Nanoscale Thermal Transport at Virginia Tech

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My group is concerned with a wide range of topics dealing with thermal management

Our work ranges from fundamental transport issues to device development

**Nanoscale Thermal Transport**
We use a femtosecond laser system for fundamental measurements of thermal transport at the nanoscale
- Nanostructures – nanotubes, films, multilayers, composites, colloidal suspensions, etc.
- Thermal conductance measurements of solid-solid and solid-liquid surfaces

**Thermoelectric (TE) Devices**
We are developing TE devices for a variety of applications including
- Electrical power generation from waste heat in vehicles
- Energy harvesting/scavenging for powering remote sensors
- Heat flux sensors
Our current projects include large scale use of TE devices on autos and nanoscale measurements

Examples of a few current projects:

- Thermoelectric power generation from waste heat in vehicles (funded by NSF/DOE)
- Fundamental measurements of interface thermal conductance using a femtosecond laser system (NSF)
- Thermal conductivity in nanostructured composites for thermal management (AFOSR)
- Thermal management for power electronics (Intel)
- Development of low conductivity materials for insulation (e.g. thermal barrier coatings)

![Image from BMW](image)

Thermoelectric energy harvesting on a vehicle
Interface thermal conductance, $G$, often dominates thermal transport at the nanoscale

Frequently use $G$ to denote interface thermal conductance (inverse of the Kapitza resistance)

$q'' = G \Delta T_{\text{interface}}$

Most solid-solid interfaces, $10 < G < 1000 \text{ MW m}^{-2} \text{ K}^{-1}$

or, in terms of resistance, $10^{-7} < R < 10^{-9} \text{ (m}^2 \text{ K}) / \text{W}$

Fig. from Lyeo & Cahill, Phys.Rev.B, 73, 144301, (2006).
Much of our experimental work at the nanoscale relies on a femtosecond laser

1. Ti:Sapphire laser \( \sim 100 \) fs pulses at 80 MHz (690 nm \(<\lambda<1040\) nm)

2. Pulses are split into “pump” and “probe” beams.

3. Pump beam is modulated at \( \sim 0.1 \) to 10 MHz to allow for lock-in detection

4. Sample is coated with aluminum

5. Pump beam heats the sample, reflectivity of the sample is \( f(T) \)

6. Arrival of probe beam at sample surface is controlled with a mechanical delay stage (up to \( \sim 3.5\) ns of delay)

7. Fraction of probe beam that is reflected to the detector gives indirect measure of the temperature at the surface of the sample as a function of delay time.

8. Additional optics are used to control divergence (lenses), align and focus the beams (CCD), and to prevent the pump beam from reaching the detector (filters).

9. Experimental data are compared with a thermal model to (generally) extract thermal conductivity and interface thermal conductance.
Time domain thermoreflectance (TDTR) gives thermal conductivity ($k$) & interface conductance ($G$)

1. Raw data also frequently gives acoustic echoes from reflections at interfaces
2. We use the ratio of the in-phase and out-of-phase signals to reduce noise.
3. Thermal model includes thermal conductivity, heat capacity, and thickness of each layer.
4. Interfaces are represented by thin layers ($h=1$ nm) with specified conductance ($G=k/h$) with negligible heat capacity.
5. Fitting the data with the thermal model typically allows determination of thermal conductivity of one layer and the interface conductance.

TDTR is useful for characterizing nanostructured composites

- Series of four samples with nickel nanoparticles embedded in a YSZ matrix
- Samples grown by pulsed laser deposition
- Oxygen not used in order to avoid formation of NiO or core-shell structures
- Five alternating layers of Ni and YSZ
- Ni nanoparticle size varied by changing number of laser pulses for each sample

- HRTEM shows abrupt interfaces without oxides
- YSZ completely surrounds each nanoparticle

We examine a series of four samples with Nickel nanoparticles embedded in YSZ

In our model we crudely approximate the nanoparticle layer as a composite layer of Ni and YSZ

Composite Layer (CL) thickness=$d_{Ni}$, $C$=weighted average of Ni & YSZ
From the TDTR data and model we find...

From the reference sample, we measure: \( k_{YSZ} = 2.5 \text{ W m}^{-1} \text{ K}^{-1} \) and \( G_{Al/YSZ} \sim 100 \text{ MW m}^{-2} \text{ K}^{-1} \)

<table>
<thead>
<tr>
<th>( d_{Ni} ) (nm)</th>
<th>( t_{YSZ} ) (nm)</th>
<th>Effective ( k ) of Ni/YSZ composite layer (W m(^{-1}) K(^{-1}))</th>
<th>Overall ( k ) of entire nanocomposite structure (W m(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>22</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>21</td>
<td>48</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>24</td>
<td>22</td>
<td>2.1</td>
<td>2.3</td>
</tr>
<tr>
<td>38</td>
<td>28</td>
<td>3.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The effective thermal conductivity of the composite layer depends on \( G_{Ni/YSZ}, k_{Ni} \), and the volume fraction.

