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

Prince E. Rouse, Jr.
J. Chem. Phys., 20 (7) 1953

2007 NNF Summer Reading Group:

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 Institute, Laboratories for Research and Development, Philadelphia, Pennsylvania
(Received January 27, 1953)

The necessary coordination of the motions of different parts of a polymer molecule is made the basis of a theory of the linear viscoelastic properties of dilute solutions of coiling polymers.

coordinates, the coordination of all the motions of the parts of a molecule is resolved into a series of modes. Each mode has a characteristic relaxation time. The theory produces equations by

"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

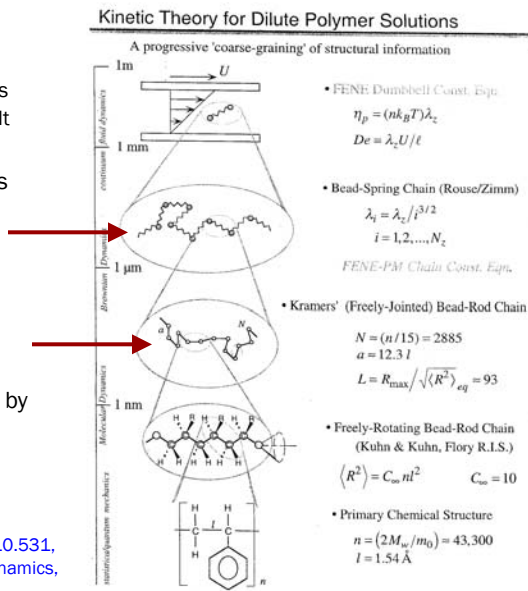"...I wrote to Rouse about this, and he quickly straightened out my error"

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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 restoring-force 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

Kinetic Theory for Dilute Polymer Solutions

A progressive 'coarse-graining' of structural information

- FENE Dumbbell Const. Eqn.
$$\eta_p = (nk_BT)\lambda_z$$
$$De = \lambda_z U/\ell$$

- Bead-Spring Chain (Rouse/Zimm)
$$\lambda_i \approx \lambda_z/i^{3/2}$$
$$i = 1,2,...,N_z$$

FENE-PM Chain Const. Eqn.

- Kramers' (Freely-Jointed) Bead-Rod Chain
$$N = (n/15) = 2885$$
$$a = 12.3\,l$$
$$L = R_{max}/\sqrt{\langle R^2\rangle}_{eq} \approx 93$$

- Freely-Rotating Bead-Rod Chain
  (Kuhn & Kuhn, Flory R.I.S.)
$$\langle R^2\rangle = C_\infty nl^2 \qquad C_\infty = 10$$

- Primary Chemical Structure
$$n = (2M_w/m_0) = 43,300$$
$$l = 1.54\,\text{Å}$$

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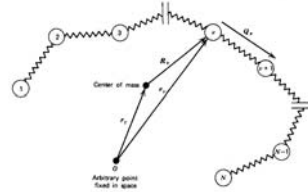
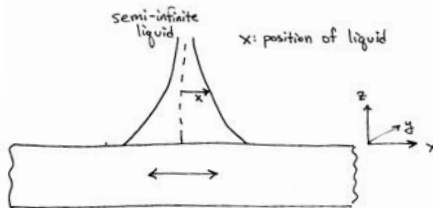Bird, Curtiss, Armstrong, and Hassager, Dynamics of Polymeric Liquids, vol. 2

$$\tau_p = \frac{\sigma^2}{24 BkT \sin^2\left(\dfrac{p\pi}{2(N+1)}\right)}$$

$$\tau_p \cong \frac{\sigma^2 N^2}{6\pi^2 BkT p^2} = \frac{\tau_1}{p^2}$$

Eq (33); approximation strictly applies only to longest 20% of relaxation times

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1. Motion of Liquid

semi-infinite liquid   x: position of liquid

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

Solution to flow problem

$$\dot{x} = v_0 e^{-\Gamma z} e^{i\omega t}, \quad \dot{y} = 0, \quad \dot{z} = 0, \quad \Gamma = (i\omega\rho_l/\eta)^{\frac{1}{2}}. \quad (1)$$

