CLASSICAL vs. QUANTUM

Lunghezza d'onda di de Broglie

$$\lambda = \frac{h}{p} \qquad \langle E_C \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{3}{2} k_B T \Rightarrow p = \sqrt{\langle p^2 \rangle} = \sqrt{3 m k_B T} \Rightarrow \lambda \approx \sqrt{\frac{h^2}{3 m k_B T}}$$

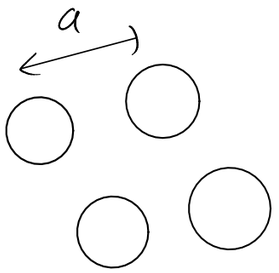
$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

TABLE 1.1. *Test of the classical hypothesis*

Liquid	T_t (K)	Λ (Å)	Λ/a	Θ_{rot}/T_t
H_2	14.05	3.3	0.97	6.1
Ne	24.5	0.78	0.26	
CH_4	90.7	0.46	0.12	0.083
N_2	63.3	0.42	0.11	0.046
Li	454	0.31	0.11	
A	84	0.30	0.083	
HCl	159	0.23	0.063	0.094
Na	371	0.19	0.054	
Kr	117	0.18	0.046	
CCl_4	250	0.09	0.017	0.0009

Λ is the de Broglie thermal wavelength at the triple-point temperature and $a = (V/N)^{1/3}$.

Hansen MacDonald



$$\rho = \frac{N}{V} \qquad a = \rho^{-1/3}$$

Approssimazione classica:

$$\Lambda \lesssim a \Rightarrow \frac{h}{\sqrt{2\pi m k_B T}} \frac{1}{a} \lesssim 1$$

$$T \gtrsim \underbrace{\frac{1}{a^2} \frac{h^2}{2\pi m k_B}}_{\tilde{T}}$$

Ar: $\tilde{T} \approx 2k$

↑ sistema denso a $\sim$ Å

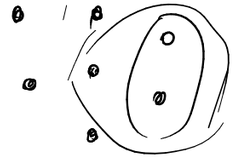
INTERAZIONI EFFETTIVE

Effettivo → riduco n. di gradi di libertà

INTERAZIONI EFFETTIVE TRA ATOMI E MOLECOLE

Energia potenziale di N particelle

$$U = \sum_{i=1}^{N} u_1(\vec{r}) + \sum_{i=1}^{N}\sum_{j>i}^{N} u_2(\vec{r}_i, \vec{r}_j) + \sum_{i=1}^{N}\sum_{j>i}^{N}\sum_{k>j}^{N} u_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$



↑ campo esterno

↑ 2 corpi

$u_2(|\vec{r}_i - \vec{r}_j|)$

↑ 3 corpi

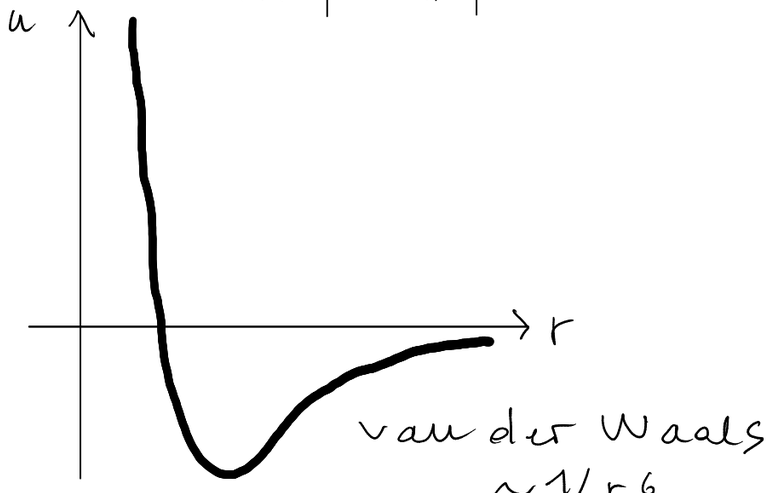
Additività a coppie

$$U \approx \sum_i u_1(\vec{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N} u_2(|\vec{r}_i - \vec{r}_j|)$$

$$U \approx \sum_i u_1(\vec{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N} \tilde{u}_2(|\vec{r}_i - \vec{r}_j|)$$ ← dipendenza dallo stato termo

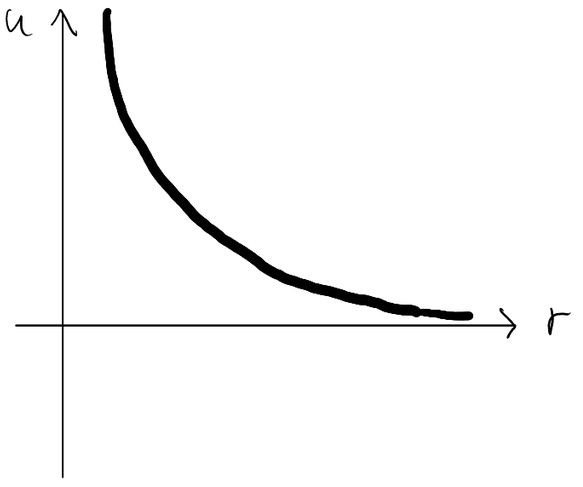
1) Lennard-Jones

Ar, CH_4



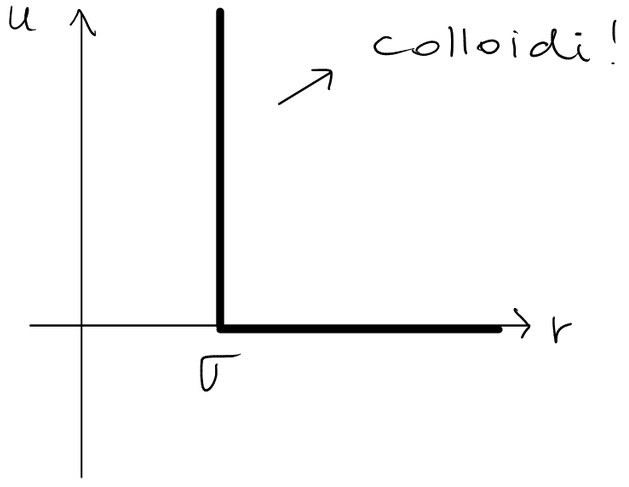
$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

2) Legge di potenza

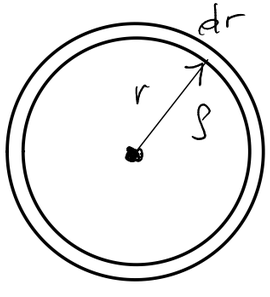


$$u(r) = \epsilon \left(\sigma/r\right)^n$$

3) Sfera dura



$$u(r) = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$



Potenziale a corto raggio

$$u \approx \int_V d\bar{r}\, \rho\, u(r) = 4\pi\rho \int_0^\infty dr\, r^{d-1} \underbrace{u(r)}_{\sim r^{-n}} \sim \int_0^\infty dr\, r^{d-1-n}$$

