Viscoelastic Material Models

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Outline

- Introduction（引言）
- Creep compliance and relaxation modulus（蠕变柔度与松弛刚度）
- Retarded elasticity（滞/粘弹性）
- Steady-state creep（稳态蠕变）
- Elastic vs. viscoelastic materials（弹性与粘弹性材料）
- Maxwell materials（Maxwell模型）
- Kelvin-voigt materials（KV模型）
- Prony series representation（Prony级数模型）
- WLF time/temperature equivalence（WLF时间/温度相当）
- Calibrating viscoelastic models（粘弹性模型校准）
- More sophisticated viscoelastic models（复杂粘弹性模型）
- Generalization to 3D（向三维模型推广）
- Response to harmonic loading（周期载荷的响应）

Introduction

- Amorphous polymers show complex time-dependent behavior when subjected to a history of stress or strain.

- Viscoelasticity theory was developed to approximate this behavior in polymers that are subjected to modest strains (less than 0.5%).

- Polymers strongly resist volume changes at all temperatures. The bulk modulus is comparable to that of metals or covalently bonded solids.

- The shear response of a polymer is strongly temperature dependent.

Shear modulus (N/m^2)

Viscoelastic

Glassy

10^9

Rubbery

10^5

Melt

Glass transition
temperature T_g
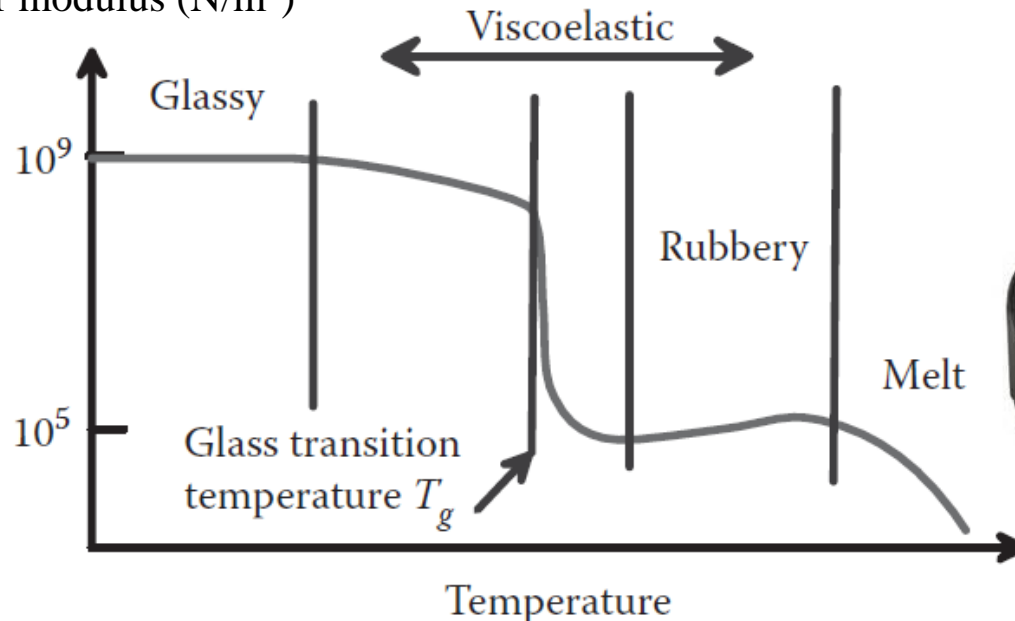
Temperature

Introduction

- At temperatures near the glass transition, the shear modulus is strongly time dependent. The time dependent shear response can be measured by applying (1) a step load or (2) a harmonic (sinusoidal) load to the specimen.

- The time-dependent modulus of polymers is also temperature dependent. Reducing the temperature is qualitatively equivalent to increasing the strain rate.

- Most amorphous polymers are isotropic.

Shear modulus (N/m^2)

