Chapter 1

INTRODUCTION TO THERMAL CONDUCTIVITY

This chapter aims to review the fundamental heat transport theory in bulk materials.

The general approach to calculate the lattice thermal conductivity is to solve the Boltzmann transport equation under the relaxation time approximation, while the scattering cross section is calculated by perturbation theory [1,2].

$$\kappa_i = \frac{1}{(2\pi)^3}\sum_n \int \left(\upsilon_{\Bbbk,n}\cdot\hat{i}\right)^2 \tau_{\Bbbk,n} C_{ph}(\Bbbk,n)\,d\Bbbk \,. \quad \mathbf{(1.1)}$$

The summation is over all the phonon modes n. $\hat{i}$ is a unit vector along a principle crystal axis and the temperature gradient. $\Bbbk$ is the wave vector. C_{ph} is the specific heat per phonon mode for frequency ω. $\upsilon_{\Bbbk,n}$ is the phonon velocity for the nth mode at wave vector $\Bbbk$. The specific heat (*vide infra*) is written as

$$C_{ph} = \frac{\hbar^2\omega^2}{k_B T^2}\frac{\exp(\hbar\omega/k_B T)}{\left[\exp(\hbar\omega/k_B T)-1\right]^2} \,. \quad \mathbf{(1.2)}$$

In case of isotropic $\upsilon_{\Bbbk}$,

$$\kappa = \frac{4\pi}{3}\frac{1}{(2\pi)^3}\sum_n \int \upsilon_{\Bbbk,n}^2 \tau_{\Bbbk,n} C_{ph}(\Bbbk,n)\, g(\Bbbk,n)\,d\Bbbk \,. \quad \mathbf{(1.3)}$$

$g(\Bbbk,n)$ is the phonon density-of-states and can be written as $g(\Bbbk,n)d\Bbbk = \left(\omega^2/\upsilon^3\right)d\omega$ in Debye's limit (i.e., $\omega = \upsilon\Bbbk$). Thus,

$$\kappa = \frac{1}{3}\frac{1}{2\pi^2}\sum_n \int_0^{\omega_{0,n}} \frac{\tau_{\omega,n}}{\upsilon_{\omega,n}} C_{ph}(\omega,n)\omega^2\, d\omega \,. \quad \mathbf{(1.4)}$$

$\omega_{0,n}$ is the maximum frequency for the n-th phonon branch.

According to equation **1.1-1.4**, accurate descriptions of the phonon band diagram and the scattering mechanisms are critical for reliable prediction and calculation of the thermal conductivity. This chapter will review the expressions for the specific heat and the scattering rates. Several important lattice thermal conductivity models and their applicable conditions are also discussed. In addition, methodologies for modeling the phonon band diagram will be briefly described.

Specific Heat C_V [2,3]

Thermodynamically, the volume specific heat is defined as

$$C_V = (\frac{\partial U}{\partial T})_V \,. \quad \mathbf{(1.5)}$$

Lattice vibrations are generally simplified as harmonic oscillators. In this model, every vibration energy level is spaced by the Planck energy $\hbar\omega$, with the zero-point energy $\frac{1}{2}\hbar\omega$. ω is the vibration frequency of the mode. For phonons, the population distribution is described by the Bose-Einstein distribution, $D_{n,\mathbb{k}}(\omega,T) = \left[\exp(\hbar\omega_{n,\mathbb{k}}/k_B T) - 1\right]^{-1}$. $D_{n,\mathbb{k}}(\omega,T)$ is called the occupation number, or, in the context of lattice dynamics, the phonon number. Thus, the total energy of the phonons in a particular branch is then given as

$$U_{n,\Bbbk}(\omega,T) = \hbar\omega_{n,\Bbbk}\left[\frac{1}{2} + D_{n,\Bbbk}(\omega,T)\right].$$ **(1.6)**

Note that the phonon number depends on temperature and the vibration frequency. The total internal energy of the crystal is the summation of $U(\omega,T)$ over all the phonon branch and wave vectors, $\sum_{n,\Bbbk} U_{n,\Bbbk}(\omega,T)$. Taking the temperature derivative of $\sum_{n,\Bbbk} U_{n,\Bbbk}$, we obtain the specific heat as

$$C_V = \sum_{n,\Bbbk} \frac{\hbar^2\omega_{n,\Bbbk}^2}{k_B T^2} \frac{\exp\left(\hbar\omega_{n,\Bbbk}/k_B T\right)}{\left[\exp\left(\hbar\omega_{n,\Bbbk}/k_B T\right) - 1\right]^2}.$$ **(1.7)**

