Rheological behaviour of molten polymer, models and experiments

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Center for Material Forming

Polymer, pastes, composites, metals

Industrial partnership

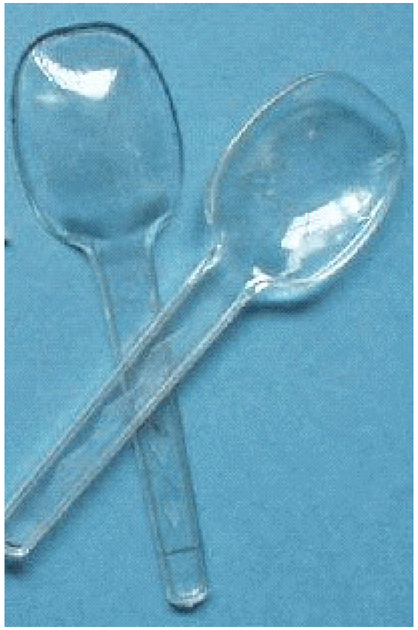
Polymer processing

Examples of polymers

Polyethylene

Polypropylene

Polystyrene



Phenomenology

Density : ~water

« **Melting** » **temperature :** ~150°C (PE, PP, PS)

Viscosity : ~10^6 water

« **Internal** » **structure :** remains/relaxes over differents timescales

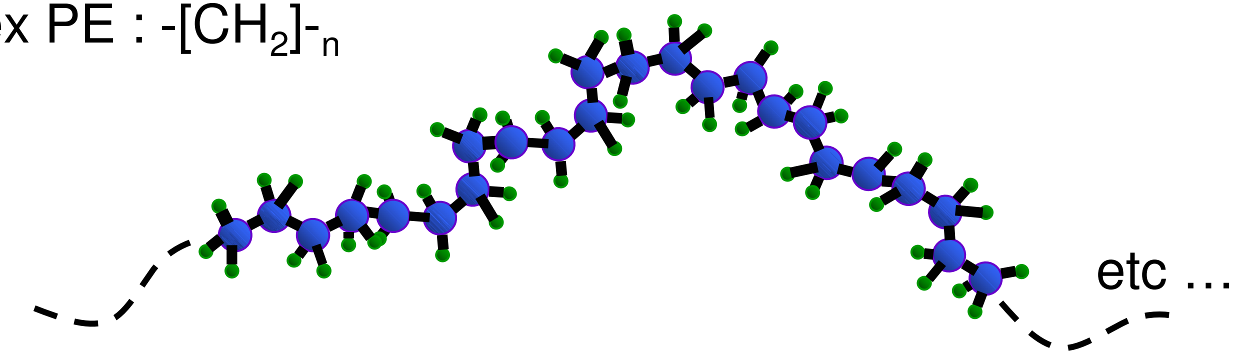
→ **memory, elasticity**

« **High** » **temperature :** viscous + elastic

→ **visco-elastic fluid**

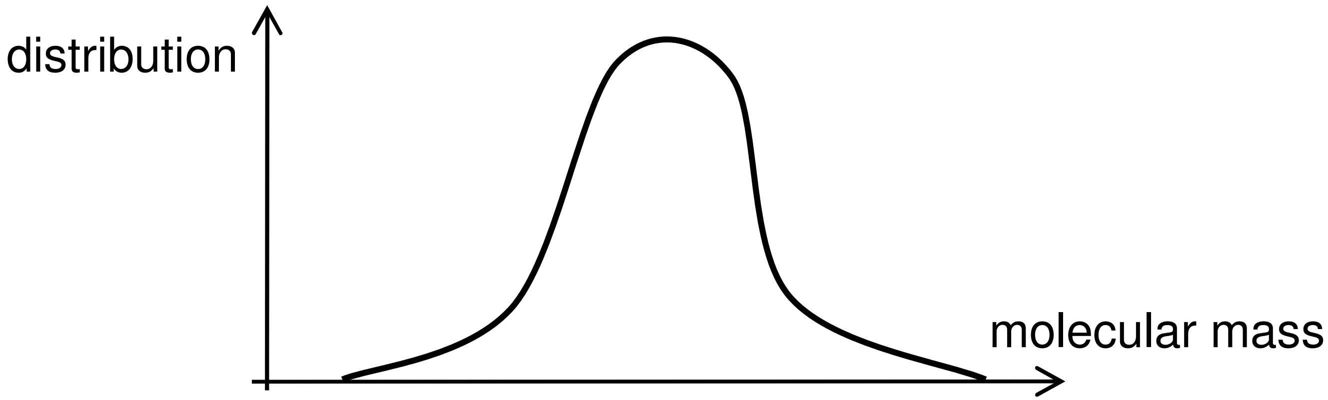
« Internal » structure ?

Macromolecules, ex PE : $-[CH_2]-_n$



… 10 000 CH_2 groups ; 10^{18} molecules per cm^3 ; very flexible

Polydispersity :



Research topics

Link between structure and rheology

Viscoelastic flows modelling

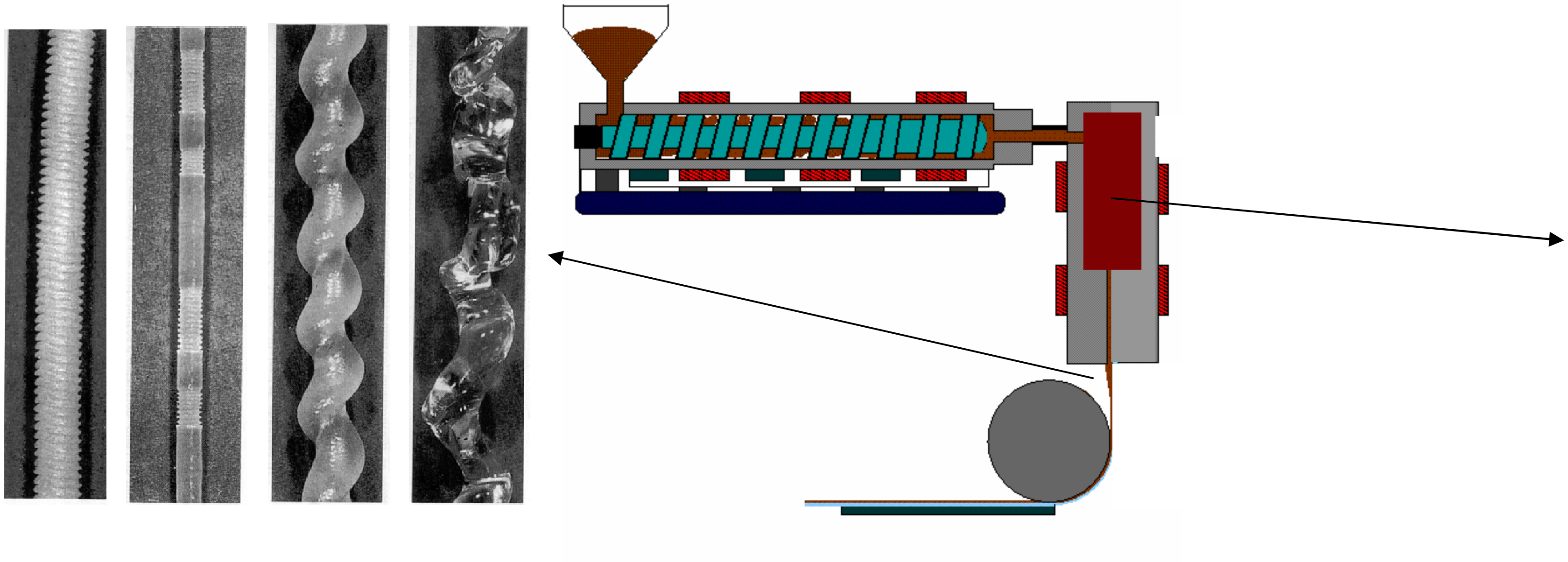
→ Polymer processing flows :

- large deformations
- large deformation rates
- complex geometries

How pertinent are viscoelastic constitutive equations ?

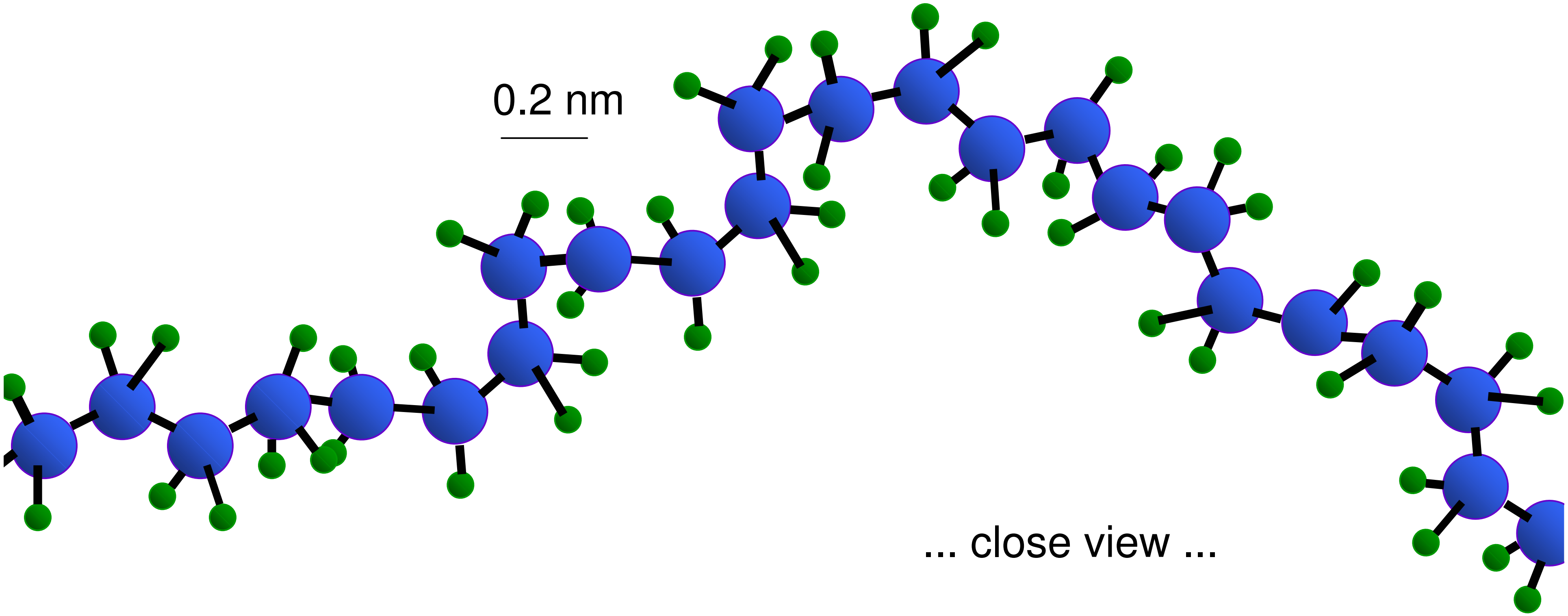
Polymer processing flows: extrusion

flow instabilites



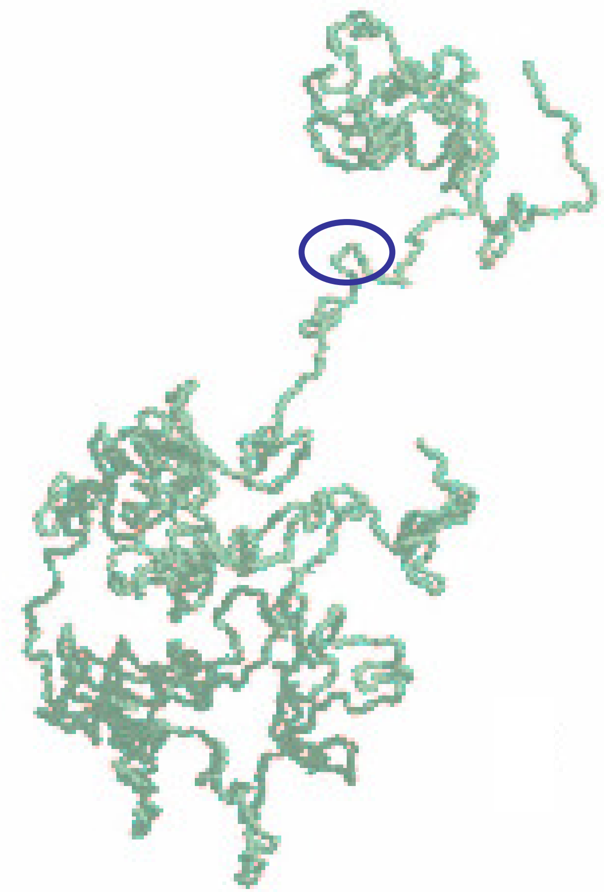
Which material ?

macromolecule :



Which material ?

macromolecule :

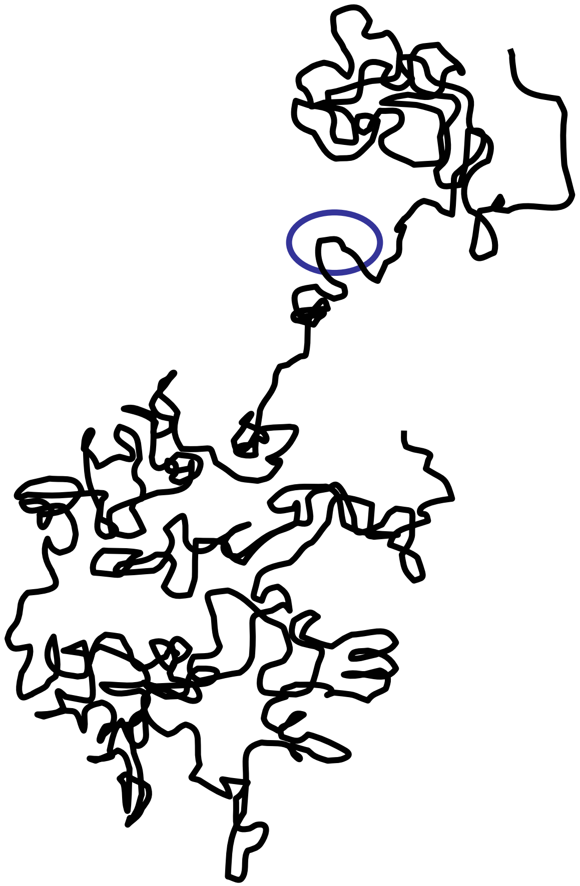


... further away.

20 nm

Which material ?

macromolecule :



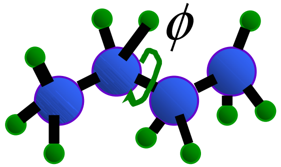
... further away :

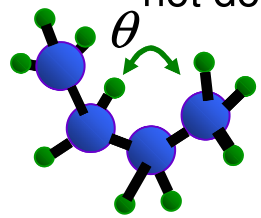
free segments

20 nm

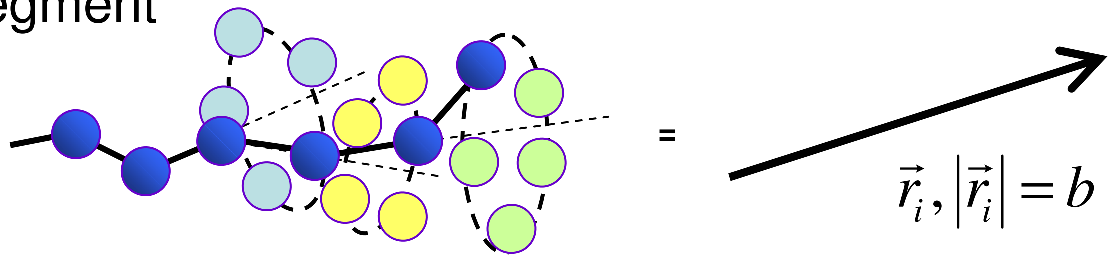
Flexible chain

Degrees of freedom



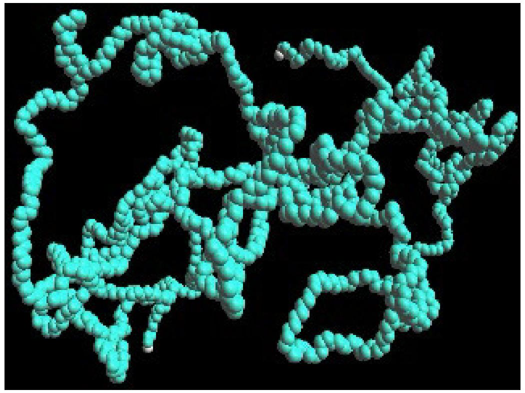


« Free » equivalent segment

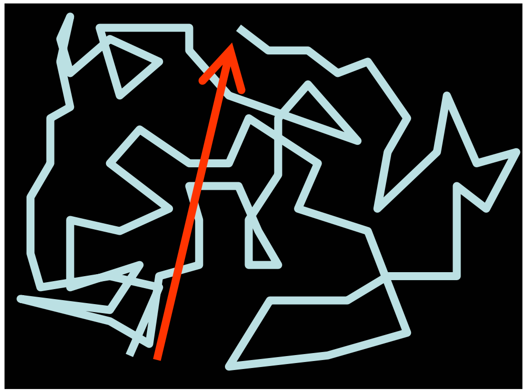


$\vec{r}_i, |\vec{r}_i| = b$

Conformation = { $\vec{r}_i$ }= "random flight" of N segments of length b

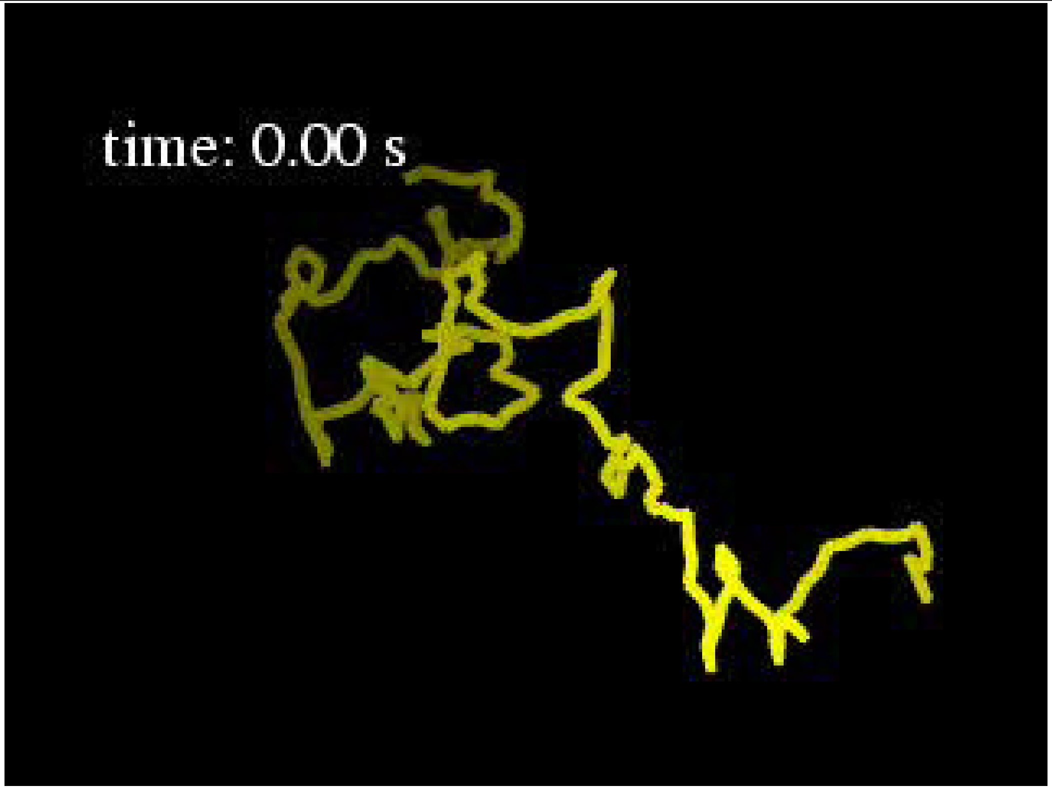


↔



$\vec{R} = \sum \vec{r}_i$

Entropic elasticity



$$\vec{R} = \sum \vec{r}_i$$

Energy kT

$$\vec{F}(\vec{R}) \cong \frac{kT}{R_0} \frac{\vec{R}}{R_0}$$

Relaxation: diffusion in the space of $\vec{R}$

Viscoelasticity

Relaxation of entropic elastic forces

Relaxation processes involve:
- which object (chain, subchain) ?
- which time ?
- which distance/which topology ?

