

Step Strain Experiment STRESS RELAXATION

Sample is initially at rest

At time $t = 0$, apply instantaneous shear strain γ_0

The shear relaxation modulus

$$G(t, \gamma_0) \equiv \sigma(t)/\gamma_0 \quad (2-1)$$

For small strains, the modulus does not depend on strain. **Linear viscoelasticity** corresponds to this small strain regime. Linear response means that stress is proportional to the strain, and thus the modulus is independent of strain.

$$\sigma(t) \equiv G(t)\gamma_0 \quad (2-3)$$

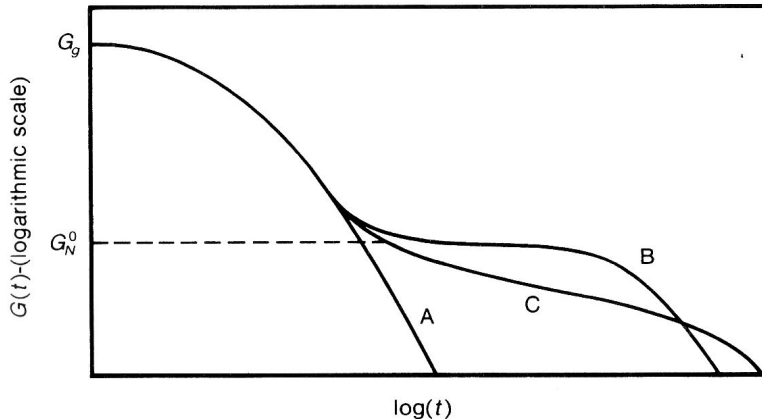


Figure 1: Stress Relaxation modulus of linear polymers. A is monodisperse with $M_w < M_C$, B is monodisperse with $M \gg M_C$, and C is polydisperse with $M_w \gg M_C$. Linear polymers are viscoelastic liquids.

Step Strain Experiment STRESS RELAXATION

RC-3 is a linear polybutadiene $M_w = 940,000$ and $M_w/M_n < 1.1$. The glass transition of this polymer is $T_g = -99^\circ\text{C}$.

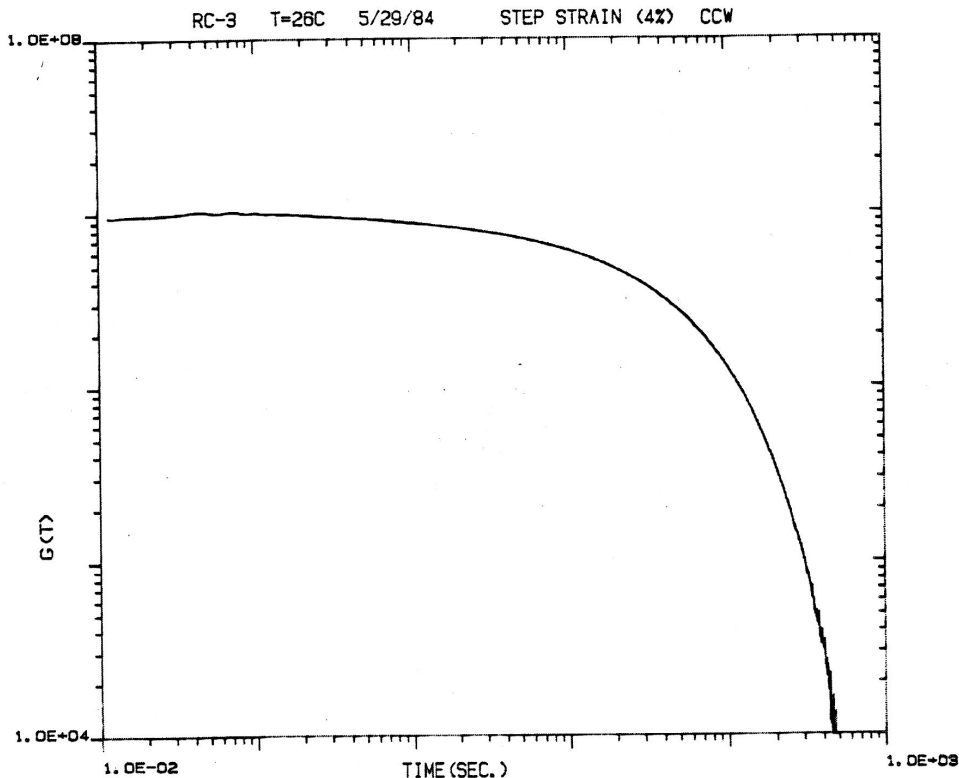


Figure 2: Stress Relaxation after a Step Strain.

