

CLASSICAL vs. QUANTUM

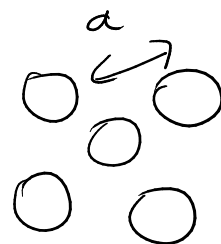
Lunghezza d'onda

$$\lambda = \frac{h}{p} = \sqrt{\frac{h^2}{3m k_B T}}$$

$$\langle \frac{p^2}{2m} \rangle = \frac{3}{2} k_B T$$

$$p = \sqrt{\langle p^2 \rangle} = \sqrt{3m k_B T}$$

Distanza tipica tra particelle



$$g = \frac{N}{V} \rightarrow a = g^{-1/3}$$



De Broglie
1923

Lunghezza d'onda
termica di Broglie

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

Approx classica ok se

$$\Lambda \lesssim a$$

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

INTERAZIONI EFFETTIVE

Effettive: eliminiamo gradi di libertà



INTERAZIONI EFFETTIVE TRA ATOMI E MOLECOLE

Interazioni interatomiche

Energia potenziale d'interazione tra N atomi

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

\uparrow campo esterno \uparrow 2 corpi \uparrow 3 corpi \rightarrow ML

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

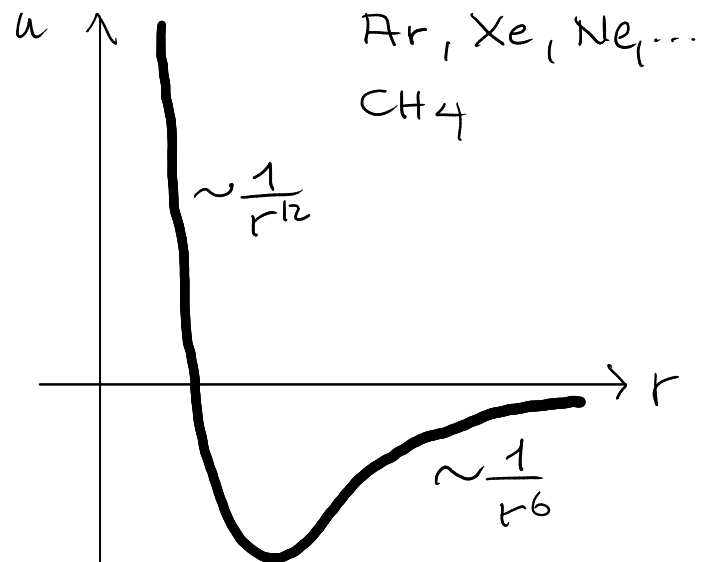


Additività a coppie:

$$U \approx \sum_{i=1}^N \sum_{j>i}^N u_2(|\vec{r}_i - \vec{r}_j|) \rightarrow \text{trascuro termini a più corpi}$$

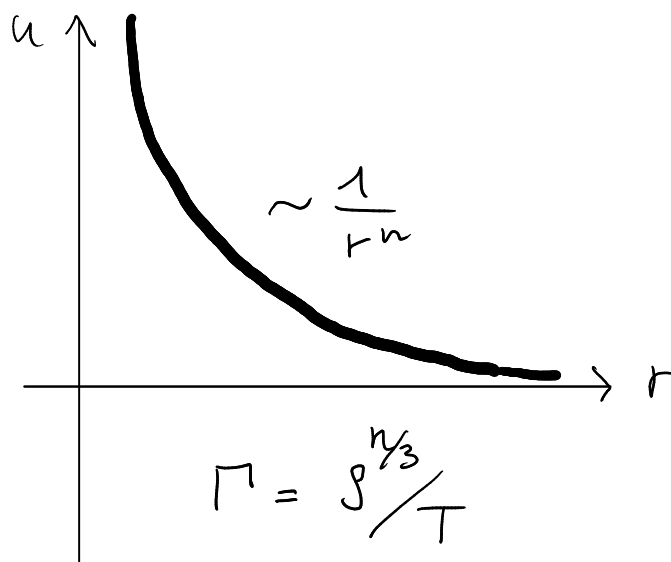
$$U \approx \sum_{i=1}^N \sum_{j>i}^N \tilde{u}_2(|\vec{r}_i - \vec{r}_j|) \rightarrow \text{li inglobo in maniera effettiva}$$

1) Lennard - Jones



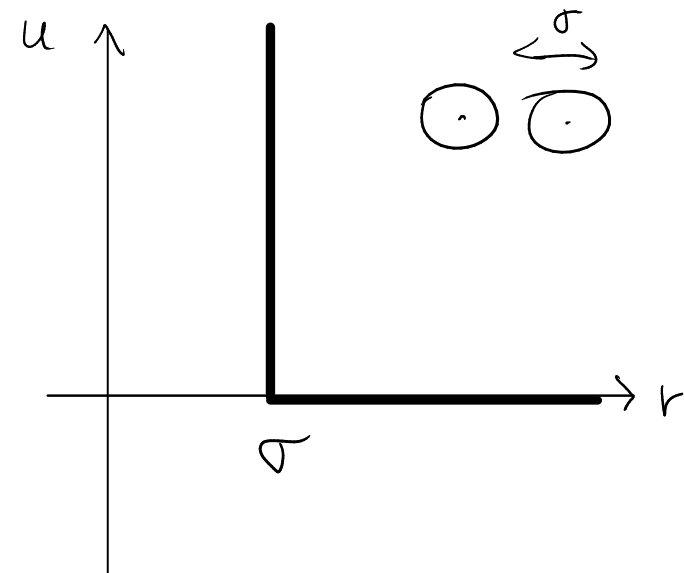
$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

2) Sfere soffici

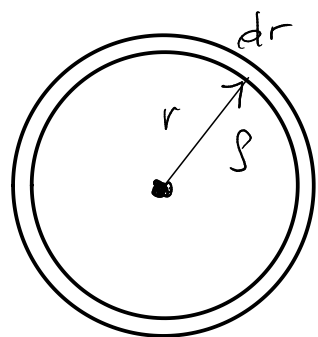


$$u(r) = \epsilon \left(\frac{\sigma}{r}\right)^n$$

3) Sfere dure



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



Portata delle interazioni

$$\frac{U}{N} \approx \int_0^\infty d\vec{r} \rho u(r) \sim \rho \int_0^\infty dr r^{d-1} \frac{1}{r^n} \sim \int_0^\infty dr \frac{1}{r^{n-d+1}}$$

$$n - d + 1 > 1 \Rightarrow n > d \quad [n > 3]$$

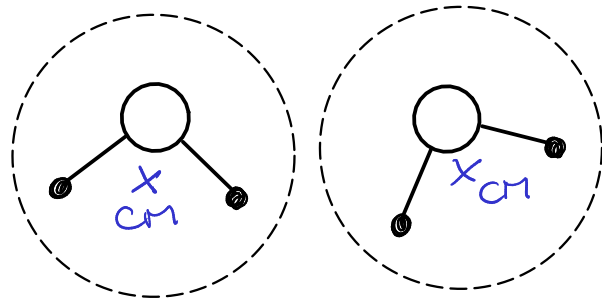
Complessità computazionale

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

$$\rightarrow \frac{N(N-1)}{2} \sim N^2 \rightarrow O(N^2)$$

se $u(r)$ è a corto raggio $\rightarrow O(N)$

Interazioni intermolecolari



α

β

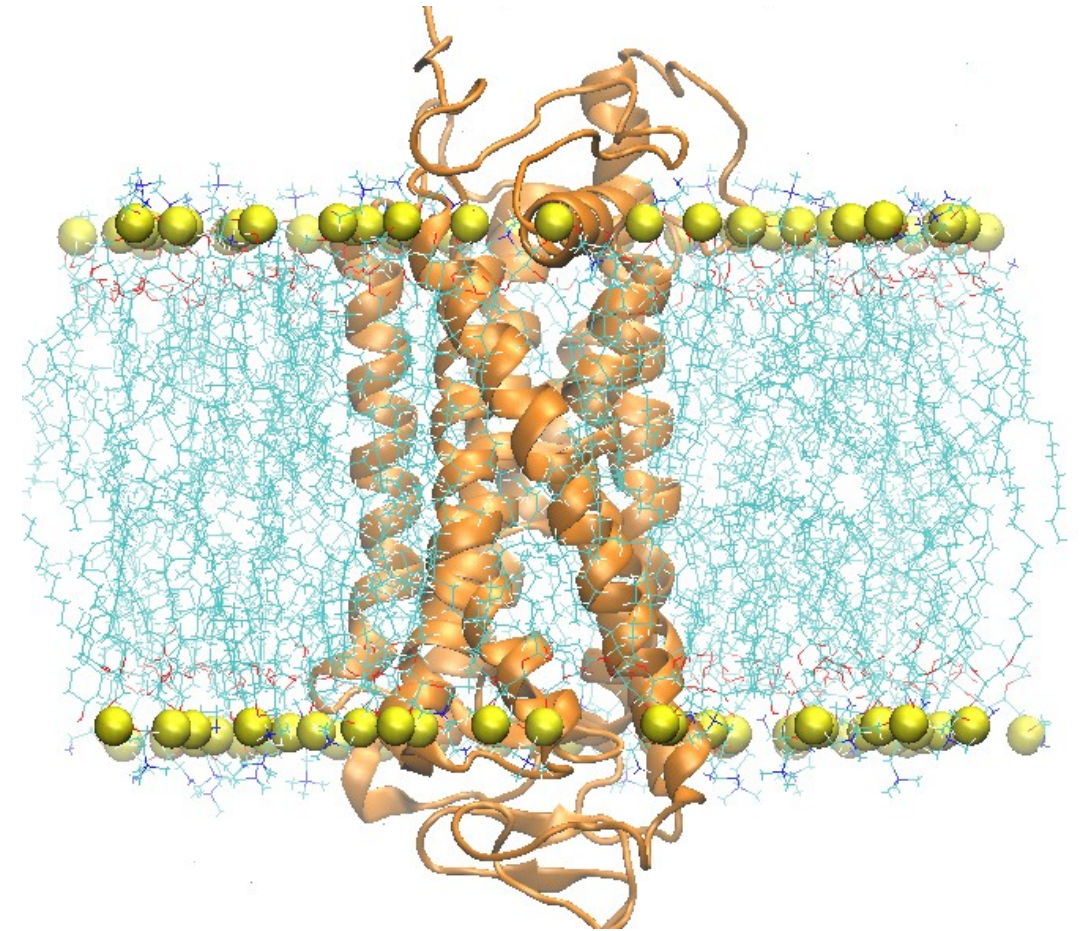
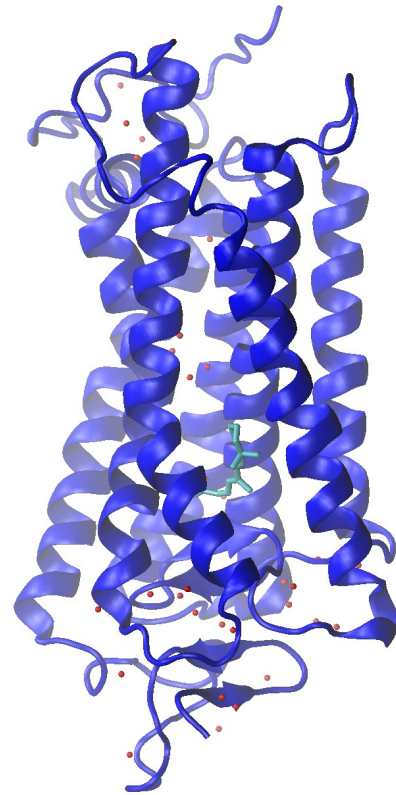
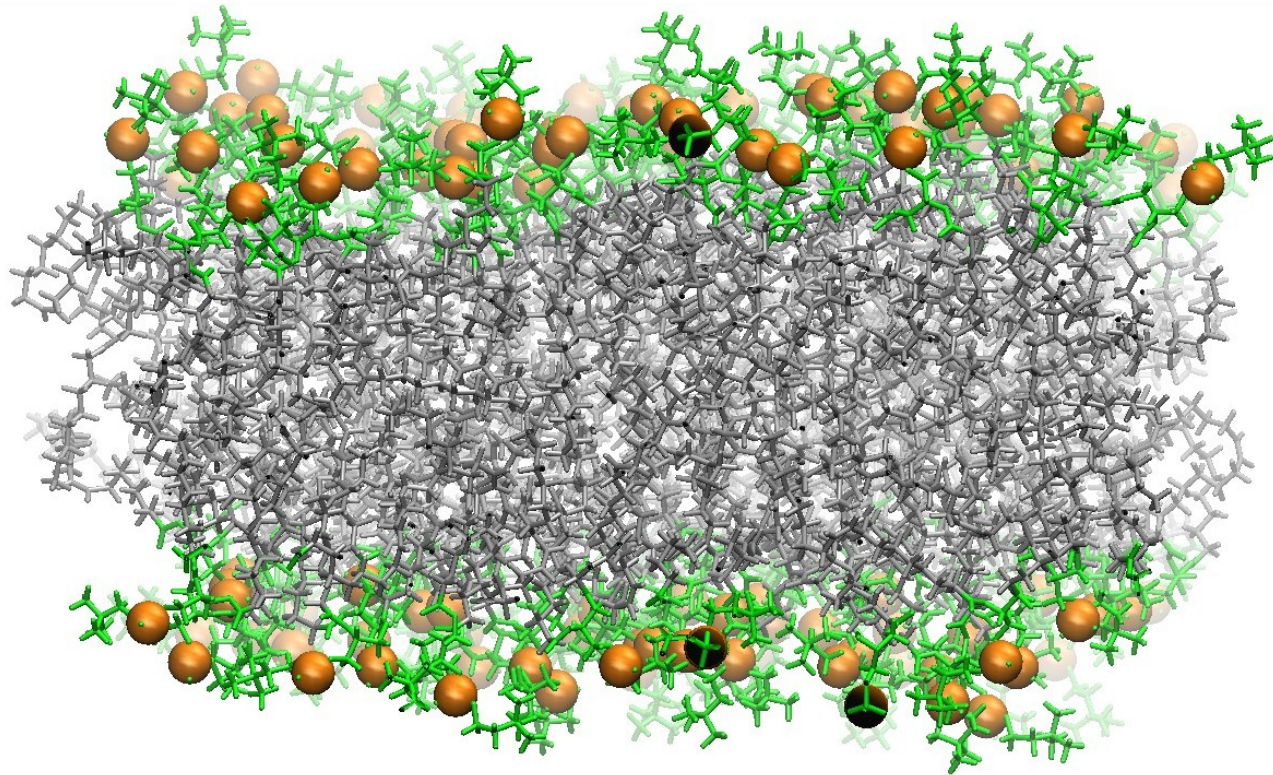
campo di forze
(FORCE-FIELD)

$$U = \underbrace{U_{\alpha\alpha} + U_{\beta\beta}}_{\text{intramolecolari}} + \underbrace{U_{\alpha\beta}}_{\text{intermolecolare}}$$

