Annual European Rheology Conference
co-organized with XV Meeting of the Italian Society of Rheology-SIR

Anisotropic Thermal Transport in Non-Linear Non-Isothermal Polymeric Flows

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MARIE CURIE ACTIONS

HORIZON 2020

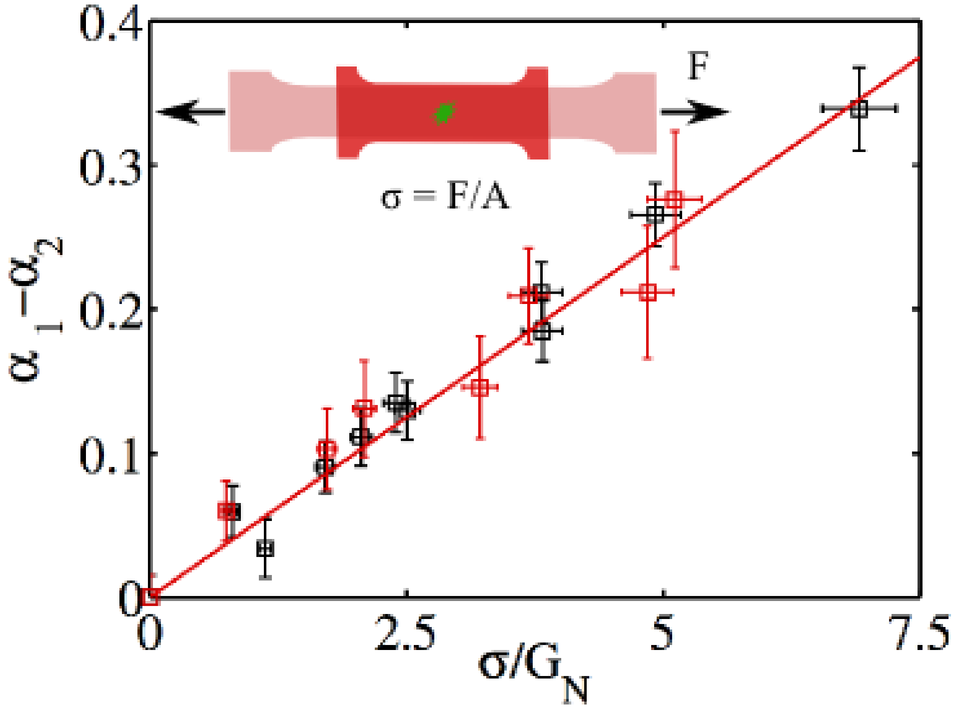
The MCIATTP project

A. Experimental investigation of thermal transport in polymers
- Anisotropy in thermal conductivity
- Stress-Thermal Rule
- Heat capacity vs. Deformation

B. Implementation of constitutive models
- Branched: eXtended Pom-Pom
- Linear: Rolie Poly
- Compare predictions with available experimental data PE, PS, PMMA...

C. Develop a deeper molecular understanding
- MD Simulations
- Why universal?
- Why beyond finite extensibility?

D. Implementation of non-homogeneous non-Isothermal flow simulations



Nieto et al. J. Heat Transfer 2014

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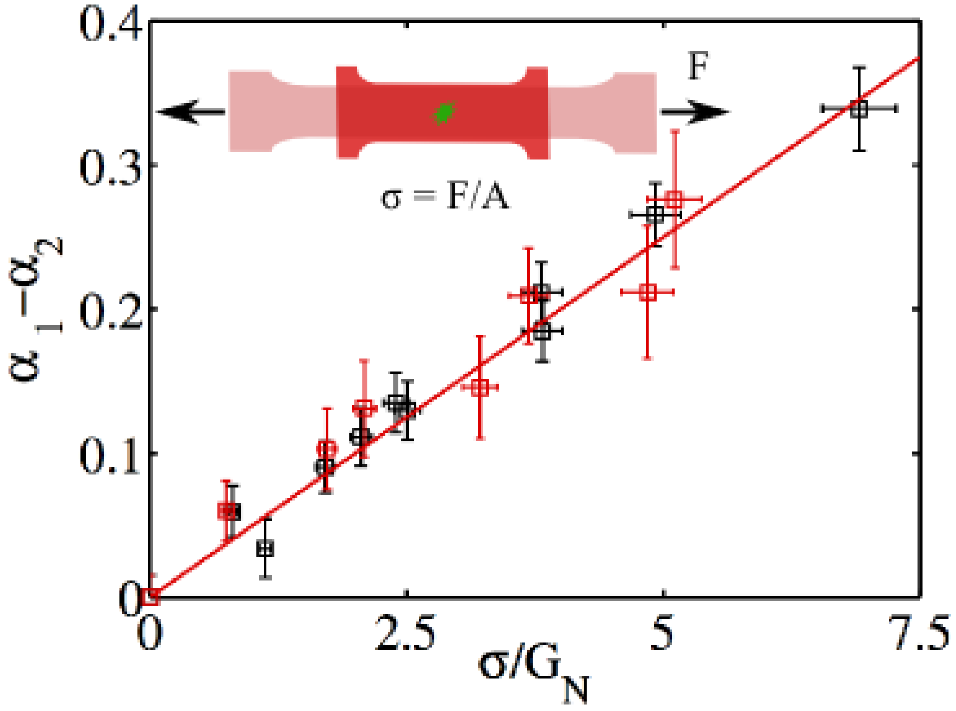

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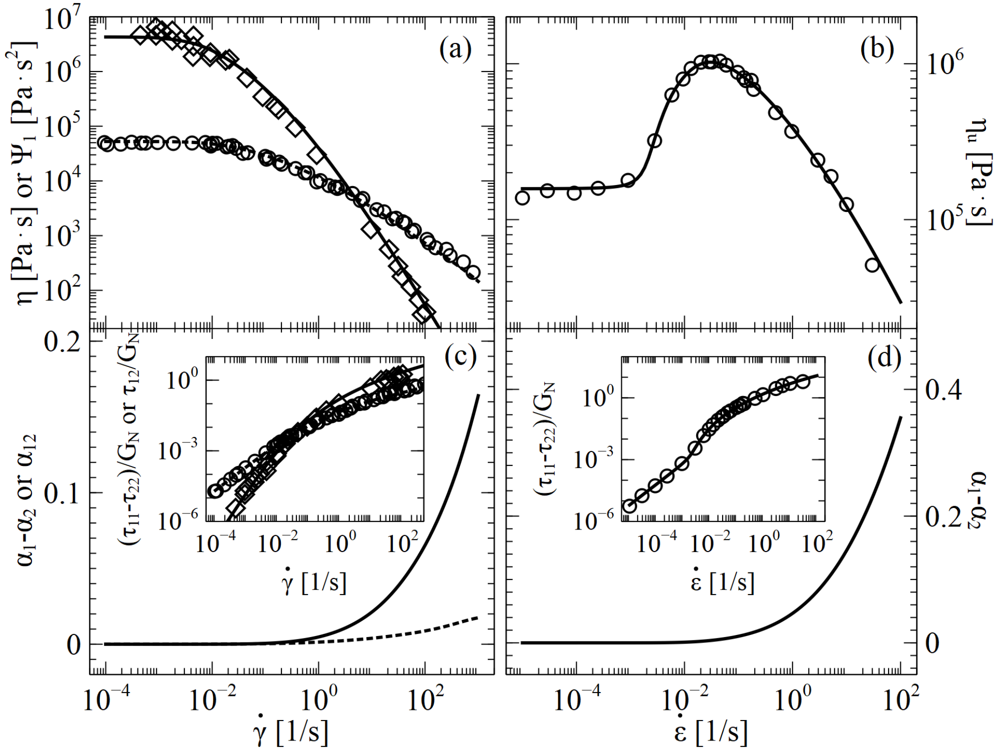

Nieto et al. Polymer Processing Society 33, 2017

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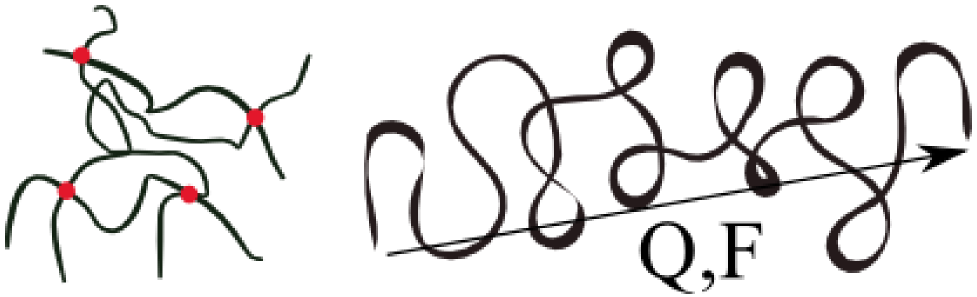

$$\boldsymbol{k} - \frac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} \propto n_i \langle \boldsymbol{R}\boldsymbol{R} \rangle_i$$

