CLASSICAL vs. QUANTUM

$|\vec{p}| \rightarrow$ relazione di Broglie : $\lambda = \frac{h}{p}$ $\quad E_c = \frac{p^2}{2m} = \frac{3}{2} k_B T \rightarrow p = \sqrt{3 m k_B T} \rightarrow \lambda = \frac{h}{\sqrt{3 m k_B T}}$

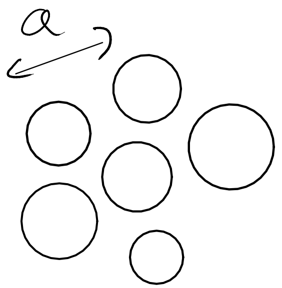
Lunghezza di Broglie $\quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$

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



Effetti quantistici trascurabili

$$\Lambda \lesssim a$$

$$\frac{h}{\sqrt{2\pi m k_B T}} \frac{1}{a} \lesssim 1 \qquad T\uparrow \quad m\uparrow$$

$$T \gtrsim \tilde{T}$$

Argon $\tilde{T} \sim 2K$

INTERAZIONI EFFETTIVE

Effettive → eliminare gradi di libertà micro

INTERAZIONI EFFETTIVE TRA ATOMI E MOLECOLE

Interazioni effettive interatomiche

→ potenziali empiriche

N punti materiali

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

↑ campo esterno, 1 corpo

↑ 2 corpi, $|\bar{r}_i - \bar{r}_j|$

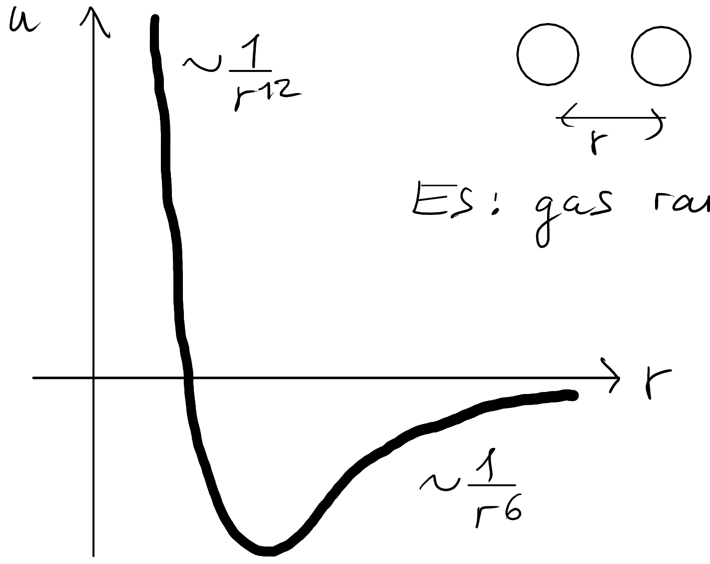
↑ 3 corpi

Appross. additività coppia

$$U \approx \sum_{i=1}^{N} \sum_{j>i} \tilde{u}_2(|\bar{r}_i - \bar{r}_j|) \leftarrow \text{dipendente dallo stato termodinamico}$$

