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

Ion-specific Effects on Biocolloidal Systems

Prof. Eduardo Rocha de Almeida Lima
Chemical Engineering Graduate Program – PPG-EQ
Rio de Janeiro State University – UERJ – Brazil
lima.eduardo@uerj.br
limaeduardo.wixsite.com/equerj/home

APS & ICTP-SAIFR Young Physicists Forum on Biological Physics: from Molecular to Macroscopic Scale (Bio2020)

Speaker

- Full Name: Eduardo Rocha de Almeida Lima
- Chemical Engineer – UEM (2005)
- D.Sc. In Chemical Engineering – UFRJ (2008)

  Thesis: “Calculation of Physicochemical Properties of Colloidal Systems via Poisson-Boltzmann Equation”
- Post-doc in Chemical Engineering at the University of California Riverside, working with classical DFT (2009).
- Professor at UERJ since 2010.

Location

- UERJ is located in Rio de Janeiro – RJ - Brazil

Research

- ✓ **LaFIT: Interfacial Phenomena and Thermodynamics Laboratory**

- ✓ 3 main lines of research:
  - ➢ **Colloids and interfacial phenomena**: interfacial tension, properties and stability emulsions, foams and sols. Applications to cosmetics, petroleum and food.
  - ➢ **Thermodynamics:** phase equilibria, asphaltene stability.
  - ➢ **Modeling and Simulation of Processes**: application to analysis and optimization of chemical engineering processes.

- ✓ E-mail: lafit.uerj@gmail.com

LaFIT

Location

- Right in front of Maracanã Stadium

- www.uerj.br
- www.visitriodejaneiro.city

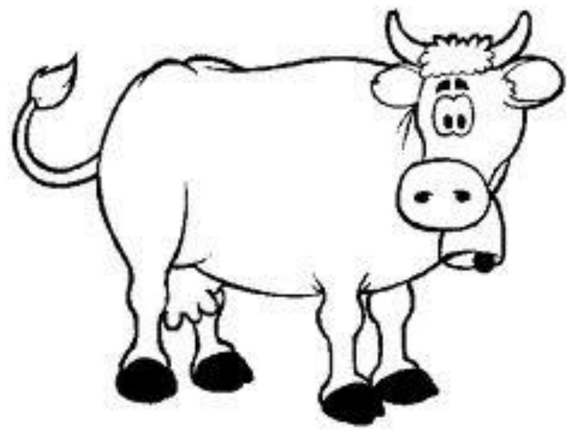
Outline (Lecture 1)

- Classical Poisson-Boltzmann equation and DLVO Theory;
- Hofmeister effects;
- Thermodynamics properties related to ion specificity.

Test: How would you estimate the volume of a cow?

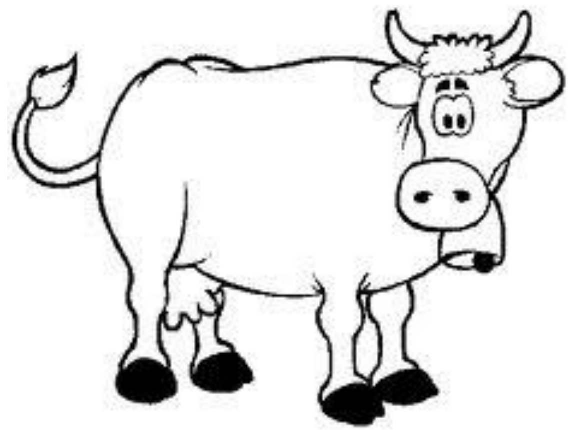
Test: How would you estimate the volume of a cow?

Mathematicians:

$\int$  dV

Test: How would you estimate the volume of a cow?

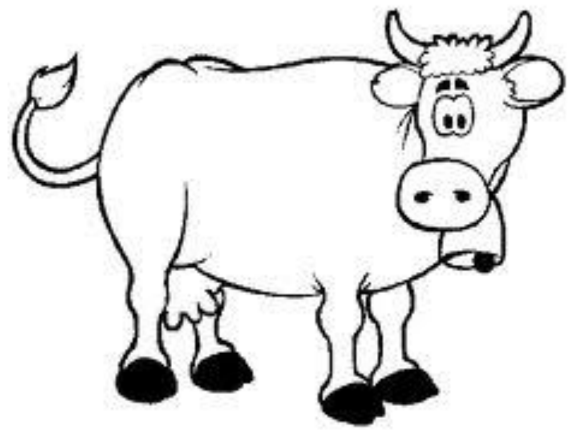
Mathematicians:

$\int$  dV

Experimental Physicists:

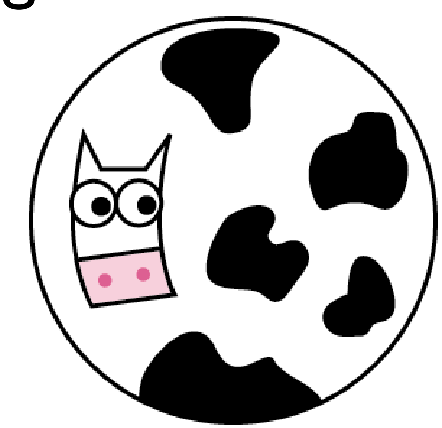
Test: How would you estimate the volume of a cow?

Mathematicians:

$\int$  dV

Experimental Physicists:

Engineers:



Colloid Science: Introduction

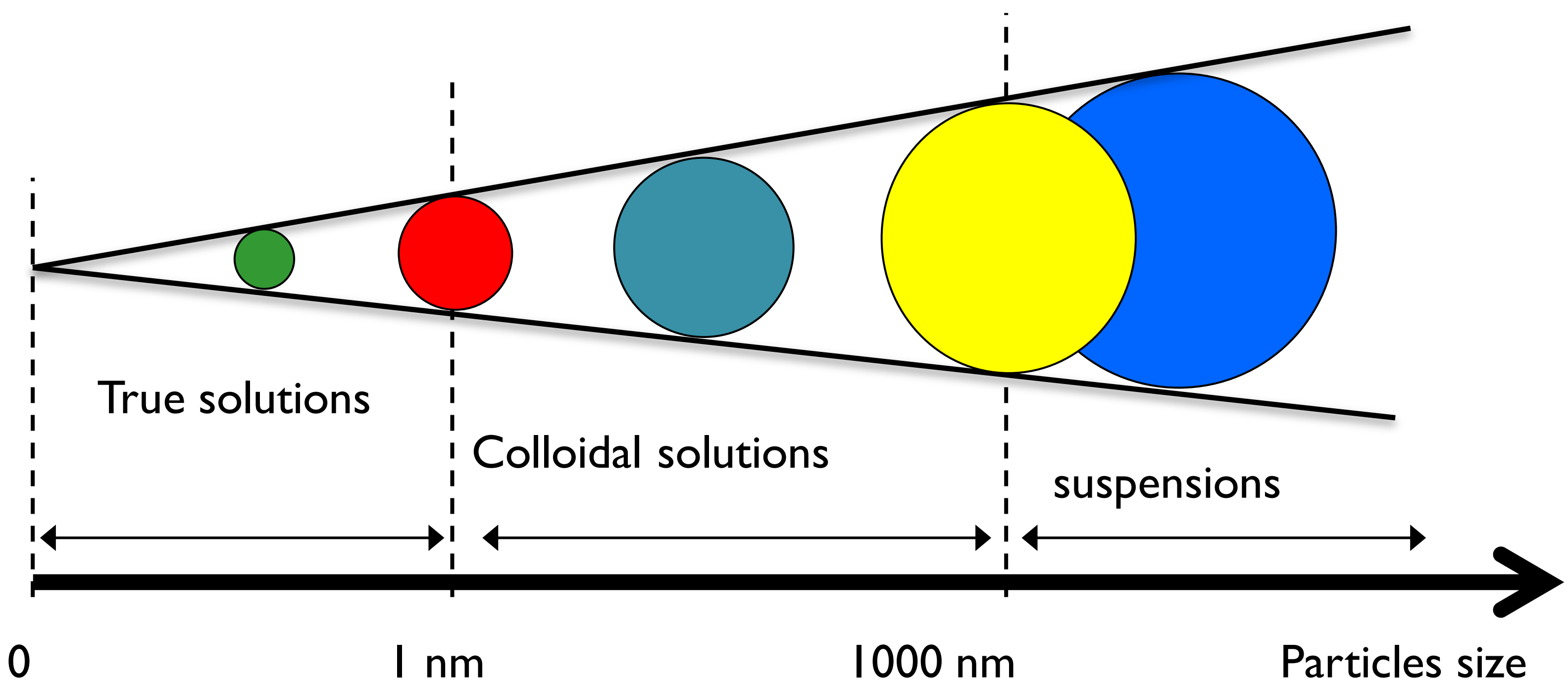
Colloids: definition

✓ **Colloids** are heterogeneous mixtures composed of at least two different phases: a **continuous phase** and a **dispersed phase**.

✓ At least one of these phases presents a dimension between 1 and 1000 nm.

✓ Despite being homogeneous systems, **macromolecules solutions** are considered colloids due to their dimensions and properties.

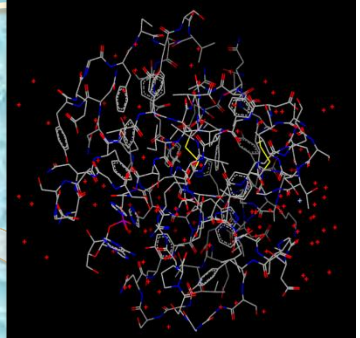
Size Scale



True solutions
Colloidal solutions
suspensions
0
1 nm
1000 nm
Particles size

Colloids Application

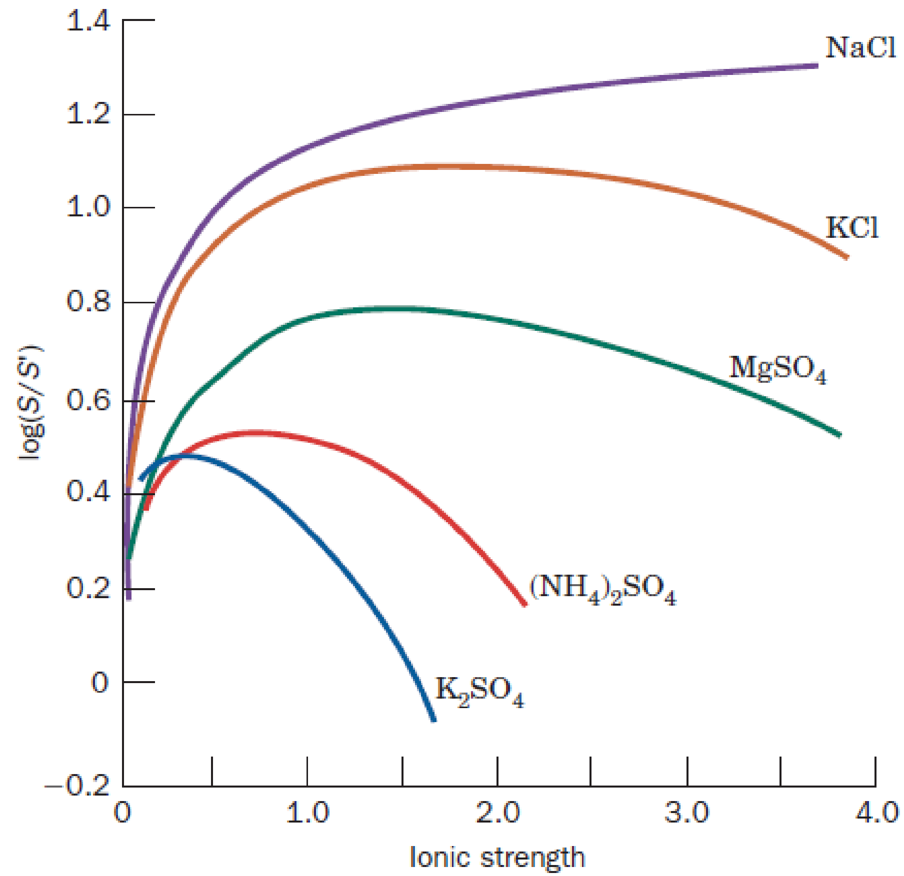
✓ Colloidal systems and phenomena are present in large quantity in nature, in our everyday life and in in industry.



