Nanoscale thermal transport and the thermal conductance of interfaces

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Outline—the big picture

Condensed matter physics

Surface and interface science

Physical chemistry

Nanoscale thermal transport

Heat transfer engineering

Thermal management

Laser processing

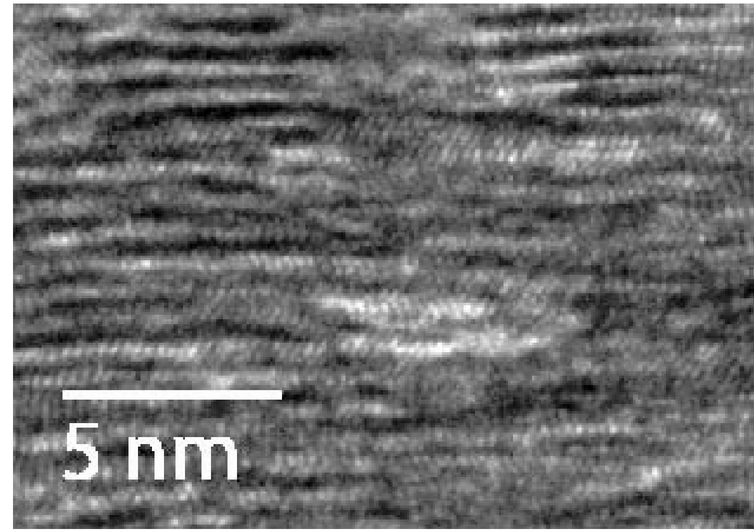
Device modeling

Outline

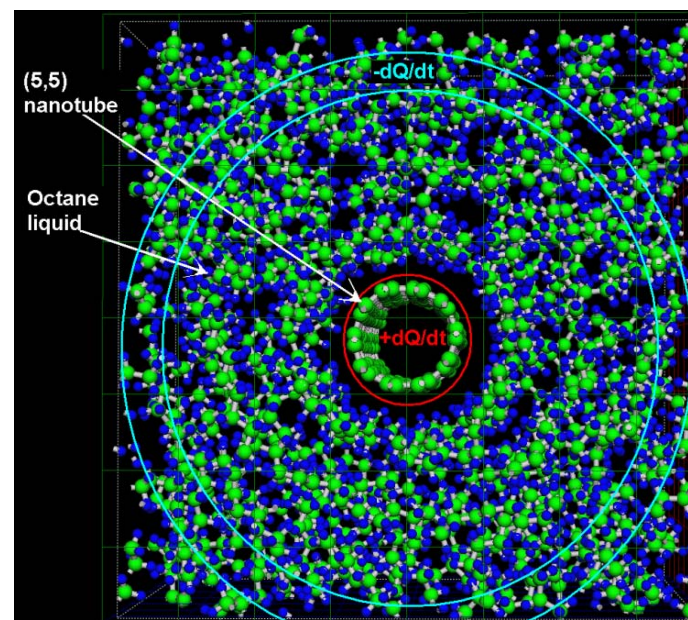
- Interface thermal conductance
- Pump probe apparatus
- Transient absorption
  - Carbon nanotubes and thermal transport at hard-soft interfaces
  - Metal nanoparticles and interfaces with water
- Time-domain thermoreflectance
  - hydrophilic and hydrophobic interfaces
- Sum-frequency vibrational spectroscopy as a probe of thermal transport across molecular layers

Interfaces are critical at the nanoscale

- Disordered layered crystals of WSe_2.
  - lowest thermal conductivity ever observed in a dense solid, only twice the conductivity of air



- Carbon nanotube composite solids and liquids for thermal management

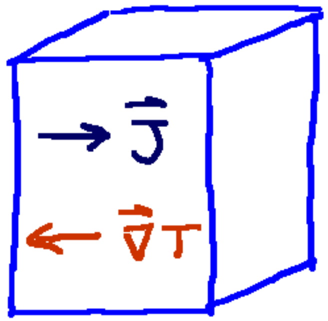


- Localization of thermal effects: medical therapy/biotechnology

Thermal transport properties

- Thermal conductivity Λ is a property of the continuum

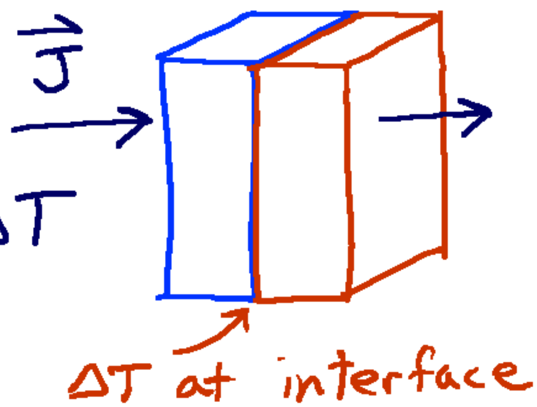
$$\vec{J} = -\Lambda \vec{\nabla} T$$



$$\Lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \vec{j}(t)\cdot\vec{j}(0)\rangle\, dt$$

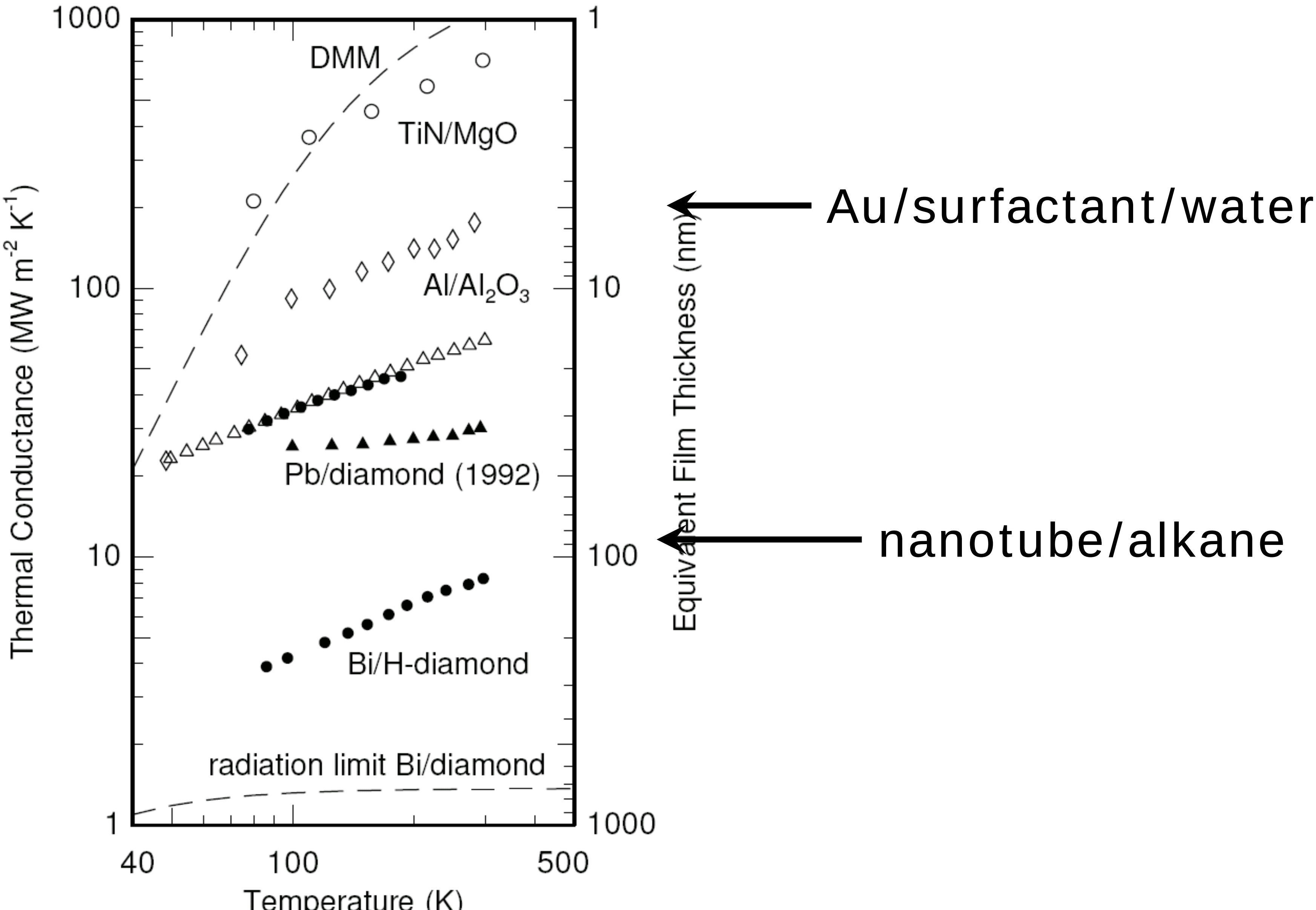
- Thermal conductance (per unit area) *G* is a property of an interface

$$J = G \Delta T$$



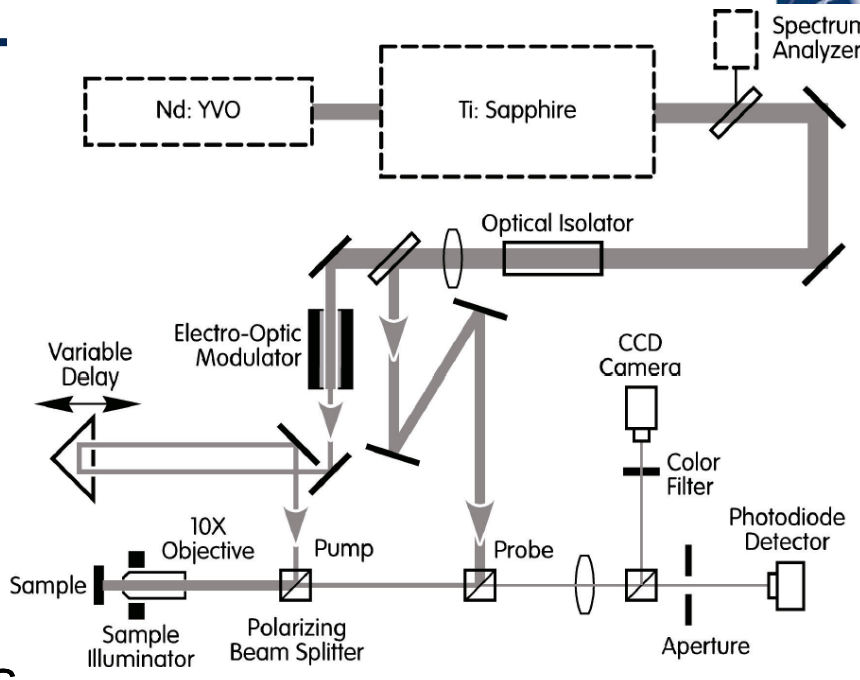
$$G = \frac{1}{Ak_BT^2}\int_0^\infty \langle q(t)q(0)\rangle\, dt$$