Role of the flow ?

Overview:
- Scalings
- Linear viscoelasticity/elastic dumbell
- Topological constraints, tube model
- Treatment of non-linear deformation (flow)
- Some examples

Entropic elasticity

Statistical conformation = $\vec{R} = \sum \vec{r}_i$ = end-to-end vector

Mean value : $\langle \vec{R} \rangle = 0$

Mean square : $\langle \vec{R}^2 \rangle = \langle (\sum \vec{r}_i)(\sum \vec{r}_j) \rangle = Nb^2 = R_0{}^2$

Gaussian density distribution : $\psi(\vec{R}) = \left(\frac{3}{2\pi R_0{}^2} \right)^{\frac{3}{2}} e^{\left(\frac{-3R^2}{2R_0{}^2} \right)}$

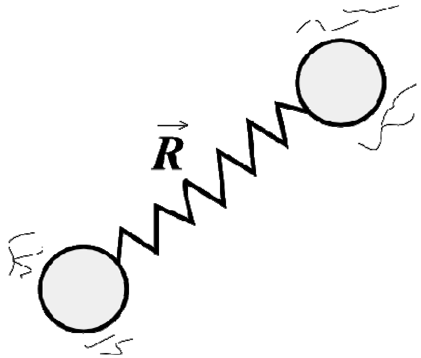
Statistical entropy : $S = k \ln\left(\Omega_{tot} \psi(\vec{R})\right)$

Thermodynamic force : $\vec{F}(\vec{R}) = -T \frac{dS}{d\vec{R}} = \frac{3kT}{R_0{}^2} \vec{R}$

Doi-Edwards 1986

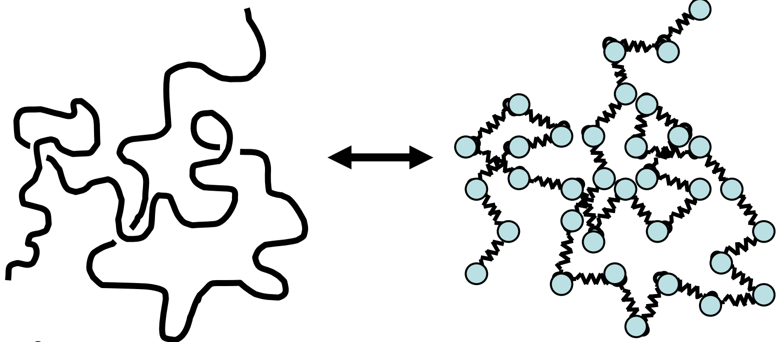
Elastic dumbbell

Force: $\vec{F}(\vec{R}) = \dfrac{3kT}{R_0^{\,2}}\vec{R}$



Spring constant: $\dfrac{3kT}{R_0^{\,2}} = \dfrac{3kT}{Nb^2}$

Einstein relation: $D = \dfrac{kT}{\zeta} = \dfrac{kT}{N\zeta_b}$

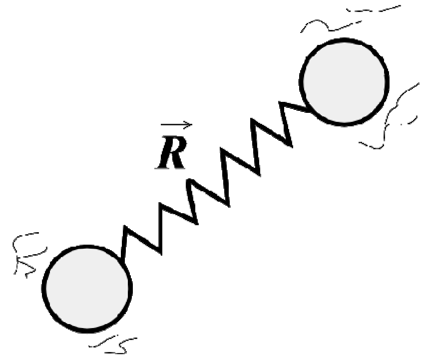


Relaxation time: $\theta = \dfrac{R_0^2}{D} = \dfrac{N^2 b^2 \zeta_b}{kT} = N^2\theta_0$

Doi-Edwards 1986

Macroscopic scale

Force: $\vec{F}(\vec{R}) = \frac{3kT}{R_0^{\ 2}}\vec{R}$



ν chains per unit volume

νR chains per unit surface

Stress: $\nu \frac{3kT}{R_0^{\ 2}}\vec{R}^2 = 3\nu kT \frac{\vec{R}^2}{R_0^{\ 2}}$

Elastic modulus: $G_0 = \nu kT$

Relaxation time: $\theta \propto N^2$

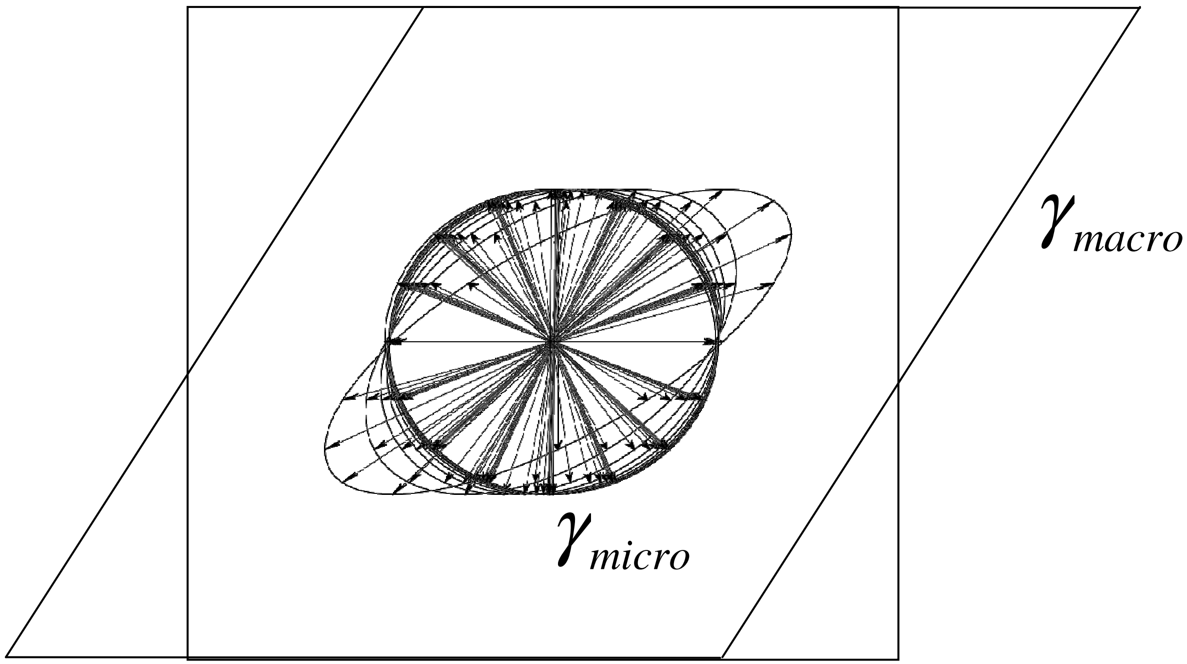
Doi-Edwards 1986

Relaxation function : experiment 1 on viscoelasticity

Response to a sudden macroscopic deformation

Stress decreases with time / Deformation / Sample stress = G_0 x microscopic strain γ_{micro} decreases

(the arrows are proportional to the chains oriented and stretched in their direction)



Whatever γ_{macro} : G(t) is constant (same ratio stress/strain)

Relaxation function : experiment 1 on viscoelasticity

Stress relaxation is faster when far from equilibrium

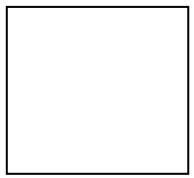
$$\frac{d\tau}{dt} = -\frac{1}{\theta}\tau$$

$$\frac{d\gamma_{micro}}{dt} = -\frac{1}{\theta}\gamma_{micro}$$

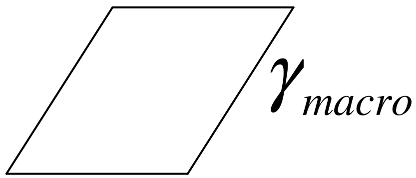
Linear (separable) response of a simple viscoelastic fluid

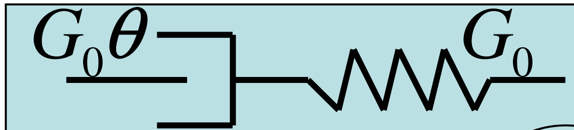
Step strain :

t=0 rest,

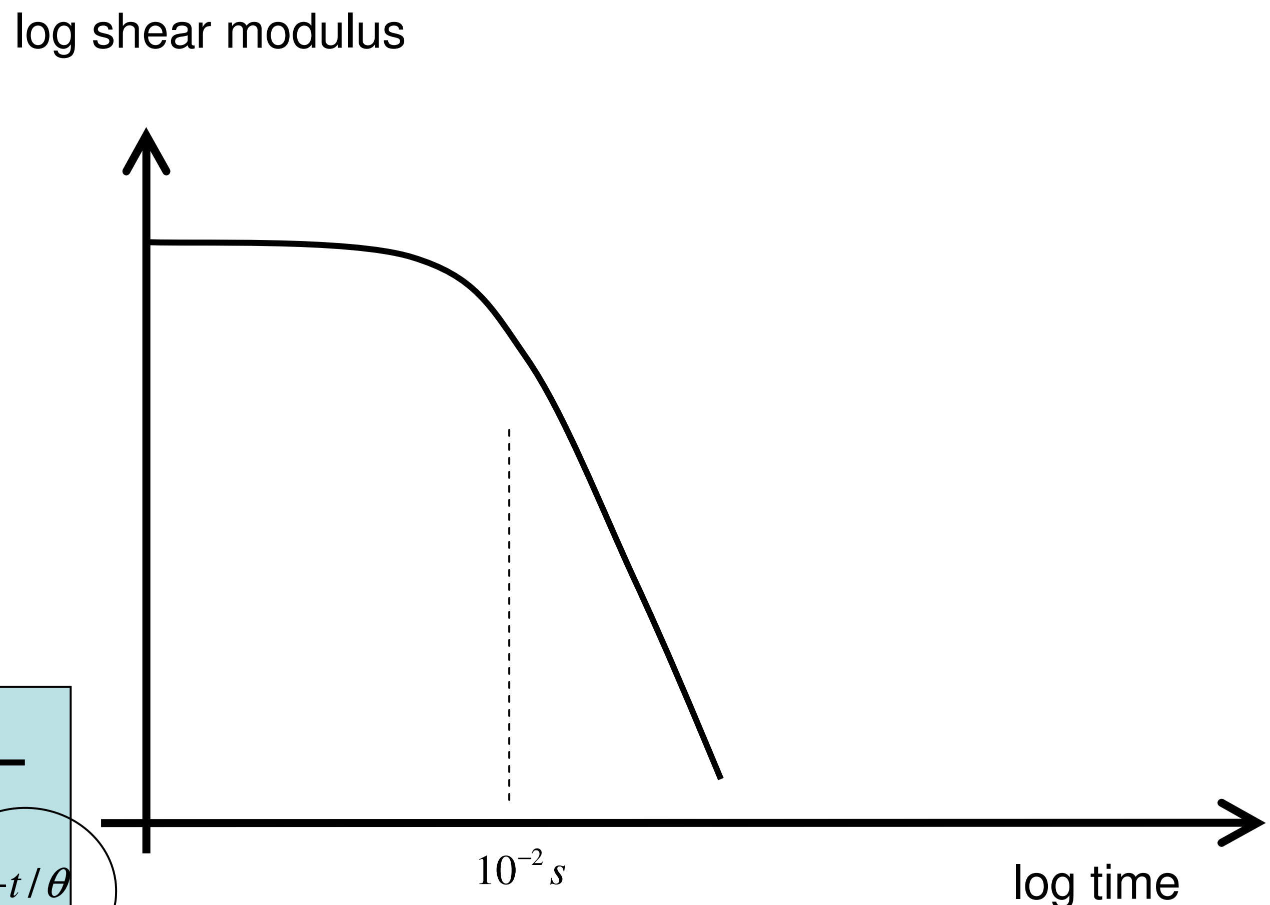


t>0 constant shear





$$\tau / \gamma = G(t) = G_0 e^{-t/\theta}$$

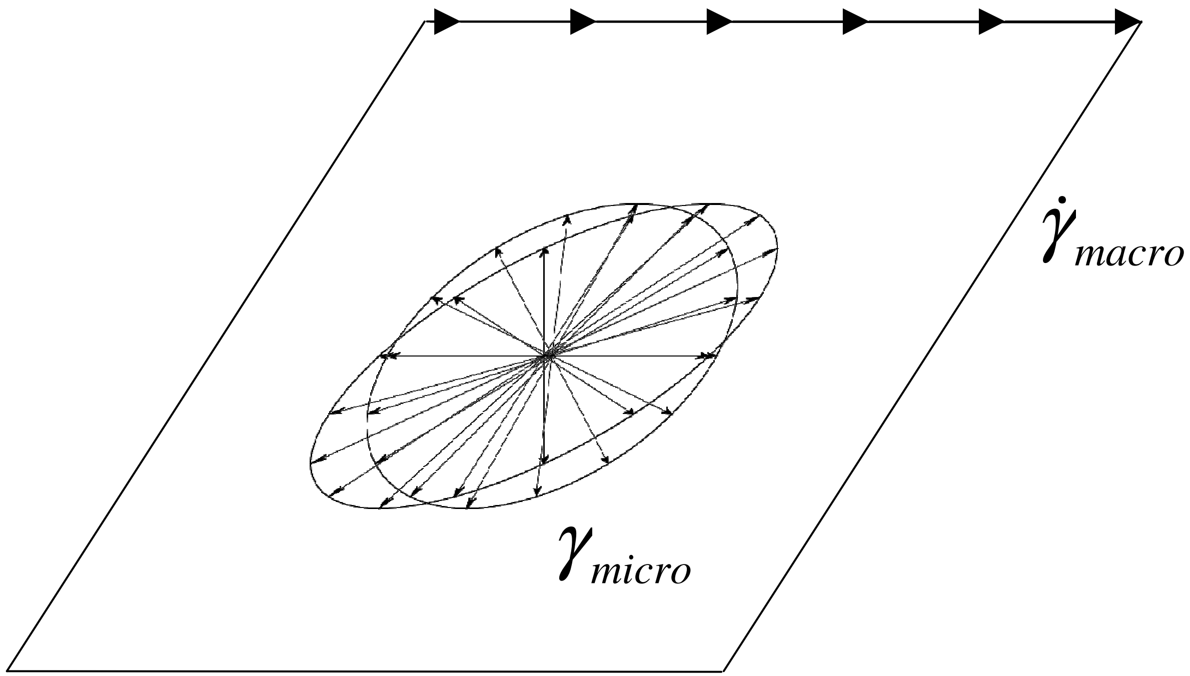


fraction of unrelaxed segments

Viscosity function : experiment 2 on viscoelasticity

Response to a continuous macroscopic deformation

Stress = $\tau = G_0 \dot{\gamma}_{macro} \theta$, $\gamma_{micro} = \dot{\gamma}_{macro} \theta$



Viscosity function : experiment 2 on viscoelasticity

Response to a continuous macroscopic deformation

drag relax

$$d\gamma_{micro} = \dot{\gamma}_{macro} dt - \frac{1}{\theta} \gamma_{micro} dt$$

Stationary : $\gamma_{micro} = \theta \dot{\gamma}_{macro}$

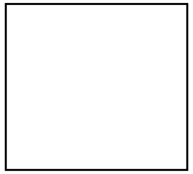
Stress : $\tau = G_0 \gamma_{micro} = G_0 \theta \dot{\gamma}_{macro}$

Viscosity : $\eta = G_0 \theta$

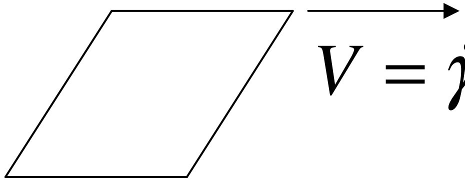
Response in steady shear

Steady shear:

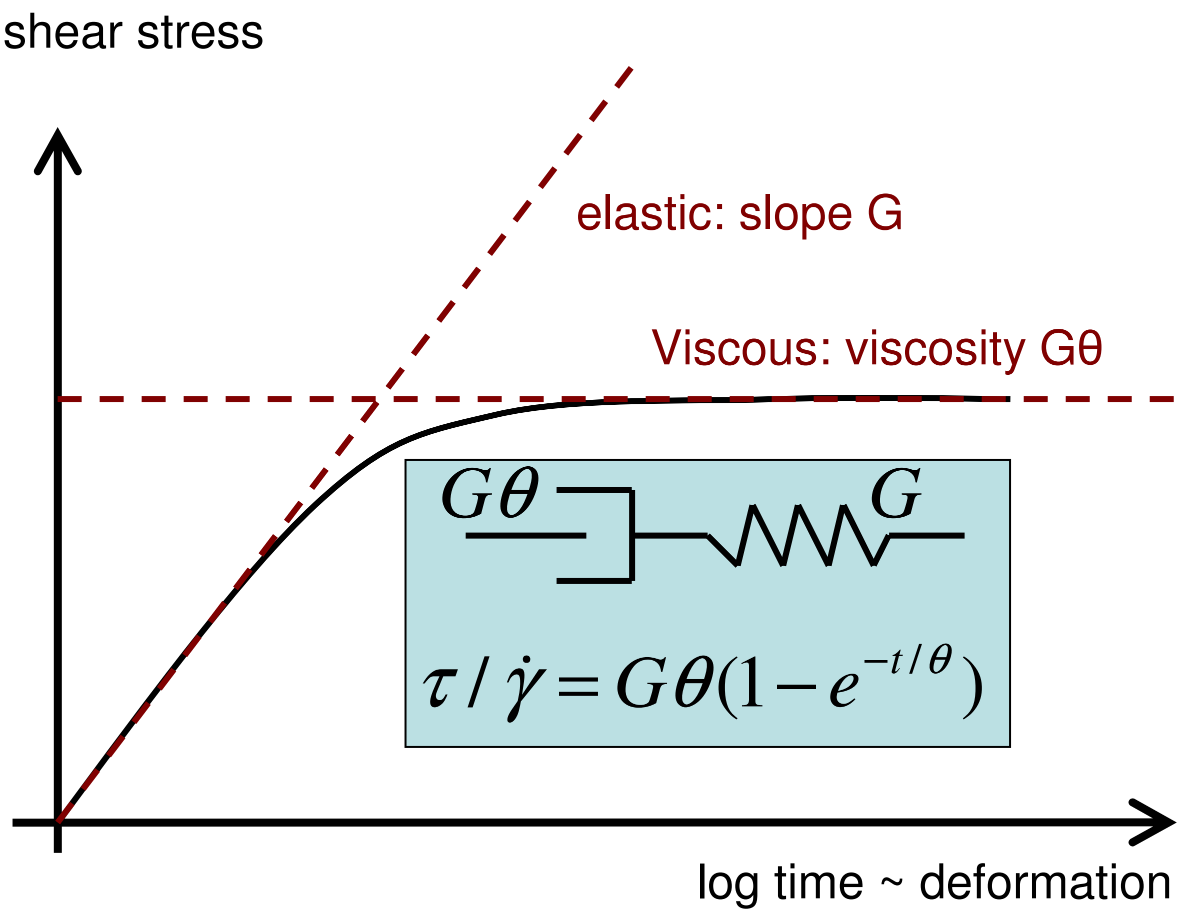
t=0 rest,



t>0 onstant shear rate,

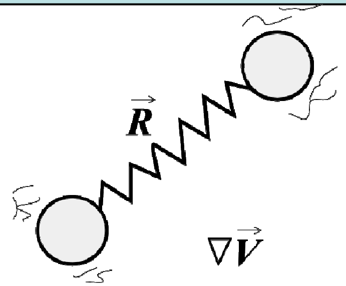


$V = \dot{\gamma} t$



Steady shear

Shear rate: $\dot{\gamma}$



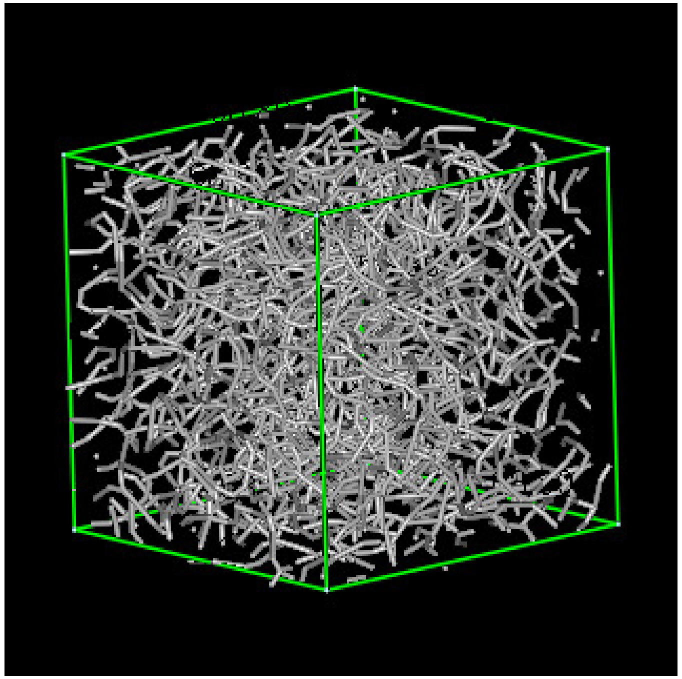
Drag (affine deformation)/relaxation balance → stress: $\tau = G_0 \dot{\gamma} \theta$

Viscosity: $\eta = G_0 \theta = \nu N b^2 N \zeta_b$

Weissenberg effect:

Long chains are *entangled*

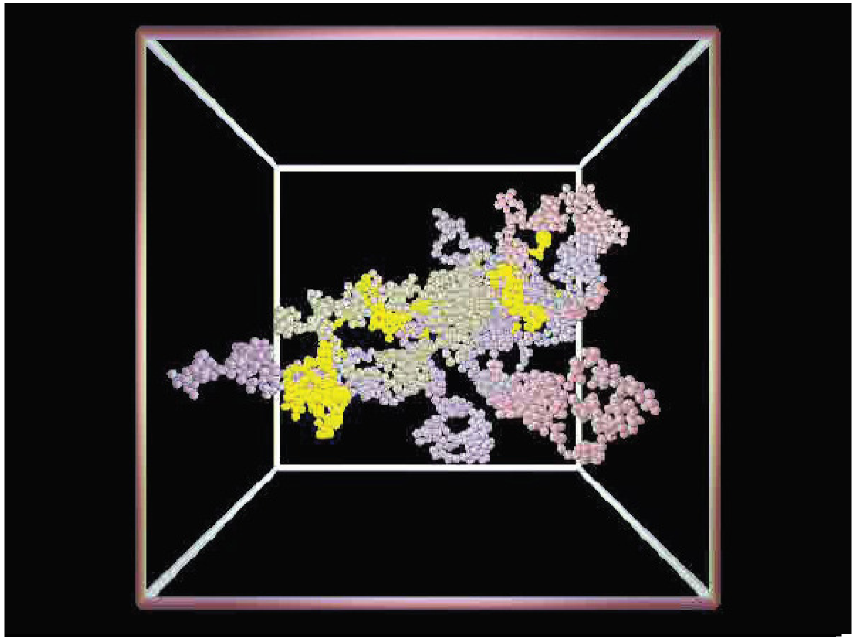
Entanglements : topological constrains between chains



Courtesy K. Kremer, from Everaers et al., Science, 2004

Long chains are *entangled*

Entanglements: topological constrains between chains

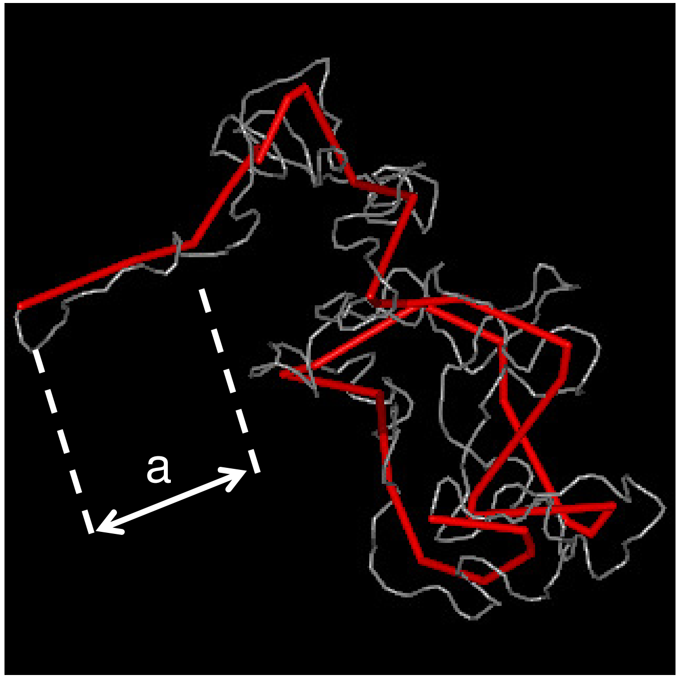


Courtesy K. Kremer, from Everaers et al., Science, 2004

Long chains are *entangled*

Entanglements: topological constrains between chains

$$\vec{F} \cong \frac{kT}{R_0}\frac{\vec{R}}{R_0} \cong \frac{kT}{a}$$



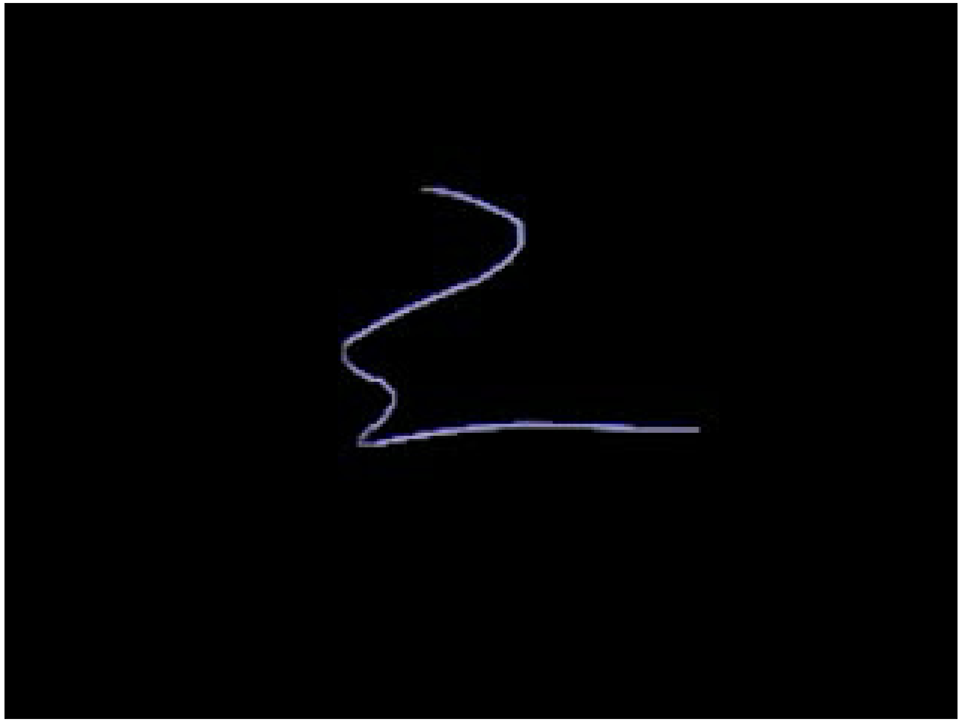
Courtesy K. Kremer, from Everaers et al., Science, 2004

Long chains are *entangled*

Entanglements: topological constrains between chains

Relaxation: diffusion out of a « tube », reptation dynamics

➔ convenient mean field model (to make self-similar !)



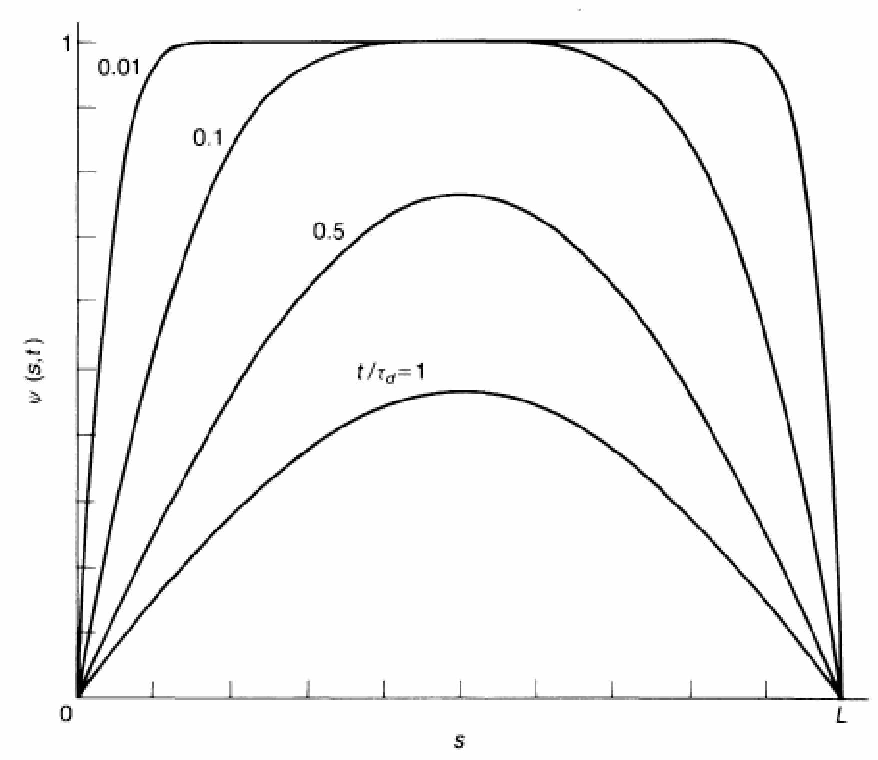
From T.C.B. McLeish group, Leeds University

Long chains are *entangled*

Entanglements: topological constrains between chains

Relaxation: diffusion out of a « tube », reptation dynamics

Tube survival probability *Doi-Edwards 1986*



Long chains are *entangled*

Entanglements: topological constrains between chains

Tube length L = Za, scales as N

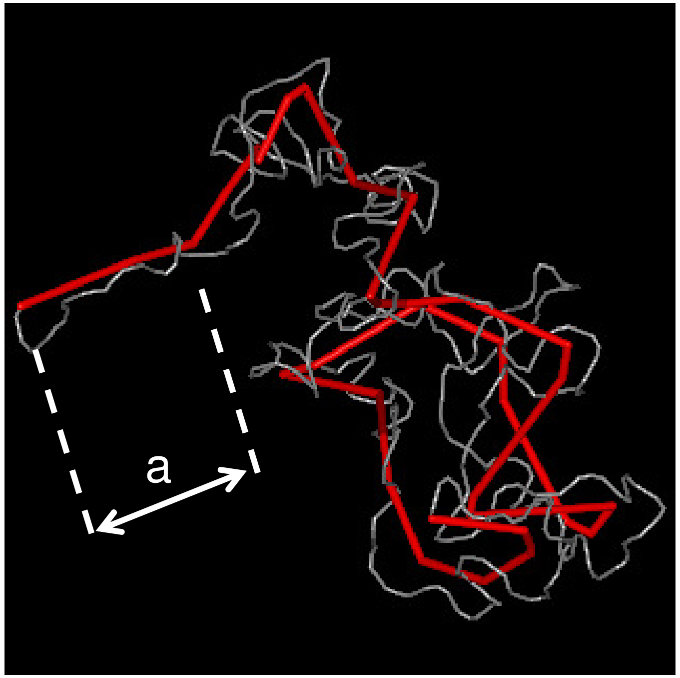
Disengagement time: $\theta_d = \frac{L^2}{D} \propto \frac{N^2 N \zeta_b}{kT} \propto N^3 \theta_0$

$a = 10^{-9}\, m$

$Z = 5 - 50$

$N / Z = 25$

$\theta_{Z=1} \approx 0.1 s$

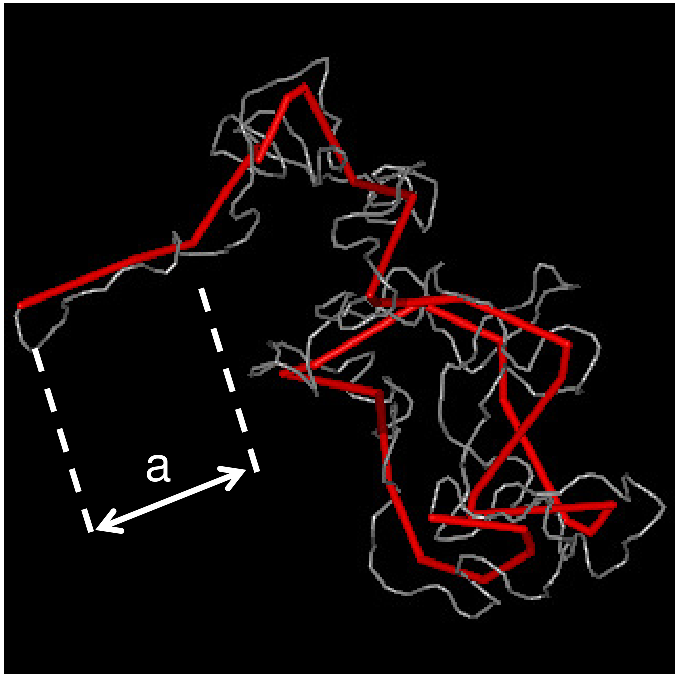


Macroscopic scale

Elastic modulus: $G_{N0} = \nu_e kT$

Relaxation time: $\theta_d \propto N^3$

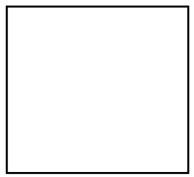
Tension on each segment: $\dfrac{3kT}{a}$



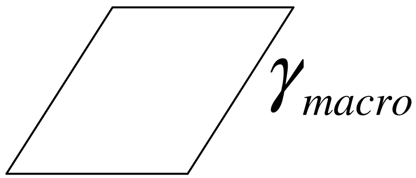
Linear response of an entangled polymer melt

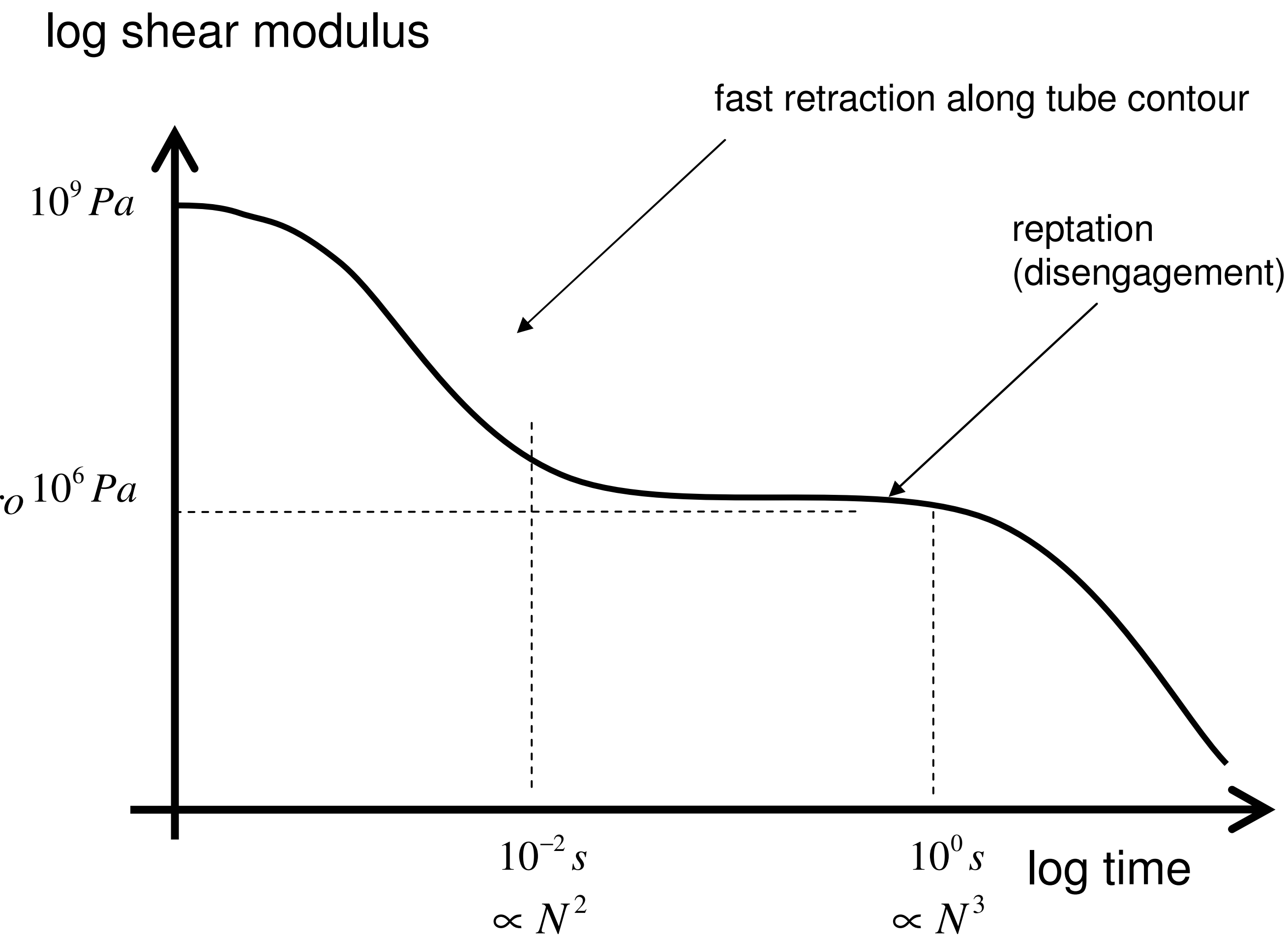
Step strain :

t=0 rest,



t>0 constant strain





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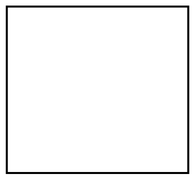
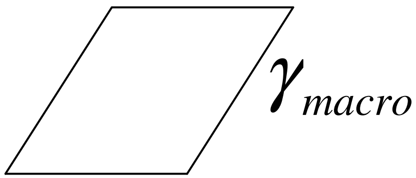
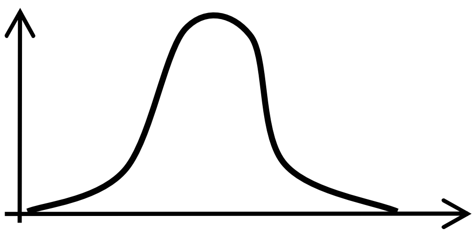


