POLIMERI

1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
Polyethylene Terephthalate	High-Density Polyethylene	Polyvinyl Chloride	Low-Density Polyethylene	Polypropylene	Polystyrene	Other
Common products: soda & water bottles; cups, jars, trays, clamshells	Common products: milk jugs, detergent & shampoo bottles, flower pots, grocery bags	Common products: cleaning supply jugs, pool liners, twine, sheeting, automotive product bottles, sheeting	Common products: bread bags, paper towels & tissue overwrap, squeeze bottles, trash bags, six-pack rings	Common products: yogurt tubs, cups, juice bottles, straws, hangers, sand & shipping bags	Common products: to-go containers & flatware, hot cups, razors, CD cases, shipping cushion, cartons, trays	Common types & products: polycarbonate, nylon, ABS, acrylic, PLA; bottles, safety glasses, CDs, headlight lenses
Recycled products: clothing, carpet, clamshells, soda & water bottles	Recycled products: detergent bottles, flower pots, crates, pipe, decking	Recycled products: pipe, wall siding, binders, carpet backing, flooring	Recycled products: trash bags, plastic lumber, furniture, shipping envelopes, compost bins	Recycled products: paint cans, speed bumps, auto parts, food containers, hangers, plant pots, razor handles	Recycled products: picture frames, crown molding, rulers, flower pots, hangers, toys, tape dispensers	Recycled products: electronic housings, auto parts,

Definizione: macromolecola composta da unità molecolari ("monomeri") connesse in forma di catena

Grado di polimerizzazione: $N \sim 10^2 - 10^6$ $\qquad p(N)$

Massa molecolare / totale: $M = mN$

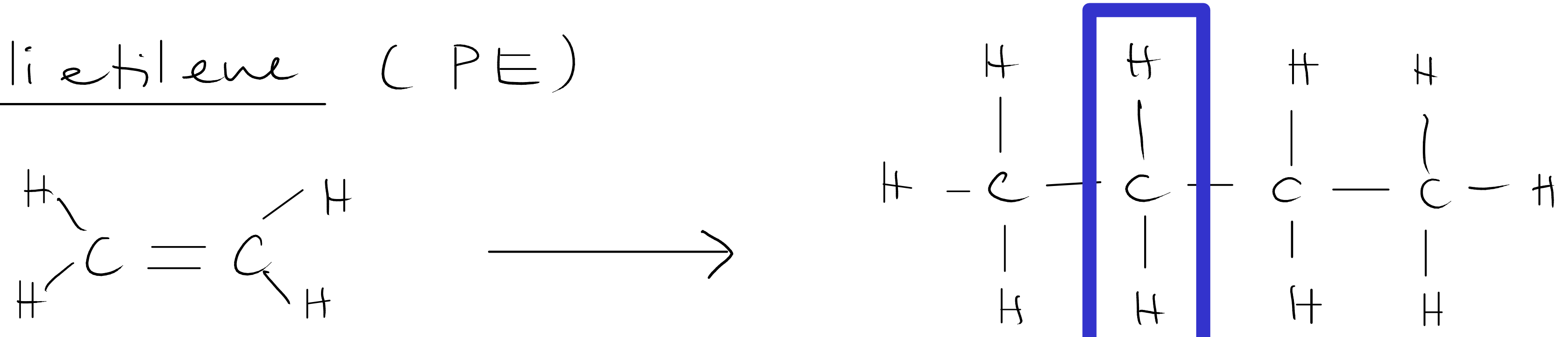
'30 : Kuhn

'71 : Flory (Nobel)

'91 : De Gennes (Nobel)

1) Polimeri sintetici

- Polietilene (PE)



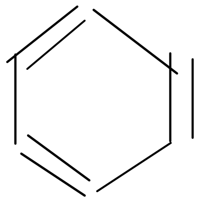
etilene C_2H_4 $\qquad [CH_2]_N$

HDPE

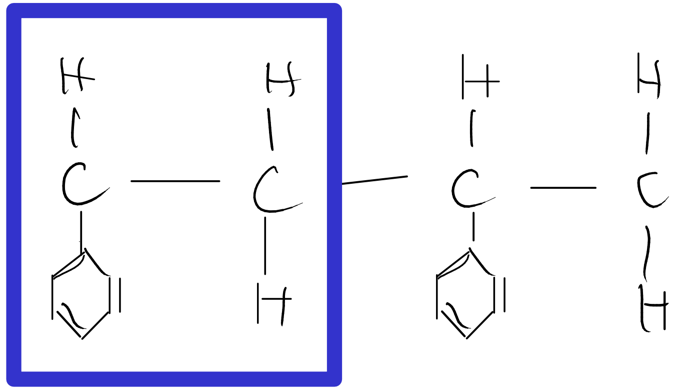
LDPE

semiflessibile

- Polistirene (PS)



benzene C_6H_6



$[C_8H_8]_N$

regolare $\Rightarrow$ XTAL

casuale $\Rightarrow$ GLASS

flessibile

Energia di legame: $\epsilon \gg k_B T$ (@Ta)

$\downarrow$

chimica

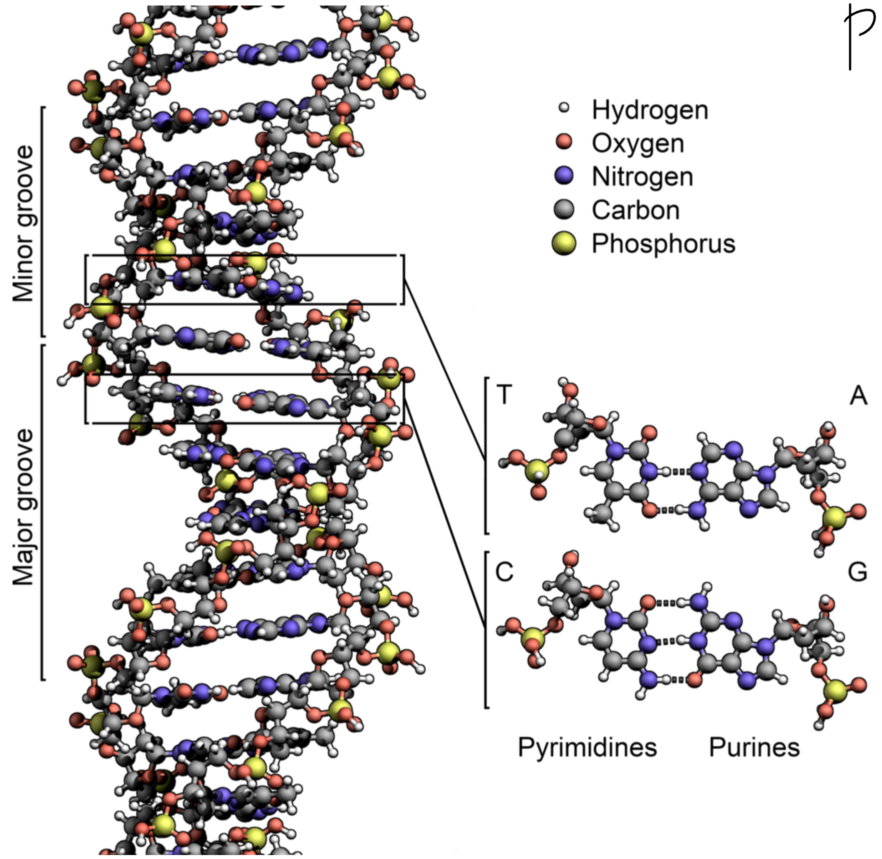
2) Biopolimeri

Es: proteine, polisaccaridi, ...