Factor of 60 range at room temperature

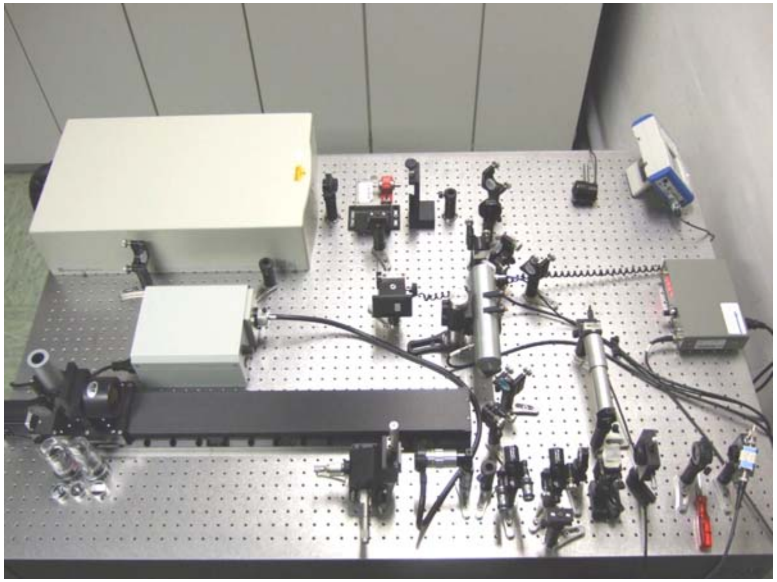


Time domain thermoreflectance since 2003

- 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



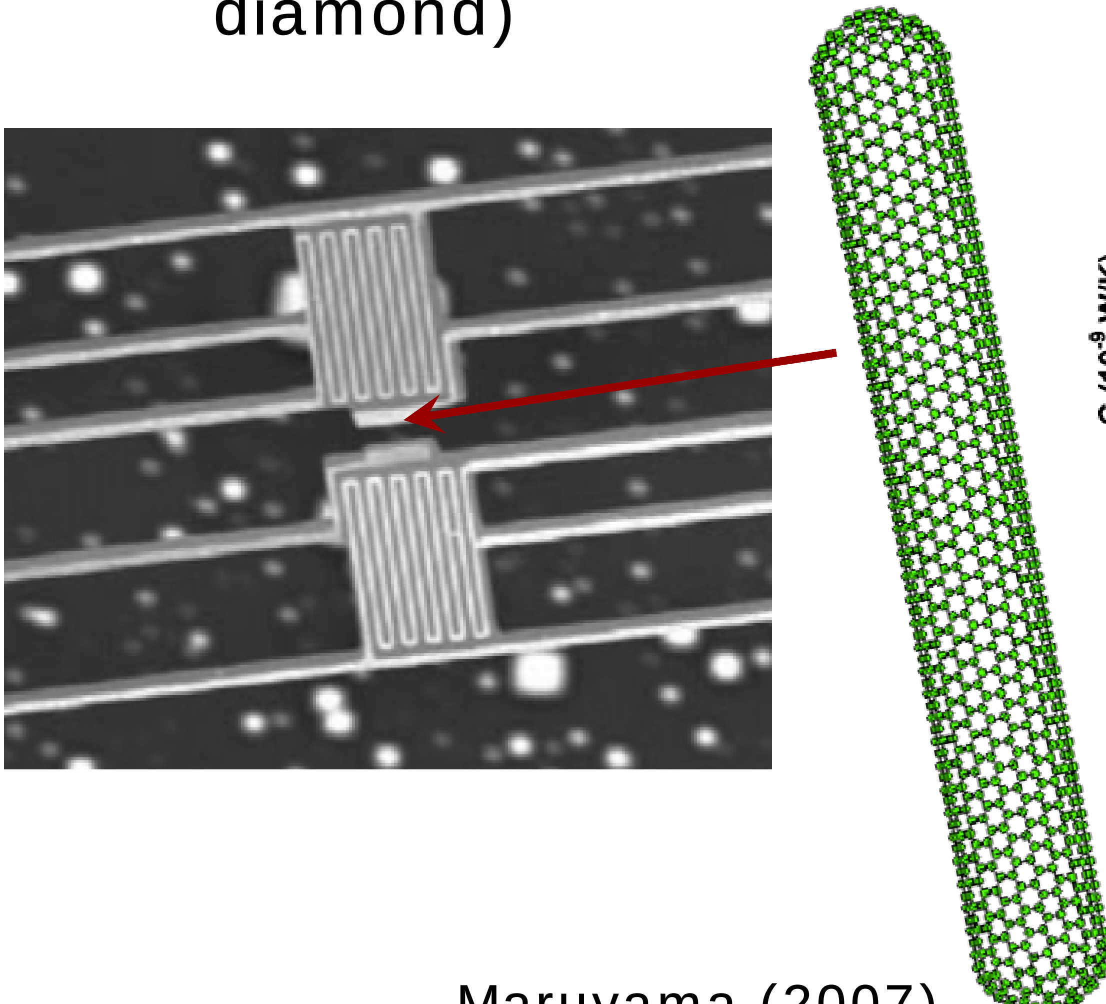
Er-fiber laser system, UIUC Nov. 2007

Solid-liquid interfaces: Two approaches

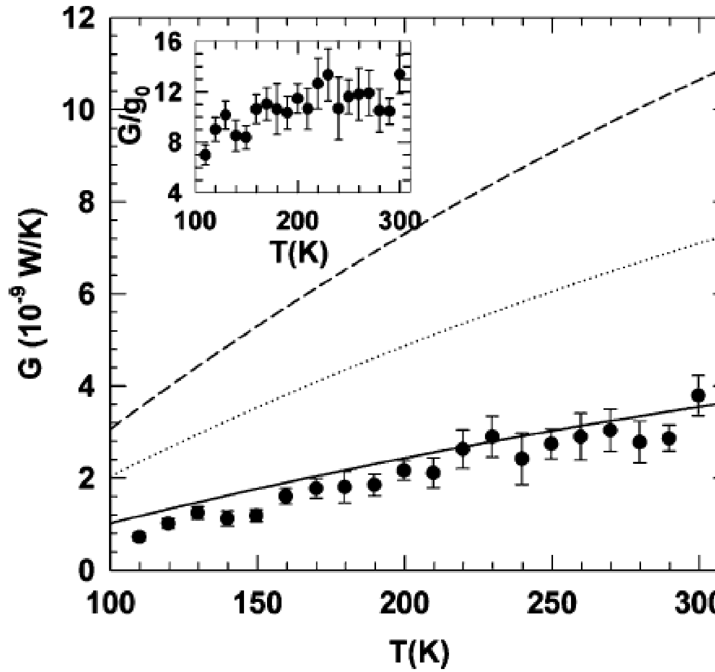
- Transient optical absorption of nanoparticles and nanotubes in liquid suspensions.
  – Measure the thermal relaxation time of a suddenly heat particle. Interface sensitive if the particle is small enough.
  – limited to interfaces that give good stability of the suspension, e.g., hydrophilic particles in H_2O
- Time-domain thermoreflectance of thin planar Al and Au films.
  – heat flows both directions: into the fluid and into the solid substrate.

Carbon nanotubes

- Evidence for the highest thermal conductivity any material (higher conductivity than diamond)



Maruyama (2007)

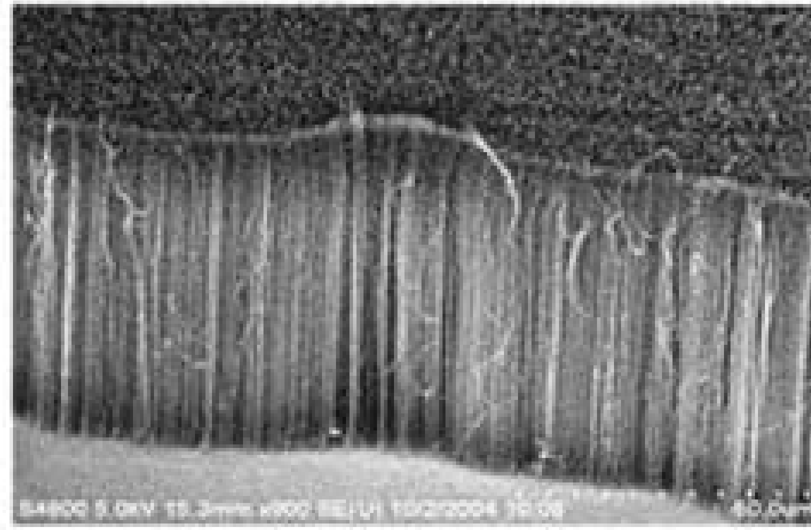


Yu et al. (2005)

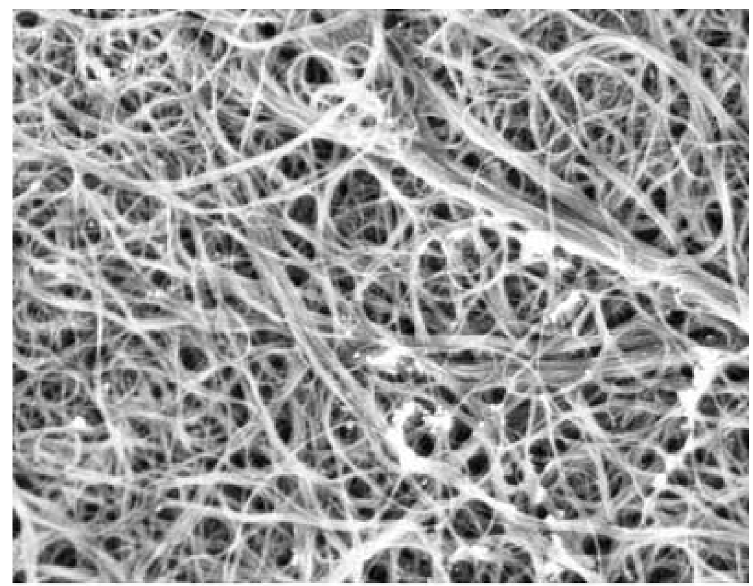
Can we make use of this?

- Much work world-wide:
  - thermal interface materials
  - so-called "nanofluids" (suspensions in liquids)
  - polymer composites and coatings

Fischer (2007)



Oriented carbon nanotube array.

