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Viscoelasticity,

Creep and Oscillation Experiment

Basic Seminar

Applied Rheology

The world leader in serving science

Overview

- Repetition of some basic terms
- Viscoelastic behavior
- Experimental approach to viscoelasticity
  - Creep- and recovery
  - Oscillation
    - Amplitude sweep
    - Frequency sweep
    - Temperature sweep
    - Time sweep
- Expansion of the measuremnent range for Oscillation
  - Time Temperature Superposition (TTS) principle
  - Cox-Merz Rule

Repetition of some basic terms

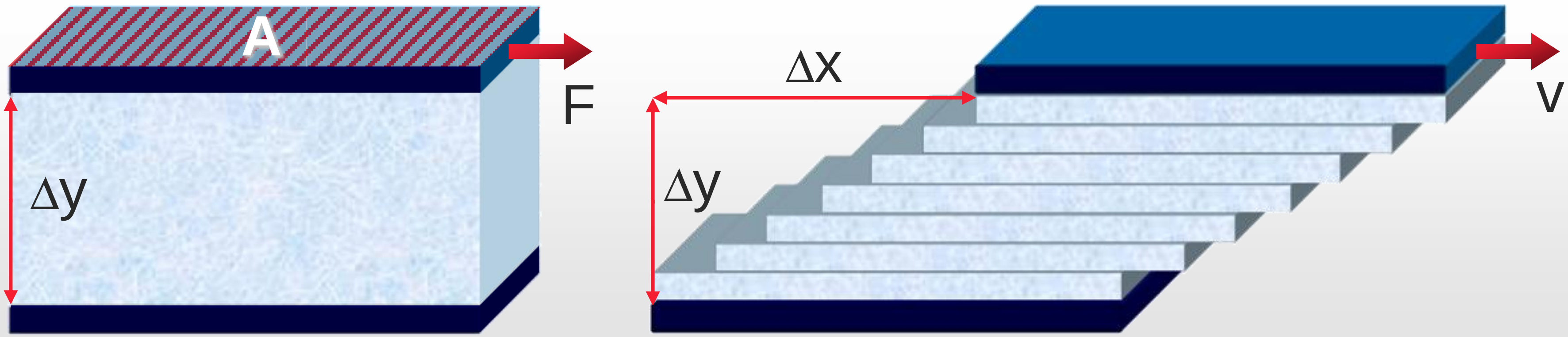
Calculation of the dynamic viscosity

Viscosity (dynamic)	η	[Pa·s]
Shear stress	τ	[Pa]
Deformation	γ	[-]
Shear rate	$\dot{\gamma}$	[1/s]

$$\Rightarrow \quad \eta = \frac{\tau}{\dot{\gamma}}$$

Repetition of some basic terms

Calculation of the dynamic viscosity



$$\tau = \frac{\text{Force}}{\text{Area}} = \frac{F}{A} \left[\frac{N}{m^2} = Pa \right]$$

$$\gamma = \frac{\text{Displacement}}{\text{Distance}} = \frac{\Delta x}{\Delta y} \left[\frac{\cancel{m}}{\cancel{m}} \right]$$

$$\dot{\gamma} = \frac{dv}{dy} = \frac{d\gamma}{dt} \left[\frac{\cancel{m}}{s \cdot \cancel{m}} = \frac{1}{s} \right]$$

Viscoelasticity

- ✓ Repetition of some basic terms
- ✓ Viscoelastic behavior
- ✓ Experimental approach to viscoelasticity
    - Creep and recovery
    - Oscillation
        - Amplitude sweep
        - Frequency sweep
        - Time sweep
        - Temperature sweep
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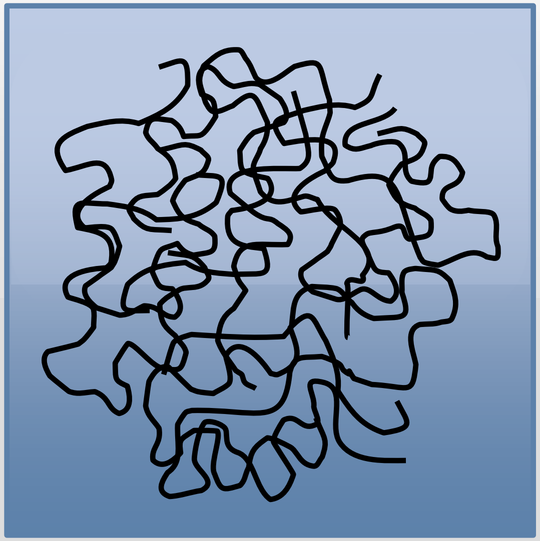
Viscoelastic behavior

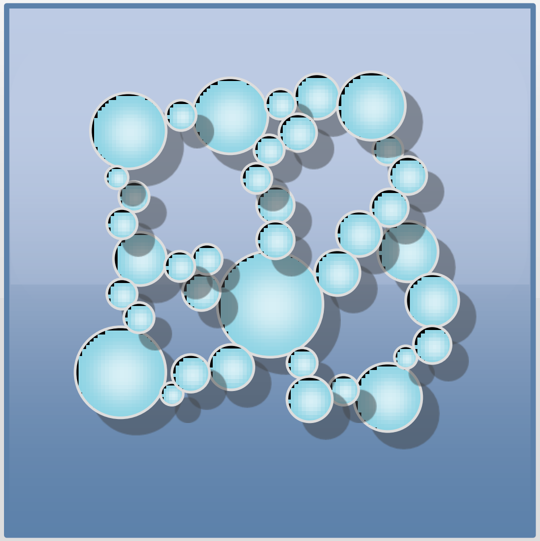
Reasons for viscoelasticity

Entenglements



- Polymer solutions
- Polymer melts

Network formation



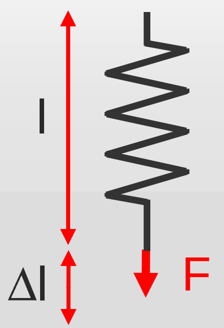
- Emulsions
- Suspensions

Viscoelastic behavior

Appying Hookke's law to rheology

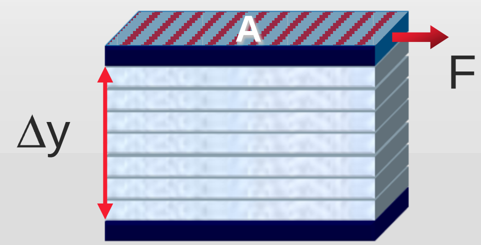
Purely elastic behavior

Spring



$$k = \text{Spring constant} = \frac{F}{\Delta l}$$

Viscoelastic behavior



$$\gamma = \frac{\Delta x}{\Delta y} \qquad \tau = \frac{F}{A}$$

Result

✓ Complex modulus G*

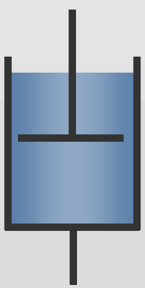
$$G^* = \frac{\tau}{\gamma} \left[Pa \right]$$

Viscoelastic behavior

Models for viscoelasticity

Viscous

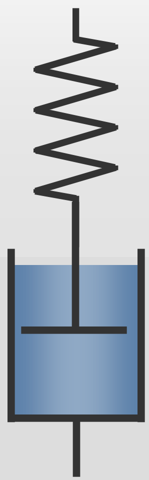
$$\tau = \eta \cdot \dot{\gamma}$$



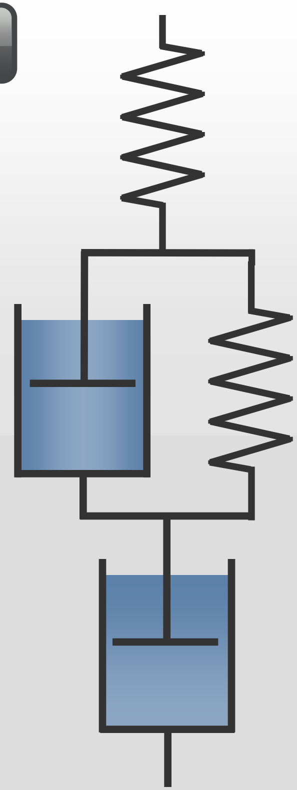
Dash pot

Viscoelastic

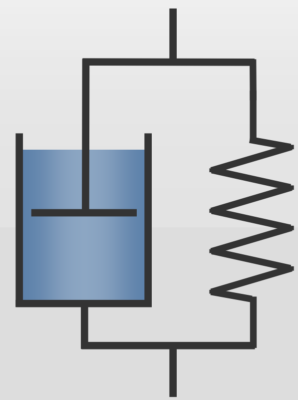
$$\tau = G^* \cdot \gamma$$



Maxwell Model



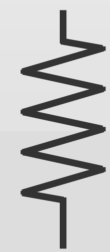
Burgers Model



Voigt/Kelvin Model

Elastic

$$F = k \cdot \Delta l$$



Spring

Viscoelasticity

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Experimental approach to viscoelasticity

Creep and recovery

The viscoelastic behavior is observed by applying instantaneous shear stress changes.

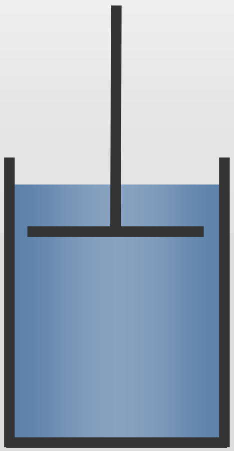
- ✓ Non-destructive method (within the LVB)
- ✓ Destinguishes between elastic and viscous properties
- ✓ Determination of the time-dependent reaction to such changes

Experimental approach to viscoelasticity

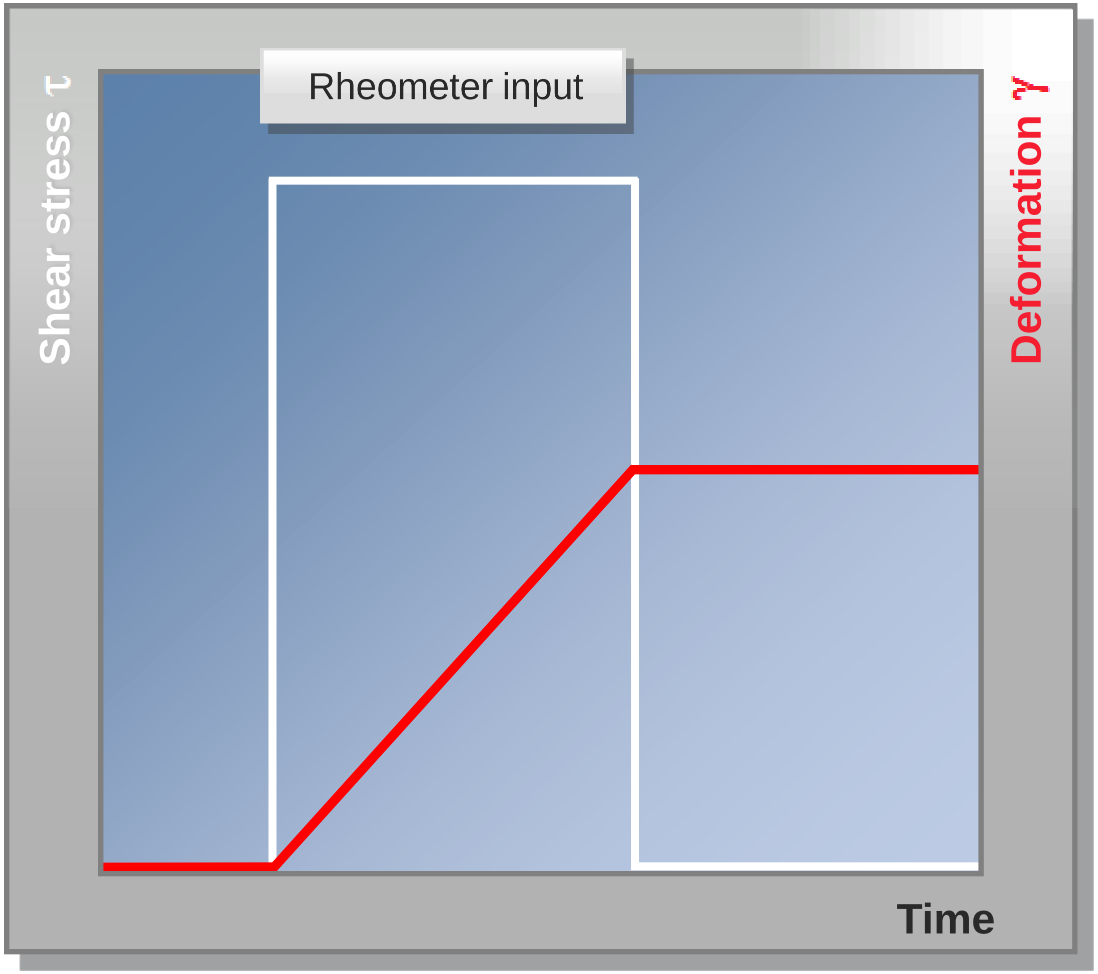
Creep and recovery

Viscous Sample

$$\tau = \eta \cdot \dot{\gamma}$$



- ✓ Irreversible deformation
- ✓ Applied energy dissipates completely



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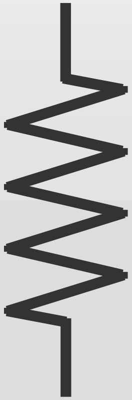
Experimental approach to viscoelasticity

