Lecture 9.
Electrostatics for salty solutions

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Main contents

- The chemistry of water
- Electrostatics for salty solutions
§9.1 The chemistry of water
pH & dissociation equilibrium

- Dissociation of $\text{H}_2\text{O}$ reflects a competition between the binding energy and the entropy of charge liberation.

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-
\]

\[
\text{Min Energy} \quad \text{Max entropy}
\]

\[
G = E - TS \quad \text{Competition between min } E \text{ and max } S
\]
• **pH**

Law of mass action

\[
\frac{[H^+][OH^-]}{[H_2O]} = \frac{[H^+]_0[OH^-]_0}{[H_2O]_0} \exp\left(-\frac{\mu^0_{H^+} + \mu^0_{OH^-} - \mu^0_{H_2O}}{k_BT}\right)
\]

Very few H\textsubscript{2}O are dissociated=> \([H_2O] = [H_2O]_0 = 55\text{M} \) (standard state)

Neutral H\textsubscript{2}O \quad \quad [H^+] = [OH^-]

Standard state \quad \quad [H^+]_0 = [OH^-]_0 = 1 \text{M}

\[
\mu^0_{H^+} + \mu^0_{OH^-} - \mu^0_{H_2O} \approx 79.9 \text{ kJ/mol}
\]

\[
[H^+] = 1.0 \times 10^{-7} \text{ M}
\]

\[
pH = -\log_{10}[H^+] = 7
\]
Charge on bio-macromolecules

- Henderson-Hasselbalch equation

\[ \text{HM} \rightleftharpoons \text{H}^+ + \text{M}^- \]

Dissociation constant

\[ K_d = \frac{[\text{H}^+][\text{M}^-]}{[\text{HM}]} \]

Dissociation strength

\[ pK = -\log_{10} K_d = -\log_{10} [\text{H}^+] - \log_{10} \frac{[\text{M}^-]}{[\text{MH}]} \]

\[ \text{pH} = pK + \log_{10} \frac{[\text{M}^-]}{[\text{MH}]} \]
• Charge state of DNA (depends on pH)

DNA molecule

\[ pK \approx 1.0 \]

At normal pH

\[ pH \approx 7 \]

\[
\text{pH} = pK + \log_{10} \left( \frac{[M^-]}{[MH]} \right)
\]

\[ \Rightarrow \log_{10} \left( \frac{[M^-]}{[MH]} \right) \approx 6 \quad \Rightarrow \frac{[M^-]}{[MH]} \approx 10^6 \]

--->

**Phosphates on the DNA backbone are essentially fully dissociated**

--->

**two electronic charges for every base pair**

--->

**linear charge density:** \[ \lambda = \frac{2e}{0.34 \text{ nm}} \]
• Charge state of amino acids (depends on pH)
§9.2 Electrostatics for salty solutions
Salt & Binding

- Salt dependence of protein–DNA binding

Equilibrium constant for Lac repressor binding to nonspecific DNA sites

Equilibrium constant for the binding of BPR (牛胰核糖核酸酶) on DNA
Gaussian law

- **General form**
  \[
  \iint E \cdot n \, dA = \iiint (\rho_q / \varepsilon) \, dV \\
  \iint E \cdot n \, dA = \iiint \nabla \cdot E \, dV
  \]

  \[\nabla \cdot E = \rho_q / \varepsilon
  \]

- **Special form**
  1. Thin sheet of negative charge lies next to a neutralizing positive layer of free counterions
    
    \[
    E \bigg|_{\text{surface}} = -\sigma_q / \varepsilon \quad \text{(surface)}
    \]
    
    \[
    \frac{dE}{dx} = \rho_q / \varepsilon \quad \text{(bulk)}
    \]

  2. Charged sphere
    
    \[
    E(r > R) = \frac{q}{4 \pi \varepsilon \, r^2}
    \]
Thermal motion to separate a neutral molecule into charged fragments

- Macroscopic objects are electrically neutral

**Problem:** Consider a raindrop of radius $R = 1\text{mm}$ suspended in air. How much work would be needed to remove one electron from 1% water molecules in the drop?

**Solution:**

$$q/e = \frac{\rho_w \times (4/3)\pi R^3}{M_w} \times 0.01 = 1.4 \times 10^{18}$$

$$\frac{e^2}{4\pi \varepsilon_0 R} = 2.3 \times 10^{-28} \text{ J m}$$

Removing electrons leaves some water molecules electrically charged. These charged water molecules crowd to the surface of the drop to get away from each other, forming a shell of charge of radius $R$.

$$V(R) = \frac{-q'}{4\pi \varepsilon_0 R} \Rightarrow dW = dq' [V(\infty) - V(R)] = \frac{q'dq'}{4\pi \varepsilon_0 R}$$

$$W = \int_0^q \frac{q'dq'}{4\pi \varepsilon_0 R} = \frac{q^2}{8\pi \varepsilon_0 R} = \frac{1}{2} (-q)V(R) \approx 10^{11} \text{ J} \gg k_B T_r$$

Thermal motion does **not disturb** electrons in macroscopic objects.
Problem: Repeat the calculation for a droplet of radius $R = 1\mu m$ in water.

$$W = \frac{q^2}{8 \pi \varepsilon_r \varepsilon_0 R}$$

$q/e \propto R^3$

$$W \propto \frac{R^5}{\varepsilon_r}$$

$$W = \left(\frac{1\mu m}{1\ mm}\right)^5 \times \frac{1}{80} \times 10^{11} \ J \approx 10^{-4} \ J$$

Problem: Repeat the calculation for a droplet of radius $R = 1nm$ in water.

$$W = \left(\frac{1nm}{1\ mm}\right)^5 \times \frac{1}{80} \times 10^{11} \ J \approx 10^{-21} \ J \approx k_B T_r$$

It is possible for thermal motion to separate a neutral molecule into charged fragments!
# In what sense DNA is “charged”?

When we put DNA in water, some of its loosely attached $H^+$ can wander away, leaving some of their electrons behind. In this case the DNA has a net negative charge and becomes a negative macroion (大分子离子). This is the sense in which DNA is charged. The lost $H^+$ are called counterions (补偿离子、平衡离子), since their net charge counters (neutralizes) the macroion.

Note: the whole solution is still neutral!
**Problem:** Consider a planar surface in water. Please estimate the electrostatic energy that counterions pay to dissociate from the surface.

**Analysis:** Assume density of surface charges $-\sigma_q$. Each counterions take charge $q$.

1. The driving energy of dissociation is the thermal energy $k_B T$.
2. We need to estimate the stored electrostatic energy per unit area.

