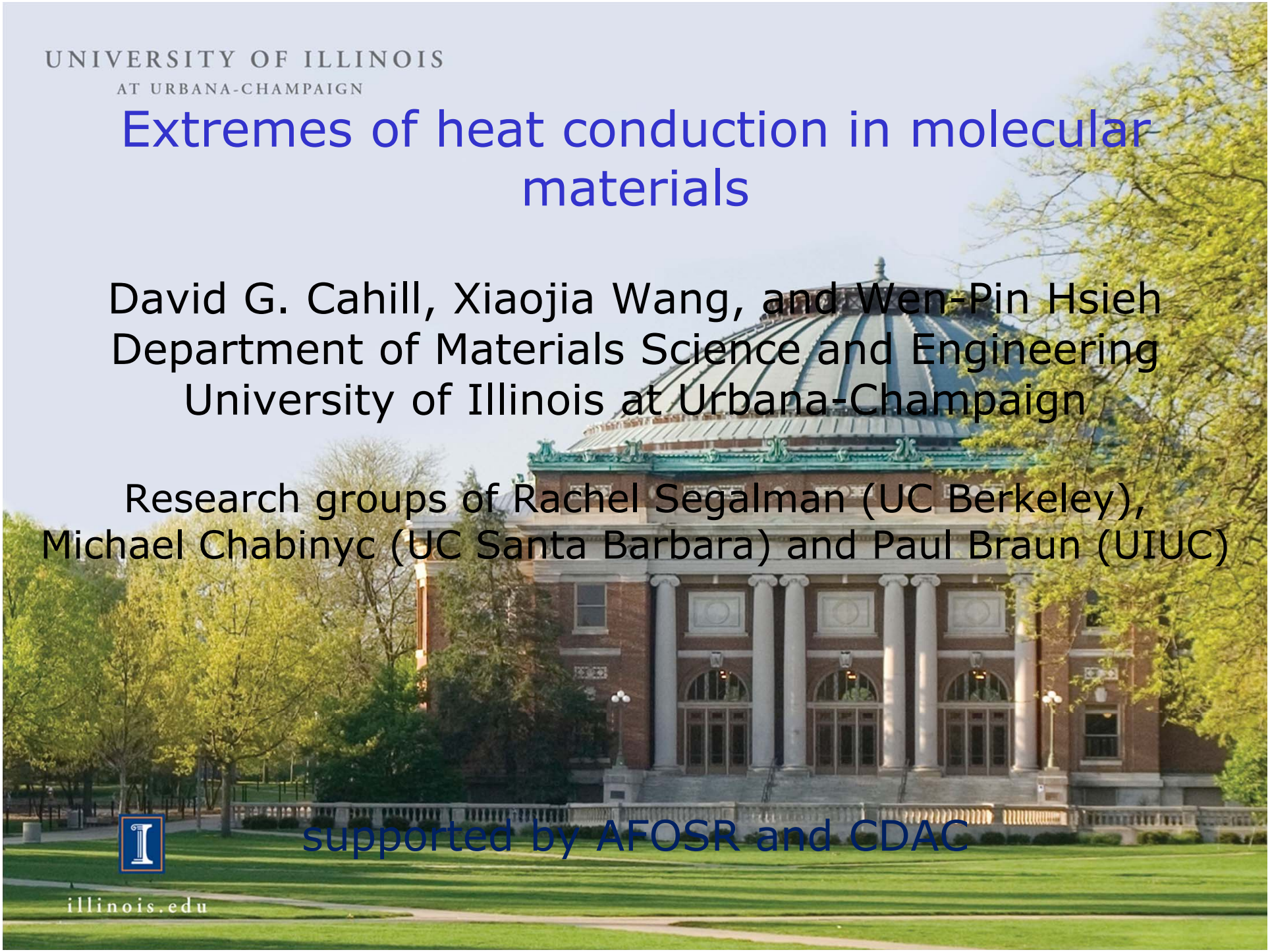

Extremes of heat conduction in molecular materials

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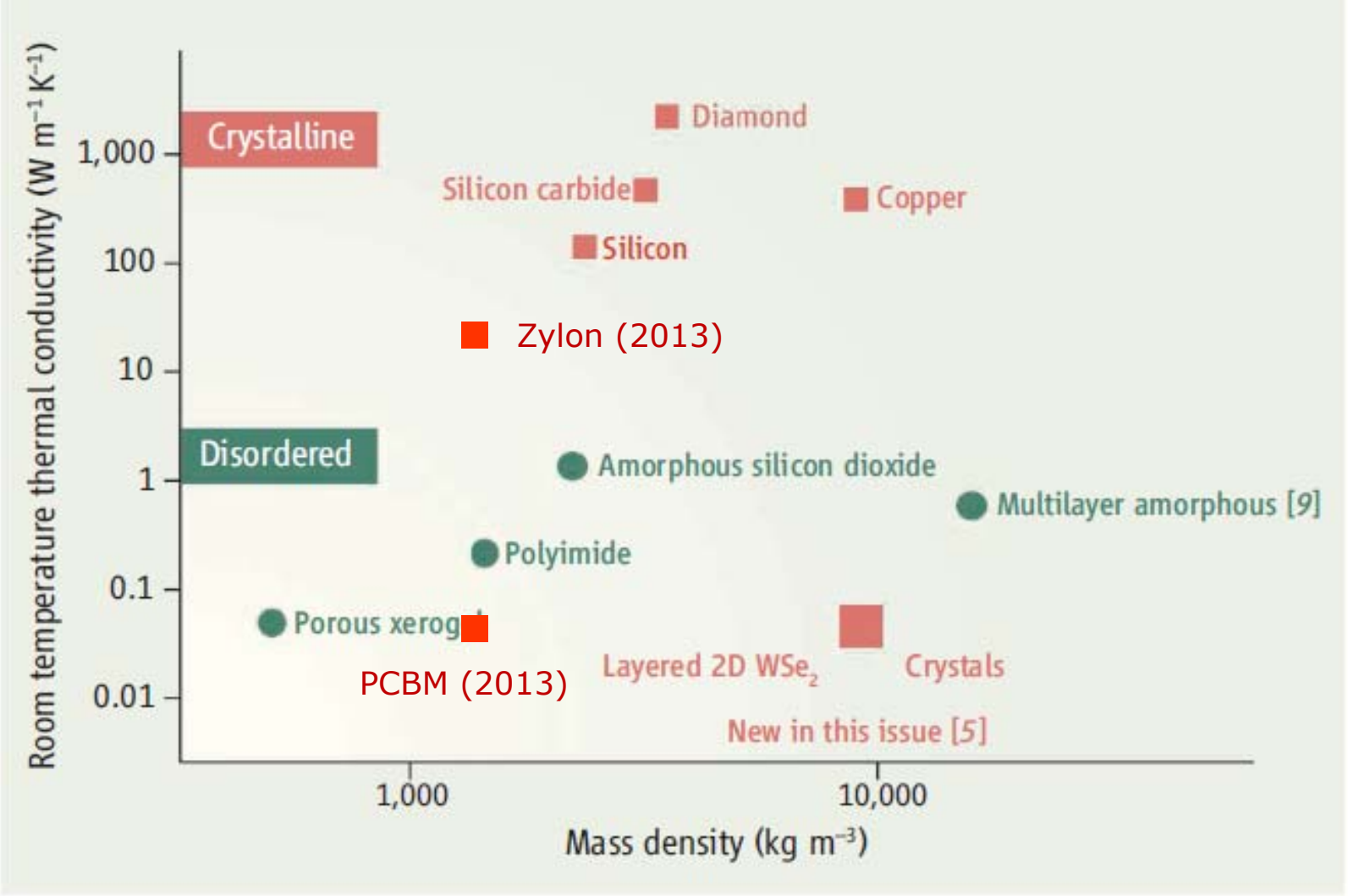
Research groups of Rachel Segalman (UC Berkeley), Michael Chabinyc (UC Santa Barbara) and Paul Braun (UIUC)

supported by AFOSR and CDAC

Outline

- Extremely low thermal conductivity in fullerene derivatives.
  - Report of 0.03 W m^{-1} K^{-1} by Duda *et al*.
  - Lowest we observe is 0.05 W m^{-1} K^{-1}
- Polymer under extreme pressure (up to 12 GPa) behaves as predicted by the minimum thermal conductivity model.
- Extremely high thermal conductivity in high modulus polymer fibers.
  - Report of 100 W m^{-1} K^{-1} by Shen *et al*.
  - Highest we observe (Zylon) is 20 W m^{-1} K^{-1}.

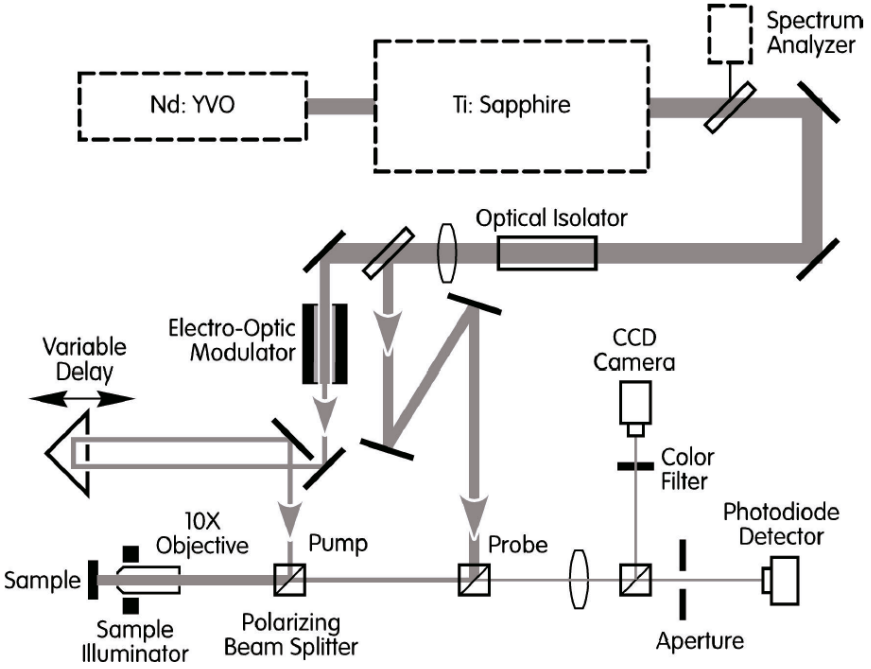
Thermal conductivities of dense solids span a range of 40,000 at room temperature

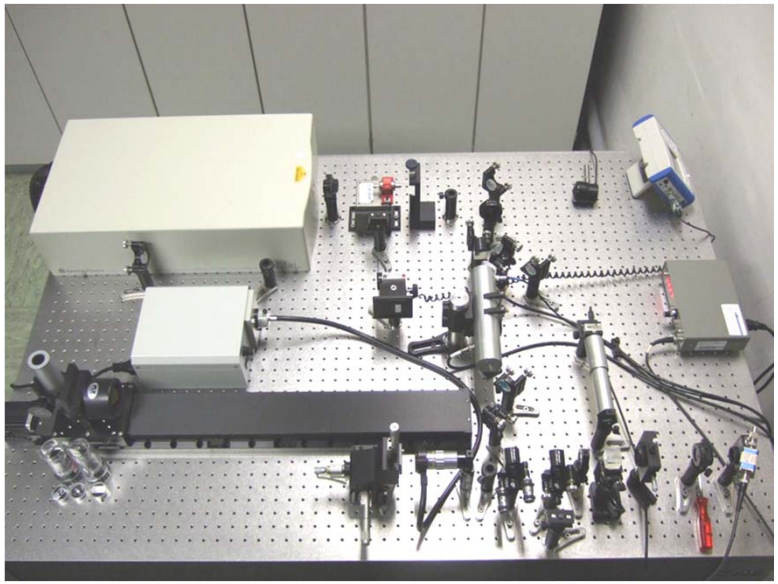


Adapted from Goodson, *Science* (2007)

