Testing the physics of heat conduction using high pressure: crystals, glasses, and interfaces

David G. Cahill, Wen-Pin Hsieh,
Mark Losego, Austin Lyons,
Paul Braun, Dallas Trinkle, Eric Pop

University of Illinois at Urbana Champaign

Bin Chen

*California Institute of Technology*

Jackie Li

University of Michigan

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 crystals

    water ice VII

  - Diffuse-mismatch model for interfaces

    Al/graphene/Si

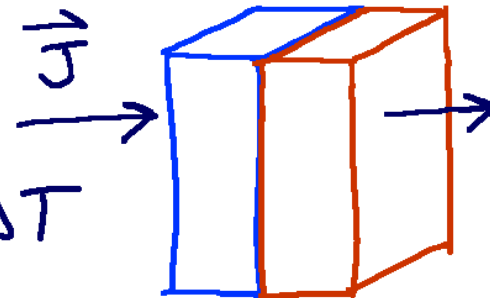# Thermal conductivity and interface thermal conductance

- Thermal conductivity Λ is a property of the continuum

$$\vec{J} = -\Lambda \vec{\nabla} T$$
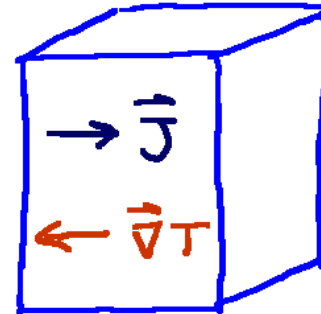
- Thermal conductance (per unit area) G is a property of an interface

$$J = G \Delta T$$

ΔT at interface

Thermal conductivity and interface thermal conductance

- Both properties are difficult to understand and control because they are integral properties.

- For example, simplest case of thermal conductivity where resistive scattering dominates

$$\Lambda = 1/3 \int C(\omega) \ v(\omega) \ \ell(\omega) \ d\omega$$

$C(\omega)$ = heat capacity of phonon mode

$v(\omega)$ = group velocity

$\ell(\omega)$ = mean-free-path

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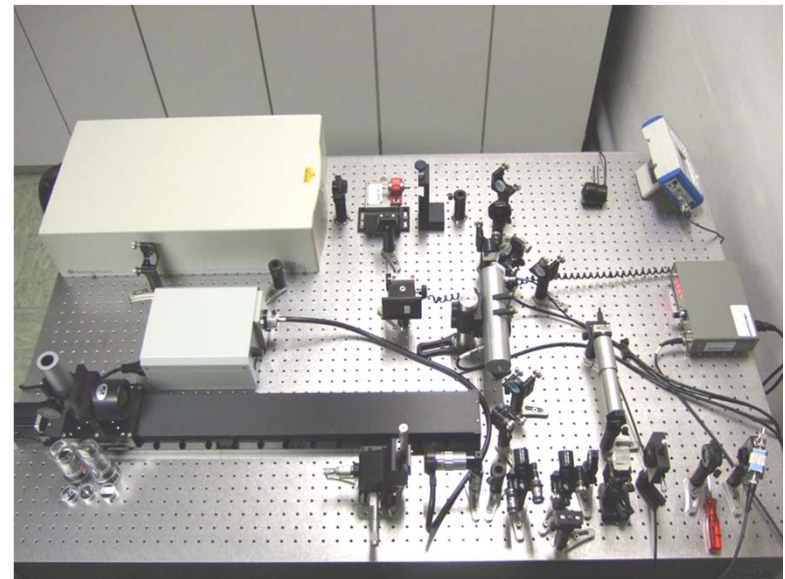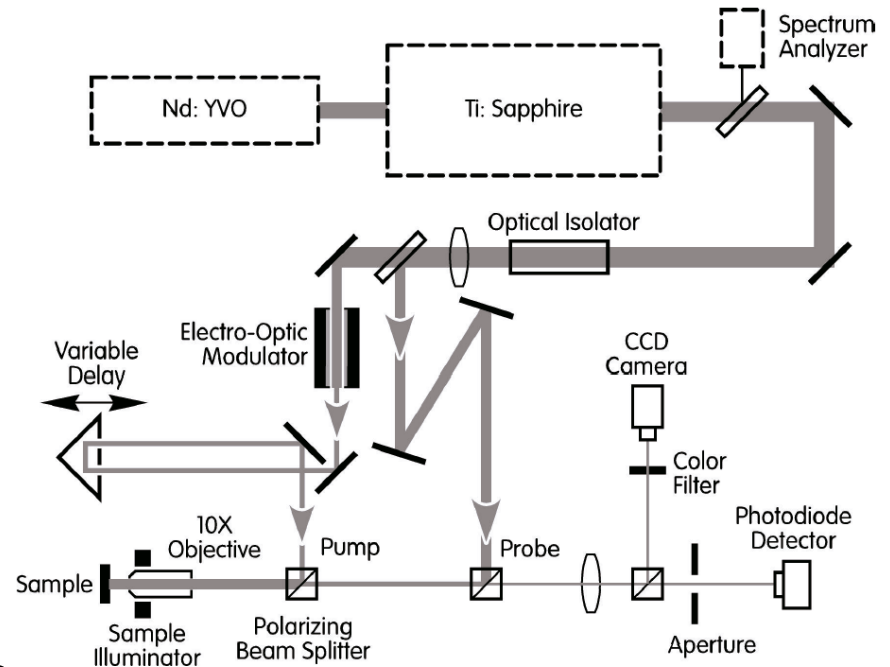
Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

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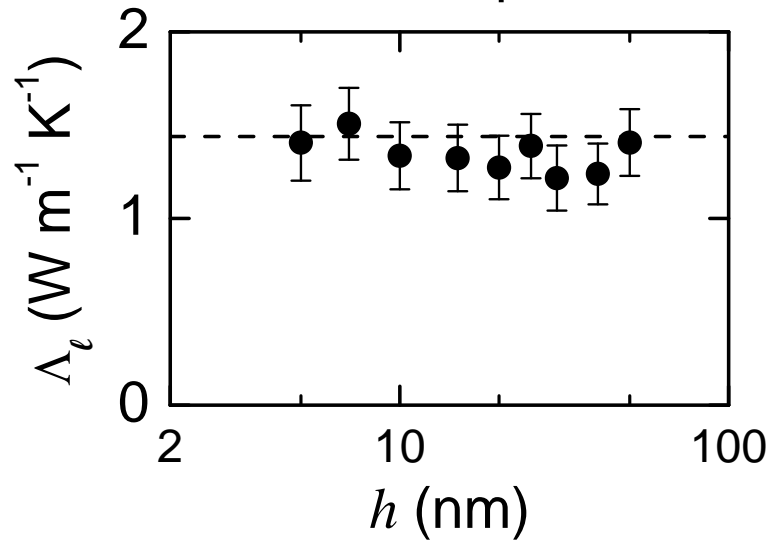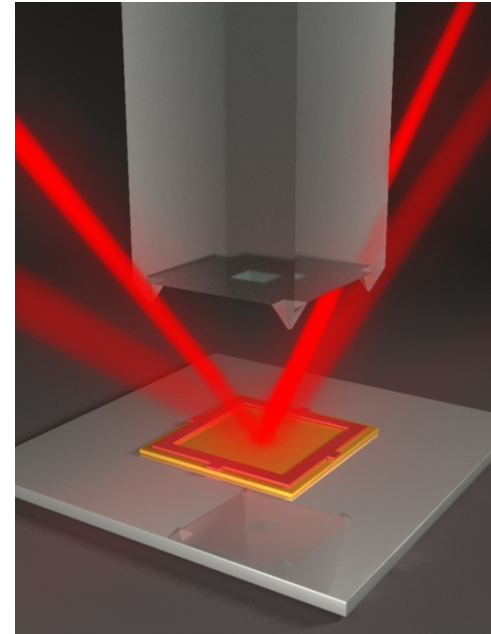

19 nm PMMA

5.1 GPa

1.3 GPa

Ambient

-V_{in} / V_{out}

Delay time (ps)

