MIT 3.071
Amorphous Materials

7: Viscoelasticity and Relaxation

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After-class reading list

- Fundamentals of Inorganic Glasses
  - Ch. 8, Ch. 13, Appendix A
- Introduction to Glass Science and Technology
  - Ch. 9 (does not cover relaxation)

> *Mathematics is the language with which God wrote the Universe.*
>
> *Galileo Galilei*

Where and why does liquid end and glass begin?

What is the nature of the glassy state?
Molecules in a glass are arranged much like those in liquids but are more tightly packed. Where and why does liquid end and glass begin?

"What don't we know?" *Science* **309**, 83 (2005).

Is glass a solid or a viscous liquid?

Solid

Elasticity

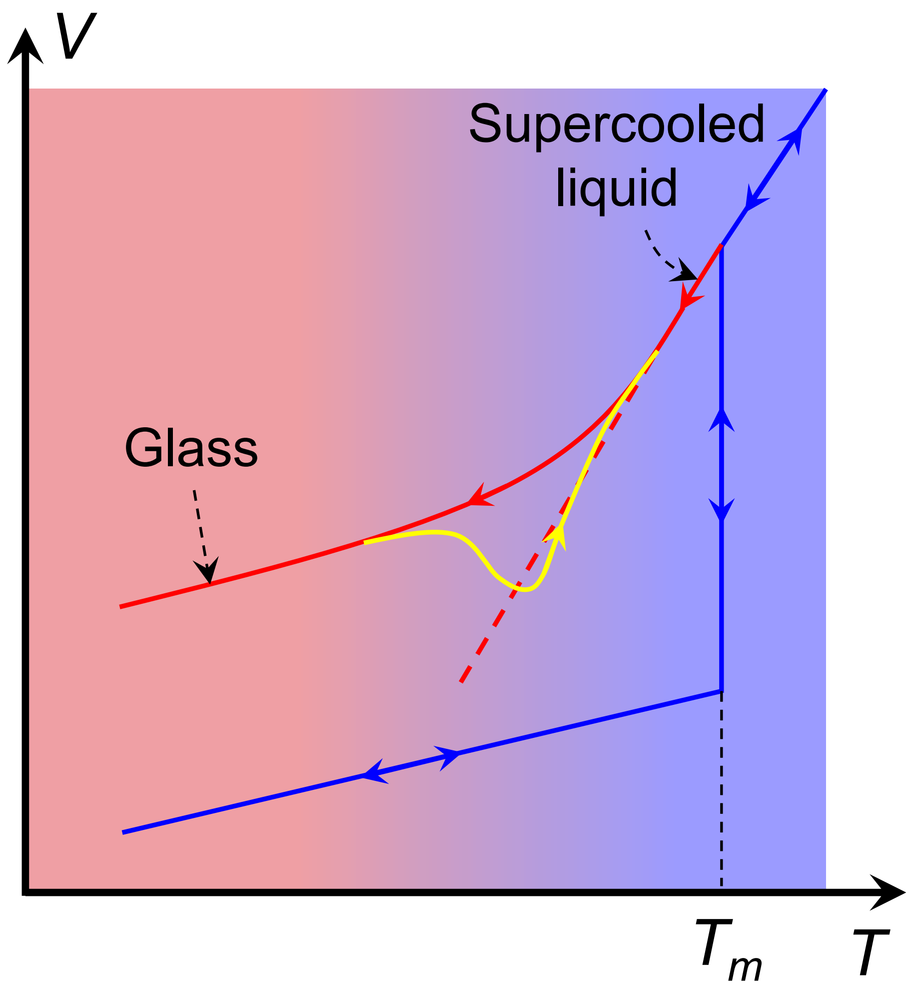
instantaneous, transient

$$\sigma_x = E\varepsilon_x$$

$$\sigma_{xy} = G\varepsilon_{xy}$$

E : Young's modulus

G : shear modulus



Liquid

Viscosity

time-dependent, permanent

$$\sigma_{xy} = \eta \cdot \frac{\partial \varepsilon_{xy}}{\partial t}$$

η : viscosity (unit: Pa·s or Poise)

Viscoelasticity: complex shear modulus

- Consider a sinusoidally varying shear strain

$$\varepsilon_{xy} = \varepsilon_0 \cdot \exp(i\omega t)$$

- Elastic response: $\sigma_{xy} = G\varepsilon_{xy} = G\varepsilon_0 \cdot \exp(i\omega t)$
- Viscous response:

$$\sigma_{xy} = \eta \frac{\partial \varepsilon_{xy}}{\partial t} = i\omega\eta \cdot \varepsilon_0 \exp(i\omega t) = i\omega\eta \cdot \varepsilon_{xy}$$

- In a general viscoelastic solid:

$$\sigma_{xy} = (G + i\omega\eta) \cdot \varepsilon_{xy} = G^* \cdot \varepsilon_{xy} \qquad G^* = G + i\omega\eta = G' + iG''$$

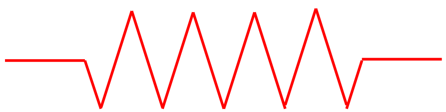
Loss modulus (G'')

Shear/storage modulus (G')

G^* : complex shear modulus

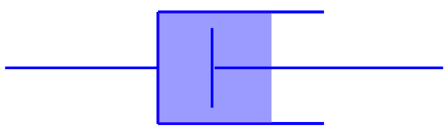
Phenomenological models of viscoelastic materials

- Elasticity: Hookean spring



$$\sigma_{xy} = G\varepsilon_{xy}$$

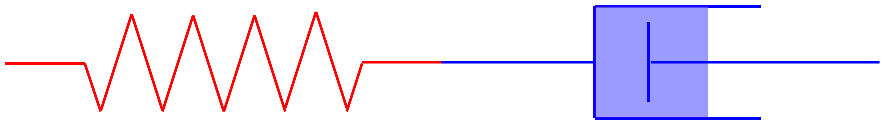
- Viscosity: Newtonian dashpot



$$\sigma_{xy} = \eta \cdot \frac{\partial \varepsilon_{xy}}{\partial t}$$

> ✓ Models assume linear material response or infinitesimal stress
>
> ✓ Each dashpot element corresponds to a relaxation mechanism

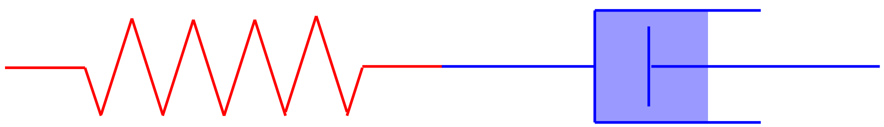
The Maxwell element



$$\sigma_E = G\varepsilon_E \qquad \sigma_V = \eta \cdot \frac{\partial \varepsilon_V}{\partial t}$$

- Serial connection of a Hookean spring and a Newtonian dashpot
- Total stress: $\sigma = \sigma_E = \sigma_V$
- Total strain: $\varepsilon = \varepsilon_E + \varepsilon_V$

The Maxwell element



$$\sigma_E = G\varepsilon_E \qquad \sigma_V = \eta \cdot \frac{\partial \varepsilon_V}{\partial t}$$

- Constant stress (creep): $\sigma = \sigma_E = \sigma_V = \text{constant} \;\left(t \geq 0\right)$

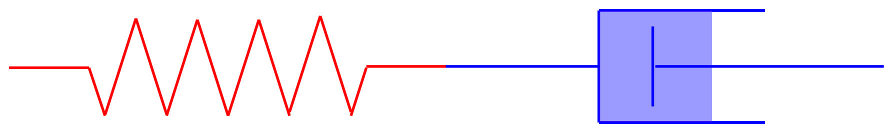
$$\varepsilon = \varepsilon_E + \varepsilon_V = \frac{\sigma}{G} + \frac{\sigma}{\eta} \cdot t$$

- Constant strain (stress relaxation): $\varepsilon = \varepsilon_E + \varepsilon_V = \text{constant} \;\left(t \geq 0\right)$

$$\varepsilon_E = \varepsilon \exp\left(-\frac{t}{\tau}\right) \qquad \varepsilon_V = \varepsilon\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \qquad \tau = \frac{\eta}{G}$$

