UNIVERSIDADE DO ESTADO DO RIO DE JANEIRO
INSTITUTO DE QUÍMICA – PPG-EQ

PPG-EQ

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:

$$\mu_i(p,T) = \mu_i^0(p,T) + k_B T \ln c_i + e z_i \psi + U_i + \mu_i^{res}$$

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

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

- ✓ Resulting in:

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

The Modified PBE

- ✓ Modified Boltzmann distribution:

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

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

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

- ✓ 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):

$$U_i^{disp} = -\frac{\mathrm{G}(x)B_i}{x^3}$$

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

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

$$U_i = \frac{-B_i}{(r_1 - r_{p1})^3\left[1 + {(r_1 - r_{p1})^3}\big/{2r_{p1}^3}\right]} + \frac{-B_i}{(r_2 - r_{p2})^3\left[1 + {(r_2 - r_{p2})^3}\big/{2r_{p2}^3}\right]}$$

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):

$$\frac{V(x)}{k_B T} = \frac{A}{(x-x')^{12}} - \frac{B}{(x-x')^{8}} + C_1(x-C_2)e^{-C_3(x-C_2)^2} + D_1 e^{-D_3(x-D_2)^2}$$

✓For two plates

$$U_i(x) = V(x) + V(L-x)$$

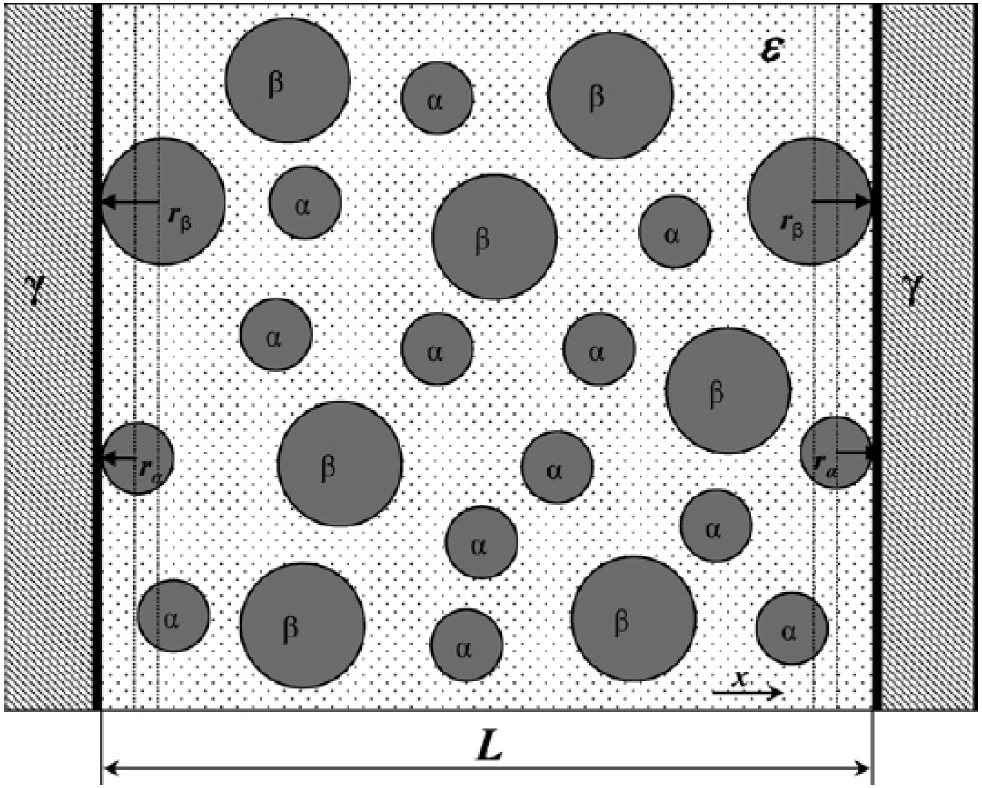
✓ These PMF include:

- ➢ van der Waals interactions;
- ➢ ionic hydration
- ➢ Self-image charge potential

Ion Size Correlation in PBE

✓ Modified Boltzmann distribution:

$$c_i = c_{\infty,\mathrm{i}}\, exp\left[-\frac{z_i e\psi + U_i + \mathrm{w_i}(\mathrm{c}(\mathbf{x}),\sigma) - \mathrm{w_i}(\mathrm{c}_\infty(\mathbf{x}),\sigma)}{k_B T}\right]$$



Alijó, Tavares, Biscaia Jr. ColSuA, 412 (2012) , 29-35

Ion Size Correlation in PBE

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

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

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

$$+ (-1 + 3{\xi_2}^2{\sigma_i}^2/{\xi_3}^2 + 2{\xi_2}^3{\sigma_i}^3/{\xi_3}^3)\ln(1-\xi_3)$$

ξ Is the packing factor, given by

$$\xi_k = \frac{\pi}{6}\sum\nolimits_i c_i(x)\sigma_i^k$$

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 D is the displacement field. For the linear response regime (for small electric fields), the displacement field is given by

$$\mathbf{D} = -\hat{\varepsilon}\nabla\psi \qquad \hat{\varepsilon} = \varepsilon(1 - \ell_c^2 \nabla^2)$$

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

Bazant, Storey, Kornyshev, Phys. Rev. Lett. 106 (2011), 046102.

