Lecture 29: Poisson-Boltzmann (PB) equation for charged surfaces (1D)

Reading for Lectures 28—29: PKT Chapter 9; Lectures 30-32: PKT Chapter 11 (skip Ch. 10)

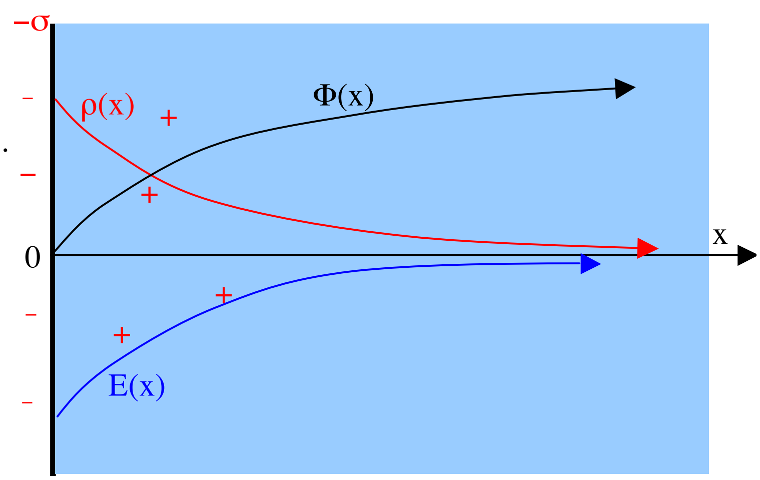
Last time we derived the PB equation. In 1D it reads $\frac{d^2\Phi(x)}{dx^2} = -\frac{1}{\varepsilon}\sum_\alpha n_\alpha^0 e^{-\frac{q_\alpha \Phi(x)}{k_B T}}$.

This is a second-order nonlinear differential equation and looks very difficult.
In tutorial, I linearized this equation and solved the resulting Debye-Huckel equation in spherical geometry and symmetric salt solution.
Surprisingly, there are some simple 1D problems for which PB can be solved exactly—without linearization. These solutions are instructive.

1. Negatively charged surface w single species of + charged counterions (e.g., q=e for H^+):
What do things look like qualitatively?

- σ is a positive number.
- overall charge neutrality: $\sigma = \int_0^\infty dx\, \rho(x)$.
- Zero of $\Phi(x)$ is arbitrary; choose $\Phi(0) = 0$.
- $E(x) = -\frac{d\Phi}{dx}$ is negative (points left).
- $E(x) = 0$ for $x < 0$, charge neutrality.
- $E(\infty) = 0$, charge neutrality.
- $E(0^+) = -\frac{\sigma}{\varepsilon}$, boundary condition.

  Note the extra factor 2 here, since there is no field to left of plate.
- $\rho(\infty) = 0$, charge neutrality.



Qualitative structure: Electric "double-layer" dipole layer next to wall.
$\Phi(x) \underset{x\to\infty}{\to} \infty$ means that you can't even linearize to D-H equation at long distances.

Why don't you get $e^{-\frac{x}{\lambda}}$ at large x? Few ions at long distance, so λ_D keeps increasing.

Poisson-Boltzmann Eq.: $\frac{d^2\Phi(x)}{dx^2} = -\frac{q}{\varepsilon} n_0 e^{-\frac{q\Phi(x)}{k_B T}}$ with $\sigma = \int_0^\infty dx\, \rho(x) = n_0 \int_0^\infty dx\, e^{-\frac{q\Phi(x)}{k_B T}}$. (sets n_0)

Scaling to dimensionless variables:

Define dimensionless potential $\phi(x) \equiv \frac{q\Phi}{k_B T}$, so $\frac{d^2\phi(x)}{dx^2} = -\frac{4\pi}{4\pi}\frac{q^2}{\varepsilon k_B T} n_0 e^{-\phi(x)} = -4\pi \ell_B n_0 e^{-\phi(x)}$,

where $\ell_B \equiv \frac{q^2}{4\pi\varepsilon k_B T}$ is the Bjerum length which is the distance between two charges so their pe equals the thermal energy (= 0.71 nm for q=e in water at room temperature).

