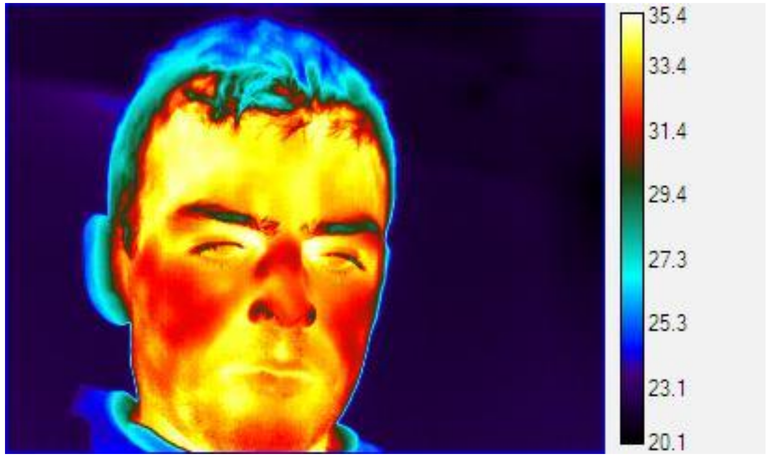
UNIVERSIDAD
DE BURGOS

13th IMT

Anisotropy in *k* and c_p induced by deformation in polymers: experimental methods, current understanding and application to numerical methods

David NIETO SIMAVILLA, David C. Venerus and Wilco M. H. Verbeeten



MARIE CURIE ACTIONS

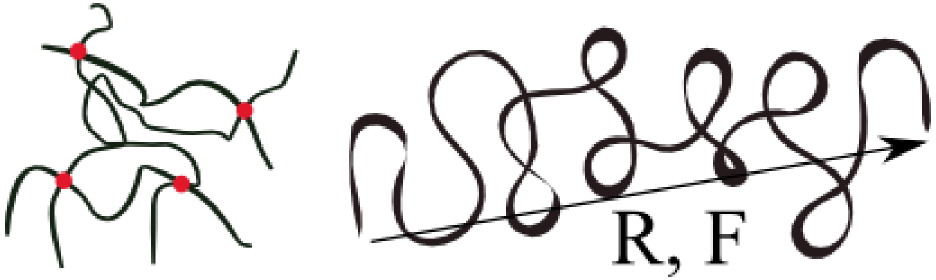
HORIZON 2020

Summary

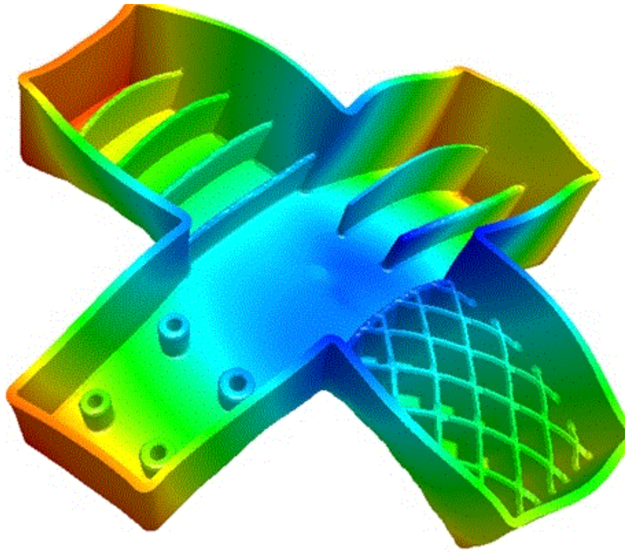
- Orientation/Stress → polymer thermo-physical properties (k, c_p)
- The MCIATTP approach:

“Molecular to Continuum Investigation of Anisotropic Thermal Transport”

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



The MCIATTP project:



Macroscopic network models

Experimental results

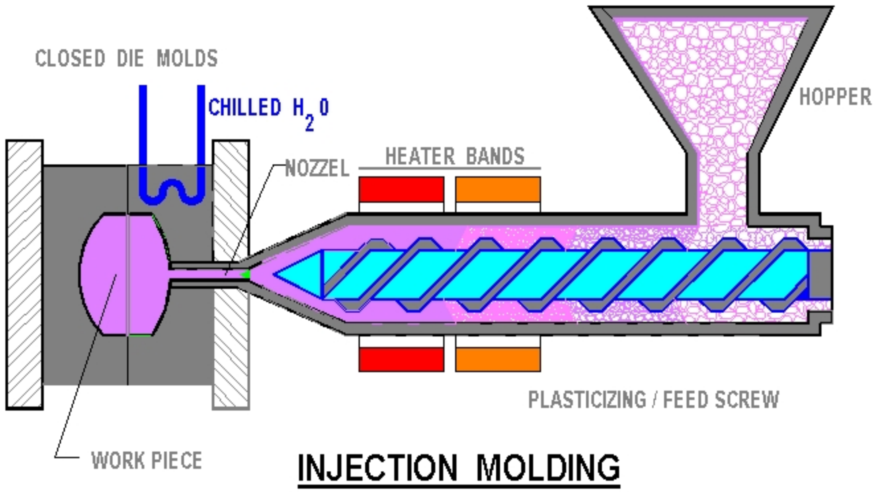
Molecular-based modelling

Molecular-macroscopic coupling

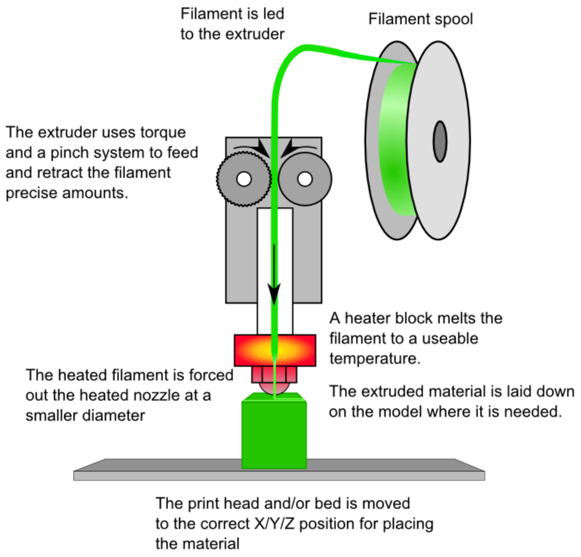
Non-homogeneous non-isothermal viscoelastic flow simulation tool

The MCIATTP Project

Motivation: Polymer Processing



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


Filament is led to the extruder

Filament spool

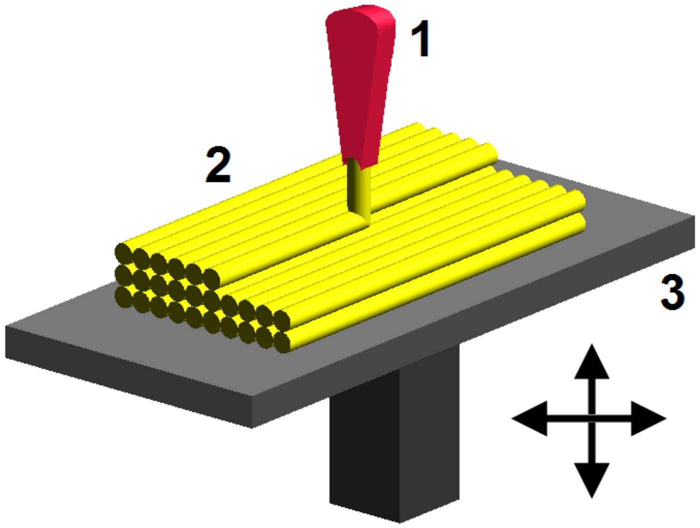
The extruder uses torque and a pinch system to feed and retract the filament precise amounts.

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



Thermal Transport Affects:
- Injection Pressure
- Cavity Flow
- Residual Stress
- Part Shrinkage

www.astra-polymers.com

Non-Isothermal Transport Phenomena

Balance Equations:

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

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

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

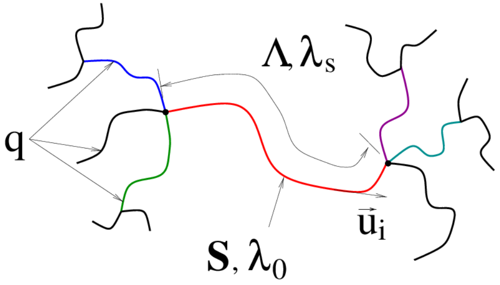
Constitutive equations:

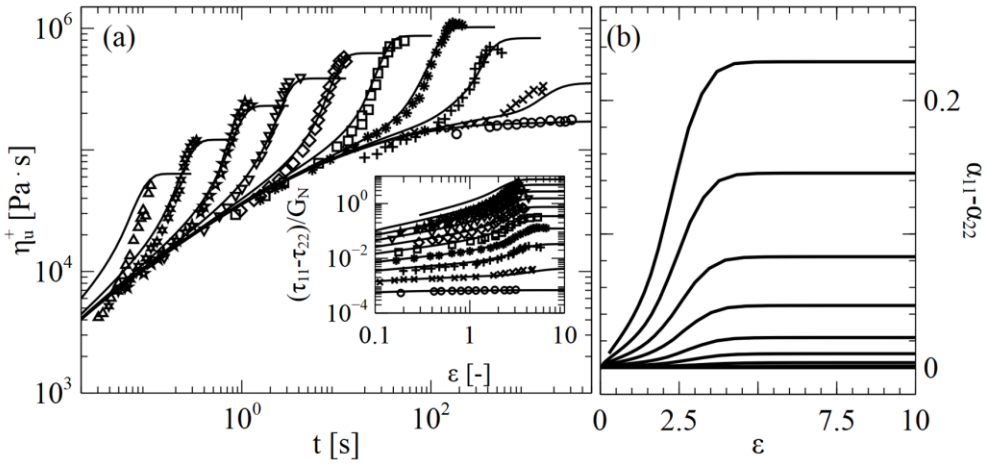
$$\boxed{\boldsymbol{q} = -k \nabla T} \qquad \boxed{\hat{c}_v = \hat{c}_v(T)} \qquad \boldsymbol{\tau} = \eta(T)\left[\nabla v + \nabla v^{\intercal}\right]$$

- High stresses & Low thermal conductivity.

