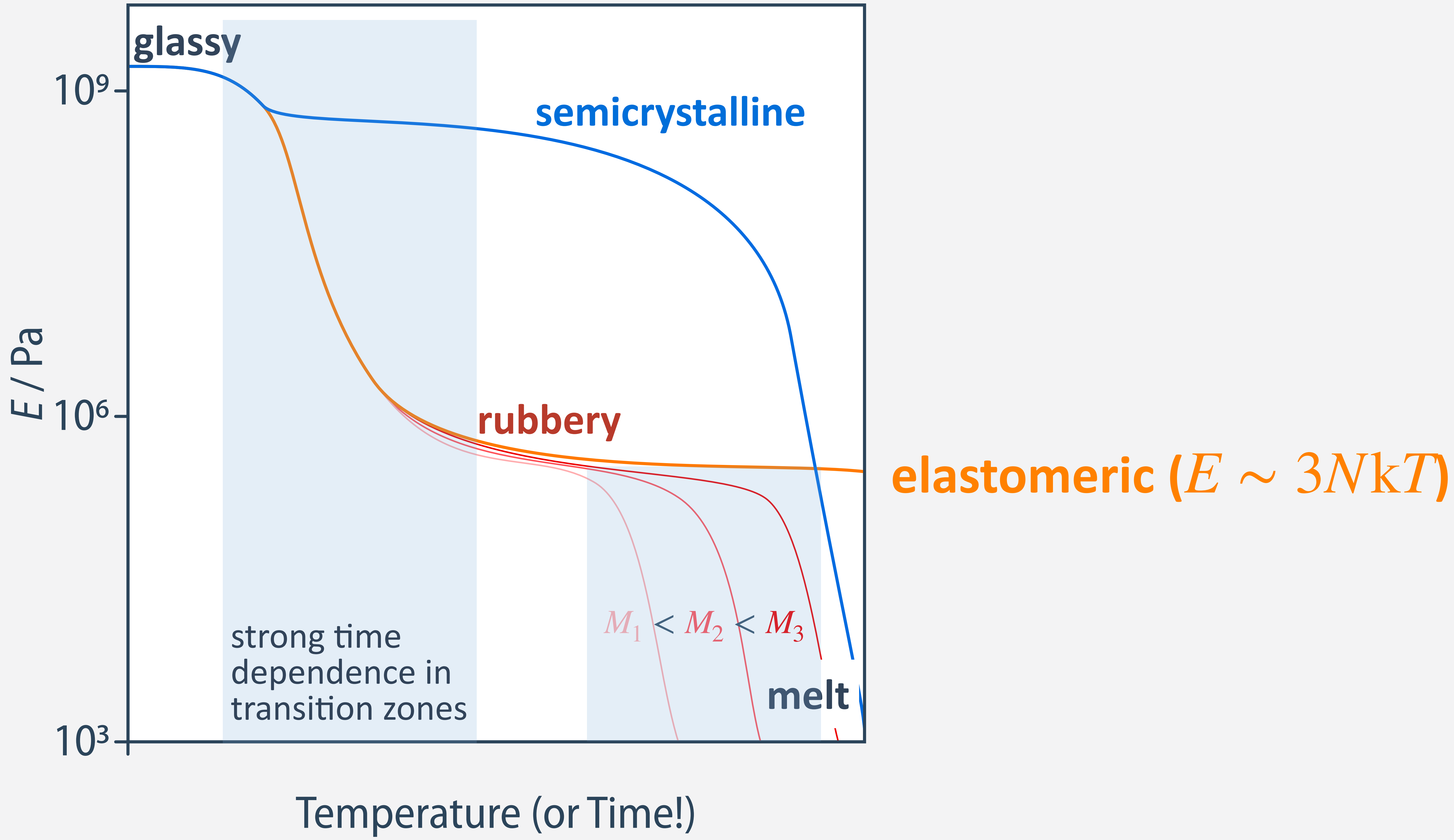
4.2

Viscoelasticity

Viscoelasticity

- **elastic solids (e.g. metals, ceramics) obey Hooke's law: $\sigma = E\epsilon$**
- the elastic modulus is independent of time t and strain rate $\mathrm{d}\epsilon/\mathrm{d}t$ (as long as T is moderate)

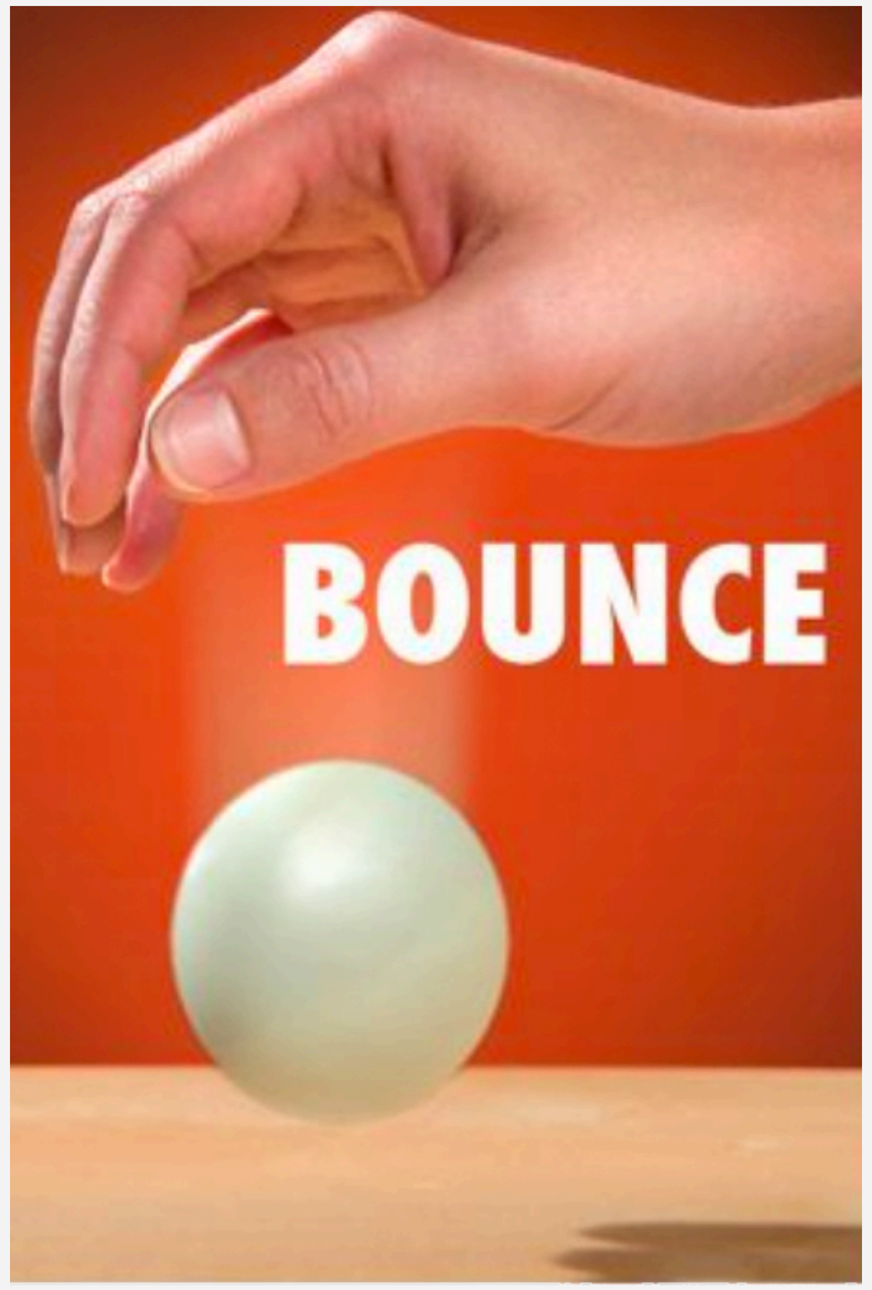


- **in contrast, polymer response depends strongly on time and strain rate, especially near transitions**

Example - Silly Putty

- silly putty exhibits different mechanical behavior depending on the time-scale of deformation

elastic solid



short time scales

deformability

"fast" strain rate

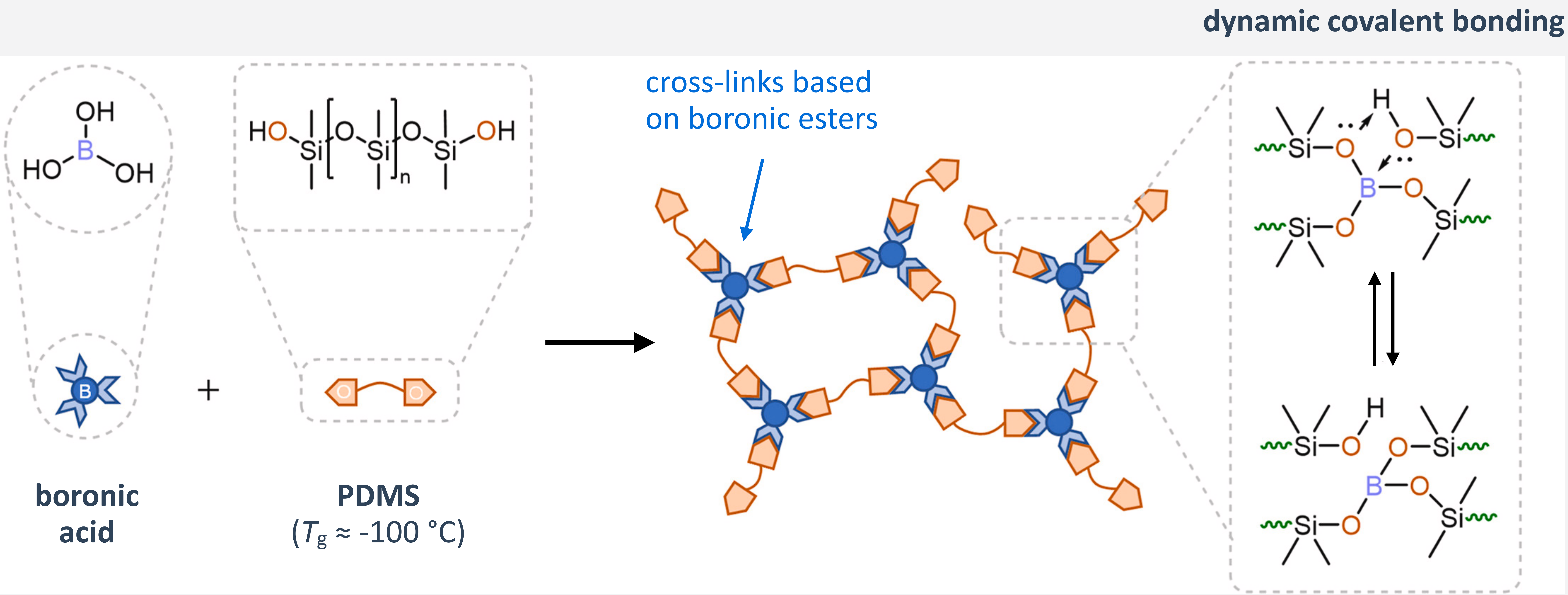
liquid flow

long time scales

- **elastic behavior dominates at short deformation times (high frequency)**
- **flow behavior dominates at long deformation times (low frequency)**

Time-Dependent Viscoelastic Behavior of Silly Putty

- networks from transiently cross-linked poly(dimethoxysiloxane) (PDMS):



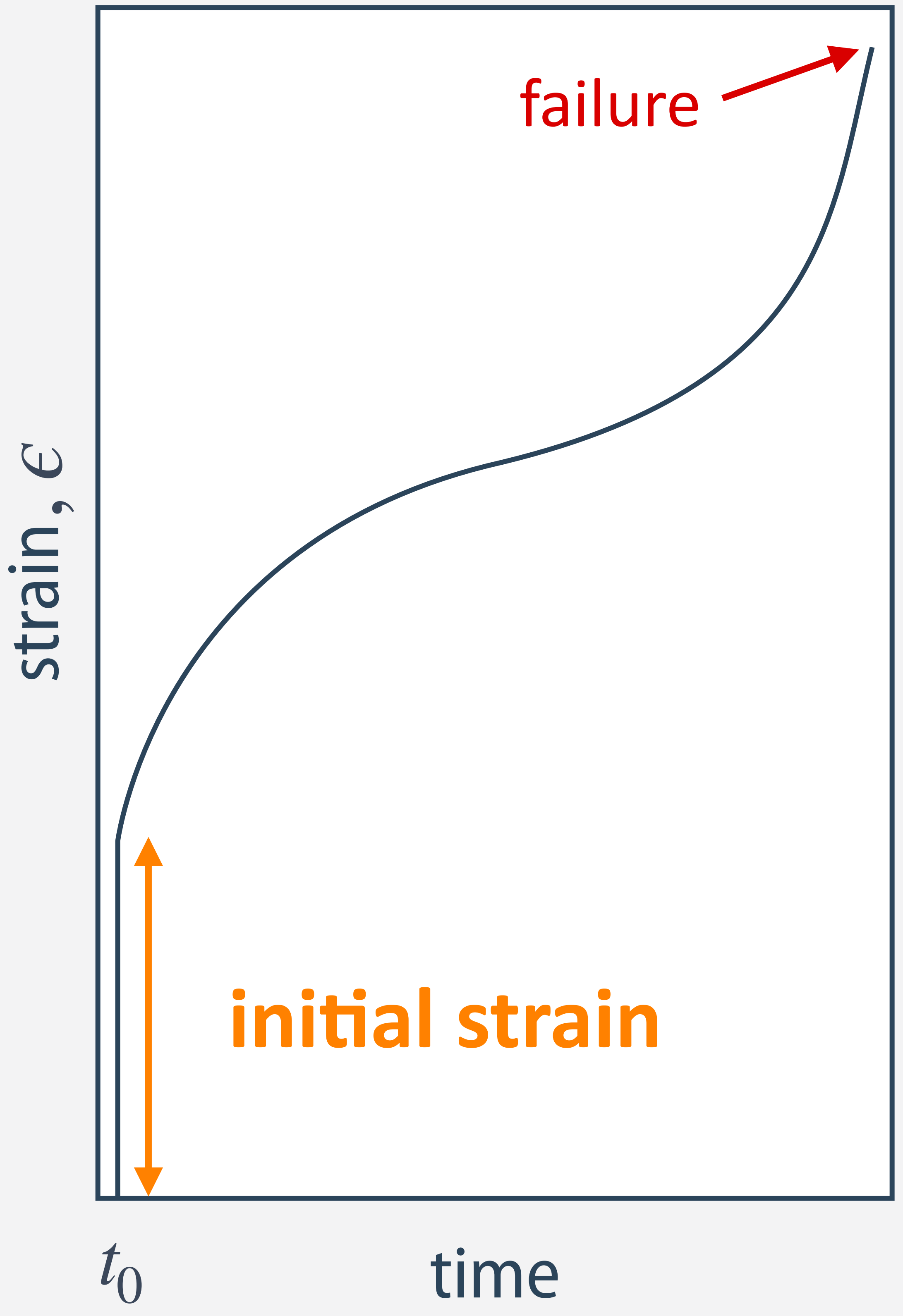
- **dynamic boronic ester bonds allow the network to flow upon bond exchange or dissociation**

Importance of Viscoelasticity

- time, frequency, and temperature jointly determine polymer performance and processing behavior

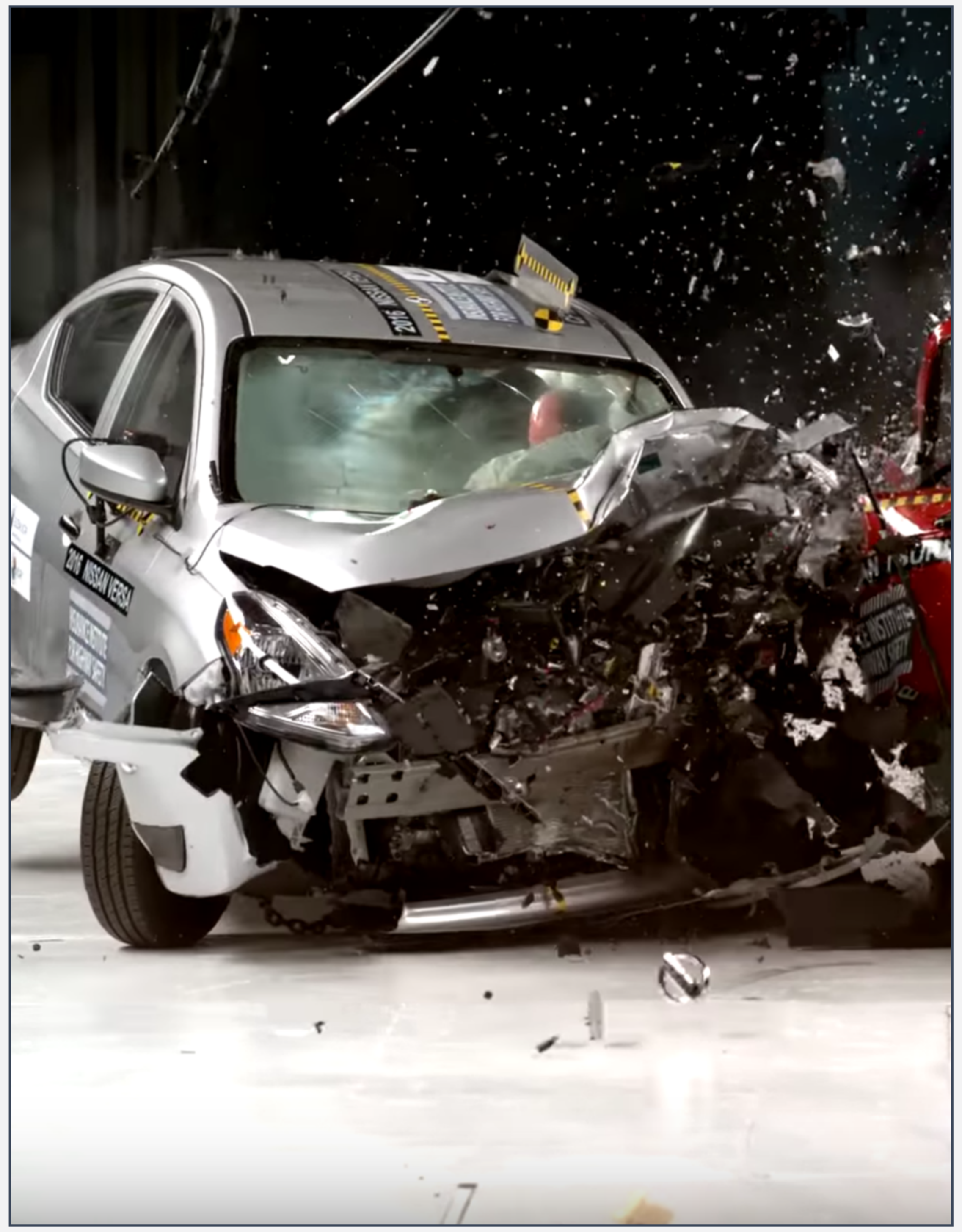
long-term properties

(creep, fatigue)



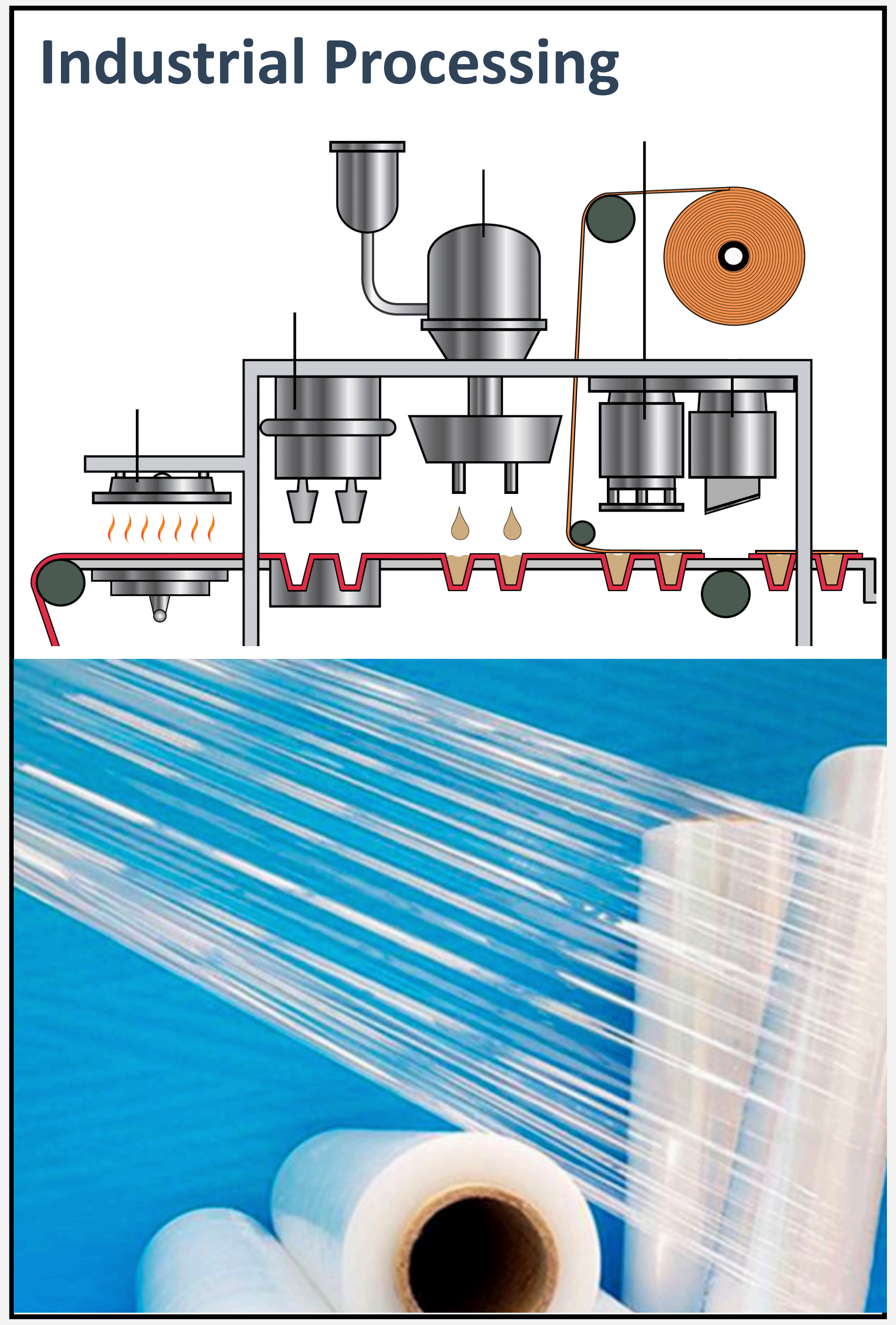
short-term properties

(impact resistance, energy dissipation, vibration,…)



