Deformation induced changes in the thermal properties of elastomers: experimental methods, current understanding and application to finite elements methods

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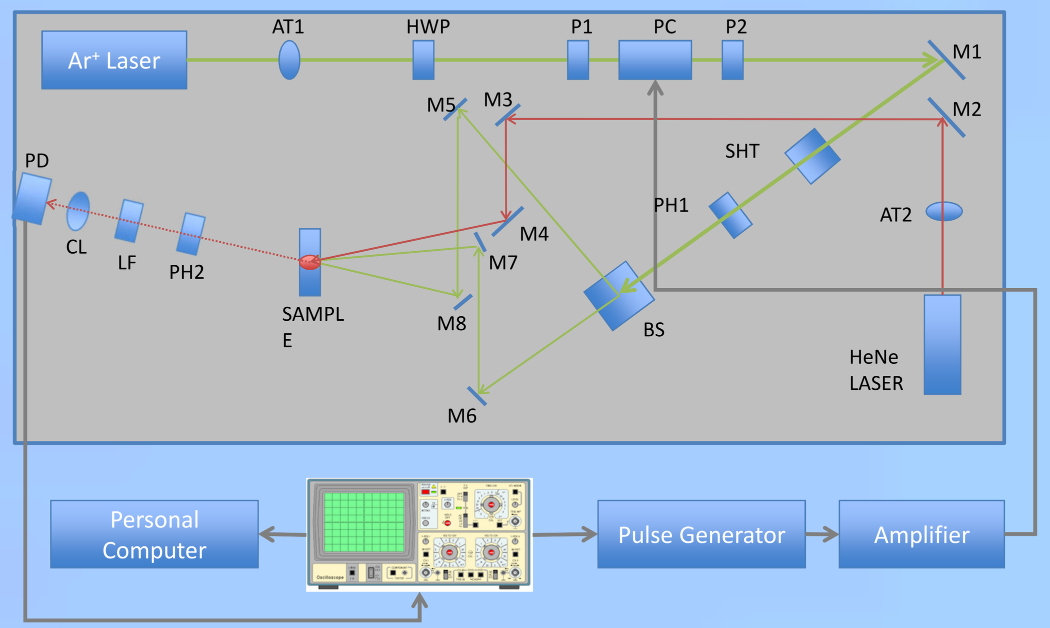
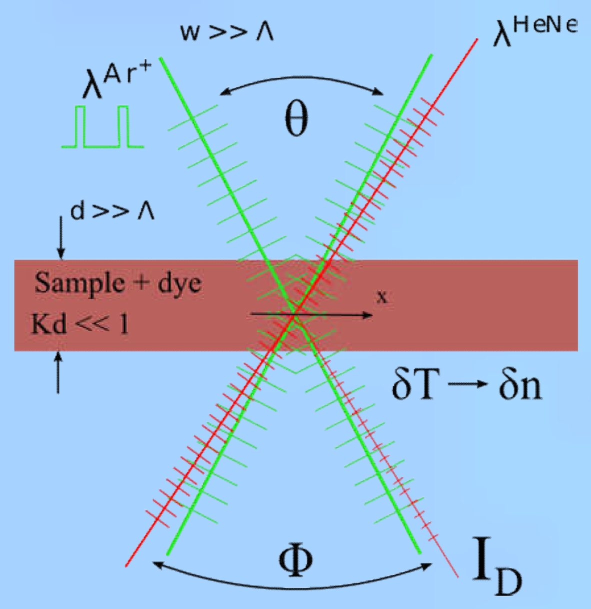
Abstract: Deformation-induced molecular orientation of polymeric materials affects thermo-physical properties, such as thermal conductivity and heat capacity. These properties influence not only the optimization of fabrication processes, but also the performance of polymeric materials during use. We introduce two complementary experimental methods to characterize the anisotropy in thermal conductivity[1,2] and its relationship to stress and deformation in elastomers subjected to uniaxial extension. Surprisingly, we find: 1) universality of a linear relationship between anisotropy in thermal conductivity and stress known as the *stress-thermal rule* and 2) that, in contrast to the analogous *stress-optic rule*, the validity of this rule extends beyond finite extensibility. Additionally, we present a transient Infrared Thermography technique[3] to investigate the dependence of heat capacity on deformation. We find that the heat capacity increases with stretching in lightly cross-linked natural rubber. Using a simple thermodynamic analysis based on classical rubber elasticity, we discuss the implications of our findings for the assumption of *purely entropic elasticity,* and the presence of an energetic contribution to the stress in deformed polymers.

