Prediction of Phonon Thermal Conductivity of Materials by Molecular Dynamics Simulation

Leila Momenzadeh

Master's Degree of Mechanics of Farm Machinery (Shiraz)

This thesis is submitted for the degree of

Doctor of Philosophy (Mechanical Engineering)

The University of Newcastle, Australia Faculty of Engineering and Built Environment School of Engineering Centre for Mass and Thermal Transport in Engineering Materials



March 2016

Statement of Originality

This is to certify that the thesis entitled "Prediction of Phonon Thermal Conductivity of Materials by Molecular Dynamics Simulation" submitted by Mrs Leila Momenzadeh contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

Leila Momenzadeh

Acknowledgment of Authorship

I hereby certify that the work embodied in this thesis contains published papers of which I am a joint author. I have written the majority of the text under the light direction of my supervisors. I carried out the calculations, prepared the figures and I was actively involved in the assessment of the outcomes of the study. My supervisors conceived the research topic and they roughly sketched the overall computational strategy. I contributed substantially to obtaining a detailed understanding of the underlying phenomena.

Professor Graeme E. Murch



Dedication

To my father, who always stood behind me. Gone but never forgotten. Thanks for all you did.

Acknowledgments

I have been undertaking research as a postgraduate student in the Centre for Mass and Thermal Transport in Engineering Materials at the University of Newcastle for four years. This has been a blissful time for me. It is my duty to acknowledge the individuals who supported me during these years.

First of all, I would like to show my appreciation to my supervisors, Professor Graeme Murch, Professor Irina Belova and Dr Alexander Evteev for their great guidance, advice, support and kindness. Their support and inspired suggestions led me towards an intelligent path. I wish to take this opportunity to thank my co-supervisor Dr Alexander Evteev. Without his patience and wisdom, I couldn't have achieved what I have now accomplished.

Further thanks go to the academic staff and my colleagues in the Faculty of Engineering and Built Environment, School of Engineering. Special thanks also to Ms Lea Petrovic, Ms Katherine Harrison, Mrs Jo Midwinter and Ms Rachel Hambleton for their support and help during the thesis process.

In addition, I am very thankful to the other members of the Centre for Mass and Thermal Transport in Engineering Materials, Dr Elena Levchenko and A/Prof. Thomas Fiedler, who provided their kind support on both a professional and personal level. I would also like to show gratitude to my friends who have made the years of studying in Australia far more enjoyable.

Furthermore, I am very grateful for the financial support provided through a postgraduate research scholarship from the University of Newcastle.

Last, but definitely not least, my special thanks go to my mother, Zahra, for her unflagging love, motivation and financial support. Furthermore, I would like to thank my lovely husband, Omid, for his love, encouragement and inspiring way of life. Without him I would not be here. In particular, I wholeheartedly thank my parents-in-law, Dariush and Giti, and my brothers, Reza and Amir, for their compassion, help and kindness during my PhD research.

Table of Contents

Statement of Originality	1
Acknowledgment of Authorship	2
Dedication	4
Acknowledgments	5
Table of Contents	6
List of Publications and Awards	8
List of Figures	10
List of Tables	15
List of Symbols	16
Abstract	24
Chapter 1: Introduction	26
1.1 Motivation and Problem Statement	26
1.2 Research Objectives and Research Significance	27
1.3 Thesis Structure	
Chapter 2: Background and Literature Review	
2.1 The Fundamental Concepts of Heat Transfer in Materials	
2.1.1 The Kinetic Theory of Thermal Conductivity	
2.1.2 The Wiedemann-Franz Law	
2.1.3 The Debye Model	
2.1.4 The Grüneisen Parameter	
2.1.5 Structure and Elastic Properties	
2.1.6 The Normal and Umklapp Processes	
2.1.7 The Boltzmann Equation	
2.1.8 Real Space and Phonon Space	
2.2 The Molecular Dynamics Method	47
	6

