



SCHOOL of ENGINEERING & APPLIED SCIENCE
UNIVERSITY of VIRGINIA

Tunable thermal transport and reversible thermal conductivity switching in topologically networked bio-inspired materials



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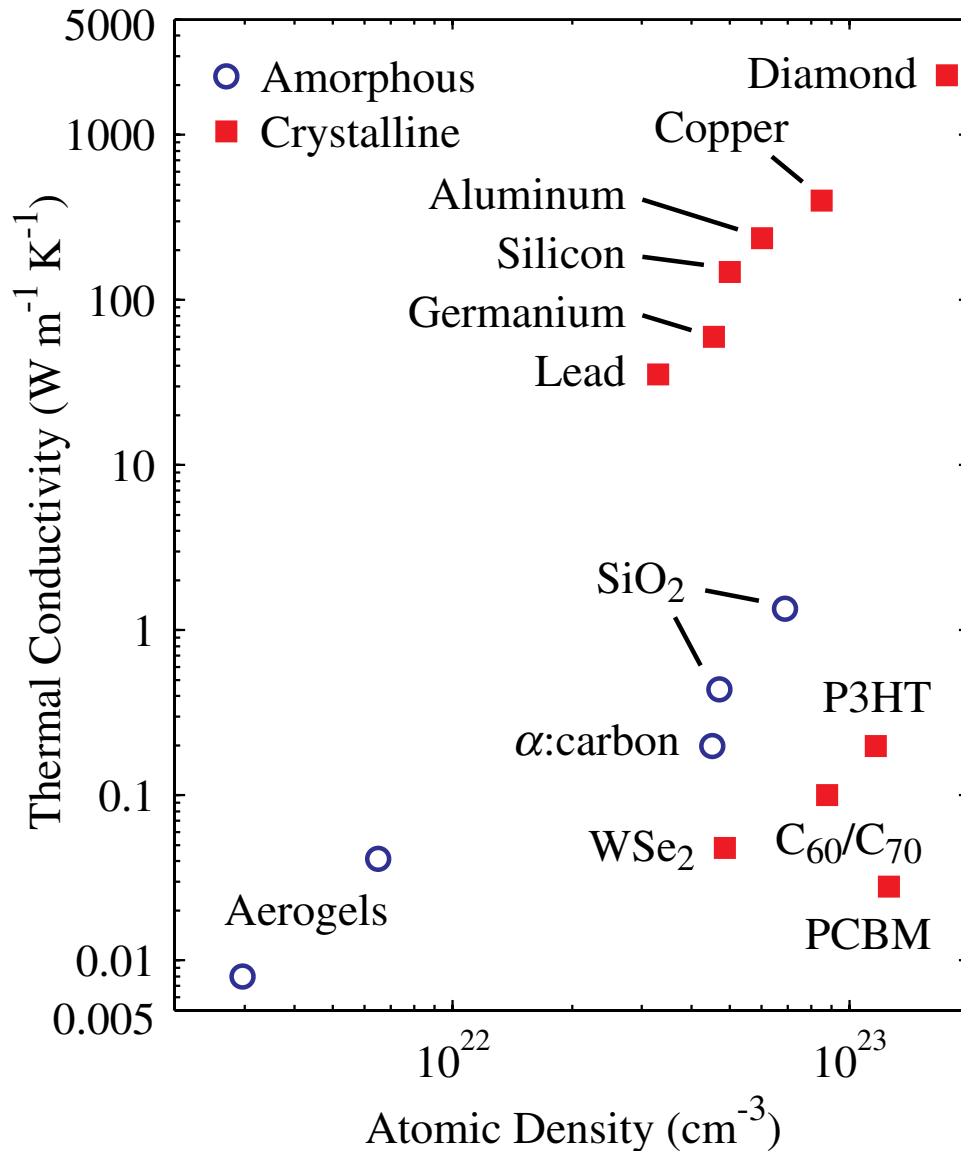
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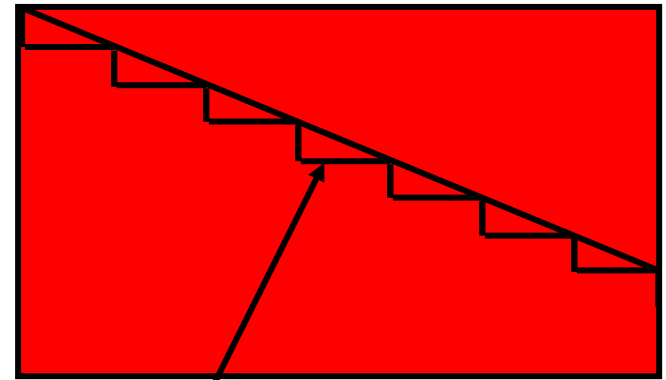
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Thermal conductivity of materials



PRL **110**, 015902 (2013)

Microscopic Picture



$\lambda = \text{Mean free path}$

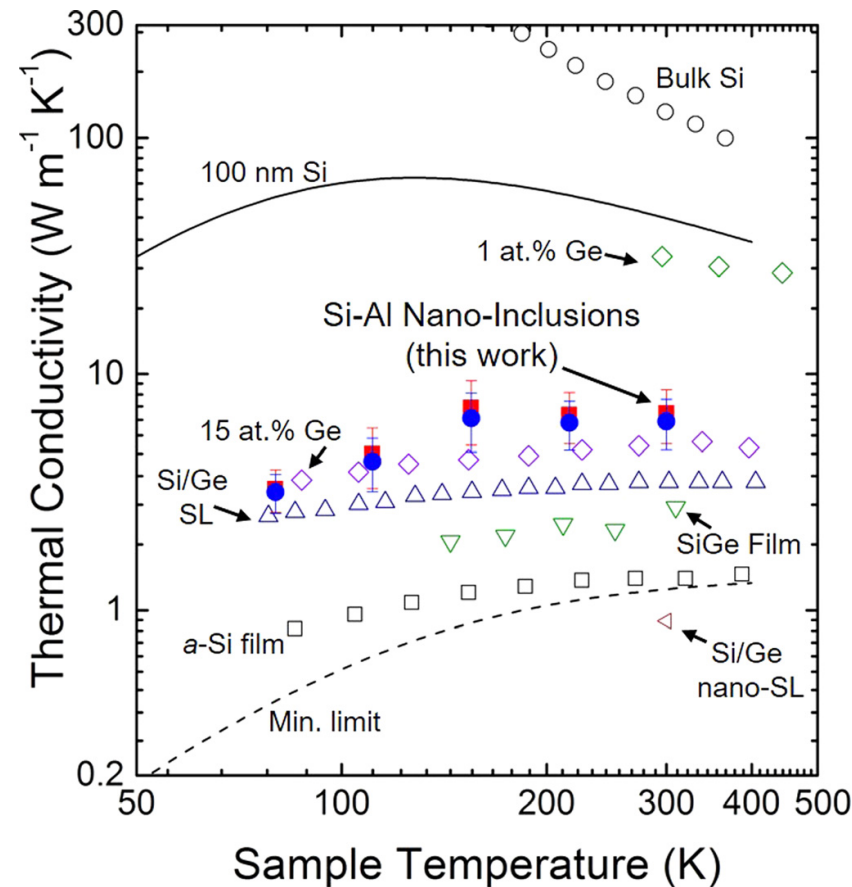
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Heat
capacity

