École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Charged Solid-Liquid Interfaces
Lesson 6

MSE 304

Francesco Stellacci

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Key Topics in the Previous Class

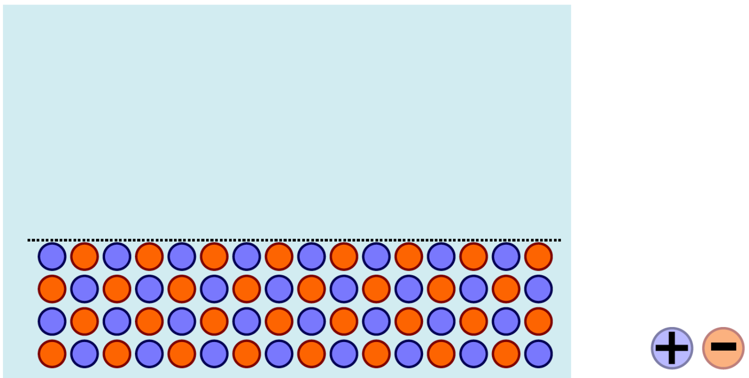
The Chemical Potential of a Real Material

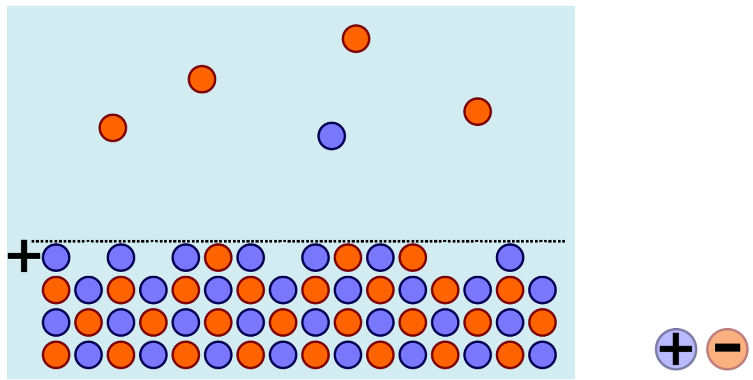
Equilibrium for Materials with Charged Interfaces

The Point of Zero Charge

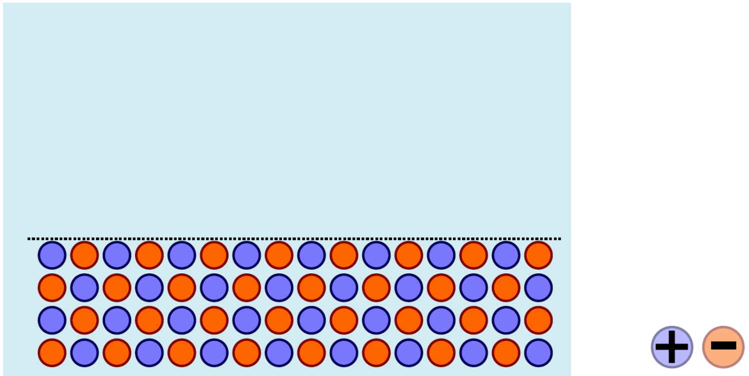
Surface Charge at an Interface

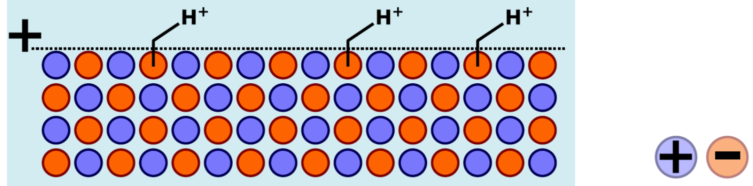
Atomistic Origin of the Surface Potential