Definition of velocity gradient

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

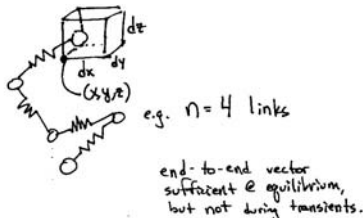Conclusion: entire polymer experiences constant velocity gradient for sufficiently low frequencies

Taylor Series Expansion of Eq (1)

$$\alpha_{z=z_0+\epsilon} = -v_0\Gamma e^{-\Gamma z_0}e^{i\omega t}\left[1 - \Gamma\epsilon + \Gamma^2\epsilon^2/2\cdots\right]. \quad (2)$$

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2. Model of Polymer Molecule

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

e.g. $n = 4$ links

end-to-end vector sufficient @ equilibrium, but not during transients.

  - End-to-End equilibrium distribution of full polymer

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

  - End-to-End distribution of *submolecule*

  $$\psi(x, y, z)dxdydz = (\beta/\pi)^{\frac{3}{2}}$$
  $$\times \exp[-\beta(x^2+y^2+z^2)]dxdydz. \quad (3)$$

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2. Model of Polymer Molecule

- Equilibrium distribution of molecular configurations:
  Gaussian at equilibrium, but modified when polymer is stretched

$$\Psi_i d\phi_i = \prod_{j=1}^{N} \psi(x_j, y_j, z_j)dx_j dy_j dz_j$$

Probability that molecular configuration lies within $d\varphi_i$

$$= (\beta/\pi)^{3N/2} \exp\left[-\beta \sum_{j=1}^{N} (x_j^2+y_j^2+z_j^2)\right] \quad (4)$$

$$\times dx_1 dy_1 dz_1 dx_2 \cdots dz_N.$$

Definition of (x_j, y_j, z_j),

Vector location of end of submolecule j

Definition of $d\varphi_i$,

differential volume surrounding each i-configuration
$(x_1, y_1, z_1), (x_2, y_2, z_2), \ldots, (x_N, y_N, z_N)$
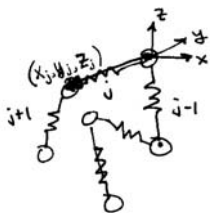
i: given configuration

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

$$(\dot{x_j})_\alpha = z_j \partial \dot{x}/\partial z = \alpha z_j.$$
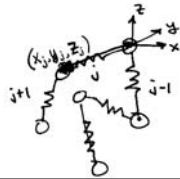
Rate of change of x-component of position vector (x_j) caused directly by gradient

Note rate of change of y_j and z_j components are zero

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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 ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

$$\Delta S = k \sum_i s_i \ln(n_i/s_i)$$

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

Definition: Average number of molecules whose points lie in $d\varphi_i$ at *equilibrium*

$$n_i = \nu \bar{\Psi}_i d\phi_i$$

Definition: Similar to n_i, but it's the average number in $d\varphi_i$ *when exposed to velocity gradient α*

$$s_i$$

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3. Motion of Polymer Molecules

Velocity Gradient ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

$$\Delta A = -T\Delta S$$

Change in Helmholtz free energy

$$\mu_i = \partial(\Delta A)/\partial s_i = kT[1+\ln(s_i/n_i)]$$

Thermodynamic potential: caused by entrance of molecule into $d\varphi_i$

$$s_i = n_i(1+\alpha f + \alpha^2 g + \alpha^3 h + \cdots)$$

Assume small variation of s_i from equilibrium n_i

$$\mu = kT[1+\ln(1+\alpha f)]$$

Rewrite energy in terms of velocity gradient

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3. Motion of Polymer Molecules