Ion-ion Electrostatic Correlation in PBE

✓ Rewriting in Cartesian coordinates:

$$\varepsilon\left(\ell_c^2\frac{\partial^4\psi}{\partial x^4}-\frac{\partial^2\psi}{\partial x^2}\right)=e\sum_{i=1}^{n_c}z_ic_i$$

that is is the Poisson–Fermi equation.

Additional boundary conditions: correlations are neglected at the surface:

$$\hat{n}\cdot\nabla\left(\nabla^2\psi\right)=0$$

Bazant, Storey, Kornyshev, Phys. Rev. Lett. 106 (2011), 046102.
Alijó, Tavares, Biscaia, Secchi, Electrochimica Acta 152 (2015) 84–92 .

Charge Regulation at the Surface

✓ The surface is uniformly charged.

✓ Basic groups = positive contributions:

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

✓ Acid groups = negative contribution:

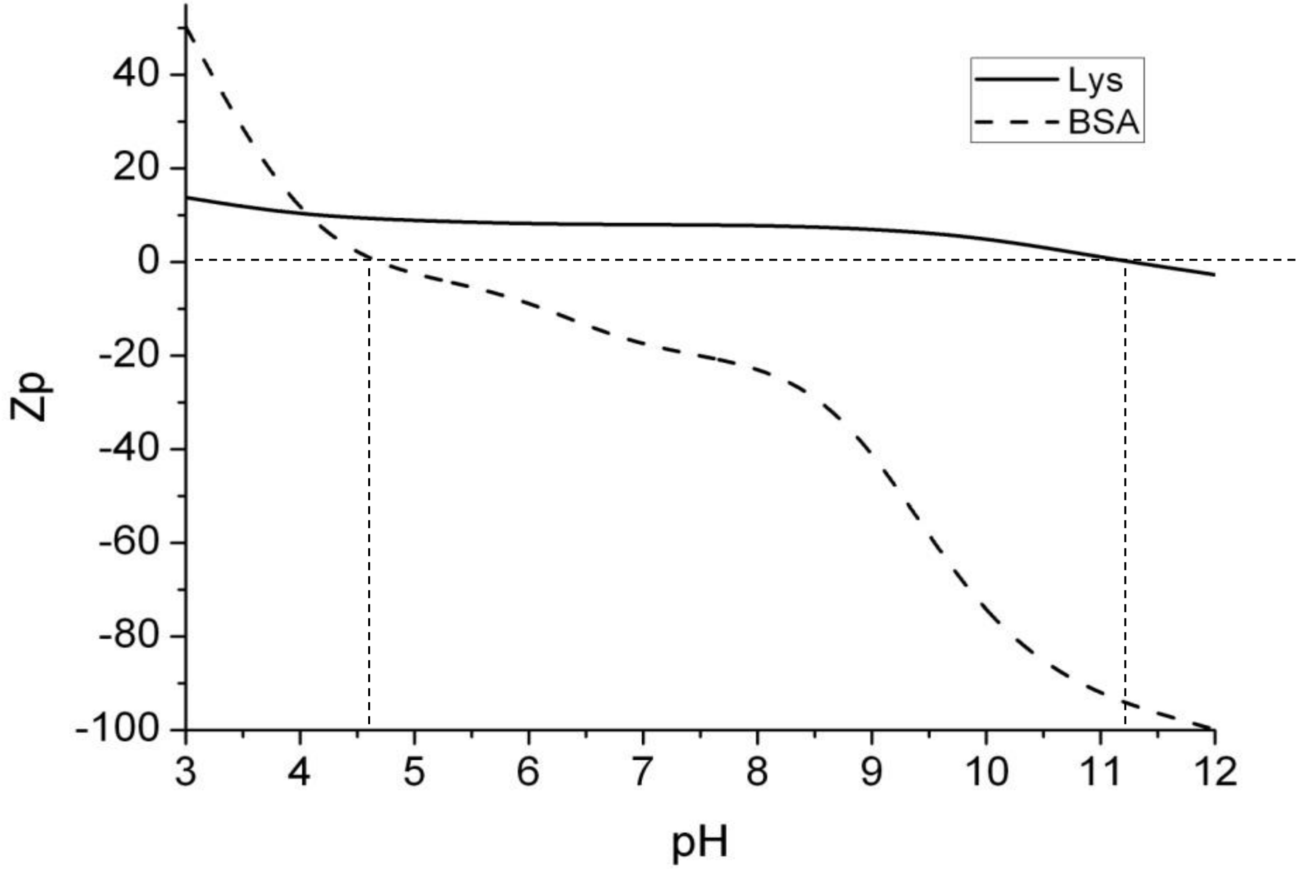
$$ez_-^i = \frac{-eK_a^i}{\left[H^+\right]_s + K_a^i}$$

