Filament Stretching Rheology: Basic Concepts

Ole Hassager
Technical University of Denmark

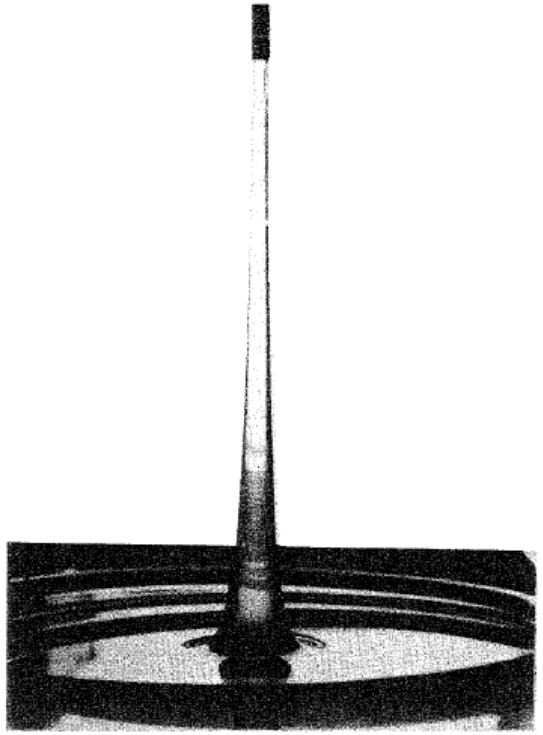


FIGURE 2.5-3. Fluid column in tubeless siphon experiment with a high molecular weight hydrocarbon polymer, AM-1 in JP-8 aviation fuel. [Reproduced from S. T. J. Peng and R. F. Landel, *J. Appl. Phys.* **47**, 4255 (1976)].

High speed image of jet break-up.
Left: Pure water. Right: Water with 200 ppm PEO.

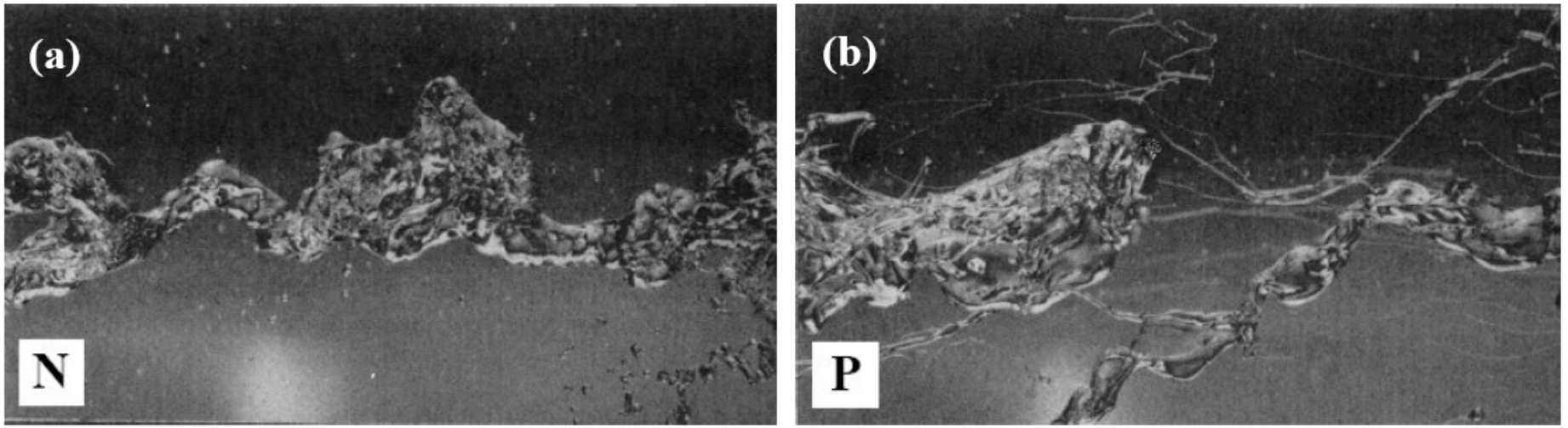
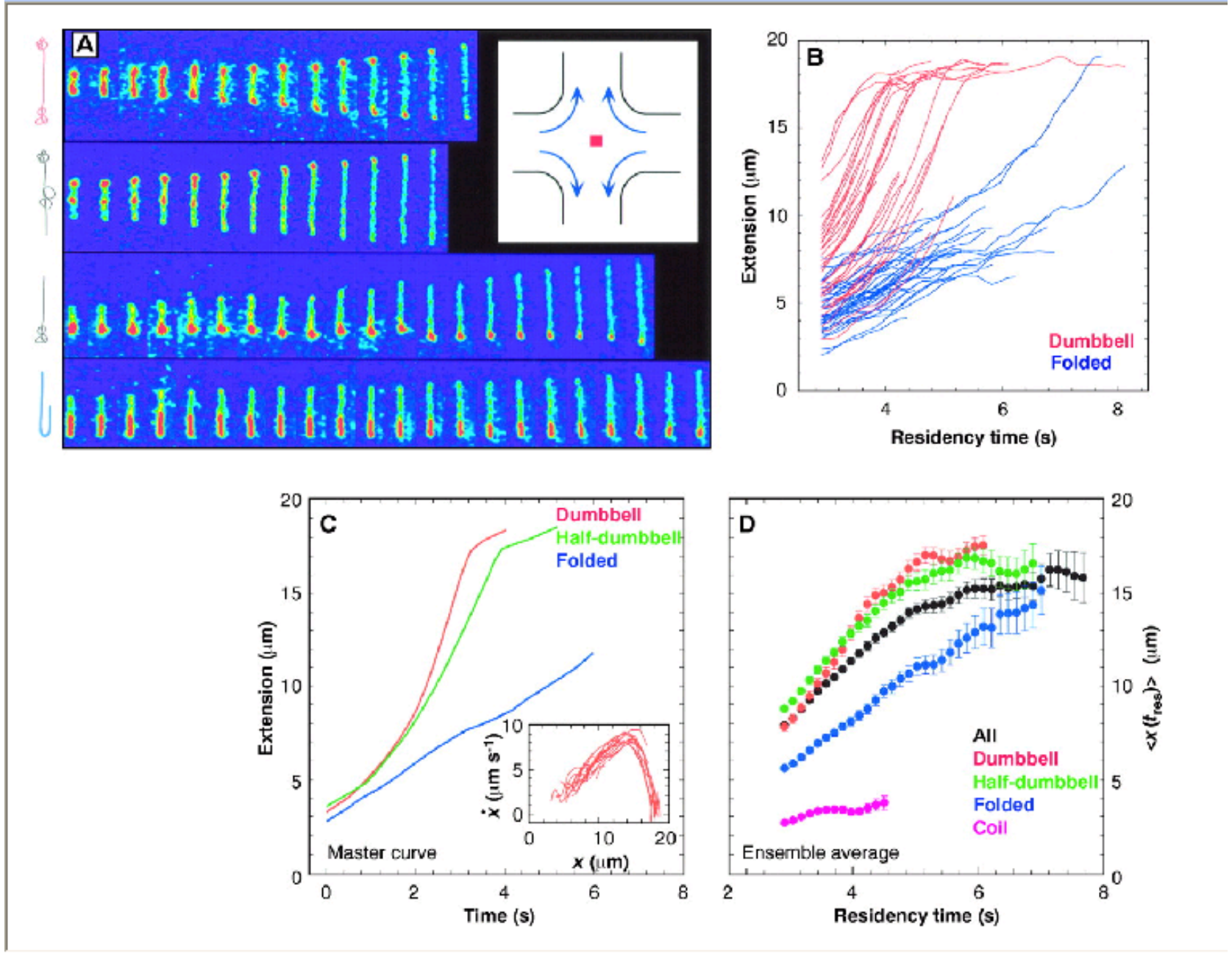


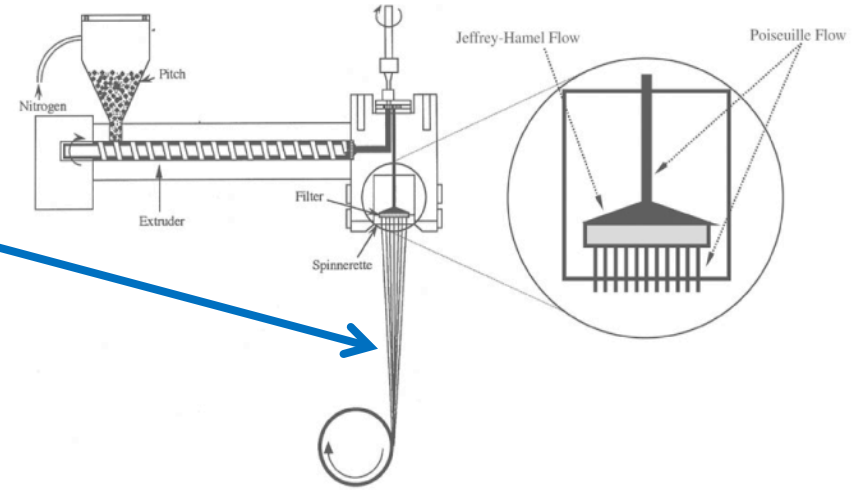
Fig. 8 (a) A turbulent jet of pure water, N for Newtonian, forming droplets. (b) A turbulent jet of water with the addition of only 200 parts per million of the macromolecule polyethylene-oxide forming filaments, from Ref. [80].



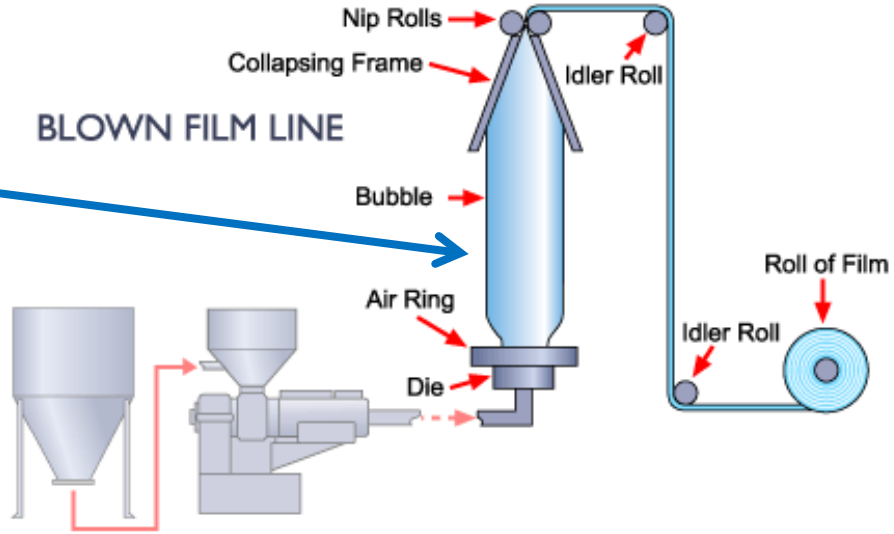
Perkins, Smith and Chu, Science, 27 June 1997, Volume 276, pp.2016-2021

Polymer processing operations with Extension:

Fibre spinning:
(draw down ratio)



Film blowing:



"The World's Strongest FibreTM"

Dyneema® is an UHMwPE (Ultra High Molecular weight Polyethylene) fibre developed by DSM in the Netherlands

High Strength: On a weight for weight basis, Dyneema® is 15 times stronger than steel wire

Water resistant: Dyneema® is hydrophobic and does not absorb water.
Chemical resistance: Dyneema® is chemically inert.

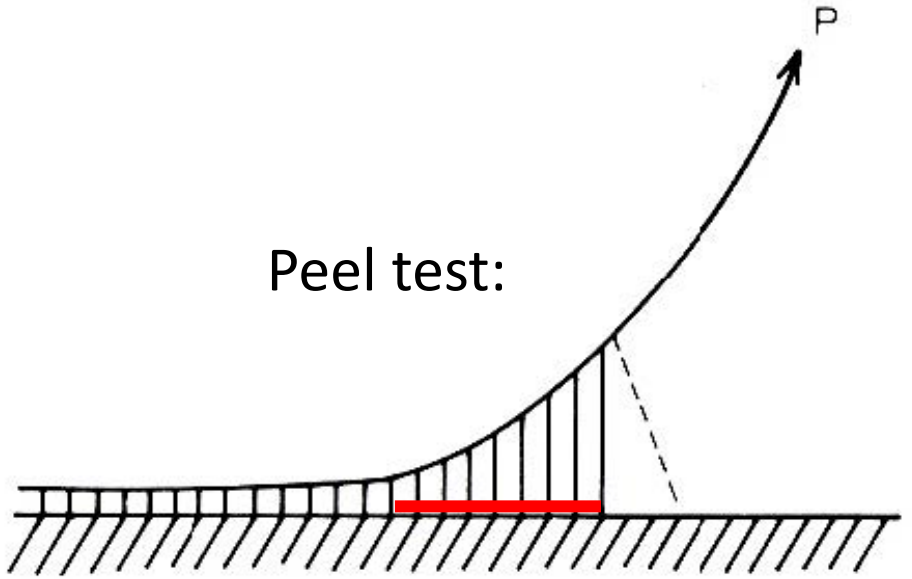
DSM Dyneema's patent: EP1699954B1.

Adhesion: Tack, stickyness, peel

Artist's perspective:

Scientist's perspective:

Peel test:



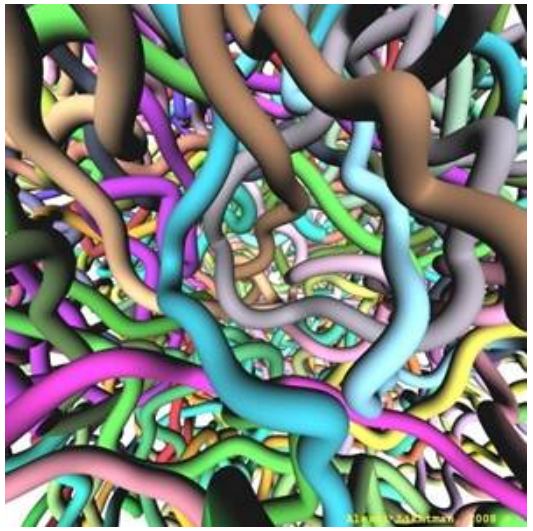
1st year DTU student: Break red chem. bonds: $\frac{3eV}{(3\text{Å})^2} \sim 5\,\frac{J}{m^2}$.