proteine ↓ DNA

polisaccaridi ↓ AMIDO, CELLULOSA

$p \sim \delta(N-N_0)$

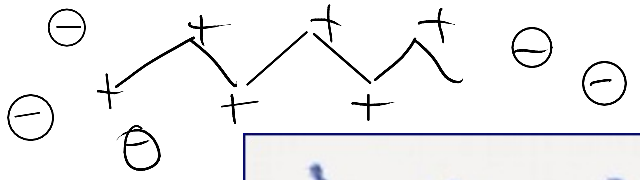


$\epsilon \sim k_B T \quad (@ T_a)$

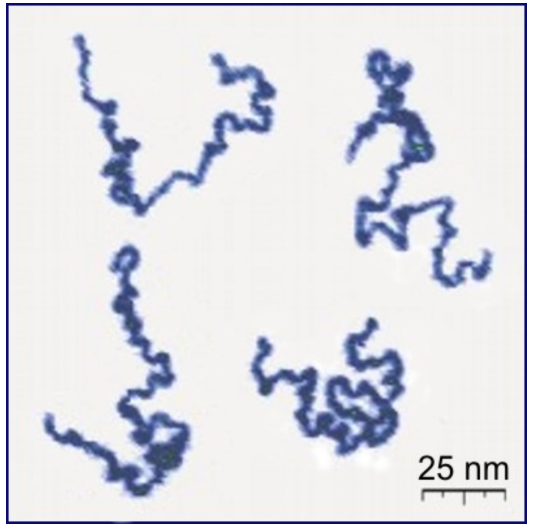
↓

fisici

3) Polielettroliti



AFM



100 nm

Roiter, Minko
J. Am. Chem. Soc. '05

Estensione

Lunghezza di legame: $a \sim 10^{-10}\,m$

Lunghezza totale: $L = N a \sim 10^{-8}\,m - 10^{-4}\,m$

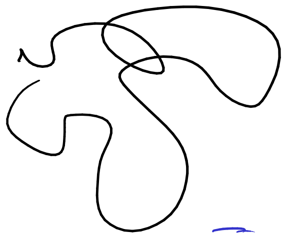
Vettore end-to-end: $\vec{R} = \vec{R}_N - \vec{R}_1$

Distanza —//— : $|\vec{R}|$

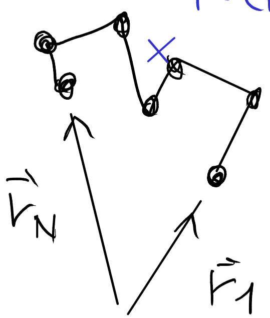
Conformazione: $\{\vec{r}_1, \dots, \vec{r}_N\}$

$\langle \dots \rangle$ ← media sulle conformazioni

Raggio di girazione: $R_g = \sqrt{\left\langle \frac{1}{N} \sum_{i=1}^{N} |\vec{r}_i - \vec{R}_{CM}|^2 \right\rangle}$



$\vec{R}_{CM} = \frac{1}{N} \sum_i \vec{r}_i$

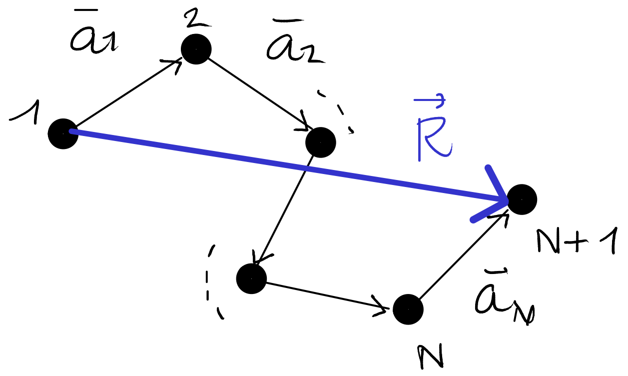


CATENA IDEALE

- N+1 monomeri
- lunghezza legame a = cost $\qquad |\bar{a}_i| = a \quad \forall i$
- orientazioni indipendenti

$$\Rightarrow \langle \vec{a}_i \cdot \vec{a}_j \rangle = a^2 \delta_{ij} \qquad \langle \vec{a}_i \rangle = \vec{0} \quad \forall i$$

$$= \langle \bar{a}_i \rangle \cdot \langle \bar{a}_j \rangle$$



$\bar{a}_i = \bar{r}_{i+1} - \bar{r}_i$

segmenti

Vettore end-to-end $\quad \vec{R} = \vec{r}_{N+1} - \bar{r}_1$

$$\langle \vec{R} \rangle = \langle \sum_{i=1}^{N} \bar{a}_i \rangle = \sum_{i=1}^{N} \langle \bar{a}_i \rangle = \vec{0}$$

Distanza end-to-end

$$\langle |\bar{R}|^2 \rangle = \langle \left(\sum_{i=1}^{N} \bar{a}_i\right) \cdot \left(\sum_{j=1}^{N} \bar{a}_j\right) \rangle = N a^2 + \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \underbrace{\langle \bar{a}_i \cdot \bar{a}_j \rangle}_{=0} = a^2 N \sim N$$

Distribuzione

$$p(\bar{R}) = p(R_x)\, p(R_y)\, p(R_z)$$

$p(\vec{R}) \approx$ gaussiana $\qquad N \gtrsim 10$ OK

$\langle |\vec{R}|^2 \rangle = 3 \langle R_x^2 \rangle \Rightarrow \langle R_x^2 \rangle = \frac{1}{3} a^2 N$

$\rightarrow |\vec{R}| \leq L = aN$ ⚠

$$p(\vec{R}) \approx \frac{1}{(2\pi a^2/3 \, N)^{3/2}} \exp\left(-\frac{3}{2a^2N} |\vec{R}|^2\right)$$

macro $\rightarrow \vec{R}$

micro $\rightarrow \{\vec{a}_1, \dots, \vec{a}_N\}$

N. conformazioni per $\vec{R}$

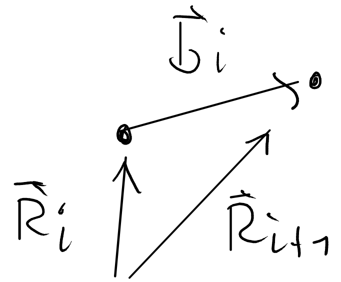
$$\Omega(\vec{R}) \sim \exp\left(-\frac{3|\vec{R}|^2}{2a^2N}\right) \Rightarrow S(\vec{R}) = K_B \ln \Omega(\vec{R}) = -\frac{3K_B|\vec{R}|^2}{2a^2N} + \text{cost}$$

$$F(\vec{R}) = -K_BT \ln \Omega(\vec{R}) = \frac{3K_BT}{2a^2N}|\vec{R}|^2 + \text{cost} \Rightarrow$$ elasticità entropica

$$= E - TS(\vec{R}) = -TS(\vec{R})$$

CATENA GAUSSIANA

- $M+1$ monomeri
- segmenti $\vec{b}_i$ indipendenti e gaussiani



$$\vec{b}_i = \vec{R}_{i+1} - \vec{R}_i$$

Distribuzione segmenti $\langle \vec{b}_i \rangle = \vec{0}$

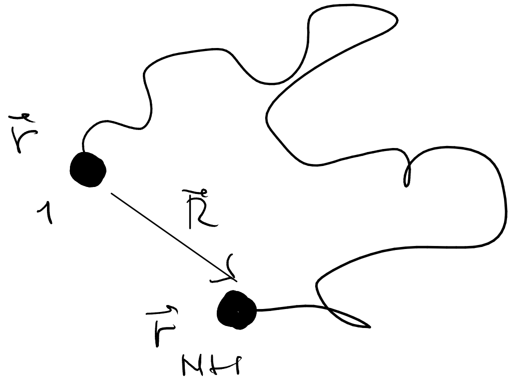
$$p(\vec{b}_i) = \frac{1}{(2\pi b^2/3)^{3/2}} \exp\left(-\frac{3|\vec{b}_i|^2}{2b^2}\right)$$

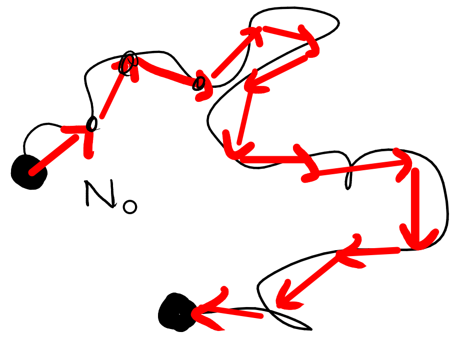
Distribuzione di $\{\vec{R}_1, \dots, \vec{R}_{M+1}\}$

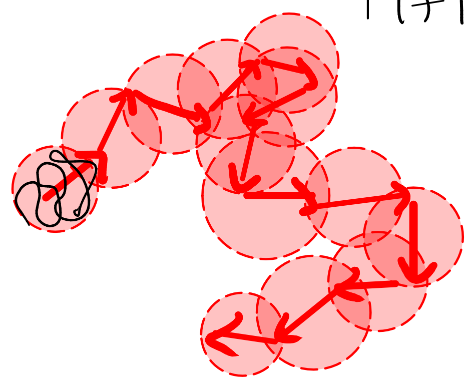
$$p(\vec{R}_1, \dots, \vec{R}_{M+1}) = \left(\frac{3}{2\pi b^2}\right)^{\frac{3N}{2}} \exp\left(-\sum_{i=1}^{M} \frac{3}{2b^2} |\vec{R}_{i+1} - \vec{R}_i|^2\right)$$

$$\Rightarrow \langle |\vec{R}|^2 \rangle = b^2 M$$

Interpretazione 1 : versione "coarse-grained" della catena ideale







$b^2 = a^2 N_0$

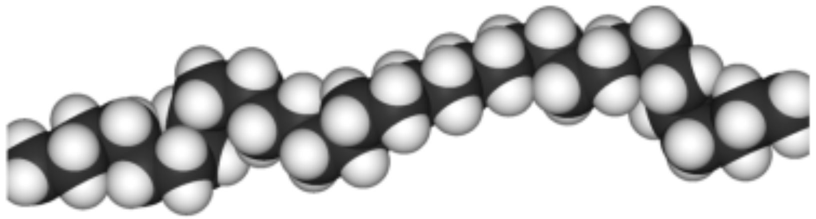
Interpretazione 2 : meccanica !

