Thermal conductance of solid-liquid interfaces

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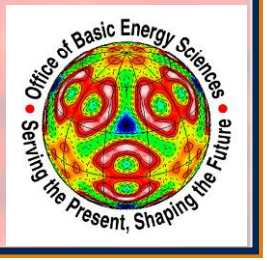
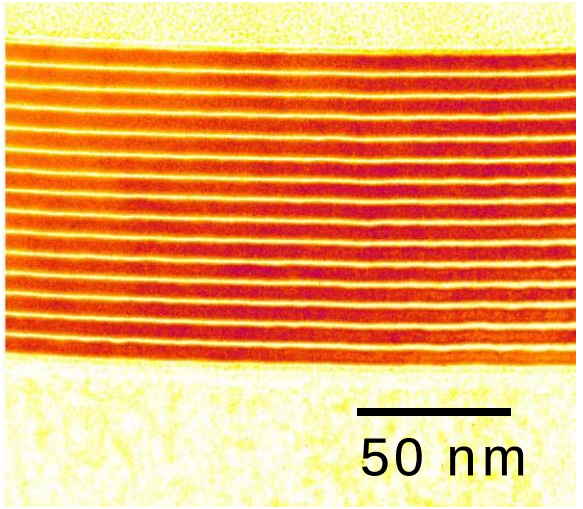


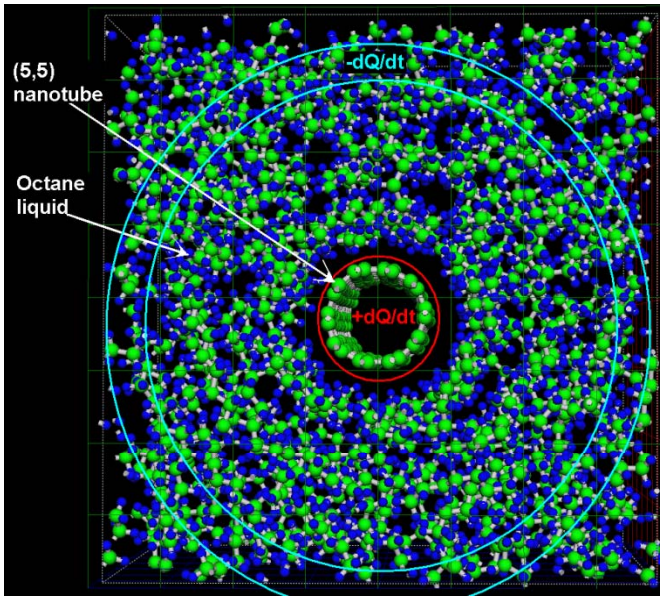
Interfaces are critical at the nanoscale

- Low thermal conductivity in nanostructured materials
  - improved thermoelectric energy conversion
  - improved thermal barriers



- High thermal conductivity composites and suspensions

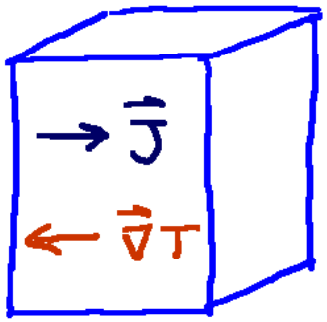
- Localization of thermal effects: medical therapy/biotechnology



Interface thermal conductance

- Thermal conductivity Λ is a property of the continuum

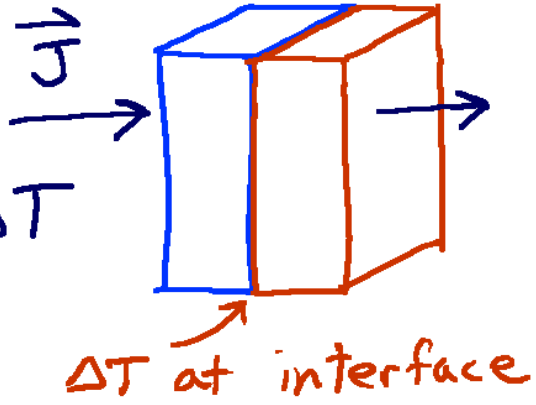
$\vec{J} = -\Lambda \vec{\nabla} T$



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

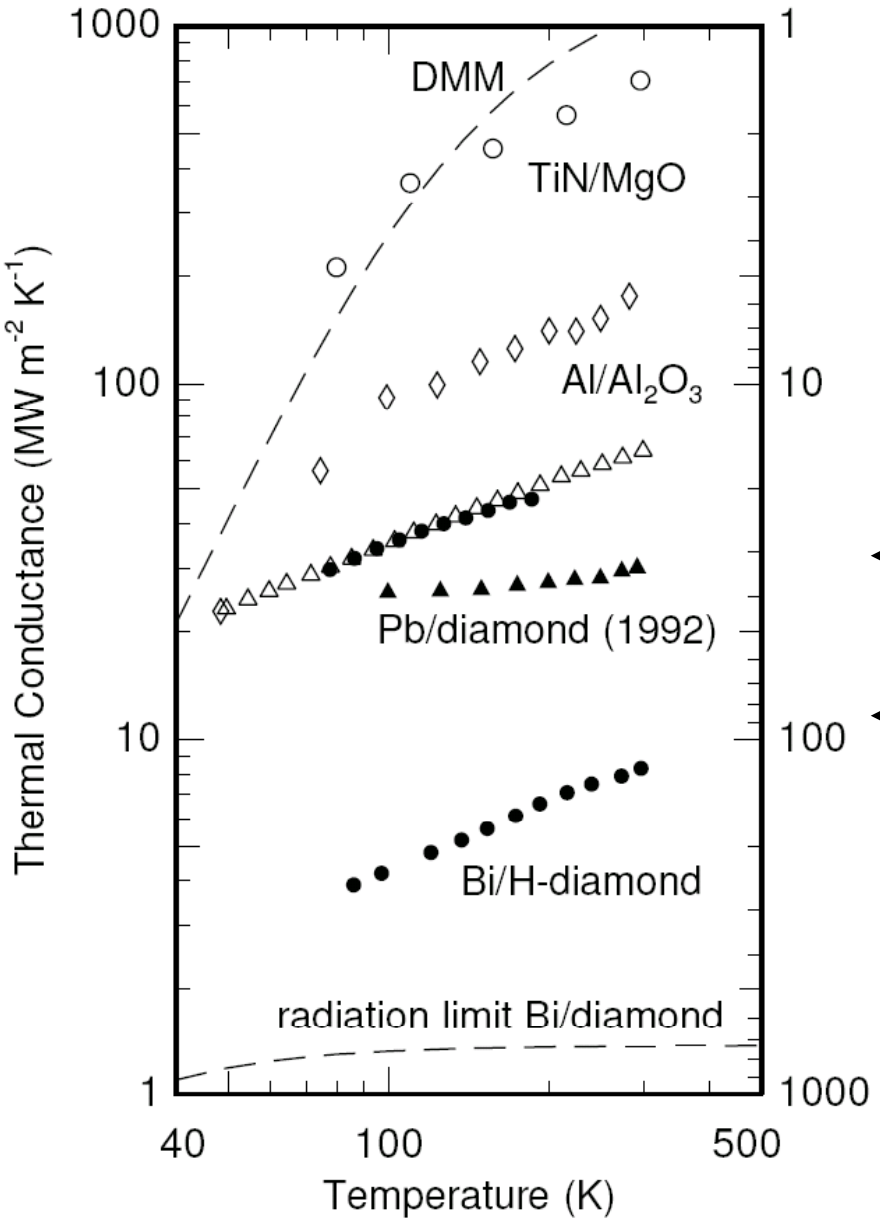
- Thermal conductance (per unit area) *G* is a property of an interface

