2.341J Lecture 6: Extensional Rheometry: From Entangled Melts to Dilute Solutions

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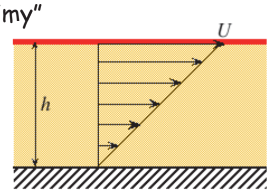
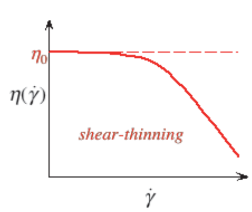
The Role of Fluid Rheology

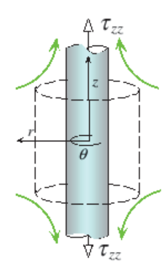
- "Slimy"



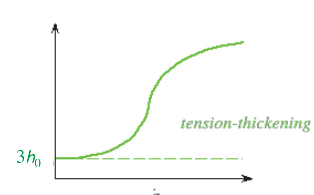
$\tau_{yx} = \eta(\dot{\gamma})\dot{\gamma}_{yx}$



- "Sticky"



$\tau_{zz} - \tau_{rr} = \overline{\eta}(\dot{\varepsilon})\dot{\varepsilon}_{zz}$



- Other manifestations: 'stringy', 'tacky', 'stranding', 'ropiness', 'pituity', 'long' vs. 'short' texture...

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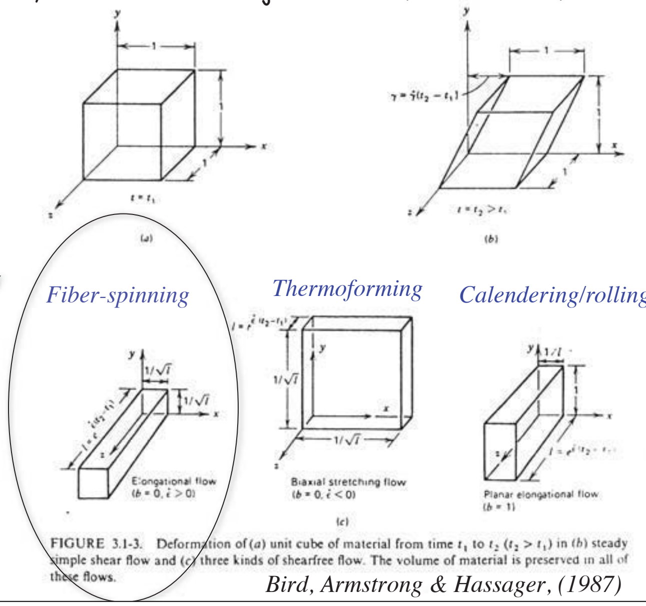
Kinematics of Deformation

- As we have seen, there are three major classes of extensional flow:

Simple Shear

$v_x = \dot{\gamma} y$



Simple Shear-Free Flow

$$v_x = -\tfrac{1}{2}\dot{\varepsilon}_0(1+b)x$$
$$v_y = -\tfrac{1}{2}\dot{\varepsilon}_0(1-b)y$$
$$v_z = \dot{\varepsilon}_0 z$$

b = *flow type parameter*

FIGURE 3.1-3. Deformation of (a) unit cube of material from time t_1 to t_2 ($t_2 > t_1$) in (b) steady simple shear flow and (c) three kinds of shearfree flow. The volume of material is preserved in all of these flows.

Bird, Armstrong & Hassager, (1987)

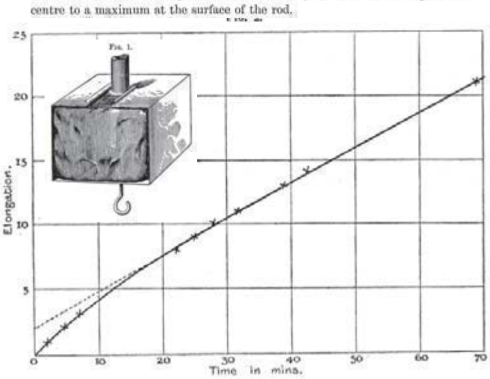
Fred Trouton (one paper on Rheology; 110 years ago)

On the Coefficient of Viscous Traction and its Relation to that of Viscosity.

By Fred. T. Trouton, F.R.S.

(Received February 12,—Read February 22, 1906.)

When experiments are made on the viscous flow of pitch and other substances of similar character, in the form of rods or cylinders, by the torsional method,* it is found that the rate of turning under torsion of these rods is not strictly proportional to the driving couple. Thus the rate of flow of the material under shearing stress cannot be in simple proportion to stress. If it is wished to investigate the exact law connecting the rate of flow with the shearing forces, by means of the torsional method, a complication is at once met with, arising from the fact that the rate of flow in a twisting rod is not of the same value everywhere, but necessarily varies from nothing at the centre to a maximum at the surface of the rod.



