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:

- Macroscopic network models
- Experimental results
- Molecular-based modelling
- Molecular-macroscopic coupling
- Non-homogeneous non-isothermal viscoelastic flow simulation tool

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

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

Balance Equations:

Mass: \[ \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \]

Momentum: \[ \frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{\tau}) \]

Internal Energy: \[ \frac{\partial \rho \hat{u}}{\partial t} = -\nabla \cdot (\rho \hat{u} \mathbf{v} + \mathbf{q}) - \mathbf{\tau} : \nabla \mathbf{v} \]

Constitutive equations:

\[ \mathbf{q} = -k \nabla T \]
\[ \hat{c}_v = \hat{c}_v(T) \]
\[ \mathbf{\tau} = \eta(T) [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \]

- High stresses & Low thermal conductivity.

Mechanical behavior and flow \[ \Leftrightarrow \] Thermal properties
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Anisotropic Thermal Conduction

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

\[ q = -k \cdot \nabla T \]

\( k \) 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:**

\[ k \propto \left\langle RR \right\rangle + \tau \propto \left\langle RR \right\rangle \]

\[ k - \frac{1}{3} \text{tr}(k)\delta = k_{eq}C_t \left[ \tau - \frac{1}{3} \text{tr}(\tau)\delta \right] \]

The Stress-Thermal Rule


Experiments: Forced Rayleigh Scattering (FRS)

Intensity/Voltage at the photodetector:

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

\[ \frac{1}{\tau_g} = D_{th} \frac{4\pi^2}{\Lambda^2} \quad D_{th} = \frac{k}{\rho c_p} \]

Experiments: Infrared Thermography (IRT)

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

\[ K I_0 w^2 / k_{eq}, \quad \text{Bi} = h d / k_{eq} \]

\[ \alpha_1 = k_{11} / k_{eq}, \quad \alpha_2 = k_{22} / k_{eq} \]

Comparison FRS and IRT

Key Findings: Universality...

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

\[ C_tG_N \sim 0.04 \]

Stress-thermal Rule:
\[ k - \frac{1}{3} \text{tr}(k)\delta = k_{eq} C_t(\tau - \frac{1}{3} \text{tr}(\tau)\delta) \]

Stress-optic Rule:
\[ n - \frac{1}{3} \text{tr}(n)\delta = C(\tau - \frac{1}{3} \text{tr}(\tau)\delta) \]

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(3) Gupta et al. Journal of Rheology 57 (2013)
The Stress-Thermal Rule can be applied:
1. Universally (just by knowing stress and $G_N$)
2. Beyond the onset of finite extensibility

Key Findings: ...Beyond Finite Extensibility

The STR stays valid where the SOR fails!

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

- Thermal conductivity method:
  - EMD: Green-Kubo
    \[ k_{ij} = \frac{1}{k_B V T^2} \int_0^\infty \langle J_i(t)J_j(0) \rangle dt \]
  - 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
    \[
    k_{ij} = \frac{1}{k_B VT^2} \int_0^\infty \langle J_i(t) J_j(0) \rangle \, dt
    \]

- 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.

**k Measurement methods:**
- EMD: Green-Kubo

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

![Graph showing stress vs. stretch ratio for different conditions](image1.png)

![Graph showing (k_{11} - k_{22})/k_{eq} vs. σ/G_N for different conditions](image2.png)
The MCIATTP project: Roadmap

- Macroscopic network models
- Experimental results
- Molecular-based modelling
- eXtended Pom-Pom
- 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?

\[ \nabla \tau + \lambda(\tau)^{-1} \cdot \tau - 2G_0 D_u = 0 \]
\[ \lambda(\tau)^{-1} = \frac{1}{\lambda_{0b}} \left[ \frac{\alpha}{G_0} \tau + f(\tau)^{-1} I + G_0 (f(\tau)^{-1} - 1) \tau^{-1} \right] \]
\[ \frac{1}{\lambda_{0b}} f(\tau)^{-1} = \frac{2}{\lambda_s} (1 - \frac{1}{\Lambda}) + \frac{1}{\lambda_{0b}} \left( \frac{1}{\Lambda^2} - \frac{\alpha I_{\tau,\tau}}{3G_0^2 \Lambda^2} \right) \]
\[ \alpha \neq 0 \rightarrow \psi_2 \neq 0 \]
\[ \Lambda = \sqrt{1 + \frac{I_{\tau}}{3G_0}} \]
\[ \lambda_s = \lambda_{0s} e^{-\frac{2}{q} (\Lambda - 1)} \]

- 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 170°C
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%.
Constitutive Model: Rolie Poly

- Rolie Poly Model: ROuse LInear Entangled POLYmers

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

Predictions

Data: Venerus et al. JOR 1999

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

Graham et al. JOR 2003
Likhtman et al. JNNFM 2003
Comparison to UE experiments: PS

\[ \kappa - \frac{1}{3} \text{tr}(\kappa) \delta = \kappa_{eq} \mathcal{C}_t \left[ \tau - \frac{1}{3} \text{tr}(\tau) \delta \right] \]

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

Predictions

\[ k - \frac{1}{3} \text{tr}(k) \delta = k_{eq} C_t \left[ \tau - \frac{1}{3} \text{tr}(\tau) \delta \right] \]

Effect of the non-zero $k_{12}$

1. Shear

2. Quench & Cut

3. Subject to $\nabla T$

$\alpha_{11} = 1.00$, $\alpha_{22} = 1.00$, $\alpha_{12} = 0.00$

$\alpha_{11} = 1.20$, $\alpha_{22} = 0.95$, $\alpha_{12} = 0.00$

$\alpha_{11} = 1.20$, $\alpha_{22} = 0.95$, $\alpha_{12} = 0.25$
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

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

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

\[
R = 1 + 8(\alpha_1 + \alpha_2)t/\tau_D + 64\alpha_1\alpha_2(t/\tau_D)^2
\]

where \( \tau_D = w^2\rho c_\lambda/k_{eq} \)

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( C_\theta ) [K]</th>
<th>( \tau_D ) [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>13 ± 0.2</td>
<td>1.60 ± 0.07</td>
</tr>
<tr>
<td>3.06</td>
<td>12 ± 0.2</td>
<td>1.77 ± 0.07</td>
</tr>
</tbody>
</table>

\[
\frac{\tau_D(\lambda)}{\tau_D(1)} = \frac{c_\lambda}{c_\lambda^0}
\]

Nieto Simavilla et al. Macromolecules 2018
Experiments: Transient Infrared Thermography

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

\[ \sigma_{\text{eng}} = \left( \frac{\partial f}{\partial \lambda} \right)_T = \left( \frac{\partial u}{\partial \lambda} \right)_T - T \left( \frac{\partial s}{\partial \lambda} \right)_T. \]

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

Nieto Simavilla et al. Macromolecules 2018
Thank you!

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