processability

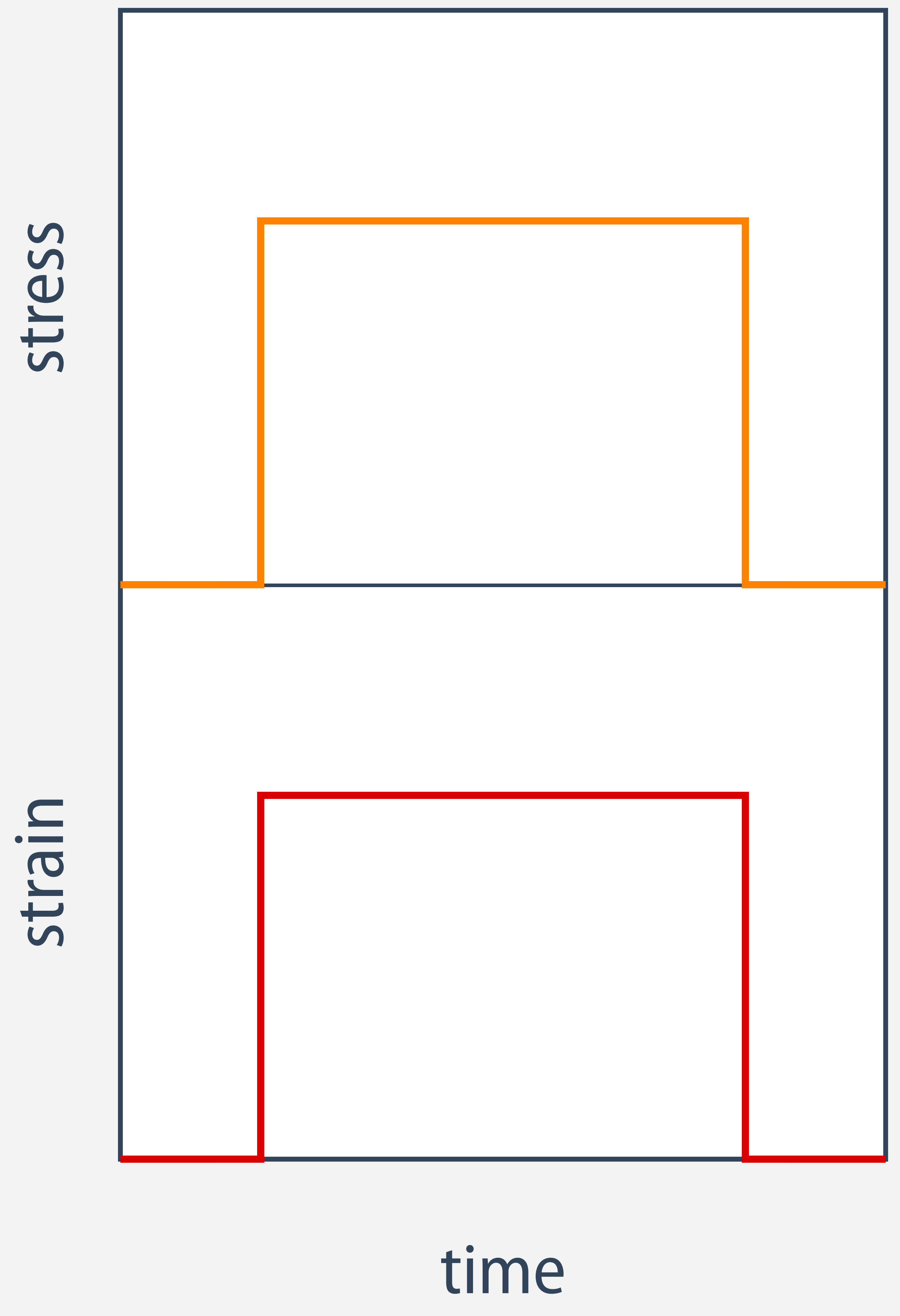
(e.g. thermoforming, fiber drawing)



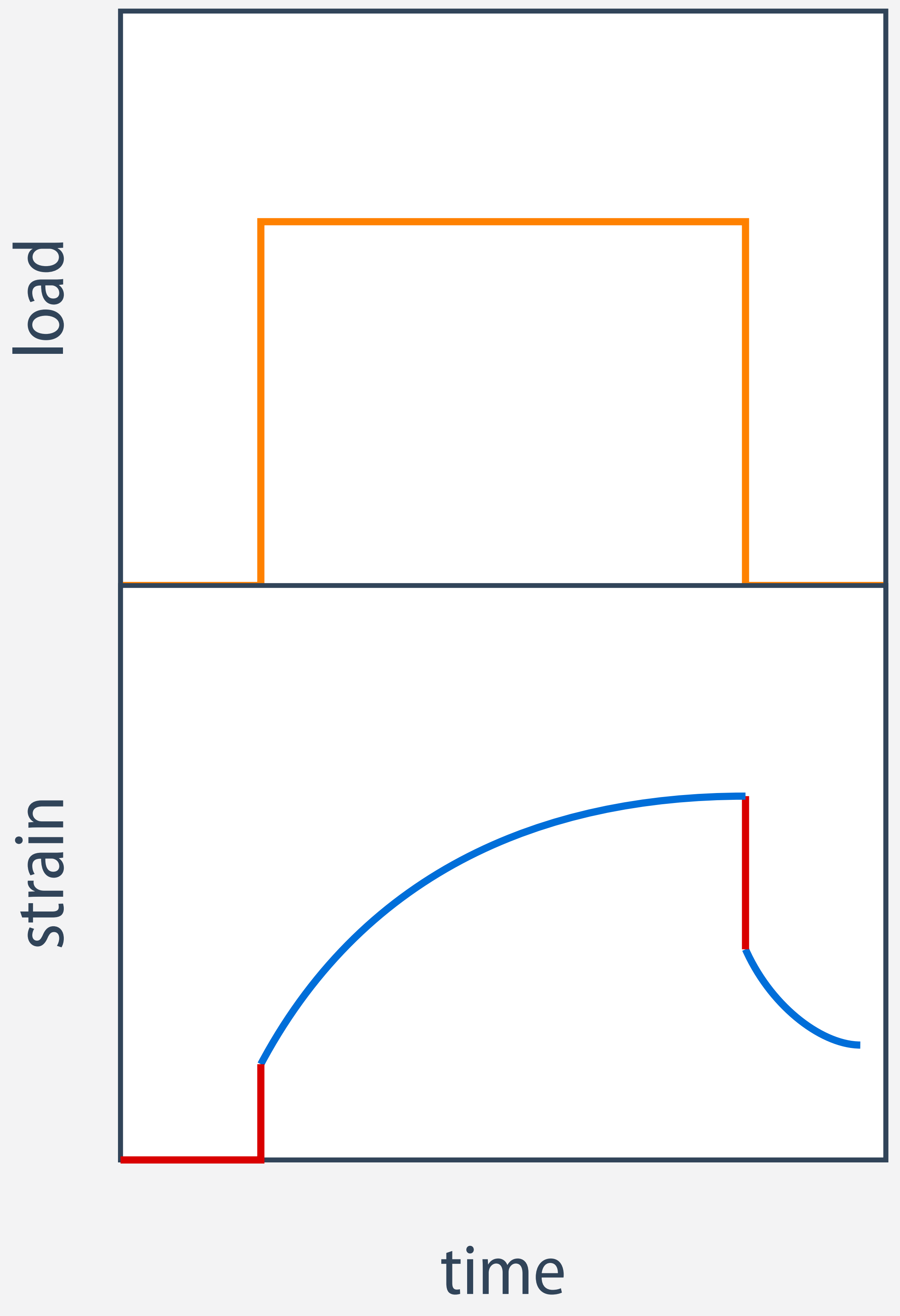
Elastic, Viscoelastic, and Viscous Responses

- creep tests illustrate the intermediate, time-dependent behavior of viscoelastic materials

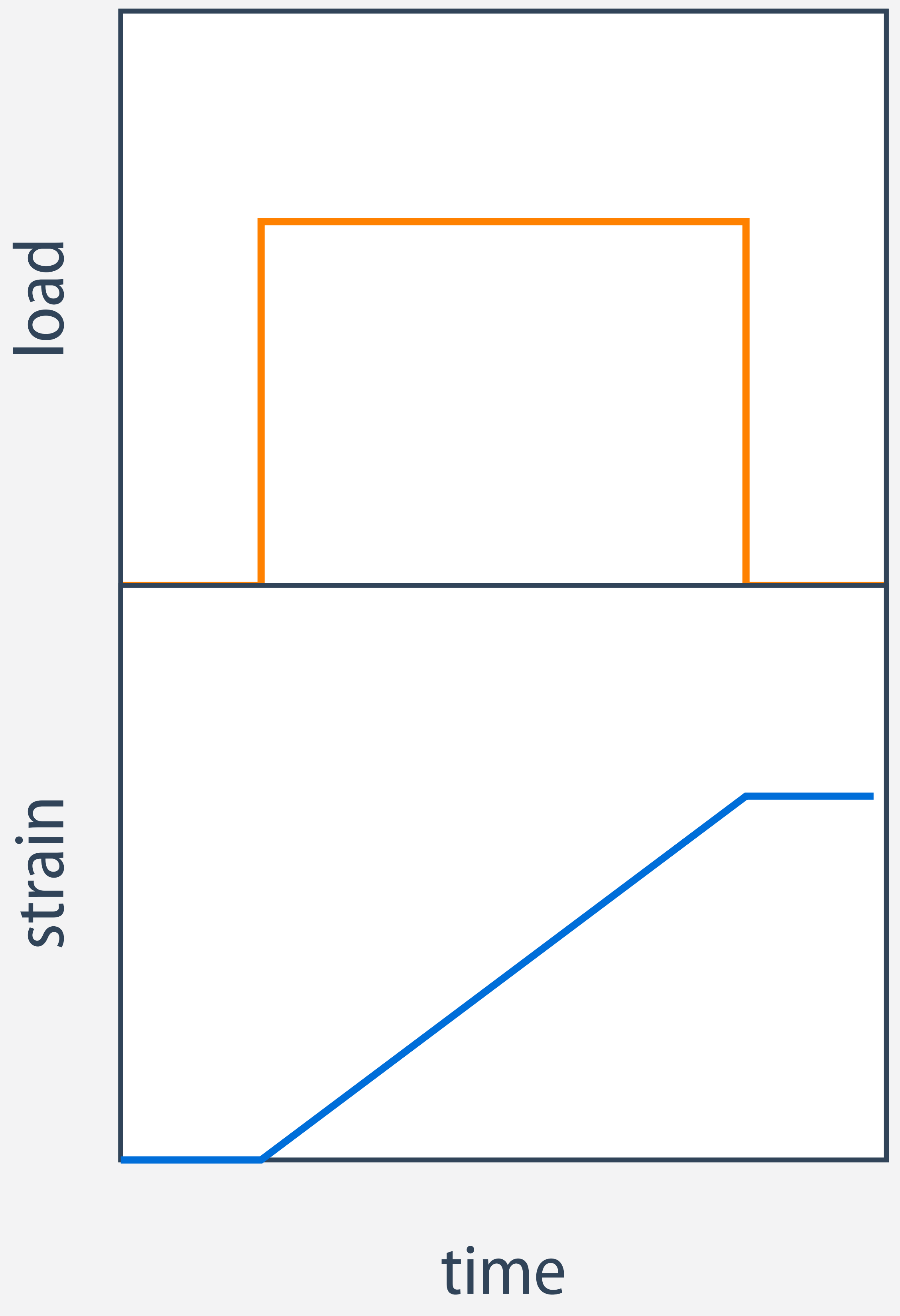
elastic solid



viscoelastic



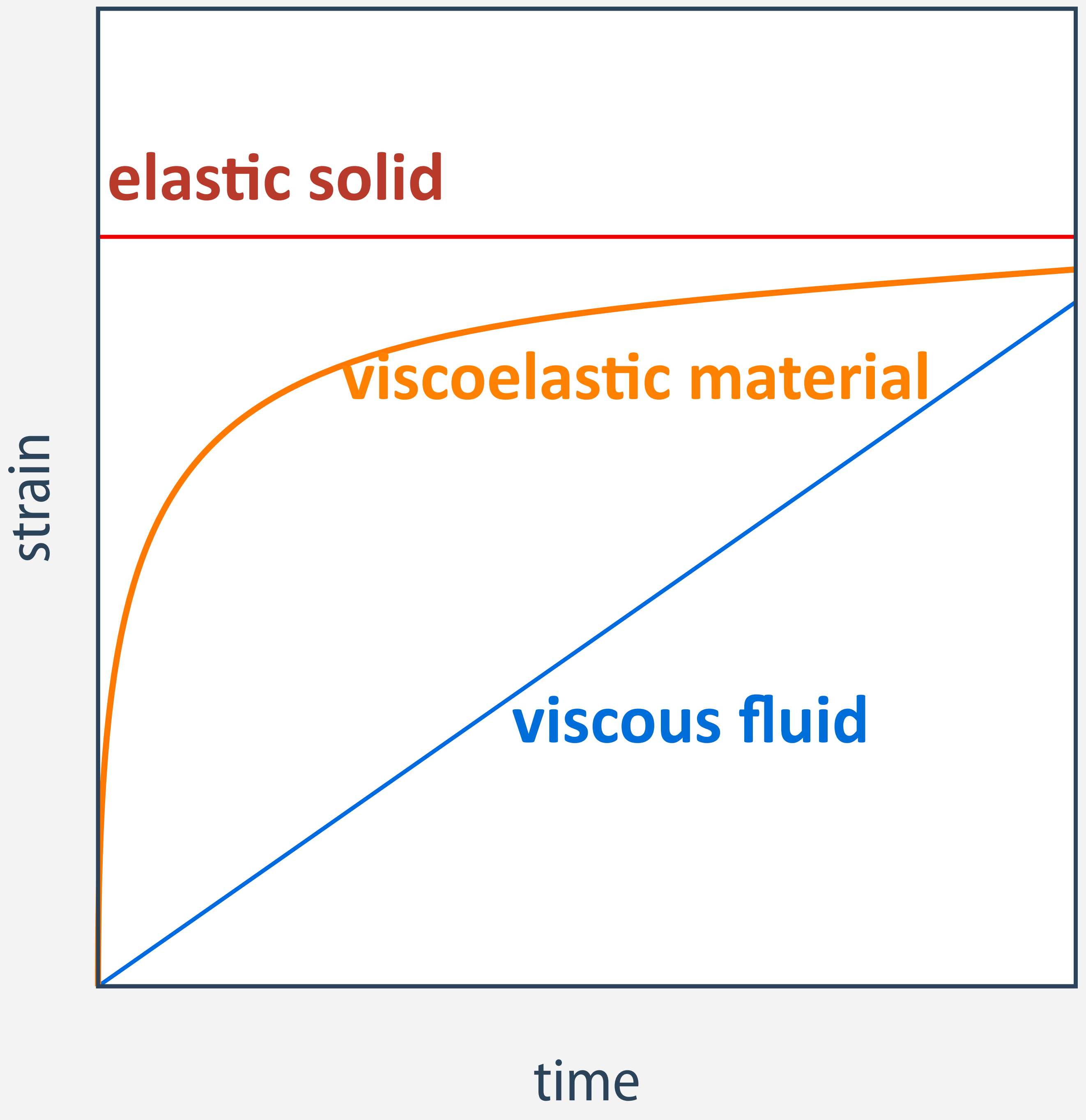
liquid flow



Phenomenological Description of Viscoelasticity

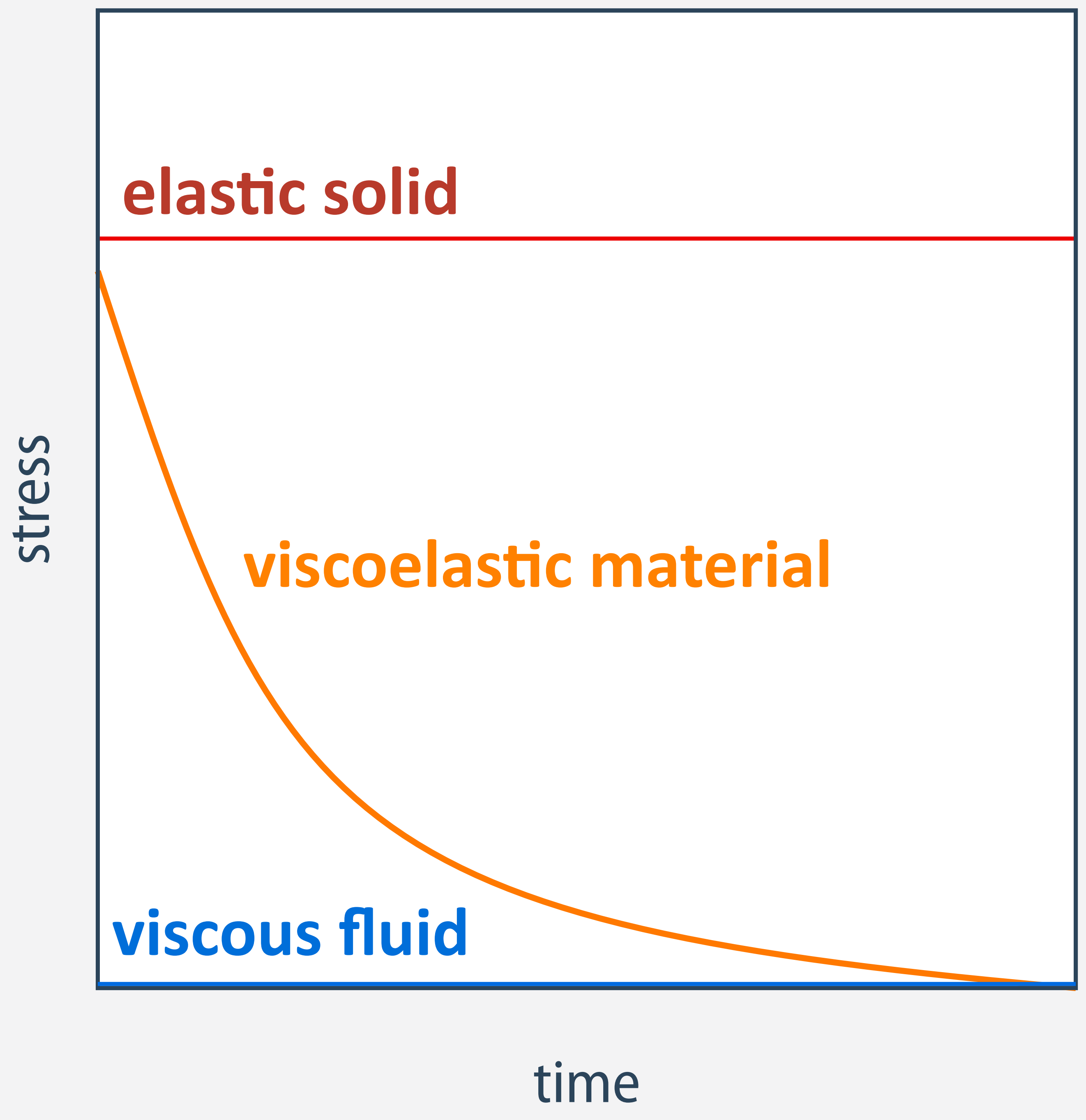
creep

(constant stress)



relaxation

(constant strain)



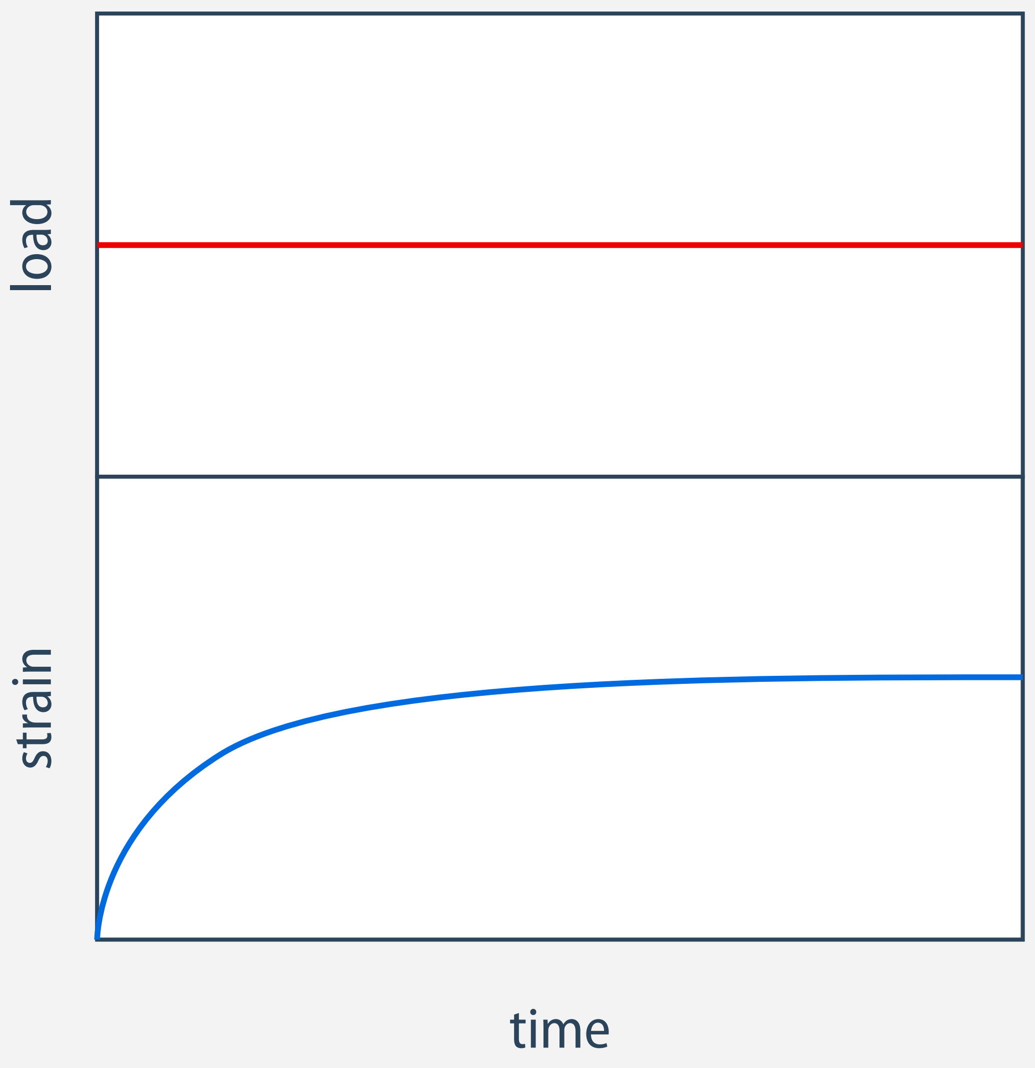
- **linear viscoelasticity: Hooke's & Newton's law apply, modulus $E = \mathrm{f}(T, t)$ is stress-independent** (valid for small deformations)
- **non-linear viscoelasticity: stress-dependent modulus $E = \mathrm{f}(T, t, \sigma)$** (large deformations)