Velocity Gradient ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

$$\left(\dot{x}_j\right)_{j-1} = B \cdot \text{restoring-force}$$

$$\text{restoring-force} \sim -d\mu/dx$$
caused by motion of $(j\text{-}1)$

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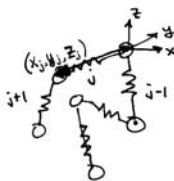
Definition: B is the *mobility* of the submolecule

$$B \equiv \left(\frac{\delta v}{\delta F}\right)_0 \sim \text{viscous drag}^{-1}$$
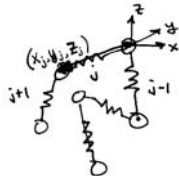
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3. Motion of Polymer Molecules

Velocity Gradient ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

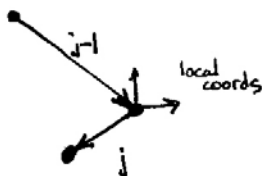$$\left(\dot{x}_j\right)_{j-1} = -B\left[\frac{\partial\mu}{\partial x_j} - \frac{\partial\mu}{\partial x_{j-1}}\right]$$

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

$$\left(\dot{x}_j\right)_D = \left(\dot{x}_j\right)_{j-1} + \left(\dot{x}_j\right)_{j+1}$$

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

Example: In simplified limit that $\sigma^2=0$

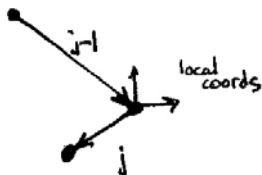$\left(\dot{x}_j\right)_{j-1}$ should be > 0, wrt local coord. system which is fixed at tail of vector (x_j, y_j, z_j)

Note: $x_j < 0$
$x_{j-1} > 0$

local coords

j-1

j

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3. Motion of Polymer Molecules

Velocity Gradient ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

Example

local coords

j-1

j

$\left(\dot{x}_j\right)_{j-1}$ should be > 0, wrt local coord. system which is fixed at tail of vector (x_j, y_j, z_j)

Note: $x_j < 0$
$x_{j-1} > 0$

μ is minimized for $x_j = 0$

In simplified limit that $\sigma^2=0$

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

$$\frac{\partial\mu}{\partial x_j} < 0$$
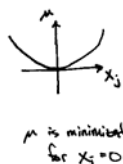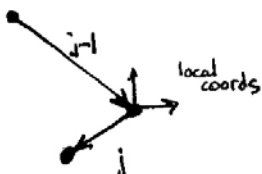
$$\frac{\partial\mu}{\partial x_{j-1}} > 0$$

$$\therefore \left(\dot{x}_j\right)_{j-1} > 0 \text{, as expected}$$

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3. Motion of Polymer Molecules

Velocity Gradient ↔ Entropy ↔ Potential Energy ↔ Force ↔ Atom Velocity

Example

Furthermore, $(\dot{x}_j)_j$ should be $>0?$ $<0?$, wrt local coords

Note: $x_j < 0$

x_{j+1} N/A

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

$\frac{\partial \mu}{\partial x_j} < 0$

$\frac{\partial \mu}{\partial x_{j+1}}$ N/A $= 0$

$\therefore (\dot{x}_j)_j > 0$, as expected

μ is minimized for $x_j = 0$

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3. Motion of Polymer Molecules

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

$$\left(\dot{x}_j\right)_D = -B\left[-\frac{\partial \mu}{\partial x_{j-1}} + 2\frac{\partial \mu}{\partial x_j} - \frac{\partial \mu}{\partial x_{j+1}}\right]$$
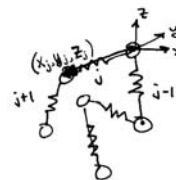
$$\mathbf{x}_t = \alpha\mathbf{z} - B\mathbf{A}\{\boldsymbol{\nabla}_x\mu\}$$