B.H.A.A. van den Brule. Rheol. Acta 1989

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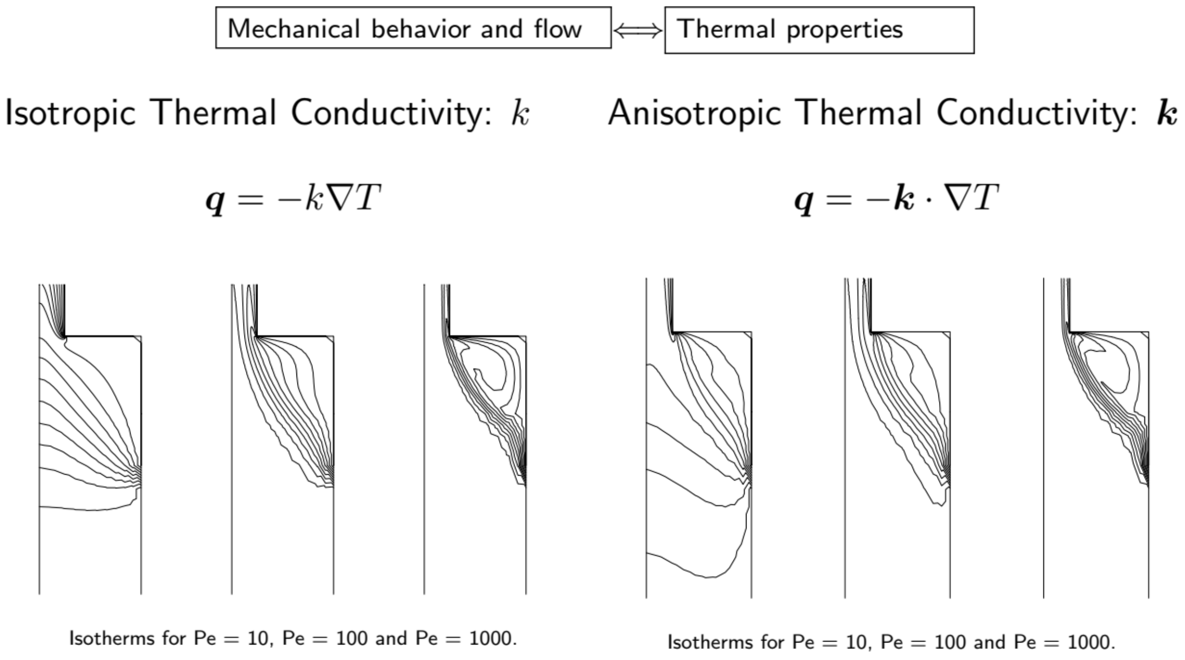
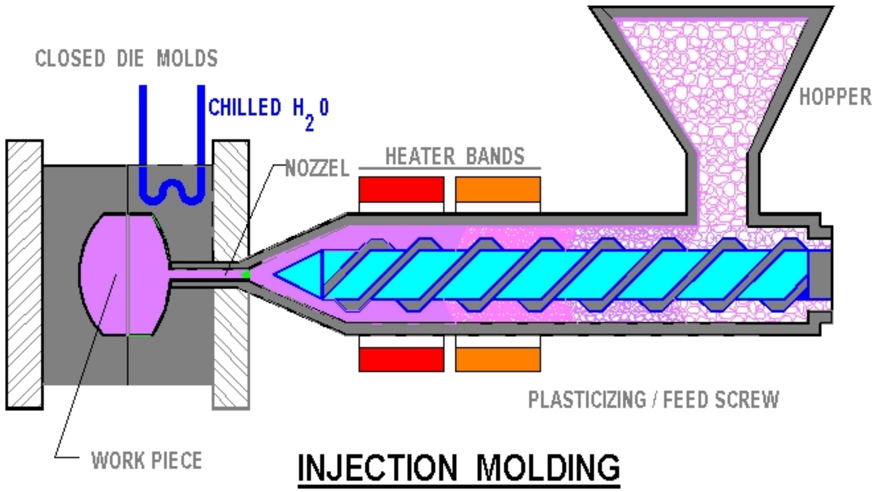
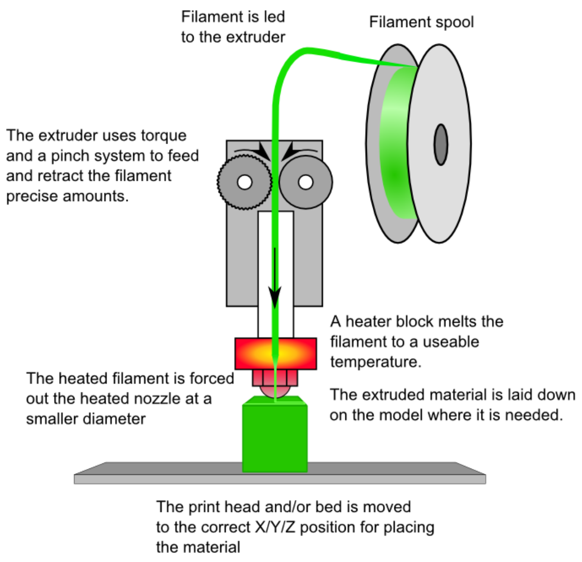
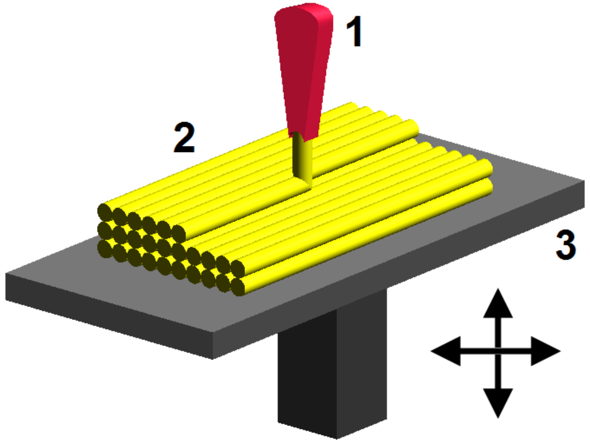


Wapperon et al. Fluid Mech. and App. 1995

Motivation: Polymer Processing







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

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:

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

- High stresses & Low thermal conductivity.

$$\boxed{\text{Mechanical behavior and flow}} \Longleftrightarrow \boxed{\text{Thermal properties}}$$

Anisotropic Thermal Conduction

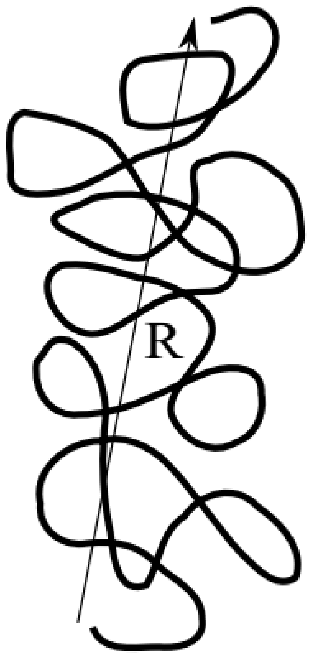
Fourier's Law: Thermal transport in deformed polymers is diffusive and anisotropic.

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

$\boldsymbol{k}$ 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:

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

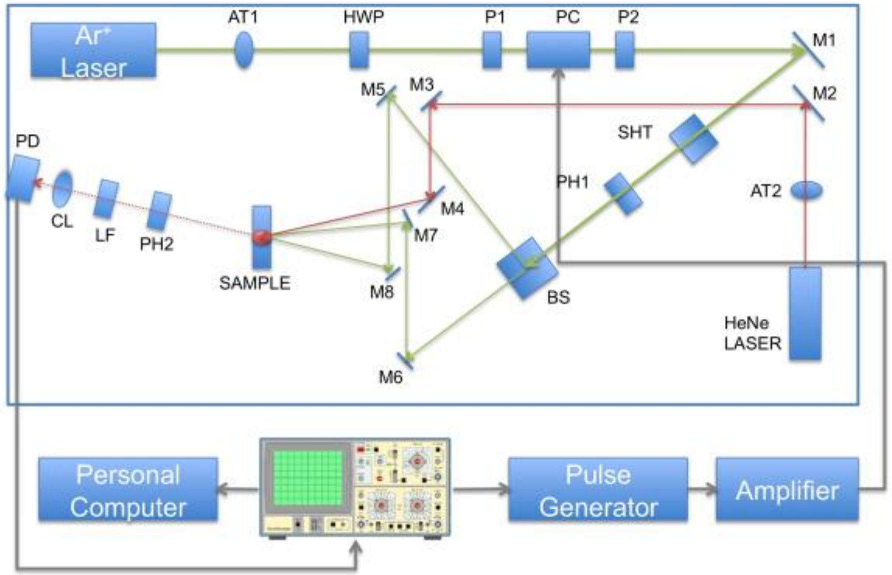
$$\boldsymbol{k} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{\mathrm{eq}} C_{\mathrm{t}} \left[\boldsymbol{\tau} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta} \right]$$

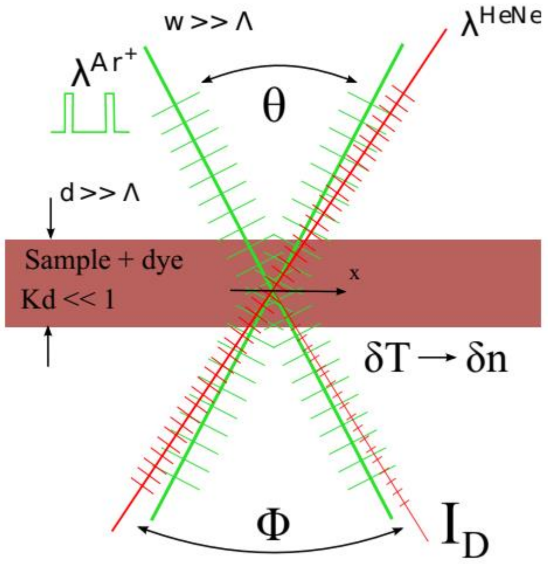
The Stress-Thermal Rule

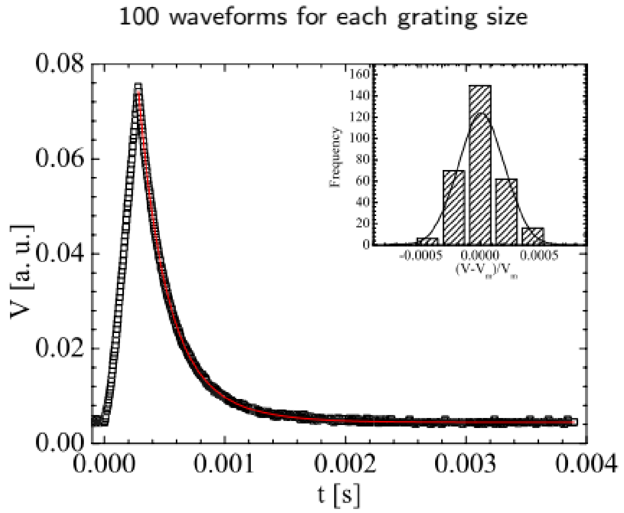
B.H.A.A. van den Brule, Rheol Acta 1989.
Öttinger and Petrillo, J. Rheol. 40 (5) 1996.
Curtiss and Bird, J. Chem. Phys. 107 (13) 1997.

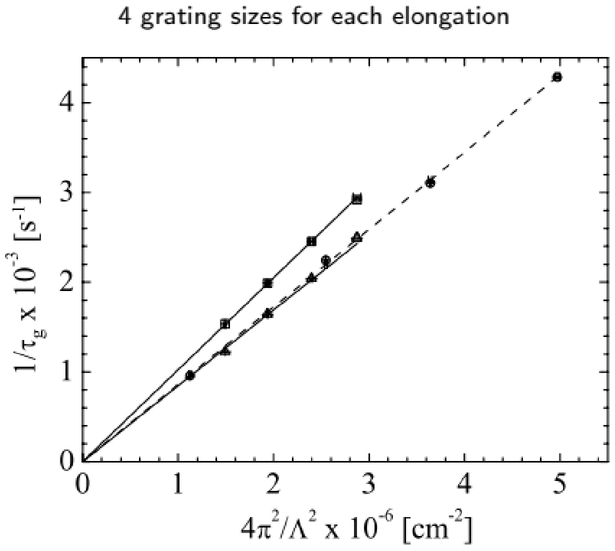
$$C_t \propto \frac{n k_B^2 T}{\zeta}$$

Experiments: Forced Rayleigh Scattering (FRS)









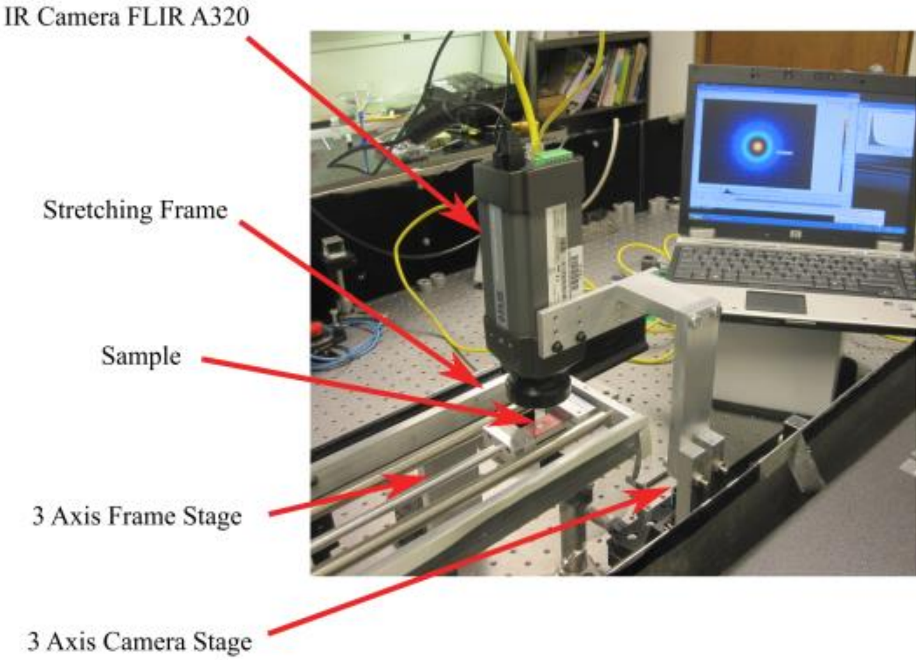
Intensity/Voltage at the photodetector:

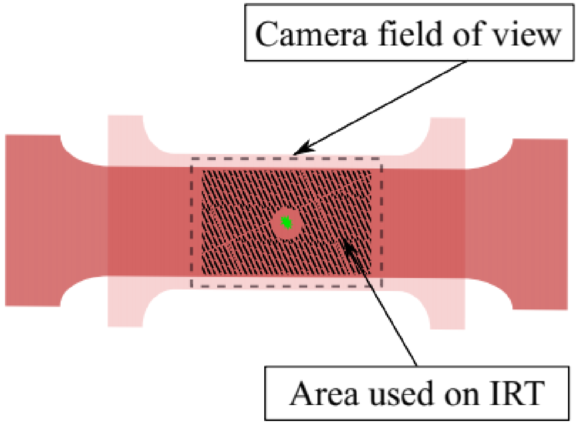
$$V(t) = \mathrm{A}\exp\left(-2\frac{t}{\tau_g}\right) + \mathrm{B}\exp\left(-\frac{t}{\tau_g}\right) + \mathrm{C}$$

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

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

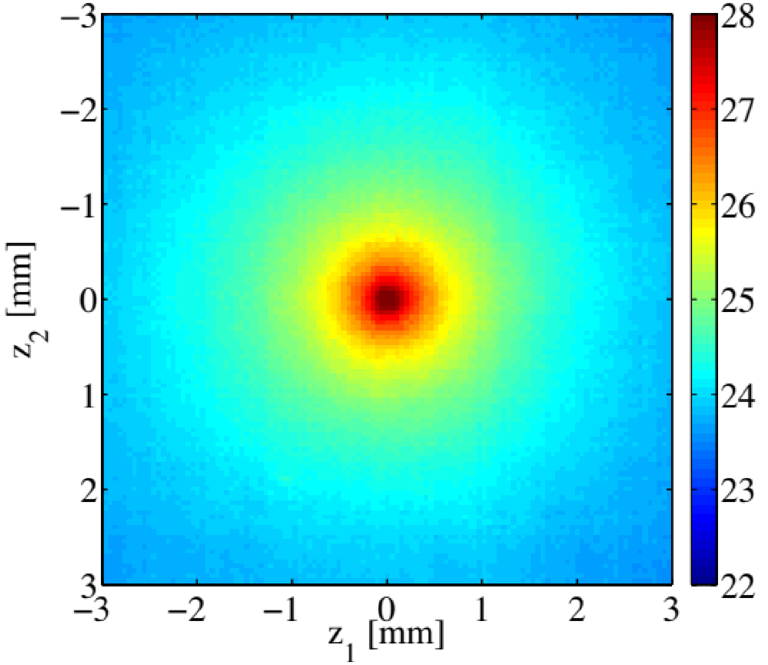
Experiments: Infrared Thermography (IRT)





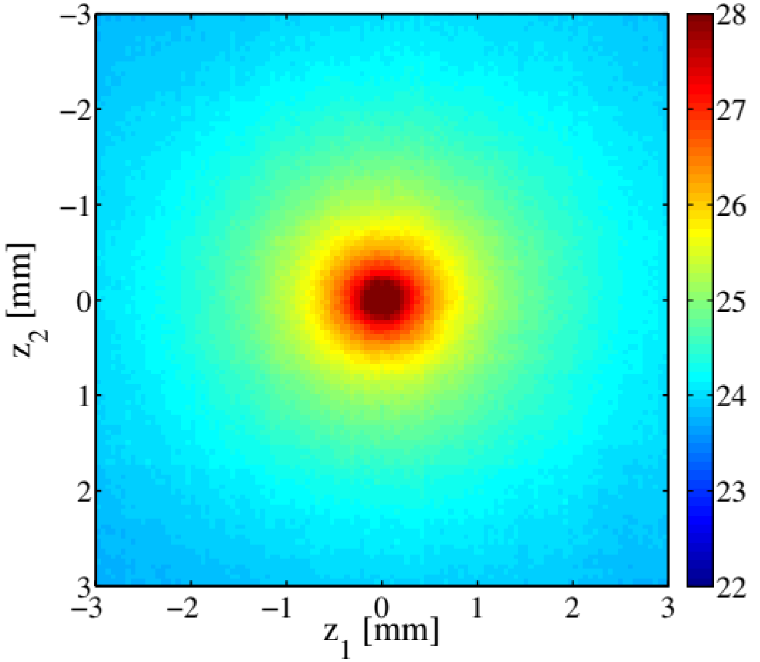
$$\theta(x_1, x_2) = \frac{1}{4\sqrt{\alpha_1\alpha_2}} K_0\left(\sqrt{2\text{Bi}(x_1{}^2/\alpha_1 + x_2{}^2/\alpha_2)}\right)$$

KI_0w^2/k_{eq}, $\text{Bi} = hd/k_{\text{eq}}$ $\qquad$ $\alpha_1 = k_{11}/k_{\text{eq}}$, $\alpha_2 = k_{22}/k_{\text{eq}}$



Un-stretched sample, $\lambda = 1$

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

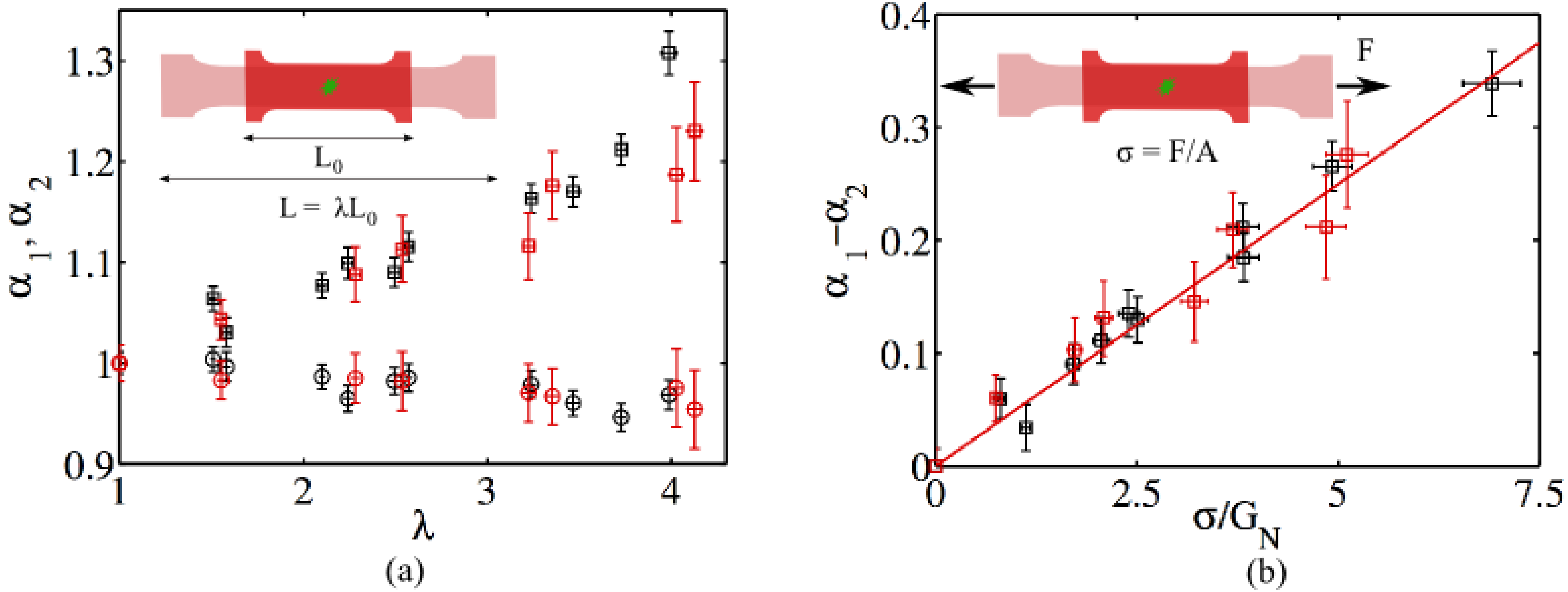


Stretched sample, $\lambda = 4.129$,

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

Nieto Simavilla et al. Journal of Heat Transfer. 2014

Comparison FRS and IRT



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}]	$C_t G_N$ –	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

$$C_t G_N \sim 0.04$$

(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)

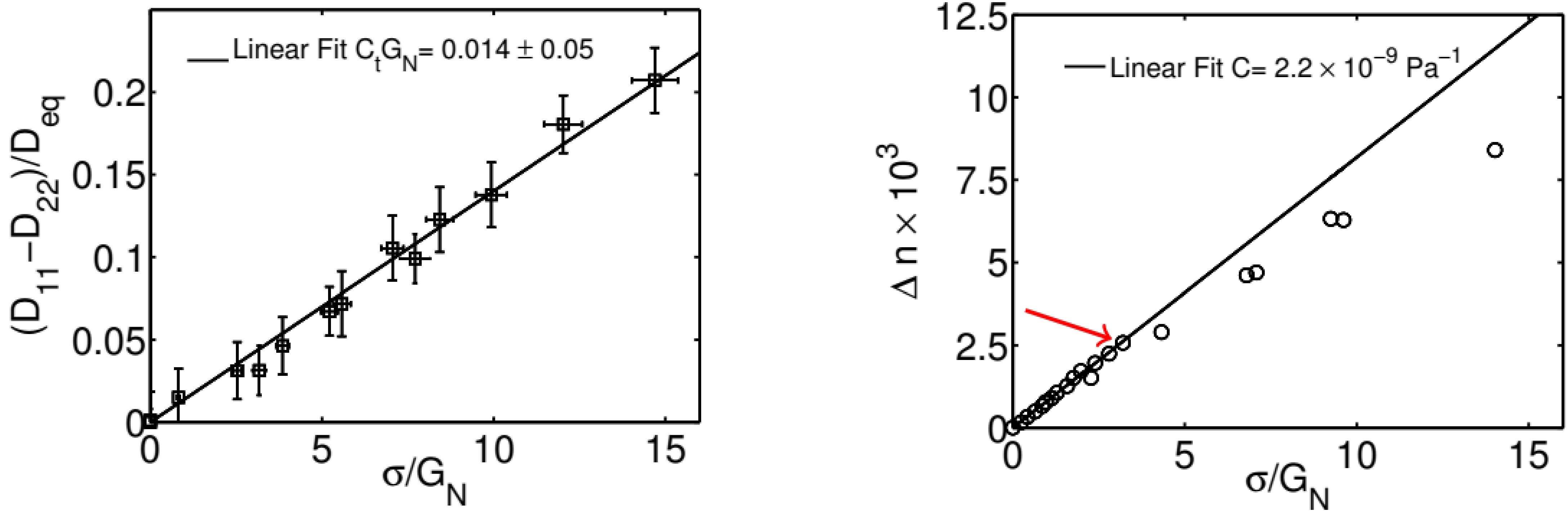
Stress-thermal Rule:

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

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

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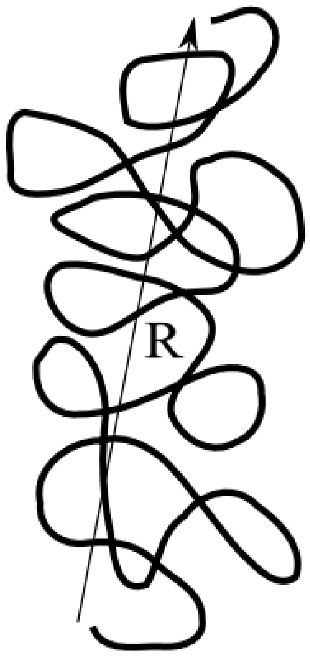

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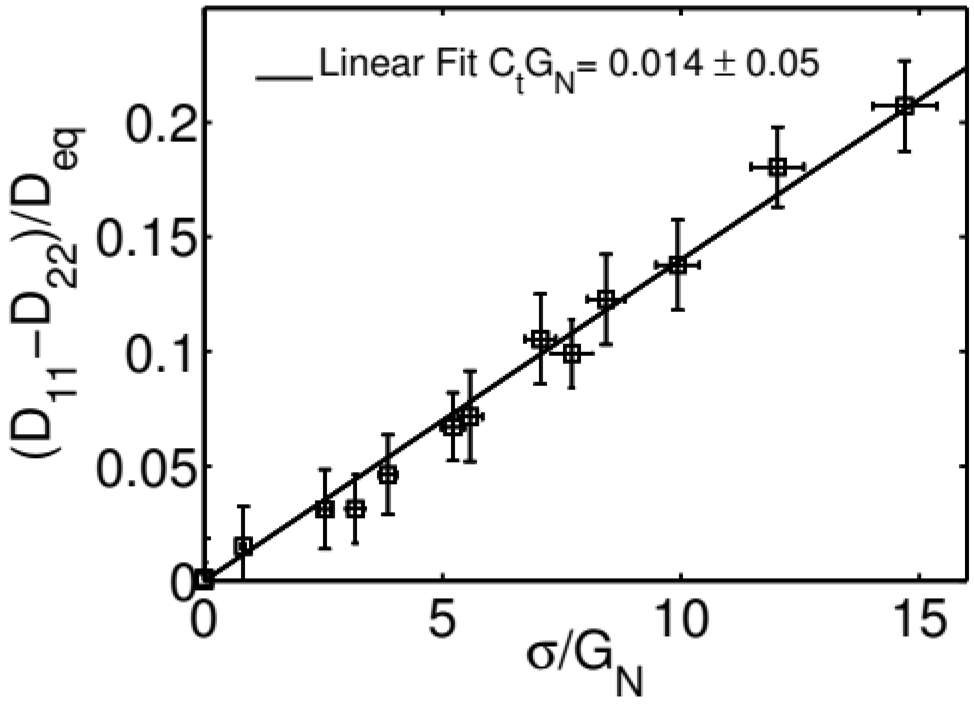
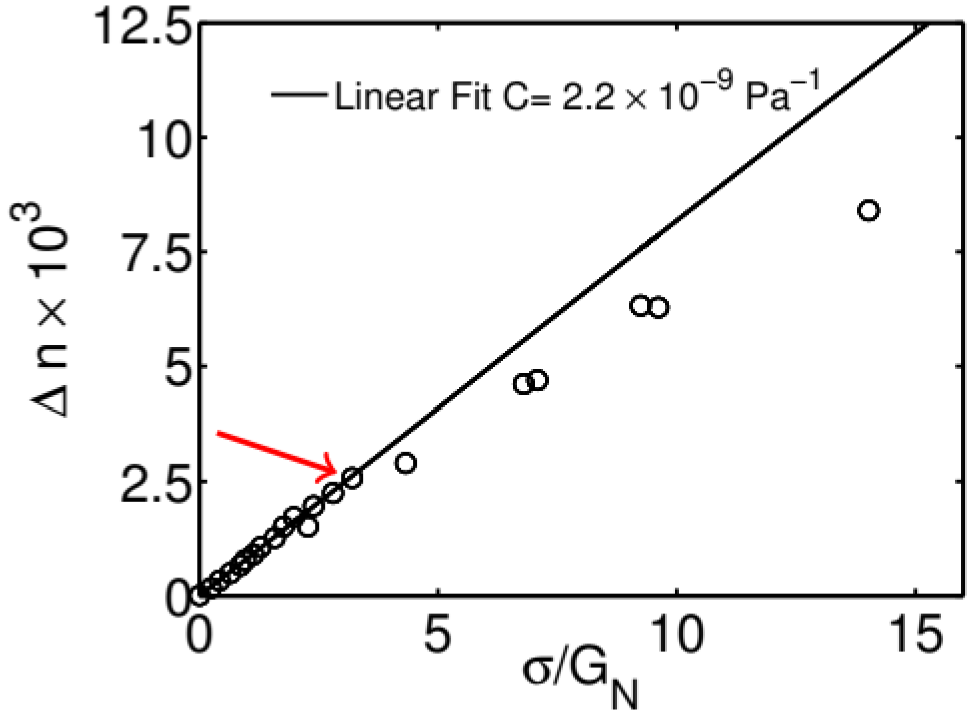




The STR stays valid where the SOR fails!

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

The Stress-Thermal Rule can be applied:

1. To any melt just by knowing stress and G_N
2. At high strain and strain rates beyond the onset of finite extensibility effects

Constitutive Model: eXtended Pom-Pom

- What physics are in the model?

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

$$\alpha \neq 0 \rightarrow \Psi_2 \neq 0$$

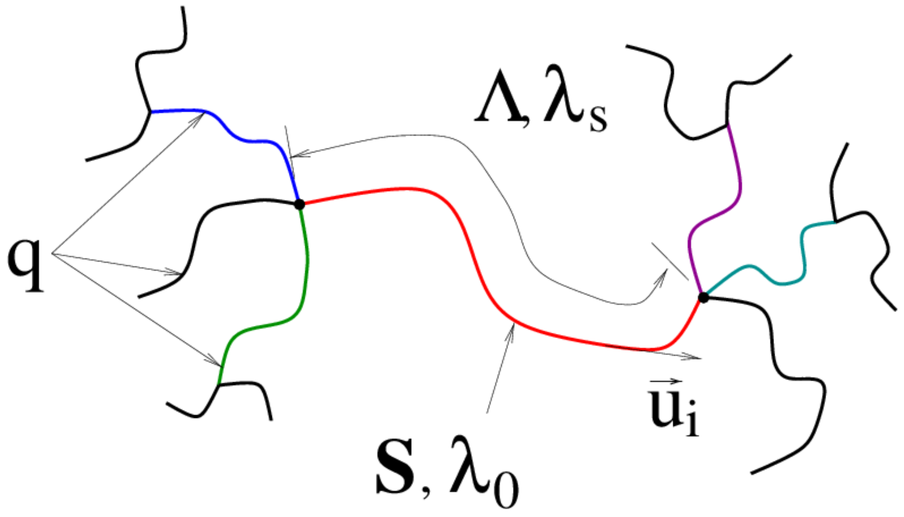
$$\boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}}\left[\frac{\alpha}{G_0}\boldsymbol{\tau} + f(\boldsymbol{\tau})^{-1}\boldsymbol{I} + G_0\left(f(\boldsymbol{\tau})^{-1} - 1\right)\boldsymbol{\tau}^{-1}\right]$$

$$\Lambda = \sqrt{1 + \frac{I_{\tau}}{3G_0}}$$

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

$$\lambda_s = \lambda_{0s}\, e^{-\frac{2}{q}(\Lambda - 1)}$$

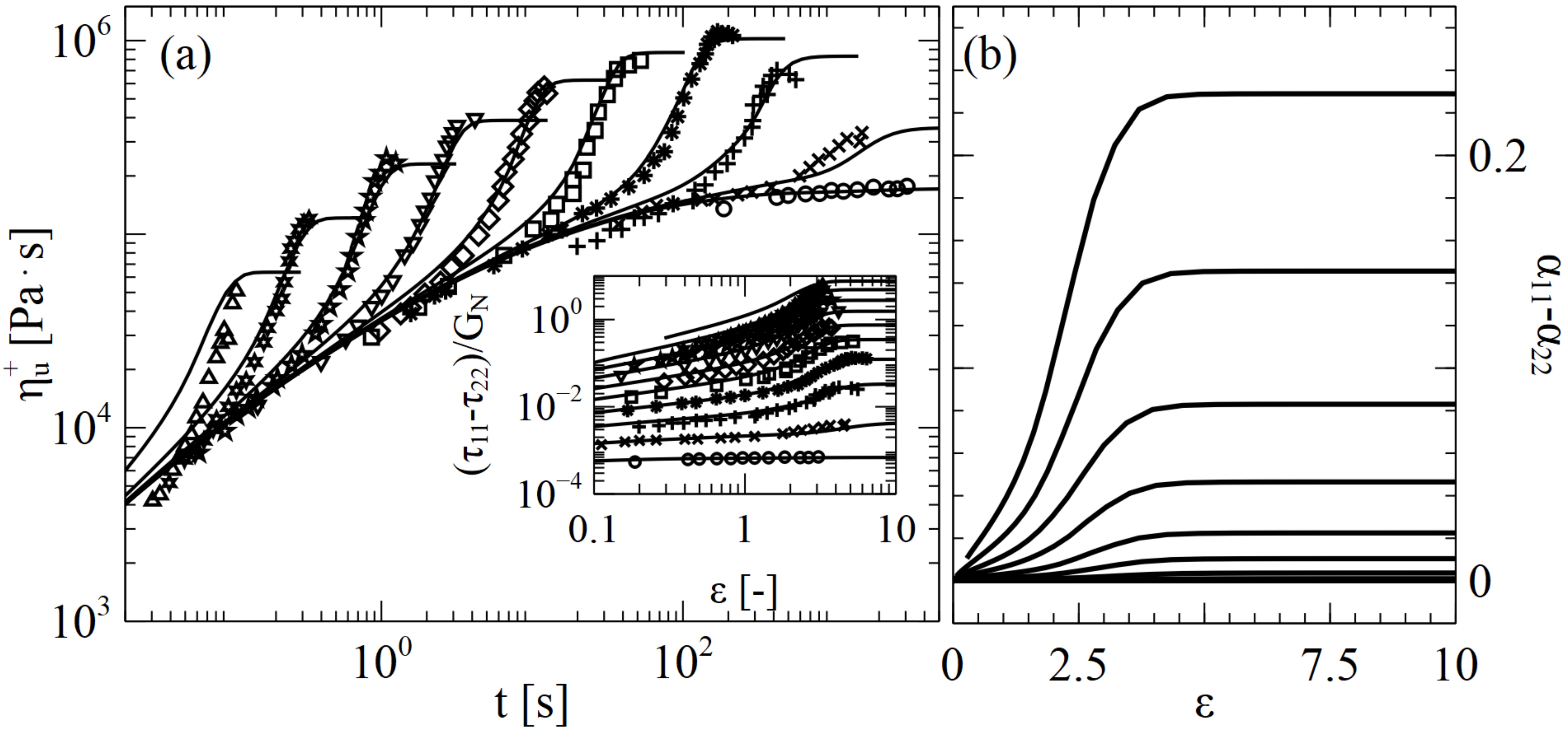
- Why XPP?
  - Amenable to FEM
  - Able to describe non-linear rheology
  - X: Avoids finite extensibility discontinuities
  - X: Includes second normal stress difference



