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 $\Lambda$ is a property of the continuum

$$\mathbf{j} = -\Lambda \nabla T$$

$$\Lambda = \frac{1}{3V k_B T^2} \int_0^\infty \langle \mathbf{j}(t) \cdot \mathbf{j}(0) \rangle \, dt$$

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

$$\mathbf{J} = G \Delta T$$

$$G = \frac{1}{Ak_B T^2} \int_0^\infty \langle q(t)q(0) \rangle \, dt$$
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 H₂O

• 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)

Yu et al. (2005)

Maruyama (2007)
Can we make use of this? Fischer (2007)

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

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

\[ G = 12 \text{ MW m}^{-2} \text{ K}^{-1} \]
• 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 is 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

\[ G = 2.0 \times 10^8 \quad G = \infty \]

\[ G = 1.8 \times 10^8 \quad G = \infty \]
Nanoparticle summary

**In water**

\[ G \approx 200 \text{ MW m}^{-2} \text{ K}^{-1} \]

\[ \Lambda/G \approx 3 \text{ nm} \]

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

**In Toluene**

\[ G \approx 15 \text{ MW m}^{-2} \text{ K}^{-1} \]
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

Distance from the DEJ (μm)

ΛC/C0 (W m⁻¹ K⁻¹)

0.0 0.5 1.0 1.5 2.0

dentin enamel

Distance from the DEJ (μm)

www.enchantedlearning.com/
Thermoreflectance of aqueous interfaces

<table>
<thead>
<tr>
<th>Water</th>
<th>SAM</th>
<th>Au</th>
<th>10nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>2nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>20nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>5nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyimide~30nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sapphire substrate 1mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>130nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Hydrophobic**
  - Au-SC<sub>18</sub>
  - 50 MW/m²-K

- **No Water**
  - Au-C<sub>11</sub>OH

- **Hydrophilic**
  - 100 MW/m²-K
• 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: \( h = \frac{\Lambda}{G} \)
  - Au/hydrophobic \( h = 12 \) nm
  - Au/hydrophilic \( h = 6 \) nm

• Difference between CH\(_3\) and OH terminal group
  - Au \( \Delta h = 6 \) nm
  - Al \( \Delta h = 7 \) nm
MD Simulation of model interfaces

Keblinski et al., RPI

water-octane

\[ G = 65 \text{ MW/m}^2\cdot\text{K} \]
Simulated vibrational spectra

<table>
<thead>
<tr>
<th>Interface</th>
<th>$G$ (MW/m²-K)</th>
<th>$\Lambda - H_2O/G$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Octane</td>
<td>65</td>
<td>9</td>
</tr>
<tr>
<td>Water Benzene</td>
<td>175</td>
<td>3.4</td>
</tr>
<tr>
<td>Water Surfactant</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>Surfactant Hexane</td>
<td>370</td>
<td>1.6</td>
</tr>
<tr>
<td>Surfactant Benzene</td>
<td>190</td>
<td>3</td>
</tr>
</tbody>
</table>

difference between water/octane and water/surfactant

$\Delta h = 7$ nm
Heat transport and ultrafast disordering of an organic molecule (with Dana Dlott)
Classic “flash diffusivity” measurement

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

50 nm Au on glass substrate

sum-frequency

visible pulse

IR pulse
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 dis Ordering 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 \( \approx 50 \) pW/K
• 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 ($\Delta h=6$ 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?