Time domain thermoreflectance since 2003

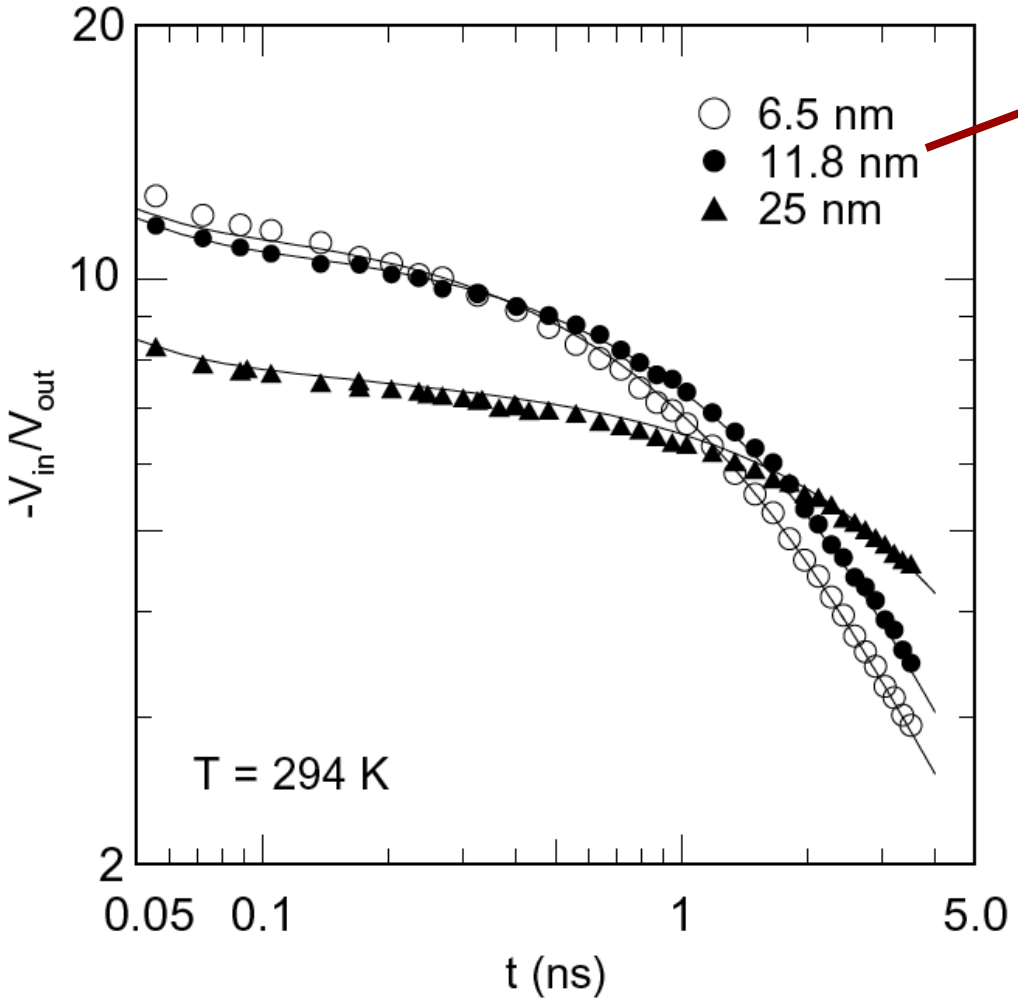
- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

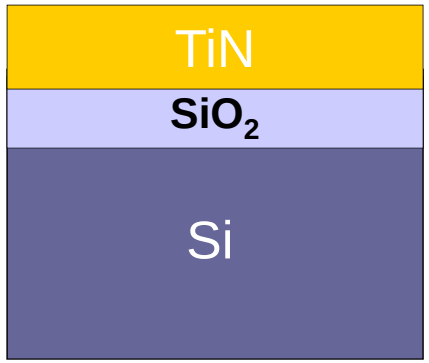




Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

Time-domain Thermoreflectance (TDTR) data for $TiN/SiO_2/Si$

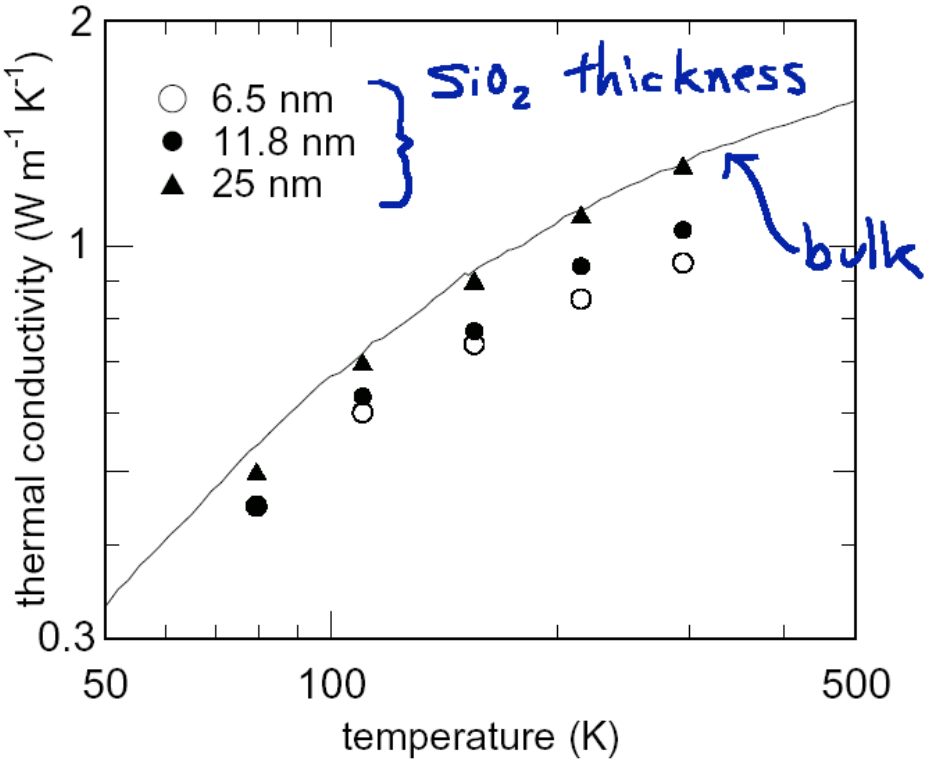


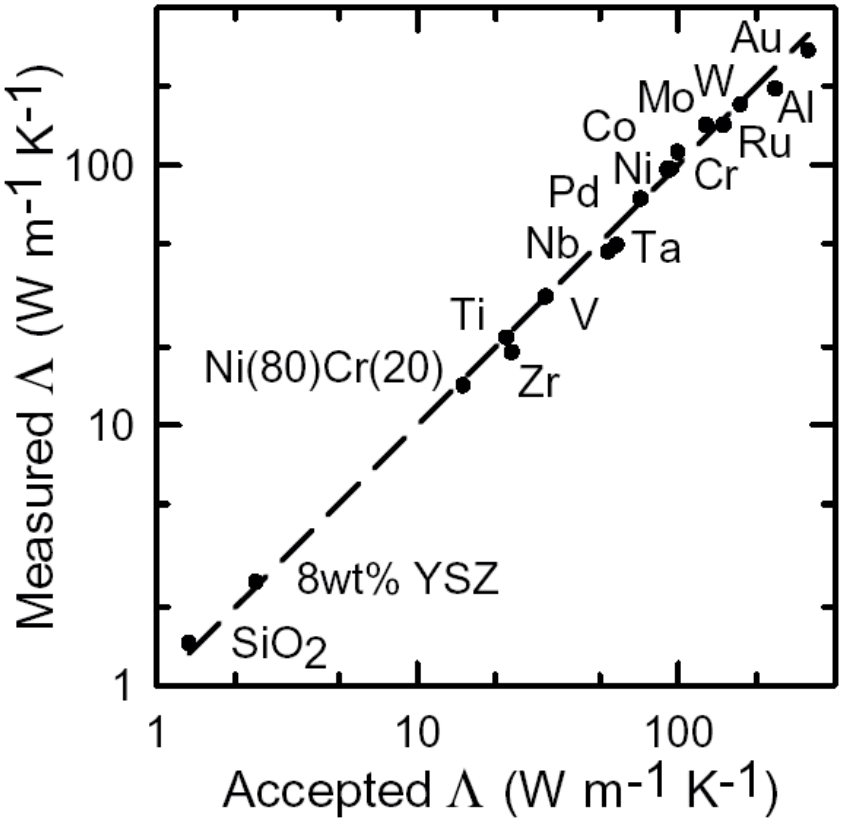


- reflectivity of a metal depends on temperature
- one free parameter: the "effective" thermal conductivity of the thermally grown SiO_2 layer (interfaces not modeled separately)

Costescu *et al*., PRB (2003)

TDTR: validation experiments

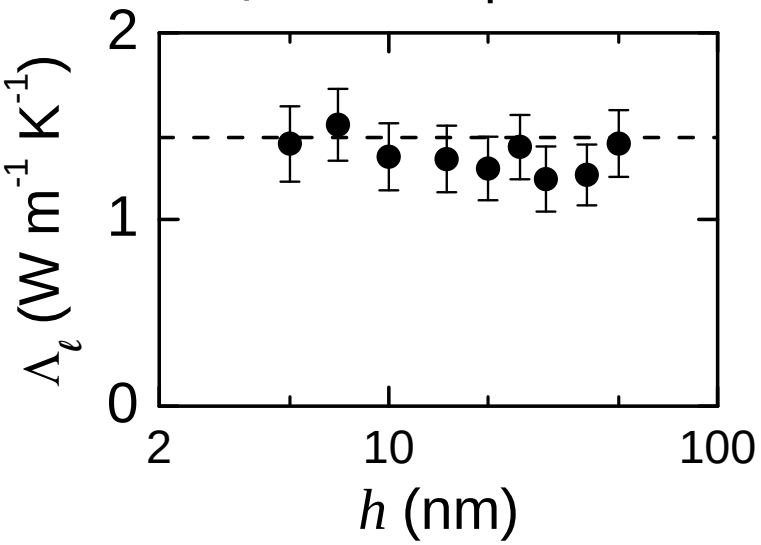




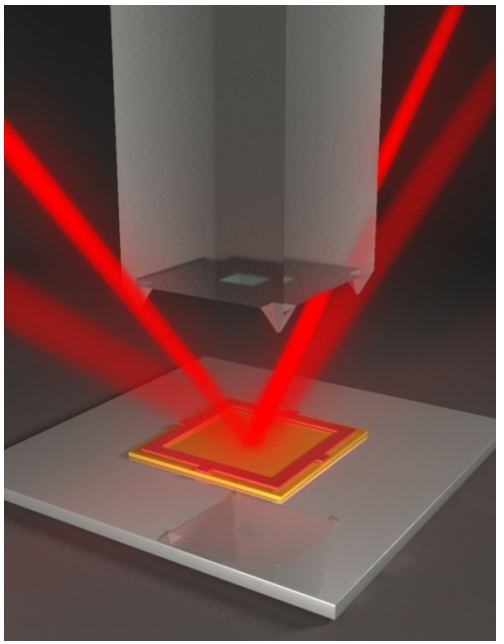
Costescu *et al*., PRB (2003)