Data: IUPAC_A LDPE melt at 170ºC
Verbeeten et al. JOR 2001

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

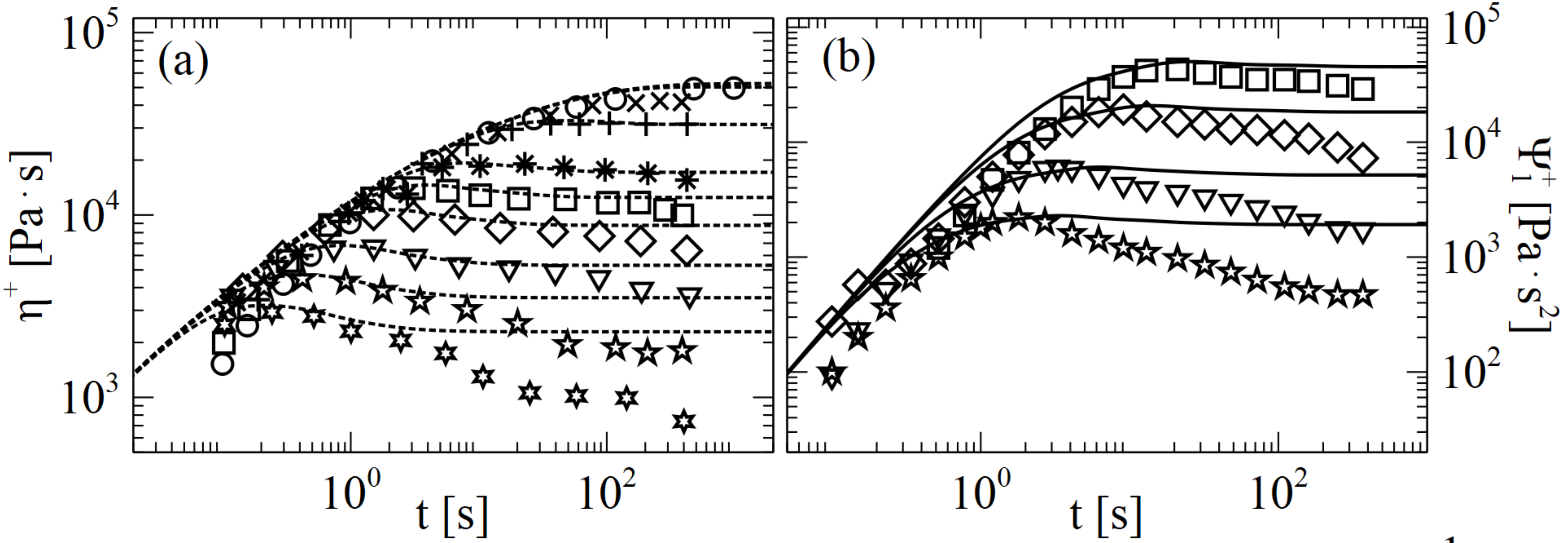
Transient Start-up: Uniaxial IUPAC_A LDPE



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 IUPAC_A LDPE



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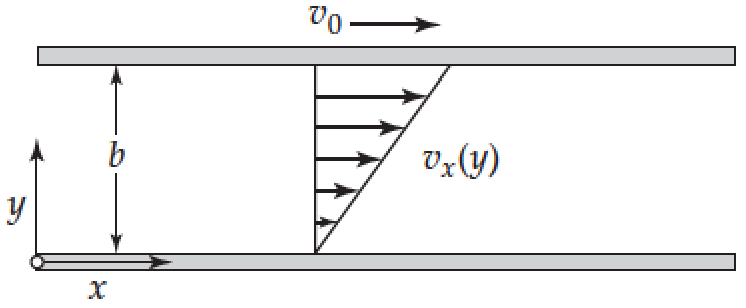
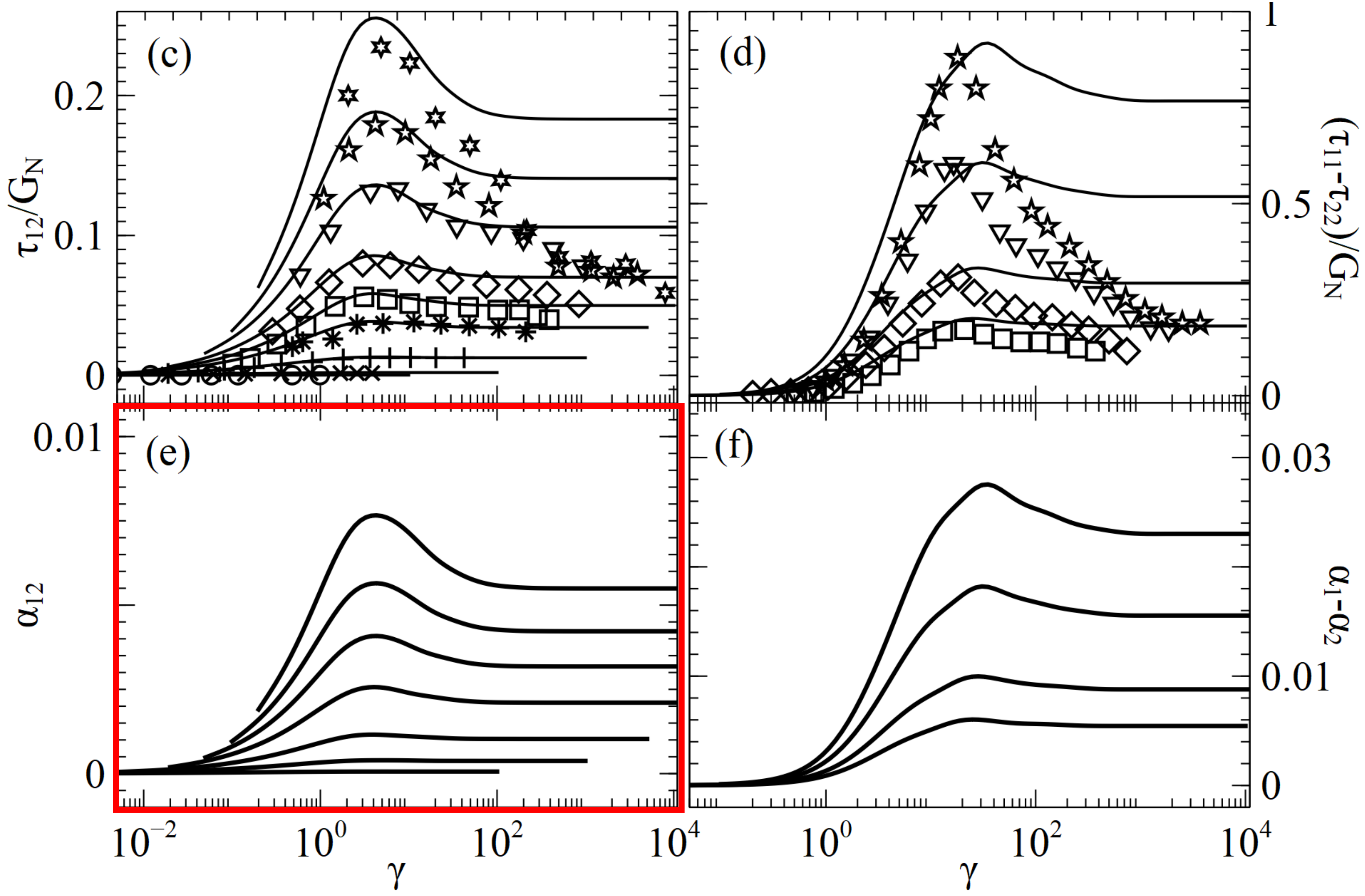


Transient Start-up: Shear IUPAC_A LDPE



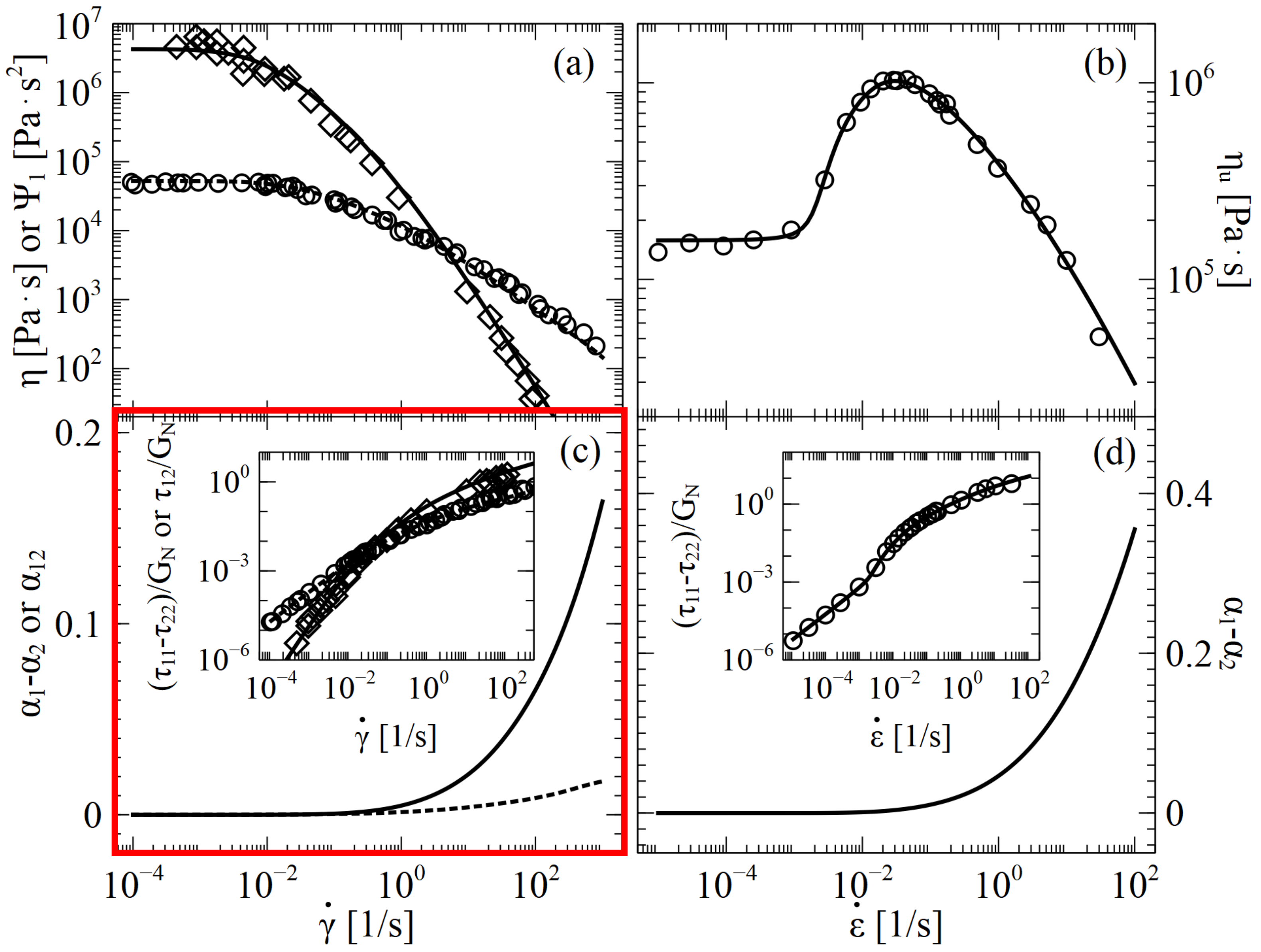
There is a non-zero off-diagonal component in shear flows