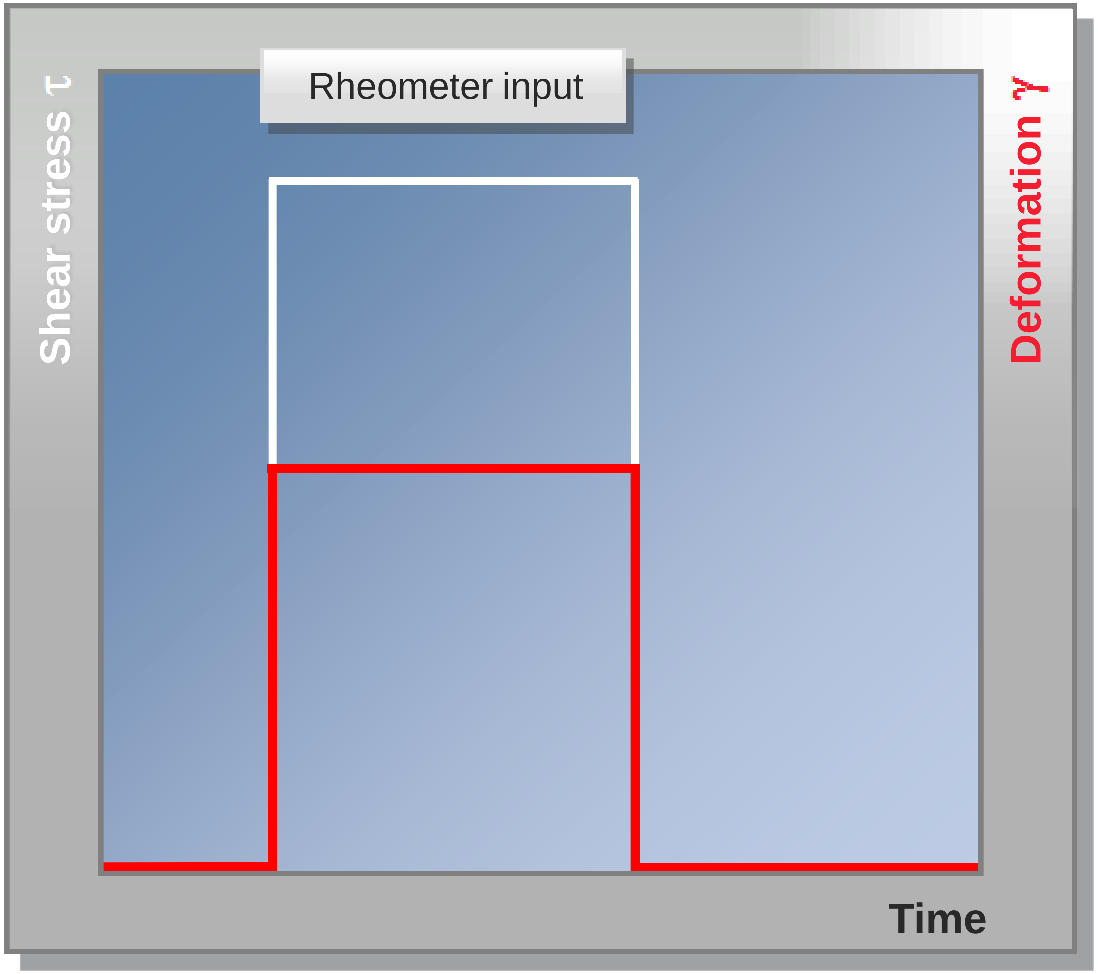
Creep and recovery

Elastic sample

$$F = k \cdot \Delta l$$

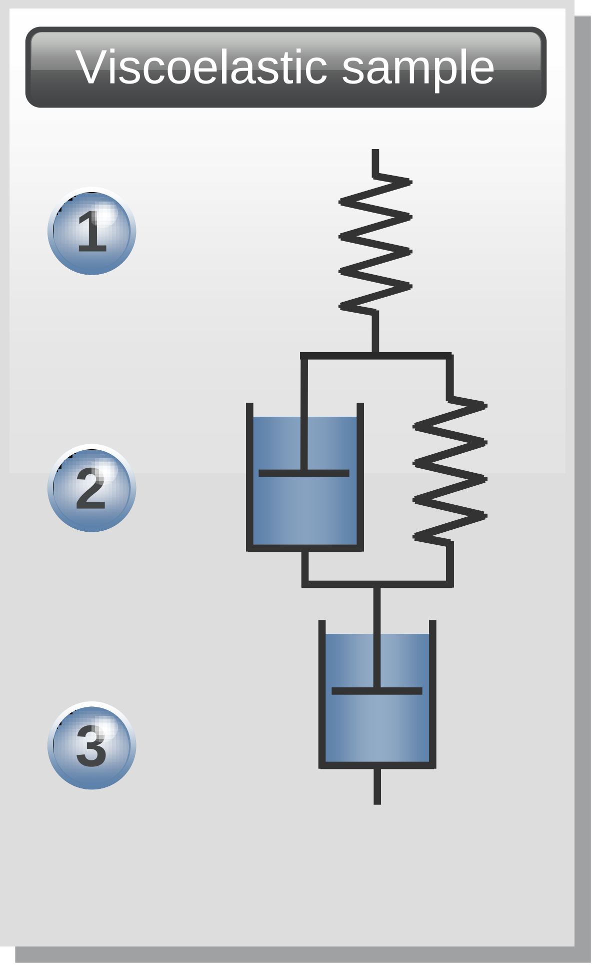


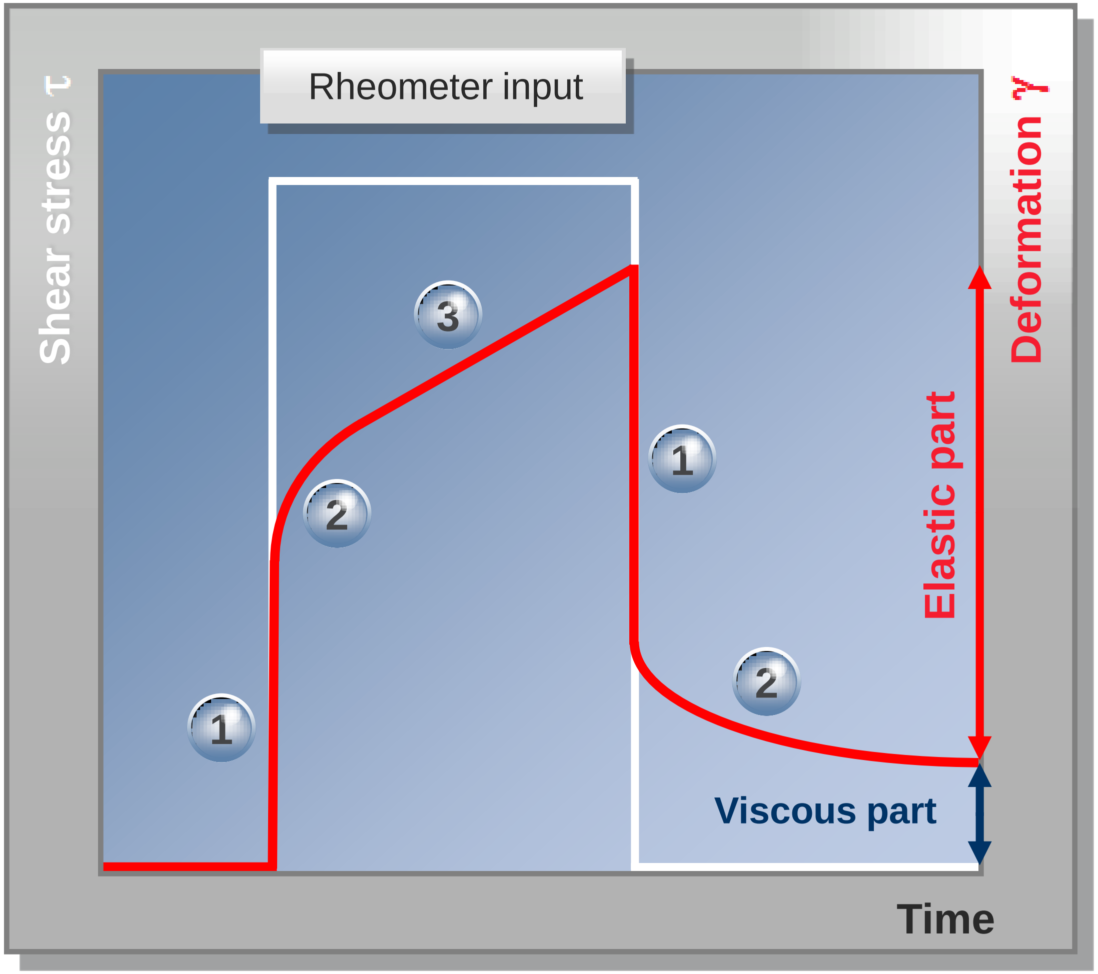
- Reversible deformation
- Applied energy is stored



Experimental approach to viscoelasticity

Creep and recovery





Experimental approach to viscoelasticity

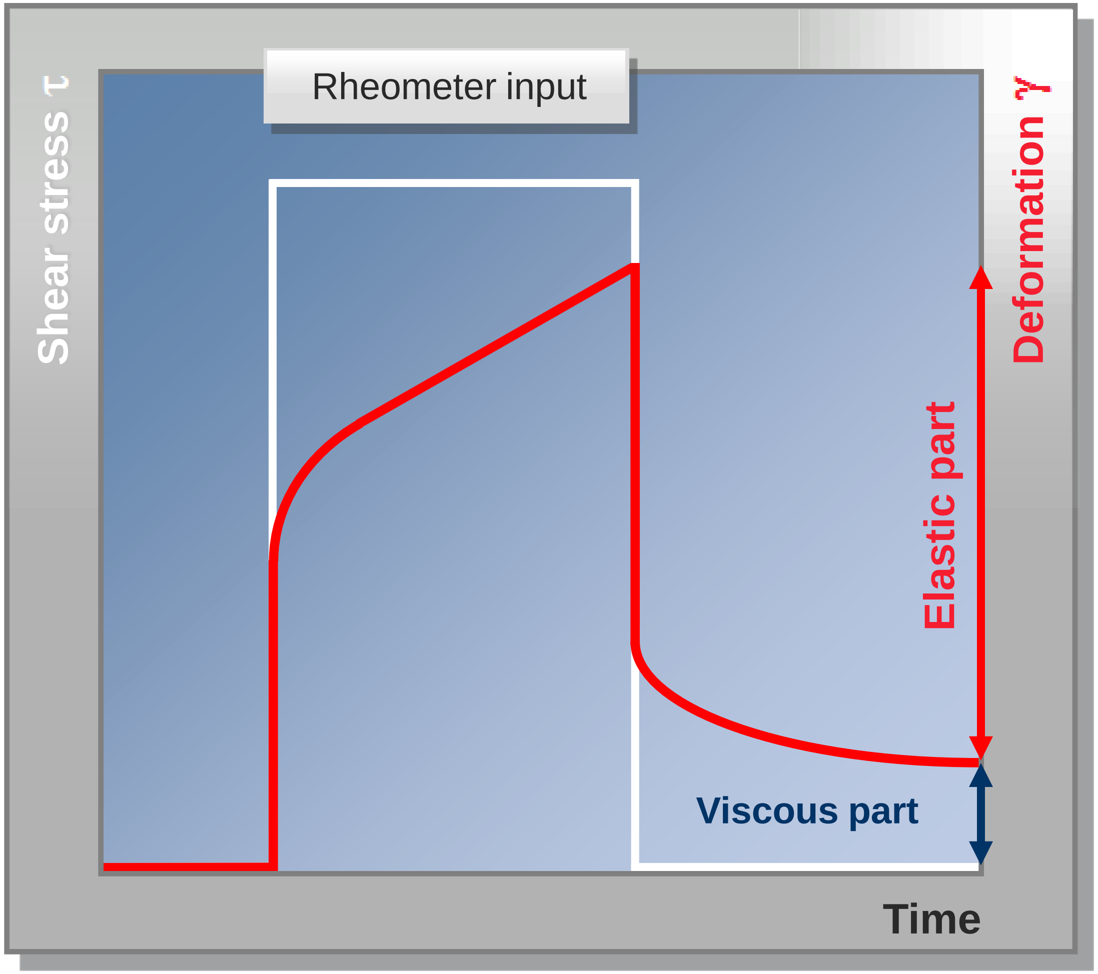
Creep and recovery

Results

- η_0 Zero shear viscosity
- γ_{e0} Equillibrium deformation
- γ_r Recoverable deformation
- λ_0 Retardation time
- G_0 Elastic modulus

Applications

- ✓ Leveling
- ✓ Sagging
- ✓ Shear stability
- ✓ Yield stress



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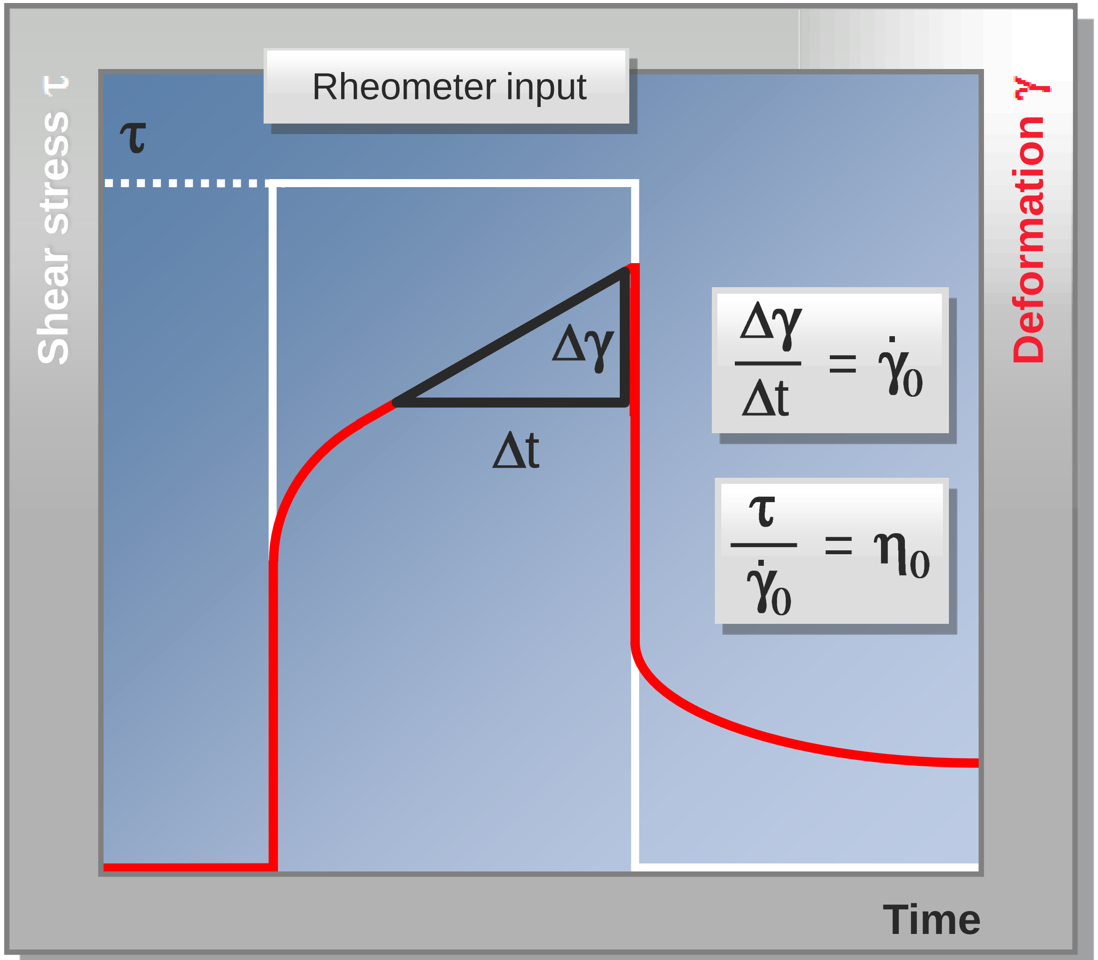

Experimental approach to viscoelasticity

Creep and recovery

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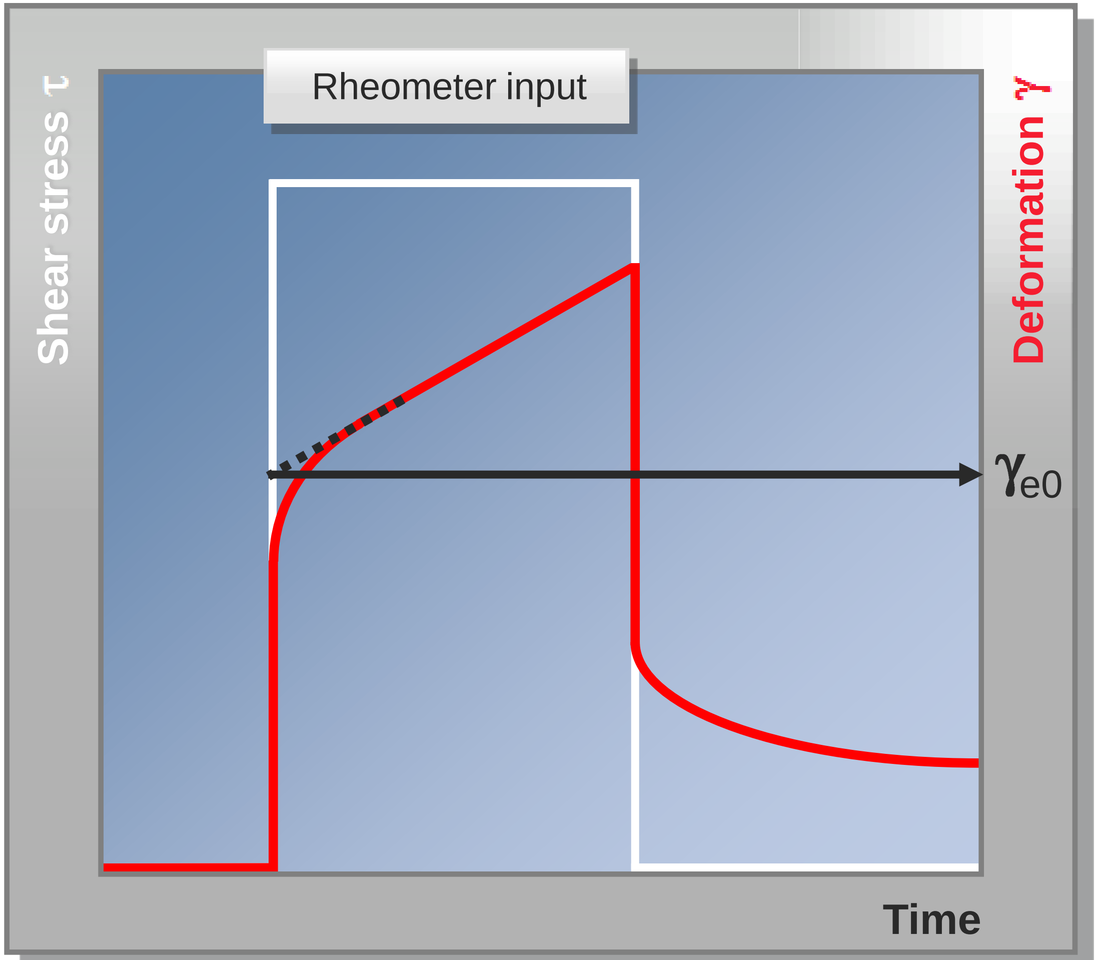

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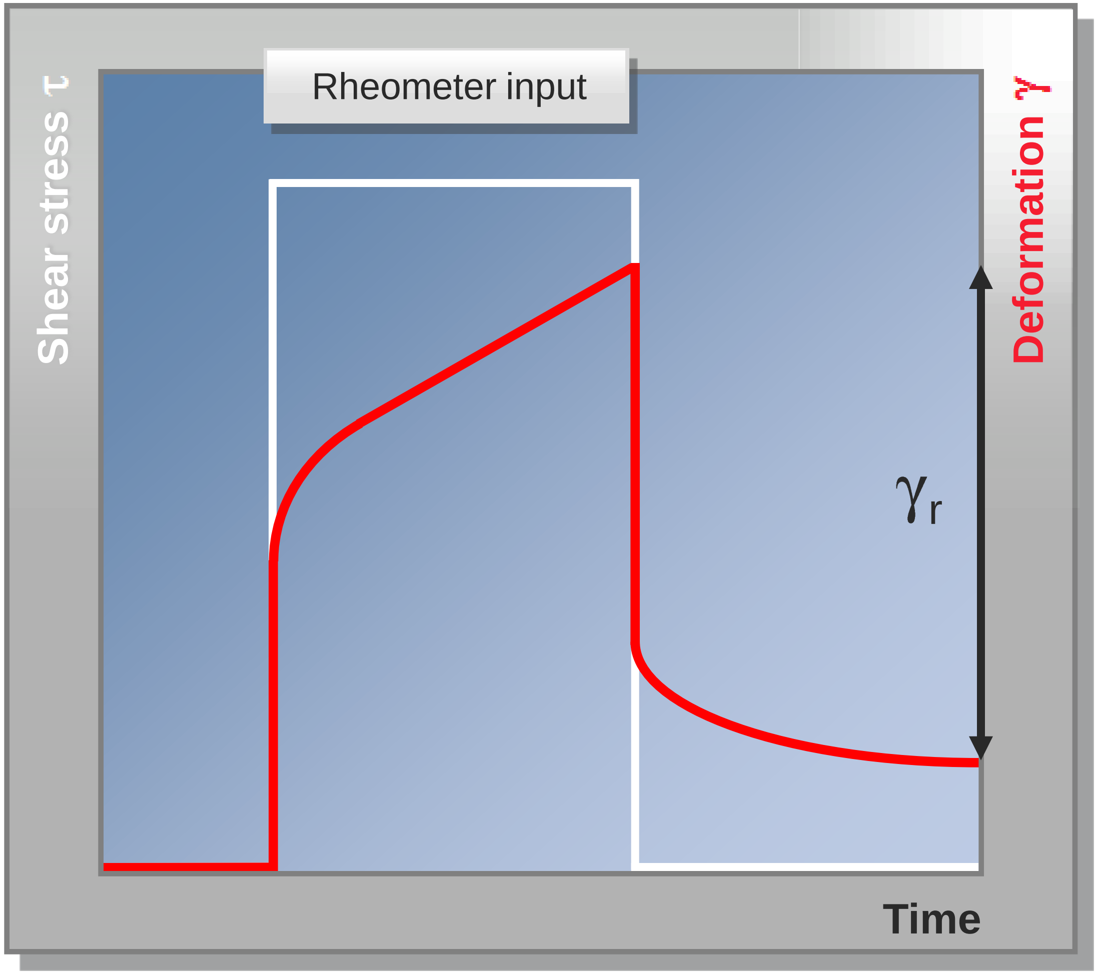

