## Molecular Constitutive Modeling

- Begin with a picture (model) of the kind of material that interests you
- Derive how stress is produced by deformation of that picture
- Write the stress as a function of deformation (constitutive equation)

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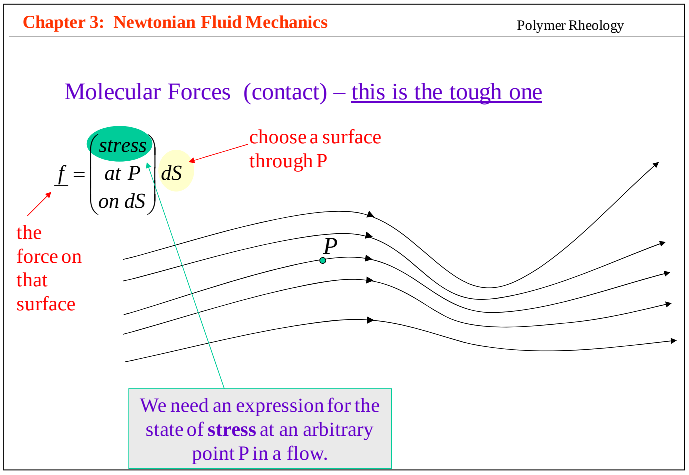
## At the beginning of the course . . .



**Chapter 3: Newtonian Fluid Mechanics**

Polymer Rheology

Molecular Forces (contact) – <u>this is the tough one</u>

$$\underline{f} = \begin{pmatrix} \textit{stress} \\ \textit{at } P \\ \textit{on } dS \end{pmatrix} dS$$

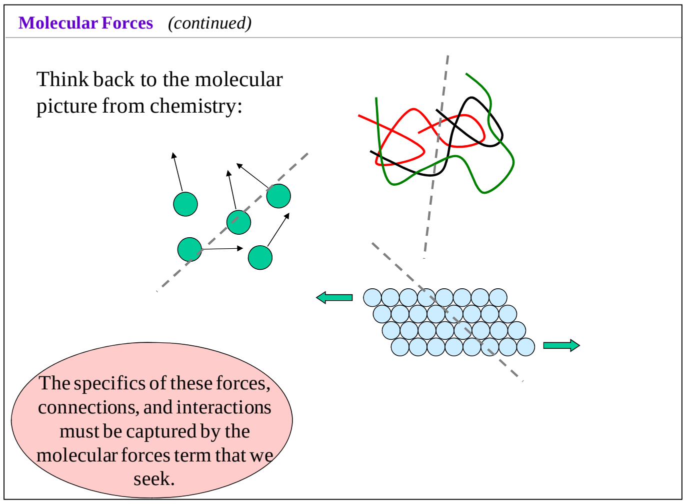
choose a surface through P

the force on that surface

We need an expression for the state of **stress** at an arbitrary point P in a flow.

## At the beginning of the course . . .

At that time we wanted to avoid specifying much about our materials.



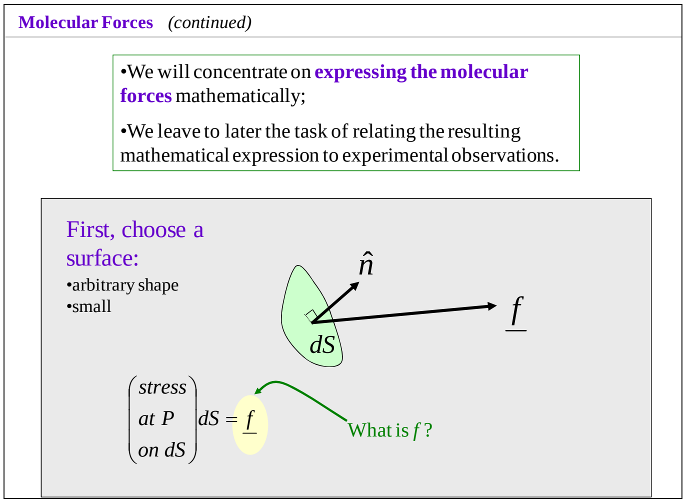
**Molecular Forces** *(continued)*

Think back to the molecular picture from chemistry:

The specifics of these forces, connections, and interactions must be captured by the molecular forces term that we seek.

---

## At the beginning of the course . . .



**Molecular Forces** *(continued)*

- We will concentrate on **expressing the molecular forces** mathematically;
- We leave to later the task of relating the resulting mathematical expression to experimental observations.

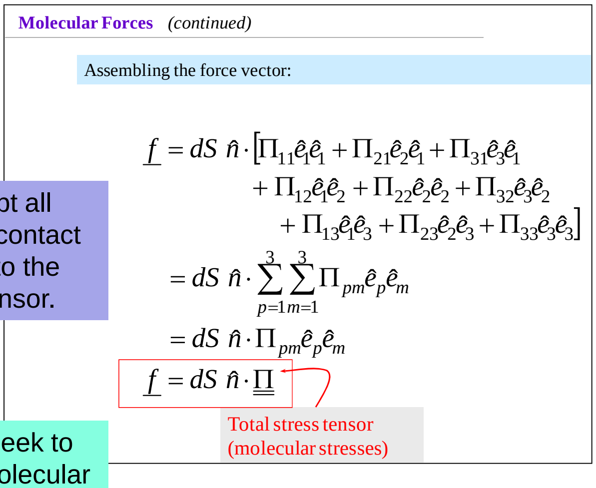
First, choose a surface:

- arbitrary shape
- small

$$\begin{pmatrix} stress \\ at\ P \\ on\ dS \end{pmatrix} dS = \underline{f}$$

What is $f$ ?

## At the beginning of the course . . .



**Molecular Forces** *(continued)*

Assembling the force vector:

$$\underline{f} = dS\ \hat{n}\cdot\big[\Pi_{11}\hat{e}_1\hat{e}_1 + \Pi_{21}\hat{e}_2\hat{e}_1 + \Pi_{31}\hat{e}_3\hat{e}_1 + \Pi_{12}\hat{e}_1\hat{e}_2 + \Pi_{22}\hat{e}_2\hat{e}_2 + \Pi_{32}\hat{e}_3\hat{e}_2 + \Pi_{13}\hat{e}_1\hat{e}_3 + \Pi_{23}\hat{e}_2\hat{e}_3 + \Pi_{33}\hat{e}_3\hat{e}_3\big]$$

$$= dS\ \hat{n}\cdot\sum_{p=1}^{3}\sum_{m=1}^{3}\Pi_{pm}\hat{e}_p\hat{e}_m$$

$$= dS\ \hat{n}\cdot\Pi_{pm}\hat{e}_p\hat{e}_m$$

$$\boxed{\underline{f} = dS\ \hat{n}\cdot\underline{\underline{\Pi}}}$$

Total stress tensor (molecular stresses)

We swept all molecular contact forces into the stress tensor.