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

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

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

Steady-State: Shear and Uniaxial Ext. IUPAC_A LDPE



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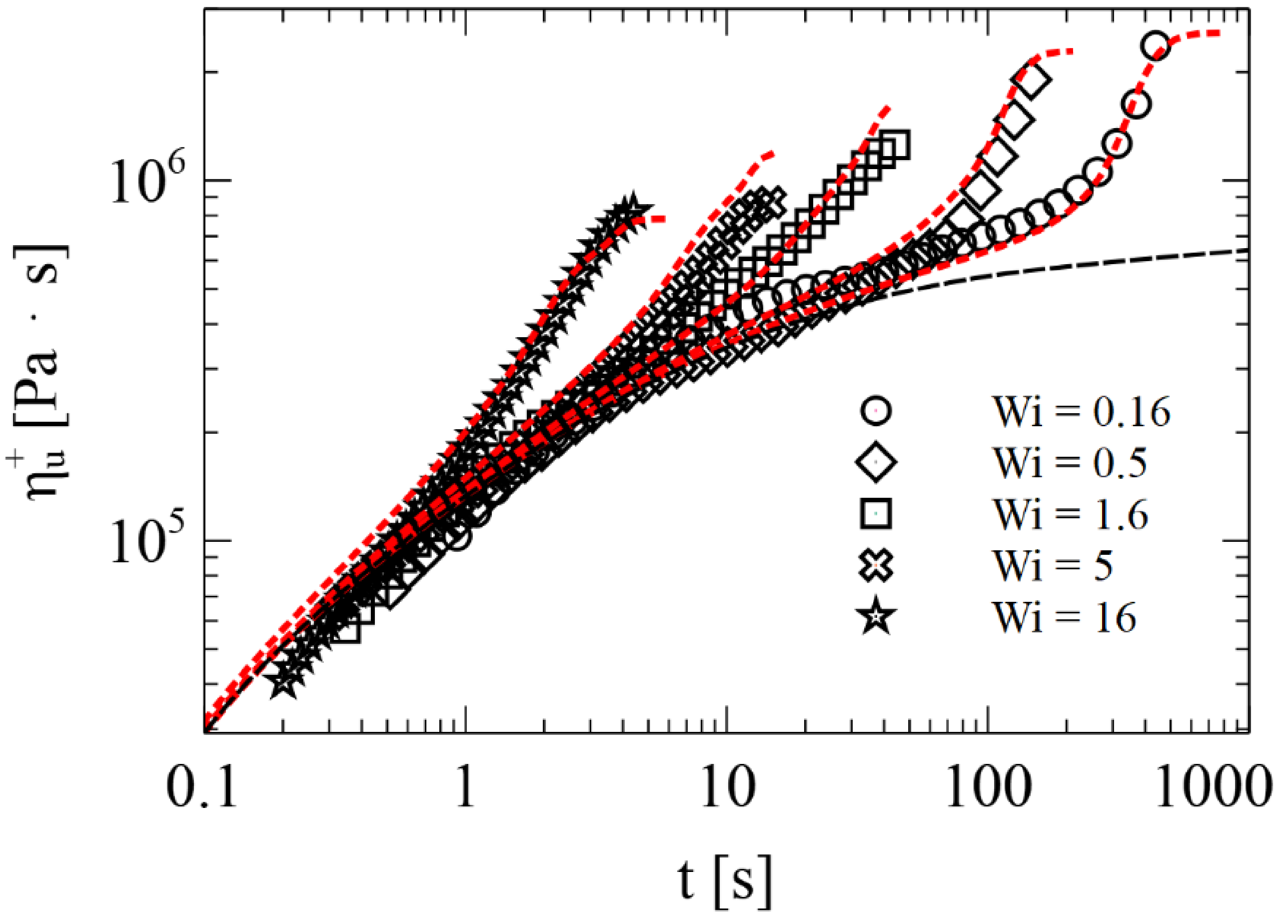
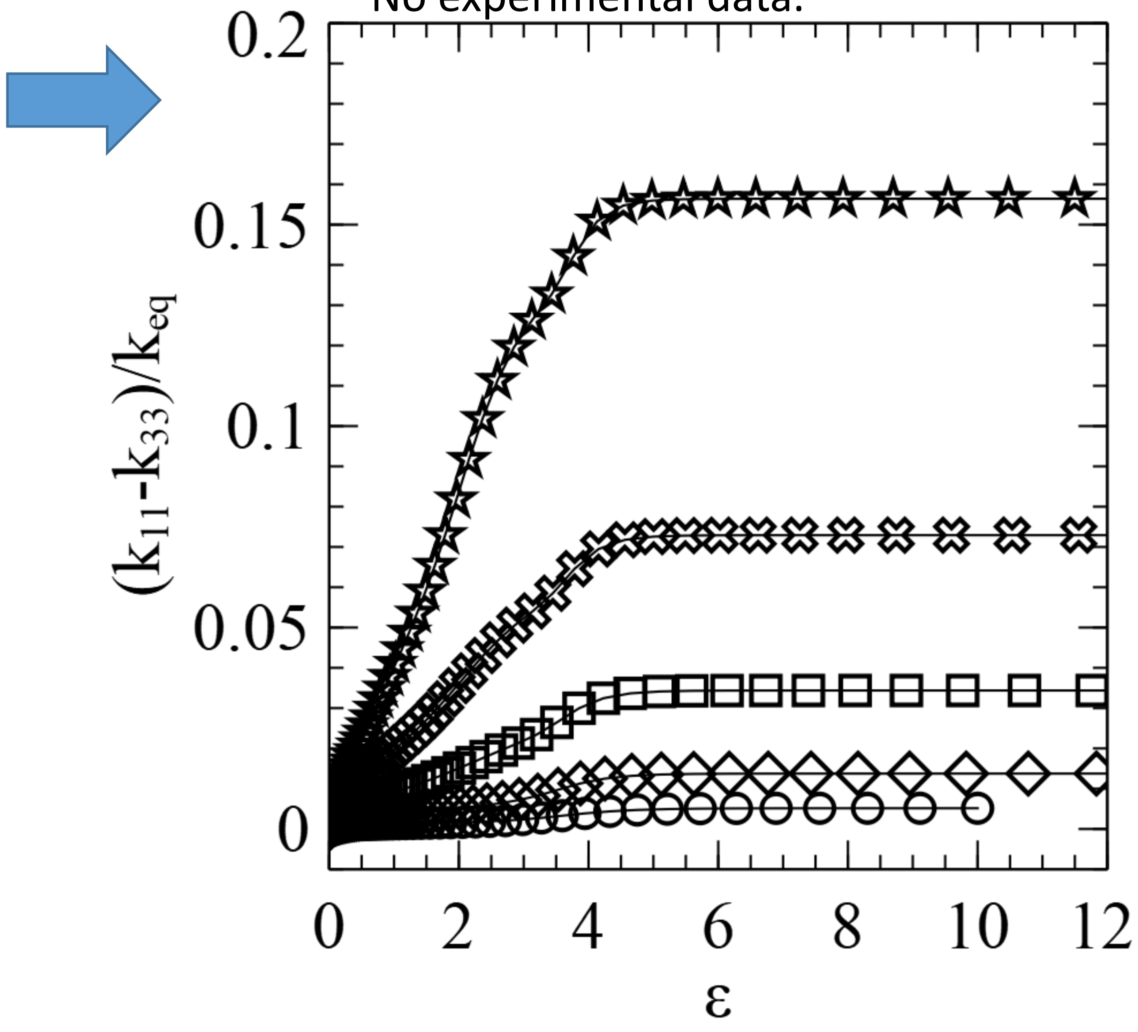
A temperature gradient in the 1-direction can generate heat flow in the 2-direction: ***Thermal Hall Effect***

Transient Start-up: Uniaxial PS158k

Dashed lines → XPP Model



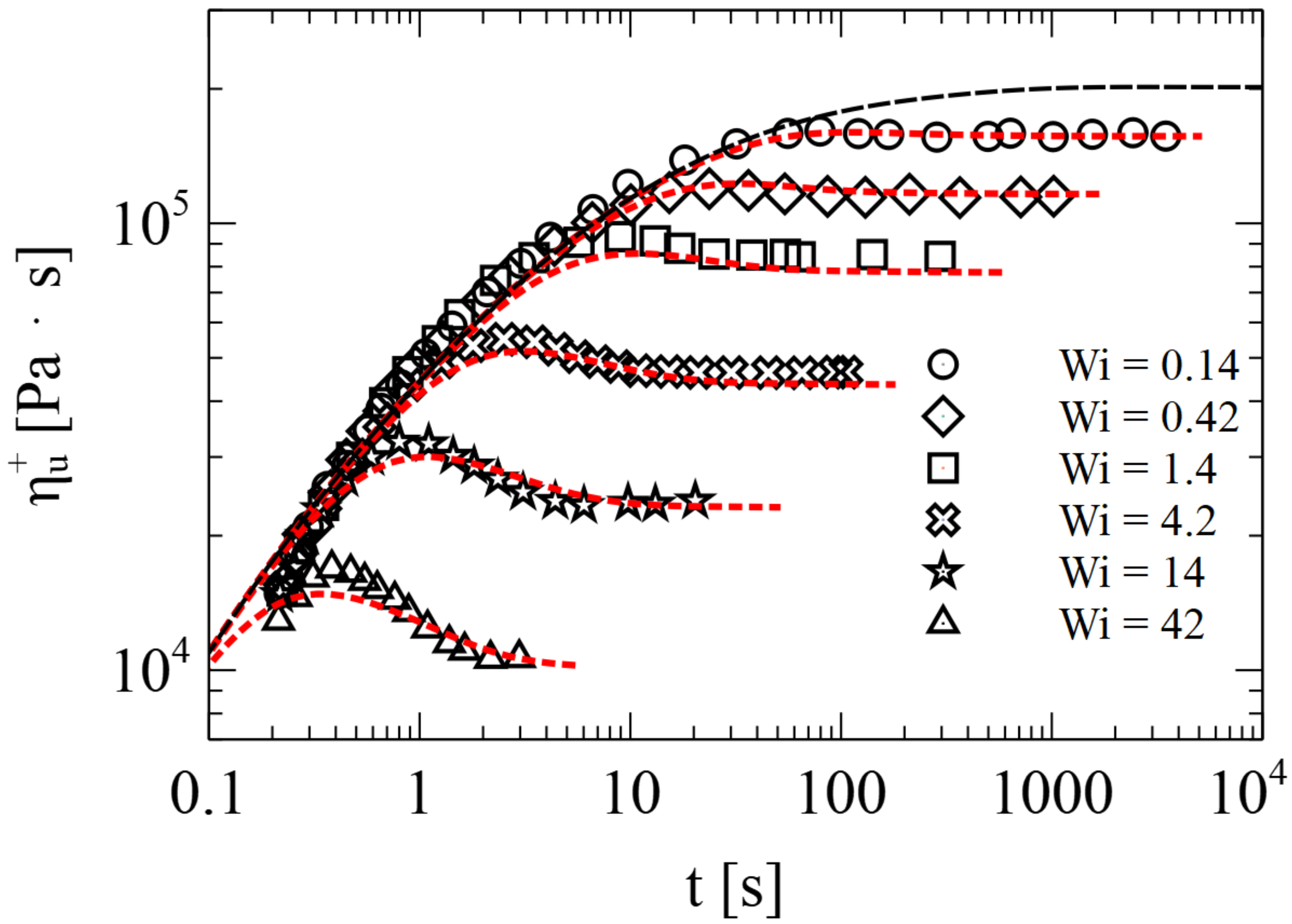
XPP + STR Model prediction.
No experimental data.



