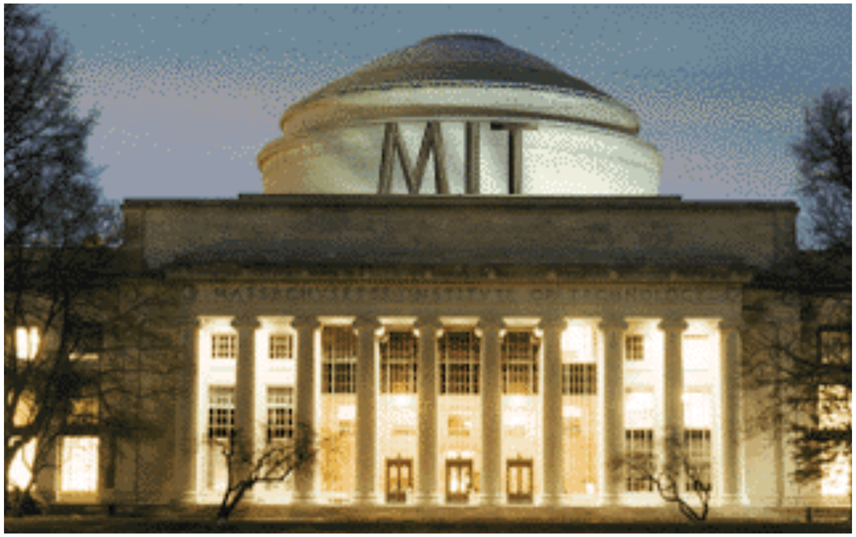
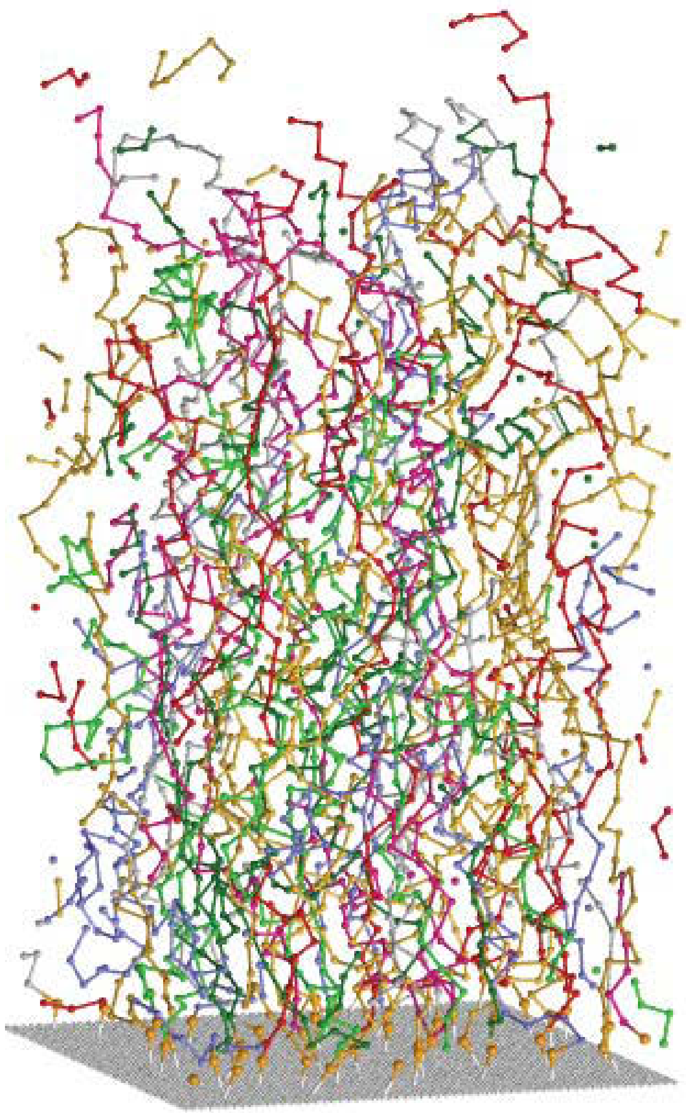
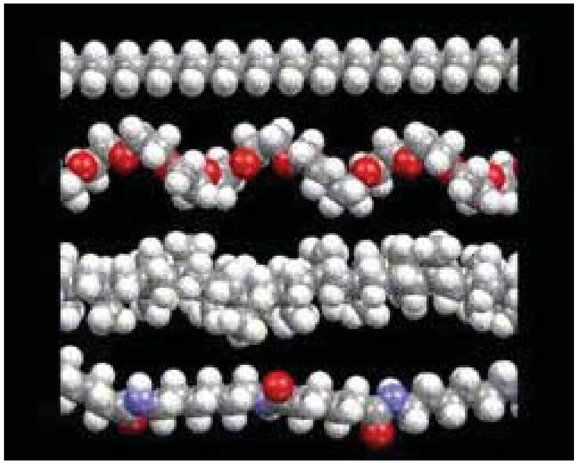
Coil-Size Scaling and Reptation of Polymer Melts

2.341J Spring 2016



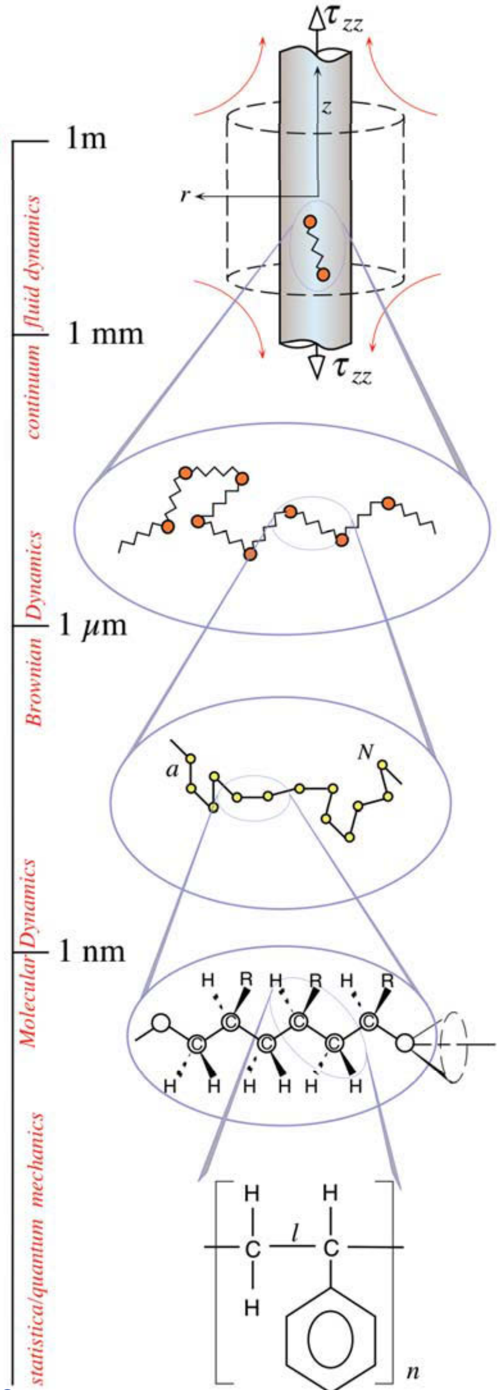
The complexity of the real problem





"Coarse Graining"

- Distill the essential physics describing the chain dynamics to simple(r) governing equations
- Chemical details and molecular specificity are collapsed into small number of chain-specific constants
- different analytic and simulation tools are appropriate to each scale



- FENE Dumbbell Const. Eqn.

$$\eta_p = (nk_BT)\lambda_z$$
$$De = \lambda_Z \dot{\varepsilon}_0$$

- Bead-Spring Chain (Rouse/Zimm)

$$\lambda_i = \lambda_z / i^{3/2}$$
$$i = 1,2,...M \approx 225$$

- Kramers' (Freely-Jointed) Bead-Rod Chain

$$N \approx (n/15) = 2885$$
$$a \approx 12.3\, l$$
$$L = R_{\max} \Big/ \sqrt{\langle R^2 \rangle}_{eq} \approx 93$$

- Freely-Rotating Bead-Rod Chain (Kuhn & Kuhn, Flory R.I.S.)

$$\langle R^2 \rangle_{eq} = C_\infty n l^2 \qquad C_\infty = 10$$

- Primary Chemical Structure

$$n = (2M_w/m_0) \approx 43{,}300$$
$$l = 1.54\,\text{Å}$$

data for Polystyrene; $M_w \approx 2.25 \times 10^6$ g/mol.

