# A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers 

Prince E. Rouse, Jr.<br>J. Chem. Phys., 20 (7) 1953<br>2007 NNF Summer Reading Group:<br>Familiar Results \& Famous Papers

August 10
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A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers Prince E. Rouse, Jr.
The Franklin Instilute, Laboratories for Research and Development, Philadelphia, Pennsylvania
(Received January 27, 1953)
The necessary coordination of the motions of different parts of coordinates, the coordination of all the motions of the parts of a polymer molecule is made the basis of a theory of the linear a molecule is resolved into a series of modes. Each mode has a a polymer molecule is made the basis of a theory of the linear a molecule is resolved into a series of modes. Each mode has a
"I found this paper very impressive, but failed to understand it fully on first reading"

Dr. Bruno H. Zimm, April 20, 1978
Citation Classic, in CC/Number 27 ; July 2, 1979
"...I wrote to Rouse about this, and he quickly straightened out my error"

## Prince Earl Rouse, Jr. 1917-?

1941, Ph.D. Univ. of Illinois, Association of Benzoic Acid in Solution
1947, J. Am. Chem. Soc., Diffusion of Vapors in Films
1953, J. Chem. Phys., Theory of LVE of Dilute Solns (Franklin Inst.)
1962, Appl. Spec., Measurement of Spectrograms (Los Alamos Lab)
1966, Society of Rheology Bingham Medal Recipient
(between E. Guth and H. Markovitz, and 6 years after B. Zimm)
1973,1975, J. Quant. Spec. Rad. Txfr., Oscillatory-strengths from line absorption in a high-temperature furnace
1976, J. Chem. Eng. Data, Detonation Properties of Explosives
1998, J. Chem. Phys., Theory of LVE of Dilute Solns, Part II
some modifications to original theory to make it more complete (contact information was a street address in Santa Fe, New Mexico)

A timeline gathered from an assortment of publications

## Big Picture: Kinetic Theory Models

- Current Topic:

Polymers in Dilute Solution

- In contrast to dilute particles
- In contrast to a polymer melt
- The focus of Rouse's paper is on linear polymers, dilutely suspended in a Newtonian background solvent
- The model for the restoringforce law comes from considerations of entropic elasticity, which is motivated by the bead-rod model

Handout for MIT course 10.531, Macromolecular Hydrodynamics, Prof. Gareth H. McKinley


## Overview of Rouse Model

- Physical model
- Polymer broken into submolecules
- Each submolecule is a chain with Gaussian end-to-end distribution, a.k.a. Gaussian chain
- "beads" and "springs" picture not introduced by Rouse, but common in texts such as DPL vol. 2 to explain Rouse's model
- Motion:
- Advection by flow of "atoms" at ends of submolecules
- Diffusion by Brownian motion, driven by minimization of free energy and inhibited by viscous drag
- Forces:
- Linear restoring force from entropic springs
- Linear viscous drag of submolecule
- Brownian force not discussed explicitly by Rouse, but captured by distribution functions
- Result
- Predicts generalized Maxwell model, with specified distribution of relaxation times
- Results given for linear viscoelastic tests
- Small amplitude oscillatory shear (SAOS)
- Zero-shear viscosity


Bird, Curtiss, Armstrong, and Hassager, Dynamics of Polymeric Llquids, vol. 2

$$
\begin{gathered}
\tau_{p}=\frac{\sigma^{2}}{24 B k T \sin ^{2}\left(\frac{p \pi}{2(N+1)}\right)} \\
\tau_{p} \cong \frac{\sigma^{2} N^{2}}{6 \pi^{2} B k T p^{2}}=\frac{\tau_{1}}{p^{2}}
\end{gathered}
$$

## 1. Motion of Liquid


$\frac{1}{\Gamma} \doteq\left[\frac{1}{\mathrm{~m}}\right] \sim$ decay length

Solution to flow problem

$$
\begin{equation*}
\dot{x}=v_{0} e^{-\Gamma z} e^{i \omega t}, \quad \dot{y}=0, \quad \dot{z}=0, \quad \Gamma=\left(i \omega \rho_{l} / \eta\right)^{\frac{1}{2}} \tag{1}
\end{equation*}
$$

