Rheology
A short Introduction

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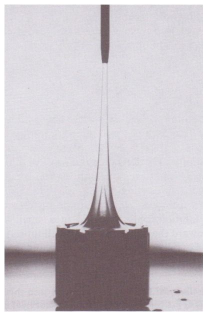

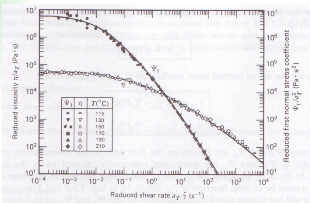

- What is Rheology
- A bit of continuum mechanics
- Rheometry / µRheology
- Structure Rheology

What is Rheology ?

Rheology is the study of the flow of matter
in response to an applied force.

It applies to substances which have a complex microstructure, such as muds, sludges, suspensions, polymers and other glass formers (e.g., silicates), as well as many foods and additives, bodily fluids (e.g., blood) or other materials which belong to the class of soft matter.

Rheology comes into play during...

- Quality control

A simple practical test will do mostly.

- Design and control of processes
- Production of materials
- Transport (e.g. pumping)

The process should be better understood, more detailed testing is imperative.

- Search for new materials and/or new applications

To tune the properties of the material, one needs understanding of the underlying microscopic processes.

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Interesting fluids (from a Rheological perspective)

plastics	dairy products, (low-fat)
polymer melts	margarine, yoghurt,
paint	cream, salad dressings,
bitumen	tomato ketchup,
emulsions	dough, cosmetics, soap

These materials contain rather tall units, like long polymers or particles of (sub-) micron size, which can interact with each other

We call them: COMPLEX FLUIDS

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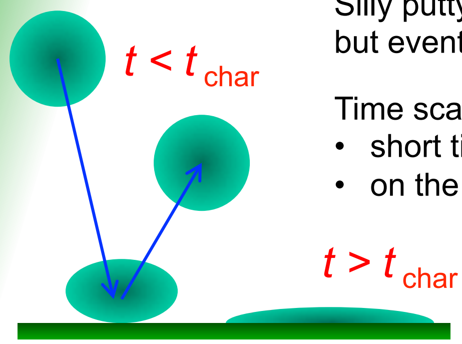
Solid, Liquid and in between…

Solid: shape preserved
Liquid: adapts it shape

Silly putty: Bounces on the table but eventually it adapts its shape.

Time scale:
- short times: solid like
- on the long run: liquid like



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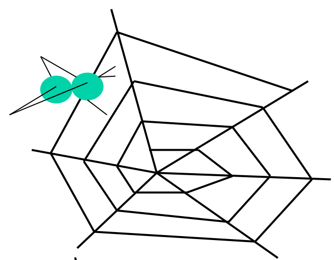
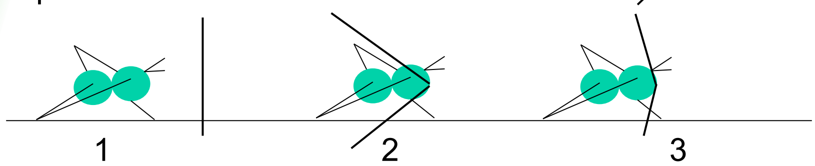
Characteristic time of the material tells you what is short and what is long:

Water	10^{-12} sec
Dough products	1 sec – 100 sec
Polymer liquids	1 – 5 min
Glacier	10 year
Glass	500 year
Bronze	2000 year



Spider web:



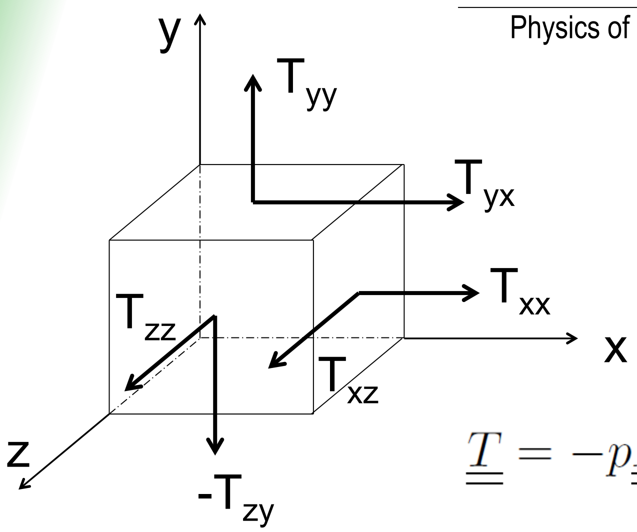
Continuum mechanics tells us how to describe stress and strain.

Stress state is described by 9 components, giving the stress tensor:

$$\underline{\underline{T}} = \sum_{a,b \in \{(x,y,z\}} T_{a,b}\, \underline{e}_a\, \underline{e}_b$$

$$T_{a,b} = T_{b,a}$$

$$\underline{\underline{T}} = \left\{ \begin{array}{ccc} \tau_{xx} - p & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \tau_{yy} - p & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \tau_{zz} - p \end{array} \right\}$$



$$\underline{\underline{T}} = -p\underline{\underline{I}} + \underline{\underline{\tau}}$$

Some components of the stress tensor

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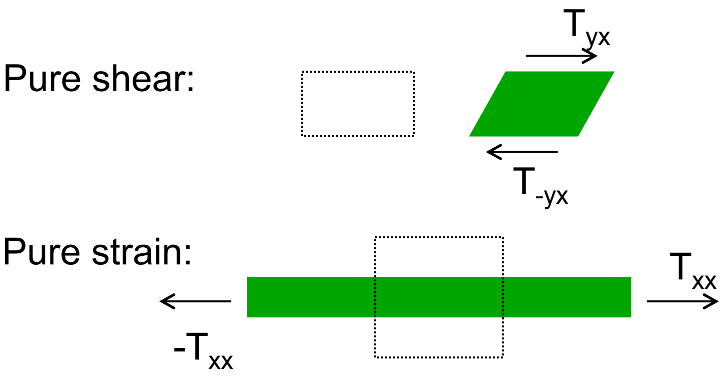
Basic forms of deformation:



C.W. Macosko: Rheology; 1994

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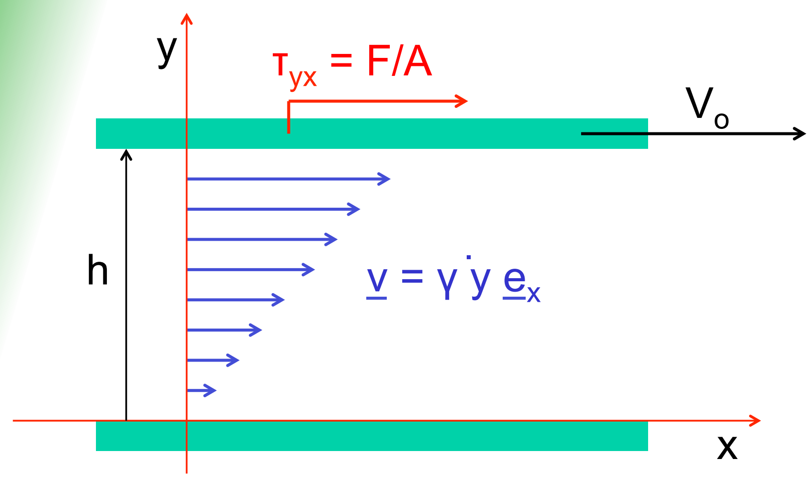
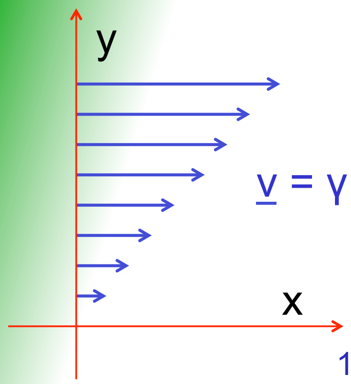
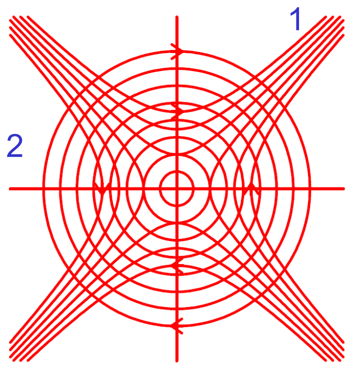
Simple shear flow



$$\dot{\gamma} = V_o / h = dv_x/dy$$



$\underline{v} = \dot{\gamma}\, y\, \underline{e}_x$



1 extension
2 rotation

$\underline{v}^{[1]} = \frac{1}{2} \dot{\gamma} (y\, \underline{e}_x + x\, \underline{e}_y)$

$\underline{v}^{[2]} = \frac{1}{2} \dot{\gamma} (y\, \underline{e}_x - x\, \underline{e}_y)$

$\underline{v} = \underline{v}^{[1]} + \underline{v}^{[2]}$

11/57

Stress tensor

in simple shear flow:

$$\underline{\underline{\tau}} = \left\{ \begin{array}{ccc} \tau_{xx} & \tau_{xy} & 0 \\ \tau_{xy} & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{array} \right\}$$

Steady state:

$$\begin{aligned} \tau_{xy} &= f(\dot{\gamma}) &= \eta(\dot{\gamma})\,\dot{\gamma} \\ \tau_{xx} - \tau_{yy} &= N_1(\dot{\gamma}) &= \Psi_1(\dot{\gamma})\,\dot{\gamma}^2 \\ \tau_{yy} - \tau_{zz} &= N_2(\dot{\gamma}) &= \Psi_2(\dot{\gamma})\,\dot{\gamma}^2 \end{aligned}$$

Newtonian liquids:
η is constant
Ψ_1 and Ψ_2 are zero

12/57

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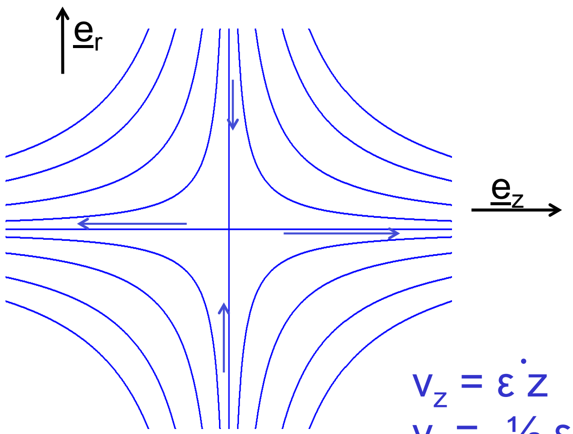
Uniaxial elongation



$v_z = \dot{\varepsilon}\, z$

$v_r = -\tfrac{1}{2}\, \dot{\varepsilon}\, r$

However, it is impossible to create
a steady extensional flow.

13/57

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About names, symbols and units

stress:	τ, σ	[Pa]
shear:	γ	[-]
shear rate:	$\dot{\gamma}$	[1/s]
strain:	ε	[-]
strain rate:	$\dot{\varepsilon}$	[1/s]
shear modulus:	G	[Pa]
viscosity:	η	[Pa s]

14/57

Flow curves of
non-Newtonian liquids

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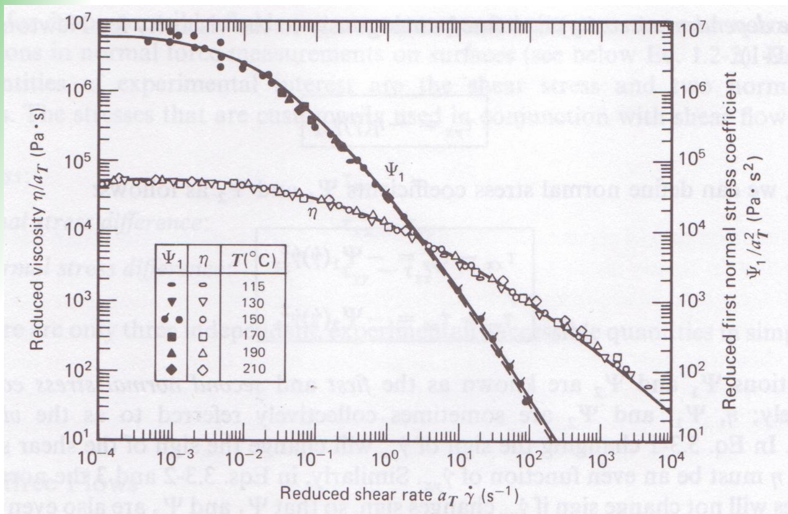

shear thinning polymer melts

shear thinning viscosity curve

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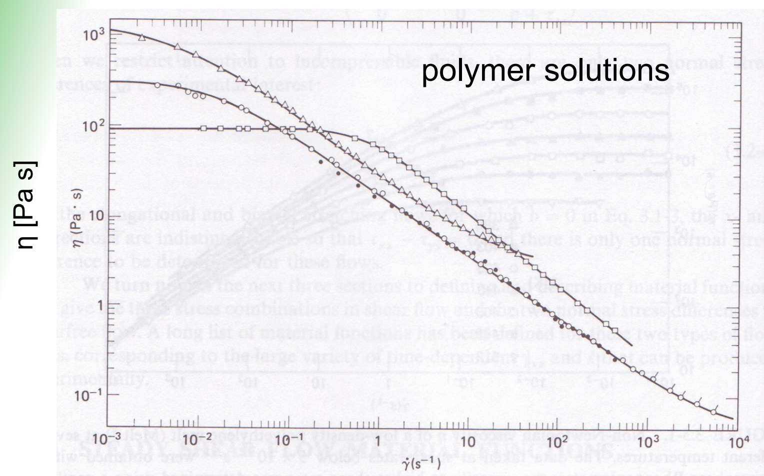

