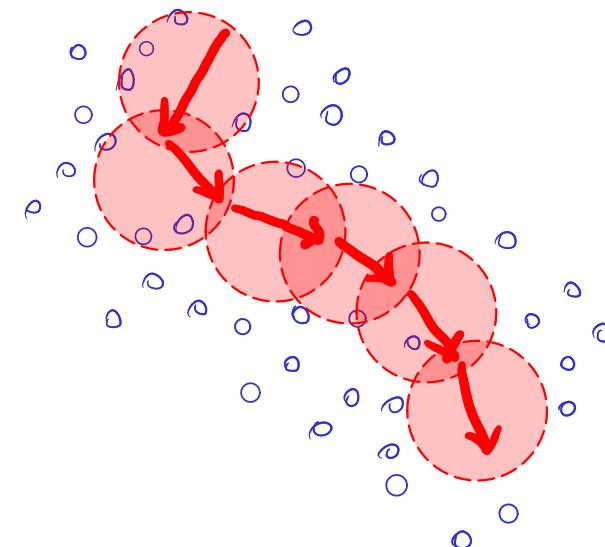
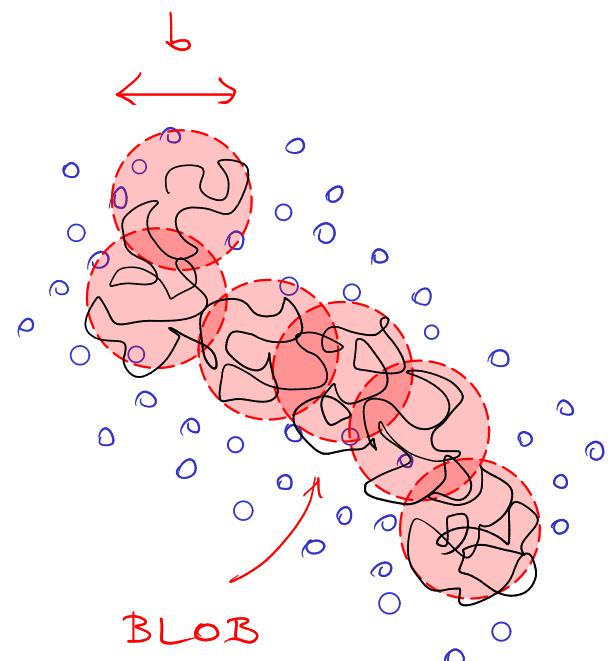
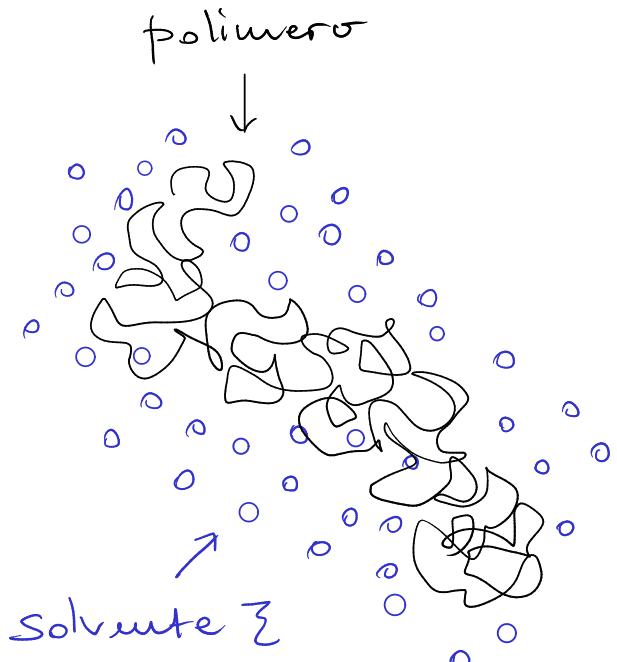
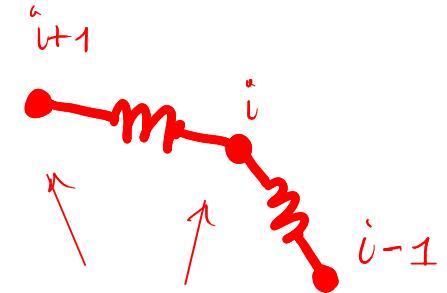


