Molecular models for the rheology of polymeric networks

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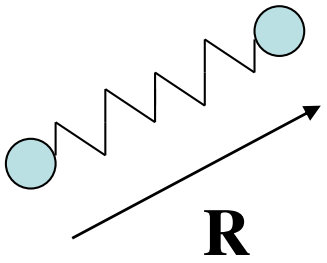
Let’s start from what we did in Crete last September

The simplest molecular model of polymer viscoelasticity. The "dumbbell" model



Two friction beads connected by a spring

End-to-end vector distribution function: $\Psi(\mathbf{R}, t)$

$$\frac{\partial \psi}{\partial t} = D \frac{\partial}{\partial \mathbf{R}} \cdot \left[\frac{\partial \psi}{\partial \mathbf{R}} + \psi \frac{\partial}{\partial \mathbf{R}} \left(\frac{E}{kT} \right) \right] - \frac{\partial}{\partial \mathbf{R}} \cdot \left(\psi \mathbf{k} \cdot \mathbf{R} \right)$$

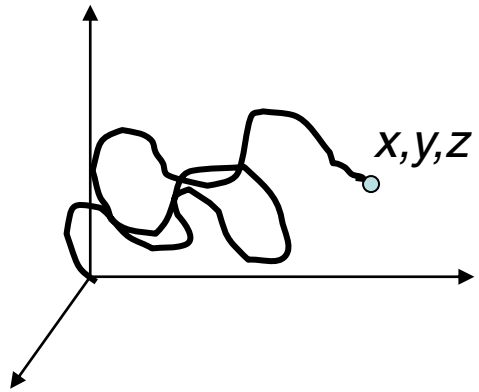
diffusion $D = kT/\zeta$

spring

convection due to velocity gradient **k**

Smoluchowski equation or Fokker-Planck equation

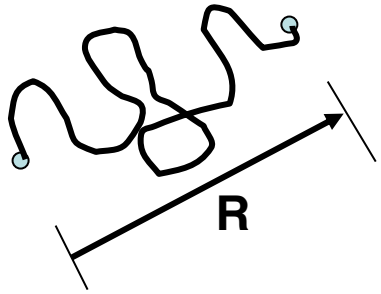
Elastic force in a Gaussian chain



$$P(x,y,z) = C\exp\left(-\frac{3}{2}\frac{x^2+y^2+z^2}{R_0^2}\right)$$

$$S = k\ln P = -\frac{3}{2}k\frac{x^2+y^2+z^2}{R_0^2} + k\ln C = -\frac{3}{2}k\frac{\mathbf{R}^2}{R_0^2} + k\ln C$$

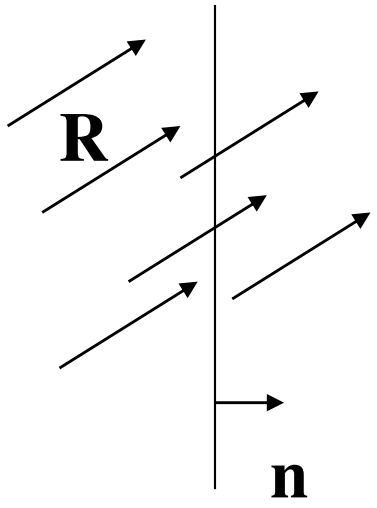
$$E = U - TS;\quad \mathbf{F} = -\frac{\partial E}{\partial \mathbf{R}} = T\frac{\partial S}{\partial \mathbf{R}}$$



$$\mathbf{F} = -\frac{3kT}{R_0^2}\mathbf{R}$$

The stress tensor **T** (for dumbbells)

Assume temporarily that all chains have the same end-to-end vector **R**



If ν is number of chain per unit volume, chains being cut per unit area are $\nu(\mathbf{R}\cdot\mathbf{n})$

If **F** is the force in each spring, the total force across unit area is $\nu\mathbf{FR}\cdot\mathbf{n}$. Hence:

$$\mathbf{T} = \nu\mathbf{FR}$$

In reality, because of distribution, it is: $\mathbf{T} = \nu \langle \mathbf{FR} \rangle$

Linear force: $\mathbf{F}=(3kT/R_0^2)\mathbf{R}$

$$\mathbf{T} = \frac{3\nu kT}{R_0^2}\langle \mathbf{RR} \rangle$$

$$\langle \mathbf{RR} \rangle = \int \mathbf{RR}\psi(\mathbf{R})d^3R$$

where $\psi(\mathbf{R})$ is the distribution function of end-to-end vector

At equilibrium, $\psi(\mathbf{R})$ is isotropic and Gaussian.

Dynamic problem = find $\psi(\mathbf{R}, t)$, from which $<\mathbf{RR}>$ as a function of time t, hence $\mathbf{T}(t)$

Recall that for a linear force: $\mathbf{T} = \frac{3\nu kT}{R_0^2}\langle \mathbf{RR} \rangle$

where: $\langle \mathbf{RR} \rangle = \int \mathbf{RR}\psi(\mathbf{R}) d^3R$

$$\frac{\partial \psi}{\partial t} = D\frac{\partial}{\partial \mathbf{R}} \cdot \left[\frac{\partial \psi}{\partial \mathbf{R}} + \psi \frac{\partial}{\partial \mathbf{R}} \left(\frac{E}{kT} \right) \right] - \frac{\partial}{\partial \mathbf{R}} \cdot (\psi \mathbf{k} \cdot \mathbf{R})$$

Multiplying **RR** to all terms, and integrating over **R** space

$$\frac{d}{dt}\langle \mathbf{RR} \rangle = 2D\mathbf{I} - \frac{6D}{R_0^2}\langle \mathbf{RR} \rangle + \mathbf{k} \cdot \langle \mathbf{RR} \rangle + \langle \mathbf{RR} \rangle \cdot \mathbf{k}^T$$

Constitutive Equation

Call relaxation time $\tau = \dfrac{R_0^2}{6D} \propto M^2$

Previous equation is rewritten as

$$\tau \frac{d}{dt}\langle \mathbf{RR} \rangle = \frac{R_0^2}{3}\mathbf{I} - \langle \mathbf{RR} \rangle + \tau\, \mathbf{k} \cdot \langle \mathbf{RR} \rangle + \langle \mathbf{RR} \rangle \cdot \tau\, \mathbf{k}^T$$

showing exponential relaxation to equilibrium value $\langle \mathbf{RR} \rangle_{eq} = \dfrac{R_0^2}{3}\mathbf{I}$

Equivalently, in terms of stress $\mathbf{T}$

$$\tau \frac{d\mathbf{T}}{dt} = \nu kT\, \mathbf{I} - \mathbf{T} + \tau\, \mathbf{k} \cdot \mathbf{T} + \mathbf{T} \cdot \tau\, \mathbf{k}^T$$

Maxwell equation

Now let's play with the Maxwell equation

Shear flows

$$\mathbf{k} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{T} = \begin{pmatrix} T_{11} & \sigma & 0 \\ \sigma & T_{22} & 0 \\ 0 & 0 & T_{33} \end{pmatrix} \qquad \mathbf{k}\bullet\mathbf{T} = \begin{pmatrix} \dot{\gamma}\sigma & \dot{\gamma}T_{22} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{T}\bullet\mathbf{k}^T = \begin{pmatrix} \dot{\gamma}\sigma & 0 & 0 \\ \dot{\gamma}T_{22} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$T_{22} = T_{33} = equilibrium\ value = \nu kT$$

$$\tau \frac{d\sigma}{dt} = -\sigma + \tau\dot{\gamma}T_{22} = -\sigma + \nu kT\tau\dot{\gamma}$$

Start up of flow at a fixed shear rate: $\sigma(t) = \nu kT\tau\dot{\gamma}\left(1 - e^{-t/\tau}\right)$

$t \to 0$ $\qquad \sigma(t) = \nu kT\dot{\gamma}t = \nu kT\gamma = G\gamma$

$t \to \infty$ $\qquad \sigma = \nu kT\tau\dot{\gamma} = \eta\dot{\gamma}$

Tangential component σ behaves like in linear viscoelasticity

Normal stress differences in steady shear flows

$$0 = \nu kT - T_{11} + 2\tau\dot{\gamma}\sigma \qquad T_{11} - \nu kT = 2\tau\dot{\gamma}\sigma = 2\tau\eta\dot{\gamma}^2$$

$$N_1 = 2\tau\eta\dot{\gamma}^2 \qquad N_2 = 0$$

Uniaxial Elongational Flows

$$\mathbf{k} = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}/2 \end{pmatrix} \qquad \mathbf{T} = \begin{pmatrix} T_{11} & 0 & 0 \\ 0 & T_{22} & 0 \\ 0 & 0 & T_{33} \end{pmatrix} \qquad \mathbf{k}\bullet\mathbf{T} = \mathbf{T}\bullet\mathbf{k}^T = \begin{pmatrix} \dot{\varepsilon}T_{11} & 0 & 0 \\ 0 & -\dot{\varepsilon}T_{22}/2 & 0 \\ 0 & 0 & -\dot{\varepsilon}T_{33}/2 \end{pmatrix}$$

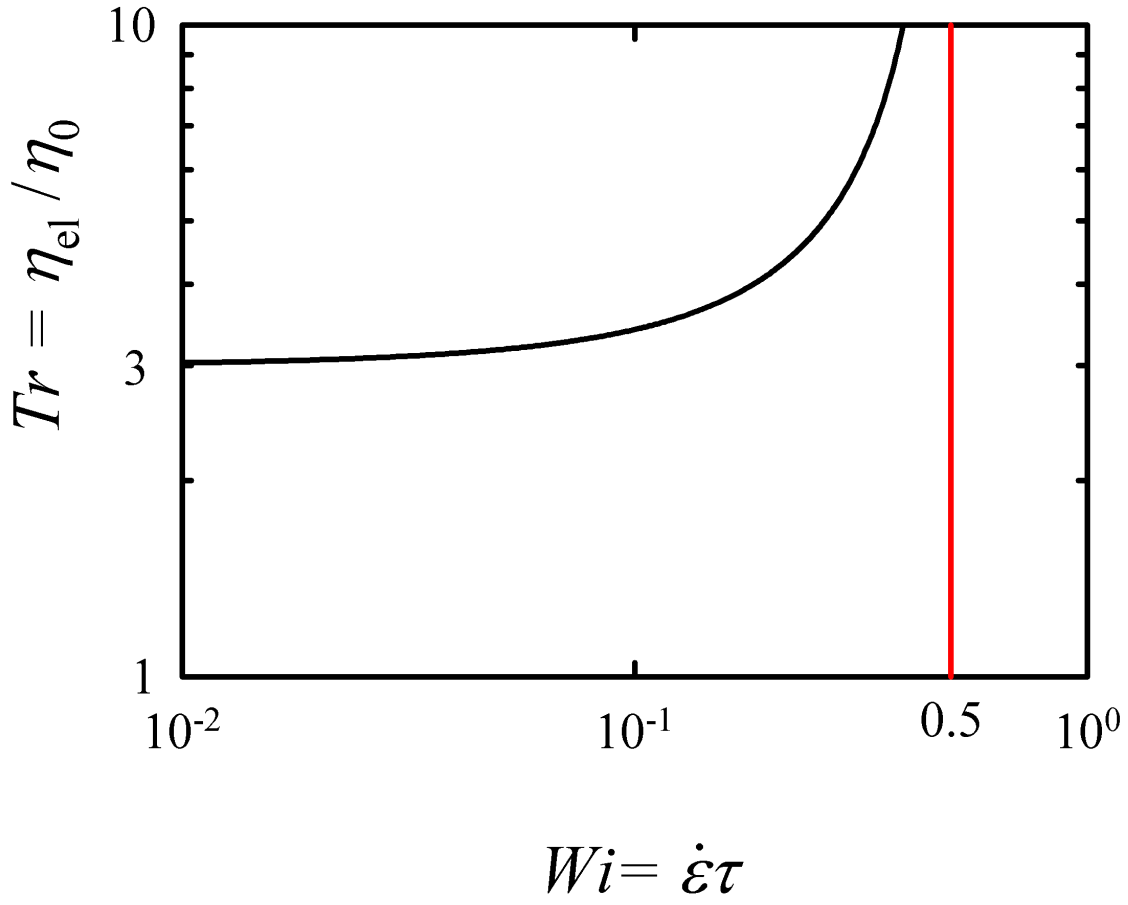
$$\tau\frac{dT_{11}}{dt} = \nu kT - T_{11} + 2\tau\dot{\varepsilon}T_{11} = \nu kT - \left(1 - 2\tau\dot{\varepsilon}\right)T_{11}$$

At steady state: $\eta_{el} = \dfrac{T_{11} - T_{22}}{\dot{\varepsilon}} = \dfrac{3}{(1 + \dot{\varepsilon}\tau)(1 - 2\dot{\varepsilon}\tau)}$

if $\tau\dot{\varepsilon} < 1/2$ T_{11} and η_{el} approaches a steady state

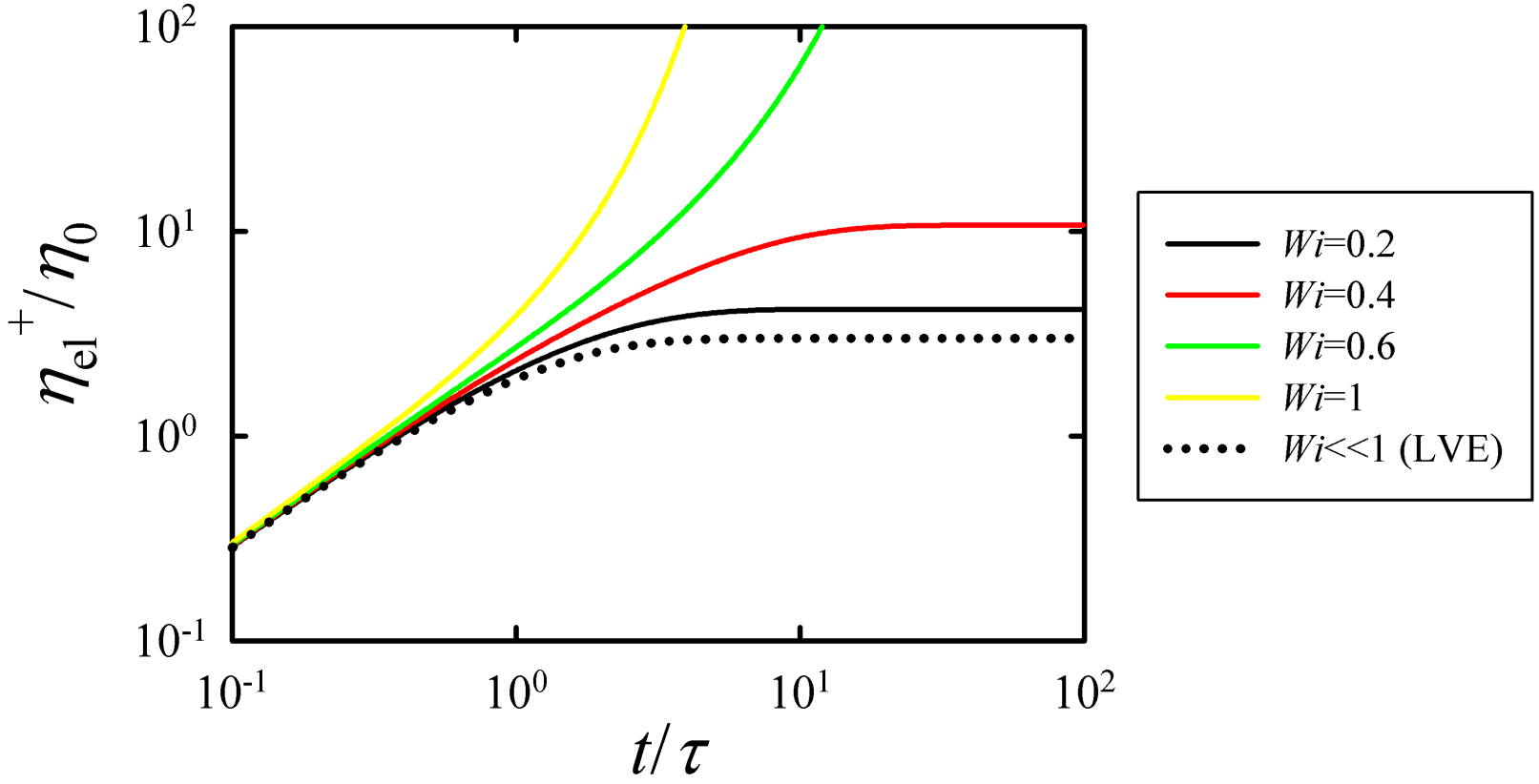
$\tau\dot{\varepsilon} \geq 1/2$ they grow without bounds

Uniaxial elongational viscosity at steady state



Extension thickening, but excessive (divergence) due to infinitely extensible spring

Transient startup



Strain hardening: viscosity higher than in the LVE limit

Conclusions on dumbbell model

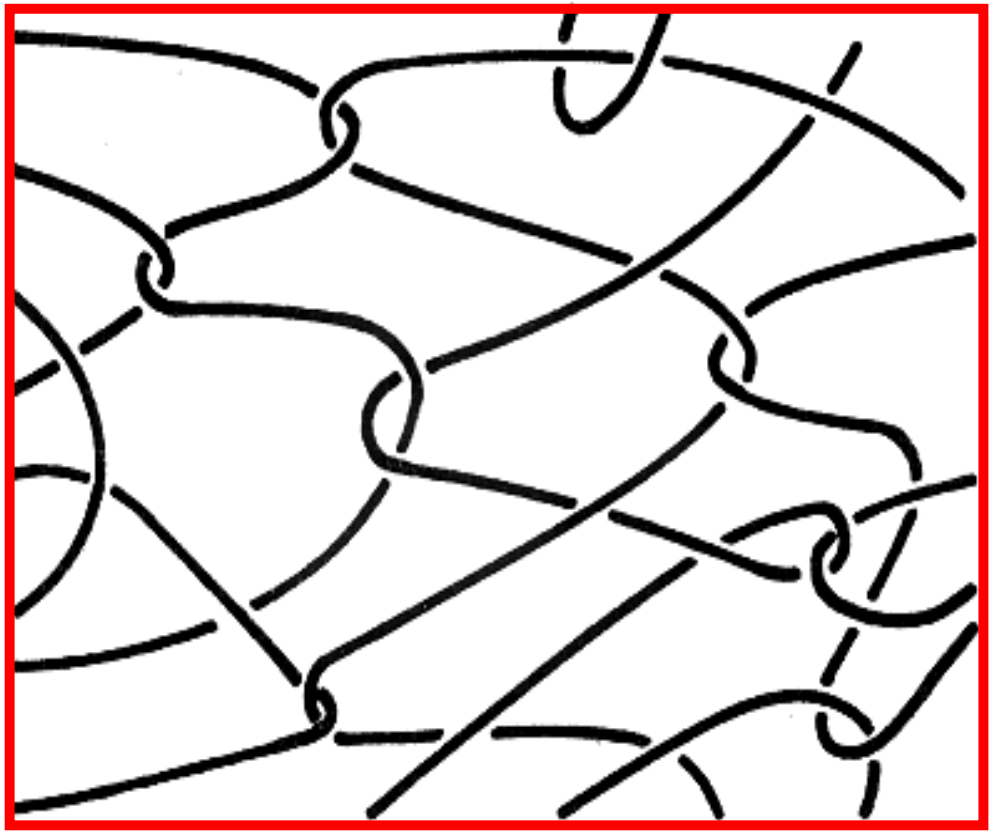
positive

- Normal stresses in shear flows
- Elongational strain hardening
- With a nonlinear force law, predicts shear thinning

negative

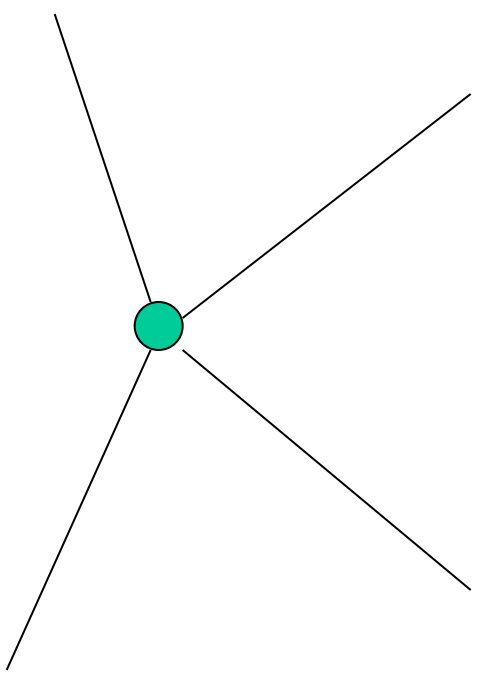
- Shear thinning should be predicted also for Gaussian chains
- No prediction of maxima in shear start up
- In any event, polymers show more than one relaxation time
- More complex models are needed

