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,
						

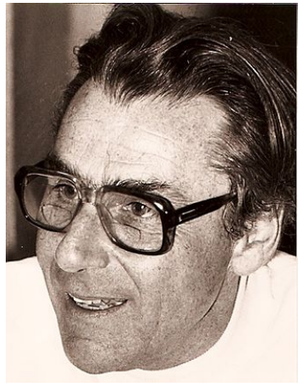
Def.: macromolecole composte da unità molecolari ("monomeri") connesse in forma di catena

Grado di polimerizzazione: $N \sim 10^2 \to 10^5$

$p(N)$

Massa molecolare: $M = mN$

Leggi di scala $\to$ N



Hans Kuhn

'30

Paul Flory

Nobel '71

(chimica)

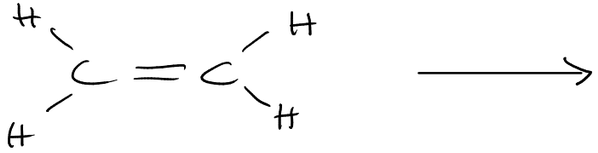
Pierre-Gilles De Gennes

Nobel '91

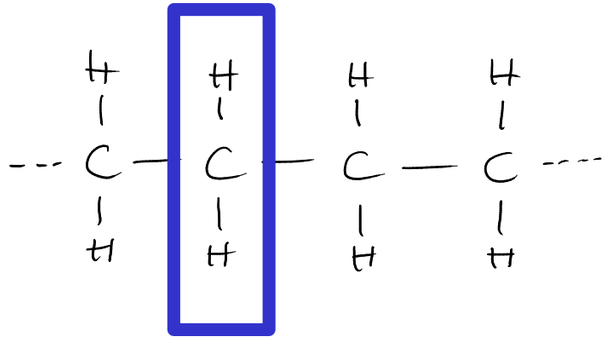
(fisica)

1) Polimeri sintetici

- Polietilene (PE)



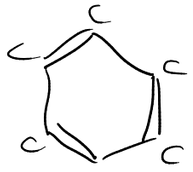
C_2H_4 etilene



$[CH_2]_N$ PE

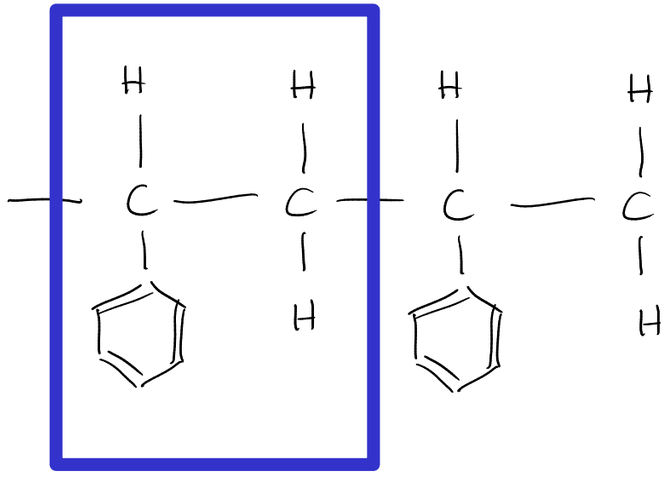
- LDPE semi-flessibile
- HDPE flessibile

- Polistirene (PS)



C_6H_6

benzene

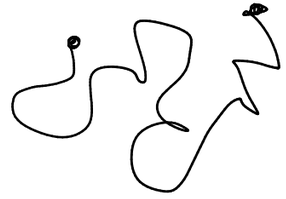


$[C_8H_8]_N$

regolare → XTAL

casuale → GLASS

flessibile



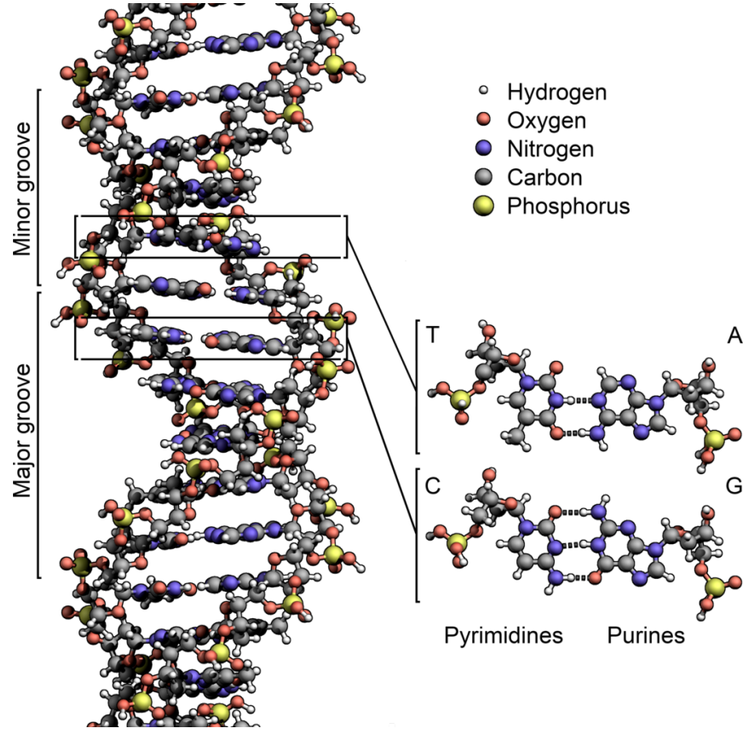
Energie di legame

$\epsilon \gg K_B T \quad @ Ta$

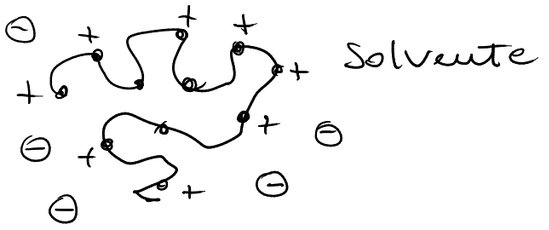
2) Biopolimeri

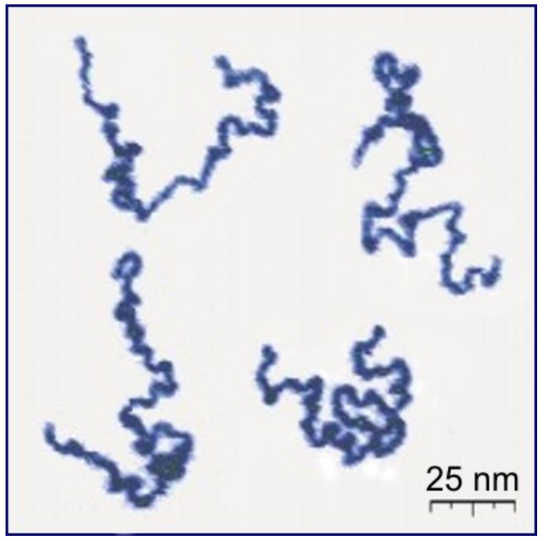
Es: proteine (DNA),
polisaccaridi (AMIDO, CELLULOSA)

