Nonlinear Viscoelasticity
SINGLE STEP SHEAR STRAIN

$$G(t, \gamma) = \frac{\sigma(t, \gamma)}{\gamma} \tag{5-1}$$

FINITE RISE TIME

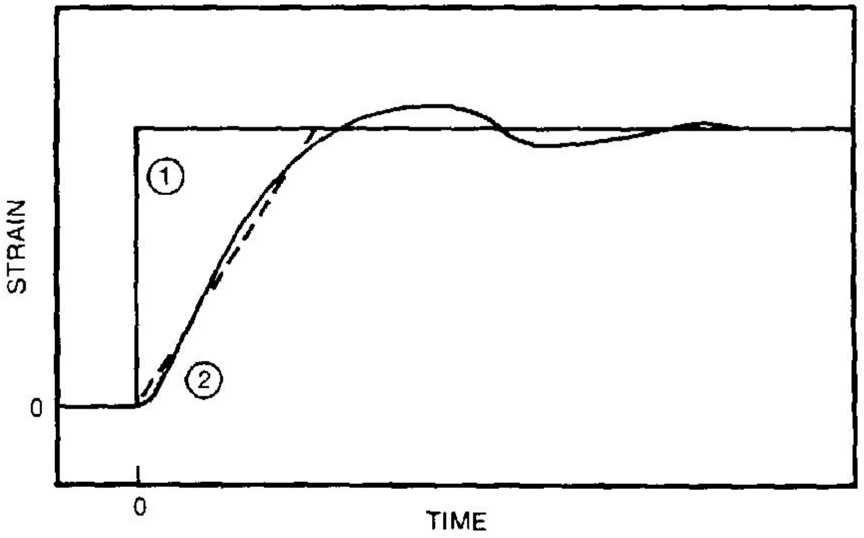

Figure 1: Comparison of Ideal Step Strain (1) with Real Strain Profile (2).

The real strain profile is approximated by a ramp.

$$\gamma(t) = \dot{\gamma} t \tag{5-2}$$

$$\text{Rise Time} \qquad \Delta t \equiv \frac{\gamma}{\dot{\gamma}} \tag{5-3}$$

Rule of Ten $\qquad t > 10\Delta t \qquad$ to be meaningful

Nonlinear Viscoelasticity
SINGLE STEP SHEAR STRAIN NONLINEAR GENERALIZED MAXWELL MODEL

$$G(t,\gamma) = \sum_i G_i(\gamma) \exp\left[\frac{-t}{\lambda_i(\gamma)}\right] \tag{5-7}$$

$$G(t,\gamma) = \sum_i h_i(\gamma) G_i \exp\left[\frac{-t}{\lambda_i(\gamma)}\right] \tag{5-8}$$

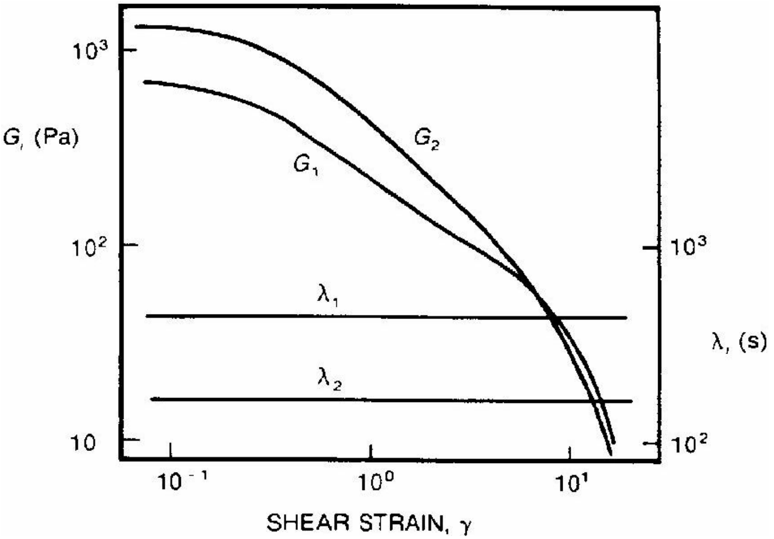

Figure 2: First Two Moduli (G_i) and Relaxation Times (λ_i) for the Nonlinear Stress Relaxation Modulus of a Polystyrene Solution.