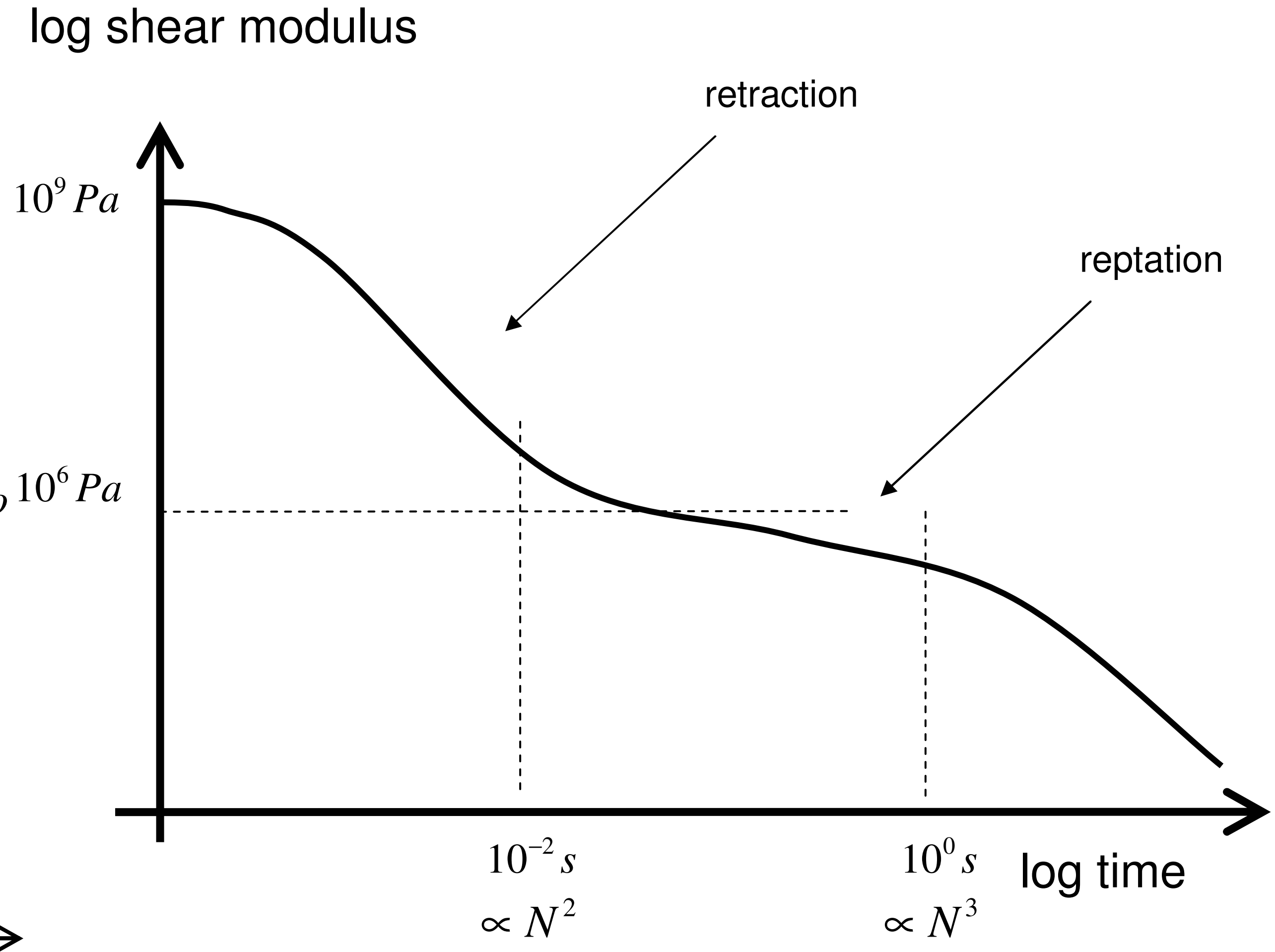
t>0 constant strain



distribution



molecular mass



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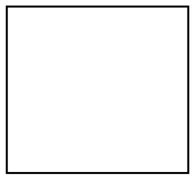
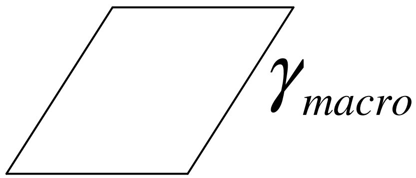
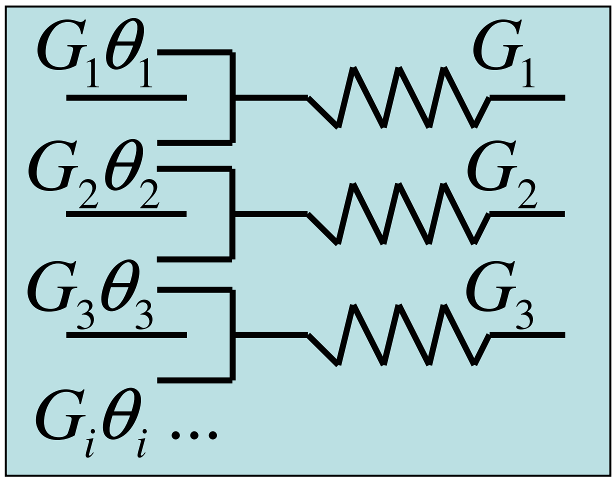
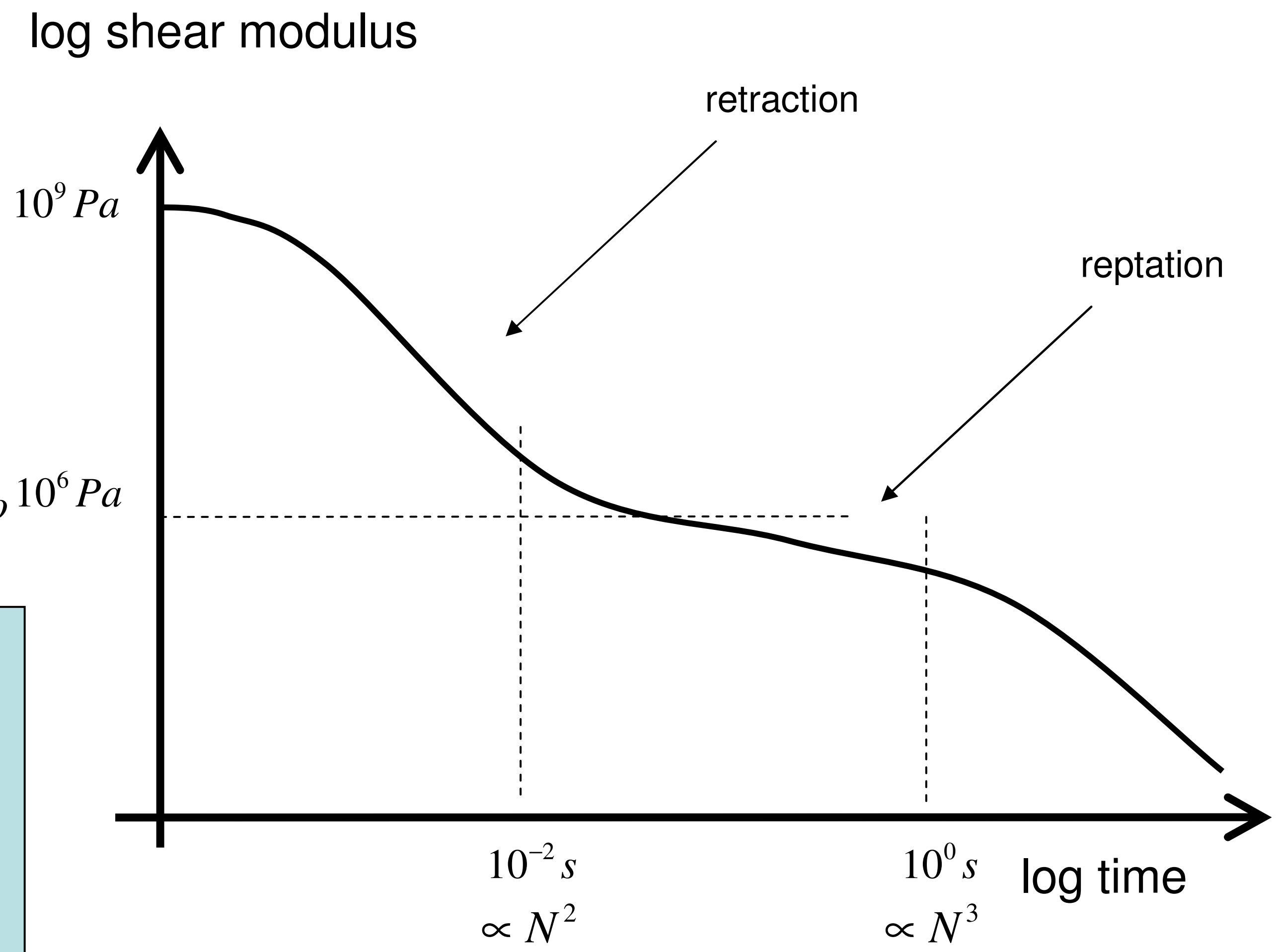


t>0 constant strain







Spectrum fitted using conventional rheometers

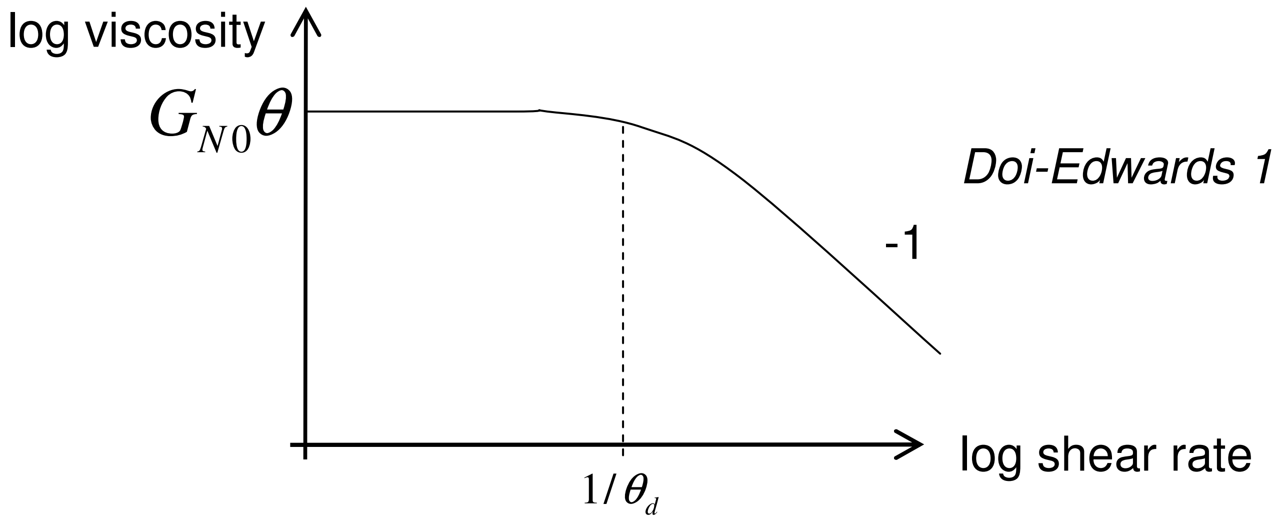
Steady shear

Shear rate: $\dot{\gamma} < 1/\theta_d$

Drag (affine deformation)/relaxation balance → stress: $\tau = G_{N0}\dot{\gamma}\theta_d$

Viscosity: $\eta = G_{N0}\theta_d$

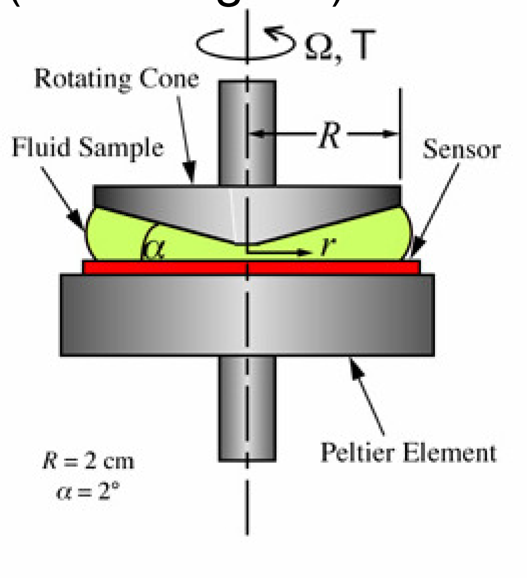
Shear thinning: $\dot{\gamma} > 1/\theta_d$ rotation of segments



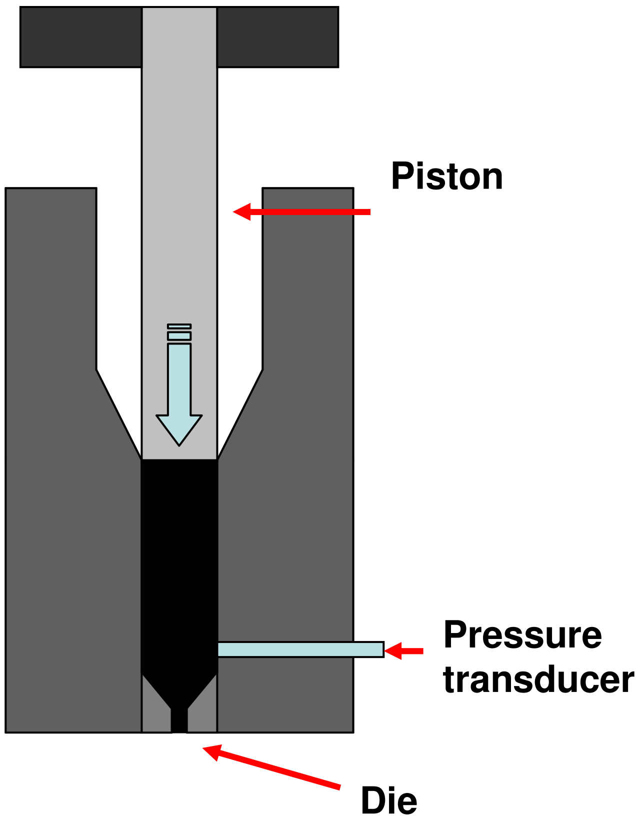
Doi-Edwards 1986

Rheometric tools

Cone-plate rheometer: mechanical spectroscopy (linear regime)



Capillary rheometer: steady shear viscosity

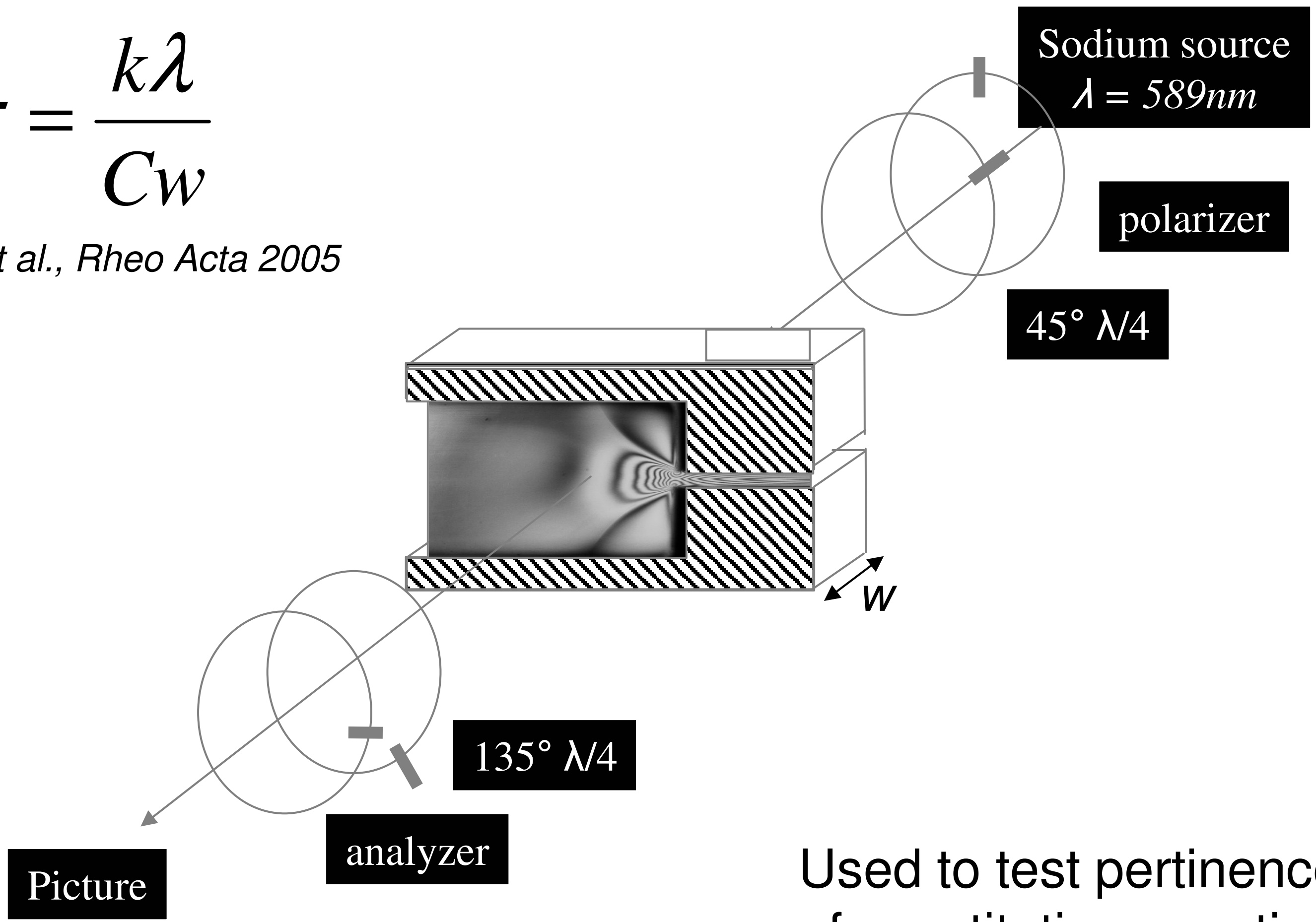


Flow-induced birefringence: stress measurements

Stress-optical law:

$$\Delta\sigma = \frac{k\lambda}{Cw}$$

Schweizer et al., Rheo Acta 2005



Used to test pertinence
of constitutive equations

Constitutive equation (3D)

