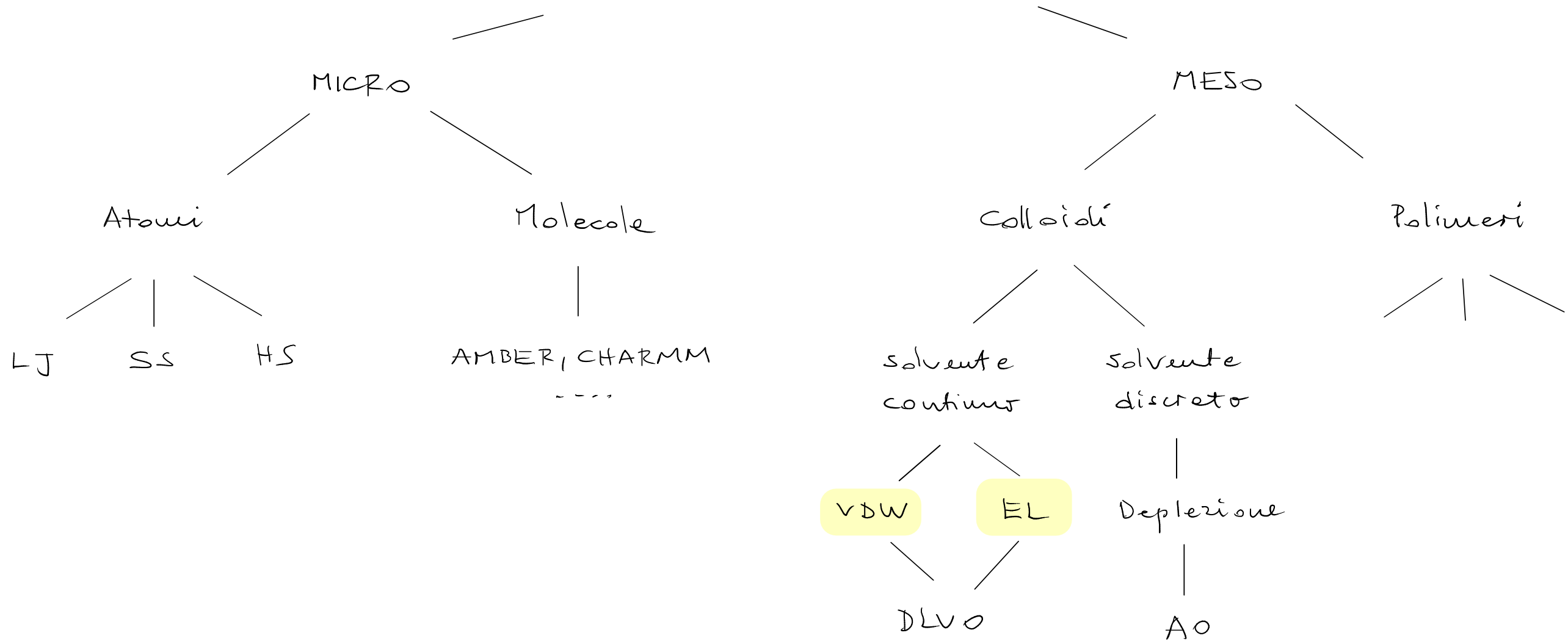
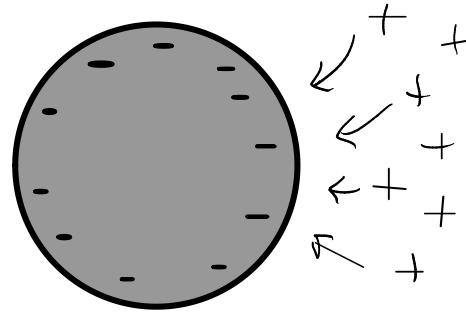


INTERAZIONI EFFETTIVE



Interazioni elettrostatiche

- Colloidi carichi Q
- Ioni in soluzione $\pm |q|$
- Soluzione $\rightarrow \epsilon$



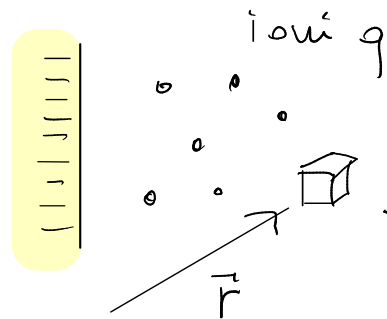
ioni \equiv gas ideale (non-interagenti) equilibrio a T

