BASICS OF RHEOLOGY

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1922

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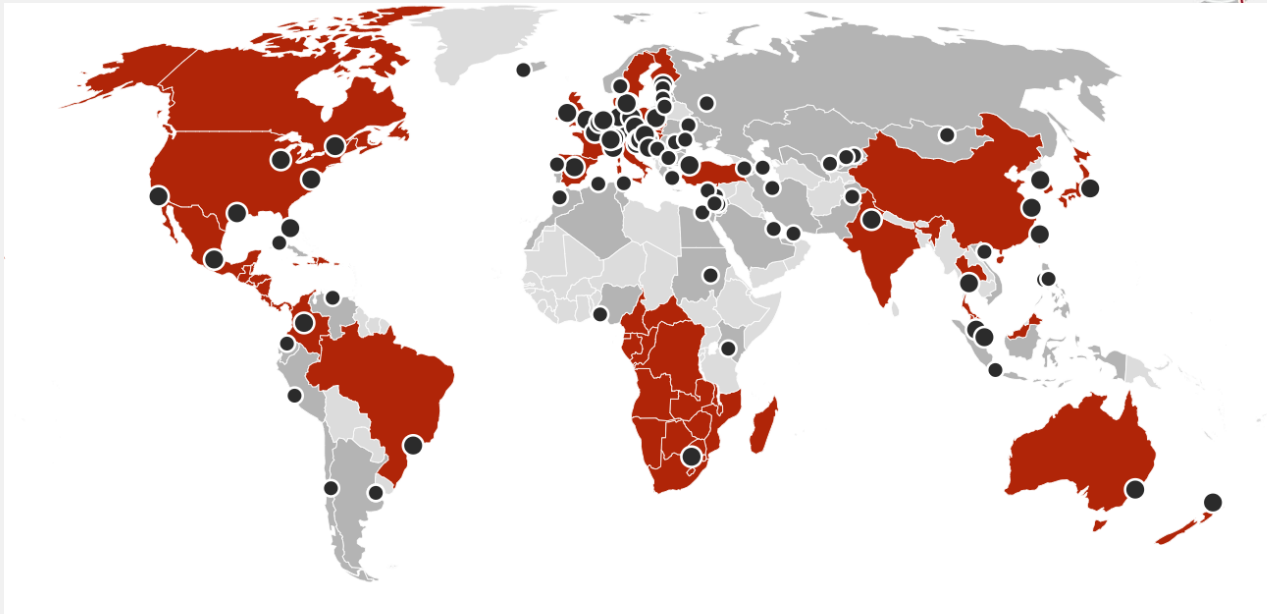

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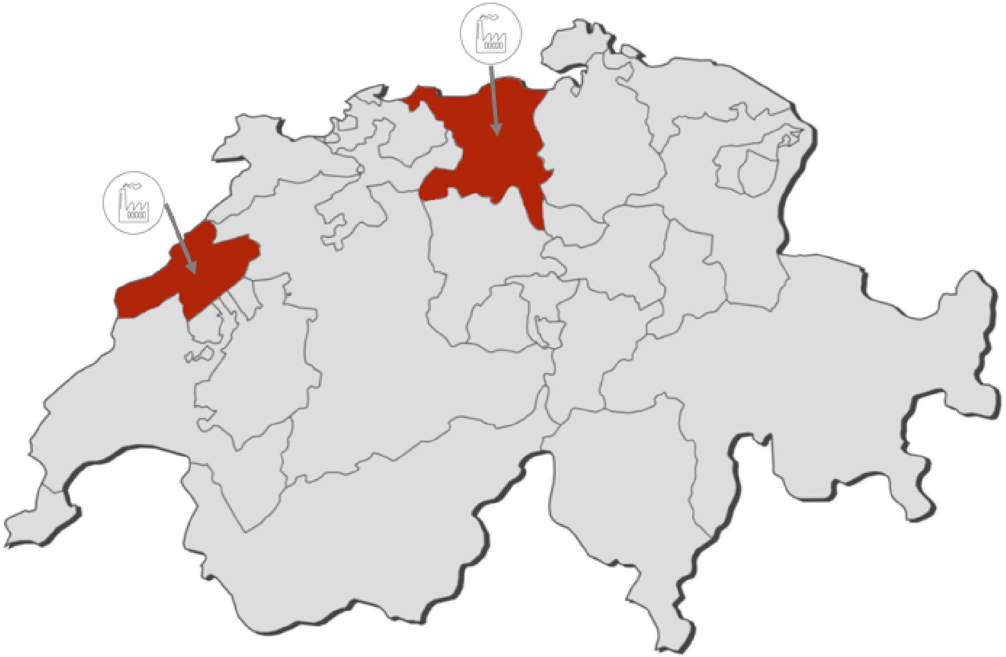
Anton Paar



2

LOCATIONS :
BUCHS (AG)
CORCELLES (NE)

1

APPLICATION
LABORATORY
CORCELLES (NE)

9

EMPLOYEES FOR
THE SALES DPT

8

EMPLOYEES FOR
THE SERVICE DPT

7

EMPLOYEES
FOR THE
ADMINISTRATION

Seminar Program 1st Part

(1) Rheology and viscous behavior
(2) Simple viscosity tests
(3) Rheometers and measuring geometries
(4) Definitions: shear stress, shear rate, (shear) viscosity
(5) Rotational tests
(6) Flow behavior
(7) (Yield point)
(8) Further flow curves and viscosity curves
(9) (Time-dependent behavior (rotation))
(10) (Temperature-dependent behavior (rotation))

Appendix: Pressure-dependent behavior (rotation)

1 Rheology and Viscous behavior

Drugstore (Apotheken) Museum
in Heidelberg, Germany

Rheology

to describe

deformation and flow behavior of all kinds of materials

rhei or rheo … to flow

Rheometry

measurement of rheological data

Rheology

is used to arrange materials in order.
Let’s go through our common household items and line up all that we can find:

on the left - the liquids **on the right - the solids**

and in between - the semi-solid substances

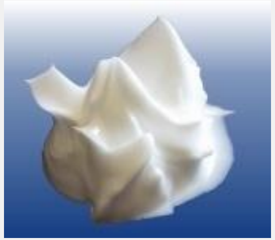
1 Rheology and Viscous behavior

The Rheology Road

viscous	viscoelastic	elastic

ideal-viscous liquids
water, oils
Viscosity Law

viscoelastic liquids
glues, shampoos



viscoelastic solids
pastes, gels, elastomers

ideal-elastic solids
stone, steel
Elasticity Law

rotational tests

oscillatory tests

1 Rheology and Viscous behavior

Anton Paar

What is viscosity ?

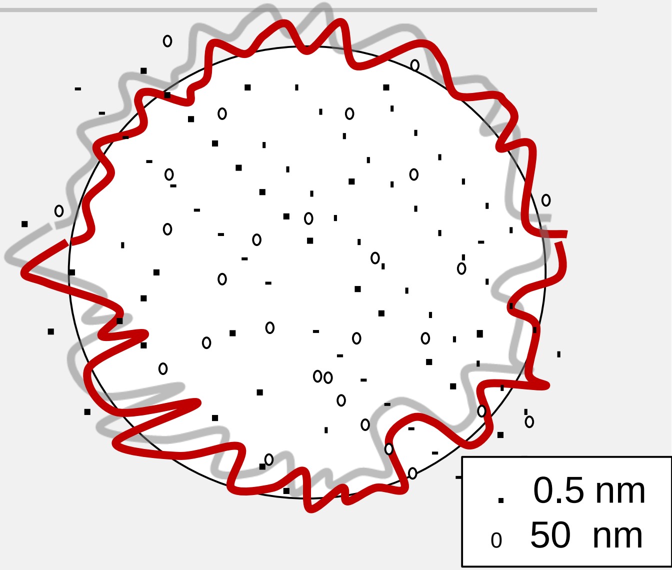
Internal friction or **flow resistance**
between the molecules and particles, when gliding along each other in a flowing state
(Newton in 1687: defectus lubricitatus)

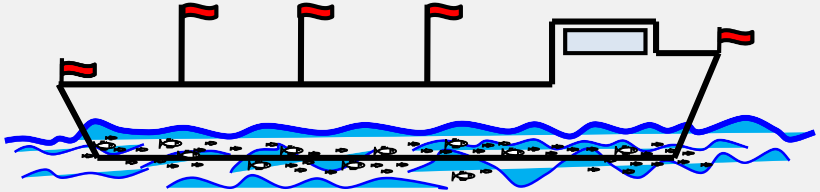
comparison of size
molecules of solvents: about 0.5 nm
macro-molecules (polymer coils): about 50 nm
particles (minerals): about 5 µm = 5000 nm

size ratio of molecules and particles
is about 1:100 to 1:10,000 (e.g. 1:1000)

illustrative comparison for 1:1000

a molecule as a	10 cm (0.1m)	long fish
a particle as a	100 m	long ship



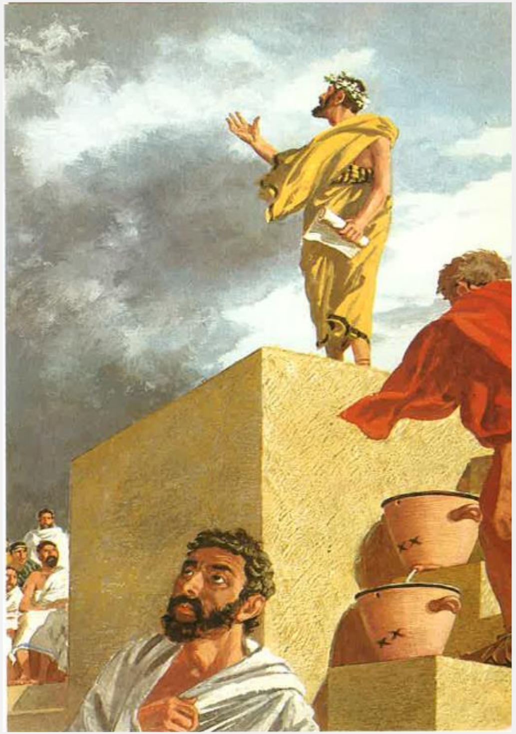


Water-clock
(in Greek: klepsýdra)

used to measure time,
since about 3500 years in Egypt,
and later e.g. at justice courts in Greece

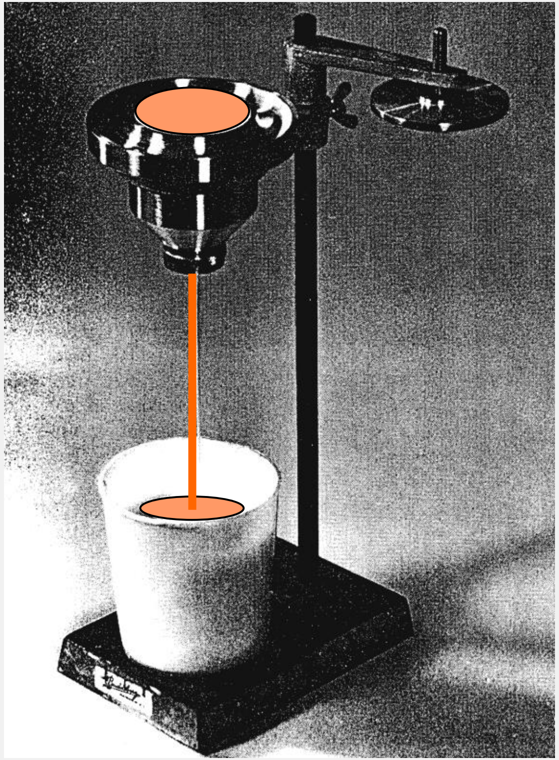
Example:
flow time
of about 6 min
for water flowing out of a 5 liter

container equipped with an outlet.



Source: Miquel, P.: So lebten sie im alten Griechenland. Tessloff Nürnberg 1982 / Librairie Hachette, Paris 1981

2 Simple Viscosity Tests



Flow cups

Measurement
flow time
of low-viscosity liquids

Result:
kinematic viscosity
weight-dependent viscosity

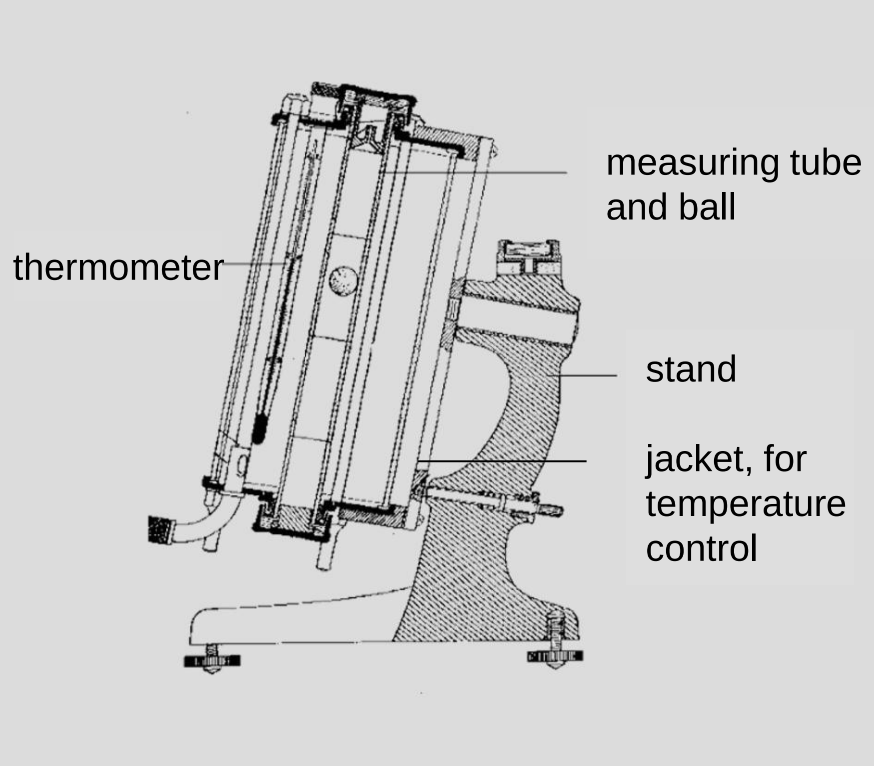
Examples:
oils, solvent-based coatings,
gravure and flexo printing inks

2 Simple Viscosity Tests

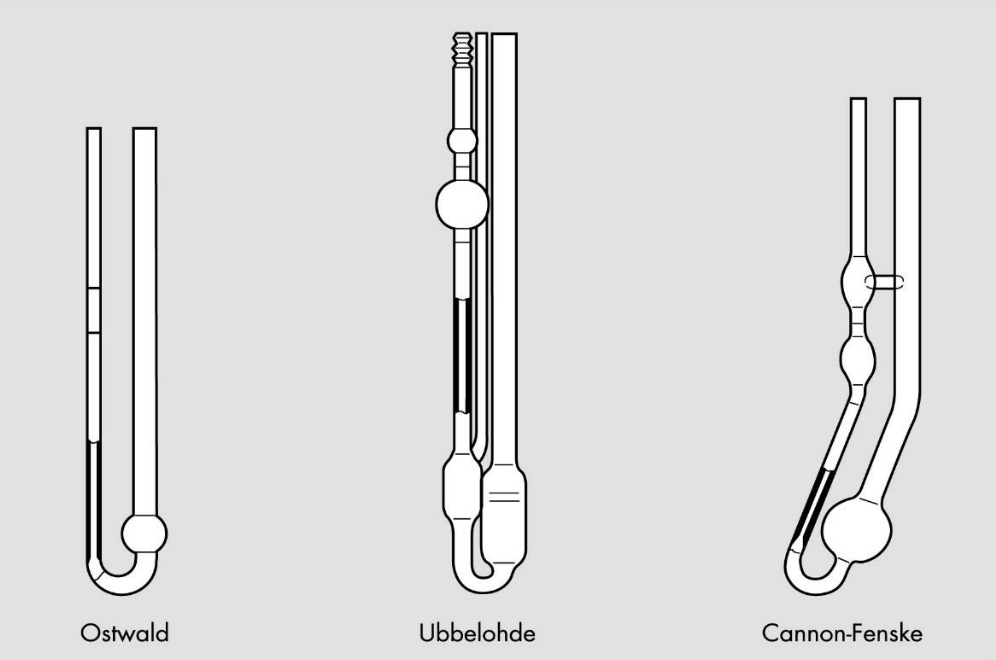
Falling-Ball Viscometers

Measurement:
falling time
of a ball through a tube
- ISO 12058
- DIN 53015

Example:
micro-falling ball viscometer Lovis
by Anton Paar for low-viscosity liquids, e.g. protein dispersions, polymer solutions, beer wort, inks



