V. Electrostatics

Lecture 25: Diffuse double layer structure

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4/6/11

Last time we showed that whenever $\lambda_D \ll L$ the electrolyte has a quasi-neutral "bulk" (or "outer") region at the geometrical scale L, where there is very little mean charge density $\rho = \sum_i z_i e c_i$ compared to the total charge density c_0, or more precisely $|\tilde{\rho}| = O(\varepsilon^2)$ where $\tilde{\rho} = \rho/ec_0, \varepsilon = \lambda_D/L \ll 1$. In order to satisfy electrostatic boundary conditions, however, diffuse charge exists in thin quasi-equilibrium double layers (which are mathematical "boundary layers").

The ion profiles are approximately in thermal equilibrium ($\mu_i \approx$ constant), even when there is a non-zero current of fluid flow, due to the small scale $\lambda_D \ll L$. [Note: the double layer can go out of equilibrium if $c_0 \to 0$ at a limiting current, or a very fast transient can occur, e.g. high frequency impedance with $\omega \sim D/\lambda_D^2$.]

1 Poisson-Boltzmann Equation

We start with an assumption of quasi-equilibrium, so that the chemical potential μ_i=constant. We separate the electric potential ϕ into two parts: $\phi = \overline{\phi} + \psi$, where $\overline{\phi}$ is the (approximately) constant bulk potential and ψ is the part due to diffuse charge. From the quasi-equilibrium assumption, the concentrations and charge density are in equilibrium with the spatially varying part ψ, so $c_i = c_i^{eq}(\psi), \rho = \rho_{eq}(\psi)$. The generalized Poisson-Boltzmann equation is derived by using this charge density in Poisson's equation (standard electro-statics) to get

$$-\nabla \cdot (\varepsilon \nabla \psi) = \rho_{eq}(\psi). \tag{1}$$

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For a dilute solution, the concentrations will follow a Boltzmann distribution,

$$c_i^{eq} = \nu_i c_0 \exp\left(-\frac{z_i e \psi}{k_B T}\right), \tag{2}$$

where ν_i is the stoichiometric coefficient defined as $c_{0,i}/c_0$, relating the bulk concentration of an individual species to the bulk salt concentration c_0 where $\psi = 0$. Using this term for the concentrations, the definition of the charge density, and assuming a constant permittivity the generalized Poisson-Boltzmann equation simplifies to

$$-\varepsilon \nabla^2 \psi = \sum_i z_i e \nu_i c_0 \exp\left(-\frac{z_i e \psi}{k_B T}\right). \tag{3}$$

For small potentials ($|\psi| \ll k_B T/e$), we can expand the exponential to get

$$-\varepsilon \nabla^2 \psi \approx \sum_i z_i e \nu_i c_0 \left[1 - \frac{z_i e \psi}{k_B T} + O(\psi^2)\right]$$

$$\approx \sum_i z_i e \nu_i c_0 - \sum_i (z_i e)^2 \nu_i c_0 \frac{\psi}{k_B T}$$

$$\approx \rho_{bulk} - \frac{\psi}{k_B T} \sum_i (z_i e)^2 \nu_i c_0. \tag{4}$$

We know that $\rho_{bulk} \approx 0$, and we can recognize the coefficient of ψ as $1/\lambda_D^2$, so

$$\lambda_D^2 \nabla^2 \psi = \psi, \qquad\qquad \lambda_D^2 = \frac{\varepsilon k_B T}{\sum_i (z_i e)^2 \nu_i c_0}. \tag{5}$$

This small voltage linearisation is known as the *Debye-Hückel Equation*, and λ_D is called the *Debye screening length*. In one dimension, the Debye-Hückel equation can be solved easily if the potential at the surface is known ($\psi(0) = \psi_D$),

$$\begin{array}{ll} \lambda_D^2 \frac{d^2\psi}{dx^2} = \psi & \qquad \psi \sim \psi_D e^{-x/\lambda_D} \\ \psi(0) = \psi_D & \implies \qquad c_i(x) = \nu_i c_0 \left[1 + \left(\frac{z_i e \psi_D}{k_B T}\right) e^{-x/\lambda_D}\right]. \end{array}$$

We can sketch this solution for the case of a binary electrolyte:
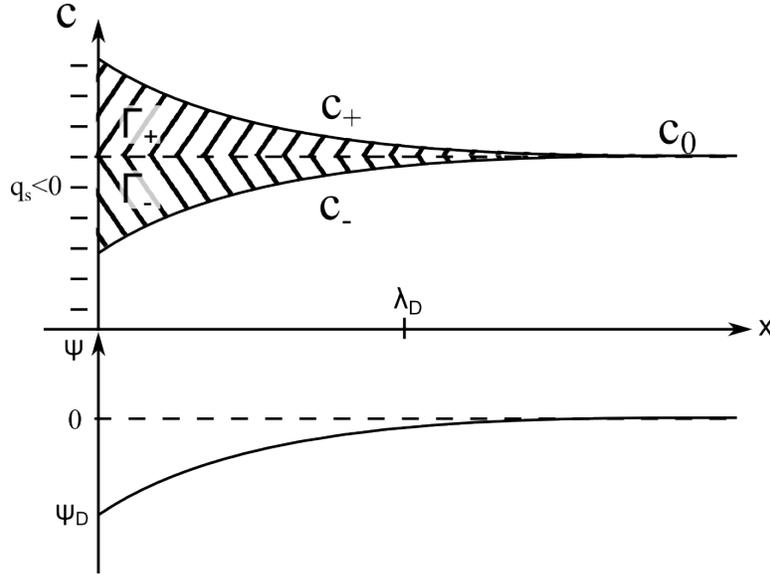
The concentration profiles relax to the bulk values at large x (which could be slowly varying, but are depicted as constant here). The integrated area of both curves tends to the same value, so that there is no net adsorption of charge near the surface in the limit of low voltage.