Linear Viscoelasticity

Time Dependence of Stress and Strain

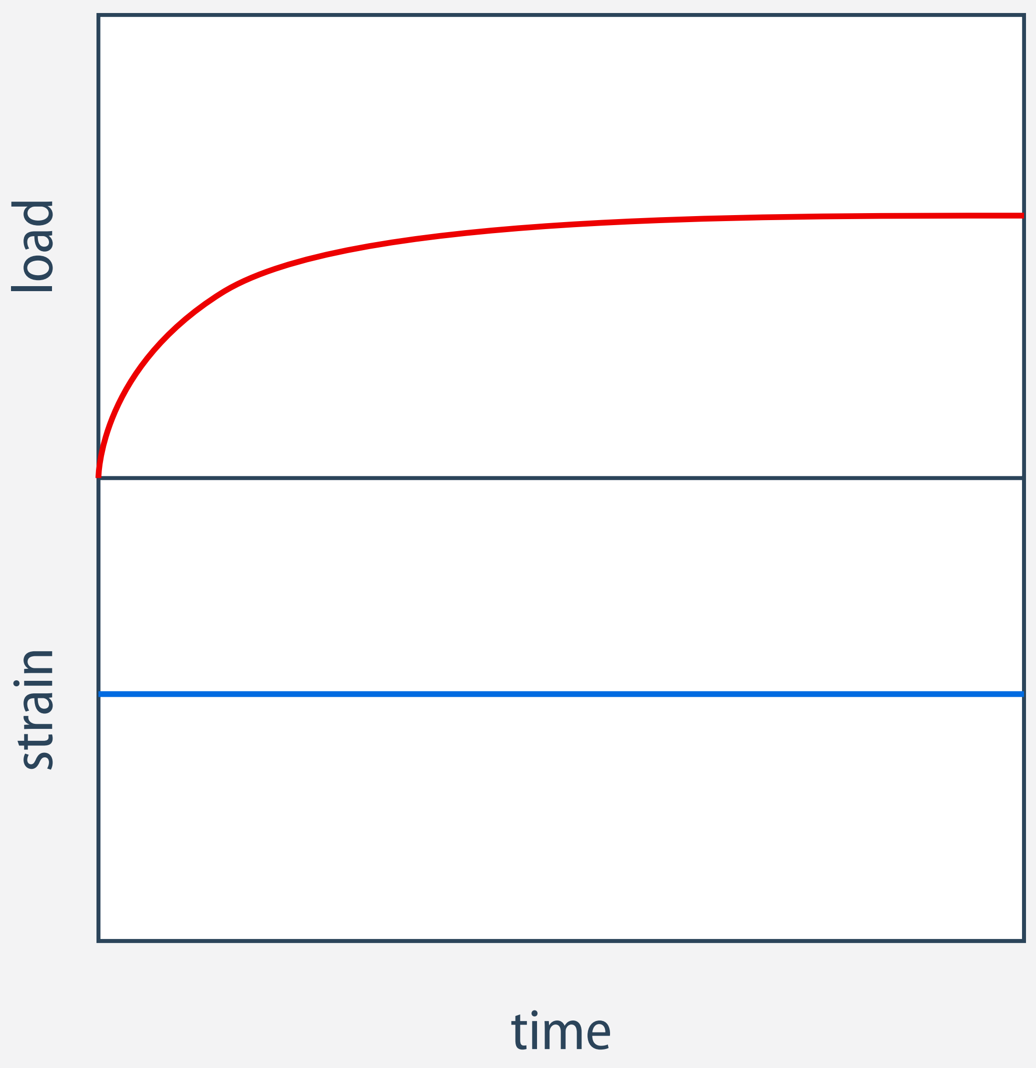
- static creep and relaxation tests define viscoelastic functions for tension and shear

Creep



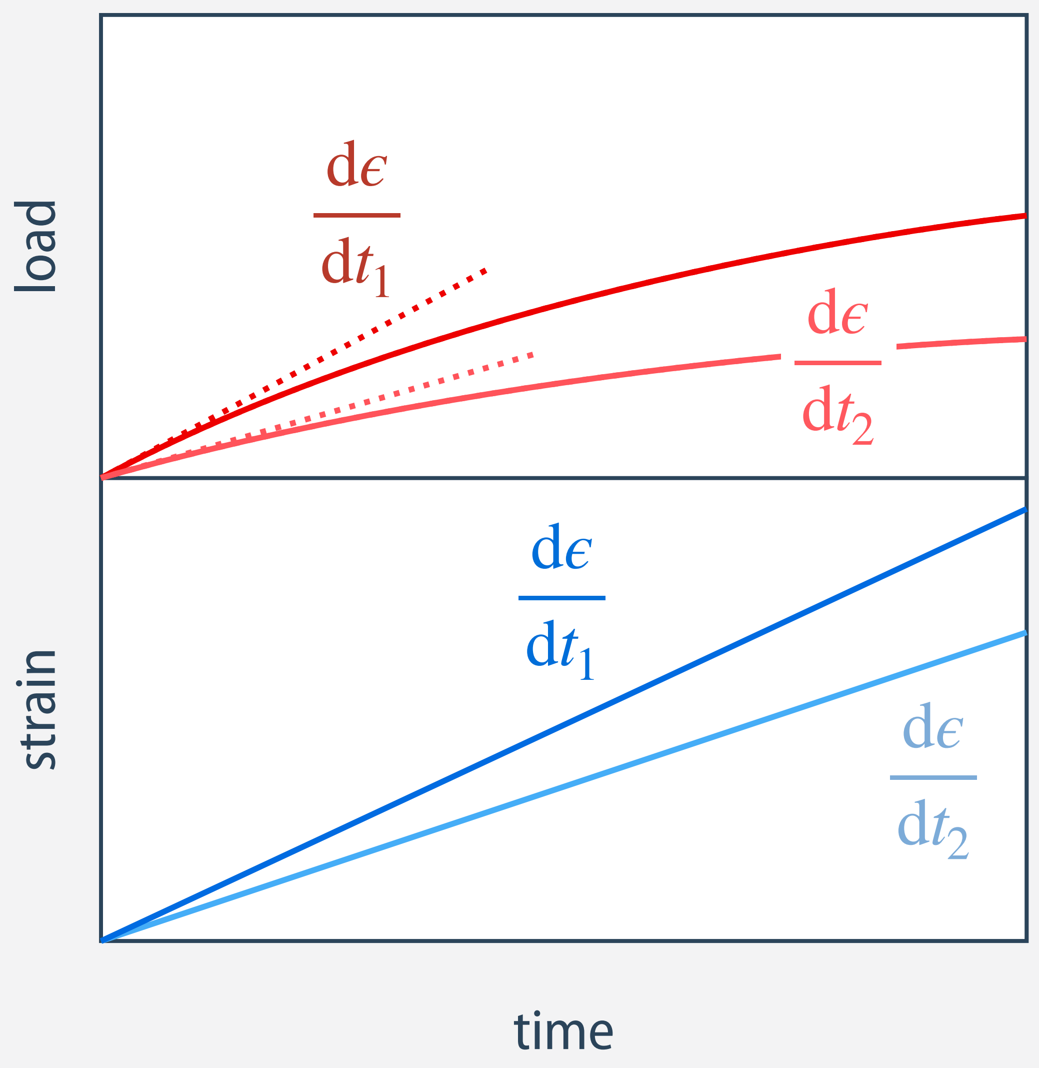
$$D(t) = \frac{\epsilon(t)}{\sigma_0} \qquad J(t) = \frac{\gamma(t)}{\sigma_0}$$

Relaxation



$$E(t) = \frac{\sigma(t)}{\epsilon_0} \qquad G(t) = \frac{\sigma(t)}{\gamma_0}$$

Constant Strain Rate

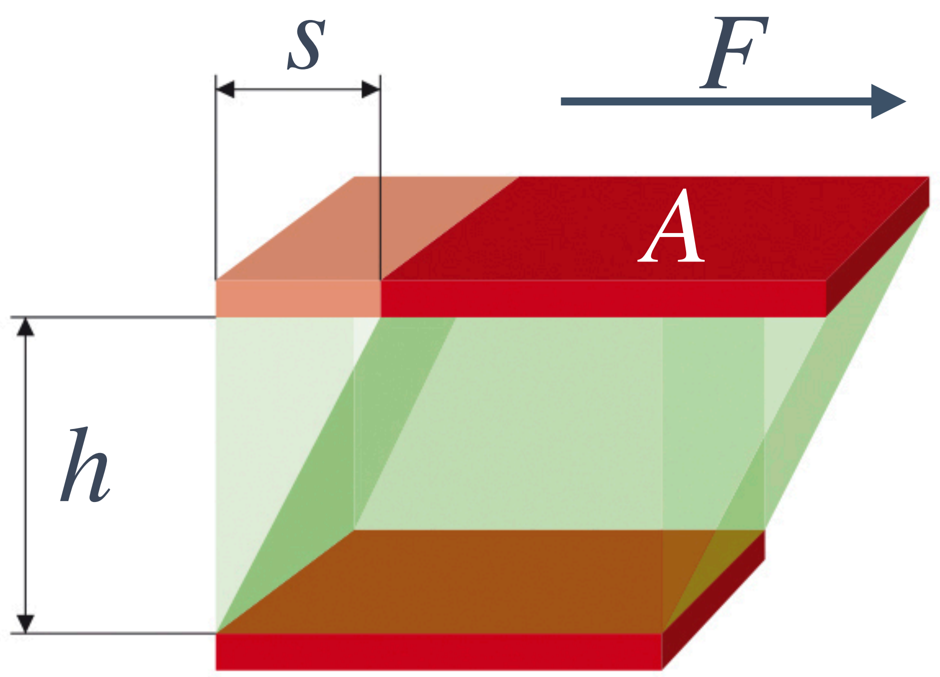


- $D(t)$ and $J(t)$: **compliances**, $E(t)$ and $G(t)$: **moduli** (compliances and moduli are independent of each other)
- do not confuse with the time-independent Young's modulus ($E = 1/D$ only for Hookean solids)

Dynamic Mechanical Analysis

Deformation under Shear

- **small strain experiments are conveniently performed under shear**



shear stress: $\sigma = \frac{F}{A}$

shear strain: $\gamma = \frac{s}{h}$

shear modulus: $G = \frac{\sigma}{\gamma}$

material	shear modulus (*G*)
very soft gel structures (salad dressing)	5-10 Pa
soft gel structures (coatings, paints)	10-50 Pa
viscoelastic gels (dispersions, lotions,…)	50-5’000 Pa
gummy bears	10-500 kPa
car tires (hard rubbers)	10-100 MPa
thermoplastic polymers	0.1-2 GPa
ceramics, glass	15 - 35 GPa
aluminum	28 GPa
steel	80 GPa

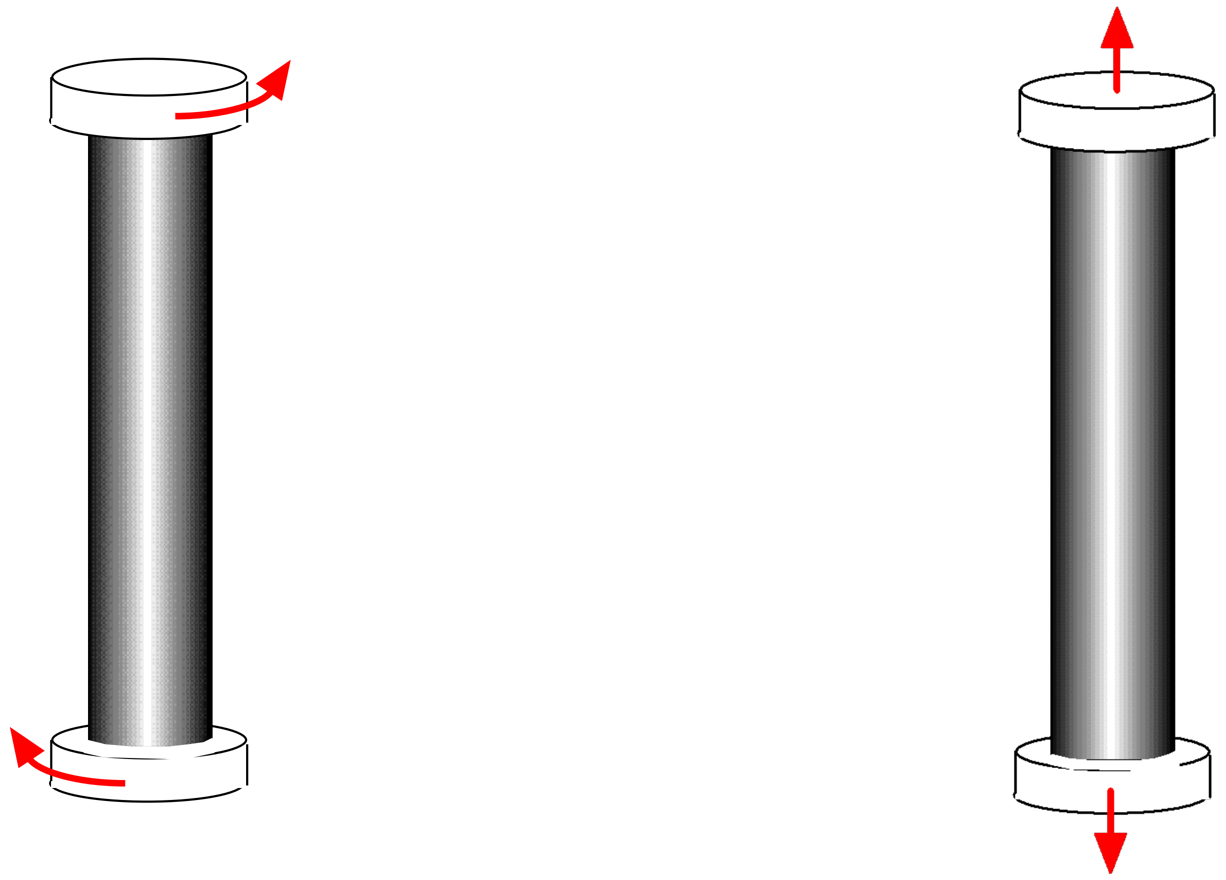
- **higher G indicates greater stiffness**

Dynamic Mechanical Measurements

- **samples are subjected to oscillatory stress or strain (shear, tension, or bending)**

dynamic mechanical analysis (DMA)

shear or tensile deformation

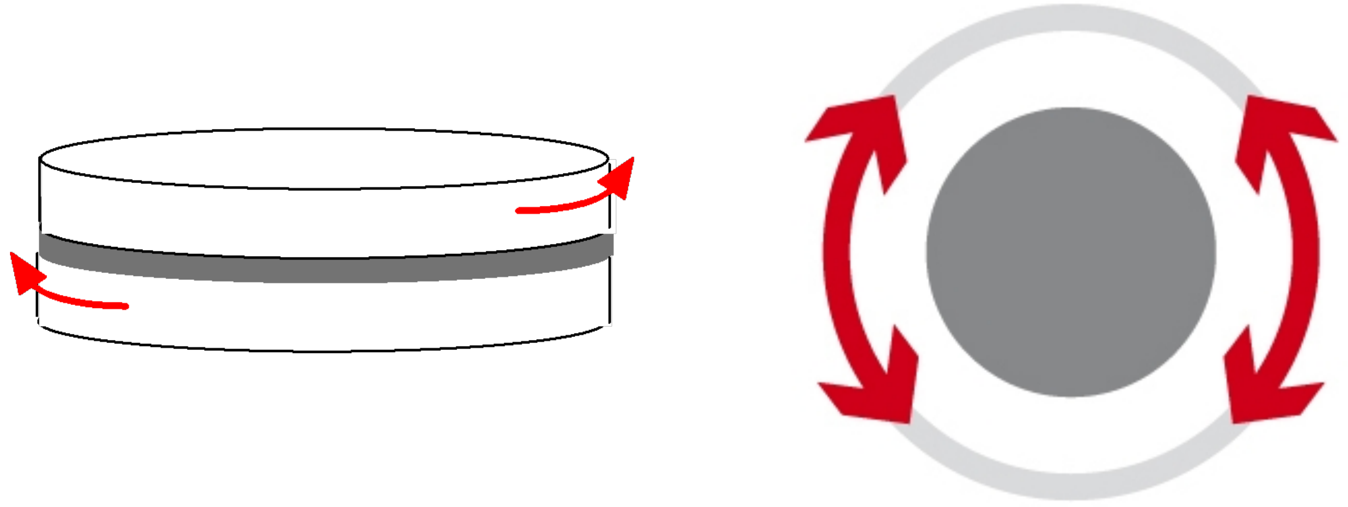


$\gamma(t) = \gamma_0 \sin(\omega t)$ $\epsilon(t) = \epsilon_0 \sin(\omega t)$

typical for solid samples

rheometry

usually shear deformation



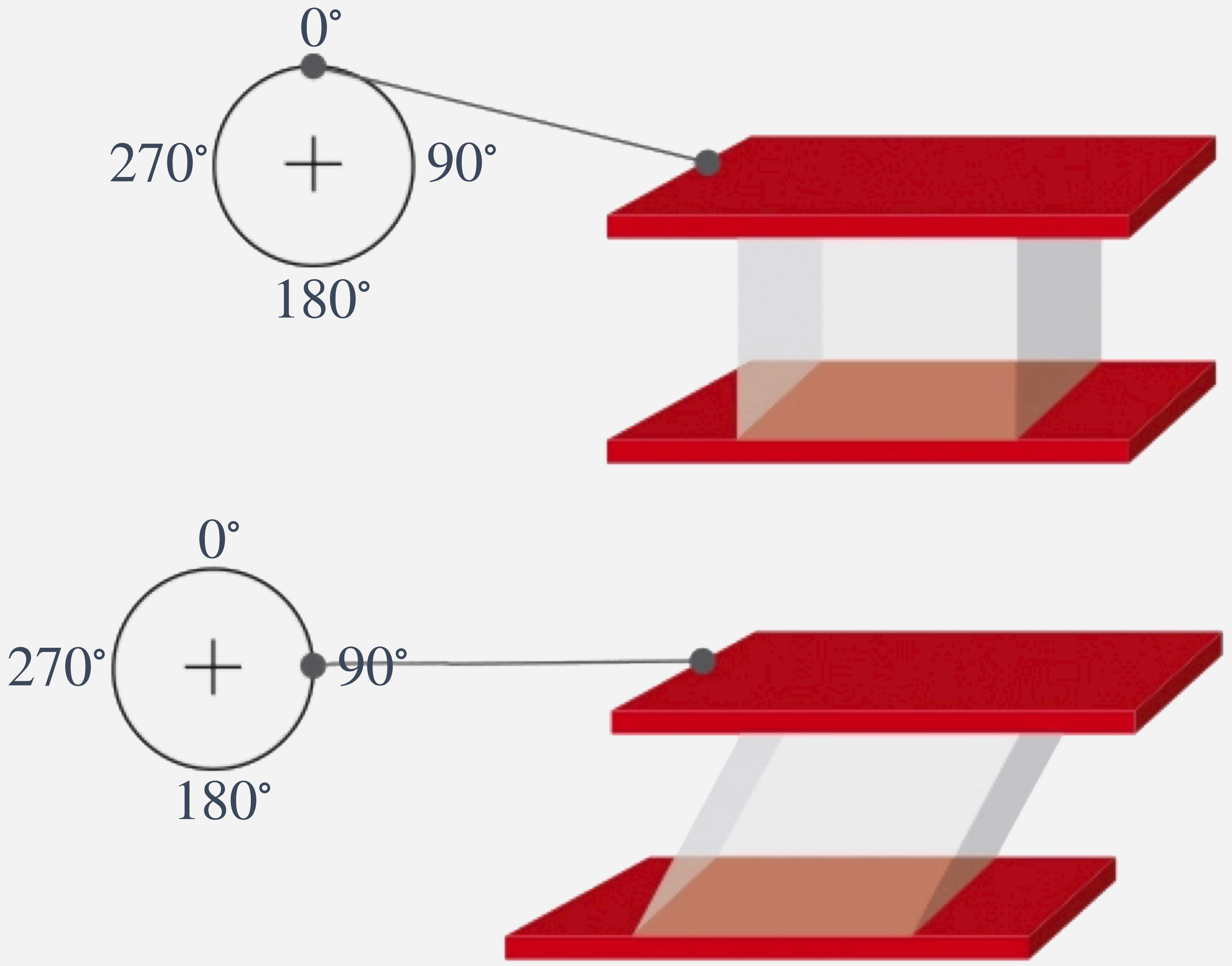
$\gamma(t) = \gamma_0 \sin(\omega t)$

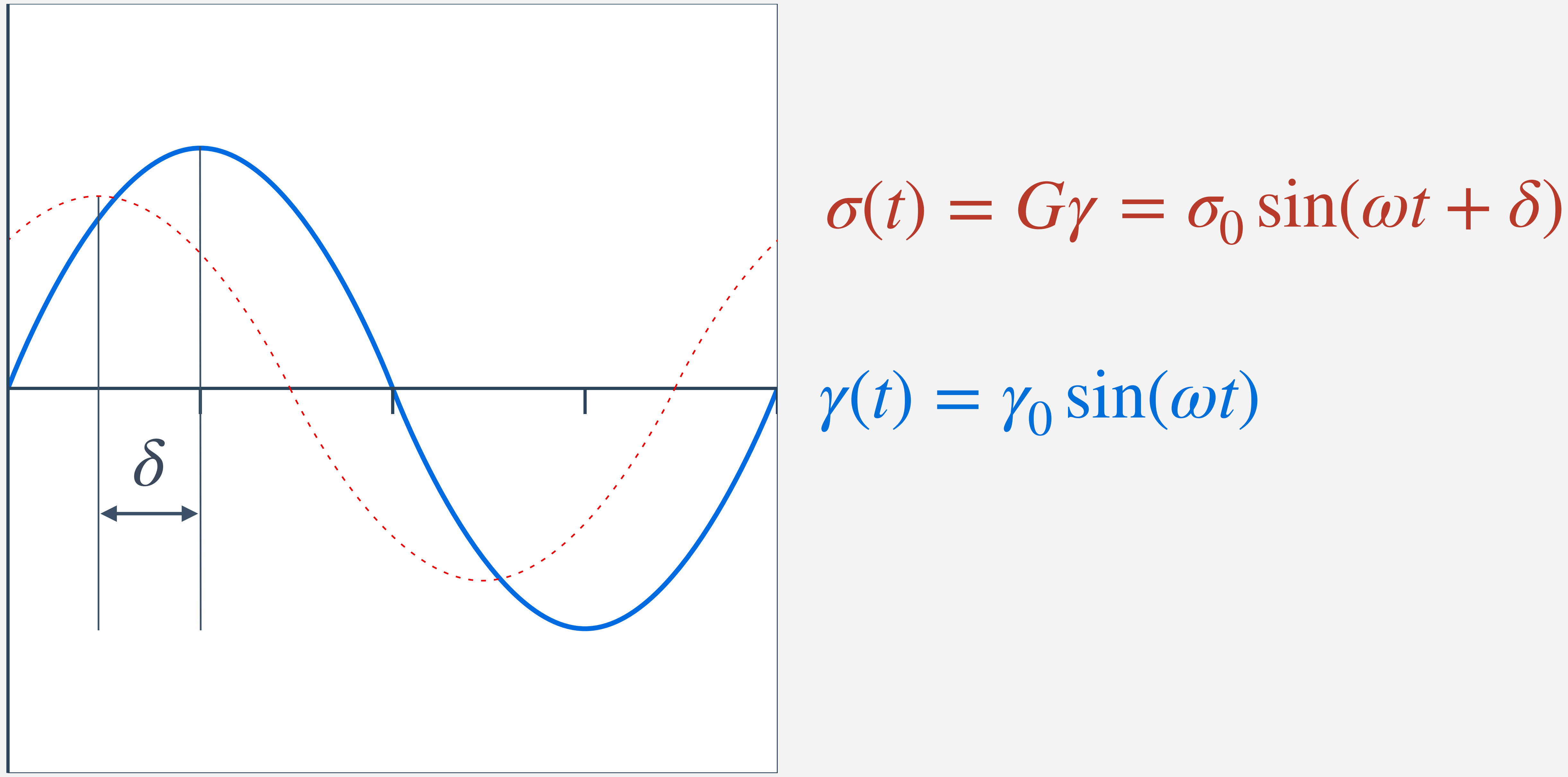
typical for liquids

- **stress is measured as a function of T (at constant ω) or of ω (at constant T)**