Now, we seek to calculate molecular contact forces directly from a molecular picture.

---

## Long-Chain Polymer Constitutive Modeling

*molecular* tension force on arbitrary surface

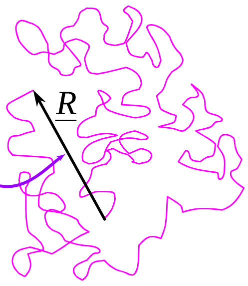
$$\underline{\tilde{f}} = dA\ \hat{n}\cdot(-\underline{\underline{\tau}})$$

stress tensor

We now attempt to calculate molecular forces by considering molecular models.

### Polymer Dynamics

end-to-end vector, $\underline{R}$

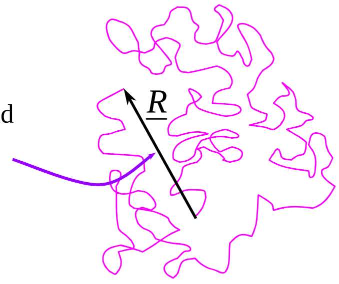


Long-chain polymers may be modeled as random walks.

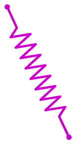
## Polymer coil responds to deformation

A polymer chain adopts the most random configuration at equilibrium.

end-to-end vector, R



When deformed, the chain tries to recover that most random configuration, giving rise to a spring-like restoring force.



spring of equilibrium length and orientation R

We will model the chain dynamics with a random walk.

---

## Gaussian Springs (random walk)

*Equilibrium configuration distribution function* - probability a walk of N steps of length *a* has end-to-end distance R

$$\psi_0(\underline{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}\cdot\underline{R}}$$

$$\beta = \frac{3}{2Na^2}$$

From an entropy calculation of the work needed to extend a random walk, we can calculate the force needed to deform a the polymer coil

$$\underline{f} = \frac{3kT}{Na^2}\underline{R}$$

If we can relate **this force**, the force to extend the spring, to the force on an arbitrary surface, we can predict rheological properties

*molecular* tension force on arbitrary surface

$$\underline{\tilde{f}} = -dA\,\hat{n}\cdot\underline{\underline{\tau}}$$

stress tensor

## *Molecular force generated by deforming chain*

$$\underline{\tilde{f}} = \begin{pmatrix}\text{Tension}\\ \text{force on } dA\end{pmatrix} = \iiint \begin{pmatrix}\text{Force on surface}\\ dA \text{ due to chains}\\ \text{of ETE } \underline{R}\end{pmatrix}$$

$$\overbrace{\begin{pmatrix}\text{Probability}\\ \text{chain of ETE } \underline{R}\\ \text{crosses surface}\\ \text{dA}\end{pmatrix}\begin{pmatrix}\text{Probability}\\ \text{chain has ETE}\\ \underline{R}\end{pmatrix}\begin{pmatrix}\text{Force exerted}\\ \text{by chain w/}\\ \text{ETE } \underline{R}\end{pmatrix}}$$

$$(\hat{n}\cdot\underline{R})\nu^{\frac{1}{3}}$$

(see next slide)

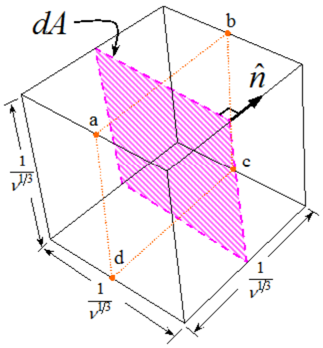
$$\psi(\underline{R})dR_1 dR_2 dR_3$$

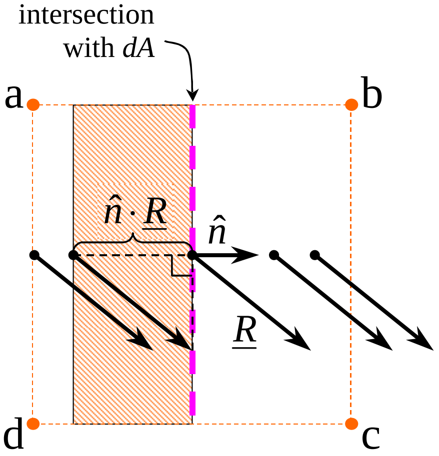
$$\underline{f} = \frac{3kT}{Na^2}\underline{R}$$

ν = number of polymer chains per unit volume

---

## Probability chain of ETE $\underline{R}$ crosses surface dA





$$\begin{pmatrix}\text{Probability}\\ \text{chain of ETE } \underline{R}\\ \text{crosses surface}\\ \text{dA}\end{pmatrix} = \frac{(\hat{n}\cdot\underline{R})\left(\nu^{-\frac{1}{3}}\right)\left(\nu^{-\frac{1}{3}}\right)}{\left(\nu^{-1/3}\right)^3}$$

1/ν = volume per polymer chain

*Molecular force generated by deforming chain*

$$\underline{\tilde{f}} = \frac{3kT\nu^{\frac{1}{3}}}{Na^2}\left(\hat{n}\cdot\langle \underline{R}\cdot\underline{R}\rangle\right)$$

$$\langle \underline{R}\cdot\underline{R}\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})\,dR_1 dR_2 dR_3$$

BUT, from before . . .

$$\underline{\tilde{f}} = -dA\,\hat{n}\cdot\underline{\underline{\tau}}$$

*molecular* tension force on arbitrary surface in terms of $\underline{\underline{\tau}}$

Comparing these two we conclude,

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle$$

$(dA = \nu^{-\frac{2}{3}})$

***Molecular force generated by deforming chain***

---

How can we convert this equation,

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle$$

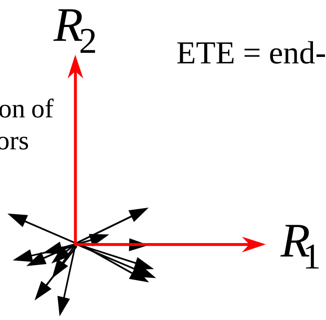
***Molecular stress in a fluid generated by a deforming chain***

which relates molecular ETE vector and stress, into a constitutive equation, which relates stress and deformation?

