PPS-33

A Combination of the eXtended Pom-Pom Model and the Stress-Thermal Rule to Predict Anisotropy in Thermal Conductivity in Non-Linear Polymeric Flows

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UNIVERSIDAD
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MARIE CURIE ACTIONS

HORIZON 2020

1. Thermal transport becomes anisotropic in polymers subjected to deformation
2. Experimental evidence of:
    - Proportionality to Stress: Stress-Thermal Rule (STR)
    - Universality
    - Beyond Finite Extensibility
3. eXtended Pom-Pom (XPP) as a constitutive model amenable for FEM simulation
4. Predictions of anisotropy for uniaxial and shear flows through combination of STR and XPP

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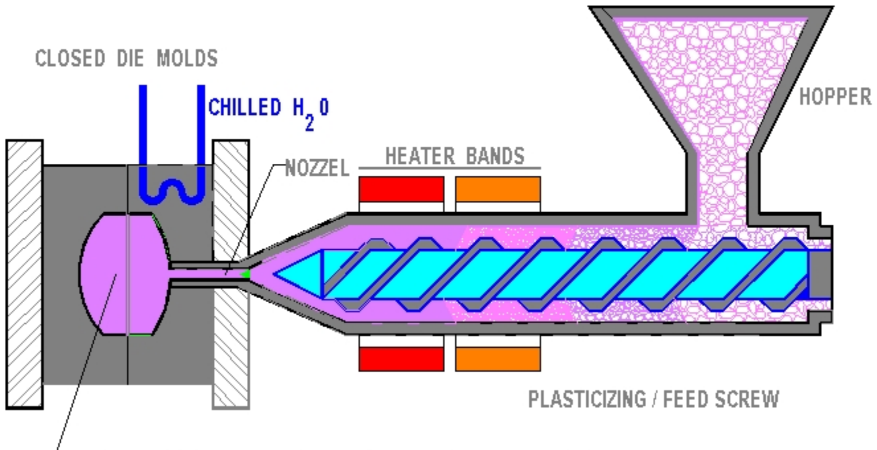
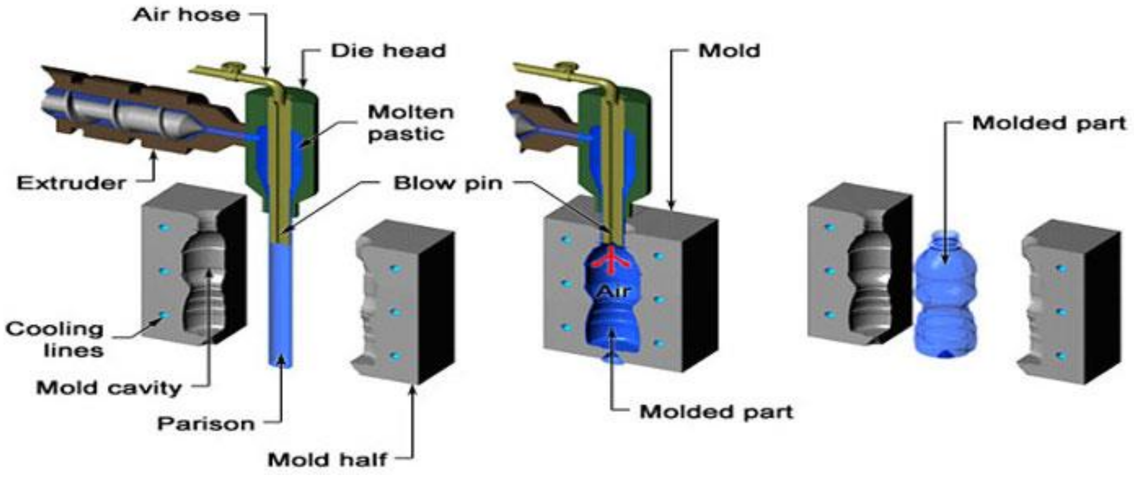
Motivation: Polymer Processing



INJECTION MOLDING



Global plastics market is expected to reach 654 billion USD by 2020

Thermal Transport Affects:

- Injection Pressure
- Cavity Flow
- Residual Stress
- Part Shrinkage

www.astra-polymers.com

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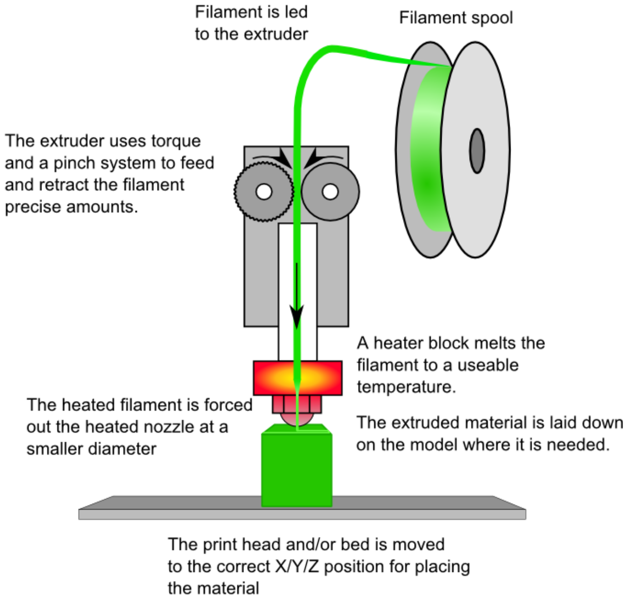

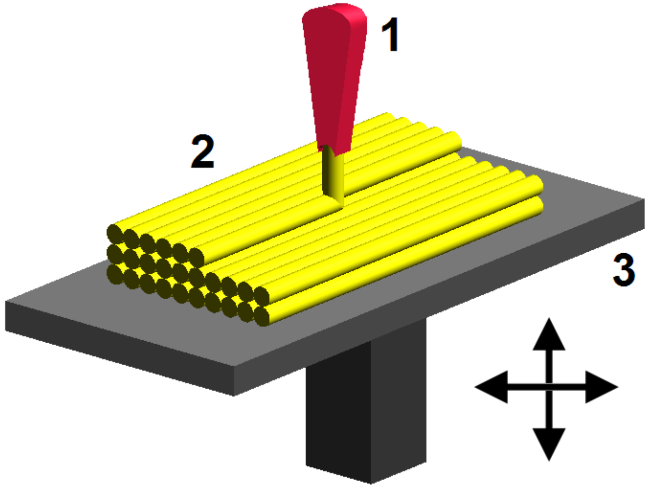

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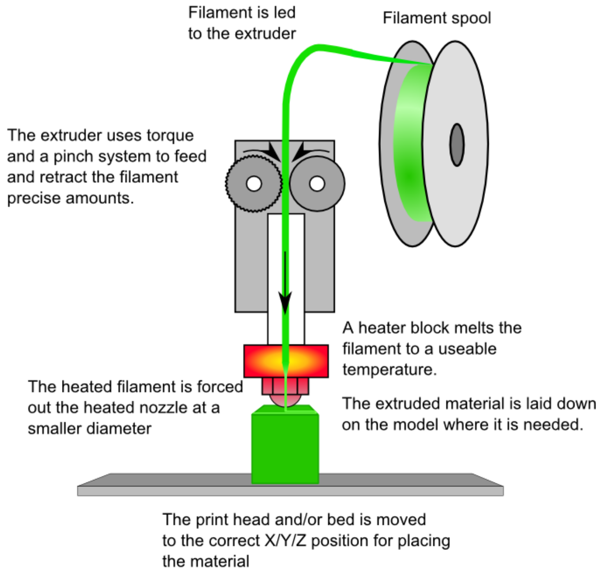


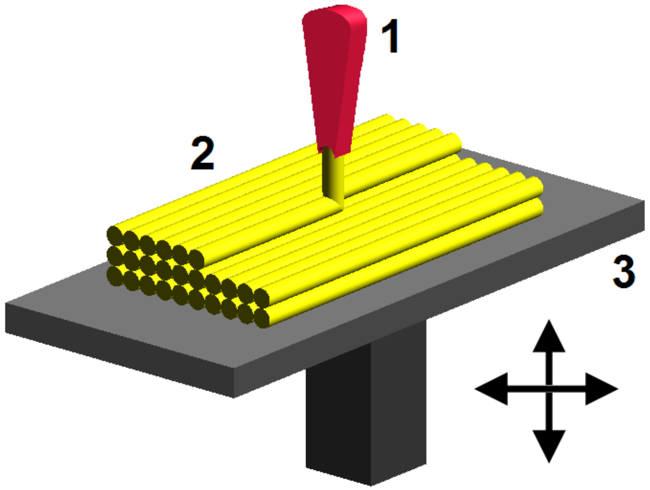
The extruder uses torque and a pinch system to feed and retract the filament precise amounts.

