Basic molecular rheology (linear regime)

Dimitris Vlassopoulos
FORTH, Institute of Electronic Structure & Laser, and
University of Crete, Department of Materials Science & Technology
Heraklion, Crete, Greece

dvlasso@iesl.forth.gr

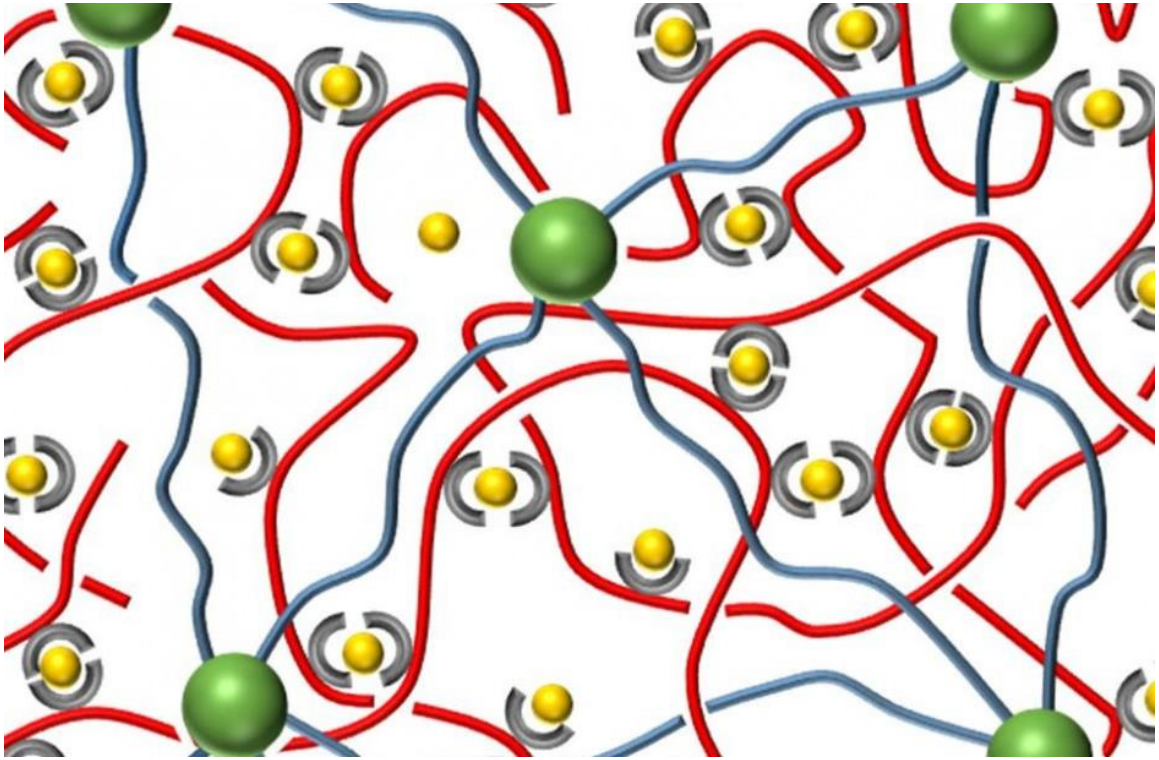
Syllabus:

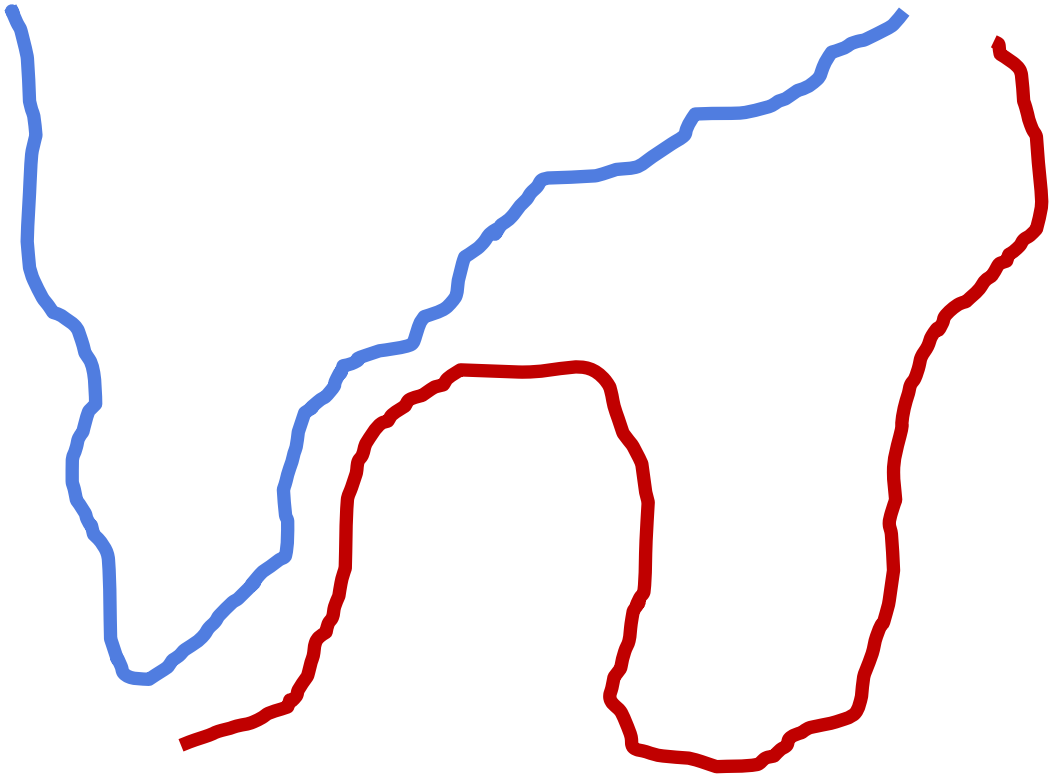
Polymers
Scales: Length, energy, modulus, time
Definitions: stress, strain, strain rate, shear, extension
Basics of linear flexible chains: molar mass, size, elasticity
Glass, Rubber-entanglements, melt
Mechanical spectroscopy: decoding visoelastic response, length and time scales
Models: Rouse,reptation and corrections
Branched polymers: stars and combs

Goals
Understand and “read” linear viscoelastic spectrum: link length and time
Appreciate difference between segments with both or one end free: diagnose material

Useful reading:

M. Rubinstein, R. H. Colby, Polymer physics, Oxford, 2003
J. M. Dealy, D. J. Read, R. G. Larson, Structure and Rheology of Molten Polymers, 2nd Edition, Hanser, 2018
W. W. Graessley, Polymeric liquids and networks: dynamics and rheology, Garland, 2008
R. G. Larson, The structure and rheology of complex fluids, Oxford, 1999
M. Doi, Introduction to polymer physics, Oxford, 2002
J. D. Ferry, Viscoelastic properties of polymers, 3rd ed., Wiley, 1980





Rheology (Heraclitus ~ 544-484 bC ….everything flows….)

(rheo = flow ; logos = study)

πάντα ῥεῖ eveything flows

Flow (and deformation) of matter (E. Bingham 1848-1945)

Flow: time and length scale
Deformation: strength (energy scale -- modulus)

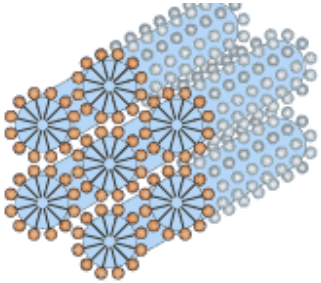
Significance:
Fluid vs Solid
Shaping materials, ordering , processing
Stability, durability, shelf life of products
Design materials for desired applications

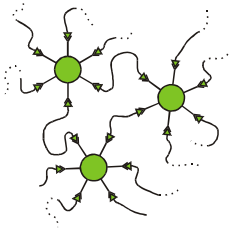
Beris, Giacomin, Appl. Rheol. 2014

Collective response + time/length scales

10^{2} s

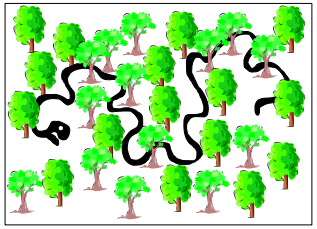
Collective motion

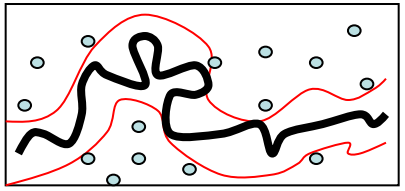




10^{1} s

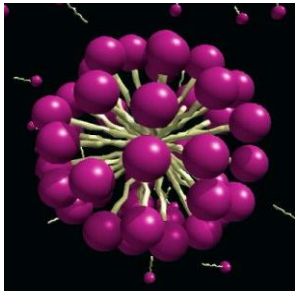
Network dynamics
("entanglements")

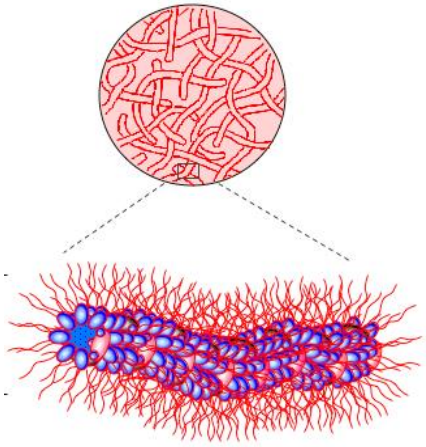




10^{-1} s

Lifetime of micelles





10^{-3} s

Exchange of molecules

10^{-6} s

(mm)

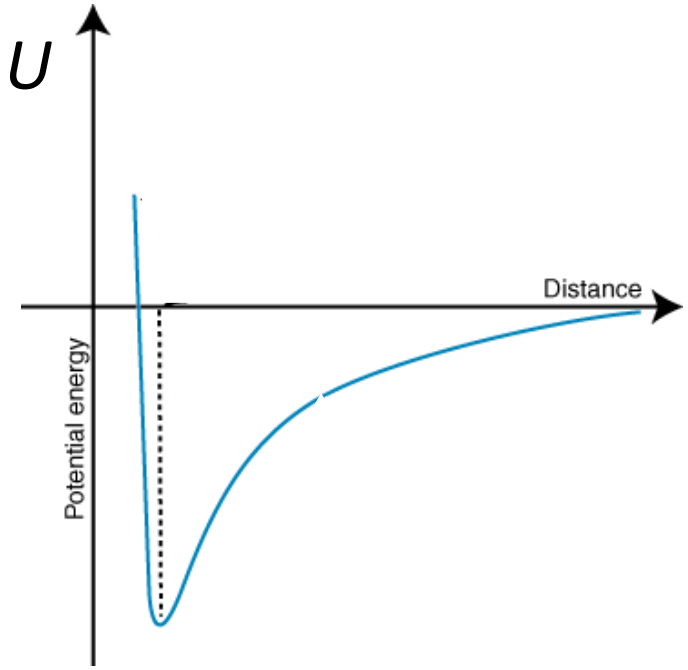
(μm)

(nm)

(Å)

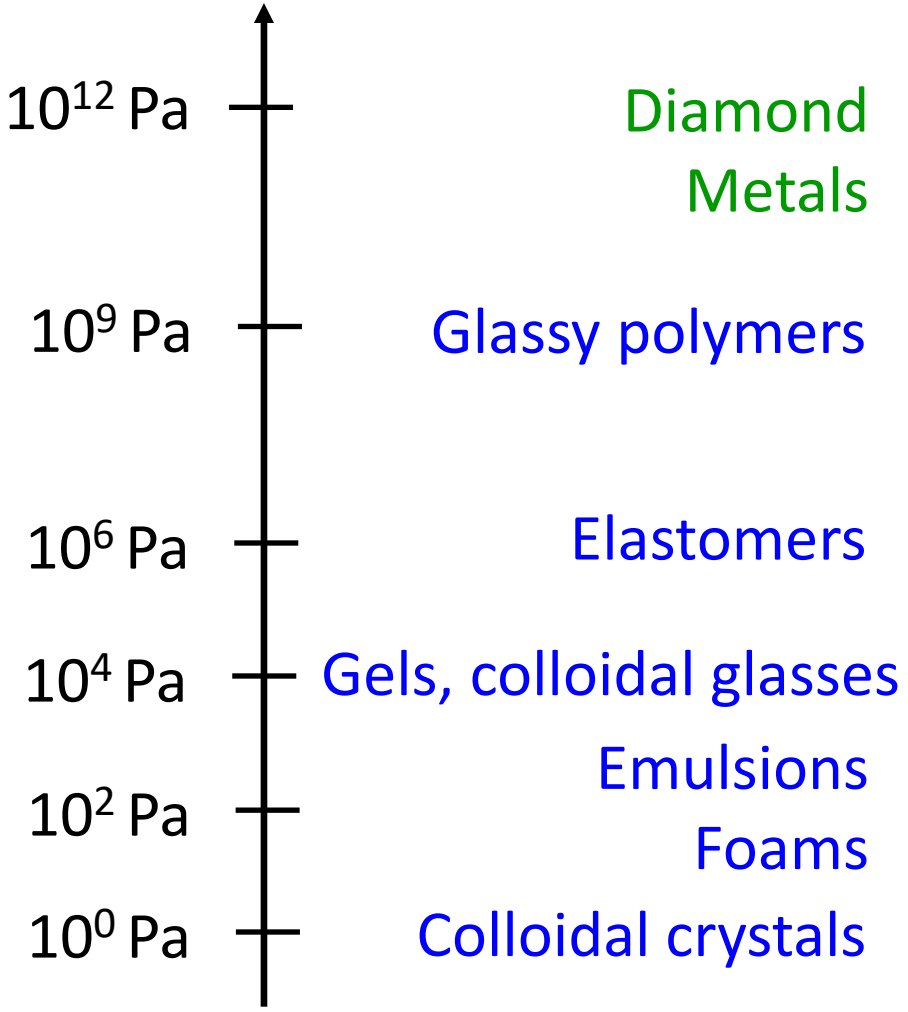
(with M. Cloitre)

Elastic energy of materials



Young modulus:

$$G = \frac{\sigma}{\gamma} = \frac{kT}{V}$$



Great sensitivity to external stimuli (mechanical stress)

Soft matter: small stimulus induces large effects (deformation)

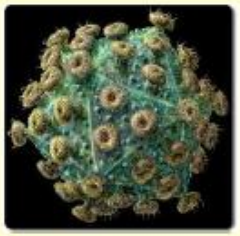
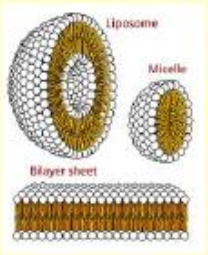
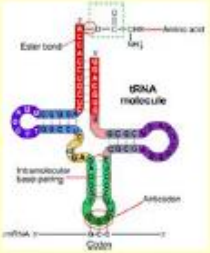
(M. Cloitre)

Polymers in materials science

# C atoms	1-5	6-15	16-25	20-50	1000 or more
@ 25°C and 1 atm	Gas	Low viscosity liquid	Very viscous liquid	Soft solid	Tough solid
Uses	Gaseous fuels	Liquid fuels and solvents	Oils and greases	Candles and coatings	Bottles…
Examples	Propane	Gasoline	Motor oil	Paraffin wax	Polyethylene
					

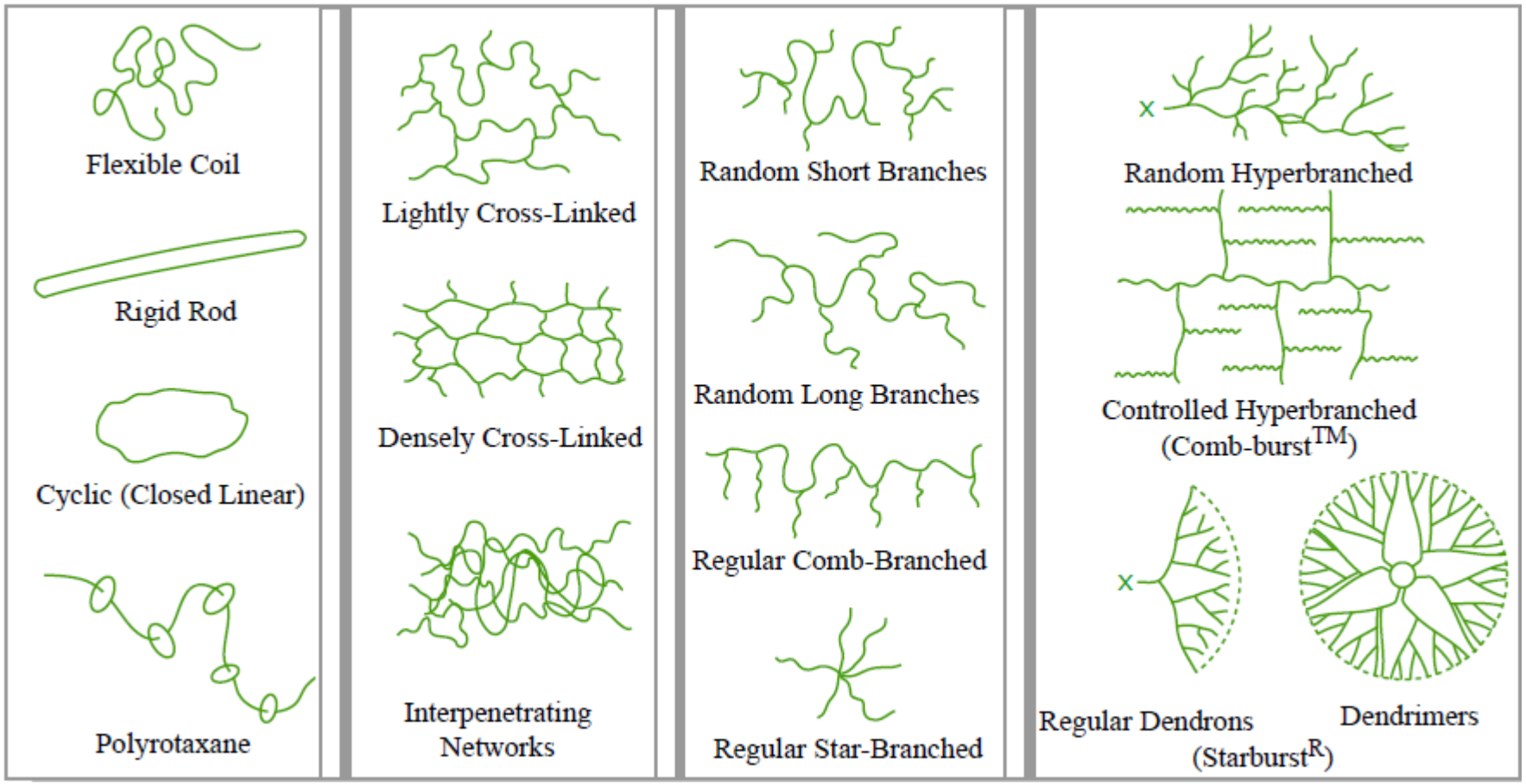
(from A. Y. Grosberg)

Polymers in nature

	DNA	RNA	Proteins	Lipids	Polysaccharides
N	Up to 10^{10}	10 to 1000	20 to 1000	5 to 100	gigantic
Nice physics models	Bioinformatics, elastic rod, charged rod, helix-coil	Secondary structure, annealed branched, folding	Proteomics, random/designed heteropolymer, HP, funnels, ratchets, active brushes	Bilayers, liposomes, membranes	??? Someone has to start
Uses					
Molecule					

(from A. Y. Grosberg)

Architecture (molecular structure)



(from MIT Mater. Sci.)

Polymer properties depend on

Chemical composition of monomer

Stereochemical configuration and tacticity

Chemical homogeneity (homopolymer vs heteropolymer)

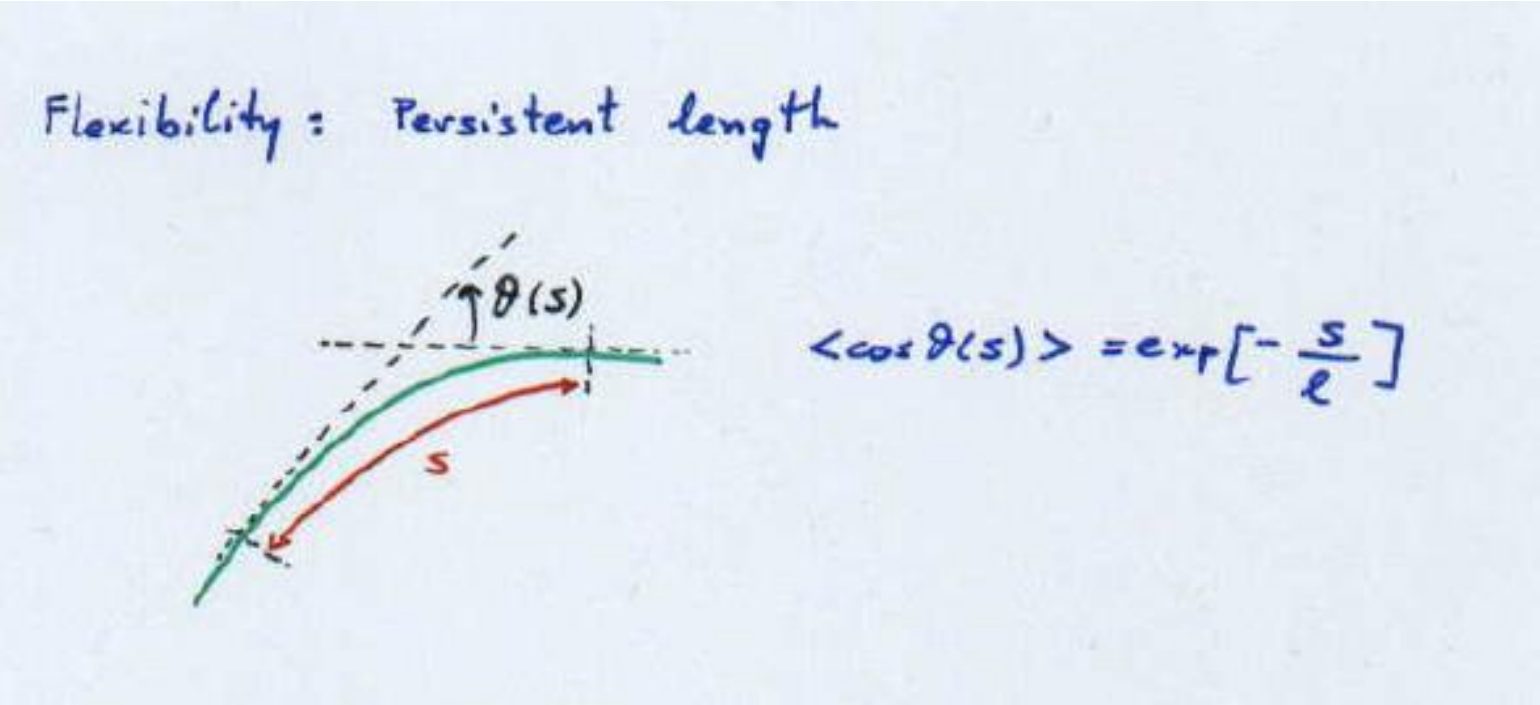
Degree of polymerization, N

Flexibility

Architecture

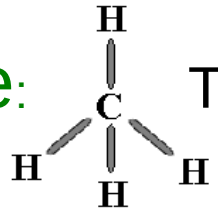
Presence of ionic groups (here: no associations)

A measure of (static) flexibility: persistence length

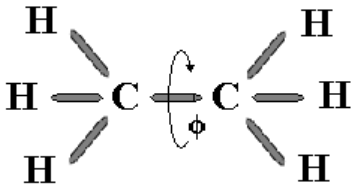


Note: what matters is the ratio l/L, with L the contour length
(e.g., DNA is semiflexible)
Indirect link to ability of chain to entangle

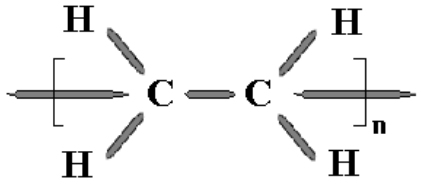
Dynamic flexibility and glass transition temperature Tg