McKinley & Sridhar, *Ann. Rev. Fluid Mechanics*, 2002

Rouse/Zimm Results (Larson, 1987)

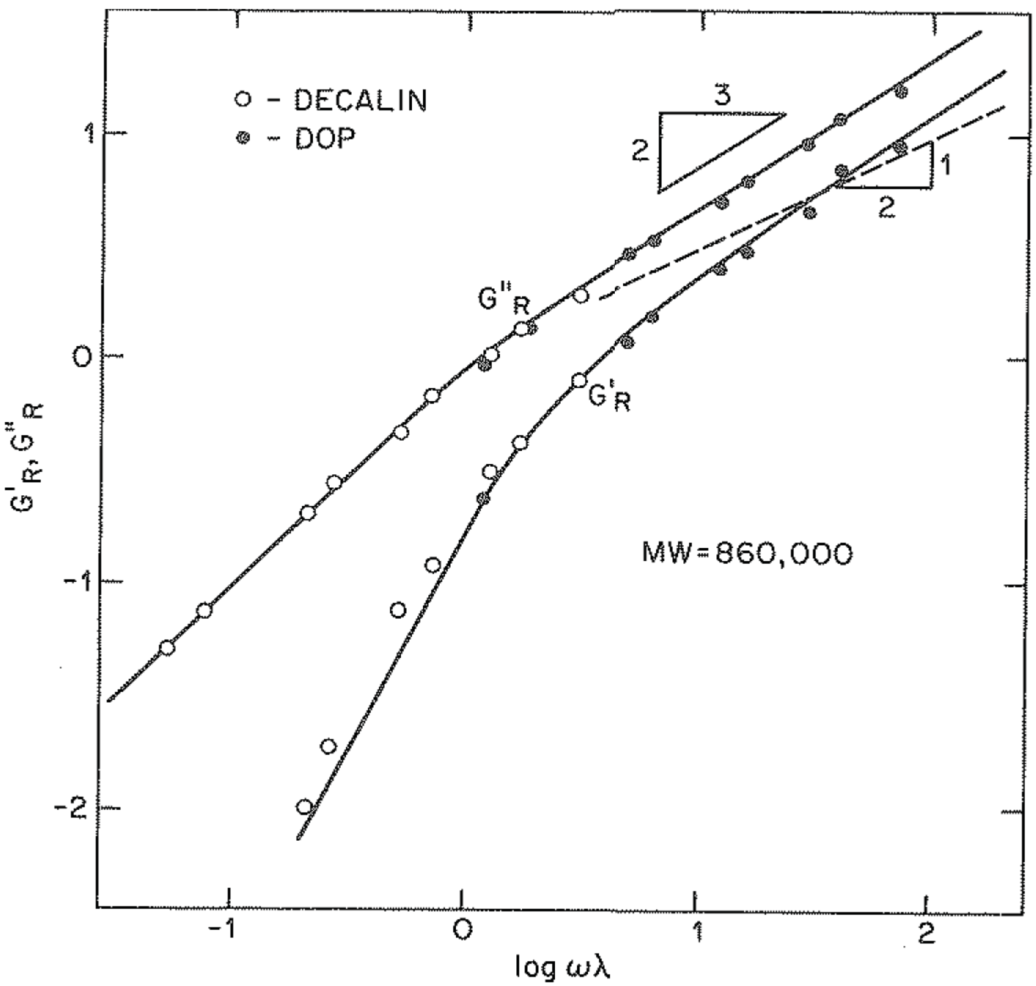
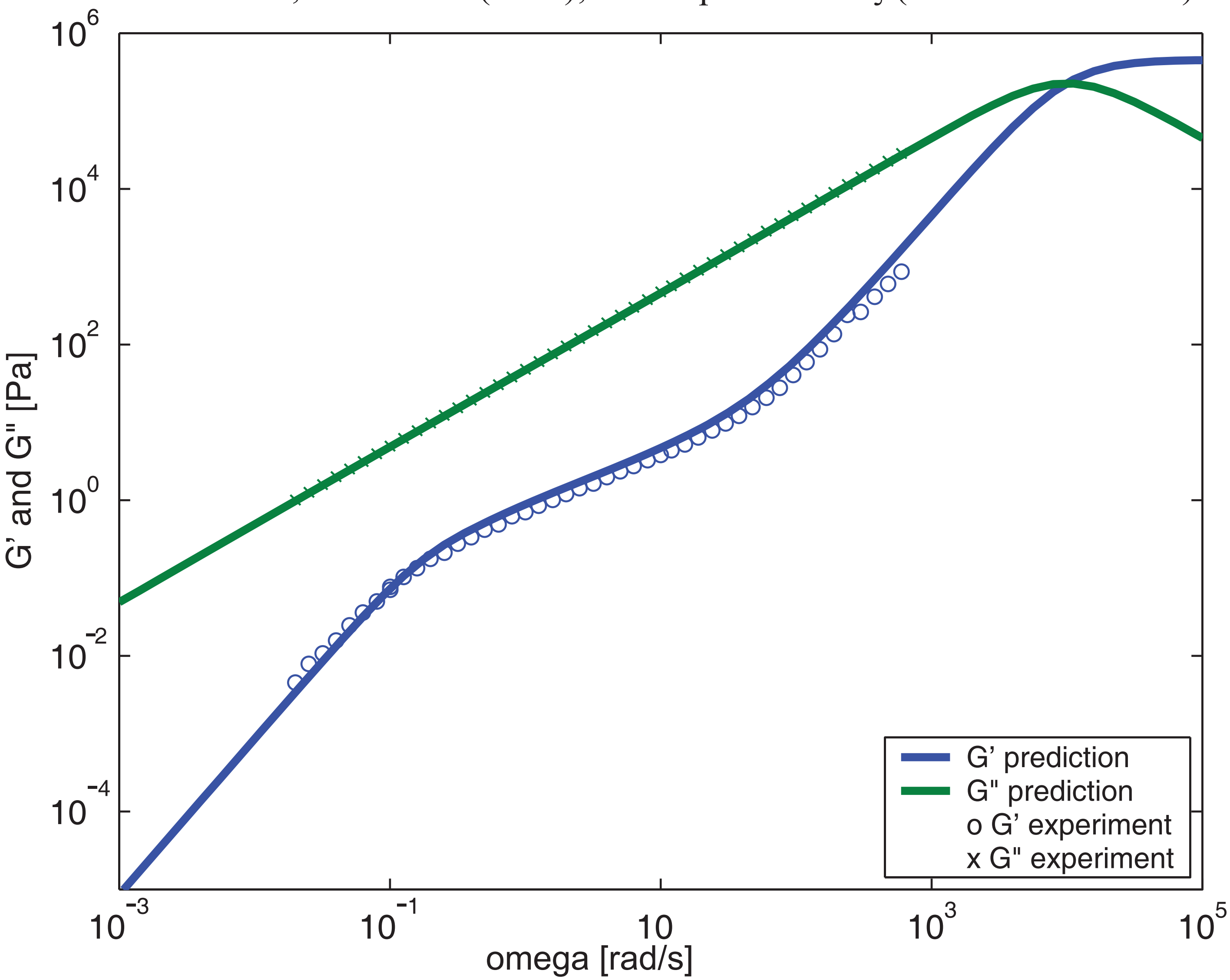