✓ Average surface charge: $Q_p = \sum_{básicos} ez_+^i + \sum_{ácidos} ez_-^i$

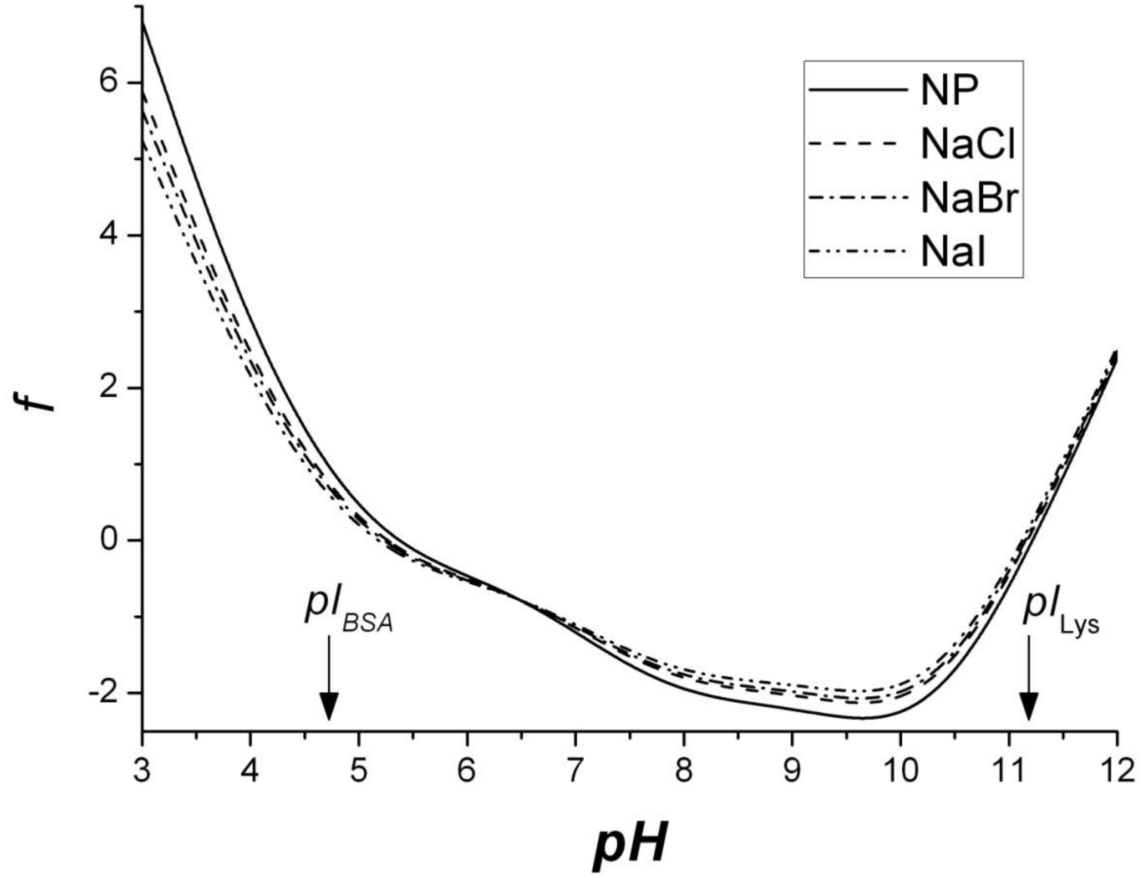
Ninham and Parsegian (1971)

Charge Regulation at the Surface

✓ Titration curve obtained from charge regulation model :



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."

$$\delta S[\rho(\boldsymbol{r})] = 0$$

J. D. van der Waals, *Verhandel. Konink. Akad. Weten. Amsterdam,* Vol. 1, No. 8, 58 (1893)
J. S. Rowlinson, *Journal of Statistical Physics, Vol. 20, No. 2, 1979*

J. D. van der Waals

Classical DFT x Electronic DFT

Classical DFT

✓Structure and thermo-physical 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 e 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.