A heater block melts the filament to a useable temperature.

The heated filament is forced out the heated nozzle at a smaller diameter

The extruded material is laid down on the model where it is needed.

The print head and/or bed is moved to the correct X/Y/Z position for placing the material



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Thermal Transport Affects:

- Injection Pressure
- Cavity Flow
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- …

Develop a Molecular to Continuum methodology to better understand and simulate this kind of flows

Non-Isothermal Transport Phenomena

Balance Equations:

$$\text{Mass:}\quad \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \boldsymbol{v})$$

$$\text{Momentum:}\quad \frac{\partial \rho \boldsymbol{v}}{\partial t} = -\nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v} + \boldsymbol{\pi})$$

$$\text{Internal Energy:}\quad \frac{\partial \rho \hat{u}}{\partial t} = -\nabla \cdot (\rho \hat{u} \boldsymbol{v} + \boldsymbol{q}) - \boldsymbol{\pi} : \nabla \boldsymbol{v}$$

Constitutive equations:

$$\boxed{\boldsymbol{q} = -k \nabla T} \qquad \boxed{\hat{c}_v = \hat{c}_v(T)} \qquad \boldsymbol{\tau} = \eta(T)\left[\nabla v + \nabla v^{\intercal}\right]$$

- High stresses & Low thermal conductivity.

Mechanical behavior and flow ⟺ Thermal properties

Anisotropic Thermal Conduction

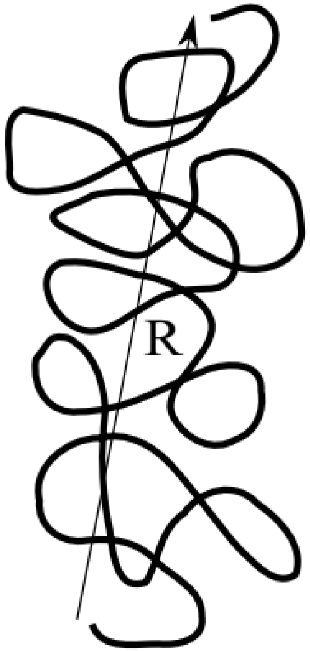
Fourier's Law: Thermal transport in deformed polymers is diffusive and anisotropic.

$$\boxed{\boldsymbol{q} = -\boldsymbol{k} \cdot \nabla T}$$

$\boldsymbol{k}$ is a tensor!

Observation: k_{eq} increases with molecular weight.

Ueberreiter & Otto-Laupenmühlen, Kolloid Z. 1953



Hypothesis: *Energy transport along the backbone of a polymer chain is more efficient than between chains.*

Simple molecular arguments:

$$\boldsymbol{k} \propto \langle \boldsymbol{R}\boldsymbol{R} \rangle \qquad + \qquad \boldsymbol{\tau} \propto \langle \boldsymbol{R}\boldsymbol{R} \rangle$$

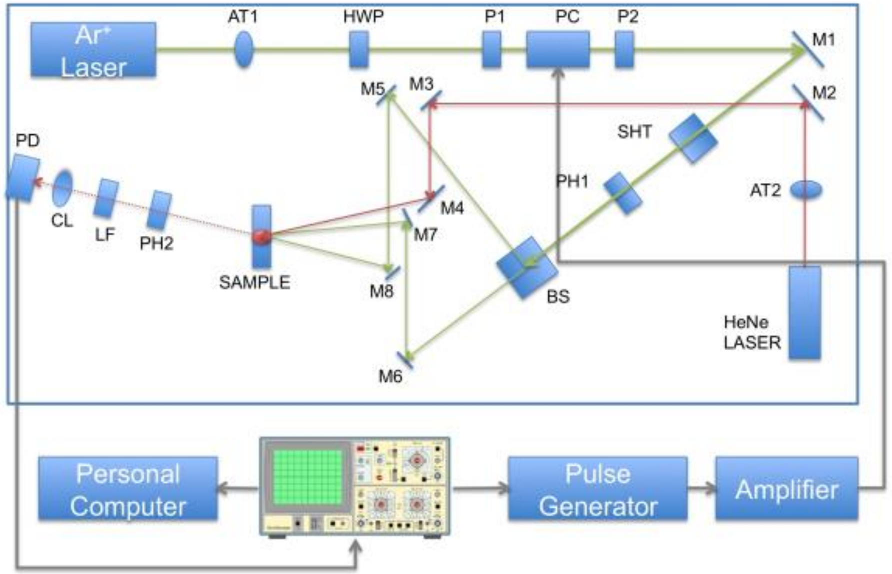
$$\boxed{\boldsymbol{k} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{\mathrm{eq}} C_{\mathrm{t}} \left[\boldsymbol{\tau} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta}\right]}$$

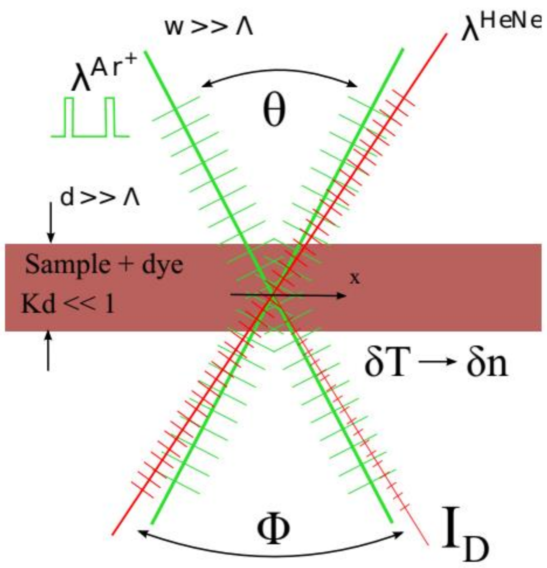
The Stress-Thermal Rule

B.H.A.A. van den Brule, Rheol Acta 1989.
Öttinger and Petrillo, J. Rheol. 40 (5) 1996.
Curtiss and Bird, J. Chem. Phys. 107 (13) 1997.