Proteins Solubility

Effects related to protein solubility:

- ✓ ionic force
- ✓ salt type (Hofmeister effects)
- ✓ pH
- ✓ Temperature
- ✓ Organic solvents



Protein Solubility: carboxi-hemoglobin
Source: Voet & Voet, 1995

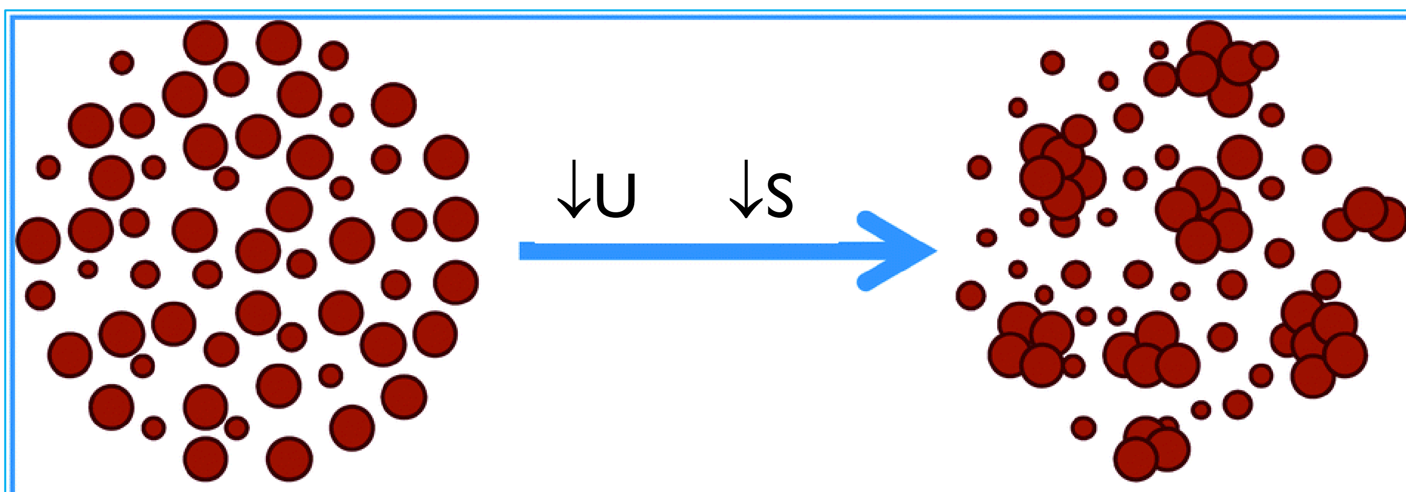
Properties of Colloidal Systems

- Most colloids are thermodynamically **metastable or unstable**.

- Some authors say that colloids are always thermodynamically unstable, but they forget the **entropic contribution**.

- Overall the stability of colloidal systems is delicate.

$$F = U - TS$$



Properties of Colloidal Systems

The properties of colloidal systems depend on:

- ✓ Interaction between phases = solvation
- ✓ Interaction between particles:
  - ➢ electrostatic (Coulomb, Poisson)
  - ➢ non-eletrostatic: van der Waals (London), solvation, steric repulsion.

Stability: DLVO Theory

DLVO Theory (Derjaguin-Landau-Verwey-Overbeek)

Two contributions:

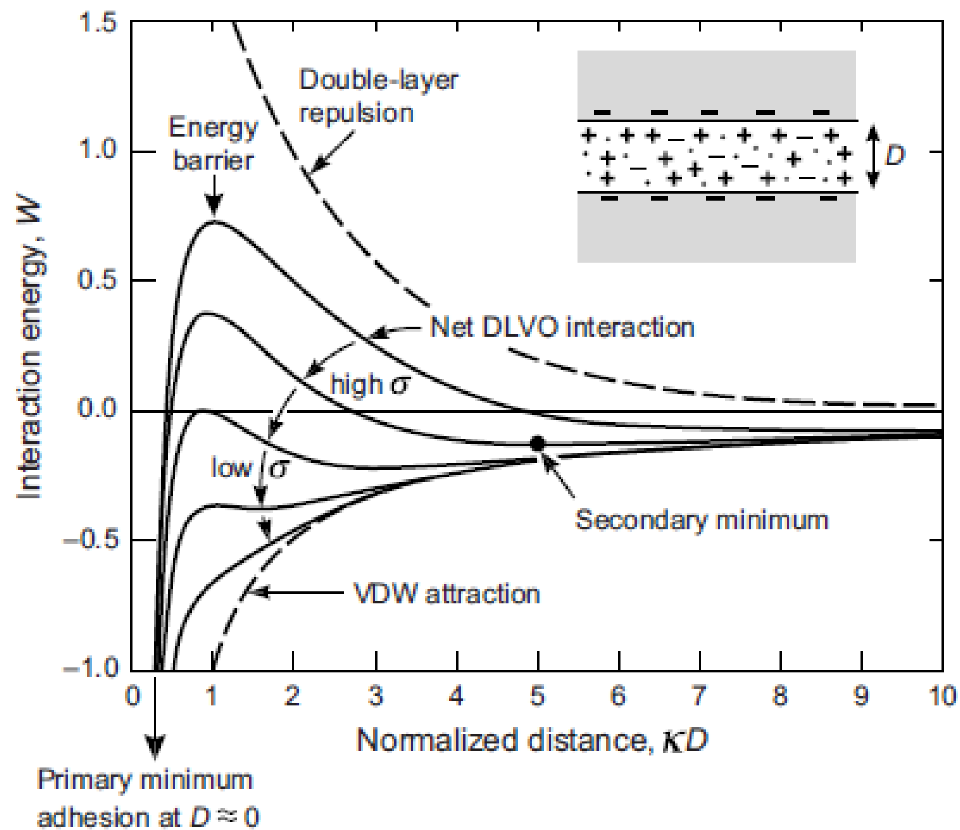
- ✓van der Waals interactions (Hamaker)
- ✓Electrostatic interactions

$$\boxed{W = W^{el} + W^{Ham} + W^{hs}}$$

The 3rd contribution refers to hard spheres:

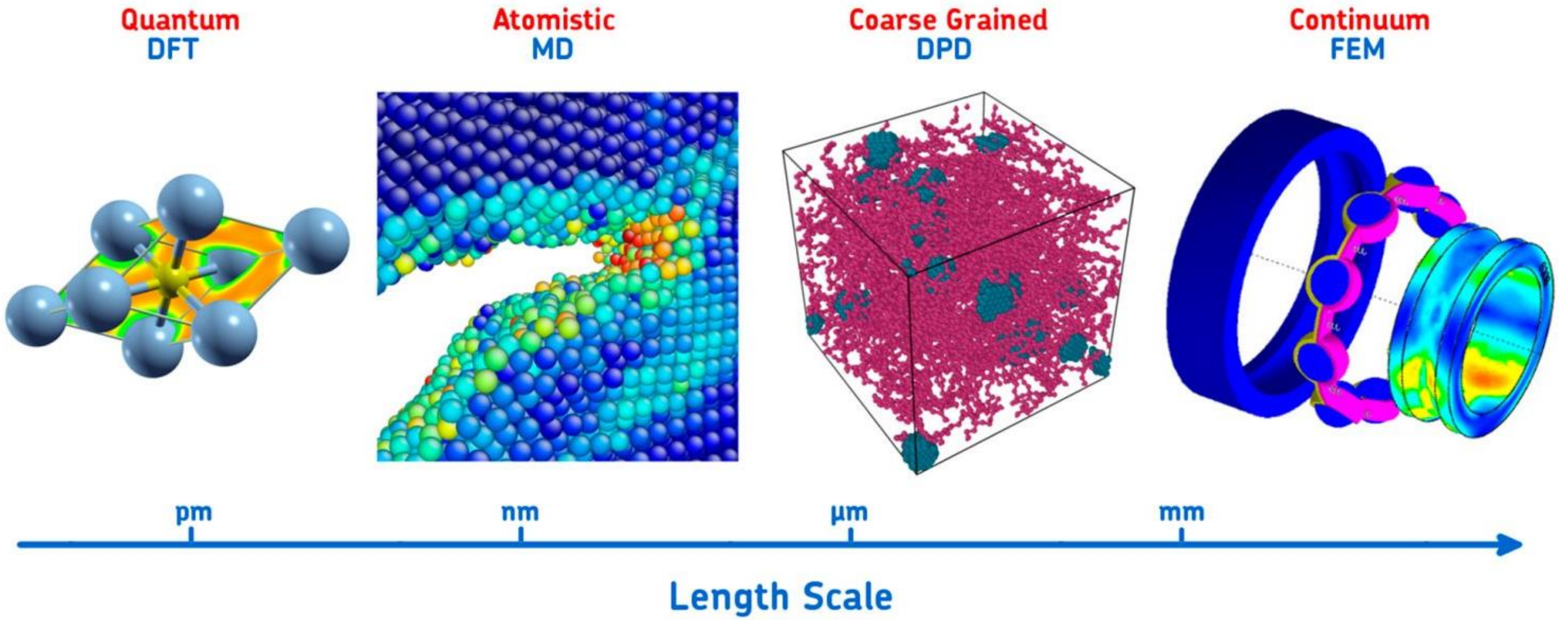
$$W^{hs} = \begin{cases} \infty, \ para \quad r < r_i + r_j \\ 0, \ para \quad r \geq r_i + r_j \end{cases}$$

Stability: DLVO Theory



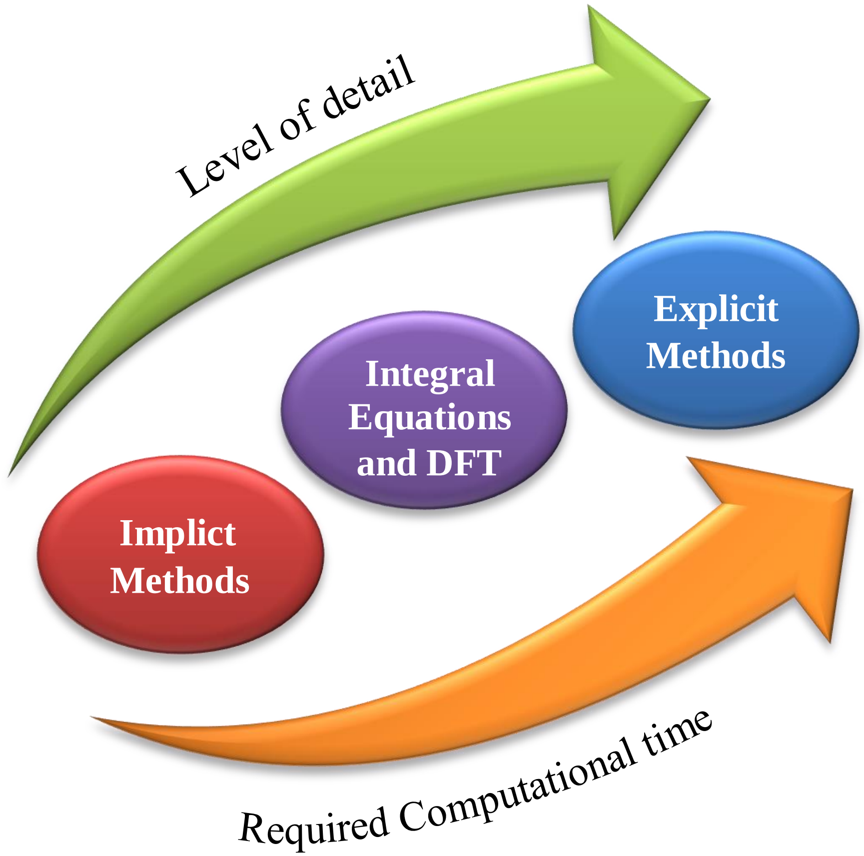
Source: Israelachvili (2011)

Different Scales



Source: http://evolution.skf.com/us/bearing-research-going-to-the-atomic-scale/

Different Scales



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

Hamaker interactions

✓ van der Waals forces play a central role in colloid science;