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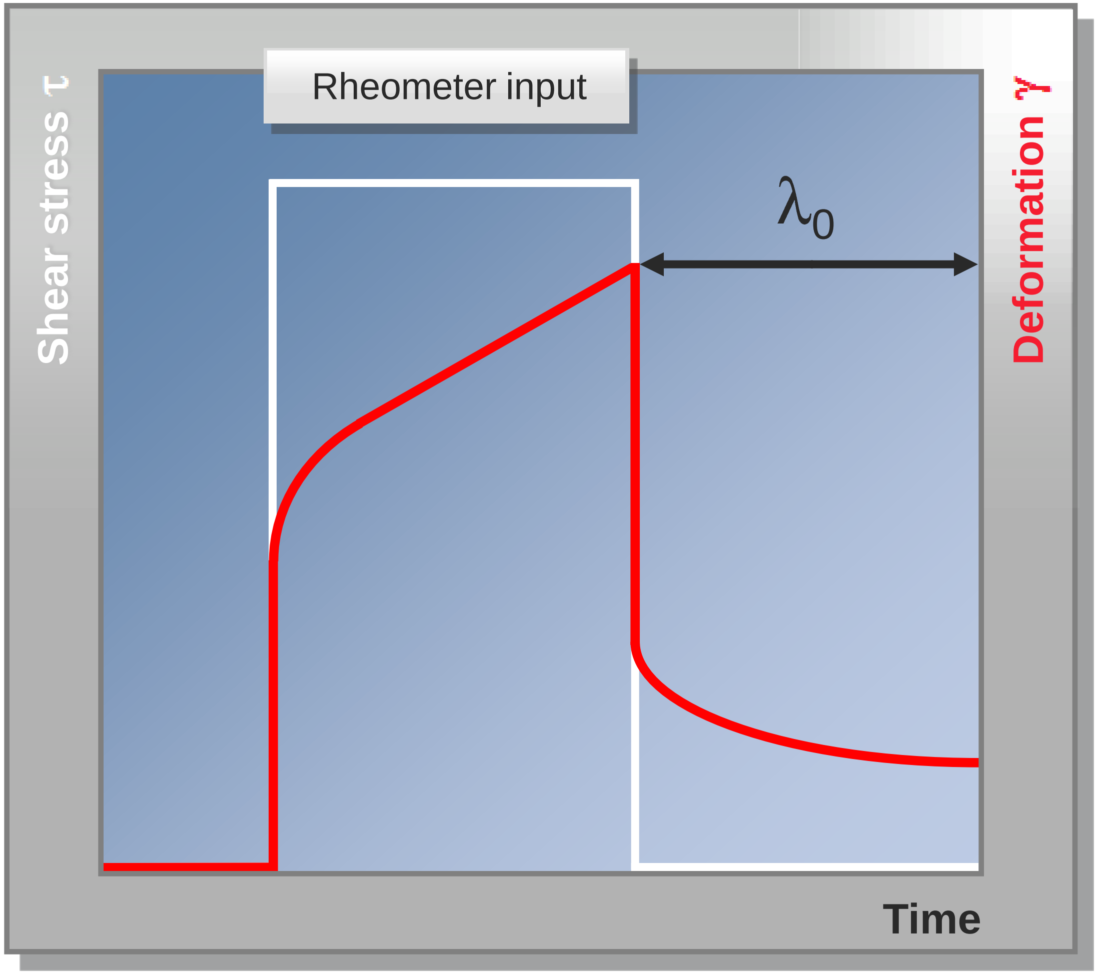

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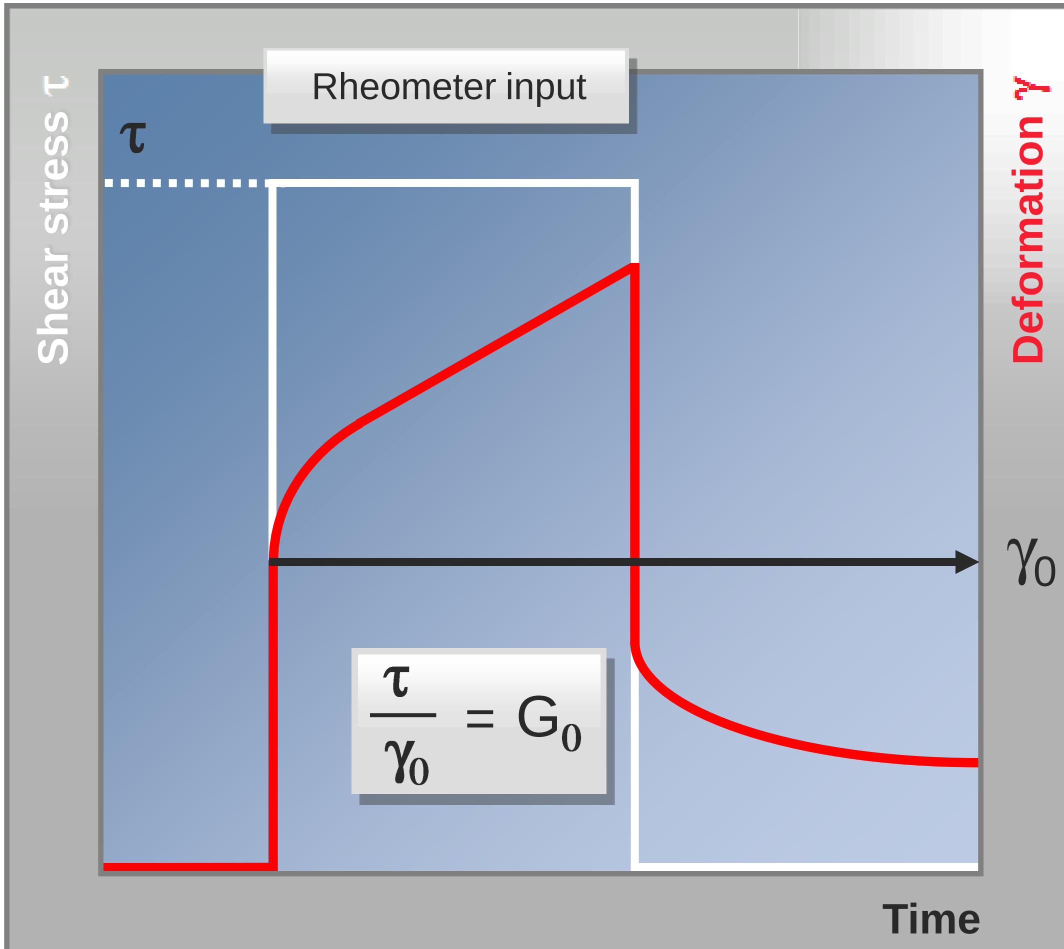


Viscoelasticity

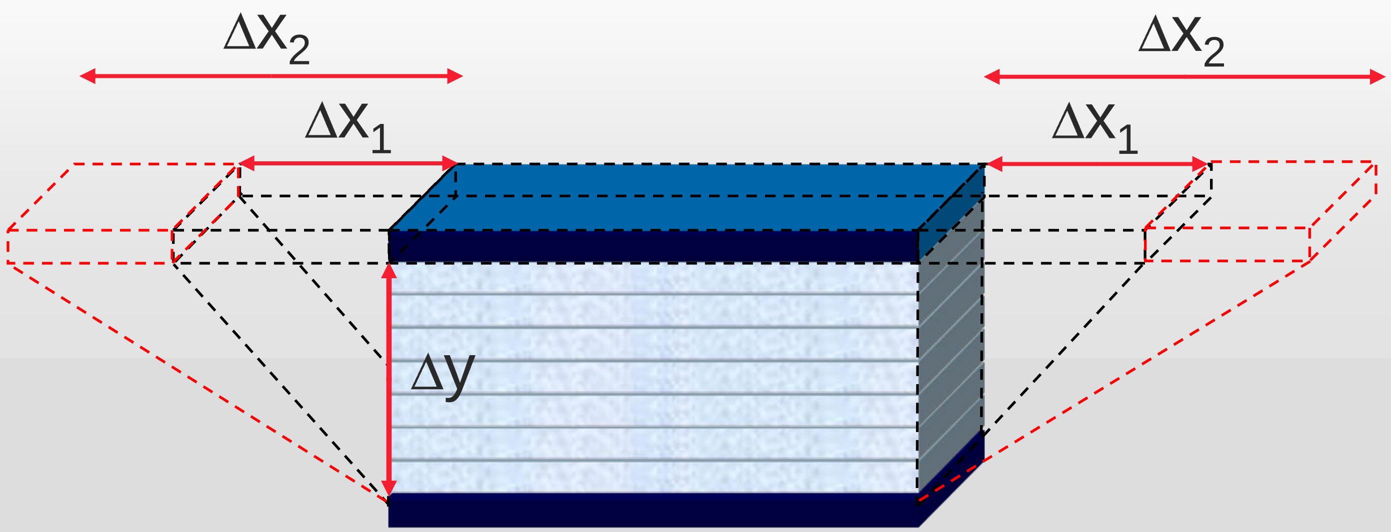
- Experimental approach to viscoelasticity

  Oscillation

Oscillation

Principle of measurement

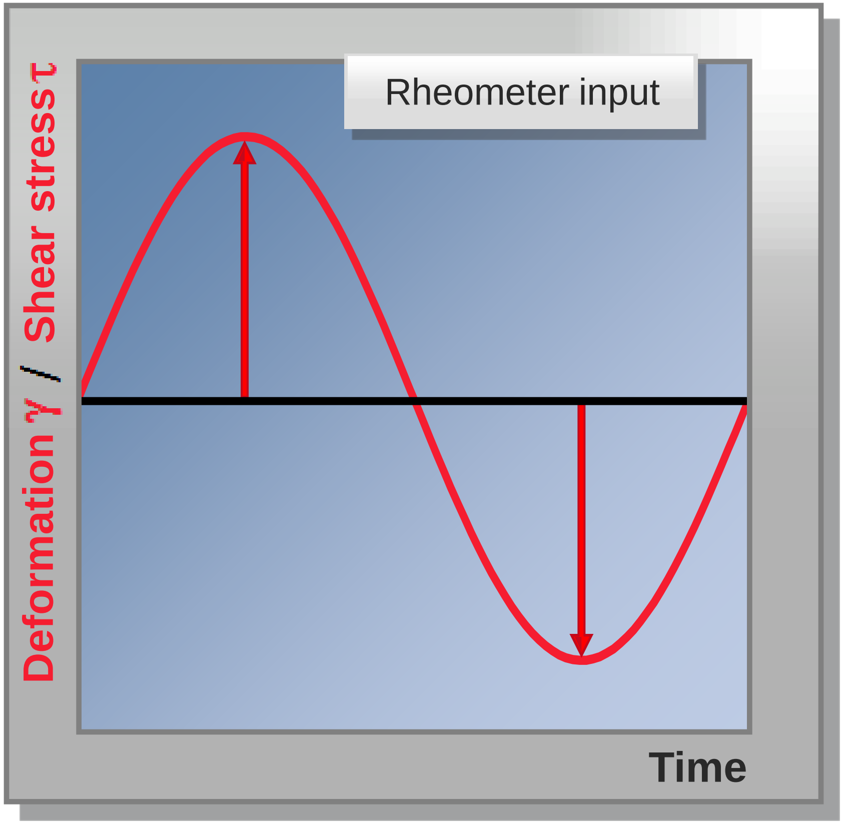
Two-Plates-Model

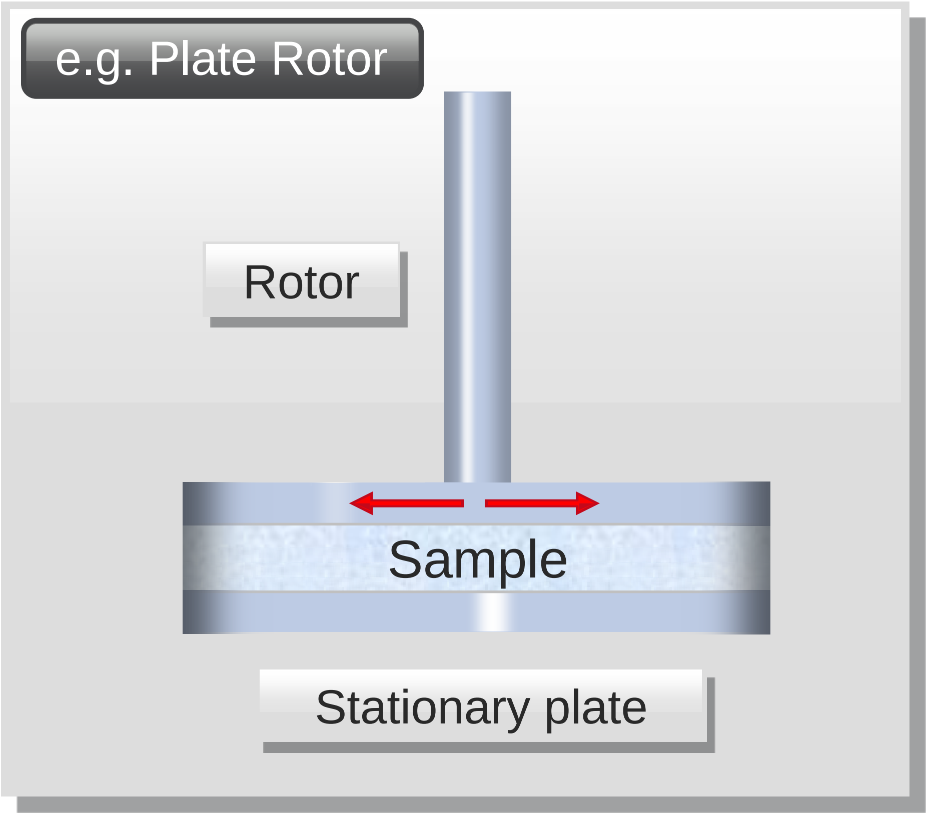


- A usually sinosoidal oscilllation is being applied by the rheometer
- Controllable parameters are the maximum amplitude (Δx_i) of the shear stress (τ) or deformation (γ) as well as the (angular) frequency (f, ω) and the temperature (T)

Oscillation

Principle of measurement





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Oscillation

Principle of measurement

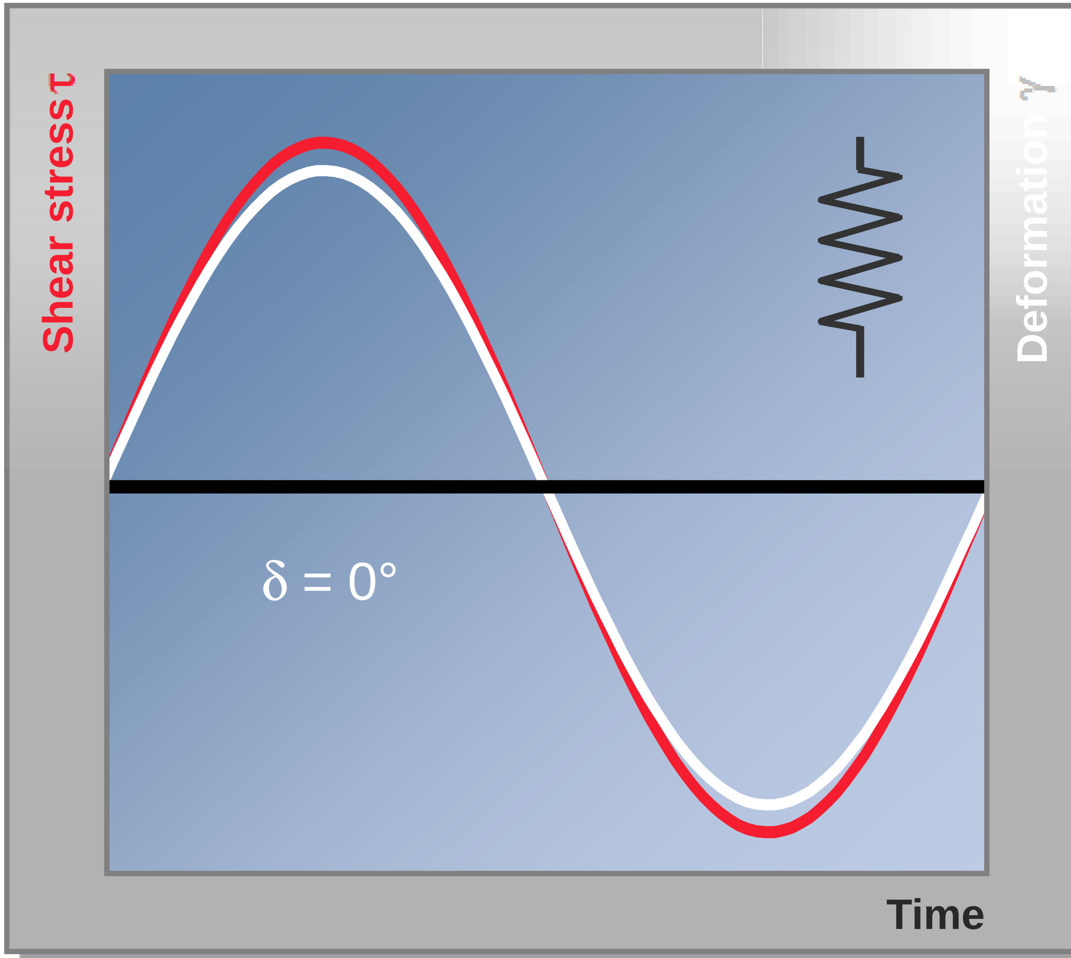
Purely elastic sample

Input

- ✓ Shear stress τ (CS)
- ✓ Deformation γ (CD) resp.

