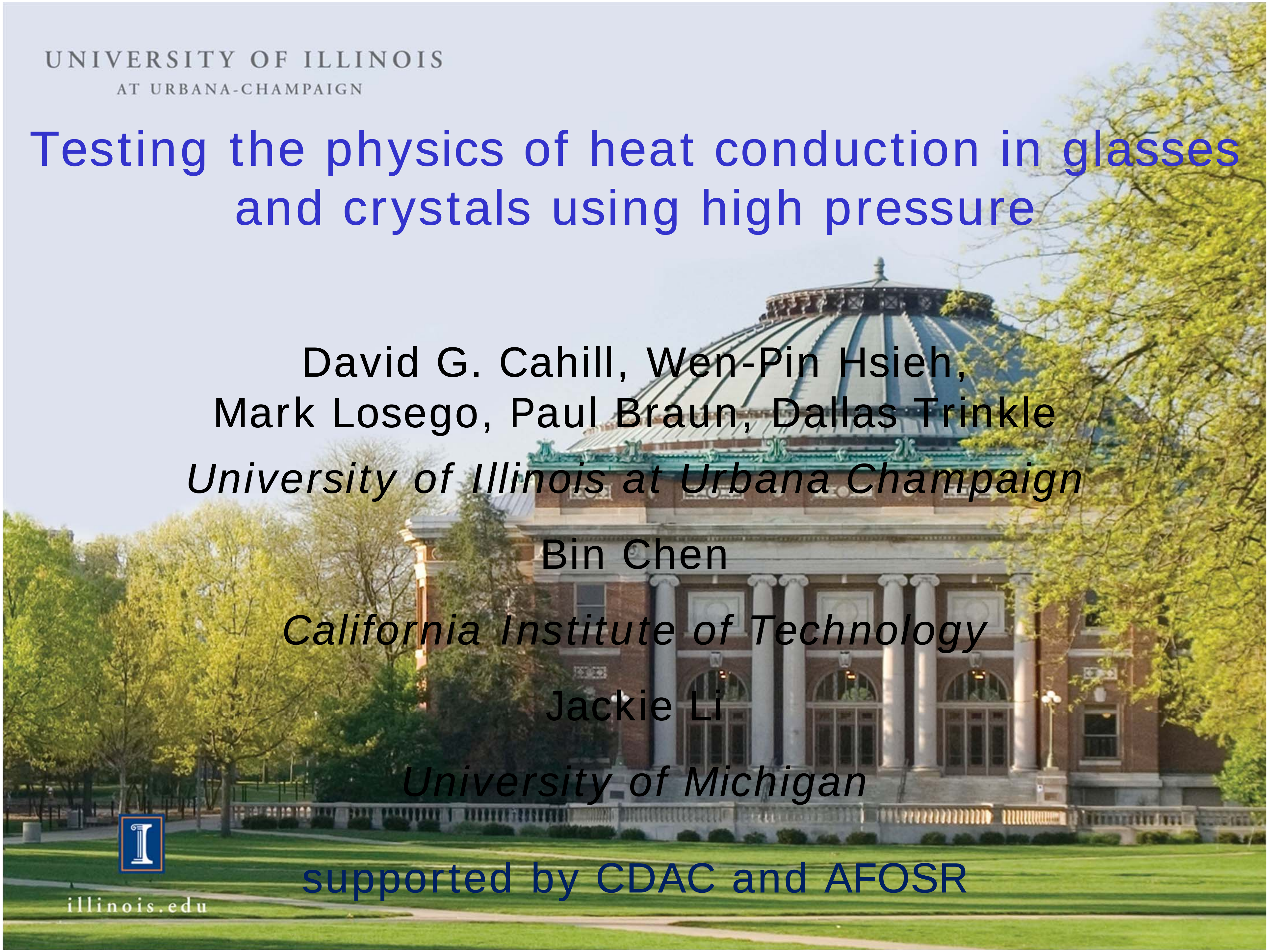

UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Testing the physics of heat conduction in glasses and crystals using high pressure

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The story...

- Use high pressure (gem anvil cells) to modify vibrational densities of states and lifetimes
- Measure the change in thermal conductivity by time-domain thermoreflectance (TDTR)
- Test classic models for heat conduction by lattice vibrations
  - Minimum thermal conductivity model for disordered materials