Frederick Thomas Trouton, FRS (1863-1922), reproduced from his Biographical Note [2] with permission of the Royal Society of London.

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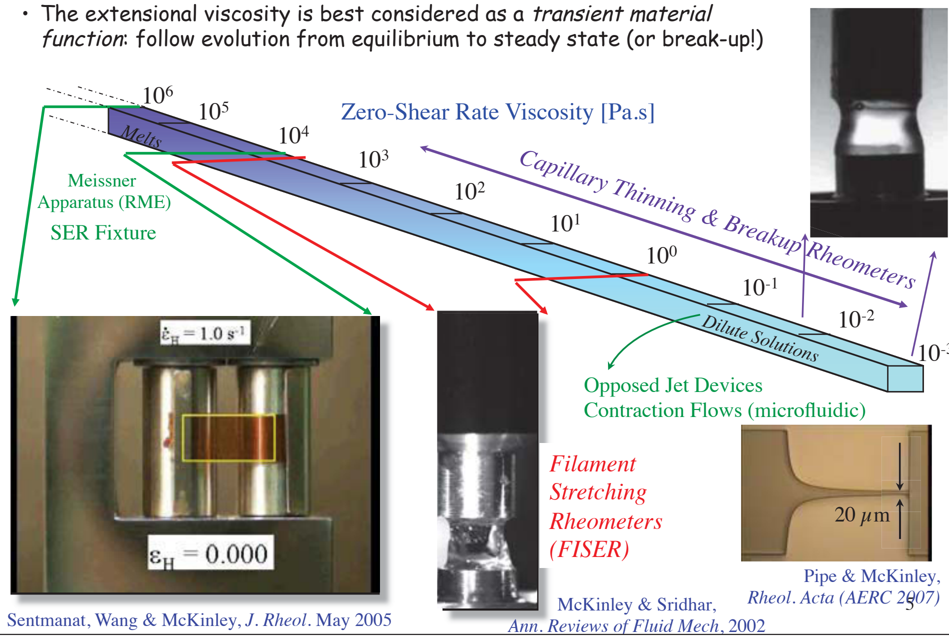
Transient Extensional Rheometry

- The extensional viscosity is best considered as a *transient material function*: follow evolution from equilibrium to steady state (or break-up!)



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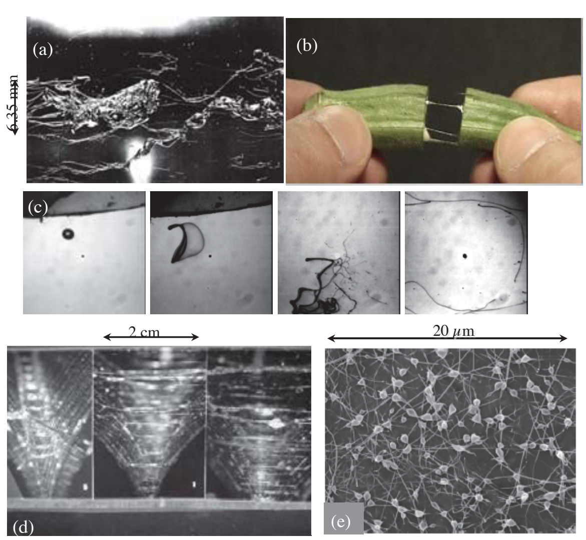
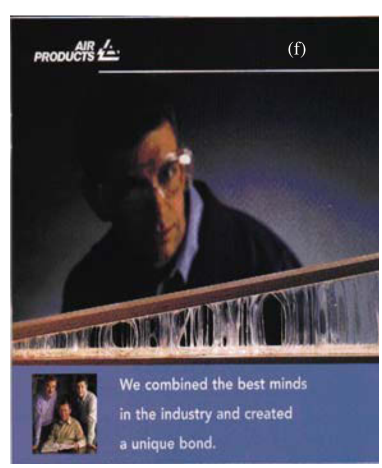
Importance of Extensional Rheology

- Dominates many processing operations
- Effects are frequently transient in nature…





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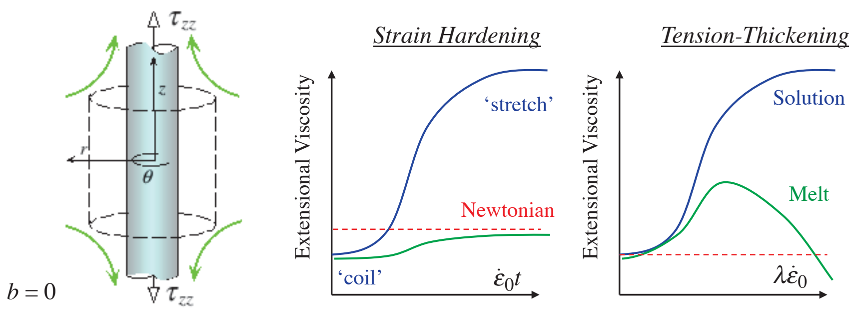
Nonlinear Extensional Viscosity