Multiple Step Strain Experiment BOLTZMANN SUPERPOSITION PRINCIPLE

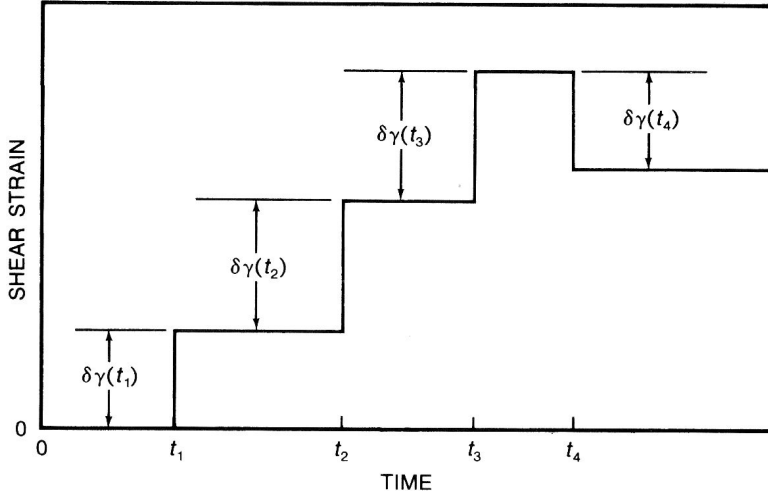


Figure 3: Sequence of Step Strains in the Multiple Step Strain Experiment.

All strains in the sequence are small so the response is linear.
The first strain $\delta\gamma(t_1)$ is applied at time t_1 .

$$\sigma(t) = G(t - t_1)\delta\gamma(t_1) \quad t_1 < t < t_2 \quad (2-4)$$

The second strain $\delta\gamma(t_2)$ is applied at time t_2 .

The Boltzmann Superposition Principle states that the stresses from the two deformations are additive:

$$\sigma(t) = G(t - t_1)\delta\gamma(t_1) + G(t - t_2)\delta\gamma(t_2) \quad t_2 < t < t_3 \quad (2-5)$$

Boltzmann Superposition holds for any combination of small strains.

$$\sigma(t) = \sum_{i=1}^N G(t - t_i)\delta\gamma(t_i) \quad t > t_N \quad (2-6)$$

For any smooth strain history we can write

$$\sigma(t) = \int_0^{\gamma(t)} G(t-t') d\gamma(t') \quad \text{text ahs typo!} \quad (2-7)$$

$d\gamma(t') = \dot{\gamma}(t') dt'$, so

$$\sigma(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (2-8)$$

The $-\infty$ integration limit reminds us that we must include all of the strain history of the sample. In practice we often start with a stress-free sample at $t = 0$, and then we write

$$\sigma(t) = \int_0^t G(t-t') \dot{\gamma}(t') dt' \quad (2-9)$$

The Boltzmann Superposition applies to more general flows

$$\tau_{ij}(t) = \int_0^{\gamma_{ij}} G(t-t') d\gamma_{ij}(t') \quad (2-10)$$

$$\tau_{ij}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}_{ij}(t') dt' \quad (2-11)$$

EXAMPLE: Simple Extension

$$\gamma_{ij}(t \geq 0) = \begin{bmatrix} 2\varepsilon_0 & 0 & 0 \\ 0 & -\varepsilon_0 & 0 \\ 0 & 0 & -\varepsilon_0 \end{bmatrix} \quad (2-12)$$

$$\tau_{ij}(t) = G(t) \begin{bmatrix} 2\varepsilon_0 & 0 & 0 \\ 0 & -\varepsilon_0 & 0 \\ 0 & 0 & -\varepsilon_0 \end{bmatrix} \quad (2-13)$$

$$\text{The extensional stress} \quad \sigma_E \equiv \tau_{11} - \tau_{22} = 3\varepsilon_0 G(t) \quad (2-14)$$

Thus Young's Modulus is three times the Shear Modulus

$$\sigma_E/\varepsilon_0 \equiv E(t) = 3G(t) \quad (2-15)$$

EXAMPLE: STEADY SIMPLE SHEAR

For all past times the strain rate tensor is:

$$\dot{\gamma}_{ij} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (2-16)$$

Thus there are two equal nonzero components of the extra stress tensor:

$$\tau_{12} = \tau_{21} = \sigma = \dot{\gamma} \int_{-\infty}^t G(t - t') dt' \quad (2-17)$$

