24 An Introduction to Nanoscale, Microscale, and Macroscale Heat Transport: Characterization and Bridging of Space and Time Scales

Christiane V.D.R. Anderson and Kumar K. Tamma

CONTENTS

24.1 Introduction ........................................................................................................ 650
24.2 Spatial and Temporal Regimes in Heat Conduction .......................................... 651
24.3 Considerations in Time–Heat Conduction ............................................................ 652
24.4 Considerations in Size–Heat Conduction ............................................................ 652
24.5 Boltzmann Transport Equation ........................................................................... 654
  24.5.1 One-Temperature Models .............................................................................. 655
  24.5.2 The C- and F-Processes Model—A Unified Theory ........................................ 657
  24.5.3 Validation of the Thermodynamics Second Law for the C- and F-Processes Model .............................................................. 660
    24.5.3.1 The Fourier Model ........................................................................ 661
    24.5.3.2 The Cattaneo Model ..................................................................... 661
    24.5.3.3 The Jeffreys-Type Model ............................................................ 661
  24.6 Two-Temperature Models .................................................................................. 662
  24.7 Relaxation Time .................................................................................................. 664
  24.8 Numerical Illustration—Two-Temperature Model and Pulse Laser Heating .............................................................. 665
  24.9 Numerical Illustration—One-Temperature Model and Heat Conduction Model Number $F_T$ ................................................................................. 667
    24.9.1 Spanning Spatial Scales .............................................................................. 669
24.1 INTRODUCTION

This chapter serves as an introduction and a prelude to understanding the fundamentals encompassing nanoscale, microscale, and macroscale heat transport. Because of the continued trend in the miniaturization of devices and rapid progress in the design and synthesis of materials and structures leading to the notion of materials by design, there is significant interest in having an improved understanding of heat transport across the broad spectrum of length scales ranging from nanoscale to macroscale regimes and time scales encompassing finite to infinite speeds of heat propagation.

Since the early work on size effects to thermal conductivity in 1938 by Haas and Biermasz and theoretical work by Casimir,1 and more recent efforts demonstrating that the thermal conductivity of thin film structures is one to two orders of magnitude less than its bulk counterpart,2 from an engineering perspective many researchers have shown a keen interest in providing an improved scientific understanding of thermal transport at small length scales such as the nanoscale regime. Some early works in the 1950s and 1960s due to Klemens,3 Callaway,4 and Holland5 emanating from the Boltzmann Transport Equation (BTE) have indeed provided viable approaches to model lattice thermal conductivity due to phonon-scattering processes. Alternately, since the early 1990s, that which emanates from the BTE with relation to the equation of radiation transfer (ERT), namely the equations for phonon radiative transfer (EPRT)6,7 and others such as Monte Carlo8–11 and molecular dynamics (MD) simulations12–16 have also received considerable research activity. While MD simulations do not require any fitting parameters, they lack the ability to perform large-scale simulations at desired length scales that are of practical interest. Alternately, the BTE-based approaches invariably need fitting parameters (for example, the relaxation time, the acoustic phonon dispersion from property of bulk medium, and the like). On the other hand, these more recent efforts since the 1990s attempt to bring such physics into an engineering perspective and follow the same methods as in Callaway4 and Holland,5 or improvements thereof, and stem serious concerns in employing phenomenological models such as the classical Fourier model and other modifications such as that due to Cattaneo–Vernotte.17,18 Consequently, these more recent efforts have directed efforts to microscopic energy transfer models, and although they also need to employ fitting parameters, they appear to show reasonably good fit to experimental data.6,9,19,20
transfer models and other formulations that have been cited in the literature since the
1990s—for example, in the prediction of thermal conductivity of very thin films—
include (1) the Fourier law overpredicts the actual heat flux, resulting in thermal
conductivity results that could be as much as two orders of magnitude greater than
experimental reported values for thin dielectric films; (2) the Cattaneo equation lacks
the ability to capture the ballistic transport process; and (3) for processes that are
small in both space and time, the energy balance fails based on the phenomenological
Fourier model. Taking some of these arguments at face value, a reference is also made
similar to issue (1) by the present authors; however, in this chapter we accurately put
into context arguments to all the preceding issues. The present chapter fundamentally
places into context and provides challenging answers to the aforementioned arguments
existing in the literature, and the reader is encouraged to go in-depth into the underlying
details and draw relevant conclusions to understanding thermal transport across the
broad range of spatial scales and also those with temporal scales ranging from finite to
infinite speeds of heat propagation.

24.2 SPATIAL AND TEMPORAL REGIMES
IN HEAT CONDUCTION

Quantum mechanics has helped us recognize that solids are composed of several
discrete particles (electrons, neutrons, and protons) at the microscopic level. Depending
on the type of solid, different mechanisms of heat transport take place in the
material in different manners and are called heat carriers. Modeling the spatial and
temporal regimes in materials can be broadly subdivided into four regimes:

- Macroscale
- Mesoscale
- Microscale
- Nanoscale

The characteristic lengths and times for these regimes are depicted in Table 24.1. In
heat conduction, two major areas have been prominent: (1) the macroscale, which
involves the modeling of macroscopic effects; and (2) the microscale, which encom-
passes all the other regimes in materials modeling (nanoscale effects are implied).

<table>
<thead>
<tr>
<th>Regime</th>
<th>Characteristic Length</th>
<th>Characteristic Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscale</td>
<td>(\geq 10^{-3}) m</td>
<td>(\geq 10^{-3}) s</td>
</tr>
<tr>
<td>Mesoscale</td>
<td>(-10^{-6}-10^{-3}) m</td>
<td>(-10^{-3}-10^{-9}) s</td>
</tr>
<tr>
<td>Microscale</td>
<td>(-10^{-6}-10^{-4}) m</td>
<td>(-10^{-4}-10^{-11}) s</td>
</tr>
<tr>
<td>Nanoscale</td>
<td>(-10^{-7}-10^{-9}) m</td>
<td>(-10^{-10}-10^{-14}) s</td>
</tr>
</tbody>
</table>

The macroscale formulation in heat conduction is based on the continuum assumption. It does not consider the size and time dependence of the heat transport. Heat is assumed to be carried by the atoms. The microscale formulation in heat conduction considers the physical mechanisms of heat transport through heat carriers where size and time dependence are crucial. This leads to the explanation of several parameters that characterize the microscopic regimes in both temporal and spatial regimes.

24.3 CONSIDERATIONS IN TIME–HEAT CONDUCTION

Besides the notion of temporal scale aspects ranging from the finite nature of heat propagation to infinite speeds of thermal transport, the important time parameters that govern the microscopic heat transport are as follows:

- The thermalization time—The time for the electrons and lattice to reach equilibrium
- The diffusion time—The time the heat information takes to travel through the specimen
- The relaxation time—The time associated with the speed at which a thermal disturbance moves through the specimen
- The heating time—The time that an external source heats the specimen
- The physical process time—The total time duration of interest

When the physical process time is comparable to any of the aforementioned times, the time effect becomes important and the process is considered to be microscopic in time. When the heating time is on the order of the thermalization time, the energy deposition must be considered. The immediate question that naturally arises from this consideration is the following: Is the energy deposited in the lattice, the electron, or both? Finally, when the heating time is comparable to the diffusion time or the relaxation time, a finite speed of the thermal propagation must be considered.