For small diameter particles, the conductivity of the composite decreases, but for the largest particles \( k_{\text{composite}} > k_{YSZ} \)

We can use effective medium theory to examine the relationship between \( k_{Ni} \) and \( G_{Ni/YSZ} \)
We can use effective medium theory to further examine the data

Effective medium theory (high volume fraction limit)

\[
(1 - f)^3 = \left( \frac{k_m}{k_c} \right)^{1+2\alpha} \times \left\{ \frac{k_c - k_p (1 - \alpha)}{k_m - k_p (1 - \alpha)} \right\}^{3 \frac{1 - \alpha}{1+2\alpha}} \alpha = \frac{k_m}{r_p G}
\]

- \( f \) = volume fraction
- \( k_m \) = matrix (YSZ) thermal conductivity
- \( k_p \) = nanoparticle thermal conductivity
- \( k_c \) = thermal conductivity of composite layer
- \( G \) = Ni/YSZ interface conductance
- \( r_p \) = nanoparticle radius

We find that interface resistance dominates if \( k_p > 30 \text{ W m}^{-1} \text{ K}^{-1} \)

We can set a lower limit on \( G \sim 170-210 \text{ MW m}^{-2} \text{ K}^{-1} \)
Example: We use TDTR to examine amorphous and crystalline metallic alloys

- Metallic alloys are melted and the cooling rate determines the structure
- Slower cooling rate creates poly-crystalline structure
- Grown by P. Liaw’s group at UT-Knoxville

\[ \text{Zr}_{47}\text{Cu}_{31}\text{Al}_{13}\text{Ni}_{9} \] alloys – same composition, different structure

\[ \text{Y}_2\text{O}_3 \] deposited using pulsed laser deposition at 400 °C by Dr. J.T. Abiade

We compare our crystalline and amorphous metallic alloys

Difference in $k$ and $G$ for the amorphous and crystalline alloys is on the order of our absolute experimental uncertainty.

However, the relative uncertainty should be low as the samples were processed together (e.g. same error in Al properties on both samples).

From the Wiedemann-Franz Law, $k_{\text{electronic}}$ for the crystalline and metallic alloys are 4.0 and 3.75 W/m-K, respectively. So roughly half of the difference in $k$ is due to $k_{\text{electronic}}$ and half is due to $k_{\text{lattice}}$. 
Measurements at a single delay time can allow for quantitative thermal imaging

- Diffusion couple made from Cr, Ti, Nb, & Si
- Annealed at 1100 °C, 4000 hrs
- Interface regions mix and diffuse when annealed
- Sample polished and coated with aluminum

- Initial TDTR measurements (left) to verify accuracy (5-10%) far from interfaces
- Only slight loss of accuracy with fit at single point
- Set pump-probe delay to \( t = 100 \) ps
- Sample placed on motorized stage and raster scanned
- Experiment measures thermal effusivity (\( kC \))

We can create thermal conductivity images with ~3 μm resolution

- Image is ~100 x 100 μm
- Measurement takes ~1 hr
- $k$ resolution ~3 μm
We have also examined the effect of self-assembled monolayers on gold-water interfaces

Five SAM’s:

- **C-11** →
- **C10-COOH** →
- **C11-OH** →
- **PUT** →
- **MMP** →

G increases ~ 3 times just by changing end group

Terminal (ω) group
Alkyl chains CH₂ at every node

A combination of pump-probe measurements can characterize cantilever structures

SUMMiT IV™ Process from Sandia National Labs
Some cantilevers are adhered to the substrate

We can also look at transient changes in absorption for nanoparticle suspensions

1. Use modified TDTR setup, move photo detector behind sample
2. Nanoparticles absorb fraction of the pump energy and heat up
3. If absorption of the nanoparticles is $f(T)$, absorbed fraction of the probe energy changes as the particles cool
4. Rate at which the particles cool gives information about the interface conductance
5. Measurements require nanoparticles that absorb in the near IR and that have a change in absorptivity with temperature
Transient absorption can examine \( G \) for suspensions of small particles

- Individual single-walled CNT’s with SDS surfactant suspended in \( \text{D}_2\text{O} \)
- Structure in the optical density leads to complicated transient absorption signal
- Temperature rise \( \sim 3 \text{ K} \)
- Two time-constant decay, \( \tau_1=45 \text{ ps}, \tau_2=250 \text{ ps} \)

Cross-section of a SWCNT with SDS surfactant

SWCNTs with an SDS surfactant behave similarly to higher order fullerenes

We can find $G$ from

$$ G = \frac{C}{A \tau} $$

$\tau_1 = 45 \text{ ps, } G \sim 12 \text{ MW m}^{-2} \text{ K}^{-1}$

Suspensions of higher order fullerenes ($C_{76}$, $C_{78}$, $C_{84}$) with no surfactant in suspensions of CS$_2$, CHCl$_3$, and toluene give similar results

$\tau = 40 \text{ ps, } G \sim 14 \text{ MW m}^{-2} \text{ K}^{-1}$

In summary, ultrafast measurements are useful tools for characterizing nanoscale thermal transport.

Time domain thermoreflectance and related ultrafast pump-probe techniques are robust and powerful measurement methods that can be used in many systems.
- Simultaneous measurements of thermal conductivity and interface thermal conductance for thin films or composites
- Quantitative thermal conductivity imaging
- Characterization of planar solid-liquid thermal conductance
- Interface conductance of nanoparticle suspensions
- Thermal conductivity of liquids
- Modified Ångström measurements of complex structures