Goal: potenziale elettrostatico $\phi(\vec{r}) \rightarrow$ densità locale $\rho_e(\vec{r})$

1) Eq. Poisson

$$\nabla^2 \phi = - \frac{\rho_e(\vec{r})}{\epsilon}$$

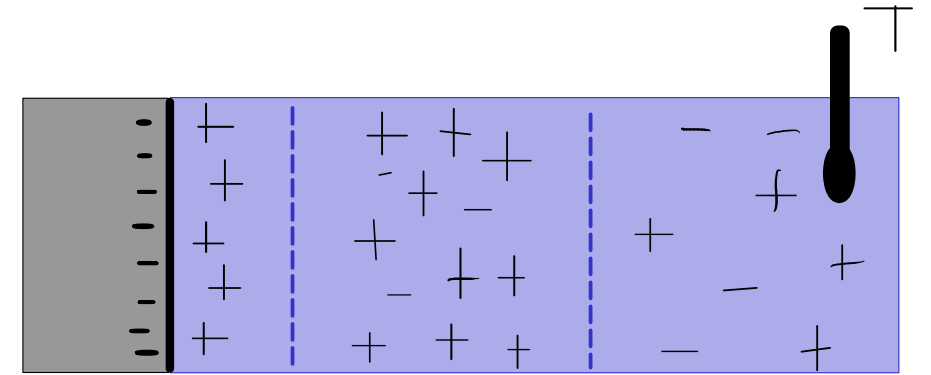
\uparrow
 $\epsilon_r \epsilon_0$



$$\rho_e(\vec{r}) = q \rho(\vec{r}) \quad \text{densità locale (di numero)}$$

2) Equilibrio: prob. trovare ione in \vec{r}

$$p(\vec{r}) \sim \exp\left(-\frac{q\phi(\vec{r})}{k_B T}\right) \Rightarrow \rho(\vec{r}) = \overset{\text{bulk}}{\rho_0} \exp\left(-\frac{q\phi(\vec{r})}{k_B T}\right)$$



① Stern rigido
② diffuso
③ bulk

$+e-$ $+e-$

electric double layer \Rightarrow Scherms

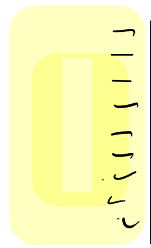
Eq. Poisson-Boltzmann

$$\nabla^2 \phi = - \frac{q \rho_0}{\epsilon} \exp\left(-\frac{q\phi}{k_B T}\right)$$

$$\rho_e(\bar{r}) = q \rho_+ (\bar{r}) - q \rho_- (\bar{r})$$

$q > 0$

$$\nabla^2 \phi = - \frac{q \rho_0}{\epsilon} \left[\exp\left(-\frac{q\phi}{k_B T}\right) - \exp\left(+\frac{q\phi}{k_B T}\right) \right] = \frac{2q \rho_0}{\epsilon} \sinh\left(\frac{q\phi}{k_B T}\right)$$



$$\phi = \phi(z) \Rightarrow \frac{d^2 \phi}{dz^2} = \frac{2q \rho_0}{\epsilon} \sinh\left(\frac{q\phi}{k_B T}\right) \rightarrow \text{BH}$$

$$\text{B.C.: } \phi(\infty) = 0 ; \phi(0) = \phi_0 < 0$$

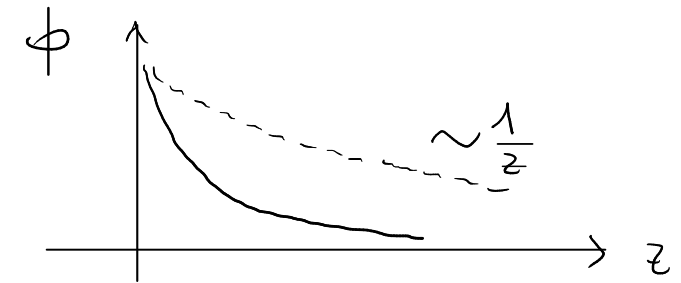
Approssimazione Debye-Hückel : $q\phi \ll k_B T$

$$\frac{d^2 \phi}{dz^2} \approx \frac{2q^2 \rho_0}{\epsilon k_B T} \phi \Rightarrow \phi(z) = \phi_0 \exp(-K_D z)$$

$$\underbrace{\quad}_{K_D^2}$$

costante di schermo
di Debye

$$\lambda_D \equiv \frac{1}{K_D} = \left(\frac{\epsilon k_B T}{2q^2 \rho_0} \right)^{1/2}$$



