Ion-specific Effects on Biocolloidal Systems

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Outline (Lecture 2)

➢ The modified Poisson-Boltzmann equation;

➢ Introduction to Classical Density Functional Theory;

➢ Size and electrostatic correlations.
The Modified Poisson-Boltzmann Equation
The Modified PBE

✓ Improvement: modifications in order to take into account several important effects such as dispersion forces, hydration, ion size effects, and electric correlation between ions.

✓ Additional contributions may be divided in two classes:

➢ external field contributions: e.g., ion-interface interactions.

➢ contributions depending on the interaction among molecules (ions): residual chemical potential.
The Modified Boltzmann Distribution

✓ Additional terms can be included in the description of the electrochemical potential:

\[ \mu_i(p, T) = \mu_i^0(p, T) + k_B T \ln c_i + e z_i \psi + U_i + \mu_{i \text{res}} \]

\[ \mu_{\infty, i}(p, T) = \mu_i^0(p, T) + k_B T \ln c_{\infty, i} + e z_i \psi_{\infty} + \mu_{\infty, i}^{\text{res}} \]

✓ Equilibrium condition: \( \mu_i(p, T) = \mu_{\infty, i}(p, T) \)

✓ Resulting in:

\[ c_i = c_{\infty, i} \exp \left[ - \frac{z_i e (\psi - \psi_{\infty}) + U_i + \mu_{i \text{res}} - \mu_{\infty, i}^{\text{res}}}{k_B T} \right] \]
The Modified PBE

✓ Modified Boltzmann distribution:

\[ c_i = c_{\infty,i} \exp\left[-\frac{z_i e(\psi - \psi_{\infty}) + U_i + \mu_{\text{res},i}^\text{res} - \mu_{\infty,i}^\text{res}}{k_B T}\right] \]

✓ Combining with Poisson Equation, we have the Modified Poisson-Boltzmann equation:

\[ \varepsilon_0 \nabla \cdot (\varepsilon \nabla \psi) = -e \sum_i z_i c_{\infty,i} \exp\left[-\frac{z_i e(\psi - \psi_{\infty}) + U_i + \mu_{\text{res},i}^\text{res} - \mu_{\infty,i}^\text{res}}{k_B T}\right] - \rho_f \]

✓ The Boundary conditions are the same as for the classical PBE.
van der Waals Interactions

Dispersion interactions between ions and a planar surface (Parsons, and Ninham, 2010):

\[ U_i^{\text{disp}} = -\frac{G(x)B_i}{x^3} \]

\[ G(x) = 1 + \frac{2x}{\sqrt{\pi r_i}} \left( \frac{2x^2}{r_i^2} - 1 \right) \exp \left( -\frac{x^2}{r_i^2} \right) - \left( 1 + \frac{4x^4}{r_i^4} \right) \text{erfc} \left( \frac{x}{r_i} \right) \]

And between two spheres (Lima et al., 2007) (without ion size correction):

\[ U_i = \frac{-B_i}{(r_i - r_{p1})^3 \left[ 1 + \frac{(r_i - r_{p1})^3}{2r_{p1}^3} \right]} + \frac{-B_i}{(r_i - r_{p2})^3 \left[ 1 + \frac{(r_i - r_{p2})^3}{2r_{p2}^3} \right]} \]

where \( B_i \) is calculated from Lifshitz Theory.
Scale integration

✓ Inclusion of ionic potential of mean force (PMF) obtained from molecular dynamics (Horinek and Netz, 2007):

\[
\frac{V(x)}{k_B T} = \frac{A}{(x - x')^2} - \frac{B}{(x - x')^8} + C_1(x - C_2)e^{-C_3(x-C_2)^2} + D_1e^{-D_3(x-D_2)^2}
\]

✓ For two plates

\[
U_i(x) = V(x) + V(L - x)
\]

✓ These PMF include:

➢ van der Waals interactions;
➢ ionic hydration
➢ Self-image charge potential
Ion Size Correlation in PBE

✓ Modified Boltzmann distribution:

\[ c_i = c_{\infty,i} \exp \left[ - \frac{z_i e \psi + U_i + w_i(c(x), \sigma) - w_i(c_{\infty}(x), \sigma)}{k_B T} \right] \]
Ion Size Correlation in PBE

The size effects are taken into account through size correlations terms by using Boublik–Mansoori–Carnahan–Starling–Leland equation of state:

\[ w_i(c(x), \sigma) = g_i = \frac{\mu_i^{res,BMCSL}}{k_B T} = \frac{(\xi_0 - \frac{\xi_2^3}{\xi_3^2})\sigma_i^3 + 3\xi_2\sigma_i + 3\xi_1\sigma_i^2}{1 - \xi_3} \]

\[ + \frac{2\xi_2^3\sigma_i^3}{\xi_3(1 - \xi_3)^3} + \frac{3\xi_1\xi_2\sigma_i^3 + 3\xi_2^2\sigma_i^2/\xi_3 + \xi_2^3\sigma_i^3/\xi_3^2}{(1 - \xi_3)^2} \]

\[ + (-1 + 3\xi_2^2\sigma_i^2/\xi_3^2 + 2\xi_2^3\sigma_i^3/\xi_3^3) \ln(1 - \xi_3) \]

