) \) is the radial density of charge per area in the conductor at \( z=0 \). This density is calculated from the two previous formulae,

\[ \sigma(r) = \frac{-qd}{2\pi \left( r^2 + d^2 \right)^{3/2}} \]

The total charge on the plate, evaluated as an area integral over \( \sigma(r) \), has the unsurprising value \( -q \).

The attractive force between the charge and the plate is just the electrostatic force acting on \( +q \) due to \( -q \),

\[ F = -\frac{q^2}{4\pi \varepsilon_0 (2d)^2} \]

and total electrostatic interaction energy is

\[ U = -\frac{q^2}{4\pi \varepsilon_0 (4a)} \]

As seen in the next section, this energy can be appreciable for ions near an ordinary interface.

b) Charge near a dielectric boundary
The image charge method can be applied to more important and complex situations, as exemplified by the case of a charge $+q$ in a medium of dielectric constant $\varepsilon'$ that contacts another medium of dielectric constant $\varepsilon''$ at a nearby planar boundary. Now, both media accumulate polarization charges at the interface.

The image charge $Q$ at $z=-d$ is no longer the negative of $+q$, a feature necessary to impose the dielectric constant asymmetry. The method finds for $z>0$,

$$\psi(r, z) = \frac{1}{4\pi\varepsilon_0\varepsilon'} \left( \frac{q}{\sqrt{r^2 + (z-d)^2}} + \frac{Q}{\sqrt{r^2 + (z+d)^2}} \right)$$

where $Q$ is given

$$Q = \frac{(\varepsilon' - \varepsilon'')}{(\varepsilon' + \varepsilon'')} q$$

If $\varepsilon'>\varepsilon''$, $Q$ is positive, not negative as before, and the charge $+q$ is repelled rather than attracted by the dielectric boundary. The charge-plate interaction force is given

$$F = \frac{(\varepsilon' - \varepsilon'') q^2}{(\varepsilon' + \varepsilon'') 4\pi\varepsilon_0 (2d)^2}$$

Using the example of a sodium ion ($a=0.2$ nm) in water ($\varepsilon'=80$) placed into contact ($d=a$) with a lipid membrane ($\varepsilon''=3$), this formula predicts an electrostatic energy of $\approx kT$; the concentration of sodium ions in the aqueous phase is thereby depleted significantly at the interface. This depletion, much larger for multivalent ions, tends to increase the surface tension as salts are added to water, a readily measured effect. The depletion is partially counteracted by the formation of neutral ion pairs at the interface.

The method of image charges can be extended to dipoles near an interface, taking advantage of the linearity of the governing equations for electrostatics in dielectric media. Each dipole is considered a pair of plus and minus point charges, each creating its own image charge.
Overview of “Screening” in Dielectric and Electrolyte Media:

Electrostatics is a field of physics, and perhaps not surprisingly, problems are often approached more from a mathematical perspective rather than a physical perspective. Actually, a broad physical perspective is pretty straightforward. In dielectric materials, polarization charge leads to a reduction (screening) of externally applied electric fields. Indeed, in one limit, metals can be considered perfect dielectric materials, as they fully screen all external electric fields by developing a static charge on their surface; this charge creates its own electric field of a magnitude need to neutralize exactly an external field. Dielectric materials develop less polarization charge than metals, allowing an external field to be experienced inside the material as a diminished internal field. If material domains are homogeneous, polarization charge only accumulates against domain boundaries. The polarization charge against these boundaries essentially produces an internal electric field that opposes the externally applied electric field, reducing the latter in inverse proportion to the material’s dielectric constant.

A molecular depiction of this perspective is sketched below for the case of a planar capacitor containing dielectric material. The external field has polarized the dielectric material’s nonpolar molecules and/or oriented its polar molecules; for middle cross sections of the material, no charge accumulation results from the polarization, but against the metal electrodes that apply the voltage difference $\Delta V$, the dipoles create layers of $+$ and $-$ polarization charge within the dielectric material. The electric field $E$ resulting from $\Delta V$ is simply $\Delta V/d$, the same as in vacuum.

The layers of polarization charge create their own electric field $E'$, directed against $E$. If the magnitude of polarization charge accumulation across the electrode areas is $q$, $E'$ is calculated

$$E' = \frac{\Delta V'}{d} = -\frac{q}{\varepsilon_o A}$$

where $A$ is the electrode area. (We derived this equation earlier.) Once again, the formula is the same as in vacuum. Everywhere away from the surfaces, the material experiences an internal field $E^*$ that sums the external and polarization-induced fields,

$$E^* = E + E' = \frac{\Delta V}{d} - \frac{q}{A\varepsilon_o} = \frac{\Delta V}{\varepsilon d}$$
The reduction of the electric field by polarization charge is captured in one material parameter, \( \varepsilon \), how easily the field polarizes molecules.

The potential field across the capacitor can be conceptually sketched,

\[
\psi(x) = V^- + \left( \frac{V^+ - V^-}{d} - \frac{q}{A\varepsilon_0} \right) x + \frac{qd}{2A\varepsilon_0}
\]

with the potential in the blue region of the curve written,

The last term on the right-hand-side is the voltage drop through each layer of polarization charge.

From this perspective, a dielectric material behaves just as vacuum, its dielectric constant a mathematical convenience to account for the charge accumulated at boundaries as a potential difference is applied.

Suppose that the dielectric medium of the previous arrangement is replaced by an electrolyte medium. Under the externally imposed potential difference between the electrodes, an electric field is experienced by the ions, causing them to move. This handout doesn’t consider electrodynamic phenomenon, so the ions are considered fixed in place at the time of analysis.

Ignoring spatial fluctuations on the size scale of \( \kappa^{-1} \) arising from the thermal motions of ions, the electrolyte’s internal electric field is macroscopically uniform, just as was the case for the dielectric medium, and at this scale, away from the boundaries, the electrolyte is also charge neutral.

Due to equilibration of the ions in the applied field, excess charge is found in the electrolyte near the electrodes, creating a double layer of characteristic thickness \( \kappa^{-1} \). (Such an arrangement is called a “electrically induced double layer”.) As discussed earlier, under the Debye-Hückel approximation there is a potential drop across this double-layer of magnitude \( \psi_s \), corresponding to charge accumulation \( q \)

\[
q = -A\varepsilon_0\kappa\psi_s
\]

Here, there are two double layers of opposite charge, one at each electrolyte. A formula analogous to the one at the top of the page again applies, i.e.,

\[
\psi(x) = V^- + \left( \frac{V^+ - V^-}{d} - \frac{2q}{A\varepsilon_0} \right) x + \frac{q\kappa^{-1}}{A\varepsilon_0}
\]
A molecular perspective similar to that given for a dielectric material is illustrated below. The bulk of the material is again neutral, with layers of charge accumulated near the electrodes. The width of these layers is much greater than for the dielectric but otherwise their electrostatic impacts are identical.

![Image](image.png)

The potential field has analogous form as well:

![Image](image.png)

The key lessons from this handout: (1) where there are regions of excess charge in a medium – whether free or from polarization – the potential drops steeply and (2) excess charge only accumulates near boundaries. Excess charge within a material causes “screening”, the weakening of electrostatic interactions. In a dielectric material, screening is immediate, whereas in an electrolyte, screening occurs over distances comparable to the Debye length.