# *Polymer Dynamics*


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(see *Adv. Phys.*, **51**, 1379-1527, (*2002*))

Boulder Summer School 2012: Polymers in Soft and Biological Matter

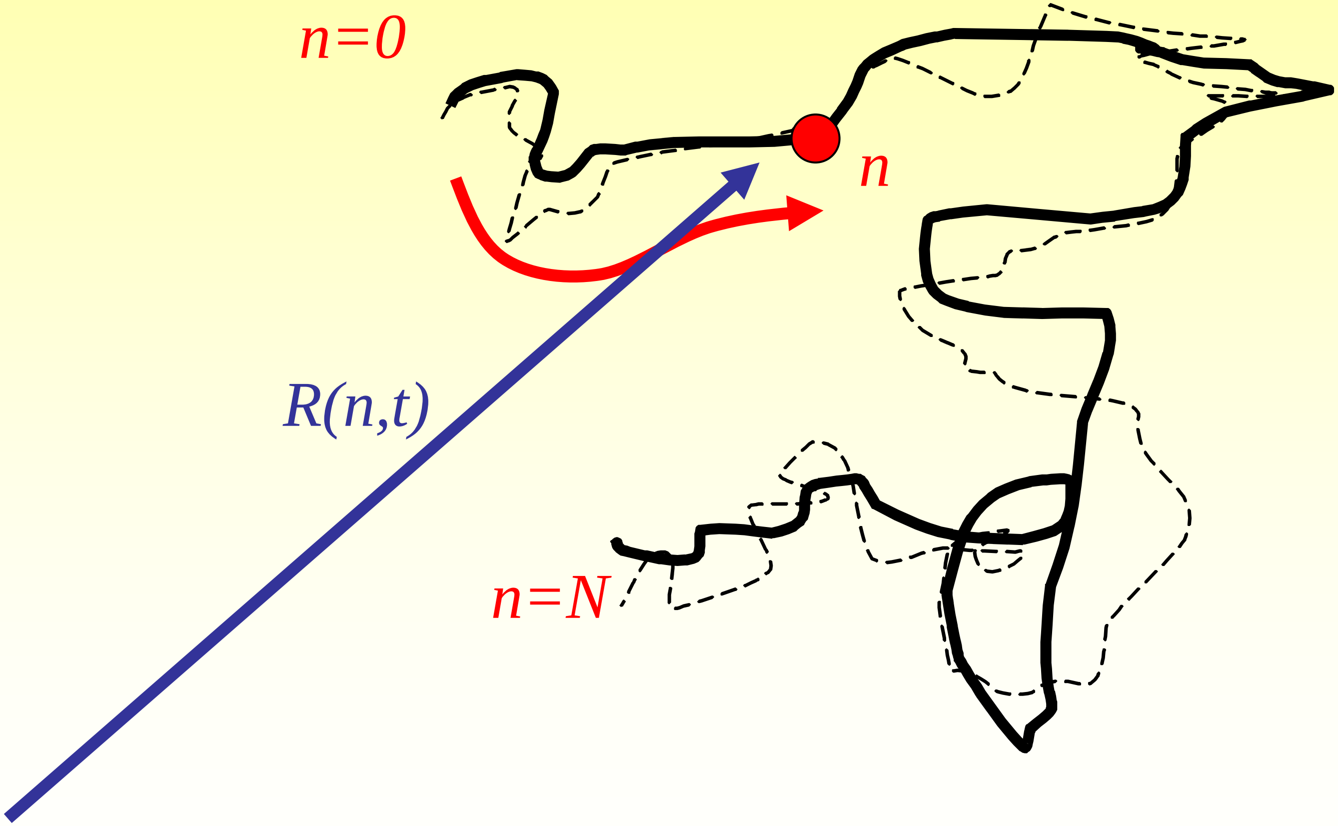
# *Schedule*

- Coarse-grained polymer physics
- Experimental probes of polymer dynamics

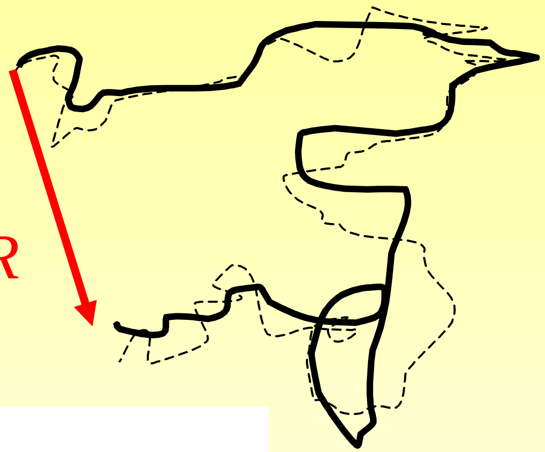
- Local friction - the Rouse chain

- Hydrodynamics - the Zimm chain
- Entangled Dynamics

# Coarse-grained Polymers



Polymers as Random Walks



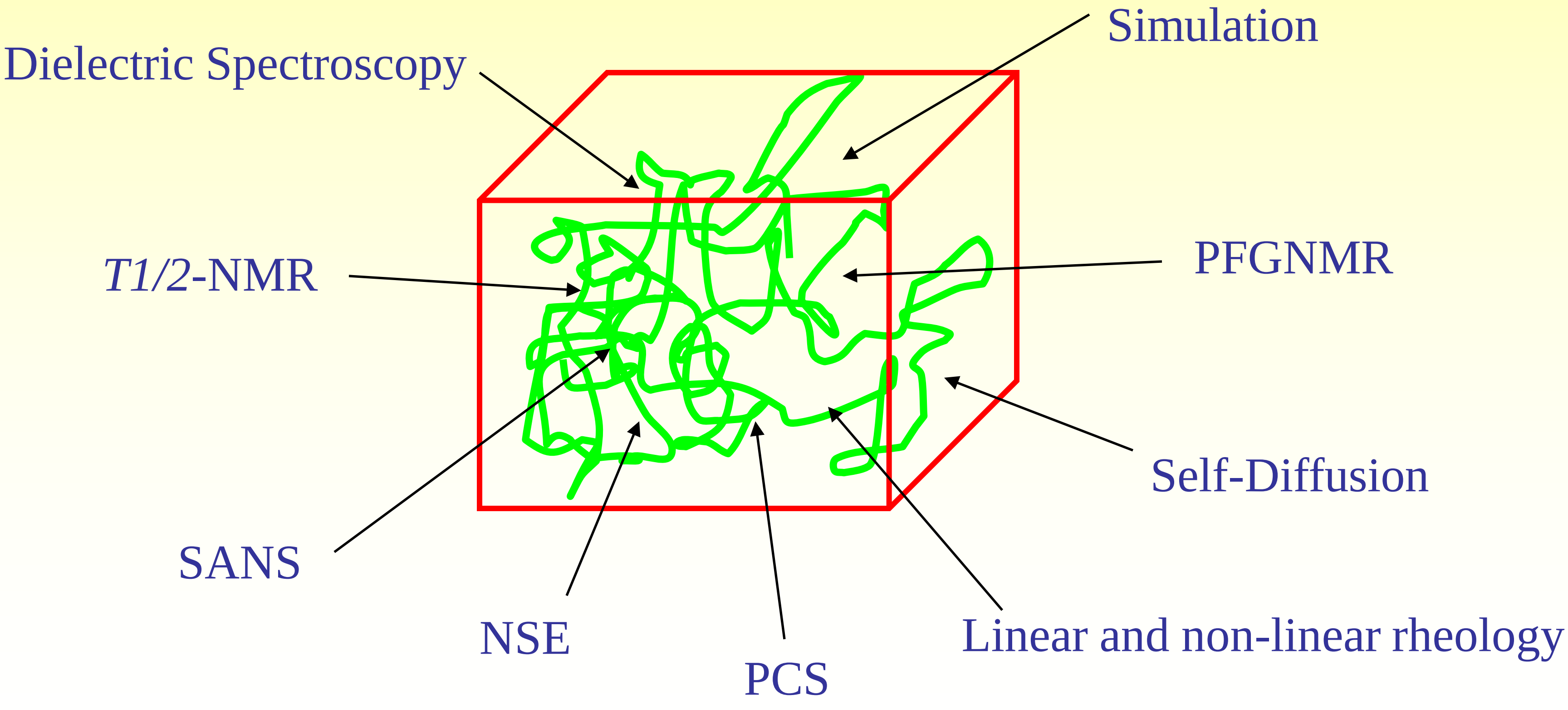

$$P(\mathbf{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(-3R^2/2Nb^2\right).$$

Force, *f*, from free energy F(**R**)=-$k_B T$lnP

$$f = -\nabla F(\mathbf{R}) = -\frac{3k_B T}{Nb^2}\mathbf{R} \quad \rightarrow \quad G_0 = k_B T C_{mon}/N_x$$

# Experiment
# - techniques that probe polymer dynamics:

- Bulk information orthogonal to rheology
- Direct Molecular information



# Rheology

## Shear

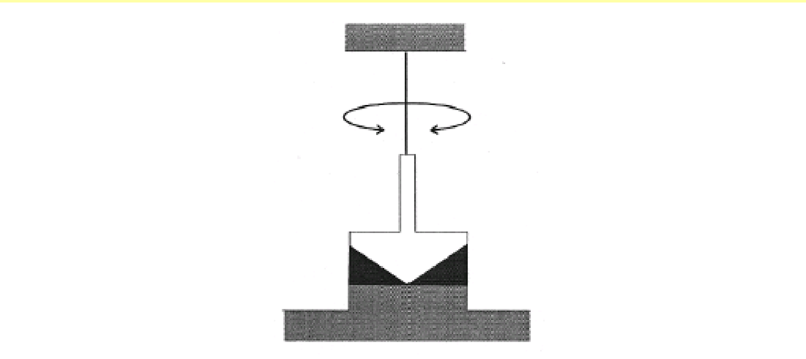
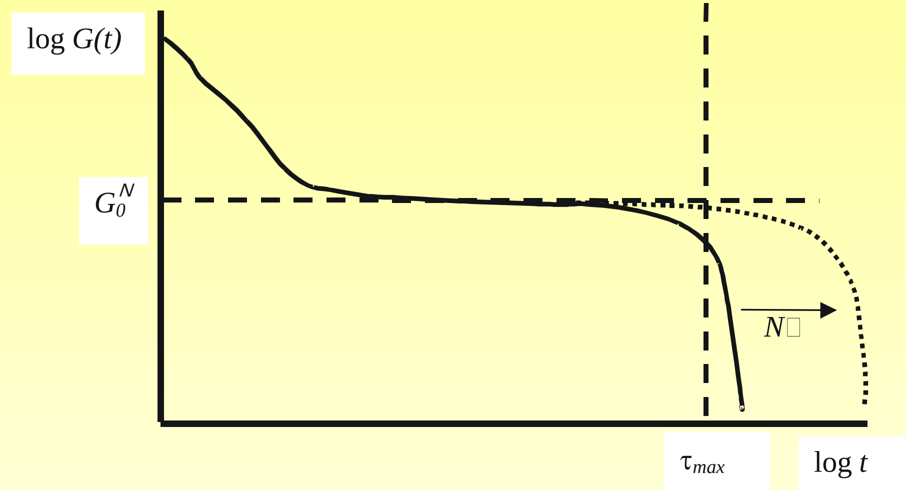
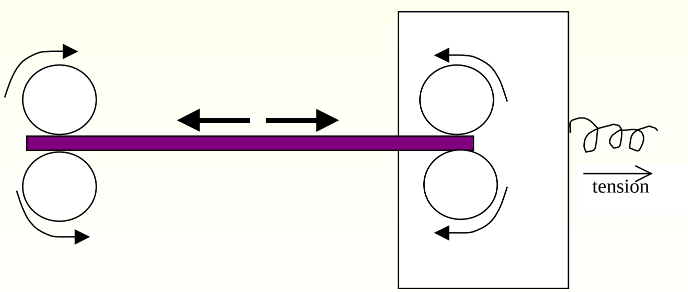
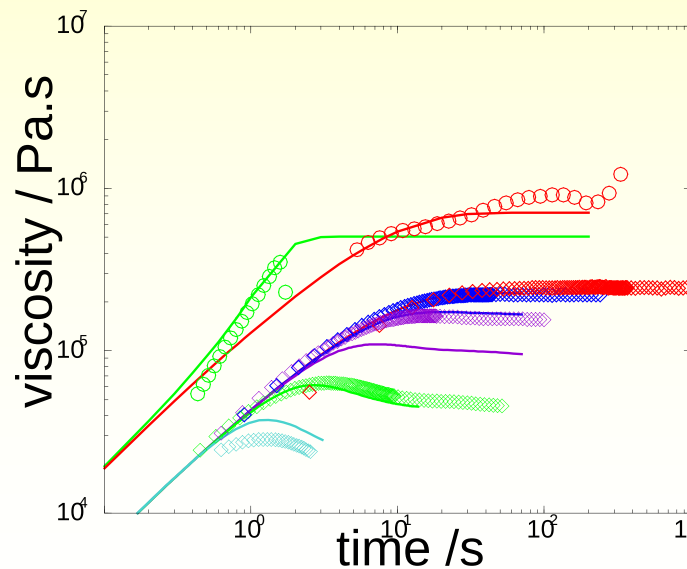


Figure 12. Schematic of a cone-and-plate shear rheometer.

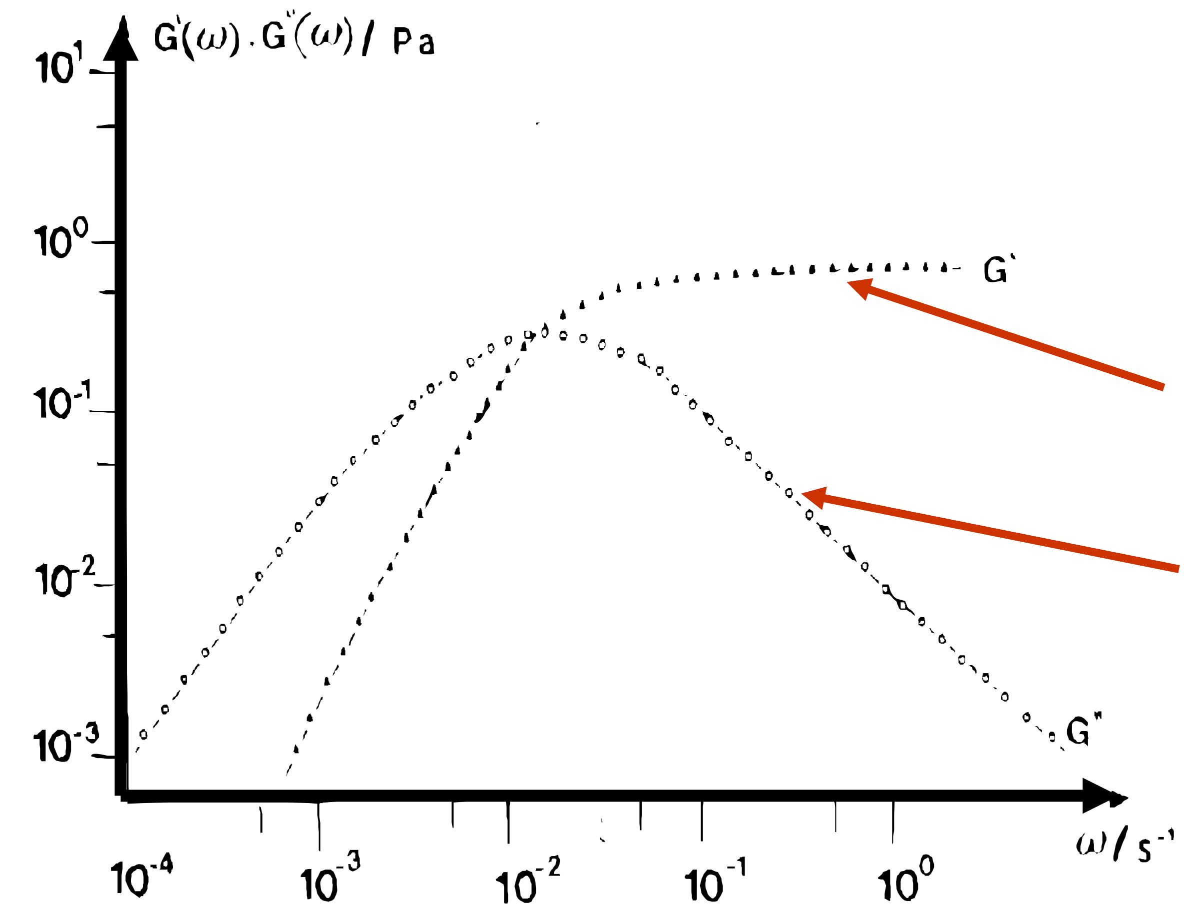



## Extension



# Frequency-dependent Shear rheology



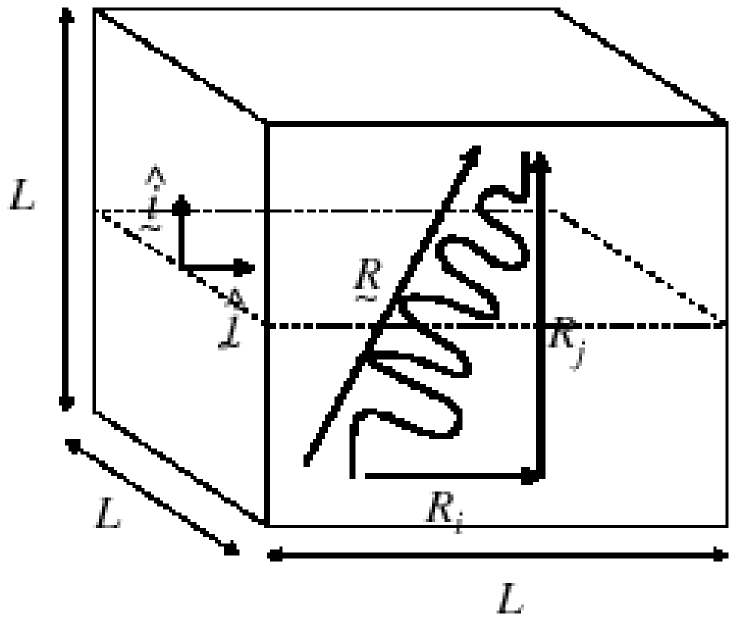

$$G(t) = G_0 e^{-t/\tau}$$

$$\Rightarrow$$

$$G'(\omega) = G_0 \frac{\omega\tau}{1+\omega^2\tau^2}$$

$$G''(\omega) = G_0 \frac{\omega^2\tau^2}{1+\omega^2\tau^2}$$

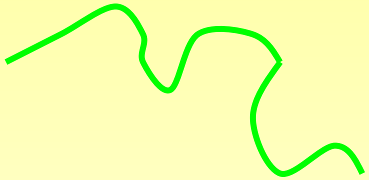
## Stress Tensor




$$\sigma_{ij} = \frac{3k_B T \mathbb{C}}{\tilde{N}^2 b^2} \langle R_i R_j \rangle .$$

$$\sim \left\langle \frac{\partial R(n,t)}{\partial n} \frac{\partial R(n,t)}{\partial n} \right\rangle$$