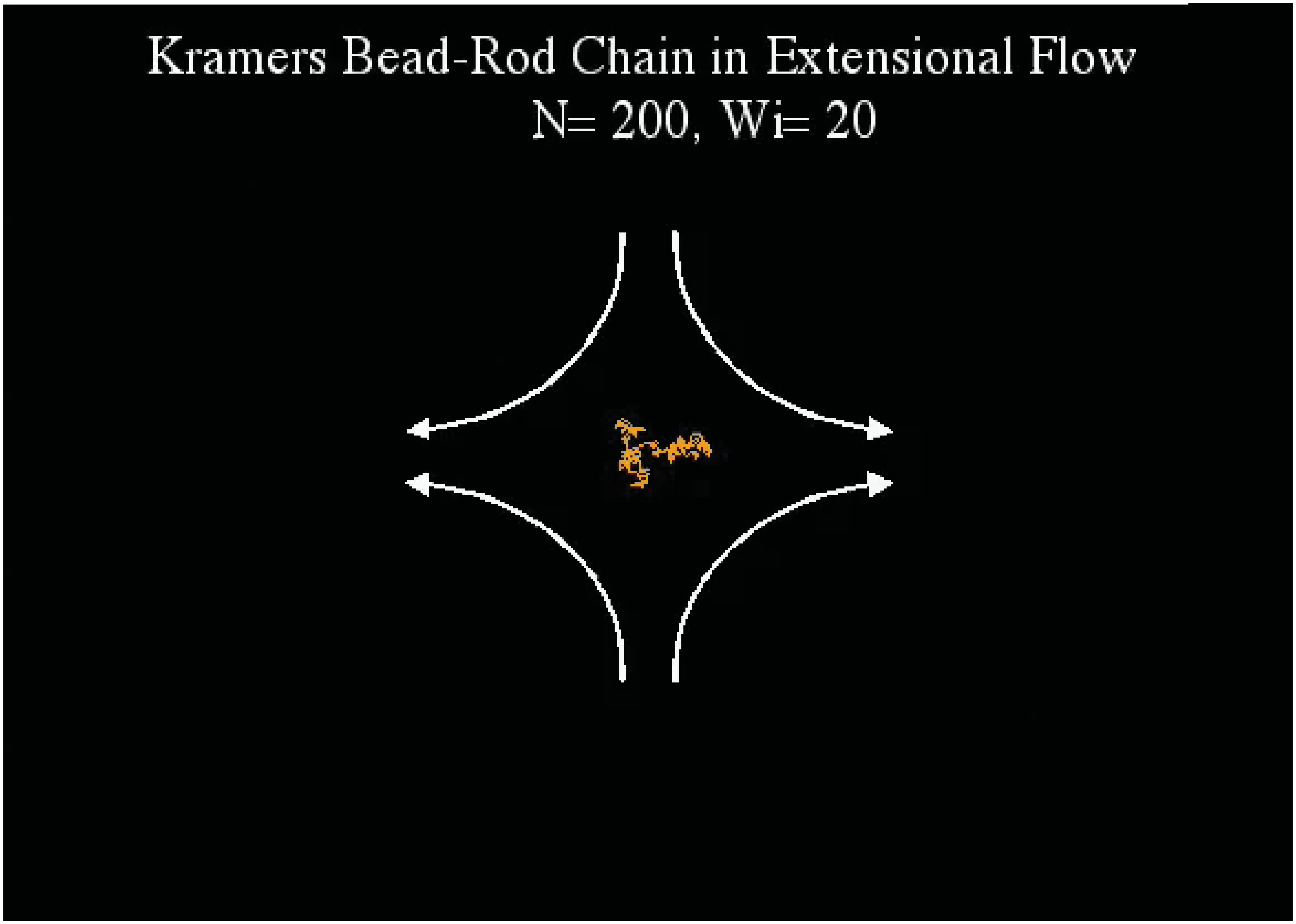
Fig. 8-1 Linear viscoelastic data for polystyrene in two theta solvents. For frequencies $\lambda\omega$ greater than 10, G' and G'' scale as $\omega^{2/3}$, in disagreement with the Rouse theory, which predicts a proportionality to $\omega^{1/2}$ in this regime. Here $G'_R \equiv G'/nkT$ and $G''_R \equiv (G'' - \eta_s\omega)/nkT$; $\lambda \equiv [\eta]_0\eta_s M/N_A kT$ (from Johnson et al.,[4] reproduced with permission from Polym. J.).

Zimm Model Fit to Experimental Data (with TTS)

Monodisperse Polystyrene in a viscous oligomeric styrene oil ("resin").
M. Verani, MS Thesis (2004); fit one parameter: ζ (friction coefficient)



Extensional Flows: (Doyle, Spiegelberg, McKinley,Shaqfeh, JNNFM 1997)



Summary (from last Class)

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SUMMARY

⇒ These are predictions that can be probed experimentally (rheometry, light scattering, viscometry)

	ROUSE	ZIMM	
	($\nu = 1/2$)	Theta Solvent ($\nu = 1/2$)	Good Solvent ($\nu = 3/5$)
Friction Coeff ζ [Ns/m]	M_w	$M_w^{1/2}$	$M_w^{3/5}$
Diffusivity $\mathcal{D}_{trans}$ [m^2/s]	M_w^{-1}	$M_w^{-1/2}$	$M_w^{-3/5}$
Relaxation time λ_{long} [s]	M_w^{2}	$M_w^{3/2}$	$M_w^{9/5}$
Intrinsic Viscosity $[\eta]$ [cm^3/g]	M_w	$M_w^{1/2}$	$M_w^{4/5}$

The Fox Flory Relation

The behavior of η_0 as a function of c and M is fairly well understood. At low concentrations an expression of the form $\eta_0 = \eta_0(c[\eta]_0)$ may be used to consolidate data for a given polymer–solvent system over a wide range of both concentration and molecular weight of the polymer. An example is the Martin equation:[13]

$$\eta_0 - \eta_s = \eta_s c[\eta]_0 e^{k'' c[\eta]_0} \qquad (3.6\text{-}15)$$

in which k'' is an arbitrary constant. Actually, a slightly better fit with data is obtained by replacing $[\eta]_0$ with $M^{a'}$ and choosing a' to fit data. It is found that a' is close to the Mark–Houwink exponent.