24.4 CONSIDERATIONS IN SIZE–HEAT CONDUCTION

The important size parameters that govern the heat transport in a device are as follows:

- The mean free path ($\lambda$)
- The characteristic dimension of the material ($L$)

From a physical viewpoint, when the mean free path is much less than the characteristic dimension of the material ($\lambda \ll L$), the heat transport is said to be macroscopic and is commonly termed the purely diffusive limit. In this limit, there exist enough scattering mechanisms within the film. In dielectrics, these scattering mechanisms help bring the phonons within the film back to equilibrium and help establish a temperature gradient.
An Introduction to Nanoscale, Microscale, and Macroscale Heat Transport

When the mean free path is on the order or much greater than the characteristic dimension of the material \( (\lambda \sim L \text{ or } \lambda >> L) \), the heat transport is said to be microscopic, and the transport presents itself in a partially diffusive-ballistic and purely ballistic manner, respectively. As the size of the material is decreased (and in comparison to \( \lambda \) becomes small), so do the scattering mechanisms within the film, and a temperature gradient might not be established at the ballistic limit. As observed at the purely ballistic limit, there exist temperature jumps at the physical boundaries (analogous to slip conditions), and the final temperature profile is characterized by 

\[
T(x=L) = \frac{T_1 + T_2}{2},
\]

Since, a temperature gradient is not established at the purely ballistic or partially ballistic-diffusive limits, then the Fourier law, in its purest definition, breaks down, thus making it impossible to predict the thermal conductivity.

These limits can be observed in Figure 24.1. The size effects to thermal conductivity were originally observed in 1938 in the experimental works of Haas and Biermasz, and the theoretical explanation shortly followed in the works of Casimir. \(^1\) Casimir identified that at the purely ballistic regime a temperature gradient could not be established, and strictly according to the Fourier law, it was not possible to prescribe the thermal conductivity. At the purely ballistic limit it was observed that the temperature at the boundaries, and not the temperature gradient within the film, governs the heat transport. Since thermodynamic equilibrium is restored due to the scattering of particles from the boundaries, the heat conduction by these particles is suggested to be similar to photons and can be analyzed as a radiative transfer model where the heat flux across the specimen can be described by

\[
q = \sigma \left(T_1^4 - T_2^4\right)
\]

(24.1)

where \( \sigma \) is the Stefan–Boltzmann constant for the heat carrier, and \( T_1 \) and \( T_2 \) are the temperatures of the faces of a thin film. This is commonly referred to as the Casimir limit.

At this juncture, some noteworthy questions naturally arise. What are the underlying issues and approaches for characterization and bridging space/time scales? When do we need to resort to nonclassical approaches and what are the limits of
the classical models? Is there a unified theory underlying heat transport that best describes the conduction of heat spanning the various scales, and what are the limitations? From a modeling and simulation viewpoint, what are the most simple yet effective formulations that are easy to implement and are not computationally intensive? Several of these issues are addressed in the text to follow and the various methods are also briefly highlighted.

### 24.5 BOLTZMANN TRANSPORT EQUATION

The heart of heat transport theory is the Boltzmann Transport Equation (BTE). The BTE determines the status of a particle via its location and velocity. The most general form of the BTE is given as

$$
\frac{\partial f}{\partial t} + v \cdot \nabla f + a \frac{\partial f}{\partial v} = \left( \frac{\partial f}{\partial t} \right)_{\text{scatt}}
$$  

(24.2)

where \( f(\vec{r}, T, \omega) \) is the nonequilibrium thermodynamic distribution function, \( v(\omega) \) is the phonon velocity (that is, the speed of sound in dielectrics), \( a(v) \) is the particle acceleration, and \( t \) is time. The first term in Equation 24.2 represents the net rate of particles over time, the second term is the convective inflow of particles in physical space, the third term is the net convective inflow due to acceleration in velocity space, and the term on the right-hand side is the net rate of change of particles inside a control volume due to collisions. The phonon velocity in a dielectric material is fairly constant over a large frequency range, and thus \( \frac{\partial f}{\partial v} \) can be neglected. Both energy and temperature gradients tend to disturb the electron distribution, and this tendency is opposed by processes that restore equilibrium, such as the scattering of electrons or phonons by lattice vibrations and crystal defects. As a result, the scattering term is approximated under the relaxation-time approximation as

$$
\left( \frac{\partial f}{\partial t} \right)_{\text{scatt}} = -\frac{f_f - f_0}{\tau}
$$  

(24.3)

where \( f_0(\vec{r}, T, \omega) \) is the thermodynamic distribution at equilibrium (Bose–Einstein distribution for boson particles [such as phonons] and Fermi–Dirac distribution for fermion particles [such as electrons]), \( \frac{\partial f_0}{\partial t} = 0 \), and \( \tau (\omega, v) \) is the rate of return to equilibrium and is called the relaxation time.

Kinetic theory is derived from the BTE under the premise that there is a local thermal dynamic equilibrium (LTE). In cases where LTE is not achieved, one solves the BTE. However, under the presence of a temperature gradient, the LTE is implied, and for simplicity in illustrating the basic concepts we consider the one-dimensional form of the BTE. The diffusion term in Equation 24.2, \( \frac{\partial f}{\partial x} \), and the \( \frac{\partial f}{\partial x} \) term can be approximated as

$$
\frac{\partial f}{\partial x} = \frac{df_0}{dT} \frac{dT}{dx}
$$  

(24.4)
The flux of particles is given by

\[ q(x) = \int_{0}^{\omega_D} v_x f(x) h \omega D(\omega) d\omega \quad (24.5) \]

The transient one-dimensional BTE under the relaxation-time approximation and the temperature gradient approximation is given by

\[ \frac{\partial f}{\partial t} + v_x \frac{df^0}{dT} \frac{dT}{dx} = \frac{f^0 - f(x)}{\tau} \quad (24.6) \]

As the temperature of a material is raised or decreased, these particles interact and collide with each other in order to return the system back to thermodynamic equilibrium (the mean time associated with these scattering processes is the relaxation time [\( \tau \)], and the mean distance associated with these scattering processes is the mean free path [\( \lambda \)]).

### 24.5.1 One-Temperature Models

Consider the Maxwell–Boltzmann, Bose–Einstein, and Fermi–Dirac distribution functions shown in Figure 24.2 where the Fermi energy is set to zero. At high frequencies (or energies), the effect of the Fermi–Dirac and the Bose–Einstein statistical functions are eliminated and all distributions converge to a Maxwell–Boltzmann distribution.

**Maxwell–Boltzmann distribution function:**

\[ f(E(\omega)) = f_{MB}(E(\omega)) := \frac{1}{E(\omega)} e^{-\frac{E(\omega)}{kT}} \quad (24.7) \]
Bose–Einstein distribution function:

\[ f(E(\omega)) = f_{BE}(E(\omega)) = \frac{1}{E(\omega)} \exp\left(\frac{E(\omega)}{k_B T}\right) - 1 \]  

(24.8)

Fermi–Dirac distribution function:

\[ f(E(\omega)) = f_{FD}(E(\omega)) = \frac{1}{E(\omega) + E_F} \exp\left(\frac{-E(\omega)}{k_B T}\right) + 1 \]  

(24.9)

where \( A \) is a normalized constant, \( k_B \) is the Boltzmann’s constant, and \( E_F \) is the Fermi energy. If the frequency \( \omega \) is large enough, in the foregoing distribution functions we have

\[ f(E(\omega)) = 0, \quad \forall \omega \in [\omega_L, \omega_R] \]  

(24.10)

Therefore, we have

\[ \frac{\partial f(E(\omega))}{\partial t} = 0, \quad \forall \omega \in [\omega_L, \omega_R] \]  

(24.11)

At high frequencies, the wavelength of the particle is short and the statistical distinction is unimportant. Multiplying Equation 24.6 by \( \nu \omega D(\omega) \) and integrating over the two separate frequency ranges \([0, \omega_L] \) and \([\omega_L, \omega_R] \), based on the physics of the actual distribution functions, because of this statistical unimportance, it is reasonable to assume that the term \( \int_{\omega_L}^{\omega_R} \nu \omega D(\omega) \frac{\partial f}{\partial \omega} \, d\omega \) equals 0, due to the observation that the distribution function is fairly constant over time for high frequencies. In other words, as the different distribution functions reach their equilibrium positions, most of the change in the distribution functions occurs at the lower frequencies, and the distributions at the high-frequency tail are fairly constant over time. Hence, the \( \partial f/\partial t \) term is neglected. Also note that as time evolves, the threshold frequency must change as the distributions reach these equilibrium stages. This is a similar analogy to the change of the Fermi energy with temperature (see Reference 27).