✓ van der Waals interaction between two particles: Hamaker

✓ Interatomic van der Waals pair potential: $w(r) = -C/r^6$

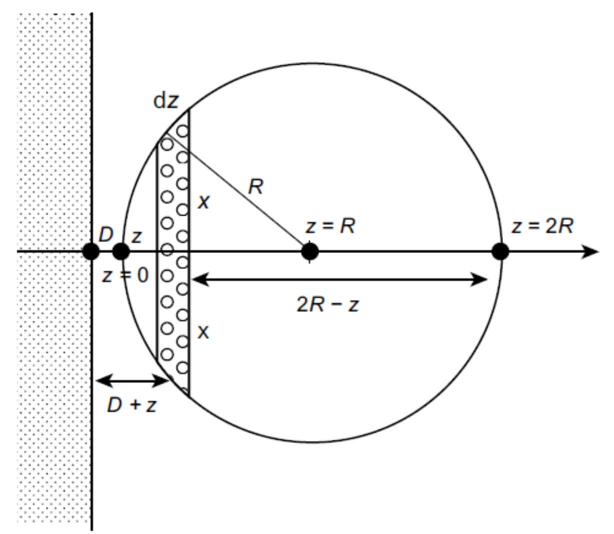
✓ Summing (integrating) the energies of all the atoms in one body with all the atoms in the other body, we have, e.g.:

- For a molecule near a flat surface:

$$w(D) = -\pi C\rho/6D^3$$

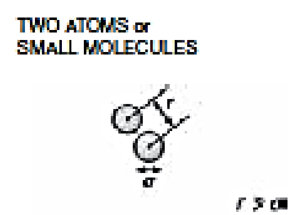
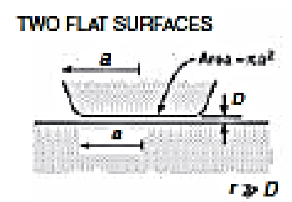
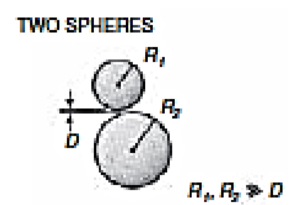
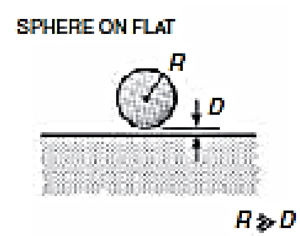
- For a sphere near a flat surface:

$$w(D) = -\underbrace{\pi^2 C\rho^2}_{\substack{A \\ \text{(Hamaker Constant)}}} R/6D$$



Source: Israelachvili (2011)

Hamaker Interactions

Geometry of bodies with surfaces D apart ($D \ll R$)		Van der Waals Interaction*	
		Energy, W	Force, $F = -dW/dD$
Two atoms or small molecules		$-C/r^6$	$-6C/r^7$
Two flat surfaces (per unit area)		$W_{\text{flat}} = -A/12\pi D^2$	$-A/6\pi D^3$
Two spheres or macromolecules of radii R_1 and R_2		$\frac{-A}{6D}\left(\frac{R_1R_2}{R_1+R_2}\right)$	$\frac{-A}{6D^2}\left(\frac{R_1R_2}{R_1+R_2}\right)$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{\text{flat}}$
Sphere or macro-molecule of radius R near a flat surface		$-AR/6D$	$-AR/6D^2$ Also $F = 2\pi RW_{\text{flat}}$

Source: Israelachvili (2011)

Electrostatic Contribution: Poisson-Boltzmann Theory

Particles charge

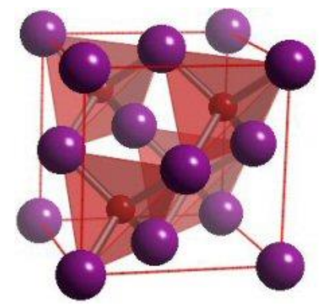
- ✓ Colloidal particles in water usually present charge.
- ✓ Where does this charge come from?
- ✓ For particles in water, is it mostly positive or negative?

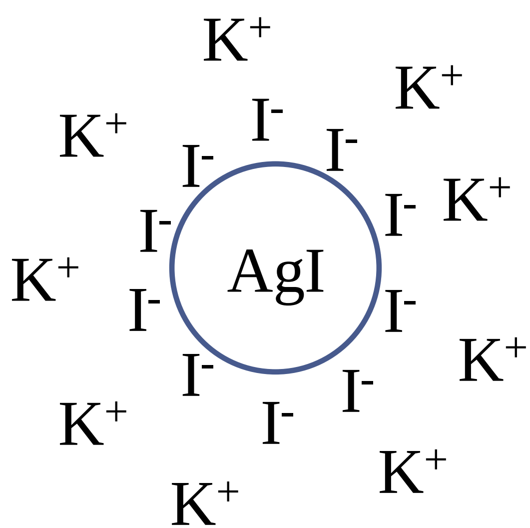
Particles charge

- ✓ Where does this charge come from?

1. Selective ions adsorption.

e.g.: AgI (s) in KI (aq)



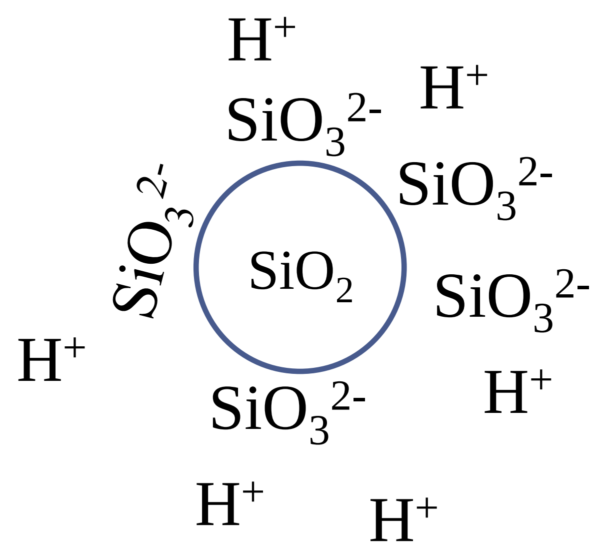


Particles charge

- ✓ Where does this charge come from?