Esempi di forme funzionali per $u_2(r)$

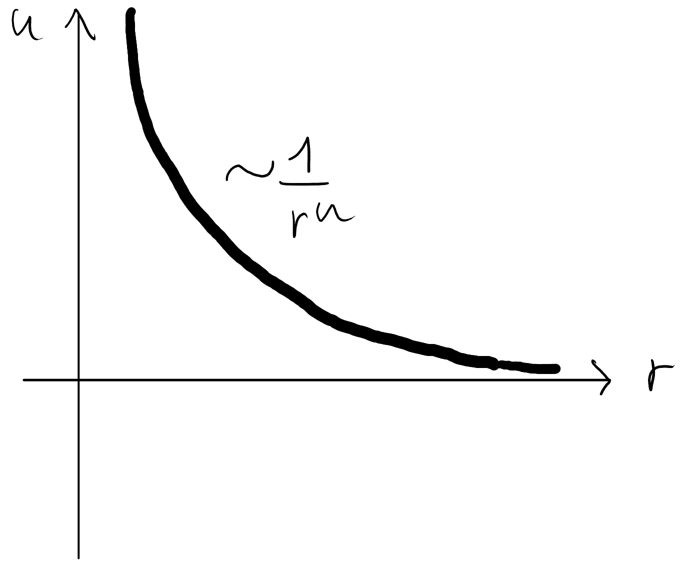
a) Lennard-Jones



Es: gas rari

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

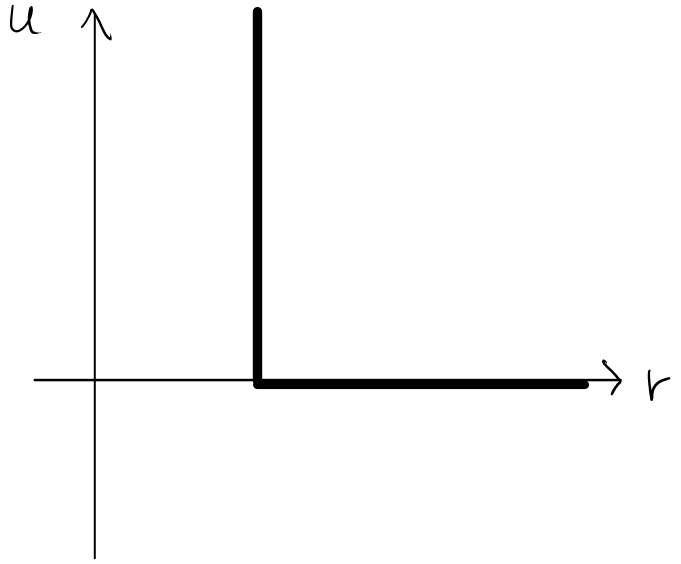
b) Sfere soffice



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

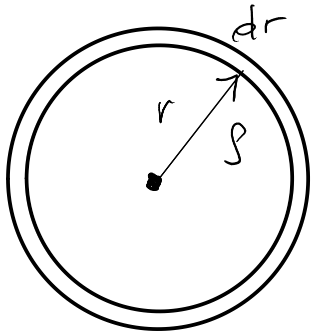
$n = 1$ Coulomb

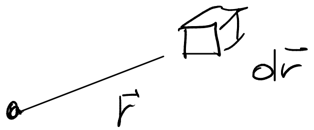
c) Sfere dure.



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

$n \to \infty$ IPL





$$U \approx \int_V u(r)\,\rho\, d\bar{r} = \rho\, 4\pi \int_{r_c}^{\infty} dr\, r^2 u(r) \sim \int_{r_c}^{\infty} dr\, \underbrace{r^{d-1} r^{-n}}_{\frac{1}{r^{n-d+1}}}$$

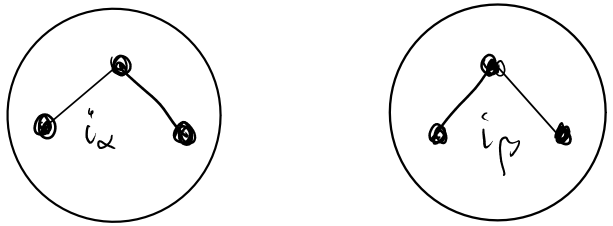
$$u(r) \sim \frac{1}{r^n}$$

$$\Rightarrow \quad n - d + 1 > 1 \quad \Rightarrow \quad n > d$$

$$\begin{cases} n > d \Rightarrow \text{corto raggio} \to \text{LJ, HS} \\ n \leq d \Rightarrow \text{lungo raggio} \to \text{Coulomb, dipolo-dipolo} \end{cases}$$

- Forma funzionale → fit parametri
  - eq. di Stato, struttura
  - ab-initio → U_{AI}, ∇U_{AI}
- Potenziali tabulati
- Machine learning

Interazioni effettive intermolecolari (forcefields)