2 Simple Viscosity Tests



Glass Capillary Viscometers

Measurement:
flow time
of liquids

Result:
Kinematic Viscosity

Examples:
mineral oils, diluted polymer solutions

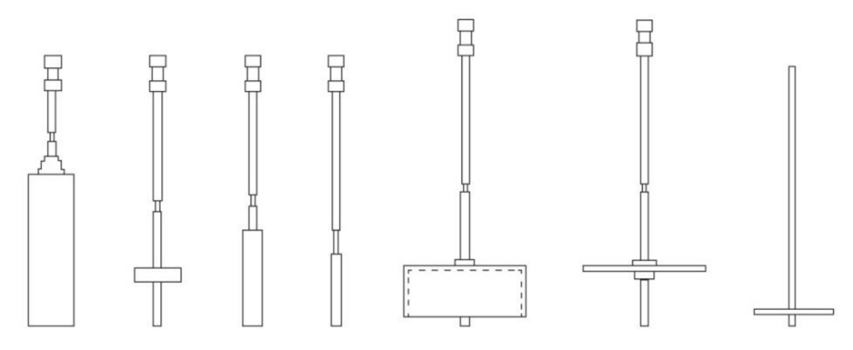
Alternative:
SVM viscometer by Anton Paar
(DIN 51659-2, EN 16894, ASTM D7042)

Anton Paar

Rotational Viscometers

Preset: rotational speed
Measurement: torque

Example: **ViscoQC** by Anton Paar

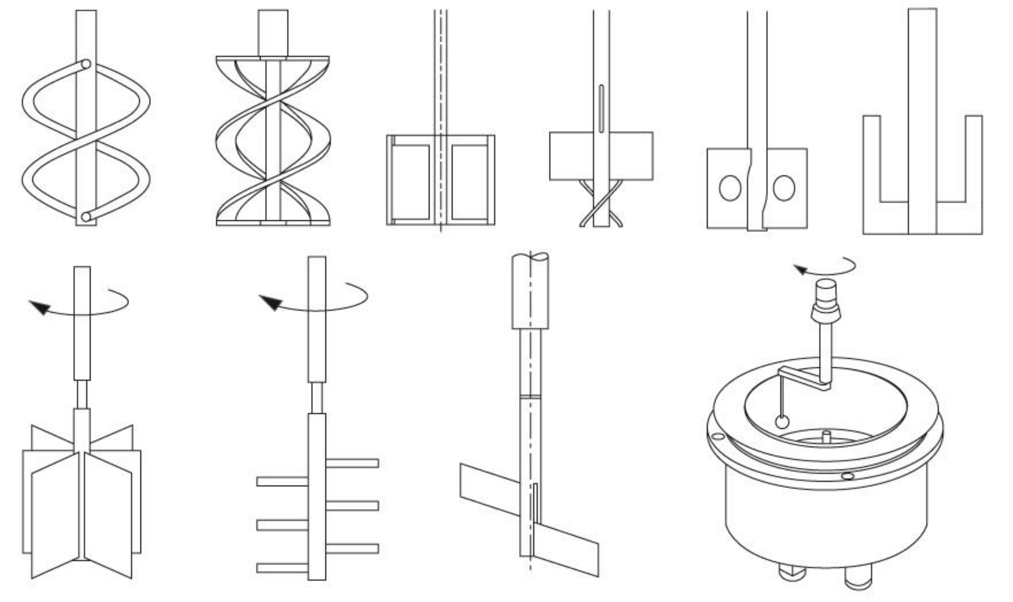


Relative Viscosity Values

- ISO 2555
- ISO 3219-2

Typical Spindles:

- cylinders
- disks
- T-bars
- pins

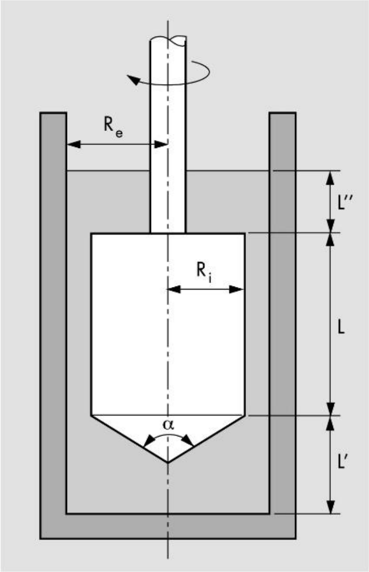


Relative Measuring Geometries

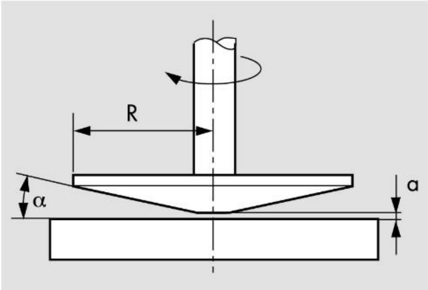
- helix (1 & 2)
- stirrer for building materials (BMC)
- starch stirrer
- blade
- anchor-shaped

- vane rotor
- pin rotor
- Krebs spindle, „paddle“
  (for coatings, Krebs units KU)
- ball (BMS)

Absolute measuring geometries (ISO 3219-2 and DIN 53019)



concentric cylinders, CC
low-viscosity liquids



cone / plate, CP
liquids, dispersions
limited particle size

Example: CP 25-1; **a** = 50 µm, max. particle size 10 % of **a**

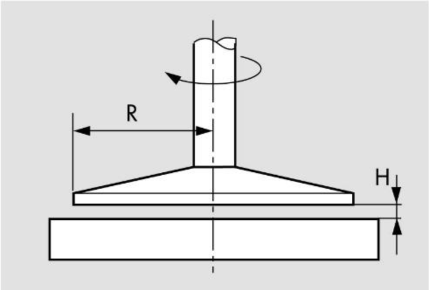
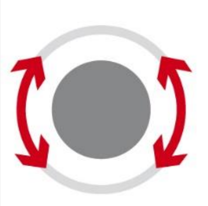


plate / plate, PP
gels, pastes, soft solids, polymer melts

3 Rheometers and Measuring Geometries

rotation

- shear tests
- tensile tests



oscillation

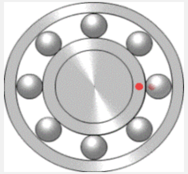
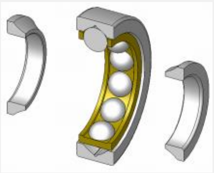
- shear tests
- torsional tests
- tensile tests

3 Rheometers and Measuring Geometries

Rheometers - each drive requires a bearing

Ball Bearing

- inner ring (rotor)
- rolling element (e.g. balls, cylinders, cones)
- outer ring (stator)

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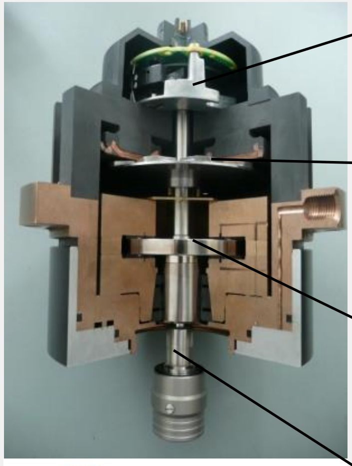
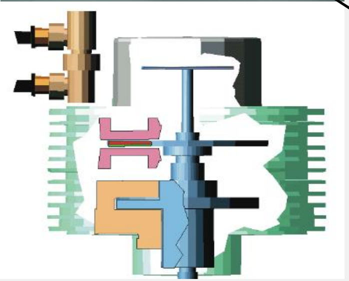



1 Encoder
opto-electronical detection of deflection angle

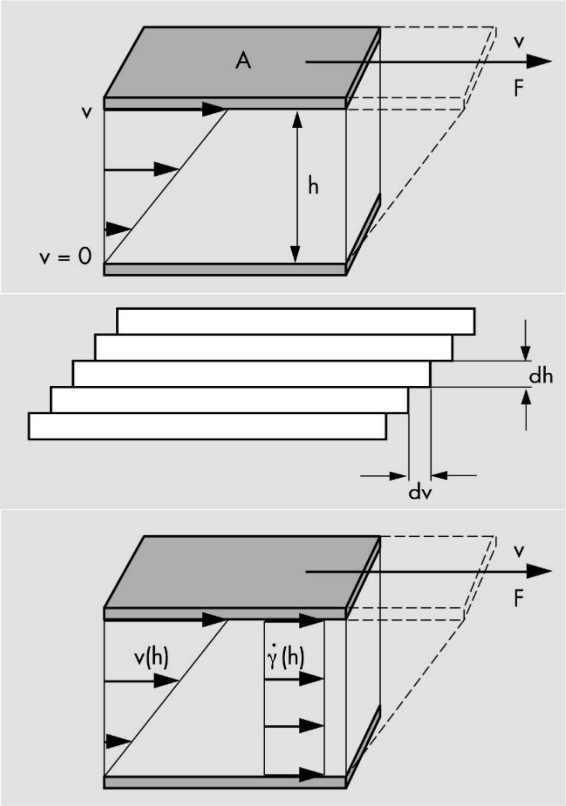
2 Measuring drive
electro-motor, torque detection

3 Air Bearing
radial and axial: pressurized air between disc (rotor) and porous graphite (stator)

An air bearing is up to 400 000 times more sensitive than a ball bearing!

4 Motor shaft
coupling for measuring geometries

4 Definitions:
Shear Stress, Shear Rate, Viscosity



The two-plates model

shear stress	$\tau = F / A$
unit:	1 N / m^2 = **1 Pa**

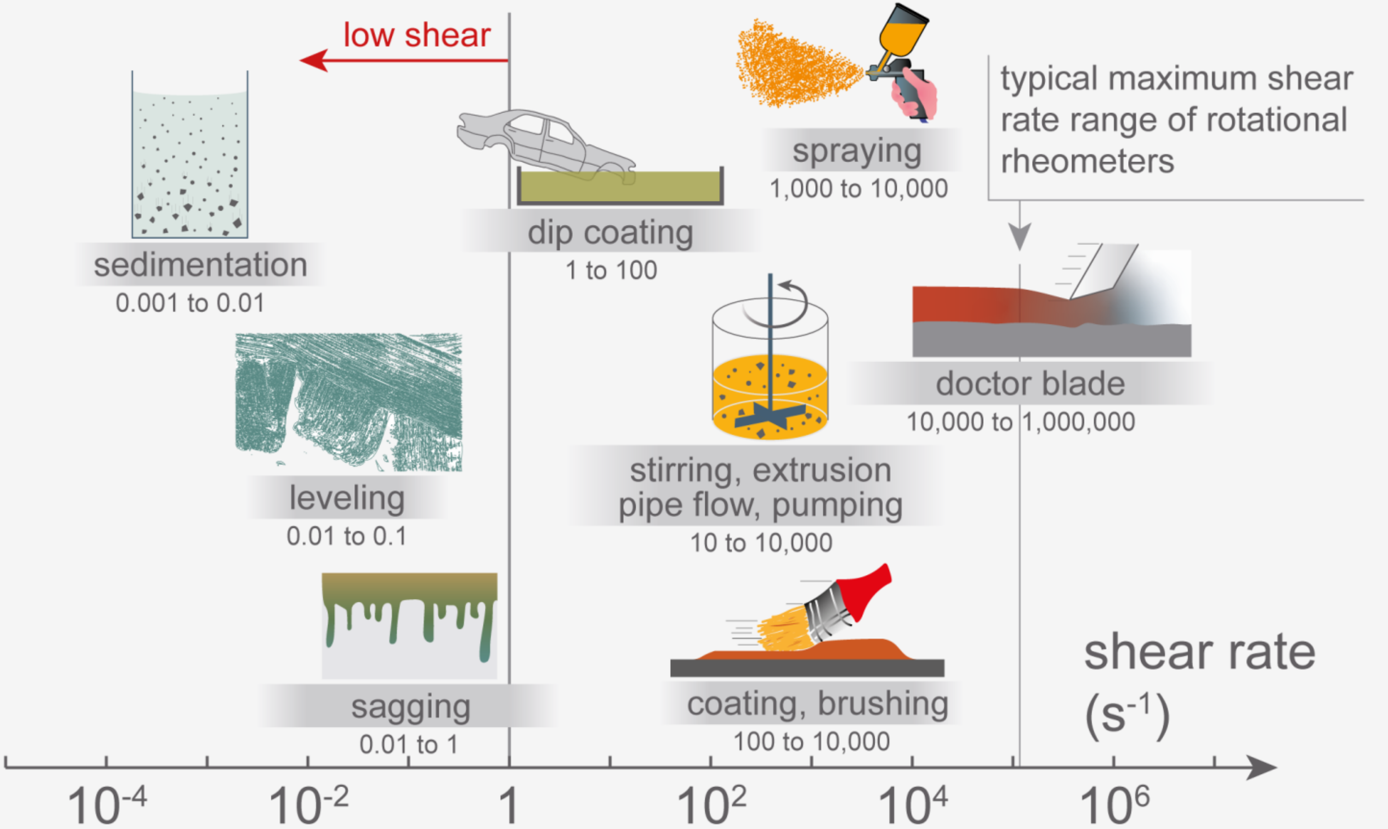
shear rate	$\dot{\gamma} = v / h$
unit:	1 m / (s·m) = **1 / s = 1 s^{-1}**

Requirement: **Laminar flow**
in contrast to **Turbulent flow**

$\dot{\gamma}$ = dv / dh = const / const = const

→ *e-learning (laminar, 2-P-M)* | → *movie (peas)* | → *movie (turbulence)*

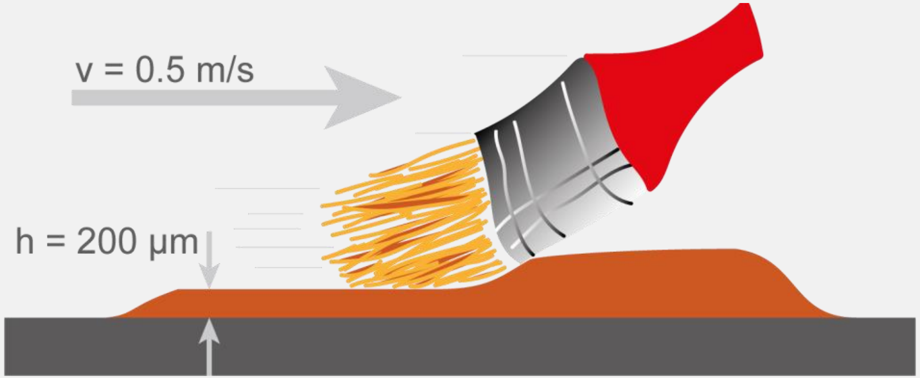
4 Definitions:
Shear Stress, Shear Rate, Viscosity



Application processes and typical shear rate ranges

4 Definitions:
Shear Stress, Shear Rate, Viscosity

Shear rates of coating processes

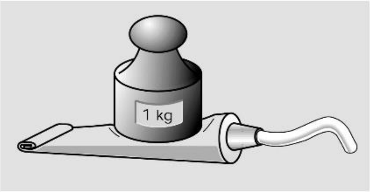


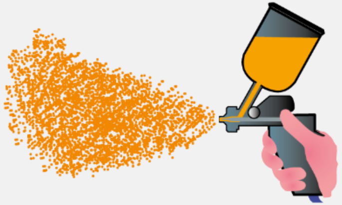
	painting with a brush	blade coating of a battery slurry
velocity v	0.5 m/s	0.1 m/s
wet layer thickness h	200 µm	10 µm
shear rate $\dot{\gamma}$	2.500 s^{-1}	10.000 s^{-1}

Shear rate calculation:
similar to the two-plates model $\dot{\gamma} = v / h$

4 Definitions: Shear Stress, Shear Rate, Viscosity

Shear rates in pipes and capillaries

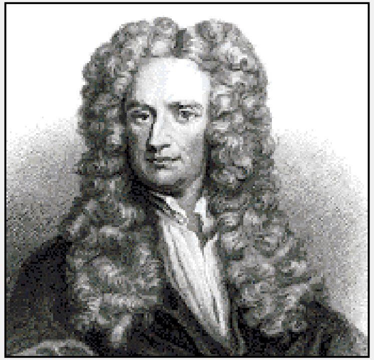




	tooth paste (squeezing)	automotive spray (pneumatic application)
flow volume V	1 cm^3 = 1 ml	250 ml
flow time t	1 s	1 min
volume flow rate V/t (or $\dot{V}$)	1 ml/s = $1 \cdot 10^{-6}$ m^3/s	250 ml/min = $4.17 \cdot 10^{-6}$ m^3/s
pipe (die) diameter d → radius R	6 mm → $3 \cdot 10^{-3}$ m	1.3 mm → $6.5 \cdot 10^{-4}$ m
shear rate $\dot{\gamma}$	47.2 s^{-1} ≈ 50 s^{-1}	19,318 s^{-1} ≈ 20,000 s^{-1}

Shear rate calculation: formula of Hagen and Poiseuille $\dot{\gamma} = (4 \cdot V) / (\pi \cdot R^3 \cdot t)$

4 Definitions: Shear Stress, Shear Rate, Viscosity



Isaac Newton
(1643 to 1727)
wrote about the
flow resistance
of fluids
(e.g. of air and water).