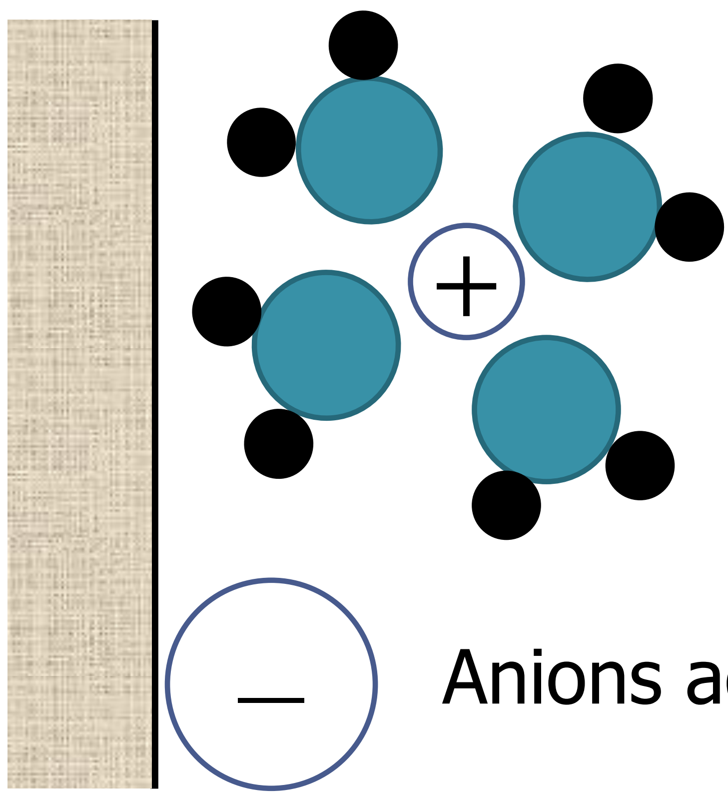
2. Ionization. E.g.: silica in water

$$SiO_2 + H_2O \rightarrow H_2SiO_3 \leftrightarrow SiO_3^{2-}{}_{(s)} + 2H^+{}_{(aq.)}$$



Particles charge

✓ For particles in water, is it mostly positive or negative?

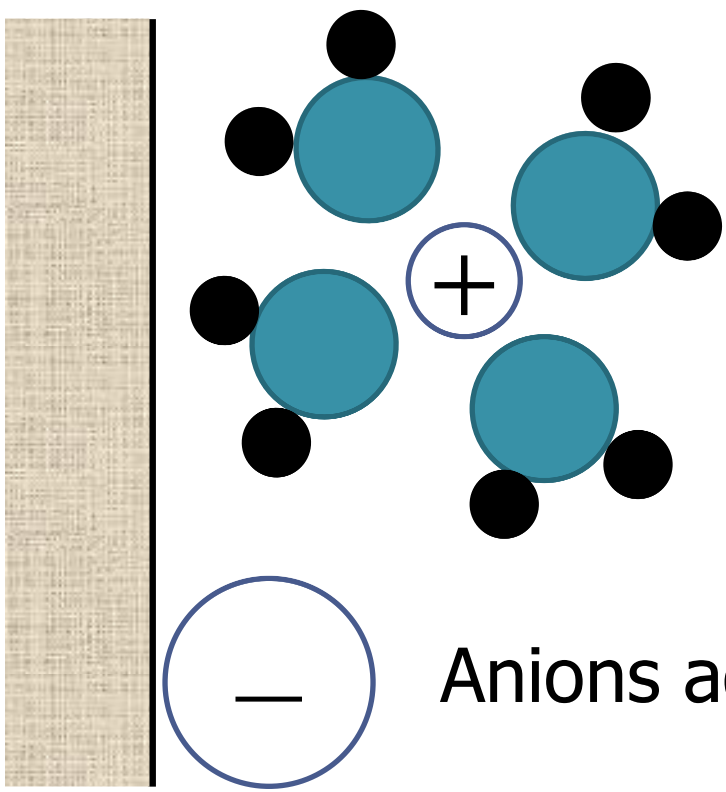


1. Polarizability
2. Hydration

Anions adsorb more than cations.

Particles charge

- ✓ For particles in water, is it mostly positive or negative?
- ✓ Answer: **negative**

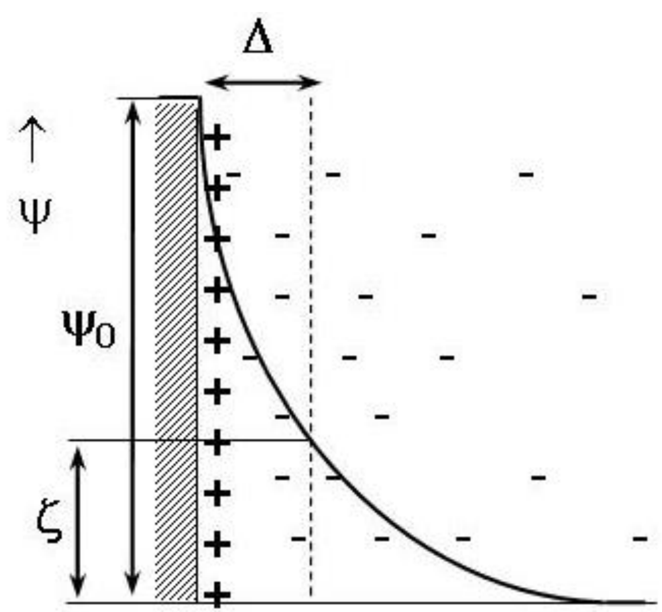


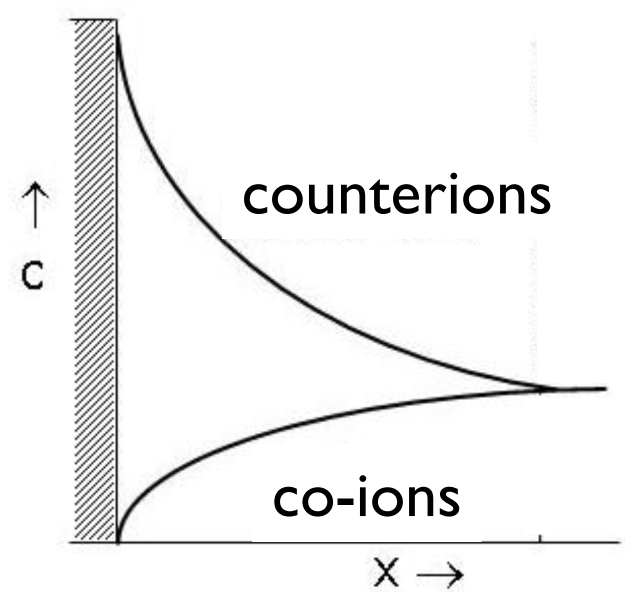
1. Polarizability
2. Hydration

Anions adsorb more than cations.