Response

- ✓ Deformation γ
- ✓ Shear stress τ resp.
- ✓ Phase angle δ



Oscillation

Principle of measurement

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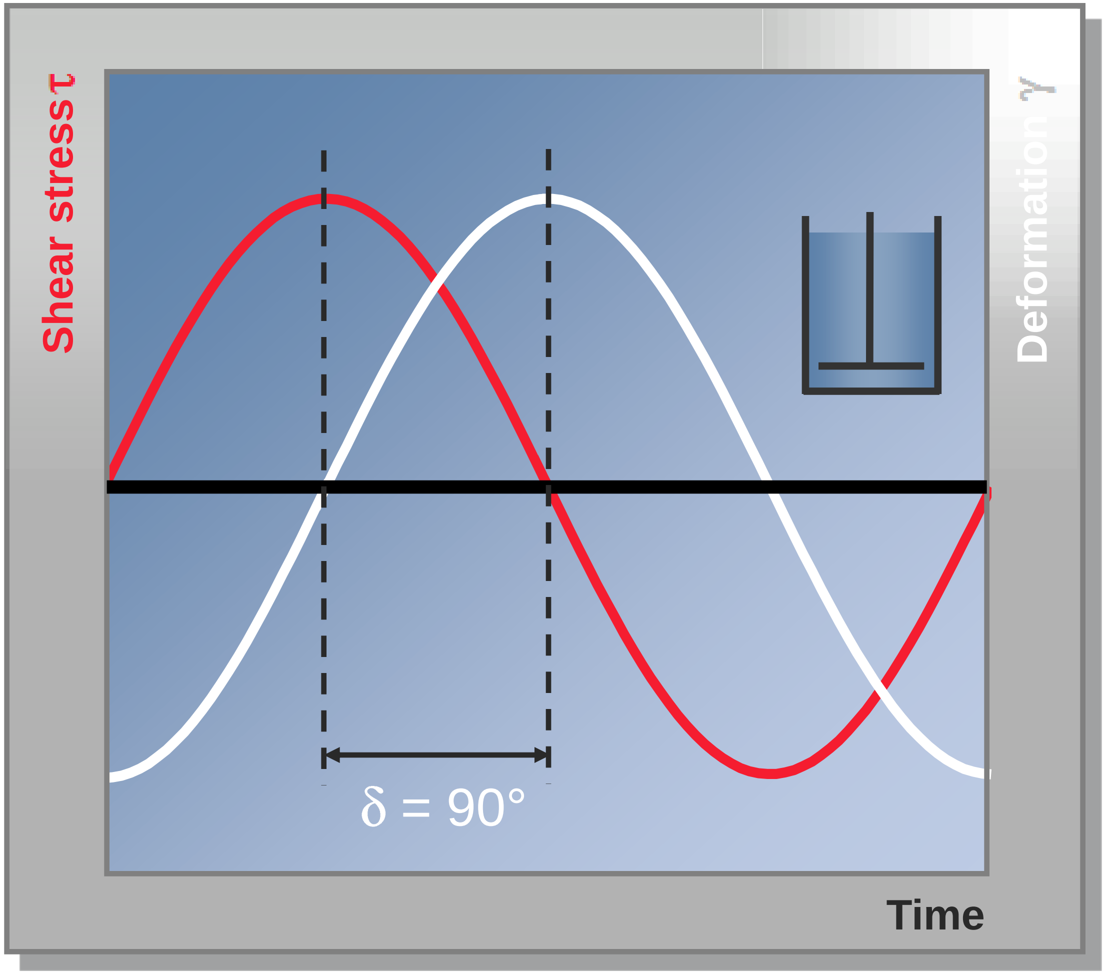

Oscillation

Principle of measurement

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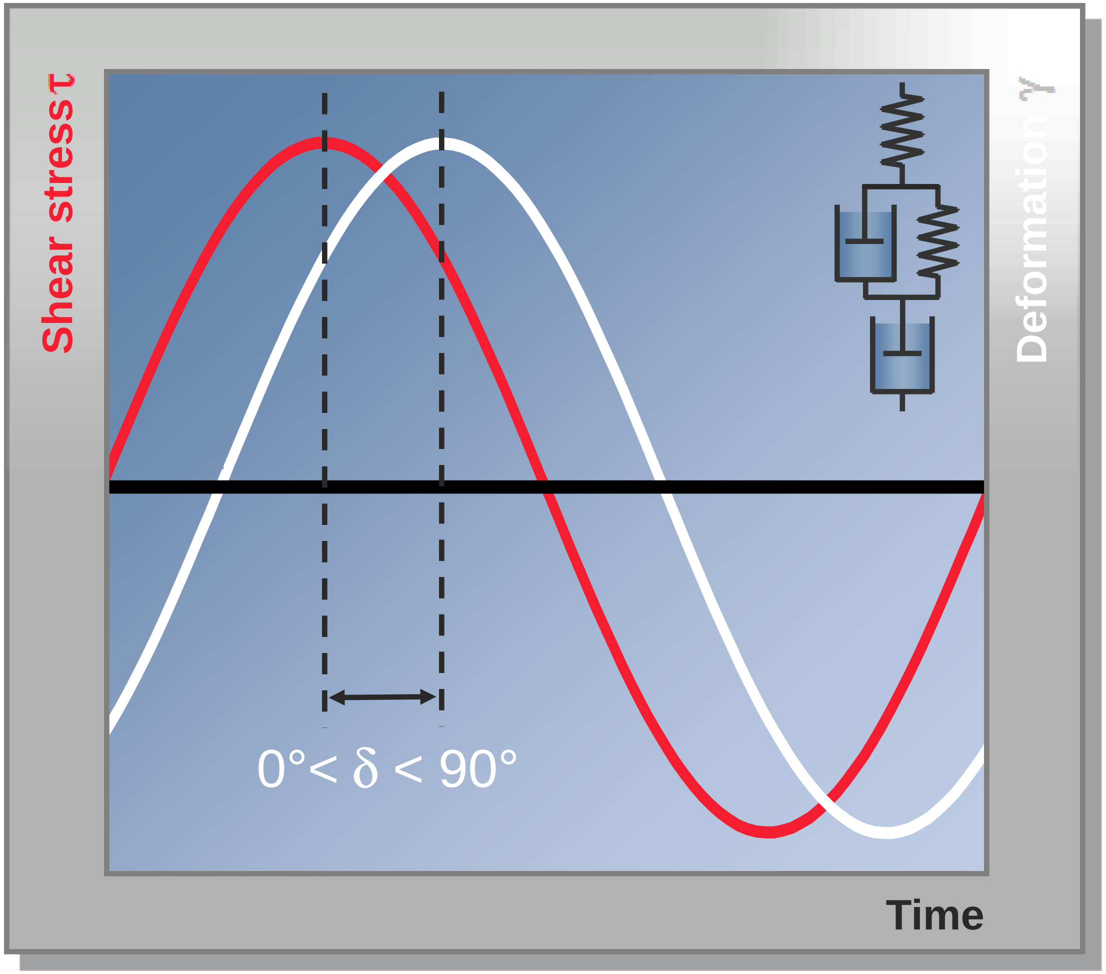

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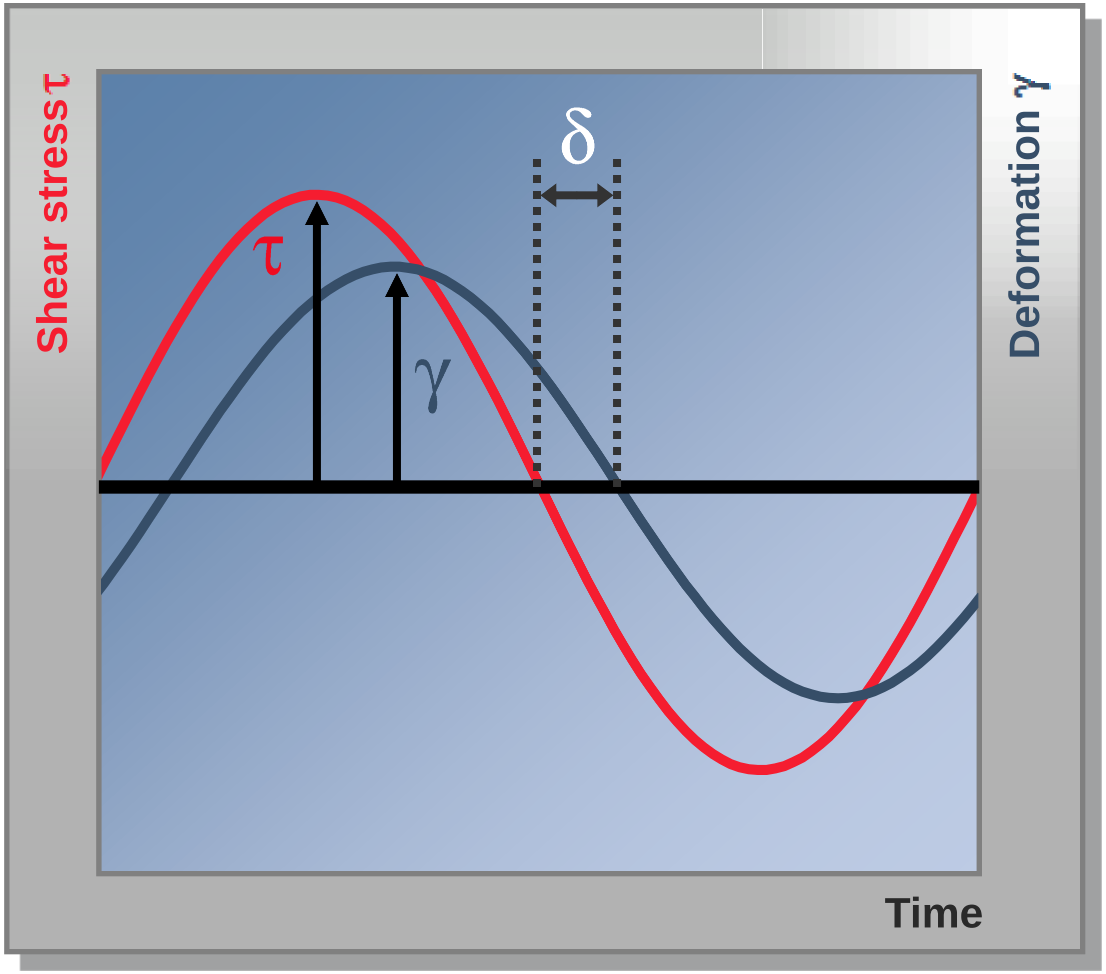
Oscillation

Principle of measurement



CS-Input

Shear stress

$$\tau(t) = \tau \cdot \sin(\omega \cdot t)$$

Response

Deformation

$$\gamma(t) = \gamma \cdot \sin(\omega \cdot t - \delta)$$

Oscillation

Results I

- Complex modulus

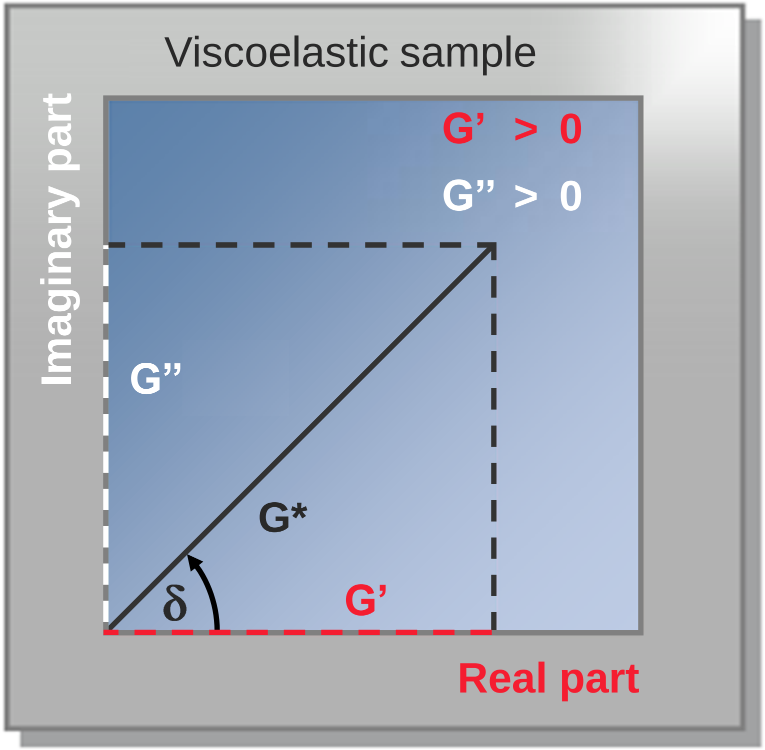
  $G^* = G' + i\,G''$ ($i^2 = -1$)

- Storage modulus

  G' (elastic part)

- Loss modulus

  G'' (viscous part, damping)



Oscillation

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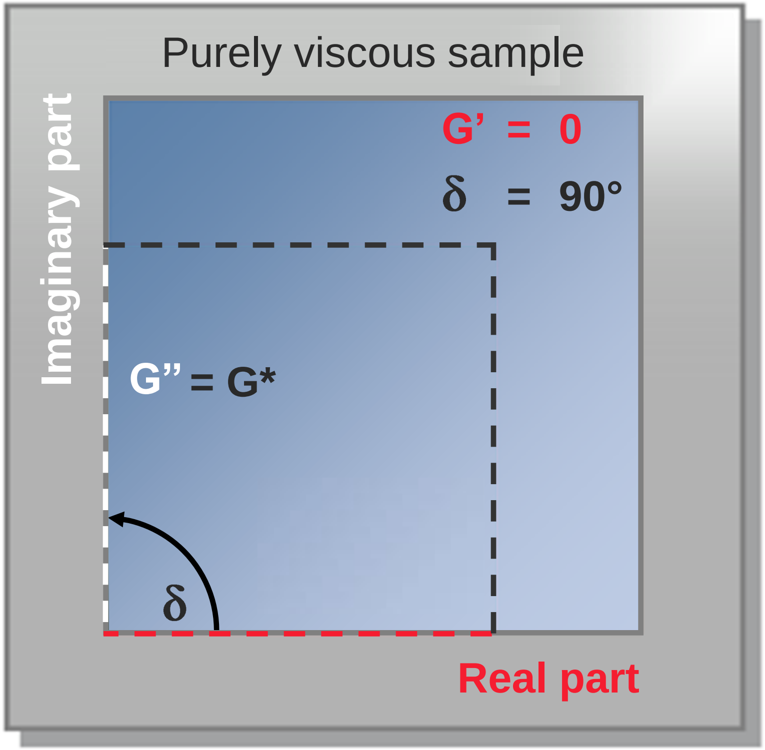

Oscillation

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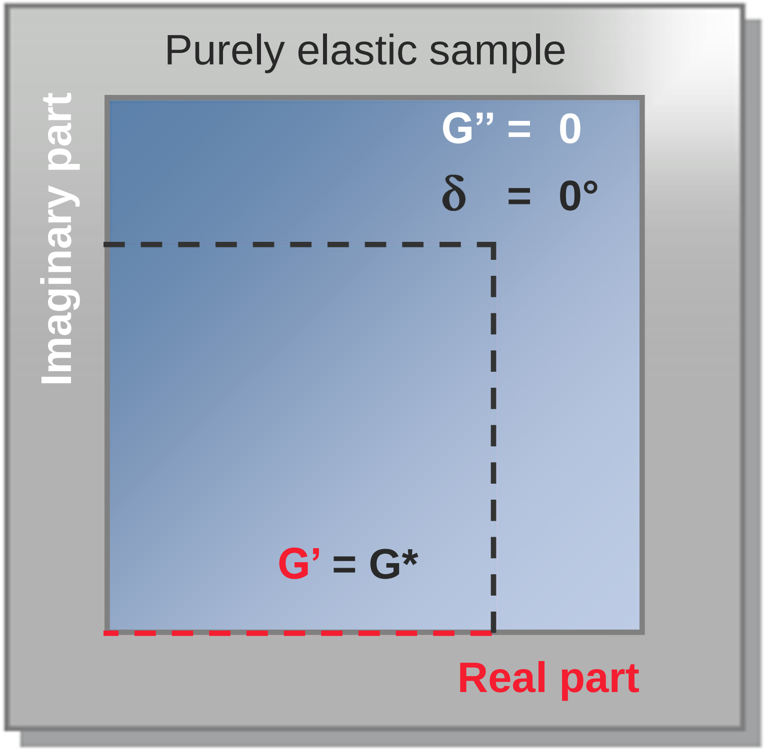