Periodic Deformation

- **oscillatory tests probe both solid-like and liquid-like responses**





Hookean solid
$\delta = 0°$

viscoelastic material
$0° < |\delta| < 90°$

Newtonian fluid
$\delta = 90°$

- **the deformation is typically applied as a sine wave**

Storage Modulus, Loss Modulus & Loss Factor

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) = \sigma_0(\sin(\omega t)\cos(\delta) + \cos(\omega t)\sin(\delta))$$

$$\frac{\sigma(t)}{\gamma_0} = \frac{\sigma_0}{\gamma_0}(\sin(\omega t)\cos(\delta)) + \frac{\sigma_0}{\gamma_0}(\cos(\omega t)\sin(\delta)) \equiv G' \sin(\omega t) + G'' \cos(\omega t)$$

storage modulus:

$$\boxed{G' = \frac{\sigma_0}{\gamma_0}\cos(\delta)}$$

loss modulus:

$$\boxed{G'' = \frac{\sigma_0}{\gamma_0}\sin(\delta)}$$

loss factor:

$$\boxed{\tan(\delta) = \frac{G''}{G'}}$$

- **storage modules G': elastic portion of the viscoelastic behavior** (stored deformation energy)
- **loss modulus G'': viscous portion of the viscoelastic behavior** (dissipated energy during viscous flow)
- **loss factor or damping factor $\tan(\delta)$: ratio between G'' and G'** (maxima often indicate transitions)

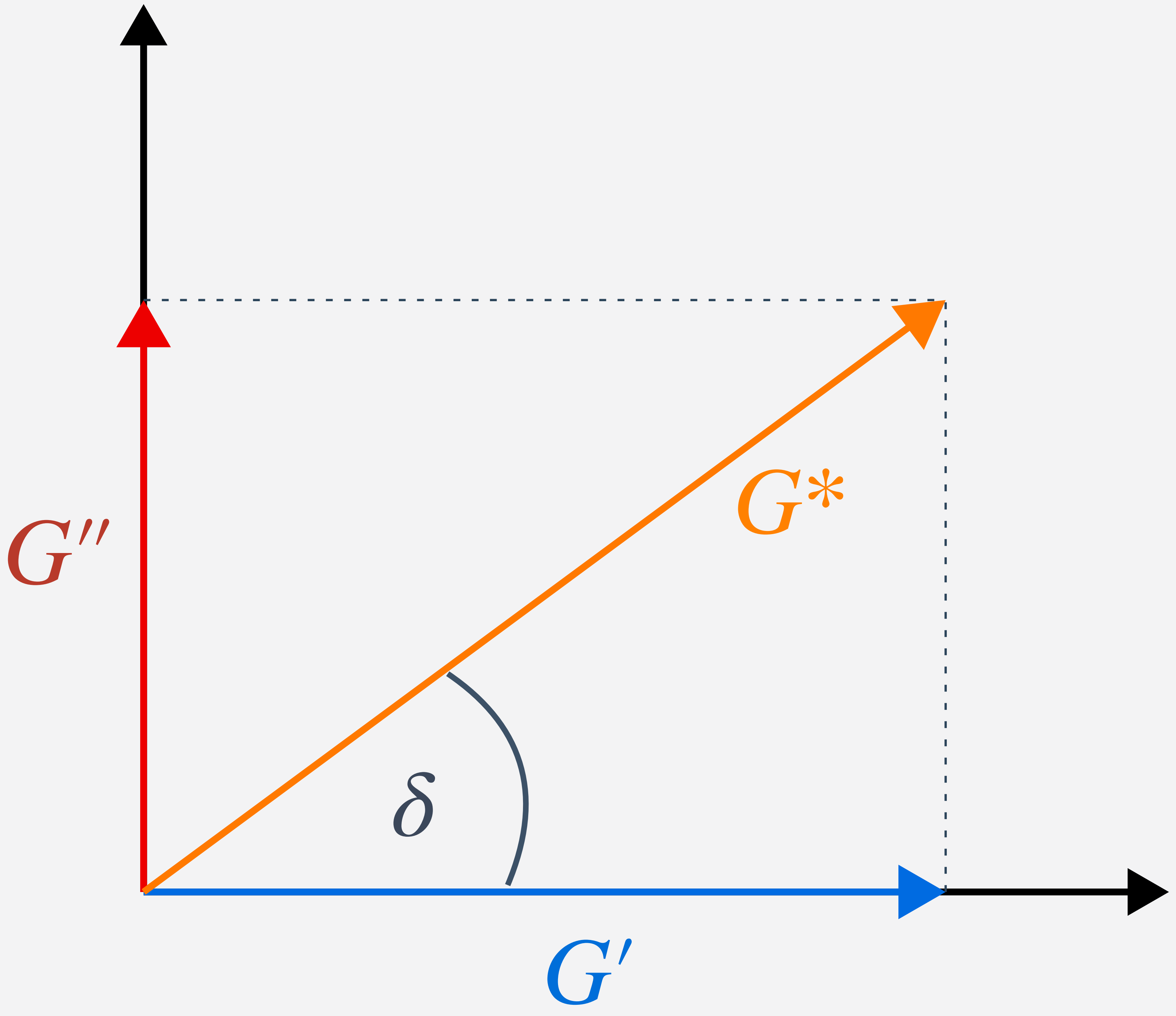
Complex Moduli

- **the entire viscoelastic response is described by the complex shear modulus** $G*$

$$G* = \frac{\sigma*}{\gamma*} = \frac{\sigma_0 e^{i(\omega t+\delta)}}{\gamma_0 e^{(i\omega t)}}$$

$$= \frac{\sigma_0 e^{(i\delta)}}{\gamma_0} = \frac{\sigma_0(\cos(\delta) + i\ \ \sin(\delta))}{\gamma_0}$$

$$= G' + iG''$$



viscoelastic solids: $G' > G''$

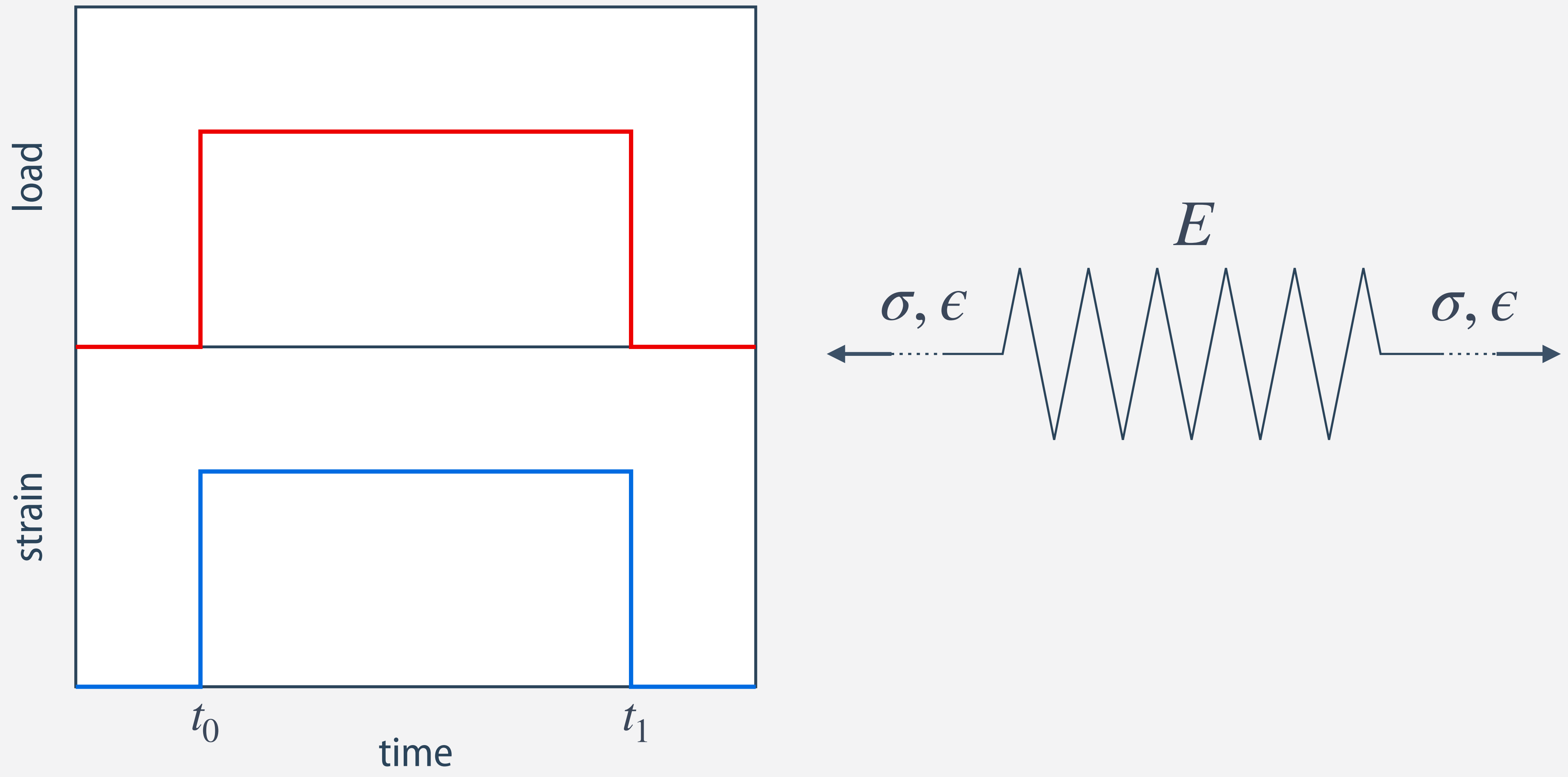
viscoelastic liquids: $G'' > G'$

- ***G'* and *G''* represent the real and imaginary components of the total response**

Simple Mechanical Models

Elastic Springs and Dashpots

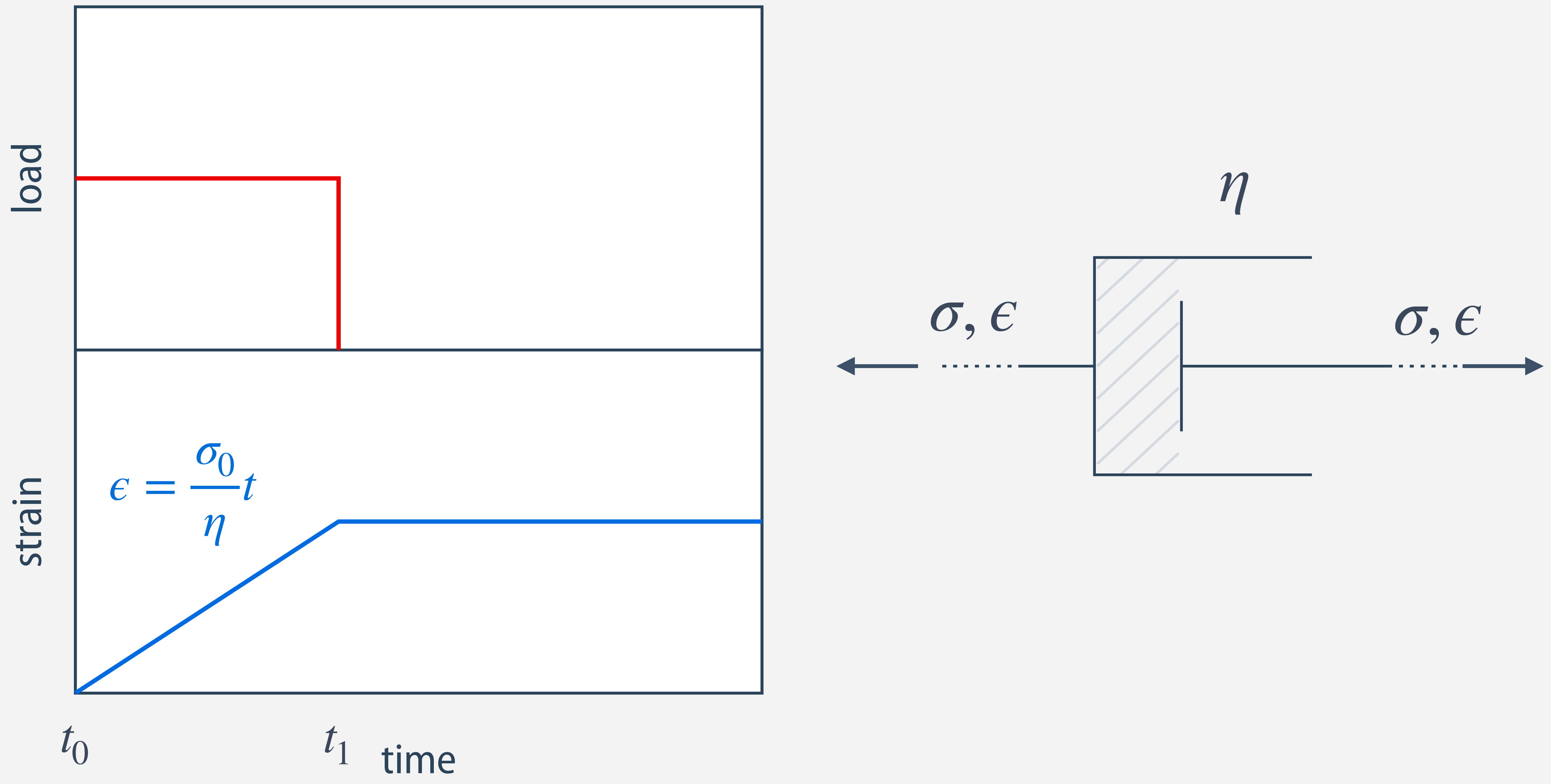
elastic solids
reversible deformation



Hooke's law:

$$\sigma = E\epsilon$$

viscous liquids
irreversible deformation



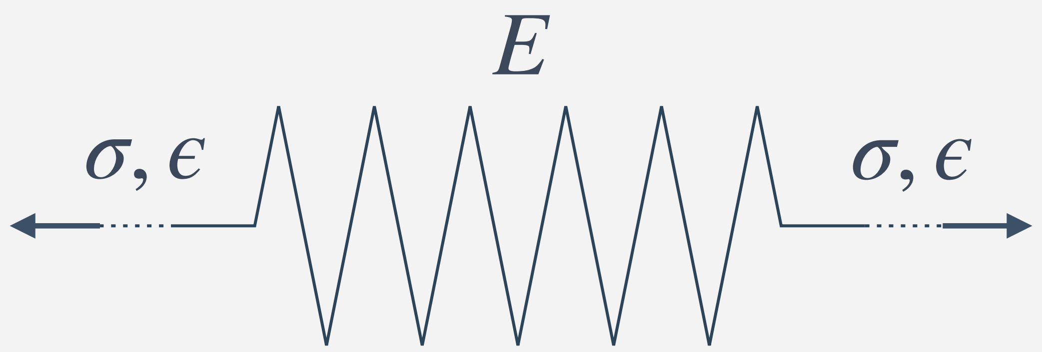
Newton's law:

$$\dot{\epsilon} = \frac{\sigma}{\eta}$$

- **mechanical analogues for elasticity (spring) and viscous flow (dashpot)**

Simple Viscoelastic Models: Linear Combinations of Dashpots & Elastic Springs

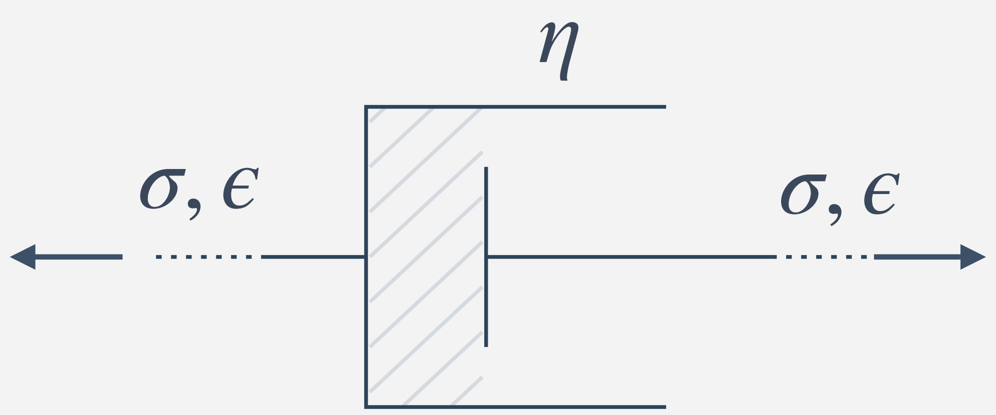
elastic solids



Hooke's law:

$$\sigma = E\epsilon$$

viscous liquids



Newton's law:

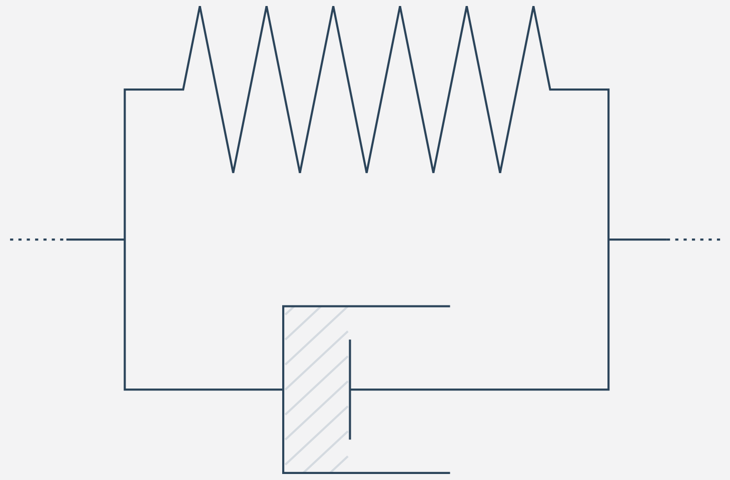
$$\dot{\epsilon} = \frac{\sigma}{\eta}$$

