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

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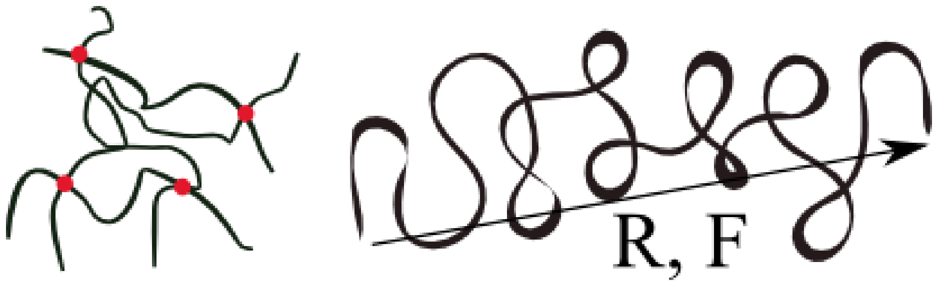
Summary

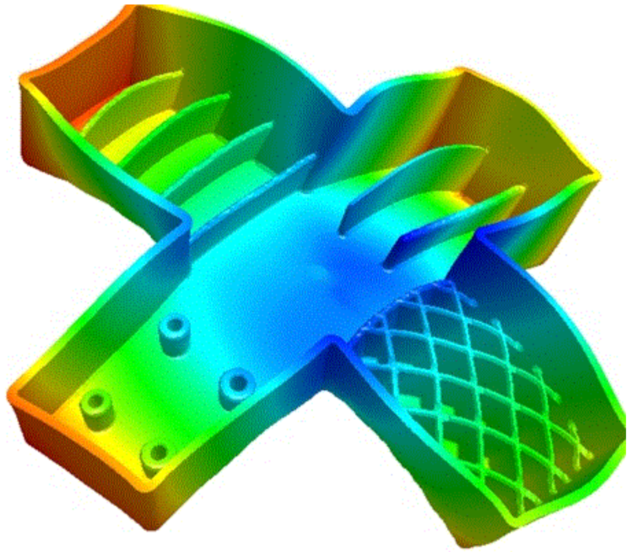
- Orientation/Stress → polymer thermo-physical properties (k, c_p)
- Our approach:

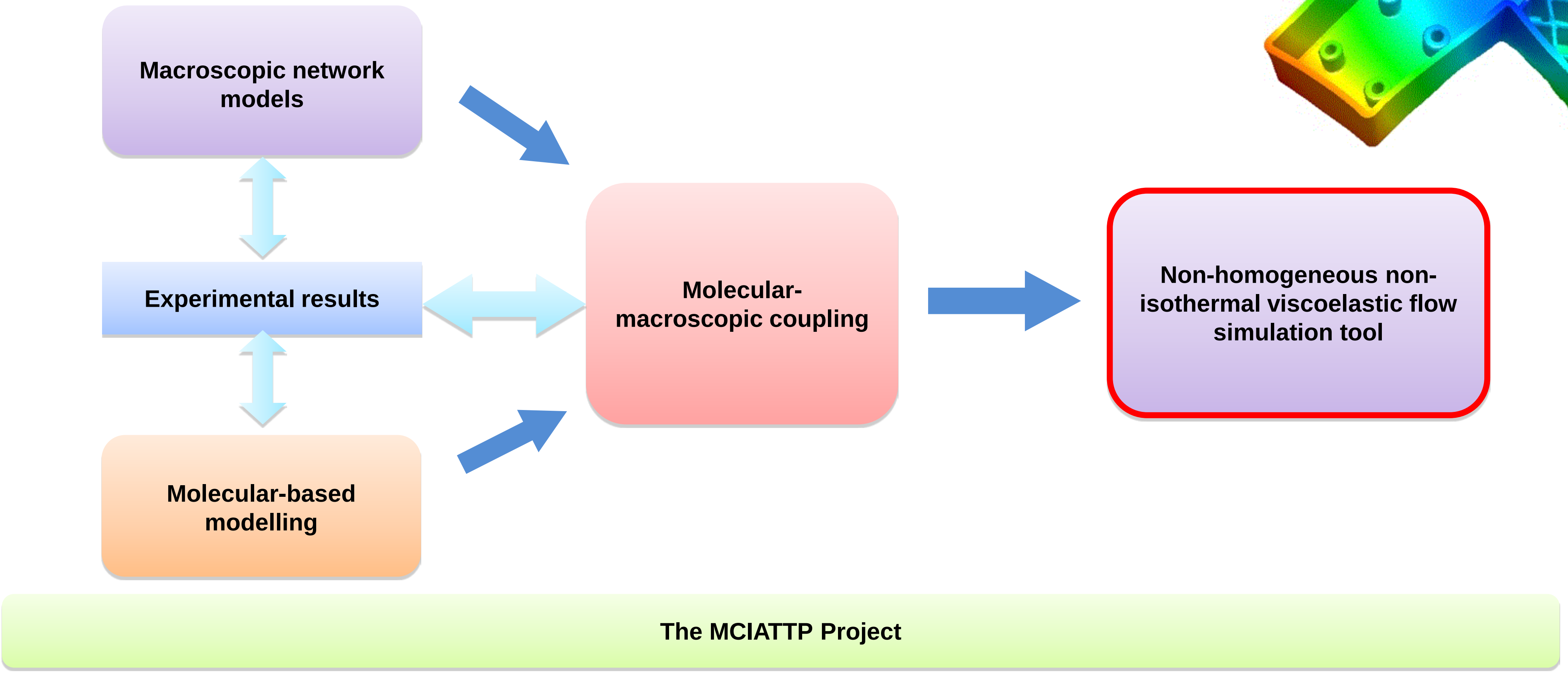
“Molecular to Continuum Investigation of Anisotropic Thermal Transport”

- Experimental work: Novel methods for quantitative measurements
- Key findings and open questions (MD Simulation work)
- The roadmap to macroscopic simulations

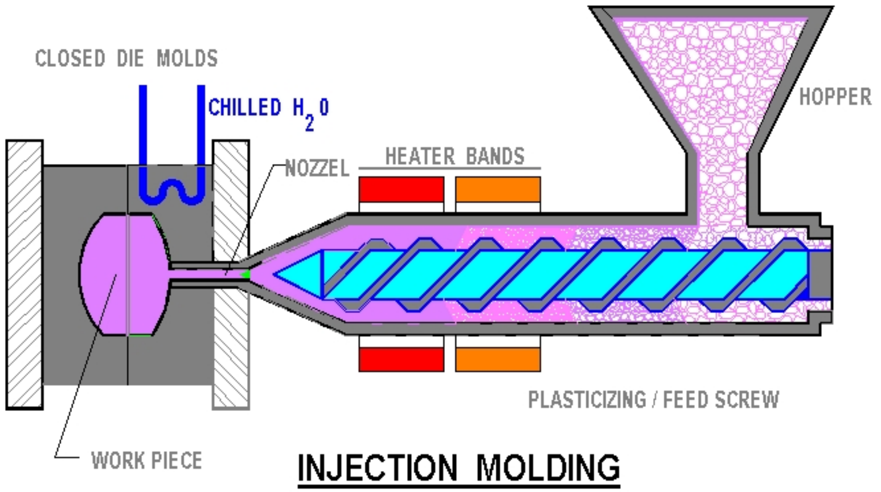


The MCIATTP project:

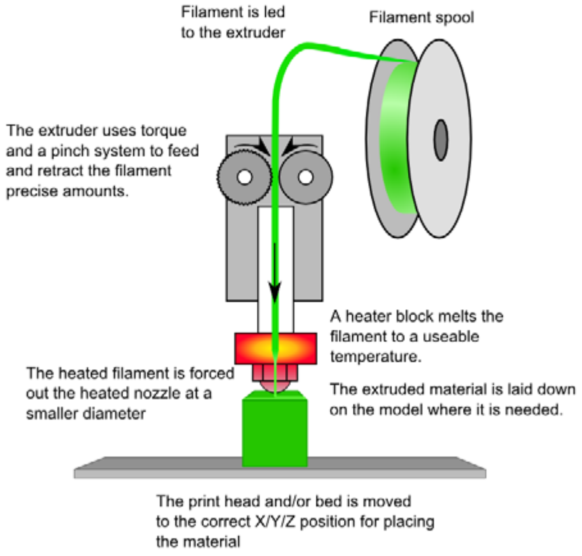


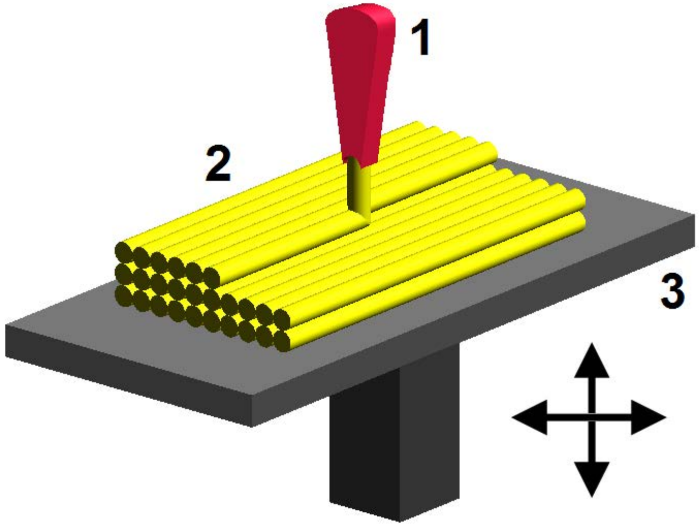


Motivation: Polymer Processing



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:

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

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

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

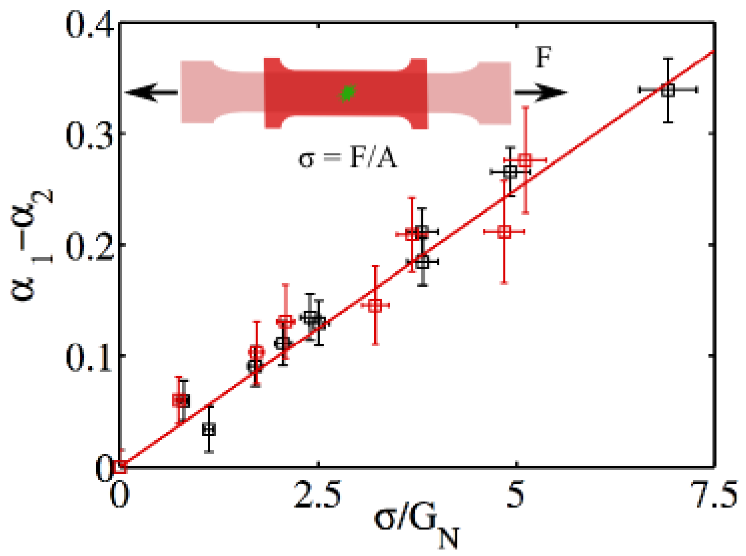
Constitutive equations:

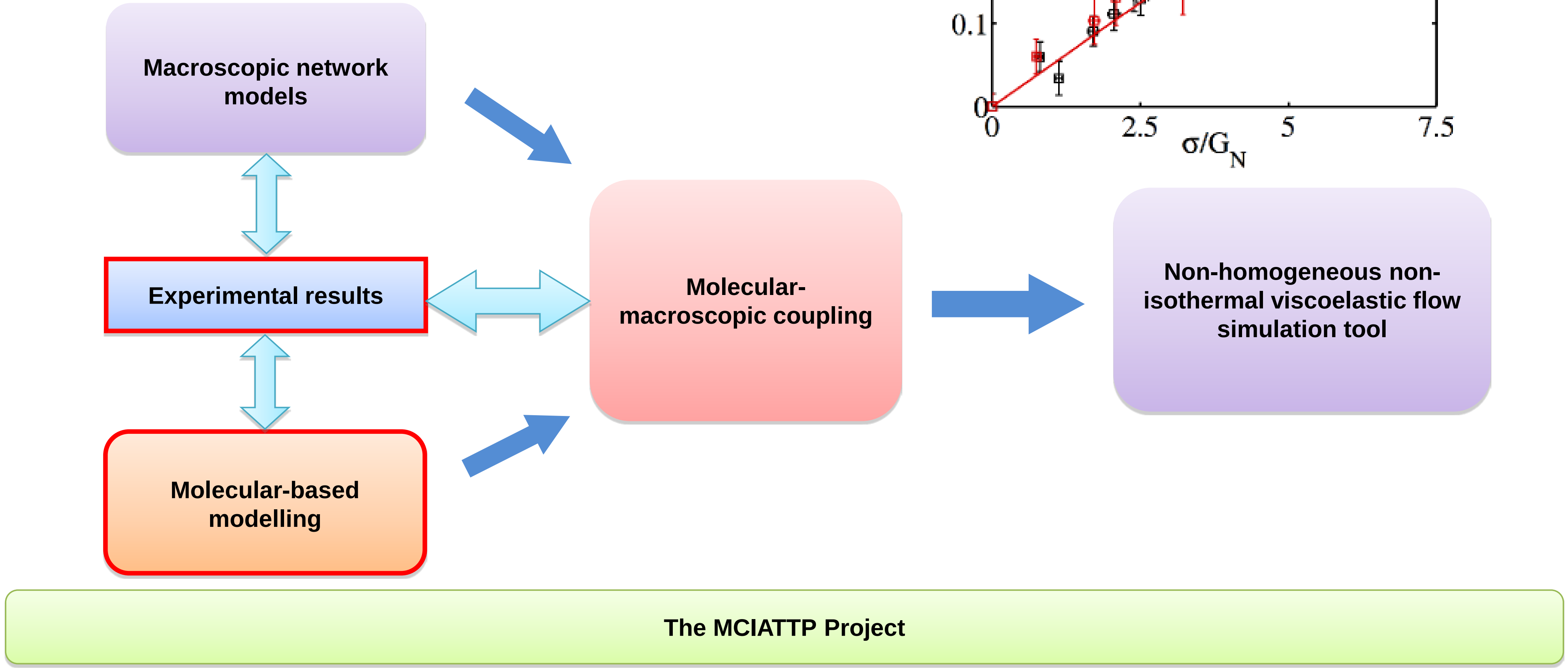
$$\boxed{\boldsymbol{q} = -k \nabla T} \qquad \boxed{\hat{c}_v = \hat{c}_v(T)} \qquad \boldsymbol{\tau} = \eta(T)\left[\nabla v + \nabla v^{\intercal}\right]$$

- High stresses & Low thermal conductivity.

Mechanical behavior and flow	$\Longleftrightarrow$	Thermal properties

The MCIATTP project:





Anisotropic Thermal Conduction

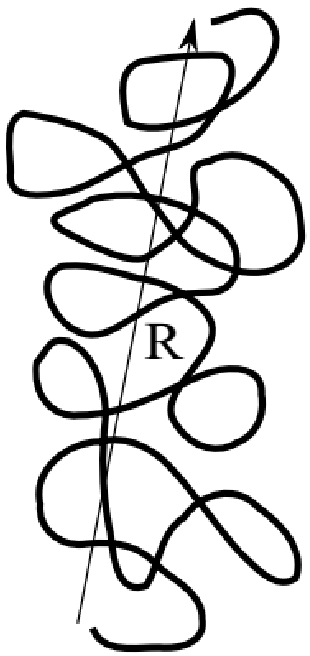
Fourier's Law: Thermal transport in deformed polymers is diffusive and anisotropic.

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

$\boldsymbol{k}$ is a tensor!

Observation: $k_{\rm eq}$ 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:

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

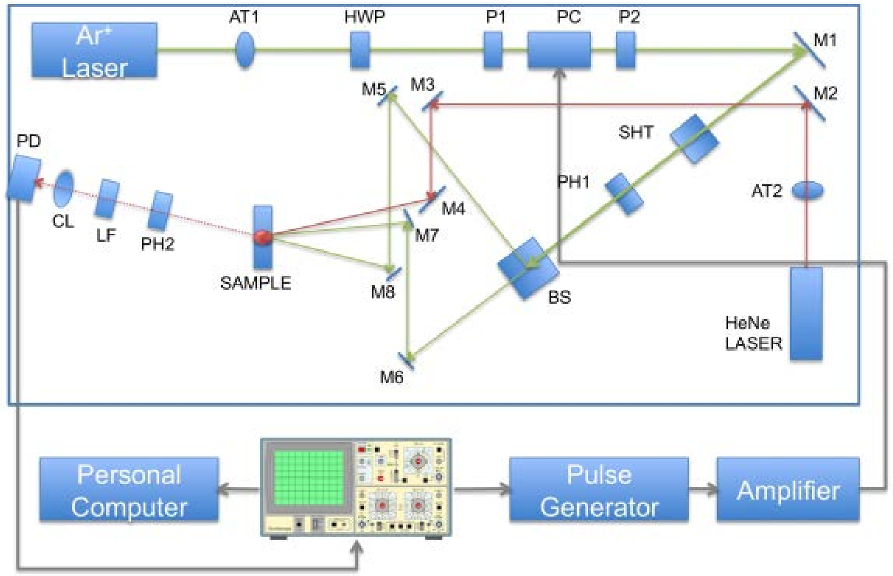
$$\boldsymbol{k} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{\rm eq} C_{\rm t} \left[\boldsymbol{\tau} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta} \right]$$

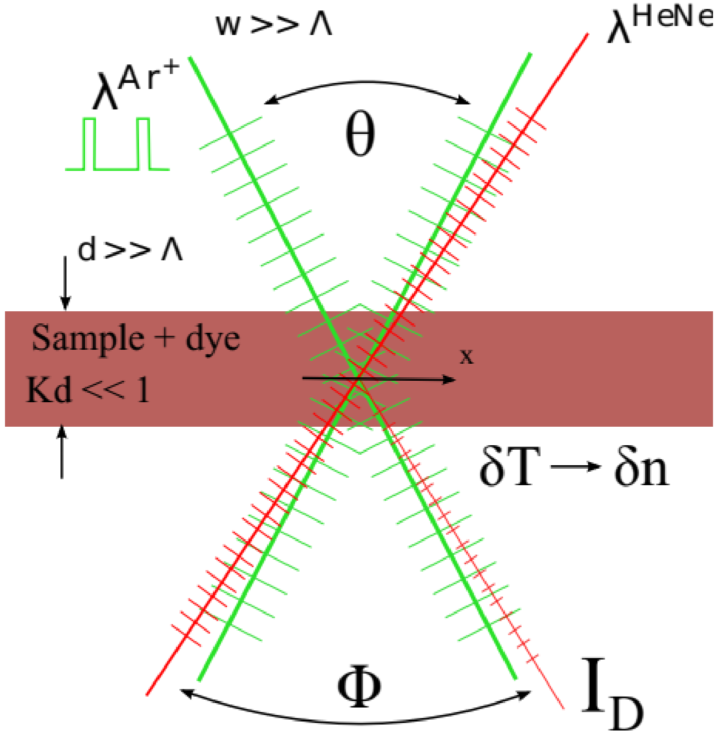
The Stress-Thermal Rule

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.

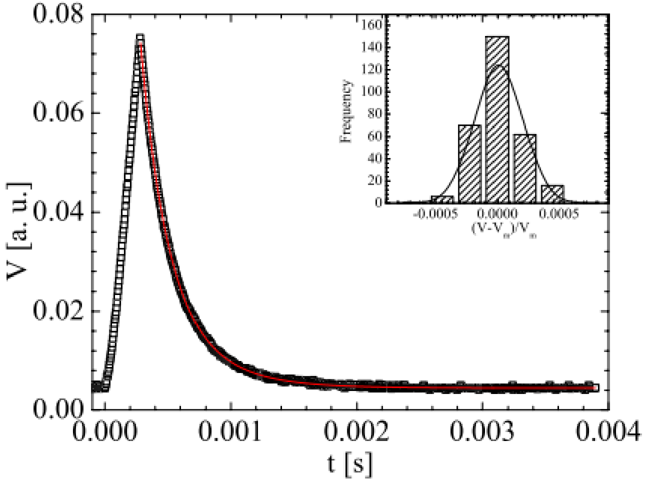
$$C_t \propto \frac{n k_B^2 T}{\zeta}$$

Experiments: Forced Rayleigh Scattering (FRS)

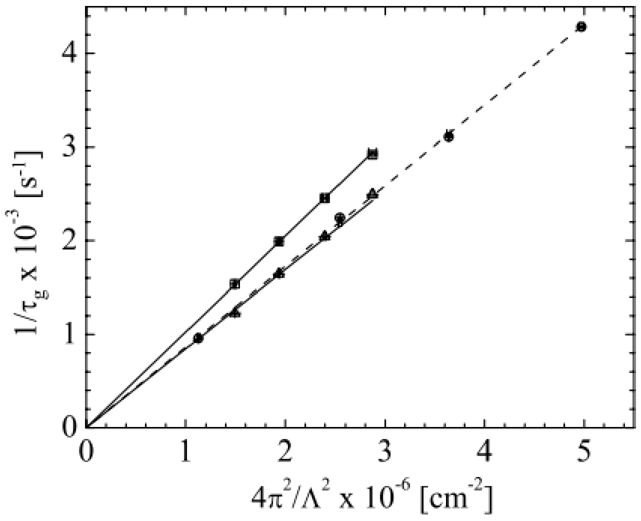




100 waveforms for each grating size



4 grating sizes for each elongation



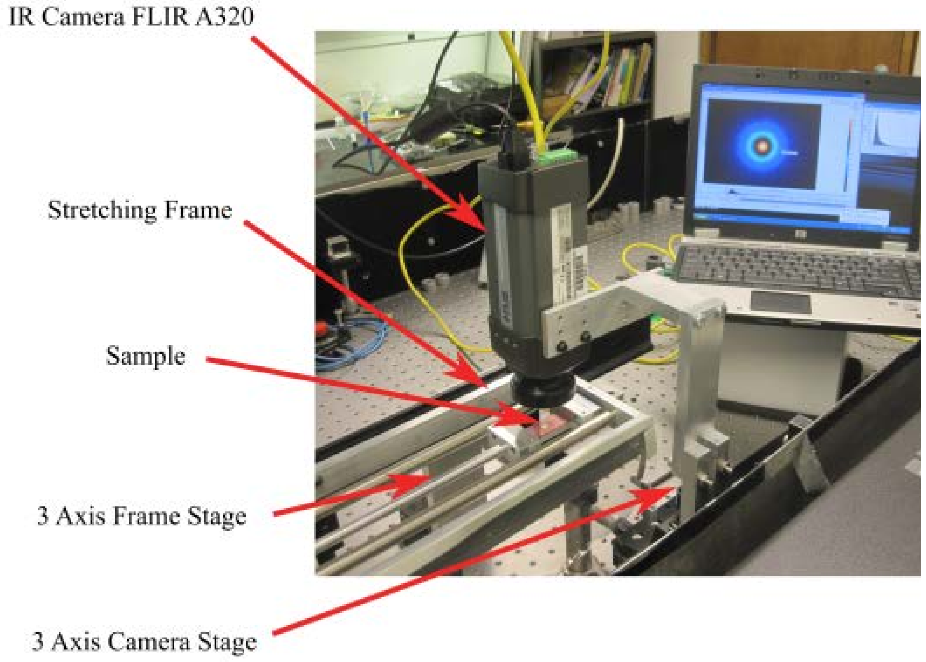
Intensity/Voltage at the photodetector:

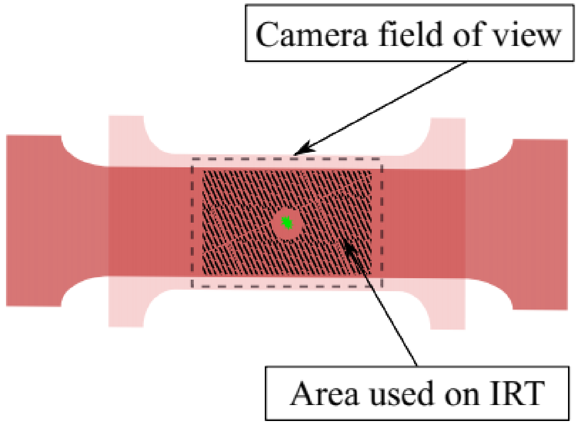
$$V(t) = \mathrm{A}\exp\left(-2\frac{t}{\tau_{\mathrm{g}}}\right) + \mathrm{B}\exp\left(-\frac{t}{\tau_{\mathrm{g}}}\right) + \mathrm{C}$$

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

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

Experiments: Infrared Thermography (IRT)