DoDyNet scientist: Study the deformation and flow of materials:

Rheology (rheo= flow, logos = learning about)

The field of molecular rheology emerges:

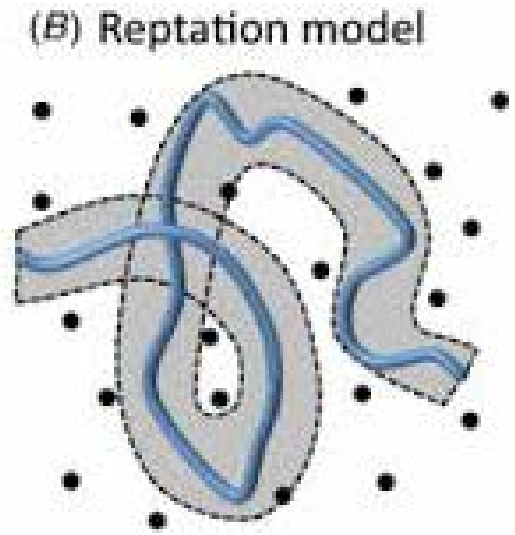
Pierre-Gilles de Gennes



Alexei Likhtmann

Nobel Prize 1991 for discovering that "methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers".

Pierre-Gilles de Gennes



- Introduced the idea of a tube surrouding a test model
- A consequence is that solvents merely increase the tube diameter whereby polymer melts can be modeled by polymer solutions.

A Chinese Nobel laureate:

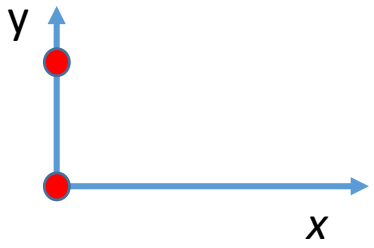
Experimental science is the foundation of all natural science.

National Museum of China, Beijing

Filament Stretching Rheology: Basic Concepts

What is the basic difference between shear and extension?:

Simple shear:

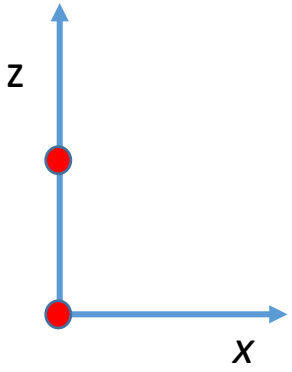


Consider two particles located at time zero both on the y-axis separated by a distance $s = y_0$. The particles are located in a simple shear flow:

$$v_x = \dot{\gamma} y$$
$$v_y = 0$$
$$v_z = 0$$

What is the difference between the particles at time t?

Simple or uniaxial extension:



Consider two particles located at time zero both on the z-axis separated by a distance $s = z_0$. The particles are located in a simple (uniaxial) extensional flow:

$$v_x = -\dot{\varepsilon} x/2$$
$$v_y = -\dot{\varepsilon} y/2$$
$$v_z = \dot{\varepsilon} z$$

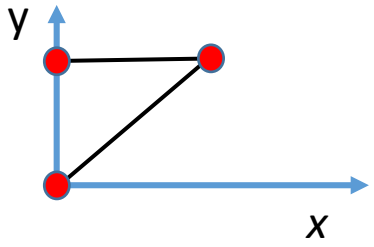
What is the difference between the particles at time t?

Filament Stretching Rheology: Basic Concepts

What is the basic difference between shear and extension?

Solution:

Simple shear:

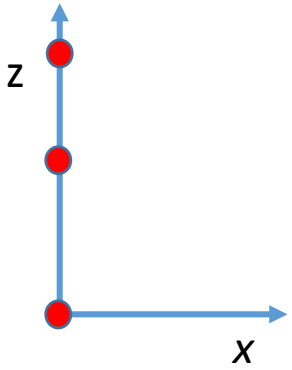


$$v_x = \dot{\gamma} y$$
$$v_y = 0$$
$$v_z = 0$$

$$\frac{dx}{dt} = \dot{\gamma} y \;\Rightarrow\; x = x_0 + \dot{\gamma} y_0 t = \dot{\gamma} y_0 t$$

$$s = \sqrt{y_0^2 + (\dot{\gamma} y_0 t)^2} \sim y_0 \dot{\gamma} t \quad \text{(large } t\text{)}$$

Simple or uniaxial extension:



$$v_x = -\dot{\varepsilon} x/2$$
$$v_y = -\dot{\varepsilon} y/2$$
$$v_z = \dot{\varepsilon} z$$

$$\frac{dz}{dt} = \dot{\varepsilon} z$$

$$\Rightarrow z = z_0 \exp(\dot{\varepsilon} t)$$

Materials functions in extension:

Extensional stress growth coefficient: $\eta_E^+(\dot{\varepsilon}, t) = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\varepsilon}}$

Extensional viscosity function: $\eta_E(\dot{\varepsilon}) = \lim_{t \to \infty} \eta_E^+(\dot{\varepsilon}, t)$ (If the limit exists)

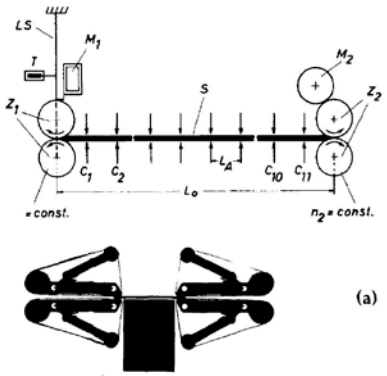
Extensional creep compliance: $J_E(t) = \varepsilon(t)/\sigma_0$

Extensional stress relaxation function.

Historical: Extensional Rheometer Designs

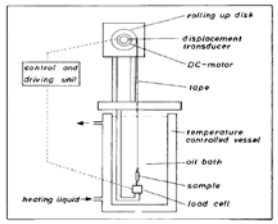
Meissner (1969), (1971), rotary clamp

$$\epsilon_{max} \approx 7$$



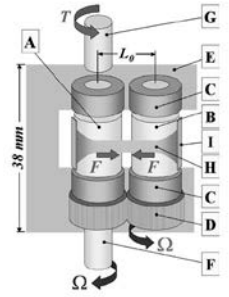
Meissner and Hostettler (1994), conveyor belt

Münstedt and Laun (1979)



Sentmanat (2004): SER
TA: EVF

$$\epsilon_{max} \approx 3.5$$



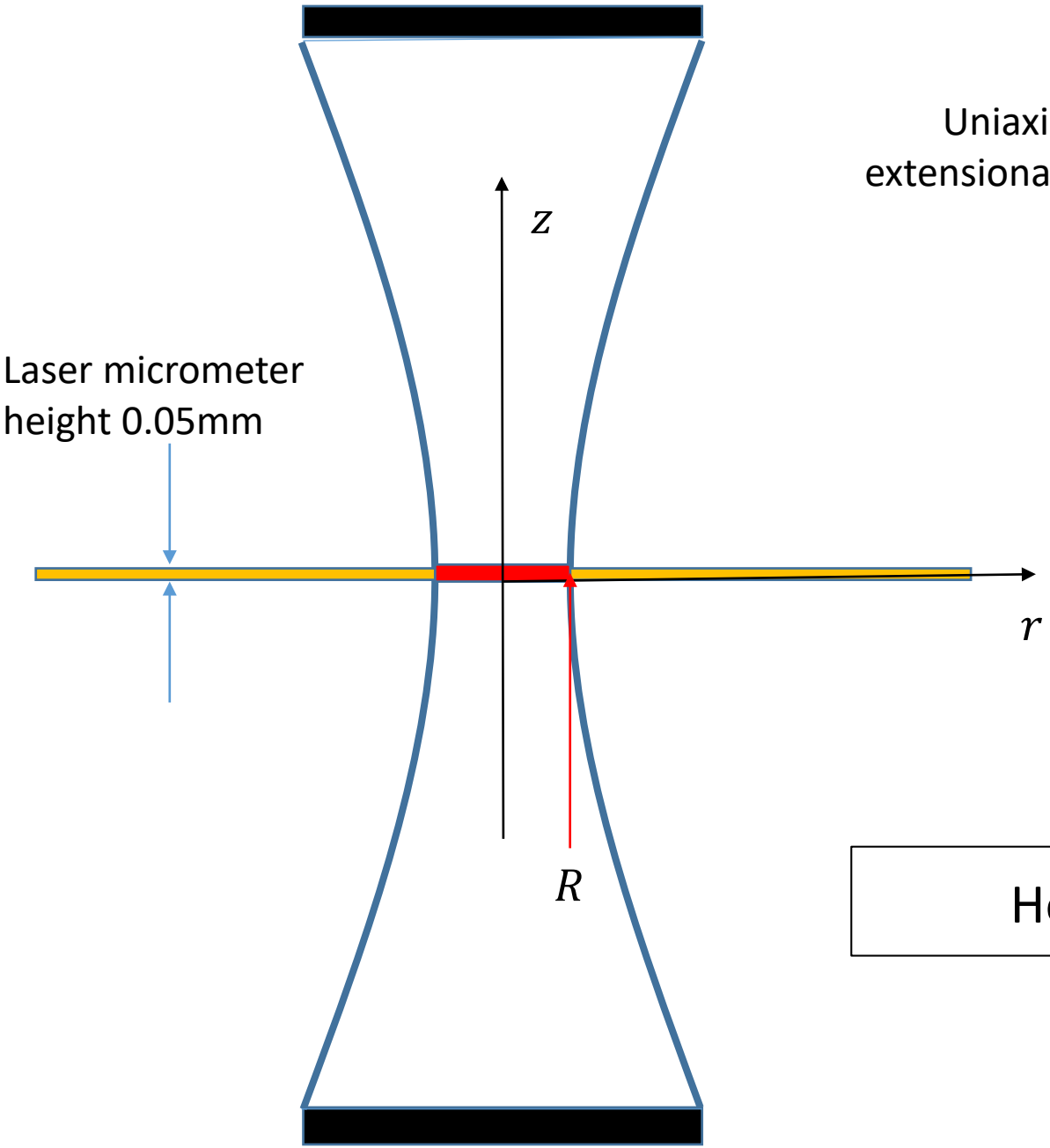
$$\epsilon_N = \log(L/L_0)$$

Filament Stretching Rheology: Basic Concepts

Enter:

1) laser technology.
2) Fast sampling and on-line control.

Spiegelberg, McKinley, Sridhar, Rasmussen, …



Uniaxial extensional flow:

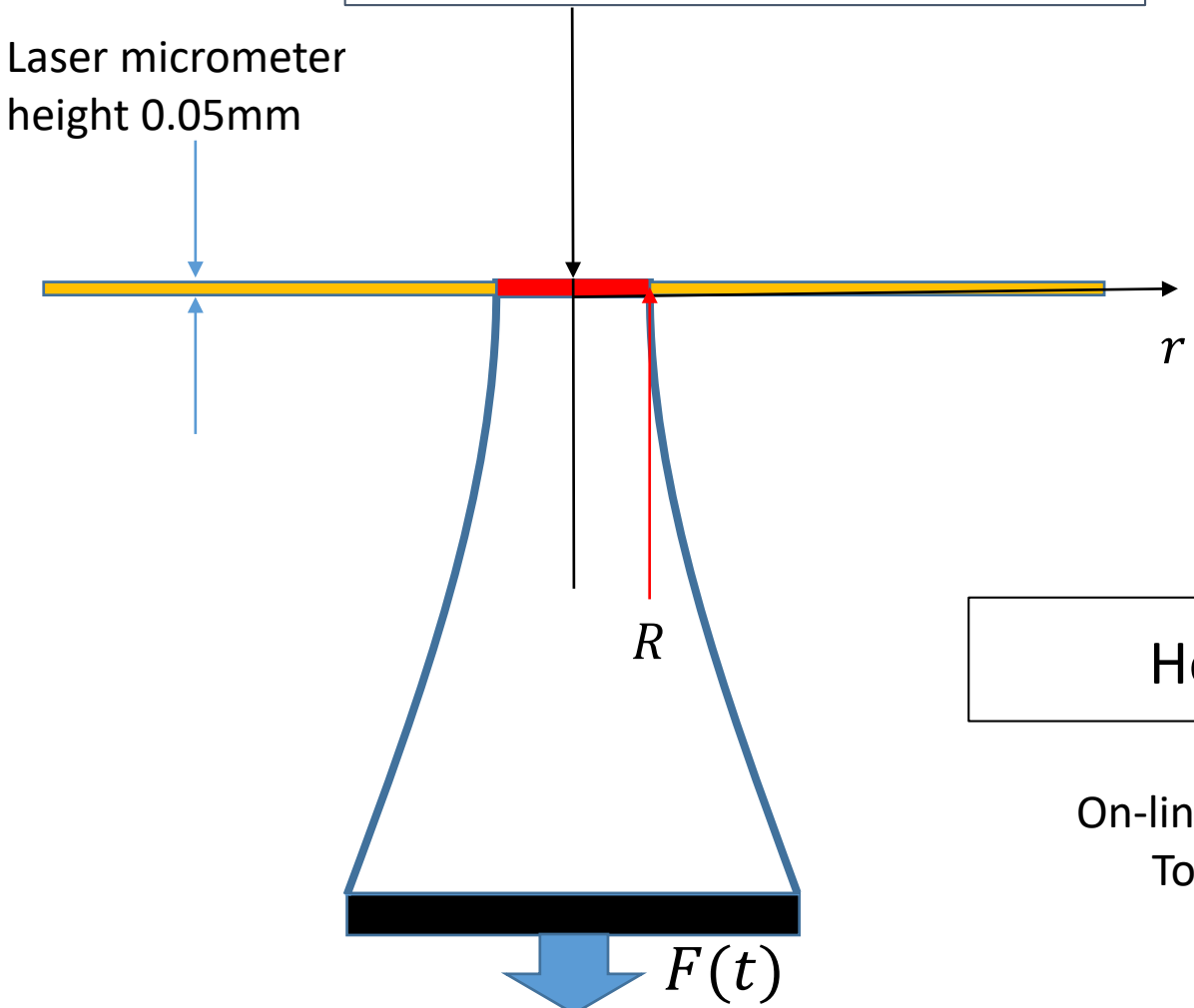
$$\begin{aligned} v_z &= \dot{\varepsilon} z \\ v_r &= -\frac{1}{2}\dot{\varepsilon} r \\ v_\theta &= 0 \end{aligned}$$

$$\dot{\varepsilon} = -2\, v_r(R)\frac{1}{R} = -2\frac{1}{R}\frac{dR}{dt} = -2\frac{d}{dt}\ln R$$

Feedback control can in principle allow for any prescribed $\dot{\varepsilon}(t)$ including a constant value.