Maxwell model

$$\sigma = \sigma_1 = \sigma_2$$

$$\epsilon = \epsilon_1 + \epsilon_2$$

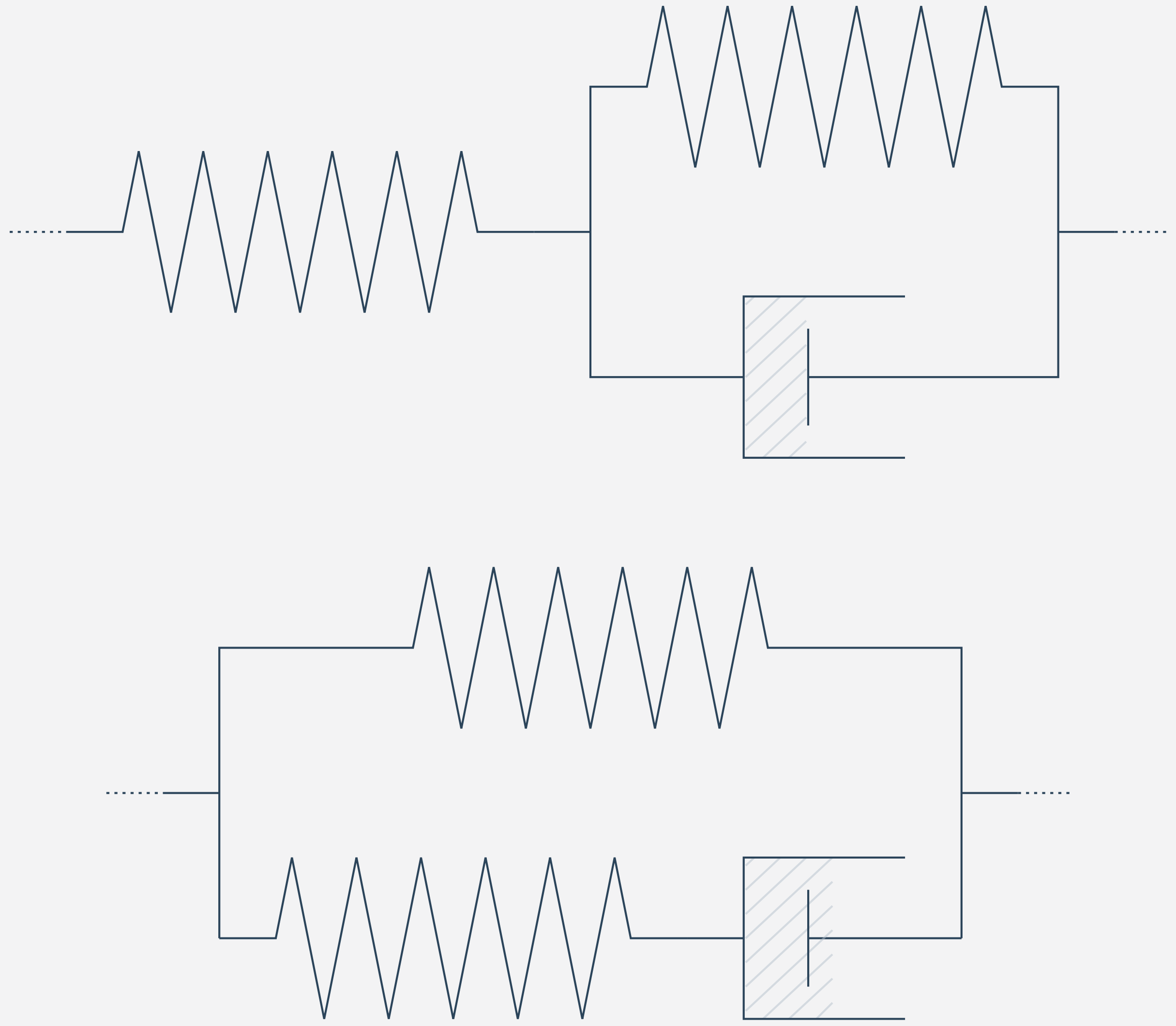
Voigt model



$$\sigma = \sigma_1 + \sigma_2$$

$$\epsilon = \epsilon_1 = \epsilon_2$$

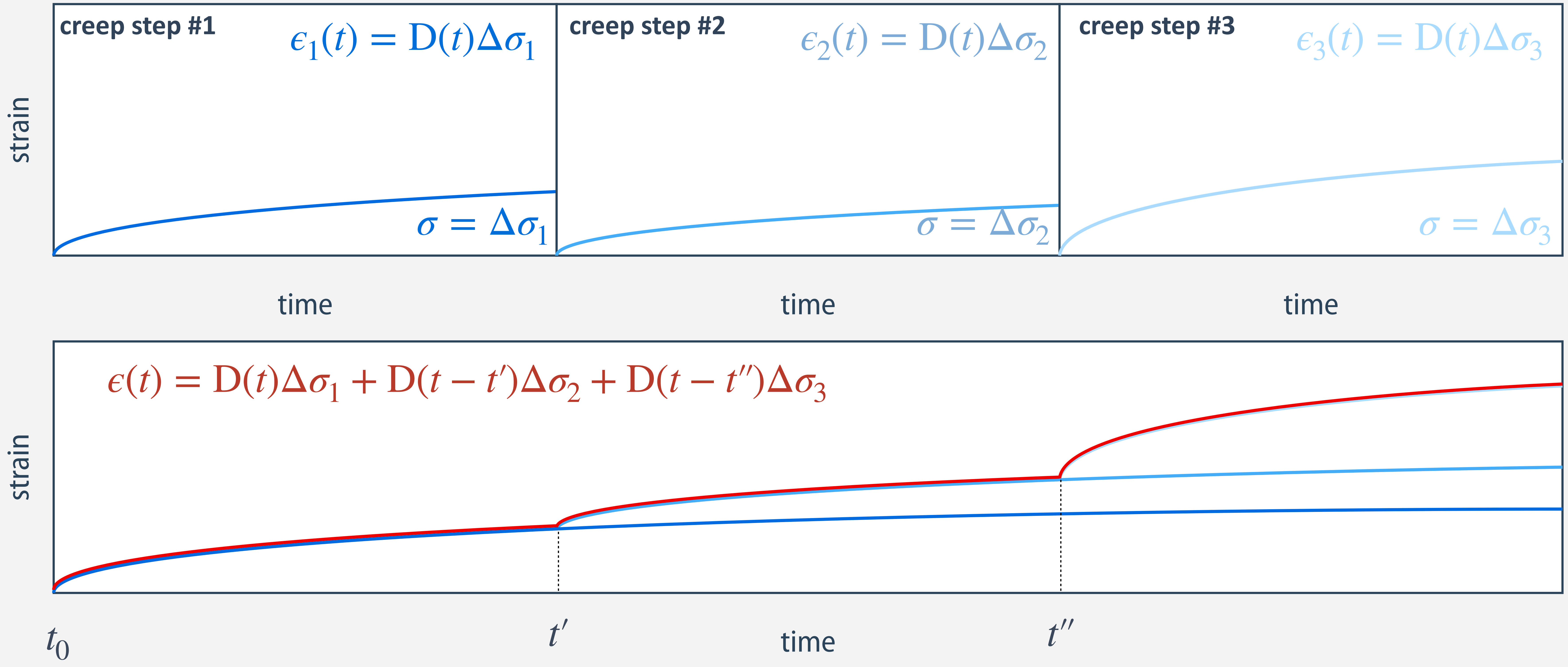
Zener models (standard linear solid)



Voigt model: see **Exercise**

Boltzmann’s Superposition Principle

- **the state of stress or strain depends on the entire loading history:**



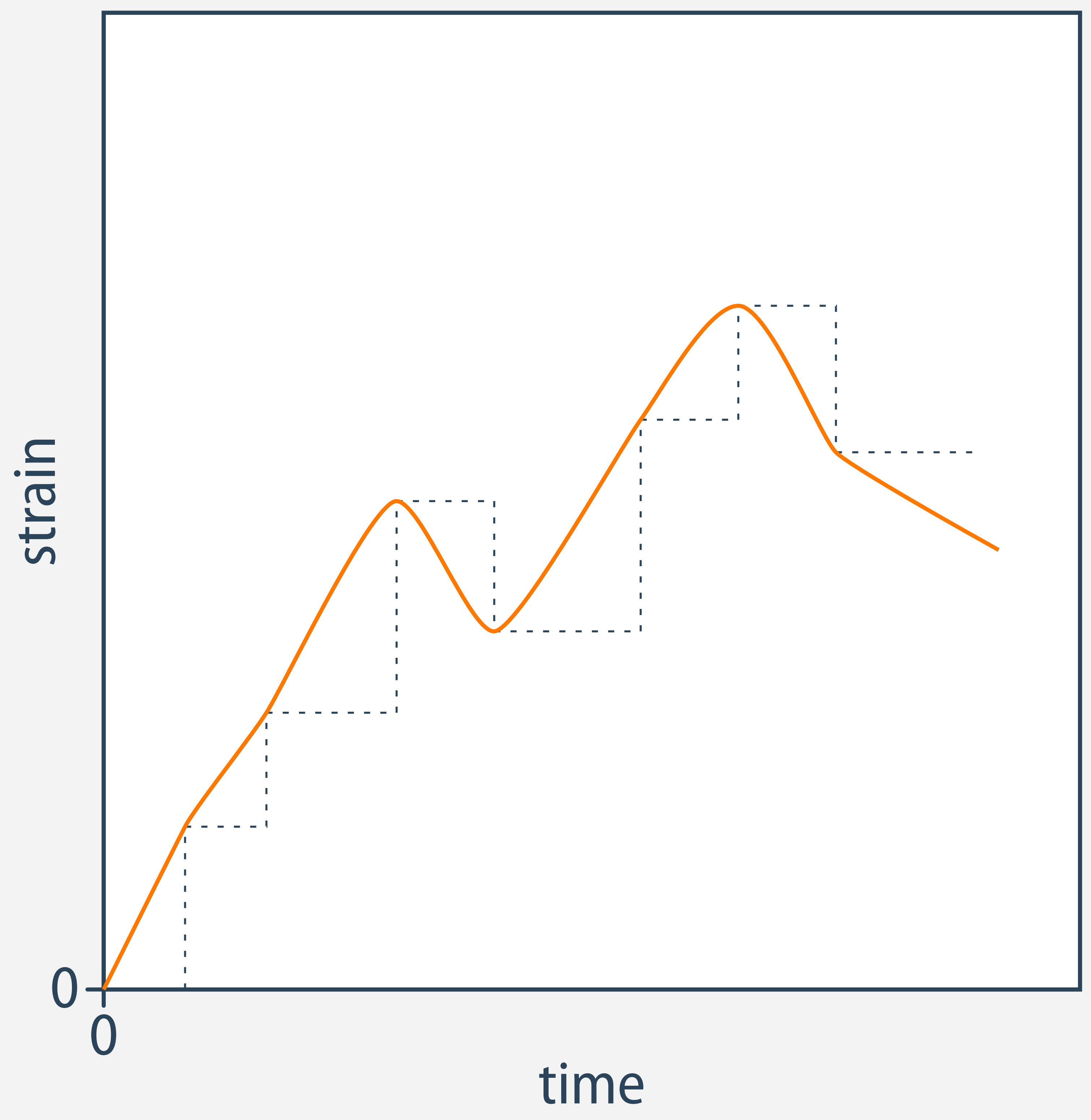
- **generalized discrete form:** $\boxed{\epsilon(t) = \sum_{n=0} \mathrm{D}(t-t_n)\Delta\sigma_n}$

- **the material “remembers” all previous stresses or or deformations**

Continuous Boltzmann Superposition

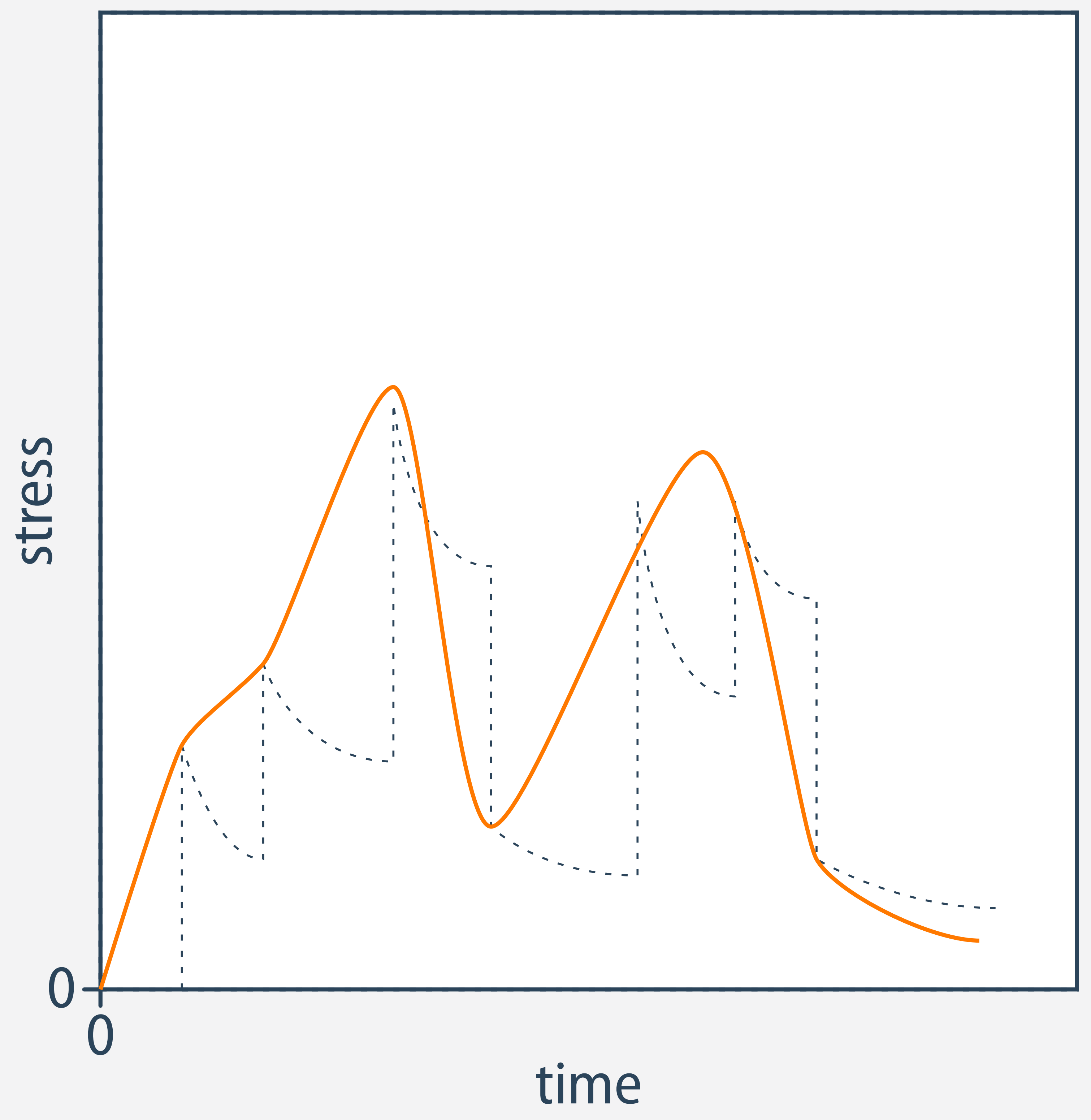
- **in the continuous limit: Boltzmann superposition integral**

creep experiment:



$$\epsilon(t) = \int_{-\infty}^{t} \mathrm{D}(t - t')\frac{\mathrm{d}\sigma}{\mathrm{d}t'}\mathrm{d}t'$$

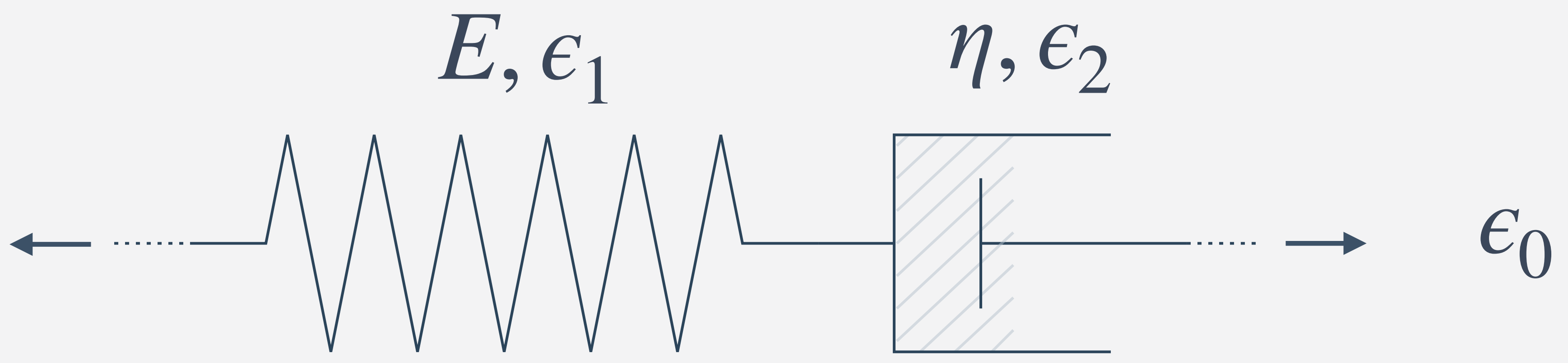
for stress relaxation



$$\sigma(t) = \int_{-\infty}^{t} \mathrm{E}(t - t')\frac{\mathrm{d}\epsilon}{\mathrm{d}t'}\mathrm{d}t'$$

Maxwell Model

- series combination of one spring and one dashpot:



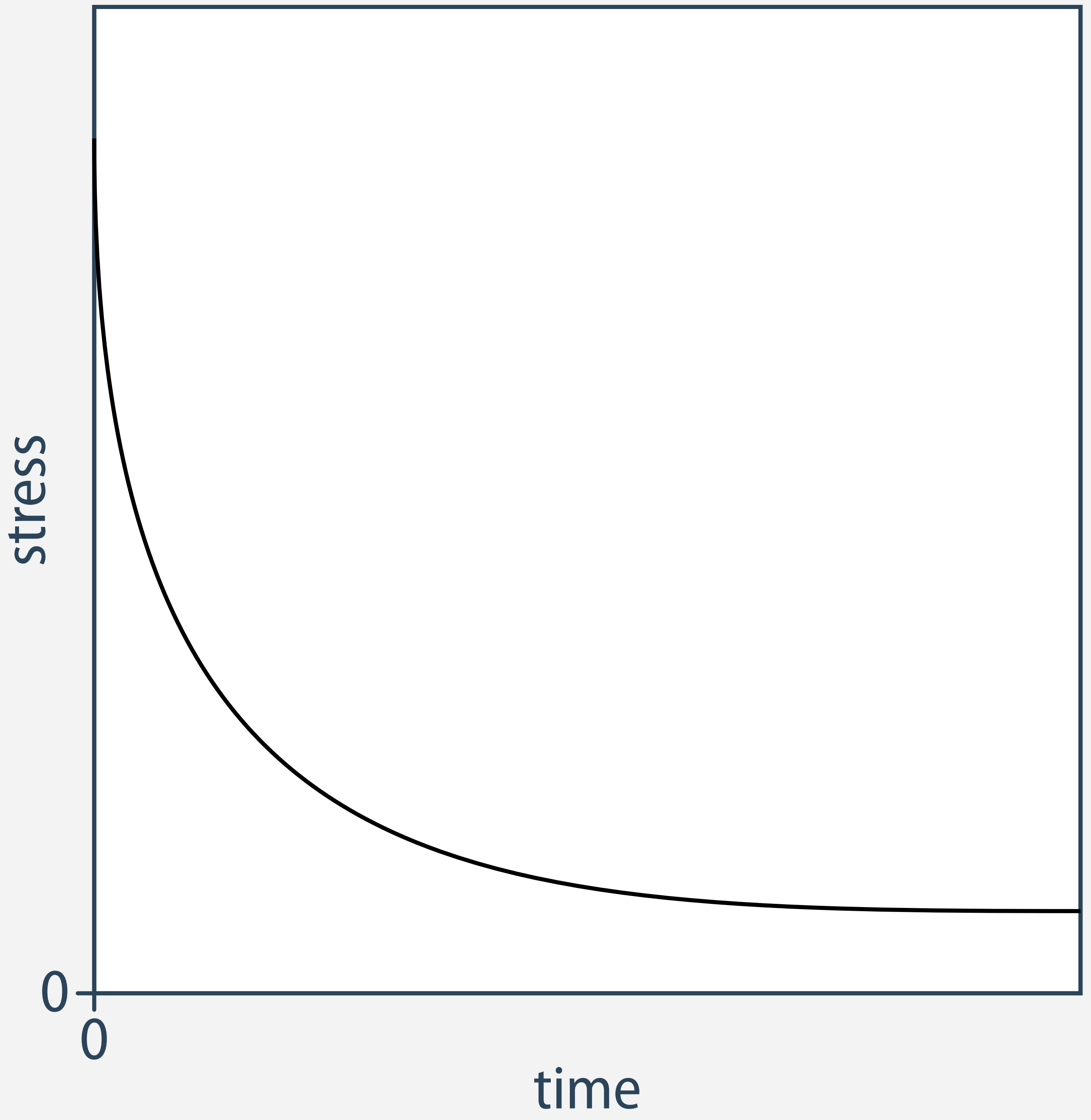
$\epsilon = \epsilon_1 + \epsilon_2 = \epsilon_0 =$ constant
(for a relaxation experiment)

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}t} = \frac{\mathrm{d}\epsilon_1}{\mathrm{d}t} + \frac{\mathrm{d}\epsilon_2}{\mathrm{d}t} = \frac{1}{E}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{\sigma}{\eta} = 0$$

$$\frac{\mathrm{d}\sigma}{\sigma} = -\frac{E}{\eta}\mathrm{d}t \quad \rightarrow \quad [\ln(\sigma)]_{\sigma_0}^{\sigma} = -\frac{E}{\eta}[t']_0^t$$

$$\sigma = \sigma_0 e^{(-t/\tau)} \quad \text{with} \quad \tau = \frac{\eta}{E}$$

$$\mathrm{E}(t) = \frac{\sigma}{\epsilon_0} = \frac{\sigma_0}{\epsilon_0} e^{(-t/\tau)} = E e^{(-t/\tau)}$$



- **describes stress relaxation, characterised by a single relaxation time τ**

Maxwell Model under Dynamic Deformation

- **for sinusoidal strain:** $\epsilon^* = \epsilon_0 e^{(i\omega t)}$ $\quad \dfrac{\mathrm{d}\epsilon^*}{\mathrm{d}t} = i\omega\epsilon_0 e^{(i\omega t)}$

- **for the stress under continuous deformation follows using the Boltzmann principle:**

$$\sigma^* = \int_{-\infty}^{t} \mathrm{E}(t-t')\frac{\mathrm{d}\epsilon^*}{\mathrm{d}t'}\mathrm{d}t' = \int_{-\infty}^{t} Ee^{-\frac{t-t'}{\tau}}\epsilon_0 i\omega e^{(i\omega t')}\mathrm{d}t'$$

$$= \frac{Ei\omega\epsilon_0}{\frac{1}{\tau}+i\omega}\left[e^{(-\frac{t-t'}{\tau}+i\omega t')}\right]_{-\infty}^{t} = \frac{Ei\omega\epsilon_0}{\frac{1}{\tau}+i\omega}e^{i\omega t} = \frac{Ei\omega\epsilon_0(\frac{1}{\tau}-i\omega)}{\frac{1}{\tau^2}+\omega^2}e^{i\omega t} = \frac{Ei\epsilon_0(\omega\tau - i(\omega\tau)^2)}{1+(\omega\tau)^2}e^{i\omega t}$$

- **the complex modulus and loss factor are then given by:**

$$E^* = \frac{\sigma^*}{\epsilon^*} = \frac{Ei(\omega\tau - i(\omega\tau)^2)}{1+(\omega\tau)^2} = \frac{E(\omega\tau)^2}{1+(\omega\tau)^2} + \frac{iE\omega\tau}{1+(\omega\tau)^2} = E' + iE''$$