Definition of velocity gradient

$$
\alpha=\partial \dot{x} / \partial z
$$

Conclusion: entire polymer experiences constant velocity gradient for sufficiently low frequencies

Taylor Series Expansion of Eq (1)

$$
\begin{equation*}
\alpha_{z=z_{0}+\mathrm{e}}=-v_{0} \Gamma e^{-\Gamma z_{0} e^{i \omega t}}\left[1-\Gamma \epsilon+\Gamma^{2} \epsilon^{2} / 2 \cdots\right] . \tag{2}
\end{equation*}
$$

## 2. Model of Polymer Molecule

- Equilibrium distribution of end-to-end vectors: all are assumed to be Gaussian

- End-to-End equilibrium distribution of full polymer

$$
p(x, y, z) d x d y d z=\left(b^{3} / \pi^{\frac{1}{2}}\right) \exp \left[-b^{2}\left(x^{2}+y^{2}+z^{2}\right)\right] d x d y d z
$$

- End-to-End distribution of submolecule

$$
\psi(x, y, z) d x d y d z=(\beta / \pi)^{\frac{3}{3}}
$$

$$
\begin{equation*}
\times \exp \left[-\beta\left(x^{2}+y^{2}+z^{2}\right)\right] d x d y d z \tag{3}
\end{equation*}
$$

## 2. Model of Polymer Molecule

- Equilibrium distribution of molecular configurations:

Gaussian at equilibrium, but modified when polymer is stretched

$$
\begin{array}{rll}
\Psi_{i} d \phi_{i}= & \prod_{j=1}^{N} \psi\left(x_{j}, y_{j}, z_{j}\right) d x_{j} d y_{j} d z_{j} & \begin{array}{l}
\text { Probability that } \\
\text { molecular configuration lies within } d \varphi_{i}
\end{array} \\
& =(\beta / \pi)^{3 N / 2} \exp \left[-\beta \sum_{j=1}^{N}\left(x_{j}{ }^{2}+y_{j}{ }^{2}+z_{j}{ }^{2}\right)\right]
\end{array}
$$

$\times d x_{1} d y_{1} d z_{1} d x_{2} \cdots d z_{N}$.

Definition of $\left(x_{\mathrm{j}}, y_{\mathrm{j}}, z_{\mathrm{j}}\right)$,
Vector location of end of submolecule $j$


Definition of $d \varphi_{\mathrm{i}}$,
differential volume surrounding each $i$-configuration

$$
\left(x_{1}, y_{1}, z_{1}\right),\left(x_{2}, y_{2}, z_{2}\right), \ldots,\left(x_{\mathrm{N}}, y_{\mathrm{N}}, z_{\mathrm{N}}\right)
$$

i: given configuration


## 3. Motion of Polymer Molecules

- Velocity gradient causes two types of polymer motion
- (1) Atoms at junctions advect with velocity identical to surrounding liquid NOTE: polymers do not affect solvent flow field,
i.e. "free-draining limit" with no "hydrodynamic interactions"
- (2) Coordinated Brownian motions of segments to drift toward their equilibrium distribution
- Model supported by observation that viscous losses tend to zero at high frequencies
- (1) Advection

$$
\left(\dot{x}_{j}\right)_{\alpha}=z_{j} \partial \dot{x} / \partial z=\alpha z_{j}
$$



Rate of change of $x$ component of position vector $\left(x_{\mathrm{j}}\right)$ caused directly by gradient

Note rate of change of $y_{\mathrm{j}}$ and $z_{\mathrm{j}}$ components are zero

## 3. Motion of Polymer Molecules

- (2) Coordinated Brownian motion: "the central part of the theory"
- When distribution of molecular configurations is perturbed it changes the thermodynamic potentials of the molecules
- Velocity Gradient $\leftrightarrow$ Entropy $\leftrightarrow$ Potential Energy $\leftrightarrow$ Force $\leftrightarrow$ Atom Velocity
$\Delta S=k \sum_{i} s_{i} \ln \left(n_{i} / s_{i}\right)$