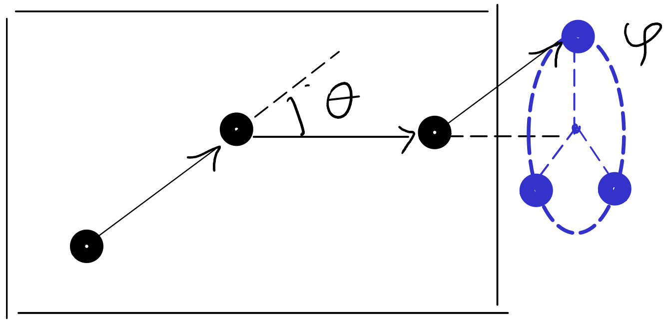
$$p(\vec{R}_1, \dots, \vec{R}_{M+1}) \sim \exp\left(-\sum_{i=1}^{M} \frac{3}{2b^2} |\vec{R}_{i+1} - \vec{R}_i|^2\right) \sim \exp\left(-\frac{H(\vec{R}_1, \dots, \vec{R}_M)}{k_B T}\right)$$

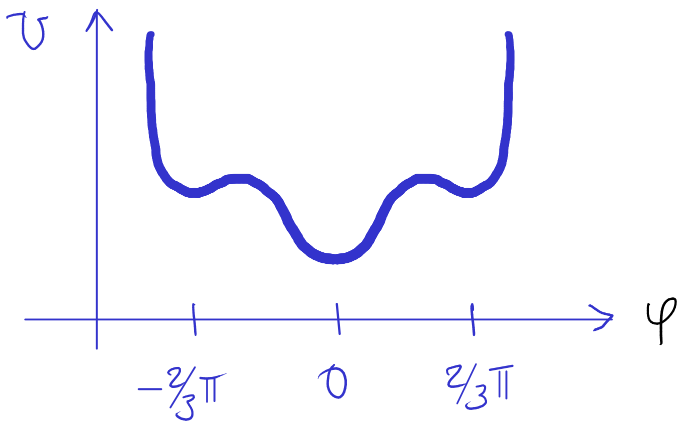
$$H = \sum_{i=1}^{N} \frac{1}{2} \underbrace{\frac{3 k_B T}{b^2}} |\vec{R}_{i+1} - \vec{R}_i|^2 \Rightarrow \text{catena oscillatori armonici accoppiati}$$

MODELLO DI KRATKY-POROD

"freely-rotating chain"







Polietilene $[CH_2]_N$

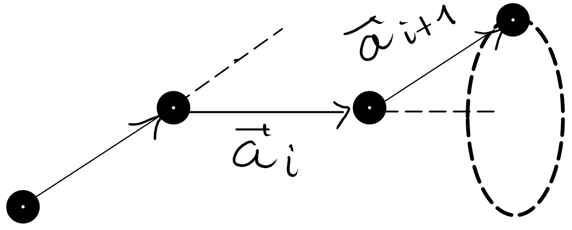
distanza di legame : $a \approx 1{,}5\ \text{Å}$

angolo di legame : $\theta \approx 68°$

- $N+1$ monomeri
- lunghezza segmenti $a = \text{cost}$
- angolo tra segmenti successivi $\theta = \text{cost}$

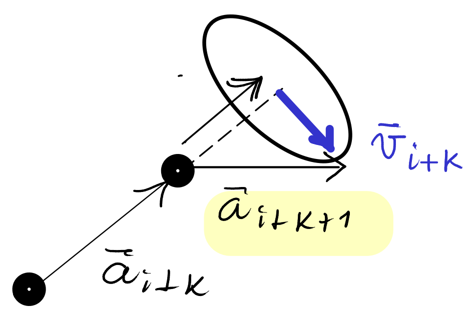
$$\langle \vec{a}_i \cdot \vec{a}_{i+1} \rangle = a^2 \cos\theta$$

$$\langle \vec{a}_i \rangle = \vec{0}$$



$$\langle \vec a_i \cdot \vec a_{i+k} \rangle = a^2 (\cos\theta)^k$$

dim. x induzione: $k \Rightarrow k+1$ $\qquad \langle \vec a_i \rangle = \vec 0$

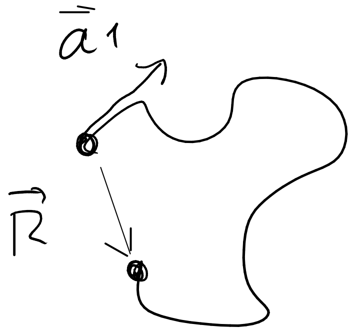


$$\begin{aligned}
\langle \vec a_i \cdot \vec a_{i+k+1} \rangle &= \langle \vec a_i \cdot (\cos\theta\, \vec a_{i+k}) \rangle + \langle \vec a_i \cdot \vec v_{i+k} \rangle \\
&= \cos\theta \langle \vec a_i \cdot \vec a_{i+k} \rangle + \vec 0 \\
&= a^2 (\cos\theta)^{k+1} \qquad \square
\end{aligned}$$

Lunghezza di persistenza

$\cos\theta < 1$

(es.) $\langle \vec a_i \cdot \vec a_{i+k} \rangle \sim \exp\left(-\frac{a}{l_p} k\right)$ $\qquad l_p \equiv$ lunghezza di persistenza



$$\begin{aligned}
\left\langle \vec R \cdot \frac{\vec a_1}{a} \right\rangle &= \frac{1}{a} \left\langle \left(\sum_{i=1}^{N} \vec a_i \right) \cdot \vec a_1 \right\rangle = \frac{1}{a} \sum_{i=1}^{N} \langle \vec a_i \cdot \vec a_1 \rangle \\
&= a \sum_{i=1}^{N} (\cos\theta)^{i-1} = a \, \frac{1 - \cos\theta^N}{1 - \cos\theta} \xrightarrow[N\to\infty]{} \underbrace{\frac{a}{1-\cos\theta}}_{= l_p}
\end{aligned}$$

$$\sum_{i=0}^{N-1} r^i = \frac{1-r^N}{1-r}$$

Distanza end-to-end

$\leftarrow N$ ⚠

$$\langle |\vec{R}|^2 \rangle = a^2 N \left[\frac{1+\cos\theta}{1-\cos\theta} - \frac{2\cos\theta}{N} \frac{1-(\cos\theta)^{N+1}}{(1-\cos\theta)^2} \right] \circledast \quad (BH)$$

$$\langle |\vec{R}|^2 \rangle = \sum_{i=1}^{N} \sum_{j=1}^{N} \langle \vec{a}_i \cdot \vec{a}_j \rangle = N a^2 + \sum_{i=1}^{N} {\sum_{j=1}^{N}}' a^2 (\cos\theta)^{|j-i|}$$

$$= N a^2 + 2 a^2 \sum_{i=1}^{N} \sum_{j>i}^{N} (\cos\theta)^{j-i} = N a^2 + 2 a^2 \sum_{i=1}^{N} (\cos\theta)^{-i} \sum_{j>i}^{N} (\cos\theta)^{j}$$

$$= \ldots = \circledast$$

(es.)

