Normal stress determination

- With constant shear rate, cone-and-plate is the ideal geometry to measure normal stress differences
- r-component of the equation of motion:

$$0 = -\frac{\partial P}{\partial r} - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\sigma_{rr}) - \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sigma_{r\theta}\sin\theta) - \frac{1}{r\sin\theta}\frac{\partial\sigma_{r\phi}}{\partial\phi} + \frac{\sigma_{\theta\theta}+\sigma_{\phi\phi}}{r}$$

- rθ- and rϕ-components of stress tensors = 0, no shear force in r-direction, flow symmetrical w/r to ϕ:

$$0 = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\Pi_{rr}) + \frac{\Pi_{\theta\theta}+\Pi_{\phi\phi}}{r}$$ with $\underline{\underline{\Pi}} = P\underline{\underline{\delta}} + \underline{\underline{\sigma}}$

Normal stress determination

$$0 = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\pi_{rr}) + \frac{\pi_{\theta\theta}+\pi_{\phi\phi}}{r}$$ (previous equation)

can also be written as:

$$\frac{\partial \pi_{rr}}{\partial \ln r} = \pi_{\theta\theta} + \pi_{\phi\phi} - 2\pi_{rr}$$

We have $\pi_{rr} - \pi_{\theta\theta} = \sigma_{rr} - \sigma_{\theta\theta}$ that is a unique function of the shear rate.

Normal stress determination

The normal stress difference is therefore a constant, and:

$$\frac{\partial \Pi_{rr}}{\partial \ln r} = \frac{\partial \Pi_{\theta\theta}}{\partial \ln r} = \frac{\partial (P+\sigma_{\theta\theta})}{\partial \ln r}$$

We have the r-component of the equation of motion:

$$\frac{\partial \Pi_{rr}}{\partial \ln r} = \Pi_{\theta\theta} + \Pi_{\phi\phi} - 2\Pi_{rr}$$

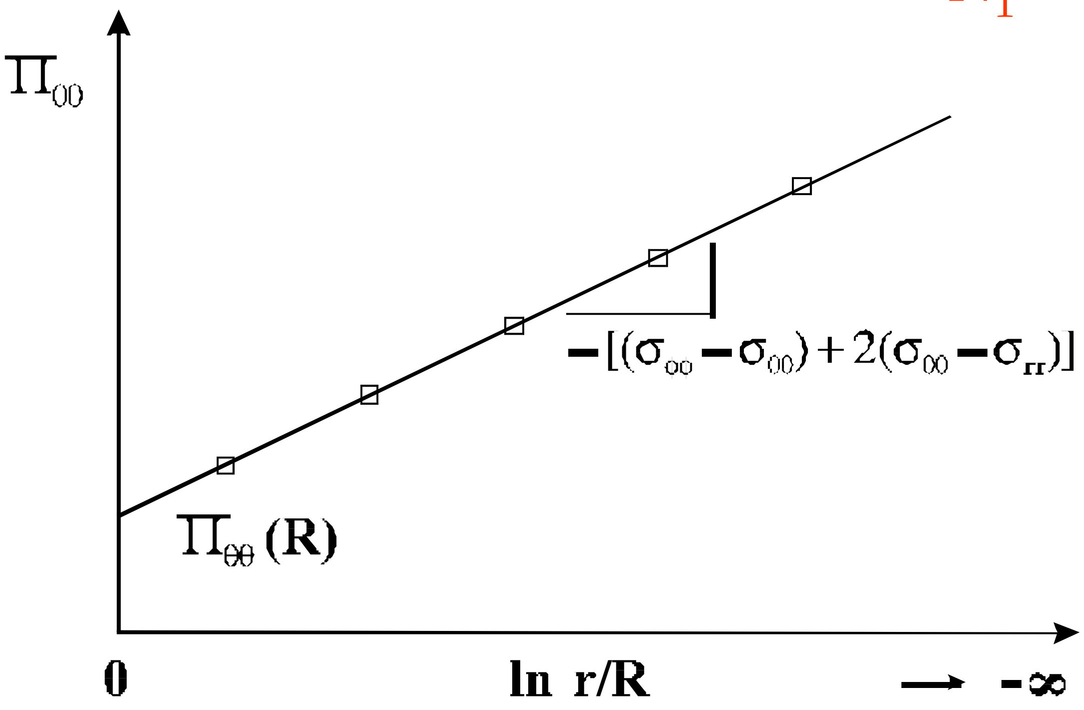
that becomes:

$$\frac{\partial}{\partial \ln r}(P+\sigma_{\theta\theta}) = (\sigma_{\phi\phi}-\sigma_{\theta\theta}) + 2(\sigma_{\theta\theta} - \sigma_{rr}) = constant$$

Normal stress determination

- The last equation is integrated from r = r to r = R:

$$\pi_{\theta\theta}(r) = (P+\sigma_{\theta\theta}) = \pi_{\theta\theta}(R) + \Big[\underbrace{(\sigma_{\phi\phi} - \sigma_{\theta\theta})}_{N_1} + 2\underbrace{(\sigma_{\theta\theta} - \sigma_{rr})}_{N_2}\Big]\ln\frac{r}{R}$$



Radial pressure profile in a cone-and-plate geometry

Normal stress determination

- Radial pressure profile is very difficult to obtain
- However, primary normal stress difference can be easily obtained from the axial force exerted on the plate:

$$F = 2\pi \int_0^R \pi_{\theta\theta}\Big|_{\theta=\pi/2} r\,dr - \pi R^2 P_a$$

- Noting that $\pi_{\theta\theta}$ is constant and using previous result for $\pi_{\theta\theta}$:

$$F = \pi R^2 \pi_{\theta\theta}(R) - \frac{1}{2}\pi R^2 \left(\pi_{\phi\phi} + \pi_{\theta\theta} - 2\pi_{rr}\right) - \pi R^2 P_a$$

Normal stress determination

- At the boundary, the internal pressure is equal to the atmospheric pressure: $\Pi_{rr}(R) = P_a$

- Therefore we can simplify the equation for F:

$$F = \pi R^2 \left[\Pi_{\theta\theta}(R) - \Pi_{rr}(R)\right] - \frac{1}{2}\pi R^2 \left[(\Pi_{\theta\theta} - \Pi_{rr}) + (\Pi_{\phi\phi} - \Pi_{rr})\right]$$

- We note: $\Pi_{\theta\theta}(R) - \Pi_{rr}(R) = \Pi_{\theta\theta} - \Pi_{rr} = \sigma_{\theta\theta} - \sigma_{rr}$;

$$\Pi_{\phi\phi} - \Pi_{rr} = (\sigma_{\phi\phi} - \sigma_{\theta\theta}) + (\sigma_{\theta\theta} - \sigma_{rr})$$

Normal stress determination

- Normal force expression reduces to:

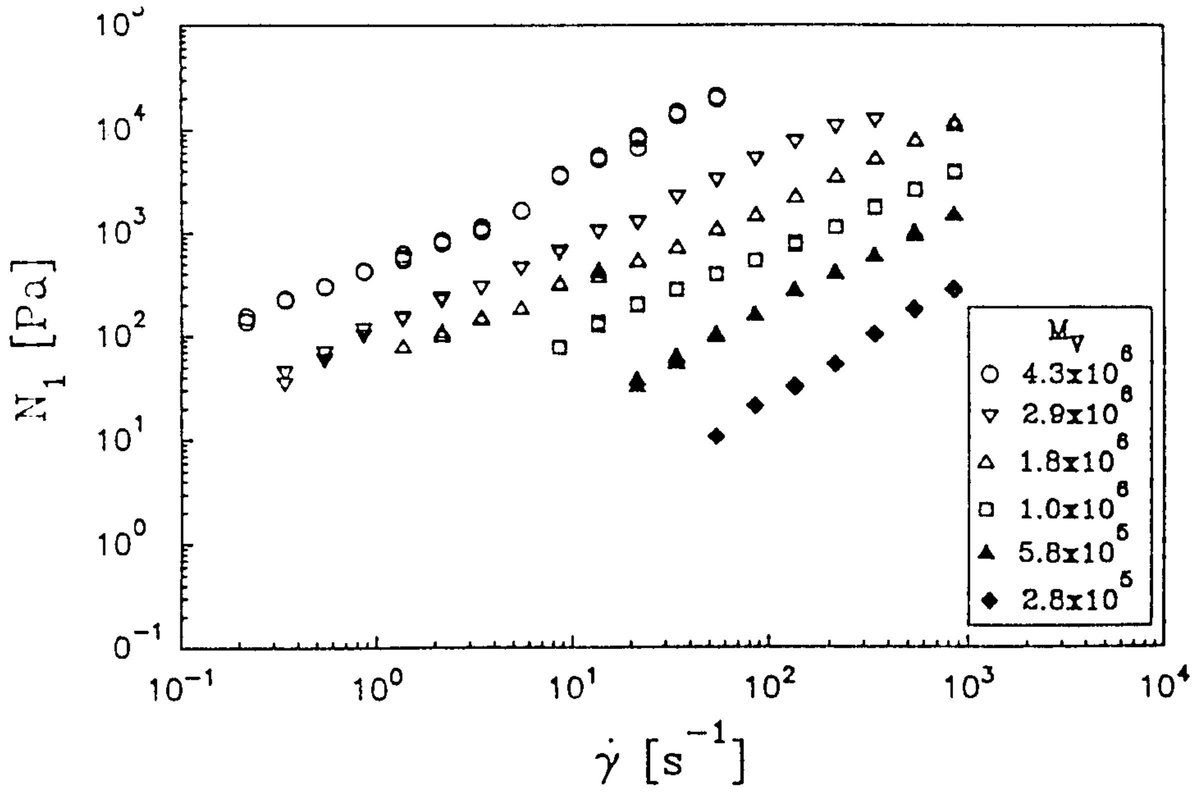
$$F = -\frac{1}{2}\pi R^2 (\sigma_{\phi\phi} - \sigma_{\theta\theta}) = -\frac{1}{2}\pi R^2 (\sigma_{11} - \sigma_{22})$$

- And primary normal stress difference is calculated from:

$$N_1 = -(\sigma_{11} - \sigma_{22}) = \frac{2F}{\pi R^2}$$

(positive quantity)

Primary normal stress difference N_1



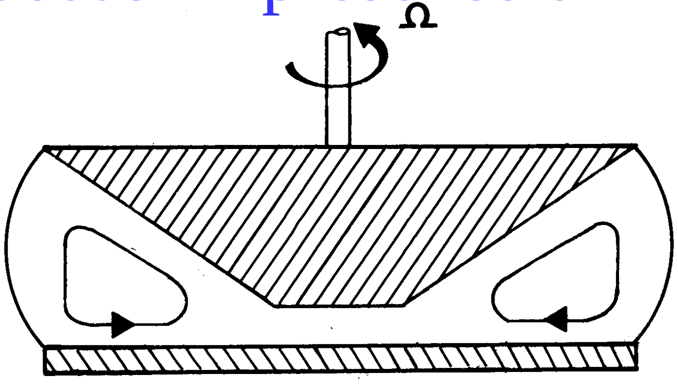
3% wt PEO solutions in water and glycerine (25°C) (Ortiz, 1992)

Inertial effects

- Linear velocity profile developed previously → neglect inertial effects

$$\frac{V_\phi}{r} = \Omega\left[\frac{(\pi/2)-\theta}{\theta_0}\right]$$

- In the presence of inertia, velocity r- and θ-components ≠ 0
- For low viscosity fluids, centrifugal force become important at high rotational speeds → presence of secondary flows

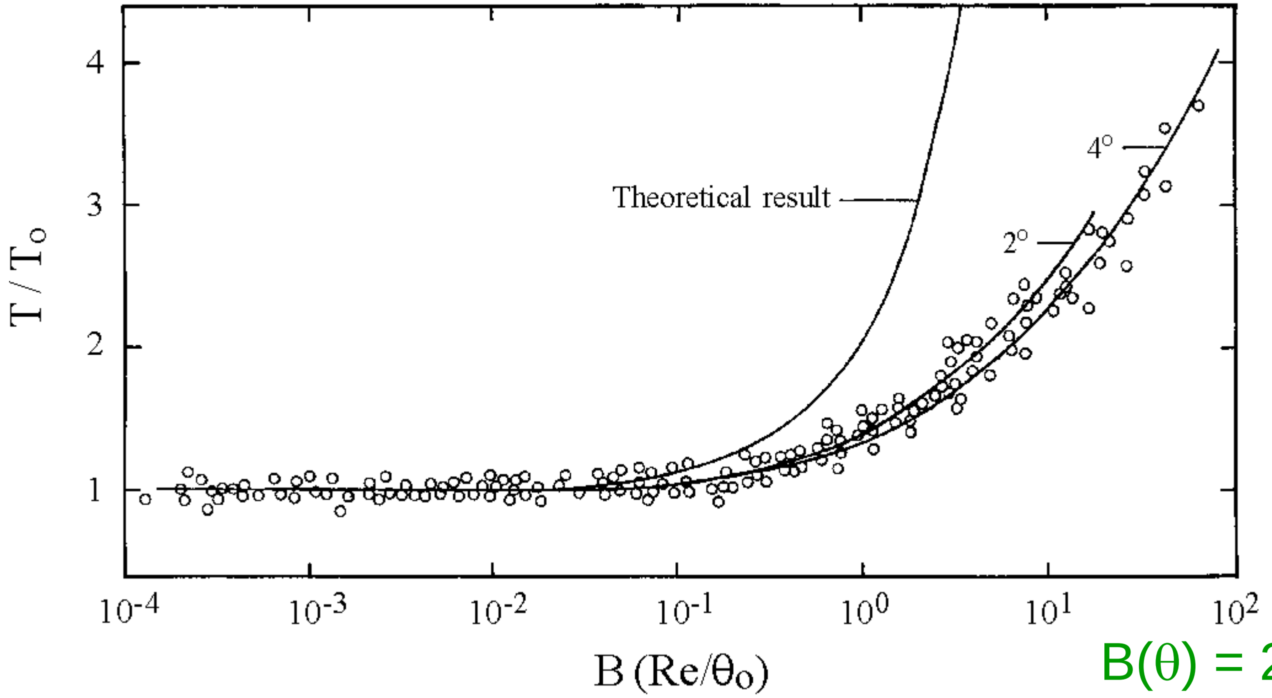


Assessment of inertial effects

- Two methods:
  - Torque correction
  - Normal force correction
- For torque correction: comparison between measured torque of low viscosity Newtonian fluids at high rotational speeds with theoretical model:

$$T = 2\pi\int_0^R \sigma_{\theta\phi} r^2 dr = \frac{2}{3}\pi R^3 \sigma_{\theta\phi}$$