Ar | Al | SiC
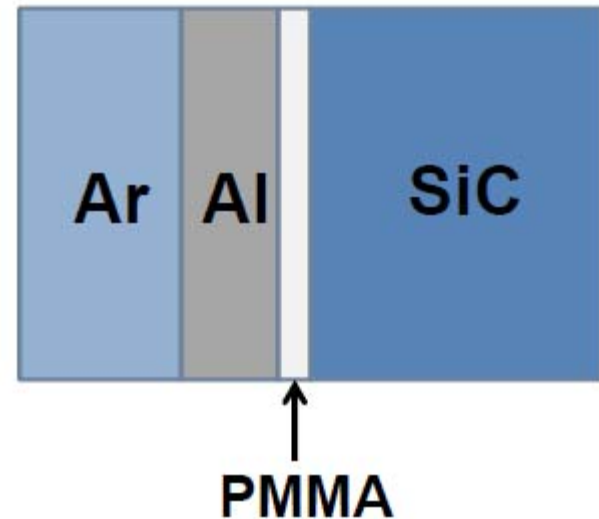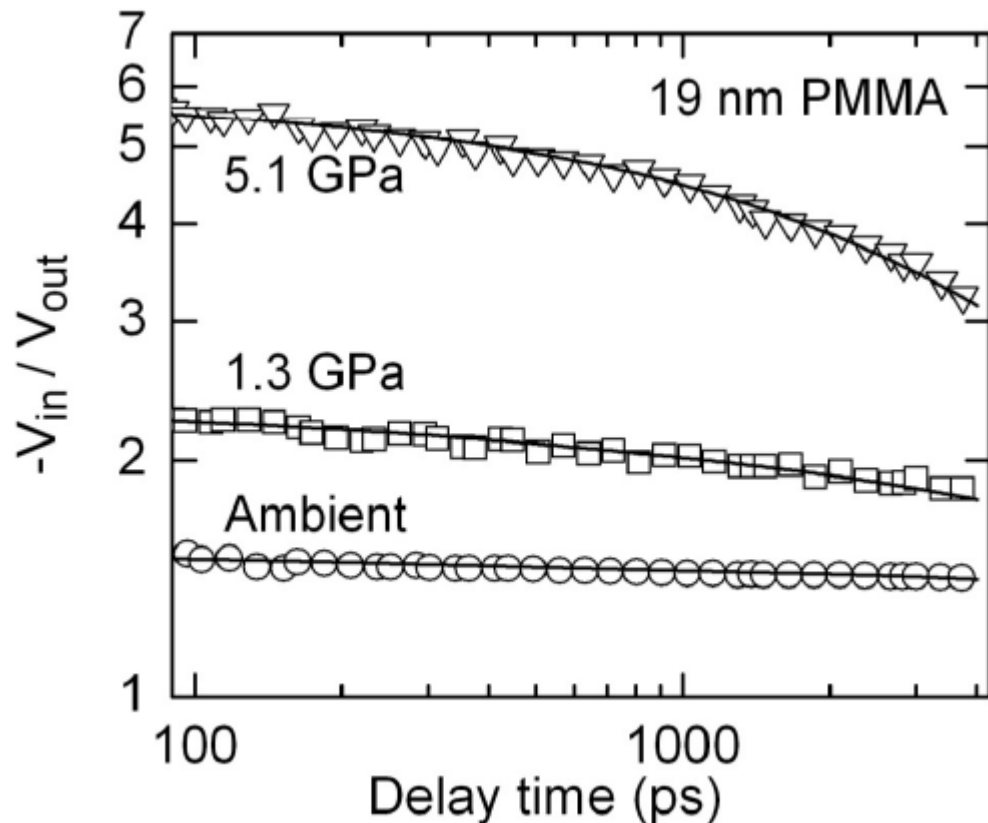
PMMA

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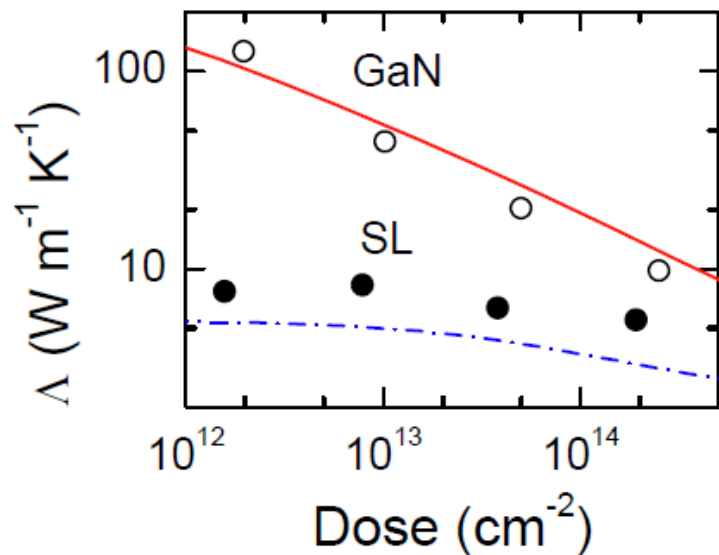D. Λ(P) of PMMA?

TDTR: Flexible, convenient, and accurate

PbTe/PbSe superlattices

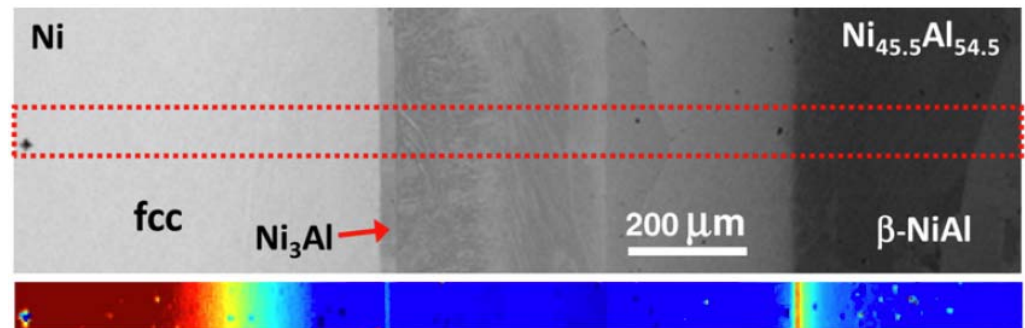## Transfer-printed interfaces

Radiation damage

High resolution mapping

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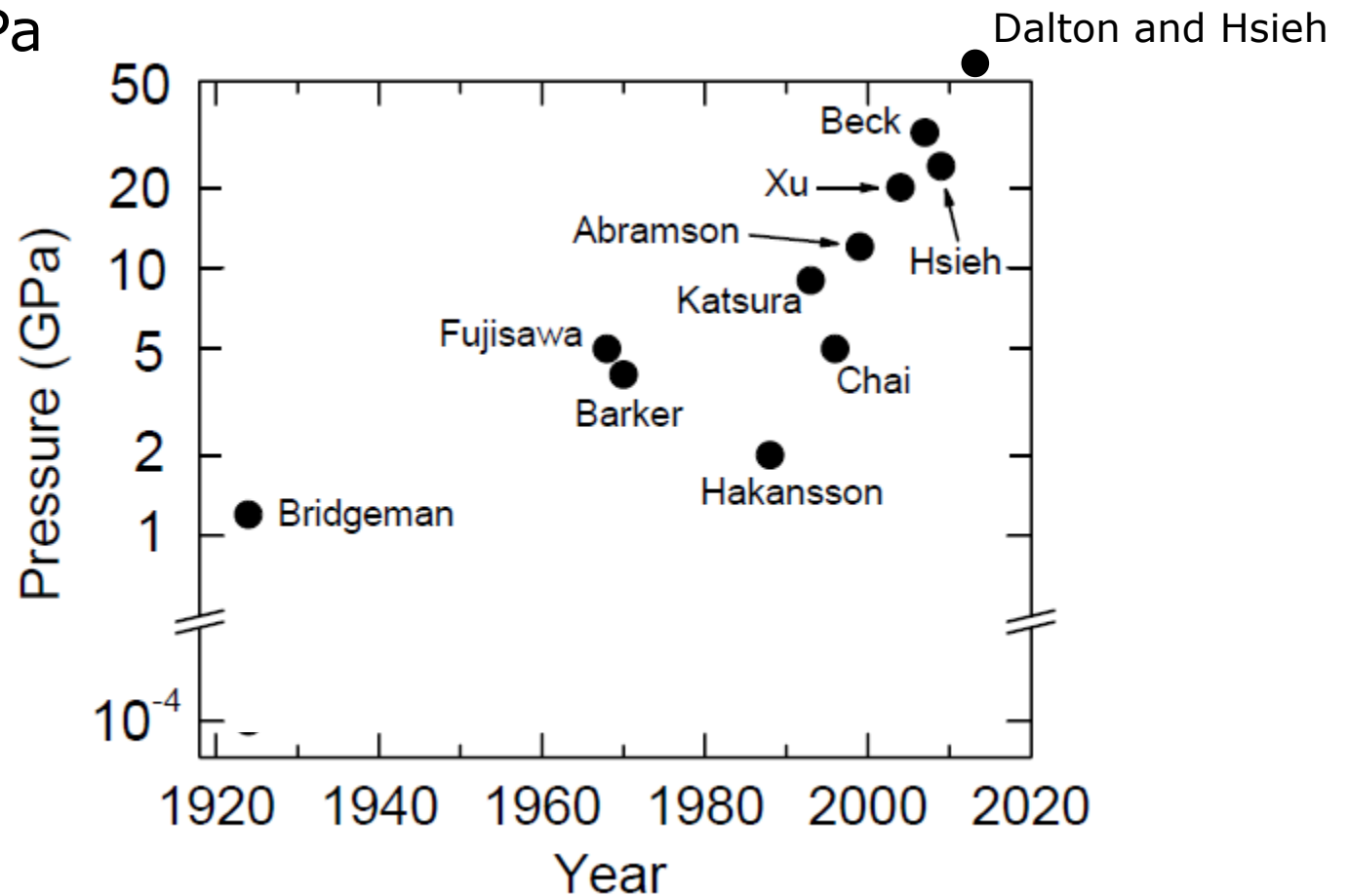
Diamond anvil cell