Limite $N \to \infty$

$$\langle |\vec{R}|^2 \rangle = a^2 \frac{1+\cos\theta}{1-\cos\theta} N = b^2 M$$

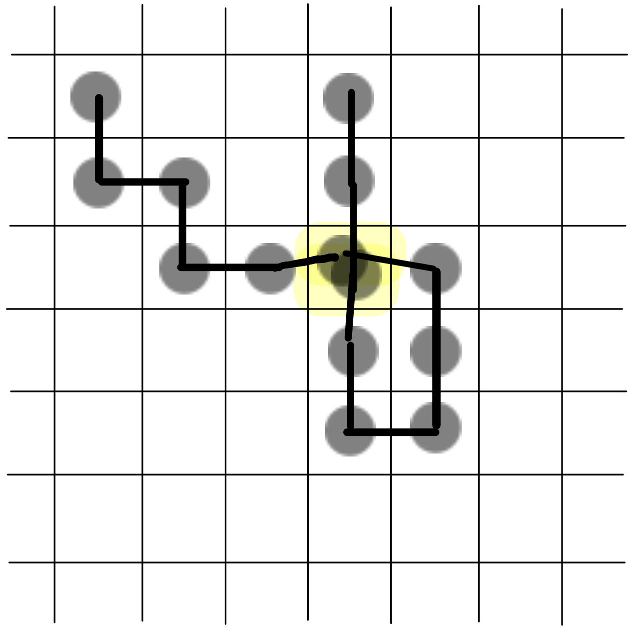
Limite $\theta \to 0$

$$\langle |\vec{R}|^2 \rangle \approx a^2 \frac{2 - \frac{\theta^2}{2}}{\theta^2/2} N \approx a^2 \frac{4}{\theta^2} N = \overbrace{\left(a \frac{4}{\theta^2}\right)^2}^{b^2} \overbrace{\frac{\theta^2}{4} N}^{M}$$

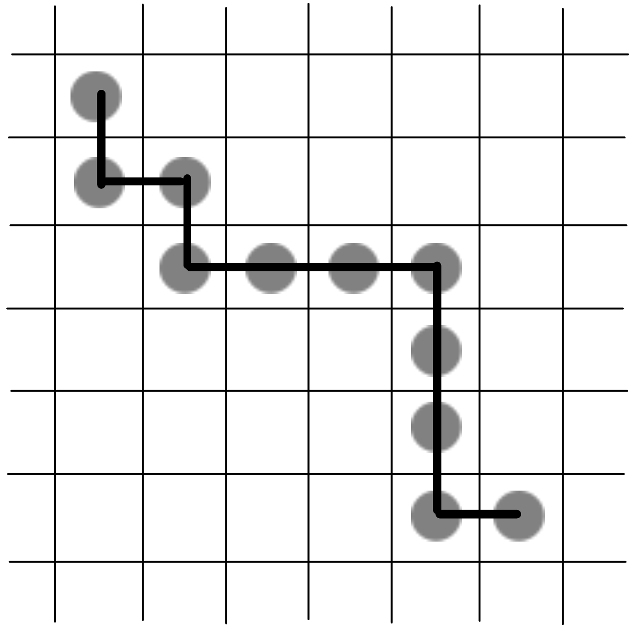
$$l_p = \frac{2}{\theta^2} = \frac{b}{2}$$

$$b = 2 l_p$$

MODELLI SU RETICOLO

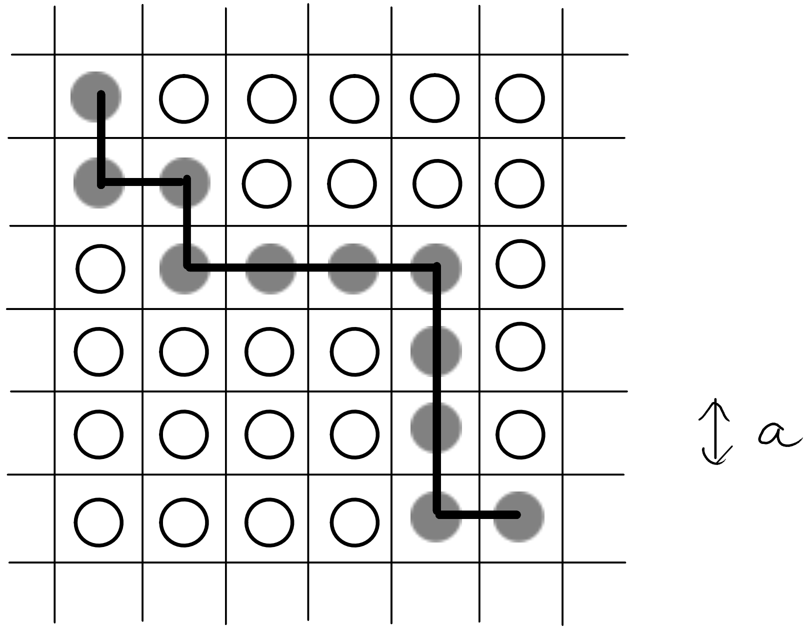


RW



SAW

Self-avoiding walk



effetti energetici

Ruolo del solvente

$$\langle |\vec{R}|^2 \rangle \sim N$$

$$N \sim R_F^{d_f} \qquad R_F \sim N^{1/2} \qquad R_F \sim N^{3/5} \qquad R_F \sim N^{\nu}$$

$\nu = 3/5$ BUONO

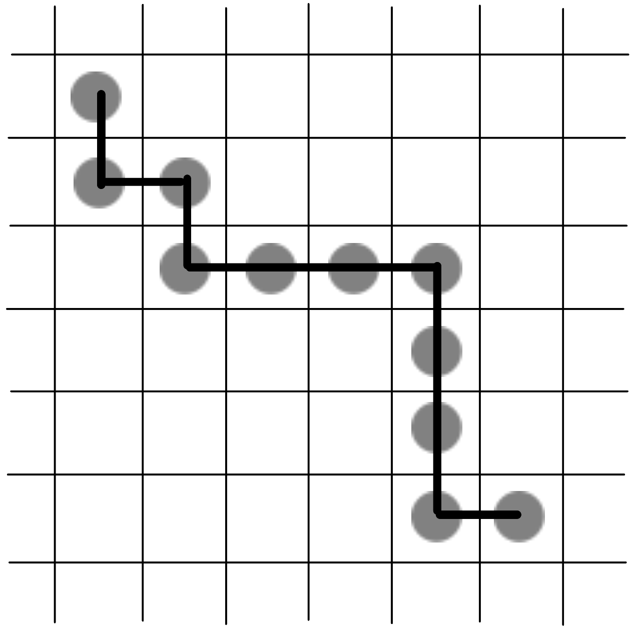
$\nu = 1/2$ θ

$\nu = 1/3$ CATTIVO

SAW

- N monomeri con $N \gg 1$
- reticolo: connettività z, volume cella $v = a^3$
- limite diluito: monomeri indipendenti

$$\rho = \frac{N}{R^3} \sim \frac{N}{N^{3/2}} \sim \frac{1}{N^{1/2}} \qquad R \sim N^{1/2}$$



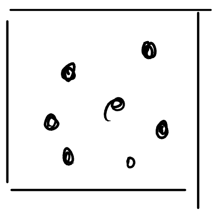
Goal: n. di conformazioni compatibili con volume escluso

Catena ideale:

$$p_{id}(\vec{R}) = \frac{1}{(2\pi a^2/_3 N)^{3/2}} \exp\left(-\frac{3}{2a^2N}|\vec{R}|^2\right) = \frac{1}{Z(N)} \exp\left(-\frac{3|\vec{R}|^2}{2a^2N}\right)$$

N. conformazioni con distanza E2E tra R e $R+dR$

$$\Omega_{id}(R) \simeq 4\pi R^2 dR \; p_{id}(R) \cdot Z(N) \qquad (N \gg 1)$$


R

monomeri independenti

n. celle : $\frac{R^3}{v} = \frac{R^3}{a^3}$

Prob. assenza overlap $N=2$: $\left(1-\frac{a^3}{R^3}\right)$

Prob. assenza overlap per N monomeri :

$$p(R) = \left(1-\frac{a^3}{R^3}\right)^{\frac{N(N-1)}{2}} = \exp\left[\frac{N(N-1)}{2}\log\left(1-\frac{a^3}{R^3}\right)\right]$$

Approx: $N \gg 1$, $\frac{a}{R} \ll 1$

$$p(R) \approx \exp\left[\frac{N^2}{2}\left(-\frac{a^3}{R^3}\right)\right]$$

N. conformazioni compatibili con volume escluso

$$\Omega(R) = \Omega_{id}(R)\cdot p(R) \sim R^2 \exp\left(-\frac{3R^2}{2a^2N} - \frac{N^2a^3}{2R^3}\right)$$