$J = G\Delta T$



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

Factor of 60 range at room temperature

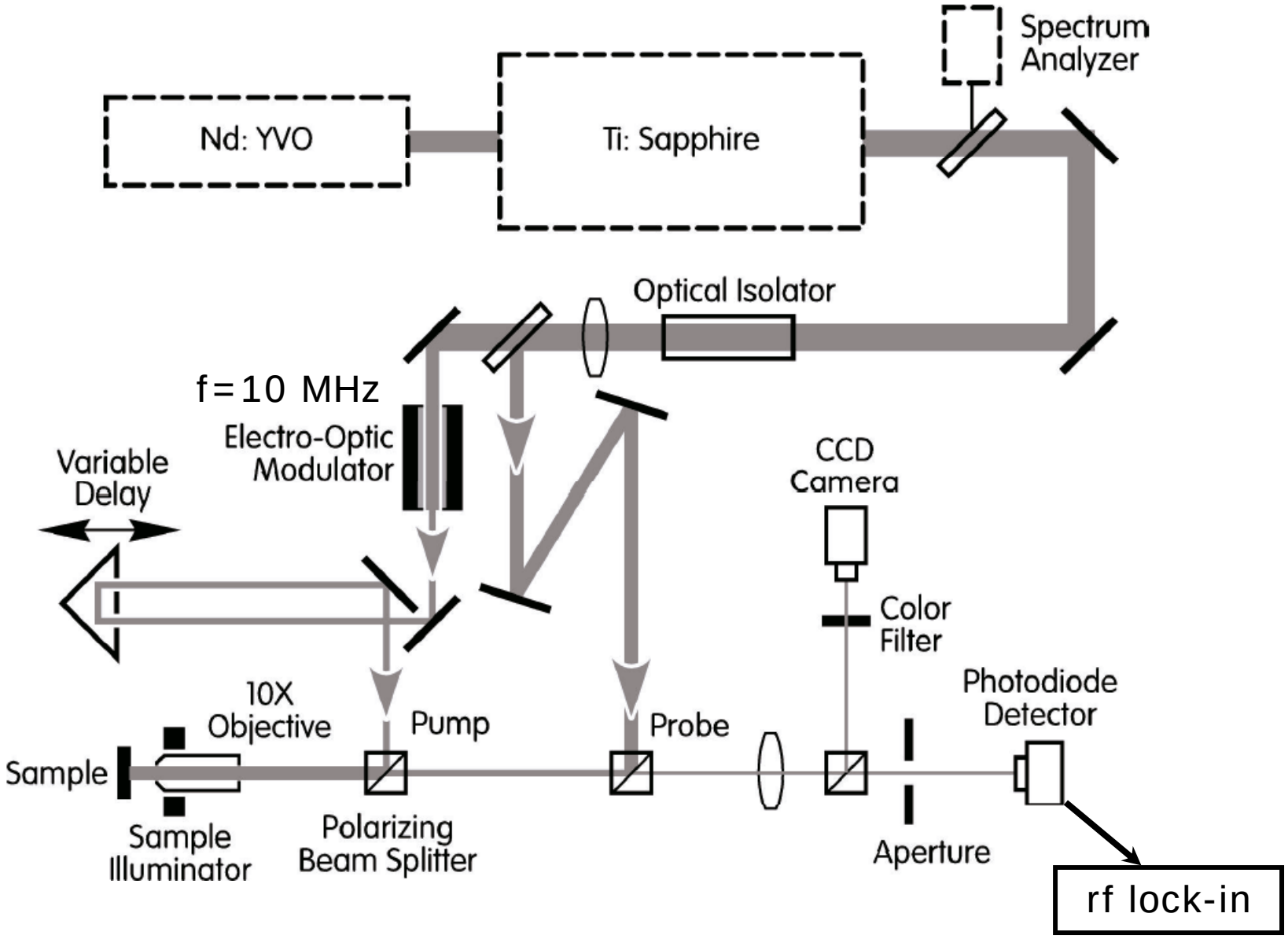


Au/surfactant/water

PMMA/Al_2O_3

nanotube/alkane

Modulated pump-probe apparatus



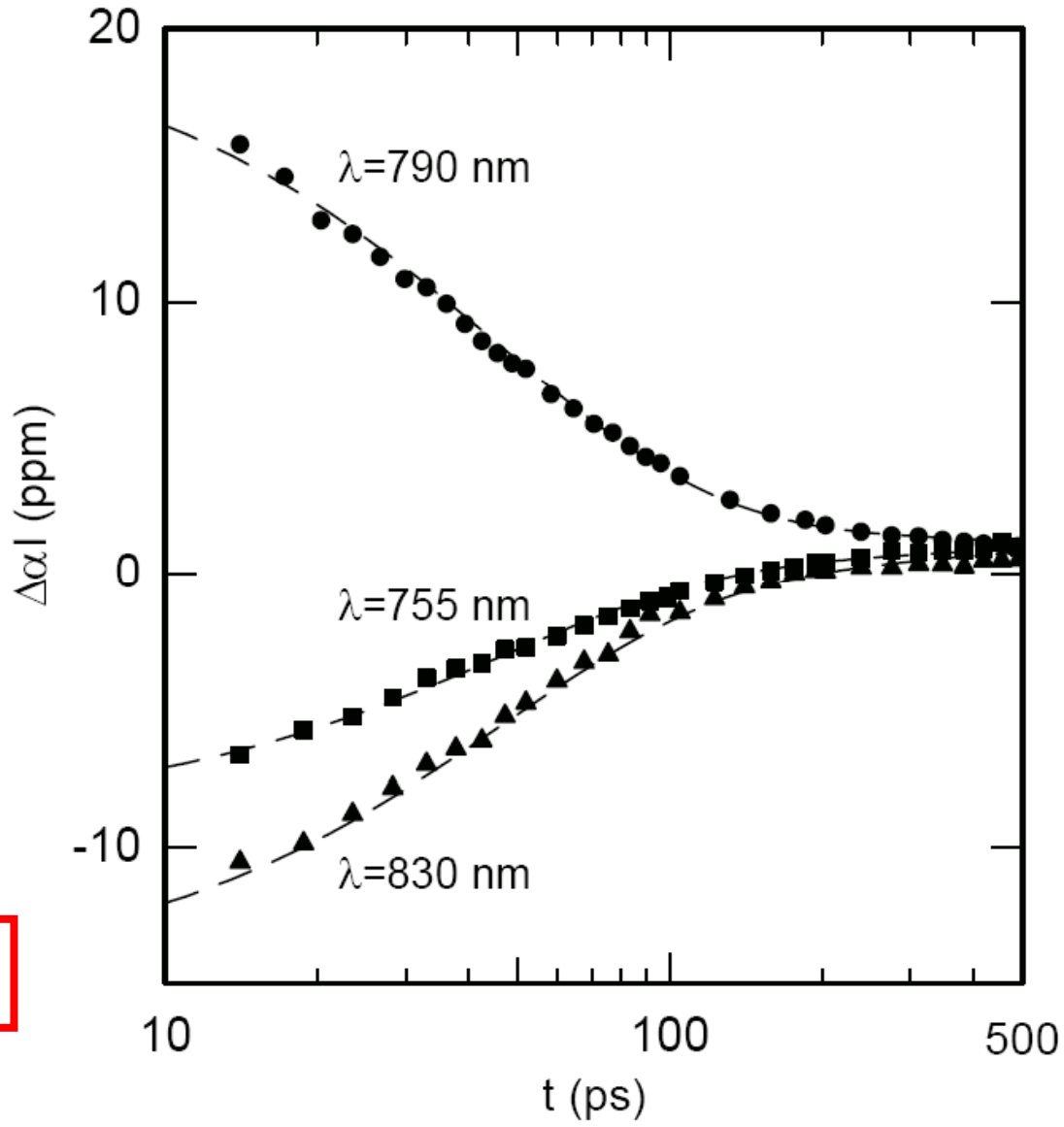
Solid-liquid interfaces: Two approaches

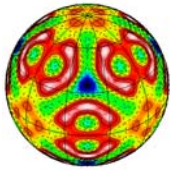
- Transient optical absorption of nanoparticles and nanotubes in liquid suspensions.
  - Measure the thermal relaxation time of a suddenly heat particle. Interface sensitive if the particle is small enough.
  - limited to interfaces that give good stability of the suspension, e.g., hydrophilic particles 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.