A growing trend in the design of polymer manufacturing processes is the use of FE simulations for the complex and non-isothermal flows involved[4]. However, while there has been a significant amount of work to include more complete rheological constitutive models into these simulations, the implementation of material thermo-physical properties that are connected to the micro-structural orientation remains a challenge. Our work is presented as a stepping-stone for the development of a molecular to continuum methodology for the simulation of industrially relevant flows.

Forced Rayleigh Scattering (FRS)[2]





Grating creation (Writing): Laser interference:

$$I = 2I_0 \cos\left(\frac{2\pi x}{\Lambda}\right) \qquad \Lambda = \frac{\lambda_w}{2\sin(\theta/2)}$$

Dye photochemistry: $\delta T \sim 0.01°C$

$$\delta T = \delta T(t_p)\exp\left(-\frac{t}{\tau_g}\right) \qquad \text{for } t \geq t_p$$

Grating Detection (Reading): $\delta T \to \delta\rho \to \delta n$

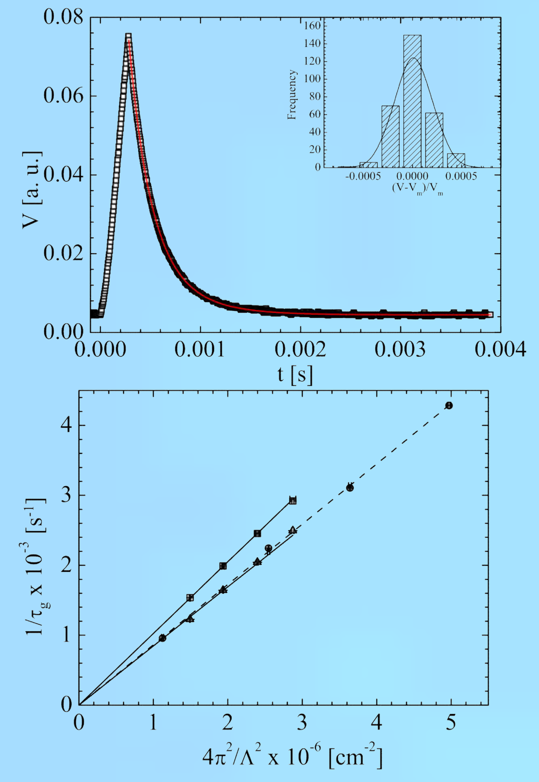
$$\delta n = \frac{\partial n}{\partial T}\Big|_P \delta T \qquad I_D \propto \delta n^2 \propto \delta T^2$$

Intensity/Voltage at the photodetector:

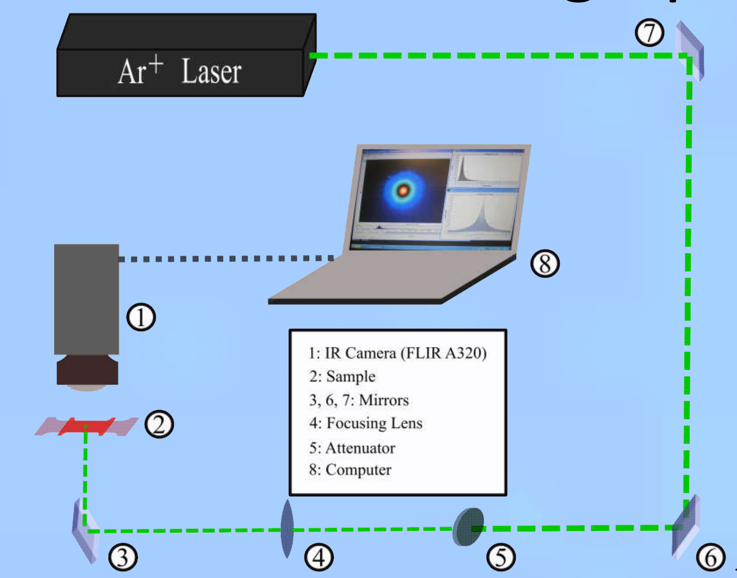
$$V(t) \propto I_D + 2\sqrt{I_C I_D}\cos\psi + I_E + I_C$$