Viscoelastic

Glassy

10^9

Rubbery

Melt

10^5

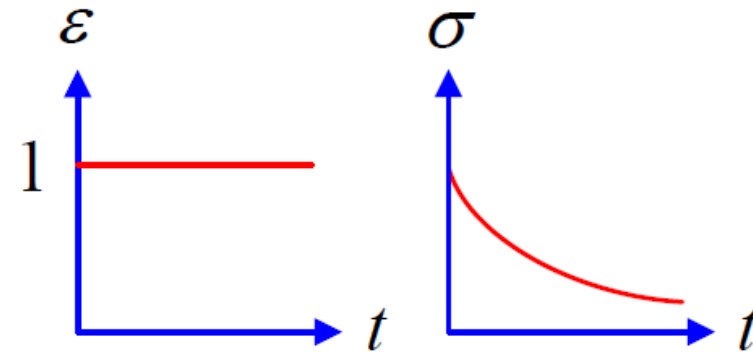Glass transition temperature T_g

Temperature
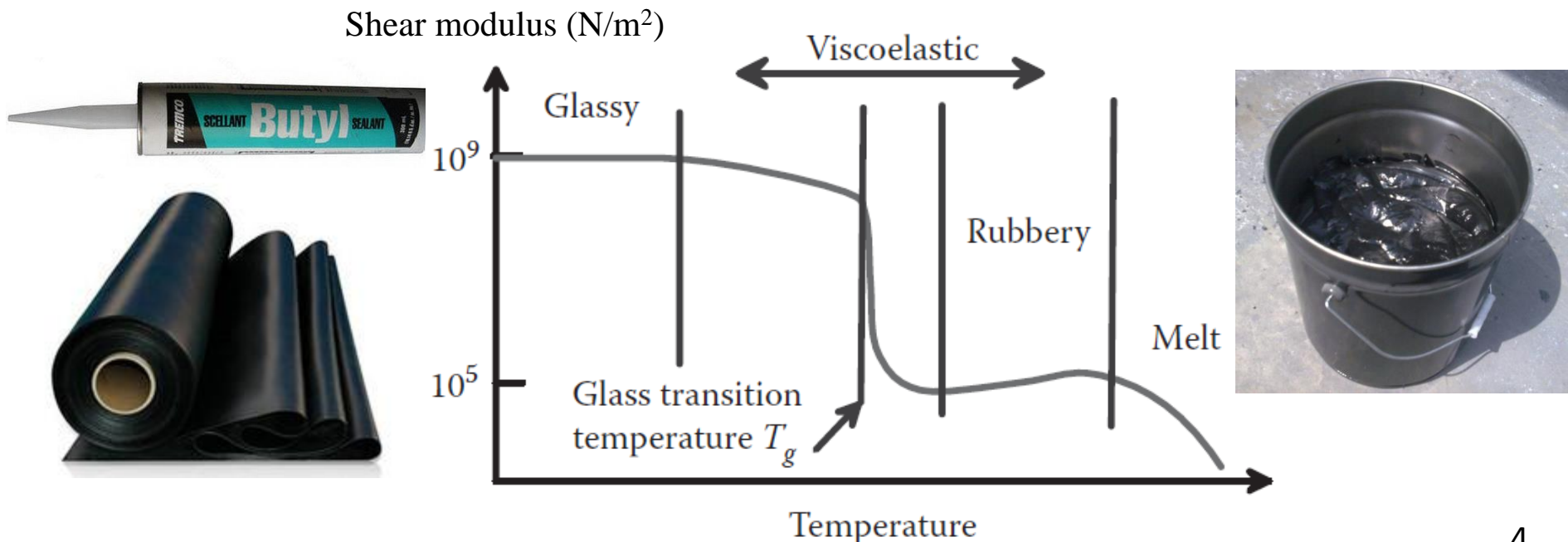
Response to Step Loading

- Creep compliance:
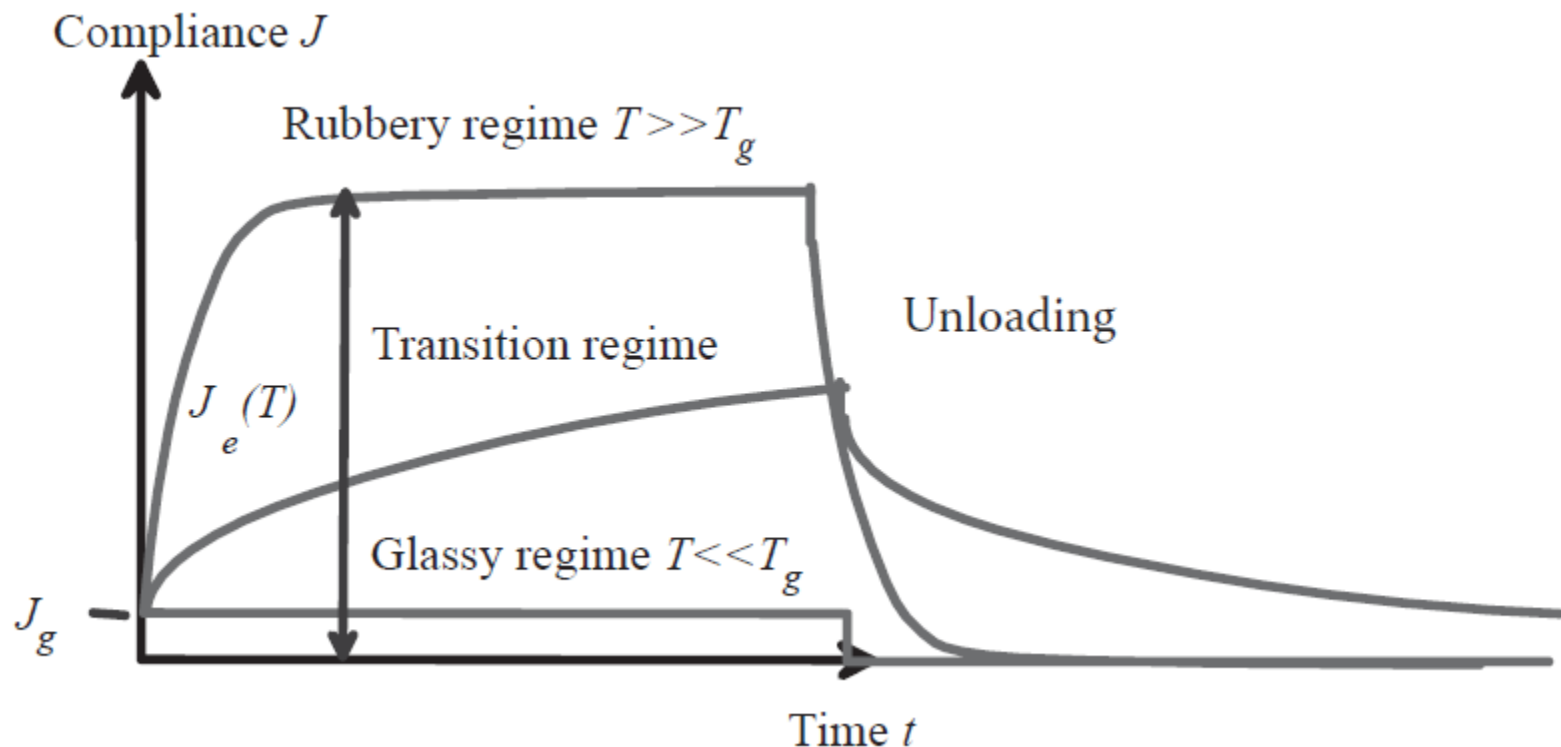the strain response to
a unit constant stress
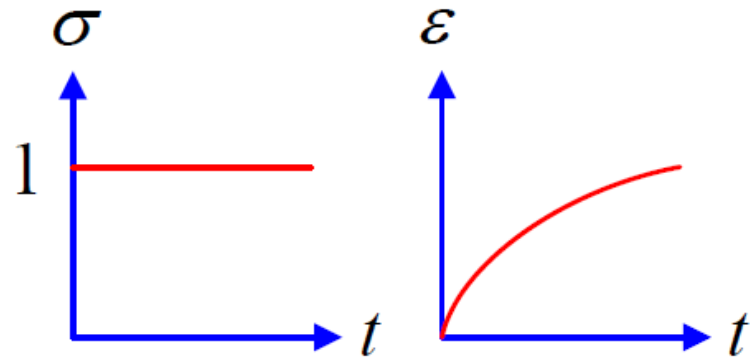
- Relaxation modulus:
the stress response to a
unit constant strain.