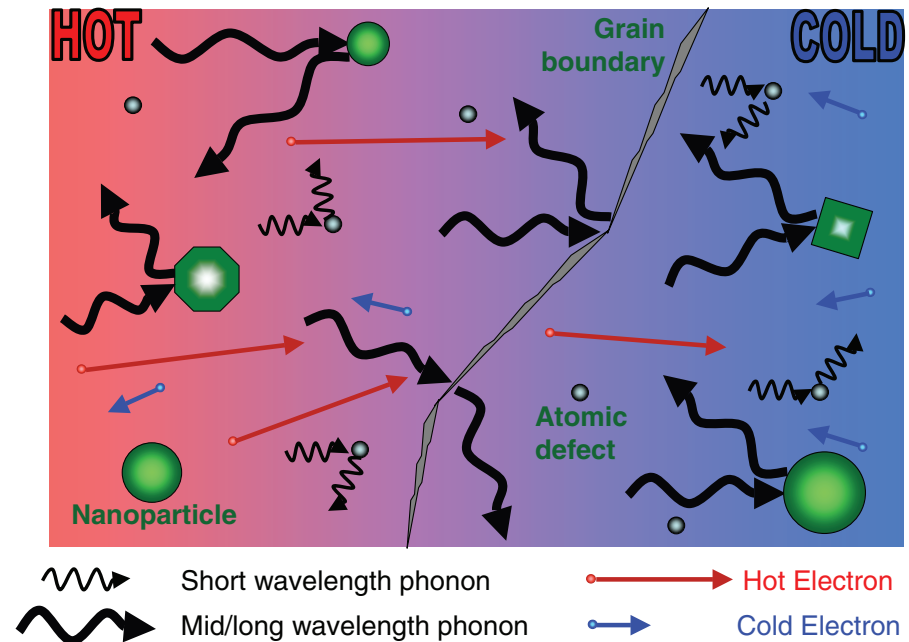
Velocity

Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity



APL **112**, 213103

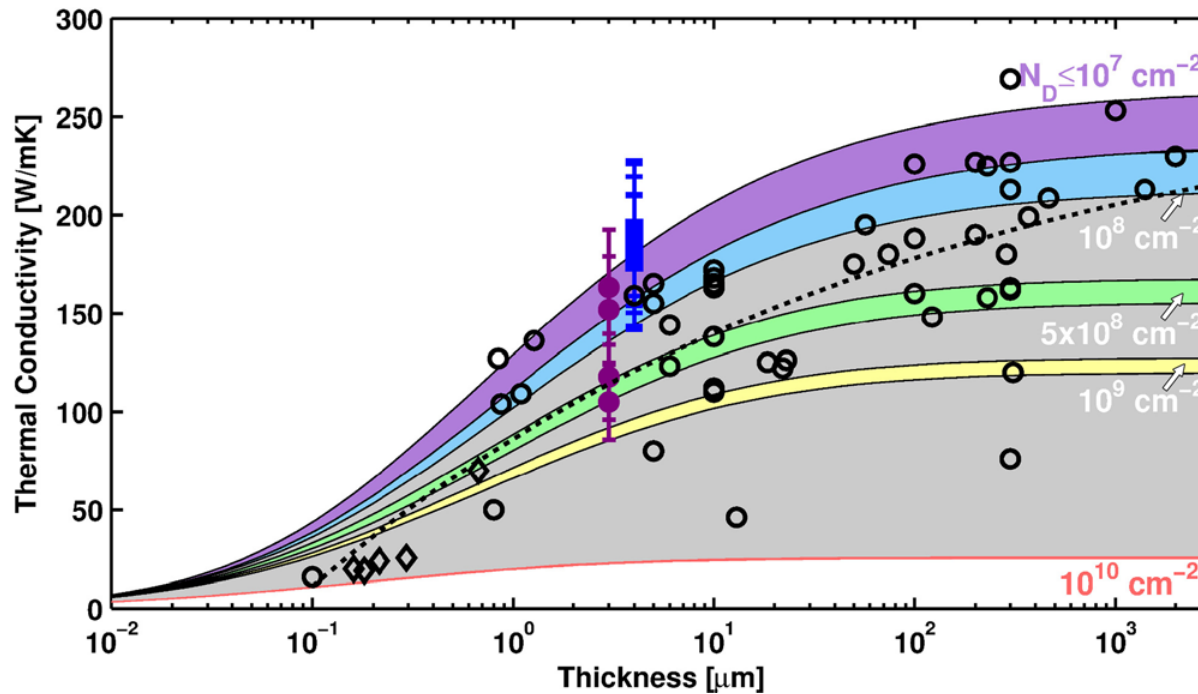


Adv. Mat. **22**, 3970

Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity

Thermal conductivity of GaN films

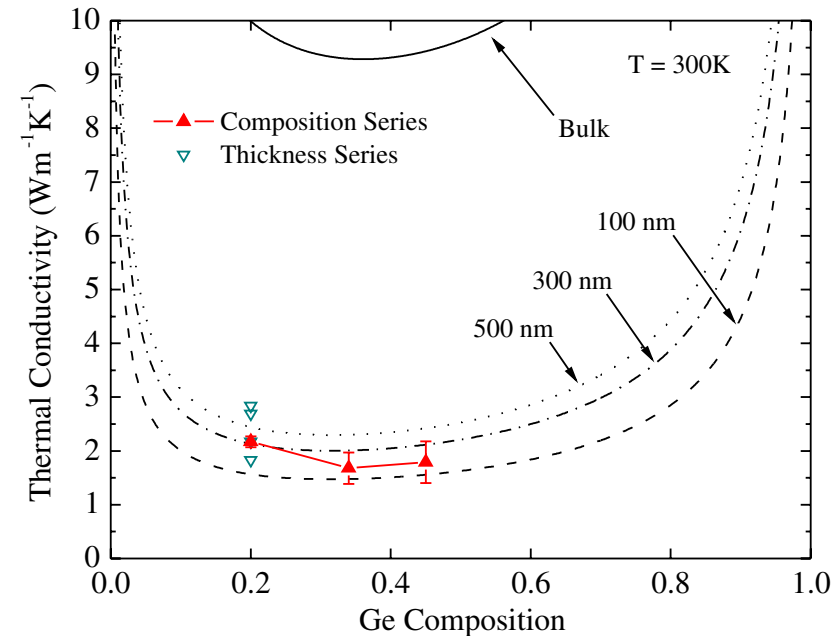


Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity

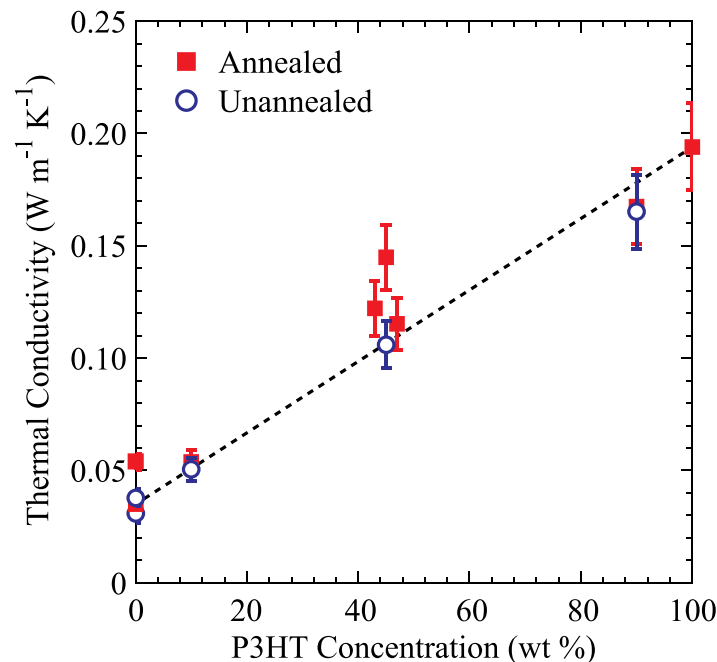
Thermal conductivity of alloy thin films

$\text{Si}_{1-x}\text{Ge}_x$

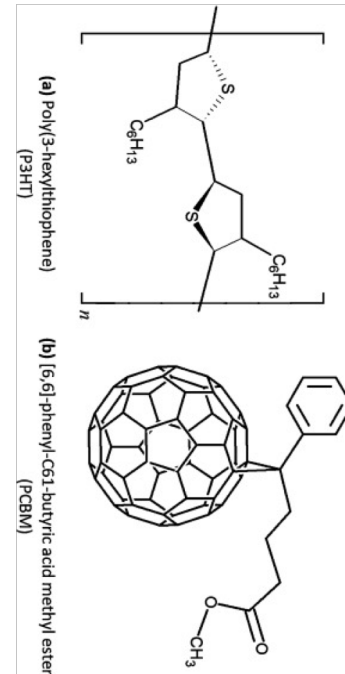


PRL 109, 195901

PCBM/P3HT



APL 102, 251912

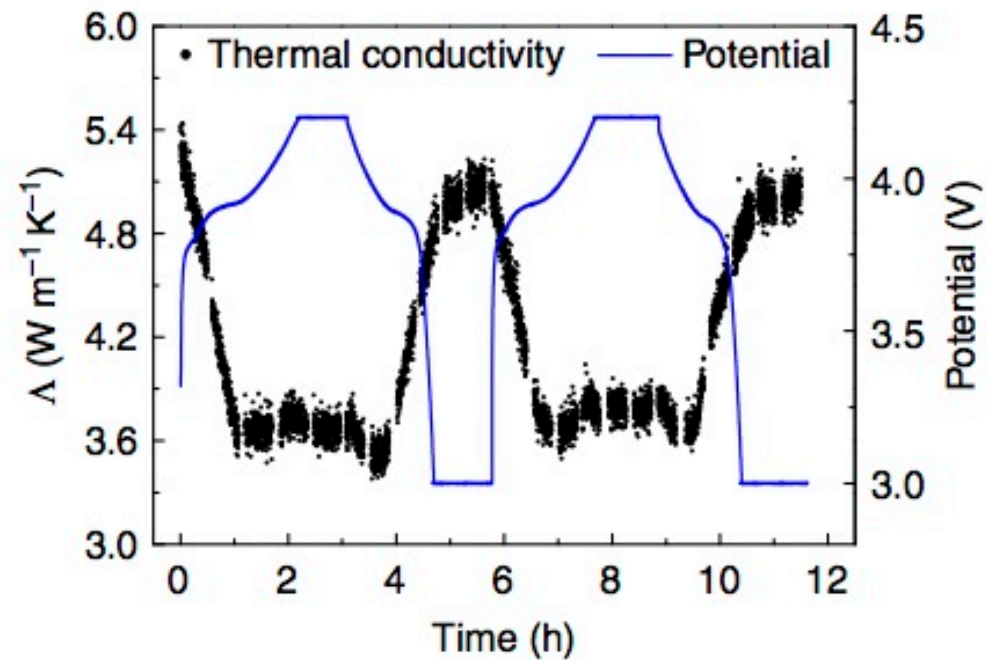
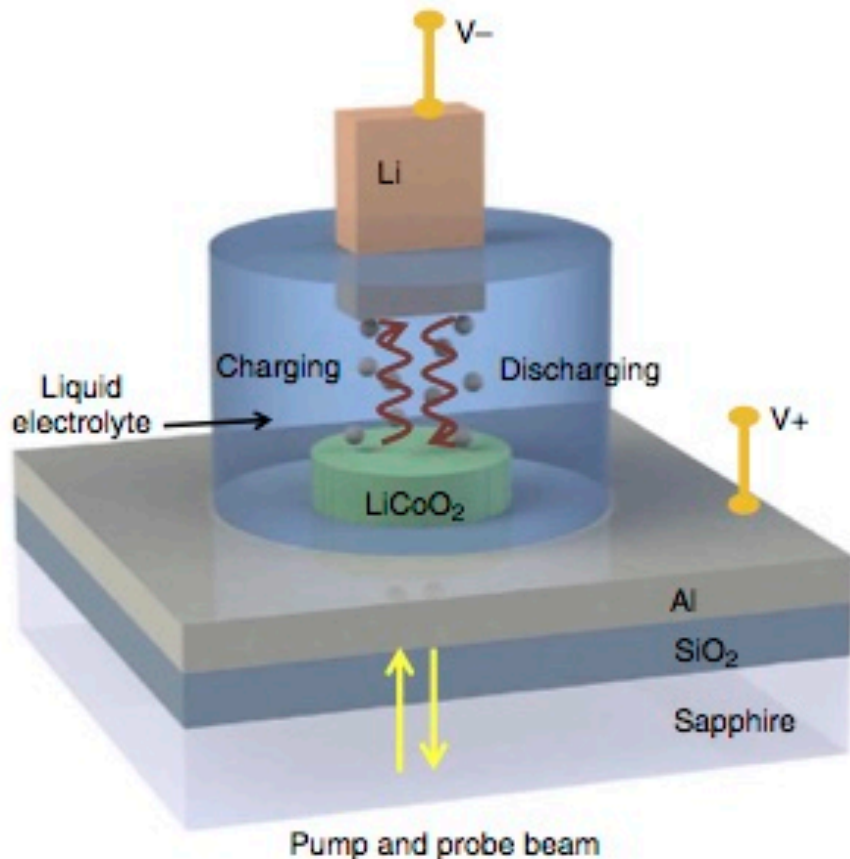