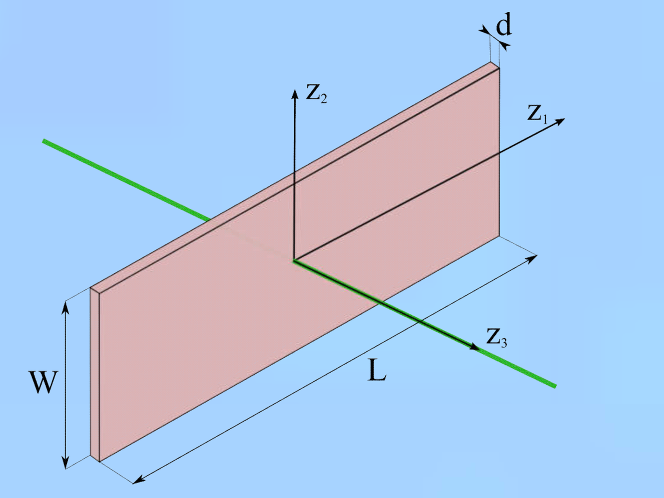
$$V(t) = A\exp\left(-2\frac{t}{\tau_g}\right) + B\exp\left(-\frac{t}{\tau_g}\right) + C$$

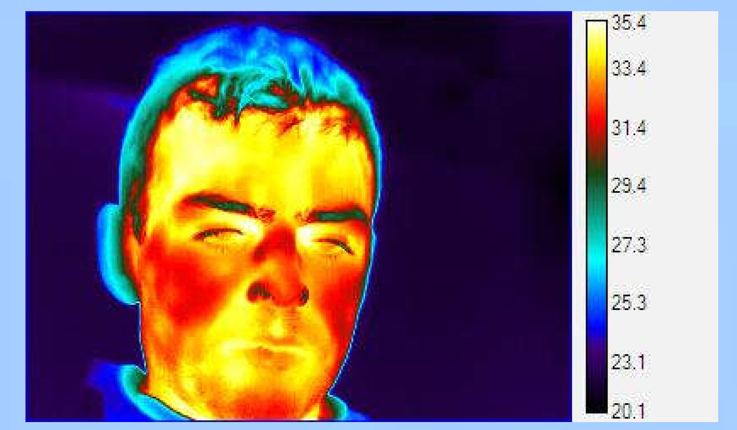
$$\frac{1}{\tau_g} = D_{th}\frac{4\pi^2}{\Lambda^2} \qquad D_{th} = \frac{k}{\rho\hat{C}_P}$$



Infrared Thermography (IRT)[1,3]







Temperature equation:

$$\rho\hat{c}_L\frac{\partial T}{\partial t} = k_{11}\frac{\partial^2 T}{\partial z_1^2} + k_{22}\frac{\partial^2 T}{\partial z_2^2} + k_{33}\frac{\partial^2 T}{\partial z_3^2} + KI_0\exp\left(-2\frac{z_1^2+z_2^2}{w^2}\right)\exp(-Kz_3),$$

Boundary and initial conditions:

$$T(\pm\infty, t) = T_0,$$

$$-k_{22}\frac{\partial T}{\partial z_3}(z_3 = \pm d/2) = \pm h[T(z_3 = \pm d/2) - T_0]$$

$$T(t \leq 0) = T_0.$$

Dimensionless variables:

$$\theta = \frac{\langle T\rangle - T_0}{KI_0 w^2/k_{eq}}, \quad x_i = z_i/L_c, \quad t^* = t/\tau_D,$$

$$\alpha_i = k_{ii}/k_{eq}, \quad \mathrm{Bi} = \frac{hd}{k_{eq}}, \quad \tau_D = w^2/D_{th}^{eq}.$$

Assumptions:

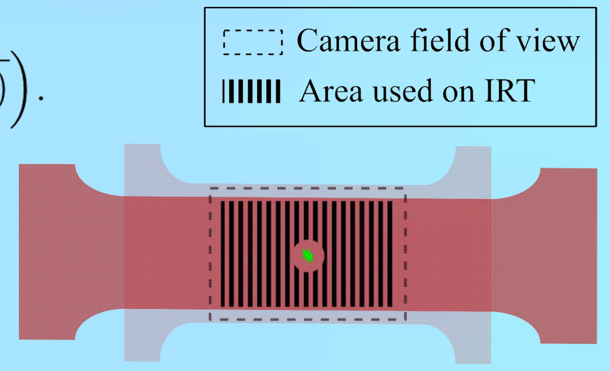
(1) Uniaxial Elongation: $\boldsymbol{k}$ diagonal and $k_{22} = k_{33}$.
(2) Fin approximation.
(3) Gaussian source propagating in the z_3 direction.
(4) Newton's law of cooling on the faces with $\mathrm{Bi} \ll 1$.

Steady-state point source solution:

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

Transient convection-free solution:

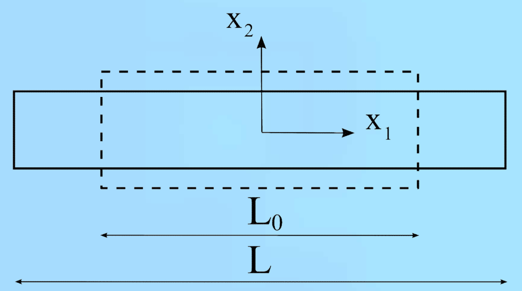
$$\theta(0,0,t^*) = \frac{1}{\sqrt{c}}\ln\left[\frac{2\sqrt{c\mathcal{R}} + 2ct^* + b}{2\sqrt{c} + b}\right]$$



Uniaxial Extension:
Lightly cross-linked elastormers are stretched in one direction and allowed to contract in the other two.

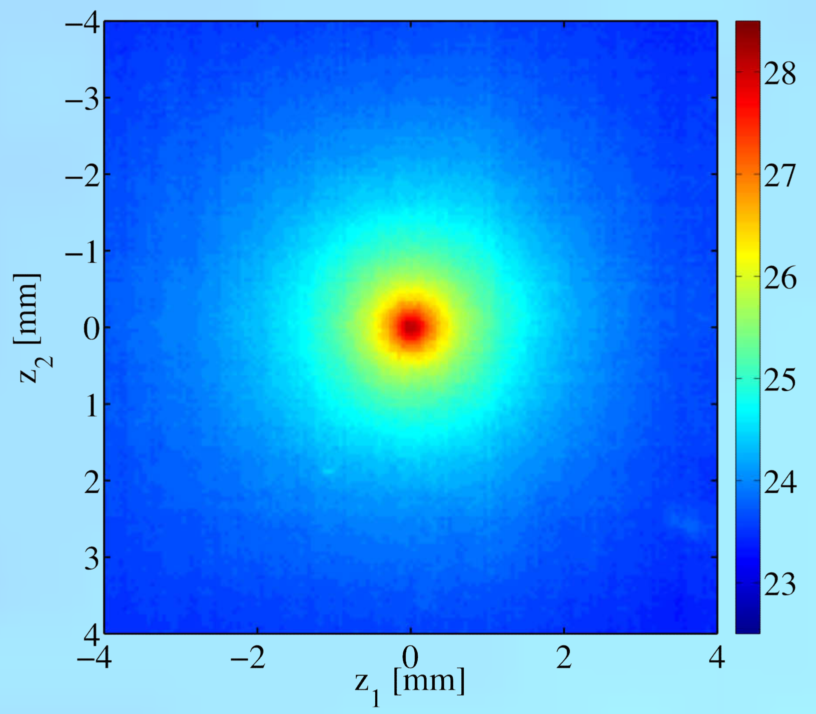
Stretch Ratio: $\lambda = L/L_0$
Tensile Stress: $\sigma = \tau_{11} - \tau_{22} = F/A$
Stress-Thermal Rule:
$\alpha_1 - \alpha_2 = C_t\sigma$