Define $s \equiv t - t'$

then $ds = -dt'$, $t' = -\infty \rightarrow s = \infty$, and $t' = t \rightarrow s = 0$

$$\sigma = \dot{\gamma} \int_0^{\infty} G(s) ds \quad (2-18)$$

Since viscosity $\eta \equiv \sigma/\dot{\gamma}$ and linear viscoelasticity corresponds to the low shear rate (Newtonian) value of the viscosity

$$\eta_0 = \int_0^{\infty} G(s) ds \quad (2-19)$$

This is the first of many examples of the results of different **linear** viscoelastic experiments being related to one another. Equation (2-19) relates the zero shear rate viscosity in steady shear to the shear relaxation modulus measured in a step strain experiment.

Owing to the long relaxation times in polymers, it is often convenient to use a logarithmic time scale, $s d(\ln s) = ds$, $s = 0 \rightarrow \ln s = -\infty$

$$\eta_0 = \int_{-\infty}^{\infty} s G(s) d(\ln s)$$

Maxwell model has

$$G(t) = G_0 \exp(-t/\lambda) \quad (2-22)$$

Thus $tG(t)$ has a maximum at roughly $t = \lambda$.

Step Strain Data on a Linear Polymer Melt INTEGRATION TO OBTAIN VISCOSITY

$$\eta_0 = \int_{-\infty}^{\infty} sG(s)d \ln s$$

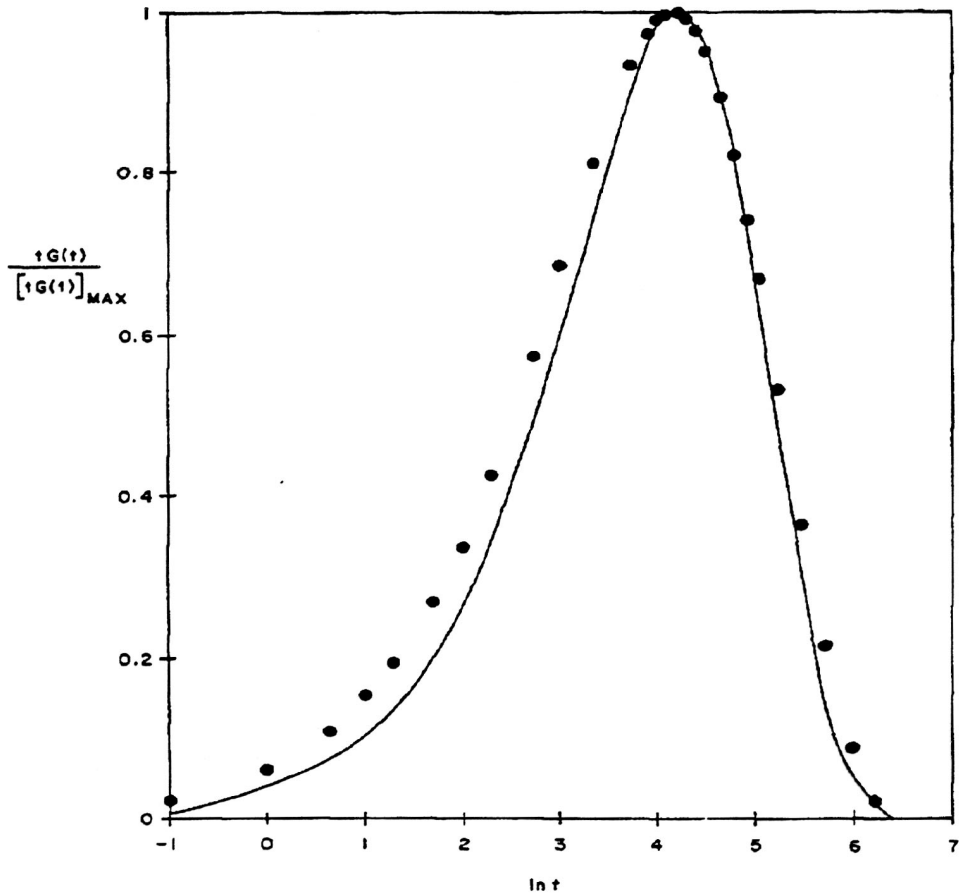


Figure 4: $tG(t)$ for a high molecular weight nearly monodisperse polybutadiene with $M_w = 940,000$. Solid curve is the Maxwell Model.