1.1 Capacitance of Double Layer (in the Debye-Hückel limit)

The capacitance is of the double layer is calculated by related the surface charge to the surface potential. The net charge brought to the surface can easily be calculated by integrated over the charge density:

$$q = \int_0^\infty \rho(\psi(x))dx = \sum_i \frac{(z_i e)^2 \nu_i c_0}{k_B T} \int_0^\infty \psi(x)dx = \frac{\varepsilon}{\lambda_D^2}(-\lambda_D \psi_D) = -\psi_D \frac{\varepsilon}{\lambda_D}$$

We expect that the net charge in the double layer should balance the surface charge, so this calculated value is also the surface charge. The capacitance is then calculated using its definition

$$C_D \equiv \frac{dq_s}{d\psi_D} = -\frac{dq}{d\psi_D}.$$

Thus, the capacitance in the Debye-Hückel limit is

$$C_D^{DH} = \frac{\varepsilon}{\lambda_D}. \tag{6}$$

Interestingly, the double layer behaves like a parallel plate capacitor of width λ_D.

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2   Double Layer at High Voltage

At large voltages, we cannot linearise the Poisson-Boltzmann equation as above. Instead, we have to solve the full nonlinear problem, which is straightforward for the case of a symmetric $(z:z)$ dilute electrolyte in one dimension, which is referred to as the *Guoy-Chapman Model*. The Poisson-Boltzmann equation in this case is

$$-\varepsilon \frac{d^2 \psi}{dx^2} = \rho_{eq} = c_0 z e \left(e^{-ze\psi/k_B T} - e^{ze\psi/k_B T} \right).$$

We first non-dimensionalize using the thermal voltage scale $(\tilde{\psi} = ze\psi/k_B T)$ and the Debye length $(\tilde{x} = x/\lambda_D)$ yielding

$$\frac{d^2 \tilde{\psi}}{d\tilde{x}^2} = \tilde{\psi}'' = \sinh \tilde{\psi} = -\tilde{\rho}. \tag{7}$$

This differential equation can be integrated by multiplying both sides by $\tilde{\psi}'$ and integrating to get

$$\tilde{\psi}'' = \sinh \tilde{\psi}$$
$$\tilde{\psi}'' \tilde{\psi}' = \sinh \tilde{\psi} \tilde{\psi}'$$
$$\frac{1}{2}(\tilde{\psi}')^2 = (\cosh \tilde{\psi} - 1) \qquad (\text{since } \tilde{\psi}' \to 0, \tilde{\psi} \to 0 \text{ as } \tilde{x} \to \infty)$$
$$\frac{1}{2}(\tilde{\psi}')^2 = 2 \sinh^2(\tilde{\psi}/2)$$
$$\tilde{\psi}' = -2 \sinh(\tilde{\psi}/2).$$

We could integrate further to get the potential, but we are most interested in the effect on capacitance, which we can find from this result. The total charge can be calculated with

$$q = \int_0^\infty \rho \, dx = -\int_0^\infty \varepsilon \frac{d^2 \psi}{dx^2} dx = \varepsilon \left. \frac{d\psi}{dx} \right|_{x=0}.$$
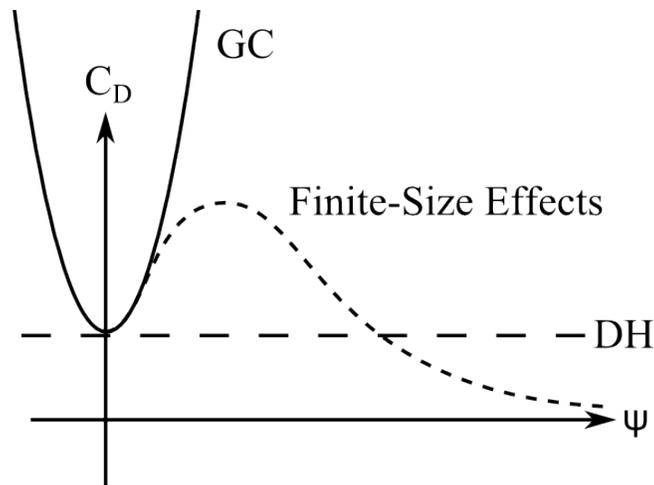
Plugging in the value of $\tilde{\psi}'$ from above, we get

$$\tilde{q} = -2 \sinh(\tilde{\psi}_D/2)$$
$$\tilde{c}_D = \frac{d\tilde{q}_s}{d\tilde{\psi}_D} = \cosh(\tilde{\psi}_D/2).$$

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Finally, we bring back the dimensional quantities to get

$$C_D^{GC} = \frac{\varepsilon}{\lambda_D} \cosh\left(\frac{ze\psi_D}{2k_BT}\right) \tag{8}$$

As expected, for small ψ_D this result simplifies to the Debye-Hückel limit from above. We can plot these equations to get to get an idea of how these various limits compare:

At large potentials ions begin to concentrate at the strongly charged surface and molecular crowding effects take over, indicated as the dashed line.

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