Atomistic Origin of the Surface Potential





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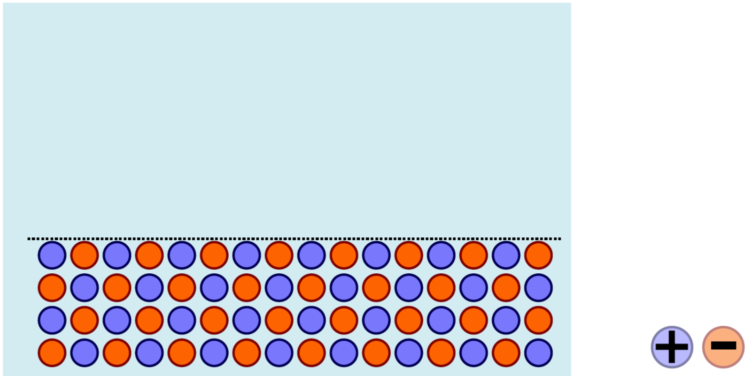
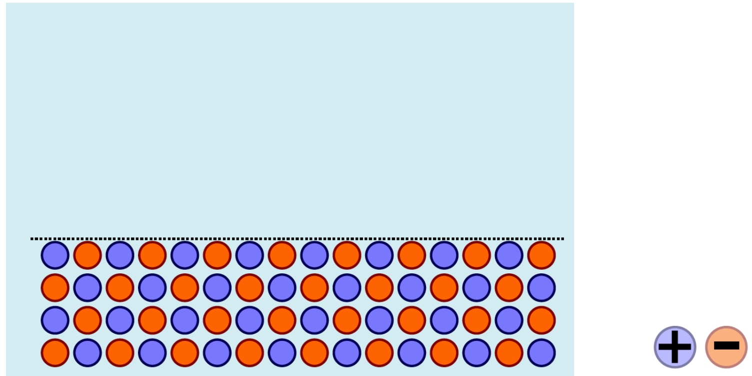
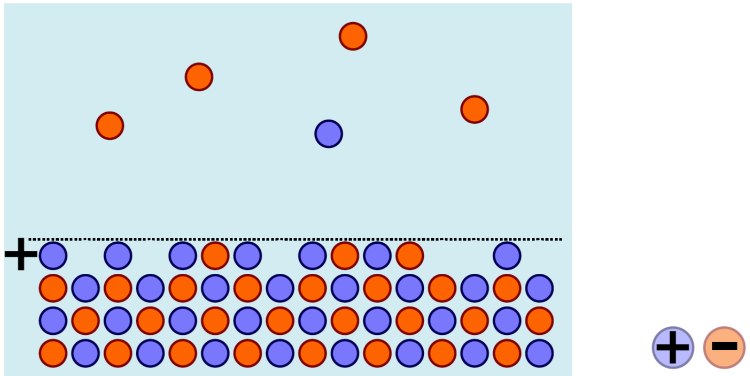
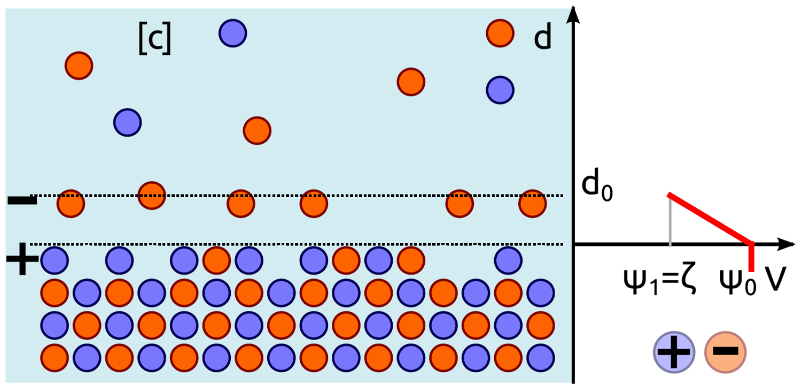
Atomistic Origin of the Surface Potential