Now, let $\frac{1}{\lambda^2} \equiv 8\pi \ell_B n_0 = \frac{2q^2}{\varepsilon k_B T} n_0$, and rescale all lengths $z \equiv \frac{x}{\lambda}$.

λ would be the Debye length if n_0 were a salt density. Here it plays a somewhat different role, since there is no salt and it depends on the counterion "normalisation factor" n_0, which (in turn) is generally determined by boundary conditions. In particular, λ can (as it will here) depend on the surface charge σ (and, as in the next section, on the distance D between two plates). In different contexts it has different names. (see below)

$$\frac{d^2\phi(z)}{dz^2} = -\frac{1}{2}e^{-\phi(z)}.$$ dimensionless P-B equation, single species. How to solve it? **29.2**

There is a trick for getting a first integral of equations like this:

c.f., mechanics, where $ma = F = -\dfrac{dV}{dx}$.

Multiply both sides by $v = \dfrac{dx}{dt}$: $m\dfrac{d^2x}{dt^2}\cdot\dfrac{dx}{dt} = -\dfrac{dV}{dx}\cdot\dfrac{dx}{dt}$ and recognize the two side as total derivatives: $\dfrac{d}{dt}\left(\dfrac{mv^2}{2}\right) = m\dfrac{d^2x}{dt^2}\cdot\dfrac{dx}{dt} = -\dfrac{dV}{dx}\cdot\dfrac{dx}{dt} = \dfrac{d}{dt}\left(-V(x)\right)$, so $\dfrac{mv^2}{2} + V(x) = E = \text{constant}$.

Similarly,

$$\frac{d^2\phi}{dz^2}\cdot\frac{d\phi}{dz} = -\frac{1}{2}e^{-\phi(z)}\cdot\frac{d\phi}{dz} \Rightarrow \frac{d}{dz}\left[\frac{1}{2}\left(\frac{d\phi}{dz}\right)^2\right] = \frac{1}{2}\frac{d}{dz}\left[e^{-\phi(z)}\right], \text{so} \left(\frac{d\phi}{dz}\right)^2 = e^{-\phi(z)} + \text{constant}.$$

Fit constant=0 by looking at z=infinity, where field E=0, anticipating that $\Phi \to \infty$, so $e^{-\phi} \to 0$.

So, $\dfrac{d\phi}{dz} = e^{-\frac{\phi(z)}{2}}$, i.e., (note that the electric field E<0, so negative square root is spurious)

$$e^{\frac{\phi}{2}}d\phi = dz \Rightarrow 2e^{\frac{\phi}{2}} = z + \text{constant},$$

$$e^{\frac{\phi}{2}} = \ln\left(\frac{z}{2} + \text{constant}\right),$$

$$\phi(z) = 2\ln\left(1 + \frac{z}{2}\right),$$

where in the last step I applied the condition $\Phi(0) = 0$.

Note that $\phi(z) \underset{z\to\infty}{\to} \infty$, so $\rho(\infty) = 0$ and the bc is OK.)

Thus, finally,

$$\Phi(x) = \frac{2k_BT}{q}\ln\left(1 + \frac{x}{2\lambda}\right),$$

$$E(x) = -\frac{d\Phi}{dx} = -\frac{k_BT}{q\lambda}\cdot\frac{1}{\left(1 + \frac{x}{2\lambda}\right)},$$

$$\rho(x) = -\varepsilon\frac{d^2\Phi}{dx^2} = \frac{\varepsilon k_BT}{2q\lambda^2}\cdot\frac{1}{\left(1 + \frac{x}{2\lambda}\right)^2}.$$

The scale factor λ (n_0) remains to be fixed by the bc's.