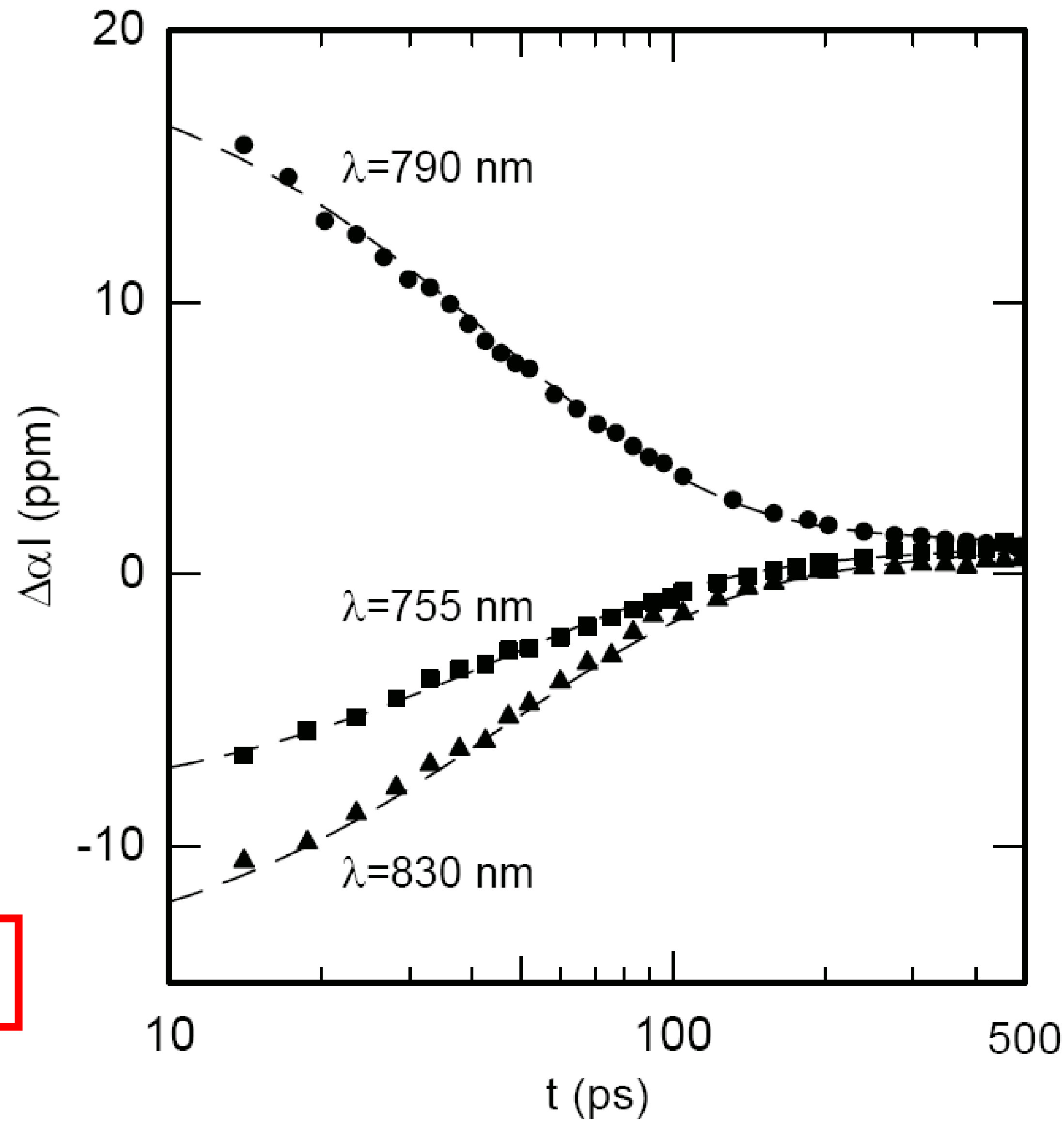


Lehman (2005)

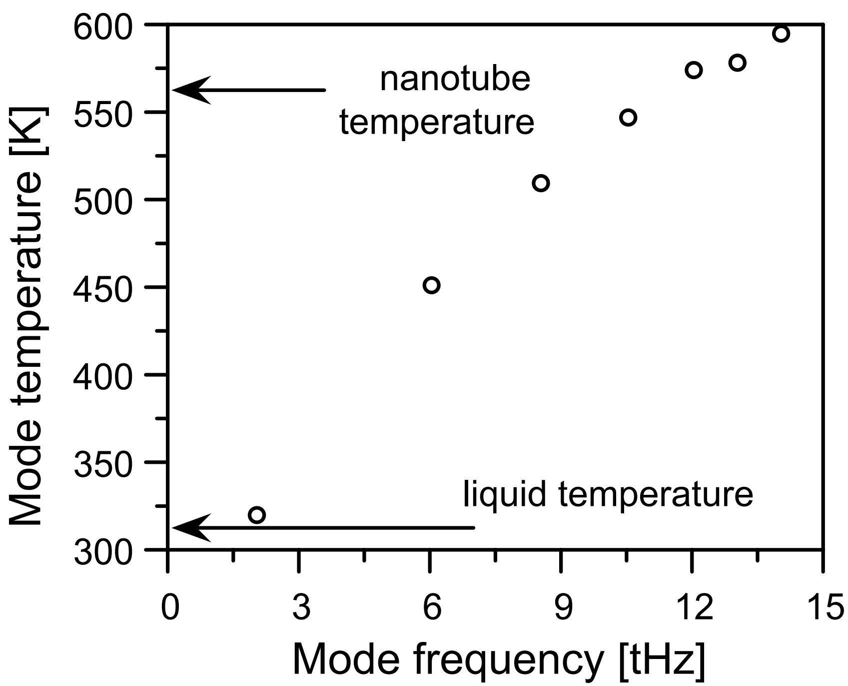
Nanotubes in surfactant in water: Transient absorption

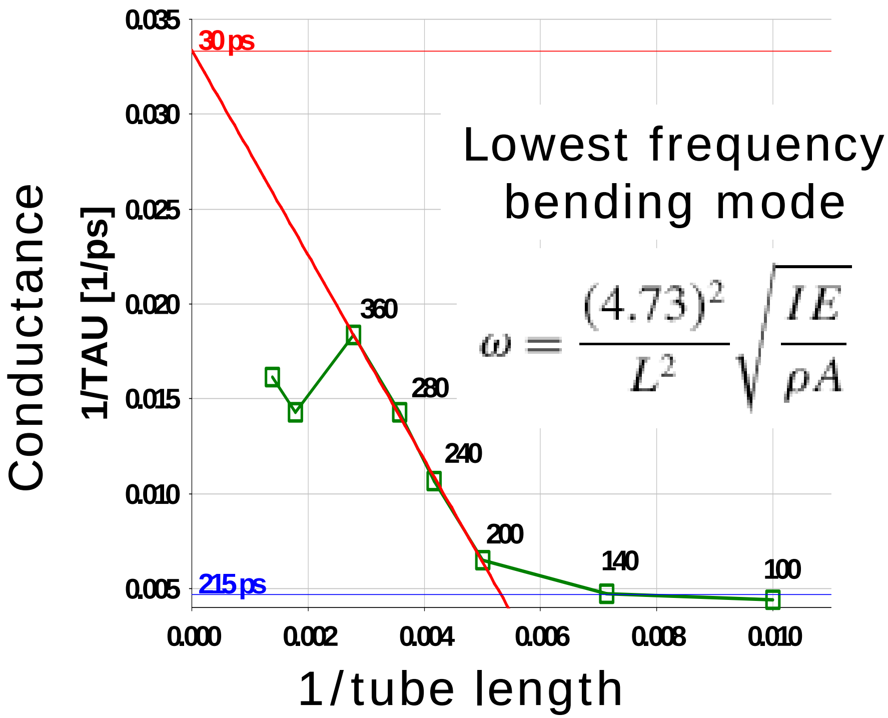
- Optical absorption depends on temperature of the nanotube
- Assume heat capacity is comparable to graphite
- Cooling rate (RC time constant) gives interface conductance

G = 12 MW m^{-2} K^{-1}



MD Simulation: Mechanisms for interface heat conduction (Keblisnki, RPI)





- Carbon nanotubes have a small number of low frequency modes associated with bending and squeezing. Only these modes can couple strongly with the liquid.

Application: Critical aspect ratio for a fiber composite

- Isotropic fiber composite with high conductivity fibers (and infinite interface conductance)

$$\Lambda_c = \frac{1}{3} V_f \Lambda_{NT}$$

- But this conductivity if obtained only if the aspect ratio of the fiber is high

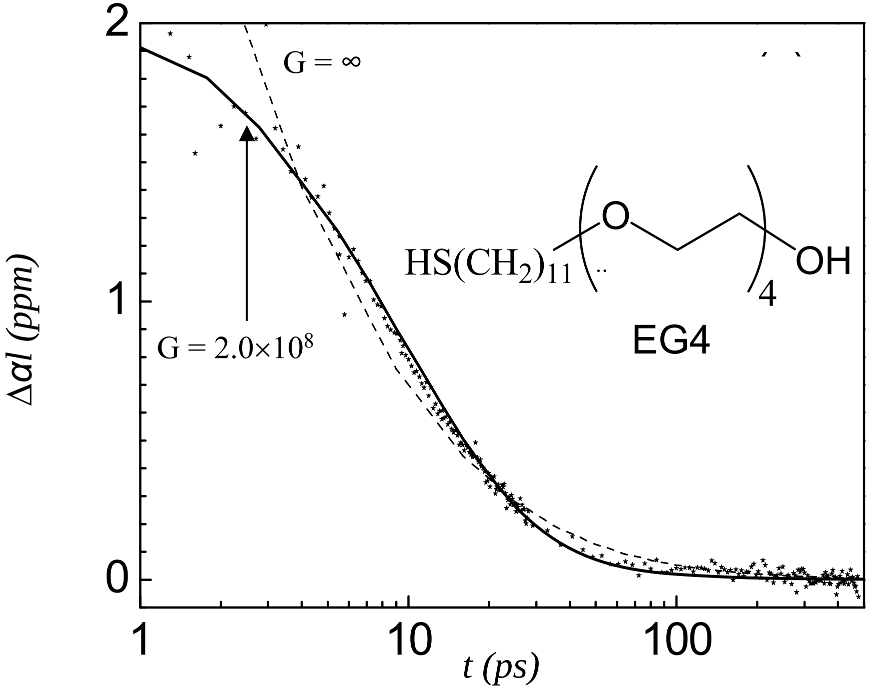
$$3\left(\frac{\Lambda_{NT}}{rG}\right)^{1/2} \approx 2000$$

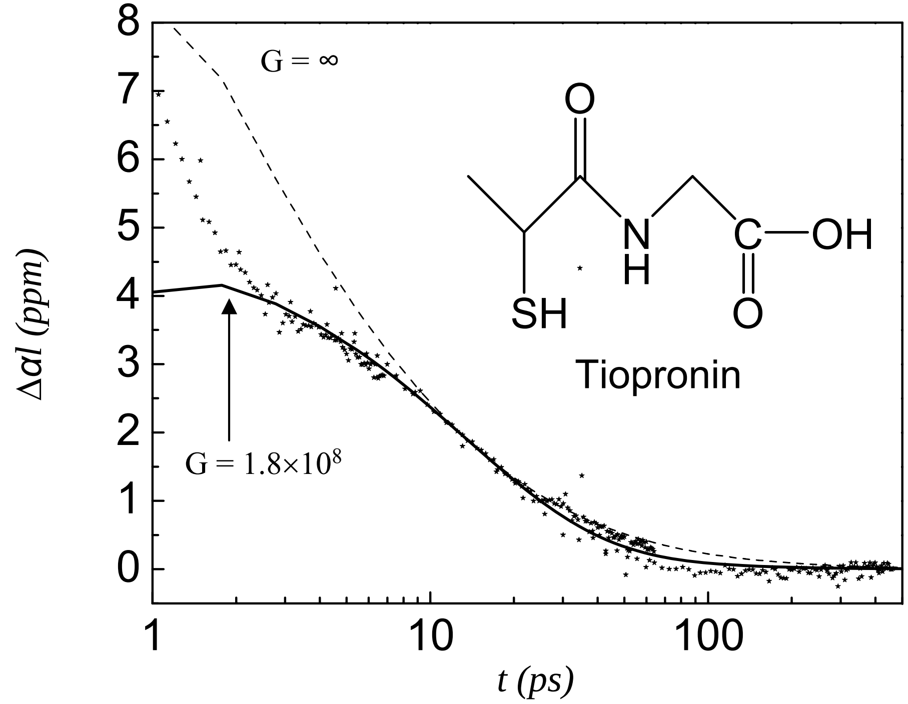
- Troubling question: Did we measure the relevant value of the conductance?