TDTR: Flexible, convenient, and accurate

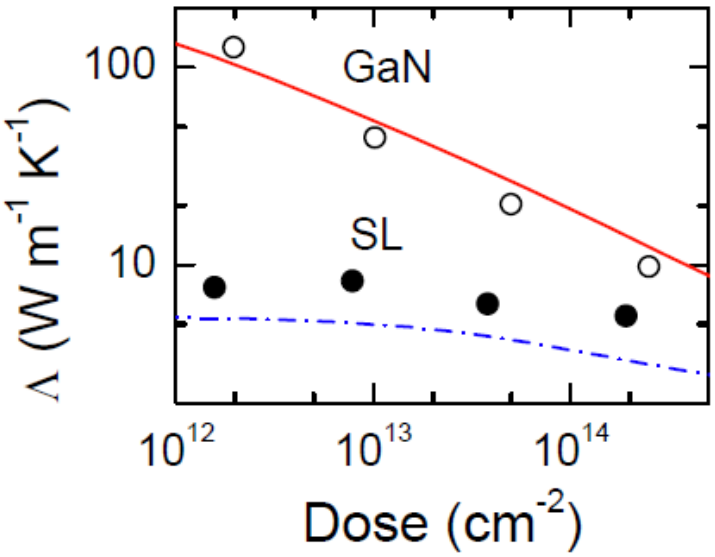
PbTe/PbSe superlattices



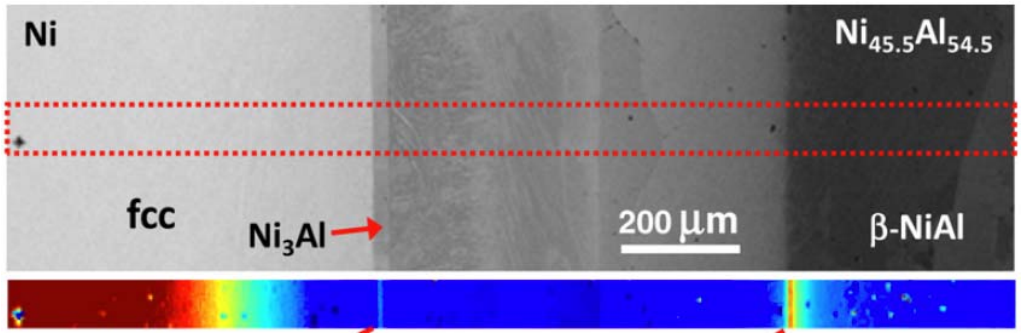
Transfer-printed interfaces



Radiation damage



High resolution mapping



Can we beat the amorphous limit of the thermal conductivity Λ_{min}

- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

High T limit

$$\Lambda_{min} = 0.40\, k_B n^{2/3} (v_\ell + 2v_t)$$

Einstein (1911)

- coupled the Einstein oscillators to 26 neighbors
- heat transport as a random walk of thermal energy between atoms; time scale of ½ vibrational period
- did not realize waves (phonons) are the normal modes of a crystal

2. *Elementare Betrachtungen über die thermische Molekularbewegung in festen Körpern;*

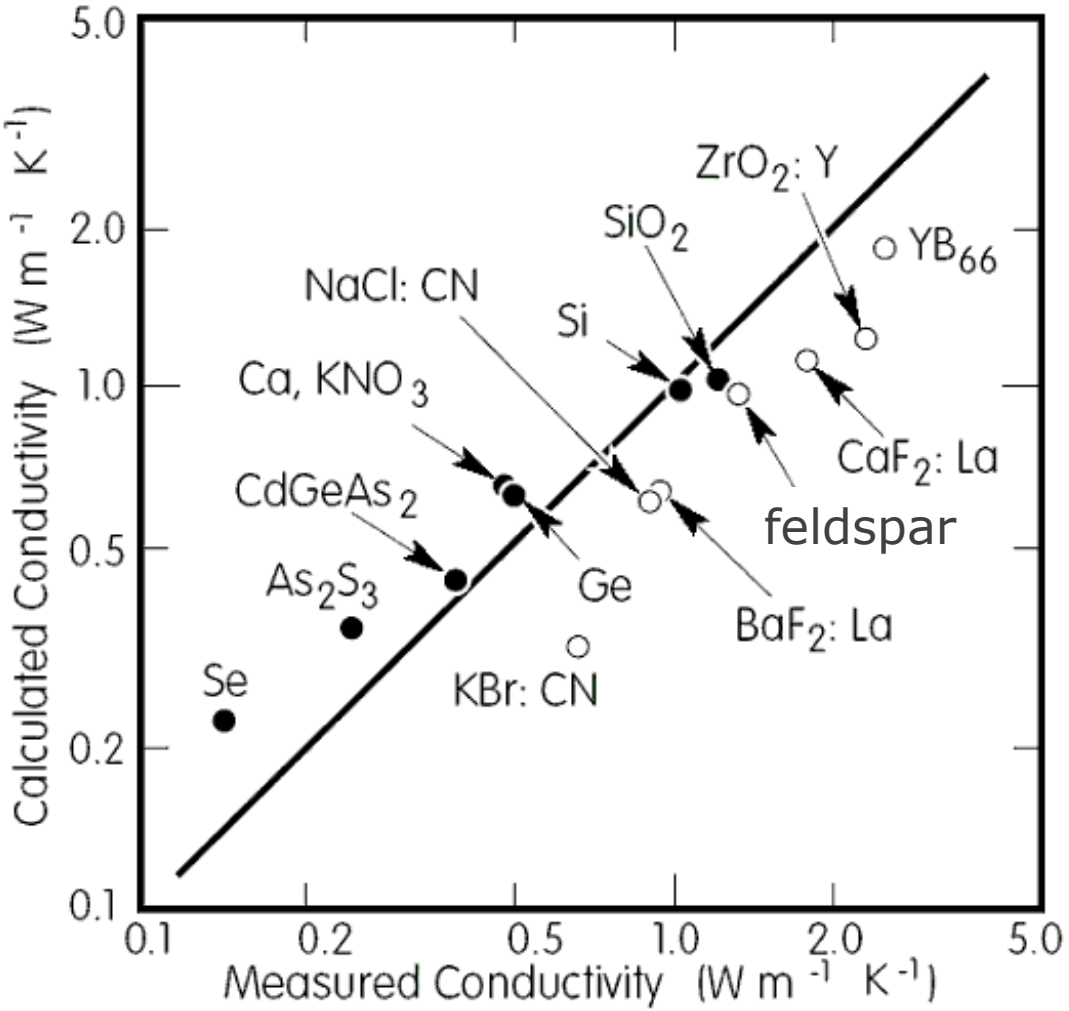
von A. Einstein.

In einer früheren Arbeit[1]) habe ich dargelegt, daß zwischen dem Strahlungsgesetz und dem Gesetz der spezifischen Wärme fester Körper (Abweichung vom Dulong-Petitschen Gesetz) ein Zusammenhang existieren müsse[2]). Die Untersuchungen Nernsts und seiner Schüler haben nun ergeben, daß die spezifische Wärme zwar im ganzen das aus der Strahlungstheorie gefolgerte Verhalten zeigt, daß aber das wahre Gesetz der spezifischen Wärme von dem theoretisch gefundenen systematisch abweicht. Es ist ein erstes Ziel dieser Arbeit, zu zeigen, daß diese Abweichungen darin ihren Grund haben, daß die Schwingungen der Moleküle weit davon entfernt sind, *monochromatische* Schwingungen zu sein. Die thermische Kapazität eines Atoms eines festen Körpers ist nicht gleich der eines schwach gedämpften, sondern ähnlich der eines stark gedämpften Oszillators im Strahlungsfelde. Der Abfall der spezifischen Wärme nach Null hin bei abnehmender Temperatur erfolgt deshalb weniger rasch, als er nach der früheren Theorie erfolgen sollte; der Körper verhält sich ähnlich wie ein Gemisch von Resonatoren, deren Eigenfrequenzen über ein gewisses Gebiet verteilt sind. Des weiteren wird gezeigt, daß sowohl Lindemanns Formel, als auch meine Formel zur Berechnung der Eigenfrequenz ν der Atome durch Dimensionalbetrachtung abgeleitet werden können, insbesondere auch die Größenordnung der in diesen Formeln auftretenden Zahlen-

1) A. Einstein, Ann. d. Phys. 22. p. 184. 1907.

2) Die Wärmebewegung in festen Körpern wurde dabei aufgefaßt als in monochromatischen Schwingungen der Atome bestehend. Vgl. hierzu § 2 dieser Arbeit.

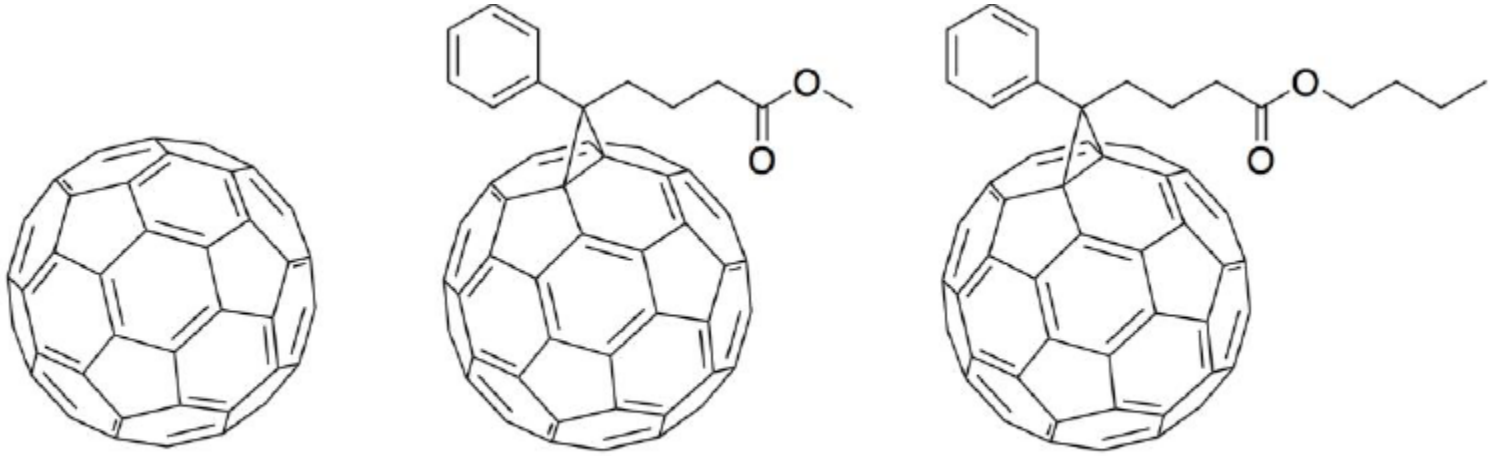
Works well for homogeneous disordered materials



- ● amorphous
- ○ disordered crystal

Fullerene derivatives have "ultralow" thermal conductivity, i.e., conductivity well below the conventional lower-limit

- Duda et al. (2013) reported 0.03 W m^{-1} K^{-1}.
- We find all samples are in the range 0.05 to 0.06 W m^{-1} K^{-1}.

