Solutions of strong electrolytes.

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Summary of perturbation theories (previous lecture)

- Unlike all previous approaches, perturbation theories improve with increasing density.
- Excellent agreement at high density and near critical point.
- WCA lacks a universal reference state but converges rapidly.
- BH possesses a universal reference state but requires higher order terms in $\beta$.
- Very good for short-ranged realistic potentials.
- Similar to previous, they fail for long-ranged potentials like Coulomb.
Solutions of strong electrolytes – preliminaries

- All previous results can be generalized to mixtures
- Electrolyte solutions are an important example of a mixture
- Virial expansion for a mixture

\[
\frac{p}{k_B T} = \rho_1 + \rho_2 + B_{11}(T)\rho_1^2 + B_{22}(T)\rho_2^2 + B_{12}(T)\rho_1\rho_2 + \cdots
\]

\[
B_{ij}(T) = -2\pi \int_0^\infty \left( e^{-\beta u_{ij}} - 1 \right) r^2 dr
\]

- Primitive model: hard sphere with a point charge in a continuum

\[
u_{12}(r) = \begin{cases} 
\infty & \text{for } r < (\sigma_1 + \sigma_2)/2 \\
\frac{q_1 q_1}{4\pi \epsilon r} & \text{for } r > (\sigma_1 + \sigma_2)/2 
\end{cases}
\]

- Correspondence imperfect gases – solutions of non-electrolytes:

\[
\frac{\Pi}{k_B T} = c_2 + \sum_{j=2}^{\infty} B_j^*(\mu_1, T) c_2^j
\]

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Lecture 9: Electrolyte solutions.
Overview of electrostatics

Electrostatic potential at an arbitrary point $\mathbf{r}$:

$$
\phi(\mathbf{r}) = \sum_j \frac{q_j^+}{4\pi\varepsilon|\mathbf{r} - \mathbf{r}_j|} + \sum_k \frac{q_k^-}{4\pi\varepsilon|\mathbf{r} - \mathbf{r}_k|}
$$

In terms of charge density $\rho(\mathbf{r})$:

$$
\phi(\mathbf{r}) = \int_V \frac{\rho^+(\mathbf{r}')}{4\pi\varepsilon|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' + \int_V \frac{\rho^-(\mathbf{r}')}{4\pi\varepsilon|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' = \int_V \frac{\rho(\mathbf{r}')}{4\pi\varepsilon|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}'
$$

Poisson’s equation:

$$
\nabla^2 \phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\varepsilon}
$$

Gauss’s law:

$$
\int \mathbf{E} \cdot d\mathbf{S} = \frac{q}{\varepsilon}
$$

Charge in the centre of a sphere:

$$
4\pi r^2 E = \frac{q}{\varepsilon}
$$

Coulomb’s law:

$$
E = \frac{q}{(4\pi\varepsilon r^2)}
$$

*Here we use SI units, McQuarrie uses Gauss units*
The Debye-Hückel theory

- Assume solvent as continuum dielectric with permittivity $\epsilon = \epsilon_0 \epsilon_r$
- Neglect molecular structure of the solvent
- Represent ions by the primitive model
- Electrostatic excess free energy ($N$ ion pairs = $2N$ particles):
  
  $$e^{-\beta(A^{el})} = e^{-\beta(A - A_0)} = \frac{Z_N}{Z_0^N} = \frac{\int \int e^{-\beta U_N} \, dr_1 \cdots dr_{2N}}{\int \int e^{-\beta U_0^0} \, dr_1 \cdots dr_{2N}}$$

where

$$U_N = \sum_{i,j > i} \frac{q_i q_j}{4\pi \epsilon |r_i - r_j|} + \sum_{i,j > i} u^0(r_{ij})$$

- $u^0(r_{ij})$ is the reference interaction potential (hard sphere)
- Electrostatic self energy of ions omitted (concentration-independent constant that adds to $A$)
The Debye-Hückel theory

Potential felt by ion $j$ at $r_j$:

$$
\psi_j(r_j) = \sum_{i \neq j} \frac{q_i}{4\pi\epsilon|r_i - r_j|}
$$

Electrostatic part of $U_N$:

$$
U_N^{el} = \sum_j q_j \psi_j(r_j)
$$

Canonical ensemble average of the electrostatic potential:

$$
\langle \psi_j \rangle = \frac{\int \cdots \int \psi_j(r_j) e^{-\beta U_N} dr_1 \cdots dr_{2N}}{\int \cdots \int e^{-\beta U_N} dr_1 \cdots dr_{2N}}
$$