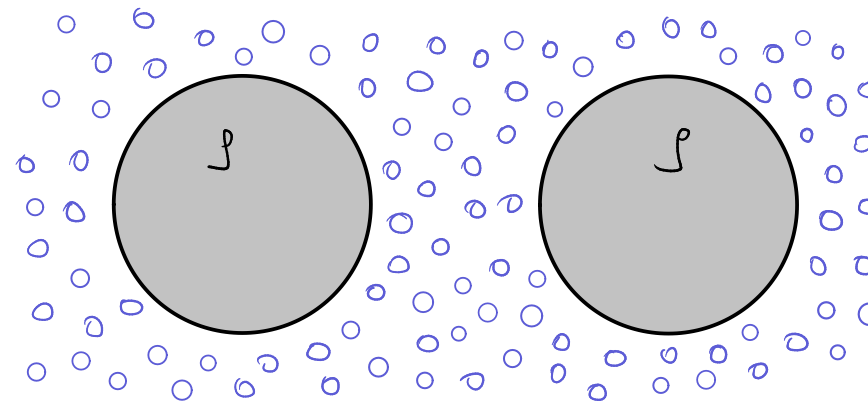
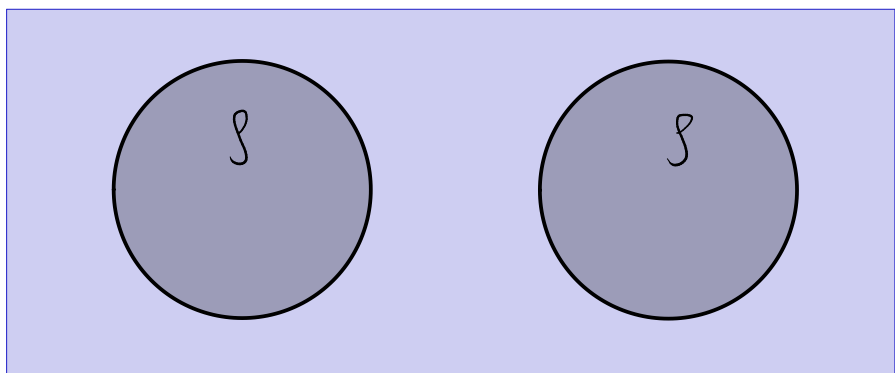
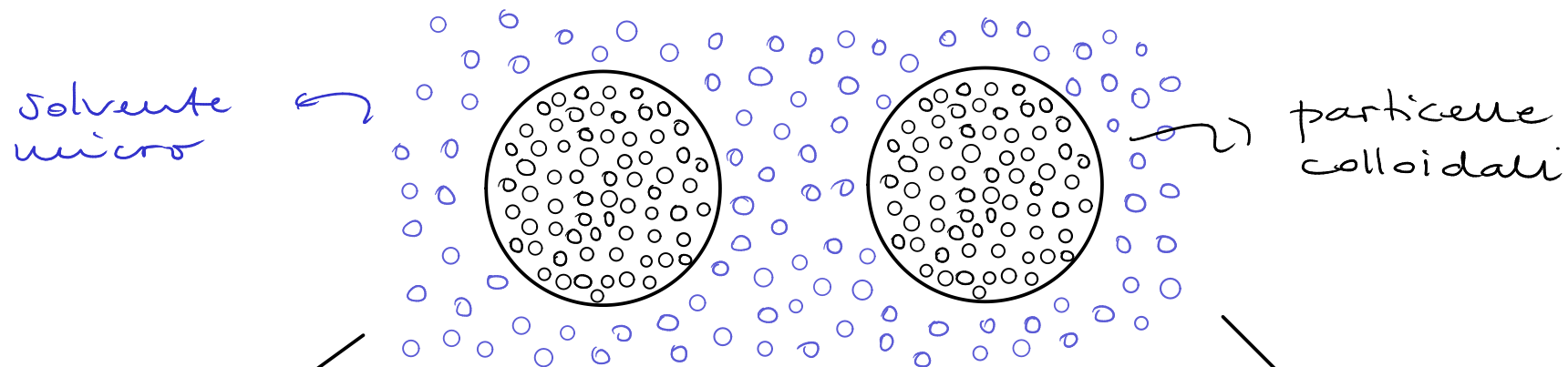
2C, 3C, 4C, LJ
(i, i+1) (i, i+1, i+2) ...

LJ, Coulomb

Campi di forze classici : AMBER, CHARMM, ...

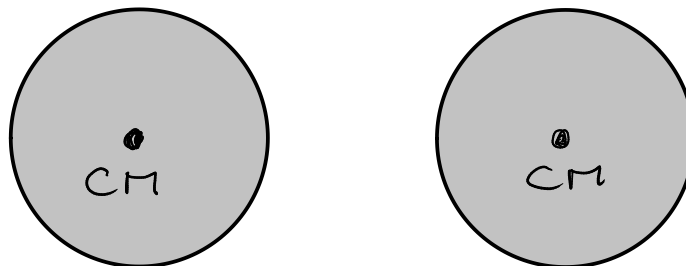


INTERAZIONI EFFETTIVE TRA COLLOIDI



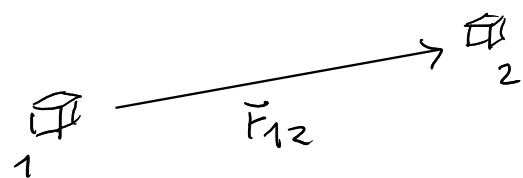
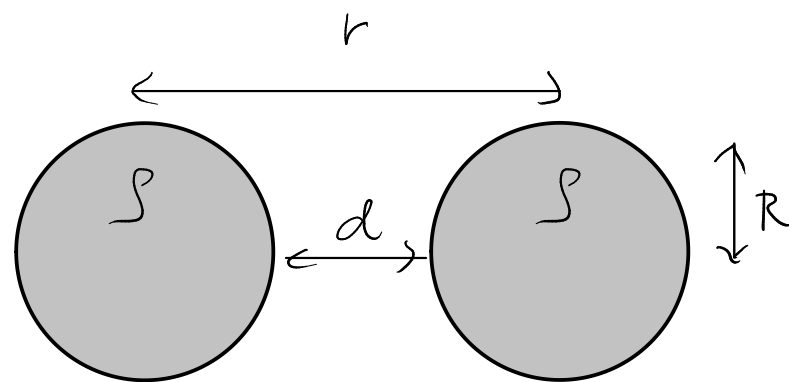
- 1) vdw
- 2) elettrostatiche

particelle
e
solvente
=
mezzi continui



- traccia sui defs
micro
- 3) deplezione

Interazioni di van der Waals



fluttuazione dipolo \rightarrow dipolo indotto

$$u_{\text{vdw}}(r) = - \frac{C}{r^6} \rightarrow \text{polarizzabilità}$$

\uparrow
attrattive

Energia potenziale totale:

$$U = \int_{V_1} d\vec{r}_1 \int_{V_2} d\vec{r}_2 g^2 u(|\vec{r}_{12}|)$$

$$U_{\text{vdw}}(r) = - \frac{A}{6} \left[\frac{2R^2}{r^2 - (2R)^2} + \frac{2R^2}{r^2} + \ln \left(1 - \frac{(2R)^2}{r^2} \right) \right] \quad \text{Hamaker 1937}$$

1) $r = 2R + d$: $d \ll \sigma$

$$U_{\text{vdw}}(r) \approx - \frac{A}{12} \frac{R}{d} = - \frac{A}{12} \frac{R}{|r - 2R|} \sim \frac{1}{|r - 2R|}$$

2) $d \gg \sigma$

$$U_{\text{vdw}}(r) \approx - \frac{A}{36} \left(\frac{2R}{r} \right)^6 \sim \frac{1}{r^6}$$

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

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

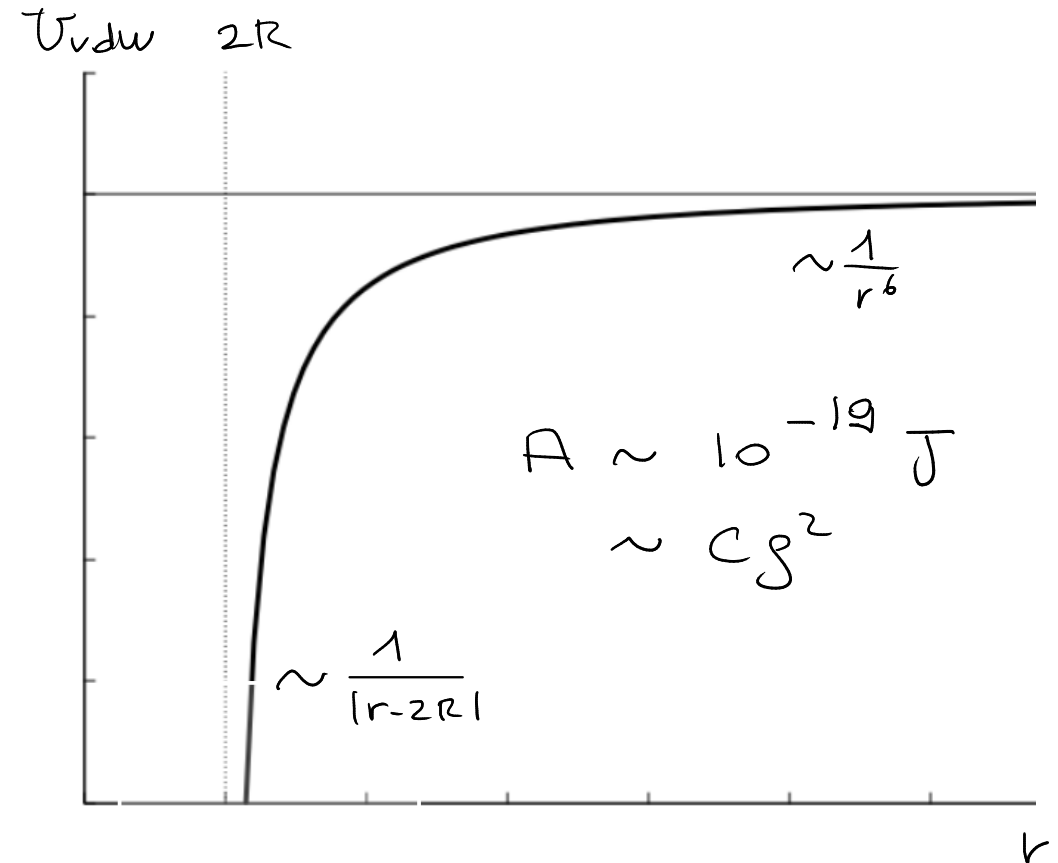
$$\approx \frac{x^2}{2} (1+x^2+x^4) + \frac{x^2}{2} - x^2 - \frac{x^4}{2} - \frac{x^6}{3} = \frac{x^2}{2} + \frac{x^4}{2} + \frac{x^6}{2} + \frac{x^2}{2} - x^2 - \frac{x^4}{2} - \frac{x^6}{3} = \frac{x^6}{6} = \frac{1}{6} \left(\frac{2R}{r}\right)^6$$

$$U_{vdw}(r) \sim \frac{1}{|r-2R|} \quad d \ll \sigma$$

$$U_{vdw}(r) \sim \frac{1}{r^6} \quad d \gg \sigma$$

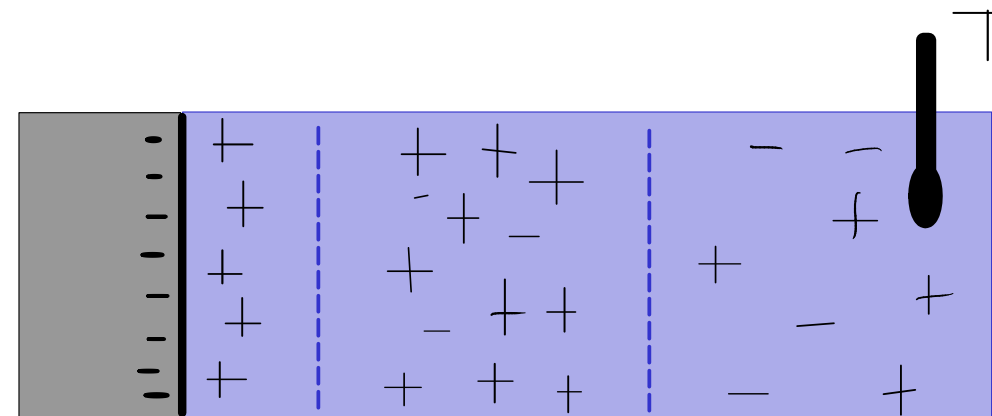
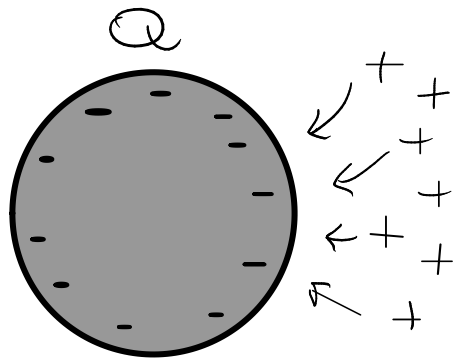
Approssimazioni:

- additività a coppie
- corpi rigidi $f = \text{cost}$
- no effetti relativistici ($\sim \frac{1}{r^7}$)
- no solvente $C = C(n_c - n_s) \rightarrow$ index matching



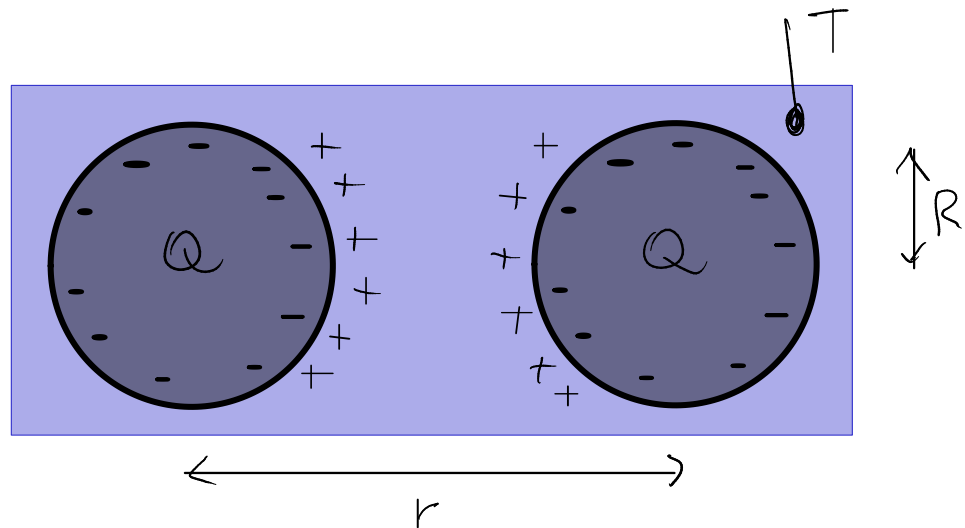
Interazioni elettrostatiche

- colloidi carichi Q
- ioni in soluzione q
- Solvente $\epsilon = \epsilon_r \epsilon_0$



Approccio Poisson - Boltzmann

- $\nabla^2 \phi = - \frac{\rho_e}{\epsilon}$
- $\rho_e(\vec{r}) \approx \rho_0 \exp\left(-\frac{q\phi(\vec{r})}{k_B T}\right)$
- approx. Debye - Hückel: $|q\phi| \ll k_B T$



