Thermal Conductivity from *ab initio* Phonon Properties

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Phonon Phenomena

- Joule Heating: Current carriers interact with atomic ions, transferring electrical energy to thermal energy.
- Superconductivity: Small phonon contribution to the photoemission kink in the copper oxide superconductors (Nature 2008)
- Entanglement: Entangling Macroscopic Diamonds at Room Temperature (Science 2011)

Experimental studies

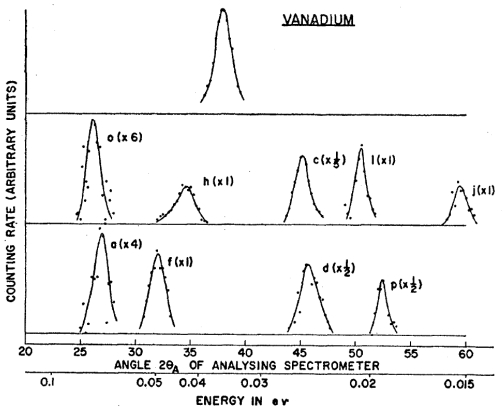
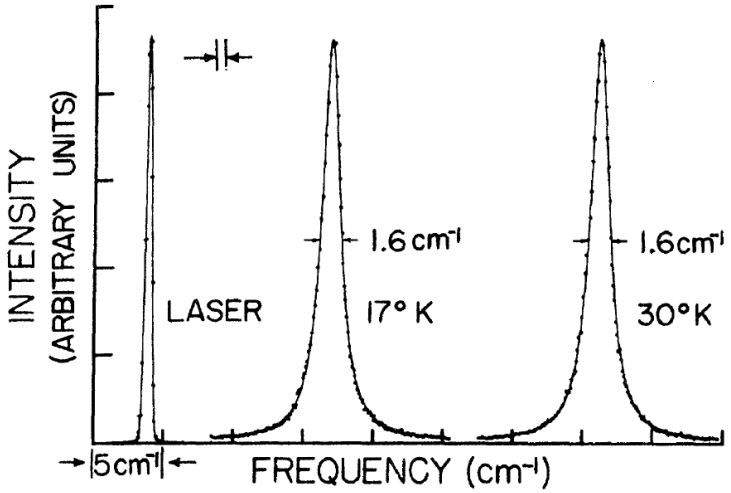


FIG. 3. Counting rates for typical neutron groups plotted as a function of the angle of the analyzing spectrometer.

(a) Neutron Scattering



(b) Raman Spectroscopy

Continuum approach

- Recall Fourier's Law of heat conduction:

$$q = -k\frac{\partial T}{\partial x}$$

- What happens when the length scales become comparable with MFP?

Boltzmann Transport Equation

- "Phonon gas" picture:

$$\frac{\partial f(\boldsymbol{\kappa},\nu)}{\partial t} + v_g(\boldsymbol{\kappa},\nu)\cdot\nabla f(\boldsymbol{\kappa},\nu) = [\frac{\partial f(\boldsymbol{\kappa},\nu)}{\partial t}]_{coll}$$

- Under the relaxation time approximation:

$$\frac{\partial f(\boldsymbol{\kappa},\nu)}{\partial t} + v_g(\boldsymbol{\kappa},\nu)\cdot\nabla f(\boldsymbol{\kappa},\nu) = \frac{f^{BE}(\boldsymbol{\kappa},\nu) - f(\boldsymbol{\kappa},\nu)}{\tau(\boldsymbol{\kappa},\nu)}$$

- Thermal conductivity:

$$k(L) = \sum_{\nu}\sum_{\kappa} c_{ph}(\boldsymbol{\kappa},\nu)v_g^2(\boldsymbol{\kappa},\nu)\tau(\boldsymbol{\kappa},\nu,L)$$

- We need phonon properties!