- Extensional flows are "strong flows" which result in extensive molecular deformation, microstructural alignment and high tensile stresses
  - Applications: fiber-spinning, blow-molding, sheet-molding, extrusion, coating



$$\eta_E^+(\dot{\varepsilon}_0, t) = \left[\tau_{zz}(t) - \tau_{rr}(t)\right] / \dot{\varepsilon}_0$$

$$\lim_{t\to\infty} \eta_E^+(\dot{\varepsilon}_0, t) \to \eta_E(\dot{\varepsilon}_0)$$

Trouton (1906): $\eta_E = 3\mu$

Transient Response

Molecular alignment increases with Hencky strain:

$$\varepsilon(t) = \int_{-\infty}^{t} \dot{\varepsilon}(t')\,dt' = \ln\frac{L(t)}{L_0}$$

Steady-State Response ?

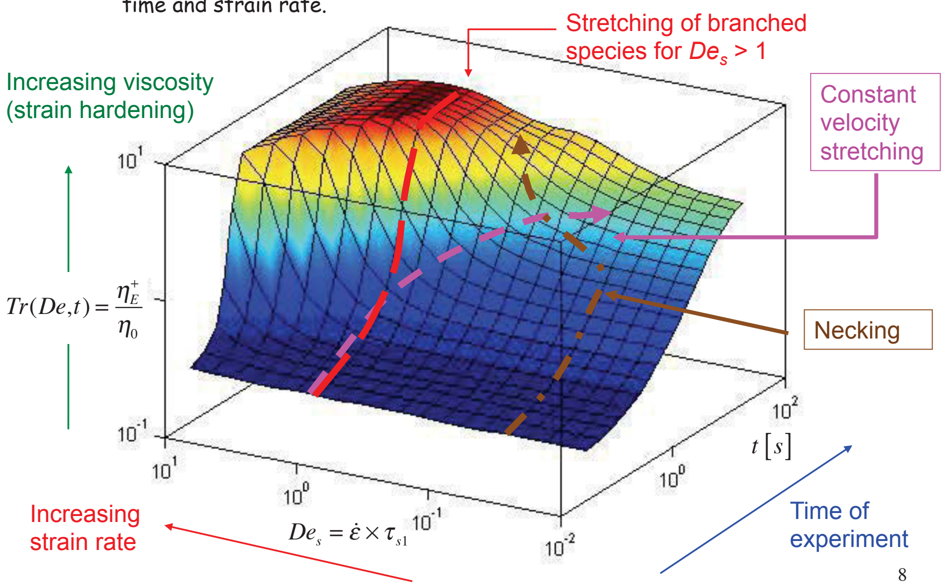
Increasing molecular alignment at higher strain rates

Deborah Number $De = \lambda\dot{\varepsilon}_0$

Tensile Stress Surface

$\eta_E(\dot{\varepsilon}_0, t) \Leftrightarrow Tr(De, \varepsilon)$

- The evolution of the extensional viscosity can be visualized as a function of time and strain rate.



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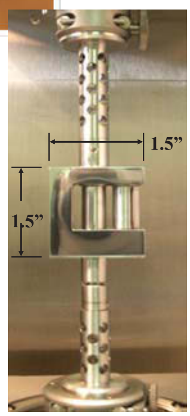
Polymer Melts

Sentmanat, Rheol. Acta (2004)

- <u>**SER** Universal Testing Platform</u>: specifically designed so that it can be easily accommodated onto a number of commercially available torsional rheometers
- TA Instruments version;
  <u>**EVF** = Extensional Viscosity Fixture</u>
- Can be housed within the host system's environmental chamber for controlled temperature experiments.
  - ❑ Requires only 5-200mg of material
  - ❑ Can be used up to temperatures of 250°C
  - ❑ Easily detachable for fixture changeover/clean-up



Validation Experiments: LDPE (BASF Lupolen® 1840H)
(Sentmanat, Wang & McKinley; JoR Mar/Apr (2005)

þM_n = 17,000; M_w = 243,000; M_w/M_n = 14.3
þCH_3/1000C = 23
þVery similar to the IUPAC A reference material
þSame polymer as that used by
Münstedt *et al.*, Rheol. Acta **37**, 21-29 (1998)
'Münstedt rheometer' (end separation method)

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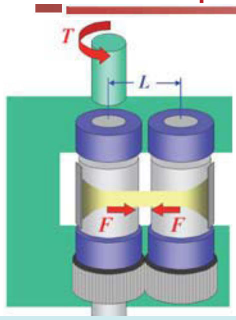
SER Principle of Operation