Methane: 

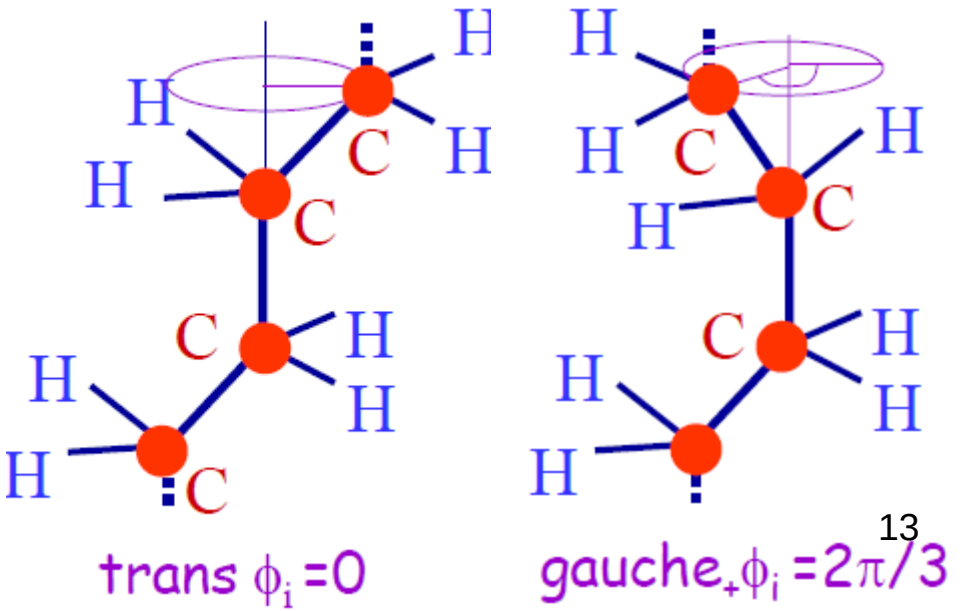
Typical fluctuations 3% in r_{C-H} and 3° in angle HCH

Ethane: 

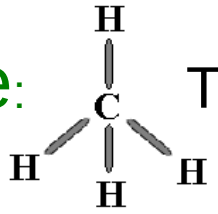
Free rotation around C-C: 3 conformations

Polyethylene: 

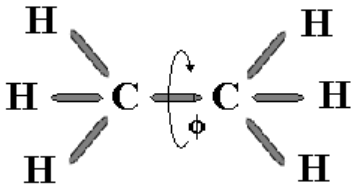
3^n possible conformations ($n \sim 10^3$)



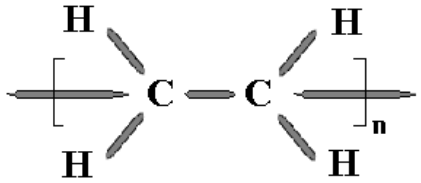
Dynamic flexibility and glass transition temperature Tg

Methane: 

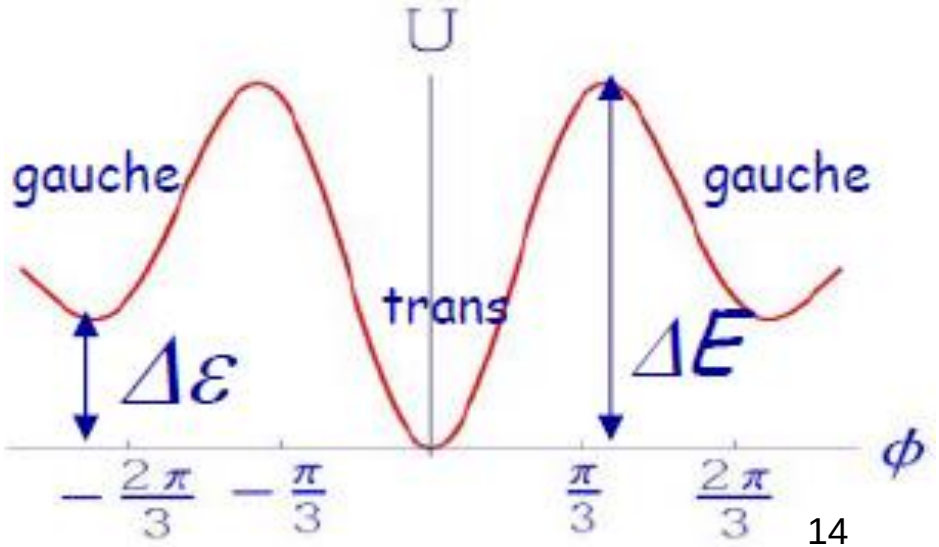
Typical fluctuations 3% in r_{C-H} and 3° in angle HCH

Ethane: 

Free rotation around C-C: 3 conformations

Polyethylene: 

3^n possible conformations ($n \sim 10^3$)



Δε: Static flexibility (PE, DNA)
(persistence length)

ΔE: Dynamic flexibility
(structure in motion - T_g)

Molar mass $M_N = M_{mon} N$

number-average M_n

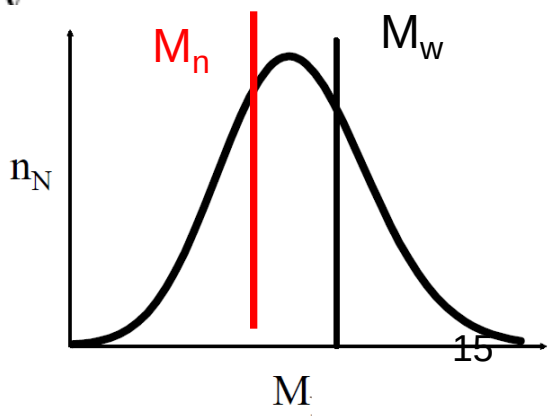
weight-average M_w

$$w_N = \frac{n_N M_N}{\sum_N n_N M_N} \qquad w_N = \frac{c_N}{c}$$

$$M_n = \sum_N n_N M_N = \frac{1}{\sum_N \frac{w_N}{M_N}}$$

$$M_w = \frac{\sum_N n_N {M_N}^2}{M_n} = \sum_N w_N M_N = \sum_N \frac{c_N}{c} M_N$$

$$PD = \frac{M_w}{M_n}$$



Molecular Weight

You have:

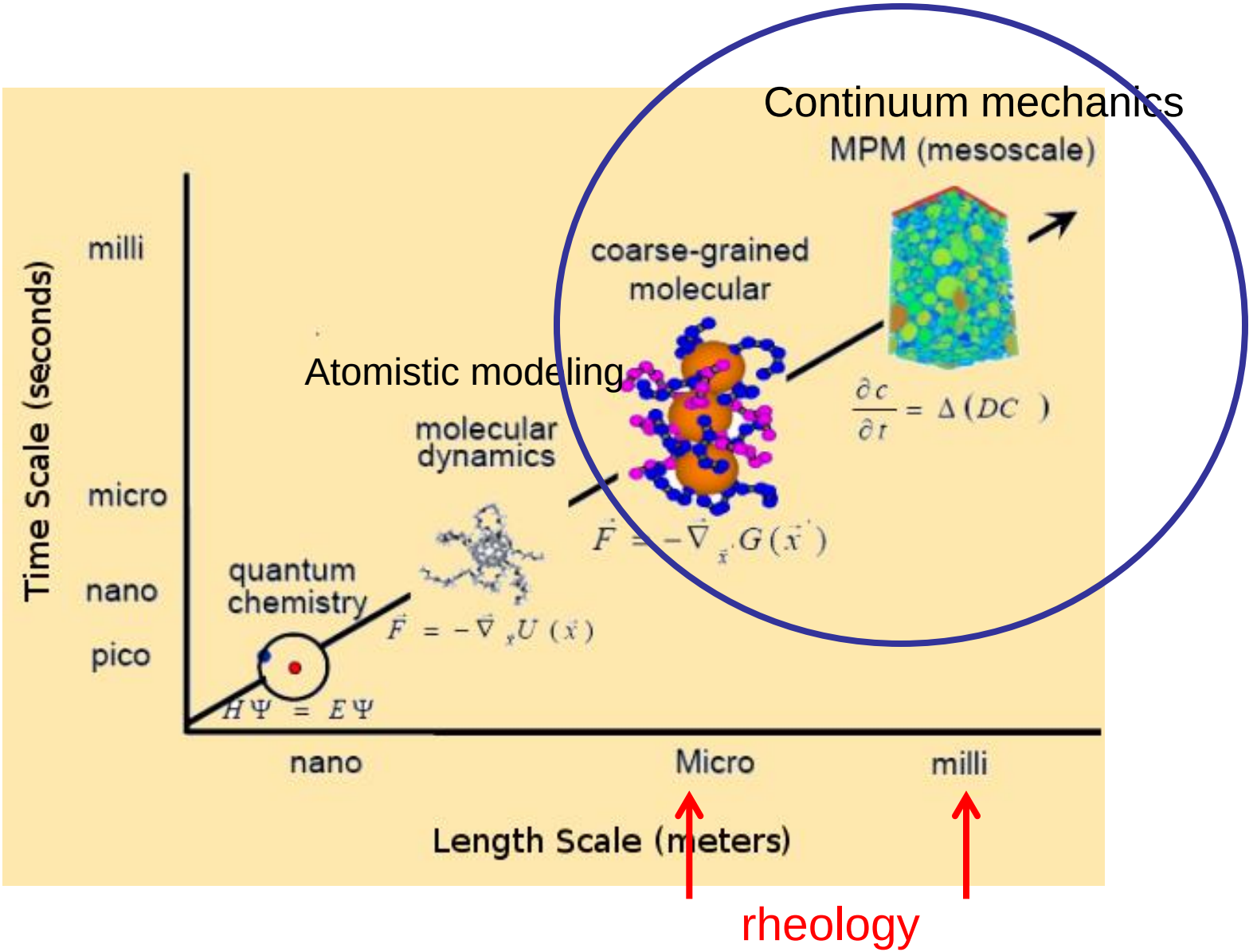
100 cherries at 9 g (each)

6 bananas at 180 g

4 watermelons at 1.2 kg

What is the average weight of a piece of fruit?

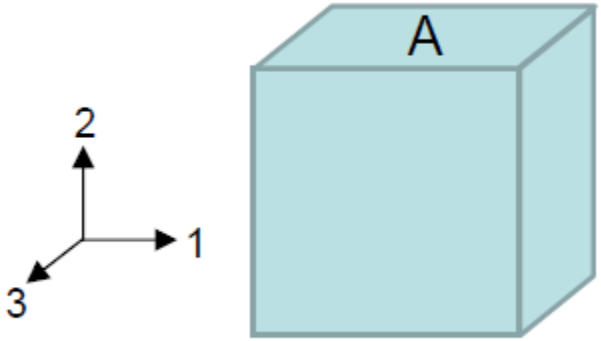
Description polymers: Coarse graining and the importance of the length scales

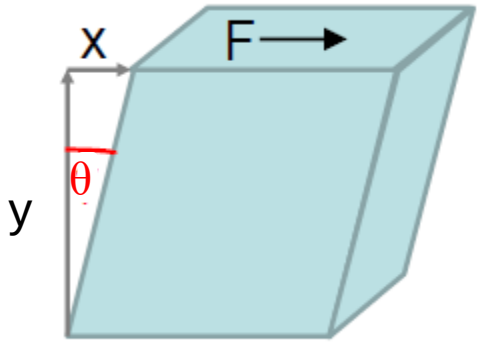


Mesoscopic world ⟶ interpretation measurement

Elementary continuum definitions:

Shear





shear stress

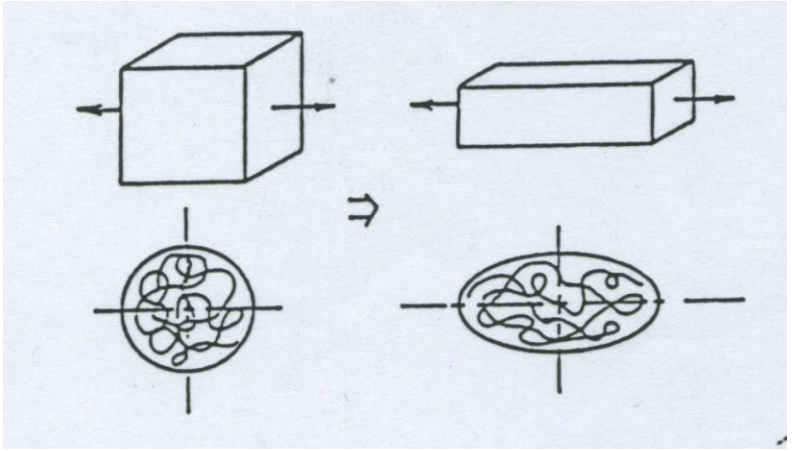
$$\sigma_{21} = \frac{F_1}{A_2} = \sigma_{12}$$

shear deformation
strain

$$\gamma = \frac{x}{y} = \tan\theta$$

shear rate
rate of strain

$$\dot{\gamma} \equiv \frac{d\gamma}{dt} = \frac{d}{dt}\left(\frac{dx}{dy}\right) = \frac{du}{dy}$$



Extension

$$v_x = -\frac{1}{2}\dot{\varepsilon}(1+b)x \quad \text{(with } 0 \le b \le 1\text{)}$$

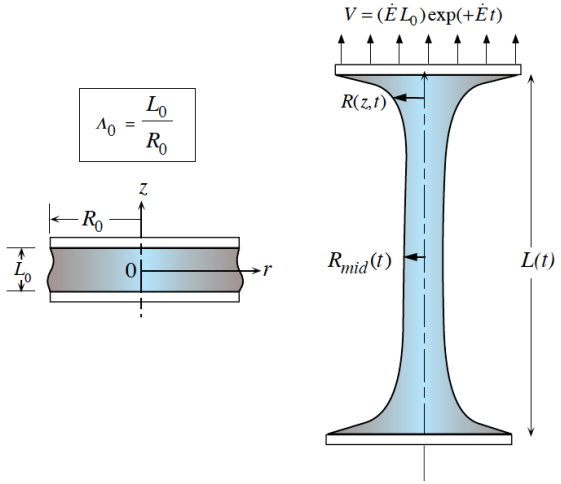
$$v_y = -\frac{1}{2}\dot{\varepsilon}(1+b)y$$

$$v_z = \dot{\varepsilon} z \quad \text{(Elongation rate)}$$

If b=0, constant rate (uniaxial elongation):

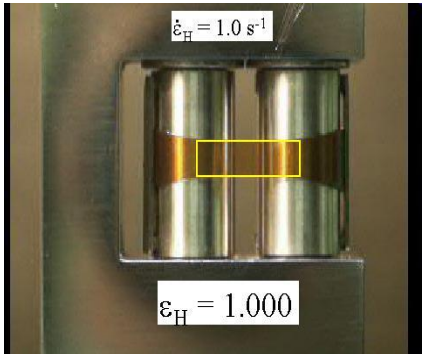
$$v_x = \frac{\partial x}{\partial t} = \frac{-1}{2}\dot{\varepsilon}x \Rightarrow x(t_2) = x(t_1)\exp\left(-\frac{\dot{\varepsilon}(t_2 - t_1)}{2}\right)$$

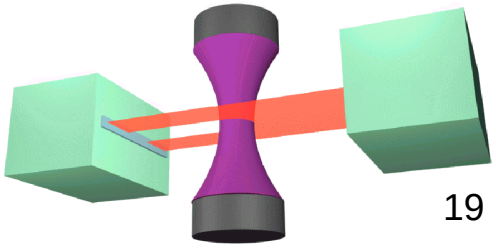
$$v_z = \dot{\varepsilon} z \Rightarrow z(t_2) = z(t_1)\exp\left(\dot{\varepsilon}(t_2 - t_1)\right)$$



[Henky strain](#)

$$\Rightarrow l(t) = l(t_0)\exp\left(\dot{\varepsilon}(\Delta t)\right)$$

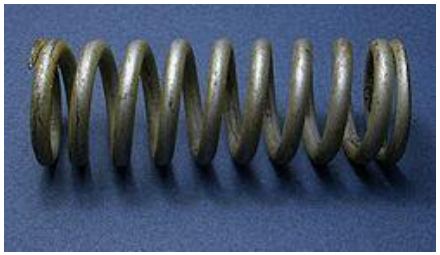




Elastic solids: constant modulus

Hooke

$$\sigma = G\gamma$$

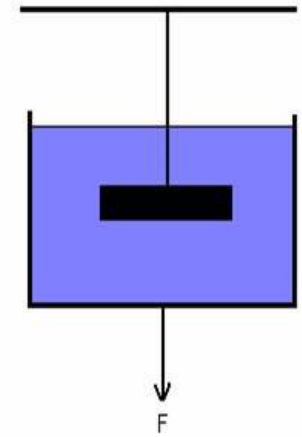


Newtonian fluids: constant viscosity

Newton

$$\eta \equiv \frac{\sigma}{\dot{\gamma}}$$

$\dot{\gamma}$: deformation rate



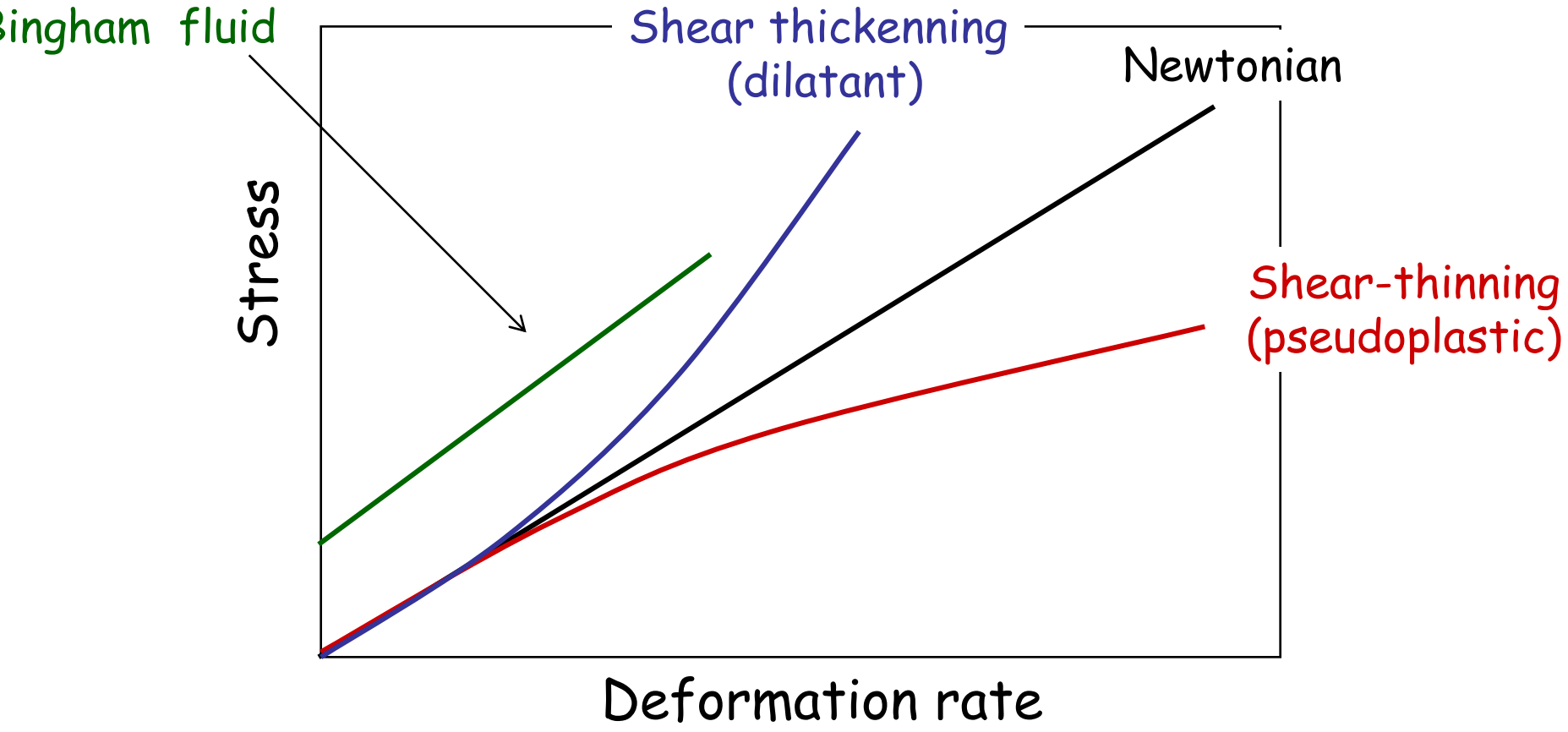
Non-Newtonian fluids:

$$\sigma = \eta(t, \dot{\gamma})\dot{\gamma}$$

Is it a solid or a liquid ?

Classify fluids from stress curve

$$\sigma = \eta\dot{\gamma} + \sigma_y$$ Yield stress



PROCESSING

stress ⟷ Deformation rate

Constitutive model (continuum, mesoscopic-molecular)

For incompressible, isothermal flow:

Momentum: $$\nabla \cdot \left\{ -p\boldsymbol{\delta} + 2\eta_s \mathbf{D} + \boldsymbol{\sigma}_p \right\} = 0$$

Mass: $$\nabla \cdot \boldsymbol{\upsilon} = 0$$

Constitutive equation: $$\frac{D\sigma_p}{Dt} = f\left(\sigma_p, \nabla \boldsymbol{\upsilon}\right)$$

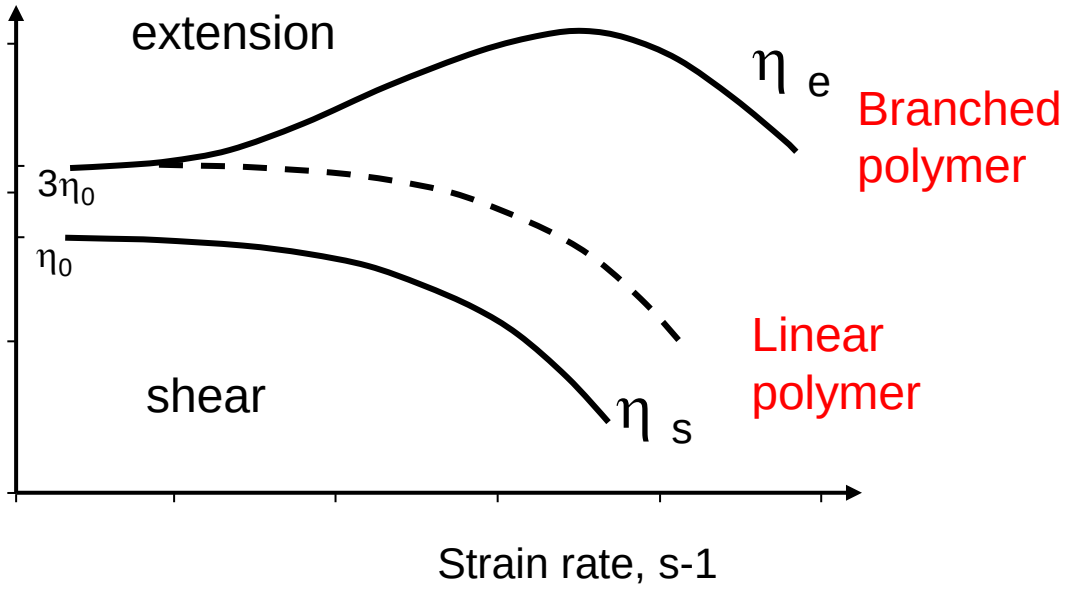
$$\sigma_p = \int_{-\infty}^{t} m(t - t')S_t(t')dt'$$

An example of polymer processing: blow molding

An example of polymer processing: blow molding

An example of polymer processing: blow molding

An example of polymer processing: blow molding

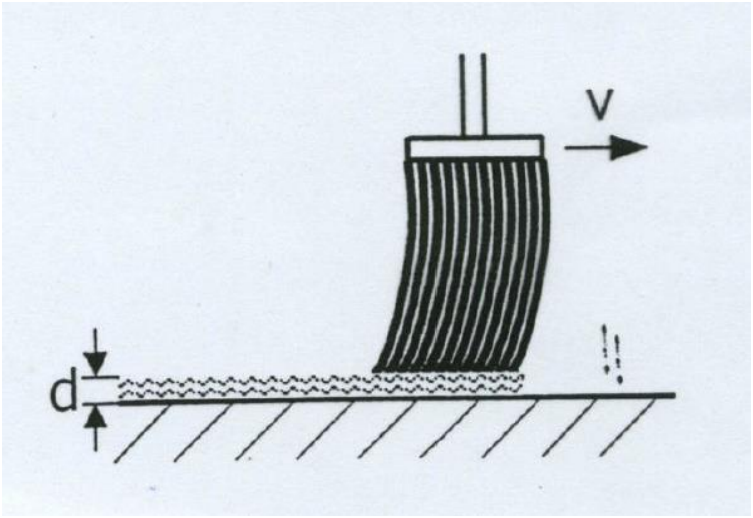


Challenge:
molecular origin of viscoelasticity, shear thinning, extension hardening

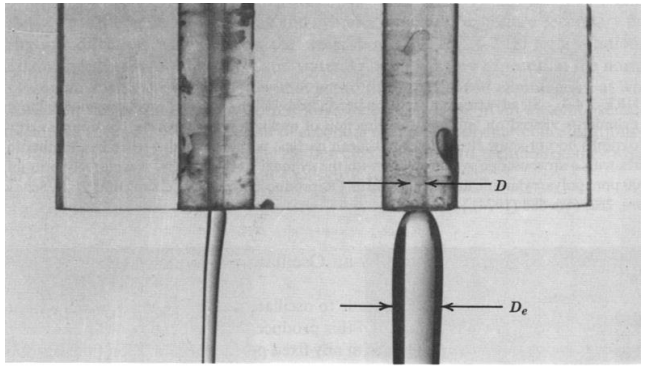
Note:
thickening and thinning characterize the response of associating polymers

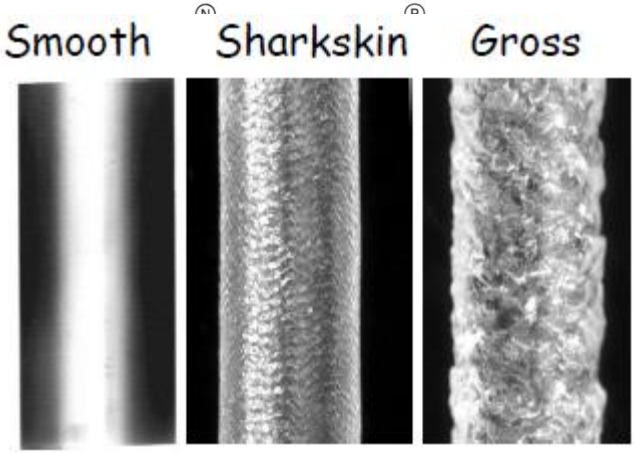
Question:

How can we rationalize a shear rate of 10^3 s^{-1}?