At high concentrations η_0 is governed by the product cM. The most striking feature of $\eta_0(cM)$ is illustrated in Fig. 3.6-4 for a variety of undiluted polymers. It is seen that η_0 goes from a linear to a 3.4 power dependence on M at some critical molecular weight M_c

DPL, Chapter §3.6

$$\begin{aligned} \eta_0 &\propto M && (M < M_c) \\ \eta_0 &\propto M^{3.4} && (M > M_c) \end{aligned} \qquad (3.6\text{-}16)$$

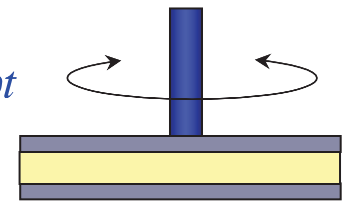
See Equations 3.6-15 and 3.6-16, and Fig. 3.6-4 in R. Byron Bird et al, *Dynamics of Polymeric Liquids*, John Wiley and Sons, Inc. removed due to copyright restrictions.

See Equations 3.6-15 and 3.6-16, and Fig. 3.6-4 in R. Byron Bird et al, *Dynamics of Polymeric Liquids*, John Wiley and Sons, Inc. removed due to copyright restrictions.

Linear Viscoelasticity from the Maxwell Model

- Input: $\gamma = \gamma_0 \sin \omega t$

  $\dot{\gamma} = (\gamma_0 \omega) \cos \omega t$



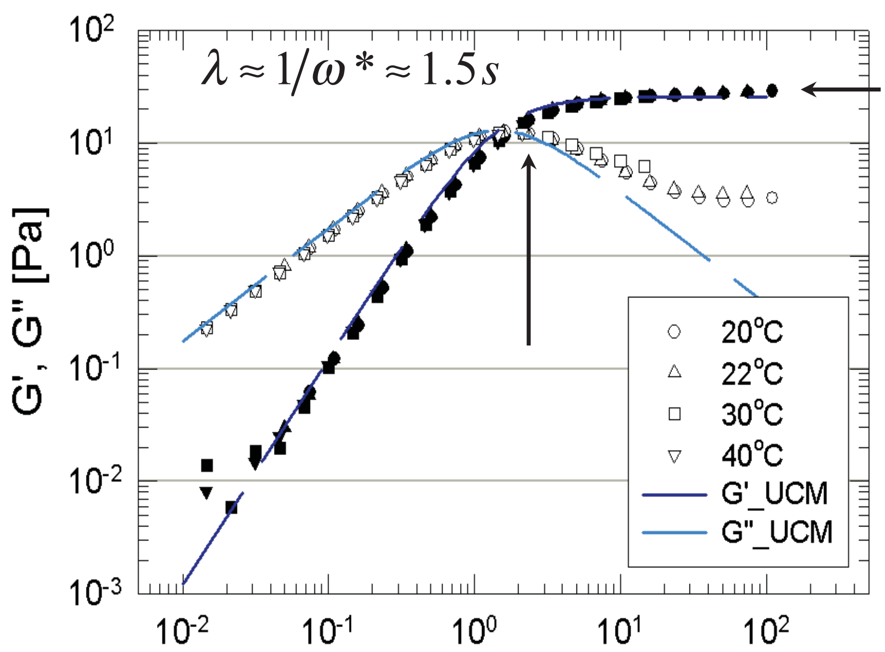
Output:

$$\tau = \gamma_0 \left[\underbrace{G''(\omega)\cos(\omega t)}_{\textit{Loss}} + \underbrace{G'(\omega)\sin(\omega t)}_{\textit{Storage}} \right]$$

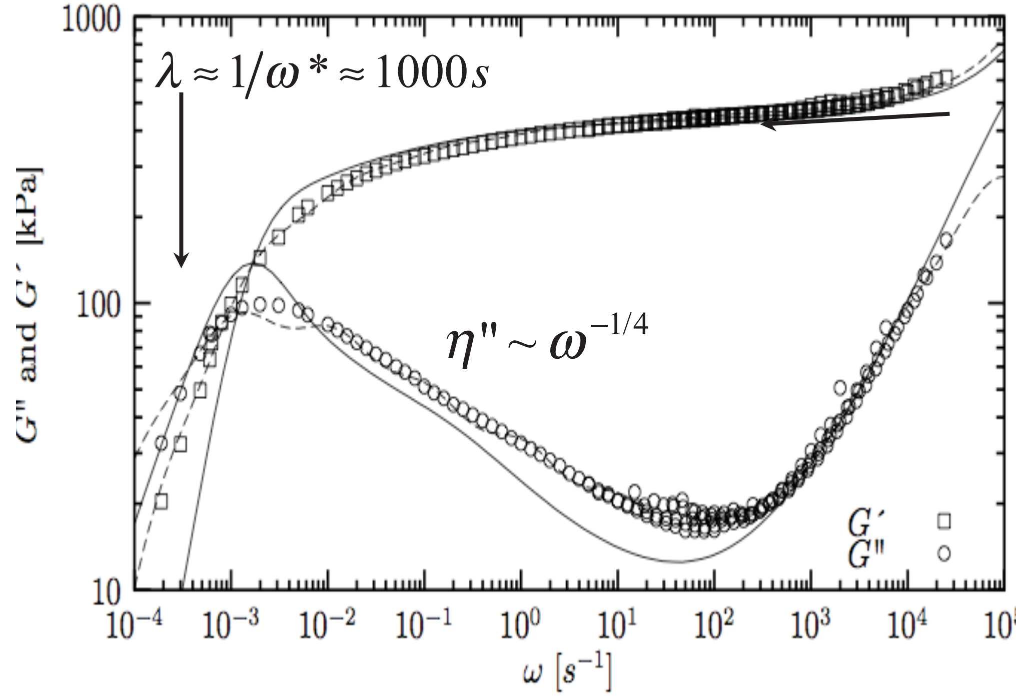
Maxwell Model

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

$$De = \lambda\omega \sim \frac{G'(\omega)}{G''(\omega)} \sim \frac{\textit{storage}}{\textit{dissipation}}$$



Wormy Micelles

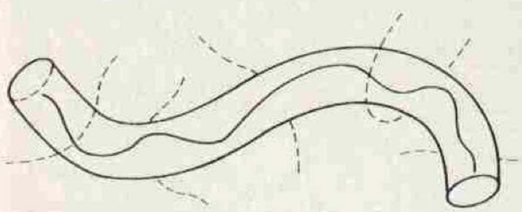


Entangled melt

Entangled Polymer Melts: *Reptation*

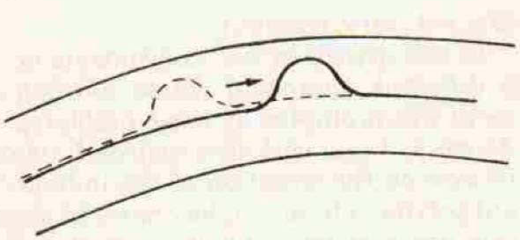
P.G. DeGennes
"Entangled Polymers", *Phys. Today* 1983

In a polymer melt, the chains can change their shape, and move, by local Brownian motion, but they cannot intersect each other. Sam Edwards was the first to point out[4] that under these conditions, each chain is confined to a "tube," as this schematic diagram shows (and the photograph on the previous page suggests).



The diameter of this tube is related to the minimum size of a knot, and is of order 50 Å for conventional melts.

If we follow one chain in the melt—call it a "test chain"—we will see it moving by snake-like motion inside its own tube.