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

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

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

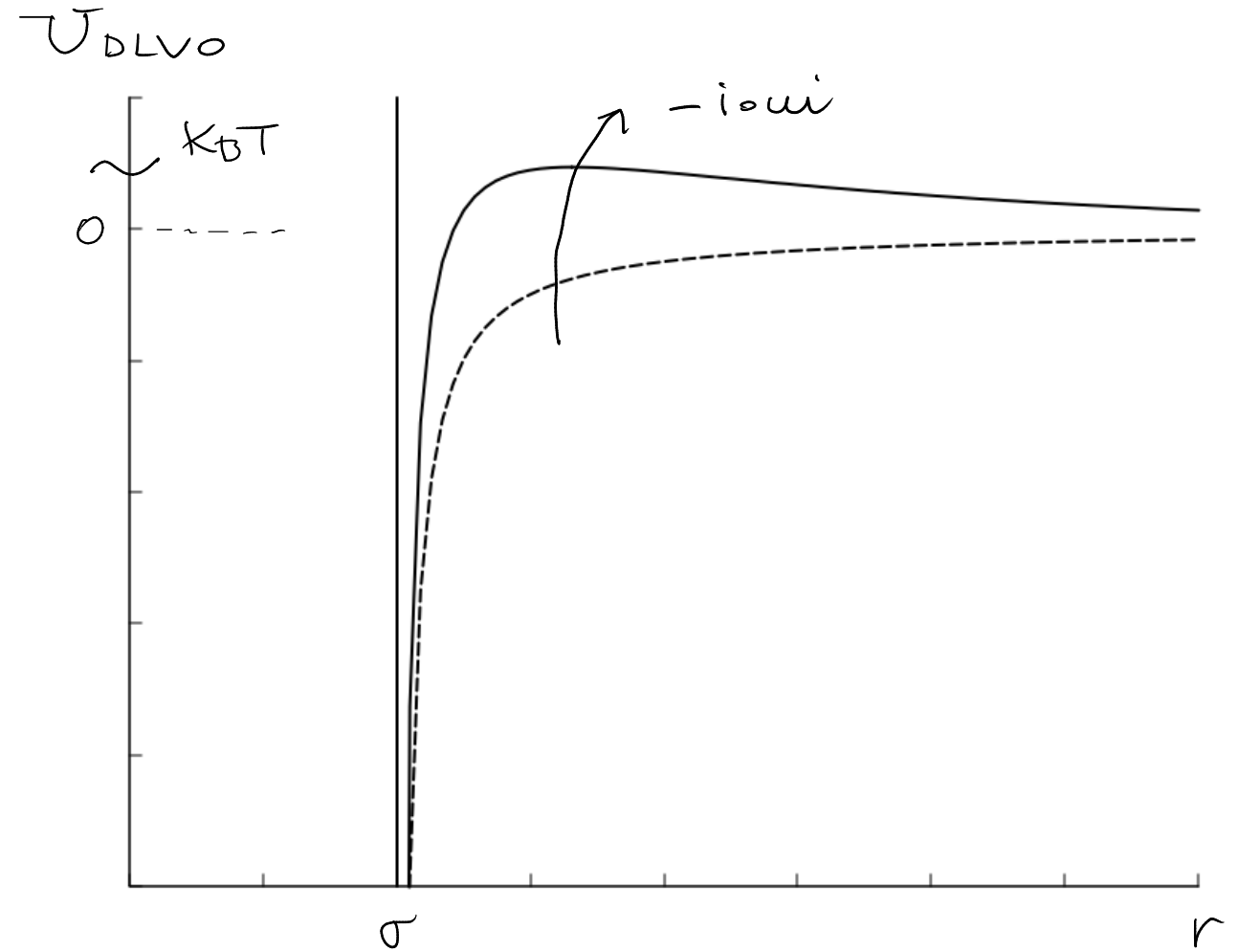
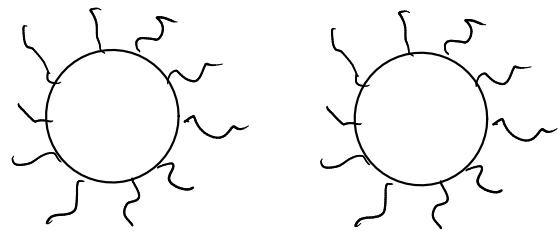
Potenziale DLVO (Derjaguin, Landau, Verwey, Overbeek)



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

stabilizzazione di carica

stabilizzazione sterica



INTERAZIONI EFFETTIVE

MICRO

MESO

Atomi

Molecole

Colloidi

Polimeri

LJ SS HS
 ••••

AMBER, CHARMM
 ••••

solvente
continuo

solvente
discreto



VDW

EL

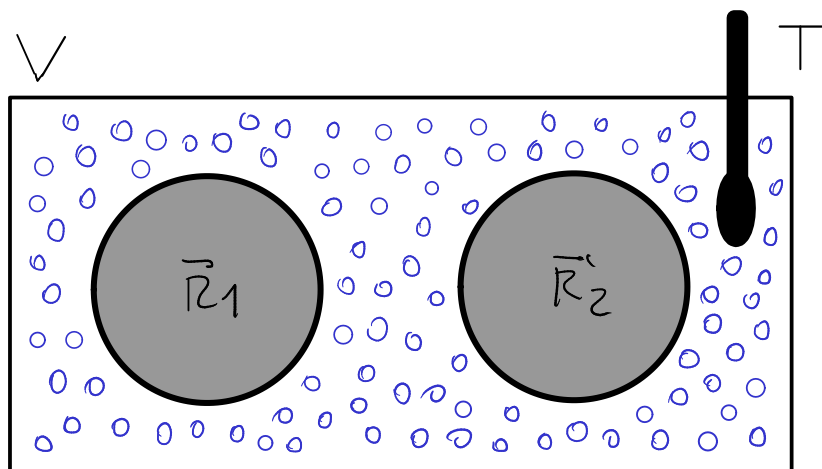
Deplezione

DLVO

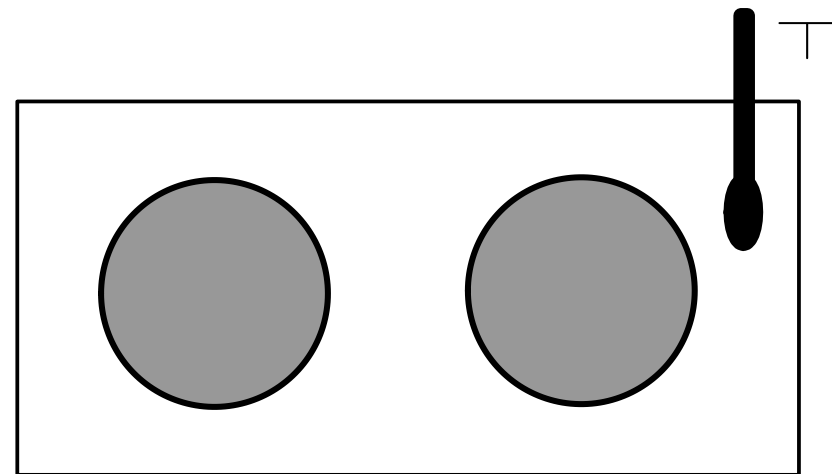
AO

Interazioni effettive tra colloidali

Miscela fortemente asimmetrica : particelle colloidali + Solvente



traccia \rightarrow



- N_c colloidali $\{ \vec{R}_i, \vec{P} \}$
- N_s solvente $\{ \vec{F}_i, \vec{p} \}$
- V, T equilibrio

Hamiltoniana

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

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

Funzione di partizione

$$\begin{aligned} Z &= \text{Tr}_c \left[\text{Tr}_s \left[e^{-\beta (H_c + H_s + U_{cs})} \right] \right] \\ &= \text{Tr}_c \left[e^{-\beta H_c} \underbrace{\text{Tr}_s \left[e^{-\beta (H_s + U_{cs})} \right]}_{Z_s(\{\vec{R}\})} \right] \end{aligned}$$

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

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

Sistema effettivo \rightarrow hamiltoniana effettiva

$$H_{\text{eff}}(\{\vec{R}, \vec{P}\}) = K_c(\{\vec{P}\}) + \underbrace{U_c(\{\vec{R}\})}_{\substack{\uparrow \\ \text{interazione} \\ \text{diretta}}} + \underbrace{F_s(\{\vec{R}\})}_{\substack{\uparrow \\ \text{interazione} \\ \text{mediata}}}$$

\rightarrow dipendono dallo stato termodinamico

H_{eff} conserva :

- termodinamica
- osservabili medie statiche

$$\Theta(\{\bar{\pi}, \vec{P}\})$$

(es.)

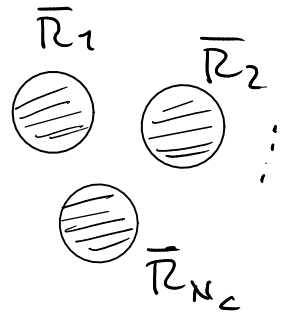
$$\langle \Theta \rangle = \frac{\text{Tr}_c [\Theta \exp(-\beta H_{\text{eff}})]}{\text{Tr}_c [\exp(-\beta H_{\text{eff}})]}$$

Interazioni effettive a 2 corpi

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

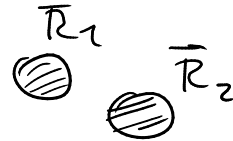
↑
termini di
volume $\rightarrow V, N_S$

⚠ termodinamica



Approx additività a coppie:

$$H_{\text{eff}} \approx K_c + U_c + F_S^{(0)} + F_S^{(2)}$$



OK se sistema diluito

$$N_c = 2 \quad ; \quad \bar{R}_1, \bar{R}_2, \vec{P}_1, \vec{P}_2$$

$$H_{\text{eff}} = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + U_c(|\bar{R}_1 - \bar{R}_2|) + F_S(\bar{R}_1, \bar{R}_2)$$

↑
vdw, EL, ...

$\{P\}$ $\{\vec{r}\}$ $\{\bar{R}_1, \bar{R}_2, \vec{r}\}$
 ↓ ↓ ↓

$$Z_S(\bar{R}_1, \bar{R}_2) = \text{Tr}_S [e^{-\beta(H_S + U_{cs})}] = \text{Tr}_S [e^{-\beta(K_S + U_S + U_{cs})}]$$

$$\begin{aligned}
&= \frac{1}{h^{3N_s} N_s!} \int d\vec{p}^{N_s} \int d\vec{r}^{N_s} e^{-\beta [K_s(\{\vec{p}\}) + U_s(\{\vec{r}\}) + U_{cs}(\vec{R}_1, \vec{R}_2, \{\vec{r}\})]} \\
&= \left(\frac{V^{N_s}}{h^{3N_s} N_s!} \int d\vec{p}^{N_s} e^{-\beta K_s} \right) \left(\frac{1}{V^{N_s}} \int d\vec{r}^{N_s} e^{-\beta (U_s + U_{cs})} \right) \\
&= Z_s^{\text{id}} \cdot Z_s^{\text{c}} \\
&\quad \uparrow \qquad \qquad \uparrow \\
&\quad \text{gas ideale} \qquad \text{configurazionale}
\end{aligned}$$

$$F_s(\vec{R}_1, \vec{R}_2) = F_s^{\text{id}} + F_s^{\text{c}} = -k_B T \ln Z_s^{\text{id}} - k_B T \ln Z_s^{\text{c}}$$

$$Z_s^{\text{id}} = \frac{V^{N_s}}{\Lambda^{3N_s} N_s!}$$

$$F_s^{\text{id}} = -k_B T [N_s \ln V - N_s \ln \Lambda^3 - \ln N_s!]$$

$$= -k_B T N_s [\ln V - \ln \Lambda^3 - \ln N_s + 1]$$

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

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

$$= k_B T \cdot \boxed{V} \left[g_S \ln(g_S \Lambda^3) - g_S \right] \quad \square$$

$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$
 volume

$$F_S(\bar{R}_1, \bar{R}_2) = F_S^{\text{id}} + \tilde{U}^{(0)} + \tilde{U}^{(2)}(|\bar{R}_1 - \bar{R}_2|)$$

Hamiltoniana effettiva

$$H_{\text{eff}} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + U_c(|\bar{R}_1 - \bar{R}_2|) + F_S^{\text{id}} + \tilde{U}^{(0)} + \tilde{U}^{(2)}(|\bar{R}_1 - \bar{R}_2|)$$

$$= K_c + F_S^{\text{id}} + \tilde{U}^{(0)} + \underbrace{U_c(|\bar{R}_1 - \bar{R}_2|) + \tilde{U}^{(2)}(|\bar{R}_1 - \bar{R}_2|)}_{\text{potenziale effettivo di coppia}}$$

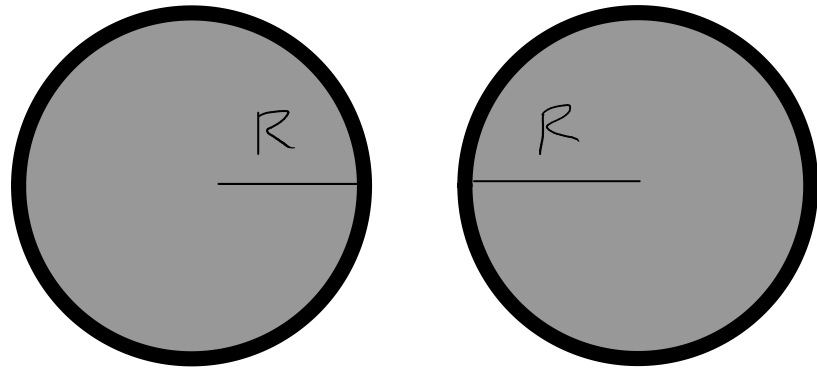
\downarrow
 volume

Forze di deplezione

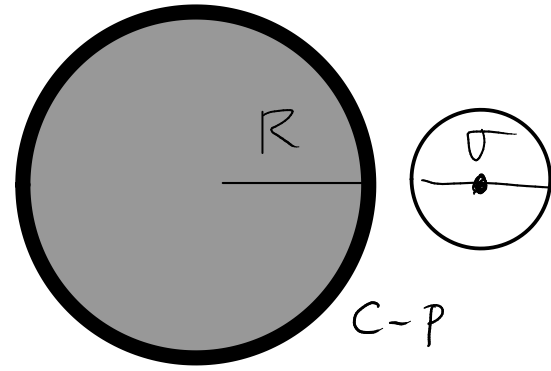
Miscela fortemente asimmetrica: **colloidi** + **polimeri** in un buon solvente

→ effetti di volume escluso

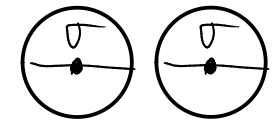
$$\downarrow \\ \sigma \approx 2Rg$$



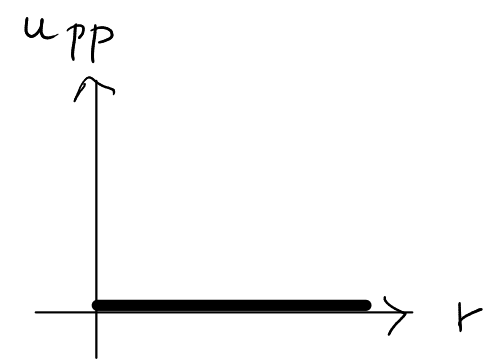
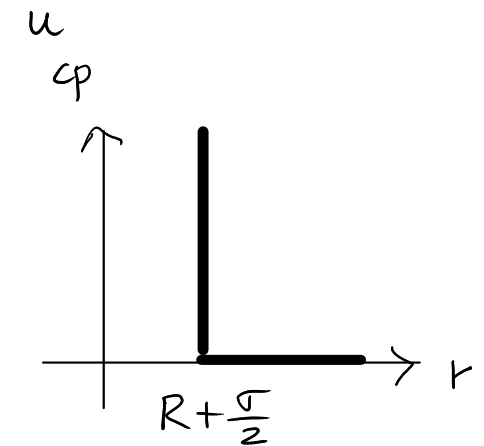
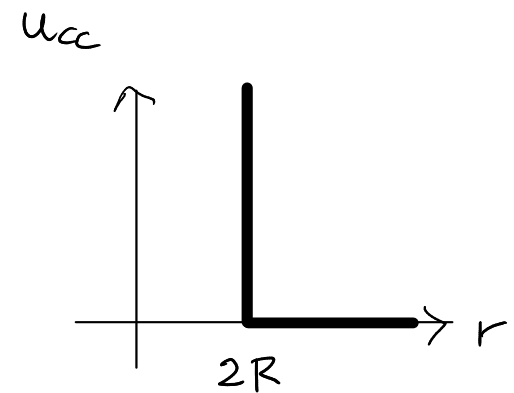
C-C
sfera dura