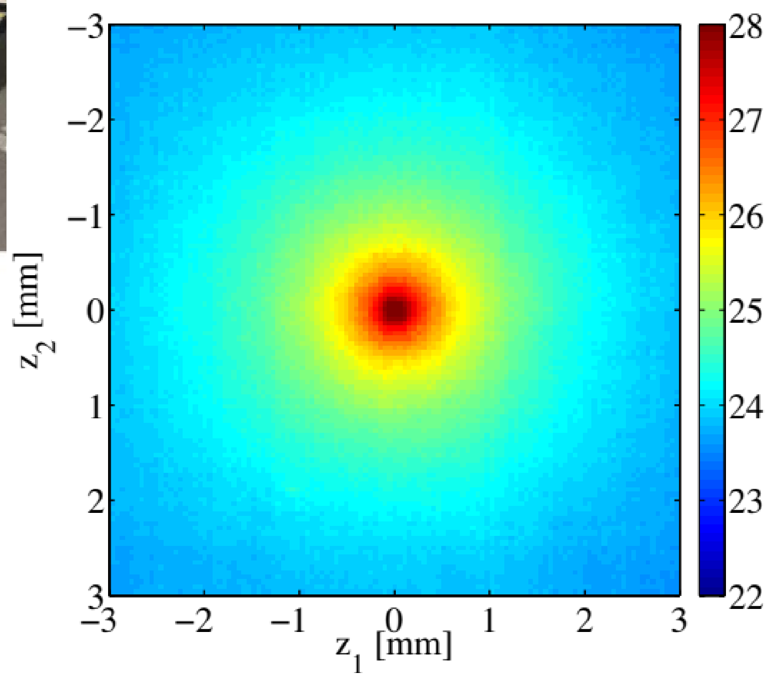




$$\theta(x_1, x_2) = \frac{1}{4\sqrt{\alpha_1\alpha_2}} K_0\left(\sqrt{2\mathrm{Bi}(x_1{}^2/\alpha_1 + x_2{}^2/\alpha_2)}\right)$$

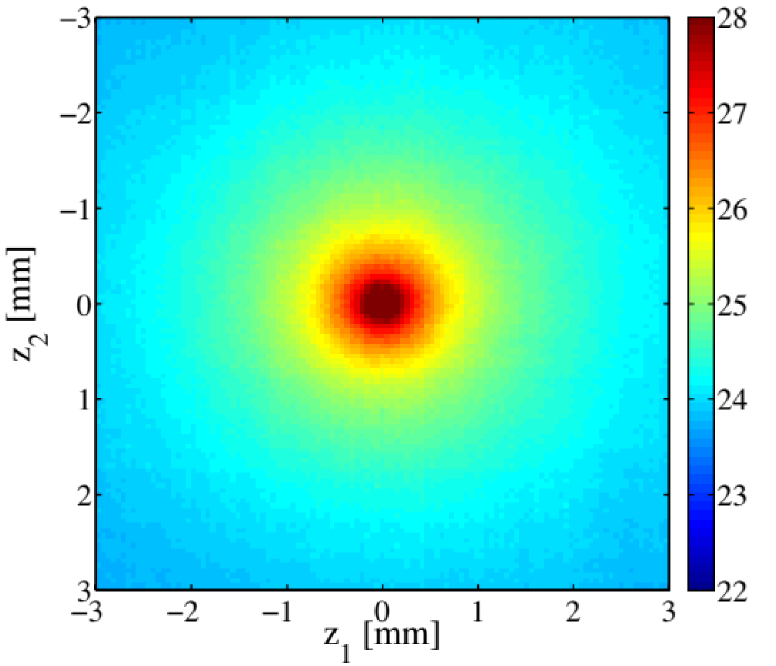
$KI_0 w^2/k_{\mathrm{eq}}, \quad \mathrm{Bi} = hd/k_{\mathrm{eq}}$

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



Un-stretched sample, $\lambda = 1$

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

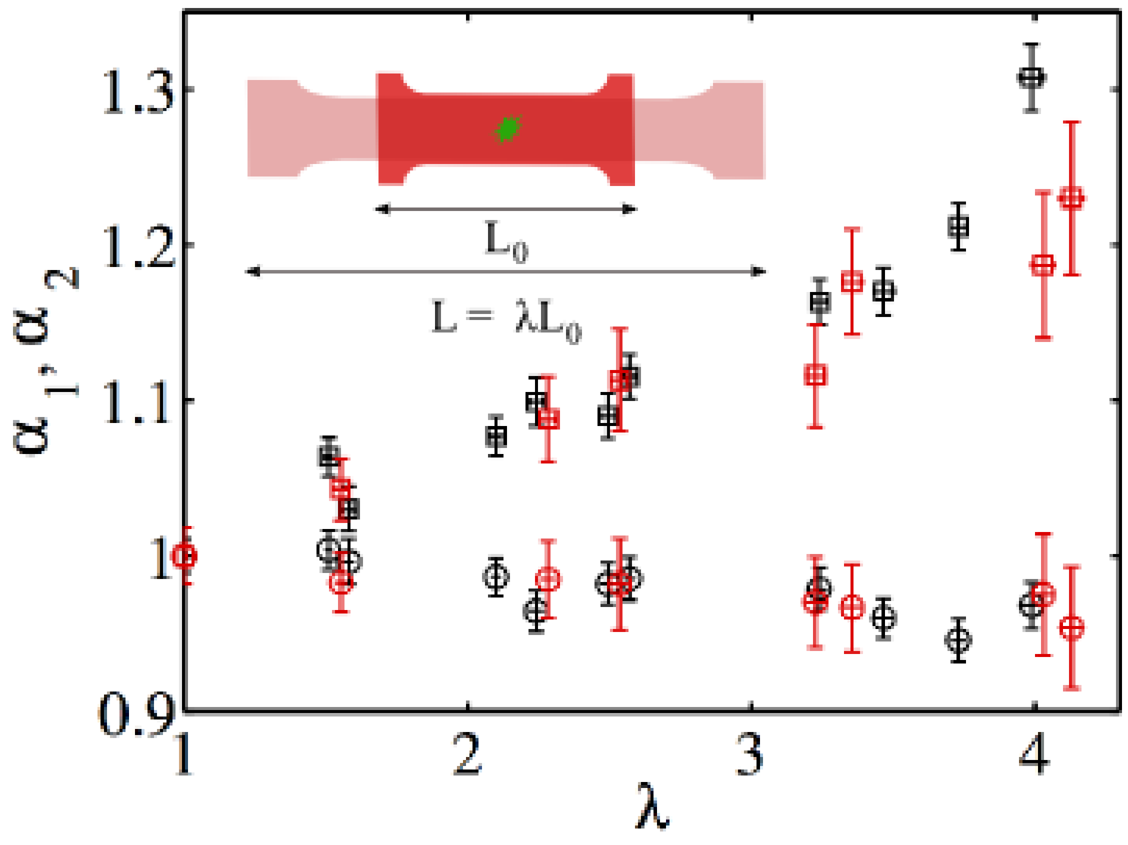


Stretched sample, $\lambda = 4.129$,

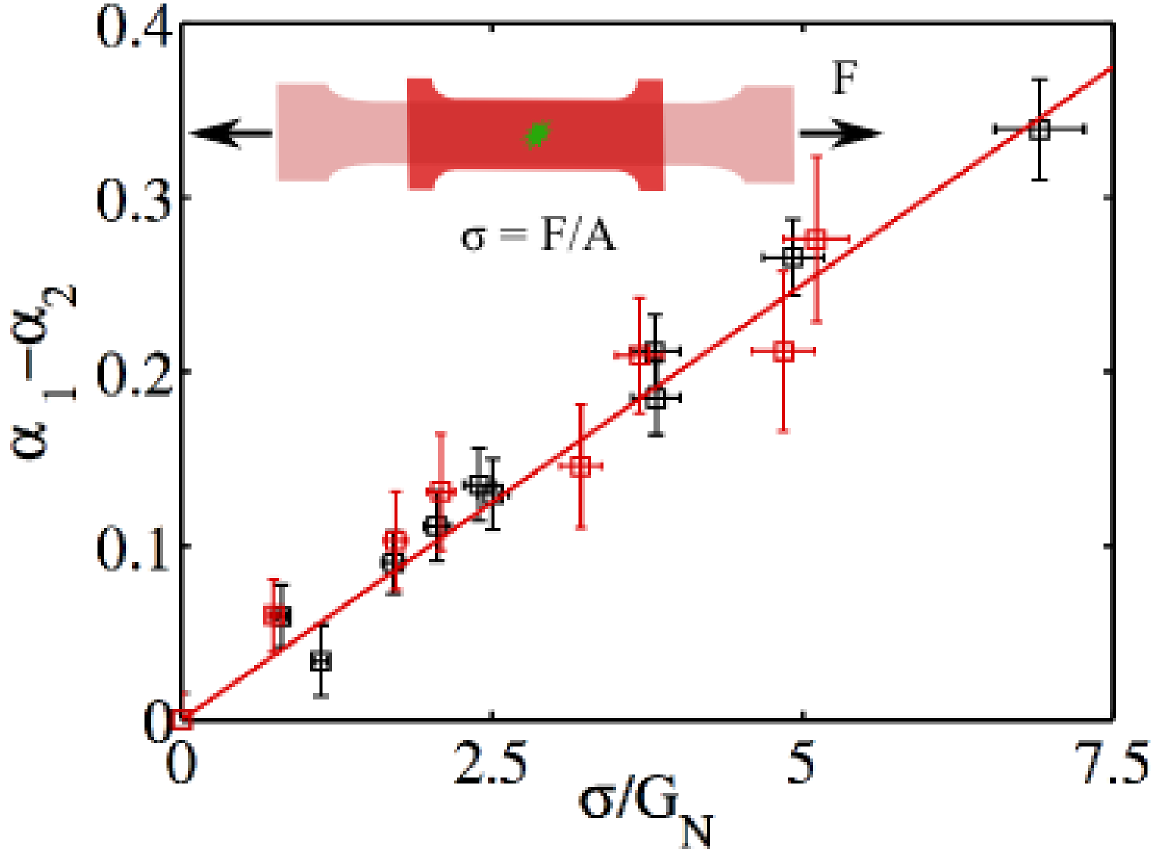
$\alpha_1 = 1.23 \pm 0.049$ and $\alpha_2 = 0.954 \pm 0.039$

Nieto Simavilla et al. Journal of Heat Transfer. 2014

Comparison FRS and IRT



(a)



(b)

PBD200k 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)

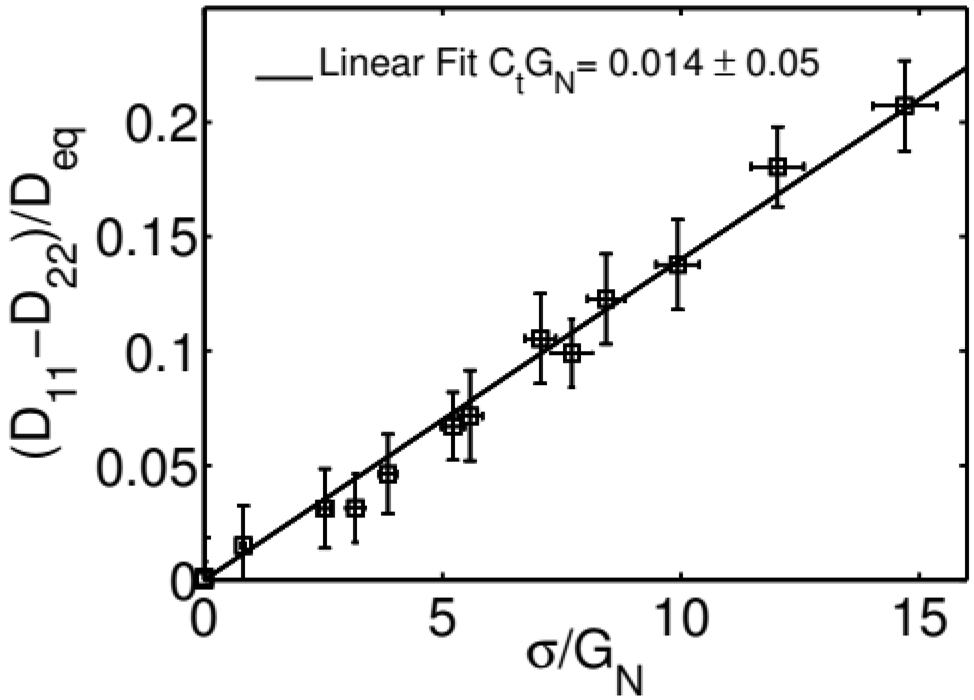
Stress-thermal Rule:

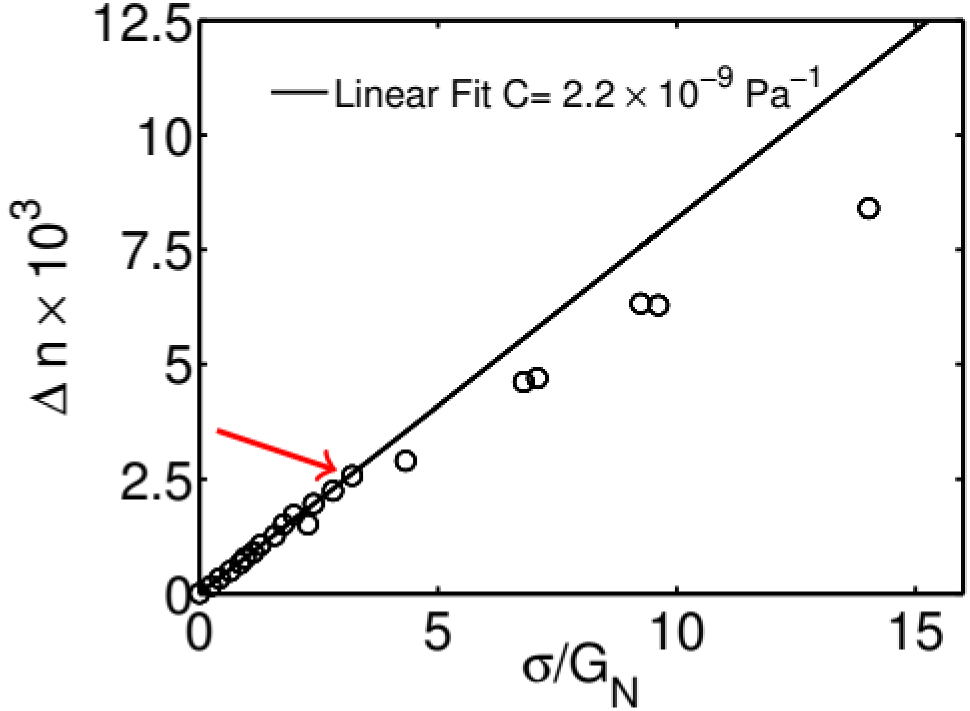
$$\boldsymbol{k} - \frac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{\mathrm{eq}} C_t (\boldsymbol{\tau} - \frac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta})$$

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

The Stress-Thermal Rule can be applied:

1. Universally (just by knowing stress and G_N)
2. Beyond the onset of finite extensibility

1st Can we reproduce the STR with MD?

- Previous MD work focuses on dimensionality, effect of chemistry, chain length, stiffness…

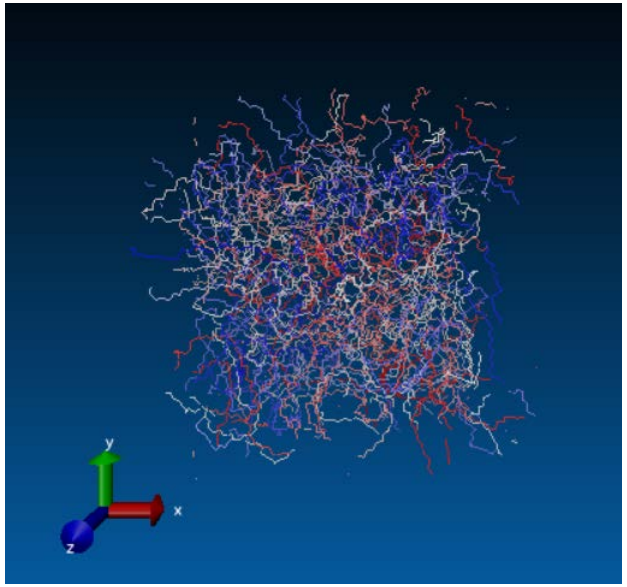
- United Atom PE with TraPPe FF

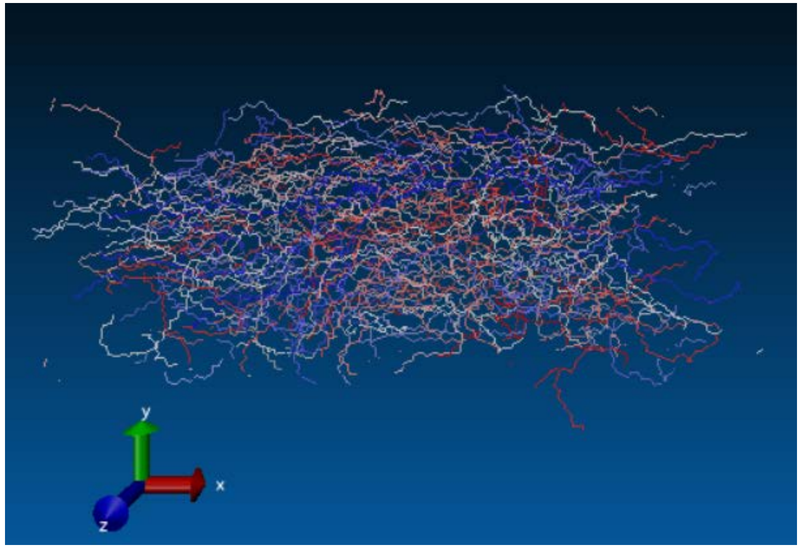
  Kyrayiannis et al. J. Chem. Phys. 2002

- Thermal conductivity method:
  - EMD: Green-Kubo

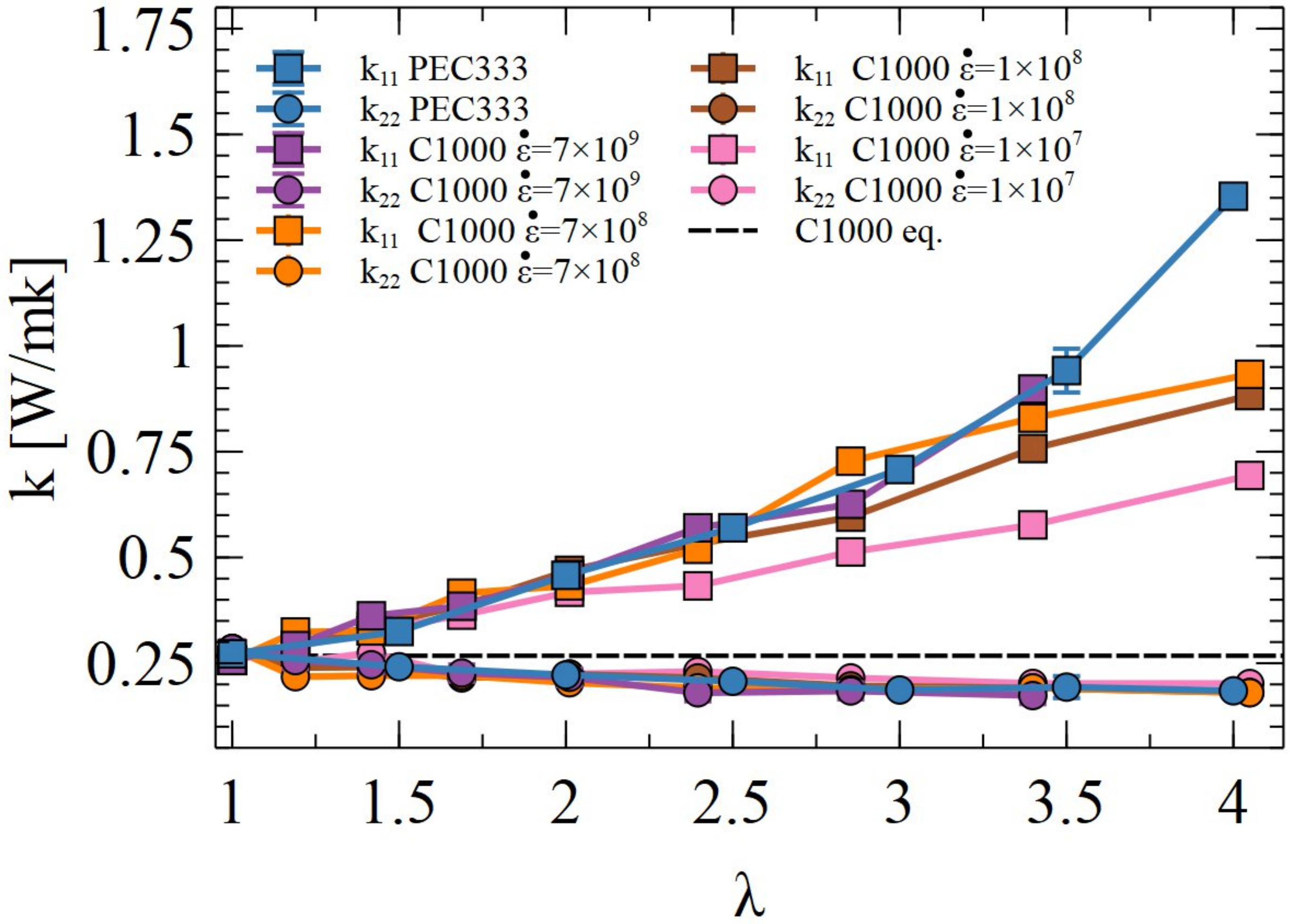
$$k_{ij} = \frac{1}{k_{\mathrm{B}} V T^2} \int_0^{\infty} \langle J_i(t) J_j(0) \rangle dt$$

  - All six components at once.
  - Less constrained by size and aspect ratio





Uniaxial extension in cross-linked and melt PE



- k Measurement methods:
  - EMD: Green-Kubo

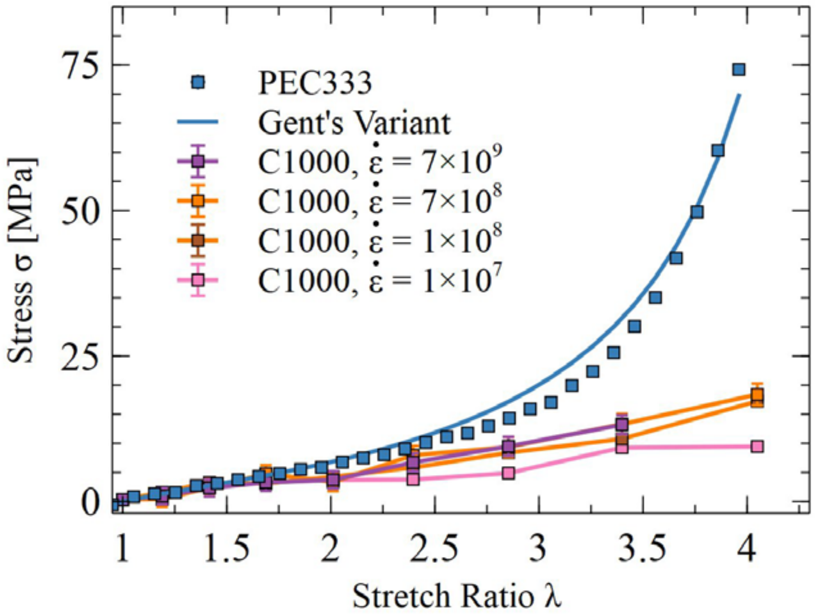
$$k_{ij} = \frac{1}{k_B V T^2} \int_0^\infty \langle J_i(t) J_j(0) \rangle dt$$

- Same qualitative behavior
- Same dependence on strain rate
- Higher anisotropy

Does the STR hold?

- Same linear response as a function of stress for all strain rates on the melt.

- Deviations at high strain/stress (i.e. finite extensibility region) for the cross-linked system.