**Dimensional Analysis:**

$$E_{\text{store}} \text{ per unit area} = \frac{k_B T}{\text{[area]}}$$

3. Construct $\text{[area]}$:

$$\begin{align*}
\left[\sigma_q\right] &= \frac{Q}{\text{[area]}} \\
\left[q/\sigma_q\right] &= \text{[area]} \\
\left[q\right] &= Q \\
\end{align*}$$

$$E_{\text{store}} \text{ per unit area} = k_B T \left(\sigma_q / q\right)$$
Screening effect in solutions

- Dilemma for counterions

  1. Diffusing *away from the macroion*, counterions *increase their entropy*. But this process will *cost lots of energy* due to pull them away from the opposite charges of macroion.

  2. If they *stay too close to the macroion*, they have *lower electrostatic energy*. However, they *won’t gain much entropy*.

  The counterions need to make a compromise (妥协) from the competition between minimizing energy and maximizing entropy.

For a large flat macroion, the compromise chosen by the counterions is to remain hanging in a cloud near the macroion’s surface.
• Screening effect

Viewed from beyond the counterion cloud, the macroion appears neutral. Thus, a second macroion won’t feel any attraction or repulsion until it gets closer than about twice the cloud’s thickness.

Even though the electrostatic interaction is of long range in vacuum, in solution the screening effect of counterions reduces its effective range, typically to about several nanometers, i.e. short range.

Counterion cloud is often called the diffused charge layer

charges left behind in the surface of macroion

electrical double double layer

• Character of forces on macroions

Mixed: partly electrostatic & partly entropic
Electrostatic interactions are crucial for proper cell functioning

- Avoid clumping catastrophe of macromolecules

Cells are filled with macromolecules and a lot of water.

A number of attractive forces (for example, depletion force or van der Waals force) are trying to stick the macromolecules together to clump into a ball of sludge.

If the macromolecules have same sign of net charge, the clumping catastrophe can be avoided.

Indeed, most of the macromolecules in a cell are negatively charged and hence repel each other.
Short-range electrostatic forces in solution are crucial for biochemical reactions in cells.

Macroions will not feel each other until they are nearby. Once they are nearby, the detailed surface pattern of positive and negative residues on a macromolecule can be felt by its neighbor, not just the overall charge.

Understand how cells organize their myriad internal biochemical reactions: only the macro-molecules with precisely matching shapes and charge distributions (i.e., match orientations) will bind and interact.

Macromolecular binding is stereospecific.
• Screen effect are crucial for DNA packing in bacteriophage

Portal motor help DNA packing

\[ W_{motor} = \text{area below the force-extension curve} \]

\[ < \frac{1}{2} \times 7000 \text{nm} \times 60 \text{pN} \approx 200000 \text{pN} \cdot \text{nm} \]

Charge of Φ29 DNA

\[ q = \frac{2e}{1 \text{bp/density}} \times 20000 \text{bp} = 40000e \]

Electrostatic energy without screen effect

\[ W_{charge} \approx \frac{q^2}{8 \pi \varepsilon R} \approx 10^8 \text{pN} \cdot \text{nm} \gg W_{motor} \]

Portal motor cannot help DNA packing if no screen effect!

≈20 nm
Charged surface and its counterion cloud in pure water

- Mean field approximation

**Question:** How to find the distribution of counterions?

**Analysis:** many-body problem

**Approximation:** we think each ion as moving independently of the others’ detailed locations, but under the influence of an electric potential created by the effective charge density. This approximate electric potential \( V(x) \) is called the mean field.

\[ c_+(x): \text{concentration of counterions at } x \]
\[ \rho_q = q c_+(x): \text{effective charge density at } x \]

\[ c_0 \equiv c_+(0) \quad \text{Take } V(0) = 0 \]
\[ q = e = 1.6 \times 10^{-19} \text{C} \]
• Poisson-Boltzmann equation

**Poisson equation:**

\[
dE / dx = \rho_q / \varepsilon \quad \text{(Gauss)}
\]

\[
E = -dV / dx
\]

**Boltzmann equation:**

\[
c_+ = c_0 e^{-qV(x)/k_B T}
\]

**Poisson-Boltzmann equation:**

\[
\frac{d^2 V}{dx^2} = -\frac{\rho_q}{\varepsilon} = -\frac{qc_+}{\varepsilon}
\]

\[
\frac{d^2 \bar{V}}{dx^2} = -4\pi l_B c_0 e^{-\bar{V}}
\]

\[
\bar{V} \equiv qV(x)/k_B T \quad \text{(reduced charge potential)}
\]

\[
l_B \equiv \frac{q^2}{4\pi \varepsilon k_B T} \quad \text{(Bjerrum length)} = 0.71 \text{ nm in water at 300K}
\]

At this length \( E_{\text{Coulomb}} = E_{\text{thermal}} \)
Boundary conditions

\[ V(0) = 0 \Rightarrow \overline{V}(0) = 0 \]  \hspace{1cm} (BC1)

\[-\frac{dV}{dx}\bigg|_{x=0} = E_{\text{surface}} = -\sigma_q/\varepsilon \Rightarrow \frac{d\overline{V}}{dx}\bigg|_{x=0} = \frac{4\pi l_B \sigma_q}{q} \]  \hspace{1cm} (BC2)

Viewed from \( \infty \), the whole system (charged surface and counterions) is neutral, thus no electrical field & its variation in \( \infty \)

\[ E(\infty) = 0 \Rightarrow -\frac{dV}{dx}\bigg|_{x=\infty} = 0 \Rightarrow \frac{d\overline{V}}{dx}\bigg|_{x=\infty} = 0 \]  \hspace{1cm} (BC3)

i.e.

\[ \frac{dE}{dx}\bigg|_{x=\infty} = 0 \Rightarrow -\frac{d^2V}{dx^2}\bigg|_{x=\infty} = 0 \Rightarrow \frac{d^2\overline{V}}{dx^2}\bigg|_{x=\infty} = 0 \]  \hspace{1cm} (BC4)

Solution to Poisson-Boltzmann equation

Problem: please find the solution to \( \frac{d^2\overline{V}}{dx^2} = -2\alpha^2 e^{-\overline{V}} \)

satisfying the above conditions
**Solution:** intuitively, the electrical field along $-x$.