*We need a idea that connects ETE vector motion to macroscopic deformation of a polymer network or melt.*

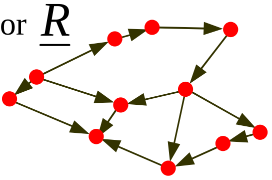
## Elastic (Crosslinked) Solid

Between every two crosslinks there is a polymer strand that follows a random walk of *N* steps of length *a*.



Distribution of ETE vectors

ETE = end-to-end vector $\underline{R}$



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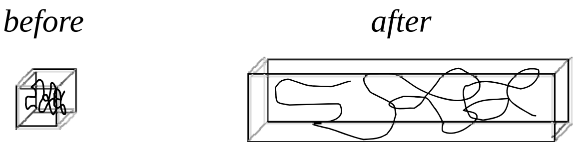
*How can we relate changes in end-to-end vector to macroscopic deformation?*

AN ANSWER: affine-motion assumption: the macroscopic dimension changes are proportional to the microscopic dimension changes



## Consider a general elongational deformation:

$$\underline{\underline{F}}^{-1} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}_{123}$$

For affine motion we can relate the components of the initial and final ETE vectors as,

ETE after

$$\lambda_1 = \frac{R_1}{R_1'} \qquad \lambda_2 = \frac{R_2}{R_2'} \qquad \lambda_3 = \frac{R_3}{R_3'} \qquad \underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

ETE before

---

We are attempting to calculate the stress tensor with this equation:

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle$$

$$\langle \underline{R}\cdot\underline{R}\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})\,dR_1 dR_2 dR_3$$

$$\underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

But, where do we get this?

Probability chain has ETE between $\underline{R}$ and $\underline{R}+d\underline{R}$: $\psi(\underline{R})dR_1dR_2dR_3$

*Configuration distribution function*

*Equilibrium configuration distribution function:*

$$\psi_0(\underline{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$$

$$\beta = \frac{3}{2Na^2}$$

But, if the deformation is **affine**, then the number of ETE vectors between $\underline{R}$ and $\underline{R}+d\underline{R}$ at time $t$ is equal to the number of vectors with ETE between $\underline{R}$' and $\underline{R}$'+$d\underline{R}$' at $t$'

Conclusion: $\psi(\underline{R}) = \psi_0(\underline{R}') = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$

---

Now we are ready to calculate the stress tensor.

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\left\langle \underline{R}\cdot\underline{R}\right\rangle$$

$$\left\langle \underline{R}\cdot\underline{R}\right\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})dR_1dR_2dR_3$$

$$R_i' = \frac{R_i}{\lambda_i}$$

$$\underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

$$\psi(\underline{R}) = \psi_0(\underline{R}') = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$$

(much algebra omitted; solved in Problem 9.57)

Final solution: $\underline{\underline{\tau}} = -\nu kT\lambda_i^2 \hat{e}_i\hat{e}_i$

Final solution for stress: $\underline{\underline{\tau}} = -\nu kT\lambda_i^2\hat{e}_i\hat{e}_i = -\nu kT\begin{pmatrix}\lambda_1^2 & 0 & 0\\ 0 & \lambda_2^2 & 0\\ 0 & 0 & \lambda_3^2\end{pmatrix}_{123}$

Compare this solution with the Finger strain tensor for this flow.

$$\underline{\underline{C}}^{-1}(t',t) = \left(\underline{\underline{F}}^{-1}\right)^T\cdot\underline{\underline{F}}^{-1} = \begin{pmatrix}\lambda_1^2 & 0 & 0\\ 0 & \lambda_2^2 & 0\\ 0 & 0 & \lambda_3^2\end{pmatrix}_{123}$$

Since the Finger tensor for **any** deformation may be written in diagonal form (symmetric tensor) our derivation is valid for all deformations.

$$\underline{\underline{\tau}} = -\nu kT\underline{\underline{C}}^{-1}$$

Which is the same as the finite-strain Hooke's law discussed earlier, with $G=\nu kT$.

---

**What about polymer melts?**

Non permanent crosslinks

Green-Tobolsky Temporary Network Model

- $\nu$ 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 $\psi_0$

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

What is the probability that a strand retains the same ETE vector between *t'* and *t'*+*Δt*?

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

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

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

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

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

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

$$\left(\begin{array}{c}\text{Stress at } t \text{ from}\\ \text{strands born}\\ \text{between } t' \text{ and}\\ t'+dt'\end{array}\right) = \left(\begin{array}{c}\text{Probability that}\\ \text{strand is born}\\ \text{between } t' \text{ and}\\ t'+dt'\end{array}\right)\left(\begin{array}{c}\text{Probability}\\ \text{that a strand}\\ \text{survives from}\\ t' \text{ to } t\end{array}\right)\left(\begin{array}{c}\text{Stress generated by}\\ \text{an affinely}\\ \text{deforming strand}\\ \text{between } t' \text{ and } t\end{array}\right)$$

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

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

Green-Tobolsky temporary network mode (Lodge model)

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Oh no, back where we started!

**NO!**

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

Green-Tobolsky temporary network mode (Lodge model)

We now know that affine motion of 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 $\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} + \frac{\alpha\lambda}{\eta_0} \underline{\underline{\tau}} : \underline{\underline{\tau}} = -\eta_0 \underline{\underline{\dot{\gamma}}}$

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)

strand slippage

$$\overset{\square}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} - \left(\nabla \underline{v}\right)^T \cdot \underline{\underline{\tau}} + \underline{\underline{\tau}} \cdot \nabla \underline{v} + \frac{\xi}{2}\left(\underline{\underline{\tau}} \cdot \underline{\underline{\dot{\gamma}}} + \underline{\underline{\dot{\gamma}}} \cdot \underline{\underline{\tau}}\right)$$