$$\frac{1}{r^{n+1-d}}$$

$$n + 1 - d > 1 \Rightarrow \underline{n > d}$$

Complessità algoritmica

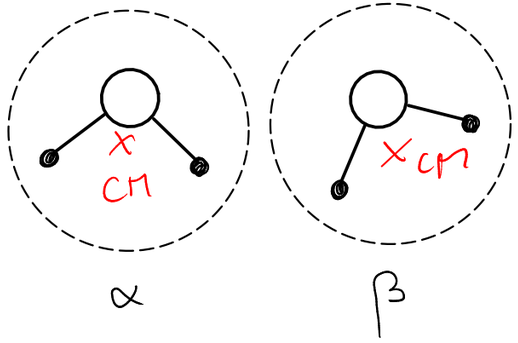
$$U = \sum_i \sum_{j>i} u(r_{ij})$$

$O(N^2) \rightarrow O(N)$ se corto raggio

Determinazione parametri

- eq. stato, struttura
- forze → ab-initio
- reti neurali

Interazioni intermolecolari



$$U = U_{\alpha\alpha} + U_{\beta\beta} + U_{\alpha\beta}$$

$U_{\alpha\alpha} + U_{\beta\beta}$: intramolecolare

$U_{\alpha\beta}$: intermolecolare

$(i, i+1)$ $(i, i+1, i+2)$ $(\dots)$ LJ + Coulomb

2c 3c 4c

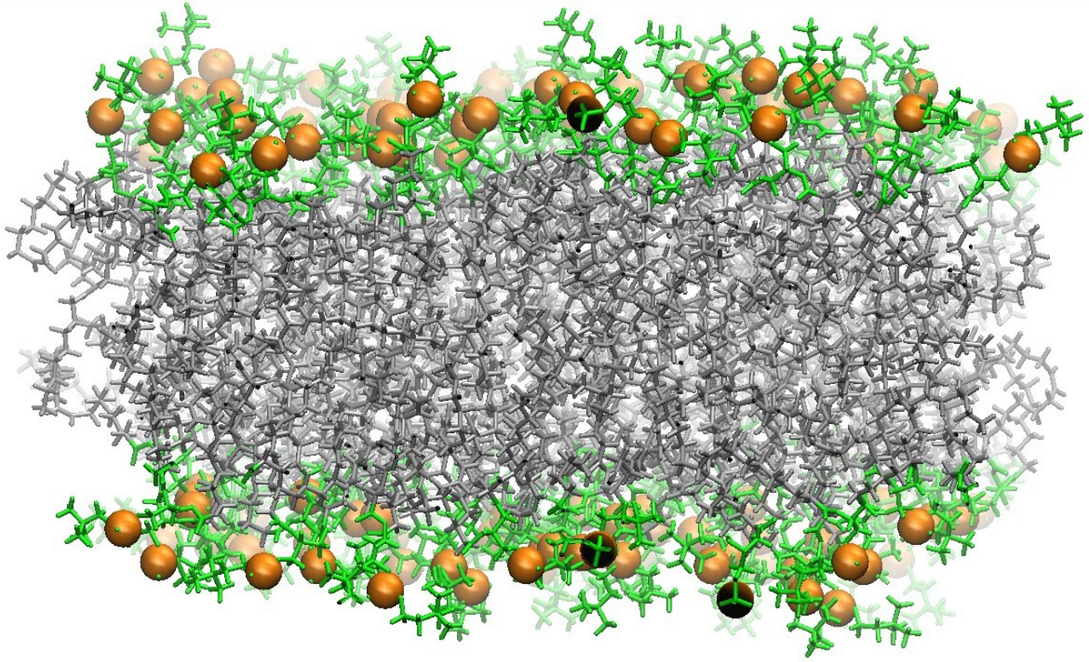
+ LJ

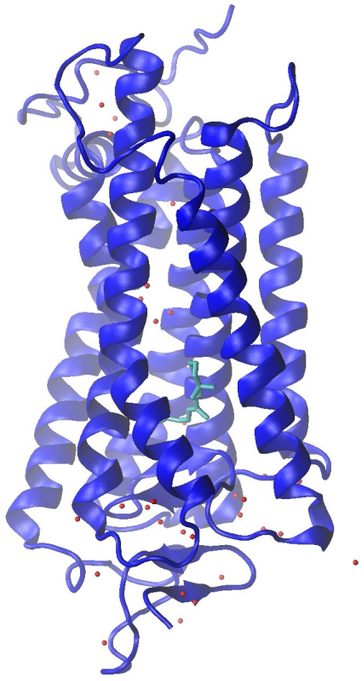
Campo di forze (force - field)

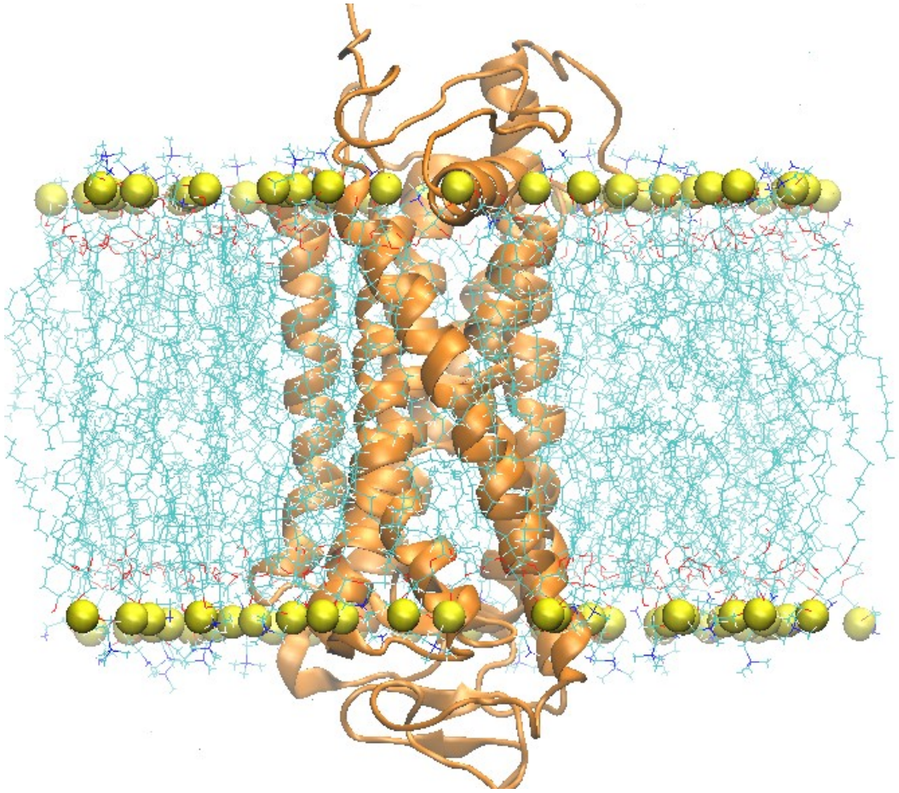
AMBER

CHARMM

....

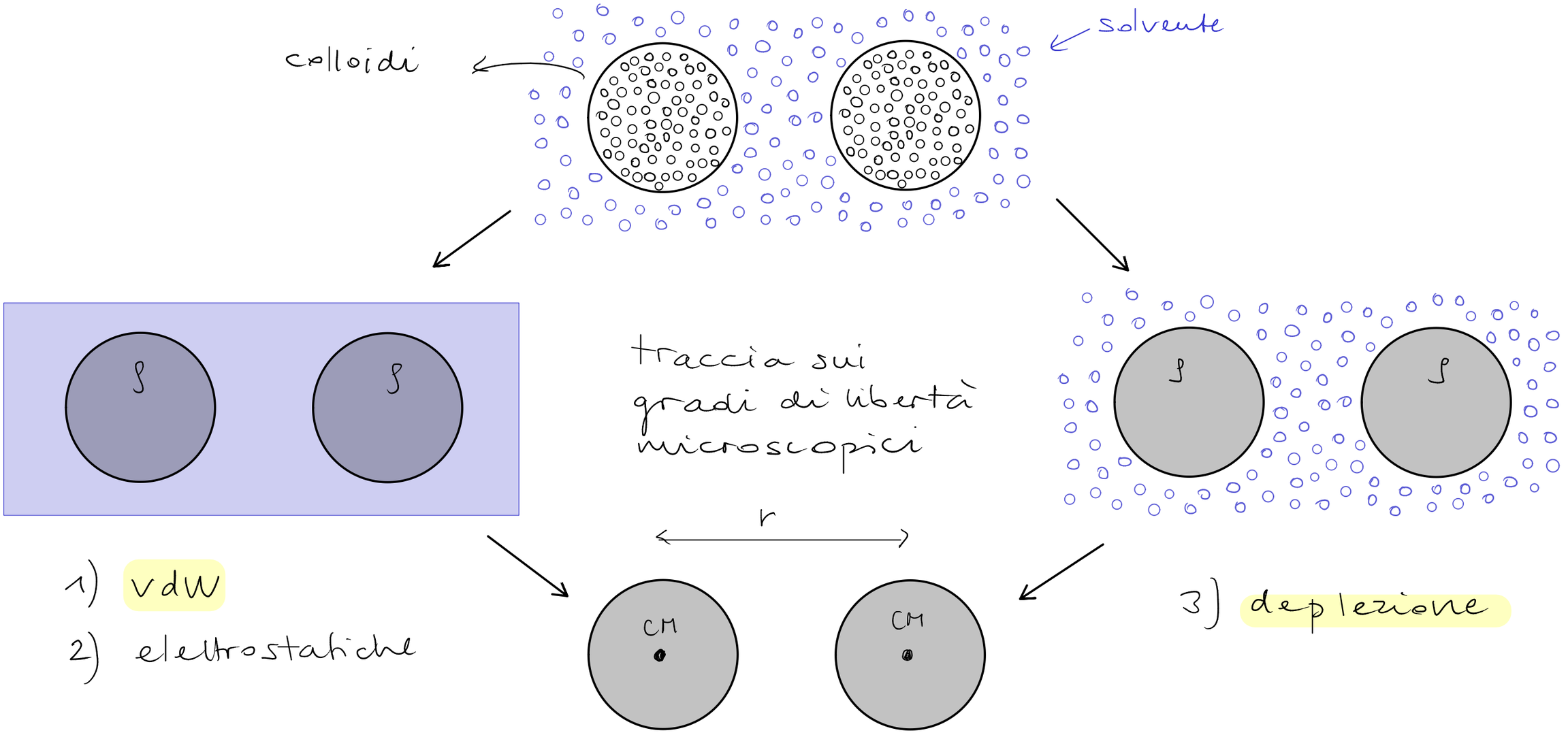






AMBERMD.ORG

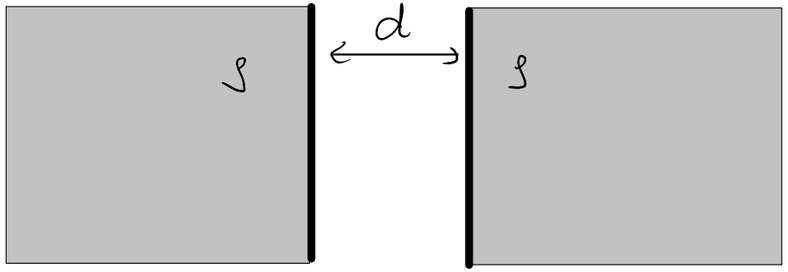
INTERAZIONI EFFETTIVE TRA COLLOIDI



Interazioni di van der Waals

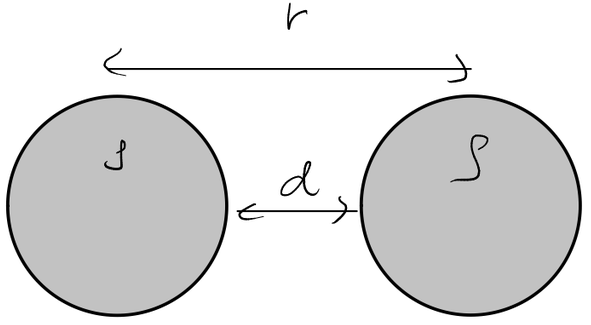
$$u_{vdw} = -\frac{C}{r^6}$$ ← polarizzabilità