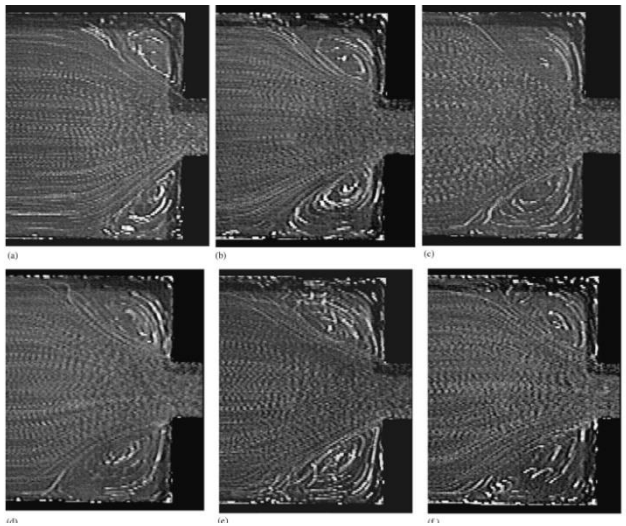


Extrudate swell & wall slip

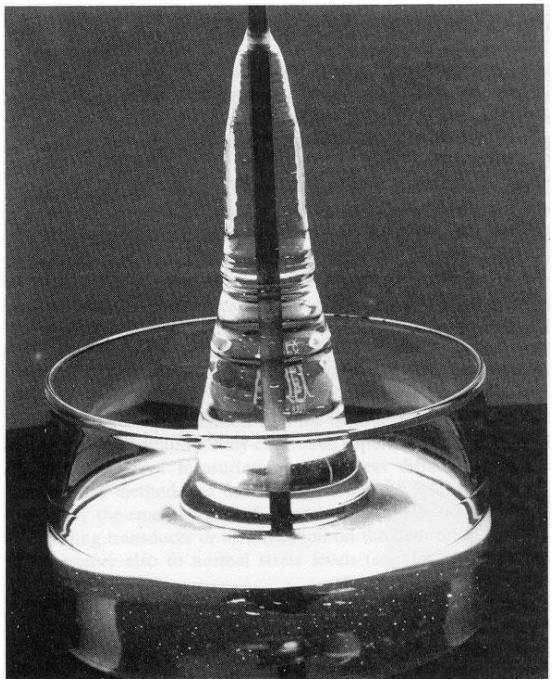




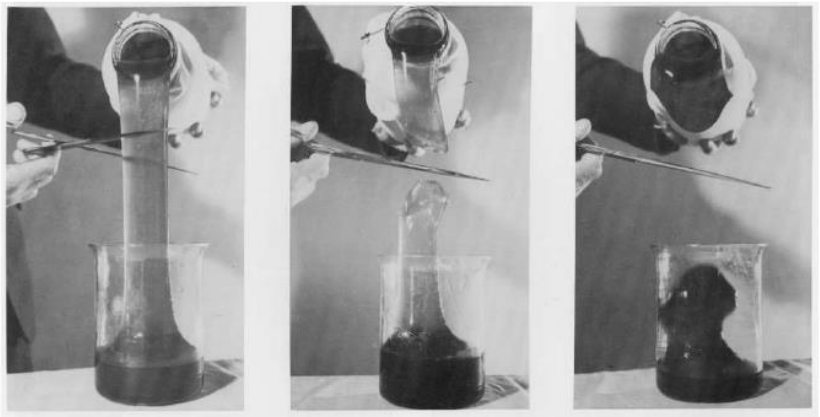
Secondary flows (vortex)



Rod climbing (Weissenberg)



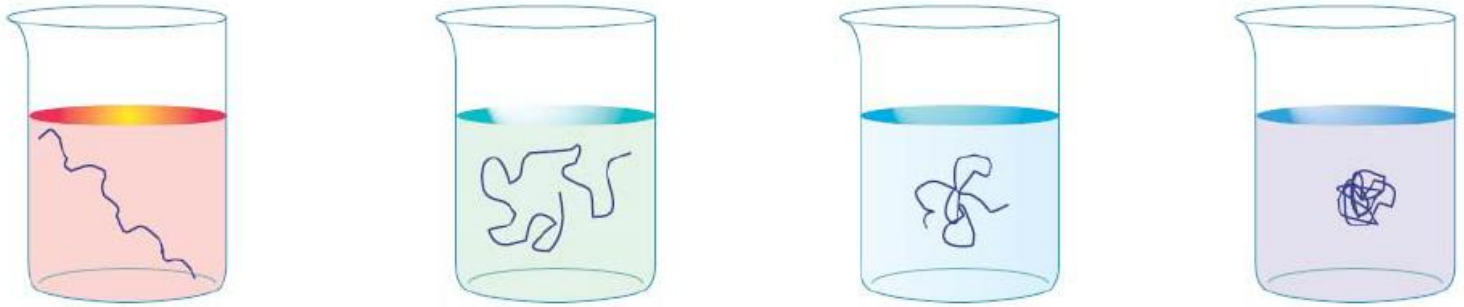
Recoil (memory)



Drag Reduction

Fig. 1.3. Enhancement of fire-hose range by addition of small amounts of polyethylene oxide to water. (Photograph, courtesy of Union Carbide Corporation.)

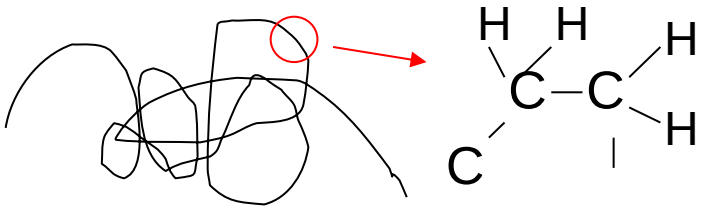
What is the size of a polymer?



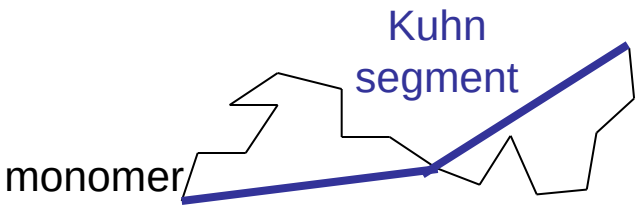
Environment matters

Can a polymer bent ? (flexible vs stiff)

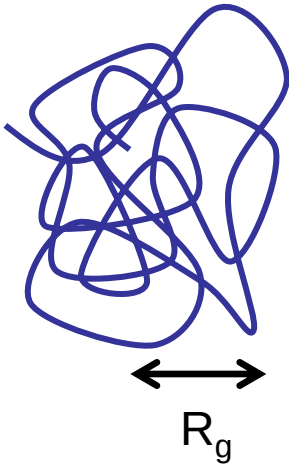
Ideal chain (Kuhn model)



Example: polyethylene $(CH_2)_n$

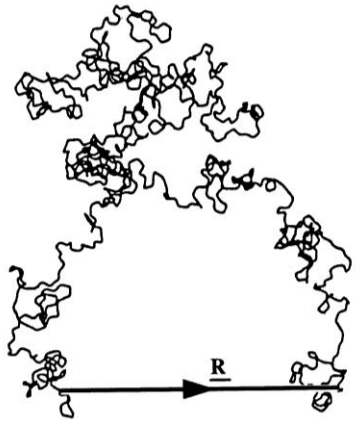


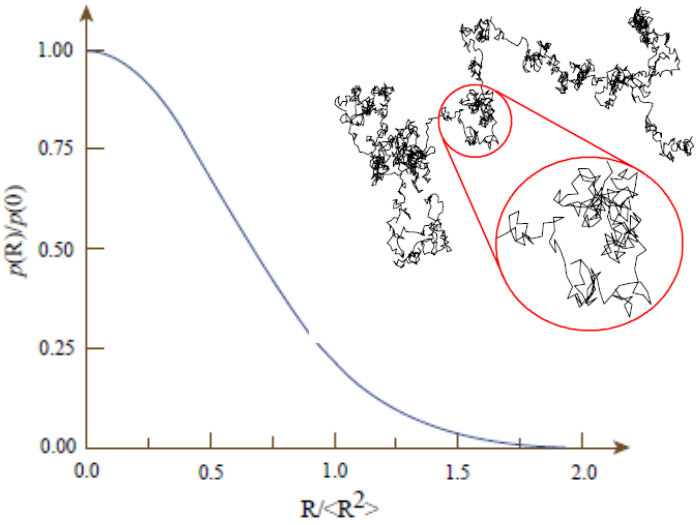
$$\left\langle \left| \underline{R} \right|^2 \right\rangle = R^2 = Nb^2$$



Random walk statistics (same step R)

$$P(\underline{R}_0 = \underline{R}) \propto \exp\left(\frac{-3\left|\underline{R}\right|^2}{2Nb^2} \right)$$





Compare:

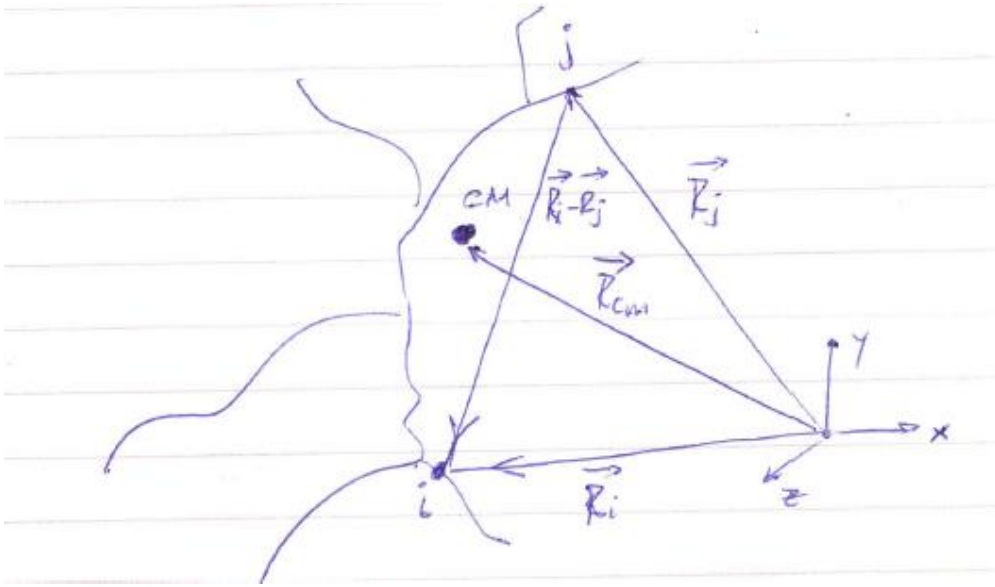
$V=Nb^3$ vs. $V=R^3=N^{3/2}b^3$

Polymers are fractal objects (here for ideal chain, $d_f=2$).

Radius of gyration

(also for nonlinear polymers)

$$R_g^2 \equiv \frac{1}{N}\sum_{i=1}^{N}\left(\vec{R}_i - \vec{R}_{CM}\right)^2$$



$$< R_g^2 >= \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N} < (R_i - R_j)^2 >$$

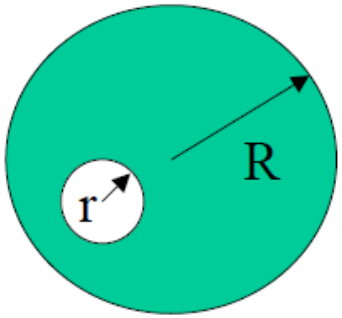
Ideal

$$< R_g^2 >= \frac{1}{N^2}\int_0^N \int_u^N < (R(u) - R(v))^2 > dvdu = Nb^2/6$$

$$< R_g^2 >= \frac{< R^2 >}{6}$$ Debye

Rod: L=Nb $<R_g^2>=L^2/12$

Polymeric fractals and self-similarity

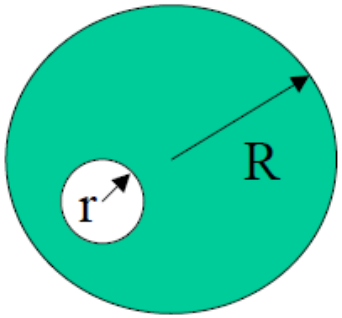


3-dimensional ball

$$m \sim r^3 \qquad m \sim r^{\mathcal{D}}$$

$$N \sim \langle R^2 \rangle$$

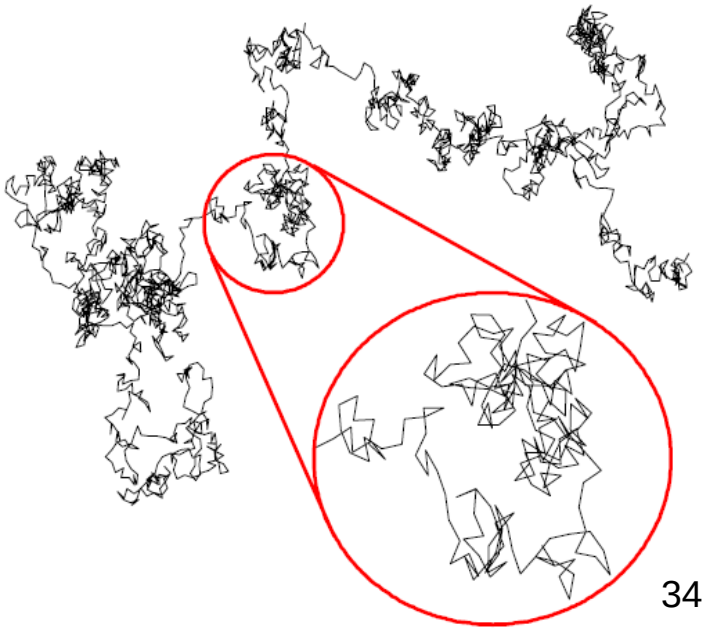
Polymeric fractals and self-similarity



3-dimensional ball

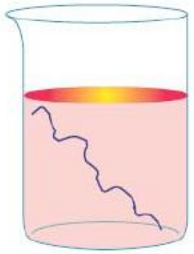
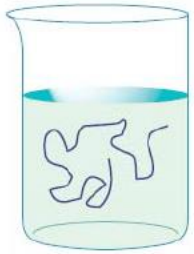
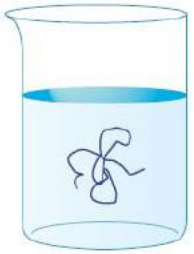
$$m \sim r^3 \qquad m \sim r^{\mathcal{D}}$$

$$N \sim \langle R^2 \rangle$$



Consider b~0.1 nm, N~10^3

Dramatic variation of polymer size

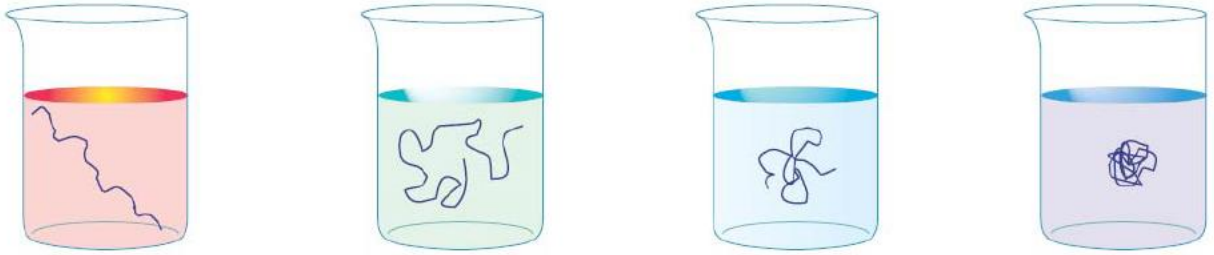
long-range repulsion	good	theta	poor
			
$R \simeq L \simeq bN$	$R \simeq bN^{3/5}$	$R \simeq bN^{1/2}$	$R \simeq bN^{1/3}$

Flexibility is important (bending)

Consider b~0.1 nm, N~10^3

Dramatic variation of polymer size

long-range repulsion | good | theta | poor



$R \simeq L \simeq bN$ | $R \simeq bN^{3/5}$ | $R \simeq bN^{1/2}$ | $R \simeq bN^{1/3}$

$$v = -\int f(\vec{r})\, d^3r = \int (1 - \exp[-U(r)/(kT)])\, d^3r$$

good: v>0 ; theta: v=0 ; poor? v<0

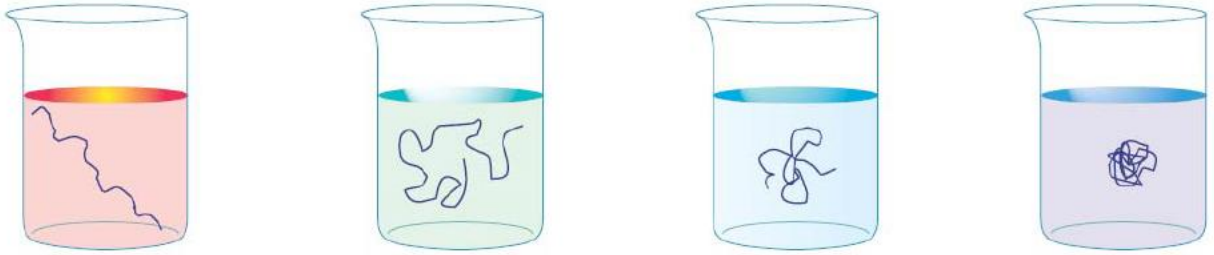
$v_{max}=b^3$ non-solvent: $v_{min}=-b^3$

Flexibility is important (bending)

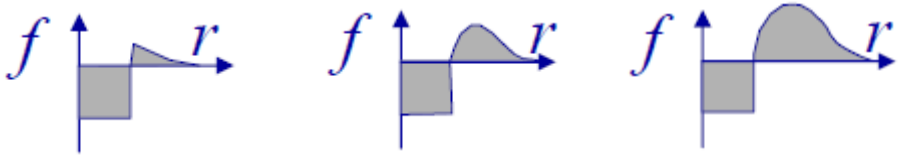
Consider b~0.1 nm, N~10^3

Dramatic variation of polymer size

long-range repulsion | good | theta | poor



$R \simeq L \simeq bN$ | $R \simeq bN^{3/5}$ | $R \simeq bN^{1/2}$ | $R \simeq bN^{1/3}$



good: v>0 ; theta: v=0 ; poor? v<0

$v_{max}=b^3$ non-solvent: $v_{min}=-b^3$

Flexibility is important (bending)

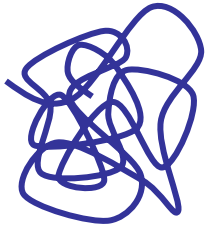
Questions:

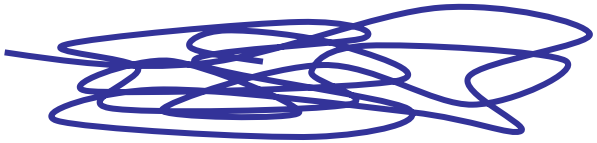
How many characteristic lengths exist in a polymer?

In how many ways could we alter the size of a polymer chain?