- Phan-Thien/Tanner
- Johnson-Segalman

**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

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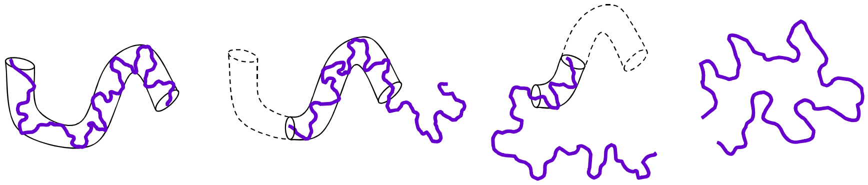
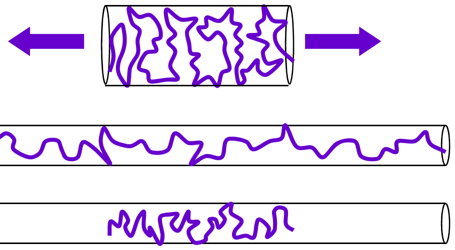
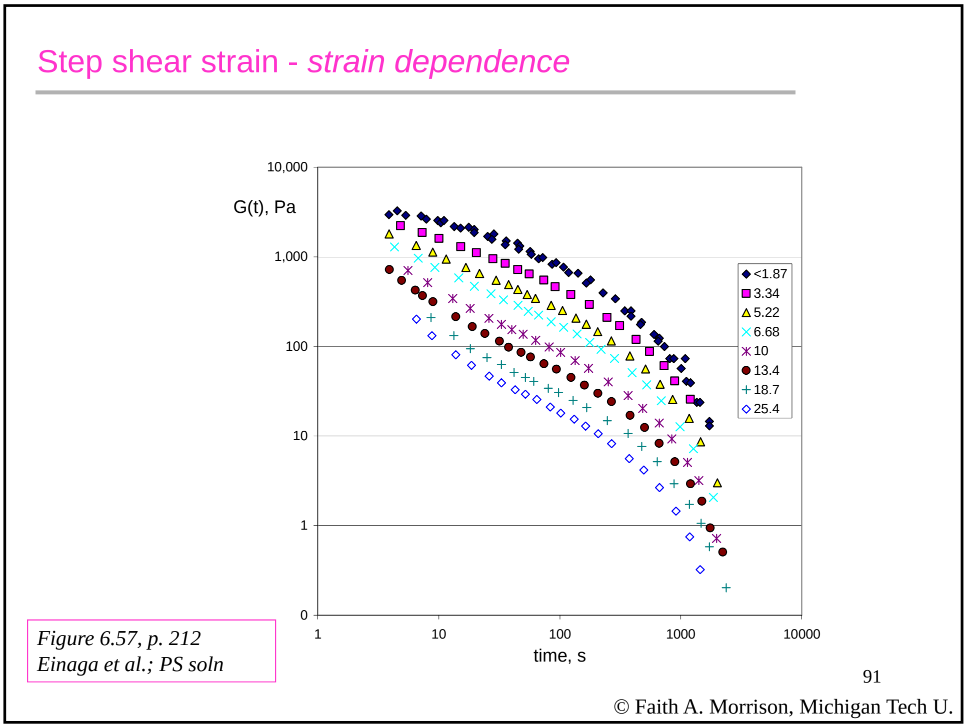
## Reptation Theory (de Gennes)



## Retraction (Doi-Edwards)

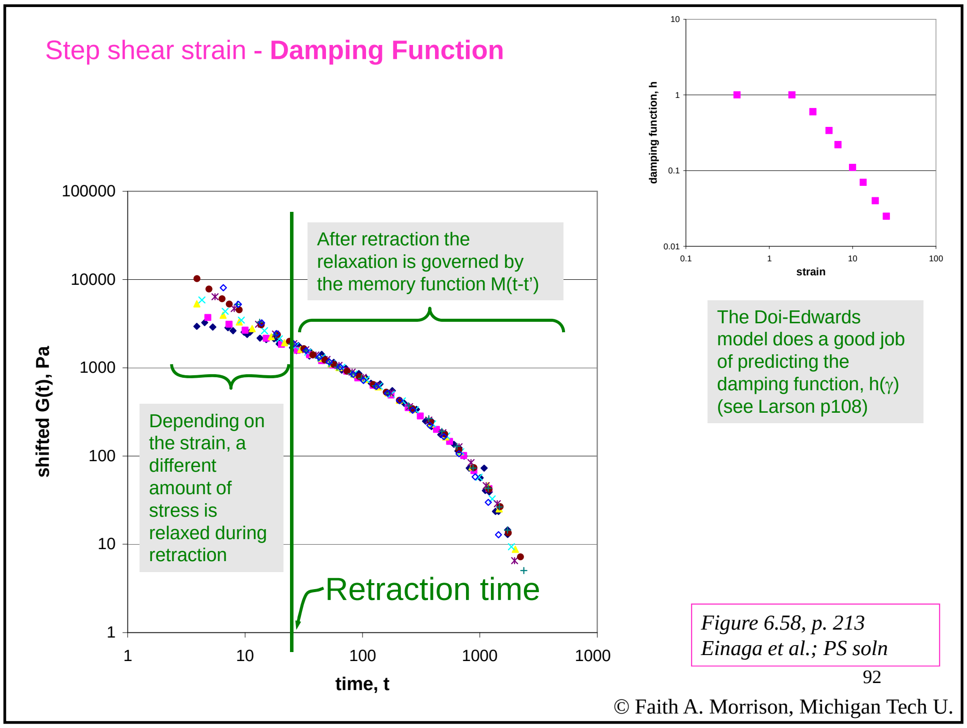


Non-affine motion



## Step shear strain - *strain dependence*

*Figure 6.57, p. 212*
*Einaga et al.; PS soln*



## Step shear strain - **Damping Function**

After retraction the relaxation is governed by the memory function M(t-t')

Depending on the strain, a different amount of stress is relaxed during retraction

The Doi-Edwards model does a good job of predicting the damping function, h(γ) (see Larson p108)

*Figure 6.58, p. 213*
*Einaga et al.; PS soln*

## Doi-Edwards Model

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

Predicts a strain measure

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

Predicts a relaxation time distribution

Predicts a memory function

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

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

*(Factorized K-BKZ type)*

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 74, 1818 (1978); ibid 74 560, 918 (1978); ibid 75, 32 (1979); ibid 75, 38 (1979)

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## Doi-Edwards Model
## Steady Shear
## SAOS

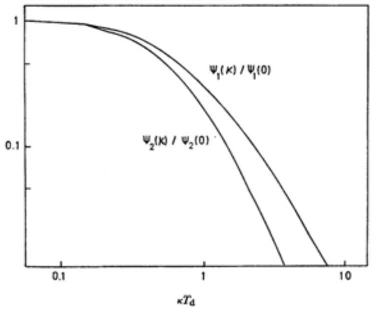

FIG. 5.—First and the second normal stress coefficients $\psi_1(\kappa)$ and $\psi_2(\kappa)$ in steady shear flow. [Note that $\psi_2(0) < 0$, so that $\psi_2(\kappa) < 0$].