Note: For FRS $\alpha_i = D_{ii}/D_{eq}$

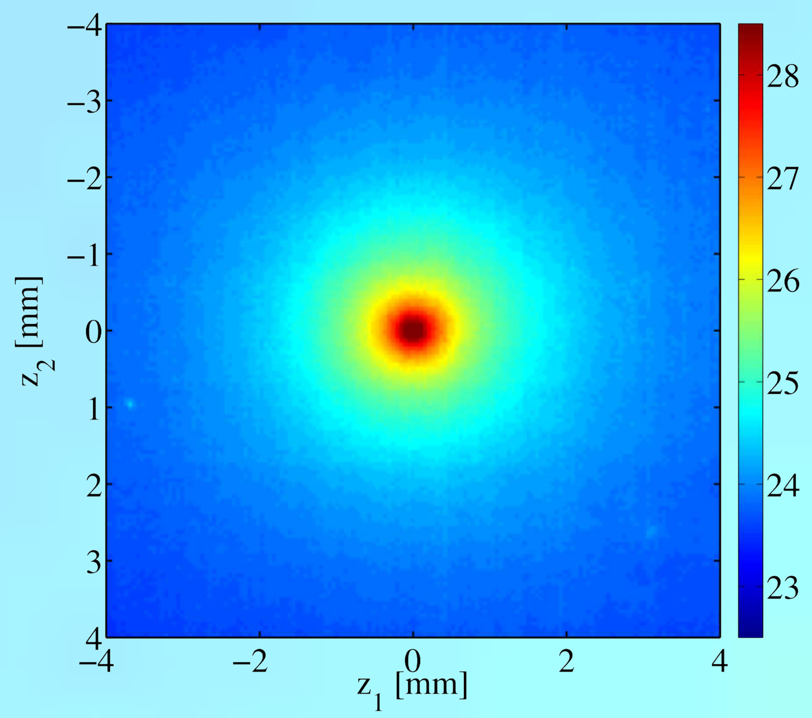


Results and Conclusions

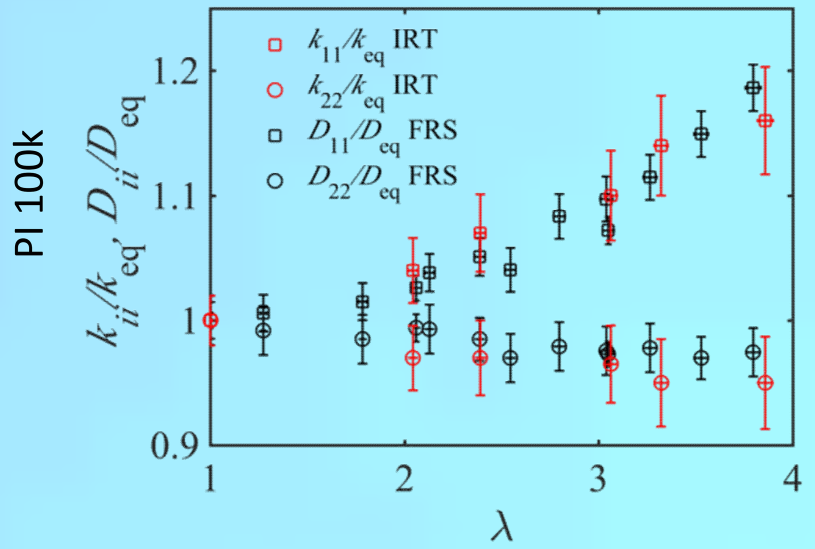
Thermograph Un-stretched sample

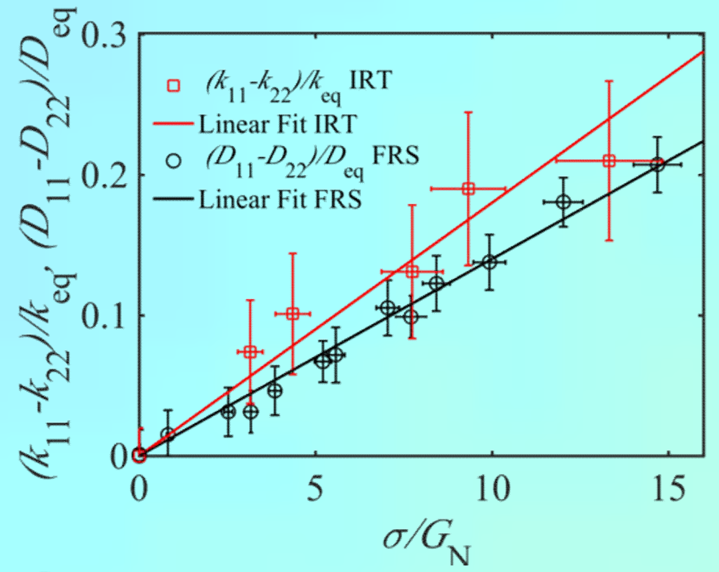


Thermograph Stretched sample



Anisotropic Thermal transport in PBD 200k and PI 100k has been studied with both FRS and IR techniques. The STR has been shown to hold for a wide range of elongations.





Stress-Thermal Rule[5]:
Energy transport along the polymer chains is more efficient than between the chains

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

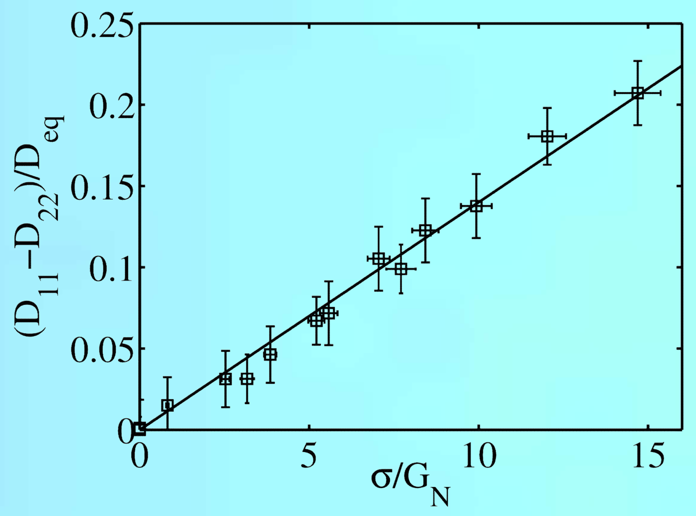
$$\boldsymbol{\tau} - \frac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta} \propto n_i\langle\boldsymbol{RR}\rangle_i$$

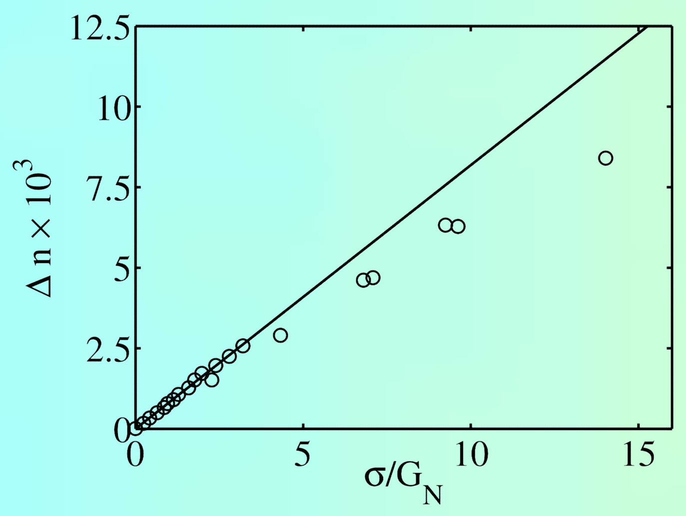
$$\boldsymbol{k} - \frac{1}{3}\mathrm{tr}(\boldsymbol{k})\boldsymbol{\delta} = k_{eq}C_t\left(\boldsymbol{\tau} - \frac{1}{3}\mathrm{tr}(\boldsymbol{\tau})\boldsymbol{\delta}\right)$$