(1) tracking with liquid (2) restoring force from Brownian motion

- e.g. N=3 submolecules

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \alpha\begin{bmatrix} z_1 \\ z_2 \\ z_3 \end{bmatrix} - B\begin{bmatrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{bmatrix}\begin{bmatrix} \partial\mu/\partial x_1 \\ \partial\mu/\partial x_2 \\ \partial\mu/\partial x_3 \end{bmatrix}$$

"Rouse Matrix"

Note: each "velocity" is with respect to the local coordinates

Note Rouse made correction in 1998, arguing that end subunits are more mobile, which changes A(1,1) = A(N,N) = 3 thus changing eigenvalues

Rouse, P.E., J. Chem. Phys., 1998

3. Motion of Polymer Molecules

- Solution requires **transformation** of original "system" of $3N$ coordinates into an **uncoupled** set of equations

    - Diagonalize Rouse Matrix, A (eigenvalue problem)

$$\mathbf{x}_t = \alpha \mathbf{z} - B\mathbf{A}\{\nabla_x \mu\}$$

$$\mathbf{R}^{-1}\mathbf{A}\mathbf{R} = \mathbf{\Lambda} = [\lambda_p \delta_{pq}]$$

$$\lambda_p = 4\sin^2\frac{p\pi}{2(N+1)}$$

    - Multiply by R^{-1}

$$\mathbf{R}^{-1}\mathbf{x}_t = \alpha\mathbf{R}^{-1}\mathbf{z} - B\mathbf{R}^{-1}\mathbf{A}\mathbf{R}\mathbf{R}^{-1}\{\nabla_x \mu\}$$

$$\mathbf{R}^{-1}\{\nabla_x \mu\} = \{\nabla_u \mu\}$$

$$\mathbf{u} = \mathbf{R}^{-1}\mathbf{x},$$
$$\mathbf{v} = \mathbf{R}^{-1}\mathbf{y},$$
$$\mathbf{w} = \mathbf{R}^{-1}\mathbf{z}.$$

    - Use above relations to rewrite an uncoupled set of equations in new "configuration coordinates"

$$\mathbf{u}_t = \alpha\mathbf{w} - B\mathbf{\Lambda}\{\nabla_u \mu\}$$

Note: each mode is NOT associated with one particular submolecule
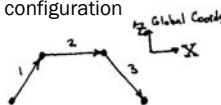
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3. Motion of Polymer Molecules

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

$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 1 \end{bmatrix} \quad \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

- In (x_j, y_j, z_j) space

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \alpha \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} - B \begin{bmatrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{bmatrix} \begin{bmatrix} \partial\mu/\partial x_1 \\ \partial\mu/\partial x_2 \\ \partial\mu/\partial x_3 \end{bmatrix} \qquad \begin{bmatrix} \dot{z}_1 \\ \dot{z}_2 \\ \dot{z}_3 \end{bmatrix} = -B \begin{bmatrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{bmatrix} \begin{bmatrix} \partial\mu/\partial z_1 \\ \partial\mu/\partial z_2 \\ \partial\mu/\partial z_3 \end{bmatrix}$$

- Eigenvalues and Eigenvectors

$$\Lambda = \begin{bmatrix} 0.59 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3.41 \end{bmatrix} \qquad R = \begin{bmatrix} 0.5 & -0.71 & -0.5 \\ 0.71 & 0 & 0.71 \\ 0.5 & 0.71 & -0.5 \end{bmatrix} \qquad R^{-1} = \begin{bmatrix} 0.5 & 0.71 & 0.5 \\ -0.71 & 0 & 0.71 \\ -0.5 & 0.71 & -0.5 \end{bmatrix}$$

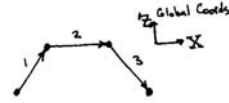| Eigenvalues	Matrix of eigenvectors	Used in transformation

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3. Motion of Polymer Molecules