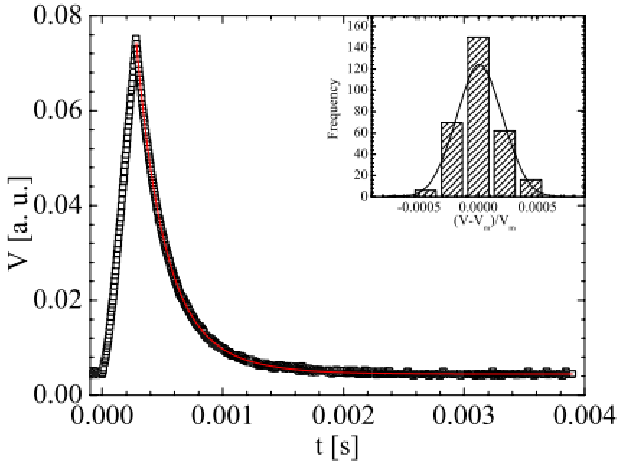
$$C_t \propto \frac{n k_B^2 T}{\zeta}$$

Experiments: Forced Rayleigh Scattering (FRS)

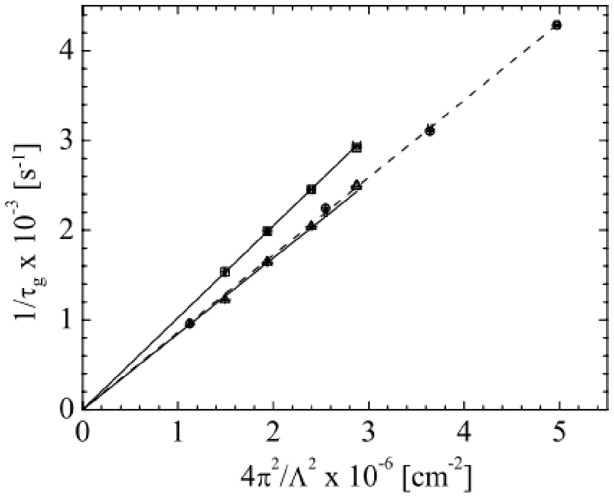




100 waveforms for each grating size



4 grating sizes for each elongation



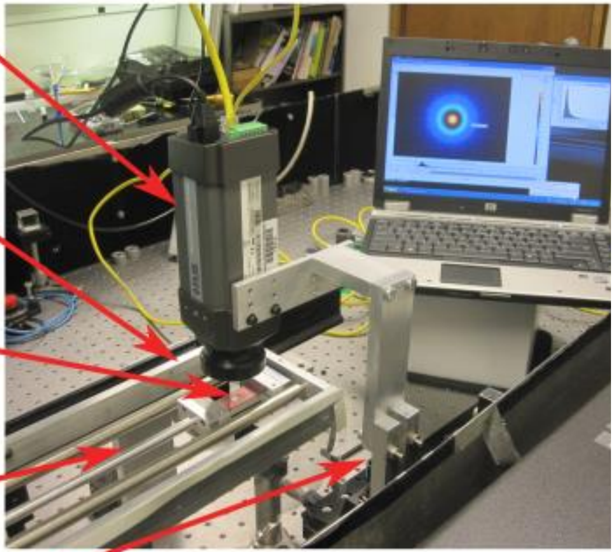
Intensity/Voltage at the photodetector:

$$V(t) = \mathrm{A}\exp\left(-2\frac{t}{\tau_{\mathrm{g}}}\right) + \mathrm{B}\exp\left(-\frac{t}{\tau_{\mathrm{g}}}\right) + \mathrm{C}$$

$$\frac{1}{\tau_{\mathrm{g}}} = \boxed{D_{\mathrm{th}}}\frac{4\pi^2}{\Lambda^2} \qquad D_{\mathrm{th}} = \frac{k}{\rho\hat{c}_p}$$

Nieto Simavilla et al. J. Pol. Sci. B 2012

Experiments: Infrared Thermography (IRT)



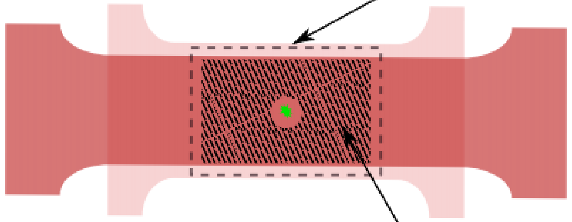
IR Camera FLIR A320

Stretching Frame

Sample

3 Axis Frame Stage

3 Axis Camera Stage



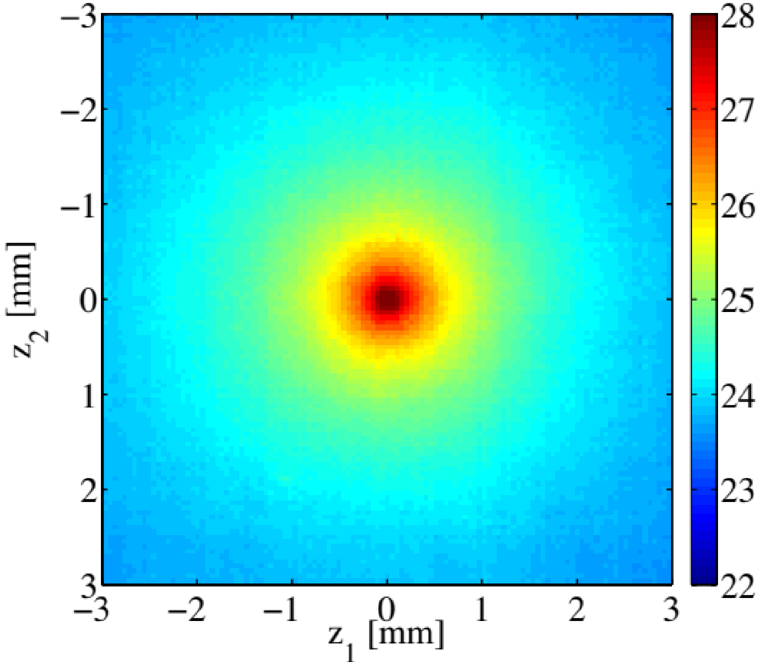
Camera field of view

Area used on IRT

$$\theta(x_1, x_2) = \frac{1}{4\sqrt{\alpha_1\alpha_2}} K_0\left(\sqrt{2\mathrm{Bi}({x_1}^2/\alpha_1 + {x_2}^2/\alpha_2)}\right)$$

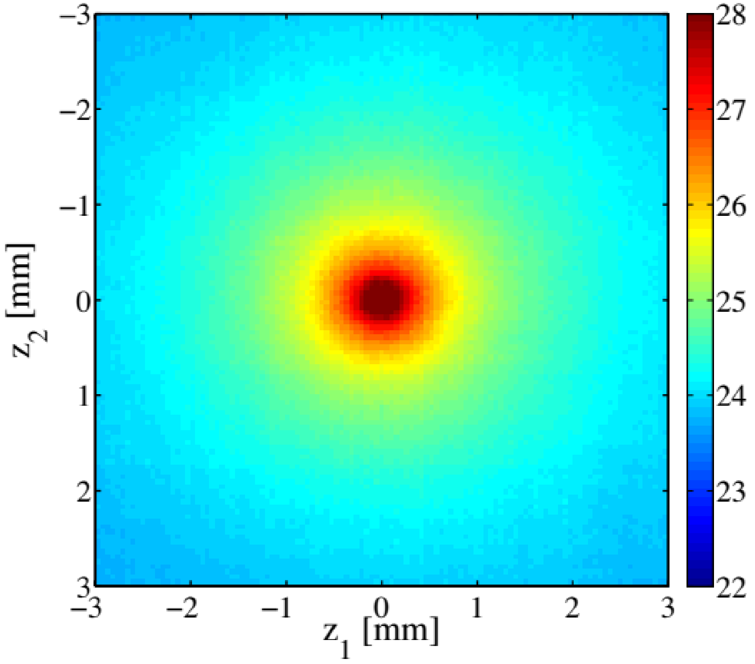
$KI_0w^2/k_{\mathrm{eq}}, \quad \mathrm{Bi} = hd/k_{\mathrm{eq}}$