In the above example (b~0.1 nm, N~10^3), estimate the size variation of a polymer

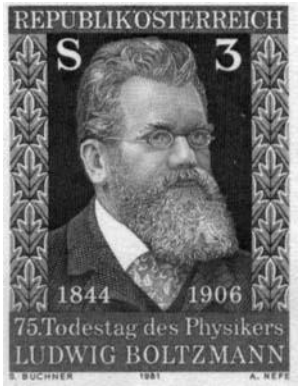
Chain elasticity:





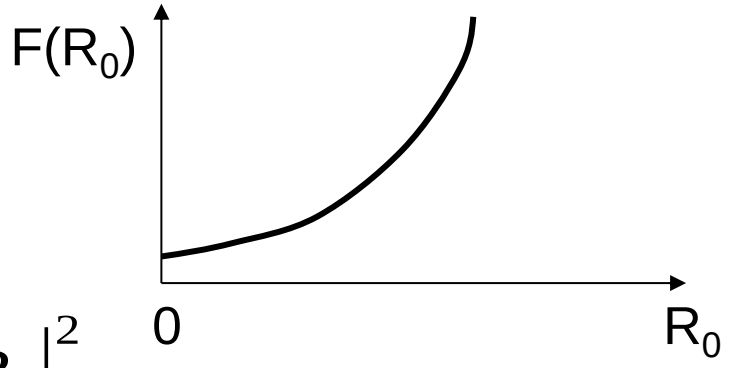
Free energy: $\Delta F = \Delta U - T\Delta S = -T\Delta S$

0 (ideal polymer)



Boltzmann:

$S = k \ln P$



$$\frac{F(\underline{R_0})}{kT} = const. + \frac{3}{2Nb^2}\left|\underline{R_0}\right|^2$$

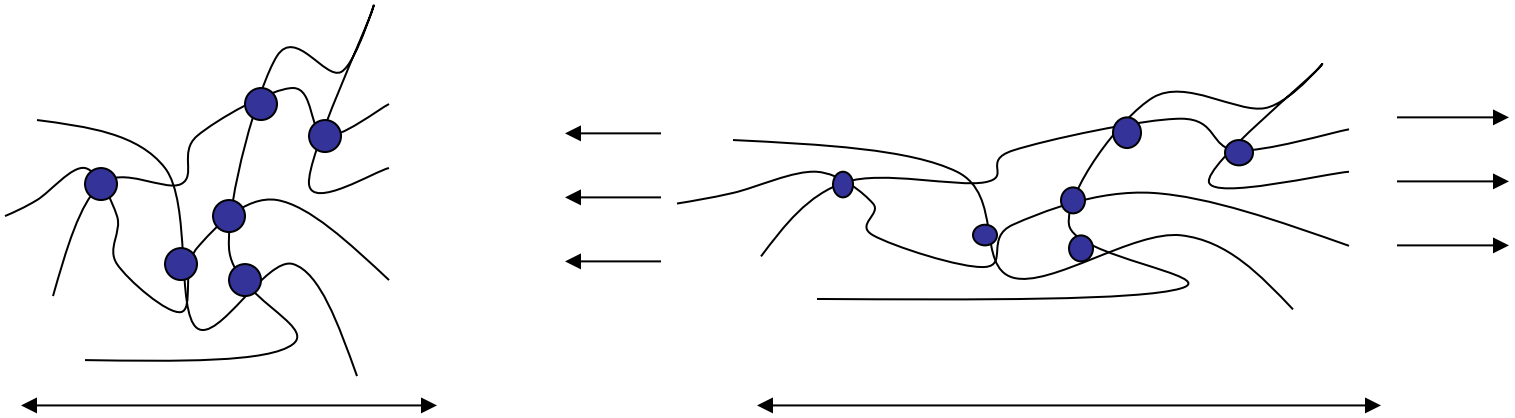
$$f = \frac{\Delta F}{\Delta R} \quad \Rightarrow \quad \sigma = \frac{3kT}{Nb^2}R$$

$$G = \frac{3kT}{Nb^2}$$

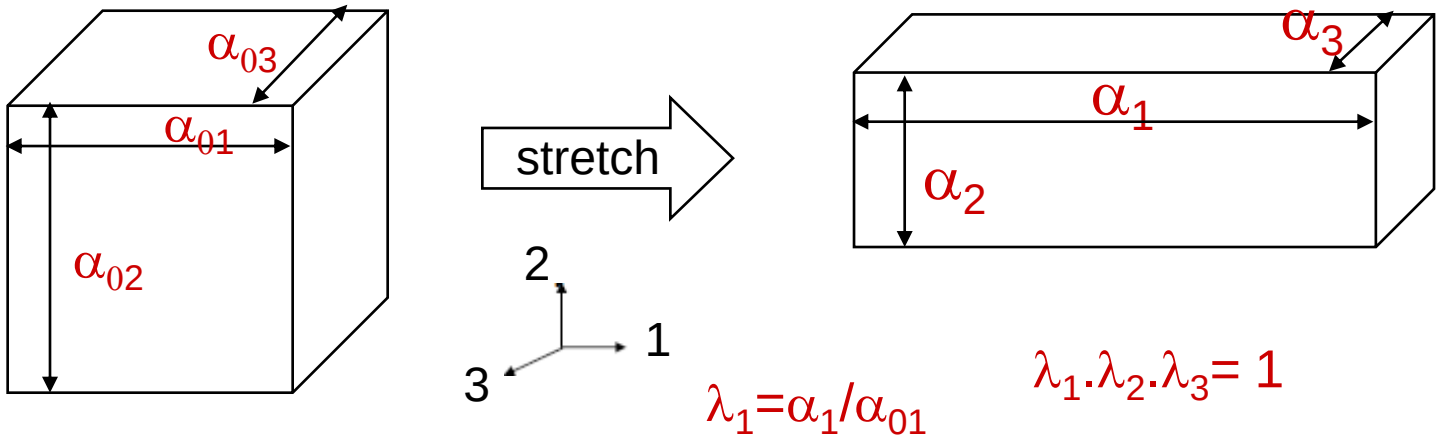
Force associated with change of conformation (thermodynamics)
Extracted from free energy, also from Hooke's law

Entropy elasticity

Rubber elasticity (main chains, crosslinked):



$< R_0^2 >^{1/2}$ $< R^2 >^{1/2}$



$\lambda_1 = \alpha_1 / \alpha_{01}$ $\lambda_1 . \lambda_2 . \lambda_3 = 1$

Use Flory's conjecture (ideal chain statistics in melt)

Green, Tobolsky J. Chem. Phys. 1946

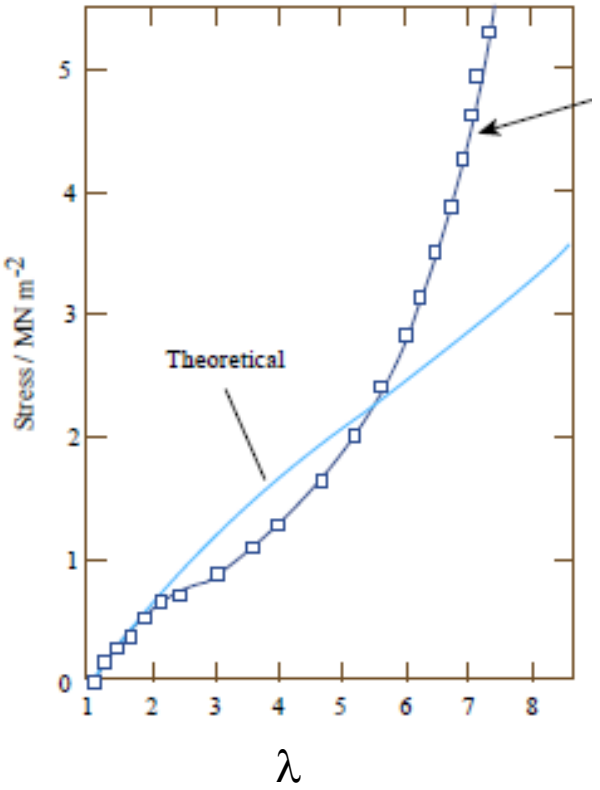
Rubber elasticity (many chains, crosslinked):

$$\sigma = 3kT\nu\frac{\Delta l}{l}$$

ν = number concentration of elastically active elements

$$\sigma_{11} = \frac{\rho N_A kT}{M_x}\left(\lambda_1 - \frac{1}{\lambda_1^{\,2}}\right)$$

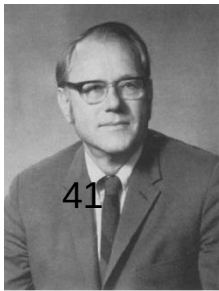
σ



$$G \approx \nu kT \qquad \nu \sim 1/\xi^3$$

$$G \approx \frac{kT}{\xi^3}$$

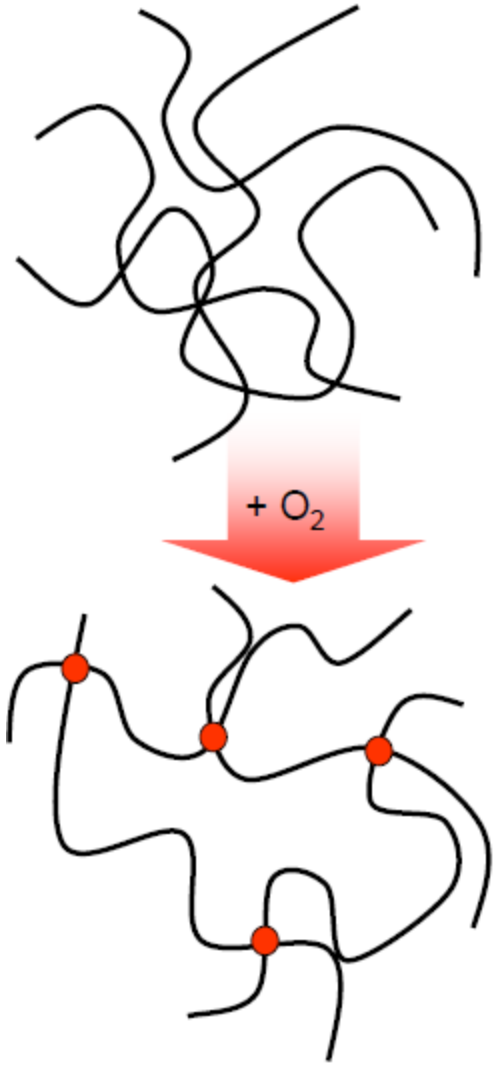
Relates modulus to size



Green, Tobolsky J. Chem. Phys. 1946
Ferry, Viscoelastic properties of polymers, 1980

Rubber (elastomer) Thermosetting polymers (chemical network)

$G \sim 10^6$ Pa



Indian ‘boot’
Amazon (~1600 bC)

Prehistoric Polymers: Rubber Processing in Ancient Mesoamerica

Dorothy Hosler,[1,2]* Sandra L. Burkett,[2] Michael J. Tarkanian[1,2]

Ancient Mesoamerican peoples harvested latex from *Castilla elastica*, processed it using liquid extracted from *Ipomoea alba* (a species of morning glory vine), and fashioned rubber balls, hollow rubber figurines, and other rubber artifacts from the resulting material. Chemical and mechanical analyses of the latex and of the processed rubber indicate that the enhanced elastic behavior of the rubber relative to the unprocessed latex is due to purification of the polymer component and to an increase in the strength and number of interchain interactions that are induced by organic compounds present in *I. alba*. These ancient peoples' control over the properties of latex and processed rubber gave rise to the Mesoamerican ball game, a central ritual element in all ancient Mesoamerican societies.

Ancient Mesoamerican peoples were processing rubber by 1600 B.C. (*1*), which predated

which contenders gambled for land, slaves other valuables.

18 JUNE 1999 VOL 284 SCIENCE

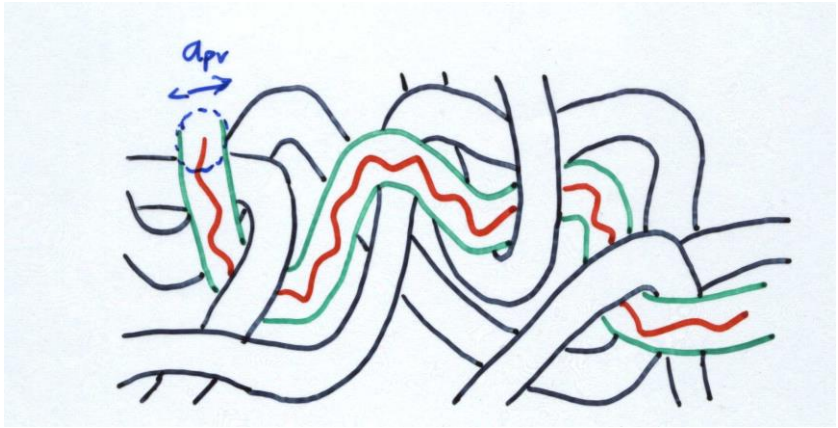
De Gennes,
Soft matter, hard science and the thrill of discovery, Spinger 1996

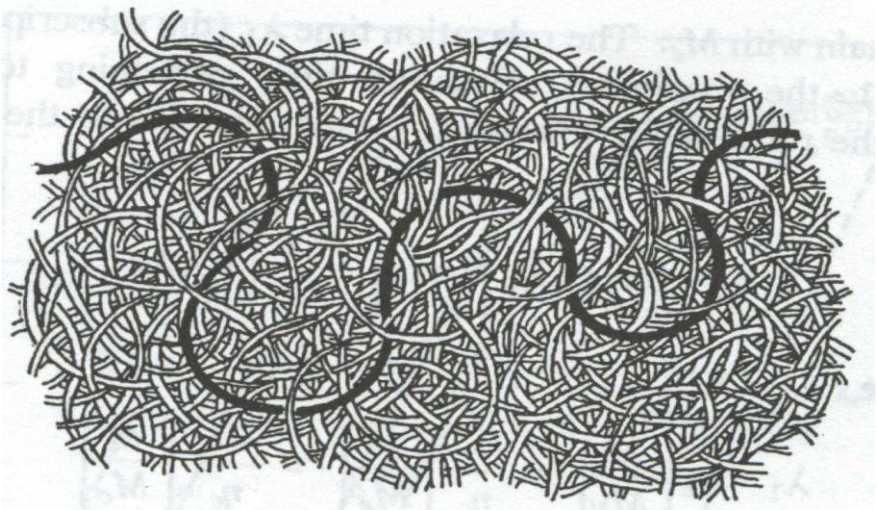
Equilibrium state in an entangled polymer melt: Plateau modulus and entanglement polymer weight

Apply Green-Tobolosky to a physical network (temporary junctions):

$$G = \nu kT$$

$$G_N^0 = \frac{\rho\ N_A\ kT}{M_e} = \frac{\rho\ R\ T}{M_e}$$





deGennes conjecture:
When chains overlap/entangle, the identity of a single chain is lost.
The network mesh size is the relevant parameter

de Gennes,
Scaling concepts in polymer physics 1979

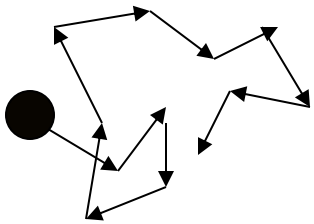
Question:

Why, for the same applied stress, a metal deforms far less than a polymer

Under a certain applied load (weight), a polymer chain (or network) deforms. We then increase the temperature. Is the (fractional) deformation going to change and how?

How do you expect the modulus to change in the presence of associations?

Simple analysis of motion: Diffusion of a small particle



Brownian motion

$$\left\langle \left[\vec{r}(t) - \vec{r}(0) \right]^2 \right\rangle = 6Dt$$

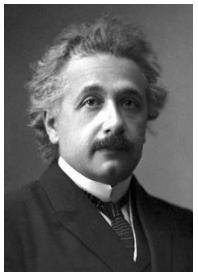
$$D = \frac{R^2}{\tau}$$

Friction coefficient:

$$\vec{F} = \zeta \vec{v}$$

$$\zeta = 6\pi\eta R$$

$$D = \frac{kT}{\zeta}$$



Stokes-Einstein-Sutherland

$$D = \frac{kT}{6\pi\eta R_h}$$

$$\tau = \frac{\eta R^3}{kT}$$

Determination of size

Linear viscoelasticity

Elastic element: $\sigma = G\gamma$

Viscous element: $\eta \equiv \frac{\sigma}{\dot{\gamma}}$

Viscoelastic element: $\sigma = \eta\dot{\gamma} = \eta\frac{\gamma}{\lambda} = G\gamma \Rightarrow \eta = G\lambda$

Key relation
in linear viscoelasticity

λ Characteristic relaxation time

Time dictates material behavior:

We can tune the state of a polymer (and hence modulus and time) with T

$T<T_g$ solid , glass [G~O(GPa)]

$T>T_g$ solid, rubber [G~O(MPa)]

$T >> T_g$ liquid [G~O(kPa)]

$$De = \frac{\tau}{t_{exp}}$$

$$Wi = \dot{\gamma}\tau$$

Alternatively, at a given temperature: very short time: glass ; very long time: liquid

This means that there is an interplay of the characteristic time of the material and the temperature:

principle of time-Temperature Superposition (tTS) - to be discussed below

Colloidal particles:

$$Pe = \dot{\gamma}\tau_0 = \frac{\dot{\gamma}R^2}{D_0} = \frac{6\pi\eta\dot{\gamma}R^3}{kT}$$

Questions:

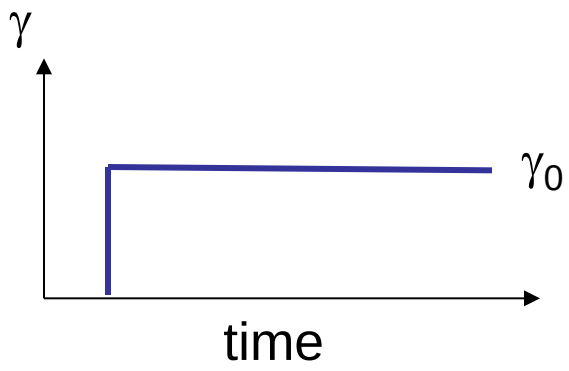
Which factors below affect the Me:
T, P, M, flexibility, concentration (solution), branching, microstructure?

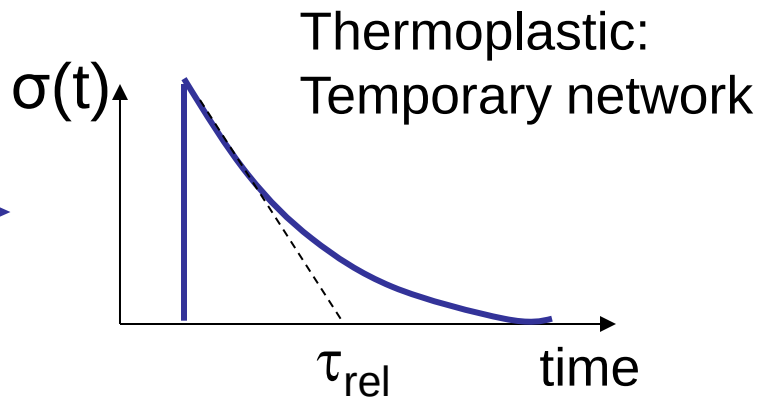
How can we probe / estimate characteristic length scales in polymers?

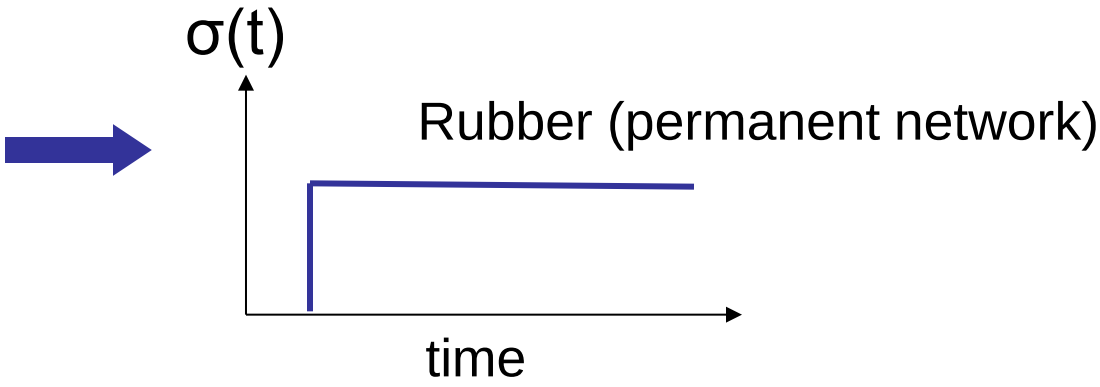
How many characteristic times exist in a polymer?

How is the time of a polymer altered?

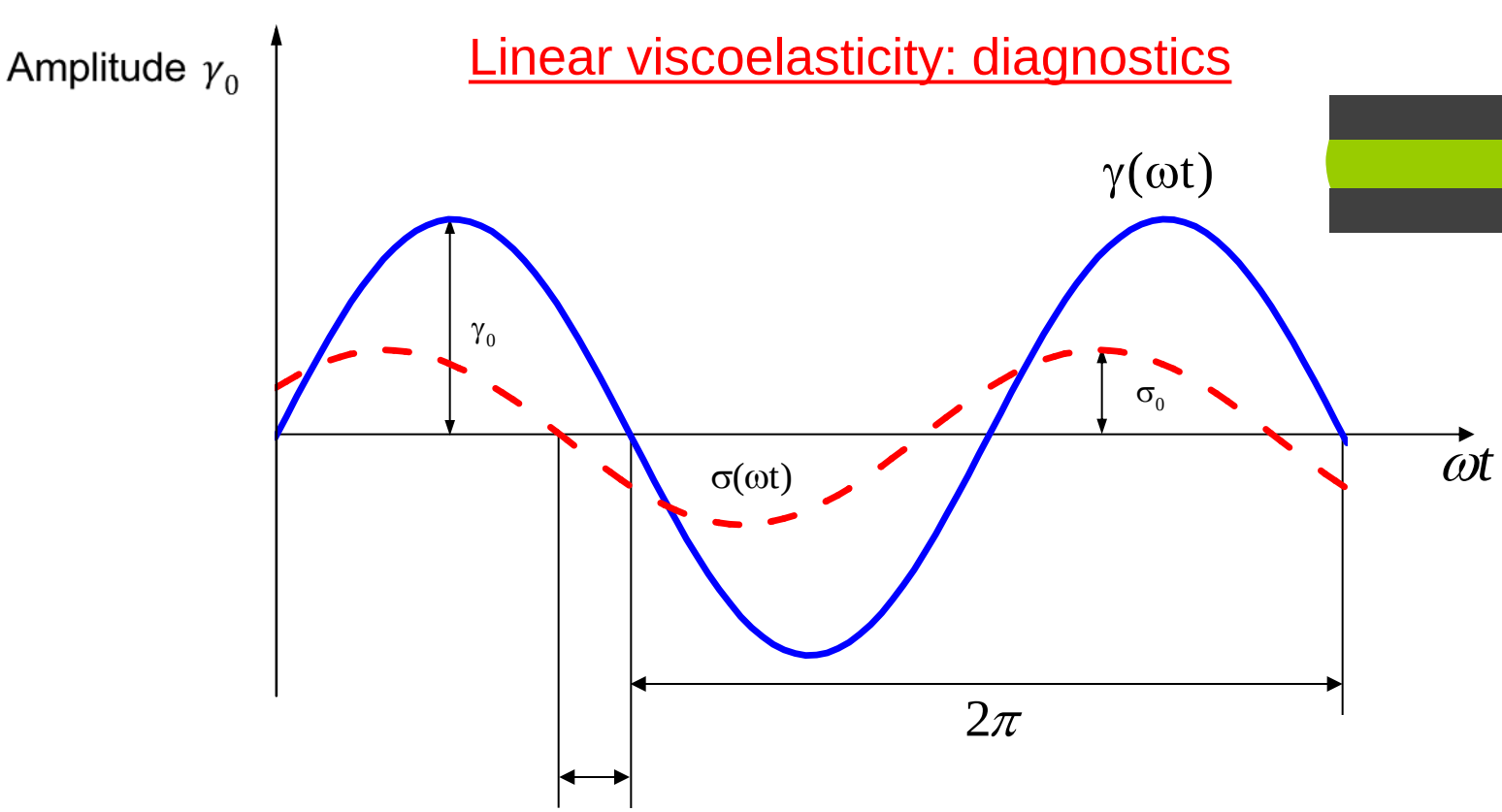
Relaxation modulus







Linear viscoelasticity: diagnostics



impose

$$\gamma(t) = \gamma_0 \cdot \sin(\omega t)$$

$$0 \le \delta \le \frac{\pi}{2}$$

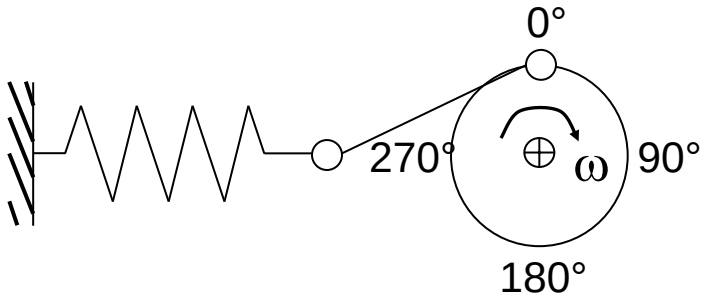
probe

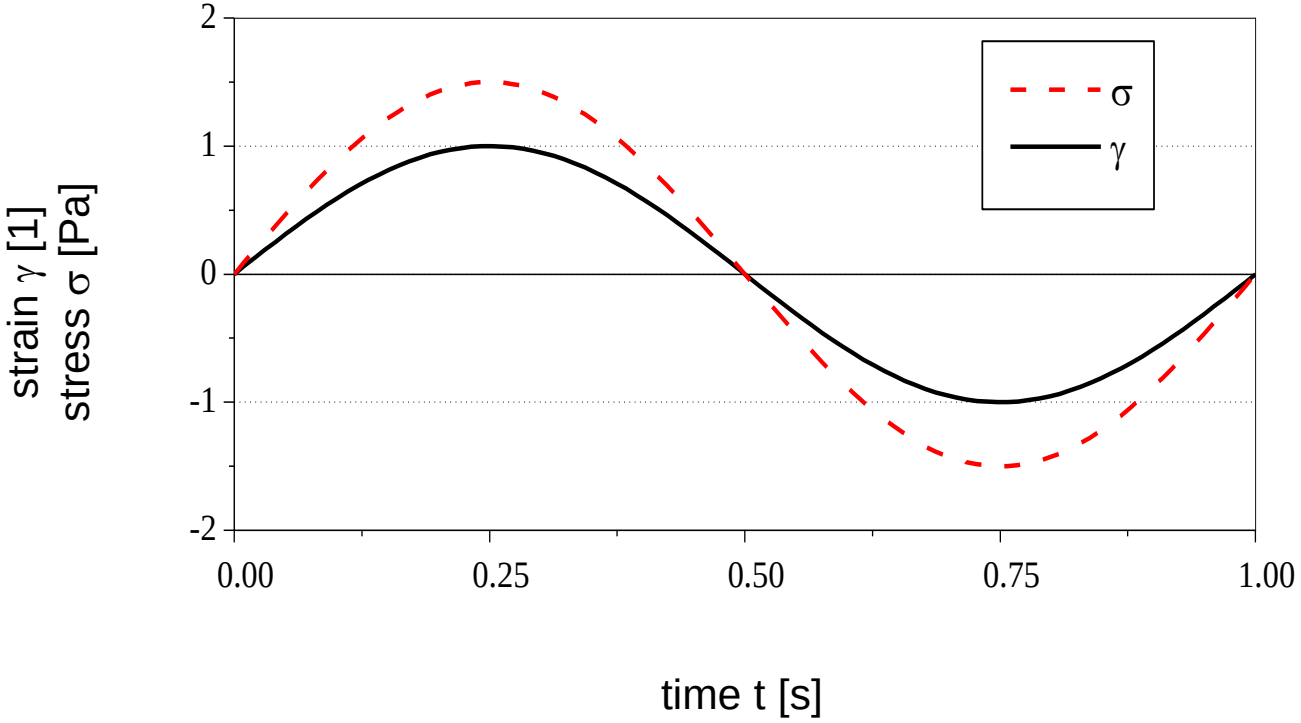
$$\sigma(t) = \sigma_0 \cdot \sin(\omega t + \delta) = \gamma_0 \cdot \overbrace{G'(\omega) \cdot \sin(\omega t)}^{\text{Elastic response}} + \gamma_0 \cdot \overbrace{G''(\omega) \cdot \cos(\omega t)}^{\text{Viscous response}}$$