$\epsilon \sim k_B T$ @Ta $p \sim \delta(N - N_0)$



3) Polielettroliti





100 nm

AFM

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

Estensione

Lunghezza di legame : a

Lunghezza totale : $L = Na$

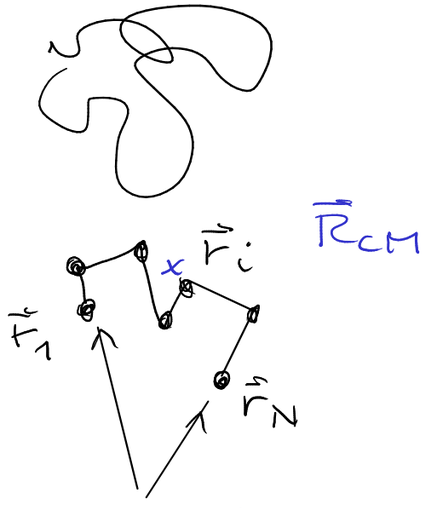
Vettore end-to-end : $\vec{R} = \vec{r}_N - \vec{r}_1$

Distanza E2E : $|\vec{R}|$

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

Medie sulle conformazioni : $\langle \ldots \rangle$

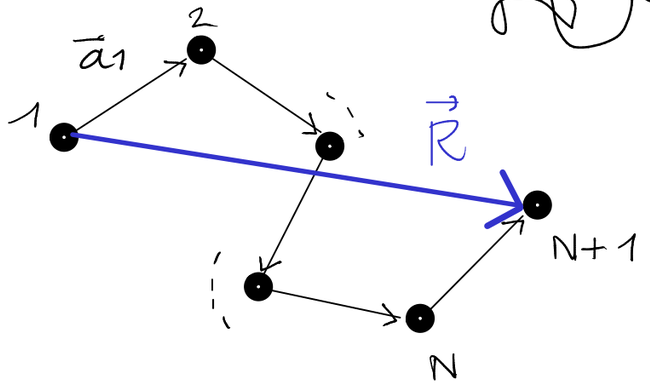
Raggio di girazione : $R_g = \left(\left\langle \frac{1}{N} \sum_{i=1}^{N} |\vec{r}_i - \vec{R}_{CM}|^2 \right\rangle \right)^{1/2} \sim |\vec{R}|$



$$\vec{R}_{CM} = \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i$$

CATENA IDEALE

"freely jointed chain"



- N+1 monomeri
- distanza legame $a = cost$ $\quad |\vec{a}_i| = a$
- orientazioni indipendenti $\quad \langle \vec{a}_i \rangle = \vec{0}$

$$\langle \vec{a}_i \cdot \vec{a}_j \rangle = a^2 \delta_{ij}$$

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

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

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

$\vec{a}_i = \vec{r}_{i+1} - \vec{r}_i$ (segmento)

RW!

Distribuzione prob. di $\vec{R}$ (pdf)

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

$p(\vec{R})$, $p(R_x) \approx$ gaussiana $\quad N \gtrsim 10$

$$\langle R_x \rangle = 0 \quad ; \quad \langle R_x^2 \rangle = \frac{1}{3} \langle |\vec{R}|^2 \rangle$$

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

microstati $\{\vec{r}_1, \dots, \vec{r}_{N+1}\} \rightarrow$ macrostato $\vec{R}$

N. conformazioni con $\vec{R}$

$$\Omega(\vec{R}) \sim \exp\left(-\frac{3}{2a^2 N} |\vec{R}|^2\right)$$

Entropia

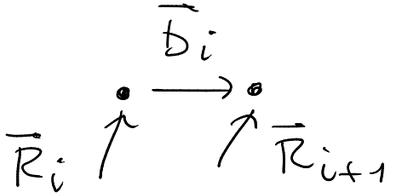
$$S(\vec{R}) = k_B \ln \Omega(\vec{R}) = \text{cost} - \frac{3 k_B}{2a^2 N} |\vec{R}|^2 \rightarrow \text{catena flessibile}$$

Energia libera

$$F(\vec{R}) = -TS = \frac{3 k_B T}{2a^2 N} |\vec{R}|^2 + \text{cost} \sim \text{elasticità entropica}$$

CATENA GAUSSIANA

- $M+1$ monomeri
- segmento $\vec{b}_i = \vec{R}_{i+1} - \vec{R}_i$
- segmenti indipendenti e gaussiani



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

$$\langle |\vec{b}_i|^2 \rangle = b^2$$

$$\langle b_{ix}^2 \rangle = \frac{1}{3} b^2$$

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

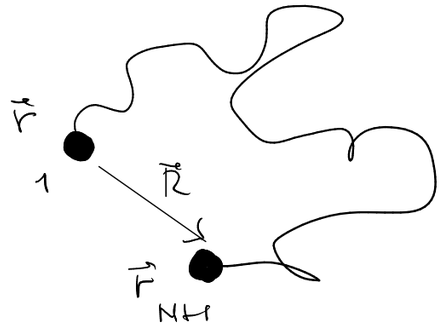
Distribuzione di $\{\vec{R}_1, \dots, \vec{R}_{M+1}\}$?

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

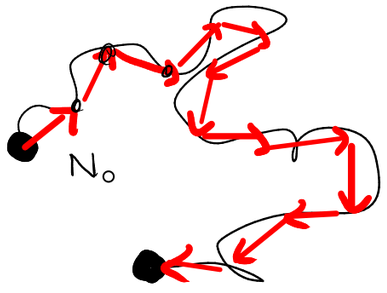
Vettore end-to-end

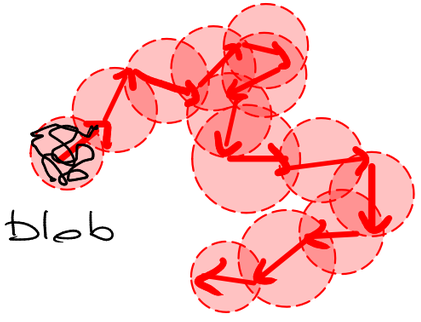
$$\langle \vec{R} \rangle = \vec{0} \qquad \langle |\vec{R}|^2 \rangle = b^2 M \sim M$$

