Viscoelasticity and Oscillation Experiment

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Overview

- Repetition of some basic terms
- Viscoelastic behavior
- Experimental approach to viscoelasticity by Oscillation
    - Amplitude sweep
    - Frequency sweep
    - Temperature sweep
    - Time sweep

Repetition of some basic terms

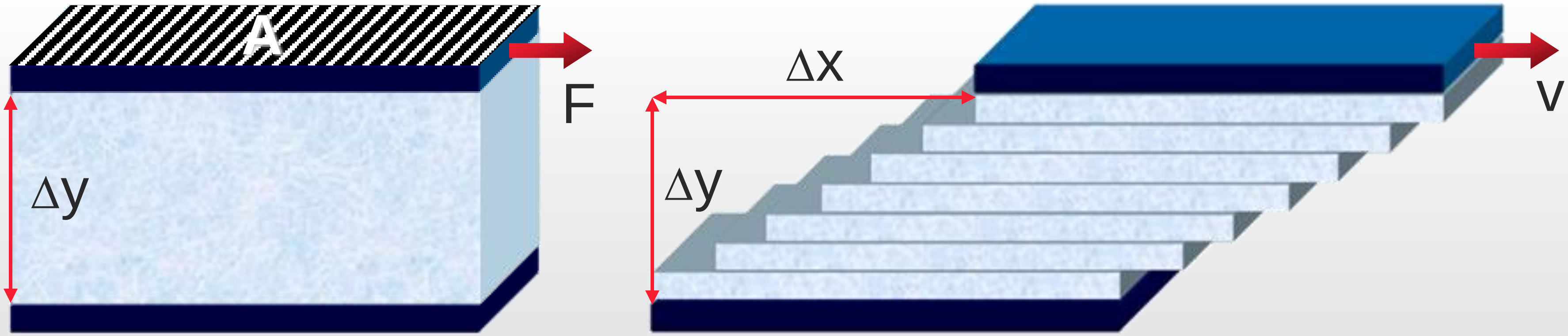
Calculation of the dynamic viscosity

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



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

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

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

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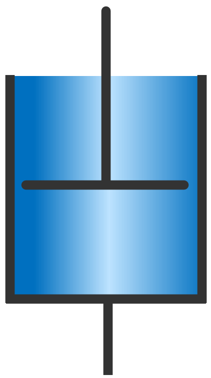
General considerations about viscoelasticity

Viscosity and elasticity

Viscosity

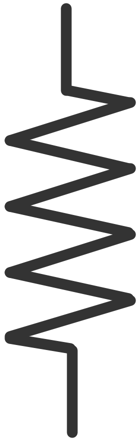
Dashpot



Investigated mainly with tests performed in rotation

Elasticity

Spring

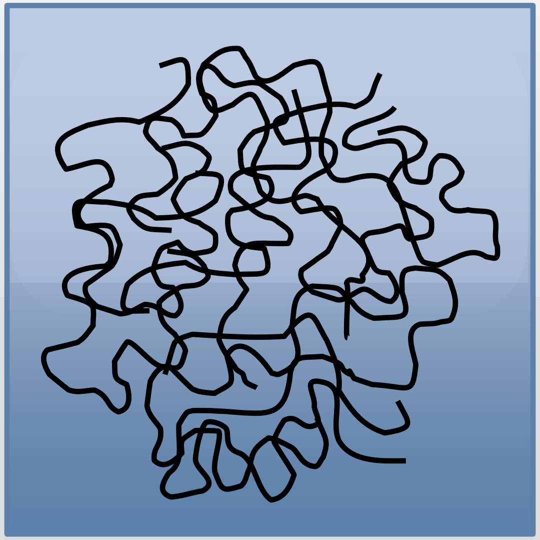


Investigated mainly with tests performed in oscillation

Viscoelastic behavior

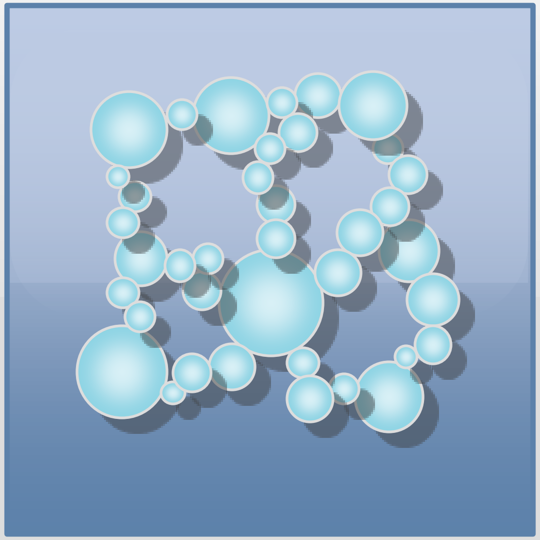
Reasons for viscoelasticity

Entenglements



- ✓ Polymer solutions
- ✓ Polymer melts

Network formation



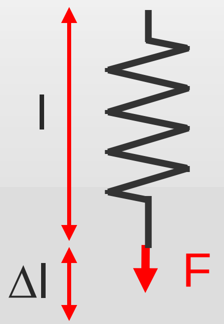
- ✓ Emulsions
- ✓ Suspensions

Viscoelastic behavior

Appying Hookke's law to rheology

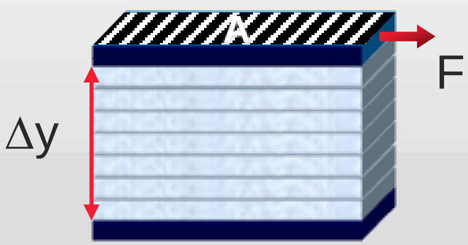
Purely elastic behavior

Spring



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

Viscoelastic behavior



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

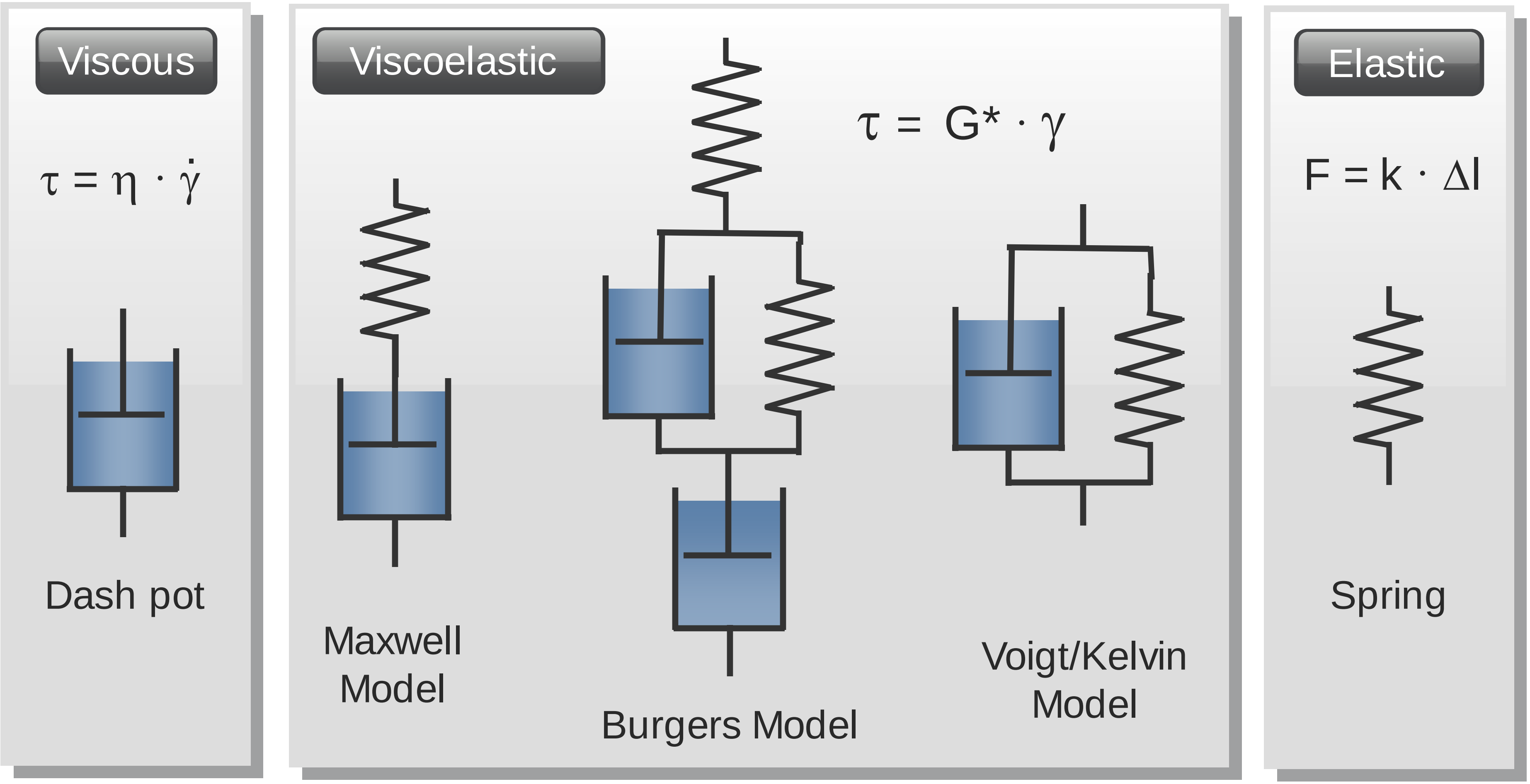
Result

✓ Complex modulus G*

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

Viscoelastic behavior

Models for viscoelasticity



Overview

- ✓ Repetition of some basic terms
- ✓ Viscoelastic behavior
- ✓ Experimental approach to viscoelasticity by Oscillation
    - Amplitude sweep
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Viscoelasticity

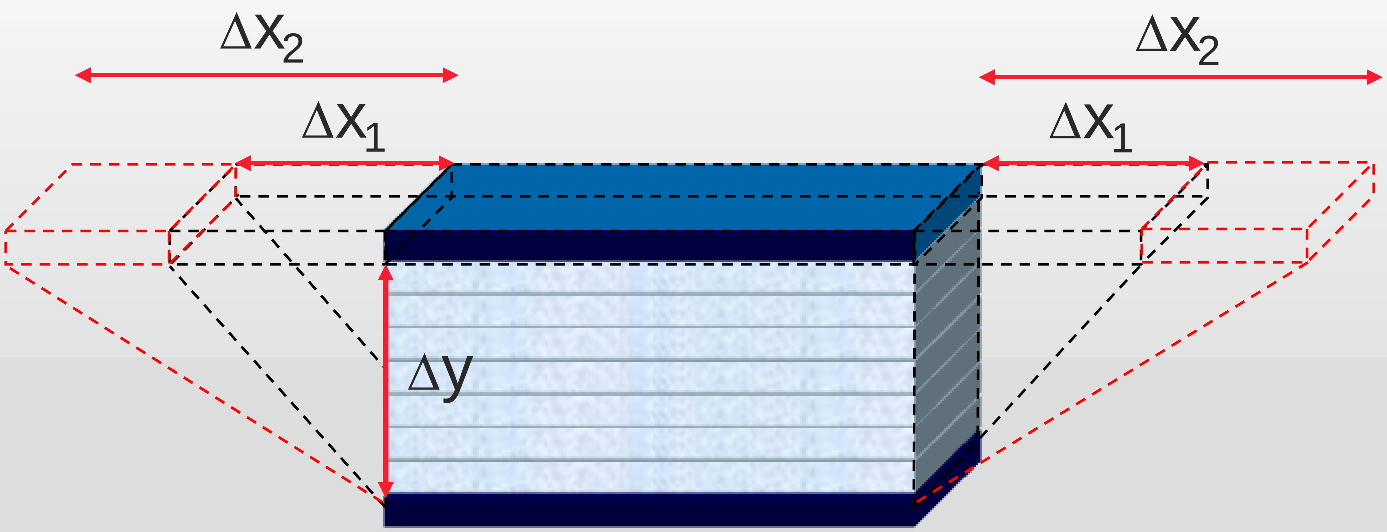
✓ Experimental approach to viscoelasticity