α $\qquad$ β

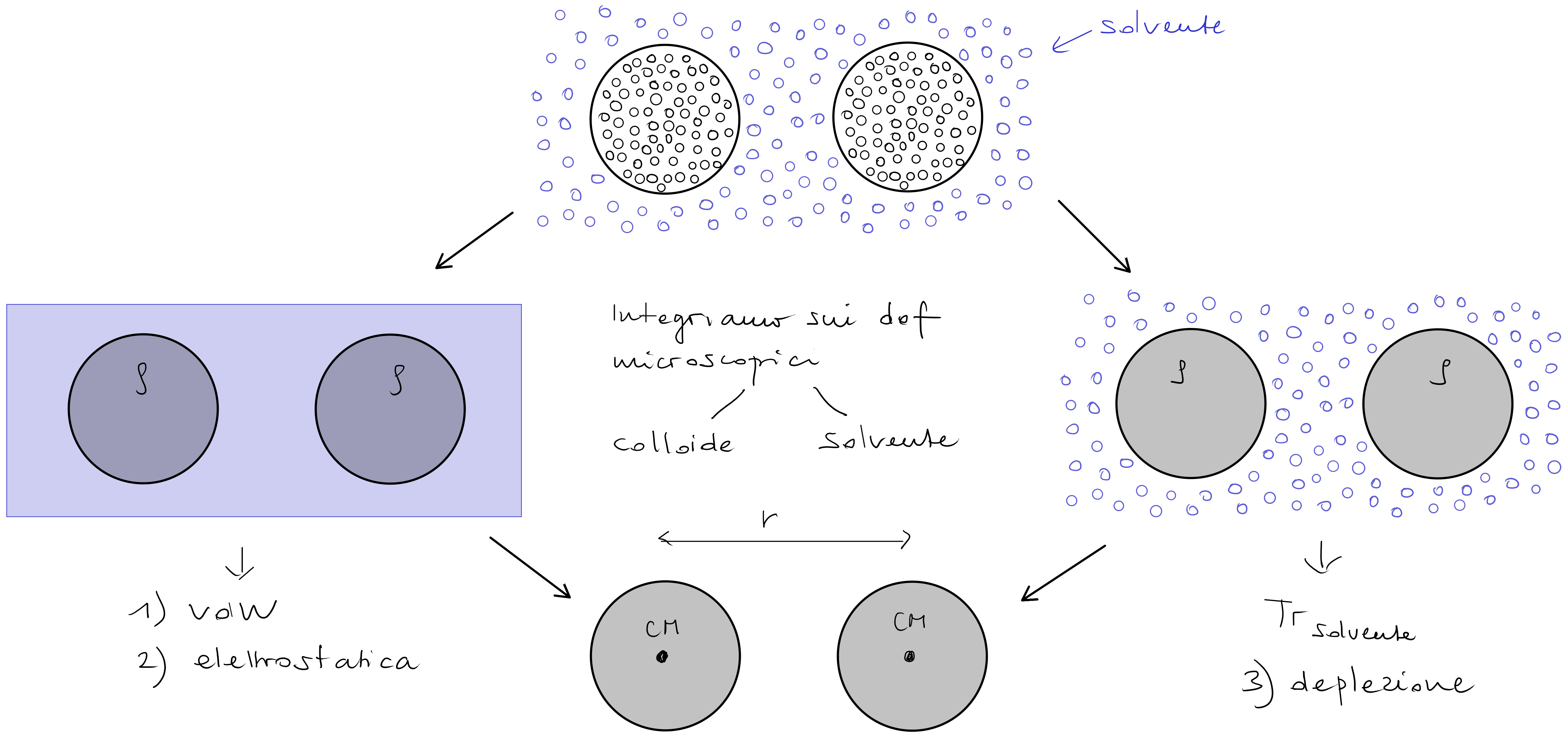
$$U = \underbrace{U_\alpha + U_\beta}_{\text{intra}} + \underbrace{U_{\alpha\beta}}_{\text{inter}} \to \text{AMBER, CHARMM, ...}$$

intra:

2C	2C	3C	4C
i-j	1-2	1-2-3	1-2-3-4
LJ			

inter: LJ, Coulomb

INTERAZIONI EFFETTIVE TRA COLLOIDI



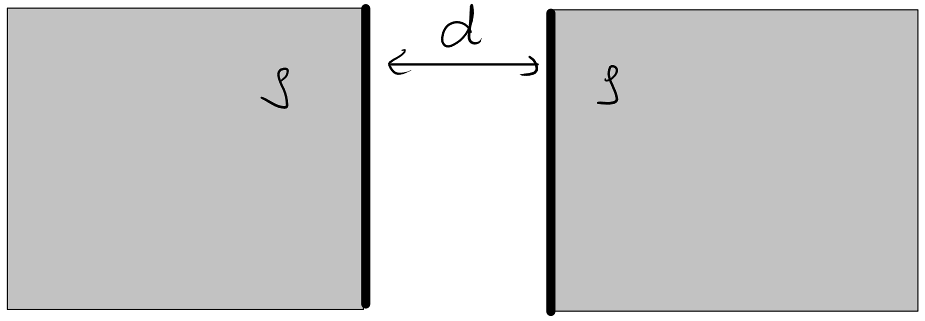
Interazioni di van der Waals

Onnipresenti e attrattive: dipolo – dipolo indotto

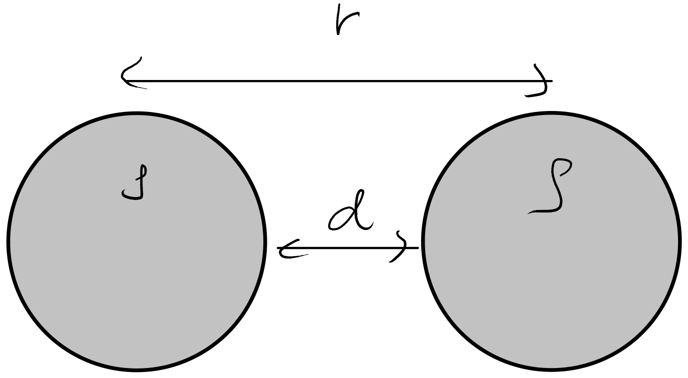
$$u(r) = -\frac{C}{r^6}$$

← polarizzabilità

← no effetti relat.

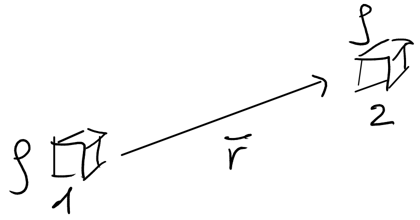


① 2 placche semi-∞



② 2 sfere

Generale:

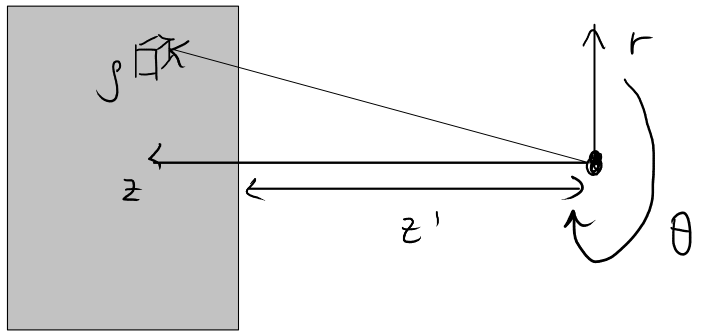


$$U = \int_{V_1}\int_{V_2} u(\bar r_1 - \bar r_2)\,\rho\, d\bar r_1\, \rho\, d\bar r_2$$