Definition: Average number of molecules whose points lie in $d \varphi_{\mathrm{i}}$ at equilibrium

Definition: Similar to $n_{i}$, but it's the average number in $d \varphi_{\mathrm{i}}$ when exposed to velocity

$$
\text { gradient } \alpha
$$

Wall's equation: change in entropy of a volume $V$

$$
n_{i}=\nu \Psi_{i} d \phi_{i}
$$

$s_{i}$

## 3. Motion of Polymer Molecules

$$
\text { Velocity Gradient } \leftrightarrow \text { Entropy } \leftrightarrow \text { Potential Energy } \leftrightarrow \text { Force } \leftrightarrow \text { Atom Velocity }
$$

$$
\begin{array}{cl}
\Delta A=-T \Delta S & \begin{array}{l}
\text { Change in Helmholtz free } \\
\text { energy }
\end{array} \\
\mu_{i}=\partial(\Delta A) / \partial s_{i}=k T\left[1+\ln \left(s_{i} / n_{i}\right)\right] & \begin{array}{l}
\text { Thermodynamic potential: } \\
\text { caused by entrance of } \\
\text { molecule into } d \varphi_{\mathrm{i}}
\end{array} \\
s_{i}=n_{i}\left(1+\alpha f+\alpha^{2} g+\alpha^{3}+\cdots\right) & \begin{array}{l}
\text { Assume small variation of } s_{\mathrm{i}} \\
\text { from equilibrium } n_{\mathrm{i}}
\end{array} \\
\mu=k T[1+\ln (1+\alpha f)] & \begin{array}{l}
\text { Rewrite energy in terms of } \\
\text { velocity gradient }
\end{array}
\end{array}
$$

## 3. Motion of Polymer Molecules

Velocity Gradient $\leftrightarrow$ Entropy $\leftrightarrow$ Potential Energy $\leftrightarrow$ Force $\leftrightarrow$ Atom Velocity
$\left(\dot{x}_{j}\right)_{j-1}=B$.restoring-force
restoring-force $\sim-d \mu / d x$ caused by motion of ( $j-1$ )


Definition: $\left(\dot{x}_{j}\right)_{j-1}$ is average velocity of line along $x_{\mathrm{j}}$ due to motion of atom at
$\left(x_{j-1}, y_{j-1}, z_{j-1}\right)$, driven by minimization of free energy

Definition: B is the mobility of the submolecule

$$
B \equiv\left(\frac{\delta v}{\delta F}\right)_{0} \sim \text { viscous drag }{ }^{-1}
$$



## 3. Motion of Polymer Molecules



Example



In simplified

$$
\begin{aligned}
&\left(\dot{x}_{j}\right)_{j-1}=-B\left[\frac{\partial \mu}{\partial x_{j}}-\frac{\partial \mu}{\partial x_{j-1}}\right] \\
& \frac{\partial \mu}{\partial x_{j}}<0 \\
& \frac{\partial \mu}{\partial x_{j-1}}>0 \\
& \therefore\left(\dot{x}_{j}\right)_{j-1}>0 \text {, as expected }
\end{aligned}
$$ limit that $\sigma^{2}=0$

## 3. Motion of Polymer Molecules



Example


Furthermore, $\left(\dot{\chi}_{j}\right)_{j}$ should be $>0$ ? , wrt leeal coords
Note: $x_{j}<0$
$\left(\dot{x}_{j}\right)_{j}=-B\left[\frac{\partial \mu}{\partial x_{j}}-\frac{\partial \mu}{\partial x_{j+1}}\right]$
$\frac{\partial \mu}{\partial x_{j}}<0$
$\frac{\partial x_{j}}{\partial x_{j+1}} N / A=0$
$\mu$ is minimivad