- The results of such a test depend on the degree of cross-linking in the polymer.

- Heavily cross-linked materials show "retarded elastic" behavior, whereas un-cross-linked materials show steady-state creep.

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Retarded Elasticity for Crosslinked Polymers

- There is always an instantaneous strain in response to a step change in stress.
- At temperatures significantly below T_g, the solid is essentially elastic.
- At temperatures significantly above T_g, the solid is very compliant.
- For a range of temperatures near T_g, the solid shows a slow transient response.
- The deformation is reversible, although this may take a very long time.

Steady-state Creep for uncrosslinked polymers

- There is always an instantaneous strain in response to a step change in stress, exactly as in crosslinked polymers.

- At temperatures well below T_g, the solid is essentially elastic and has a very low compliance, comparable with J_g.

- At temperatures above T_g, the solid is very compliant. For most practical ranges of loading, the compliance will increase more or less linearly with time. The slope of compliance is strongly temperature dependent.

- Above the glass transition temperature T_g, the deformation is irreversible.
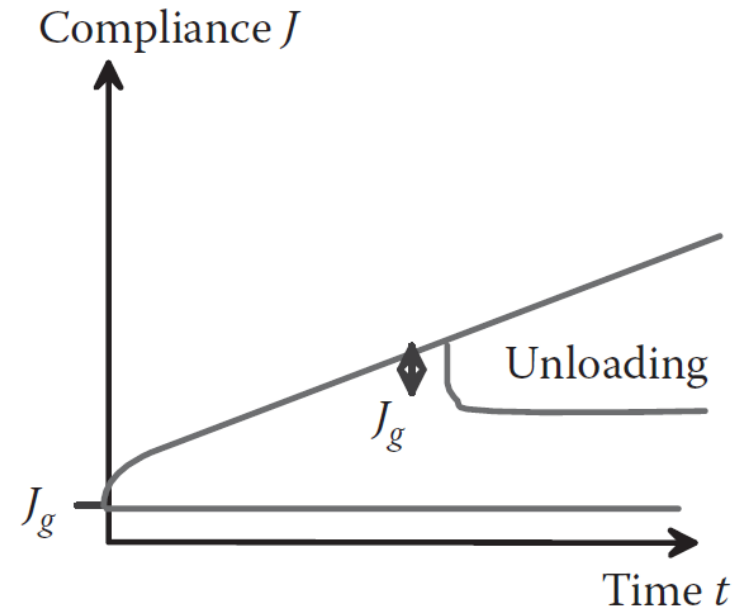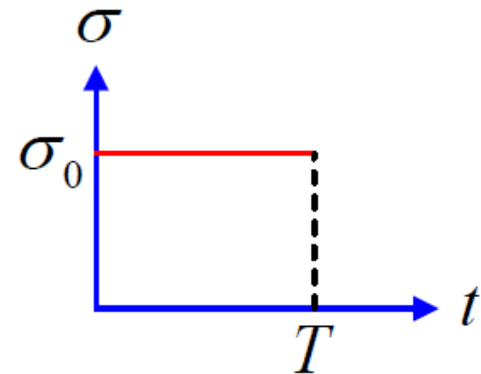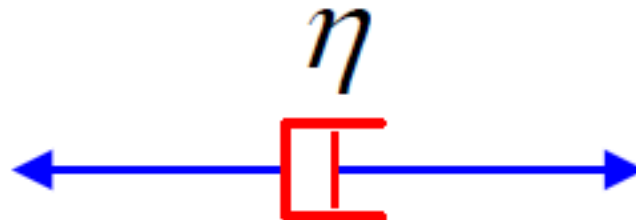
Elastic vs. Viscoelastic Materials

- For a constant loading acting from time 0 to T,

- The strain responses of elastic materials:

$$\sigma = E\varepsilon \quad \Rightarrow \varepsilon = \frac{\sigma}{E}$$
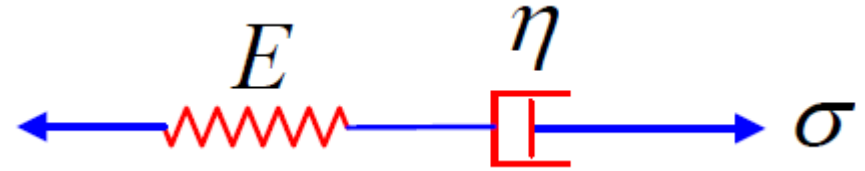
- The strain responses of **viscoelastic** materials:

$$\sigma = \eta\dot{\varepsilon} \quad \Rightarrow \dot{\varepsilon} = \frac{\sigma}{\eta}$$
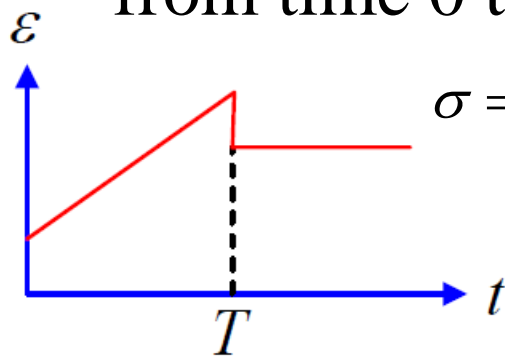
Viscoelastic Models

- **Maxwell model** (steady-state creep of uncrosslinked polymers)

$$\dot{\varepsilon} = \dot{\varepsilon}_E + \dot{\varepsilon}_\eta = \frac{\dot{\sigma}}{E} + \frac{\sigma}{\eta}$$