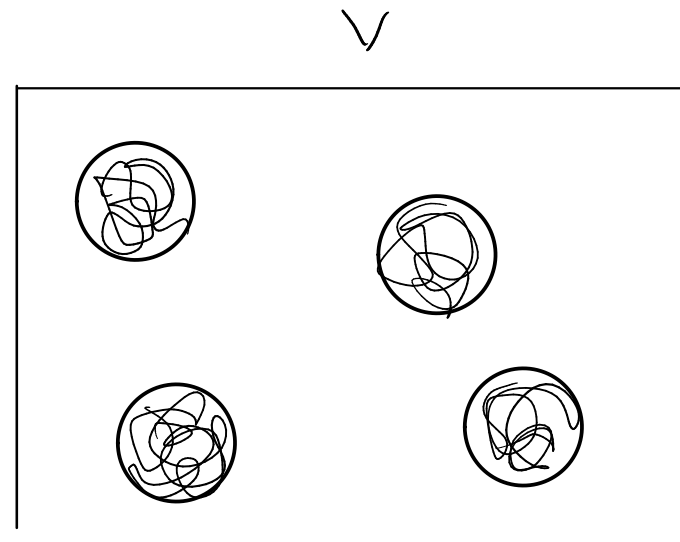


C-P
sfera dura

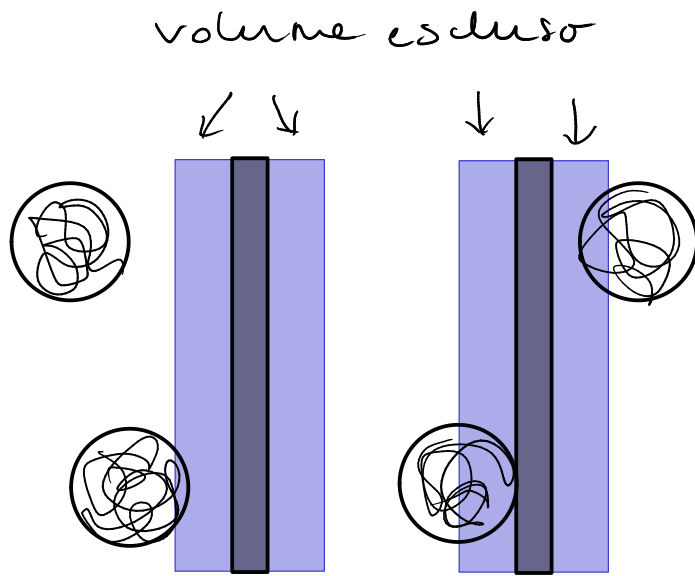


P-P
gas non interagente

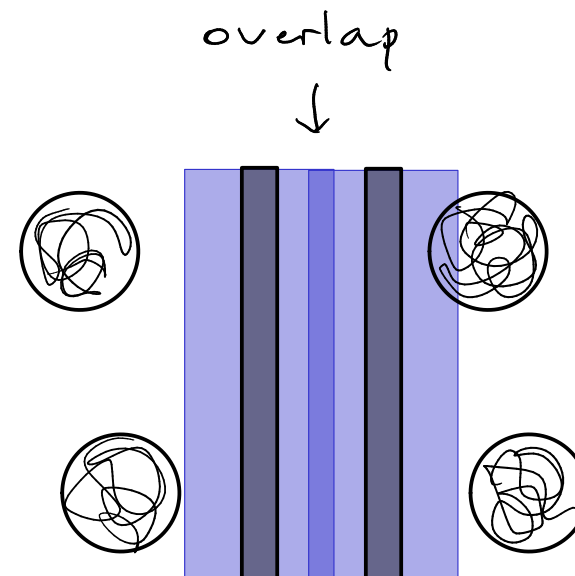




F_p



$\nearrow F_p$



$\searrow F_p$

\Downarrow

attrattivo

INTERAZIONI EFFETTIVE

MICRO

MESO

Atomi

Molecole

Colloidi

Polimeri

LJ

SS
.....

HS

AMBER, CHARMM
.....

solvente
continuo

solvente
discreto

polimeri lineari
dendrimeri
polimeri a stella
polielettroliti

VDW

EL

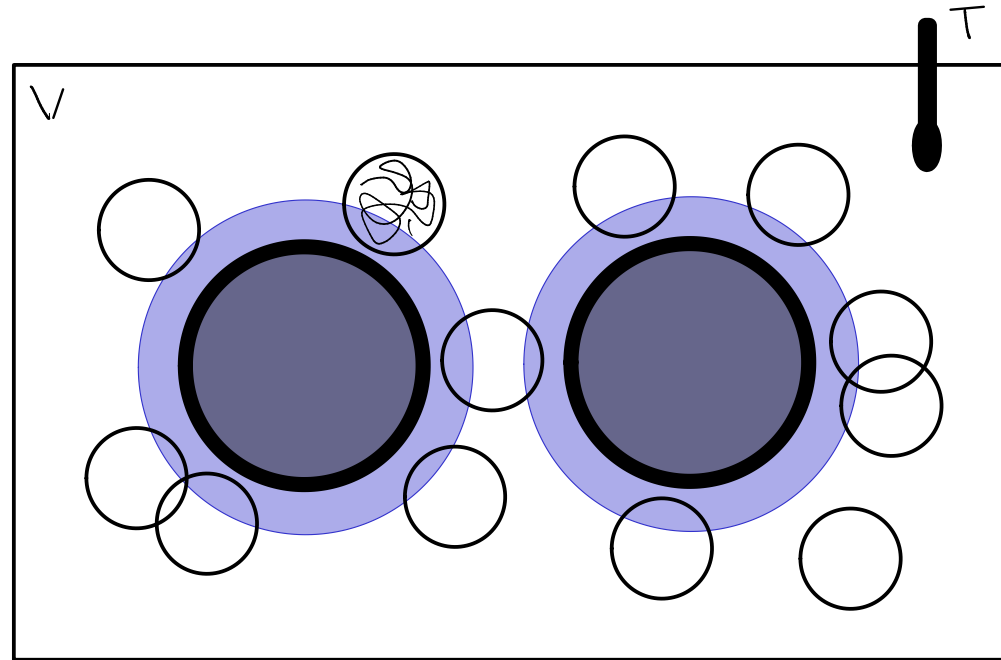
Deplezione

DLVO

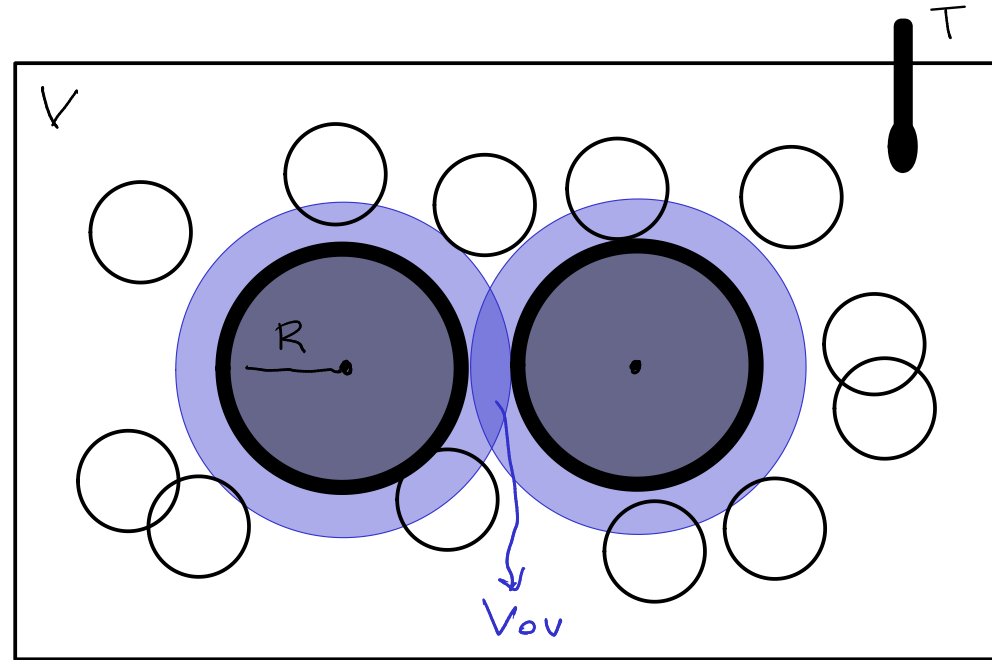
AO

Potenziale di Asakura-Oosawa:

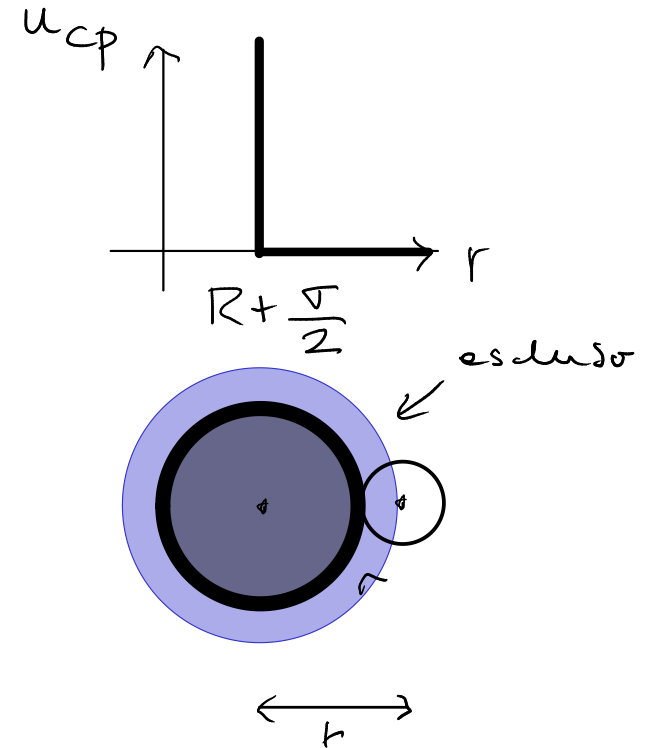
$$N_c = 2 \quad \{\bar{R}_1, \bar{R}_2\} \quad N_p \equiv N \quad \{\bar{F}_i, \bar{P}_i\} \quad i=1, \dots, N$$



$$r > 2R + \sigma = D$$



$$\leftarrow r \rightarrow$$



$$Z_p(\bar{R}_1, \bar{R}_2) = \frac{1}{h^{3N} N!} \int d\bar{P}^N \int d\bar{F}^N \exp[-\beta (H_p + U_{cp}(\{\bar{F}_i\}, \bar{R}_1, \bar{R}_2))]]$$

$$Z_p^{id} = \frac{V^N}{\Lambda^{3N} N!}$$

$$Z_p^c = \frac{1}{V^N} \int d\bar{F}^N \exp[-\beta (U_p(\{\bar{F}_i\}) + U_{cp}(\{\bar{F}_i\}, \bar{R}_1, \bar{R}_2))]]$$

$$Z_p = Z_p^{id} \cdot Z_p^c$$

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

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

$= \begin{cases} 1 & \text{fuori da volume escluso} \\ 0 & \text{dentro il volume escluso} \end{cases}$

$$F_P(\vec{r}_1, \vec{r}_2) = F_P^{\text{id}} + F_P^c = F_P^{\text{id}} - N k_B T \ln \left[\frac{V - V_e}{V} \right]$$

$$r > 2R + \sigma = D \quad : \quad V_e = 2 \cdot \frac{4}{3} \pi \left(\frac{D}{2} \right)^3 = \frac{\pi}{3} D^3 = 2 \frac{\pi}{6} D^3$$

$$2R < r < D \quad : \quad V_e = 2 \frac{\pi}{6} D^3 - V_{ov}$$

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

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

$$F_p^c(\bar{R}_1, \bar{R}_2) = -N k_B T \ln \left[1 - \frac{\pi D^3}{6V} \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right) \right] \quad V_e \sim D^3 \ll V$$

$$\approx N k_B T \frac{\pi D^3}{6V} \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right)$$

$$= \underbrace{\rho}_{\uparrow} \cdot \underbrace{k_B T}_{\uparrow} \cdot \frac{\pi D^3}{6} \left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3} + c - c \right)$$

Stato termodinamico

$$= \tilde{U}^{(0)} + \tilde{U}_{A0}(|\bar{R}_1 - \bar{R}_2|)$$

$$\tilde{U}_{A0}(r=D) = 0$$

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

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

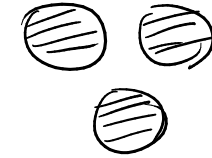
$$\tilde{U}_{A0}(r) = \rho \cdot k_B T \cdot \frac{\pi D^3}{6} \left(-1 + \frac{3r}{2D} - \frac{r^3}{2D^3} \right) = - \rho k_B T \frac{\pi D^3}{6} \left(1 - \frac{3r}{2D} + \frac{r^3}{2D^3} \right)$$

\Rightarrow forza di deplezione attrattiva

$$\tilde{U}_{A0} < 0 \quad r < D$$

$$H_{\text{eff}} = K_c + U_c(r) + F_p^{\text{id}} + \tilde{U}^{(0)} + \tilde{U}_{A0}(r) = K_c + F_p^{\text{id}} + \tilde{U}^{(0)} + \tilde{U}_{\text{eff}}(r)$$

$$U_{\text{eff}}(r) = \begin{cases} 0 & r > D \\ \tilde{U}_{A0}(r) & 2R < r \leq D \\ \infty & r \leq 2D \end{cases} \quad N_c > 2$$

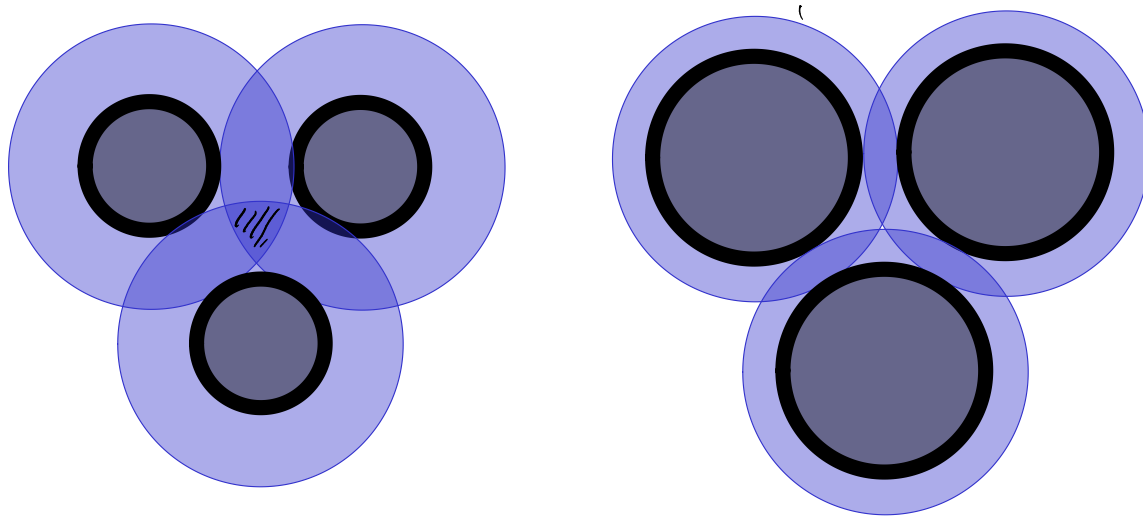


- Dato R , $\exists \sigma^* t.c. \sigma < \sigma^*$ non ci sono termini $F_c^{(n)}$ non nulli con $n > 2$

