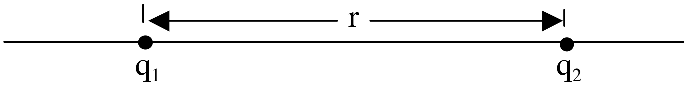
Lecture 28: Electrostatic effects in Aqueous Solution

Reading for Lectures 28—29: PKT Chapter 9

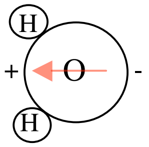
Key point: In the macroscopic world, matter is almost always neutral. The reason for this is that it costs a lot of energy to separate unlike charges. Why do ions form so easily in solution?

Review:

Consider two charges q_1 and q_2 a distance r apart. Coulomb's law asserts that these particles interact with a force of magnitude $F = \frac{|q_1 q_2|}{4\pi\varepsilon r^2}$ which points along the line of centers and is repulsive for like charges and attractive for unlike charges. The constant ε is called the permittivity and has units of C^2/Jm. For the vacuum (or air) $\varepsilon_0 = 8.85\times10^{-12}$ C^2/Jm, which is called the **permittivity of free space**. For other media, $\varepsilon = D\varepsilon_0$, where D is called the dielectric constant (PKT terminology).



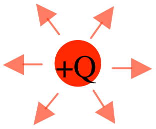
For water, $D \approx 80$, which means that the force between two charges in water is much reduced from what it would be in vacuum. The reason for this reduction is that water is **polar**, i.e., water molecules carry an electric dipole.



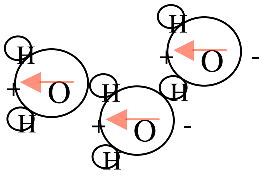
Important Comment:

This dipole is critical to biology in two ways:

(a) it reduces the forces between charges by partially shielding the charges. Note that it can't neutralize the charge, since H_2O is overall uncharged. It just "spreads it out".



(b) Because of the dipole moment, water molecules like to organize into a hydrogen-bonded networks. These bonding networks can be formed in many different ways, thus have a relatively high entropy (as well as a slightly lower energy). Anything which disrupts this netwrk structure increases the energy and decreases the entropy, both of which have the effect of increasing the Helmholz free energy F=E-TS. This is a key contribution to the hydrophobic effect which is the organizing/driving force for protein folding and membrane formation.



As a consequence of the Coulomb force, there is a potential energy involved in separating unlike charges off to infinite distance (or forcing like charges together from infinite distance):

$\Delta U = \int_r^\infty dr F(r) = \frac{|q_1 q_2|}{4\pi\varepsilon}\int_r^\infty \frac{dr'}{(r')^2} = \frac{|q_1 q_2|}{4\pi\varepsilon r}$, so (taking infinite separation as U=0, we find a potential energy $U(r) = \frac{q_1 q_2}{4\pi\varepsilon r}$, which is positive for like charges (which have to be "pushed" together from infinite, thus storing pe) and negative for unlike charges (which have to be "pulled" apart to get to infinite separation).

Consider two charges +e and -e a distance r apart, e.g., in a molecule in free space. Such charges have a negative potential energy, so it requires a positive energy to separate them, i.e., to ionize the molecule. The energy required to separate these charges in vacuum (or air) to a large distance is $E_{\text{ionization}} = \frac{1}{4\pi\varepsilon_0}\frac{q^2}{r}$. Thus, for two elementary charges at a characteristic distance of 0.1 nm,

$$E_{\text{ionization}} = \frac{1}{4\pi\varepsilon_0}\frac{q^2}{r} = \frac{1}{4\pi\left(8.85\times10^{-12}\right)}\frac{\left(1.60\times10^{-19}\right)^2}{10^{-10}} = \boxed{2.3\times10^{-18}\ J.}$$

Corresponds to the energy of taking one electron away from a molecule of size 0.1 nm (e.g., H). Of course, it is easier to remove the electron from an object 10x larger, like a large molecule.

Compare this with thermal energy at room temperature: $k_B T_{\text{room}} = 1.38\times10^{-23}(300) = 4\times10^{-21}$ J, which is smaller by a factor $\frac{E_i}{k_B T_r} = \frac{2.3\times10^{-18}}{4\times10^{-21}} \sim 570$.

Thus, the probability of finding this electron ionized due to thermal fluctuations carries a factor $P_i \propto e^{-\frac{E_i}{k_B T}} \sim e^{-570} \sim 10^{-250}$.

Upshot: It is VERY unlikely that you will find H-atom ionized at room temperature.

Comments:

- This would be very different at the surface of the sun where T~6000 K and even more so at T=10^8 K in the interior.