Electrical Double Layer: Gouy-Chapman Theory

- ✓ Electric field attracts counterions and repels co-ions.
- ✓ Thermal energy randomly disperses the ions.
- ✓ Combined effect = nonlinear distribution





Boltzmann Distribution

Electrochemical potential near a charged surface (Mcmillan-Mayer reference):

$$\mu_i = \mu_i^0 + k_B T \ln c_i + e z_i \psi$$

Chemical potential at bulk:

$$\mu_{\infty,i} = \mu_i^0 + k_B T \ln c_{\infty,\mathrm{i}}$$

Equilibrium: $\mu_i = \mu_{\infty,i}$

Hence: $c_i = c_{\infty,\mathrm{i}}\, exp\left(-\frac{z_i e \psi}{k_B T}\right)$

Poisson-Boltzmann Equation

Siméon Denis **Poisson**
(1781-1840)

- ✓ Boltzmann distribution:

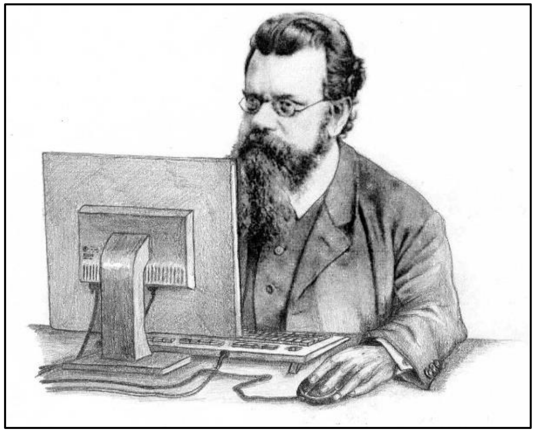
$$c_i = c_{\infty,\mathrm{i}}\, exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

- ✓ Poisson Equation:

$$\varepsilon_0 \nabla \cdot \left(\varepsilon \nabla \psi\right) = -\rho$$, where $$\rho = e \sum_i z_i c_i$$

Poisson-Boltzmann Equation:

$$\varepsilon_0 \nabla \cdot (\varepsilon \nabla \psi) = -e \sum_i z_i c_{\infty,\mathrm{i}}\, exp\left(-\frac{z_i e\psi}{k_B T}\right)$$



Ludwig **Boltzmann**
(1844-1906)

Boundary Conditions

a) Specified surface electrostatic potential (Dirichlet):

$$\psi|_{surface} = \psi_0 \qquad \psi|_{\infty} = 0$$

b) Specified surface charge density (Neumann):

$$(\varepsilon \nabla \psi)|_{surface} = -\frac{\sigma}{\varepsilon_0} \qquad \nabla \psi|_{\infty} = 0$$

Adimensionalizing PBE

For planar geometry, uniform dielectric constant and symmetric electrolyte (z:z)

$$\frac{\mathrm{d}^2\psi}{dx^2} = -\frac{ezc_\infty}{\varepsilon_0\varepsilon}\left[exp\left(-\frac{ze\psi}{k_BT}\right) - exp\left(\frac{ze\psi}{k_BT}\right)\right]$$

or

$$\frac{\mathrm{d}^2\psi}{dx^2} = \frac{2ezc_\infty}{\varepsilon_0\varepsilon} sinh\left(\frac{ze\psi}{k_BT}\right)$$

Defining $\kappa^2 = \frac{e^2\sum c_{\infty,\mathrm{i}} z_i^2}{\varepsilon_0\varepsilon k_BT}$; $X = \kappa x$; $\varphi = \frac{z_i e\psi}{k_BT}$

Results in $\frac{\mathrm{d}^2\varphi}{dX^2} = sinh(\varphi)$

Poisson-Boltzmann X Debye-Hückel

Analytical solution of PBE:

$$\psi(x) = \frac{2k_B T}{ez} \ln\left[\frac{1+\gamma \exp(-\kappa.x)}{1-\gamma \exp(-\kappa.x)}\right]$$

$$\gamma = tgh\left(\frac{ez\psi_0}{4k_B T}\right) = \frac{\exp\left(\frac{ez\psi_0}{2k_B T}\right)-1}{\exp\left(\frac{ez\psi_0}{2k_B T}\right)+1}$$

Debye-Hückel equation = linearization of PBE :

$$\frac{d^2\varphi}{dX^2} = \varphi$$

whose solution is $\psi = \psi_o \exp(-\kappa x)$

Force Between two Particles

From the solution of PBE (ψ) we calculate ionic concentration profiles:

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

and the free Energy of the System:

$$A - A^o = \frac{e}{2}\int \psi \sum_i c_\mathrm{i} z_i \, dV + \int \sum_i c_\mathrm{i} U_i \, dV + k_B T \int \sum_i \left[c_i ln\left(\frac{c_i}{c_{\infty,\mathrm{i}}}\right) - (c_\mathrm{i} - c_{\infty,\mathrm{i}})\right] dV$$

Mean Force between the particles: $F = -\frac{\partial A}{\partial L} = -\frac{\partial (A - A^o)}{\partial L}$