Using this fundamental basis, we now highlight a novel C- and F-processes model, which is based on the hypothesis that upon the application of a temperature gradient, there simultaneously coexist both slow processes (at low energies and termed C-processes) and fast processes (at high energies and termed F-processes) associated with the heat carriers and evolving with time as the processes proceed from a finite nature of propagation to those involving infinite speeds.17–19 The spanning of space scales is in the sense of characterizing ballistic to diffusive limits, and the spanning of the time scales is in the sense of characterizing finite to infinite speeds of heat propagation. As with BTE-based approaches, certain limitations exist; nonetheless, coupling of the simple yet effective C- and F-processes model with computationally attractive variants of MD or lattice dynamics to avoid the need for fitting parameters may provide extensions to circumvent some of the limitations and provide extensions for multiscale capabilities.
24.5.2 THE C- AND F-PROCESSES MODEL—A UNIFIED THEORY

Following the previous discussion, we now define the total heat flux as

\[ q = \int_0^{\alpha_T} v_f \omega D(\omega) d\omega + \int_{\alpha_T}^{\infty} v_f \omega D(\omega) d\omega = q_c + q_f \]  (24.12)

where the postulation made here is that the integral up to a threshold frequency \( \omega_T \) involves the slow C-processes and is termed \( q_c \), and that the integral from the threshold to infinity involves the fast F-processes and is termed \( q_f \).

As discussed previously, considering the total heat conduction process, the BTE can be multiplied by \( v_f \omega D(\omega) \) and integrated over the entire frequency range. Also, note that \( \int_{\alpha_T}^{\infty} v_f \omega D(\omega) \frac{df}{d\omega} d\omega = 0 \) (not detailed here) due to the observation that the distribution function is constant over time for high frequency; therefore, \( df/dt = 0 \).

Next, introducing the nondimensional heat conduction model number \( F_T \) as the following ratio, we have

\[ F_T = \frac{\int_{\alpha_T}^{\infty} v_f^2 \frac{df}{d\omega} \omega D(\omega) d\omega}{\int_0^{\infty} v_f^2 \frac{df}{d\omega} \omega D(\omega) d\omega} \]  (24.13)

This is physically depicted in Reference 28 and has the interpretation

\[ F_T = \frac{K_f}{K_f + K_c} \]

Further, the following is defined

\[ K = \int_0^{\alpha_T} v_f^2 \frac{df}{d\omega} \omega D(\omega) d\omega + \int_{\alpha_T}^{\infty} v_f^2 \tau \frac{df}{d\omega} \omega D(\omega) d\omega = K_c + K_f \]  (24.15)

Upon application of the heat flux of particles given in Equation 24.12 and the thermal conductivity given in Equation 24.15, with the definition from Equation 24.13, the transient BTE finally yields the C- and F-processes heat conduction constitutive model in terms of the heat conduction model number as

\[ q = q_c + q_f \]  (24.16)

\[ q_f = -F_T K \frac{dT}{dx} \]  (24.17)

\[ q_c + \tau \frac{dq_c}{dt} = -(1 - F_T) K \frac{dT}{dx} \]  (24.18)
In general, the C- and F-processes heat conduction constitutive model is given by

\begin{align}
q_F &= -F \tau K T \\
q_C + \tau \frac{dq_C}{dt} &= -(1 - F) \tau K T \\
q &= q_F + q_C
\end{align}

which explains the present derivation based on fundamental physical principles emanating from the Boltzmann transport equation.

In the previous equations, \( q \) is the total heat flux due to the mechanism of heat conduction (which is composed of that associated with each of the Fourier-type fast processes and the Cattaneo-type slow processes), and \( K \) is the total conductivity, which is the sum of the Fourier (effective) conductivity, \( K_F \), and the Cattaneo (elastic) conductivity, \( K_C \). Thus, \( K = K_F + K_C \).

When \( F = 1 \), the right-hand side of Equation 24.20 is zero and the total heat flux is given by the Fourier law. This implies that the conductivity associated with the slow C-processes \( K_C = 0 \), or in other words, most of the dominant transport with evolution of time to steady state is via the fast F-processes. On the other hand, when \( F = 0 \), the right-hand side of Equation 24.19 is zero and the total heat flux is given by the Cattaneo law. Consequently, \( K_F = 0 \) and most of the dominant transport with the evolution of time to steady state is via the slow C-processes. Thus, in the limiting cases of \( F \) the C- and F-processes model can recover both Cattaneo and Fourier laws.

The combined representation of the C- and F-processes model can be shown by adding Equations 24.17 and 24.18 to yield

\begin{equation}
q + \tau \frac{dq_C}{dt} = -K \nabla T
\end{equation}

By substituting the C- and F-processes postulation that the total heat flux is a combination of the flux associated with the low-energy processes and the high-energy processes (see Equation 24.12) where \( q_C = q - q_F \), and the high-energy processes are described by a Fourier-like heat flux given by \( q_F = -K \tau \frac{dT}{dx} \), Equation 24.22 reduces to

\begin{equation}
q + \tau \frac{d(q - (-K_F \tau T))}{dt} = -K \nabla T
\end{equation}

Rearranging Equation 24.23, we obtain the so-called Jeffreys model of heat conduction as

\begin{equation}
q + \tau \frac{dq}{dt} = -K \left[ \nabla T + \tau \frac{K_F}{K} \frac{dT}{dt} \right]
\end{equation}
where the flux \( q \), the thermal conductivity \( K \), and the relaxation time \( \tau \) are the total contributions, and \( \tau K_f/K \) is defined as the retardation time \( \tau_R \). By adhering to the notion of the heat conduction model number, it is finally possible to characterize the energy transport of the heat conduction process from transient to steady state.

It is noteworthy to mention that the Jeffreys model also reduces to the Cattaneo model when \( K_f = 0 \). However, when \( K_f = K \) it only reduces to a Fourier-like model that contains the elusive relaxation time parameter \( \tau \), unlike the C- and F-processes model, which identically yields the Fourier model.

By substituting Equations 24.19–24.21 into the energy equation, we eliminate the flux and obtain the generalized one-step (GOS) C- and F-processes one-temperature formulation as

\[
L_1(T) = f_1(T, \dot{T}, \ddot{T}, T_{xx}, K, \alpha, c_r, S, \dot{S}, \tau, F_r), \quad \text{for } F_r < 1
\]

\[
L_2(T) = f_2(T, \dot{T}, \ddot{T}, T_{xx}, K, \alpha, S), \quad \text{for } F_r = 1
\]

where \( T \) is the total temperature, \( K \) is the total thermal conductivity given by kinetic theory as \( K = C v^2 \tau/3 \), the temperature propagation speed is given by \( c_r = \sqrt{K/\rho c} \), the thermal diffusivity is given by \( \alpha = K/\rho c \), \( C \) is the specific heat of the heat carrier, \( \rho \) is the density of the heat carrier, \( S \) is the external heat source, and the retardation time is given by \( \tau_R = \tau F_r \).

In conjunction with the C- and F-processes model, we argue following the initial work by Klitsner and colleagues on phonon radiative heat transfer where heat conduction by phonons can be analyzed as radiative transfer that the phonons are emitted from the surface and that the boundary conditions are developed based on an energy balance at the surface as \( q_n = q_{rad} \), where

\[
q_n = \hat{q} \cdot \hat{n} = f(C, v, T, T_\infty), \quad \text{for } x = 0, L
\]

where \( T \) represents the surface temperatures of the left and right sides of the film, and \( T_\infty \) is the ambient temperature on the right and left of the film. It is assumed that the thermalizing black boundaries (the ambient) are the boundaries of the metal film between which the dielectric film is enclosed.