Ideal elastic solid

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

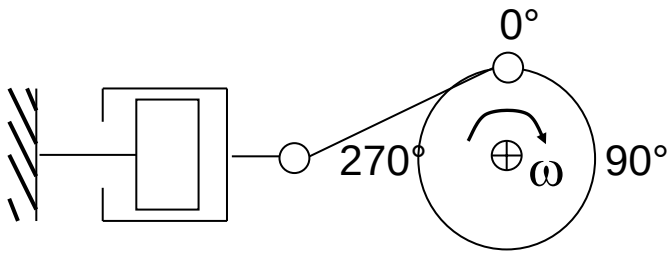
$$\sigma(t) = G \cdot \gamma(t) = G \cdot \gamma_0 \sin(\omega t)$$



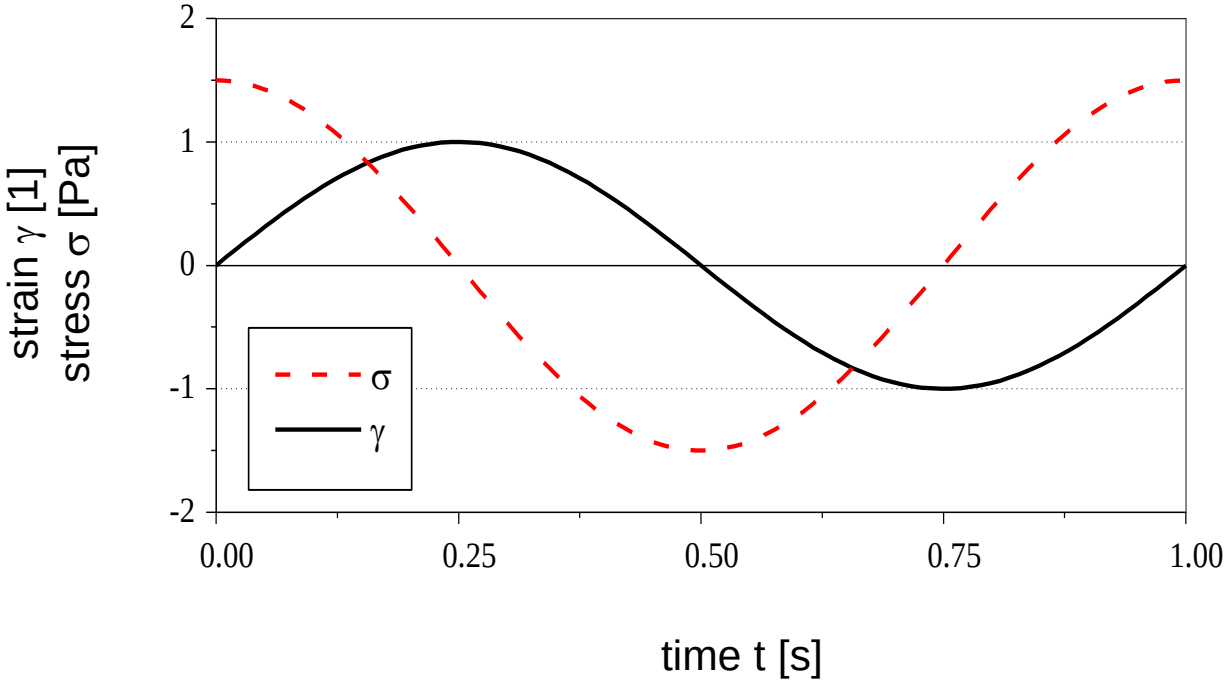


Ideal viscous liquid

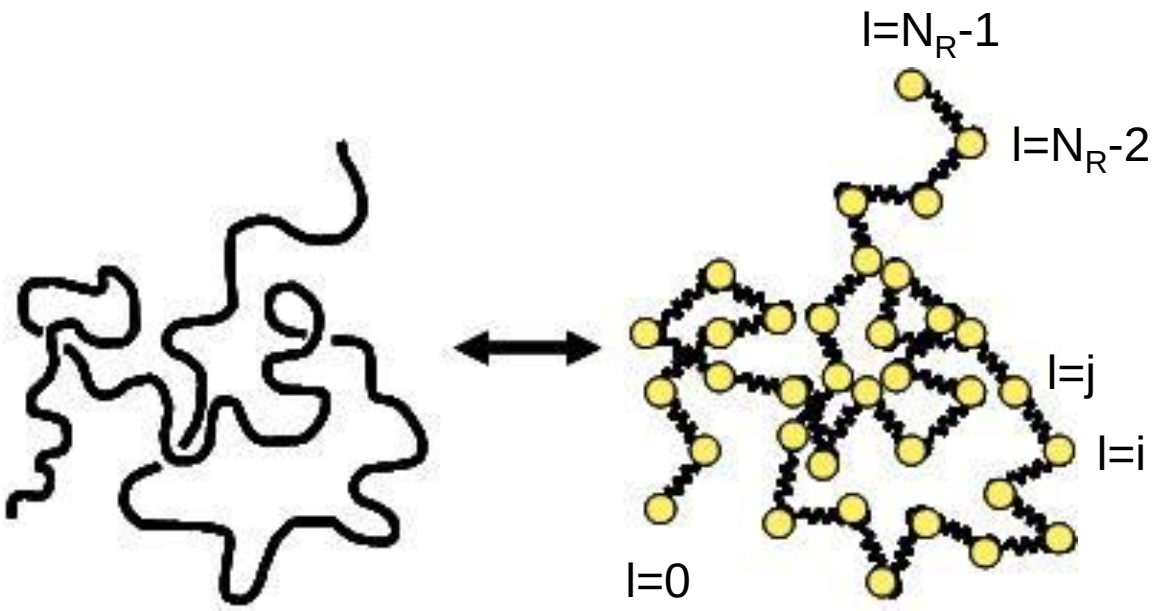
$$\gamma(t) = \gamma_0 \sin(\omega t)$$



$$\sigma(t) = \eta \cdot \dot{\gamma}(t) = \eta \cdot \gamma_0 \omega \cos(\omega t) = \eta \cdot \gamma_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right)$$



Coarse graining: Mesoscopic bead-spring models



Spring (constant k → G) : elastic element
Bead (friction ζ → η): viscous element

Each of the elements (bead-spring) of the chain satisfies at equilibrium:

$$\overrightarrow{f_{el}} = \overrightarrow{f_{fr}}$$

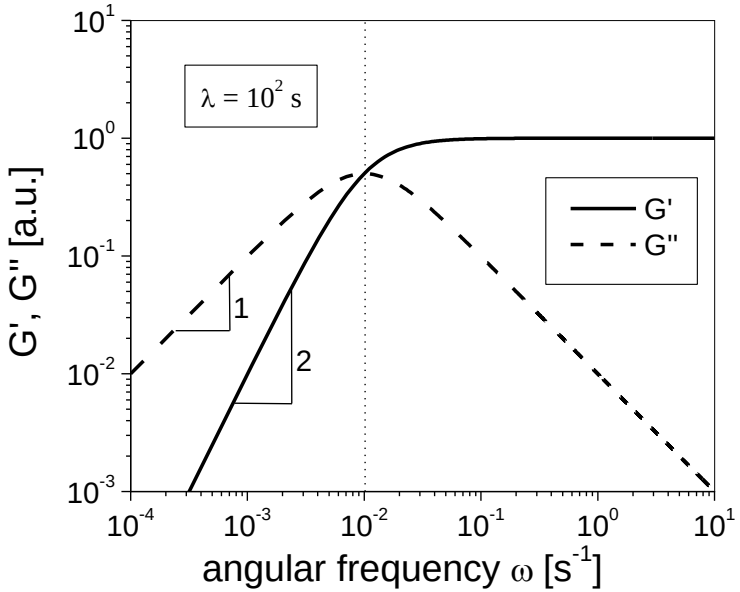
Simplest viscoelastic liquid: Maxwell element

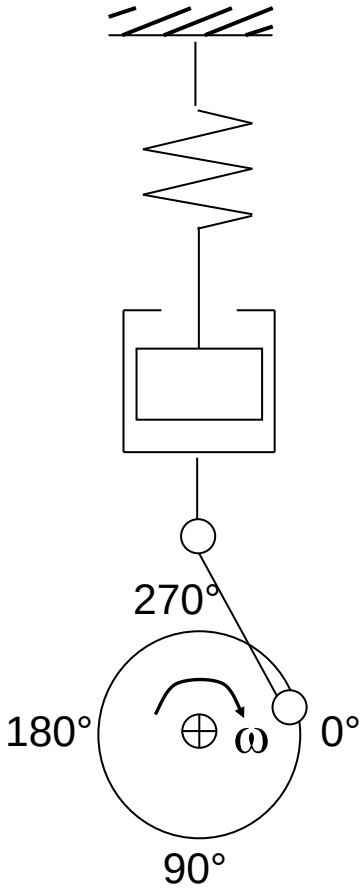
$$\sigma = \sigma_F = \sigma_D \qquad \gamma = \gamma_F + \gamma_D$$

$$\frac{d\gamma}{dt} = \frac{1}{G}\cdot\frac{d\sigma}{dt} + \frac{\sigma}{\eta} \qquad \gamma_0\omega\cos(\omega t) = \frac{1}{G}\cdot\frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$\sigma = \left[\frac{G\cdot\lambda^2\cdot\omega^2}{1+\lambda^2\cdot\omega^2}\right]\cdot\sin(\omega t) + \left[\frac{G\cdot\lambda\cdot\omega}{1+\lambda^2\cdot\omega^2}\right]\cdot\cos(\omega t)$$

$$\sigma = G'(G,\lambda,\omega)\cdot\sin(\omega t) + G''(G,\lambda,\omega)\cdot\cos(\omega t)$$



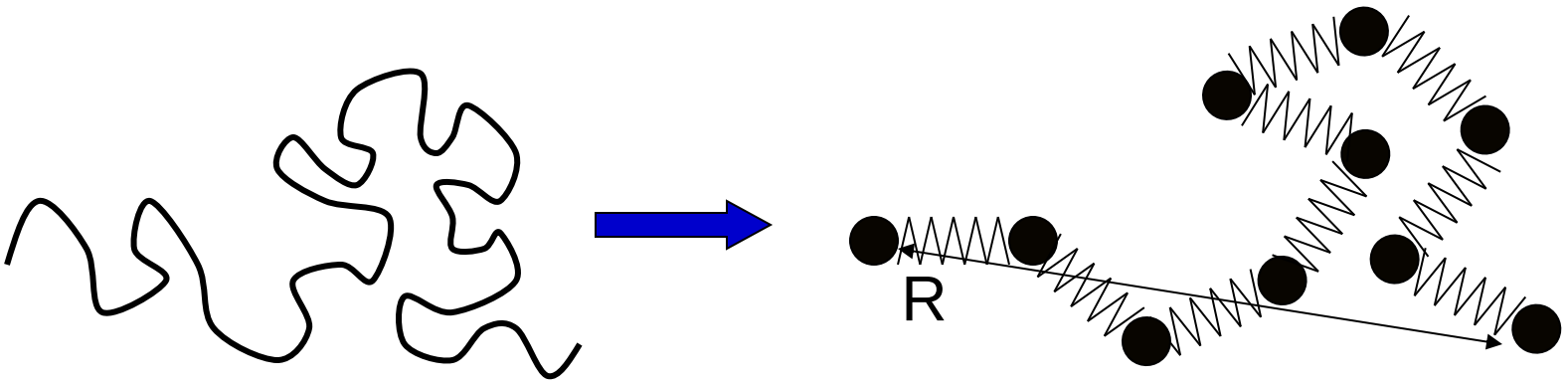


Importance of time (frequency):

Span time ←→ Span responding length scale

Spectroscopy

Rouse model for an unentangled polymer chain



N beads of length b

- Each bead has its own friction ζ
- Total friction: $\zeta_R = N\zeta \rightarrow D_R = \frac{kT}{N\zeta}$
- Rouse time: $\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2}{kT/N\zeta} = \frac{\zeta}{kT} NR^2$

$t < \tau_{Rouse}$: viscoelastic modes $t > \tau_{Rouse}$: diffusive motion

- Stokes law: $\zeta \approx \eta_s b$
- Kuhn monomer relaxation time: $\tau_0 \approx \frac{\zeta b^2}{kT} = \frac{\eta_s b^3}{kT} \rightarrow \tau_R \approx \tau_0 N^2$

(E. van Ruymbeke)

Rouse relaxation modes:

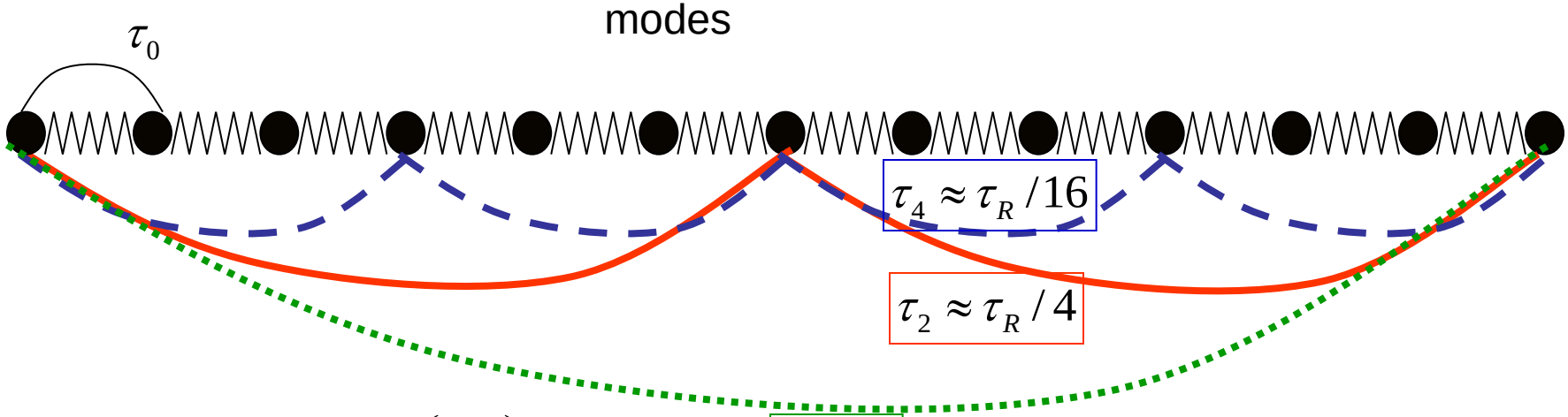
The longest relaxation time: $\tau_R \approx \tau_0 N^2$

For relaxing a chain section of N/p monomers:

$$\tau_p \approx \tau_0 \left(\frac{N}{p}\right)^2$$ (p = 1,2,3,…,N)

$\tau_1 \approx \tau_R$ $\tau_i < \tau_{i-1}$

N relaxation modes



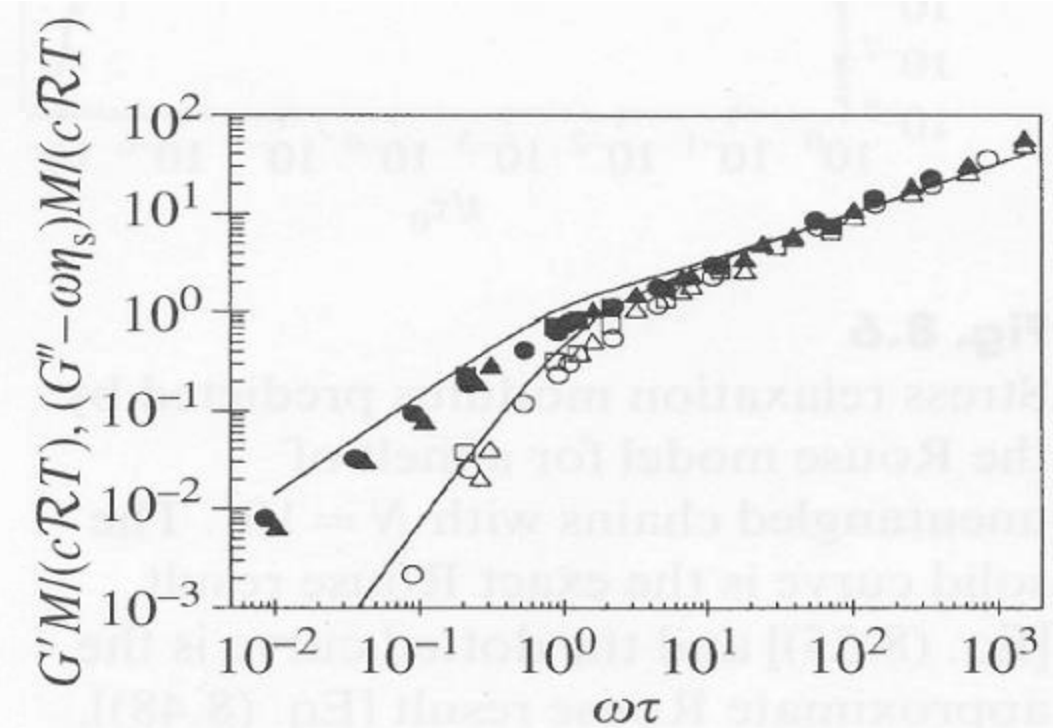
$$G(t) = \frac{kT}{Nb^3}\nu \sum_{p=1}^{N} \exp\left(\frac{-t}{\tau_p}\right)$$

$$\tau_p = \frac{\zeta b^2 N^2}{6\pi^2 kT p^2}$$

(E. van Ruymbeke)

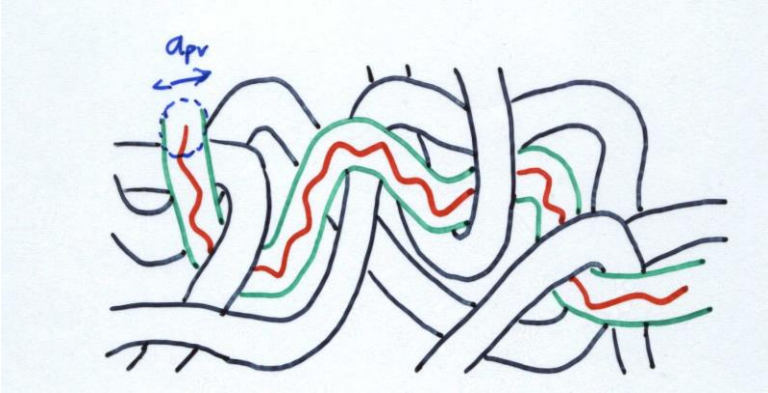
$$G'(\omega) \simeq G''(\omega) \sim \omega^{1/2}$$ For $1/\tau_R < \omega < 1/\tau_0$

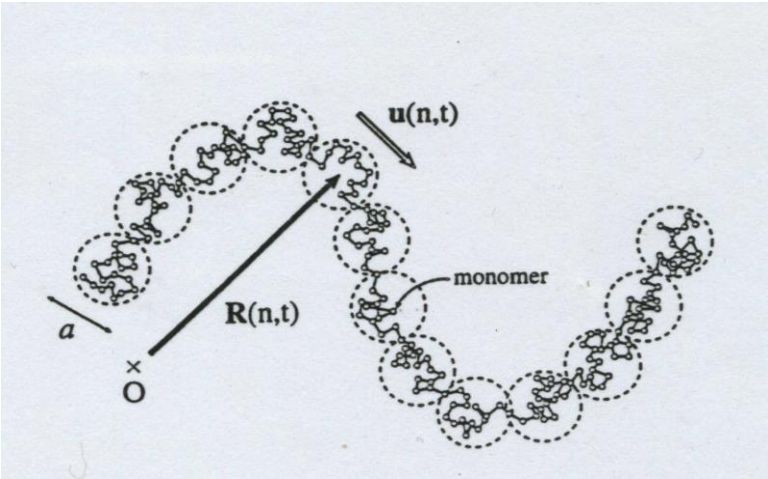
$$\begin{cases} G'(\omega) \sim \omega \\ G''(\omega) \sim \omega^2 \end{cases}$$ For $\omega < 1/\tau_R$



Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus G' and filled symbols are the loss modulus G''. Squares have $c = 0.5\ \mathrm{g\,L^{-1}}$, triangles have $c = 1.0\ \mathrm{g\,L^{-1}}$, and circles have $c = 2.0\ \mathrm{g\,L^{-1}}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

Reptation model in a tube (de Gennes): How to treat topological interactions





Ideal chain: Random walk $R = bN^{1/2}$

Tube: topological constraints / uncrossability

Chain in a tube: $\alpha = bN_e^{1/2}$ (tube diameter)

