V. Electrostatics

Lecture 24: Diffuse Charge in Electrolytes

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1. Poisson-Nernst-Planck Equations

The Nernst-Planck Equation is a conservation of mass equation that describes the influence of an ionic concentration gradient and that of an electric field on the flux of chemical species, specifically ions. We can start with the general conservation of mass equation for an incompressible fluid ($\nabla . u = 0$):

$$\frac{\partial c_i}{\partial t} + u \nabla c_i + \nabla . F_i = 0$$

The background velocity in the convection term ($\nabla . (u c_i)$) is relatively easy to define in a dilute solution, where it is just the (mass averaged) velocity of the solvent. However, this velocity becomes more difficult to define in concentrated solutions, since the distinction between the "flux" of an ion and relative to the "flow" of the solvent becomes blurred. More general prescriptions are available that treat all molecules (ions and solvent) on an equal footing, such as the Stefan-Maxwell equations for coupled fluxes or the de Groot-Mazur equations of nonequilibrium thermodynamics, but we neglect such complexities here, since most electrolytes are dilute enough to be well described.

The flux density for the Nernst-Planck Equation can be generally expressed as

$$F_i = M_i c_i \nabla \mu_i$$

Using the Einstein relation,

$$M_i = \frac{D_i}{k_B T},$$

and the gradient of the chemical potential for a dilute solution,

$$\nabla \mu_i = \frac{k_B T}{c_i} \nabla c_i + z_i e \nabla \phi ,$$

we can rewrite the flux as

$$F_i = -D_i \left(\nabla c_i + \frac{z_i e c_i}{k_B T} \nabla \phi \right),$$

where the first term on the RHS is the flux due to diffusion and the second term on the RHS is the flux due to electromigration (the nonlinear term). We can now insert this expression for the flux into the conservation of mass equations and we will obtain the Nernst-Planck Equation for a dilute solution:

$$\frac{\partial c_i}{\partial t} + u \nabla c_i - \nabla \cdot \left[D_i \left(\nabla c_i + \frac{z_i e c_i}{k_B T} \nabla \phi \right) \right] = 0$$

The Nernst-Planck Equation gives us i equations with i+1 unknowns. Hence, in order to solve the system of equations, we need to come up with one more equation. We can describe the electrostatic potential by using the Poisson Equation (a mean field approach),

$$\rho = \nabla \cdot D ,$$

where ρ is the free charge density and **D** is the is the electric displacement field vector.
If we assume that we have a linear dielectric material, we can describe the electric displacement field vector as

$$D = \varepsilon E ,$$

where ε is the permittivity of the material (mainly the solvent), and **E** is the electric field generated by charges in the system. For electrostatics we also know that

$$\nabla \times E = 0$$

$$E = -\nabla \phi$$

Hence we can rewrite the expression for the electric displacement field vector as

$$D = -\varepsilon \nabla \phi$$

We can now insert this expression into the Poisson Equation to arrive at our final form for this equation:

$$\rho = -\nabla \cdot (\varepsilon \nabla \phi)$$

Using a mean field approximation, we can get another equation for the free charge density, defined in terms of the mean (volume averaged) ion concentrations,

$$\rho = \sum_i z_i e c_i$$

This equation sums up all the charges of all the ions per unit volume. Combining this equation and the Poisson equation, we can get a new equation for the electrostatic potential to combine with the Nernst Planck Equations:

$$-\nabla \cdot (\varepsilon \nabla \phi) = \sum_i z_i e c_i$$

Our full set of *Poisson-Nernst-Planck* (PNP) Equations is then:

$$\frac{\partial c_i}{\partial t} + u \nabla c_i - \nabla \cdot \left[D_i \left(\nabla c_i + \frac{z_i e c_i}{k_B T} \nabla \phi \right) \right] = 0$$

$$-\nabla \cdot (\varepsilon \nabla \phi) = \sum_i z_i e c_i$$

The system is now fully specified with matching numbers of equations and variables.