Relaxation time

The Maxwell element



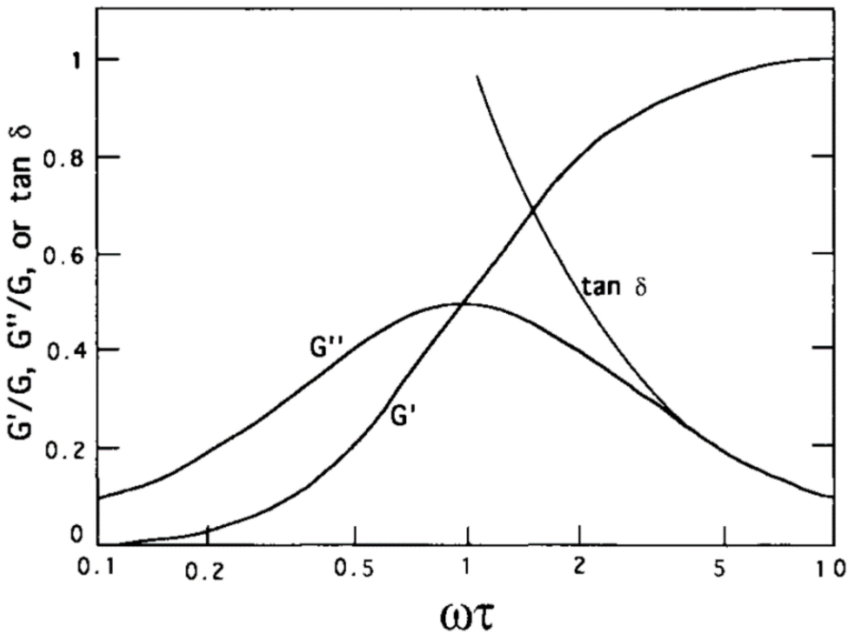
$$\sigma_E = G\varepsilon_E \qquad \sigma_V = \eta \cdot \frac{\partial \varepsilon_V}{\partial t}$$

- Oscillatory strain:

$$\varepsilon = \varepsilon_E + \varepsilon_V = \varepsilon_0 \exp(i\omega t)$$

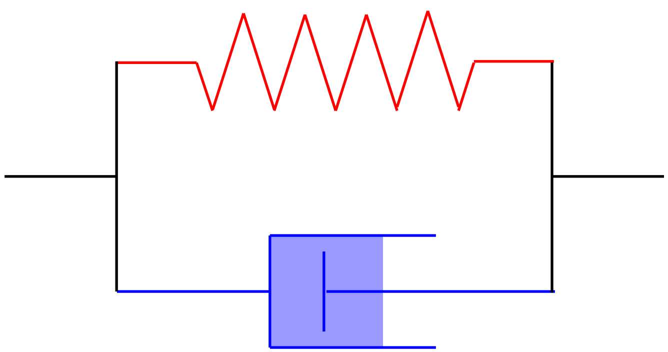
$$G' = \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \cdot G$$

$$G'' = \frac{\omega\tau}{1+\omega^2\tau^2} \cdot G$$



The Voigt-Kelvin element

$$\sigma_E = G\varepsilon_E$$



$$\sigma_V = \eta \cdot \frac{\partial \varepsilon_V}{\partial t}$$

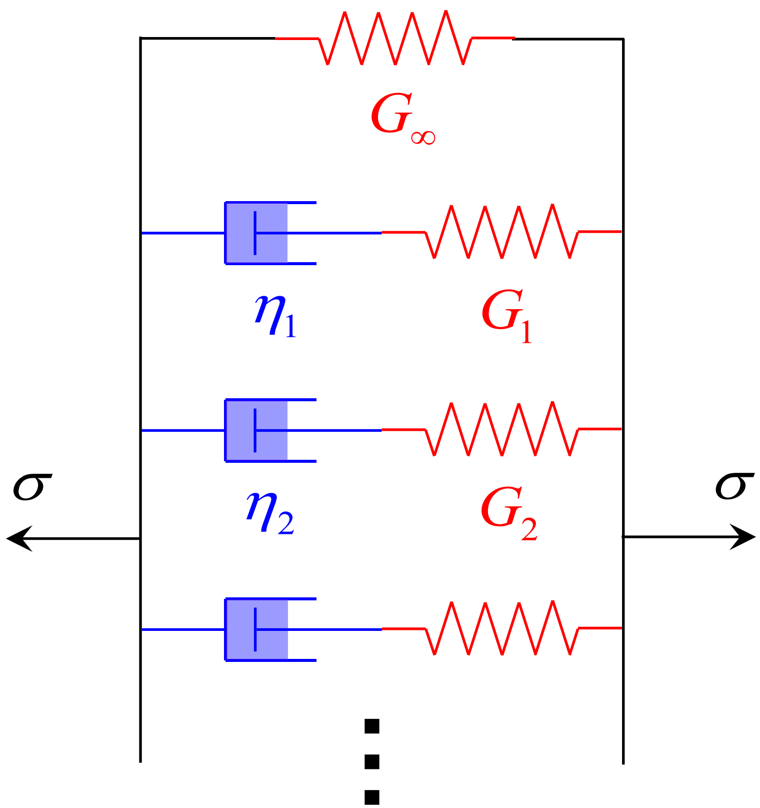
- Parallel connection of a Hookean spring and a Newtonian dashpot
- Total stress: $\sigma = \sigma_E + \sigma_V$
- Total strain: $\varepsilon = \varepsilon_E = \varepsilon_V$
- Constant strain: $\sigma = G\varepsilon$
- Constant stress:

$$\varepsilon = \frac{\sigma}{G}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

- Oscillatory strain: $\varepsilon = \varepsilon_0 \exp(i\omega t)$

$G' = G \qquad G'' = \omega\tau \cdot G$

Generalized Maxwell model



- For each Maxwell component:

$$\frac{\partial \varepsilon_i}{\partial t} = \left(\frac{1}{G_i} \frac{\partial}{\partial t} + \frac{1}{\eta_i} \right) \sigma_i$$

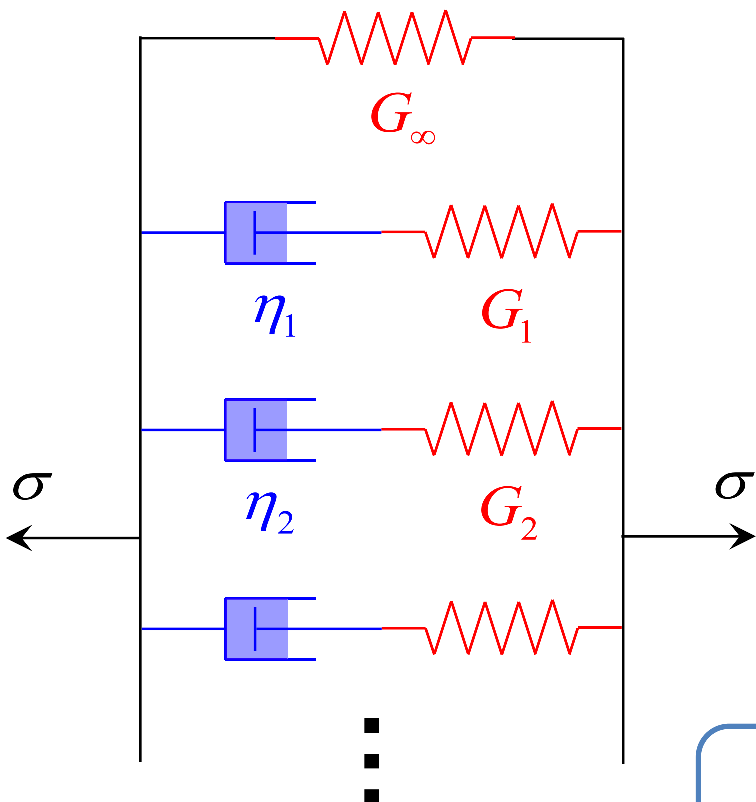
$$= \left(\frac{\partial}{\partial t} + \frac{1}{\tau_i} \right) \cdot \frac{\sigma_i}{G_i} \qquad \tau_i = \frac{\eta_i}{G_i}$$

$$\varepsilon_1 = \ldots = \varepsilon_i = \ldots = \varepsilon$$

- Total stress:

$$\sigma = G_\infty \varepsilon + \sigma_1 + \ldots + \sigma_i + \ldots$$

Generalized Maxwell model



- Stress relaxation:

$$\varepsilon = \text{constant} \quad (t \geq 0)$$

- Prony series:

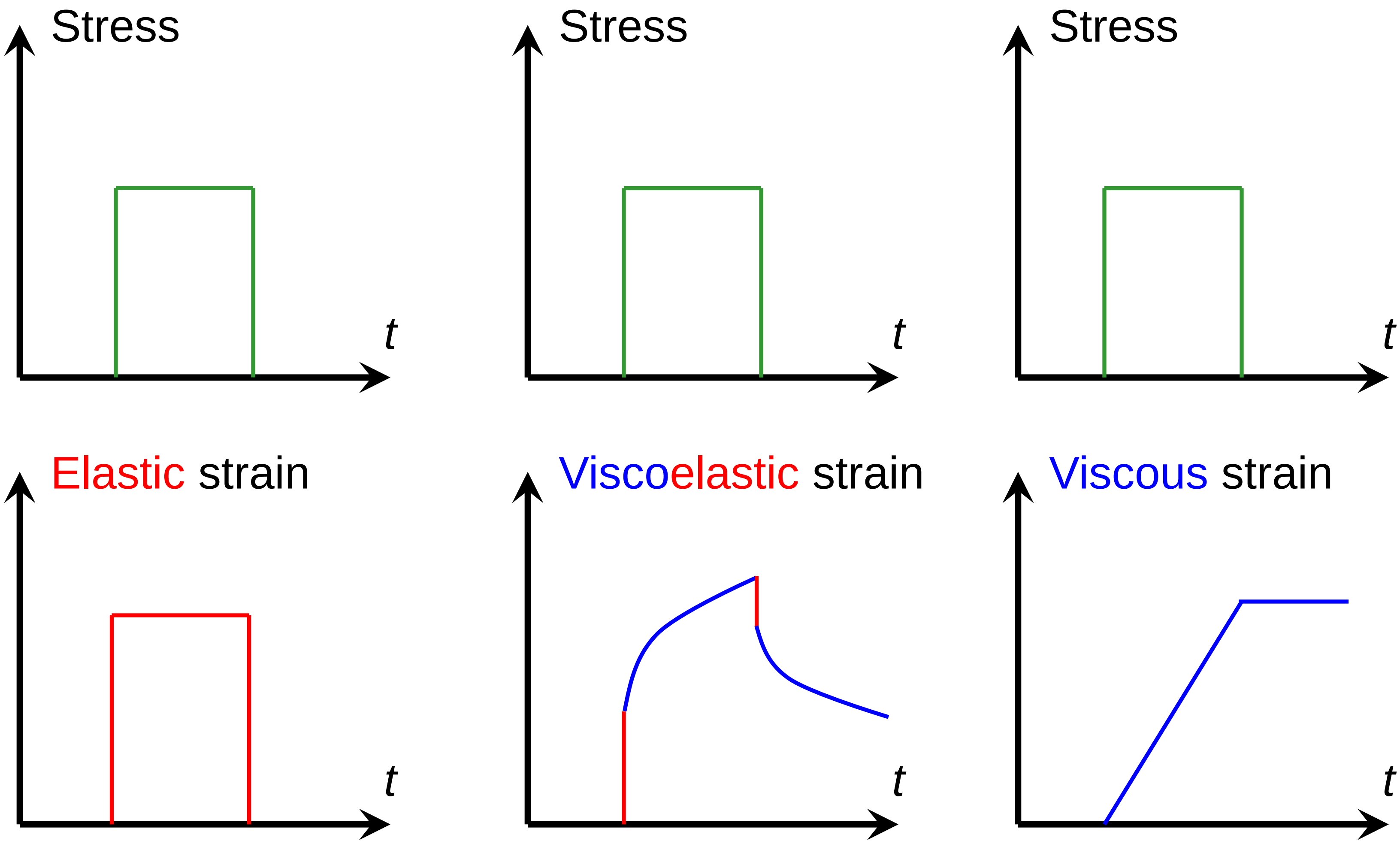
$$\sigma = G_\infty \varepsilon + \sigma_1 + \ldots + \sigma_i + \ldots$$

$$= \left[G_\infty + \sum_{i>0} \exp\left(-\frac{t}{\tau_i} \right) \cdot G_i \right] \cdot \varepsilon$$

$$= \left[G_\infty + \exp\left[-(t/\tau)^\beta \right] \cdot G_R \right] \cdot \varepsilon$$

In real solids, a multitude of microscopic relaxation processes give rise to dispersion of relaxation time (stretched exponential)

Elastic, viscoelastic, and viscous responses



Viscoelastic materials

Mozzarella cheese

Human skin

Turbine blades

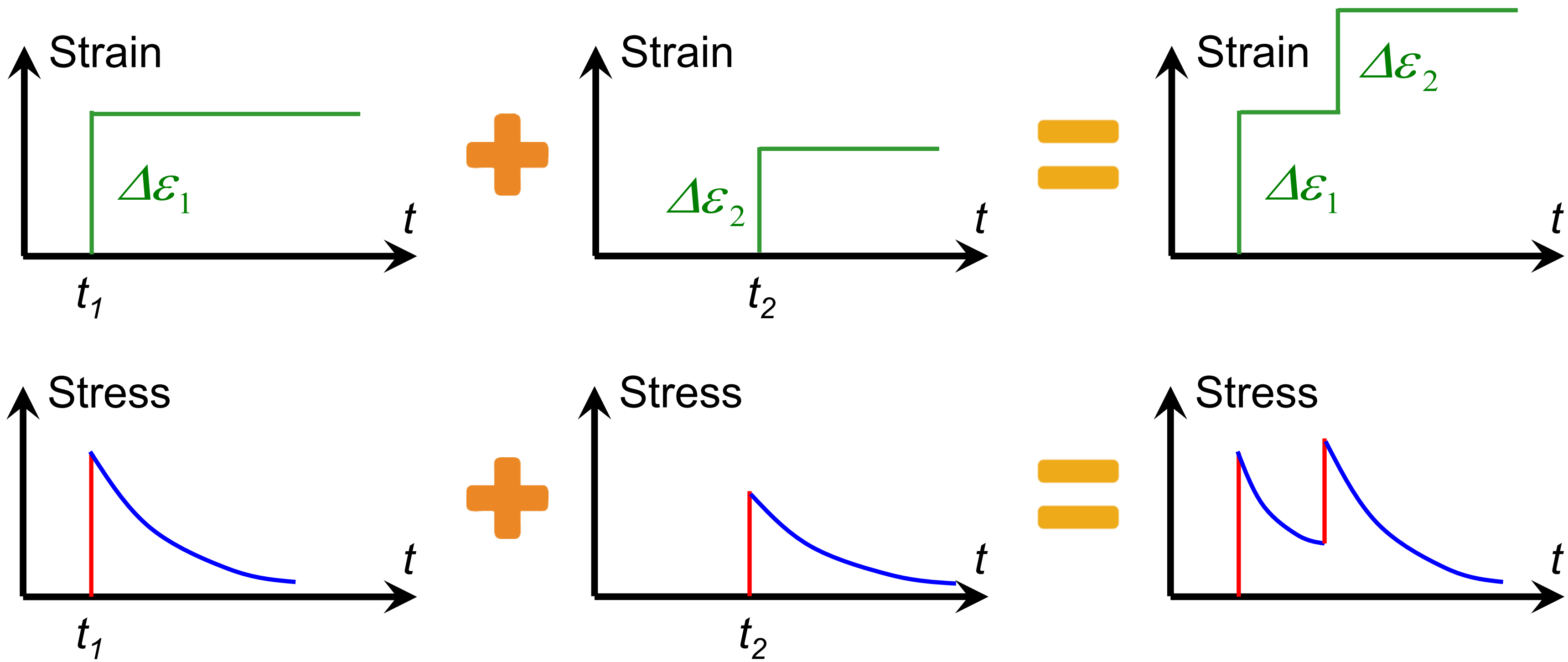
Volcanic lava

Naval ship propellers

Memory foams

Boltzmann superposition principle

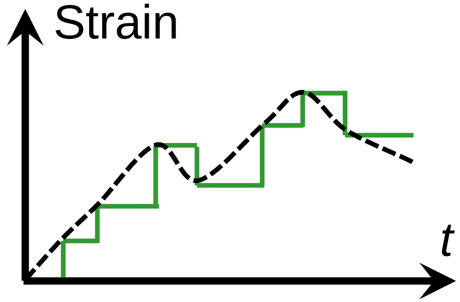
- In the linear viscoelastic regime, the stress (strain) responses to successive strain (stress) stimuli are additive



$$\Delta\sigma_1 = G\Delta\varepsilon_1 \cdot \Psi\left(t - t_1\right) \qquad \Delta\sigma_2 = G\Delta\varepsilon_2 \cdot \Psi\left(t - t_2\right) \qquad \sigma = \Delta\sigma_1 + \Delta\sigma_2$$