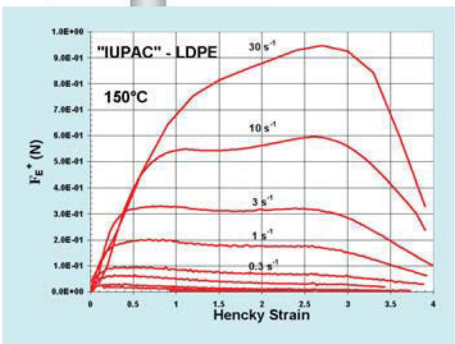


- "Constant Sample Length" Extensional Rheometer
- Ends of sample affixed to windup drums, such that for a constant drum rotation:

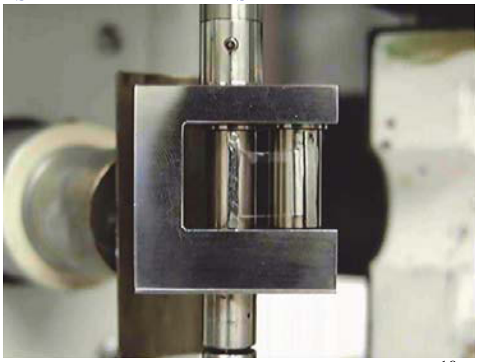
$$\dot{\varepsilon}_0 = 2\Omega R/L$$

- Resulting torque on transducer (attached to housing)

$$T = 2(F + F_{friction})R$$



SER Fixture with ARES Rheometer



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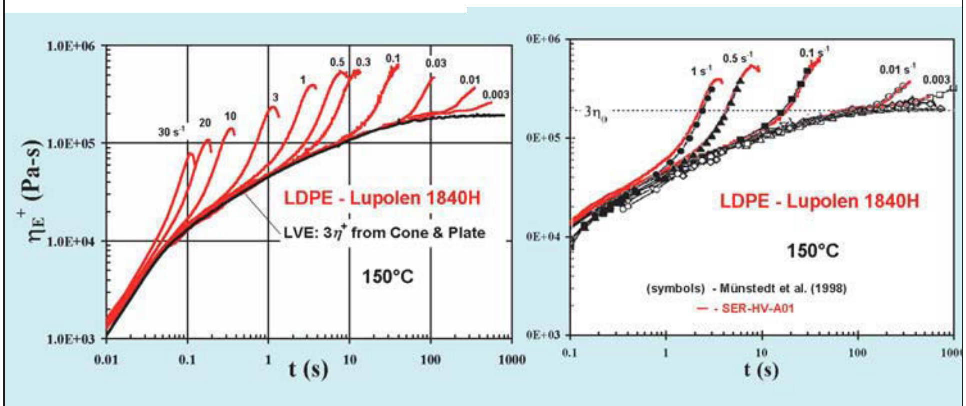
Comparison of LDPE Stress Growth Curves

- Good agreement with LVE response at short times ($t \geq 0.01$ s) $\eta_E^+ = 3\eta^+(t)$
- Increasing strain-hardening and sample rupture at high rates



- The results with the SER (red curves) show excellent agreement with literature results from Münstedt et al. (black symbols & lines)

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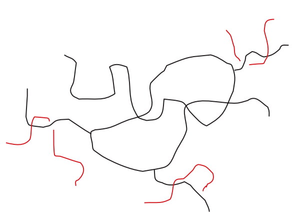
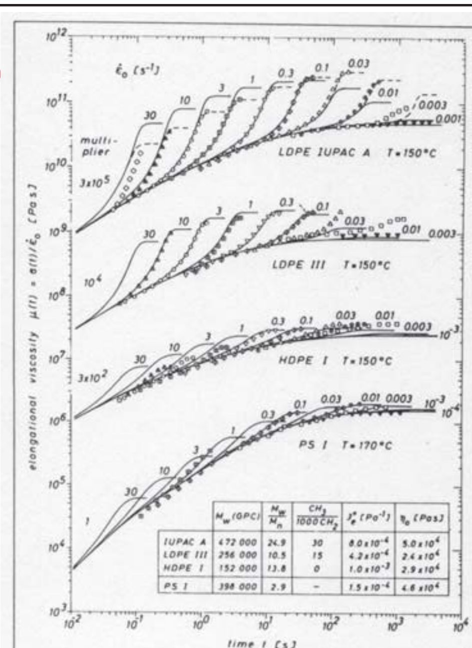
The Role of Chain-Branching

- Extensional stress growth is a strong function of the level of molecular branching.
- Branch points act as 'crosslinks' that efficiently elongate chains and transmit stress…
  - Provided they are long enough to be entangled



H.M. Laun, *Int. Cong. Rheol.* 1980



	M_w (GPC)	M_w/M_n	$CH_3/1000\,CH_2$	J_e^0 [Pa⁻¹]	η_0 [Pa s]
IUPAC A	472 000	24.9	30	8.0×10^{-4}	5.0×10^4
LDPE III	256 000	10.5	15	4.2×10^{-4}	2.4×10^4
HDPE I	152 000	13.8	0	1.0×10^{-3}	2.9×10^4
PS I	398 000	2.9	–	1.5×10^{-4}	4.6×10^4