$$
\therefore\left(\dot{x}_{j}\right)_{j}>0 \text {, as expected }
$$

## 3. Motion of Polymer Molecules

- Combine submolecule distortion from (1) advection and (2) diffusion in matrix representation

$$
\left(\dot{x}_{j}\right)_{D}=-B\left[-\frac{\partial \mu}{\partial x_{j-1}}+2 \frac{\partial \mu}{\partial x_{j}}-\frac{\partial \mu}{\partial x_{j+1}}\right]
$$

$$
\mathbf{x}_{i}=\underbrace{\alpha \mathbf{z}}-\underbrace{B \mathbf{A}\left\{\mathbf{\nabla}_{x} \mu\right\}}
$$

$$
\begin{aligned}
\text { (1) tracking } & \text { (2) restoring force } \\
\text { with liquid } & \text { from Brownian motion }
\end{aligned}
$$

- e.g. $\mathrm{N}=3$ submolecules

$$
\left[\begin{array}{l}
\dot{x}_{1} \\
\dot{x}_{2} \\
\dot{x}_{3}
\end{array}\right]=\alpha\left[\begin{array}{l}
z_{1} \\
z_{2} \\
z_{3}
\end{array}\right]-B \underbrace{\left[\begin{array}{ccc}
2 & -1 & 0 \\
-1 & 2 & -1 \\
0 & -1 & 2
\end{array}\right]}\left[\begin{array}{l}
\partial \mu / \partial x_{1} \\
\partial \mu / \partial x_{2} \\
\partial \mu / \partial x_{3}
\end{array}\right]
$$


"Rouse Matrix"

## 3. Motion of Polymer Molecules

- Solution requires transformation of original "system" of 3 N coordinates into an uncoupled set of equations
- Diagonalize Rouse Matrix, A (eigenvalue problem)

$$
\mathbf{x}_{t}=\alpha \mathbf{z}-B \mathbf{A}\left\{\boldsymbol{\nabla}_{x} \mu\right\}
$$

- Multiply by $R^{-1}$

$$
\begin{aligned}
& \mathbf{R}^{-1} \mathbf{A} \mathbf{R}=\boldsymbol{\Lambda}=\left[\lambda_{p} \delta_{p q}\right] \\
& \lambda_{p}=4 \sin ^{2} \frac{p \pi}{2(N+1)}
\end{aligned}
$$

$$
\mathbf{R}^{-1} \mathbf{x}_{t}=\alpha \mathbf{R}^{-1} \mathbf{z}-B \mathbf{R}^{-1} \mathbf{A} \mathbf{R} \mathbf{R}^{-1}\left\{\boldsymbol{\nabla}_{x} \mu\right\}
$$



- Use above relations to rewrite an uncoupled set
$\mathbf{W}=\mathbf{R}^{-1} \mathbf{z}$. of equations in new"configuration coordinates"

$$
\mathbf{u}_{t}=\alpha \mathbf{w}-B \mathbf{\Lambda}\left\{\boldsymbol{\nabla}_{u} \mu\right\}
$$

Note: each mode is NOT associated with one particular submolecule

## 3. Motion of Polymer Molecules

What does this transformation look like?
An illustrative example, again take $\sigma^{2}=0$ for illustrative purposes

- Coupled "coordinate" system, $N=3$ submolecules, arbitrary configuration

$$
\left[\begin{array}{l}
x_{1} \\
y_{1} \\
z_{1}
\end{array}\right]=\left[\begin{array}{l}
1 \\
0 \\
1
\end{array}\right] \quad\left[\begin{array}{l}
x_{2} \\
y_{2} \\
z_{2}
\end{array}\right]=\left[\begin{array}{l}
1 \\
0 \\
0
\end{array}\right] \quad\left[\begin{array}{l}
x_{3} \\
y_{3} \\
z_{3}
\end{array}\right]=\left[\begin{array}{c}
1 \\
0 \\
-1
\end{array}\right]
$$