2.2.1 Thermodynamic Ensembles and Equations of Motion		
2.2.2 Periodic Boundary Condition	49	
2.2.3 The Limitations of the MD Method	50	
2.2.4 The Interaction Model: Lennard-Jones Potential	51	
2.2.5 The Embedded-Atom Method (EAM)		
2.2.6 The Direct Method		
2.2.7 The Green-Kubo Method		
2.2.8 Overview of Previous Works	54	
Chapter 3: Research Methodology	59	
Chapter 4: The Heat Current Autocorrelation Function (HCACF)	71	
Chapter 5: The Decomposition Model for Lattice Thermal Conductivity81		
5.1 Thermal Conductivity Decomposition	90	
5.2 Time Constant	94	
5.3 Analysis of the Phonon Thermal Conductivity Decomposition	98	
Chapter 6: Spectral Representation	122	
Chapter 7: Links to the Experimental Data and Assessment of the Scaling Re	elations of	
the Lattice Thermal Conductivity	157	
Chapter 8: Conclusions and Recommendations for Future Research	170	
8.1 Conclusions	170	
8.2 Future Research	172	
References	174	

List of Publications and Awards

Awards

2013 Postgraduate Research Prize, University of Newcastle, Australia, Faculty of Engineering and Built Environment

Invited Talks

Iran Telecommunication Industries Institute of Applied Science Affiliated with the University of Applied Science, Shiraz, Iran - Prediction of Phonon Thermal Conductivity of Materials by Molecular Dynamics Simulation.

Conference Papers (Poster)

L. Momenzadeh, A.V. Evteev, E.V. Levchenko, T. Ahmed, I.V. Belova, and G.E. Murch, Prediction of Phonon Thermal Conductivity of F.C.C. Al by Molecular Dynamics Simulation. ICTHT 2015: 17th International Conference on Thermophysics and Heat Transfer on May, 14-15, 2015 at Amsterdam, The Netherlands. p. 701.

Conference Papers (Oral)

T. Ahmed, A.V. Evteev, E.V. Levchenko, **L. Momenzadeh**, I.V. Belova, and G.E. Murch, Molecular Dynamics Study of Thermal Transport in Liquid Ni-Al Alloys, 4th International Conference on Material Science and Engineering Technology (ICMSET 2015), October 26-28, 2015, Singapore. ID Number: ICMSET2015-211-A.

A. V. Evteev, **L. Momenzadeh**, E. V. Levchenko, I. V. Belova and G. E. Murch, Phonon Thermal Transport in a Monatomic Lattice. EMRS conference, Computer modelling in nanoscience and nanotechnology: an atomic-scale perspective III (short: CMNN3), fall 2014, Warsaw, Poland.

Journal Papers

This thesis is based on the following papers. I warrant that I have obtained, where necessary, permission from the copyright owners to use any part of my own published work in which the copyright is held by another party.

- L. Momenzadeh, A.V. Evteev, E.V. Levchenko, I.V. Belova, and G.E. Murch, Y.H. Sohn, *Phonon Thermal Conductivity of f.c.c. Cu by Molecular Dynamics Simulation*. Defect and Diffusion Forum, 2013. 336: p. 169-184.
- A.V. Evteev, L. Momenzadeh, E.V. Levchenko, I.V. Belova, and G.E. Murch, *Molecular dynamics prediction of phonon-mediated thermal conductivity of f.c.c. Cu.* Philosophical Magazine, 2014. 94: p. 731-751.
- A.V. Evteev, L. Momenzadeh, E.V. Levchenko, I.V. Belova, and G.E. Murch, *Decomposition Model for Phonon Thermal Conductivity of a Monatomic Lattice*. Philosophical Magazine, 2014. 94: p. 3992-4014.
- A.V. Evteev, L. Momenzadeh, E.V. Levchenko, I.V. Belova, and G.E. Murch, Vibrational contribution to thermal transport in liquid copper: Equilibrium molecular dynamics study. Computational Materials Science, 2015. 96: p. 229-236.
- A.V. Evteev, E.V. Levchenko, L. Momenzadeh, I.V. Belova, and G.E. Murch, Molecular Dynamics Study of Phonon-Mediated Thermal Transport in Ni₅₀Al₅₀ Melt: case analysis of the influence of the process on the kinetics of solidification. Philosophical Magazine, 2015. 95: p. 90-111.
- E.V. Levchenko, A.V. Evteev, L. Momenzadeh, I.V. Belova, and G.E. Murch. *Phonon-Mediated Heat Dissipation in a Monatomic Lattice: Case Study on Ni*. Philosophical Magazine, 2015. 95(32): p. 3640-3673.
- A.V. Evteev, E.V. Levchenko, L. Momenzadeh, I.V. Belova, and G.E. Murch, *Insight into Lattice Thermal Impedance via Equilibrium Molecular Dynamics: Case Study on Al.* Philosophical Magazine, 2015, DOI: 10.1080/14786435.2016.1143569.