Relaxation Time Spectrum

$F(\lambda)d\lambda$ represents the mode strengths between λ and $\lambda + d\lambda$.

$$G(t) = \int_0^{\infty} F(\lambda) [\exp(-t/\lambda)] d\lambda \quad (2-28)$$

Defining $H(\lambda) \equiv F(\lambda)\lambda$, $H(\lambda)d(\ln \lambda) = F(\lambda)d\lambda$, $\lambda = 0 \Rightarrow \ln \lambda = -\infty$

$$G(t) = \int_{-\infty}^{\infty} H(\lambda) [\exp(-t/\lambda)] d(\ln \lambda) \quad (2-29)$$

Equations (2-28) and (2-29) are continuous versions of the Generalized Maxwell Model. Many methods for calculating $H(\lambda)$ from experimental data are found in J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley (1980).

Relaxation spectra are discussed extensively in the literature, despite the fact that calculation of $H(\lambda)$ or $F(\lambda)$ is

MATHEMATICALLY ILL-POSED.

Many $H(\lambda)$ describe the same $G(t)$.

Furthermore, molecular theories of viscoelasticity predict $G(t)$ directly, so the relaxation spectrum is nearly obsolete.

Shear Relaxation Modulus of Polymer Gels CROSSLINKED ELASTOMERS (p. 1)

Crosslinked polymers are **viscoelastic solids**. They exhibit time-dependent stress relaxation, but do not relax to a zero stress state.

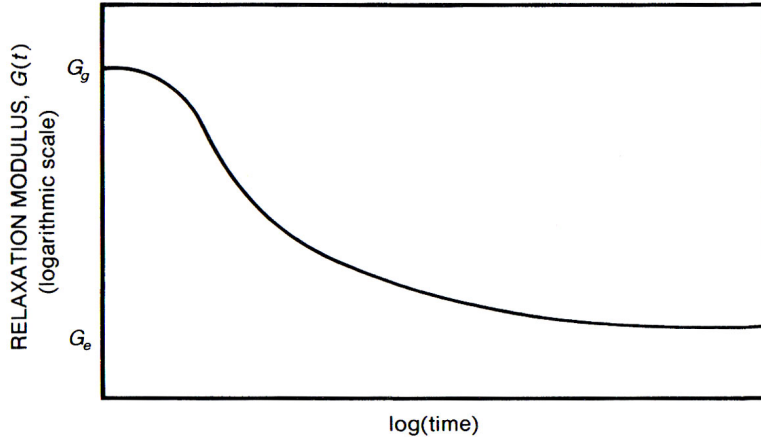


Figure 5: Stress Relaxation of a Crosslinked Gel

The (short time) **glassy modulus** is

$$G_g \cong \frac{kT}{b^3} \quad kT \text{ per monomer}$$

k is the Boltzmann's constant

T is the absolute temperature

b is a length scale that is roughly the size of a monomer

Typical G_g for polymers are 10^9 - 10^{10} dynes/cm², which corresponds to $b \cong 3\text{\AA}$.

A general relation links length scale l and modulus scale G

$$G \cong \frac{kT}{Pl^3}$$

Shear Relaxation Modulus of Polymer Gels CROSSLINKED ELASTOMERS (p. 2)

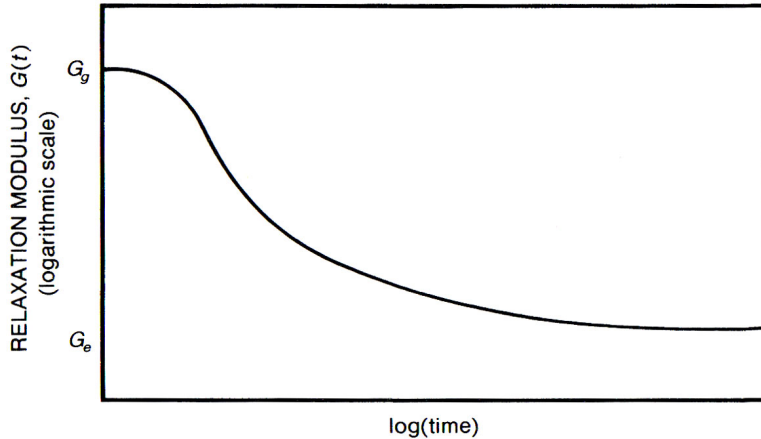


Figure 6: Stress Relaxation of a Crosslinked Gel

The (long time) **gel modulus** is

$$G_e = \nu kT = \frac{\rho R T}{M_x} \quad kT \text{ per network strand}$$

$\nu = \rho N_A / M_x$ is the number density of network strands

$R \equiv N_A k$, with N_A Avogadro's number

ρ is the polymer density

M_x is the molecular weight of a network strand.

