Interazioni effettive a 2 corpi

$$H_{eff} = K_c + U_c(\{\bar{R}_i\}) + F_s(\{\bar{R}_i\}) \longrightarrow F_s = F_s^{(0)} + F_s^{(2)} + F_s^{(3)} + \dots$$

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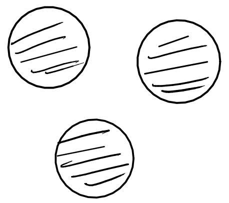


$F_s^{(0)}$: termine di volume; $F_s^{(2)}$: $\sum_{i=1}^{N_c} \sum_{j>i} \dots$

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

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

$$F_s = -K_B T \ln Z_S(\bar{R}_1, \bar{R}_2)$$

$$Z_s = Z_s^{id} \cdot Z_s^c = \frac{1}{h^{3N_s} N_s!} \int d\bar{p}^{N_s} \int d\bar{r}^{N_s} e^{-\beta(K_s + U_s + U_{cs})}$$

$$= \underbrace{\left(\frac{V^{N_s}}{h^{3N_s} N_s!} \int d\bar{p}^{N_s} e^{-\beta K_s} \right)}_{Z_s^{id}} \underbrace{\left(\frac{1}{V^{N_s}} \int d\bar{r}^{N_s} e^{-\beta(U_s + U_{cs})} \right)}_{Z_s^{c}}$$

$$\left(\frac{\sqrt{2\pi m K_B T}}{h} \right)^{3N_s}$$

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

Stirling $\ln N! \approx N \ln N + N$ $\qquad \rho_s = \frac{N_s}{V}$

$$F_s^{id} = -K_B T \left[N_s \ln\left(\frac{V}{\Lambda^3}\right) - \ln(N_s!) \right] \approx -K_B T N_s \left[\ln\left(\frac{V}{\Lambda^3}\right) - \ln N_s - 1 \right]$$

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

$$F_S = F_{id} - K_B T \ln\left(Z_S^c\right) = F_{id} + \tilde{U}^{(0)} + \tilde{U}^{(2)}(\underbrace{\bar{R}_1, \bar{R}_2}_{|\bar{R}_1 - \bar{R}_2|})$$

$$\Rightarrow \quad H_{eff} = K_c + U_c + F_S^{id} + \underbrace{\tilde{U}^{(0)} + \tilde{U}^{(2)}}_{\text{potenziale effettivo d'interazione a 2 corpi}}$$

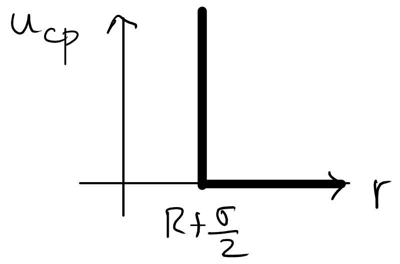
Forze di deplezione

Effetti di volume escluso in miscele asimmetriche

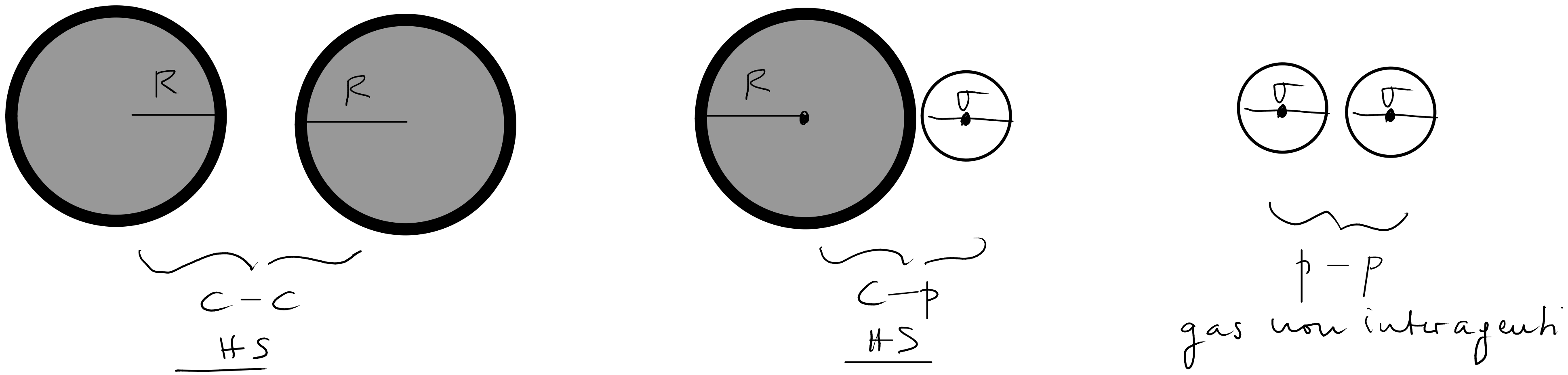
- colloidi → c
- polimeri → p
- solvente