$$G(t,\gamma) = \sum_i h_i(\gamma) G_i \exp\left[\frac{-t}{\lambda_i}\right] \tag{5-9}$$

Nonlinear Viscoelasticity
MULTIPLE STEP SHEAR STRAIN

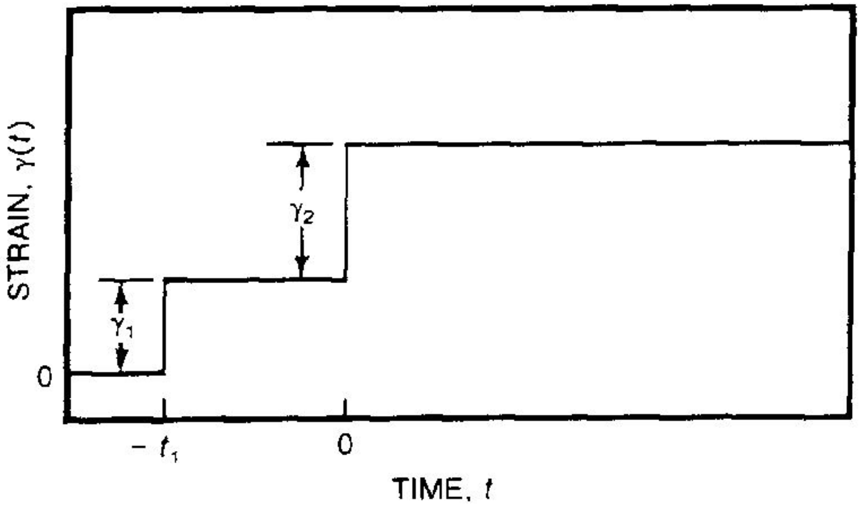

Figure 3: Double Step Strain Experiment.

Boltzmann Superposition works if the steps are small enough to correspond to linear viscoelasticity.

$$\sigma(t) = G(t + t_1)\gamma_1 + G(t)\gamma_2 \qquad (5\text{-}13)$$

For two nonlinear (large) steps:

$$\sigma(t) = (\gamma_1 + \gamma_2)h(\gamma_1 + \gamma_2)G(t + t_1) + \gamma_2 h(\gamma_2)[G(t) - G(t + t_1)] \qquad (5\text{-}14)$$

Equation (5-14) works fine with the damping function predicted by the tube model, **if the second step was in the same direction as the first step**.

Nonlinear Viscoelasticity
MULTIPLE STEP SHEAR STRAIN

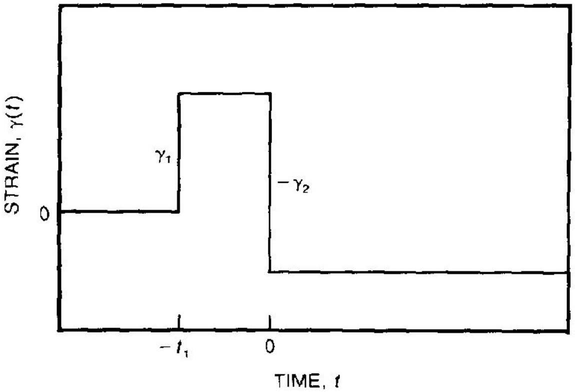

Figure 4: Double Step Strain Experiment with Reversal.

The double step strain with reversal is a simple experiment that **all** theories of nonlinear viscoelasticity fail to predict.

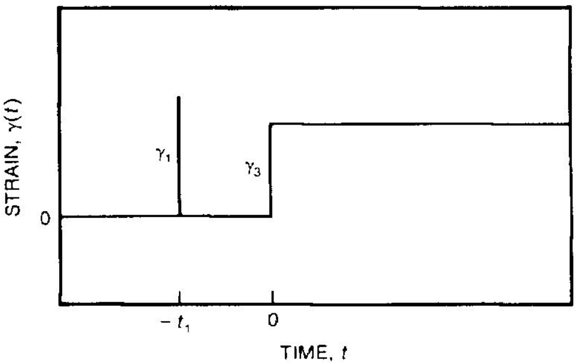

Figure 5: Spike Strain Test.