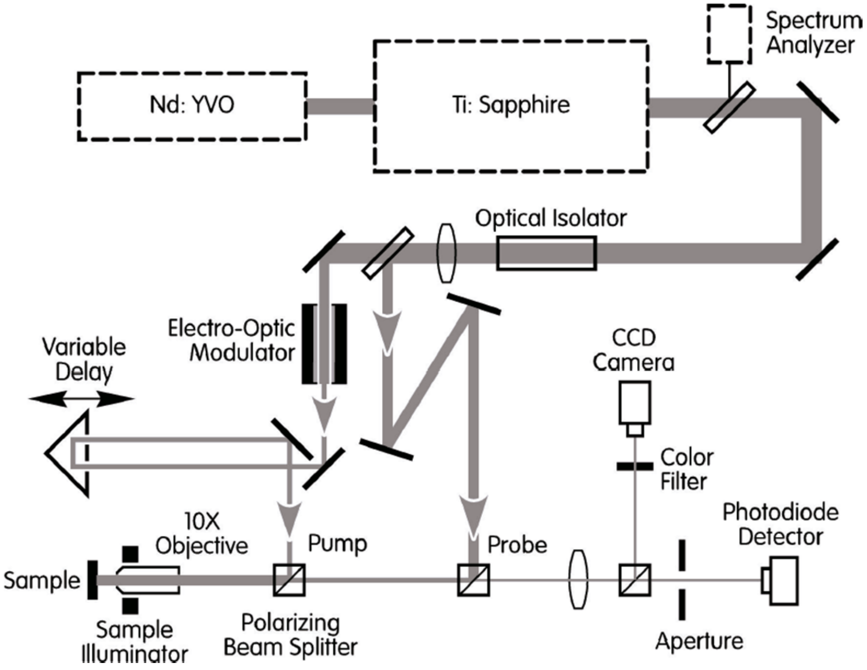
    PMMA polymer

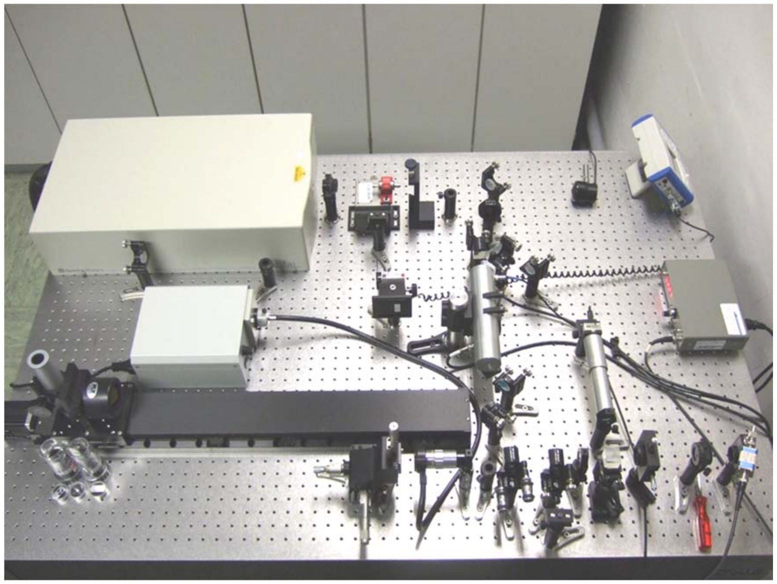
  - Leibfried-Schlömann equation for perfect crystals

