Methods of Improving Constitutive Equations

Maxwell Model

We can improve with new time derivatives or new strain measures.

$$\begin{cases} \underline{\underline{\tau}} + \lambda \frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \dot{\underline{\underline{\gamma}}} \\ \underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{\gamma}}(t,t')dt' \end{cases}$$

We can also change the basic equation:

- *linear modifications*
- *non-linear modifications*

Other Constitutive Approaches

Simple Maxwell Model, shear

$$\tau_{21} + \lambda \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \dot{\gamma}_{21}$$

Upper-Convected Maxwell Model, general

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

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retardation time

Simple Jeffreys Model, shear

$$\tau_{21} + \lambda_1 \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \left(\dot{\gamma}_{21} + \lambda_2 \frac{\partial \dot{\gamma}_{21}}{\partial t} \right)$$

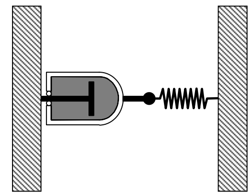
Upper-Convected Jeffreys Model, general

(Oldroyd B Fluid)

$$\underline{\underline{\tau}} + \lambda_1 \overset{\nabla}{\underline{\underline{\tau}}} = -\eta_0 \left(\dot{\underline{\underline{\gamma}}} + \lambda_2 \overset{\nabla}{\dot{\underline{\underline{\gamma}}}} \right)$$

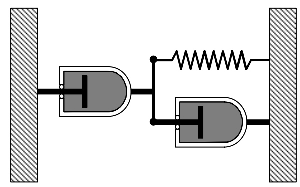
Maxwell Model - Mechanical Analog

$$\tau_{21} + \lambda \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \dot{\gamma}_{21}$$



Jeffreys Model - Mechanical Analog

$$\tau_{21} + \lambda_1 \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \left(\dot{\gamma}_{21} + \lambda_2 \frac{\partial \dot{\gamma}_{21}}{\partial t} \right)$$



Unfortunately, this change only modifies G(t-t');
the Jeffreys Model is a GLVE model

Simple Jeffreys Model (not frame-invariant) $\underline{\underline{\tau}} + \lambda_1 \frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \frac{\partial \underline{\underline{\dot{\gamma}}}}{\partial t} \right)$

Now, solving for τ_{21} explicitly we obtain,

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \underbrace{\left[\frac{\eta_0}{\lambda_1}\left(1 - \frac{\lambda_2}{\lambda_1}\right) e^{-\frac{t-t'}{\lambda_1}} + \frac{2\eta_0 \lambda_2}{\lambda_1} \delta(t-t') \right]}_{G(t-t')} \underline{\underline{\dot{\gamma}}}(t')\,dt'$$

Other linear modifications of the Maxwell model motivated by springs and dashpots in series and parallel modify G(t-t') but do not otherwise introduce new behavior.

(Might as well use the Generalized Maxwell model)

Non-linear modifications of the Maxwell Model

White-Metzner Model

$$\underline{\underline{\tau}} + \frac{\eta(\dot{\gamma})}{G_0}\overset{\nabla}{\underline{\underline{\tau}}} = -\eta(\dot{\gamma})\underline{\underline{\dot{\gamma}}}$$

Oldroyd 8-Constant Model

$$\underline{\underline{\tau}} + \lambda_1 \overset{\nabla}{\underline{\underline{\tau}}} + \frac{1}{2}(\lambda_1 - \mu_1)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\tau}} + \underline{\underline{\tau}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\mu_0\left(\mathrm{tr}\underline{\underline{\tau}}\right)\underline{\underline{\dot{\gamma}}} + \frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}$$
$$= -\eta_0\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\nabla}{\underline{\underline{\dot{\gamma}}}} + (\lambda_2 - \mu_2)\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\nu_2\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}\right)$$

The Oldroyd 8-constant contains many other constitutive equations as special cases.