Boltzmann superposition principle

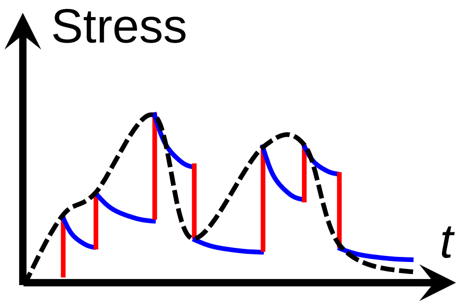
- In the linear viscoelastic regime, the stress (strain) responses to successive strain (stress) stimuli are additive



$$\varepsilon = \sum_i \Delta\varepsilon_i$$

$$\varepsilon = \int_0^t \frac{d\varepsilon_i}{dt'} \cdot dt'$$

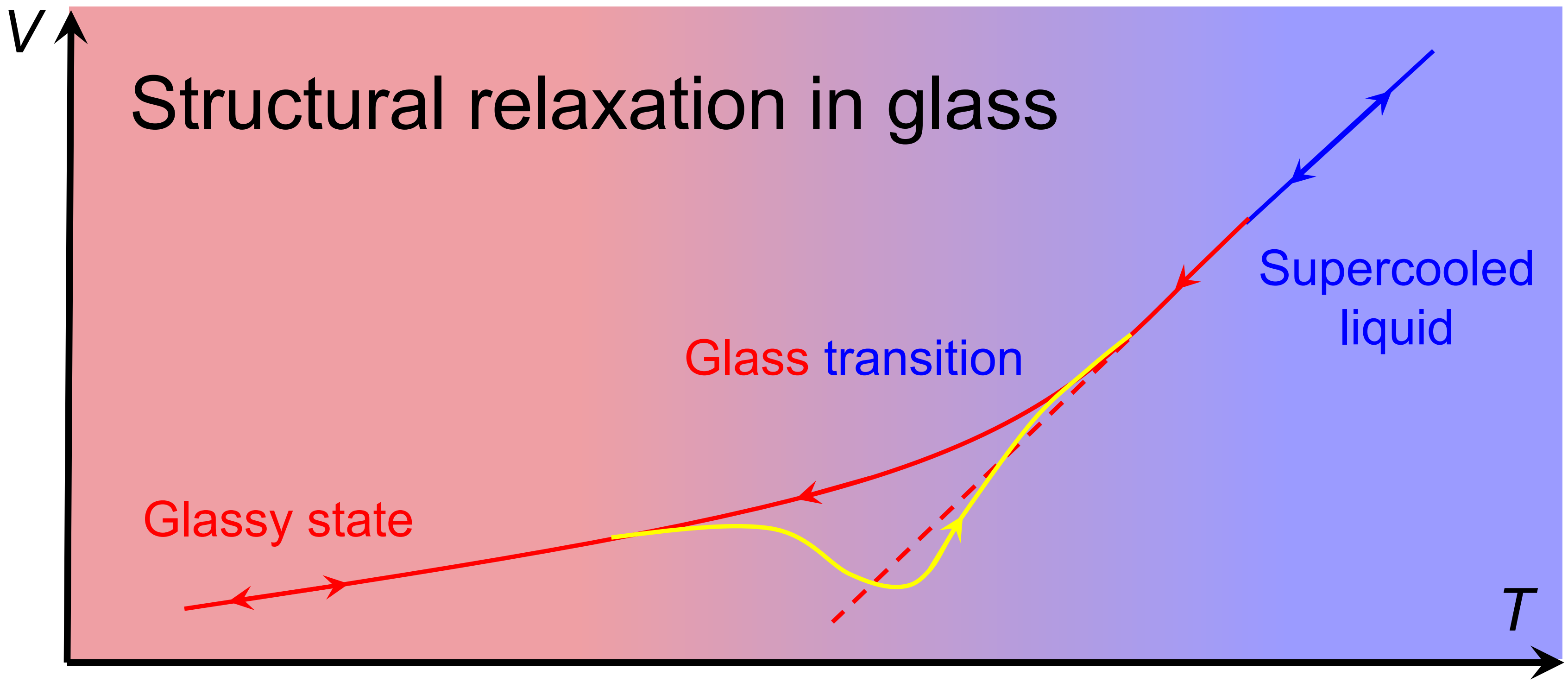
- ✓ Viscoelastic response is history-dependent
- ✓ Relaxation function Ψ dictates time-domain response



$$\sigma = \sum_i \Delta\sigma_i = \sum_i G\Delta\varepsilon_i \cdot \Psi\left(t - t_i\right)$$

$$\sigma = \int_0^t \frac{d\sigma_i}{dt} \cdot dt = \int_0^t G \frac{d\varepsilon}{dt'} \cdot \Psi\left(t - t'\right) \cdot dt'$$

Structural relaxation in glass



Elastic regime

$$\tau_{re} >> t_{obs}$$

All mechanical and thermal effects only affect atomic vibrations

Viscoelastic regime

$$\tau_{re} \sim t_{obs}$$

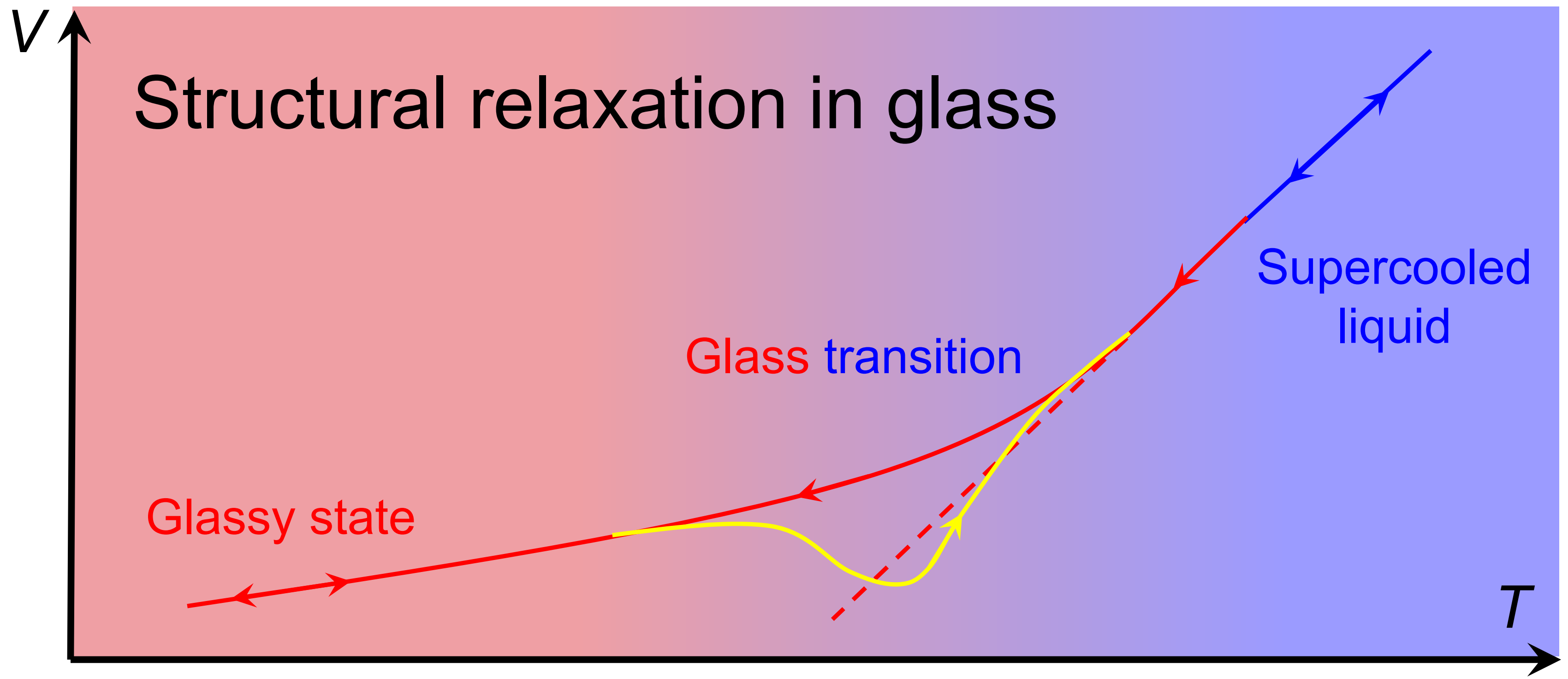
Glass structure and properties are **history-dependent**