This was later known as:
Viscosity Law "of Newton"
was formulated in the 19. century
(e.g. by G.G. Stokes in 1845).

(shear) viscosity

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

unit: 1 Pa / (1/s) = **1 Pas = 1000 mPas**

Previously used unit (not SI):
1 cP (centi-poise) = 1 mPas

4 Definitions: Shear Stress, Shear Rate, Viscosity

materials	viscosity η
gases / air	0.01 to 0.02 / 0.018 **mPas**
water at 20 °C (0 / 60 / 100 °C)	**1.0 mPas** (1.8 / 0.47 / 0.28 mPas)
milk, coffee creams	2 to 10 mPas
olive oils	≈ 100 mPas
motor oils, e.g. SAE 10W-30, at 23 / 100 °C	175 / 20 mPas
polymer melts (dependent on T and $\dot{\gamma}$)	10 to 10,000 Pas
bitumen (at T = 80 / 40 / 0 °C)	200 **Pas** / 20 **kPas** / 1 **MPas**

→ *e-learning (visco-turtles)*

5 Rotational Tests

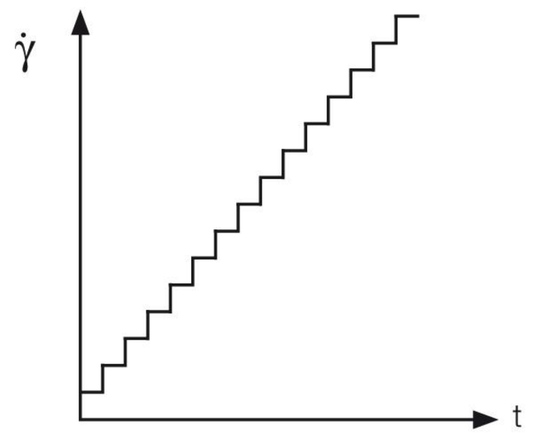
rotation CSR controlled shear rate	test preset	result
raw data	**rotational speed n** [min^{-1}]	**torque M** [Nm]
rheological parameters	shear rate $\dot{\gamma}$ [s^{-1}]	shear stress τ [Pa]

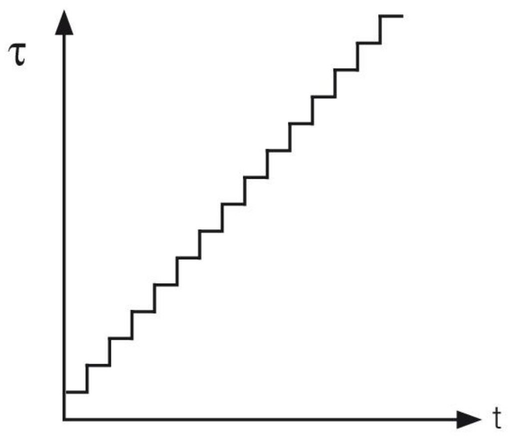
rotation CSS controlled shear stress	test preset	result
raw data	**torque M** [Nm]	**rotational speed n** [min^{-1})
rheological parameters	shear stress τ [Pa]	shear rate $\dot{\gamma}$ [s^{-1}]

torque M: 1 Nm = 1000 mNm = 1,000,000 µNm = 1,000,000,000 nNm

For each measuring geometry there are **two conversion factors**: M → τ and n → $\dot{\gamma}$

5 Rotational Tests





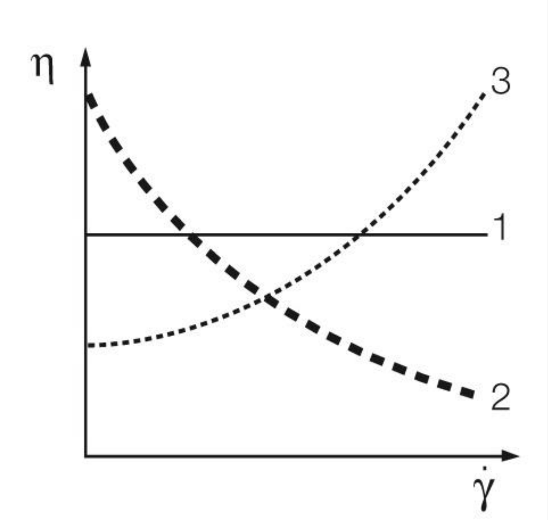
rotational speed preset

shear rate ramp
step-like upwards or downwards
CSR: controlled shear rate

torque preset

shear stress ramp
step-like upwards or downwards
CSS: controlled shear stress

6 Flow Behavior



Viscosity curves

1	ideal-viscous	(Newtonian)
2	shear-thinning	(pseudoplastic)
3	shear-thickening	(dilatant)

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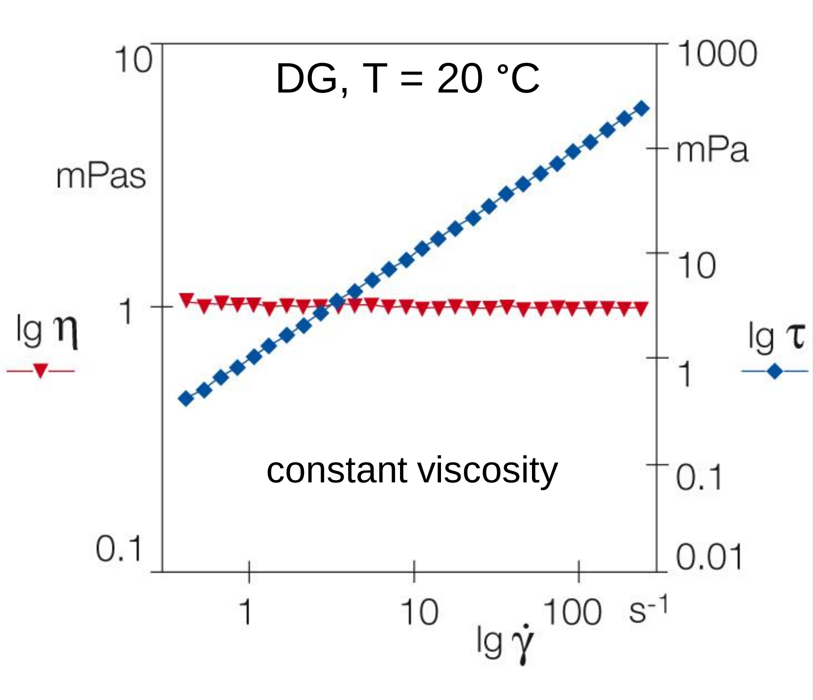
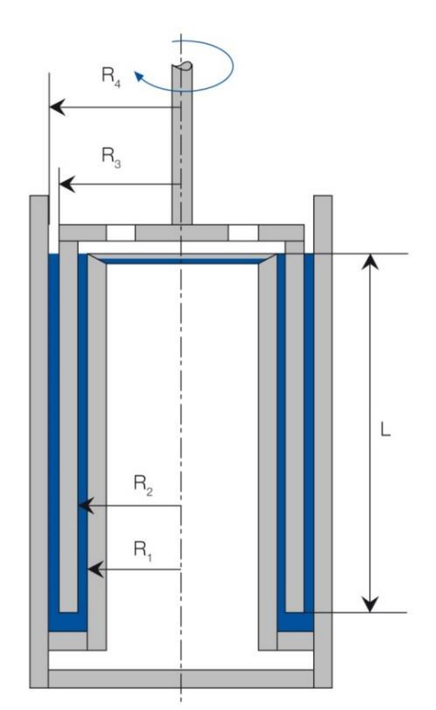


Water

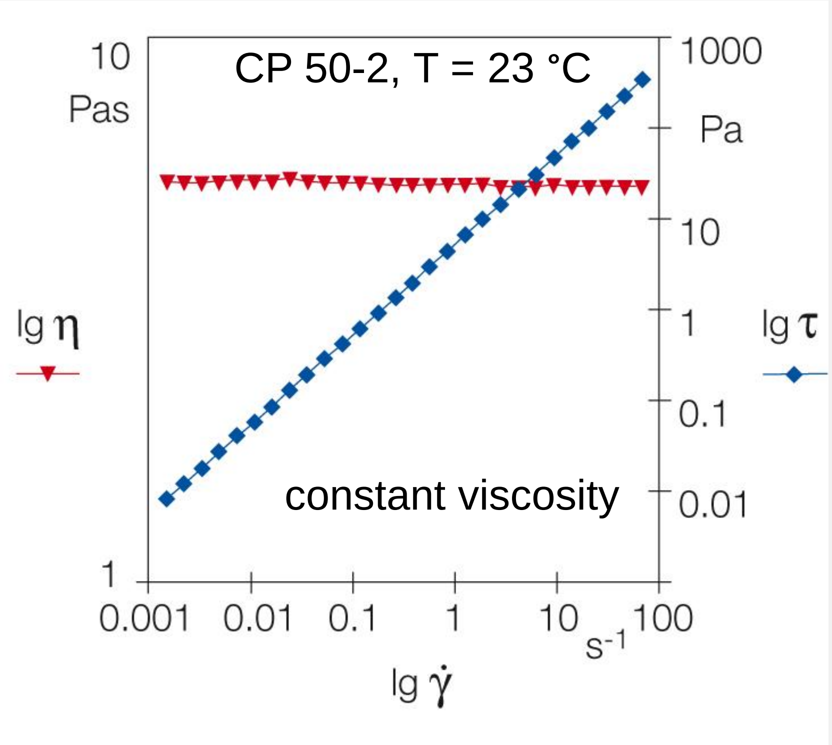
Double-gap measuring geometry DG for low-viscosity liquids

ISO 3219-2



→ *movie (Taylor vortices, via PIV, particle imaging velocimetry*

6 Flow Behavior



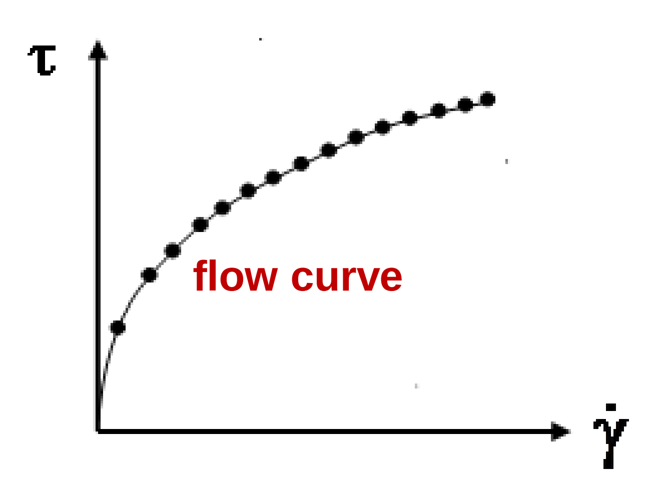
Silicone oil

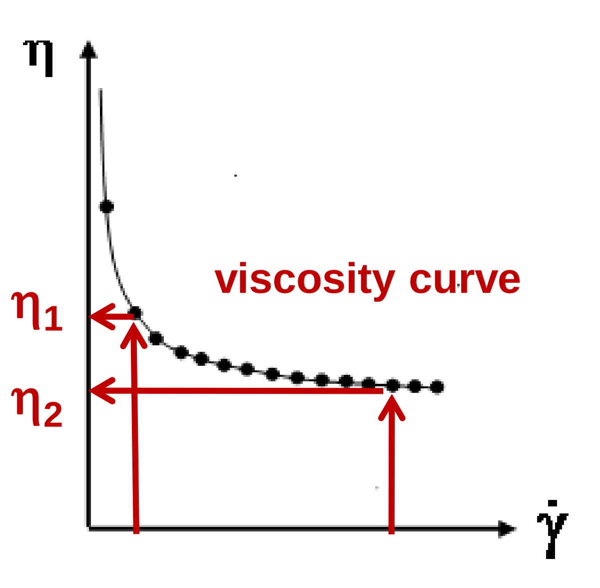
logarithmic scale

Advantage:
Very low values
can be displayed

cone / plate
measuring
geometry, CP

6 Flow Behavior





- **shear-thinning**
- pseudoplastic

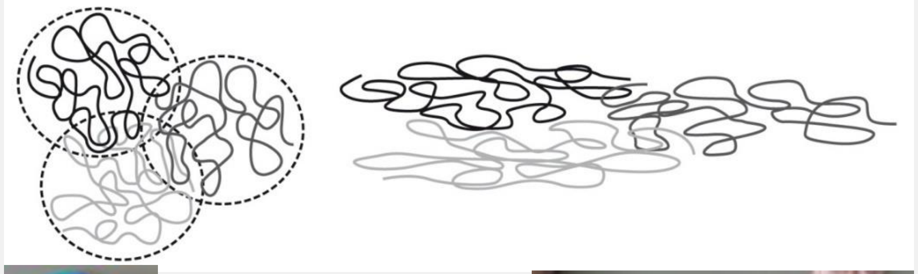
$$\eta_1(\dot{\gamma}) > \eta_2(\dot{\gamma})$$

6 Flow Behavior

Polymers: chain-like macro-molecules

at rest | when shearing

molecules are coiled, entanglements



deformation in shear direction, disentanglements

Consequence: shear-thinning flow behavior, decreasing viscosity

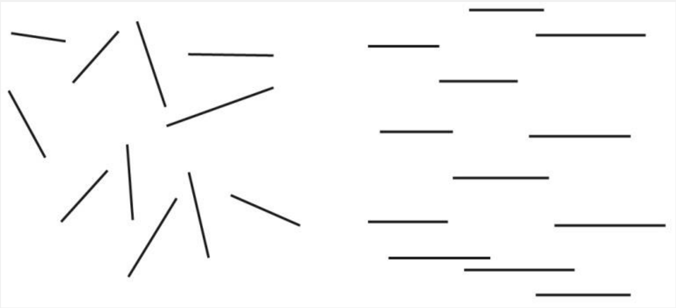
Typical size: molecule coil, hydrodynamic diameter 5 nm to 50 nm
PE, M = 100 kg/mol, L = 1000 nm (stretched), d = 0.5 nm, ratio L/d = 2000:1
comparison: spaghetti noodles, 1 mm thick and 2 m long

6 Flow Behavior

Suspensions: with needle- or platelet-shaped particles

at rest   when shearing

particles are suspended randomly (when without interaction forces)



particles are oriented in flow direction

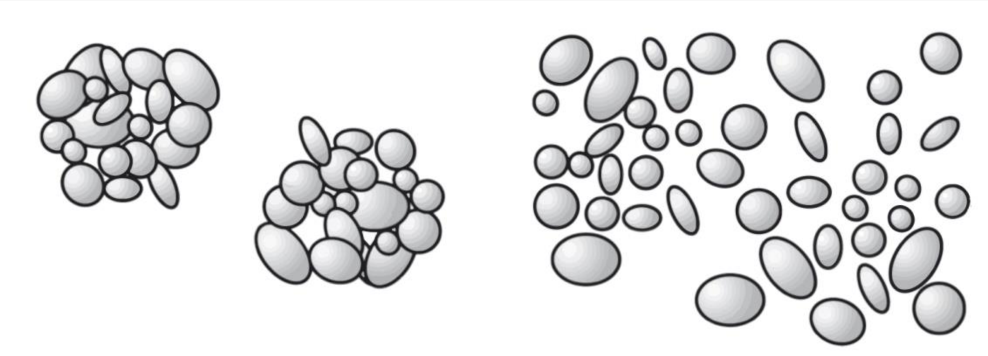
Consequence: shear-thinning flow behavior, decreasing viscosity

Typical size:
(1) metallic-effect pigments, aluminum flakes
diameters d = 7 to 30 μm, thickness h = 0.2 to 1 μm, ratio d/h = 30:1
(2) ceramics, such as Bentonite: length / width / thickness, L x b x h = 800 x 800 x 1 nm

