

***Ab Initio* Calculation of Lattice Thermal Conductivity**

GUO QIONG^{1, a}

¹Shanghai Aircraft Design and Research Institute, Commercial Aircraft Cooperation of China (COMAC)

^aemail: guoqiong@comac.cc

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Abstract. An *ab-initio*-based theoretical approach was presented to accurately describe phonon thermal transport. Harmonic and anharmonic interatomic force constants (IFCs) are the only inputs required for exact solution of phonon Boltzmann equation, thus the crucial elements required to calculate thermal conductivity. In this work, first principles using density functional perturbation theory was employed to calculate the harmonic IFCs. The third order anharmonic IFCs are determined by 2n+1 theorem. The calculated lattice thermal conductivities for Si and Ge, both isotopically enriched and naturally occurring, are in excellent agreement with experimental data.

Introduction

In semiconductors, heat is carried by the vibrating lattice. Such material's lattice thermal conductivity is an essential component in determining its potential utility for thermal management applications. So a predictive theoretical approach to calculate the lattice thermal conductivity in these materials is of tremendous importance for modern science and technology[1].

For over half a century, models of phonon thermal transport in bulk and nanostructured materials have commonly employed single-mode phonon relaxation time approximations[2,3](RTA) to bypass the difficulty in solving the phonon BTE. However, RTA introduces adjustable constants by fitting to existing experimental data, so it has limited predictive power. Improved approximate solutions of the phonon BTE have been achieved using variational approaches[4,5]. However, the accuracy of these depends on the choice of trial functions used, and simple trial functions cannot be constructed to reflect the full non-equilibrium distribution of phonons and nonlinear phonon dispersions characterizing most semiconductors. After that an iterative approach to solve exactly the linearized phonon BTE has been achieved[6-8]. The only inputs are the harmonic and anharmonic interatomic force constants (IFCs). More recently, molecular dynamics (MD) approaches have been introduced to calculate the lattice thermal conductivity of materials. However, they typically rely on empirical interatomic potentials[9] (EIPs) that are fit to experimental properties of materials, which are only available for a small number of already well-studied materials. These factors motivate *ab initio* calculations of the IFCs, removing the necessity of adjustable parameters, as well as providing more accurate results for its accurate representations of IFCs instead of that obtained from the empirical interatomic potentials.

In this paper, a predictive theoretical approach is presented to calculate lattice thermal conductivity free of adjustable parameters and is valid over a wide temperature range around room temperature. The methodology is illustrated first, then the calculation results of Si and Ge are compared with experimental results to test the approach.

Methodology

This session illustrated the *ab initio* approach to calculate the harmonic and third-order anharmonic IFCs in the framework of density-functional perturbation theory (DFPT), and calculating thermal conductivity through the Boltzmann transport theory.

A. Interatomic Force Constant

The reciprocal-space harmonic IFCs is a combination of electronic and ionic parts, can be written as

$$\Phi_{\alpha\beta}(\vec{q}) = \Phi_{\alpha\beta}^{el}(\vec{q}) + \Phi_{\alpha\beta}^{ion}(\vec{q}) = \frac{1}{N} \frac{\partial^2 E}{\partial u_{\kappa}^{\alpha} \partial u_{\kappa'}^{\beta}} \quad (1)$$

where N is the number of unit cells.

The real-space harmonic IFCs are found by using the fast Fourier transformation technique, using which to construct the reciprocal-space dynamical matrix given by

$$D_{\alpha\beta}(\kappa\kappa', \vec{q}) = \sum_{\ell'} \Phi_{\alpha\beta}(0\kappa; \ell' \kappa') e^{-i\vec{q} \cdot \vec{R}_{\ell'}} \quad (2)$$

with \vec{R}_i being the position vector of the i^{th} unit cell, κ indicating the atom with mass M_{κ} within the i^{th} unit cell and the real-space harmonic IFCs being described by $\Phi_{\alpha\beta}$.