In Einstein's model proposed in 1907, every atom is oscillating independently at a same frequency, ω_E. The internal energy of the system is then given as

$$U = 3N\hbar\omega_E\left(D(\omega_E,T) + \frac{1}{2}\right) = 3N\frac{\hbar\omega_E}{\exp(\hbar\omega_E/kT) - 1} + 3N\frac{\hbar\omega_E}{2}.$$ **(1.8)**

N is the number of atoms. From equation **1.8**, the specific heat could be derived as

$$C_V = \frac{\partial U}{\partial T} = 3Nk\left(\frac{\hbar\omega_E}{kT}\right)^2 \frac{\exp(\frac{\hbar\omega_E}{kT})}{\left(\exp(\frac{\hbar\omega_E}{kT}) - 1\right)^2}.$$ **(1.9)**

In the low temperature limit, $T \to 0$

$$C_{V,ph} \approx e^{-\hbar\omega_E/kT}.$$ **(1.10)**

In this model, the specific heat drops exponentially as temperature goes to absolute zero. However, such fast decay does not fit well to the experimental results, which demonstrate that the specific heat decreases with T^3 dependence rather than the activation process-like decay.

As in equation **1.6**, the internal energy of the crystal lattice is a function of phonon frequency. It is thus convenient to re-write equations **1.6** and **1.7** as integrals of the phonon frequencies:

$$U = \int \hbar\omega \left[\frac{1}{2} + D(\omega,T) \right] g(\omega) d\omega \, . \, \textbf{(1.11)}$$

$$C_{V,ph} = \frac{\partial}{\partial T} \int \hbar\omega D(\omega,T) g(\omega) d\omega \, . \, \textbf{(1.12)}$$

$g(\omega)$ is defined as the density-of-states. As such, the number of phonon modes within ω and $\omega + d\omega$ is $g(\omega)d\omega$. For a 3-dimensional isotropic crystal,

$$g(\omega)d\omega = \frac{\int d^3k}{\Delta^3 k} = \frac{\int d^3k}{(2\pi / a)^3} \, . \, \textbf{(1.13)}$$

a is the lattice constant of the crystal. Further mathematical deduction yields that

$$g(\omega)d\omega = \frac{a^3}{2\pi^2} \frac{k^2}{d\omega / dk} d\omega \, . \, \textbf{(1.14)}$$

In the Debye model, rather than treating the phonons as individual random oscillators, the atoms vibrate collectively in a wave-like fashion. The phonon branch is assumed to be non-dispersive (i.e., $\omega = \upsilon k$). Thus,

$$g(\omega) = a^3\omega^2 / 2\pi^2\upsilon^3 \, . \, \textbf{(1.15)}$$

The linear dispersion is applicable to acoustic phonons at low frequencies. The Debye model fails to predict the specific heat for high-frequency phonons, as the dispersion at high frequencies deviate from linearity. Approximating the first Brillouin zone by a sphere with the same volume, we can now calculate the specific heat of the lattice vibrations (two transverse modes and one longitudinal mode) in Debye's model by integrating equation **1.11**,

$$U = \frac{3a^3}{2\pi^2 \upsilon^3} \int_0^{\omega_D} \omega^2 \frac{\hbar\omega}{\exp(\frac{\hbar\omega}{kT}) - 1} d\omega = 9NkT(\frac{T}{\theta})^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1}. \textbf{(1.16)}$$

N is the number of atoms in the first BZ; θ is the Debye temperature of the material ($\theta = \frac{\hbar\omega_D}{k_B} = \frac{\hbar\upsilon_g}{k}\sqrt[3]{6\pi^2 N}$). ω_D is the vibration frequency at the Debye temperature. $x_D \equiv \hbar\omega_D / kT$. In equation **1.16**, the $\int \frac{1}{2}\hbar\omega g(\omega) d\omega$ term is omitted for simplicity, as our goal here is to find the expression for specific heat. Taking the temperature derivative of equation **1.16**, we find:

$$C_{V,ph} = \frac{1}{2\pi^2\upsilon^3} \int_0^{\omega_D} \frac{\hbar^2\omega^4}{k_B T^2} \frac{\exp(\hbar\omega / k_B T)}{\left[\exp(\hbar\omega / k_B T) - 1\right]^2} d\omega = 9Nk \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4 e^4}{\left(e^x - 1\right)^2} dx.$$

Debye's model predicts a T^3 dependency of thermal conductivity when $T \to 0$.