- 3-corpi è repulsivo

Sovrastimo V_{0v}

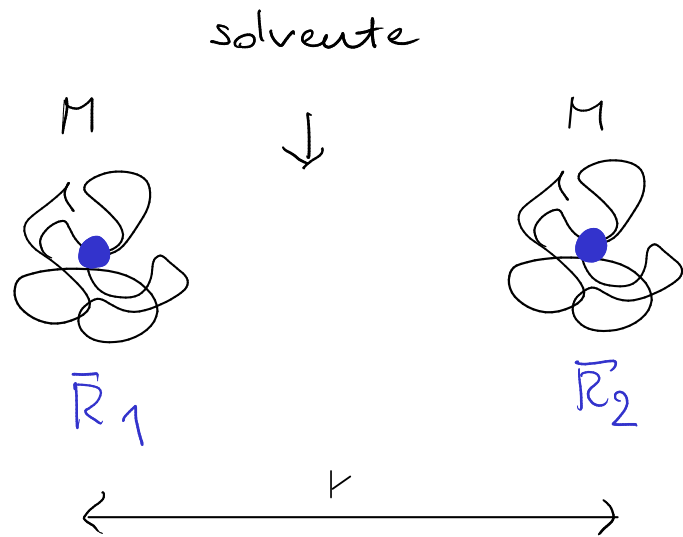
\Rightarrow sovrastimo F_c



$$F_c \approx F_c^{(0)} + F_c^{(2)} + F_c^{(3)}$$

\uparrow
 \tilde{U}_{A0}

INTERAZIONI EFFETTIVE TRA POLIMERI



Centri di massa di 1 e 2:

$$\{ \vec{F}_{1i} \}, \{ \vec{F}_{2i} \}$$

$$\bar{R}_1 = \frac{1}{M} \sum_{i=1}^M \vec{F}_{1i}$$

$$\bar{R}_2 = \frac{1}{M} \sum_{i=1}^M \vec{F}_{2i}$$

Hamiltoniana:

$$H = H_1 + H_2 + U_{12}$$

Funzione di partizione vincolata

$$Z(\bar{R}_1, \bar{R}_2) = \text{Tr}_1 \left[\text{Tr}_2 \left[e^{-\beta H} \delta\left(\bar{R}_1 - \frac{1}{M} \sum_{i=1}^M \vec{F}_{1i}\right) \delta\left(\bar{R}_2 - \frac{1}{M} \sum_{i=1}^M \vec{F}_{2i}\right) \right] \right]$$

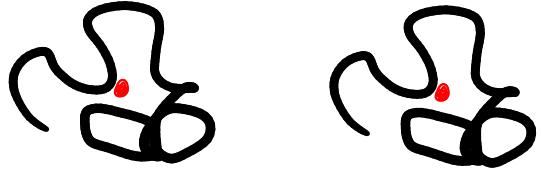
$$Z = \int d\bar{R}_1 \int d\bar{R}_2 Z(\bar{R}_1, \bar{R}_2)$$

$$\mapsto \tilde{U}^{(2)}(r) \rightarrow 0 \quad r \rightarrow \infty$$

$$U_{\text{eff}}(|\bar{R}_1 - \bar{R}_2|) = -k_B T \ln Z(\bar{R}_1, \bar{R}_2) = \tilde{U}^{(0)} + \tilde{U}^{(2)}(|\bar{R}_1 - \bar{R}_2|)$$

Esempi di potenziali effettivi di coppia

1. Polimeri lineari



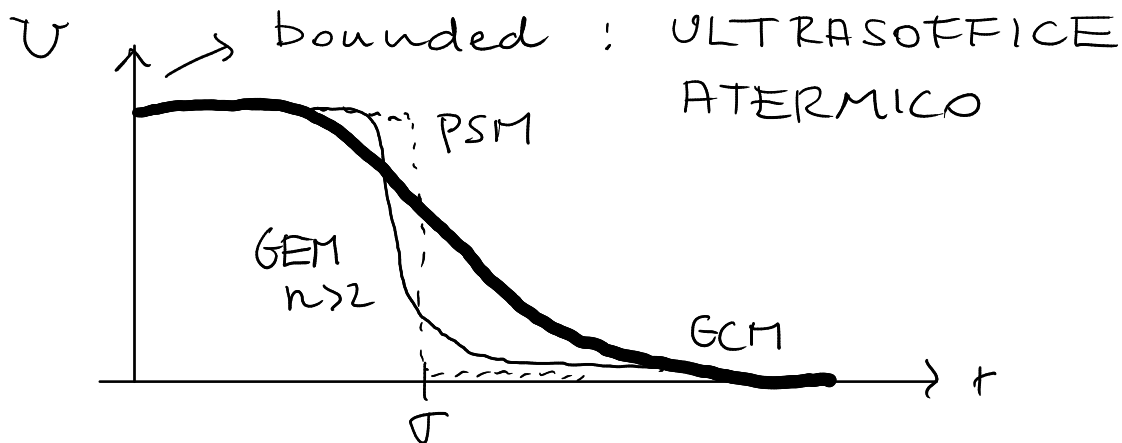
$$\sigma \sim R_g$$

170 Stillinger
Gaussian core
model (GCM)

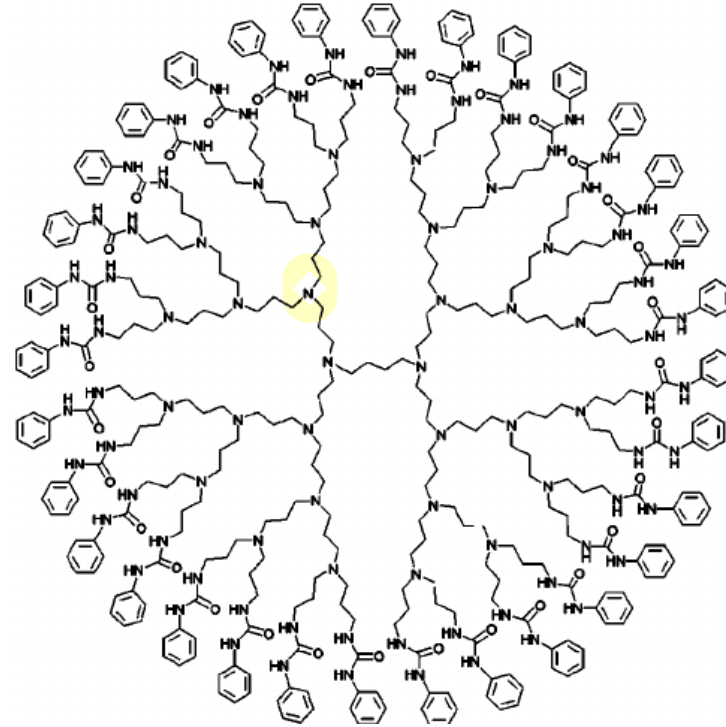
$$U(r) = \epsilon \exp\left[-\left(\frac{r}{\sigma}\right)^2\right]$$

$$\uparrow$$

$$\epsilon \sim k_B T$$



2. Dendrimeri



Likos, Ballauff
2005

$$U(r) = \epsilon \exp\left[-\left(\frac{r}{\sigma}\right)^n\right]$$

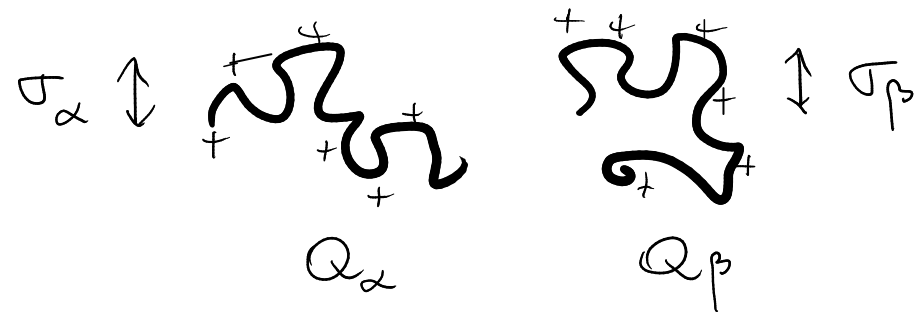
Generalized
exponential
model (GEM)

$$n \approx 3-4$$

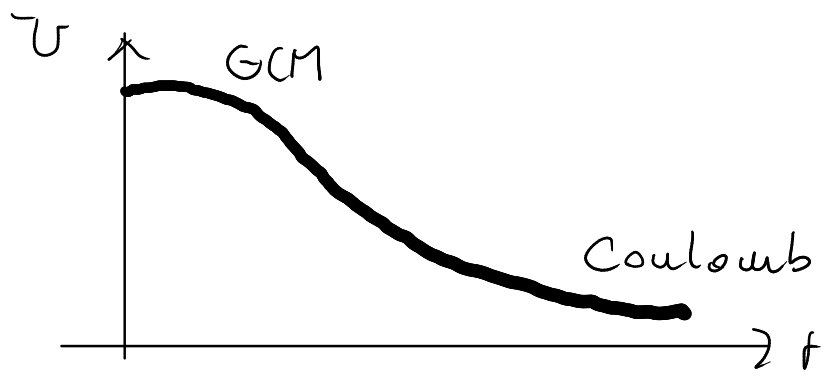
$$U(r) = \begin{cases} \epsilon & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

Penetrable
sphere
model (PSM)

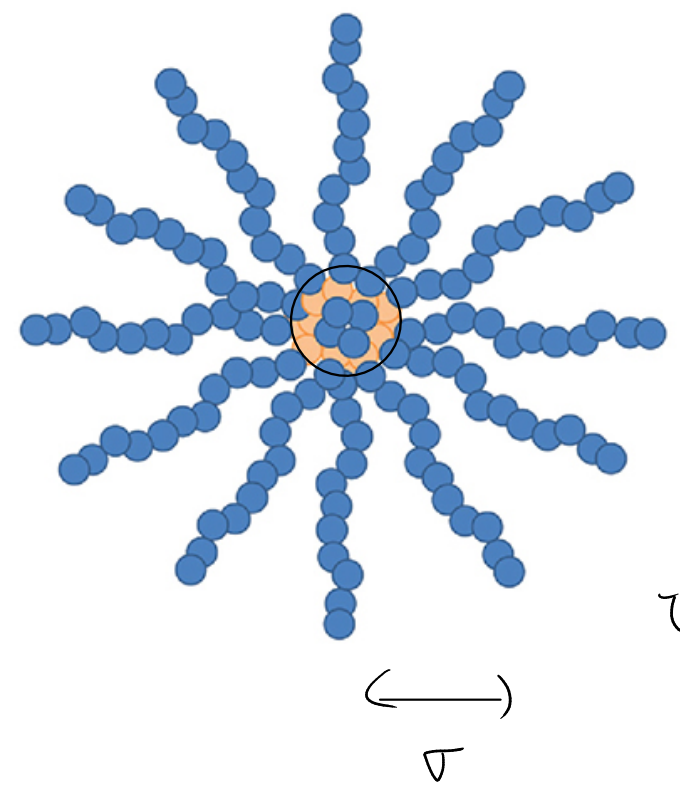
3. Polielettroliti



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

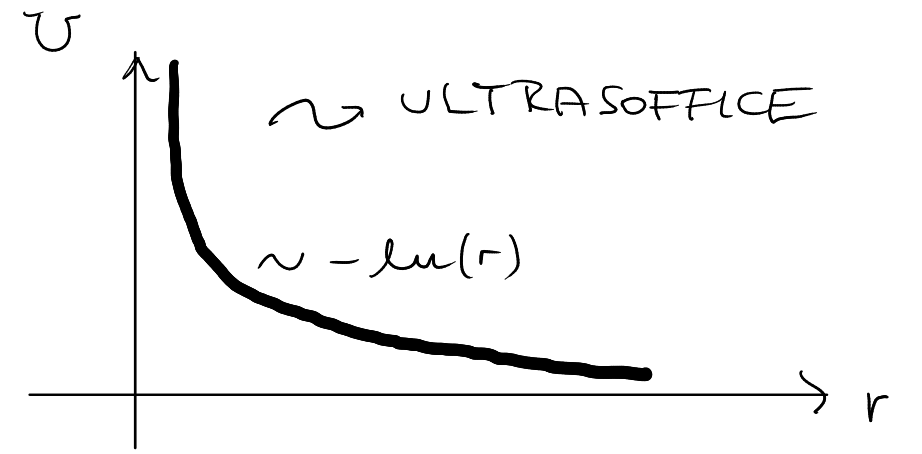


4. Polimeri a stella



$f = n. \text{ braccia}$

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

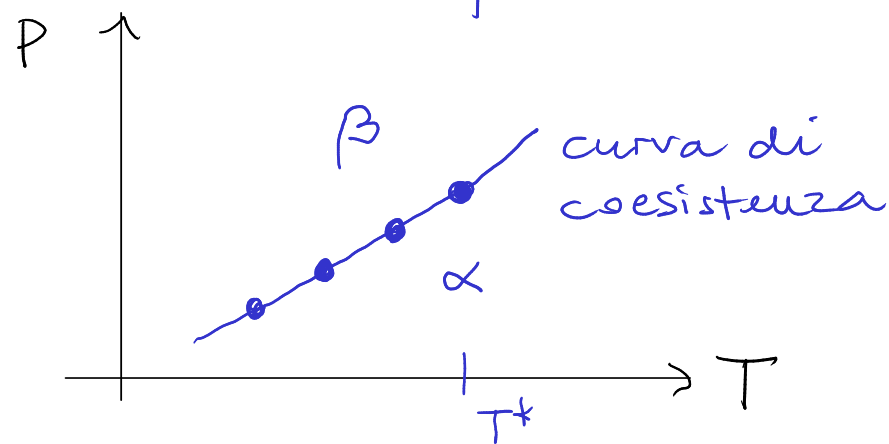
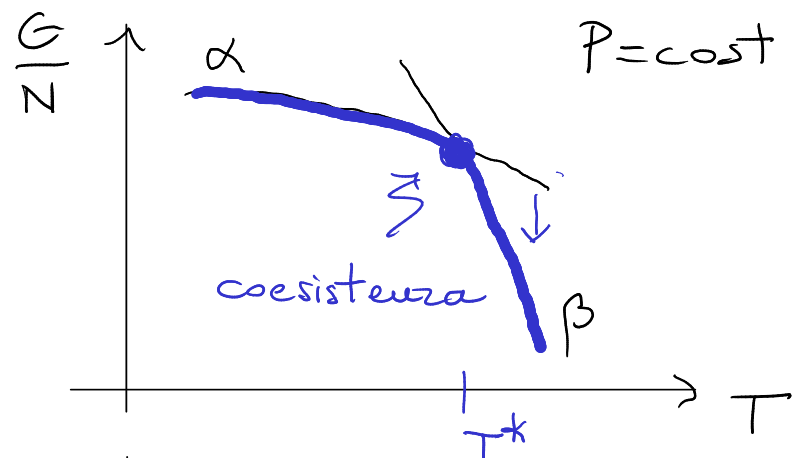


DIAGRAMMI DI FASE

α β coesistenza di fase : $T_\alpha = T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha = \mu_\beta$