The phonon frequencies and eigenvectors are solutions to the eigenvalue equation

$$\sum_{\beta\kappa'} \frac{1}{\sqrt{M_{\kappa}M_{\kappa'}}} D_{\alpha\beta}(\kappa\kappa', \vec{q}) e_{\beta\kappa'}(\vec{q}) = \omega^2 e_{\alpha\kappa}(\vec{q}) \quad (3)$$

The third-order anharmonic IFCs are evaluated first in reciprocal space,

$$\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\vec{q}, \vec{q}', \vec{q}'') = \frac{\partial^3 E_{tot}}{\partial u_{\kappa}^{\alpha}(\vec{q}) \partial u_{\kappa'}^{\beta}(\vec{q}') \partial u_{\kappa''}^{\gamma}(\vec{q}'')} \quad (4)$$

The “2n+1” theorem provides an analytic expression for these third-order anharmonic IFCs. We first use the Fourier transform expression,

$$\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\vec{q}, \vec{q}', \vec{q}'') = \delta_{\vec{q} \pm \vec{q}' \pm \vec{q}'' + \vec{K}} \sum_{l'l''} \Phi_{\alpha\beta\gamma}(0\kappa, l' \kappa, l'' \kappa) e^{\pm i\vec{q} \cdot \vec{R}_l} e^{i\vec{q}' \cdot \vec{R}_{l'}} \quad (5)$$

And the $\Phi_{\alpha\beta\gamma}^{\kappa\kappa'\kappa''}(\vec{q}, \vec{q}', \vec{q}'')$ are calculated as described in [10].

B. Linearized Boltzmann Equation

The linearized BTE is.

$$v_{\lambda} \cdot \nabla T \frac{\partial n_{\lambda}}{\partial T} = \sum_{\lambda'\lambda''} \left[W_{\lambda\lambda'\lambda''}^{+} (\Psi_{\lambda''} - \Psi_{\lambda'} - \Psi_{\lambda}) + \frac{1}{2} W_{\lambda\lambda'\lambda''}^{-} (\Psi_{\lambda''} + \Psi_{\lambda'} - \Psi_{\lambda}) \right] + \sum_{\lambda'} W_{\lambda\lambda'}^{imp} (\Psi_{\lambda'} - \Psi_{\lambda}) \quad (6)$$

The lowest-order anharmonic scattering process involves three phonons. Three-phonon scattering satisfies both energy and crystal momentum conservation,

$$\omega_j(\vec{q}) \pm \omega_{j'}(\vec{q}') = \omega_{j''}(\vec{q}''), \quad \vec{q} \pm \vec{q}' = \vec{q}'' + \vec{K} \quad (7)$$

Where \vec{q} , j , $\omega_j(\vec{q})$ and are the phonon momentum, branch index, and frequency, and \vec{K} is a reciprocal

lattice vector that is zero for normal process and nonzero for umklapp processes. Umklapp scattering is the dominant process for thermal resistivity at high temperatures for low defect crystals.

Three-phonon scattering rates are determined from Fermi's golden rule with the anharmonic IFCs as an input.

$$W_{\lambda\lambda'\lambda''}^{\pm} = \frac{\hbar\pi}{4N} \frac{(n_{\lambda}^0 + 1)(n_{\lambda'}^0 + \frac{1}{2} \pm \frac{1}{2})n_{\lambda''}^0}{\omega_{\lambda}\omega_{\lambda'}\omega_{\lambda''}} |\Phi_{\lambda\lambda'\lambda''}^{\pm}|^2 \delta(\omega_{\lambda} \pm \omega_{\lambda'} - \omega_{\lambda''}) \quad (8)$$

Where N is the number of unit cells and the delta function ensures energy conservation. The three-phonon matrix elements, $\Phi_{\pm}(\lambda, \lambda', \lambda'') = \Phi(j, -\vec{q}; j', \mp \vec{q}'; j'', \vec{q}'')$, measure the strength of the

scattering processes and are given by

$$\Phi(j, \vec{q}; j', \vec{q}'; j'', \vec{q}'') = \sum_{\kappa} \sum_{l'\kappa'} \sum_{l''\kappa''} \sum_{\alpha\beta\gamma} \Phi_{\alpha\beta\gamma}(0\kappa, l' \kappa', l'' \kappa'') e^{i\vec{q}' \cdot \vec{R}_{l'}} e^{i\vec{q}'' \cdot \vec{R}_{l''}} \frac{e_{\alpha\kappa}^j(\vec{q}) e_{\beta\kappa'}^{j'}(\vec{q}') e_{\gamma\kappa''}^{j''}(\vec{q}'')}{\sqrt{M_{\kappa}M_{\kappa'}M_{\kappa''}}} \quad (9)$$

where M_{κ} is the mass of the κ th atom and R_{ℓ} is a lattice vector. The $\Phi_{\alpha\beta\gamma}(0\kappa, l' \kappa', l'' \kappa'')$ are third order

anharmonic IFCs for the indicated triplets of atoms, and the e 's are phonon eigenvectors.