Random walk of N_e entanglement segments

Primitive path: $l = \frac{N}{N_e}\alpha \sim N$

Curvilinear Diffusion (1-D along tube):

$$D = \frac{kT}{\zeta_p} = \frac{kT}{N\zeta} \sim N^{-1}$$

$$\tau = \frac{l^2}{D} \sim N^3 \qquad \eta = G\tau \sim N^3$$

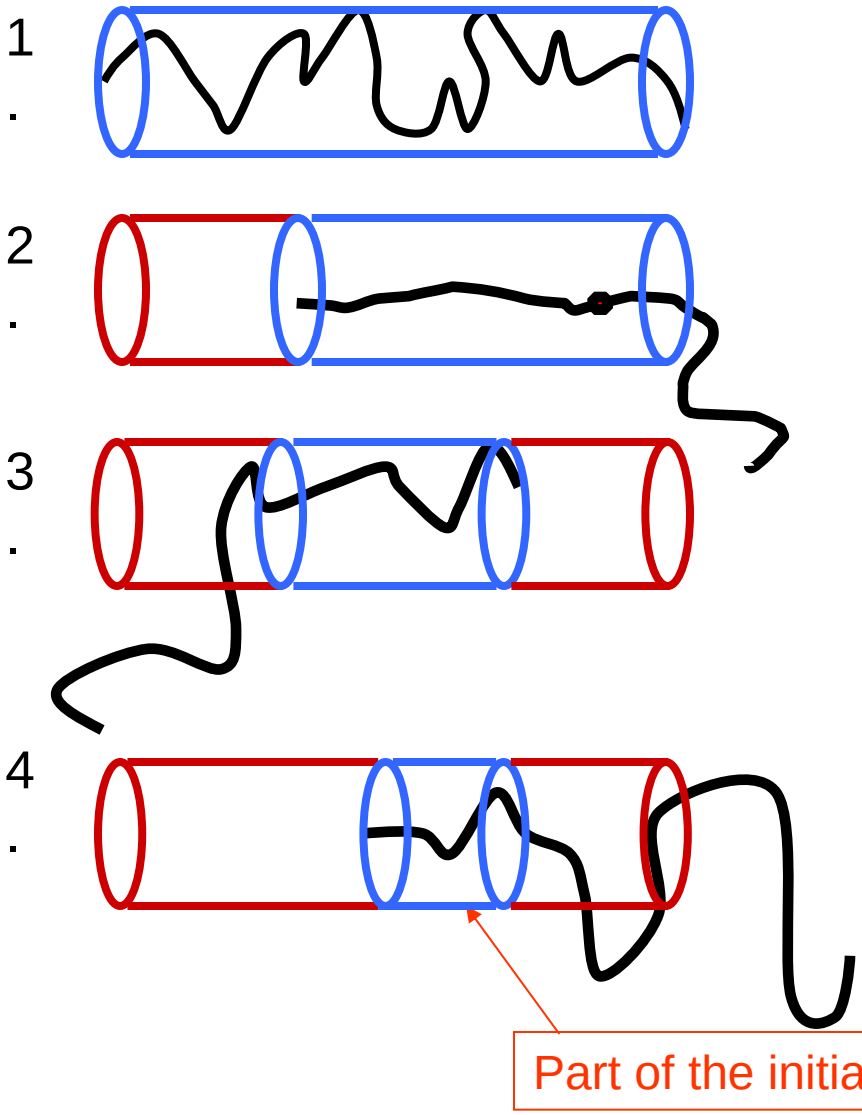
stronger N-dependence !
(compared to Rouse)

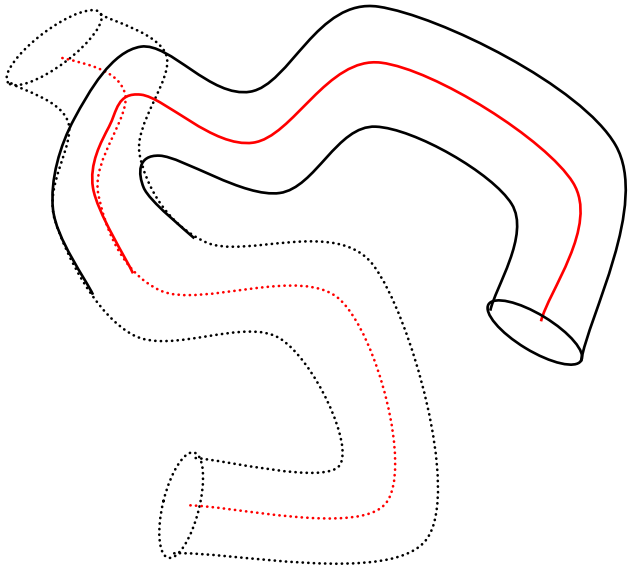
De Gennes, Polymer concepts in polymer physics 1979
Doi, Edwards, The theory of polymer dynamics 1986

Reptation
Doi-Edwards model

$$G(t) = G_N^0 P(t)$$

$$P(t) = \sum_{i,odd} \frac{8}{\pi^2 i^2} \exp\left[-i^2 t/\tau\right]$$





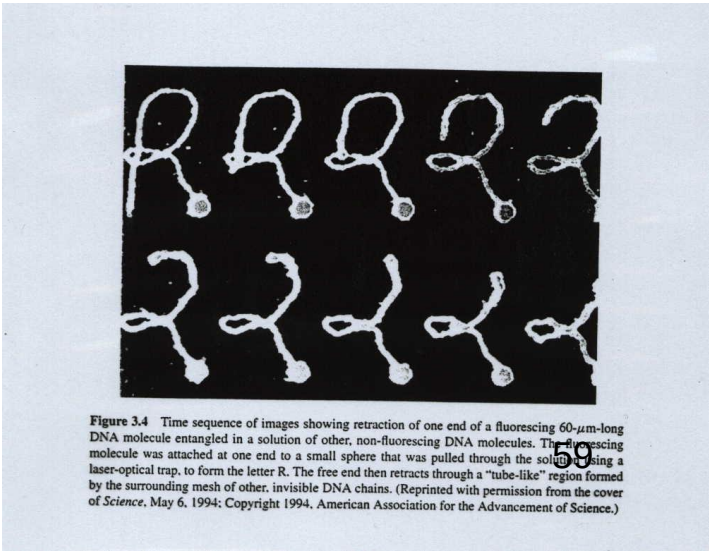


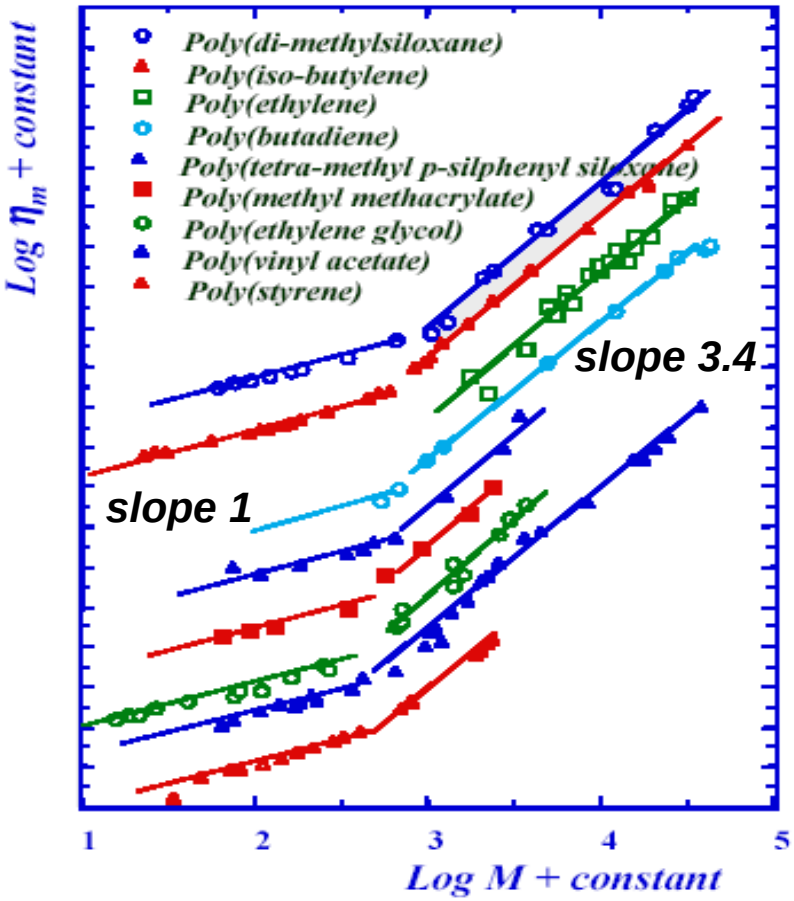
Figure 3.4 Time sequence of images showing retraction of one end of a fluorescing 60-μm-long DNA molecule entangled in a solution of other, non-fluorescing DNA molecules. The fluorescing molecule was attached at one end to a small sphere that was pulled through the solution using a laser-optical trap, to form the letter R. The free end then retracts through a "tube-like" region formed by the surrounding mesh of other, invisible DNA chains. (Reprinted with permission from the cover of *Science*, May 6, 1994; Copyright 1994, American Association for the Advancement of Science.)

(E. van Ruymbeke)

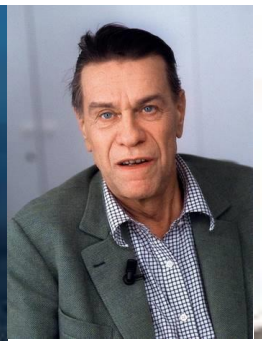
Consequences of Entanglements

$M < M_e$ Rouse

Zero-shear viscosity vs. M (note change of slope)



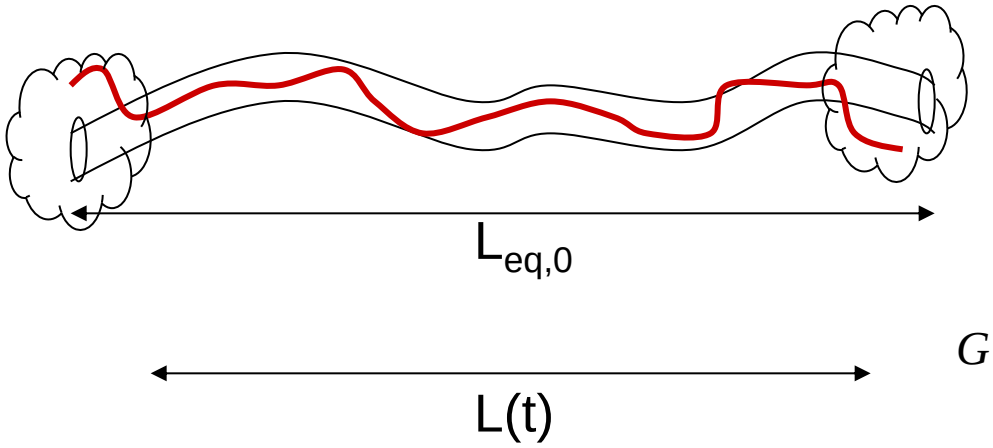
$M > M_e$ Edwards deGennes Doi



Berry, Fox, Adv. Polym. Sci. 1968

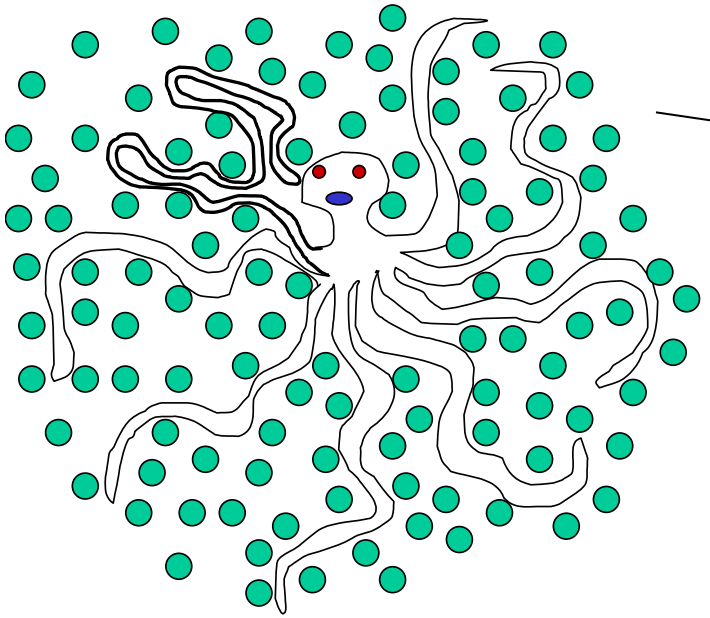
Doi, Edwards, The theory of polymer dynamics 1986

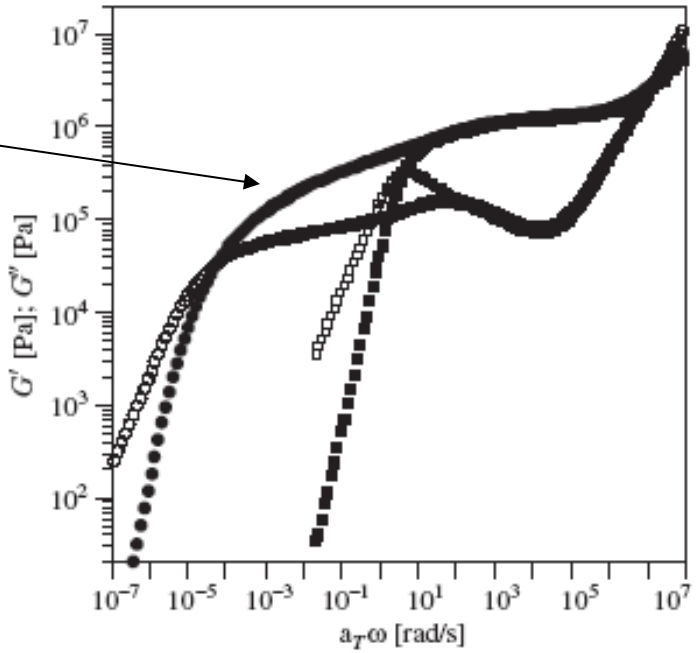
contour length fluctuations (CLF)



deGennes
Doi, 1984
Rubinstein, Colby, Viovy, 1991

$$G(\tau_R) \approx G_N^0 \left(1 - \frac{N_e}{N}\left(\frac{\tau_R}{\tau_e}\right)^{1/4}\right) \approx G_N^0 \left(1 - \mu\sqrt{\left(\frac{N_e}{N}\right)}\right)$$



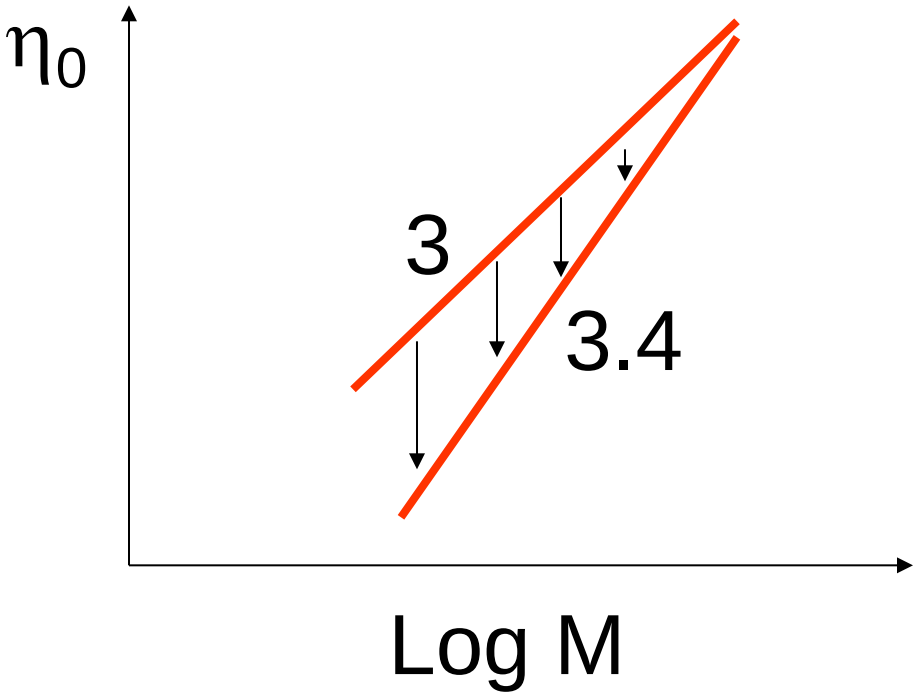


Rubinstein, Colby: Polymer Physics, 2003

Non-reptative modes: Contour length fluctuations

$$\tau_{reptf}(Z) \cong \tau_{rept}(Z)\left(1-\frac{2C_1}{\sqrt{Z}}+\frac{C_2}{Z}+\ldots\right)$$

CLF: affect more the smaller chains



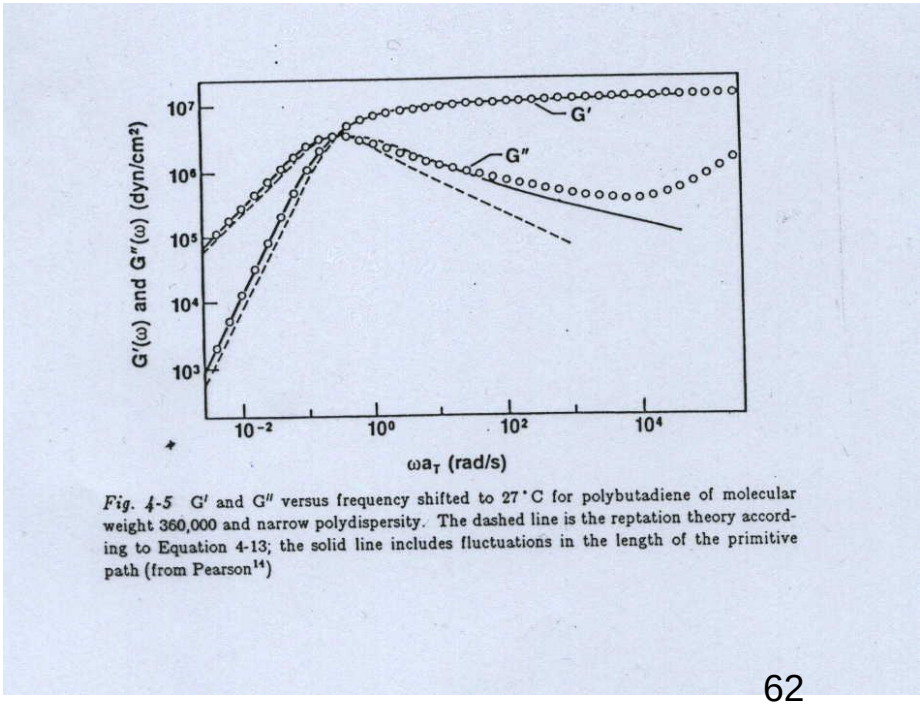
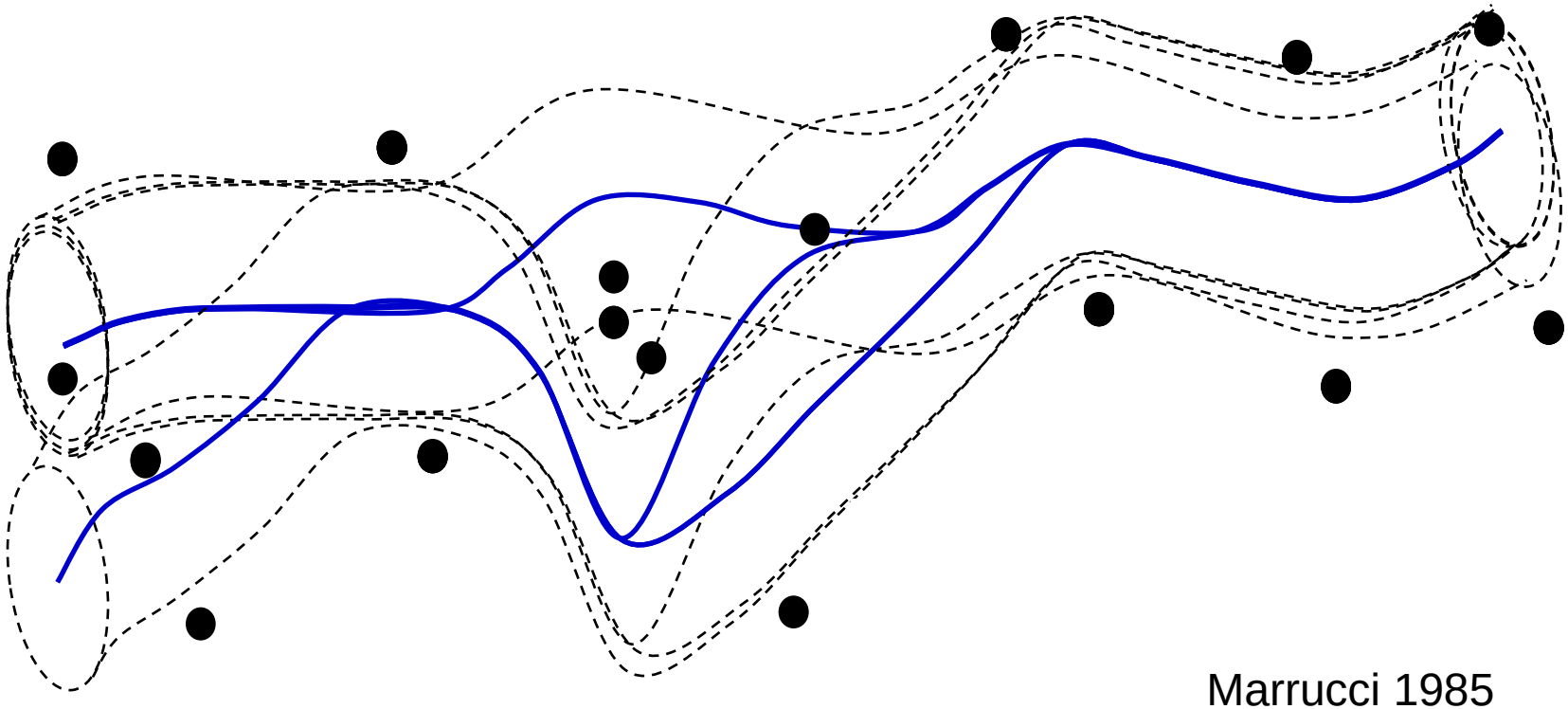


Fig. 4-5 G′ and G″ versus frequency shifted to 27 °C for polybutadiene of molecular weight 360,000 and narrow polydispersity. The dashed line is the reptation theory according to Equation 4-13; the solid line includes fluctuations in the length of the primitive path (from Pearson[14])

Constraint Release
Dynamic dilution



Marrucci 1985
Rubinstein , Colby 1988
Viovy et al. 1991
Likhtman-McLeish 2002

Initial D&E model (with CR)

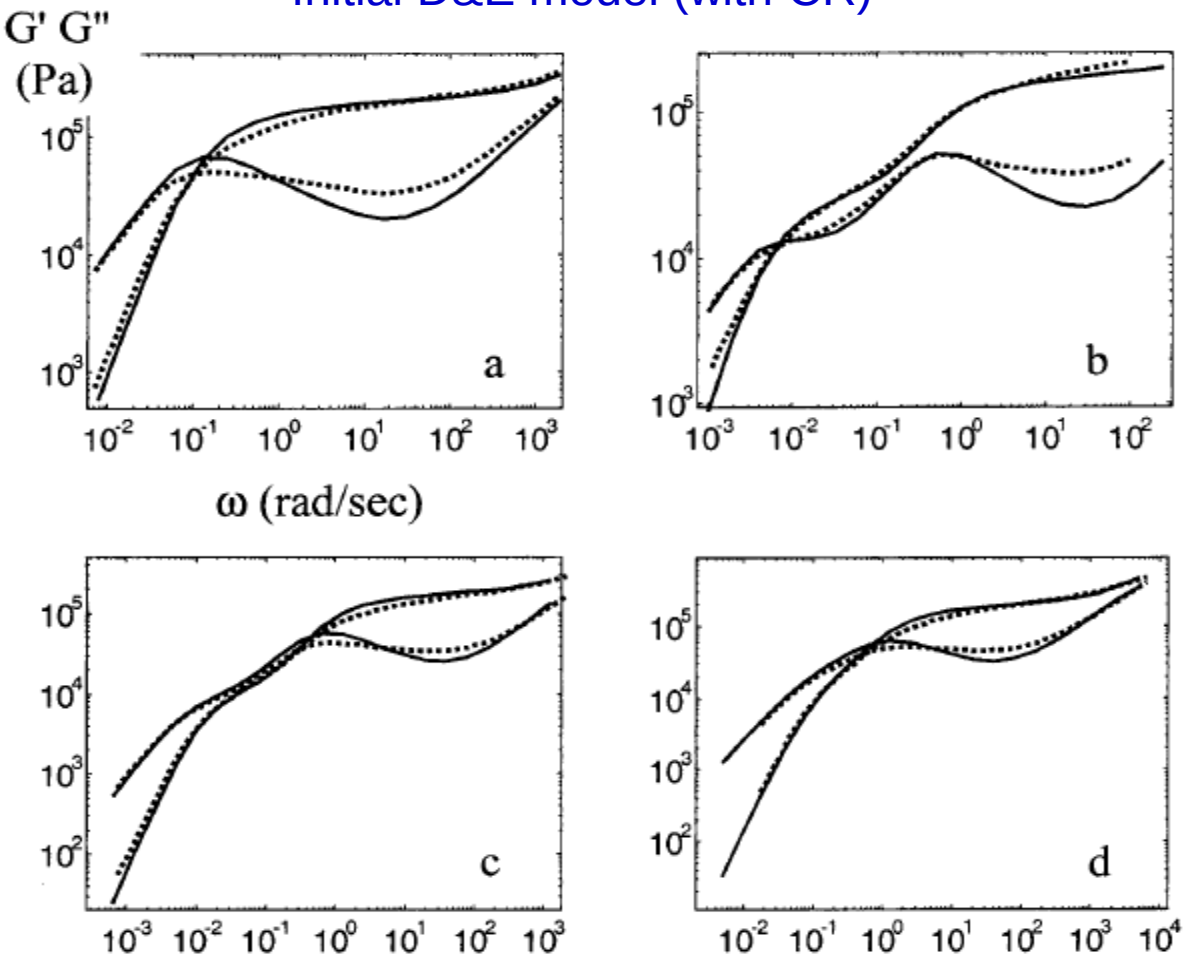


Figure 2. Experimental (···) and predicted (—) dynamic moduli using the Doi and Edwards kernel (eq 2) and double reptation (eqs 1 and 5) for (a) PS1, (b) PS9, (c) PS12, and (d) PS13.