Comparison of calculated time dependent elongational viscosities with experimental data

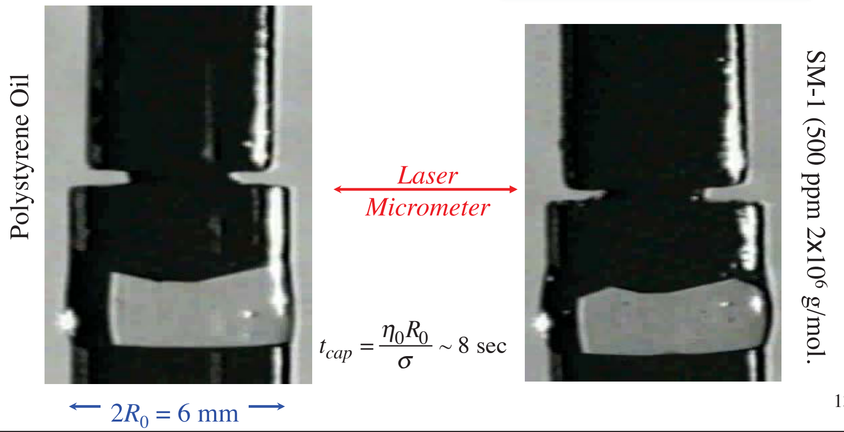
Results for Simple Fluids

- Newtonian Fluids
  - McKinley & Tripathi, *J Rheol.*, 2000

$$\frac{R_{mid}}{R_0} = 0.0709\frac{\sigma}{\eta_s R_0}(t_c - t)$$

- Ideal Elastic Fluids
  - Entov & Hinch, *JNNFM*, 1997

$$\frac{R_{mid}}{R_0} = \left(\frac{GR_0}{\sigma}\right)^{1/3}\exp\left(-\frac{t}{3\lambda_1}\right)$$



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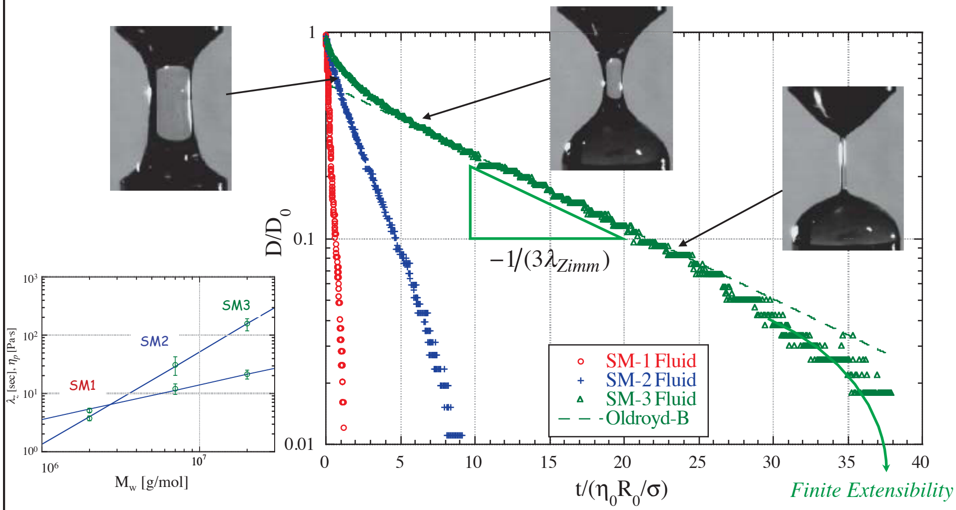
Dilute Polymer Solutions

- Increasing molecular weight delays elasto-capillary breakup
- Measured time-scale agrees quantitatively with Zimm relaxation time



- Important in many biological processes (saliva, spinning of spider silk)

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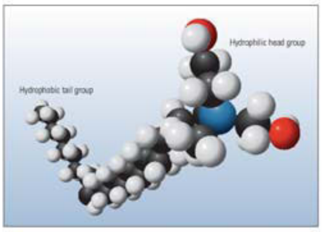
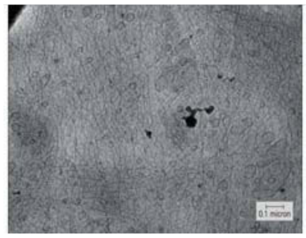
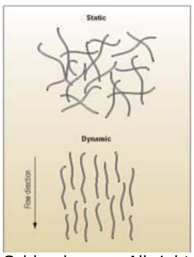
Flow Through Porous Media

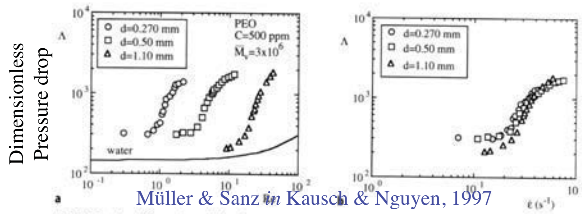
- Solutions of flexible polymers and self-assembling wormlike surfactants are commonly used in *enhanced oil recovery* (EOR) and reservoir fracturing operations.