Maximum pressure achieved in thermal conductivity measurements

1 atm=bar

1 bar=100 kPa

1 Mbar=100 GPa

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

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

I. Works well for homogeneous disordered materials but is this model valid for glassy polymers?
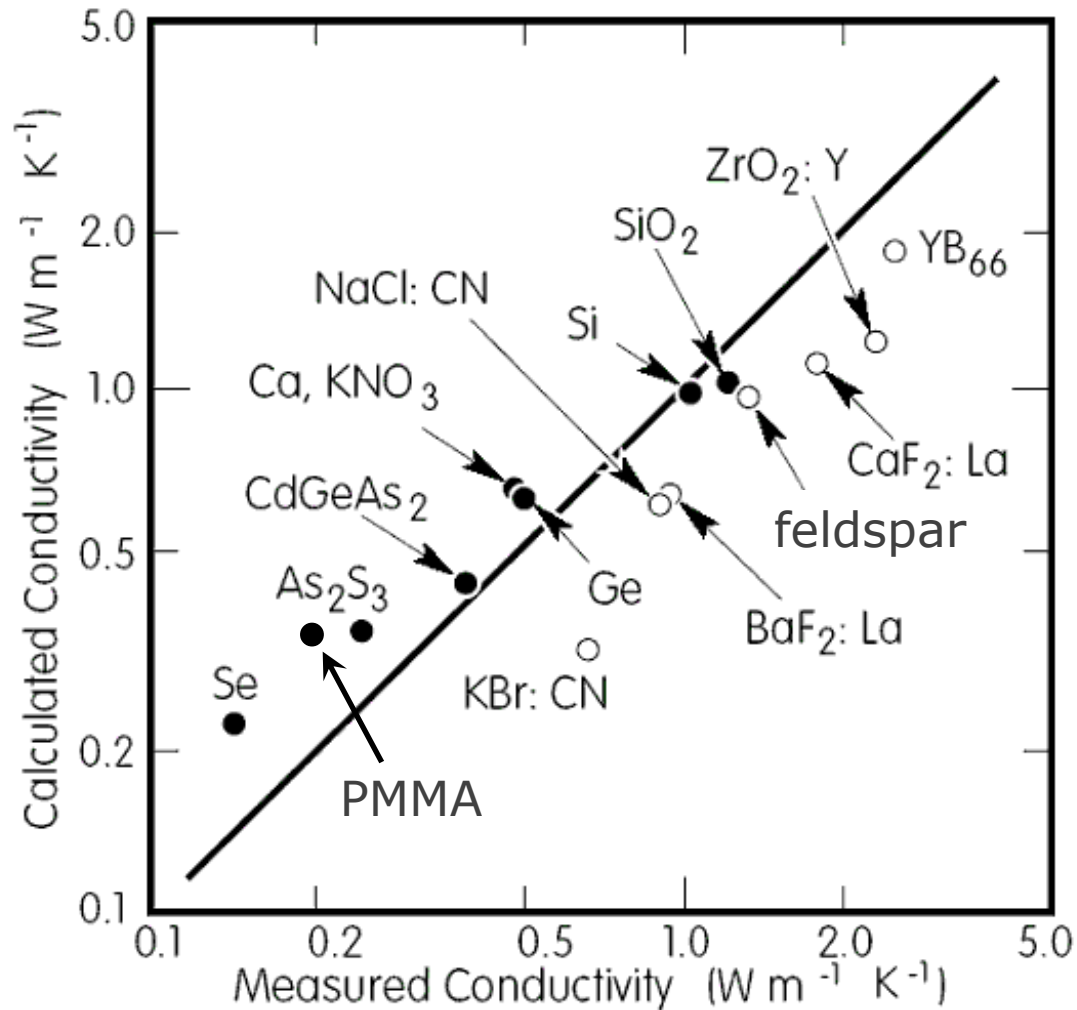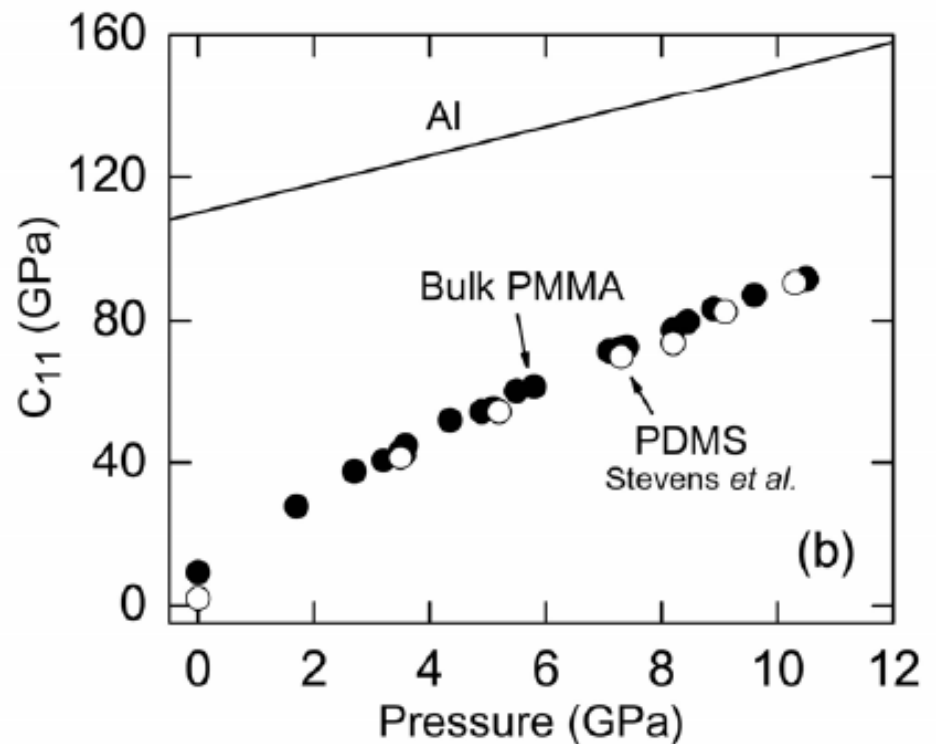

- ● amorphous
- ○ disordered crystal

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.
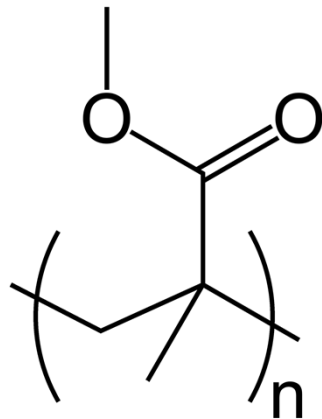
C_{11} data for PMMA from picosecond interferometry