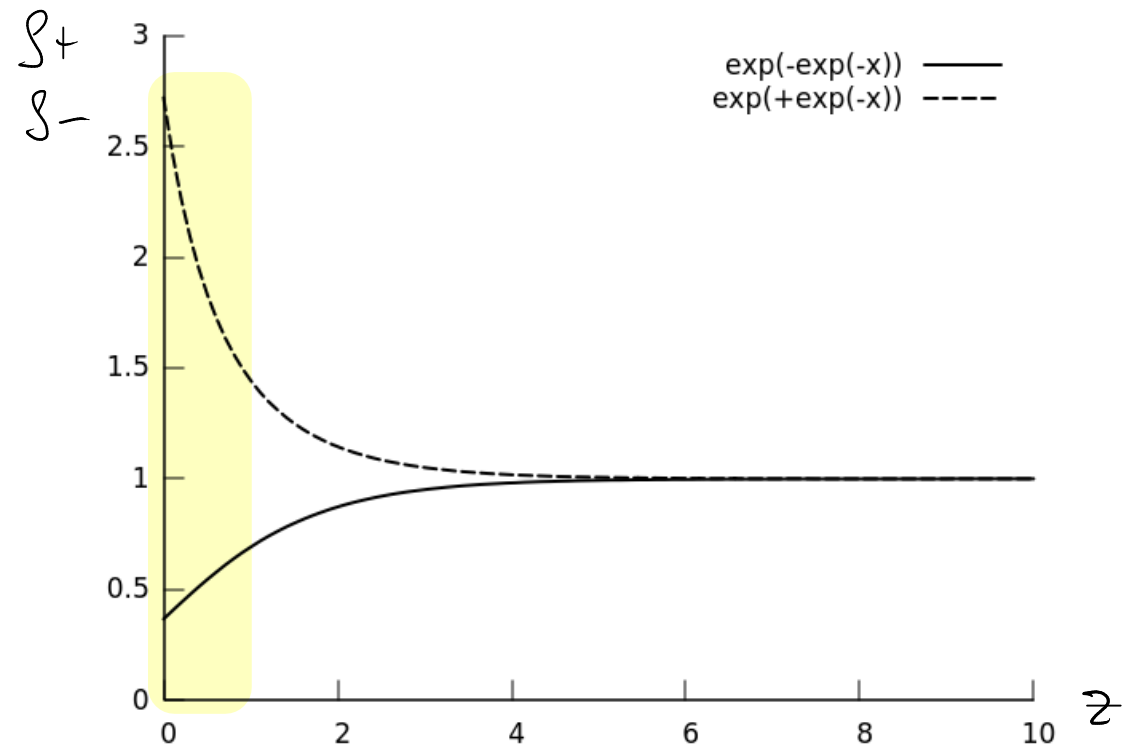
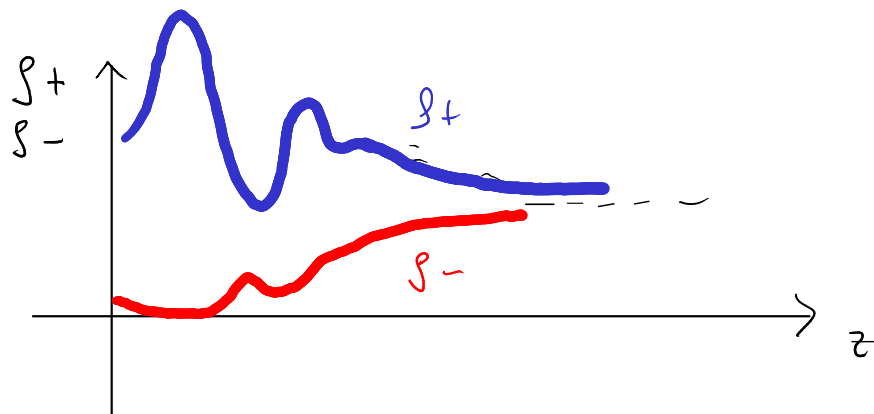
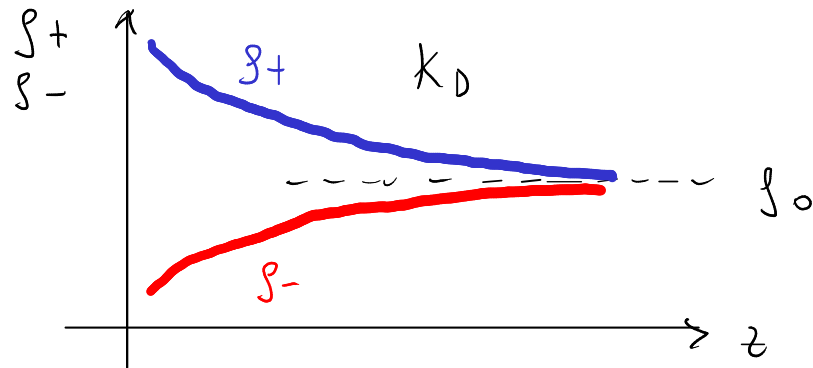
\rightarrow spessore electric layer
diffuso