\( \xi \) is the packing factor, given by

\[ \xi_k = \frac{\pi}{6} \sum_i c_i(x)\sigma_i^k \]
Ion-ion Electrostatic Correlation in PBE

✓ Modified Poisson equation (equivalent to a Poisson–Fermi equation):

\[ \nabla \cdot \mathbf{D} \equiv \varepsilon (\ell_c^2 \nabla^2 - 1) \nabla^2 \psi = \rho. \]

where \( \mathbf{D} \) is the displacement field. For the linear response regime (for small electric fields), the displacement field is given by

\[ \mathbf{D} = -\hat{\varepsilon} \nabla \psi \quad \hat{\varepsilon} = \varepsilon (1 - \ell_c^2 \nabla^2) \]

\( \ell_c \) = scaling factor: empirical parameter that establishes a characteristic length scale in which the electrostatic correlations are relevant.

Ion-ion Electrostatic Correlation in PBE

✓ Rewriting in Cartesian coordinates:

\[ \varepsilon \left( \ell_c^2 \frac{\partial^4 \psi}{\partial x^4} - \frac{\partial^2 \psi}{\partial x^2} \right) = e \sum_{i=1}^{n_c} z_i C_i \]

that is is the Poisson–Fermi equation.

Additional boundary conditions: correlations are neglected at the surface:

\[ \hat{n} \cdot \nabla (\nabla^2 \psi) = 0 \]

Charge Regulation at the Surface

✓ The surface is uniformly charged.

✓ Basic groups = positive contributions:

\[ e z^i_+ = \frac{e[H^+]_s}{[H^+]_s + K_a^i}, \text{ where } [H^+]_s = 10^{-pH} \exp \left( -\frac{e\psi_s}{k_B T} \right) \]

✓ Acid groups = negative contribution:

\[ e z^i_- = \frac{-eK_a^i}{[H^+]_s + K_a^i} \]

✓ Average surface charge: \( Q_p = \sum_{\text{bási cos}} e z^i_+ + \sum_{\text{ácidos}} e z^i_- \)

Ninham and Parsegian (1971)
Charge Regulation at the Surface

✓ Titration curve obtained from charge regulation model:

![Titration curve graph](image)
Force between a Lysozyme and a BSA
Density Functional Theory
Density Functional Theory

“Matter distributes itself in space in such a way that, for a given energy, the entropy attains a maximum.”

\[ \delta S[\rho(r)] = 0 \]


Classical DFT
✓ Structure and thermophysical properties
✓ Statistical Mechanics
✓ Density of matter

van der Waals (1893) Nobel Prize (1910)
Onsager (1949) Nobel Prize (1968)
Mermin (1965)-Ebner-Saam-Stroud (1976)

Electronic DFT
✓ Spectroscopic, electronic and optoelectronic properties
✓ Quantum Mechanics
✓ Electronic density

Thomas-Fermi (1920s) Nobel Prize (1938)
Hohenberg and Kohn (1964)
Kohn and Sham (1965) Nobel Prize (1998)
Classical Density Functional Theory (DFT)

✓ Structure and thermodynamic properties from a molecular perspective.
✓ Can be applied to several kinds of systems: polymers, electrolytes, polyelectrolytes and biomacromolecules.
✓ Takes into account microscopic details without dealing explicitly with thermal fluctuations.
Hohenberg-Kohn Theorem (1964)

✓ Originally established in the quantum mechanics of the ground-state energy of electrons at 0K.
✓ Generalization to a finite temperature by Mermin (1965).
✓ Equally applicable to classical systems (Evans, 1979).

“The one-body potential can be uniquely determined by a density profile that minimizes the grand-potential functional.”

**Consequence:** the Helmholtz energy can be expressed as a unique functional of the density profiles.

Fundamentals of DFT

✓ Helmholtz Energy = functional of density profiles of molecules.

\[ F = F \left[ \rho \left( \vec{r} \right) \right] \]

✓ Molecular density profile: ensemble average of instantaneous molecular densities (Wu, 2006):

\[ \rho \left( \vec{r} \right) = \langle \sum_i \delta \left( \vec{r} - \vec{r}_i \right) \rangle \]
Fundamentals of DFT

✓ Central task: derive an analytical expression for the grand potential of an open system as a functional of the density profiles:

\[ \Omega[\{\rho_i(\vec{r})\}] = F[\{\rho_i(\vec{r})\}] + \sum_{i=1}^{N} \int \rho_i(\vec{r})[\psi_i(\vec{r}) - \mu_i(\vec{r})] d\vec{r} \]