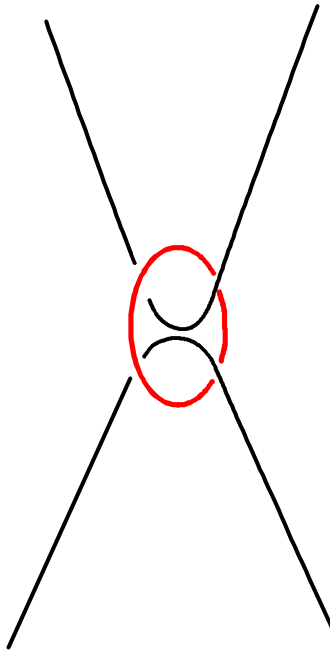
Polymeric networks



Permanent *vs.* impermanent interactions

cross-links





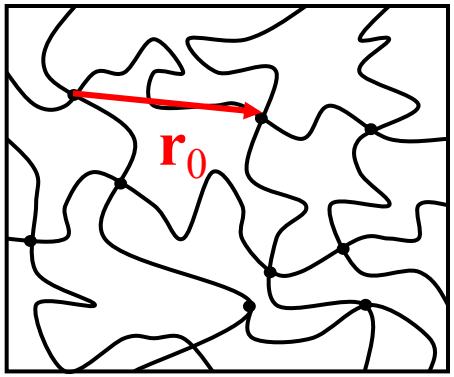
entanglements,
…

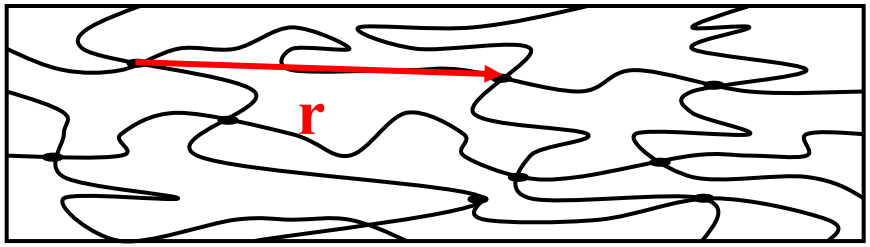
Monomers can slide through the ‘sliplink’

Rubber elasticity

Neo-Hookean constitutive equation

The simplest example: Rubber elasticity





Deformed state

Affinity assumption: Chain end-to-end vectors change according to macroscopic deformation:

$$\mathbf{r} = \mathbf{E} \cdot \mathbf{r}_0$$

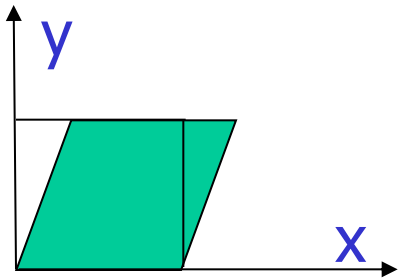
where **E** is deformation gradient tensor

Deformation gradient tensor **E**

$$\|E\| = \begin{vmatrix} \partial x/\partial x_0 & \partial x/\partial y_0 & \partial x/\partial z_0 \\ \partial y/\partial x_0 & \partial y/\partial y_0 & \partial y/\partial z_0 \\ \partial z/\partial x_0 & \partial z/\partial y_0 & \partial z/\partial z_0 \end{vmatrix}$$

For example, for a shear deformation, coordinates of a material point change as:

$$x = x_0 + \gamma\, y_0$$
$$y = y_0$$
$$z = z_0$$



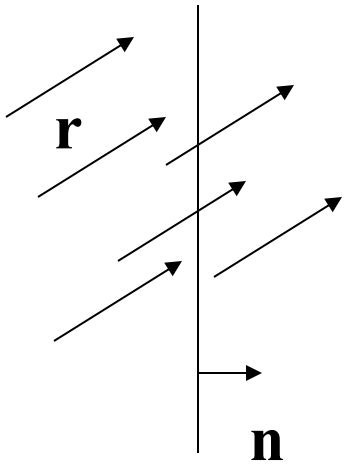
Hence, the matrix of **E** is:

$$\|E\| = \begin{vmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

Tensor **E** reduces to the unity (or identity) tensor **I** in the absence of deformation.

The stress tensor **T**

Assume temporarily that all chains have the same end-to-end vector **r**



If ν is number of chain per unit volume, the chains cut per unit area are $\nu(\mathbf{r}\cdot\mathbf{n})$

If **F** is the force in each spring, the total force across unit area is $\nu\mathbf{F}\mathbf{r}\cdot\mathbf{n}$. Hence:

$$\mathbf{T} = \nu\mathbf{F}\mathbf{r}$$

In reality, because of distribution, it is: $\mathbf{T} = \nu \langle \mathbf{F}\mathbf{r} \rangle$

Gaussian chains have a linear force **F**

$$\mathbf{F} = \frac{3kT}{nb^2}\mathbf{r}$$

n is monomer number

b is monomer length

Hence the average for the stress becomes:

$$\mathbf{T} = 3\nu kT\left\langle \frac{\mathbf{rr}}{nb^2} \right\rangle$$

Recalling the definition of deformation tensor **E**, we can write

$$\left\langle \frac{\mathbf{rr}}{nb^2} \right\rangle = \left\langle \frac{1}{nb^2}\mathbf{E}\cdot\mathbf{r}_0\mathbf{E}\cdot\mathbf{r}_0 \right\rangle = \left\langle \frac{1}{nb^2}\mathbf{E}\cdot\mathbf{r}_0\mathbf{r}_0\cdot\mathbf{E}^{\dagger} \right\rangle = \mathbf{E}\cdot\left\langle \frac{\mathbf{r}_0\mathbf{r}_0}{nb^2} \right\rangle\cdot\mathbf{E}^{\dagger} = \frac{1}{3}\mathbf{E}\cdot\mathbf{E}^{\dagger}$$

where we have used the fact that in the undeformed rubber the tensor $\langle \mathbf{r}_0\,\mathbf{r}_0 \rangle$ is isotropic, and given by

$$\begin{pmatrix} \frac{nb^2}{3} & 0 & 0 \\ 0 & \frac{nb^2}{3} & 0 \\ 0 & 0 & \frac{nb^2}{3} \end{pmatrix}$$

Replacing <**rr**> into the expression for the stress **T** we obtain the simple result:

$$\mathbf{T} = \nu kT\, \mathbf{E}\cdot\mathbf{E}^{\dagger} = G\,\mathbf{B} \qquad (1)$$

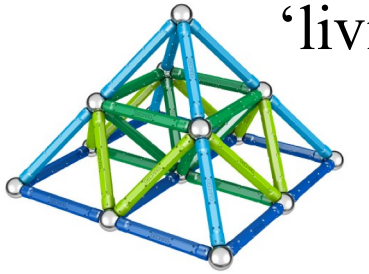
where G=νkT is the shear modulus, and **B**

$$\mathbf{B} = \mathbf{E}\cdot\mathbf{E}^{\dagger}$$

is a quadratic deformation tensor called Finger tensor. For a shear deformation we find

$$|B| = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\cdot\begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Eq.(1) is the constitutive equation of the ideal rubber, also called neo-Hookean, which predicts nonlinear effects. For example we find a normal force in the sheared rubber, quadratic in the shear deformation γ.



Impermanent networks

Let's assume that a rubber-like network is impermanent, i.e., that chains occasionally detach, and then reattach to the network. If:

1. Chains attach and reattach stochastically with a mean frequency $1/\tau$
2. Such renewal frequency remains unaffected when chains are stretched
3. Chains reattaching to the network have equilibrium conformations

Then, after a step deformation **E** at time 0, instantly creating the stress **T**=G**B** as in a rubber, the stress will subsequently decay in time as:

$$\mathbf{T}(t) - G\mathbf{I} = G\exp(-t/\tau)(\mathbf{B} - \mathbf{I}) = G(t)(\mathbf{B} - \mathbf{I}) \qquad (1)$$

The exponential term gives the fraction of chain segments that at time t have not yet detached from the network. G(t) is called "relaxation modulus", and in general is not given by a single negative exponential, but by a weighted sum of different exponentials.

For a general flow or deformation history, Eq.(1) becomes

$$\mathbf{T}(t) = \frac{G}{\tau}\int_{-\infty}^{t} \exp\left(-\frac{t-t'}{\tau}\right)\mathbf{B}(t,t')\,dt' \qquad (2)$$

Where does Eq. (2) come from?

In Eq.(2), **B**(t,t') is the Finger tensor between time t' in the past and present time t, and is representative of the "history of deformation".

The constitutive equation, Eq.(2), is explained as follows. In a time interval dt', a fraction dt'/τ of chains is renewed. If such event has occurred at time t' in the past, the fraction of surviving chains at the present time t is:

$$\frac{dt'}{\tau}\exp(-\frac{t-t'}{\tau})$$

Those chains carry a deformation **B**(t,t'). Now, if all chains of the network were equally deformed, the stress **T** would be G**B**(t,t') like in a permanent rubber network. But since only the above fraction of chains carries the strain **B**(t,t'), their contribution to the stress is

$$\frac{dt'}{\tau}\exp(-\frac{t-t'}{\tau})\,G\mathbf{B}\left(t,t'\right)$$

from which Eq.(2) is obtained by summing over all contributions from past reattachment events.

Uniaxial extensional flow

Eq.(2) predicts strong nonlinearities in fast elongational flows. The velocity field in uniaxial extensional flow is written as

$$v_x = \dot{\varepsilon}\, x, \qquad v_y = -\frac{\dot{\varepsilon}}{2} y, \qquad v_z = -\frac{\dot{\varepsilon}}{2} z$$

But since: $v_x = dx/dt$, $v_y = dy/dt$, $v_z = dz/dt$, the above equations are readily integrated in time. If the stretching rate is constant in time we obtain:

$$x = x_0 \exp\left(\dot{\varepsilon}\, t\right), \qquad y = y_0 \exp\left(-\dot{\varepsilon}\, t/2\right), \qquad z = z_0 \exp\left(-\dot{\varepsilon}\, t/2\right)$$

From which:

$$\left|E(t)\right| = \begin{pmatrix} e^{\dot{\varepsilon} t} & 0 & 0 \\ 0 & e^{-\dot{\varepsilon} t/2} & 0 \\ 0 & 0 & e^{-\dot{\varepsilon} t/2} \end{pmatrix}, \qquad \left|B(t)\right| = \begin{pmatrix} e^{2\dot{\varepsilon} t} & 0 & 0 \\ 0 & e^{-\dot{\varepsilon} t} & 0 \\ 0 & 0 & e^{-\dot{\varepsilon} t} \end{pmatrix}$$

Eq.(2) then gives for the stress component in the stretching direction x :

$$T_{xx}(t) = \frac{G}{\tau}\int_{-\infty}^{t} \exp(-\frac{t-t'}{\tau})\, B_{xx}(t,t')\,dt'$$

$$= \frac{G}{\tau}\int_{-\infty}^{t} \exp\left[-\frac{t-t'}{\tau} + 2\dot{\varepsilon}(t-t')\right]dt'$$

which predicts a divergent behavior if the flow is fast, i.e., if:

$$\tau\dot{\varepsilon} \geq \frac{1}{2}$$

corresponding to a situation where chains are stretched faster than they can detach from the network.

It should be noted that a similar behavior is in fact observed in polymeric liquids in fast elongational flows.

Also note that this result is the same as for the dumbbell model.

Behavior predicted in shear flows is not realistic

In a shear flow with a shear rate constant in time, the Finger strain history is

$$\left|B(t,t')\right| = \begin{pmatrix} 1+\dot{\gamma}^2(t-t')^2 & \dot{\gamma}(t-t') & 0 \\ \dot{\gamma}(t-t') & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Then Eq.(2) gives:

$$T_{xy}(t) = \frac{G}{\tau}\dot{\gamma}\int_{-\infty}^{t}(t-t')\exp(-\frac{t-t'}{\tau})\,dt' = G\tau\dot{\gamma} = \eta\dot{\gamma}$$

$$N_1(t) = T_{xx} - T_{yy} = \frac{G}{\tau}\dot{\gamma}^2\int_{-\infty}^{t}(t-t')^2\exp(-\frac{t-t'}{\tau})\,dt' = 2G\tau^2\dot{\gamma}^2 = \psi_1\dot{\gamma}^2$$

The first of these equations predicts that the viscosity $\eta = G\tau$ remains constant for all values of shear rate, which is unrealistic since most polymeric liquids exhibit a non-Newtonian viscosity.

The second equation predicts that the first normal stress difference N_1 is quadratic in the shear rate, which in practice is true only in slow flows.

Finally, the Finger tensor wrongly predicts a zero second normal stress difference N_2

Here again, we find the same results of the dumbbell model.

Indeed, the C.E. of Eq.(2) is the integral form of the differential C.E. of the dumbbell.

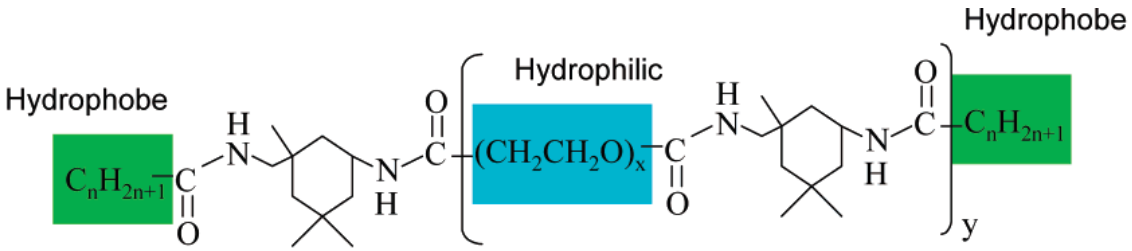
Polymers with special interactions generate impermanent networks

- Polymers (actually co-polymers) may contain special groups that interact strongly
- Very effective viscosizers are copolymers with the structure A-B-A, where B is a water soluble (hydrophilic) long chain, whereas A is a short segment insoluble in water (hydrophobic)
- When the polymer is dissolved in water, segments A tend to segregate by clustering together (polymers with “sticky” points)

One type of associating polymer
(among many others we will not discuss)

Hydrophobically-modified **E**thoxylated **UR**ethane (HEUR)

One variety of HEUR's are "telechelic" polymers, actually 3-block copolymers

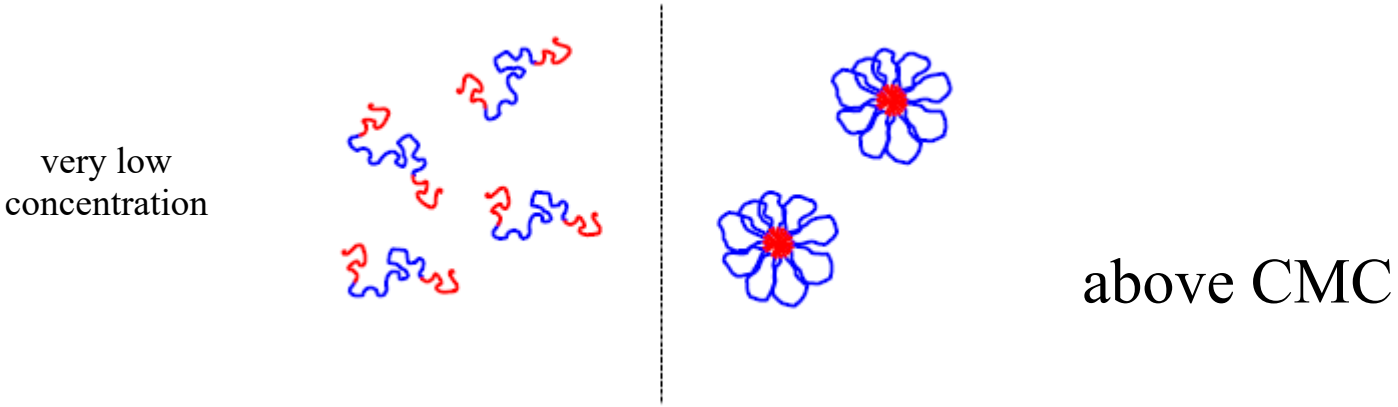


The central block is a relatively *long* water-soluble (hydrophilic) polymer. The end blocks are water-insoluble (hydrophobic) *short* chains.

For reasons that will become apparent, HEUR's are used as *thickeners* in several commercial products, like paints, personal care articles, etc.

HEUR's form micelles

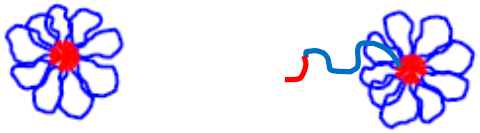
Because the hydrophilic central segment is much longer than the hydrophobic ends, HEUR molecules are soluble in water



At extremely low concentrations molecules will be separate, but above a critical (still very small, a few ppm) concentration (called CMC) they will prefer to form micelles. Each micelle contains a (nearly) fixed number of molecules. All hydrophobic ends are packed together in the micelle *core* (thus excluding water), while the hydrophilic polymers happily float in the water.

The micelles of these telechelic HEUR's are also called *flowers*.

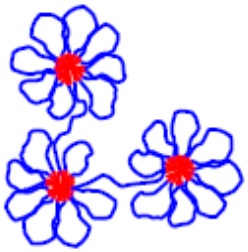
Thermal motion plays a role. Micelles can aggregate.



Because of thermal motion, periodically the hydrophobic ends detach from the micellar core, and move about in the surroundings.