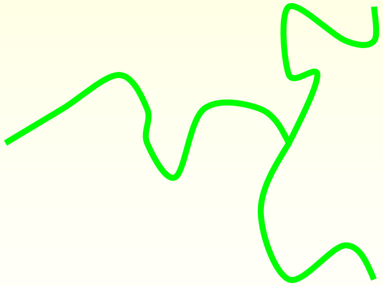
Linear Polymers



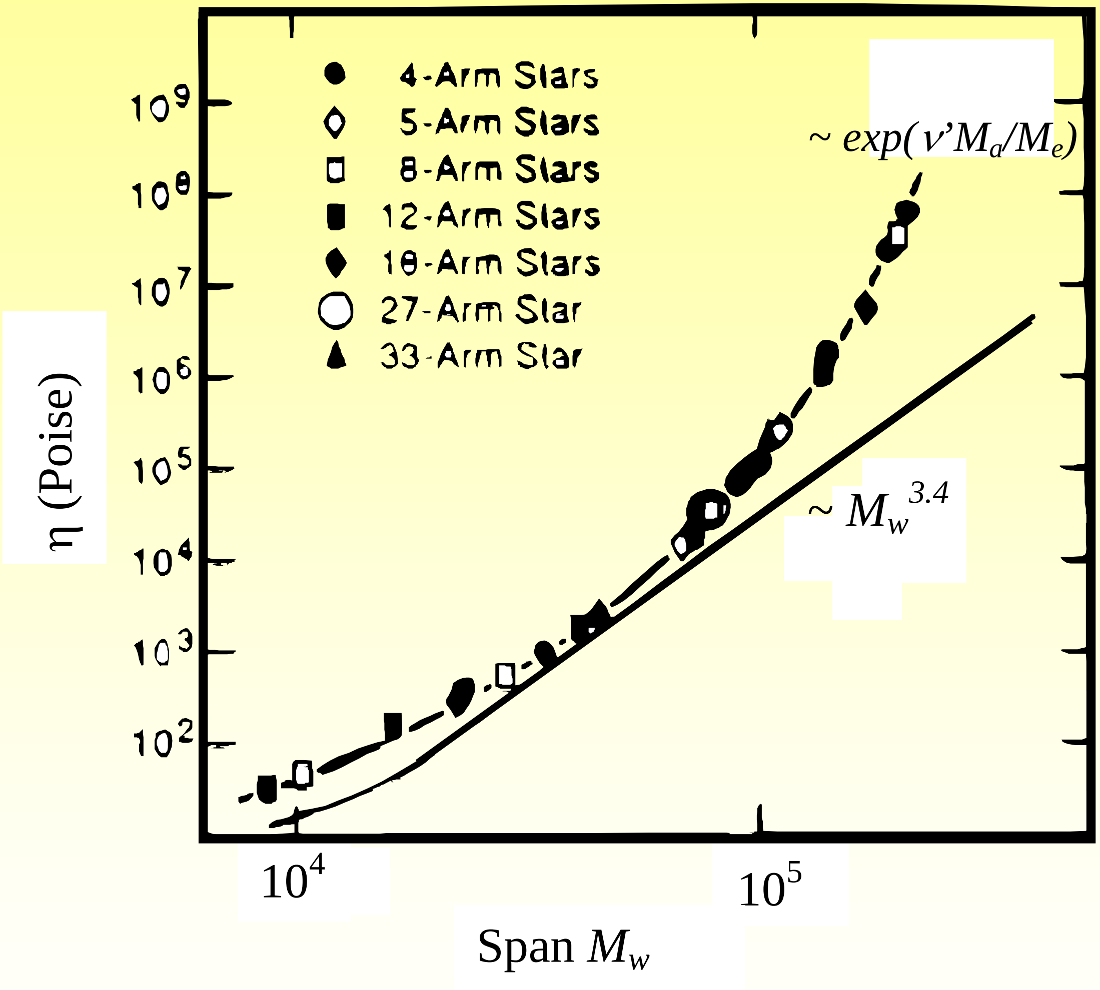
$$\left.\begin{array}{ll} \eta \sim M^{1} & M < M_{c} \\ \eta \sim M^{3.4} & M > M_{c}. \end{array}\right\}$$

$$M_{c} \simeq 2M_{e}.$$

Branched Polymers



$$\eta \sim \exp\left[\nu(M_{a}/M_{e})\right] \quad M_{a} > M_{c}$$

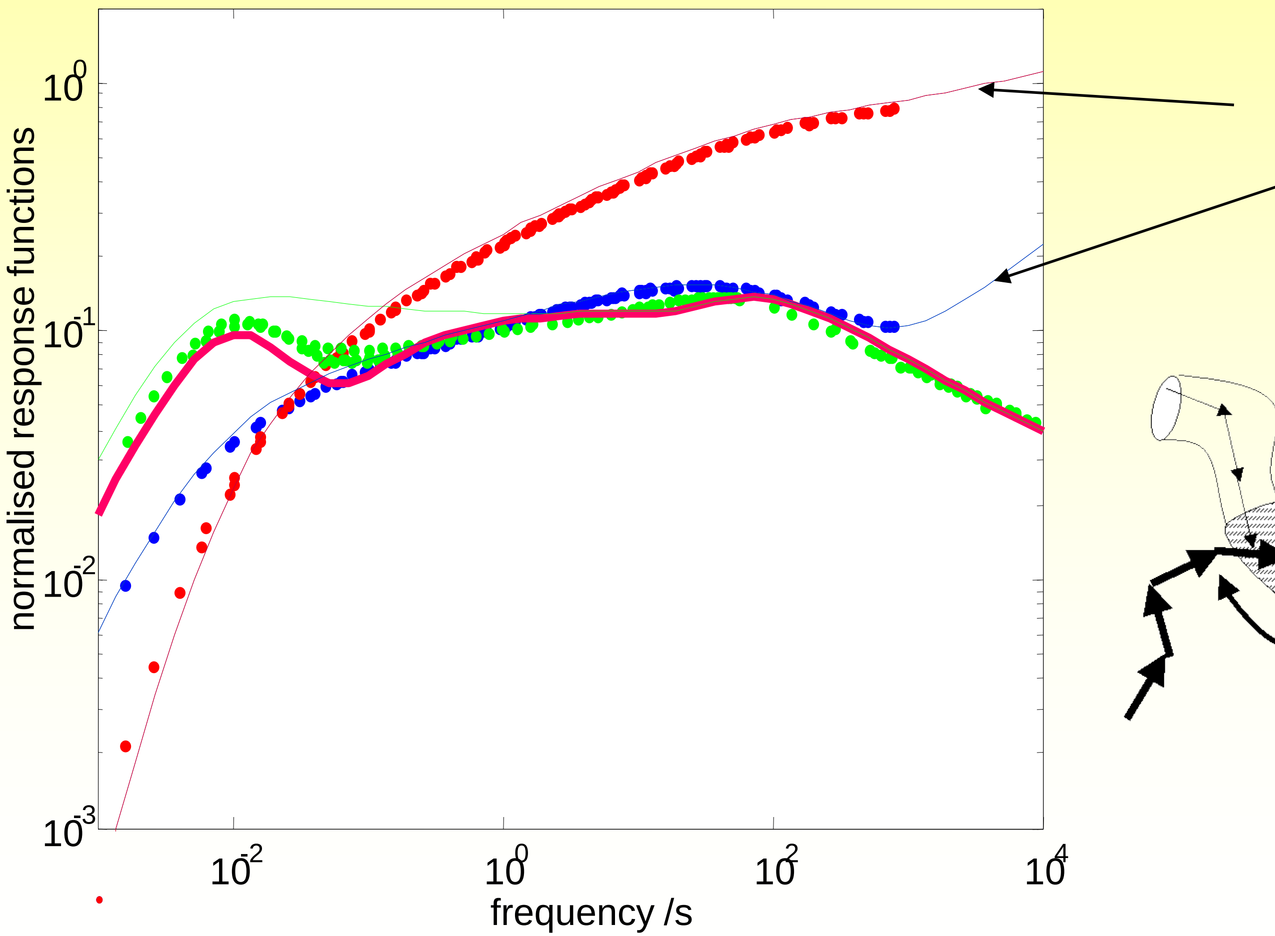


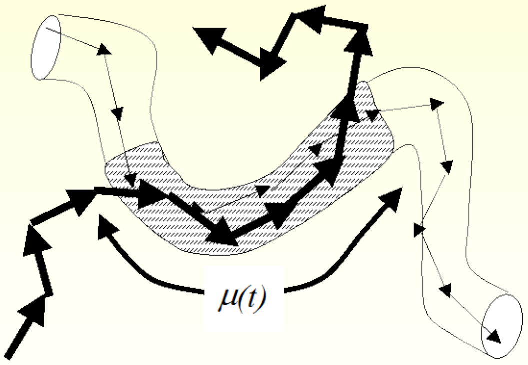

Fetters and Pearson (1983)

# Dielectric Spectroscopy for *Z*=16 stars

(Watanabe 2002)

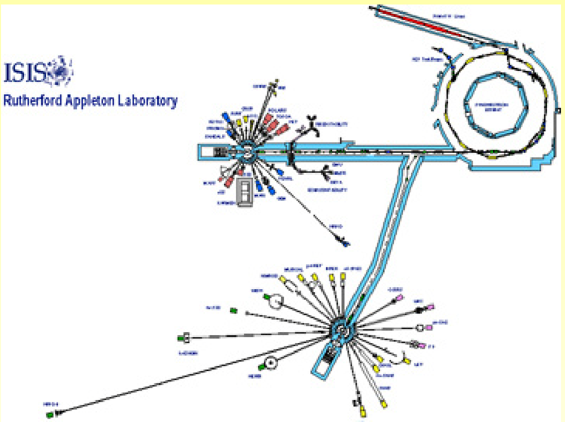
$$\left\langle \frac{\partial R(n',t)}{\partial n'} \frac{\partial R(n,0)}{\partial n} \right\rangle$$



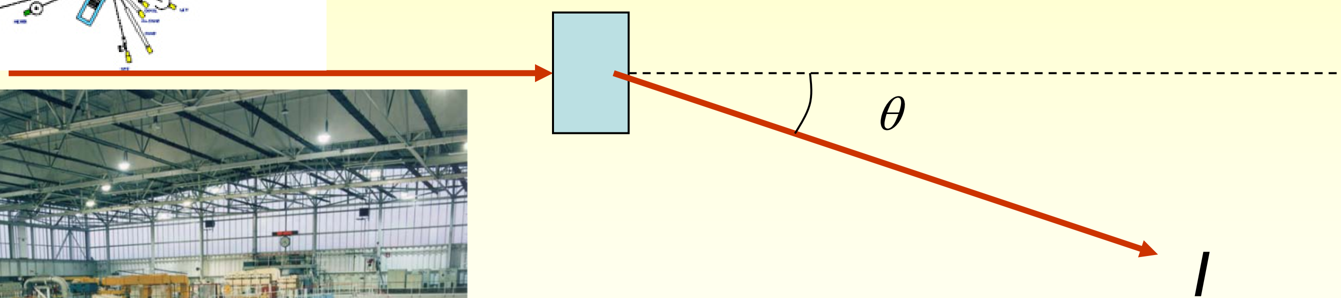



# Neutron Scattering

$$I(q) = FourierTransform(density\_correlations)$$

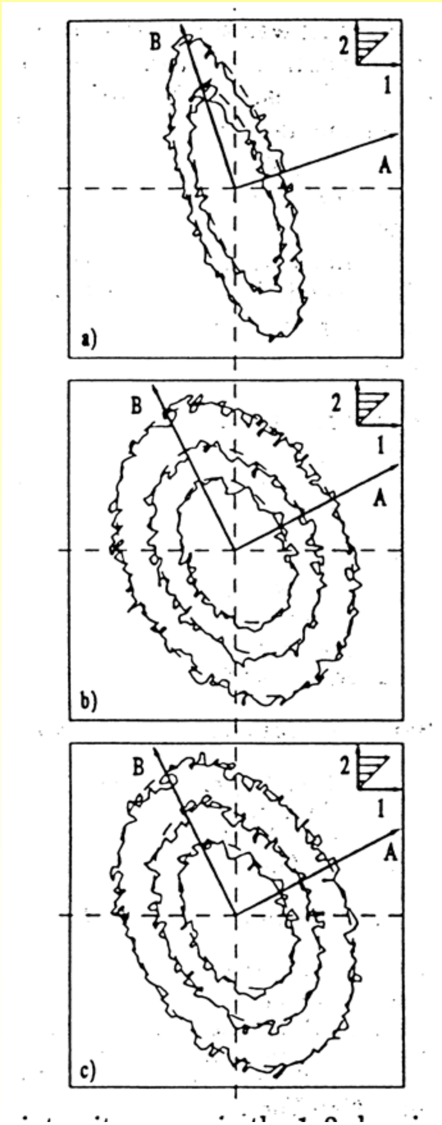



$$q = \frac{4\pi}{\lambda} \sin\theta$$



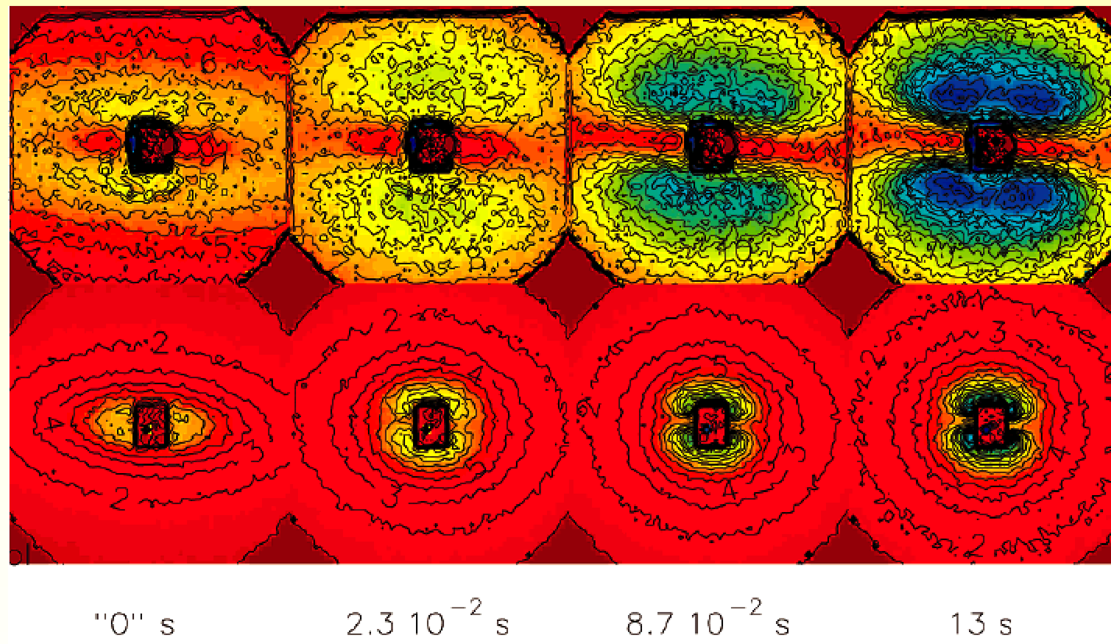

Sees inside the chain (“higher *q*”)

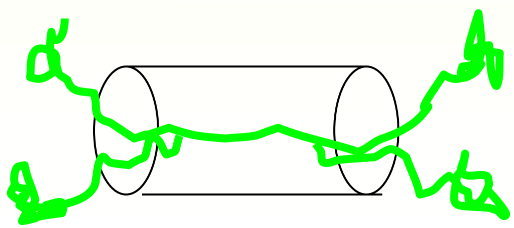
# SANS on Deformed Chains




$$\frac{1}{N^2}\left\langle \int_0^N dn \int_0^N dn' \exp\{i\boldsymbol{q}.[\boldsymbol{R}(n,t)-\boldsymbol{R}(n',t)]\} \right\rangle$$

Linears - Muller *et al.* (1993)