Controlling thermal conductivity - Dynamic

The thermal conductivity switch

Reversibly switching the thermal conductivity of a material via an external stimulus

Defect diffusion, e.g., “de-litiation” of LiCoO_2



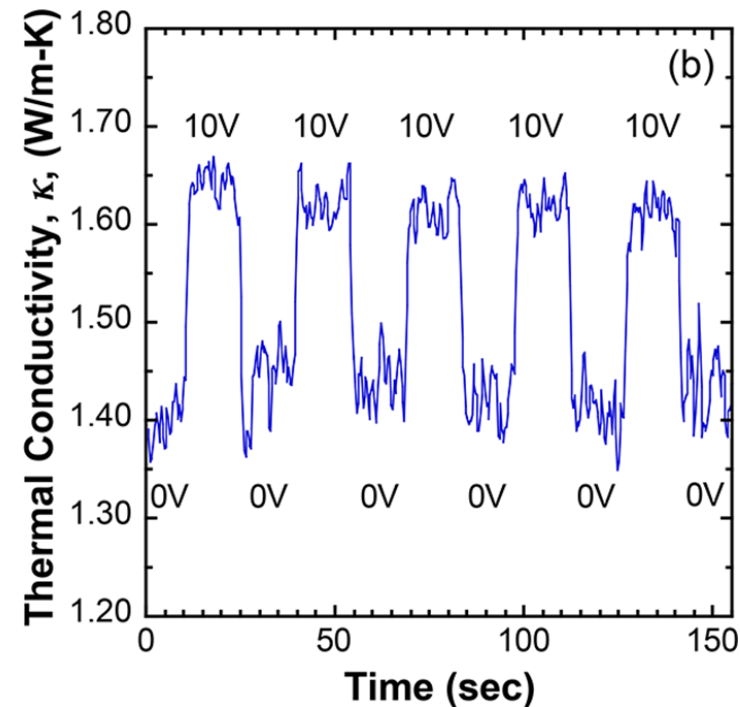
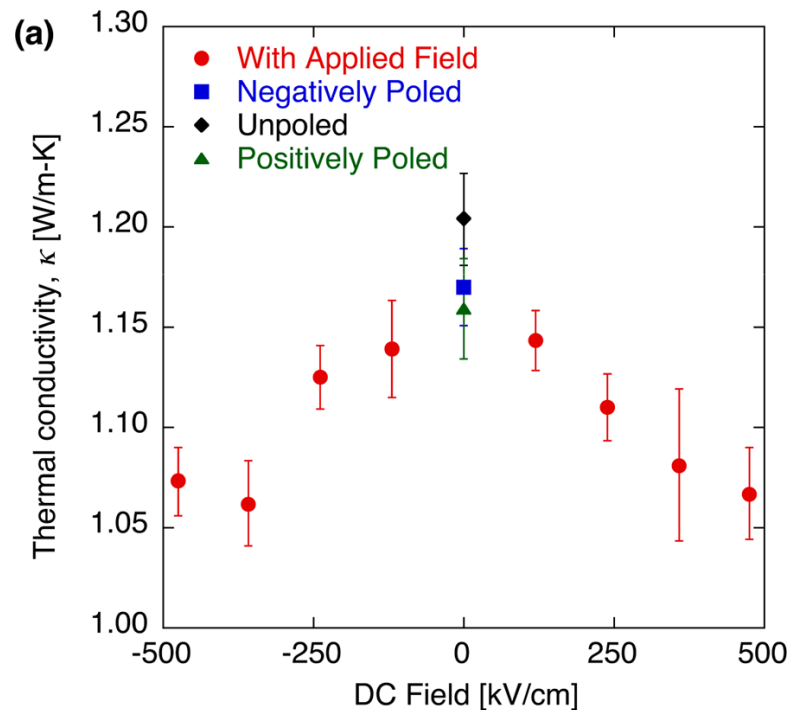
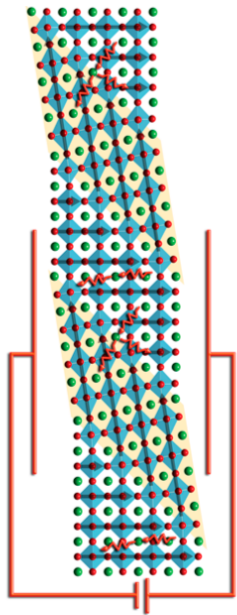
Nat. Comm. **5**, 4035

Controlling thermal conductivity - Dynamic

The thermal conductivity switch

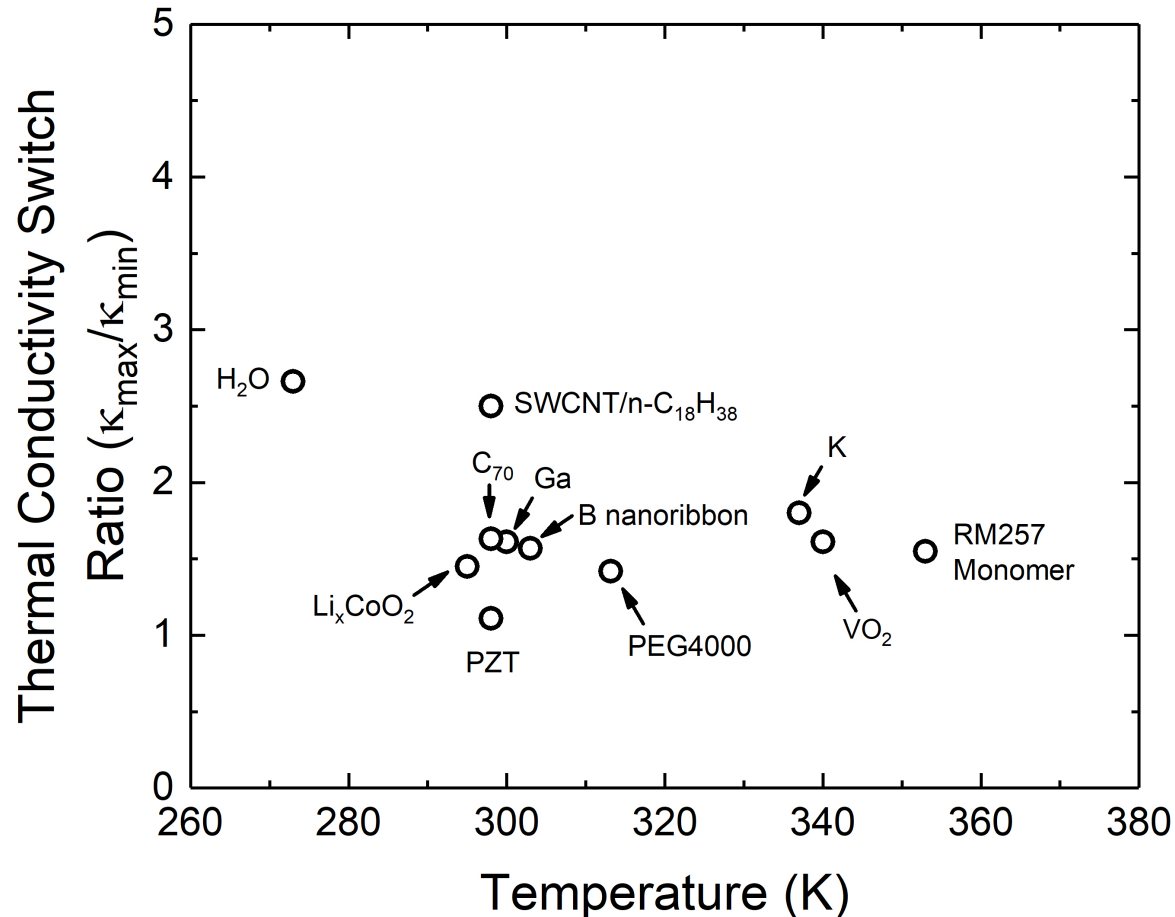
Reversibly switching the thermal conductivity of a material via an external stimulus