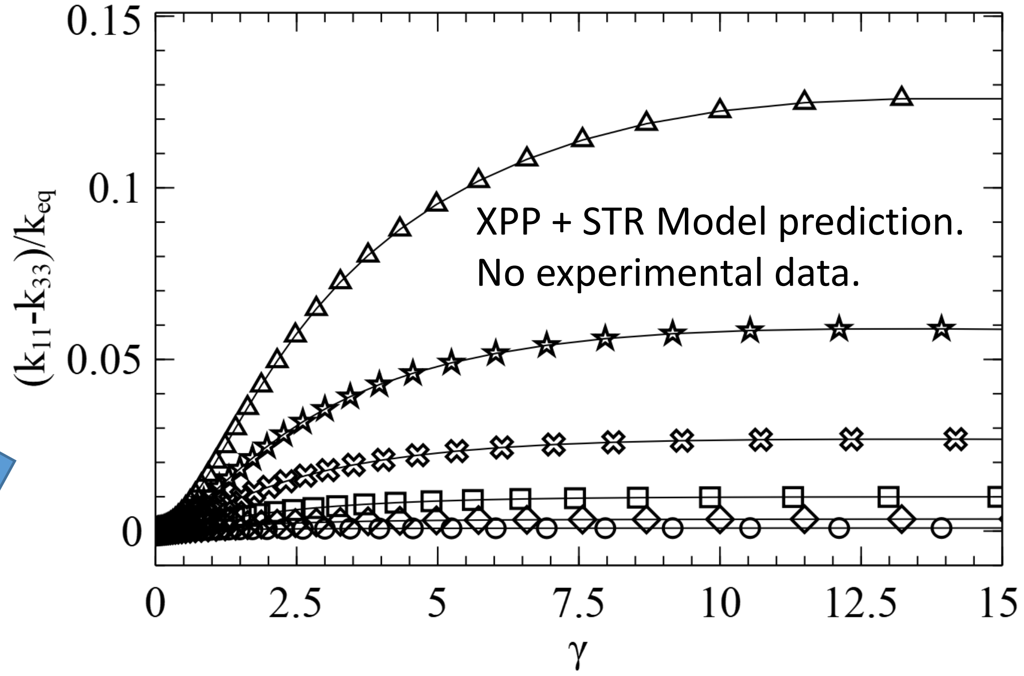
Data: Venerus et al. JOR 1999

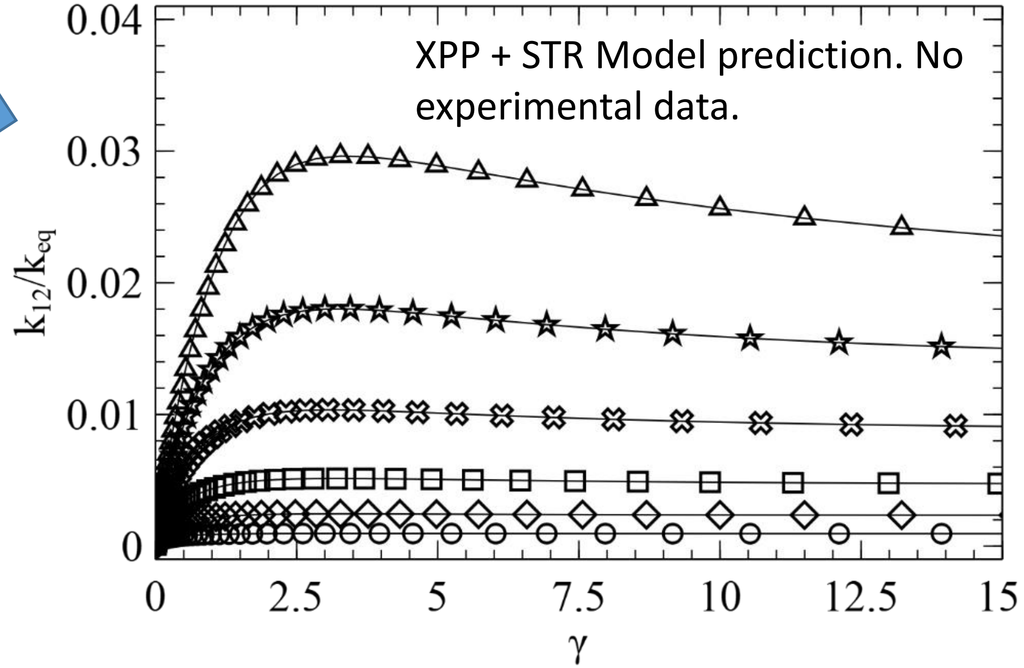
Transient Start-up: Shear Rheology PS158k