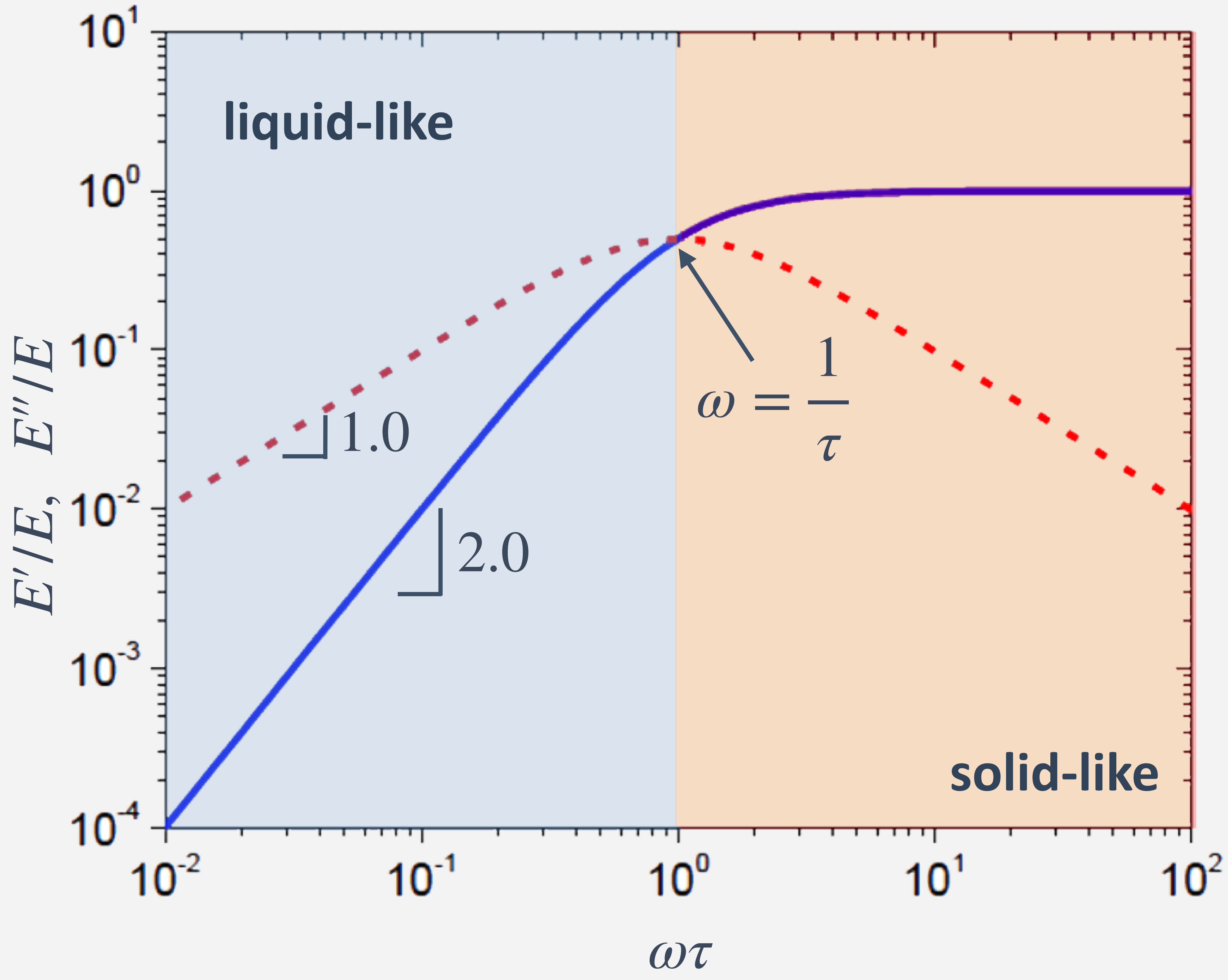
$$\tan(\delta) = \frac{E''}{E'} = \frac{1}{\omega\tau}$$

Modeling Rheology Curves

- **for the complex modulus it follows:**

$$= E^* = \frac{\sigma^*}{\epsilon^*} = \frac{Ei\omega}{\frac{1}{\tau} + i\omega}$$

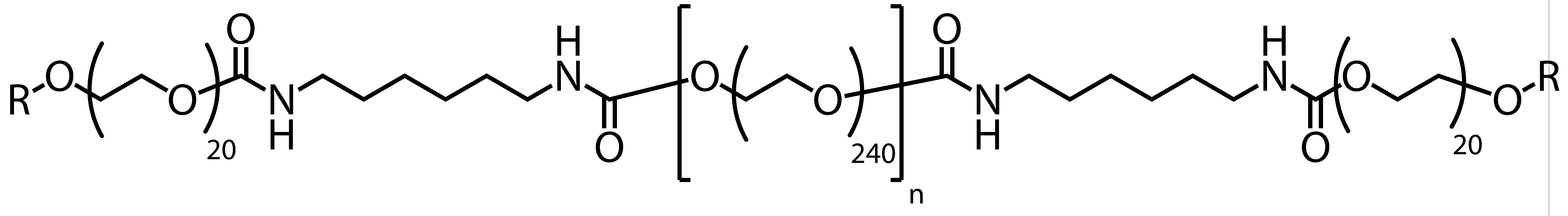
$$= E' + iE'' = \frac{E(\omega\tau)^2}{1 + (\omega\tau)^2} + \frac{iE\omega\tau}{1 + (\omega\tau)^2}$$



- **relaxation time τ marks the transition from liquid-like to solid-like behavior**
- **E' and E'' show universal frequency dependence in the terminal regime ($\omega \ll \tau$)**

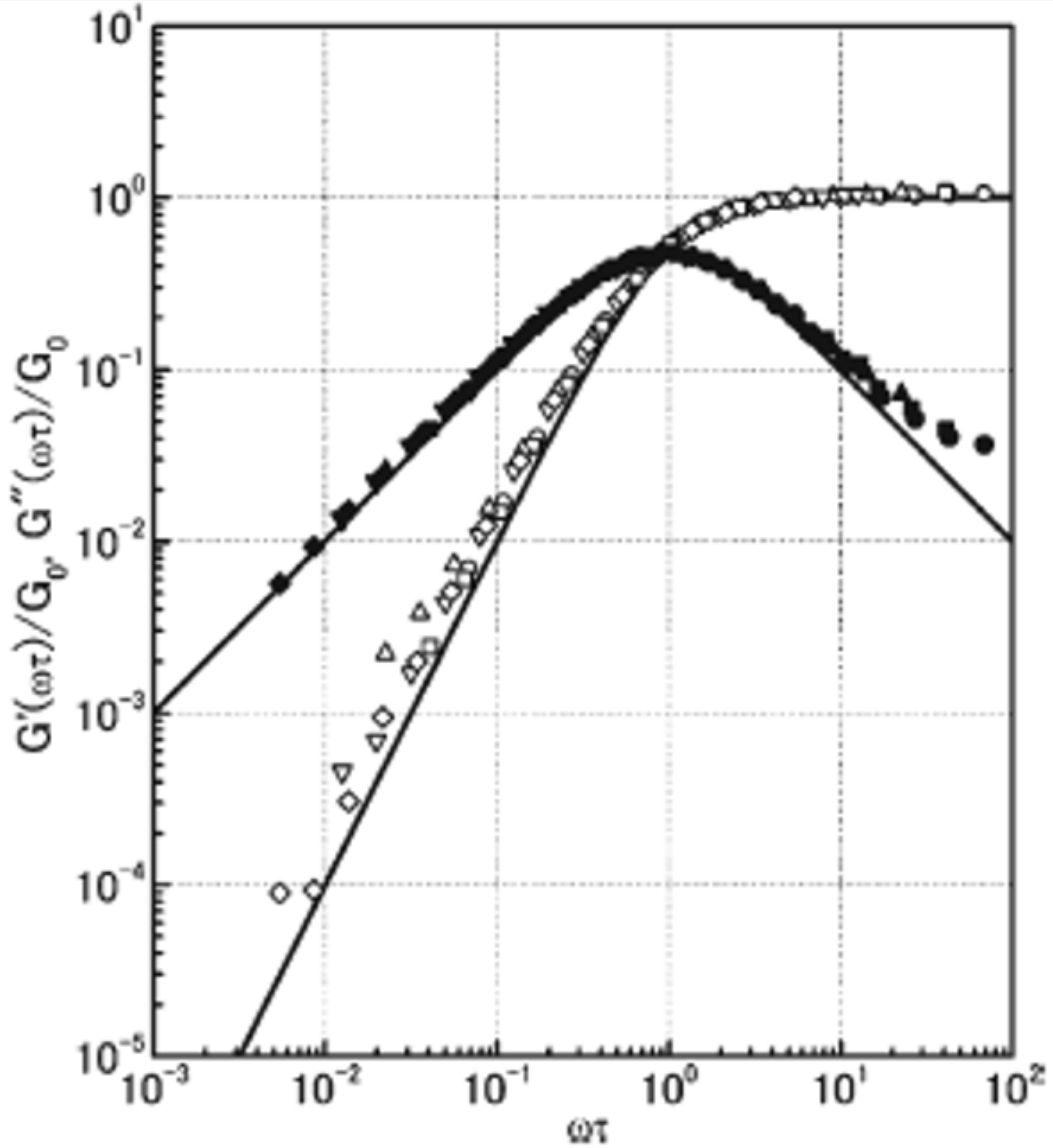
Experimental Validation

- **Maxwell behavior is often encountered in temporary networks from small molecules (due to the formation of hydrogen-bonds, for example) with a single relaxation time τ**



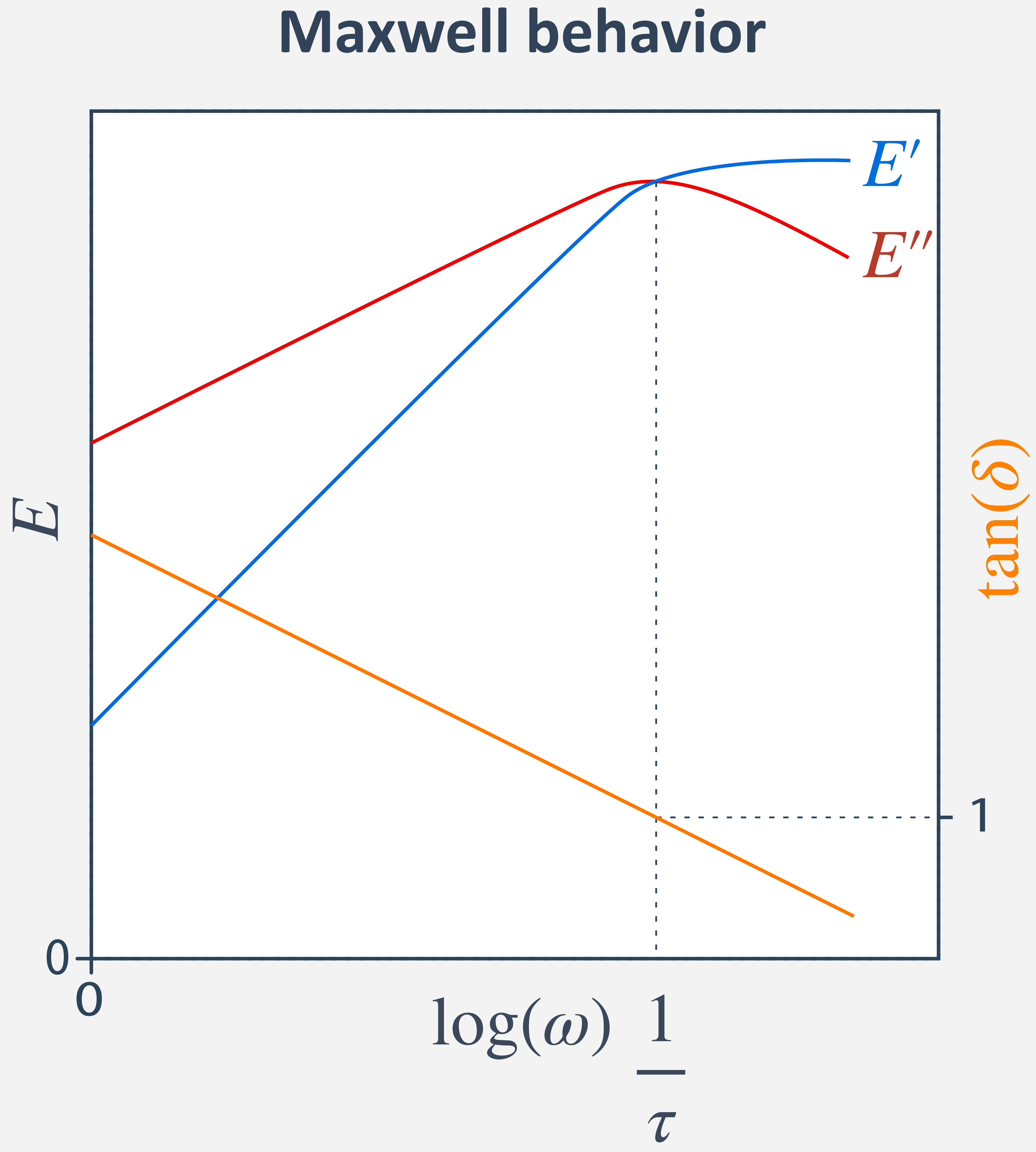
+

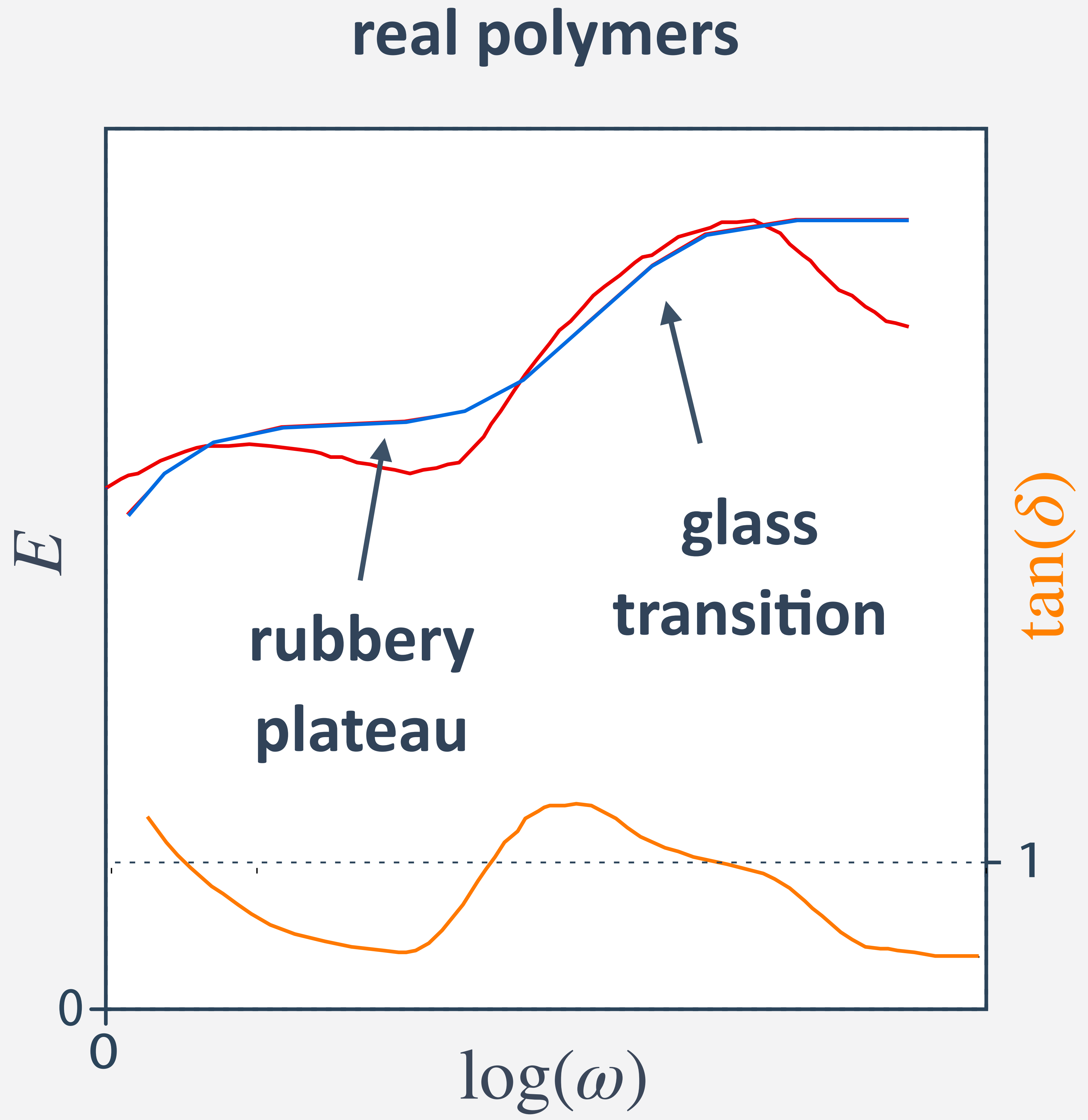
MeOH



Rheol. Acta **2012**, *51*, 89-96.

Limitations

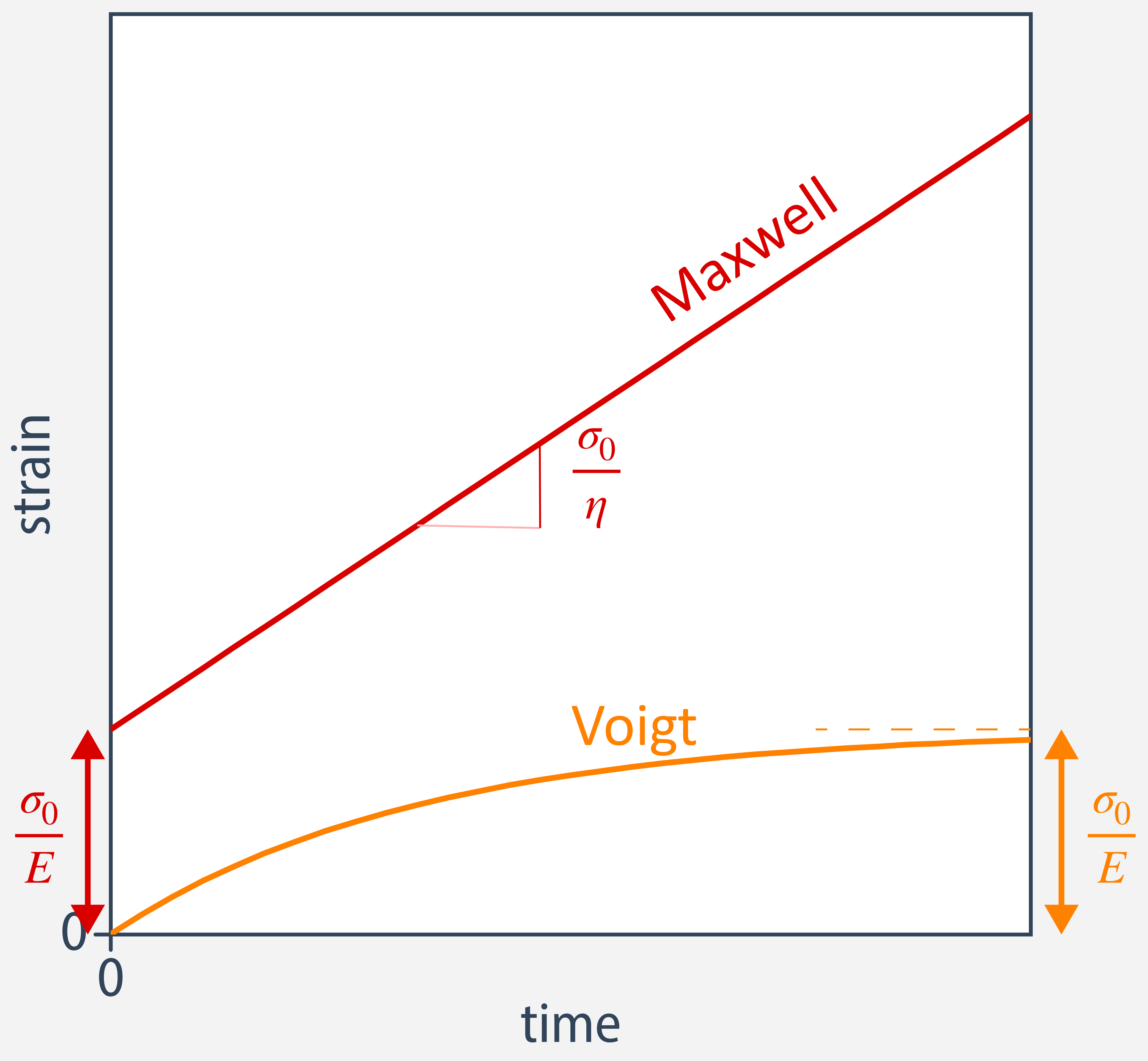




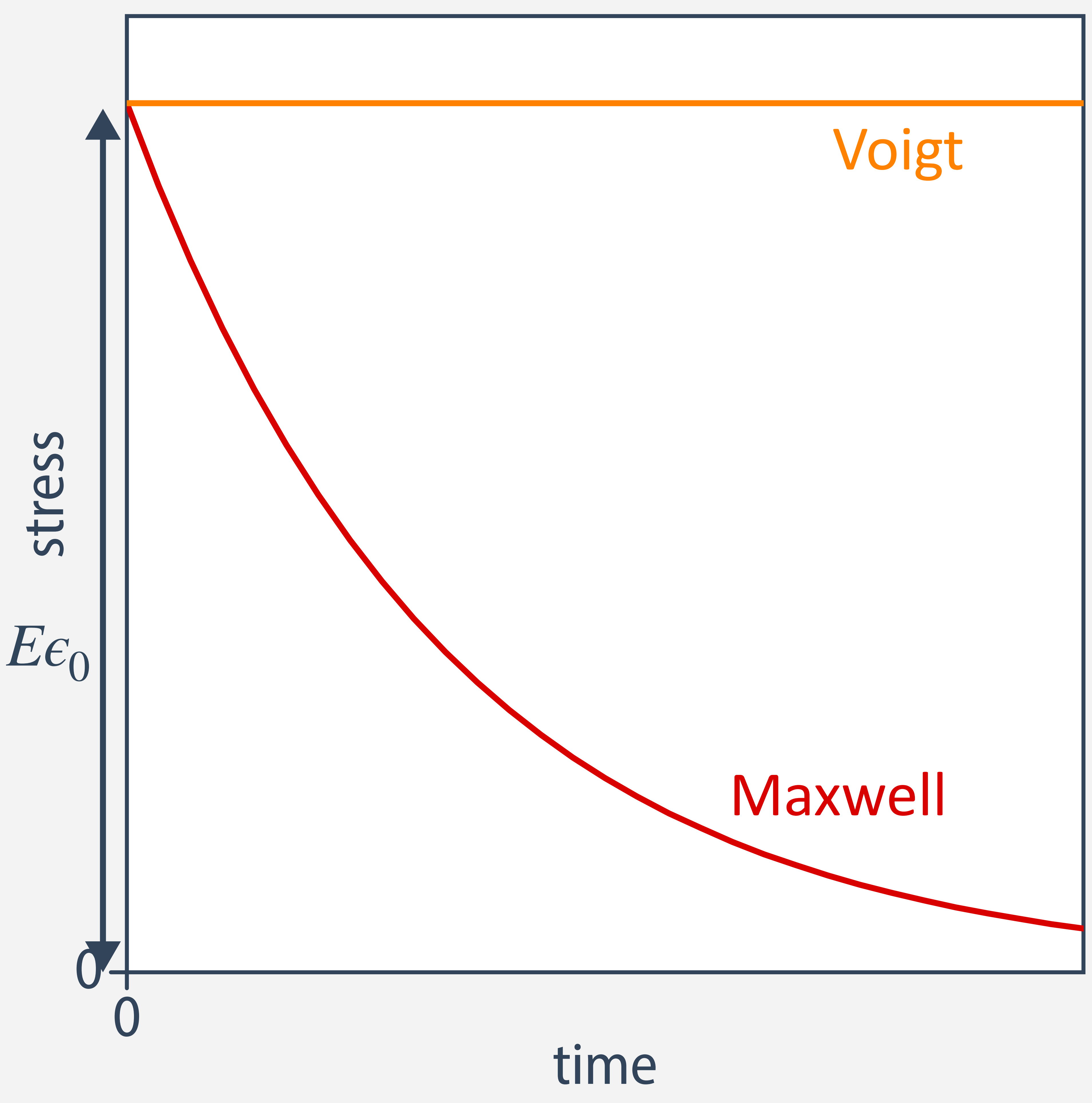
- the Maxwell model is oversimplified for real polymers
- the Voigt model (parallel arrangement of spring and dashpot) also fails (see Exercise)