Hencky strain: $\varepsilon(t) = \int_{t'=0}^{t} \dot{\varepsilon}(t')dt'.$

$$\langle \sigma_{zz} - \sigma_{rr} \rangle = \frac{F(t) - mg}{\pi R^2}$$



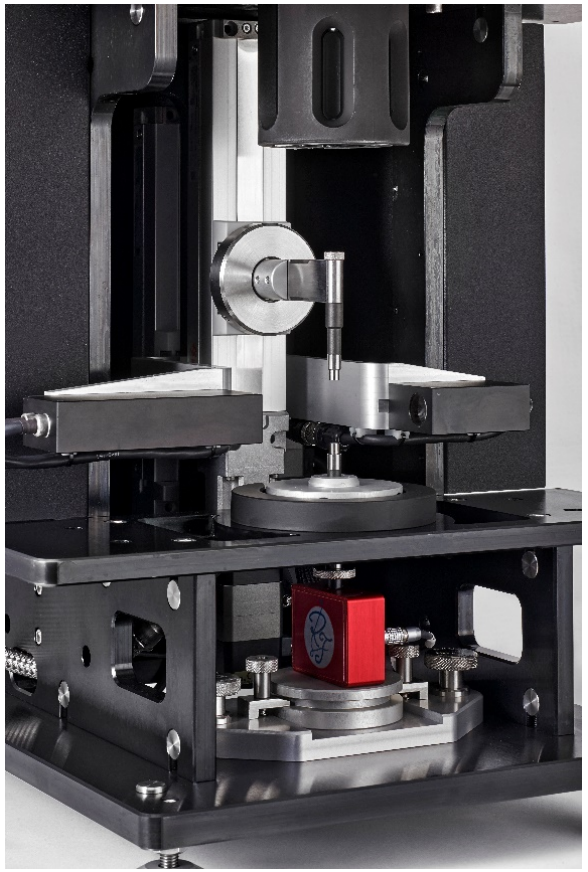
Surface tension and inertia meglected here may by included in force balance by Szabo, Rheol. Acta (1997).

$$\dot{\varepsilon} = -2\, v_r(R) \frac{1}{R} = -2 \frac{1}{R} \frac{dR}{dt} = -2 \frac{d}{dt} \ln R$$

Hencky strain: $\varepsilon(t) = \int_{t'=0}^{t} \dot{\varepsilon}(t')dt'.$

On-line control of Nominal Hencky strain: $\varepsilon_N = \log(L/L_0)$
To obtain desired true Hencky strain function $\varepsilon(t)$.

How can that be done in practice?



www.rheofilament.com

So what could possibly go wrong?

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- End-plate slip-off
- End-plate instability
- Highly localized necking
- Filament fracture
- Residual solvent
- Humidity
- Sample impurity
- Bubbles in sample
- Sample degradation
- Phase separation
- Non-isothermal effects
- Force too low
- Gravitational sagging

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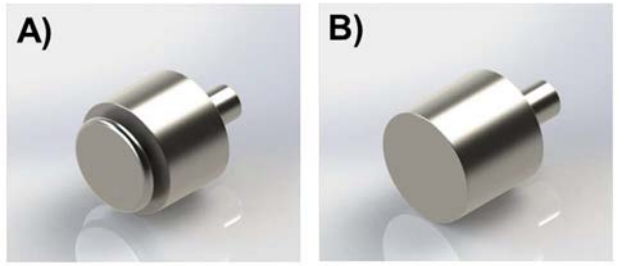

Fig. 1. Sketch of plate designs. (a) The mushroom plate design developed for stretching of non-sticky samples. (b) The original plate design for sticky samples.

Stress and strain measured here!

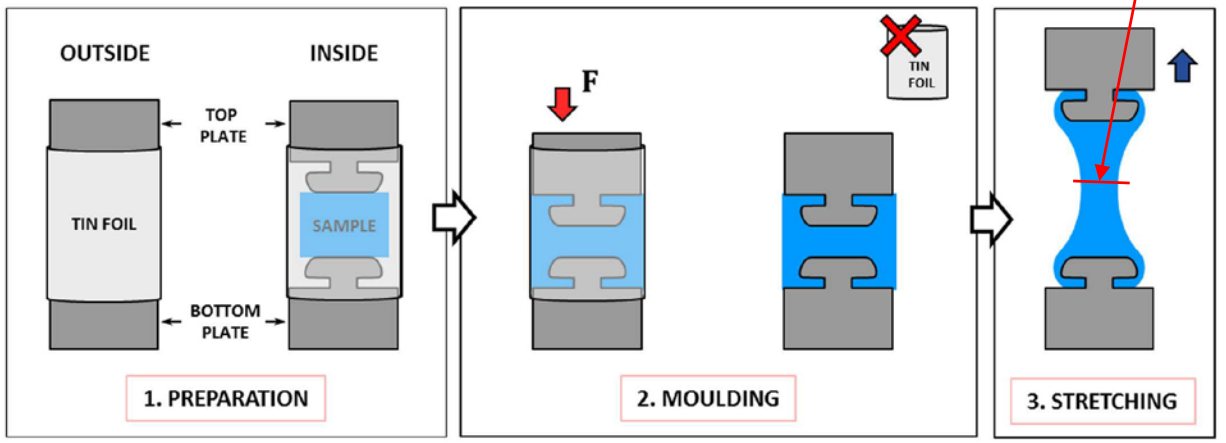

Fig. 2. Sketch of moulding procedure in the FSR using the mushroom plates. 1. Preparation: Initial placement of the polymer disc between the bottom and top plates with a piece of tin foil wrapped around it. 2: Moulding: (left) Moulding procedure where the sample is heated above T_m and the top plate is lowered by applying a force F. (right) after moulding where the tin foil has been removed. 3. Stretching: The anchoring effect of the mushroom during stretching preventing slip-off.

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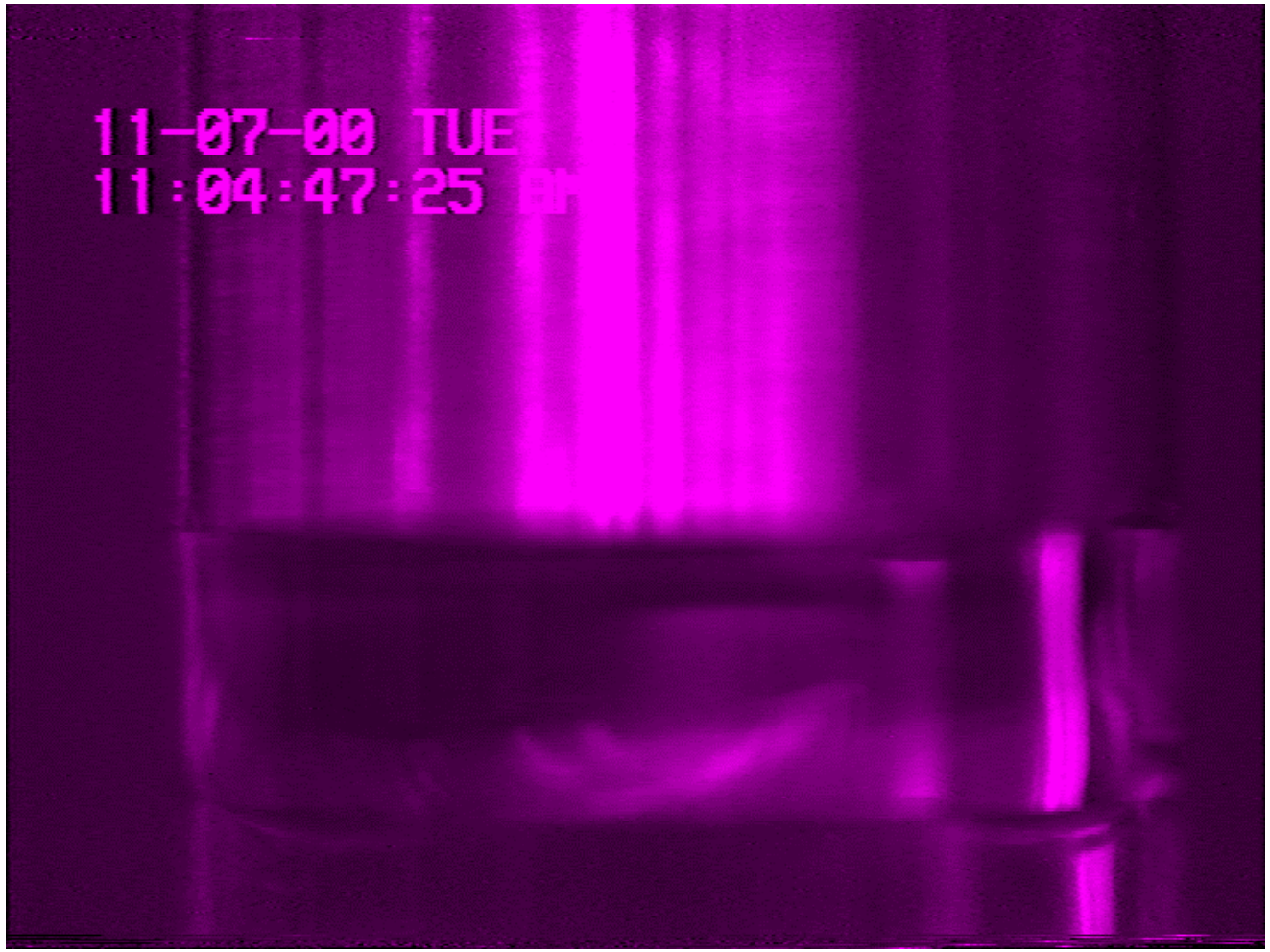
Very strongly strain hardening polymer solutions (UCM, Oldroyd B)



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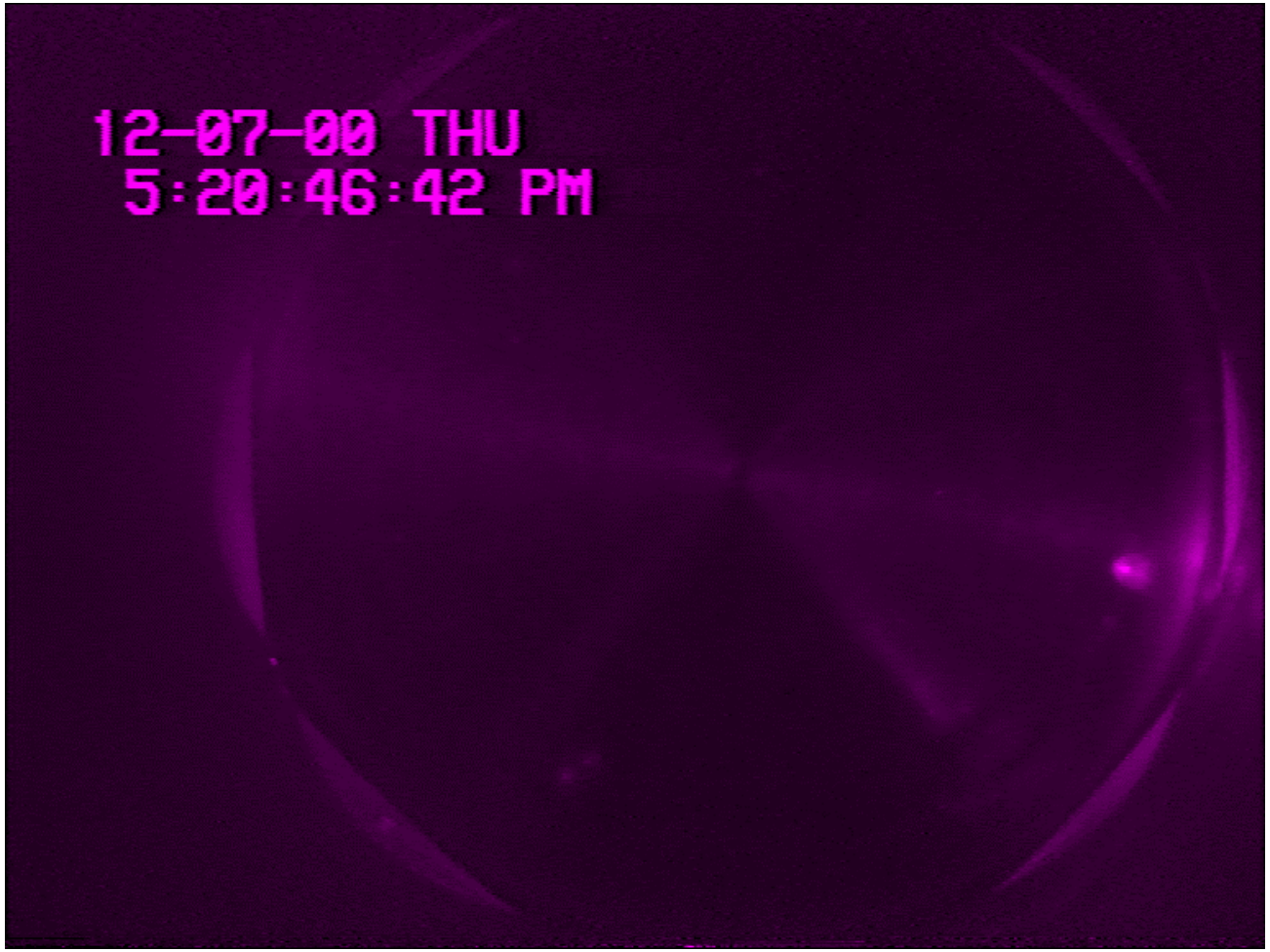

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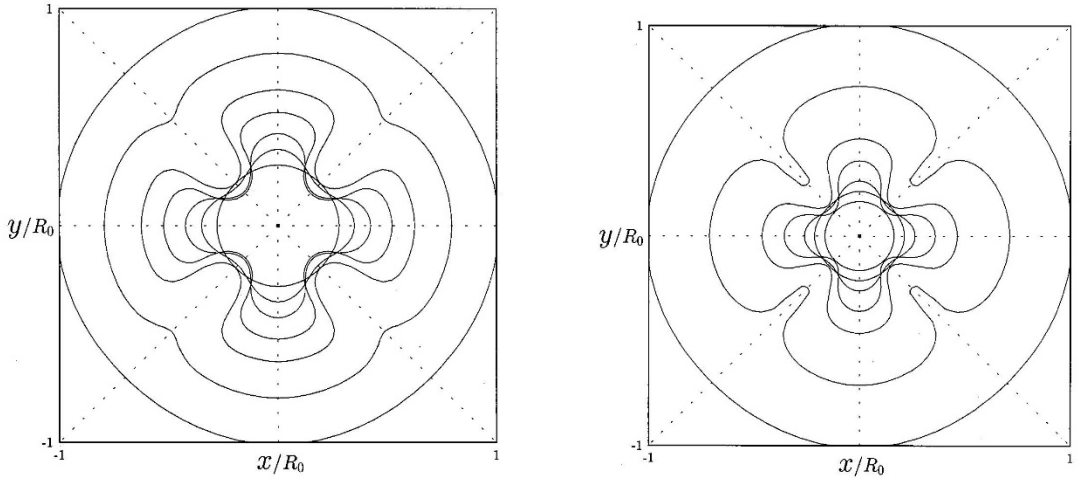

Simulated surface profiles for the distance z/R_0 from the end plate equal to 0, 0.05, 0.1, 0.2, 0.5 and 1, and at the symmetry plane with (left) and without (right) surface tension. Note the larger mid-filament diameter with surface tension.
Material: UCM. $\phi = \gamma/(R_0 G_0)$ 0.1 and 0.0 respectively.
Rasmussen and Hassager, J. Rheol., (2001)

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On the ”Considere criterion”: Conditions for necking

McKinley and Hassager, J.Rheol. (1999):

Abstract:

In the limit of rapid elongation such that **no molecular relaxation occurs**, the external work applied is all stored elastically and the Considere criterion originally developed in solid mechanics can be used to quantitatively predict the critical Hencky strain to failure.