Distanza E2E tipica R_* = più probabile

$$F(R) = -K_B T \ln[\Omega(R)] = -TS(R)$$

$$= \underbrace{F_0(N) - 2K_B T \ln R + \frac{3K_B T}{2a^2 N} R^2}_{F_{id}(R)} + \underbrace{\frac{K_B T N^2 a^3}{2R^3}}_{F_{ex}(R)}$$

Caso ideale:

$R_*^2 \sim N$

$$\frac{dF}{dR} = -\frac{2K_B T}{R} + \frac{3K_B T}{a^2 N} R \Rightarrow \frac{2\cancel{K_B T}}{R_*} = \frac{3\cancel{K_B T} R_*}{a^2 N} \Rightarrow R_*^2 = \frac{2}{3} a^2 N$$

$\langle |\vec{R}|^2 \rangle$

SAW: argomento Flory

$R_* \sim N^\nu$ $\quad N^{2\nu-1}$ $\quad N^{2-3\nu}$

$$\frac{2}{R_*} = \frac{3R_*}{a^2 N} - \frac{3N^2 a^3}{2R_*^4} \qquad \frac{2}{3} = \frac{R_*^2}{a^2 N} - \frac{N^2 a^3}{2R_*^3} \qquad O(1) \sim \frac{R_*^2}{N} - \frac{N^2}{R_*^3}$$

Trascuriamo 2/3

$$\frac{R_*^2}{a^2 N} = \frac{N^2 a^3}{2 R_*^3} \Rightarrow R_*^5 \sim N^3 \Rightarrow R_* \sim N^{3/5}$$

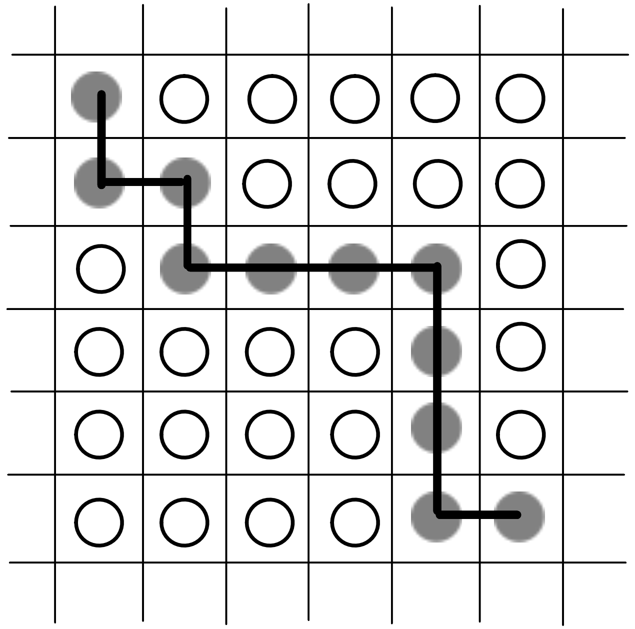
$R_* \sim N^{\nu} \leftarrow \nu \equiv$ esponente di Flory

d dimensioni : $R_* \sim N^{\frac{3}{d+2}}$

Argomento di Flory : $\nu \sim 0.6$

Gruppo di rinormalizzazione : $\nu = 0.588$

EFFETTI ENERGETICI



- SAW
- Interazioni : monomero – monomero ϵ_{mm}
  monomero – solvente ϵ_{ms}
  solvente – solvente $\epsilon_{ss} = 0$
- Approssimazione campo medio : trascuriamo fluttuazioni

Energia interazione per conformazione α

$$U_\alpha = \frac{1}{2} \sum_{i=1}^{N} \epsilon_{mm} n_{mm}^{(i)} + \sum_{i=1}^{N} \epsilon_{ms} n_{ms}^{(i)}$$

Energia media per R data

$$U(R) = \frac{1}{2} \sum_{i=1}^{N} \epsilon_{mm} \langle n_{mm}^{(i)} \rangle + \sum_{i=1}^{N} \epsilon_{ms} \langle n_{ms}^{(i)} \rangle$$

Energia libera

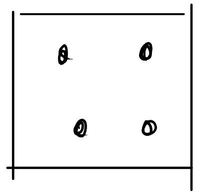
$$F(R) = F_{saw}(R) + U(R) \quad \Leftarrow \text{MF}$$

$$= F_{id}(R) + F_{ex}(R) + U(R)$$

Approx. campo medio

$$U(R) = \frac{1}{2} N \epsilon_{mm} \langle n_{mm} \rangle + N \epsilon_{ms} \langle n_{ms} \rangle$$

Bassa densità



R frazione siti occupati: $\frac{a^3 N}{R^3} = \phi$

$$\left.\begin{aligned} \langle n_{mm} \rangle &= z\phi \\ \langle n_{ms} \rangle &\simeq z(1-\phi) \end{aligned}\right\} \Rightarrow U(R) = \frac{1}{2} N \epsilon_{mm} z \frac{a^3 N}{R^3} + N \epsilon_{ms} z \left(1 - \frac{a^3}{R^3} N\right)$$

$$U(R) = \frac{1}{2} z \big(\underbrace{\epsilon_{mm} - 2\epsilon_{ms}}_{-\epsilon}\big) \frac{a^3}{R^3} N^2 + \underbrace{\epsilon_{ms} z N}_{\mathrm{cost}(N)}$$

interazioni

$$V(R) = -\frac{1}{2}\epsilon z \frac{a^3}{R^3} N^2 + \text{cost}(N)$$

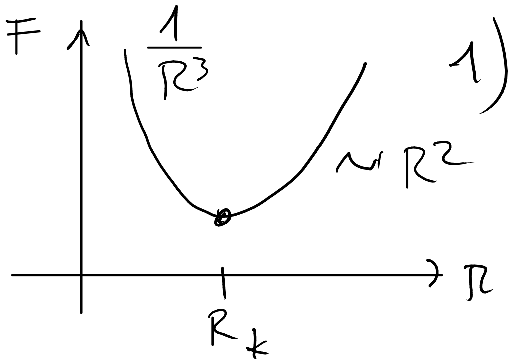
$$F(R) = F_0(N) - 2K_BT \ln R + \frac{2K_BT}{3a^2N} R^2 + \frac{1}{2} k_BT \frac{a^3}{R^3} \underbrace{\left(1 - \frac{\epsilon z}{k_BT}\right)} N^2$$

$$v_{eff} = a^3\left(1 - \frac{\epsilon z}{K_BT}\right)$$

$$F(R) = F_0(N) - 2K_BT \ln R + \frac{2K_BT}{3a^2N} R^2 + \frac{1}{2} k_BT \frac{a^3}{R^3} \left(1 - \frac{\epsilon z}{k_BT}\right) N^2$$

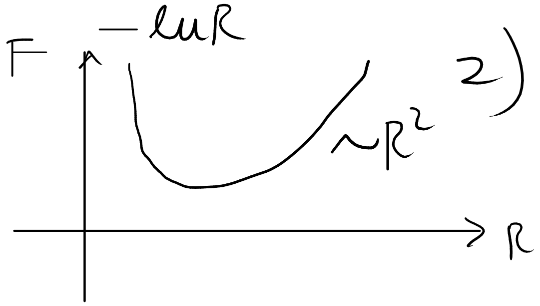
Ruolo del solvente

$$v_{eff} = v\left(1 - \frac{z\epsilon}{k_B T}\right) \qquad \epsilon = -\underbrace{\epsilon_{mm}}_{>0} + 2\underbrace{\epsilon_{ms}}_{>0} > 0$$



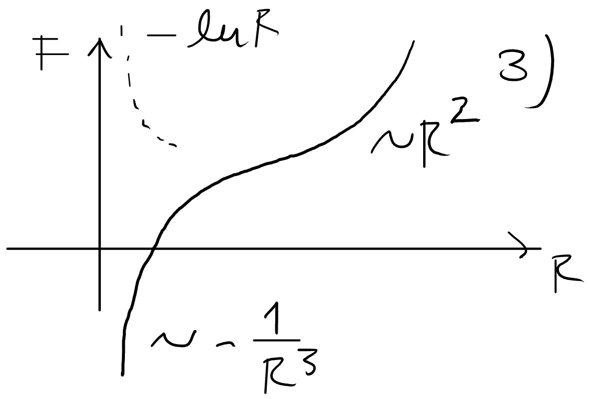
1) $k_B T \gg z\epsilon$ $\qquad v_{eff} > 0$