Suspensions containing agglomerated particles

at rest when shearing

agglomerates entrap
and immobilize
part of the liquid

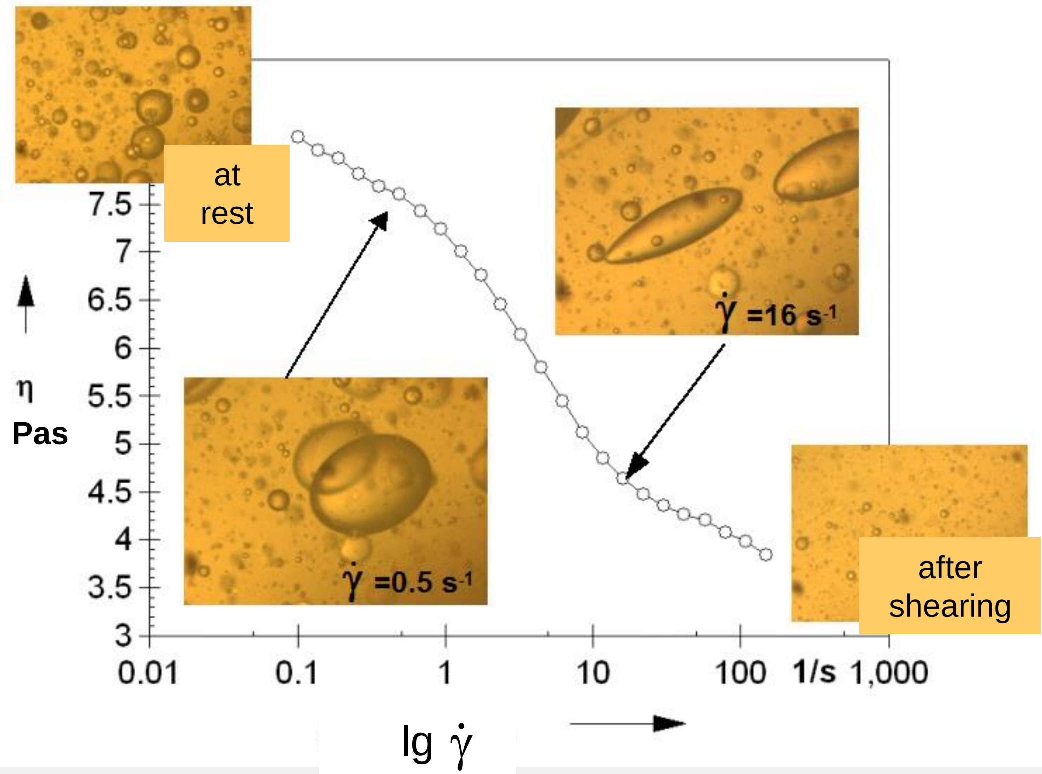


agglomerates
are disintegrated

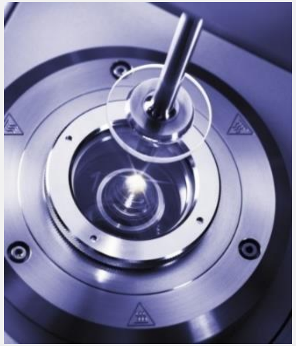
Consequence: shear-thinning flow behavior, decreasing viscosity

Typical size:
primary particles 1 to 10 nm, aggregates up to 100 nm, agglomerates up to 100 µm = 0.1 mm

6 Flow Behavior



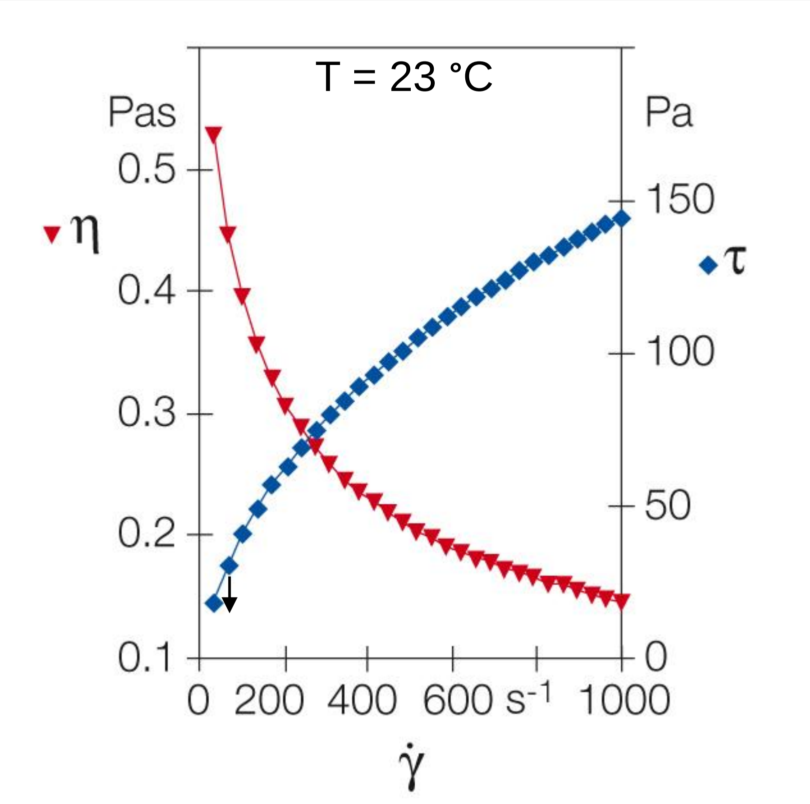
Rheo-microscopy



Emulsion: water in silicone oil

Size and shape of the droplets are dependent on sample preparation and shear rate.

Increase of the volume specific surface ratio due to decreasing droplet size
→ **viscosity may increase** at rest after shearing.



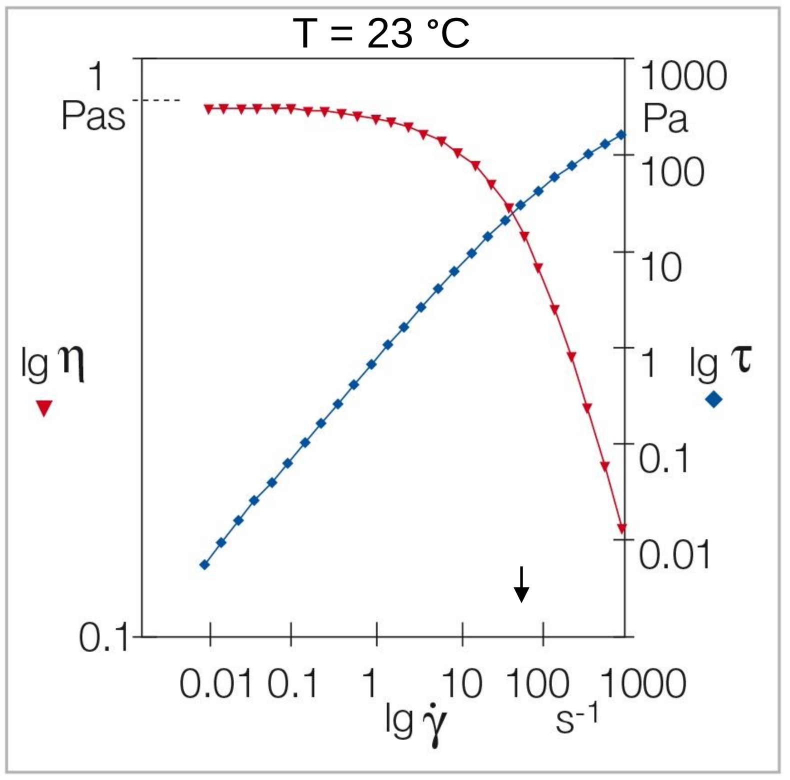
Wall paper paste

aqueous methylcellulose solution

uncrosslinked polymer

typical behavior of
polymer solutions
→ continued shear-thinning

6 Flow Behavior



Wall paper paste

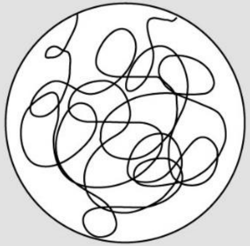
aqueous methylcellulose solution

uncrosslinked polymer

for $\dot{\gamma} < 0.1\ s^{-1}$
plateau of the zero-shear viscosity

logarithmic scale
focus on low-shear range

1



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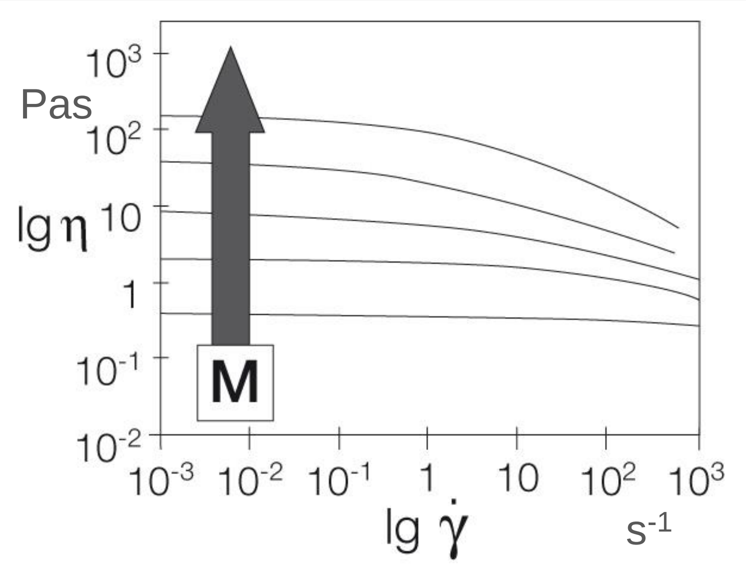
Uncrosslinked polymers in the low-shear range, zero-shear viscosity

Superposition of two processes

(1) Orientation of the macromolecules under shear load
→ **disentanglements**
→ viscosity decreases

(2) Re-coiling due to visco-**elastic** behavior
→ **re-entanglements**
→ viscosity increases

Result:
no change of viscosity in the low-shear range
→ **η_0 value**
usually observed for $\dot{\gamma} < 1\ s^{-1}$

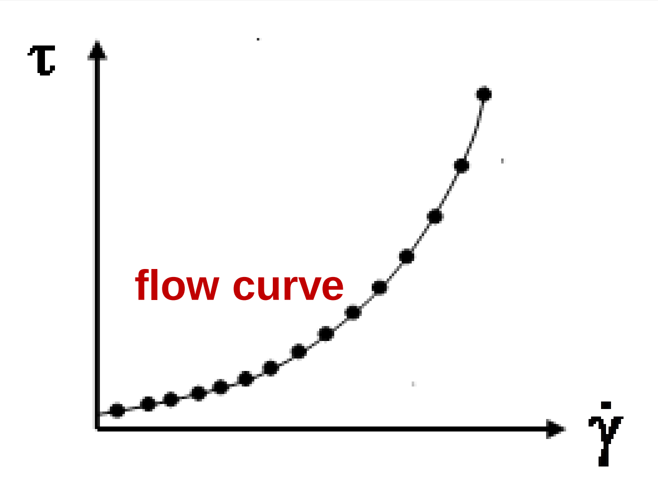


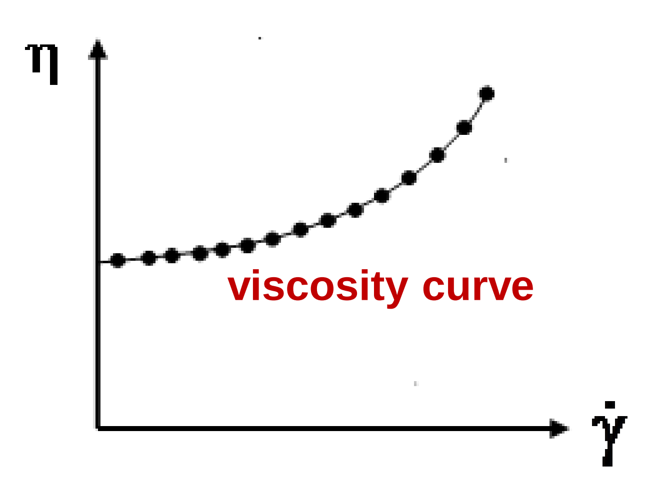
Uncrosslinked polymers

An increasing average
molar mass M
results in a higher value of the
zero-shear viscosity.

(for a constant polymer concentration)

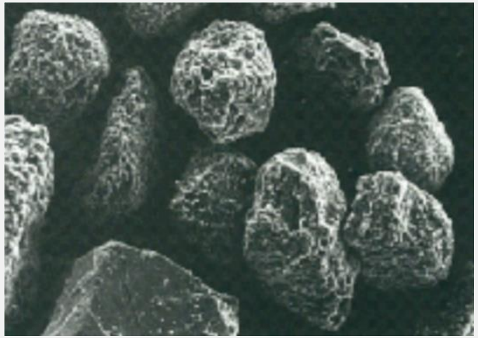
6 Flow Behavior





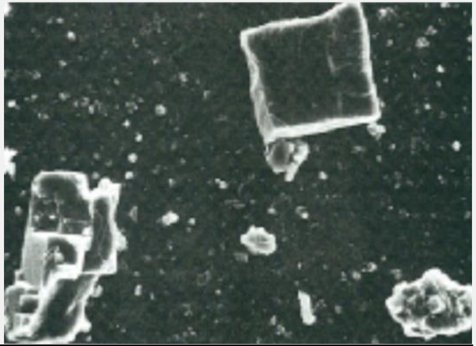
- **shear-thickening**
- dilatant

→ *movie (starch dispersion)*



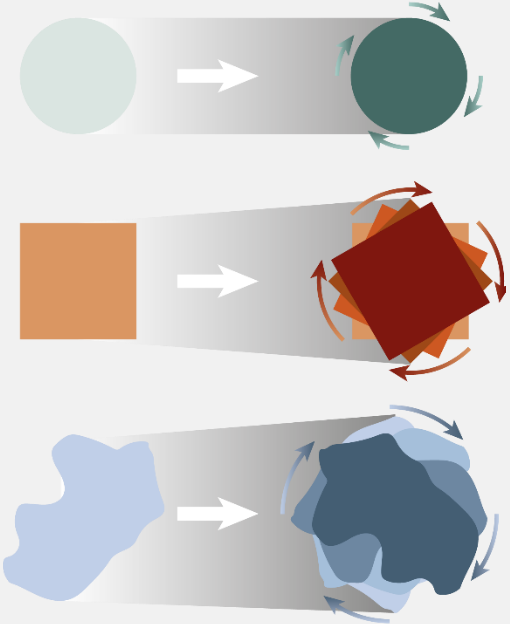
(1)

(2)



Source: REM images, University of Karlsruhe

Influence of the particle shape



Aqueous chalkstone suspensions

(1) spherical particles

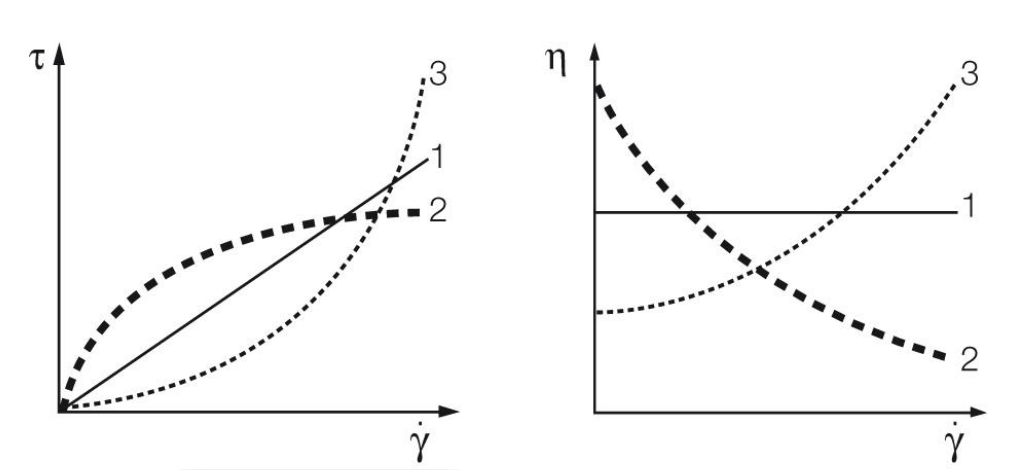
(2) cube-shaped particles

Comparison:
Same solid concentration, suspension (2) showed **shear-thickening** already at lower shear rates.