Stress: $\tau = 3G_{N0}\left\langle \frac{\vec{R}\vec{R}^T}{R_0^2} \right\rangle = 3G_{N0}B$ (autocorrelation)

B conformation tensor: $\left\langle \frac{\vec{R}\vec{R}^T}{R_0^{\ 2}} \right\rangle = \int_{\vec{R}} \frac{\left(\vec{R}\vec{R}^T\right)}{R_0^{\ 2}} \psi\left(\vec{R}\right) d\vec{R}^3$

$$d\vec{f} = \tau\vec{n}ds = 3G_{N0}\left\langle \frac{\vec{R}\vec{R}^T\vec{n}}{R_0^2} \right\rangle ds$$

At rest: $B = \frac{1}{3}I$

Affine deformation: $\frac{dB}{dt} = \left\langle \frac{\nabla\vec{v}\vec{R}\vec{R}^T}{R_0^{\ 2}} \right\rangle + \left\langle \frac{\vec{R}\left(\nabla\vec{v}\vec{R}\right)^T}{R_0^{\ 2}} \right\rangle = \nabla\vec{v}B + B\nabla^T\vec{v}$

Because $\frac{d}{dt}\left(\psi\left(\vec{R}\right) d\vec{R}^3\right) = 0$ when no relaxation

Constitutive equation (3D)

Stress: $\tau = 3G_{N0}\left\langle \frac{\vec{R}\vec{R}^T}{R_0^2} \right\rangle = 3G_{N0}B$

B conformation tensor: $\left\langle \frac{\vec{R}\vec{R}^T}{R_0{}^2} \right\rangle = \int_{\vec{R}} \frac{\left(\vec{R}\vec{R}^T\right)}{R_0{}^2}\psi\left(\vec{R}\right)d\vec{R}^3$

$d\vec{f} = \tau\vec{n}ds = 3G_{N0}\left\langle \frac{\vec{R}\vec{R}^T\vec{n}}{R_0^2} \right\rangle ds$

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Relaxation: $\frac{dB}{dt} = \nabla\vec{v}B + B\nabla^T\vec{v} - \frac{1}{\theta}\left(B - \frac{1}{3}I\right)$ ⟶ Upper-convected Maxwell model

Why choosing differential models for B ?

Maxwell model: closed form from Smoluchowski equation

But general kinetic theory models (Likthman et al., Öttinger & Kröger et al, etc ..) involve too many refinements for polymer processing and require closure approximations

Integral models (KBKZ 1962-63, Doi-Edwards 1986, Wagner et al. 1976-2012) require lots of computational ressources to be solved in practice

Constitutive equation (3D)

Evolution equation for $B = \left\langle \frac{\vec{R}\vec{R}^T}{R_0^2} \right\rangle$, tube model:

- take Maxwell model $\frac{dB}{dt} = \nabla\vec{v}B + B\nabla^T\vec{v} - \frac{1}{\theta}\left(B - \frac{1}{3}I\right)$
- trace(B) is mean square chain stretch: $trB = \left\langle \frac{\vec{R}.\vec{R}}{R_0^2} \right\rangle$
- $\frac{dtrB}{dt} = 2tr(\nabla\vec{v}B) - \frac{1}{\theta}(trB - 1)$
- rescale B so that trB=1

Larson 1988

$$\frac{dB}{dt} = \nabla\vec{v}B + B\nabla^T\vec{v} - 2tr(\nabla\vec{v}B)B - \frac{1}{\theta}\left(B - \frac{1}{3}I\right)$$

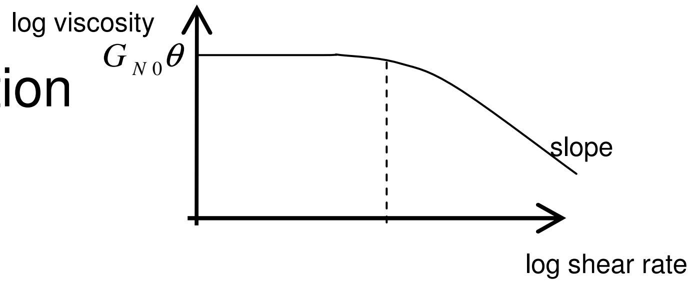
Test of reptation differential model

Evolution equation for $B = \left\langle \frac{\vec{R}\vec{R}^T}{R_0^2} \right\rangle$, tube model:

- $\frac{dB}{dt} = \nabla\vec{v}B + B\nabla^T\vec{v} - 2tr(\nabla\vec{v}B)B - \frac{1}{\theta}\left(B - \frac{1}{3}I\right)$

- Marrucci & Ianniruberto (1996): convective constrain release

relaxation is accelerated by retraction



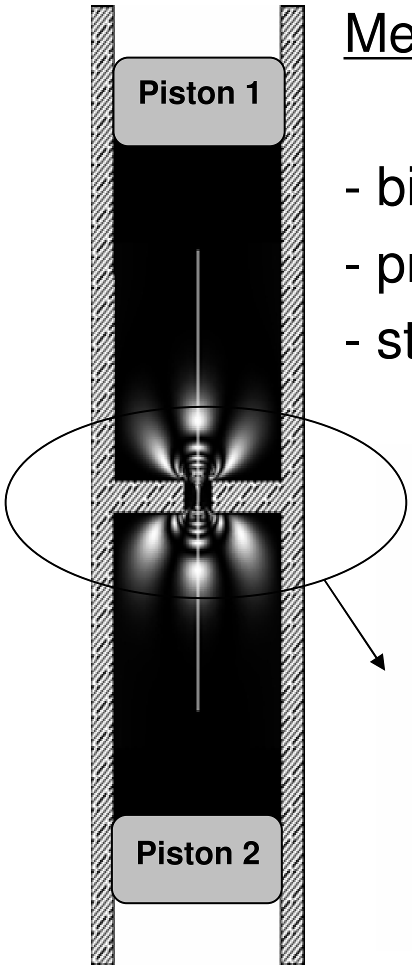
- $\frac{1}{\theta} = \frac{1}{\theta_d} + |\nabla u|$

➔ $\frac{1}{\theta} = \frac{1}{\theta} + 2\beta|tr(\nabla uB)|$

- linear viscoelasticity spectrum + β fitted from steady shear

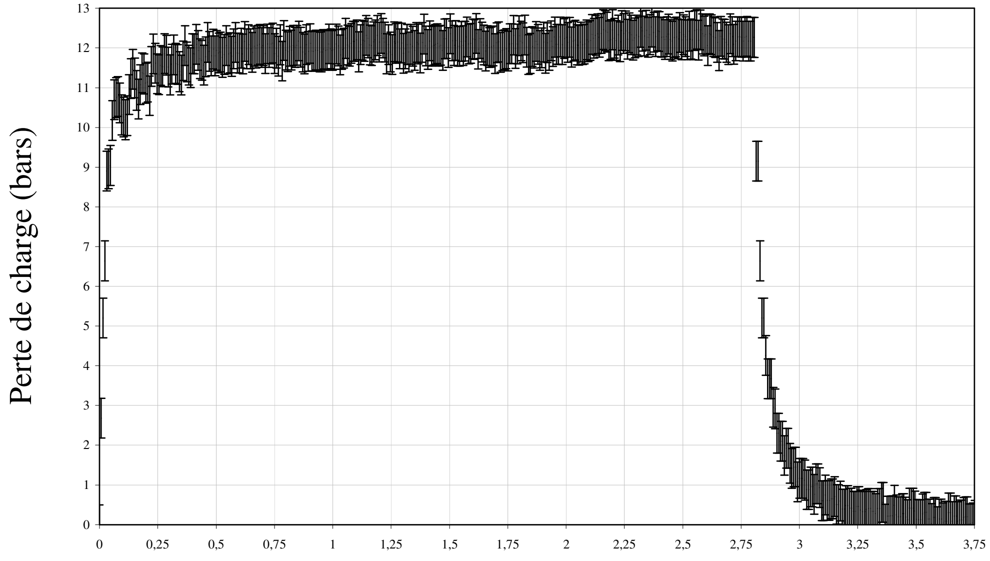
Valette, Mackley, Hernandez 2006

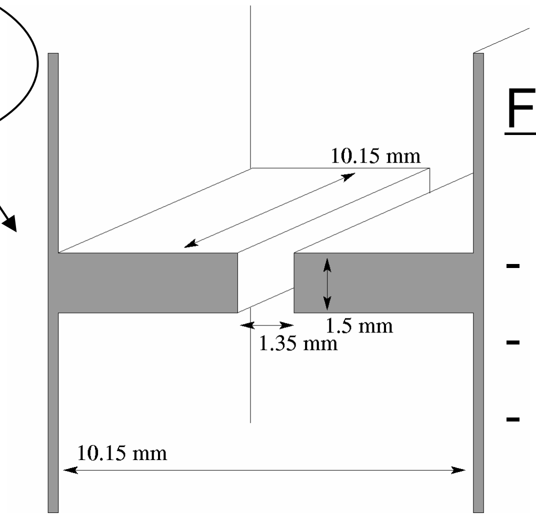
Valette, Mackley, Hernandez, JNNFM 2006



Measure:

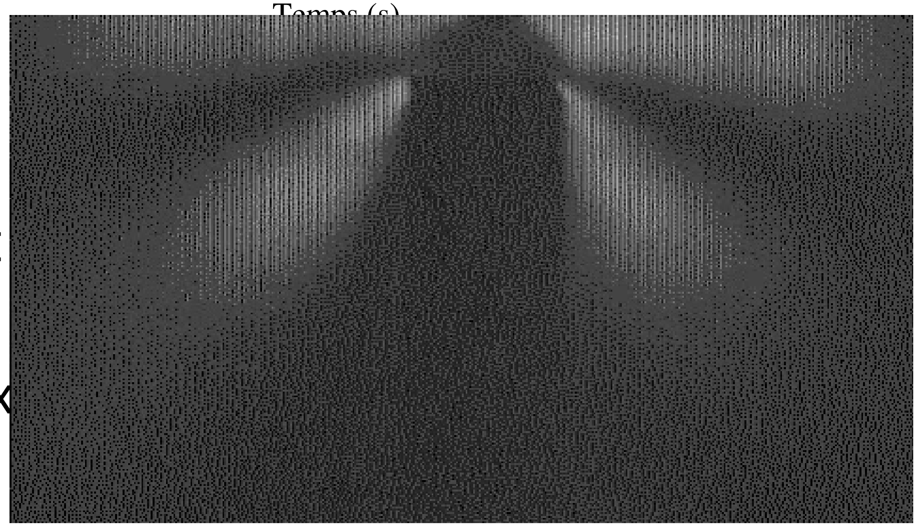
- birefringence
- pressure drop
- strain rate ~$1/\theta_d$





Flow:

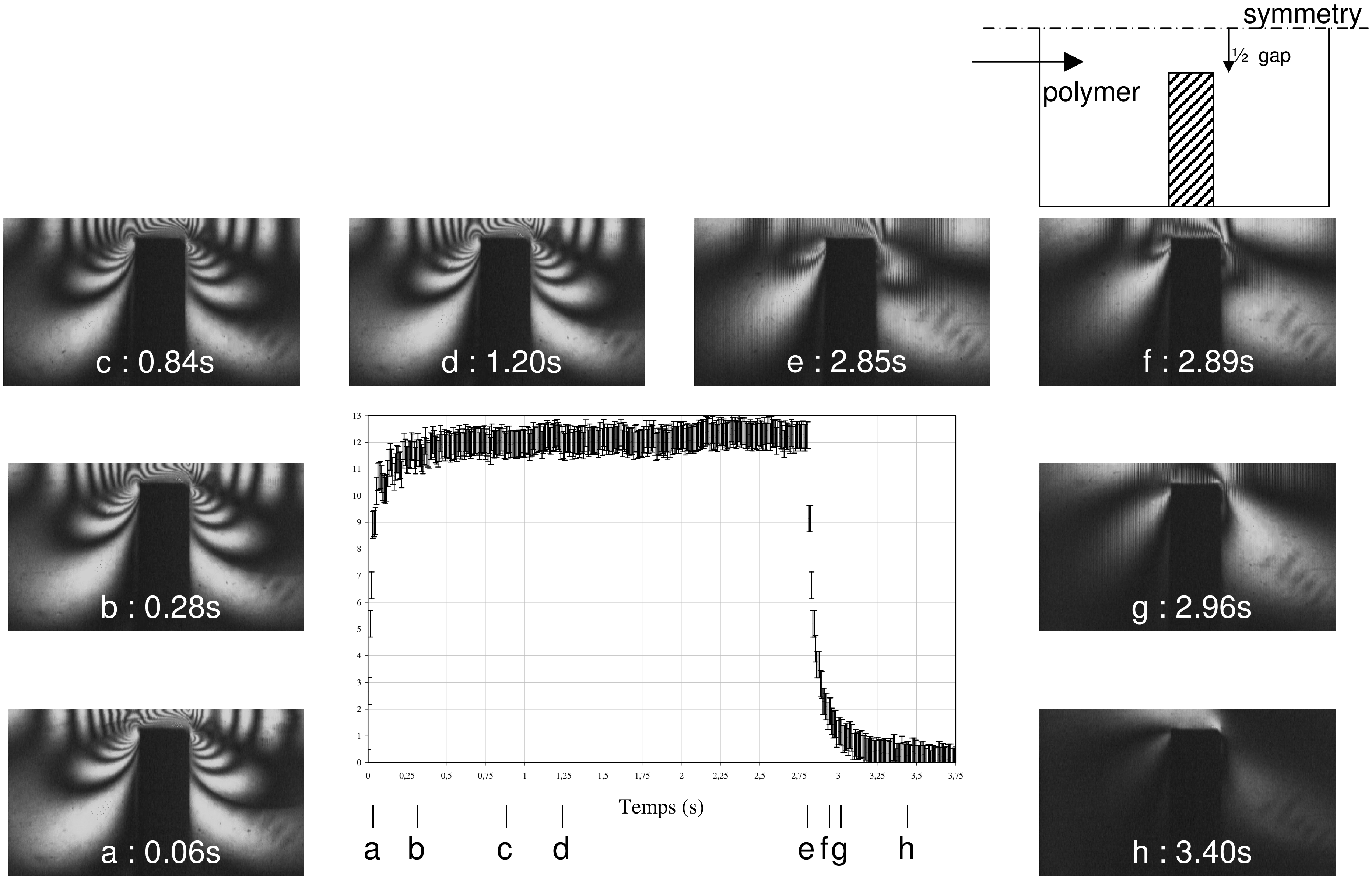
- start
- flow
- relax



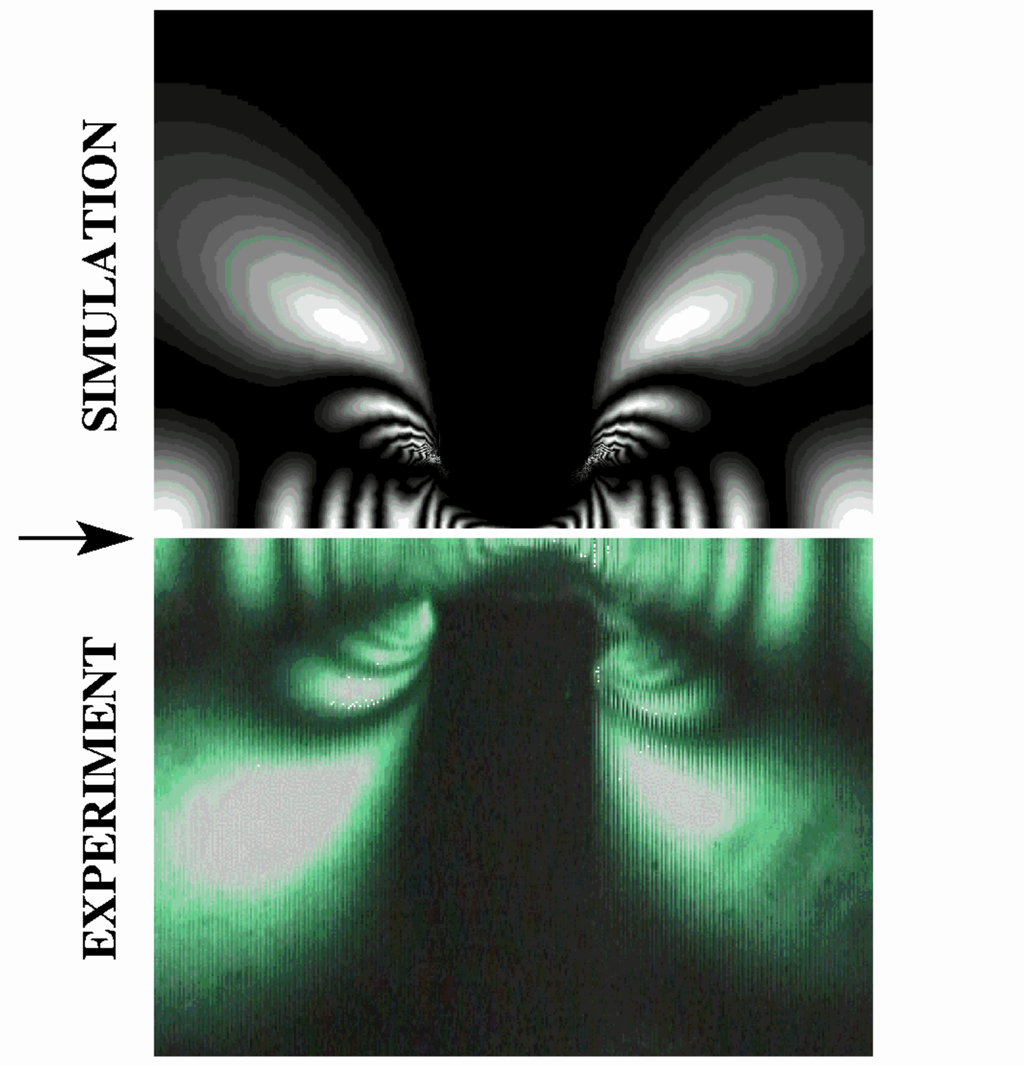
Numerics: finite elements

Equations	: momentum equation incompressibility transport equations for conformation tensors
Splitting	: Perturbed Stokes problem ← extra-stress
Stabilization	: « solvent » part (discretization) SUPG (transport)
Time	: implicit Euler
Approximation	: P, Conformation (linear continuous) Velocity (quadratic continuous)