Kefi *et al*. (2004) Oilfield Review

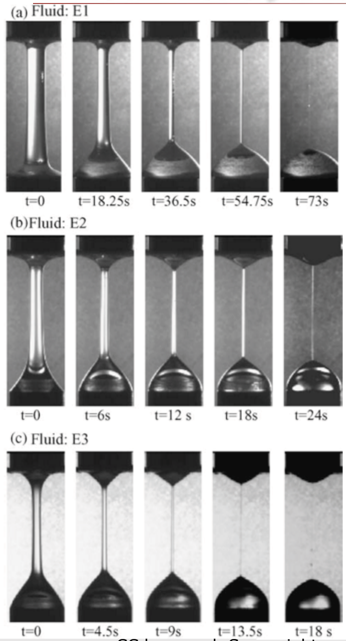




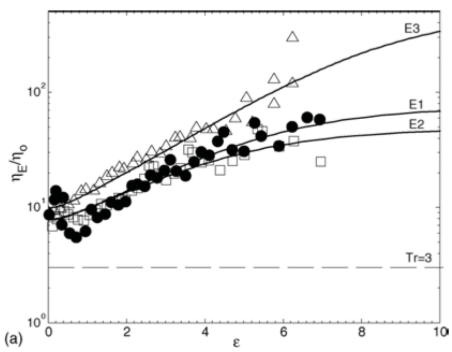
Müller & Sanz *in* Kausch & Nguyen, 1997

Fig. 11.22 a, b. Effect of particle size on resistance coefficient for PEO solutions: **a** as a function of Reynolds number; **b** as a function of average strain rate [10]

Extensional Viscosity of Wormlike Surfactants



- Solutions of EHAC (Schlumberger VES "clearfrac",) in brine



$$D_{mid}(t) \Rightarrow \dot{\varepsilon}(t) = -\frac{2}{D_{mid}}\frac{dD_{mid}}{dt} \Rightarrow \eta_{E,apparent}(t)$$

Yesilata, Clasen & McKinley, *JNNFM* **133**(2) 2006
Kim, Pipe, McKinley; *Kor-Aust Rheol. J*, 2010

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Drag Reduction and Jet Breakup

- Extensional effects from polymer additives can dramatically reduce the extent of turbulent dissipation in high Reynolds number flows
- Applications include:
  - ❑ Wake reduction: sailing, submarines, high-speed swimming (dolphins)
  - ❑ Flow-rate enhancement: storm drains, firehoses...

Union-Carbide "Rapid Water"!!

Enhancement of fire-hose range by addition of small amounts of polyethylene oxide to water. (Photograph, courtesy of Union Carbide Corporation.)

From W.R. Schowalter "Non-Newtonian Fluid Mechanics"(Pergamon) 1978

Commercial Interest in Jet (?) Breakup

New York Times, Dec 4th, 1984

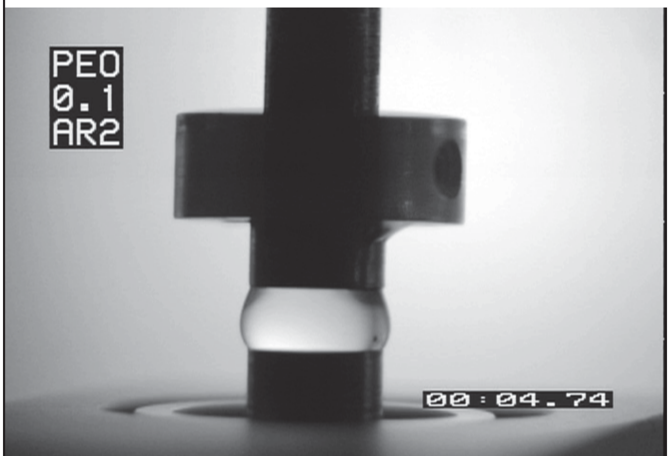
"..if a few pieces of spaghetti are withdrawn gently there is little resistance. But if you jerk it out, it pulls on more than you have hold of. The resistance Is much higher." (*strain-hardening*)

Break Up of Low Viscosity Liquids

- 0.1 wt% PEO (2×10^6 g/mol) in water
  - Standard test fluid; $\eta_0 \approx 1.10\times10^{-3}$ Pa.s
  - Plate diameter R_0 = 3mm; Aspect Ratio L = 2.3