- $\operatorname{In}\left(\mathrm{x}_{\mathrm{j}}, \mathrm{y}_{\mathrm{j}}, \mathrm{z}_{\mathrm{j}}\right)$ space
$\left[\begin{array}{l}\dot{x}_{1} \\ \dot{x}_{2} \\ \dot{x}_{3}\end{array}\right]=\alpha\left[\begin{array}{c}1 \\ 0 \\ -1\end{array}\right]-B\left[\begin{array}{ccc}2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2\end{array}\right]\left[\begin{array}{l}\partial \mu / \partial x_{1} \\ \partial \mu / \partial x_{2} \\ \partial \mu / \partial x_{3}\end{array}\right] \quad\left[\begin{array}{l}\dot{z}_{1} \\ \dot{z}_{2} \\ \dot{z}_{3}\end{array}\right]=-B\left[\begin{array}{ccc}2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2\end{array}\right]\left[\begin{array}{l}\partial \mu / \partial z_{1} \\ \partial \mu / \partial z_{2} \\ \partial \mu / \partial z_{3}\end{array}\right]$
- Eigenvalues and Eigenvectors

$$
\Lambda=\underbrace{\left[\begin{array}{ccc}
0.59 & 0 & 0 \\
0 & 2 & 0 \\
0 & 0 & 3.41
\end{array}\right]}_{\text {Eigenvalues }} \quad R=\underbrace{\left[\begin{array}{ccc}
0.5 & -0.71 & -0.5 \\
0.71 & 0 & 0.71 \\
0.5 & 0.71 & -0.5
\end{array}\right]}_{\text {Matrix of }} \quad R^{-1}=\underbrace{\left[\begin{array}{ccc}
0.5 & 0.71 & 0.5 \\
-0.71 & 0 & 0.71 \\
-0.5 & 0.71 & -0.5
\end{array}\right]}_{\begin{array}{c}
\text { Used in } \\
\text { eigenvectors }
\end{array}}
$$

## 3. Motion of Polymer Molecules

An illustrative example, again take $\sigma^{2}=0$ for illustrative purposes

- In $\left(\mathrm{u}_{\mathrm{j}}, \mathrm{v}_{\mathrm{j}}, \mathrm{w}_{\mathrm{j}}\right)$ space

$$
\begin{aligned}
& u=R^{-1} x=\left[\begin{array}{ccc}
0.5 & 0.71 & 0.5 \\
-0.71 & 0 & 0.71 \\
-0.5 & 0.71 & -0.5
\end{array}\right]\left[\begin{array}{l}
1 \\
1 \\
1
\end{array}\right]=\left[\begin{array}{c}
1.71 \\
0 \\
-0.2929
\end{array}\right] \\
& w=R^{-1} z=\left[\begin{array}{ccc}
0.5 & 0.71 & 0.5 \\
-0.71 & 0 & 0.71 \\
-0.5 & 0.71 & -0.5
\end{array}\right]\left[\begin{array}{c}
1 \\
0 \\
-1
\end{array}\right]=\left[\begin{array}{c}
0 \\
-1.41 \\
0
\end{array}\right]
\end{aligned}
$$

- Transformed "coordinates"

$$
\begin{aligned}
& {\left[\begin{array}{l}
\dot{u}_{1} \\
\dot{u}_{2} \\
\dot{u}_{3}
\end{array}\right]=\alpha\left[\begin{array}{c}
0 \\
-1.41 \\
0
\end{array}\right]-B\left[\begin{array}{ccc}
0.59 & 0 & 0 \\
0 & 2 & 0 \\
0 & 0 & 3.41
\end{array}\right]\left[\begin{array}{l}
\partial \mu / \partial u_{1} \\
\partial \mu / \partial u_{2} \\
\partial \mu / \partial u_{3}
\end{array}\right]} \\
& {\left[\begin{array}{l}
\dot{w}_{1} \\
\dot{w}_{2} \\
\dot{w}_{3}
\end{array}\right]=-B\left[\begin{array}{ccc}
0.59 & 0 & 0 \\
0 & 2 & 0 \\
0 & 0 & 3.41
\end{array}\right]\left[\begin{array}{l}
\partial \mu / \partial w_{1} \\
\partial \mu / \partial w_{2} \\
\partial \mu / \partial w_{3}
\end{array}\right]}
\end{aligned}
$$