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

Ar Al SiC
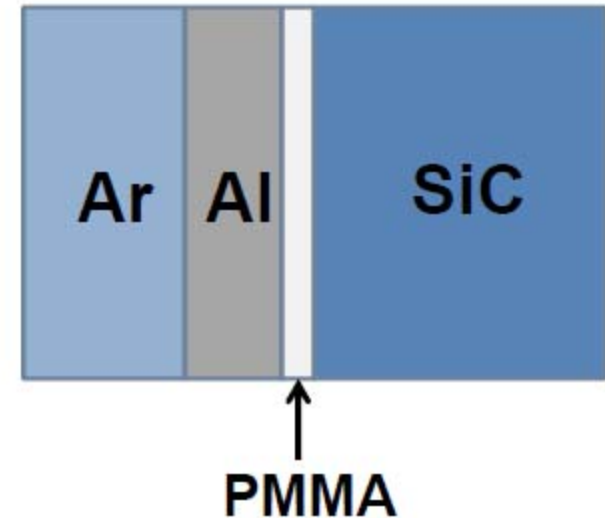
PMMA

Nanoscale polymer brushes "grafted from" the SiC anvil
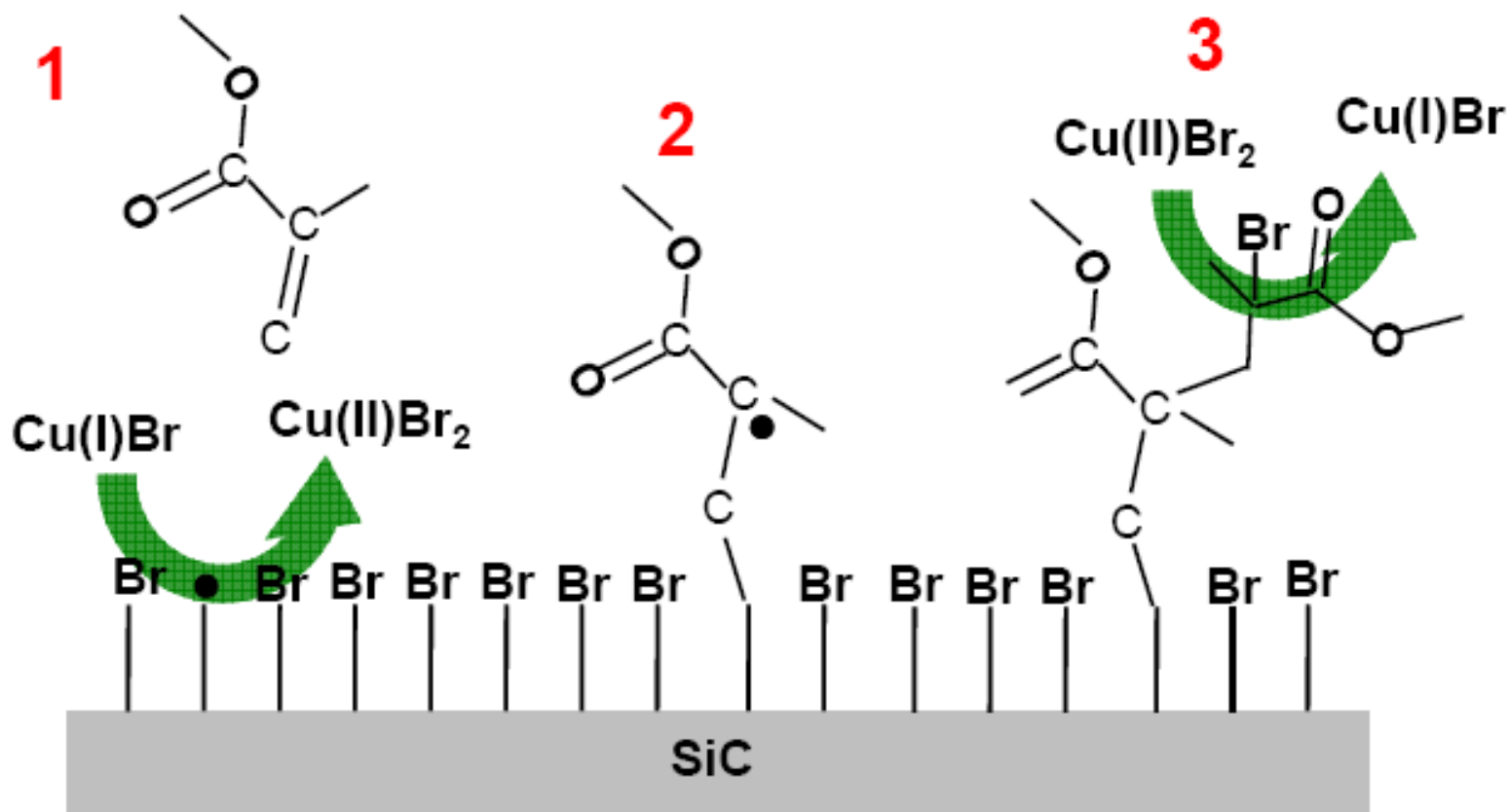
Thermal conductivity of PMMA polymer is independent of thickness and agrees well with the predicted scaling with $(C_{11})^{1/2}$
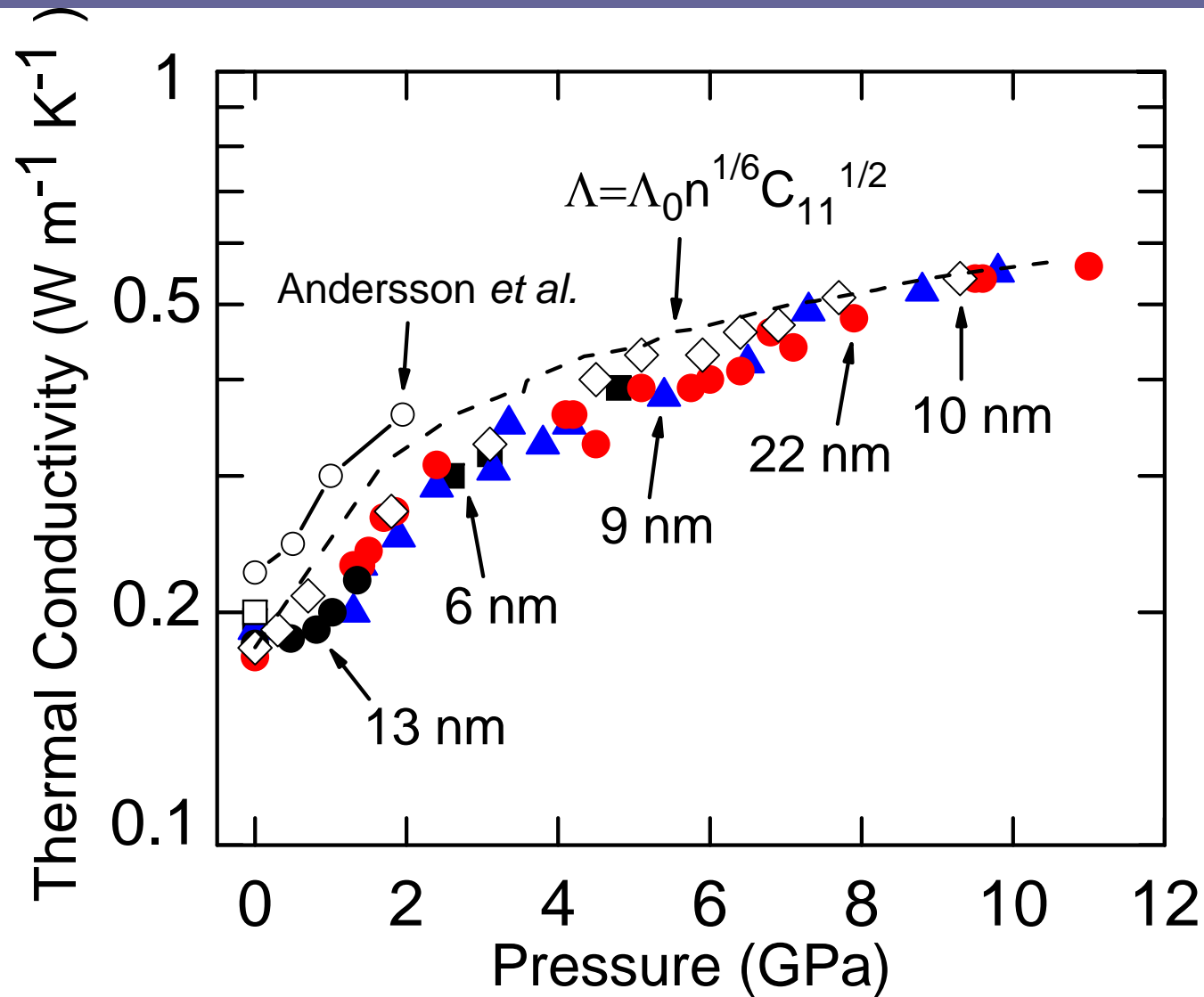
- Leibfried-Schlömann equation