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

The MCIATTP project:





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The MCIATTP Project

Constitutive Model: eXtended Pom-Pom

- What physics are in the model?

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

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

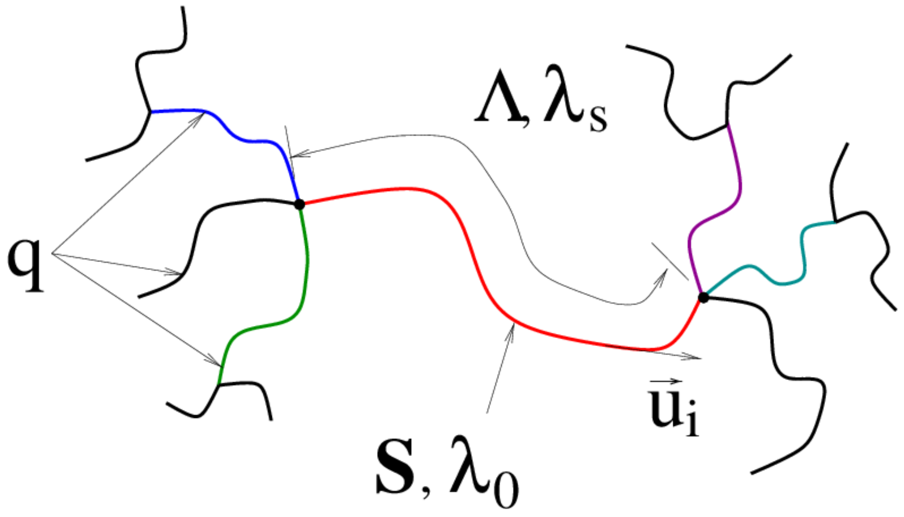
$$\boldsymbol{\lambda}(\boldsymbol{\tau})^{-1} = \frac{1}{\lambda_{0b}}\left[\frac{\alpha}{G_0}\boldsymbol{\tau} + f(\boldsymbol{\tau})^{-1}\boldsymbol{I} + G_0\left(f(\boldsymbol{\tau})^{-1} - 1\right)\boldsymbol{\tau}^{-1}\right]$$

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

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

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

- 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

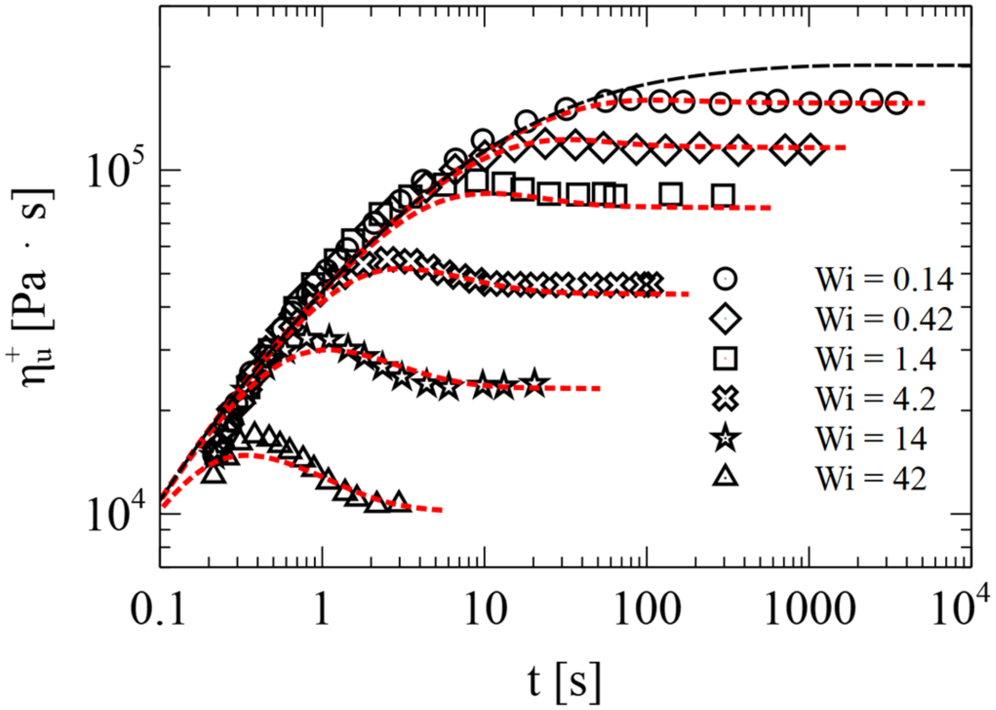
Constitutive Model: Rolie Poly

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

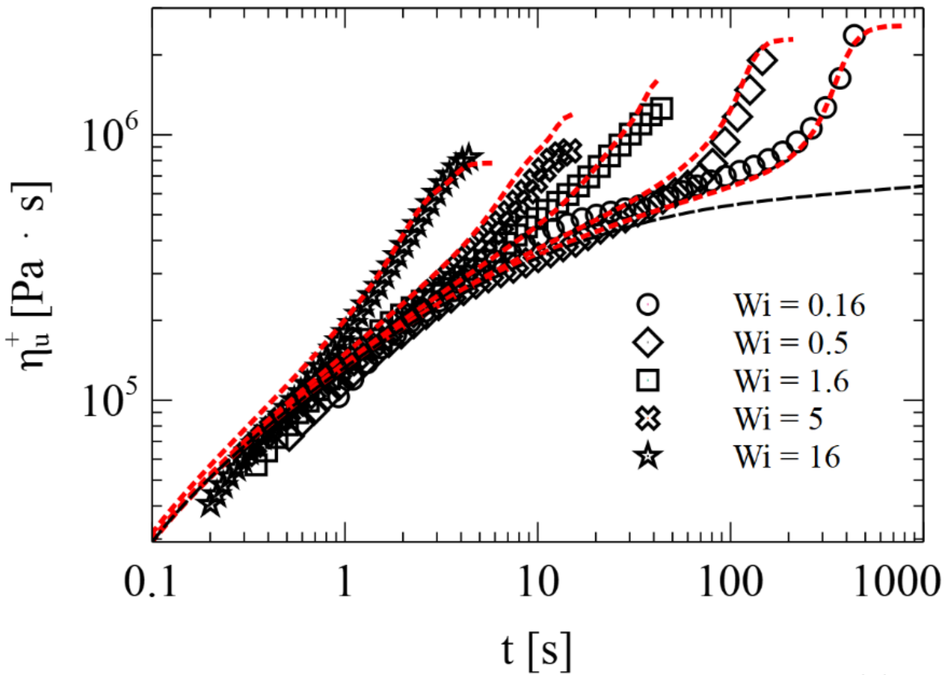
- Rolie Poly Model: ROuse LInear Entangled POLYmers

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

- Predictions



Data: Thomas Schweizer Rheol. Acta 2002

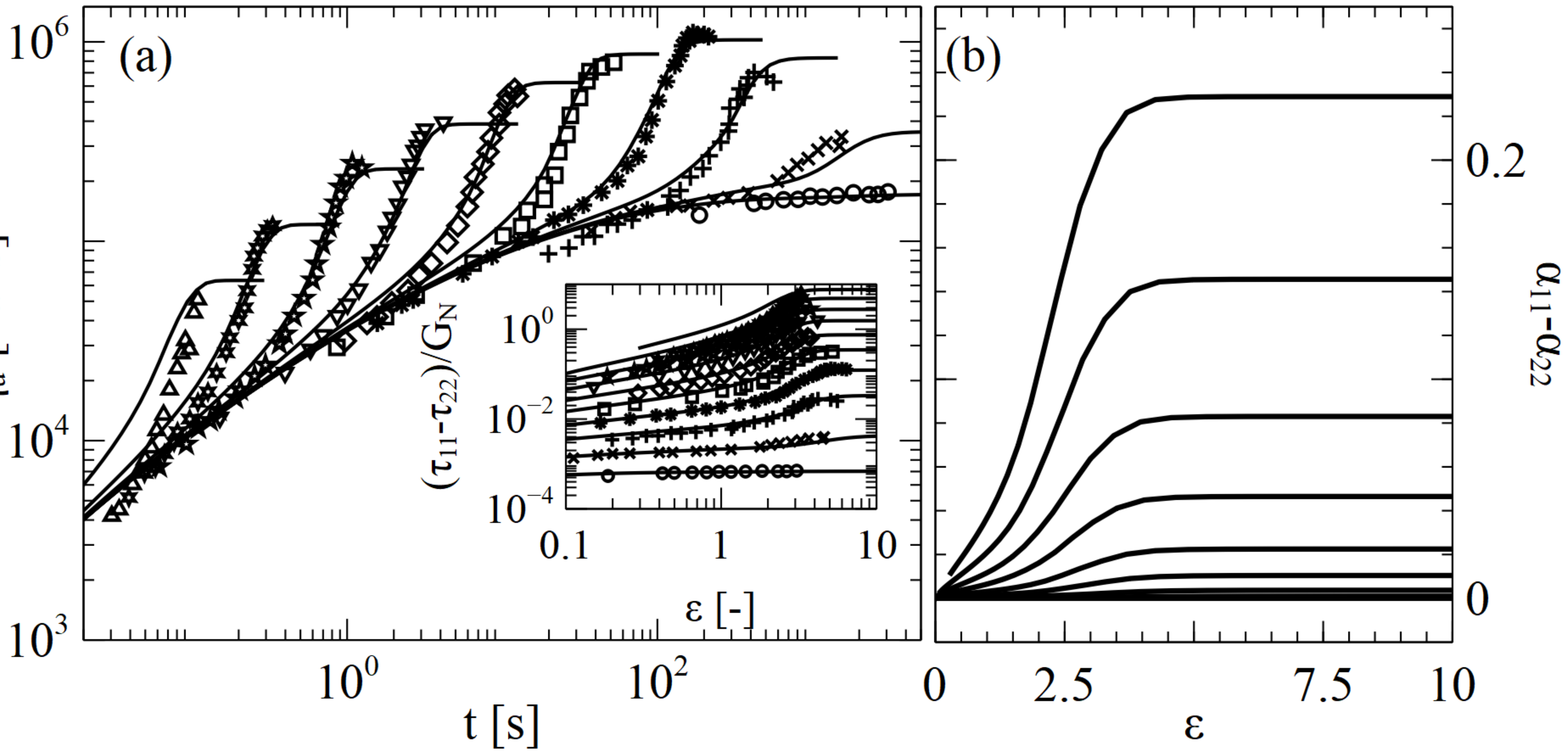


Data: Venerus et al. JOR 1999

- Implement Finite extensibility.