Finally, after the correct heat flux is computed via the C-F model (which must be a constant across the film due to the radiative equilibrium assumption at steady state), an effective thermal conductivity is obtained as follows. We invoke the following proposition that the thermal conductivity provided by the C-F model is due to the heat flux within the film based on the established boundary temperatures divided by the temperature gradient based on the imposed ambient temperatures. Thus,

\[
K_{C,F} = \frac{\text{true heat flux within the film due to established boundary temperatures}}{\text{temperature gradient due to the imposed ambient temperatures}}
\]
24.5.3 Validation of the Thermodynamics Second Law for the C- and F-Processes Model

The thermodynamics second law is represented in terms of the Clausius–Duhem inequality as

\[ \rho \left( \frac{Ds}{Dt} - rT^{-1} \right) \geq - \nabla \cdot (T^{-1} \mathbf{q}) \]  

(24.29)

where \( s \) is the entropy, and \( r \) is the heat source.

It can be shown that for a solid,

\[ \rho \left( T \frac{Ds}{Dt} - r \right) + \nabla \cdot \mathbf{q} = 0 \]  

(24.30)

The thermodynamics second law can also be represented in the form

\[ \rho (T \dot{s} - r) + \nabla \cdot \mathbf{q} - T^{-1} \mathbf{q} \cdot \nabla T \geq 0 \]  

(24.31)

Therefore, the thermodynamics second law can be simply decoupled to yield the following two sufficient conditions:

\[ \rho (T \dot{s} - r) + \nabla \cdot \mathbf{q} = 0 \]  

(24.32)

\[ \mathbf{q} \cdot \nabla T \leq 0 \]  

(24.33)

where the first equation represents no viscous dissipation of kinetic energy into thermal energy, and the second condition represents that in heat conduction, the heat flow is from a high-temperature region to a low-temperature region. From the previous section, we showed that the C-processes and F-processes in the C- and F-processes heat conduction model belong to two different frequency ranges. Therefore, the F-processes and the C-processes are independent, and either of the processes indeed satisfy the thermodynamics second law independently, namely,

\[ \mathbf{q}_F \cdot \nabla T = -F_T k (\nabla T)^2 \leq 0 \]  

(24.34)

\[ \mathbf{q}_C \cdot \nabla T = -\left(1 - F_T\right) k \int_{\infty}^{\infty} e^{-\frac{s-x}{\tau}} \nabla T(x,s) ds \leq 0 \]  

(24.35)

To satisfy the thermodynamics second law, the heat conduction model number \( F_T \) must strictly satisfy the bounds \( F_T \in [0, 1] \). For other cases such as \( F_T < 0 \) or \( F_T > 1 \), the thermodynamics second law will be violated. To be consistent with the second law of thermodynamics, one must ensure \( 0 \leq k_F \) and \( 0 \leq k_C \); hence, \( 0 \leq k = k_F + k_C \). Thus, from its basic underlying definition, the bounds are strictly \( F_T \in [0, 1] \). For the
case of \( F_T < 0 \), it leads to \( 0 < -k_F < k_C \) or \( 0 < -k_C < k_F \), and for the case of \( 1 < F_T \), it leads to \( 0 < k_F < -k_C \) or \( 0 < k_C < k_F \). For either of the previous two underlying cases, the second law of thermodynamics is violated, and hence it is neither valid nor physically acceptable. Some existing classical models in the literature are highlighted next, which can all be readily explained via the C- and F-processes model as described previously.

### 24.5.3.1 The Fourier Model

Under the assumption of a macroscopic continuum formulation, this phenomenological model proposed by Fourier is given by

\[
q = -k \nabla T
\]  

(24.36)

where \( k \) is the conductivity tensor, \( q \) is the heat flux, and \( T \) is temperature, which together with the energy equation yields the parabolic one-step [POS] heat conduction equation or the parabolic heat conduction [PHC] equation and is diffusive with the notion of infinite speed of propagation of thermal disturbances.

### 24.5.3.2 The Cattaneo Model

Because of the anomalies associated with the Fourier model and in order to account for a finite temperature propagation speed, the Cattaneo-type model is based on the notion of relaxing the heat flux and is given as

\[
\tau \frac{\partial q}{\partial t} = -q - k \nabla T
\]  

(24.37)

where \( \tau \) is the relaxation time (Cattaneo originally developed this model for gases).

For the Cattaneo model, the temperature propagation speed is given as

\[
c_T = \sqrt{\frac{k}{\rho c \tau}}
\]  

(24.38)

where \( \rho \) is the material density, and \( c \) is the heat capacity. Together with the energy equation, it yields the hyperbolic one-step [HOS] heat conduction equation or the hyperbolic heat conduction [HHC], which is propagative with the notion of a finite speed of heat propagation.

### 24.5.3.3 The Jeffreys-Type Model

The original Jeffreys model was introduced by Jeffreys, who originally proposed this for studying the wave propagation in the earth’s mantle, and is given as

\[
\sigma + \lambda \frac{\partial \sigma}{\partial t} = \eta \left( \dot{\gamma} + \lambda \frac{\partial \dot{\gamma}}{\partial t} \right)
\]  

(24.39)
which relates the stress and the rate of strain tensor \((\sigma, \dot{\gamma})\), and \(\eta_0\) is the zero shear rate viscosity. In this constitutive model originally proposed in 1929, \(\lambda_1\) is defined as the relaxation time and \(\lambda_2\) is defined as the retardation time; no mention was ever made by Jeffreys relating this to the notion of heat. Based on experiences in viscoelastic fluids, a Jeffreys-type heat flux phenomenological model drawn from the original Jeffreys equation (Equation 24.39) was subsequently proposed and introduced by Joseph and Preziosi\(^\text{29}\) for heat conduction, which appears as

\[
\mathbf{q} + \tau \frac{\partial \mathbf{q}}{\partial t} = -k \left[ \nabla T + K \frac{\partial (\nabla T)}{\partial t} \right] \tag{24.40}
\]

where \(\tau\) is the relaxation time and \(K = \frac{\tau k}{k}\) is the retardation time. It is important to note that in the original Jeffreys model proposed by Jeffreys,\(^\text{33}\) which relates stress and strain rate, or in the corresponding heat flux model introduced by Joseph and Preziosi,\(^\text{29}\) which relates the heat flux to the temperature gradient, the retardation time can never exceed the relaxation time as it makes the physical interpretation meaningless if violated. When selecting the retardation time, \(K = 0\), the Jeffreys-type model degenerates to the Cattaneo model as

\[
\tau \frac{\partial \mathbf{q}}{\partial t} = -\mathbf{q} - k \nabla T \tag{24.41}
\]

and when selecting the retardation time equal to the relaxation time, \(K = \tau\), the Jeffreys-type model only degenerates to a Fourier-like diffusive model with relaxation as

\[
\mathbf{q} + \tau \frac{\partial \mathbf{q}}{\partial t} = -k \left[ \nabla T + \tau \frac{\partial (\nabla T)}{\partial t} \right] \tag{24.42}
\]

### 24.6 TWO-TEMPERATURE MODELS

Likewise, there also exists the so-called microscale two-temperature theory (namely, the two-step temperature equations describing nonequilibrium behavior between electrons and phonons). From a microscale viewpoint, the pioneering work of the two-temperature diffusive formulation of Anisimov et al.,\(^\text{34}\) who seem to have developed the first parabolic two-step [PTS] energy balance equations, are significant and given as

\[
C_e(T_e) \frac{\partial T_e}{\partial t} = -\frac{\partial \mathbf{q}}{\partial \mathbf{r}} - G(T_e - T_\text{r}) + S(\mathbf{r}, t) \tag{24.43}
\]

\[
C_e \frac{\partial T_e}{\partial t} = G(T_e - T_\text{r}) \tag{24.44}
\]

\[
\mathbf{q}_e = -k_e \nabla T_e \tag{24.45}
\]
where $S(r,t)$ is the internal heating due to a laser pulse and is an integral part of the 
two-temperature theory, $C_e$ is the electron heat capacity and $C_l$ is lattice heat capacity 
(with $C = C_e + C_l$), $G$ is the electron-lattice coupling factor whose experimental 
determination has been challenged,$^{35,36}$ and $k_e$ is associated with the electron thermal 
conductivity in steady state. The electron heat flux $q_e$ pertains to the Fourier model, 
and diffusion in the lattice is neglected during the interested transient duration.