Diatomic Chain

- Equations of Motion:

$$M\frac{\partial^2 u_n}{\partial t^2} = -K1(U_n - u_n) - K2(U_n - u_{n-1})$$
$$m\frac{\partial^2 u_n}{\partial t^2} = -K1(u_n - U_n) - K2(u_n - U_{n+1})$$

- General solutions:

$$U_n = \sum_{\kappa} \tilde{U}_{\kappa} e^{i(\kappa na - \omega t)} \qquad u_n = \sum_{\kappa} \tilde{u}_{\kappa} e^{i(\kappa na - \omega t)}$$

Diatomic Chain

- Eigenvalue problem representation:

$$\begin{bmatrix} -M\omega_\kappa^2 & 0 \\ 0 & -m\omega_\kappa^2 \end{bmatrix} \begin{bmatrix} \tilde{U}_\kappa \\ \tilde{u}_\kappa \end{bmatrix} = \begin{bmatrix} -(K1+K2) & K1+K2e^{-i\kappa a} \\ -(K1+K2) & K1+K2e^{-i\kappa a} \end{bmatrix} \begin{bmatrix} \tilde{U}_\kappa \\ \tilde{U}_\kappa \end{bmatrix}$$

- General version:

$$\omega^2(\kappa,\nu)e(\kappa,\nu) = D(\kappa)e(\kappa,\nu)$$

- The spring constant is determined by a material specific empirical potential

Simple Phonon Properties

- Group Velocity:

$$v_g(\boldsymbol{\kappa}, \nu) = \frac{\partial \omega(\boldsymbol{\kappa}, \nu)}{\partial \boldsymbol{\kappa}}$$

- Specific Heat:

$$c_{ph}(\boldsymbol{\kappa}, \nu) = \frac{\partial E}{V \partial T} = \frac{\hbar \omega(\boldsymbol{\kappa}, \nu)}{V} \frac{\partial f^{BE}(\boldsymbol{\kappa}, \nu)}{\partial T}$$

- We still need the phonon lifetimes $\tau(\boldsymbol{\kappa}, \nu, L)$!

What exactly is τ

- Matthiesen rule:

$$\frac{1}{\tau(\boldsymbol{\kappa}, \nu, L)} = \frac{1}{\tau_{p-p}(\boldsymbol{\kappa}, \nu)} + \frac{1}{\tau_b(\boldsymbol{\kappa}, \nu, L)} + \frac{1}{\tau_{p-e}(\boldsymbol{\kappa}, \nu)}$$

- Boundary Scattering:

$$\tau_b(\boldsymbol{\kappa}, \nu, L) = \frac{L/2}{|v_g(\boldsymbol{\kappa}, \nu)|}$$

- Electron-Phonon Scattering (low doping levels):

$$\frac{1}{\tau_{p-e}} = \frac{n_e \epsilon_1^2 \omega}{\rho V_g^2 k_B T} \sqrt{\frac{\pi m^* V_g^2}{2 k_B T}} exp(-\frac{m^* V_g^2}{2 k_B T})$$

- How can we find τ_{p-p} numerically? Go beyond the harmonic approximation!

Anharmonicity

- Selection Rules:

$$\hbar\omega(\boldsymbol{\kappa},\nu) + \hbar\omega(\boldsymbol{\kappa}',\nu') = \hbar\omega(\boldsymbol{\kappa}'',\nu'')$$
$$\boldsymbol{\kappa} + \boldsymbol{\kappa}' = \boldsymbol{\kappa}'' + \boldsymbol{g}$$

- Thermal expansion and Finite Thermal conductivity:

$$E = N\phi + \sum_{s\geq 1} \frac{1}{s!} \frac{\partial^s \phi}{\partial u^s} \sum_n (u_n - u_{n+1})^s$$

- Fermi's golden rule (empirical potentials are inadequate):

$$\tau_{p-p}(\boldsymbol{\kappa},\nu) \propto \frac{\partial^3 \phi(\boldsymbol{\kappa},\boldsymbol{\kappa}',\boldsymbol{\kappa}'')}{\partial u(\boldsymbol{\kappa})\partial u(\boldsymbol{\kappa}')\partial u(\boldsymbol{\kappa}'')}$$