Oscillation

Oscillation

Principle of measurement

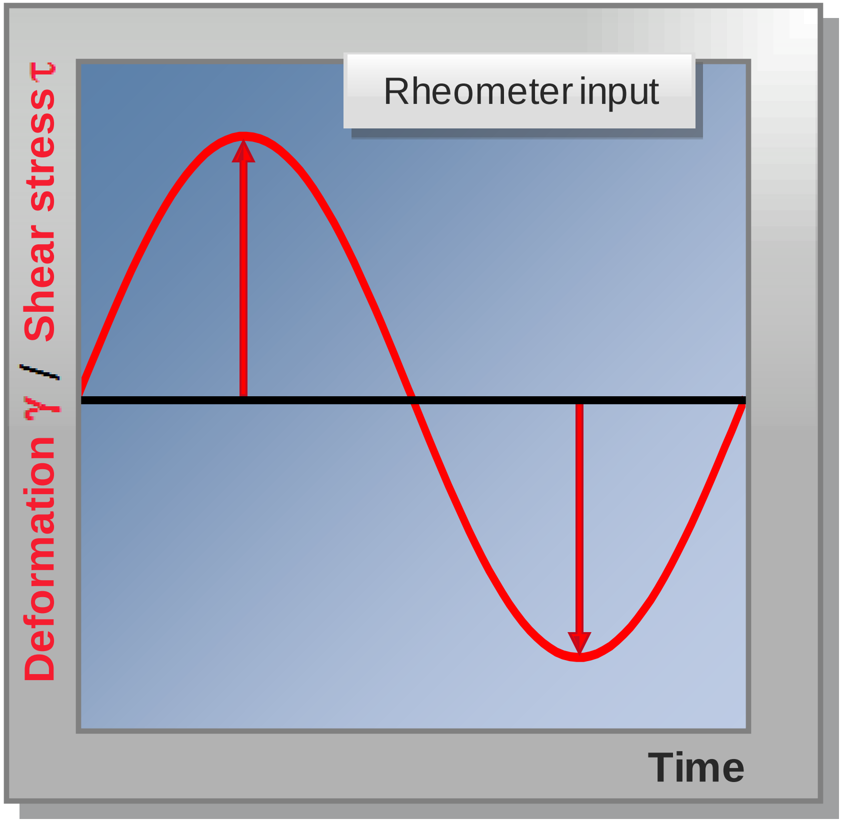
Two-Plates-Model

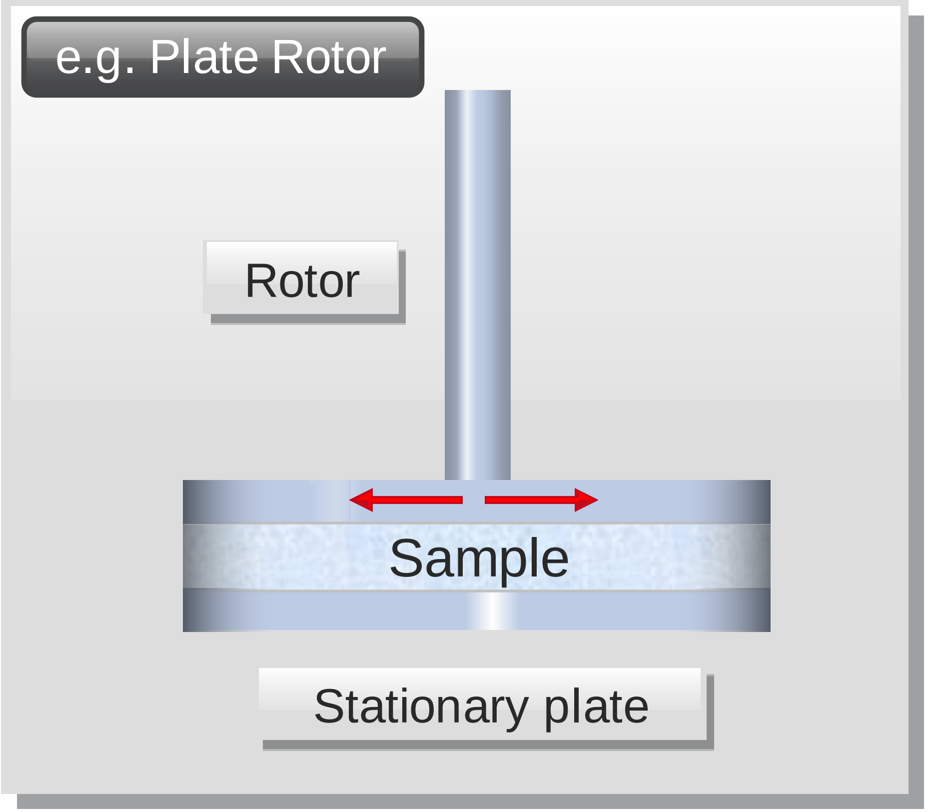


- A usually sinosoidal oscilllation is being applied by the rheometer
- Controllable parameters are the maximum amplitude (Δx_i) of the shear stress (τ) or deformation (γ) as well as the (angular) frequency (f, ω) and the temperature (T)