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

- In (u_j, v_j, w_j) space

$$u = R^{-1}x = \begin{bmatrix} 0.5 & 0.71 & 0.5 \\ -0.71 & 0 & 0.71 \\ -0.5 & 0.71 & -0.5 \end{bmatrix}\begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 1.71 \\ 0 \\ -0.2929 \end{bmatrix}$$

$$w = R^{-1}z = \begin{bmatrix} 0.5 & 0.71 & 0.5 \\ -0.71 & 0 & 0.71 \\ -0.5 & 0.71 & -0.5 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} = \begin{bmatrix} 0 \\ -1.41 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 1 \end{bmatrix} \quad \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

- Transformed "coordinates"

$$\begin{bmatrix} \dot{u}_1 \\ \dot{u}_2 \\ \dot{u}_3 \end{bmatrix} = \alpha \begin{bmatrix} 0 \\ -1.41 \\ 0 \end{bmatrix} - B \begin{bmatrix} 0.59 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3.41 \end{bmatrix}\begin{bmatrix} \partial\mu/\partial u_1 \\ \partial\mu/\partial u_2 \\ \partial\mu/\partial u_3 \end{bmatrix}$$

$$\begin{bmatrix} \dot{w}_1 \\ \dot{w}_2 \\ \dot{w}_3 \end{bmatrix} = - B \begin{bmatrix} 0.59 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 3.41 \end{bmatrix}\begin{bmatrix} \partial\mu/\partial w_1 \\ \partial\mu/\partial w_2 \\ \partial\mu/\partial w_3 \end{bmatrix}$$

Compare to coupled result before:

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \alpha \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} - B \begin{bmatrix} 2 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 2 \end{bmatrix}\begin{bmatrix} \partial\mu/\partial x_1 \\ \partial\mu/\partial x_2 \\ \partial\mu/\partial x_3 \end{bmatrix}$$

But how does μ depend on (u,v,w)? Through f!

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3. Motion of Polymer Molecules

- Now we'll use
  - Uncoupled expression for configuration evolution $\mathbf{u}_t = \alpha\mathbf{w} - B\Lambda\{\nabla_u\mu\}$
    with
  - Continuity $\dot{\rho} = -\text{div}(\rho\mathbf{V})$
    to
  - Solve for f (which requires differentiation, neglecting α^2 terms and higher, and solving a differential equation).

  - Solution:

$$f = \sum_{p=1}^{N} \frac{u_p w_p}{2D_p(1+i\omega\tau_p)}$$

$$\tau_p = (4\beta D_p)^{-1} = \sigma^2(6BkT\lambda_p)^{-1}$$

We will soon see that τ_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

$$\mu = kT[1+\ln(1+\alpha f)]$$

$$\mathbf{u}_t = \alpha\mathbf{w} - B\Lambda\{\nabla_u\mu\}$$

4. The Viscoelastic Properties

- Represent rate of work done per unit volume, P, by application of a shearing stress using linear viscoelastic parameter notation

$$S = Re\{\eta^* \alpha\} = \alpha_0[\eta_1 \cos\omega t + \eta_2 \sin\omega t]$$

Definition of viscoelastic notation.
S: shear stress
Relation to common notation: $\eta' = \eta_1$
$$\eta'' = \eta_2$$

$$P = S\alpha_0 \cos\omega t$$
$$= \alpha_0^2[\eta_1 \cos^2\omega t + \eta_2 \sin\omega t \cos\omega t]$$

Power per unit volume = stress * shear-rate

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

$$\underbrace{\mathbf{V}_l \cdot \boldsymbol{\nabla}\mu}_{} \; \underbrace{n\Psi(1+\alpha f)d\phi_i}_{}$$