For concentrated solutions or solids, we must replace concentrations with activities in the flux expression (in brackets) and account for the dependence of the diffusivity on activity coefficients, as in previous lectures. The Poisson equation may also require modification to go beyond the mean field approximation, as will be discussed in an upcoming lecture on electrostatic correlations.

2. Dimensionless Form

We can now non-dimensionalize the PNP equations. Let's use the following non-dimensional variables:

$$\tilde{x} = \frac{x}{L}, \quad \tilde{c}_i = \frac{c_i}{c_{i,ref}}, \quad \tilde{\varepsilon} = \frac{\varepsilon}{\varepsilon_{ref}}, \quad \tilde{D}_i = \frac{D_i}{D_{i,ref}}, \quad \tilde{F}_i = \frac{F_i}{(D_{i,ref} c_{i,ref} / L)}, \quad \tilde{u} = \frac{u}{u_{ref}}, \quad \tilde{t} = \frac{t}{(L^2 / D_{ref})},$$

$$\tilde{\phi} = \frac{e\phi}{k_B T}, \quad \tilde{\nabla} = L\nabla$$

Using these, we can rewrite the Poisson-Nernst-Planck Equations in non-dimensional form. The dimensionless conservation of mass equation is:

$$\frac{\partial \tilde{c}_i}{\partial \tilde{t}} + Pe_i \tilde{u} \tilde{\nabla} \tilde{c}_i = -\tilde{\nabla} \tilde{F}_i$$

where Pe_i is the Peclet number for species i and is defined as

$$Pe_i = \frac{u_{ref} L}{D_{i,ref}}$$

If Pe << 1, the convection term can be neglected and hence ion transport will not be affected by fluid flow. There will however still be fluid flow (without feedback) due to the electrostatic body force exerted due to ionic charge.

The non-dimensional flux is

$$\tilde{F}_i = -\tilde{D}_i (\tilde{\nabla} \tilde{c}_i + z_i \tilde{c}_i \tilde{\nabla} \tilde{\phi})$$

and the non-dimensional Poisson equation is

$$-\frac{\varepsilon_{ref} k_B T}{eL^2} \tilde{\nabla}.(\tilde{\varepsilon} \tilde{\nabla} \tilde{\phi}) = e \sum_i z_i c_{i,ref} \tilde{c}_i$$

If we divide both sides by $\sum_i z_i^2 e c_{i,ref}$, we arrive at the following equation:

$$-\tilde{\lambda}_D^2 \tilde{\nabla}.(\tilde{\varepsilon} \tilde{\nabla} \tilde{\phi}) = \tilde{\rho} = \frac{\sum_i z_i c_{i,ref} \tilde{c}_i}{\sum_i z_i^2 c_{i,ref}}$$

where $\tilde{\lambda}_D^2$, a quantity that is usually much smaller than 1, is defined as

$$\tilde{\lambda}_D^2 = \left(\frac{\lambda_D}{L}\right)^2 = \frac{\varepsilon_{ref} k_B T}{eL^2 \sum_i z_i^2 e c_{i,ref}}$$

$$\lambda_D = \sqrt{\frac{\varepsilon_{ref} k_B T}{\sum_i (z_i e)^2 c_{i,ref}}}$$

λ_D describes the thickness of the double layer and is called the *Debye screening length*. It tends to be very small (Note $\lambda_D \propto \sqrt{\varepsilon}$). For example, for water this screening length tends to be on the order of 0.5-50 nm. The screening length increases as the dilute solution become more dilute $\left(\lambda_D \propto \left(\sum c_i\right)^{-1/2}\right)$.