- UCM
- UCM + terms = UCJ

The Oldroyd 8-Constant model contains all terms *linear* in stress tensor and at most *quadratic* in rate-of-deformation tensor that are also consistent with frame invariance.

$$\underline{\underline{\tau}} + \lambda_1 \overset{\nabla}{\underline{\underline{\tau}}} + \frac{1}{2}(\lambda_1 - \mu_1)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\tau}} + \underline{\underline{\tau}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\mu_0\left(\mathrm{tr}\underline{\underline{\tau}}\right)\underline{\underline{\dot{\gamma}}} + \frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}$$
$$= -\eta_0\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\nabla}{\underline{\underline{\dot{\gamma}}}} + (\lambda_2 - \mu_2)\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\nu_2\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}\right)$$

Giesekus Model

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} + \frac{\alpha\lambda}{\eta_0}\underbrace{\underline{\underline{\tau}}:\underline{\underline{\tau}}}_{\text{quadratic in stress}} = -\eta_0\underline{\underline{\dot{\gamma}}}$$

quadratic in stress

The only way to choose among these nonlinear models is to compare predictions.

We can also **modify integral models** to add non-linearity and thus produce new constitutive equations.

Factorized Rivlin-Sawyers Model

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t')\left(\Phi_2(I_1, I_2)\underline{\underline{C}} - \Phi_1(I_1, I_2)\underline{\underline{C}}^{-1}\right)dt'$$

Factorized K-BKZ Model

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t')\left(2\frac{\partial U}{\partial I_2}\underline{\underline{C}} - 2\frac{\partial U}{\partial I_1}\underline{\underline{C}}^{-1}\right)dt'$$

I_1, I_2 are the invariants of the Finger or Cauchy strain tensors (these are related).

Again, the only way to choose among these nonlinear models is to compare predictions
(see R. G. Larson, Constitutive Equations for Polymer Melts).

Choosing Constitutive Equations

We have fixed all the obvious flaws in our constitutive equations, and now we have too many choices!

We could make predictions and compare with experimental data, but some of the models (Rivlin Sawyer, K-BKZ) have undefined functions that must be specified.

How to proceed? ***We need some guidance.***

All along we have taken a *continuum-mechanics approach*. We have run that course all the way through. Now we must go back and seek some insight from molecular ideas of relaxation and polymer dynamics.

Molecular Approach to Polymer Constitutive Modeling

molecular tension force on arbitrary surface

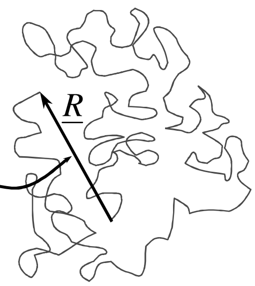
$$\underline{\tilde{f}} = -dA\,\hat{n}\cdot\underline{\underline{\tau}}$$

stress tensor

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

Polymer Dynamics

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

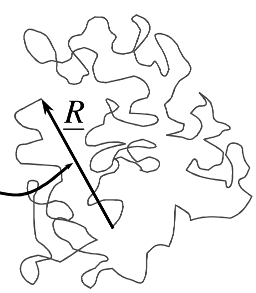


polymers may be modeled as random walks.

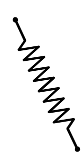
Polymer coil responds to deformation

A polymer chain adopts the most random configuration at equilibrium.

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



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 $\underline{R}$

We will model the chain dynamics with a random walk.

Gaussian Springs

Equilibrium configuration distribution function - probability a walk has end-to-end distance R

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

From an entropy calculation on a random walk we can calculate the force needed to deform a Gaussian spring