↑ attrattiva



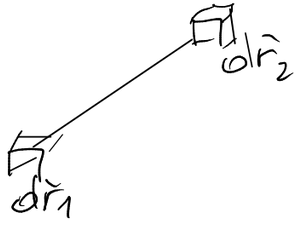
① 2 placche semi-∞

nel solvente ↓ nel vuoto



② 2 sfere

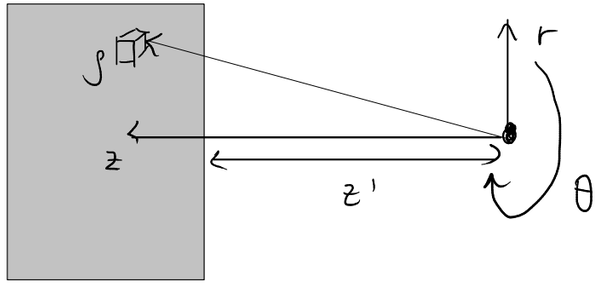
Energia potenziale totale



$$U = \int_{V_1}\int_{V_2} \rho\, d\bar{r}_1\, \rho\, d\bar{r}_2\, u(|\bar{r}_1 - \bar{r}_2|) = \int_V d\bar{r} \int_{V'} d\bar{r}'\, \rho^2\, u(|\bar{r} - \bar{r}'|)$$

$$= \int_{V'} d\bar{r}' \rho \int_V d\vec{r}\; u'(|\bar{r} - \bar{r}'|)$$

①

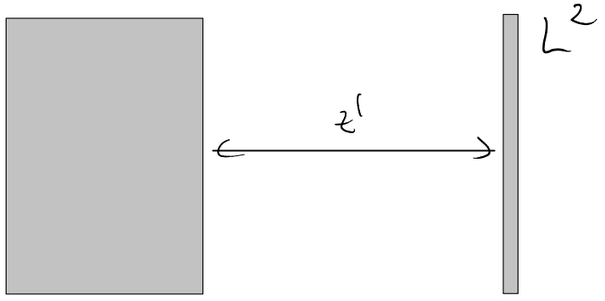


$$w' = \rho \int_0^{2\pi} d\theta \int_{z'}^{\infty} dz \int_0^{\infty} dr\, r \left(-\frac{C}{(z^2+r^2)^3} \right)$$

$$= -\pi C \rho \int_{z'}^{\infty} dz \int_0^{\infty} dr \frac{2r}{(z^2+r^2)^3}$$

$$= -\pi C \rho \int_{z'}^{\infty} dz \left[-\frac{1}{2} \frac{1}{(z^2+r^2)^2} \right]_0^{\infty}$$

$$= -\frac{\pi C \rho}{2} \int_{z'}^{\infty} dz \frac{1}{z^4} = -\frac{\pi C \rho}{6} \left[-\frac{1}{z^3} \right]_{z'}^{\infty} = -\frac{\pi C \rho}{6} \frac{1}{z'^3}$$

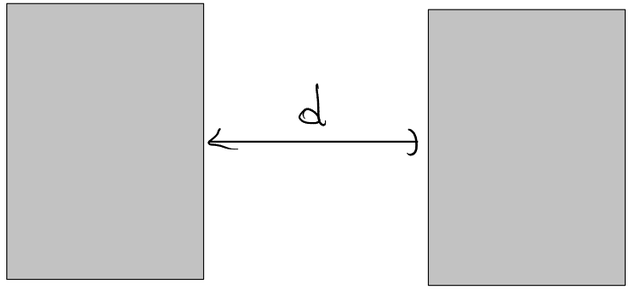


$$U = \int_0^L dx' \int_0^L dy' \int_d^{\infty} dz' \left(-\frac{\pi C \rho^2}{6} \right) \frac{1}{z'^3}$$

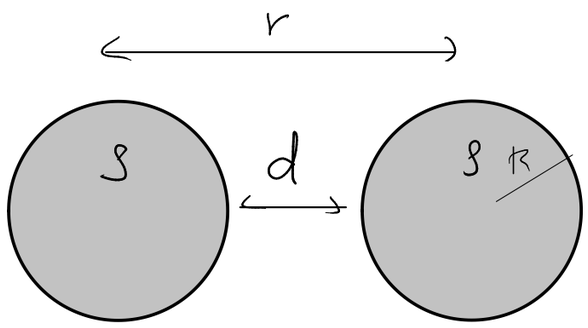
$$= -\frac{\pi C \rho^2 L^2}{6} \int_d^{\infty} dz' \frac{1}{z'^3}$$

$A \equiv$ costante di Hamaker

$$\frac{U}{L^2} = -\frac{\pi C \rho^2}{12} \left[-\frac{1}{z'^2} \right]_d^{\infty} = -\frac{\pi^2 C \rho^2}{12\pi} \frac{1}{d^2} = -\frac{A}{12\pi} \frac{1}{d^2}$$



(2)



Hamaker 1937

$$U_{vdw}(r) = -\frac{A}{6}\left[\frac{2R^2}{r^2-(2R)^2} + \frac{2R^2}{r^2} + \ln\left(1-\frac{(2R)^2}{r^2}\right)\right]$$

1) contatto : $r \equiv 2R + d \qquad 2R \equiv \sigma \qquad d \ll \sigma$

$$U_{vdw} \approx -\frac{AR}{12}\frac{1}{d} = -\frac{AR}{12}\frac{1}{|r-\sigma|}$$

2) grandi distanze : $d \gg \sigma$

$$U_{vdw} \approx -\frac{A}{36}\left(\frac{\sigma}{r}\right)^6$$

$\ln(1-x^2) \approx -x^2 - \frac{x^4}{2} - \frac{x^6}{3} \qquad \frac{1}{1-x^2} \approx 1 + x^2 + x^4$

$$\frac{2R^2}{r^2-(2R)^2} + \frac{2R^2}{r^2} + \ln\left(1-\frac{4R^2}{r^2}\right) = \frac{1}{2}\frac{(2R/r)^2}{1-(2R/r)^2} + \frac{1}{2}\left(\frac{2R}{r}\right)^2 + \ln\left[1-\left(\frac{2R}{2}\right)^2\right] \approx \qquad x = \frac{2R}{r}$$

$$\approx \frac{x^2}{2}(1+x^2+x^4) + \frac{x^2}{2} - x^2 - \frac{x^4}{2} - \frac{x^6}{3} = \frac{x^2}{2} + \frac{x^4}{2} + \frac{x^6}{2} + \frac{x^2}{2} - x^2 - \frac{x^4}{2} - \frac{x^6}{3} = \frac{x^6}{6} = \frac{1}{6}\left(\frac{2R}{r}\right)^6$$

Approssimazioni

- additività a coppie
- no effetti relativistici

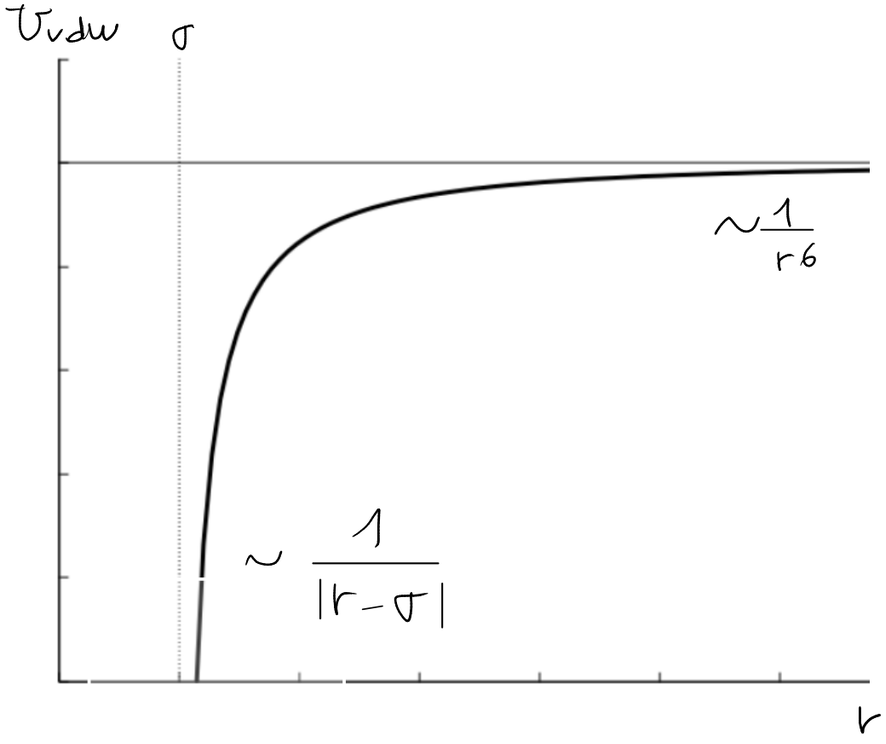
$$\nu = \frac{1}{\Delta t} \qquad \Delta t < \frac{r}{c} \Rightarrow \quad \nu > \frac{c}{r}$$

$$\Rightarrow \quad \frac{1}{r^7}, \quad \frac{1}{r^3}$$

- ruolo del solvente

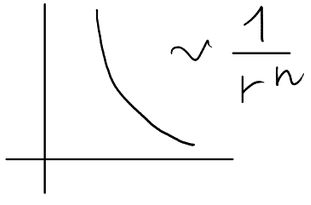
$$C = C(n_C - n_S)$$

indici di rifrazione



INTERAZIONI EFFETTIVE

- MICRO
  - Atomi
    - LJ
    - SS
    - HS
    - ....
  - Molecole
    - AMBER, CHARMM
    - ....
- MESO
  - Colloidi
    - solvente continuo
      - VDW
      - EL
      - DLVO
    - solvente discreto
      - Deplezione
      - AO
  - Polimeri