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

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

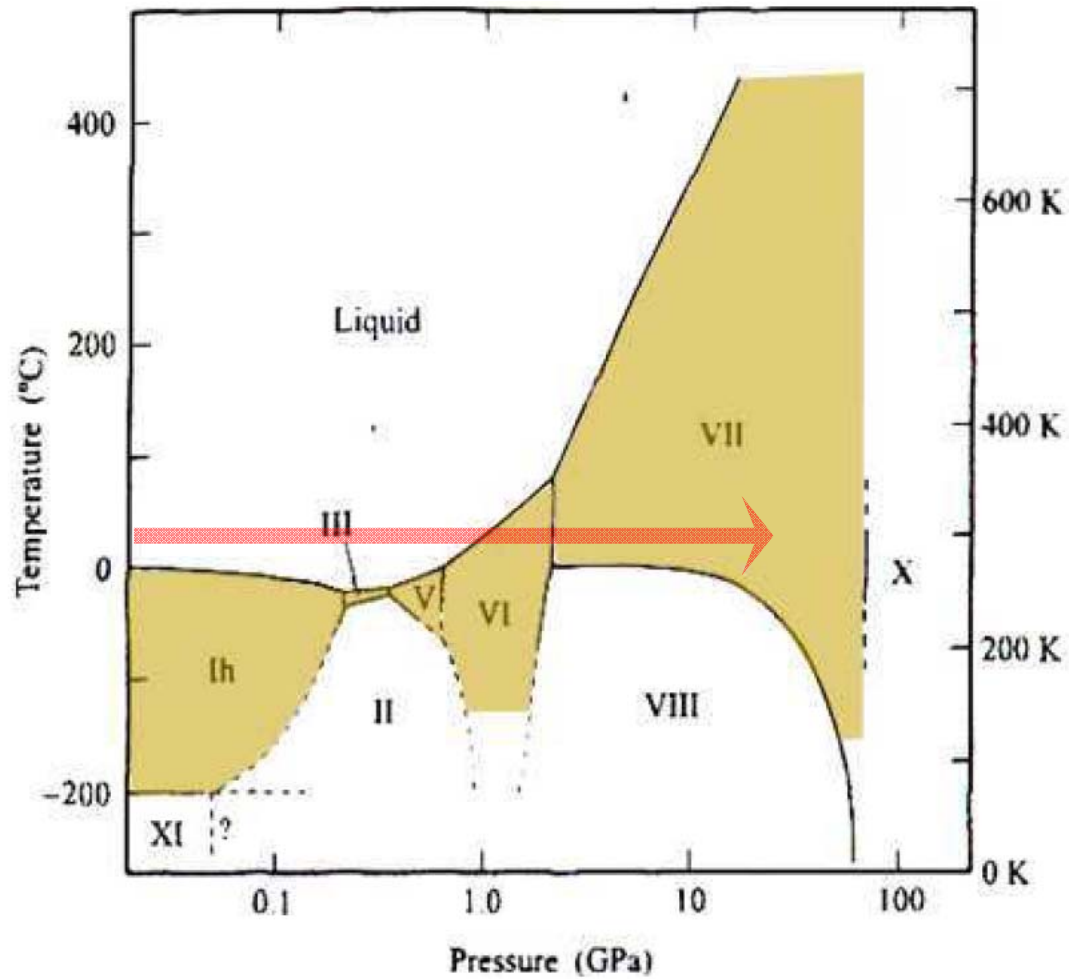$V = $ molecular volume

$\omega = $ Debye frequency

$\gamma = $ Grüneisen parameter

- Test using relative low modulus water ice that is compressed by 33% at P=22 GPa.

Water ice has a remarkably rich phase diagram
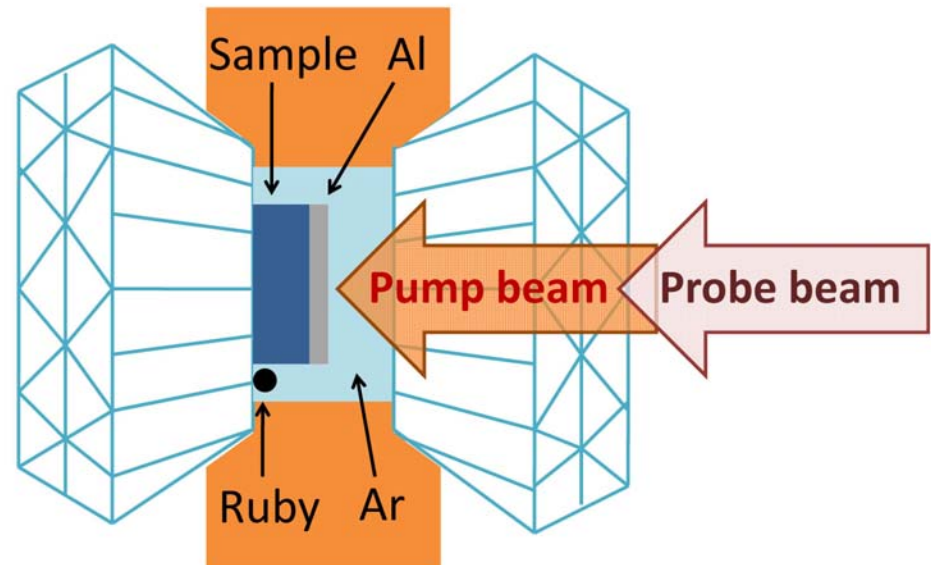

Petrenko and Whitworth (1999)

Ice VII, cubic with two interpenetrating but not interconnected bcc sub-lattices

- Hydrogen-bonding in ice VII is disordered
- Ice VIII is the proton ordered form
- Ice X is thought to be "polymeric": H-bond is symmetric