- Creep compliance due to a constant loading σ_0 acting from time 0 to T

$$\sigma = \sigma_0 \;\Rightarrow\; \dot{\sigma} = 0 \;\Rightarrow\; \dot{\varepsilon} = \frac{\sigma_0}{\eta} \;\Rightarrow\; \varepsilon[t] = \begin{cases} \dfrac{\sigma_0}{\eta}t + \dfrac{\sigma_0}{E}, & 0 < t \le T \\[2mm] \dfrac{\sigma_0}{\eta}T, & t > T \end{cases}$$

$$\Rightarrow \boxed{J[t] = \frac{\varepsilon[t]}{\sigma_0} = \frac{1}{\eta}t + \frac{1}{E}}$$

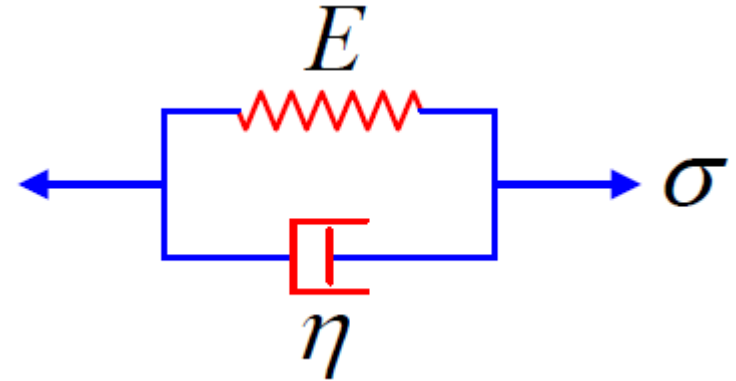- Relaxation modulus due to a constant strain ε_0

$$\varepsilon = \varepsilon_0 = \text{const} \;\Rightarrow\; \frac{\dot{\sigma}}{E} = -\frac{\sigma}{\eta} \;\Rightarrow\; \frac{\dot{\sigma}}{\sigma} = -\frac{E}{\eta} \;\Rightarrow\; \ln\sigma = -\frac{Et}{\eta} + \ln C \;\Rightarrow\; \sigma[t] = Ce^{-Et/\eta}$$

$$\sigma[0] = E\varepsilon_0 = C \;\Rightarrow\; \sigma[t] = E\varepsilon_0 e^{-Et/\eta} \;\Rightarrow\; G[t] = \frac{\sigma[t]}{\varepsilon_0} = Ee^{-Et/\eta}$$

Kelvin-Voigt Model (Retarded Elasticity of Crosslinked Polymers)

$$\sigma = \sigma_\eta + \sigma_E = \eta\dot{\varepsilon} + E\varepsilon$$

- Creep compliance due to a constant loading σ_0 acting from time 0 to T
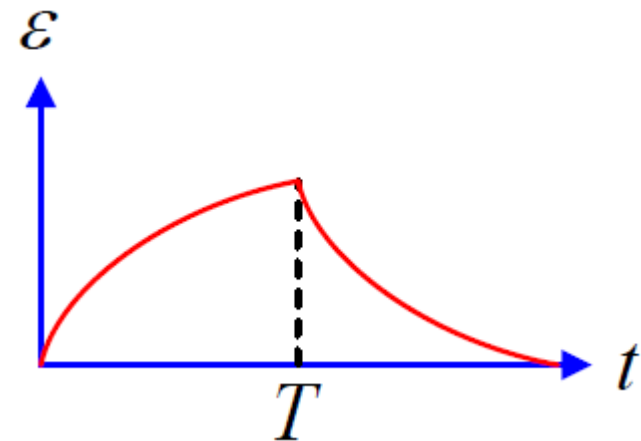
$$0 < t \leq T: \quad \eta\dot{\varepsilon} + E\varepsilon = \sigma_0 \quad \Rightarrow e^{Et/\eta}\left(\dot{\varepsilon} + \frac{E}{\eta}\varepsilon\right) = e^{Et/\eta}\left(\frac{\sigma_0}{\eta}\right)$$

$$\Rightarrow \frac{d}{dt}\left(e^{Et/\eta}\varepsilon\right) = \frac{\sigma_0}{\eta}e^{Et/\eta} \quad \Rightarrow \varepsilon[t] = \frac{\sigma_0}{E} + Ce^{-Et/\eta}$$

$$\varepsilon[0] = \frac{\sigma_0}{E} + C = 0 \quad \Rightarrow C = -\frac{\sigma_0}{E} \quad \Rightarrow \varepsilon[t] = \frac{\sigma_0}{E}\left(1 - e^{-Et/\eta}\right)$$

$$t > T: \quad \eta\dot{\varepsilon} + E\varepsilon = 0 \quad \Rightarrow \frac{\dot{\varepsilon}}{\varepsilon} = -\frac{E}{\eta} \quad \Rightarrow \varepsilon[t] = De^{-Et/\eta}$$

$$\varepsilon[T] = De^{-ET/\eta} = \frac{\sigma_0}{E}\left(1 - e^{-ET/\eta}\right) \Rightarrow \varepsilon[t] = \frac{\sigma_0}{E}\left(e^{ET/\eta} - 1\right)e^{-Et/\eta} \Rightarrow \boxed{J[t] = \frac{e^{-Et/\eta}}{E}\left(e^{ET/\eta} - 1\right)}$$
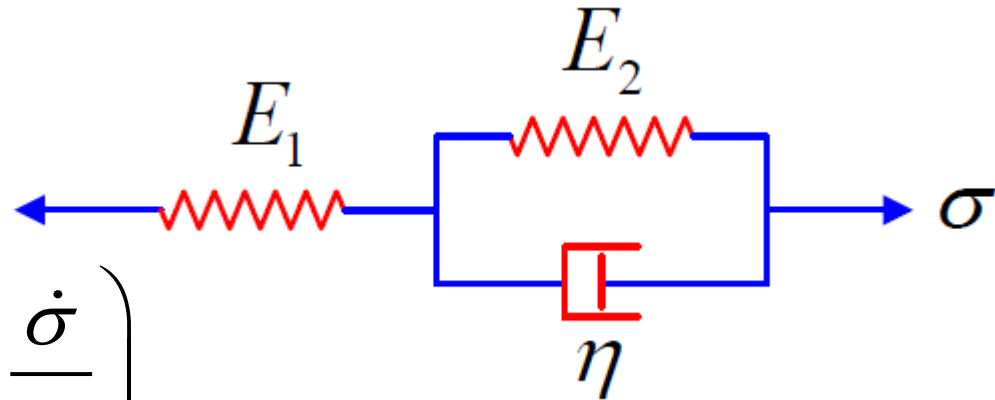
Standard Linear Solid Model