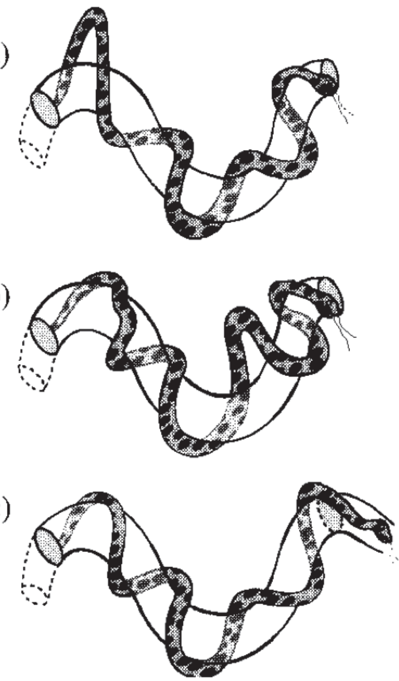


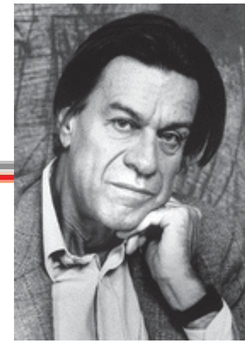
Fig. 9.1
Reptation steps: (a) formation of a loop at the tail of the snake and elimination of the tail segment of the confining tube; (b) propagation of the loop along the contour of the tube; (c) release of the loop at the head of the snake and formation of a new section of the confining tube.

Pierre-Gilles de Gennes (1932-2007)
Nobel Prize 1991
"The Founding Father of Soft Matter"

https://web.archive.org/web/20130621152528/http://www.rsc.org/chemistryworld/Issues/2007/July2007/PierreGillesDeGennes.asp

Reptare: to wriggle like a snake

Entangled Polymers



P.G. DeGennes

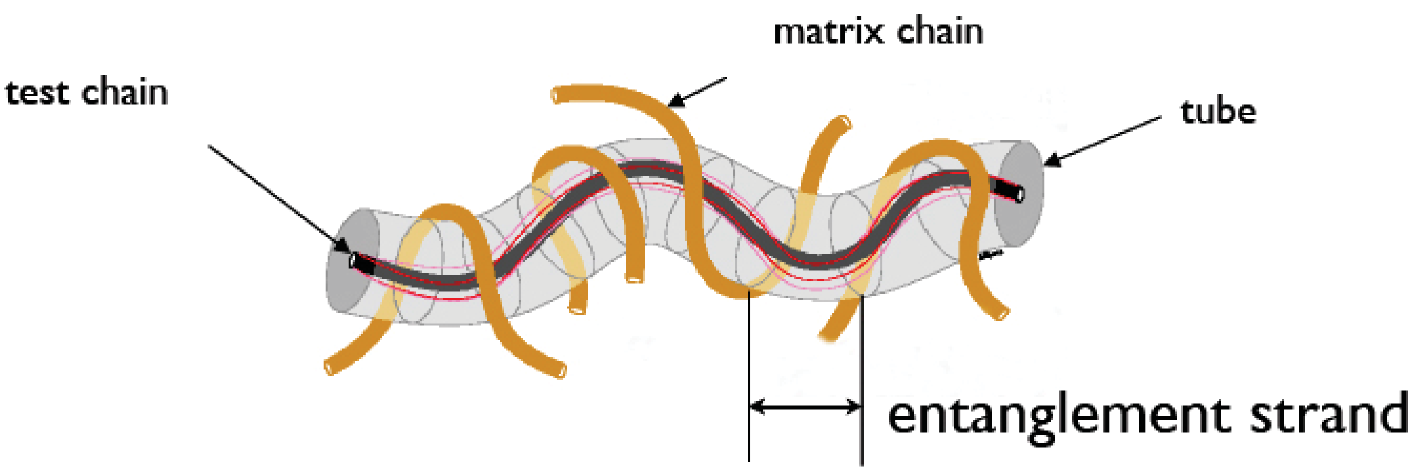
M. Doi & S.F. Edwards

Molecular Dynamics

https://www.youtube.com/watch?v=Y7XAroFgVQs

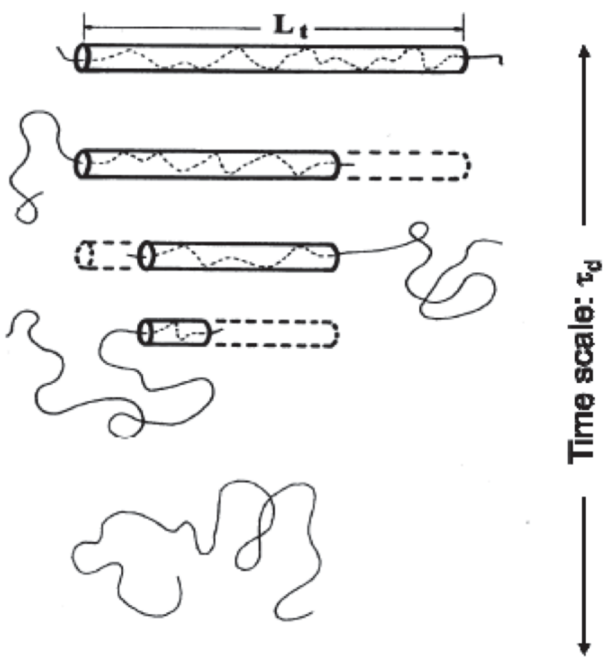
LAMMPS (Open Source)

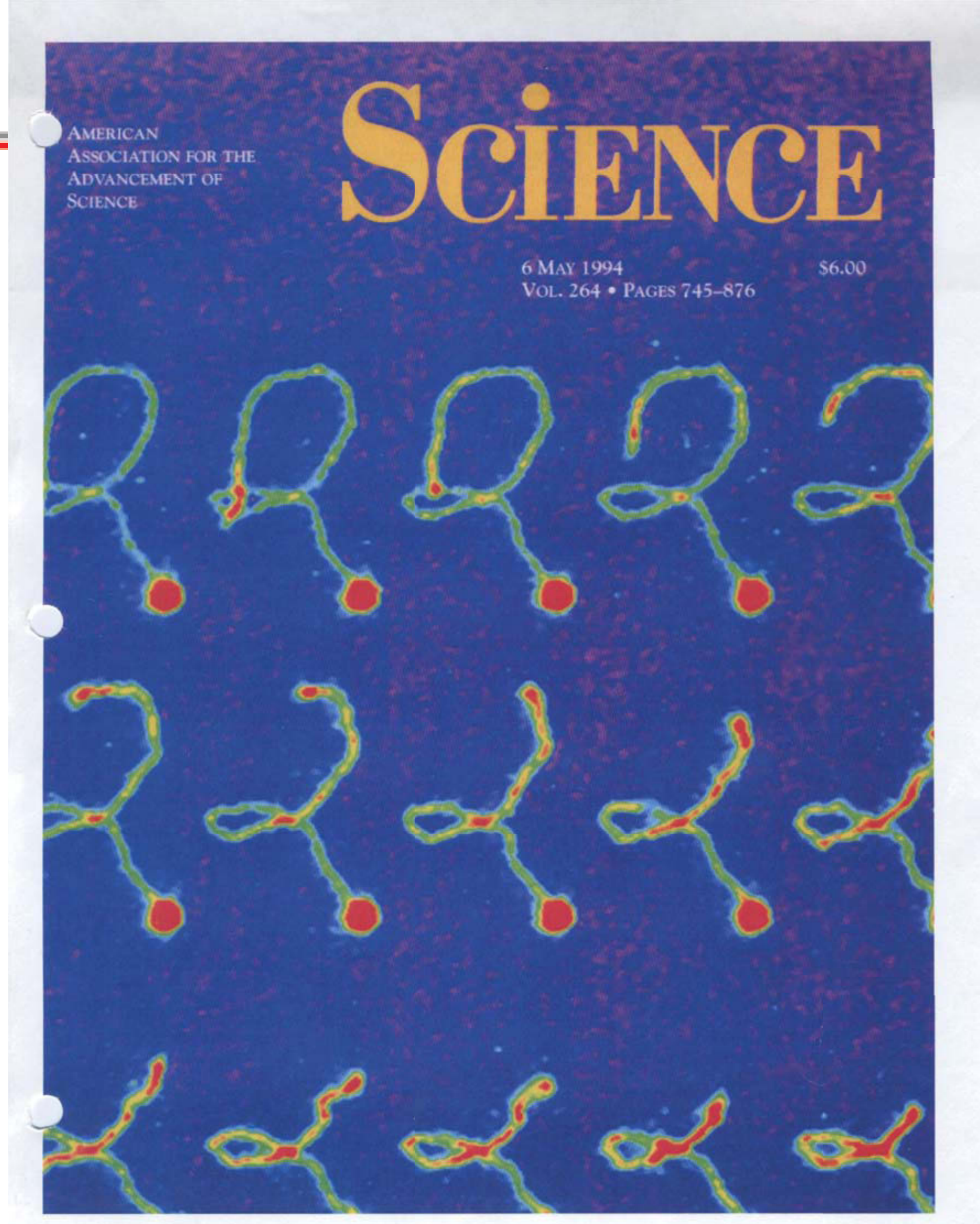
https://www.youtube.com/watch?v=oB79II_63rM