Reason:
difference in required volume

→ **in flowing dispersions, particles are permanently in a rotational motion**

flow curves / viscosity curves



1	ideal-viscous	(Newtonian)
2	shear-thinning	(pseudoplastic)
3	shear-thickening	(dilatant)

Summary: Seminar Program 1st part

Anton Paar

(1) Rheology and viscous behavior *viscosity as flow resistance, internal friction; “Rheology Road”*
(2) Simple viscosity tests *flow cups, falling-ball & glass-capillary viscometers; rotational viscometers, relative measuring geometries*
(3) Rheometers and measuring geometries *absolute measuring geometries; concentric cylinders, cone/plate, plate/plate; ball bearing & air bearing*
(4) Definitions: shear stress, shear rate, (shear) viscosity *laminar & turbulent flow, shear rate range & technical applications; viscosity law, kinematic viscosity*
(5) Rotational tests *raw data and rheological parameters; controlled shear rate (CSR), controlled shear stress (CSS)*
(6) Flow behavior *ideal-viscous, Newtonian; shear-thinning, pseudoplastic; shear-thickening, dilatant; rheo-microscopy; zero-shear viscosity*
(7) Yield point (via flow curves and via γ/τ - diagrams) *as interception on the stress-axis, mathematical curve fitting, regression models; crossover of fitting lines*
(8) Further flow curves and viscosity curves *effect of rheology additives; transient viscosity peak*
(9) Time-dependent behavior (rotation) *step tests, structure recovery, thixotropic behavior; curing*
(10) Temperature-dependent behavior (rotation) *softening; crystallization; gelation, curing; pour point (oils)*

Appendix: Pressure-dependent behavior (rotation)

Seminar Program 2nd part

(11) Viscoelastic behavior
(12) Definitions: deformation, shear strain, shear modulus
(13) Yield point via γ / τ - diagram
(14) Oscillatory tests
(15) Amplitude sweeps
(16) Frequency sweeps
(17) (Time-dependent behavior (oscillation))
(18) Temperature-dependent behavior (oscillation)

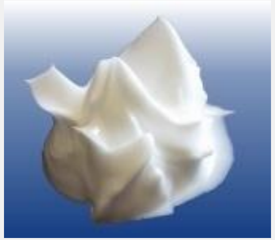
Appendix:
(19) DMA in torsion (on solid specimens)
(20) (DMA in tension)

The Rheology Road

viscous — **viscoelastic** — **elastic**

ideal-viscous liquids
water, oils
Viscosity Law

viscoelastic liquids
glues, shampoos



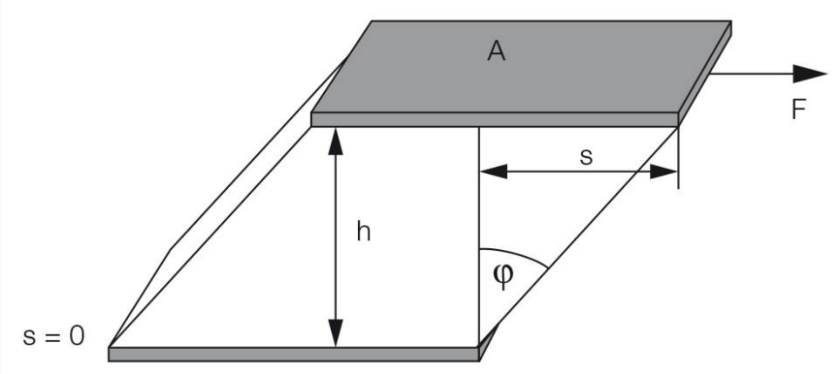
viscoelastic solids
pastes, gels, elastomers

ideal-elastic solids
stone, steel
Elasticity Law

rotational tests

oscillatory tests

12 Definitions: Deformation, Strain, Shear Modulus



Two-plates model

shear stress

$$\tau = F / A$$

unit: $1\ N / m^2$ = **1 Pa**

shear deformation or **shear strain**

$$\gamma = s / h$$

unit: 1 m / m = **1 = 100 %**

12 Definitions: Deformation, Strain, Shear Modulus

Robert Hooke (1635 to 1703),
in 1676 he states **for solids proportionality of force and deformation**.

The later so-called
Elasticity Law of Hooke
was formulated in the
19. century (e.g. by T. Young in 1807, or A.L. Cauchy in 1827).

Shear modulus

$$G = \tau / \gamma$$

unit: (1 Pa / 1 =) **1 Pa**

1 GPa = 1000 MPa = 10^6 kPa = 10^9 Pa

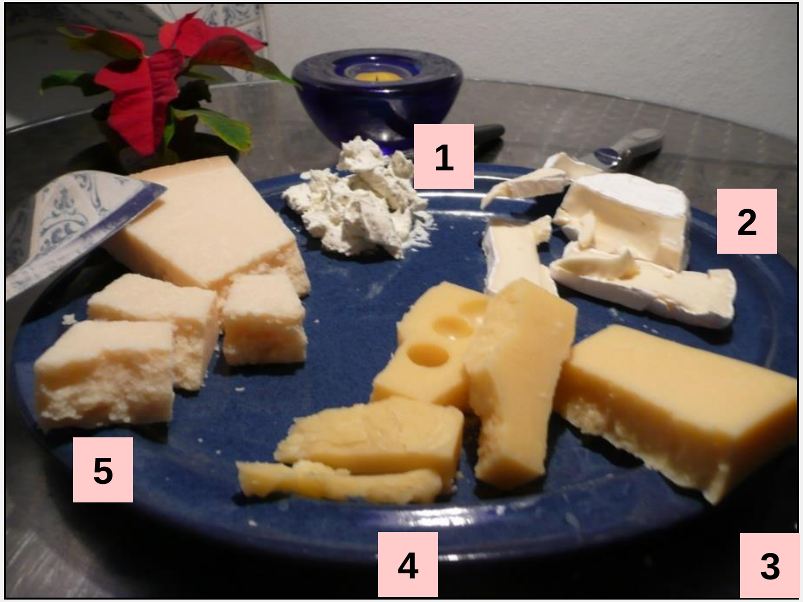
Giga-pascal, Mega-pascal, kilo-pascal

spring force	F
deflection path	s
spring constant	C (stiffness)
law of springs:	F / s = C

12 Definitions: Deformation, Strain, Shear Modulus

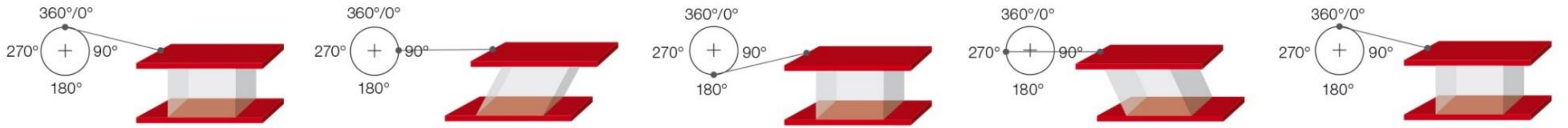
Material stiffness and shear moduli

cheese type	example	shear modulus (around)
1 cream	spread cheese	1 kPa
2 soft	French Camembert	10 kPa
3 semi-hard	Holland Gouda (young)	0.1 MPa
4 hard	Swiss Emmentaler	0.5 MPa
5 extra hard	Italian Parmigiano	1 MPa



→ *e-learning (cheese mice)*

14 Oscillatory Tests

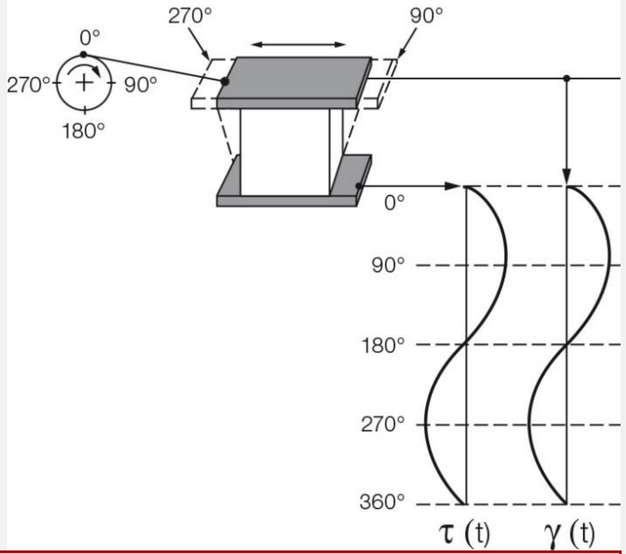


Two- plates model, equipped with two sensors,
top preset of deflection path (strain or deformation)
bottom measurement of resulting force (shear stress)

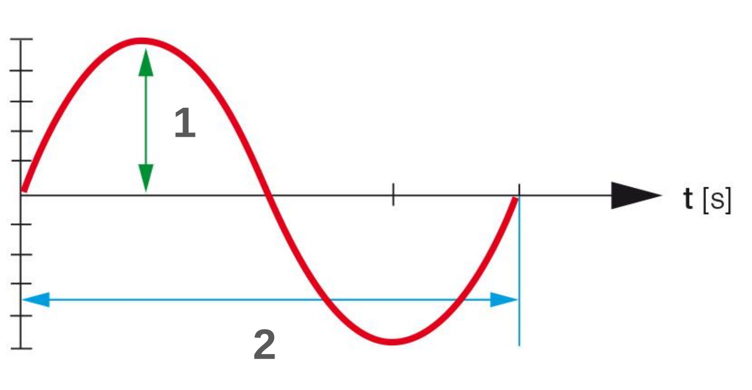
sinusoidal preset

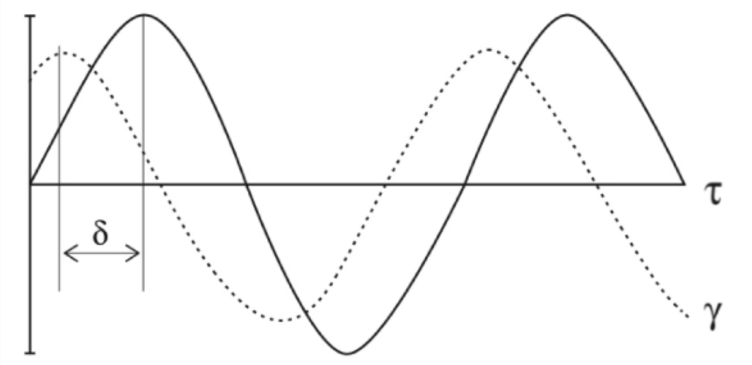
ideal-elastic behavior
stiff sample (e.g. a stone or steel):
no time shift between the sine curves of
preset strain and resulting shear stress:

the curves of γ and τ are "in phase"



→ *movie (2-plates-model, ideal-elastic behavior)*





Preset
constant amplitude (1) and constant frequency (2)

Result
Most samples show
viscoelastic behavior
with a
phase shift δ
between the maxima of the sine curves as the
retardation of the measuring response
compared to the preset.

→ *movie (2-plates-model, viscoelastic behavior)*

14 Oscillatory Tests

phase shift angle

90° ≥ δ ≥ 0°

ideal-viscous behavior

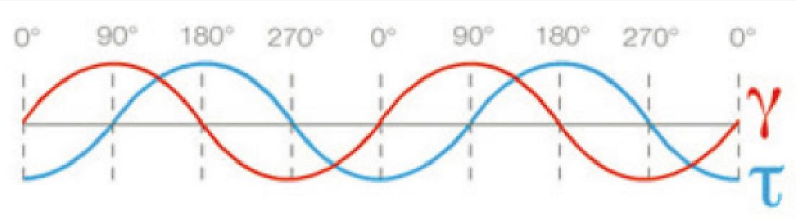
fluid, liquid: **90° ≥ δ > 45°**

and

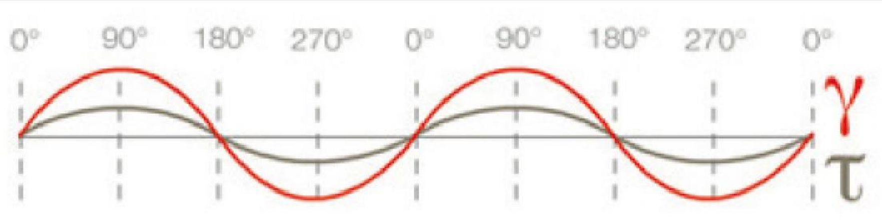
ideal-elastic behavior

solid, gel-like: **45° > δ ≥ 0°**

Illustrative concept: δ as the "street number in Rheology Road"



ideal-viscous: δ = 90°



ideal-elastic: δ = 0°

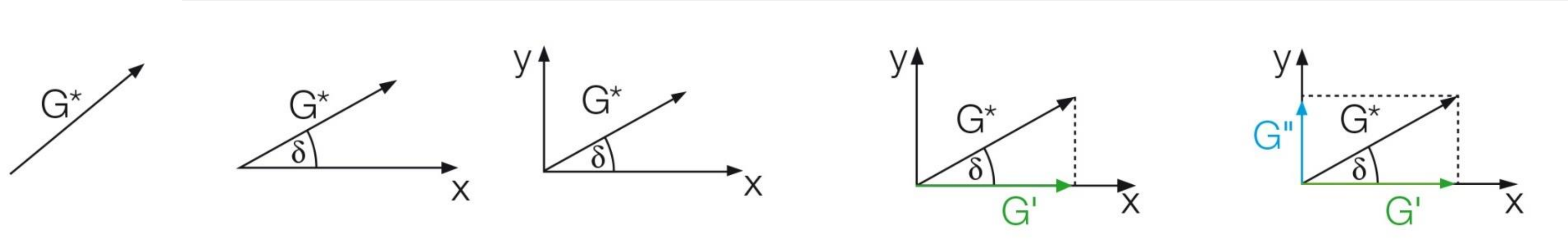
Anton Paar

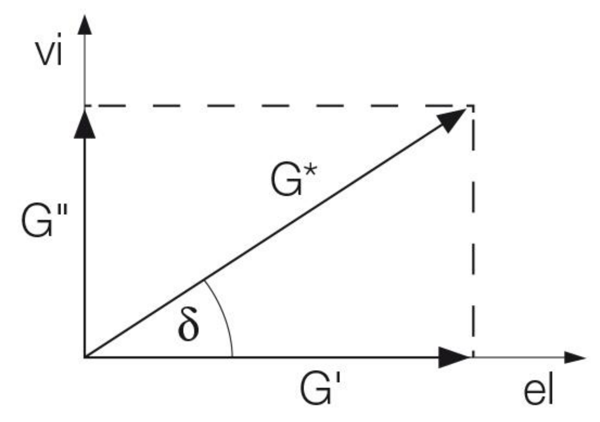
Vector diagram
to determine the parameters G' and G'' based on the Elasticity Law

- preset of γ_A
- measurement of τ_A and phase shift angle δ
  (index A for amplitude)

Calculation:
complex shear modulus G*

$$G^* = \tau_A / \gamma_A$$





Molecules
left: freely moveable, uncrosslinked
right: crosslinked

Vector diagram

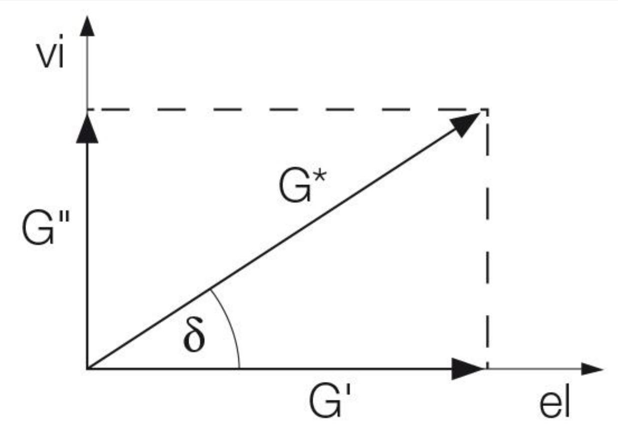
G* **complex shear modulus, viscoelastic behavior in total**

G' **(shear) storage modulus, elastic shear modulus**

G'' **(shear) loss modulus, viscous shear modulus**

G' (G-prime) for the **stored**,
G'' (G-double prime) for the **lost** (dissipated)

deformation energy
internal friction when flowing



$\tan\delta$ = G''/ G'

loss factor (or **damping factor**)

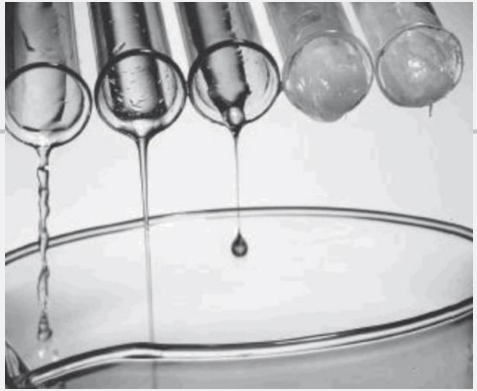
tangent delta
unit: dimensionless (or 1)