$$C_{V,ph} = \frac{12\pi^4}{5} Nk(\frac{T}{\theta})^3 \propto T^3. \textbf{(1.17)}$$

In the high-temperature limit, defined as $\hbar\omega \gg k_B T$, $\frac{1}{2} + D_{n,\Bbbk}(\omega,T)$ approaches $k_B T / \hbar\omega$, thus, $U_{n,\Bbbk}(\omega,T) \approx k_B T$. As a result, all the phonon modes have the same energy as $k_B T$ at the high-temperature limit. Since the number of normal modes equals the number of degree of freedom 3N (N: number of atoms), $\sum_{n,\Bbbk} U_{n,\Bbbk} \approx 3Nk_B T$, $C_{V,ph} \approx 3Nk_B$ at high temperatures. This is the Dulong-Petit law, which empirically states that at high temperatures all the specific heat saturates to a constant independent of the material.

Phonon Relaxation Time τ

The phonon relaxation time is a collective parameter governed by various phonon scattering processes. It is highly dependent on the material systems, and the dominant mechanisms in most cases are the isotope/impurity scattering, the boundary scattering, the Umklapp process, and the three-phonon normal process. Matthiessen's rule proposes that the resistivity of a system with distinct scattering mechanisms is the sum of the individual resistivities alone [2]. Thus,

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} . \quad \textbf{(1.18)}$$

In cases when τ is wave vector $\mathbb{k}$ dependent, the conductivity is proportional to some average $\bar{\tau}$. Thus, Matthiessen's rule is modified as

$$\frac{1}{\tau} = \sum_i \frac{1}{\bar{\tau}_i} . \quad \textbf{(1.19)}$$

Developing the expressions for the relaxation times is non-trivial, especially for the three-phonon processes. In the following paragraphs, we discuss the scattering time expressions for the various processes in some commonly seen models. Due to the fact that many of the relaxation processes are dependent on the phonon frequencies, as well as the characteristics of the dispersions of the phonon branches, some fundamental assumptions are applied in the scattering time expressions in each model that limit the validity of the expressions to certain phonons at particular temperature ranges.

Lattice Thermal Conductivity Models

The behavior of the lattice thermal conductivity is qualitatively described by the early work of Debye and Peierls: (1) the lattice thermal conductivity at very low temperatures depends strongly on the size and shape of the crystal (long phonon mean-free-path) and increases with the specific heat (T^3 dependence) as temperature goes up. (2) The lattice thermal conductivity starts to decline as the temperature reaches high enough (~ $0.1\theta_D$), when the Umklapp processes start being dominate. (3) At the peak of the thermal conductivity, its value is sensitive to crystal imperfection such as impurities, isotopes, and defects. Following Debye and Peierls' work, several models have been proposed to better describe the thermal conductivity characteristics:

1. The Klemens Model [4]

In the Klemens model, the thermal conductivity for different scattering mechanisms are calculated separately and the total thermal conductivity in this model is given as

$$\frac{1}{\kappa} = \sum_i \kappa_i^{-1} . \textbf{ (1.20)}$$

In the Klemens model the phonon-point defect (defects with mass difference such as isotopes, impurities, etc.) scattering is given as

$$\frac{1}{\tau_{I,j}} = \frac{\pi}{6} V'\Gamma g(\omega)\omega^2 = \frac{V'\Gamma}{4\pi \upsilon_j^3}\omega^4 . \textbf{ (1.21)}$$

$$\Gamma = \frac{\sum_i (c_i M_i)^2 - \left(\sum_i c_i M_i\right)^2}{\left(\sum_i c_i M_i\right)^2} . \textbf{ (1.22)}$$

$\tau_{I,j}$ is the phonon-impurity relaxation time of the j phonon branch; V' is the atomic volume; Γ is the so-called mass-fluctuation phonon scattering parameter. c_i and M_i denote the concentration and the mass of the point defects (e.g., isotopes or the impurities). In equation **1.20**, the Debye model phonon density-of-state (equation **1.15**) is assumed. Under such assumption, the expression fails for the zone edge high frequency phonons as the dispersion curve turns convex-up, rendering a higher density-of-state.

Note that the point-defect scattering *is strongly dependent on the phonon frequency, group velocity, and impurity content*. The $\tau^{-1} \propto \omega^4$ relation is similar to the Rayleigh scattering in photons. It has been experimentally confirmed that the impurity level has a large effect on the thermal conductivity. For example, the highly enriched ^{70}Ge (99.99%) sample has maximum thermal conductivity 14 times higher than the $^{70/76}$Ge sample (43% of ^{70}Ge; 48% of ^{76}Ge; 9% others) [1].