The Helmholtz Plane





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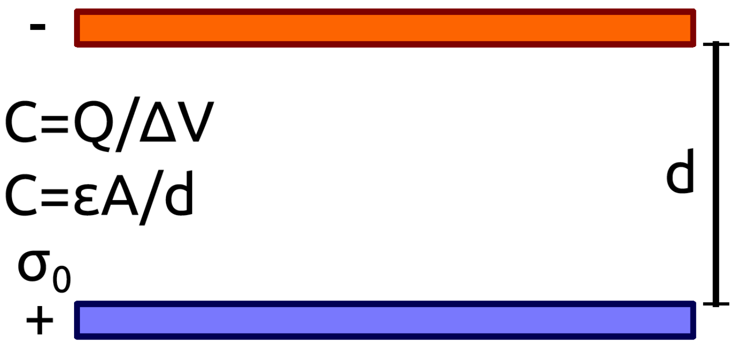
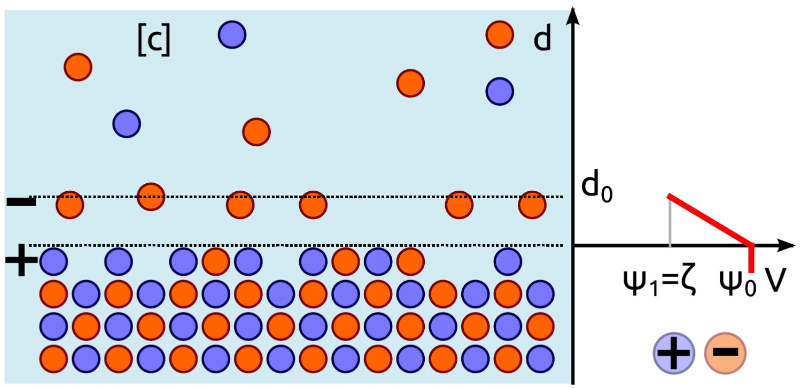
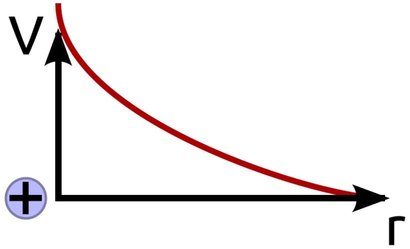


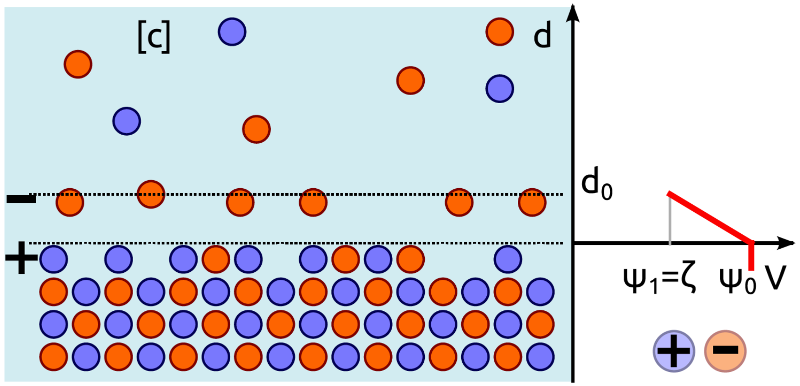


The Helmholtz Plane

$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$

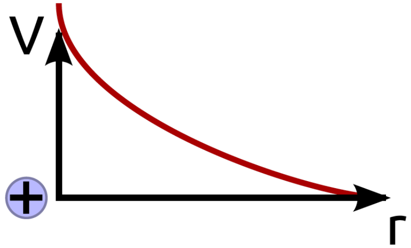


- Electric potential induced by an ion in a dielectric medium



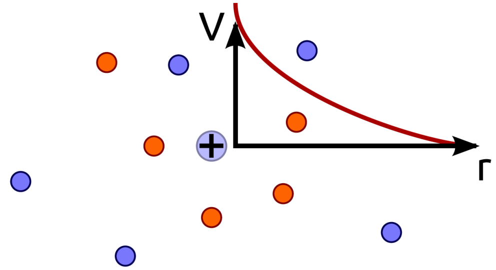
Debye-Hückel Theory

$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$



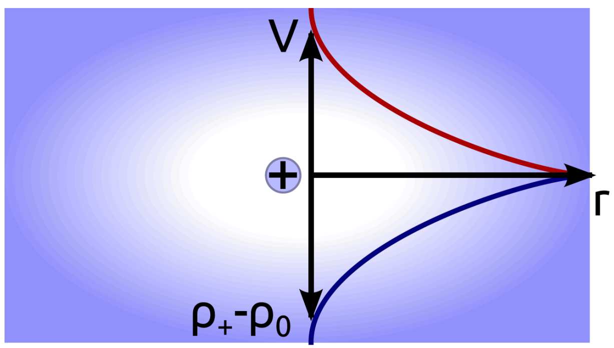
- Electric potential induced by an ion in a dielectric medium