Viscous regime

$$\tau_{re} << t_{obs}$$

Structural changes are instantaneous: equilibrium state can be quickly reached

Ergodicity breakdown



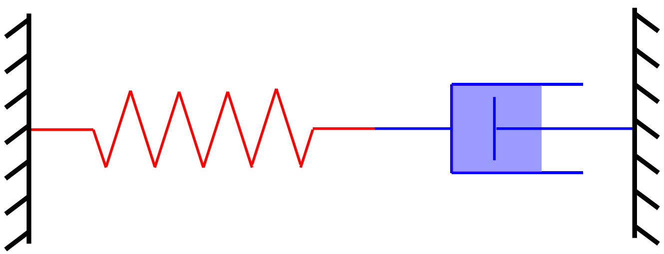
Elastic regime | Viscoelastic regime | Viscous regime

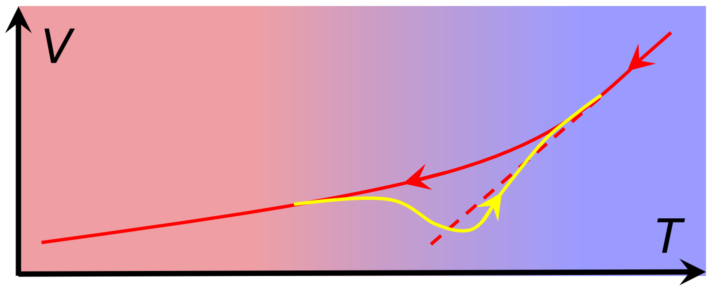
$DN >> 1$ | $DN \sim 1$ | $DN << 1$

Debroah number (DN): $DN = \tau_{re} / t_{obs}$

"… the mountains flowed before the Lord…"
Prophetess Deborah (Judges 5:5)

Comparing stress relaxation and structural relaxation

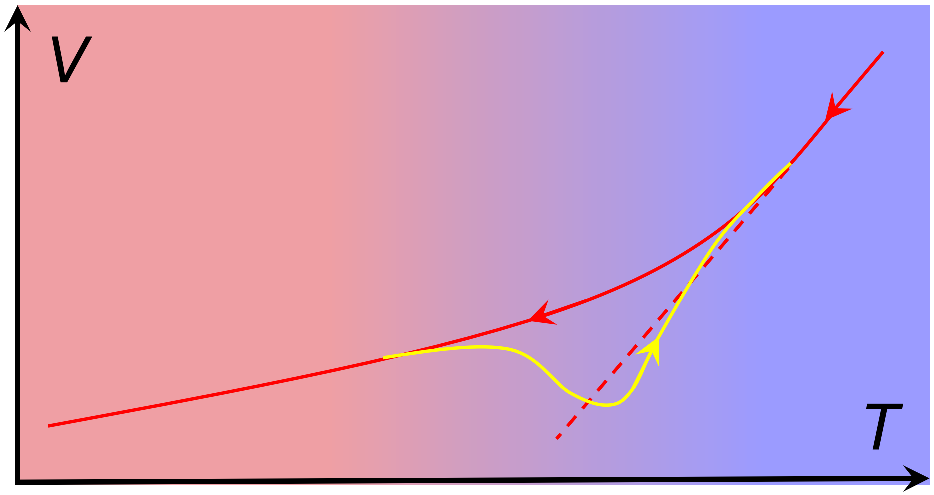




- "Equilibrium" state
  - Zero stress state
- Driving force
  - Residual stress
- Relaxation kinetics
  - Exponential decay with a single relaxation time
  - Relaxation rate scales with driving force

- "Equilibrium" state
  - Supercooled liquid state
- Driving force
  - Free volume $V_f = V - V_e$
- Relaxation kinetics
  - Exponential decay with a single relaxation time
  - Relaxation rate scales with driving force

Free volume model of relaxation (first order kinetic model)



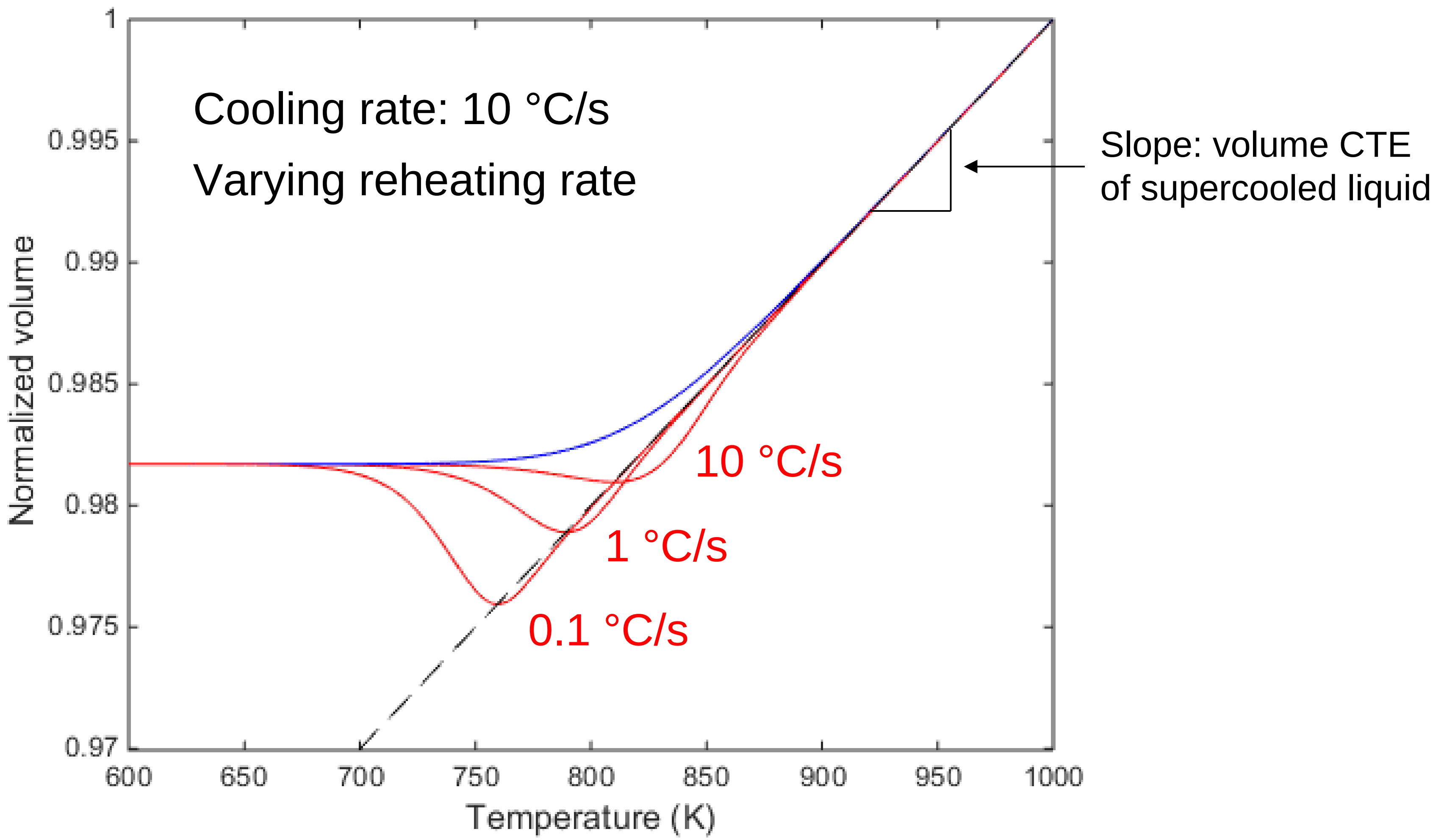
- Relaxation kinetics at constant temperature

$$V_f(t) = V(t) - V_e$$
$$= V_f(t=0)\cdot\exp(-t/\tau_{re})$$
$$\Rightarrow \frac{\partial V_f}{\partial t} = -\frac{V_f}{\tau_{re}}$$