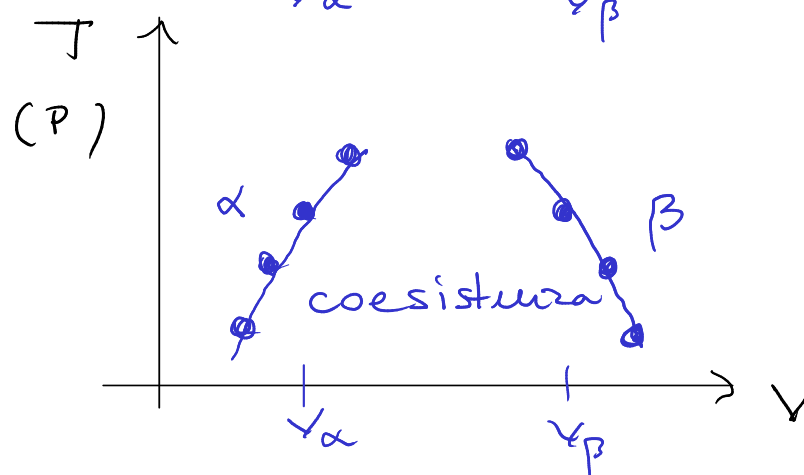
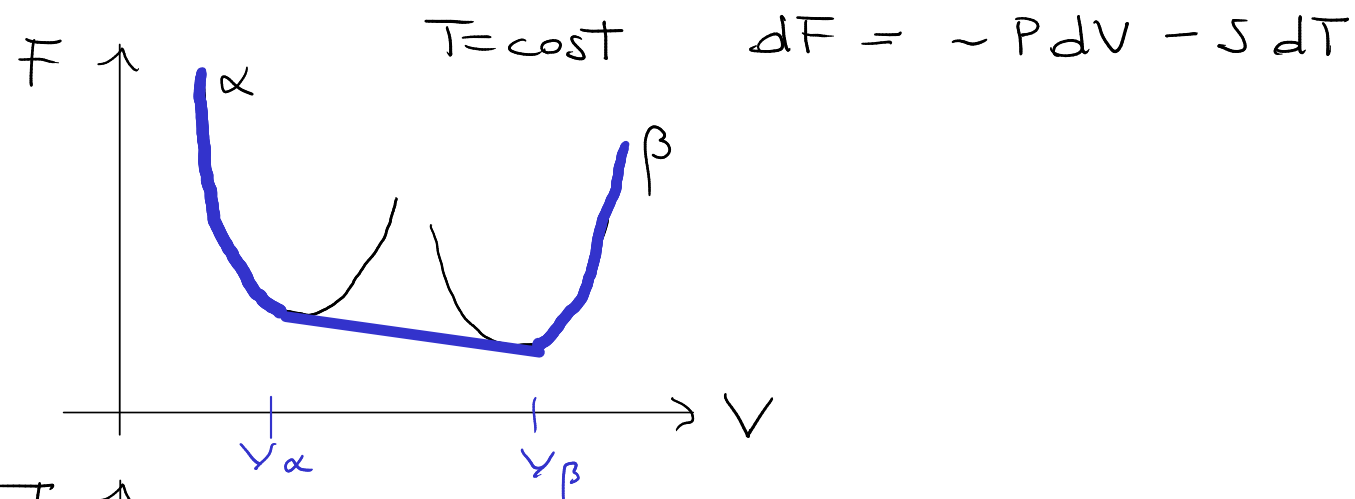
1. **Potenziale di Gibbs** : $G = E - TS + PV$

Se P, T fissate, equilibrio = $\min \{G\}$



2. **Potenziale di Helmholtz** : $F = E - TS$

Se V, T fissati, equilibrio = $\min \{F\}$



Equazione di Clausius-Clapeyron

Eq. differenziale per la pressione di coesistenza $P = P(T)$

$$\frac{dP}{dT} = \frac{L_{\alpha \rightarrow \beta}}{(v_{\beta} - v_{\alpha}) T}$$

$\left\{ \begin{array}{l} L_{\alpha \rightarrow \beta} = \text{calore latente } \alpha \rightarrow \beta \\ v_{\alpha}, v_{\beta} = \text{volumi specifici} \end{array} \right.$

$$v = \frac{V}{N}$$

Costruzione della tangente comune

$$\left\{ \begin{array}{l} \frac{dF}{dV} \Big|_{V_{\alpha}} = \frac{dF}{dV} \Big|_{V_{\beta}} \quad (P_{\alpha} = P_{\beta}) \\ F(V_{\alpha}) = F(V_{\beta}) + \frac{dF}{dV} \Big|_{V_{\beta}} (V_{\alpha} - V_{\beta}) \end{array} \right.$$

$$F(V_{\alpha}) - \frac{dF}{dV} \Big|_{V_{\beta}} V_{\alpha} = F(V_{\beta}) - \frac{dF}{dV} \Big|_{V_{\beta}} V_{\beta}$$

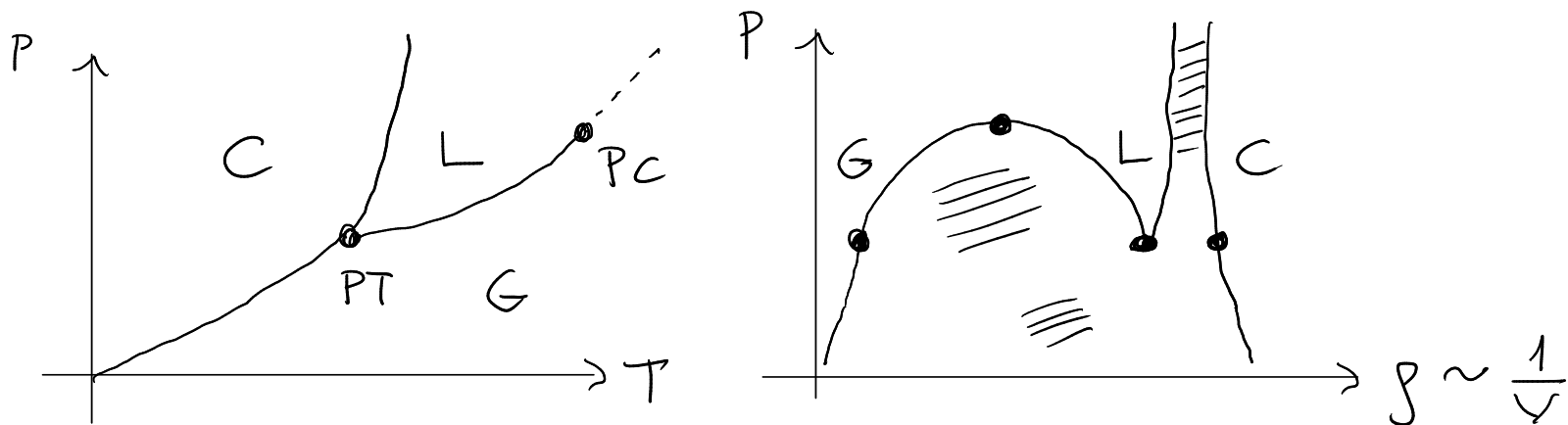
$$F_{\alpha} + P_{\alpha} V_{\alpha} = F_{\beta} + P_{\beta} V_{\beta}$$

$$G_{\alpha} = G_{\beta}$$

TOPOLOGIA DEI DIAGRAMMI DI FASE

Sistemi atomici / molecolari

1. Sistemi "normali" (es. Argon)

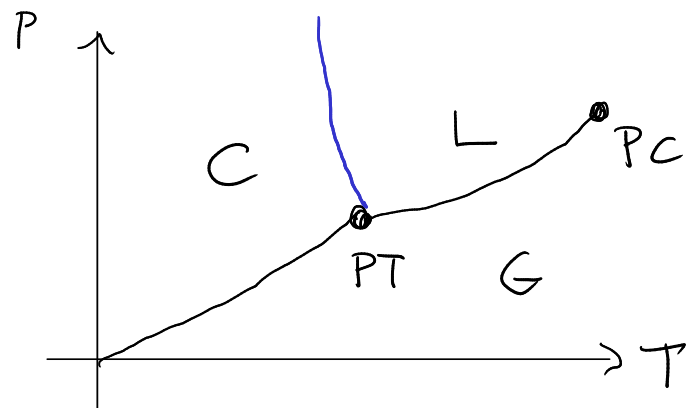


Coesistenza C-L $\alpha=C, \beta=L$

$$\frac{dP}{dT} = \frac{L_{CL}}{(v_L - v_C)T} > 0$$

$$v_L > v_C \quad \rho_L < \rho_C$$

2. Sistemi "anomali" (es. H₂O, Si, Ge, ...)

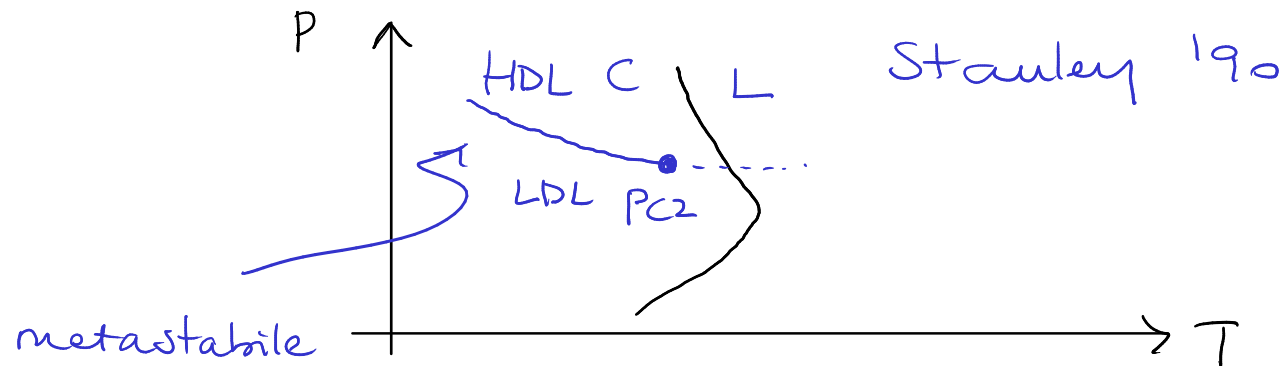


$$\frac{dP}{dT} < 0 !!$$

$$\rho_L > \rho_C$$

$$v_L - v_C < 0$$

3. Transizioni liquido-liquido (es. H₂O, Si, Ge, S, P, ...)



Princeton

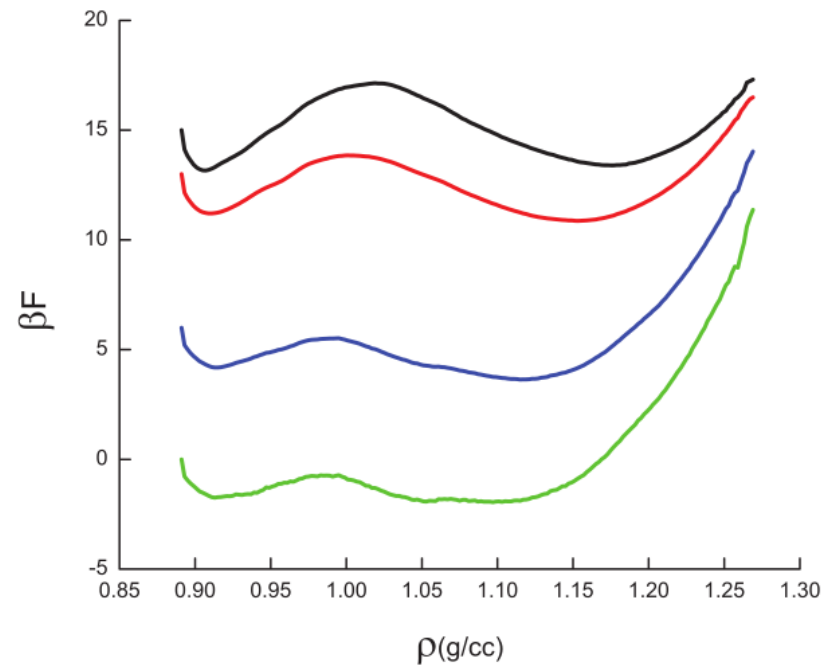
214505-6 Liu *et al.*J. Chem. Phys. **137**, 214505 (2012)

FIG. 4. Density dependence of the contracted free energy obtained by integrating over Q_6 [see Eq. (7)] at phase coexistence conditions. Black curve: 224 K, 2.3 kbar; red curve: 228.6 K, 2.19 kbar; blue curve: 235 K, 2.0 kbar; green curve: 238 K, 1.9 kbar. The relative vertical location of each isotherm is arbitrary.

consistent with free energy vs. density calculations on the ST2 model using reaction field treatment of long-ranged electrostatic interactions.⁶²

Berkeley

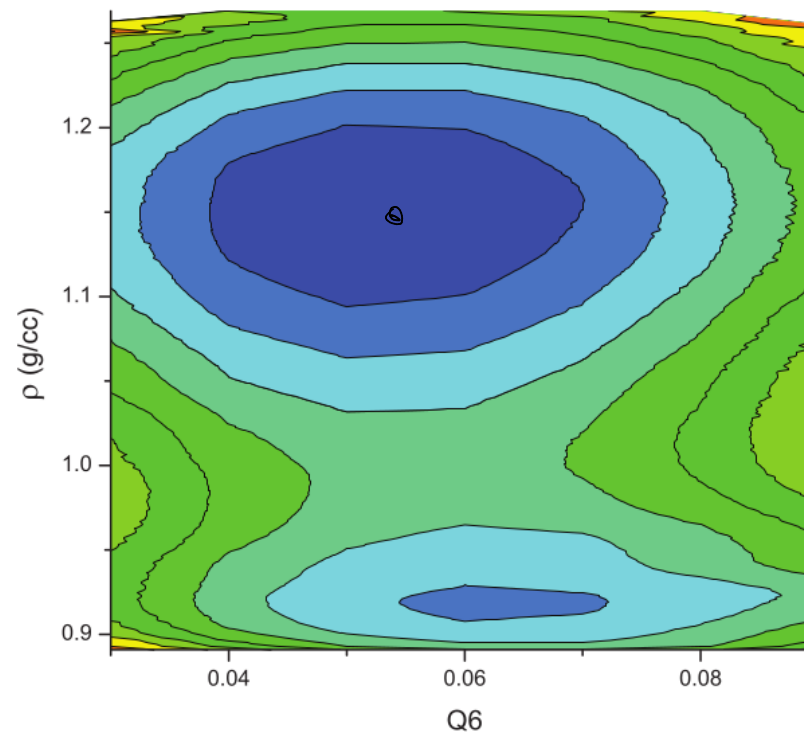
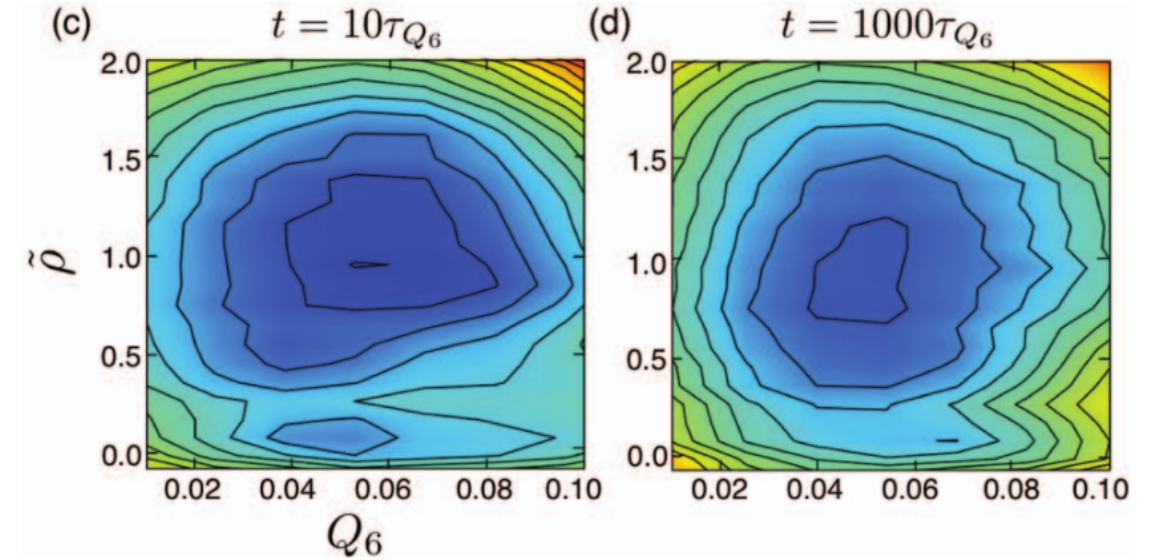
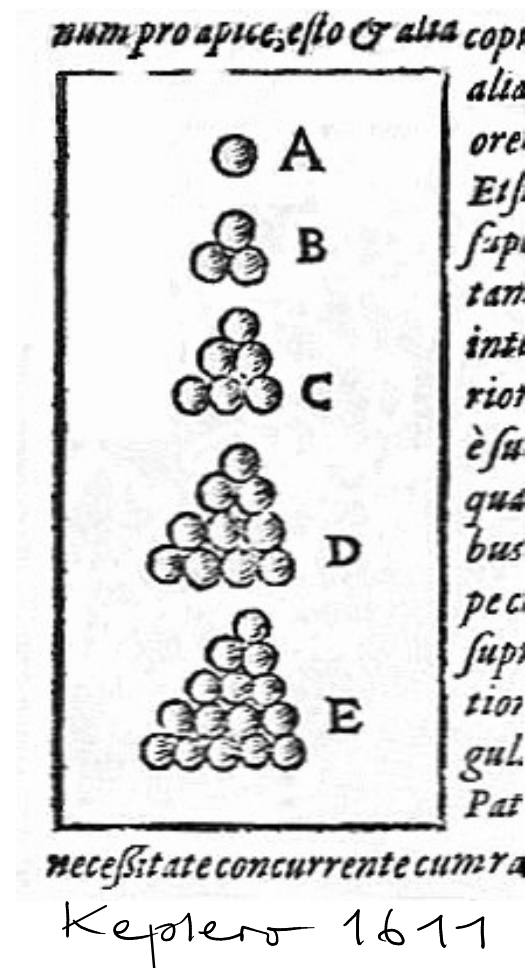
214504-3 D. T. Limmer and D. Chandler J. Chem. Phys. **138**, 214504 (2013)

