II. Phonon engineering and heat conduction

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The Phononic heat conduction

- Phononic thermal conductivity → spectrum!
- Phonon scattering mechanisms → intrinsic
- Phonons at nanoscale → solve BTE
- Phonon transmission at interfaces → diffuse?
- Phonons in novel materials → better transport?
- Heat transfer phonons and measurements → techniques
Thermal conductivity $k$ has different contributions:

$$k = k_{\text{phonon}} + k_{\text{electron}}$$

Wiedemann-Franz law for an approximation of electronic contribution in the thermal conductivity

$$L_0 = \frac{k_{el}}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.44 \cdot 10^{-8} \text{W} \Omega K^{-2}$$

Silicon (undoped)

- $k_{Si} = 149 \text{ Wm}^{-1}\text{K}^{-1}$
- $\sigma_{Si} = 10^{-3} \text{ \Omega}^{-1}\text{m}^{-1}$

Graphite

- $k_{\text{C_graphite}} = 140 \text{ Wm}^{-1}\text{K}^{-1}$
- $\sigma_{\text{C_graphite}} = 6.1 \cdot 10^4 \text{ \Omega}^{-1}\text{m}^{-1}$

Wiedemann-Franz law approximations:

$$\frac{k_{Si,e^-}}{k_{Si}} = \frac{L_0 T_e \sigma_{Si}}{\lambda_{Si}} \ll 1$$

$$\frac{k_{\text{C_graphite},e^-}}{k_{\text{C_graphite}}} = \frac{L_0 T_e \sigma_{\text{C_graphite}}}{k_{\text{C_graphite}}} \approx 0.3\%$$
The model of the thermal conductivity

- Solution of a Boltzmann transport equation (Peierls)

\[
\frac{\partial f}{\partial t} + \nabla \cdot \vec{v} f + \frac{\vec{F}}{m} \cdot \nabla \vec{v} f = \frac{\partial f}{\partial t}_\text{coll} = -\frac{f - f_0}{\tau(\omega)}
\]  

(Relaxation time approximation)

\[
f = f_0 - \tau(\omega) \cdot (\vec{v} \cdot \vec{\nabla}_r f_0)
\]

\[
\phi = \sum_i E_i f_i \vec{v}_{i,x} = \sum_{i,\text{pol}} \int_{0}^{\infty} g(\omega, p) E(\omega) f(\omega) \vec{v}_{i,x}(\omega, p) d\omega
\]

\[
f_0(\omega, T) = \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1}
\]

Bose-Einstein statistics

\[
k = \sum_{\text{pol.}} \int_{0}^{\infty} \frac{\hbar \omega}{3} \cdot \frac{df_0}{dT} \cdot (v \tau) \cdot g(\omega) \cdot v d\omega
\]

\[
\vec{\phi} = k \cdot \vec{\nabla}_r T
\]

NB: Isotropic approx. for v, \(\tau,\ldots\)
The model of the thermal conductivity

- Solution of a Boltzmann transport equation (Peierls)

\[
\frac{\partial f}{\partial t} + \vec{v} \cdot \vec{\nabla} f + \frac{F}{m} \vec{\nabla} \cdot \vec{v} f = \frac{\partial f}{\partial t}_{\text{coll}} = \frac{f - f_0}{\tau(\omega)}
\]

(Relaxation time approximation)

\[
k = \sum_{\text{pola}} \int_0^{+\infty} \frac{1}{3} \hbar \omega \cdot \frac{df_0}{dT} \cdot (v \tau) \cdot g(\omega) \cdot v d\omega
\]

\[
f_0(\omega, T) = \frac{1}{e^{\hbar \omega/k_B T} - 1}
\]

Bose-Einstein statistics

Planck’s law for phonons

Wien’s law for phonons

\[
\lambda_D = \frac{h v_s}{2.8 k_B T}
\]

\[
v_{s, Si} \sim 4.5 \times 10^3 \text{ ms}^{-1}
\]
Phononic thermal conductivity

Phonon spectrum

MD calculations with bulk Si

Calculated phonon density of states (D) in a e=37 nm Si nanowire

Henry and Chen,

Lü, JAP 104, 054314 (2008)
**Which phonons?**

The acoustic phonons are carrying the heat.

\[
\begin{align*}
  k &= \sum_{\text{pola.}} \frac{1}{3} \int_0^{+\infty} \hbar \omega \cdot \frac{df_0}{dT} \cdot (v \tau) \cdot g(\omega) \cdot v d\omega \\
  &= \int_0^{+\infty} \frac{1}{3} c_\omega v(v \tau) d\omega \quad \rightarrow \quad k = \frac{1}{3} \rho c_p v_s \Lambda
\end{align*}
\]

NB: Different from the specific heat!