Oscillation

Results II

Phase angle	δ (0° ≥ δ ≤ 90°)
Loss factor	$\tan\delta = G''/ G'$
Complex viscosity	$\eta^* = G^* / i\,\omega$
Angular frequency	$\omega = 2\pi f$
	(f = frequency)

Viskoelastizität

Oscillation

Amplitude sweep

Oscillation

Amplitude sweep

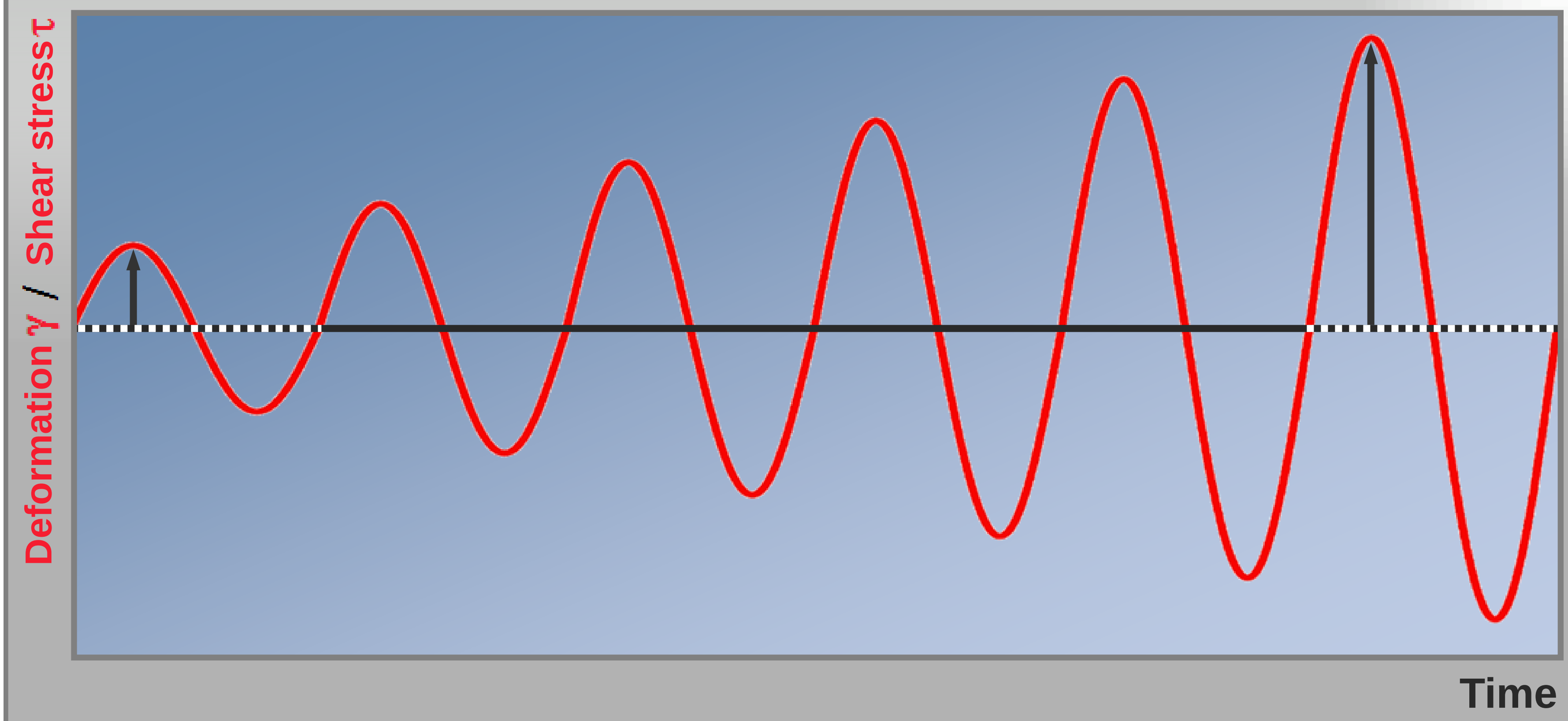
Increasing amplitude in shear stress τ (CS) or deformation γ (CD) with constant frequency

- ✓ Determination of the linear-viscoelastic range (LVR), where material functions (G‘,G“, δ) are independent of the stress or the deformation applied
- ✓ Information about product stability e.g. gel strength

Oscillation

Amplitude sweep

Increasing amplitude inshear stress τ (CS) or deformation γ (CD) with const. frequency



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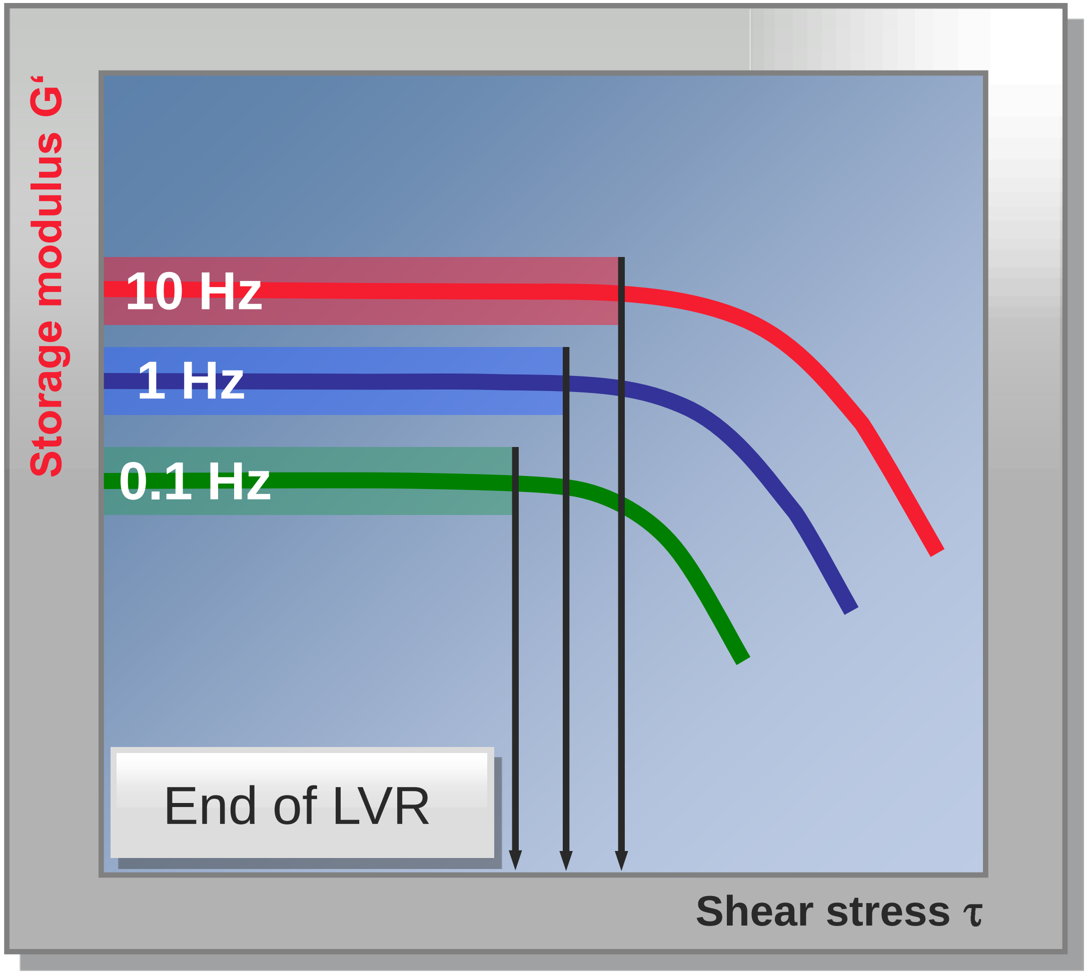
Oscillation

Amplitude sweep



Plotted over τ

Width of the linear-viscoelastic regime (LVB) depends on the frequency

Plotted over γ

Width of LVB is less frequency depending

Viskoelastizität

✓ Oscillation

Frequency sweep

Oscillation

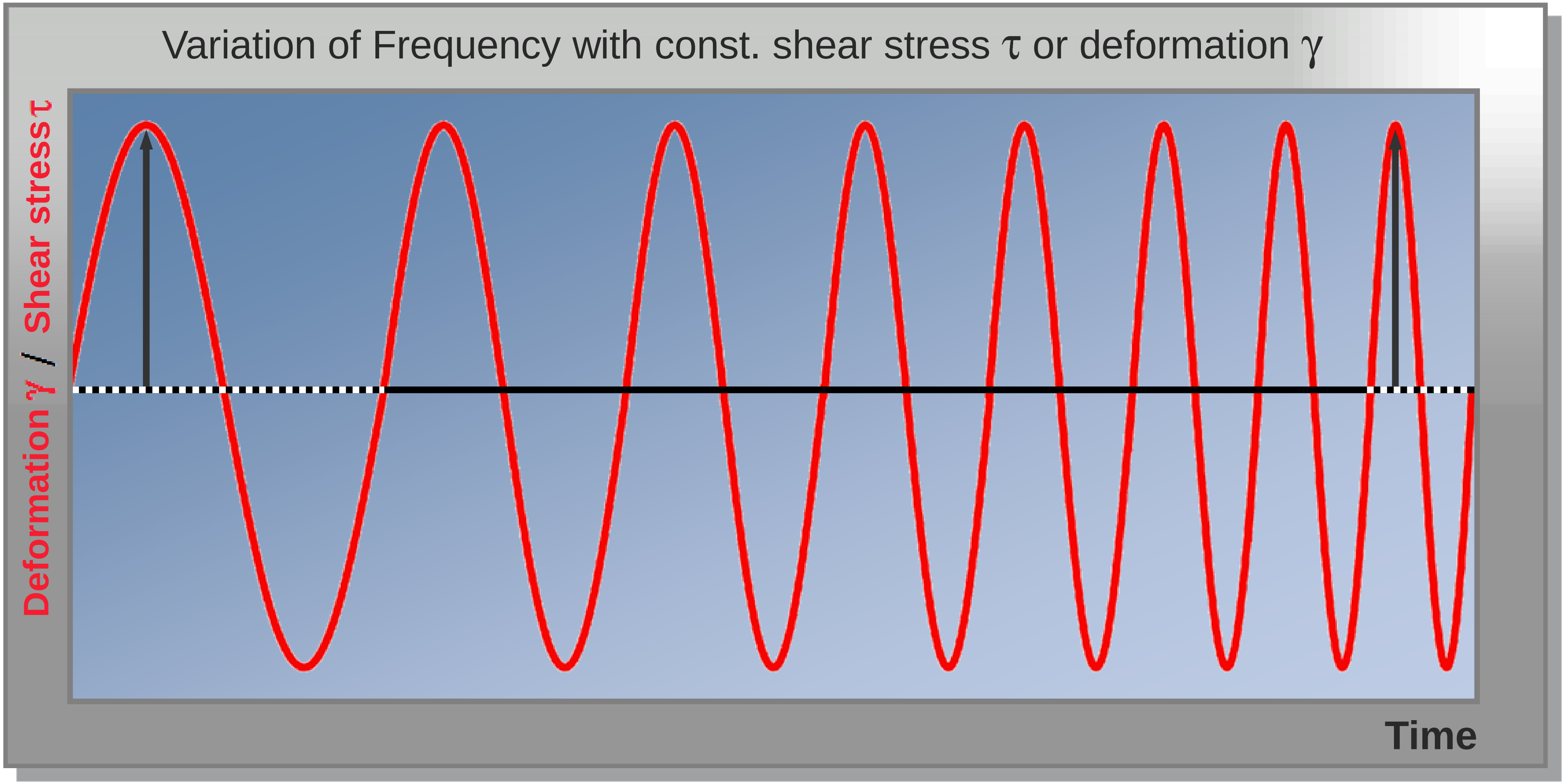
Frequency sweep

Variation of frequency with constant shear stress τ or deformation γ respectively

- ✓ Determination of material‘s structure
- ✓ Determination of material’s properties, which cannot be measured in shear

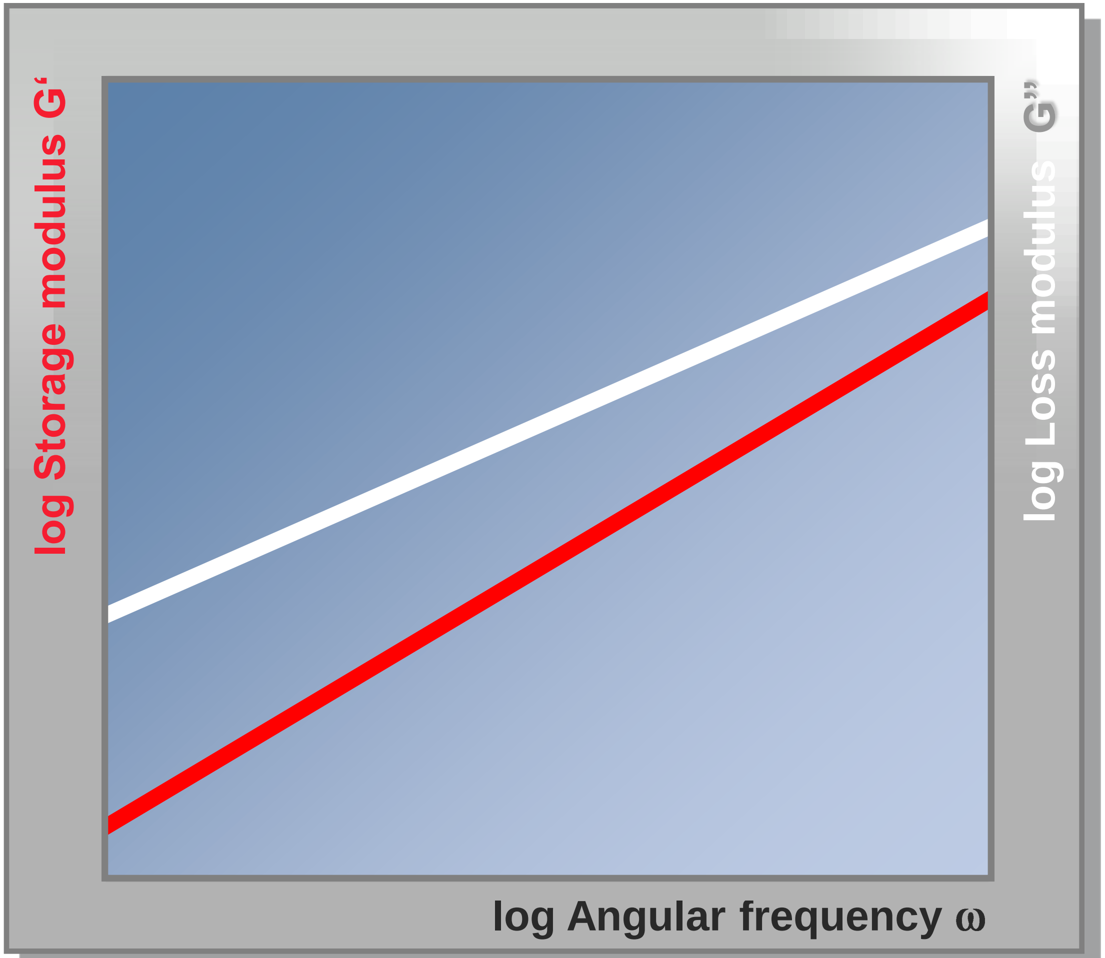
Oscillation

Frequency sweep



Oscillation

Frequency sweep



Viscous Flow

The samples behaves mainly viscous over the entire measuring range

G' < G''