$$\downarrow$$

$$u(r) = -\frac{C}{|\bar r_1 - \bar r_2|^6}$$

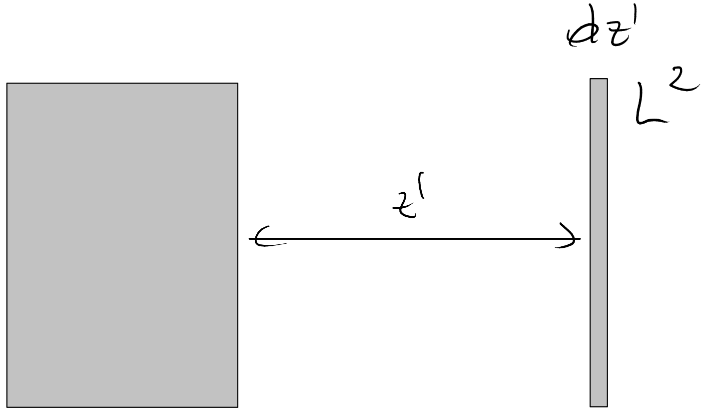
1



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

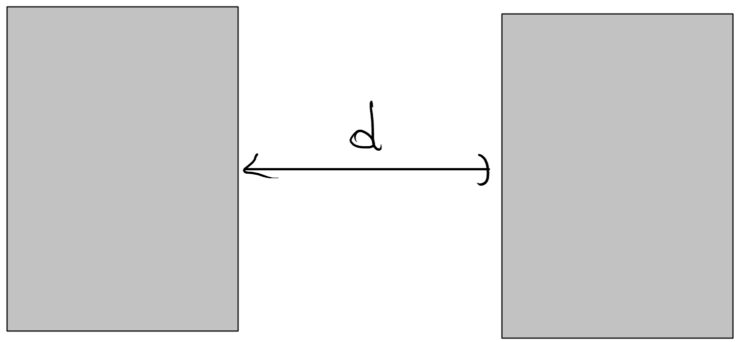
$$= -\pi C \rho \int_{z'}^\infty dz \left[-\frac{1}{2}\frac{1}{(r^2+z^2)^2}\right]_0^\infty = -\frac{\pi C \rho}{2}\int_{z'}^\infty dz \frac{1}{z^4}$$

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



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

$$\frac{du}{L^2}$$

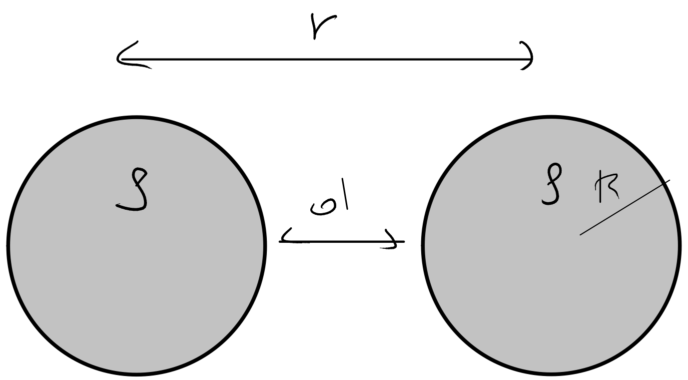


$$\frac{U}{L^2} = -\frac{\pi C \rho^2}{6}\int_d^\infty dz' \frac{1}{z'^3} = -\frac{\pi C \rho^2}{12}\left[-\frac{1}{z'^2}\right]_d^\infty$$

$$= -\frac{\pi^2 C \rho^2}{12\pi}\frac{1}{d^2} = -\frac{A}{12\pi}\frac{1}{d^2}$$

$A \equiv$ costante di Hamaker

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) $r \to 2R \equiv \sigma$ $\quad r = 2R + d \quad$ contatto $\quad d \ll \sigma$

$$\left[\underbrace{\frac{2R^2}{2(2R)d+d^2}}_{\sim \frac{R}{2d}} + \underbrace{\frac{2R^2}{(2R+d)^2}}_{\to \frac{1}{2}} + \underbrace{\ln\left(1-\frac{(2R)^2}{(2R+d)^2}\right)}_{\sim \ln\left(\frac{d}{R}\right)}\right] \longrightarrow 1 - \frac{(2R)^2}{(2R)^2+2(2R)d+d^2} \approx 1 - \frac{1}{1+\frac{d}{R}} \approx \frac{d}{R}$$