$$
\left[\begin{array}{l}
x_{1} \\
y_{1} \\
z_{1}
\end{array}\right]=\left[\begin{array}{l}
1 \\
0 \\
1
\end{array}\right] \quad\left[\begin{array}{l}
x_{2} \\
y_{2} \\
z_{2}
\end{array}\right]=\left[\begin{array}{l}
1 \\
0 \\
0
\end{array}\right] \quad\left[\begin{array}{l}
x_{3} \\
y_{3} \\
z_{3}
\end{array}\right]=\left[\begin{array}{c}
1 \\
0 \\
-1
\end{array}\right]
$$

Compare to coupled result before:
$\left[\begin{array}{l}\dot{x}_{1} \\ \dot{x}_{2} \\ \dot{x}_{3}\end{array}\right]=\alpha\left[\begin{array}{c}1 \\ 0 \\ -1\end{array}\right]-B\left[\begin{array}{ccc}2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2\end{array}\right]\left[\begin{array}{l}\partial \mu / \partial x_{1} \\ \partial \mu / \partial x_{2} \\ \partial \mu / \partial x_{3}\end{array}\right]$

But how does $\mu$ depend on ( $u, v, w$ )? Through $f$ !

## 3. Motion of Polymer Molecules

- Now we'll use
- Uncoupled expression for configuration evolution $\quad \mathbf{u}_{t}=\alpha \mathbf{w}-B \mathbf{\Lambda}\left\{\boldsymbol{\nabla}_{u} \mu\right\}$ with
- Continuity $\dot{\rho}=-\operatorname{div}(\rho \mathbf{V})$ to
- Solve for $f$ (which requires differentiation, neglecting $\alpha^{2}$ terms and higher, and solving a differential equation).
- Solution:

$$
f=\sum_{p=1}^{N} \frac{u_{p} w_{p}}{2 D_{p}\left(1+i \omega \tau_{p}\right)}
$$

$$
\tau_{p}=\left(4 \beta D_{p}\right)^{-1}=\sigma^{2}\left(6 B k T \lambda_{p}\right)^{-1}
$$

We will soon see that $\tau_{\mathrm{p}}$ are relaxation times, but this has not been proven yet

- Now everything is known, and we will use
$f \leftrightarrow$ thermodynamic potential $\leftrightarrow$ velocity in diffusion space

$$
\begin{aligned}
& \mu=k T[1+\ln (1+\alpha f)] \\
& \mathbf{u}_{t}=\alpha w-B \mathbf{\Lambda}\left\{\boldsymbol{\nabla}_{u} \mu\right\}
\end{aligned}
$$

## 4. The Viscoelastic Properties

- Represent rate of work done per unit volume, $P$, by application of a shearing stress using linear viscoelastic parameter notation
$S=\operatorname{Re}\left\{\eta^{*} \alpha\right\}=\alpha_{0}\left[\eta_{1} \cos \omega t+\eta_{2} \sin \omega t\right]$
Definition of viscoelastic notation. $S$ : shear stress Relation to common notation: $\eta^{\prime}=\eta_{1}$

$$
\begin{aligned}
P & =S \alpha_{0} \cos \omega t \\
& =\alpha_{0}^{2}\left[\eta_{1} \cos ^{2} \omega t+\eta_{2} \sin \omega t \cos \omega t\right]
\end{aligned}
$$

$$
\eta^{\prime \prime}=\eta_{2}
$$

Power per unit volume $=$ stress * shear-rate

- Represent the same quantity, $P$, using result of kinetic theory

$P_{s}^{-}=\eta_{s} \alpha_{0}^{2} \cos ^{-} \omega t$
$P_{m}=\alpha_{0}{ }^{2} n k T \sigma^{2} \sum_{p=1}^{N} \frac{\cos ^{2} \omega t+\omega \tau_{p} \sin \omega t \cos \omega t}{6 D_{p}\left(1+\omega^{2} \tau_{p}^{2}\right)}$

$$
\begin{aligned}
& \frac{\partial \mu}{\partial u_{p}}=\frac{\alpha_{0} k T w_{p}}{2 D_{p}\left(1+\omega^{2} \tau_{p}{ }^{2}\right)}\left(\cos \omega l+\omega \tau_{p} \sin \omega t\right) \\
& \dot{u}_{p}=\alpha_{0} w_{p} \cos \omega t
\end{aligned}
$$