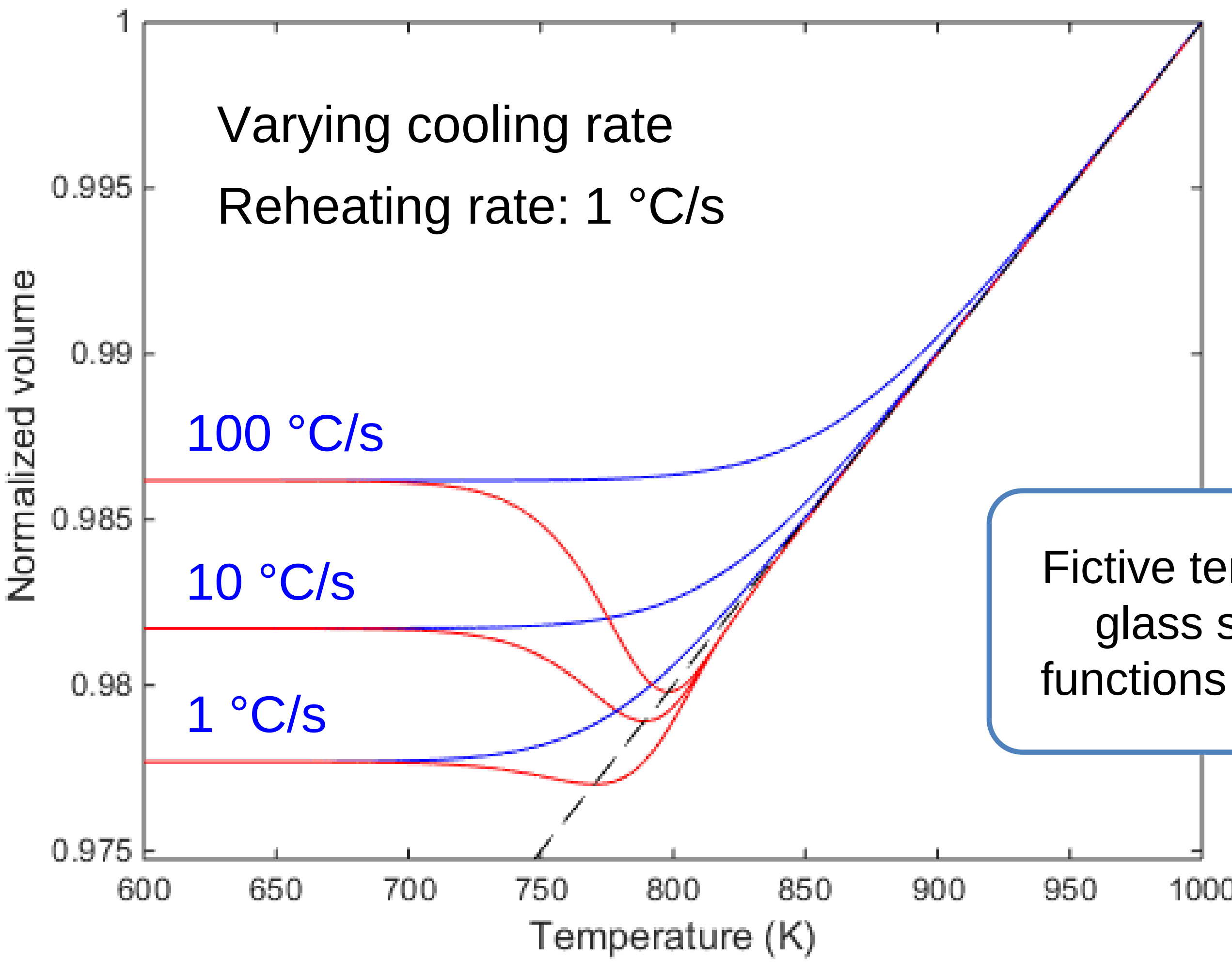
- Temperature dependence of relaxation

$$\tau_{re} = \tau_0 \exp\left(\frac{\Delta E_a}{k_B T}\right) \Rightarrow \frac{\partial V}{\partial t} = \frac{\partial V_f}{\partial t} = -\frac{V_f}{\tau_0}\cdot\exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

Model predicted relaxation kinetics

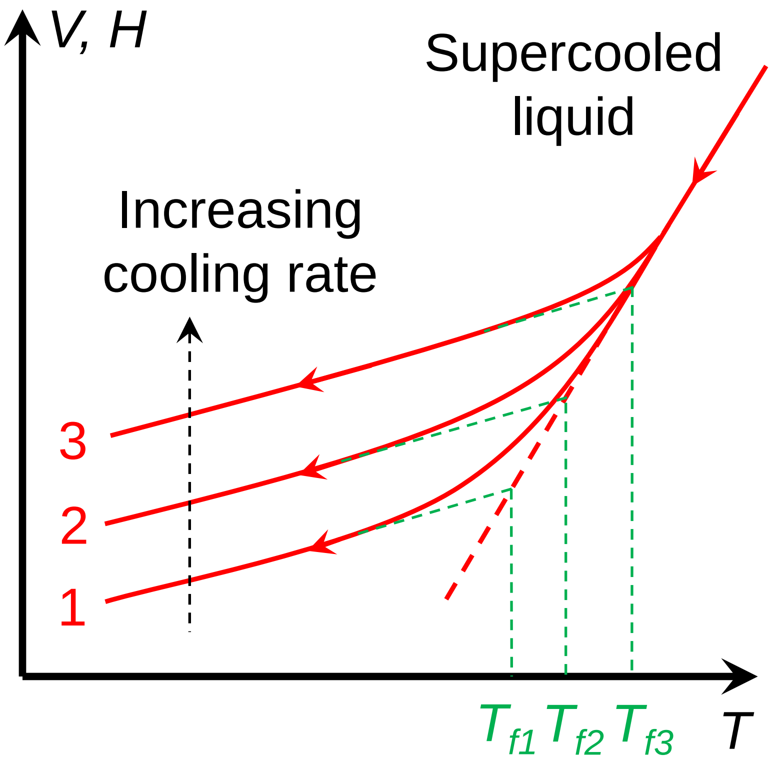


Model predicted relaxation kinetics



Fictive temperature and glass structure are functions of cooling rate

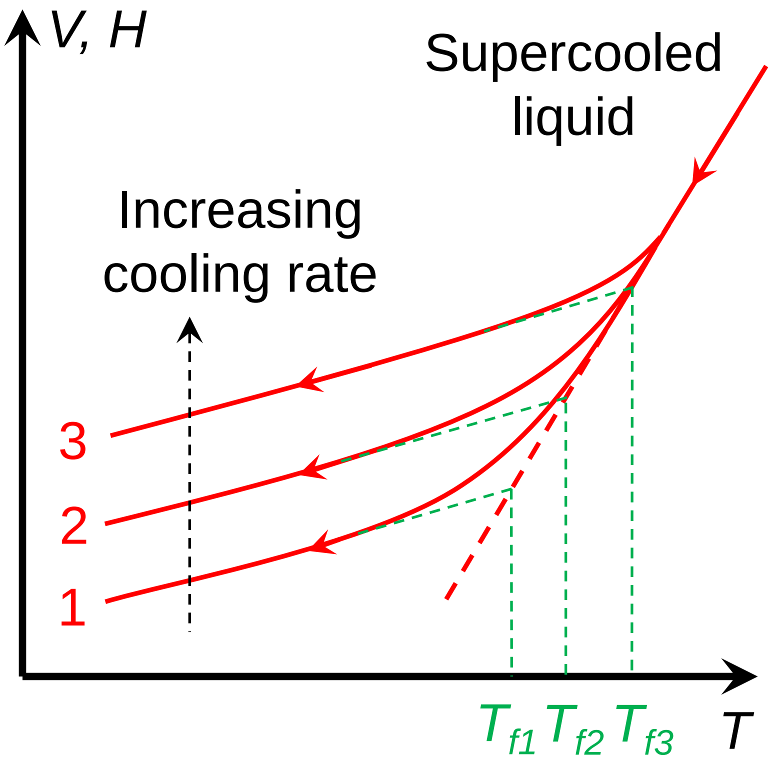
Tool's Fictive temperature theory



$$V = V\left(T, T_f\right) \qquad H = H\left(T, T_f\right)$$

- Fictive temperature T_f : the temperature on the supercooled liquid curve at which the glass would find itself in equilibrium with the supercooled liquid state if brought suddenly to it
- With increasing cooling rate:
  - $T_{f1} < T_{f2} < T_{f3}$
- A glass state is fully described by thermodynamic parameters (T, P) and T_f
- Glass properties are functions of temperature and T_f (structure)

Tool's Fictive temperature theory



$$V = V\left(T, T_f\right) \qquad H = H\left(T, T_f\right)$$

- Glass property change in the glass transition range consists of two components
  - Temperature-dependent property evolution without modifying glass structure