Chen, JHT (1998)
Finiteness of the thermal conductivity..?

- Critical parameter: The phonon relaxation time as without it the propagation would be infinite!

In this absence of defects, it is due to the nonlinearity of the force field between atoms

NB: $k$ has a 3D meaning...

→ FPI (Fermi Pasta Ulam) paradox of the atomic chain

$k$ does not always exist when nonlinearity!

$k \sim L^\alpha$, $\alpha$ not always 0.

see Lepri etc.
Scattering mechanisms
that do not conserve the momentum

Origin of the different terms in the mean free path

• Umklapp (Klemens model)
  Origin: Nonlinearity=Anharmonicity !!

\[ \tau_U(\omega)^{-1} \sim A_1 e^{-\theta_D/bT} \Gamma^m \omega^m \]

\[ \hbar \omega_1 + \hbar \omega_2 = \hbar \omega_3 \]
\[ \vec{k}_1 + \vec{k}_2 = \vec{k}'_3 \text{ but } \vec{k}_3 \text{ in the end} \]

(Very schematic !!)
Scattering mechanisms

Origin of the different terms in the mean free path

- Umklapp (Klemens model)
  Origin: Nonlinearity=Anharmonicity !!
  \[ \tau_U(\omega)^{-1} \sim A_1 e^{-\theta_D/\hbar T^3} \omega^2 \]

- Boundary scattering of the particle
  \[ \tau_B(\omega)^{-1} \sim A_2 \nu(\omega)/D \]

To be taken into account only in crude model if dispersion relation have not been calculated!
Scattering mechanisms

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- 'Rayleigh' scattering due to impurities
  Similar to electromagnetics \( \rightarrow \) Mie theory
  \[ \tau_I(\omega)^{-1} \sim A_3 \omega^4 (d_{\text{part}}<<\lambda) \]

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Majumdar, JAP (2005)

NIPS Summer school, August 2010
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  \[ \tau_I(\omega)^{-1} \sim A_3 \omega^4 (d_{\text{part}}<<\lambda) \]

• Electron-phonon interaction
  \[ \tau_{\text{e-\text{ph}}}(\omega)^{-1} \sim T \]
Scattering mechanisms

Origin of the different terms in the mean free path

- **Umklapp (Klemens model)**
  
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- **Electron-phonon interaction**

  \[ \tau_{e-ph}(\omega)^{-1} \sim T \]

Usually: Mathiessen rule of the relaxation time \( \tau(\omega)^{-1}=\Sigma \tau_i(\omega)^{-1} \)

NB: Curious: Same treatment of elastic, inelastic etc. lifetime
Phonon scattering mechanisms

Scattering mechanisms (2)

Leading mean free paths...

$\Lambda = \nu_g \tau$

10nm Si particles in a matrix of Ge

J.Y. Duquesne, INSP, Paris

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Phonon scattering mechanisms

**Mean free path distribution**

\[ \Lambda = v_g \tau \]

MD calculations with bulk Si

**Figure:**

- Graph showing mean free path distribution with curves for 300 K and 1000 K.
- Legend indicating different temperatures: 300 K and 1000 K.

How to deal with BTE at low D?

- At small scale (space/time), the Fourier approach breaks down!
  - Dispersion relation → wave effect
  - Phonon density of states

  Limitation of the approach: \( L \sim 2\pi v/\omega \) [0–20nm]
  \( L \sim \Lambda \) [10–1000nm?]

- One needs then
  - 'Grey approximation'

<table>
<thead>
<tr>
<th>to solve the BTE (long !)</th>
<th>to use a simulation method at the atomic scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Probabilistic: Monte-Carlo method</td>
<td>- Molecular dynamics</td>
</tr>
<tr>
<td>- Approx: Discrete ordinate (Radiation)</td>
<td>- Lattice dynamics</td>
</tr>
<tr>
<td>- Approx.: Ballistic-diffusive equation</td>
<td>- Atomistic Green’s function method</td>
</tr>
</tbody>
</table>

- ‘Grey approximation’ \( \tau(\omega) = \tau \)
Fourier vs BTE at nanoscale
Examples taken from Lacroix, Joulain, PRB (2005)

NB: Cattaneo-Vernotte
\[ \frac{1}{\tau} \frac{\partial T}{\partial t} + \frac{\rho c}{\partial t} \frac{\partial^2 T}{\partial t^2} = k \Delta T \]
also incomplete

Stationary temperature profile between two parallel thermalized media

Propagation of heat

Transverse

Longitudinal

‘Temperature jump’
Reducing the thermal conductivity
Impurities or nanoparticles

• Useful for the generation of thermoelectricity!