R.B. Bird et al.: Dynamics of polymeric liquids, 1987

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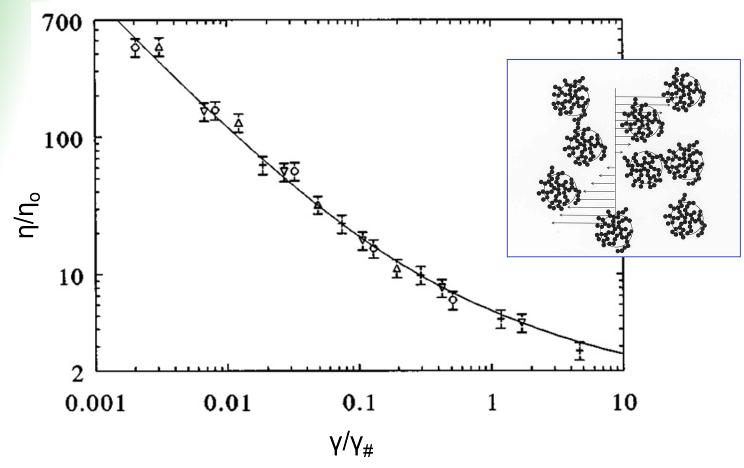
plastic behavior



Wolters et al. 1996

17/57

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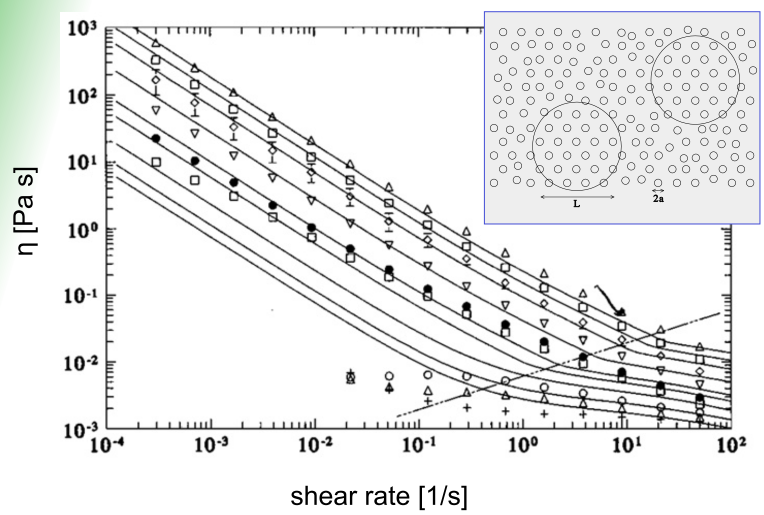
plastic behavior



van der Vorst et al., 1997

18/57

Flow behavior

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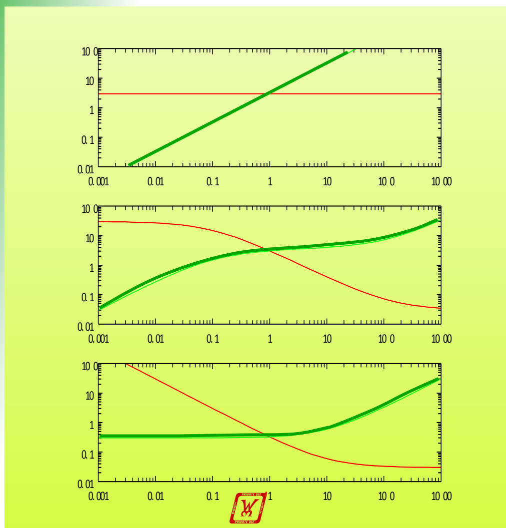
green: shear stress red: viscosity



Newtonian

$\square = \square_o \, \square'$

Shear thinning

$\square = (c\,\square'^{\,n})\;\square'$ (power law)

Plastic

$\square = \square_o + \square_o \, \square'$

19/57

non-Newtonian phenomena

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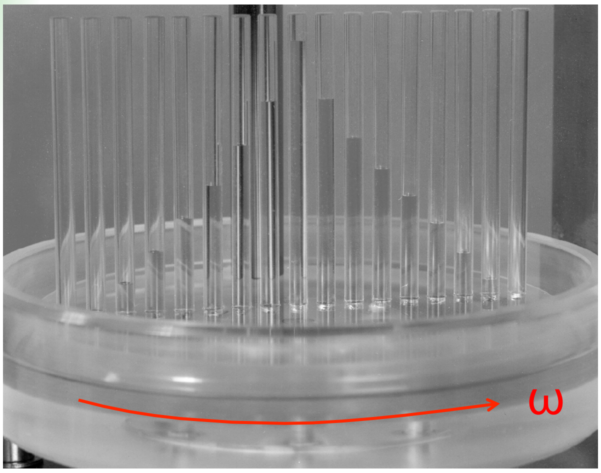
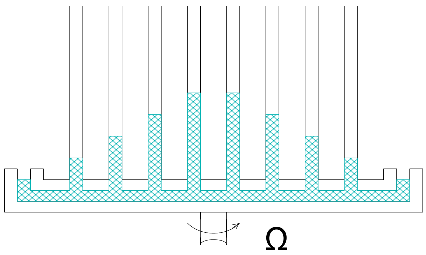


Normal stesses in a PMMA solution

20/57

Normal stresses



Due to the rotating lower disk, a shear flow exists between the disks. In case of visco-elastic fluids, this gives rise to normal stress differences.