Shear Relaxation Modulus of Polymer Melts

CHAIN ENTANGLEMENT

Long linear polymers have universal linear viscoelastic response that depends on their chain length and chain length distribution, **independent of the chemical details**.

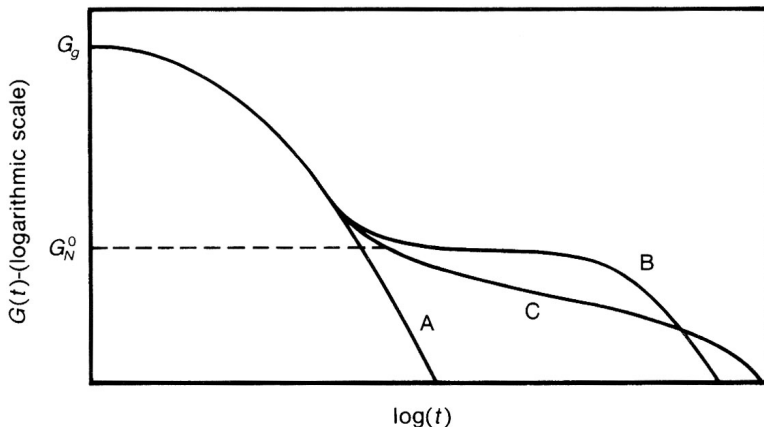


Figure 7: Stress Relaxation Modulus of Polymers

Curve A is a monodisperse unentangled polymer ($M < M_C$).

Relaxation is rapid, with no sign of a rubbery plateau.

Curve B is a monodisperse entangled polymer ($M > M_C$).

At short times the relaxation is identical to the short chain, but terminal relaxation is delayed by the rubbery plateau.

The **plateau modulus** is

$$G_N^0 = \frac{\rho RT}{M_e} \quad kT \text{ per entanglement strand} \quad (2-20)$$

where M_e is the molecular weight of an entanglement strand.

Curve C is a polydisperse entangled polymer ($M_w > M_C$).

Zero Shear Rate Viscosity of Linear Polymers UNIVERSAL BEHAVIOR

$$\eta_0 \sim \begin{cases} M_w & M_w < M_C \\ M_w^{3.4} & M_w > M_C \end{cases}$$

INDEPENDENT OF MONOMER CHEMISTRY!

