What about polymer melts?

Non permanent crosslinks

Green-Tobolsky Temporary Network Model

- ν junction points per unit volume = constant
- ETE vectors have finite lifetimes
- when old junctions die, new ones are born
- newly born ETE vectors adopt the equilibrium distribution ψ_0

$$\begin{pmatrix}\text{Probability per unit} \\ \text{time that strand dies} \\ \text{and is reborn at} \\ \text{equilibrium}\end{pmatrix} \equiv \frac{1}{\lambda} \qquad \begin{pmatrix}\text{Probability that strand} \\ \text{retains same ETE from t'} \\ \text{to t (survival probability)}\end{pmatrix} \equiv P_{t',t}$$

What is the probability that a strand retains the same ETE vector between t' and $t'+\Delta t$?

$$P_{t',t+\Delta t} = \begin{pmatrix}\text{Probability that strand} \\ \text{retains same ETE from } t' \\ \text{to } t \text{ (survival probability)}\end{pmatrix}\begin{pmatrix}\text{Probability that} \\ \text{strand does not die} \\ \text{over interval } \Delta t\end{pmatrix}$$

$$P_{t',t+\Delta t} = P_{t',t}\left(1 - \frac{1}{\lambda}\Delta t\right)$$

$$\frac{dP_{t',t}}{dt} = -\frac{1}{\lambda}P_{t',t}$$

$$\ln P_{t',t} = -\frac{t}{\lambda} + C_1$$

$$\boxed{P_{t',t} = e^{-\frac{(t-t')}{\lambda}}}$$

The contribution to the stress tensor of the individual strands can be calculated from,

$$\begin{pmatrix}\text{Stress from}\\ \text{strands born}\\ \text{between } t' \text{ and}\\ t'+dt'\end{pmatrix} = \begin{pmatrix}\text{Probability that}\\ \text{strand is born}\\ \text{between } t' \text{ and}\\ t'+dt'\end{pmatrix}\begin{pmatrix}\text{Probability}\\ \text{that a strand}\\ \text{survives from}\\ t' \text{ to } t\end{pmatrix}\begin{pmatrix}\text{Stress generated by}\\ \text{an affinely}\\ \text{deforming strand}\\ \text{between } t' \text{ and } t\end{pmatrix}$$

$$d\underline{\underline{\tau}} = \left[\frac{1}{\lambda}dt'\right]\left[e^{-\frac{(t-t')}{\lambda}}\right]\left[-G\underline{\underline{C}}^{-1}(t',t)\right]$$

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t}\frac{G}{\lambda}e^{-\frac{(t-t')}{\lambda}}\underline{\underline{C}}^{-1}(t',t)\,dt'$$

Green-Tobolsky temporary network mode (Lodge model)

Back where we started!

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t}\frac{G}{\lambda}e^{-\frac{(t-t')}{\lambda}}\underline{\underline{C}}^{-1}(t',t)\,dt'$$

Green-Tobolsky temporary network mode (Lodge model)

NO!

We now know that affine motion off strands with equal birth and death rates gives a model with no shear-thinning, no second-normal stress difference.

To model shear-thinning, N_2, etc., therefore, we must add something else to our physical picture, e.g.,

- •Anisotropic drag
- •nonaffine motion of various types

Anisotropic drag - Giesekus

In a system undergoing deformation, the surroundings of a given molecule will be anisotropic; this will result in the drag on any given molecule being anisotropic too.

Starting with the dumbbell model (gives UCM), replace $\frac{8kT\beta^2}{\zeta}$ with an anisotropic mobility tensor $\frac{\underline{\underline{B}}}{\lambda}$. Assume also that the anisotropy in $\underline{\underline{B}}$ is proportional to the anisotropy in $\underline{\underline{\tau}}$.

$$\underline{\underline{B}} - \underline{\underline{I}} = \frac{\alpha}{G}\underline{\underline{\tau}}$$

Giesekus Model $$\underline{\underline{\tau}} + \lambda\overset{\triangledown}{\underline{\underline{\tau}}} + \frac{\alpha\lambda}{\eta_0}\underline{\underline{\tau}} : \underline{\underline{\tau}} = -\eta_0\dot{\underline{\underline{\gamma}}}$$

see Larson, "Constitutive equations for polymer melts, Butterworths, 1988

Constitutive equations incorporating non-affine motion include:

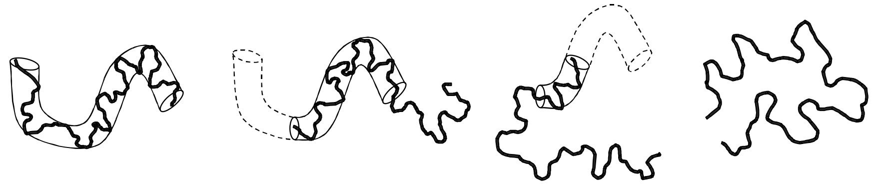
Gordon and Schowalter: "strands of polymer slip with respect to the deformation of the macroscopic continuum"; see Larson, p130 (this model has problems in step-shear strains)