Differentiate $A^{el} = (A - A_0)$ with respect to $q_j$ to show that

$$
\left( \frac{\partial A^{el}}{\partial q_j} \right)_{V,T} = -\frac{1}{\beta} \left( \frac{\partial \ln Z_N}{\partial q_j} \right)_{V,T} = -\frac{1}{\beta Z_N} \left( \frac{\partial Z_N}{\partial q_j} \right)_{V,T}
$$

Define coupling parameter $\lambda$ such that $dq_j = q_j d\lambda$, to obtain

$$
A^{el} = A - A_0 = \sum_j q_j \int_0^1 \langle \psi_j(\lambda) \rangle d\lambda
$$

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Lecture 9: Electrolyte solutions.
The Debye-Hückel theory

Potential felt by ion \( j \) at \( \mathbf{r}_j \):

\[
\psi_j(\mathbf{r}_j) = \sum_{i \neq j} \frac{q_i}{4\pi\varepsilon|\mathbf{r}_i - \mathbf{r}_j|}
\]

Electrostatic part of \( U_N \):

\[
U_{N}^{el} = \sum_{j} q_j \psi_j(\mathbf{r}_j)
\]

Canonical ensemble average of the electrostatic potential:

\[
\langle \psi_j \rangle = \frac{\int \cdots \int \psi_j(\mathbf{r}_j) e^{-\beta U_N} \, d\mathbf{r}_1 \cdots d\mathbf{r}_{2N}}{\int \cdots \int e^{-\beta U_N} \, d\mathbf{r}_1 \cdots d\mathbf{r}_{2N}} = \frac{\int \cdots \int \left( \frac{\partial U_N}{\partial q_j} \right) e^{-\beta U_N} \, d\mathbf{r}_1 \cdots d\mathbf{r}_{2N}}{Z_N}
\]

Differentiate \( A_{el} = (A - A_0) \) with respect to \( q_j \) to show that

\[
\left( \frac{\partial A_{el}}{\partial q_j} \right)_{V,T} = -\frac{1}{\beta} \left( \frac{\partial \ln Z_N}{\partial q_j} \right)_{V,T} = -\frac{1}{\beta Z_N} \left( \frac{\partial Z_N}{\partial q_j} \right)_{V,T} = \langle \psi_j \rangle, \ j = 1, 2, \ldots, 2N
\]

Define coupling parameter \( \lambda \) such that \( dq_j = q_j d\lambda \), to obtain

\[
A_{el} = A - A_0 = \sum_{j} q_j \int_{0}^{1} \langle \psi_j(\lambda) \rangle d\lambda
\]
The Debye-Hückel theory

Consider electrostatic potential at arbitrary point \( r \)

\[
\psi(r) = \sum_i \frac{q_i}{4\pi \varepsilon |r - r_i|}
\]

Ensemble average \( \psi(r) \) with particle 1 fixed at \( r_1 \):

\[
1\langle \psi(r, r_1) \rangle = \frac{\int \cdots \int \psi(r, r_1)e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}{\int \cdots \int e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}
\]

Take its Laplacian and substitute \( \nabla^2 \psi(r) = -\rho(r)/\varepsilon \) (Poisson’s eq.)

\[
\nabla^2 \left( 1\langle \psi(r, r_1) \rangle \right) = \frac{\int \cdots \int \nabla^2 \psi(r, r_1)e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}{\int \cdots \int e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}
\]

\[
= \frac{\int \cdots \int -\frac{1}{\varepsilon} \rho(r, r_1)e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}{\int \cdots \int e^{-\beta U_N} \, dr_2 \cdots dr_{2N}}
\]

\[
= -\frac{1}{\varepsilon} 1\langle \rho(r, r_1) \rangle
\]
The Debye-Hückel theory

Average electrostatic potential with particle 1 fixed at \( r_1 \):

\[
1\langle \psi(r, r_1) \rangle
\]

Average electrostatic potential due to all other particles except 1:

\[
1\langle \psi(r) \rangle = 1\langle \psi(r, r_1) \rangle - \frac{q_1}{4\pi \epsilon |r - r_1|}
\]

Average electrostatic potential acting upon particle 1 fixed at \( r_1 \):

\[
1\langle \psi(r_1) \rangle = \langle \psi_1 \rangle \text{ for an isotropic fluid}
\]

Set \( r_1 = 0 \) and express charge density, \( \rho(r) \), in terms of \( g(r) \) for \( r > 0 \)

\[
\nabla^2 \left( 1\langle \psi(r) \rangle \right) = \nabla^2 \left( 1\langle \psi(r, r_1) \rangle \right) = -\frac{1}{\epsilon} 1\langle \rho(r, r_1) \rangle
\]

\[
= -\frac{1}{\epsilon} \sum_{s=1}^{2} q_s c_s g_{1s}(r, r_1) = -\frac{1}{\epsilon} \sum_{s=1}^{2} q_s c_s e^{-\beta w_{1s}(r)}
\]

\[\dagger\text{Note: } \nabla^2 (r - r_1)^{-1} = -4\pi \delta^3(r - r_1), \text{ therefore } \nabla^2 \langle \psi(r) \rangle = \nabla^2 \langle \psi(r, r_1) \rangle, r > 0 \]
The Debye-Hückel theory