“viscoelastic ratio”

of viscous and elastic portions

use case
point of phase transition

G' = G'' or **$\tan\delta$ = 1** or **δ = 45°**



viscous		viscoelastic		elastic
G'' >> G'	G'' > G'	G'' = G'	G' > G''	G' >> G''
liquid, fluid state		sol / gel transition	gel-like, solid state	

$\tan\delta = G'' / G'$

$\tan\delta >> 1$ $\rightarrow \infty$	$\tan\delta > 1$	$\tan\delta = 1$	$\tan\delta < 1$	$\tan\delta << 1$ $\rightarrow 0$

ideal-viscous: $\tan\delta > 100:1 = 100$
for scientists: $\tan\delta > 1000$

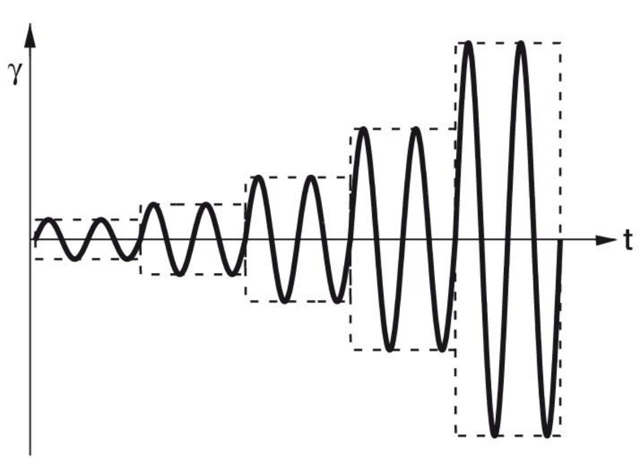
ideal-elastic: $\tan\delta < 1:100 = 0.01$
for scientists: $\tan\delta < 0.001$

Source: Society of Cosmetic Chemists: Viscosity, Rheology and Rheology Modifiers

Oscillation CSD contr. shear deformation	test preset		result	
raw data	**deflection angle φ(t)**	[rad]	**torque M(t)** **phase shift δ**	[Nm] [degrees]
rheological parameters	Deformation/strain γ(t)	[%]	shear stress τ(t) phase shift δ	[Pa] [degrees]

Oscillation CSS controlled shear stress	test preset		result	
raw data	**torque M(t)**	[Nm]	**deflection angle φ(t)** **phase shift δ**	[rad] [degrees]
rheological parameters	shear stress τ(t)	[Pa]	deformation/strain γ(t) phase shift δ	[%] [degrees]

φ in degrees or in 1 rad; 360° corresponds to 2π rad



Preset

constant frequency

(e.g. angular frequency ω = 10 rad/s)

variable strain (deformation)

strain sweep

or variable stress

stress sweep

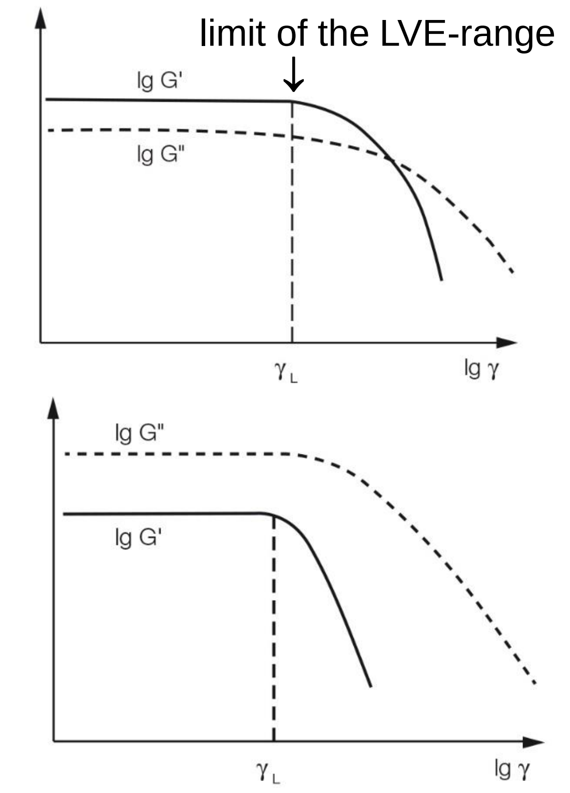
Frequency conversion: $\omega = 2\pi \cdot f$

with **angular frequency ω in rad/s** (or s^{-1}) and **frequency f in Hz**

Please note: Hz is not a SI unit.

→ *movie (amplitude sweep)*

15 Amplitude Sweeps



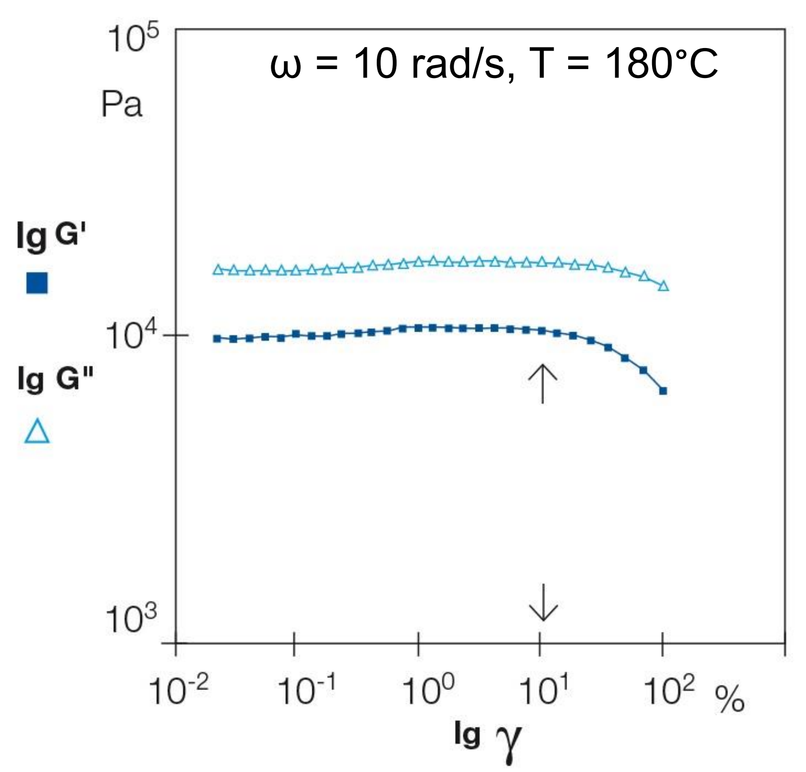
Result

storage modulus **G'** (elastic behavior)
loss modulus **G''** (viscous behavior)

limiting value of the
linear viscoelastic (LVE-) range when reaching γ_L
linearity limit of shear strain

at **given** conditions,
i.e., at the **preset** frequency

in the LVE-range
top: **G' > G'' (gel-like, solid structure)**
bottom: **G'' > G' (liquid, fluid structure)**



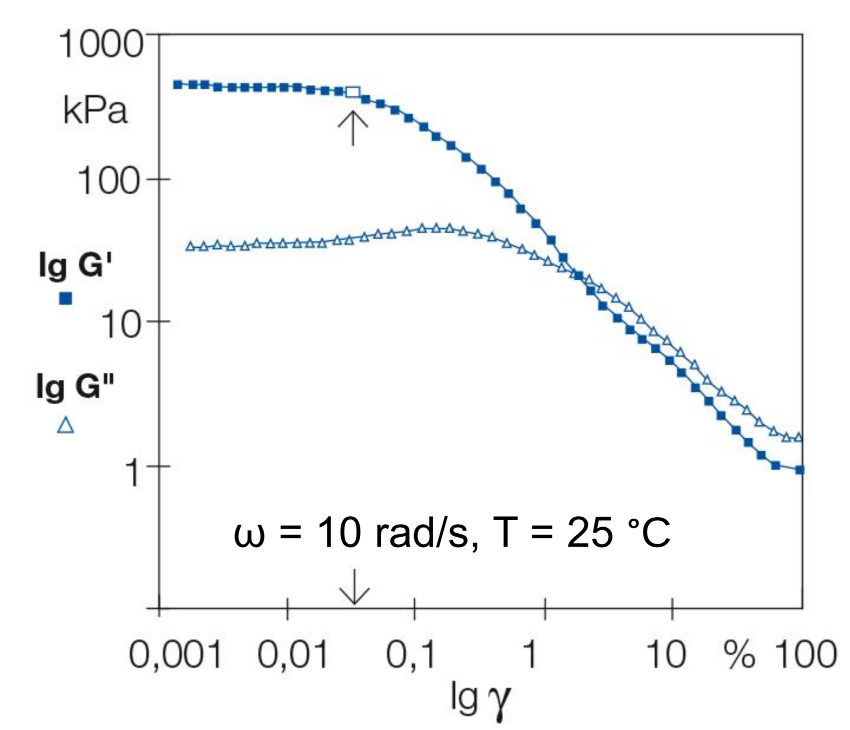
Polymer melt

liquid state
because G'' > G'

viscoelastic fluid

limit of the LVE range at
γ_L = 10 % = 0.1

15 Amplitude Sweeps

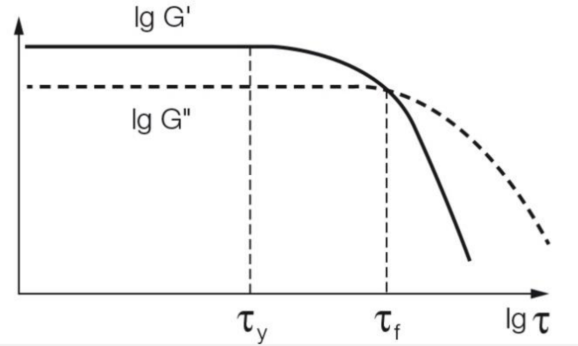


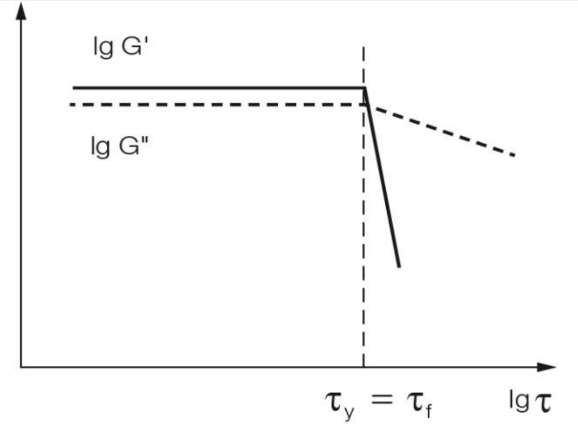
Sealant

in the LVE range
gel-like or pasty state
because G' > G''

limit of the LVE-range at
$\gamma_L = 0.026\ \%$

15 Amplitude Sweeps





- **yield point τ_y**
  value at the **limit of the LVE-range,**
  or **linearity limit of shear stress**
  (also as τ_L)

- **flow point τ_f**
  value at the **crossover point G' = G"**
  (also as τ_{co})

For both values:
At **given** test conditions,
i.e. **preset** frequency

Brittle fracture if $\tau_y = \tau_f$

Oscillatory tests: calculation of shear rate values

$\dot{\gamma} = \gamma_A \cdot \omega$

unit: 100 % · (1 rad/s) = 1 · (1/s) = 1 s^{-1}

Example

amplitude sweep

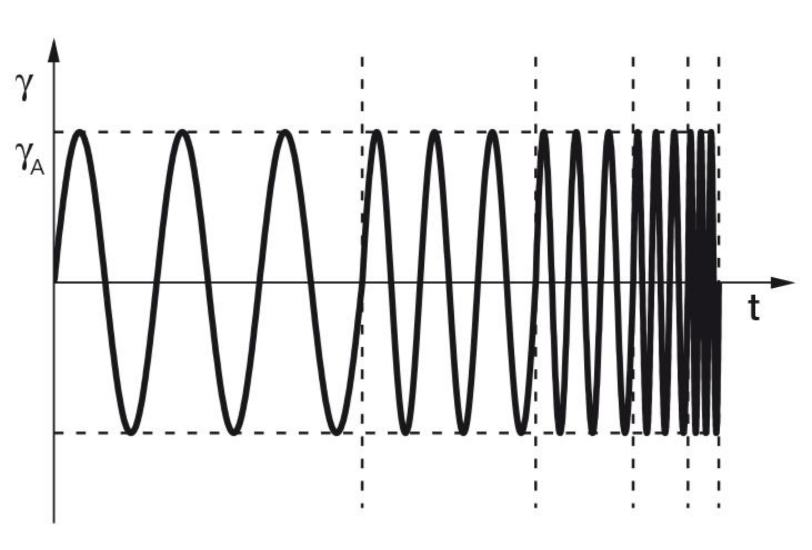
γ_A = 10 %

ω = 10 rad/s

$\dot{\gamma}$ = 10 % · 10 rad/s = 0.1 · 10 s^{-1} = **1 s^{-1}**

Summary:

Usually oscillatory tests are performed in the low-shear range.



Preset

constant amplitude

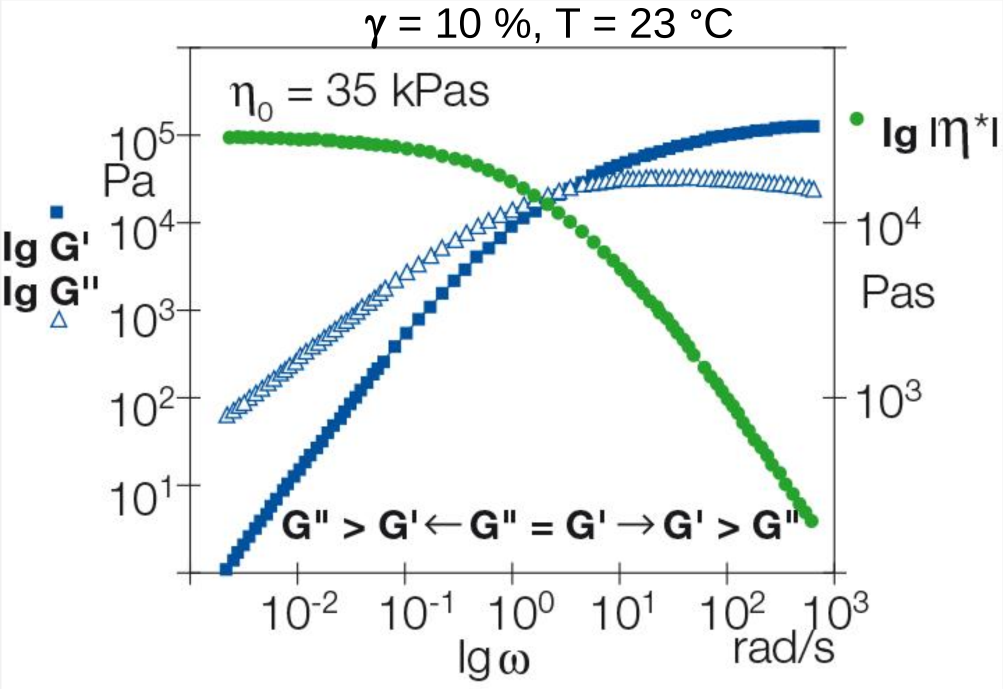
shear strain (or shear stress)
within the LVE-range

and

variable frequency

Precondition:
LVE-range has been checked by an amplitude sweep.

