

Problem 8.34 Understanding Rheology

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This problem references the Rouse model. The Rouse model is one of the classic molecular models. There is an excellent discussion of the Rouse model in Ronald G. Larson's book "Constitutive Equations for Polymer Melts and Solutions" (Butterworths, 1988). The figures and text attached to this note are from this book.

The physical system that is the basis of the Rouse model is shown in Larson's Figure 8.1 below. The inertia and drag of a polymer chain is captured in beads connected by linear springs. Larson derives the constitutive equation and the linear viscoelastic spectrum, the g_i, λ_i .

$g_i = G_0 = \text{constant}$ for all values of i

$\lambda_i = \lambda_0 / i^2$ for all values of $i = 1, 2, 3, \dots$

(see discussion around equations 2-71 and 2-72)

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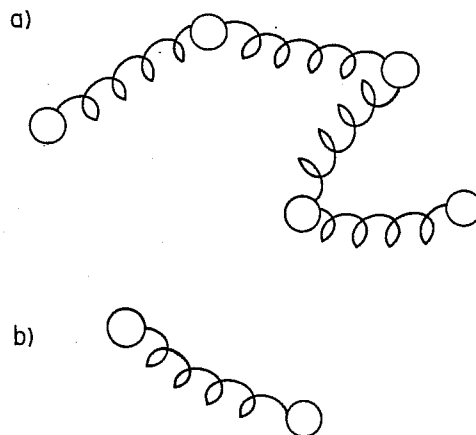


Fig. 2-6 (a) The Rouse beads and springs model for a polymer molecule; (b) the elastic dumbbell.

As Larson discusses, this linear viscoelastic spectrum results in G' and G'' that are equal to each other and proportional to the square root of frequency at high frequencies. This is what I have asked you to show by plotting the spectrum given in problem 8.34. You may choose anything you like for G_0 and λ_0 . Your plot should look like Larson's Figure 2-7.

Some real systems show this behavior as can be seen in Larson's Figure 4.3 for a concentration of 0.124. Other materials are different as seen at other concentrations and in Figure 8-1, but the discussion of their behavior is in terms of deviations from Rouse behavior; thus knowing what Rouse behavior is and where it comes from is important in polymer solution and melt rheology.

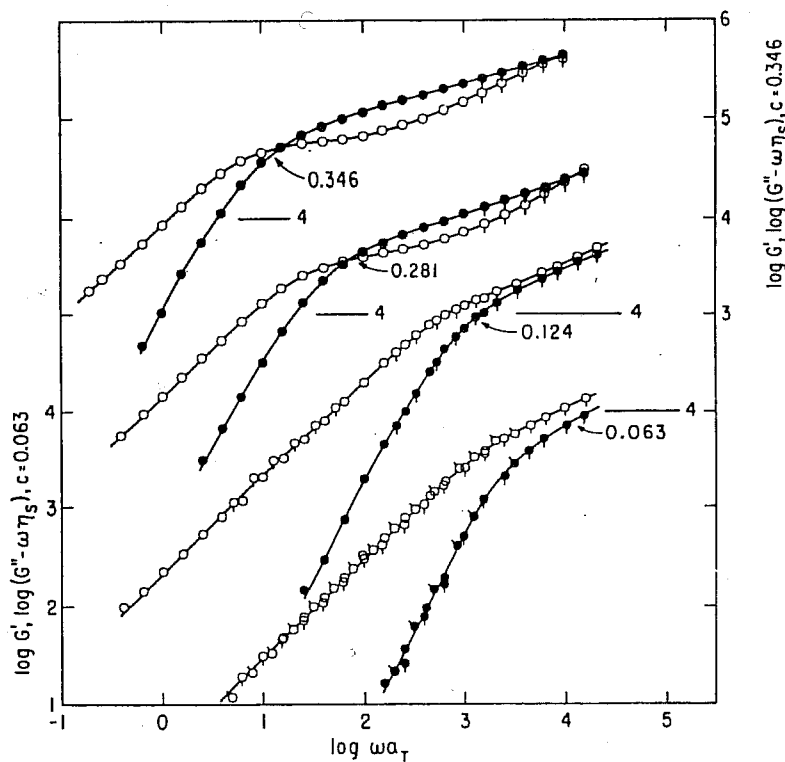


Fig. 4-3 G' and $G'' - \omega\eta_s$ versus frequency for polystyrene of molecular weight 267,000 dissolved in chlorinated diphenyl at the concentrations shown (in gm/cm³). Ordinates are shifted vertically (from Holmes, et al.,¹² reprinted from J. Polym. Sci., ©1971 by permission of John Wiley & Sons, Inc.).