Maxwell vs. Voigt Model

creep experiment
(constant stress σ_0)



relaxation experiment
(constant strain ϵ_0)

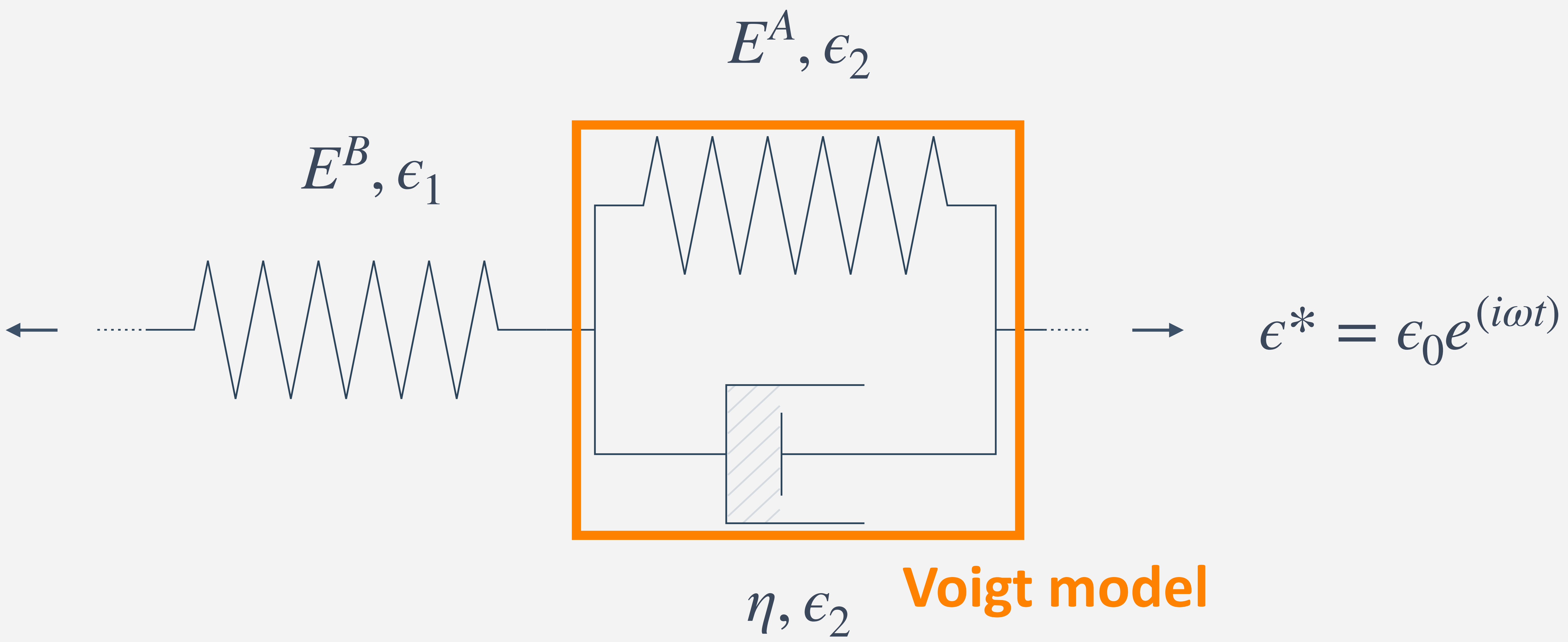


see corresponding **Exercise** for details

Three Element Models

- **Example: Zener model**

  (combined Maxwell and Voigt elements)



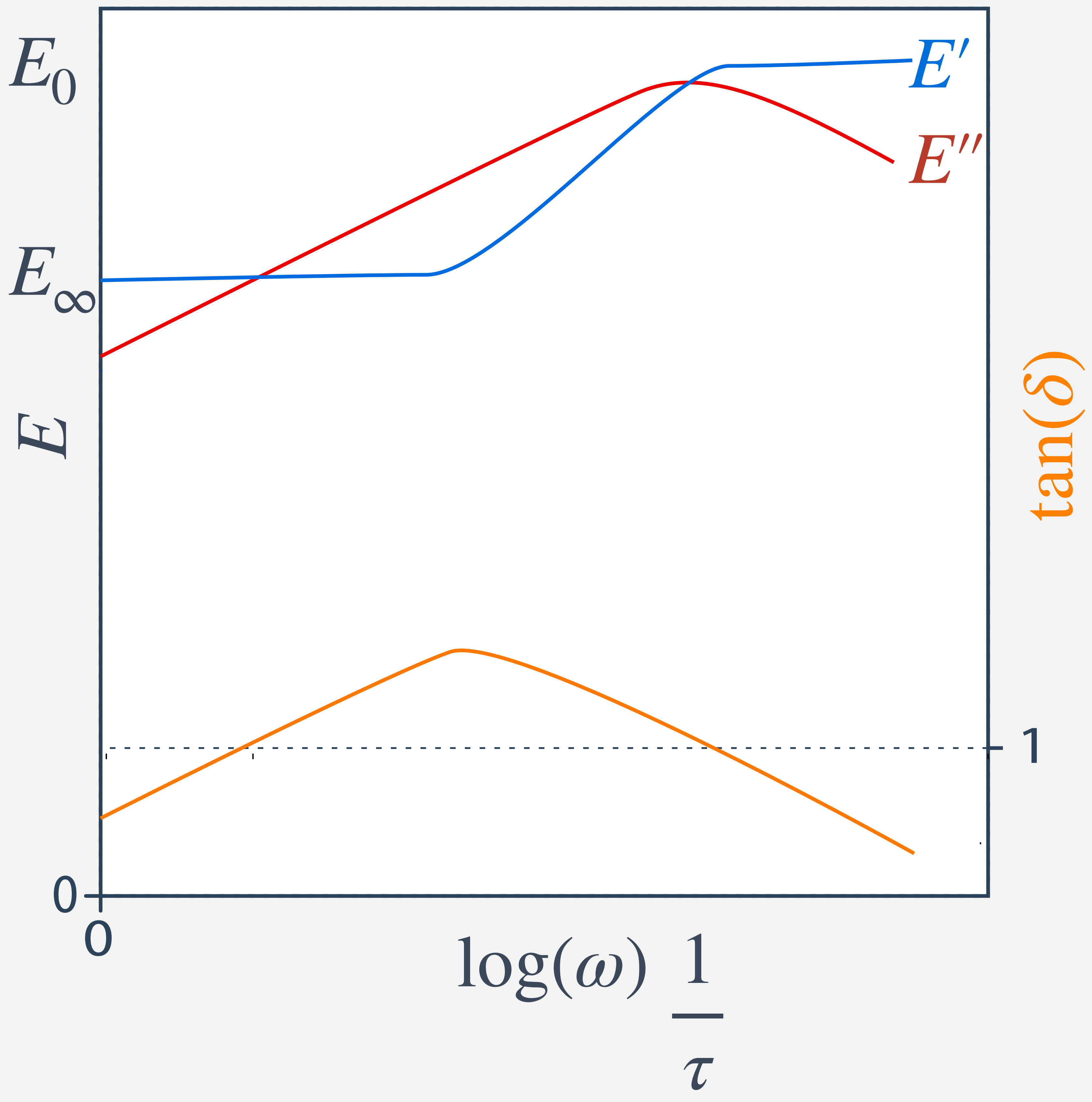
- **we use:** $E_0 = E^B$ $\quad E_\infty = \dfrac{E^A E^B}{E^A + E^B}$ $\quad \tau_\delta = \dfrac{\eta(E_0 - E_\infty)}{E_0^2}$

- **after some calculations, we find:**

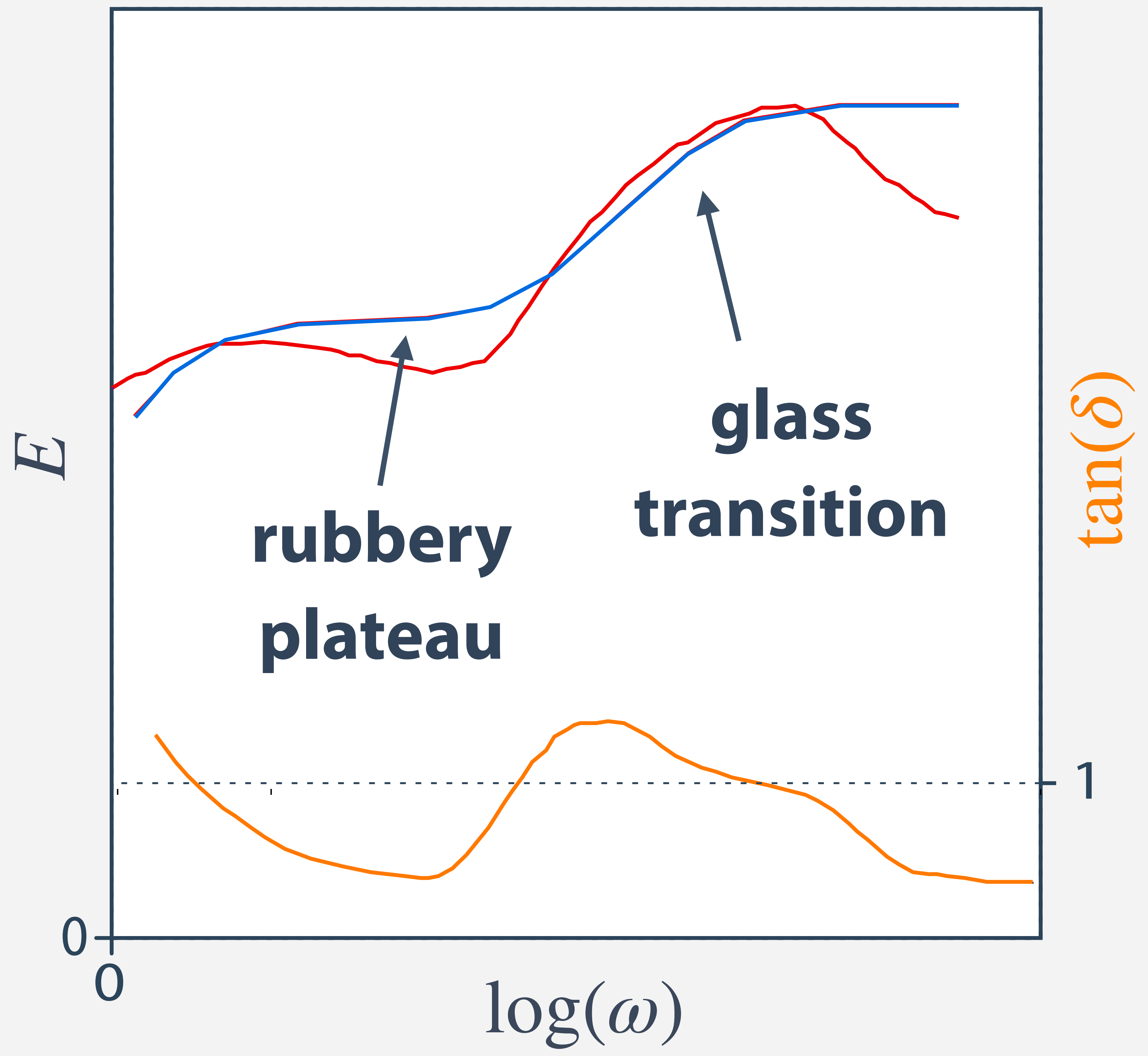
$$E' = E_0 - \frac{E_0 - E_\infty}{1 + (\omega\tau_\delta)^2} \qquad E'' = \omega\tau_\delta \frac{E_0 - E_\infty}{1 + (\omega\tau_\delta)^2} \qquad \tan(\delta) = \frac{\omega\tau_\delta(E_0 - E_\infty)}{\sqrt{E_0 E_\infty}(1 + (\omega\tau_\delta)^2)}$$

Basic Mechanical Behavior

Zener model



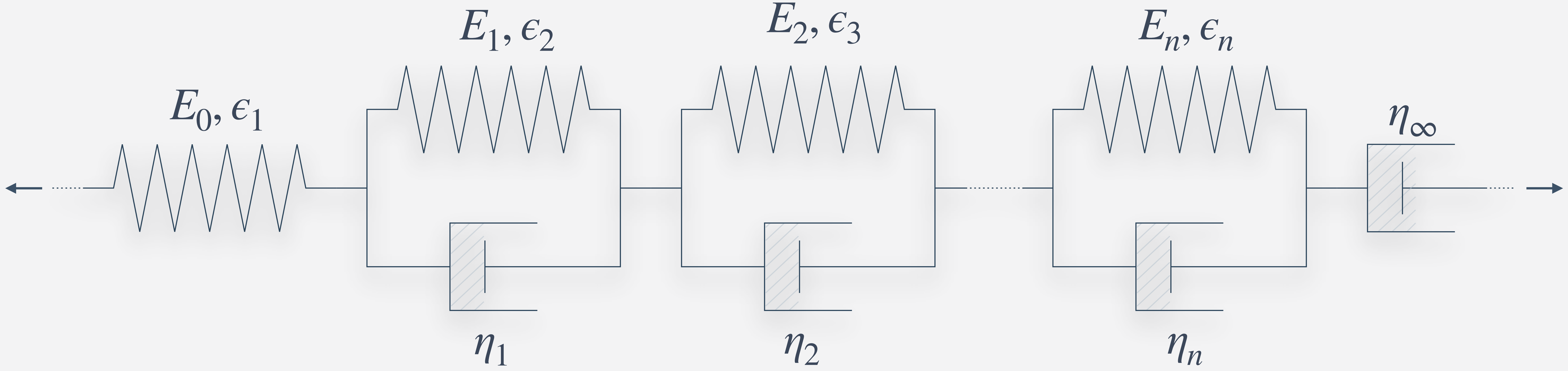
real polymers



- E'' always peaks at the glass transition
- $E' \rightarrow E_0$ for $\omega \ll 1/\tau_\delta$, equals Maxwell model when $E^A = 0$

Generalised Voigt-Maxwell Model

- **multiple relaxation times describe more realistic behavior:**



$$\mathrm{E}(t) = E_\infty + \sum_{1}^{n} E_i e^{\left(-\frac{t}{\tau_i}\right)}$$

- **for continuous conditions, we get the relation to a relaxation time spectrum $H(\tau)$:**

$$\mathrm{E}(t) = E_\infty + \int_{-\infty}^{\infty} H(\tau) e^{-\frac{t}{\tau}} \mathrm{d}\ln\tau$$

- **Cole-Cole equation as another empirical equation:**

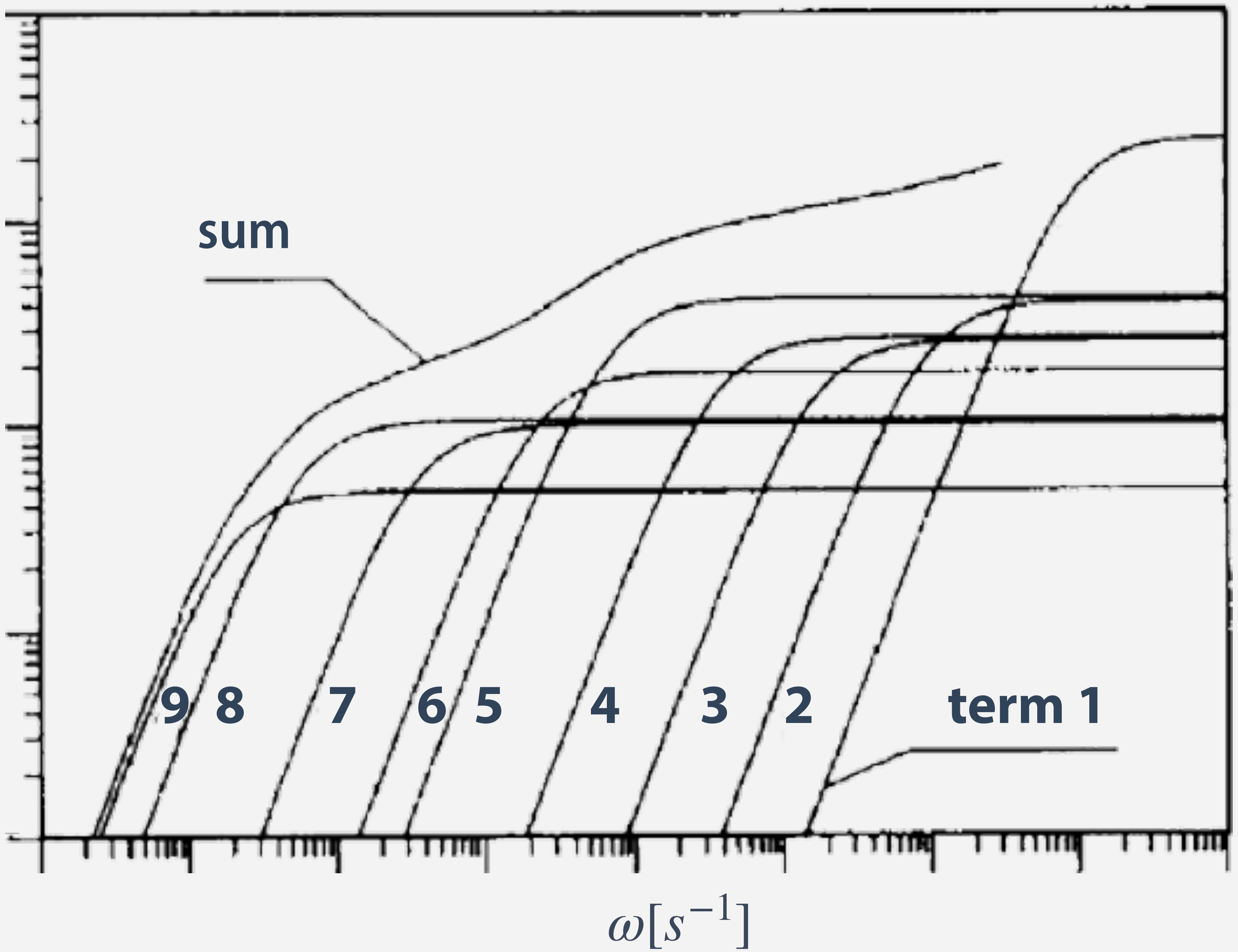
$$\frac{E^* - E_0}{E_\infty - E_0} = \frac{1}{e + (i\omega\tau)^\beta}$$

Generalised Voigt-Maxwell Model Under Dynamic Conditions

$$\mathrm{G}(t) = \sum_{i=1}^{N} G_i e^{-\frac{t}{\tau_i}}$$

$$G'(t) = \sum_{i=1}^{N} G_i \frac{(\omega\tau_i)^2}{1+(\omega\tau_i)^2}$$

$$G''(t) = \sum_{i=1}^{N} G_i \frac{\omega\tau_i}{1+(\omega\tau_i)^2}$$

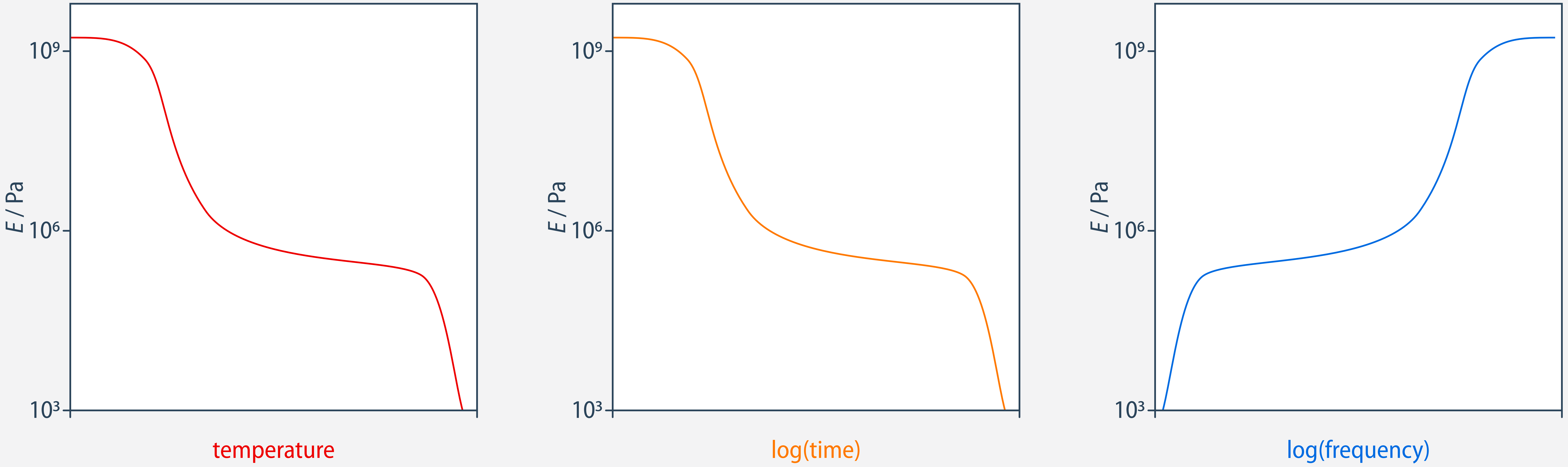


- low-frequency behavior dominated by the longest relaxation time τ
- G_i and τ_i are empirical, often with limited physical meaning