C.J. Knight, *Ph.D. thesis* (2009)
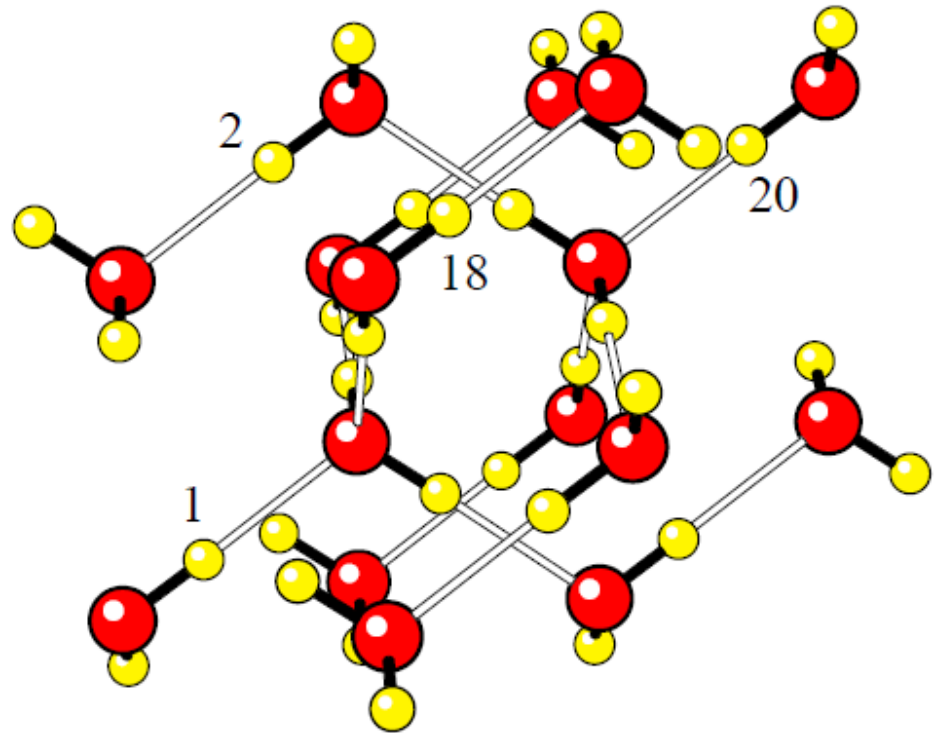
Use Al-coated mica as a substrate. Measure using Ar and then with ice.
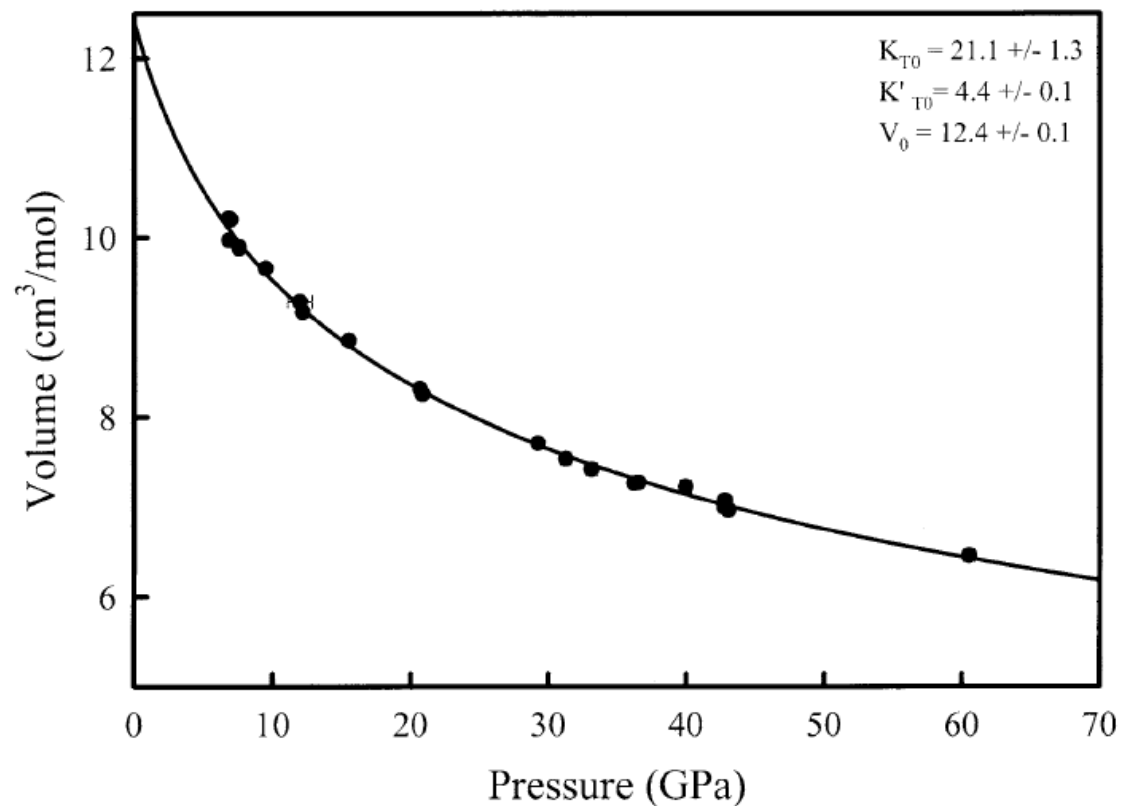
Diamond anvil cell

Measuring thermal conductivity of 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 ice as the pressure medium
5. use density functional theory to calculate changes in H_2O heat capacity per unit volume
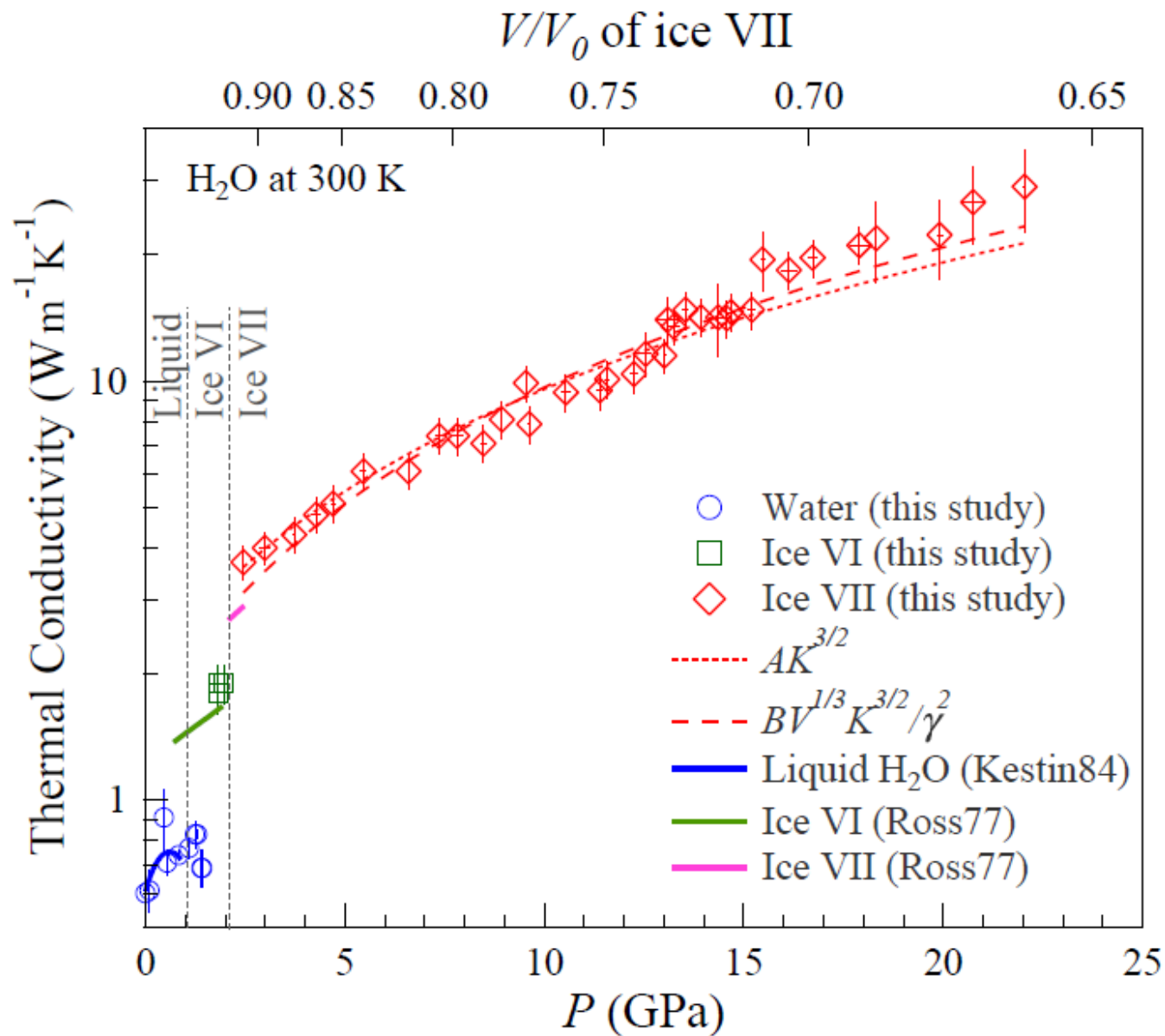6. analyze the data
7. repeat...

Derive changes in Debye frequency ω_D and Grüneisen parameter γ from equation of state $V(P)$

- Data for $V(P)$ are fit to a model (e.g., Birch-Murnaghan)
- Assume ω_D scales with $K^{1/2}$
- γ is derived from a second derivative of the $V(P)$ curve.

$V(P)$ of ice VII by synchrotron x-ray diffraction

$K_{T0} = 21.1 +/- 1.3$
$K'_{T0} = 4.4 +/- 0.1$
$V_0 = 12.4 +/- 0.1$

Frank *et al.*, Geochimica et Cosmochimica Acta, 2004

V/V_0 of ice VII

H$_2$O at 300 K

Thermal Conductivity (W m^{-1}K^{-1})

Liquid
Ice VI
Ice VII

○ Water (this study)
□ Ice VI (this study)
◇ Ice VII (this study)
------- $AK^{3/2}$
- - - $BV^{1/3}K^{3/2}/\gamma^2$
—— Liquid H$_2$O (Kestin84)
—— Ice VI (Ross77)
—— Ice VII (Ross77)

P (GPa)

- Elastic constants and phonon spectra of typical materials do not change much between 0 <P <10 GPa.