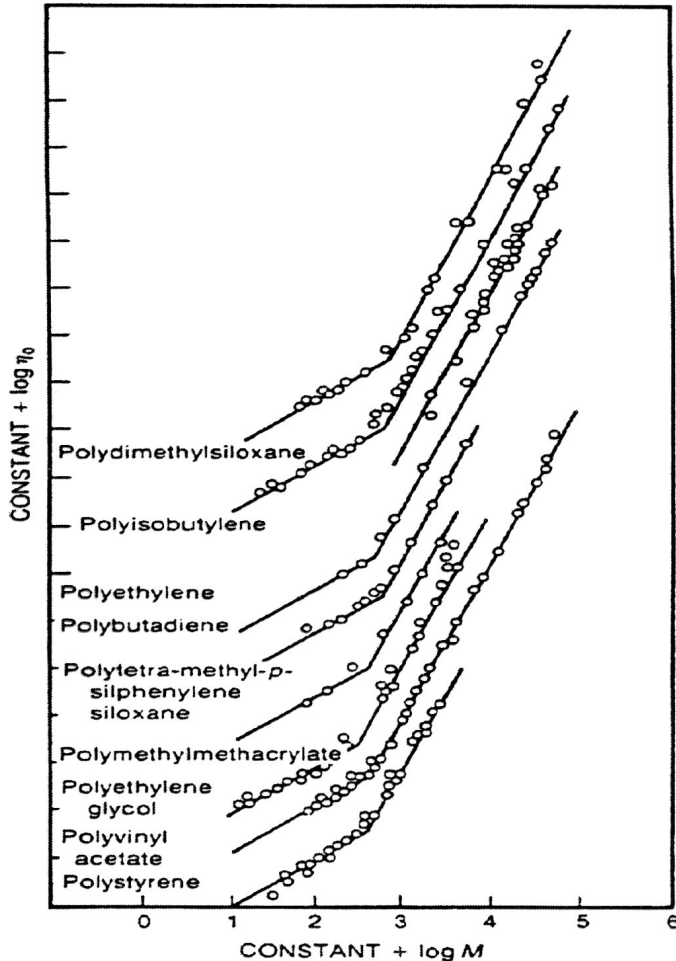


Figure 8: Viscosity - Molecular Weight Relation for various Linear Polymers

Relaxation Time Distribution THE GENERALIZED MAXWELL MODEL

The (single mode) Maxwell model has

$$G(t) = G_0 \exp(-t/\lambda) \quad (2-22)$$

Multiple relaxation times are described by the Generalized Maxwell Model

$$G(t) = \sum_{i=1}^N G_i \exp(-t/\lambda_i) \quad (2-25)$$

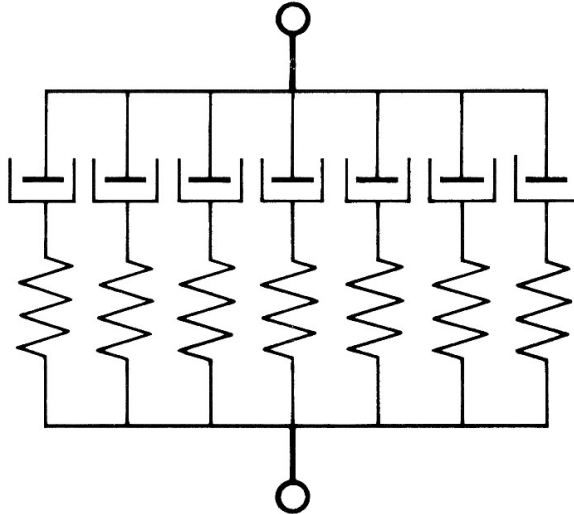


Figure 9: Generalized Maxwell Model

By using a sufficient number of modes, one can empirically describe any viscoelastic liquid with the Generalized Maxwell Model.

Creep and Creep Recovery

SHEAR COMPLIANCE

Apply a **constant stress** σ for all times $t > 0$.

Shear Creep Compliance $J(t) \equiv \gamma(t)/\sigma$ units $cm^2/dyne$ (2-31)

Linear viscoelasticity $\Rightarrow J(t)$ is independent of σ

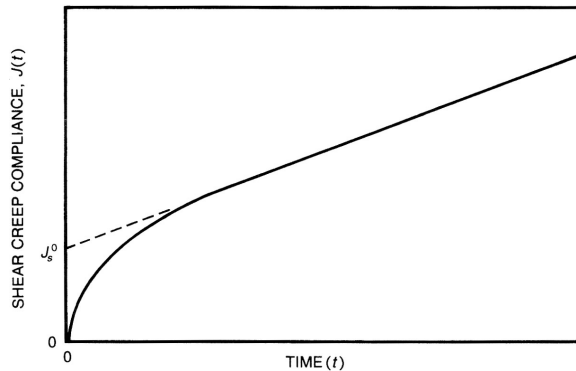


Figure 10: Creep Compliance of a Polymer Melt.

The long-time creep behavior of a viscoelastic liquid is linear in time.

$$J(t) = J_S^0 + t/\eta_0 \quad (2-32)$$

J_S^0 is the steady state compliance, and provides a measure of the terminal (long-time) elastic energy in the system.

Boltzmann Superposition makes

$$J_S^0 = \frac{1}{\eta_0^2} \int_0^\infty G(s) s ds = \frac{\int_0^\infty G(s) s ds}{\left[\int_0^\infty G(s) ds \right]^2} \quad (2-33)$$

Once again, a logarithmic time scale is often convenient.