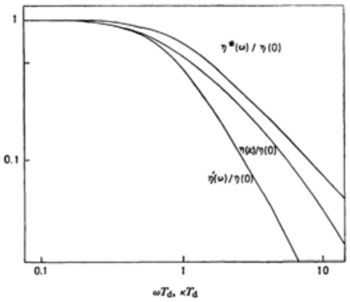

FIG. 3.—Non-linear viscosity $\eta(\kappa)$ in steady state, the modulus, $|\eta^*(\omega)|$, and the real part, $\eta'(\omega)$ of the linear dynamic viscosity. All quantities are normalized by the steady state viscosity at zero shear rate, $\eta(0)$.

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)

## Doi-Edwards Model
## Shear Start Up

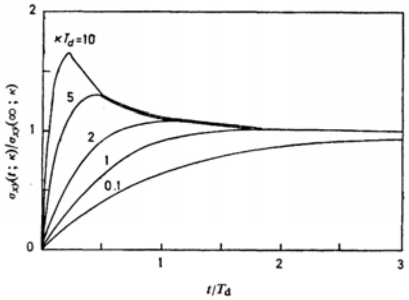

FIG. 6.—Shear stress when a shear flow is started at $t = 0$ with shear rate $\kappa$.

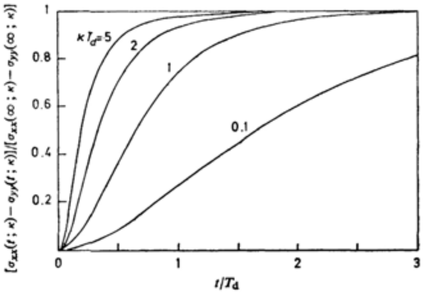

FIG. 7.—Growth of the first normal stress component when a shear flow is started at $t = 0$ with shear rate $\kappa$.

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)

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## Doi-Edwards Model
## Steady Elongation
## Elongation Startup

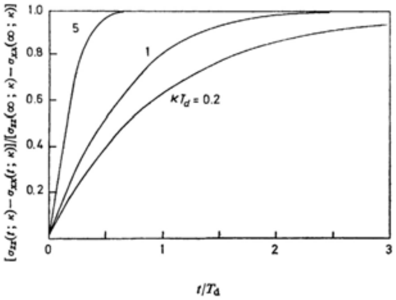

FIG. 13.—Growth of stress when an elongational flow is started at $t = 0$.

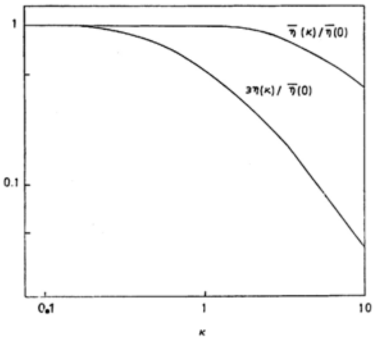

FIG. 12.—Steady elongational viscosity $\bar{\eta}(\kappa)$ and the steady shear viscosity $3\eta(\kappa)$. Both are normalized by $\bar{\eta}(0) = 3\eta(0)$.

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)

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## Doi-Edwards Model
## Large-Amplitude Step Shear

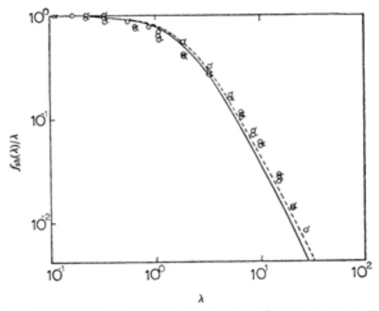


FIG. 6.—Strain dependent part of the stress relaxation function for simple shear [eqn (6.7)]. Circles, observed values [after ref. (11): sample, polystyrene solution in diethyl phthalate; molecular weight, $3 \times 10^6$; concentration, ◌ 0.166 g cm$^{-3}$, ○ 0.221 g cm$^{-3}$, ○ 0.275 g cm$^{-3}$]. Solid curve, eqn (6.8). Broken curve, eqn (7.4). In the ideal gaussian rubber $f_{sh}/\lambda$ is constant.

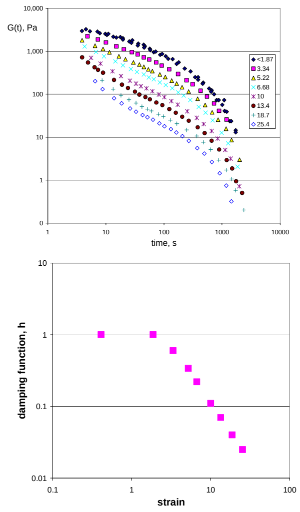


Figure 6.58, p. 213 Einaga et al.; PS soln

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 74, 1802 (1979)

## Doi-Edwards Model

*Correctly predicts:*

- Ratio of $\Psi_1/\Psi_2$
- shape of start-up curves
- shape of h($\gamma_0$) (nonlinear step strain, damping function)
- predicts $\eta = AM^3$
- shear thinning of $\eta$, $\Psi_1$
- tension-thinning elongational viscosity

!!!!