2. The Callaway model [5]

In 1959 Joseph Callaway developed a model to calculate the lattice thermal conductivity valid at low temperatures (2.5K to 100K). In Callaway's model, an isotropic Debye-like phonon spectrum is assumed, i.e., no distinction between longitudinal and transverse phonons and the phonon branches are non-dispersive. The scattering mechanisms considered in this model are:

a. Isotope/point impurity scattering

In Callaway's model, the isotope scattering takes the form proposed by Klemens (i.e., $\tau_I^{-1} = A\omega^4$). A is a fitting parameter which depends on the mass-fluctuation phonon scattering parameter and the phonon velocity as in the Klemens model.

Assumptions and validity: (I) Debye-like phonon spectrum and the Debye's description of the density-of-states. Therefore, this expression applies to low temperature region where Debye's model is valid. (II) An averaged phonon velocity for longitudinal and transverse branches.

b. Boundary scattering

$\tau_B^{-1} = \upsilon_B / L_0$; υ_B is the average speed of sound. L_0 is the characteristic length of the sample.

Assumptions and validity: (I) Since no specularity factor is incorporated, the Callaway model assumes that the scattering at the surface boundary is purely diffusive. (II) Again, the speed of sound is the averaged phonon velocity for longitudinal and transverse branches.

c. Three-phonon normal process

$\tau_N^{-1} = B_2 T^3 \omega^2$ B_2 is a fitting parameter which depends on the Gruneisen constant and the phonon velocity. The expression was derived by Herring [6] for longitudinal phonon scattering under momentum conservation conditions at low temperatures.

Assumptions and validity: Low-temperature longitudinal phonons.

d. Umklapp process

$\tau_U^{-1} = B_1 T^3 \omega^2$ B_1 is a fitting parameter which contains the exponential temperature factor $\exp\left(-\theta / bT\right)$ as suggested by Peierl, the phonon velocity, the Gruneisen constant, and the Debye temeperature.

Assumptions and validity: The Umklapp process expression in Callaway's model is neither a high-temperature nor a low-temperature assumption; thus, the model fails to describe the Umklapp process, limiting the model to the low-temperature region where the Umklapp process is negligible.

The overall relaxation time is

$$\tau = \left(\upsilon_B L_0^{-1} + B_1 T^3 \omega^2 + A\omega^4 + B_2 T^3 \omega^2\right)^{-1}. \quad \textbf{(1.23)}$$

The thermal conductivity can thus be expressed as [7]

$$\kappa = \frac{1}{2\pi^2 \upsilon_B} \int_0^{\omega_D} \frac{\hbar^2 \omega^4 k_B T^{-2}}{\upsilon_B L_0^{-1} + \left(B_1 + B_2\right) T^3 \omega^2 + A\omega^4} \frac{\exp(\hbar\omega / k_B T)}{\left[\exp\left(\hbar\omega / k_B T\right) - 1\right]^2} d\omega. \quad \textbf{(1.24)}$$

The three-phonon normal process is incorporated in equation **1.24**; such treatment assumes the normal process as a resistive scattering process. However, the three-phonon normal process does not contribute to thermal resistance, since the phonon momentum is conserved. Thus, in the original Callaway's model, an additional correction term was introduced to counteract errors by treating the normal process as entirely resistive. The correction term is usually neglected because it is found to be small in most cases, where the normal process relaxation time is much longer than the resistive process [5].

The Callaway's model assumes a non-dispersive phonon spectrum with no distinction in the phonon modes. Therefore, the model fails to explain the thermal conductivity of materials with highly dispersive phonon spectrums at high temperatures such as germanium and silicon. Moreover, the relaxation time expressions for the three-phonon normal and Umklapp processes are over-simplified from reality. *Thus the model predicts the thermal conductivity behavior well only at low temperatures (*$\leq 0.1\theta_D$*) where the Debye-like phonon spectrum is a good approximation and only the isotope/impurity scattering and boundary scattering are important.*

3. The Holland model [2]

Distinct from the Klemens and the Callaway models, the analysis of lattice thermal conductivity in Holland's model explicitly considers the contribution by both the transverse and longitudinal phonons.

a. Isotope scattering

   $\tau_I^{-1} = A\omega^4$

b. Boundary scattering

   $\tau_B^{-1} = \upsilon_B / FL_0$

   The speed of sound is defined as the average phonon velocity $\upsilon_B^{-1} = (1/3)\left(2\upsilon_T^{-1} + \upsilon_L^{-1}\right)$. T , L represents the transverse and longitudinal acoustic phonons respectively. F is the specularity parameter introduced for partially diffusive boundary scattering.