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

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





Application: Critical aspect ratio for a fiber composite

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

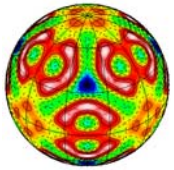
$$\Lambda_c = \frac{1}{3} V_f \Lambda_{NT}$$

- 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"



Comparisons between experiment and simulation: general considerations

Experiment

- optical pulse creates electronic excitations which decay
  - electron-phonon
  - phonon-phonon
- high frequency vibrations are quantized
- interfaces are difficult to prepare and characterize

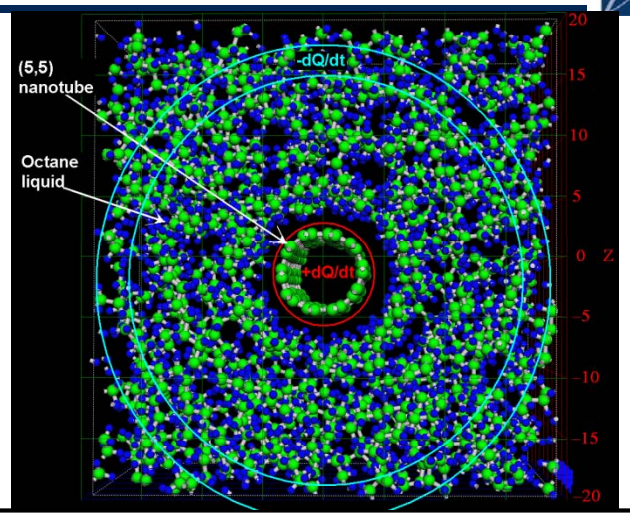
Simulation

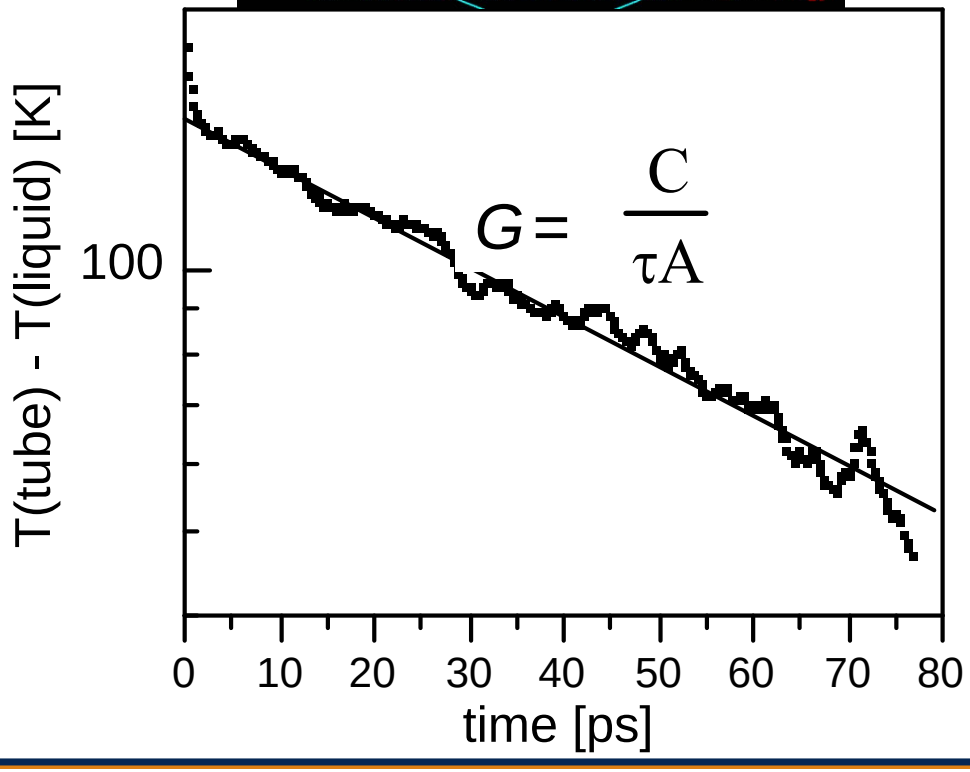
- no electrons but can add heat any way we want
- all vibrational modes are thermally excited.
- uncertainties in potentials
- finite-size simulation cell removes lowest-frequency vibrations and creates problems for long mean-free-paths

Simulation: relaxation time

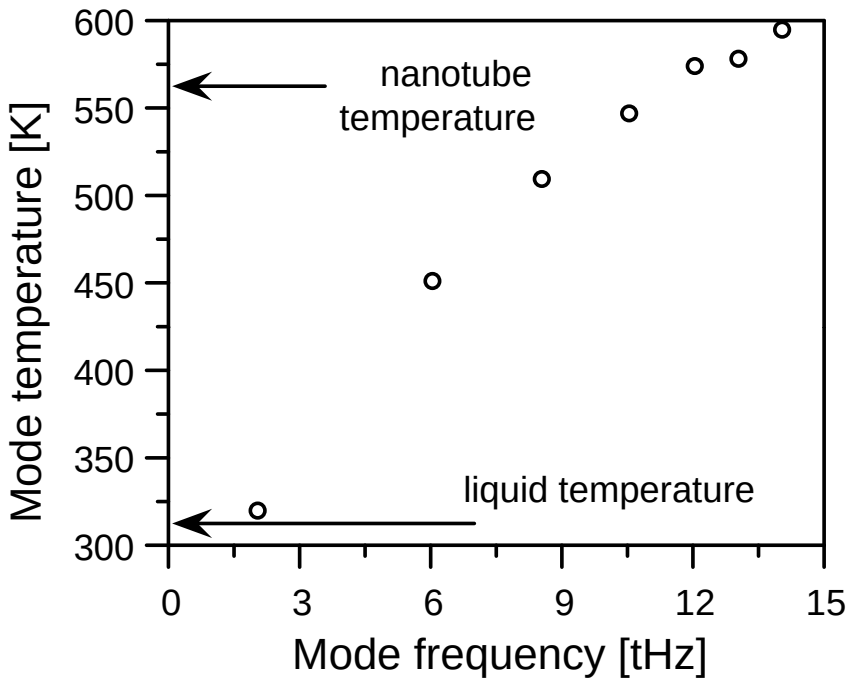
- Mimic the experiment: heat nanotube suddenly and let system equlibrate
- Use experimental heat capacity to convert time constant to G. For long tubes:

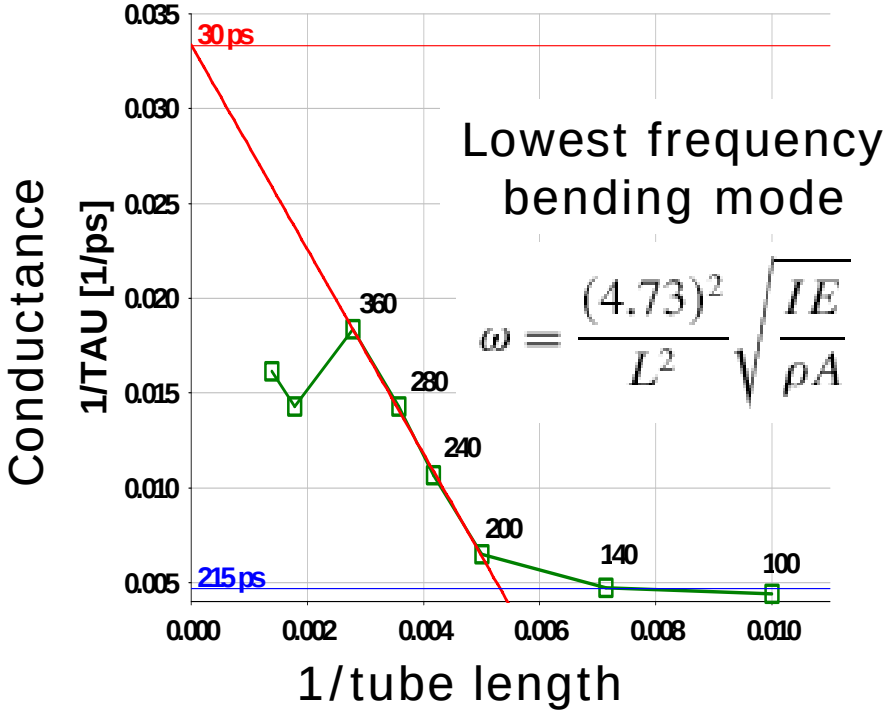
  G = 22 MW m^{-2} K^{-1}





Simulation: Mechanisms for interface heat conduction

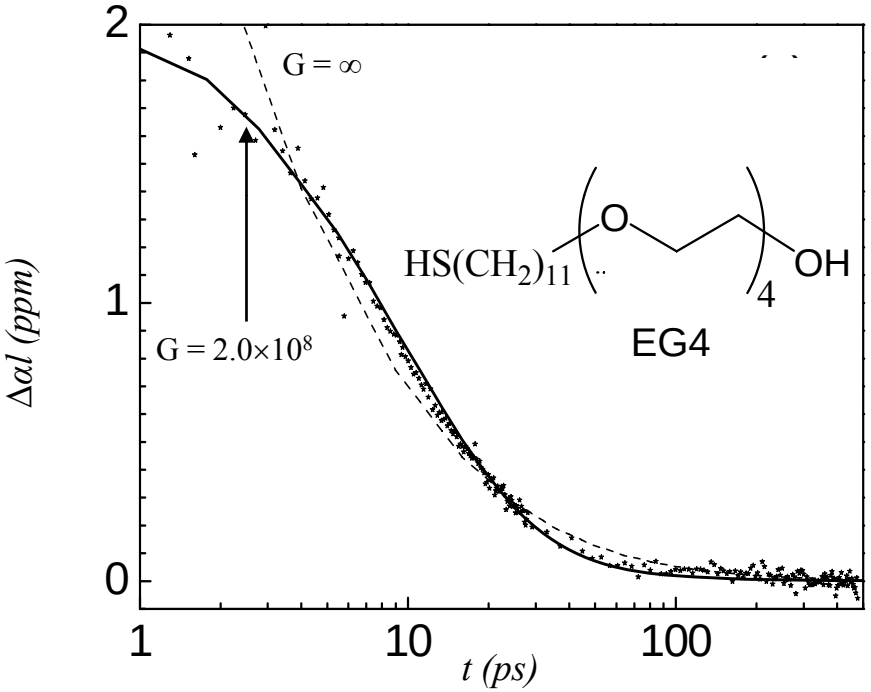


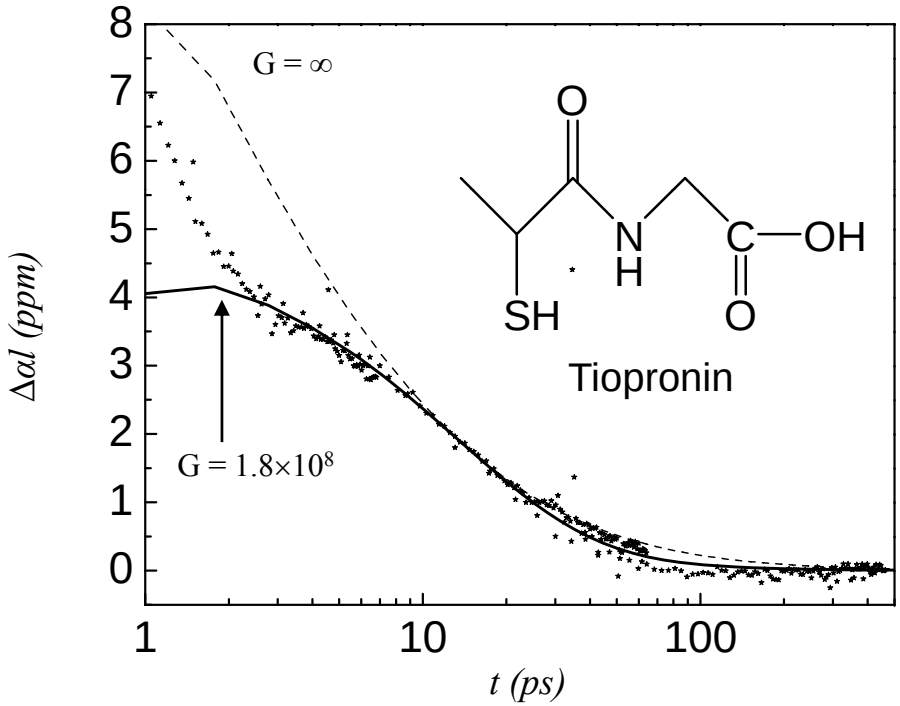


- Carbon nanotubes have a small number of low frequency modes associated with bending and squeezing. Only these modes can couple strongly with the liquid.

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

- transient absorption data

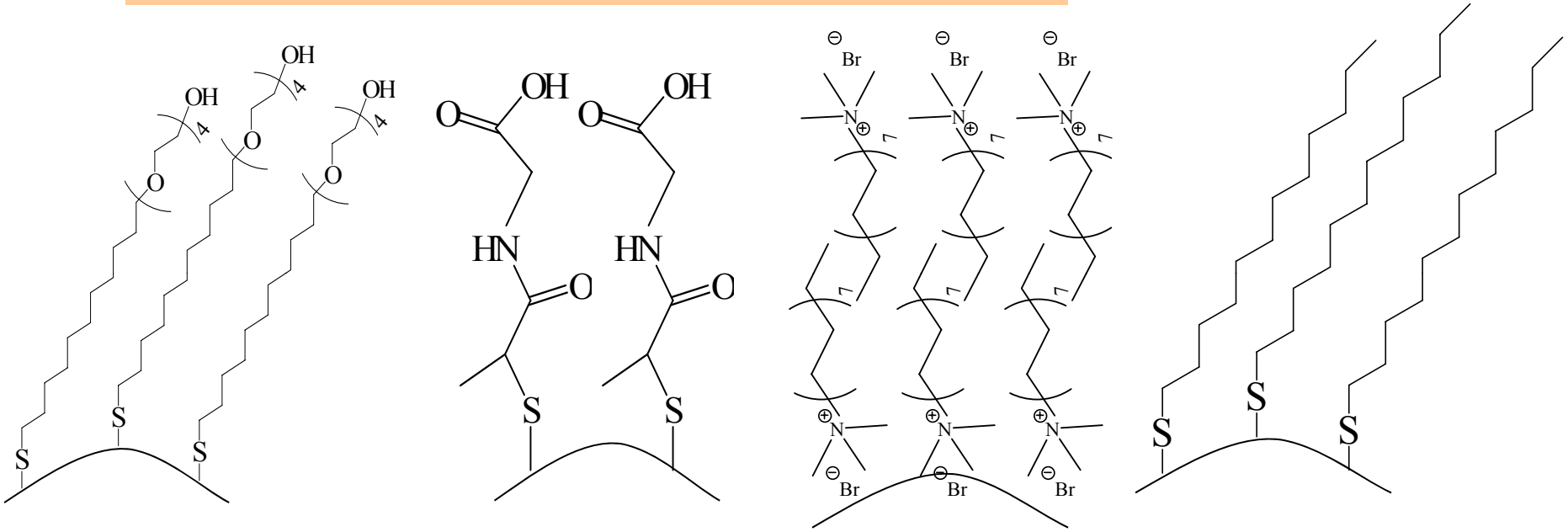




Nanoparticle summary

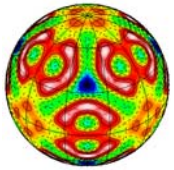
In water

In Toluene



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

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



Application: Critical particle radius for a nanofluid

- Interface conductance and thermal conductivity of the fluid determine a critical particle radius

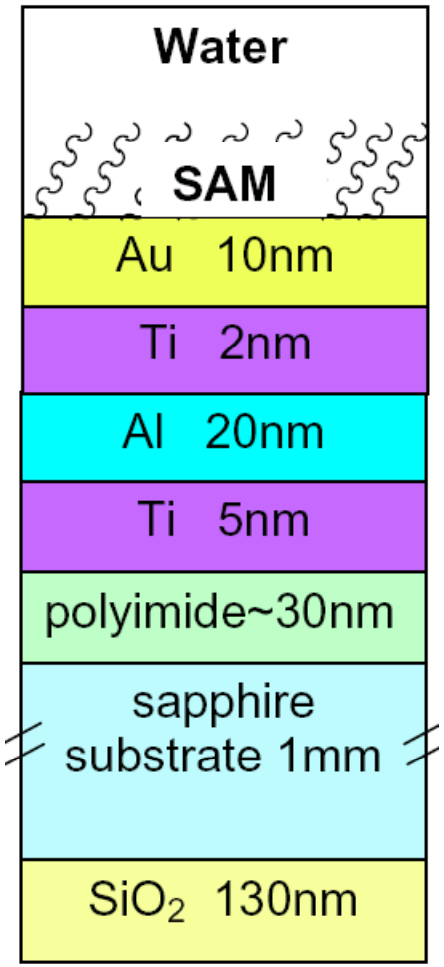
$$r_c = \Lambda/G$$

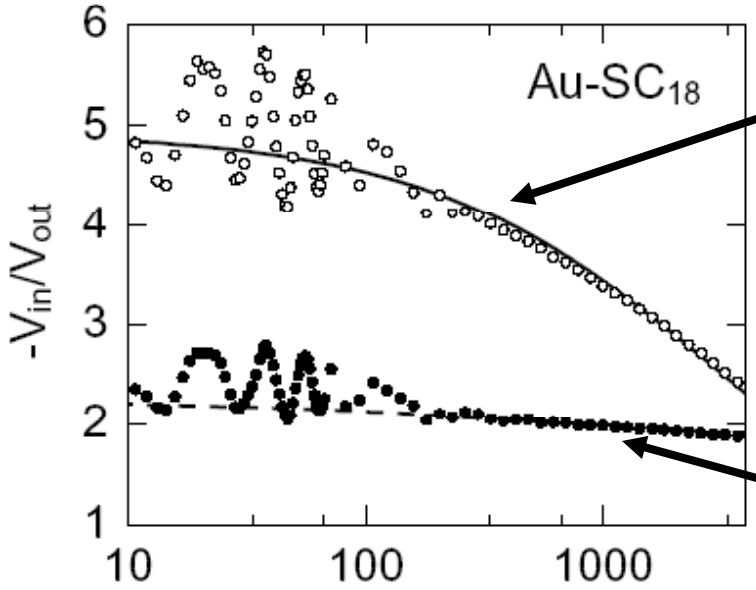
- For particles in water, r_c = 3 nm.
- For high thermal conductivity particles, dilute limit of effective medium theory