Direct Observation

Perkins, Smith, Chu, Science 1994





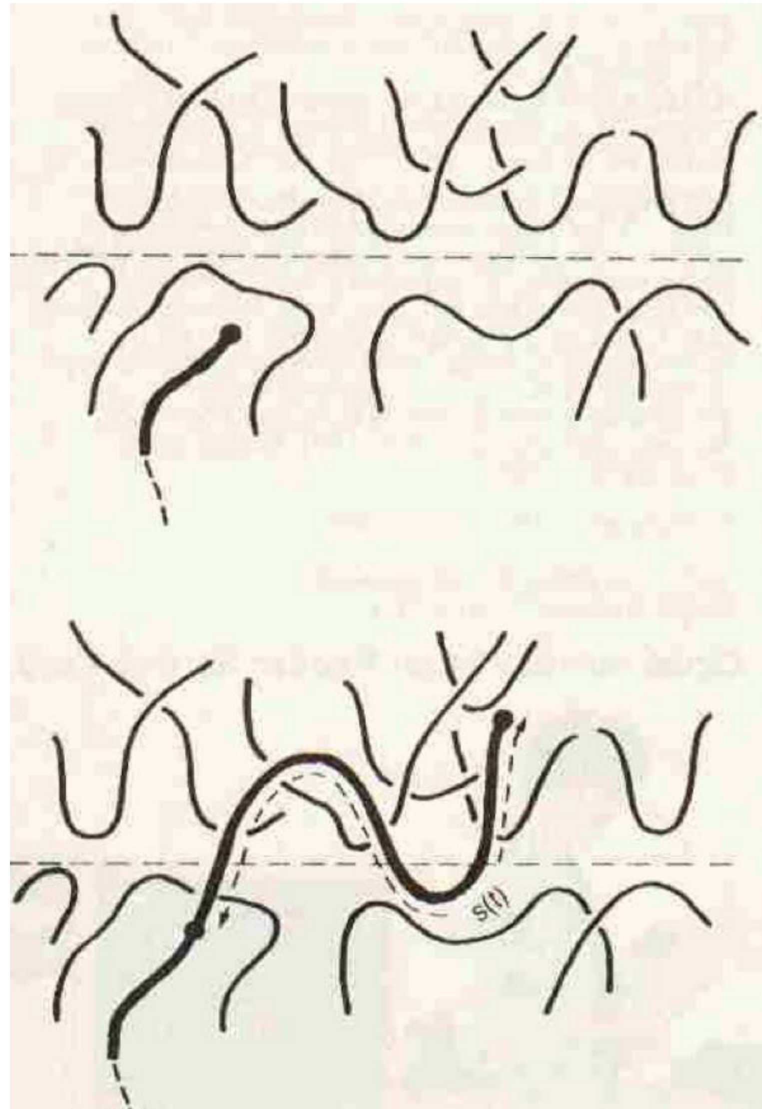
Indirect Observation: "Polymer Welding"

Polymer–polymer welding. One can weld a pair of polymer blocks by bringing them into close contact and maintaining them slightly above the glass transition temperature for a certain time t. Interdiffusion takes place, and the junction develops mechanical strength. The essential difference with the preceding case is that for the purposes of welding, the interesting time interval t is *smaller* than the reptation time τ. In other words, the thickness of the mixing layer is smaller than the size of a coil.

In some experiments[15] carried out in Lausanne, Switzerland, researchers monitored the state of the mixing layer by fracturing the junction and measuring the fracture energy per unit area, G, as a function of the welding time. Experimentally $G(t)$ saturates after one reptation time τ, and increases at earlier times according to

$$G \simeq G_{\max} (t/\tau)^{1/2} \qquad (t < \tau)$$

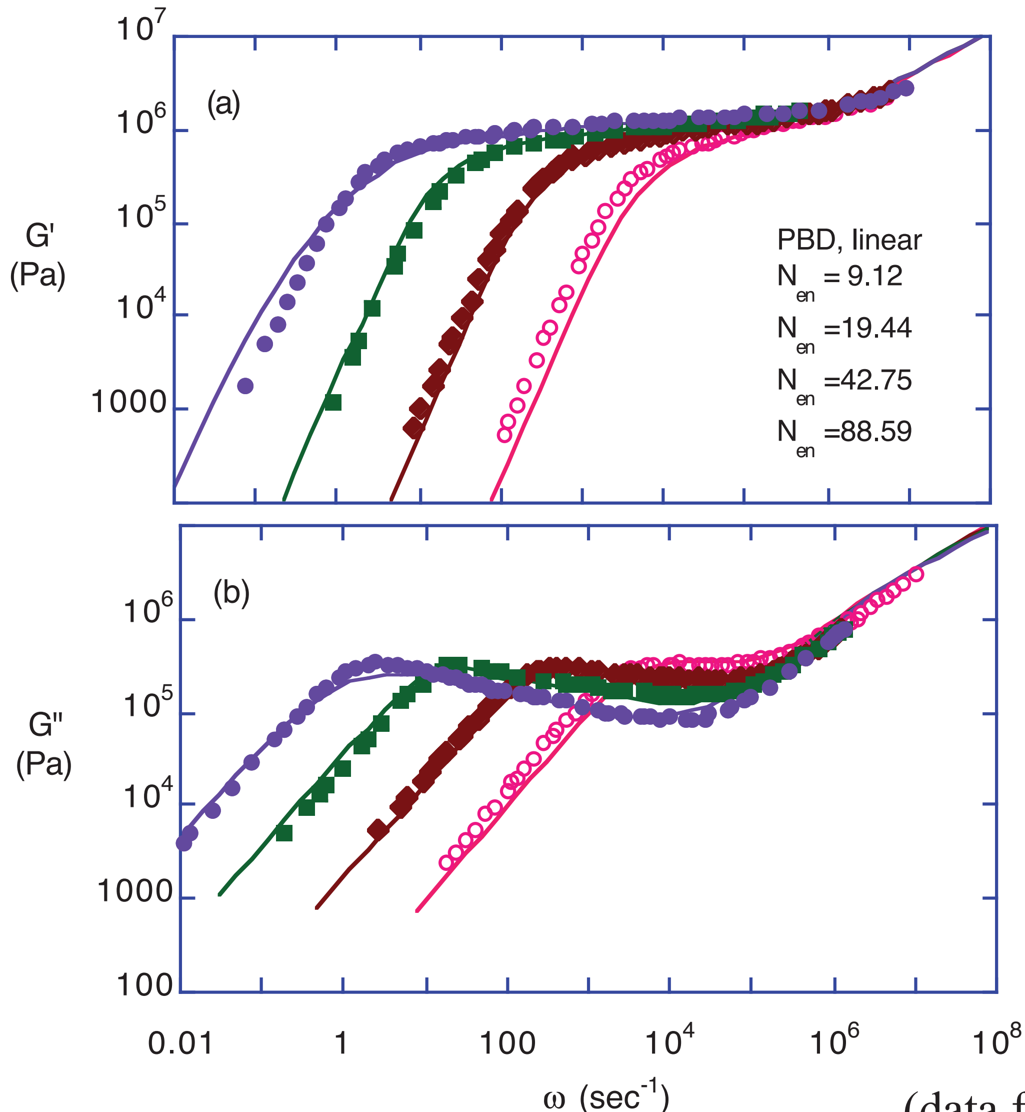
The following sketch suggests a microscopic picture of the welding process.