SAW rinormalizzato $\qquad R_k \sim N^{3/5}$ $\qquad$ BUON SOLVENTE



2) $k_B T = z\epsilon$ $\qquad v_{eff} = 0$

Catena ideale $\qquad R_k \sim N^{1/2}$ $\qquad$ SOLVENTE Θ



3) $k_B T \ll z\epsilon$

Collasso catena $\qquad R_k \sim N^{1/3}$ $\qquad$ CATTIVO SOLVENTE

→ "globule"

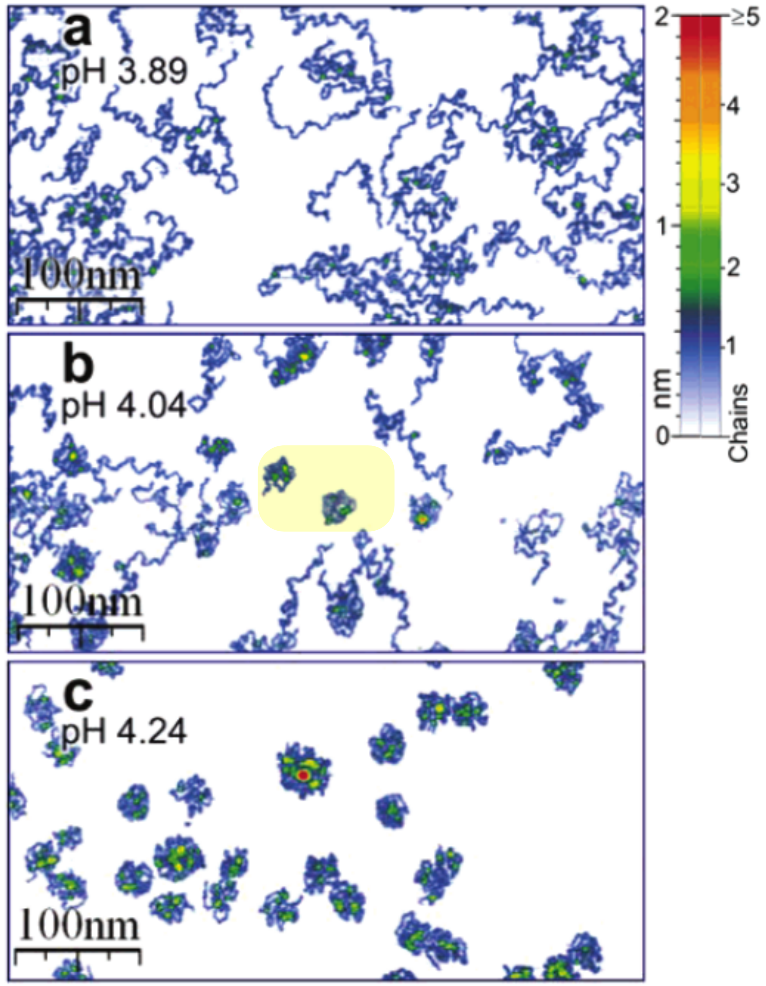


Figure 2. AFM-visualized conformations of adsorbed P2VP molecules: (a) pH 3.89, extended coils; (b) pH 4.04, intermediate state; (c) pH 4.24, compact coils. Z-scale bar shows a number of superposed chains assuming the height increment of 0.4 nm.

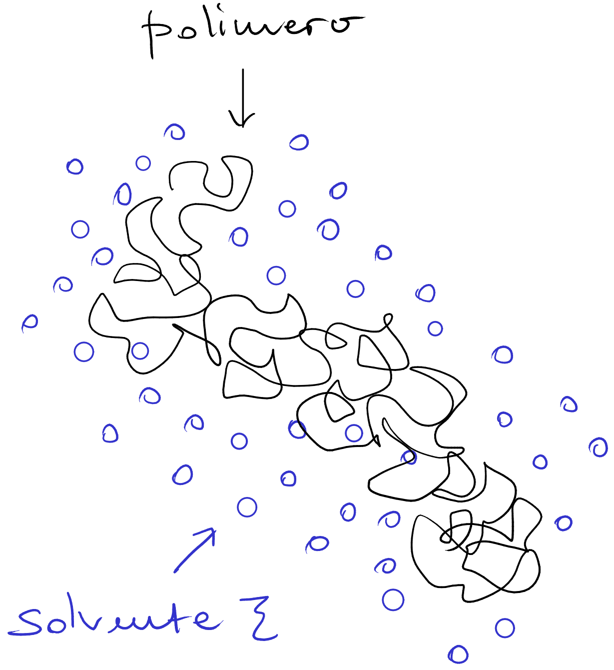
Roiter Minko JACS 2005

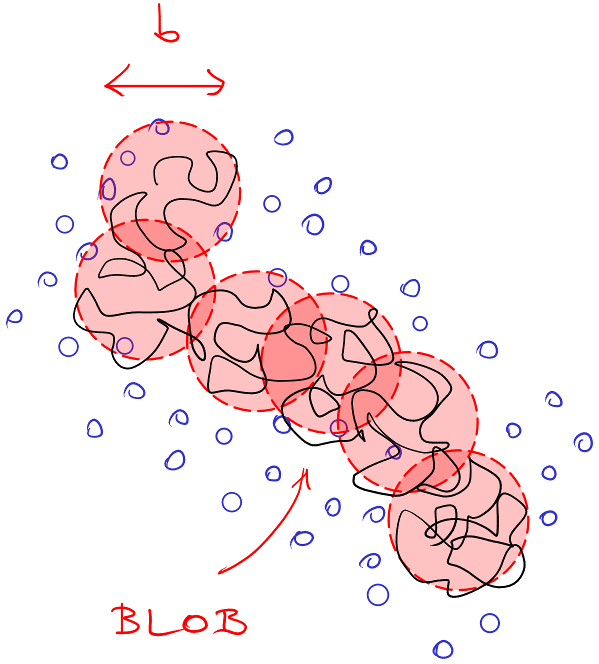
COIL – GLOBULE transition

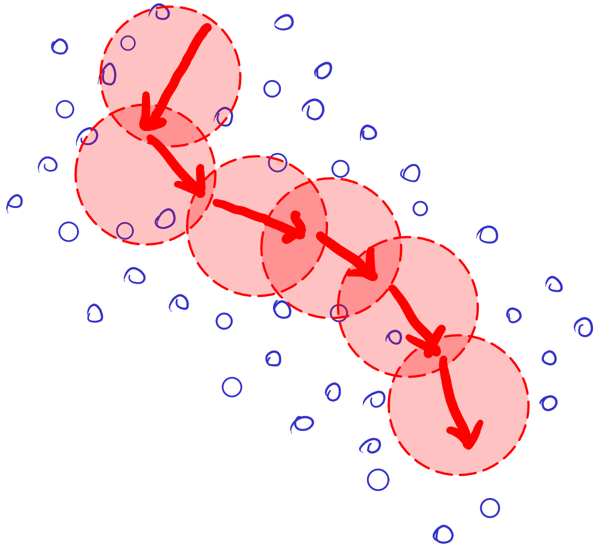
MODELLO DI ROUSE

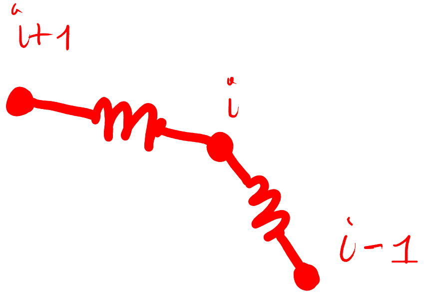
Dinamica di una catena gaussiana in un solvente

$$\frac{1}{2}\,\frac{3k_BT}{b^2}\,|\vec{R}_{i+1}-\vec{R}_i|^2$$









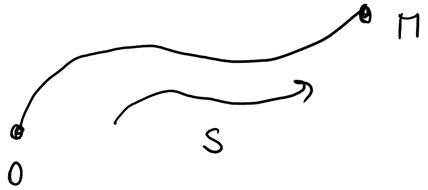
$$\xi \frac{\partial \vec{R}_i}{\partial t} = \vec{F}_i + \vec{\theta}_i(t) \qquad \langle \vec{\theta}_i \rangle = \vec{0} \qquad \langle \theta_{\alpha i}(t)\,\theta_{\beta j}(t') \rangle = 2\,\overbrace{k_BT\,\xi}^{\theta_0}\,\delta_{\alpha\beta}\,\delta_{ij}\,\delta(t-t')$$