List of Figures

Figure 3.2: Basic structure of the MD simulation.....70

Figure 4.2: Comparison of the normalized HCACF of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag calculated at three different temperatures with the simulation blocks containing 4,000 (black solid line) and 32,000 (blue dashed line) atoms.

Figure 5.2: Double-logarithmic plot of the temperature dependence of the thermal conductivity, k_{ph} , of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and

Figure 6.1: Normalized power spectrum $VS_X(\omega)/2k_B = R(\omega)$ of the spontaneously fluctuating thermodynamic force X(t) in thermal equilibrium at different temperatures

Figure 6.4: Temperature dependences of the characteristic frequencies ω_c (circles), ω_R (diamonds), ω_{01} (solid downward facing triangles), ω_{d1} (squares), and $\omega'_{01} = \omega_c \sqrt{1 - (\omega_c \tau_1)^{-2}}$ (upward facing triangles) for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag in a wide temperature range (see Table 3.1). Open downward facing triangles show an estimation of ω_{01} on the basis of ω_c (via ω'_{01}) and τ_1 according to an approximate relation given by the quartic equation $(\omega_{01}/\omega'_{01})^4 - (\omega_{01}/\omega'_{01})^3 - (\omega_{01}/\omega'_{01})(\omega'_{01}\tau_1)^{-4} - (\omega'_{01}\tau_1)^{-2} = 0$. See text for further details.

Figure 6.5: Spectra of the power dissipation $S_{Power}(\omega) = \frac{3V}{2\pi k_B T} S_J(\omega) S_X(\omega)$ for the equilibrium thermal fluctuations at different temperatures above T_D for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag predicted on the basis of the

analytical model for the heat current autocorrelation function given by Equation 5.1..

Figure 7.1: (a₁), (b₁), (c₁), (d₁) and (e₁) show the decomposition of the total thermal conductivity, *k* (solid circles), of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag [11], respectively, into the electronic, k_{el} (upward facing open triangles), and phonon, k_{ph} (solid diamonds), components. This decomposition is based on: (i) the relation $k = k_{el} + k_{ph}$; (ii) the calculations of the phonon thermal conductivity, k_{ph-ph} (open squares), limited by the phonon scattering; and (iii) a simplified model of electron-phonon scattering in a metal [14, 17, 21] (see text for details). As a result, it is assumed that $k_{el} \approx k_{el-ph}$ and $k_{ph} = (k_{ph-ph}^{-1} + k_{ph-el}^{-1})^{-1}$, where k_{el-ph} is the electron thermal conductivity limited by the phonon scattering, while k_{ph-el} (downward facing open triangles) is the phonon thermal conductivity limited by the relative contribution of the phonon component to the total thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag, respectively. Solid diamonds and open squares show the ratios k_{ph}/k and k_{ph-ph}/k , respectively.