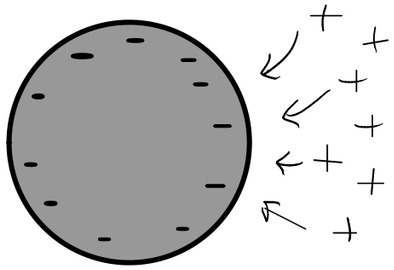


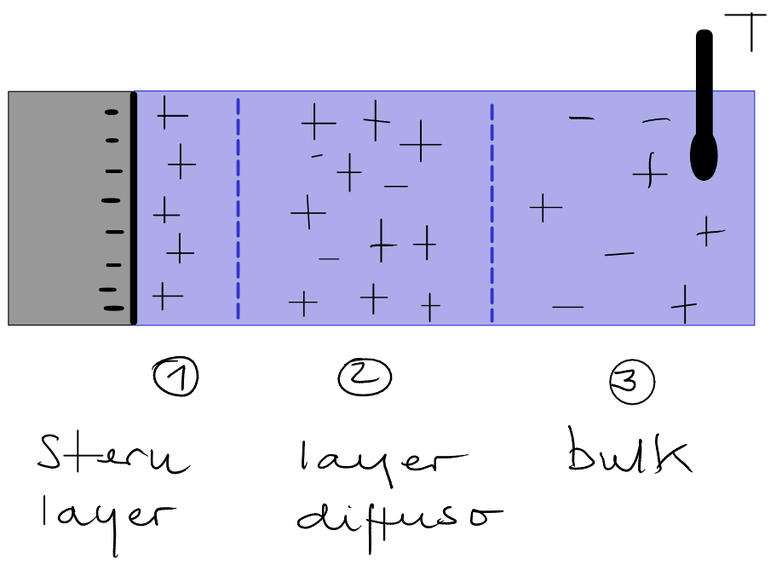
$A \sim 10^{-20}$ J

index matching

Interazioni elettrostatiche

- colloidi carichi Q
- ioni in soluzione $\pm |q|$
- soluzione $\rightarrow \epsilon$





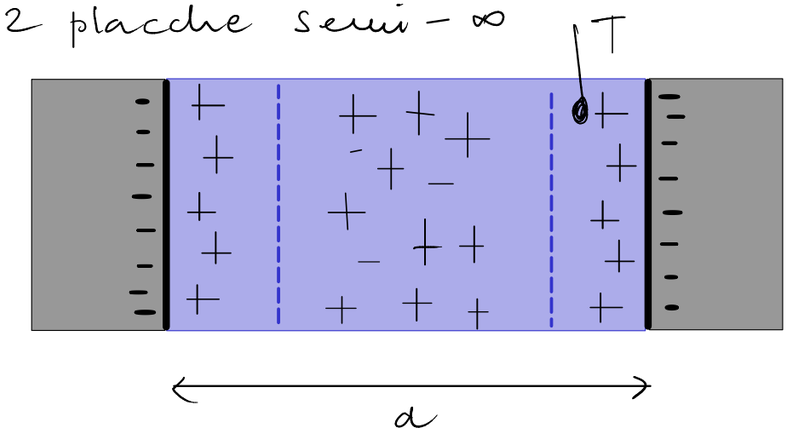
Poisson - Boltzmann (BH) $\rightsquigarrow$ $\rho_e(\vec{r})$

- $\nabla^2 \phi = -\frac{\rho_e}{\epsilon}$ $\qquad \epsilon = \epsilon_r \epsilon_0$
- $\rho_e \approx \rho_0 \exp\left(-\frac{q\phi}{K_B T}\right)$

Approssimazione di Debye - Hückel: $|q\phi| \ll K_B T$

Esempi:

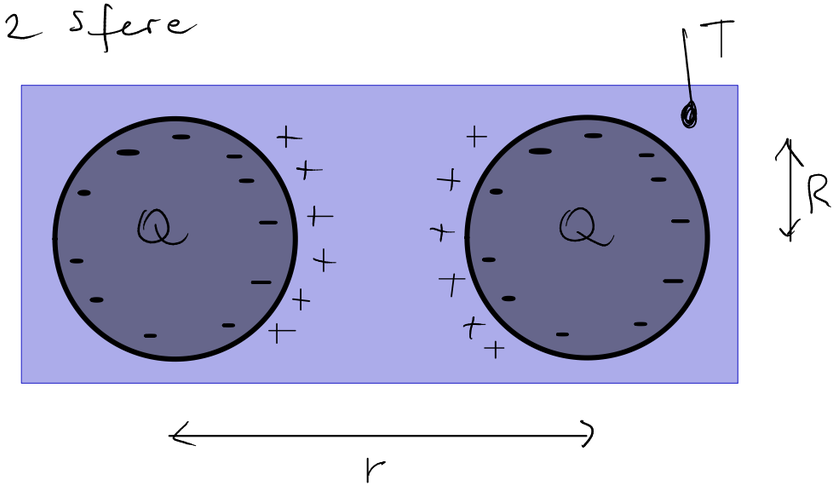
1) 2 placche semi-∞



costante di schermo Debye $\sim \frac{\sqrt{I_s}}{\sqrt{T}}$

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

2) 2 sfere



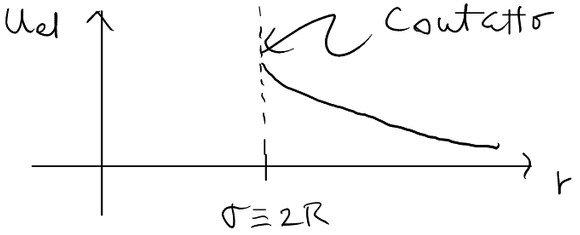
approssimazione di Debye-Hückel:

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

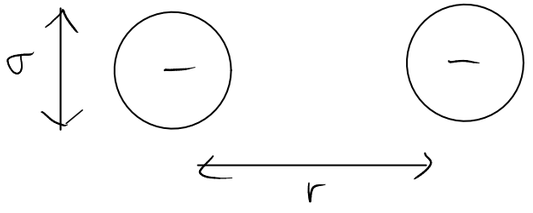
$$= \frac{Q'^2}{4\pi\varepsilon} \frac{\exp(-K_D r)}{r}$$

Yukawa

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



Potenziale DLVO (Derjaguin, Landau, Verwey, Overbeek)

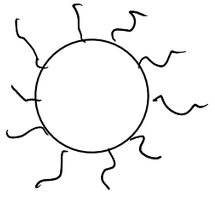


VdW + EL + HS

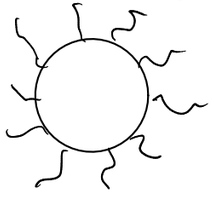
$$U_{DLVO}(r) = \begin{cases} \infty & r \leq \sigma \\ U_{vdw} + U_{el} & r > \sigma \end{cases}$$