Now let's consider a low dielectric liquid (such as many organic solvents) with ε_{ref} much smaller than that of water. The reduced permittivity would tend to reduce the Debye screening length, but this is counteracted by the poor solvation characteristics of the liquid, which leads to typically smaller ion concentrations $\{c_i\}$. As a result, λ_D may be of the same order as in water, or larger. In very dilute systems, such as surfactant-stabilized charged colloids in oils, the Debye screening length can be tens of microns. In typical electrolytes, however, the Debye length is much smaller, at the nanoscale, so that double layers are typically "thin" compared to most geometrical length scales – a crucial fact whose consequences we address below. In solvent-free room-temperature ionic liquids, which consist of large (~1nm) soft ions, the ion concentration is so large that the Debye length is smaller than the ion size and thus loses its physical significance. In such liquids, correlations between discrete ions are critical, and the ion size is the most relevant length scale, for not only specific chemical interactions, but also electrostatic correlations, as we will discuss in Lecture 28.

It is interesting to note that the Debye screening length acts as a natural length scale for diffusion/migration in the PNP equations. This is in contrast to classical convection/diffusion of neutral species, where there is no natural length scale (aside from the particle size) and mass transfer is controlled mainly by the geometrical length scale L.

The expression for the Debye screening length can be rewritten as:

$$\lambda_D = \sqrt{\frac{\varepsilon_{ref} k_B T}{2I}}$$

where I is the ionic strength, a measure of conductivity. It is defined as

$$I = \frac{1}{2} \sum_i (z_i e)^2 c_{i,ref}$$

An alternative way to get an idea of the Debye screening length is based on a scaling argument that is based on balancing electrostatic energy density and entropy/osmotic pressure. This approach can be conceptualized by an electric field that is trying to "squash" ions against a surface. The ions, having finite size, want to diffuse away both due to overcrowding of the layer adjacent to the surface in addition to the ions being at a finite, nonzero temperature. The length scale at which these two phenomena balance is the Debye screening length.

$$\frac{1}{2}\varepsilon_{ref}E^2 \sim k_B T c_{ref}$$

This is a balance of the electrostatic and thermal energy densities. Furthermore, we also know that

$$\lambda_D E \sim \frac{k_B T}{ze}$$

which is a balance of the voltage due to electrostatics (the electric field) and the thermal voltage. In effect this is a balance of forces. Upon rearranging, we recover the same expression as above, in the case of a z:z electrolyte

$$\lambda_D \sim \sqrt{\frac{\varepsilon_{ref} k_B T}{2(ze)^2 c_{ref}}}$$

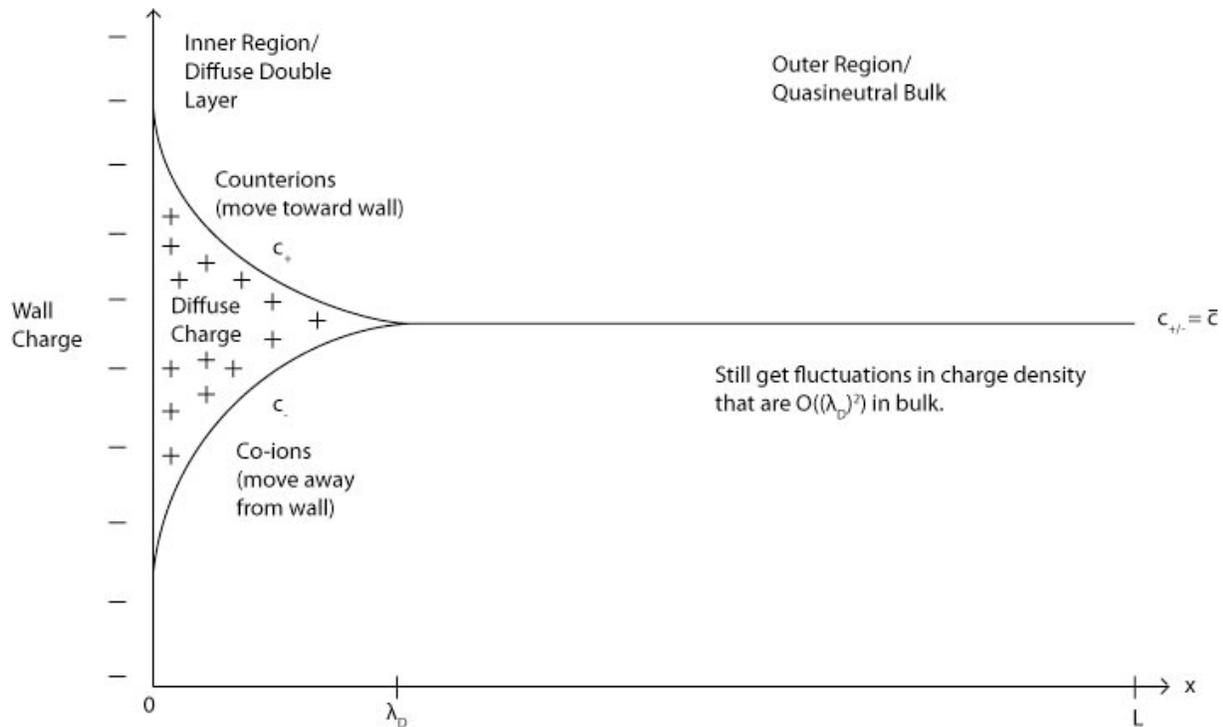which demonstrates the power of these scaling arguments.