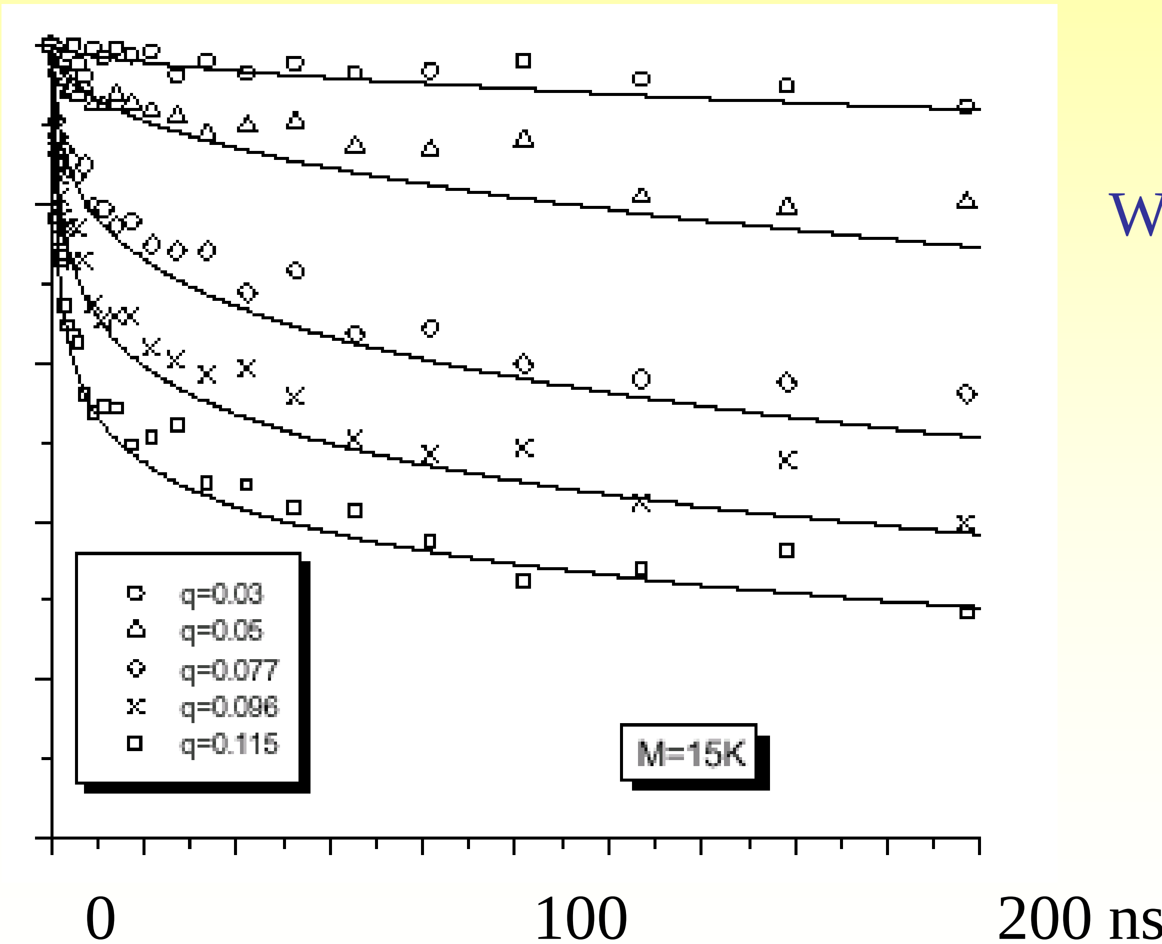


Hs - Heinrich *et al.* (2002)

# Neutron Spin Echo

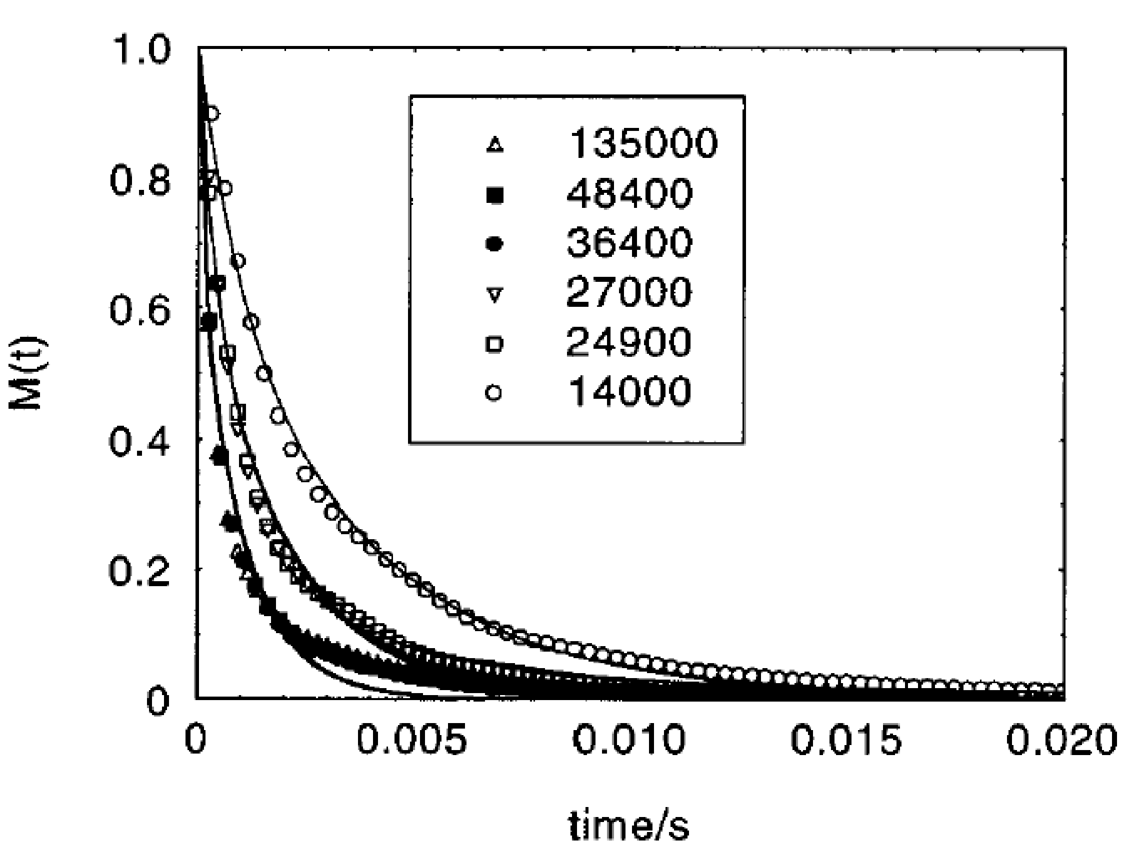
$$\frac{1}{N^2}\left\langle \int_0^N dn \int_0^N dn' \exp\{i\boldsymbol{q}.[\boldsymbol{R}(n,t)-\boldsymbol{R}(n',0)]\}\right\rangle$$




Wischnewski *et al.* (2002)

# Transverse (*T2*) NMR

$$\left\langle \cos\left[\frac{3\Delta_b}{2b^2}\int_0^t dt'\left(\frac{\partial \boldsymbol{R}(n,t')}{\partial n'}.\boldsymbol{L}.\frac{\partial \boldsymbol{R}(n,t')}{\partial n}\right)\right]\right\rangle$$




Klein *et al.* (1998)

# Diffusion Measurements (NMR, NR, SIMS..)

$$D_{CM} = \lim_{t \to \infty} \frac{\left\langle \frac{1}{N} \sum_{n=1}^{N} [\mathbf{R}(n,t) - \mathbf{R}(n,0)]^2 \right\rangle}{6t}$$

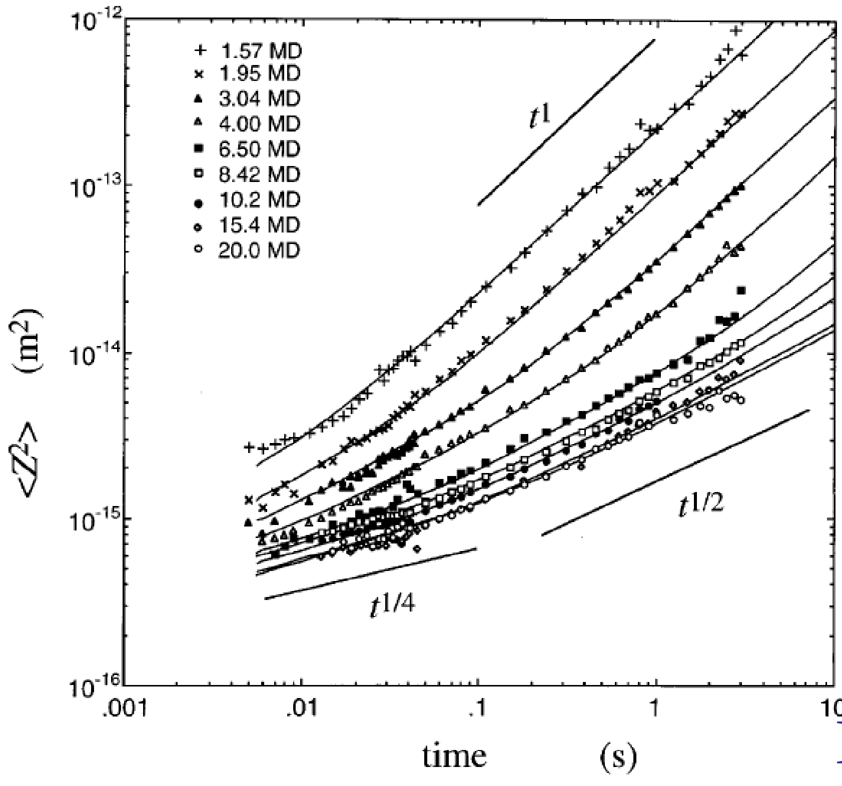



FIG. 6. $\log(\langle Z^2 \rangle)$ vs $\log(t)$, for nine different molar masses (see legend for molar mass labels) where, in the case of the $10\times10^6$, $15\times10^6$, and $20\times10^6$ dalton polymers, the small spin diffusion correction has been made to the stimulated echo experiment data sets. Asymptotic scaling exponents are shown in the straight line tangents. Clear $t^{1/4}$ to $t^{1/2}$ and $t^{1/2}$ to $t^1$ transitions are apparent as the changing molar masses sweep the Rouse and tube disengagement times across the NMR window. The data are fitted to Eq. (12) using the two parameters $\tau_d$ and $a$ as given in Table I.

Komlosh and Callaghan (1999)

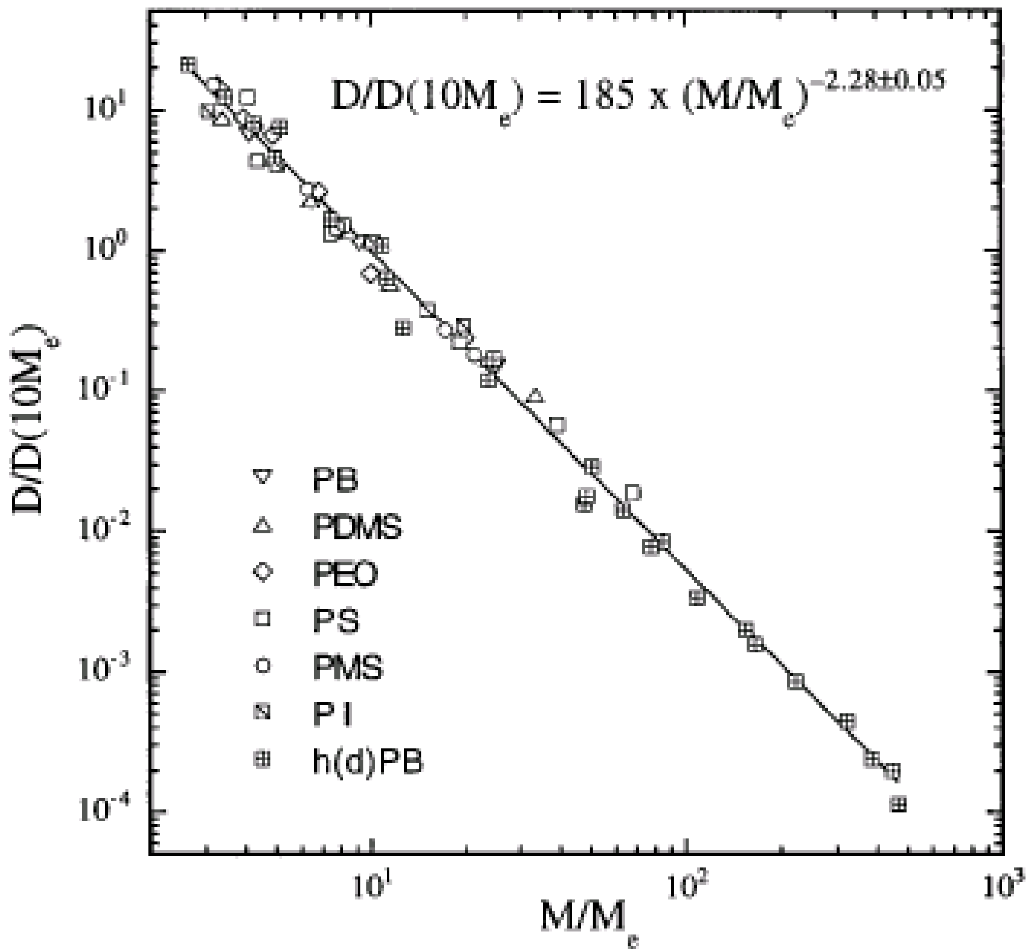


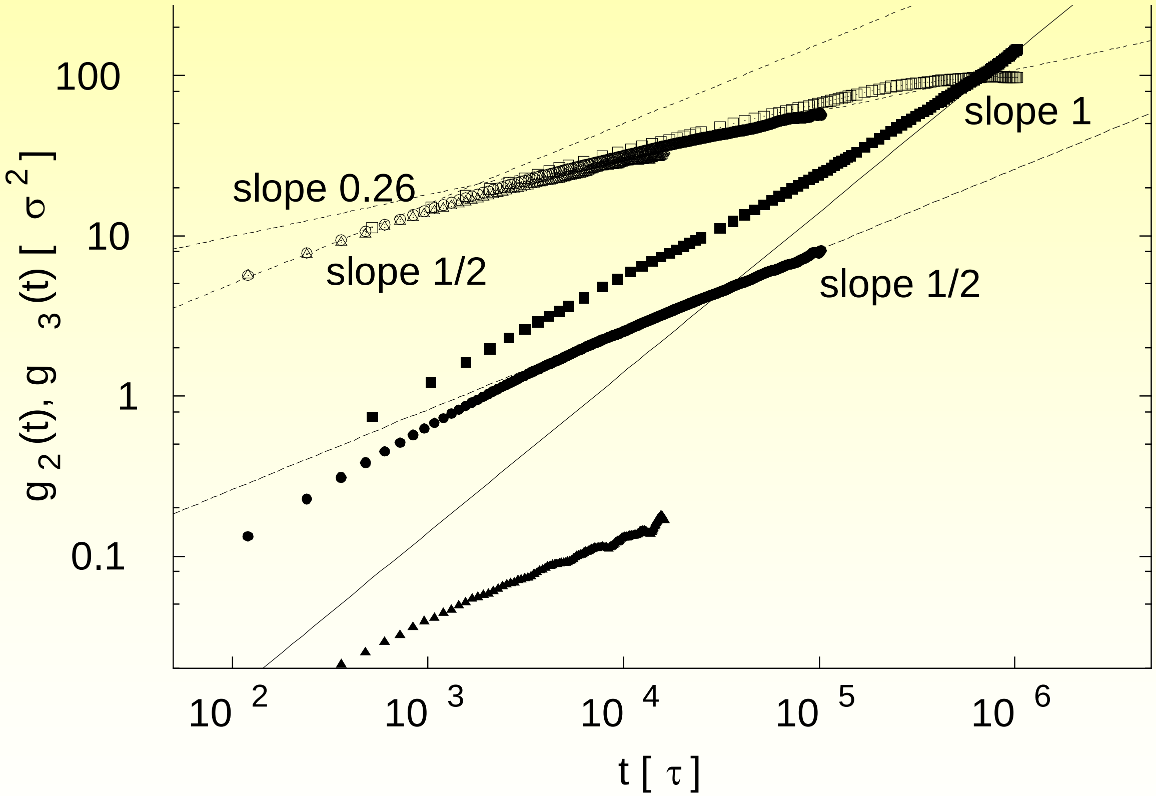

FIG. 3. Data from Fig. 1, combined with data for six other polymers from the literature, along with the global power law fit.

Lodge (1999)

# Simulation

$$\left\langle \left( \boldsymbol{R}(n,t) - \boldsymbol{R}(n,0) \right)^2 \right\rangle$$

(in this case …)



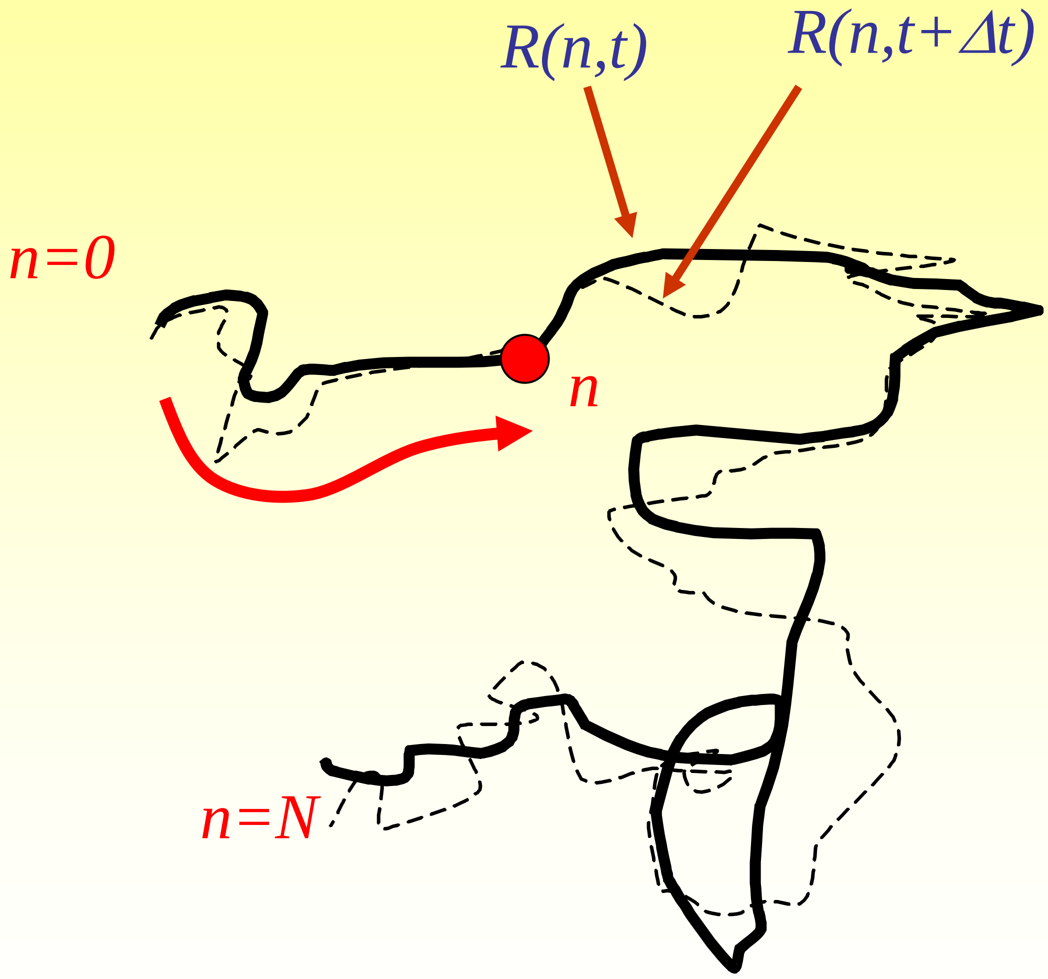

Putz *et al.* (2000)