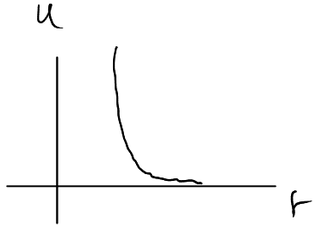
stabilizzazione di carica

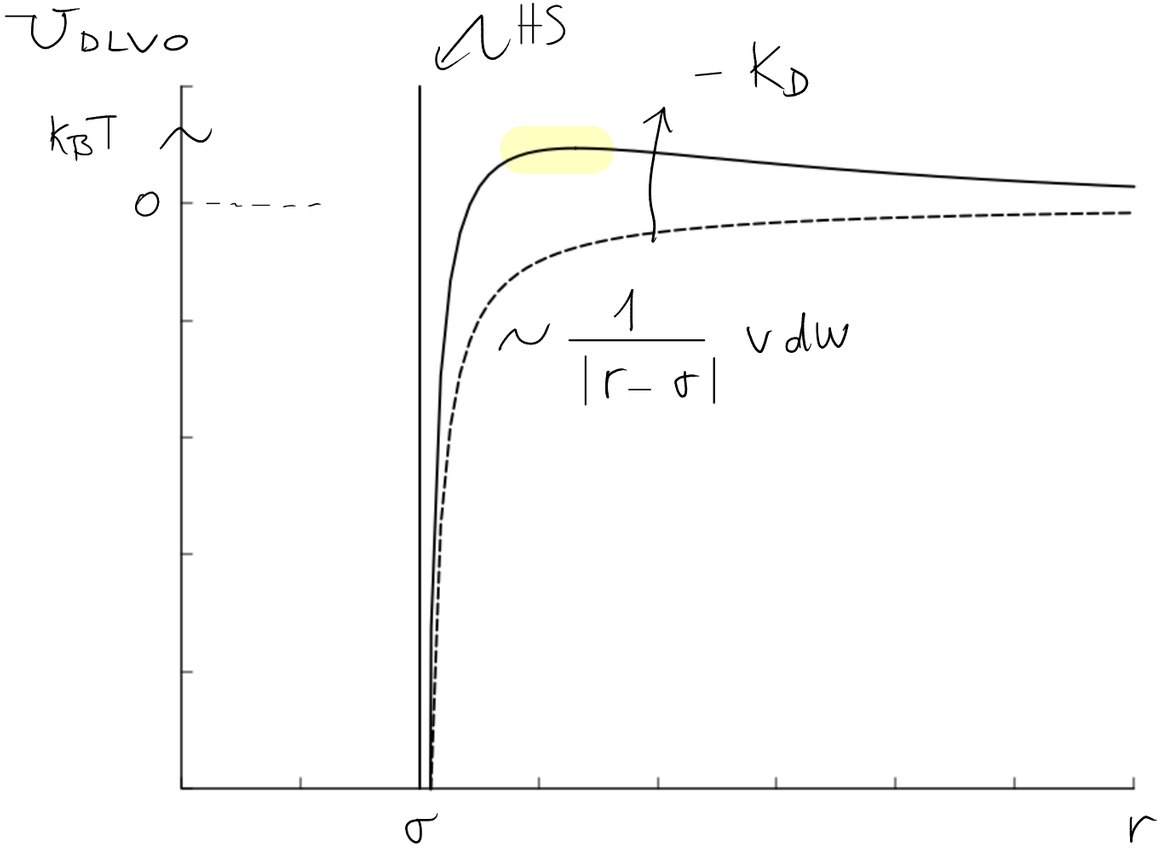
stabilizzazione sterica



SAW

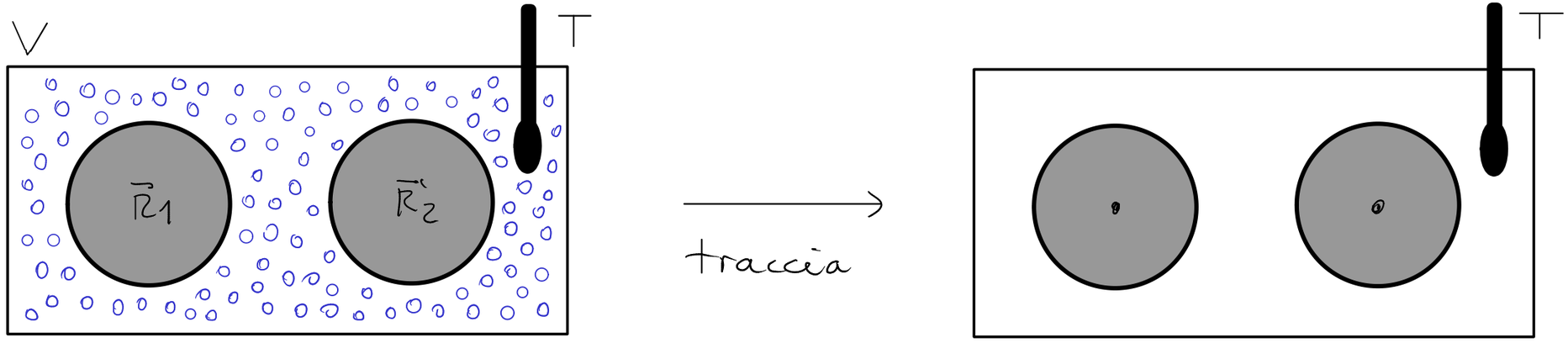






Interazioni effettive tra colloidi

Miscela asimmetrica: colloidi + solvente micro



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

$$Z = Tr_C\left[Tr_S\left[e^{-\beta H} \right] \right]$$

Traccia

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

$$Z = Tr_c \left[e^{-\beta H_c} \underbrace{Tr_s \left[e^{-\beta (H_s + U_{cs})} \right]}_{Z_s(\{\vec{R}\})} \right]$$

$$F_s(\{\vec{R}\}) = -k_B T \ln \left[Z_s(\{R\}) \right] \quad \Rightarrow \quad Z_s = e^{-\beta F_s}$$

$$Z = Tr_c \left[e^{-\beta H_c} e^{-\beta F_s} \right] = Tr_c \left[e^{-\beta (\underbrace{H_c + F_s}_{H_{eff}(\{\vec{R},\vec{P}\})})} \right]$$

Sistema effettivo

$$H_{eff} = K_c + U_c + F_s$$

U_c: interazione diretta

F_s: interazione mediata

→ preserva termodinamica

→ preserva medie statiche $\theta(\{\vec{R},\vec{P}\})$

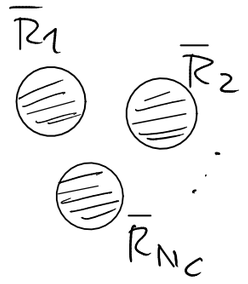
$$Tr_c \left[Tr_s [\dots] \right] \leftarrow \langle \theta \rangle = \frac{Tr_c \left[\theta \exp(-\beta H_{eff}) \right]}{Tr_c \left[\exp(-\beta H_{eff}) \right]} \quad \text{(es.)}$$

Interazioni effettive a 2 corpi

$$H_{eff} \simeq K_c + U_c + F_S(\{\vec{R}\}) = K_c + U_c + F_S^{(0)} + F_S^{(2)} + F_S^{(3)} + \dots$$

↑ dipende dallo stato

↑ volume $S, T, \dots$



Approx di additività a coppie

$$F_S \approx F_S^{(0)} + F_S^{(2)}$$

$N_C = 2$

$\{\vec{R}_1, \vec{R}_2\}, \{\vec{P}_1, \vec{P}_2\}$

$$H_{eff} = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + U_c(|\vec{R}_1 - \vec{R}_2|) + F_S(\vec{R}_1, \vec{R}_2)$$

$$F_S = -K_B T \ln[Z_S(\vec{R}_1, \vec{R}_2)]$$

$$Z_S = Tr_S\left[e^{-\beta(H_S+U_{CS})}\right] = Tr_S\left[e^{-\beta K_S}\, e^{-\beta(U_S+U_{CS})}\right]$$

$$= \frac{1}{h^{3N_S}\, N_S!}\int d\bar{p}^{N_S}\, e^{-\beta K_S}\int d\bar{r}^{N_S}\, e^{-\beta(U_S+U_{CS})}$$

$$= \left(\frac{V^{N_S}}{h^{3N_S}\, N_S!}\int d\bar{p}^{N_S}\, e^{-\beta K_S}\right)\left(\frac{1}{V^{N_S}}\int d\bar{r}^{N_S}\, e^{-\beta(U_S+U_{CS})}\right)$$

$$= Z_S^{id}\cdot Z_S^{C}$$

$$F_S = F_S^{id} + F_S^{C} = -k_B T \ln Z_S^{id} - k_B T \ln Z_S^{C}$$

$$Z_S^{id} = \frac{V^{N_S}}{\Lambda^{3N_S}\, N_S!} \rightarrow F_S^{id} = -k_B T \ln\left[\frac{V^{N_S}}{\Lambda^{3N_S}\, N_S!}\right]$$

$$= -k_B T\left\{N_S \ln\left(\frac{V}{\Lambda^3}\right) - \ln(N_S!)\right\}$$

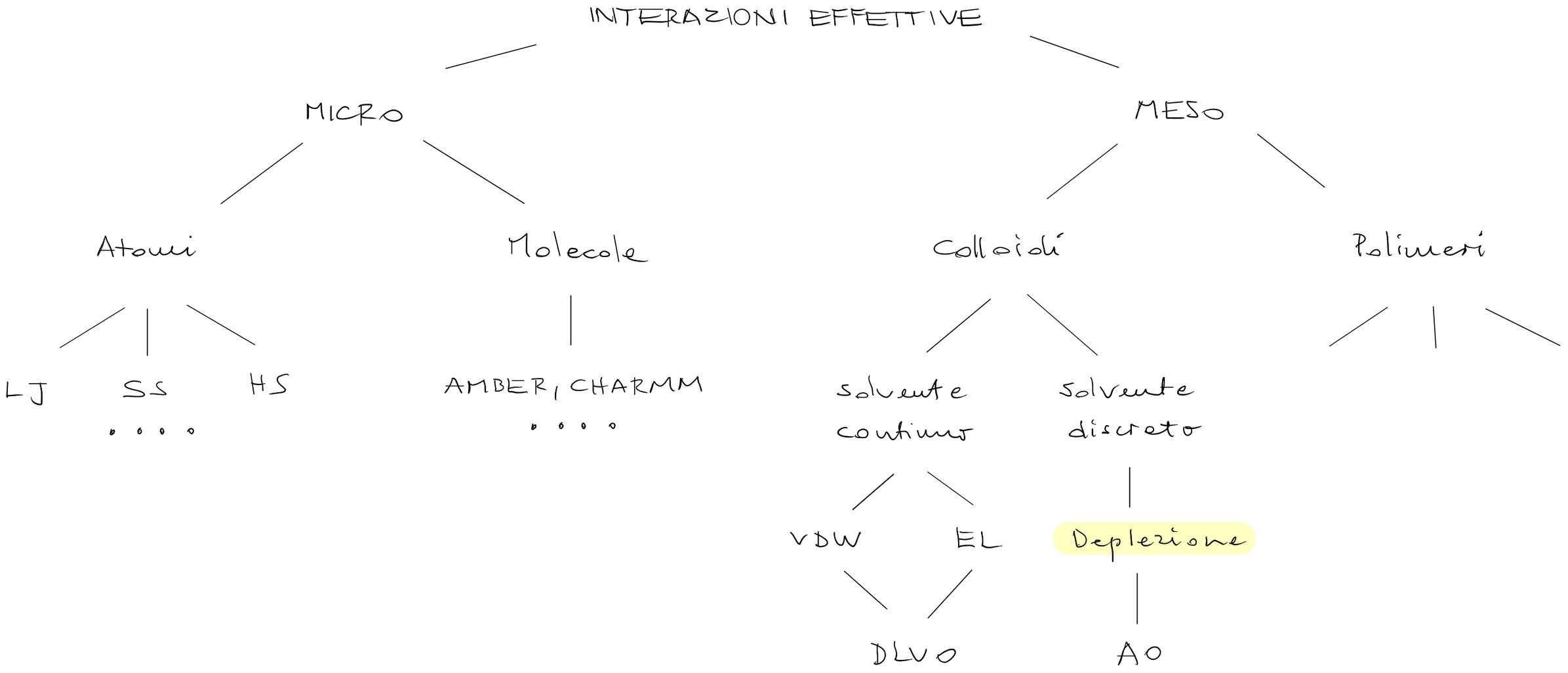
Stirling $\rightarrow$ $$= -k_B T\, N_S\left[\ln\left(\frac{V}{\Lambda^3}\right) - \ln N_S + 1\right]$$

$$F_s^{id} = -K_B T V \left[\rho_s \ln\left(\frac{V}{\Lambda^3}\right) - \rho_s \ln N_s + \rho_s \right]$$

$$= -K_B T V \left[-\rho_s \ln(\Lambda^3 \rho_s) + \rho_s \right] = K_B T V \left[\rho_s \ln(\Lambda^3 \rho_s) - \rho_s \right]$$

$$F_S(\vec{R}_1, \vec{R}_2) = F_S^{id} - K_B T \ln Z_S^c \equiv F_s^{id} + \tilde{U}^{(0)} + \tilde{U}^{(2)}(|\vec{R}_1 - \vec{R}_2|)$$