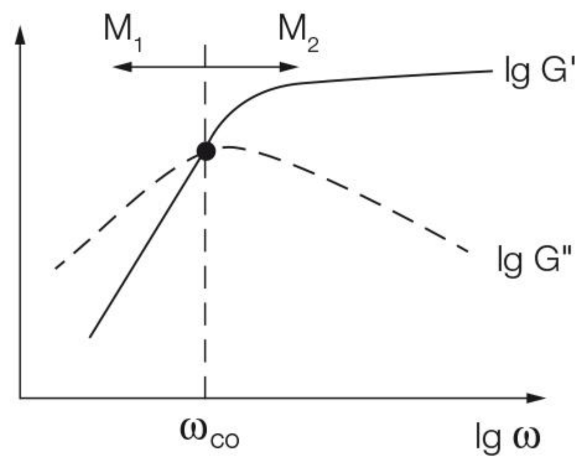
→ *movie (frequency sweep)*



PDMS
poly-
di-methyl
siloxane

typical behavior of
uncrosslinked polymers
showing a crossover point G' = G''

16 Frequency Sweeps

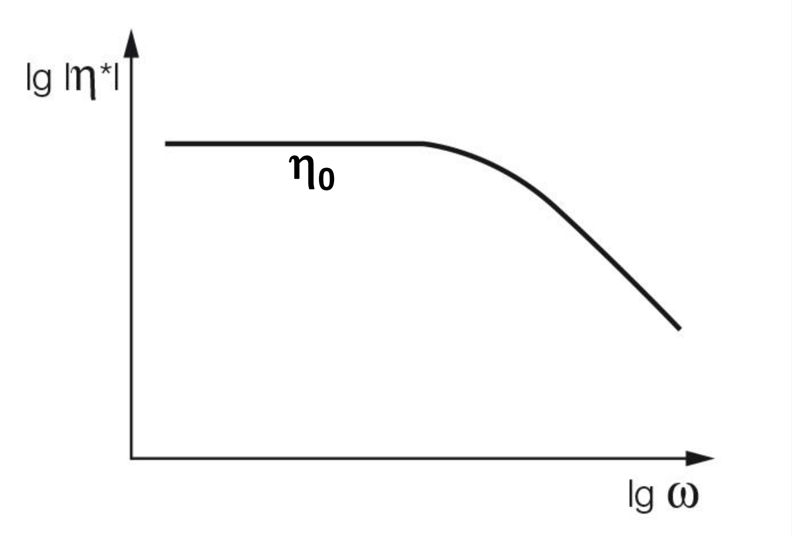


uncrosslinked polymers

average molar mass M

position of the crossover point G' = G"
depends on M (here: $M_1 > M_2$)

relaxation time $\lambda = 1 / \omega_{co}$



Uncrosslinked polymers
complex viscosity η*

$$|\eta^*| = G^* / \omega$$

unit: 1 Pas = 1 Pa / (1/s)

Maxwellian fluids show a
plateau of the zero-shear viscosity η_0
at low frequencies

η_0 is proportional to the molar mass M
(at the same polymer concentration),
as for viscosity curves $\eta(\dot{\gamma})$ in rotation.

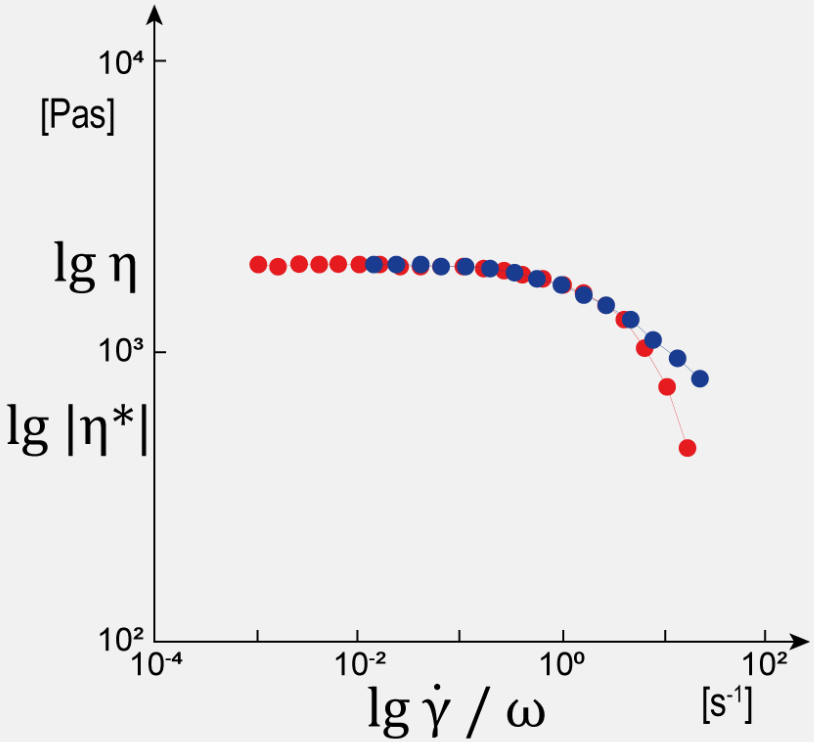
Cox / Merz relation

In the low-shear range, for uncrosslinked polymers:

The plateau of the zero-shear viscosity η_0 is on the same level for both.

(1) shear viscosity $\eta(\dot{\gamma})$ (in rotation)
(2) complex viscosity $|\eta^*(\omega)|$ (in oscillation)

Reason: In the low-shear range or the LVE-range, respectively, applies: $\eta(\dot{\gamma}) = |\eta^*(\omega)|$



Cox / Merz relation

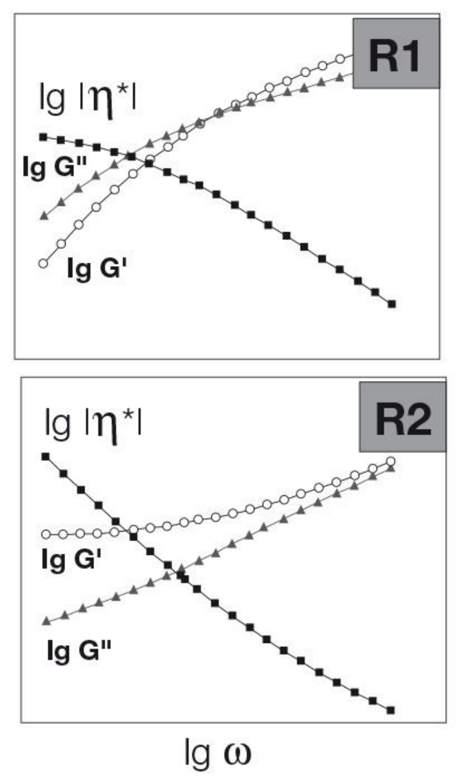
Polymer melt

oscillation
frequency sweep
complex viscosity $|\eta^*(\omega)|$

rotation
shear rate dependent
(shear) viscosity $\eta(\dot{\gamma})$

Summary:
Same plateau value of the zero-shear viscosity in the low-shear range

Source: Cox, W.P., Merz, E.H.: J. Polym. Sci., 1958



Behavior-at-rest of two resins
problem: bad start of pumping
→ check low frequency range

top: uncrosslinked molecules G" > G'

η^* shows plateau of the zero-shear viscosity η_0
→ **viscoelastic liquid**

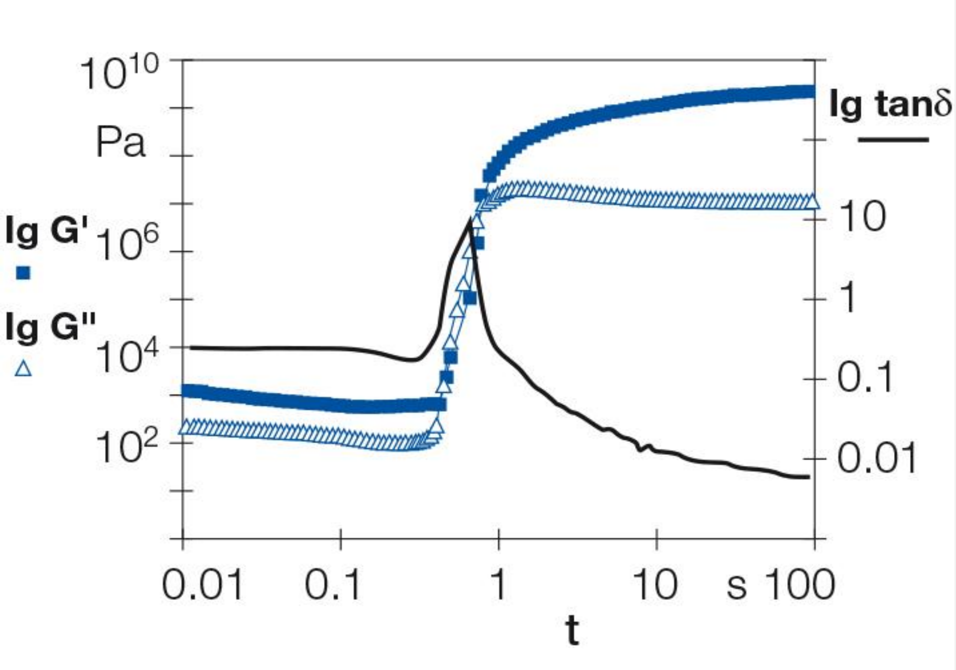
bottom: cross-linked molecules G' > G"

η^* rises towards infinity
→ **solid structure**

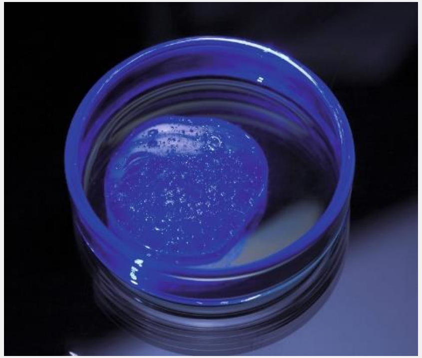
Comment: Values of η^* are not useful where G' > G".

17 Time-dependent Behavior (Oscillation)

D-PP 08, γ = 0.02 %, ω = 63 rad/s (or f = 10 Hz)



UV-curing resin

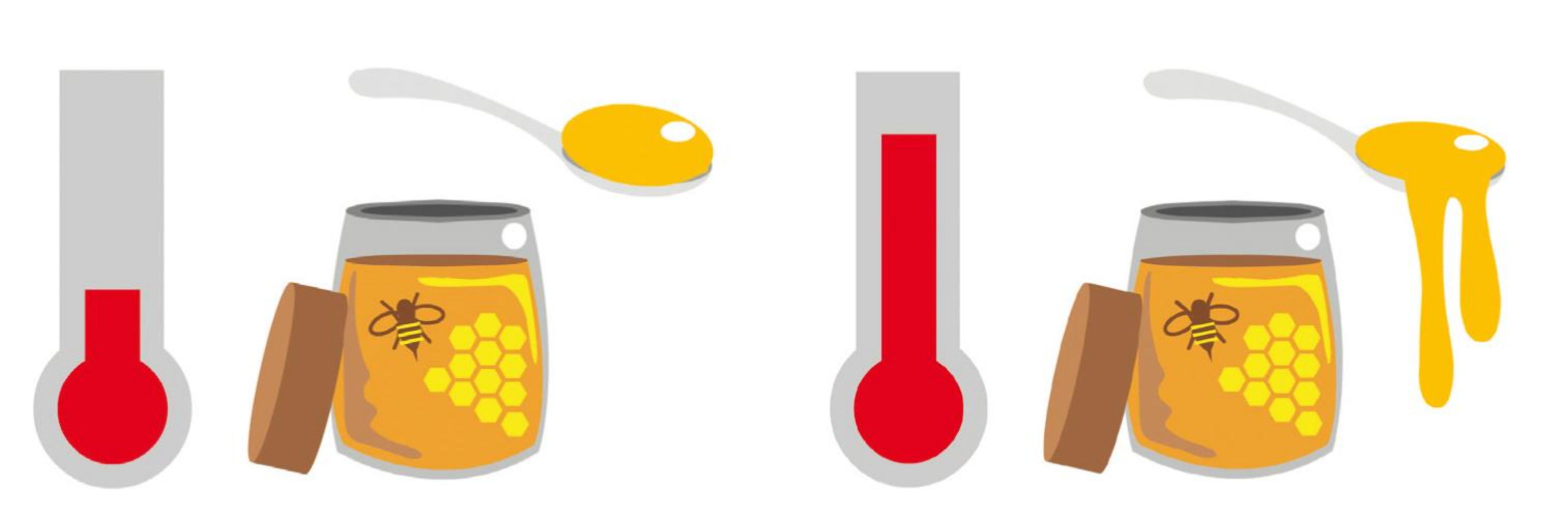


fast curing reaction

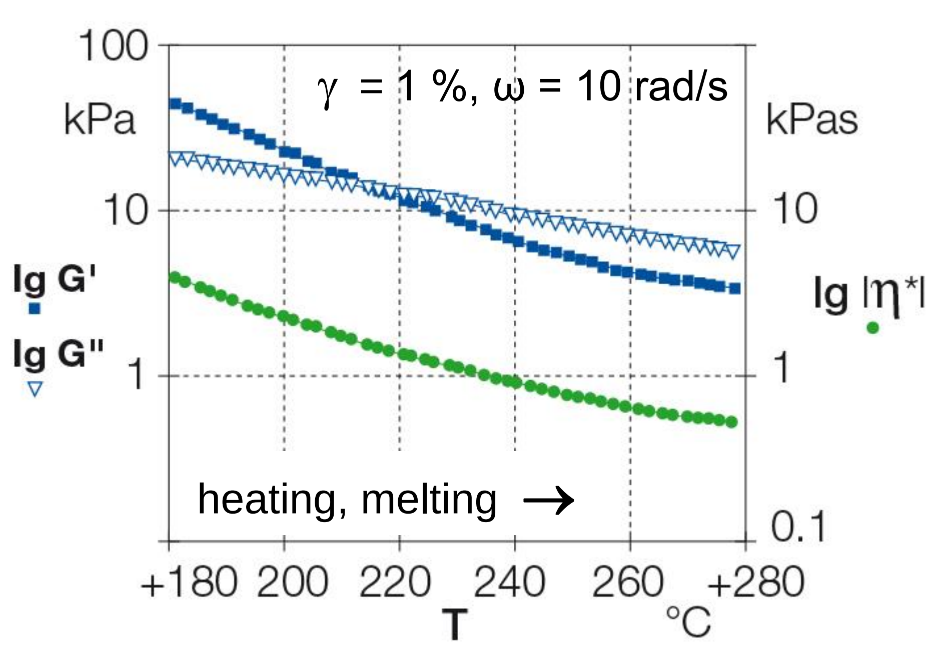
main reaction in 0.5 s
finally very rigid, since G' > 1 GPa

$\tan\delta = G'' / G'$

18 Temperature-dependent Behavior (Oscillation)



18 Temperature-dependent Behavior (Oscillation)



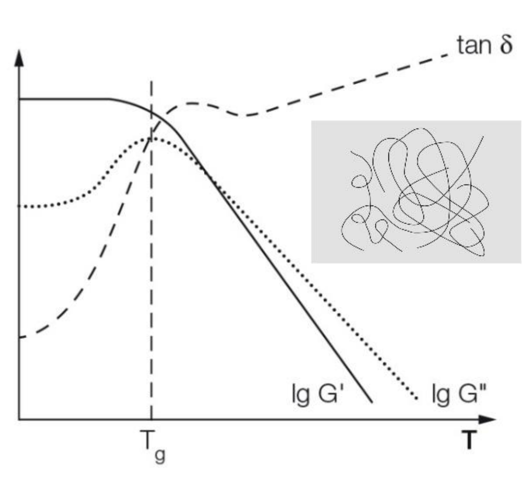
ABS resin

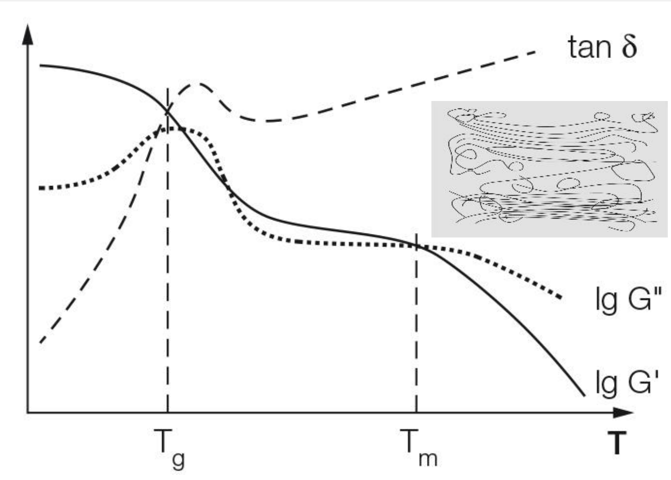
blend of 3 immiscible polymers

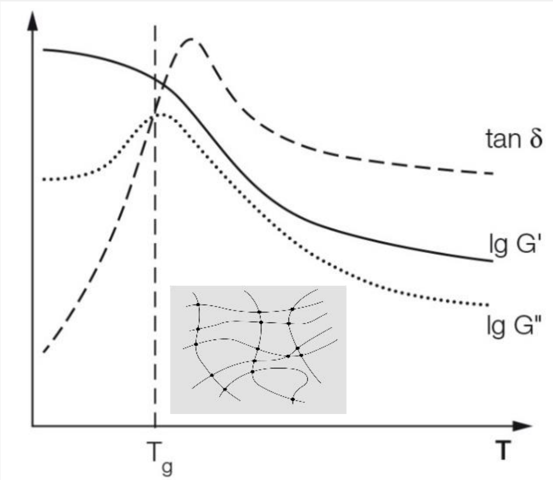
softening temperature

T = 215 °C
at the crossover point G' = G''

Polymers (dynamic-mechanical analysis DMA, acc. to ISO 6721-1)