Main text:

This criterion states that homogenous uniaxial elongation of a **visco**elastic filament is guaranteed provided the strain is less than that at which a maximum occurs in the force versus extension curve, Vincent (1960); Cogswell and Moore (1972); Malkin and Petrie (1997)

Hoyle and Fielding, JNNFM (2017)

However, in failing to take account of the *rate* of extension, this criterion is unable to address necking in viscoelastic materials, in which the *rate* at which the strain is applied (compared with the material's intrinsic rate of stress relaxation) is an important variable, alongside the total accumulated strain.

Considere violated but Filament Stretching Rheometry with feed-back works!

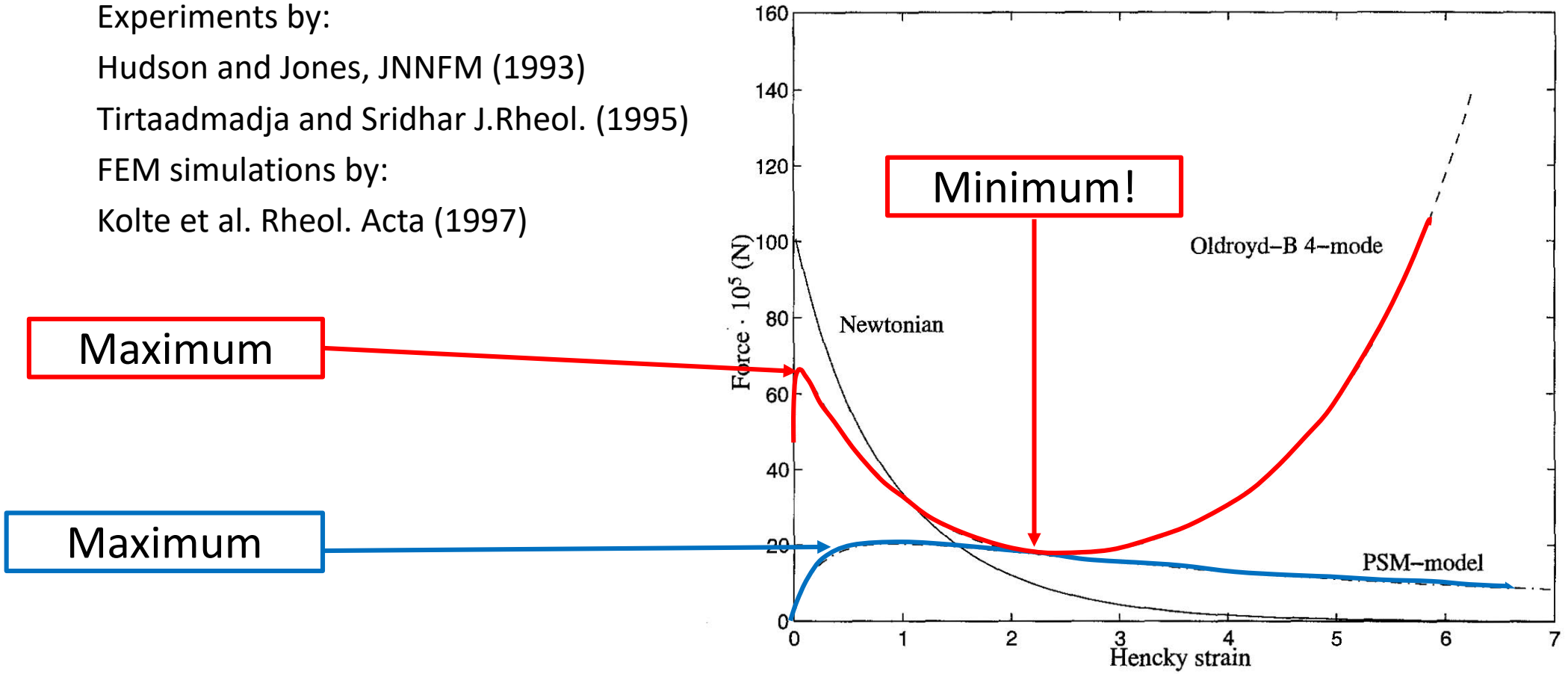
Experiments by:

Hudson and Jones, JNNFM (1993)

Tirtaadmadja and Sridhar J.Rheol. (1995)

FEM simulations by:

Kolte et al. Rheol. Acta (1997)



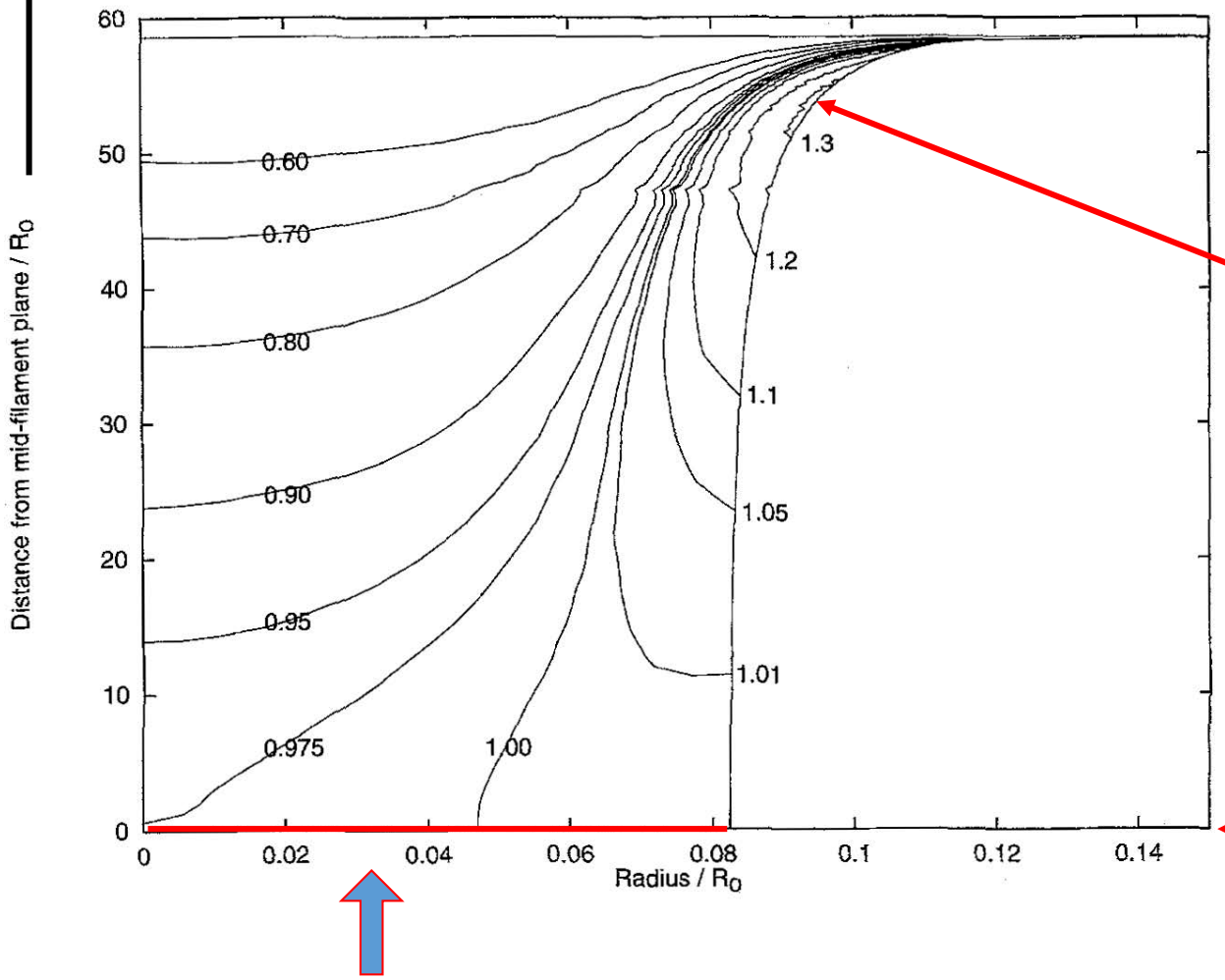
Oldroyd-B: 0.31% PIB, Mw ~ 1.2 10^6 solution (”Boger fluid”) (maximum and minimum)

PSM: Semidilute 2.0% PIB, Mw 4.3 10^6 (Papanastasiou, Scriven, Macosko) (single maximum)

FEM simulations by Kolte et al., Rheol. Acta (1997)

Contour plots for $\frac{\mathrm{tr}\,(\sigma)_{experimental}}{\mathrm{tr}(\sigma)_{ideal}}$, "Boger fluid"

Top plate



Dilute PIB solution modeled as 4-component Oldroyd B

Maximum!

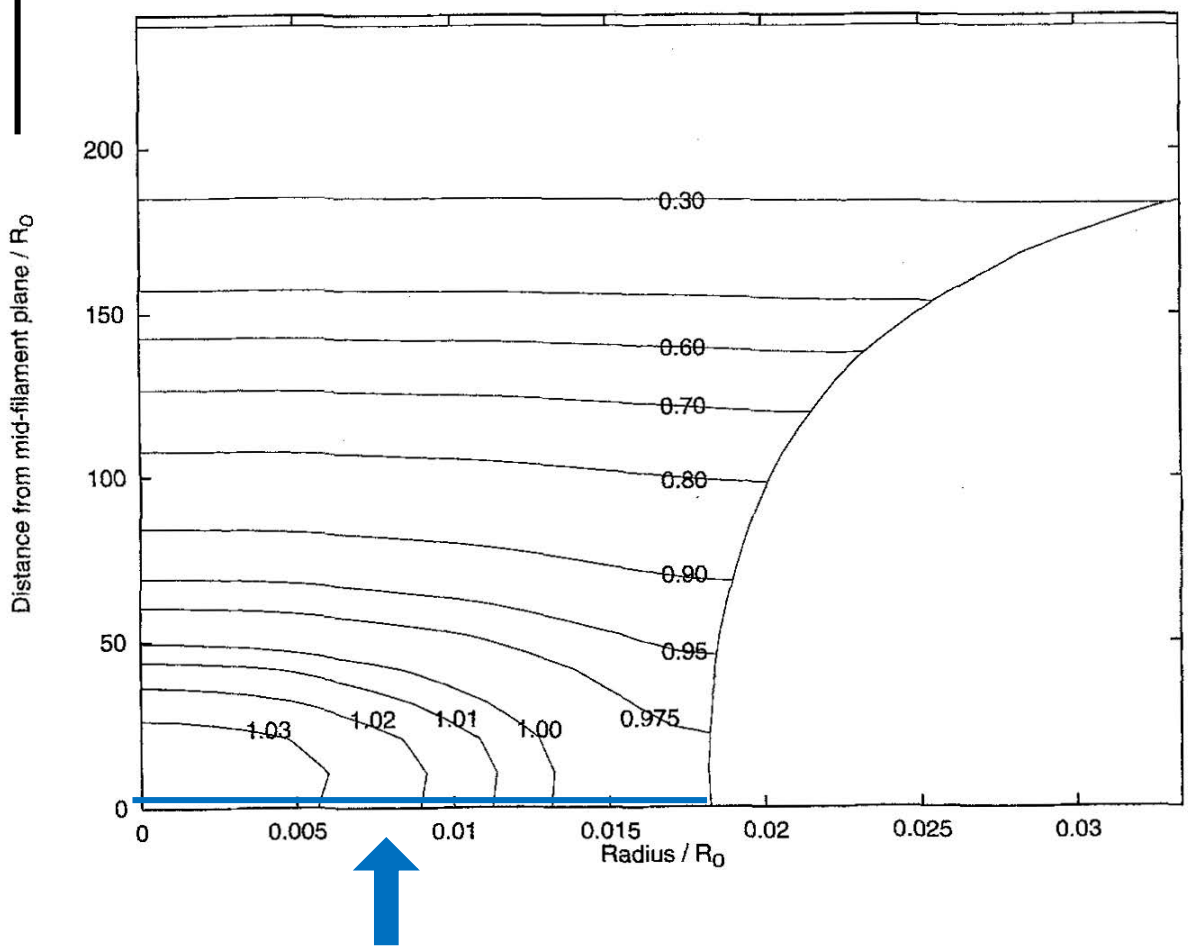
Symmetry plane

$\mathrm{tr}\,(\sigma)$ less than 3% deviation from ideal in symmetry plane!