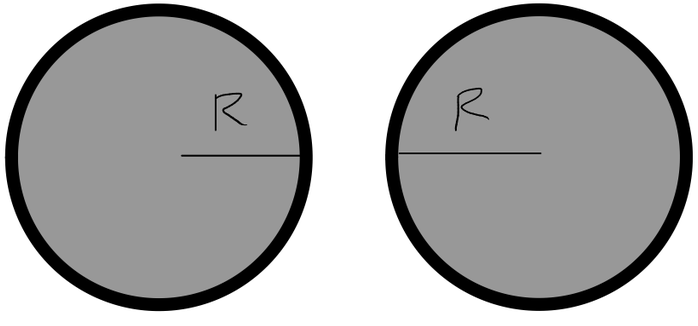
$$H_{eff} = K_c + \underbrace{F_s^{id} + \tilde{U}^{(0)}}_{\text{volume}} + \underbrace{U_c(|\vec{R}_1 - \vec{R}_2|) + \tilde{U}^{(2)}(|\vec{R}_1 - \vec{R}_2|)}_{\tilde{U}_{eff}(|\vec{R}_1 - \vec{R}_2|)}$$


INTERAZIONI EFFETTIVE
MICRO
MESO
Atomi
Molecole
Colloidi
Polimeri
LJ
SS
HS
. . . .
AMBER, CHARMM
. . . .
solvente continuo
solvente discreto
VDW
EL
Deplezione
DLVO
AO

Forze di depleziore

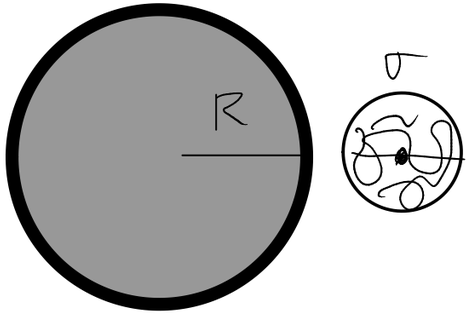
Miscele fortemente asimmetriche → colloidi + polimeri + solvente ("buon")

$\sigma \approx 2R_g$ estensione polimeri $c_1 p$



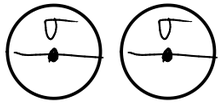
C–C

HS



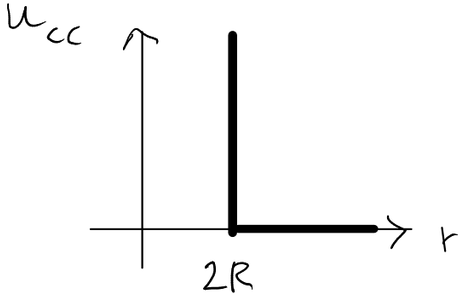
C–P

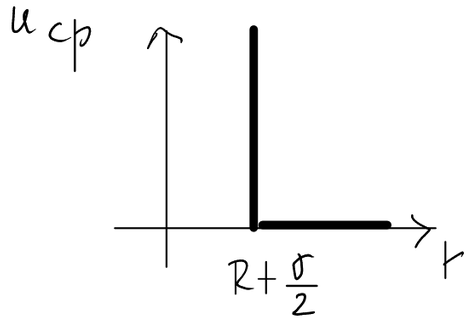
HS

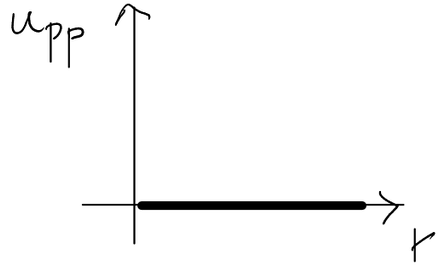


P–P

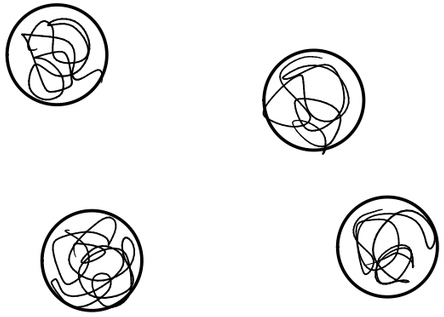
gas non interagente



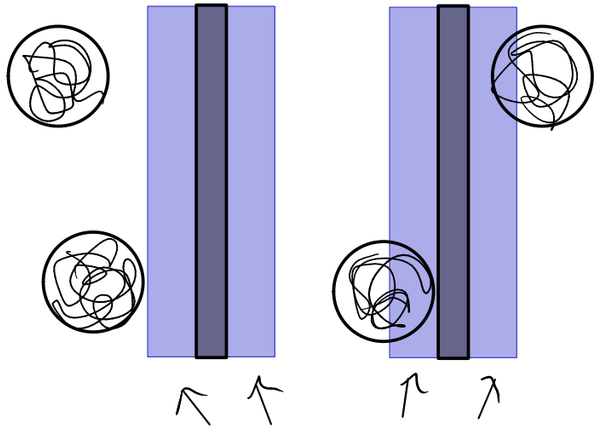




Depletion

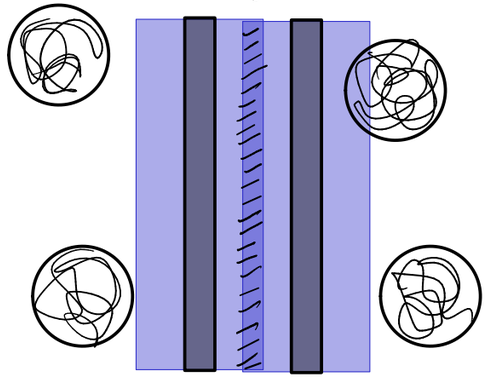


F_p



volume escluso

$\nearrow F_p$



overlap

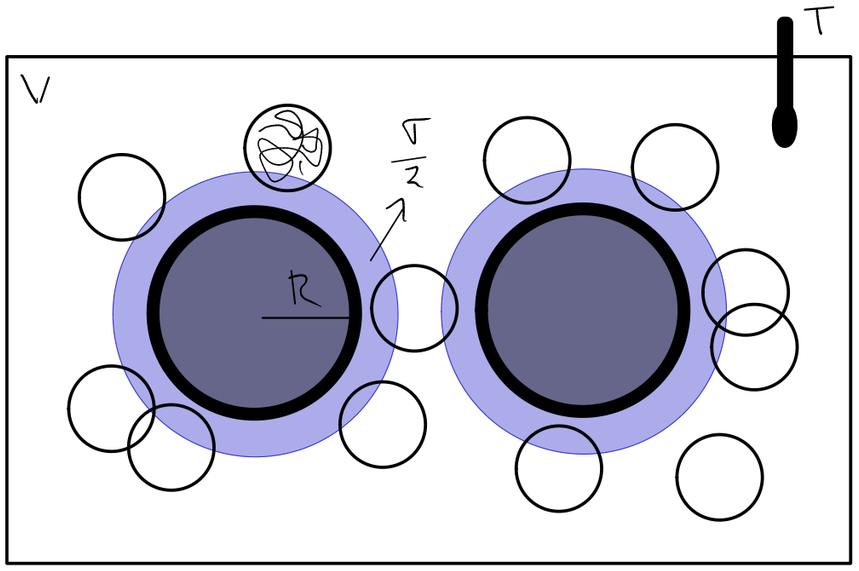
volume escluso

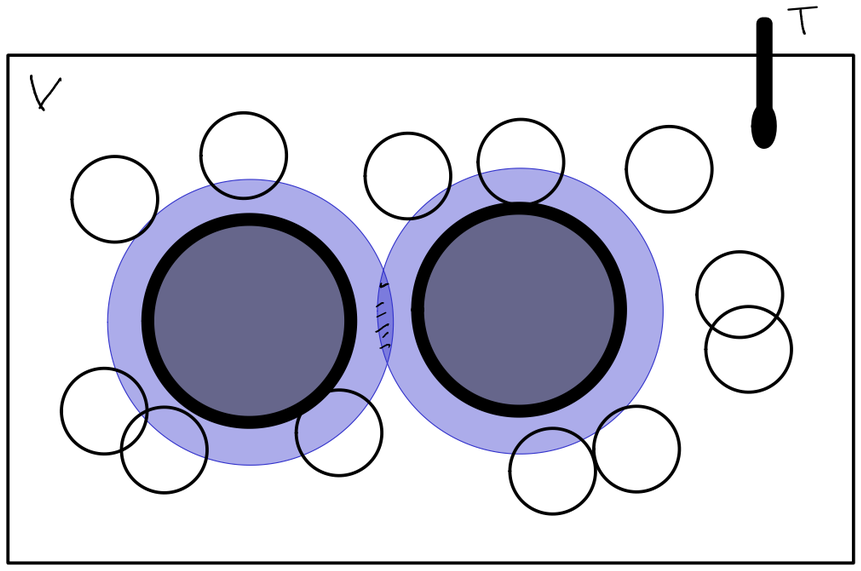
$\searrow F_p$

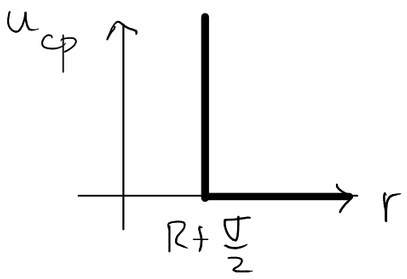
$\Rightarrow$ attrazione

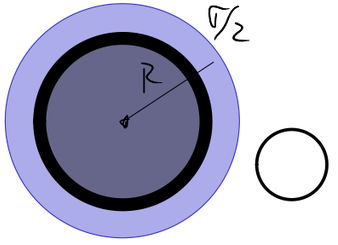
Potenziale di Asakura – Oosawa

$N_c = 2 \quad \{\vec{R}_1, \vec{R}_2\} \qquad N \equiv N_p \quad \{\vec{r}_i, \vec{p}_i\} \quad i = 1, \dots, N$