## MODELLO DI ROUSE

1955: dinamica di una catena gaussiana in solvente  $\rightarrow$  M+1 monomeri  $\rightarrow$  interazione



$$\frac{1}{2} \frac{3K_B T}{b^2} |\bar{R}_{i+1} - \bar{R}_i|^2$$



monomeri effettivi

Idea: eq. Langevin per i monomeri effettivi  $\rightarrow$  Serra-amortita

$$\zeta \frac{d\bar{R}_i}{dt} = \underbrace{\frac{3K_B T}{b^2} (\bar{R}_{i+1} - \bar{R}_i) + \frac{3K_B T}{b^2} (\bar{R}_{i-1} - \bar{R}_i)}_{\text{oscillatori armonici}} + \bar{\theta}_i(t) \rightarrow$$

↑  
solvente

- no volume escluso
- no attrazione

$\Rightarrow$  solvente  $\theta$

$$\begin{cases} \langle \bar{\theta}_i \rangle = \bar{\theta} \\ \langle \theta_{i\alpha}(t) \cdot \theta_{i\beta}(t') \rangle = \end{cases}$$

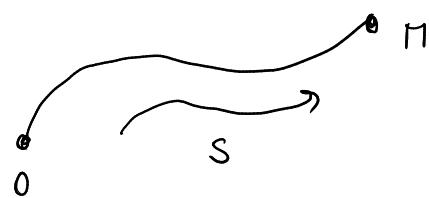
$$2\theta_0 \delta_{\alpha\beta} \delta_{ij} \cdot \delta(t-t')$$

$$\uparrow \\ \theta_0 = K_B T \cdot \zeta$$

$$i=1 \rightarrow i=M-1$$

monomeri fantasma :  $\bar{R}_{-1} = \bar{R}_0$   $\bar{R}_{M+1} = \bar{R}_M$

$$\int ds \rightarrow \sum_i$$



$$\bar{R}_i = \bar{R}(s)$$

$$\bar{R}_{i+1} = \bar{R}(s+ds)$$

$$\bar{R}_{i-1} = \bar{R}(s-ds)$$

$$\sum_i \frac{d\bar{R}}{dt} = \frac{3k_B T}{b^2} [\bar{R}(s+ds) + \bar{R}(s-ds) - 2\bar{R}(s)] + \bar{\theta}(s,+)$$

$$\sum_i \frac{d\bar{R}}{dt} \approx \frac{3k_B T}{b^2} \frac{\partial^2 \bar{R}}{\partial s^2} + \bar{\theta}(s,+)$$

Modi di Rouse : serie Fourier  $\rightarrow$  coordinate generalizzate

$$\bar{R}(s,t) = \bar{x}_0(t) + 2 \sum_{p=1}^{\infty} \cos\left(\frac{\pi p}{M}s\right) \bar{x}_p(t) + \sum \cancel{\sin(\cdot)} \quad \leftarrow \text{B.C.}$$

$$\begin{aligned} \int_0^M ds \cos\left(\frac{\pi q}{M}s\right) \bar{R}(s,t) &= \int_0^M ds \cos\left(\frac{\pi q}{M}s\right) \bar{x}_0(t) + 2 \sum_{p=1}^{\infty} \int_0^M ds \cos\left(\frac{\pi q}{M}s\right) \cos\left(\frac{\pi p}{M}s\right) \bar{x}_p(t) \\ &= \delta_{q0} M \bar{x}_0(t) + 2 \sum_{p=1}^{\infty} \underbrace{\frac{M}{\pi} \frac{\#}{2} \delta_{qp}}_{\frac{M}{\pi} \frac{\#}{2} \delta_{pq}} (1 - \delta_{po}) \cdot \bar{x}_p(t) \\ &= \delta_{q0} M \bar{x}_0(t) + (1 - \delta_{q0}) M \bar{x}_q(t) = M \bar{x}_q(t) \end{aligned}$$