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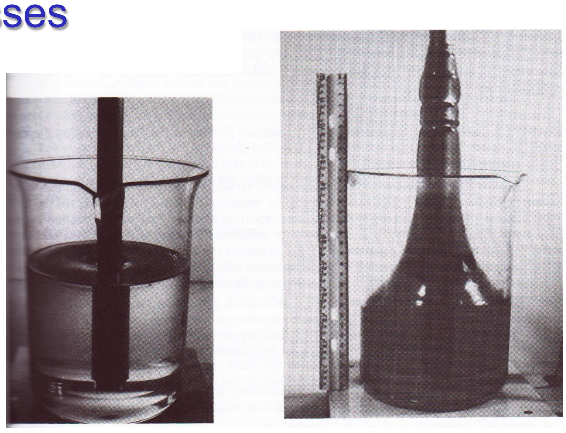
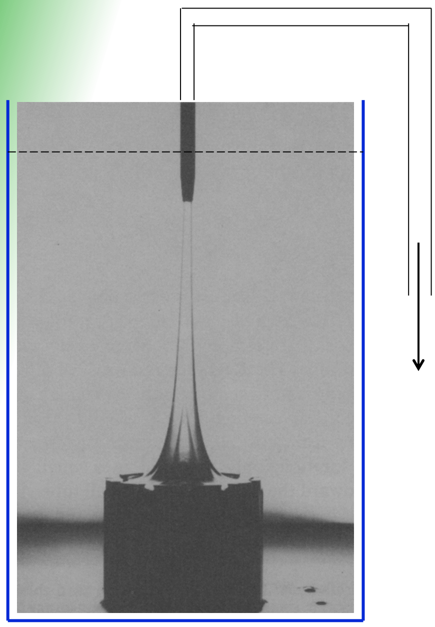
Rod climbing due to normal stresses



Newtonian visco-elastic

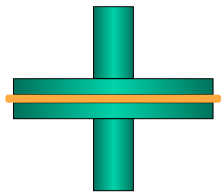
Dough for bread baking, shows rod climbing during its preparation.



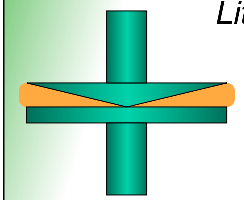
Another visco-elastic effect: the tubeless siphon

Rheometry

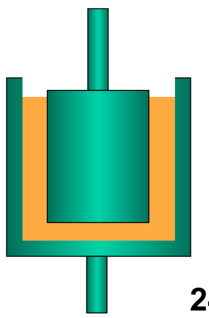
Geometries for nearly simple shear flow



- Plate-plate
  Shear rate not constant
  Little sample needed



- Cone-plate
  Shear rate constant
  Little sample needed



- Couette geometry
  Shear rate nearly constant
  More sample needed
  Higher sensitivity

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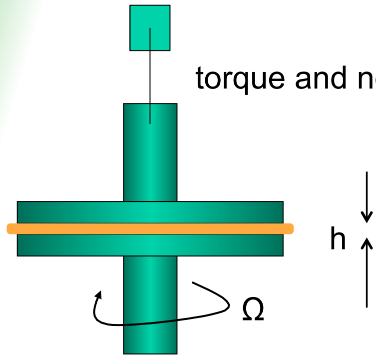
plate-plate geometry



shear rate: $\dot{\gamma}(r) = \Omega\, r/h$
torque: $M = 2\pi \int r^2\, \tau(r)\, dr$

Can be used for normal force measurements

25/57

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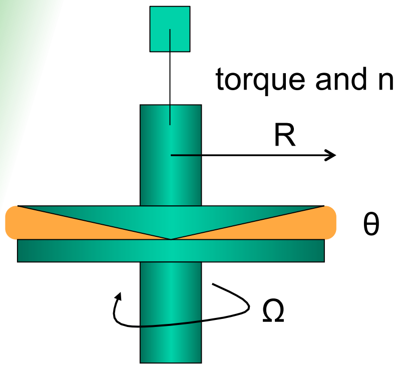
cone-plate geometry

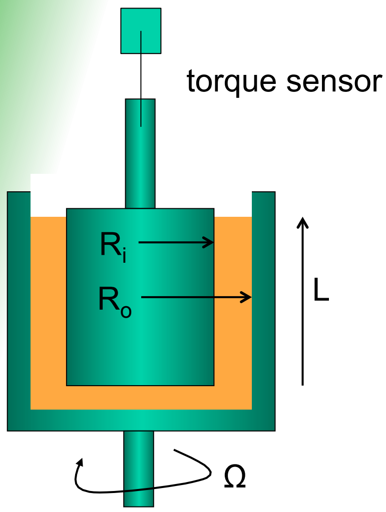


shear rate: $\dot{\gamma}(r) = \Omega/\theta$
torque: $M = 2\pi/3\, R^3\, \tau$

Can be used for normal force measurements

26/57

Couette geometry



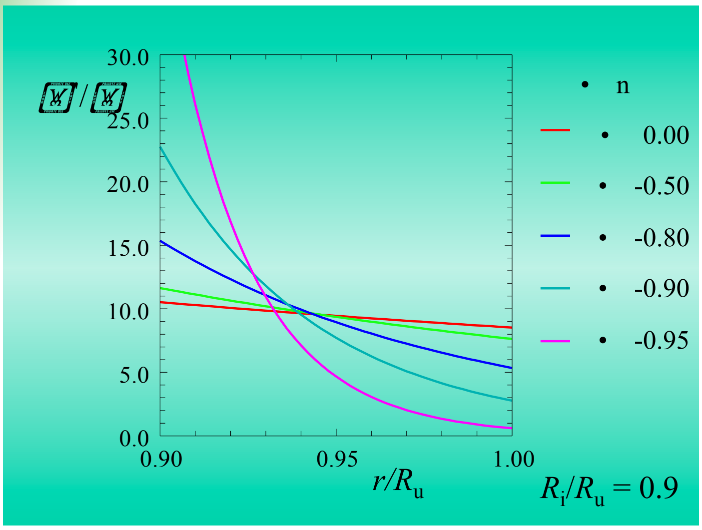
shear rate:
$\dot{\gamma}(r) \approx \frac{1}{2}\Omega(R_o+R_i)/(R_o-R_i)$

torque:
$M = 2\pi r^2 L\tau(r)$

end effects cause trouble !!

Shear rate in Couette for a power law fluid with index n

$\tau = (c\,\dot{\gamma}^{n})\,\dot{\gamma}$



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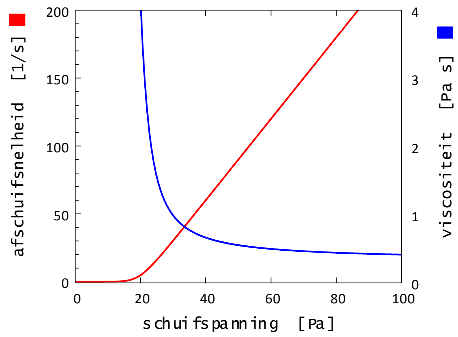
"controled shear rate" :
shear rate is applied
resulting stress is measured.