Oscillation

Principle of measurement

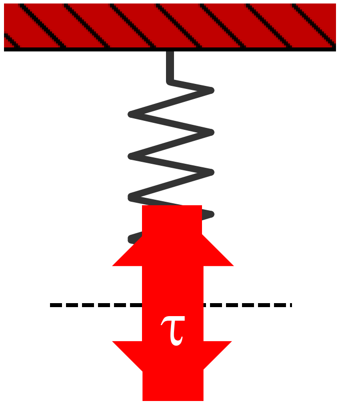


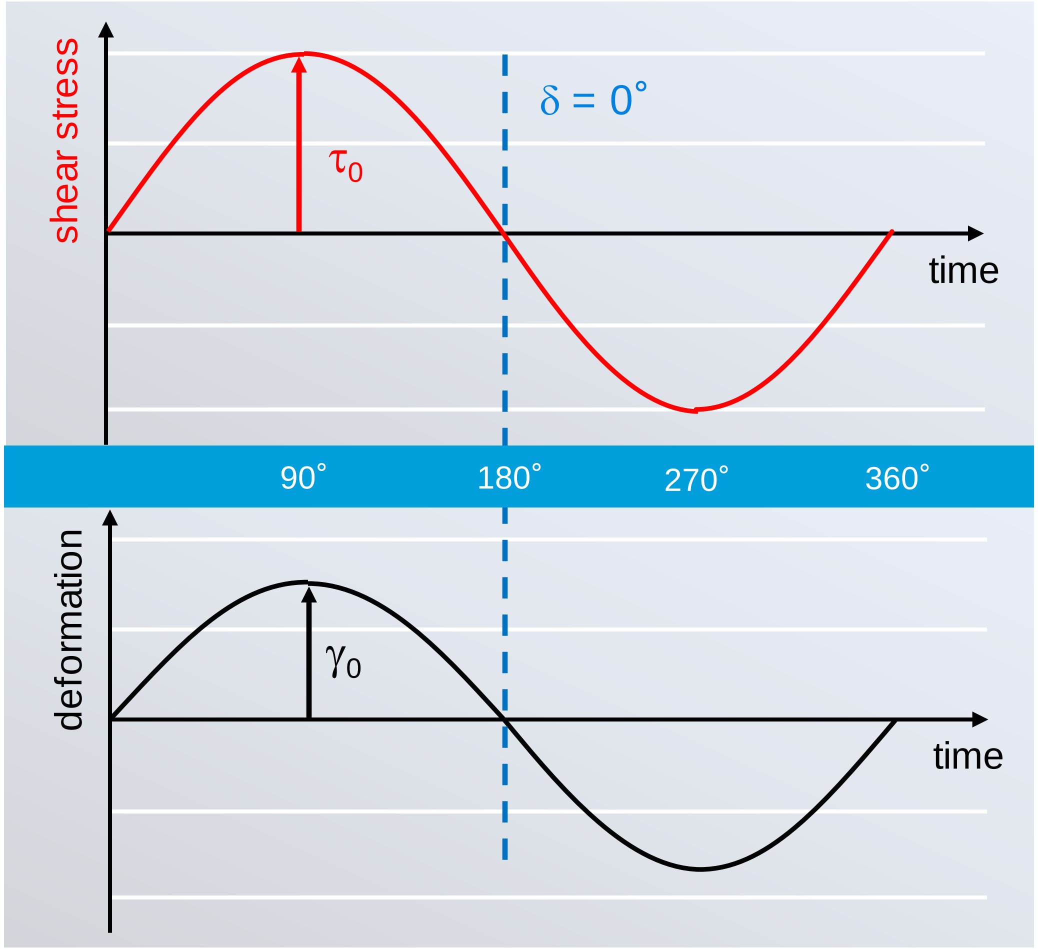


Oscillatory experiments

Principle of measurement

Purely elastic material



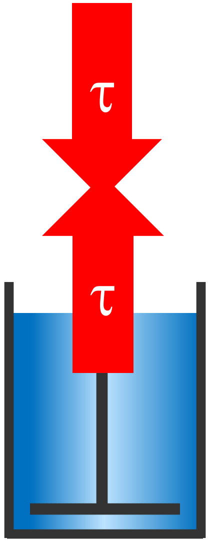


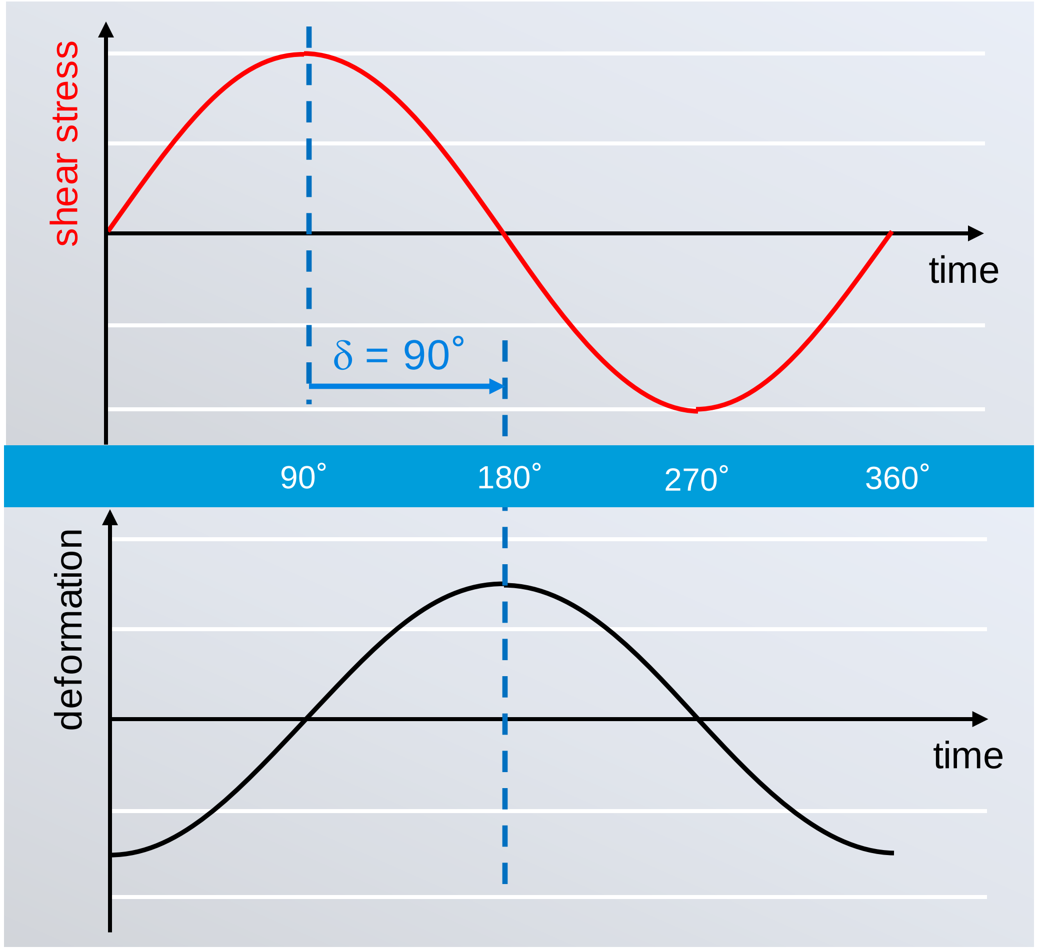
No phase shift between input and response

Oscillatory experiments

Principle of measurement

Purely viscous material





Phase shift (δ) between stress and deformation signal is 90°

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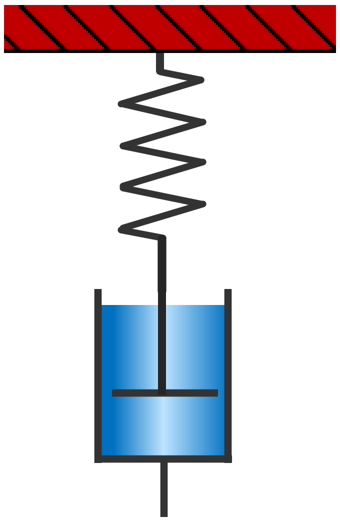
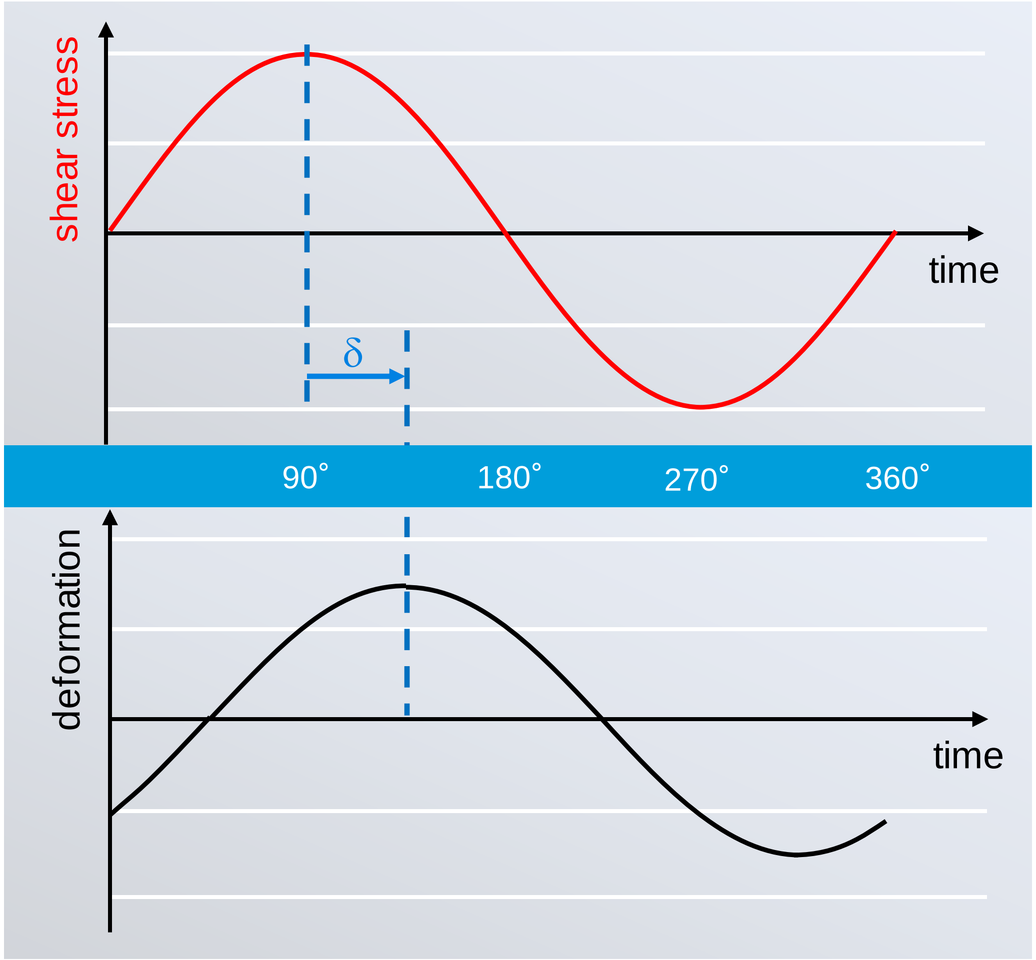
Oscillatory experiments

Principle of measurement

Viscoelastic sample



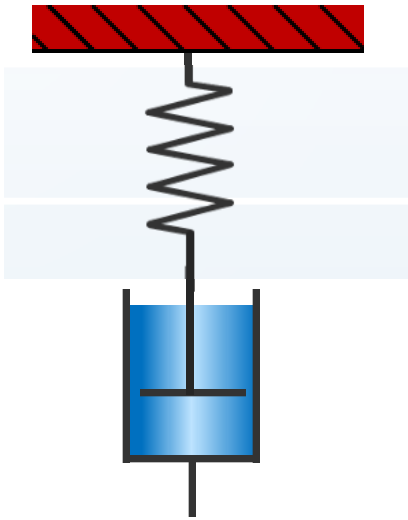
Phase shift (δ) between stress and deformation signal is between 0° and 90°

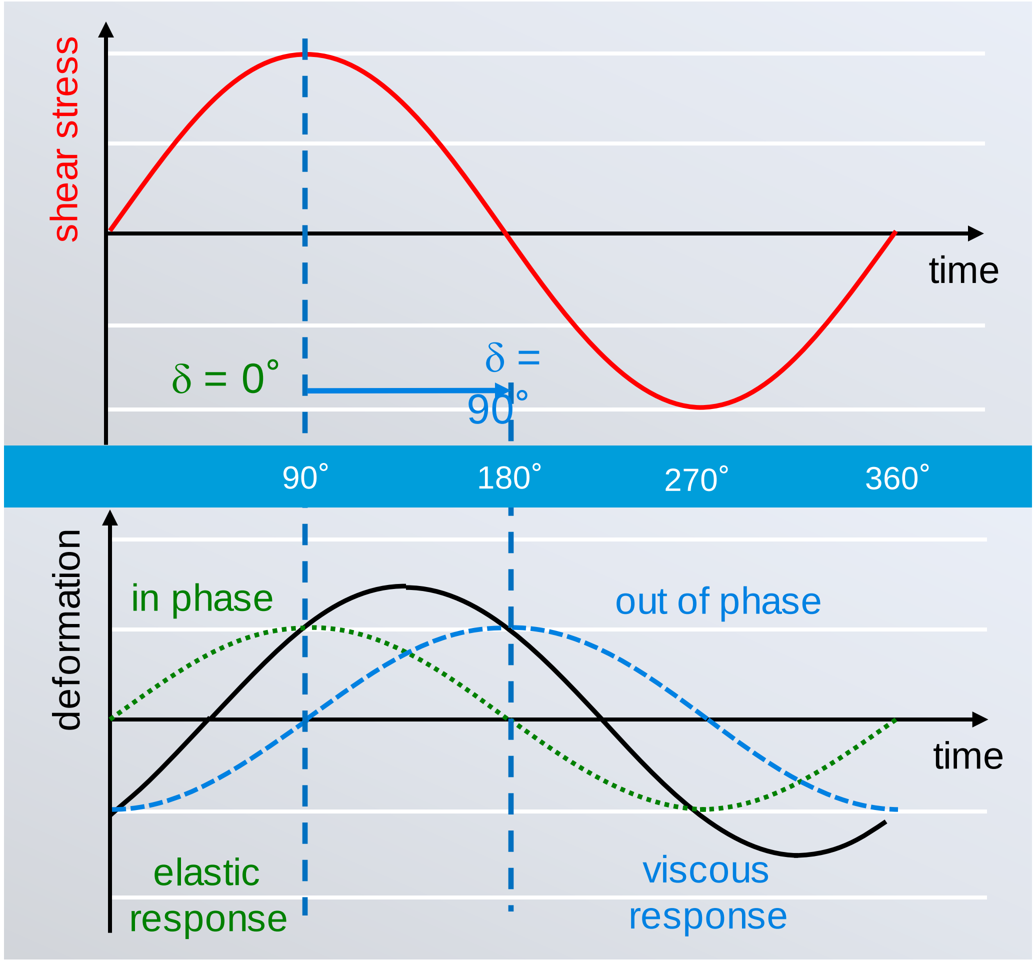


Oscillatory experiments

Principle of measurement

Viscoelastic sample





Phase shift (δ) between stress and deformation signal is between 0° and 90°

Oscillation

Results I

- Complex modulus

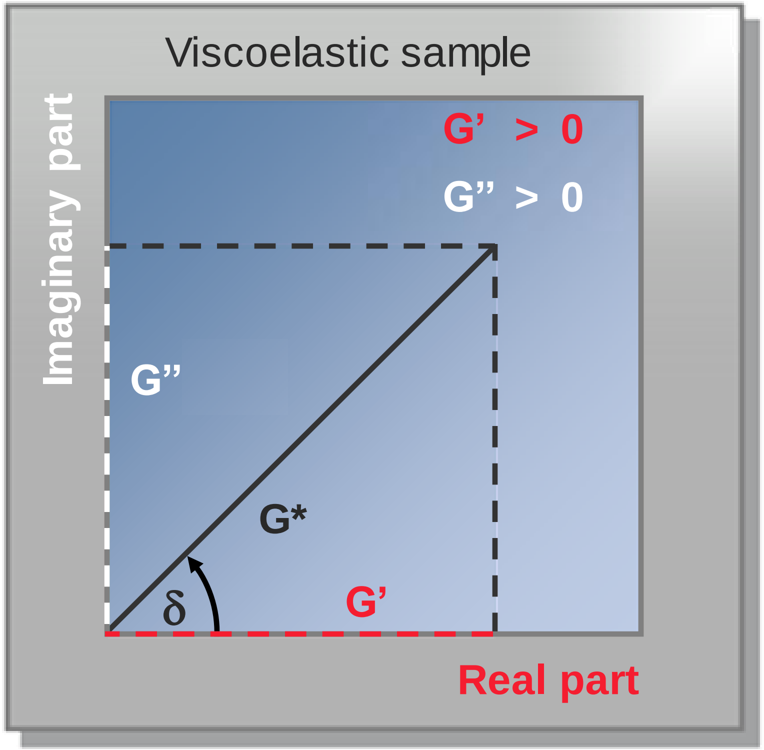
  $G^* = G' + i\,G''$ ($i^2 = -1$)