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

If we can relate **this force** to the arbitrary force on a surface, we can connect these two

molecular tension force on arbitrary surface

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

stress tensor

Molecular force generated by deforming chain

$$\underline{\tilde{f}} = \left(\begin{array}{c}\text{Tension}\\ \text{force on } dA\end{array}\right) = \iiint \left(\begin{array}{c}\text{Force on surface}\\ dA \text{ due to chains}\\ \text{of ETE } \underline{R}\end{array}\right) dR_1 dR_2 dR_3$$

$$\left(\begin{array}{c}\text{Probability}\\ \text{chain of ETE } \underline{R}\\ \text{crosses surface}\\ \text{dA}\end{array}\right)\left(\begin{array}{c}\text{Probability}\\ \text{chain has ETE}\\ \underline{R}\end{array}\right)\left(\begin{array}{c}\text{Force exerted}\\ \text{by chain w/}\\ \text{ETE } \underline{R}\end{array}\right)$$

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

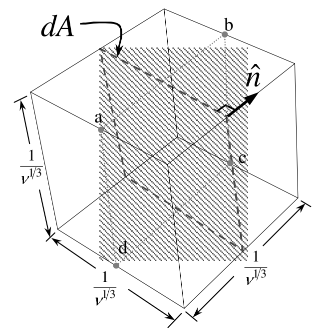
(see text)

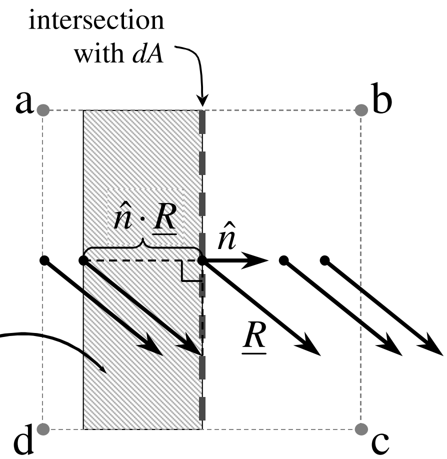
$dA = \nu^{-\frac{2}{3}}$

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

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

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





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

volume $= \nu^{-1}$

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,

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

Molecular force generated by deforming chain

How can we convert this equation,

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

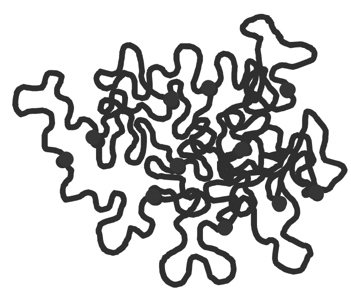
Molecular force generated by deforming chain

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

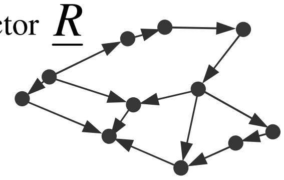
We need a idea that connects ETE vector motion to macroscopic deformation of a polymer network or melt.

Elastic (Crosslinked) Solid

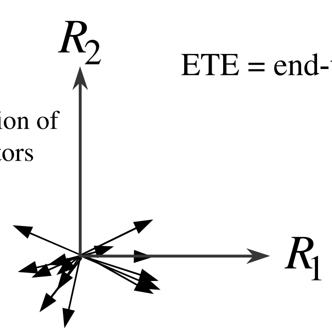
Between every two crosslinks there is a polymer strand that follows a random walk of *N* steps of length *a*.



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

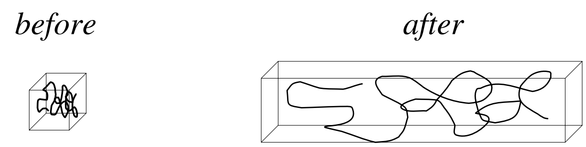


Distribution of ETE vectors



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

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

$$\lambda_1 = \frac{R_1}{R_1'} \qquad \lambda_2 = \frac{R_2}{R_2'} \qquad \lambda_3 = \frac{R_3}{R_3'}$$

ETE before

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

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

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

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

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

But, where do we get this?

Probability chain has ETE between $\underline{R}$ and $\underline{R}+d\underline{R}$: $\psi(\underline{R})dR_1 dR_2 dR_3$

Configuration distribution function

Equilibrium configuration distribution function:

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

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.

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

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

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

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

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

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

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

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 $G=\nu kT$.