"heat capacity G" vs. "heat conduction G"

Hydrophilic metal nanoparticles: 4 nm diameter Au:Pd nanoparticles in water

transient absorption data

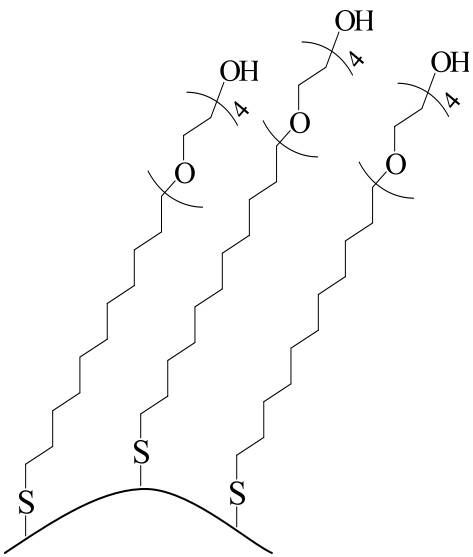


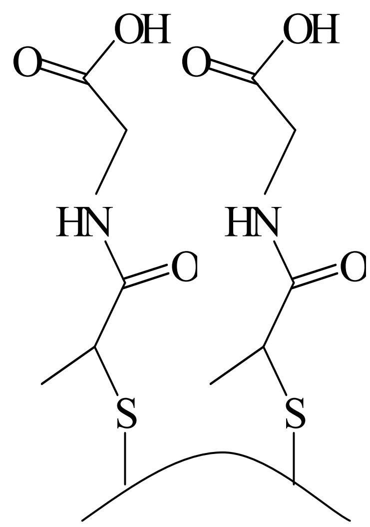


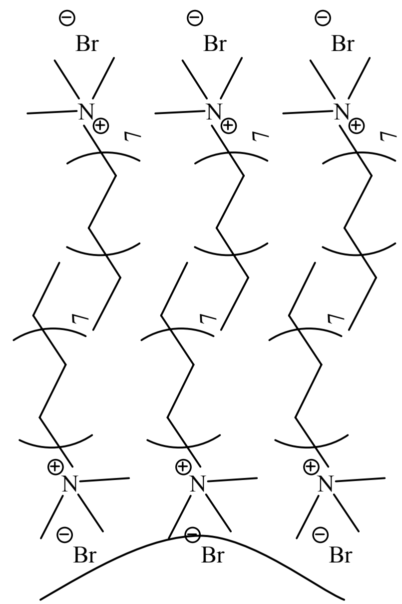
Nanoparticle summary

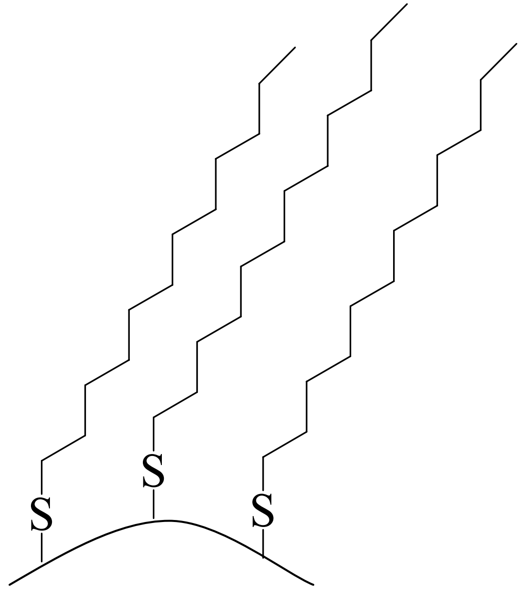
In water

In Toluene









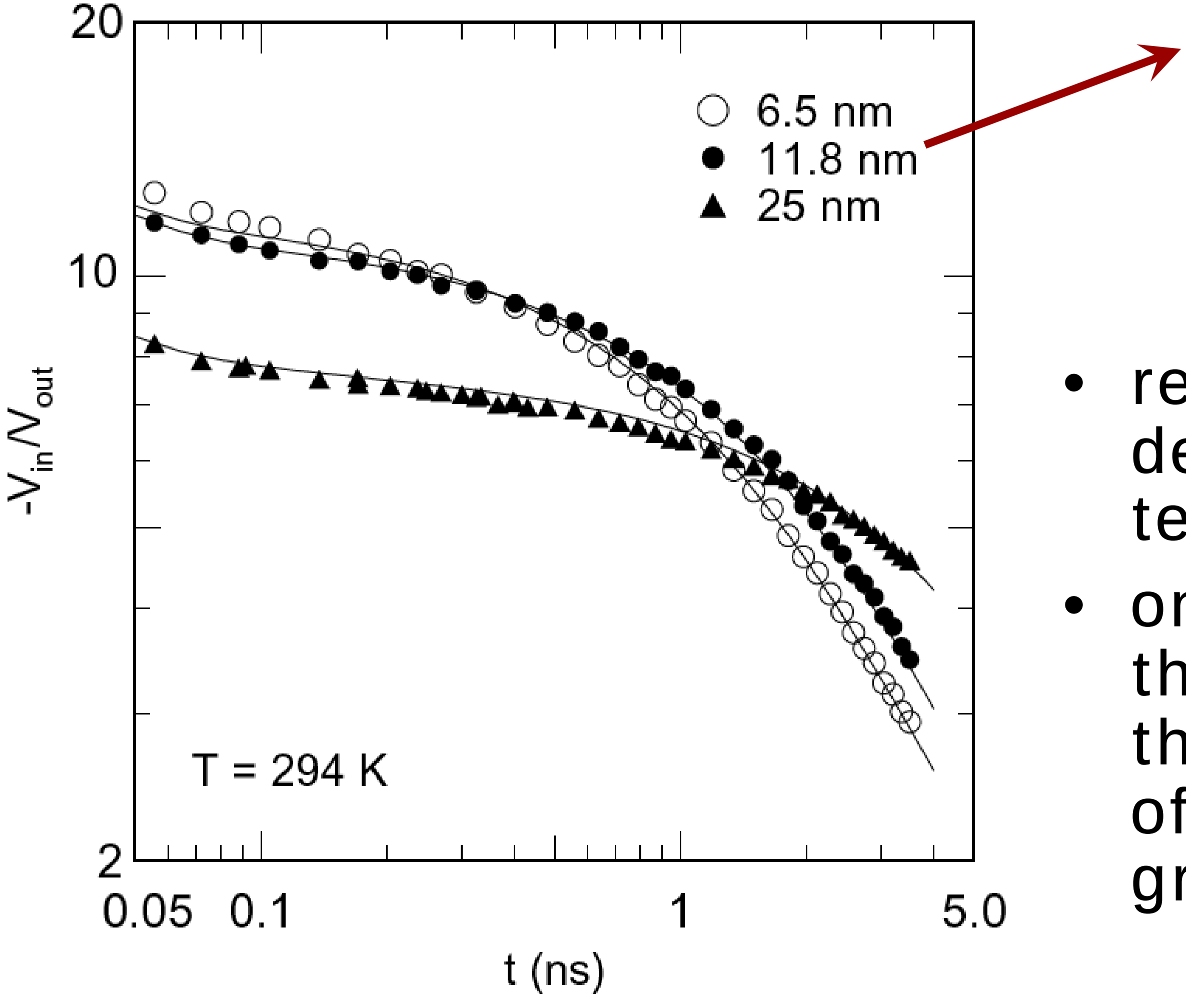
G ~ 200 MW m^{-2} K^{-1}

G ~ 15 MW m^{-2} K^{-1}

$\Lambda/G \approx 3$ nm

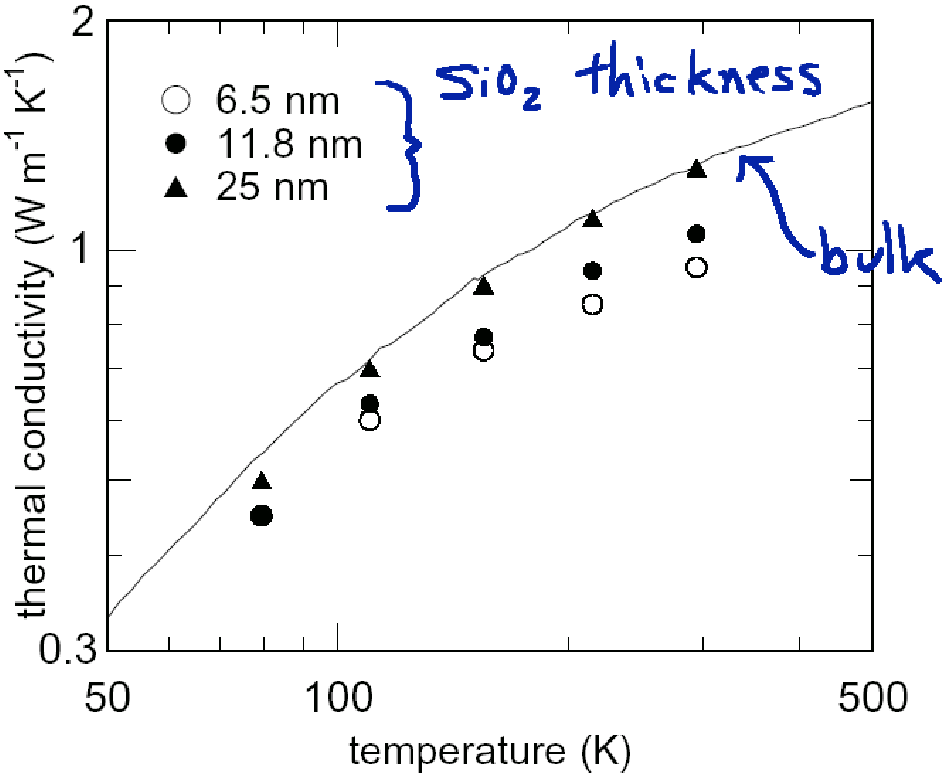
Hydrophilic interfaces are surprisingly similar despite differences in molecular structure of the surfactants