"controled stress" :
torque (shear stress) is applied
resulting shear rate
is measured.

Useful in case of
yield measurements.



29/57

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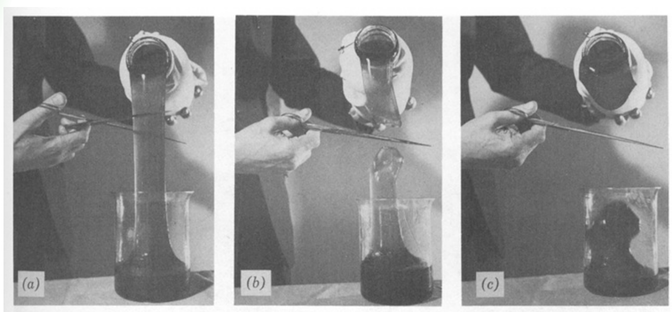
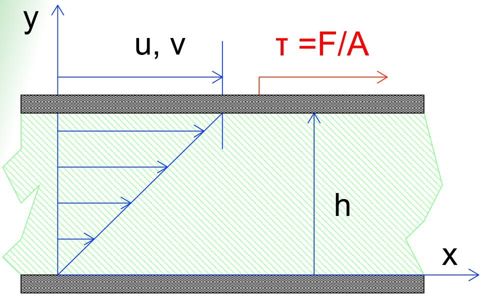
Linear Visco-elasticity



30/57

Elasticity and viscosity



$\gamma = u/h, \quad \gamma = \dot{v}/h$

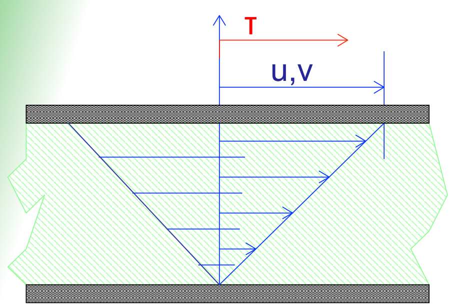
Ideal elastic Hookean behavior

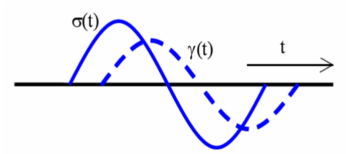
$F = G\,(A/h)\,u \qquad \tau = G\gamma$

Ideal viscous Newtonian behavior

$F = \eta\,(A/h)\,v \qquad \tau = \eta\gamma$.

Visco-elastic measurements:
reveal important time scales.





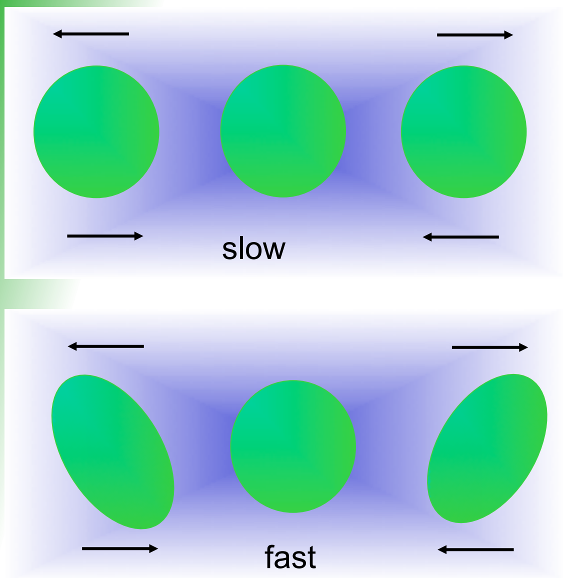
But how?

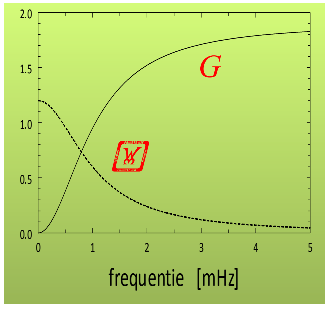
$\gamma = u/h, \quad \gamma = \dot{v}/h$

If you aply $\quad \gamma = \gamma_o \cos(\omega t)$

you measure $\quad \tau = \tau_o \cos(\omega t + \varphi)$

Emulsion droplet





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Stress is a functional of the shear history.
For small shear this functional is linear:

$$\tau(t) = \int_0^\infty G(t')\,\dot{\gamma}(t-t')\,dt'$$

Relaxation function

Or equivalently for small stresses:
shear is a linear functional of the stress history:

$$\gamma(t) = \int_0^\infty J(t')\,\dot{\tau}(t-t')\,dt'$$

Retardation function

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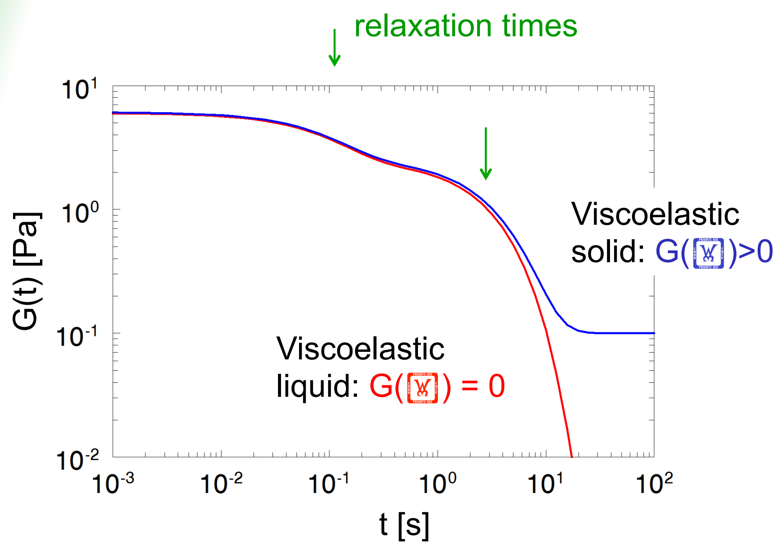
G(t): relaxation function



35/57

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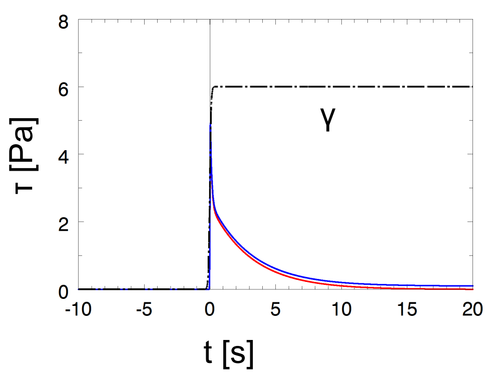
How to measure the relaxation function G(t)?