# Summary of Probes of Polymer Dynamics

Table 1. Summary of techniques for study of entangled dynamics.

| Technique | Coarse-grained chain correlation | Spatial scale | Timescale |
|---|---|---|---|
| Rheology | $S_{xy} \equiv \left\langle \frac{\partial R_x(n,t)}{\partial n} \frac{\partial R_y(n,t)}{\partial n} \right\rangle$ | — | $10^{[illegible]}$–$10^{[illegible]}$ s |
| Optics | $S_{xy} \equiv \left\langle \frac{\partial R_x(n,t)}{\partial n} \frac{\partial R_y(n,t)}{\partial n} \right\rangle$ | — | $10^{[illegible]}$–$10^{[illegible]}$ s |
| SANS | $S(\mathbf{q};t) = \left\langle \frac{1}{N^2} \int_0^N dn \int_0^N dm \cdot \exp[i\mathbf{q} \cdot (\mathbf{R}(n,t) - \mathbf{R}(m,t))] \right\rangle$ | 1–500 nm | — |
| NSE | $S_{coh}(\mathbf{q},t) = \left\langle \int_0^N \frac{dn}{N} \int_0^N \frac{dm}{N} \cdot \exp[i\mathbf{q} \cdot (\mathbf{R}(n,t) - \mathbf{R}(m,0))] \right\rangle$ | 1–500 nm | 1–300 ns |
| | $S_{inc}(\mathbf{q},t) = \left\langle \int_0^N \frac{dn}{N} \cdot \exp[i\mathbf{q} \cdot (\mathbf{R}(n,t) - \mathbf{R}(n,0))] \right\rangle$ | | |
| DLS | $S_{DLS}(\mathbf{q},t) = \int \exp(-i\mathbf{q} \cdot \mathbf{r}) \langle \rho_{DLS}(\mathbf{r},t) \rho_{DLS}(\mathbf{0},0) \rangle \, d^3\mathbf{r}$ | 1–$10^{[illegible]}$ μm | $10^{[illegible]}$–$10^{[illegible]}$ s |
| DS | $\Phi(t) = \frac{1}{b^2} \left\langle \frac{\partial \mathbf{R}(n,t)}{\partial n} \cdot \frac{\partial \mathbf{R}(n',0)}{\partial n'} \right\rangle$ | 10–100 nm | $10^{[illegible]}$–$10^{[illegible]}$ s |
| $T_2$-NMR | $M(t) = \left\langle \cos \left[ \frac{3\Delta_0}{2b^2} \int_0^t dt' \left( \frac{\partial \mathbf{R}(n,t')}{\partial n} \cdot \mathbf{L} \cdot \frac{\partial \mathbf{R}(n,t')}{\partial n} \right) \right] \right\rangle$ | 10–100 nm | $10^{[illegible]}$–$10^{[illegible]}$ s |
| SNR | $D_{self} = \lim_{t\to\infty} \frac{\left\langle \frac{1}{N} \sum_{n=0}^{N} [\mathbf{R}(n,t) - \mathbf{R}(n,0)]^2 \right\rangle}{6t}$ | 1–500 nm | $10^{[illegible]}$–$10^{[illegible]}$ s |
| PGNMR | $\phi_n(t) = \langle [\mathbf{R}(n,t) - \mathbf{R}(n,0)]^2 \rangle$ | 10–$10^{[illegible]}$ nm | $10^{[illegible]}$–10 s |
| Simulation | All of the above | variable | variable |

# The Rouse Model




$$(\Delta R)^2 \approx Dt$$

$$D_{eff} \approx \frac{1}{n(t)} \approx \frac{1}{(\Delta R)^2}$$

$$\Rightarrow (\Delta R)^2 (\Delta R)^2 \approx t$$

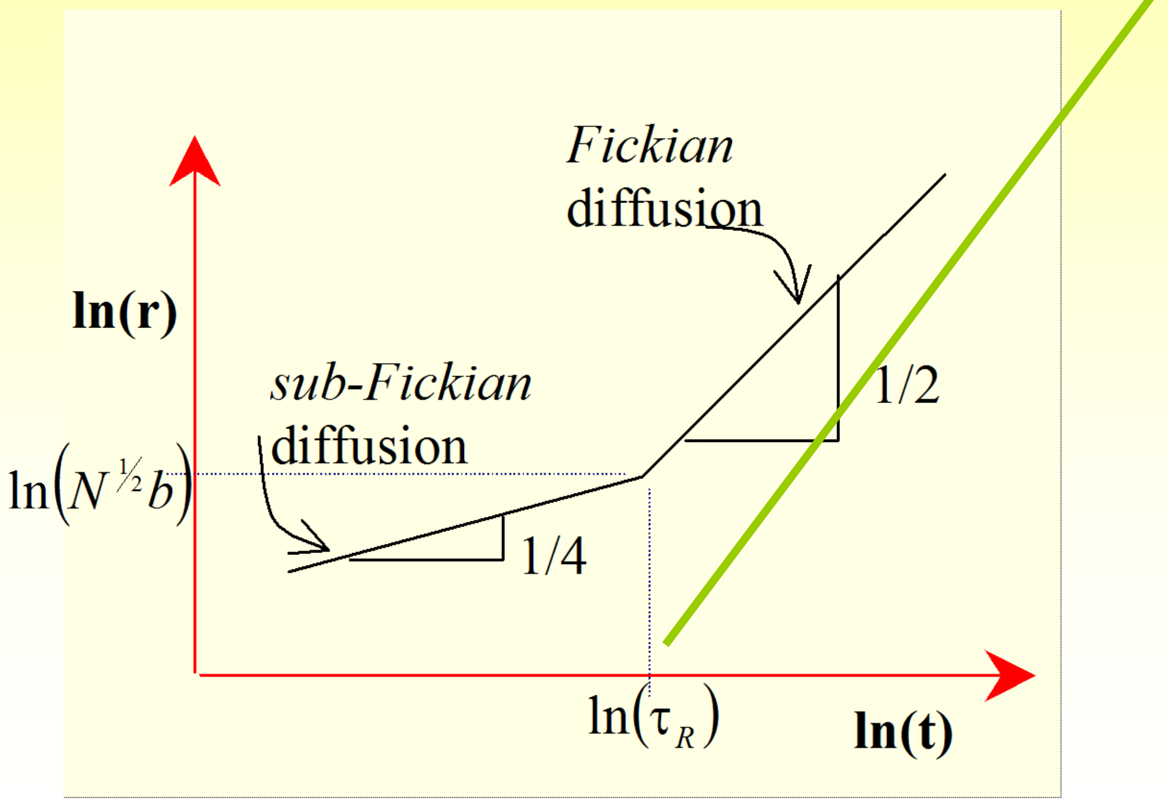
$$\Rightarrow (\Delta R) \approx t^{1/4}$$

# Diffusion in the Rouse Model

Rouse Time

$$\tau_R \cong \frac{R^2}{D_{cm}} \cong \frac{Nb^2}{\left(\frac{kT}{N\zeta_0}\right)}$$

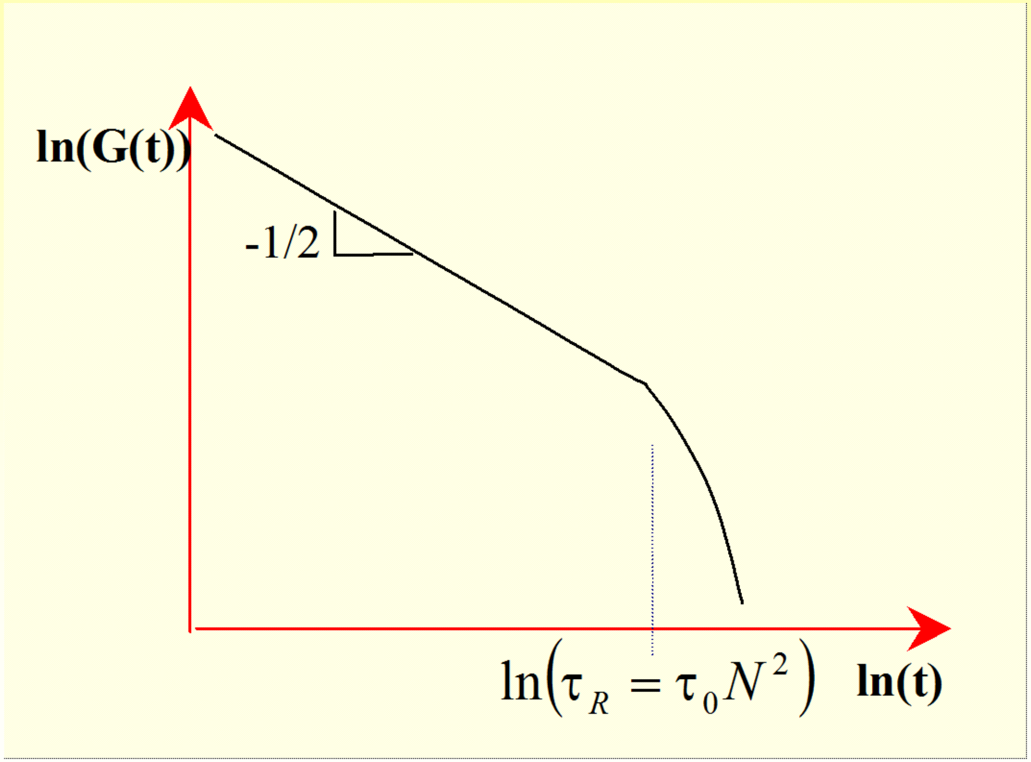
$$\cong \frac{N^2 b^2}{kT}$$



# Stress Relaxation in the Rouse Model

$$G(t) \cong c_N kT \frac{N}{n(t)}$$

$$\cong c_N kT \left(\frac{\tau_R}{t}\right)^{\frac{1}{2}}$$



# *Polymer solutions and Hydrodynamics: The Zimm Chain*

- Polymers in solution: scaling, correlations
- Dynamics: Zimm model, dilute and semi-dilute regimes

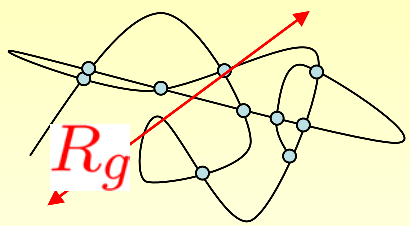
*References:*


M Rubinstein and R Colby, *Polymer Physics (2003)*

R Larson, *The Structure and Rheology of Complex Fluids*

# *Polymers in Solution: excluded volume*

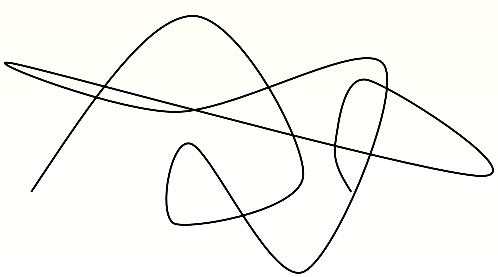
- Real polymer chains: excluded volume parameter $v$




$$R_g \sim \tilde{b} N^{\nu}$$
$$\sim b \left(\frac{v}{b^3}\right)^{2\nu - 1} N^{\nu}$$
$$(\nu = 0.588 \simeq 3/5)$$

Flory: balance contact energy with chain entropy ) **Swollen chains**

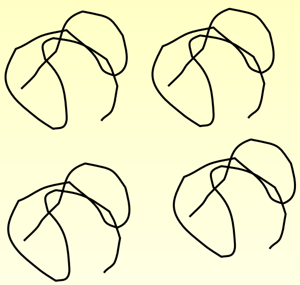
- Phantom coil: Melt, near Θ-point $(v = 0)$



$$R_g \sim b N^{1/2}$$

# *Semi-dilute regime* $\phi > \phi^*$

- Onset of multi-chain behaviour, interactions, enhanced viscoelasticity.



$$c^* = \frac{1}{V_{\text{chain}}} \sim \frac{1}{R_g^3}$$

$$\rho^* = M c^*$$

$$\phi^* = \frac{N b^3}{R_g^3} \sim N^{1-3\nu}$$

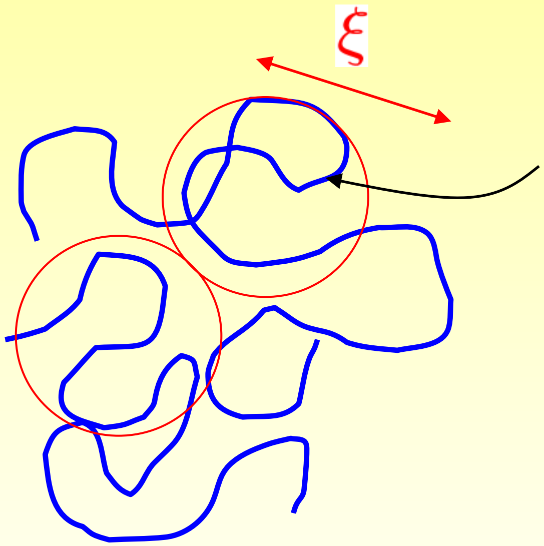
$$= \begin{cases} \frac{1}{N^{0.5}} & \text{(ideal, } \Theta\text{-solvent)} \\ \frac{1}{N^{0.76}} & \text{(good solvent)} \end{cases}$$

*e.g.* Raise *T* ) swell ) induce overlap increase viscosity!

$\phi > \phi^*$

# *Chain correlations*

- Sections of chain only see themselves at short distances:




$g$ monomers in a “blob”

$\xi \sim g^{\nu}$ Flory/single chain scaling inside blob

$\phi \sim \frac{g b^3}{\xi^3}$ blobs fill space

$$\xi \sim \phi^{\frac{-\nu}{3\nu - 1}} = \begin{cases} \frac{1}{\phi^{0.76}} & \text{(good)} \\ \frac{1}{\phi} & \Theta \text{ solvent} \end{cases}$$

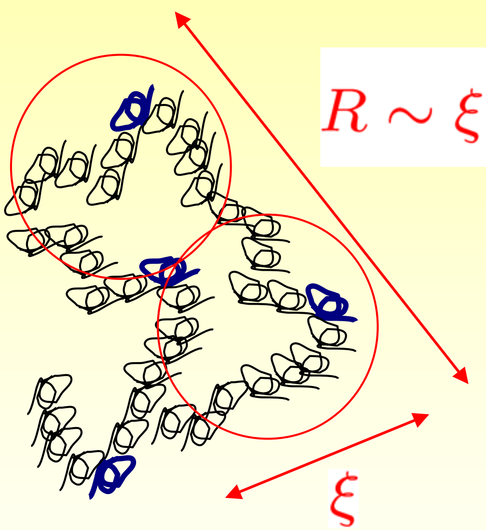
Correlation length (e.g. light scattering)

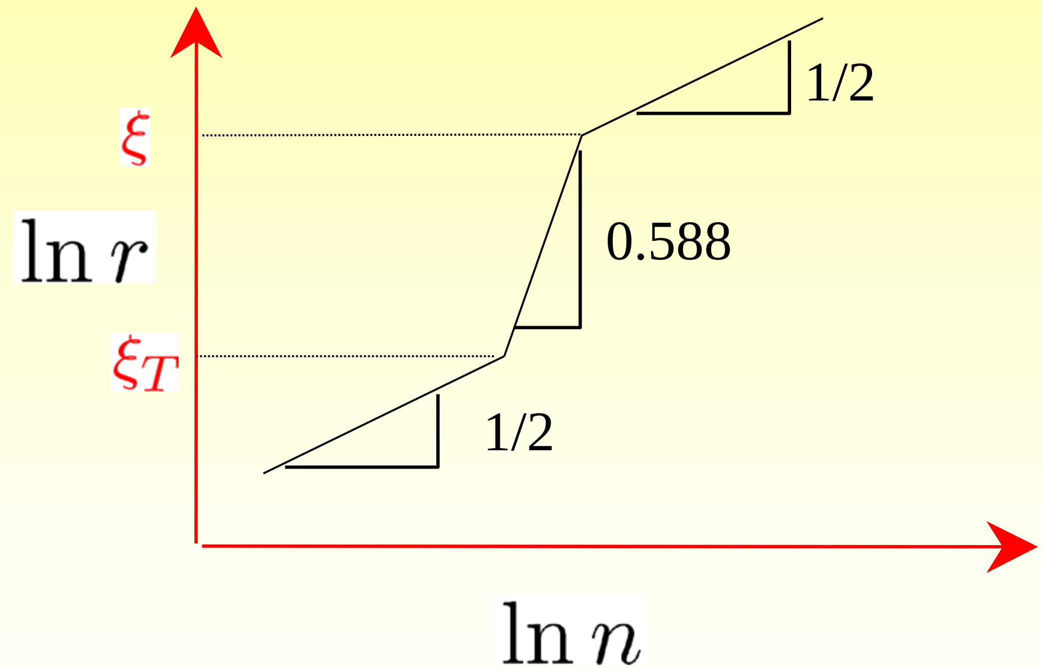
**Small distances:** excluded volume negligible $r < \xi_T$

$$\xi_T \sim \frac{b^4}{v}$$

**Large distances:** Random walk of blobs $r > \xi$

$$R \sim \xi \left(\frac{N}{g}\right)^{1/2}$$



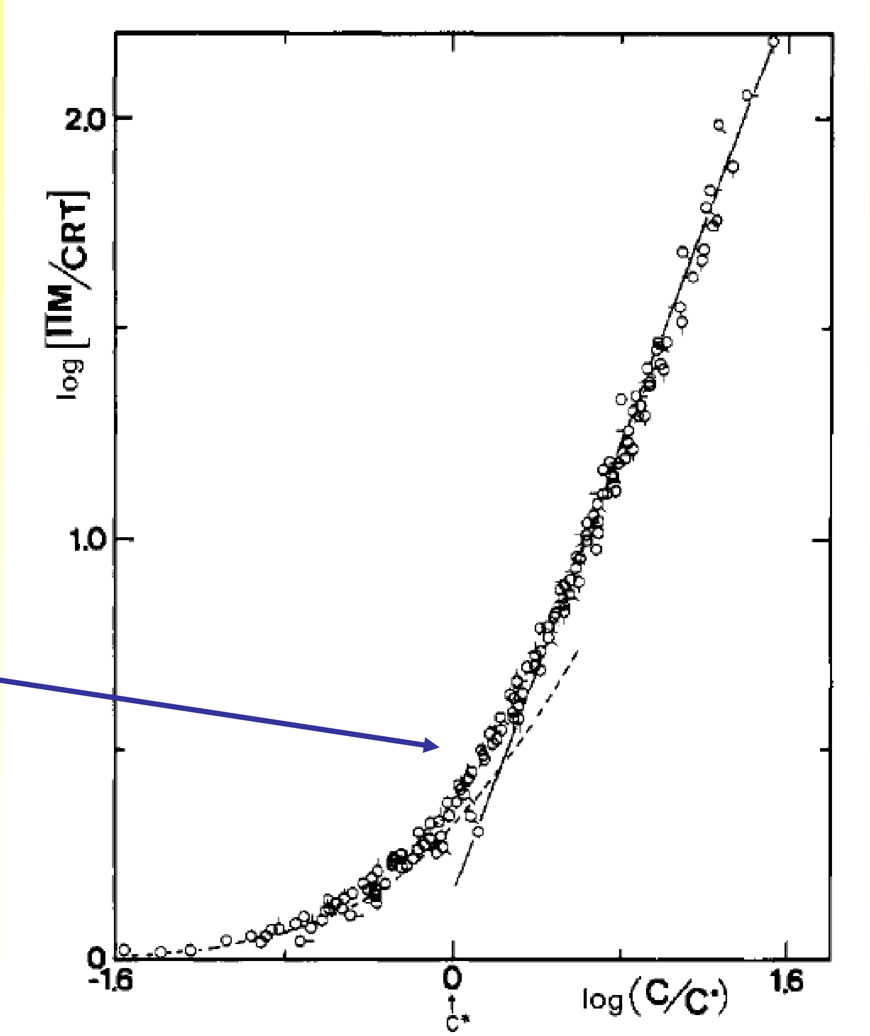




**Crossover to melt when:** $\xi \sim \frac{1}{\phi^{0.76}} \sim \xi_T$ (Edwards screening)

# Semi-dilute solutions: osmotic pressure

$$\Pi = \left.\frac{\partial F}{\partial V}\right|_N \sim \frac{k_B T}{\xi^3} \sim \phi^{2.3}$$