- There is an important entropic component of the ionization probability, ignored here. In fact, all atoms will ionize in empty space because of the translational entropy available to the ionized electron:

  Simple model: This is just the ligand receptor problem with a single ligand (the electron) and a single receptor (the ion). $Z = e^{\beta E_{ioniz}} + \frac{V}{\lambda_{th}^3}$, so the probability of ionization is

  $P_{ioniz} = \frac{1}{Z}\frac{V}{\lambda_{th}^3} = \frac{1}{1+\frac{\lambda_{th}^3}{V}e^{\beta E_{ionize}}}$. When $\beta E_{ioniz} >> 1$ (as it is here) $P_{ioniz} \sim \frac{V}{\lambda_{th}^3} e^{-\beta E_{ionize}}$.

  But, notice that P_{ioniz} always goes to unity for large-enough V! (qm corrections!)

Now compare with aqueous solution:

In aqueous solution, the permittivity is 80x larger than in vacuum (air) $\varepsilon_{water} = D\varepsilon_0$ with $D = 80$.

Thus, $E_{ionization} = \frac{2.3\times10^{-18}}{80} = 2.9\times10^{-20}$ J and $\frac{E_i}{k_B T_r} \sim \frac{570}{80} \sim 7$, so $P_i \propto e^{-\frac{E}{k_B T}} \sim e^{-7} \sim 10^{-3}$.

And, even larger for larger molecule!

Upshot: It is common for molecules to become charged in aqueous solution.

Two important effects:

(a) Some solutes separate into ionic species when they dissolve, e.g., $NaCl \rightarrow Na^+ + Cl^-$.

(b) Some macromolecular groups ionize in solution leaving a macro-ion and a relatively mobile counterion, e.g., proteins containing the ionic amino acids, Aspartic acid (Asp) and Glutamic acid (Glu), which contain $-C(=O)O^- + H^+$ ionized hydroxyl groups, and Arginine (Arg), Lysine (Lys), and Histidine (His), which contain $-NH^+ + OH^-$ ionized amide groups. These processes, which produce H^+ and OH^- are regulated by the water pH, i.e., groups may or may not ionize depending on ambient pH.

- These charged species, charged macro-ions, released counterions, and salts/electrolytes, are common in the biological world:
- Charged surfaces release counterions of opposite charge, leading to electric double-layers (dipole layers).
- Mobile charges in solution (from salts, etc.) screen charges, so that charge effects fall off as $e^{-\kappa r}$ instead of the purely Coulombic 1/r.
- Polyvalent ions play a particularly important role when they are present.

These diffuse charge clouds play an important role in controlling the macromolecular stereo-specific interactions which govern protein (and DNA/RNA) interactions/function and the way in which these molecules interact with surfaces, especially soft surfaces such as membranes.

Technical points to keep in mind:

- Treatment of these charge clouds involves both classical electrostatics and thermal/statistical/diffusive effects.
- At long distances, the role of these clouds can be included in an average ("mean-field") continuum way; at short distances, the discreteness of charge and the specific pattern of charges plays an important role.

The Poisson-Boltzmann Equation and the equilibrium particle distributions:

The mechanics of charge clouds is coupled:

A. Electrostatics:

The distribution of charge $\rho(\vec{r})$ produces an **electrical potential** $\Phi(\vec{r}) \equiv V(\vec{r})$ (PKT).

Note: PKT use Φ for the electric-field flux, which is entirely different.

B. Statistical mechanics:

This potential $\Phi(\vec{r})$ in turn determines the equilibrium distribution of the charges.

Comment:

At short distance scales, the charge distribution is always discrete and the corresponding electrical potential is singular at the points of the charge distribution.

At long distance scales (i.e., for average behavior) both can often be replaced approximately by smooth distributions $\langle\rho(\vec{r})\rangle, \langle\Phi(\vec{r})\rangle$, which are "mean fields" and do not include "correlations."

I'll drop the "average" notation; however, keep it in the back of your mind.

Suppose you have several charged species α with particle density $n_\alpha(\vec{r})$ and charge q_α, respectively. Then, the charge-density distribution is $\rho(\vec{r}) = \sum_\alpha q_\alpha n_\alpha(\vec{r})$.

Recall that electrical potential is defined in such a way that in a potential field $\Phi(\vec{r})$ a particle of charge q at position $\vec{r}$ has an (electrostatic) energy $U_{electric}(\vec{r}) = q\Phi(\vec{r})$.

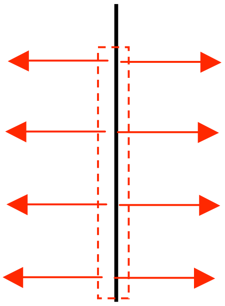
It follows that the (electrostatic) energy of a particle of type α is $q_\alpha\Phi(\vec{r})$.

If these particles are effectively ideal (non-interacting) and have no other forces (walls, etc.) acting on them, then they will be distributed according to $n_\alpha(\vec{r}) = n_\alpha^0 e^{-\frac{q_\alpha\Phi(\vec{r})}{k_BT}}$ (Boltzmann distribution, c.f., gravitational distribution), where the prefactor sets the overall number of particles of type α.

Thus, the equilibrium charge-density distribution is $\boxed{\rho_{eq}(\vec{r}) = \sum_\alpha q_\alpha n_\alpha(\vec{r}) = \sum_\alpha q_\alpha n_\alpha^0 e^{-\frac{q_\alpha\Phi(\vec{r})}{k_BT}}}$.