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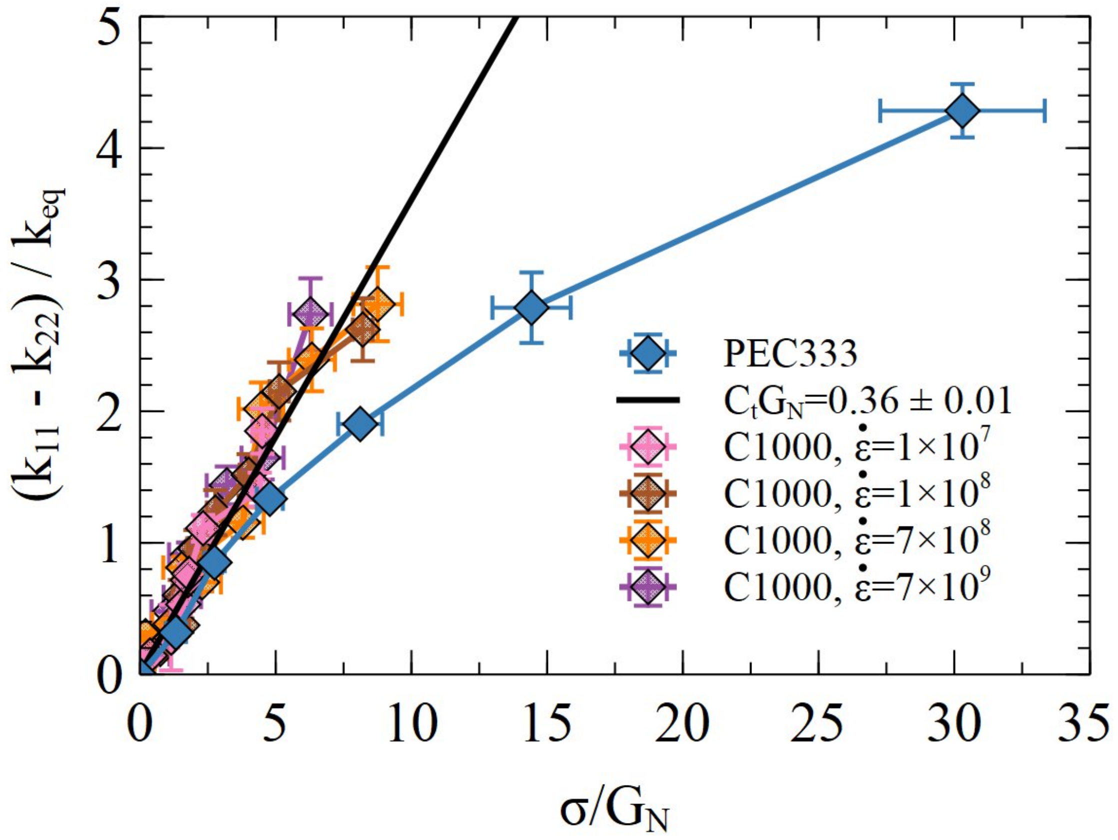
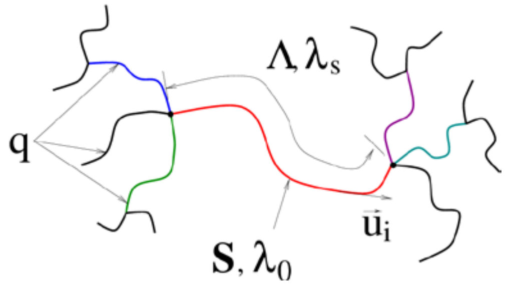
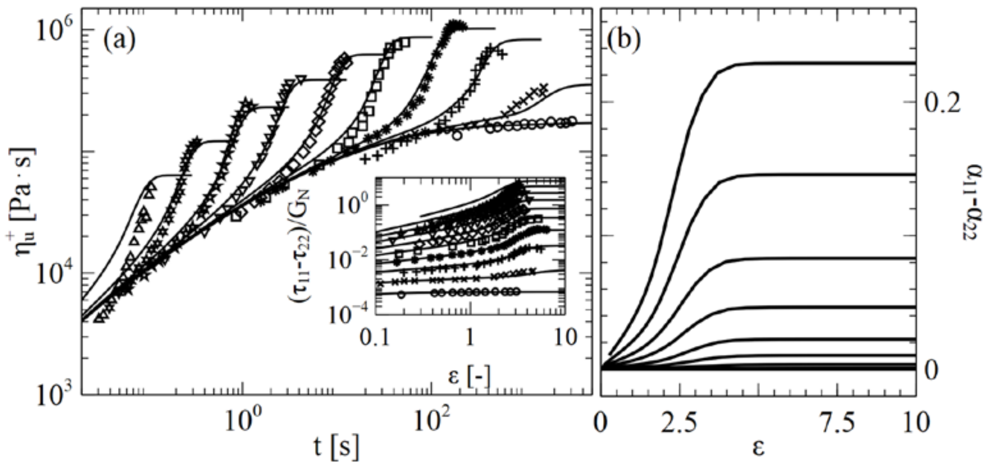


The MCIATTP project: Roadmap



eXtended Pom-Pom



Macroscopic network models

Experimental results

Molecular-based modelling

Molecular-macroscopic coupling

Non-homogeneous non-isothermal viscoelastic flow simulation tool

The MCIATTP Project

Constitutive Model: eXtended Pom-Pom

- What physics are in the model?

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

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

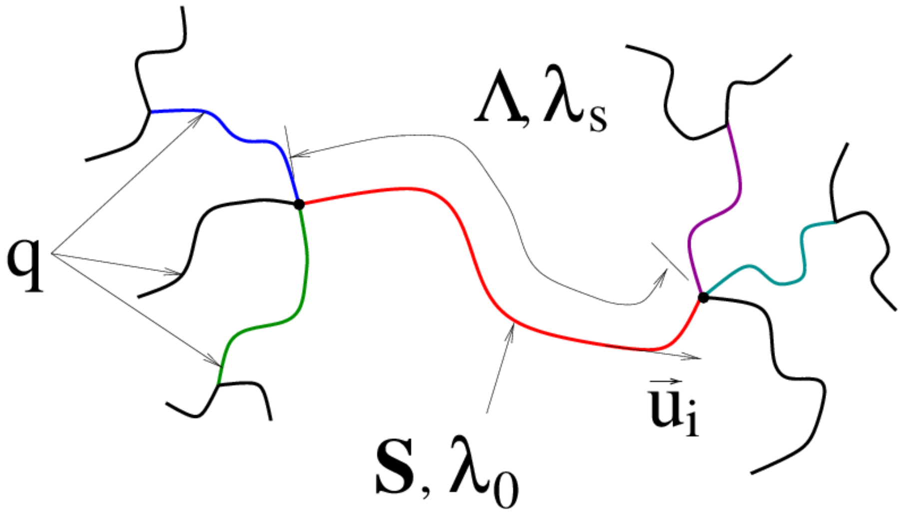
$$\boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}} \left[\frac{\alpha}{G_0} \boldsymbol{\tau} + f(\boldsymbol{\tau})^{-1} \boldsymbol{I} + G_0 \left(f(\boldsymbol{\tau})^{-1} - 1 \right) \boldsymbol{\tau}^{-1} \right]$$

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

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

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

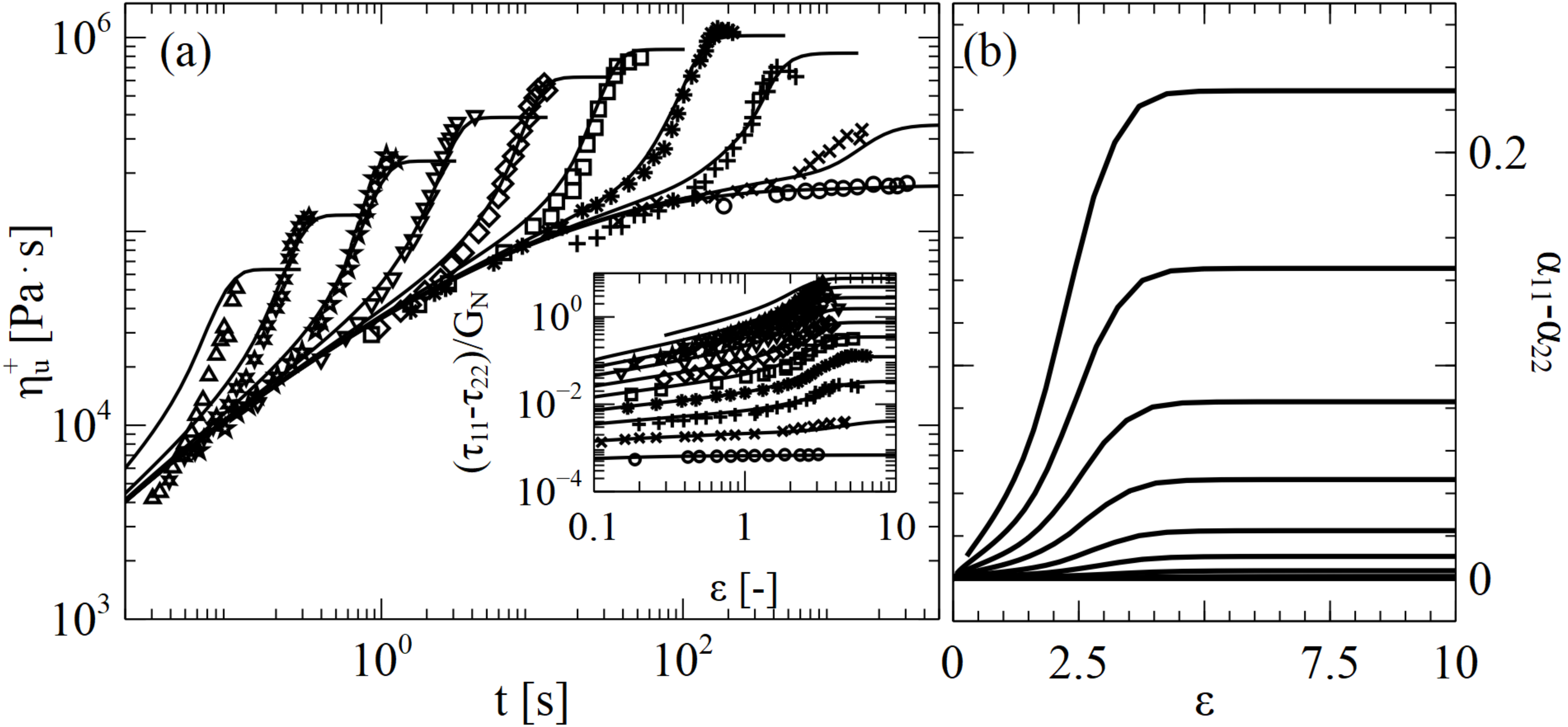
- Why XPP?
  - Amenable to FEM
  - Able to describe non-linear rheology
  - X: Avoids finite extensibility discontinuities
  - X: Includes second normal stress difference



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.