Soon, the floating end will be captured again by the micellar core.

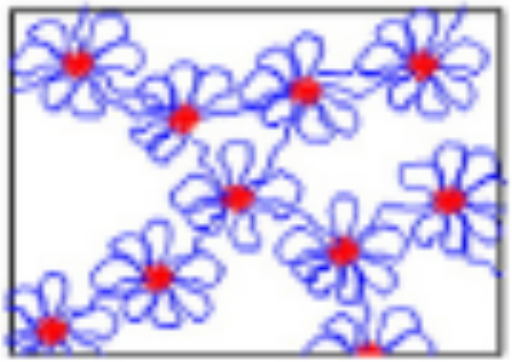
However, if the concentration is such that micelles are frequently close to one another, the floating end can be captured by the core of a *different* micelle, and a *bridging* chain is then created.



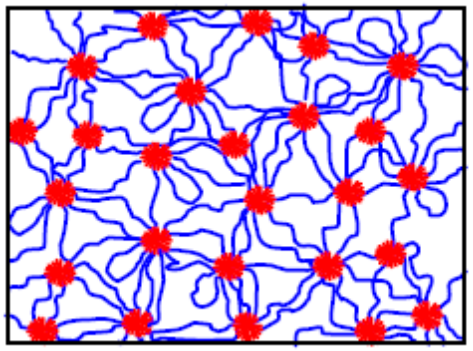
In other words, at some concentration (higher than CMC) micelles start to aggregate into *clusters*.
Although each cluster is not a permanent object (bridging chains will periodically detach and reattach elsewhere), on average clusters will become larger with increasing concentration, and the solution viscosity will rise increasingly steeply.

Percolation. The impermanent network

Eventually, with further increasing concentration, bridging chains (and/or bridging micellar chains or super-bridges) will percolate the whole volume, and a network will be formed:



network of super-bridges (weaker)

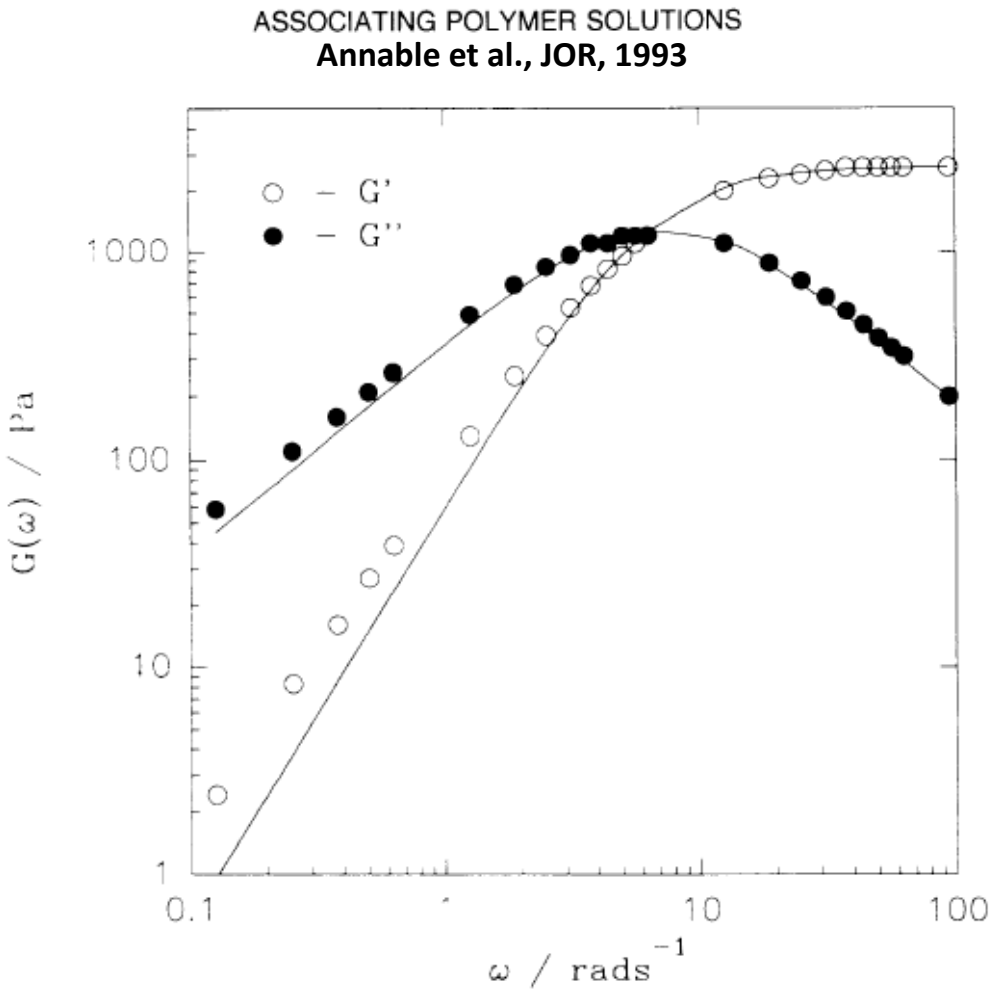


network of bridging chains (stronger)

The network is rubber-like, but it is not a permanent network like that of a crosslinked rubber. Indeed, since bridging chains detach and reattach continuously, the network is *impermanent*, i.e., the system remains a liquid.

However, a high viscosity is expected from such a structured liquid.

Linear viscoelasticity of the HEUR impermanent network



While ordinary polymers typically show a spectrum of relaxation times, here a ***single*** relaxation time is (essentially) found.

Indeed, these data obey the well-known Maxwell equations:

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

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

A single relaxation time implies that friction processes are not involved, and chemistry dominates. The detachment-reattachment frequency must be the rate-controlling step.

FIG. 4. Real and imaginary parts of the complex modulus as a function of frequency for C16/35 K at [illegible]% w/v. Lines: best fit to a Maxwell model ($T = 298$ K).

C16/35K means: mass of central polymer (PEG) is 35K, ends are 16 carbon-atom hydrocarbons.

Nonlinear effects

- The structure of the impermanent network gets modified in fast flows
- Most frequently, the network is somehow disrupted. Hence, shear thinning results
- In some cases, flow favors further aggregation, and shear thickening may be observed

Steady shear viscosity of HEUR solutions

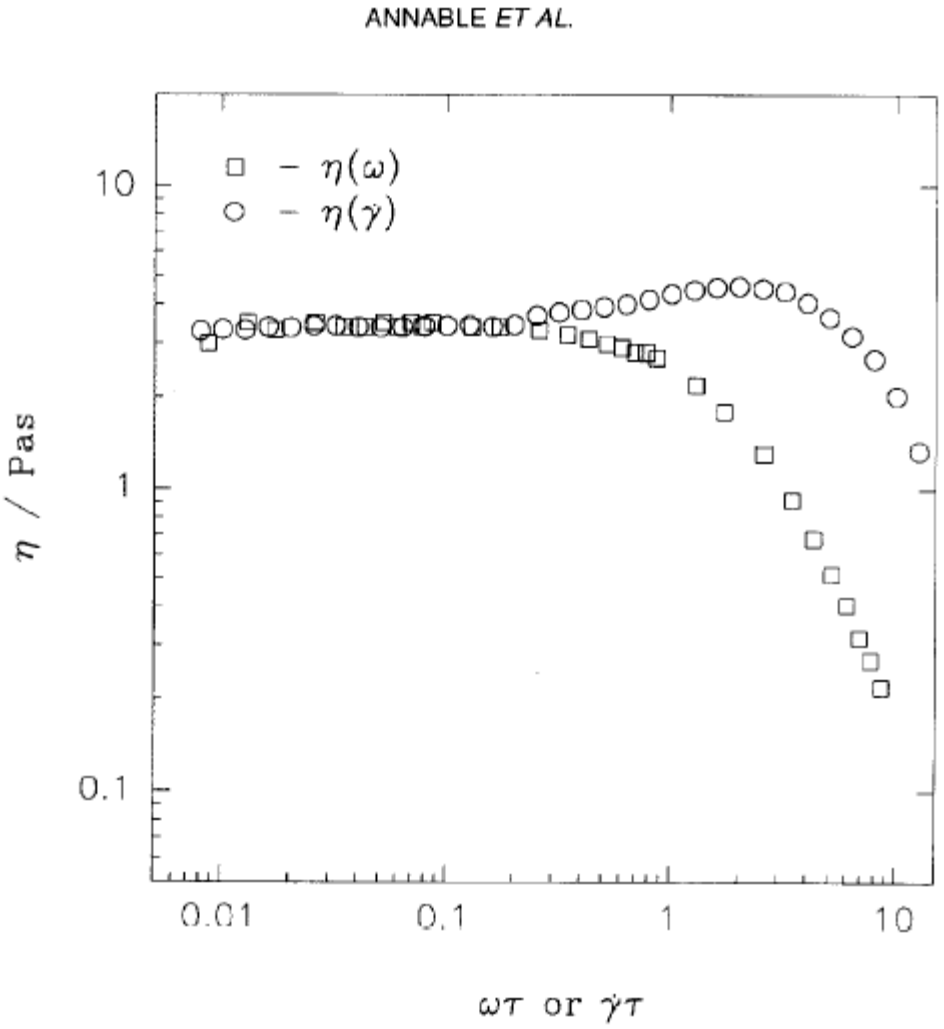


FIG. 3. Comparison of steady shear and dynamic viscosities as a function of reduced shear rate or frequency for C16/35 K at 1.5%w/v. $T = 298$ K.

Cox-Merz rule is not obeyed

In some cases (like this one), a region of weak shear-thickening can be found, before shear-thinning prevails with further increasing the shear rate.

Models of nonlinear viscoelasticity that include the possibility of shear thickening were developed by Vaccaro and Marrucci, *JNNFM*, 2000, by Tanaka and co-workers (many papers), and by McKinley and co-workers, *Macromolecules*, 2006.

Theories of nonlinear response for impermanent networks

Green and Tobolsky, *J. Chem. Phys*., 1946
Yamamoto, *J. Phys. Soc. Jpn*, 1956
Tanaka and Edwards, *Macromolecules* 1992, *JNNFM* 1992

Such theories assume that the network deforms *affinely*, and that chains attach and detach from the network. Detached chains *relax* the stress.

Unfortunately those theories *do not predict shear thickening*, but only shear thinning.

In 1995 van den Brule and Hoogerbrugge performed Brownian simulations of the impermanent network and found (*JNNFM*, 1995) that shear thickening originated from the fact that the *probability for a pendant chain of being recaptured by the network is proportional to its end-to-end distance R* since the *velocity* by which the free chain-end explores the surrounding space (hence the *volume* explored per unit time) grows with increasing *R*.

The analytic model of Vaccaro and Marrucci (2000) is based on such result, and that of Tripathi, Tam, and McKinley (2006) on some variant of it.

Equations for two populations of chains

$\psi(\boldsymbol{R}, t)$ = distribution function of end-to-end vector $\boldsymbol{R}$ of *attached* chains
$\varphi(\boldsymbol{R}, t)$ = distribution function of end-to-end vector $\boldsymbol{R}$ of *pendant* chains

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial \boldsymbol{R}} \cdot (\psi \boldsymbol{k} \cdot \boldsymbol{R}) - \beta(R)\psi + \alpha(R)\varphi$$

affine deformation — detachment rate — attachment rate

$$\frac{\partial \varphi}{\partial t} = -\frac{\partial}{\partial \boldsymbol{R}} \cdot \left(-D \frac{\partial \varphi}{\partial \boldsymbol{R}} + \varphi \frac{D}{k_B T} \boldsymbol{F}(R) + \varphi \boldsymbol{k} \cdot \boldsymbol{R} \right) - \alpha(R)\varphi + \beta(R)\psi$$

diffusion — retraction due to force ***F***

Assumptions on detachment rate, *i.e.* on $\beta(R)$, are essential in determining shear-thinning

Assumptions on attachment rate, *i.e.* on $\alpha(R)$, are essential in determining shear-thickening

Detachment frequency $\beta(R)$

At equilibrium: $\beta_0 = \Omega \exp\left(-\frac{E}{k_B T}\right)$

Away from equilibrium: $\beta = \Omega \exp\left(-\frac{E - Fl}{k_B T}\right) = \beta_0 \exp\left(\frac{Fl}{k_B T}\right)$

(where $F(R)$ is the elastic force and is related to the length of the hydrophobic tail)
In the nonlinear range, since $_0$, detachment becomes more frequent, and (other things remaining the same) shear-thinning prevails. (For a constant the viscosity would remain constant).

Assumptions for $\alpha(R)$ are less clear. As mentioned previously, $\alpha(R)$ growing with R induces shear-thickening.

Expressions for α and β appeared in the literature

Table 1. Comparison of Creation and Destruction Rate for Various Models[a]

model	probability rate of creation $L(\underline{Q},t)$	probability rate of destruction $M(\underline{Q},t)$
Green and Tobolsky[32]	$1/\tau_E$	$1/\tau_E$
Tanaka and Edwards[28−31]	c_1/τ_E	$\exp(c_2Q)/\tau_E$ $(c_3 + 1.5c_4Q^2)/\tau_E$
Wang[34]	$(c_1 + c_2\tau_E^2\dot{\gamma}^2)/\tau_E$	$(1 + c_3Q^2/Q_{eq}^2)/\tau_E$
Ahn and Osaki[37]	$\exp(c_1\gamma)/\tau_E$	$\exp(c_2\gamma)/\tau_E$
van den Brule and Hoogerbrugge[38]	$(c_1Q/Q_{eq})/\tau_E$	$2/\tau_E$
Hatzikiriakos and Vlassopoulos[49]	$2Q^3n_1\dot{\gamma}/3$	$4D/Q^2 \exp(-W/k_BT)$
Vaccaro and Marrucci[40]	$(c_1 + c_2Q/Q_{eq})/\tau_E$	f/τ_E
Hernandez-Cifre et al.[39]	$1 - \exp\{-(c_1 + c_2fQ)\Delta t\}$	$1 - \exp\{-2\Delta t \exp(c_3f^2)/\tau_E\}$

[a] Here c_1, c_2, c_3, and c_4 are model specific constants; γ is the total strain; $\dot{\gamma}$ is the shear rate; f is given in eq 9; n_1 is the concentration of single molecules; D is the translational diffusivity of a molecule; W is the energy of interaction of two molecules; $Q = \sqrt{\langle Q^2 \rangle}$ is the ensemble average length of the bridged chain; Δt is the simulation time step.

The stress tensor *T* can be obtained from previous equations

For a network containing ν elastically-active chains per unit volume, the stress tensor $\boldsymbol{T}$ is given by ($\boldsymbol{R}$ is the end-to-end vector, and $\boldsymbol{F}$ the corresponding elastic force, in a chain):

$$\boldsymbol{T} = \nu\langle \boldsymbol{FR} \rangle = \nu \frac{3k_B T}{Nb^2} \langle f\boldsymbol{RR} \rangle = \frac{3G}{Nb^2} \langle f\boldsymbol{RR} \rangle$$

The scalar factor f accounts for non-Gaussian behavior (f >1), and $G = \nu\, k_B T$ is the elastic modulus.

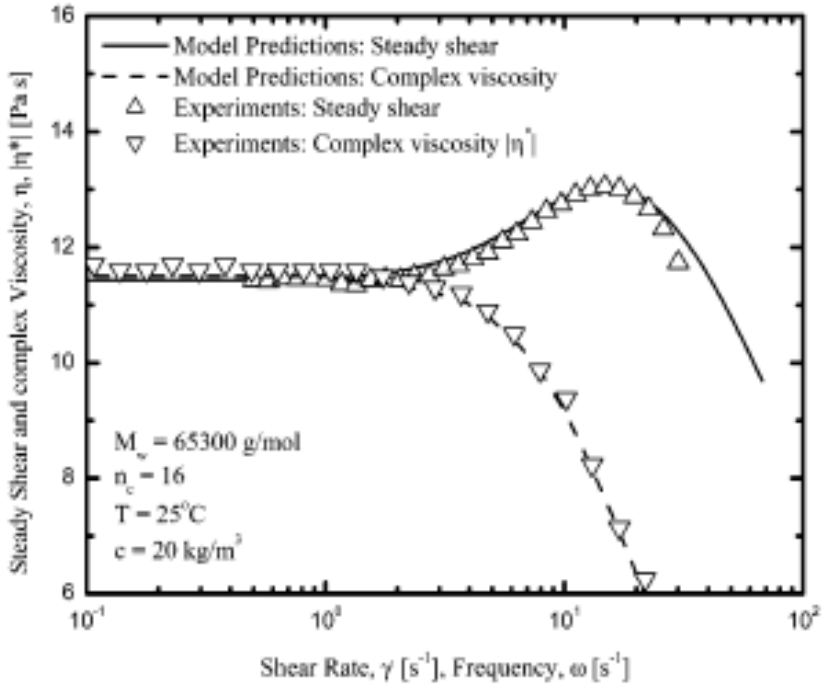
A similar equation is written for the pendant chains, and the ensemble averages $\langle \cdot \rangle$ appearing in these expressions are calculated through the distribution functions $\psi(\boldsymbol{R}, t)$ and $\varphi(\boldsymbol{R}, t)$ previously defined.

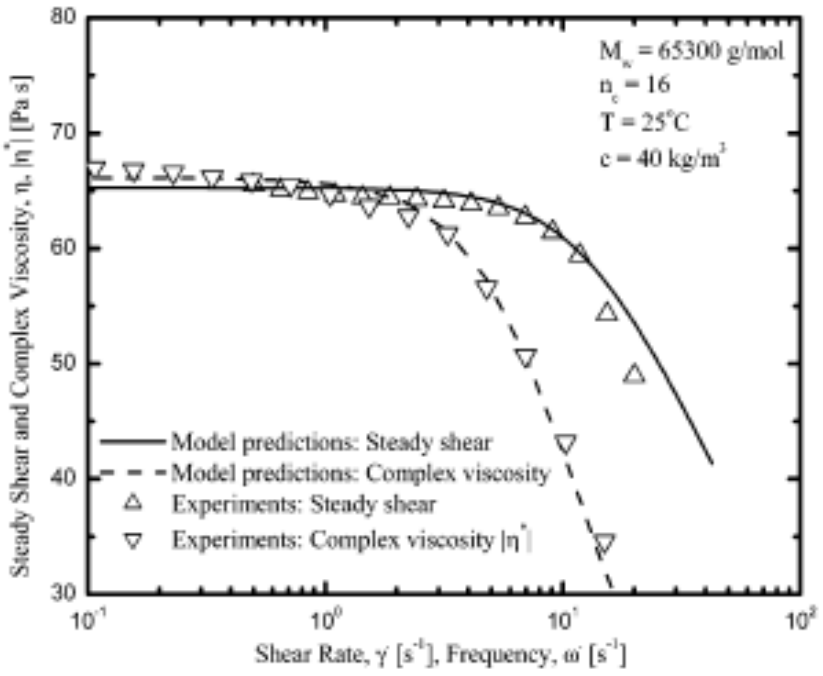
In practice, instead of solving the PDE's for $\psi(\boldsymbol{R}, t)$ and $\varphi(\boldsymbol{R}, t)$, simpler ODE's for the relevant averages can be derived by using suitable decoupling approximations.