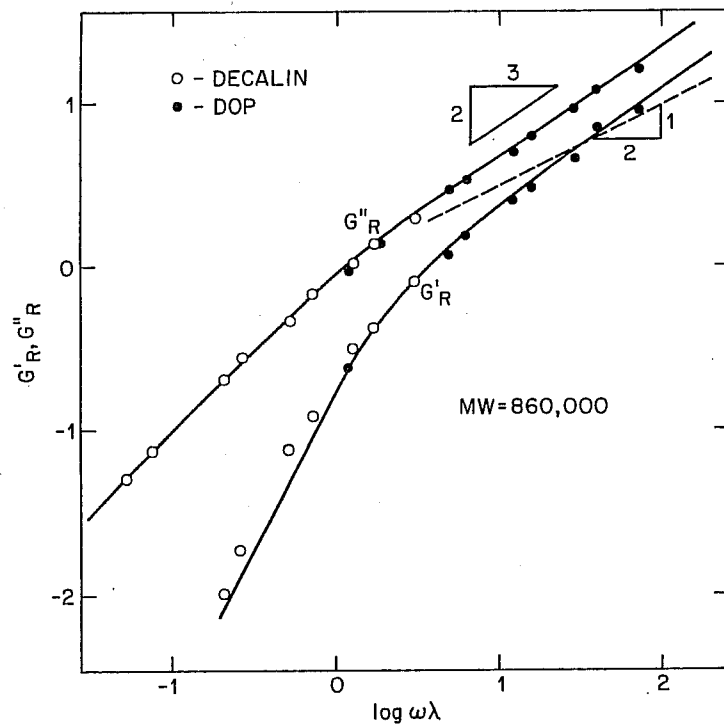


Fig. 8-1 Linear viscoelastic data for polystyrene in two theta solvents. For frequencies $\lambda\omega$ greater than 10, G' and G'' scale as $\omega^{2/3}$, in disagreement with the Rouse theory, which predicts a proportionality to $\omega^{1/2}$ in this regime. Here $G'_R \equiv G'/nkT$ and $G''_R \equiv (G'' - \eta_s\omega)/nkT$; $\lambda \equiv [\eta]_0\eta_s M/N_A kT$ (from Johnson et al.,⁴ reproduced with permission from Polym. J.).

2.7 THE ROUSE MODEL

2.7.1 The Langevin Equation

We now return to the Rouse multiple-spring-bead model of Figure 2-6a. In this case, the Langevin equation for the end-to-end vector of a given spring is coupled to the equations for the neighboring springs, because beads attached to the given spring feel forces from the neighboring springs. The average Langevin equation, the counterpart to Equation 2-40 for the dumbbell model, is

$$\zeta(\dot{\tilde{R}}_i - R_i \cdot \nabla v) + kT \sum_{j=1}^N A_{ij} \left[2\beta^2 R_j + \frac{\partial \log \psi}{\partial R_j} \right] = 0 \quad (2-50)$$

where

$$A_{ij} = \begin{cases} 2 & \text{if } i=j \\ -1 & \text{if } i=j+1 \text{ or } i=j-1 \\ 0 & \text{otherwise} \end{cases} \quad (2-51)$$

and R_j is the end-to-end vector of the j th spring in the chain. N is the number of springs. Equation 2-50 can be thought of as a matrix equation with off-diagonal terms.

2.7.2 Normal Mode Transformation

Rouse discovered a transformation that diagonalized this matrix equation into uncoupled equations, that is, into N normal modes:

$$\zeta(\dot{\tilde{R}}_i - R_i \cdot \nabla v) + 4kT \sin^2\left(\frac{i\pi}{2(N+1)}\right) \left[2\beta^2 R_i + \frac{\partial \log \psi}{\partial R_i} \right] = 0 \quad (2-52)$$

where R_i is a transformed end-to-end vector. The first mode, $i=1$, corresponds to cooperative relaxation of the entire chain. The other normal modes, $i=2,3,\dots$, correspond to relaxations of successively smaller portions of the chain. An analogy can be drawn to a vibrating string, which has a fundamental mode corresponding to vibration of the whole string, and a series of higher harmonics that correspond to vibrations of successively smaller fractions of the string.