We must now apply the condition giving the charge (-σ) on the plate: $E\left(0^+\right) = -\dfrac{\sigma}{\varepsilon}$, which fixes the previously unknown constant n_0: $E(0) = -\dfrac{k_BT}{q\lambda} = -\dfrac{\sigma}{\varepsilon}$, so $\lambda = \dfrac{\varepsilon k_BT}{\sigma q}$.

Finally,

$$\Phi(x) = \frac{2k_BT}{q}\ln\left(1+\frac{q\sigma x}{2\varepsilon k_BT}\right),$$

$$E(x) = -\frac{\sigma}{\varepsilon}\cdot\frac{1}{\left(1+\frac{q\sigma x}{2\varepsilon k_BT}\right)},$$

$$\rho(x) = \frac{q\sigma^2}{2\varepsilon k_BT}\cdot\frac{1}{\left(1+\frac{q\sigma x}{2\varepsilon k_BT}\right)^2}; \quad n(x) = \frac{\sigma^2}{2\varepsilon k_BT}\cdot\frac{1}{\left(1+\frac{q\sigma x}{2\varepsilon k_BT}\right)^2}.$$

Final results, single surface.

Check charge neutrality: $\sigma = \int_0^\infty dx\, \rho(x)$.

Check that these formulas look like graphs.

Power-law decay of E and ρ at large distance .

Comment on divergence of potential: $\rho(x) \sim e^{-\frac{q\Phi}{k_BT}} = e^{-\frac{q}{k_BT}\cdot\frac{2kT}{q}\ln\left(1+\frac{x}{2\lambda}\right)} = \frac{1}{\left(1+\frac{x}{2\lambda}\right)^2}$.

Upshot:

- Charge cloud whose density dies off as x^{-2} at large distance.
- The characteristic scale is $2\lambda = \frac{2\varepsilon k_BT}{e\sigma}\cdot\frac{2\pi}{2\pi} = \frac{1}{2\pi\ell_B n_\sigma}$, where $n_\sigma \equiv \sigma/e$ is the number of unit charges (e) per unit surface area.
- In this context, 2λ is called the "Gouy-Chapman length."
- The positive-charge cloud is referred to as a Gouy-Chapman layer.
- It is a result of a competition between energetic effects which want to squeeze the thickness down and the entropy effect which wants to expand it.

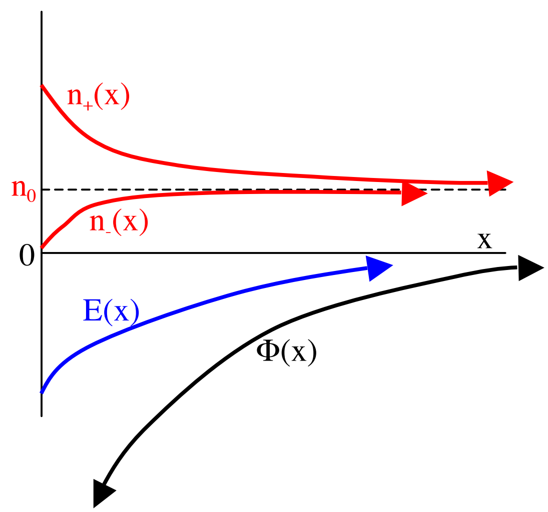
Now, add salt, i.e., extrinsic source of additional ions:

2. Single charged surface with bulk salt.

Assume there are (only) two kinds of ions +q AND –q, i.e., the positive salt ion is the same as the wall counter ion. They are in equal concentration at large x, so n_0 is now fixed by the amount of salt in solution (no longer determined by boundary condition).

It follows that

$$\rho(x) = qn_+(x) - qn_-(x) = qn_0\left(e^{-\frac{q\Phi(x)}{k_BT}} - e^{\frac{q\Phi(x)}{k_BT}}\right),$$



so, $\frac{d^2\Phi(x)}{dx^2} = -\frac{q}{\varepsilon}n_0\left(e^{-\frac{q\Phi(x)}{k_BT}} - e^{\frac{q\Phi(x)}{k_BT}}\right) = \frac{2qn_0}{\varepsilon}\sinh\left(\frac{q\Phi}{k_BT}\right)$, since $n_\pm(x) = n_0 e^{\mp\frac{q\Phi}{k_BT}}$.