$r \leq 2R + \sigma \equiv D$

$$H_{eff} = K_c + U_c + F_p(\vec{R}_1, \vec{R}_2)$$

$$F_p = -K_B T \ln\left(Z_p^{id} \cdot Z_p^c\right) \quad \rightarrow \quad Z_p^{id} = \frac{V^N}{\Lambda^{3N} N!}$$

$$Z_p^c = \frac{1}{V^N} \int d\vec{r}^N \exp\left[-\beta\left(U_{cp} + \underbrace{U_{pp}}_{=0}\right)\right]$$

1 se non esclusione
0 se esclusione

$$= \frac{1}{V^N} \int d\vec{r}^N \exp\left[-\beta \sum_{i=1}^{N} u_{cp}(\vec{r}_i; \vec{R}_1, \vec{R}_2)\right] = \left(\frac{1}{V} \int d\vec{r}_1 \exp\left[-\beta u_{cp}(\vec{r}_1; \vec{R}_1, \vec{R}_2)\right]\right)^N$$

$$\simeq \left(\frac{V - V_e}{V} \right)^N \quad \Rightarrow \quad F_p^c = -N k_B T \ln \left(\frac{V - V_e}{V} \right)$$

$r > 2R + \sigma = D$

$$V_e = 2 \cdot \frac{4}{3}\pi \left(\frac{D}{2} \right)^3 = 2 \cdot \frac{\pi}{6} D^3$$

$2R < r < D$

$$V_{ov} \simeq \frac{\pi}{6} (2R + \sigma)^3 \left[1 - \frac{3r}{2(2R+\sigma)} + \frac{r^3}{2(2R+\sigma)^3} \right] = \frac{\pi}{6} D^3 \left(1 - \frac{3r}{2D} + \frac{r^3}{2D^3} \right)$$

$$V_e = 2\frac{\pi}{6} D^3 - \frac{\pi}{6} D^3 \left(1 - \frac{3r}{2D} + \frac{r^3}{2D^3} \right) = \frac{\pi}{6} D^3 \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right) \quad \text{(es.)}$$

$$F_p^c = -N K_B T \ln \left[1 - \frac{\pi D^3}{6V} \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right) \right] \qquad V \gg V_e$$

$$\approx +N K_B T \frac{\pi D^3}{6V} \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right) = \rho K_B T \frac{\pi D^3}{6} \left(\underbrace{1 + \frac{3r}{2D} - \frac{r^3}{2D^3}} + c - c \right)$$

$$F_p^c = \tilde{U}^{(0)} + \tilde{U}_{AO}(r) \leftarrow \text{Asakura - Oosawa}$$

$\tilde{U}^{(0)}$: termine volume

$\tilde{U}_{AO}(r=D) = 0$

$$1 + \frac{3D}{2D} - \frac{D^3}{2D^3} + c = 0 \quad \Rightarrow \quad c = -2$$

$$\tilde{U}_{AO}(r) = \rho K_B T \frac{\pi D^3}{6} \left(-1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right)$$

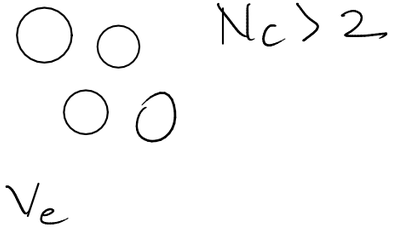
$$\tilde{U}_{AO}(r) = -\rho K_B T \frac{\pi D^3}{6} \left(1 - \frac{3r}{2D} + \frac{r^3}{2D^3} \right) \qquad \tilde{U}_{AO}(2R) < 0 \qquad 2R < r \leq D$$

Hamiltoniana effettiva

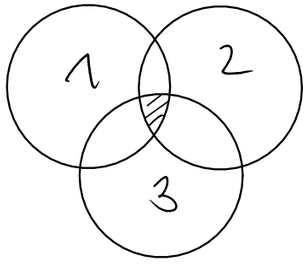
$$H^{eff} = K_C + U_{CC} + F_p^{id} + \tilde{U}^{(0)} + \tilde{U}_{AO}(r) \quad \Rightarrow \quad U_{eff} = U_{CC}(r) + \tilde{U}_{AO}(r)$$

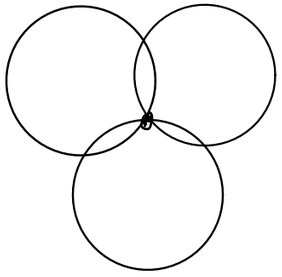
F_p^{id}, $\tilde{U}^{(0)}$: termini volume

$$V_{eff} = \begin{cases} \infty & r \leq 2R \\ \tilde{V}_{A0}(r) & 2R < r < D \\ 0 & r \geq D \end{cases}$$



- $N_c = 3$ → termine a 3 corpi repulsivo : approssimazione di coppia sovrastima V_{ov} ⇒ sovrastima attrazione





Dato R, $\exists\ \sigma^*$ t.c. se $\sigma < \sigma^*$ non ci sono interazioni a $n \geq 3$ corpi

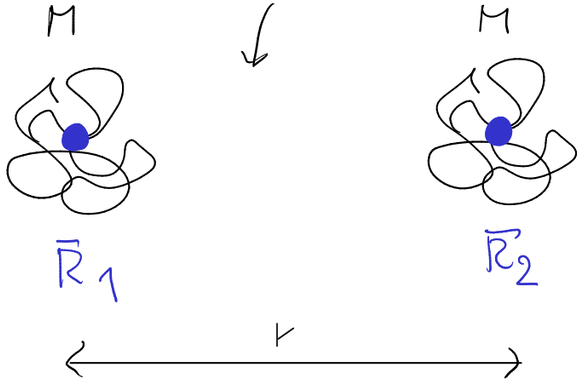
- Per N_c finito, il termine a 2 corpi resta $\tilde{V}_{A0}$

$$F_p^c = \tilde{V}^{(0)} + \tilde{V}^{(2)} + \tilde{V}^{(3)} + \dots$$

$$\tilde{V}^{(2)} \uparrow \tilde{V}_{A0}$$

INTERAZIONI EFFETTIVE TRA POLIMERI

buon solvente



Traccia sui monomeri (M)

$$\vec{R}_1^{CM} = \frac{1}{M}\sum_{i=1}^{M} \vec{r}_{1i} \qquad \vec{R}_2^{CM} = \frac{1}{M}\sum_{i=1}^{M} \vec{r}_{2i}$$

Hamiltoniana

$$H = H_1 + H_2 + U_{12} \qquad \{\vec{r}_{1i}, \vec{r}_{2i}\}$$

Funzione di partizione vincolata

$$Z(\vec{R}_1,\vec{R}_2) \propto Tr_1\left[Tr_2\left[e^{-\beta H}\, \delta\left(\vec{R}_1 - \frac{1}{M}\sum_{i=1}^{M}\vec{r}_{1i}\right)\delta\left(\vec{R}_2 - \frac{1}{M}\sum_{i=1}^{M}\vec{r}_{2i}\right)\right]\right]$$

$$Z = \int d\vec{R}_1 \int d\vec{R}_2\, Z(\vec{R}_1,\vec{R}_2)$$

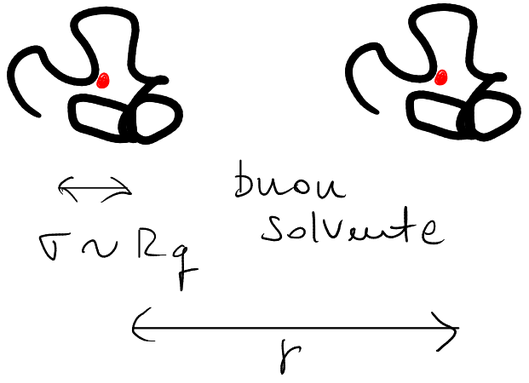
$$U_{eff}(\vec{R}_1,\vec{R}_2) \equiv -K_B T \ln Z(\vec{R}_1,\vec{R}_2) \qquad Z(\vec{R}_1,\vec{R}_2) = e^{-\beta U_{eff}}$$

$$U_{eff} \equiv \tilde{U}^{(0)} + \tilde{U}^{(2)}(|\vec{R}_1 - \vec{R}_2|) \quad \text{con} \quad \tilde{U}^{(2)} \to 0 \ \text{se} \ |\vec{R}_1 - \vec{R}_2| \to \infty$$

$p(\vec{R}_1, \vec{R}_2) \sim e^{-\beta U_{eff}} \Rightarrow U_{eff}$ energia libera di Landau