Field controlled ferroelastic domain mobility in PZT



The thermal conductivity switch

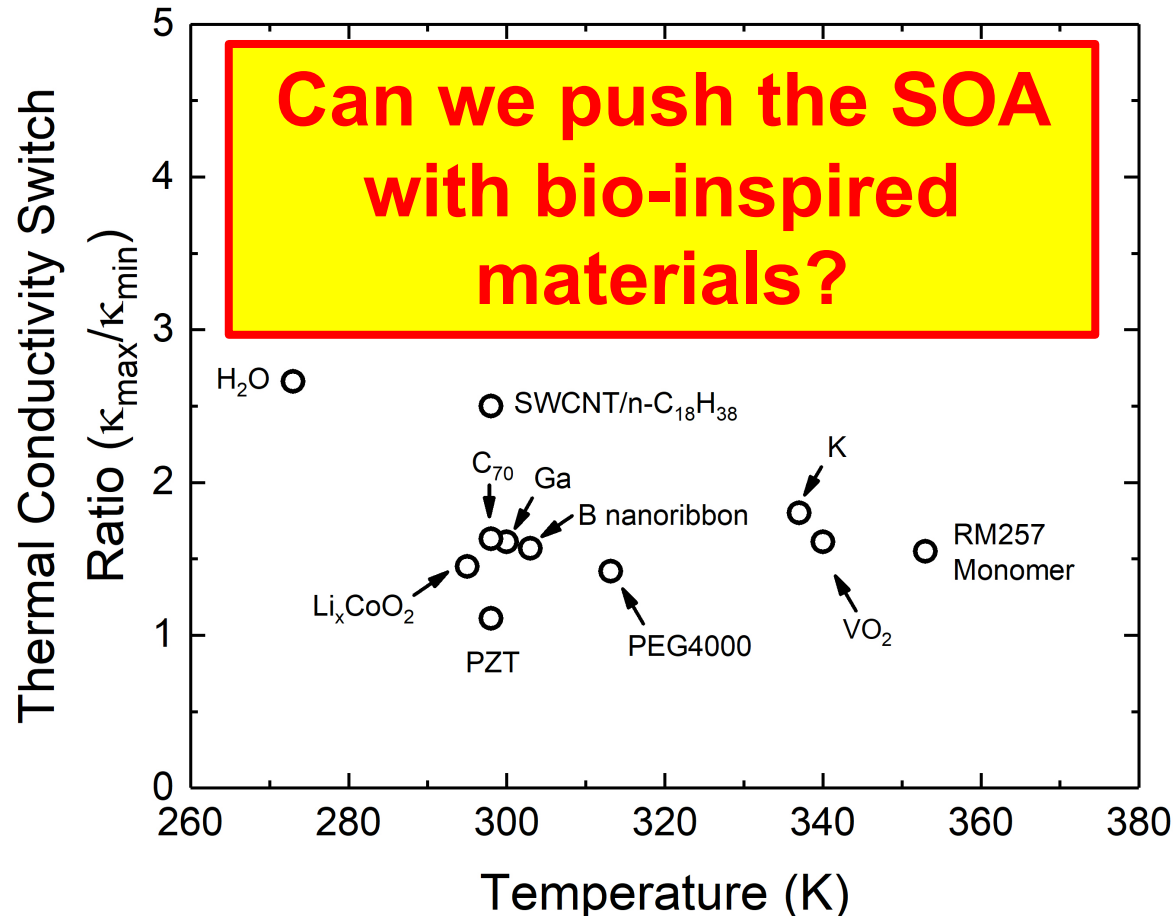
State of the art around biologically relevant temperatures



Controlling thermal conductivity - Dynamic

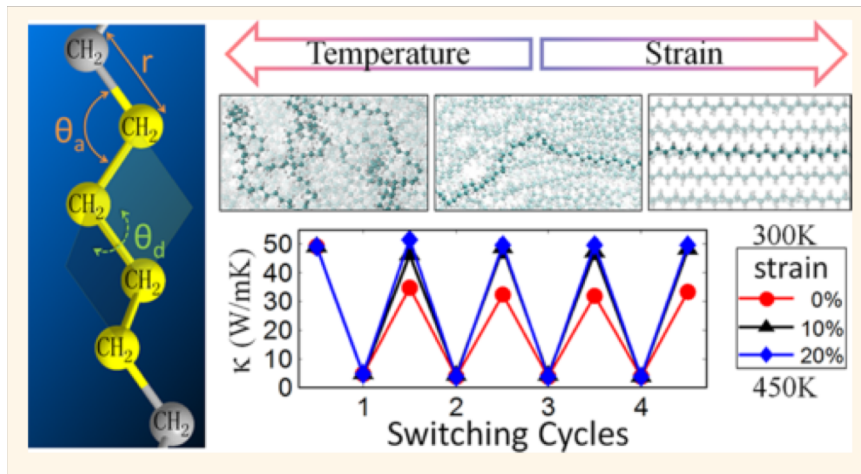
The thermal conductivity switch

State of the art around biologically relevant temperatures



Nature Nanotechnology **13**, 959 (2018)

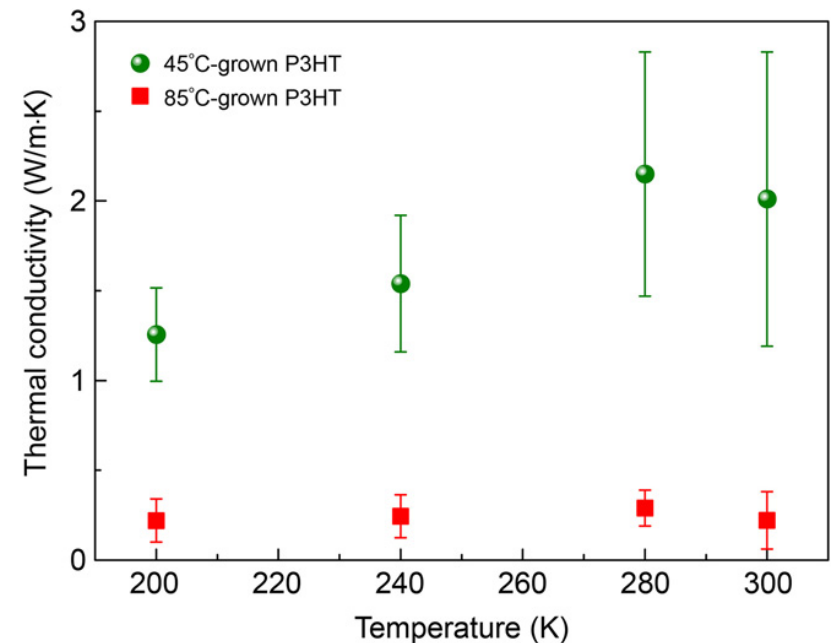
Heat transfer and thermal conductivity in polymers



ACS Nano **7**, 7592

Increased inter- and intramolecular bonding has been shown to **create polymers with ~10x higher κ than conventional polymers**

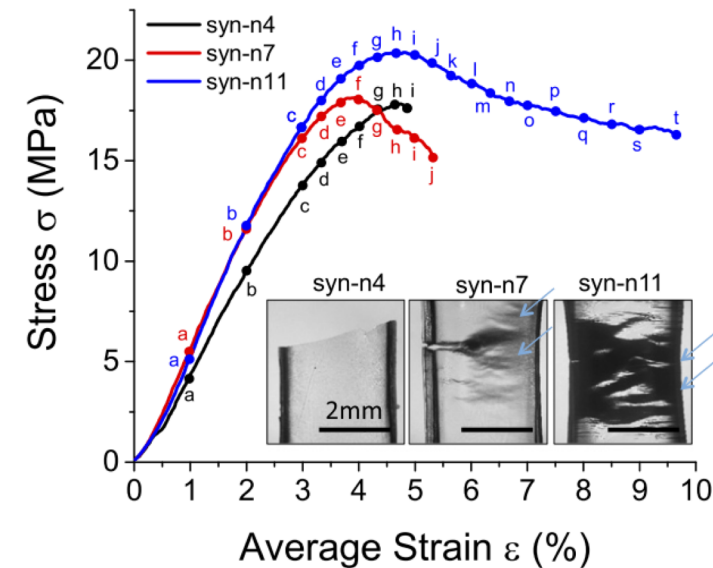
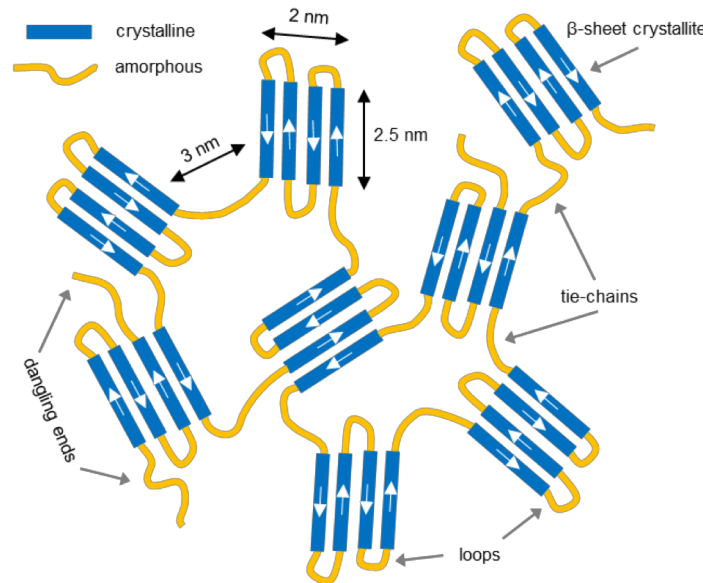
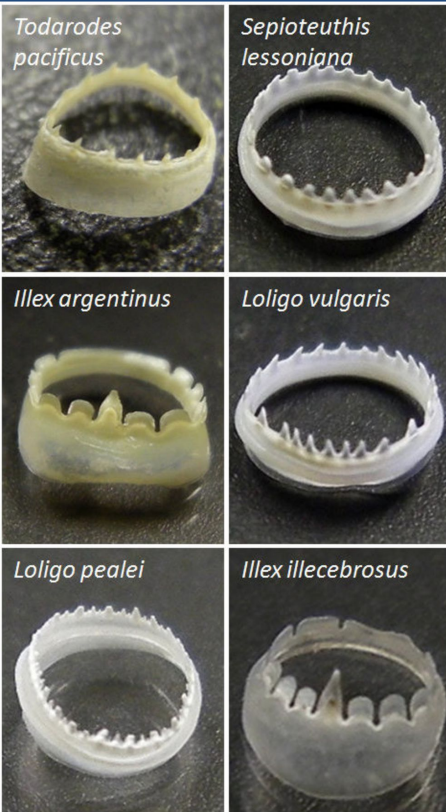
Polyethylene predicted to vary thermal conductivity by **a factor of 12**



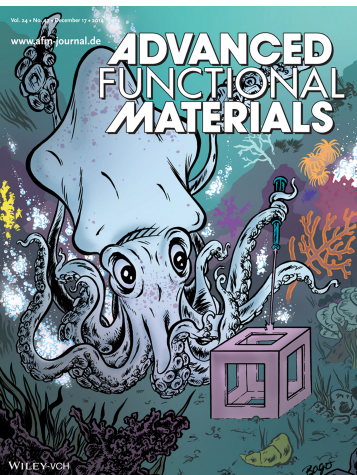
Science Advances **4**, eaar3031

Strain, chain alignment and crystallinity lead to large changes in polymer thermal conductivity (static)