  Kabameni et al. Rheol Acta 2009

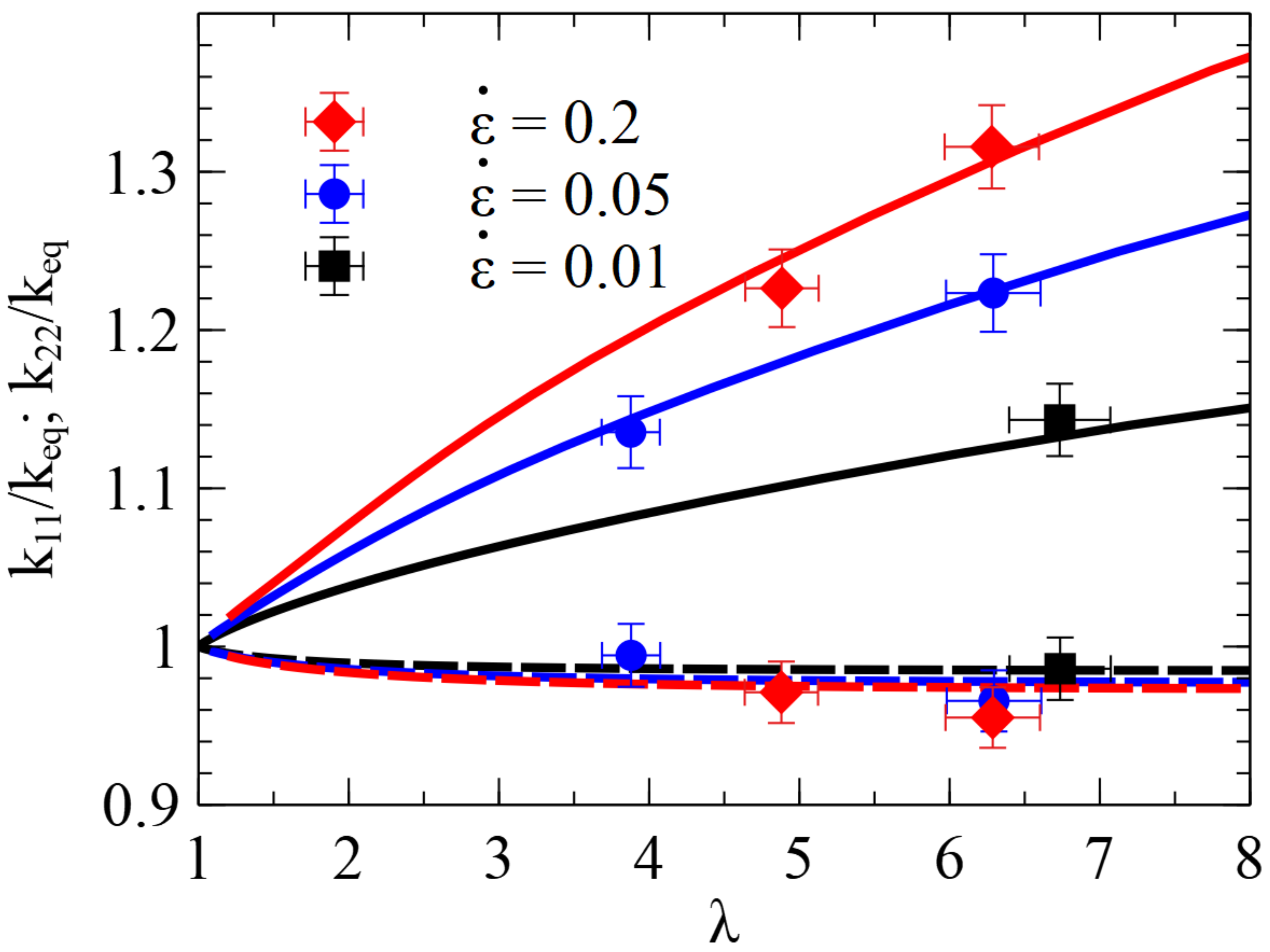
Transient Start-up: Uniaxial IUPAC_A LDPE



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

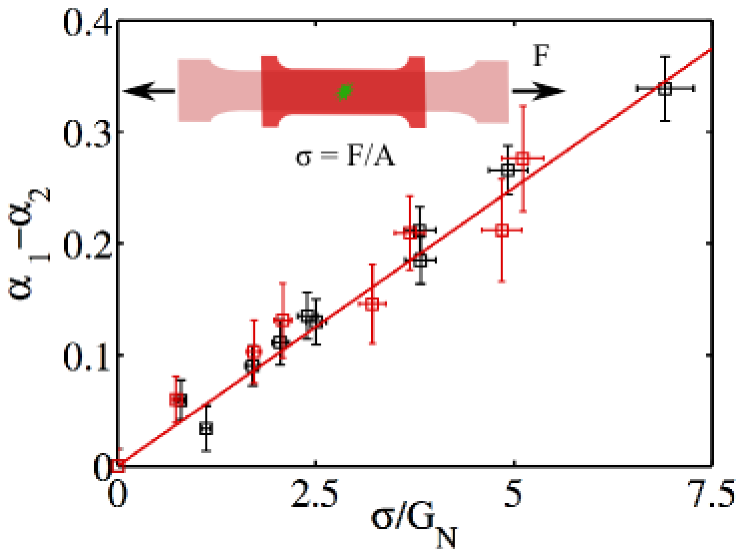
Gupta et al. Journal of Rheology 57, 2013.

Comparison to experiments: PS



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

The MCIATTP project:



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Anisotropic Thermal Conduction

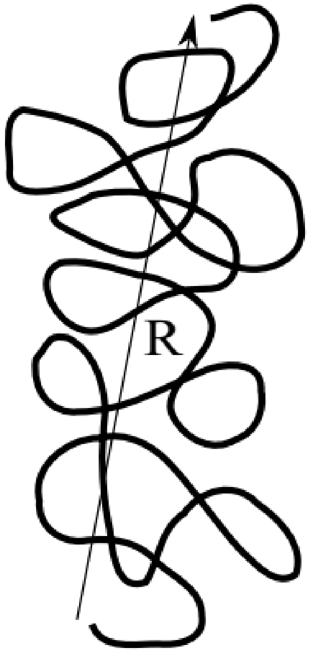
Fourier's Law: Thermal transport in deformed polymers is diffusive and anisotropic.

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

$\boldsymbol{k}$ 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:

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

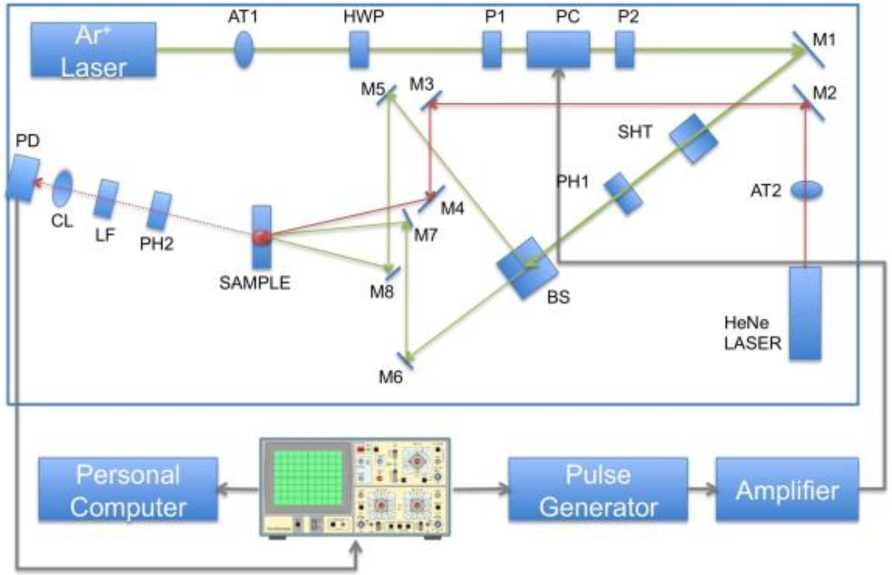
$$\boxed{\boldsymbol{k} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{\mathrm{eq}} C_{\mathrm{t}} \left[\boldsymbol{\tau} - \tfrac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta}\right]}$$

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.