1: step response: $\dot{\gamma}(t) = \delta(t)$ (γ is a step)

$$\tau(t) = \int_0^\infty G(t')\,\delta(t-t')\,dt' = G(t)$$



36/57

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2: harmonic driving:

$$\gamma(t) = \gamma_0 \sin\omega t \qquad \dot\gamma(t) = \omega\gamma_0 \cos\omega t$$

$$\begin{aligned}
\tau(t) &= \gamma_0 \int_0^\infty \omega\, G(t') \cos(\omega t - \omega t')\, dt' \\
&= \gamma_0 \int_0^\infty \omega\, G(t') \sin\omega t'\, dt' \sin\omega t + \gamma_0 \int_0^\infty \omega\, G(t') \cos\omega t'\, dt' \cos\omega t
\end{aligned}$$

$$G'(\omega) = \int_0^\infty \omega\, G(t) \sin\omega t\, dt = \omega\, \eta''(\omega)$$ storage modulus

$$G''(\omega) = \int_0^\infty \omega\, G(t) \cos\omega t\, dt = \omega\, \eta'(\omega)$$ loss modulus

$$\tau(t) = G'(\omega)\,\gamma(t) + \frac{G''(\omega)}{\omega}\,\dot\gamma(t)$$

37/57

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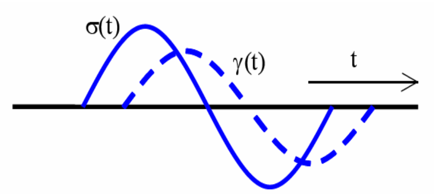
harmonic shear experiment

$$\gamma(t) = \gamma_0 \sin(\omega t) \qquad \sigma(t) = \sigma_0 \sin(\omega t + \varphi)$$



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

$$\begin{aligned}
\sigma_0 \cos\varphi &= G'\gamma_0 \\
\sigma_0 \sin\varphi &= G''\gamma_0
\end{aligned}$$

38/57

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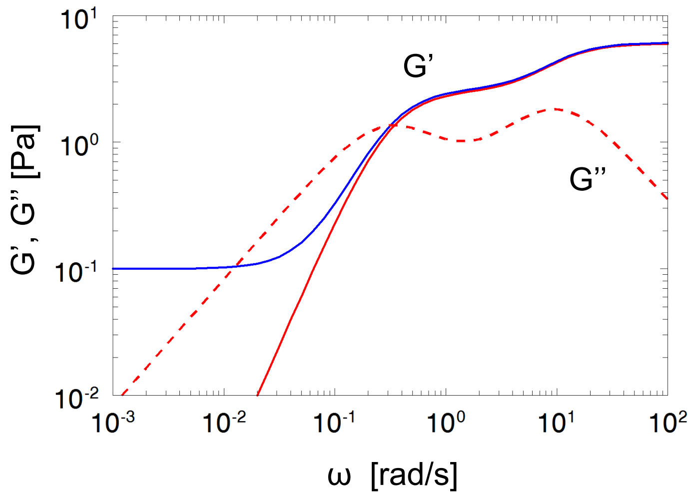

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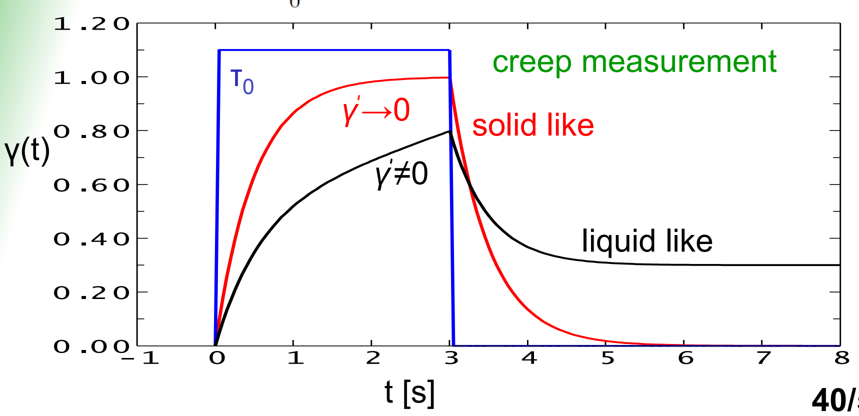
How to measure the retardation function J(t)?

step response: $\dot{\tau}(t-t') = \tau_0\,\delta(t-t')$ (τ is a step)

$$\gamma(t) = \tau_0 \int_0^\infty J(t')\,\delta(t-t')\,dt' = \tau_0\,J(t)$$



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Relation between G(t) and J(t)

$$\tau(t) = \int_0^\infty G(t')\,\dot\gamma(t-t')\,dt' \qquad \gamma(t) = \int_0^\infty J(t')\,\dot\tau(t-t')\,dt'$$

Laplace transform

$$\hat\tau(s) = s\hat G(s)\,\hat\gamma(s) \qquad \hat\gamma(s) = s\hat J(s)\,\hat\tau(s)$$

$$s^2\,\hat G(s)\,\hat J(s) = 1$$

$$j\omega\,\hat G(j\omega) = j\omega\,\eta^\star(\omega) = G^\star(\omega) \;= G' + jG''$$

$$-j\omega\,\hat J(j\omega) = J^\star(\omega) \;= J' - jJ''$$

41/57

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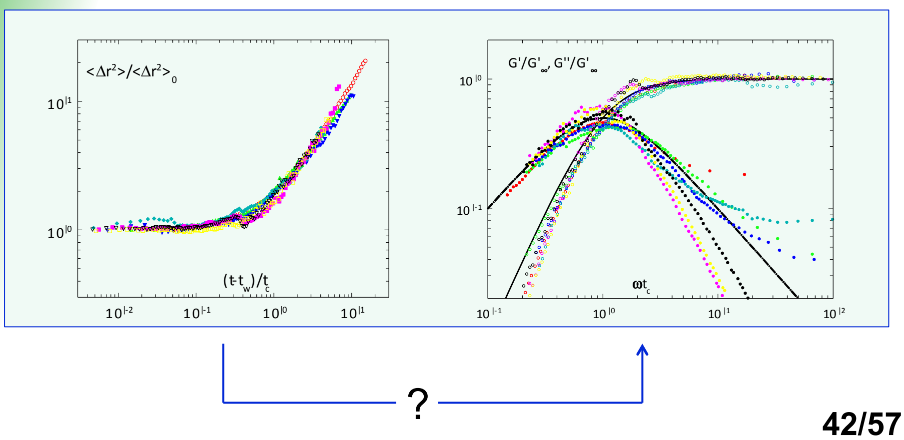
Generalized Stokes Einstein Relation and particle tracking micro-rheology