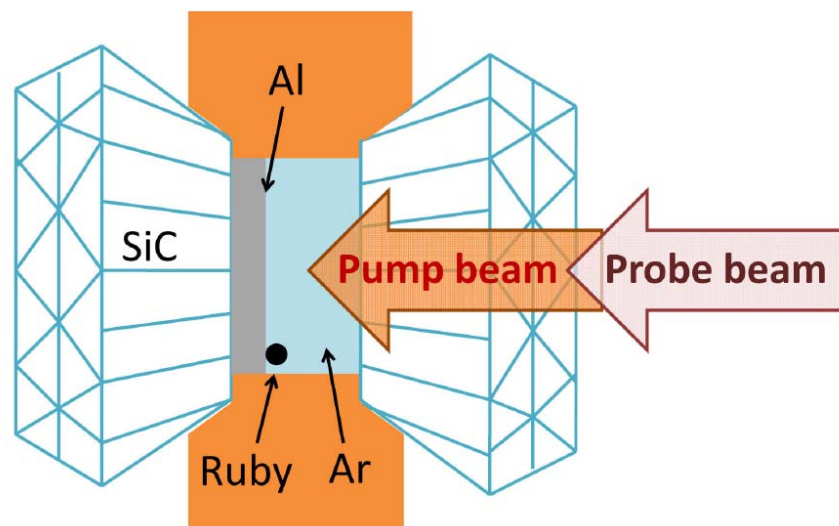- But weak interface bonds are expected to be highly anharmonic (more like PMMA than diamond)
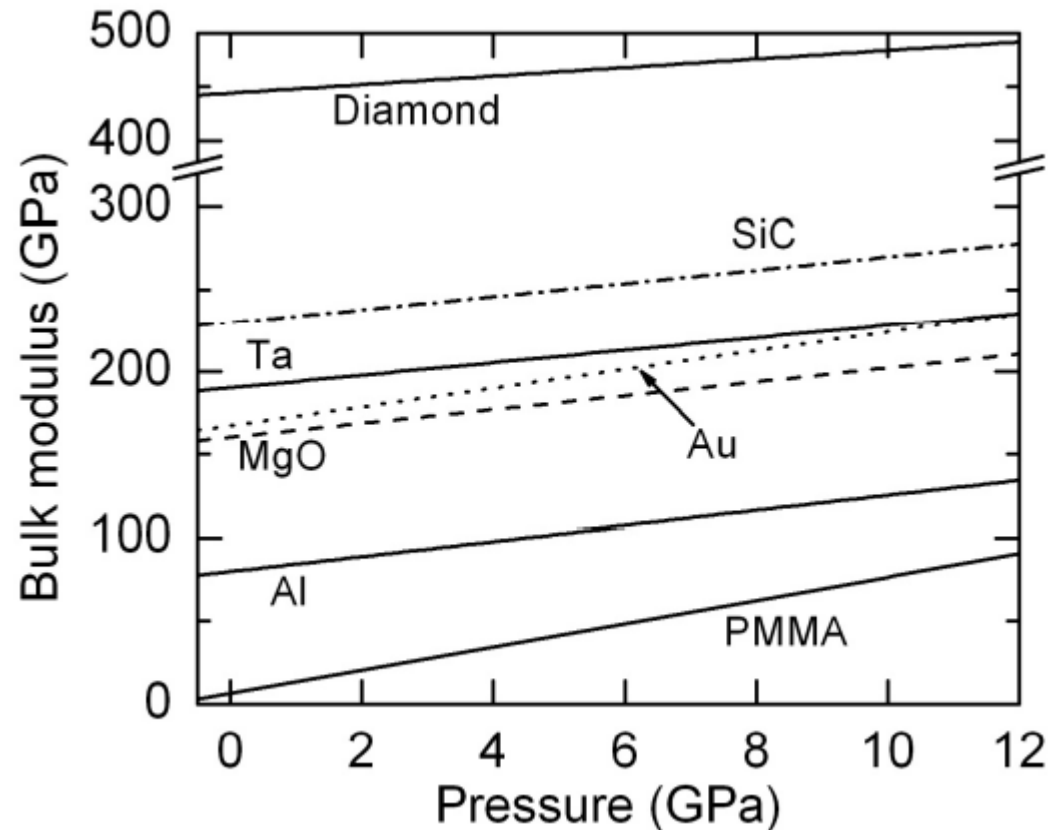
Interface stiffness *s* is analogous to interface thermal conductance *G*

apply pressure, P

displacement, d

$$\Delta d = \frac{1}{s(P)} P$$

z

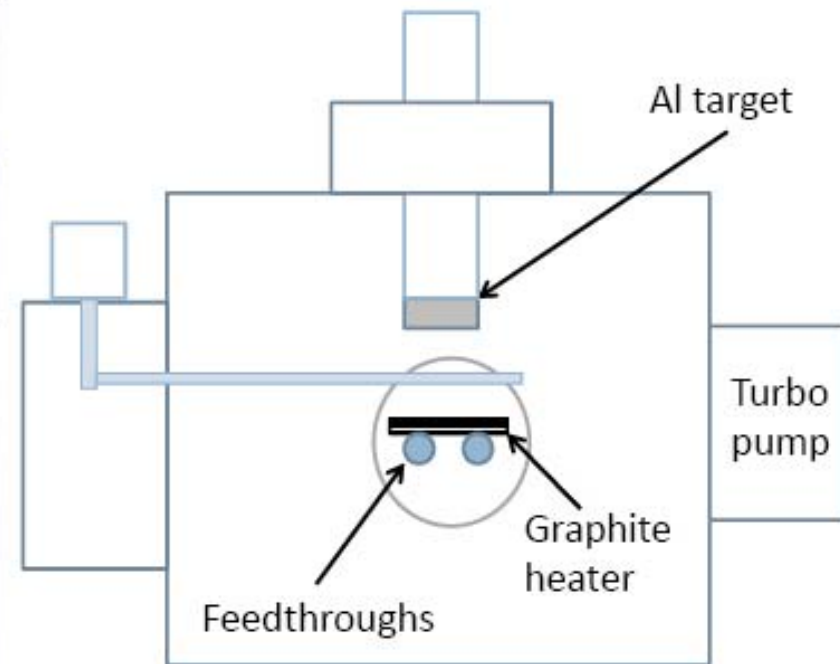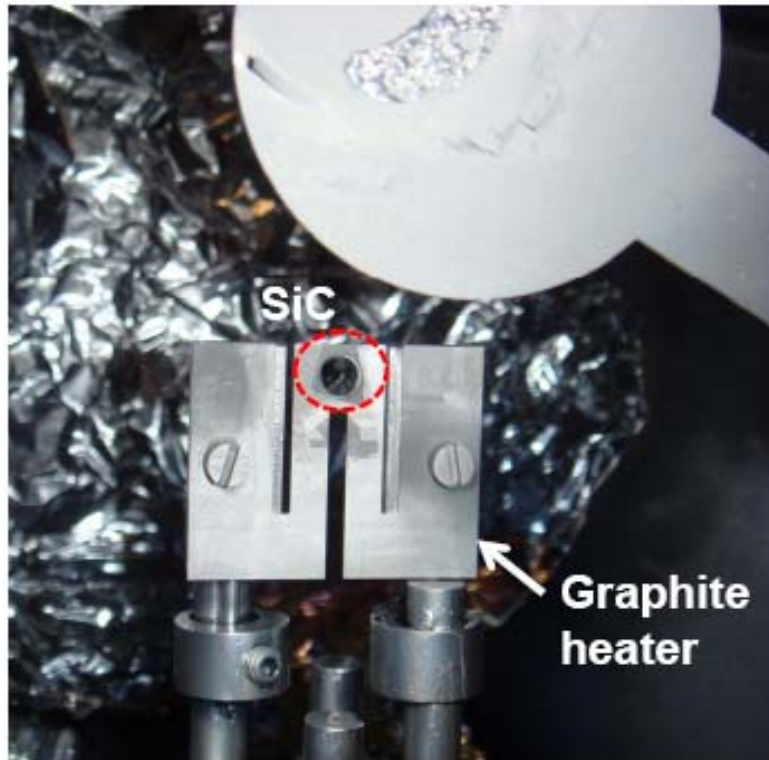apply heat flux, J