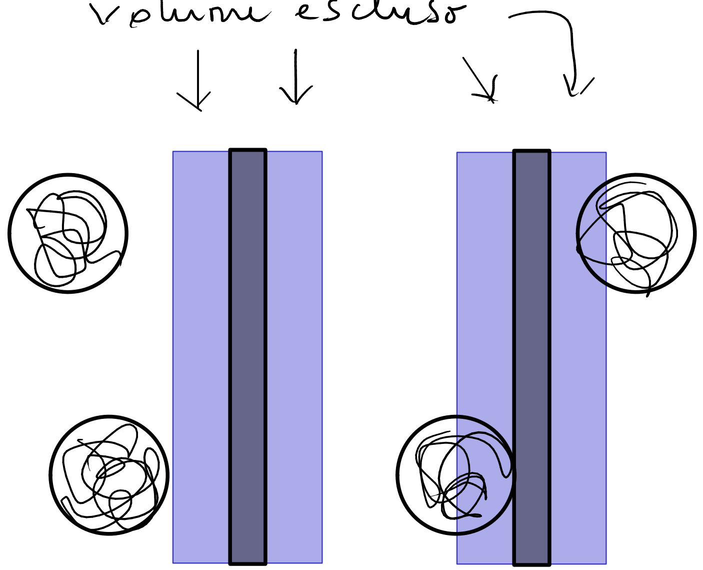
polimero buon solvente

$R_g \simeq \sigma/2$



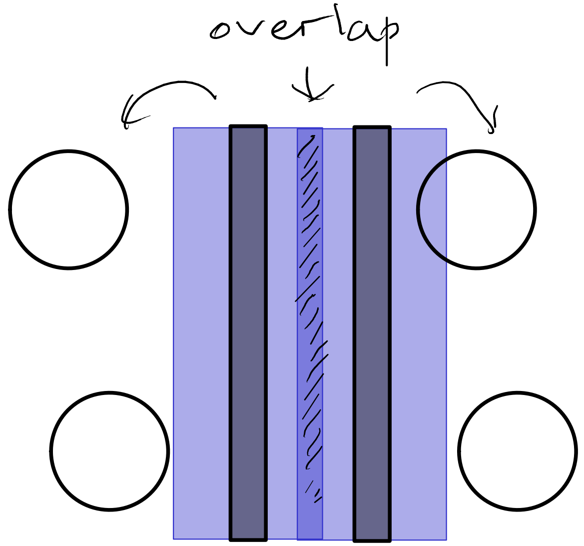
Modello d' interazione :