Recap from the previous slide:

\[ \nabla^2 \left( \frac{1}{\langle \psi(r) \rangle} \right) = -\frac{1}{\epsilon} \sum_{s=1}^{2} q_s c_s g_{1s}(r, r_1) = -\frac{1}{\epsilon} \sum_{s=1}^{2} q_s c_s e^{-\beta w_{1s}(r)} \]

Up to this point, everything was exact.

**First approximation** (mean field)
– set the potential of mean force to \( \frac{1}{\langle \psi(r) \rangle} \)

\[ w_{1s}(r) = q_s \frac{1}{\langle \psi(r) \rangle} \equiv q_s \phi_1(r) \quad \text{for } r > a \]

Use the Poisson equation to obtain the Poisson-Boltzmann (PB) eq.:

\[ \nabla^2 \phi_1(r) = -\frac{1}{\epsilon} \sum_{s=1}^{2} q_s c_s e^{-\beta q_s \phi_1(r)} \quad \text{for } r > a \]
The Debye-Hückel theory

**Second approximation** – linearize RHS of the PB equation

\[
\sum_{s=1}^{2} q_s c_s e^{-\beta q_s \phi_1(r)} \approx \sum_{s=1}^{2} q_s c_s - \beta \sum_{s=1}^{2} q_s^2 c_s \phi_1(r)
\]

First term vanishes due to electroneutrality.

Linearized PB equation:

\[
\nabla^2 \phi_1(r) = \kappa^2 \phi_1(r) = \phi_1(r)/\lambda_D^2 \quad \text{for } r > a
\]

where we introduced the **Debye screening length** \( \lambda_D = \kappa^{-1} \):

\[
\kappa^2 = \frac{\beta \epsilon}{2} \sum_{s=1}^{2} q_s^2 c_s = \frac{\beta}{2\epsilon} I , \quad \text{where } I \text{ is the ionic strength}
\]

Finally, we note that inside the particle we have

\[
\nabla^2 \phi_1(r) = 0 \quad \text{for } r < a
\]
The Debye-Hückel theory

\( \phi_1(r) \) is spherically symmetric, so we rewrite the linearized PB equation:

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\phi_1}{dr} \right) = \begin{cases} 
\kappa^2 \phi_1(r) & \text{for } r > a \\
0 & \text{for } r < a 
\end{cases}
\]

With boundary conditions (\( a \) is the particle size – hard sphere):

\[
\phi_1(r \to \infty) \to 0, \quad \phi_1(r \to a^+) = \phi_1(r \to a^-)
\]

**Primitive model:** \( a > 0 \), **restricted primitive model:** \( a = 0 \)

Its solution then becomes (see textbook for derivation):

\[
\phi_1(r) = \begin{cases} 
\frac{q_1}{4\pi \varepsilon r} - \frac{q_1 \kappa}{4\pi \varepsilon (1 + \kappa a)} & \text{for } 0 < r < a \\
\frac{q_1 e^{-\kappa (r-a)}}{4\pi \varepsilon r (1 + \kappa a)} & \text{for } r > a
\end{cases}
\]

and finally we obtain \( \langle \psi_j \rangle \) – excess free energy contribution \( A_{\text{el}} \)

\[
\text{for } r < a \quad \langle \psi_j \rangle = \phi_j(r) - \frac{q_j}{4\pi \varepsilon r} = \frac{q_j \kappa}{4\pi \varepsilon (1 + \kappa a)}
\]
Remarks on the Debye-Hückel approximation

- Primitive model: \( a > 0 \), restricted primitive model: \( a = 0 \)
- For \( c \to 0 \) DH is an exact limiting law.
- Then \( \kappa a \ll 1 \), so we obtain:

\[
\lim_{c \to 0} w_{ij}(r) = \frac{q_i q_j e^{-\kappa r}}{4\pi \epsilon r}
\]

(Yukawa screened potential)

- As soon as the particle volume \( a \) becomes important, the assumption \( w_{1s}(r) = q_s \phi_1(r) \) breaks down
- Self-consistency conditions:

\[
q_j \langle \psi_s \rangle = q_s \langle \psi_j \rangle, \quad \frac{\partial \langle \psi_i \rangle}{\partial q_j} = \frac{\partial \langle \psi_j \rangle}{\partial q_i}
\]