$\alpha_1 = k_{11}/k_{\mathrm{eq}}, \quad \alpha_2 = k_{22}/k_{\mathrm{eq}}$



Un-stretched sample, $\lambda = 1$

and $\mathrm{Bi}_0 = 0.029 \pm 0.001$

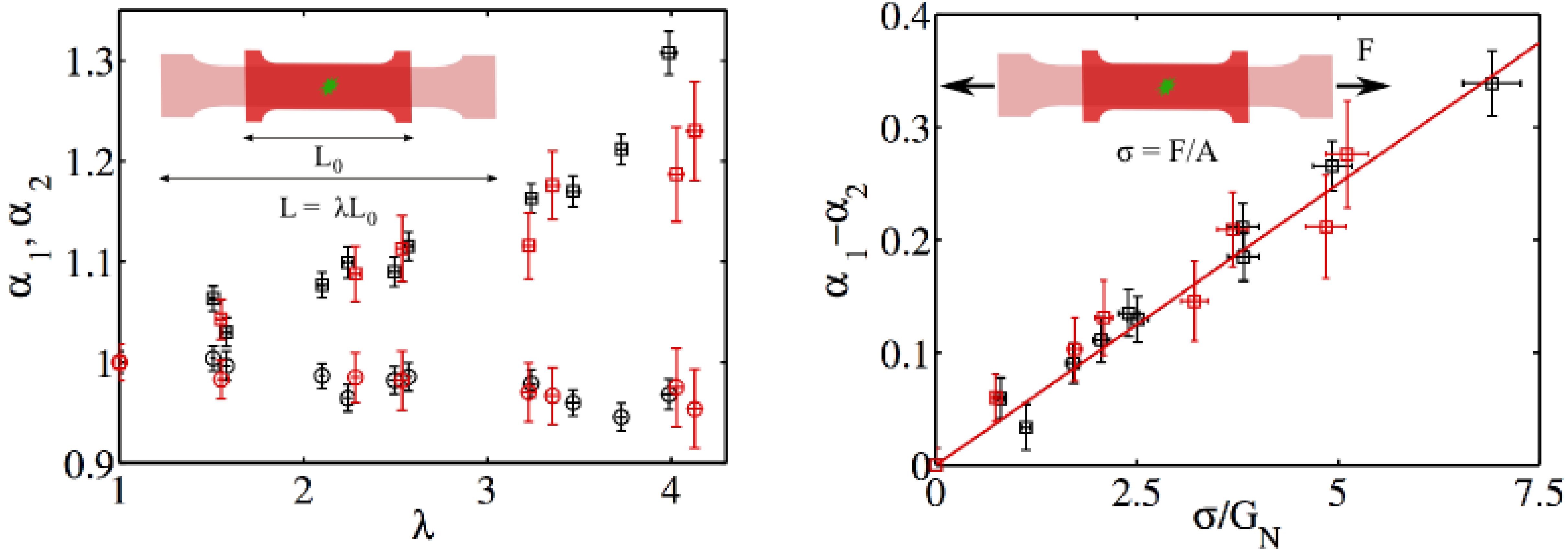


Stretched sample, $\lambda = 4.129$,

$\alpha_1 = 1.23 \pm 0.049$ and $\alpha_2 = 0.954 \pm 0.039$

Nieto Simavilla et al. Journal of Heat Transfer. 2014

Comparison FRS and IRT



(a)

(b)

Nieto Simavilla et al. Journal of Heat Transfer. 2014

Key Findings: Universality…

Stress-Thermal Coefficients for several polymeric materials

Material	Deformation –	G_N [kPa]	C_t x 10^4 [kPa^{-1}]	$C_\mathrm{t}G_\mathrm{N}$ –	C x 10^9 [Pa^{-1}]
PIB 85k[7]	Shear	320 [1]	1.9	0.061 ± 0.024	1.45
PIB 130k[7]	Shear	320 [1]	1.2	0.038 ± 0.022	1.45
xl-PDMS[6]	Uniax.	200 [1]	1.3	0.026 ± 0.008	0.13-0.26
xl-PBD 200k[5]	Uniax.	760 [1]	0.73	0.051 ± 0.011	3.5
xl-PBD 150k[5]	Uniax.	760 [1]	0.93	0.059 ± 0.014	3.5
xl-PI 100k[4]	Uniax.	370 [2]	0.37	0.014 ± 0.005	2.2
PS 260k[3]	Uniax.	200 [1]	1.65	0.033 ± 0.007	-4.8
PMMA 83k[3]	Uniax.	310 [1]	1.7	0.054 ± 0.011	0.16

$$\boxed{C_\mathrm{t}G_\mathrm{N} \sim 0.04}$$

(1) Fetters et al. Macromolecules 27, 17 (1994)
(2) Fetters et al. Macromolecules 37 (2004)
(3) Gupta et al. Journal of Rheology 57 (2013)
(4) Nieto Simavilla et al. J. Pol. Sci. B 50 (2012)
(5) Venerus et al. Macromolecules 42 (2009)
(6) Broerman et al. J.Chem. Phys. 111 (1999)
(7) Venerus et al. Phys. Rev. Lett. 82 (1999)

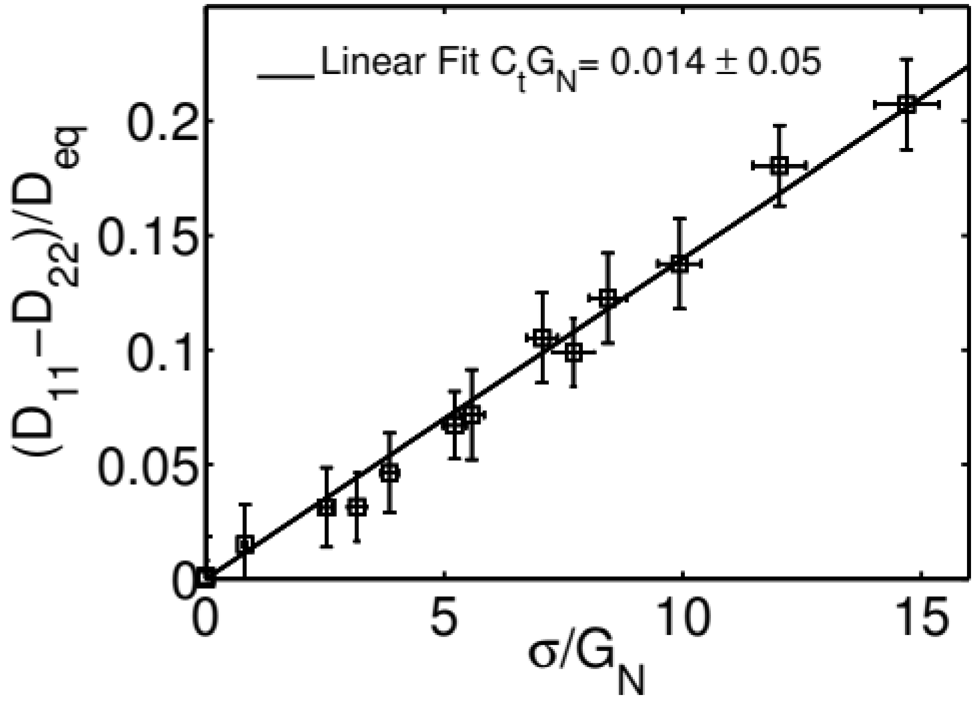
Stress-thermal Rule:

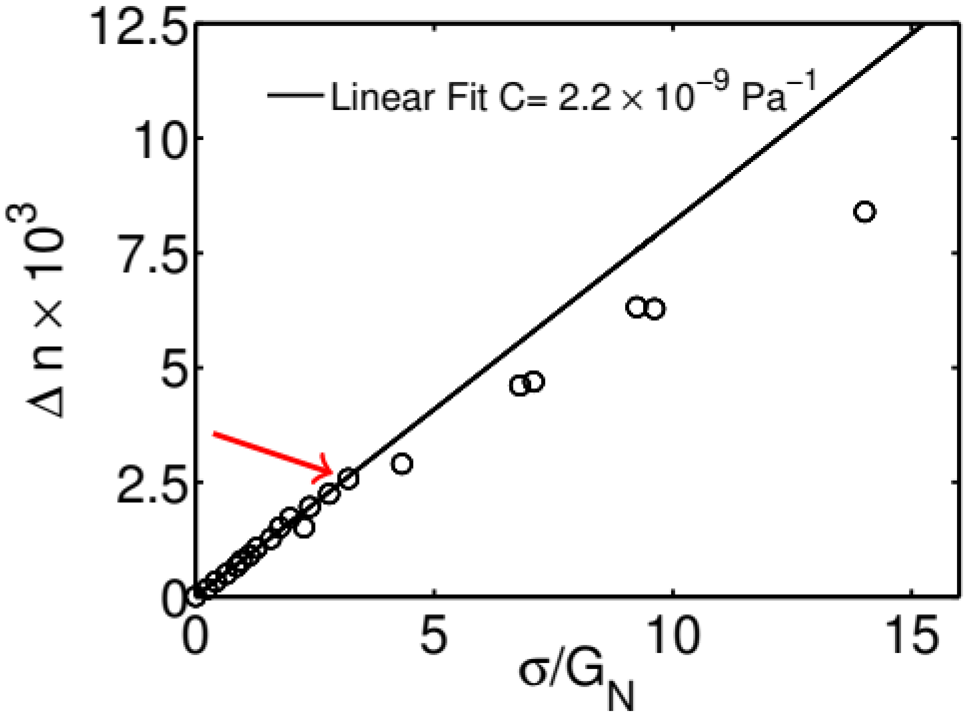
$$\boldsymbol{k} - \frac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_\mathrm{eq}C_\mathrm{t}(\boldsymbol{\tau} - \frac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta})$$