Valette, Mackley, Hernandez, JNNFM 2006

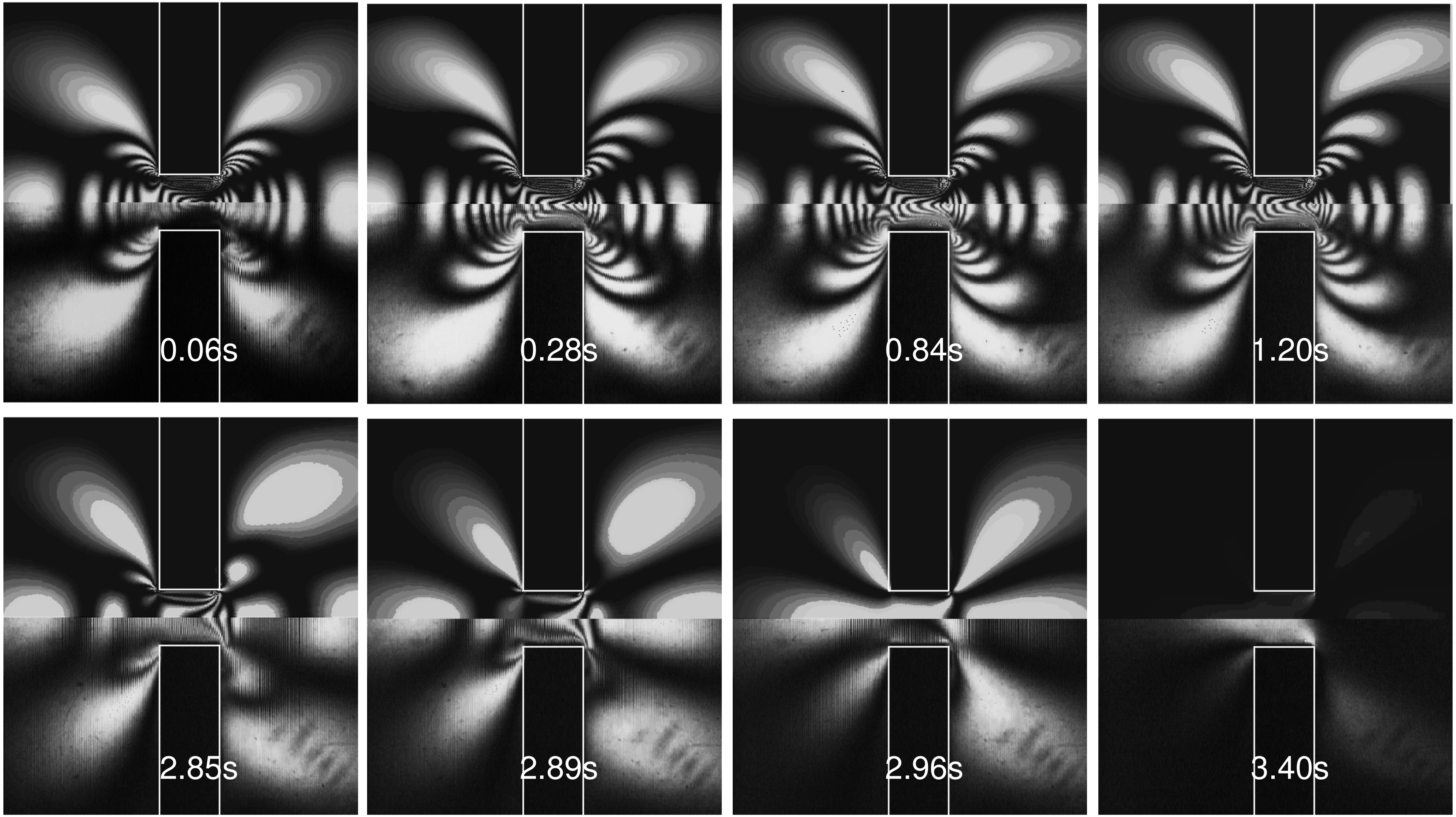


Valette, Mackley, Hernandez, JNNFM 2006



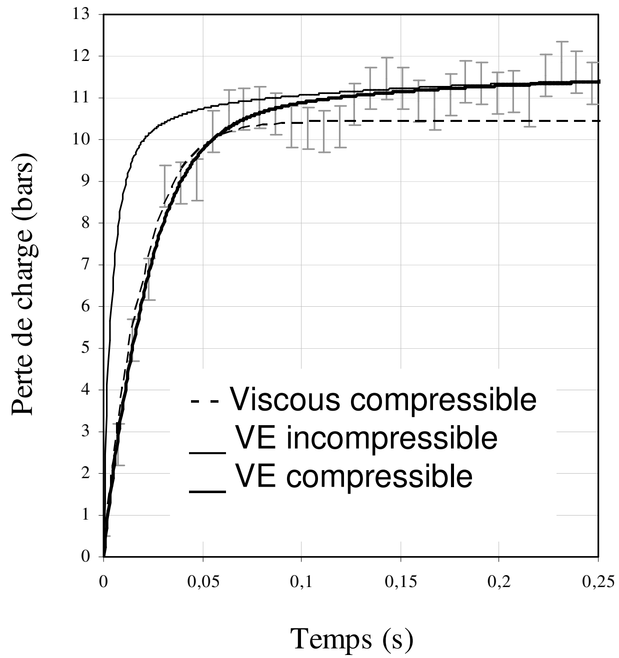
Valette, Mackley, Hernandez, JNNFM 2006

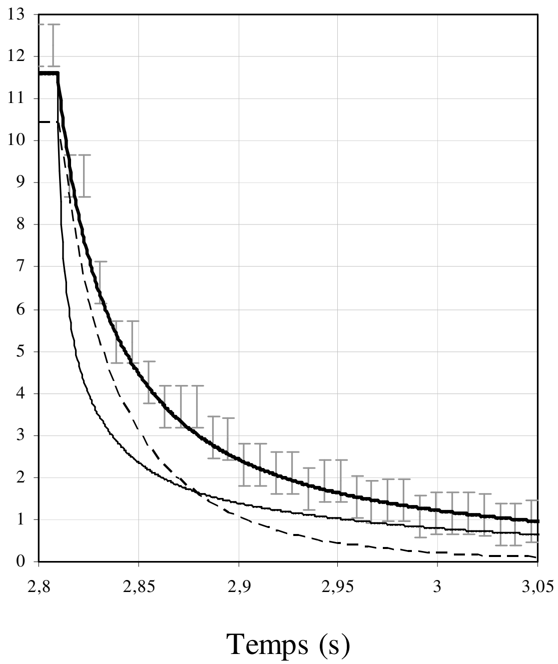
Solving it with suitable numerical methods, then compute birefringence

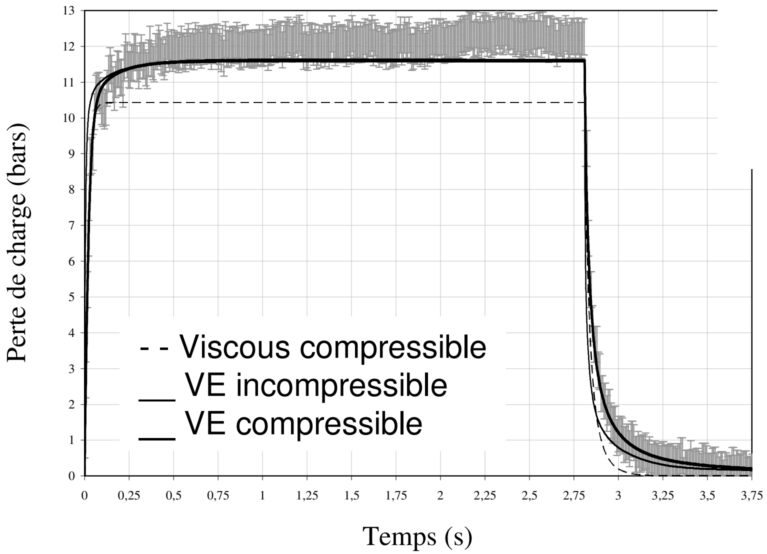


Valette, Mackley, Hernandez, JNNFM 2006

Solving it with suitable numerical methods, then compute pressure drop

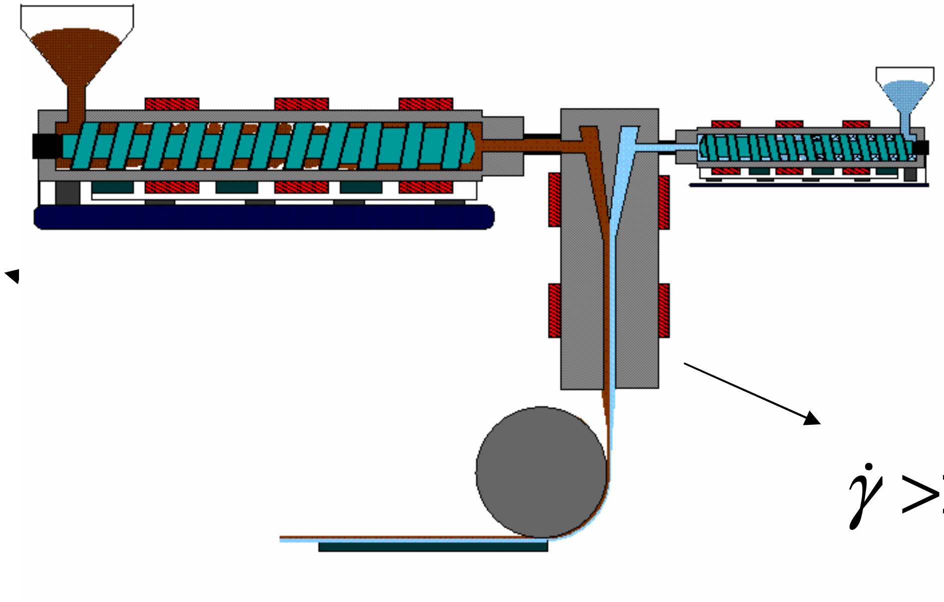






Predictions of tube-based differential models are ≈ OK

Flows were not as strong as polymer processing flows:



$$\dot{\gamma} >> 1/\theta_d$$

Birefringence:

- measure of stress
- not linked to a measure of strain (rate)

Flows stronger than $1/\theta_d$

Take chain retraction dynamics into account:

- stress is still $\tau = 3GB$
- partition of B: $B = \lambda^2 S$ — *McLeish & Larson 1998*
- $\frac{dB}{dt} = \nabla\vec{v}B + B\nabla^T\vec{v} - 2(\nabla\vec{v} : B)B - \frac{1}{\theta_d}\left(B - \frac{1}{3}I\right)$
- $\frac{d\lambda}{dt} = tr(\nabla\vec{v}B) - \frac{1}{\theta_r}(\lambda - 1)$

- not really satisfactory predictions — *Koventry, Valette, Mackley 2004*

Planar elongational flow Coventry, Mackley, Valette 2004

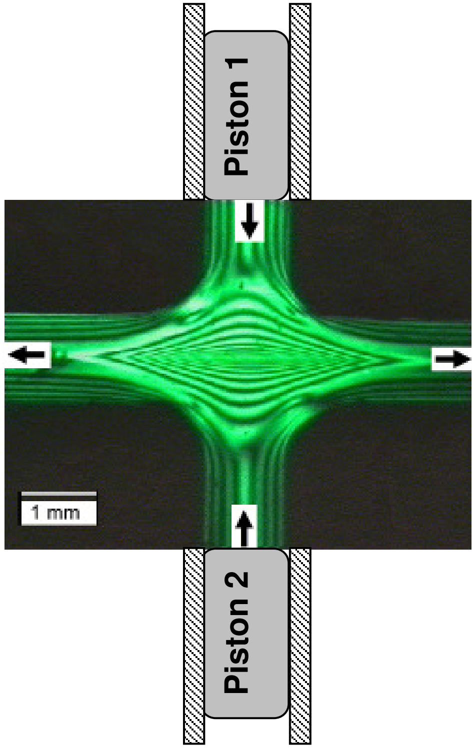
« Purely » elongational :

- $3\ s^{-1}$

- birefringence

- polystyrene

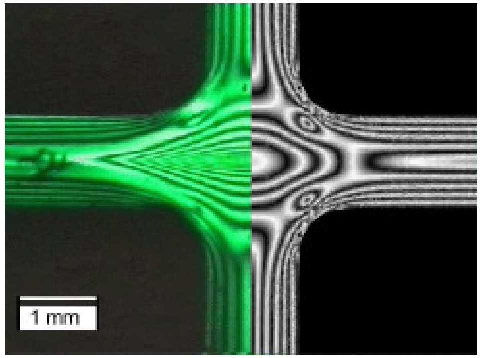
- compare different models



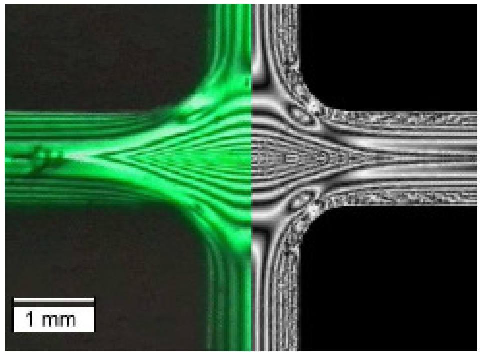
Planar elongational flow Coventry, Mackley, Valette 2004

<u>Same physics, different expressions</u>
(closure approximation) :

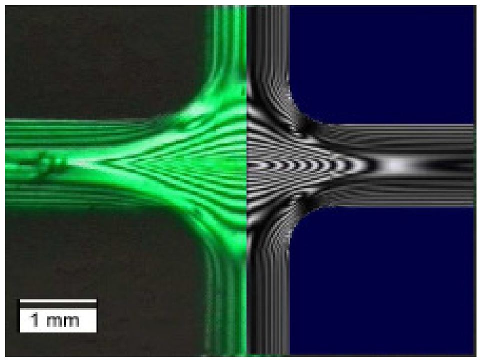
- Rolie-Poly



- Pompom



- DXPompom



Too many adjustable parameters !!!!

Flows stronger than $1/\theta_d$

Take chain retraction dynamics and finite extensibility into account:

- stress is still $\tau = 3GB$

Marrucci & Ianniruberto 2003

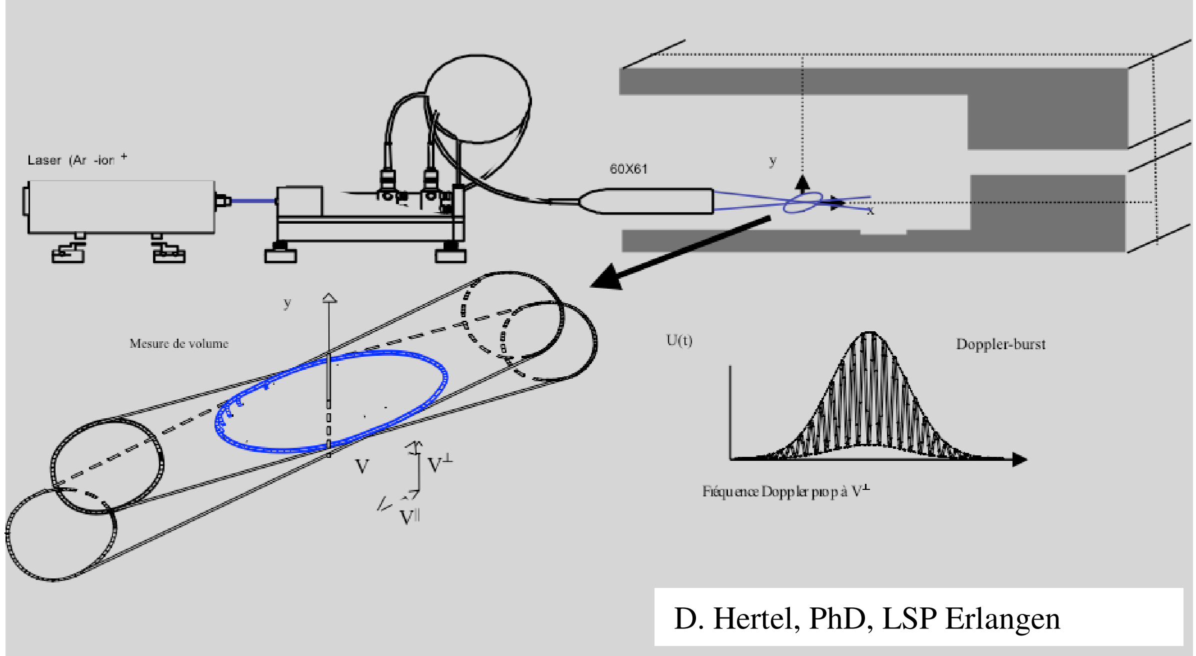
- finite extensibility: chains are no more Gaussian:
  - rest dimension $R_0 = \sqrt{N} b$
  - unfolded chain length $R_{\max} = Nb$
  - max extension square $(R_{\max} / R_0)^2 = N$
  - modulus $G \to G \dfrac{N-1}{N - trB} = Gf$

- single equation partition for B:

$$\frac{dB}{dt} = \nabla \vec{v} B + B \nabla^T \vec{v} - \frac{f}{\theta}\left(B - \frac{trB}{3} I\right) - \frac{1}{3\theta_r}\left(ftrB - 1\right) I$$

$$\frac{1}{\theta} = \frac{1}{\theta_d} + \left(\frac{1}{\theta_r} - \frac{1}{\theta_d}\right) \frac{\beta\left(ftrB - 1\right)}{1 + \beta\left(ftrB - 1\right)}$$

Test constitutive equations using LDV



Measure Vx (axial)
Spatial resolution 35 µm, velocity resolution 50µm/s

Optical rheometer

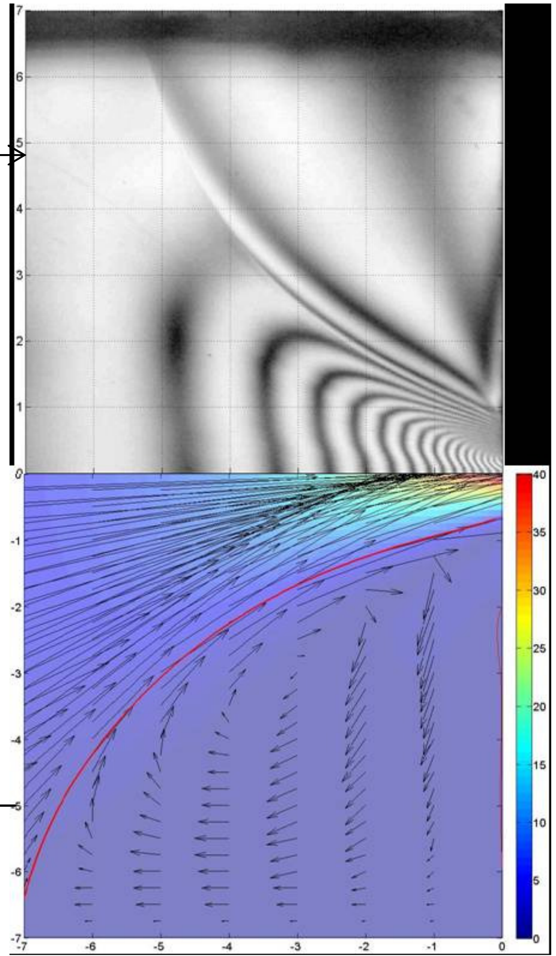
Stress

?