The probability flux is the sum over the contributions from all modes:

$$J/\psi = \sum_{i=1}^N \dot{R}_i \quad (2-53)$$

which can be substituted into the probability continuity equation, Equation 2-42. Because each mode is independent, the probability distribution has a factorable solution:

$$\psi(R_1, R_2, \dots, R_N) = \prod_{i=1}^N \psi_i(R_i) \quad (2-54)$$

Each ψ_i satisfies its own Smoluchowski equation:

$$\frac{\partial \psi_i}{\partial t} + \frac{\partial}{\partial R_i} \cdot \left\{ R_i \cdot \nabla v \psi_i - \frac{4kT}{\zeta} \sin^2\left(\frac{i\pi}{2(N+1)}\right) \left[2\beta^2 R_i + \frac{\partial \log \psi_i}{\partial R_i} \right] \right\}$$

2.7.3 The Stress Tensor and Constitutive Equation

The polymeric contribution to the stress tensor is a sum of contributions all the springs:

$$\sigma_p = 2\nu kT \beta^2 \sum_{i=1}^N \langle R_i R_i \rangle$$

It is a property of the normal-mode decomposition that

$$\sum_{i=1}^N \langle R_i R_i \rangle = \sum_{i=1}^N \langle R_i' R_i' \rangle$$

Thus the stress can be broken down into a sum of contributions,

$$\sigma_p = \sum_{i=1}^N \sigma_i$$

each contribution coming from a distinct normal mode,

$$\sigma_i = 2\nu kT \beta^2 \langle R_i' R_i' \rangle$$

Because the distribution function, ψ_i , associated with mode i satisfies a Smoluchowski equation similar to the Smoluchowski equation for dumbbells, σ_i an upper-convected Maxwell equation (see Section 1.6.2),

$$\nabla \cdot \left(\sigma_i + \frac{1}{\lambda_i} (\sigma_i - G\delta) \right) = 0$$

where

$$\lambda_i = \frac{\zeta}{16kT \beta^2 \sin^2(i\pi/2(N+1))}, \quad G = \nu kT$$

Equations 2-58, 2-60, and 2-61 therefore constitute the constitutive equation Rouse model.

2.7.4 Approximation for Slow Modes

In the Rouse constitutive equation, there are N independent contributions to the stress tensor, each having its own relaxation time, λ_i . For N large, the many long relaxation times for which $i < N$, and therefore

$$\sin^2\left(\frac{i\pi}{2(N+1)}\right) \approx \frac{i^2\pi^2}{4(N+1)^2} \quad (2-62)$$

The longer relaxation times are therefore approximately

$$\lambda_i \approx \frac{\zeta(N+1)^2}{4\pi^2\beta^2 i^2 kT}, \quad G_i = G = \nu kT. \quad (2-63)$$

This equation for λ_i shows an *apparent* dependence on N , the number of submolecules into which the chain is subdivided. N is not a purely molecular property, but depends on how many beads and springs one chooses to describe the molecule. Fortunately, the apparent dependence of λ_i on N disappears. This is so because for a given polymer molecule, as one increases N , the number of submolecules, the fully extended length of each submolecule decreases as $1/N$. Then β^{-2} , which is proportional to the mean square end-to-end distance of the submolecule, is proportional to $1/N$. Also ζ , the bead friction coefficient, is inversely proportional to N , since as one increases the number of beads used to describe a given polymer molecule, the amount of friction that must be assigned to each bead decreases. Equation 2-63 can therefore be rearranged to a form that shows no dependence on N :

$$\lambda_i \approx \frac{\zeta_0 P^2 \ell^2}{6\pi^2 i^2 kT} = \frac{6(\eta - \eta_s)}{\pi^2 i^2 \nu kT} \quad (2-64)$$

Here P is the number of monomers in the whole chain, ℓ is the monomer length and ζ_0 is the friction coefficient per monomer. $\eta - \eta_s$ is the polymer contribution to the shear viscosity. The second equality in 2-64 is derived from the relationship $\eta - \eta_s = \nu kT \sum \lambda_i$ and the identity $\sum \lambda_i = \lambda_1 \sum 1/i^2 = \pi^2 \lambda_1 / 6$.

This equation for λ_i is only valid if i/N is small. For large i/N , that is, for modes that describe the relaxation of only a few submolecules, the approximation in Equation 2-64 does not hold, and λ_i for each of these modes depends on N , the arbitrary number of submolecules. Thus the Rouse model is only valid for the longer relaxation modes.