Coordinate di Rouse

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

$$\begin{aligned} p=0 &> \int_0^{\pi} dx \cos(px) \cos(qx) = \frac{\pi}{2} \delta_{pq} (1 + \delta_{p0}) \\ p \neq 0 & \frac{1}{2} \left\{ \frac{\sin[(p-q)x]}{p-q} + \frac{\sin[(p+q)x]}{p+q} \right\} \end{aligned}$$

## Equazioni del moto

$$\frac{\partial \vec{X}_P}{\partial t} = \frac{\partial}{\partial t} \left[ \frac{1}{m} \int^m ds \cos\left(\frac{p\pi}{m}s\right) \vec{R}(s, t) \right]$$

$$= \frac{3k_B T}{\varepsilon M b^2} \int_0^M ds \cos\left(\frac{p\pi}{M}s\right) \frac{\partial^2 \bar{F}}{\partial s^2} + \frac{1}{\varepsilon M} \int_0^M ds \cos\left(\frac{p\pi}{M}s\right) \bar{\theta}(s, t)$$

①

②

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

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

$$\Rightarrow - \frac{3 k_B T p^2 \pi^2}{\sum m^2 g^2} \vec{x}_p(t)$$

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

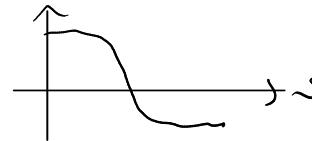
$$\langle \bar{\theta}_p(t) \rangle = 0$$

$$\begin{aligned} \langle \theta_{\alpha p}(t) \theta_{\beta q}(t') \rangle &= \frac{1}{M^2} \int_0^M ds \int_0^M ds' \cos\left(\frac{p\pi s}{M}\right) \cos\left(\frac{q\pi s'}{M}\right) \langle \theta_{\alpha p}(s, t) \theta_{\beta q}(s', t') \rangle \\ &= \frac{2 k_B T \varepsilon}{M^2} \underbrace{\int_0^M ds \cos\left(\frac{p\pi s}{M}\right) \cos\left(\frac{q\pi s}{M}\right)}_{\frac{M}{\pi} \frac{\pi}{2} \delta_{pq}} \delta(t-t') \delta_{\alpha\beta} \\ &= \frac{k_B T \varepsilon}{M} \delta_{pq} (1 + \delta_{po}) \delta(t-t') \delta_{\alpha\beta} \end{aligned}$$

Eq. moto per  $\vec{x}_p$

$$\frac{d\vec{x}_p}{dt} = - \frac{3 k_B T p^2 \pi^2}{\varepsilon M^2 b^2} \vec{x}_p(t) + \frac{1}{\varepsilon} \vec{\theta}_p(t) \quad \rightarrow \text{eq. Langevin sorda-aumentate disaccoppiate}$$

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



$$p=0 : \bar{X}_0(t) = \frac{1}{M} \sum_{i=0}^M \bar{R}_i(s_i) \rightarrow \frac{1}{M} \sum_{i=0}^M \bar{R}_i(t) \text{ CM del polimero} \quad p=1 : \sim \text{dipolo}$$

$$\frac{\partial \bar{X}_0}{\partial t} = \frac{1}{\zeta} \bar{\theta}_0(t) \rightarrow \bar{X}_0(t) = \bar{X}_0(0) + \frac{1}{\zeta} \int_0^t ds \bar{\theta}_0(s)$$

diffusivo

Spost. quadratico medio del CM

$$\langle |\bar{X}_0(t) - \bar{X}_0(0)|^2 \rangle = \frac{1}{\zeta^2} \int_0^t ds \int_0^t ds' \langle \bar{\theta}_0(s) \cdot \bar{\theta}_0(s') \rangle = \frac{6 k_B T}{\zeta M} \int_0^t ds = 6 \frac{K_B T}{\zeta M} t$$

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

$\equiv D_{CM}$

Autocorrelazione modi Rouse :

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

$$\langle \bar{X}_p(t) \cdot \bar{X}_p(0) \rangle = \dots = \langle |\bar{X}_p(0)|^2 \rangle \exp(-t/\tau_p) \quad \tau_p \propto p^{-1} \quad \text{tempo di correlazione}$$