<u>Rheometry</u> :
Linear regime: spectrum
Capillary: steady shear

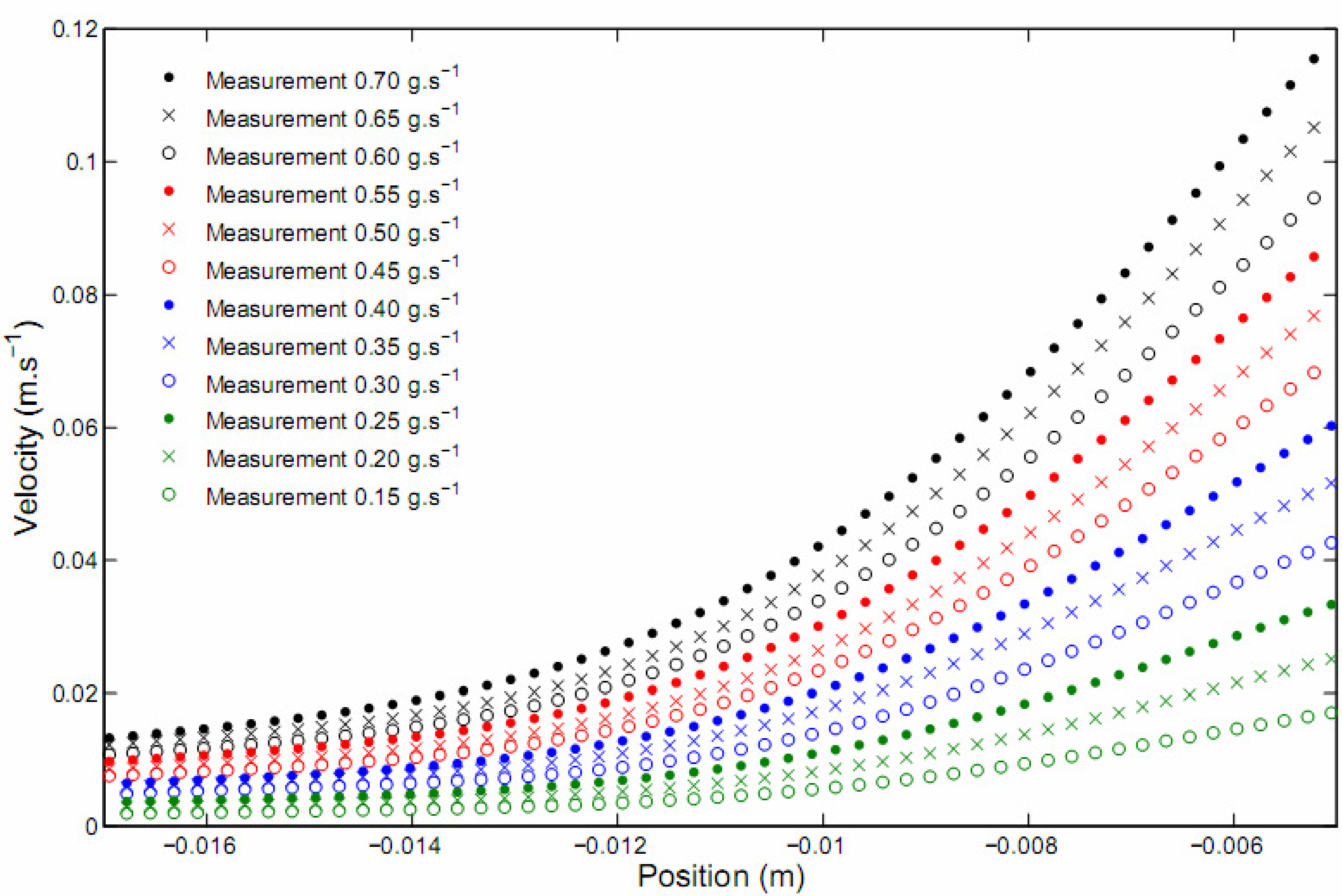
Computation

Velocity
+gradients



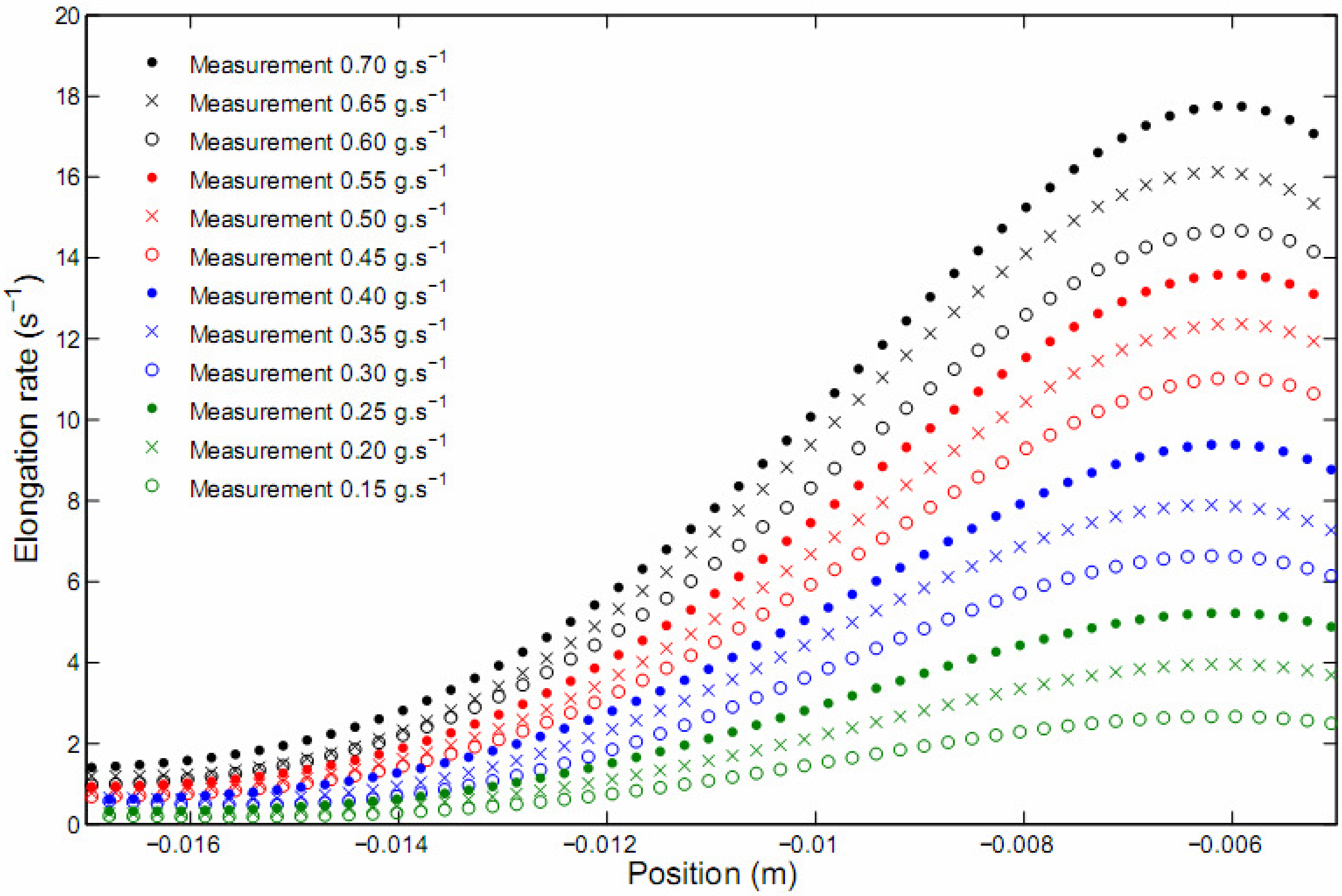
Boukellal, Durin, Valette, Agassant 2011

Optical rheometer: on symmetry axis get velocity



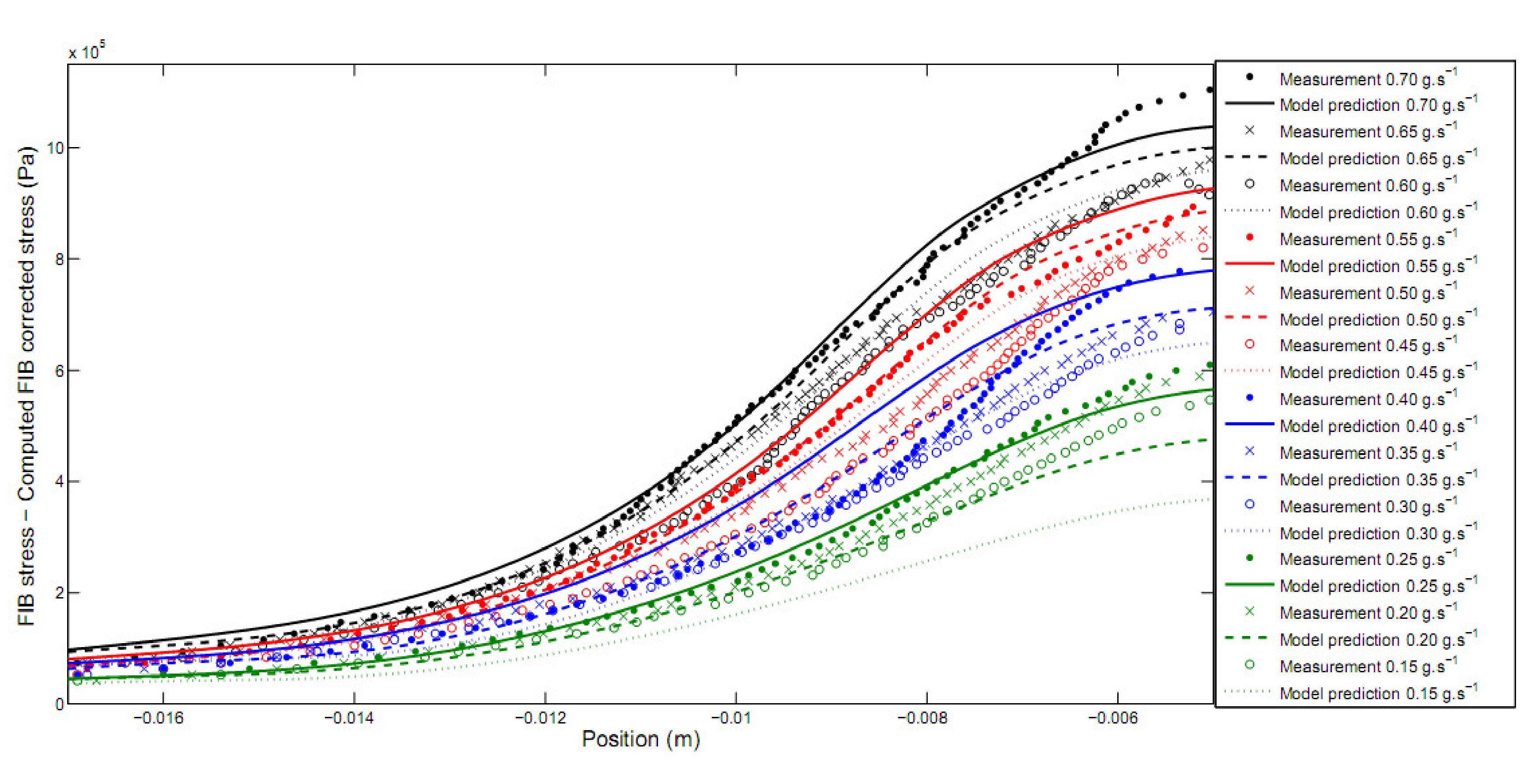
Boukellal, Durin, Valette, Agassant 2011

Optical rheometer: on symmetry axis deduce strain rate



Boukellal, Durin, Valette, Agassant 2011

Optical rheometer: compute stress and compare



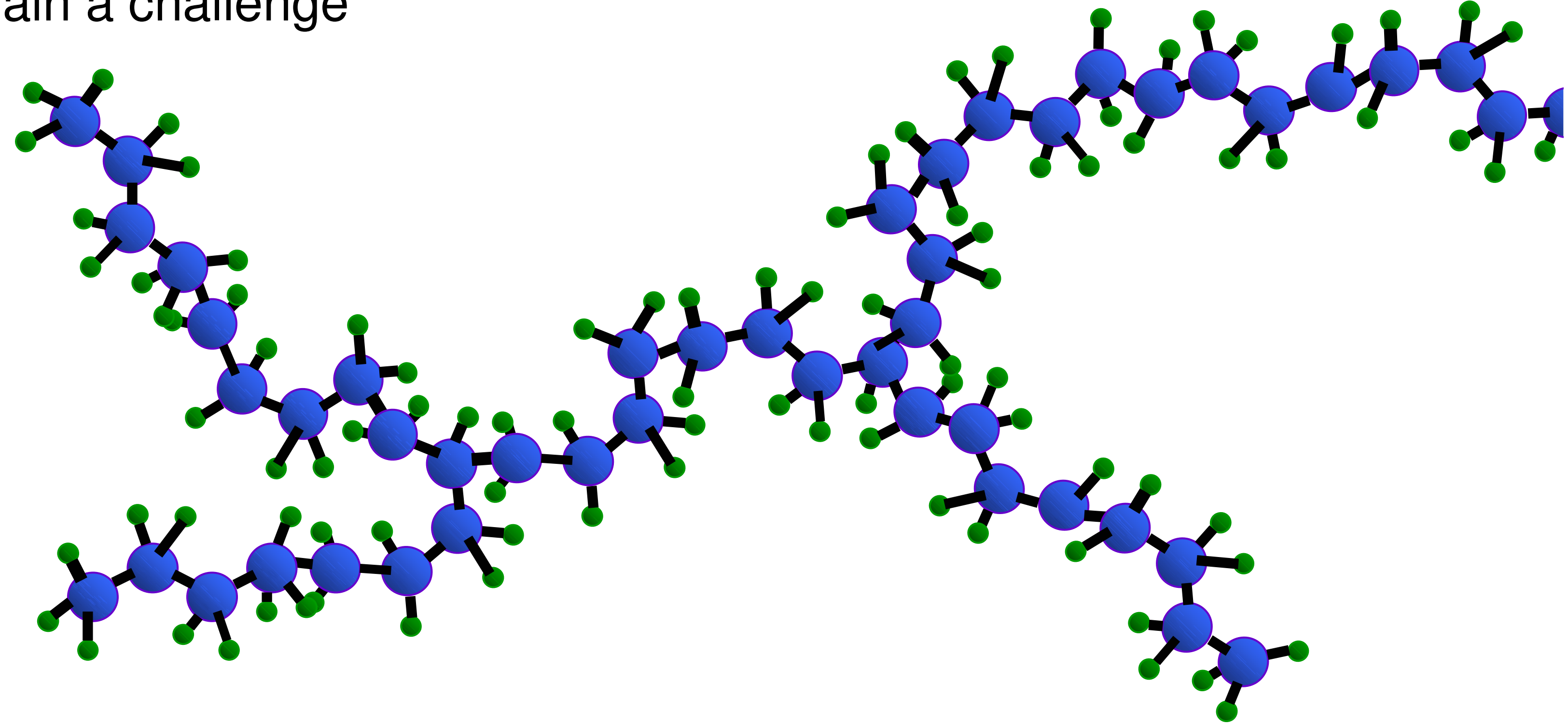
Boukellal, Durin, Valette, Agassant 2011

Conclusion

Models are OK for moderately fast flows and simple chain topologies

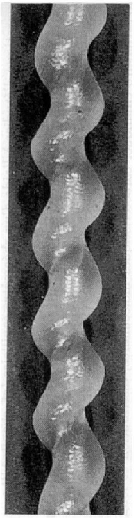
No adjustable parameters (modulo uncertainties)

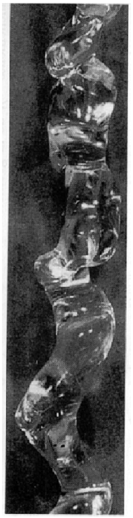
Predictive constitutive models for complex topologies and faster flows remain a challenge