Boltzmann superposition predicts no effect of the spike, but experimentally there is an effect when γ_1 is large enough.

Nonlinear Viscoelasticity
START-UP OF STEADY SHEAR

Shear Stress Growth Function $$\sigma^+(t,\dot\gamma) \equiv \sigma(t,\dot\gamma) \tag{5-17}$$

Shear Stress Growth Coefficient $$\eta^+(t,\dot\gamma) \equiv \frac{\sigma^+}{\dot\gamma} \tag{5-18}$$

First Normal Stress Growth Function $$N_1^+(t,\dot\gamma) \equiv \sigma_{11}(t,\dot\gamma) - \sigma_{22}(t,\dot\gamma) \tag{5-19}$$

First Normal Stress Growth Coefficient $$\Psi_1^+(t,\dot\gamma) \equiv \frac{N_1^+}{\dot\gamma^2} \tag{5-20}$$

Linear Viscoelastic Limits:

$$\lim_{\dot\gamma\to 0}\left[\eta^+(t,\dot\gamma)\right] = \eta^+(t) \tag{5-23}$$

$$\lim_{\dot\gamma\to 0}\left[N_1^+(t,\dot\gamma)\right] = 0$$

Long Time Limits:

$$\lim_{t\to\infty}\left[\eta^+(t,\dot\gamma)\right] = \eta(\dot\gamma) \tag{5-24}$$

$$\lim_{t\to\infty}\left[N_1^+(t,\dot\gamma)\right] = N_1(\dot\gamma) \tag{5-25}$$

Nonlinear Viscoelasticity
START-UP OF STEADY SHEAR

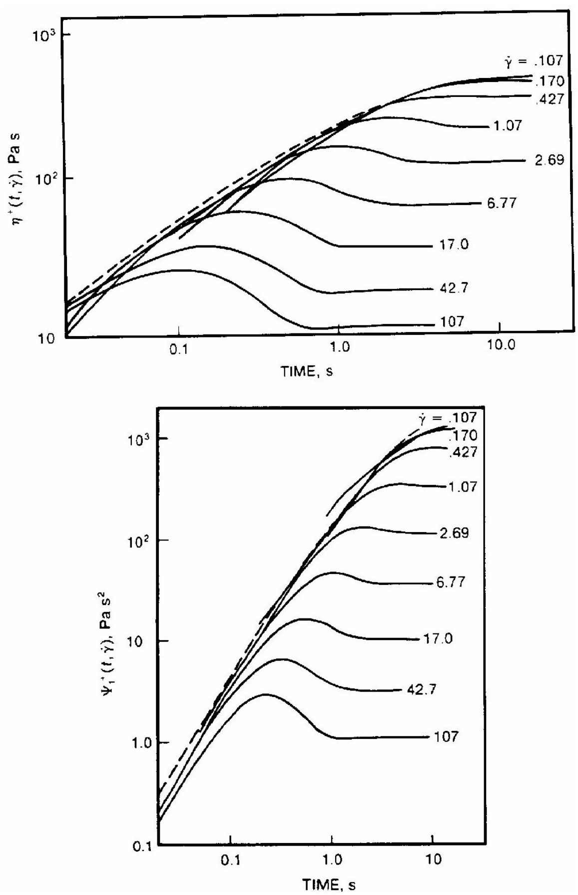

Figure 6: Shear Stress Growth and Normal Stress Growth Coefficients for the Start-Up of Steady Shear of a Polystyrene Solution.

Both functions show stress overshoots that indicate short-time relaxation processes are activated in steady shear.

Nonlinear Viscoelasticity
CESSATION OF STEADY SHEAR

Shear Stress Decay Function $\sigma^{-}(t,\dot{\gamma}) \equiv \sigma(t,\dot{\gamma})$ (5-33)

Shear Stress Decay Coefficient $\eta^{-}(t,\dot{\gamma}) \equiv \dfrac{\sigma^{-}}{\dot{\gamma}}$ (5-34)

First Normal Stress Decay Function $N_1^{-}(t,\dot{\gamma}) \equiv \sigma_{11}(t,\dot{\gamma}) - \sigma_{22}(t,\dot{\gamma})$ (5-35)