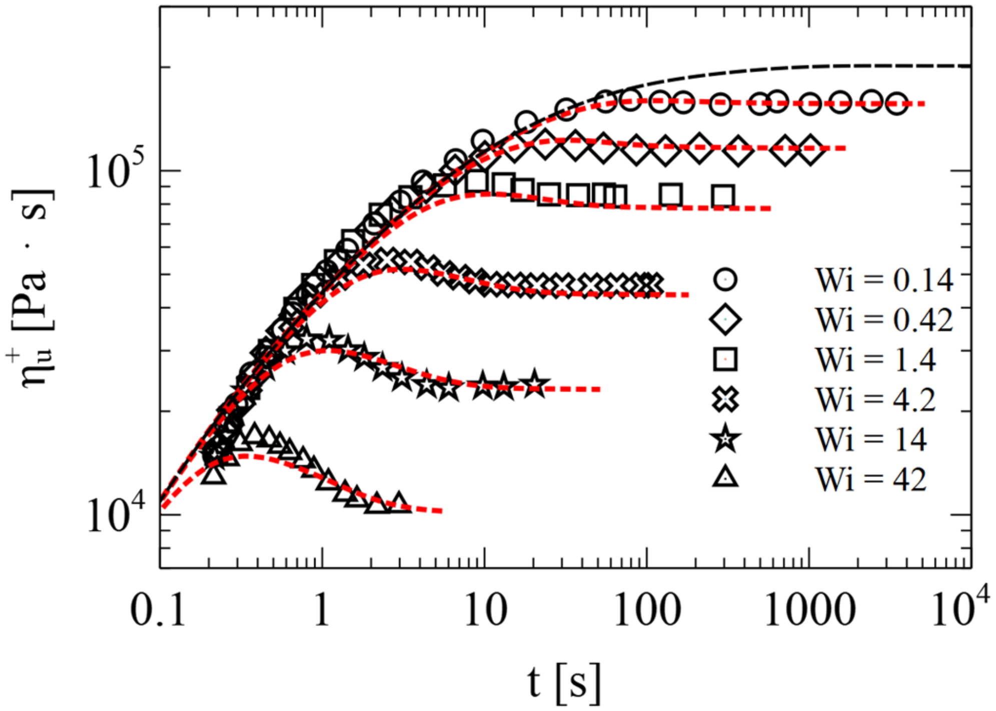
Constitutive Model: Rolie Poly

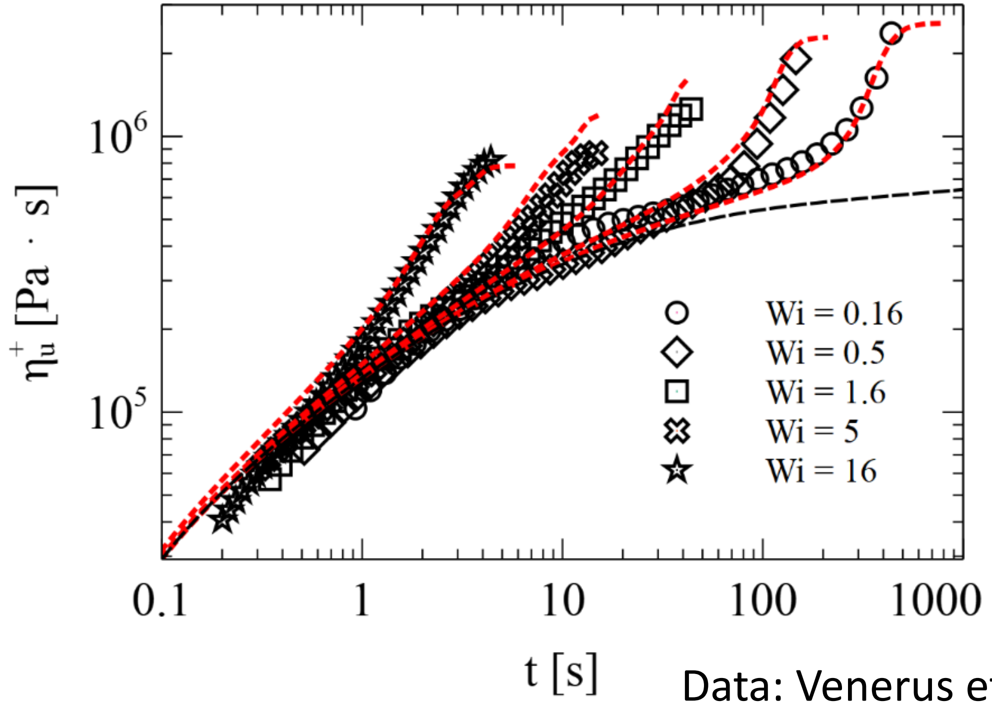
Graham et al. JOR 2003
Likhtman et al. JNNFM 2003

- Rolie Poly Model: ROuse LInear Entangled POLYmers

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

Predictions



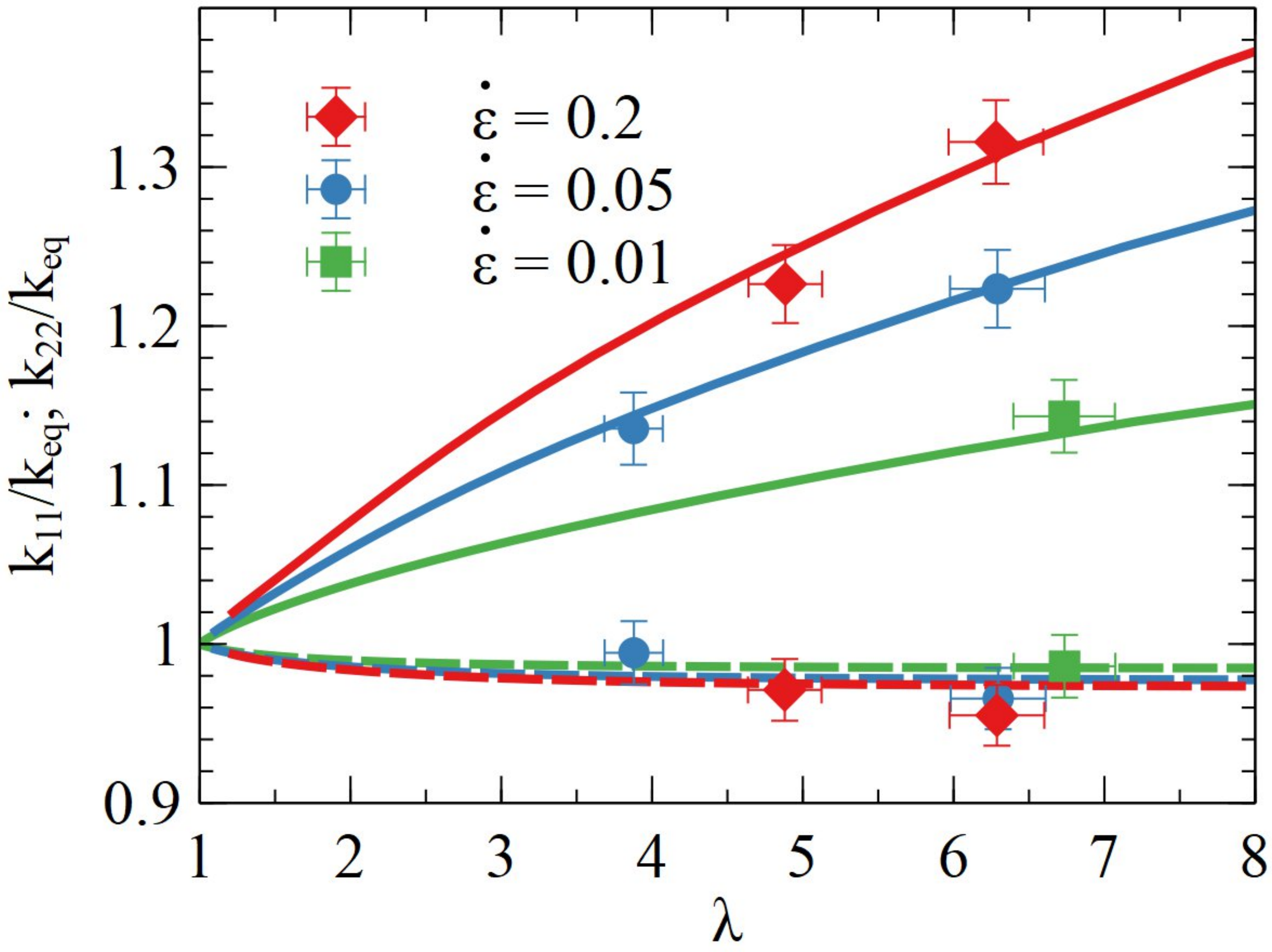


Data: Venerus et al. JOR 1999

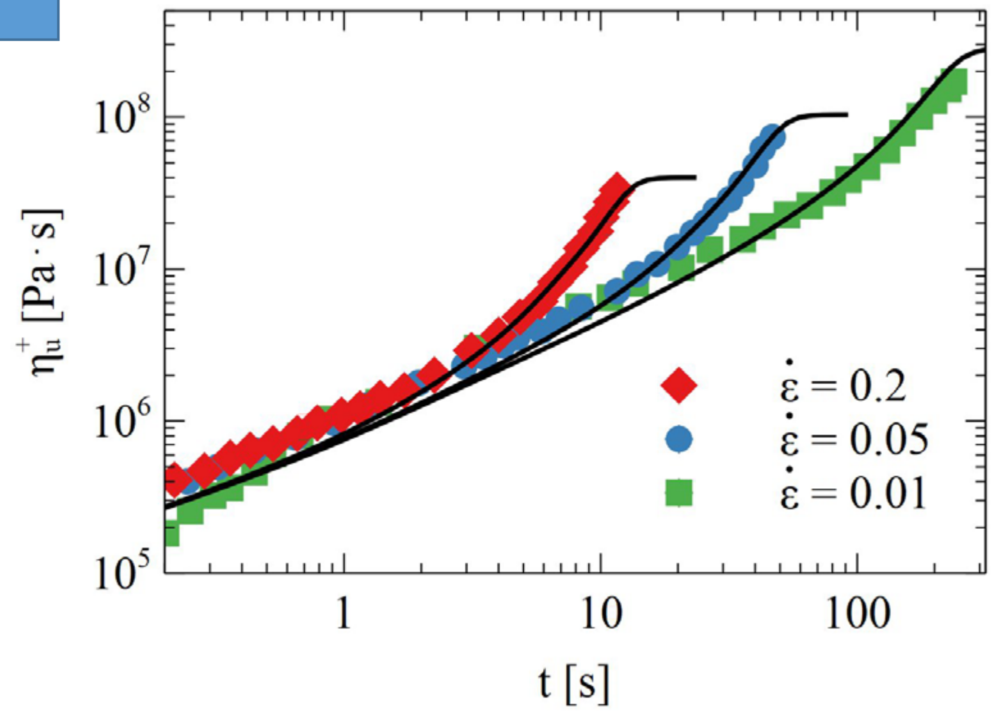
Data: Thomas Schweizer Rheol. Acta 2002

- Implement Finite extensibility.
  Kabameni et al. Rheol Acta 2009

Comparison to UE experiments: PS



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

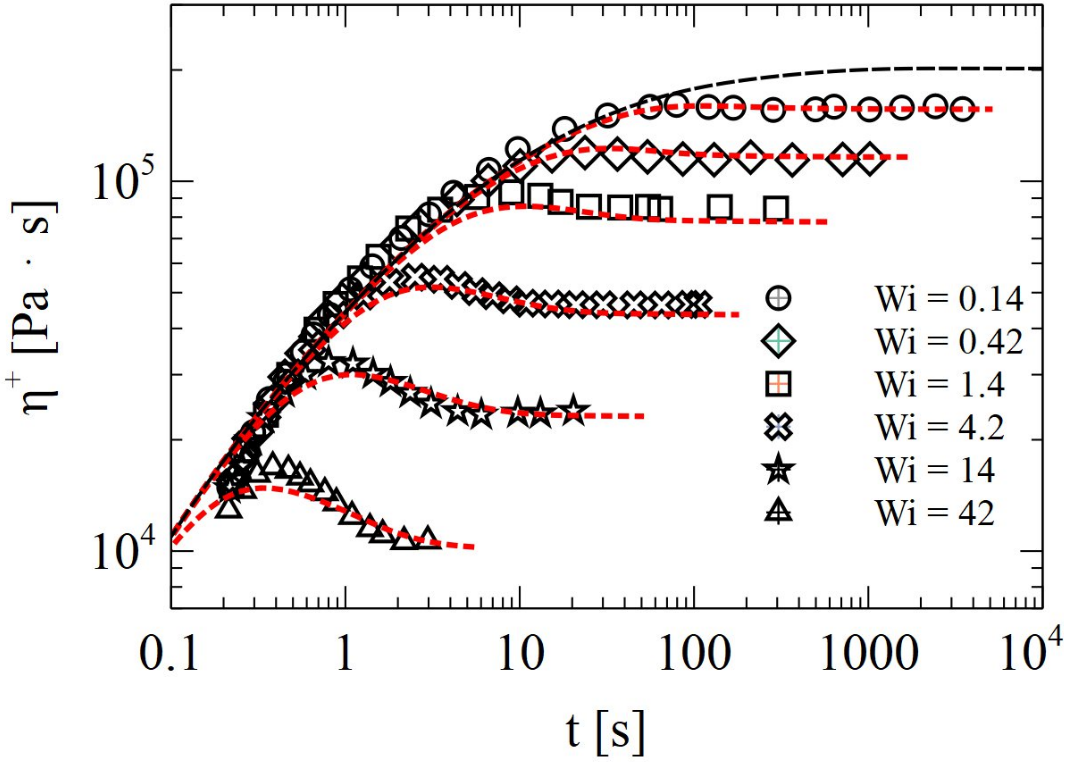


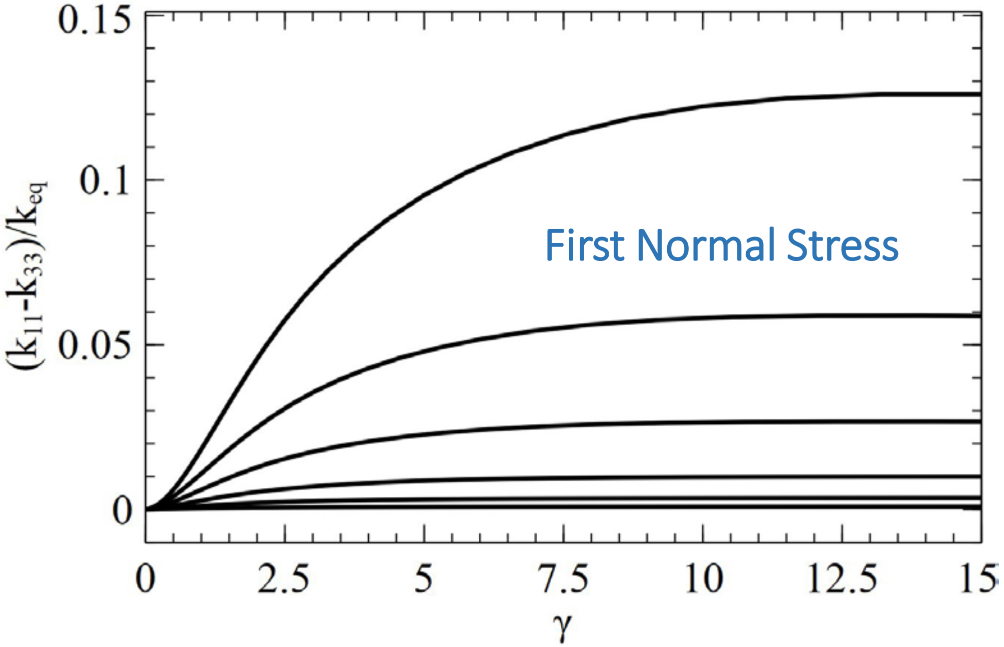
FRS Measurements after quenching. Data from Gupta et al. JOR 2013