Hohenberg P, Kohn W (1964) Phys Rev 136:B864
Mermin ND (1965) Phys Rev 127:A1441
Evans R (1979) Adv Phy 28:143

Fundamentals of DFT

- ✓ Helmholtz Energy = functional of density profiles of molecules.

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

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

$$\rho(\vec{r}) = < \sum_i \delta(\vec{r} - \vec{r}_i) >$$

Fundamentals of DFT

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

$$\Omega[\{\rho_i(\vec{r})\}] = F[\{\rho_i(\vec{r})\}] + \sum_{i=1}^{N} \int \rho_i(\vec{r}) \underbrace{[\psi_i(\vec{r}) - \mu_i(\vec{r})]}_{\text{One-body potential}} \mathrm{d}\vec{r}$$

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

$$\left.\frac{\delta\Omega[\{\rho_i(\vec{r})\}]}{\delta\rho_i(\vec{r})}\right|_{\rho_i^{eq}} = 0$$

Fundamentals of DFT

Or in terms of Helmholtz free energy (F):

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

The ideal contribution for the Helmholtz energy is:

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

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

Solving for the density profiles:

$$\rho_i(\vec{r}) = exp\left[\beta\mu_i - \beta\psi_i - \frac{\delta\beta\mathrm{F}^{\mathrm{ex}}[(\rho_i(\vec{r})]}{\delta\rho_i(\vec{r})}\right]$$

Density Functional Theory (DFT)

The Helmholtz functional can be split in four parts:

$$F = F^{id} + \underbrace{F_{hs}^{ex} + F_{C}^{ex} + F_{el}^{ex}}_{F^{ex}}$$

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:

$$c_i(x) = exp\left[\left(\mu_i - \Psi_i(x) - \frac{\delta F^{ex}}{\delta c_i(x)}\right)/k_B T\right]$$

Defining the mean electrostatic potential:

$$\mathrm{z_i e}\psi(x) = \Psi_i(x) + \frac{\delta F_C^{ex}}{\delta c_i(x)}$$

DFT x Boltzmann Distribution

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

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

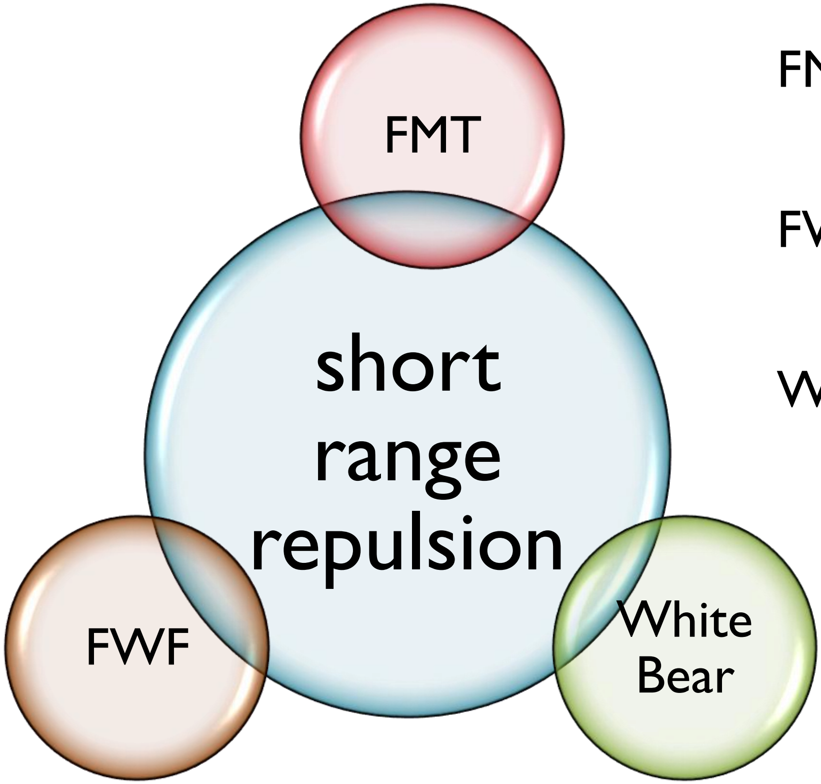
✓ Helmholtz energy F simplifies to that used in Poisson-Boltzmann theory and the expression for the density profile of ions simplifies to

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

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:



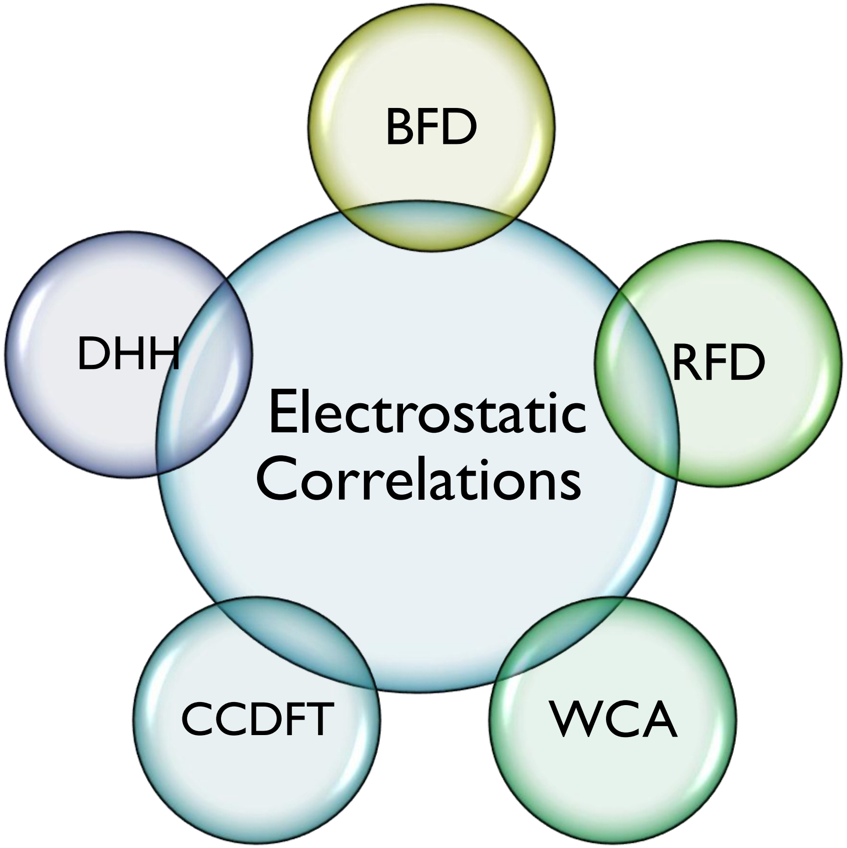
FMT →Rosenfeld's fundamental measure theory

FWF → Forsman, Woodward and Freasier methods

White Bear → modification of FMT using EoS for bulk hard-sphere fluids by Boublik, Mansoori, Carnahan, Starling and Leland (BMCSL).