Densità di ioni

$$\rho_{\pm}(z) = \rho_0 \exp \left[\mp \frac{q\phi_0}{k_B T} \exp(-K_D z) \right]$$

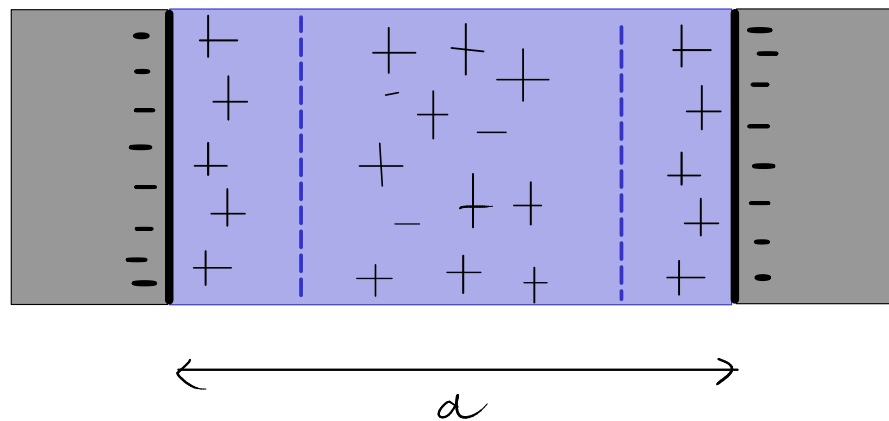
Taylor I ordine

$$\rho_{\pm}(z) \approx \rho_0 \left[1 \mp \frac{q\phi_0}{k_B T} \exp(-K_D z) \right] = \rho_0 \pm \frac{\rho_0 q |\phi_0|}{k_B T} \exp(-K_D z)$$



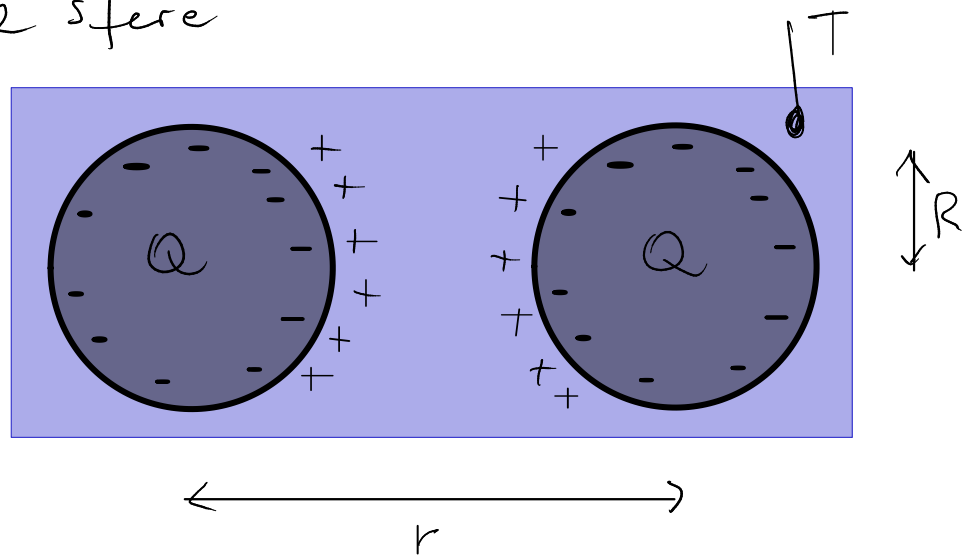
Esempi:

1) 2 placche semi- ∞



$$\frac{U_{el}}{L^2} \sim \downarrow K_B T \exp(-K_D d) \quad (DH)$$

2) 2 sfere



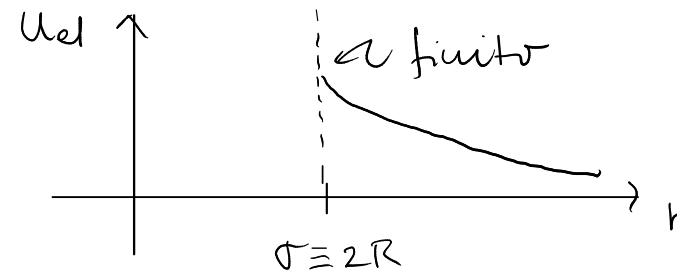
approssimazione DH:

$$U_{el} \approx \frac{Q^2}{4\pi\epsilon} \left(\frac{\exp(K_D r)}{1 + K_D R} \right)^2 \frac{\exp(-K_D r)}{r}$$

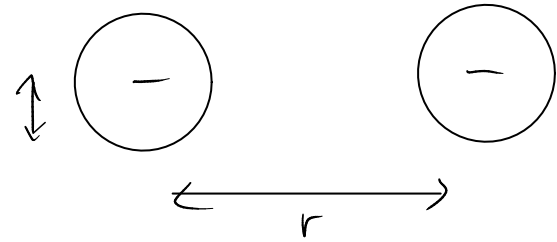
$\underbrace{\hspace{10em}}_{\text{Yukawa}}$