FEM simulations by Kolte et al., Rheol. Acta (1997)

Contour plots for $\frac{\mathrm{tr}\,(\sigma)_{experimental}}{\mathrm{tr}(\sigma)_{ideal}}$, shear thinning fluid

Top plate



Semi-dilute PIB solution:

Linear spectrum: BSW.

Non-linear model: PSM.

Symmetry plane

$\mathrm{tr}\,(\sigma)$ less than 4% deviation from ideal in symmetry plane!

FEM simulations by Kolte et al., Rheol. Acta (1997)

Conclusion so far for the FSR with feed-back control:

There is no immediate conflict between necking and the operation of the FSR for rheometry as long as the filament remains axis-symmetric.

Hoyle and Fielding: Criteria for necking.

Yellow: Homogeneous deformation stable. White: Necking

Two instability modes: ”Stress curvature mode” and ”Elastic Considere mode”

Stress curvature neutral condition

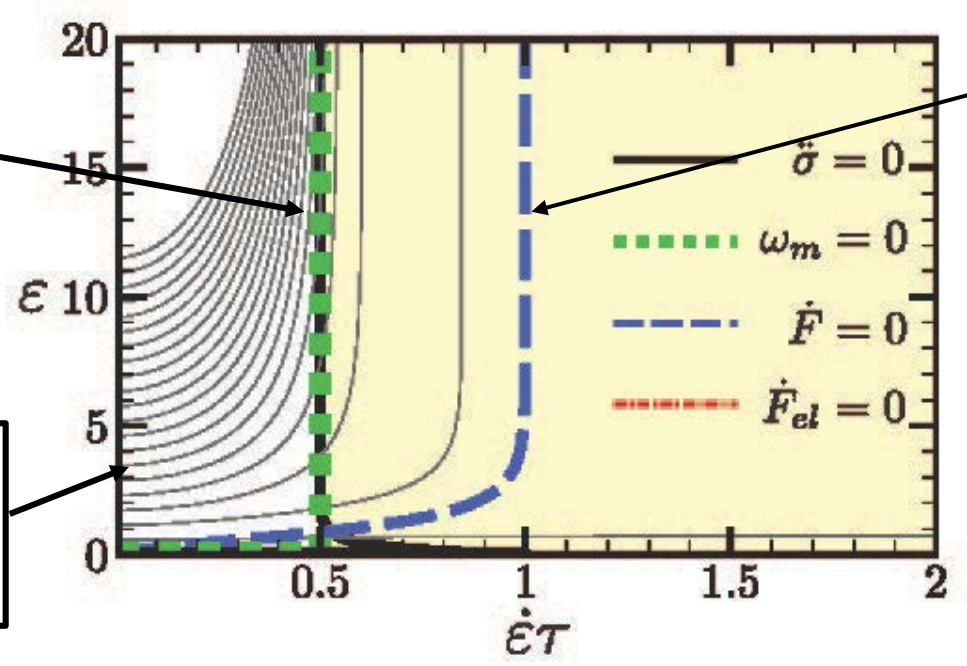
Incorrect prediction of original Considere

No elastic Considere mode for Oldroyd B

Newtonian liquids do not exhibit ductile failure

(in absence of surface tension).

Hassager, Kolte & Renardy (1998)



(a) Oldroyd-B

Hoyle and Fielding, J. Rheol. (2016)

5.1.1 Newtonian

Should show necking according to stress curvature condition

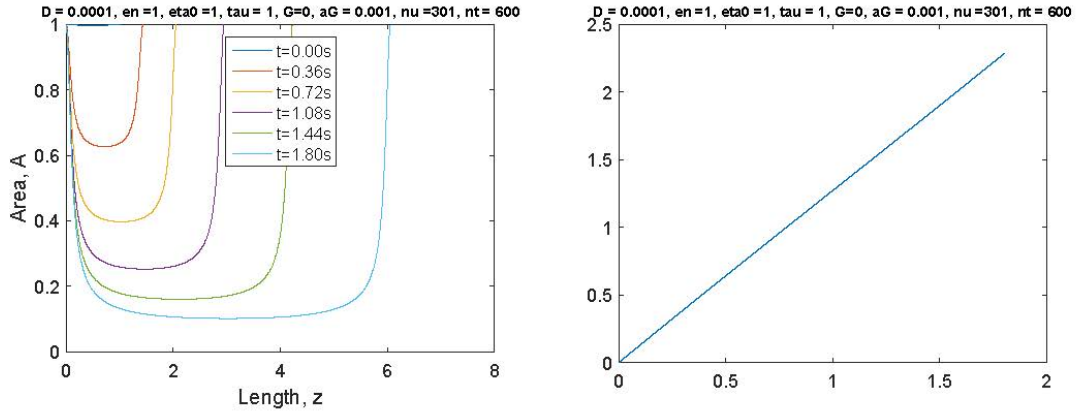


Figure 6: Area as function of height and ϵ as function of time.

Potential for end-plate instability

5.1.2 Oldroyd B

Should not show necking according to stress curvature condition

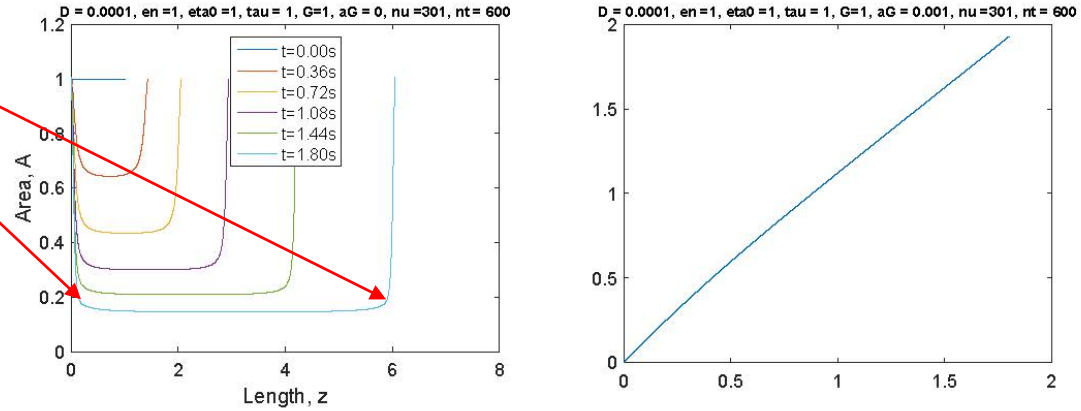
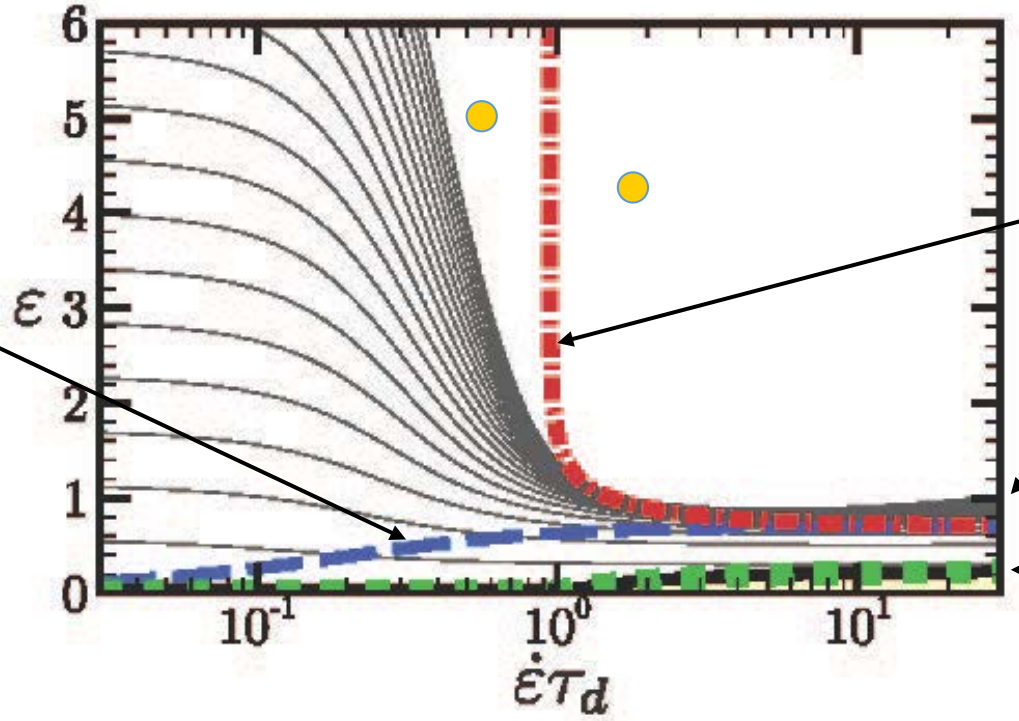


Figure 7: Area as function of height and ϵ as function of time.

Hoyle and Fielding: Criteria for necking.

Yellow: Homogeneous deformation stable. White: Necking

A material with stress saturation. Non-stretch DE or Rolie-Poly



(d) non-stretch Rolie-Poly

Original Considere

Elastic Considere

For Wi → ∞ elastic Considere and original Considere coincide with $\boldsymbol{\varepsilon_c} \approx 0.9$ as for the DE-model (McKinley and Hassager)

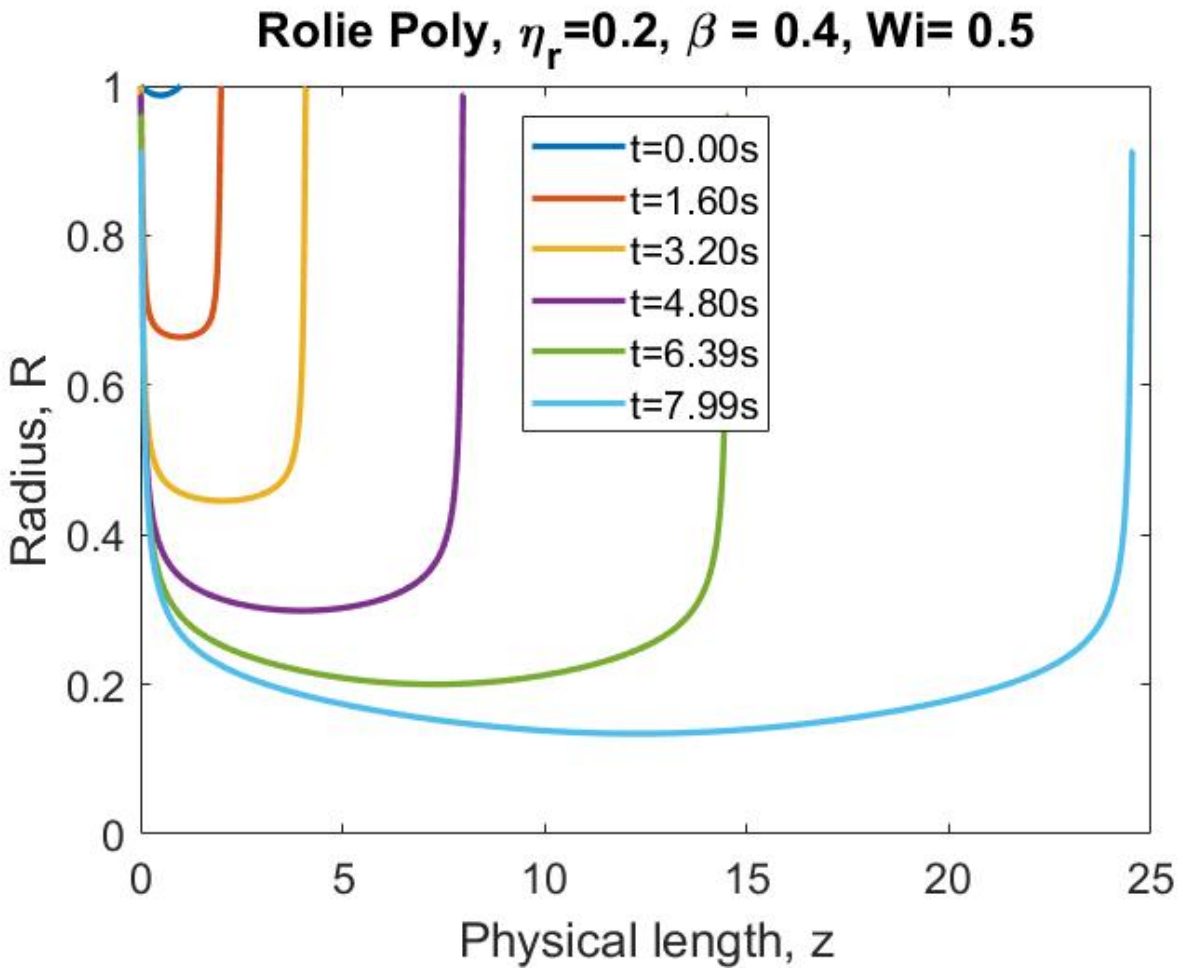
Stress curvature condition

"Unsafe at Any Speed", Ralph Nader (1965)

Non-stretch Rolie-Poly model: Slender Filament Approximation by Hoyle and Fielding:
Example of stress material with stress saturation