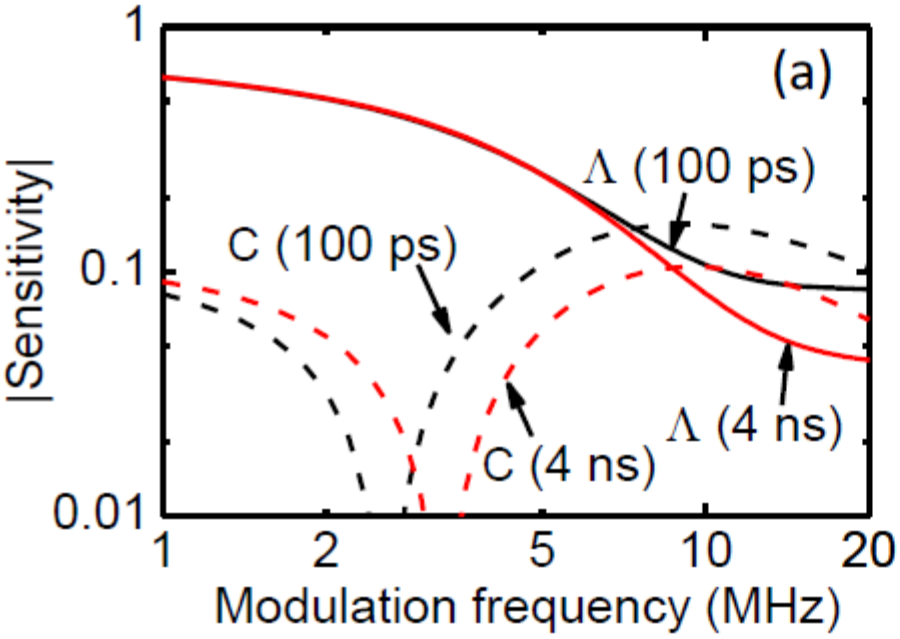


C60 PCBM PCBNB

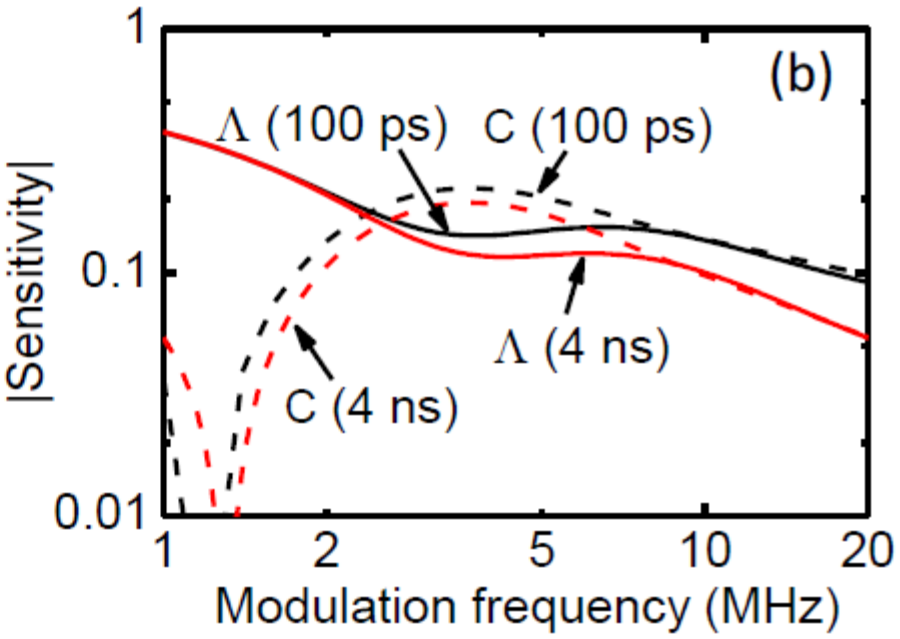
Use thin films (≈60 nm and ≈120 nm thick) and variable modulation frequency to separate thermal conductivity and heat capacity

$$S_\alpha = \frac{d\ln(-V_{in}/V_{out})}{d\ln(\alpha)}$$

60 nm

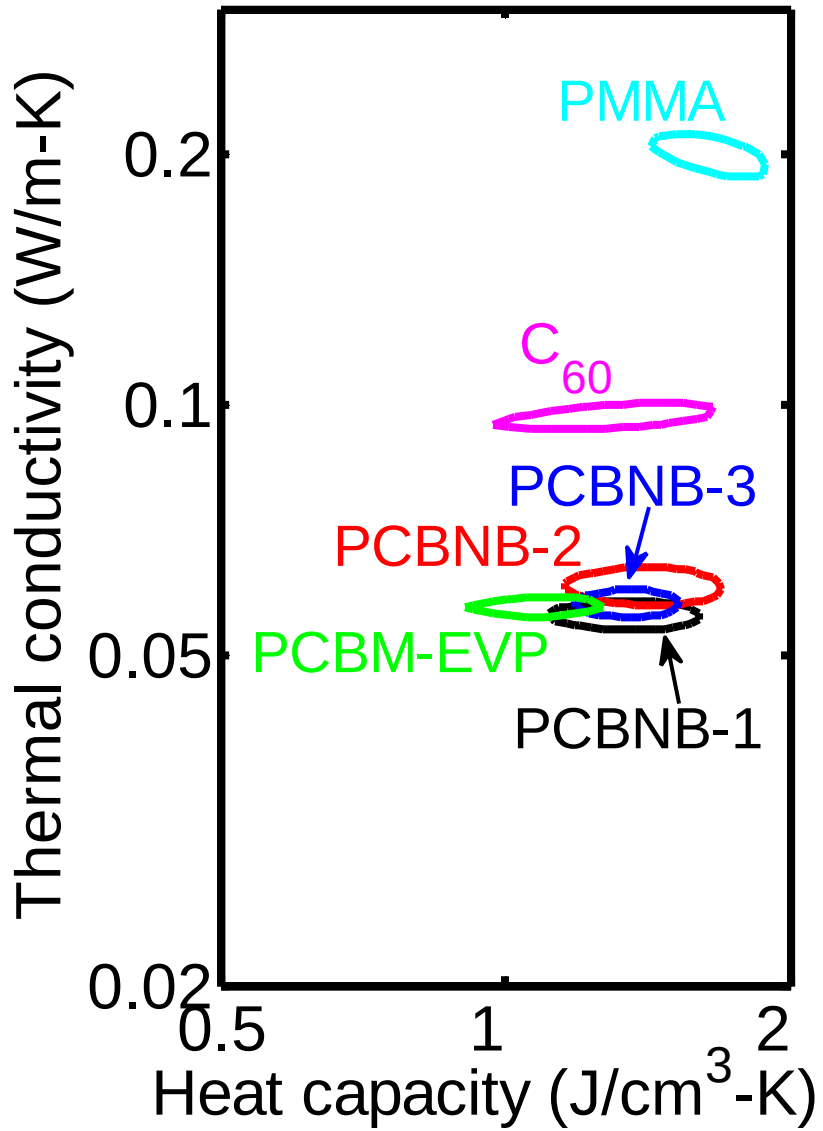


120 nm



Wang *et al*., PRB, in press.

Fit two parameters (C and Λ) to multiple data sets (modulation frequency, thickness)

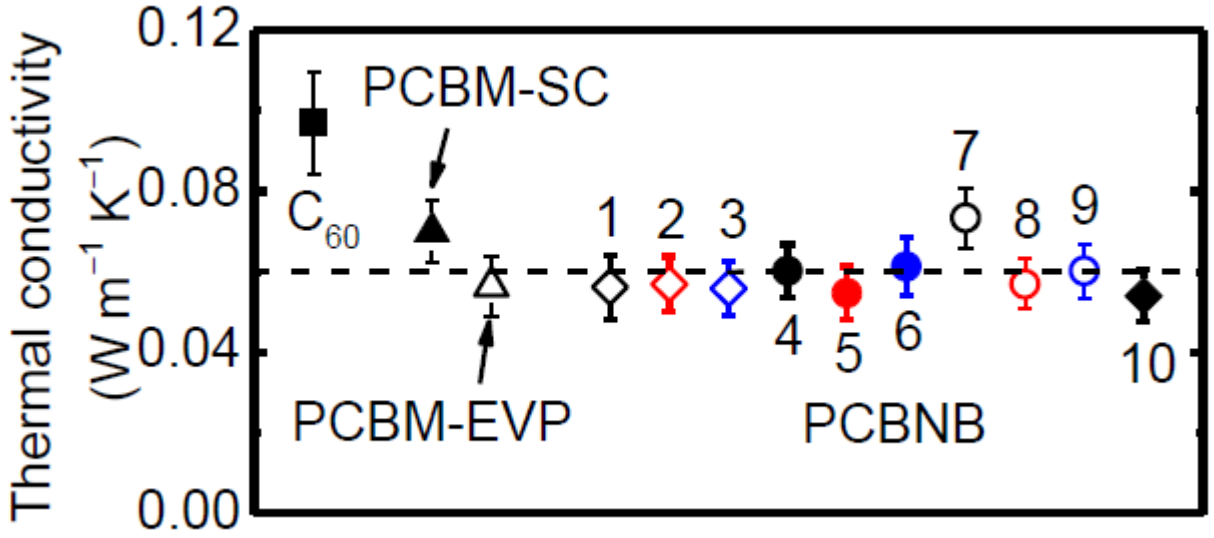


- Assume heat capacity C doesn't depend on thickness but allow thermal conductivity to vary with thickness.

Wang *et al*., PRB, in press.

Surprising result: fullerene derivative thermal conductivity (0.05 to 0.06 W m^{-1} K^{-1}) is smaller than either C_{60} (by a factor of 2) or bulk polymer (by a factor of 3-4)

- Lowering of sound velocities (v_l of PCBNB is 70% of v_l for C60) but hard to explain the suppression of conductivity based on sound velocities alone.



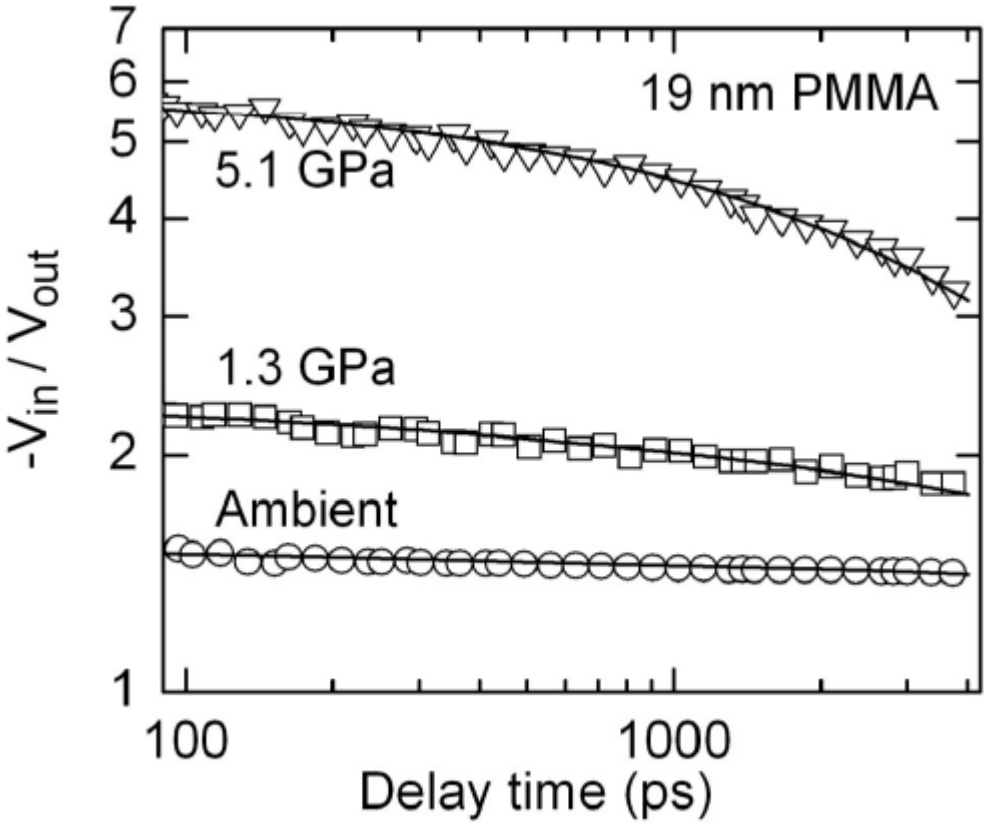
Wang *et al*., PRB, in press.