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

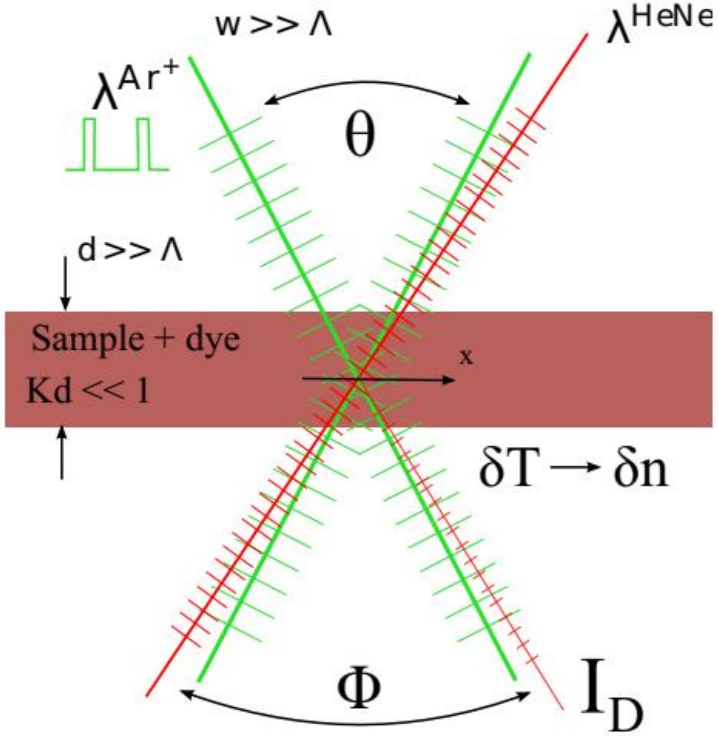
Experiments: Forced Rayleigh Scattering (FRS)



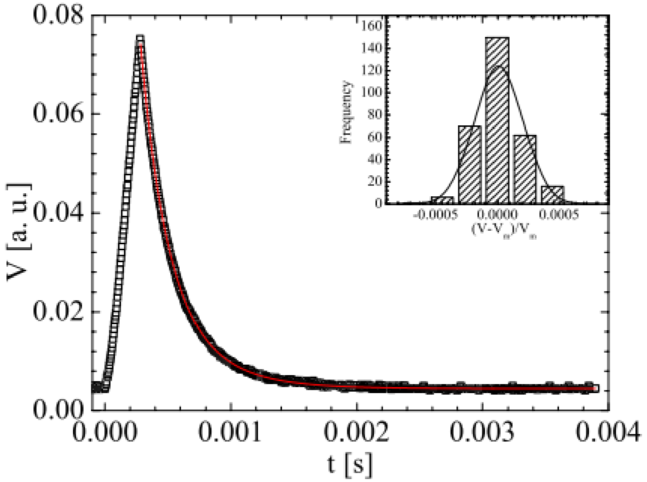
Intensity/Voltage at the photodetector:

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

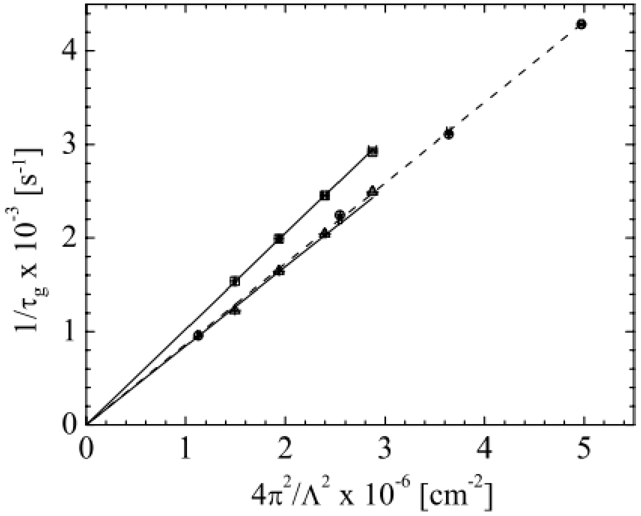
$$\frac{1}{\tau_\mathrm{g}} = \boxed{D_\mathrm{th}}\frac{4\pi^2}{\Lambda^2} \qquad D_\mathrm{th} = \frac{k}{\rho\hat{c}_p}$$



100 waveforms for each grating size

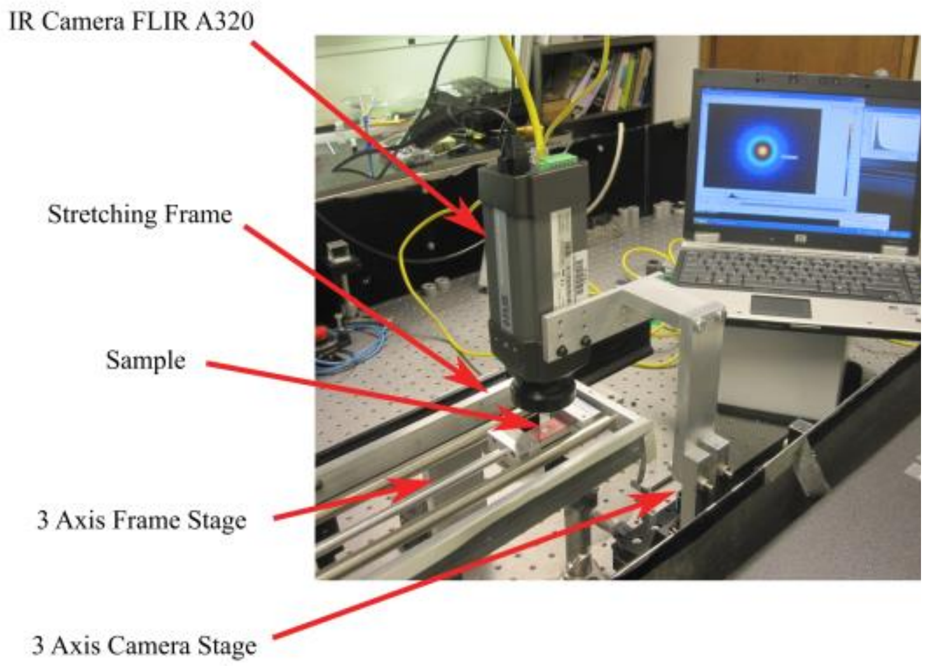


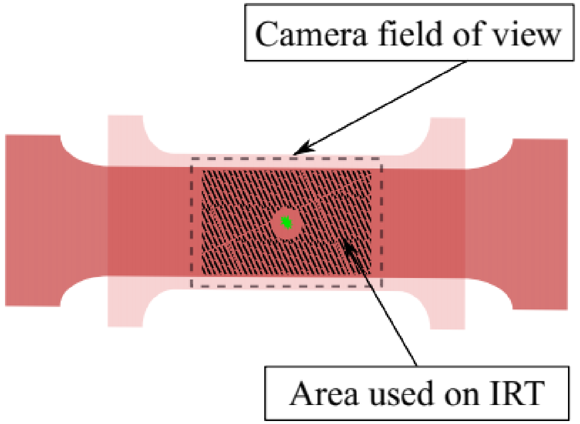
4 grating sizes for each elongation



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

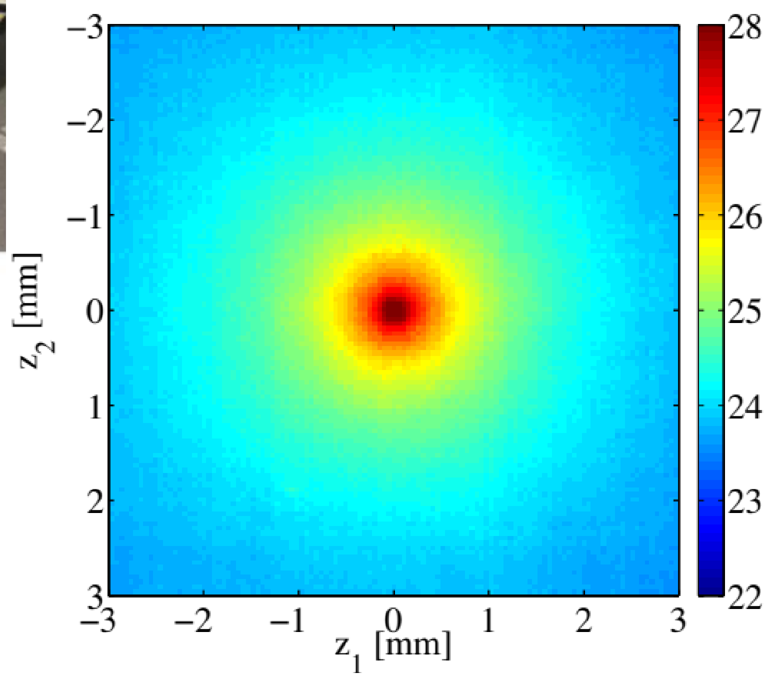
Experiments: Infrared Thermography (IRT)



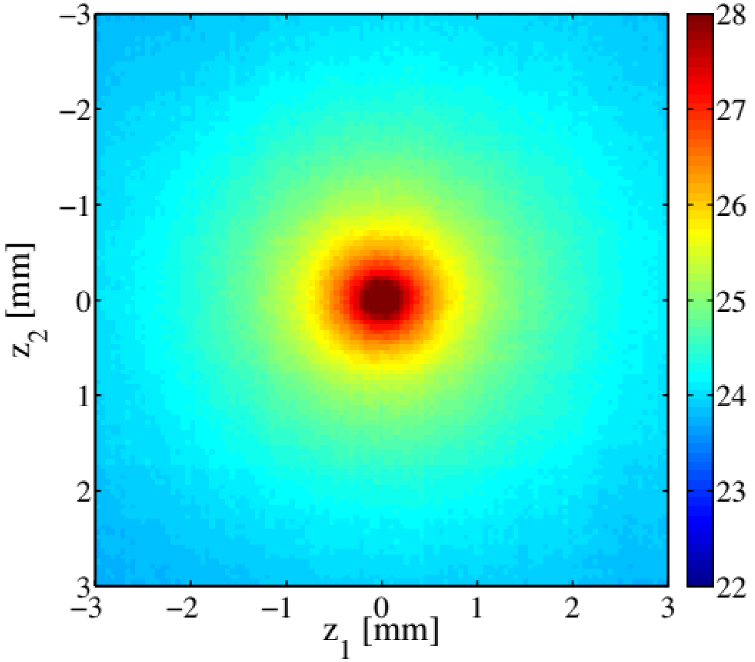


$$\theta(x_1, x_2) = \frac{1}{4\sqrt{\alpha_1\alpha_2}} K_0\left(\sqrt{2\mathrm{Bi}(x_1{}^2/\alpha_1 + x_2{}^2/\alpha_2)}\right)$$