Change now to dimensionless units, $\frac{d^2\phi(z)}{dz^2} = \sinh\phi$, **29.4**

where $z = \frac{x}{\lambda_D}$ with $\lambda^{-2} = \lambda_D^{-2} = \frac{2q^2 n_0}{\varepsilon k_B T}$.

Note that now n_0 does NOT depend on surface charge, etc., since it is set by the amount of salt (electrolyte) in the solution. In this context λ is called the "Debye length" and denoted λ_D. Note that $\lambda_D \sim \sqrt{k_B T}$.

The first integration goes through as for case 1: $\left(\frac{d\phi}{dx}\right)^2 = 2\cosh\phi + \text{constant}$

The boundary condition at large distance on the potential $\Phi(\infty) = 0$ and the field $E(\infty) = 0$ determine constant =-2.

The remaining boundary condition on the field:

$E(0) = -\frac{\sigma}{\varepsilon}; E(\infty) = 0$ (or, equivalently, $\sigma = q\int_0^\infty dx\left(n_+(x) - n_-(x)\right)$).

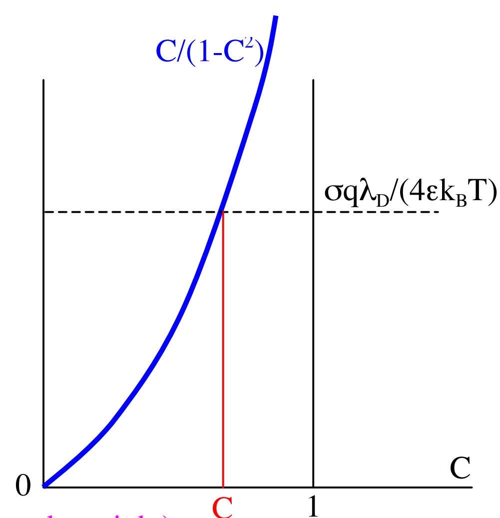
Thus, $\left(\frac{d\phi}{dz}\right)^2 = 2(\cosh\phi - 1) \Rightarrow \frac{d\phi}{\sqrt{\frac{1}{2}(\cosh\phi - 1)}} = 2dz$.

Solution of this which satisfies bc $\phi(\infty) = 0$ is $\phi(z) = 2\ln\left(\frac{1 - Ce^{-z}}{1 + Ce^{-z}}\right)$, so so

$$\Phi(x) = \frac{2k_B T}{q}\ln\left(\frac{1 - Ce^{-\frac{x}{\lambda_D}}}{1 + Ce^{-\frac{x}{\lambda_D}}}\right),$$

$$E(x) = -\frac{2k_B T}{q\lambda_D}\cdot\frac{2Ce^{-\frac{x}{\lambda_D}}}{\left(1 - C^2 e^{-\frac{2x}{\lambda_D}}\right)} \underset{x\to 0}{\to} -\frac{4k_B T}{q\lambda_D}\cdot\frac{C}{1 - C^2},$$

$$n_\pm(x) = n_0 e^{\mp\frac{q\Phi(x)}{k_B T}} = n_0\left(\frac{1 + Ce^{-\frac{x}{\lambda_D}}}{1 - Ce^{-\frac{x}{\lambda_D}}}\right)^{\pm 2} \underset{x\to 0}{\to} n_0\left(\frac{1 + C}{1 - C}\right)^{\pm 2}.$$



(C is a constant of integration to be determined below, see graph at right)

The constant C(σ)>0 is now set from the BC on E(0): $-E(0) = \frac{4k_B T}{q\lambda_D}\cdot\frac{C}{\left(1 - C^2\right)} = \frac{\sigma}{\varepsilon}$.