The ODE's become algebraic equations when steady states are considered.

Comparison of nonlinear model with data
McKinley *et al*., *Macromolecules*, 2006

Macromolecules, Vol. 39, No. 5, 2006

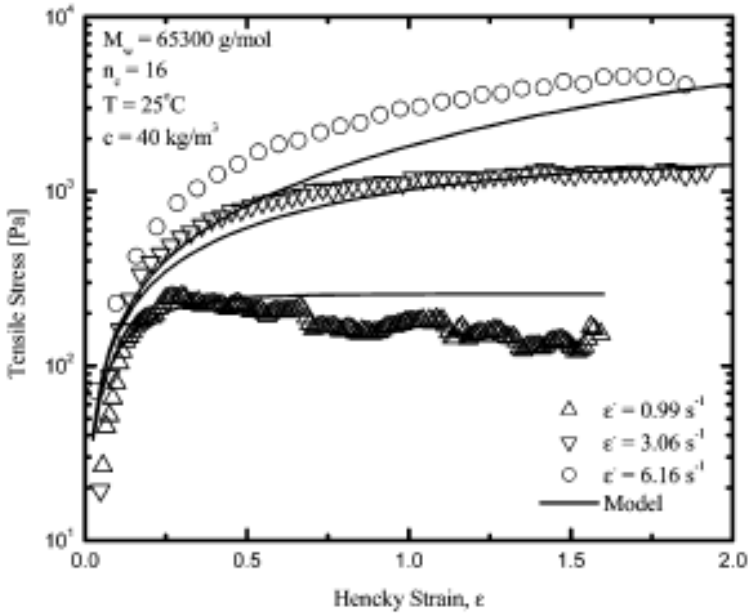


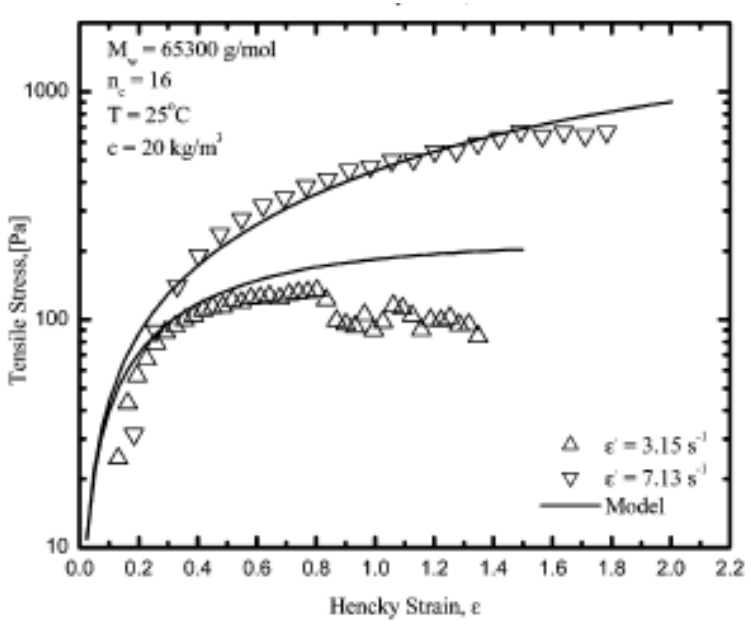


Same polymer at two different concentrations. One is shear-thickening, the other is not. The model describes both data quite well by choosing suitable different values of an arbitrary parameter (the meaning of which remains somewhat obscure).

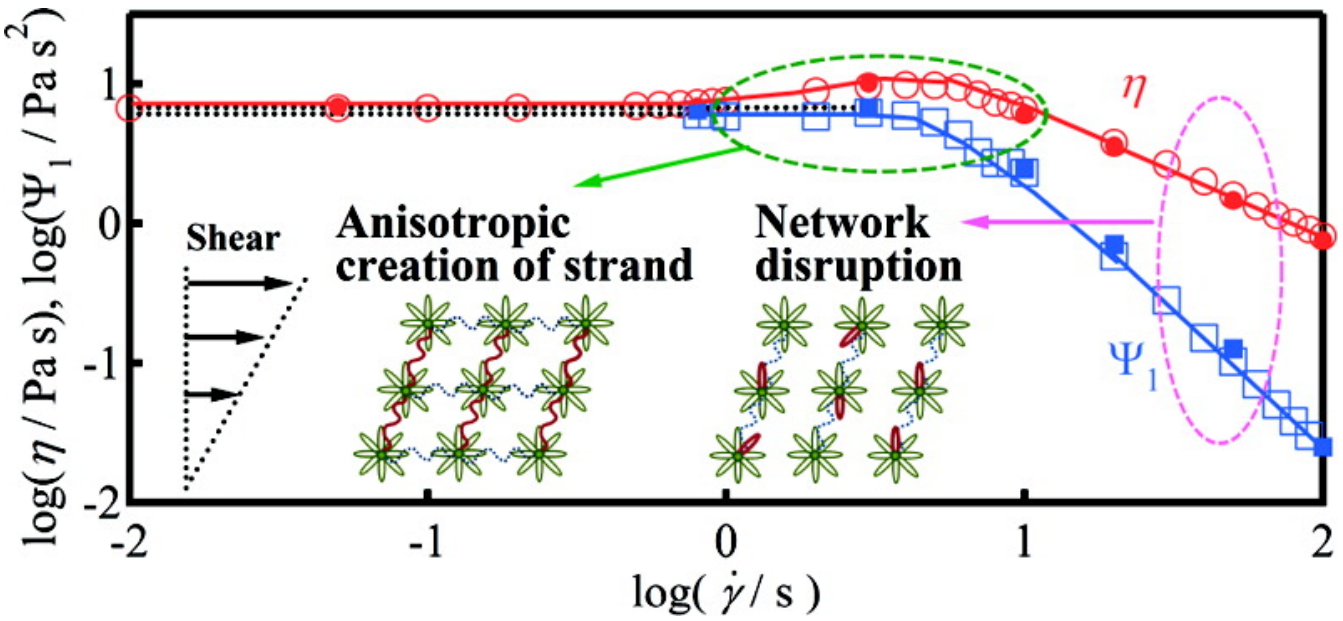
For all situations, Cox-Merz rule does not hold true.

Some elongational data





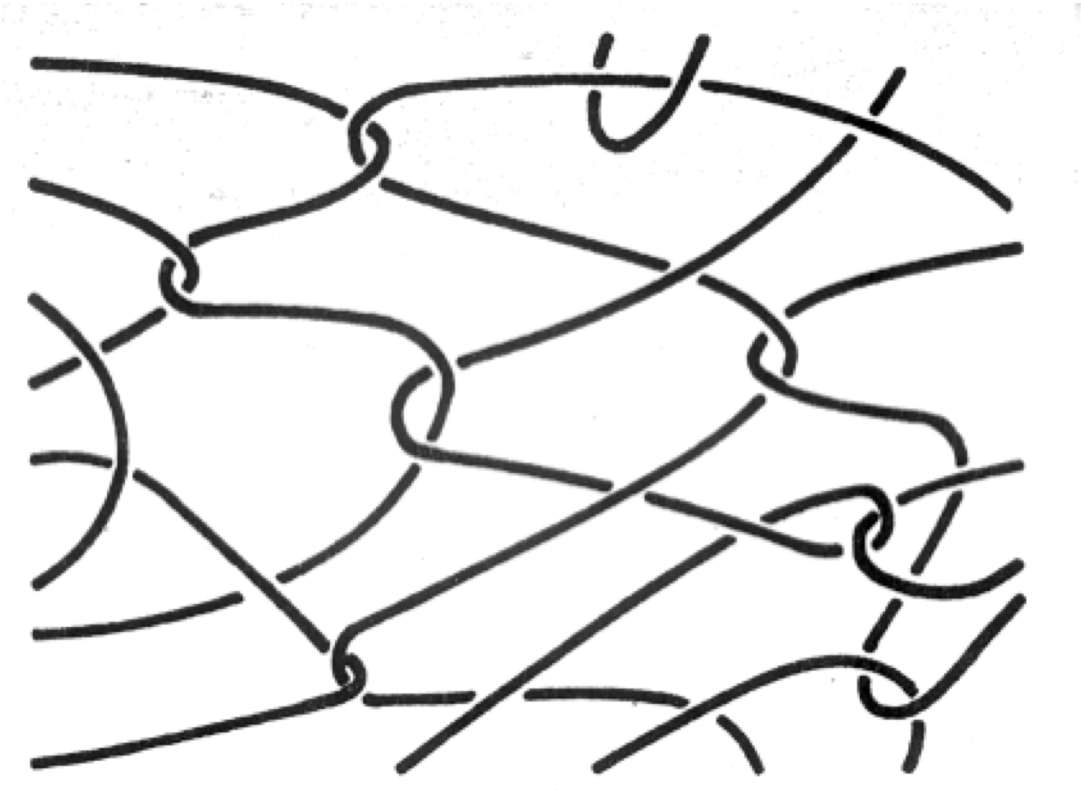
More recent data by Watanabe and coworkers (*Macromolecules* 2012)



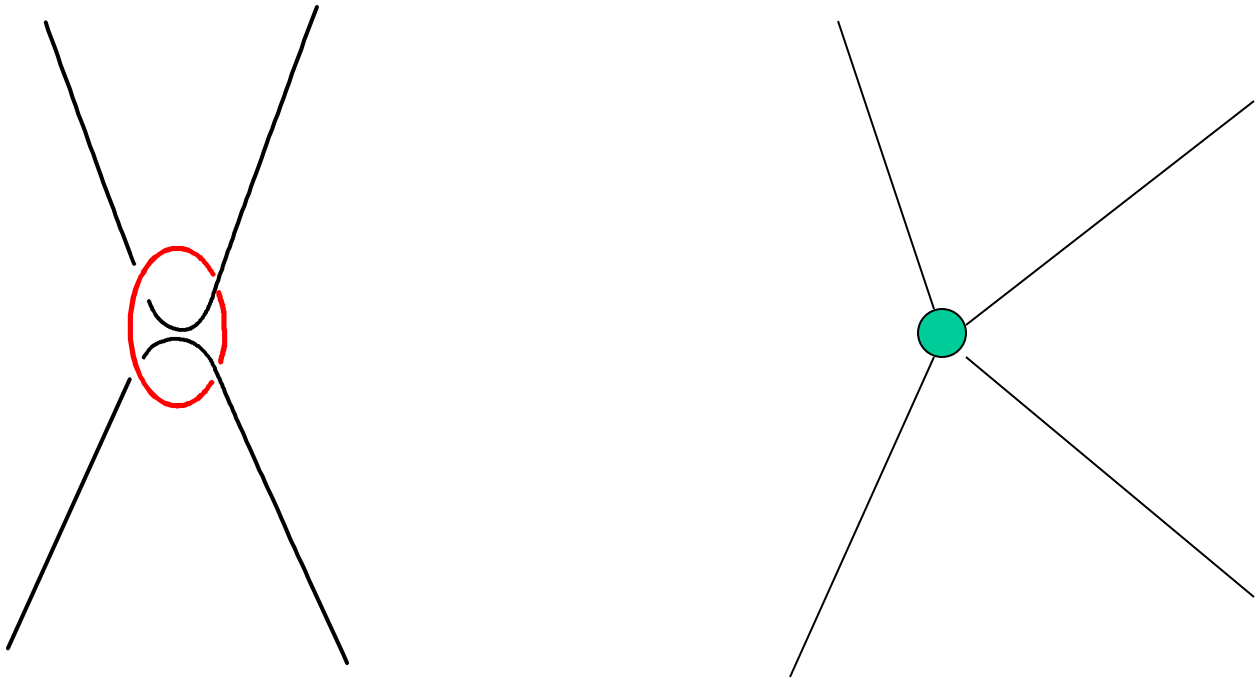
The viscosity is shear thickening while the first normal stress difference is not (or barely so). Watanabe *et al*. explain the effect by invoking an anisotropic creation of bridges.

Constitutive equations for entangled polymeric networks

Network of entangled polymers

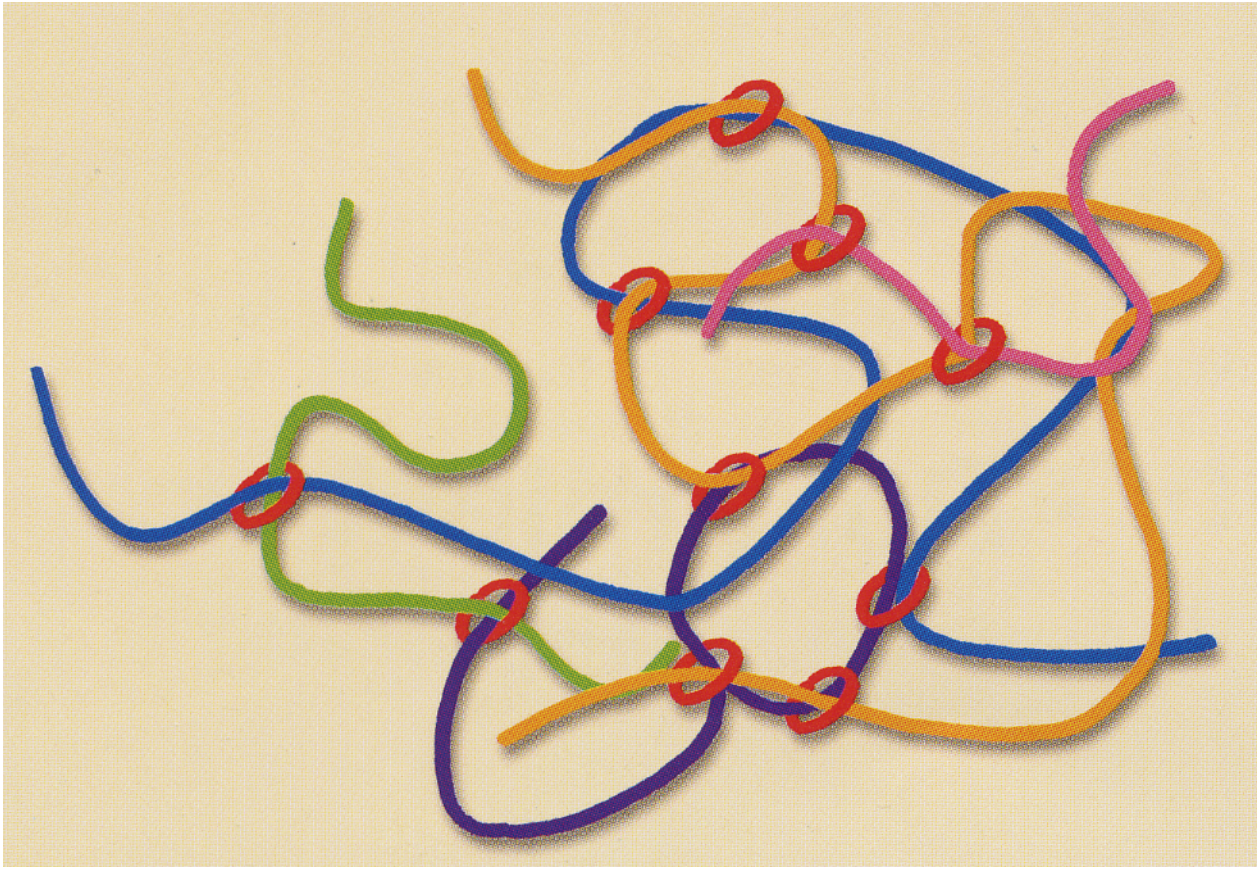


Nodes of the rubberlike network are “sliplinks” (entanglements) instead of crosslinks



Crucial difference: Monomers can slide through the sliplink

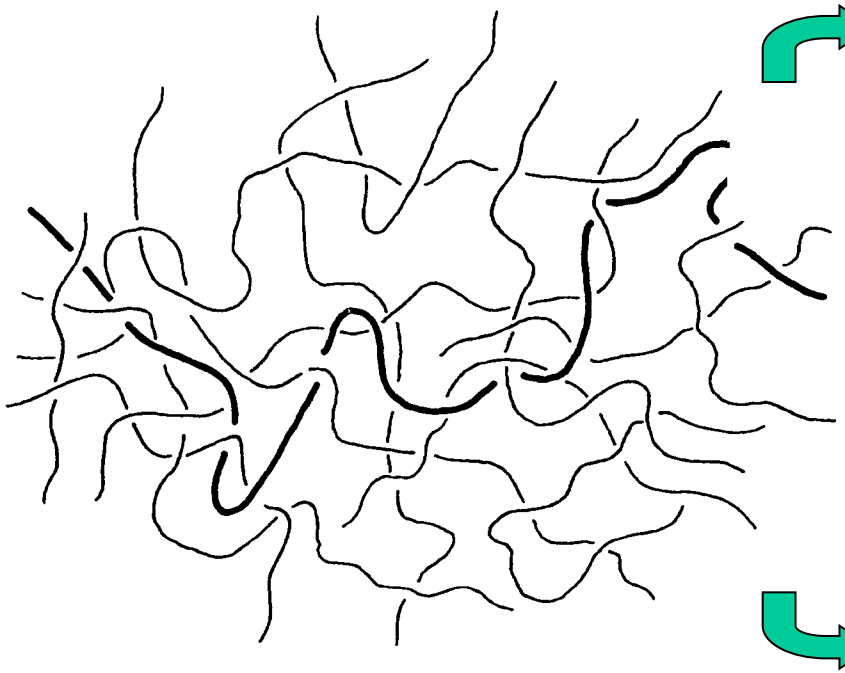
Entangled network

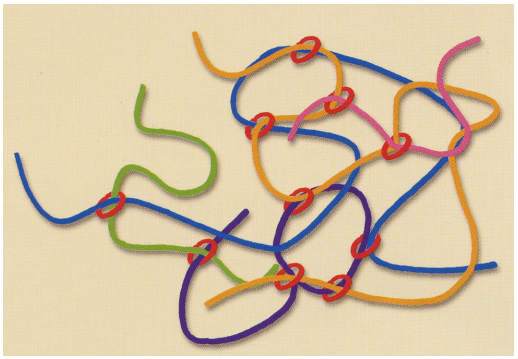


Picture referring to Brownian simulations of Masubuchi *et al.*
(NAPLES code)

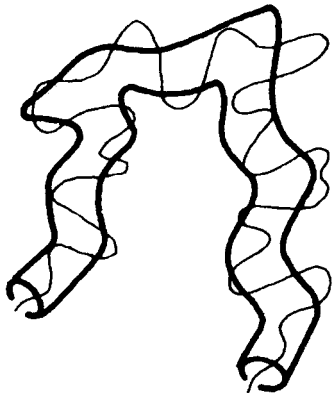
Polymers with entanglements

(melts or solutions)