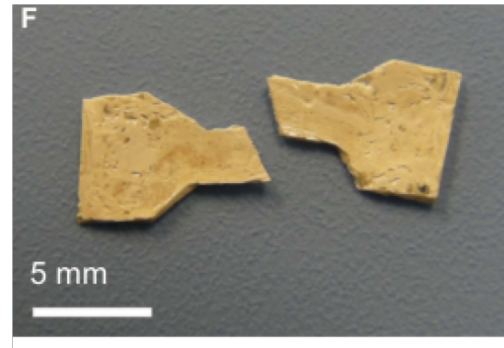
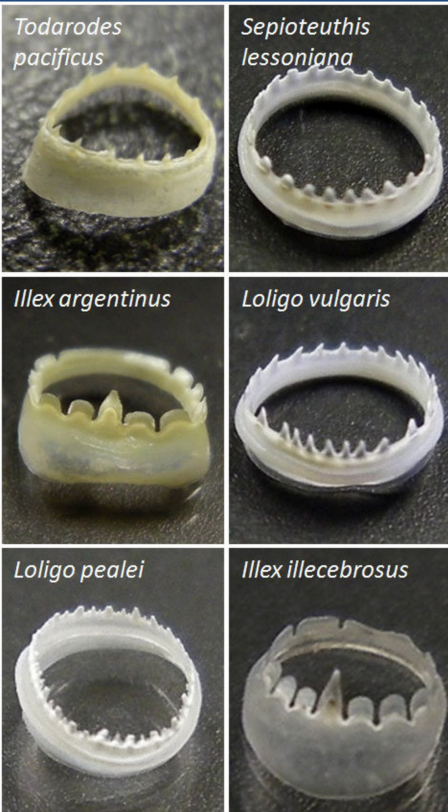
Squid ring teeth proteins – Prof. Melik Demirel (Penn State)



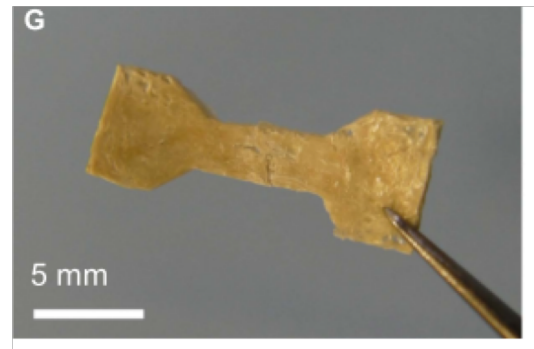
High strength protein due to semi crystalline (beta sheets) hydrogen bonded network



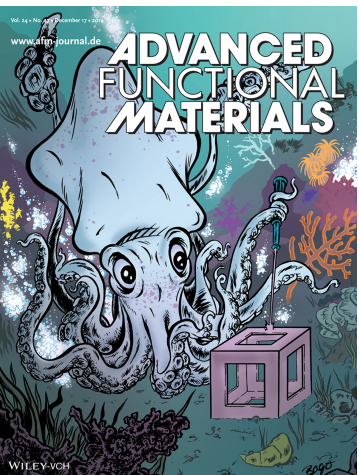
Squid ring teeth proteins – Prof. Melik Demirel (Penn State)



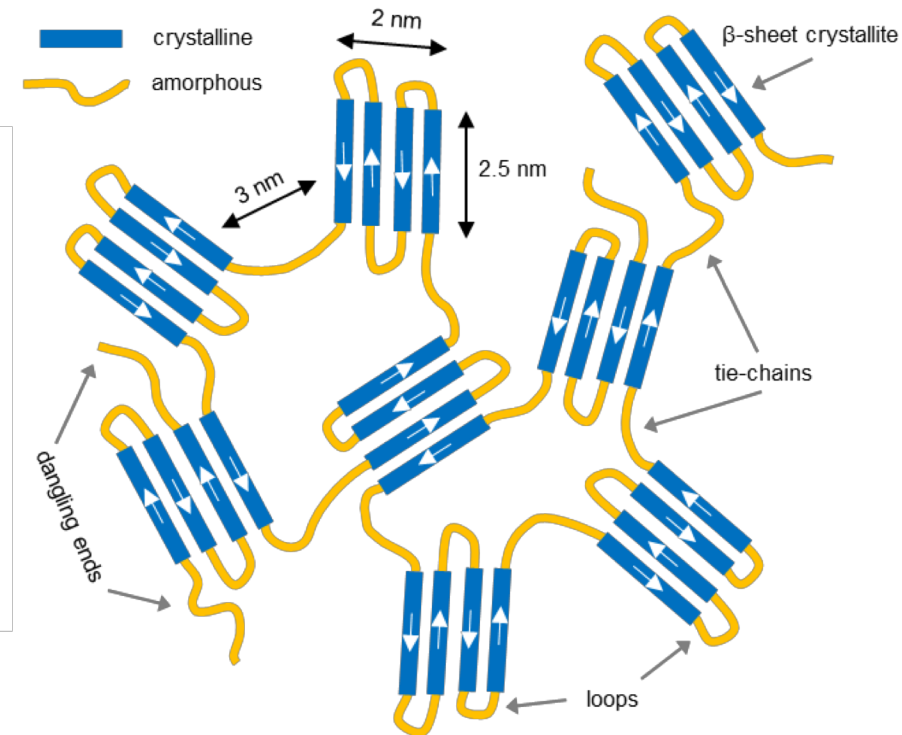
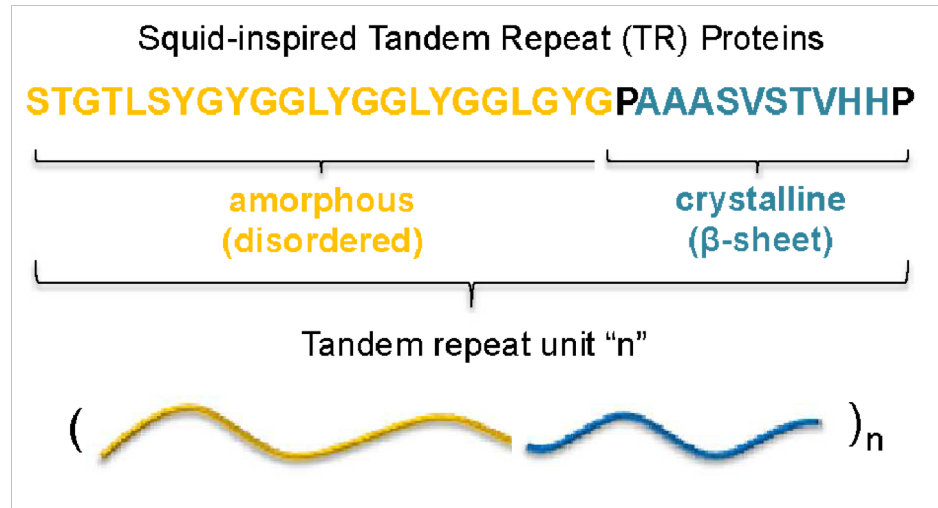
Add water!



Self healing when hydrated
(with a little bit of heat)



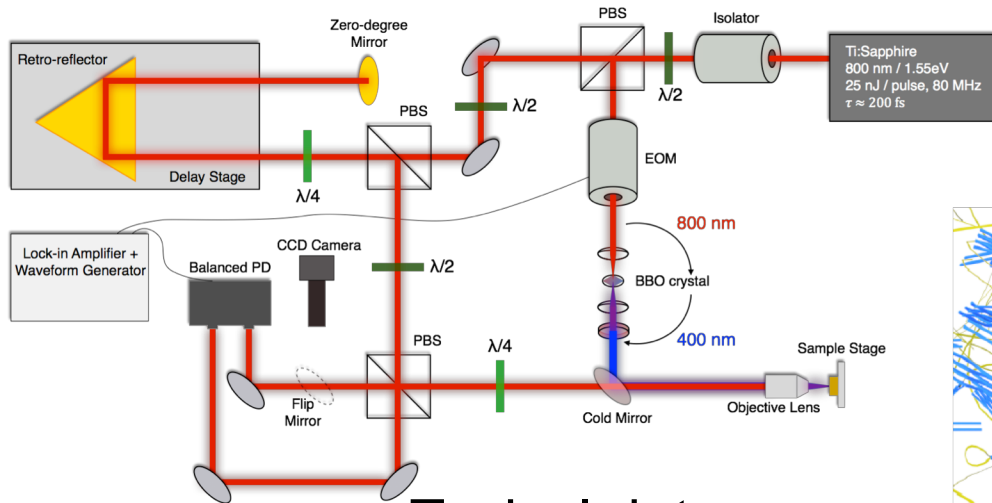
Squid ring teeth proteins – Prof. Melik Demirel (Penn State)