## 4. The Viscoelastic Properties

- Comparing the two expressions for $P$ gives the result for the viscoelastic parameters

$$
\begin{aligned}
\text { Dynamic Viscosity } & \text { Dynamic Moduli } \\
\eta_{1}=\eta_{s}+n k T \sum_{p=1}^{N} \frac{\tau_{p}}{1+\omega^{2} \tau_{p}^{2}} & G_{1}=n k T \sum_{p=1}^{N} \frac{\omega^{2} \tau_{p}^{2}}{1+\omega^{2} \tau_{p}{ }^{2}} \\
\eta_{2}=n k T \sum_{p=1}^{N} \frac{\omega \tau_{p}^{2}}{1+\omega^{2} \tau_{p}^{2}} & G_{2}=\omega \eta_{s}+n k T \sum_{p=1}^{N} \frac{\omega \tau_{p}}{1+\omega^{2} \tau_{p}^{2}}
\end{aligned}
$$

- Results
- This shows that $\tau_{\mathrm{p}}$ are relaxation times
- Moduli represented by a generalized Maxwell model
- Found result independently of the distribution of $\tau_{\mathrm{p}}$
- Happens that Zimm model only changes distribution of $\tau_{\mathrm{p}}$

$$
\tau_{p}=\sigma^{2}\left[24 B k T \sin ^{2} \frac{p \pi}{2(N+1)}\right]^{-1}
$$

## 4. The Viscoelastic Properties

- Take limit of $\omega \rightarrow 0$ to determine the steady-flow viscosity

$$
\begin{aligned}
\eta_{0} & =\eta_{s}+\frac{n \sigma^{2}}{24 B} \sum_{p=1}^{N}\left[\sin \frac{p \pi}{2(N+1)}\right]^{-2} \\
& =\eta_{s}+\frac{n \sigma^{2} N(N+2)}{36 B} .
\end{aligned}
$$

- Contribution of first mode $\tau_{1}$ is very large

$$
\begin{aligned}
& \left(\eta_{0}\right)_{\tau_{1}}=n \sigma^{2}\left[24 B \sin ^{2} \frac{\pi}{2(N+1)}\right]^{-1} \\
& \frac{\left(\eta_{0}\right)_{\tau_{1}}}{\eta_{0}} \cong \frac{6(N+1)^{2}}{\pi^{2} N(N+2)} \cong \frac{6}{\pi^{2}} \approx 61 \%
\end{aligned}
$$

## 4. The Viscoelastic Properties

- Approximation Argument: most information is contained in long modes
- Very fast relaxation processes are excluded from the model
- The longest $20 \%$ of the relaxation times (i.e. $p<N / 5$ ) account for majority of response up to one decade before reaching maximum frequency allowed by theory
- Use this to simplify expressions for relaxation times, providing workable analytical results
- For $p<N / 5$

$$
\tau_{p} \cong \frac{\sigma^{2}(N+1)^{2}}{6 \pi^{2} p^{2} B k T} \cong \frac{\sigma^{2} N^{2}}{6 \pi^{2} p^{2} B k T}
$$

$$
\eta_{1}=\eta_{s}+\frac{6\left(\eta_{0}-\eta_{s}\right)}{\pi^{2}} \sum_{p==1}^{N} \frac{p^{2}}{p^{4}+\omega^{2} \tau_{1}^{2}},
$$

$$
G_{1}=n k T \sum_{p=1}^{N} \frac{\omega^{2} \tau_{1}{ }^{2}}{p^{4}+\omega^{2} \tau_{1}{ }^{2}}
$$