- $M+1$ monomeri effettivi
- no volume escluso / attrazione
- catena gaussiana
- forze stocastiche indipendenti

$$\xi \frac{\partial \vec{R}_i}{\partial t} = \frac{3k_BT}{b^2}(\vec{R}_{i+1}-\vec{R}_i) + \frac{3k_BT}{b^2}(\vec{R}_{i-1}-\vec{R}_i) + \vec{\theta}_i(t)$$

$$0 < i < M$$

$$\begin{cases} \overline{R}_{-1} = \overline{R}_0 \\ \overline{R}_{M+1} = \overline{R}_M \end{cases} \Rightarrow$$



$$\vec{R}(s,t) \equiv \overline{R}_i(t)$$

$$\overline{R}(s+ds,t) \equiv \overline{R}_{i+1}(t) \quad \overline{R}(s-ds,t) \equiv \overline{R}_{i-1}(t)$$

$$\zeta \frac{\partial \overline{R}}{\partial t} = \frac{3K_BT}{b^2}\left[\overline{R}(s+ds,t) + \overline{R}(s-ds,t) - 2\overline{R}(s,t)\right] + \vec{\theta}(s,t)$$

$$\zeta \frac{\partial \overline{R}}{\partial t} \approx \frac{3K_BT}{b^2} \frac{\partial^2 \vec{R}}{\partial s^2} + \vec{\theta}(s,t) \qquad \text{B.C.:} \quad \left.\frac{\partial \overline{R}}{\partial s}\right|_0 = \left.\frac{\partial \overline{R}}{\partial s}\right|_M = \vec{0}$$

Soluzione in spazio di Fourier:

$$\vec{R}(s,t) = \overline{X}_0(t) + 2\sum_{p=1}^{\infty} \cos\left(\frac{p\pi}{M}s\right) \vec{X}_p(t) + \sum \cancel{\sin}() \left[\int ds \cos\left(\frac{q\pi}{M}s\right) \dots\right]$$

$$\tilde{X}_p(t) = \frac{1}{M}\int_0^M ds \cos\left(\frac{p\pi}{M}s\right) \overline{R}(s,t)$$

$$\int_0^{\pi} dx \cos(px)\cos(qx) = \frac{\pi}{2}\delta_{pq}(1+\delta_{p0})$$

$$\frac{1}{2}\left\{ \frac{\sin[(p-q)x]}{p-q} + \frac{\sin[(p+q)x]}{p+q} \right\}$$

Equazioni del moto

$$\frac{\partial \vec{X}_p}{\partial t} = \frac{1}{M}\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\frac{\partial \vec{R}}{\partial t} = \frac{3k_BT}{\xi M b^2}\underbrace{\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\frac{\partial^2 \vec{R}}{\partial s^2}}_{1}$$

$$+\ \underbrace{\frac{1}{M\xi}\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\vec{\theta}(s,t)}_{2}$$

1 $\displaystyle\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\frac{\partial^2 \vec{R}}{\partial s^2} = \frac{p\pi}{M}\int_0^{p\pi} dt \cos t\,\frac{\partial^2 \vec{R}}{\partial t^2} = \frac{p\pi}{M}\left\{\underbrace{\left[\sin t\,\frac{\partial^2 \vec{R}}{\partial t^2}\right]_0^{p\pi}}_{=0} - \int_0^{p\pi} dt \sin t\,\frac{\partial \vec{R}}{\partial t}\right\}$

$$t = \frac{p\pi}{M}s\ ;\quad \frac{\partial^2 R}{\partial s^2} = \left(\frac{p\pi}{M}\right)^2\frac{\partial^2 \vec{R}}{\partial s^2}$$

$$= \frac{p\pi}{M}\left\{\underbrace{\left[\cos t\,\frac{\partial \vec{R}}{\partial t}\right]_0^{p\pi}}_{=0} - \int_0^{p\pi} dt \cos t\,\vec{R}(t)\right\} = -\left(\frac{p\pi}{M}\right)^2\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\vec{R}(s)$$

perchè $\frac{\partial \vec{R}}{\partial t} = 0$ se $t = p\pi$ $(s = M)$

e $t = 0$ $(s = 0)$

$$\rightarrow\ -\frac{3k_BT}{\xi M b^2}\,\frac{p^2\pi^2}{M}\,\vec{X}_p(t)$$

② $\bar{\theta}_p(t) \equiv \frac{1}{M}\int_0^M ds\, \cos\left(\frac{p\pi}{M}s\right)\bar{\theta}(s,t)$

$$\begin{cases} \langle \bar{\theta}_p(t)\rangle = 0 \\ \langle \theta_{\alpha p}(t)\,\theta_{\beta q}(t')\rangle = \frac{1}{M^2}\int_0^M ds\int_0^M ds'\,\cos\left(\frac{p\pi s}{M}\right)\cos\left(\frac{q\pi s'}{M}\right)\langle \theta_{\alpha p}(s,t)\,\theta_{\alpha q}(s',t')\rangle \end{cases}$$

$$= \frac{2 k_B T \xi}{M^2}\underbrace{\int_0^M ds\,\cos\left(\frac{p\pi s}{M}\right)\cos\left(\frac{q\pi s}{M}\right)}_{\frac{M}{\pi}\frac{\pi}{2}\delta_{qp}(1+\delta_{p0})}\delta(t-t')\,\delta_{\alpha\beta}$$

$$= \frac{k_B T \xi}{M}\,\delta_{qp}\,(1+\delta_{p0})\,\delta(t-t')\,\delta_{\alpha\beta}$$

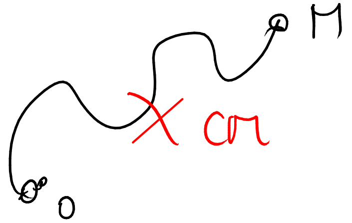
$$\frac{\partial \bar{X}_p}{\partial t} = -\frac{3 k_B T}{\xi M b^2}\,\frac{p^2\pi^2}{M}\,\bar{X}_p(t) + \frac{1}{\xi}\bar{\theta}_p(t)$$

Modi di Rouse:

$$\vec{X}_p(t) = \frac{1}{M}\int_0^M ds \cos\left(\frac{p\pi}{M}s\right)\vec{R}(s,t)$$

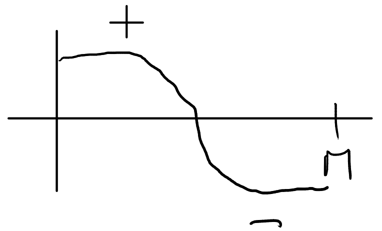
$p=0$:

$$\vec{X}_0(t) = \frac{1}{M}\int_0^M ds\, \vec{R}(s,t)$$



$$\frac{1}{M}\sum_{i=0}^{M} \vec{R}_i(t) = CM$$

$p=1$:



$$\frac{\partial \vec{X}_p}{\partial t} = -\frac{3k_BT}{\xi M b^2}\frac{p^2\pi^2}{M}\vec{X}_p(t) + \frac{1}{\xi}\vec{\theta}_p(t) = -\frac{1}{\tau_p}\vec{X}_p(t) + \frac{1}{\xi}\vec{\theta}_p(t)$$

$$\langle \theta_{\alpha p}(t)\,\theta_{\beta q}(t')\rangle = \frac{k_BT\,\xi}{M}\,\delta_{qp}\,(1+\delta_{p0})\,\delta(t-t')\,\delta_{\alpha\beta}$$

Moto del CM: $p = 0$

$$\frac{\partial \vec{x}_p}{\partial t} = \frac{1}{\xi} \vec{\theta}_0(t) \Rightarrow \vec{x}_0(t) = \vec{x}_0(0) + \frac{1}{\xi}\int_0^t dt' \, \vec{\theta}_0(t)$$

$$\langle |\vec{x}_0(t) - \vec{x}_0(0)|^2 \rangle = \frac{1}{\xi^2}\int_0^t dt' \int_0^t dt'' \langle \vec{\theta}_0(t') \cdot \vec{\theta}_0(t'') \rangle$$

$$= 6 \frac{1}{\xi^2} \frac{K_B T \xi}{M} t = 6 \underbrace{\frac{K_B T}{\xi M}}_{D_{CM}} t \sim t \qquad \underline{D_{CM} \sim \frac{1}{M}}$$