Interpretazione 1 : versione coarse-grained della catena ideale

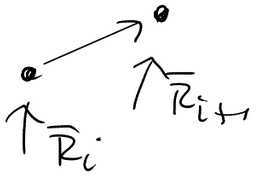


$N_0 \gtrsim 10$





$b^2 = a^2 N_0$



Interpretazione 2 : meccanica

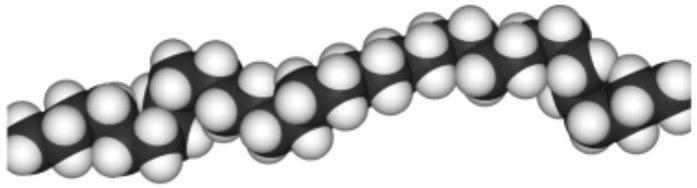
$$p(\vec{R}_1, \dots, \vec{R}_{N+1}) \sim \exp\left(-\frac{3}{2b^2}\sum_{i=1}^{M} |\vec{R}_{i+1} - \vec{R}_i|^2\right) \sim \exp\left(-\frac{H(\vec{R}_1, \dots, \vec{R}_{N+1})}{k_B T}\right)$$

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

catena oscillatori armonici accoppiati

MODELLO DI KRATKY - POROD

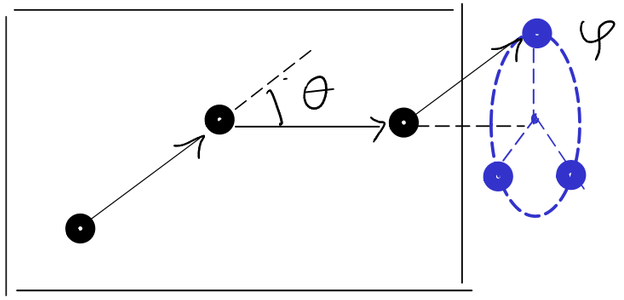
"freely rotating chain"

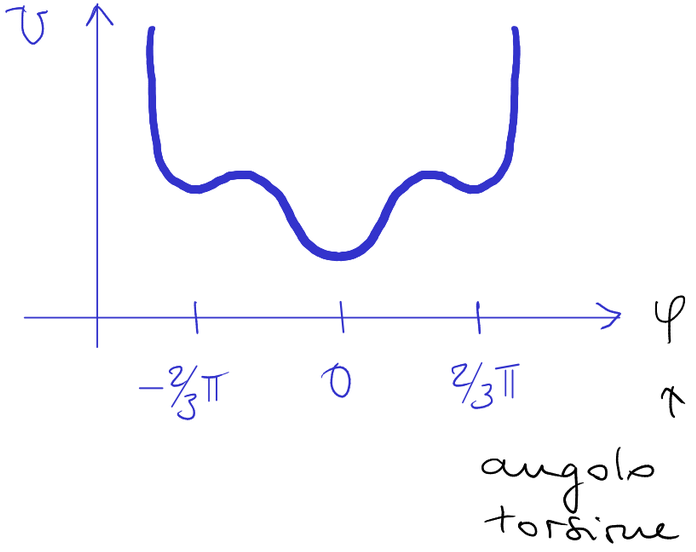


Polietilene $[CH_2]_N$

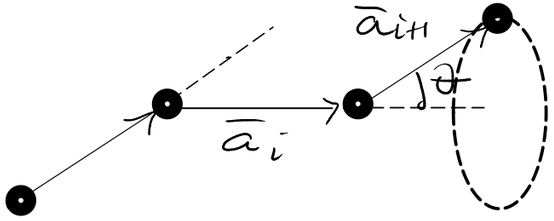
distanza di legame: $a \approx 1{,}5$ Å

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





- N+1 monomeri
- lunghezza legame $a = cost$ $\qquad \langle \bar{a}_i \cdot \bar{a}_{i+1} \rangle = 0$
- correlazione tra segmenti: $\langle \bar{a}_i \cdot \bar{a}_{i+1} \rangle = a^2 \cos\theta$



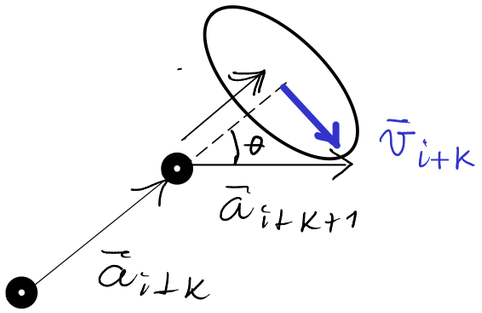
$$\langle \bar{a}_i \cdot \bar{a}_{i+k} \rangle = a^2 (\cos\theta)^k \qquad \cos\theta < 1$$

Dim. per induzione: $k \Rightarrow k+1$

$$\langle \bar{a}_i \cdot \bar{a}_{i+k+1} \rangle = \cos\theta \langle \bar{a}_i \cdot \bar{a}_{i+k} \rangle + \langle \bar{a}_i \cdot \bar{v}_{i+k} \rangle$$

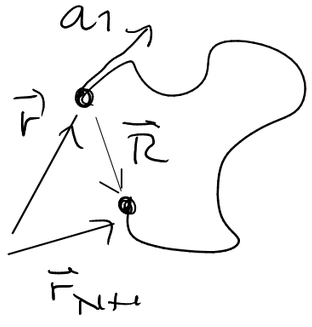
$$\bar{a}_{i+k+1} = \cos\theta\, \bar{a}_{i+k} + \bar{v}_{i+k} \qquad = 0$$

$$= a^2 (\cos\theta)^{k+1} \quad \square$$



Lunghezza di persistenza

$$\left\langle \frac{\bar{a}_1}{a} \cdot \vec{R} \right\rangle = \frac{1}{a} \left\langle \bar{a}_1 \cdot \left(\sum_{i=1}^{N} \bar{a}_i \right) \right\rangle = \frac{1}{a} \sum_{i=1}^{N} \langle \bar{a}_1 \cdot \bar{a}_i \rangle$$



$$= \frac{a^2}{a} \sum_{i=1}^{N} (\cos\theta)^{i-1} = a \frac{1-(\cos\theta)^N}{1-\cos\theta} \xrightarrow[N\to\infty]{} \frac{a}{1-\cos\theta} = l_p$$

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

l_p ↑ lunghezza di persistenza

Distanza end-to-end

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

$$= \langle \left(\sum_{i=1}^{N} \vec{a}_i\right) \cdot \left(\sum_{j=1}^{N} \vec{a}_j\right) \rangle = a^2 N + \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \langle \vec{a}_i \cdot \vec{a}_j \rangle$$

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

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

Limite $N \to \infty$:

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

$2 l_p$

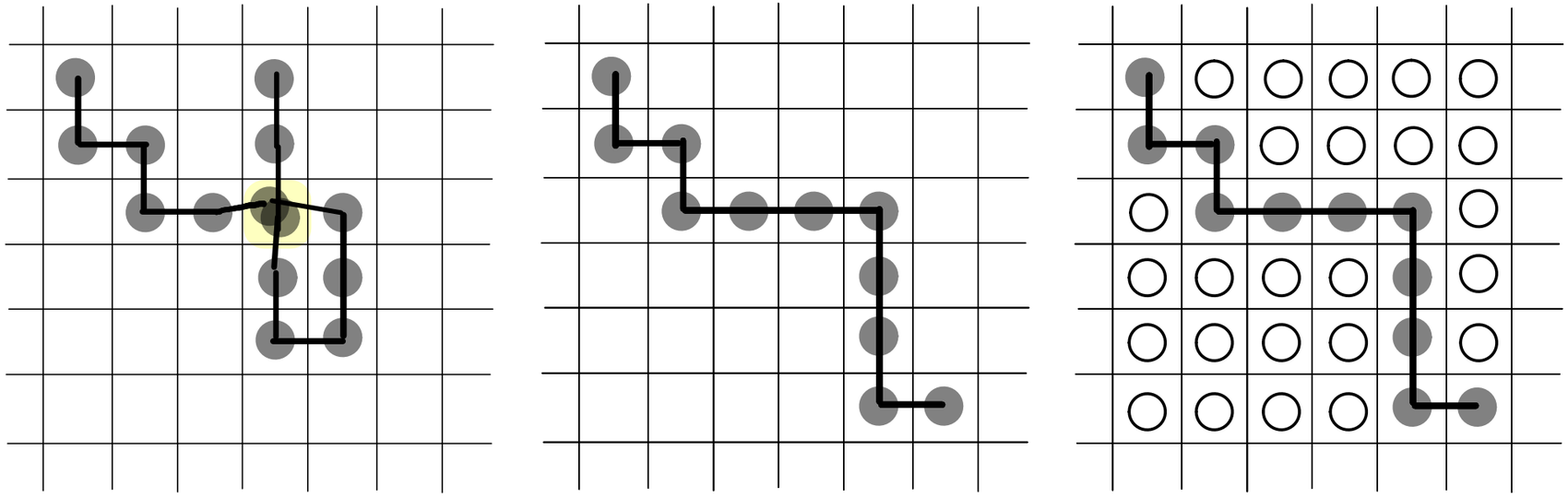
Limite $\theta \to 0$ (forte persistenza) : $l_p \approx \frac{a}{\theta^2/2} = a \frac{2}{\theta^2}$ $\quad b^2 = \left(2 \frac{2a}{\theta^2}\right)^2$

$$\langle |\vec{R}|^2 \rangle \simeq a^2 \frac{1+1-\theta^2/2}{\theta^2/2} N = a^2 \frac{2-\theta^2/2}{\theta^2/2} N \approx a^2 \frac{4}{\theta^2} N = a^2 \left(\frac{4}{\theta^2}\right)^2 \left(\frac{\theta^2}{4}\right) N$$

$$= b^2 M$$

$$\begin{cases} b = 2\ell_p \\ M = \left(\frac{\theta^2}{4}\right) N \end{cases}$$

MODELLI SU RETICOLO



RW

SAW

self-avoiding walk

Effetti energetici

solvente

$R_f \sim N^{\nu}$

$N \sim R_f^{d_f}$

dimensione frattale

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

$R_f \sim N^{1/2}$

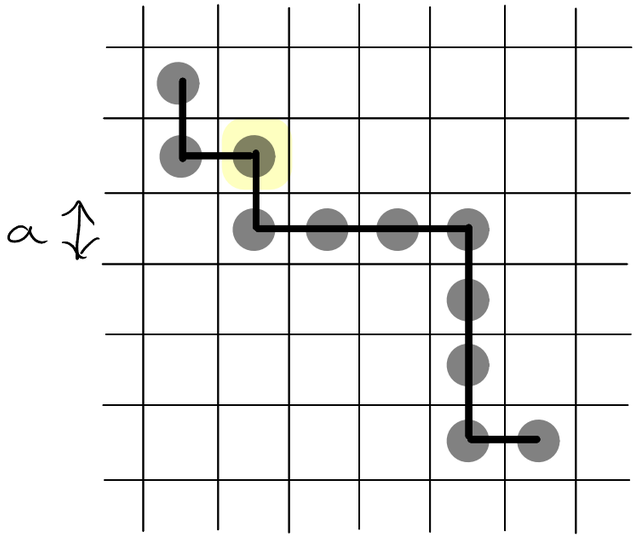
$R_f \sim N^{3/5}$

$R_f \sim N^{\nu}$ — BUON SOLVENTE: $\frac{3}{5}$; θ: $\frac{1}{2}$; CATTIVO SOLVENTE: $\frac{1}{3}$

SAW

- N monomeri $N \gg 1$
- reticolo: z connettività, celle lunghezza lineare a
- regime diluito: monomeri indipendenti

$$\rho = \frac{N}{R^3} \sim \frac{N}{N^{3\nu}} \sim N^{1-3\nu} \to 0 \quad N \gg 1$$



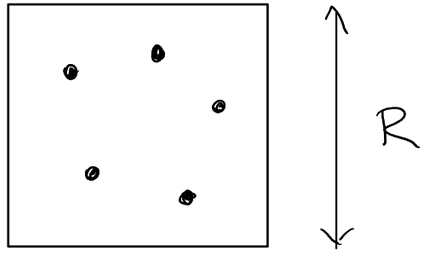
Goal: n. conformazioni compatibili con vincolo di volume escluso

Catena ideale: per $N \gg 1$

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

N. conf. con distanza E2E tra R e R+dR

$$\Omega_{id}(R) = 4\pi R^2 dR \cdot p_{id}(|\vec{R}|)$$



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

N = 2 : prob. che non ci sia overlap

$\left(1 - \frac{a^3}{R^3}\right)$

$\frac{N(N-1)}{2}$ coppie indipendenti

Prob. che non ci siano overlaps

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

Siccome $N \gg 1$, $R \gg a$

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

N. conformazioni compatibili con vincolo volume escluso

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

Distanza E2E "tipica" = più probabile

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

$$= \underbrace{F_0 - 2k_BT \ln R + \frac{3k_BT}{2a^2N} R^2}_{F_{id}(R)} + \underbrace{\frac{k_BT a^3 N^2}{2} \frac{1}{R^3}}_{F_{ex}(R)}$$