- Spring + Kelvin

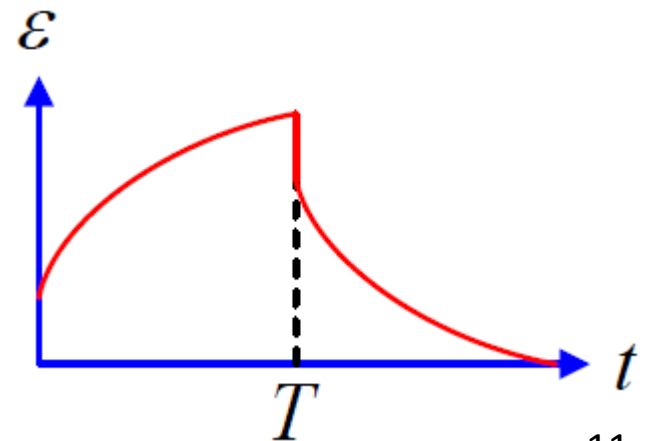$$\sigma = \sigma_{E_1} = \sigma_{E_2} + \sigma_\eta$$

$$= E_2 \varepsilon_2 + \eta \dot{\varepsilon}_2$$

$$= E_2 \left(\varepsilon - \frac{\sigma}{E_1} \right) + \eta \left(\dot{\varepsilon} - \frac{\dot{\sigma}}{E_1} \right)$$

$$\Rightarrow \boxed{ \left(E_1 + E_2 \right) \sigma + \eta \dot{\sigma} = E_1 E_2 \varepsilon + E_1 \eta \dot{\varepsilon} }$$

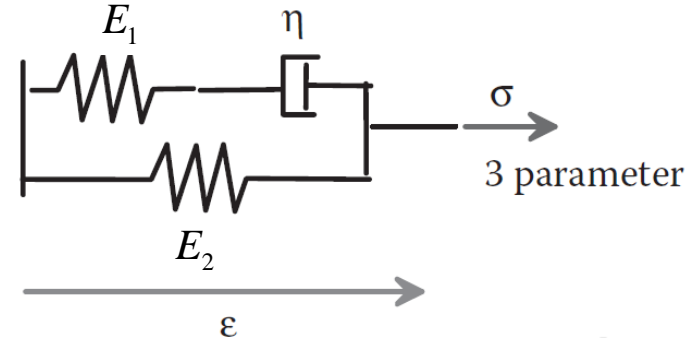- Strain response to a constant loading σ_0 acting from time 0 to T

Three-parameter Model

- Spring // Maxwell

$$\dot{\varepsilon} = \dot{\varepsilon}_{E_2} = \dot{\varepsilon}_{E_1} + \dot{\varepsilon}_\eta = \frac{\dot{\sigma}_1}{E_1} + \frac{\sigma_1}{\eta} = \frac{\dot{\sigma} - E_2\dot{\varepsilon}}{E_1} + \frac{\sigma - E_2\varepsilon}{\eta}$$

3 parameter

$$\Rightarrow \boxed{E_1\sigma + \eta\dot{\sigma} = E_1E_2\varepsilon + \left(E_1 + E_2\right)\eta\dot{\varepsilon}}$$

- Relaxation modulus due to a constant strain ε_0

$$\varepsilon = \varepsilon_0 = \text{const} \quad \Rightarrow E_1\sigma + \eta\dot{\sigma} = E_1E_2\varepsilon_0 \quad \Rightarrow e^{E_1 t/\eta}\left(\frac{E_1}{\eta}\sigma + \dot{\sigma}\right) = e^{E_1 t/\eta}\frac{E_1E_2\varepsilon_0}{\eta}$$

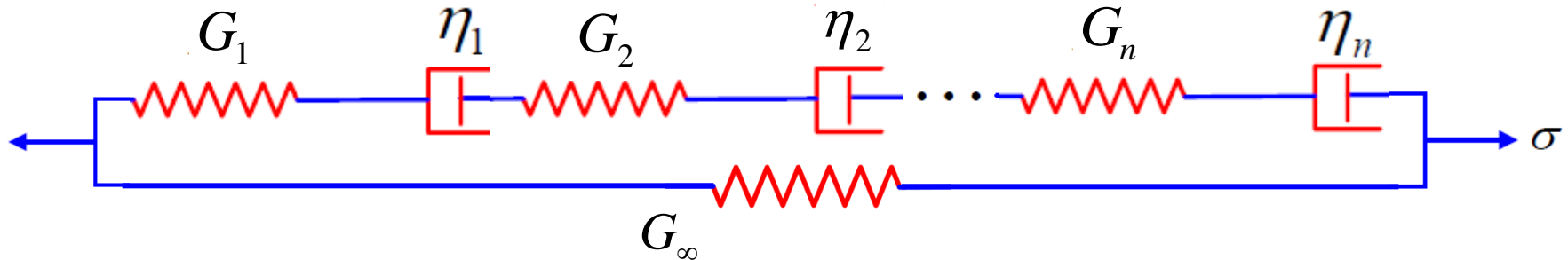$$\Rightarrow \frac{d}{dt}\left(e^{E_1 t/\eta}\sigma\right) = e^{E_1 t/\eta}\frac{E_1E_2\varepsilon_0}{\eta} \quad \Rightarrow e^{E_1 t/\eta}\sigma = e^{E_1 t/\eta}E_2\varepsilon_0 + C \quad \Rightarrow \sigma[t] = E_2\varepsilon_0 + Ce^{-E_1 t/\eta}$$