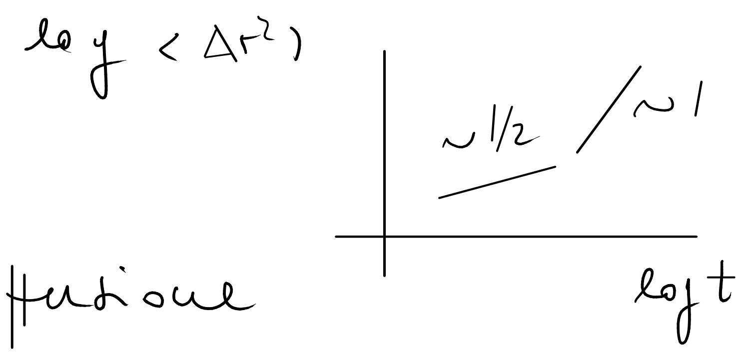
Dinamica dei modi di Rouse $(p \geq 1)$

$$\langle \vec{x}_p(t) \cdot \vec{x}_p(0) \rangle = \ldots = \langle |\vec{x}_p(0)|^2 \rangle e^{-t/\tau_p}$$

$$\tau_p \equiv \frac{\xi M^2 b^2}{3 K_B T p^2 \pi^2}$$ tempo di correlazione di Rouse $\qquad \underline{\tau_p \sim M^2} \sim \frac{1}{p^2}$

Dinamica segmentale

$\to \quad \vec{R}(s,t) \quad \to \quad \vec{R}_i(t)$



$t \gg \tau_1 \qquad \langle |\vec{R}_i(t) - \vec{R}_i(0)|^2 \rangle \sim t \qquad$ (es.)

$t \ll \tau_1 \qquad \langle |\vec{R}_i(t) - \vec{R}_i(0)|^2 \rangle \sim t^{1/2} \qquad$ sotto-diffusione

Dinamica rotazionale

$\vec{R}(t) = \vec{R}(M,t) - \vec{R}(0,t)$ vettore end-to-end

$$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle = 16 \sum_{p=1,3,\dots} \langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle \qquad t_R \sim \tau_1 \sim M^2$$

$$\vec{R}(t) = \cancel{\vec{X}_0} + 2 \sum_{p=1}^{\infty} \cos(p\pi)\, \vec{X}_p(t) - \cancel{\vec{X}_0} - 2 \sum_{p=1}^{\infty} \vec{X}_p(t)$$

$$= 2 \sum_{p=1}^{\infty} [\cos(p\pi) - 1]\, \vec{X}_p(t) = -4 \sum_{p=1,3,5,\dots} \vec{X}_p(t)$$

-2 disp.

0 pari

Modello Rouse

$$\begin{cases} D_{CM} \sim \frac{1}{M} \\ \tau_R \sim M^2 \end{cases}$$

Esperimenti

$$\begin{cases} D_{CM} \sim \frac{1}{M^{\nu}} \\ \tau_R \sim M^{2\nu+1} \end{cases}$$

TABLE 2: Experimental Values of α and $d_F = 1/\alpha$ As Found in the Literature or in This Study

molecule family	α	d_F	range	source
globular proteins	0.39	2.56	2.04	PDB[13]
globular proteins	0.39	2.56	1.46	this work
PS in toluene	0.41	2.45	2.93	this work
PMMA in acetone below 30 kD	0.46	2.17	1.68	this work
PS in acetone	0.47	2.15	1.72	this work
PS in $CDCl_3$ below 20 kD	0.47	2.12	1.62	this work
PMMA in $CDCl_3$ below 30 kD	0.48	2.07	1.68	this work
oligosaccharides[a]	0.48	2.07	2.17 (3.40)[b]	NMR[3]
PS in THF below 20 kD	0.50	2.01	1.72	this work
PEO in D_2O	0.54	1.86	3.90	this work
small molecules in D_2O[a]	0.54	1.84	1.39	NMR[5]
PMMA in acetone above 25 kD	0.54	1.84	1.81	this work
PEO in water	0.55	1.82	2.80	NMR[6]
small molecules in $CDCl_3$[a]	0.56	1.77	1.60	NMR[5]
DNA	0.57	1.75	1.69	fluorescence[12]
PEO in $CDCl_3$	0.58	1.73	4.13	this work
denatured peptide[a,c]	0.58	1.71	1.15	NMR[2]
PMMA in $CDCl_3$ above 25 kD	0.61	1.65	1.81	this work
PS in $CDCl_3$ above 20 kD	0.61	1.63	2.63	this work
PS in THF above 20 kD	0.62	1.61	2.00	this work
Linear alcanes	0.71	1.41	0.50 (C8−C26)	this work

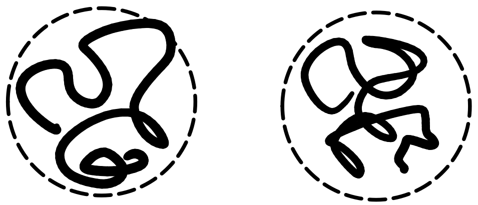
Modello di Zimm

→ MF interazioni idrodinamiche

$$D_{CM} \sim \frac{1}{M^{\alpha}} \sim \frac{1}{M^{1/2}}$$

REGIMI DI DENSITÀ

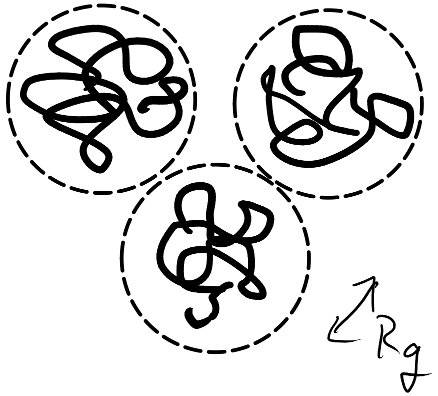
Diluito



$\rho \lesssim \rho^*$

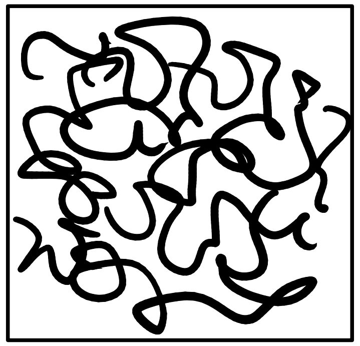
ρ^*

Semi-diluito



$\rho \gtrsim \rho^*$

Concentrato

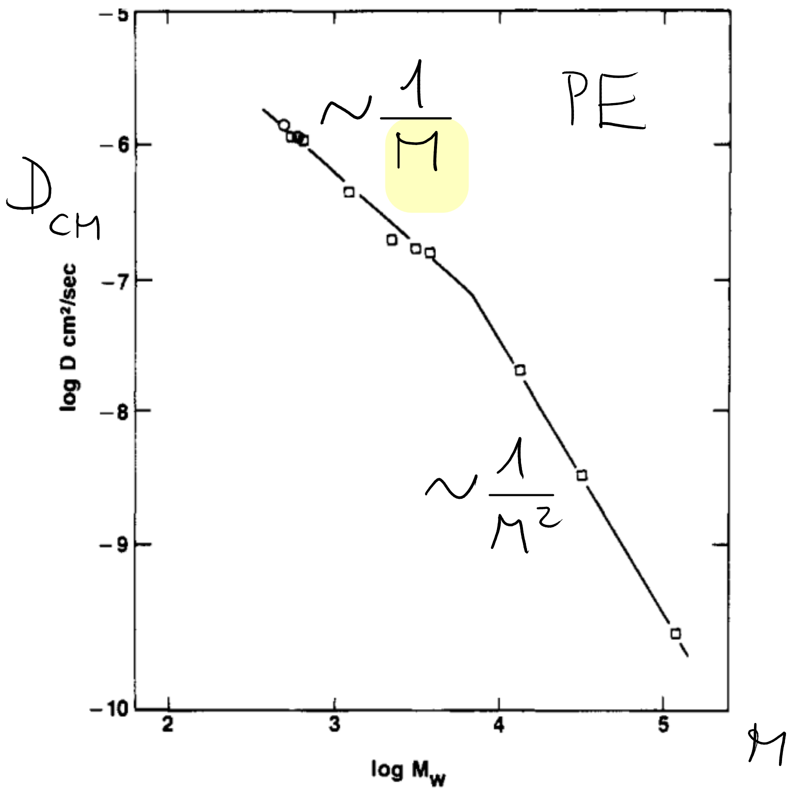


$\rho \gg \rho^*$

MELT

De Gennes

"Reptation"



ıre 11. Self-diffusion coefficient corrected to the temperature hich the friction factor for viscosity equals 2.3×10^{-9} dyn·s/cm. ıperatures are listed in Table III. Symbols are same as Figure

Pearson et al.

Macromolecules