Stress-optic Rule:

$$\boldsymbol{n} - \frac{1}{3}\mathrm{tr}(\boldsymbol{n})\boldsymbol{\delta} = C(\boldsymbol{\tau} - \frac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta})$$

Key Findings: …Beyond Finite Extensibility





The STR stays valid where the SOR fails!

Nieto Simavilla et al. J. Pol. Sci. B 2012

Constitutive Model: eXtended Pom-Pom

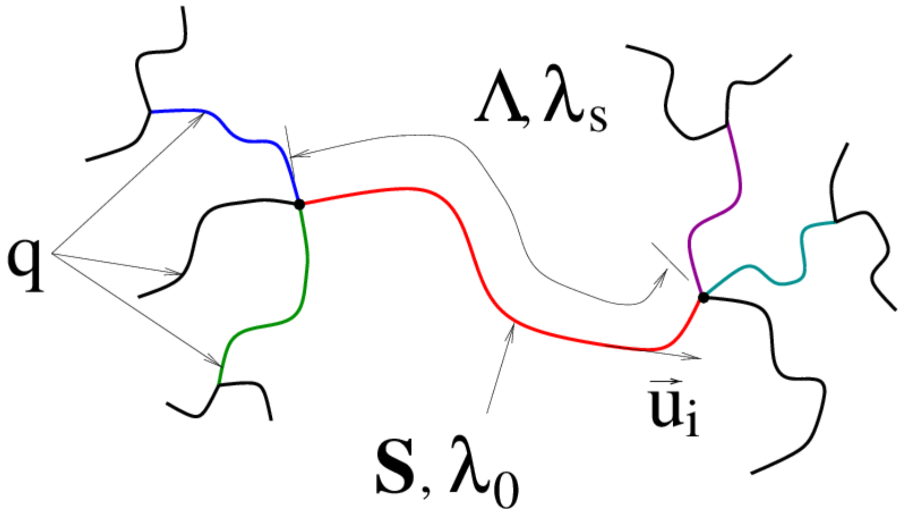
- What physics are in the model?

$$\overset{\nabla}{\boldsymbol{\tau}} + \boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} \cdot \boldsymbol{\tau} - 2G_0\mathbf{D}_u = \mathbf{0} \qquad \alpha \neq 0 \rightarrow \Psi_2 \neq 0$$

$$\boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}}\left[\frac{\alpha}{G_0}\boldsymbol{\tau} + f(\boldsymbol{\tau})^{-1}\boldsymbol{I} + G_0\left(f(\boldsymbol{\tau})^{-1} - 1\right)\boldsymbol{\tau}^{-1}\right] \qquad \Lambda = \sqrt{1 + \frac{I_{\tau}}{3G_0}}$$

$$\frac{1}{\lambda_{0b}} f(\boldsymbol{\tau})^{-1} = \frac{2}{\lambda_s}\left(1 - \frac{1}{\Lambda}\right) + \frac{1}{\lambda_{0b}}\left(\frac{1}{\Lambda^2} - \frac{\alpha I_{\boldsymbol{\tau}\cdot\boldsymbol{\tau}}}{3G_0^2\Lambda^2}\right) \qquad \lambda_s = \lambda_{0s}\, e^{-\frac{2}{q}(\Lambda - 1)}$$

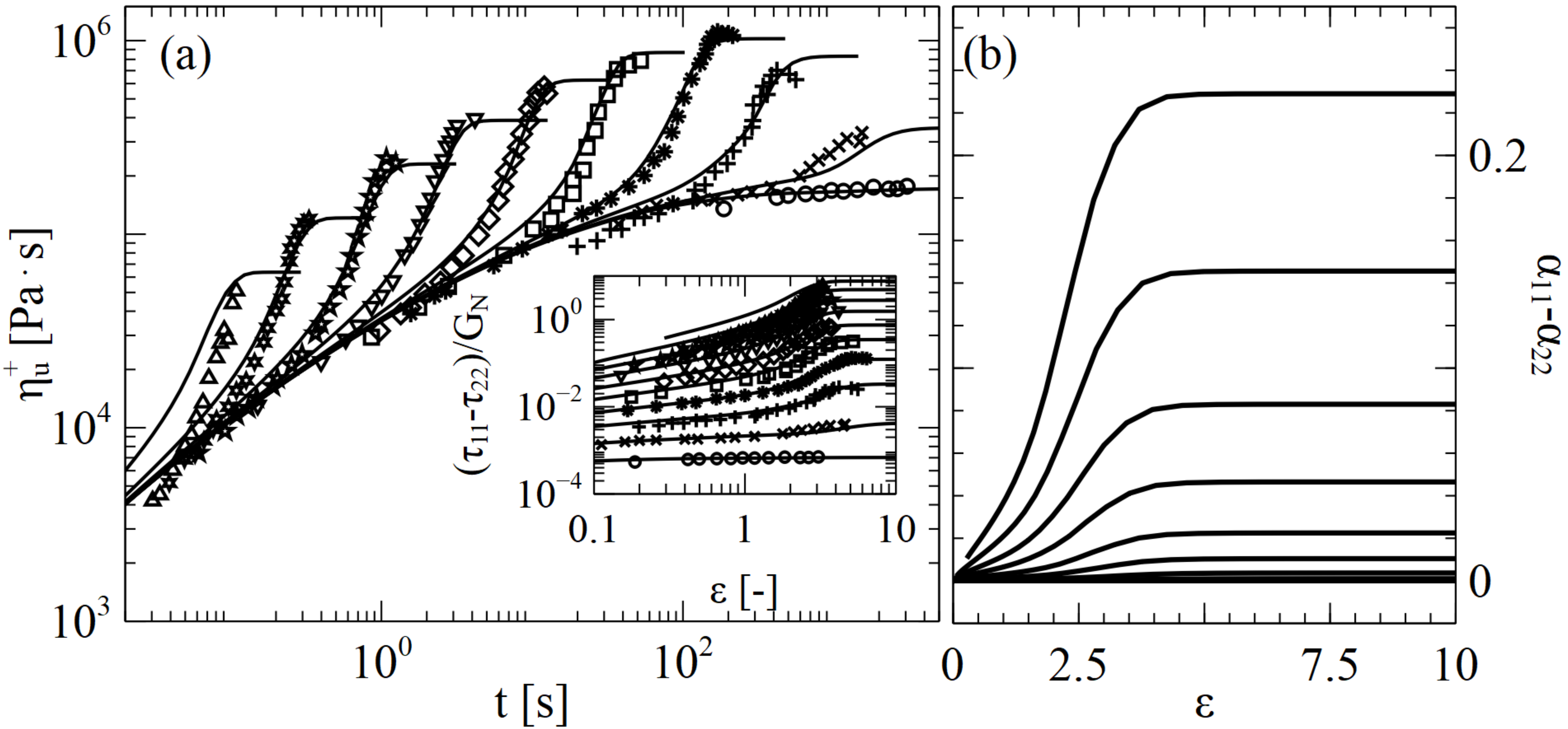
- Why XPP?
  - Amenable to FEM
  - Able to describe non-linear rheology
  - X: Avoids finite extensibility discontinuities
  - X: Includes second normal stress difference