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



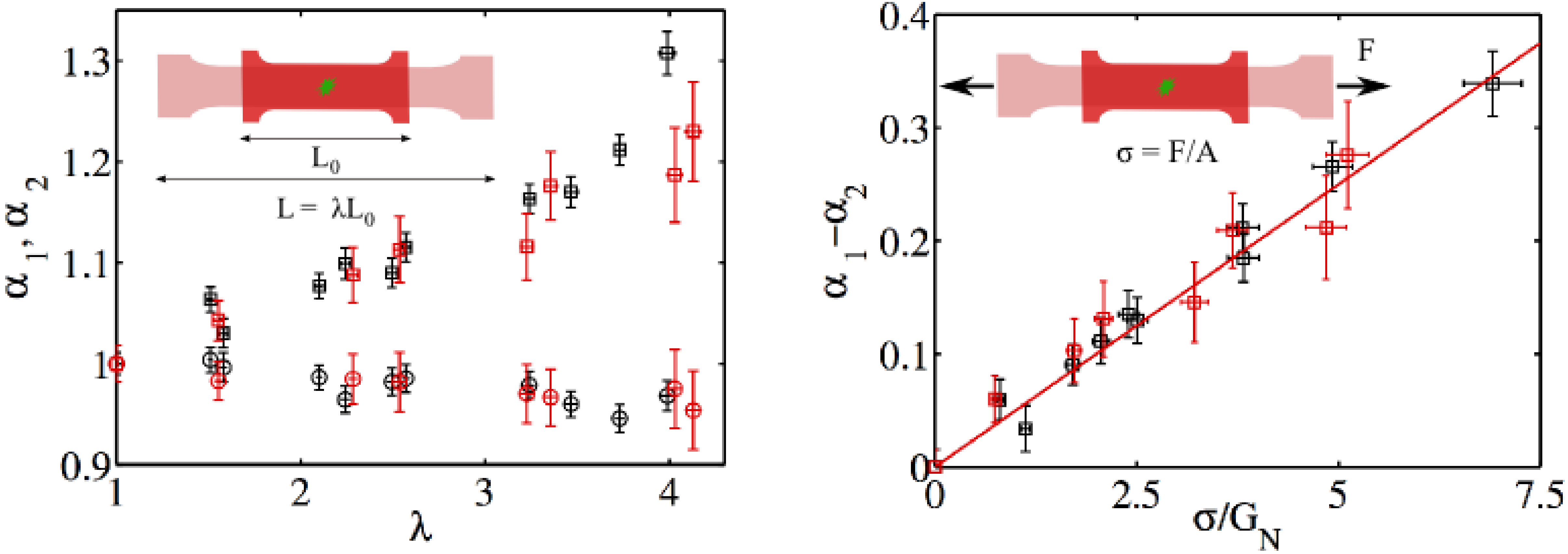
Un-stretched sample, $\lambda = 1$ and $\mathrm{Bi}_0 = 0.029 \pm 0.001$



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}]	$C_t G_N$ –	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

$$\boxed{C_t G_N \sim 0.04}$$

(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:

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

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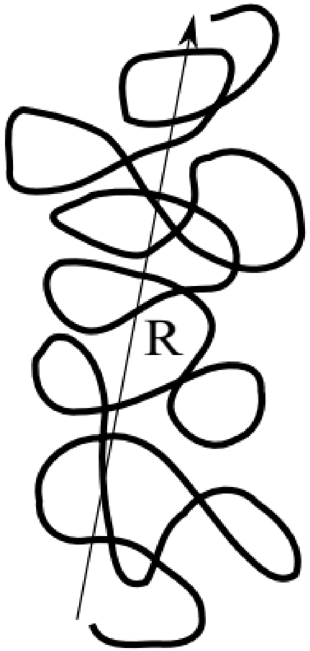

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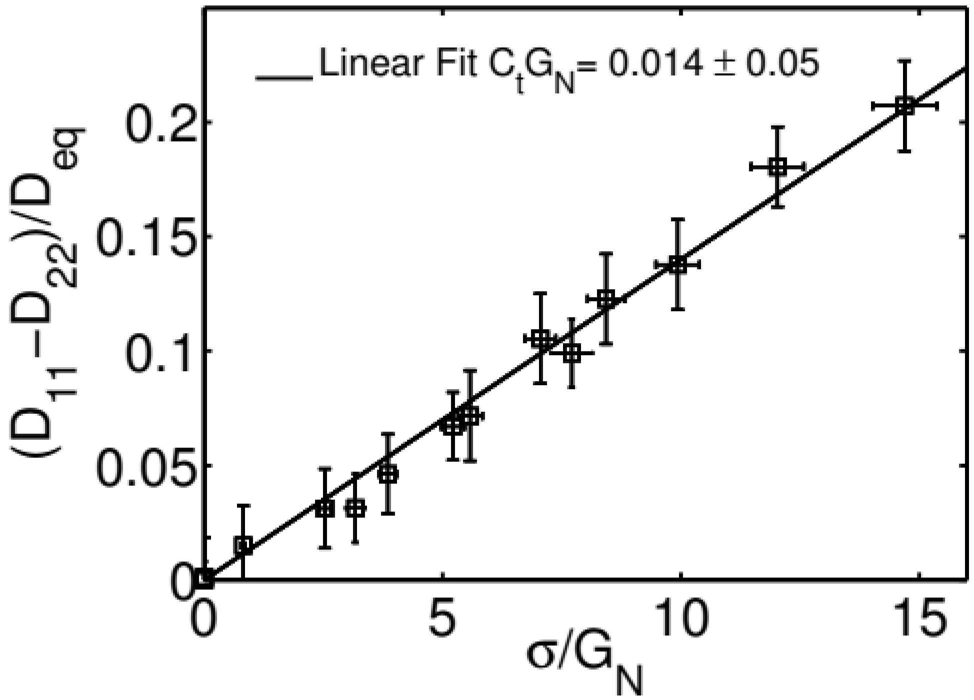
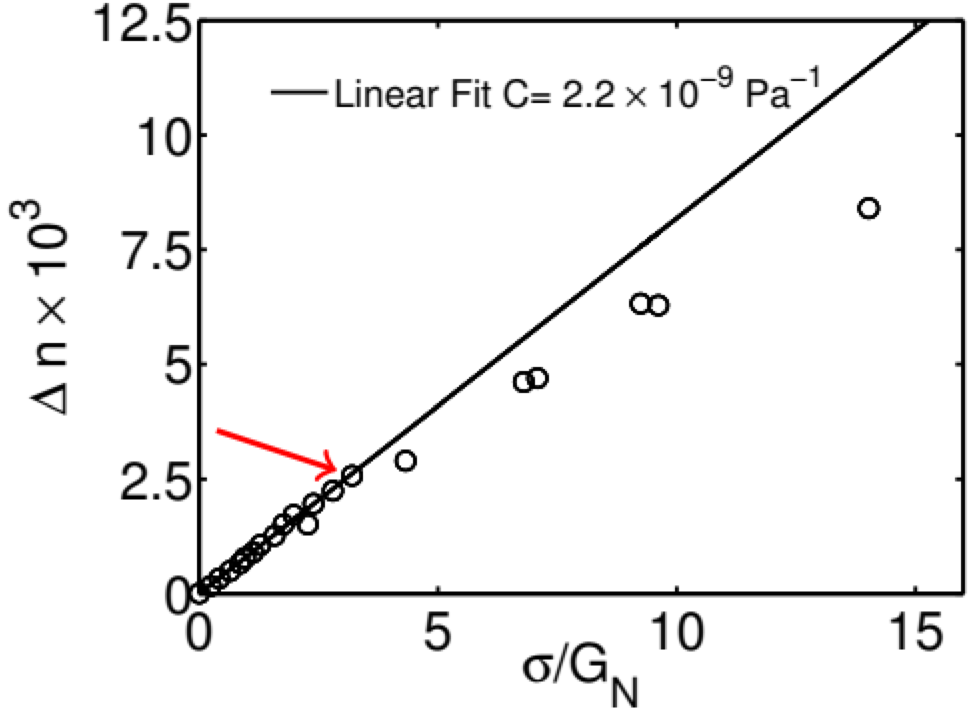
Key Findings: …Beyond Finite Extensibility





The STR stays valid where the SOR fails!