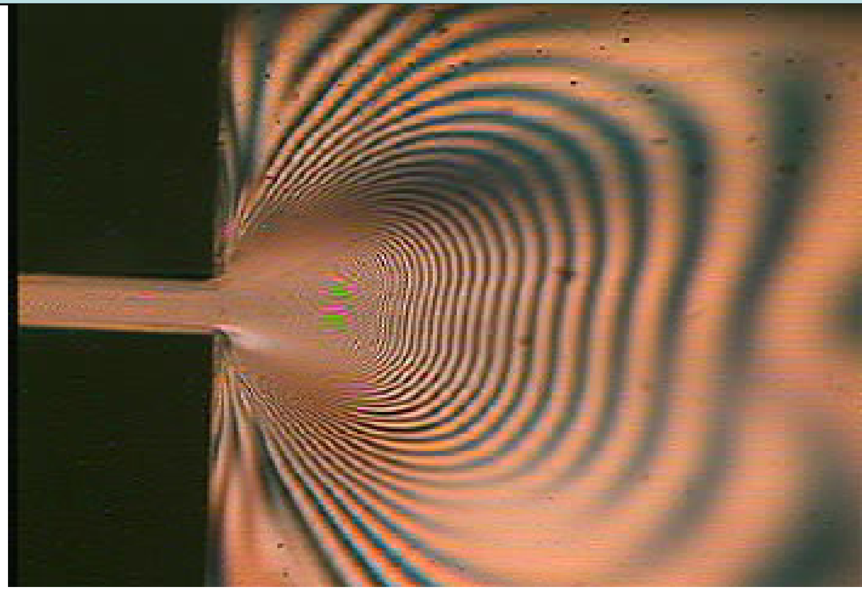


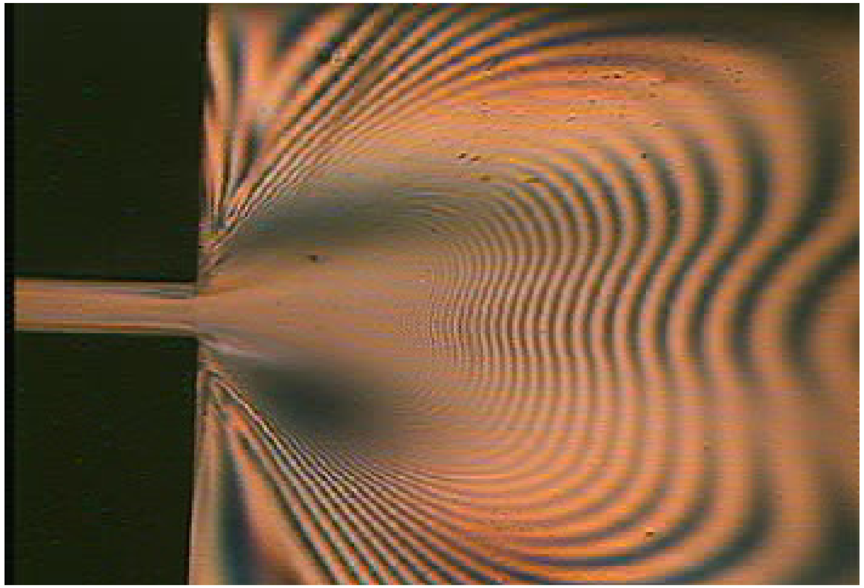
Polymer processing flows: instabilities

Very strong flows $\dot{\gamma} >> 1/\theta_r$







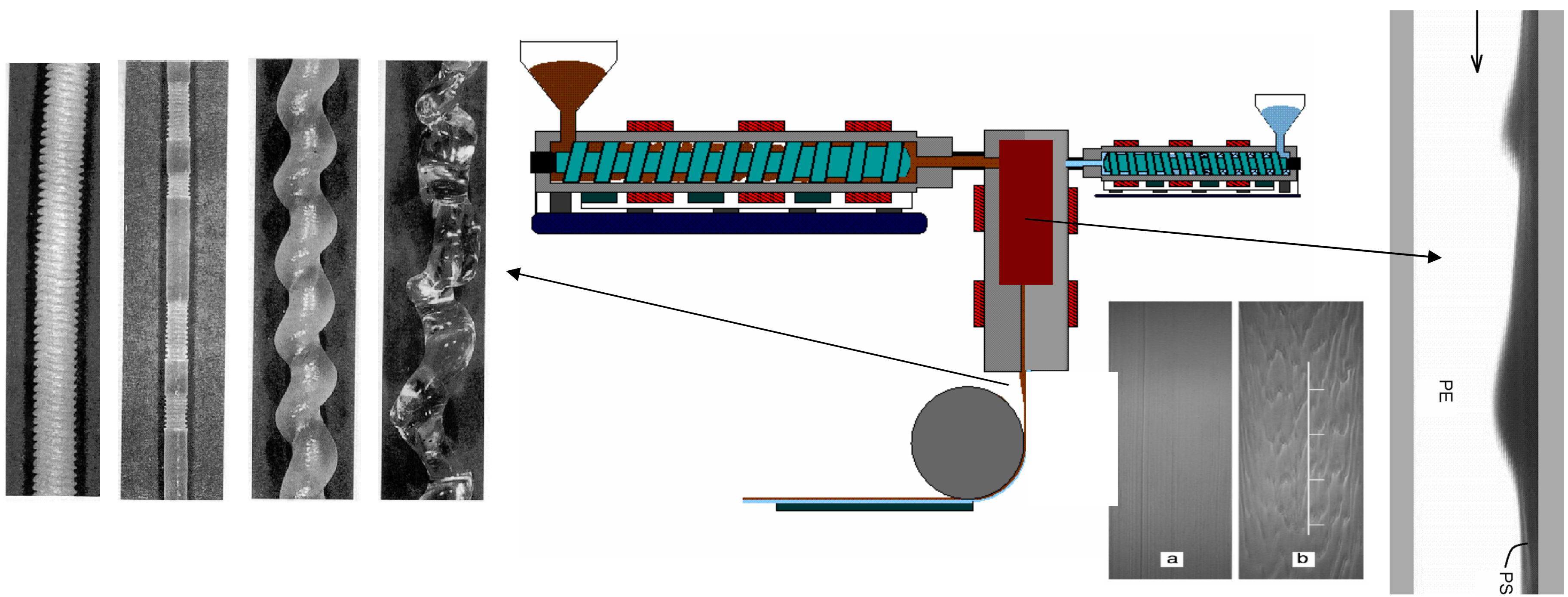


Combeaud, Demay, Vergnes 2004

Polymer processing flows: instabilities

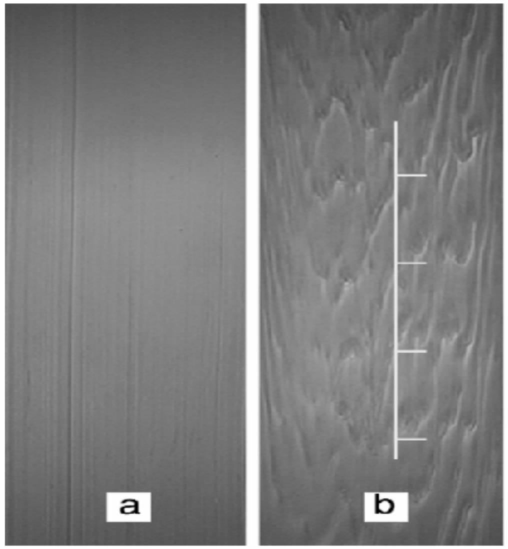
flow instabilites

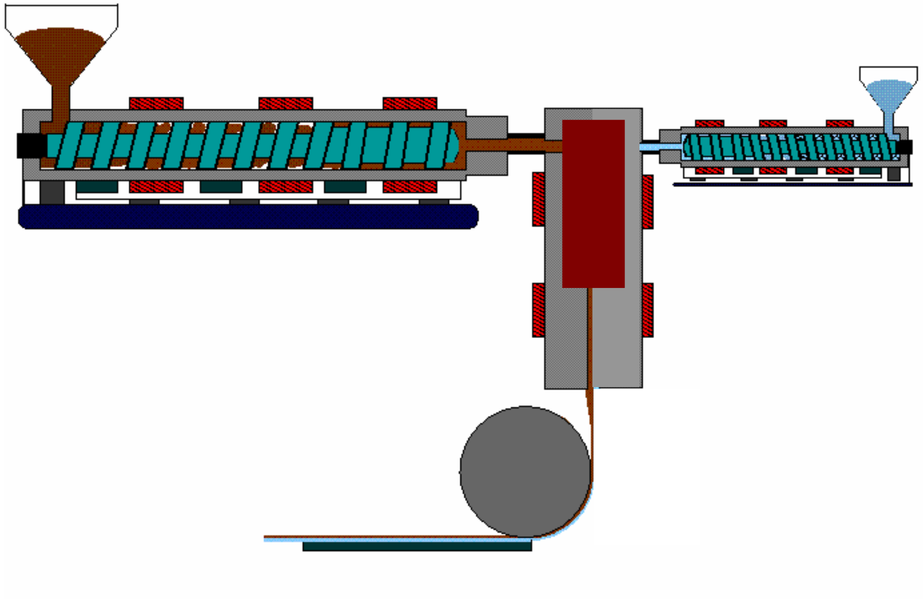
interfacial instabilities



Polymer processing flows: coextrusion instabilities

interfacial instabilities



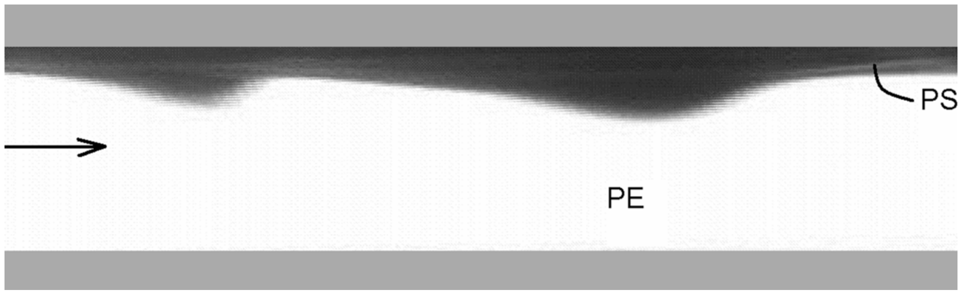


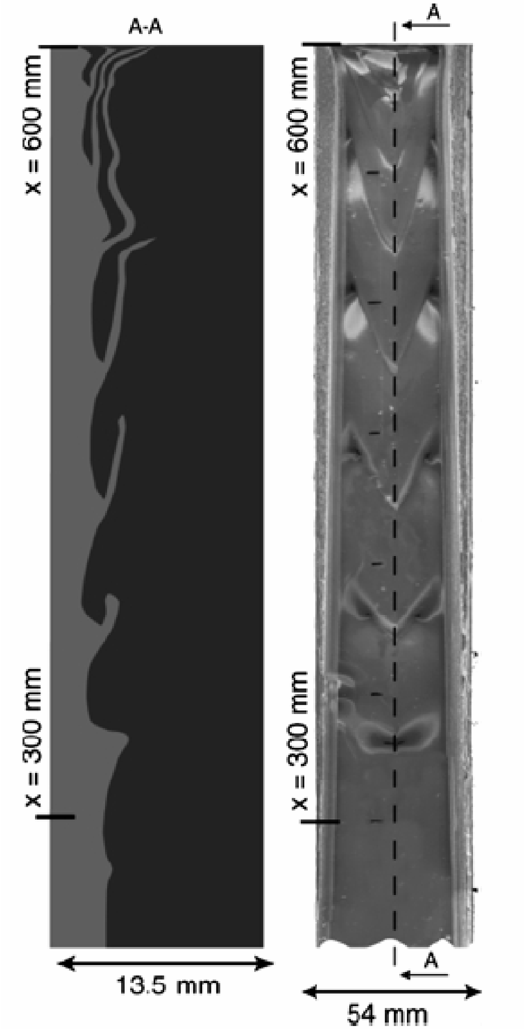
Valette, Laure, Demay, Agassant 2003

Polymer processing flows: coextrusion instabilities

interfacial instabilities

inside flow cell / after cooling



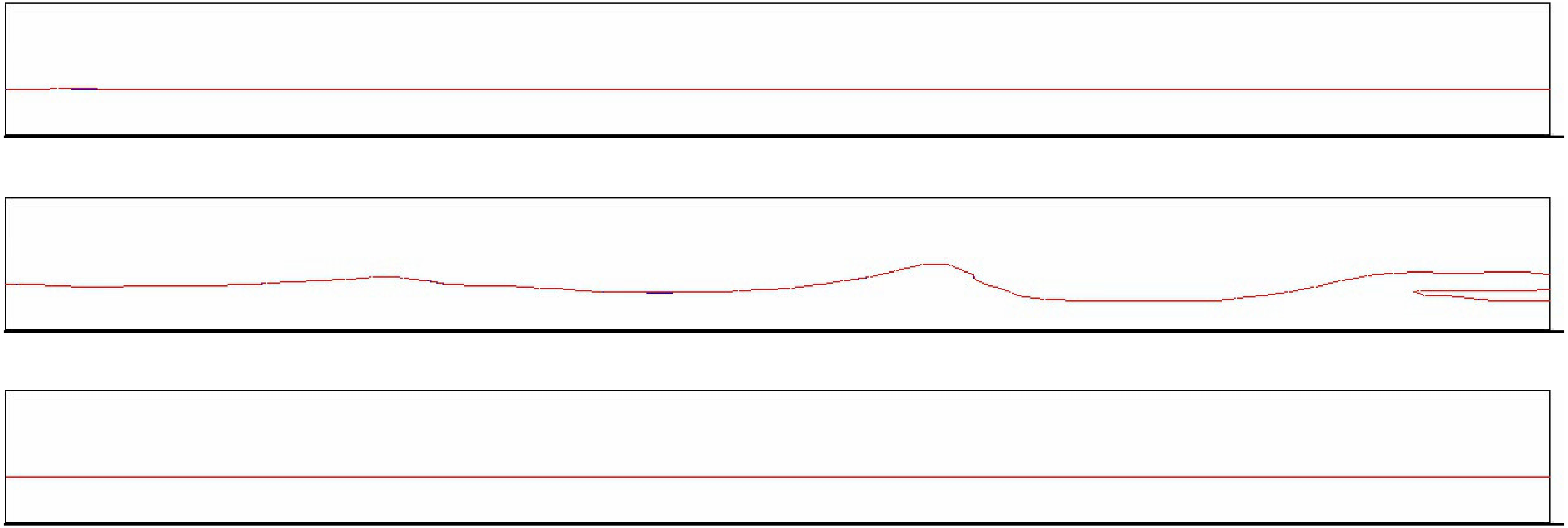


Valette, Laure, Demay, Agassant 2004a

Polymer processing flows: coextrusion instabilities

interfacial instabilities: solve direct model -> convective instability

forced system: Level-set + SUPG method

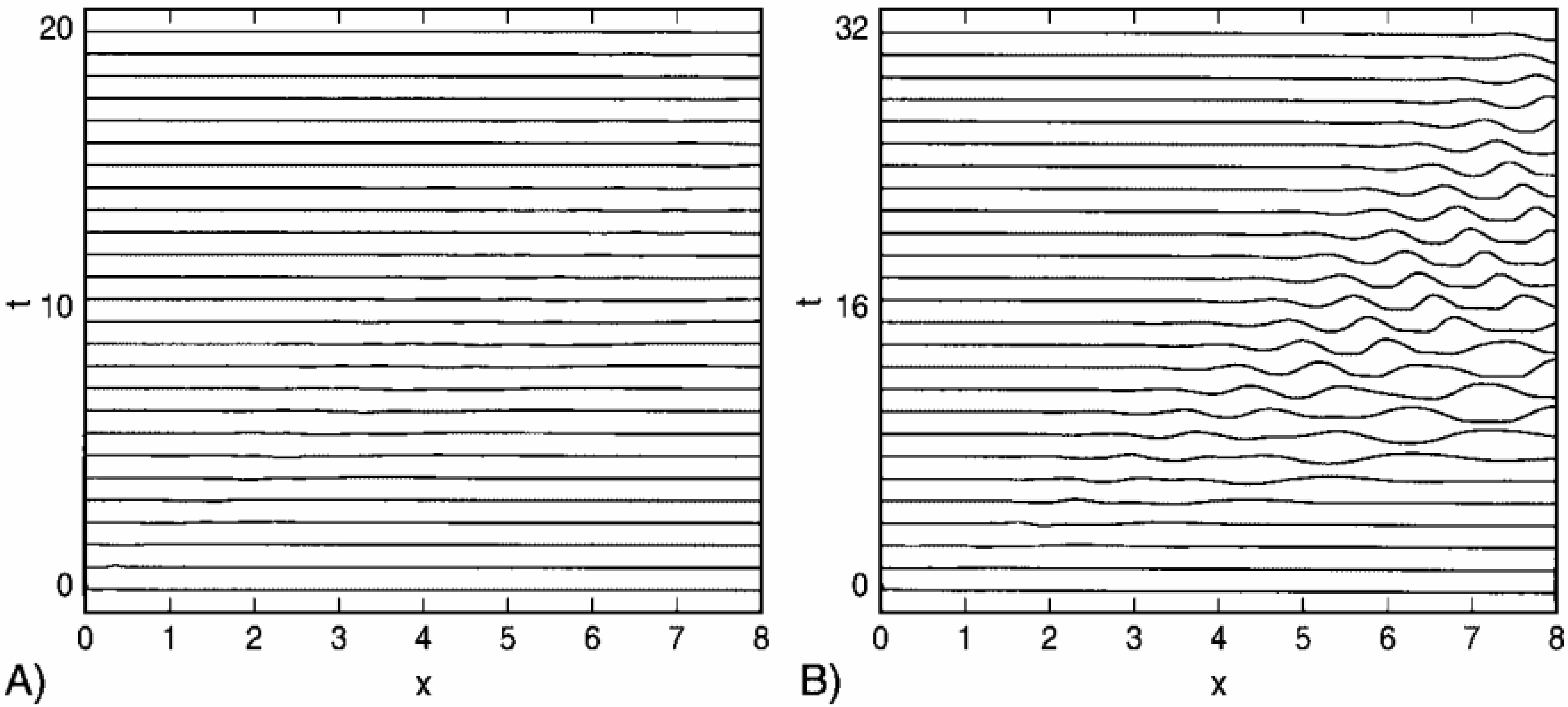


Valette, Laure, Demay, Fortin 2002

Polymer processing flows: coextrusion instabilities

interfacial instabilities: solve direct model -> convective instability

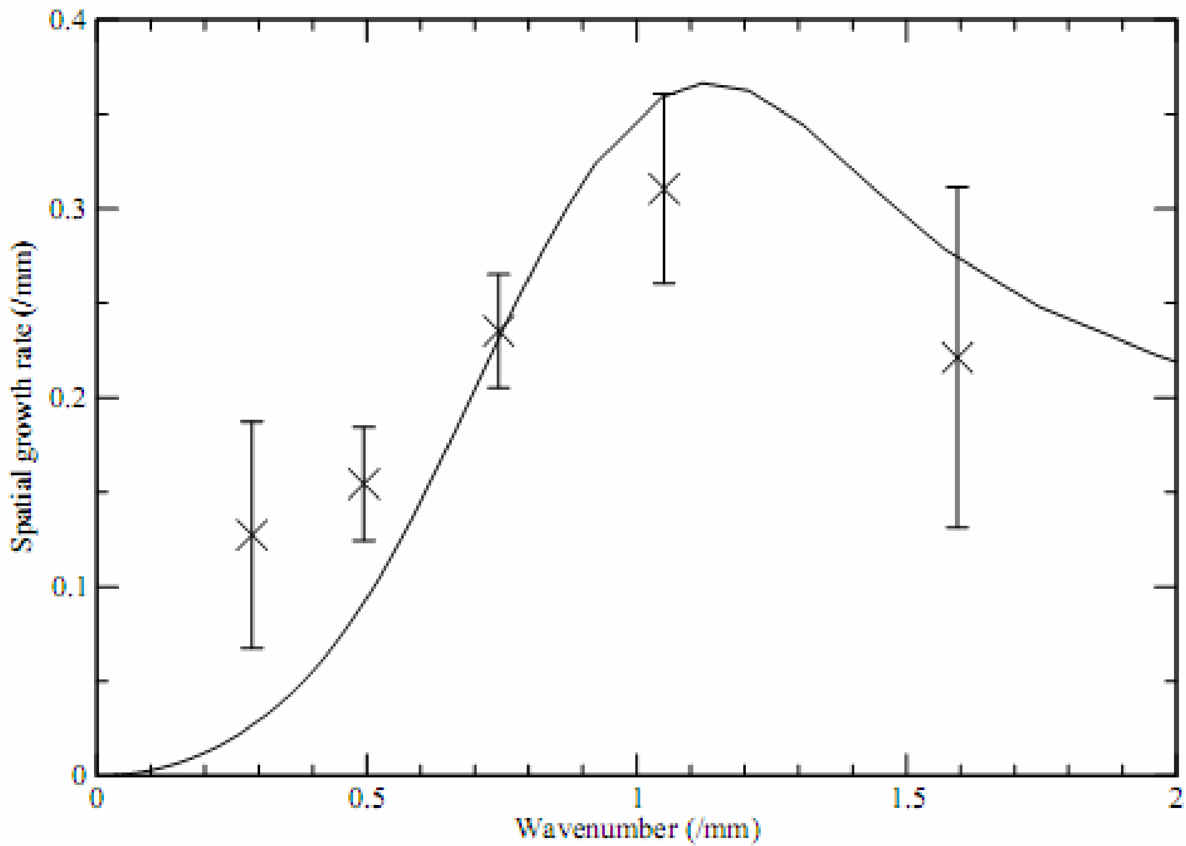
wavepacket: Discontinuous Galerkin method



Valette, Laure, Demay, Fortin 2001

Polymer processing flows: coextrusion instabilities

interfacial instabilities: linear stability of 2 layer viscoelastic Poiseuille flow



Valette, Laure, Demay, Agassant 2004b

Polymer processing flows: instabilities

flow instabilites

interfacial instabilities