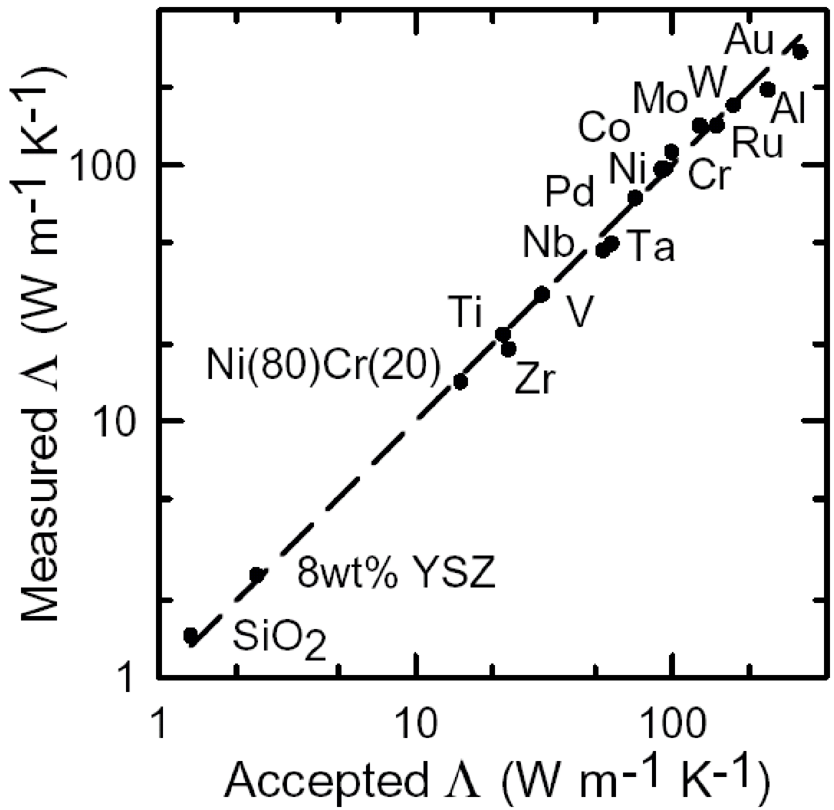
Time-domain Thermoreflectance (TDTR) data for TiN/SiO_2/Si



- reflectivity of a metal depends on temperature
- one free parameter: the "effective" thermal conductivity of the thermally grown SiO_2 layer

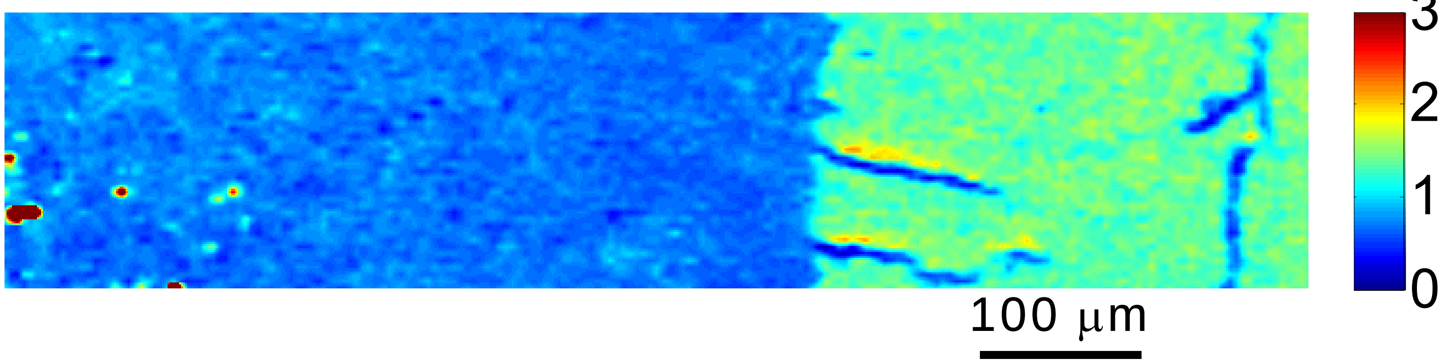
TDTR: Flexible, convenient, and accurate

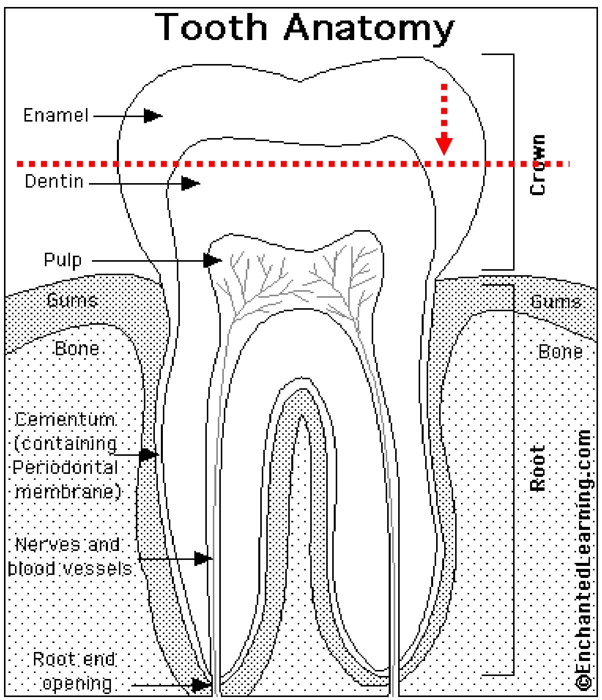




...with 3 micron spatial resolution

Thermal conductivity map of a human tooth





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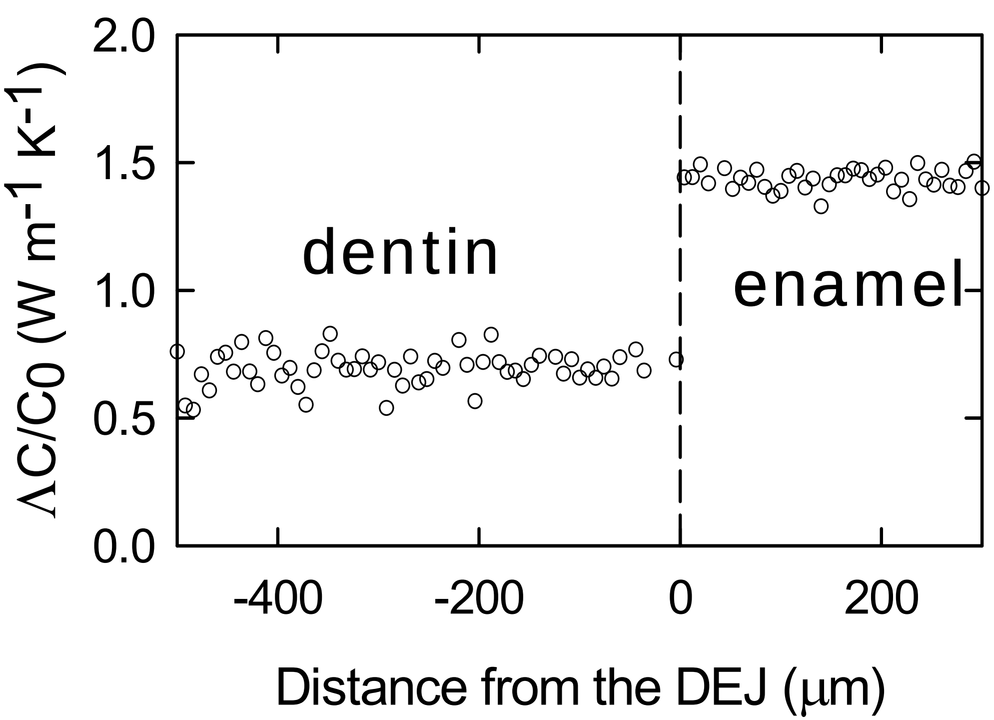
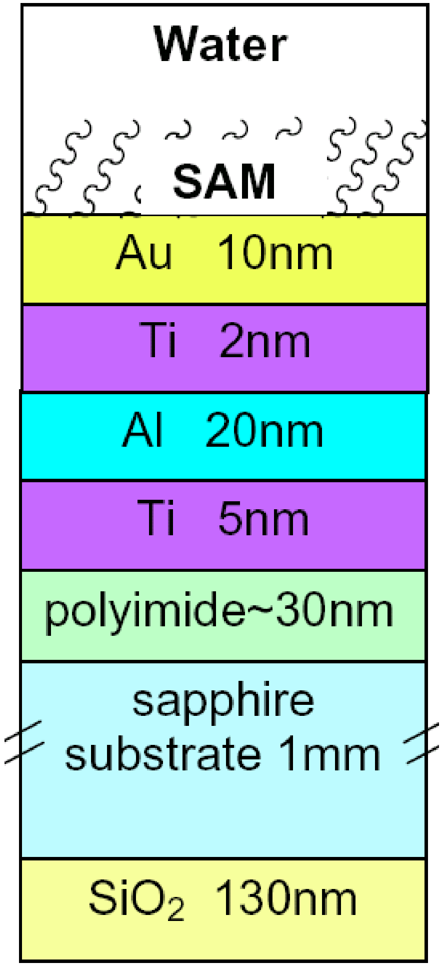
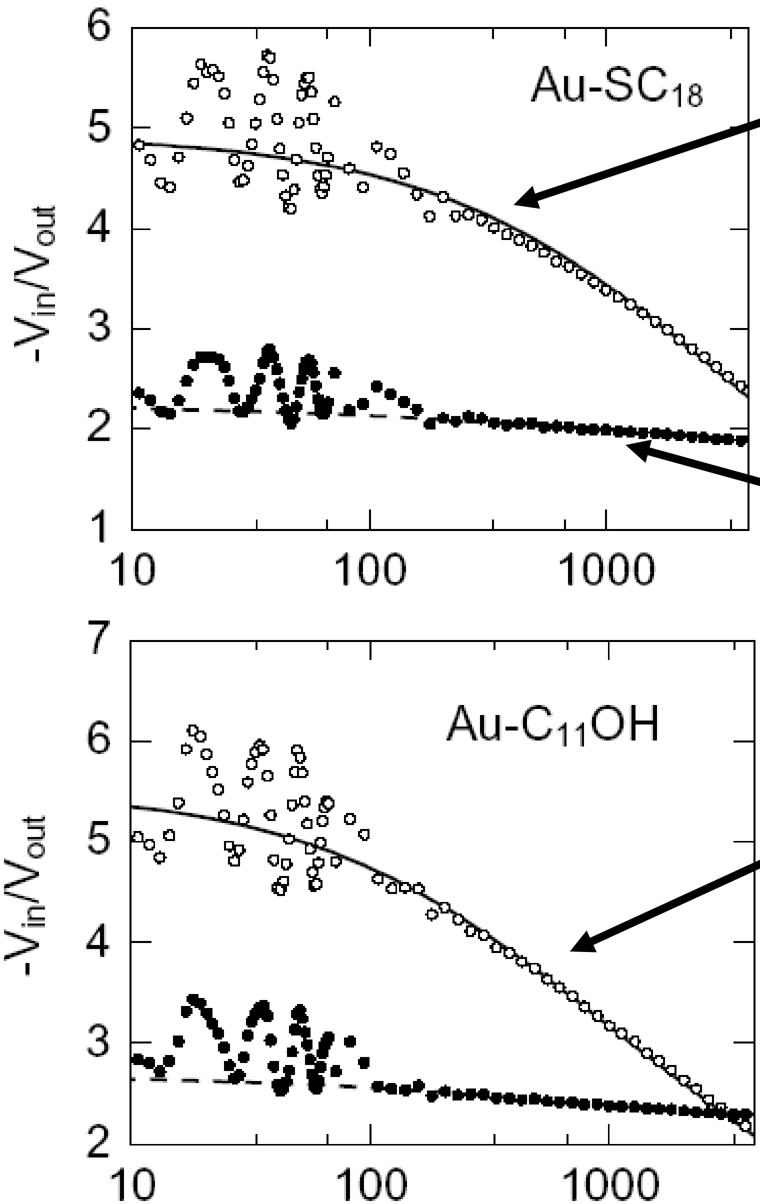