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

The Stress-Thermal Rule can be applied:

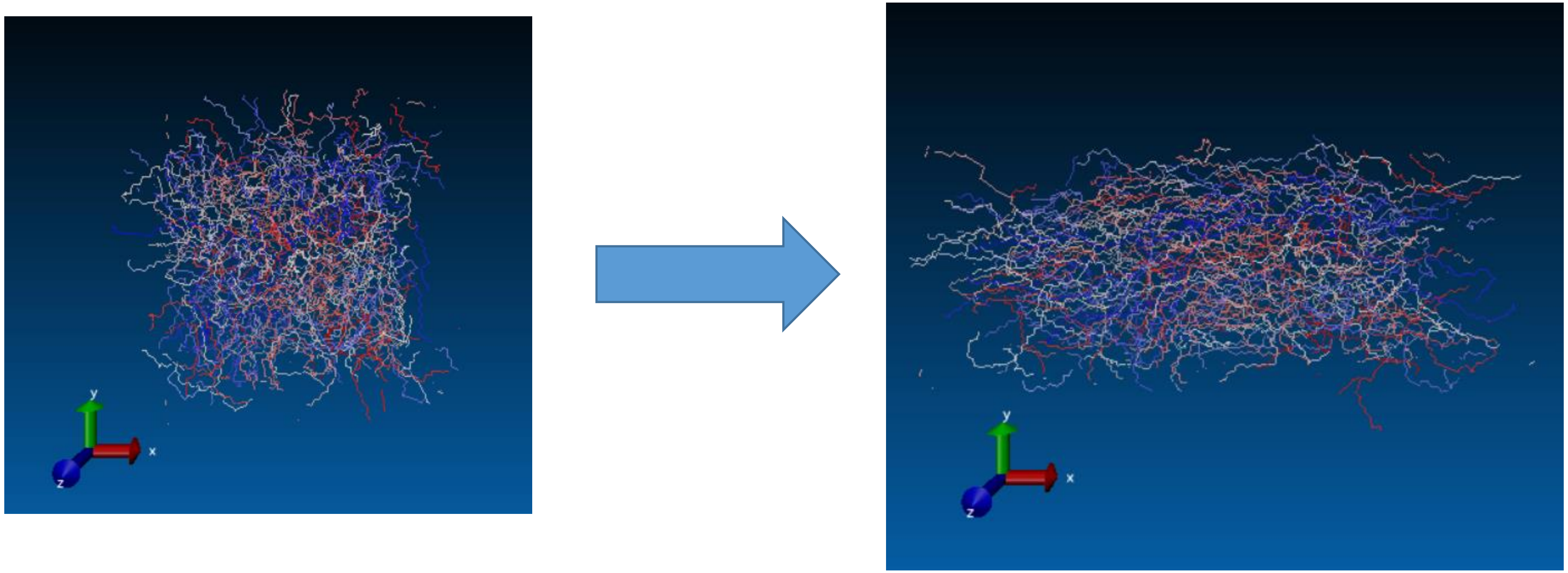
1. To any melt just by knowing stress and G_N
2. At high strain and strain rates beyond the onset of finite extensibility effects

MD Simulation work on XL and melt PE

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

- k Measurement methods:
  - EMD: Green-Kubo

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



Crnjar et al. Phys. Rev. Mat. 2018

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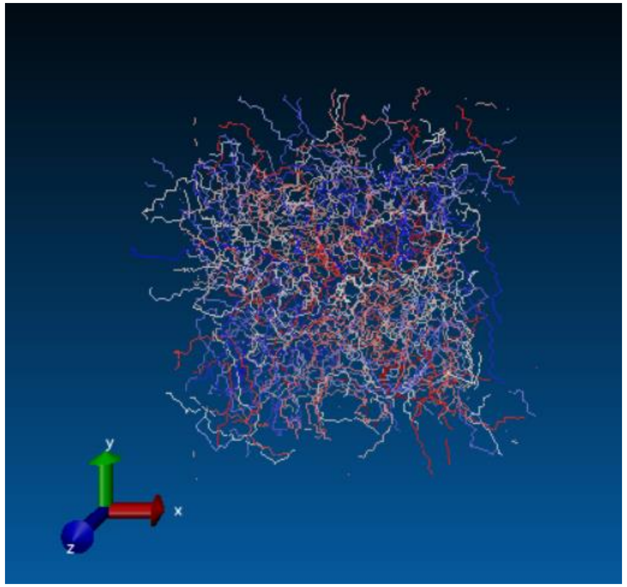

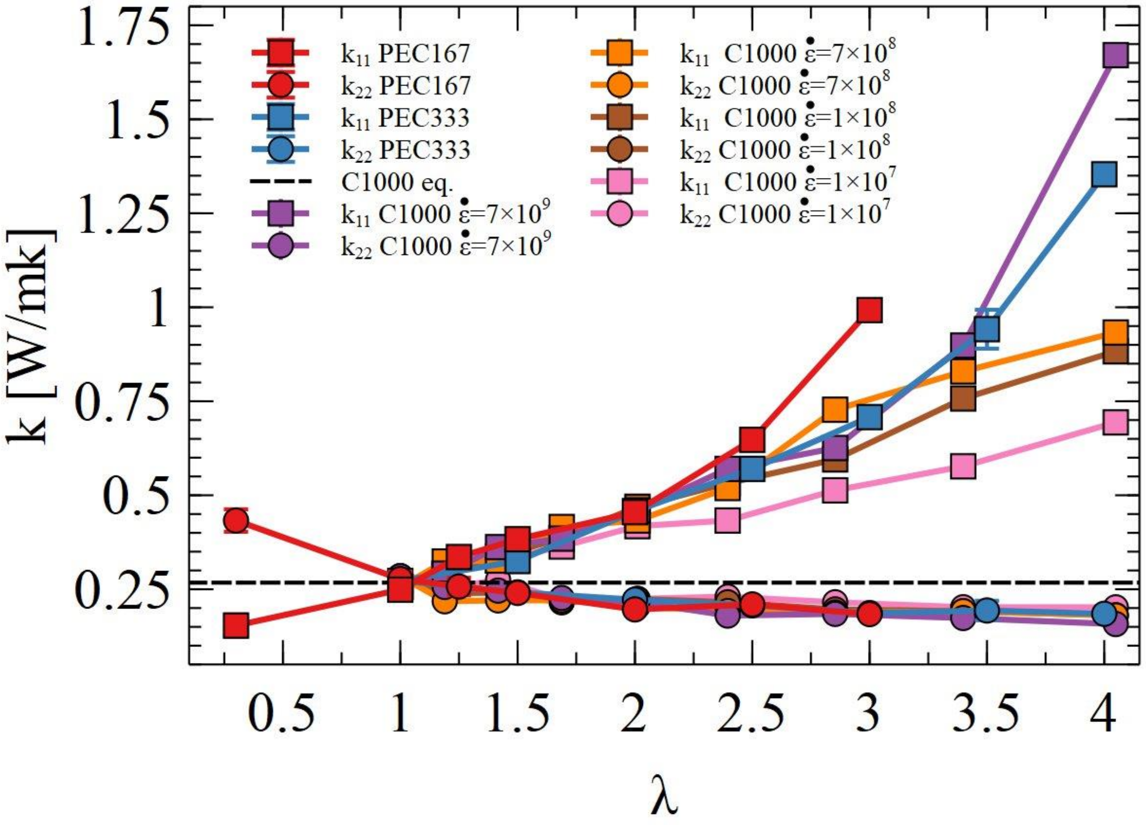

Crnjar et al. Phys. Rev. Mat. 2018

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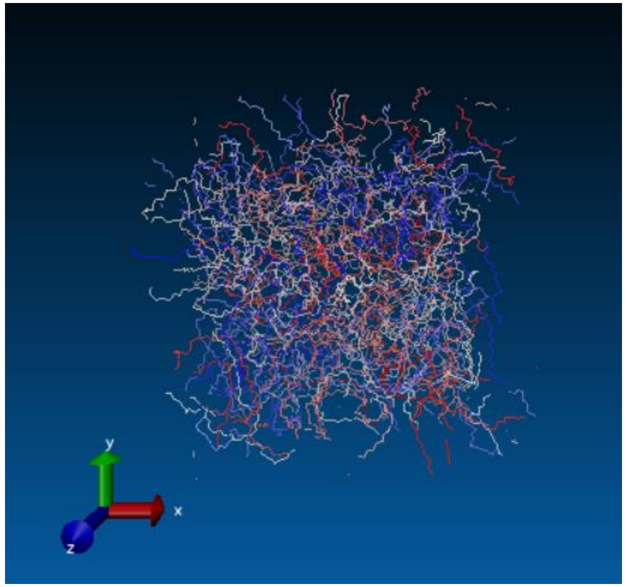
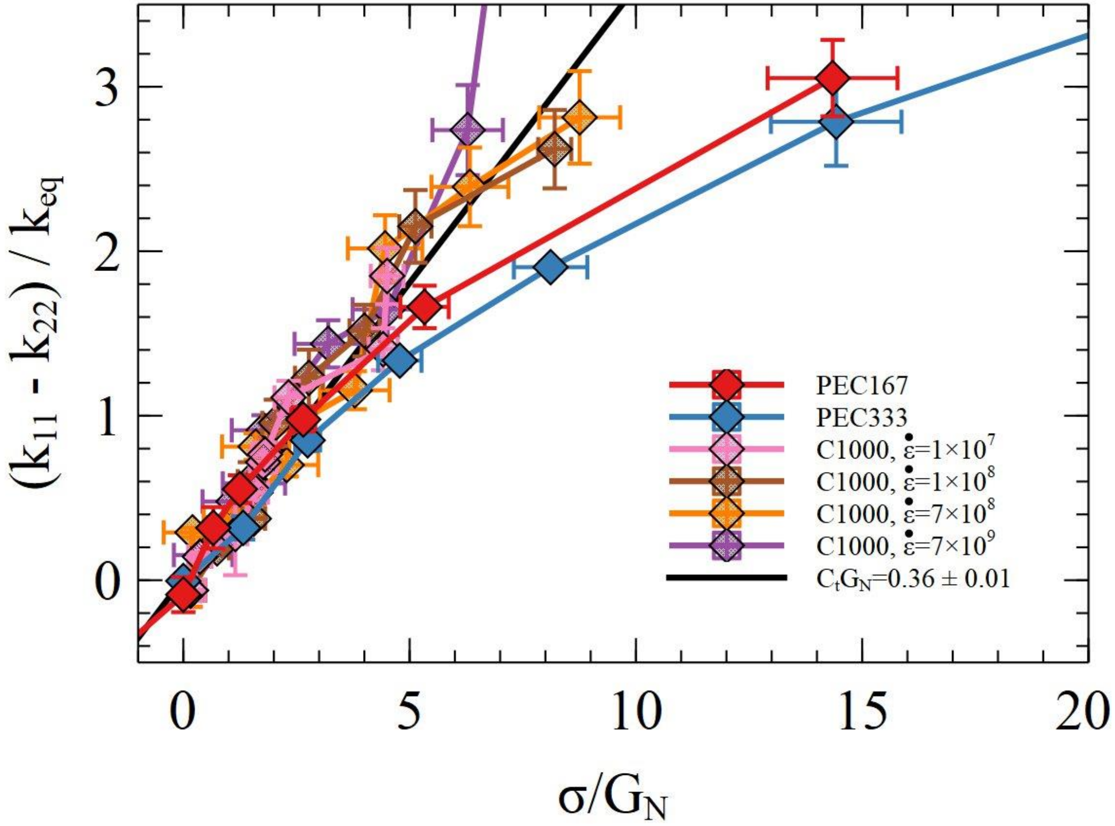