Fig. 1. Ion concentration profiles in a quasi-neutral bulk electrolyte with thin double layers, where the Debye length is much smaller than the system size. In order to satisfy the electrostatic (or electrochemical) boundary conditions at a charged surface, the ion profiles adjust so as to create a narrow layer of diffuse charge, which decays away from the surface over the scale of the Debye length. The diffuse charge is equal and opposite to the surface charge, so that the two regions form a "double layer" that acts like a parallel plate capacitor at the surface.

3. Thin Double Layers

As noted above, for most electrolytes, the Debye length is much smaller than the geometrical length scale, $\lambda_D \ll L$ and hence $\tilde{\lambda}_D^2 \ll 1$.

If we assume that everything is scaled correctly, then $\tilde{\lambda}_D^2$ is a small parameter in the Poisson equation,

$$-\tilde{\lambda}_D^2 \tilde{\nabla}.(\tilde{\varepsilon}\tilde{\nabla}\tilde{\phi}) = \tilde{\rho}$$

which multiplies the highest derivatives (2nd order) in the dimensionless PNP equations and thus corresponds to a "singular perturbation". With proper scalings, all the terms in the PNP equations are O(1), except the terms in the Poisson equation where $\tilde{\rho} = $ O($\tilde{\lambda}_D^2$). This would seem to imply electroneutrality; however, setting ρ equal to zero means that you can no longer impose boundary conditions, because you have lost the mathematical ability to do so, since the number of independent variables is reduced by one. It is also tempting to assume that the potential satisfies Laplace's equation $\nabla^2\phi = 0$ in a neutral electrolyte, but we shall see that this too is incorrect, if the ion concentrations are nonuniform.

The question is how the system can be electroneutral while still satisfying Poisson's equation. In essence, we can assume electroneutrality in the bulk; however, when we get close to a charged surface, this assumption starts to break down. Therefore, we have to use the method of matched asymptotic expansion ("boundary-layer theory", singular perturbation theory) to solve this problem.

Physically, the picture looks something like figure 1, which shows that we have a quasi-neutral bulk of concentration $\overline{c}_i$ and potential $\overline{\phi}$, but also that we have a wall charge at which this assumption of quasi-neutrality breaks down. A wall charge can be induced by opposing or applying a voltage or via fluctuations in charge density of O($\tilde{\lambda}_D^2$) (even in the outer solution). Furthermore, the double layer acts like a capacitor, since there is a separation of charge.