Thermoreflectance of aqueous interfaces





hydrophobic
50 MW/m^2-K

no water

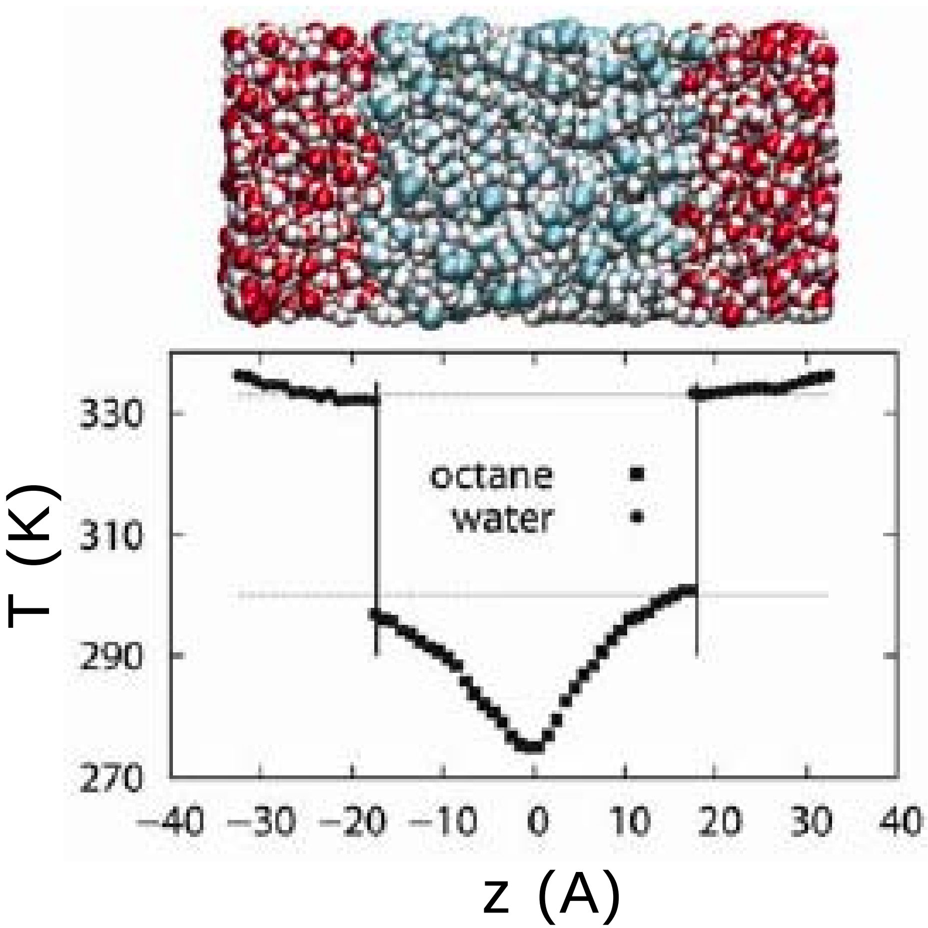
hydrophilic
100 MW/m^2-K

Thermoreflectance of solid/H_2O interfaces

- Experiments contain many interfaces and layers so look at the difference in the conductance created by changing from hydrophobic to hydrophilic.
- Define Kapitza length, equivalent thickness of water: $h = \Lambda / G$
  - Au/hydrophobic h = 12 nm
  - Au/hydrophilic h = 6 nm
- Difference between CH_3 and OH terminal group
  - Au Δh=6 nm
  - Al Δh=7 nm

MD Simulation of model interfaces

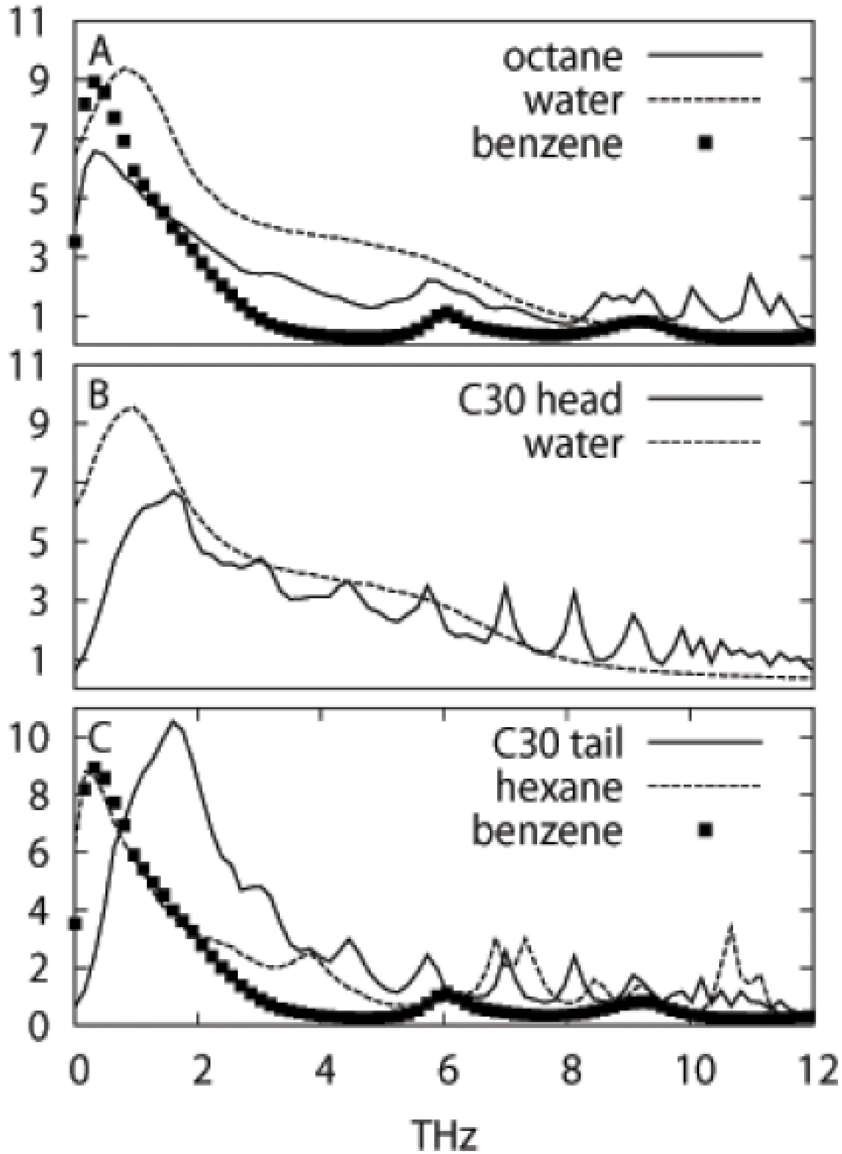
Keblinski et al., RPI



water-octane

G = 65 MW/m^2-K

Simulated vibrational spectra

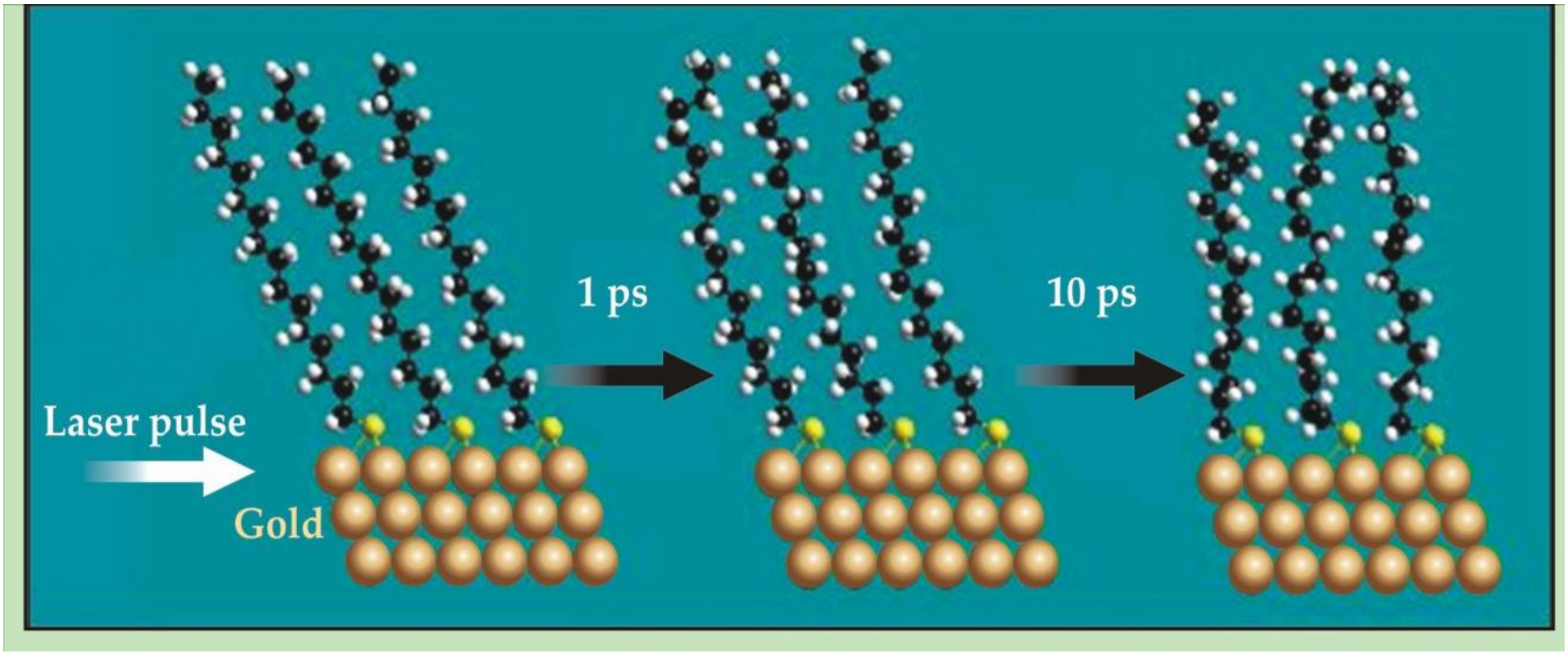


Interface	G (MW/m^2-K)	Λ-H_2O/G (nm)
Water Octane	65	9
Water Benzene	175	3.4
Water Surfactant	300	2
Surfactant Hexane	370	1.6
Surfactant Benzene	190	3