Larson: uses nonaffine motion that is a generalization of the motion in the Doi Edwards model; see Larson, Chapter 5

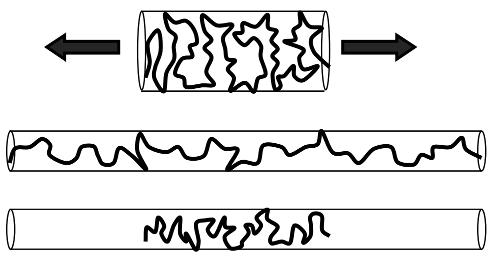
Wagner: uses irreversible nonaffine motion; see Larson, Chapter 5

see Larson, "Constitutive equations for polymer melts, Butterworths, 1988

Reptation Theory (de Gennes)



Retraction (Doi-Edwards)



Doi-Edwards Model

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} M(t-t')\,\underline{\underline{Q}}(t',t)\,dt'$$

$$\underline{\underline{Q}}(t',t) = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} 5\left(\frac{\hat{u}'\cdot\underline{\underline{F}}^{-1}\;\hat{u}'\cdot\underline{\underline{F}}^{-1}}{\left|\hat{u}'\cdot\underline{\underline{F}}^{-1}\right|^2}\right)\sin\theta\; d\theta d\phi$$

$$M(t-t') = \sum_{i\,odd}\frac{G_i}{\lambda_i}e^{-\frac{t-t'}{\lambda_i}} \qquad G_i = \frac{8G_N^0}{\pi^2 i^2} \qquad \lambda_i = \frac{\lambda_1}{i^2}$$

$\hat{u}' =$ unit vector that gives orientation of strands at time *t'*

(Factorized K-BKZ type)

Doi-Edwards Model

Correctly predicts:

- Ratio of Ψ_1/Ψ_2
- shape of start-up curves
- shape of $h(\gamma_0)$
- predicts $\eta = AM^3$
- shear thinning of η, Ψ_1
- tension-thinning elongational viscosity

Fails to predict:

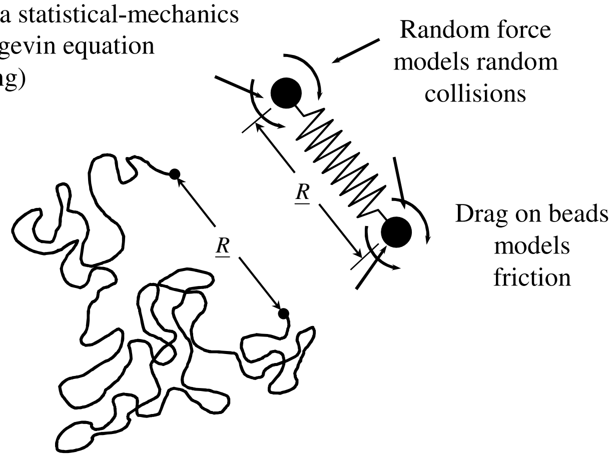
- $\eta = AM^{3.4}$
- shape of shear thinning of η, Ψ_1
- reversing flows

Also, calculations of flow fields is quite involved.

What about polymer solutions?

- Dilute solutions: chains do not interact
- collisions with solvent molecules are modeled stochastically
- calculate $\psi(\underline{R})$ by a statistical-mechanics solution to the Langevin equation (ensemble averaging)

Elastic Dumbbell Model



Elastic Dumbbell Model for Dilute Polymer Solutions results in:

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} = -\eta_0 \dot{\underline{\underline{\gamma}}}$$

Upper-Convected Maxwell Model

$$G = \nu kT$$ (ν: number of dumbbells/volume)

$$\lambda = \frac{\zeta}{8kT\beta^2}$$ (ζ: bead friction factor)

$$\beta^2 \equiv \frac{3}{2Na^2}$$ from random walk

Summary

Molecular models may lead to familiar constitutive equations

- Rubber-elasticity theory = Finite-strain Hooke's law model
- Green-Tobolsky temporary network theory = Lodge equation
- Reptation theory = K-BKZ type equation
- Elastic dumbbell model for polymer solutions = upper-convected Maxwell

Model parameters have greater meaning when connected to a molecular model

- G = νkT
- G_i, λ_i specified by model

Molecular models are essential to narrowing down the choices available in the continuum-based models (e.g. K-BKZ, Rivlin-Sawyers, etc.)

Caution: correct stress predictions do not imply that the molecular model is correct

Stress is proportional to the second moment of $\psi(R)$, but different functions may have the same second moments.

As always, the proof is in the prediction.

see Larson, esp. Ch 7

Rheometry

measurement

Shear - capillary, parallel plate, cone-and-plate, Couette

Elongational - melt stretching, filament stretching, MBER, lubricated squeezing, stagnation flows, contraction flows

Flow Birefringence - applicable for both shear and elongation flows

What is measured depends on what is measurable.

Flow Birefringence - a non-invasive way to measure stresses

no net force, isotropic chain,
isotropic polarization

force applied, anisotropic chain,
anisotropic polarization = *birefringent*