Numerical Methods for solving PBE

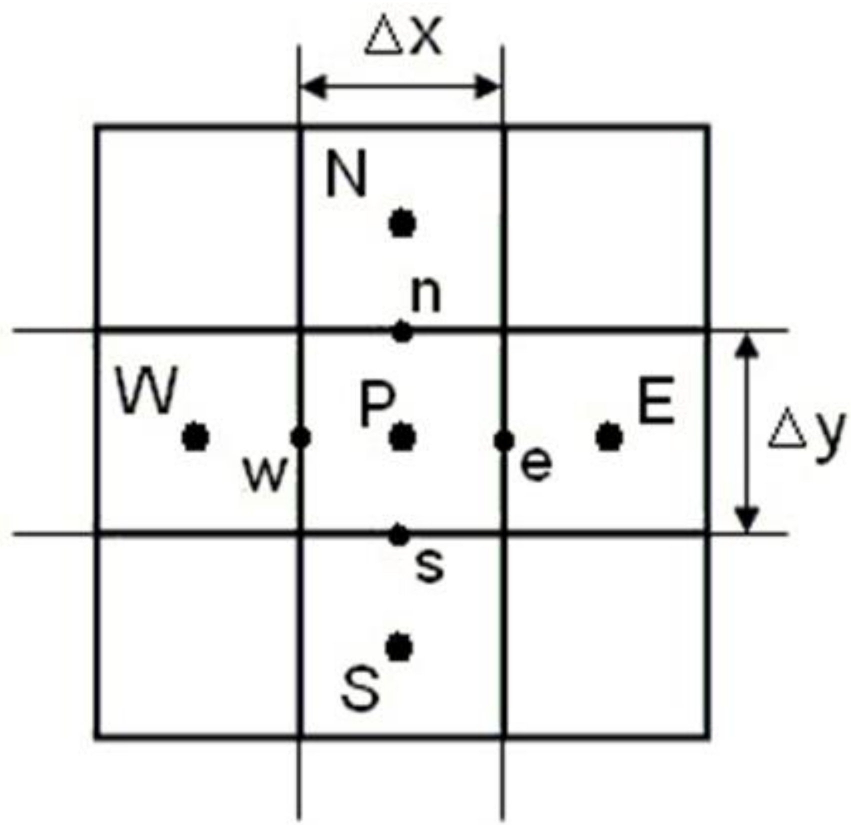
✓ Poisson-Boltzmann Equation:

- elliptic second order partial differential equation;
- can be solved by discretization methods.

✓ Most used methods:

- Finite difference method
- Finite Volume method
- Finite Element Method

Finite Volume Method



Bi-dimensional finite volume P and its neighbours

Lima et al. (2007), PCCP, 9, 3174

Finite Volume Method

$$\frac{\partial}{\partial x}\left(\Gamma_1 \frac{\partial \psi}{\partial x}\right) + \frac{\partial}{\partial y}\left(\Gamma_2 \frac{\partial \psi}{\partial y}\right) + S = 0$$

$$\int_s^n \left(\Gamma \frac{\partial \psi}{\partial x}\right)_w^e dy + \int_w^e \left(\Gamma \frac{\partial \psi}{\partial y}\right)_s^n dx + \int_s^n \int_w^e S\, dx dy = 0$$

$$S = S_P \psi_p + S_c$$

$$\left(\Gamma \frac{\partial \psi}{\partial x}\right)_w^e \Delta y + \left(\Gamma \frac{\partial \psi}{\partial y}\right)_s^n \Delta x + (S_P \phi_p + S_c)\Delta x \Delta y = 0$$

Lima et al. (2007), PCCP, 9, 3174

Hofmeister Effects

✓ Ion-specific effects:

biology, biochemistry, chemistry, chemical engineering …

✓ Hofmeister *et al.* (1880-1890):

Interactions between proteins are more affected by some salts than from others ⇒ lyotropic series or Hofmeister series.

Franz Hofmeister (1850-1922)

monovalent cations	$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$
Divalent cations	$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$
Monovalent anions	$Cl^- < Br^- < NO_3^- < I^- < SCN^-$

Hofmeister Effects

✓ Boström et al. (2002, 2003, 2004, 2005):

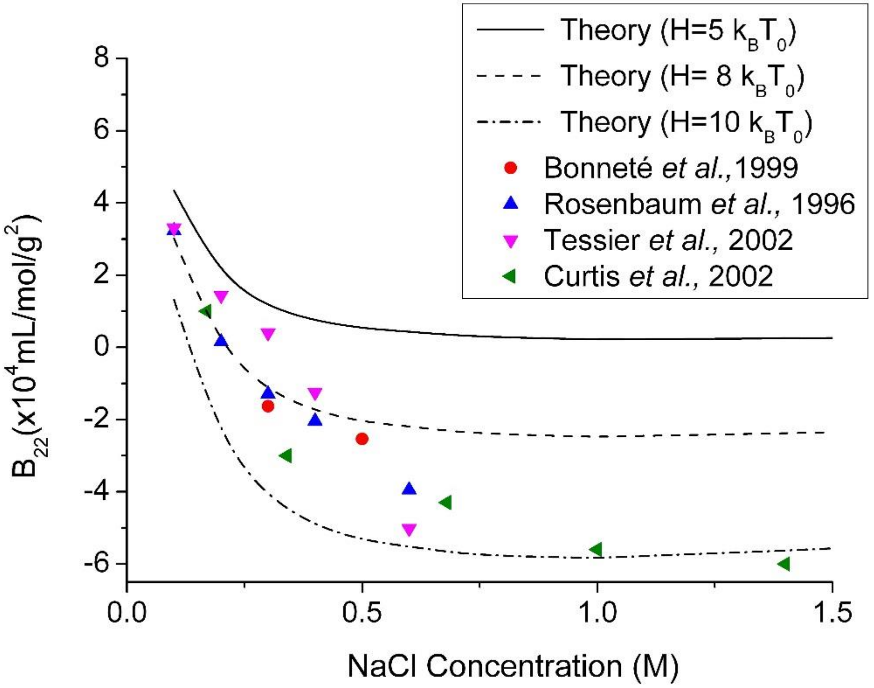
- When van der Waals interactions between ions and surface are treated at the same nonlinear level as the double layer interactions, being included at the Poisson-Boltzmann equation, the origin of ion-specific effects finally comes into sight.

Ion-Specific Effects

- ✓ Ion specificity in classical theories:
  - ➢PBE: ion valence
  - ➢DFT: ion valence and ion size.
- ✓ Addressing **Hofmeister effects** requires other ion-surface interactions as it will be discussed in the next lecture.

Thermodynamic properties related to ion specificity

- ✓ Stability: micellization, coagulation, coalescence.
- ✓ Properties: free energy, osmotic pressure, osmotic second virial coefficient.



$$\frac{W^{PB}}{k_B T} = \frac{\varepsilon\varepsilon_0 k_B T \sigma}{e^2} \int_{\infty}^{r/\sigma} f \cdot d\left(\frac{r}{\sigma}\right)$$

$$W = W^{PB} + W^{Ham} + W^{hs}$$

$$B_{22} = \frac{N_A}{2M^2} \int_0^{\infty} \left(1 - e^{-W(r)/k_B T}\right) 4\pi r^2 dr$$