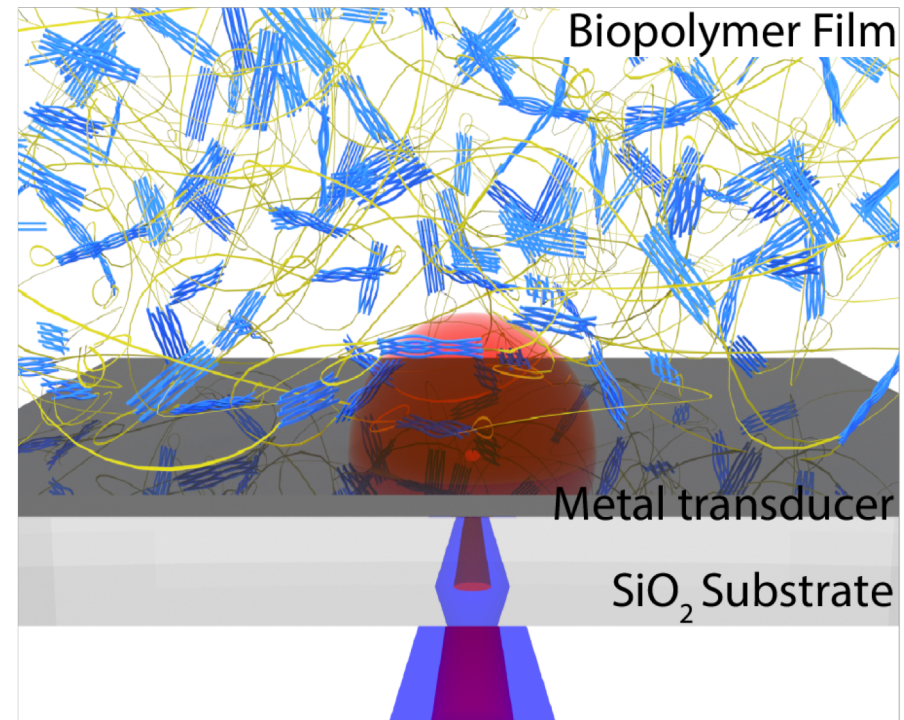
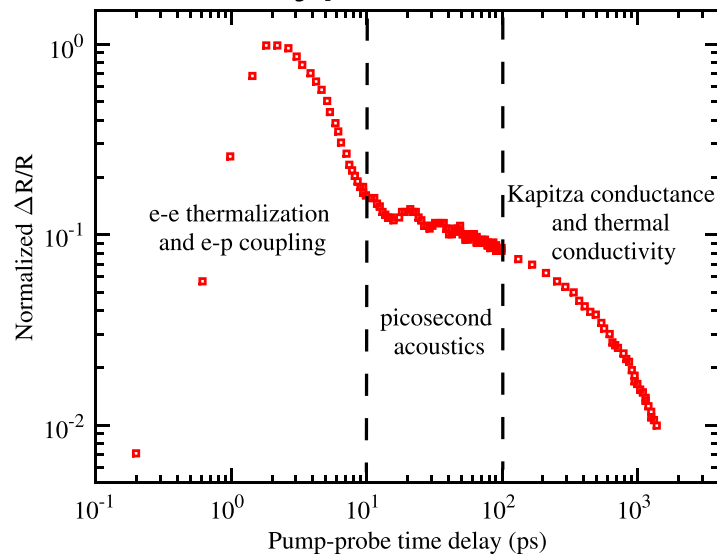
- Can we tune the thermal conductivity by changing the molecular structure? (static)
- Can we dynamically control the thermal conductivity with hydration? (dynamic thermal conductivity switch)

Time domain thermoreflectance (TDTR)

A typical sub-picosecond pump-probe system

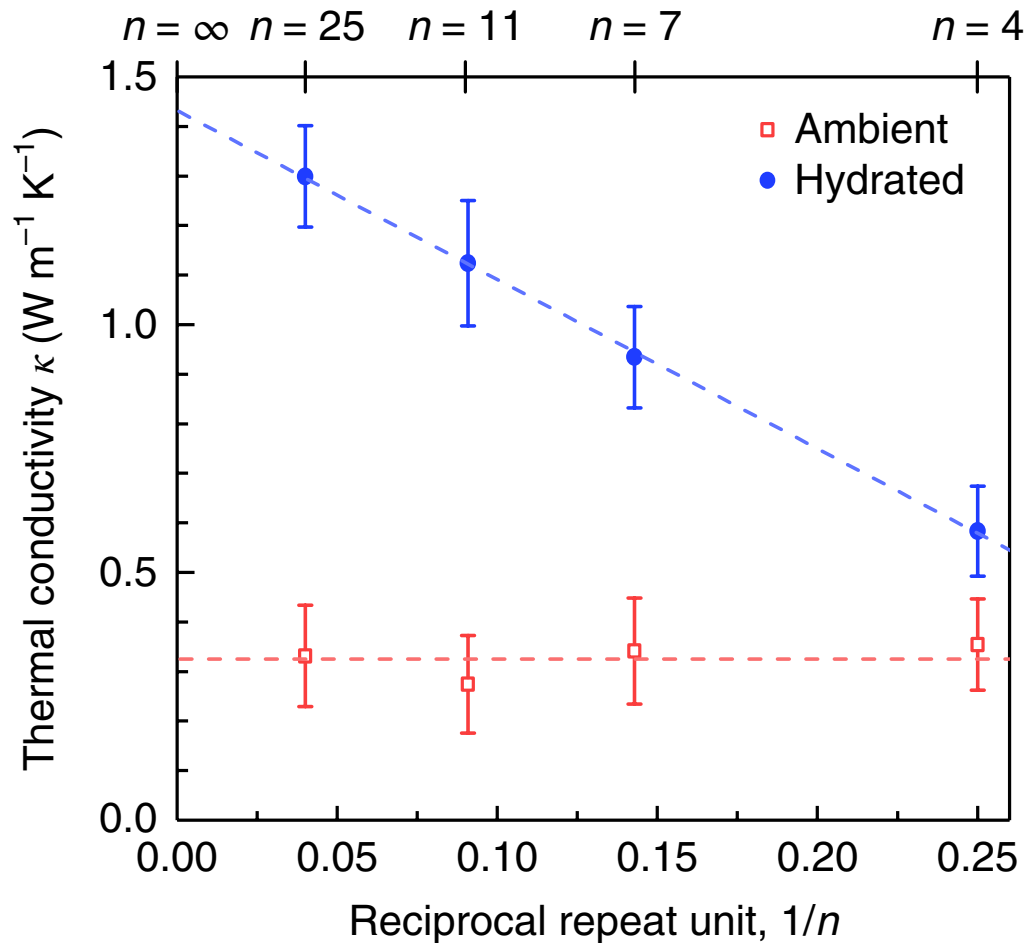


Typical data



Data from: Giri *et al.* *J. Appl. Phys.* **117**, 105105 (2015)

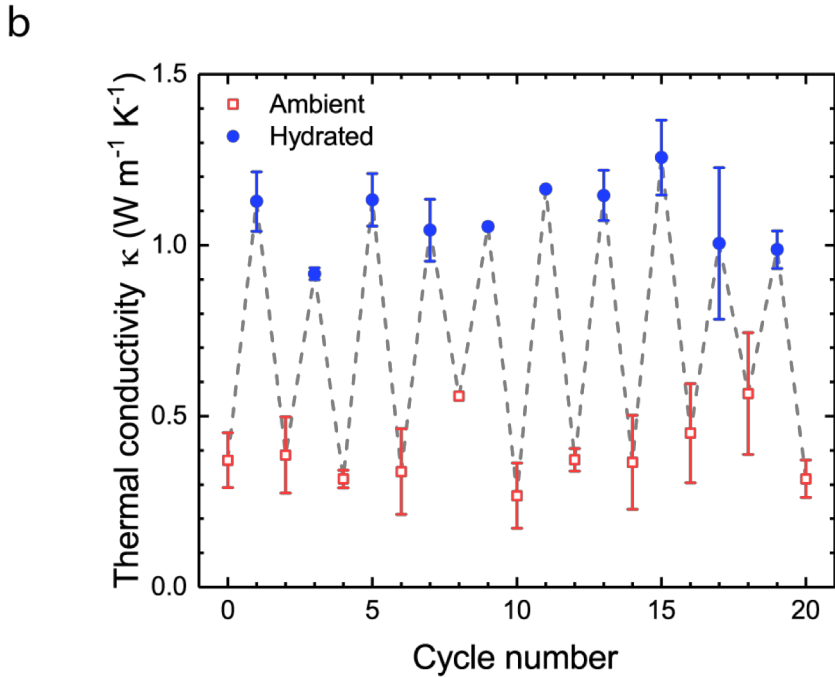
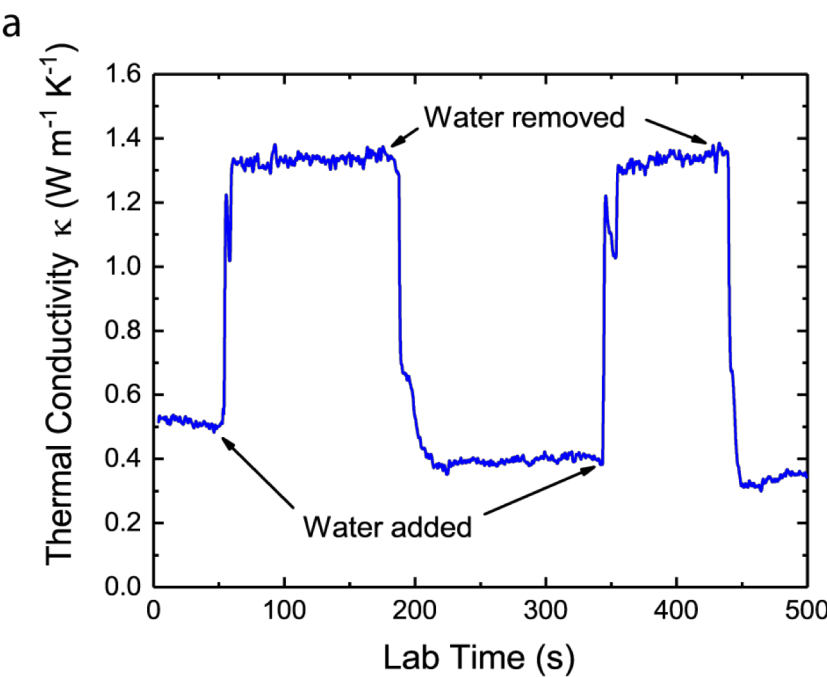
Results – Programmable thermal conductivity