Effect of inertia on torque measurements



Newtonian fluids, two different cone angles (Cheng, 1968)

$$\frac{T}{T_0} = 1 + B(\theta_0)\left(\frac{4\rho R^2 \Omega}{\mu}\right)^2$$

B(θ) = 2.505 x 10^{-10} for 2° cone

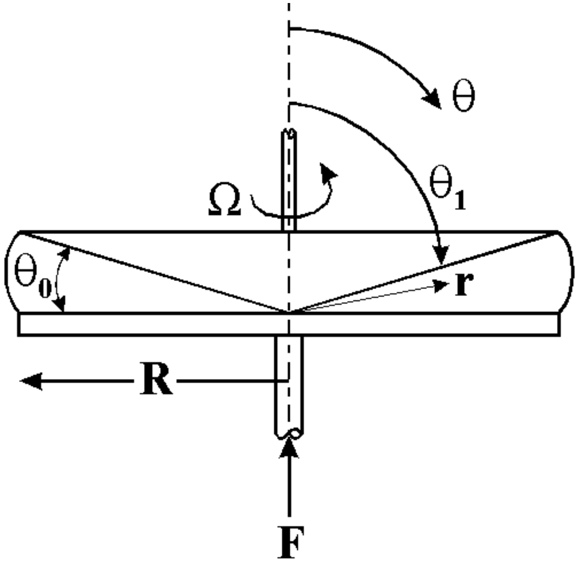
Normal force corrections

- Approximate solution for Newtonian fluids
- r-component of the equation of motion with a linear velocity profile:

$$\frac{1}{\rho}\frac{\partial P}{\partial r} = \frac{V_\phi^2}{r} = r\Omega^2\left(\frac{\Theta_0 - \Theta}{\Theta_0}\right)^2$$

- Integrating with respect to r and noting that P = P_a at r = R:

$$P - P_a = \frac{1}{2}\rho\Omega^2 R^2\left[\left(\frac{r}{R}\right)^2 - 1\right]\left(\frac{\Theta_0 - \Theta}{\Theta_0}\right)^2$$



Normal force corrections

- Previous equation averaged over θ (approximate solution since velocity profile is no longer linear):

$$\langle P \rangle - P_a = \frac{\frac{1}{2}\rho\Omega^2 R^2 \left[\left(\frac{r}{R}\right)^2 - 1 \right]}{\theta_0} \int_0^{\theta_0} \left(\frac{\theta_0 - \theta}{\theta_0} \right)^2 d\theta$$

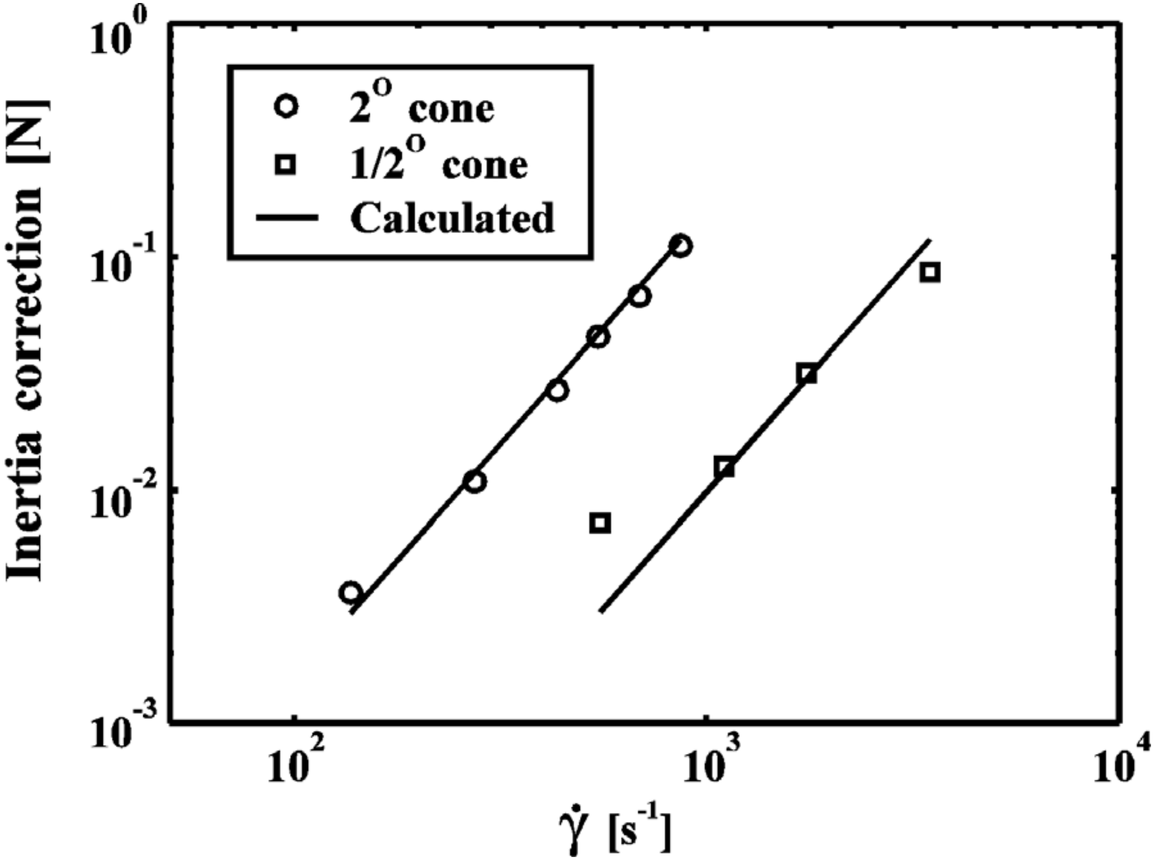
$$= \frac{1}{6}\rho\Omega^2 R^2 \left[\left(\frac{r}{R}\right)^2 - 1 \right]$$

- The normal force due to inertial effects is then:

$$F_{inertia} = 2\pi \int_0^R \left(\langle P \rangle - P_a \right) r\,dr$$

$$F_{inertia} = -\frac{1}{12}\pi\rho\Omega^2 R^4$$ (negative force)

Normal force for glycerine (25°C)



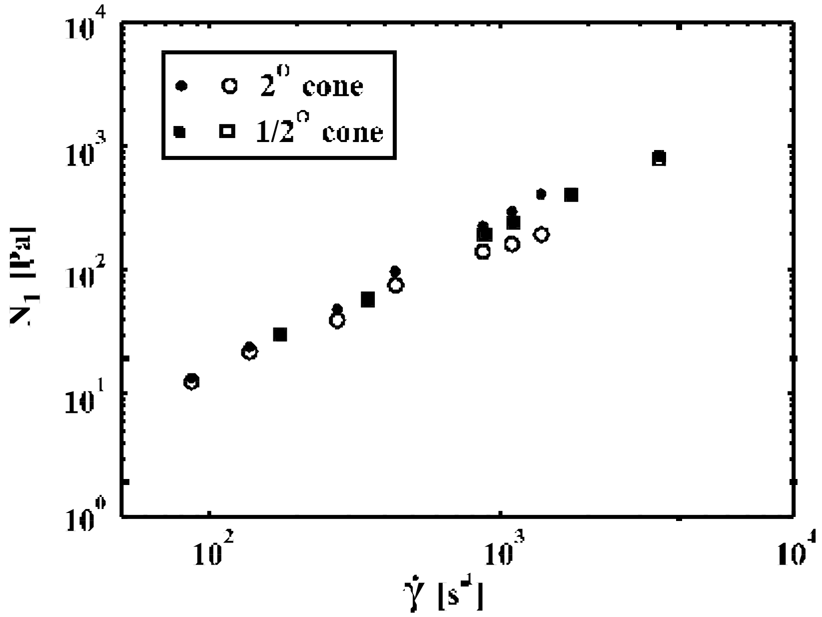
Lines are from theoretical result:

$$F_{inertia} = -\frac{1}{12}\pi\rho\Omega^2 R^4$$

Viscoelastic fluids

- Possible to use previous equation for viscoelastic fluids in the absence of other experimental evidence or viscoelastic calculations
- Equation for $F_{inertia}$ can be used to estimate corrections to add (opposite signs) to the normal force measurements