Polymer motions not described by the Rouse model include bond rotations and coordinated movements of several backbone atoms. These motions are sometimes called "glassy modes" since they account for much of the relaxation that occurs in bulk polymers that have been vitrified, i.e., cooled to the point of solidification into a glass. The temperature at which a fluid vitrifies is called the *glass transition temperature*.

2.7.5 Assumptions of the Rouse Model

The assumptions underlying the Rouse model are:

1. Excluded volume and polymer-solvent interactions are neglected; the coil has a Gaussian equilibrium distribution of configurations.
2. The deformations are not so severe that they distort the chain conformation beyond the limit of Gaussian behavior. The distortions can thus be modeled by the displacements of a discrete set of frictional beads connected by submolecules

that act as springs.

3. The frictional drag on a bead is proportional to the velocity of the minus the ambient solvent velocity, that is, the velocity the solvent would have the absence of that bead.

4. The influence of the drag that other beads have on the ambient solvent velocity around a given bead is neglected; i.e., hydrodynamic interaction is accounted for.

5. Brownian forces keep each bead in thermal equilibrium with the solvent; each bead maintains the Maxwell distribution of velocities corresponding to solvent temperature.

Finally, we have tacitly assumed that

6. The topological restrictions that prohibit one part of the chain from passing through another are neglected; the Rouse molecule is therefore a "phantom chain."

For modest deformations, the weakest of these assumptions are the neglect of solvent effects and the neglect of hydrodynamic interaction. Corrections to these are discussed in Chapter 8. The effects of the phantom chain assumption are uncertain.¹⁷

2.8 LINEAR VISCOELASTICITY

2.8.1 Distribution of Relaxation Times

2.8.1.1 The Rouse spectrum The Rouse model is more complete than the model of Green and Tobolsky, because it yields values for the relaxation times and moduli, $G_i = G = \nu kT$, for all i . These values constitute what is called *distribution or spectrum of relaxation times*. The Rouse relaxation spectrum is a distinctive feature of the model that can be tested experimentally. The simple and most accurate type of experiment that tests this spectrum is the *amplitude oscillatory deformation*. This can be performed in shear, for example, on the cone and plate geometry of Fig. 1-5, by an oscillatory rotation of the about its axis of symmetry. In this way the shear becomes a sinusoidal function of time:

$$\gamma = \gamma_0 \sin \omega t$$

here γ_0 , the maximum shear strain, is called the *strain amplitude*; ω is the *frequency*.

The response of the shear stress for the upper-convected Maxwell equal such a strain history, and hence the response of a single mode, say mode i , in the Rouse model, is

$$\sigma = \gamma_0 \left[G_i \frac{\omega^2 \lambda_i^2}{\omega^2 \lambda_i^2 + 1} \sin \omega t + G_i \frac{\omega \lambda_i}{\omega^2 \lambda_i^2 + 1} \cos \omega t \right]$$

The shear stress is therefore proportional to the strain amplitude, γ_0 , no matter how large the value of γ_0 . This result is a peculiar, and unrealistic, feature

upper-convected Maxwell equation. Nevertheless for all constitutive equations that obey the postulates of viscoelastic simple fluid theory, and perhaps more to the point, for virtually all real polymer melts and solutions, the shear stress is proportional to $\dot{\gamma}_0$ if $\dot{\gamma}_0$ is small. The region of small $\dot{\gamma}_0$ where σ is proportional to $\dot{\gamma}_0$ is called the *regime of linear viscoelasticity*, since σ in this regime is linear in $\dot{\gamma}_0$.* Note in Equation 2-66 that the linear viscoelastic shear stress has two terms. In general,

$$\sigma = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t] \quad (2-67)$$

where G' and G'' (the prime here does *not* denote differentiation) are called the *storage modulus* and the *loss modulus*, respectively. These names derive from the fact that the term involving G' is *in phase with the strain*; that involving G'' is *in phase with the strain rate*. For a perfectly elastic material that *stores* all mechanical energy imparted to it, $G'' = 0$. For a Newtonian liquid, which *instantly loses* all mechanical energy, $G' = 0$.

For the Rouse model, Equation 2-60, we find

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \lambda_i^2}{\omega^2 \lambda_i^2 + 1} \quad (2-68)$$

$$G''(\omega) = \sum_i G_i \frac{\omega \lambda_i}{\omega^2 \lambda_i^2 + 1} \quad (2-69)$$

G' and G'' are thus determined by the values of G_i and λ_i , that is by the relaxation spectrum.