$$r >> r_c \qquad \Delta\Lambda = (1+3\phi)\Lambda$$

$$r << r_c \qquad \Delta\Lambda = (1-1.5\phi)\Lambda$$

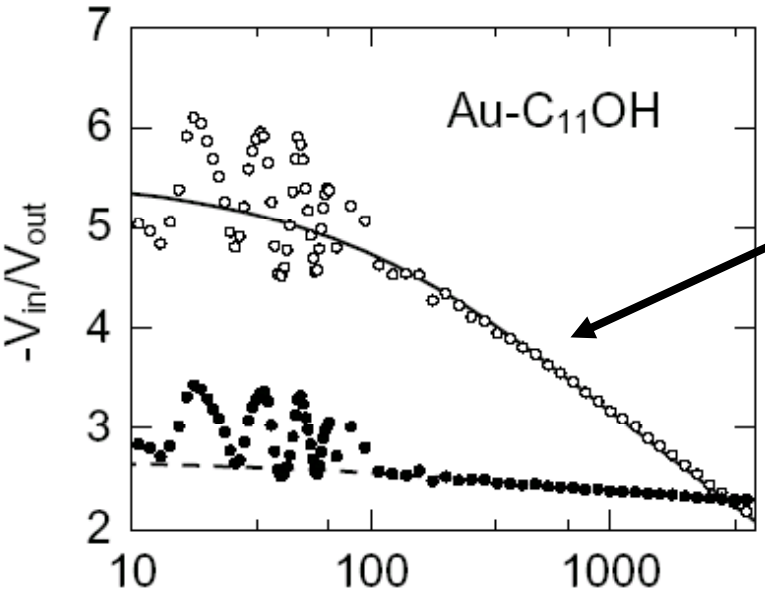
Thermoreflectance of solid/H_2O interfaces





hydrophobic
50 MW/m^2-K

no water

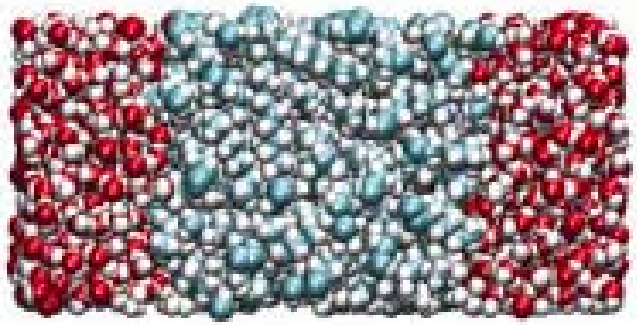


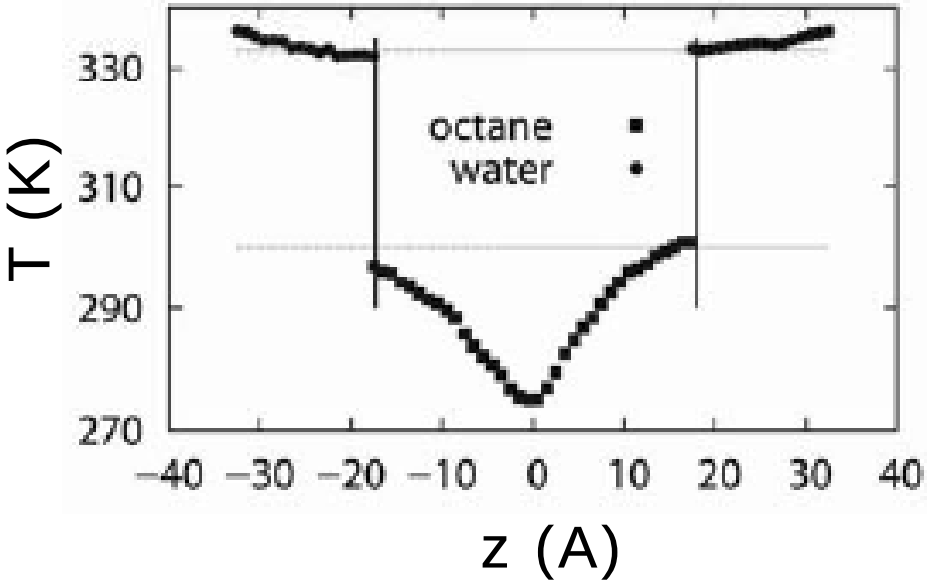
hydrophilic
100 MW/m^2-K

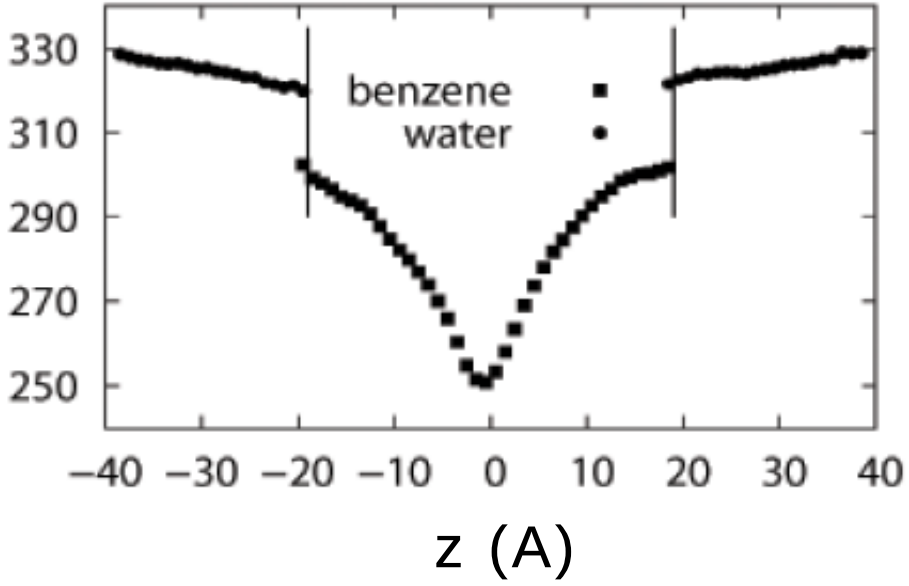
Thermoreflectance of solid/H_2O interfaces