↑ volume escluso

↑ F_s



↓ volume escluso

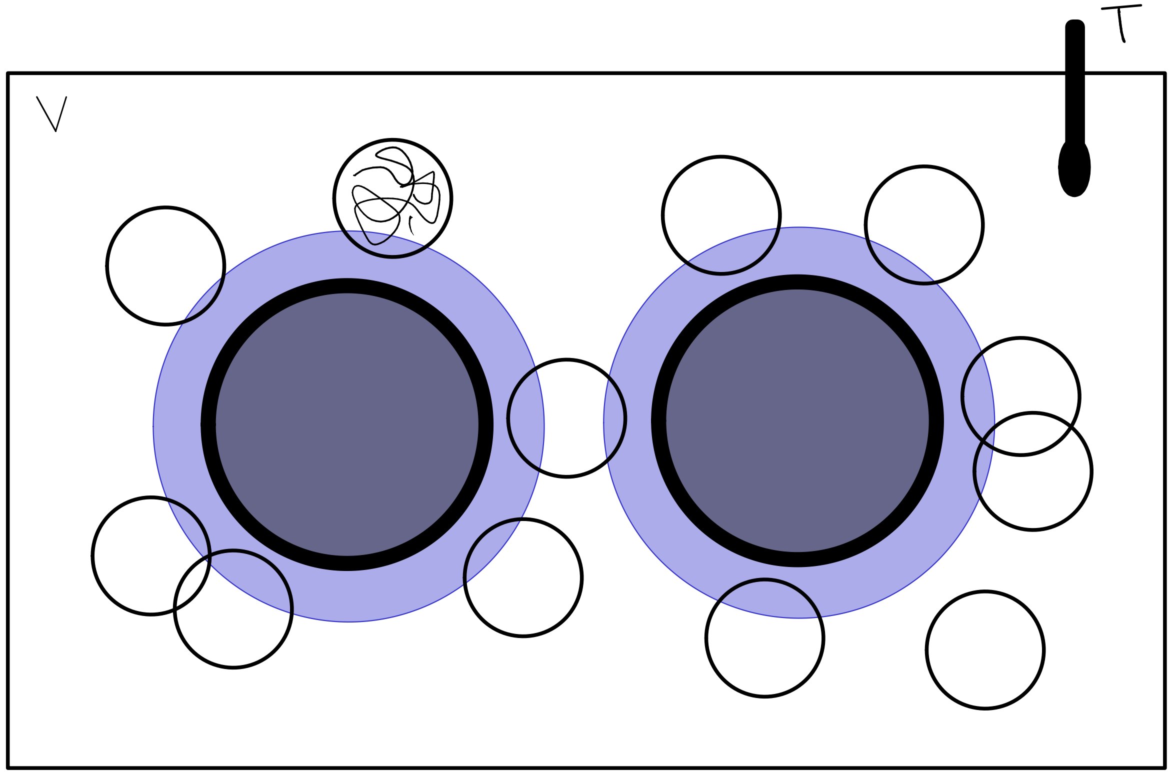
↓ F_s

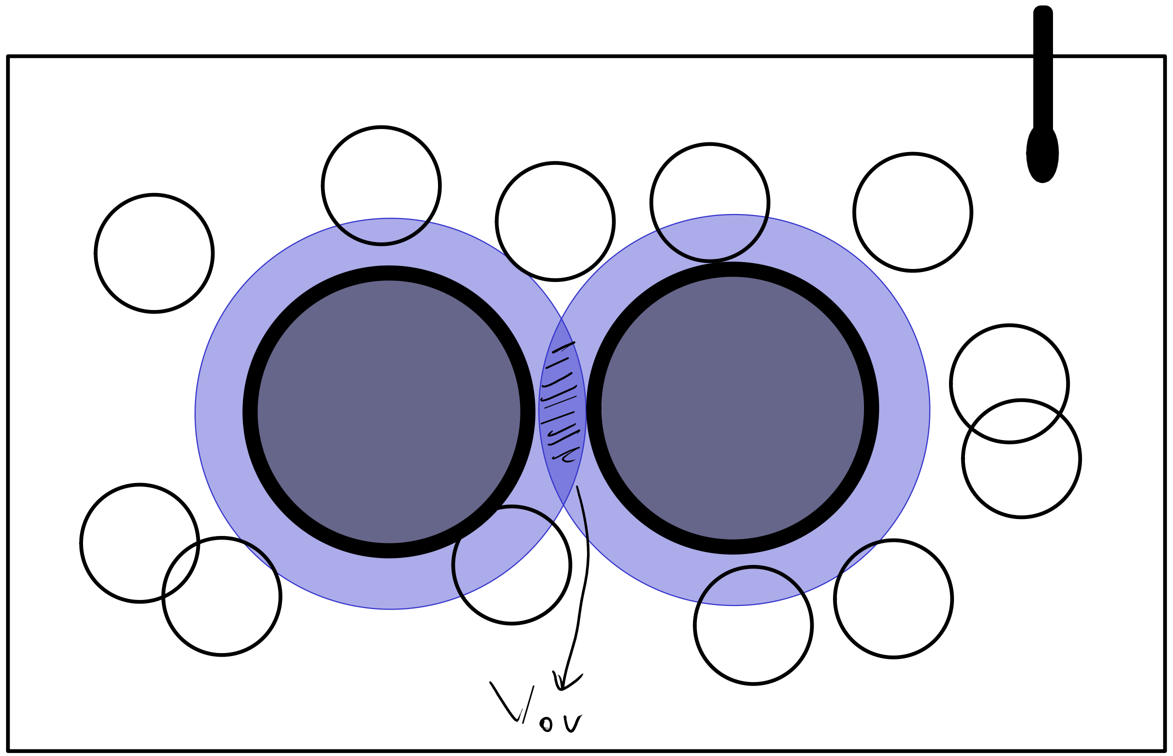
⇓

attrazione

Potenziale di Asakura – Oosawa: (~1950) $N_c = 2$, $\bar{R}_1, \bar{R}_2$; $N_p = N$, $\{\bar{r}_i, \bar{p}_i\}$