    water ice VII

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

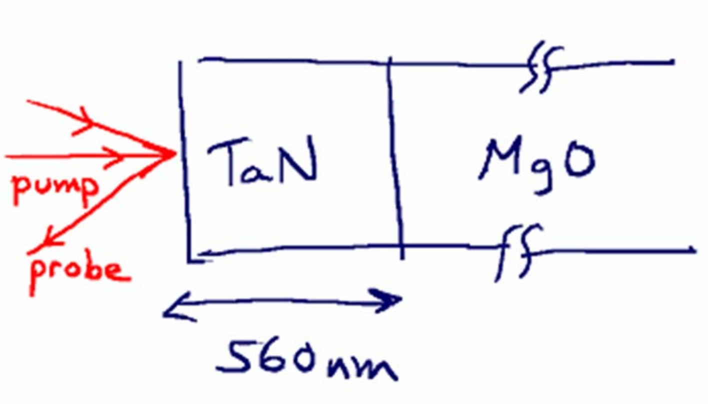


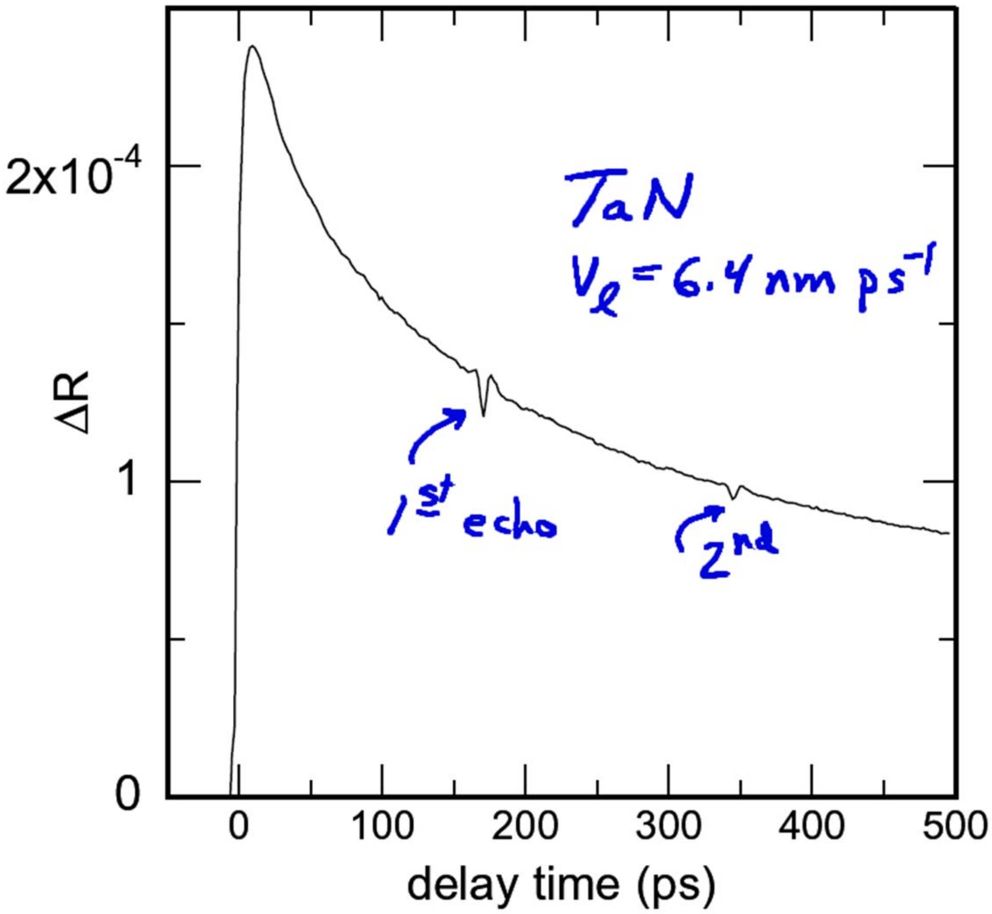


Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

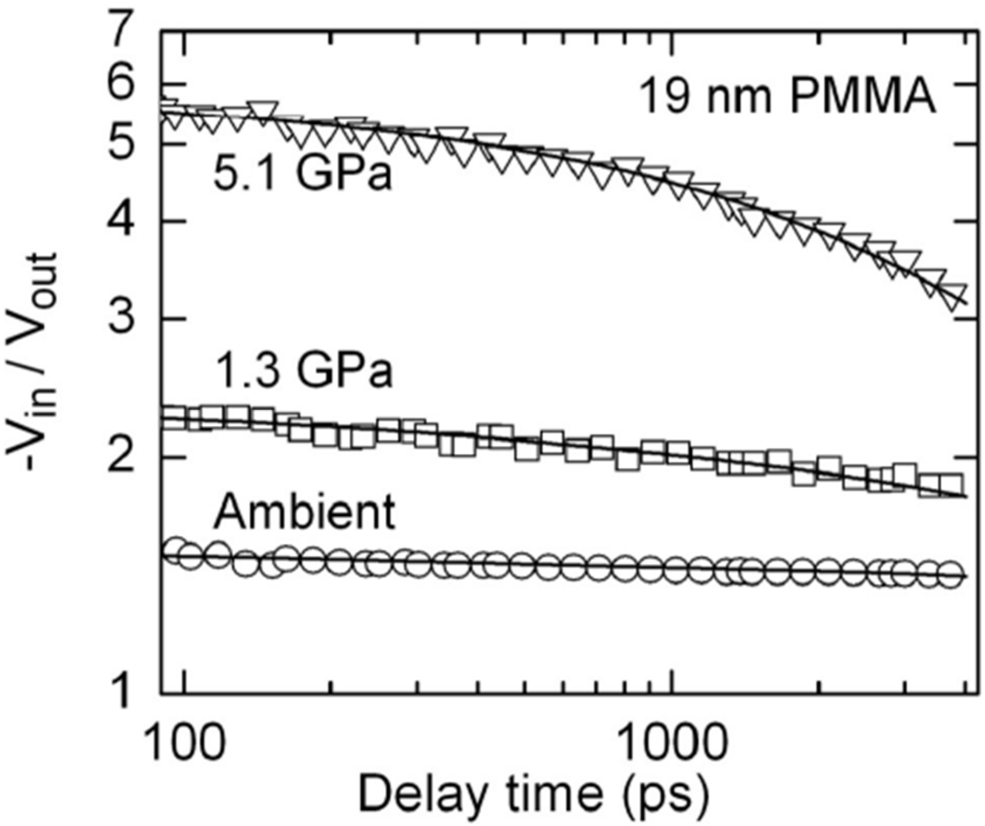
psec acoustics and time-domain thermoreflectance

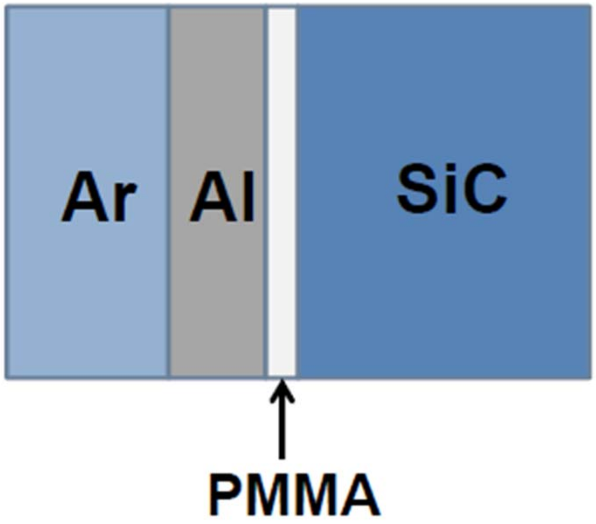
- Optical constants and reflectivity depend on strain and temperature
- Strain echoes give acoustic properties or film thickness
- Thermoreflectance dR/dT gives thermal properties





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





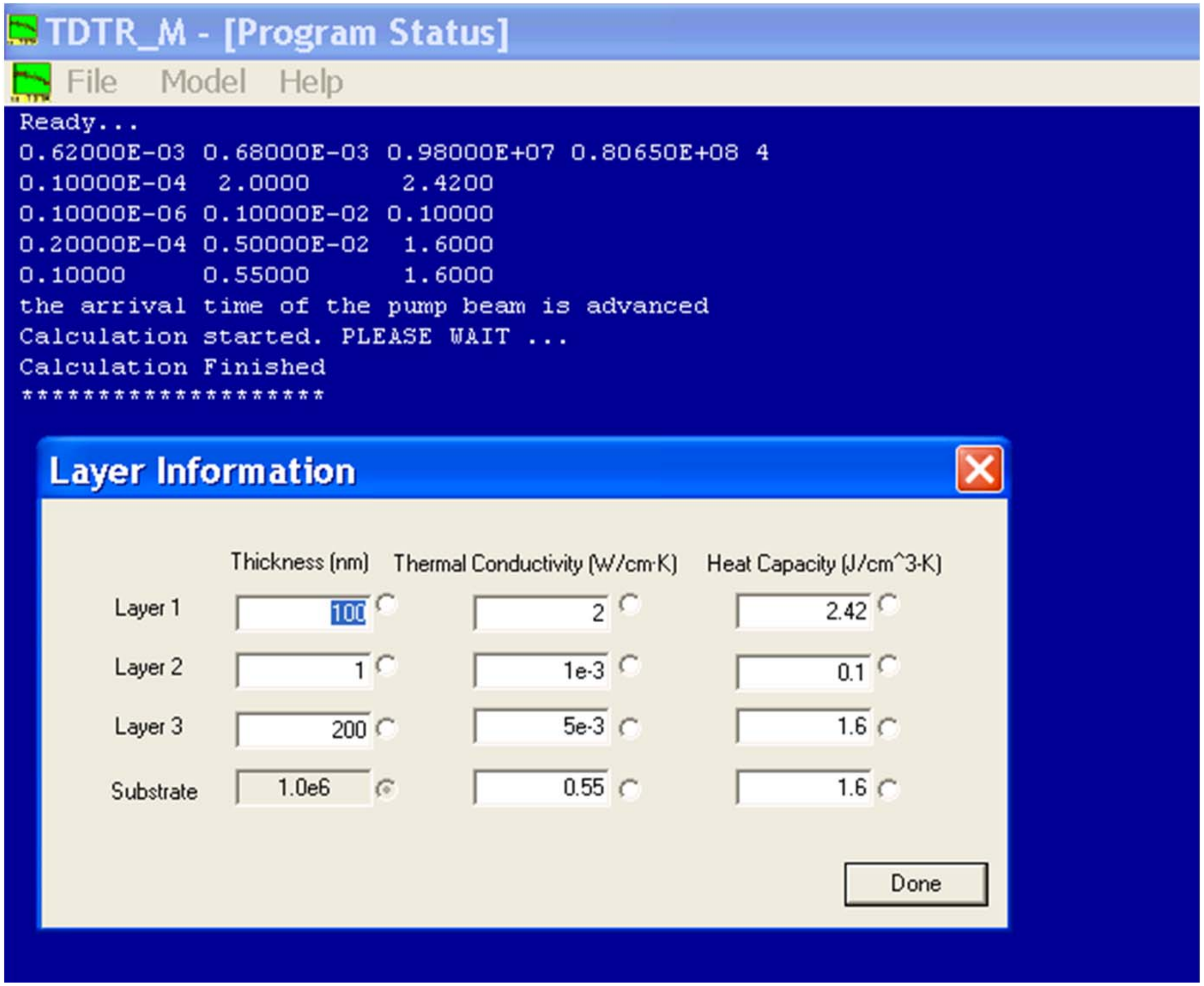
Thermal Model:

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

Windows software

author: Catalin Chiritescu,

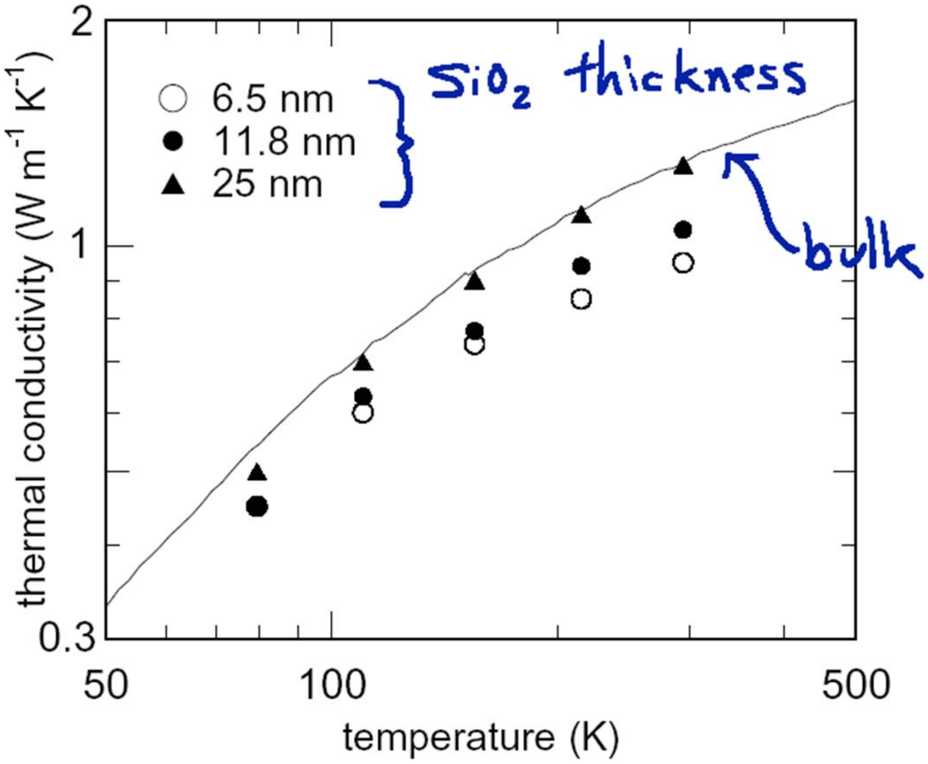
users.mrl.uiuc.edu/cahill/tcdata/tdtr_m.zip

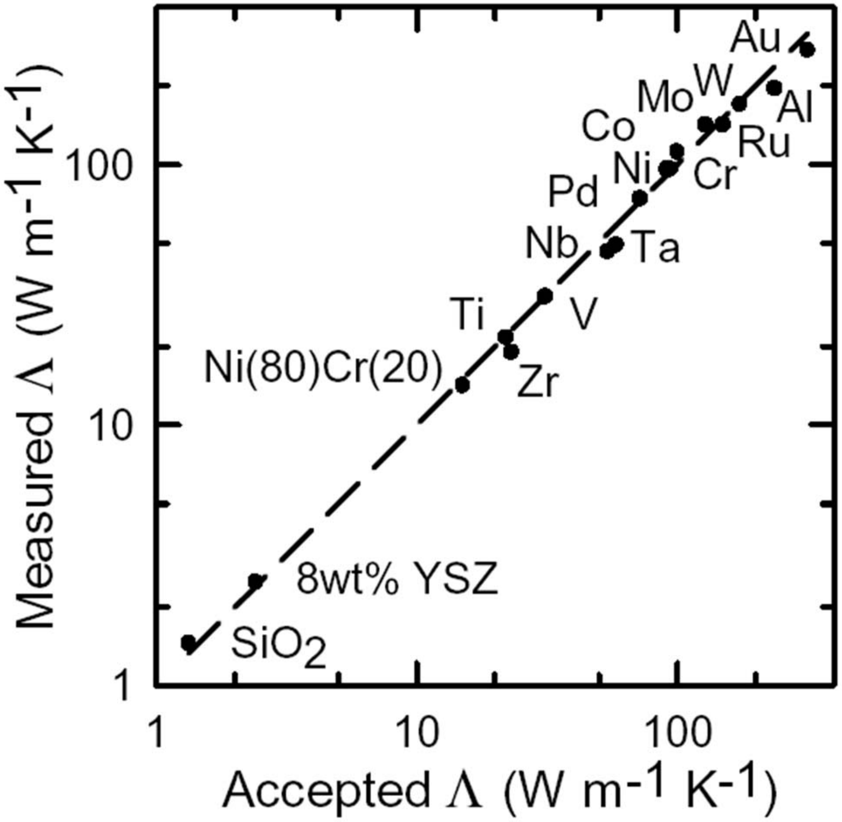


```
Ready...
0.62000E-03 0.68000E-03 0.98000E+07 0.80650E+08 4
0.10000E-04  2.0000       2.4200
0.10000E-06 0.10000E-02 0.10000
0.20000E-04 0.50000E-02  1.6000
0.10000     0.55000      1.6000
the arrival time of the pump beam is advanced
Calculation started. PLEASE WAIT ...
Calculation Finished
********************
```

	Thickness (nm)	Thermal Conductivity (W/cm-K)	Heat Capacity (J/cm^3-K)
Layer 1	100 ○	2 ○	2.42 ○
Layer 2	1 ○	1e-3 ○	0.1 ○
Layer 3	200 ○	5e-3 ○	1.6 ○
Substrate	1.0e6 ●	0.55 ○	1.6 ○