Temperature, T

$$\Delta T = \frac{1}{G} J$$

z
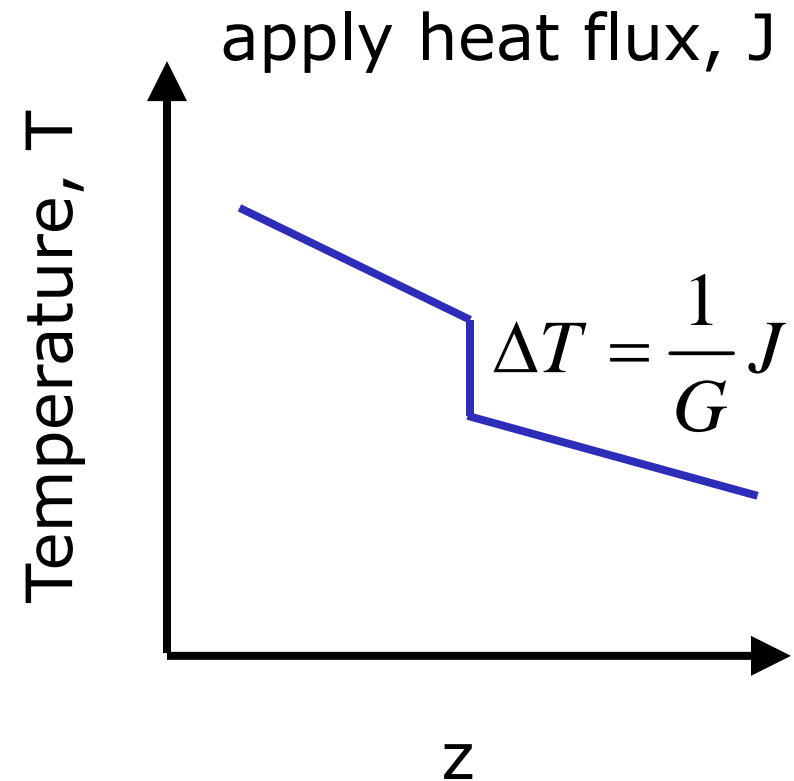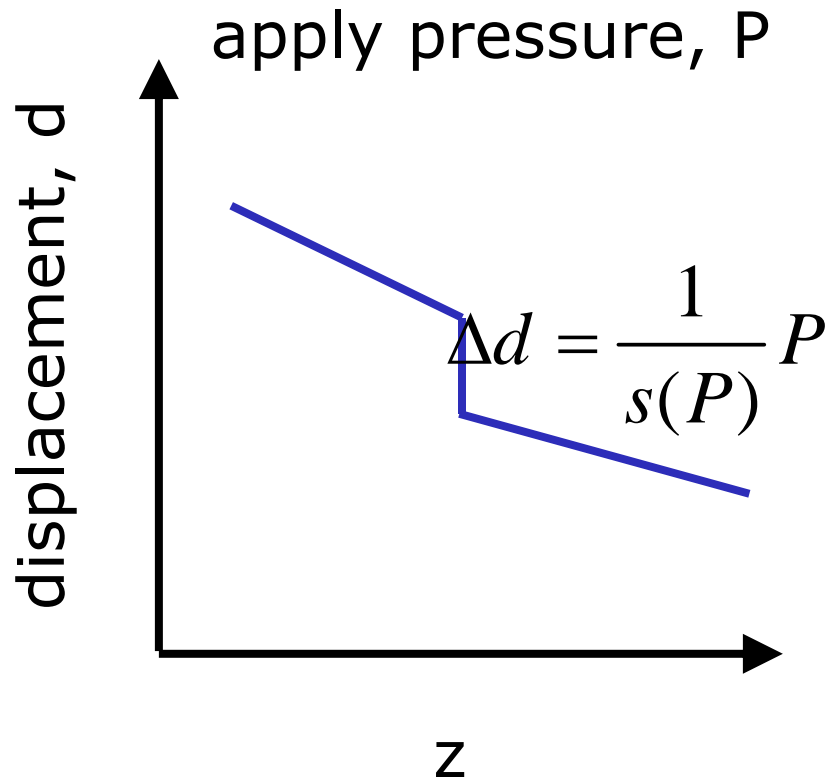
Deposit Al on SiC with and without coating with monolayer CVD graphene by transfer-printing

Diamond anvil cell

Clean SiC anvil at high temperatures and deposit Al film *in-situ* by sputtering

Compare clean interface with a layer of CVD graphene inserted at the interface

- Clean interface has the weak pressure dependence expected from diffuse-mismatch (DMM) calculations.

- Insert graphene: low conductance and strong pressure dependence.

- At P>8 GPa, "weak" interface becomes "strong" and conductance is high.
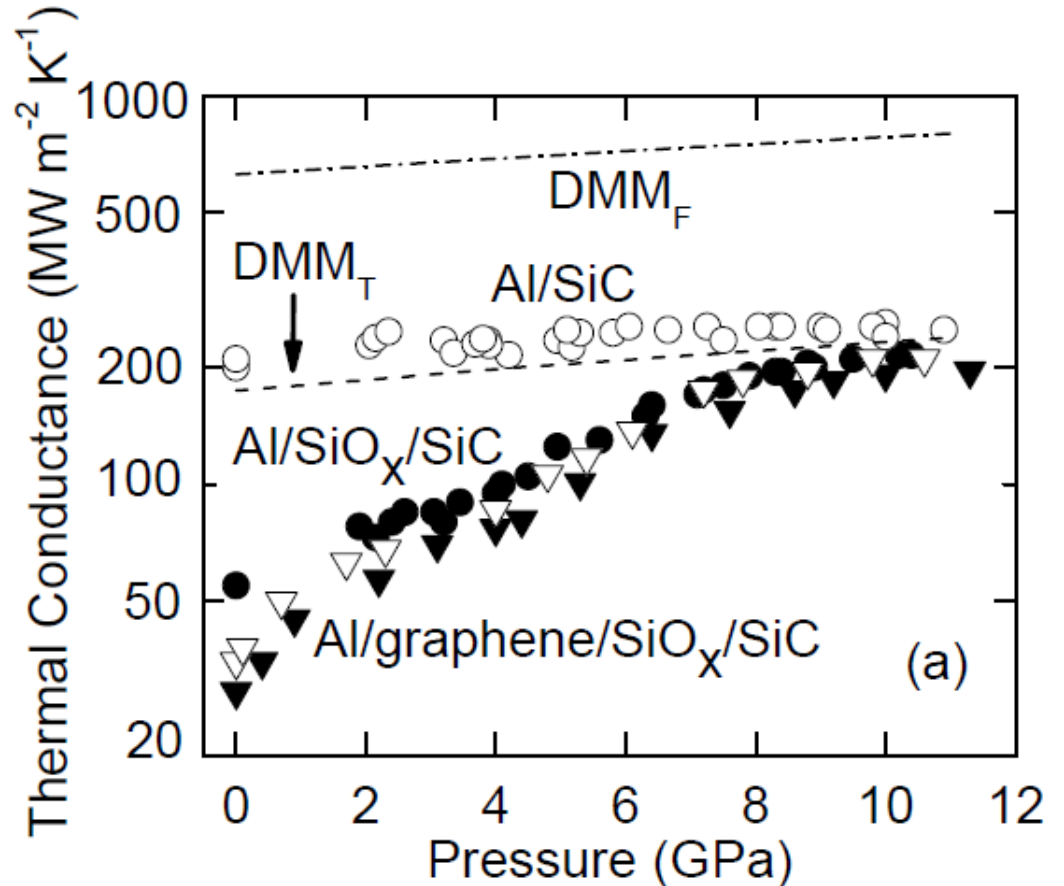
Summary

- 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?

- Pressure dependence of typical (dirty, weakly bonded) interfaces is in poor agreement with the diffuse mismatch model

  - Weak interfacial bonding suppresses heat conduction at interfaces. Pressure can be used to vary the strength of interface bonding.