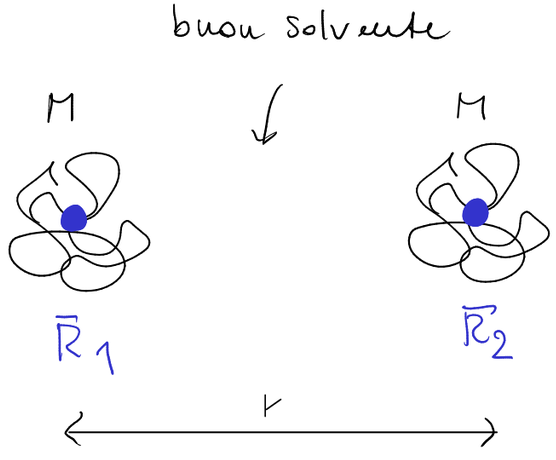
INTERAZIONI EFFETTIVE TRA POLIMERI



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

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

$$\begin{cases} H_1 = \dfrac{3k_BT}{2b^2}\sum_{i=1}^{M} |\bar{r}_{1,i+1} - \bar{r}_{1,i}|^2 + \dfrac{1}{2}k_BT\sum_{i=1}^{M}\sum_{j\neq i} v(|\bar{r}_{1i} - \bar{r}_{1j}|) \\ \text{catena gaussiana} \\ H_2 = \text{----} \;//\; \text{----} \qquad 1 \to 2 \\ U_{12} = \dfrac{1}{2}k_BT\sum_{i=1}^{M}\sum_{j=1}^{M} v(|\bar{r}_{1i} - \bar{r}_{2j}|) \end{cases}$$

Funzione di partizione vincolata

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

$$Z = Tr_1\left[Tr_2\left[e^{-\beta H}\right]\right] = \int d\bar{R}_1 \int d\bar{R}_2\, Z(\bar{R}_1, \bar{R}_2) = \int d\bar{R}_1 \int d\bar{R}_2\, e^{-\beta U_{eff}(\bar{R}_1, \bar{R}_2)}$$

$$U_{eff}(\bar{R}_1, \bar{R}_2) = -k_BT \ln\left[Z(\bar{R}_1, \bar{R}_2)\right] + U_0$$

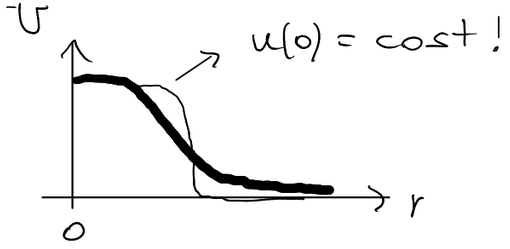
potenziale effettivo (energia libera di Landau)

$$p(\bar{R}_1, \bar{R}_2) = \frac{e^{-\beta U_{eff}(\bar{R}_1, \bar{R}_2)}}{\int d\bar{R}_1 \int d\bar{R}_2\, e^{-\beta U_{eff}(\bar{R}_1, \bar{R}_2)}}$$

1. Polimeri lineari

$\updownarrow \sigma \sim R_g$

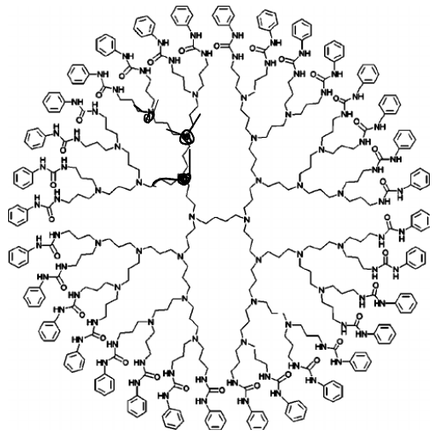
buon solvente



$U(r) = \epsilon\, e^{-(r/\sigma)^2}$ → ultrasoffice $\epsilon \sim K_B T$

'to Stillinger: **Gaussian core model**

2. Dendrimeri



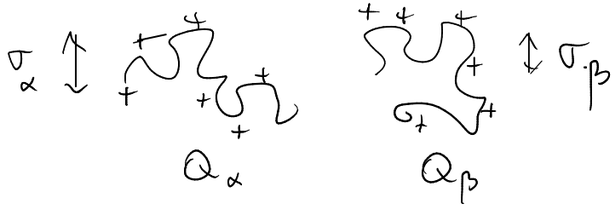
Likos, Ballauff

$U(r) = \epsilon\, e^{-(r/\sigma)^n}$

$n \simeq 3 - 4$

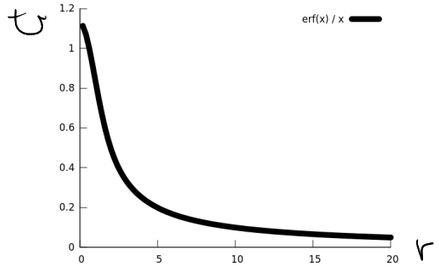
Generalized exponential model ↓ ultrasoffice

3. Polielettroliti

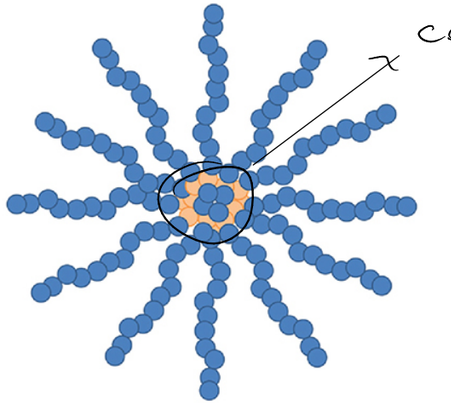


Ultrasoft primitive model

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



4. Polimeri a stella



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