TDTR: Flexible, convenient, and accurate



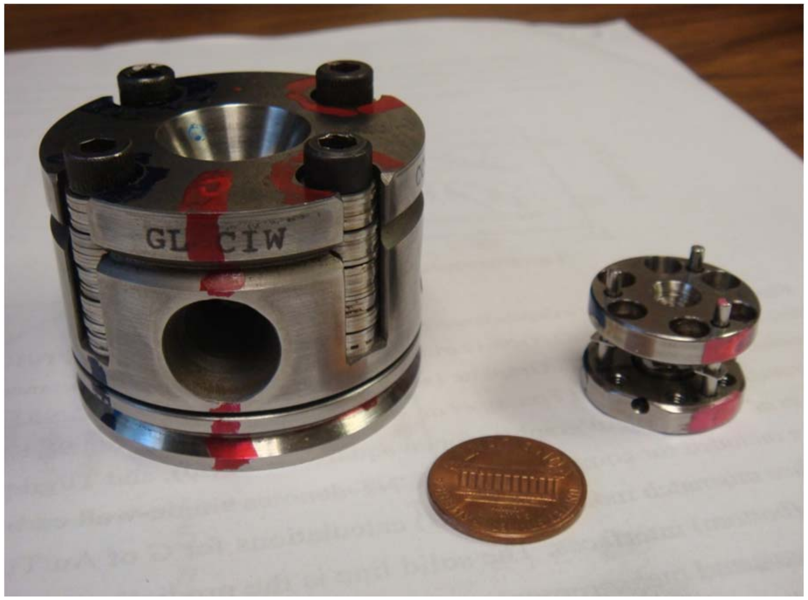


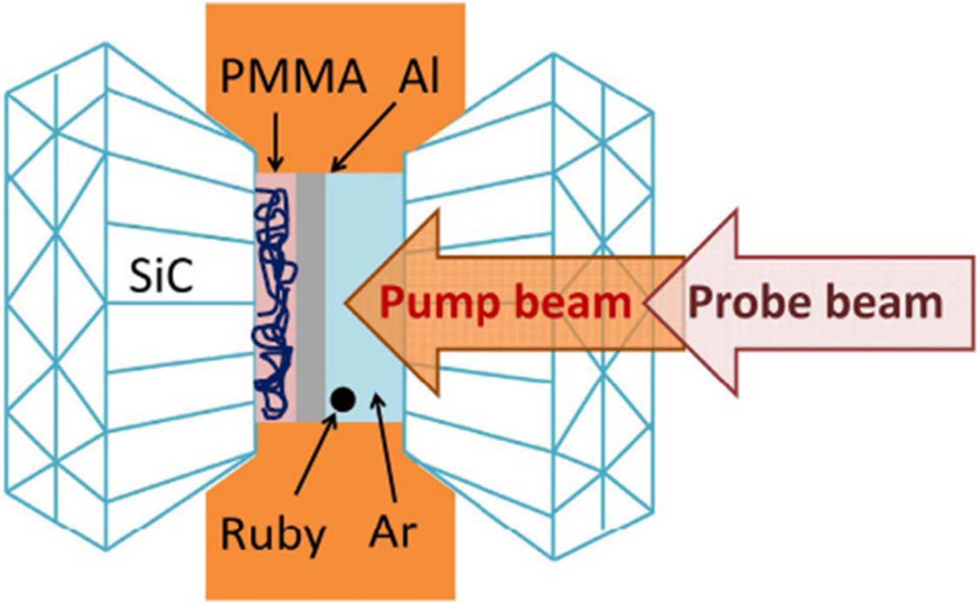
Costescu *et al*., PRB (2003)

Zhao *et al*., Materials Today (2005)