- Storage modulus

  G' (elastic part)

- Loss modulus

  G'' (viscous part, damping)



Oscillation

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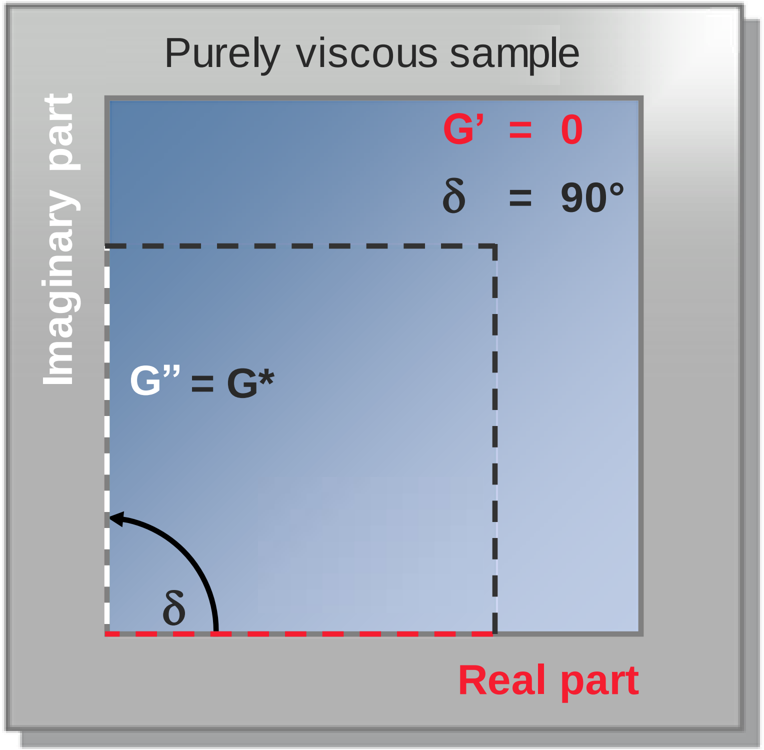

Oscillation

Results I

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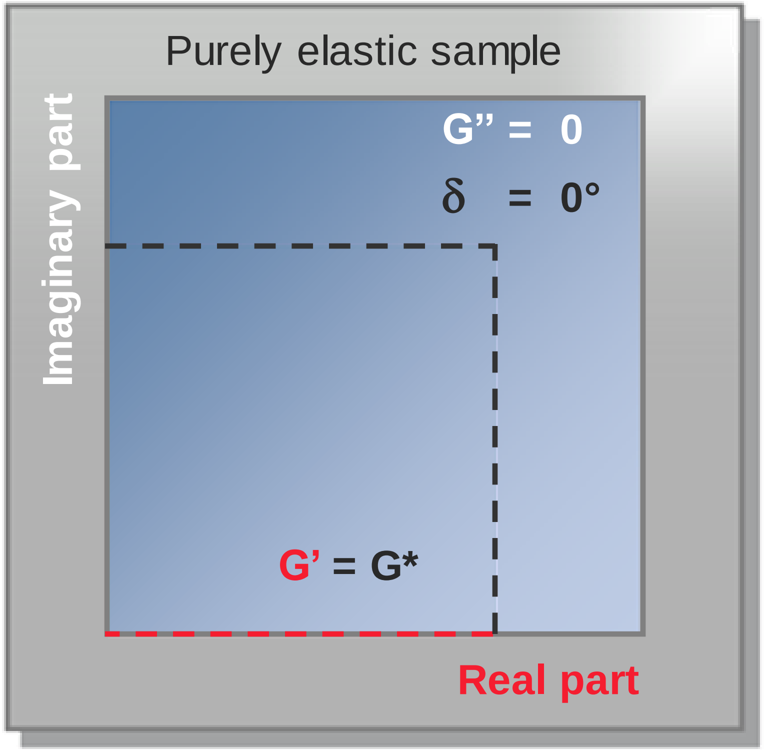


Oscillation

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)

Oscillatory experiments

When to perform oscillatory measurements

- When information about viscoelasticity is wanted
- When the material's behavior at rest is of interest
- When a phase transition of a material is investigated
- When rotational experiments cannot be performed because
    - the investigated material is too elastic
    - the investigated material shows wall slip effects

Oscillatory experiments

Oscillatory test methods

Oscillatory tests in controlled deformation CD or controlled stress CS

Amplitude Sweep	Frequency Sweep	Temperature sweep	Time Sweep
G', G'', δ… = f (γ_0 or τ_0)	G', G'', δ… = f (f or ω)	G', G'', δ… = f (T)	G', G'', δ… = f (t)

Amplitude Sweep

- Increasing the amplitude of applied stress or deformation signal
- Determination of linear viscoelastic range (LVR)

Frequency Sweep

- Changing frequency while keeping amplitude constant
- Determination of material character at different time scales

Temperature sweep

- Determination of temperature depending phase transitions and structural changes

Time Sweep

- Investigation of curing and cross linking reactions
- Stability tests

Viskoelastizität

✓ Oscillation

Amplitude sweep

Oscillation

Amplitude sweep

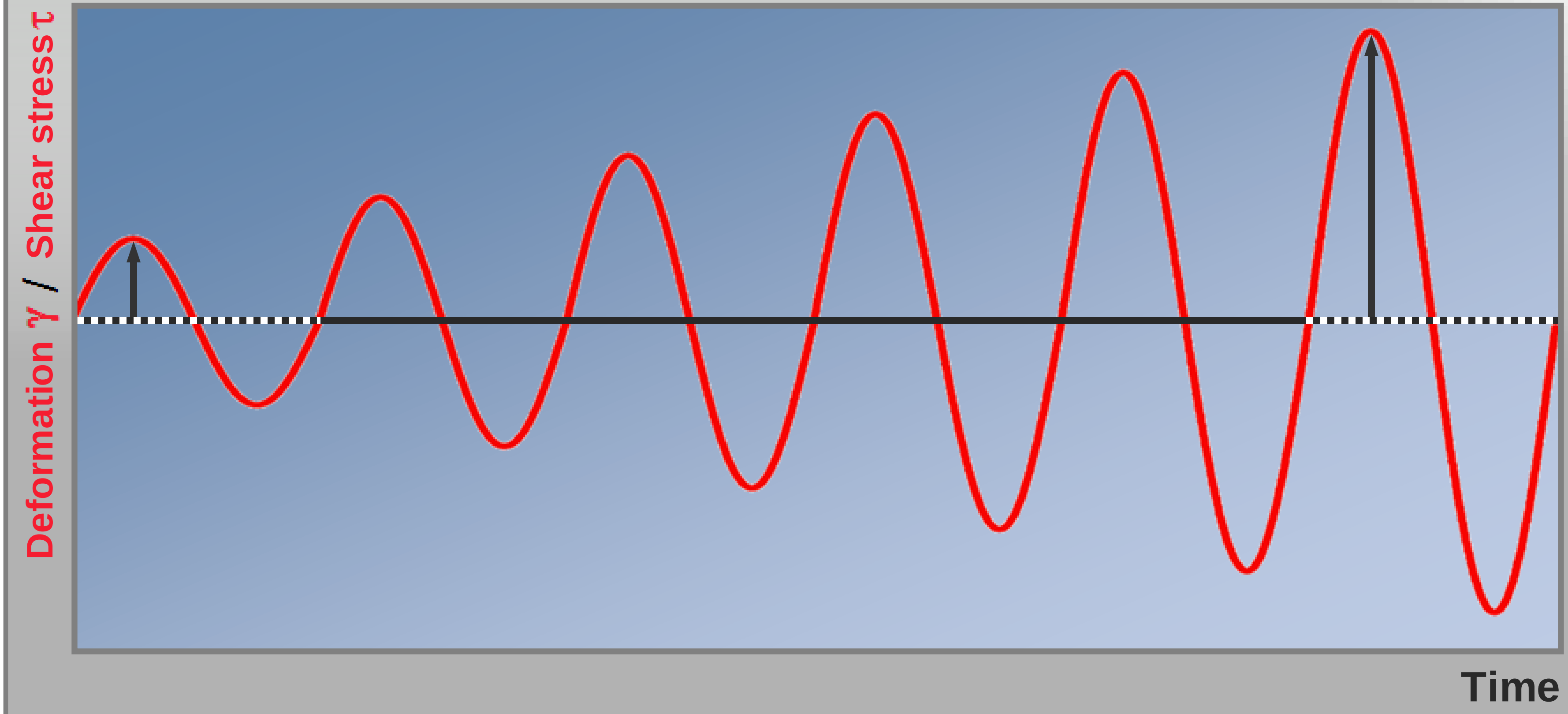
Increasing amplitude in shear stress τ (CS) or deformation γ (CD) with constant frequency

