Step Strain Experiment
STRESS RELAXATION

Sample is initially at rest
At time $t = 0$, apply instantaneous shear strain $\gamma_0$
The shear relaxation modulus

$$G(t, \gamma_0) \equiv \sigma(t)/\gamma_0$$  \hspace{1cm} (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.

$$\sigma(t) \equiv G(t)\gamma_0$$  \hspace{1cm} (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.
RC-3 is a linear polybutadiene $M_w = 940,000$ and $M_w/Mn < 1.1$. The glass transition of this polymer is $T_g = -99^\circ C$.

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

$$\sigma(t) = \int_0^{\gamma(t)} G(t - t')d\gamma(t')$$

This equation has a typo! (2-7)

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

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

$$\sigma(t) = \int_{0}^{t} G(t - t')\dot{\gamma}(t')dt'$$ (2-9)

The Boltzmann Superposition applies to more general flows

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

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

EXAMPLE: Simple Extension

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

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

The extensional stress

$$\sigma_E \equiv \tau_{11} - \tau_{22} = 3\varepsilon_0 G(t)$$ (2-14)

Thus Young’s Modulus is three times the Shear Modulus

$$\sigma_E/\varepsilon_0 \equiv E(t) = 3G(t)$$ (2-15)
EXAMPLE: STEADY SIMPLE SHEAR

For all past times the strain rate tensor is:

\[
\dot{\gamma}_{ij} = \begin{bmatrix}
0 & \dot{\gamma} & 0 \\
\dot{\gamma} & 0 & 0 \\
0 & 0 & 0 
\end{bmatrix}
\]  

(2-16)

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

\[
\tau_{12} = \tau_{21} = \sigma = \dot{\gamma} \int_{-\infty}^{t} G(t-t') dt'
\]  

(2-17)

Define \( s \equiv t - t' \)

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

\[
\sigma = \dot{\gamma} \int_{0}^{\infty} G(s) ds
\]  

(2-18)

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

\[
\eta_0 = \int_{0}^{\infty} G(s) ds
\]  

(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, \( sd(ln s) = ds, s = 0 \rightarrow ln s = -\infty \)

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

Maxwell model has

\[
G(t) = G_0 \exp(-t/\lambda)
\]  

(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 $\lambda$ and $\lambda + d\lambda$.

$$G(t) = \int_0^\infty F(\lambda) \left[ \exp(-t/\lambda) \right] d\lambda$$  \hspace{1cm} (2-28)

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

$$G(t) =\int_{-\infty}^{\infty} H(\lambda) \left[ \exp(-t/\lambda) \right] d(\ln \lambda)$$  \hspace{1cm} (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.
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

\[ G_g \approx \frac{kT}{b^3} \]

\( k \) 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/cm\(^2\), which corresponds to \( b \approx 3 \text{Å} \).

A general relation links length scale \( l \) and modulus scale \( G \)

\[ G \approx \frac{kT}{l^3} \]
The (long time) gel modulus is

\[ G_e = \nu kT = \frac{\rho RT}{M_x} kT \text{ per network strand} \]

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

\( R \equiv N_A k \), with \( N_A \) Avogadro’s number

\( \rho \) 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.

![Stress Relaxation Modulus of Polymers](image)

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

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

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

\[ G(t) = G_0 \exp(-t/\lambda) \]  \hspace{1cm} (2-22)

Multiple relaxation times are described by the Generalized Maxwell Model

\[ G(t) = \sum_{i=1}^{N} G_i \exp(-t/\lambda_i) \]  \hspace{1cm} (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 $\sigma$ 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 $\sigma$

Figure 10: Creep Compliance of a Polymer Melt.

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

$$J(t) = J_S^0 + t/\eta_0$$

(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

$$J_S^0 = \frac{1}{\eta_0^2} \int_0^\infty G(s)sds = \frac{\int_0^\infty G(s)sds}{[\int_0^\infty G(s)ds]^2}$$

(2-33)

Once again, a logarithmic time scale is often convenient.

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

$$J_S^0 = \frac{1}{\eta_0^2} \int_{-\infty}^\infty s^2G(s)d\ln s$$
Step Strain Data on a Linear Polymer Melt
INTEGRATION TO OBTAIN THE STEADY STATE COMPLIANCE

$$J^0_0 = \frac{1}{\eta_0^2} \int_{-\infty}^{\infty} s^2 G(s) d\ln s$$

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 \( G(t), J(t), \text{etc.} \) contains all information about the linear viscoelastic response of a material.

**EXAMPLE: VISCOSITY AND STEADY STATE COMPLIANCE**

Long-time creep

\[
J(t) = J^0_S + t/\eta_0 \tag{2-32}
\]

determines both \( \eta_0 \) and \( J^0_S \).

They can also be determined from the shear relaxation modulus

\[
\eta_0 = \int_0^\infty G(s)ds \tag{2-19}
\]

\[
J^0_S = \frac{1}{\eta_0^2} \int_0^\infty G(s)sds \tag{2-33}
\]

**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 $\gamma_r(t)$

$$R(t) \equiv \gamma_r(t)/\sigma ~~~~ (2-39)$$

Boltmann Superposition makes

$$R(t) = J(t) - t/\eta_0 ~~~~ (2-40)$$

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

$$\lim_{t \to \infty} [R(t)] = J_0^s ~~~~ (2-41)$$

The terminal (longest) relaxation time is

$$\lambda_1 \approx \eta_0 J_0^s ~~~~ (2-35)$$

Figure 12: Creep and Creep Recovery for a Viscoelastic Liquid. Stress $\sigma_0$ is applied at $t = 0$, and removed at $t = t_2$. Note that $J_0^e = J_0^s$. 

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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 \( \sigma_0 \) is applied at \( t = 0 \), and removed at either \( t = t_1 \) or \( t_2 \).
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 $M_w \gg M_C$. 

Creep and Creep Recovery
LOGARITHMIC PLOTS