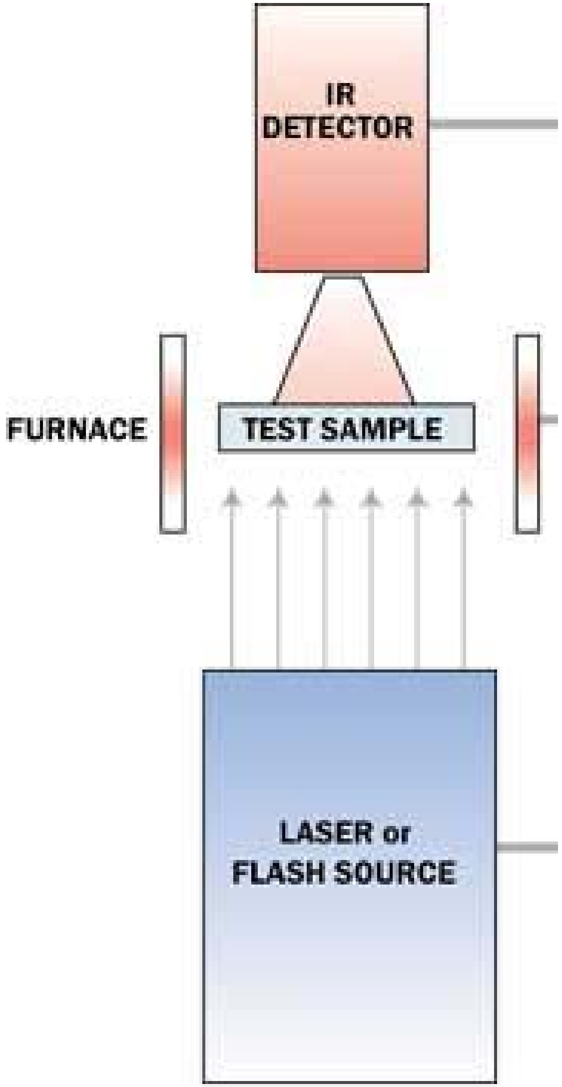
difference between water/octane and water/surfactant

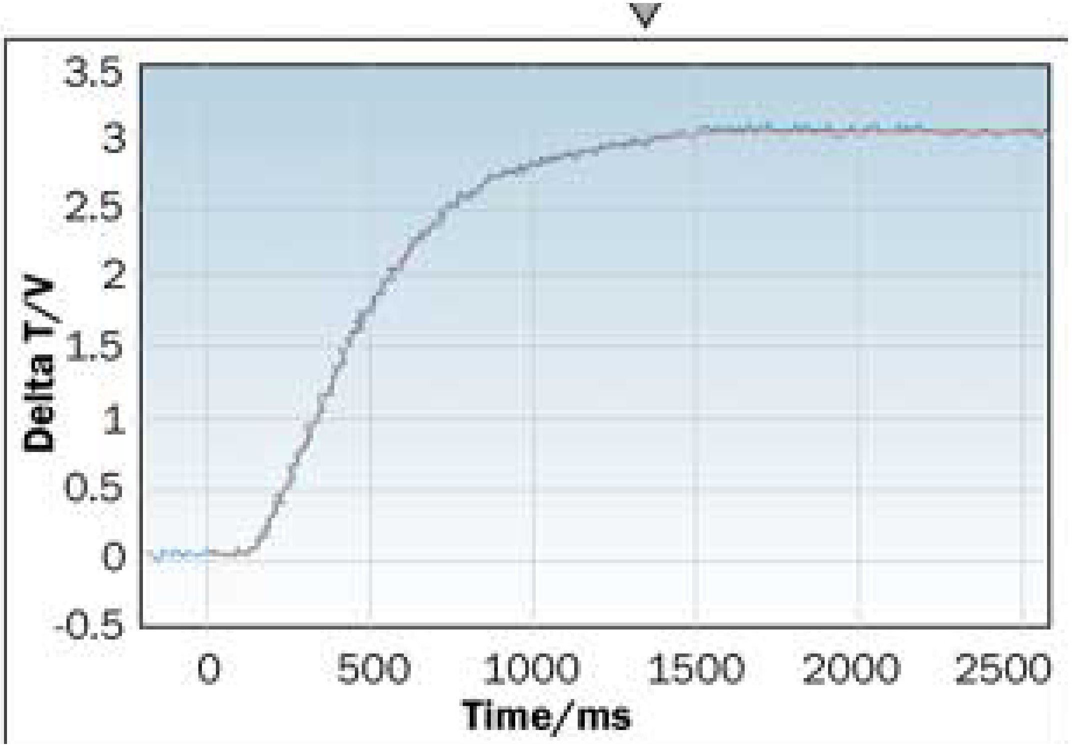
Δh = 7 nm

Heat transport and ultrafast disordering of an organic molecule (with Dana Dlott)