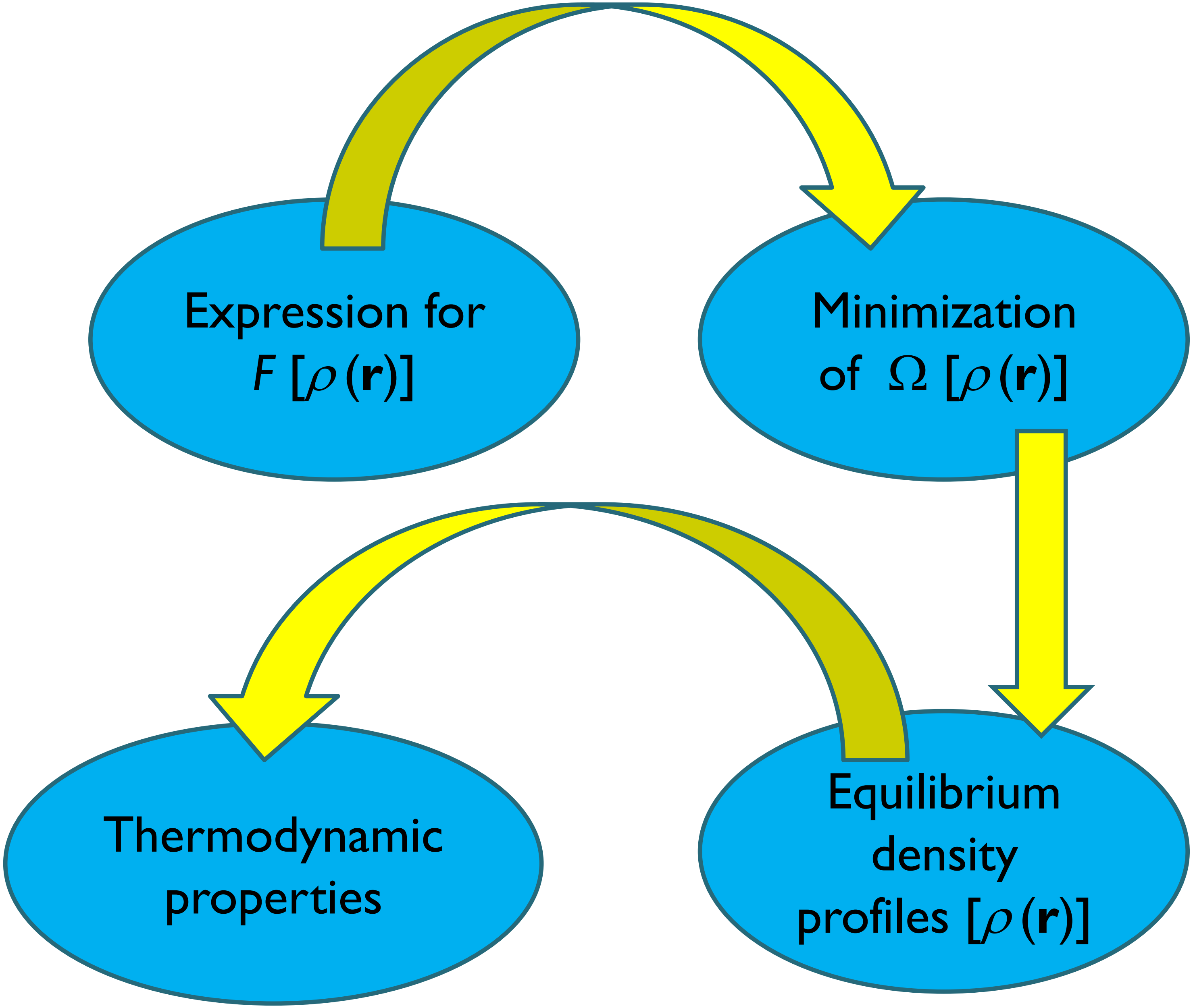
Density Functional Theory

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 $F\,[\rho(\mathbf{r})]$

Minimization of $\Omega\,[\rho(\mathbf{r})]$

Equilibrium density profiles $[\rho(\mathbf{r})]$

Thermodynamic properties

Picard Method

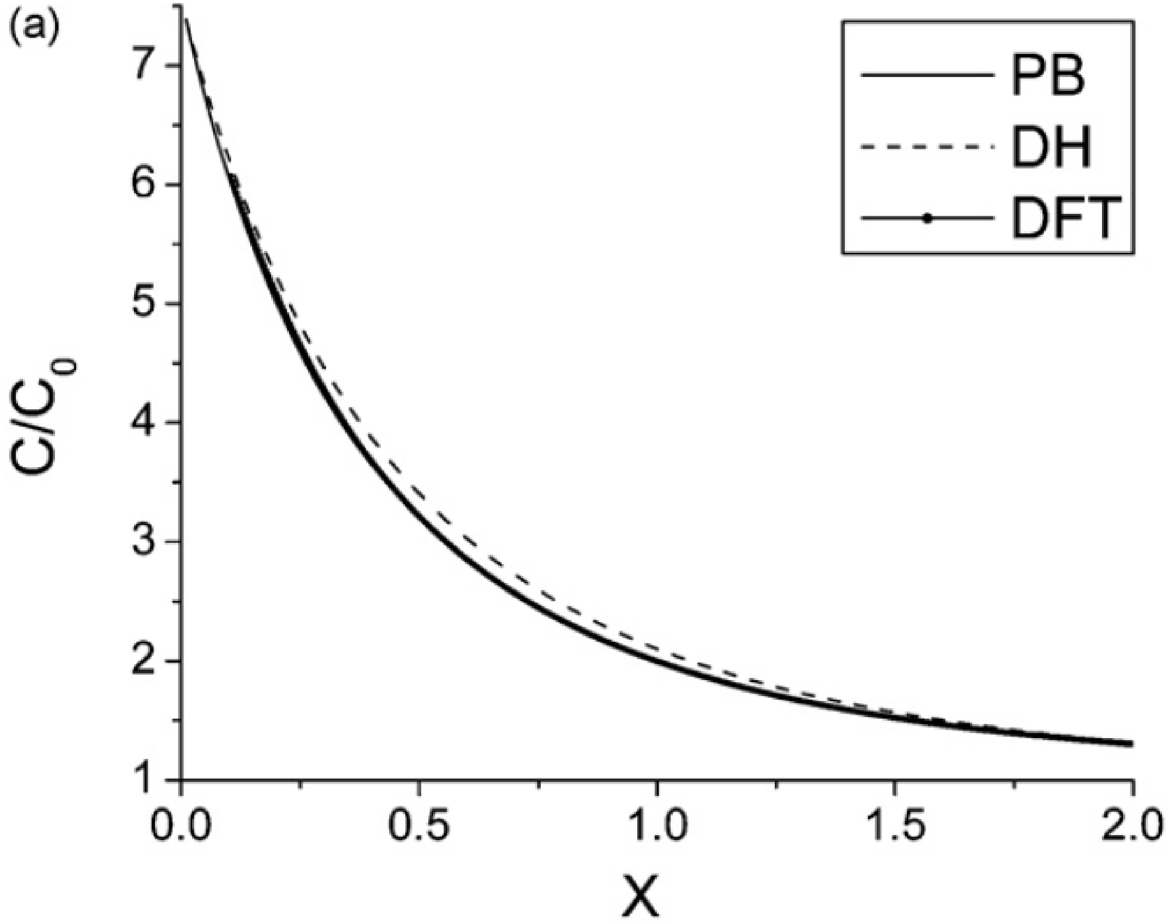
- Conventional method to converge to the equilibrium density profiles → Picard method.