	polydispersity	M_w (g/mol)	M_n (g/mol)
PS1	1.02	355 500	346 200
PS2	1.02	191 300	187 600
PS3	1.09	886 900	813 500
PS4	1.04	176 700	169 900
PS5	1.03	60 400	58 600
PS6	1.03	58 400	56 900
PS7	1.02	146 400	143 300
PS8	1.04	676 000	650 900

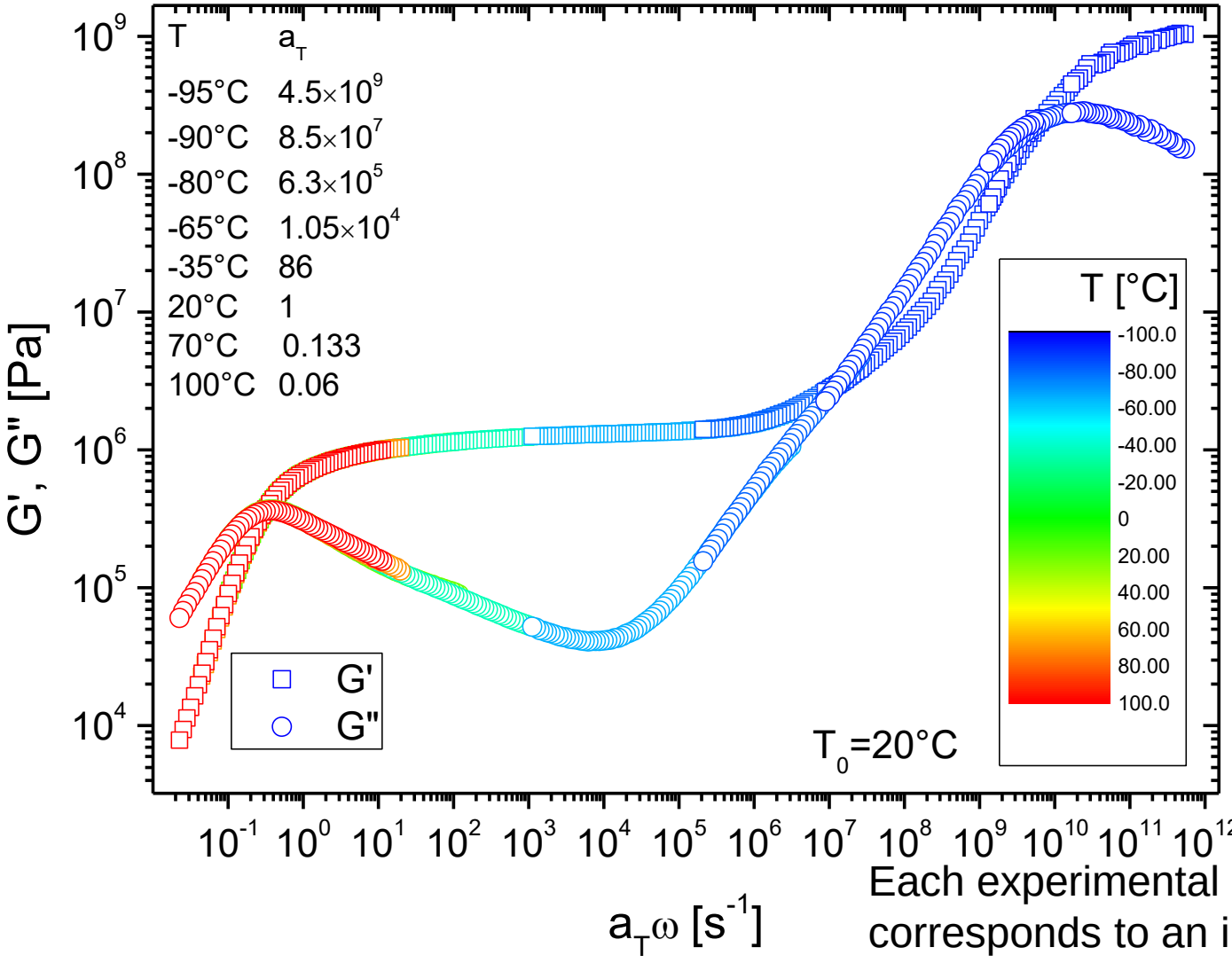
(b) Bi- or Tridisperse

	composition
PS9	50% PS2, 50% PS3
PS10	20% PS4, 80% PS5
PS11	80% PS4, 20% PS5
PS12	65% PS2, 35% PS8
PS13	30% PS7, 30% PS2, 40% PS1

Mechanical Spectroscopy

Entanglements
(physical) network

Complete master curve of PBd 430kg/mol (~220 Me)



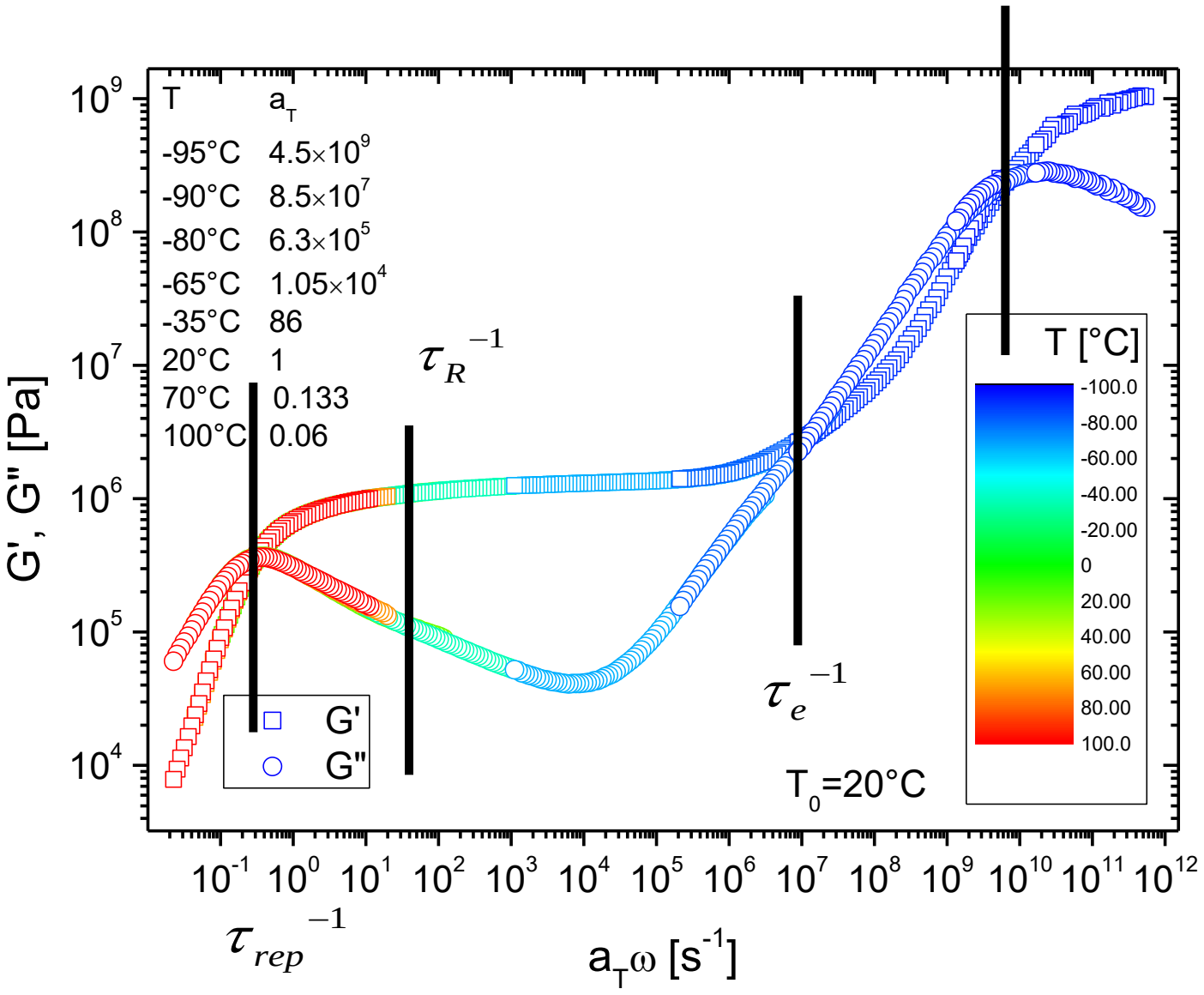
Each experimental frequency corresponds to an inverse characteristic time of the polymer

Data: F. Stadler, E. vanRuymbeke

Mechanical Spectroscopy

Entanglements
(physical) network

Complete master curve of PBd 430kg/mol (~220 Me)

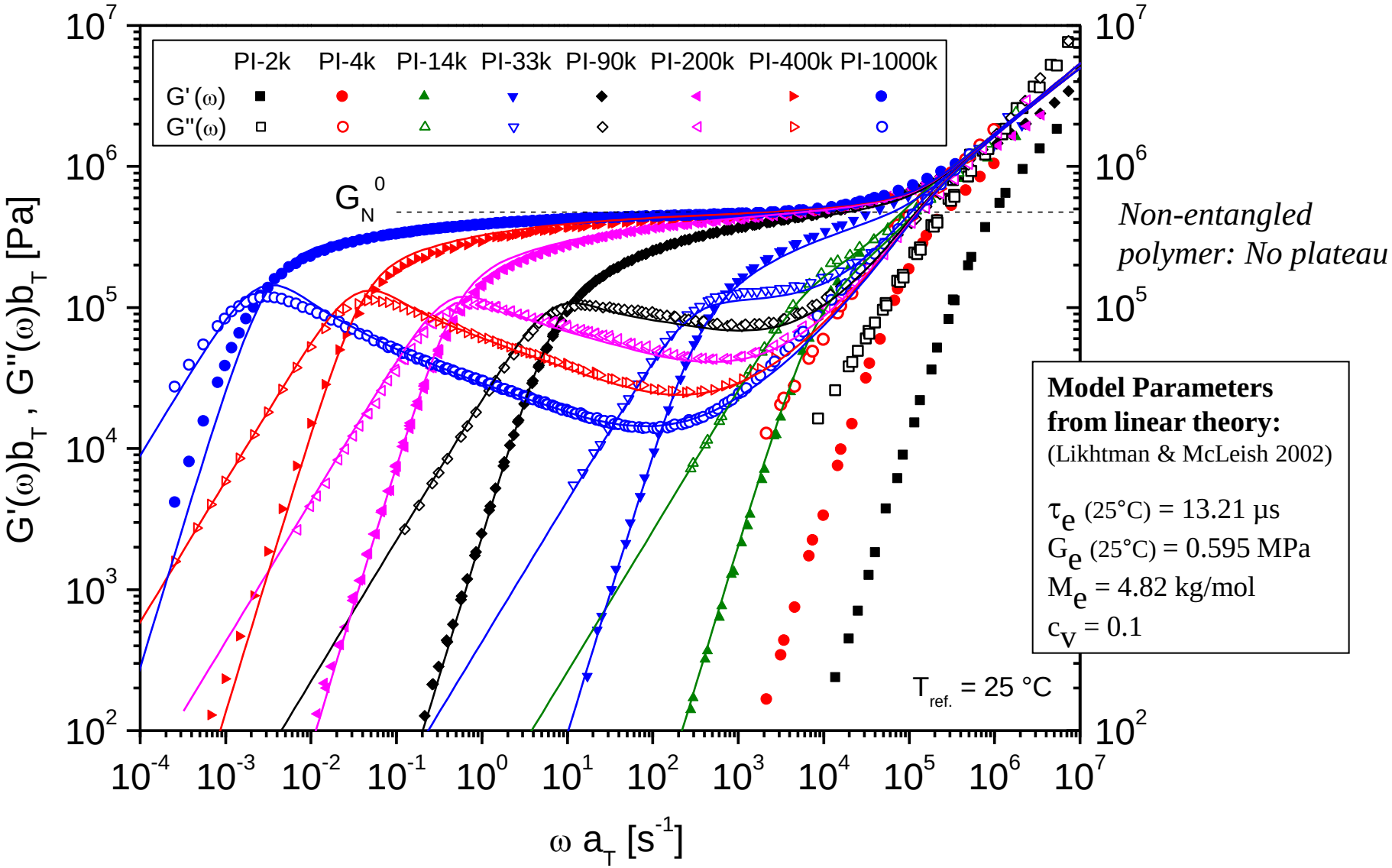


Data: F. Stadler, E. vanRuymbeke

How does the plateau region depend on MW?

How can we obtain mechanical spectra extending over many decades in frequency and modulus?

Shear rheology of narrow PI

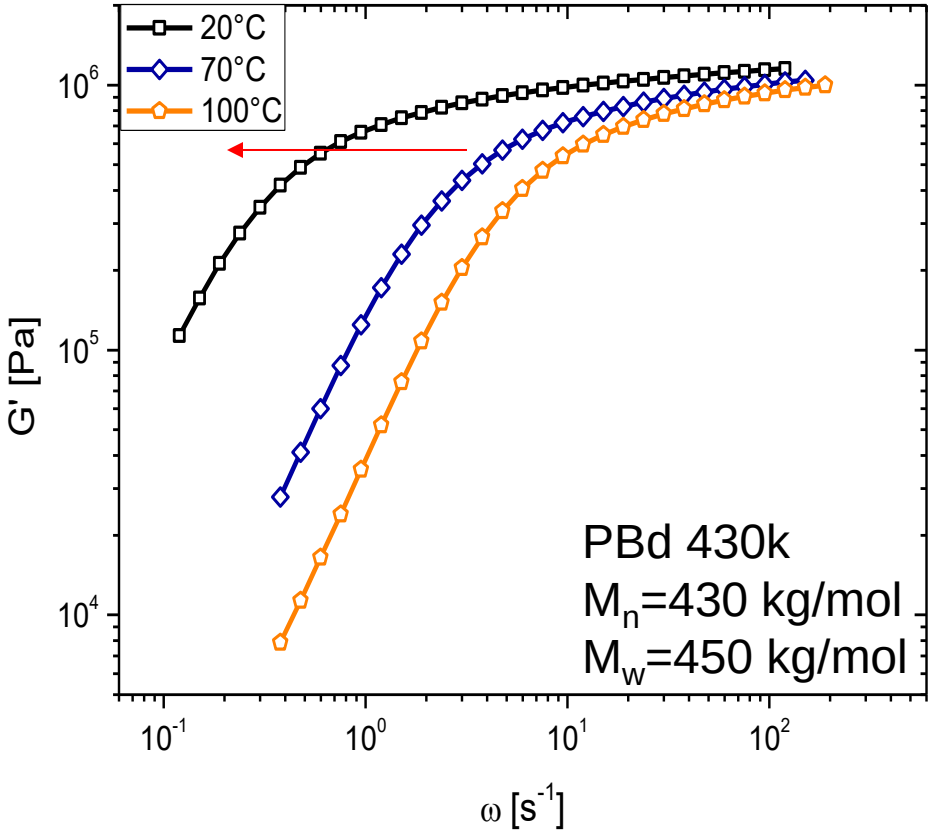


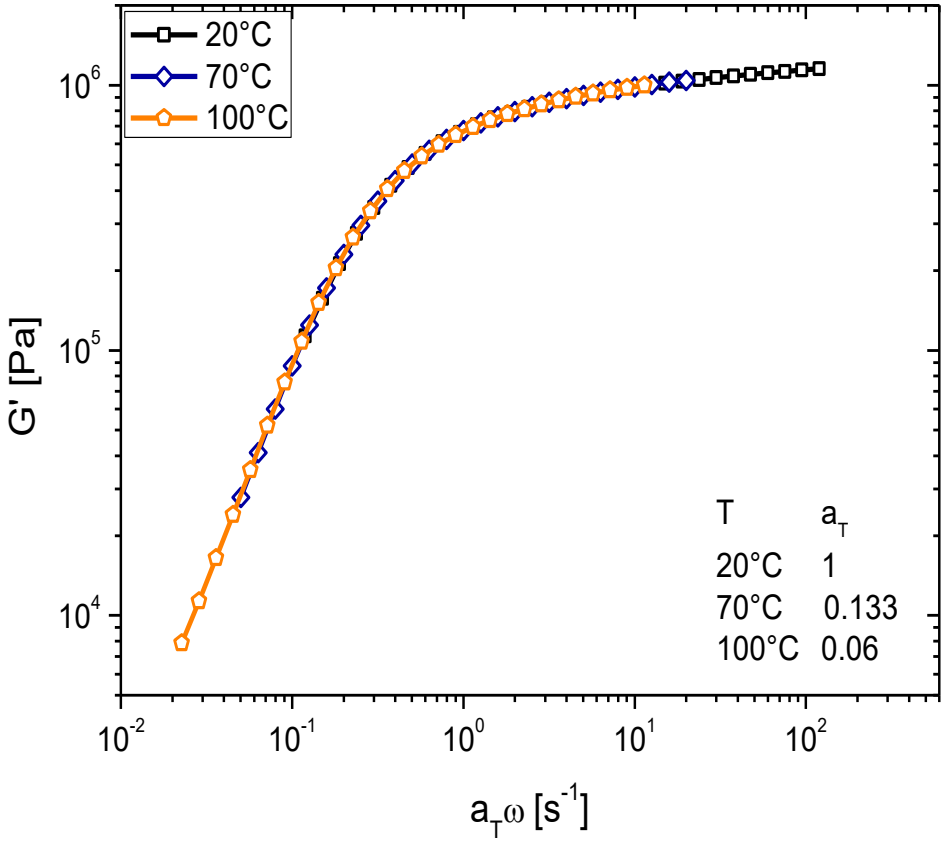
RepTate: Alexei Likhtman, Jorge Ramirez

Auhl, et al.
J. Rheol. (2008)

Time Temperature Superposition (TTS)

Shifted storage modulus G'(ω) at different temperatures (horizontal)

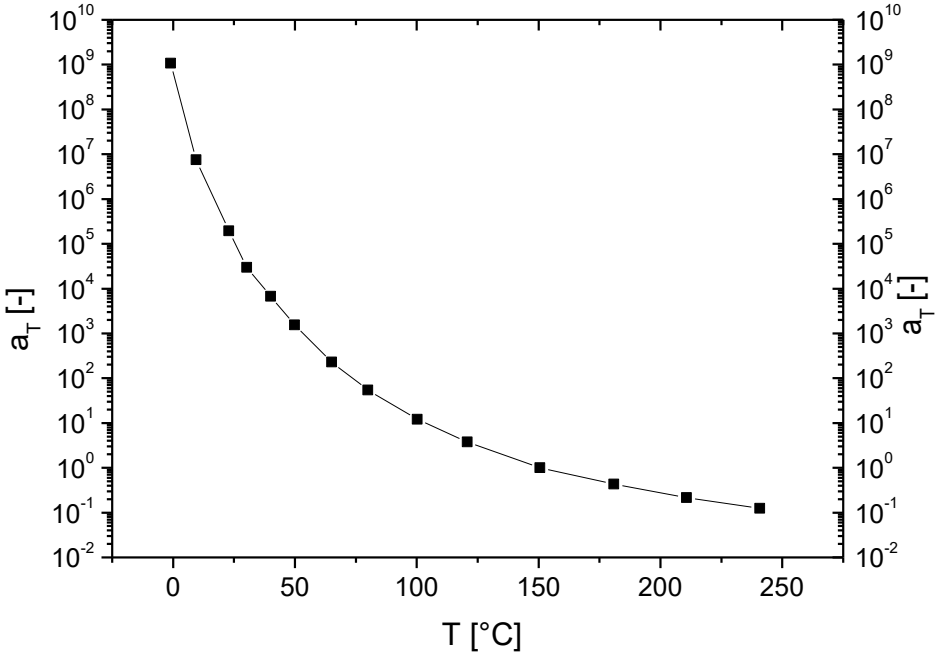


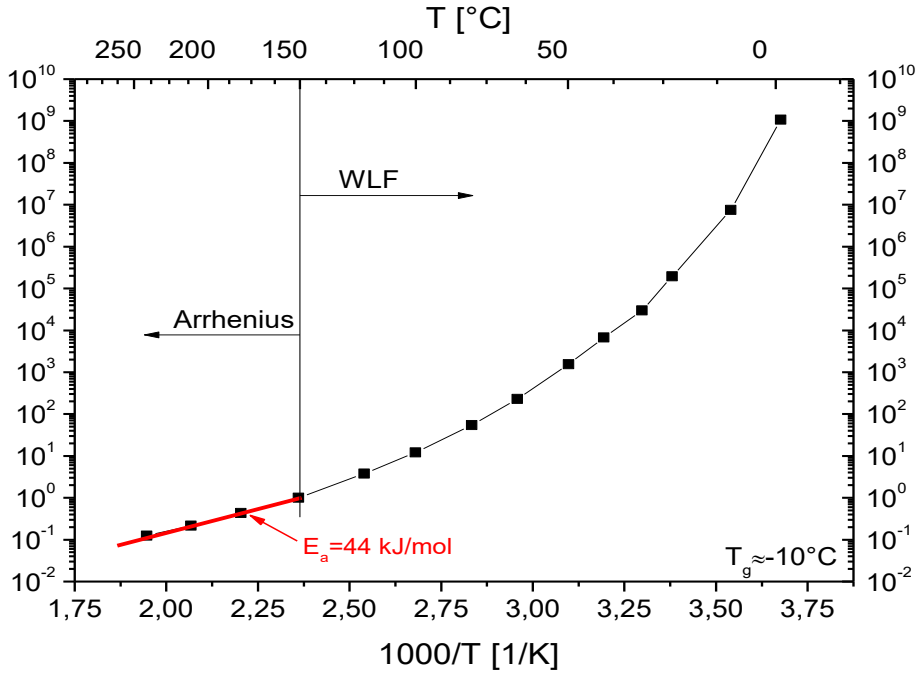


Data: F. Stadler, E. vanRuymbeke

Horizontal shift factor

WLF- and Arrhenius dependencies of the shift factors





$$\log a = -\frac{c_1 \cdot (T - T_{ref})}{c_2 + (T - T_{ref})}$$

(Williams-Landel-Ferry equation: WLF)

- c_1, c_2: depends on the nature of the polymer melts (not on the structure)
- Thermo-rheologically simple

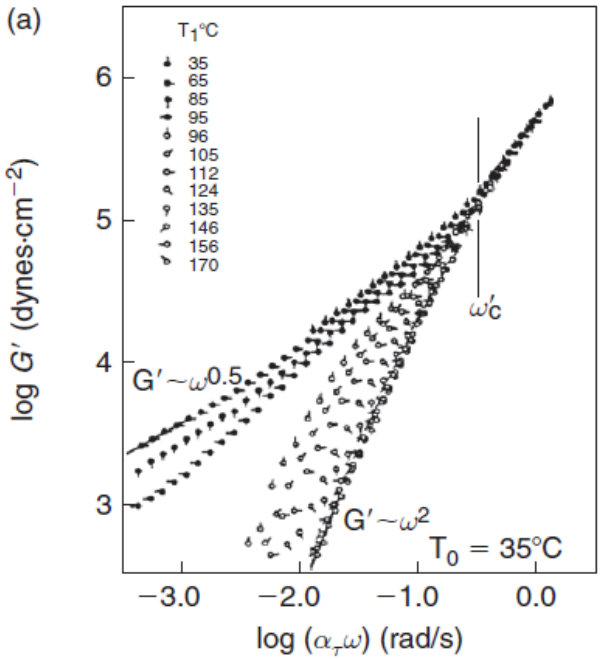
J. D. Ferry, Viscoelastic properties of polymers, Wiley, 1980