Data: IUPAC_A LDPE melt at 170ºC

PP: McLeish and Larson. JOR 1998
xPP: Verbeeten et al. JOR 2001

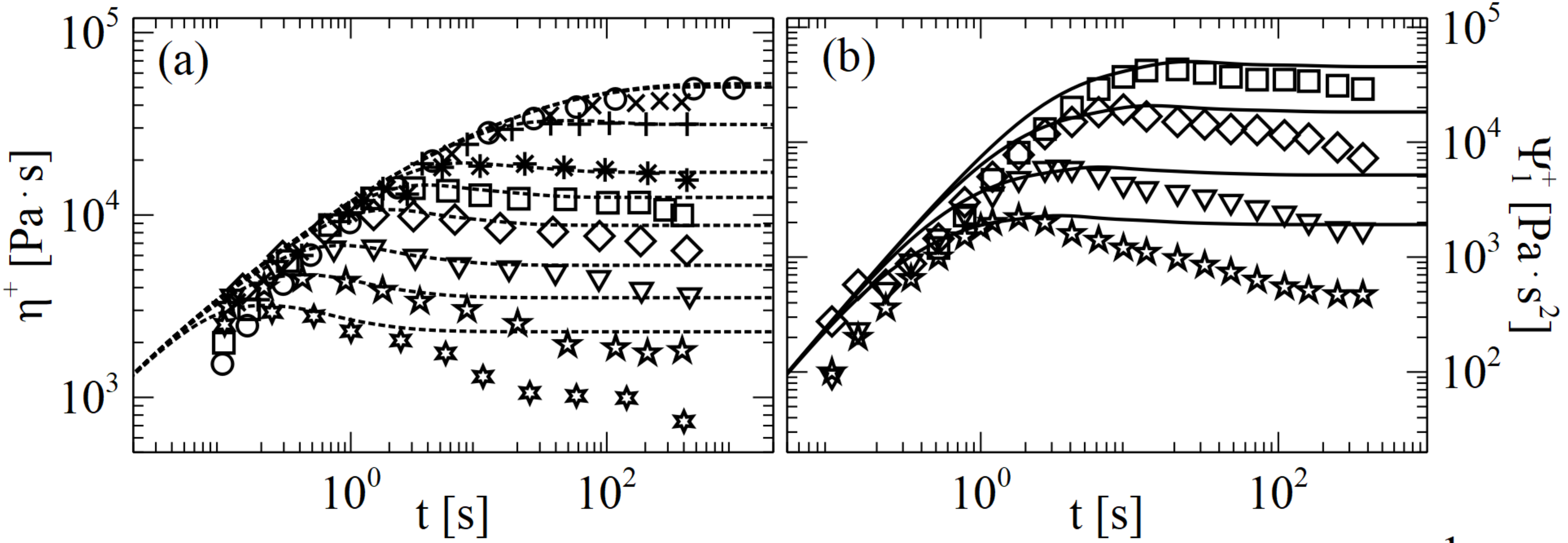
Transient Start-up: Uniaxial



The anisotropy in TC is comparable to that observed in PS and PMMA melts ~20%.

Gupta et al. Journal of Rheology 57, 2013.

Transient Start-up: Shear Rheology



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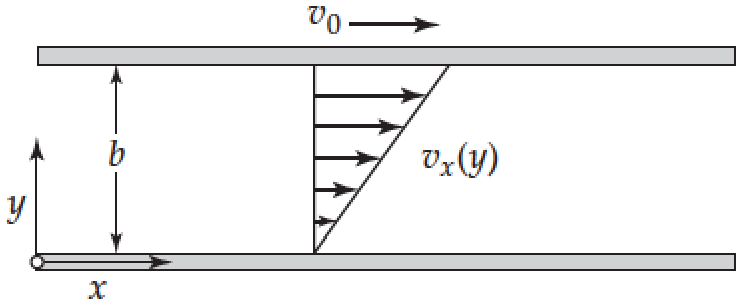
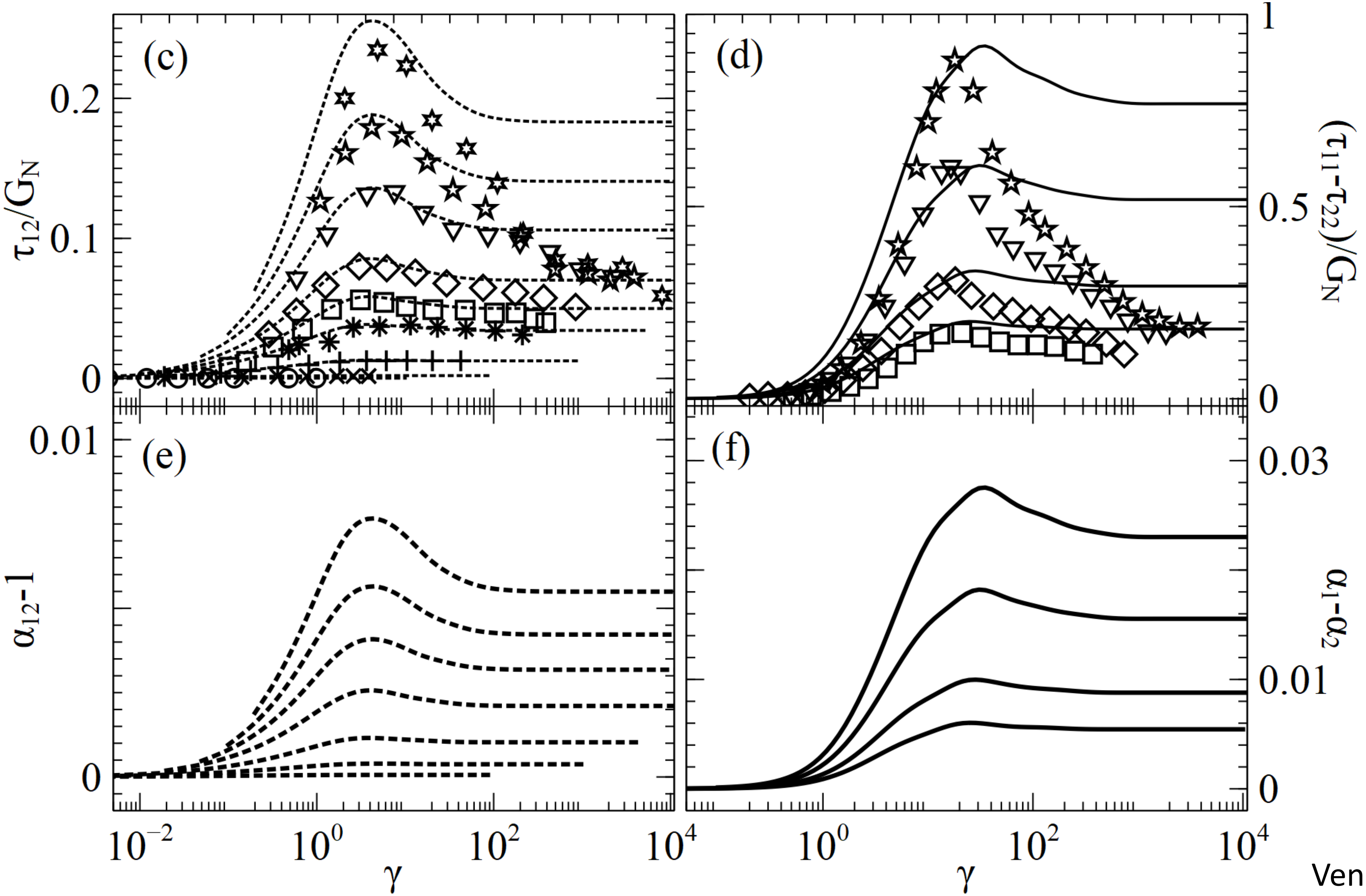