P.G. DeGennes "Entangled Polymers", Phys. Today 1983

Reptation Model Fit

- Monodisperse Polyisoprene (Baumgaertel & H. Winter, U.Mass, 1992)



Rubbery Modulus (G_N) almost unchanged

$M_e \sim 4{,}800$ g/mol

$M_w = 20{,}000$ to $300{,}000$

$$\tau_d \propto M_w^{3.4}$$

(data from Baumgaertel et al. 1992)

Recent Developments

- Contour Length Fluctuations (CLF); reptation (curvilinear diffusion) along a tube of f uctuating length
  - Kuzuu & Doi, 1983
  - Milner & McLeish, 1998 PRL **81**(3).

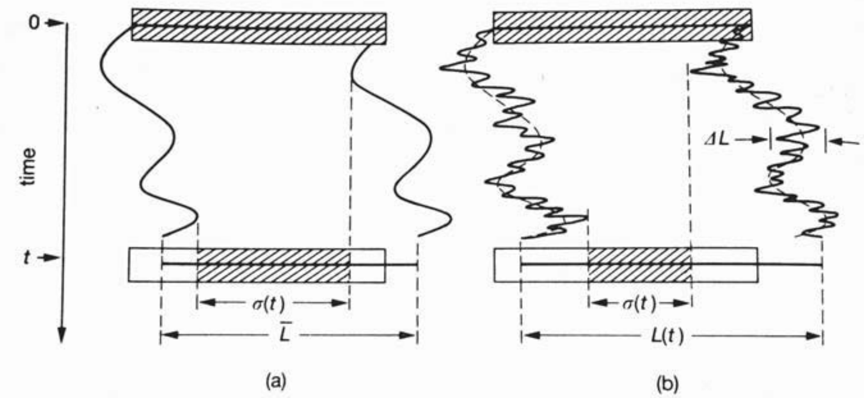


Fig. 6.9. The Brownian motion of a primitive chain with (a) fixed contour length, and (b) fluctuating contour length. The oblique lines denote the region that has not been reached by either end of the primitive chain. Obviously the length of this region $\sigma(t)$ decreases faster in (b) than in (a). Reproduced from ref. 15.

Reptation and Contour-Length Fluctuations in Melts of Linear Polymers

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(Received 14 January 1998)

We present an analytical theory of stress relaxation in monodisperse linear polymer melts that contains contributions from both reptation and contour-length fluctuations, modeled as in our previous work on arm retraction in star polymers. Our approach resolves two long-standing problems with reptation theory: it predicts a zero-shear viscosity η scaling as $\eta \sim N^{3.4}$ over a broad range in chain length N before reaching an asymptotic N^3 dependence, and a power law $\omega^{-\alpha}$ in the dynamic loss modulus $G''(\omega)$ with $0 < \alpha < 1/4$ depending on chain length, in agreement with experiment. [S0031-9007(98)06599-5]

CLF Results

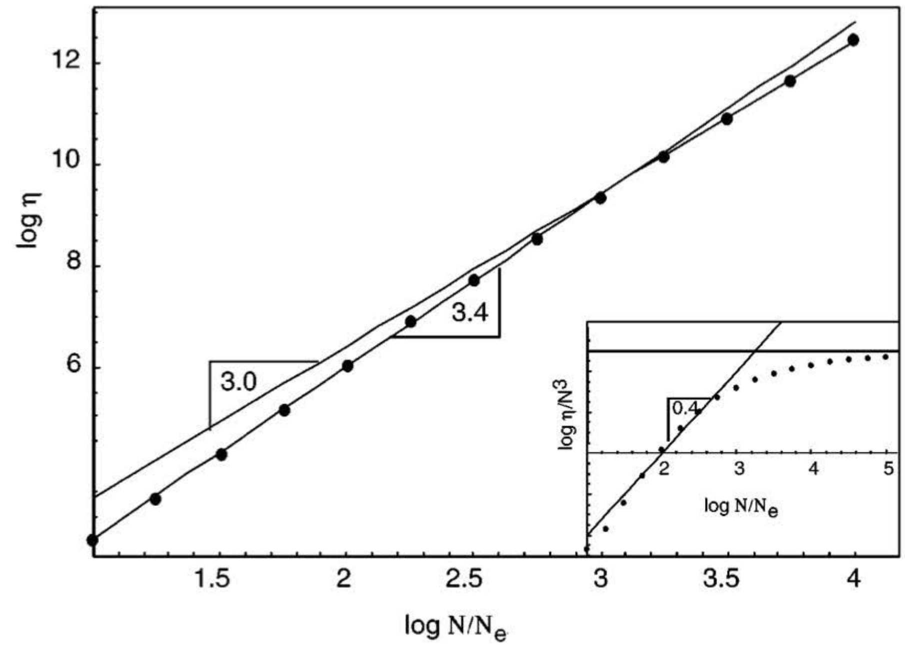
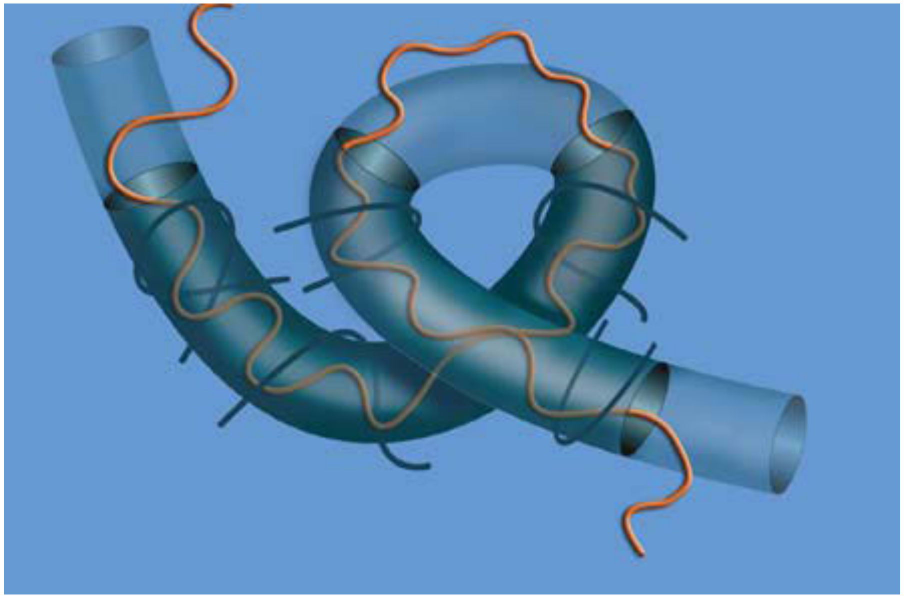