$$\sigma[0] = E_2\varepsilon_0 + C = E_1\varepsilon_0 + E_2\varepsilon_0 \quad \Rightarrow C = E_1\varepsilon_0 \quad \Rightarrow \sigma[t] = E_2\varepsilon_0 + E_1\varepsilon_0 e^{-E_1 t/\eta}$$

$$\Rightarrow \boxed{G[t] = \frac{\sigma[t]}{\varepsilon_0} = E_2 + E_1 e^{-E_1 t/\eta}}$$

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Prony Series for the Relaxation Modulus

- Spring // lots of Maxwell elements

- Relaxation modulus due to a constant strain ε_0

$$G[t] = \sigma[t]/\varepsilon_0 = G_\infty + \sum_{i=1}^{n} G_i e^{-t/t_i}, \quad t_i = \eta_i/G_i$$

- These parameters are used directly as the properties of the material.

- The sum of exponentials is known as the *Prony series*.

Williams–Landell–Ferry Time/Temperature Equivalence

- At temperature T_1, subject a specimen to a step change in shear strain and measure the relaxation modulus.
- Repeat the experiment at several higher temperatures.
- The double log plot demonstrates that, if you simply shift the modulus curves for the higher temperatures to the right, the data collapse onto a single master curve.
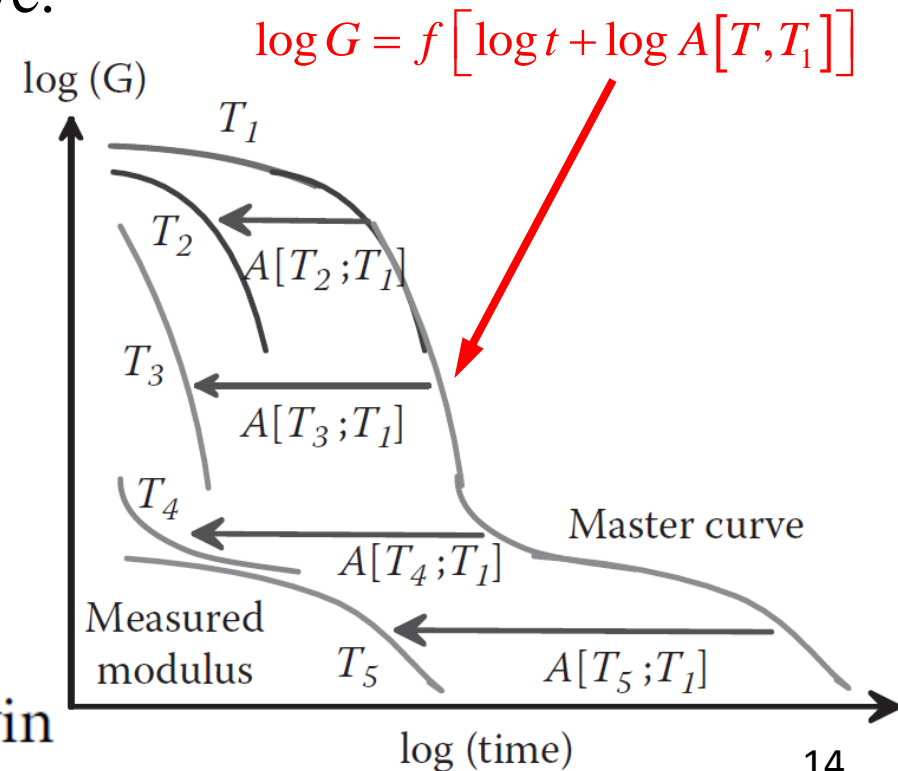
- WLF shift function:

$$\log A[T, T_1] = -\frac{C_1(T - T_1)}{C_2 + T - T_1}$$

- More convenient to use T_g as the reference temperature

$$\log A[T, T_g] = -\frac{C_1^g(T - T_g)}{C_2^g + T - T_g}$$

$$C_1^g \approx 10 - 40 \text{ and } C_2^g \approx 50 - 100 \text{ Kelvin}$$

$$\log G = f\left[\log t + \log A[T, T_1]\right]$$

log (G)

T_1

T_2

$A[T_2; T_1]$

T_3

$A[T_3; T_1]$

T_4

Master curve

$A[T_4; T_1]$

Measured modulus

T_5

$A[T_5; T_1]$
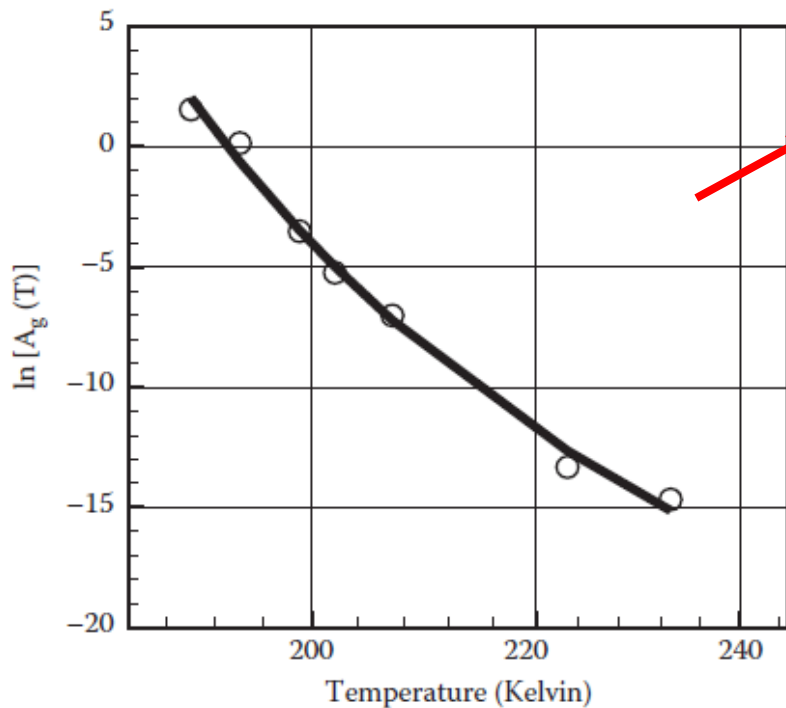
log (time)