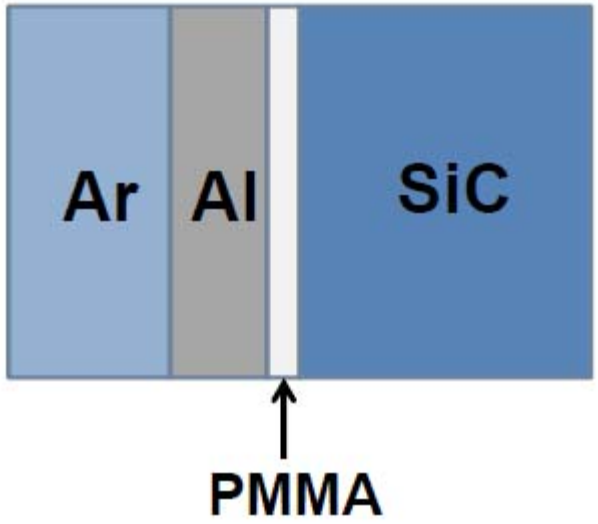
Why is the thermal conductivity a factor of 2 less than disordered C_{60} and a factor of 4 less than a glassy polymer?

- Heat capacity per unit volume is almost the same.
- Longitudinal sound velocities are 2.8 nm/ps, 40% smaller than C_{60}. So lower vibrational frequencies of the C_{60} center of mass explains some of the difference.
- Vibrational states of the polymer chains do not seem to be contributing to the heat transport.
- Computational studies would be useful to understand the mechanism and optimize the polymer chain molecular weight.

Wang *et al*., PRB, in press.

Analyze ratio V_{in}/V_{out} using an exact solution of the heat diffusion equation



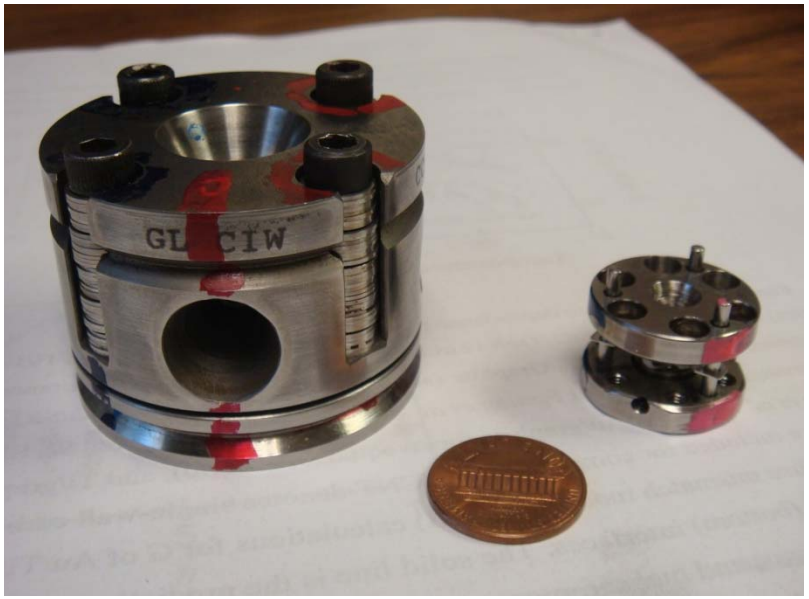


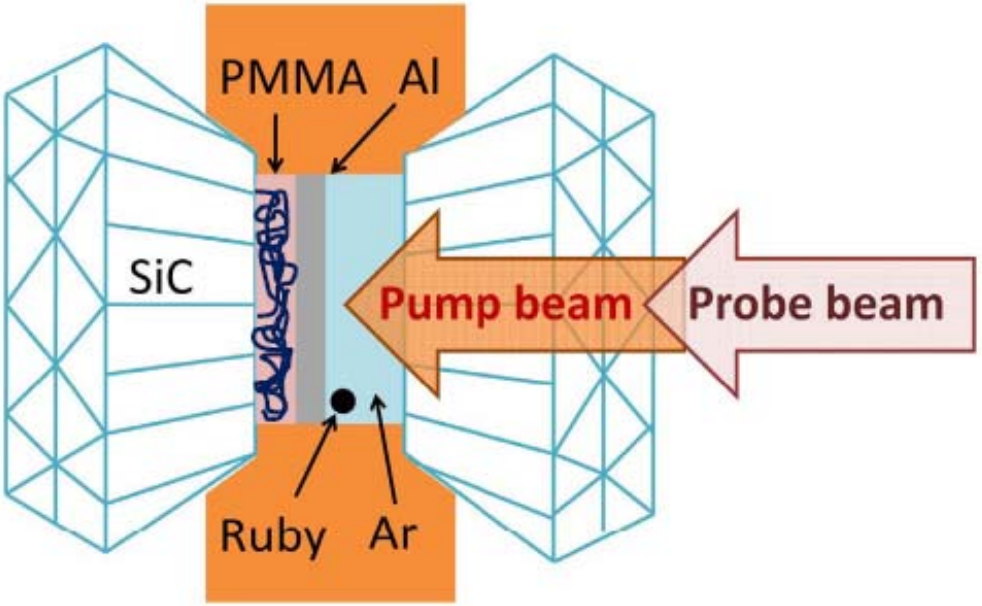
Thermal Model:

A. Laser spot size
B. Thickness and C(P) of Al
C. Interface conductance
D. Λ(P) of PMMA?

TDTR is all optical method: adaptable to "extreme" environments such as high pressure