That completes part B of the derivation. On to part A!

Back now to electrostatic fundamentals:



If you have the electrical potential, you find the electric field by taking $\vec{E} = -\nabla\Phi$, i.e., $E = -\frac{d\Phi(x)}{dx}$ if everything is varying in one dimension only.

But, how do you relate the charge density $\rho(\vec{r})$ to $\Phi(\vec{r})$.

I'll do this in 1D and tell you the general result.

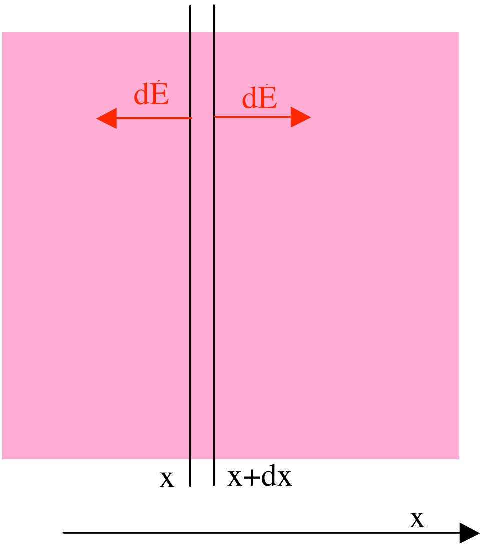
What is the electric field from a flat 2D surface of charge density σ?

Symmetry requires that it points perpendicularly away from the plane, symmetrically in both directions.

Remember Gauss's theorem, which says that, if you surround a charge q with a surface which is always perpendicular to the electric field, then the sum over the surface of the product of the area element times the electric field strength equals $\frac{q}{\varepsilon_0}$ in a vacuum (or $\frac{q}{\varepsilon}$ in a uniform medium of permittivity ε).

In this situation $2AE = \frac{q}{\varepsilon} = \frac{A\sigma}{\varepsilon}$, so $E = \frac{\sigma}{2\varepsilon}$, which is independent of x.

Future Ref: If E=0 on one side, then $E = \frac{\sigma}{\varepsilon}$ on the other.



Each infinitesimal slab of thickness dx has an (infinitesimal) charge density $\sigma(x) = dx\rho(x)$, which contributes an electric field $dE' = \frac{dx\rho(x)}{2\varepsilon}$.

All the slabs contribute additiely to the total field E(x).

It follows that $E(x+dx) - E(x) = 2dE' = dx\frac{\rho(x)}{\varepsilon}$, so

$\frac{dE(x)}{dx} = \frac{\rho(x)}{\varepsilon}$, so finally $\boxed{\frac{d^2\Phi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon}.}$

Generally, $\boxed{\nabla^2\Phi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon}.}$

This is called the Poisson equation (part A of our calculation).

Putting together parts A and B:

$$\boxed{\frac{d^2\Phi(x)}{dx^2} = -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_\alpha^0 e^{-\frac{q_\alpha\Phi(x)}{k_BT}}} \text{ or } \boxed{\nabla^2\Phi(\vec{r}) = -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_\alpha^0 e^{-\frac{q_\alpha\Phi(\vec{r})}{k_BT}}.}$$

Poisson-Boltzmann equation

Once you solve for Φ, you can resubstitute in $n_\alpha(\vec{r}) = n_\alpha^0 e^{-\frac{q_\alpha\Phi(\vec{r})}{k_BT}}$ to find ion distributions.

This ugly second-order NON-linear differential equation governs the shape of the charge clouds.

Comments:

1. Looks hopeless; however, it turns out that we can make progress in simple cases:
2. When the potential is weak-enough, $\left|\frac{q_\alpha\Phi}{k_BT}\right| << 1$, then the exponential can be expanded,

$e^{-\frac{q_\alpha\Phi}{k_BT}} \approx 1 - \frac{q_\alpha\Phi}{k_BT} + \ldots$, giving

$$\nabla^2\Phi(\vec{r}) = -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_\alpha^0\left[1 - \frac{q_\alpha\Phi(\vec{r})}{k_BT} + \ldots\right] \approx -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_\alpha^0 + \frac{1}{\varepsilon k_BT}\left(\sum_\alpha q_\alpha^2 n_\alpha^0\right)\Phi(\vec{r}).$$

In practice, considerations of carge neutrality often cancel the first term on the right, leaving

$\nabla^2\Phi(\vec{r}) = \frac{1}{\varepsilon k_BT}\left(\sum_\alpha q_\alpha^2 n_\alpha^0\right)\Phi(\vec{r}) = \frac{1}{\lambda_D^2}\Phi(\vec{r})$, where $\frac{1}{\lambda_D^2} = \frac{1}{\varepsilon k_BT}\left(\sum_\alpha q_\alpha^2 n_\alpha^0\right)$.

This equation is known as the Debye-Huckel equation and λ_D is called the “Debye length.”