i.e. $E(x) = -(k_B T / q) \bar{V}' \leq 0 \Rightarrow \bar{V}' \geq 0$

$\bar{V}'' = -2 \alpha^2 e^{-\bar{V}} \Rightarrow 2 \bar{V}'' \bar{V}' = -4 \alpha^2 e^{-\bar{V}} \bar{V}'$

$\Rightarrow [(\bar{V}')^2]' = 4 \alpha^2 [e^{-\bar{V}}]' \Rightarrow \bar{V}' = 2 \alpha (e^{-\bar{V}} - A)^{1/2}$

BC3: $\bar{V}'(\infty) = 2 \alpha (e^{-\bar{V}(\infty)} - A)^{1/2} = 0 \Rightarrow A = e^{-\bar{V}(\infty)}$

BC4: $\bar{V}''(\infty) = -2 \alpha^2 e^{-\bar{V}(\infty)} = 0 \Rightarrow \bar{V}(\infty) = \infty$  

$\Rightarrow e^{\bar{V}/2} \bar{V}' = 2 \alpha \Rightarrow 2 [e^{\bar{V}/2}]' = 2 \alpha \Rightarrow \bar{V} = 2 \ln \alpha \left( x - A_2 \right)$

BC1: $\bar{V}(0) = 0 \Rightarrow A_2 = -1 / \alpha$

BC2: $\bar{V}'(0) = 4 \pi l_B \sigma_q / q \Rightarrow \alpha = 2 \pi l_B \sigma_q / q$

$\begin{cases} 
\bar{V} = 2 \ln \left( 1 + x / x_0 \right) \Rightarrow V(x) = (2k_B T / q) \ln \left( 1 + x / x_0 \right) \\
x_0 \equiv q / 2 \pi l_B \sigma_q \quad \text{(Gouy–Chapman length)}
\end{cases}$
Solution: intuitively, the electrical field along -x.

\[ E(x) = -(k_B T / q) \bar{V}' \leq 0 \Rightarrow \bar{V}' \geq 0 \]

\[ \bar{V}'' = -2 \alpha^2 e^{-\bar{V}} \Rightarrow 2 \bar{V}'' \bar{V}' = -4 \alpha^2 e^{-\bar{V}} \bar{V}' \]

\[ \Rightarrow [ (\bar{V}')^2 ]' = 4 \alpha^2 [ e^{-\bar{V}} ]' \Rightarrow \bar{V}' = 2 \alpha (e^{-\bar{V}} - A)^{1/2} \]

BC3: \[ \bar{V}'(\infty) = 2 \alpha (e^{-\bar{V}(\infty)} - A)^{1/2} = 0 \Rightarrow A = e^{-\bar{V}(\infty)} \]

BC4: \[ \bar{V}''(\infty) = -2 \alpha^2 e^{-\bar{V}(\infty)} = 0 \Rightarrow \bar{V}(\infty) = \infty \]

\[ \Rightarrow e^{\bar{V}/2} V' = 2 \alpha \Rightarrow 2 [ e^{\bar{V}/2} ]' = 2 \alpha \Rightarrow \bar{V} = 2 \ln \alpha (x - A_2) \]

BC1: \[ \bar{V}(0) = 0 \Rightarrow A_2 = -1 / \alpha \]

BC2: \[ \bar{V}'(0) = 4 \pi l_B \sigma_q / q \Rightarrow \alpha = 2 \pi l_B \sigma_q / q \]

\[ \begin{align*}
\bar{V} &= 2 \ln \left( 1 + x / x_0 \right) \Rightarrow V(x) = (2 k_B T / q) \ln \left( 1 + x / x_0 \right) \\
x_0 &= q / 2 \pi l_B \sigma_q \quad \text{(Gouy–Chapman length)}
\end{align*} \]
Problem: please find $c_0$ and $c(x)$, then draw figures $V(x)$, $E(x)$ and $c(x)$.

\[
\frac{d^2 \bar{V}}{dx^2} = -4 \pi l_B c_0 e^{-\bar{V}}
\]
\[
\frac{d^2 \bar{V}}{dx^2} = -2 \alpha^2 e^{-\bar{V}}
\]

\[
\alpha = \frac{2 \pi l_B \sigma_q}{q}
\]
\[
c_0 = \frac{\alpha^2}{2 \pi l_B}
\]
\[
c_0 = \frac{2 \pi l_B \sigma_q^2}{2 l_B}
\]
\[
V(x) = \frac{2 k_B T}{q} \ln \left(1 + \frac{x}{x_0}\right)
\]

\[
c_+ = c_0 e^{-qV(x)/k_B T} = \frac{2 \pi l_B \sigma_q^2}{q^2} e^{-2\ln(1+x/x_0)} = \frac{2 \pi l_B \sigma_q^2}{q^2} \frac{1}{(1+x/x_0)^2}
\]

$V(x)$

$x/x_0$

$E(x)/|E(0)|$

$c_+ / c_0$

$x/x_0$
Problem: please prove that the whole system is electrically neutral.

Solution:

\[ c_+ = \frac{2\pi l_B \sigma^2}{q^2} \left( \frac{1}{1 + x/x_0} \right)^2 \Rightarrow \rho_q = q c_+ = \frac{2\pi l_B \sigma^2}{q} \left( \frac{1}{1 + x/x_0} \right)^2 \]

\[ x_0 \equiv \frac{q}{2\pi l_B \sigma q} \]

\[ Q_+ = \iiint \rho_q \, dx dy dz = A \times \int_0^\infty \rho_q \, dx = A \sigma_q \]

\[ Q_- = -A \sigma_q \]

\[ Q_{total} = 0 \]

Problem: please discuss the relation between \( c(x) \) and temperature.

Solution:

\[ l_B \equiv \frac{q^2}{4\pi \varepsilon k_B T} \Rightarrow x_0 \equiv \frac{q}{2\pi l_B \sigma q} = \frac{2 \varepsilon k_B T}{q \sigma q} \]

(1): the higher \( T \), the larger \( x_0 \) ==> the wider distribution of counterions

(2): vice versa. (3): \( T \to \infty \), uniform distribution

(4): \( T \to 0 \), \( c_+ = (\sigma_q / q) \delta (x - 0) \) (entropy dominated)

(5): \( c_+ = (\sigma_q / q) \delta (x - 0) \) (electrostatic energy dominated)
**Problem:** Reconsider a planar surface in water. Please estimate the electrostatic energy that counterions pay to dissociate from the surface.