## 5. Discussion of Results

- Relaxations times do not depend on $N$, the number of subdivisions, so long as the length of a submolecule is sufficiently long to allow for a Gaussian end-to-end vector distribution

$$
\tau_{p} \cong \frac{\sigma^{2} N^{2}}{6 \pi^{2} p^{2} B k T}
$$

$\sum$| $B=K N$ |
| :--- |
| $\sigma^{2} N=S^{2}$ |

$$
\tau_{p}=S^{2} /\left(6 K \pi^{2} p^{2} k T\right)
$$



$$
\tau_{1} \propto M W^{2}
$$

## 5. Discussion of Results

- Predicted viscoelastic moduli frequency response


Fjg. 2. Contribution of the polymer to the components of the complex rigidity relative to the contribution of a single relaxation mode to the instantaneous rigidity.

## 5. Discussion of Results

- Each mode contributes $n k T$ at sufficient frequency


From MIT course 10.531,
Macromolecular Hydrodynamics,
Prof. Gareth H. McKinley

## Comparison with Experimental Data

Despite the various limitations suggested by Rouse, the primary disagreement with experimental data is apparently due to hydrodynamic interactions between submolecules, an effect added by Zimm

Note that both Rouse and Zimm predict a generalized Maxwell equation, the primary difference being in the form of the relaxation time distribution

$$
\begin{aligned}
& \tau_{\text {Rouse }} \cong \frac{\tau_{1}}{p^{2}} \\
& \tau_{\mathrm{Zimm}} \cong \frac{\tau_{1}}{p^{3 / 2}}
\end{aligned}
$$

Zimm, B.H., J. Chem. Phys, 1956
 Free-Draining Hydrodynamic Interactions


Experimental data for polystyrene Larson, R. G., Constitutive Equations, Ch. 8

## Irony

- Rouse intended his theory to apply for DILUTE solutions, but researchers have discovered that it can be even more useful for concentrated solutions which are not entangled.
- No hydrodynamic interactions to consider
- Relaxations not affected by entanglements, so idea of "mobility" still adequate

Rouse did not approve of applying his theory to concentrated solutions, undiluted linear polymers, or networks. However, others did not hesitate to try modifications. For an undiluted amorphous polymer, simple substitution of density for concentration provided approximate agreement in a limited frequency range with viscoelastic properties when the molecular weight was less than the critical value for manifestation of entanglements. 58,59
Ferry,J.D., Macromolecules, 1991

Ferry, J.D., Landel, R.F., Williams, M.L., J. App. Phys., 1955

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Exteasions of the Rouse Theory of Viscoelastic Properties to Undiluted Linear Polymers*






## Overview of Rouse Model

- Physical model
- Polymer broken into submolecules
- Each submolecule is a chain with Gaussian end-to-end distribution, a.k.a. Gaussian chain
- "beads" and "springs" picture not introduced by Rouse, but common in texts such as DPL vol. 2 to explain Rouse's model
- Motion:
- Advection by flow of "atoms" at ends of submolecules
- Diffusion by Brownian motion, driven by minimization of free energy and inhibited by viscous drag
- Forces:
- Linear restoring force from entropic springs
- Linear viscous drag at junction points
- Brownian force not discussed explicitly by Rouse, but captured by distribution functions
- Result
- Predicts generalized Maxwell model, with specified distribution of relaxation times
- Results given for linear viscoelastic tests
- Small amplitude oscillatory shear (SAOS)
- Zero-shear viscosity

$$
\begin{aligned}
& \tau_{p}=\frac{\sigma^{2}}{24 B k T \sin ^{2}\left(\frac{p \pi}{2(N+1)}\right)} \\
& \tau_{p} \cong \frac{\sigma^{2} N^{2}}{6 \pi^{2} B k T p^{2}}=\frac{\tau_{1}}{p^{2}}
\end{aligned}
$$