Classic "flash diffusivity" measurement

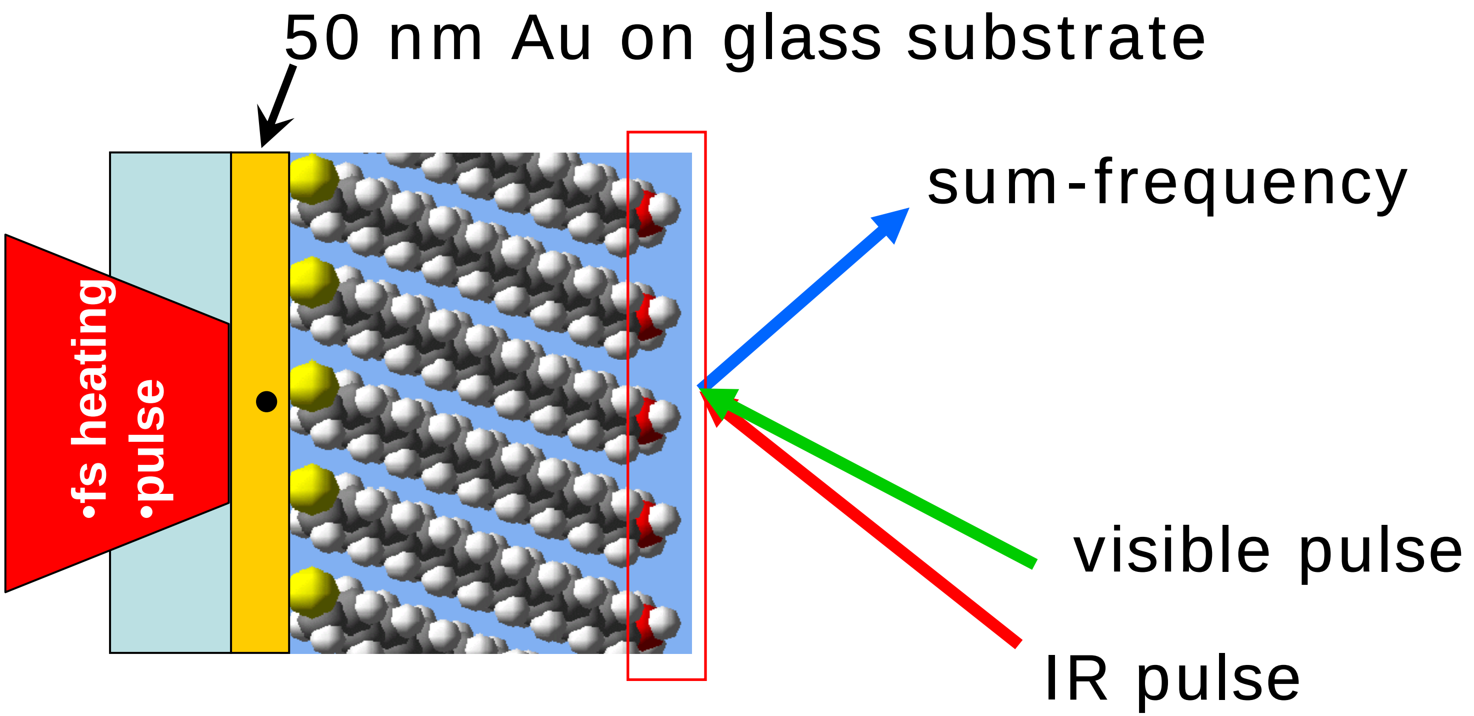




http://electronics-cooling.com/articles/2002/2002_may_a4.php

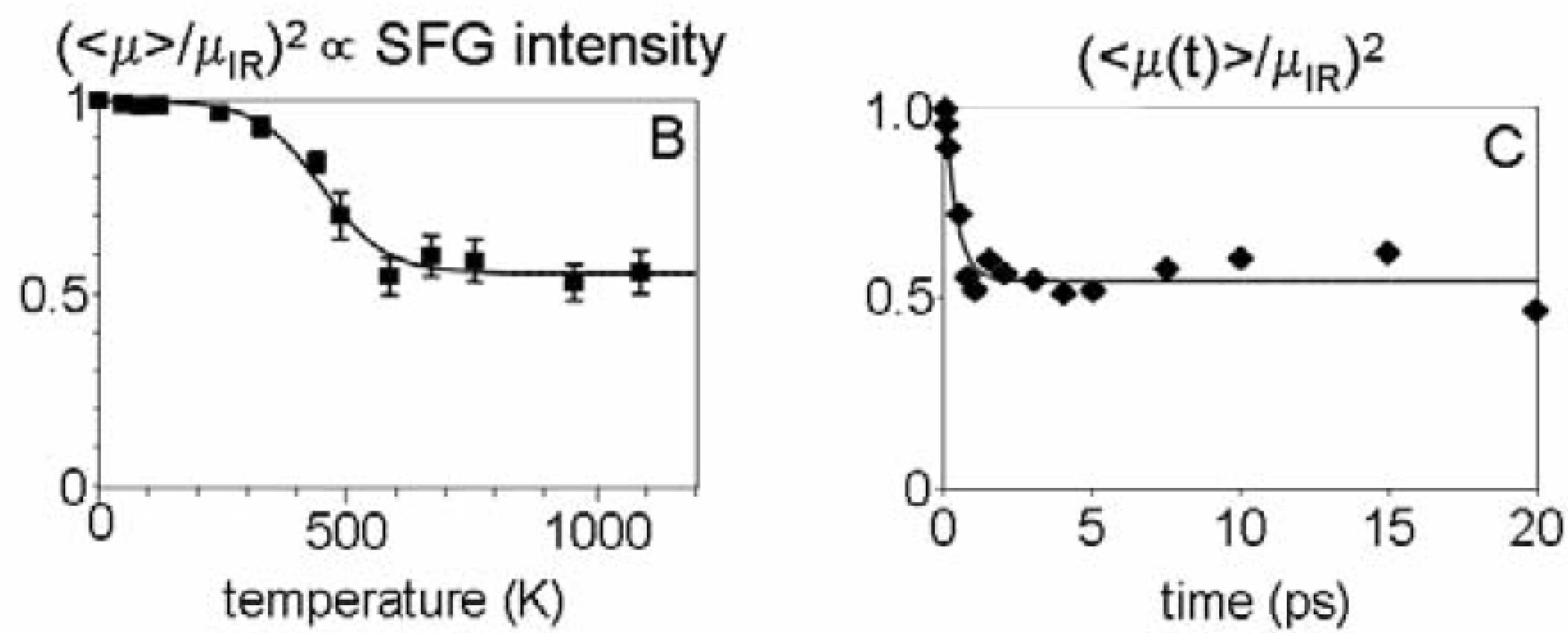
Broad-band sum-frequency generation (SFG) vibrational spectroscopy

- tunable (2.5-18 μm) broad-band IR pulse
- fixed (800 nm) narrow band
- sum-frequency signal analyzed by spectrograph

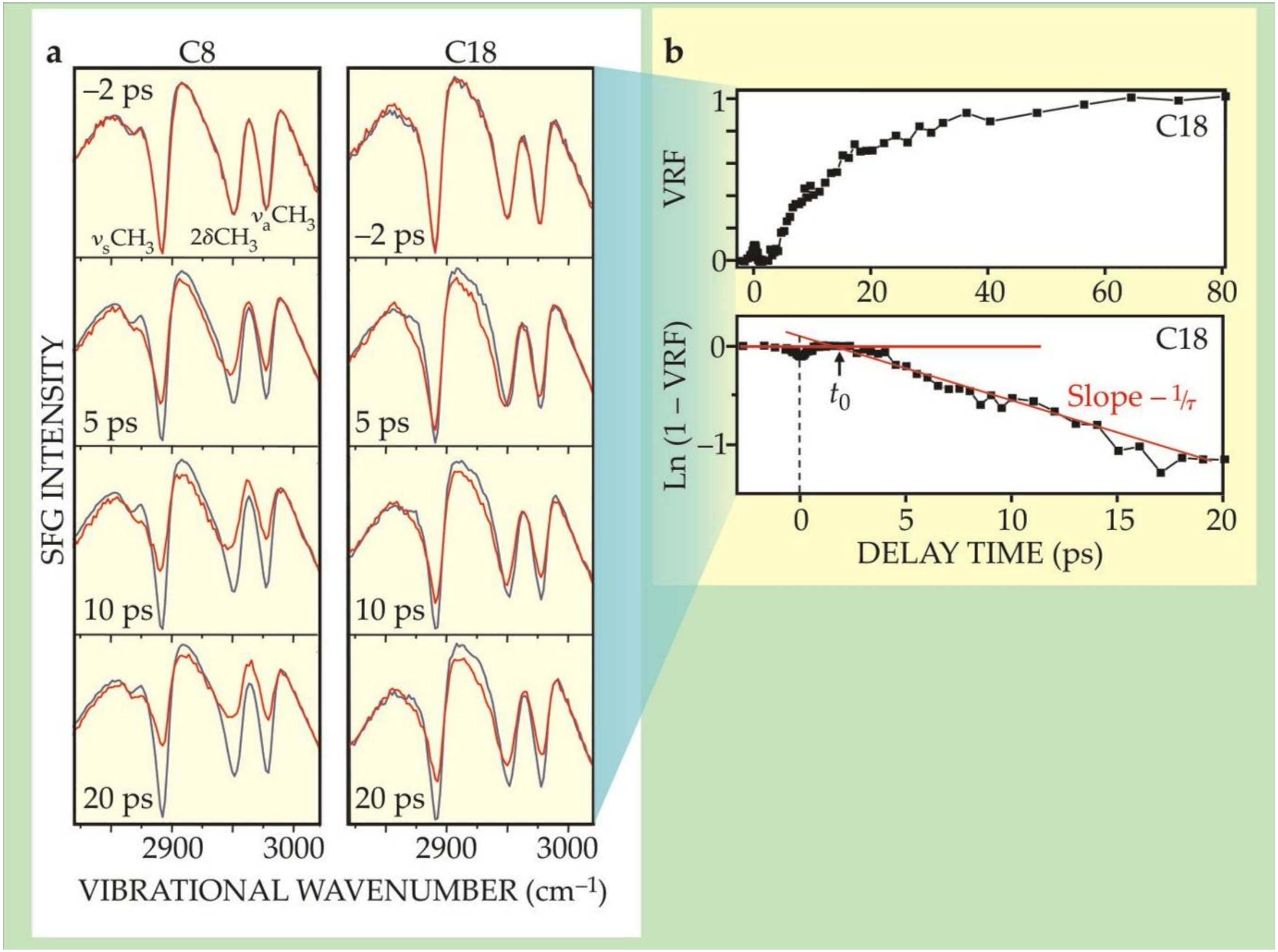


Complicated thermometer

- MD simulation of suddenly heated alkane molecules: greatest sensitivity near 500 K.
- Disordering occurs in 1 ps for large(>300 K) temperature excursion

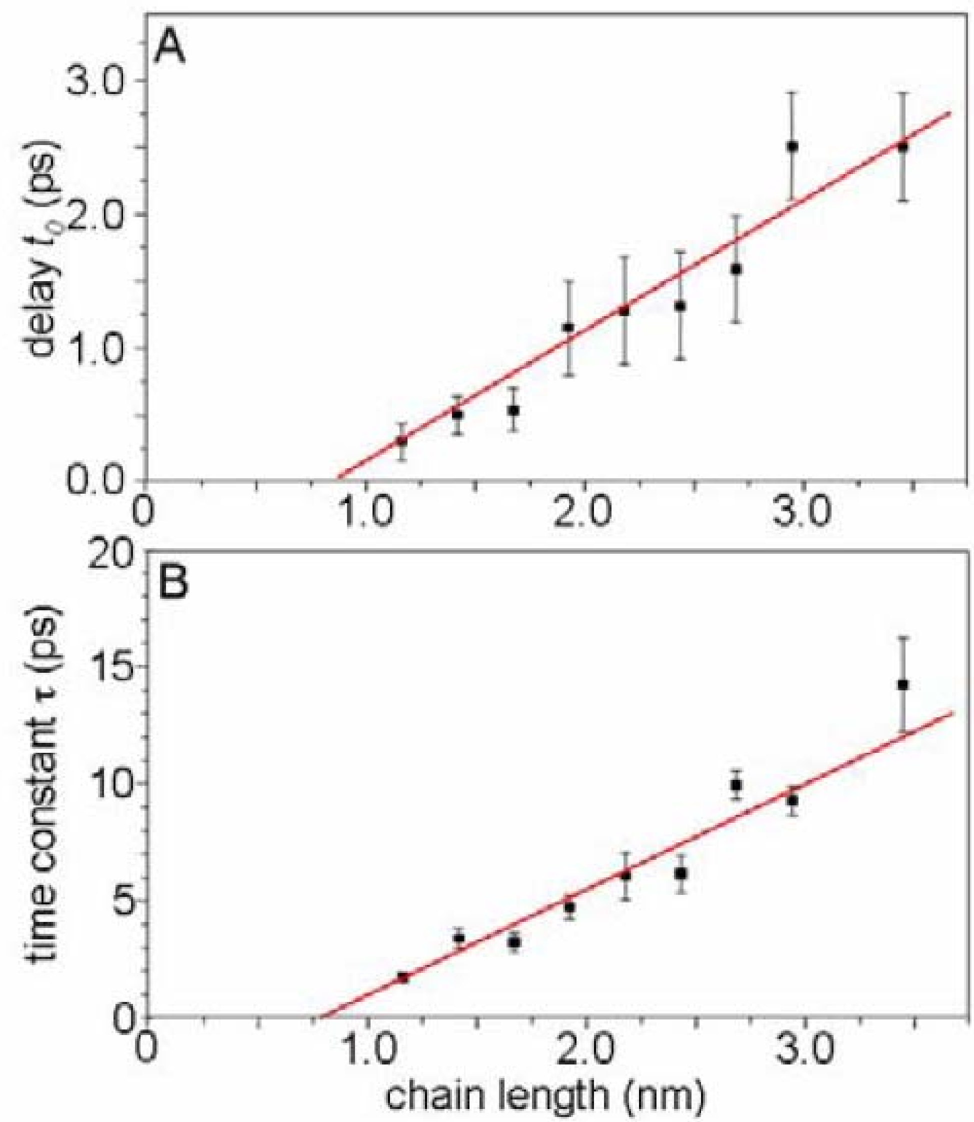


Time-resolved sum-frequency spectroscopy



Interface limited heat transport

- Both onset and time-constant of disordering are approximately linear in chain length
- Suggests heat transport is controlled by the interface (not diffusive in the molecule)
- Estimate of molecule heat capacity gives thermal conductance of ≈50 pW/K



Summary, needs, and questions

- Thermal conductance of Pb/diamond is much higher than radiation limit. Need a quantitative theory for the anharmonic channel for heat transport.
- Low conductance of hard/soft interfaces limits the applications of carbon nanotubes for thermal management. How can we measure the relevant conductance for the heat carrying phonons?
- The difference in Kapitza lengths for hydrophobic and hydrophilic interfaces is large at the molecular scale (Δh=6 nm) but rules out significant “drying” of hydrophobic interfaces.
- Demonstrated sum-frequency generation as the world’s thinnest thermometer. Can we find a thin and fast thermometer that is easier to calibrate?