The generalized two step (GTS) pulse heating model for metals recently proposed 
by Tamma and Zhou$^{37}$ permits taking into account not only choices of propagation 
or diffusion transport mechanisms at the microscale levels but also transitions via the 
simultaneous introduction of microscale relaxation/retardation times.

We next introduce the physical notion of a *heat conduction model number*, $F_{Te}$, 
associated with the electron heat flux involving F-processes and C-processes as

$$q_e = -k_e \nabla T_e - \tau \frac{\partial q_e}{\partial t} - \tau k_{pe} \frac{\partial}{\partial t} (\int VT_e)$$

$$= -k_e \left[ \nabla T_e \tau + \frac{\tau}{k_e} \frac{\partial q_e}{\partial t} + \tau F_{Te} \frac{\partial}{\partial t} (\int VT_e) \right]$$  \hspace{1cm} (24.46)

For microscale heat transport it now has a different physical meaning than in the 
macroscale formulation, although it has similarities with the associated macroscale 
formulation and is physically defined in terms of a *heat conduction model number*, 
$F_{Te} \in [0,1]$, as

$$F_{Te} = \frac{k_{eF}}{k_{eF} + k_{eC}}$$  \hspace{1cm} (24.47)

where $k_{eF}$ and $k_{eC}$ are contributions of the F-processes and C-processes to the total 
electron thermal conductivity given by $k_e = k_{eF} + k_{eC}$. Furthermore, the aforementioned constitutive formulation for the two-step theory also has a different physical 
meaning than that of the macroscale formulation in the following sense.

We consider for microscale heat transport

$$q_{eF} = -k_{eF} \nabla T_e = -F_{Te} k_e \nabla T_e$$

$$q_{eC} + \tau \frac{\partial q_{eC}}{\partial t} = -k_{eC} \nabla T_e = -(1 - F_{Te}) k_e \nabla T_e$$  \hspace{1cm} (24.48)

$$q_e = q_{eF} + q_{eC}$$

where $q_e$ is the total electron heat flux and is composed of the sum of the electron 
heat flux associated with the F-processes, $q_{eF}$, and the C-processes, $q_{eC}$, respectively.

Employing this constitutive model into the Anisimov et al.$^{34}$ two-step energy 
equations yields the generalized microscale electron/lattice two-step model equations
Nanoengineering of Structural, Functional, and Smart Materials

with \( F_{\text{Te}} \in [0, 1] \) of which the GTS pertains to the range \( F_{\text{Te}} \in (0, 1) \), which is parabolic (diffusive) in nature:

\[
C_{\text{r}}(T_{\text{r}}) \frac{\partial T_{\text{r}}}{\partial t} = - \frac{\partial q_{\text{r}}}{\partial x} - G(T_{\text{r}} - T_{\text{r}}) + S
\]

\[
C_{\text{e}} \frac{\partial T_{\text{e}}}{\partial t} = G(T_{\text{e}} - T_{\text{e}})
\]  

(24.49)

\[
q_{\text{r}} = -k_{\text{r}} \left[ \nabla T_{\text{r}} + \frac{\tau}{k_{\text{e}}} \frac{\partial q_{\text{e}}}{\partial t} + \tau F_{\text{Te}} \frac{\partial}{\partial t} (\nabla T_{\text{e}}) \right]
\]

The preceding GTS model is parabolic (diffusive), and the transmission of information is immediately felt everywhere. It is also to be noted that by approximate mathematical manipulations, the aforementioned equations may be combined to lead to a single equation for the determination of the electron or lattice temperatures, respectively.

### 24.7 RELAXATION TIME

The first step in solving for the heat transport at the different length scales is to approximate the elusive relaxation time, \( \tau \). Accounting for all the scattering mechanisms within a film can approximate the relaxation time. Accurately quantifying and qualifying all the possible scattering mechanisms proves to be the most difficult task in solving the C-F model, or any model derived from BTE for that matter.\(^3\)\(^-\)\(^6\)\(^9\) This task can be simplified by accounting for all the internal scattering processes within a specimen by assuming that all scattering mechanisms are independent. And, using Matthiessen’s rule, which inversely adds all scattering contributions as \( 1/\tau = \sum_{j} 1/\tau_{i,j} \) where \( \tau_{i,j} \)’s are the contributions of the various scattering mechanisms based on \( i \), the modes of polarizations of the phonons, and \( j \), the different types of scattering rates. These scattering mechanisms contribute to the total resistance to the heat transport.

Many researchers\(^1\)\(^,\)\(^3\)\(^-\)\(^4\)\(^2\)\(^3\)\(^8\)\(^-\)\(^4\)\(^2\) describe all the different scattering mechanisms that have been used for predicting relaxation times for doped and undoped single and polycrystalline dielectric films. In a nutshell, most of the scattering is due to crystal imperfections or interactions with other phonons, and at low temperatures (or for films where the \( \lambda - L \) the boundary of a crystal. For the results shown here, we assume that these are the main scattering mechanisms

\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{defect}}} + \frac{1}{\tau_{U}} + \frac{1}{\tau_{\text{GB}}}
\]  

(24.50)

where the scattering due to defects is given as

\[
\tau_{\text{defect}} = \frac{1}{\alpha \sigma_{\tau} \eta v}
\]  

(24.51)
where $\alpha$ is a constant (usually one), $\sigma_s$ is the scattering cross section, $\eta$ is the level of impurity in the medium (in other words, it is the number of scattering sites in the medium), and $v$ is the speed of the phonons, which for dielectrics is the speed of sound. The scattering cross section is approximated as:

$$\sigma_s = \pi R^2 \left( \frac{s^4}{s^4 + 1} \right)$$

(24.52)

where $R$ is the radius of the lattice imperfection, $s$ is the size parameter given by $s = 2\pi R/\Lambda_{\text{dominant}}$, and $\Lambda_{\text{dominant}}$ is the dominant wavelength of phonons, which is given by $\hbar v \sim \Lambda_{\text{dominant}} K_B T$, where $K_B$ is the Boltzmann constant, and $\hbar$ is Planck’s constant.

The scattering due to other phonons is accounted by the U-process scattering as:

$$\tau_U = A \frac{T}{\theta_D} e^{\frac{\theta_D}{k_B T}}$$

(24.53)

where $A$ is a nondimensional constant that depends on the atomic mass, the lattice spacing, and the Grünessen constant; $\theta_D$ is the Debye temperature; $\omega$ is the frequency; $T$ is the temperature; and $a$ is a parameter representing the effect of the crystal structure.

Finally, the grain boundary scattering is given as:

$$\tau_{GB} = \frac{d_s}{v_s}$$

(24.54)

where $v_s$ is the average phonon velocity, and $d_s$ is the sample size in the direction perpendicular to heat flow.

### 24.8 NUMERICAL ILLUSTRATION—TWO-TEMPERATURE MODEL AND PULSE LASER HEATING

For the experiment by Brorson et al.,

\[ C_e = 1.84E + 4(J/m^3K), C_i = 2.5E + 6(J/m^3K), \delta = 15.3 \text{ nm}, G = 2.6E + 16(W/m^3K), J = 10(J/m^2), k_{\text{e0}} = 310(W/mK), L = 0.1 \mu m, \text{ and } R = 0.093 \text{ were employed. Also, } t_p = 96 \text{ fs was used except when the source was that of case (1) as described subsequently; } t_p = 100 \text{ fs was employed for the experimental simulations.} \]

For the selected experiment from Brorson et al. for short-pulse laser heating of thin gold films, the following were investigated:

**Case 1:** For the source, the actual measured autocorrelation of the laser pulse was first employed.

**Case 2:** The source was specifically selected as

$$S = 0.94 \left( \frac{1 - R}{t_p \delta} \right) J e^{-\frac{t_p^2}{2 \gamma}} \left( \frac{\tau_p}{t_p} \right)^2$$

(24.55)
where \( t_p \) is the full width at half maximum of the pulse duration and \( \delta \) is the radiation penetration depth.