First Normal Stress Decay Coefficient $\Psi_1^{-}(t,\dot{\gamma}) \equiv \dfrac{N_1^{-}}{\dot{\gamma}^2}$ (5-36)

Linear Viscoelastic Limits:

$$\lim_{\dot{\gamma}\to 0}\left[\eta^{-}(t,\dot{\gamma})\right] = \eta^{-}(t)$$

$$\lim_{\dot{\gamma}\to 0}\left[N_1^{-}(t,\dot{\gamma})\right] = 0$$

Short Time Limits:

$$\lim_{t\to 0}\left[\eta^{-}(t,\dot{\gamma})\right] = \eta(\dot{\gamma})$$

$$\lim_{t\to 0}\left[N_1^{-}(t,\dot{\gamma})\right] = N_1(\dot{\gamma})$$

Nonlinear Viscoelasticity
CESSATION OF STEADY SHEAR

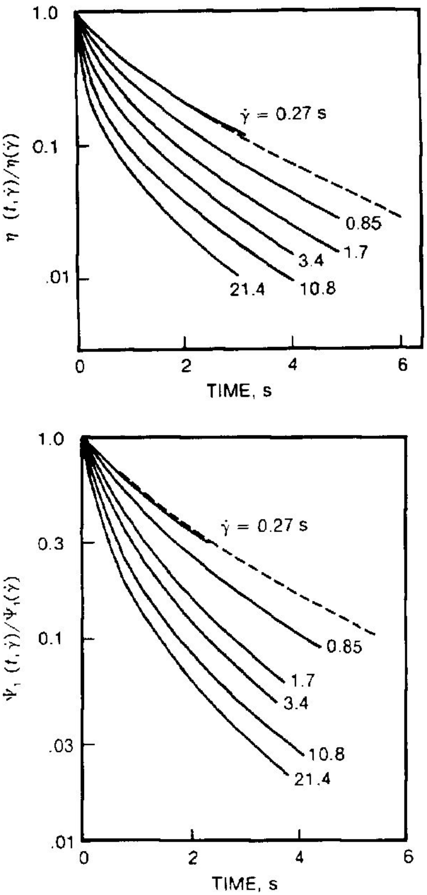

Figure 7: Shear Stress Decay and Normal Stress Decay Coefficients for Cessation of Steady Shear Flow of a Polyisobutylene Solution.

Both functions show stresses decaying **faster** at larger shear rates, consistent with long relaxation modes being replaced by shorter-time relaxation processes that are activated in steady shear.

Nonlinear Viscoelasticity
NONLINEAR CREEP

Larger $\sigma \Rightarrow$ Larger $\dot{\gamma} \Rightarrow$ Lower η

$$J(t, \sigma) \geq J(t)$$

Larger $\sigma \Rightarrow$ More Dissipation Processes (**less stored energy**)

$$J_s^0(\sigma) \leq J_s^0$$

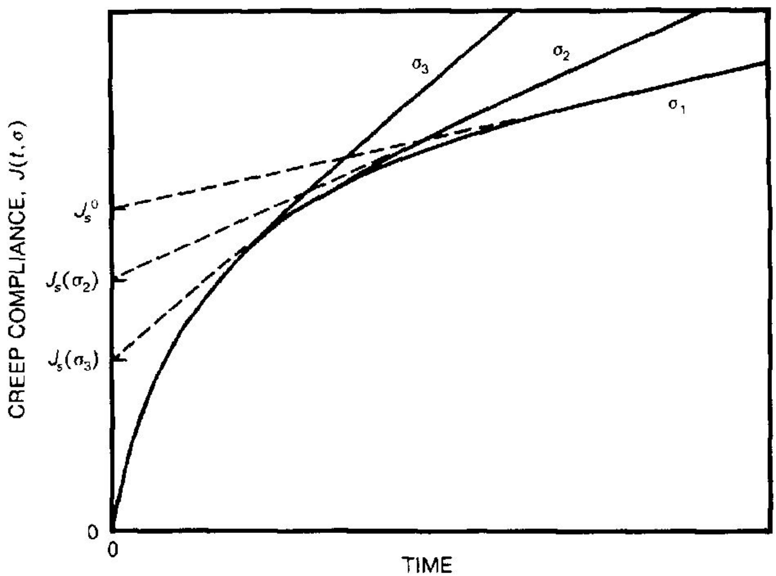

Figure 8: Creep Compliance at a Linear Viscoelastic Stress σ_1 and two Nonlinear Stresses with $\sigma_3 > \sigma_2 > \sigma_1$.