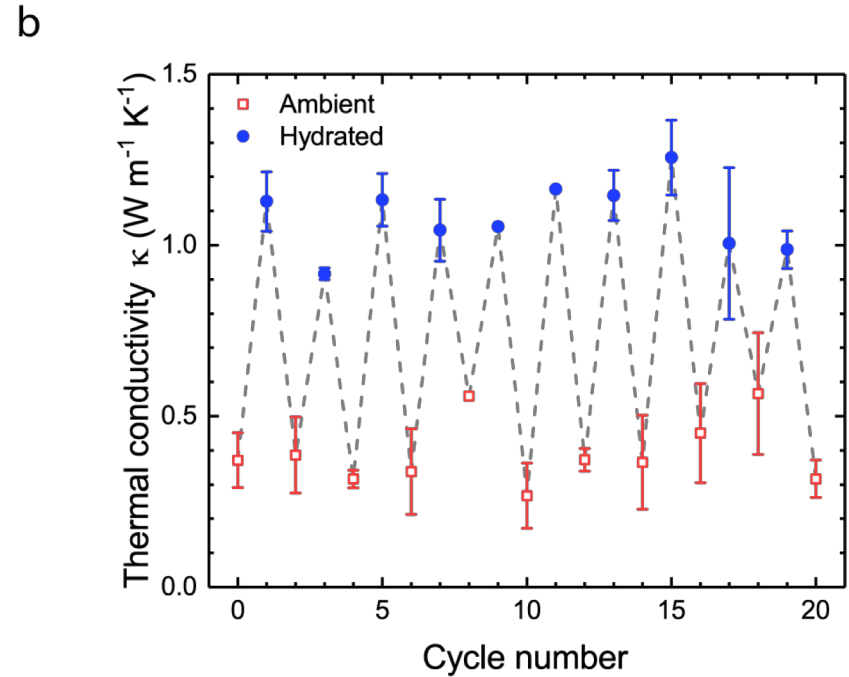
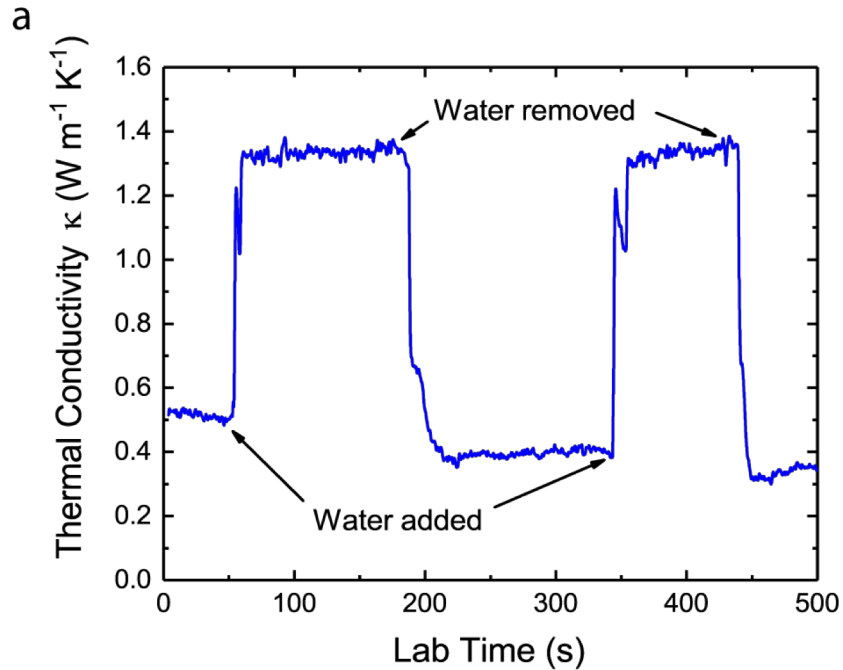
- κ ambient
- No dependence on n
 - Typical κ for polymer/protein
 - Disorder dominates

- κ hydrated
- Linear dependent on $1/n$
 - Up to 4X increase in κ compared to ambient

Results – Switchable thermal conductivity

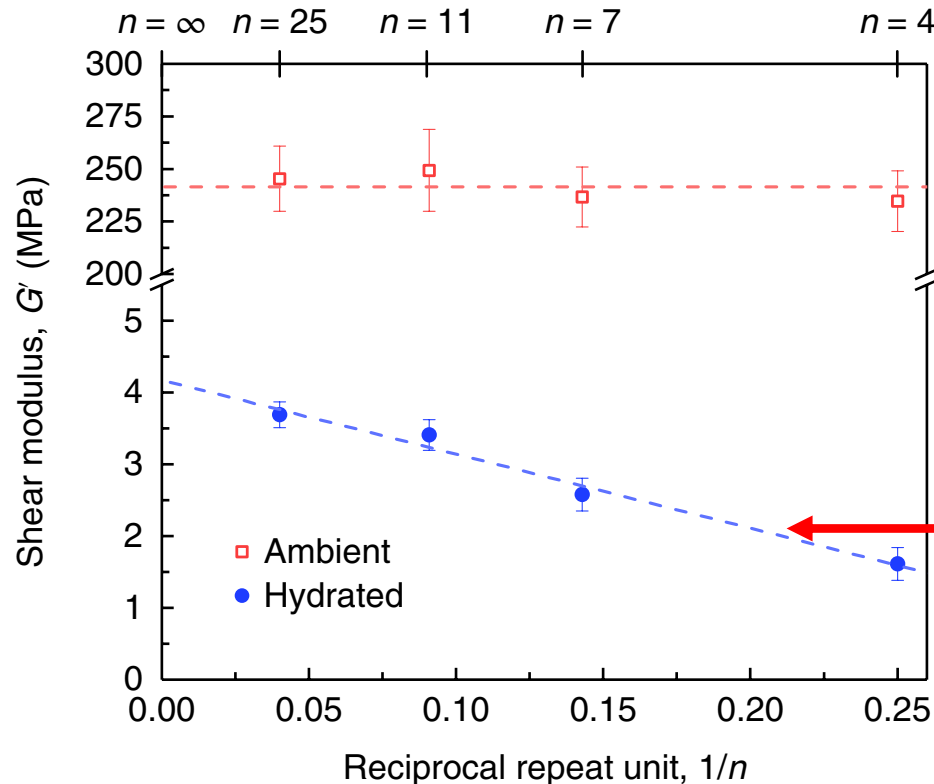


Results – Switchable thermal conductivity

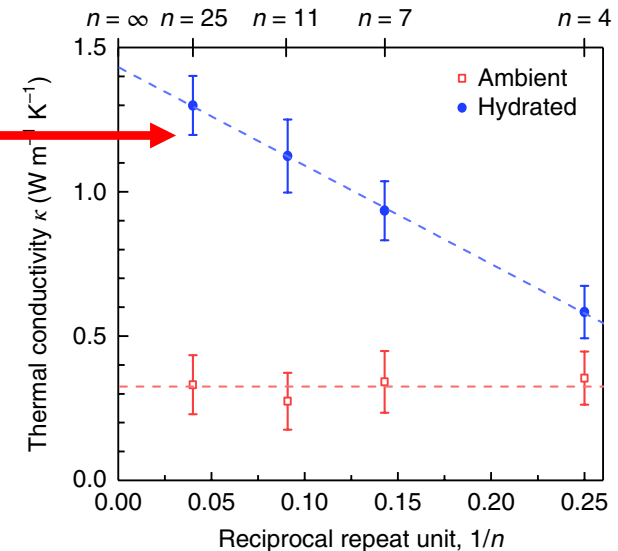


But why???

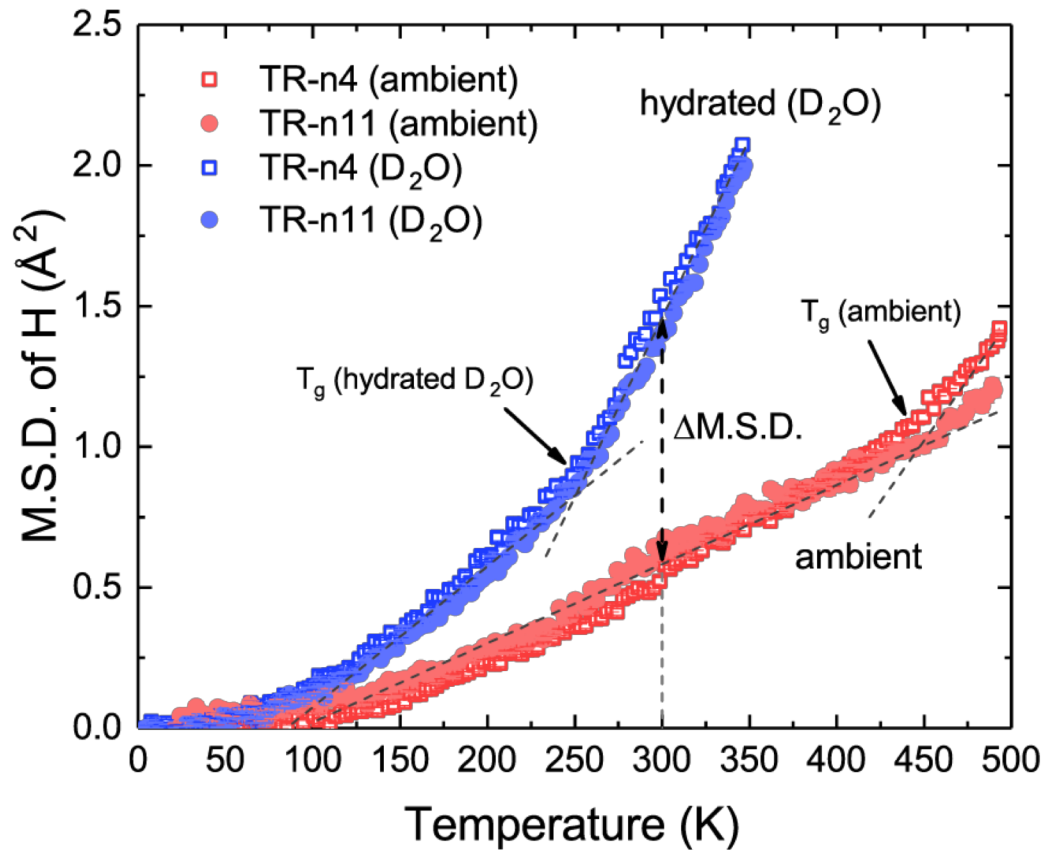
Results – Rheology



- $\kappa \sim G'$
- Diamond = Strong bonds = high κ
 - Polymers = weak bonds = low κ
 - κ trends with $G'(1/n)$
 - **Why does κ increase with hydration?**