42/57

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Stokes Einstein relation

$$D = \frac{k_B T}{6\pi\eta R}$$

links a transport coefficient (η)
to an equilibrium property (D)

$$\langle \Delta x^2(t) \rangle = 2D\,t = \frac{k_B T}{3\pi R}\,\frac{t}{\eta}$$

43/57

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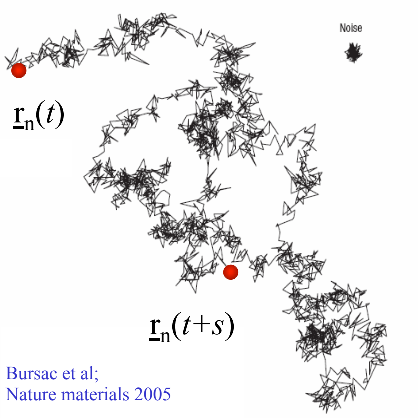
particle tracking μ-rheology



Bursac et al;
Nature materials 2005

● : fluoresent tracer
observed by CSLM
$\underline{r}_n = (x_n, y_n)$

Stokes Einstein Relation
(Newtonian fluid):

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi R}\,\frac{t}{\eta}$$

Generalized Stokes
Einstein Relation:

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi R}\,J(t)$$

< >: ensemble averaging
and/or time
averaging

44/57

Retardation function of a Newtonian fluid

$$J(t) = \frac{\gamma(t)}{\tau_0} = \frac{1}{\tau_0}\int_0^t \dot{\gamma}(t')\,dt' = \frac{t}{\eta}$$

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi R}\,\frac{t}{\eta}$$

generalization

$$\langle \Delta x^2(t) \rangle = \frac{k_B T}{3\pi R}\,J(t)$$

prove via Laplace transforms; T.G. Mason, 2000

concentrated emulsion

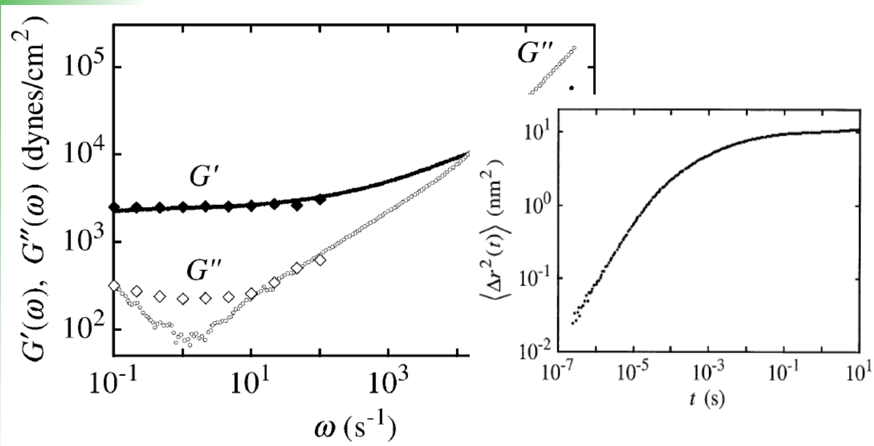


Fig. 3 The frequency-dependent storage modulus, $G'(\omega)$, (solid symbols) and loss modulus, $G''(\omega)$, (open symbols) for the concentrated emulsion obtained from $\langle \Delta r^2(t) \rangle$ in Fig. 1 using the estimates for the generalized Stokes–Einstein equation, Eqs. (10) and (11) (small circles), and by mechanical measurements (large diamonds)

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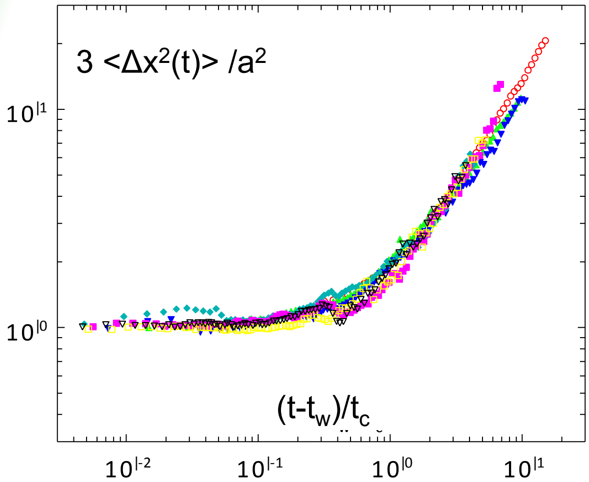
Dense suspension of polyNipam microgel particles



47/57

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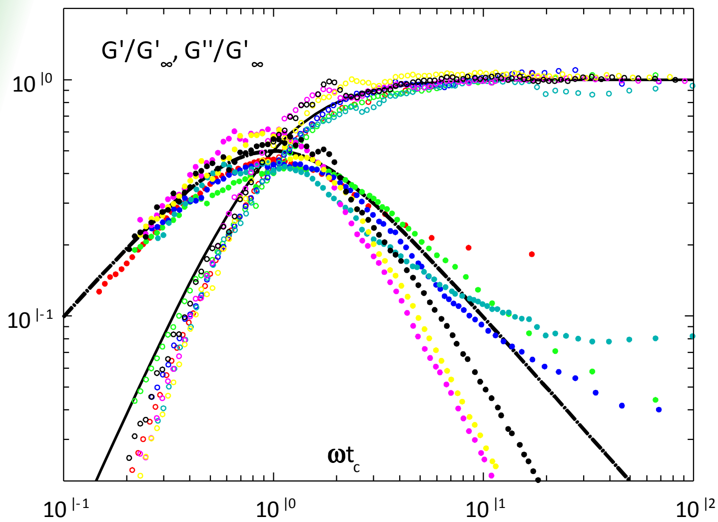
the resulting G'and G"



48/57

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Two critical assumptions:

- GSER $\langle \Delta r^2(t) \rangle = \frac{k_B T}{\pi a} J(t)$
- Complex fluid around probe can be considered as a continuum

If valid:

- You measure from equilibrium properties a non-equilibrium transport property
- There exist several approaches to calculate $J^*(\omega)$ from J(t)