For the Rouse model, G_i and λ_i are given by Equation 2-63. For materials that do not obey the Rouse model, Equations 2-68 and 2-69 can be *fit* to the measured $G'(\omega)$ and $G''(\omega)$ by appropriately choosing a set of relaxation times, $\{\lambda_i\}$, and moduli, $\{G_i\}$. These sets of relaxation times and moduli constitute a *discrete representation* of the relaxation spectrum. The measurement of G' and G'' as functions of frequency is thus a means of determining the distribution of relaxation times. Note that the contribution of mode i to G'' is maximum when $\omega = 1/\lambda_i$. Thus G'' is sensitive to relaxation processes with relaxation times around $1/\omega$. By varying ω over a wide range of frequencies, the strengths, G_i , of relaxation mechanisms occurring over a correspondingly wide range of times are probed.

Figure 2-7 shows $G'(\omega)$ and $G''(\omega)$ for the Rouse model. The model predicts that at low frequencies,

$$G' \propto \omega^2; \quad G'' \propto \omega \quad (2-70)$$

* Outside of the linear viscoelastic regime, higher powers of $\dot{\gamma}_0$ appear, as well as *higher harmonics*, that is higher powers of $\sin \omega t$ and $\cos \omega t$.

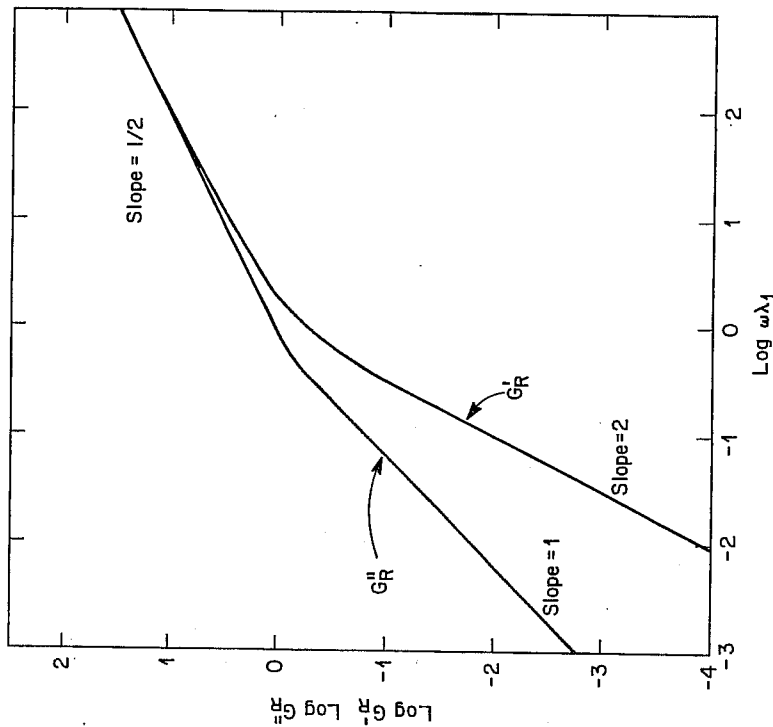


Fig. 2-7 The Rouse predictions for the dimensionless storage and loss moduli G'_R and G''_R as functions of dimensionless frequency, $\omega\lambda_1$, where λ_1 is the longest relaxation time. The moduli are made dimensionless by dividing G' and G'' by the modulus $G = \nu kT$ (from Ferry¹⁸ reprinted from *Viscoelastic Properties of Polymers*, 3rd Ed., © 1980 by permission of John Wiley & Sons, Inc.).

This result is not unique to the Rouse model, but is true any time there is a longest relaxation time that dominates at small ω . The region of frequency in which this limiting behavior occurs is called the *terminal zone*.¹⁸

At high frequencies, the Rouse model gives the distinctive prediction

$$G' = G'' \propto \omega^{1/2} \quad (2-71)$$

This prediction is a consequence of the spacing of relaxation times in the Rouse model, namely, $\lambda_i \propto 1/i^2$; see Equation 2-63. In general, if $\lambda_i \propto 1/i^p$, and $G_i = G$ is independent of i , then

$$G' \propto G'' \propto \omega^{1/p} \quad (2-72)$$

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