Power per molecule   Molecules per volume per configuration

$$\overline{P}_s = \eta_s \alpha_0^2 \cos^2\omega t$$
$$P_m = \alpha_0^2 nkT\sigma^2 \sum_{p=1}^{N} \frac{\cos^2\omega t + \omega\tau_p \sin\omega t \cos\omega t}{6D_p(1+\omega^2\tau_p^2)}$$

$$\frac{\partial\mu}{\partial u_p} = \frac{\alpha_0 kT w_p}{2D_p(1+\omega^2\tau_p^2)}(\cos\omega t + \omega\tau_p \sin\omega t)$$

$$\dot{u}_p = \alpha_0 w_p \cos\omega t$$

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4. The Viscoelastic Properties

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

Dynamic Viscosity

$$\eta_1 = \eta_s + nkT \sum_{p=1}^{N} \frac{\tau_p}{1+\omega^2\tau_p^2}$$

$$\eta_2 = nkT \sum_{p=1}^{N} \frac{\omega\tau_p^2}{1+\omega^2\tau_p^2}$$

Dynamic Moduli

$$G_1 = nkT \sum_{p=1}^{N} \frac{\omega^2\tau_p^2}{1+\omega^2\tau_p^2}$$

$$G_2 = \omega\eta_s + nkT \sum_{p=1}^{N} \frac{\omega\tau_p}{1+\omega^2\tau_p^2}$$

- Results
  - This shows that τ_p are relaxation times
  - Moduli represented by a generalized Maxwell model
  - Found result independently of the distribution of τ_p
  - Happens that Zimm model only changes distribution of τ_p

$$\tau_p = \sigma^2\left[24BkT \sin^2\frac{p\pi}{2(N+1)}\right]^{-1}$$

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4. The Viscoelastic Properties

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

$$\eta_0 = \eta_s + \frac{n\sigma^2}{24B} \sum_{p=1}^{N} \left[\sin\frac{p\pi}{2(N+1)} \right]^{-2}$$

$$= \eta_s + \frac{n\sigma^2 N(N+2)}{36B}.$$

- Contribution of first mode τ_1 is very large

$$\left(\eta_0 \right)_{\tau_1} = n\sigma^2 \left[24B \, \sin^2\frac{\pi}{2(N+1)} \right]^{-1}$$

$$\frac{\left(\eta_0 \right)_{\tau_1}}{\eta_0} \cong \frac{6(N+1)^2}{\pi^2 N(N+2)} \cong \frac{6}{\pi^2} \approx 61\%$$

---

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

$$\tau_p \cong \frac{\sigma^2 (N+1)^2}{6\pi^2 p^2 BkT} \cong \frac{\sigma^2 N^2}{6\pi^2 p^2 BkT}$$

$$\eta_1 = \eta_s + \frac{6(\eta_0 - \eta_s)}{\pi^2} \sum_{p=1}^{N} \frac{p^2}{p^4 + \omega^2 \tau_1^2},$$