Furthermore, for the relaxation parameter, \( \tau \), the following were investigated:
(1) \( \tau \) accounts for the temperature dependence with data taken from Pells and Shiga, and (2) \( \tau = 0.04 \) ps (constant value). In all the situations, temperature dependence of the electron thermal conductivity and heat capacity was assumed.

Employing the GTS, studies were conducted to demonstrate the theoretical consequences alluded to earlier, including efforts to further plausibly shed light on the characterization of the heat transport behavior in these experiments. Figure 24.3 shows the comparative results of the Brorson et al. experimental results of the front surface with the GTS \( (F_{Te} = 0 \text{ and permitting } \tau = \tau [T])) \), \( F_{Te} = 1 \), which implies \( \tau = 0 \); and \( F_{Te} = 0.5 \) with \( \tau = \tau [T] \). In this figure, the source was selected from the actual measured autocorrelation of the laser probe (Case 1). Although not clearly distinguishable, the cases of \( F_{Te} = 1 \) and \( F_{Te} = 0.5 \) (arbitrarily selected) seem to be somewhat closer than \( F_{Te} = 0 \) at very early times in the transient.

Also based on the theoretical premise that there simultaneously exist fast and slow transport processes, the added objective was to characterize (admittedly, it is a first attempt and a crude manner) the microscale heat conduction model number, namely the \( F_{Te} \) value, and select this to match closely to the experiment. For example, if \( F_{Te} = 0.1 \) was a close match, then \( k_{ef} = 0.1k_e = 0.1(k_{ef} + k_{ec}) \), which implies that

**FIGURE 24.3** Comparative results for experiment due to Brorson et al. \[Brorson et al., 1987\] with \( \tau = \tau (T) \) and heat source, case(i).
An Introduction to Nanoscale, Microscale, and Macroscale Heat Transport

plausibly 90% pertains to transport associated with $k_{EC}$ and 10% pertains to transport associated with $k_{EF}$. Since that which is customarily measured experimentally is the total thermal conductivity, such a plausible challenge was undertaken. However, based on very limited experiments conducted to date, no bounds on errors are available (and that too with the existence of possible experimental errors), and hence only a quantitative check could be made but no conclusive results or inferences could be drawn.

Figure 24.4 next shows the comparative results with the source selected instead from Case 2. The results are in reasonable agreement in the initial part of the transient; however, some in-depth studies drawing comparisons with the measured autocorrelation of the laser pulse need to be further investigated.

24.9 NUMERICAL ILLUSTRATION—ONE-TEMPERATURE MODEL AND HEAT CONDUCTION MODEL NUMBER $F_T$

Consider the following thought experiment. Since literature on experimental results describing the transient behavior at the ballistic limit is mostly nonexistent to our knowledge, we next present a systematic analysis of the significance of $F_T$ spanning the temporal-ballistic limits for the case of a diamond film of 1 µm (hypothetical case).
Considering the film structure in Figure 24.5(a), assume that the curve shown in Figure 24.5(b) represents the characteristic thermal conductivity data at room temperature for the diamond film spanning the ballistic to diffusive limits (asymptotically approaching the bulk data provided by Reference 46 as shown). For the 1-µm diamond film, suppose that the total thermal conductivity $K \approx 2100$ W/m/K. Note that the steady-state prediction is independent of $F_T$. We assume that the correct transient behavior can be characterized by $F_T$ in the C-F model where these responses are depicted in Figure 24.5(c) with evolution of time to steady state. In the case of the 1-µm diamond film, say that $F_T = 0.5$ will correctly characterize the transient to

\[ \text{FIGURE 24.5 One Temperature Model and the Heat Conduction Model Number, } F_T. \]
steady-state temperature response of the experiment across the film thickness. The information that this thought experiment has provided is that the actual transport behavior for this film that is in the partially diffusive-ballistic region (due to the observed temperature jump on boundaries at steady state) also provides a transient response that is 50% wavelike at a finite speed and 50% diffusive as an infinite speed of heat propagation. Since $F_T = 0.5$, $K_F = 0.5(K)$. That is, in obtaining the total conductivity, the conductivity associated with the fast F-processes is half the total conductivity (the other half is due to the conductivity associated with the slow C-processes). Based on the definition of $F_T$, for the first time it is now possible to characterize the elastic component of the thermal conductivity and provide a fundamental understanding of the role of the fast F-processes and slow C-processes in the propagation of heat transport leading to the thermal conductivity property obtained for the given film.

### 24.9.1 Spanning Spatial Scales

At steady state, the nondimensional temperature profiles (under the boundary conditions in Equation 24.27, which are of the third kind) of type IIa diamond films spanning lengths from 0.001 to 1000 $\mu$m based on the C-F model implementation are shown in Figure 24.6. At room temperature, the mean free path of diamond films for experiments performed by Anthony et al. is ~0.447 $\mu$m (see Table 24.2). At these film thicknesses, we observe that the temperature plots span both the ballistic ($\lambda \gg L$) and diffusive ($\lambda \ll L$) limits. At steady state, all temperature profile results for various values of $F_T \in [0,1]$ are equal as shown in Figure 24.6.
FIGURE 24.6 Steady-state results for several diamond film thicknesses using C-F model with boundary conditions of the third kind. The non-dimensional thickness \( l/L \) where \( l \) is the x-axis position and \( L \) is the film thickness.
24.10 MULTILAYERS AND SUPERLATTICES

We also demonstrate applications relevant to the interface conditions in multilayers and superlattices via the C- and F-processes model based on two schools of thought: (1) the use of contact conduction/contact resistance of layered structures based on geometric, mechanical load, and thermal aspects,\textsuperscript{47} and (2) the consideration of phonon transport in nanostructures.\textsuperscript{48} In both cases, it is assumed that the interface of dissimilar materials of the multifilm structure has imperfect thermal contact at $x_i$ between layers $(i - 1)$ and $(i)$. Via the present C-F model, for method 1 the appropriate interface conditions are given as

\begin{align}
K^{(i-1)} \left[ \frac{\partial \dot{T}^{(i-1)}}{\partial x} + \tau^{(i-1)} F_T^{(i-1)} \frac{\partial \dot{T}^{(i-1)}}{\partial x} \right] &= K^{(i)} \left[ \frac{\partial \dot{T}^{(i)}}{\partial x} + \tau^{(i)} F_T^{(i)} \frac{\partial \dot{T}^{(i)}}{\partial x} \right] \quad \text{at } x_i \quad (24.56) \\
K^{(i-1)} \left[ \frac{\partial \dot{T}^{(i-1)}}{\partial x} + \tau^{(i-1)} F_T^{(i-1)} \frac{\partial \dot{T}^{(i-1)}}{\partial x} \right] &= \frac{1}{R_{i-1-(i)}} \left( T_i - T_{i-1} + \frac{\sigma T_i^2}{R_{i-1-(i)}} \left( \dot{T}_i - \dot{T}_{i-1} \right) \right) \quad (24.57)
\end{align}

for $i = 1, 2, \ldots, n$. As applicable to the C-F model,\textsuperscript{47} Equation 24.56 represents the continuity of the interface heat flux, and Equation 24.57 states that the difference between the two surfaces temperatures is proportional to the heat flux. The proportionality coefficient is the thermal contact resistance $R_{i-1-(i)}$ between the two layers, which is a function of forces acting on layer $(i - 1)$ due to layer $(i)$ and vice versa.

\begin{table}[h]
\centering
\caption{Data Used in the Prediction of the Relaxation Time of Diamond Type IIa Films}
\begin{tabular}{|l|c|}
\hline
\textbf{Constant} & \textbf{Properties} \\
\hline
Bulk $K^b$ & 3320 W/m/K \\
Lattice constant & 3.567 Å \\
Specific heat & 517.05 J/kg/K \\
Mass density & 3510 kg/m$^3$ \\
Phonon velocity$^c$ & 12,288 m/s \\
Constant $A$ (Eq. 24.53) & 188.06$^a$ \\
Effective mean free path & 0.447 µm \\
$\eta^b$ (Eq. 24.51) & $0.154 \times 10^{26}$ atoms/m$^3$ \\
$a$ (Eq. 24.53) & 1.58 \\
Debye temperature & 1860 K \\
\hline
\end{tabular}
\footnotesize{$^a$ This value is slightly different than the one reported in Reference 6 because we have chosen to compute all parameters based on the phonon velocity set to 12.288 m/s.~\textsuperscript{6} $^b$ Anthony, T.R. et al., \textit{Phys. Rev. B}, 42, 1104–1111, 1990. $^c$ Majumdar, A., \textit{J. Heat Transfer}, 115, 7–16, 1993.}
\end{table}
Usually, this is a parameter obtained by experiments and is an unknown in this formulation.