$s \to p$



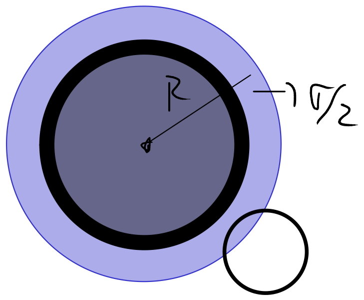


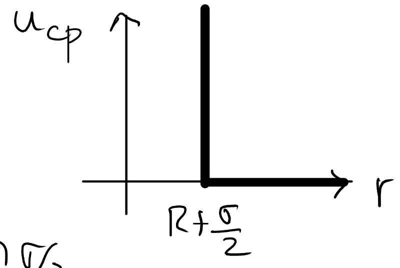
$$Z_p^{id} = \frac{V^N}{\Lambda^{3N} N!}$$

$$Z_p^{c} = \frac{1}{V^N}\int d\bar{r}^N e^{-\beta(\overset{0}{\downarrow}U_p + U_{cp})} = \frac{1}{V^N}\int d\bar{r}^N e^{-\beta \sum_{i=1}^{N} \overset{HS}{u_{cp}}(\bar{r}_i, \bar{R}_1, \bar{R}_2)}$$

$$= \frac{1}{V^N}\left(\int d\bar{r}_1 \, e^{-\beta u_{cp}(\bar{r}_1, \bar{R}_1, \bar{R}_2)}\right)^N$$

$$e^{-\beta u_{cp}} = \begin{cases} 0 & \text{se overlap} \\ 1 & \text{se no overlap} \end{cases}$$





$$= \frac{1}{V^N}\left(V - V_e\right)^N = \left(\frac{V-V_e}{V}\right)^N \qquad V_e \equiv \text{volume escluso totale}$$

$$F_p^c = -K_B T \ln Z_p^c = -K_B T N \ln\left(\frac{V-V_e}{V}\right)$$

Distanza tra colloidi $r > 2R+\sigma \equiv D$

$$V_e = 2 \times \frac{4}{3}\pi\left(R+\frac{\sigma}{2}\right)^3 = 2\,\frac{4}{3}\pi\left(\frac{D}{2}\right)^3 = 2\,\frac{\pi}{6}D^3$$

Se $2R < r < D$:

$$V_e = 2\,\frac{\pi}{6}D^3 - V_{ov}$$

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

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

$$\tilde{U}_{AO}(|R_1 - R_2| = r) \equiv F_p^c = -N K_B T \ln\left[1 - \frac{\pi D^3}{6V}\left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3}\right)\right]$$

$$V_c << V \Rightarrow \tilde{U}_{A0}(r) \approx + K_B T\, N \frac{\pi D^3}{6V}\left(1 + \frac{3r}{2D} - \frac{r^3}{2D^3}\right) = \underset{\text{dipendente da stato termodinamico}}{\underbrace{\rho\, K_B T}} \frac{\pi D^3}{6}\left(1 + \frac{3r}{2D} - \underset{+c}{\frac{r^3}{2D^3}}\right)$$

$$\rho \to \frac{N_p}{V}$$

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

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

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

$$\tilde{U}_{A0}(r) = -\rho\, K_B T \frac{\pi D^3}{6}\left(1 - \frac{3r}{2D} + \frac{r^3}{2D^3}\right) \qquad 2R < r < 2R + \sigma \equiv D$$

$$\tilde{U}_{eff} = U_c + F_p^c = \underset{HS}{U_c} + \tilde{U}_{A0} = \begin{cases} \infty & r \leq 2R \\ \tilde{U}_{A0} & 2R < r < D \\ 0 & r \geq D \end{cases}$$

$$H_{eff} = K_c + \tilde{U}_{eff} + F_p^{id}$$