Wi= 0.5

Stress curvature condition: Unstable
Elastic Considere condition: Not unstable



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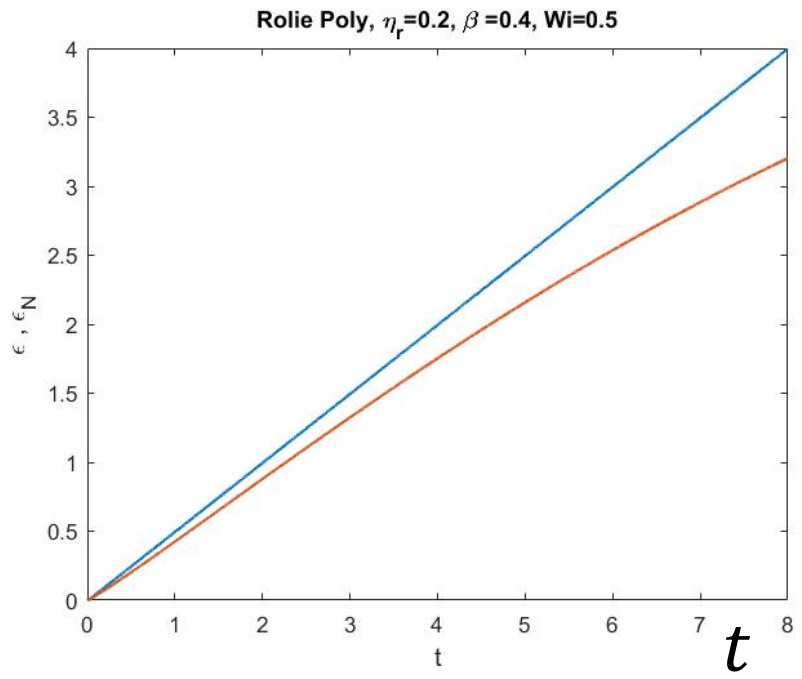
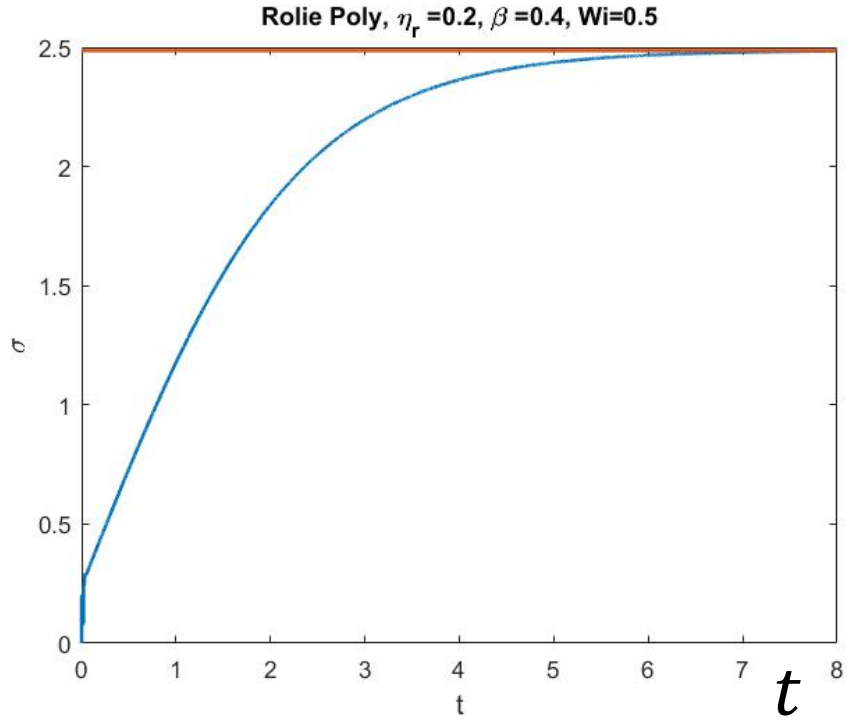


Blue line: True Hencky strain $\varepsilon = 2\ln(R_0/R)$
Red line: Nominal Hencky strain $\varepsilon_N = \ln(L/L_0)$

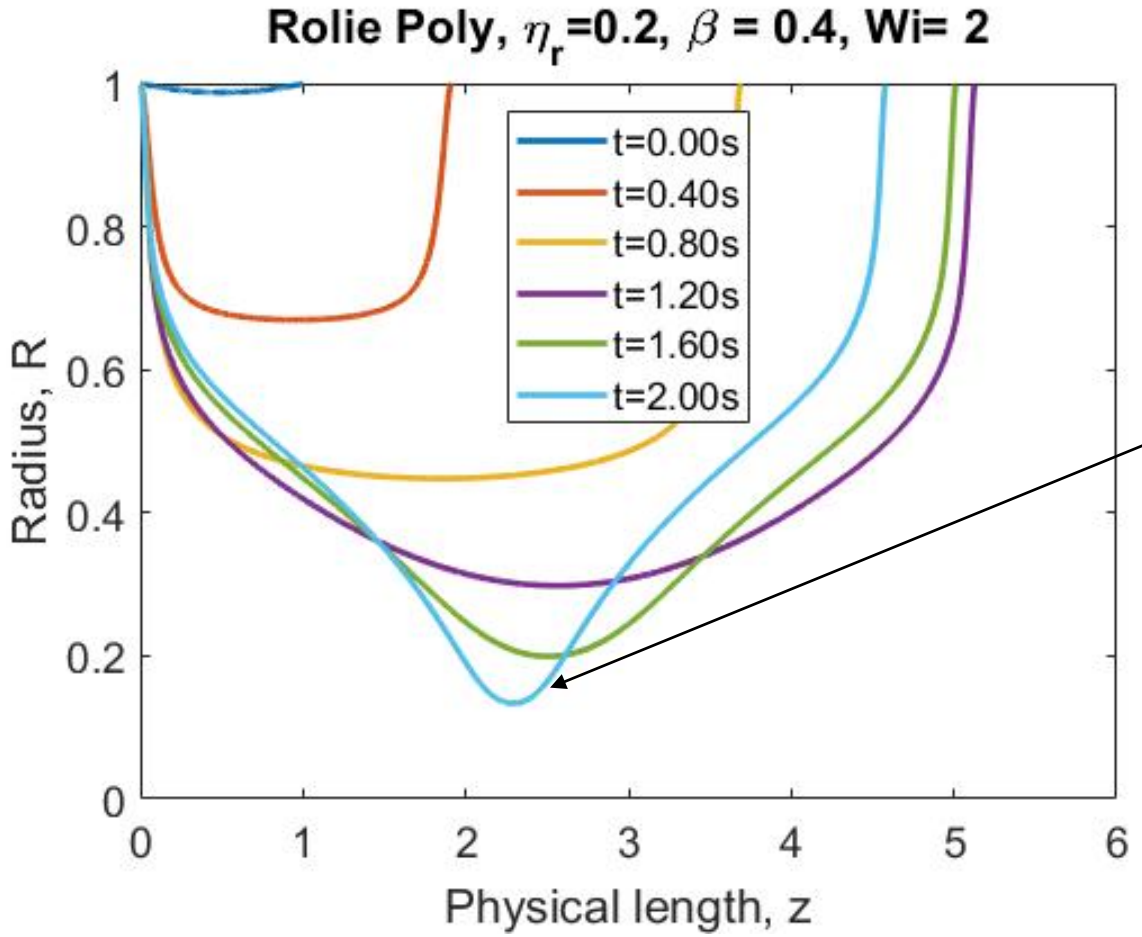


True stress as function of time.
Red line: From theoretical steady extensional viscosity

Non-stretch Rolie-Poly model: Slender Filament Approximation by Hoyle and Fielding:
Example of stress material with stress saturation

Wi= 2

Stress curvature condition: Unstable
Elastic Considere condition: Unstable

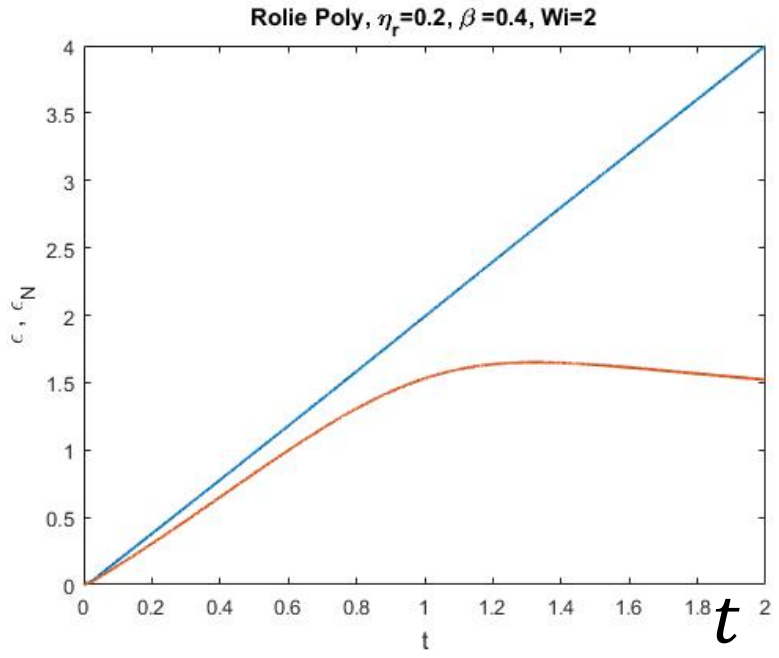


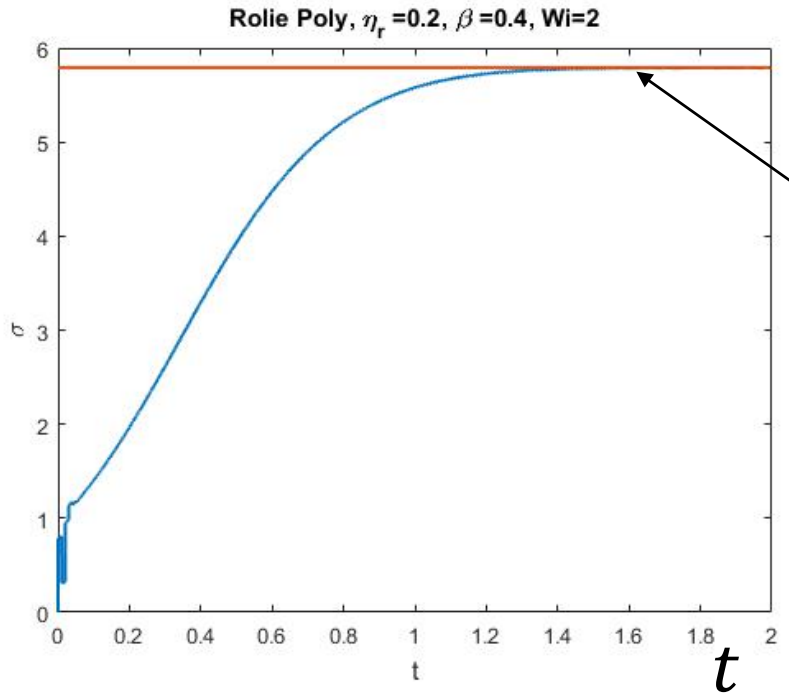
Development of highly localized neck

Non-stretch Rolie-Poly model: Slender Filament Approximation by Hoyle and Fielding:
Example of stress material with stress saturation

Wi= 2

Stress curvature condition: Unstable
Elastic Considere condition: Unstable



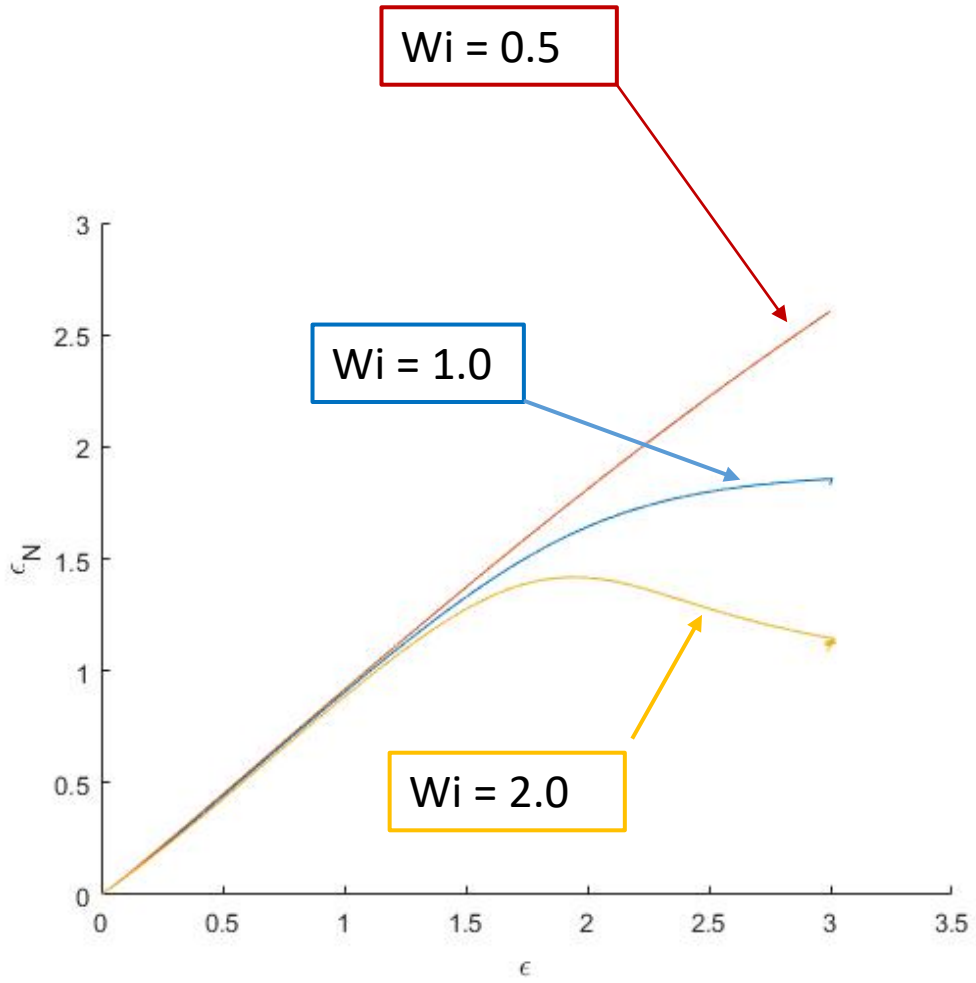


Still possible to measure steady extensional viscosity!