Primary normal stress difference



3% wt polyisobutylene in decalin (25°)

Open symbols: uncorrected data

Closed symbols: corrected data

- Uncorrected normal stress data show differences for the 2° cone, mostly at high shear rates (rotational speeds)

Measurements of transient viscometric functions

- Major problems with cone-and-plate geometry:
  - Not possible to generate true step changes of the speed of the rotating assembly (time t_s required)
  - Existence of a lag time (t_r) between the time of the command and the effective initiation
  - Lack of torsional and axial rigidities of the rheometer → coupling between the instrument and the fluid properties (torsional and axial response times t_t and t_a)

Measurements of transient viscometric functions

- Torsional and axial response times t_t and t_a:

$$t_t = \frac{20\pi\eta_0 R^3}{3K_t\theta_0}$$

$$t_a = \frac{6\pi\eta_0 R}{K_a\theta_0^3}$$

with K_t and K_a the torsional and axial compliances of the instrument, θ_0 the angle of the cone, R the plate radius and η_0 the viscosity of a Newtonian fluid

Criteria for transient experiments

- We define τ_n and τ_t the characteristic times of the normal force and torque responses of the fluid during transient experiments
- For a test to be valid, we should have
  - $\tau_n >> t_s$
  - $\tau_t >> t_s$
  - $\tau_n >> t_a$
  - $\tau_t >> t_a$

Criteria for transient experiments

- Approximation from convected Maxwell model (Chap. 6):

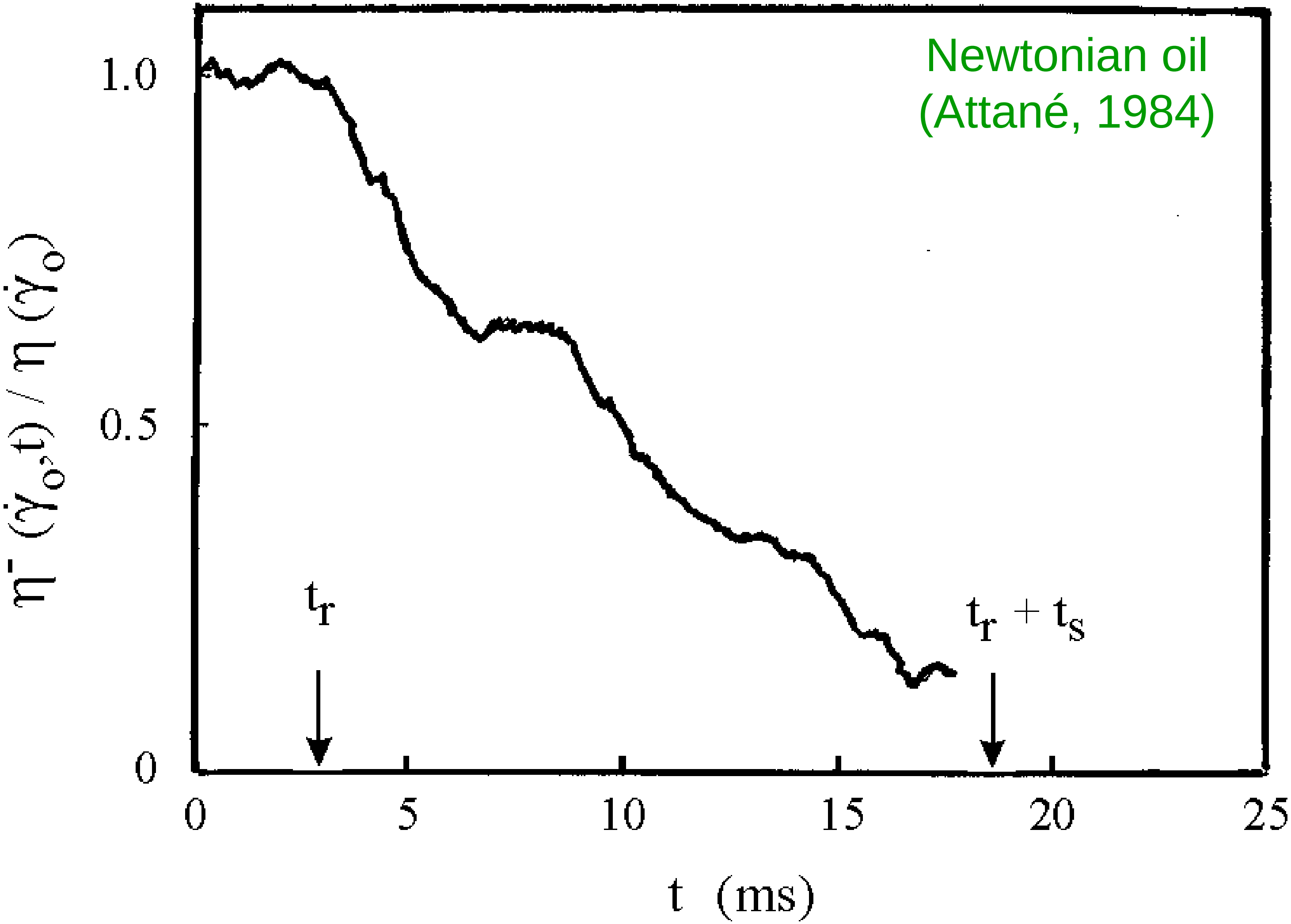
$$\tau_n = \tau_t = \lambda_w = J_e^0 \eta_0 = \frac{\psi_{10}}{2\eta_0}$$

with J_e^0: steady-state compliance, ψ_{10}: zero shear first normal stress coefficient

- The criteria become:

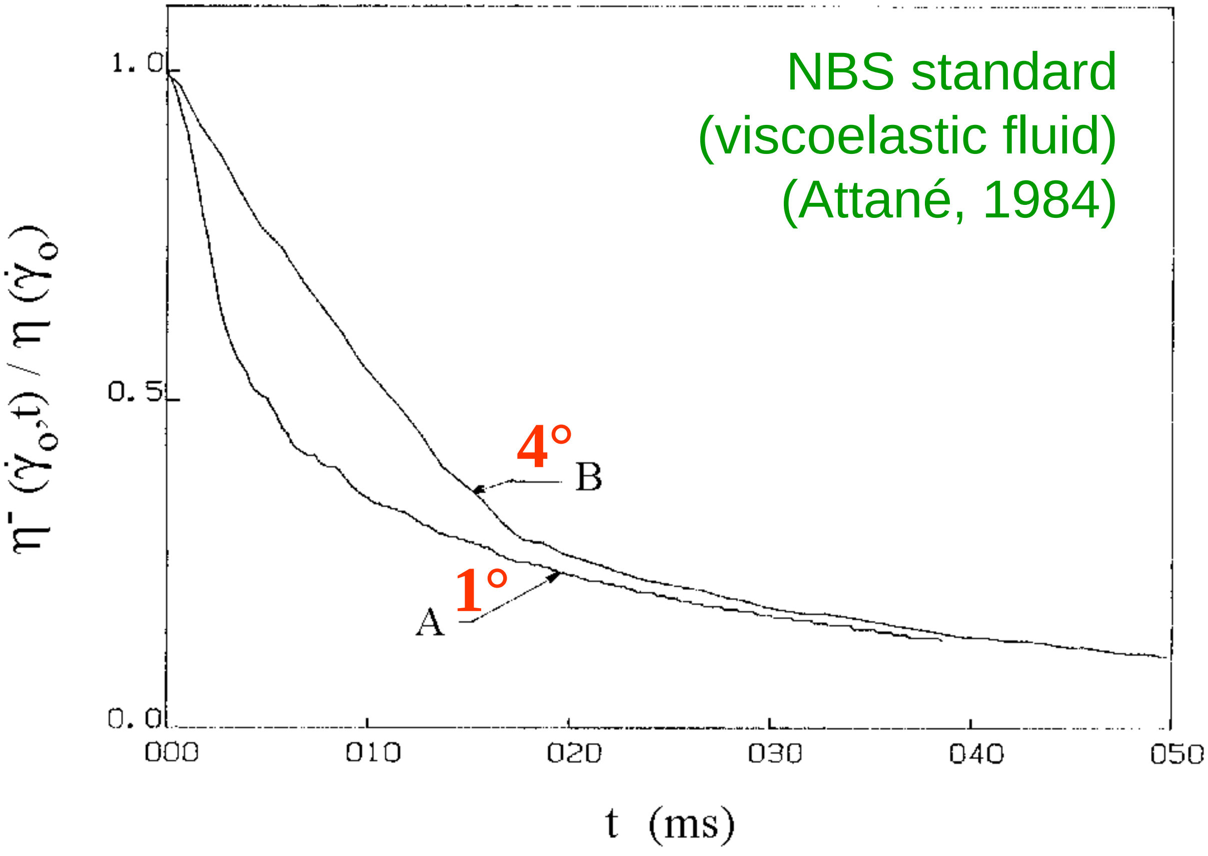
$$J_e^0 \eta_0 >> t_s, \qquad J_e^0 >> \frac{20\pi R^3}{3K_t\theta_0}, \qquad J_e^0 >> \frac{6\pi R}{K_a\theta_0^3}$$

Shear stress relaxation following cessation of steady shear (560 s^{-1})



Newtonian fluid should relax instantly
→Relaxation response of instrument (~ 16 ms)

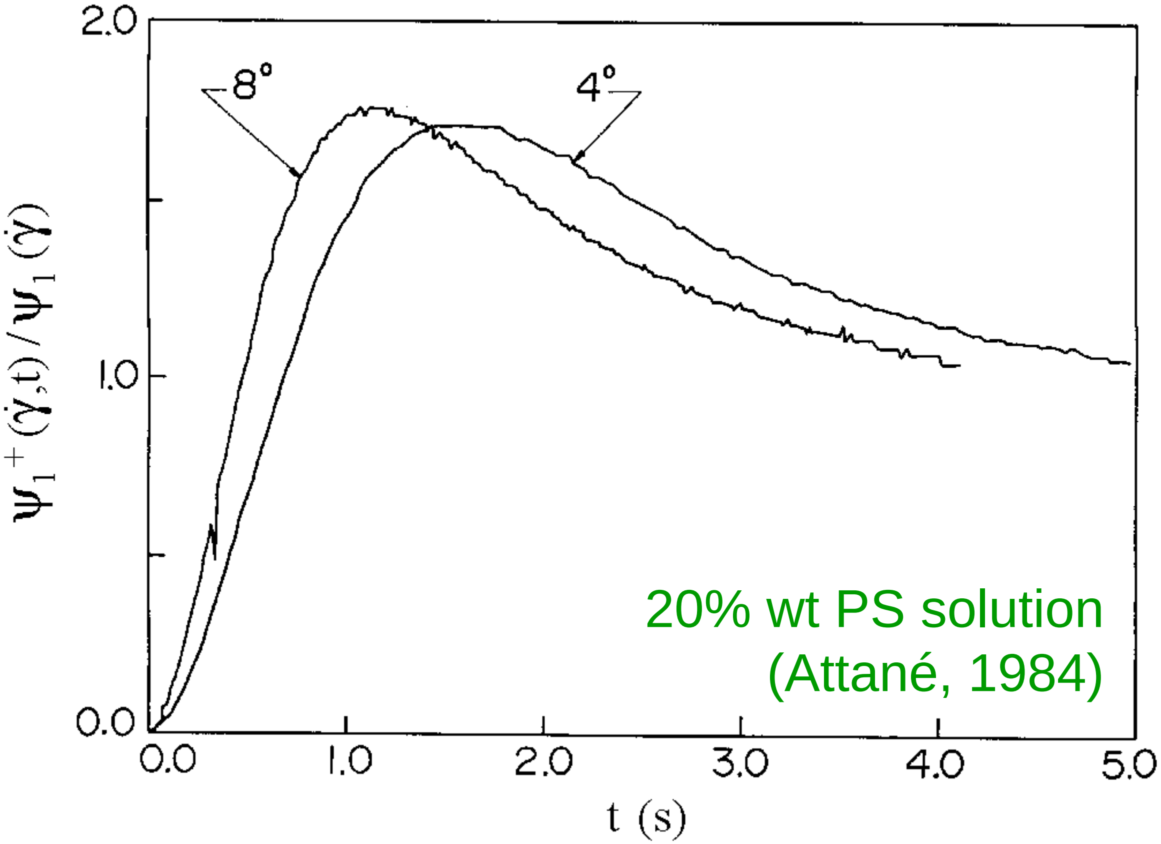
Reduced shear relaxation



For 1° cone: instrument response time (t_s) ~ 6 ms

For 4° cone: ~ 13 ms

Reduced primary normal stress growth function



Important coupling effects for the 4° cone, overshoot affected

More reliable data with 8° cone

Transient experiments with cone-and-plate geometries

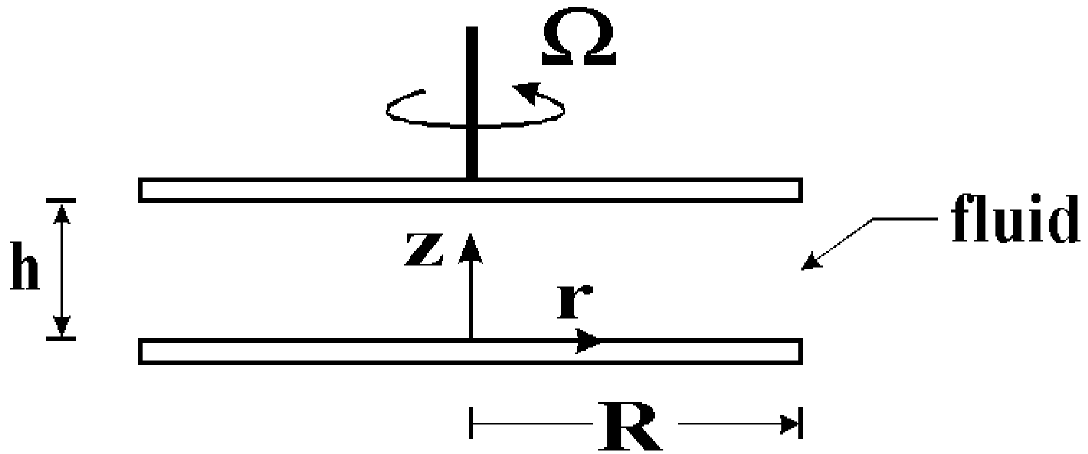
- Summary:
  - Relaxation of viscoelastic fluids with relaxation time < 0.1 s is not possible
  - For times in excess of $2t_s$, the relaxation properties should be correctly determined
  - Balance between axial and torsional instrument stiffness and sensitivity