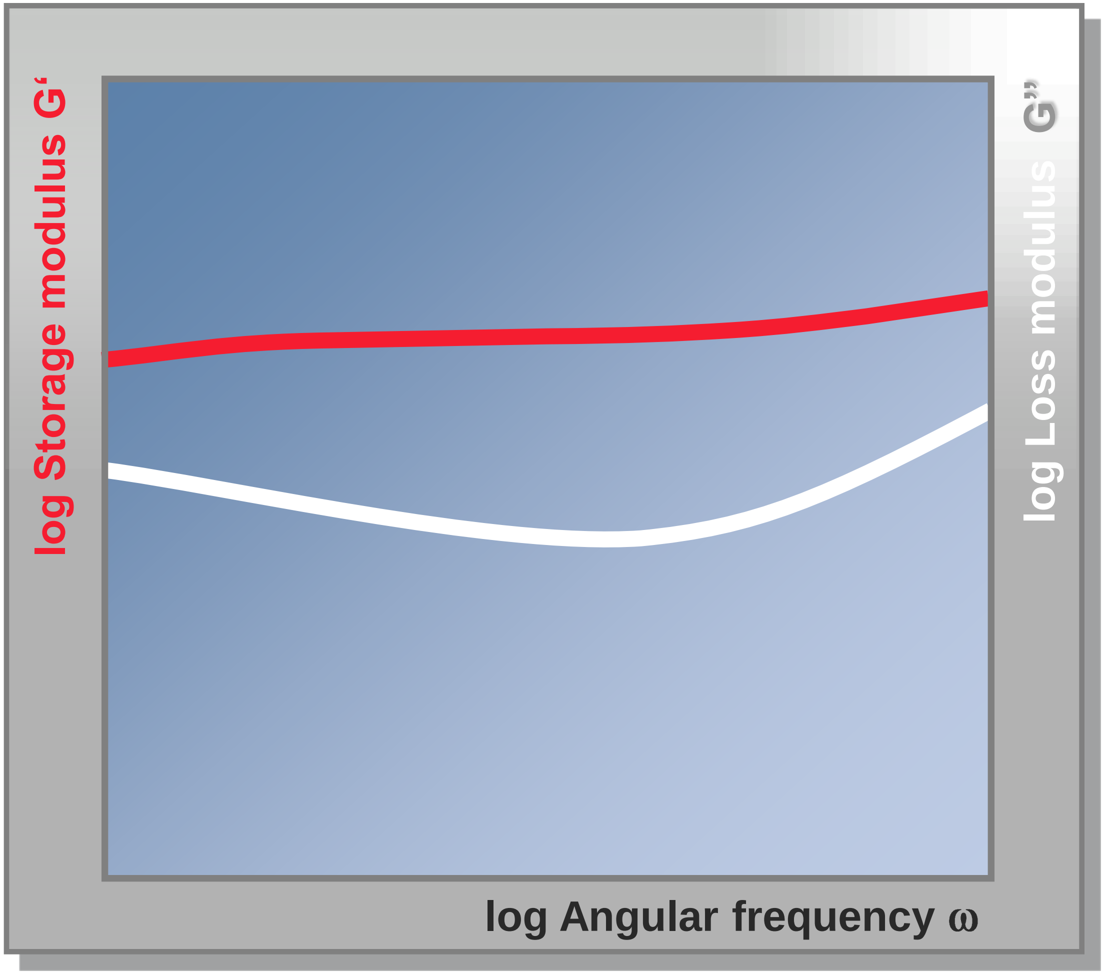
For ideal viscous samples:

Slope G'(ω) = 2

Slope G''(ω) = 1

Oscillation

Frequency sweep



Elastic Plateau

Sample behavior is dominated by the elastic properties

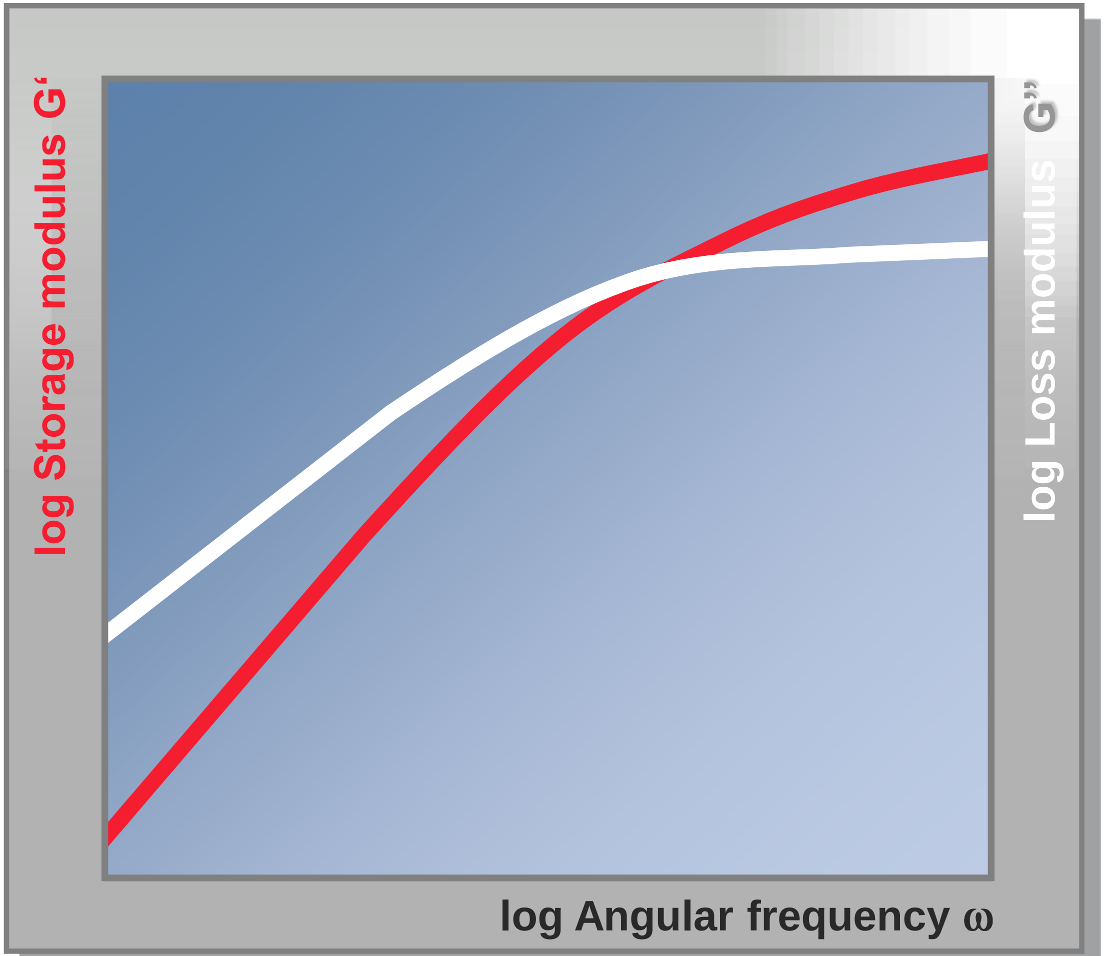
G' > G''

Examples:

- ✓ Cross linked Polymers
- ✓ Physical Networks

Oscillation

Frequency sweep



Viscoelastic behavior

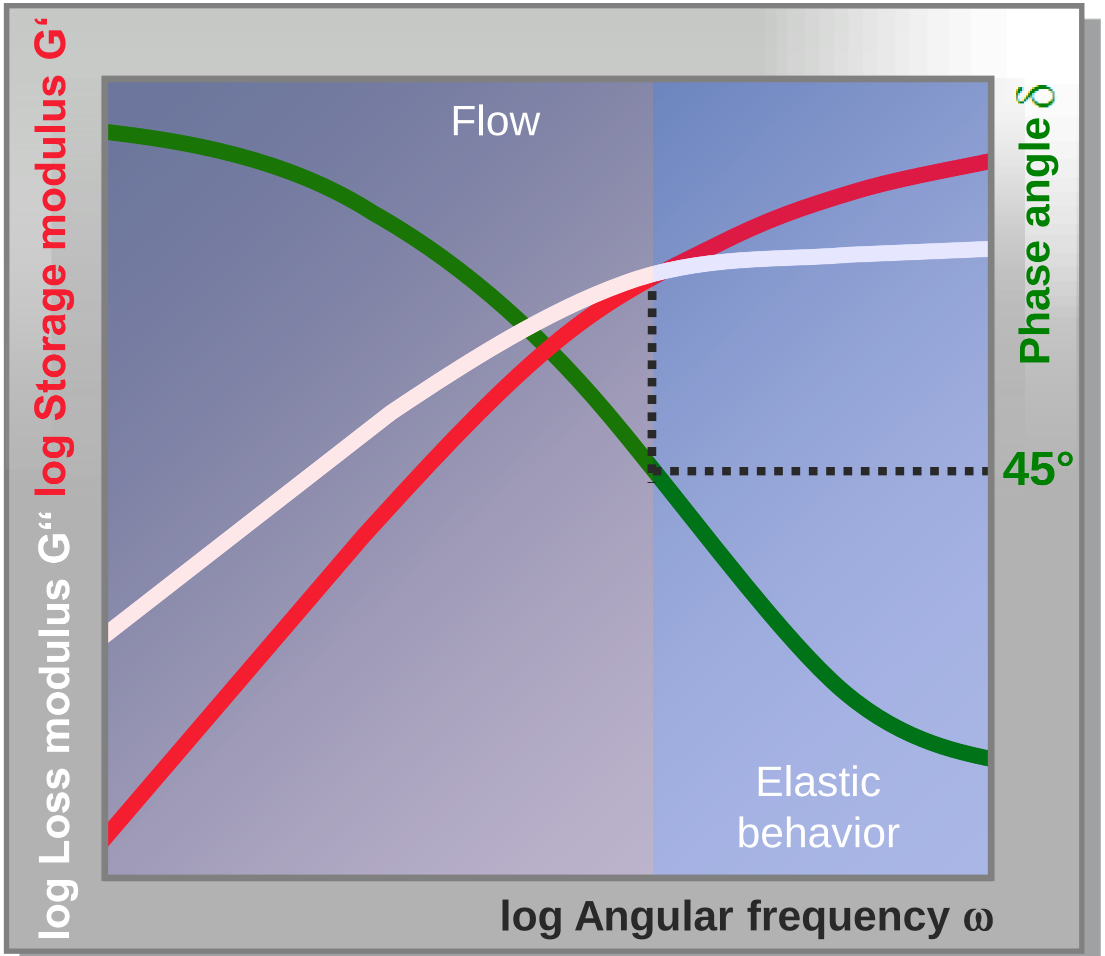
In the region of low frequencies the sample behaves viscous

At high frequencies the elastic behavior predominates

Cross-Over-Point G' = G''

Oscillation

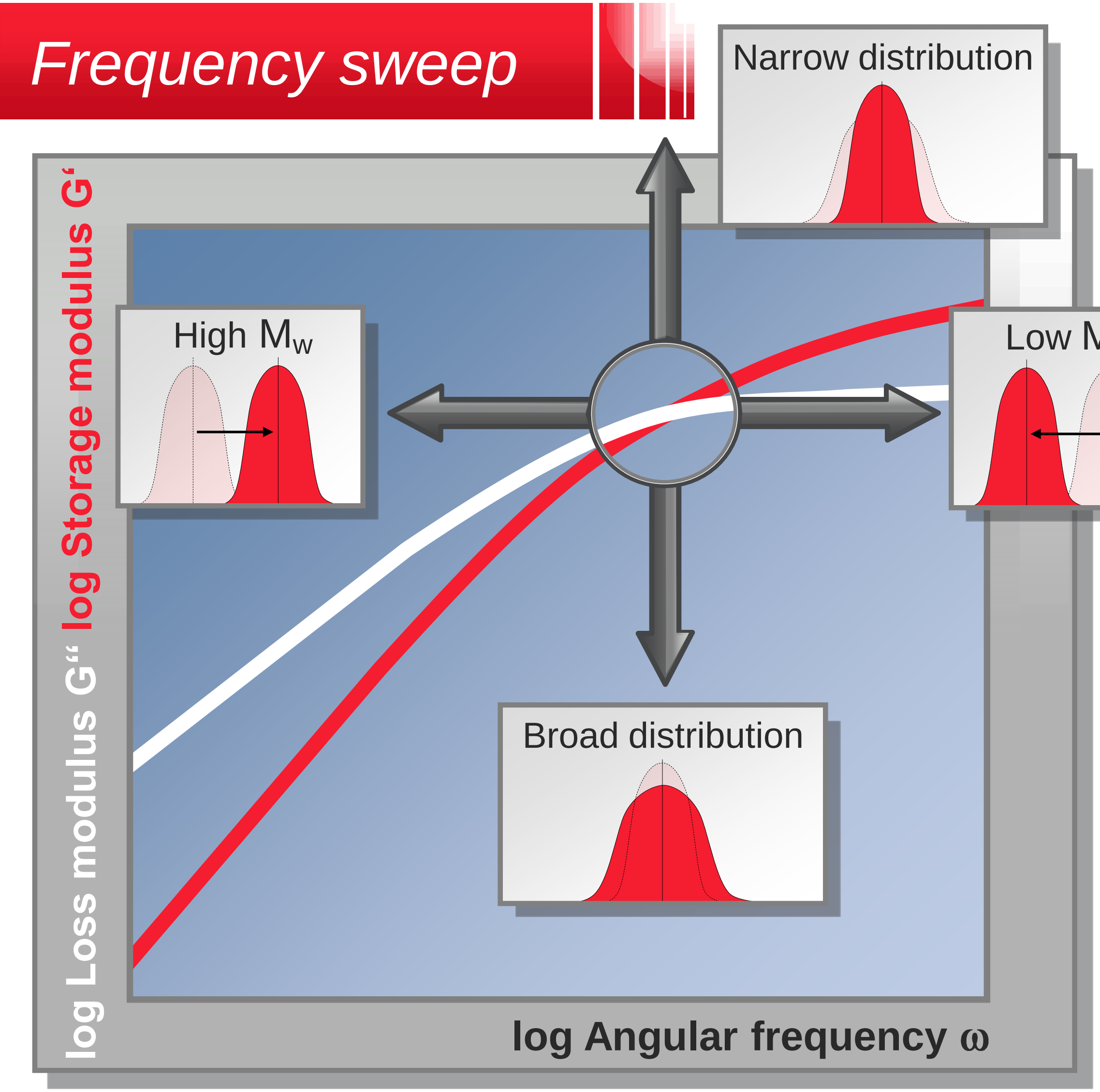
Frequency sweep



Cross-Over-Point

The Cross-Over-Point G' = G'' separates viscous flow at low frequencies and elastic behavior at higher frequencies

Oscillation



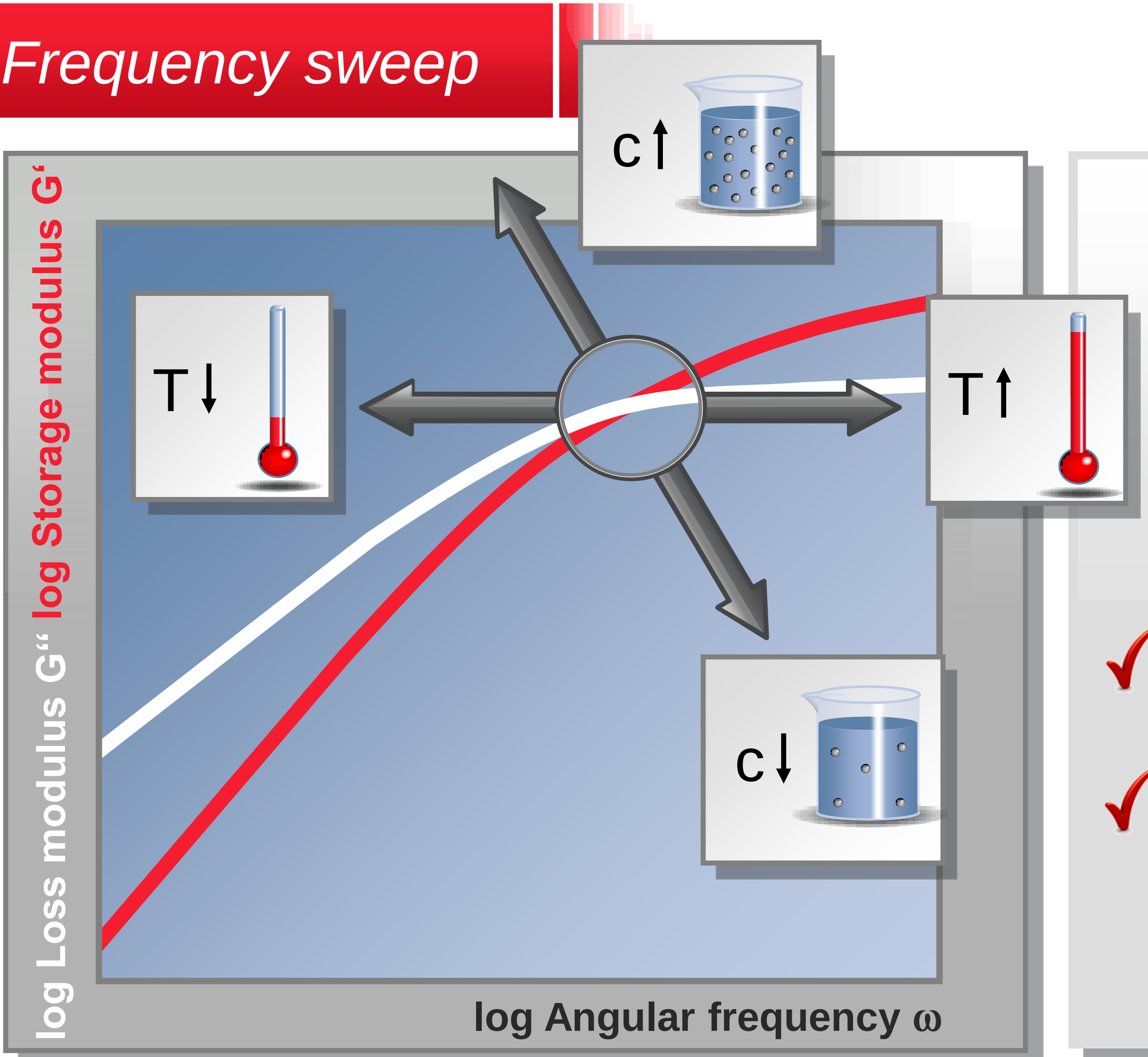
Polymer Fluids

The location of the cross over point depends on:

- ✓ The average molecular weight (M_w)
- ✓ The molecular weight distribution (MWD)

Oscillation

Frequency sweep



Polymere Fluide

The location of the cross over point depends on:

- ✓ The temperature T
- ✓ The polymer concentration c (for polymer solutions)

Viskoelastizität

✓ Oscillation

Temperature sweep

Oscillation

Temperature sweep

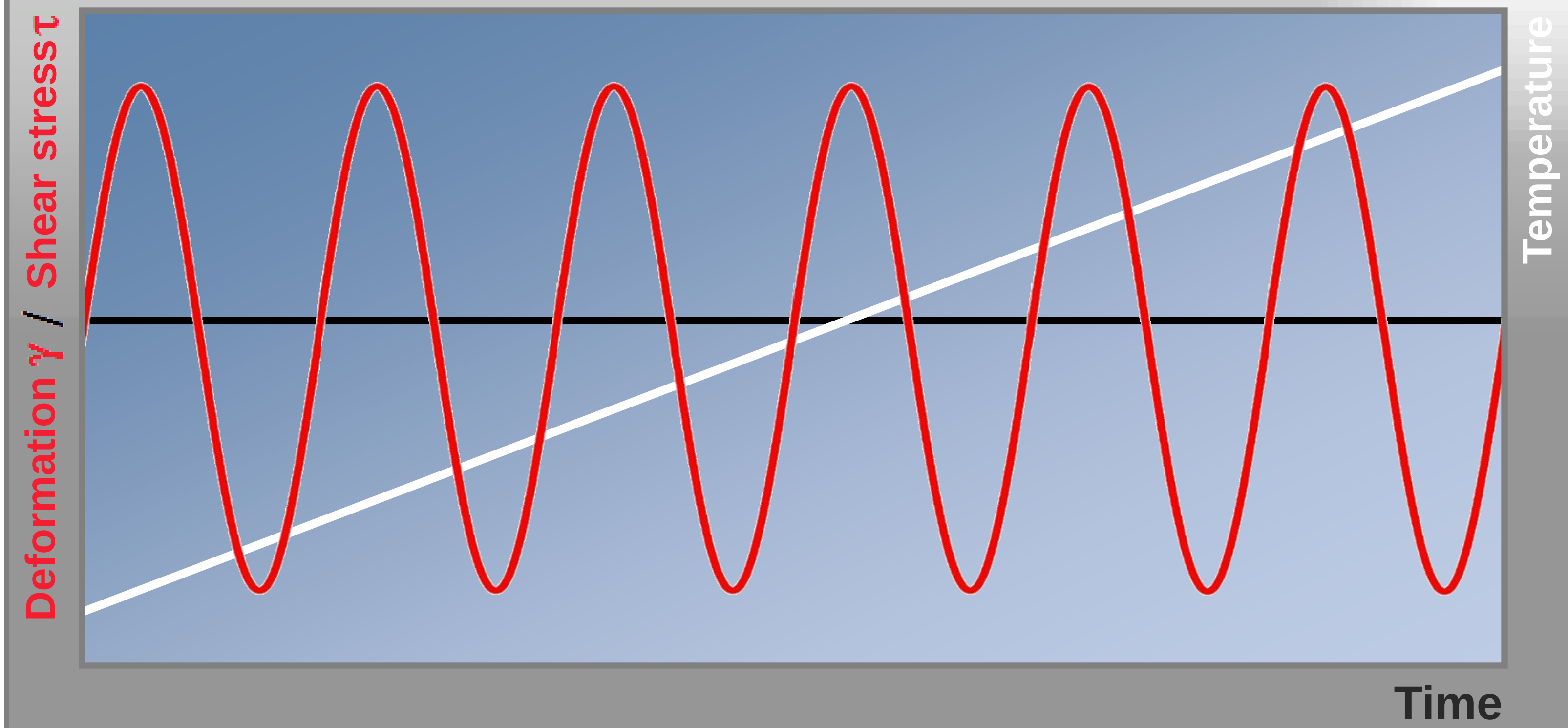
Variation of the temperature with constant shear stress τ or deformation γ and (angluar) frequency ω,f

- ✓ Determination of the temperature depending sample charteristics
- ✓ Determination of the glas transition, softening and melting temperature
- ✓ Investigation of chrystallization processes and sol-gel transitions

Oscillation

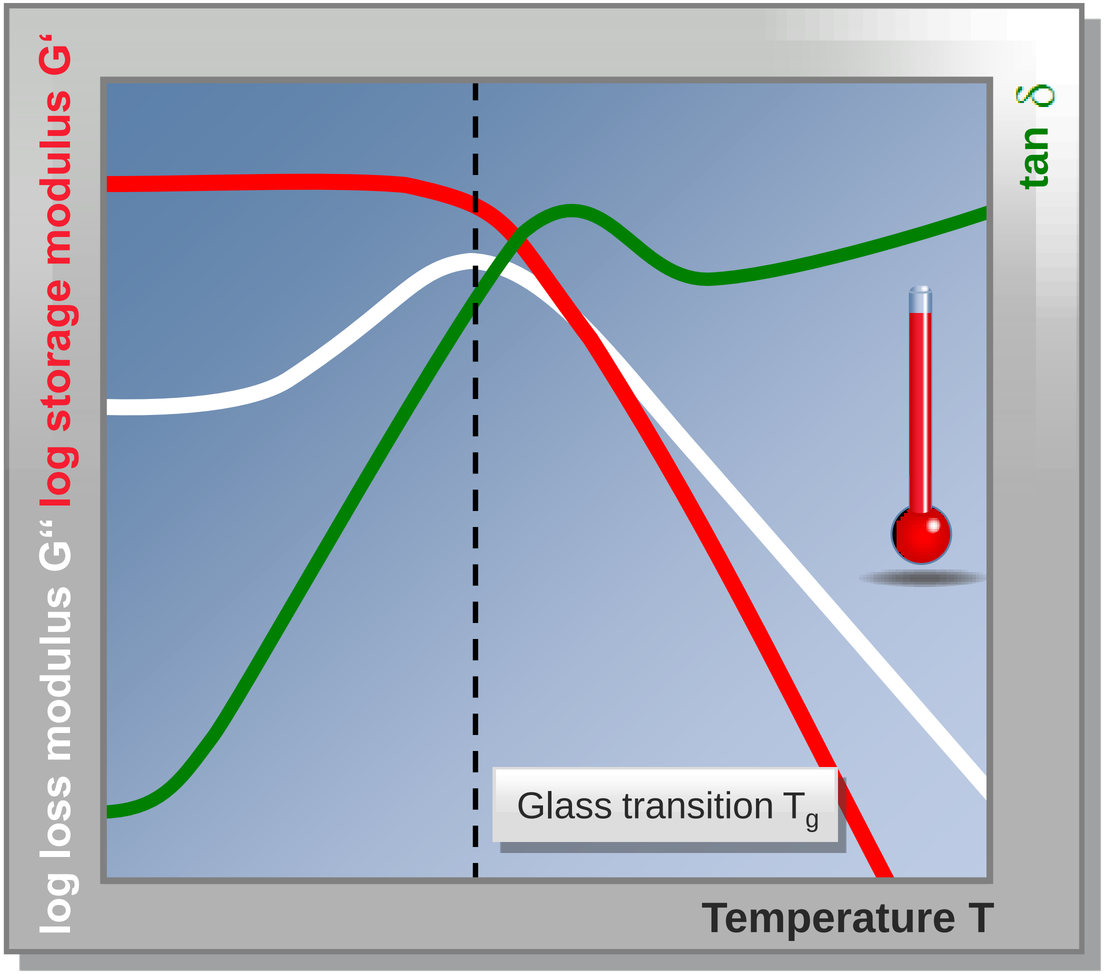
Temperature sweep

Variation of the temperatur with const. shear stress τ or deformation γ and (agular) frequency ω,f



Oscillation

Temperature sweep



Amorphous polymers

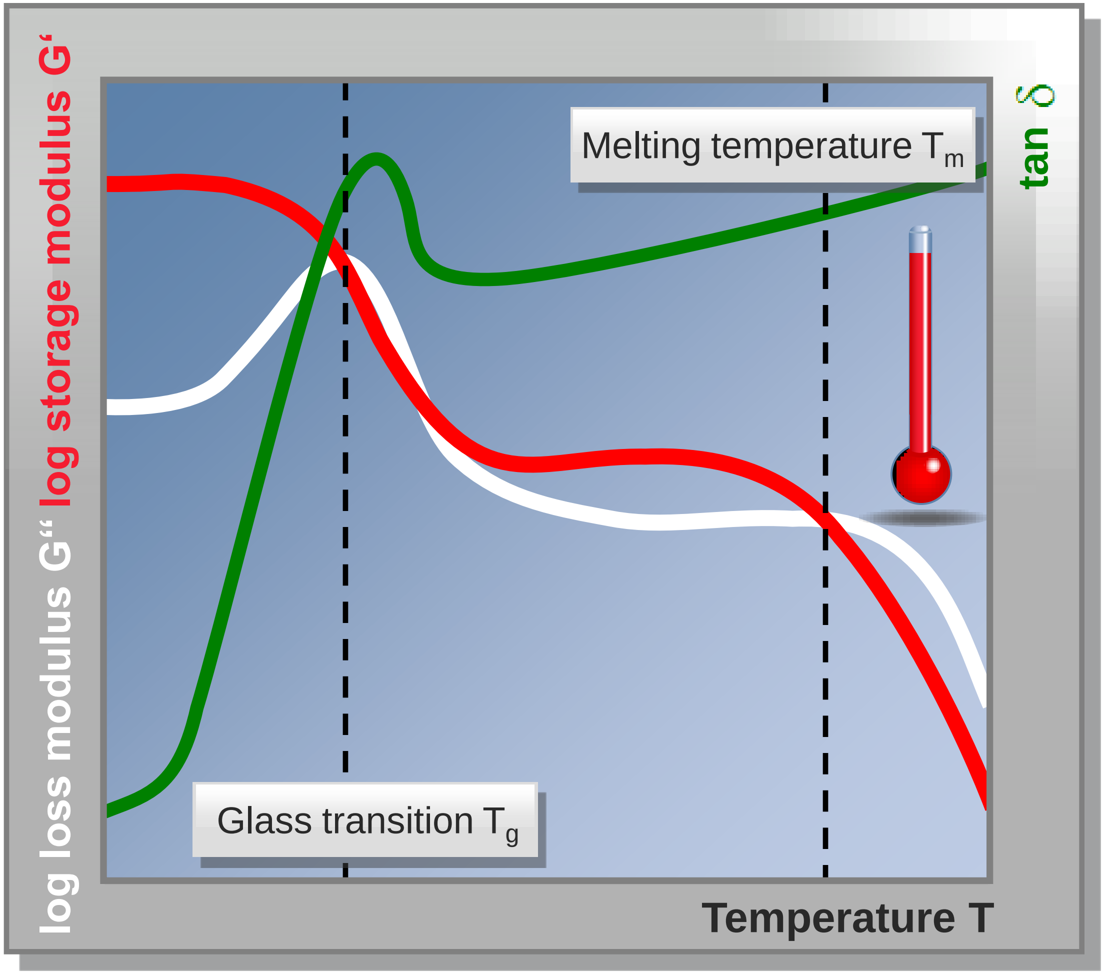
- ✓ Not cross linked
- ✓ No positional order
- ✓ Random orientation

Examples:

- ✓ Polystyrene
- ✓ Polyvinylchloride
- ✓ Polycarbonate

Oscillation

Temperature sweep



Semi crystalline Polymers

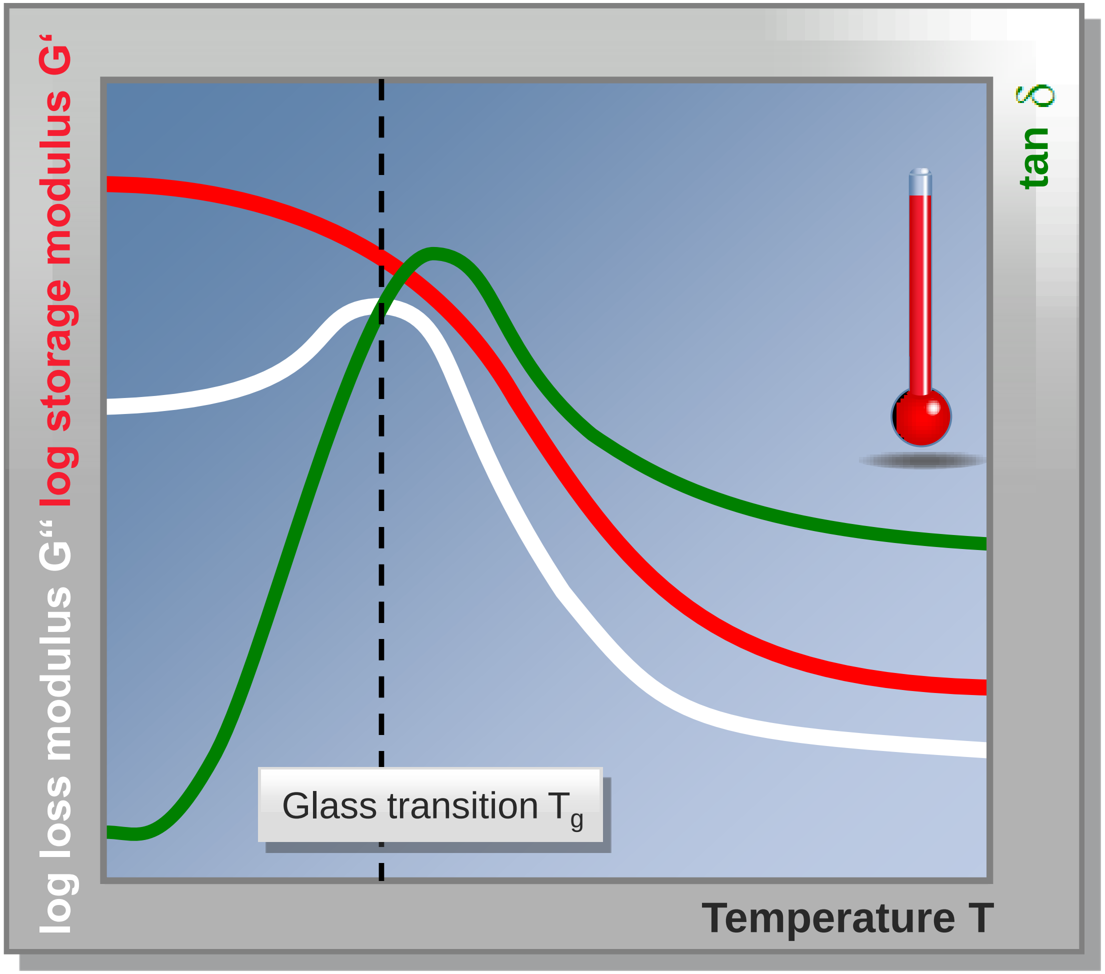
- ✓ Not cross linked
- ✓ Partially ordered structure
- ✓ Partially oriented

Examples:

- ✓ Low Density Polyethylen
- ✓ High Density Polyethylen
- ✓ Polypropylen

Oscillation

Temperature sweep



Cross-linked Polymers

Via covalent or ionic bonds cross-linked macro molecules

Examples:

Depending on the cross-link density

Elastomers (wide-meshed)

Thermosets (close-meshed)

Viscoelasticity

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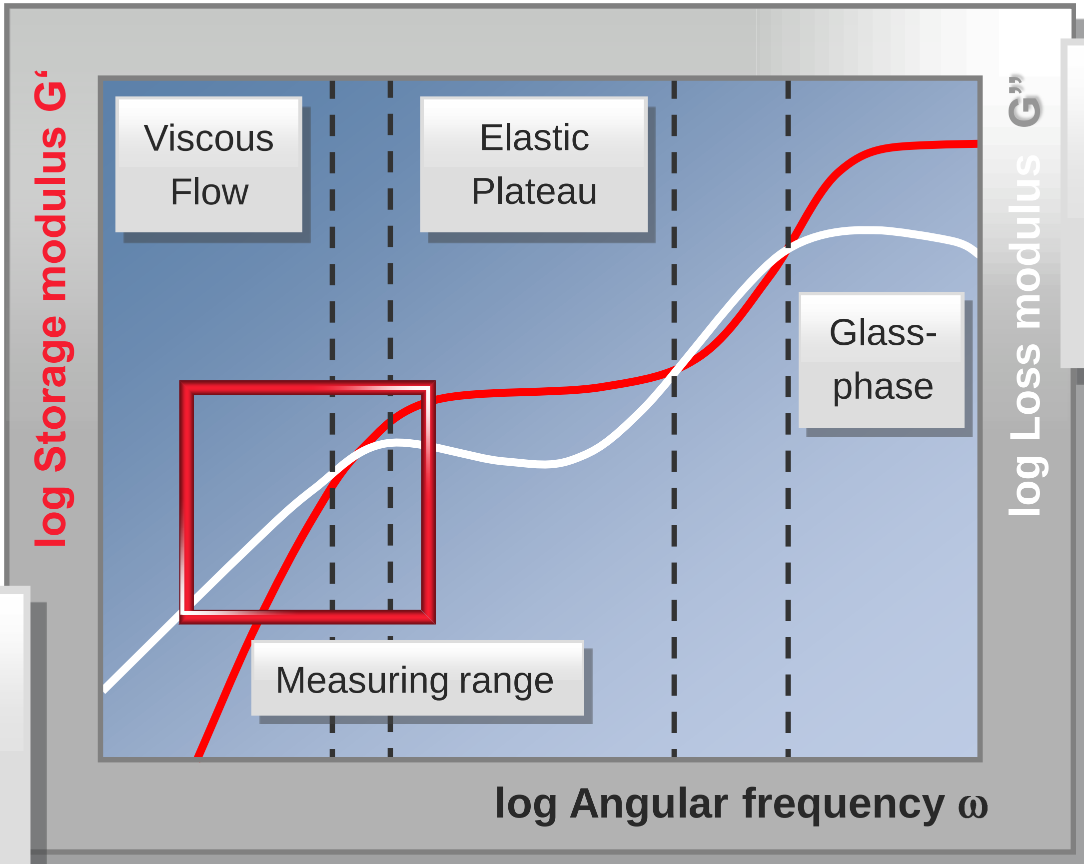
Oscillation