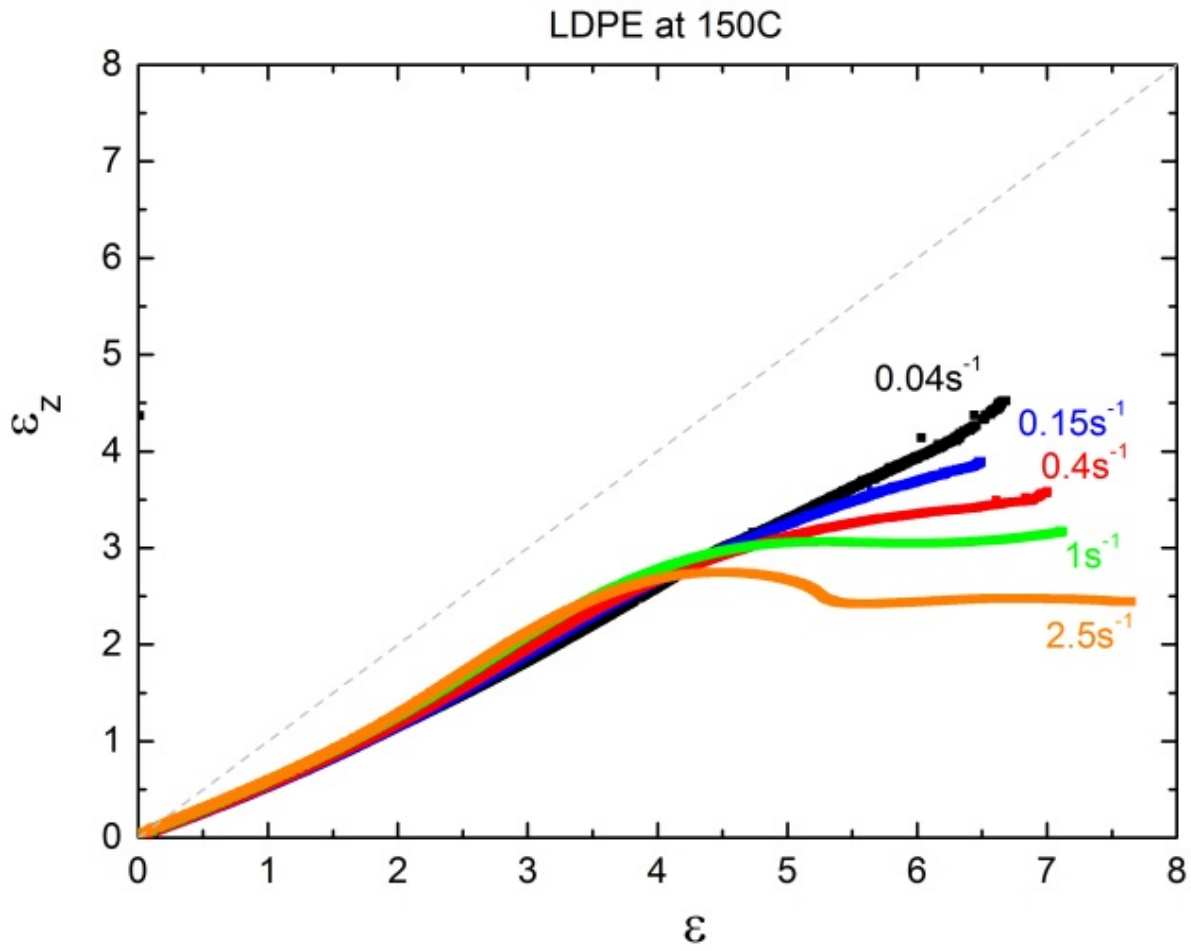
Blue line: True Hencky strain $\varepsilon = 2\ln(R_0/R)$
Red line: Nominal Hencky strain $\varepsilon_N = \ln(L/L_0)$

True stress as function of time.
Red line: From theoretical steady extensional viscosity

RoliePoly $\beta = 0.4$



Low Density Polyethylene
$d\epsilon/dt = const.$



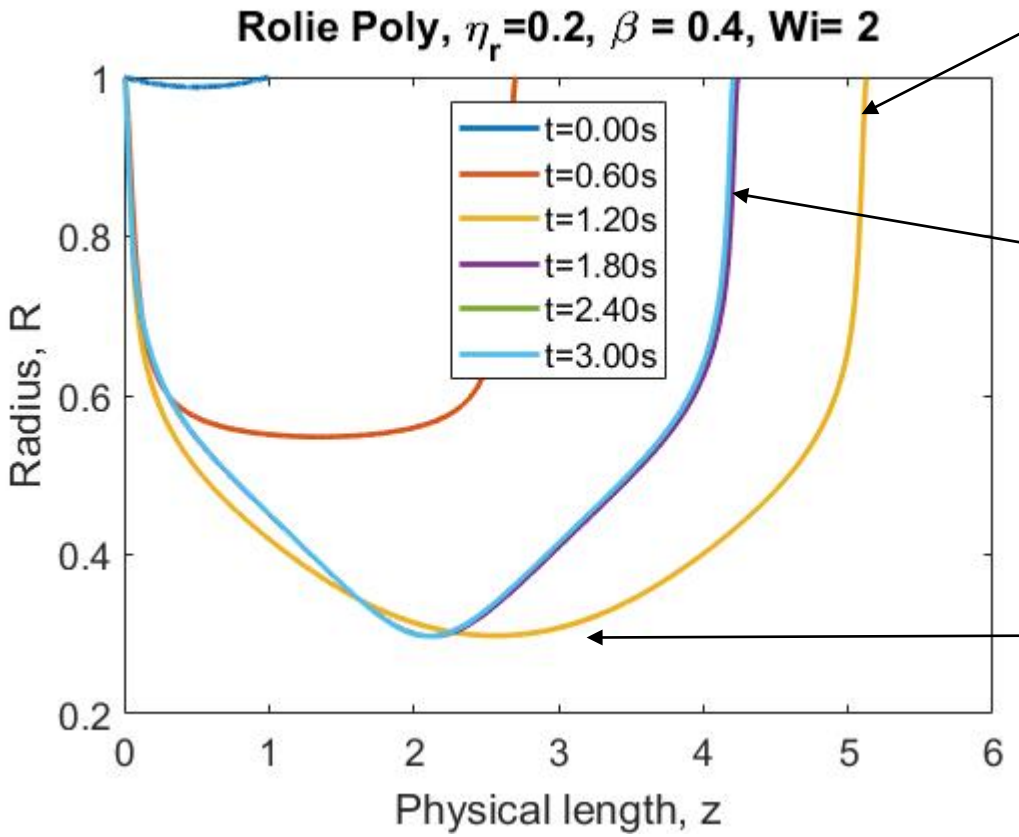
Conclusion so far for the FSR with feed-back control:

There is no immediate conflict between necking and the operation of the FSR for rheometry as long as the filament remains axis-symmetric even for materials with stress saturation!

Non-stretch Rolie-Poly model: Slender Filament Approximation by Hoyle and Fielding:
Example of stress material with stress saturation

Wi= 2

Stress relaxation after Hencky strain 2.4



Profile at initiation of relaxation

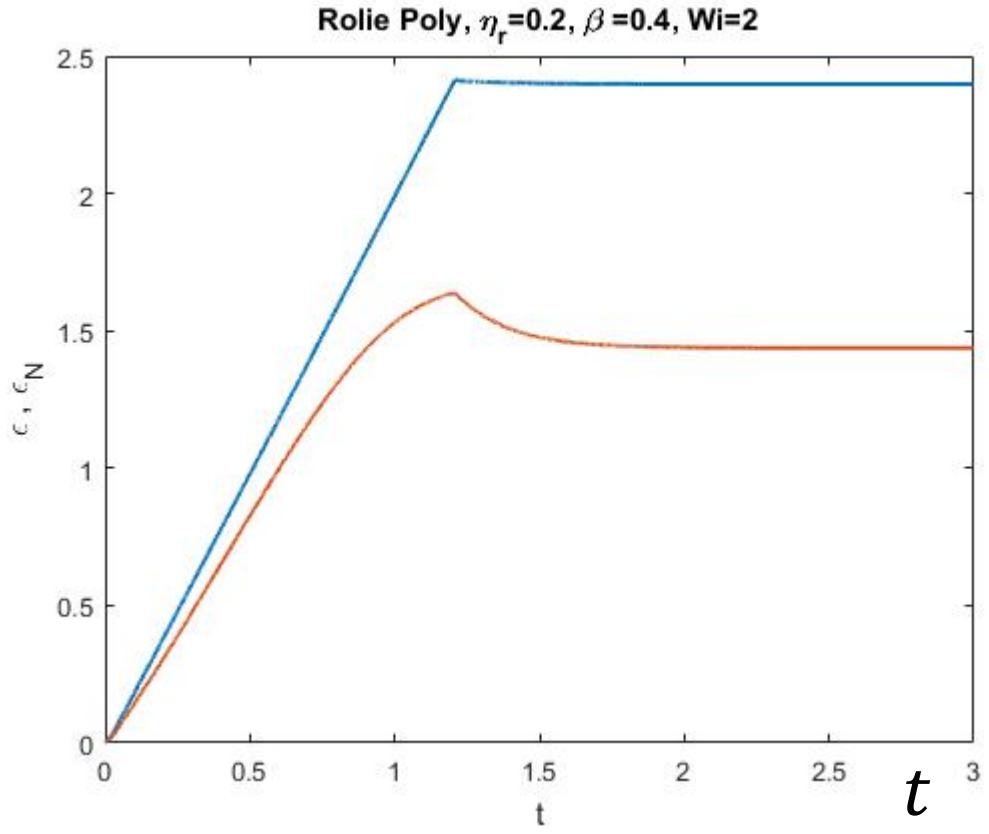
Adjustment of nominal Hencky strain needed to keep true Hencky strain constant.

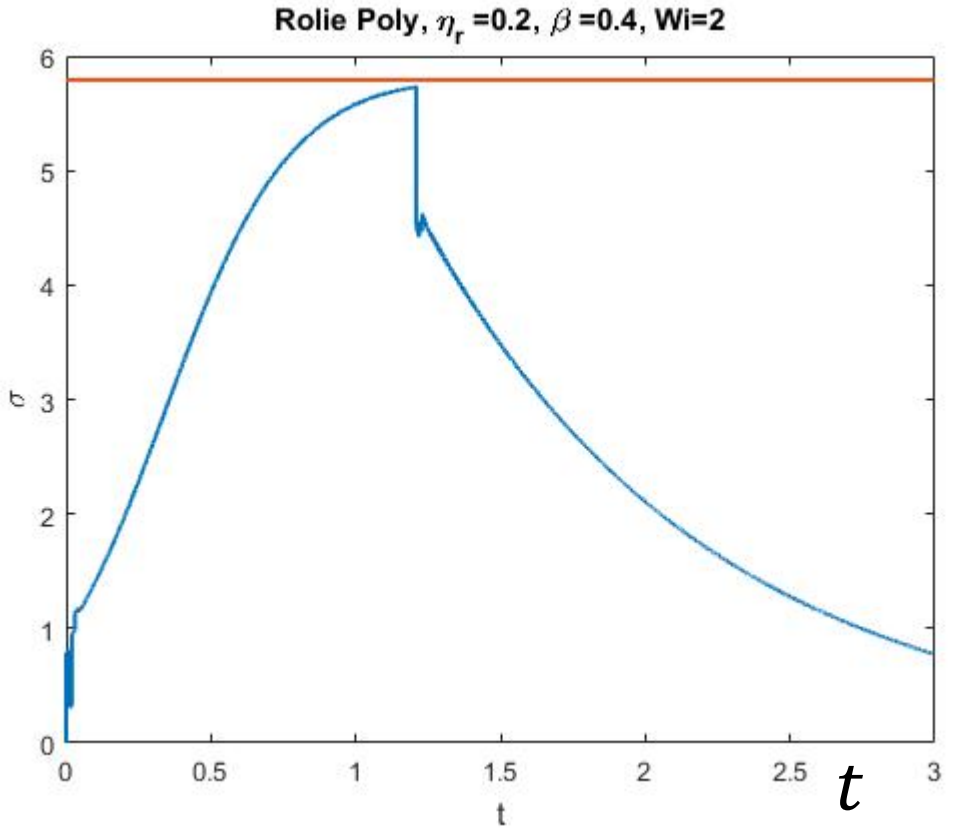
$R = \exp(-2.4/2) \approx 0.30$

See also Hoyle and Fielding, JNNFM (2017)

Non-stretch Rolie-Poly model: Slender Filament Approximation by Hoyle and Fielding:
Example of stress material with stress saturation

Stress relaxation after Hencky strain 2.4





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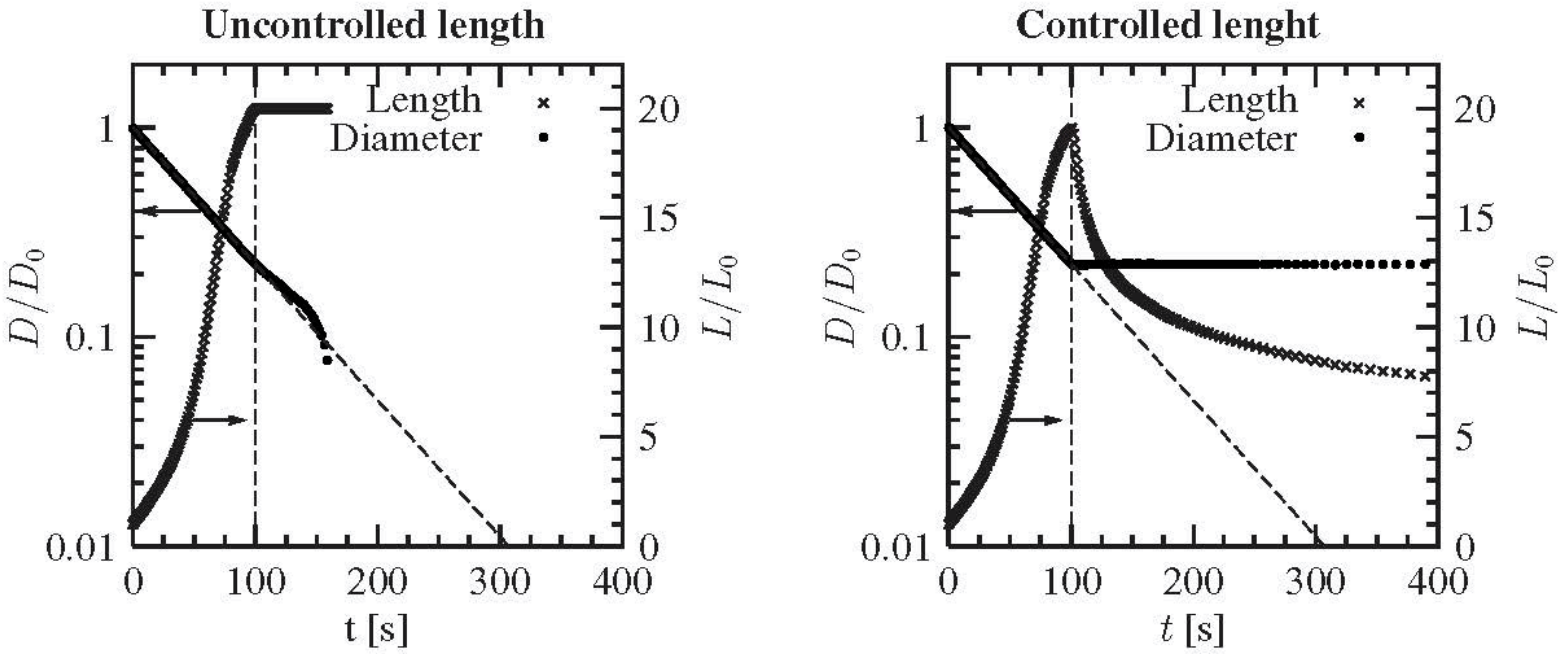
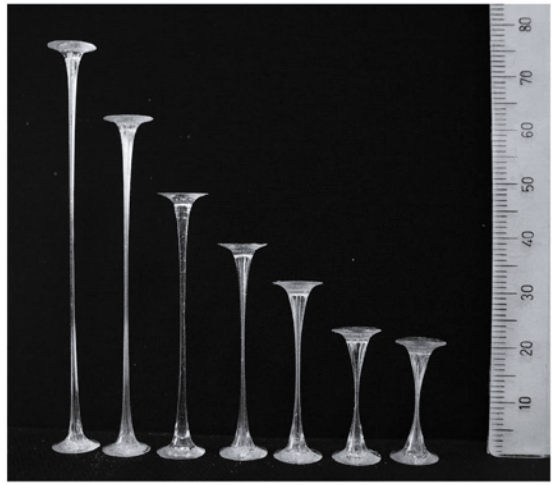
True stress as function of time.
Red line: From theoretical steady extensional viscosity