Alternatively, for method 2, via the C-F model the phonon transmission across the interface can be accounted based on the effect of diffusive scattering as

\[ \alpha_{(i-1)-i} K^{(i-1)} \left[ \frac{\partial T^{(i-1)}}{\partial x} + \tau^{(i-1)} F_T^{(i-1)} \frac{\partial T^{(i-1)}}{\partial x} \right] = \alpha_{(i-1)-i} K^{(i)} \left[ \frac{\partial T^{(i)}}{\partial x} + \tau^{(i)} F_T^{(i)} \frac{\partial T^{(i)}}{\partial x} \right] , \] at \( x \)

(24.58)

where \( \alpha_{(i-1)-i} \) is the phonon transmissivity across the rough gap from the \((i - 1)\) to the \((i)\) layer. Method 2 formulation does not require direct knowledge of the thermal boundary resistance, and after solving for the unknown temperatures it can be obtained from Reference 48. As an illustration, GaAs/AlAs temperature profiles spanning space scales and the prediction of thermal conductivity are shown in Figure 24.7. Thus far, we have demonstrated that the C- and F-processes model can (1) explain the heat transport behavior from ballistic limit (Casimir limit: \( \lambda >> L \)) to the diffusive limit (Fourier limit: \( \lambda \ll L \)) for the prediction of the thermal conductivity, (2) span time scales explaining finite to infinite speeds of heat propagation, and (3) overall provide a balanced energy equation with the inclusion of a nondimensional heat conduction model number, which is given as the ratio of the conductivity associated with fast processes to the total conductivity, which is composed of both fast and slow processes. It is simple to implement and circumvents many of the deficiencies existing in the literature.

24.11 THE EQUATION OF PHONON RADIATIVE TRANSFER (EPRT)

In thin dielectric films, the major heat carriers are phonons. The thermodynamic equilibrium distribution for these carriers follows the Bose–Einstein distribution, which is similar to the distribution of photons. Under this premise the equation of phonon radiative transfer (EPRT) is originally described in Reference 49 based on the correlation between the radiation theory (i.e., the equation of radiative transfer [ERT]) and the transport theory in dielectric thin films. The major assumption made regarding solving the transport properties in very thin films is that the problem can be solved as a one-dimensional gray medium between black walls at specified temperatures under radiative equilibrium. This condition arises when a dielectric film is sandwiched between two metallic films. The following is a detailed derivation of this theory.

The intensity of photons, that is, the radiation emitted in any direction by a wave packet, is given by

\[ I(\theta, \phi, \omega, x, t) = \sum_p v(\theta, \phi) f(x, t) \hbar \omega D(\omega) \]  

(24.59)
An Introduction to Nanoscale, Microscale, and Macroscale Heat Transport

**FIGURE 24.7** Representative C- and F-Processes model results for GaAs/AlAs superlattices.

(a) Schematic diagram of a two-layer film of thickness L between dissimilar ambient temperatures.

(b) Temperature plots spanning space scales.

(c) Thermal conductivity spanning space scales.
where the summation is over the photon polarizations, \( v(\theta, \phi) \) is the velocity vector in the direction of \( \theta \) and \( \phi \) within a unit solid angle, \( \hbar \omega \) is the energy at which the photons propagate, and \( D(\omega) \) is the density of states per unit volume. The frequency dependency of the phonon intensity is eliminated by assuming that the film medium acts as a gray body.

For cases where \( \lambda \gg L \), the EPRT appears to model microscale aspects encompassing the ballistic to diffusive limits. In these cases, the thermal conductivity for thin films is obtained at steady state due to scattering of phonons from the boundaries, which returns the system to thermodynamic equilibrium. This suggests that the heat conduction by phonons is similar to that of photons and thus can be analyzed as a radiative transfer problem.\(^{26}\)

Applying the analogy between photons and phonons and multiplying Equation 24.6 by \( v, \hbar \omega D(\omega) \) and using the intensity definition (Equation 24.59), the equation of phonon radiative transfer is obtained as

\[
\frac{\partial I(x, \mu)}{\partial t} + v \frac{\partial I(x, \mu)}{\partial x} = \frac{I^0(T(x)) - I(x, \mu)}{\tau}
\]  

(24.60)

where the velocity in the direction of the phonon propagation is \( v = v\mu, \mu = \cos \theta, \theta \) is the angle between the phonon propagation and the \( x \)-direction, and \( I^0 \) is the equilibrium intensity.

At steady-state, Equation 24.60 reduces to

\[
v\mu \tau \frac{\partial I(x, \mu)}{\partial x} + I(x, \mu) = I^0(T(x))
\]  

(24.61)

Majumdar \(^{[6]}\) analyzed the EPRT for both acoustically thin (\( \lambda \gg L \)) and acoustically thick (\( \lambda \ll L \)) limits and shows that the EPRT does indeed provide results that span both limiting cases where the Casimir and the Fourier laws are applicable.

### 24.12 CALLAWAY/HOLLAND’S MODEL

Heat conduction in solids is well understood to follow the kinetic formula

\[
K = \frac{1}{3} Cv \lambda
\]

(24.62)

where \( K \), the thermal conductivity of an ensemble of heat carriers, is given by the total specific heat \( C \), the average speed of the heat carries \( v \), and the mean free path \( \lambda \). When the assumption that all phonons have the same energy and velocity is not desired it is possible to account for the phonon dispersion where \( C, v, \) and \( \lambda \) are frequency dependent. Equation 24.62 can be modified by including the summation over all phonon branches (one longitudinal and two transverse) and by integrating
over the phonon spectrum width of each branch as presented in the early works of Peierls in 1929,

\[ K = \frac{1}{3} \sum_p \int C(\omega)v(\omega)\lambda(\omega)d\omega \]  

(24.63)

The temperature-dependent thermal conductivities of silicon and germanium films can be modeled based on the approximated solutions to the Boltzmann Transport Equation (BTE) where the frequency-dependent relaxation times represent the phonon-scattering events. The most widely used model for determining the thermal conductivity is a method first proposed by Callaway,\(^4\) which assumes that the N-processes dominate the scattering and the total thermal conductivity can be expressed as a sum of \( K = K_1 + K_2. \)

The first modified form of Callaway’s model, known as Holland’s model,\(^5\) assumes that \( K_2 = 0 \) and includes the three phonon polarizations in \( K_1: \)

\[ K_1 = K_{TO} + K_{TU} + K_L \]  

(24.64)

Note that Holland’s and the modified Callaway/Holland’s models are a solution of the steady-state version of the BTE and can only provide the temperature-dependent results of thermal conductivity and therefore only address the issue of microscopic size, i.e., they can only determine thermal conductivity as a function of size.