Transient Start-up: Shear



There is a non-zero off-diagonal component in shear flows

$$\boldsymbol{k} = \begin{pmatrix} k_{11} & k_{12} & k_{13} \\ & k_{22} & k_{23} \\ & & k_{33} \end{pmatrix}$$

$$\boldsymbol{q} = \boldsymbol{k} \cdot \boldsymbol{\nabla} T$$

Venerus et al. Phys. Rev. Lett. 1999

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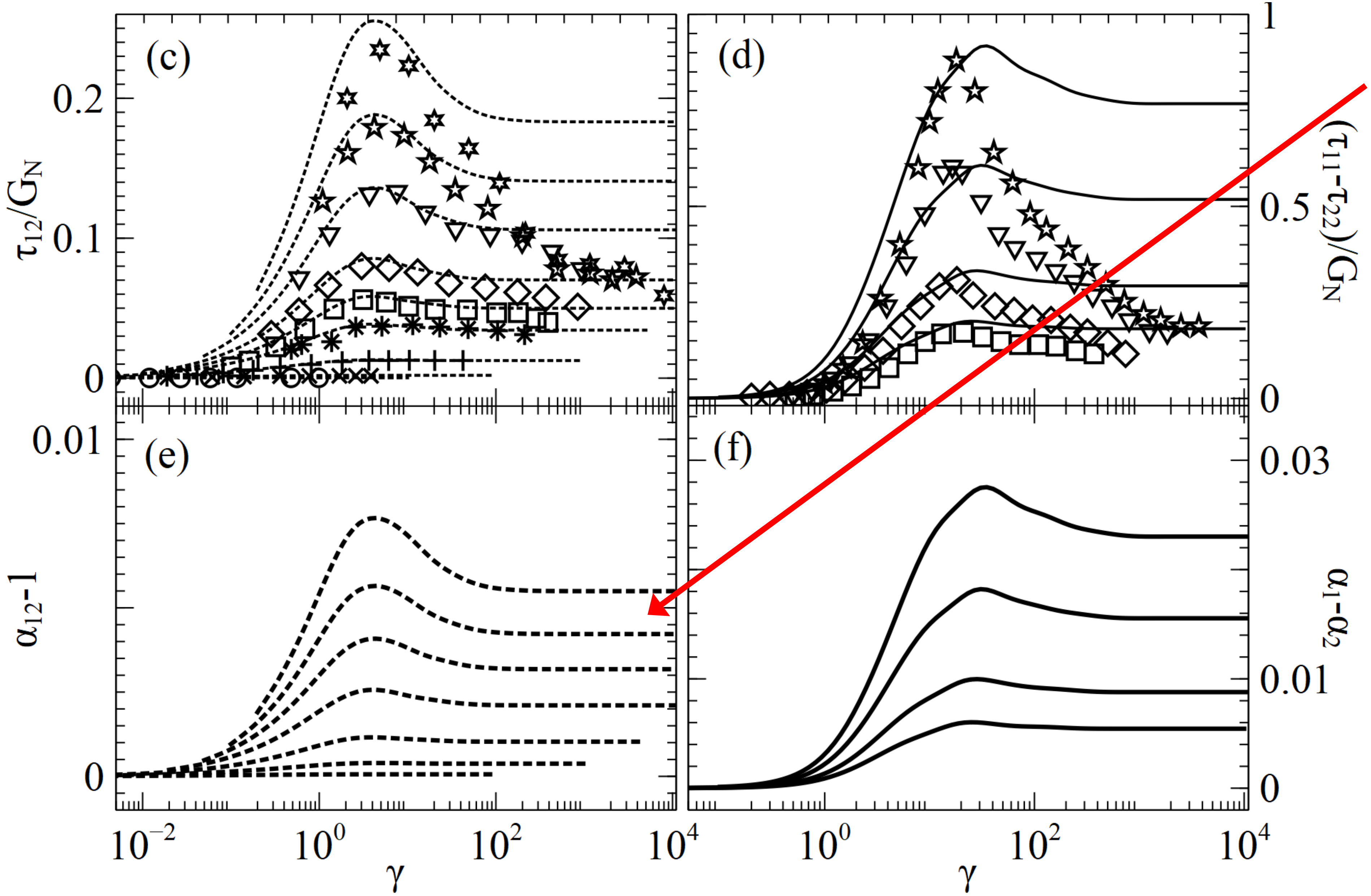

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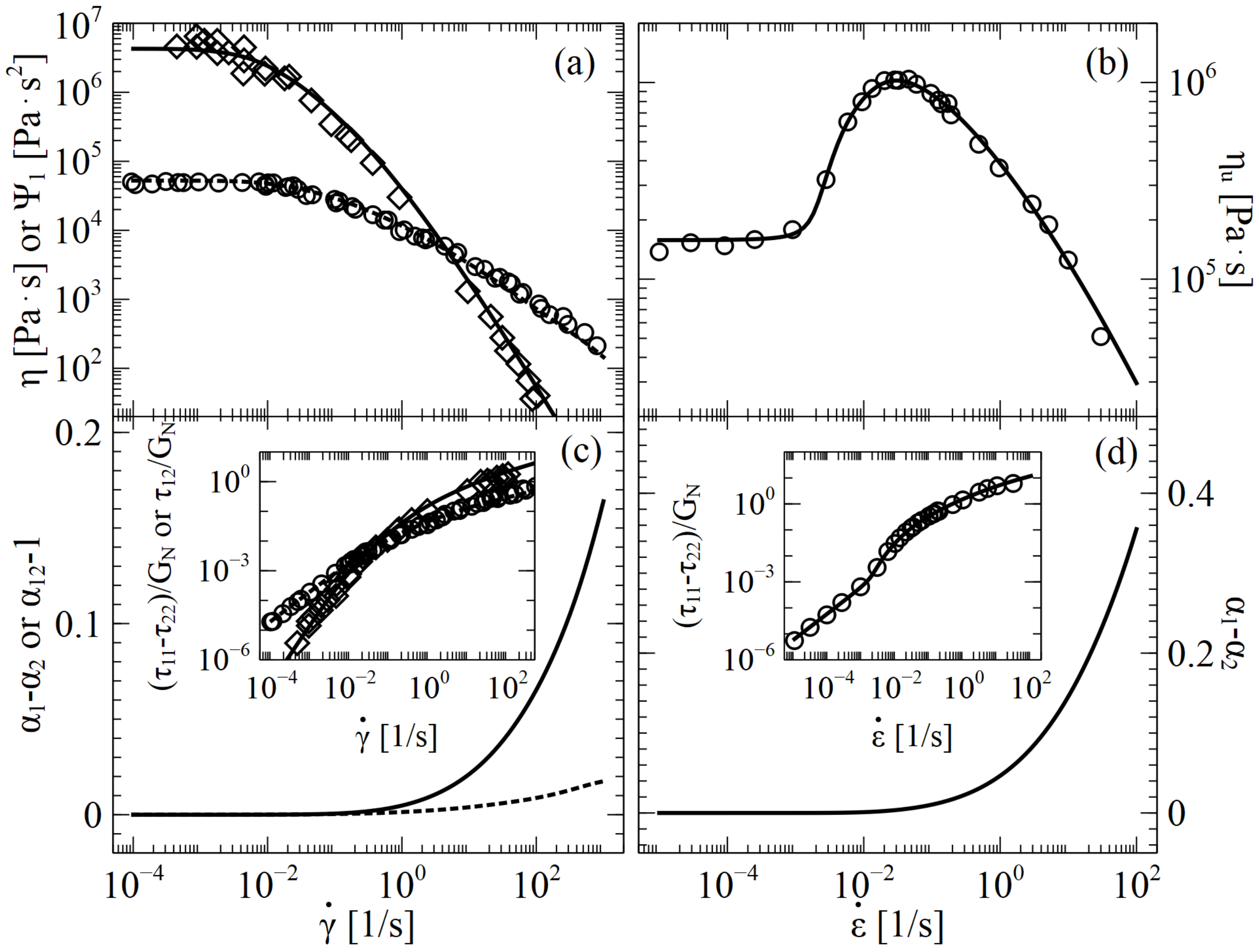
A temperature gradient in the 1-direction can generate heat flow in the 2-direction: ***Thermal Hall Effect***