Cone-and-plate geometries

- Sources of errors:
  - Slow secondary motion
  - Problem for less viscous flows (inertial effects)
  - Use of a cone angle too large, as basic equations are derived assuming very small angle ($< 3°$)
  - Edge fracture: flow instability at high deformation or high shear rate

3.4 Concentric disk geometry

- Frequently used for measuring rheological properties of polymer melts and multiphase polymer systems
- Consists of two parallel concentric disks of radius R separated by a constant gap h



The flow is viscometric in cylindrical coordinates

Concentric disk geometry

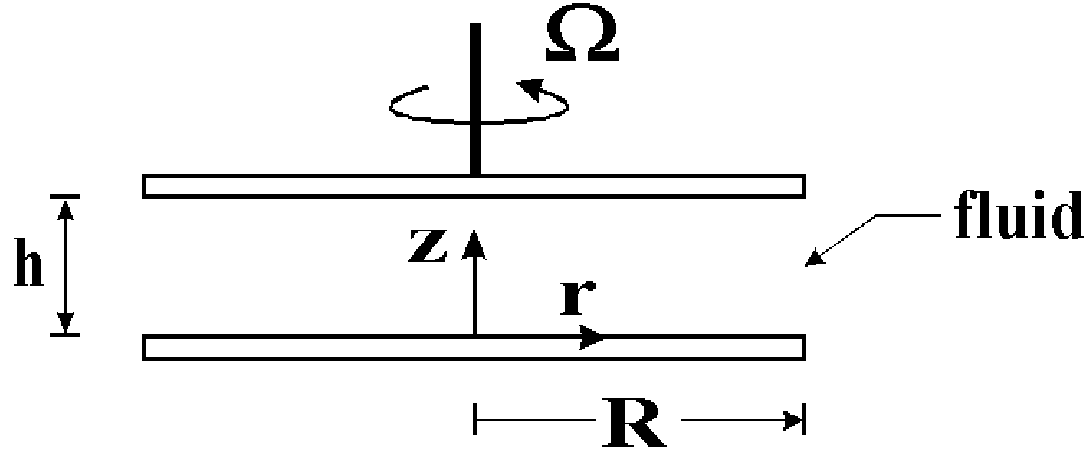
- Upper or lower plate rotates
- Torque and and normal force can be measured at either one
- Gap can be varied (1-2 mm for 25 mm disks)
- Geometry advantageous at high temperature (minimized thermal expansion effects) and for multiphase systems:

$$\frac{d_p}{h} << 1$$

(d_p = particle or domain diameter)

Concentric disk geometry

- Disadvantages
  - Flow is not homogeneous within the gap ($V_\theta = f(r,z)$)
  - Shear rate varies linearly with the radial position
  - Viscoelastic materials will not stay within the gap at high shear rates



Velocity profile and shear rate

- For a small enough gap (h/R<<1) or low rotational speed, inertia can be neglected
- For steady-state conditions:

$$V_\theta = \Omega r\left(1 - \frac{z}{h}\right)$$

$$\dot{\gamma} = \dot{\gamma}_{z\theta} = \Omega\frac{r}{h}$$

Viscosity determination

- For non-Newtonian fluids, because shear rate varies with the radial position, viscosity no longer proportional to the torque
- Rabinowitsch-type development must be used
- The torque is given by:

$$T = 2\pi \int_0^R -\sigma_{z\theta}(r)\, r^2\, dr$$

$$= 2\pi \int_0^R \frac{\eta(r)\,\Omega r^3}{h}\, dr$$

Viscosity determination

- Making a change of variable $r \rightarrow \dot{\gamma}(= \Omega r / h)$ the torque is expressed as:

$$T = 2\pi \left(\frac{h}{\Omega} \right)^3 \int_0^{\dot{\gamma}_R} \eta(\dot{\gamma}) \dot{\gamma}^3 d\dot{\gamma}$$

$$T = 2\pi \left(\frac{R}{\dot{\gamma}_R} \right)^3 \int_0^{\dot{\gamma}_R} \eta(\dot{\gamma}) \dot{\gamma}^3 d\dot{\gamma}$$

- Taking the derivative w/r to the shear rate at the wall and using Leibnitz's rule:

$$\frac{d(T/2\pi R^3)}{d\dot{\gamma}_R} = \eta(\dot{\gamma}_R) - 3\dot{\gamma}_R^{-4} \int_0^{\dot{\gamma}_R} \eta(\dot{\gamma}) \dot{\gamma}^3 d\dot{\gamma}$$

Viscosity determination

- Using the equation for the torque, and rearranging to obtain the final expression for the viscosity:

$$\eta(\dot{\gamma}_R) = \frac{T}{2\pi R^3 \dot{\gamma}_R}\left[3 + \frac{d\ln(T/2\pi R^3)}{d\ln\dot{\gamma}_R}\right]$$

- To obtain the viscosity of a non-Newtonian fluid, we must first plot ln(T) vs. ln(shear rate at the wall)
- The viscosity is then calculated using the local value of the slope

Power-law fluid

- For a power-law fluid, the torque is expressed as:

$$T = 2\pi m \int_0^R (\dot{\gamma}_{z\theta})^n r^2 dr$$

and

$$\ln T \sim n \ln \dot{\gamma}_R$$

- The viscosity is given by: $\eta(\dot{\gamma}_R) = \frac{T}{2\pi R^3 \dot{\gamma}_R}\left[3 + n\right]$

- Most commercial software packages assume n = 1

if n = 0.3, error of 22%

Normal stress difference determination

- Neglecting inertial forces, the shear rate is given by:

$$\dot{\gamma} = \dot{\gamma}_{z\theta} = \Omega \frac{r}{h}$$

- We assume that the only non-zero shear component is $\sigma_{z\theta}(r) = \sigma_{\theta z}(r)$
- r-component of the equation of motion:

$$0 = -\frac{\partial P}{\partial r} - \left(\frac{1}{r} \frac{\partial}{\partial r} (r\sigma_{rr}) - \frac{\sigma_{\theta\theta}}{r} \right)$$

Normal stress difference determination

- The equation can be written as:

$$\frac{\partial}{\partial r}(P+\sigma_{rr}) = -\frac{(\sigma_{rr}-\sigma_{\theta\theta})}{r} = \frac{(\sigma_{\theta\theta}-\sigma_{zz})}{r} + \frac{(\sigma_{zz}-\sigma_{rr})}{r}$$

$$= -\frac{(\psi_1+\psi_2)}{r}\dot{\gamma}^2$$

- Normal stresses can not be measured in the radial direction, therefore we replace:

$$\sigma_{rr} = \psi_2\dot{\gamma}^2 + \sigma_{zz}$$

Normal stress difference determination

- The previous equation

$$\frac{\partial}{\partial r}(P + \sigma_{rr}) = -\frac{(\sigma_{rr} - \sigma_{\theta\theta})}{r} = \frac{(\sigma_{\theta\theta} - \sigma_{zz})}{r} + \frac{(\sigma_{zz} - \sigma_{rr})}{r}$$

$$= -\frac{(\psi_1 + \psi_2)}{r}\dot{\gamma}^2$$

is integrated as followed:

$$(P + \psi_2\dot{\gamma}^2 + \sigma_{zz})\Big|_0^r = -\int_0^r \frac{\psi_1 + \psi_2}{r}\dot{\gamma}^2 dr$$

Normal stress difference determination

- Written in terms of the total pressure:

$$\pi_{zz}(r) - \pi_{zz}(0) = -\psi_2\dot{\gamma}^2 - \int_0^r \frac{\psi_1 + \psi_2}{r}\dot{\gamma}^2\,dr$$

