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 $\Lambda$ is a property of the continuum

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

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

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

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

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

$\Delta T$ at interface
Factor of 60 range at room temperature

- Au/surfactant/water
- PMMA/Al$_2$O$_3$
- nanotube/alkane
Modulated pump-probe apparatus

- Nd: YVO
- Ti: Sapphire
- Optical Isolator
- Electro-Optic Modulator
- Variable Delay
- Sample Illuminator
- 10X Objective
- Pump
- Probe
- Polarizing Beam Splitter
- CCD Camera
- Color Filter
- Aperture
- Photodiode Detector
- rf lock-in
- Spectrum Analyzer

f = 10 MHz
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.
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

\[ G = 12 \text{ MW m}^{-2} \text{ K}^{-1} \]
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"
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>• optical pulse creates electronic excitations which decay</td>
<td>• no electrons but can add heat any way we want</td>
</tr>
<tr>
<td>– electron-phonon</td>
<td>• all vibrational modes are thermally excited.</td>
</tr>
<tr>
<td>– phonon-phonon</td>
<td>• uncertainties in potentials</td>
</tr>
<tr>
<td>• high frequency vibrations are quantized</td>
<td>• finite-size simulation cell removes lowest-frequency vibrations and creates problems for long mean-free-paths</td>
</tr>
<tr>
<td>• interfaces are difficult to prepare and characterize</td>
<td></td>
</tr>
</tbody>
</table>
Simulation: relaxation time

- Mimic the experiment: heat nanotube suddenly and let system equilibrate.
- Use experimental heat capacity to convert time constant to $G$. For long tubes:
  $G = 22 \text{ MW m}^{-2} \text{ K}^{-1}$
• Carbon nanotubes have a small number of low frequency modes associated with bending and squeezing. Only these modes can couple strongly with the liquid.
Hydrophilic metal nanoparticles:
4 nm diameter Au:Pd nanoparticles in water

- transient absorption data

\[ G = \infty \]

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

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

In water

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

In Toluene

\[ \text{G} \sim 15 \text{ MW m}^{-2} \text{ K}^{-1} \]
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, \( r_c = 3 \text{ nm} \).
- For high thermal conductivity particles, dilute limit of effective medium theory
  \[ r >> r_c \quad \Delta\Lambda = (1+3\phi)\Lambda \]
  \[ r << r_c \quad \Delta\Lambda = (1-1.5\phi)\Lambda \]
Thermoreflectance of solid/H$_2$O interfaces

Water
- SAM
- Au 10nm
- Ti 2nm
- Al 20nm
- Ti 5nm
- polyimide~30nm
- sapphire substrate 1mm
- SiO$_2$ 130nm

Hydrophobic:
- Au-SC$_{18}$: 50 MW/m$^2$-K

Hydrophilic:
- Au-C$_{11}$OH: 100 MW/m$^2$-K

Graphs showing variations in $-V_{in}/V_{out}$ for different materials and conditions.
Thermoreflectance of solid/H$_2$O 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

\[ G = 65 \text{ MW/m}^2\text{-K} \]

\[ G = 175 \text{ MW/m}^2\text{-K} \]
$G_{\text{H}_2\text{O-surf}} = 300 \pm 30 \text{ MW/m}^2\text{-K}$

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

High conductivity of the ordered surfactant

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

$\Lambda_{\text{hexane}} = 0.11 \text{ W/m-K}$

(0.09 exp)
**Simulated vibrational spectra**

<table>
<thead>
<tr>
<th>Interface</th>
<th>( G ) (MW/m(^2)-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**

\[ \Delta h = 7 \text{ nm} \]
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

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

\[
\frac{\langle \mu \rangle}{\mu_{IR}} \propto \text{SFG intensity}
\]

\[
\frac{\langle \mu(t) \rangle}{\mu_{IR}}^2
\]

![Graphs showing the relationship between SFG intensity and temperature/time.](image-url)
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