Why does it work:

$$\lambda_i(T) = \frac{R^2}{D} = \frac{R^2}{k_B T}\zeta_i(T)$$

$$\lambda(T) \sim \sum \lambda_i(T) \sim \sum \zeta_i(T)$$

Exceptions: Determine transitions
(e.g., block copolymers, crystallization)



Rosedale + Bates, Macromolecules 1984

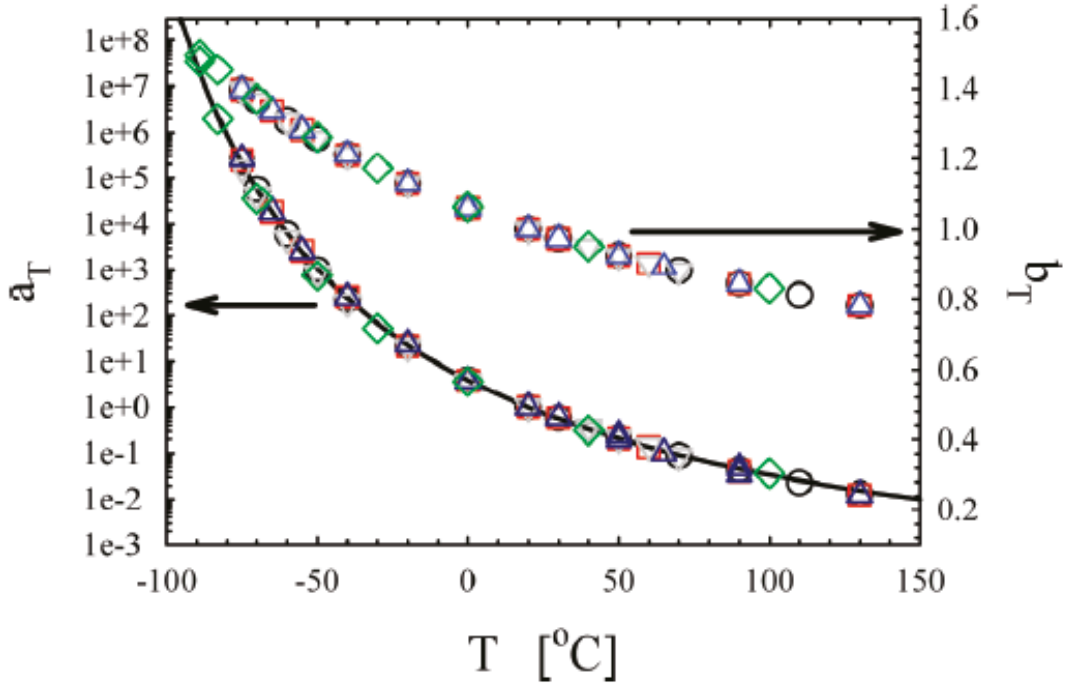
Key: homogeneous distribution of friction with same T-dependence

(works with systems of same single microscopic friction, e.g. homopolymers

-- but there are issues near the glass transition)

Kremer, Schoenhals, Broadband dielectric spectroscopy 2003
Ferry, Viscoelastic properties of polymers 1980
Plazek, J. Rheol. 2000
McKenna, J. Rheol. 2010

Vertical shift factor



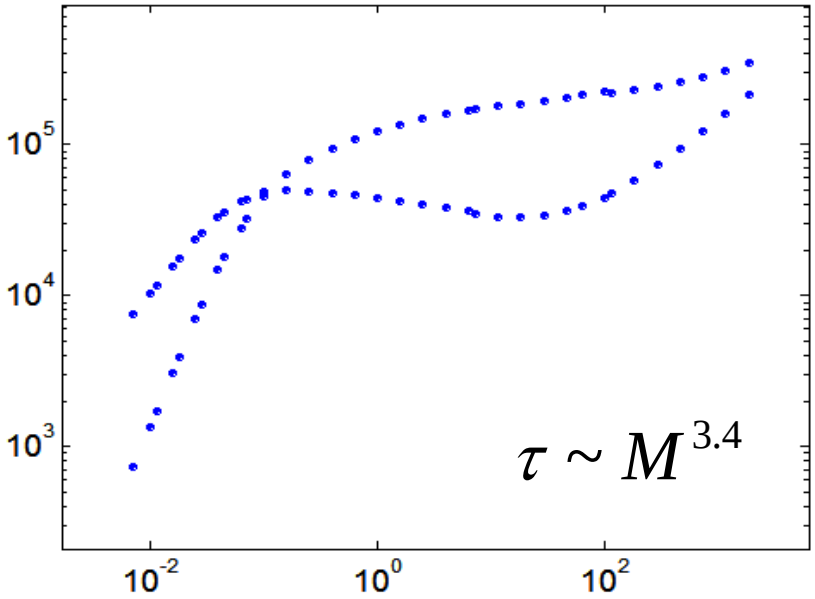
Snijkers et al, Macro 2011

Plateau modulus: $G_N^0 = \nu kT = \rho RT/M_e$ Green-Tobolsky 1958; Edwards 1968

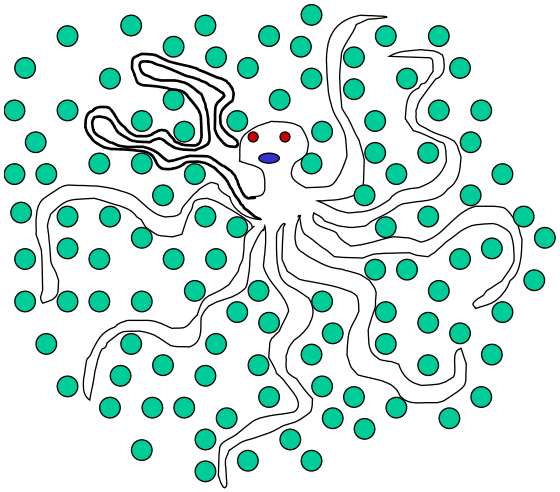
$$b_T = \frac{\rho(T_{ref})T_{ref}}{\rho(T)T}$$

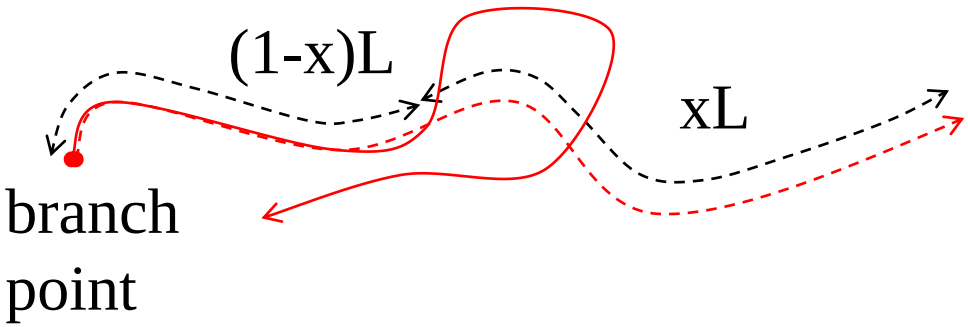
Compare linear and star polymers:

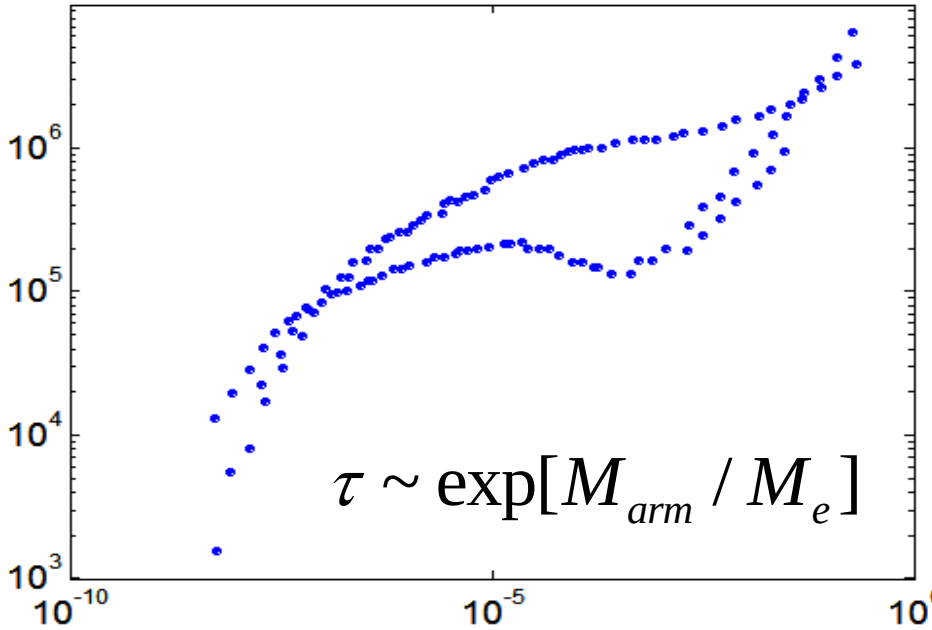
reptation - power law vs. retraction (fluctuations)– exponential



Linear







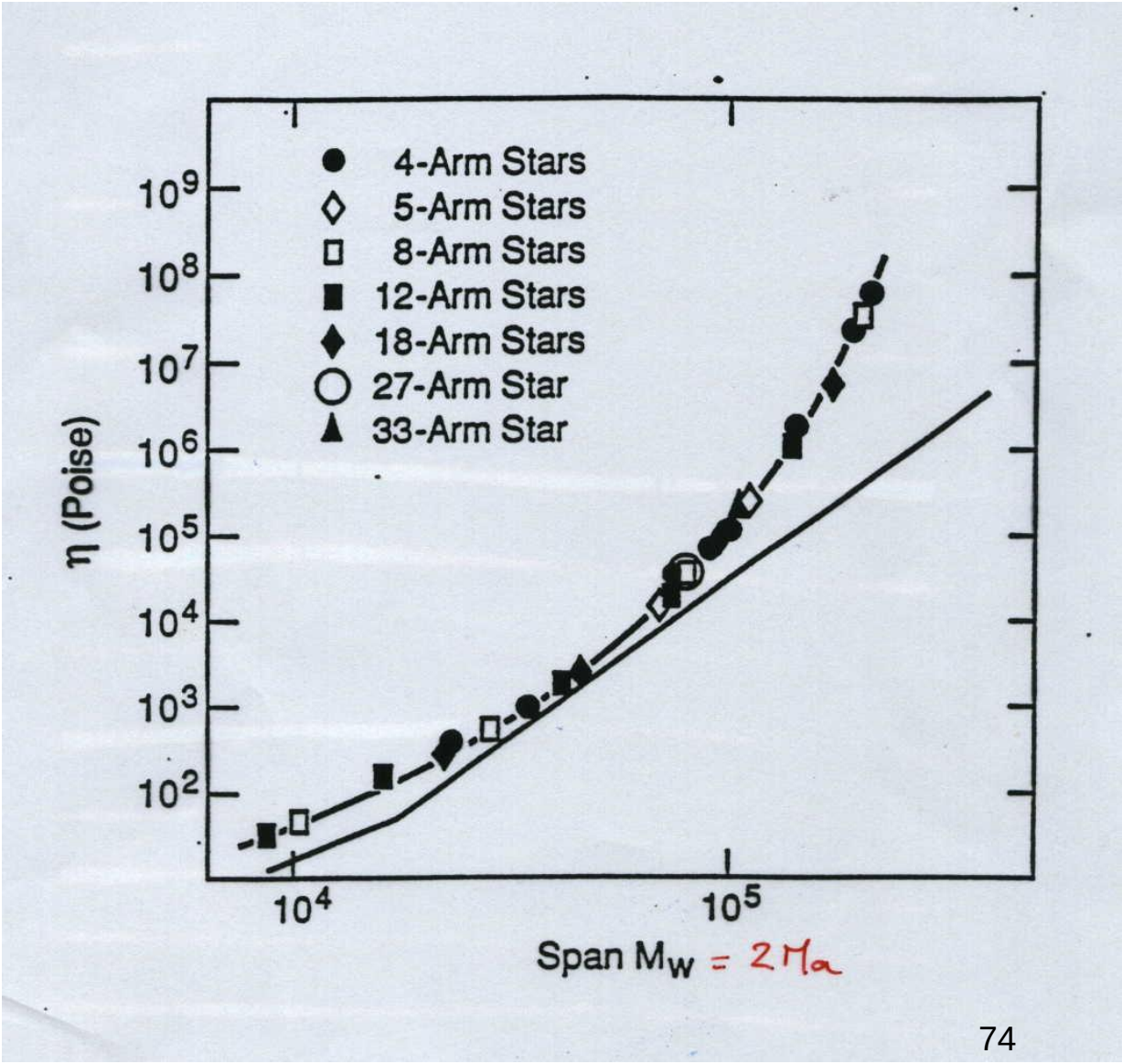
Star (no reptation)

Consequence 1:

Star has larger viscosity which does not depend on number of arms!

$$\tau \sim \exp[M_{arm} / M_e]$$

$$\tau \sim M_{arm}^{3.4}$$

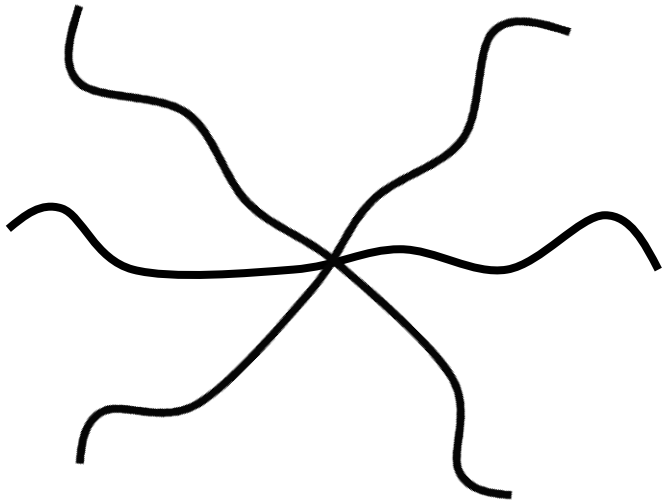


Not true for
f > 36 (roughly)

Fetters et al. Macromolecules 1993 ; Pakula et al. Macromolecules 1998

Consequence 2:

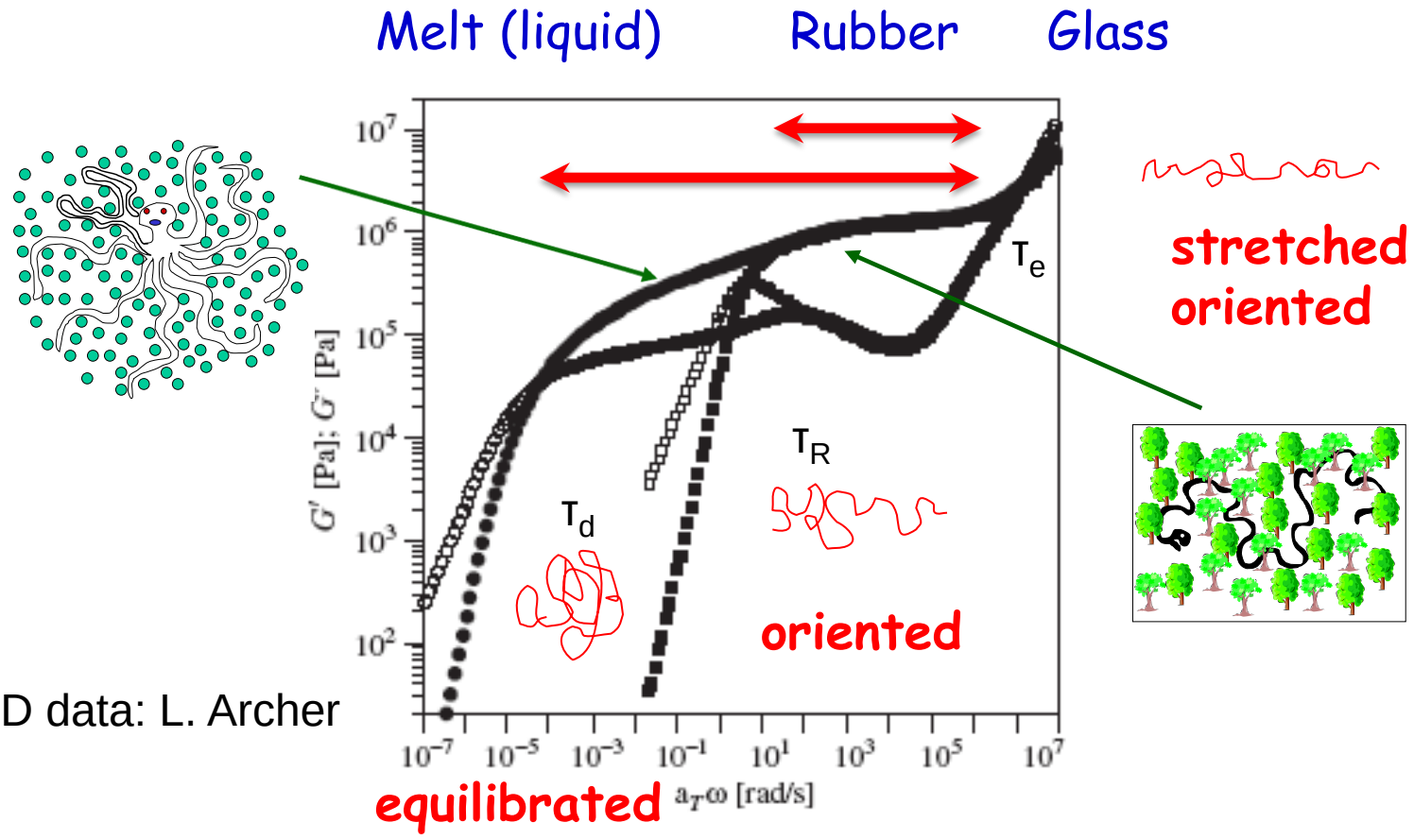
Star with same total molar mass as linear, but several arms (>3) may have smaller viscosity!



Wider application to hyperbranched polymers: viscosity "control"

Dorgan et al. Macromolecules 2003

Linear viscoelasticity: link to macromolecular conformation



PBD data: L. Archer

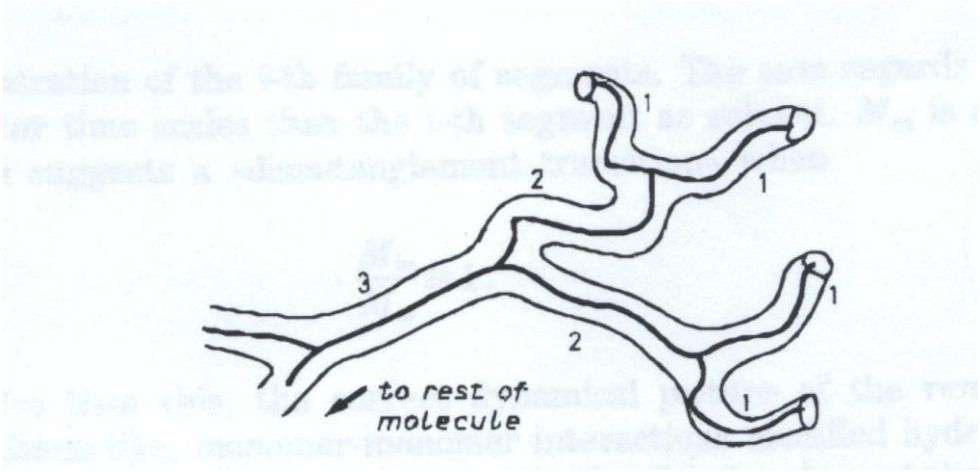
Entangled linear chains – reptation + fluctuations + CR $\eta \sim N^{3.4}$

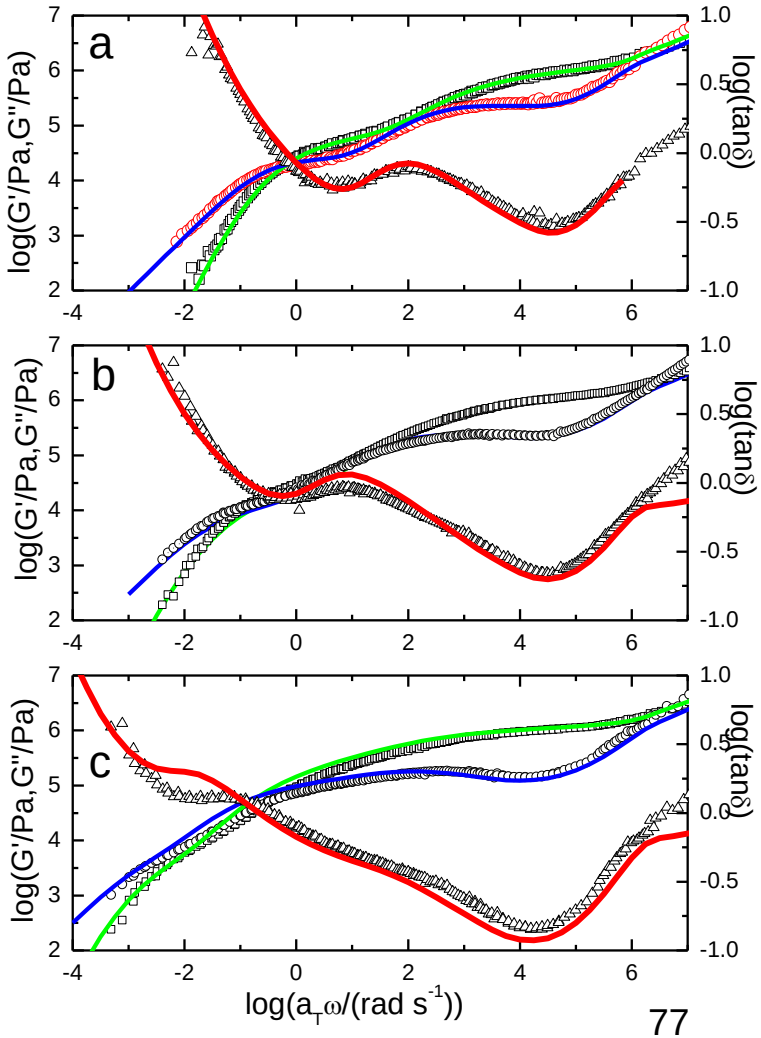
Entangled stars – arm retraction $\eta \sim \exp[N_{arm} / N_e]$

Edwards, deGennes, Doi, Pearson, Graessley, Marrucci
Rubinstein, McLeish, Milner, Larson, Colby, Watanabe, Likhtman

Branched polymers:

Combine reptation + retraction (and account for some important "details"





McLeish, EPL 1988

Van Ruymbeke et al., 2006+ ; Kapnistos, 2005

Questions:

Which are the key differences between polymers and colloids?
(length, time, energy, interactions)

We discussed De, Wi, Pe. How do they compare?

Are there rheological (and other) differences between polymeric and colloidal glasses?

What is the analogy of entanglement-response of polymers to colloidal response?

Summary:

Synthesis: N, b

Size: $R=N^{1/2}b$

Distribution: $P(R) \propto \exp\left(\frac{-3R^2}{2Nb^2}\right)$

Modulus: $G=vkT=kT/\xi^3$

Diffusion: $\boxed{D = \frac{kT}{\zeta} = \frac{R^2}{\tau}}$

Hooke: $\sigma=G\gamma$

Newton: $\eta \equiv \frac{\sigma}{\dot{\gamma}}$

Viscoelasticity: $\eta = G\lambda$

$\eta \sim N$

$\eta \sim N^{3.4}$

$\eta \sim \exp[N_{arm} / N_e]$