**Analysis:**

\[
V(x) = \frac{2k_B T}{q} \ln \left(1 + \frac{x}{x_0}\right) \Rightarrow E(x) = -\frac{dV}{dx} = -\frac{2k_B T}{q(x+x_0)}
\]

\[
\frac{E_{store}}{\text{Area}} = \frac{1}{2} \int_{0}^{\infty} \varepsilon E^2 \, dx = \frac{2\varepsilon k_B^2 T^2}{q^2 x_0}
\]

\[
x_0 = \frac{2\varepsilon k_B T}{q \sigma_q}
\]

This result is the same as that we obtained from the dimensional analysis!

**Eg:** A fully dissociating lipid bilayer can have one unit of charge per lipid head group, i.e., \(\sigma_q/q = 0.7 \text{ nm}^{-2}\). For a spherical vesicle of radius 10 \(\mu\text{m}\), the total stored energy is \(4\pi \times (10\mu\text{m})^2 \times 0.7 \text{ nm}^{-2} k_B T \approx 10^9 k_B T\). (huge!)
Charged surface and its counterion cloud in electrolyte (电解质) solutions

Character: the density is none-zero in $\infty$

In ultimate case, $T \rightarrow 0$, the + and – charges can align to alternated layers

Taking $V(\infty)=0$, in equilibrium, we have

Boltzmann:
$$c_+ = c_\infty e^{-qV(x)/k_BT} \quad \text{and} \quad c_- = c_\infty e^{qV(x)/k_BT}$$

Poisson:
$$\frac{d^2 V}{dx^2} = -\frac{\rho_q}{\varepsilon} = -\frac{q(c_+ - c_-)}{\varepsilon}$$

Viewed from $\infty$, the whole system (charged surface, counterions, and $\pm$ salt ions) is neutral, thus no electrical field & its variation in $\infty$

$$E(\infty) = 0 \Rightarrow -\frac{dV}{dx}\bigg|_{x=\infty} = 0$$

i.e.
$$-\frac{dE}{dx}\bigg|_{x=\infty} = 0 \Rightarrow -\frac{d^2 V}{dx^2}\bigg|_{x=\infty} = 0 \Rightarrow c_+ = c_- \equiv c_\infty$$

Contribution from electrolyte
Poisson-Boltzmann equation:
\[
\frac{d^2 \bar{V}}{dx^2} = \frac{\sinh \bar{V}}{\lambda_D^2}
\]
\[
\lambda_D = \left(8\pi l_B c_\infty\right)^{-1/2}
\]
(Debye screening length)

Boundary conditions:
\[
\bar{V}(\infty) = 0 \quad \frac{d\bar{V}}{dx}\bigg|_{x=\infty} = 0 \quad \frac{d\bar{V}}{dx}\bigg|_{x=0} = \frac{4\pi l_B \sigma_q}{q}
\]

Solution:
\[
\bar{V}'' = \frac{\sinh \bar{V}}{\lambda_D^2} \Rightarrow \bar{V}'' \bar{V}' = \sinh \bar{V} \bar{V}' / \lambda_D^2 \Rightarrow [(\bar{V}')^2]' = 2 \left[ \cosh \bar{V} \right]' / \lambda_D^2
\]
\[
\Rightarrow (\bar{V}')^2 = 2 (\cosh \bar{V} - A_1) / \lambda_D^2
\]
\[
\Rightarrow (\bar{V}')^2 = \frac{4}{\lambda_D^2} \sinh^2 \frac{\bar{V}}{2} \Rightarrow \bar{V}' = -\frac{2}{\lambda_D} \sinh \frac{\bar{V}}{2}
\]

Discuss: why not take + sign? Hint: + sign makes $\bar{V}' \leq 0$
Poisson-Boltzmann equation:

\[
\frac{d^2 \bar{V}}{dx^2} = \frac{\sinh \bar{V}}{\lambda_D^2} \quad \quad \lambda_D = (8\pi \ l_B \ c_\infty)^{-1/2}
\]

(Debye screening length)

Boundary conditions:

\[
\bar{V}(\infty) = 0 \quad \quad \frac{d \bar{V}}{dx}\bigg|_{x=\infty} = 0 \quad \quad \frac{d \bar{V}}{dx}\bigg|_{x=0} = \frac{4\pi l_B \ \sigma_q}{q}
\]

Solution:

\[
\bar{V}'' = \frac{\sinh \bar{V}}{\lambda_D^2} \Rightarrow \bar{V}'' \bar{V}' = \sinh \bar{V} \ \bar{V}' / \lambda_D^2 \Rightarrow [(\bar{V}')^2]' = 2 [\cosh \bar{V}]' / \lambda_D^2
\]

\[
\Rightarrow (\bar{V}')^2 = 2 (\cosh \bar{V} - A_1) / \lambda_D^2
\]

\[
\bar{V}'(\infty) = 0 \quad \& \quad \bar{V}(\infty) = 0
\]

\[
A_1 = 1 \quad \cosh^2 \frac{\bar{V}}{2} + \sinh^2 \frac{\bar{V}}{2} = \cosh \bar{V}
\]

\[
(\bar{V}')^2 = 2 (\cosh \bar{V} - 1) / \lambda_D^2
\]

\[
\Rightarrow (\bar{V}')^2 = \frac{4}{\lambda_D^2} \sinh^2 \frac{\bar{V}}{2} \Rightarrow \bar{V}' = \frac{2}{\lambda_D} \sinh \frac{\bar{V}}{2}
\]

Discuss: why not take + sign? Hint: + sign makes \( \bar{V}' \leq 0 \).
\[ \int \frac{d(\bar{V}/2)}{\sinh(\bar{V}/2)} = -\int \frac{dx}{\lambda_D} \Rightarrow \ln \left( -\tanh \frac{\bar{V}}{4} \right) = -\frac{x + x^*}{\lambda_D} \Rightarrow \bar{V} = 2 \ln \tanh \frac{x + x^*}{2 \lambda_D} \]

\[ \bar{V}' = -\frac{2}{\lambda_D} \sinh \frac{\bar{V}}{2} \Rightarrow \bar{V}'(0) = -\frac{2}{\lambda_D} \sinh \frac{\bar{V}(0)}{2} = -\frac{2}{\lambda_D} \sinh \ln \tanh \frac{x^*}{2 \lambda_D} = \frac{4\pi l_B \sigma_q}{q} \]

\[ \Rightarrow x_* = \lambda_D \ln \left[ \frac{1 + \sqrt{1 + \zeta^2}}{\zeta} \right], \quad \zeta = 2\pi l_B \lambda_D \sigma_q / q \]