$$U^0_{\pm}(r) = ez_{\pm}\psi_0(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\frac{z_{\pm}z_+}{r}$$

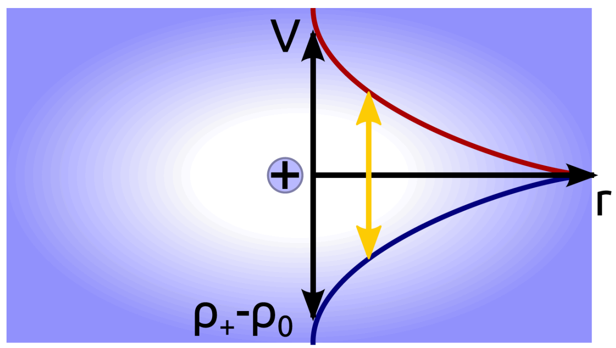


- Other ions interact with this potential

$$\rho_{\pm}(r) = \exp -\frac{ez_{\pm}}{k_B T}\psi(r)$$



$$\nabla^2\psi = -\frac{\rho}{\epsilon_0\epsilon_r} = -\frac{e}{\epsilon_0\epsilon_r}\left[z_+\rho_+ + z_-\rho_-\right]$$

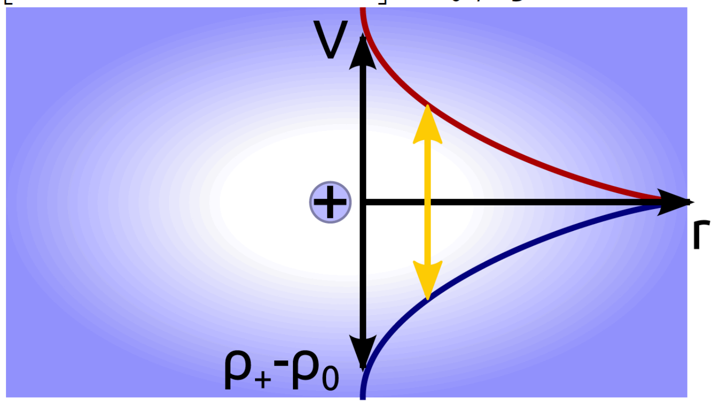


- Mean-field model: ion distribution represented by a Boltzmann density

Debye-Hückel Theory

$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

$$\nabla^2\psi = -\frac{eC}{\epsilon_0\epsilon_r}\left[z_+n_+e^{-\frac{ez_+}{k_BT}\psi} + z_-n_-e^{-\frac{ez_-}{k_BT}\psi}\right] \approx \frac{e}{\epsilon_0\epsilon_r}\frac{eC}{k_BT}\left[n_+z_+^2 + n_-z_-^2\right]\psi = \kappa^2\psi$$