- ✓ 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

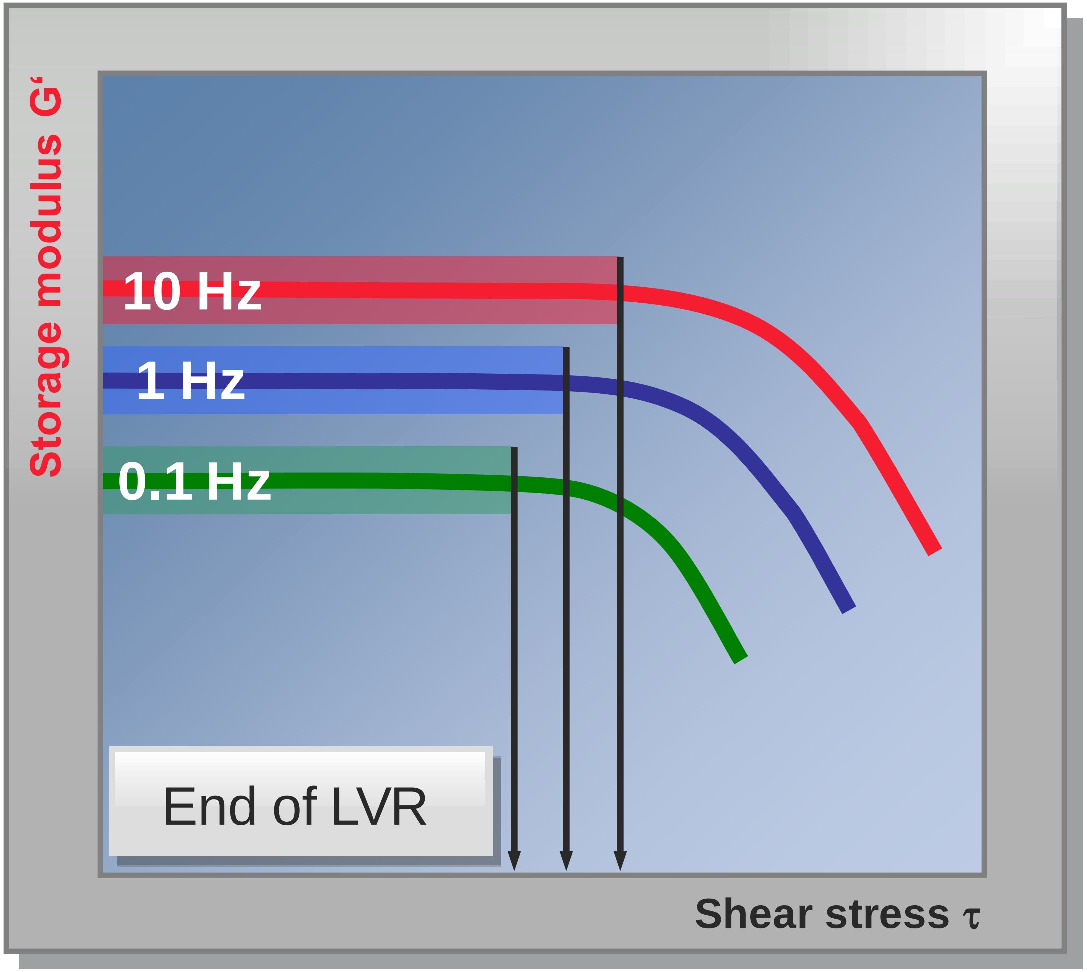
Amplitude sweep

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



Oscillation

Amplitude sweep



Plotted over τ

Width of the linear-viscoelastic range (LVR) depends on the frequency

Plotted over γ

Width of LVR is less frequency depending

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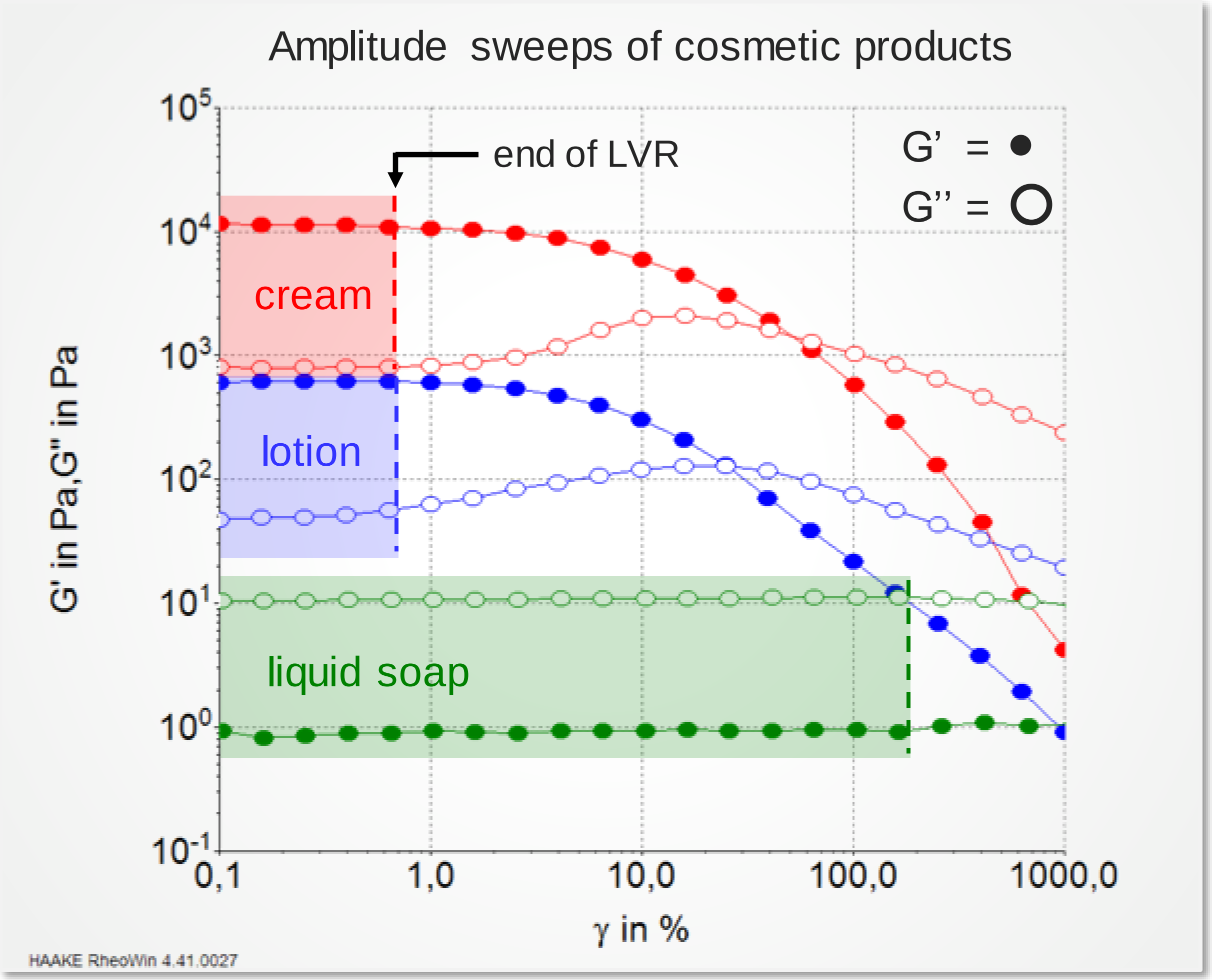
Oscillatory experiments

Oscillatory test methods

Amplitude Sweep

G', G'', δ... = f (γ_0 or τ_0)

- Determination of the linear viscoelastic range (LVR)
- Within LVR rheological parameters are independent of applied deformation / stress
- Within LVR microstructure of sample does not change