Calibrating Viscoelastic Models

TABLE 3.8   Viscoelastic Properties of Polyisobutylene

WLF parameters: $C_1^g = 36.9$ $C_2^g = 57.6$ Kelvin $T_g = 193$ Kelvin

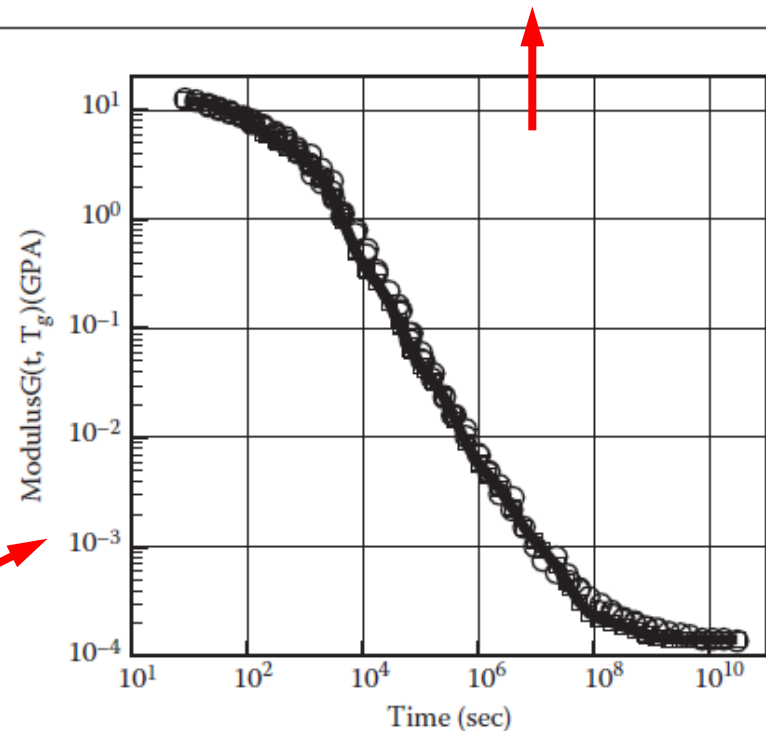$G_\infty = 0.143\,\mathrm{MNm^{-2}}$ $G_1 = 7.3\,\mathrm{GNm^{-2}}$ $t_1 = 100\,\mathrm{sec}$

$G_2 = 4.9\,\mathrm{GNm^{-2}}$ $t_2 = 2000\,\mathrm{sec}$ $G_3 = 0.48\,\mathrm{GNm^{-2}}$ $t_3 = 2 \times 10^4\,\mathrm{sec}$

$G_4 = 57\,\mathrm{MNm^{-2}}$ $t_4 = 2 \times 10^5\,\mathrm{sec}$ $G_5 = 6.4\,\mathrm{MNm^{-2}}$ $t_5 = 2 \times 10^6\,\mathrm{sec}$

$G_6 = 1.3\,\mathrm{MNm^{-2}}$ $t_6 = 2 \times 10^7\,\mathrm{sec}$ $G_7 = 0.1\,\mathrm{MNm^{-2}}$ $t_7 = 4 \times 10^8\,\mathrm{sec}$

Experimental and fitted WLF shift function for polyisobutylene
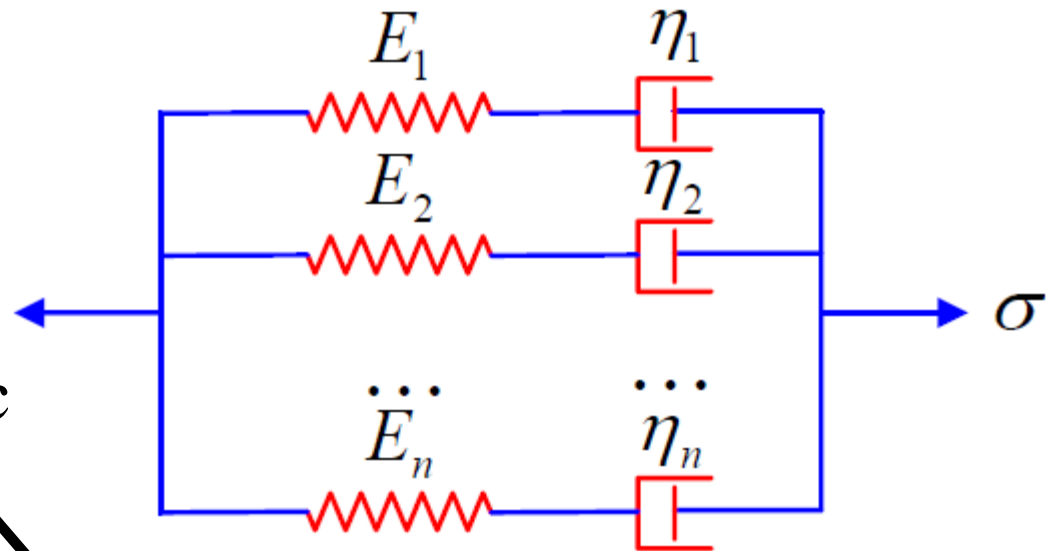
Experimental and fitted relaxation modulus (seven-term Prony series) of polyisobutylene at T_g