2) $r \to \infty$ $\quad \Rightarrow \quad U_{vdw} \sim \frac{1}{r^6}$

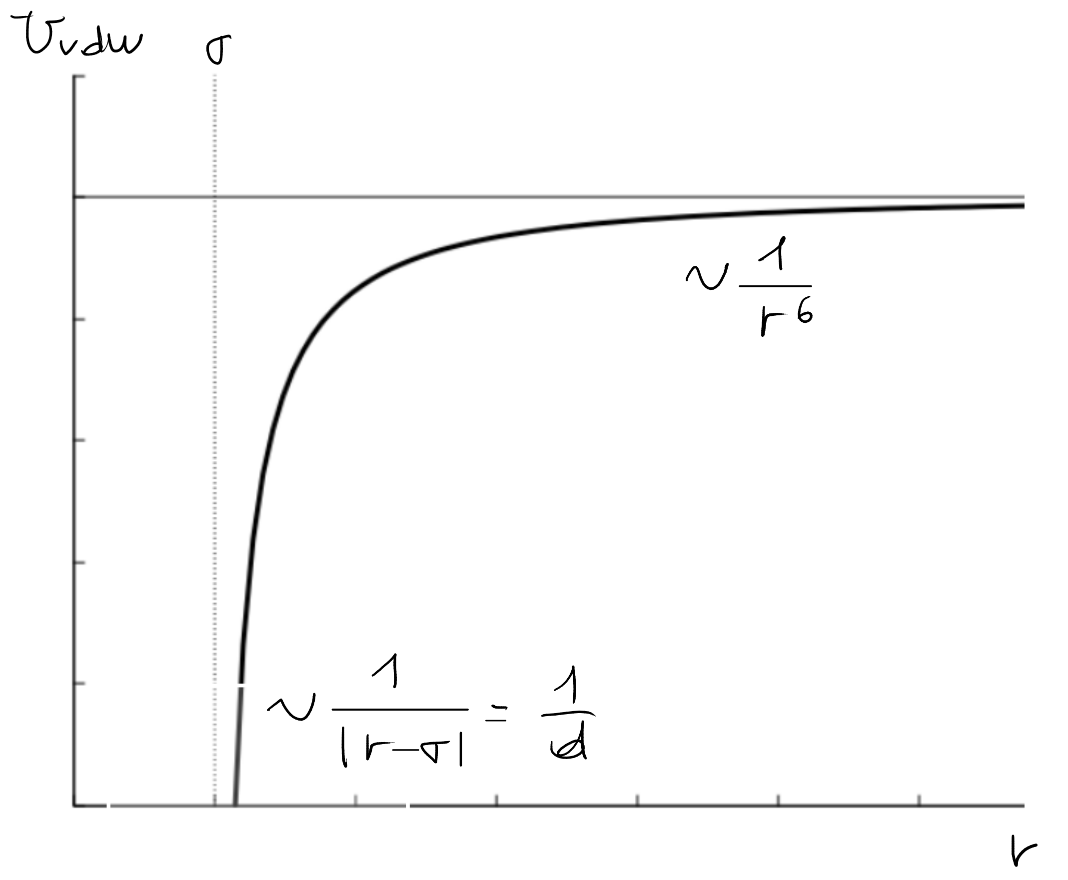
$$\ln(1-x^2) \approx -x^2 - \frac{x^4}{2} - \frac{x^6}{3} \qquad \frac{1}{1-x^2} \approx 1 + x^2 + x^4$$

$$x = \frac{2R}{r}$$

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

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

$$\begin{cases} d \ll \sigma & \Rightarrow \quad U_{vdw} \sim -\dfrac{A}{12}\dfrac{R}{d} = -\dfrac{A}{12}\dfrac{R}{|r-\sigma|} \\ d \gg \sigma & \Rightarrow \quad U_{vdw} \sim -\dfrac{A}{36}\left(\dfrac{\sigma}{r}\right)^6 \end{cases}$$



Approssimazioni:

- additiva a coppie
- no effetti relativistici $\quad \Delta t = \dfrac{r}{c} \quad \nu > \dfrac{1}{\Delta t}$

  $\rightarrow \dfrac{1}{r^7} \quad \Rightarrow \quad \dfrac{1}{r^3}$

- solvente $\rightarrow C_1 (n_c - n_s) \quad \Rightarrow$ stabilizzazione

  $\uparrow$ indici di rifrazione $\qquad$ index-matching $n_c \simeq n_s$