- However we need a more useful expression in terms of the measurable normal force. We start with:

$$\pi_{zz}(r) - \pi_{zz}(R) = -\psi_2\dot{\gamma}^2(r) + \psi_2\dot{\gamma}^2(R) - \int_R^r \frac{\psi_1 + \psi_2}{r}\dot{\gamma}^2\,dr$$

Normal stress difference determination

- From the definition of the secondary normal stress coefficient:

$$\psi_2 \dot{\gamma}^2 (R) = -\left[\pi_{zz}(R) - \pi_{rr}(R)\right]$$

- At the boundary, the internal pressure is equal to the outside (atmospheric) pressure:

$$\pi_{rr}(R) = P_a$$

Normal stress difference determination

- Combining previous results:

$$\Pi_{zz}(r) = -\Psi_2\dot{\gamma}^2(r) + P_a - \int_R^r \frac{\Psi_1 + \Psi_2}{r}\dot{\gamma}^2 dr$$

- With the change of variable

$$r \rightarrow \dot{\gamma}(=\Omega r / h)$$

the equation is rewritten:

$$\Pi_{zz}(r) = -\Psi_2\dot{\gamma}^2(r) + P_a + \int_{\dot{\gamma}}^{\dot{\gamma}_R} (\Psi_1 + \Psi_2)\dot{\gamma}\, d\dot{\gamma}$$

Normal stress difference determination

- The net axial force on the plate is:

$$F = 2\pi\int_0^R \left[\Pi_{zz}(r) - P_a\right] r\,dr$$
$$= -2\pi\int_0^R \psi_2\,\dot{\gamma}^2(r)\,r\,dr + 2\pi\int_0^R\int_{\dot{\gamma}}^{\dot{\gamma}_R}(\psi_1+\psi_2)\,\dot{\gamma}\,d\dot{\gamma}\,r\,dr$$

- Again a change of variable: $r \rightarrow \dot{\gamma}(= \Omega r / h)$

to obtain:

$$F = \frac{2\pi R^2}{\dot{\gamma}_R^2}\left(-\int_0^{\dot{\gamma}_R}\psi_2\,\dot{\gamma}^3\,d\dot{\gamma} + \int_0^{\dot{\gamma}_R}\int_{\dot{\gamma}}^{\dot{\gamma}_R}(\psi_1+\psi_2)(\xi)\,\xi\,d\xi\,\dot{\gamma}\,d\dot{\gamma}\right)$$

Normal stress difference determination

- Changing the order of integration (in the double integral):

(ξ is an integration variable)

$$F = \frac{2\pi R^2}{\dot{\gamma}_R^2}\left(-\int_0^{\dot{\gamma}_R}\psi_2\,\dot{\gamma}^3 d\dot{\gamma} + \int_0^{\dot{\gamma}_R}\int_0^{\xi}(\psi_1+\psi_2)\,(\xi)\,\dot{\gamma}\, d\dot{\gamma}\,\xi\, d\xi\right)$$

$$= \frac{2\pi R^2}{\dot{\gamma}_R^2}\left(-\int_0^{\dot{\gamma}_R}\psi_2\,\dot{\gamma}^3 d\dot{\gamma} + \frac{1}{2}\int_0^{\dot{\gamma}_R}(\psi_1+\psi_2)\,\dot{\gamma}^3 d\dot{\gamma}\right)$$

$$= \frac{\pi R^2}{\dot{\gamma}_R^2}\left(\int_0^{\dot{\gamma}_R}(\psi_1-\psi_2)\,\dot{\gamma}^3 d\dot{\gamma}\right)$$

Normal stress difference determination

- Finally we take the derivative with respect to $\dot{\gamma}$:

$$\frac{d}{d\dot{\gamma}_R}(F\dot{\gamma}_R^2) = \pi R^2 (\psi_1 - \psi_2)\dot{\gamma}_R^3$$

$$= \dot{\gamma}_R F \frac{d\ln F}{d\ln\dot{\gamma}_R} + 2\dot{\gamma}_R F$$

$$= \pi R^2 (N_1 - N_2)\dot{\gamma}_R$$

and obtain the difference between the normal stresses:

$$N_1(\dot{\gamma}_R) - N_2(\dot{\gamma}_R) = \frac{2F}{\pi R^2}\left(1 + \frac{1}{2}\frac{d\ln F}{d\ln\dot{\gamma}_R}\right)$$

Normal stress difference determination

- For negligible N_2 (Weissenberg hypothesis):

$$N_1(\dot{\gamma}_R) = \psi_1(\dot{\gamma}_R)\dot{\gamma}_R^2 \approx \frac{2F}{\pi R^2}\left(1 + \frac{1}{2}\frac{d\ln F}{d\ln \dot{\gamma}_R}\right)$$

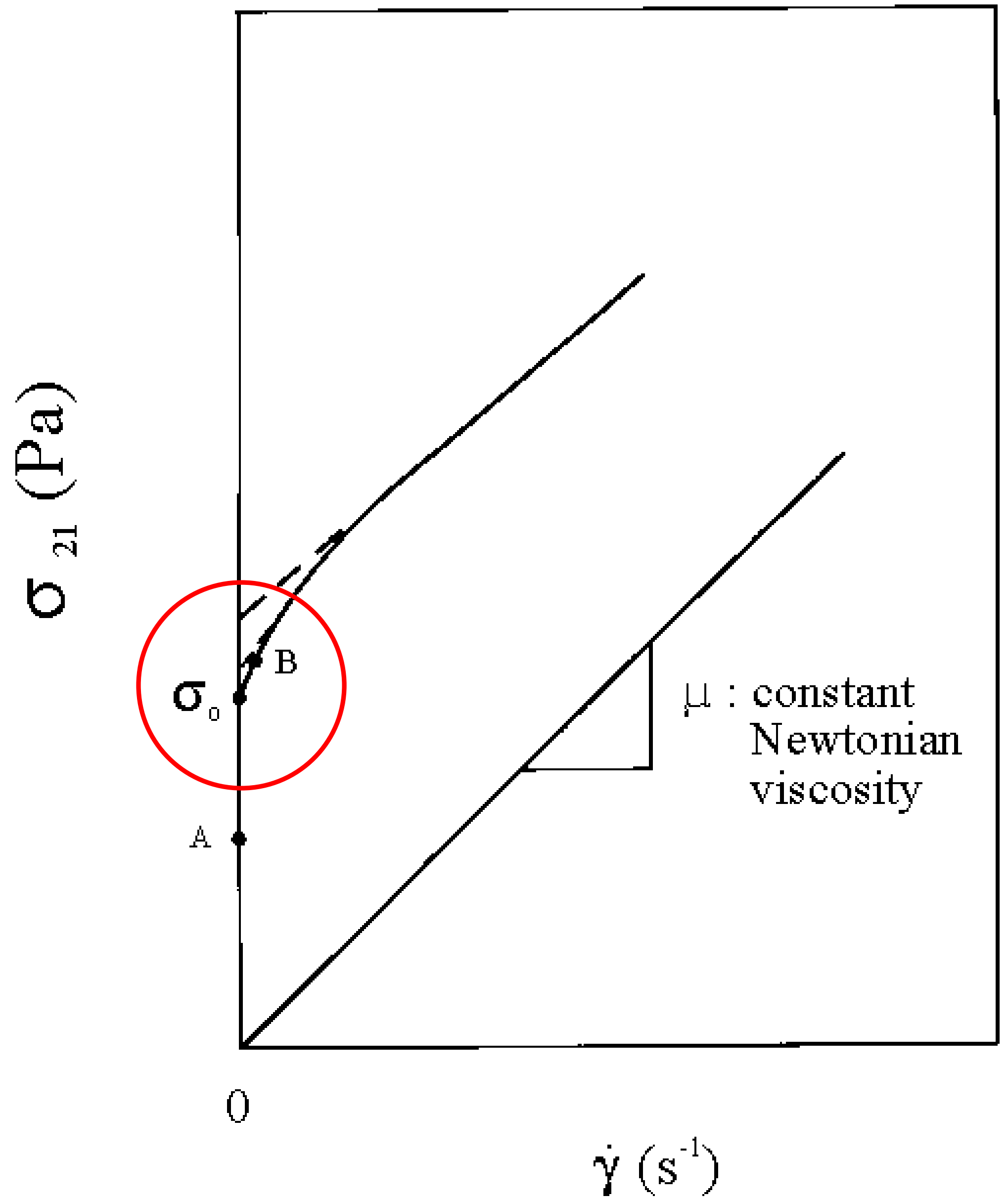
in which the derivative is determined from the slope of ln(F) vs. ln(shear rate at the wall) (~ Ω)