49/57

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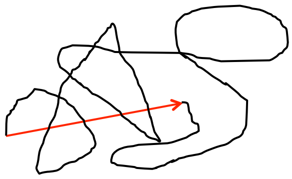
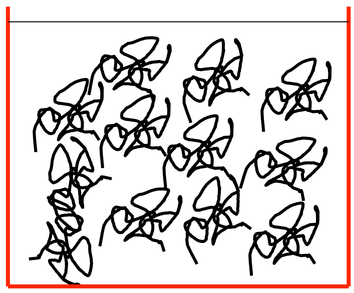
Microscopic view on the stress tensor

We consider a polymer solution





end to end vector

50/57

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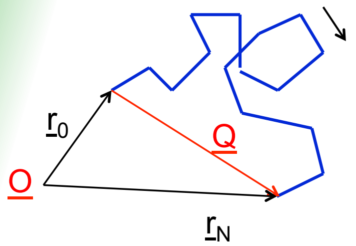
polymer as a
freely jointed chain



$\underline{u}_i = \underline{r}_i - \underline{r}_{i-1}$

N segments with length b

$$\langle \underline{u}_i \cdot \underline{u}_j \rangle = \delta_{ij}\, b^2$$

$$\underline{Q} = \sum_{i=1}^{N} \underline{u}_i$$

$$\langle Q^2 \rangle = \langle \sum_{i,j=1}^{N} \underline{u}_i \cdot \underline{u}_j \rangle = b^2 \sum_{i,j=1}^{N} \delta_{ij} = N\, b^2$$

51/57

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equipartition of energy:

$$\frac{1}{2}\kappa \langle Q^2 \rangle = \frac{3}{2} k_B T$$

spring constant of
the entropic spring:

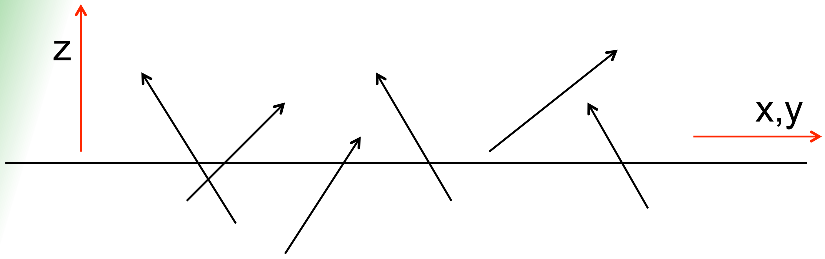
$$\kappa = \frac{3 k_B T}{N b^2}$$

Gaussian probability distribution:

$$p(\underline{Q}) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} \exp\left(\frac{-3Q^2}{2\, N b^2} \right)$$

52/57

Consider the vectors $\underline{Q}$ near imaginairy interface:



the number of vectors with value $\underline{Q}$ punching through the interface: $n(\underline{Q})Q_z d^3Q$.
so, $dT_{z\beta} = n(\underline{Q})Q_z F_\beta\, d^3Q$

$$T_{z\beta} = \int n(\underline{Q})\, Q_z F_\beta\, d^3Q$$

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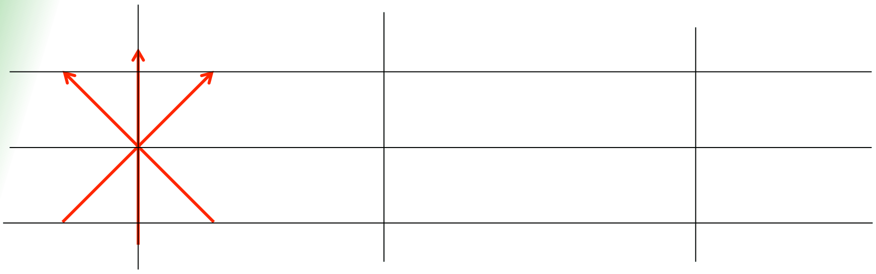
Polymer contribution
to the stress tensor:

$$\begin{aligned} T_{\alpha\beta} &= n \int p(\underline{Q})\, (Q_\alpha F_\beta)\, d^3Q \\ &= \frac{3nk_BT}{Nb^2} \int p(\underline{Q})\, (Q_\alpha Q_\beta)\, d^3Q \end{aligned}$$

Hence, the rheologist
should study
the probability distribution p($\underline{Q}$,$\dot{\gamma}$)

Probability distribution p($\underline{Q}$,$\dot{\gamma}$)

At rest this probability is fully symmetric,
so $\underline{T}$ contains only diagonal components.



rest small $\dot{\gamma}$ large $\dot{\gamma}$

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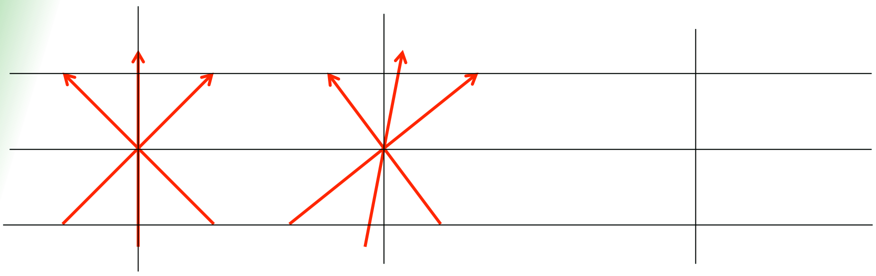
Under small shear rate the distribution
streches along the velocity direction,
leading to a linear increase of the shear stress



rest small $\dot{\gamma}$ large $\dot{\gamma}$

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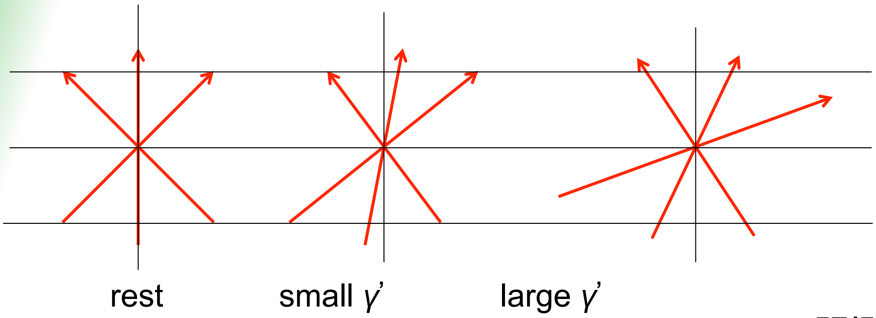
Under large shear rate the streched distribution rotates towards the velocity direction,
leading to shear thinning and a normal stress difference.



57/57