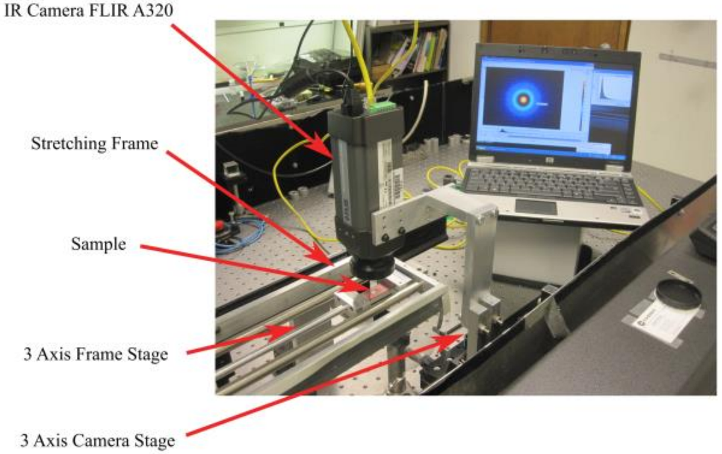
$$k_{ij} \propto C_{k,p} v^{i}_{k,p} \lambda^{j}_{k,p}$$

$$\lambda_j \propto L_{\mathrm{e}}?$$



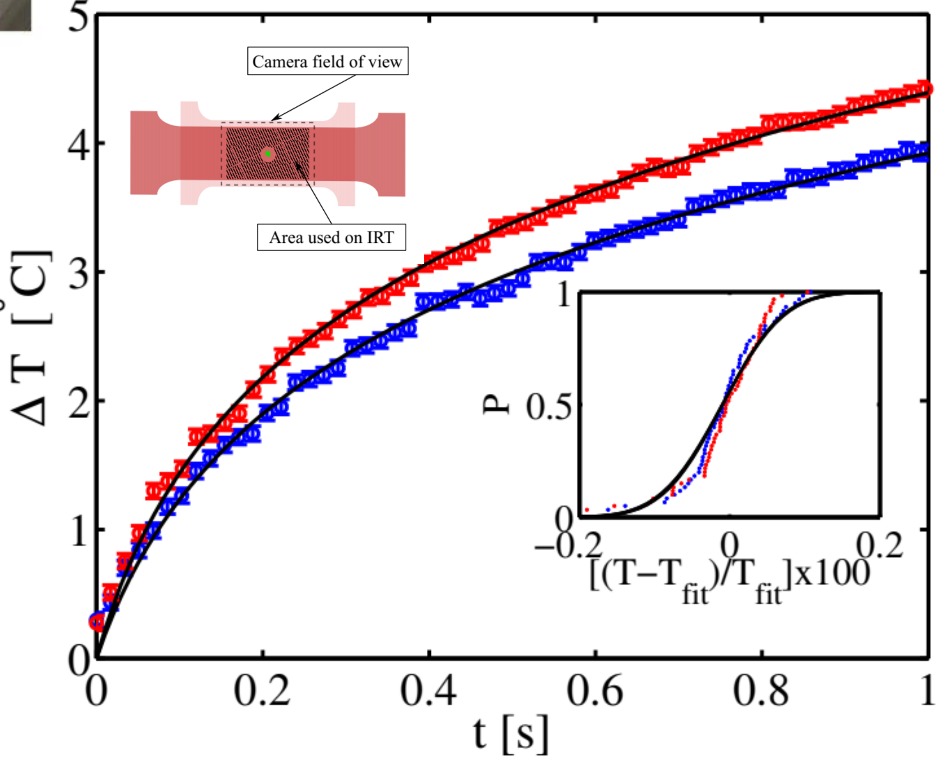
Crnjar et al. Phys. Rev. Mat. 2018

Experiments: Transient Infrared Thermography



$$\theta(0,0,t^*) = \frac{\langle T\rangle(0,0,t)-T_0}{KI_0w^2/k_{\mathrm{eq}}} = \frac{1}{\sqrt{c}}\ln\left[\frac{2\sqrt{c\mathcal{R}}+2ct/\tau_{\mathrm{D}}+b}{2\sqrt{ca}+b}\right]$$

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



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

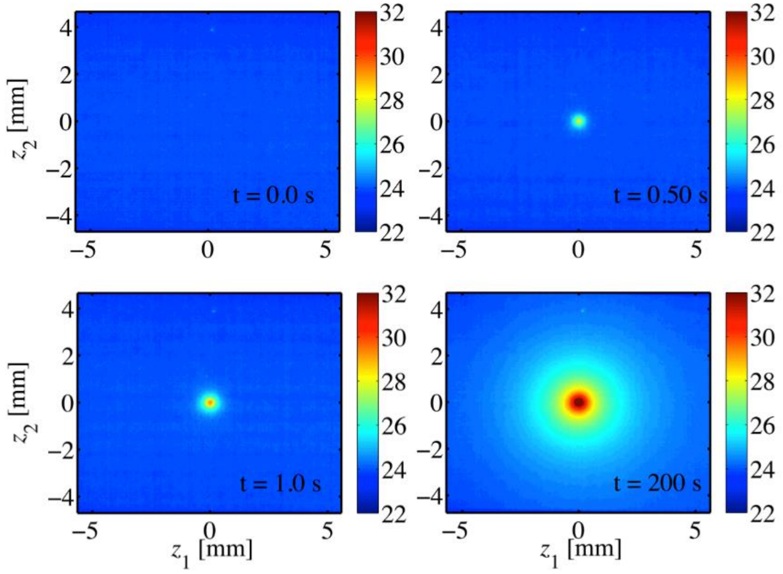
where $\tau_{\mathrm{D}} = w^2\rho\hat{c}_\lambda/k_{\mathrm{eq}}$

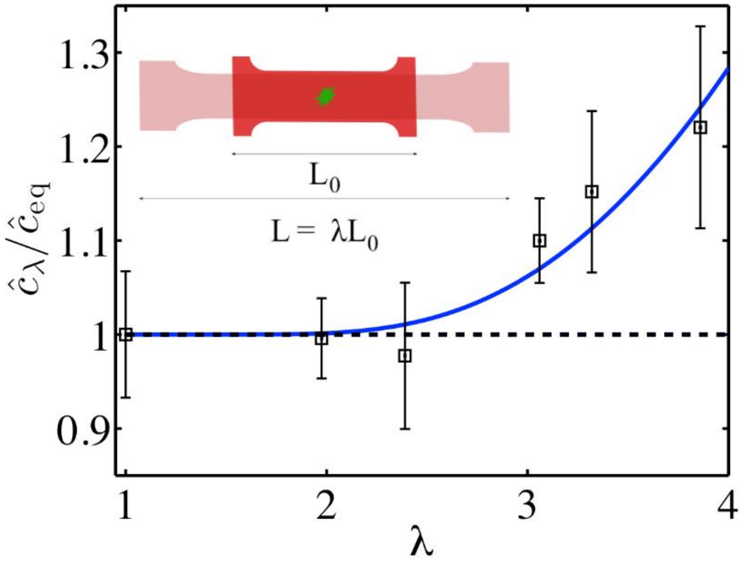
λ	C_θ [K]	τ_{D} [s]
○ 1.00	13 ±0.2	1.60 ± 0.07
○ 3.06	12 ±0.2	1.77 ± 0.07

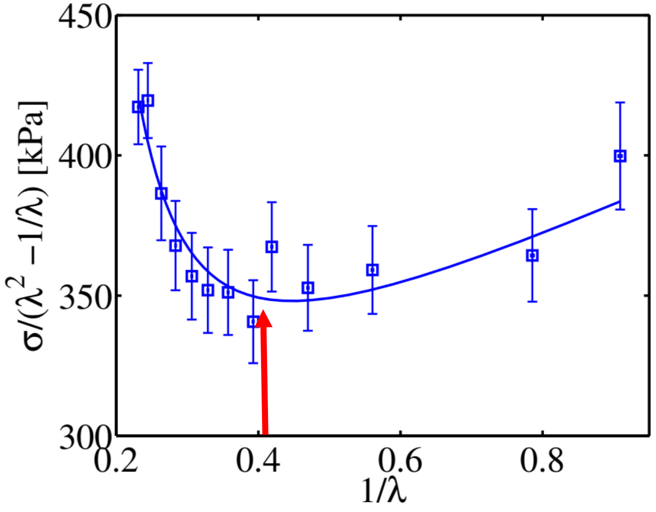
$$\frac{\tau_{\mathrm{D}}(\lambda)}{\tau_{\mathrm{D}}(1)} = \frac{\hat{c}_\lambda}{\hat{c}^0_\lambda}$$