**Problem:** Find the asymptotic behavior of \( \bar{V} \) for large \( \lambda_D \)

**Solution:** \( \lambda_D = (8\pi l_B c_\infty)^{-1/2} \) large \( \Rightarrow \) \( c_\infty \) small

\[ \psi \ll 1 \Rightarrow \tanh \psi \approx \frac{e^\psi - e^{-\psi}}{e^\psi + e^{-\psi}} \approx \frac{(1+\psi) - (1-\psi)}{(1+\psi) + (1-\psi)} = \psi \]

\[ \bar{V} = 2 \ln \tanh \frac{x + x^*}{2 \lambda_D} \approx 2 \ln \frac{x + x^*}{2 \lambda_D} = 2 \ln \left( \frac{x^*}{2 \lambda_D} \right) + 2 \ln \left( 1 + \frac{x}{x_*} \right) \]

\[ x_* = \lambda_D \ln \left[ \frac{1 + \sqrt{1 + \zeta^2}}{\zeta} \right] \approx \lambda_D / \zeta = q / 2\pi l_B \sigma_q = x_0 \]

\[ \bar{V} = 2 \ln \left( 1 + \frac{x}{x_0} \right) \] (omit the unimportant constant) \( \Rightarrow \) self-consistent!
\[
\Rightarrow \int \frac{d(\bar{V}/2)}{\sinh(\bar{V}/2)} = -\int \frac{dx}{\lambda_D} \Rightarrow \ln \left(-\tanh \frac{\bar{V}}{4}\right) = -\frac{x + x_*}{\lambda_D} \Rightarrow \bar{V} = 2 \ln \tanh \frac{x + x_*}{2\lambda_D}
\]

\[\bar{V}' = -\frac{2}{\lambda_D} \sinh \frac{\bar{V}}{2} \Rightarrow \bar{V}'(0) = -\frac{2}{\lambda_D} \sinh \frac{\bar{V}(0)}{2} = -\frac{2}{\lambda_D} \sinh \ln \tanh \frac{x_*}{2\lambda_D} = \frac{4\pi l_B \sigma_q}{q}
\]

\[\Rightarrow x_* = \lambda_D \ln \left[\frac{(1 + \sqrt{1 + \zeta^2})}{\zeta}\right], \quad \zeta = 2\pi l_B \lambda_D \sigma_q / q
\]

**Problem:** Find the asymptotic behavior of \(\bar{V}\) for large \(\lambda_D\)

**Solution:** \(\lambda_D = (8\pi l_B c_\infty)^{-1/2}\) large \(\Rightarrow c_\infty\) small

\[\psi \ll 1 \Rightarrow \tanh \psi = \frac{e^\psi - e^{-\psi}}{e^\psi + e^{-\psi}} \approx \frac{(1 + \psi) - (1 - \psi)}{(1 + \psi) + (1 - \psi)} = \psi
\]

\[\bar{V} = 2 \ln \tanh \frac{x + x_*}{2\lambda_D} \approx 2 \ln \frac{x + x_*}{2\lambda_D} = 2 \ln \left(\frac{x_*}{2\lambda_D}\right) + 2 \ln \left(1 + \frac{x}{x_*}\right)
\]

\[x_* = \lambda_D \ln \left[\frac{(1 + \sqrt{1 + \zeta^2})}{\zeta}\right] \approx \lambda_D / \zeta = q / 2\pi l_B \sigma_q = x_0
\]

\[\bar{V} = 2 \ln \left(1 + \frac{x}{x_0}\right) \text{ (omit the unimportant constant)} \quad \text{self-consistent!}
\]
Problem: Find the asymptotic behavior of $\bar{V}$ for $x \gg \lambda_D$

Solution: $\psi \gg 1 \Rightarrow \tanh \psi = \frac{e^\psi - e^{-\psi}}{e^\psi + e^{-\psi}} = 1 - \frac{2 e^{-\psi}}{e^\psi + e^{-\psi}} \approx 1 - 2 e^{-2\psi}$

$$\ln \tanh \psi \approx \ln \left(1 - 2 e^{-2\psi}\right) \approx -2 e^{-2\psi}$$

$$\bar{V} = 2 \ln \tanh \frac{x + x_*}{2 \lambda_D} \approx -4 e^{-(x + x_*)/\lambda_D} \approx -\left(4 e^{-x_*/\lambda_D}\right) e^{-x/\lambda_D}$$

The electric fields far outside a charged surface in an electrolyte are exponentially screened at distances greater than the Debye length $\lambda_D$

$$\bar{V} = -\left(4 e^{-x_*/\lambda_D}\right) e^{-x/\lambda_D} \quad \lambda_D = \left(8\pi l_B c_\infty\right)^{-1/2}$$

$c_\infty \uparrow \Rightarrow \lambda_D \downarrow \Rightarrow \bar{V}$ decays more quickly

Increasing the concentration of electrolyte shortens the effective range of the electrostatic interaction
Homework: estimate the electrostatic energy of a spherical shell with \( Q \) negative charges

Hints: (1). prove Poisson equation in spherical coordinates

\[
\frac{1}{r} \frac{d}{dr} \left( r \frac{dV(r)}{dr} \right) = -\frac{\rho(r)}{\epsilon_r \epsilon_0}
\]

(2). write \( c_+(r) \) and \( c_-(r) \) in terms of Boltzmann distribution

then prove \( \rho = e(c_+ - c_-) \approx -\frac{2 e^2 c_\infty}{k_B T} V(r) \)

valid for \( eV(r) \ll k_B T \)

(3). combining (1) and (2), write Debye-Hückel equation

\[
\frac{d^2(rV(r))}{dr^2} = \frac{1}{\lambda_D^2} (rV(r))
\]

(4). Solve equation to obtain \( V(r) = \frac{A}{r} e^{-r/\lambda_D} \)

(5). Using Gaussian law to obtain the BC at surface \( -\frac{dV(r)}{dr} \bigg|_R = \frac{Q}{4\pi \epsilon_0 \epsilon_r R^2} \)

then obtain \( A = \frac{Q e^{R/\lambda_D}}{4\pi \epsilon_0 \epsilon_r (1 + R/\lambda_D)} \) and \( V(R) = \frac{1}{4\pi \epsilon_0 \epsilon_r} \frac{Q}{R} \frac{\lambda_D}{R + \lambda_D} \)

(6). Find the electrostatic energy in terms of \( U(R) = \frac{1}{2} Q V(R) \)
Energy for assembling viral capsid

\[
U(R) = \frac{1}{2} Q V(R) = \frac{1}{2} k_B T \left( \frac{Q}{e} \right)^2 \frac{l_B \lambda_D}{R(R + \lambda_D)} \approx \frac{1}{2} k_B T \left( \frac{Q}{e} \right)^2 \frac{l_B \lambda_D}{R^2}
\]

\[
\lambda_D = \frac{1}{\sqrt{8\pi l_B c}} \quad \Rightarrow \quad U(R) \propto c^{-1/2}
\]

\[
\Delta G_{\text{capsid}} = \Delta G_{\text{contact}} + U(R)
\]
Repulsion of like-charged surfaces

Each surface, together with its counterion cloud, is an electrically neutral object! If $T \to 0$, the cloud will collapse down to the surfaces, rendering them neutral. No interaction!