$s d \ln s = ds$, $s = 0 \Rightarrow \ln s = -\infty$

$$J_S^0 = \frac{1}{\eta_0^2} \int_{-\infty}^\infty s^2 G(s) d \ln s$$

Step Strain Data on a Linear Polymer Melt

INTEGRATION TO OBTAIN THE STEADY STATE COMPLIANCE

$$J_S^0 = \frac{1}{\eta_0^2} \int_{-\infty}^{\infty} s^2 G(s) d \ln s$$

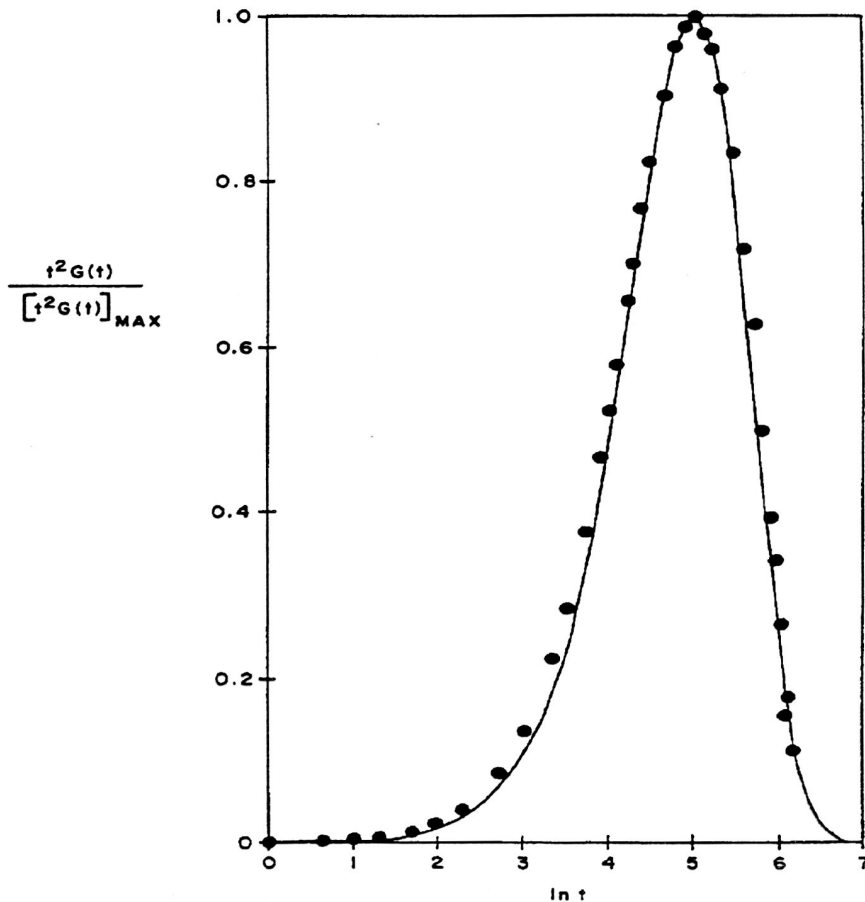


Figure 11: $t^2 G(t)$ for a High Molecular Weight Nearly Monodisperse Polybutadiene with $M_w = 940,000$. Solid Curve is the Maxwell Model.

Relations between Creep Compliance and Relaxation Modulus

Each measurable viscoelastic function ($G(t)$, $J(t)$, etc.) contains all information about the linear viscoelastic response of a material.

EXAMPLE: VISCOSITY AND STEADY STATE COMPLIANCE

Long-time creep

$$J(t) = J_S^0 + t/\eta_0 \quad (2-32)$$

determines both η_0 and J_S^0 .

They can also be determined from the shear relaxation modulus

$$\eta_0 = \int_0^\infty G(s)ds \quad (2-19)$$

$$J_S^0 = \frac{1}{\eta_0^2} \int_0^\infty G(s)sds \quad (2-33)$$

RELATIONS BETWEEN $G(t)$ AND $J(t)$

The same information is contained in both functions, so there must be a general relationship. One form involves Laplace Transforms

$$\int_0^\infty J(t) \exp(-ts)dt = \frac{1}{s^2 \int_0^\infty G(t) \exp(-ts)dt}$$

The other forms are convolution integrals

$$\int_0^t G(\lambda)J(t-\lambda)d\lambda = t$$

$$\int_0^t J(\lambda)G(t-\lambda)d\lambda = t$$

This implies a simple inequality

$$J(t)G(t) \leq 1$$

Creep and Creep Recovery RECOVERABLE COMPLIANCE OF A VISCOELASTIC LIQUID

After reaching steady state in creep, we remove the stress and measure the **elastic recoil strain** $\gamma_r(t)$

$$\text{RECOVERABLE COMPLIANCE} \quad R(t) \equiv \gamma_r(t)/\sigma \quad (2-39)$$

$$\text{Boltmann Superposition makes} \quad R(t) = J(t) - t/\eta_0 \quad (2-40)$$