- Second condition is satisfied by the linearized PB equation
- But it is not satisfied by the non-linearized one
The ionic atmosphere

- Amount of charge within distance $r$ from a selected ion

$$p(r) dr \propto \frac{1}{\langle \rho(r) \rangle} 4\pi r^2 dr = -\frac{q_1 \kappa^2 r}{1 + \kappa a} e^{-\kappa (r-a)} dr$$

- Maximum around $r \approx \lambda_D = \kappa^{-1}$ from the reference ion $q_1 = -1e$
Thermodynamic functions from DH theory

\[ A - A_0 = \sum_j q_j \int_0^1 \langle \psi_j(\lambda) \rangle d\lambda = \sum_j \frac{q_j^2}{4\pi \epsilon} \int_0^1 \frac{\lambda \kappa(\lambda)}{1 + \kappa(\lambda) a} d\lambda \]

\[ \frac{\beta A^\text{el}}{V} = \frac{\beta A - A_0}{V} = -\frac{\kappa^3}{12\pi} \tau(\kappa a) \approx -\frac{\kappa^3}{12\pi} \]

where

\[ \tau(\kappa a) = \frac{3}{\kappa^3 a^3} \left( \ln(1 + \kappa a) - \kappa a + \frac{\kappa^2 a^2}{2} \right) \]

\[ \kappa \to 0 \approx 1 - \frac{3}{4} \kappa a + \frac{3}{5} (\kappa a)^2 + \cdots \]

Electrostatic (excess) chemical potential

\[ \mu_j^\text{el} = \left( \frac{\partial A^\text{el}}{\partial N_j} \right)_{V,T} = \frac{V}{\beta} \left( \frac{\partial}{\partial N_j} \left( \frac{\beta A^\text{el}}{V} \right) \right)_{V,T} \approx \frac{\kappa q_j^2}{8\pi \epsilon (1 + \kappa a)} \]
Thermodynamic functions from DH theory

\[ \mu_j \xrightarrow{\kappa \to 0} k_B T \ln \Lambda^3 + k_B T \ln c_j - \frac{\kappa q_j^2}{8\pi \epsilon (1 + \kappa a)} \]

\[ \ln \gamma_j \xrightarrow{\kappa \to 0} -\frac{\kappa q_j^2}{8\pi k_B T \epsilon (1 + \kappa a)} \]

\[ \ln \gamma_+ \approx -|q+q-| \frac{\kappa}{8\pi k_B T \epsilon} \]

\[ G^\text{el} = \sum_j N_j \mu_j^\text{el}, \quad \frac{\beta G^\text{el}}{V} = \sum_j N_j \mu_j^\text{el} = -\frac{\kappa^3}{8\pi (1 + \kappa a)} \]

\[ \frac{\beta G^\text{el}}{V} = \frac{\beta A^\text{el}}{V} + \beta p^\text{el} \]

\[ \beta p^\text{el} = -\frac{\kappa^3}{24\pi} \left( \frac{3}{1 + \kappa a} - 2\tau (\kappa a) \right) \xrightarrow{\kappa \to 0} -\frac{\kappa^3}{24\pi} \]

\[ \frac{p}{k_B T} \xrightarrow{\kappa \to 0} c_1 + c_2 - \frac{\kappa^3}{24\pi}, \quad \phi = \frac{p}{k_B T (c_1 + c_2)} \xrightarrow{\kappa \to 0} 1 - \frac{\kappa^3}{24\pi (c_1 + c_2)} \]
Particle volume vs. electrostatics

- Simulation: Lennard-Jones particles with diameter $\sigma$
- Bjerrum length: $\lambda_B = \frac{e^2}{(4\pi k_B T r)}$

![Diagram showing the relationship between $\mu_{ex}$ and $c_s$ for different values of $\sigma/\lambda_B$.](Image)

Extended DH
Exp. (NaCl)
$\sigma/\lambda_B = 2.0$
$\sigma/\lambda_B = 1.0$
$\sigma/\lambda_B = 0.5$

Picture from publication: P. Košovan et. al., Macromolecules (2015), DOI:10.1021/acs.macromol.5b01428
Advanced statmech. theories of ionic solutions

- Analogue of the virial expansion (1950s)
- Generalization of integral equations (1960s)

\[ w(r) = \frac{1}{r} - \frac{\kappa^2}{4\pi} \int_{|r-r'|>a} \frac{w(|r-r'|)}{r'} \, dr' \]

- Perturbation approaches (1970s)
- All compare with experiment much better than DH
- DH can be obtained as a specific truncation of the virial expansion or closure of the integral equations