- 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 $\Delta h = 6$ nm

Simulation of model interfaces







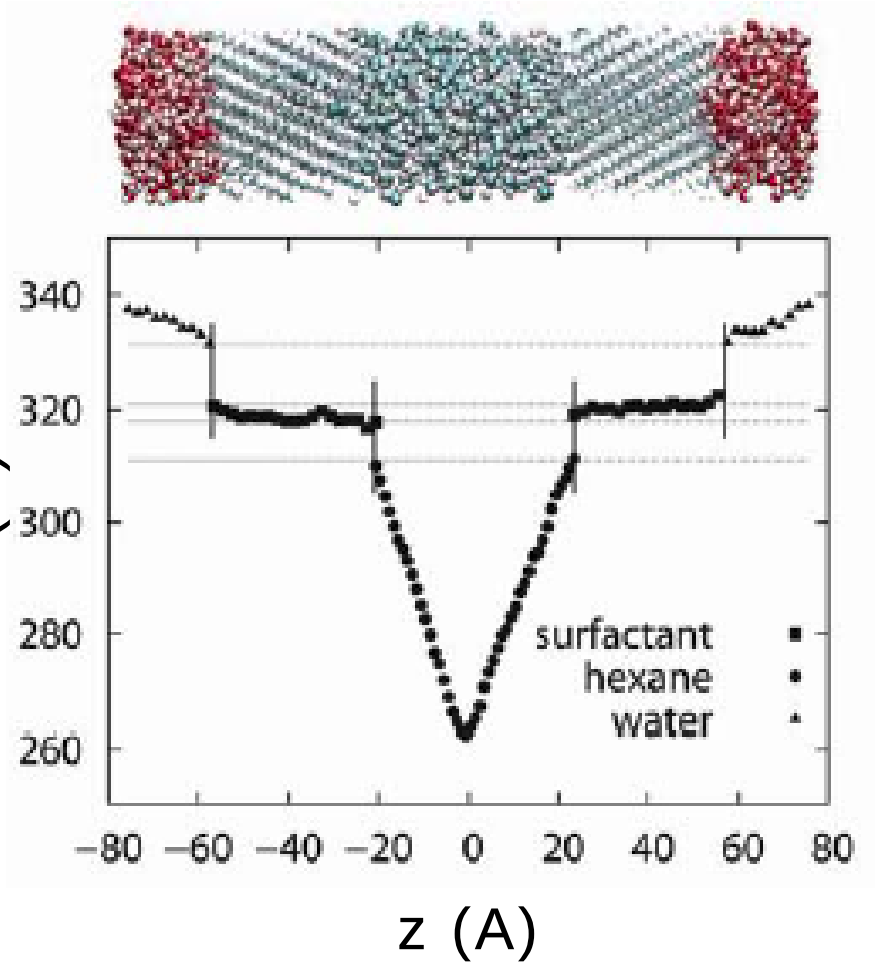
water-octane

G = 65 MW/m^2-K

water-benzene

G = 175 MW/m^2-K

Water - Surfactant - Hexane Interface



$G_{H_2O\text{-surf}}$ = 300 ± 30 MW/m^2-K

$G_{surf\text{-}hex}$ = 370 ± 30 MW/m^2-K

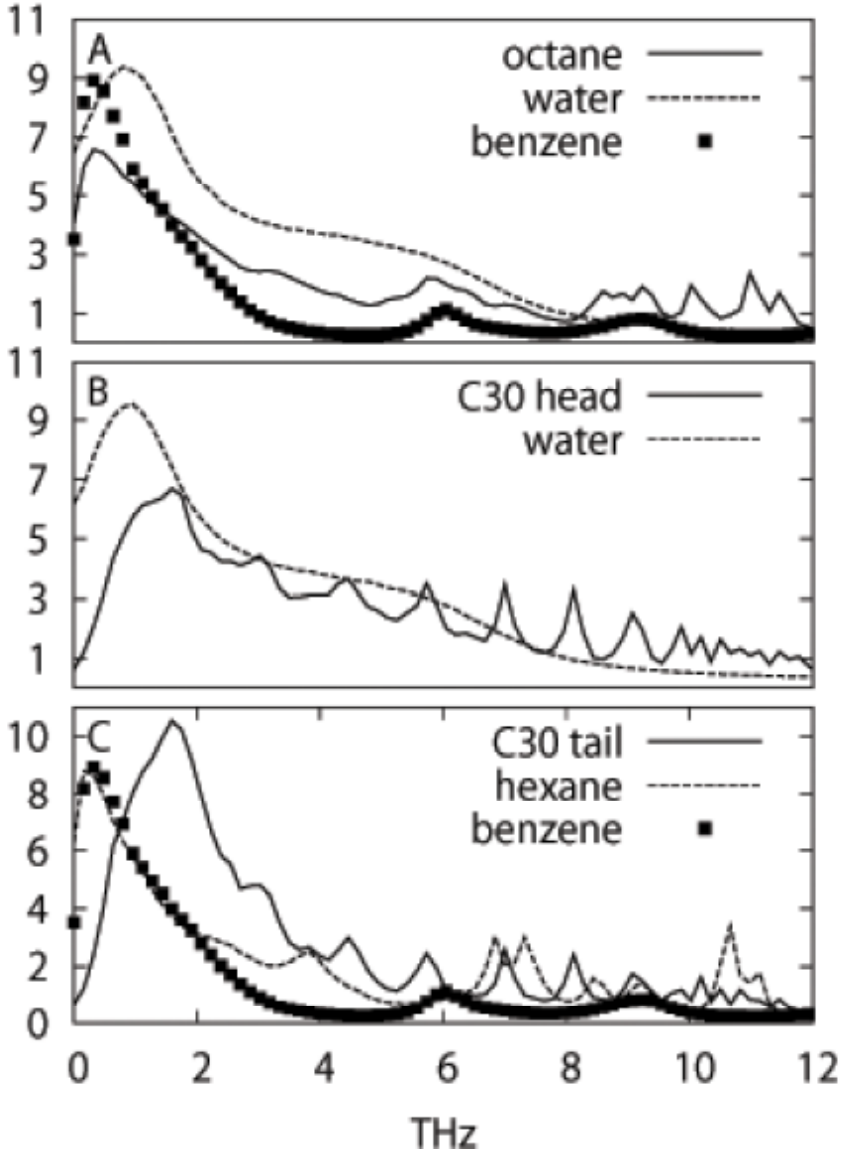
High conductivity of the ordered surfactant

$\Lambda_{surfactant}$ = 9 W/m-K

Λ_{hexane} = 0.11 W/m-K

(0.09 exp)

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

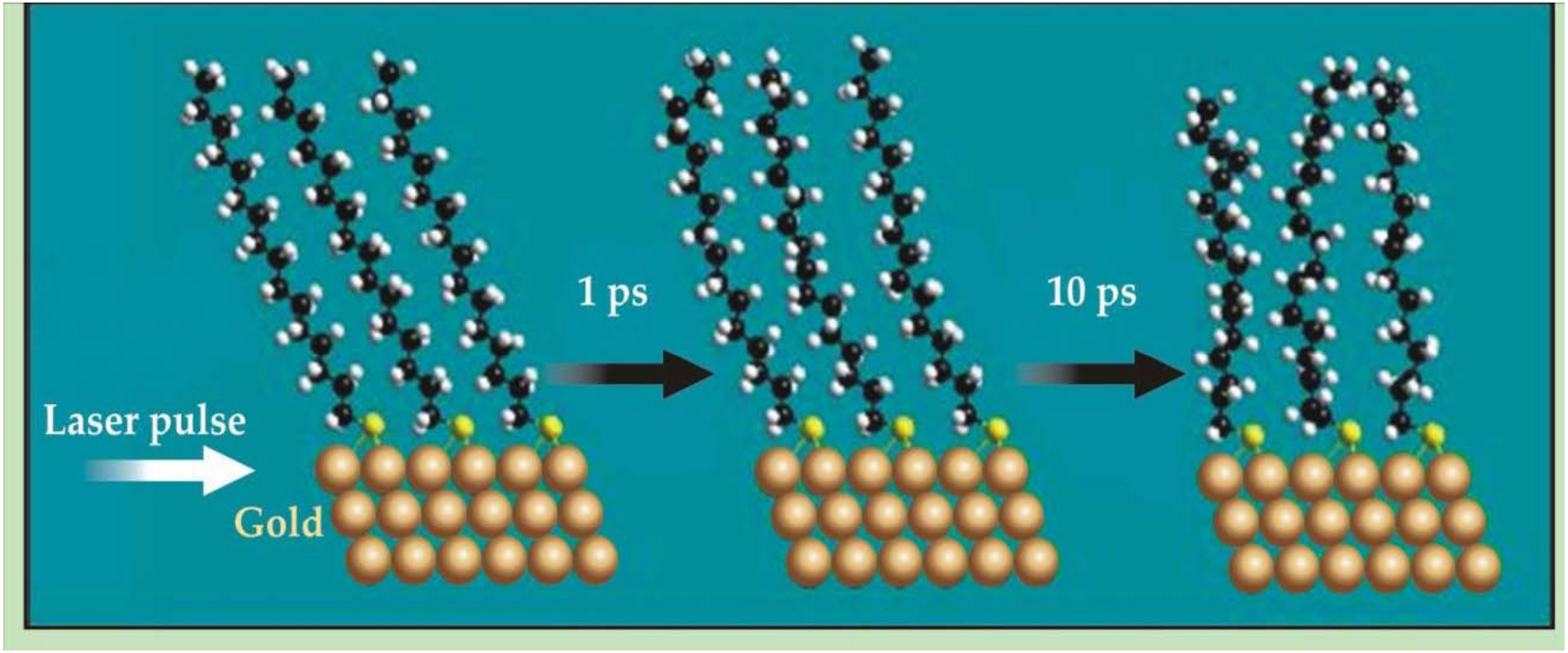
difference between water/octane and water/surfactant