*Fails to predict:*

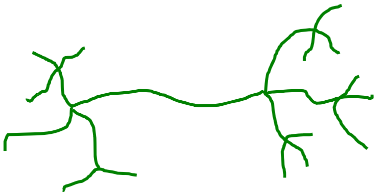
- $\eta = AM^{3.4}$
- shape of shear thinning of $\eta$, $\Psi_1$
- reversing flows
- Elongational strain hardening (branched polymers)

Tentatively conclude: shear thinning is an issue of non-affine motion

## Advanced Models

Long-chain branched polymers

**Pom-Pom Model** (McLeish and Larson, *JOR* 42 81, 1998)
Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



- Single backbone with multiple branches
- Backbone can readily be stretched in an extensional flow, producing strain hardening
- In shear startup, backbone stretches only temporarily, and eventually collapses, producing strain softening
- Based on reptation ideas; two decoupled equations, one for orientation, one for stretch; separate relaxation times for orientation and stretch)

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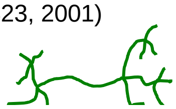
Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



Predicts elongational strain hardening

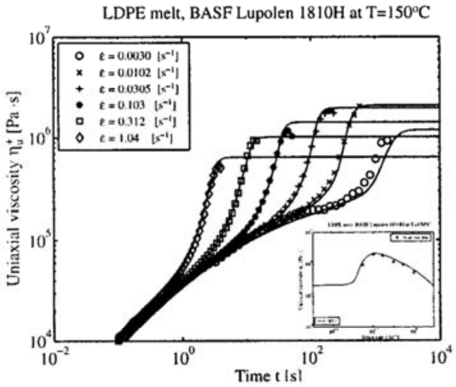
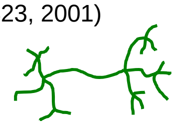


**FIG. 5.** Transient and quasisteady state (*inset*) uniaxial elongational viscosity $\eta_u$ of the XPP model for Lupolen 1810H melt at $T = 150\,°\text{C}$. $\nu_i = 2/q_i$, $\varepsilon = 0.0030,\ 0.0102,\ 0.0305,\ 0.103,\ 0.312,\ 1.04\ \text{s}^{-1}$.

Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



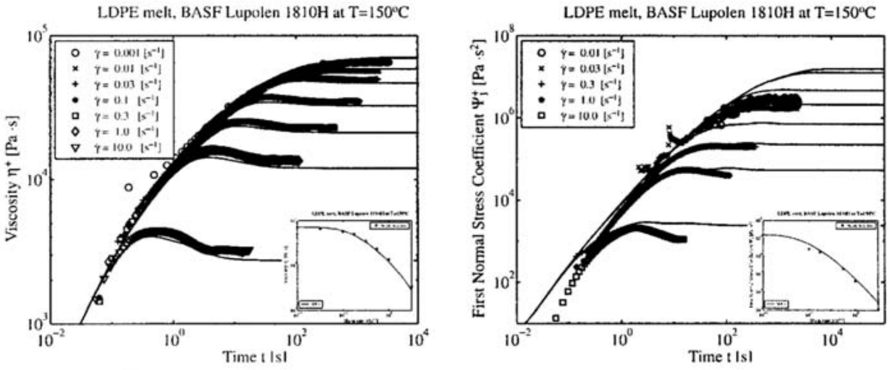


**FIG. 8.** Transient and steady state (*inset*) shear viscosity $\eta$ (*left*) and first normal stress coefficient $\Psi_1$ (*right*) of the XPP model for Lupolen 1810H melt at $T = 150\,°\mathrm{C}$. $\nu_i = 2/q_i$. $\gamma = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10\ \mathrm{s}^{-1}$.

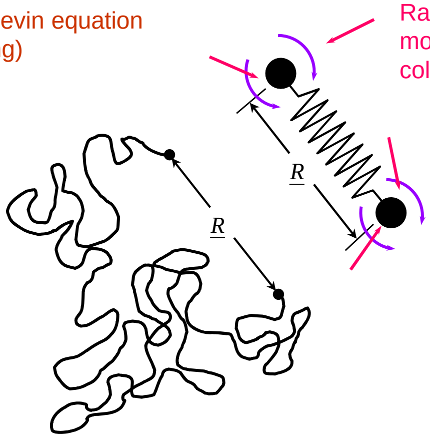
---

## What about polymer solutions?

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

**Elastic Dumbbell Model**

W. Kuhn, 1934



Random force models random collisions

Drag on beads models friction

## Elastic Dumbbell Model

Continuum modeling

Momentum balance on a control volume (Navier-Stokes Equation)

$$\rho\left(\frac{\partial \underline{v}}{\partial t} + \underline{v}\cdot\nabla\underline{v}\right) = -\nabla p + \mu\nabla^2\underline{v} + \rho\underline{g}$$

Inertia = surface + body

Mixed Continuum/Stochastic modeling (Langevin Equation)

Momentum balance on a discrete body (mass *m*, velocity *u*)

In a fluid continuum (velocity field v)

$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^2\underline{R} + \underline{A}$$

Inertia = drag + spring + random (Brownian)

Construct an ensemble of dumbbells and seek the probability of a given ETE at *t*

Construct an ensemble of dumbbells and seek the probability of a given ETE at *t*

## Elastic Dumbbell Model

Langevin Equation

$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^2\underline{R} + \underline{A}$$

To solve, (see Larson pp41-45). Consider an ensemble of dumbbells and seek the probability $\psi$ that a dumbbell has an ETE R at a given time t. The equation for $\psi$ is the Smoluchowski equation:

$$\frac{\partial\psi}{\partial t} + \frac{\partial}{\partial\underline{R}}\cdot\left[\underline{R}\cdot\nabla\underline{v}\,\psi - \frac{4kT\beta^2}{\zeta}\underline{R}\,\psi - \frac{2kT}{\zeta}\frac{\partial\psi}{\partial\underline{R}}\right] = 0$$

We can calculate stress from: $\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})\,dR_1dR_2dR_3$

If we multiply the Smoluchowski equation by $\underline{R}\cdot\underline{R}$ and integrate over R space, we obtain an expression for $\underline{\underline{\tau}}$ (i.e. the constitutive equation for this model)

Integration yields:

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

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

Upper-Convected Maxwell Model!