    Volume: $\left(\partial V / \partial T\right)_{T_f} = \alpha_{V,g}$

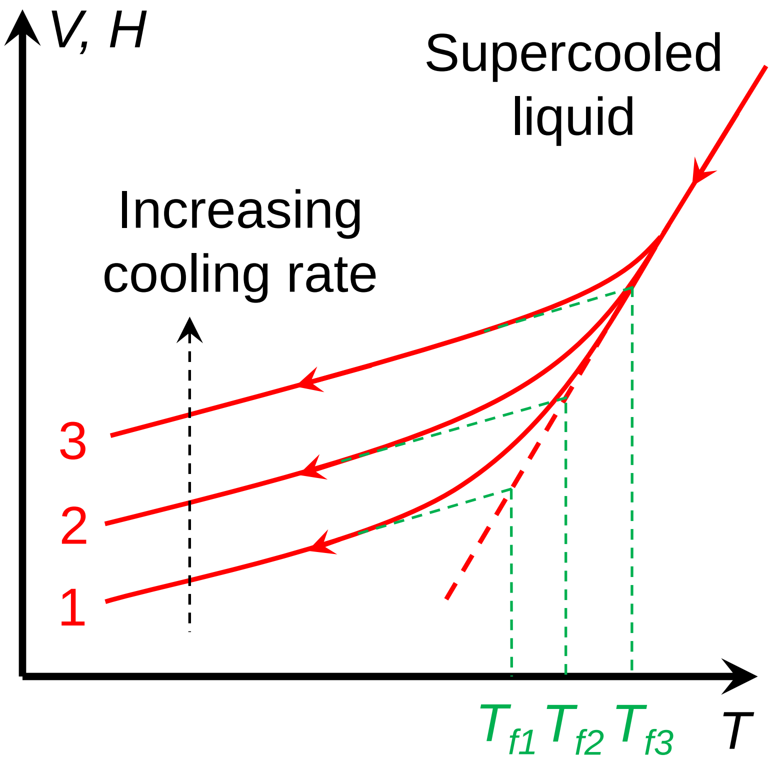
    Enthalpy: $\left(\partial H / \partial T\right)_{T_f} = C_{P,g}$

  - Property change due to relaxation (T_f change)

    Volume: $\left(\partial V / \partial T_f\right)_T = \alpha_{V,e} - \alpha_{V,g}$

    Enthalpy: $\left(\partial H / \partial T_f\right)_T = C_{P,e} - C_{P,g}$

Tool's Fictive temperature theory



$$V = V\left(T, T_f\right) \quad H = H\left(T, T_f\right)$$

- Glass property change in the glass transition range consists of two components

$$\frac{dV\left(T,T_f\right)}{dT} = \left(\frac{\partial V}{\partial T}\right)_{T_f} + \left(\frac{\partial V}{\partial T_f}\right)_T \cdot \frac{dT_f}{dT}$$

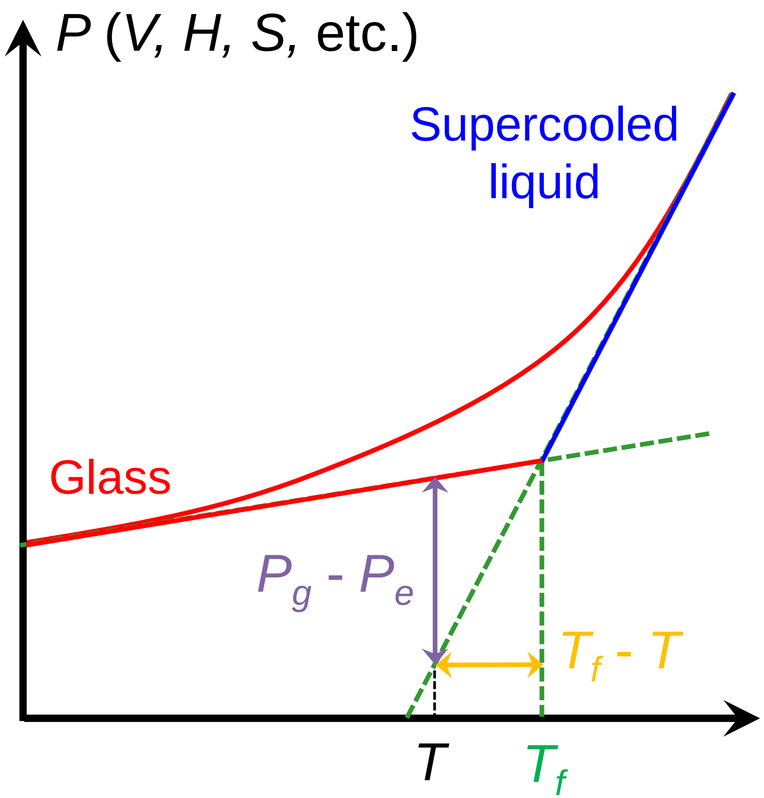
$$= \alpha_{V,g} + \left(\alpha_{V,e} - \alpha_{V,g}\right) \cdot \frac{dT_f}{dt} \Big/ \frac{dT}{dt}$$

$$\frac{dH\left(T,T_f\right)}{dT} = \left(\frac{\partial H}{\partial T}\right)_{T_f} + \left(\frac{\partial H}{\partial T_f}\right)_T \cdot \frac{dT_f}{dT}$$

$$= C_{P,g} + \left(C_{P,e} - C_{P,g}\right) \cdot \frac{dT_f}{dt} \Big/ \frac{dT}{dt}$$

Predicting glass structure evolution due to relaxation: Tool's equation

Consider a glass sample with Fictive temperature T_f



$$P_g - P_e = \left(\frac{\partial P_e}{\partial T} - \frac{\partial P_g}{\partial T} \right) \cdot \left(T_f - T \right)$$

Take time derivative:

$$\Rightarrow \frac{dP_g}{dt} = \left(\frac{\partial P_e}{\partial T} - \frac{\partial P_g}{\partial T} \right) \cdot \frac{dT_f}{dt}$$

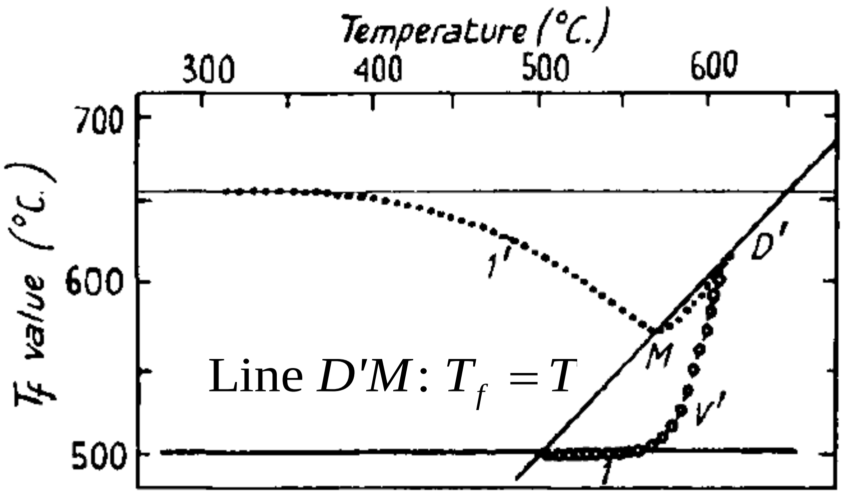
Assume first-order relaxation:

$$\frac{dP_g}{dt} = -\frac{P_g - P_e}{\tau_{re}}$$

$$\Rightarrow \frac{dT_f}{dt} = -\frac{T_f - T}{\tau_{re}}$$

Tool's equation

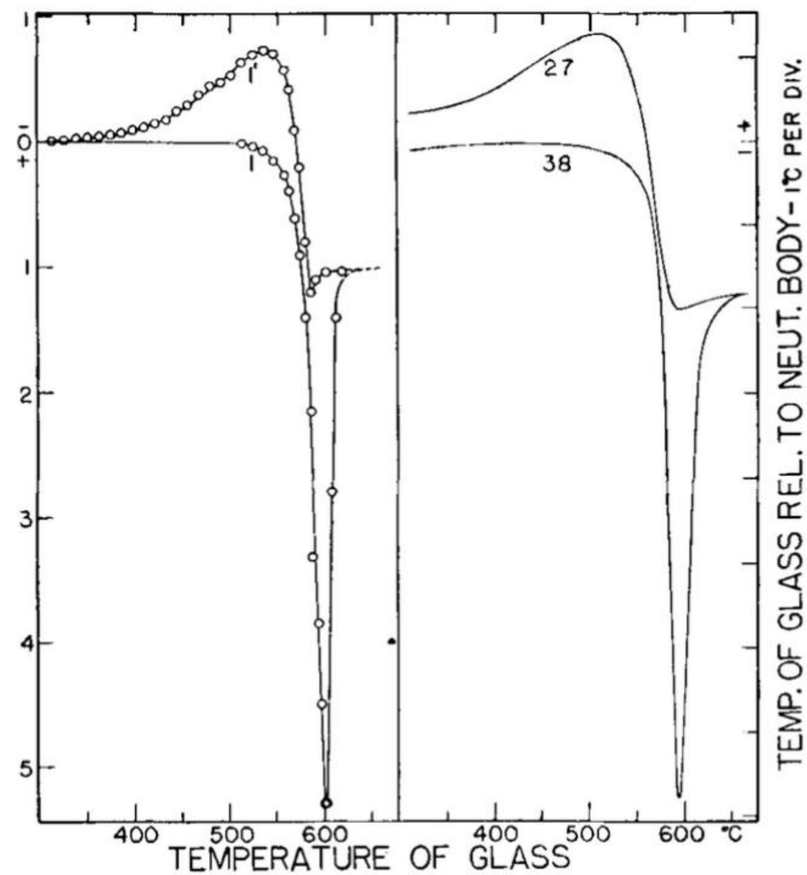
Tool's Fictive temperature theory



$$\frac{dT_f}{dt} = -\frac{T_f - T}{\tau_{re}}$$ Tool's equation

$$\frac{dH\left(T, T_f\right)}{dT} = \left(\frac{\partial H}{\partial T}\right)_{T_f} + \left(\frac{\partial H}{\partial T_f}\right)_T \cdot \frac{dT_f}{dT}$$