Δh = 7 nm

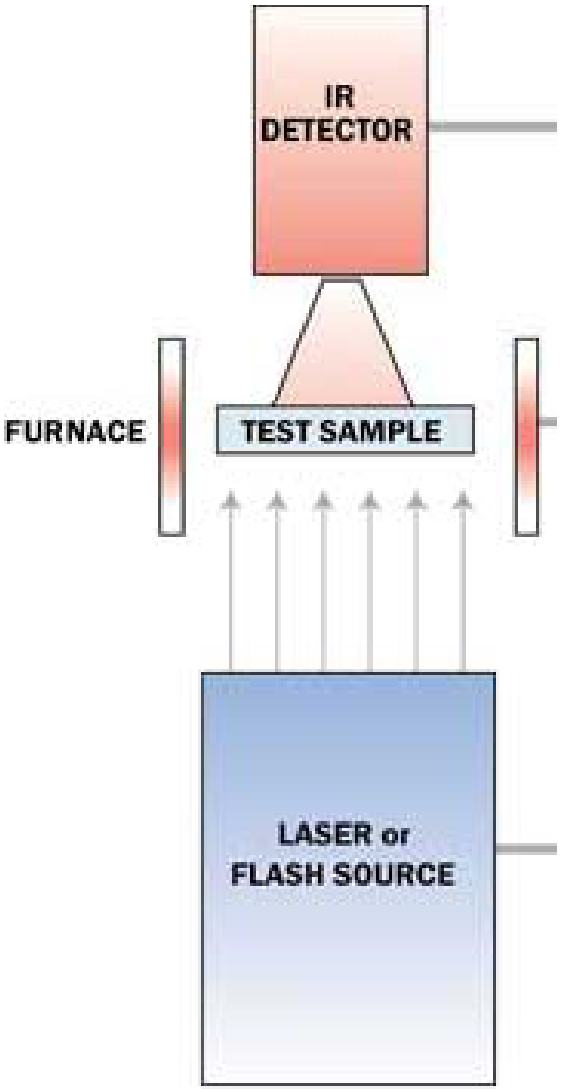
Summary (so far)

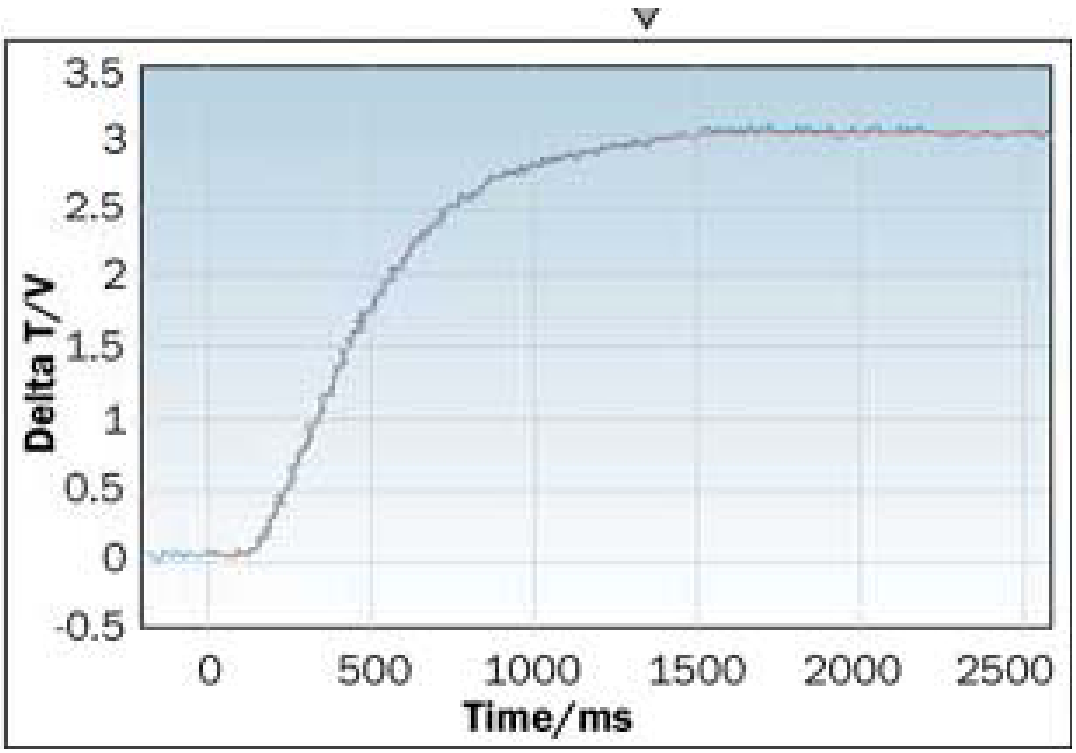
- Simulations of nanotube/octane show twice the conductance of experiment on nanotube/alkane-surfactant.
  - experiment: nanotubes form small bundles? large electron-to-phonon-to-phonon resistance?
  - simulation: lack of quantization?
  - both: surfactant structure?
- The difference in Kapitza lengths for hydrophobic and hydrophilic interfaces is nearly identical in simulation and experiment.
  - experiment 6 nm (for Au) and 7 nm (for Al)
  - simulation 7 nm
- Large discrepancy for organic-organic interfaces: need to revisit the experiments.