Two different models give the same constitutive equation (because stress only depends on the second moment of $\psi$, not on details of $\psi$)

$$G = \nu k T$$

number of dumbbells/volume

$$\lambda = \frac{\zeta}{8kT\beta^2}$$

bead friction factor

$$\beta^2 \equiv \frac{3}{2Na^2}$$

from random walk

---

## Elastic Dumbbell Model for Dilute Polymer Solutions

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

Polymer contribution

$$\underline{\underline{\tau}}_s = -\eta_s \underline{\underline{\dot{\gamma}}}$$

Solvent contribution

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s$$

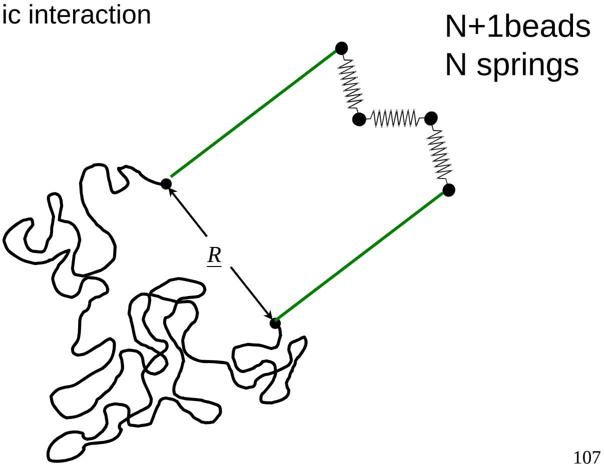
Dumbbell Model
(Oldroyd B)

See problem 9.49

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

## Rouse Model

- Multimodal bead-spring model
- Springs represent different sub-molecules
- Drag localized on beads (Stokes)
- No hydrodynamic interaction



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## Rouse Model

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

- Rouse wrote the Langevin equation for each spring. Each spring's equation is coupled to its neighbor springs which produces a matrix of equations to solve.

Langevin Equation

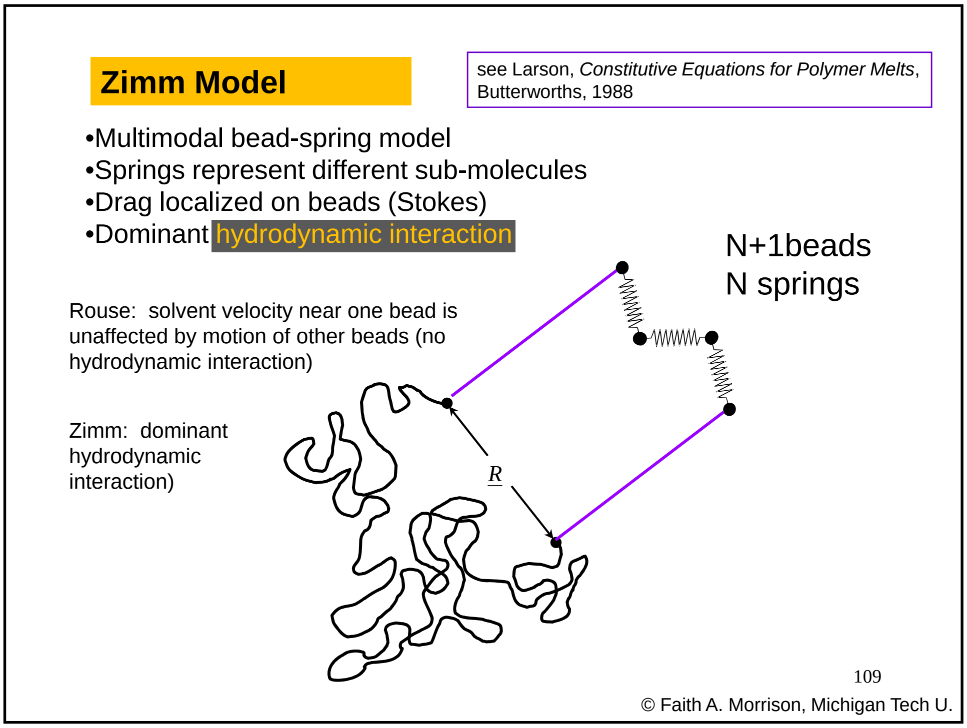
$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^2\underline{R} + \underline{A}$$

- Rouse found a way to diagonalize the matrix of the averaged Langevin equations; this allowed him to find a Smoluchowski equation for each transformed "mode" $\tilde{\underline{R}}_i$ of the Rouse chain
- Each Smoluchowski equation gives a UCM for each of the modes $\tilde{\underline{R}}_i$

$$\underline{\underline{\tau}} = \sum_{i=1}^{N} \underline{\underline{\tau}}_i \qquad G = \nu kT$$

$$\underline{\underline{\tau}}_i + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_i = -G\underline{\underline{I}} \qquad \lambda_i = \frac{\zeta}{16kT\beta^2 \sin^2(i\pi/2(N+1))}$$

Rouse Model for polymer solutions (multi-mode UCM)



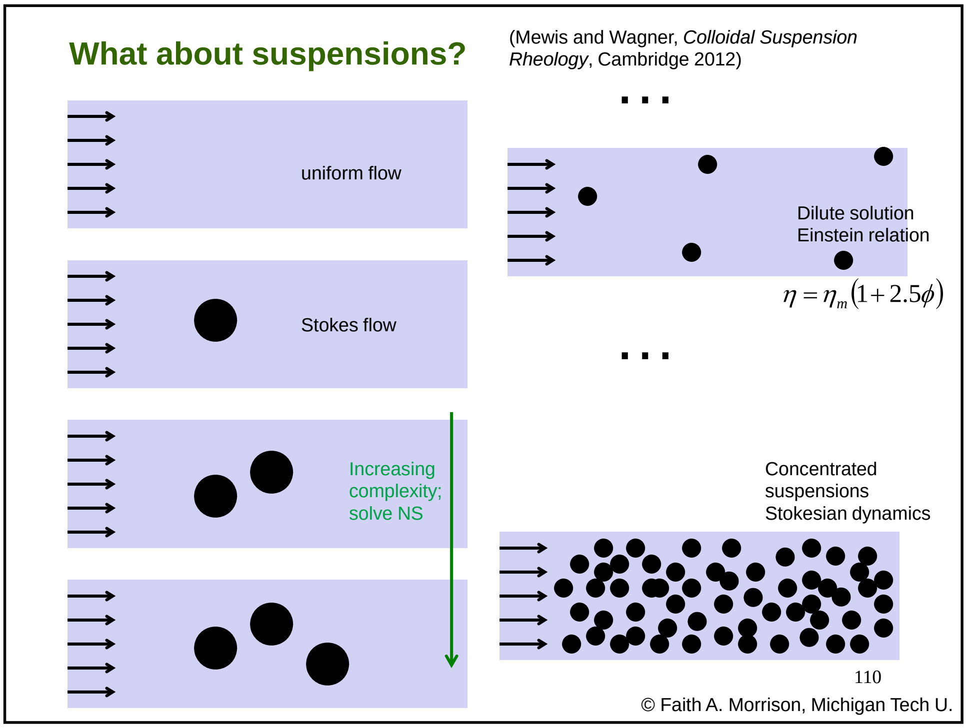
## Zimm Model

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

- Multimodal bead-spring model
- Springs represent different sub-molecules
- Drag localized on beads (Stokes)
- Dominant hydrodynamic interaction