Dashed lines → XPP Model

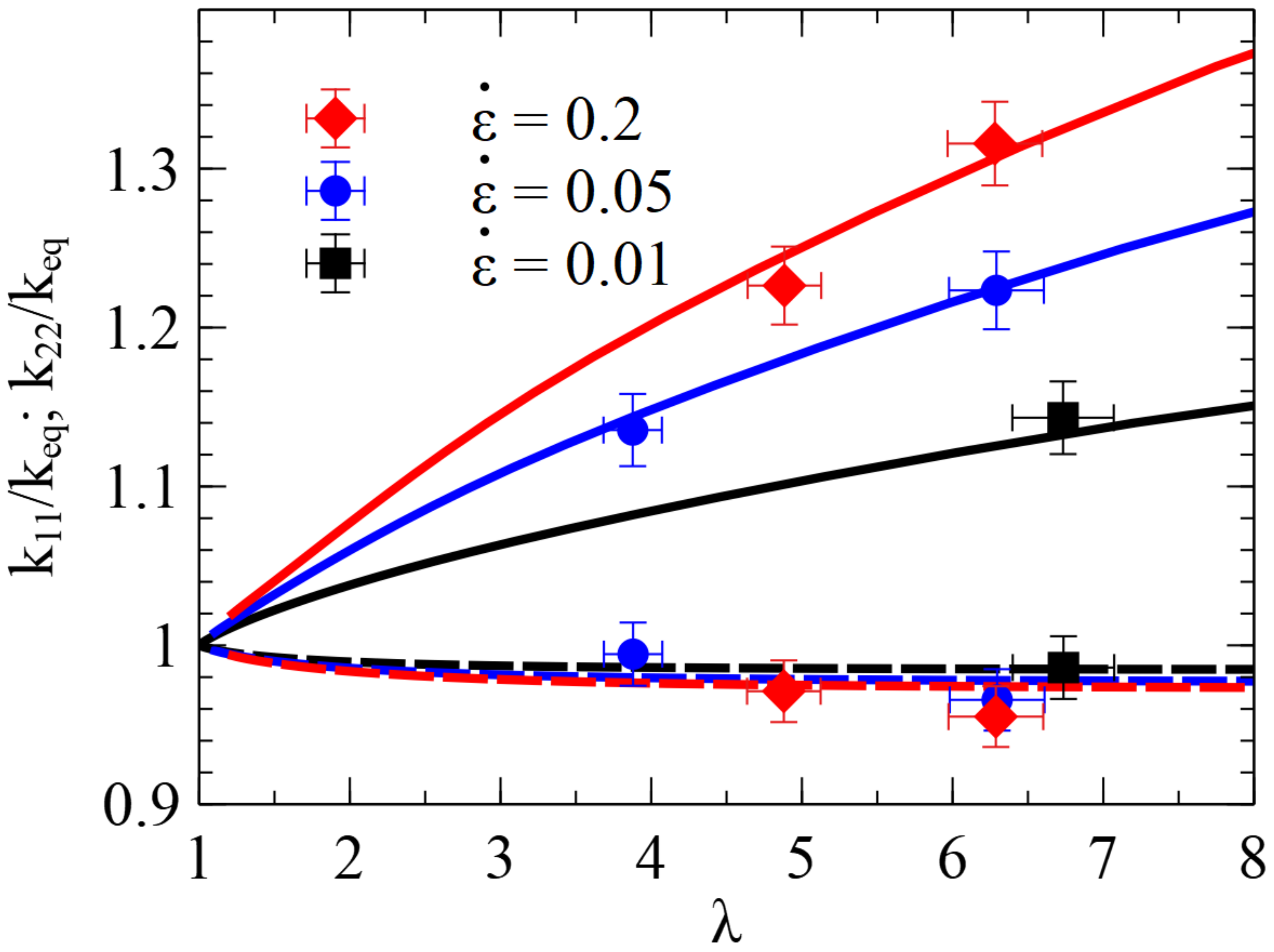


Data: Thomas Schweizer Rheol. Acta 2002





Comparison to experiments: PS260k



FRS Measurements after quenching. Data from Gupta et al. JOR 2013

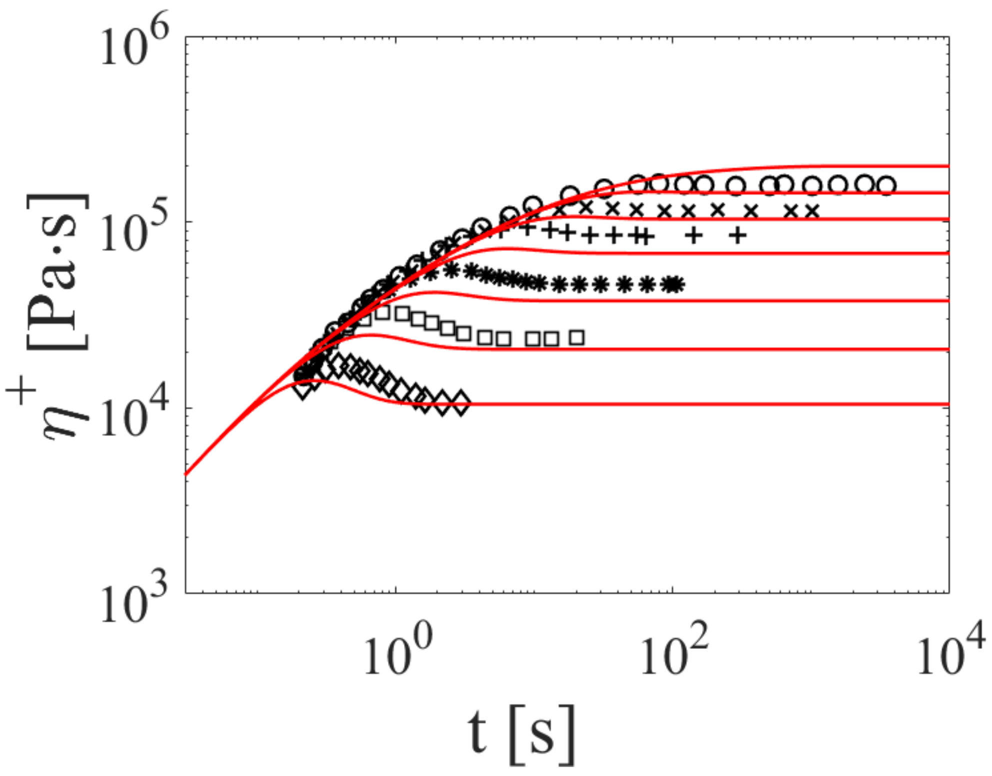
Constitutive Model: Rolie Poly

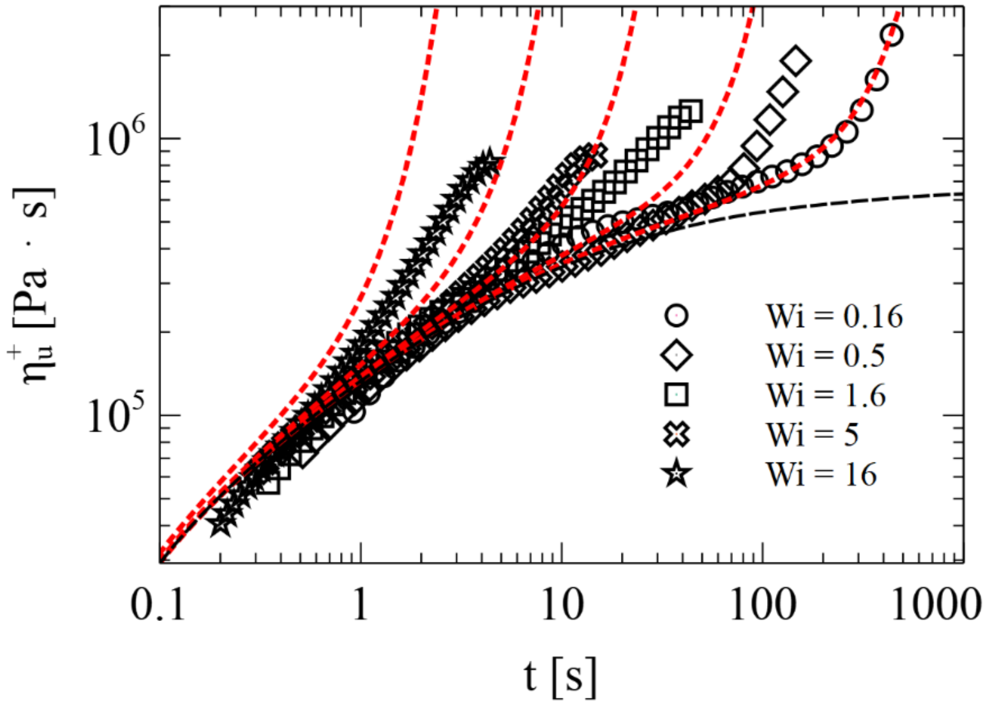
Graham et al. JOR 2003
Likhtman et al. JNNFM 2003

- Rolie Poly Model: ROuse LInear Entangled POLYmers

$$\frac{d\boldsymbol{\sigma}}{dt} = \boldsymbol{\kappa}\cdot\boldsymbol{\sigma} + \boldsymbol{\sigma}\cdot\boldsymbol{\kappa}^T - \frac{1}{\tau_d}(\boldsymbol{\sigma} - \boldsymbol{I}) - \frac{2\left(1-\sqrt{(3/\mathrm{tr}\boldsymbol{\sigma})}\right)}{\tau_R}\left(\boldsymbol{\sigma} + \beta\left(\frac{\mathrm{tr}\boldsymbol{\sigma}}{3}\right)^{\delta}(\boldsymbol{\sigma} - \boldsymbol{I})\right)$$

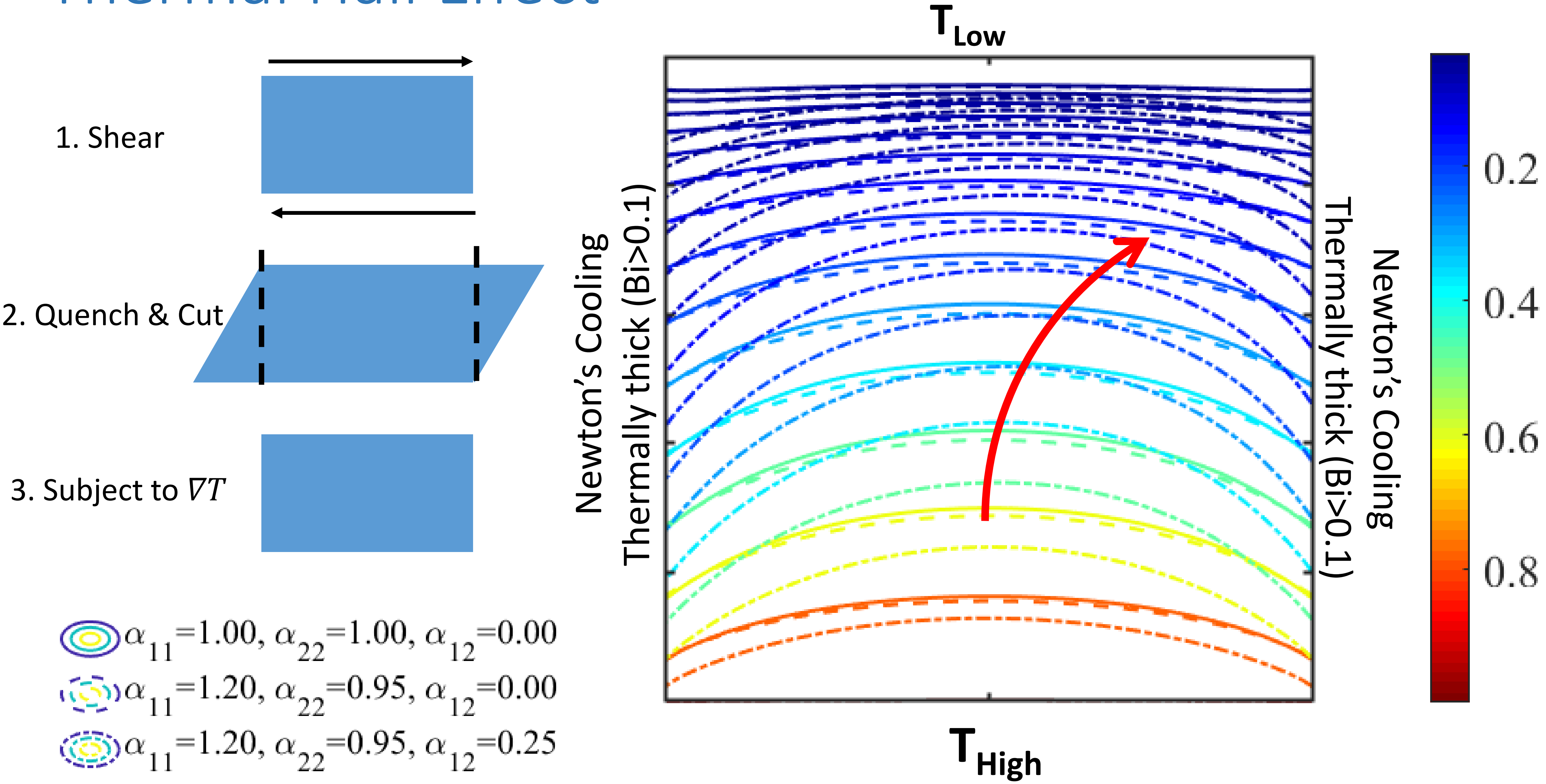
- Predictions





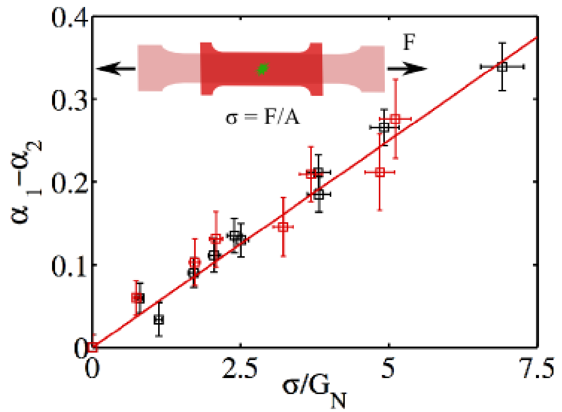
- Future Work: Implement Finite extensibility. Kabameni et al. Rheol Acta 2009

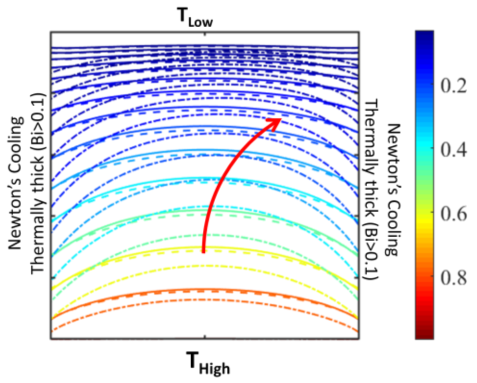
Thermal Hall Effect

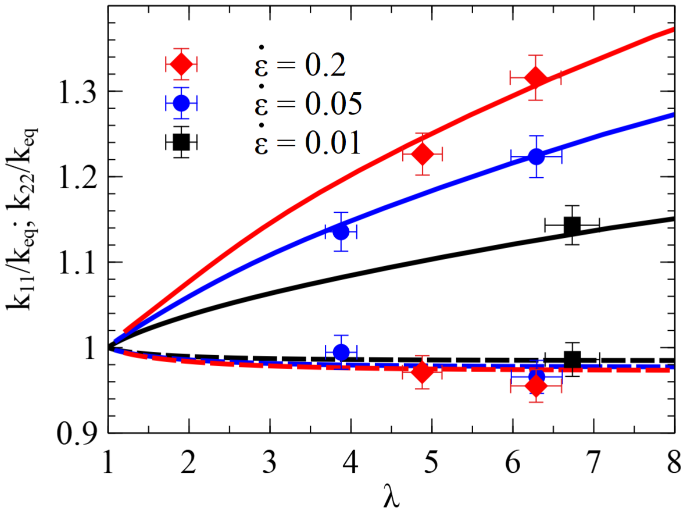


Conclusions

1. Thermal transport becomes anisotropic in polymers subjected to deformation
2. Flow induced anisotropy has significant implications in polymer processing
3. Experimental evidence of:
   - Proportionality to Stress: Stress-Thermal Rule (STR)
   - Universality
   - Beyond Finite Extensibility
4. We can use constitutive models (XPP, RP…), that are amenable to numerical flow simulations, in combination with the STR to include anisotropy in thermal conductivity in non-isothermal flows







Thank you!

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UNIVERSIDAD DE BURGOS

MARIE CURIE ACTIONS

HORIZON 2020