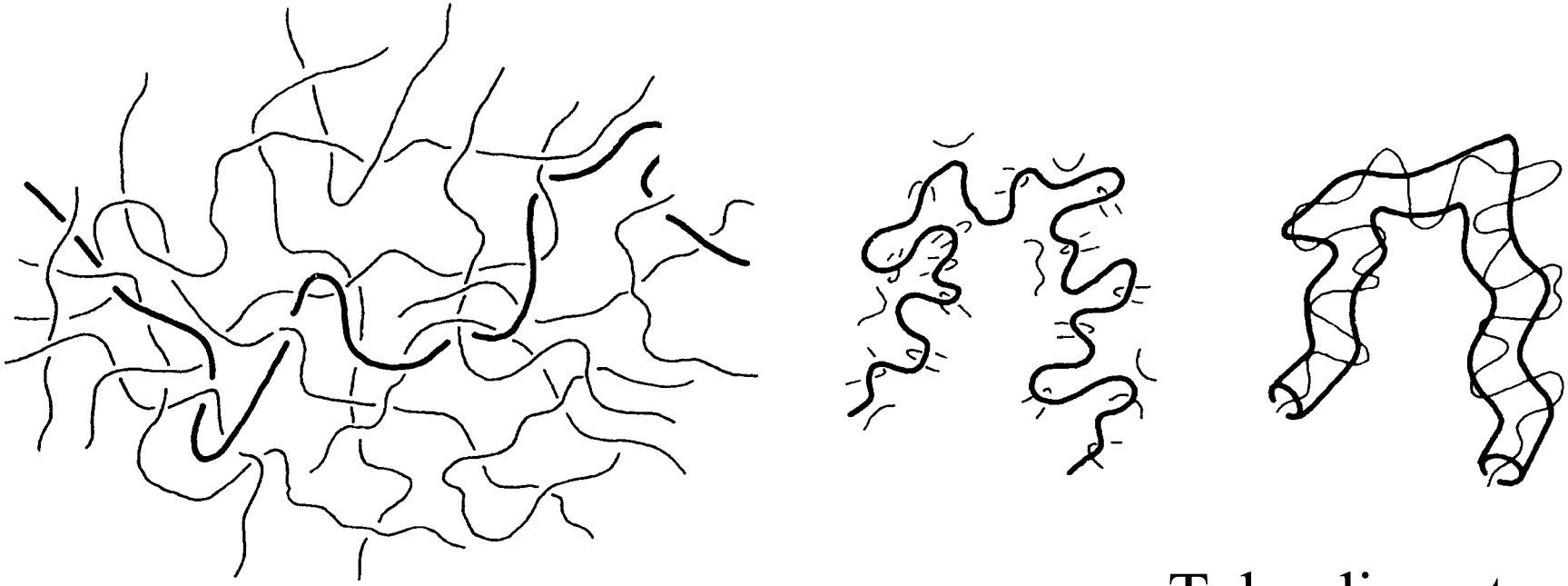


Many-chain simulations



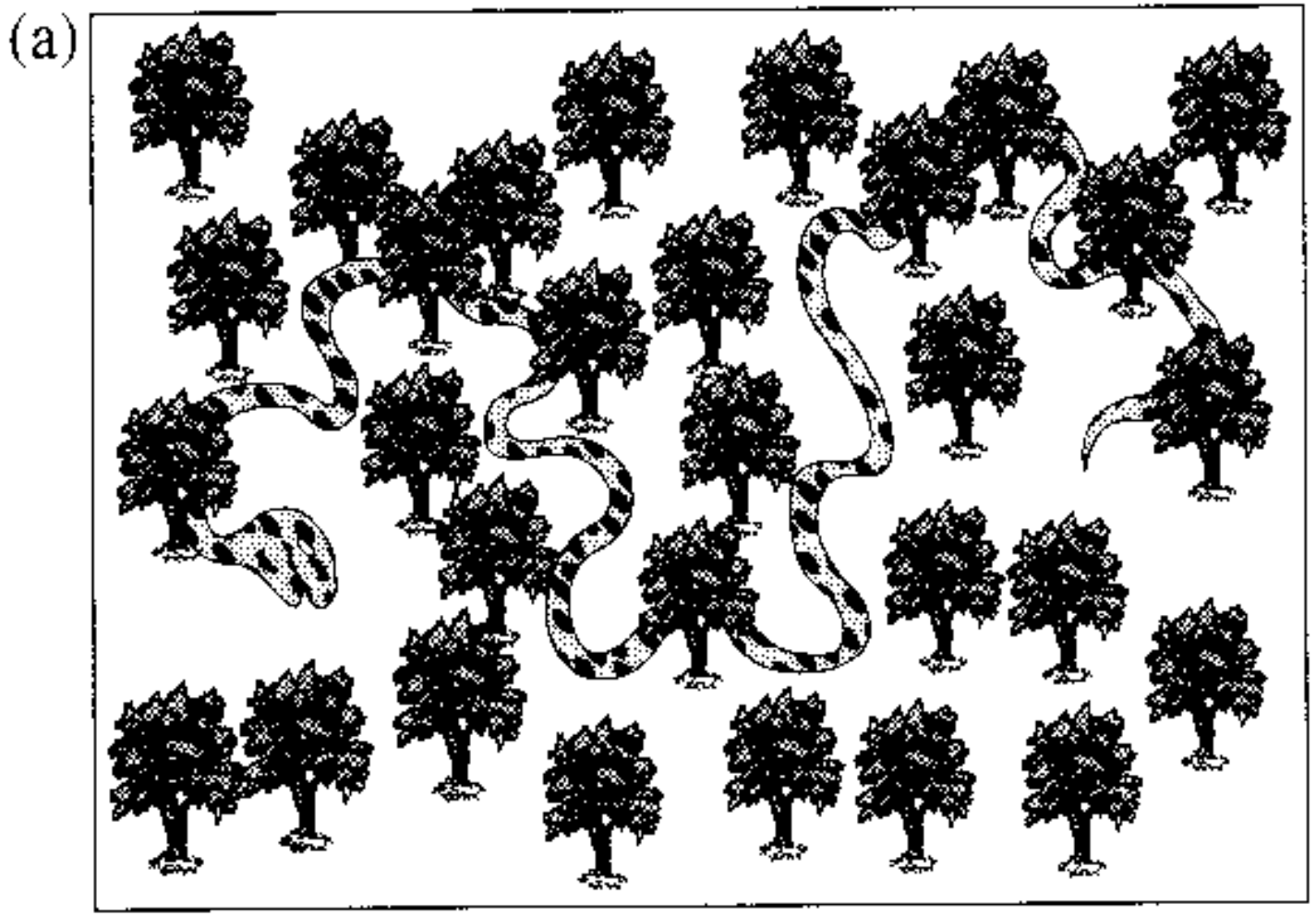
Single-chain models (constitutive equations)

The “tube” idea (Edwards 1967)

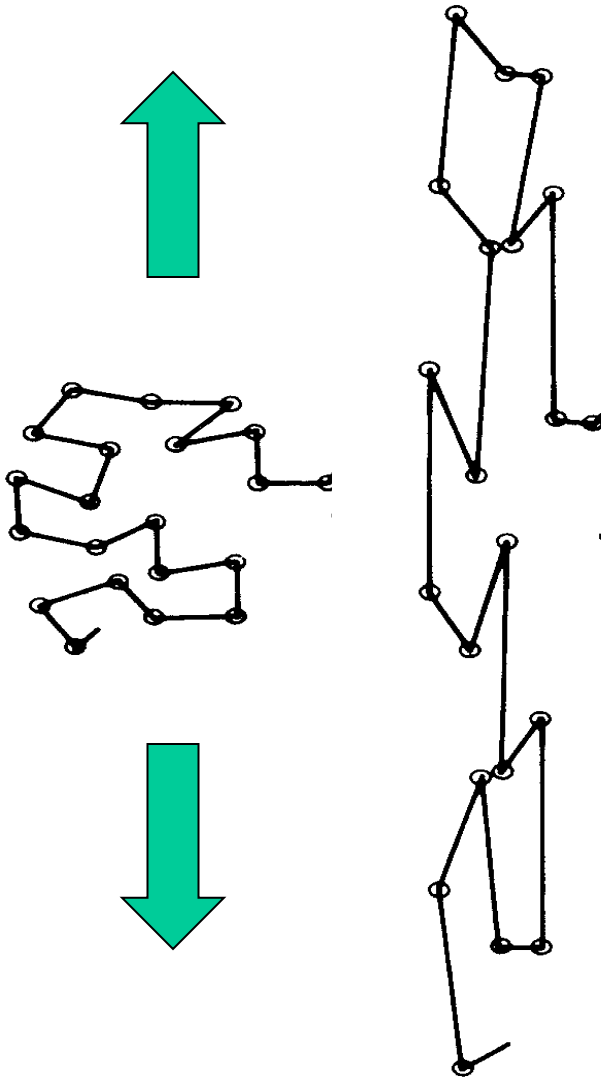


Tube diameter = a

Reptation dynamics (de Gennes 1971)



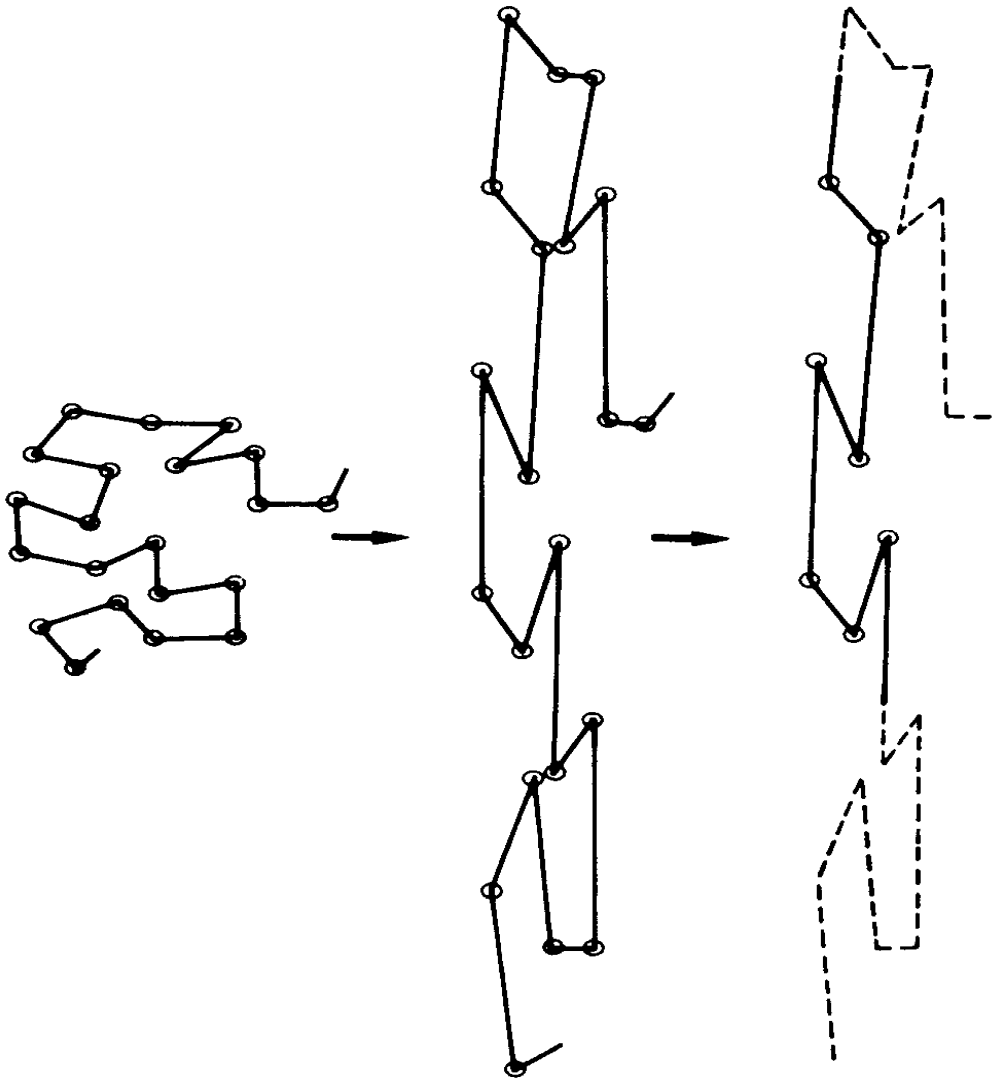
Doi-Edwards theory (1978)



Affine deformation of tube axis (or primitive chain)

Tube diameter remains fixed at equilibrium value

Chain stretch soon relaxes



Chain wants to retract to original tube length (to regain equilibrium tension and monomer density)

This is a **fast** process, only involving friction (no topological obstacles)

Relaxation after a step in shear

Tube is represented through slip-links

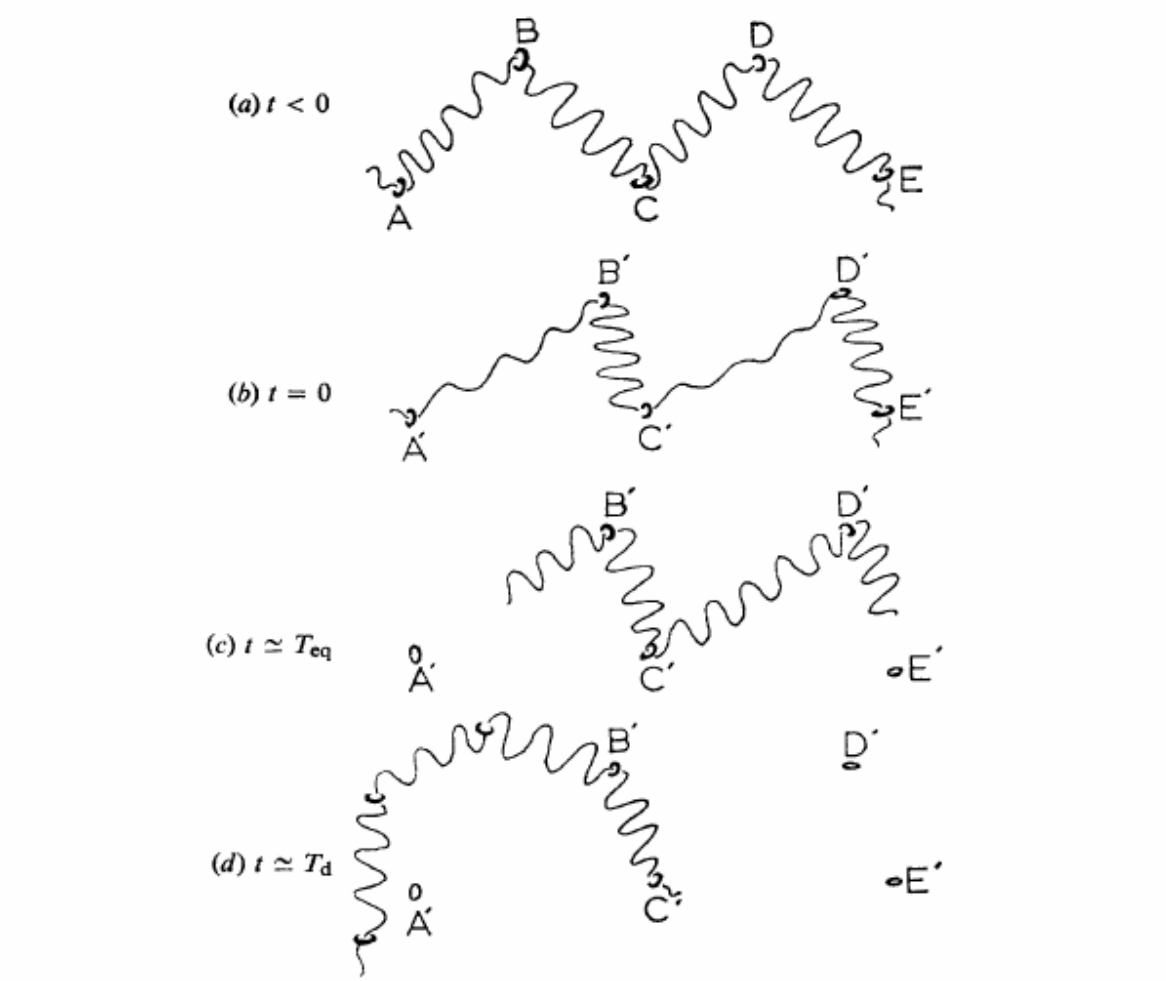
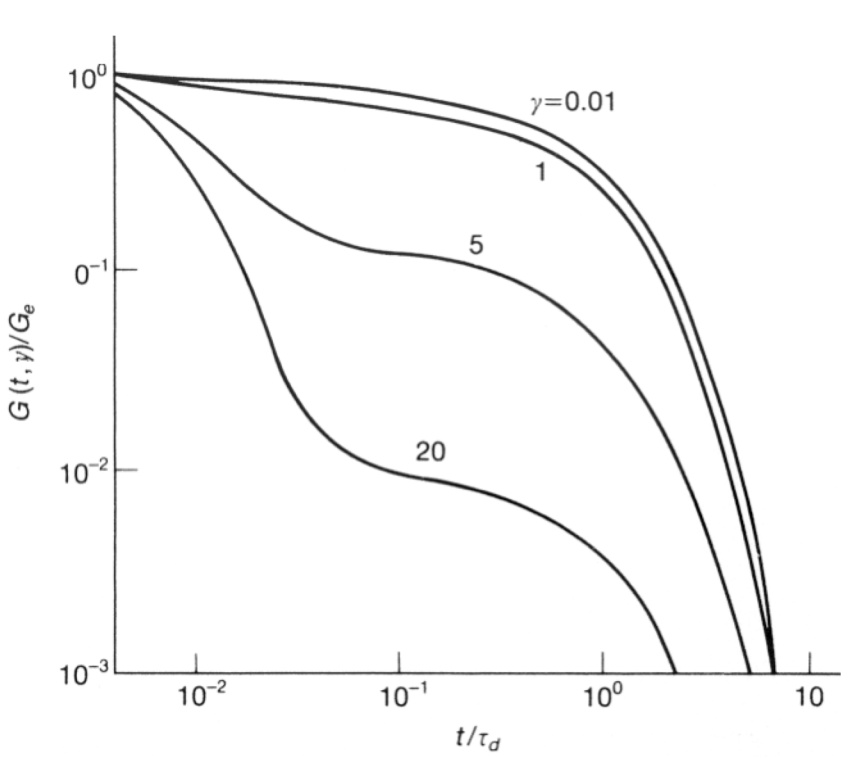
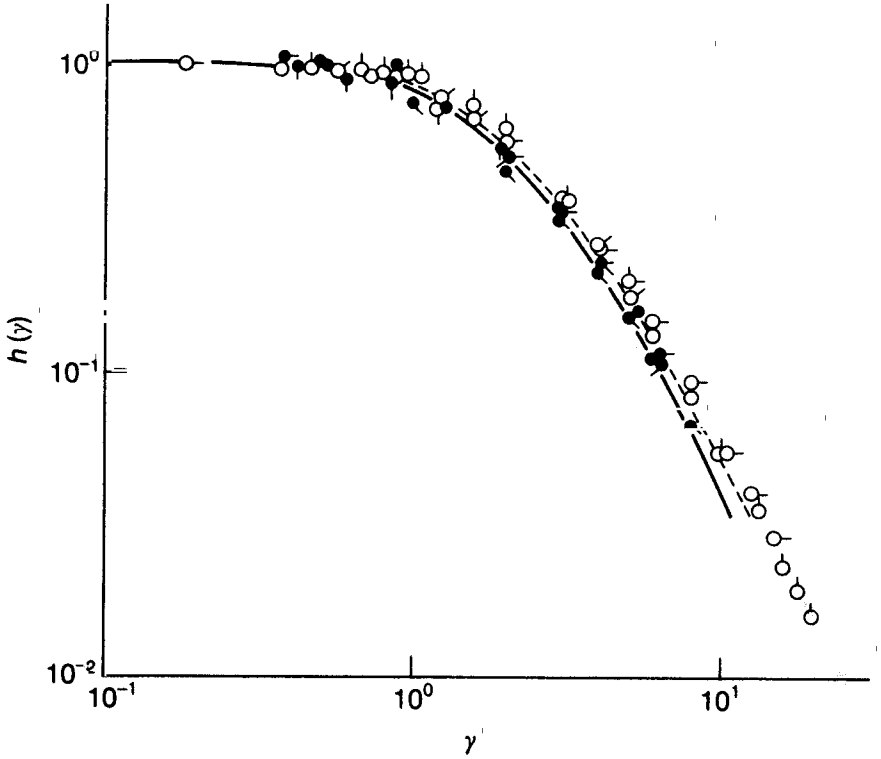


FIG. 3.—Schematic illustration of the relaxation process after the sudden deformation. (*a*) Initial equilibrium state, (*b*) immediately after the deformation: each part of the chain is stretched or compressed, (*c*) after the first relaxation process: the primitive chain recovers its equilibrium arc length, but the conformation of the primitive chain is still in a non-equilibrium state, (*d*) the second relaxation process: the chain disengages from the deformed slip-links and returns to the final equilibrium state.