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

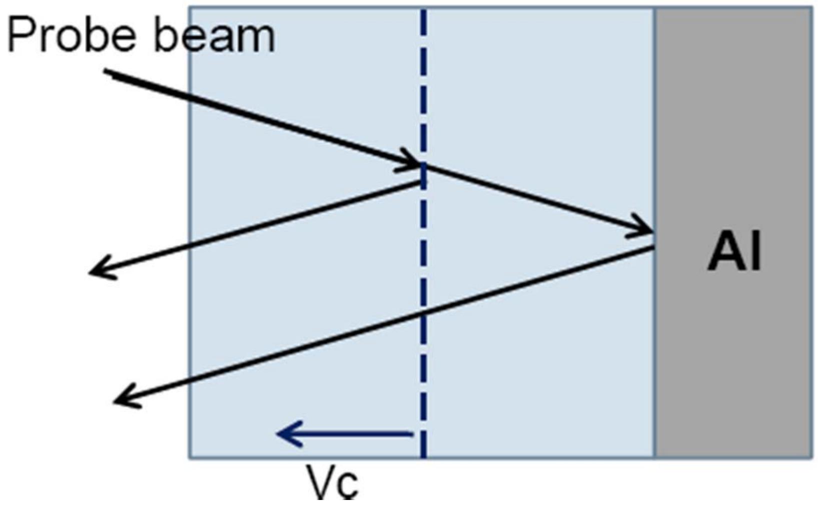
Diamond anvil cell



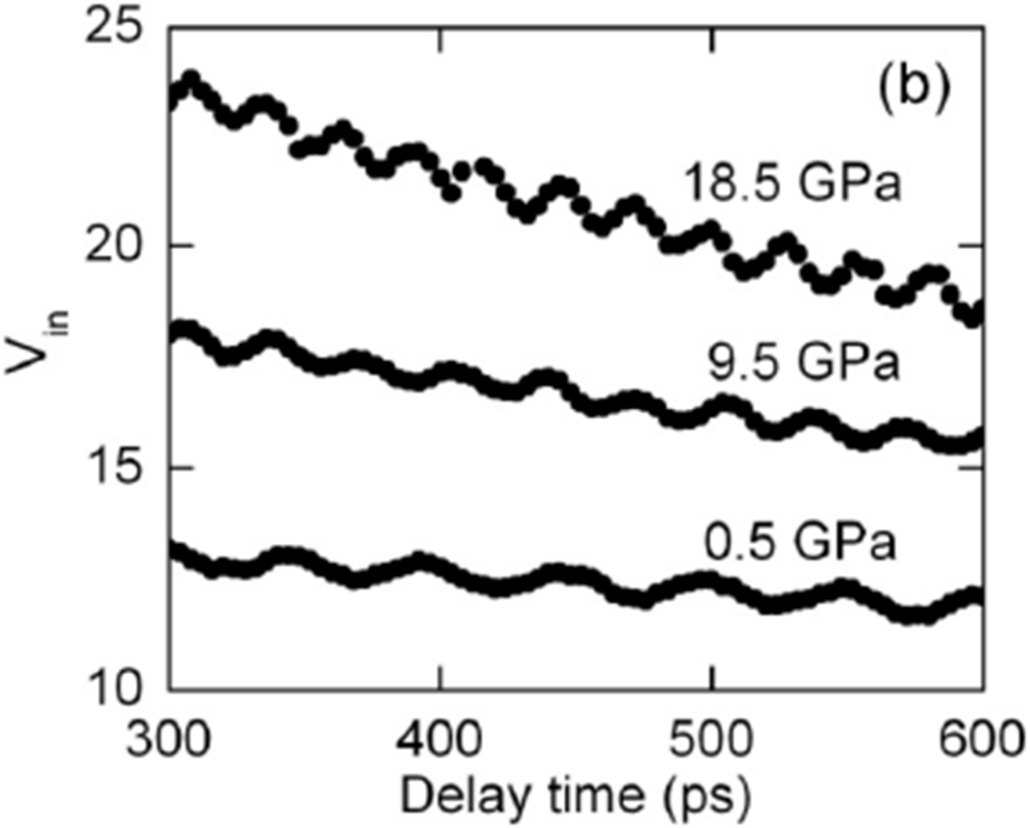


Time-domain stimulated Brillouin scattering (picosecond interferometry)

muscovite mica



muscovite mica



Hsieh *et al*., PRB (2009)

Model of the minimum thermal conductivity

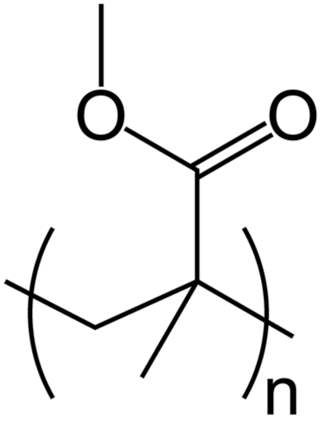
- Einstein (1911): random walk of thermal energy
- Not good for crystals: Debye (1914)
- but does work for amorphous solids, Birch and Clark (1940); Kittel (1948)
- and crystals with strong atomic-scale disorder, Slack (1979); Cahill and Pohl (1988).

High T limit

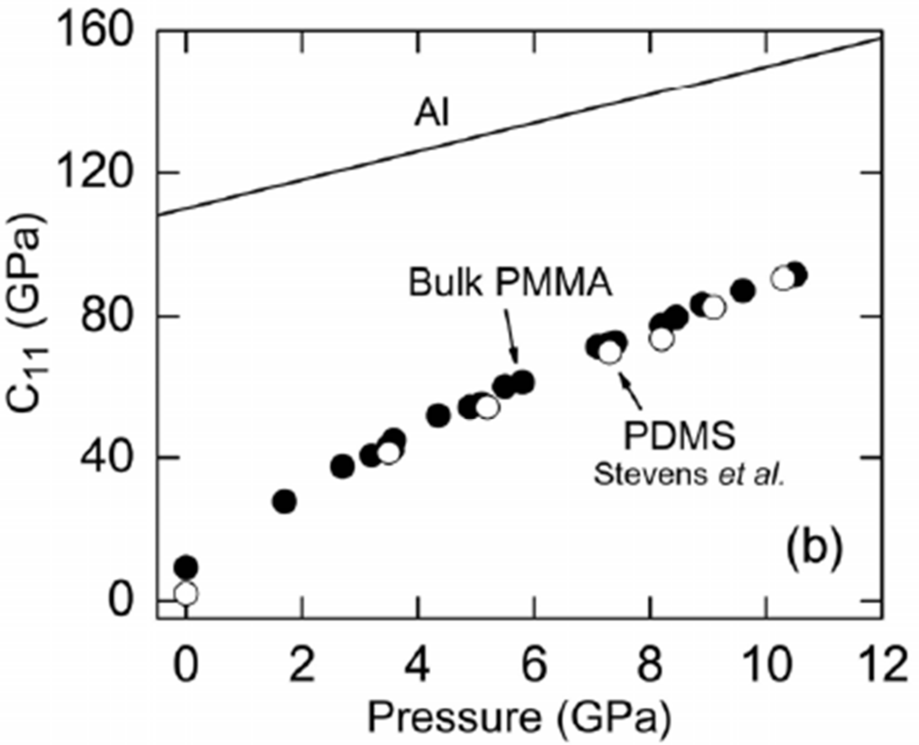
$$\Lambda_{min} = 0.40 k_B n^{2/3} (v_l + 2v_t)$$

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.



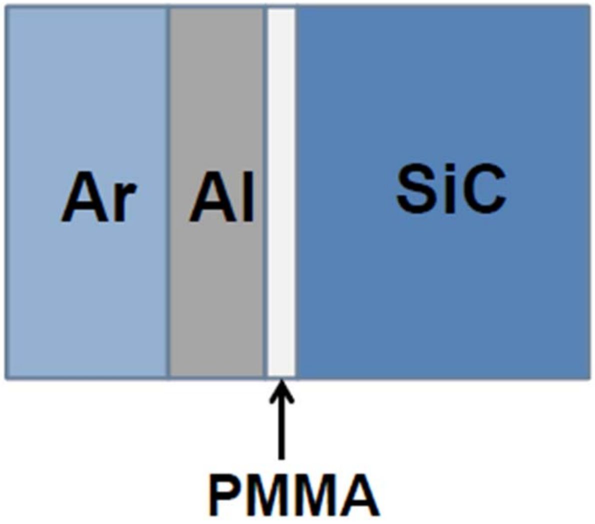
C_{11} data for PMMA from picosecond interferometry