Slope = 1.32

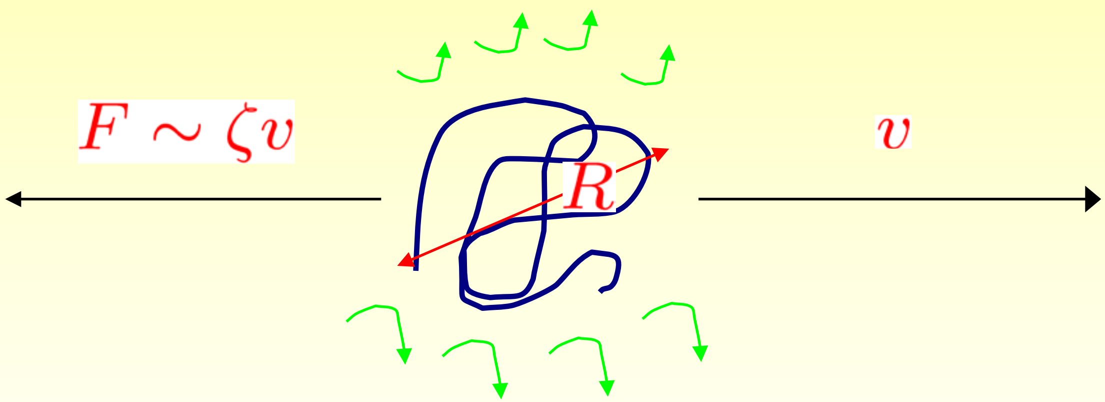



*Nocho* et al., Macromolecules 1981

# Diffusion: Zimm model

- Local drag coefficient in Rouse model: $\zeta_R = N\zeta_0$
- In solution, include **long range** hydrodynamic drag: $\zeta_Z = 6\pi\eta_s R$

(Stokes)




- Einstein Relation:

$$D = \frac{k_B T}{\zeta_Z} \Rightarrow \tau_Z = \frac{R^2}{D} = \underbrace{\frac{\eta_s b^3}{k_B T}}_{\tau_0} N^{3\nu}$$

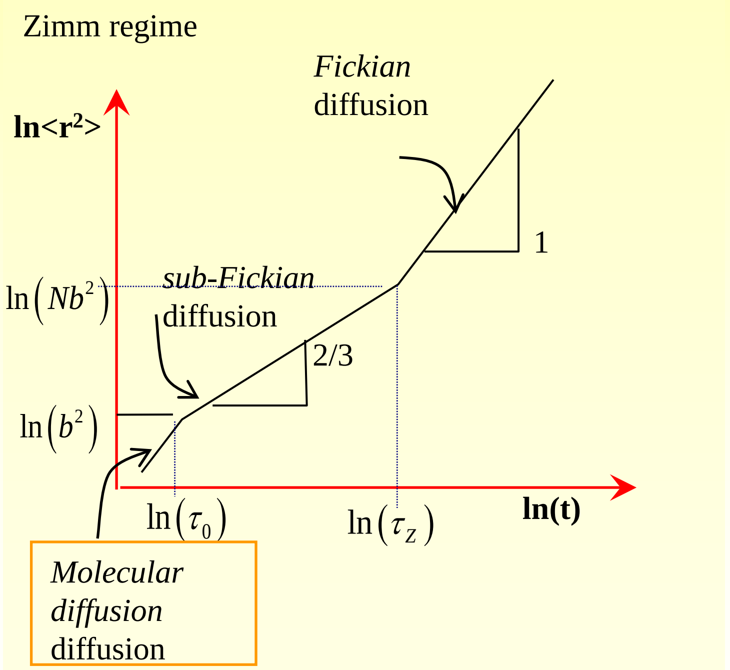
# Zimm or Rouse……who cares?!

$$\tau_Z(N) = \tau_0 N^{3\nu} = \tau_0 N^{1.76}$$
$$\tau_R(N) \simeq \tau_0 N^2$$

$$\tau_Z < \tau_R$$

- Relax by Zimm modes (faster)
- Monomer diffusion up to a Zimm time :

$$\langle r^2(n,t)\rangle \equiv \langle |r(t) - r(0)|^2\rangle = D(n)t \sim \frac{k_B T}{6\pi R(n)} t \sim \frac{k_B T}{6\pi R(n)} t \sim \frac{k_B T}{\left[\left(\frac{t}{\tau_0}\right)^{\frac{1}{3\nu}}\right]^{\nu}} t \sim t^{2/3}$$




(recall Rouse sub-Fickian $t^{1/4}$)

# *Stress relaxation* G(t)

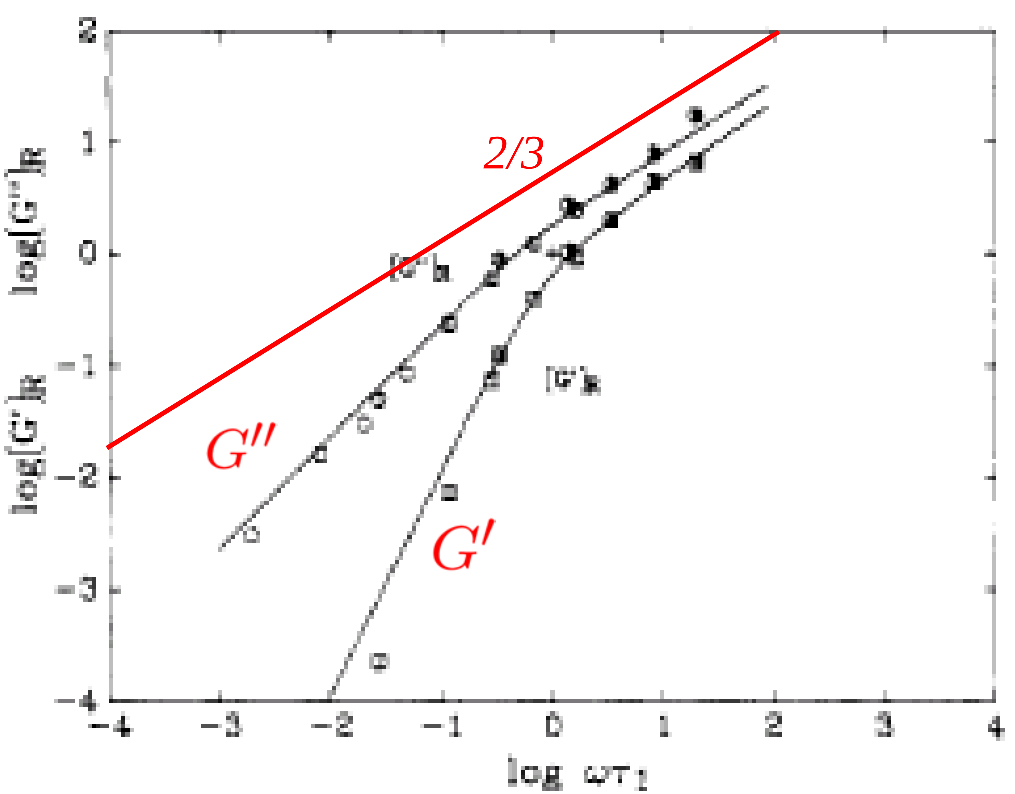
Count number of unrelaxed chain segments *N/n(t)*

$$G(t) \sim ck_BT\,\frac{N}{n(t)} \sim \frac{\phi k_BT}{Nb^3}\,\frac{N}{(t/\tau_Z)^{1/3\nu}}$$

$$\sim \frac{\phi k_BT}{b^3}(t/\tau_Z)^{-1/3\nu}$$

$$\sim \begin{cases} t^{-2/3} & (\Theta\text{-solvent}) \\ t^{-0.57} & (\text{good solvent}) \end{cases}$$

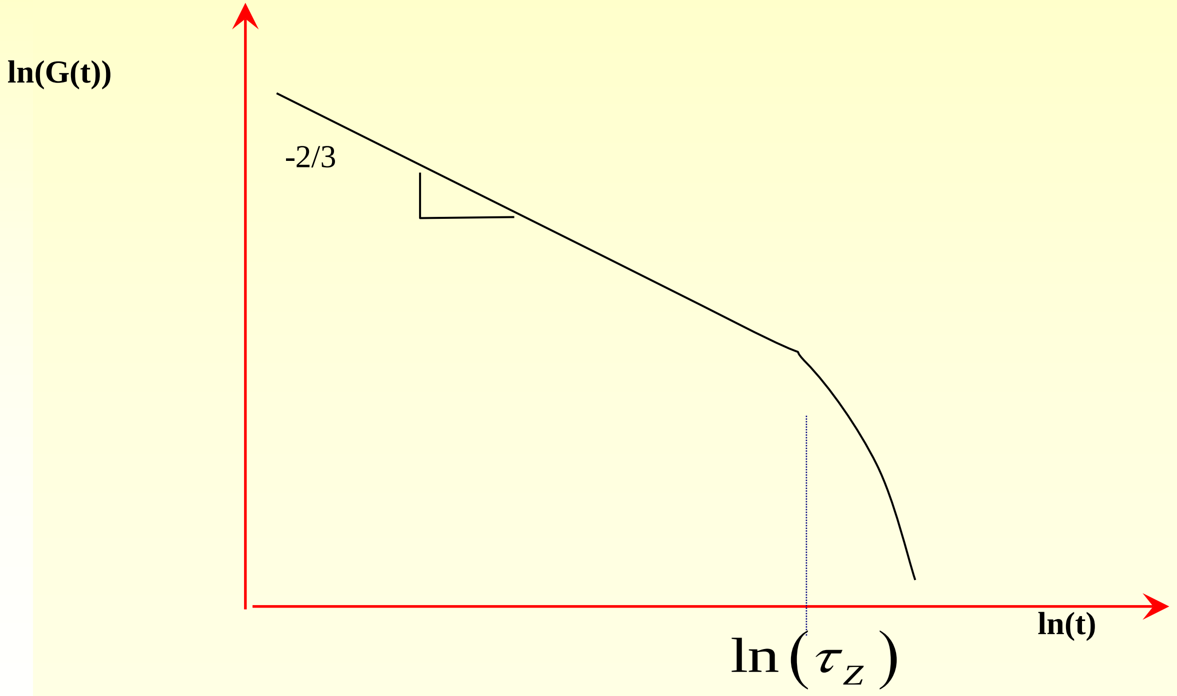
[Decalin in Θ-solvent, Hair & Amis, 1989]



# Stress relaxation at later times…..

After Zimm time…..not much stress left!

$$G(t) \simeq \frac{\phi k_B T}{b^3}(t/\tau_Z)^{-1/3\nu} e^{-t/\tau_Z}$$



# *Intrinsic viscosity (dilute solution)*

$$\eta = \eta_s \left(1 + [\eta]\, c + \mathcal{O}(c^2)\right)$$

- Einstein calculation for colloids (spheres), only due to surrounding hydrodynamics: $[\eta] = 2.5\phi$
- Polymeric contribution in dilute solution:

$$\eta - \eta_s \simeq G\,\tau \simeq k_B T \frac{\phi}{N b^3} \tau$$

$$\Rightarrow \quad [\eta] = \frac{k_B T N_A}{\eta_s M} \tau \qquad (c = \text{mass/volume})$$

$$\simeq \begin{cases} \frac{b^3 N_{av} N^2}{M} \sim N & \text{Rouse} \\ \frac{R^3 N_{av}}{M} \sim N^{3\nu - 1} & \text{Zimm} \end{cases}$$

# *Dilute solution )*
# *Melt in Good Solvent?*

dilute — $\phi^*$ — semi-dilute — $\phi^{**}$ — melt

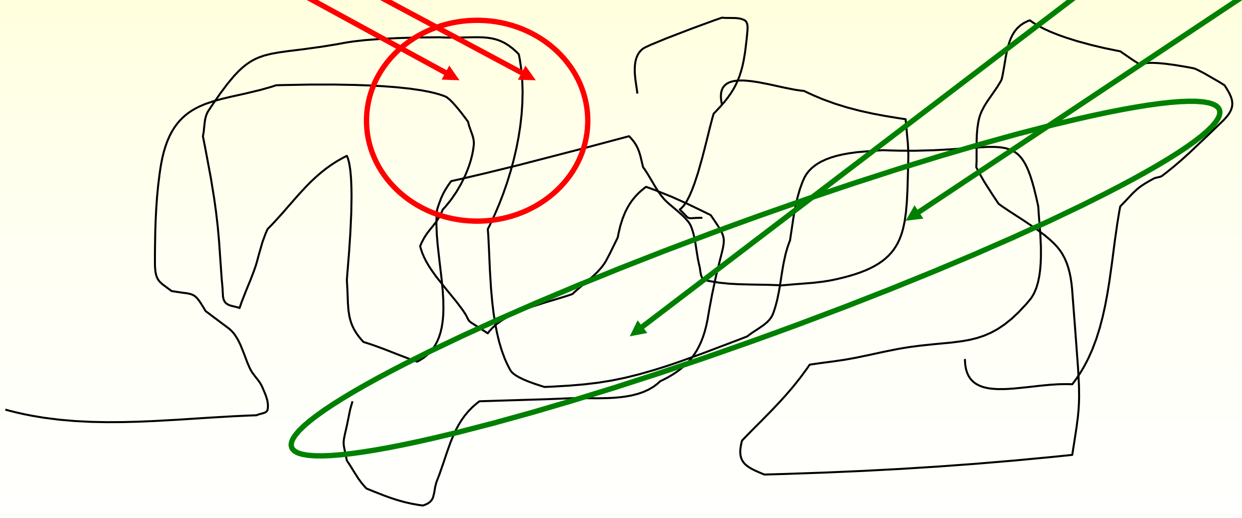
**Zimm**

$R \sim N^{\nu}$

screening $\begin{cases} \xi_{\text{hydrodynamic}} \\ \xi_{\text{excluded volume}} \end{cases}$