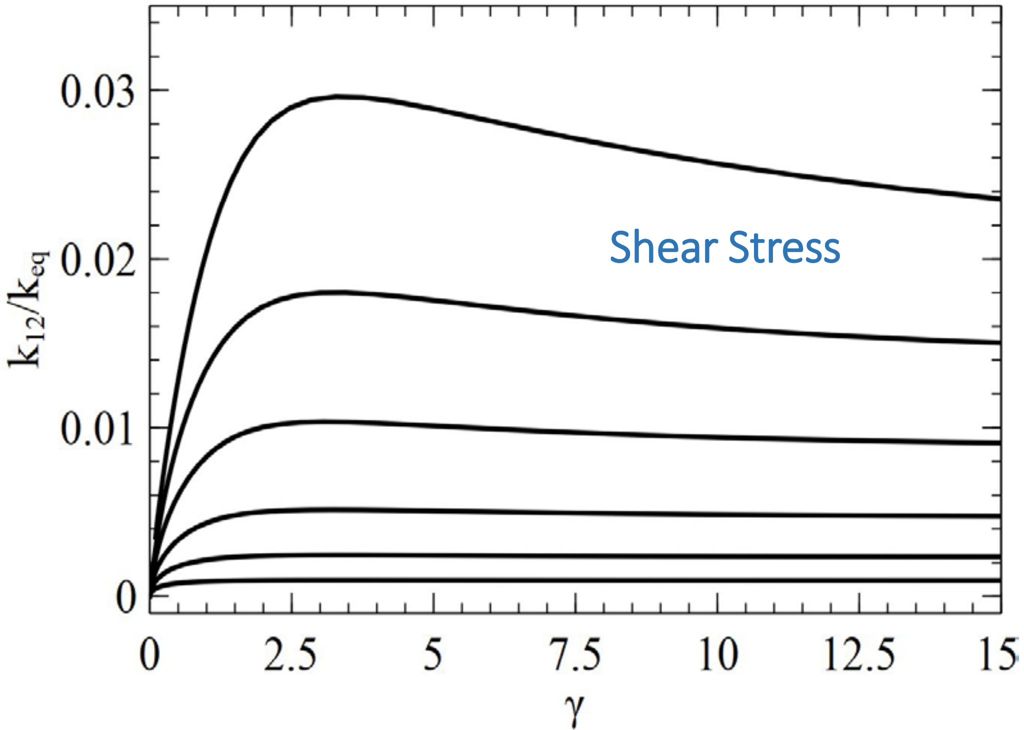
Effects under shear

Predictions

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

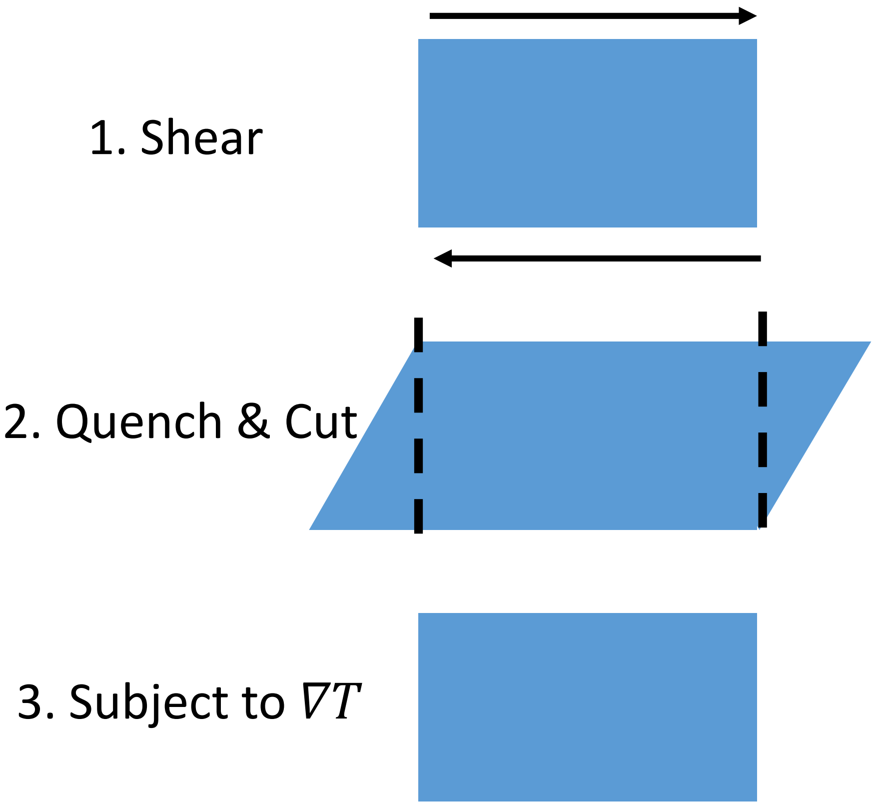


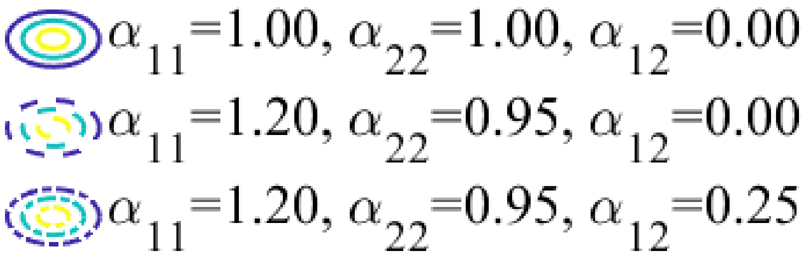


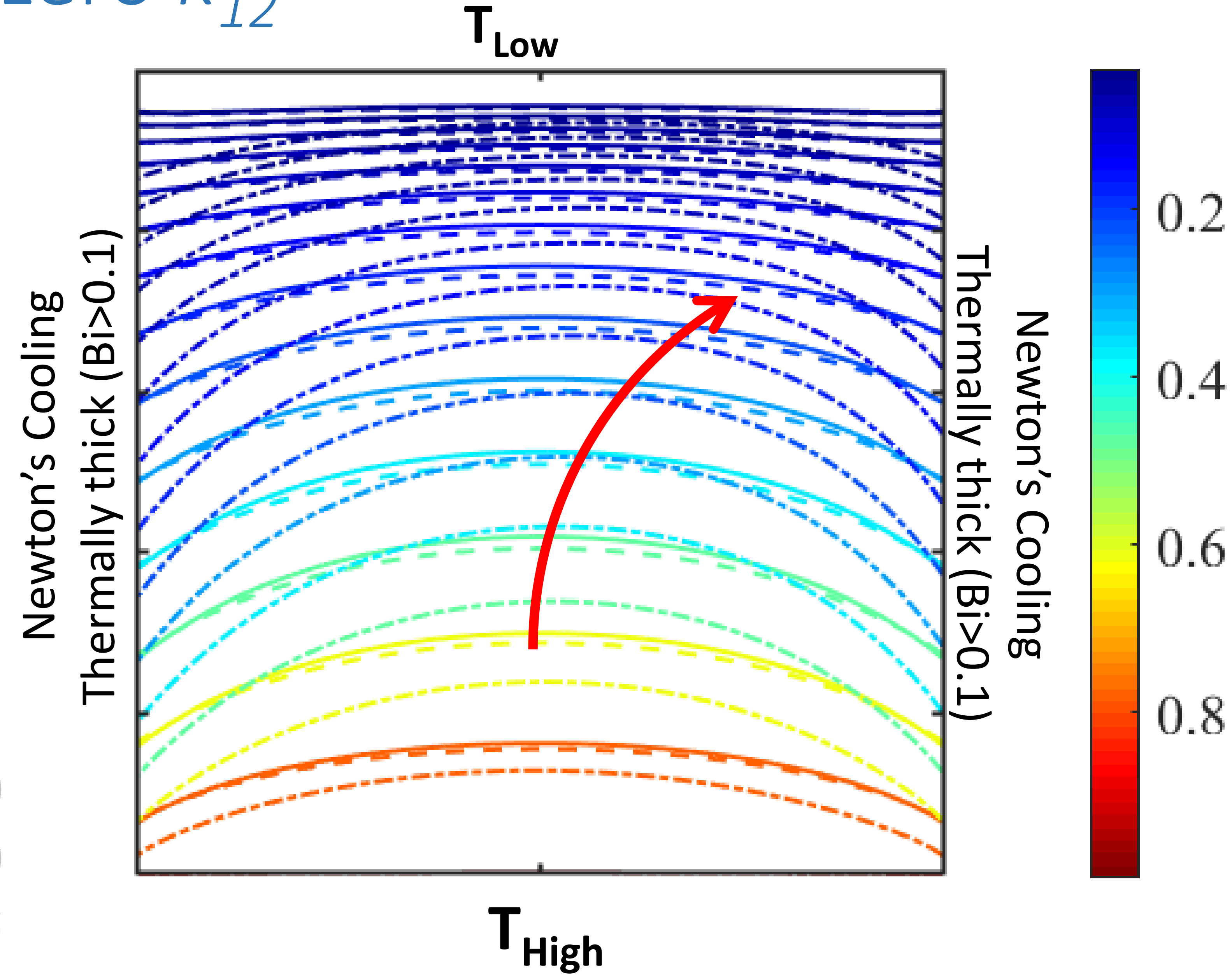


Data: Thomas Schweizer Rheol. Acta 2002

Effect of the non-zero k_{12}

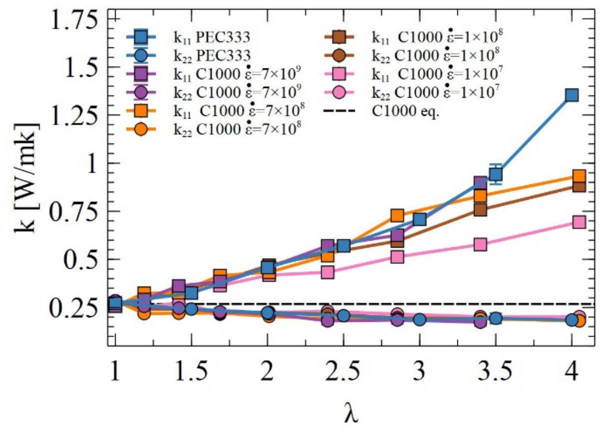


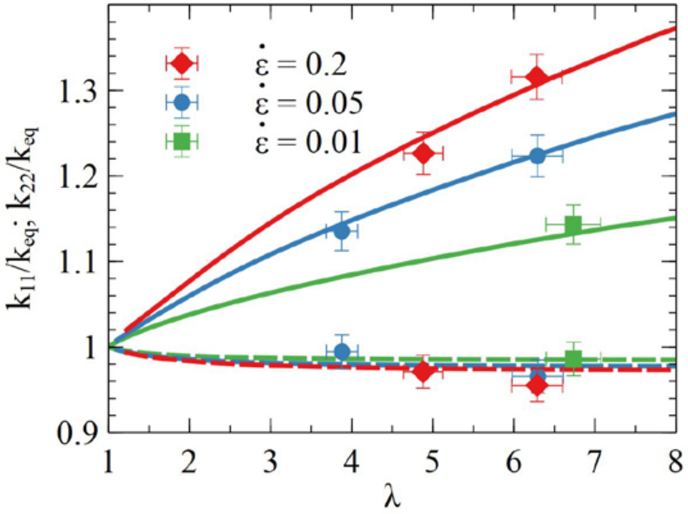


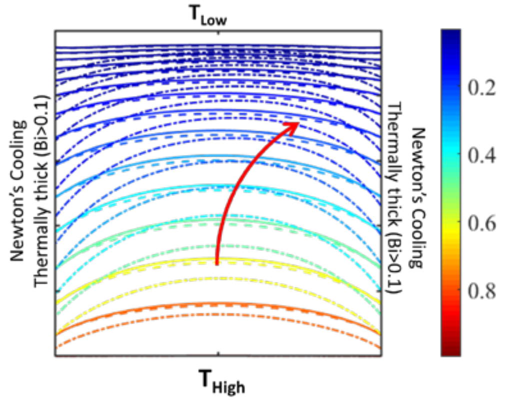


Conclusions

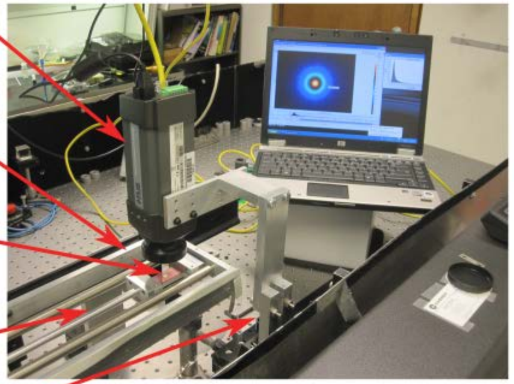
1. Thermal transport becomes anisotropic in polymers subjected to deformation
2. Flow induced anisotropy has significant implications in polymer processing
3. Experimental evidence of:
   - Proportionality to Stress: Stress-Thermal Rule (STR)
   - Universality
   - Beyond Finite Extensibility
4. MD simulations represent a unique tool to gain insight into the open questions regarding thermal transport in polymeric materials.
5. Roadmap to combine constitutive models (XPP, RP…) with the STR to include anisotropy in thermal transport in non-isothermal flows





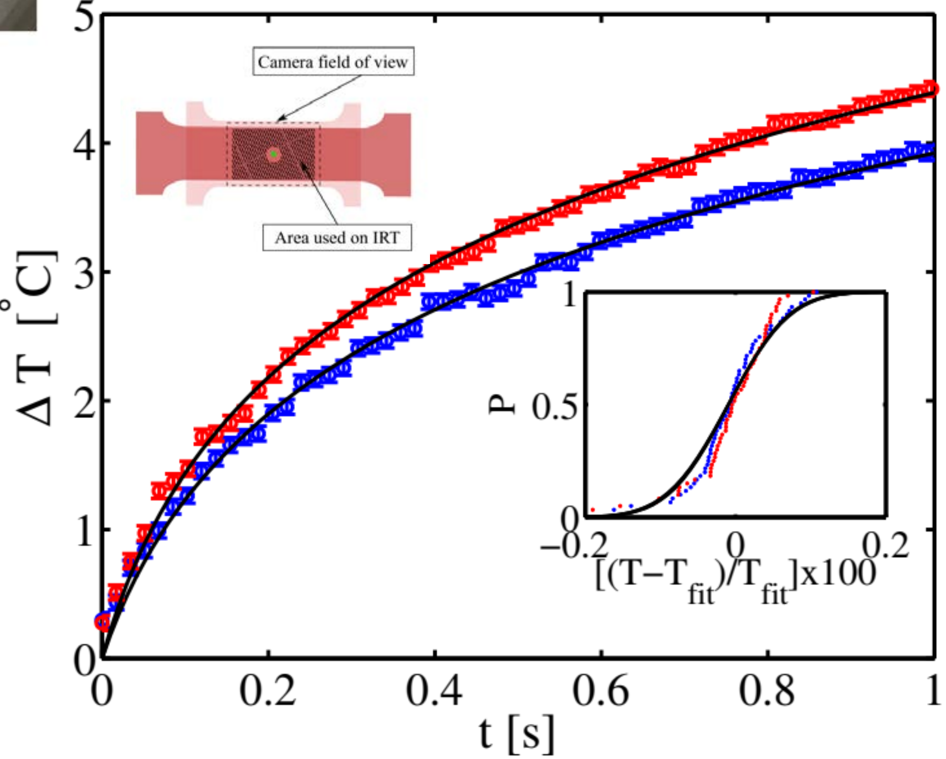


Experiments: Transient Infrared Thermography



$$\theta(0,0,t^*) = \frac{\langle T\rangle(0,0,t) - T_0}{K I_0 w^2/k_{\mathrm{eq}}} = \frac{1}{\sqrt{c}} \ln\left[\frac{2\sqrt{c\mathcal{R}} + 2ct/\tau_{\mathrm{D}} + b}{2\sqrt{ca} + b}\right]$$