Diamond anvil cell



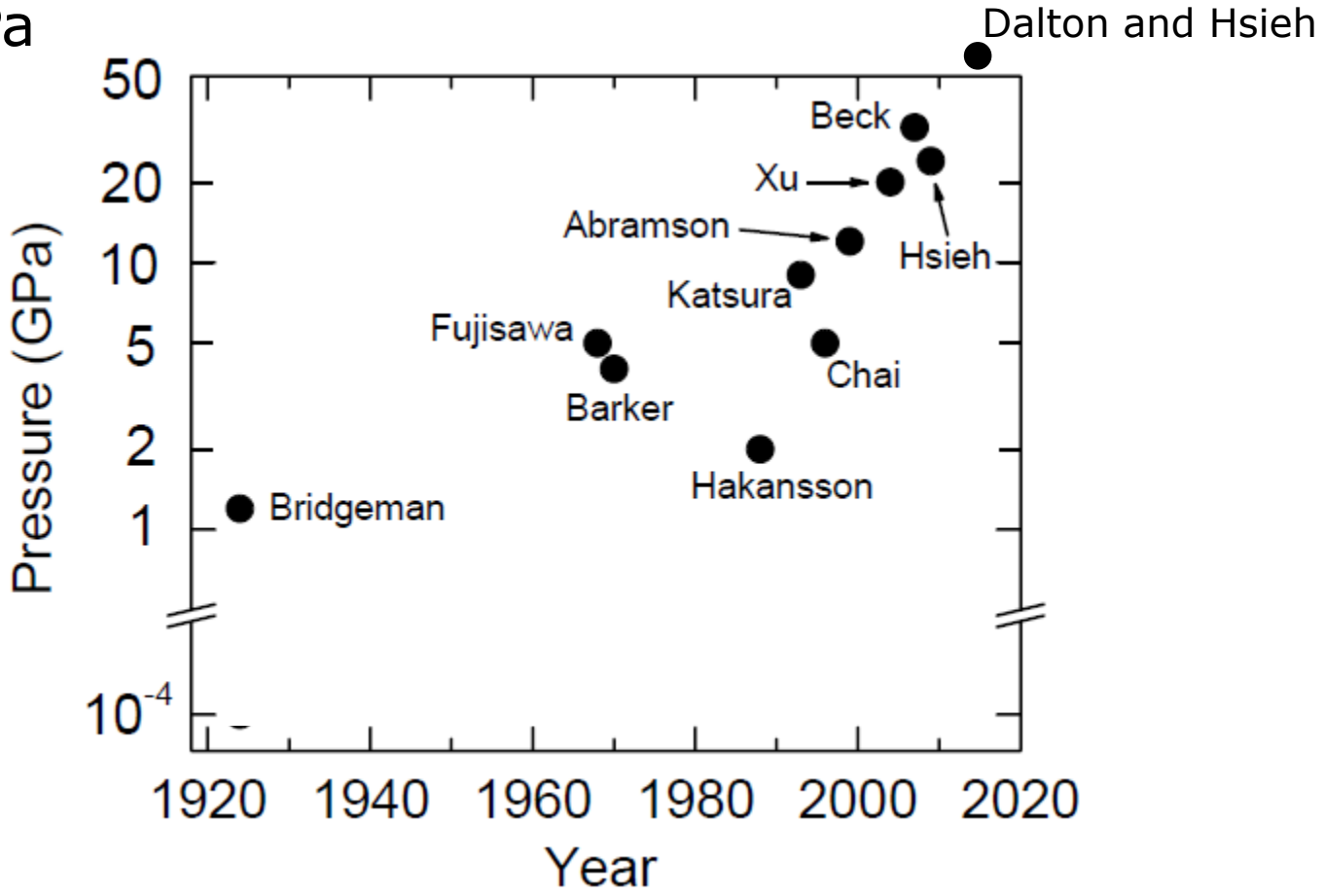


Maximum pressure achieved in thermal conductivity measurements

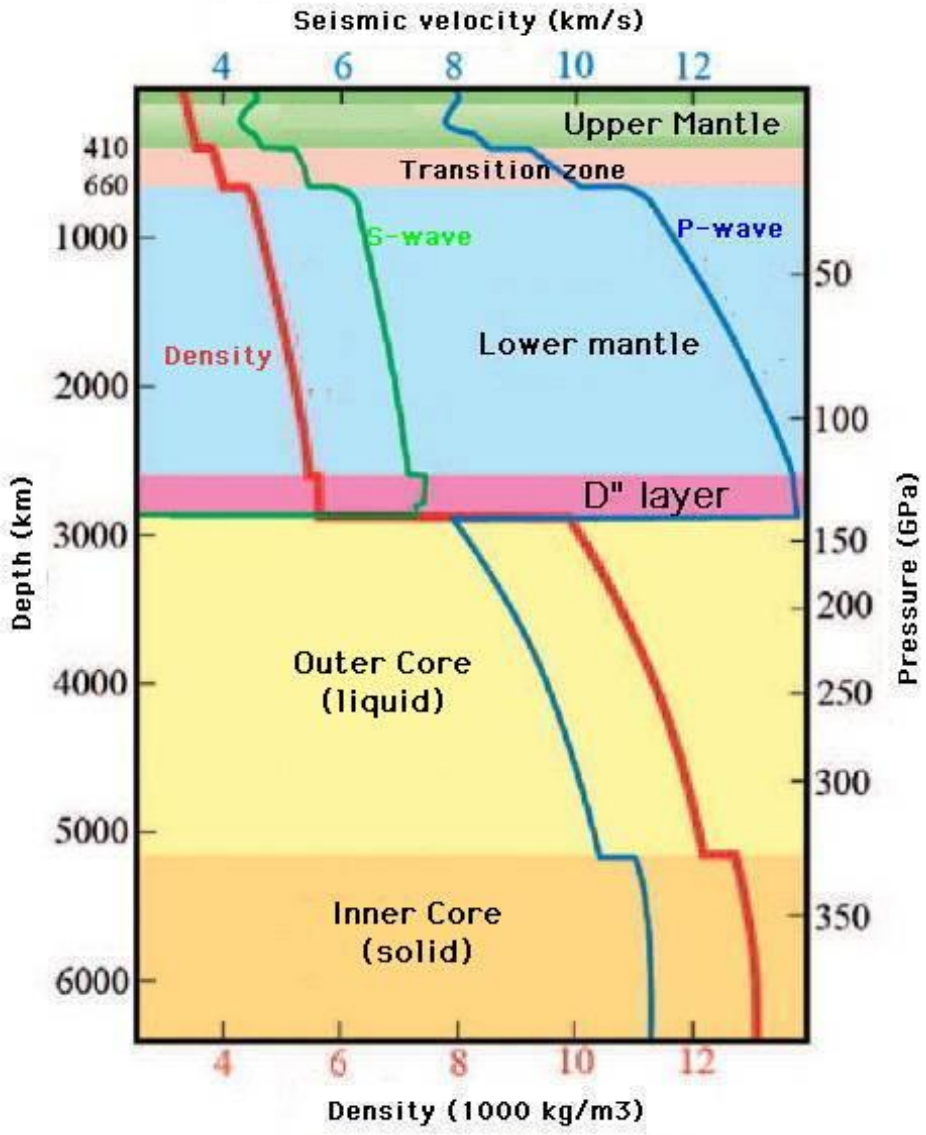
1 atm=bar

1 bar=100 kPa

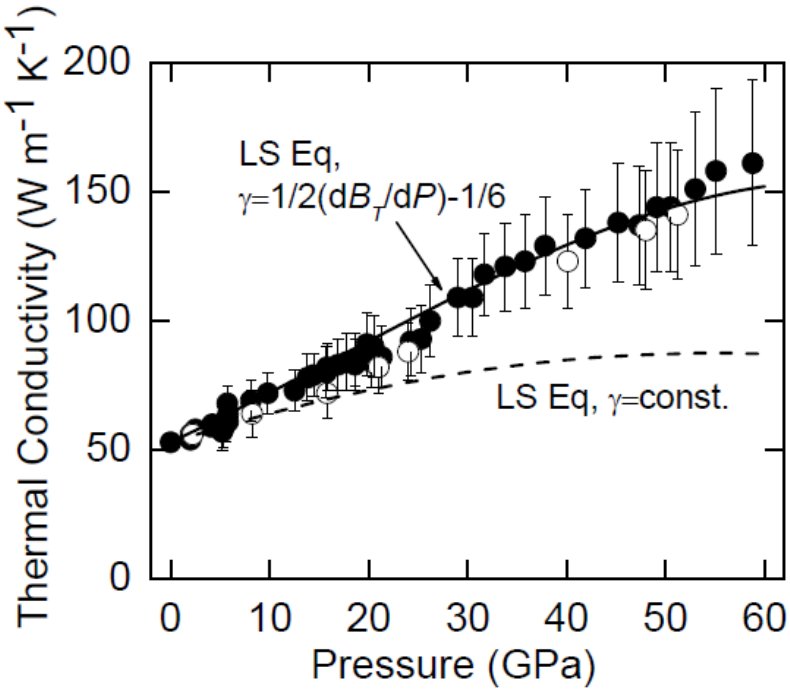
1 Mbar=100 GPa



Core-mantle boundary is ≈135 GPa



TDTR data for MgO

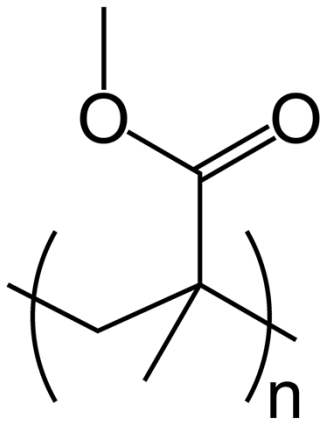


Currently working on (Mg,Fe)O

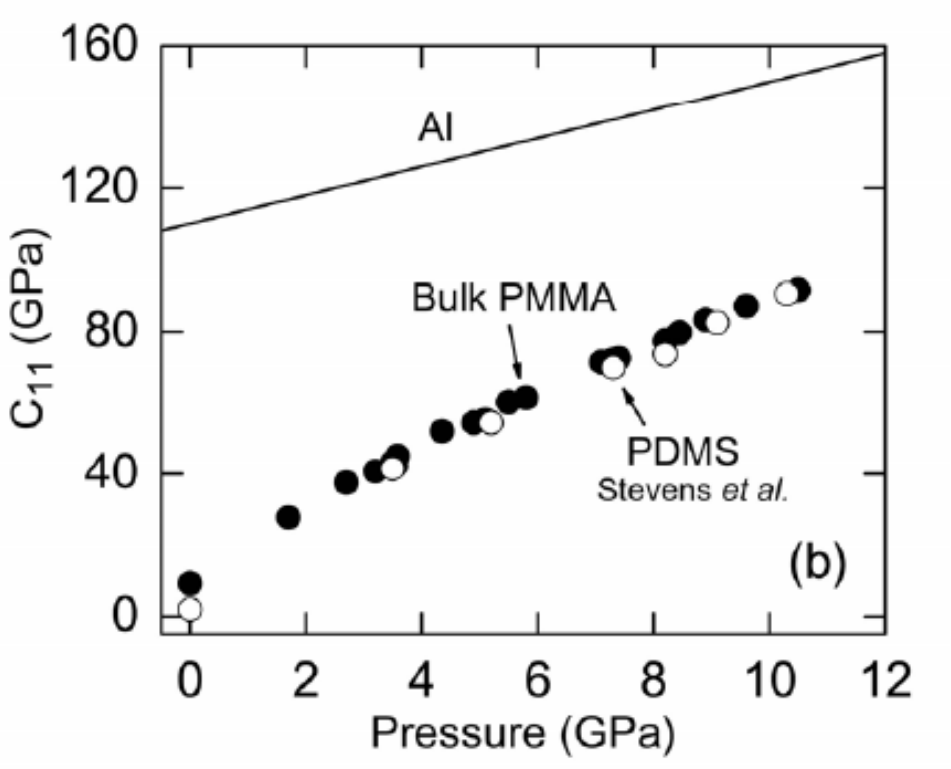
http://my.opera.com/nielsol/blog/2008/11/13/core-mantle-boundary

Test the applicability of the model for glassy polymers

- Polymers combine strong covalent bonds along the backbone (and within the side groups) and weak "non-bonded" interactions between chains.
- At high pressures, this strong inhomogeneity in bond strength is reduced.



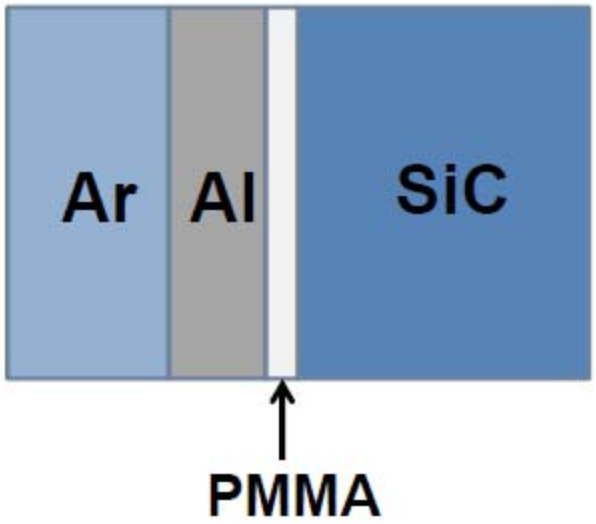
C_{11} data for PMMA from picosecond interferometry



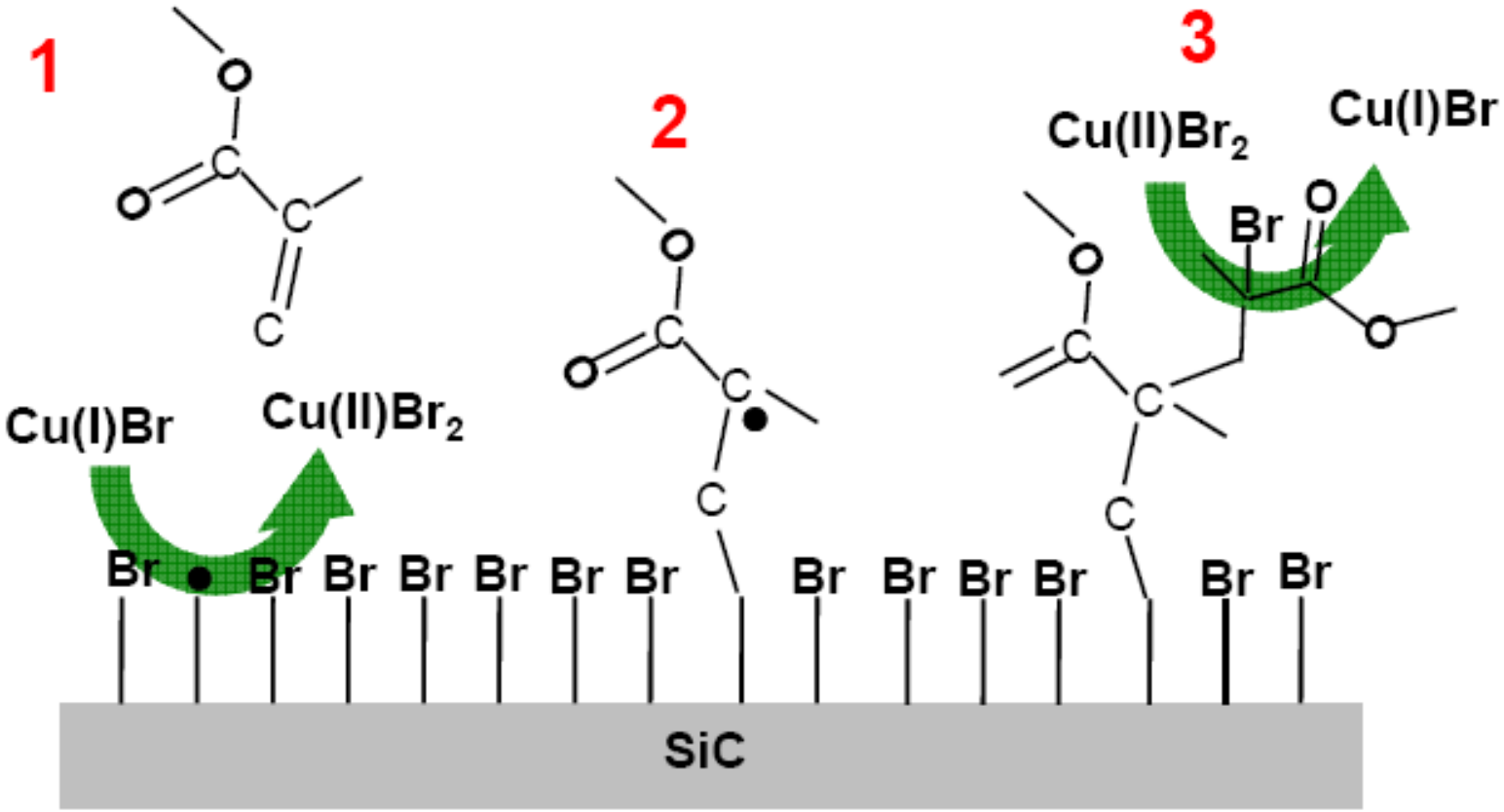
Stevens *et al.*, J. Chem. Phys. 127 104906 (2007)