Figure 7.2: Double-logarithmic plot for the scaling relations of the lattice thermal conductivity k_{ph} with (a) the coefficient of the thermal expansion α_P and (b) the isothermal bulk modulus B_T . Plots show the ratio of the lattice thermal conductivities $k_{ph}(M)/k_{ph}(Cu)$ as a function of (a) the ratio of the coefficients of the thermal expansion $\alpha_P(M)/\alpha_P(Cu)$ and (b) the ratio of the isothermal bulk moduli $B_T(M)/B_T(Cu)$ calculated for the f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag models at 500, 700 and 900 K (M denotes Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag). The symbols show the calculated data (data for Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag are marked as 1, 2, 3, 4 and 5, respectively) while the lines show the linear fit of the data. The small symbols and solid lines represent data at 500 K, the medium symbols and dashed lines represent data at 900 K......169

List of Tables

Table 2.1: Basic information about lattice structures	37
Table 3.1: Temperature ranges for f.c.c. Cu, Al, NiEAM1, NiEAM2 and Ag.	62
Table 3.2: Atomic volume parameters for the quadratic equations (see Equation 3.5) the cases of f.c.c. Cu, Al, Ni _{EAM1} , Ni _{EAM2} and Ag.	in 62
Table 3.3: Details of the HCACF calculations	66

Table 5.1: Details of the linear fits of the average phonon velocities (v_0, α_v), Debye frequencies (ω_D) and Debye temperatures (T_D) at zero temperature......108

List of Symbols

Arabic Symbols	
Symbol	Description
а	Lattice parameter, Lattice constant
$\overline{a_i}$	Acceleration
Α	Constant number
<i>A</i> ₁	Strength (1, refer to acoustic short-range phonons)
<i>A</i> ₂	Strength (2, refer to acoustic long-range phonons)
B_T	Isothermal bulk modulus
<i>C</i> ₁	Partial heat capacity of acoustic short-range phonon modes
<i>C</i> ₂	Partial heat capacity of acoustic long-range phonon modes
C_{11} , C_{12} and C_{44}	Elastic constants
C_D	Debye heat capacity
$C_{\rm DP}$	Classical lattice heat capacity known as Dulong and Petit value
C_{ijkl}	Tensor of elastic constants
C_{JJ_1}	Contribution into the HCACF decay due to the acoustic short-
	range phonon modes
C_{JJ_2}	Contribution into the HCACF decay due to the acoustic long-
	range phonon modes
C_P	Heat capacity at constant pressure
C_V	Heat capacity at constant volume
$D(\omega)$	Density of state
e_i	Total energy of the <i>i</i> -th atom
Ε	Total energy
f_1	Fraction of the acoustic short-range phonon modes
f_2	Fraction of the acoustic long-range phonon modes
\mathbf{F}_i	Force
F_{α}	The embedding function for type α
g	Reciprocal lattice vector
$g(\omega,T)$	Density of phonon modes
$g_1(\omega,T)$	Density of the acoustic short-range phonon modes
	I

$g_2(\omega,T)$	Density of the acoustic long-range phonon modes
J	Microscopic heat current vector per unit volume
J_1	Heat current due to acoustic short-range phonon modes
J ₂	Heat current due to acoustic long-range phonon modes
k	Thermal conductivity
<i>k</i> ₁	Thermal conductivity (1, refer to acoustic short-range phonons)
<i>k</i> ₂	Thermal conductivity (2, refer to acoustic long-range phonons)
$k_{ m B}$	Boltzmann constant
k _{el}	Electron thermal conductivity
k _{el-ph}	Electronic thermal conductivity when limited by phonon
	scattering
k_{ph}	Phonon thermal conductivity
k_{ph-el}	Phonon thermal conductivity when limited by electron scattering
k_{ph-ph}	Lattice thermal conductivity determined by the phonon-phonon
	scattering processes
L ₀	Lorenz Constant
m	Mass of atom
m_i	Mass of atom <i>i</i>
n	Number of atoms in the specimen, Phonon distribution
n_e	Free electron per atom
n_0	Equilibrium phonon distribution
n'_0	Displaced phonon distribution
Ν	Number of atoms
<i>N</i> ₁	Acoustic short-range phonon modes
<i>N</i> ₂	Acoustic long-range phonon modes
Р	Pressure
p_1 and p_2	Probabilities
\mathbf{p}_i	Momentum vectors
P _{set}	Pressure
q	Wave vector
Q	Heat flux
\boldsymbol{r}_i	Position vectors, radius-vector of the <i>i</i> -th atom