Steady-State: Shear and Uniaxial Extension



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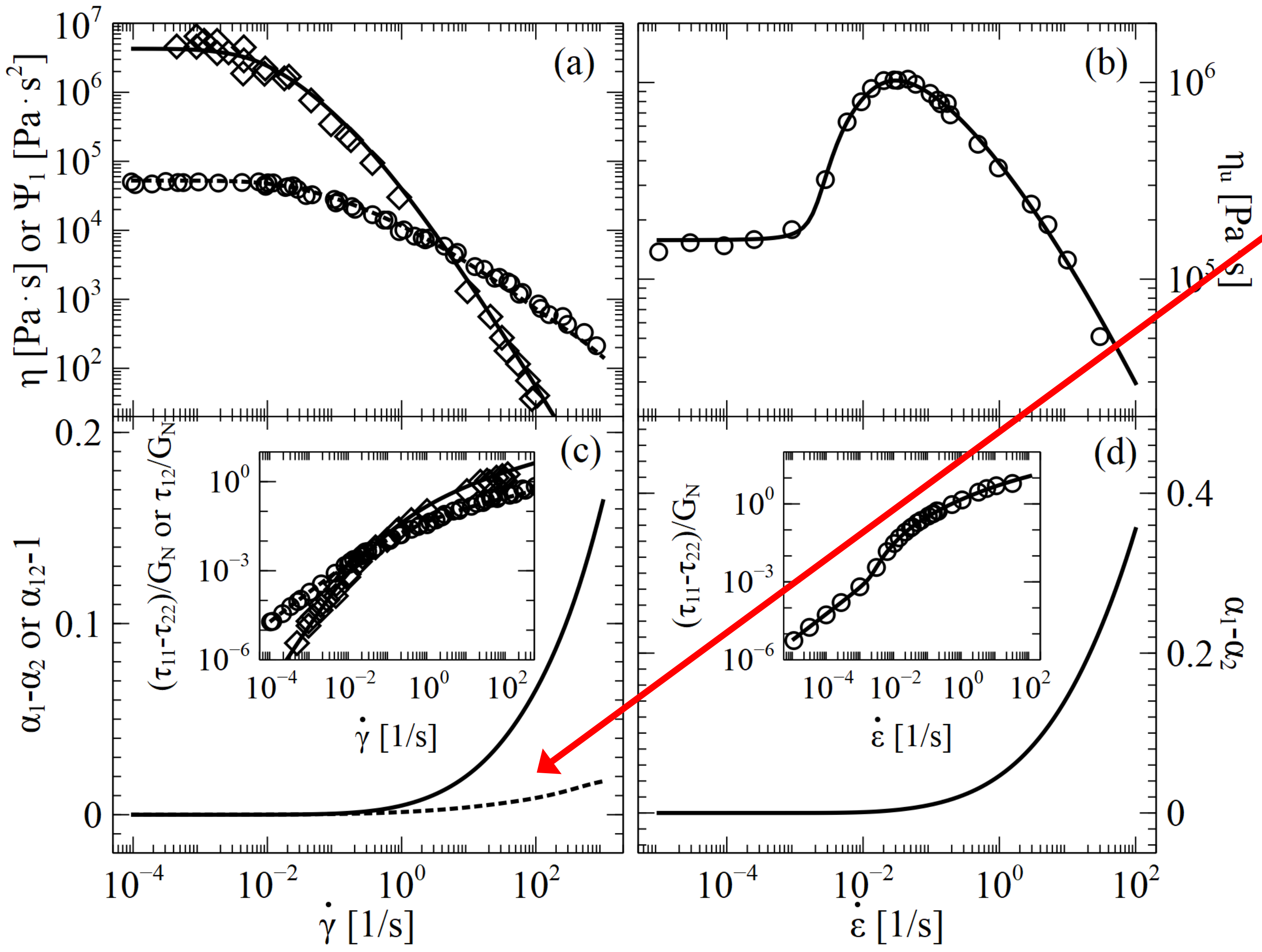

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Future Work: MTCIATTP project

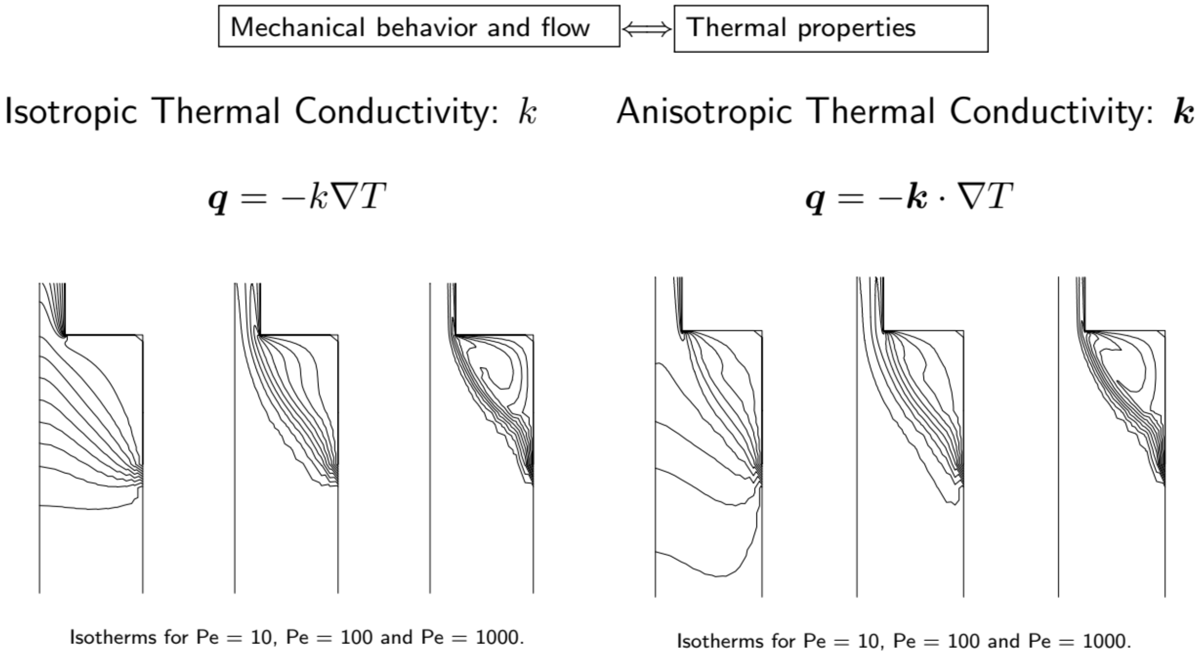
A. Implementation of New Constitutive Models

- Other polymer architectures: Rolie Poly
- Compare predictions with available experimental data PS, PMMA...

B. Develop a deeper understanding at the molecular level

- Why universal?
- Why beyond finite extensibility?

C. Implementation of Non-Isothermal Flow Simulations (FEM)


Mechanical behavior and flow $\Longleftrightarrow$ Thermal properties

Isotropic Thermal Conductivity: k

$$\boldsymbol{q} = -k\nabla T$$

Anisotropic Thermal Conductivity: $\boldsymbol{k}$

$$\boldsymbol{q} = -\boldsymbol{k}\cdot\nabla T$$

Isotherms for Pe = 10, Pe = 100 and Pe = 1000.

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Wapperon et al. Fluid Mech. and App. 1995

Conclusions

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Thank you!

David C. Venerus and Jay D. Schieber (Illinois Institute of Technology)

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Wilco M.H. Verbeeten (Universidad de Burgos)

Molecular to Continuum Investigation of Anisotropic Thermal Transport in Polymers
“MCIATTP”
Project # 750985

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