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Viskoelastizität

✓ Oscillation

Frequency sweep

Oscillation

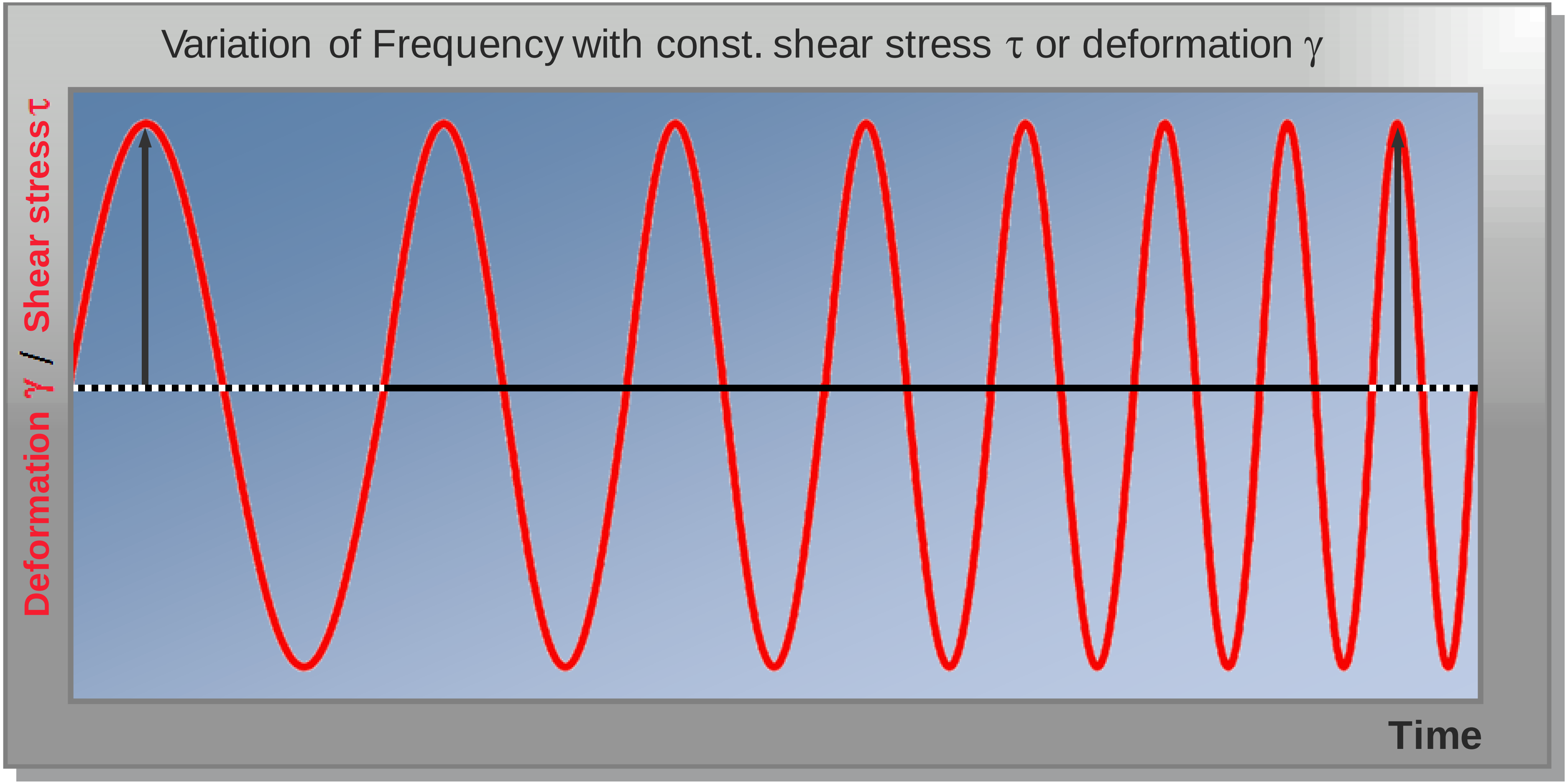
Frequency sweep

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

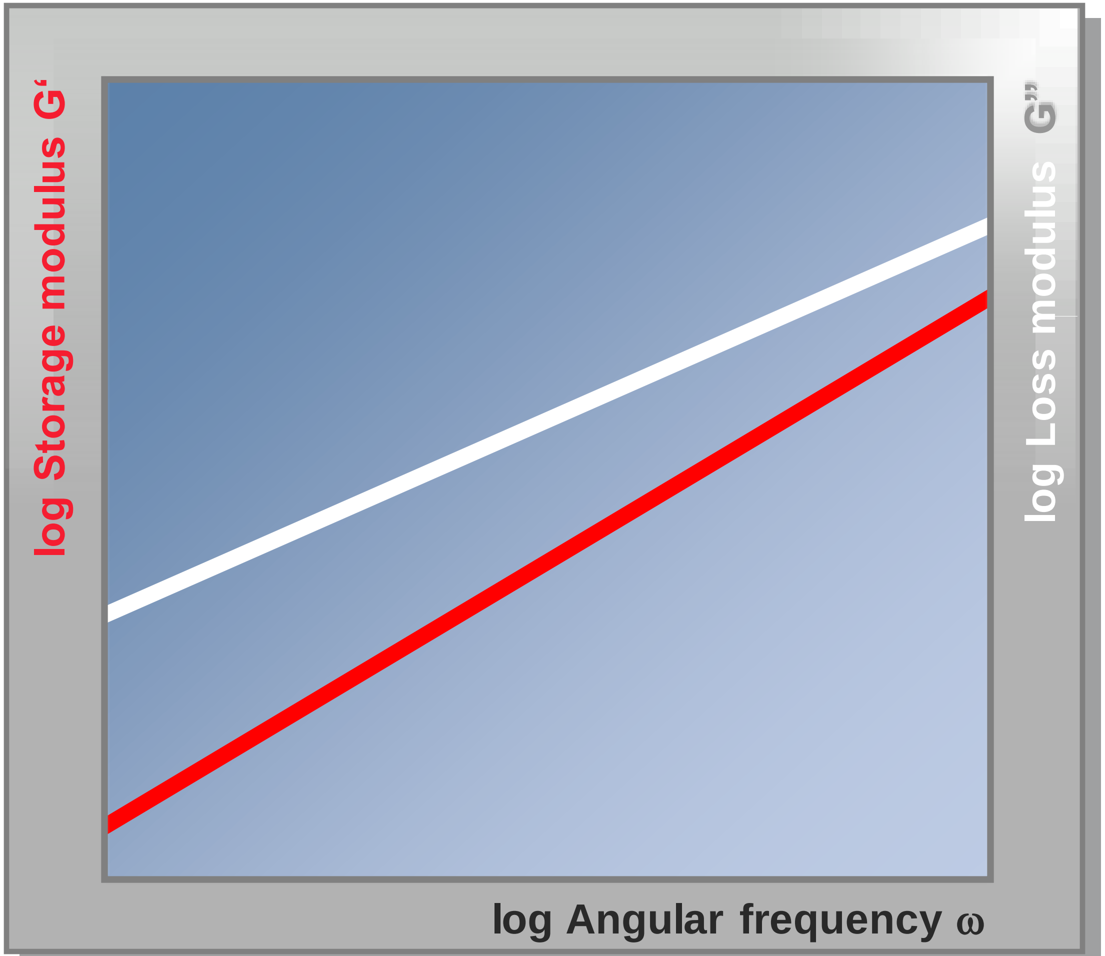
Oscillation

Frequency sweep



Oscillation

Frequency sweep



Viscous Flow

The samples behaves mainly viscous over the entire measuring range

G' < G''

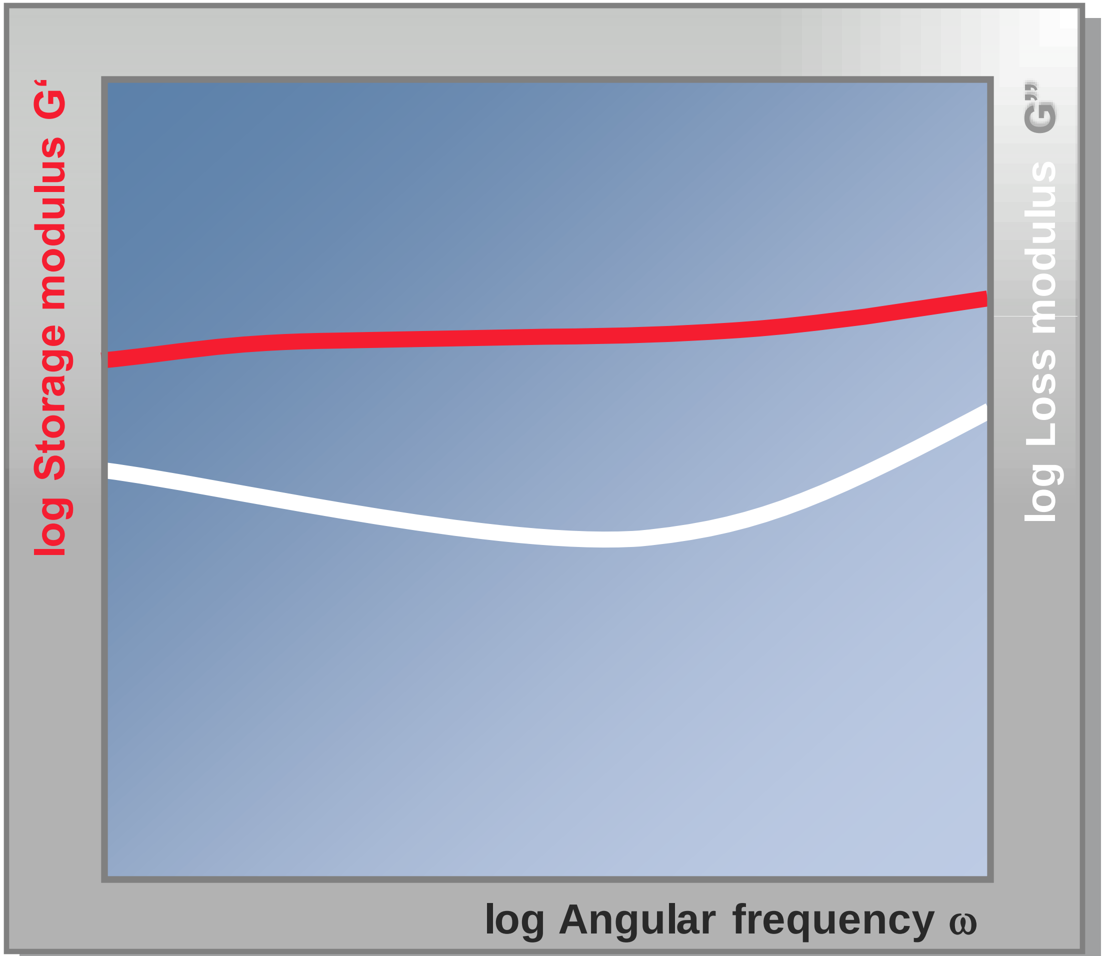
For ideal viscous samples:

Slope G'(ω) = 2

Slope G''(ω) = 1

Oscillation

Frequency sweep



Elastic Plateau

Sample behavior is dominated by the elastic properties

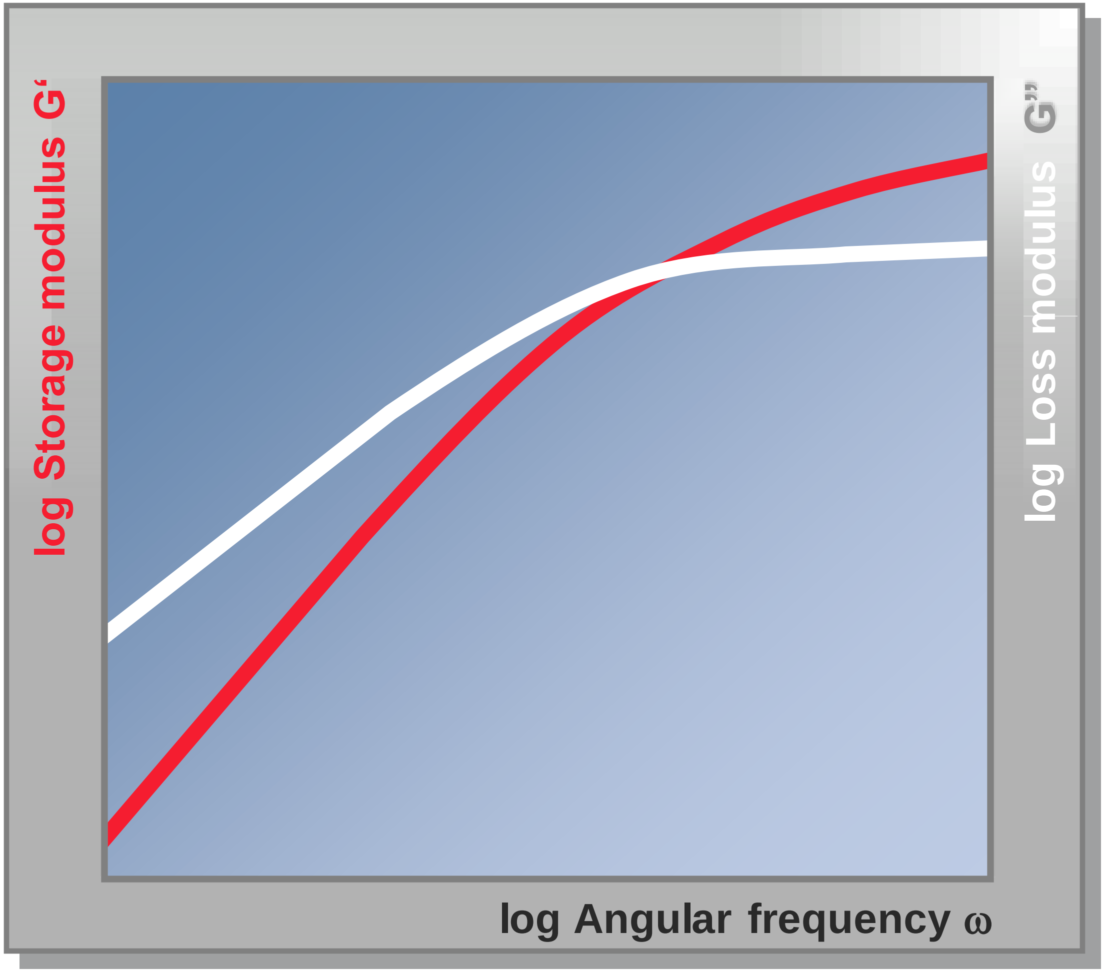
G' > G''

Examples:

- ✓ Cross linked Polymers
- ✓ Physical Networks

Oscillation

Frequency sweep



Viscoelastic behavior

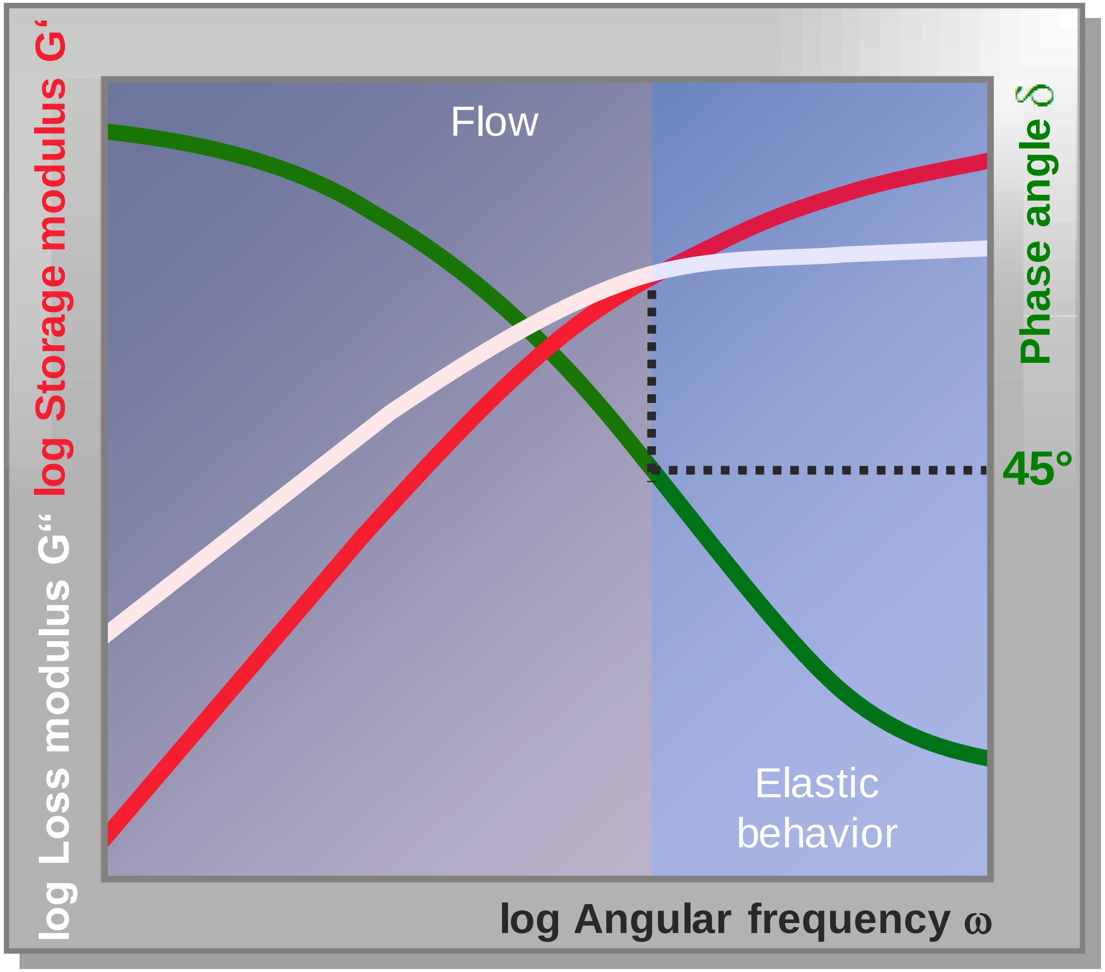
In the region of low frequencies the sample behaves viscous

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

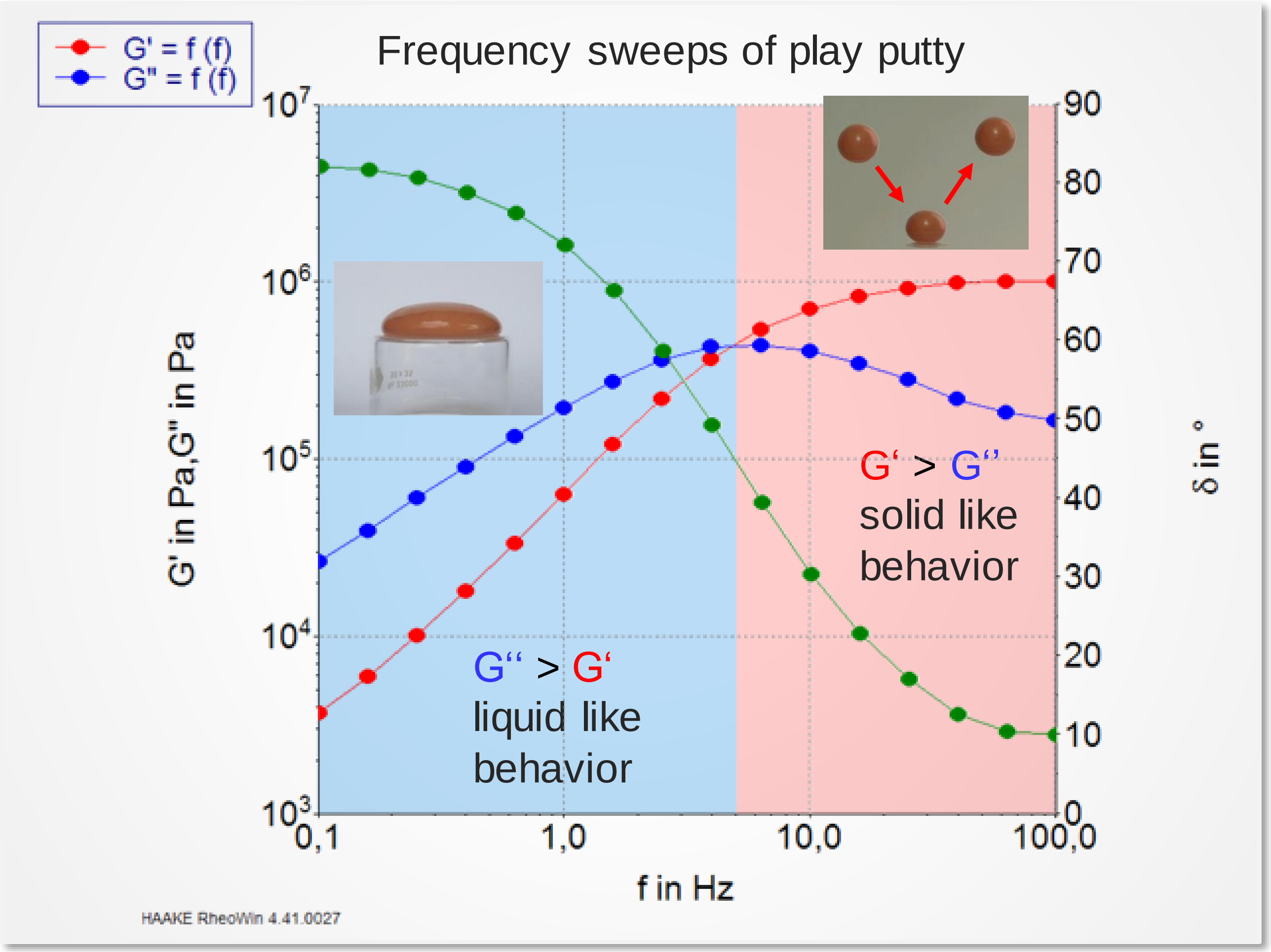
Oscillatory experiments

Oscillatory test methods

Frequency Sweep

G', G'', δ… = *f* (f or ω)

- Performed within LVR
- Within LVR rheological parameters are independent of applied deformation or stress



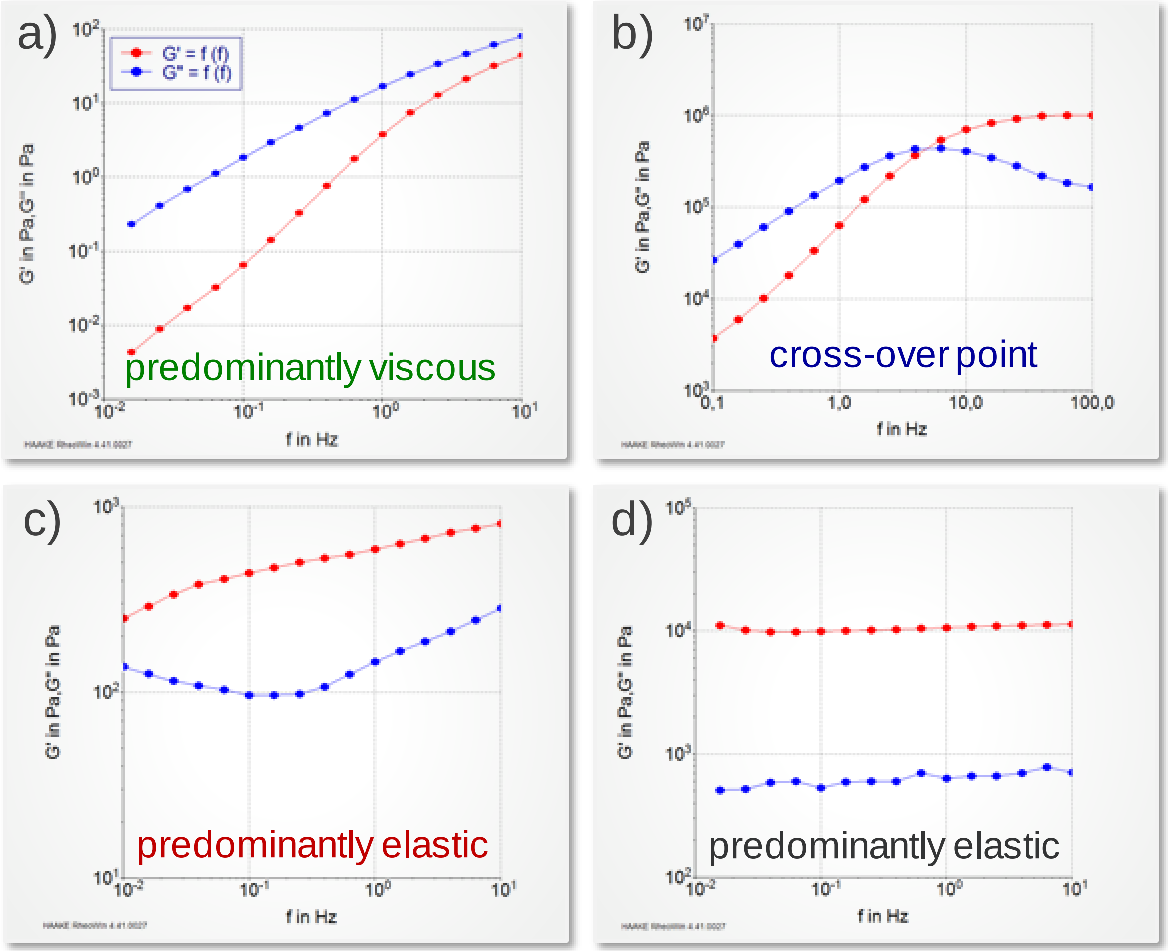
Oscillatory experiments

Oscillatory test methods

Frequency Sweep

G', G'', δ… = f (f or ω)

- a) viscoelastic fluid
  liquid soap
- b) viscoelastic fluid
  play putty
- c) viscoelastic solid
  soft lotion
- d) viscoelastic solid
  stiff cream



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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

