

# STATISTICAL MOLECULAR THERMODYNAMICS

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Video 11.7

Debye-Hückel Theory 1

# ELECTROLYTES



Peter Debye

How do ions  
distribute  
themselves in  
dilute solutions?

*Let's assume  
that the ions are  
point charges  
and the solvent  
can be  
represented as  
a dielectric  
continuum*



Erich Hückel

## WHERE ARE THE IONS?

Consider a central ion,  $i$ . Near to  $i$ , the density of ions of opposite charge will be enriched, while the density of ions of like charge will be depleted (for simplicity, we'll consider only a single type of anion and a single type of cation). At equilibrium, we should see a Boltzmann distribution, so that the charge density (charge per unit volume)  $\rho$  at a distance  $r$  from ion  $i$  will be:

$$\rho_i(r) = \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T}$$

The diagram shows the equation  $\rho_i(r) = \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T}$  with three red arrows pointing to specific parts of the equation. The first arrow points to the summation index  $j=+,-$  and is labeled "charge". The second arrow points to the concentration term  $C_j$  and is labeled "bulk number density (concentration)". The third arrow points to the exponent  $-q_j \psi_i(r)/k_B T$  and is labeled "electrostatic potential from ion  $i$ ".

# Self-assessment

First, from intuition, what do you expect the charge density to be very, very far from ion  $i$ ? Next, use the equation below to prove that.

$$\rho_i(r) = \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T}$$

# Self-assessment Explained

Very far from ion  $i$  we would expect *no* charge density, i.e., no preference for positive vs. negative charge, because it is too far away to exert an influence. In the below equation, that's equivalent to  $\psi = 0$ .

$$\begin{aligned}\rho_i(r) &= \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T} \\ &= \lim_{\psi \rightarrow 0} \sum_{j=+,-} q_j C_j \\ &= 0\end{aligned}$$

} *by electroneutrality*

# THE POISSON EQUATION

The Poisson equation fundamentally relates a charge density in a dielectric medium to an electrostatic potential. In a spherically symmetric system, the Poisson equation is

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\psi_i(r)}{dr} \right] = - \frac{\rho_i(r)}{\epsilon_0 \epsilon}$$

$\nabla^2 \psi$  permittivity of free space (units) dielectric constant of medium (solvent)

Assuming a weak potential, so that we may truncate the exponential in the charge density, we have


$$\begin{aligned} \rho_i(r) &= \sum_{j=+,-} q_j C_j e^{-q_j \psi_i(r)/k_B T} \approx \sum_{j=+,-} q_j C_j - \sum_{j=+,-} q_j C_j \frac{q_j \psi_i(r)}{k_B T} \\ &= - \frac{\psi_i(r)}{k_B T} \sum_{j=+,-} q_j^2 C_j \end{aligned}$$

# THE SCREENED POTENTIAL

Solution of the Poisson equation with that density leads to a general solution of the differential equation of

$$\psi_i(r) = \frac{B}{r} e^{\kappa r} + \frac{A}{r} e^{-\kappa r} \quad \text{where} \quad \kappa^2 = \frac{1}{\epsilon_0 \epsilon k_B T} \sum_{j=+,-} q_j^2 C_j$$

*number  
density  
(i.e.,  $c_j N_A$ )*



For the potential to go to zero at large  $r$ , it must be true that  $B = 0$ . For the potential to go to Coulomb's Law at infinite dilution ( $\kappa = 0$ ), it must be true that:

$$A = \frac{q_i}{4\pi\epsilon_0\epsilon}$$

and thus: 
$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\epsilon_0\epsilon r}$$

## THE INVERSE DEBYE LENGTH

Note that  $\kappa$  has units of inverse distance. The term involving  $\kappa$  in the numerator of the potential indicates that the potential of ion  $i$  is increasingly “screened” with increasing ionic strength.

$$\psi_i(r) = \frac{q_i e^{-\kappa r}}{4\pi\epsilon_0\epsilon r}$$
$$\kappa^2 = \frac{1}{\epsilon_0\epsilon k_B T} \sum_{j=+,-} q_j^2 C_j$$

With a little calculus, one can show that  $\kappa^{-1}$  is the distance at which there is the highest probability of finding a counterion vs an ion of like charge around ion  $i$ . Note that for a given concentration of a 1:1 electrolyte (like NaCl), that distance would shrink by a factor of 2 for a 2:2 electrolyte (like CaSO<sub>4</sub>). Thus, the counterion charge cloud “shrinks” for more highly charged species and screens them more rapidly.



$$dU = \delta q + \delta w$$



*Next: Debye-Hückel Theory 2*