Rayleigh Time Scale

$$t_R \approx \sqrt{\frac{\rho R_0^3}{\sigma}} \approx 0.020\,s$$



Rodd, Cooper-White, McKinley; *Applied Rheol*. **15**(1), 12-27; 2005

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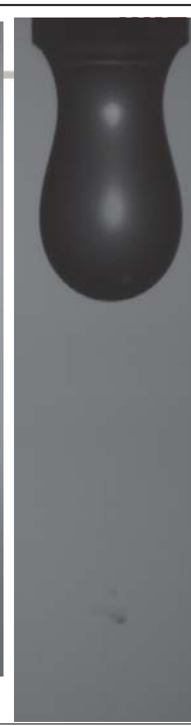
Low Viscosity Fluids

- Critical to Inkjet Printing
  - 100-1000 drops per second
  - Drop volume 2-10 picoliter
  - Eliminate formation of spray and "satellite droplets"
- Identical viscosities and surface tensions
  - One contains Poly(ethylene oxide) (PEO) M_w = 1,000,000 g/mol, c = 100 ppm

$$\frac{\text{Elastic effects}}{\text{Inertio-capillary effects}} \qquad De_0 = \frac{\lambda}{\sqrt{\rho R_0^3/\sigma}} \sim O(1)$$

$$\frac{\text{Viscous effects}}{\text{Inertio-capillary effects}} \qquad Oh = \frac{\eta_0}{\sqrt{\rho\sigma R_0}} << 1$$

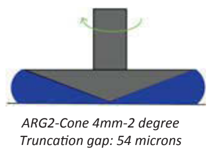
- Viscous effects are never important compared to inertial, capillary, elastic effects!!
  - ***Inviscid Viscoelastic Fluids….***

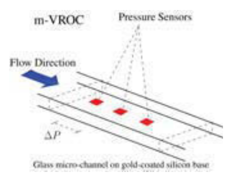


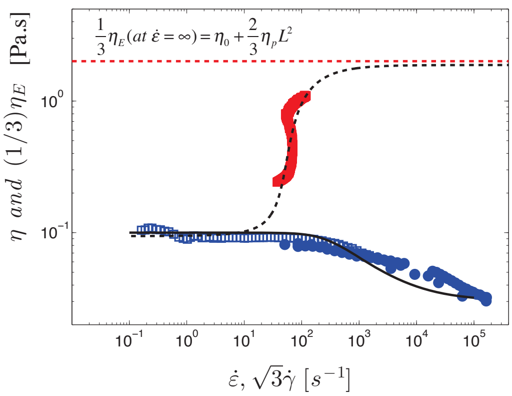
V. Tirtaatmadja, J.J. Cooper-White *et al*., *Phys Fluids* **18** (2006)

Comparing Theory (still to come…) & Experiments

Measure Shear & Extensional Viscosity of a typical commercial paint







FENE-P Model Parameters: (both shear and extensional)

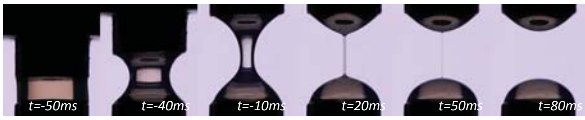
$\eta_0 = 0.1\ Pa.s$

$\eta_s = 0.03\ Pa.s$

$L = 3.8$

$\tau = 0.01\ s$

Capillary Thinning Experiments



- □ Shear Data-ARG2
- ■ Shear Data-mVROC
- ○ CaBER Data-Extensional Viscosity
- —— Shear Viscosity FENE-P Model
- - - Extensional Viscosity FENE-P Model

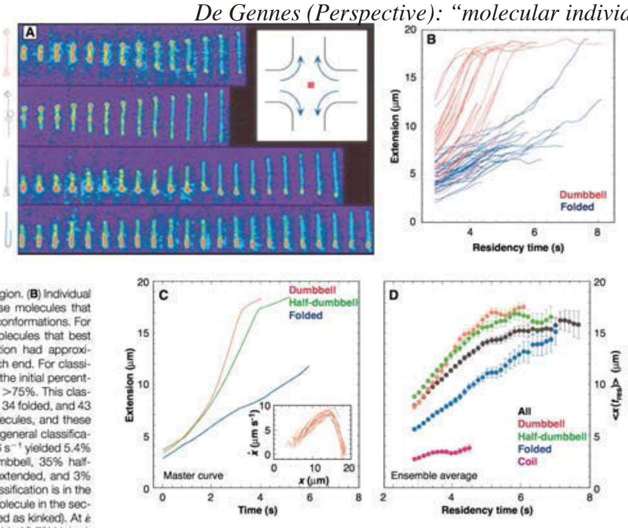
The limit of infinite dilution: single molecule experiments

- Label DNA as a model "supersized" single flexible molecule

The Cross Slot Apparatus: A free-standing stagnation point : Perkins, Smith Chu, *Science* 1997

De Gennes (Perspective): "molecular individualism"