Universality

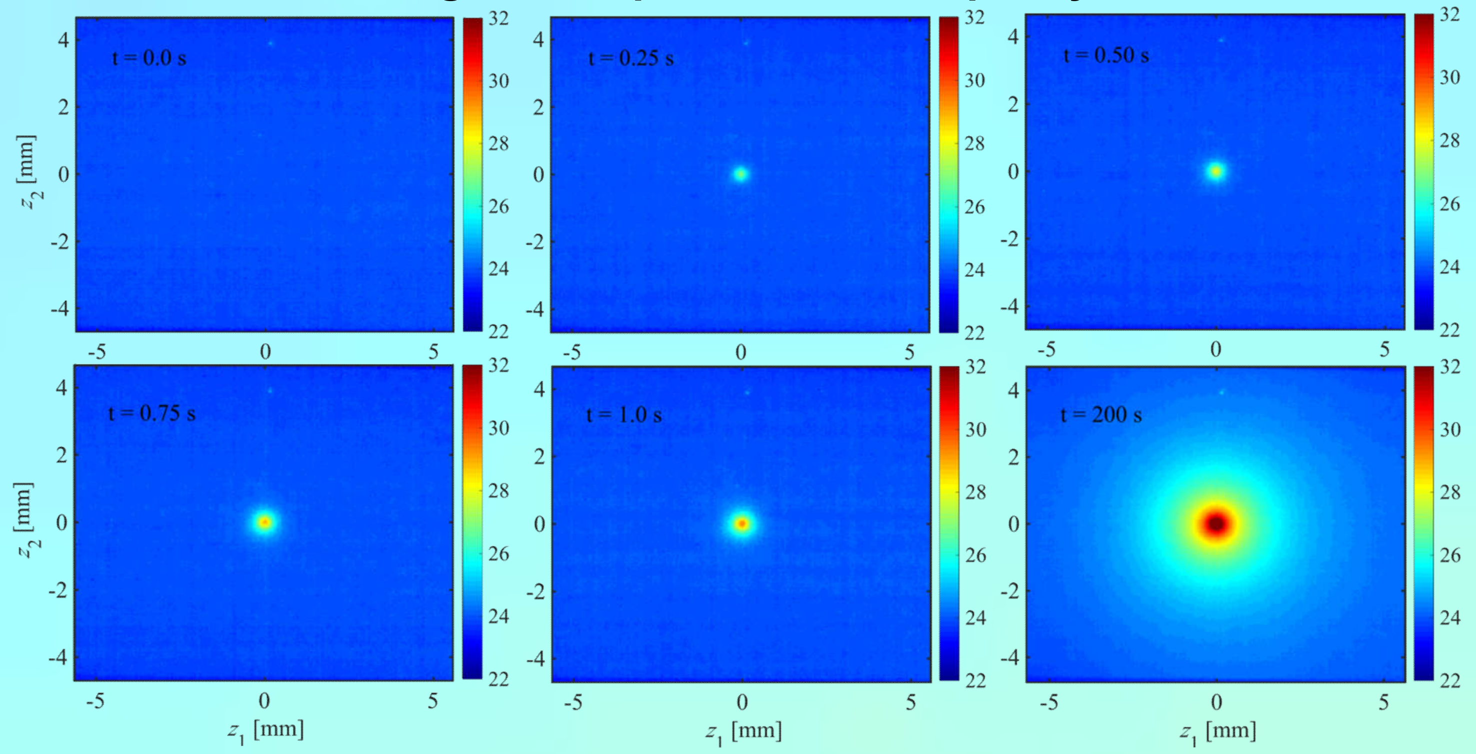
Material	Deformation (kPa)	G_N –	C_t x 10^4 (kPa^{-1})	C_tG_N –	C x 10^6 (kPa^{-1})
PIB 85k	Shear	320 [1]	1.9 ± 0.67	0.061 ± 0.024	1.7
PIB 130k	Shear	320 [1]	1.2 ± 0.67	0.038 ± 0.022	1.7
xl-PDMS	Uniax.	200 [1]	1.3 ± 0.30	0.026 ± 0.008	0.2
xl-PBD 200k	Uniax.	760 [1]	0.73 ± 0.15	0.051 ± 0.011	3.3
xl-PBD 150k	Uniax.	760 [1]	0.93 ± 0.19	0.059 ± 0.014	3.3
xl-PI 100k	Uniax.	370 [2]	0.37 ± 0.10	0.014 ± 0.005	1.9
PS	Uniax.	200 [1]	1.65 ± 0.10	0.033 ± 0.007	-5
PMMA	Uniax.	310 [1]	1.7 ± 0.10	0.054 ± 0.011	0.16