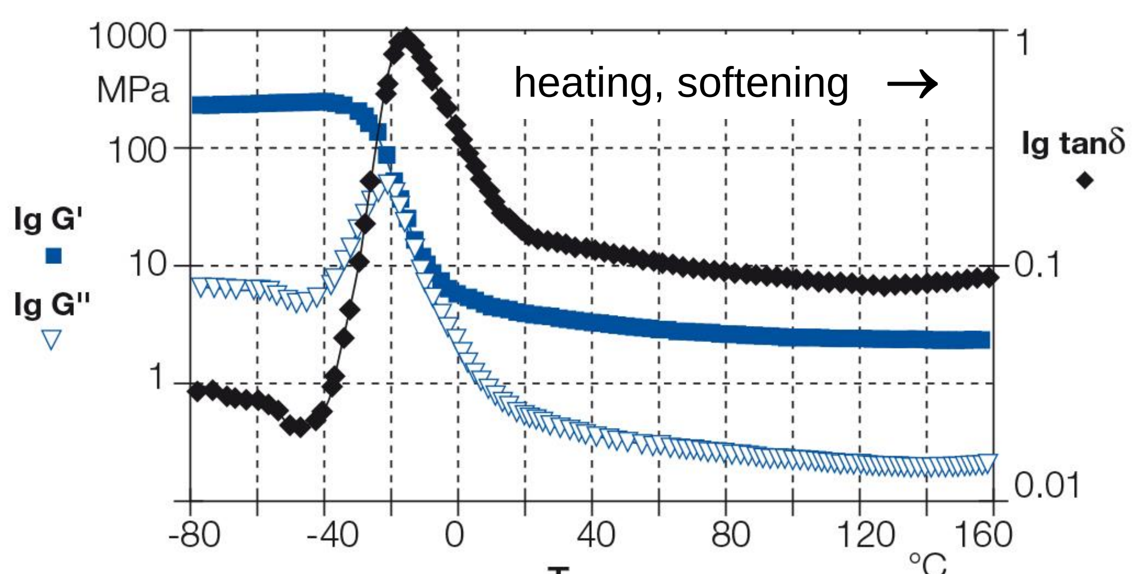
amorphous
uncrosslinked, no order

partially crystalline
uncrosslinked, partially ordered

chemically cross-linked
covalent primary bonds

T_g glass transition temperature at the G" maximum (peak): ISO 6721-11
T_m melting temperature

18 Temperature-dependent Behavior (Oscillation)



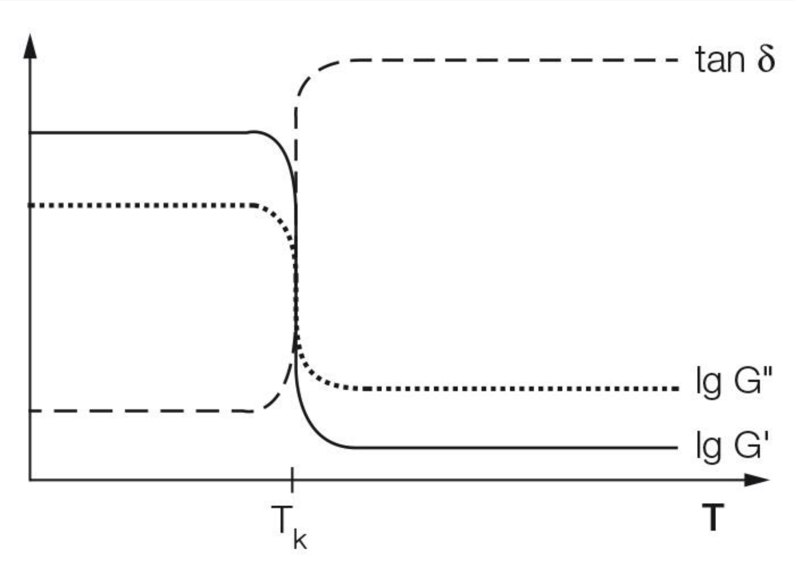
γ = 0.25 %, ω = 10 rad/s

Rubber

crosslinked polymer

T_g = -22 °C (G'' max)
T_g = -16 °C (tanδ max)
no T_m

18 Temperature-dependent Behavior (Oscillation)



Melting or crystallization
crystallizing substances

Preset
constant dynamic-mechanical
shear conditions

- amplitude in the LVE-range
- usually ω = 10 rad/s

Result
steeply decreasing or increasing curves
in a relatively narrow temperature range

T_k crystallization temperature

Appendix: Further Tests besides Shear Tests

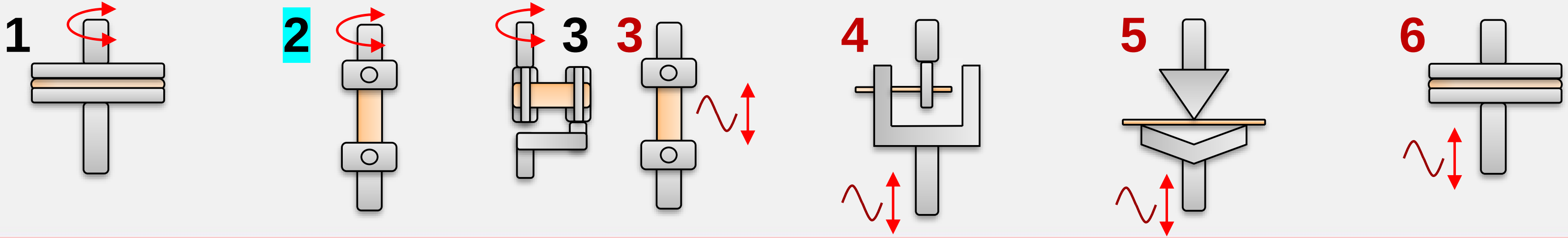
Overview: Test modes according to ISO 6721

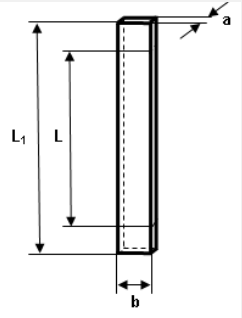
with oscillation, to measure dynamic-mechanical properties
as **DMA** or **DMTA**, dynamic-mechanical (thermal) analysis (oscillatory or unidirectional)

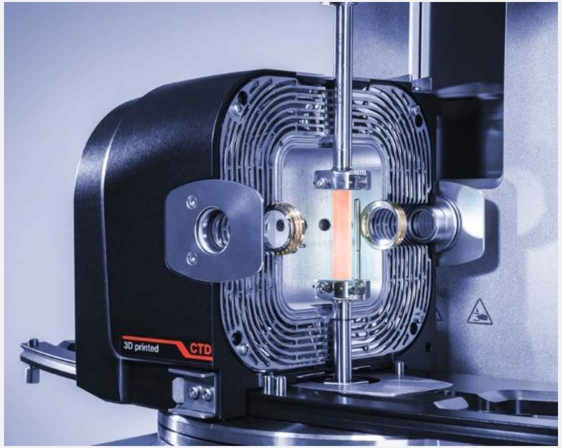
	Test mode	Samples	Measured moduli
1.	**Shear**	liquids, dispersions, soft solids	**G**
2.	**Torsion**	solids	**G**
3./3.	**Tension / extension**	highly viscous liquids, films, solids	**E**
4.	**Cantilever bending**	solids	**E**
5.	**3-point bending**	solids	**E**
6.	**Compression**	rubber, solids	E_C

rotational drive (1.–3.)

linear drive (3.–6.)





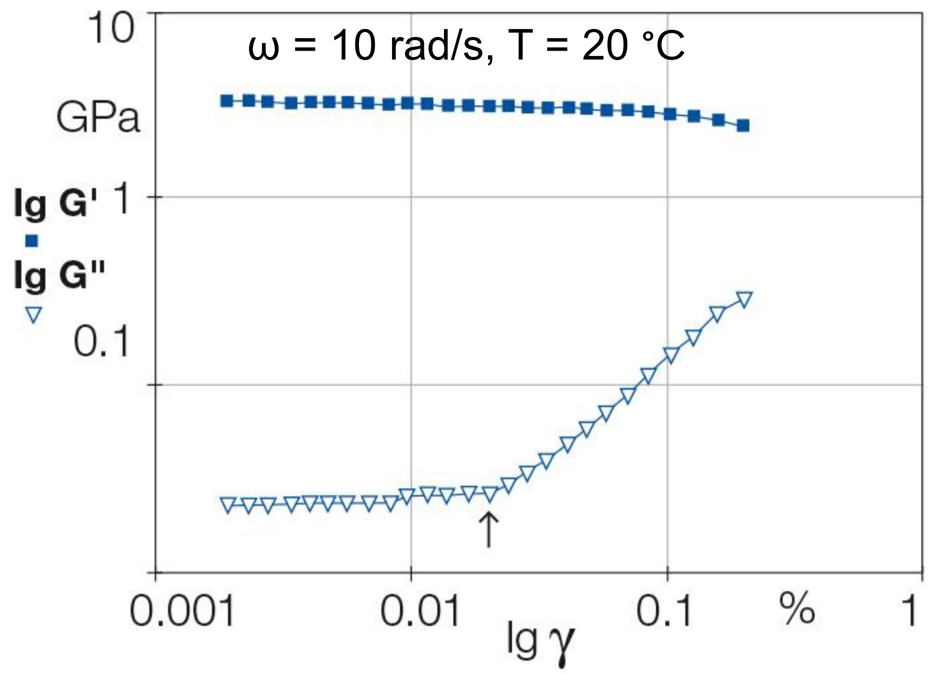


Solid Torsion bars

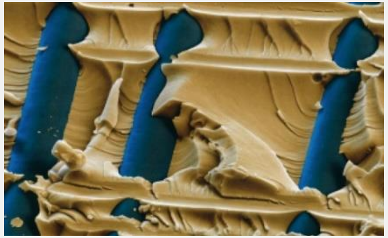
measuring geometry SRF
(solid rectangular fixture)

typical dimensions:
54 x 10 x 1 (L_1 x b x a, in mm),
with L = 40 mm free length, between the clamps
total length L_1 = L + (2 x 7) mm

19 DMA in Torsion



Fiber-reinforced resin



resin matrix and fibers
Source: BASF calendar 2013

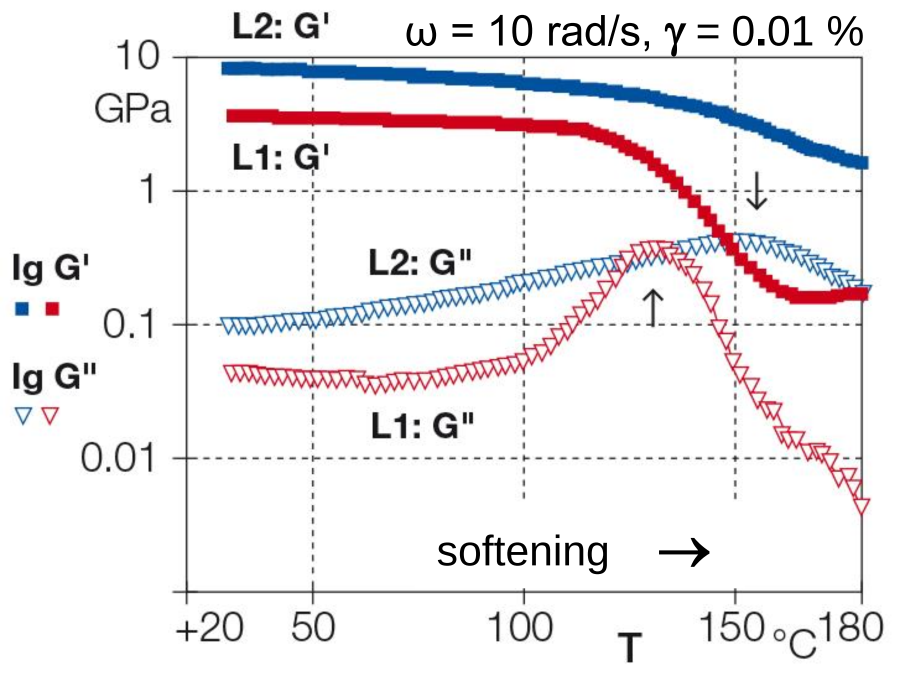
Amplitude Sweep

LVE-range up to $\gamma = 0.02$ %

Rising G'':
increasing consumption of deformation energy (lost energy) due to the formation of

micro-cracks

19 DM(T)A in Torsion



Laminates

unmodified laminate	L1
reinforced laminate	L2

increase of G' from 3 GPa to 8 GPa

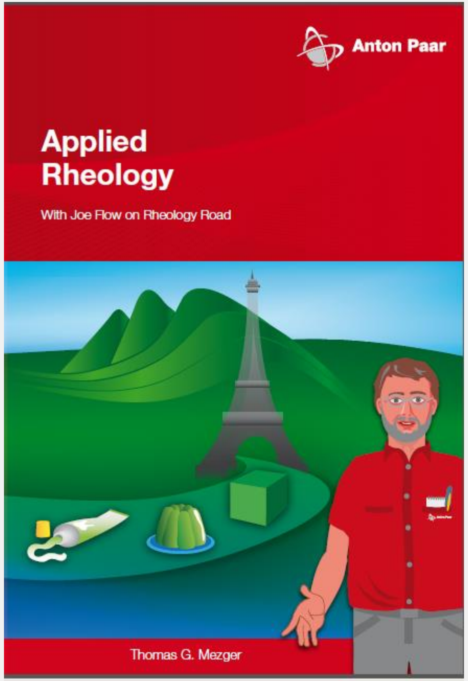
→ **harder surface, less abrasion**

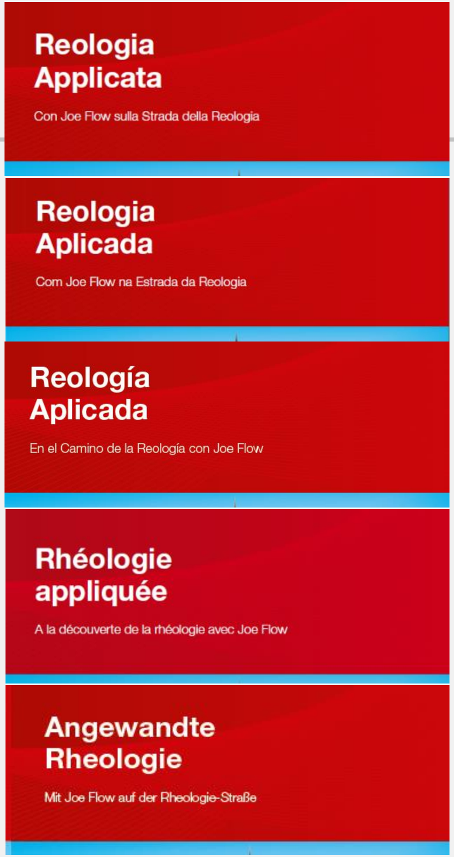
Summary: Seminar Program 2nd part

(11) Viscoelastic behavior *“Rheology Road”, stringiness, rod climbing or Weissenberg-effect, extrudate swelling, melt fracture*
(12) Definitions: deformation, shear strain, shear modulus *elasticity law*
(13) Yield point via γ / τ - diagram *straight fitting line in the linear-elastic deformation range*
(14) Oscillatory tests *phase shift; raw data and rheological parameters; shear storage modulus, shear loss modulus, loss factor or damping factor; sol / gel transition*
(15) Amplitude sweeps *LVE-range, gel strength, brittle break behavior, G”-maximum; yield point & flow point*
(16) Frequency sweeps *uncrosslinked polymers: average molar mass, Maxwellian behavior; complex viscosity, zero-shear viscosity; cross-linked polymers; dispersion stability, syneresis*
(17) Time-dependent behavior (oscillation) *step tests, structure recovery, thixotropic behavior; ORO-test; curing, UV-curing*
(18) Temperature-dependent behavior (oscillation) *softening, melting, T_g -values; crystallization; high-temperature tests; gelation, curing*

Appendix:
(19) DMA in torsion *solid torsion bars; DMA and DMTA in torsion; T_g values*
(20) DMA in tension *extensional rate, ext. viscosity, strain softening, strain hardening; tensile stress, elongation, E-modulus, Young’s modulus, Poisson’s ratio; DM(T)A in extension; E’ & E” moduli, T_g values*

Rheo-Books





9 languages available: German, English, Chinese, Korean, French, Spanish, Portuguese, Italian, Japanese
additionally: **The Rheology Handbook** (5^{th} ed., publisher Vincentz, Hanover, 432 p.) also available in German

End of the Rheo-Seminar

Have a nice day…