3.1 Outer Region (Quasineutral Bulk)

We can describe the bulk region by an expansion of $\tilde{c}_i$ and $\tilde{\phi}$ and we let $\tilde{\lambda}_D \to 0$

$$\tilde{c}_i \sim \overline{c}_i = \overline{c}_i^{(0)} + \tilde{\lambda}_D \overline{c}_i^{(1)} + \tilde{\lambda}_D^2 \overline{c}_i^{(2)} + \dots$$

$$\tilde{\phi} \sim \overline{\phi} = \overline{\phi}^{(0)} + \tilde{\lambda}_D \overline{\phi}^{(1)} + \tilde{\lambda}_D^2 \overline{\phi}^{(2)} + \dots$$

We then plug these expansions into the governing equations to get relations (governing equations) for all the terms. At leading order (O(1)) in the bulk/outer region, we have essentially the same form of the Nernst-Planck equations:

$$\frac{\partial \overline{c}_i^{(0)}}{\partial \tilde{t}} + Pe_i \tilde{u} \tilde{\nabla} \overline{c}_i^{(0)} = -\tilde{\nabla} \overline{F}_i$$

$$\overline{F}_i = -\tilde{D}_i (\tilde{\nabla} \overline{c}_i^{(0)} + z_i \overline{c}_i^{(0)} \tilde{\nabla} \overline{\phi}^{(0)})$$

However, at leading order the Poisson equation reduces to the electroneutrality condition:

$$\overline{\rho}^{(0)} = \frac{\sum_i z_i c_{i,ref} \overline{c}_i^{(0)}}{\sum_i z_i^2 c_{i,ref}} = 0$$

$$\sum_i z_i c_{i,ref} \overline{c}_i^{(0)} = 0$$

which implicitly determines the potential. This is a scalar condition, however, so we are not allowed to impose any additional electrostatic boundary conditions on the quasi-neutral bulk, without considering matching with the double layers.

Only once we get beyond the leading order in the bulk, will we start moving away from the quasi-neutrality condition. For example, for the term that is O($\tilde{\lambda}_D^2$), we get:

$$-\tilde{\nabla} \cdot (\tilde{\varepsilon} \tilde{\nabla} \overline{\phi}^{(0)}) = \overline{\rho}^{(2)} = \frac{\sum_i z_i c_{i,ref} \overline{c}_i^{(2)}}{\sum_i z_i^2 c_{i,ref}}$$

Hence, even the bulk is not electroneutral, due to nonzero charge at higher order, and the leading-order potential does not satisfy Laplace's equation. Instead, we can combine the Nernst-

Planck equations with the leading-order electroneutrality condition to show that the potential is determined by the condition of charge conservation, since the leading order current density,

$$\tilde{J}^{(0)} = \sum_i z_i \tilde{F}_i^{(0)} \quad \text{satisfies} \quad \tilde{\nabla} \cdot \tilde{J}^{(0)} = 0$$

so that no bulk charge is created over time.

3.2 Inner Region (Quasi-equilibrium Diffuse Double Layer)

To find solutions for the diffuse double layer, we need to introduce a new set of spatial coordinates. Let us define these as follows:

$$\hat{x} = \frac{x}{\lambda_D} = \frac{\tilde{x}}{\tilde{\lambda}_D} \rightarrow Then \, \hat{\nabla} = \tilde{\lambda}_D \tilde{\nabla}$$

We do a similar expansion as in the bulk region:

$$\tilde{c}_i \sim \hat{c}_i(\hat{x}, \tilde{t}) = \hat{c}_i^{(0)} + \tilde{\lambda}_D \hat{c}_i^{(1)} + \tilde{\lambda}_D^2 \hat{c}_i^{(2)} + ...$$

$$\tilde{\phi} \sim \hat{\phi}(\hat{x}, \tilde{t}) = \hat{\phi}^{(0)} + \tilde{\lambda}_D \hat{\phi}^{(1)} + \tilde{\lambda}_D^2 \hat{\phi}^{(2)} + ...$$

For this analysis, we will also assume that **u** = 0 in the diffuse double layer.