r _{ij}	Distance between the centres of the two particles
r _{i,j}	Distance between atom i and j
$R(\omega)$	Thermal resistance
$R_1(\omega)$	Thermal resistance of the acoustic short-range phonon modes
$R_2(\omega)$	Thermal resistance of the acoustic long-range phonon modes
S	Speed of sound
S _{e,b}	Speed of sound in the direction of $e = \frac{q}{ q }$ for polarization b
$S_{l,\delta}$	Phonon speed of the longitudinal mode at given direction
S _{ph}	Phonon velocity
$s_{t_1,\delta}$ and $s_{t_2,\delta}$	Phonon speeds of the two transvers mode at given direction
S	Seebeck coefficient
$S_J(\omega)$	The power spectrum of the equilibrium fluctuations of the total
	heat flux $J(t)$
S _{Power}	Spectrum of power dissipation
$S_X(\omega)$	The power spectrum of the spontaneously fluctuating
	thermodynamic force $X(t)$
t	Time
Т	Absolute temperature
T_D	Debye temperature
T_m	Melting temperature
T _{set}	Desired temperature
u	Drift velocity in the direction of the heat flow
U	Thermal energy
U_{ij}	Lennard-Jones potential
V	Volume of the simulation cell
v_i	Absolute value of the velocity vector of the atom
v_{ilpha} or v_{ieta}	Components of the vectors \boldsymbol{v}_i
v_g	Phonon velocity
v_G	Group velocity
v_P	Phonon phase velocity
$x_{i\alpha}$	Components of the vectors r_i
$x_{ij\alpha}$ or $x_{ij\beta}$	Components of the vectors r_{ij}
1	

X	Thermodynamic force
$Y(\omega)$	Thermal reactance
$Y_1(\omega)$	Thermal reactance of the acoustic short-range phonon modes
$Y_2(\omega)$	Thermal reactance of the acoustic long-range phonon modes
$Z(\omega)$	Thermal Impedance
$Z_1(\omega)$	Thermal impedance of the acoustic short-range phonon modes
$Z_2(\omega)$	Thermal impedance of the acoustic long-range phonon modes

Greek Symbols	
Symbol	Description
α _Ω	Parameters of atomic volume quadratic equation
α_P	Coefficient of thermal expansion
α_V	Coefficient of thermal expansion
α and β	The element types of atoms i and j
eta_Ω	Parameters of atomic volume quadratic equation
β_T	Isothermal compressibility
δ	Given direction
δ_2	Dimensionless factor which should be less than unity
$\delta(\omega+\omega')$	Dirac delta function
Λ	Mean free path
∇T	Temperature gradient
ε	Depth of the potential well
ε_{xx} and ε_{yy}	Compression strain
E _{xy}	Shear strain
ε	Time history of parameter
$arphi_1$	Contribution of the acoustic short-range phonon modes into the
	lattice heat capacity
$arphi_2$	Contribution of the acoustic long-range phonon modes into the
	lattice heat capacity
$\phi_{lphaeta}$	Pair-wise potential function
γ	Gruneisen parameter
ħ	Reduce Plank constant
λ_D	Shortest wavelength
μ	Phonon mobility
η	Damping parameter
Ω	Atomic volume
Ω_0	Parameters of atomic volume quadratic equation
ρ	Mass density
$ar{ ho}_i$	Host electron density
I	I description of the second