Need thin (<20 nm) layers of PMMA

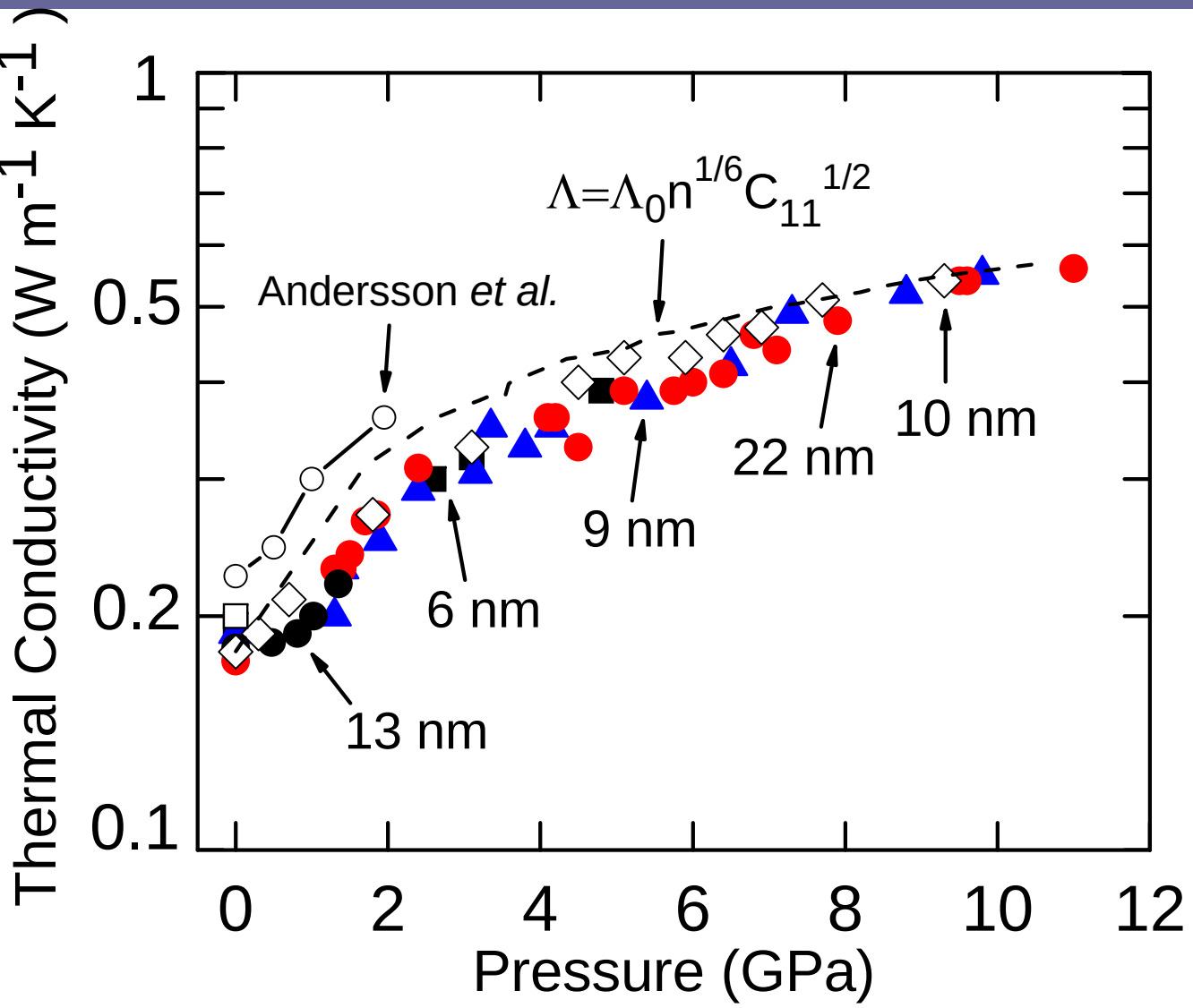
- PMMA thermal conductivity is smaller than the pressure medium (H_2O or Ar)
- For good sensitivity, we need most of the heat to flow through the polymer layer and into the SiC anvil
- Polymer "brushes" provide an elegant solution for controlling the polymer thickness



Nanoscale polymer brushes “grafted from” the SiC anvil



Thermal conductivity of PMMA polymer is independent of thickness and agrees well with the predicted scaling with $(C_{11})^{1/2}$



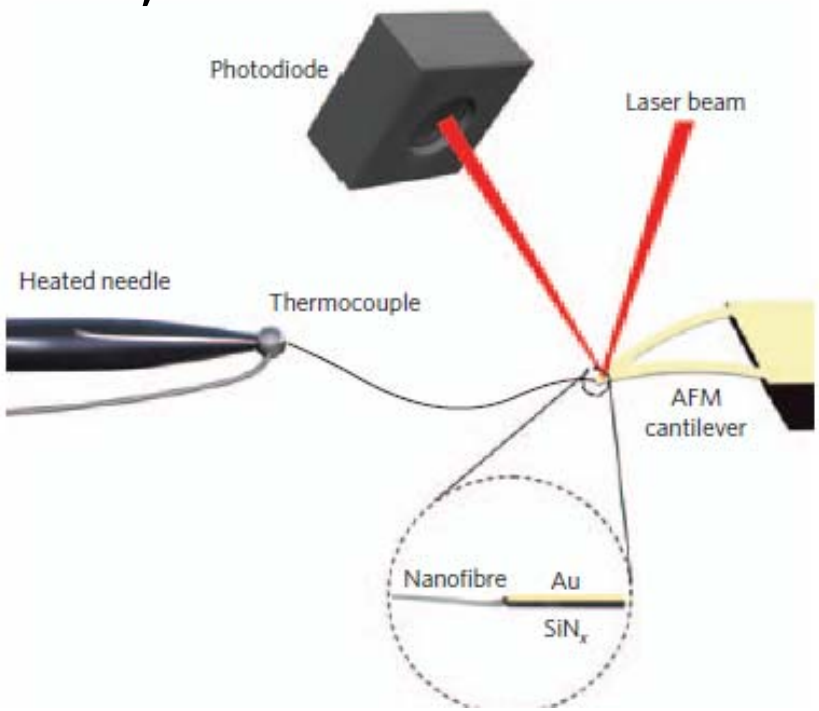
Reports of extremely high thermal conductivity in polymer fibers

- Fujishiro *et al*., Jpn. J. Appl. Phys. (1997) Dyneema polyethylene fibers

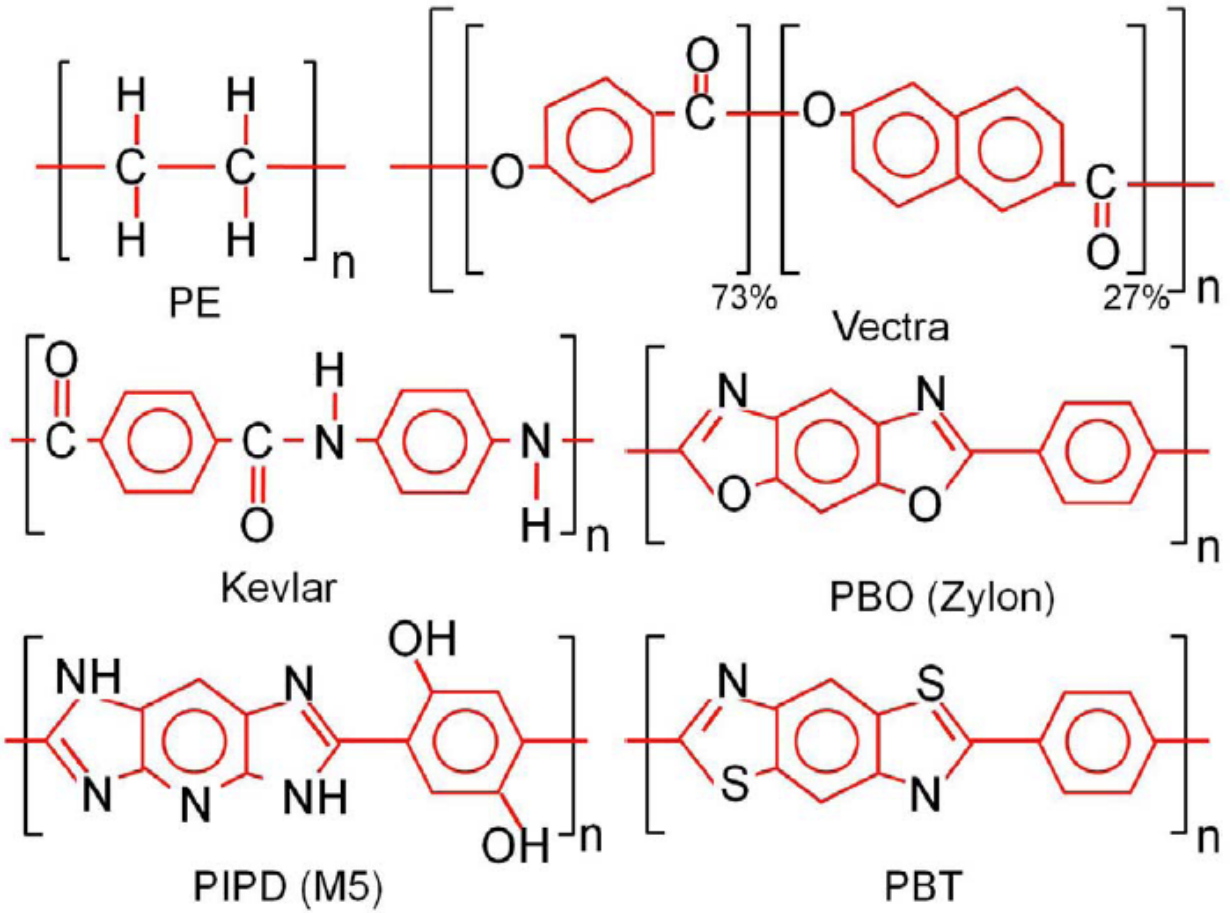
  60 W/m-K

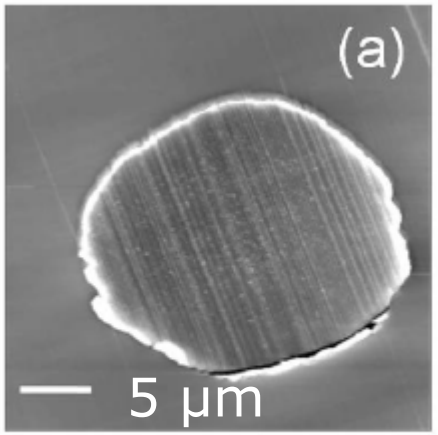
- Shen *et al*., Nature Nanotechnol. (2010) individual polyethylene nanofiber,