$$\rho_{i,in}{}^{(k)}(\vec{r}) = \rho_{i,out}{}^{(k-1)}(\vec{r})f + \rho_i{}^{(k-1)}(\vec{r})(1-f)$$

- 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 ρ.

Some results applying the Classical Theories

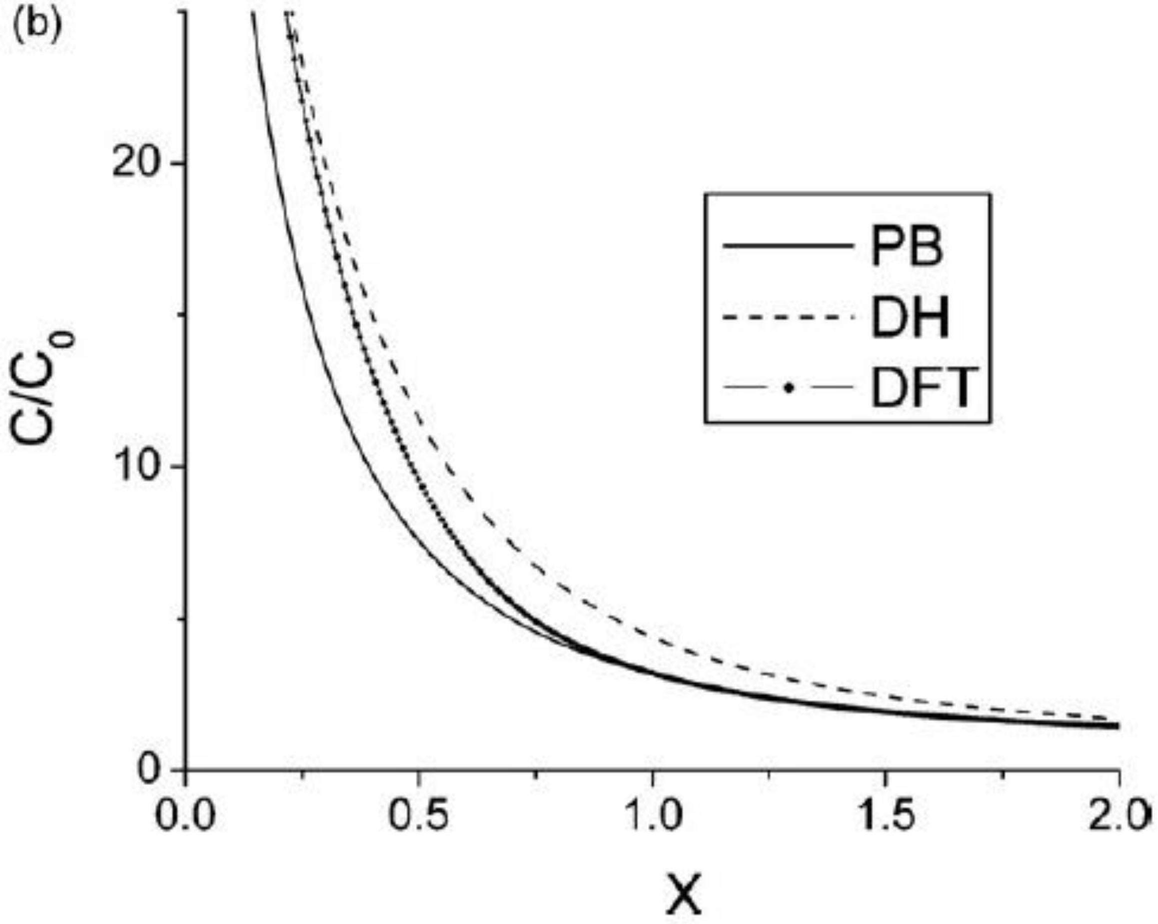
Counterion Concentration profile



1:1 salt; $\varphi_0 = 2$; $C_0 = 0.1$ mol/L; D = 2Å

Tavares, Boström, Lima, Biscaia. FPE (2010).