Isotopic impurities introduce elastic scattering of phonons. The scattering rate due to such impurities is calculated as

$$W_{\lambda\lambda'}^{imp} = \frac{\pi}{2} g_2 \omega_{\lambda} \omega_{\lambda'} n_{\lambda}^0 (n_{\lambda'}^0 + 1) \sum_{\kappa} |\hat{e}_{\kappa\lambda}^* \cdot \hat{e}_{\kappa\lambda'}^*|^2 \delta(\omega_{\lambda'} - \omega_{\lambda}) \quad (10)$$

The linearized phonon BTE is solved with an iterative procedure with harmonic and anharmonic IFCs obtained from *ab initio* DFPT calculations. Using the substitution, $n_{\lambda}^1 = n_{\lambda}^0(n_{\lambda}^0 + 1)\beta\bar{F}_{\lambda} \cdot \nabla T$, the phonon

BTE can be rearranged, we obtain the three equations,

$$F_{\lambda\alpha} = F_{\lambda\alpha}^0 + \Delta F_{\lambda\alpha} \quad (11)$$

$$F_{\lambda\alpha}^0 = \frac{\hbar\omega_{\lambda}n_{\lambda}^0(n_{\lambda}^0 + 1)v_{\lambda\alpha}}{TQ_{\lambda}} \quad (12)$$

$$\Delta F_{\lambda\alpha} = \frac{1}{Q_{\lambda}} \left\{ \sum_{\lambda'\lambda''} \left[W_{\lambda\lambda'\lambda''}^{+} (F_{\lambda'\alpha} - F_{\lambda''\alpha}) + \frac{1}{2} W_{\lambda\lambda'\lambda''}^{-} (F_{\lambda'\alpha} - F_{\lambda''\alpha}) \right] + \sum_{\lambda'} W_{\lambda\lambda'}^{imp} \right\} \quad (13)$$

And the total scattering rate is,

$$Q_{\lambda} = \sum_{\lambda'\lambda''} (W_{\lambda\lambda'\lambda''}^{+} + \frac{1}{2} W_{\lambda\lambda'\lambda''}^{-}) + \sum_{\lambda'} W_{\lambda\lambda'}^{imp} \quad (14)$$

We consider a temperature gradient along the [001] (z) direction. The iterative procedure is initiated by setting $F_{\lambda z}^1 = F_{\lambda z}^0 = 0$. The result zero-order solution is inserted into the $\Delta F_{\lambda\alpha}$ to obtain the first-order

solution. The iteration procedure is repeated until convergence is achieved. The phonon scattering time is related to $F_{\lambda z}$ as $\tau_{\lambda z} = TF_{\lambda z} / \hbar\omega_{\lambda}v_{\lambda z}$. It is used to calculate the lattice thermal conductivity as

$$\kappa_{zz} = \frac{1}{V} \sum_{\lambda} C_{\lambda} v_z^2 \tau_{\lambda z} \quad (15)$$

where $C_{\lambda} = k_B n_{\lambda}^0(n_{\lambda}^0 + 1)(\hbar\omega_{\lambda}\beta)^2$ is the specific heat per mode, $\beta = 1/(k_B T)$, and V is the crystal volume.

C. Computational Details

For all density functional calculations, the ion-electron and exchange-correlation effects are modeled in the framework of pseudopotential theory and local-density approximation. An 8*8*8 Monkhorst-Pack mesh was used in the Brillouin Zone. An cutoff energy of 24Ry was used for the plane wave expansion. We calculated the thermal conductivity of Si and Ge for heat current parallel to the direction of the temperature gradient, which is taken to lie along the [001] (z) direction.