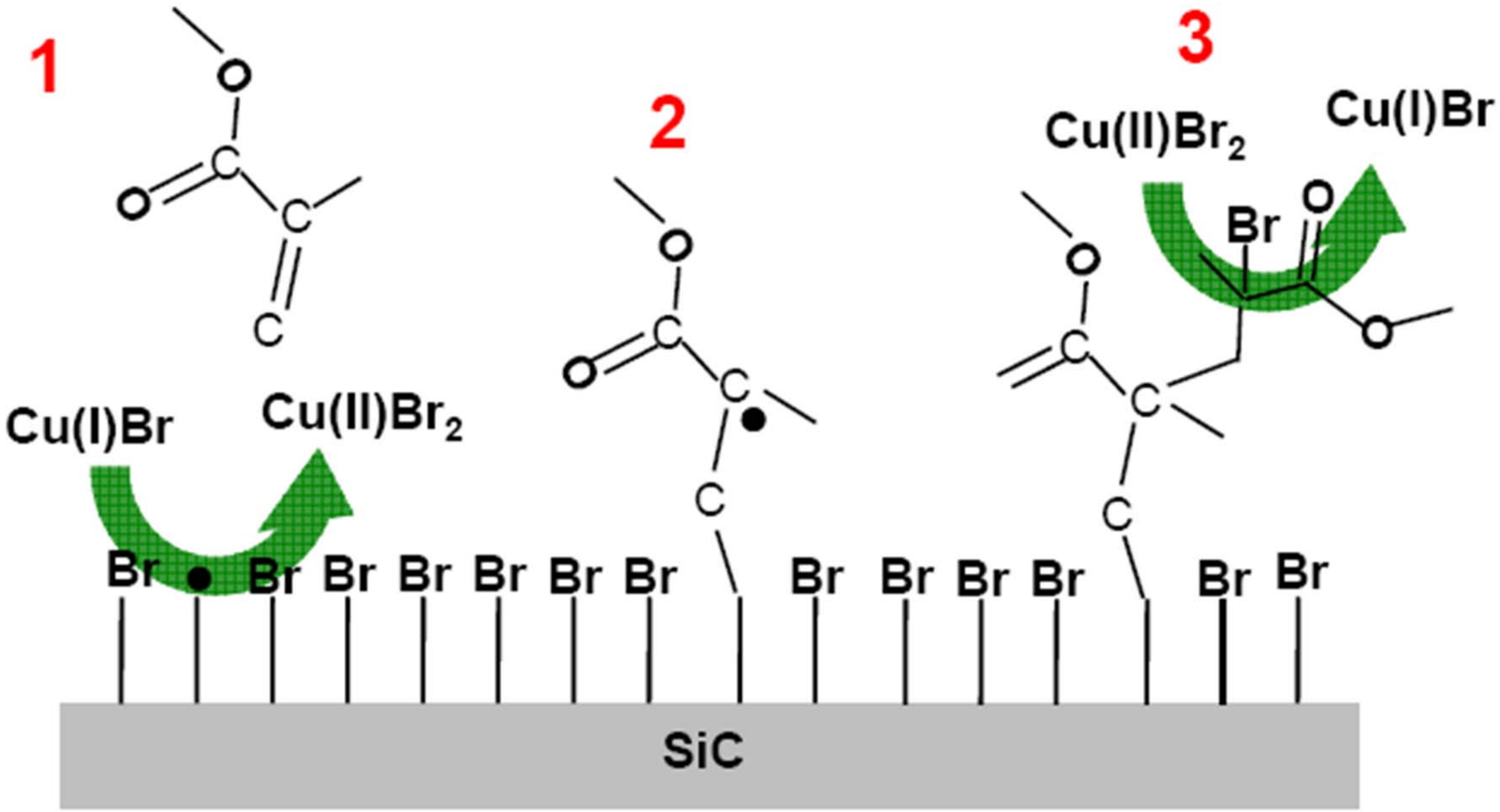
Stevens *et al.*, J. Chem. Phys. 127 104906 (2007)

Need thin (<20 nm) layers of PMMA

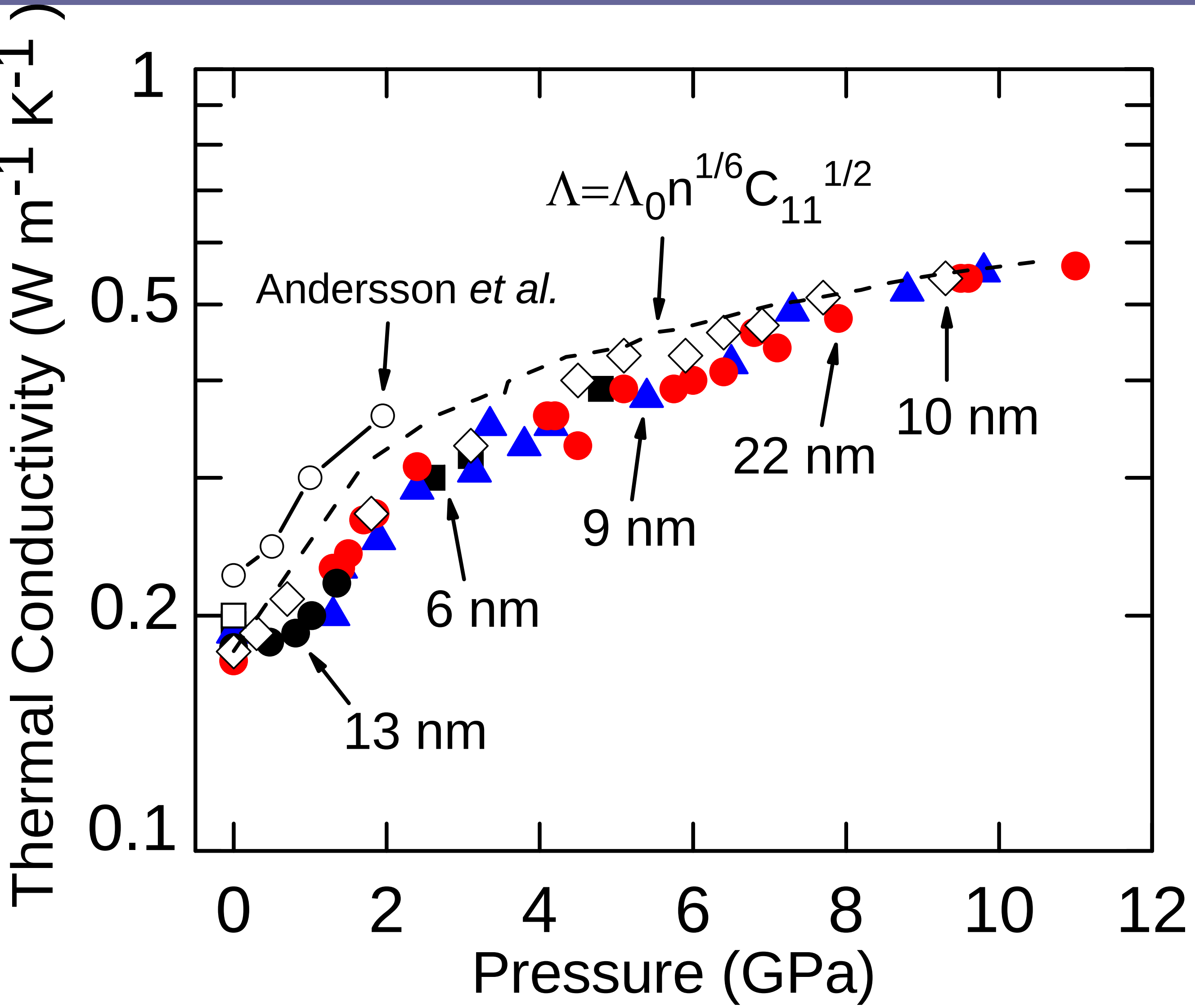
- PMMA thermal conductivity is smaller than the pressure medium (H_2O or Ar)
- For good sensitivity, we need most of the heat to flow through the polymer layer and into the SiC anvil
- Polymer “brushes” provide an elegant solution for controlling the polymer thickness