Large-strain relaxation occurs in two steps:
stretch relaxation (Rouse time τ_R)
orientation relaxation (disengagement time τ_d)

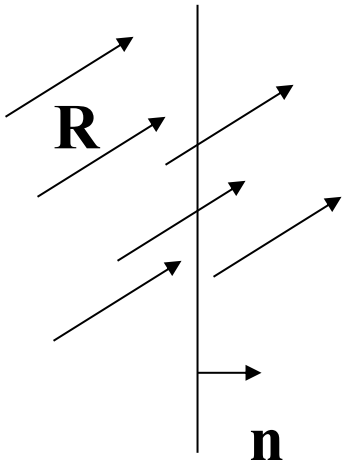




Time-deformation separability at long times defines the “damping function”

The stress tensor **T**

Assume temporarily that all subchains have the same end-to-end vector **R**



If ν is number of subchains per unit volume, subchains "cut" by a plane of unit area are $\nu(\mathbf{R}\cdot\mathbf{n})$

If **F** is the force in each subchain, the total force across unit area is $\nu\mathbf{FR}\cdot\mathbf{n}$.

Hence: $\mathbf{T} = \nu\mathbf{FR}$

In reality, because of distribution, it is: $\mathbf{T} = \nu\langle\mathbf{FR}\rangle$

Linear force: $\mathbf{F}=(3kT/nb^2)\mathbf{R}$

$$\mathbf{T} = 3\nu kT\left\langle \frac{\mathbf{RR}}{nb^2} \right\rangle$$

The orientation of a subchain is described by the unit vector **u** = **R**/R. Hence we may rewrite **T** as:

$$\mathbf{T} = 3\nu kT\left\langle \frac{R^2}{nb^2}\mathbf{uu} \right\rangle = 3\nu kT\left\langle \Lambda^2\,\mathbf{uu} \right\rangle$$

where **Λ** is the stretch of a subchain. If the stretch is relaxed (as in Doi-Edwards constitutive equation), Λ = 1, and **T** reduces to:

$$\mathbf{T} = 3\nu kT\left\langle \mathbf{uu} \right\rangle = 3\nu kT\,\mathbf{S} = G\,\mathbf{S}$$

where **S** = <**uu**> is the orientation tensor of the entangled network. **S** has a unit trace, and reduces to **I**/3 in the isotropic equilibrium state.

Doi-Edwards constitutive equation

Doi and Edwards derived the so-called **Q** tensor that describes the orientation in an entangled network soon after a step strain, when chain stretch is relaxed. Hence, for the step strain, it is **S** = **Q** at $t = 0^+$. Next, during orientational relaxation due to disengagement, **S**(t) is given by:

$$\mathbf{S}(t) - \mathbf{I}/3 = \psi(t)(\mathbf{Q} - \mathbf{I}/3) \cong \exp(-t/\tau_d)(\mathbf{Q} - \mathbf{I}/3)$$

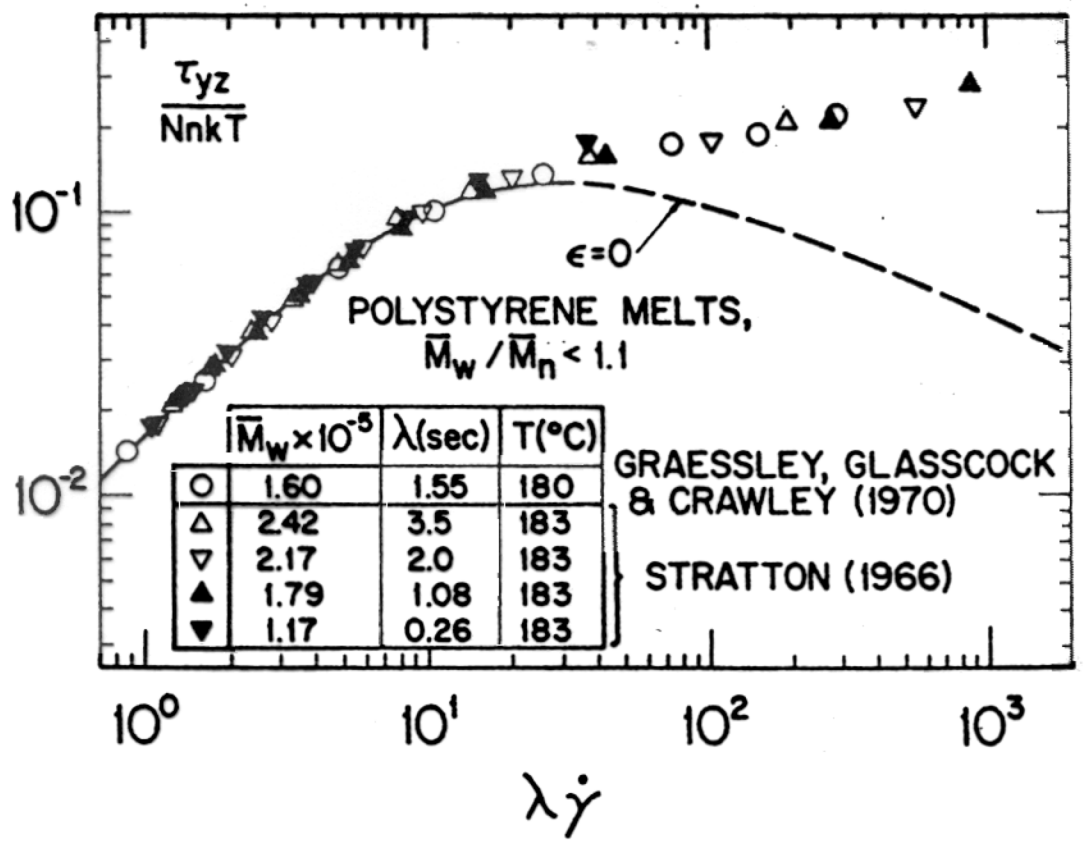
where $\psi(t)$ gives the fraction of chain segments that at time t have not yet disengaged from the old entanglements. For simplicity, $\psi(t)$ can be approximated by the single negative exponential that dominates reptation dynamics.

For a general flow or deformation history, we find

$$\mathbf{S}(t) = \frac{1}{\tau_d}\int_{-\infty}^{t} \exp\left(-\frac{t - t'}{\tau_d}\right)\mathbf{Q}\left[\mathbf{E}(t, t')\right]dt'$$

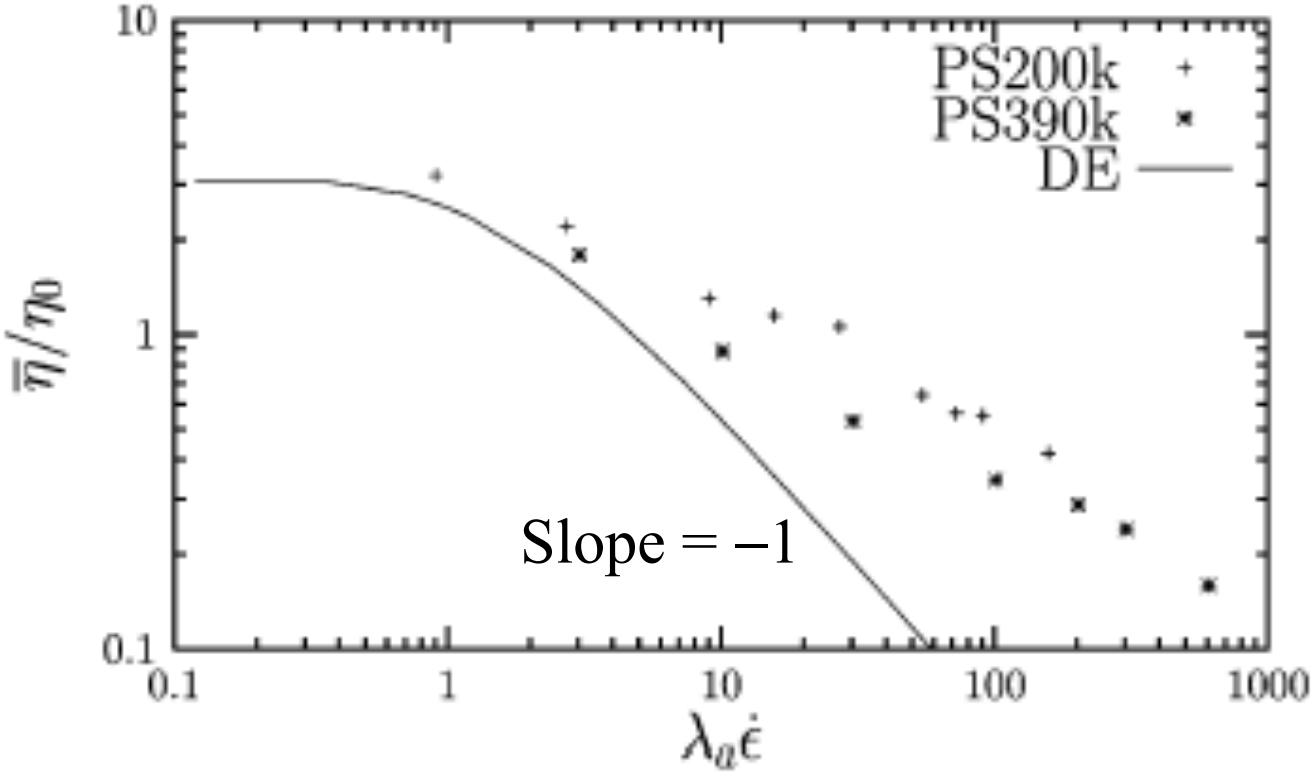
which, except for the restriction to a single exponential, is the DE C.E.

Steady shear flows



Doi-Edwards theory predicts a <u>maximum</u> of shear stress at the onset of nonlinear response

Steady elongational flows



$$\sigma_{plateau} = G$$

Chain stretch

If the flow is fast, specifically if the magnitude of the velocity gradient **k** approaches the retraction rate $1/\tau_R$, then also chain stretch becomes important in determining the stress **T**

By decoupling stretch and orientation contributions

$$\mathbf{T} = G\left\langle \Lambda^2 \mathbf{uu} \right\rangle \approx G\,\lambda^2 \left\langle \mathbf{uu} \right\rangle = G\lambda^2 \mathbf{S} \qquad \lambda^2 = \left\langle \frac{R^2}{nb^2} \right\rangle$$

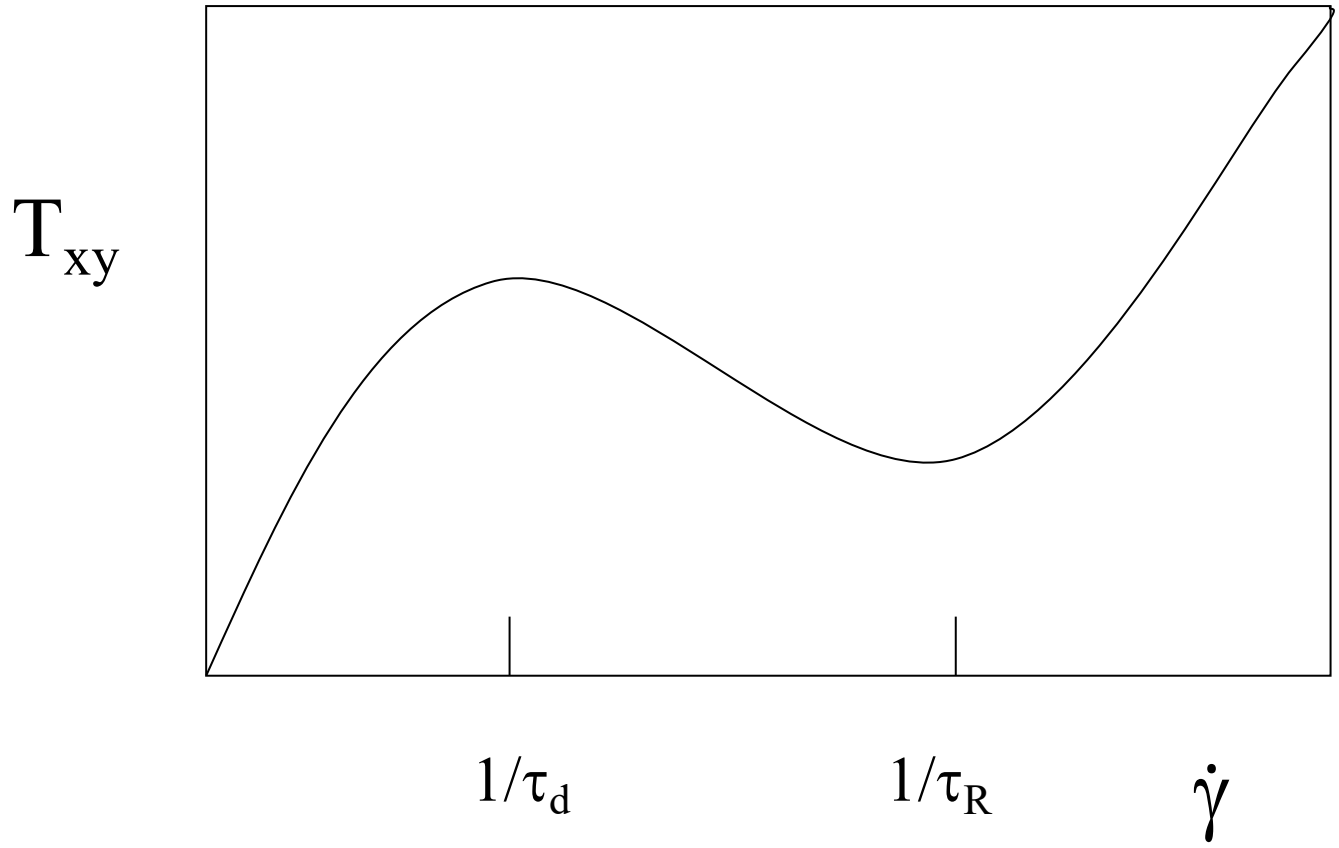
Hence we also need an equation to predict λ. A force balance on the whole chain gives

$$\frac{d\lambda}{dt} = (\mathbf{k} : \mathbf{S})\lambda - \frac{\lambda - 1}{\tau_R}$$

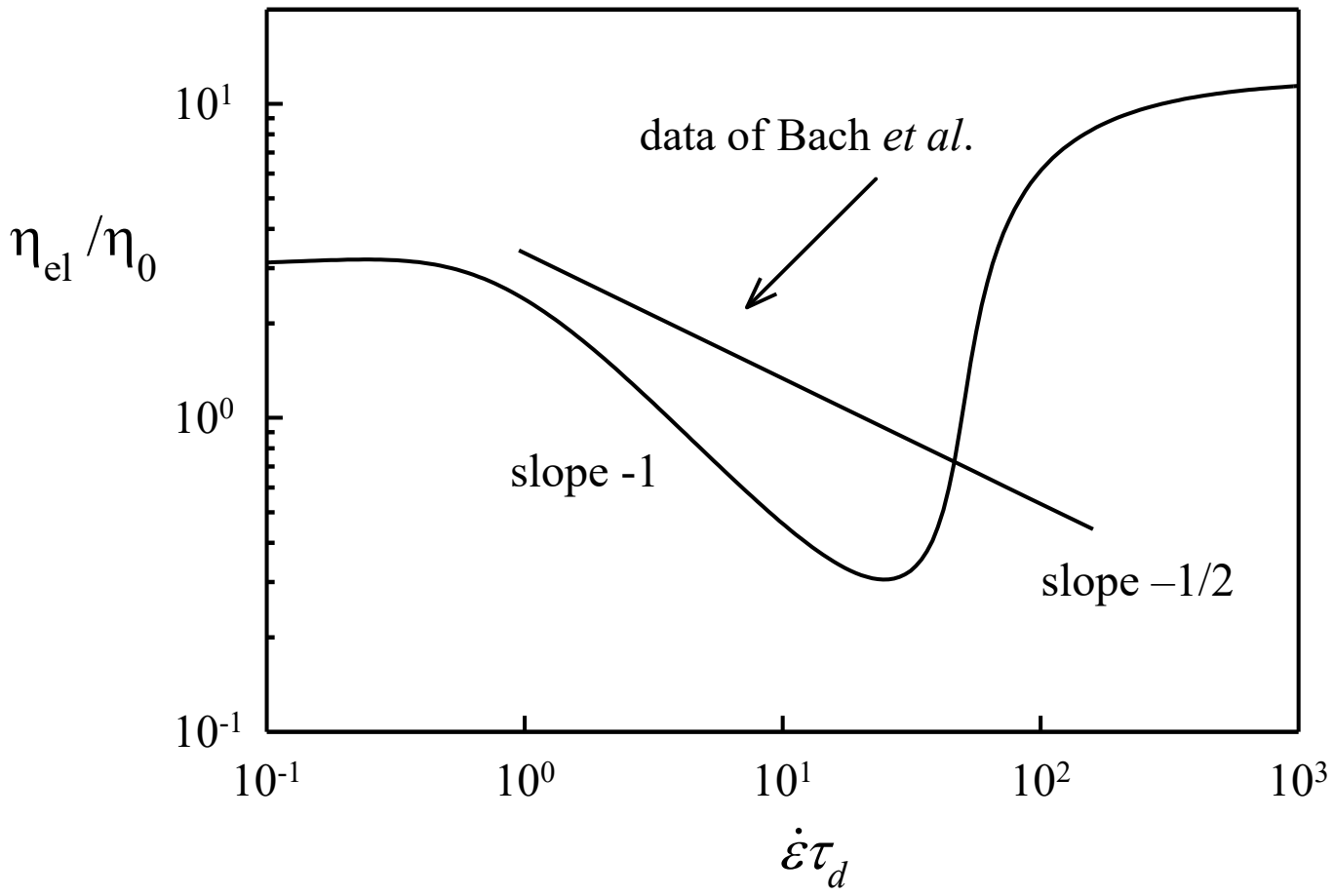
The first term on the r.h.s. is the affine stretching term, driving λ towards values larger than unity.
The last (negative) term describes relaxation of the stretch λ back to unity.