If we plug the expansions into the Nernst-Planck equations, we obtain for the leading order term:

$$\nabla \cdot \mathbf{F}_i^{(0)} = \tilde{\lambda}_D \frac{\partial c_i^{(0)}}{\partial \tilde{t}} = O\left(\tilde{\lambda}_D\right)$$

Since we know this to be true, it is necessary that $\nabla . \hat{F}_i$ is small, but nonzero. Plugging the expansions into the expression for flux, we get as our leading order expression:

$$\mathbf{F}_i^{(0)} = -\tilde{D}_i(\nabla c_i^{(0)} + z_i c_i^{(0)} \nabla \phi^{(0)})$$

This expression again tells us that $\tilde{D}_i(\hat{\nabla} \hat{c}_i^{(0)} + z_i \hat{c}_i^{(0)} \hat{\nabla} \hat{\phi}^{(0)})$ must be small (O($\tilde{\lambda}_D$)). Furthermore, since we know that fluxes must be continuous, this inner flux must be equal to the outer flux at their respective asymptotic limits. This means we have to match the outer flux as it approaches the surface to the inner flux as it moves away from the surface. In mathematical terms we get:

$$\tilde{\lambda}_D \lim_{\tilde{x} \to 0} \overline{\mathbf{F}}_i = \lim_{x \to \infty} \mathbf{F}_i$$

which is essentially matching the two solutions at their respective asymptotic limits.

As $\tilde{\lambda}_D \to 0$ again the inner flux expression vanishes $\tilde{D}_i(\hat{\nabla} \hat{c}_i^{(0)} + z_i \hat{c}_i^{(0)} \hat{\nabla} \hat{\phi}^{(0)}) \to 0$, so that the double layer ion profiles correspond to *quasi-equilibrium*. Setting this term equal to zero is essentially equivalent to setting the flux equal to zero, which is the equilibrium condition. The intuitive physical reason as to why this is the case is that the double layers are thin enough that they can quickly equilibrate in response to any dynamical changes in the bulk (as long as they have much longer time scales). Therefore, this even holds under conditions where you have a macroscopic flux, since at the microscopic level the length scale dictates molecular behavior. This actually explains why the Gouy-Chapman model (an equilibrium model which we will study in upcoming lectures) still holds for thin double layers.

Setting the flux equal to zero at leading order in the double layer gives a Boltzmann distribution for the concentration:

$$\hat{c}_i^{(0)} = \hat{c}_i^{(0)}(\infty)e^{-z_i\hat{\phi}^{(0)}} \sim (const)e^{-\frac{z_i e\phi}{k_B T}}$$

if $\hat{\phi}^{(0)} = 0$ in the bulk, just outside the double layer. The inner problem for the PNP equations is then the equilibrium problem (assume $\tilde{\varepsilon} = 1$):

$$-\hat{\nabla}^2\hat{\phi}^{(0)} = \hat{\rho} = \frac{\sum_i z_i c_{i,ref}\hat{c}_i^{(0)}}{\sum_i z_i^2 c_{i,ref}}$$

This equation is called the Poisson-Boltzmann Equation. It describes the self-consistent mean electric field generated by the mean ion concentrations in Boltzman equilibrium in the potential.

In summary, if the Debye length is much smaller than the geometrical scale size, then the electrolyte breaks into two distinct regions: a quasineutral bulk solution and thin quasi-equilibrium double layers with diffuse charge.

For more reading on matched asymptotic expansions for electrochemical transport problems, see

1. Bazant, Chu, Bayly, SIAM J Appl Math 65 (2005) 1463-1484. (steady state)
2. Bazant, Thornton, Ajdari, Phys. Rev. E 70 (2004) 021506. (DC transients)
3. Olesen, Bazant, Bruus, Phys. Rev. E 82 (2010) 011501. (AC transients)

10.626 Electrochemical Energy Systems

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