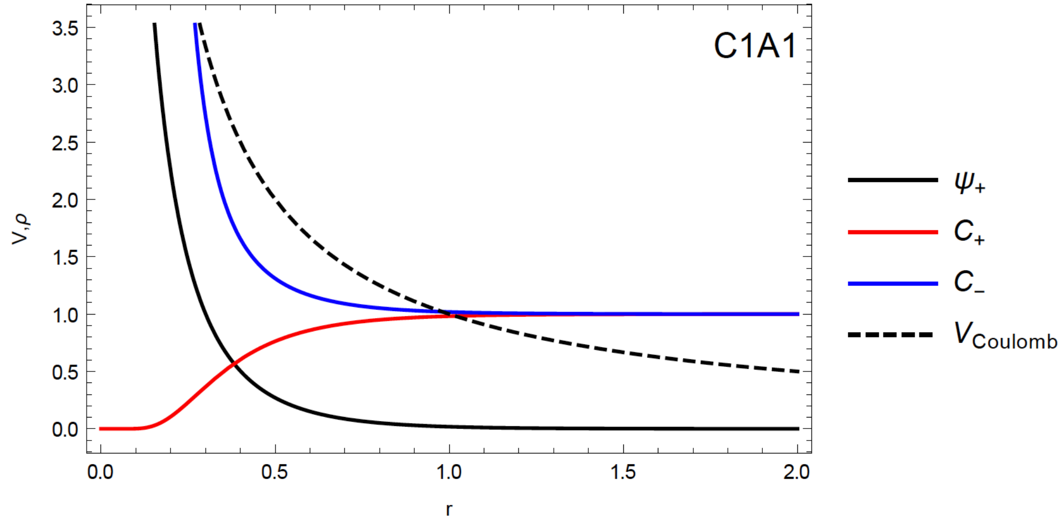
- Can be solved analytically if **linearized**

Debye Length

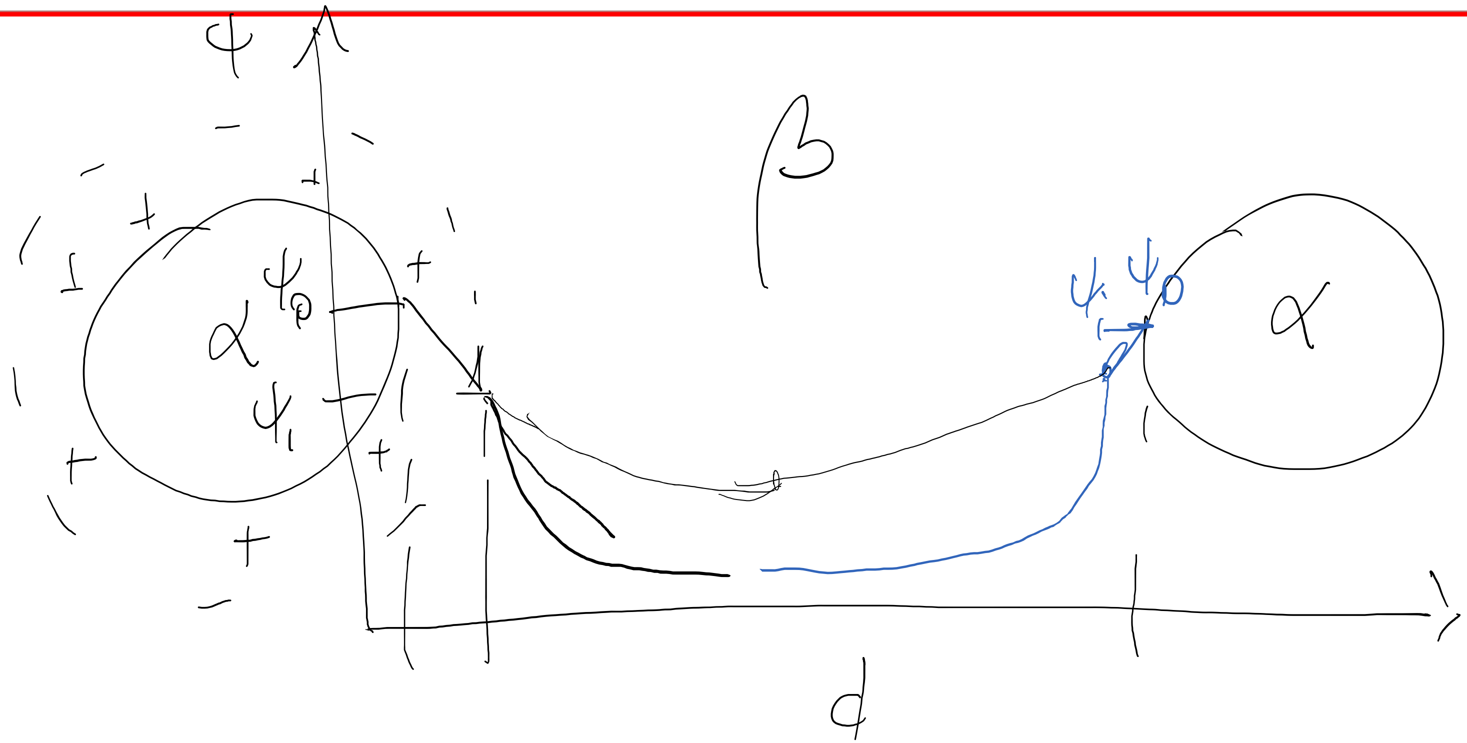
$$\nabla^2 \psi = 2 \frac{n^\infty z e}{\varepsilon_1 \varepsilon_0} \sinh\left(\frac{z e \psi}{kT}\right)$$