The long-time limit of the recoverable strain is thus the steady state compliance

$$\lim_{t \rightarrow \infty} [R(t)] = J_s^0 \quad (2-41)$$

The terminal (longest) relaxation time is

$$\lambda_1 \cong \eta_0 J_s^0 \quad (2-35)$$

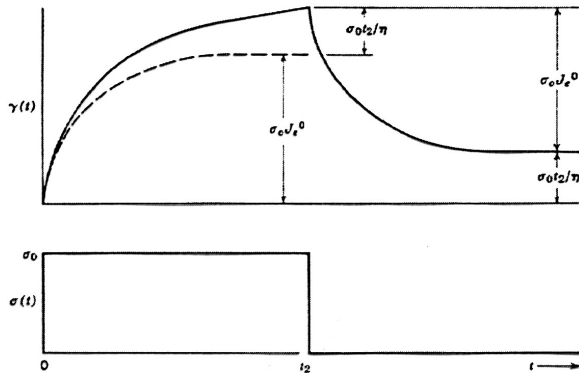


Figure 12: Creep and Creep Recovery for a Viscoelastic Liquid. Stress σ_0 is applied at $t = 0$, and removed at $t = t_2$. Note that $J_e^0 = J_s^0$.

Creep and Creep Recovery RECOVERABLE COMPLIANCE OF A VISCOELASTIC SOLID

A viscoelastic solid has infinite viscosity, so

$$R(t) = J(t)$$

and the long-time limits of each are the equilibrium compliance J_e^0 .

$$R(\infty) = J(\infty) = J_e^0$$

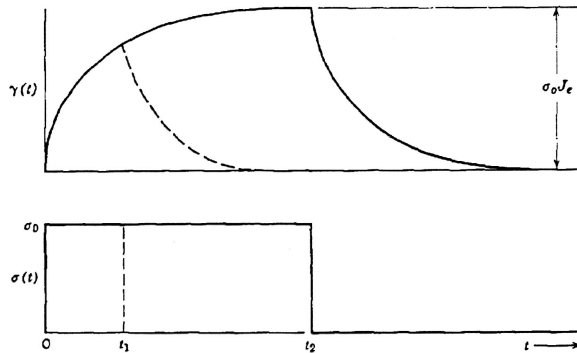


Figure 13: Creep and Creep Recovery for a Viscoelastic Solid. Stress σ_0 is applied at $t = 0$, and removed at either $t = t_1$ or t_2 .

Creep and Creep Recovery LOGARITHMIC PLOTS

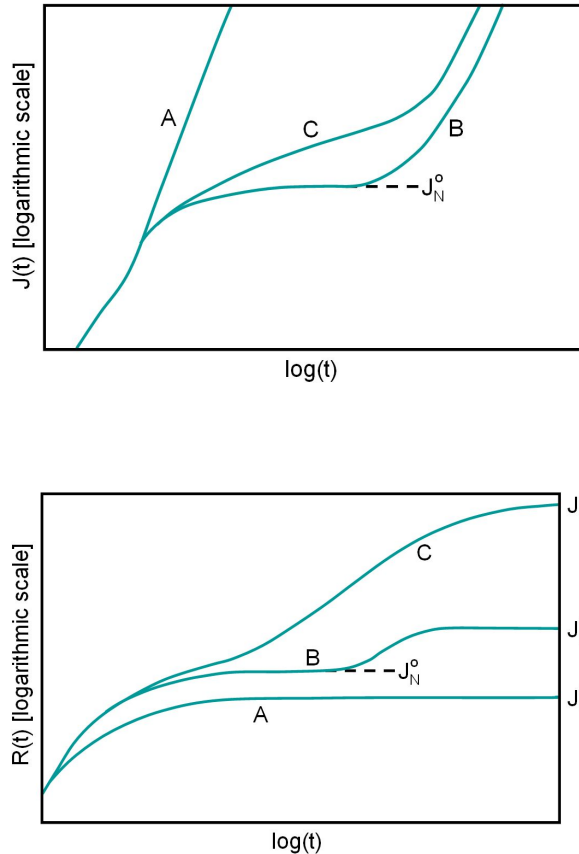


Figure 14: Figures 2-6 and 2-7 in text have **numerous mistakes**. A is monodisperse with $M < M_C$, B is monodisperse with $M \gg M_C$, and C is polydisperse with $M_w \gg M_C$.