Efficiency depends on figure-of-merit ZT

\[ Z = \frac{S^2 \sigma}{k_{el} + k_{ph}} \]

Strategies to decrease \( k_{ph} \)
(without impact on \( \sigma \) and \( S \))

Adding impurities or nanoparticles!

→ impacts the high-frequency acoustic phonons

Majumdar, PRL (2007)

ErAs in InGaAs

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Reducing the thermal conductivity
Boundaries

• Useful for the generation of thermoelectricity!
  Efficiency depends on figure-of-merit ZT
  \[ Z = \frac{S^2 \sigma}{(k_{el} + k_{ph})} \]

Strategies to decrease \( k_{ph} \)
(without impact on \( \sigma \) and \( S \))

Adding boundaries → impacts all phonons

Ball-milling

Chen and Ren, Science (2008)

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Reducing the thermal conductivity
Boundaries

• Useful for the generation of thermoelectricity!
  Efficiency depends on figure-of-merit ZT

\[ Z = \frac{S^2 \sigma}{(k_{el} + k_{ph})} \]

Strategies to decrease \( k_{ph} \)
(without impact on \( \sigma \) and \( S \))

Adding boundaries
  \( \rightarrow \) impacts all phonons

Here in nanowires

Majumdar, APL (2003)

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Reducing the thermal conductivity
Roughness

• Useful for the generation of thermoelectricity!
  Efficiency depends on figure-of-merit ZT
  \[ Z = \frac{S^2 \sigma}{(k_{el} + k_{ph})} \]

Strategies to decrease \( k_{ph} \)
(without impact on \( \sigma \) and \( S \))

Adding amorphous layers at the boundaries
  → further reduces the thermal conductivity!

Majumdar, Nature (2009)
See also Heat, same issue
Phonon transmission at interfaces?

- Wave model for the low-frequency phonons

\[ T = \frac{4Z_1Z_2}{(Z_1+Z_2)^2} \]

Acoustic wave!

\[ Z_1 = \rho_1 c_1 \]

\[ Z_2 \]

Thermal boundary resistance

NB: Terminology issue:
- Kapitza resistance (fluid-solid)
- Thermal interface resistance (thick interface)

Kapitza resistance (fluid-solid)
Thermal interface resistance (thick interface)

Transistor level
Polymer-based layer
Heat spreader

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Phonon transmission at interfaces?

- More difficulty for the high frequency acoustic phonons

Diffuse mismatch model
= limit of strong diffuse scattering
Acoustic mismatch and diffuse mismatch models

DMM: ‘All correlations between ingoing and outgoing phonons are ignored’

\[
t_{12}(\omega) = r_{21}(\omega) = 1 - t_{21}(\omega)
\]

\[
t_{12} = \frac{1}{1 + \frac{1}{c_1^2} + \frac{1}{c_2^2}}
\]

(With assumption on the DOS)

<table>
<thead>
<tr>
<th>$R_{\beta_d} T^3$ with units $K^4/(W/cm^2)$.</th>
<th>Sapphire AMM</th>
<th>DMM</th>
<th>Quartz AMM</th>
<th>DMM</th>
<th>Silicon AMM</th>
<th>DMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>21.0</td>
<td>*</td>
<td>21.4</td>
<td></td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>18.5</td>
<td>24.4</td>
<td>9.77</td>
<td>13.8</td>
<td>14.5</td>
<td>18.9</td>
</tr>
<tr>
<td>Copper</td>
<td>18.5</td>
<td>20.1</td>
<td>8.66</td>
<td>9.43</td>
<td>14.3</td>
<td>14.6</td>
</tr>
<tr>
<td>Gold</td>
<td>18.9</td>
<td>*</td>
<td>18.1</td>
<td></td>
<td>7.48</td>
<td></td>
</tr>
<tr>
<td>Indium</td>
<td>20.4</td>
<td>17.7</td>
<td>7.19</td>
<td>7.10</td>
<td>12.1</td>
<td>12.2</td>
</tr>
<tr>
<td>Lead</td>
<td>18.8</td>
<td>17.8</td>
<td>7.67</td>
<td>7.14</td>
<td>12.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Nickel</td>
<td>19.7</td>
<td>21.1</td>
<td>9.32</td>
<td>10.5</td>
<td>15.5</td>
<td>15.6</td>
</tr>
<tr>
<td>Platinum</td>
<td>20.8</td>
<td>18.7</td>
<td>13.0</td>
<td>8.10</td>
<td>21.3</td>
<td>13.2</td>
</tr>
<tr>
<td>Rhodium</td>
<td>20.8</td>
<td>*</td>
<td>23.6</td>
<td></td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>18.2</td>
<td>18.7</td>
<td>8.66</td>
<td>8.06</td>
<td>13.8</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Swartz and Pohl, RMP (1987)