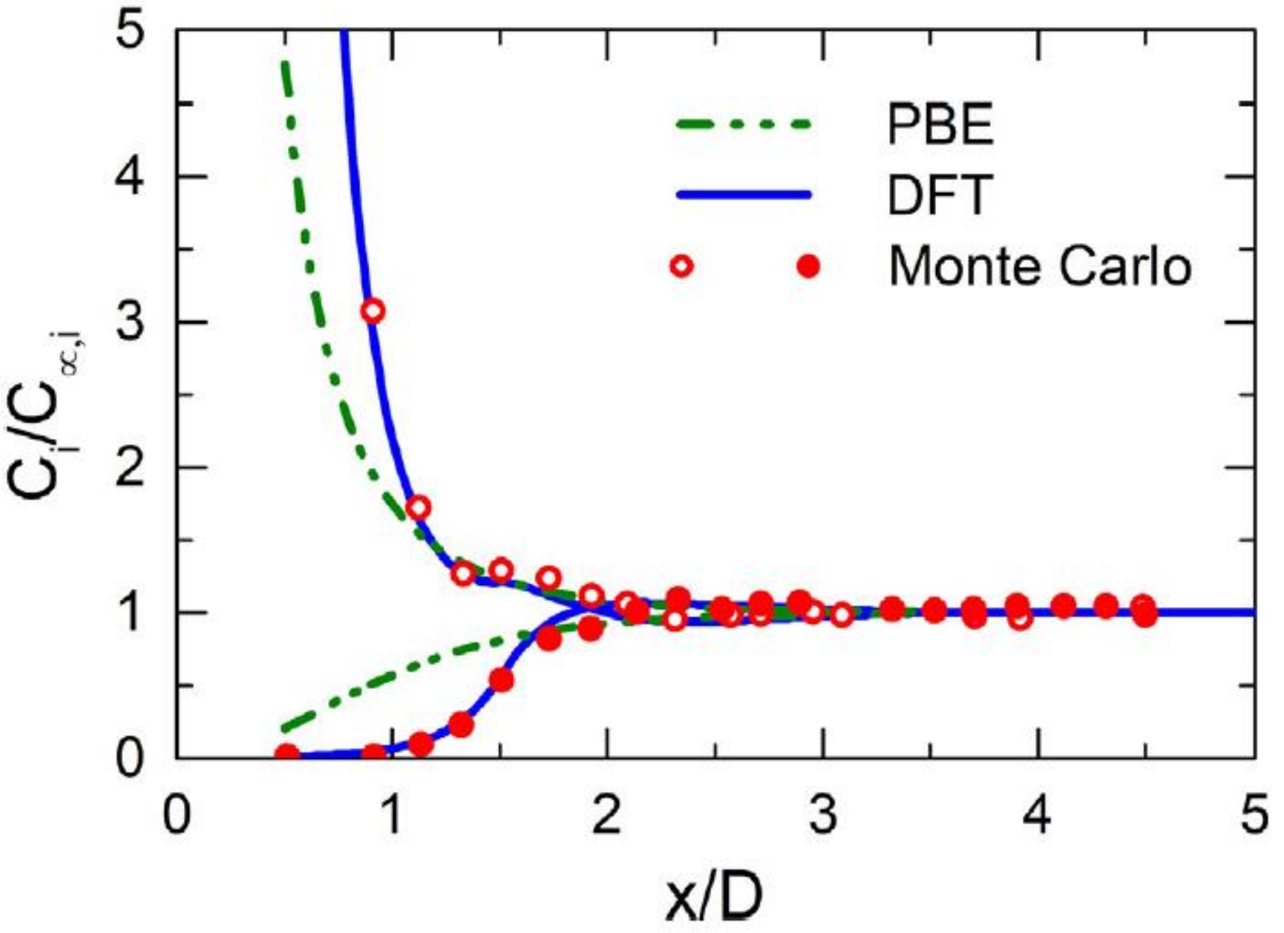
Counterion Concentration profile



2:2 salt; $\varphi_0 = 2$; $C_0 = 0.1$ mol/L; D = 2Å

Tavares, Broström, Lima, Biscaia. FPE (2010).

Ionic Concentration profiles



1:1 salt; Q = 0.35 C/m^2; C_∞ = 2mol/L.;T = 298.15 K.; D = 4.25 Å.

Barbosa, Lima, Tavares (2017). doi: 10.1016/B978-0-12-409547-2.13915-0.

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