$$\Delta T = \langle T\rangle(0,0,t) - T_0 = \frac{C_\theta}{\sqrt{c}} \ln\left[\frac{2\sqrt{c\mathcal{R}} + 2ct/\tau_{\mathrm{D}} + b}{2\sqrt{ca} + b}\right] \Rightarrow C_\theta, \tau_{\mathrm{D}}$$



$$\mathcal{R} = 1 + 8(\alpha_1 + \alpha_2)t/\tau_{\mathrm{D}} + 64\alpha_1\alpha_2(t/\tau_{\mathrm{D}})^2$$

where $\tau_{\mathrm{D}} = w^2 \rho \hat{c}_\lambda / k_{\mathrm{eq}}$

λ	C_θ [K]	τ_{D} [s]
○ 1.00	13 ±0.2	1.60 ± 0.07
○ 3.06	12 ±0.2	1.77 ± 0.07

$$\frac{\tau_{\mathrm{D}}(\lambda)}{\tau_{\mathrm{D}}(1)} = \frac{\hat{c}_\lambda}{\hat{c}_\lambda^0}$$

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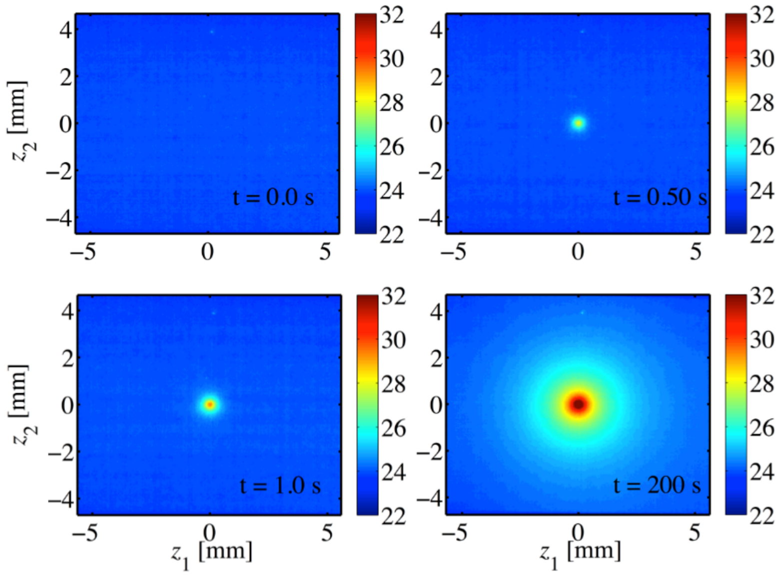
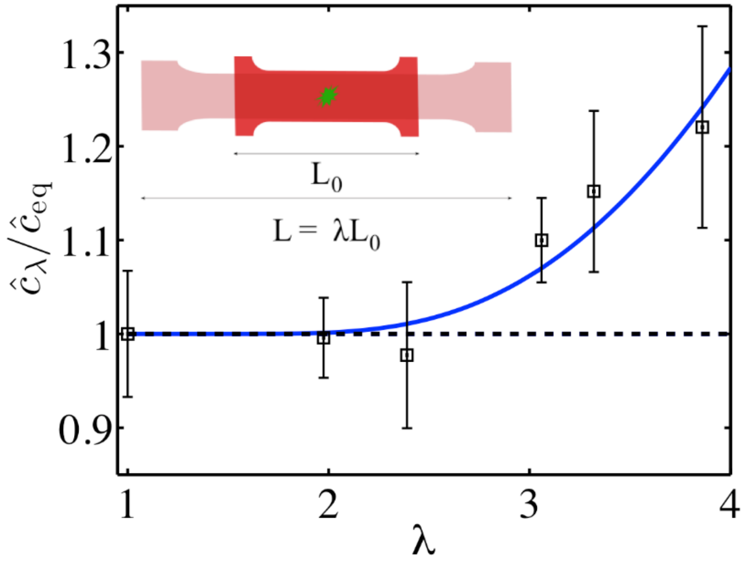
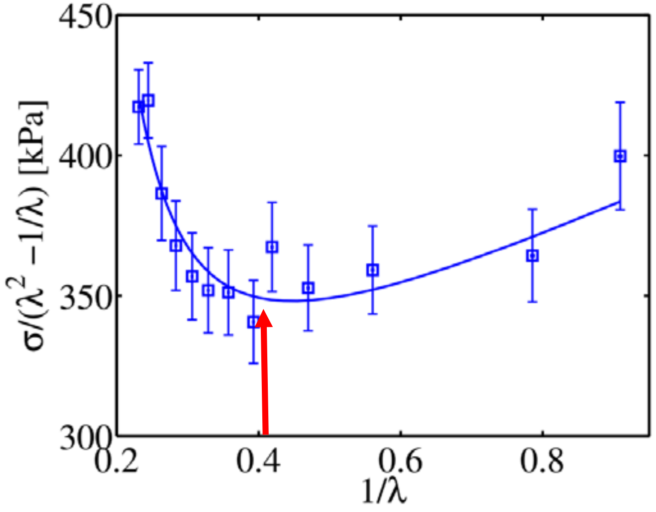
Experiments: Transient Infrared Thermography



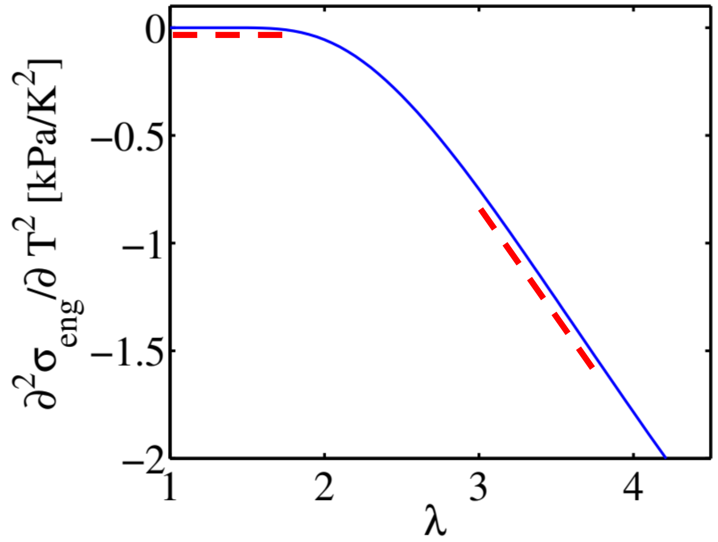




$$\rho \hat{c}_\lambda = \rho \hat{c}_{eq} - T \int_1^\lambda \left(\frac{\partial^2 \sigma_{eng}}{\partial T^2} \right)_{\lambda'} d\lambda'.$$

$$\sigma_{eng} = \left(\frac{\partial f}{\partial \lambda} \right)_T = \left(\frac{\partial u}{\partial \lambda} \right)_T - T \left(\frac{\partial s}{\partial \lambda} \right)_T$$

Not *Purely Entropic Elasticity* -> internal energy contribution to stress is required



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Thank you!

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"MCIATTP"
Project # 750985

UNIVERSIDAD DE BURGOS

MARIE CURIE ACTIONS

HORIZON 2020