DE with chain stretch in steady shear

(Marrucci & Grizzuti, 1988; Cates et al., 1993)



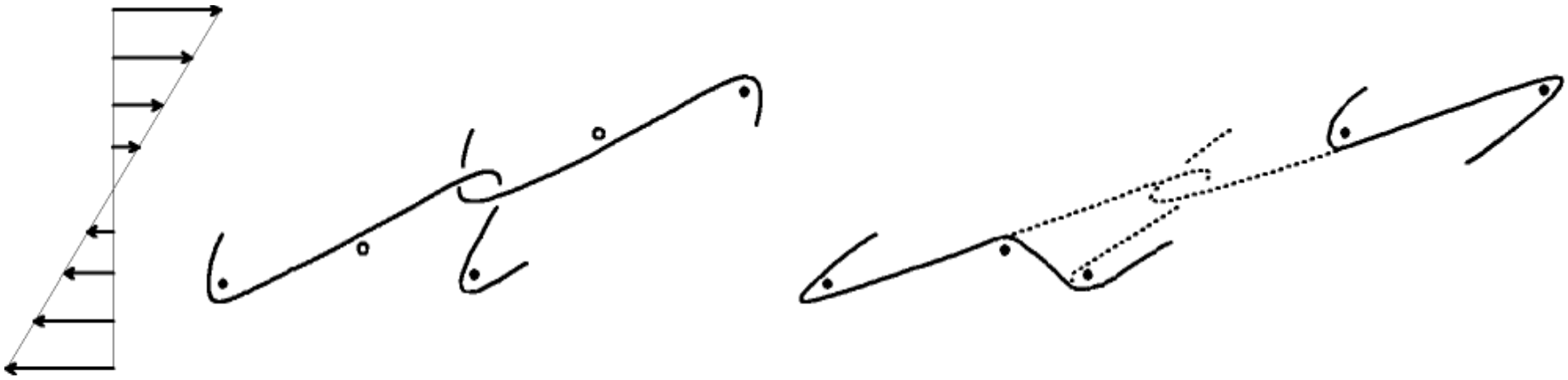
DE theory *vs.* PS melt data in elongation



saturation due to finite extendibility

i) Different slope; ii) no upturn

Convective constraint release
(Marrucci & Ianniruberto 1996)



$$\frac{1}{\tau} = \frac{1}{\tau_d} + \dot{\gamma}$$

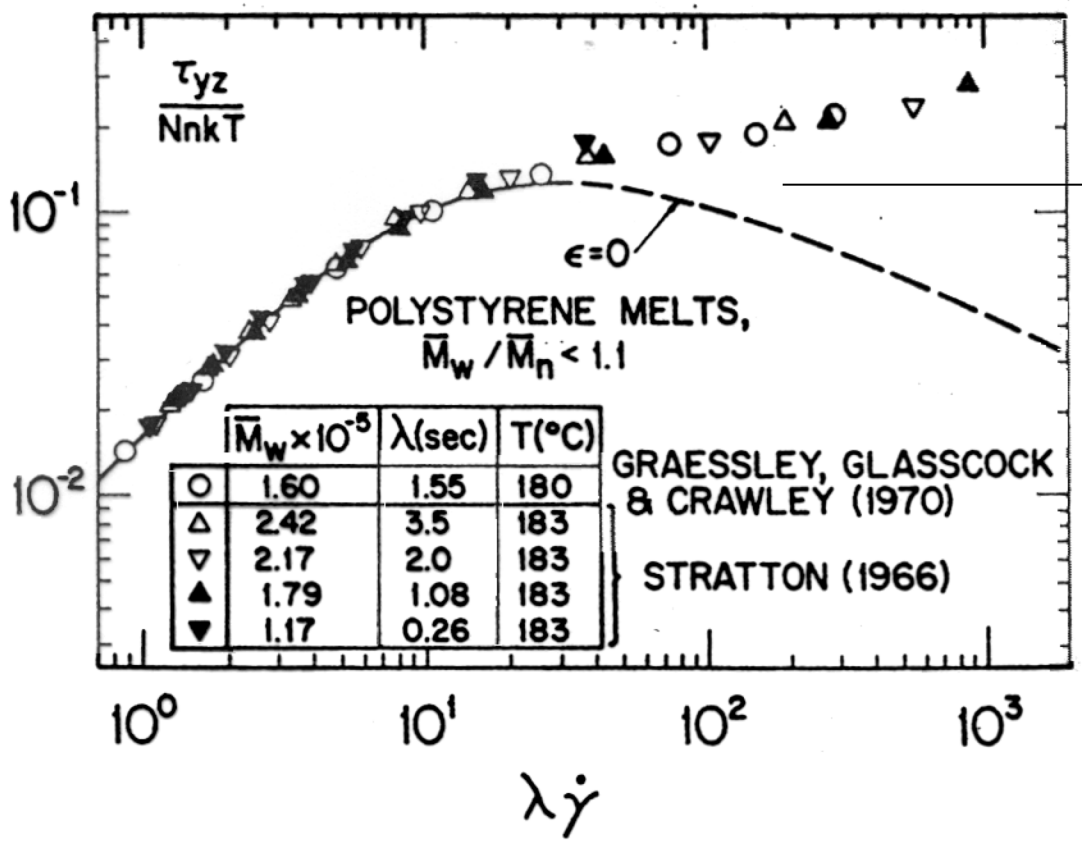
In fast flows

$\eta = G\tau = G/\dot{\gamma}$

$\sigma = \eta\dot{\gamma} = G$

CCR plateau

Steady shear flows



Plateau due to CCR

Whether or not a shallow maximum remains depends on an unknown numerical factor of the CCR contribution

Mead-Larson-Doi model (1998)

$$\mathbf{T} = 3G_e\lambda^2\mathbf{S}$$

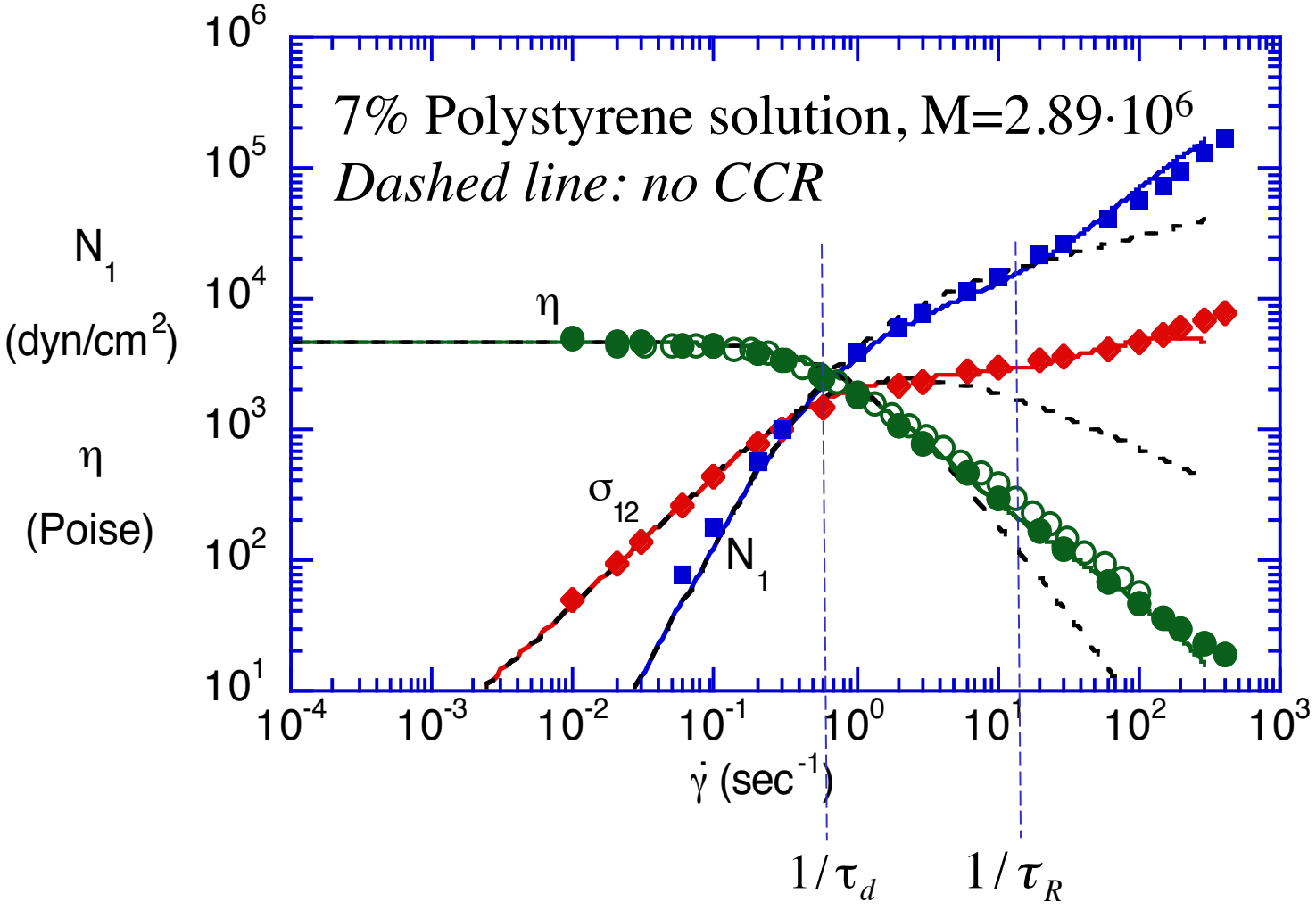
$$\mathbf{S}(t) = \int_{-\infty}^{t} \mathbf{Q}\left[\mathbf{E}(t',t)\right]\frac{\partial\psi(t',t)}{\partial t'}dt'$$

$$\frac{\partial\psi(t',t)}{\partial t} = -\frac{\psi(t',t)}{\tau} = -\left[\frac{1}{\lambda^2\tau_d} + f(\lambda)\left(\mathbf{k}:\mathbf{S} - \frac{\dot{\lambda}}{\lambda}\right)\right]\psi(t',t)$$

$$\dot{\lambda} = \mathbf{k}:\mathbf{S}\lambda - \frac{\lambda-1}{\tau_R} - \frac{1}{2}\left(\mathbf{k}:\mathbf{S} - \frac{\dot{\lambda}}{\lambda}\right)(\lambda-1)$$

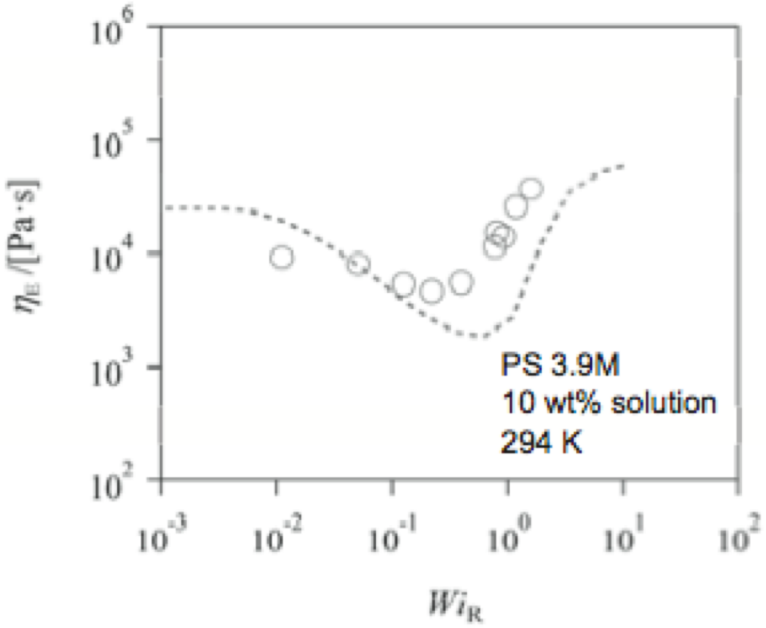
- MLD introduce the switch function $f(\lambda)$, switching off CCR with increasing λ.
- The last term in the stretch equation accounts for CCR-induced relaxation effects on stretch

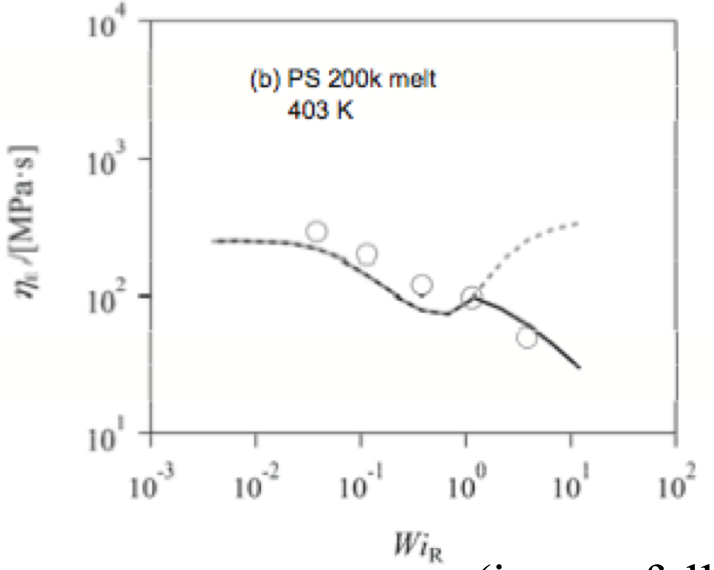
MLD model *vs.* data in steady shear



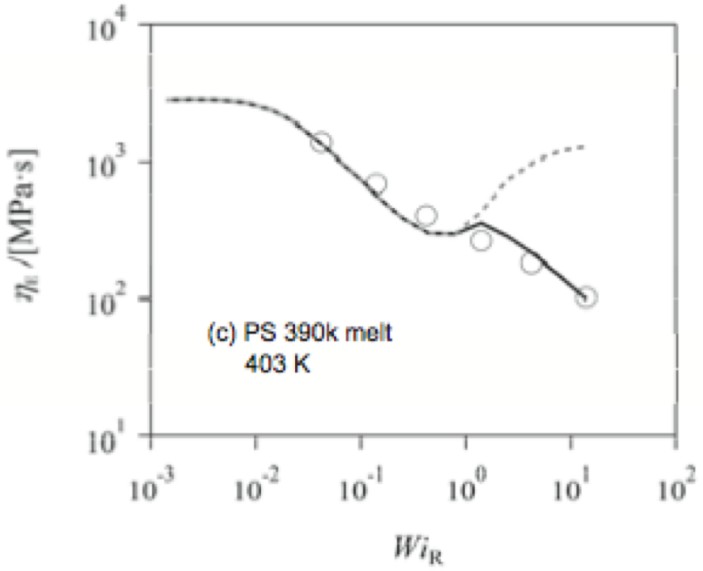
MLD model *vs.* steady elongation data

(Yaoita *et al.*, 2014)





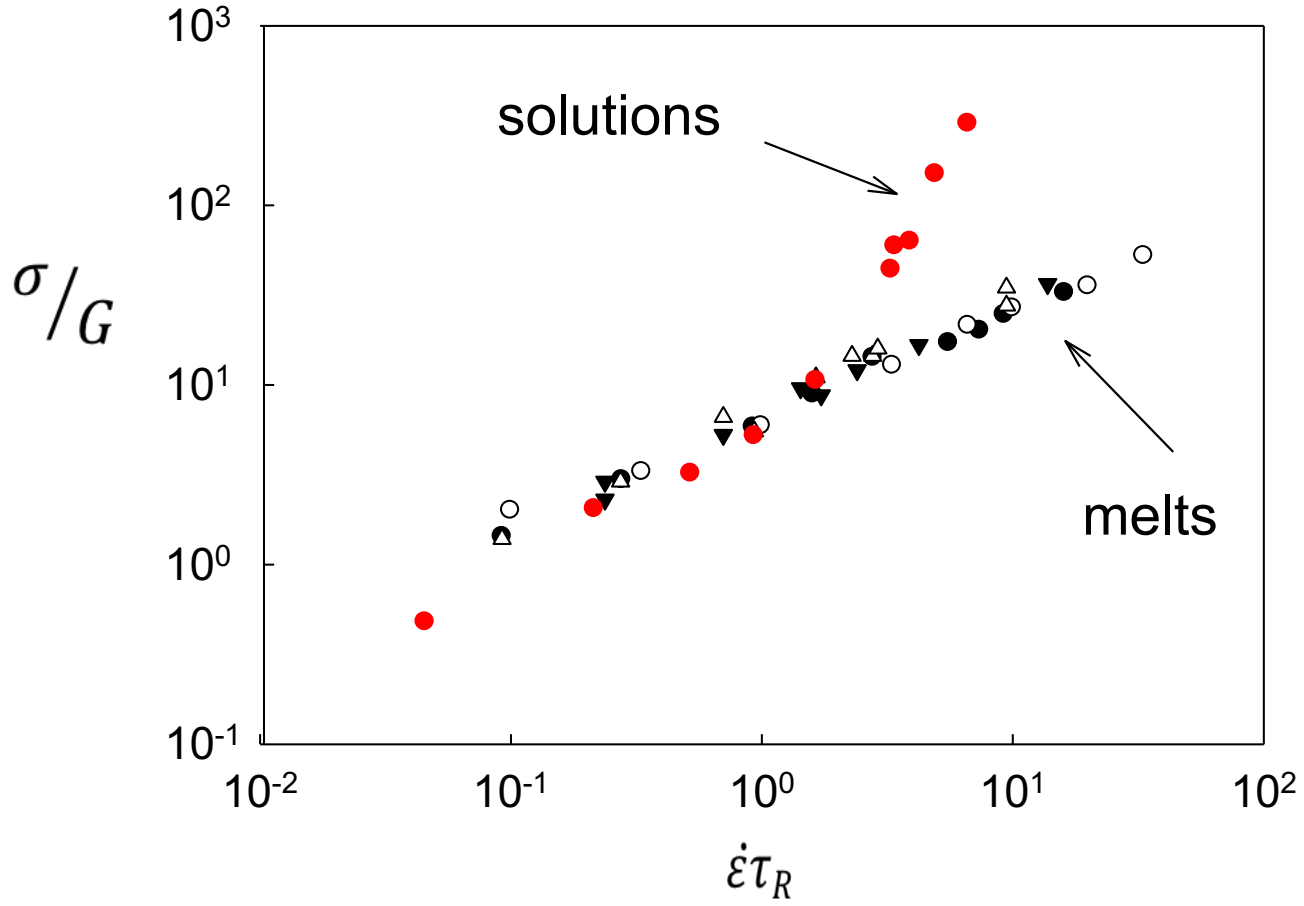
(ignore full lines)