- **Origin of repulsion**

  The repulsion between like-charged surfaces can only arise as an entropic effect. As the surfaces get closer than twice their Gouy–Chapman length, their counterion clouds get squeezed. The cloud resists the squeezing and exhibits an “osmotic” pressure.

- **Poisson-Boltzmann equation**

  $$c_+ = c_0 e^{-qV(x)/k_BT} \quad [\text{Taking } V(0)=0]$$

  $$V'' = -\frac{qc_+}{\varepsilon} \quad \Rightarrow \quad \bar{V}'' = -4\pi l_B c_0 e^{-\bar{V}}$$
• Boundary conditions

Symmetry: $V(x)$ is even function, $E(x)$ is odd function

$\bar{V}(0)=0$ \hspace{1cm} (BC1)

$E(0)=0 \Rightarrow V'(0)=0$ \hspace{1cm} (BC2)

$V'(-D)=4\pi l_B \sigma_q / q$, $V'(D)=-4\pi l_B \sigma_q / q$ \hspace{1cm} (BC3)

• Solution

Problem: please find solution to $\bar{V}''=-2\alpha^2 e^{-\bar{V}}$ satisfying the above BCs.

Solution: \[ \bar{V}'=2\alpha \left( e^{-\bar{V}} - A \right)^{1/2} \]

BC1+BC2

Taking $e^{-\bar{V}/2}=\sec \psi \Rightarrow d \bar{V}=-2 \tan \psi \ d \psi$

$d \ \psi = \alpha \ dx \ \Rightarrow \psi = \alpha (x + A_2) \ \Rightarrow \bar{V}=2 \ln \cos \alpha (x + A_2)$

BC1=>$ A_2=0 \Rightarrow \bar{V}=2 \ln \cos \alpha \ x$

BC3=>$2 \alpha \tan \alpha D = 4\pi l_B \sigma_q / q \Rightarrow \alpha \tan \alpha D = 2\pi l_B \sigma_q / q$
• Boundary conditions

**Symmetry:** $V(x)$ is **even** function, $E(x)$ is **odd** function

$\bar{V}(0) = 0$ \hspace{1cm} (BC1)

$E(0) = 0 \Rightarrow V'(0) = 0$ \hspace{1cm} (BC2)

$V'(-D) = 4\pi l_B \sigma_q / q, \quad V'(D) = -4\pi l_B \sigma_q / q$ \hspace{1cm} (BC3)

• Solution

**Problem:** please find solution to $\bar{V}'' = -2 \alpha^2 e^{-\bar{V}}$ satisfying the above BCs.

**Solution:**

$\bar{V}' = 2\alpha (e^{-\bar{V}} - A)^{1/2}$

$\bar{V}'(0) = 0 \Rightarrow A = 1$

$\bar{V}' = 2\alpha (e^{-\bar{V}} - 1)^{1/2}$

Taking $e^{-\bar{V}/2} = \sec \psi \Rightarrow d \bar{V} = -2 \tan \psi d \psi$

$d \psi = \alpha dx \Rightarrow \psi = \alpha (x + A_2) \Rightarrow \bar{V} = 2 \ln \cos \alpha (x + A_2)$

BC1=> $A_2 = 0 \Rightarrow \bar{V} = 2 \ln \cos \alpha x$

BC3=> $2 \alpha \tan \alpha D = 4\pi l_B \sigma_q / q \Rightarrow \alpha \tan \alpha D = 2\pi l_B \sigma_q / q$
Profiles of electric potential and the density of counterions

\[ \bar{V} = 2 \ln \cos \alpha x \Rightarrow c_+ = c_0 e^{-\bar{V}} = c_0 \sec^2 \alpha x \]

With parameter \( \alpha D = 0.5 \)

**Problem:** find the repulsion pressure

**Solution:**

\[ p_A = -\frac{dF}{d(2D)} \]

\[ F = \frac{1}{2} \left( -\sigma_q A \right) V(D) + \frac{1}{2} \left( -\sigma_q A \right) V(-D) + \int_{-D}^{D} \frac{1}{2} q c_+ V' Adx + k_B T \int_{-D}^{D} c_+ \ln \frac{c_+}{c_*} Adx \]

- electrostatic self-energy of two surfaces
- Electrostatic energy of counterions
- Contribution of entropy

\( c_*: \) to ensure \( c_+/c_* \) dimensionless
\[
\frac{F}{k_B T A} = -\frac{\sigma_q}{2q} \left[ \bar{V}(D) + \bar{V}(-D) \right] + \int_{-D}^{D} \left( \frac{1}{2} c_+ \bar{V} + c_+ \ln \frac{c_+}{c_*} \right) dx
\]

\[
\bar{V} = 2 \ln \cos \alpha x \Rightarrow c_+ = c_0 e^{-\bar{V}} = c_0 \sec^2 \alpha x \quad \alpha = \sqrt{2\pi l_B c_0}
\]

\[
c_+ \ln \frac{c_+}{c_*} = c_+ \ln \frac{c_0 e^{-\bar{V}}}{c_*} = c_+ \ln \frac{c_0}{c_*} - c_+ \bar{V} \Rightarrow \frac{1}{2} c_+ \bar{V} + c_+ \ln \frac{c_+}{c_*} = c_+ \ln \frac{c_0}{c_*} - \frac{1}{2} c_+ \bar{V}
\]

\[
\int_{-D}^{D} c_+ \ln \left( \frac{c_0}{c_*} \right) dx = \ln \left( \frac{c_0}{c_*} \right) \int_{-D}^{D} c_+ dx = \frac{2 \sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right)
\]

\[
\bar{V}'' = -2 \alpha^2 e^{-\bar{V}} \Rightarrow c_+ = \frac{-c_0}{2 \alpha^2} \bar{V}'' \Rightarrow \frac{1}{2} c_+ \bar{V} = -\frac{c_0}{4 \alpha^2} \bar{V}'' \bar{V}
\]