$$= \frac{Q'^2}{4\pi\epsilon} \frac{\exp(-K_D r)}{r}$$

$$Q' = Q \frac{\exp(K_D R)}{1 + K_D R}$$



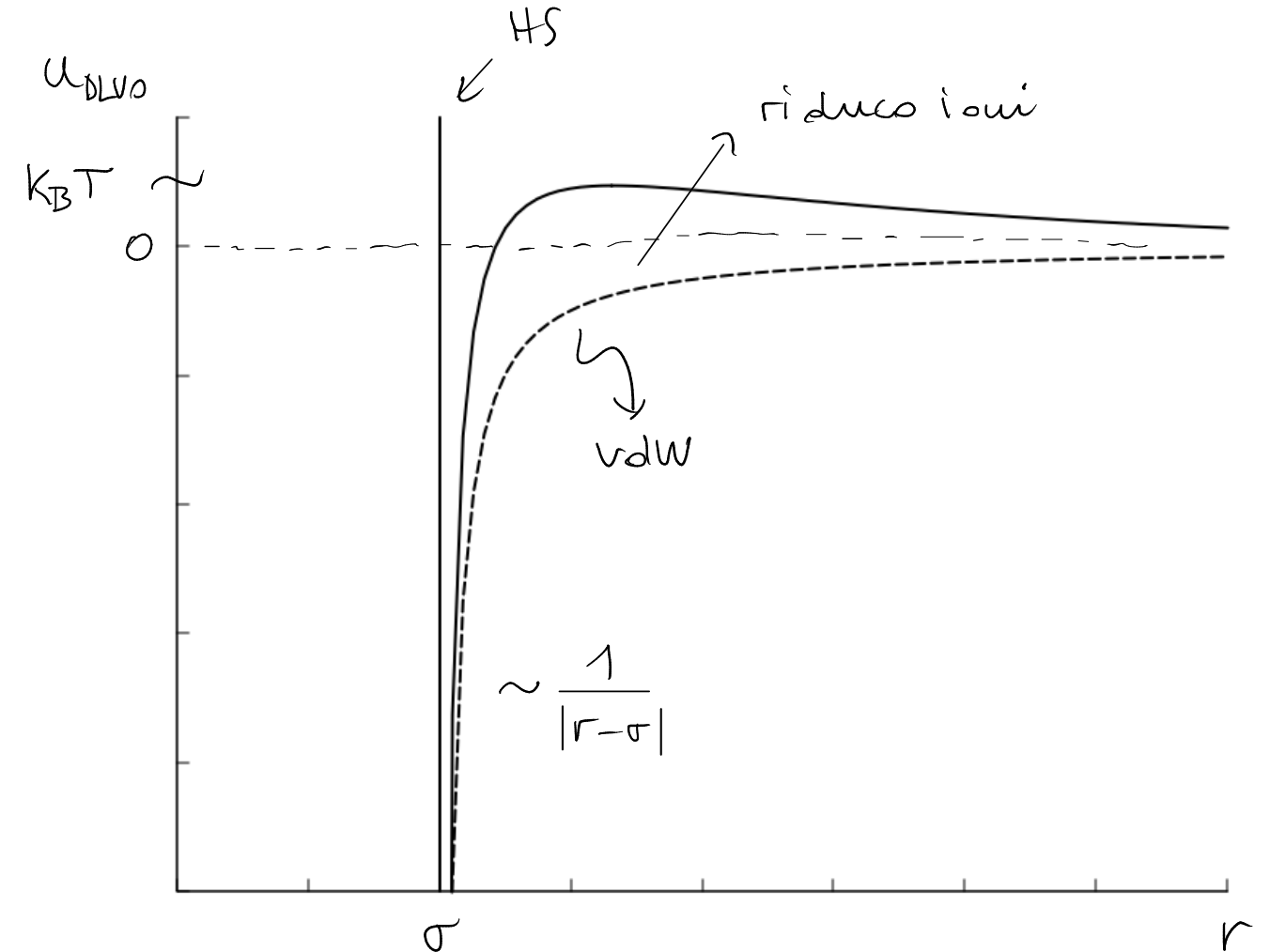
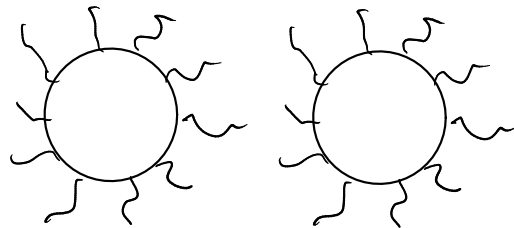
Potenziale DLVO (Derjaguin, Landau, Verwey, Overbeek)



vdW + el + HS

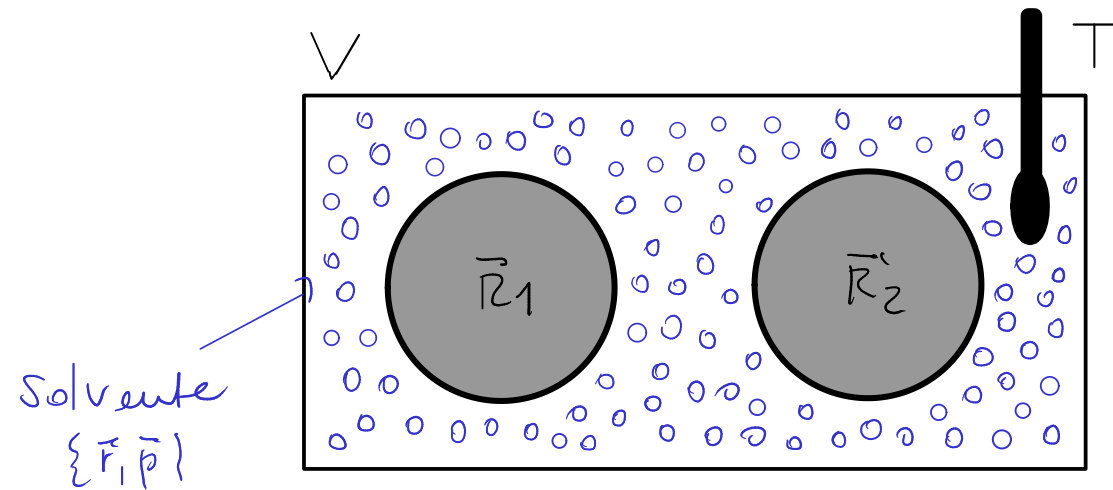
$$u_{DLVO}(r) = \begin{cases} \infty & r \leq \sigma \\ u_{vdW}(r) + u_{el}(r) & r > \sigma \end{cases}$$