Nieto Simavilla et al. Macromolecules 2018

Experiments: Transient Infrared Thermography



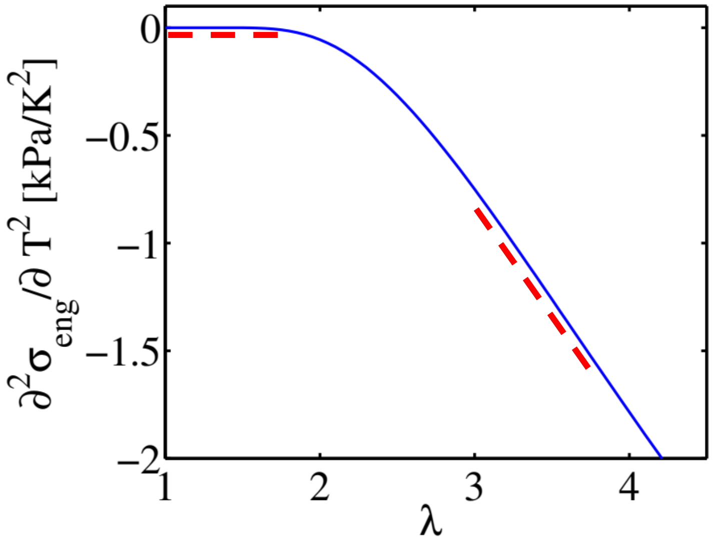




$$\rho\hat{c}_\lambda = \rho\hat{c}_{\mathrm{eq}} - T\int_1^\lambda \left(\frac{\partial^2\sigma_{\mathrm{eng}}}{\partial T^2}\right)_{\lambda'} d\lambda'.$$

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

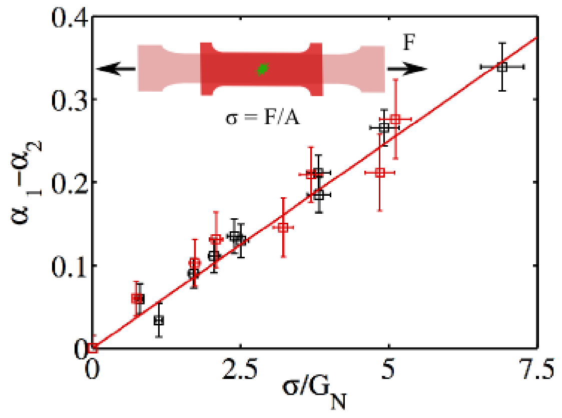
Not Purely Entropic Elasticity -> internal energy contribution to stress is required

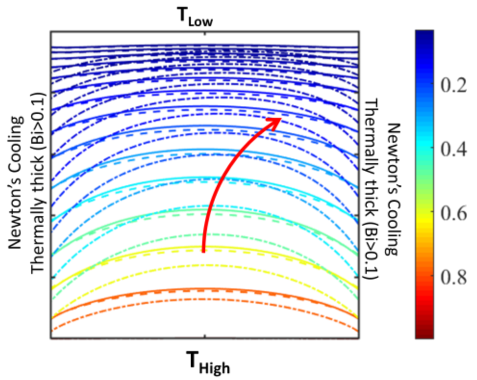


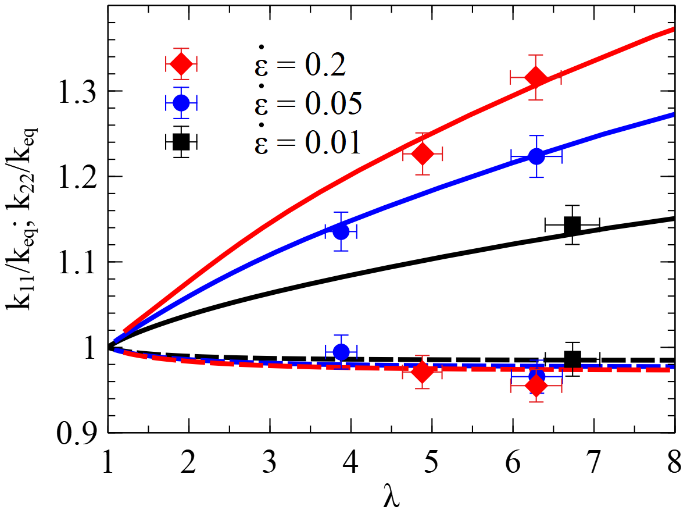
Nieto Simavilla et al. Macromolecules 2018

Conclusions

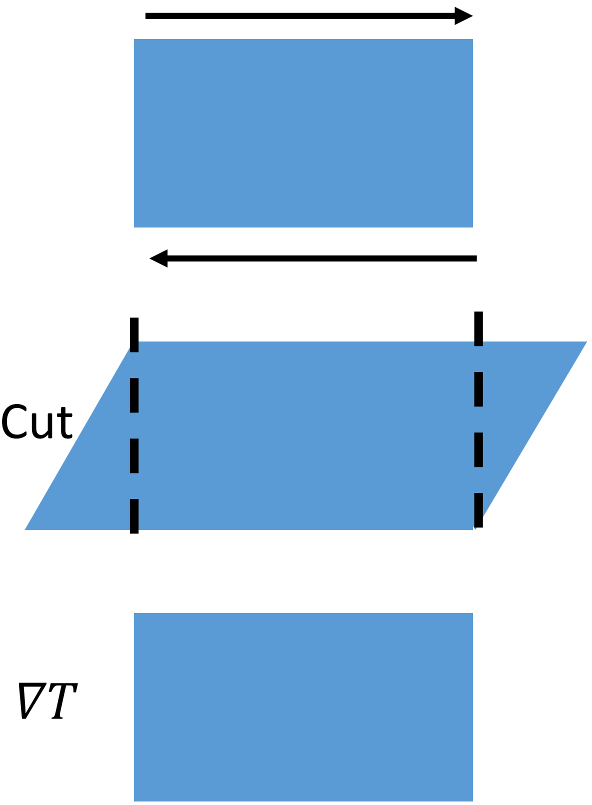
1. Thermal transport becomes anisotropic in polymers subjected to deformation
2. Flow induced anisotropy has significant implications in polymer processing
3. Experimental evidence of:
    - Proportionality to Stress: Stress-Thermal Rule (STR)
    - Universality
    - Beyond Finite Extensibility
4. We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







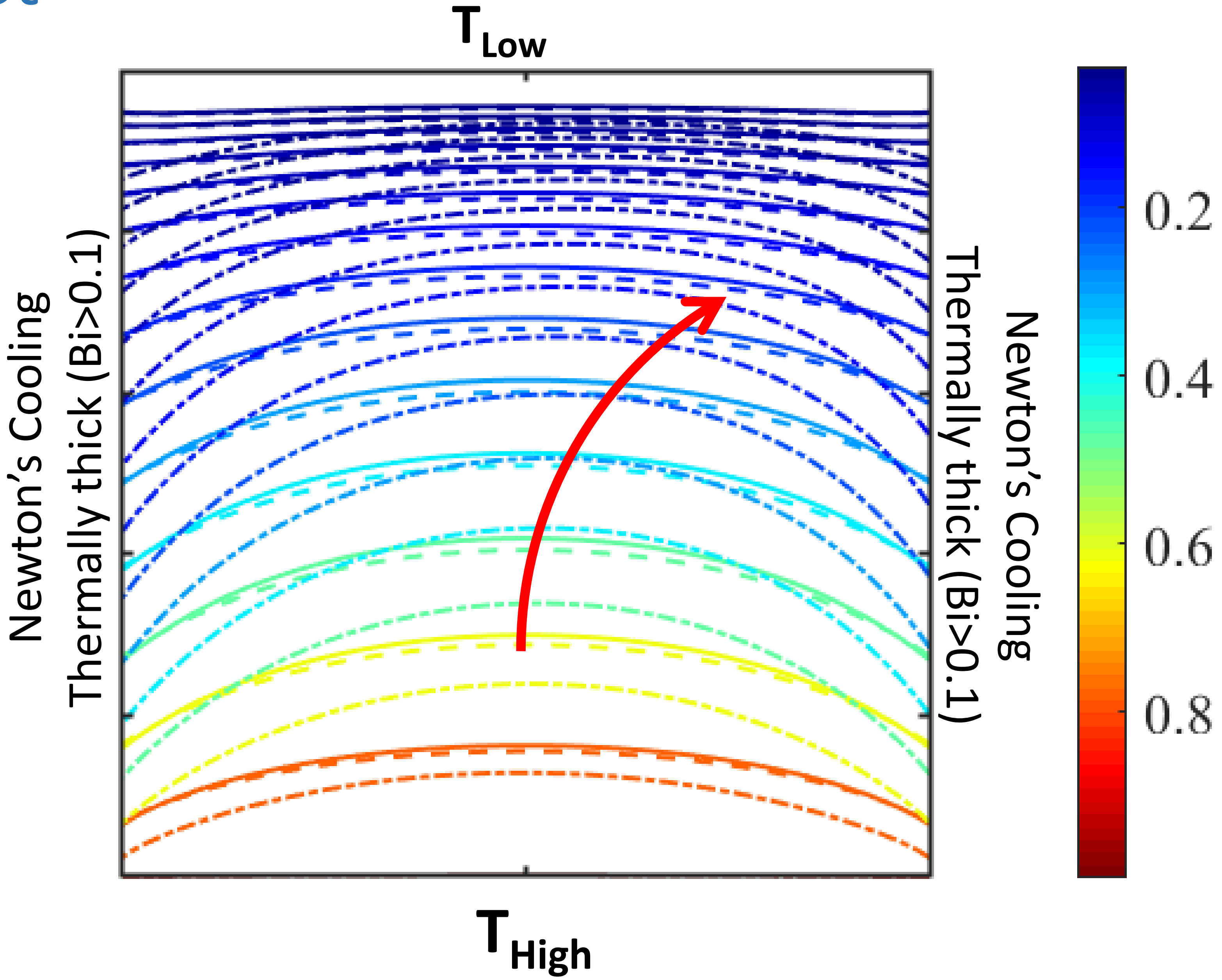
Thermal Hall Effect



1. Shear

2. Quench & Cut

3. Subject to ∇T



α_{11}=1.00, α_{22}=1.00, α_{12}=0.00

α_{11}=1.20, α_{22}=0.95, α_{12}=0.00

α_{11}=1.20, α_{22}=0.95, α_{12}=0.25

Thank you!

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

UNIVERSIDAD
DE BURGOS

MARIE CURIE **ACTIONS**

HORIZON 2020