\[
\int_{-D}^{D} \bar{V}'' \bar{V} dx = \bar{V} \bar{V}''|_{-D}^{D} - \int_{-D}^{D} (\bar{V}'')^2 dx = -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - \int_{-D}^{D} (2 \alpha \tan \alpha x)^2 dx
\]

\[
= -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - 4 \alpha^2 \int_{-D}^{D} (\sec^2 \alpha x - 1) dx = -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) + 8 \alpha^2 D - 8 \alpha \tan \alpha D
\]

\[
\Rightarrow \frac{F}{k_B T A} = -\frac{\sigma_q}{q} \bar{V}(D) + \frac{2 \sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) - \frac{c_0}{4 \alpha^2} \left[ \frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - 8 \alpha^2 D + 8 \alpha \tan \alpha D \right]
\]

\[
= -\frac{2 \sigma_q}{q} \bar{V}(D) + \frac{2 \sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) + 2 D c_0 - \frac{1}{\pi l_B} \alpha \tan \alpha D
\]
\[
\Rightarrow \frac{F}{k_B T A} = -\frac{\sigma_q}{2q} [\bar{V}(D) + \bar{V}(-D)] + \int_{-D}^{D} \left( \frac{1}{2} c_+ \bar{V} + c_+ \ln \frac{c_+}{c_*} \right) dx
\]

\[
\bar{V} = 2 \ln \cos \alpha x \Rightarrow c_+ = c_0 e^{-\bar{V}} = c_0 \sec^2 \alpha x \quad \alpha = \sqrt{2\pi l_B c_0}
\]

\[
c_+ \ln \frac{c_+}{c_*} = c_+ \ln \frac{c_0 e^{-\bar{V}}}{c_*} = c_+ \ln \frac{c_0}{c_*} - c_+ \bar{V} \Rightarrow \frac{1}{2} c_+ \bar{V} + c_+ \ln \frac{c_+}{c_*} = c_+ \ln \frac{c_0}{c_*} - \frac{1}{2} c_+ \bar{V}
\]

\[
\int_{-D}^{D} c_+ \ln \left( \frac{c_0}{c_*} \right) dx = \ln \left( \frac{c_0}{c_*} \right) \int_{-D}^{D} c_+ dx = \frac{2\sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right)
\]

\[
\bar{V}'' = -2 \alpha^2 e^{-\bar{V}} \Rightarrow c_+ = -\frac{c_0}{2\alpha^2} \bar{V}'' \Rightarrow \frac{1}{2} c_+ \bar{V} = -\frac{c_0}{4\alpha^2} \bar{V}'' \bar{V}
\]

\[
\int_{-D}^{D} \bar{V}'' \bar{V} dx = \bar{V} \bar{V}' \bigg|_{-D}^{D} - \int_{-D}^{D} (\bar{V}'')^2 dx = -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - \int_{-D}^{D} (2 \alpha \tan \alpha x)^2 dx
\]

\[
= -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - 4\alpha^2 \int_{-D}^{D} (\sec^2 \alpha x - 1) dx = -\frac{8\pi l_B \sigma_q}{q} \bar{V}(D) + 8\alpha^2 D - 8\alpha \tan \alpha D
\]

\[
\Rightarrow \frac{F}{k_B T A} = -\frac{\sigma_q}{q} \bar{V}(D) + \frac{2\sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) - \frac{c_0}{4\alpha^2} \left[ \frac{8\pi l_B \sigma_q}{q} \bar{V}(D) - 8\alpha^2 D + 8\alpha \tan \alpha D \right]
\]

\[
= -\frac{2\sigma_q}{q} \bar{V}(D) + \frac{2\sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) + 2D c_0 - \frac{1}{\pi l_B} \alpha \tan \alpha D
\]
\[ \alpha \tan \alpha D = 2 \pi l_B \sigma_q / q \equiv \gamma \quad \alpha = \sqrt{2 \pi l_B c_0} \]

\[ \Rightarrow \frac{F}{k_B T A} = -\frac{2 \sigma_q}{q} \bar{V}(D) + \frac{2 \sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) + 2 D c_0 - \frac{1}{\pi l_B} \alpha \tan \alpha D \]

\[ = 2 D c_0 + (\gamma / \pi l_B) \left[ \ln \left( \frac{c_0}{c_*} \right) - \bar{V}(D) - 1 \right] \]

\[ \bar{V}(D) = 2 \ln \cos \alpha D = -\ln \left( 1 + \tan^2 \alpha D \right) = -\ln \left( 1 + \alpha^2 \tan^2 \alpha D / \alpha^2 \right) = -\ln \left( 1 + \frac{\gamma^2}{2 \pi l_B c_0} \right) \]

\[ \Rightarrow \frac{F}{k_B T A} = 2 D c_0 + \frac{\gamma}{\pi l_B} \left[ \ln \left( \frac{c_0}{c_*} \right) + \ln \left( 1 + \frac{\gamma^2}{2 \pi l_B c_0} \right) - 1 \right] = 2 D c_0 + \frac{\gamma}{\pi l_B} \ln \left( c_0 + \frac{\gamma^2}{2 \pi l_B} \right) + \text{const.} \]

\[ \Rightarrow \frac{p}{k_B T} = \frac{-d}{d(2 D)} \left( \frac{F}{k_B T A} \right) = -c_0 - \left( D + \frac{\gamma}{\alpha^2 + \gamma^2} \right) \frac{d c_0}{d D} + \left( \alpha / \alpha^2 + \gamma^2 \right) \frac{d \alpha}{D} \]

\[ \alpha \tan \alpha D = \gamma \Rightarrow \frac{d \alpha}{d D} = -\frac{\alpha (\alpha^2 + \gamma^2)}{\gamma + D (\alpha^2 + \gamma^2)} \]

\[ \alpha = \sqrt{2 \pi l_B c_0} \Rightarrow \frac{d c_0}{d \alpha} = \frac{\alpha}{\pi l_B} \]

\[ \therefore \frac{p}{k_B T} = -c_0 + \frac{\alpha^2}{\pi l_B} = 0 \]

\[ \Leftrightarrow p = c_0 k_B T \]
\[
\alpha \tan \alpha D = 2 \pi l_B \sigma_q / q \equiv \gamma \\
\alpha = \sqrt{2 \pi l_B c_0}
\]