Viskoelastizität

✓ Oscillation

Temperature sweep

Oscillation

Temperature sweep

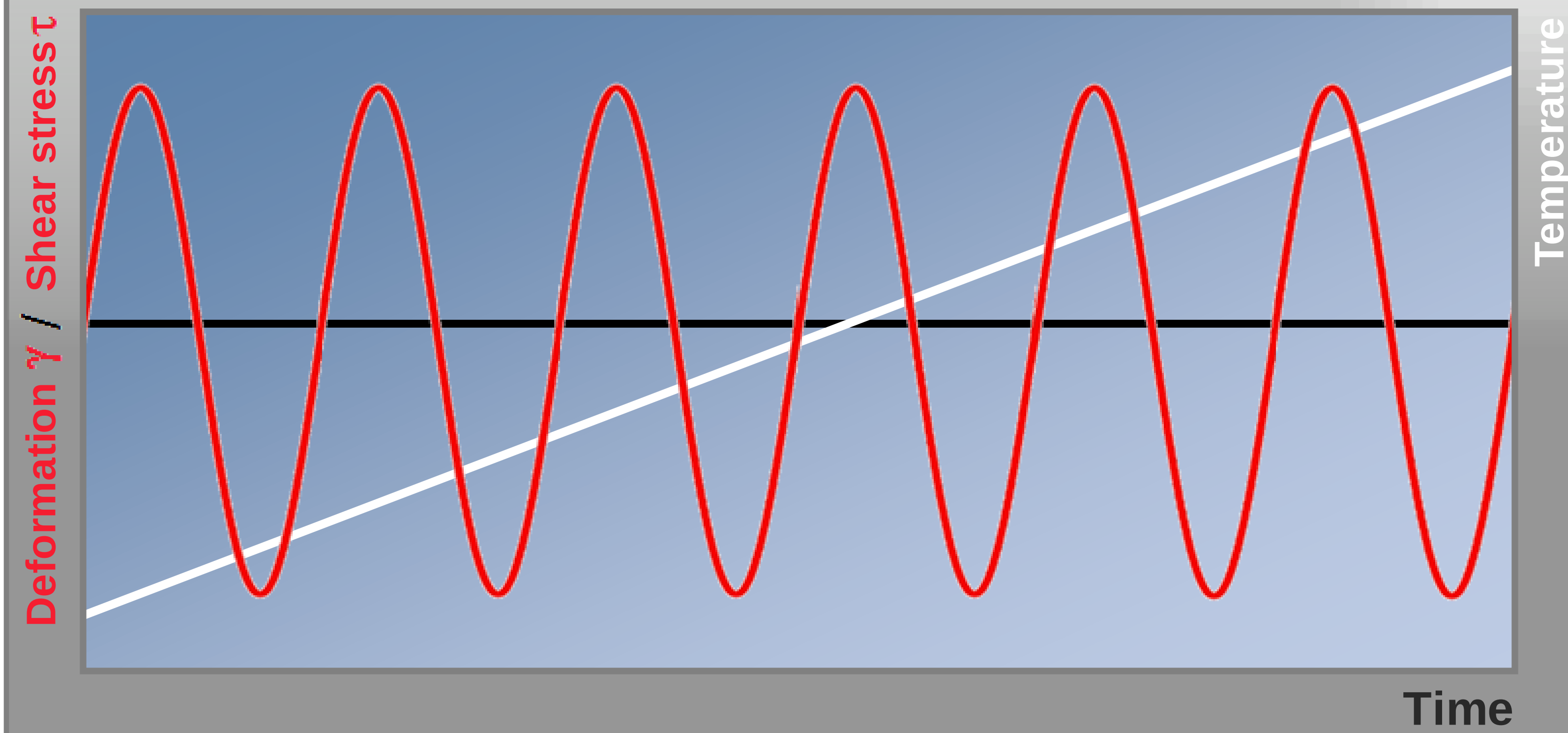
Variation of the temperature with constant shear stress τ or deformation γ and (angluar) frequency ω,f

- ✓ 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



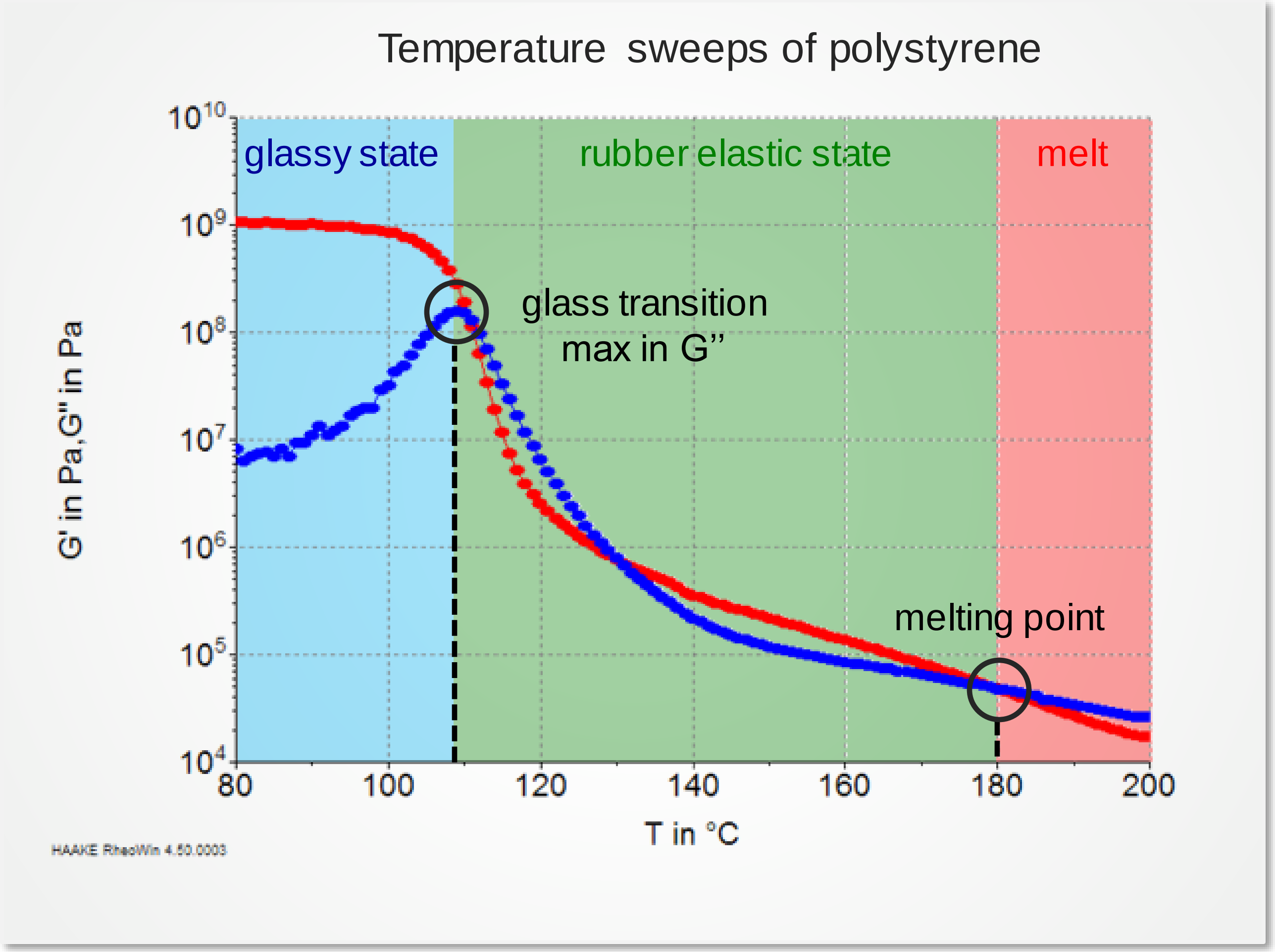
Oscillatory experiments

Oscillatory test methods

Temperature sweep

G', G'', δ… = *f* (T)

- Determination of major phase transitions like
  - Melting point
  - Glass transition
- Monitoring temperature induced crystallization



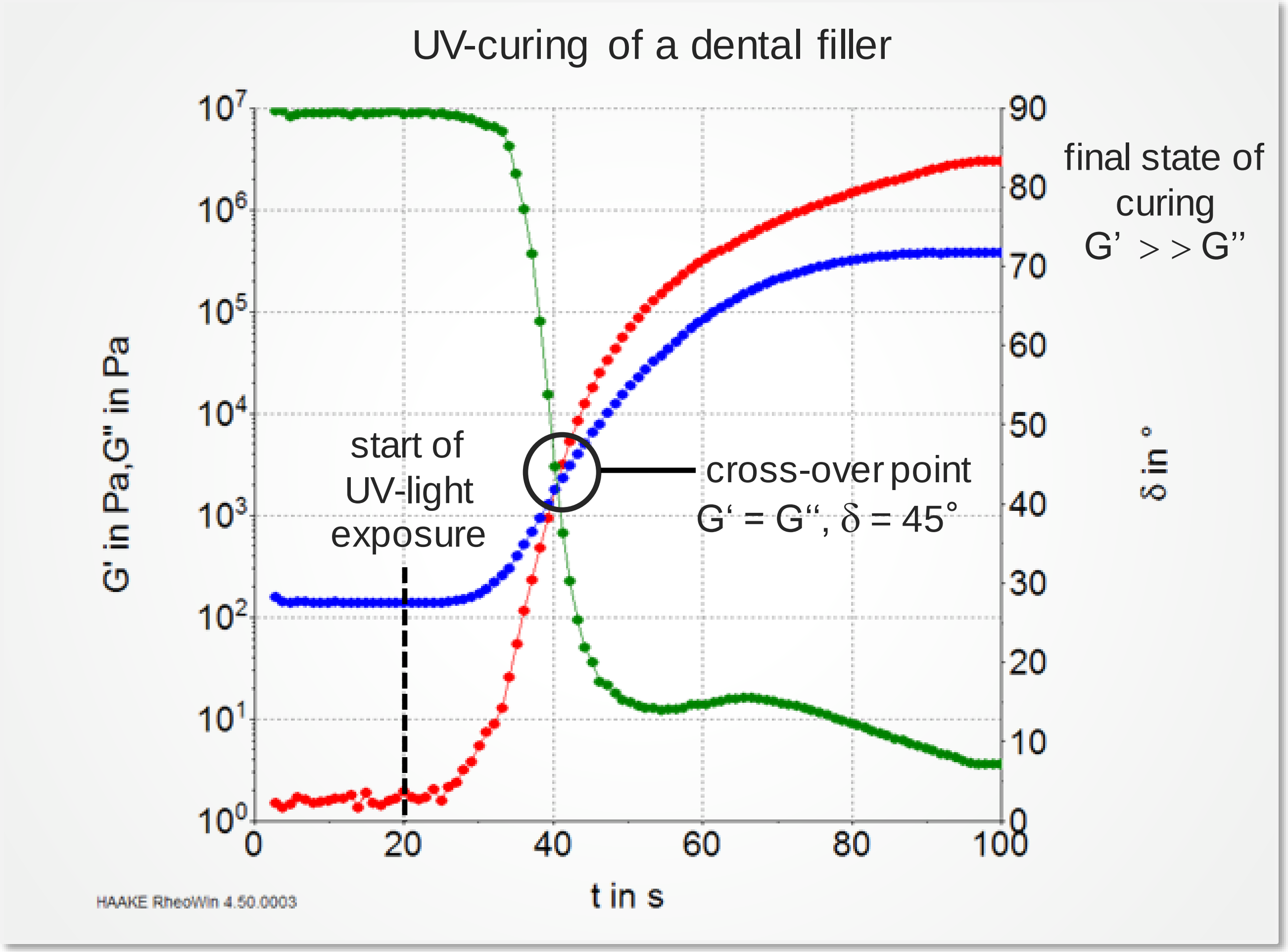
Oscillatory experiments

Oscillatory test methods

Time Sweep

G', G'', δ... = *f* (t)

- Monitoring curing and cross-linking reactions
- Phase transition from liquid to solid like
- Cross-over point is often referred to as gel point



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Any questions ?

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Thank you for your attention