**24.12.1 Comparison of Results Between Holland Model and EPRT**

Figure 24.8(a) depicts the experimental and analytical results obtained by Asheghi and colleagues\(^42\) for crystalline silicon layers of thicknesses 0.42, 0.83, and 1.6 µm. In their study, yet another modification to Callaway’s temperature-dependent thermal conductivity model is employed, which considers the possibility of specular reflection through the surface. Their results show the peak in the conductivity for the thin films to occur at 70 K. The recommended bulk conductivity reaches a maximum of 5500 W/m/K at 30 K.\(^42\)

Figure 24.8(b) shows the results from the finite-element implementation of the steady-state EPRT compared with the experimental and analytical results given by Reference 42. Although the results in Figure 24.8(b) present values that are higher than those seen in the results of Asheghi and colleagues, they provide a better fit of the data at low temperatures. The current study of the EPRT did not include effects of grain boundary scattering. This demonstrates that the addition of the grain boundary scattering reduces the thermal conductivity by adding more sites for the thermal resistance. The results obtained by the EPRT method seem to be more appropriate to be used with films of the 1 µm range. Note that at room temperature the mean free path of silicon and diamond films are 0.0409 and 0.39 µm, respectively. Hence, films thinner than 1 µm will present microscopic ballistic behavior at room temperature.
The results shown by using the finite-element method (FEM) are based on experimental thermal conductivity data available from work by Anthony and colleagues.\textsuperscript{46} (Table 24.3).

24.13 MOLECULAR DYNAMICS

Molecular dynamics (MD) is a computer simulation technique where the time evolution of a set of interacting atoms is followed by integrating their classical equations of motion. This equation corresponds to the second law of classical mechanics formulated by Sir Isaac Newton in 1687.

\[
\bar{F}_i (\vec{r}_i) = m_i \ddot{\vec{r}}_i
\]  

(24.65)
where $\vec{F}$ is the force acting on the atom $i$ at a given time in a system containing $N$ atoms, $m_i$ is the atom mass, and $\vec{a}_i$ is the atom acceleration given by

$$\vec{a}_i = \frac{d^2 \vec{r}_i}{dt^2}$$

with $\vec{r}_i$ as the atom position.

However, the motion of molecules is quite complicated and the forces involved are nonlinear and depend on the position of the other atoms. Therefore, a different form of the classical equations of motion is used and follows Hamilton’s equation where particles are described by their positions $\vec{r}$ and momenta $\vec{p} = m\vec{v}$. The forces on the particles are obtained from the gradient of the interatomic potential energy surface $U(r_1, r_2, \ldots, r_N)$ as a function of the positions of all the atoms:

$$\vec{F}_i = -\nabla_{\vec{r}_i} U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$  \hspace{1cm} (24.66)

where $\nabla_{\vec{r}_i}$ operates on the position $r_i$ of atom $i$. Any change in the potential energy that results from a displacement of atom $i$ contributes to the force acting on atom $i$.

In order to develop a molecular dynamics simulation, it is necessary to specify both the atomic structure of the nanotubes where atoms are arranged at specific positions and the interatomic potential, which, for carbon nanotubes, is based on the Tersoff-Brenner functional form with parameters fitted from experimental and quantum mechanical data to reflect good structural, mechanical, and thermal properties of nanotubes. A pristine nanotube is illustrated in this work. After the initial conditions and the interaction potential are defined, the equations of motion are numerically integrated and solved using a predictor-corrector algorithm with fixed time steps of 0.2 fs. The molecular dynamics simulation provides information at the microscopic level via the positions and velocities of all atoms as a function of time,

$$\vec{r}_i(t), \vec{v}_i(t)$$
In order to obtain thermal conductivity results from the information provided at the microscopic level, a nonequilibrium molecular dynamics simulation–based direct method\textsuperscript{12,13} is used. The direct method emulates the actual experimental situation by setting two regions of hot and cold atoms.

### 24.13.1 Pristine Nanotube

The results for thermal conductivity shown here are for (10,10) single-wall carbon nanotube (SWNT). The theoretical expectation for SWNTs at room temperature (300 K) is either about 2000–3000 W/m/K\textsuperscript{12,14} or about 6000 W/m/K\textsuperscript{15}. As mentioned earlier, results reported for the peak value of thermal conductivity in Reference 15 are an order of magnitude larger than the results reported in other work\textsuperscript{12,14} and in recent experiments.\textsuperscript{16} This is because an extremely small sample of carbon nanotubes was used in that simulation, and extrapolation of the data was performed, which was probably erroneous. It is noteworthy to mention that in running a MD simulation it was observed that the thermal conductivity is highly dependent on the size of the nanotube and the temperature gradient chosen, as shown in Figure 24.9. The temperature gradient, used for obtaining the thermal conductivity results in Figure 24.9(b), is kept constant at 2.03 K/nm, and the size of the nanotube is varied from 98.4 to 787.0 Å (1600 to 12,800 atoms). As the size of the nanotube is increased, the thermal conductivity appears to asymptotically approach a constant value. This is an interesting finding, which is in agreement with experimental results found in thin films, where the thermal conductivity is size dependent. As the film size approaches a critical value, the thermal conductivity equals that of its bulk counterpart. This concept is worthy of further investigation in nanotubes, because the idea of “bulk” nanotube size is still under investigation. Here we note that, for a given thermal gradient, which can be determined from the experimental conditions, the thermal conductivity as a function of length converges to a constant value within 40–80 nm for a (10,10) SWNT.

Figure 24.9(c) shows the change in thermal conductivity as a function of the temperature gradient for a nanotube under periodic boundary conditions with 3200 atoms. Based on the expected room temperature thermal conductivity provided in Reference 14, it appears that it would be more appropriate to choose a temperature difference between 40 and 60 K for pristine nanotubes with 3200 atoms, instead of 80 K as shown in the results of Figure 24.9(b). This finding, along with the question of what will happen to nanotubes of other sizes, is being further investigated.

### 24.14 Concluding Remarks

An introduction that serves as a prelude to an improved understanding of nanoscale, microscale, and macroscale thermal transport was presented. Since the early work in the 1930s, there has been a quest to provide an improved scientific understanding of size effects in thermal conductivity. More notably, with the advent of nanotechnology, since the 1990s there is a surge of research interest and activity in the area of thermal transport. Although limitations exist in many of the methods, it is time to take a critical and in-depth look at the various investigations, questions, and concerns raised in the literature. The present chapter highlights some of the recent
(a) Typical carbon nanotube (picture courtesy of the National Center of Competence in Research (NCCR) 4).

(b) Thermal conductivity versus nanotube length.

(c) Thermal conductivity versus temperature gradient.

FIGURE 24.9 Thermal conductivity of carbon nanotubes.
advances in thermal transport analysis and also provides some challenging solutions to various issues appearing in the literature. It is hoped that this chapter fosters future research in the directions discussed.

PROBLEMS

1. Identify the various methods (classical and nonclassical) existing in the literature for the prediction of thermal conductivity at scales ranging from nanoscale to macroscale regimes.

2. Conduct a thorough literature review and point out the limitations cited in the literature for the classical models. Verify these limitations using examples in the literature. Conduct the same for nonclassical models.

3. Derive the C- and F-processes constitutive model and understand the notion of spanning ballistic to diffusive limits and finite to infinite speeds of heat propagation. Since the method is not computationally intensive, verify some numerical examples such as thin films, superlattices, thermal contact conduction/resistance, and the like.

4. Investigate methods that are not computationally intensive yet do not require fitting parameters. For example, look into coupling the C- and F-processes model with variants that are less cumbersome to molecular dynamics to circumvent potential limitations.

5. Develop multiscale methods suited for modeling and simulation of large-scale applications on modern high-performance computing (HPC) platforms.

ACKNOWLEDGMENTS

The support for this work is in the form of computer grants from the Minnesota Supercomputer Institute (MSI) and in part by the Army High Performance Computing Research Center (AHPCRC) under the auspices of the Department of the Army, Army Research Laboratory (ARL) (DAAD19-01-2-0014). The content does not necessarily reflect the position or the policy of the government, and no official endorsement should be inferred. Special thanks are due to X. Zhou for related technical discussions. Thanks are also due to D. Srivastava for collaborations on the MD simulations. Special thanks are due to Amit Jain for the preparation of the chapter.

REFERENCES