Notes:

- Agrees with qualitative expectations.
- You can easily solve this problem in the linear approximation (Debye-Huckel, see HW?). The result is $\Phi(x) = -\frac{\sigma\lambda_D}{\varepsilon}e^{-\frac{x}{\lambda_D}}$, and corresponds to the limit of small C, which allows the ln to be expanded. You can think of this as the low-σ limit. Thus, we expect significant deviations

from the linearized form at high σ. I find, e.g., $\Phi_{DH}(0) = -\frac{\sigma\lambda_D}{\varepsilon}$, while for large σ,

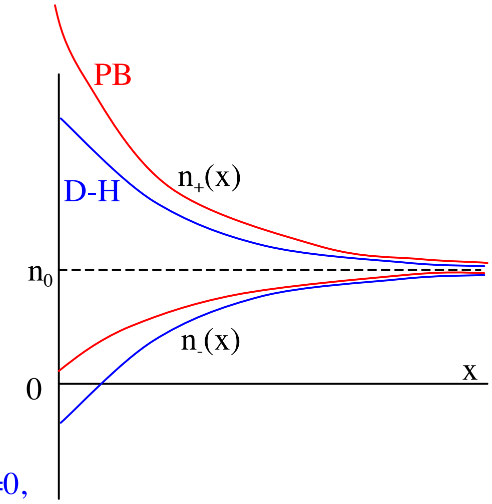
$\Phi_{PB}(0) = -\frac{2k_BT}{q}\ln\left(\frac{\sigma q\lambda_D}{k_BT\varepsilon}\right)$, which diverges for $\sigma \to \infty$ but much more slowly than $\Phi_{DH}(0)$.

- What's the difference between the H-D treatment and the PB treatment at large σ?

  As σ increases, C approaches 1 in the PB solution.

Thus,
$$n_+(x=0) = n_0\left(\frac{1+C}{1-C}\right)^2 \to n_0\left(\frac{2}{1-C}\right)^2$$
$$n_-(x=0) = n_0\left(\frac{1-C}{1+C}\right)^2 \to n_0\left(\frac{1-C}{2}\right)^2$$
for PB,

while
$$n_+(x=0) = n_0\left(1+\frac{q\sigma\lambda_D}{\varepsilon k_BT}\right)$$
$$n_-(x=0) = n_0\left(1-\frac{q\sigma\lambda_D}{\varepsilon k_BT}\right)$$
for D-H.



What you see is that, at large σ, the linearized (DH) treatment eventually leads to (unphysical) negative values of $n_-(x)$ near x=0, while in the exact (PB) keeps $n_-(0)>0$, while allowing $n_+(0)$ to increase above the DH value. PB approaches DH at large x.

Long-distance fall offs for charge-neutral electrolytes are always of the form $e^{-\frac{x}{\lambda_D}}$ (sometimes written $e^{-\kappa_D x}$).

This can be seen generically wherever the potential is weak by linearizing original equation, as was done in the 3D case in tutorial:

$$\nabla^2\Phi(\vec{r}) = -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_0^\alpha e^{-\frac{q_\alpha\Phi(\vec{r})}{k_BT}} = -\frac{1}{\varepsilon}\sum_\alpha q_\alpha n_0^\alpha\left(1-\frac{q_\alpha\Phi(\vec{r})}{k_BT}\right) = 0 + \Lambda_D^{-2}\Phi(\vec{r})$$ with $\Lambda_D^{-2} \equiv \frac{1}{\varepsilon k_BT}\sum_\alpha q_\alpha^2 n_0^\alpha$, so

variation goes as $e^{\pm\frac{x}{\Lambda_D}}$ in 1D and similarly in 3D.

This is the general form of the Debye length; note that it agrees with more-specific definition above, where there are only two kinds of ions (both with charge |q|), so $\Lambda_D^{-2} \equiv \frac{1}{\varepsilon k_BT}2q^2 n_0 = \lambda_D^{-2}$.

This will lead to exponentially decaying (screened) surface interactions ($\Pi(D) \sim e^{-\frac{D}{\Lambda_D}}$)

Comment: Similar exponential screening of charged ions in electrolyte solutions.