Distanza E2E tipica R_* per la catena ideale

$$\frac{dF_{id}}{dR} = -\frac{2k_BT}{R} + \frac{3k_BT}{a^2N} R \Rightarrow \frac{3k_BT}{a^2N} R_* = \frac{2k_BT}{R_*} \Rightarrow R_*^2 = \frac{2}{3} a^2 N$$

$$R_*^2 \sim N$$

$$R_*^2 = \frac{2}{3} \langle |\bar{R}|^2 \rangle$$

Distanza tipica R_* per SAW

$$\frac{dF}{dR} = -\frac{2 k_B T}{R} + \frac{3 k_B T}{a^2 N} R - \frac{3 k_B T a^3 N^2}{2} \frac{1}{R^4} = 0 \qquad R = R_*$$

$$\frac{3 k_B T}{a^2 N} R_* - \frac{3 k_B T a^3 N^2}{2} \frac{1}{R_*^4} = \frac{2 k_B T}{R_*}$$

$$\frac{1}{a^2 N} R_*^2 - \frac{a^3 N^2}{2} \frac{1}{R_*^3} = \frac{2}{3} \longrightarrow O(N^{2\nu-1}) - O(N^{2-3\nu}) = \underbrace{O(1)}$$

Trascuriamo $\frac{2}{3}$

$$R_*^5 \sim N^3 \Rightarrow R_* \sim N^{3/5} \qquad R_* \sim N^{\nu} \rightarrow \text{esponente di Flory}$$

check:

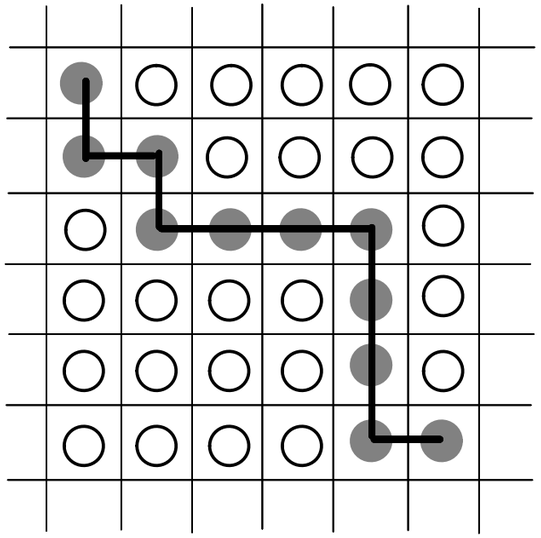
$$\begin{cases} 2\nu - 1 > 0 & \nu > 1/2 = 0.5 \\ 2 - 3\nu > 0 & \nu < 2/3 = 0.\overline{6} \end{cases}$$

SAW: $\nu = 0.6$ in 3 d $\boxed{V}$

RG: $\nu = 0.588$!!

EFFETTI ENERGETICI

- SAW : regime diluito
- Interazioni : monomero – monomero ϵ_{mm}
  monomero – solvente ϵ_{ms}
  solvente – solvente $\epsilon_{ss} = 0$

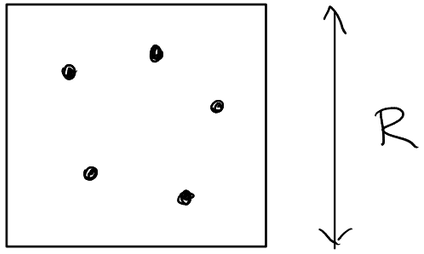


Energia conformazione α

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

Energia media per R data

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



monomeri indipendenti

concentrazione $\phi = \frac{N}{R^3/a^3} = \frac{a^3}{R^3} N$

$$\langle n_{mm}^{(i)} \rangle = z \cdot \phi$$

$$\langle n_{ms}^{(i)} \rangle = z \cdot (1-\phi)$$

$$U(R) = \frac{1}{2} \epsilon_{mm} N z \frac{a^3}{R^3} N + \epsilon_{ms} N z \left(1 - \frac{a^3}{R^3} N\right)$$

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

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

Energia libera

$$F(R) = F_{SAW}(R) + U(R)$$

$$= \underbrace{F_0 + F_{el}(R)}_{\text{ideale}} + F_{ex}(R) + U(R)$$

volume escluso

↑ energia media

$$= F_0 - 2K_BT \ln R + \frac{3K_BT}{2a^2N} R^2 + \frac{1}{2} K_BT a^3 \frac{N^2}{R^3} - \frac{1}{2} z\epsilon a^3 \frac{N^2}{R^3}$$

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

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

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

Ruolo del solvente

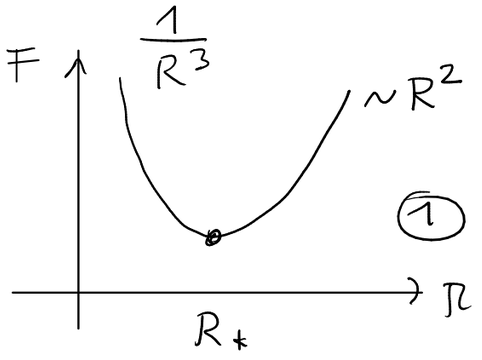
$$v_{eff} = v\left(1 - \frac{z\epsilon}{k_B T}\right) \qquad \epsilon = -(\epsilon_{mm} - 2\epsilon_{ms}) > 0$$

($\epsilon_{mm} < 0$, $\epsilon_{ms} > 0$)

1) $k_B T > z\epsilon$

SAW RINORMALIZZATO

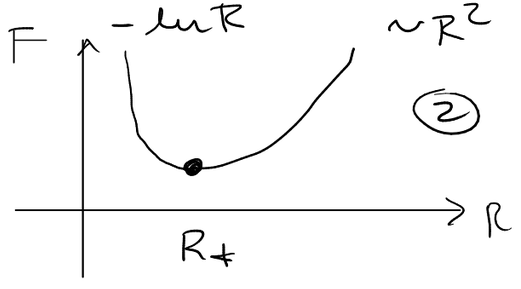
$R_* \sim N^{3/5}$ "BUON SOLVENTE"



2) $k_B T = z\epsilon$

CATENA IDEALE

$R_* \sim N^{1/2}$ " SOLVENTE θ "