Stress relaxation of 145kg/mol monodisperse polystyrene in FSR



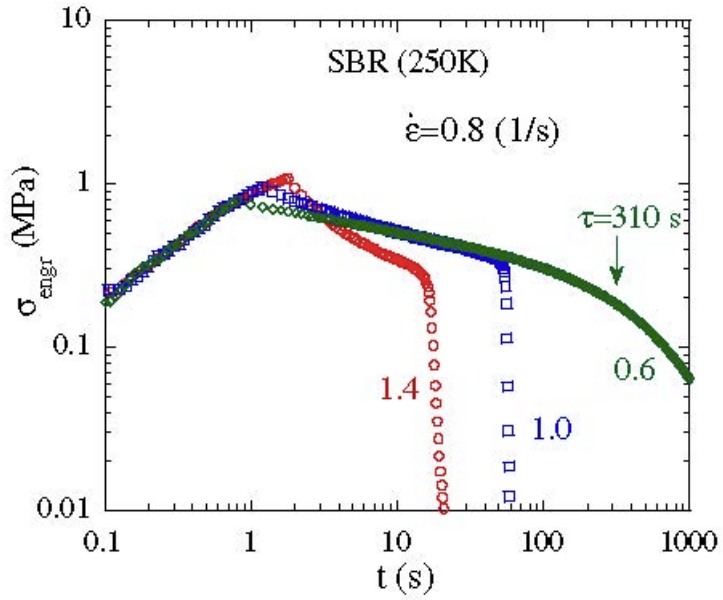
Evolution of filament diameter, *D(t)*, and plate separation, *L(t)*, for an elongational rate of 0.03 s−1 at 120C, stretched for 100 s and then relaxed. D_0=3.40 mm and L_0=8.82 mm.



Quenched polystyrene filaments after cessation of flow.

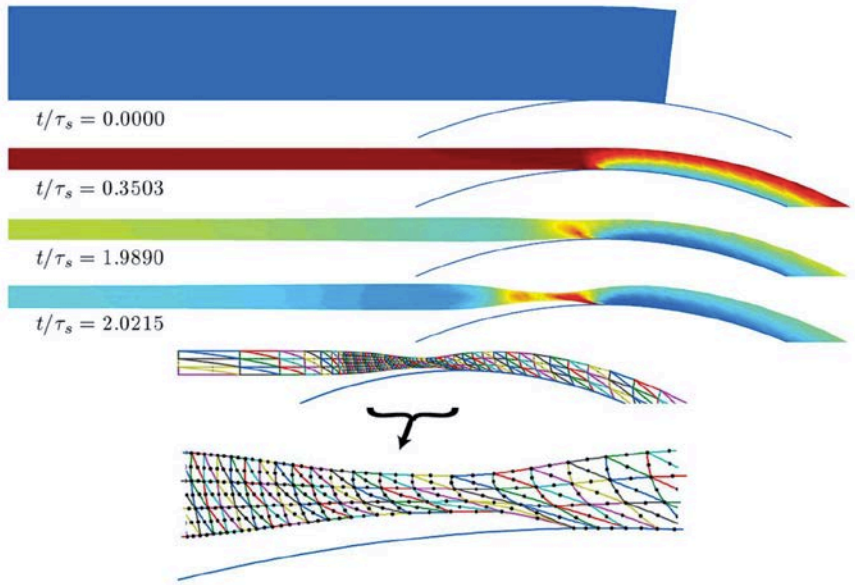
Relaxed 0 s 7 s 47 s 126 s 350 s 3000 s 7000 s before quenching.

Attempt of stress relaxation in 250kg/mol SBR:



Wang, Boukani, Wang and Wang, PRL 99, 237801 (2007)

SER fixture coupled to an Anton Paar MCR 301 rotational rheometer.



Lyhne, Rasmussen and Hassager PRL 102, 138301 (2009)

See also Hoyle and Fielding, JNNFM (2017)

Conclusion so far for the FSR with feed-back control:

There is no immediate conflict between necking and the operation of the FSR for rheometry as long as the filament remains axis-symmetric even for materials with stress saturation!

Care should be exercised with the SER or EVF in stress relaxation of certain materials.

So what could possibly go wrong?

- End-plate slip-off
- End-plate instability
- Highly localized necking
- Filament fracture (tomorrow!)
- Residual solvent (vacuum dry powder if possible – diffusion length!)
- Humidity
- Sample impurity
- Bubbles in sample
- Sample degradation
- Phase separation
- Non-isothermal effects
- Force too low
- Gravitational sagging

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Non-isothermal effects in filament stretching.

Energy balance:

$$\rho C_p \frac{dT}{dt} = \dot{\varepsilon}[\sigma_{zz}(t) - \sigma_{rr}(t)] - \frac{2h_w(T - T_b)}{R}$$

Reformulate in terms of strain:

$$\rho C_p \frac{dT}{d\varepsilon} = [\sigma_{zz}(\varepsilon) - \sigma_{rr}(\varepsilon)] - \frac{2h_w(T - T_b)}{\dot{\varepsilon} a_T R_0} a_T \exp(\varepsilon/2)$$

1 2 3

Terms 1 and 2 give the adiabatic temperature increase. Terms 3 represents the energy loss to surroundings.

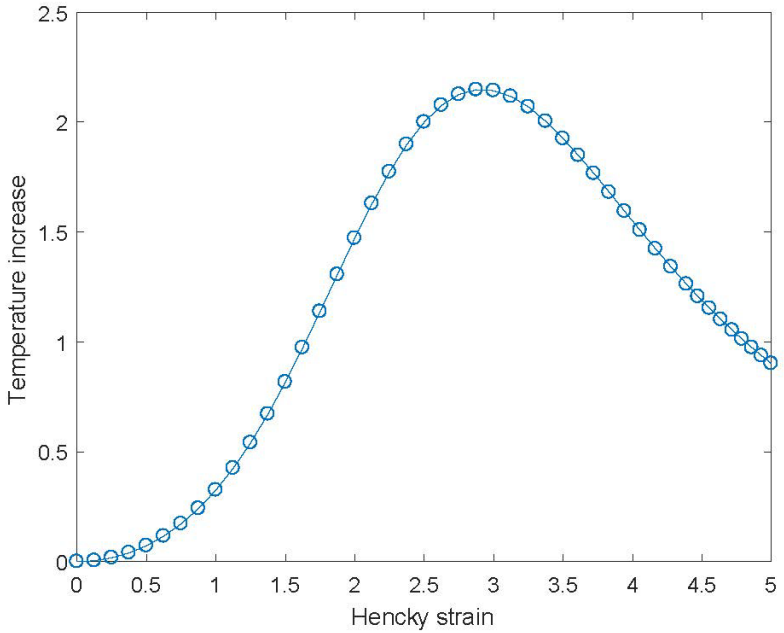
Assume TTS works in non-linear range. Then for example for PS perform experiments at 130C and 150C with same value of $\dot{\varepsilon} a_T$. Since $a_T(130)/a_T(150) \approx 40$ is follows that the heat loss term has about 40 times stronger weight at 130C than at 150C (the experiment lasts 40 times longer). Therefore the temperature increase will be smaller at 130C at the same Weissenberg number. On the other hand the temperature sensitivity of the rheology is greater at 130C than at 150C.

The energy equation can be cast in the alternative form for the temperature increase $y = T - T_b$:

$$\frac{dy}{d\varepsilon} + H\exp(\varepsilon/2)\, y = S(\varepsilon) \tag{1}$$

$$S = \frac{\sigma_{zz} - \sigma_{rr}}{\rho C_p} \qquad H = \frac{2h_w}{\rho C_p \dot{\varepsilon} R_0}$$

The constant H is a non-dimensional measure of the cooling rate or equivalently departure from adiabatic heating. Simulations of (1) seem to indicate that heating effects are small provided $H > 1$.



Example of simulated temperature increase for PS390k in VADER

VADER: $h \approx 80\ \mathrm{W/m^2K}$

So what could possibly go wrong?

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- Sample impurity
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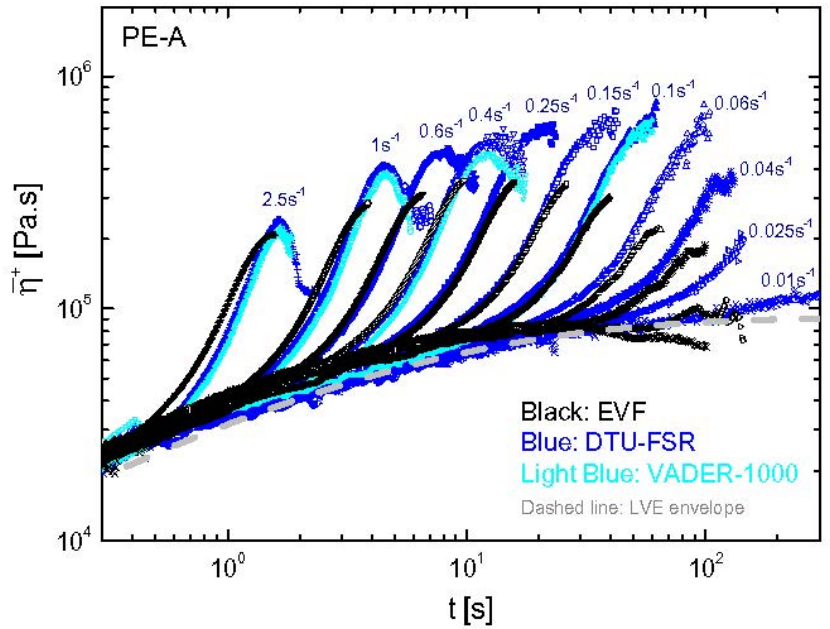
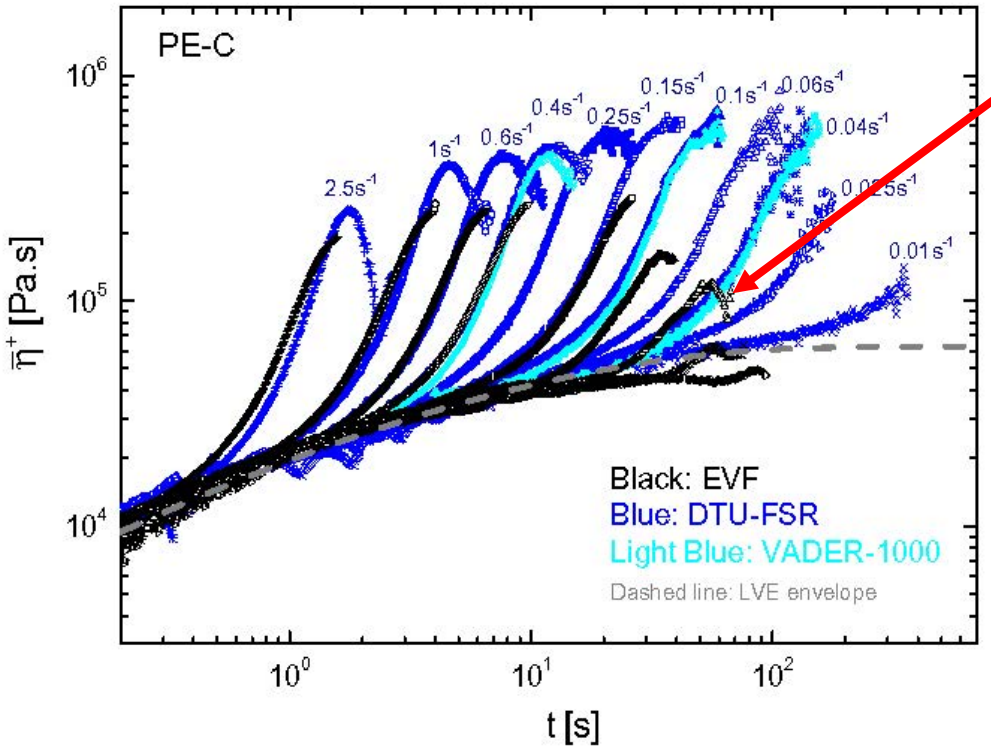
Lower limit on rate in FSR: $\dot{\varepsilon}_s = \frac{\rho g L_0}{6\eta_0} e^{\varepsilon}$

Compare with LVE envelope
(see also EVF)



Huang et al., Rheol. Acta (2016)



Gravitational sagging in EVF fixture

A simple model indicates a characteristic time for sagging $\tau = \frac{\eta_0}{9\varrho g L_0}$ where L_0 is the distance between cylinders. However data indicate that sagging is a serious problem at least up to stretch rates 10 times τ^{-1}.

Conclusion: EVF or SER geometry is much more prone to sagging than the FSR geometry. Possibly because the gravity in EVF and SER is perpendicular to the direction of stretching.