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 $(C_{11})^{1/2}$



For good crystals, the theory is more complicated but should be correct if optical phonons are not too important

- Leibfried-Schlömann equation
  - acoustic phonons dominant heat carriers
  - three phonon anharmonic scattering between acoustic modes controls phonon mean-free-path

$$\Lambda = f\,\frac{V^{1/3}\omega_D^3}{\gamma^2 T}$$

$V =$ molecular volume

$\omega =$ Debye frequency

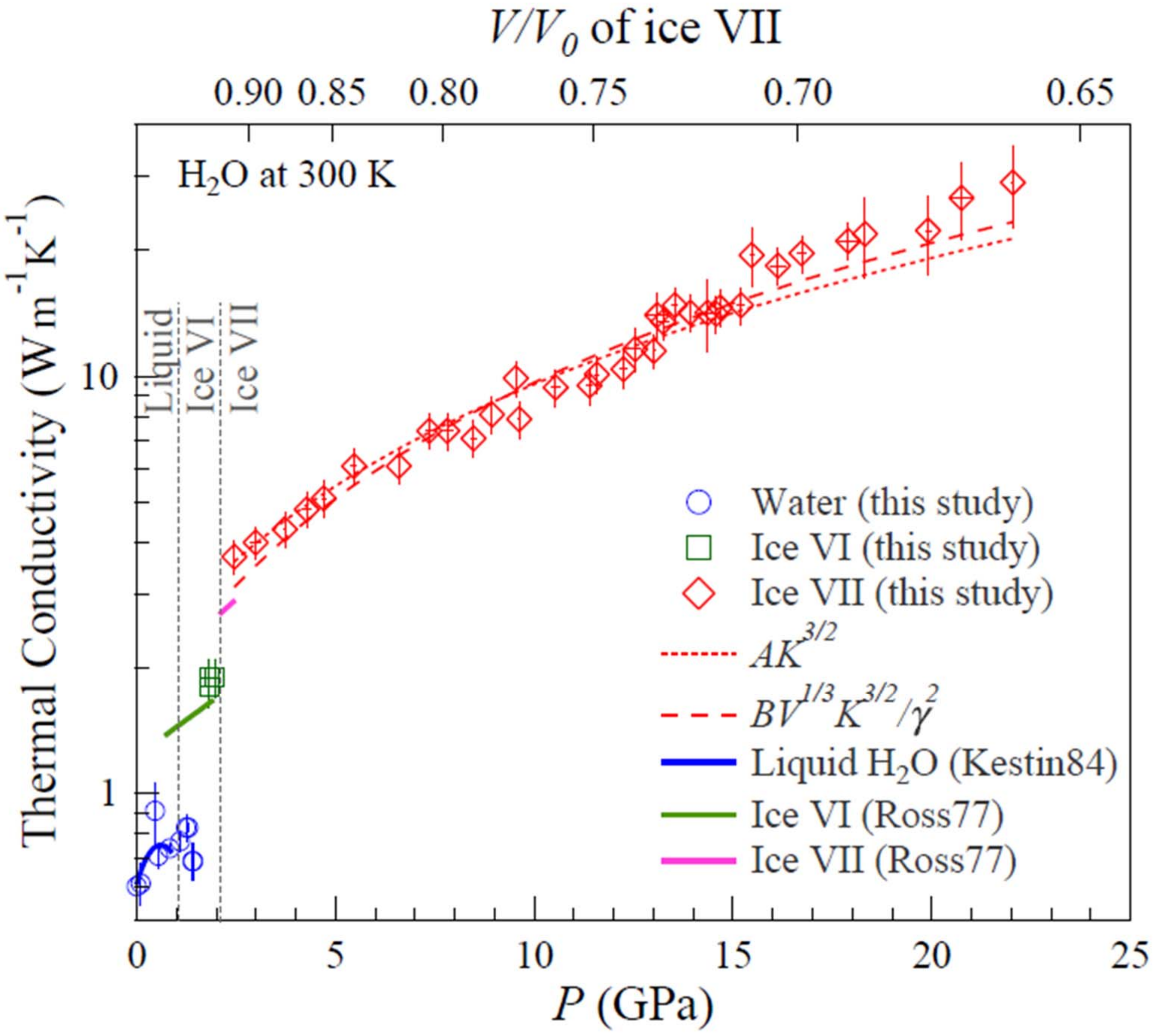
$\gamma =$ Grüneisen parameter

Now test a crystal: water ice VII

- Experimental details are complicated

1. coat thin mica substrate with Al
2. measure mica with Ar pressure medium
3. use published MD simulation of Ar thermal conductivity to analyze the data for mica
4. measure again with H_2O as the pressure medium
5. Use simulation to calculate changes in H_2O heat capacity per unit volume (result: essentially constant)
6. Repeat a few times...

Good agreement with LS equation over wide range of compression



Summary

- Time domain thermoreflectance (TDTR) is a powerful method for measuring thermal conductivity under extreme conditions.
- Pressure dependence of PMMA polymer in good agreement with the model of the minimum thermal conductivity
  - Polymers do not resemble the atomic solids the model was originally intended for. Why is this model is so robust?
- Pressure dependence of ice VII in good agreement with Leibfried-Schlömann equation
  - Optical phonons are not an important factor for thermal conductivity of water ice either as carriers or scattering mechanisms. Will this be true for oxide minerals?