$$G_1 = nkT \sum_{p=1}^{N} \frac{\omega^2 \tau_1^2}{p^4 + \omega^2 \tau_1^2},$$

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

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

$$B = KN$$

$$\sigma^2 N = S^2$$

$$\tau_p = S^2/(6K\pi^2 p^2 kT)$$

$$S^2 \propto MW$$

$$B \propto 1/MW$$

$$\tau_1 \propto MW^2$$

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5. Discussion of Results

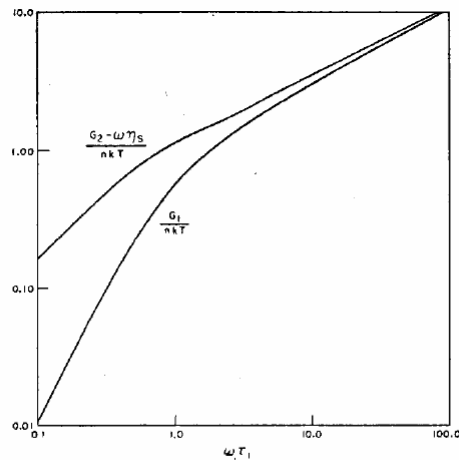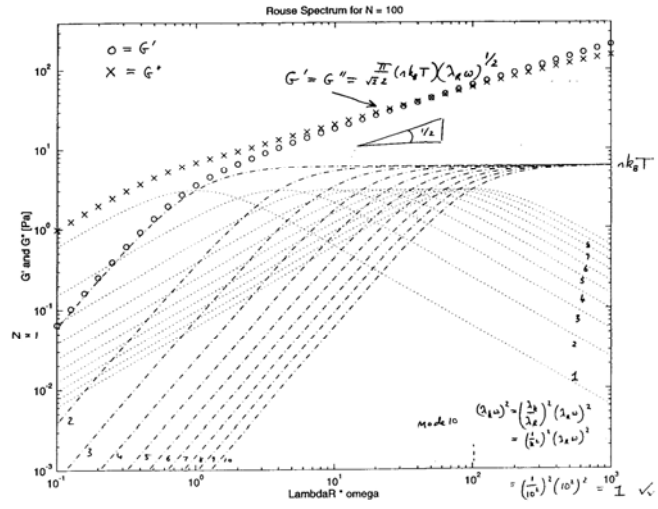- Predicted viscoelastic moduli frequency response

FIG. 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.

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5. Discussion of Results

- Each mode contributes nkT at sufficient frequency
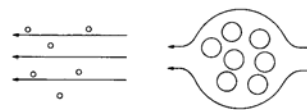
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Comparison with Experimental Data

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

Rouse:
Free-Draining

Zimm:
Hydrodynamic Interactions

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

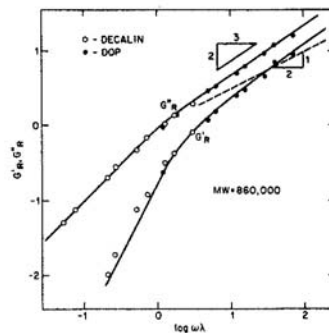$$\tau_{\text{Rouse}} \cong \frac{\tau_1}{p^2}$$

$$\tau_{\text{Zimm}} \cong \frac{\tau_1}{p^{3/2}}$$

Zimm, B.H., J. Chem. Phys, 1956

Experimental data for polystyrene

Larson, R. G., Constitutive Equations, Ch. 8

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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

Journal
of
Applied Physics

Extensions of the Rouse Theory of Viscoelastic Properties to Undiluted Linear Polymers*
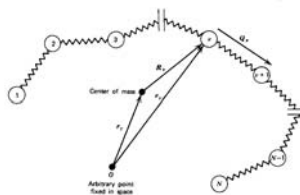
John D. Ferry, Robert F. Landel, and Malcolm L. Williams†
Department of Chemistry, University of Wisconsin, Madison, Wisconsin
(Received May 5, 1954)

The Rouse theory for viscoelastic properties of very dilute solutions is modified for application to undiluted linear polymers. With the effective segment mobility expressed in terms of steady-flow viscosity, the theory is applied to polymers of rather low molecular weight essentially without further change. In high molecular weight polymers, it is assumed that for modes of motion with relaxation times above a critical value the effective segment mobility drops abruptly, in accordance with the effect of entanglement coupling on steady-flow viscosity as described by Bueche. Properties in both the transition region between glasslike and rubberlike consistency and the rubberlike or plateau region are predicted semiquantitatively with no arbitrary parameters. In an alternative application to the transition region, the average effective friction coefficient per monomer unit can be calculated for both linear and lightly cross-linked systems.

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

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

$$\tau_p = \frac{\sigma^2}{24 BkT \sin^2\left(\dfrac{p\pi}{2(N+1)}\right)}$$

$$\tau_p \cong \frac{\sigma^2 N^2}{6\pi^2 BkT p^2} = \frac{\tau_1}{p^2}$$

Eq (33); approximation strictly applies only to longest 20% of relaxation times