As stress increases, the viscosity drops and the recoverable strain drops, consistent with large stresses inducing additional dissipation mechanisms.

Nonlinear Viscoelasticity
NONLINEAR RECOVERY

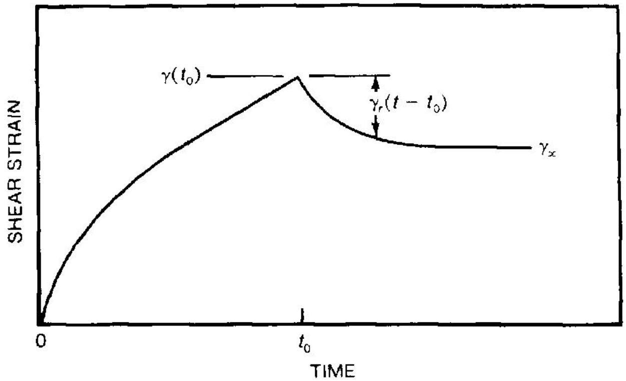

Figure 9: Creep and Creep Recovery.

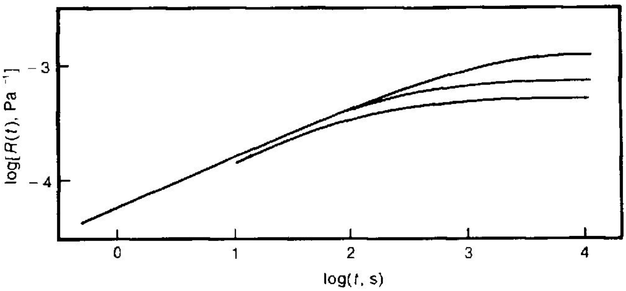

Figure 10: Recoverable Compliance after Creep at Three Stress Levels (Increasing Creep Stress from Top to Bottom).

Recoverable compliance is lower at larger creep stresses because the large stress induces additional short-time relaxation processes, meaning that a smaller fraction of the deformation is stored.

Nonlinear Viscoelasticity
RECOIL DURING START-UP OF SHEAR

$$\gamma_r \equiv \gamma(t_0) - \gamma(t) = \gamma_r(t - t_0, t_0, \dot{\gamma}) \tag{5-64}$$

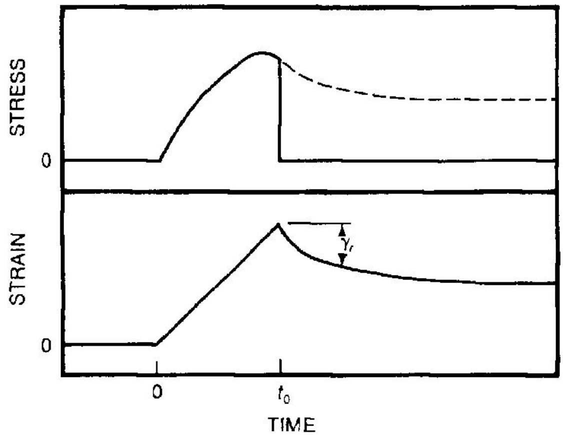

Figure 11: Recoil Part-Way Through Start-Up.

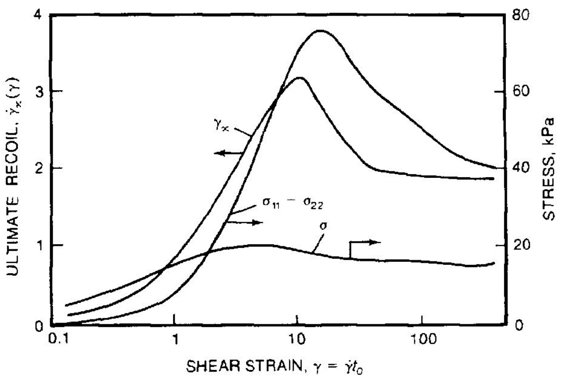

Figure 12: Ultimate Recoil During Start-Up Compared with the Shear and Normal Stress Growth Functions for LDPE.