FIG. 6. Free energy surface in the (ρ, Q_6) plane at (228.6 K, 2.2 kbar), calculated with the same HDL-region histograms used to generate Figure 2 and separate LDL-region histograms obtained from simulations in the LDL windows ($0.90 \leq \rho^* \leq 0.94$ g/cc) that were first started from HDL configurations ($1.13 \leq \rho^* \leq 1.16$ g/cc) and subsequently biased to the LDL region. The agreement with the free energy surface shown in Figure 2 is an indication that the simulations properly sample equilibrated phases.



⇓

WRONG



Congettura di
Keplero
FCC
74%
massimo

When presenting the progress of his project in 1996, Hales said that the end was in sight, but it might take "a year or two" to complete. In August 1998 Hales announced that the proof was complete. At that stage, it consisted of 250 pages of notes and 3 gigabytes of computer programs, data and results.

Despite the unusual nature of the proof, the editors of the *Annals of Mathematics* agreed to publish it, provided it was accepted by a panel of twelve referees. In 2003, after four years of work, the head of the referee's panel, Gábor Fejes Tóth, reported that the panel were "99% certain" of the correctness of the proof, but they could not certify the correctness of all of the computer calculations.

Hales (2005) published a 100-page paper describing the non-computer part of his proof in detail. Hales & Ferguson (2006) and several subsequent papers described the computational portions. Hales and Ferguson received the Fulkerson Prize for outstanding papers in the area of discrete mathematics for 2009.

Sfere dure

3d, monocomponente, σ , $u^{(1)}(\vec{r}) = 0$

$$u_{HS}(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

$$\exp \left[- \frac{1}{k_B T} \sum_{i=1}^N \sum_{j \neq i}^N u_{HS}(r_{ij}) \right]$$

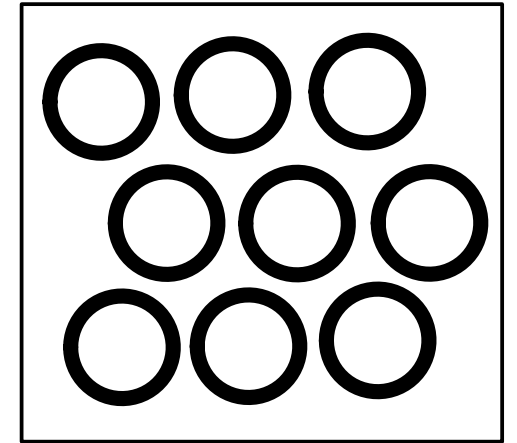
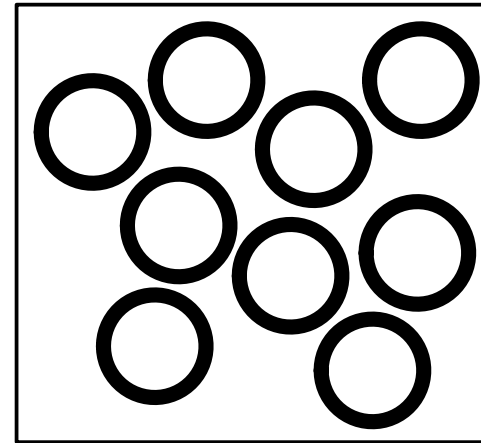
$$= \begin{cases} 1 & \text{se no overlaps} \\ 0 & \text{se overlaps} \end{cases}$$

\Rightarrow ATERMICO

Frazione d'impaccamento

$$\phi = \frac{\frac{4}{3} \pi \left(\frac{\sigma}{2}\right)^3 N}{V} = \frac{\pi}{6} \sigma^3 \rho$$

V, T fissati



$$F = \cancel{E} - TS$$

$$S_{\text{fcc}} > S_{\text{fluids}} !!$$

Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

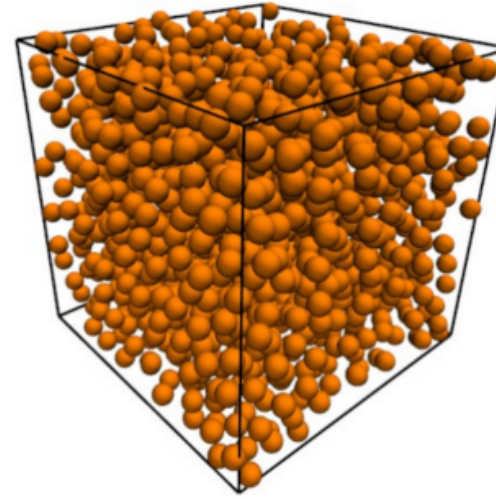
University of California Radiation Laboratory, Livermore, California

(Received August 12, 1957)

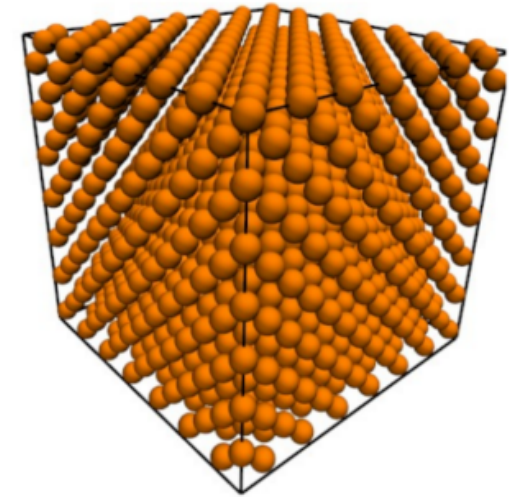
A CALCULATION of molecular dynamic motion has been designed principally to study the relaxations accompanying various nonequilibrium phenomena. The method consists of solving exactly (to the number of significant figures carried) the simultaneous classical equations of motion of several hundred particles by means of fast electronic computers. Some of the



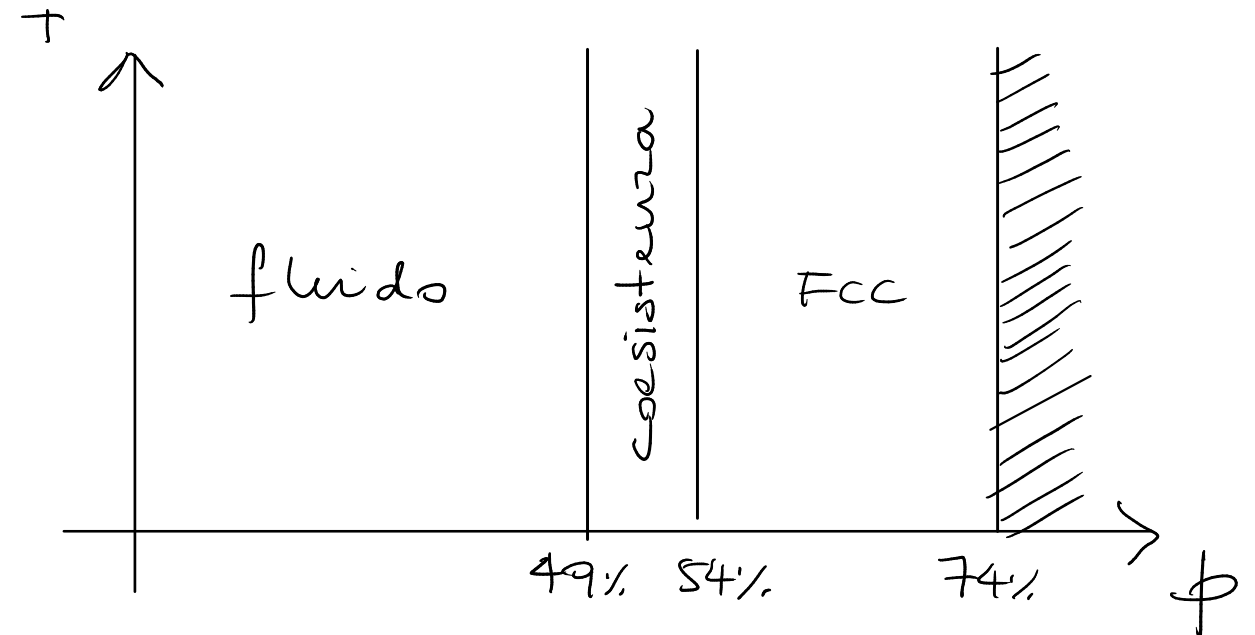
Alder



fluido



FCC



Diagrammi di fase dei materiali soffici

1. Colloidi duri

Particelle di PMMA :

$R = 305 \pm 10 \text{ nm}$ (3%)

stabilizzazione sterica

index matching \rightarrow No vdw

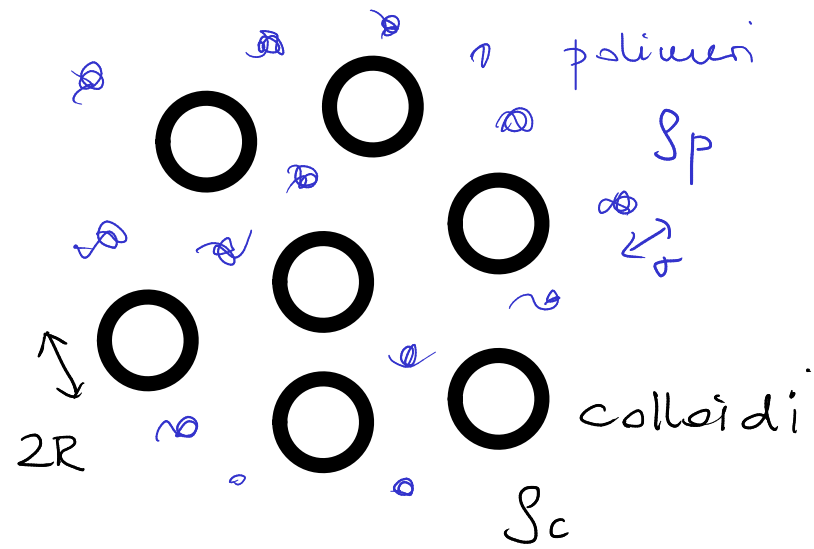
\Downarrow

$$U_{\text{eff}} = u_{\text{HS}}(r)$$



Pusey Van Meegen Science 1986

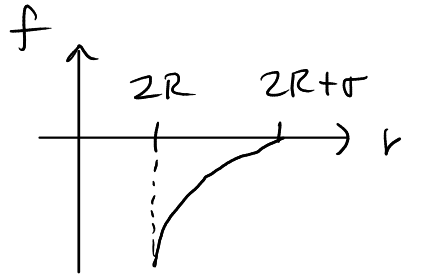
2. Colloidi attrattivi



→ colloidi + polimeri

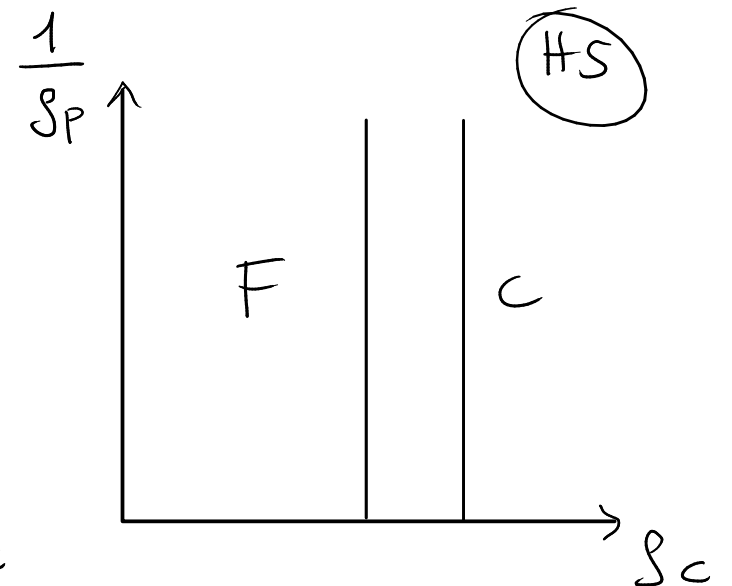
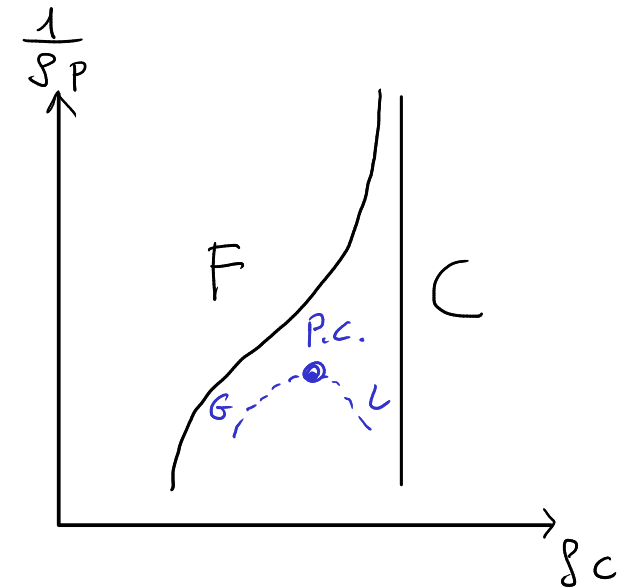
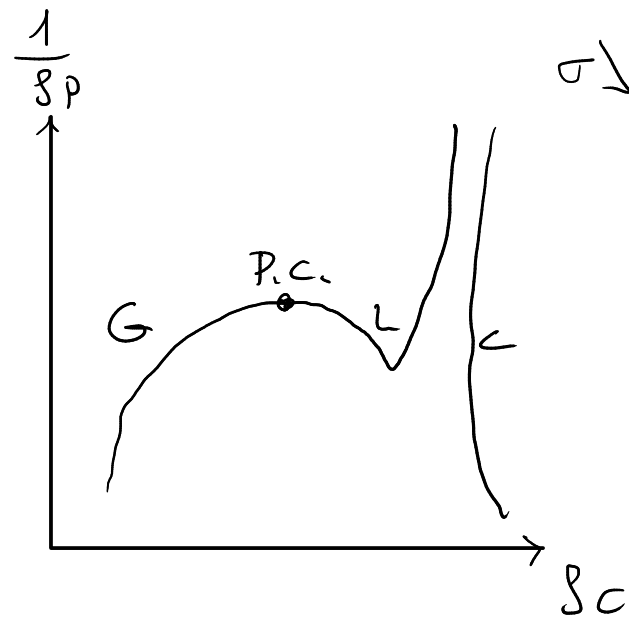
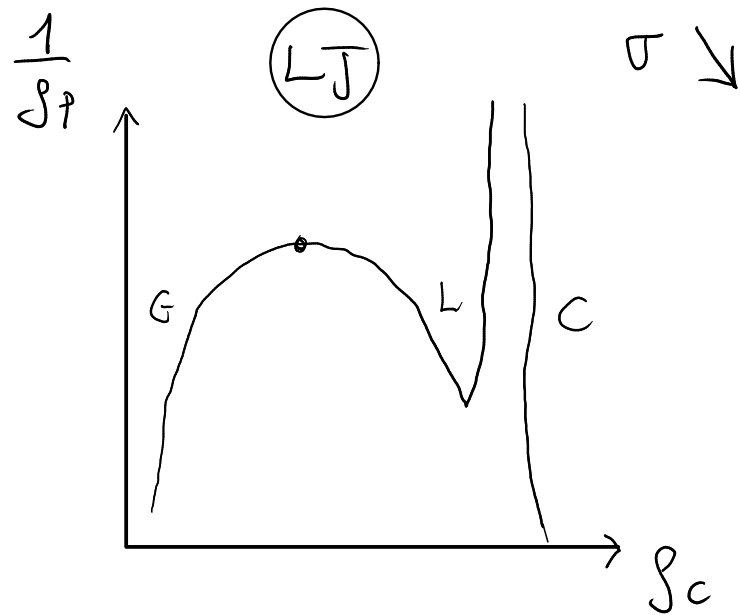
$$U_{\text{eff}}(r) = u_{\text{HS}}(r) + u_{\text{AO}}(r)$$