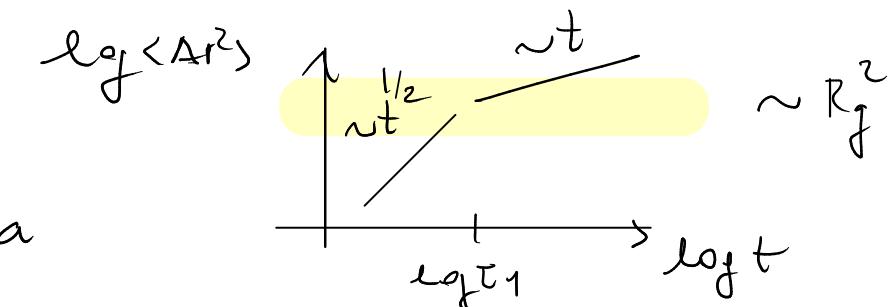
(es.)

Dinamica dei singoli monomeri (dinamica segmentale)

$$\langle |\bar{R}_i(t) - \bar{R}_i(0)|^2 \rangle \quad (\text{es}) \quad \text{Doi}$$

$$t \gg \tau_1 : \langle |\Delta \bar{R}_i|^2 \rangle \sim t$$

$$t \ll \tau_1 : \langle |\Delta \bar{R}_i|^2 \rangle \sim t^{1/2} \rightarrow \text{diffusione anomala}$$



Dinamica rotazionale

$$\bar{R} \equiv \bar{R}_H - \bar{R}_O = \cancel{\bar{x}_o} + 2 \sum_{p=1}^{\infty} \cos(\pi p) \bar{x}_p - \cancel{\bar{x}_o} - 2 \sum_{p=1}^{\infty} \bar{x}_p =$$

$$\langle \bar{R}(t) \cdot \bar{R}(0) \rangle = 16 \sum_{p=1,3,\dots} \langle \bar{x}_p(t) \cdot \bar{x}_p(0) \rangle = 2 \sum_{p=1}^{\infty} (\cos(\pi p) - 1) \bar{x}_p = -4 \sum_{p=1,3,\dots} \bar{x}_p$$

$$= 16 \langle |\bar{x}_p(0)|^2 \rangle \sum_{p=1,3,\dots} \exp(-t/\tau_p) \rightarrow \text{dominata da } p=1 \Rightarrow \tau_R \sim t_1$$

$\tau_R \sim M^2$

## Modello Rouse

$$\left\{ \begin{array}{l} D_{CM} \sim \frac{1}{M} \\ \tau_R \sim M^2 \end{array} \right.$$

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

## Eperimenti

$$\left\{ \begin{array}{l} D_{CM} \sim \frac{1}{M^\alpha} \\ \tau_R \sim M^{2\alpha+1} \end{array} \right.$$

## Interazioni idrodinamiche

Zimmo → ok!

1916 J. Phys. Chem. B, Vol. 113, No. 7, 2009

Augé et al.

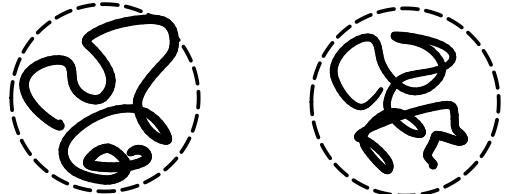
TABLE 2: Experimental Values of  $\alpha$  and  $d_F = 1/\alpha$  As Found in the Literature or in This Study

molecule family	$\alpha$	$d_F$	range	source
globular proteins	0.39	2.56	2.04	PDB <sup>13</sup>
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 <sup>a</sup>	0.48	2.07	2.17 (3.40) <sup>b</sup>	NMR <sup>3</sup>
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 $D_2O$ <sup>a</sup>	0.54	1.84	1.39	NMR <sup>5</sup>
PMMA in acetone above 25 kD	0.54	1.84	1.81	this work
PEO in water	0.55	1.82	2.80	NMR <sup>6</sup>
small molecules in $CDCl_3$ <sup>a</sup>	0.56	1.77	1.60	NMR <sup>5</sup>
DNA	0.57	1.75	1.69	fluorescence <sup>12</sup>
PEO in $CDCl_3$	0.58	1.73	4.13	this work
denatured peptide <sup>a,c</sup>	0.58	1.71	1.15	NMR <sup>2</sup>
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 alkanes	0.71	1.41	0.50 (C8–C26)	this work