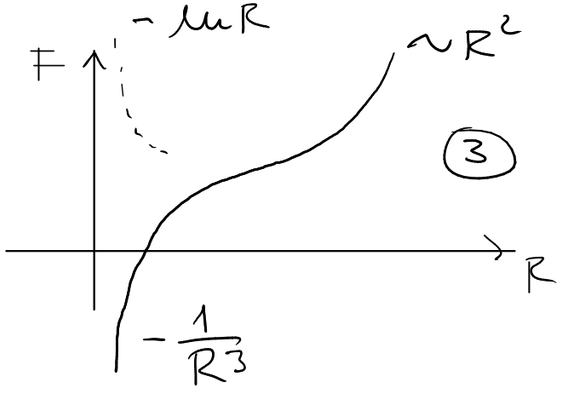
3) $k_B T < z\epsilon$

COLLASSO GLOBULO

oggetto compatto

$R_* \sim N^{1/3}$

" CATTIVO SOLVENTE "



polielettroliti

transizione

coil - globule

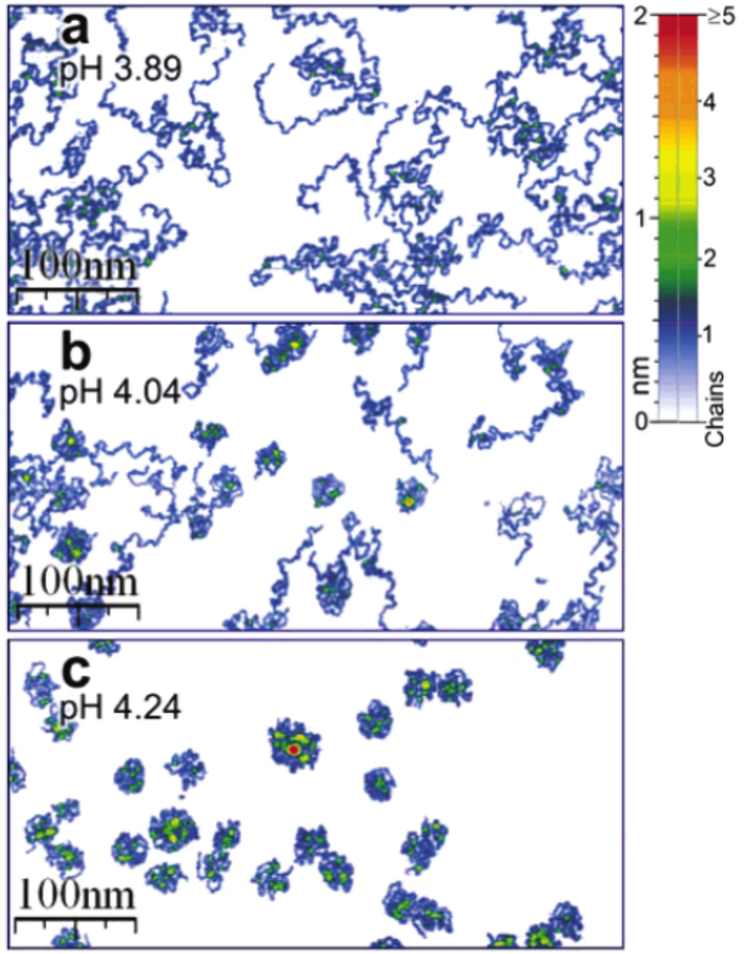
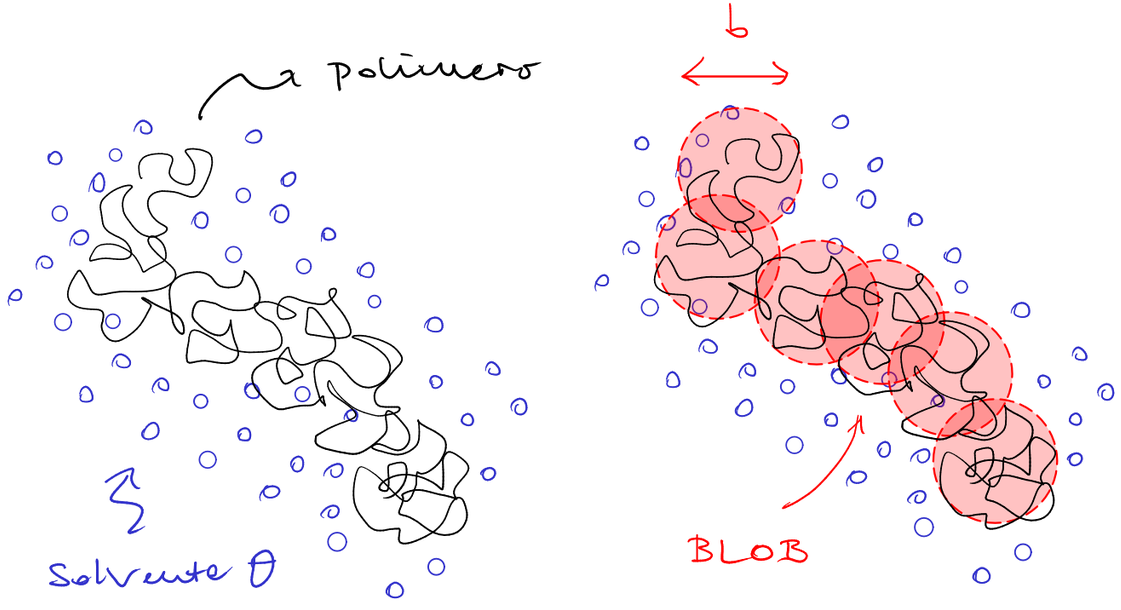


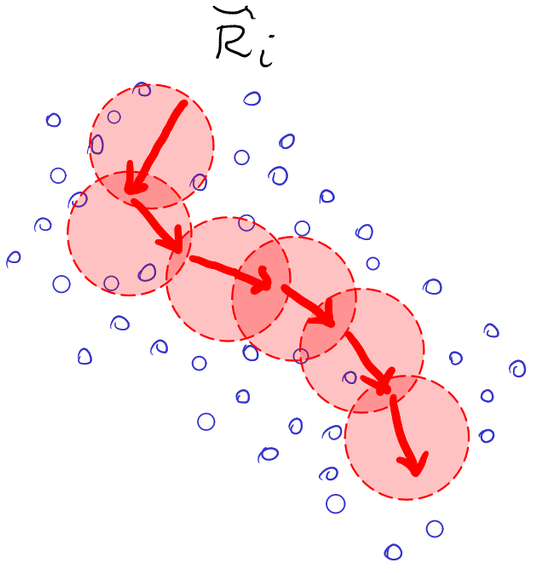
Figure 2. AFM-visualized conformations of adsorbed P2VP molecules: (a) pH 3.89, extended coils; (b) pH 4.04, intermediate state; (c) pH 4.24, compact coils. Z-scale bar shows a number of superposed chains assuming the height increment of 0.4 nm.