Fig. 2. Conformation-dependent rate of stretching: (**A**) Images of molecular configurations spaced every 0.13 s at the highest strain rate investigated ($\dot{\epsilon}$ = 0.86 s^{-1}). We classified these configurations as (from top to bottom) dumbbell, kinked, half-dumbbell, and folded. The molecular extension of the last image in the first row is 13.9 µm. Sketches of possible molecular configurations are shown on the left. (**Inset**) A schematic illustration of the flow pattern where the red rectangle indicates the observation region. (**B**) Individual traces of x versus t_{res} for those molecules that best typify dumbbell or folded conformations. For classification purposes, the molecules that best typified a dumbbell configuration had approximately symmetric "coils" at each end. For classification as folded, we required the initial percentage of the folded section to be >75%. This classification yielded 30 dumbbells, 34 folded, and 43 half-dumbbells out of 992 molecules, and these molecules were reanalyzed. A general classification of all molecules at $\dot{\epsilon}$ = 0.86 s^{-1} yielded 5.4% kinked, 24% folded, 20% dumbbell, 35% half-dumbbell, 8.3% uniform, 5% extended, and 3% coils where precedence for classification is in the listed order (for example, the molecule in the second row of Fig. 2A was classified as kinked). At $\dot{\epsilon}$ = 0.51s^{-1}, this classification yielded 3.7% kinked, 10% folded, 31% dumbbells, 33% half-dumbbells, 9.8% uniform, 3.7% ex-



The rate of extension $\dot{x}$ for each dumbbell molecule in Fig. 2B was calculated by

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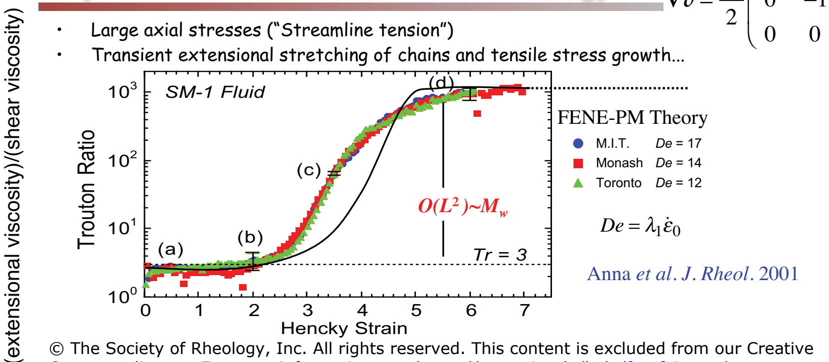
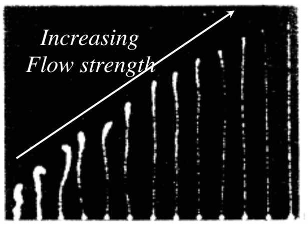
Polymer Additives and Extensional Rheology

$$\nabla v = \frac{\dot{\varepsilon}_0}{2}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +2 \end{pmatrix}$$

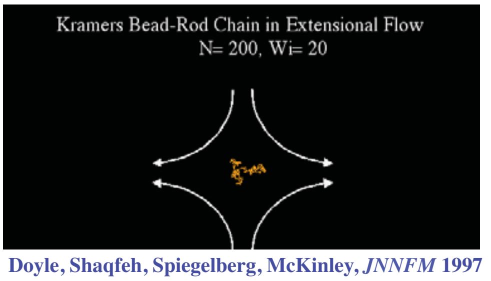
- Large axial stresses ("Streamline tension")
- Transient extensional stretching of chains and tensile stress growth…



Anna *et al*. *J. Rheol*. 2001



Smith, Chu, Larson, *Science* 1997

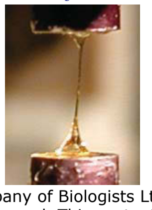


Doyle, Shaqfeh, Spiegelberg, McKinley, *JNNFM* 1997

Summary

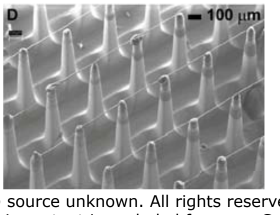
- A number of well-characterized instruments now exist for performing measurements of transient extensional rheometry for fluids spanning range from dilute solution to the melt
  - 'constant volume' devices: e.g. FISER, CABER, Münstedt Rheometer
  - 'constant length' devices: e.g. EVF, SER, RME = Meissner Rheometer
- Understanding the kinematics imposed by the instrument and the dynamics of filament evolution is essential in order to extract the true material functions
- Challenges still remain:
  - Theory for filament deformation and rupture at very high strains
  - Measurements for 'weakly elastic' materials "non-spinnable materials"
  - Understanding and exploiting extensional viscosity on the microscale:

N. Kojic et al.



L. Mahadevan, Harvard

R. Cohn, U. Louisville



2.341J / 10.531J Macromolecular Hydrodynamic
Spring 2016