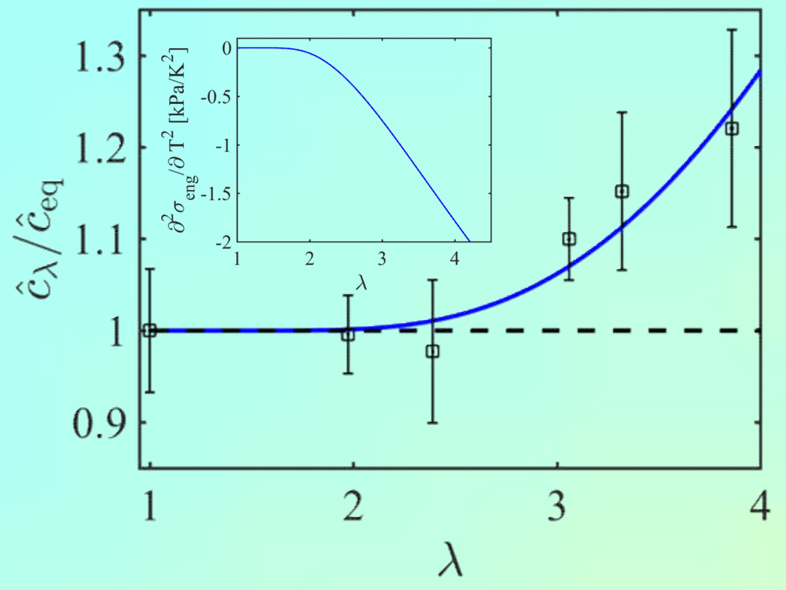
Stress-thermal and stress-optic rules[2]





Transient IRT: Elongation dependent heat capacity[3]





$$\rho\hat{c}_\lambda = T\left(\frac{\partial s}{\partial T}\right)_\lambda = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_\lambda$$

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

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

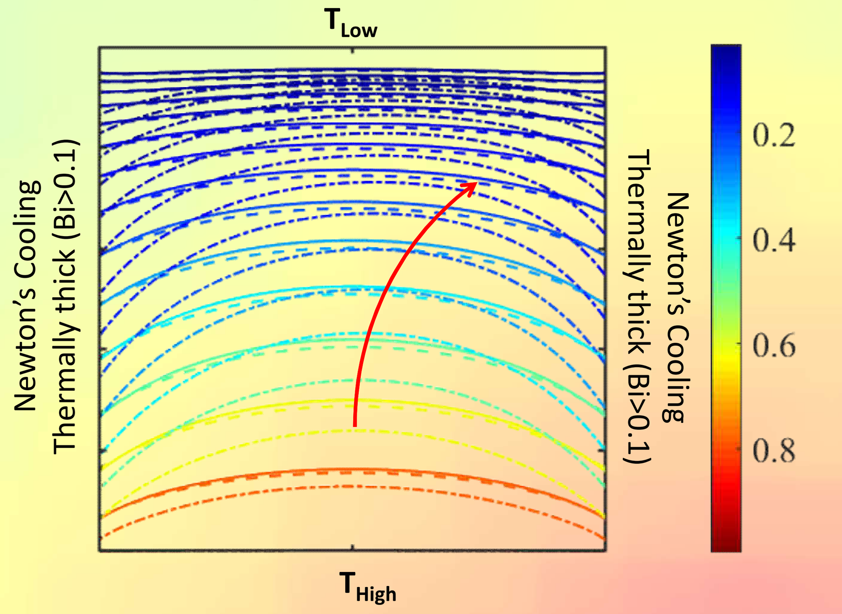
- Scattering experiments show that the increase in heat capacity are not due to strain-induced crystallization.
- The increase in heat capacity is observed at roughly the same strains where finite extensibility is present in the specimens mechanical tests.

Application to FE: Temperature profiles of anisotropic solid (quenched) samples subjected to a simple temperature gradient

The *stress-thermal rule suggests that sheared samples present an off-diagonal term in the thermal conductivity tensor proportional to the shear stress.*

$$k_{11}k_{22} - k_{12}^2 > 0$$

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



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