Concentric disk geometry

- Mostly used to measure linear viscoelastic properties (Chap. 5)
- Sources of errors:
  - Instrument compliance (as for cone-and-plate)
  - Shear rate function of radial position often not corrected

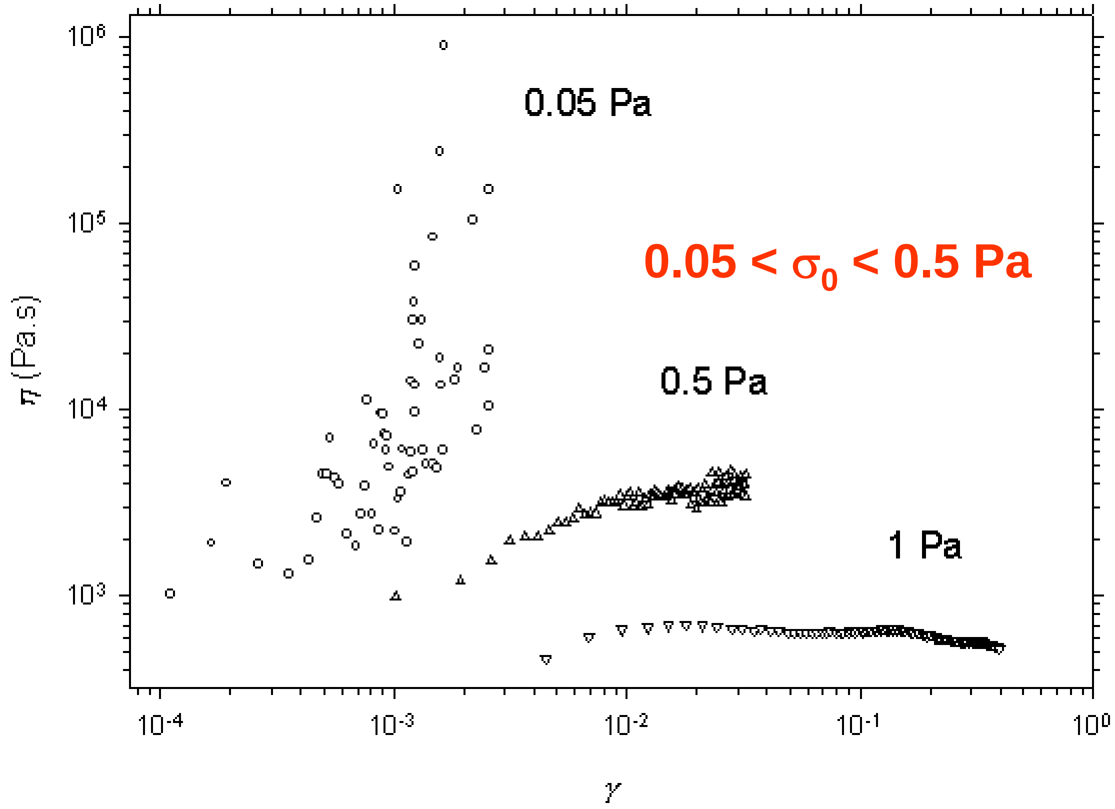
3.5 Yield stress measurements

- Materials such as suspensions, coatings, foodstuffs → 3-D structure ~ solid-like properties
- Can break under applied forces → viscoplastic materials
- Dynamic measurement of yield stress using extrapolation is not very reliable



Yield stress measurements

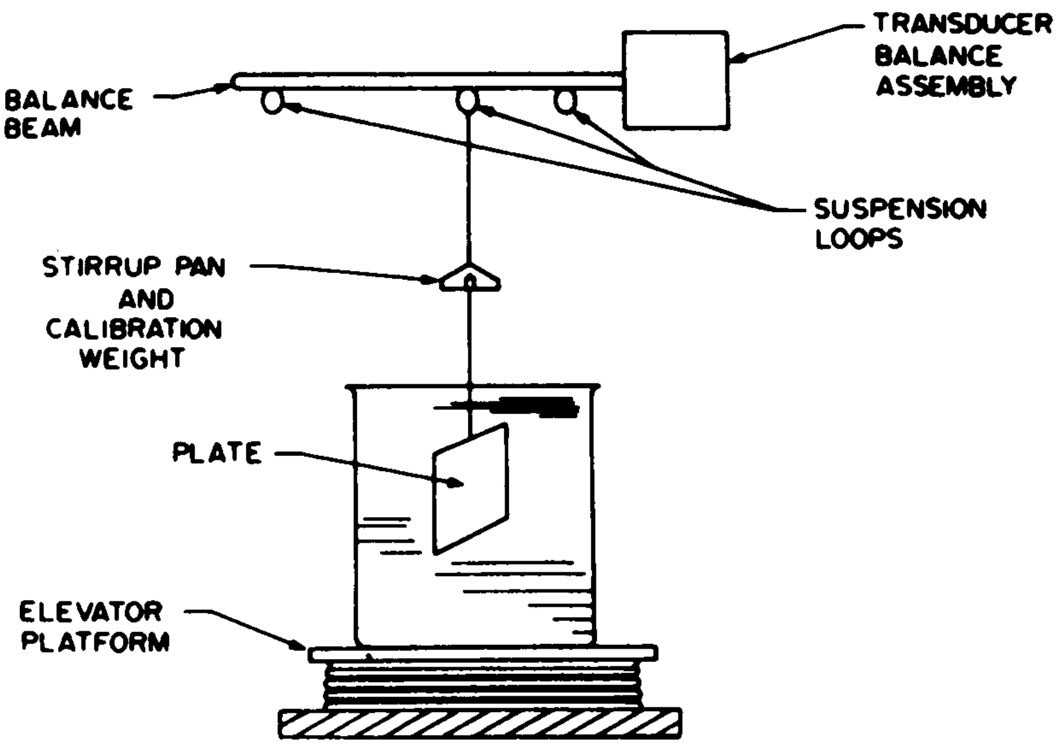
- Static measurements (undisturbed microstructure) and without extrapolation are preferable
- Can be achieved by controlling shear stress instead of shear rate → static yield stress under creep



(Craciun, 2003)

Static method for measuring yield stress (De Kee, 1986)

- At beginning of the test, plate is supported by the sample (zero load registered)
- Platform is lowered → sample exerts a force on the plate
- Net force is recorded



Static method for measuring yield stress (De Kee, 1986)

- When the acting force exceeds the yield stress, flow begins
- Characterized by a change in slope, at $t = t_r$
- Yield stress: $\sigma_0 = \frac{F_r}{S}$

  (S = area of the plate)
- Correction for the buoyant force: $F_b = \rho V g$

  (V = volume of displaced sample)