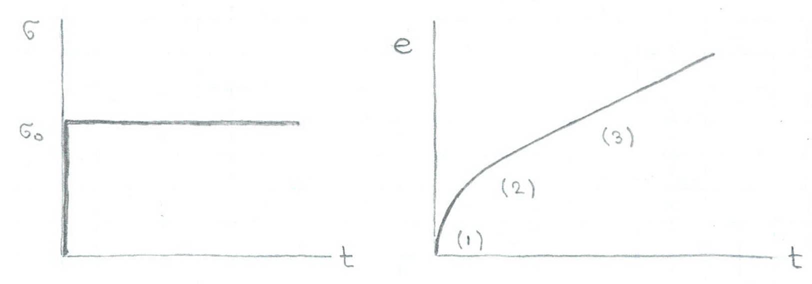
Polymer Viscoelasticity: Linear Response [pln52]

Creep compliance: $J(t)$

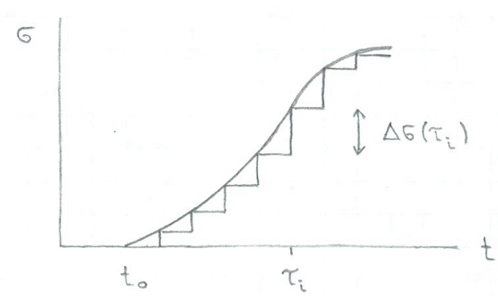
- Constant stress applied abuptly: $\sigma(t) = \sigma_0 \theta(t)$.
- Linear time-dependent strain: $e(t) = J(t)\sigma_0$.
- Regimes of linear strain response (see graph):
  (1) fast elastic response,
  (2) creep response (crossover),
  (3) long-time asymptotic viscous response.
- Phenomenological model: $J(t) = bt + c\sqrt{t}, \quad b, c \geq 0$.



Time-dependent stress $\sigma(t)$ of arbitrary profile.

Linear strain response constructed via superposition principle:

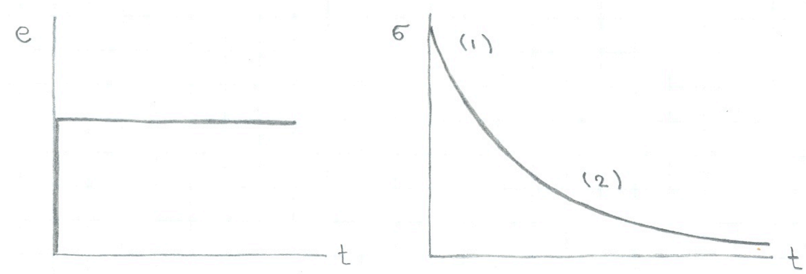
$$e(t) = \sum_i \Delta\sigma(\tau_i) J(t - \tau_i) \;\to\; \int_{\sigma(t_0)}^{\sigma(t)} d\sigma(\tau) J(t-\tau) = \int_{t_0}^{t} d\tau\, J(t-\tau) \frac{d\sigma}{d\tau}.$$



Strain response for linear and oscillatory stress profiles explored in [pex35].

Stress relaxation modulus: $G(t)$

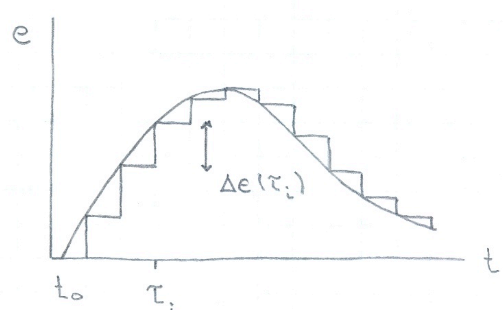
- Constant strain applied abruptly: $e(t) = e_0\theta(t)$.
- Linear time-dependent stress: $\sigma(t) = e_0 G(t)$.
- Regimes of linear stress response (see graph):
  (1) instant elastic response,
  (2) stress relaxation due to viscous flow.
- Phenomenological models of stress relaxation:
  ▷ $G(t) = e^{-t}$ (fast),
  ▷ $G(t) = (1+t)^{-1}$ (slow).



Time-dependent strain $e(t)$ of arbitrary profile.

Linear stress response constructed via superposition principle:

$$\sigma(t) = \sum_i \Delta e(\tau_i) G(t-\tau_i) \ \to \ \int_{e(t_0)}^{e(t)} de(\tau) G(t-\tau) = \int_{t_0}^{t} d\tau G(t-\tau)\frac{de}{d\tau}.$$



Stress response for model strain profiles explored in [pex36].

Oscillatory strain: $e(t) = \sin(\omega t)$.

Steady-state stress response: $\sigma(t) = G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)$.

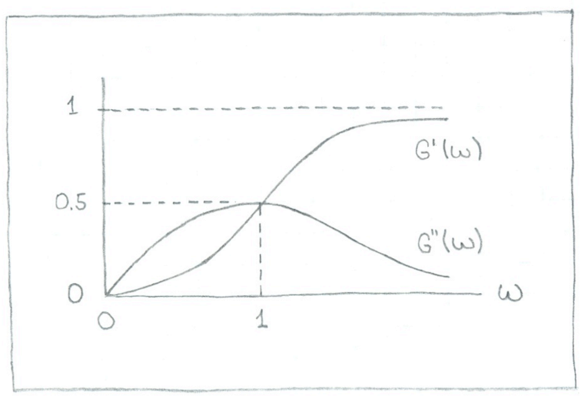
- $G'(\omega)$: storage modulus describes elastic response,
- $G''(\omega)$: loss modulus describes viscous response.

Example: $G(t) = e^{-t}$.

$$\Rightarrow \ \sigma(t) = \frac{\omega}{1+\omega^2}\Big[e^{-t} + \omega\sin(\omega t) + \cos(\omega t)\Big],$$

where the first term represents a transient response and the two remaining terms the steady-state response with moduli

$$G'(\omega) = \frac{\omega^2}{1+\omega^2}, \quad G''(\omega) = \frac{\omega}{1+\omega^2}.$$



Zero-shear viscosity η_0 defined via $\sigma \doteq \eta_0\,(de/d\tau)$ for circumstances where it is justified to assume that a constant strain rate produces a constant steady-state stress.

$$\sigma = \eta_0 \frac{de}{d\tau} = \int_{-\infty}^{t} d\tau\, G(t-\tau)\,\frac{de}{d\tau} = \int_0^\infty dt' G(t')\,\frac{de}{d\tau}$$

$$\Rightarrow \ \eta_0 = \int_0^\infty dt\, G(t).$$

[extracted in part from Jones 2002]