Rouse: solvent velocity near one bead is unaffected by motion of other beads (no hydrodynamic interaction)

Zimm: dominant hydrodynamic interaction)



## What about suspensions?

(Mewis and Wagner, *Colloidal Suspension Rheology*, Cambridge 2012)

$$\eta = \eta_m (1 + 2.5\phi)$$

Brady and Bossis, *Ann. Rev. Fluid Mech*, 20 111 1988
Wagner and Brady, *Phys. Today* 2009, p27

## Stokesian Dynamics

Langevin Equation for Dumbbells

$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^{2}\underline{R} + \underline{A}$$

Inertia = drag + spring + random (Brownian)

Another Langevin Equation
Stokesian Dynamics for Concentrated Suspensions

$$\underline{\underline{M}}\cdot\frac{d\underline{U}}{dt} = \underline{F}_{hydrodynamic} + \underline{F}_{particle} + \underline{F}_{Brownian}$$

Hydrodynamic = everything the suspending fluid is doing (including drag)
Particle = interparticle forces, gravity (including spring forces)
Brownian = random thermal events

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## Stokesian Dynamics

Brady and Bossis, *Ann. Rev. F*
*Mech*, 20 111 1988

Spanning clusters
increase viscosity

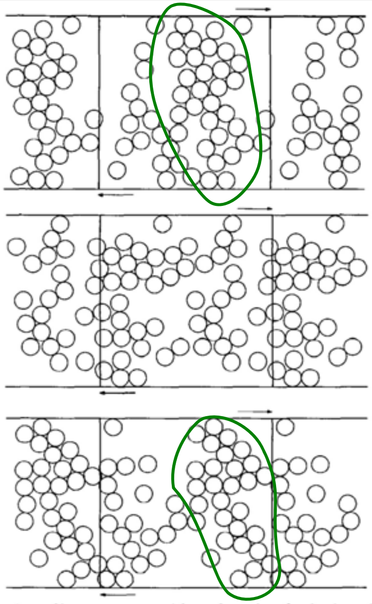


*Figure 14* Snapshots of instantaneous particle configurations for the sheared suspension of Figure 13. The sequence (from top to bottom) corresponds in time to that indicated by the arrows in Figure 13. These arrows correspond to the maxima and minima of the viscosity fluctuations. Both the top and bottom frames show the presence of a spanning cluster—a connected path from one wall to the other—and give rise to large viscosities. In the middle frame, no spanning cluster is present and the viscosity is relatively low.

## 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 (UCM)
- •Reptation theory = K-BKZ type equation
- •Elastic dumbbell model for polymer solutions = Oldroyd B equation

**Model parameters have greater meaning when connected to a molecular model**

- •$G = \nu kT$
- •$G_i$, $\lambda_i$ 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.)**

As always, the proof is in the prediction.

***see Larson, esp. Ch 7***

**Modeling may lead directly to information sought (without ever calculating the stress tensor)**

---

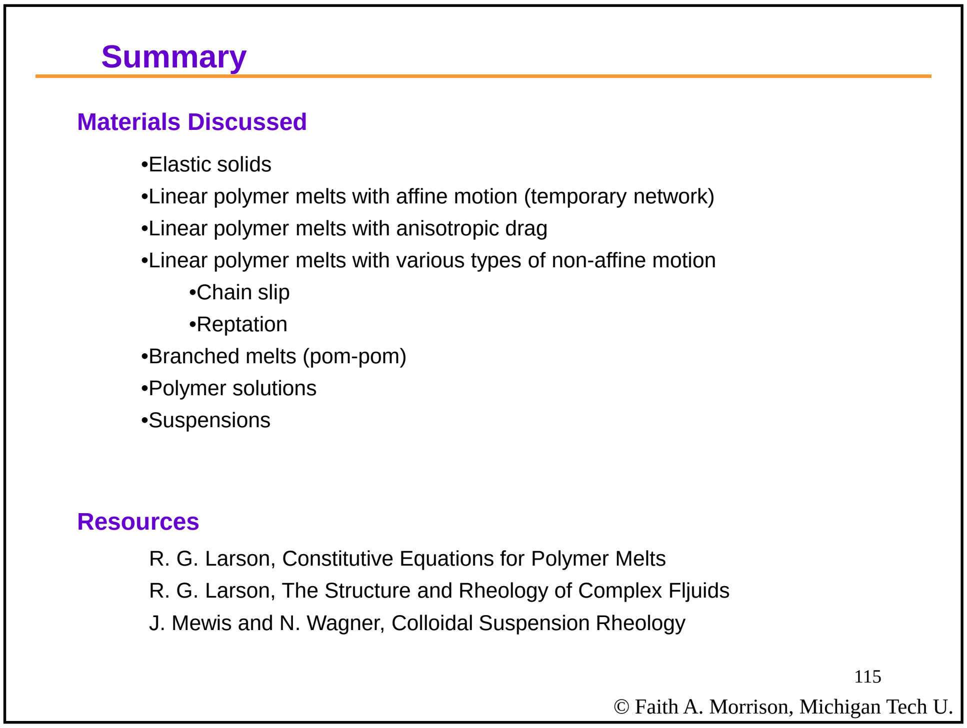
## Summary

**Molecular models may lead to familiar constitutive equations**

- •Rubber-elasticity theory = Finite-strain Hooke’s law model
- •Green-Tobolsky temporary network theory = Lodge equation (UCM)
- •Reptation theory = K-BKZ type equation
- •Elastic dumbbell model for polymer solutions = Oldroyd B equation (UCM)

**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.



## Summary

### Materials Discussed

- Elastic solids
- Linear polymer melts with affine motion (temporary network)
- Linear polymer melts with anisotropic drag
- Linear polymer melts with various types of non-affine motion
  - Chain slip
  - Reptation
- Branched melts (pom-pom)
- Polymer solutions
- Suspensions

### Resources

R. G. Larson, Constitutive Equations for Polymer Melts
R. G. Larson, The Structure and Rheology of Complex Fljuids
J. Mewis and N. Wagner, Colloidal Suspension Rheology