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



Classic “flash diffusivity” measurement

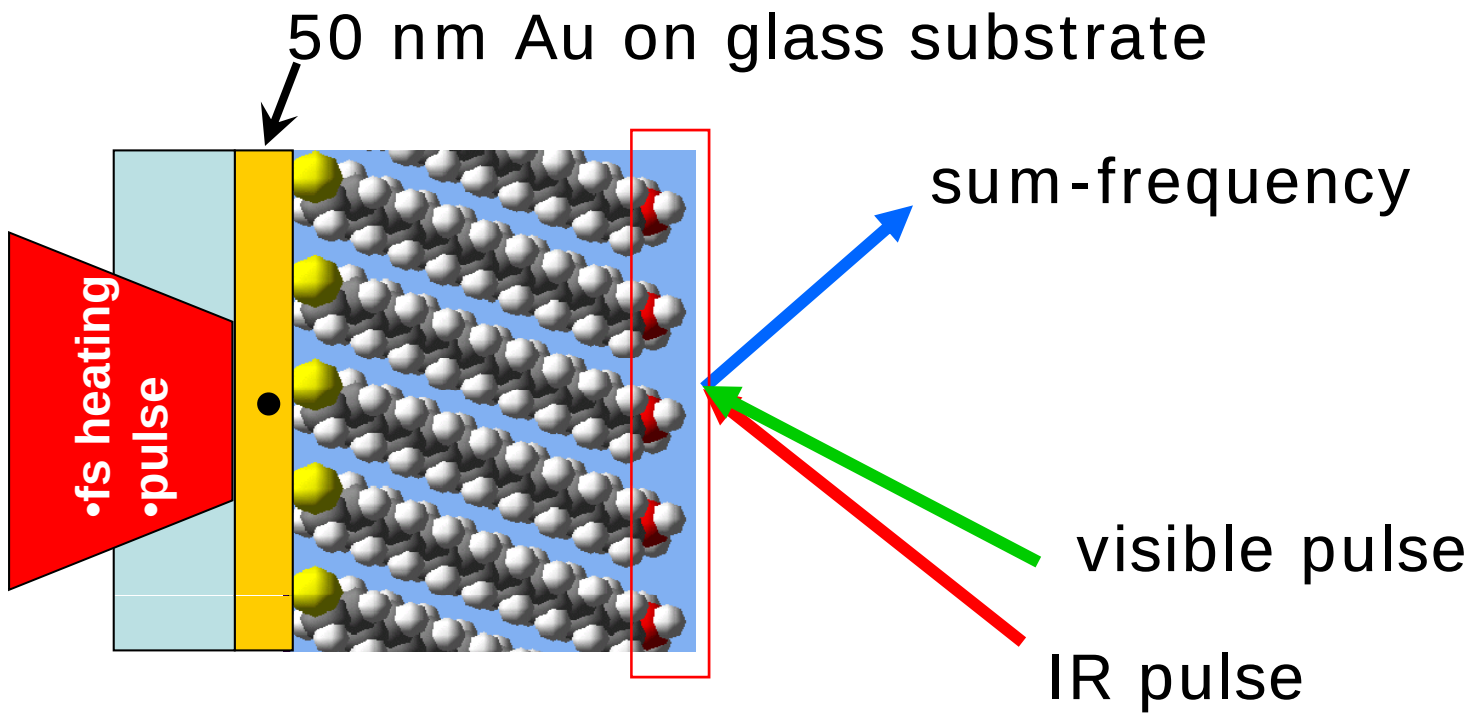




http://electronics-cooling.com/articles/2002/2002_may_a4.php

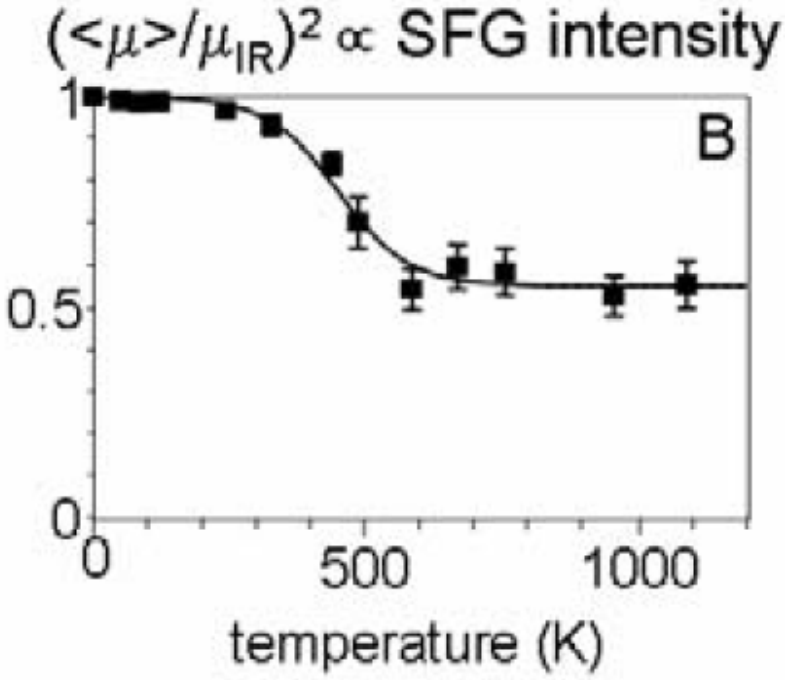
Broad-band sum-frequency generation (SFG) vibrational spectroscopy

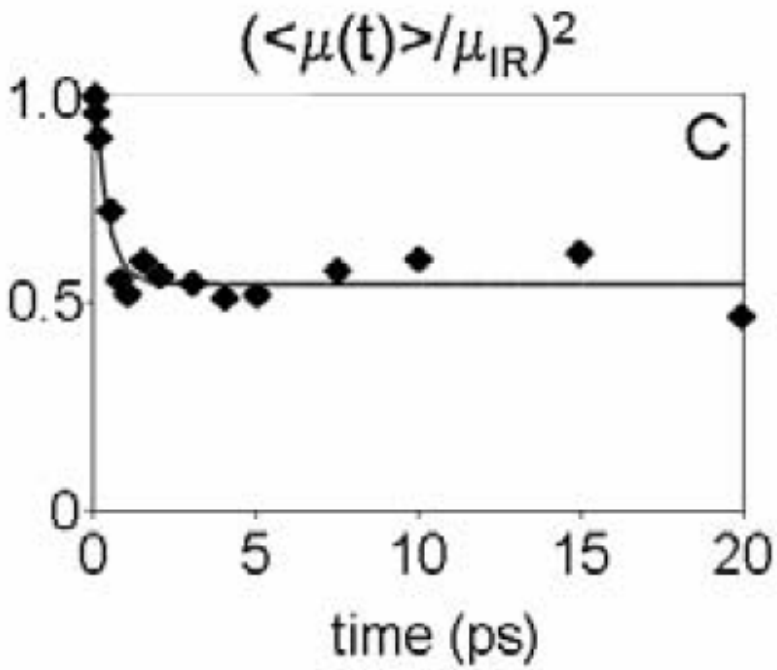
- tunable (2.5-18 μm) broad-band IR pulse
- fixed (800 nm) narrow band
- sum-frequency signal analyzed by spectrograph



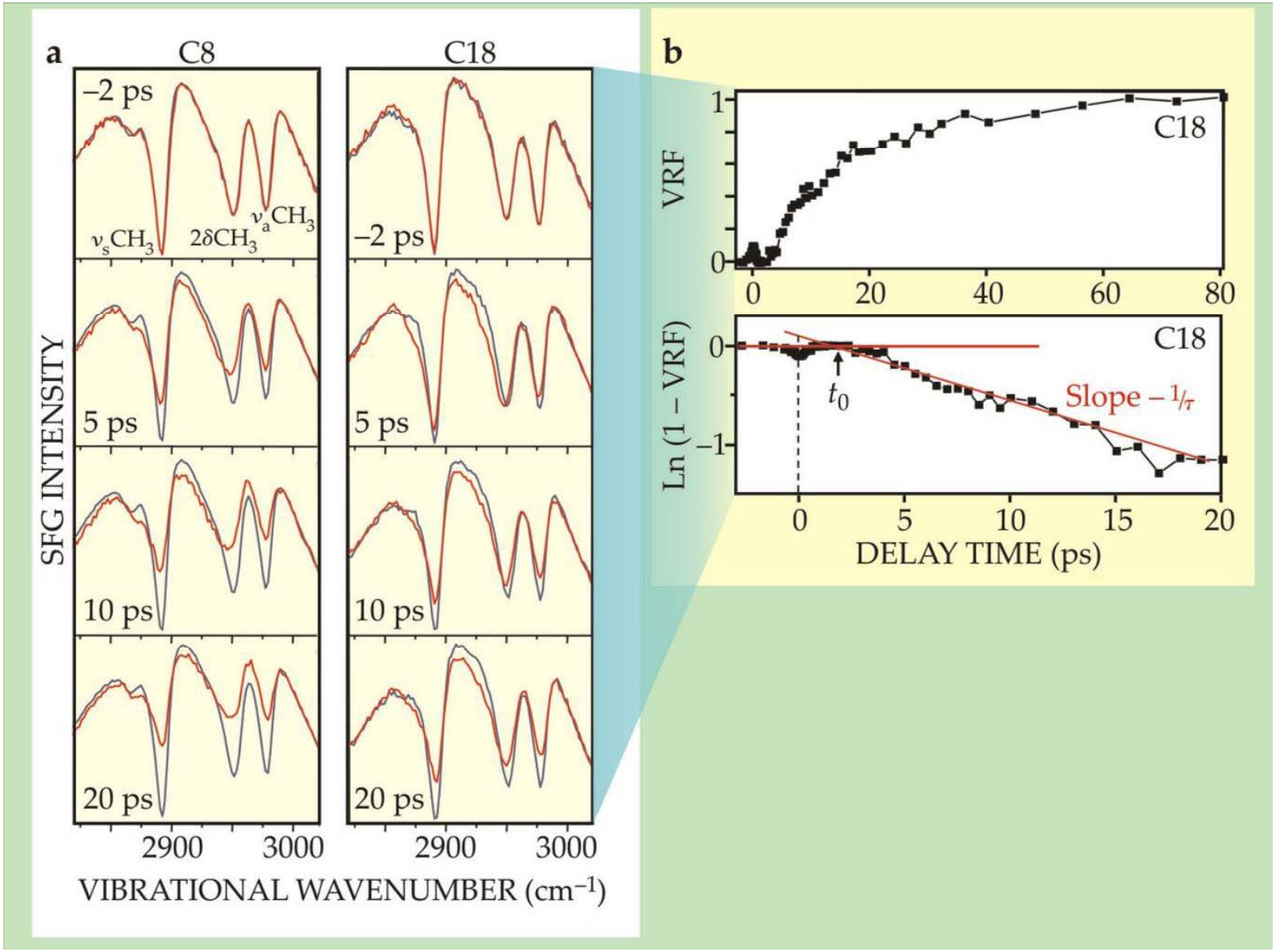
Complicated thermometer

- 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 approximately 50 pW/K