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More Sophisticated Models
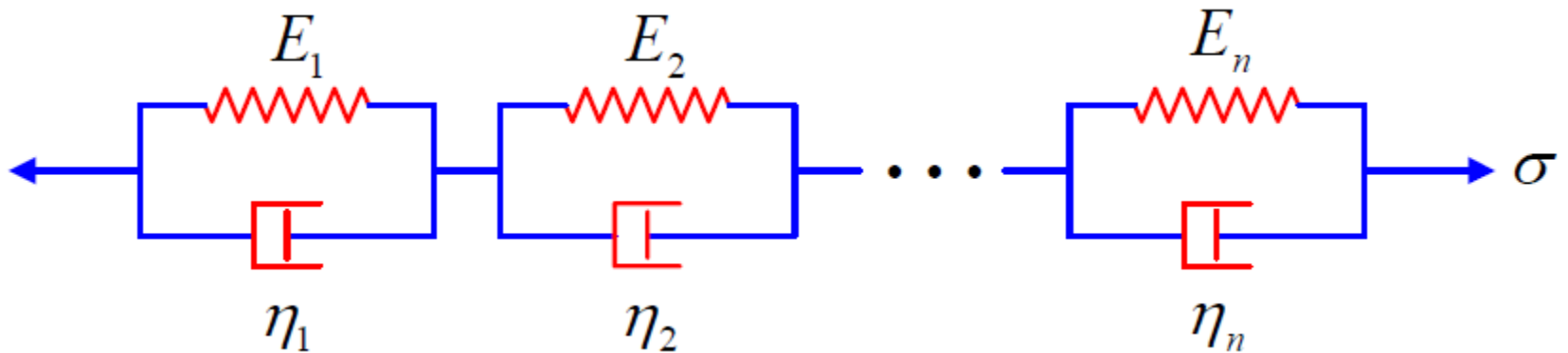
- General mathematical structure of viscoelastic models:

$$\left(p_0 + p_1 \frac{\partial}{\partial t} + p_2 \frac{\partial^2}{\partial t^2} + \cdots + p_n \frac{\partial^n}{\partial t^n} \right)\sigma = \left(q_0 + q_1 \frac{\partial}{\partial t} + q_2 \frac{\partial^2}{\partial t^2} + \cdots + q_n \frac{\partial^n}{\partial t^n} \right)(E\varepsilon)$$

Generalization to 3D

- 1D linear elastic

$$\sigma = E\varepsilon$$

- 3D linear elastic

$$\sigma_{kk} = 3K\varepsilon_{kk};$$
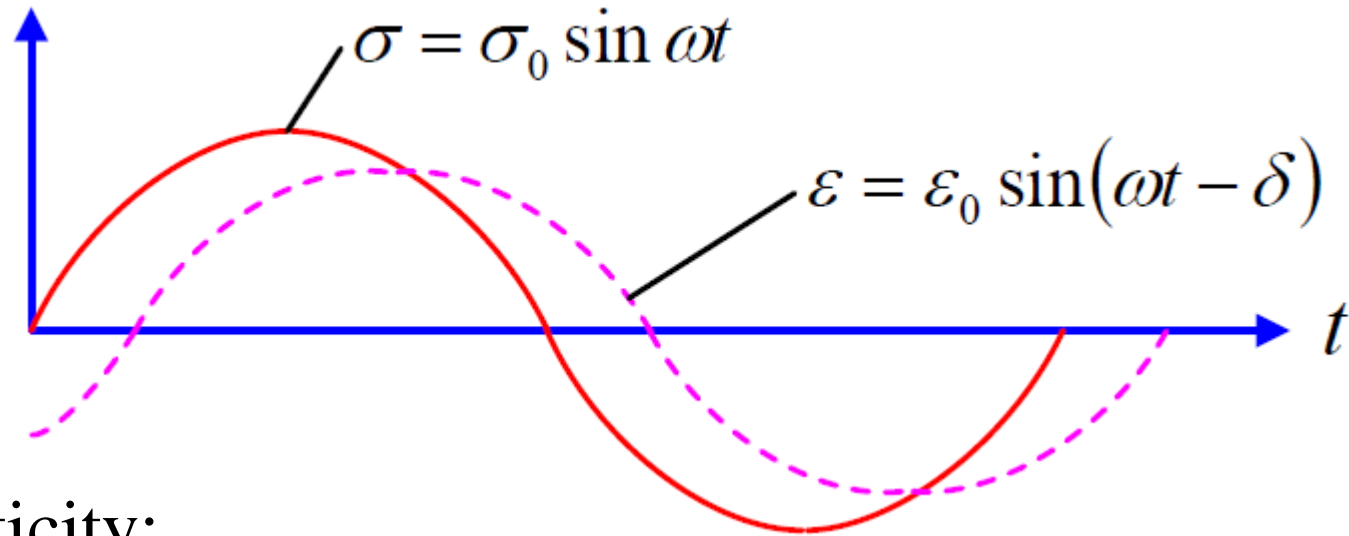$$\sigma'_{ij} = 2G\varepsilon'_{ij}.$$

- 1D linear viscoelastic

$$P\sigma = Q(E\varepsilon)$$

- 3D linear viscoelastic

$$P\sigma_{kk} = Q(3K\varepsilon_{kk});$$
$$P\sigma'_{ij} = Q(2G\varepsilon'_{ij}).$$

Response to Harmonic Loading

$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

- Elasticity:

$$\sigma = \sigma_0 \sin \omega t, \quad \varepsilon = \frac{\sigma_0}{E} \sin \omega t = \varepsilon_0 \sin \omega t \quad \text{(no delay for strain response)}$$

- Viscoelasticity: $\varepsilon = \varepsilon_0 \sin(\omega t - \delta) = \varepsilon_0 \cos \delta \sin \omega t - \varepsilon_0 \sin \delta \cos \omega t$

- Storage compliance: $\varepsilon_0 \cos \delta / \sigma_0$

- Loss compliance: $\varepsilon_0 \sin \delta / \sigma_0$