  100 W/m-K

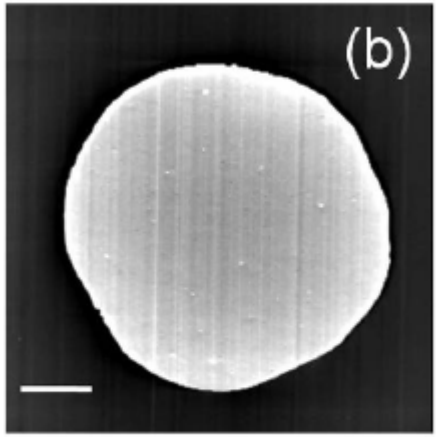


High throughput measurements of polymer fibers by time-domain thermoreflectance





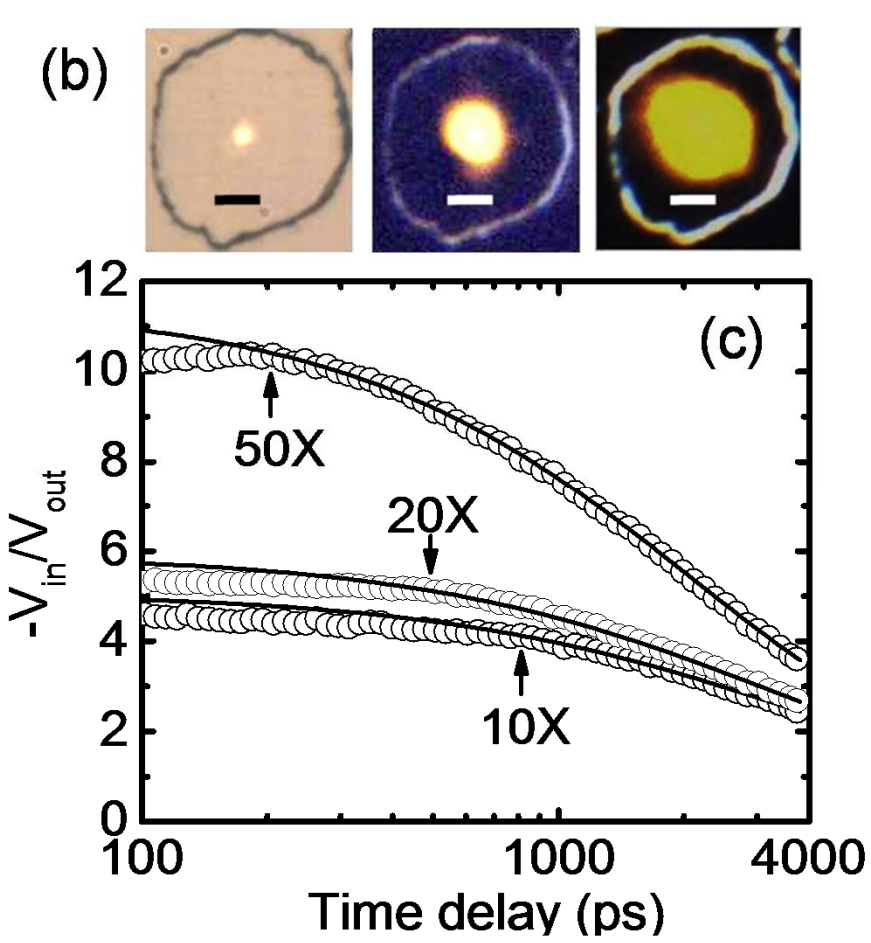
PE (Dyneema)

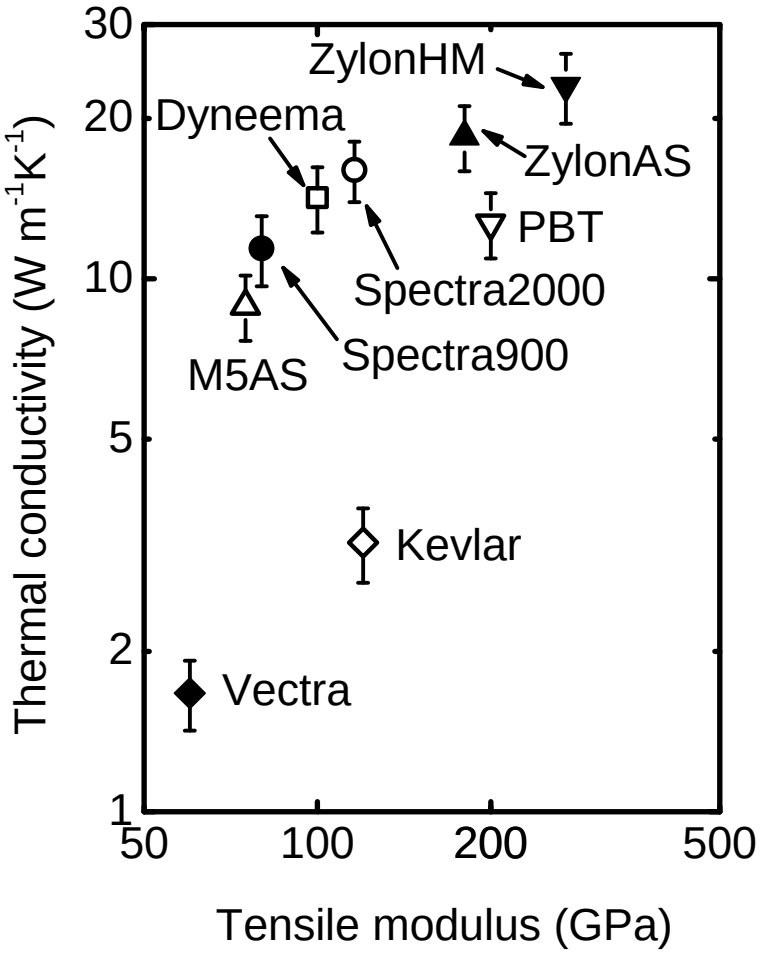


Vectra

Wang *et al*., Macromolecules (2013)

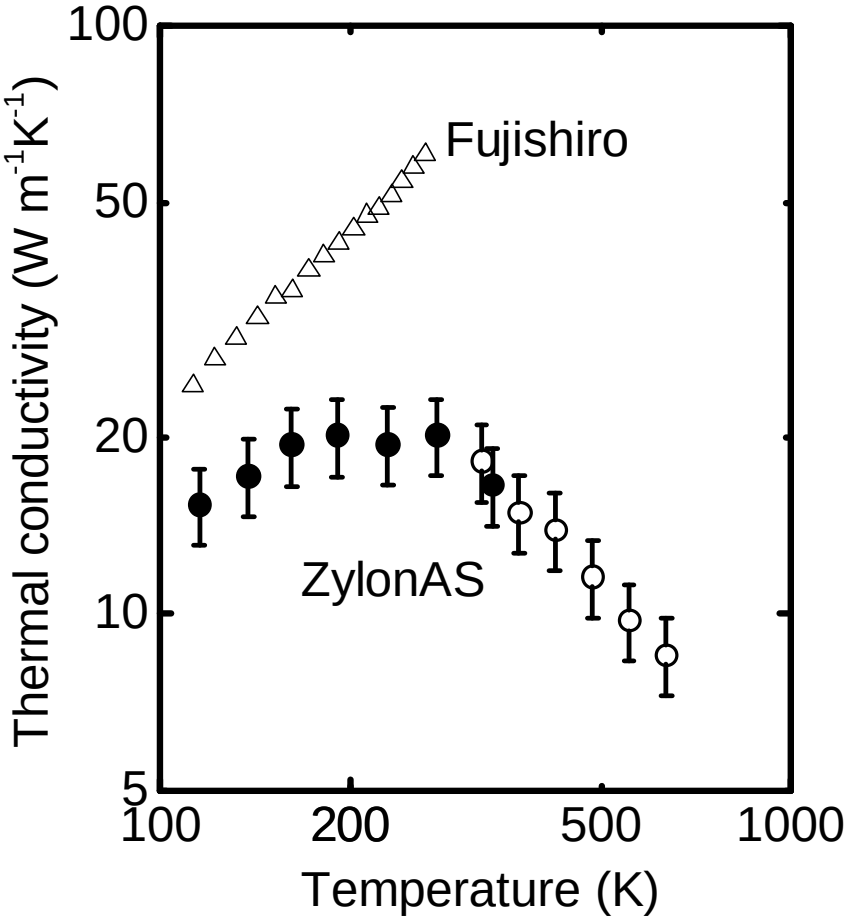
High throughput measurements of polymer fibers by time-domain thermoreflectance

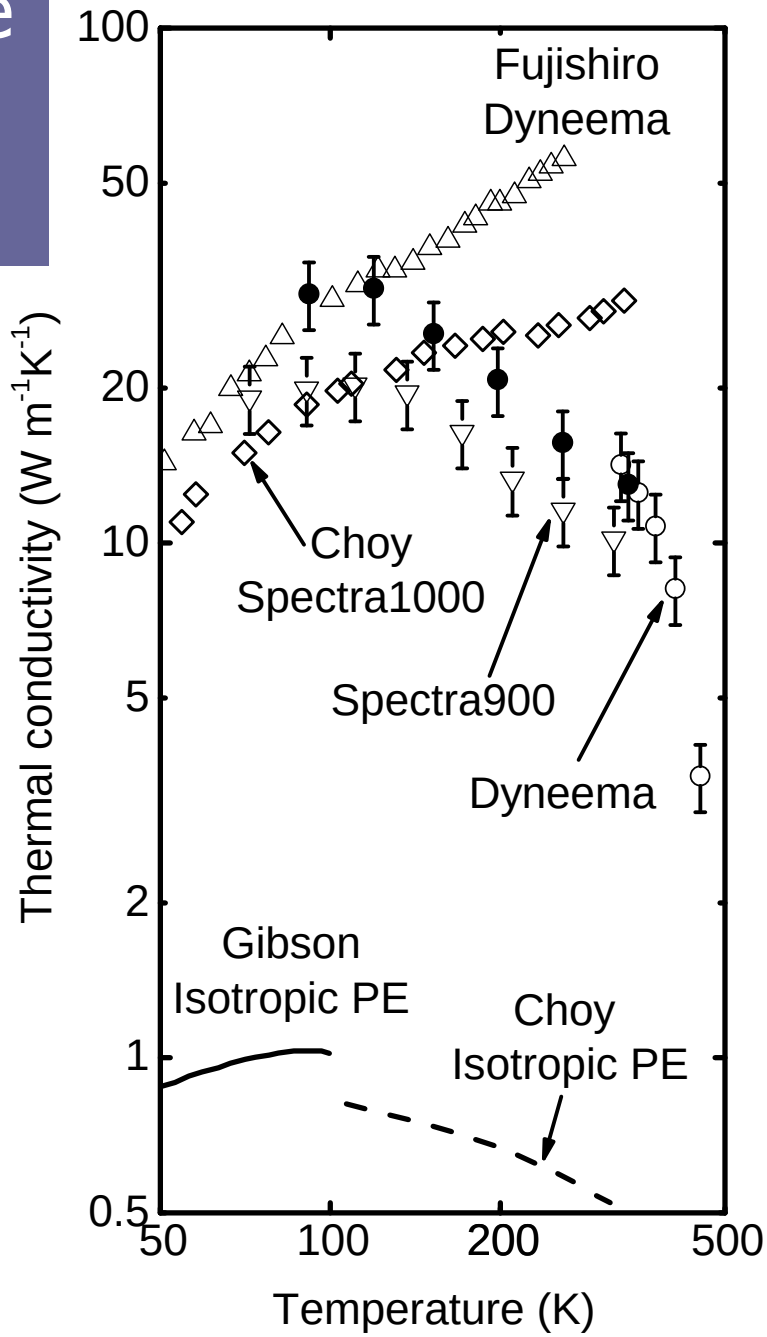




Wang *et al*., Macromolecules (2013)

1/*T* temperature dependence suggests intrinsic behavior governed by anharmonicity





Wang *et al*., Macromolecules (2013)

Work backwards to estimate vibrational state lifetime and mean-free-path

- Assume high velocity longitudinal modes dominate the thermal transport
- Average velocity in the *z*-direction (fiber axis) is c_z.

$$\frac{c_z}{c_x} \gg 1, \left\langle v_z^2 \right\rangle \approx c_z^2 \qquad \Lambda = \left\langle v_z^2 \right\rangle \int C(\omega)\tau(\omega)d\omega$$

- Make the usual Debye approximation but assume that only a small fraction of C is due to longitudinal acoustic modes, $C \approx 0.06$ J cm^{-3} K^{-1} for PBO
- With $v_z = 10^4$ m s^{-1}: $\tau \approx 3$ ps and $v_z\tau \approx 30$ nm

Wang *et al*., Macromolecules (2013)

Summary

- Working to push the lower and upper limits of thermal conduction in molecular materials
  - Current range of reproducible results is a factor of 400: 0.05 W m^{-1} K^{-1} for PCBM/PCBNB to 20 W m^{-1} K^{-1} for Zylon fiber
- Mechanisms are not yet clear in either case.
  - Why is the thermal conductivity of PCBNB lower than both C60 and polymer?
  - 1^{st} observation of 1/T dependence in high modulus fibers suggests intrinsic behavior, i.e., defects are not important. Is this true?
- High hydrostatic pressure provide a powerful approach for systematically modifying vibrational states and testing models.