The expressions of isotope scattering and boundary scattering in the Holland model are essentially the same as those in the Callaway model, except that the boundary scattering is not fully diffusive in the Holland model.

The Holland model attempts to capture the high-temperature ($T > 0.1\theta_D$) characteristic of the thermal conductivity behavior. Therefore, the expressions for the three-phonon normal and Umklapp processes are modified from the Callaway model.

c. Three-phonon normal process

$$\tau_{N,T}^{-1} = B_T \omega T^4 \text{ for } 0 \le \omega < \omega_1$$

$$\tau_{N,L}^{-1} = B_L \omega^2 T^3 \text{ for } 0 \le \omega \le \omega_3$$

These relaxation time expressions were derived by Herring [6] for *low- temperature longitudinal and transverse acoustic phonons.* Note that in the Callaway model, only the longitudinal acoustic phonon is considered in the normal process. Although these expressions are derived for low-temperature acoustic phonons, it is sufficient for fitting the thermal conductivities, since at high temperatures the normal process becomes negligible.

d. Umklapp scattering

$$\tau_{U,T}^{-1} = \frac{B_{U,T}\omega^2}{\sinh(x)} \text{ for } \omega_1 \le \omega \le \omega_2$$

$$\tau_{U,T}^{-1} = 0 \text{ for } \omega < \omega_1$$

In the Holland model, the Umklapp process is absent at $\omega \le \omega_1$ (or $\theta \le \theta_1$) and only the transverse modes are considered.

Combining the scattering mechanisms, one gets

$$\tau_T^{-1} = \upsilon_B / FL + A\omega^4 + \tau_{U,T}^{-1}$$

$$\tau_L^{-1} = \upsilon_b / FL + A\omega^4 + B_L \omega^2 T^3 .$$

As stated earlier, the Holland model takes into account the contribution of thermal conductivity from both the transverse and longitudinal phonons [2]:

$$\kappa = \kappa_T + \kappa_L$$

$$\kappa = \frac{2}{3}\int_0^{\theta_T/T} \frac{C_T T^3 x^4 e^x (e^x-1)^{-2} dx}{\tau_T^{-1}} + \frac{1}{3}\int_0^{\theta_L/T} \frac{C_L T^3 x^4 e^x (e^x-1)^{-2} dx}{\tau_L^{-1}} .$$

The thermal conductivity can be further written as

$$\kappa = \frac{2}{3}\int_0^{\theta_1/T} \frac{C_1 T^3 x^4 e^x (e^x-1)^{-2} dx}{\upsilon_B / FL + A m^4 x^4 T^4 + B_{N,T} m x T^5} + \frac{2}{3}\int_{\theta_1/T}^{\theta_2/T} \frac{C_2 T^3 x^4 e^x (e^x-1)^{-2} dx}{\upsilon_B / FL + A m^4 x^4 T^4 + \frac{B_{U,T} m^2 x^2 T^2}{\sinh(x)}} +$$

$$\frac{1}{3}\int_0^{\theta_L/T} \frac{C_L T^3 x^4 e^x (e^x-1)^{-2} dx}{\upsilon_B / FL + A m^4 x^4 T^4 + B_{N,L} m^2 x^2 T^5}$$

$i = T, L$; $x = \hbar\omega / k_B T$; $\theta_i = k_B \omega_i / \hbar$; $C_i = \left(k_B / 2\pi^2 \upsilon_i\right)\left(k_B / \hbar\right)^3$.

Assumption: In the Holland model, the transverse acoustic phonon is assumed to have three constant velocities depending on the phonon frequency range - i.e., the transverse phonon has a constant velocity at low frequencies $\omega < \omega_1$, and the velocity decreases abruptly and remains constant between ω_1 and ω_2. For phonons with frequencies above ω_2 the phonon velocity is zero.

In summary, the Holland model considers the contribution of thermal conductivity both from the longitudinal and the transverse phonons. It also applies two averaged phonon group velocities to crudely describe the phonon dispersions. Distinct from the Callaway model, the Holland model uses different expressions for the relaxation mechanisms. Overall speaking, the Holland model captures the thermal conductivity characteristics better than the Callaway model at higher temperatures.

Following Callaway and Holland, there have been several modifications to the thermal conductivity model. These modifications are aimed to better capture the temperature dependence over a broader range. Basically, the focus of the later work has been primarily on achieving a better description in the phonon dispersions rather than developing new thermal conductivity models.

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