→ In bulk systems, the resistances with DMM and AMM are similar (30%)
Phonon transmission at interfaces

Metal dielectric interface

- Measured values higher than prediction

Maxwell-Garnett approximation

\[ \alpha = \lambda_3 \frac{\rho_2}{R} \]

Thermal "surface resistance"

Chapuis

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(Phonon particule)
Thermal conductivity of ‘new’ materials

- Porous materials to harvest energy
- Other types of low-thermal conductivity materials (beating the ‘Einstein limit’ of amorphous materials)

Chiritescu, Science (2007)  
Goodson, Science (2007)

Disordered layered crystal

$k_{\text{air}}(300 \text{ K}) = 0.025 \text{ Wm}^{-1}\text{K}^{-1}$

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Thermal conductivity of ‘novel’ materials

- Carbon nanotubes
  - MWCNT: Kim et al, PRL(2001)
  - $k = 3000 \text{ Wm}^{-1}\text{K}^{-1}$

- Graphene
  - $k \sim 5 \times 10^3 \text{ W/mK}$
  - Balandin, Nano Letters (2008)

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Other types of engineering

- Rectification?

Carbon nanotubes loaded with gradient of molecule density:

Chang, .., Majumdar, Zettl, Science 2006

- Phonon-based motor?

For the moment only due to the thermal gradient

Usual methods for heat transport characterisation

- 3ω method (Cahill, RSI, 1989)
  Based on $R = R_0 (1 + \alpha \Delta T)$
  and $\Delta T \propto P = R [ I_0 \cos \omega t ]^2$
  $\Rightarrow U_{3\omega} = \alpha / 2 R_0 I_0 \Delta T_{2\omega}$

- Suspended microresistors (Shi and Majumdar)

- Ultrafast pump-probe spectroscopy

S. Dilhaire (Bordeaux)
Heat transfer phonons and measurements

THE 3ω METHOD

- \( R(T) = R_0 \left( 1 + \alpha \Delta T \right) \) 
  Resistance depends on temperature

- \( I = I_0 \cos(\omega t) \) \( \to P(t) = R I(t)^2 = \frac{1}{2} R \left( 1 + \cos(2\omega t) \right) \)
  \( \to T(t) = T_0 + T_{DC} + T_{2\omega} \cos(2\omega t + \phi_{2\omega}) \)
  Joule heating of an electric wire

- \( U = RI = R_0 I_0 \left[ 1 + \alpha \left( T_{DC} + T_{2\omega} \cos(2\omega t + \phi_{2\omega}) \right) \right] \cos(\omega t) \)
  \[ = R_0 I_0 \left[ (1 + \alpha T_{DC}) \cos(\omega t) + \frac{1}{2} \alpha T_{2\omega} \cos(\omega t - \phi_{2\omega}) + \frac{1}{2} \alpha T_{2\omega} \cos(3\omega t + \phi_{2\omega}) \right] \]
  \[ = U_{\omega} + \frac{1}{2} \alpha R_0 I_0 T_{2\omega} \cos(3\omega t + \phi_{2\omega}) \]

- Temperature of the wire = \( f(\text{heat flux to the sample}) \)
Wave behaviour superimposed to the quasiparticle behaviour

Research driven by thermoelectric community and the quest for better insulator [lower k] or by microelectronics for better conductors [higher k]

Still plenty of room...
- Demonstration of the Boltzmann transport equation for phonons?
- Phonon relaxation time/mean free path
- Degree of diffusivity at the interface
- Filters and interference effects
- Localization etc.
- Amorphous materials... [not tackled here !]
Useful references

- **Books**
  - G. Chen, Nanoscale energy transport and conversion
  - S. Volz (ed), Microscale and Nanoscale Heat Transfer
  - S. Volz (ed), Thermal Nanosystems and Nanomaterials
  - Z.M. Zhang, Nano/Microscale heat transfer
  - ...

- **Reviews or interesting articles**
  - ...

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