Esempi di potenziali effettivi di coppia

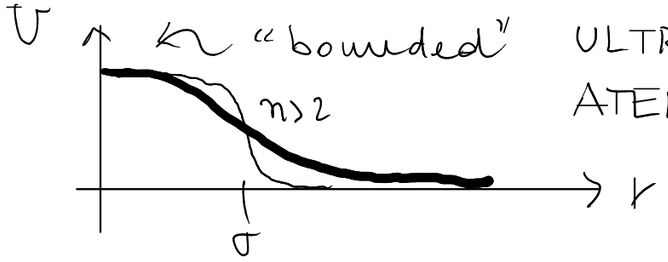
1. Polimeri lineari



Stillinger 1976
Gaussian core model (GCM)

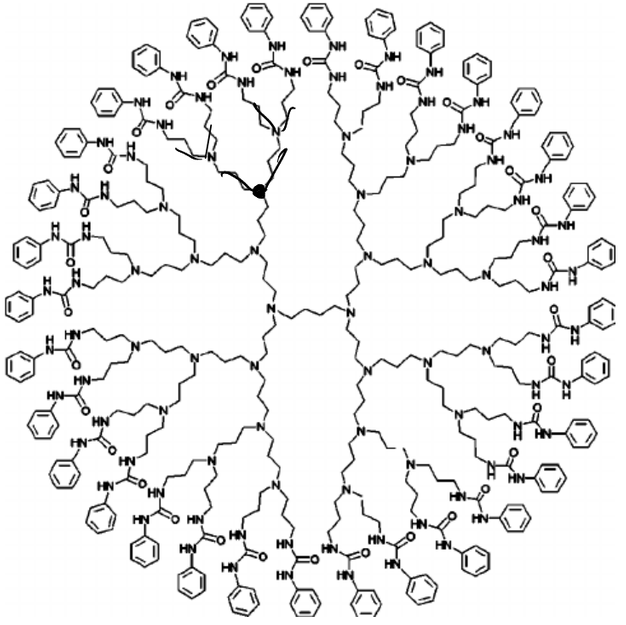
$$U(r) \approx \epsilon \exp\left[-\left(r/\sigma\right)^2\right]$$

$\epsilon \sim K_B T$



ULTRASOFFICE
ATERMICO

2. Dendrimeri



Likos, Ballauff
2005

$$U \approx \epsilon \exp\left[-\left(r/\sigma\right)^n\right]$$

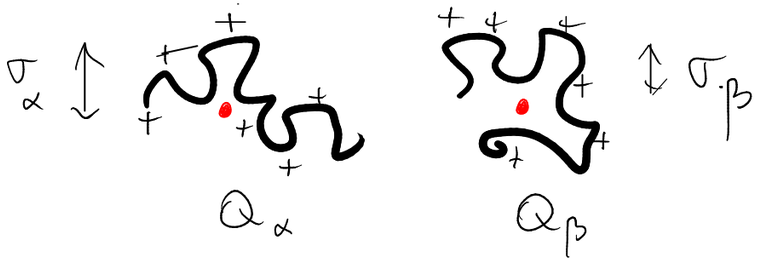
$n \sim 3-4$

Generalized exponential model (GEM)

$$U = \begin{cases} \epsilon & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

Penetrable sphere model (PSM)

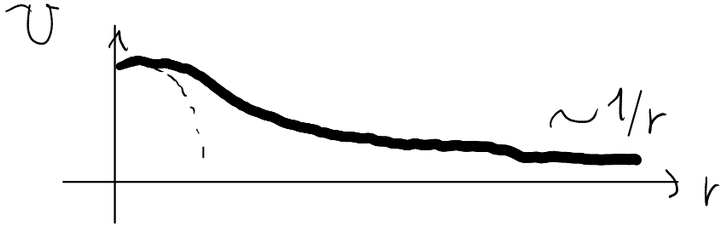
3. Polielettroliti



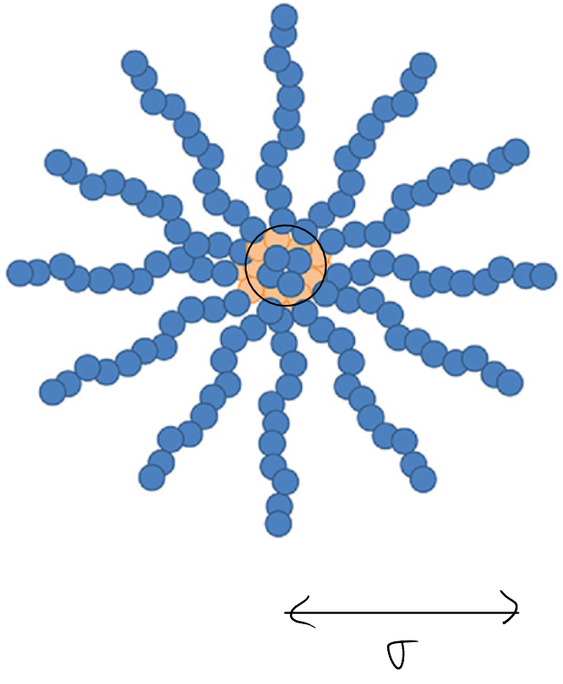
$$U(r) = \frac{Q_\alpha Q_\beta}{\varepsilon} \frac{\operatorname{erf}\left(\frac{r}{2\sigma}\right)}{r}$$

$\sigma_\alpha = \sigma_\beta = \sigma$

JCP '11

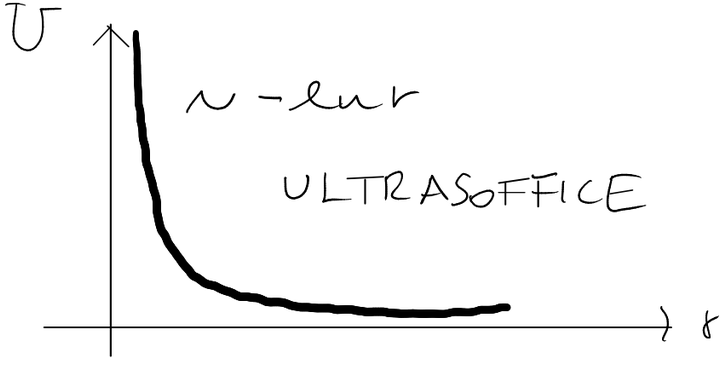


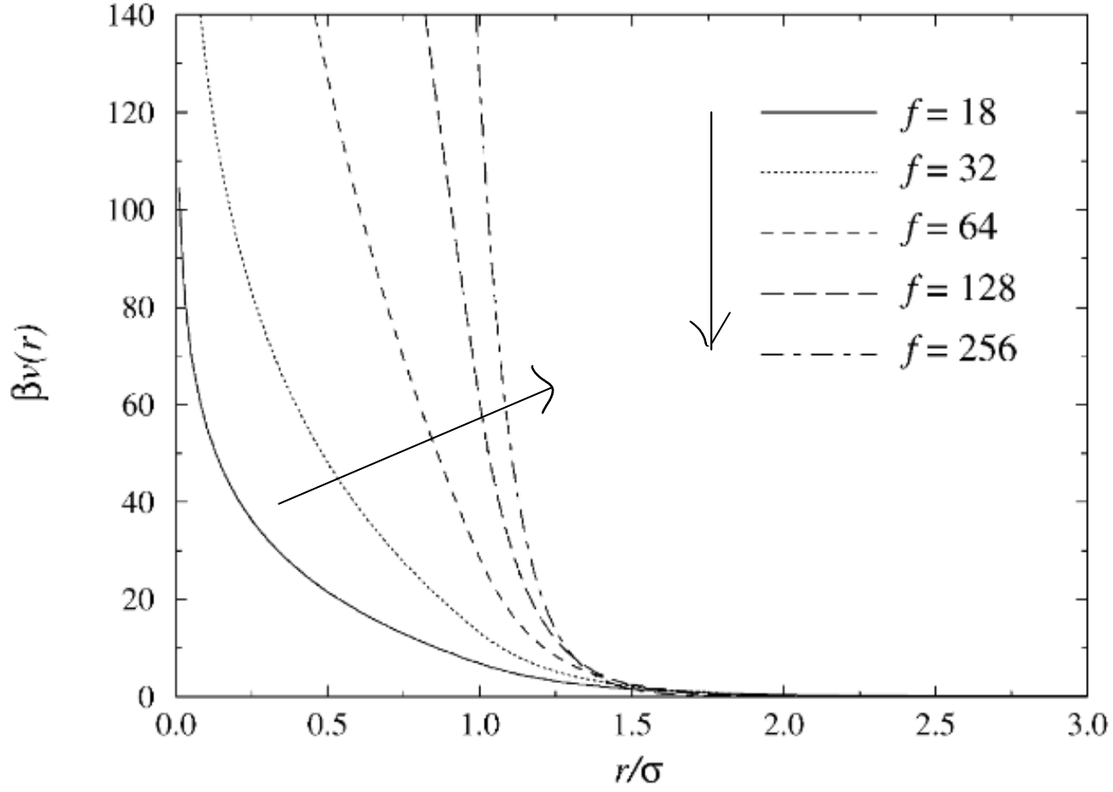
4. Polimeri a stella



f ≡ funzionalità

$$U(r) \sim \begin{cases} -\ln\left(\frac{r}{\sigma}\right) & r \lesssim \sigma \\ \frac{\exp\left(-\frac{r-\sigma}{\sigma}\right)}{r} & r > \sigma \end{cases}$$




140
120
100
80
60
40
20
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
βv(r)
r/σ
f = 18
f = 32
f = 64
f = 128
f = 256

Likos 2001