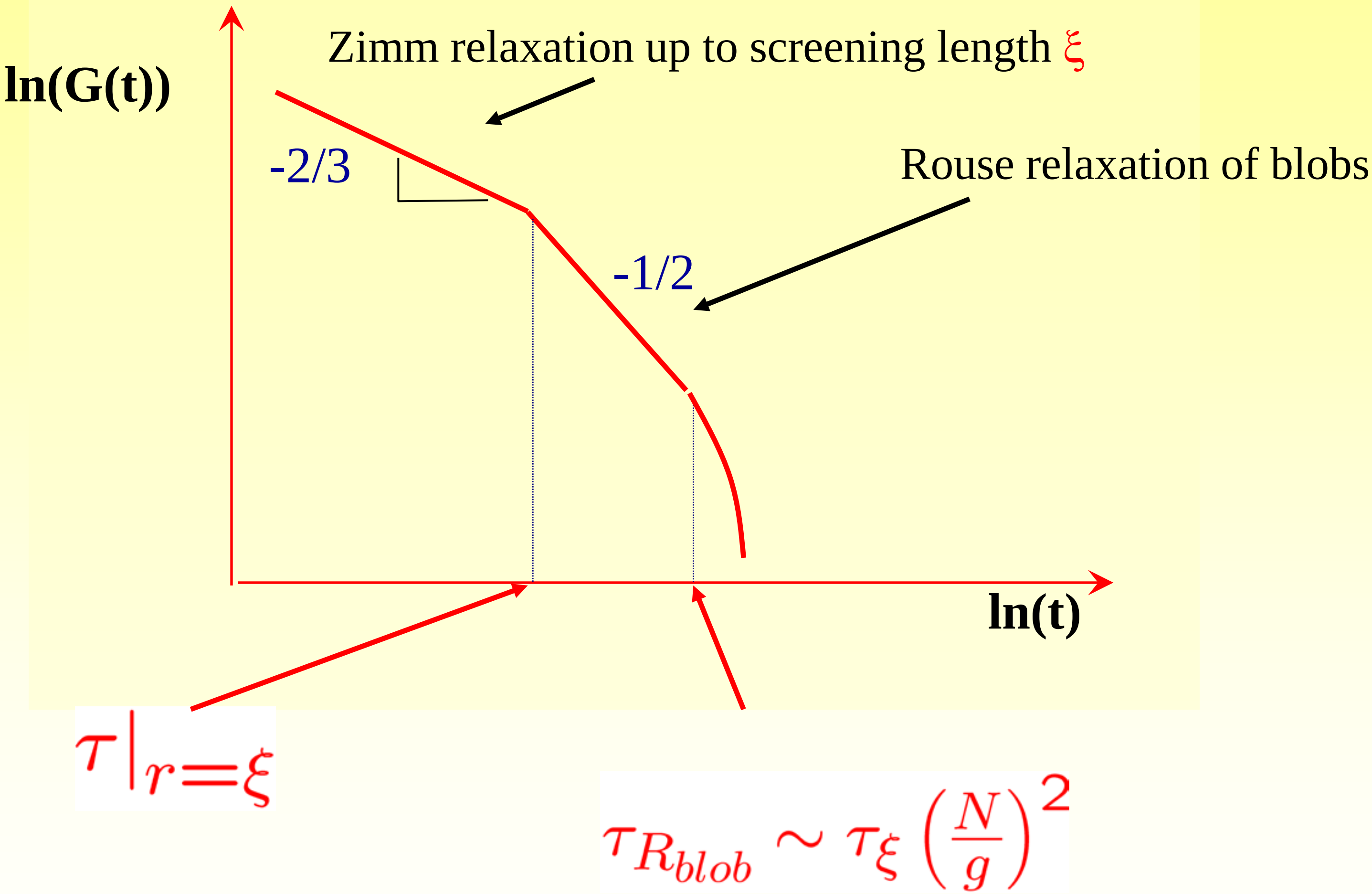
**Rouse**

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

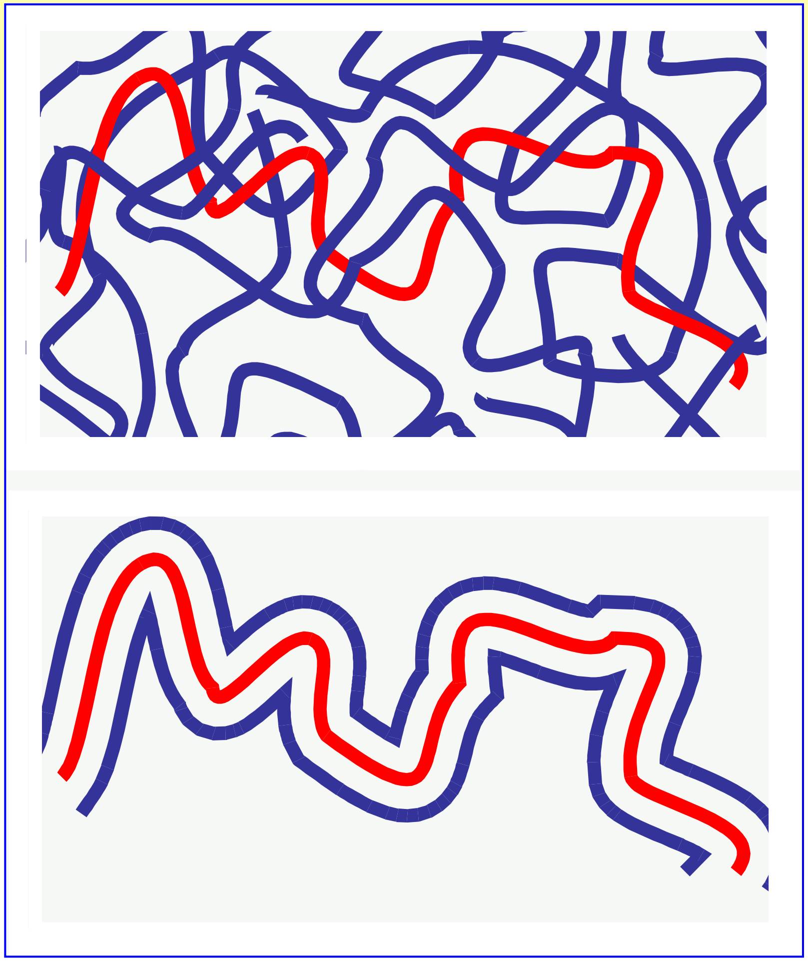


$\xi_{\text{hydro}} \simeq \xi_{\text{excl}}$ (??)

# *Rouse/Zimm together*



# *Entangled Dynamics*

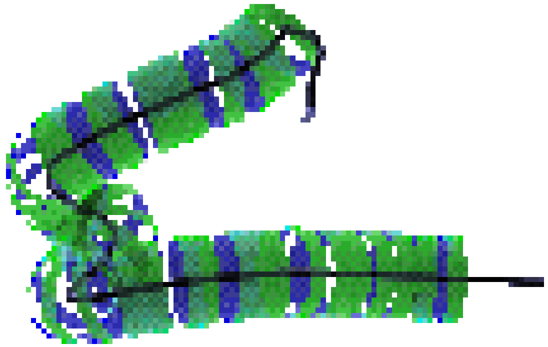


The Problem

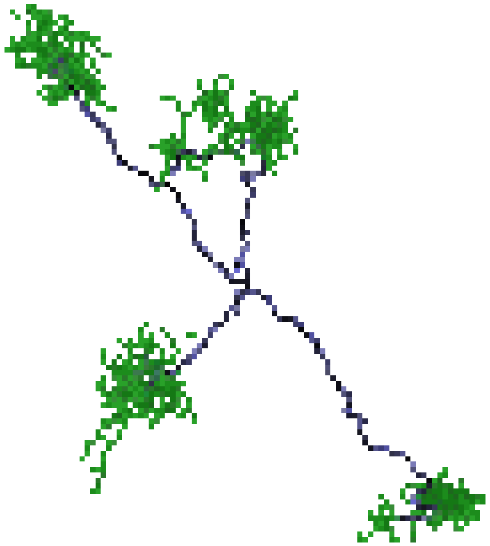
The “Solution”

## *Chain motions*

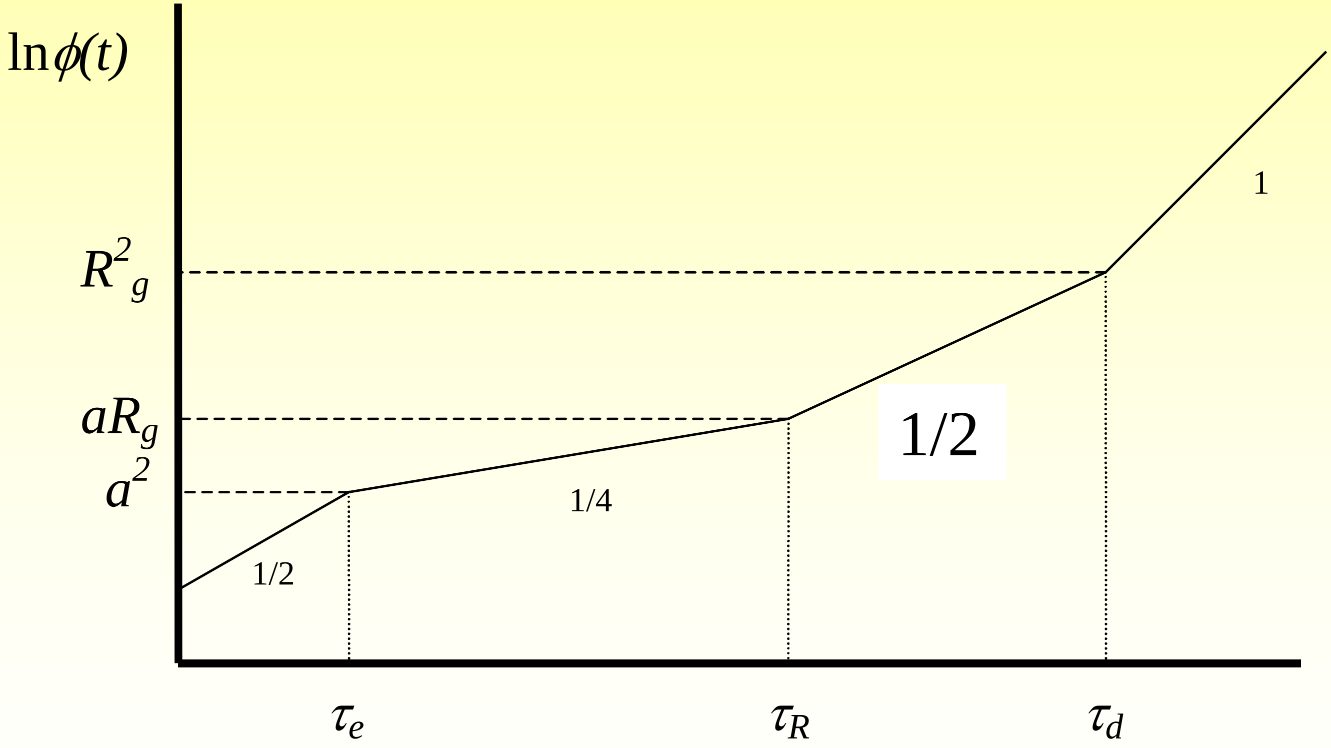
- Linear polymers: reptation



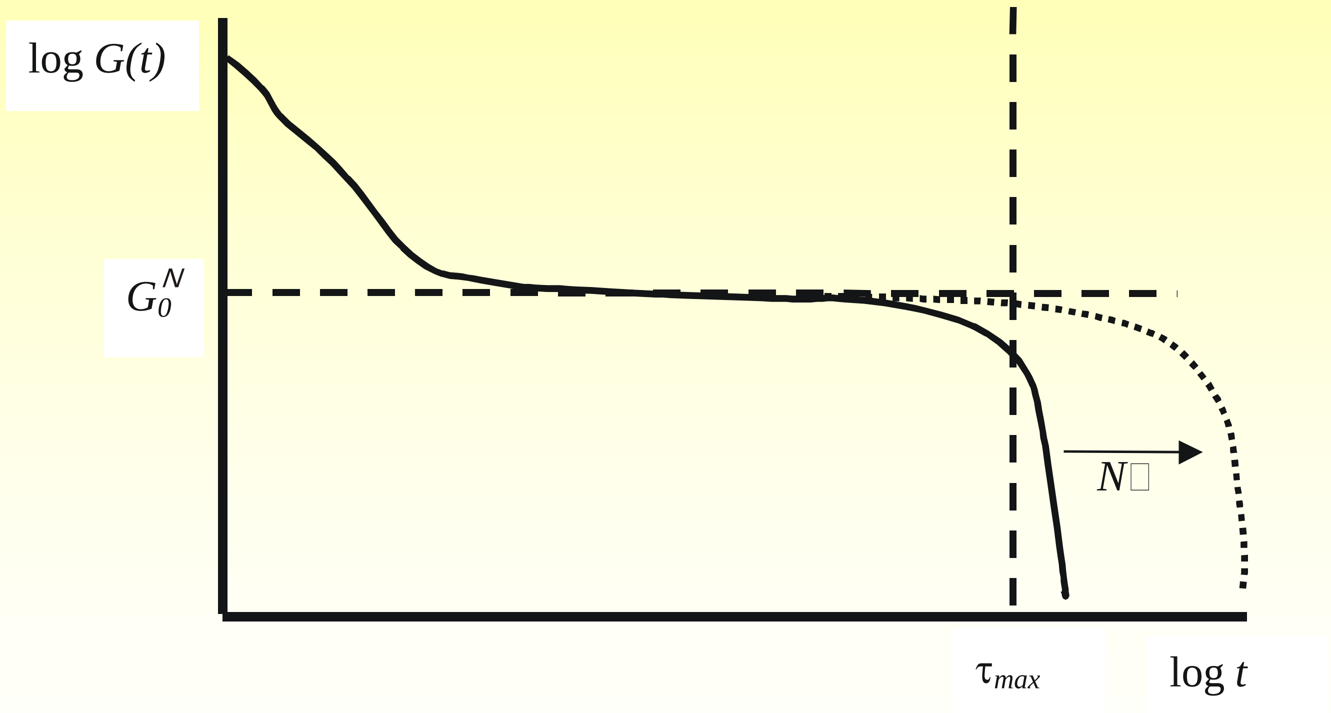
- Branched polymers: arm retraction



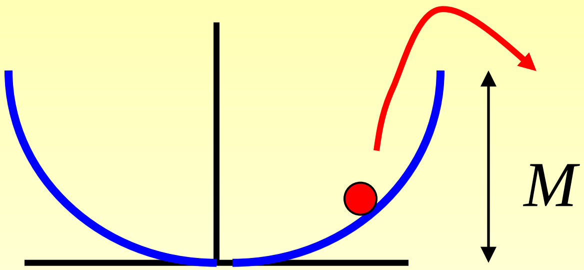
# Diffusion in the reptation Model



# Stress Relaxation in the reptation Model

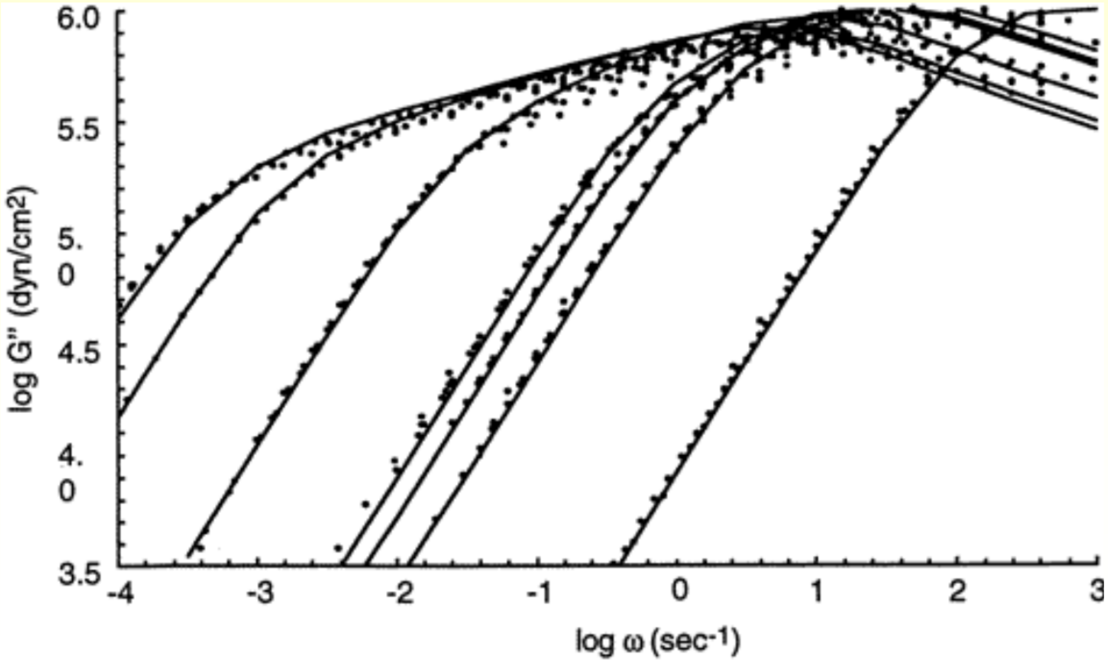


# *Star Polymers*

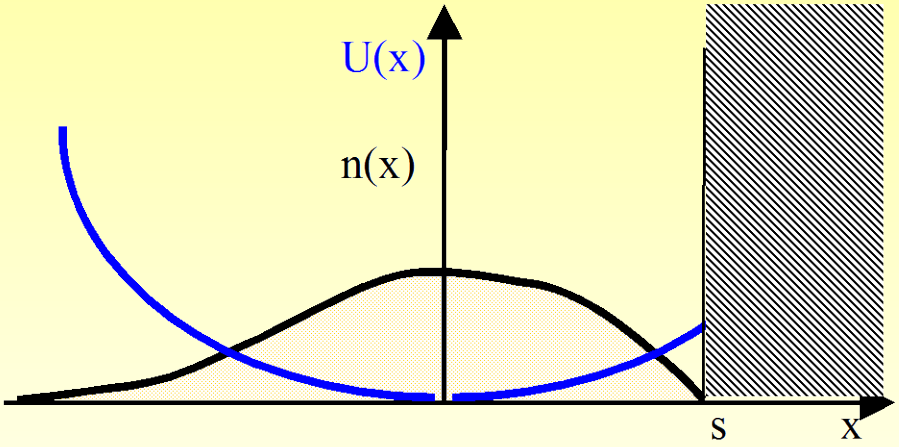



End-retraction is an "activated process" over a thermal barrier ~*M*

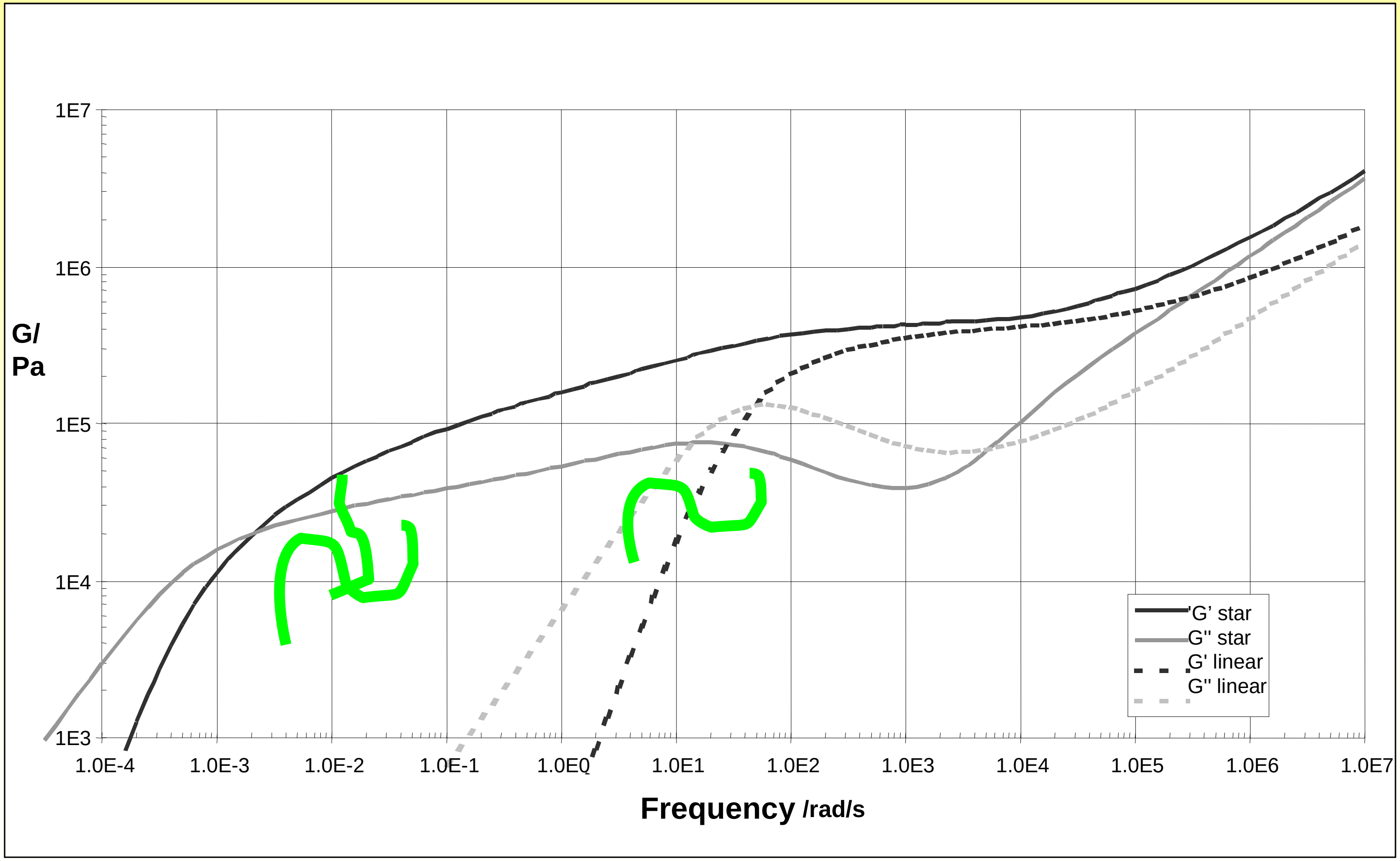
$$\therefore \quad \tau \sim \exp(\nu M)$$