- stabilizzazione di carica
- stabilizzazione sterica

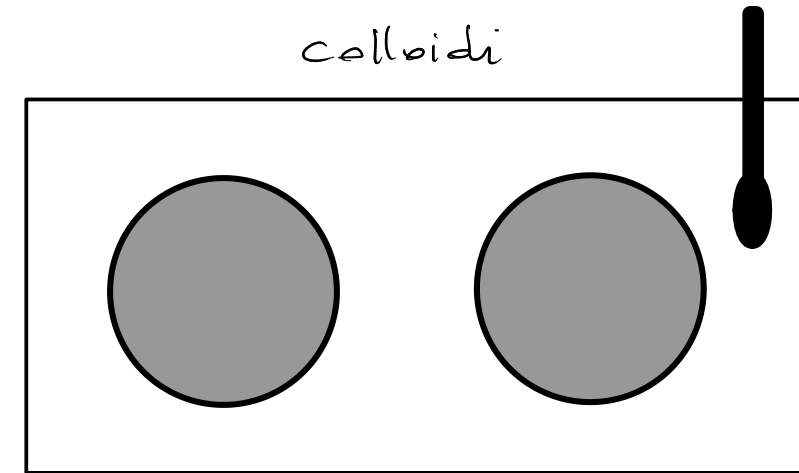


Interazioni effettive tra colloidi

Miscela asimmetrica: colloidi + solvente \rightarrow Christos LIKOS



traccia \rightarrow



Hamiltoniana effettiva H_{eff}

dof colloidi: $\{\vec{R}, \vec{P}\}$ N_c
dof solvente: $\{\vec{r}, \vec{p}\}$ N_s

Hamiltoniana

$$H = H_c(\{\vec{R}, \vec{P}\}) + H_s(\{\vec{r}, \vec{p}\}) + U_{cs}(\{\vec{R}\}, \{\vec{r}\})$$

Funzione di partizione

$$Z = \text{Tr}_c [\text{Tr}_s [e^{-\beta H}]] = \text{Tr}_c [e^{-\beta H_c} \text{Tr}_s [e^{-\beta H_s} e^{-\beta U_{cs}}]]$$

$$\text{Tr} [\dots] = \frac{1}{h^{3N} N!} \int_V d\vec{r}^N \int d\vec{p}^N$$

$$Z_s(\{\vec{R}\}) \equiv \text{Tr}_s [e^{-\beta H_s} e^{-\beta U_{cs}}]$$

$$F_s(\{\vec{R}\}) = -k_B T \ln(Z_s) \Rightarrow Z_s = e^{-\beta F_s}$$

$$Z = \text{Tr}_c [e^{-\beta H_c} e^{-\beta F_s}] = \text{Tr}_c [e^{-\beta (H_c + F_s)}] = \text{Tr}_c [e^{-\beta H_{\text{eff}}}]$$

Hamiltoniana effettiva

$$H_{\text{eff}} = H_c(\{\vec{R}, \vec{P}\}) + F_s(\{\vec{R}\}) = K_c + U_c(\{\vec{R}\}) + F_s(\{\vec{R}\})$$

↓

dirette tra
colloidi

↓

mediate
dal solvente

↓

indipendenti da T, ρ

riproduce

— termodinamica

— $\langle \Theta(\{\vec{R}, \vec{P}\}) \rangle$

↑

osservabili STATICHE

$$\Rightarrow \langle \Theta \rangle \stackrel{\text{(es.)}}{=} \frac{\text{Tr}_c [\Theta \exp(-\beta H_{\text{eff}})]}{\text{Tr}_c [\exp(-\beta H_{\text{eff}})]}$$

$$\text{Tr}_c [\text{Tr}_s [\dots]]$$