Roiter Minko JACS 2005

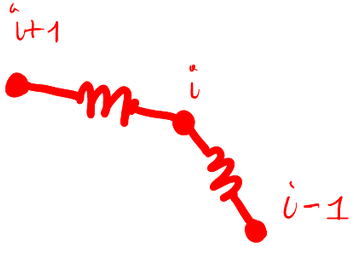
MODELLO DI ROUSE (1955)

Goal: dinamica catena polimerica in un solvente θ





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



- M+1 monomeri effettivi
- catena gaussiana → oscillatori accoppiati
- Langevin sovra-smorzato
- forze stocastiche indipendenti

$$\zeta\,\frac{\partial \vec{R}_i}{\partial t} = \vec{F}_i + \vec{\theta}_i(t) \qquad \theta_0 = k_B T \cdot \zeta$$

equilibrio

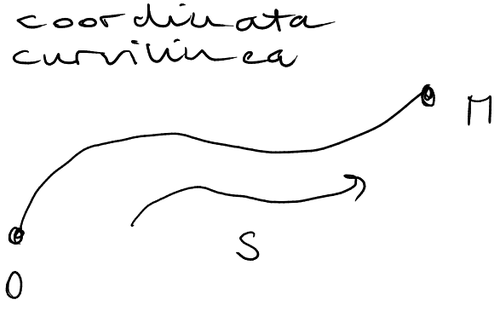
$$\begin{cases} \langle \vec{\theta}_i(t) \rangle = \vec{0} \\ \langle \theta_{i\alpha}(t)\,\theta_{j\beta}(t') \rangle = 2\theta_0\,\delta_{\alpha\beta}\,\delta(t-t')\,\delta_{ij} \end{cases}$$

$$\zeta \frac{\partial \vec{R}_i}{\partial t} = \frac{3 k_B T}{b^2} (\vec{R}_{i+1} - \vec{R}_i) + \frac{3 k_B T}{b^2} (\vec{R}_{i-1} - \vec{R}) + \vec{\theta}_i(t) \qquad 0 < i < M$$

$$\zeta \frac{\partial \vec{R}_i}{\partial t} = \frac{3 k_B T}{b^2} (\vec{R}_{i+1} + \vec{R}_{i-1} - 2\vec{R}) + \vec{\theta}_i(t) \qquad 0 \le i \le M$$

$\uparrow$

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



$$\begin{cases} \vec{R}_{i+1}(t) = \vec{R}(s+ds, t) \\ \vec{R}_{i-1}(t) = \vec{R}(s-ds, t) \\ \vec{R}_i(t) = \vec{R}(s, t) \end{cases}$$

$$\vec{R}(s+ds,t) + \vec{R}(s-ds,t) - 2\vec{R}(s,t) \approx \frac{\partial^2 \vec{R}}{\partial s^2}$$

$$\frac{\partial \vec{R}}{\partial t} \approx \frac{3 k_B T}{\zeta b^2} \frac{\partial^2 \vec{R}}{\partial s^2} + \frac{1}{\zeta} \vec{\theta}(s,t) \qquad \text{B.C.:} \quad \left.\frac{\partial \vec{R}}{\partial s}\right|_0 = \left.\frac{\partial \vec{R}}{\partial s}\right|_M = 0$$

Trasformazione di Fourier

$$\begin{cases} \vec{R}(s,t) = \vec{X}_0(t) + 2 \sum_{p=1}^{\infty} \cos\left(\frac{p\pi}{M} s\right) \vec{X}_p(t) + \cancel{\sum \text{sin}\left(\frac{p\pi}{M} s\right) \vec{X}_p(t)} \qquad \int ds \cos\left(\frac{q\pi}{M} s\right) \dots \\ \vec{X}_p(t) = \frac{1}{M} \int_0^M ds \cos\left(\frac{p\pi}{M} s\right) \vec{R}(s,t) \rightarrow \text{modi di Rouse} \end{cases}$$

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

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

Equazioni del moto

Mostro che le equazioni del moto dei modi di Rouse sono disaccoppiate

$$\frac{\partial \vec{R}}{\partial t} = \frac{3 K_B T}{\zeta b^2} \frac{\partial^2 \vec{R}}{\partial s^2} + \frac{1}{\zeta}\vec{\Theta}(s,t)$$

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

$$\frac{\partial \bar{X}_p}{\partial t} = \frac{3 K_B T}{M \xi b^2} \underbrace{\int_0^M ds \cos\left(\frac{p\pi}{M} s\right) \frac{\partial^2 \bar{R}}{\partial s^2}}_{①} + \frac{1}{M\xi} \underbrace{\int_0^M ds \cos\left(\frac{p\pi}{M} s\right) \bar{\theta}(s,t)}_{②}$$

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

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

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

perché $\frac{\partial \bar{R}}{\partial t} = 0$ se $t = p\pi$ $(s = M)$
e $t = 0$ $(s = 0)$

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

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

$\left\{ \langle \bar{\theta}_p(t) \rangle = 0 \right.$

$\left(\langle \theta_{\alpha p}(t)\, \theta_{\beta q}(t') \rangle = \frac{1}{M^2} \int_0^M ds \int_0^M ds' \cos\left(\frac{p\pi s}{M}\right) \cos\left(\frac{q\pi s'}{M}\right) \langle \theta_{\alpha p}(s,t)\, \theta_{\alpha q}(s',t') \rangle \right.$

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

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

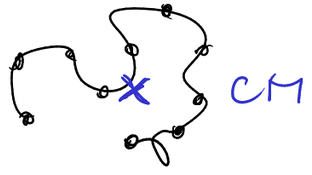
$\left\{ \frac{\partial \bar{X}_p}{\partial t} = -\frac{3\pi^2 k_B T\, p^2}{M^2 \zeta b^2} \bar{X}_p(t) + \frac{1}{\zeta} \vec{\theta}_p(t) \right.$ → eq. di Langevin per i singoli modi

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

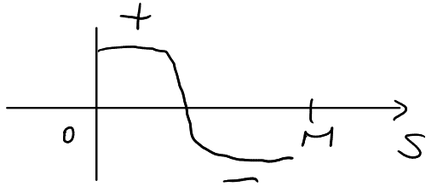
Modi di Rouse: interpretazione fisica

$p=0$: $\vec{X}_0(t) = \frac{1}{M}\int_0^M ds\, \vec{R}(s,t) \rightarrow \frac{1}{M}\sum_{i=0}^{M} \vec{R}_i(t)$

centro di massa: CM!



$p=1$: $\vec{X}_1(t) = \frac{1}{M}\int_0^M ds \cos\left(\frac{\pi}{M}s\right) \vec{R}(s,t)$



...