# The Star-arm fluctuation potential




$$U(z) = \frac{3kT}{2Nb^2}z^2 - \frac{3kT}{a}z = \frac{3kT}{2Nb^2}s^2 + \text{const.},$$

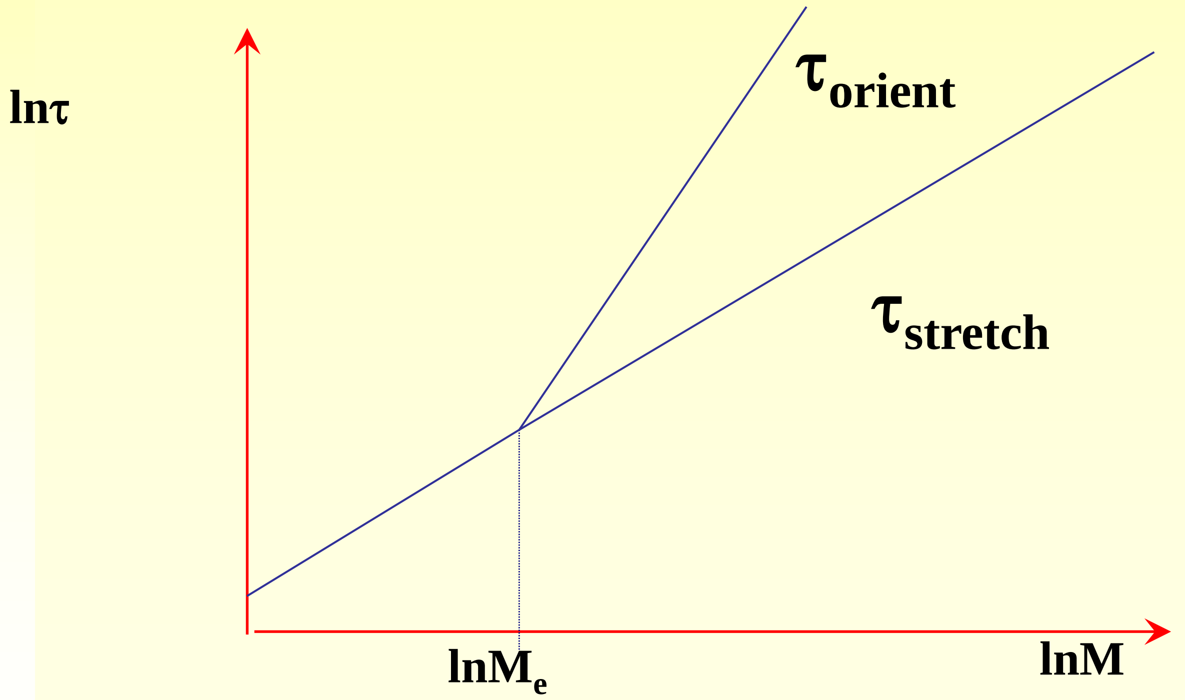

1E7
1E6
1E5
1E4
1E3
G/
Pa
1.0E-4
1.0E-3
1.0E-2
1.0E-1
1.0E0
1.0E1
1.0E2
1.0E3
1.0E4
1.0E5
1.0E6
1.0E7
Frequency /rad/s
'G' star
G'' star
G' linear
G'' linear

# *Further Topics*

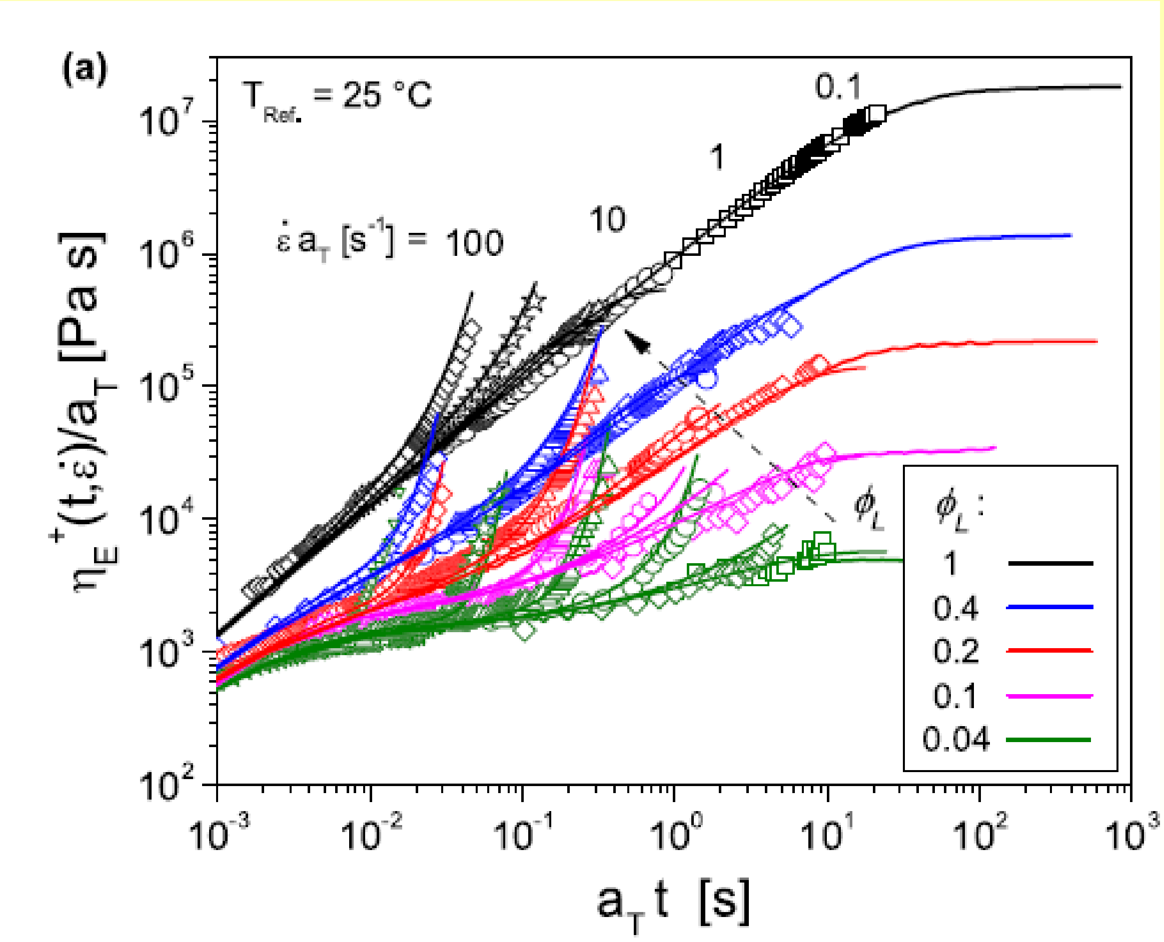
- Non-linear Rheology
- Quantitative Linear Entangled Dynamics
- Rheology, Topology and the Pom-Pom model
- Workshop problems….

# *A non-linear view of entanglement:*

- Bifurcation of Stretch and Orientation relaxation times

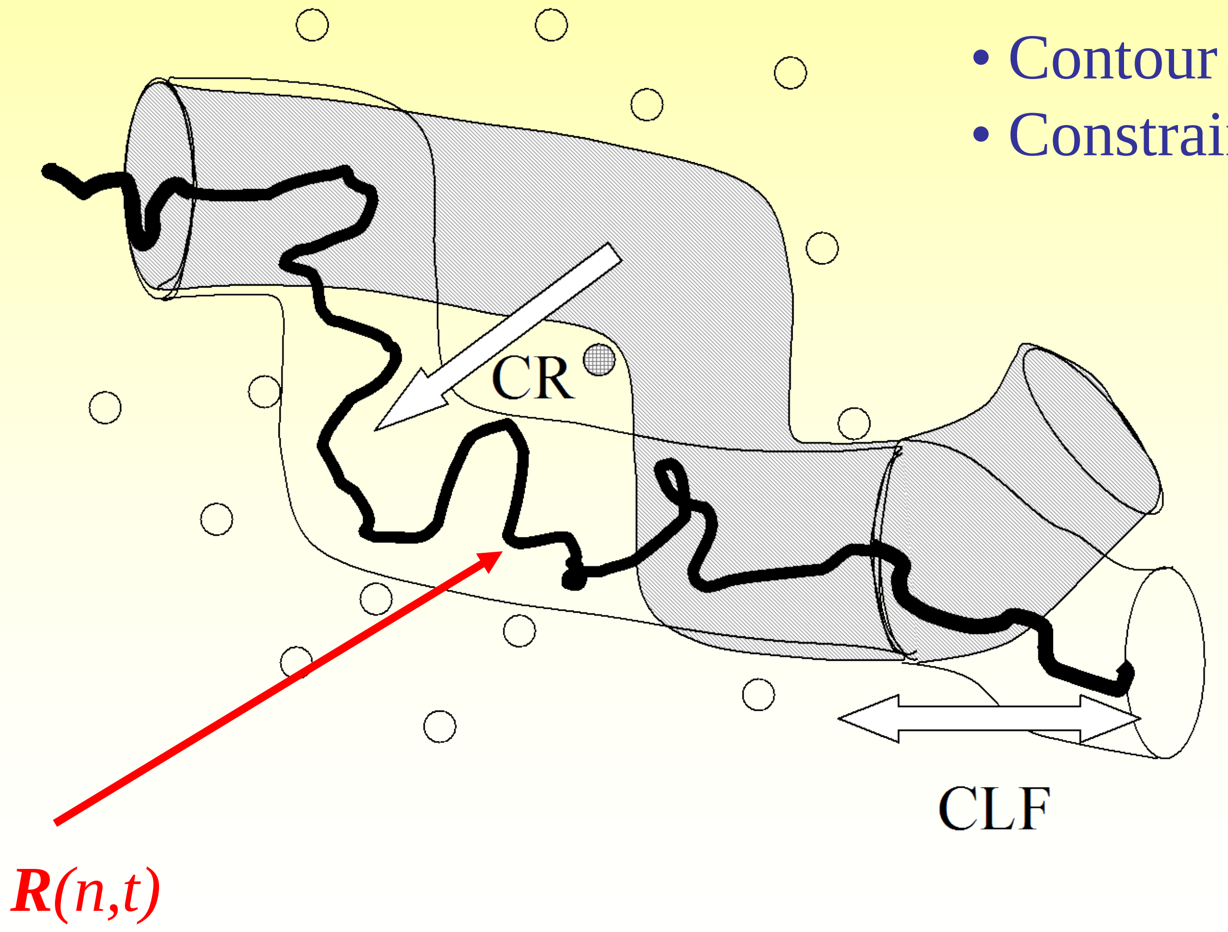


# *Startup of extensional flow shows* two nonlinearities in rate*:*



# Quantative Theory:  New Physical Processes

- Contour length fluctuation
- Constraint Release

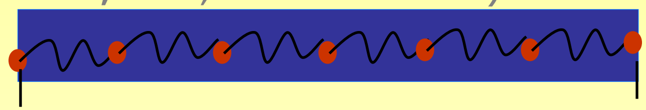


# Linear Rheology

$$\left\langle \frac{\partial R(n,t)}{\partial n}\frac{\partial R(n,t)}{\partial n}\right\rangle$$

•Linear regime -

(Likhtman and McLeish, Macromolecules **2002**, *35*, 6332-6343)

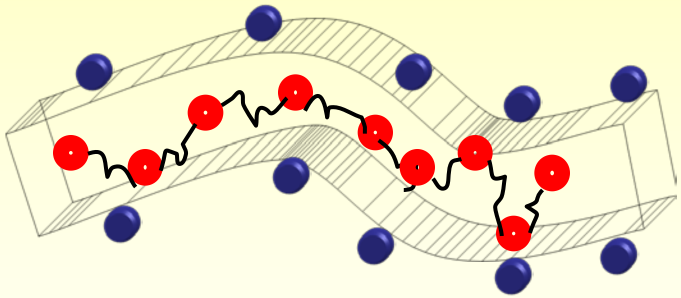


- numerical solution of CLF

??? $\mu(t)=L(t)/L(0)$ - fraction of tube segments survived after time $t$

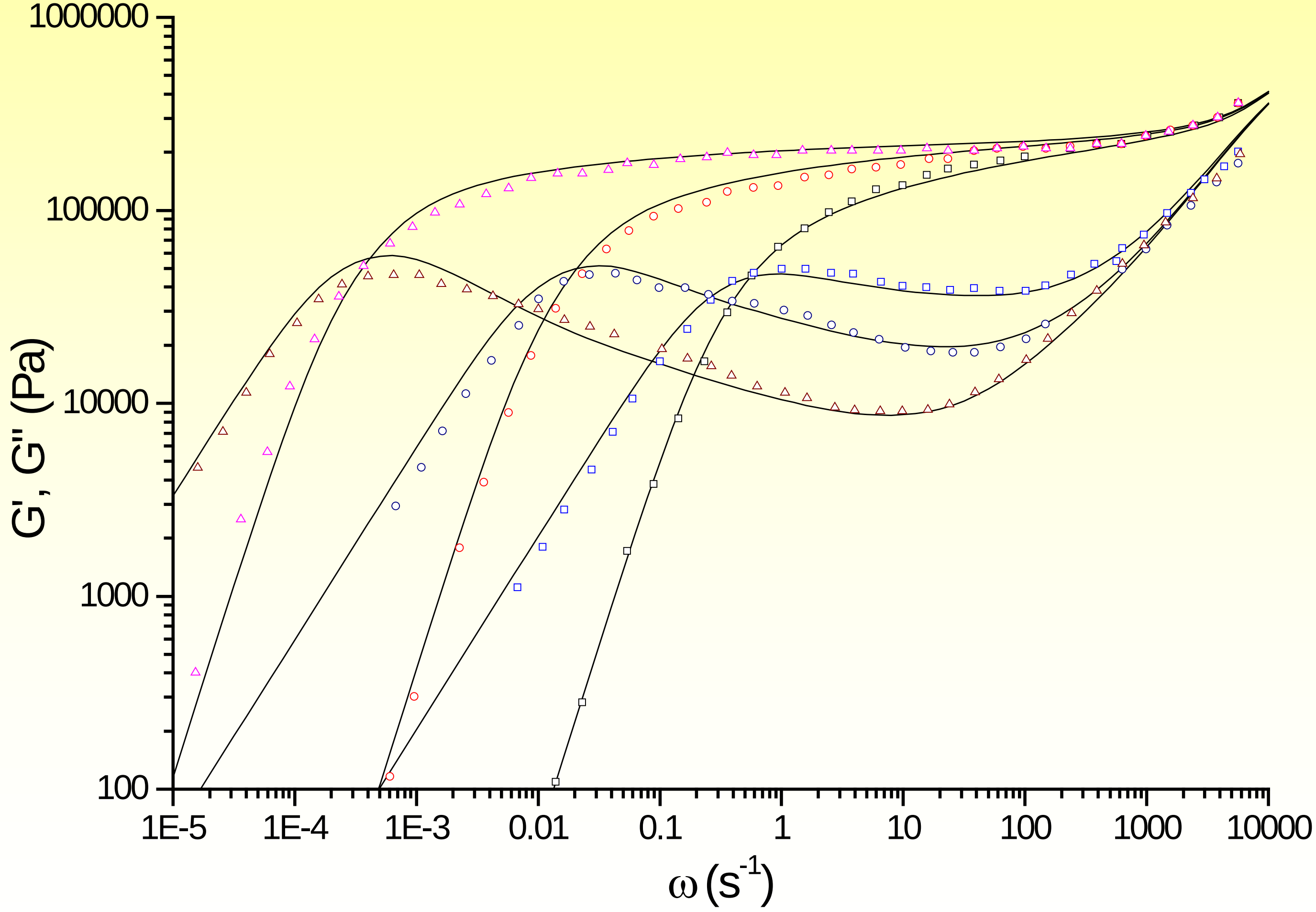
- CR: Rubinstein and Colby (1988)