These IFCs were obtained from first-principles using DFPT. The Quantum Espresso package is used to calculate all ground-state energies and harmonic IFCs. While the anharmonic IFCs are first evaluated on a reciprocal mesh and then been transformed into real space with triplet interactions out to seventh nearest neighbors, exploiting the 2n+1 theorem and following the method described in [10]. For each temperature, κ_z was calculated using the iterative solution to the phonon Boltzmann equation

as outlined in Sec.B and incorporating *ab initio* IFCs described in Sec.A. The phase space search for all allowed phonon-phonon scattering events was performed on a Gaussian quadrature grid for all three components of \vec{q} and the x and y component of \vec{q}' . The z component of \vec{q}' was chosen from a

finer linear grid. The final calculations were performed using a 32 point GAUSSIAN quadrature for each q component and a maximum of 200 points in the linear \vec{q}_z grid.

Results and Discussions

Fig.1 shows the calculated phonon dispersion for Si along high symmetry directions compared with measured data. The excellent agreement between *ab initio* theory and experiment highlights the accuracy of present approach. The calculated intrinsic lattice thermal conductivities for Si and Ge between 100K and 300 K are compared with measured values in Fig. 2. The agreement between theory and experiment is exceptionally good.

Fig.3 shows the lattice thermal conductivity of naturally occurring and isotopically enriched Si and Ge compared with the corresponding experimental values. The agreement between theory and experiment is extremely good for both the naturally occurring and isotopically enriched Si and Ge. It

is evident that the isotope effect is more obvious in Ge than Si, as the difference gap is larger for Ge. This is due to the spread of isotopes in the naturally occurring Ge. As the temperature increases, the calculations for both cases converge because the U scattering is strengthened with increasing temperatures and consequently drives the thermal conductivity.

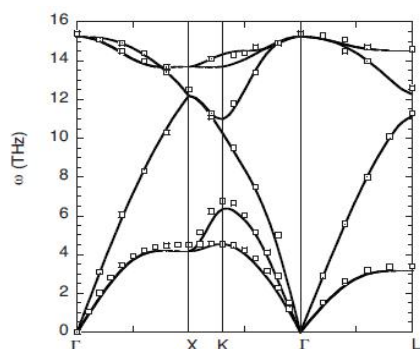


Fig.1 Phonon dispersion of Si. *Ab initio* calculations (solid line) and experiment[11] (open square).

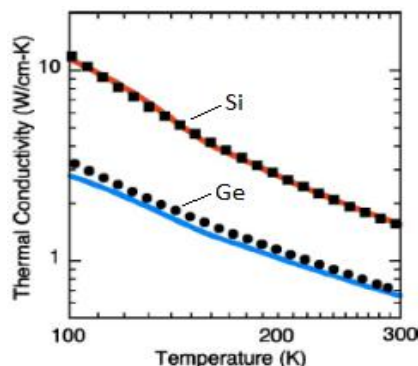


Fig.2 Lattice thermal conductivity as a function of temperature. The red line and solid squares are the calculated and measured of Si respectively, while the blue line and the solid circles are the corresponding quantities for Ge[12].

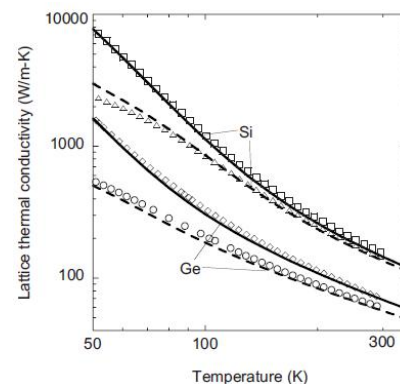


Fig.3 Lattice thermal conductivity of isotopically enriched (solid line) and naturally occurring (dashed line). Measured[13] (open diamond and open arrow for Si; open square and open circle for Ge) versus calculations.

Conclusions

In conclusion, an *ab initio* approach is proposed to calculate the lattice thermal conductivity using DFPT approach for harmonic and anharmonic IFCs combined with an exact solution of linearized phonon BTE. This approach has predictive capability without any adjustable parameters. Excellent agreement has been found in comparing *ab initio* calculated dispersion curves with experimental data. The method was then tested in getting thermal conductivity of Si and Ge. Good agreement with measured thermal conductivity has been found over a wide temperature range for both isotopically enriched and naturally occurring samples. The isotope effect in Ge is more obvious than Si. The demonstrated accuracy of our theory applied to Si and Ge suggests its predictive potential for calculating thermal conductivity of many other bulk and nanostructured materials of scientific and technological interest.

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