Moto del CM

$$\frac{\partial \vec{X}_0}{\partial t} = \frac{1}{\zeta}\vec{\Theta}_0(t) \rightarrow \vec{X}_0(t) = \vec{X}_0(0) + \frac{1}{\zeta}\int_0^t dt'\, \vec{\Theta}_0(t')$$

Spostamento quadratico medio del CM

$$\langle |\vec{X}_0(t) - \vec{X}_0(0)|^2 \rangle = \frac{1}{\zeta^2}\int_0^t dt' \int_0^t dt'' \langle \vec{\Theta}_0(t') \cdot \vec{\Theta}_0(t'') \rangle = 6\frac{k_B T}{\zeta M} t \sim t$$

$\rightarrow D_{CM} \sim \frac{1}{M}$

$$\langle \Theta_{\alpha p}(t)\, \Theta_{\beta q}(t') \rangle = \frac{k_B T \cdot \zeta}{M} \delta_{qp}(1+\delta_{p0})\,\delta(t-t')\,\delta_{\alpha\beta}$$

coeff. di diffusione del CM

Dinamica dei modi di Rouse $p \geq 1$

$$\frac{\partial \vec{X}_p}{\partial t} = - \underbrace{\frac{3\pi^2 k_B T\, p^2}{N^2 \zeta b^2}}_{1/\tau_p} \vec{X}_p(t) + \frac{1}{\zeta} \vec{\theta}_p(t) = - \frac{1}{\tau_p} \vec{X}_p(t) + \frac{1}{\zeta} \vec{\theta}_p(t) \qquad \langle \vec{X}_p(0) \cdot \ldots \rangle$$

$$\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle$$

$$\langle \frac{\partial \vec{X}_p}{\partial t} \cdot \vec{X}_p(0) \rangle = - \frac{1}{\tau_p} \langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle + \frac{1}{\zeta} \underbrace{\langle \vec{\theta}_p(t) \cdot \vec{X}_p(0) \rangle}_{=0}$$

$$\frac{\partial}{\partial t} \langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle = - \frac{1}{\tau_p} \langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle$$

$$\langle \vec{X}_p(t) \cdot \vec{X}_p(0) \rangle = \langle |\vec{X}_p(0)|^2 \rangle \exp\left(- t/\tau_p\right) \qquad \tau_p = \text{tempo di correlazione di Rouse}$$

$$\tau_p = \frac{N^2 \zeta b^2}{3\pi^2 k_B T\, p^2} \sim N^2 \sim \frac{1}{p^2}$$

Dinamica rotazionale

(es.)

$\vec{R} \neq \vec{R}(s,t)$

$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$ decade sulla scala di tempo di τ_1 (più lento)

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

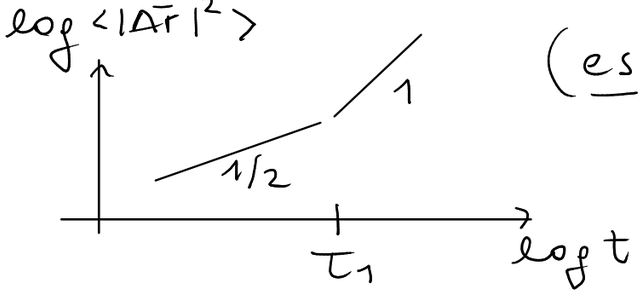
vettore end-to-end

tempo di correlazione rotazionale: $\tau_R \sim M^2$

Dinamica segmentale

$$\langle |\vec{R}_i(t) - \vec{R}_i(0)|^2 \rangle \sim \begin{cases} t & t \gg \tau_1 \\ t^{1/2} & t \ll \tau_1 \end{cases}$$

sotto-diffusione



(es.)

Modello Rouse

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

Esperimenti

Solvente Θ

$$\begin{cases} D_{CM} \sim \dfrac{1}{M^{1/2}} \\ \tau_R \sim M^{3/2} \end{cases}$$

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

Solvente Θ: $D_{CM} \sim \dfrac{1}{M^{1/2}}$ $\qquad D_{CM} \sim \dfrac{1}{M^{\alpha}}$

Modello di Zimm: interazioni idrodinamiche (mediate dal solvente)

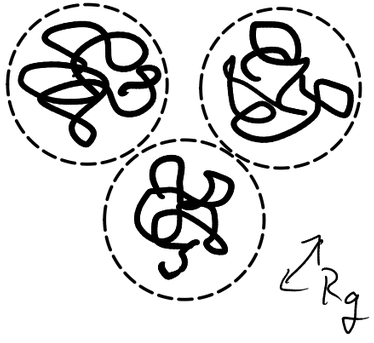
$D_{CM} \sim \dfrac{1}{M^{1/2}}$ $\qquad \tau_R \sim M^{3/2}$

REGIMI DI DENSITA'

Diluito

$\rho \approx \rho^*$

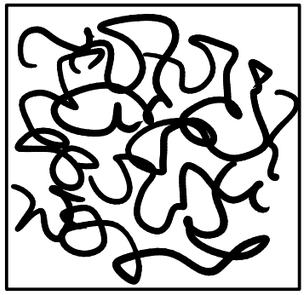
Semi-diluito



ρ^*

$\rho \gtrsim \rho^*$

Concentrato

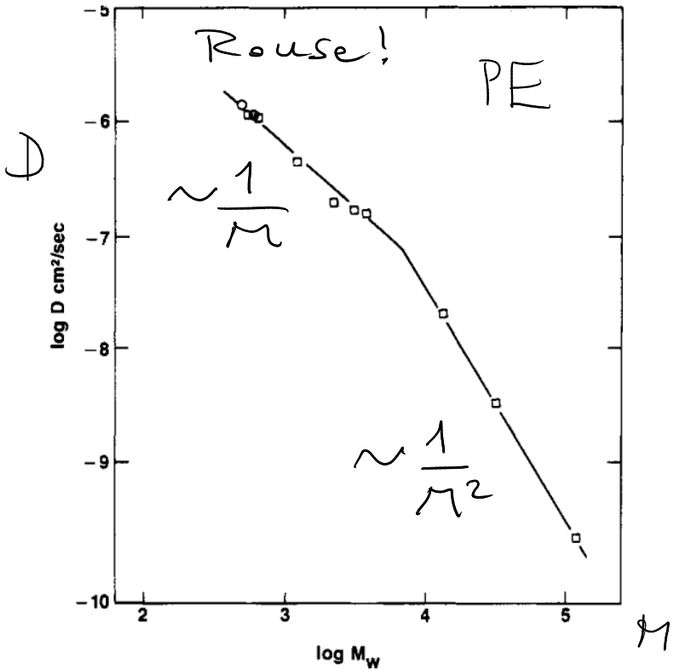


$\rho >> \rho^*$

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