- Solving the Poisson-Boltzmann equation.

$$\psi(r) = \frac{e z_+}{4\pi\epsilon_0\epsilon_r} \frac{e^{-\kappa r}}{r}, \qquad \kappa^2 = \frac{e^2 C}{\epsilon_0 \epsilon_r} \frac{n_+ z_+^2 + n_- z_-^2}{k_B T}$$



Colloidal Particles



Colloidal Particles

$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

κa

TABLE 5.1 Solutions to the Poisson–Boltzmann equation for microparticles and nanoparticles

	Small κa	Large κa
Low potentials	$\psi(r) = \psi_0 \frac{a}{r}\exp[-\kappa(r-a)]$	$\psi(x) = \psi_0 \exp(-\kappa x)$
High potentials	$\nabla^2\psi = \frac{2zn^\infty e}{\varepsilon_r\varepsilon_0}\sinh\left(\frac{e\psi}{kT}\right)$	$\tanh\left(\frac{ze\psi(x)}{4kT}\right) = \tanh\left(\frac{ze\psi_0}{4kT}\right)\exp(-\kappa x)$
	where $\kappa^2 = \frac{2z^2e^2n^\infty}{\varepsilon_r\varepsilon_0 kT}$	

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Colloidal Particles

$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

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	where $\kappa^2 = \frac{2z^2e^2n^\infty}{\varepsilon_r\varepsilon_0 kT}$	

$$V_{rep} = 4\pi\varepsilon_1\varepsilon_0\zeta^2\frac{a^2}{r}\exp\left[-\kappa a\left(\frac{r}{a}-2\right)\right]$$

Unfortunately they attract by van der Waals forces:

$$V_{att} = -\frac{A}{6}\left[\frac{2a^2}{r^2-4a^2}+\frac{2a^2}{r^2}+\ln\left(1-\frac{2a^2}{r^2}\right)\right]$$

A is the Hamaker constant.

why is there an attraction potential

Colloidal Particles

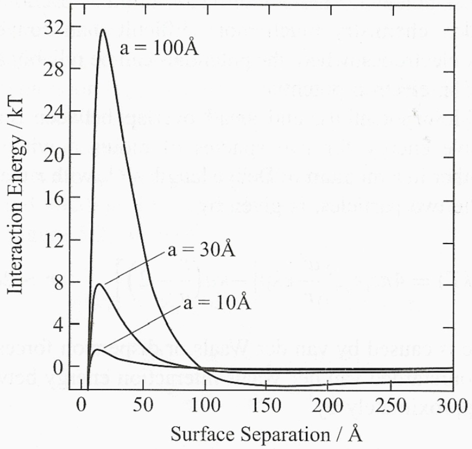

FIGURE 5.4 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation, for several particle radii. Hamaker constant $= 25 \times 10^{-20}$ J, $I = 1$ mM, $\psi_0 = 0.10$ V, $a = 1.0$ nm, 3.0 nm, and 10.0 nm, Debye length = 10 nm. Note that the secondary minimum is negligible for nanoparticles, but becomes important above 10 nm.

Conclusions