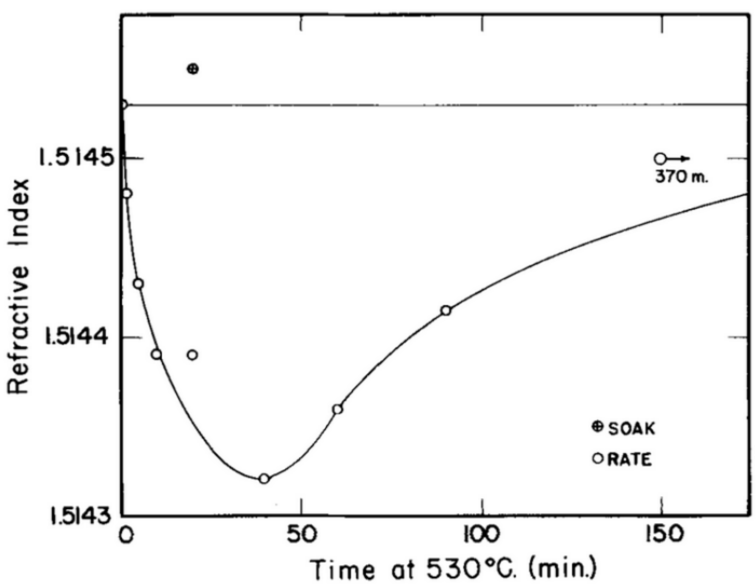
$$= C_{P,g} + \left(C_{P,e} - C_{P,g}\right) \cdot \frac{dT_f}{dt} \Big/ \frac{dT}{dt}$$



J. Am. Ceram. Soc. **29**, 240 (1946)

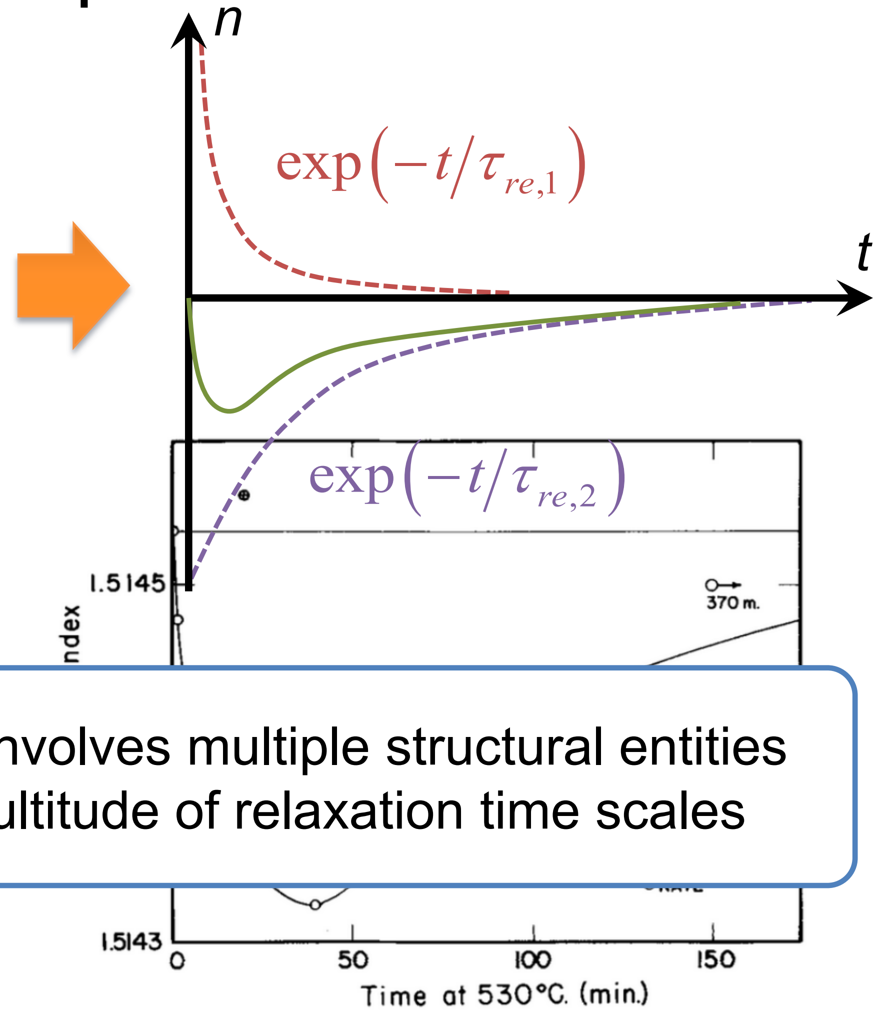
Difficulties with Tool's T_f theory

- Ritland experiment: two groups of glass samples of identical composition were heat treated to obtain the same refractive index via two different routes
  - Group A: kept at 530°C for 24 h
  - Group B: cooled at 16°C/h through the glass transition range
- Both groups were then placed in a furnace standing at 530°C and their refractive indices were measured as a function of heat treatment time
- Glass structure cannot be fully characterized by the single parameter T_f



J. Am. Ceram. Soc. **39**, 403 (1956).

Explaining the Ritland experiment



Structural relaxation in glass involves multiple structural entities and is characterized by a multitude of relaxation time scales

Read More

Tool-Narayanaswamy-Moynihan (TNM) model

What is relaxation?

Relaxation: return of a perturbed system into equilibrium

- Examples
  - Stress and strain relaxation in viscoelastic solids
  - Free volume relaxation in glasses near T_g
  - Glass structural relaxation (T_f change)
- Time-dependent, occurs even after stimulus is removed
- Debroah Number: $DN = \tau_{re} / t_{obs}$
  - *DN* >> 1: negligible relaxation due to sluggish kinetics
  - *DN* << 1: system always in equilibrium
  - *DN* ~ 1: system behavior dominated by relaxation

Modeling relaxation

Relaxation rate $\frac{\partial P}{\partial t} = -\frac{P - P_e}{\tau_{re}}$ Driving force

- Maxwellian relaxation models

$$P(t) = (P_0 - P_e) \cdot \exp\left(-\frac{t}{\tau_{re}}\right) + P_e$$

$$P(t) = (P_0 - P_e) \cdot \exp\left(-\frac{t}{\tau_{re}}\right)^{\beta} + P_e$$

- Boltzmann superposition principle in linear systems

$$\sigma = G\Psi(t - t') \cdot \frac{d\varepsilon}{dt} \cdot \Delta t \qquad R = IRF(t - t') \cdot S \cdot \Delta t$$

$$\sigma = \int_0^t \frac{d\sigma}{dt} \cdot dt = \int_0^t G\Psi(t - t') \cdot \frac{d\varepsilon}{dt'} dt' \qquad R = \int_0^t IRF(t - t') \cdot S(t') \cdot dt'$$

“The Nature of Glass Remains Anything but Clear”

- Free volume relaxation theory

$$\frac{\partial V}{\partial t} = -\frac{V_f}{\tau_0} \cdot \exp\left(-\frac{\Delta E_a}{k_B T}\right)$$

- Tool’s Fictive temperature theory
  - Uses a single parameter T_f to label glass structure
  - Tool’s equation (of T_f relaxation)

$$\frac{dT_f}{dt} = -\frac{T_f - T}{\tau_{re}}$$

- Structural relaxation in glass involves multiple structural entities and is characterized by a multitude of relaxation time scales
  - The Ritland experiment

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