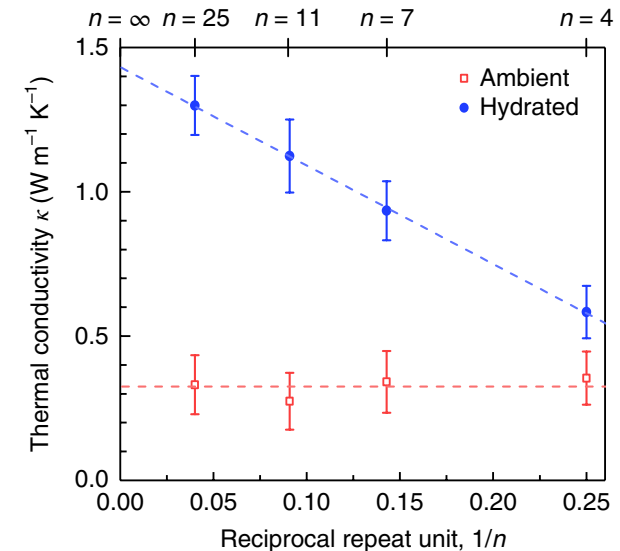


Results – Neutron scattering (NIST)



$$\kappa \sim \text{MSD}$$

- QENS in ambient and hydrated environments
- Hydration increases mean square displacement of hydrogen atoms in network



Mechanisms of thermal conductivity switching

Thermal conductivity of
crystalline/ordered solids

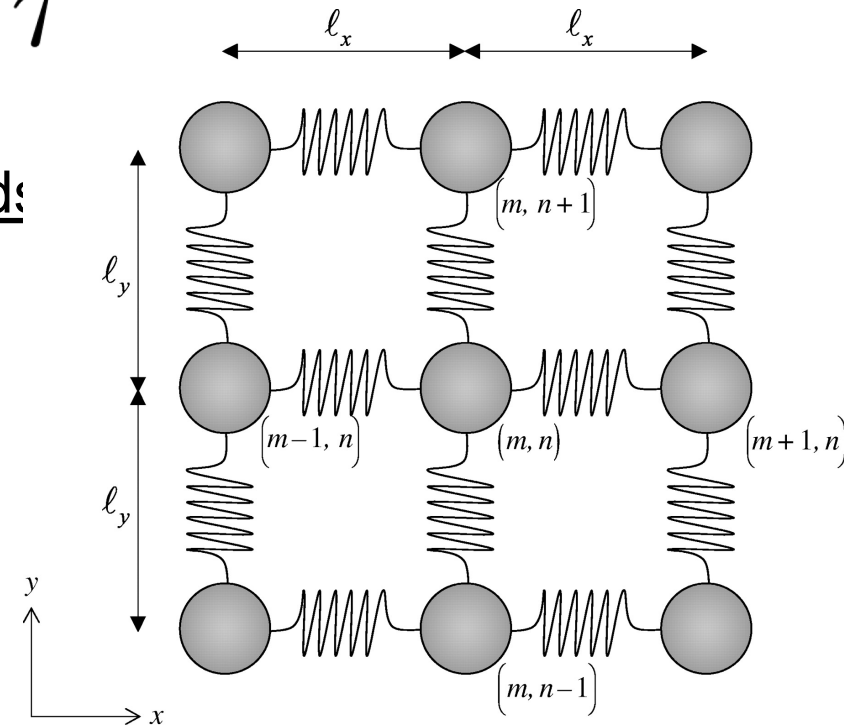
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Thermal conductivity of disordered solids

$$\kappa_{\text{Diffuson}} \propto \sum C_{\omega} D_{\omega}$$

D_{ω} = Mode Diffusivity

$$D_{\omega} \propto \text{MSD} \times G'^2$$



Mechanisms of thermal conductivity switching

Competing effects

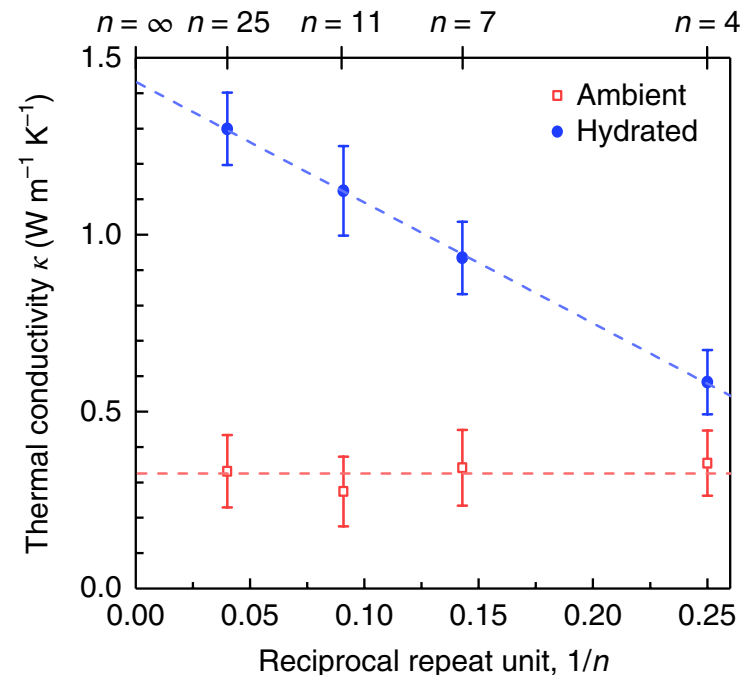
- Increase in κ due to increase in MSD
- Decrease in κ (trend in $1/n$) due to decrease in G'

Thermal conductivity of disordered solids

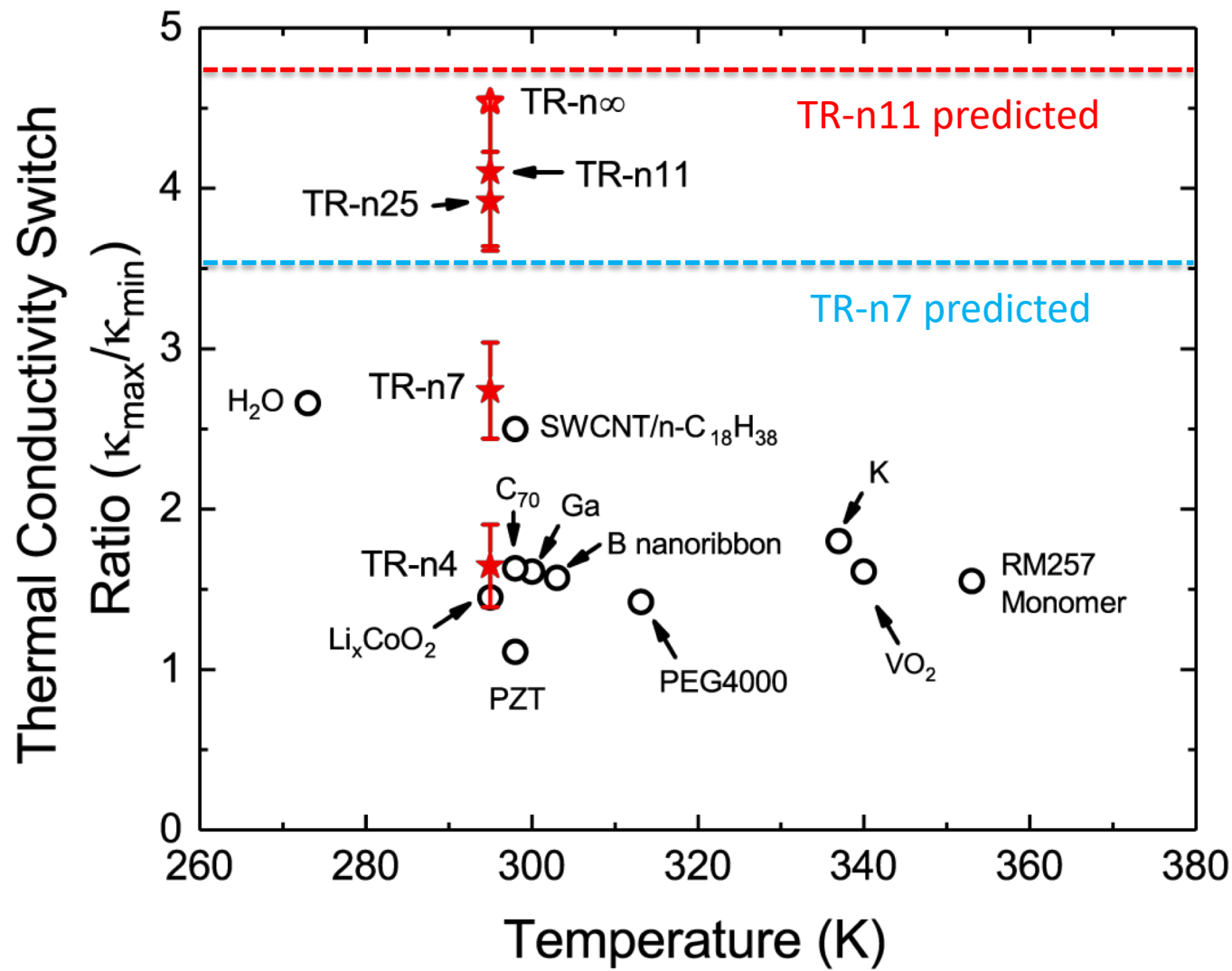
$$\kappa_{\text{Diffuson}} \propto \sum C_{\omega} D_{\omega}$$

D_{ω} = Mode Diffusivity

$$D_{\omega} \propto \text{MSD} \times G'^2$$



Redefining the SOA of κ switches with SRT





nature
nanotechnology

ARTICLES

<https://doi.org/10.1038/s41565-018-0227-7>

Tunable thermal transport and reversible thermal conductivity switching in topologically networked bio-inspired materials

John A. Tomko^{1,0}, Abdon Pena-Francesch^{2,3,10}, Huihun Jung^{2,3}, Madhusudan Tyagi^{4,5}, Benjamin D. Allen^{6,7}, Melik C. Demirel^{2,3,7*} and Patrick E. Hopkins^{1,8,9*}