Time-Temperature Equivalence

Time-Temperature Equivalence

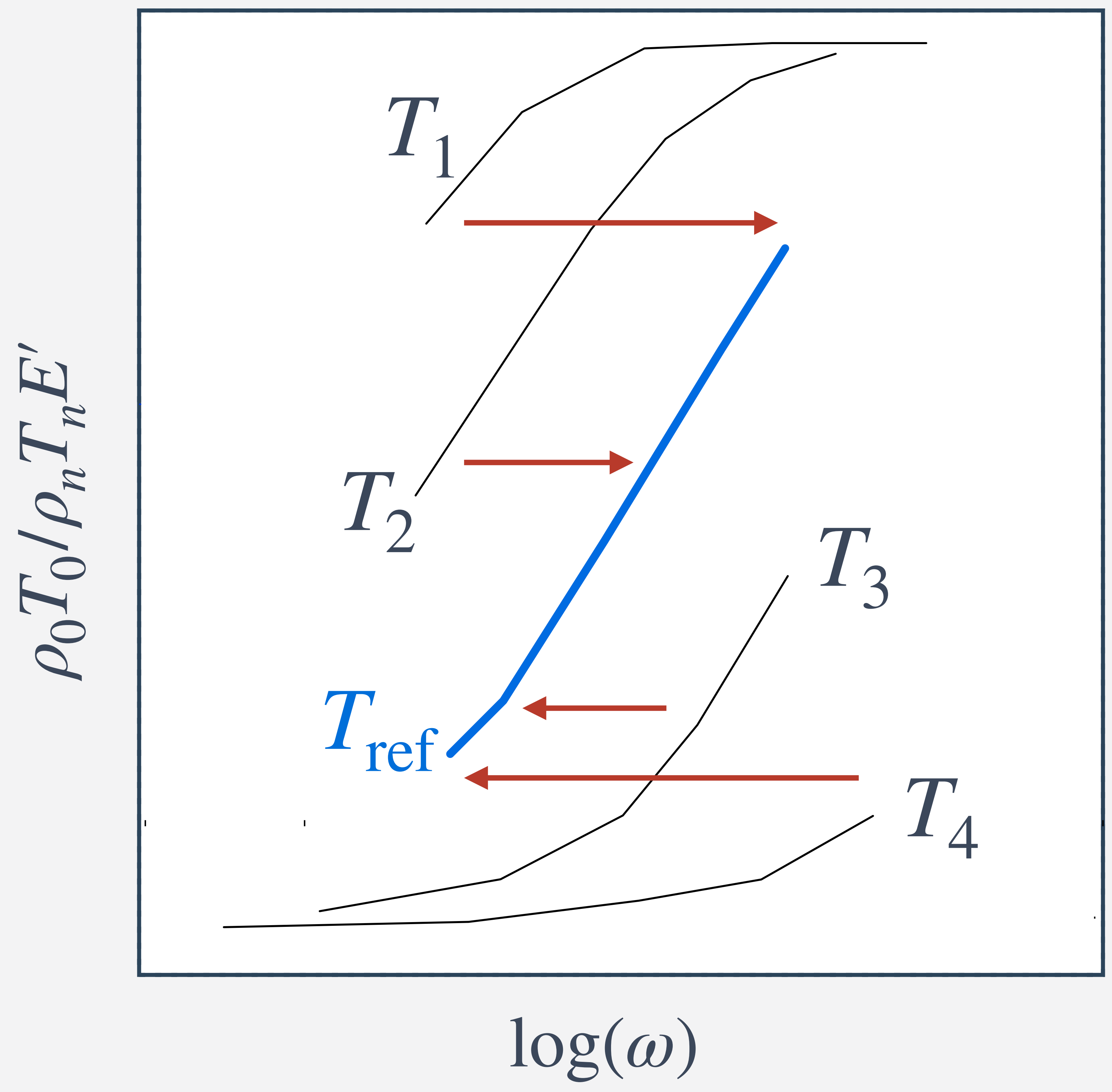
- increasing **temperature** or **time** (or decreasing **frequency**) produces similar effects on E

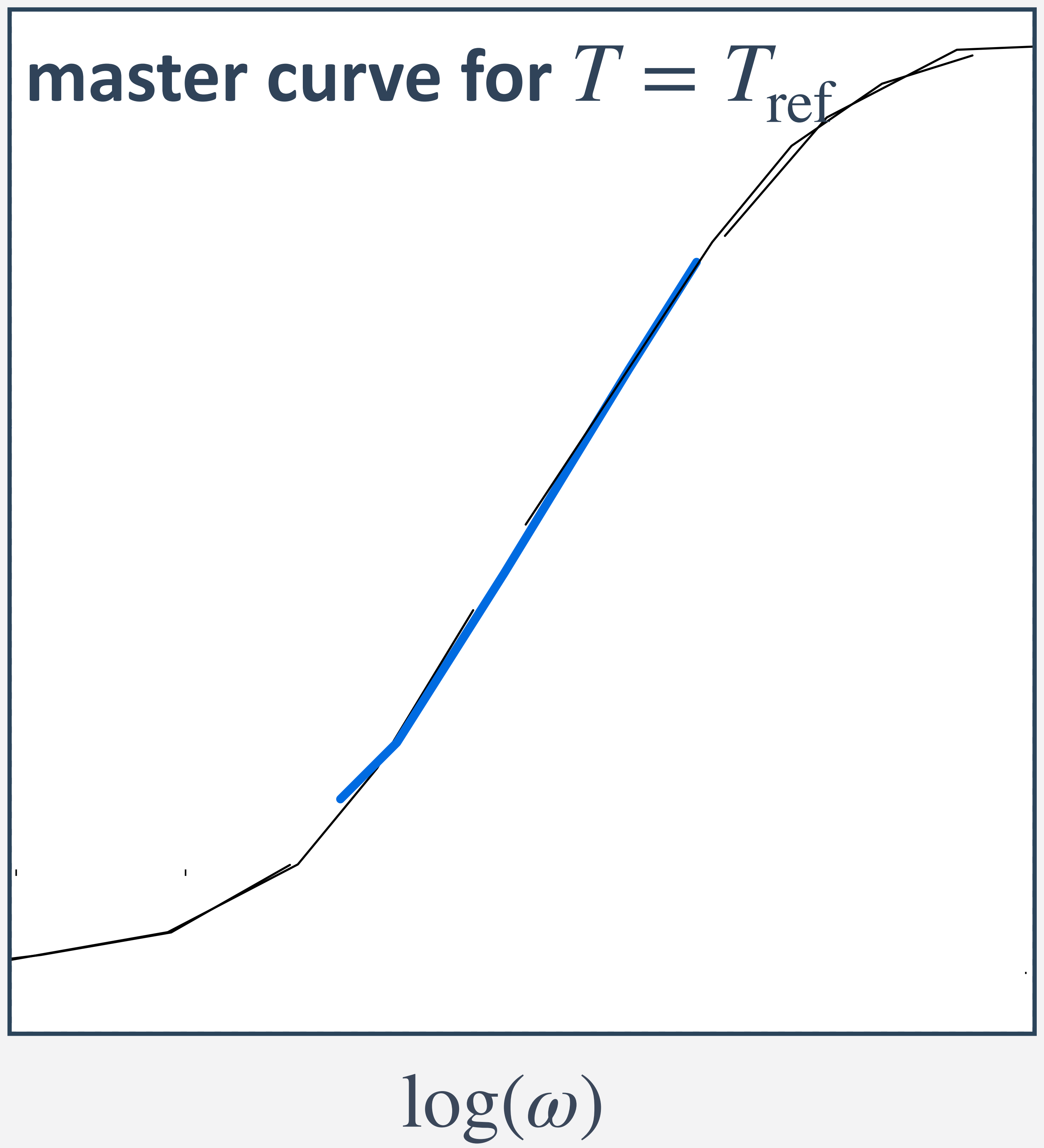


- can we relate time (or frequency) and temperature quantitatively?

Time-Temperature Superposition

- measurements of E' as function of frequency at several temperatures

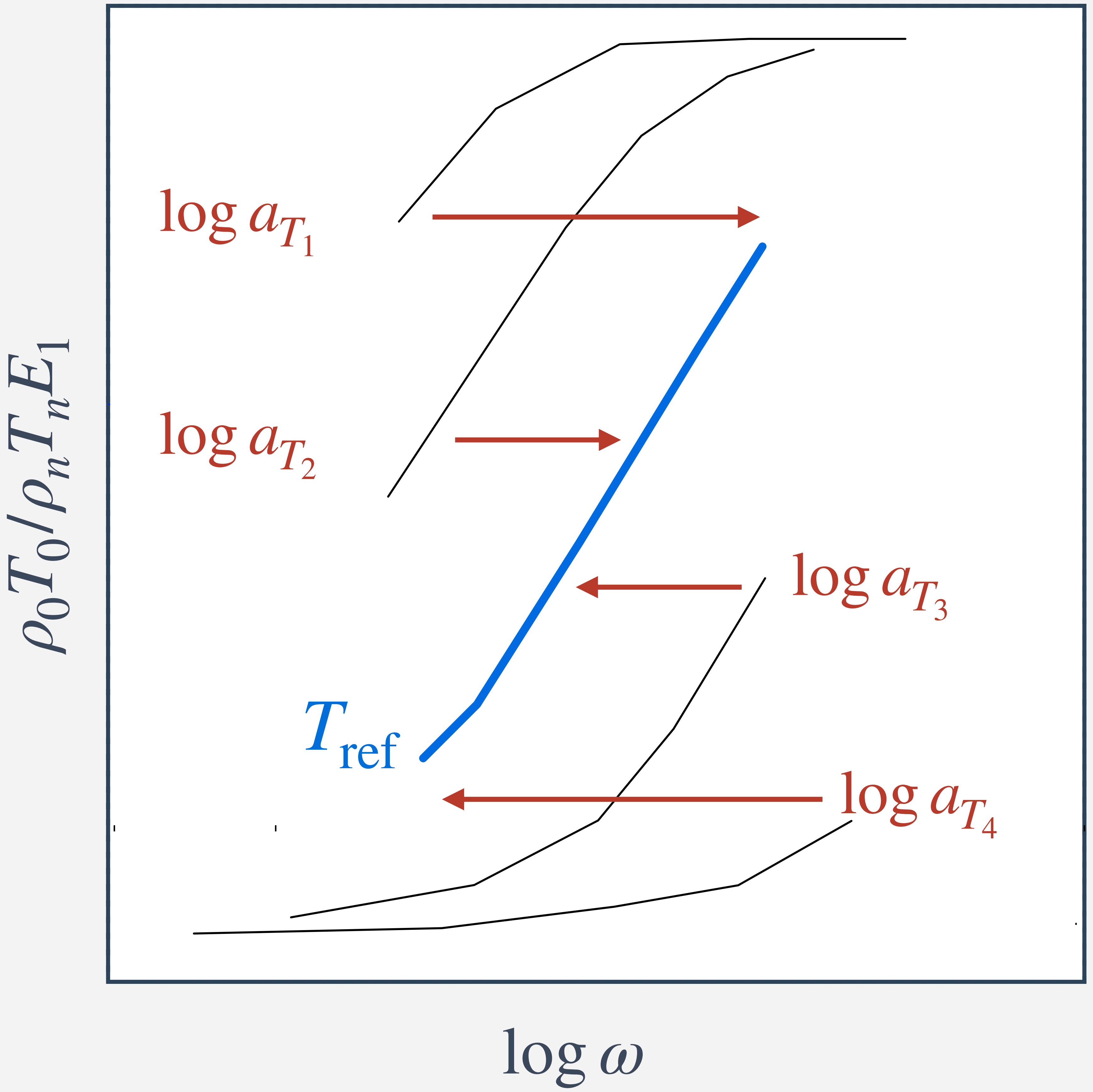




- **after correction for ρT, superimposed curves by horizontal shifts along $\log(\omega)$ to form a master curve**
- **extends the accessible frequency range**

Williams-Landel-Ferry (WLF) Equation

- **shift factors follow the empirical WLF relation:**



$$\log(a_T) = \log(\omega_{\mathrm{ref}}) - \log(\omega) = \log\left(\frac{\omega_{\mathrm{ref}}}{\omega}\right)$$

$$\boxed{\log(a_T) = -\frac{\mathrm{C}_1(T - T_{\mathrm{ref}})}{\mathrm{C}_2 + T - T_{\mathrm{ref}}}}$$

for $T_{\mathrm{ref}} = T_{\mathrm{g}}$:

$$\log(a_T) = -\frac{17.44(T - T_{\mathrm{ref}})}{51.6 + T - T_{\mathrm{ref}}}$$

- **using T_{g} as reference temperature gives near-universal constants** $\mathrm{C}_1 = 17.44$ **and** $\mathrm{C}_2 = 51.6\ \mathrm{K}$

Interpretation by Free Volume Theory

- the WLF equation, though empirical, can be justified by free volume considerations:
- **from free Volume Theory:** $\tau(T) = \tau_0 e^{\frac{v_0}{v_f}} = \tau_0 e^{\frac{\Delta\alpha^{-1}}{T - T_0}}$ see **Slide 152**
- **let** $T_0 = T_\mathrm{g} - \mathrm{A}$, $\tau(T) = \tau_0 e^{\frac{\Delta\alpha^{-1}}{\mathrm{A} + T - T_\mathrm{g}}}$, $\tau(T_\mathrm{g}) = \tau_0 e^{\frac{\Delta\alpha^{-1}}{\mathrm{A}}}$:
- **we saw:** $a_T = \frac{\omega(T_\mathrm{g})}{\omega(T)} = \frac{\tau(T)}{\tau(T_\mathrm{g})}$ $\ln a_T = \ln \tau(T) - \ln \tau(T_\mathrm{g}) = \frac{\Delta\alpha^{-1}}{\mathrm{A} + T - T_\mathrm{g}} - \frac{\Delta\alpha^{-1}}{\mathrm{A}}$

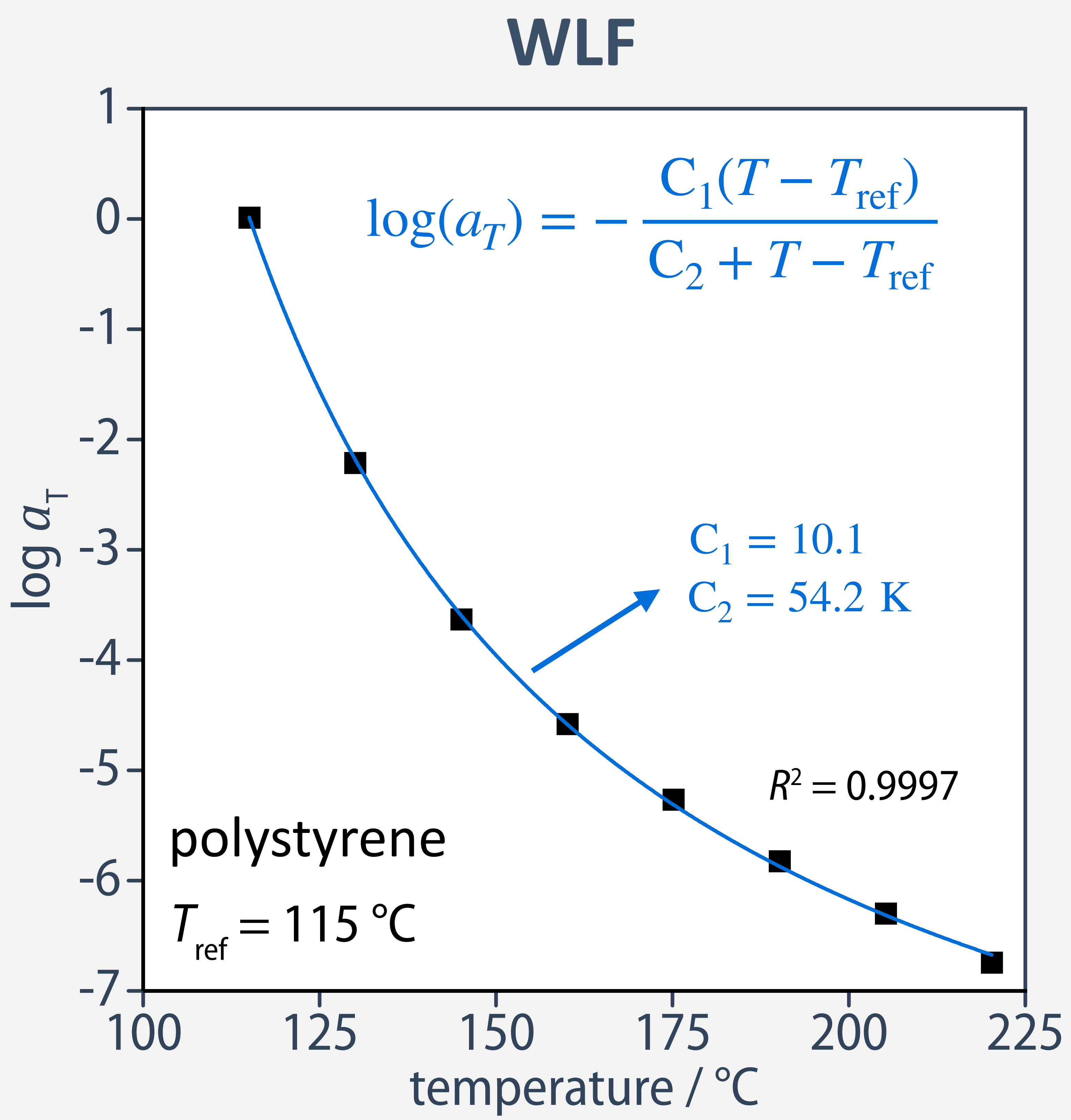
$$\ln a_T = -\frac{\mathrm{A}^{-1}\Delta\alpha^{-1}(T - T_\mathrm{g})}{\mathrm{A} + T - T_\mathrm{g}}$$

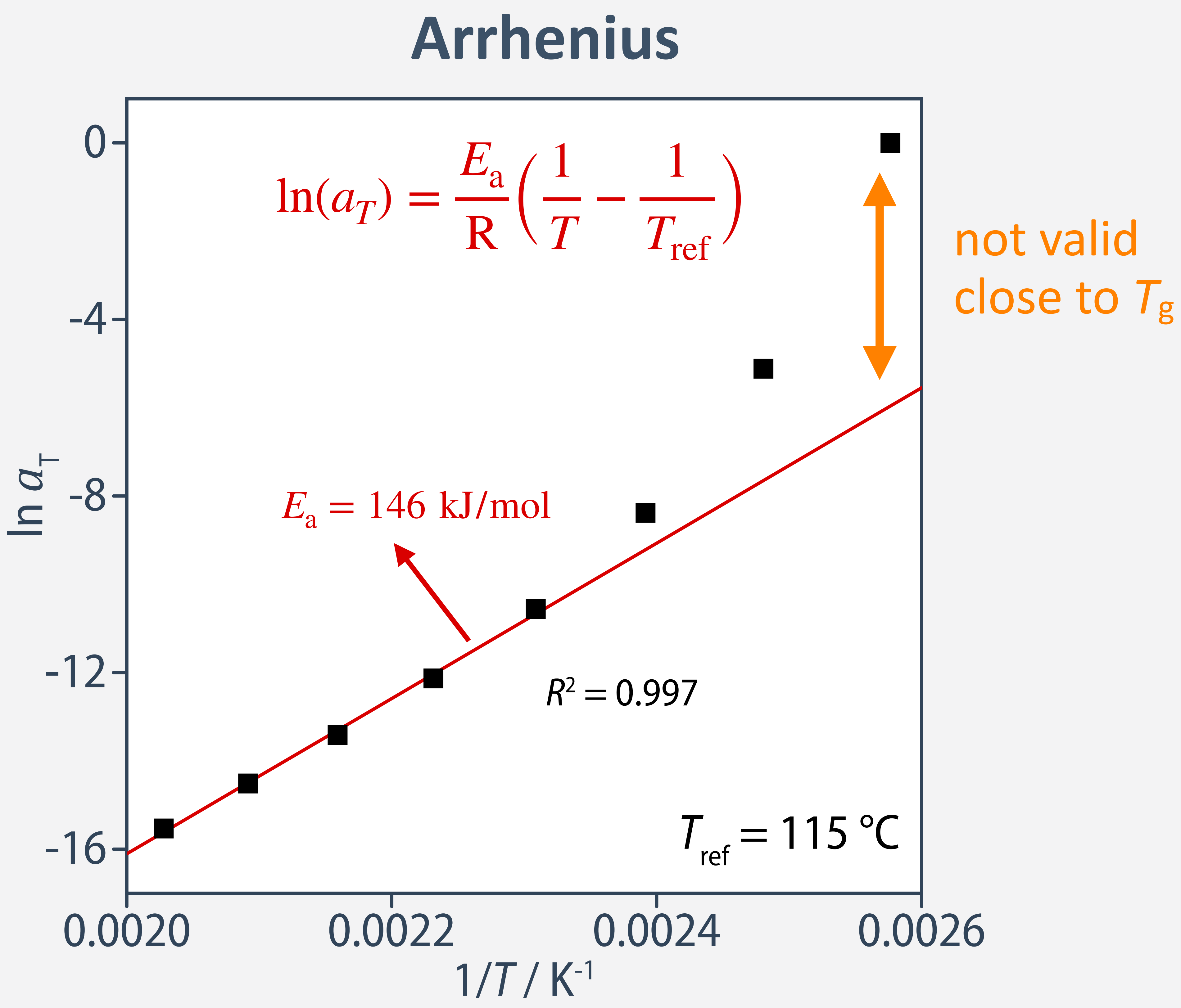
compare with the WLF equation:

$$\log(a_T) = -\frac{\mathrm{C}_1(T - T_\mathrm{ref})}{\mathrm{C}_2 + T - T_\mathrm{ref}}$$

see reader on WLF Equation

Analysis of Horizontal Shift Factors





- **WLF plot: describes free-volume-controlled dynamics near T_g**
- C_1 ("sensitivity to heating") and C_2 ("distance to the glass") depend on T_{ref}
- **Arrhenius plot: describes thermally activated conformational motion at high temperatures**

see reader on WLF Equation

Implications and Limitations of the WLF Equation

- **Experimental time or frequency windows are limited: the WLF approach extends these ranges and enables prediction of long-term (creep) behavior.**
- **valid approximately for** $T_\mathrm{g} < T < T_\mathrm{g} + 50 - 100\ \mathrm{K}$
- **deviations from "universal" constants are common and depend on** T_ref
- **not applicable to non-linear behavior** (large deformations)
- **thermorheological simplicity required: all viscoelastic quantities (**$E', E'', \tan(\delta)$**) must shift by the same factor**
- **The WLF equation is an empirical yet powerful tool, best used within its valid window around** T_g

Learning Outcome

- polymers are viscoelastic materials, their mechanical response depends strongly on the timescale of the measurement.
- linear viscoelasticity applies for small deformations, enabling simple mechanical models to describe time-dependent behavior.
- time-temperature equivalence is a hallmark of polymer dynamics: it justifies time-temperature superposition, which allows extending measurements across otherwise inaccessible time or frequency ranges.