- longitudinal stress relaxation

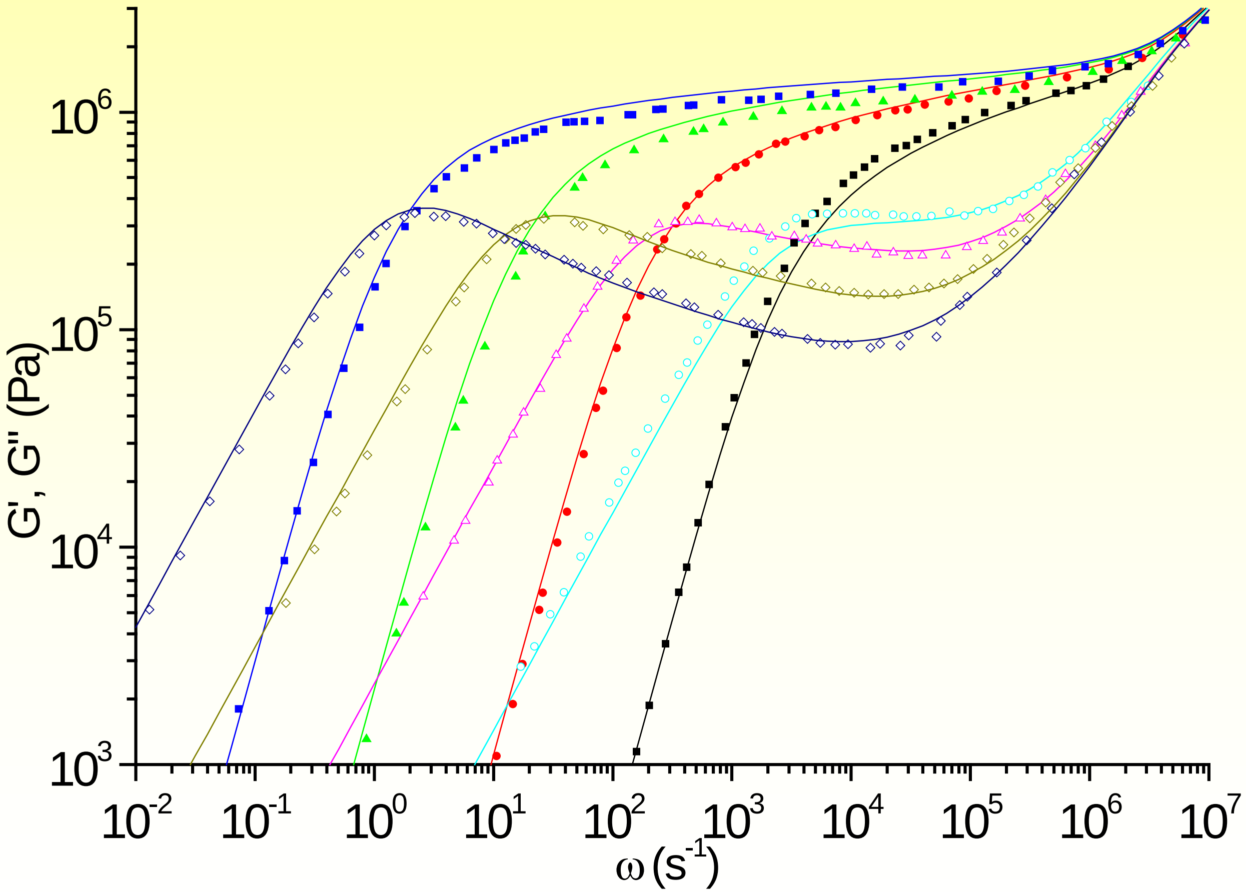


$$G(t,c_\nu)=\frac{\rho RT}{M_e}\left(\frac{4}{5}\mu(t)R(t,c_\nu)+\frac{1}{5Z}\sum_{p=1}^{Z-1}\frac{1}{p^2}e^{-\frac{p^2t}{\tau_R}}+\frac{1}{Z}\sum_{p=Z}^{N}\frac{1}{p^2}e^{-\frac{2p^2t}{\tau_R}}\right)$$

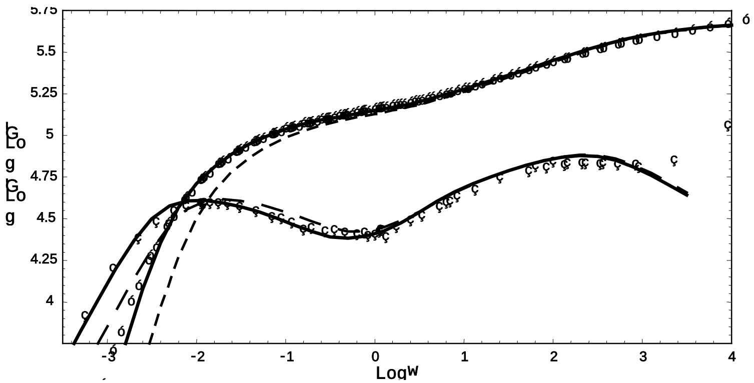
# Polystyrene, Shausberger et al, 1985, Mw=290K, 750K and 2540K, Me=13K



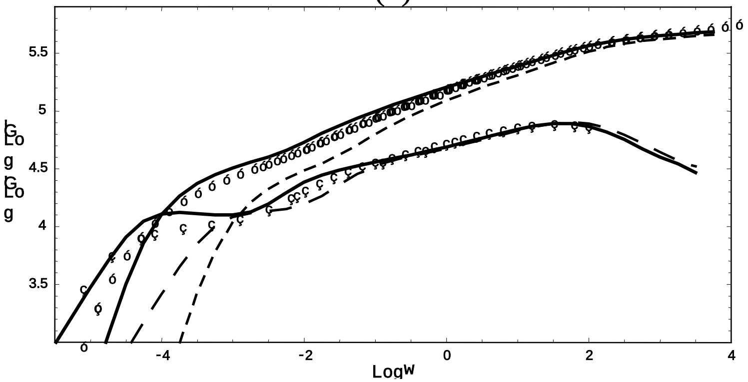
***Polybutadiene, Baumgaertel et al, 1992,***
***Mw=20.7K, 44.1K, 97K and 201K***



# Rheology and Topology

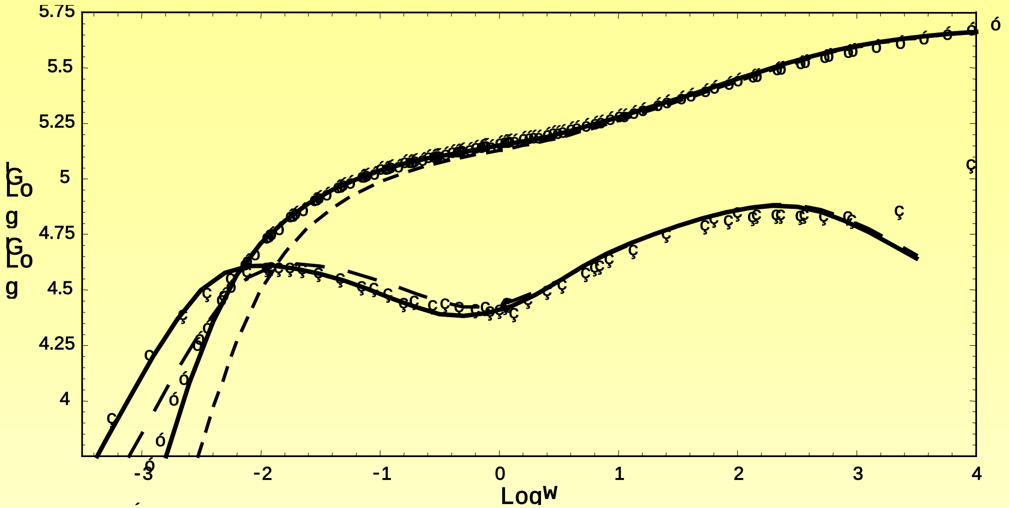


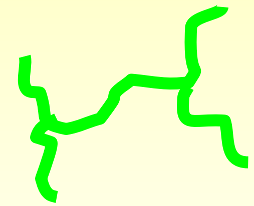

(a)




(b)

Figure 8  Experimental and theoretical complex moduli for the two H-polymers of the table. Fitting parameters of $G_0$ and $\tau_e$ were consistent with literature values, the number of entanglements along arm and crossbar, $s_a$ and $s_b$ together with their polydispersities $\varepsilon_a$ and $\varepsilon_b$ determined by GPC and SALS. Theoretical curves accounting for polydispersity are dashed; those without are solid.

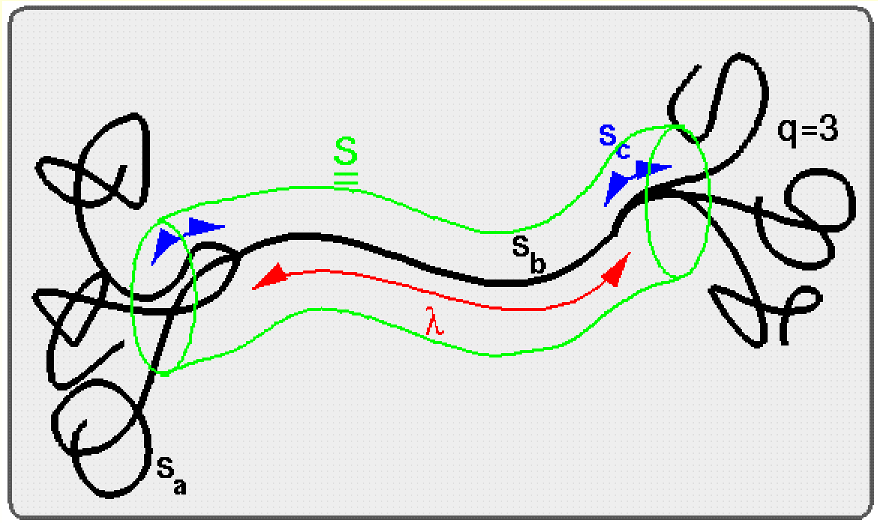


## *LCB Polymers in non-linear flow*

# Pom-pom constitutive equation

- highly entangled branch points
- long flexible backbone sections
- dangling ends



Stretch

$$\dot{\lambda} = \langle \mathbf{K} : \mathbf{S} \rangle \lambda - \frac{1}{\tau_s}(\lambda - 1)$$

Orientation

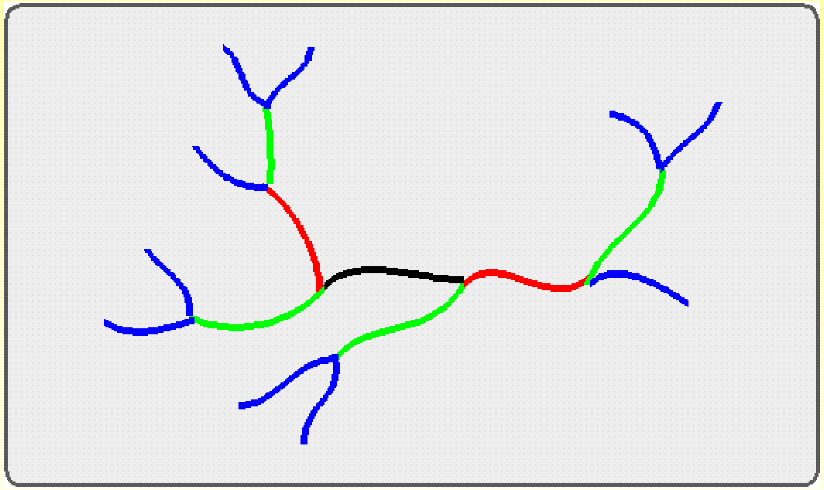
$$\frac{D}{Dt}\mathbf{A} - \mathbf{K} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{K}^T = -\frac{1}{\tau_b}(\mathbf{A} - \mathbf{I})$$

$$\mathbf{S}(t) = \frac{\mathbf{A}(t)}{\mathrm{trace}(\mathbf{A}(t))}.$$

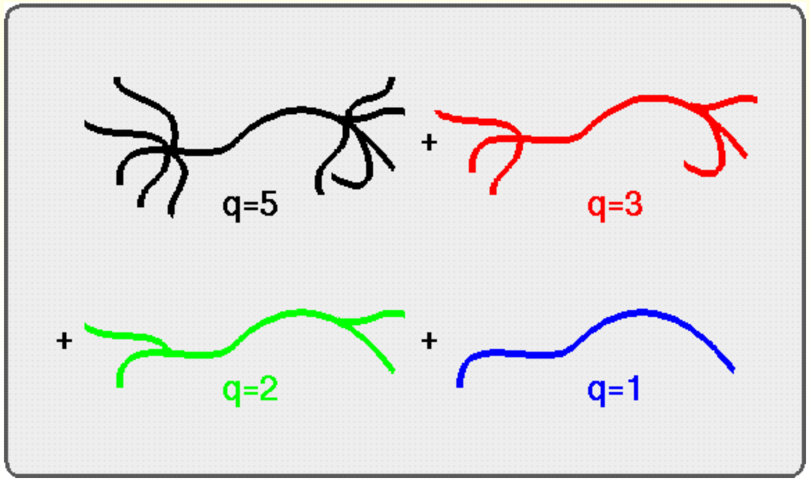
Stress

$$\sigma(t) = G[\lambda(t)]^2 \mathbf{S}(t)\left(1 + 2\frac{Z_c(t)}{L_0 \lambda(t)}\right),$$

# Represent a polydisperse (branched) polymer as a spectrum of pom-poms

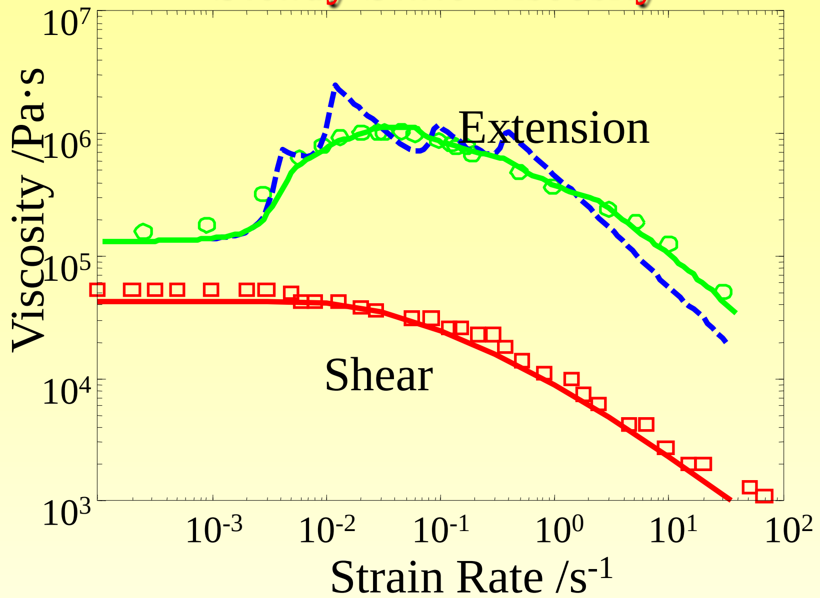


- Linear relaxation spectrum => $\tau_{bi}$, $g_i$
- 'decorate' these modes using nonlinear extensional data => $q_i$, $\tau_{si}$

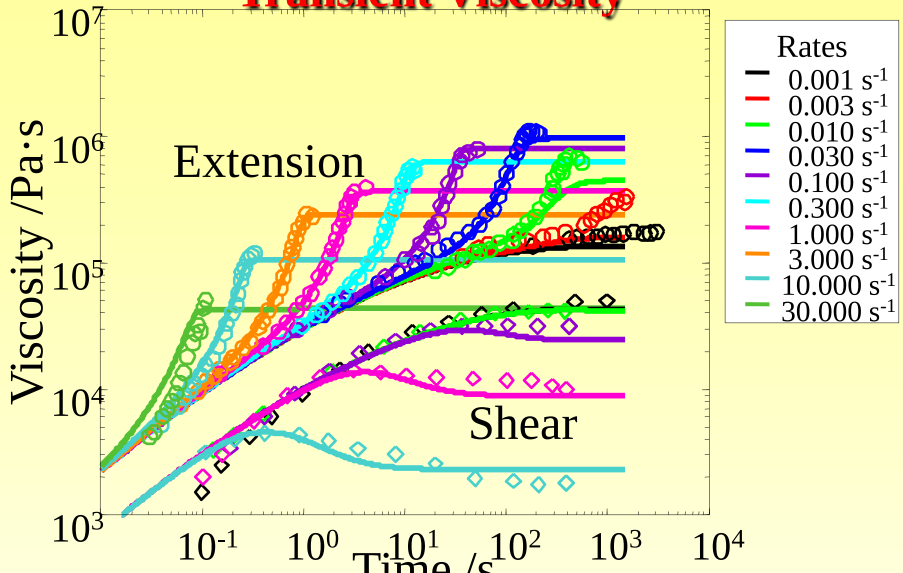


# Multi-mode pompom - an example

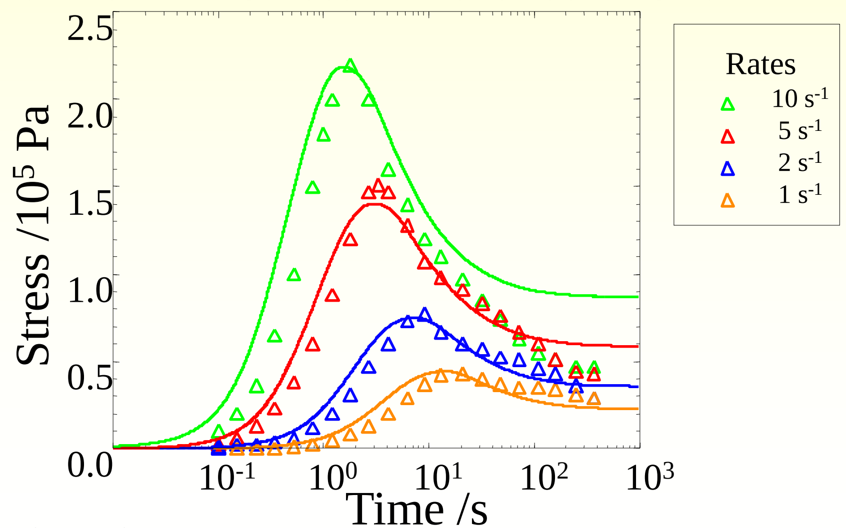
## Steady State Viscosity




## Transient Viscosity




## First Normal Stress Difference in Shear




Data from Meissner (1972, 1975) and Münstedt and Laun (1979).

# Classes of LCB and *q*-Spectra