Frequency sweep



Inertia effects of rheometer limit the measurement range towards high frequencies

Long Measurement times limit the measurement range towards small frequencies

Oscillation

Frequency sweep

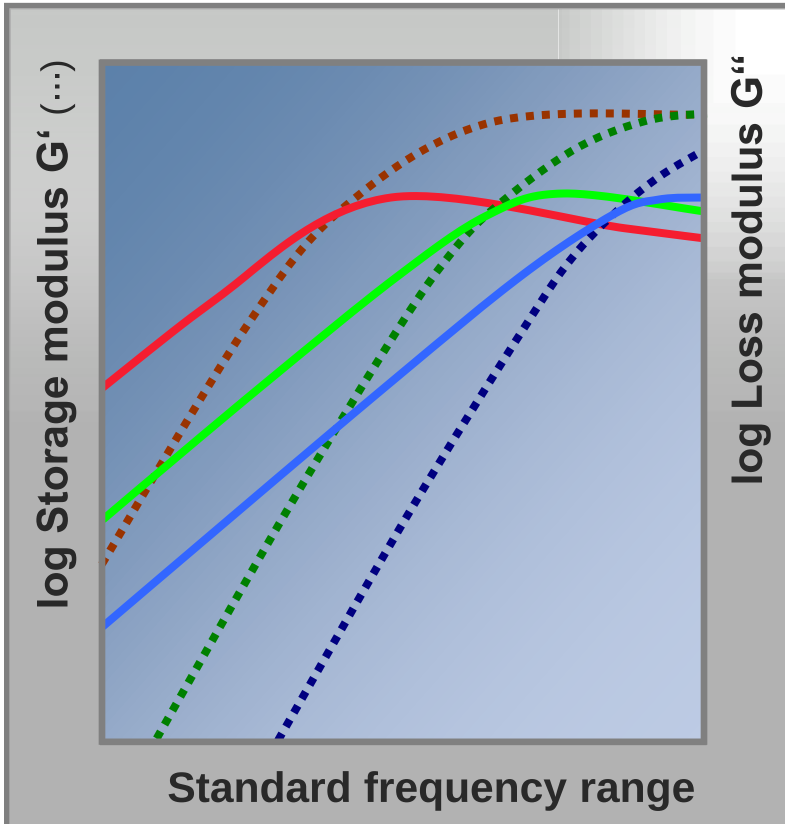
Freq. [Hz]	Time [s]	Time [min]	Time [h]	Time [d]
100	0.01			
10	0.1			
1	1			
0.1	10	0.17		
0.01	100	1.67		
0.001	1000	16.7	0.28	
0.0001	10000	167	2.78	0.12
0.00001	100000	1670	27.8	1.2
0.000001	1000000	16700	278	12

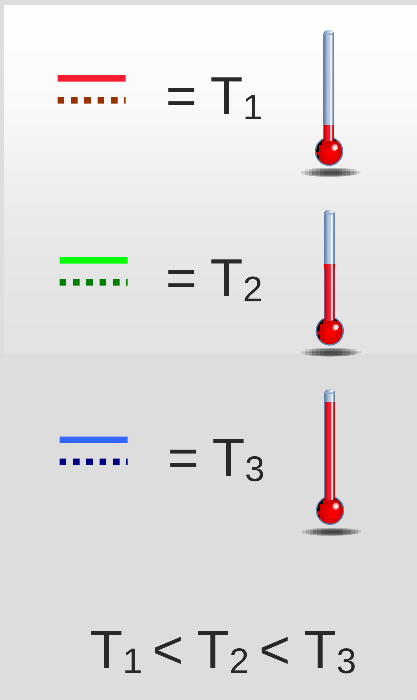
Expansion of the measurement range

Time Temperature Superposition (TTS)

Performance

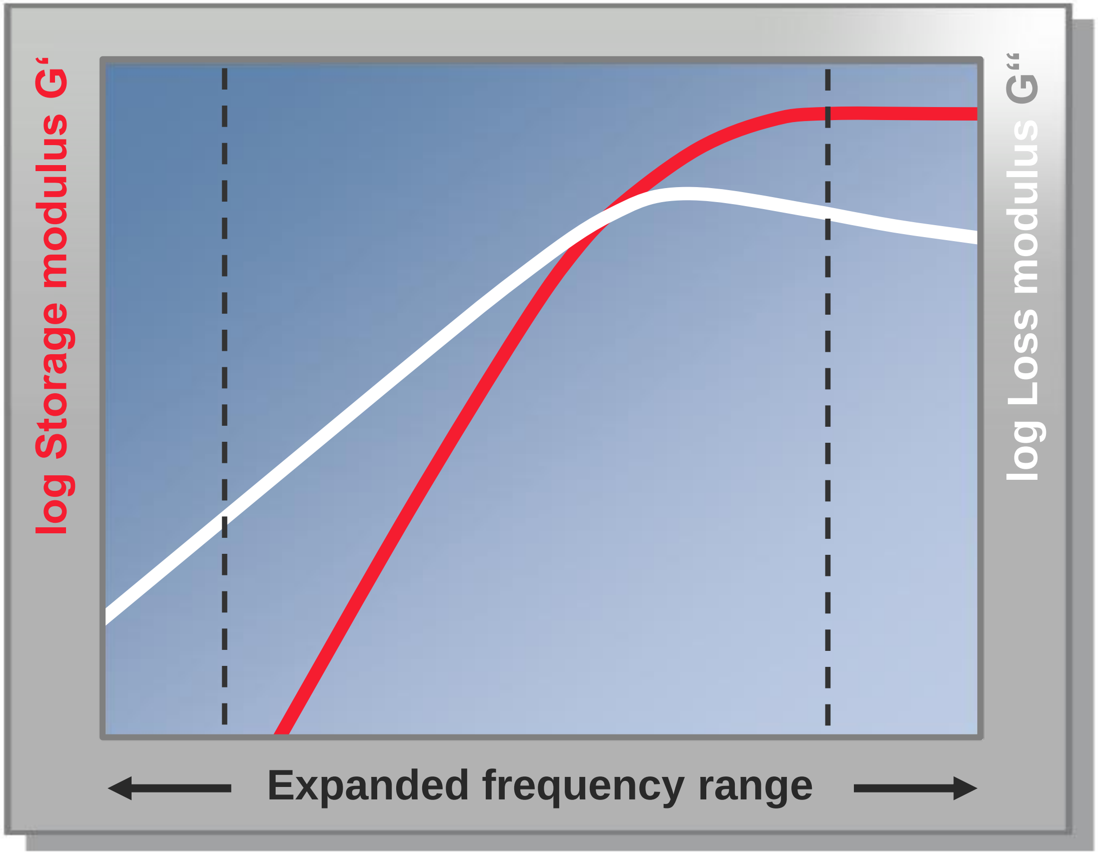
Several frequency sweeps are being performed at different temperatures





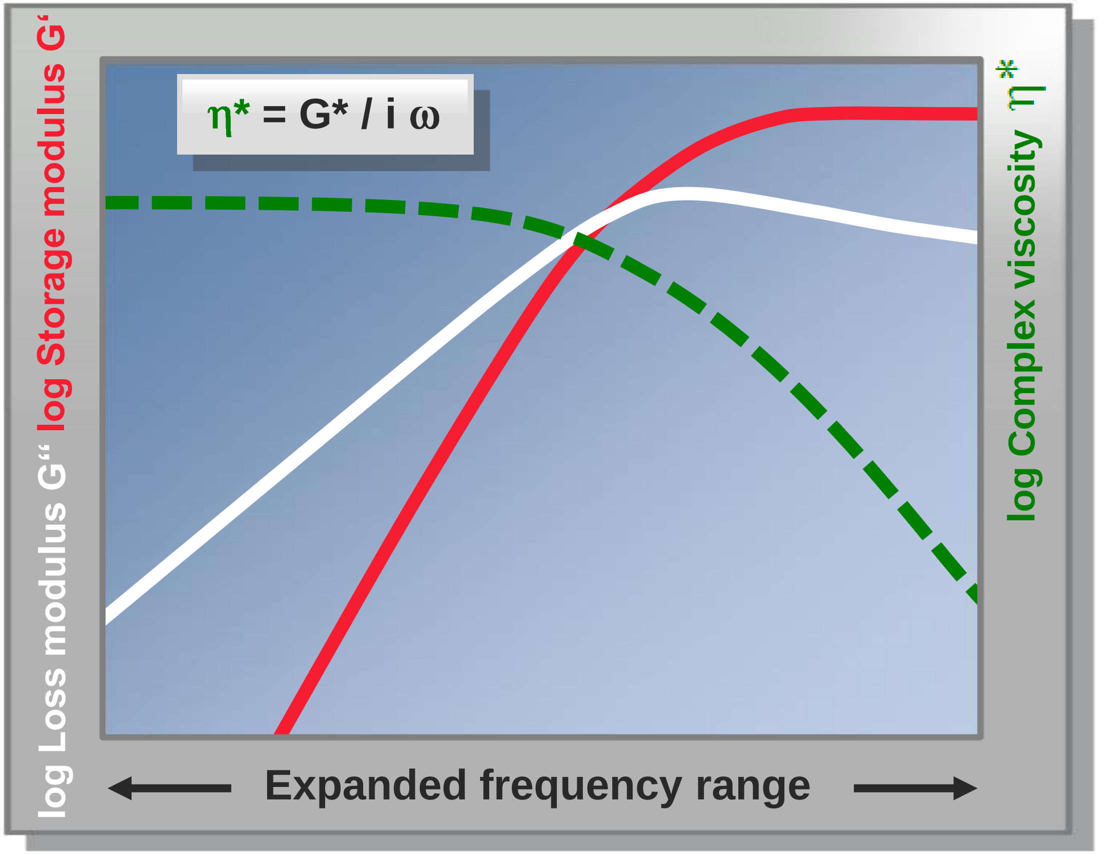
Expansion of the measurement range

Time Temperature Superposition (TTS)



Expansion of the measurement range

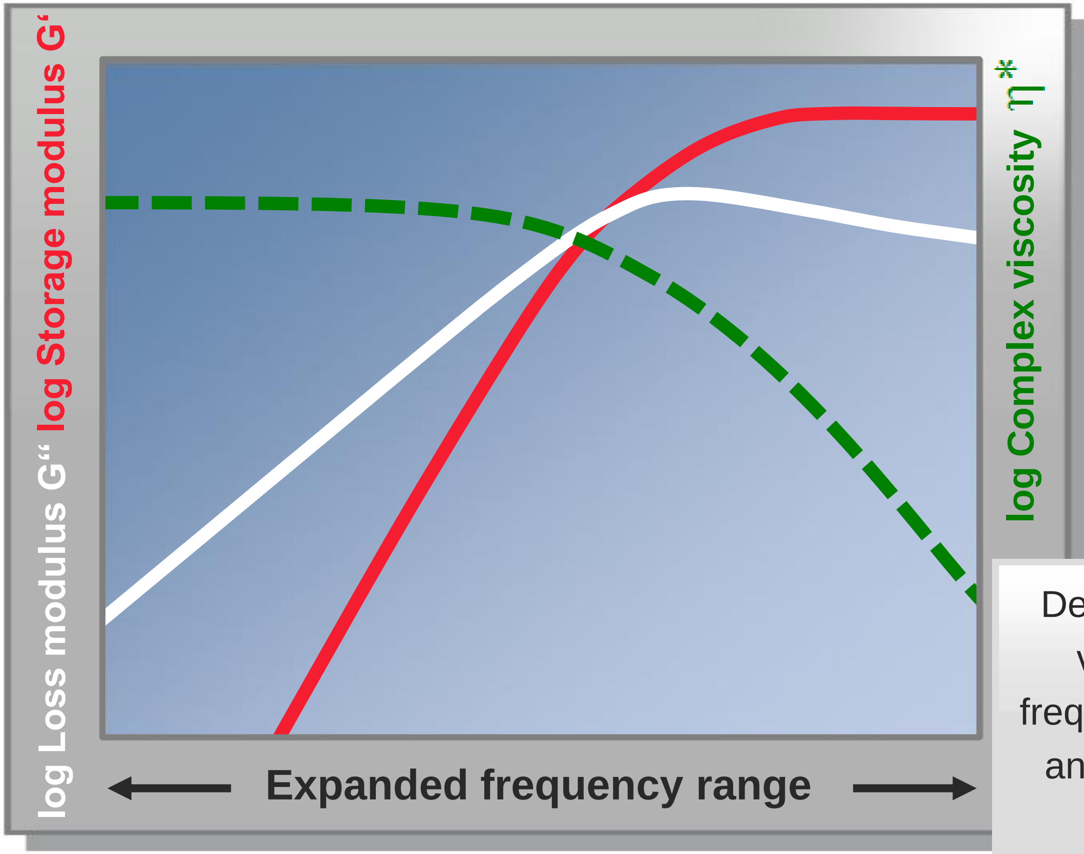
Time Temperature Superposition (TTS)



Expansion of the measurement range

Time Temperature Superposition (TTS)

Determination of the zero shear viscosity η_0



Determination of the viscosity at high frequencies / velocities and short relaxation times

Expansion of the measurement range

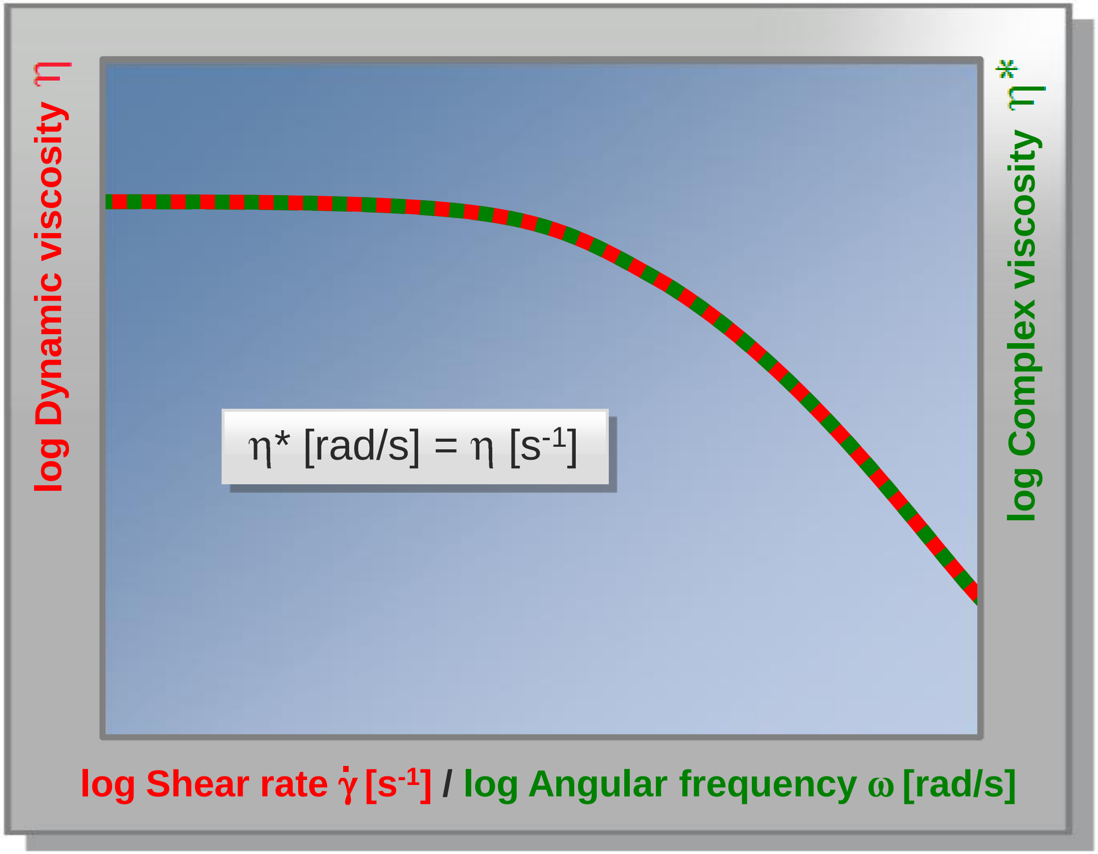
Cox-Merz Rule

Empiric Rule

Valid for numerous unfilled polymer melts and polymer solutions

Validity in the Non-Newtonian may vary

Not valid for dispersions, suspensions and gels



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Any questions ?

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Thank you for your attention