Solutions are OK
Melts are NOT

PS solutions vs PS melts

(Bhattacharjee et al., *Macromolecules* 2002; Bach *et al., Macromolecules* 2003; Luap et al., *Rheologica Acta* 2006)



"Non universal" behaviour

Non universal behaviour in fast flows

Sridhar et al., ICR Monterey 2008

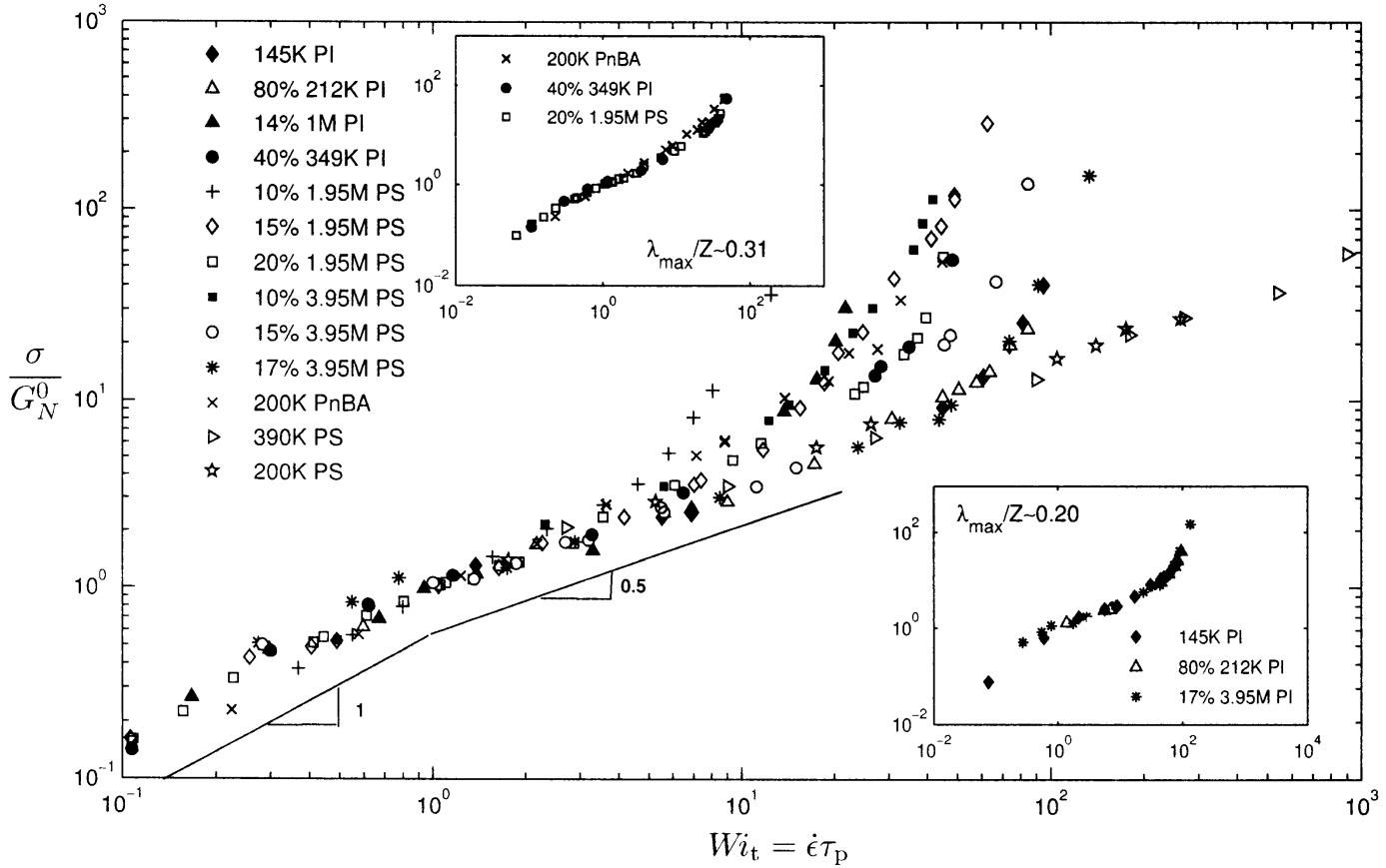
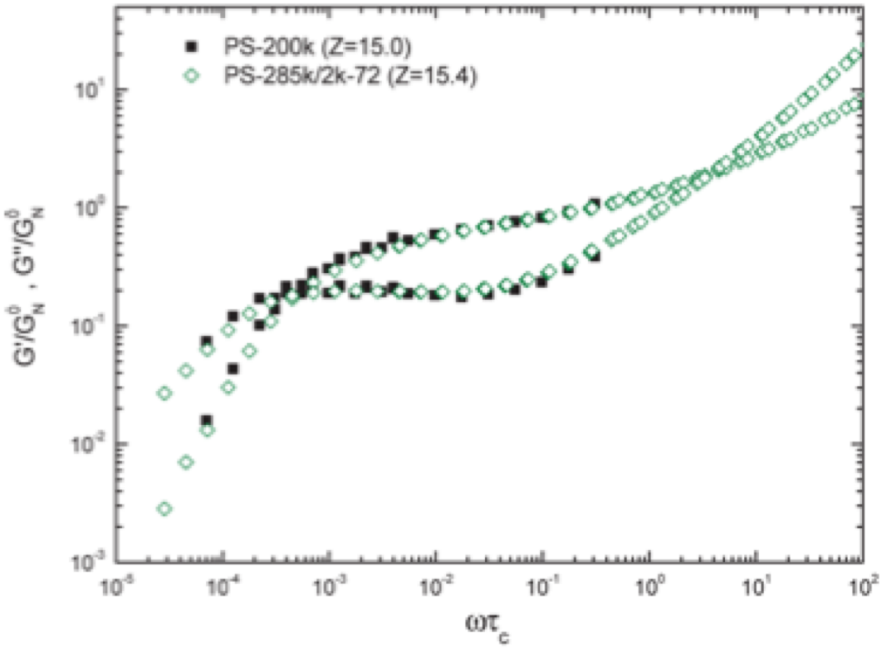
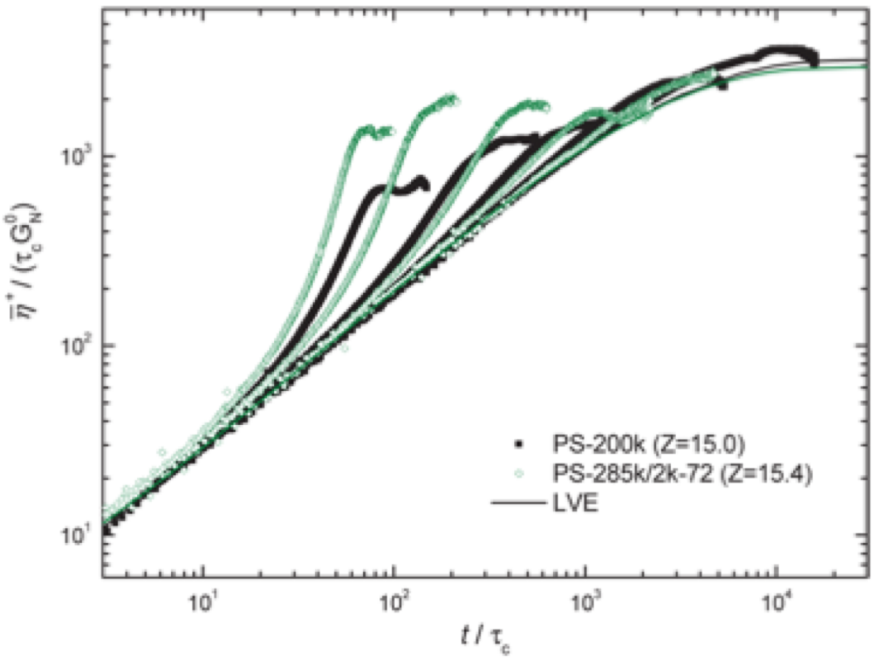


FIG. 2: Comparison of the steady state non-dimensional stress against Weissenberg number, Wi_{t} (strain rate non-dimensionalized by τ_{p}) for various systems including Polystyrene and Polyisoprene entangled solutions and melts. Lines of slope 1 and 0.5 are drawn to highlight different regimes. The insets show the selected data of systems with nearly equal $\lambda_{\max}/Z$ values ($\sim$ 0.20 and 0.31).

Melts *vs.* "solutions" with same *Z*

Huang et al., Macromolecules 2013





Differences in the nonlinear range cannot be explained by classical DE theory

Working hypothesis on monomeric friction coefficient

- Why should friction coefficient be insensitive to molecular alignment induced by fast flows?
- For the case of PS melts, we expect that ζ decreases with increasing monomeric orientational order
- Solutions and melts behave differently because solvent molecules remain randomly oriented

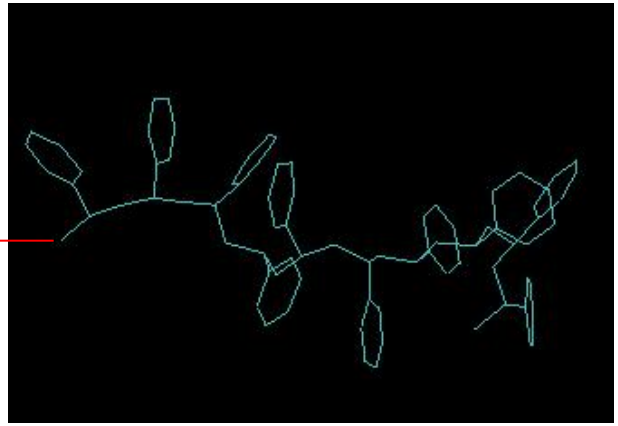
Investigation on flow-induced friction change

- The effect of flow on friction is expected to depend on the specific chemistry
- The technique of choice is then atomistic molecular dynamics
- We focus on molecular dynamics simulations of (by necessity) short polymers, specifically PS oligomers
- Shear flows are here considered

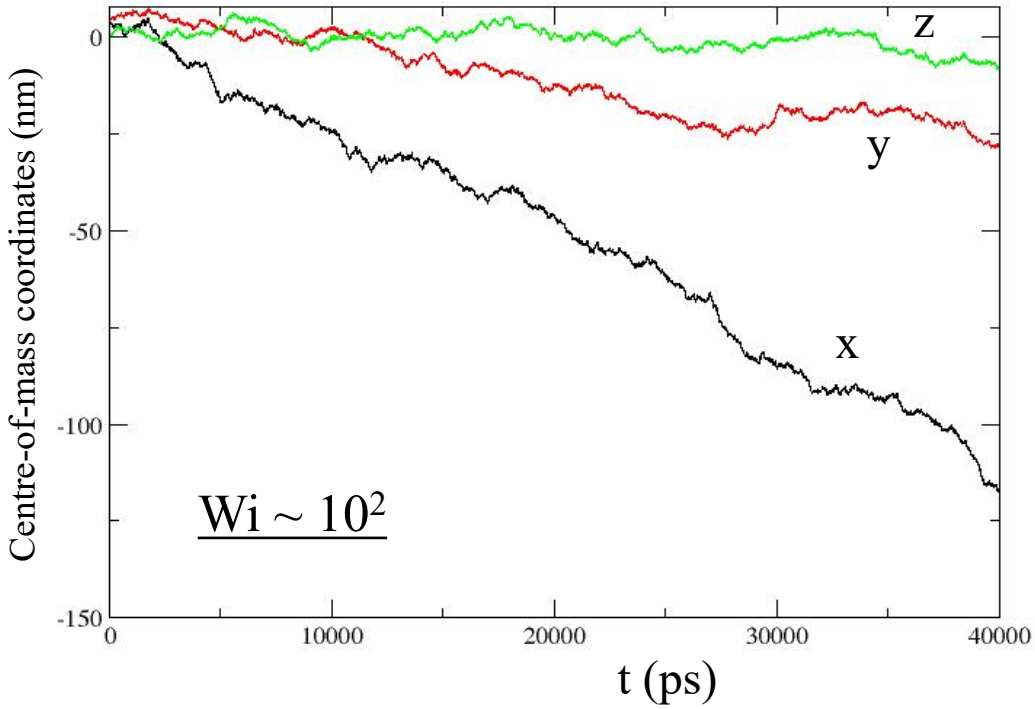
Flow-induced friction change

Molecular Dynamics

F_x



PS decamer

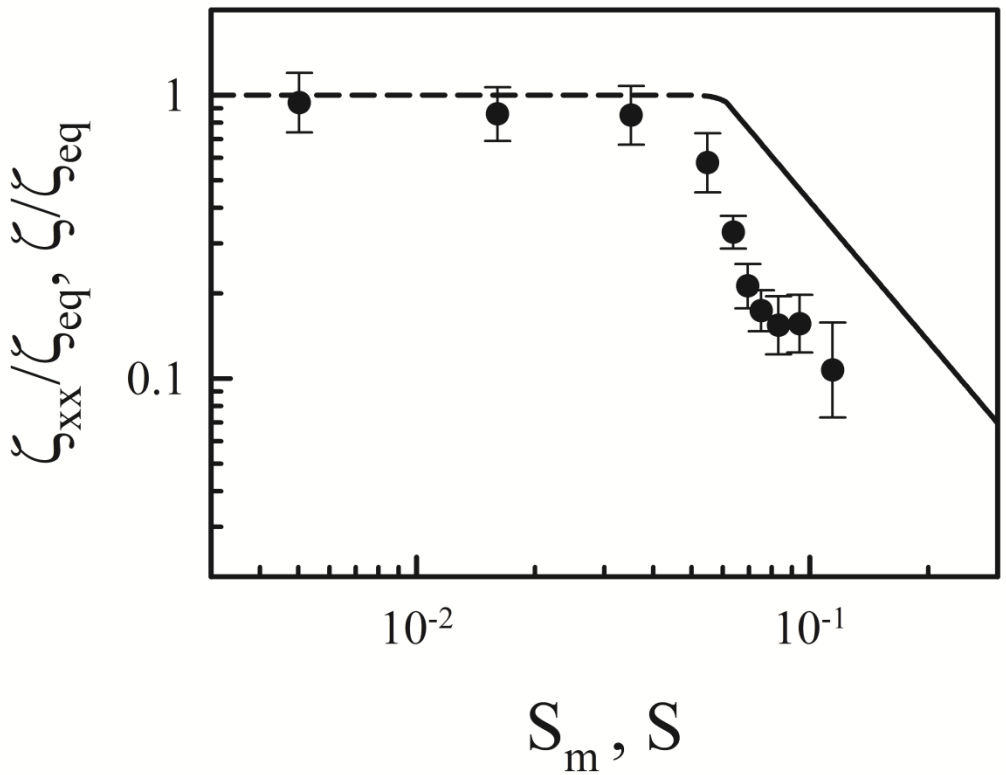


The average slope gives the velocity v_x, hence the friction coefficient:

$$\zeta = \frac{F_x}{v_x}$$

Comparison between decamer result and polymer prediction

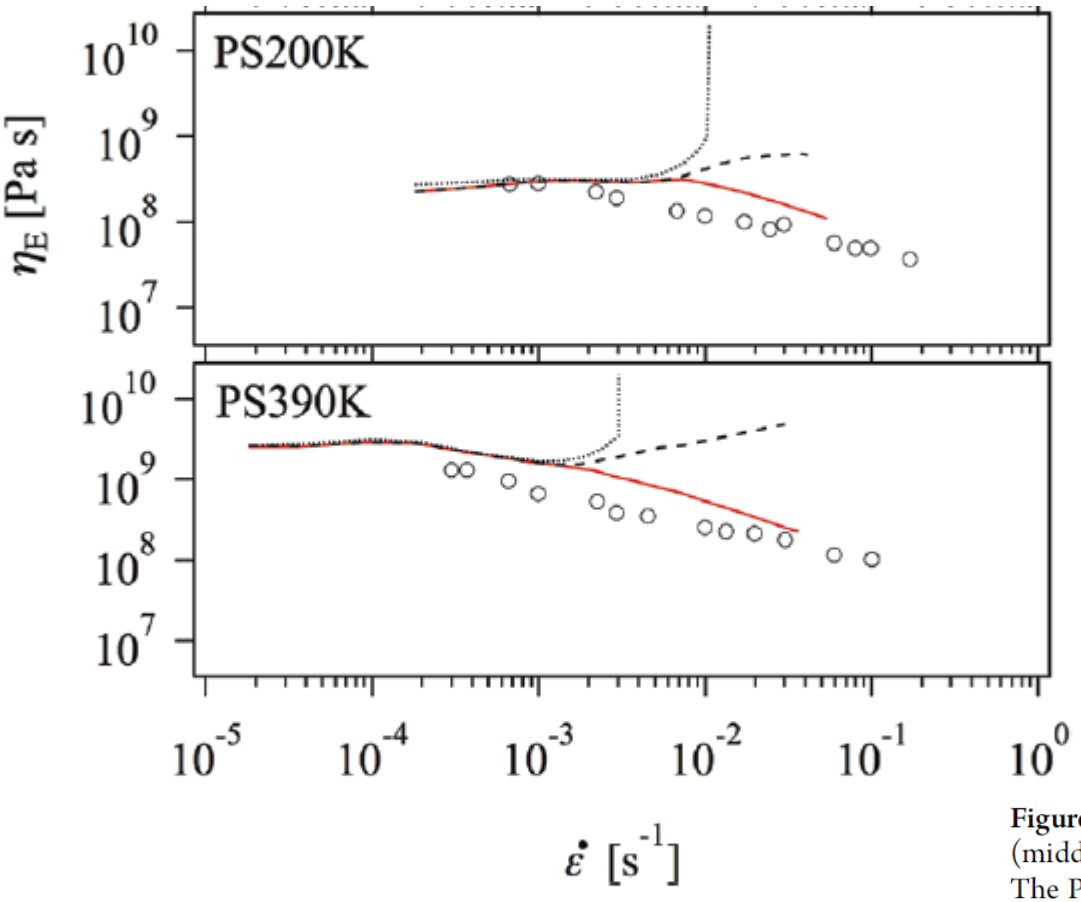
(based on an analysis of stress-optical data of entangled PS melts)



Ianniruberto *et al.* (2012)

(where $\zeta_{xx}/\zeta_{eq}=M_{eq}/M_{xx}$)

After “measuring” the friction coefficient in MD, we run again the NAPLES simulations with the new friction



With and without friction reduction (dashed includes finite extendibility)

Figure 10. Steady elongational viscosity for PS100K (top), PS200K (middle) and PS390K (bottom) at 130 °C plotted against strain rate. The PCN simulation results without FENE and ζ reduction are shown with thin dotted curves. The PCN-FENE results without and with the stretch/orientation-induced reduction of friction are indicated with thick dashed and solid (red) curves, respectively. Experimental data from ref 3 are shown with unfilled circles.

Conclusions

- Rheology of polymeric networks is a fascinating subject, with surprising features
- We have here considered networks of entangled polymers and networks of telechelic, unentangled associating polymers
- More complex associating networks (including double dynamics networks) will be discussed in Capri
- Extensional flows, ubiquitous in processing operations, represent a very severe test for constitutive equations