$$u_{\text{AO}}(r) = s_p \cdot k_B T \cdot f(r) \quad 2R < r < 2R + \sigma$$



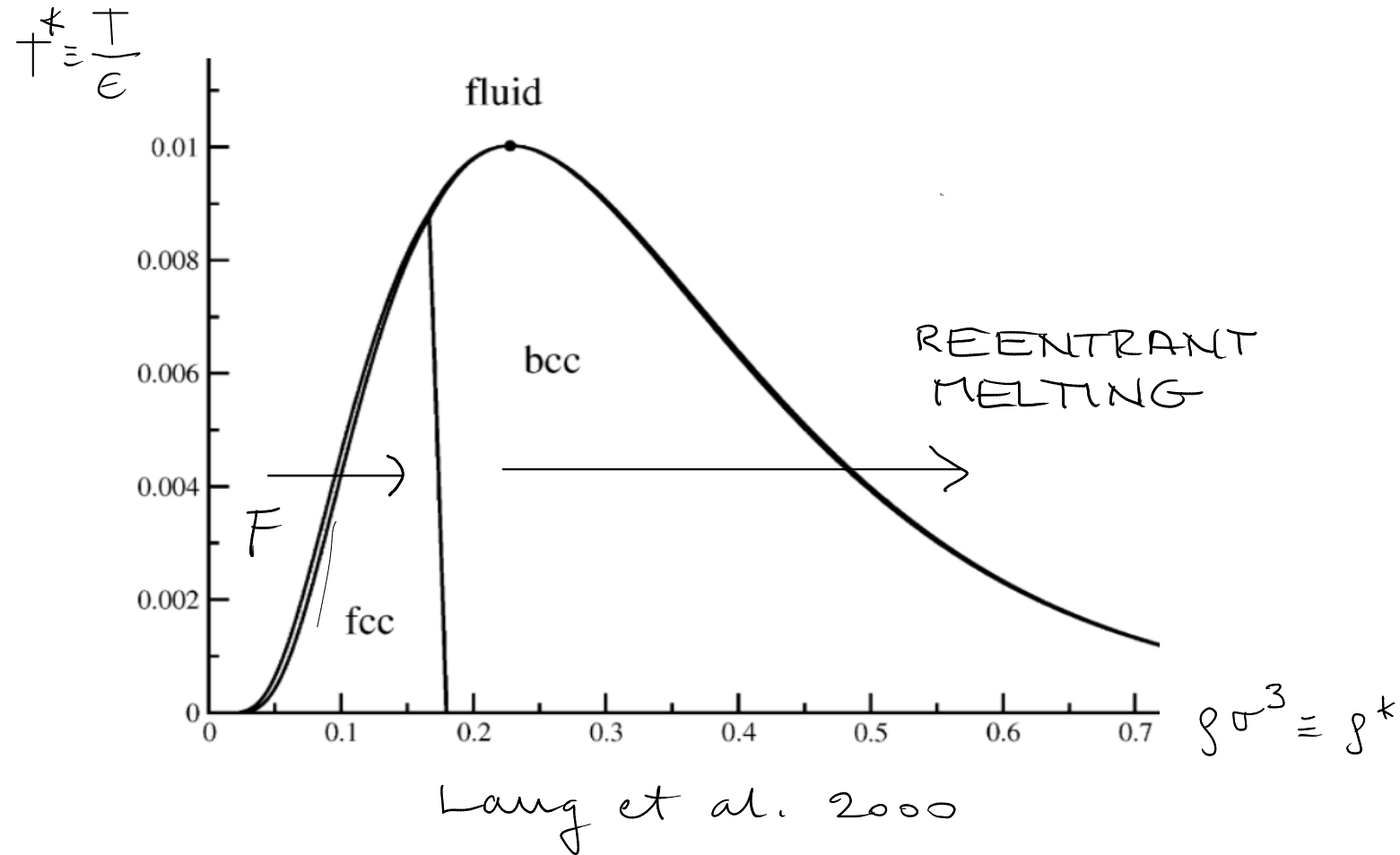
$$\exp \left[- \frac{1}{k_B T} s_p \sum_i \sum_j f(r_{ij}) \right] \quad \frac{1}{s_p} \rightarrow T$$

ATERMICO



3. colloidi ultrasoffici

Polimeri lineari, dendrimeri, microgels



EOM

$$u(r) = \epsilon \exp \left[- \left(\frac{r}{\sigma} \right)^2 \right]$$

↑
 $\epsilon \sim k_B T$



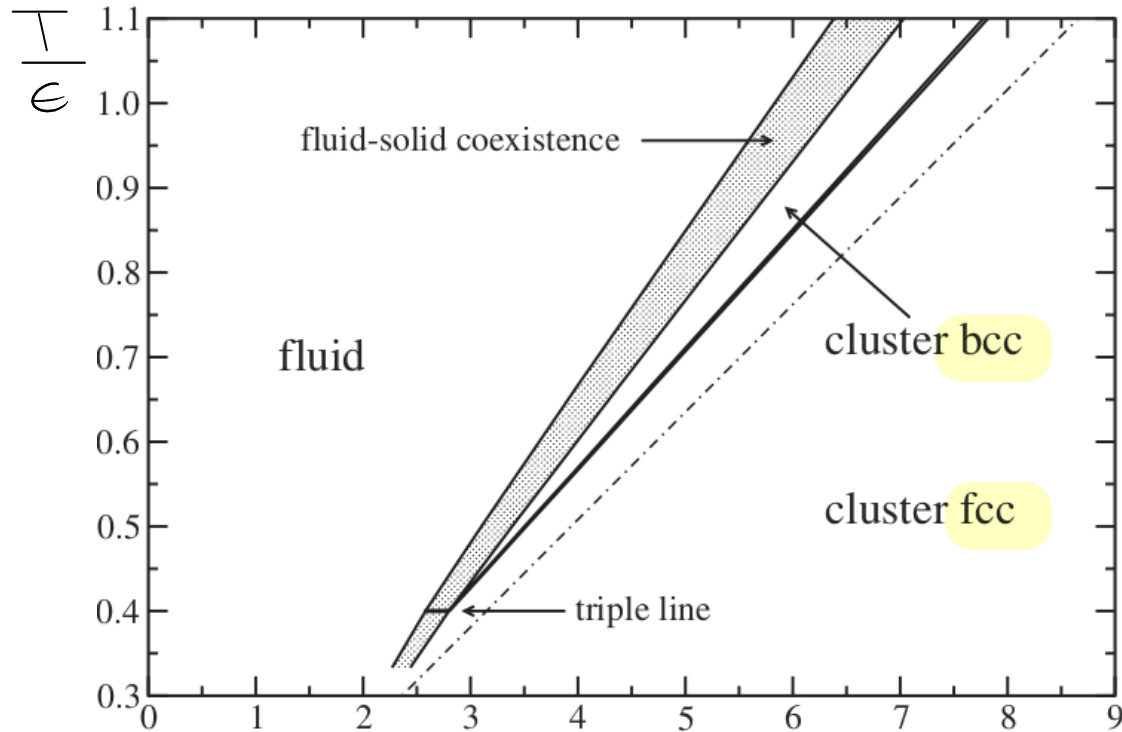
70 Stillingner:
freezing a bassa g e T

$$T_f \sim \exp \left(- \frac{0.94}{g_f^{2/3}} \right)$$

GEM

$$u(r) = \epsilon \exp[-(r/\sigma)^n]$$

$$n \sim 3-4$$



$$\tilde{\rho} = \rho \sigma^3$$

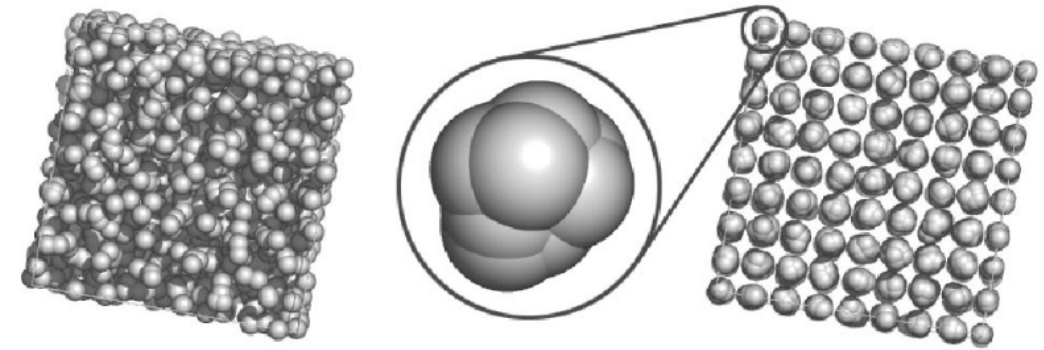


FIG. 2. Two simulation snapshots of a GEM-4 system for $T^* = 0.4$ and $\rho^* = 2.5$ and 7 (left and right). The middle panel shows a close-up of one cluster. Particle diameters are not drawn to scale but are chosen to optimize the visibility of the structures.

PRL **96**, 045701 (2006)

Self assembling cluster crystals from DNA based dendritic nanostructures

Emmanuel Stiakakis¹, Niklas Jung², Nataša Adžić³, Taras Balandin⁴, Emmanuel Kentzinger⁵, Ulrich Rücker⁵, Ralf Biehl⁶, Jan K. G. Dhont^{1,7}, Ulrich Jonas² & Christos N. Likos³

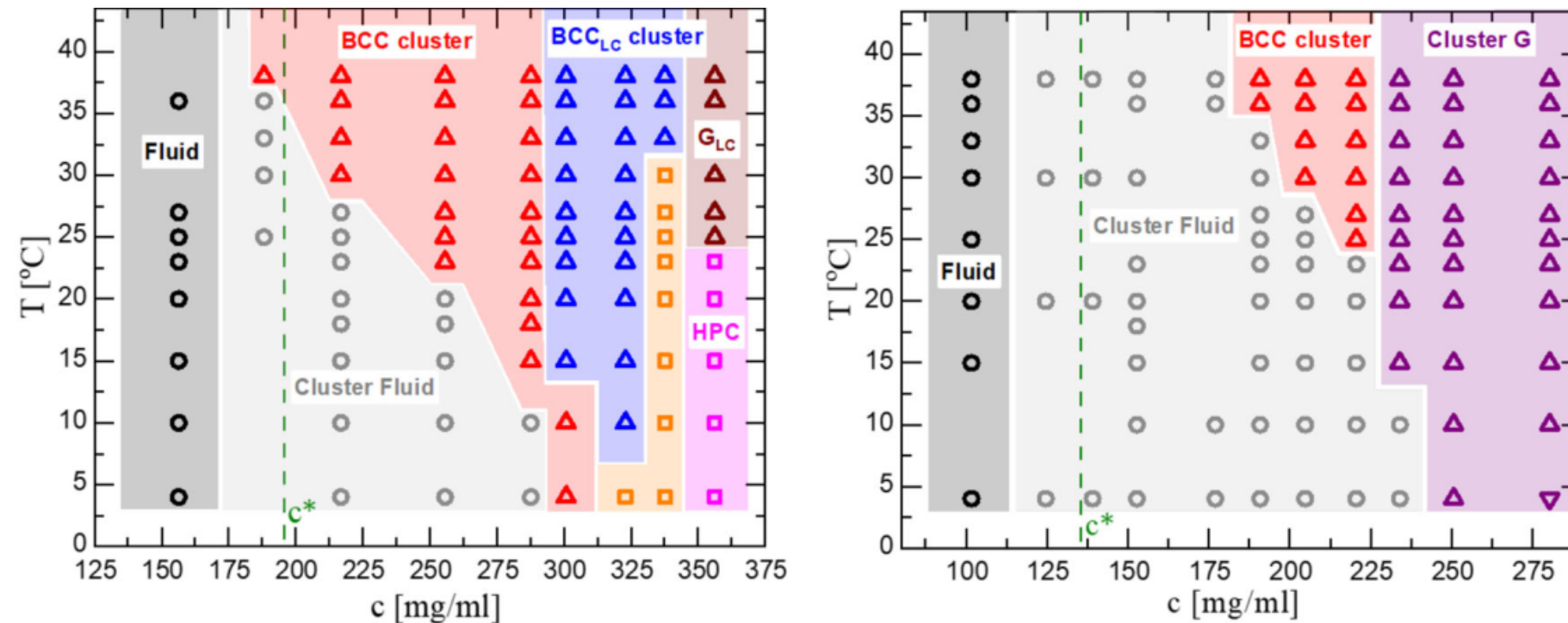


Fig. 6 Phase diagrams of G1-P-G1 and G2-P-G2. A concentration-temperature phase diagram of aqueous solutions of G1-P-G1 (a) and G2-P-G2 (b). The following phases are indicated: Fluid (black circles), cluster fluid (gray circles), BCC cluster crystal (red triangles), liquid crystalline BCC-like cluster crystal (BCC_{LC} cluster, blue triangles), liquid crystalline glass-like (G_{LC} , brown triangles), non-birefringent glass-like (Cluster G, purple triangles) and hexagonal packed cylinder (HPC, magenta squares). The corresponding background colors are added to assist in identifying the various phases. The structural assignment of the orange region in the G1-P-G1 phase diagram based solely on the SAXS data was not possible. The green-dashed lines indicate the DNA overlap concentration c^* of G1-P-G1 and G2-P-G2 (see Methods, “System parameters” section).