\[
\Rightarrow \frac{F}{k_B T A} = -\frac{2 \sigma_q}{q} V(D) + \frac{2 \sigma_q}{q} \ln \left( \frac{c_0}{c_*} \right) + 2 D c_0 - \frac{1}{\pi l_B} \alpha \tan \alpha D
\]

\[
= 2 D c_0 + (\gamma / \pi l_B) \left[ \ln \left( \frac{c_0}{c_*} \right) - \bar{V}(D) - 1 \right]
\]

\[
V(D) = 2 \ln \cos \alpha D = -\ln \left( 1 + \tan^2 \alpha D \right) = -\ln \left( 1 + \frac{\alpha^2 \tan^2 \alpha D}{\alpha^2} \right) = -\ln \left( 1 + \frac{\gamma^2}{2 \pi l_B c_0} \right)
\]

\[
\Rightarrow \frac{F}{k_B T A} = 2 D c_0 + \frac{\gamma}{\pi l_B} \left[ \ln \left( \frac{c_0}{c_*} \right) + \ln \left( 1 + \frac{\gamma^2}{2 \pi l_B c_0} \right) - 1 \right] = 2 D c_0 + \frac{\gamma}{\pi l_B} \ln \left( c_0 + \frac{\gamma^2}{2 \pi l_B} \right) + \text{const.}
\]

\[
\Rightarrow \frac{p}{k_B T} = -\frac{d}{d(2D)} \left( \frac{F}{k_B T A} \right) = -c_0 \left( D + \frac{\gamma}{\alpha^2 + \gamma^2} \right) \frac{dc_0}{dD}
\]

\[
\alpha \tan \alpha D = \gamma \Rightarrow \frac{d \alpha}{dD} = -\frac{\alpha (\alpha^2 + \gamma^2)}{\gamma + D (\alpha^2 + \gamma^2)}
\]

\[
\alpha = \sqrt{2 \pi l_B c_0} \Rightarrow \frac{dc_0}{d \alpha} = \frac{\alpha}{\pi l_B}
\]

\[
\Leftrightarrow p = c_0 k_B T
\]
\[ \alpha \tan \alpha D = 2\pi l_B \sigma_q / q \equiv \gamma \]

\[ D_1 > D_2 \Rightarrow \alpha_1 < \alpha_2 \]

Decreasing distance induces larger \( \alpha \)

\[ \alpha = \sqrt{2\pi l_B c_0} \quad \text{Then gives larger } c_0 \]

\[ p = c_0 k_B T \quad \text{Then gives larger } p \]

The repulsive pressure increases as the plate separation decreases!

- **Experiment validates the theory**
  
  The surfaces are egg lecithin (卵磷脂) bilayers containing phosphatidylglycerol (磷酸酰甘油).
  
  The lines are fitting curves with one parameter \( \sigma_q \).

  At \( 2D > 2 \) nm the purely electrostatic theory fits the data well!
  
  [Data: Cowley et al., 1978]
  
  At \( 2D < 2 \) nm the surfaces begin to touch and other forces besides the electrostatic one appear.
Estimate $W_{\text{charge}}$ of Φ29 DNA packing considering the counterion cloud

Electrostatic interaction $\leftrightarrow p = c k_B T \Rightarrow p V = N k_B T$

$W_{\text{charge}} = N k_B T \ln \frac{V_1}{V_2}$

$V_1 = L \pi [(R_{DNA} + \lambda_D)^2 - R_{DNA}^2] \approx 64000 \text{nm}^3$

$V_2 = \frac{4\pi}{3} R_{\text{capsid}}^3 - L \pi R_{DNA}^2 \approx 12000 \text{nm}^3$

$W_{\text{charge}} \approx 65000 k_B T \approx W_{\text{motor}} = 50000 k_B T$
Attraction of opposite-charged surfaces

As the surfaces approach from infinity, each presents neutral; no long-range force.

As the surfaces approach, counterion pairs form, which still preserve the system’s neutrality.

The counterion pairs escape from the gap and so gain entropy without changing the electrostatic energy. This process can lower the free energy and so drive the surfaces together.

If the charge densities are equal and opposite, the process proceeds until the surfaces are in tight contact with no counterions left at all. The electrostatic self-energy stored in each surface is released. We have already estimated that this energy is substantial.

Electrostatic binding between surfaces of matching shape and charge distribution can be very strong.
§ Summary & further reading
Summary

- Electrostatic force
  - Charged surface in water: counterion cloud weakens the electrostatic interaction.
  - Adding electrolyte shortens the thickness of counterion cloud and make electrostatic interaction decay exponentially.
  - The repulsion of like-charged surfaces arises from compressing their ion clouds
  - Oppositely charged surfaces attract by releasing counterion pairs.
• Mean field approximation
  - we think of each ion as moving independently of the others’ detailed locations, but under the influence of an electric potential created by the effective charge density
• Poisson-Boltzmann equation
  - Charged surface with counterion cloud in water

\[
\bar{V}'' = -4\pi l_B c_0 e^{-\bar{V}}
\]

\[
\bar{V} = 2 \ln \left(1 + \frac{x}{x_0}\right)
\]

\[
x_0 \equiv \frac{q}{2\pi l_B \sigma_q}
\]

\[
p = c_0 k_B T
\]

\[
c_0 = \alpha^2 / 2\pi l_B
\]

\[
\bar{V} = 2 \ln \cos \alpha x
\]

\[
\alpha \tan \alpha D = 2\pi l_B \sigma_q / q
\]
Poisson-Boltzmann equation (continued)

- Charged surface with counterion cloud in monovalent (单价) salt solution

\[
\frac{d^2 \bar{V}}{dx^2} = \frac{\sinh \bar{V}}{\lambda_D^2}
\]

\[
\lambda_D = \left(8\pi l_B c_\infty\right)^{-1/2}
\]

\[
\bar{V} = 2 \ln \tanh \frac{x + x_*}{2 \lambda_D}
\]

\[
x_* = \lambda_D \ln \left[\frac{1 + \sqrt{1 + \zeta^2}}{\zeta}\right], \quad \zeta = 2\pi l_B \lambda_D \frac{\sigma_q}{q}
\]

For \(x >> \lambda_D\):

\[
\bar{V} = -\left(4 e^{-x_*/\lambda_D}\right) e^{-x/\lambda_D}
\]

For dilute solution, \(\lambda_D \propto c_\infty^{-1/2} \to \infty\):

\[
\bar{V} = 2 \ln \left(1 + x/x_0\right) + \text{const.}
\]
Further reading

- Phillips et al., Physical Biology of the Cell, Ch9
- Nelson, Biological Physics, Ch7