One-body potential

✓ The equilibrium density profile of inhomogeneous fluid is given by the minimum condition (Euler-Lagrange equation):

\[ \frac{\delta \Omega[\{\rho_i(\vec{r})\}]}{\delta \rho_i(\vec{r})} \bigg|_{\rho_i^{eq}} = 0 \]
Fundamentals of DFT

Or in terms of Helmholtz free energy (F):

\[
\frac{\delta F[(\rho_i(\vec{r}))]}{\delta \rho_i(\vec{r})} + \psi_i(\vec{r}) - \mu_i(\vec{r}) = 0
\]

The ideal contribution for the Helmholtz energy is:

\[
\beta F^{id} = \beta \Omega^{id} - \int \rho(\vec{r}) \beta \varphi(\vec{r}) d\vec{r} = - \int \rho(\vec{r}) d\vec{r} + \int \rho(\vec{r}) \ln[\rho(\vec{r})\Lambda^3] d\vec{r}
\]

\[
= \int \rho(\vec{r})\{\ln[\rho(\vec{r})\Lambda^3] - 1\} d\vec{r}
\]

Solving for the density profiles:

\[
\rho_i(\vec{r}) = \exp \left[ \beta \mu_i - \beta \psi_i - \frac{\delta \beta F^{ex}[(\rho_i(\vec{r}))]}{\delta \rho_i(\vec{r})} \right]
\]
Density Functional Theory (DFT)

The Helmholtz functional can be split in four parts:

\[ F = F^d + F_{hs}^{ex} + F_C^{ex} + F_{el}^{ex} \]

The electrostatic contribution is composed by two contributions:

- **Direct Coulomb interactions**: \( F_C^{ex} \)
- **Electrostatic correlations**: \( F_{el}^{ex} \)
Density Functional Theory (DFT)

Using the same notation as for PB Theory, the Euler-Lagrange functions for the density of ions are given by:

\[ c_i(x) = \exp \left[ \left( \mu_i - \psi_i(x) - \frac{\delta F_{e}^{ex} }{\delta c_i(x)} \right)/k_B T \right] \]

Defining the mean electrostatic potential:

\[ z_i e\psi(x) = \psi_i(x) + \frac{\delta F_{c}^{ex} }{\delta c_i(x)} \]
DFT x Boltzmann Distribution

✓ Neglecting size correlations: $\frac{\delta F_{hs}^{ex}}{\delta c_i} = 0$

and electrostatic correlations: $\frac{\delta F_{el}^{ex}}{\delta c_i} = 0$

✓ Helmholtz energy $F$ simplifies to that used in Poisson-Boltzmann theory and the expression for the density profile of ions simplifies to

$$ c_i(x) = c_{\infty,i} \exp \left[ -\frac{z_i e \psi(x)}{k_B T} \right] $$

that is the classical Boltzmann distribution
Short range repulsion

✓ Different Approaches usually used for the short range repulsion contribution to the excess Helmholtz free energy:

- FMT $\rightarrow$ Rosenfeld’s fundamental measure theory
- FWF $\rightarrow$ Forsman, Woodward and Freasier methods
- White Bear $\rightarrow$ modification of FMT using EoS for bulk hard-sphere fluids by Boublik, Mansoori, Carnahan, Starling and Leland (BMCSL).
Density Functional Theory

Approaches used for the ion-ion electrostatic correlations

- **WCA** → Weighted correlation approach
- **BFD** → bulk fluid density approach
- **RFD** → reference fluid density approach
- **CCDFT** → contact-corrected DFT approach
- **DHH** → hole corrected Debye-Hückel theory
Density Functional Theory (DFT)

Expression for $F[\rho(r)]$

Minimization of $\Omega[\rho(r)]$

Equilibrium density profiles $[\rho(r)]$

Thermodynamic properties
Picard Method

- Conventional method to converge to the equilibrium density profiles → Picard method.

\[ \rho_{i,\text{in}}^{(k)}(\vec{r}) = \rho_{i,\text{out}}^{(k-1)}(\vec{r})f + \rho_{i}^{(k-1)}(\vec{r})(1 - f) \]

- This method belongs to the class of successive substitution methods and uses a “mixture parameter” \( f \) that is the weight of a weighted average between the new and old estimates of \( \rho \).
Some results applying the Classical Theories
1:1 salt; $\varphi_0 = 2; C_0 = 0.1$ mol/L; $D = 2\text{Å}$

Tavares, Boström, Lima, Biscaia. FPE (2010).
2:2 salt; \( \varphi_0 = 2 \); \( C_0 = 0.1 \) mol/L; \( D = 2 \) Å
Tavares, Broström, Lima, Biscaia. FPE (2010).
1:1 salt; $Q = 0.35 \text{ C/m}^2$; $C_\infty = 2\text{ mol/L.}; T = 298.15 \text{ K.}; D = 4.25 \text{ Å.}$


Monte Carlo results from Torrie and Valleau (1980) cited therein