Density Functional Theory

- Theorem 1: The ground-state energy from Schrodinger's equation is a unique function of the electron density.
- Theorem 2: The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrodinger equation.
- The Kohn-Sham single electron equations have the form:

$$[\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

Iteration procedure in DFT

- A trial electron density is chosen: $n_1(r)$
- Solve Kohn-Sham with initial guess:

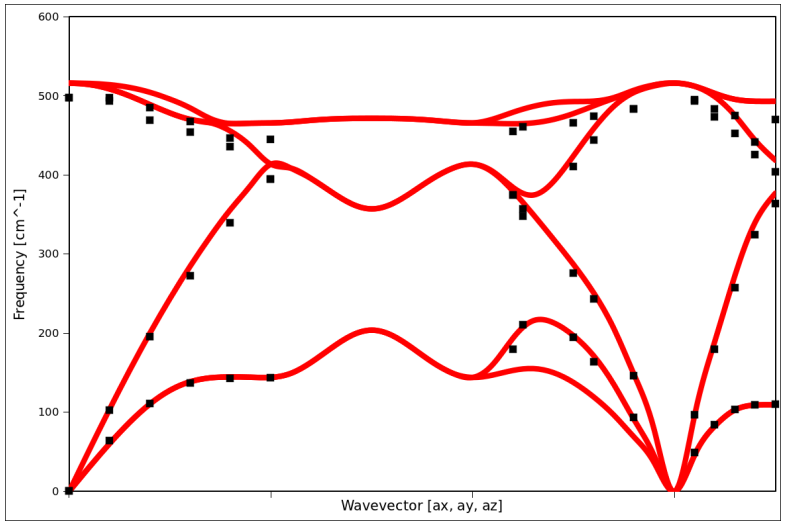
$$[\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + e^2 \int \frac{n_1(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3\vec{r'} + V_{XC}^{electrongas}[n_1(\vec{r})]]\psi_i(\vec{r}) = \epsilon_i\psi_i$$

- Recaculate electron density:

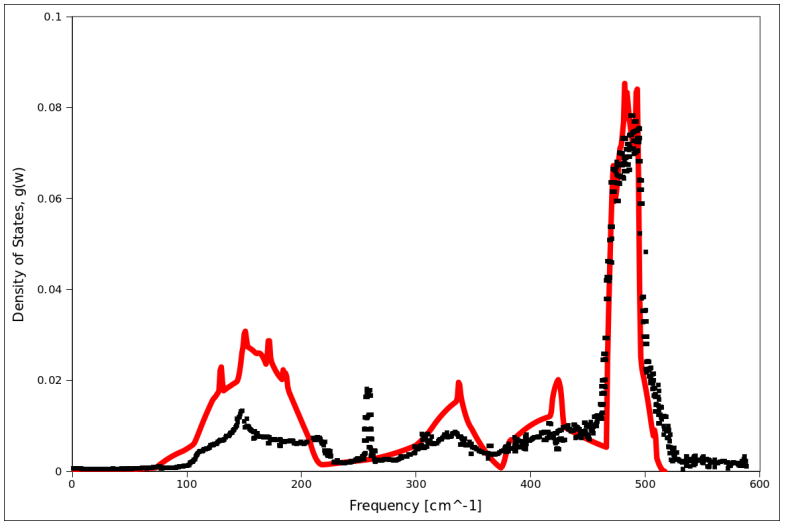
$$n_2(\vec{r}) = 2\sum_i \psi_i^*(\vec{r})\psi_i(\vec{r})$$

- Iterate until $n_{p+1}(\vec{r}) = n_p(\vec{r})$

Bulk Silicon from DFT



(c) Dipersion



(d) Density of States

Silicon cont.

- Lifetimes????

So What Just Happened?

- DFT for bulk phonon properties
- Lifetimes are not any easy task
- Extend this approach to the nanoscale