FIG. 1. Predicted viscosity η as a function of chain length N/N_e shows without adjustable parameters an effective exponent of 3.4. Plotted as η/N^3 versus N/N_e, crossover occurs at around $N/N_e = 200$, as in experiment [15].

$$\eta \sim N^{3.4} \text{ or } \eta \sim (N/N_e)^{3.4} = Z^{3.4}$$



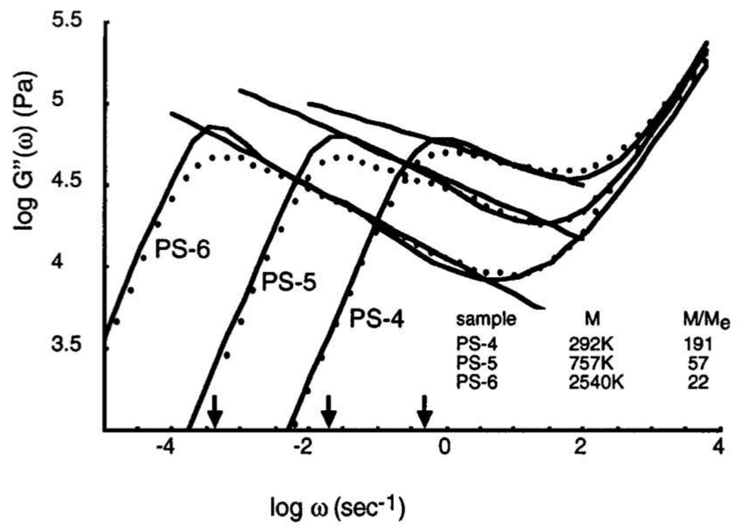
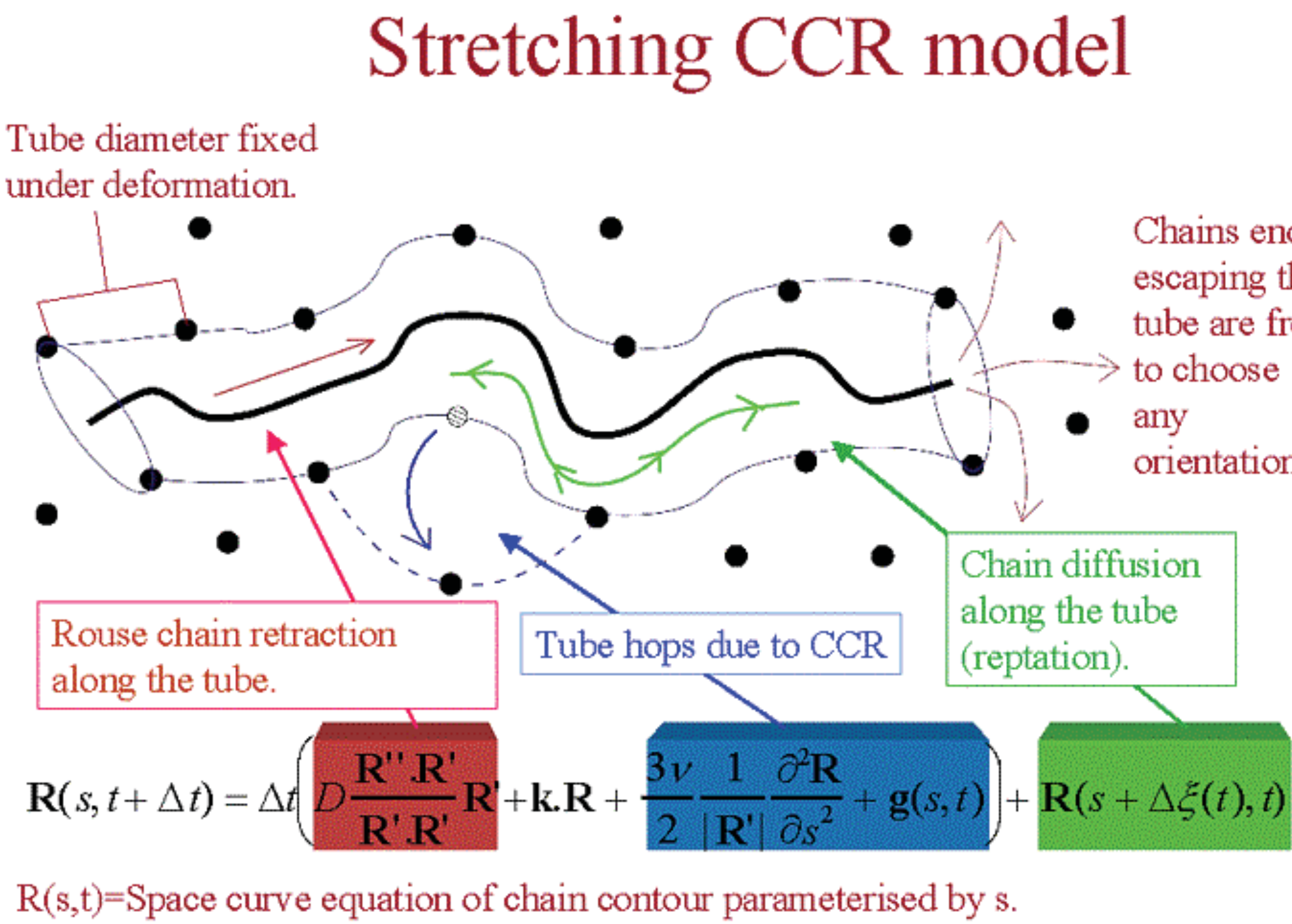


FIG. 2. Computed loss modulus $G''(\omega)$ compared to data of Ref. [16] for narrow-MWD polystyrene melts. A common value of τ_e and G has been taken for the three curves. The variation in slope above $\omega\tau_d = 1$ results from "contamination" of the $-1/4$ behavior by Rouse modes inside the tube. Arrows mark $\omega\tau_d = 1$. (Lines are guides to the eye of slope 1/8, 1/5.5, 1/4.5).

"Fully Loaded Model"

- Reptation + Contour Length Fluctuations + Convective Constraint Release + Finite Extensibility (+ Anisotropic Tube Deformation!)
- Marrucci & coworkers; McLeish & coworkers"Rolie-Poly" Model;



The Graessley Diagram

- W. Graessley, *Polymer*, **21** (1980); pp.258-262
- All polymeric f uids can be characterized by their location on a diagram representing effects of (c, M_w)
- Solvent quality exponent, ν

Ideal Gaussian chain (random walk) $\nu = 1/2$

−1.25 to −2

$$c^* \sim M_w^{1-3\nu} \Leftrightarrow M_w \sim (c^*)^{1/(1-3\nu)}$$

$$c^\infty \sim M_w^{-2} \Leftrightarrow M_w \sim (c^\infty)^{-1/2}$$