0.5       $\theta$   
 $\nu$       .  
 $\nu$       .  
0.68      burr  
solvente

## REGIMI DI DENSITÀ

Diluito

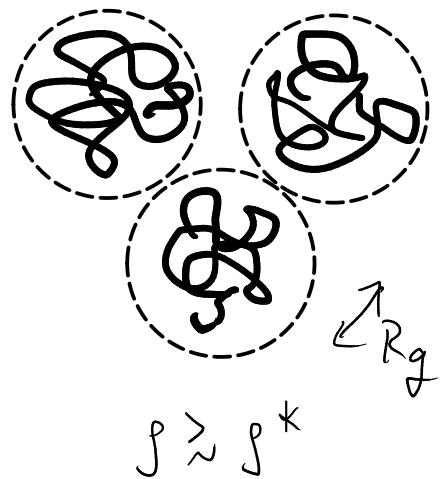


$$\rho \ll \rho^*$$

$$\frac{\frac{4}{3}\pi R_g^3 N}{V} = \phi_* \approx 1$$

$$\rho^* \approx \frac{3}{4\pi} \frac{1}{R_g^3}$$

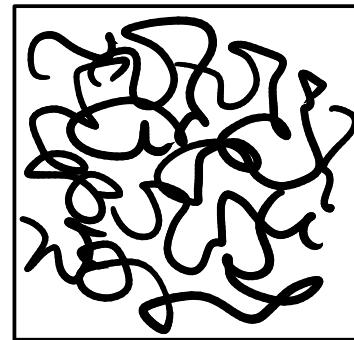
Semi-diluito



$$\rho \approx \rho^*$$

$$\rho \gtrsim \rho^*$$

Concentrato



$$\rho \gg \rho^*$$

polymer melt

liquido

vetro

cristallo

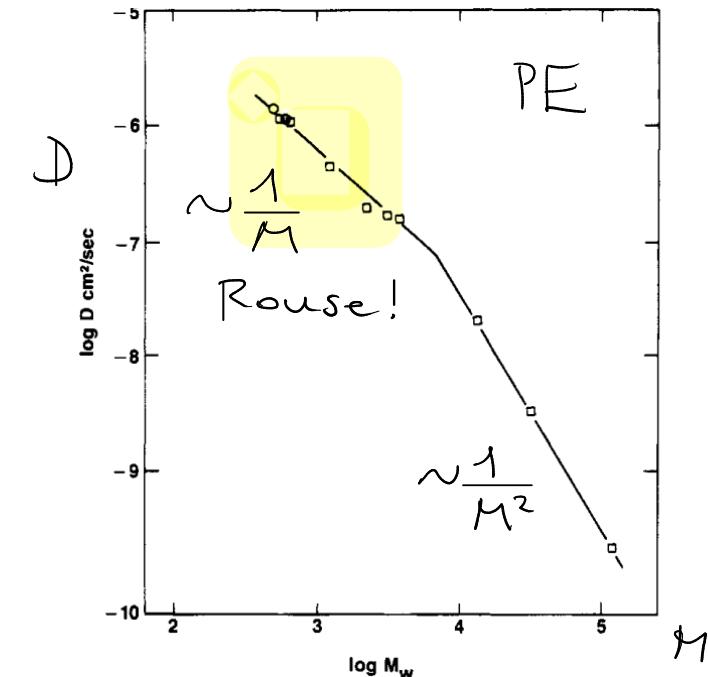


Figure 11. Self-diffusion coefficient corrected to the temperature at which the friction factor for viscosity equals  $2.3 \times 10^{-9} \text{ dyn}\cdot\text{s}/\text{cm}$ . Temperatures are listed in Table III. Symbols are same as Figure

Pearson et al.  
Macromolecules

$$\begin{aligned} \text{grandi } M : D &\sim \frac{1}{M^2} \\ \text{piccoli } M : D &\sim \frac{1}{M} \end{aligned}$$