$ ho_{eta}$	The electron density from one atom of type β at location of the
	other atom
$ ho_{\mu_j}(r_{ij})$	Electron density induced by an atom j at the location of atom i
σ	Finite distance, Entropy
σ_{el}	Electrical conductivity
$\sigma^{(p)}_{ilphaeta}$	Potential energy contribution to the components of the stress
	tensor of atom <i>i</i>
σ_{xx} and σ_{yy}	Compression stress
σ_{xy}	Shear stress
τ	Relaxation time
$ au_1$	Time constant (1, refer to acoustic short-range phonons)
$ au_2$	Time constant (2, refer to acoustic long-range phonons)
$ au_1'$	Average relaxation time
$ au_{2N}$	Relaxation time for a given acoustic long range phonon mode to
	restore the same perturbed phonon distribution $n(q, b, T)$ to the
	displaced distribution $n'_0(\boldsymbol{q}, \boldsymbol{b}, \boldsymbol{u}, T)$ via N-processes
$ au_{1U}$	Relaxation time for a given acoustic short-range phonon mode to
	restore a perturbed phonon distribution $n(q, b, T)$ to the
	equilibrium distribution $n_0(\boldsymbol{q}, \boldsymbol{b}, T)$ via U-processes
$ au_{2U}$	Relaxation time for a given acoustic long-range phonon mode to
	restore the displaced distribution $n'_0(\boldsymbol{q}, b, \boldsymbol{u}, T)$ to the equilibrium
	distribution $n_0(\boldsymbol{q}, \boldsymbol{b}, T)$ via U-processes
$ au_{c}$	Characteristic time constant
$ au_{C}$	Combined relaxation time
$ au_M$	Effective relaxation time for a given phonon mode
$ au_N$	Mode-dependent relaxation time for N-processes
$ au_P$	Barostate time constant
$ au_T$	Reservoir-system time constant
$ au_U$	Mode-dependent relaxation time for U-processes
$ au^*$	Phonon relaxation time
\boldsymbol{v}_i	Velocity vector of the <i>i</i> -th atom
ω	Angular frequency

ω_1	Low-frequency phonon mode
ω_2 and ω_3	High-frequency phonon mode
$\omega(\boldsymbol{q},b)$	Angular frequency which is a function of the phonon wave vector
	\boldsymbol{q} and the phonon polarization \boldsymbol{b}
$\omega_{\rm c}$	Characteristic angular frequency
ω_D	Debye frequency
ω_{d1}	Maximum location of $S_{J_1}(\omega)$, Damped resonance frequency
ω_{d2}	Maximum location of $S_{J_2}(\omega)$
ω_R	Maximum location of power spectrum
ω_{01}	Undamped resonance frequency
ω'_{01}	Minimum of $ Z_1(\omega) $, where $Y_1(\omega)$ passes via zero value
ω_{02}	Minimum location of impedance $ Z_2(\omega) $ of the acoustic long rang
	phonon modes

Abbreviations		
Abbreviation	Description	
Ag	Silver	
Al	Aluminium	
Ar	Argon	
b.c.c.	Body-centred cubic	
Cu	Copper	
EAM	Embedded-atom method	
f.c.c.	Face-centred cubic	
Ge	Germanium	
HCACF	Heat current autocorrelation function	
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator	
MD	Molecular dynamics	
N-processes	Normal processes	
Ni	Nickel	
Ni _{EAM1}	f.c.c. Ni that describe by EAM interatomic potential developed	
	by Mishin et al, (published in 1999)	
Ni _{EAM2}	f.c.c. Ni that describe by EAM interatomic potential developed	
	by Mishin et al, (published in 2004)	
NPT	Isobaric-isothermal ensemble	
NVE	Micro canonical ensemble	
NVT	Canonical ensemble	
ps	picosecond	
SC	Simple cubic	
Si	Silicon	
SiGe	Silicon germanium	
THz	Terahertz	
U-processes	Umklapp processes	

Abstract

In this study, the phonon dynamics and lattice thermal conductivity of f.c.c. Copper (Cu), Aluminium (Al), Nickel (Ni) and Silver (Ag), as case studies, are investigated over a wide range of temperatures in detail. Calculations are performed within the framework of equilibrium molecular dynamics simulations in conjunction with the Green-Kubo formalism. To describe the interatomic interaction, the most reliable embedded-atom method potentials are used. It should be noted that for Ni two different embedded-atom method interatomic potentials are considered. Hereafter, the first potential is referred to as Ni_{EAM1} (published in 1999) while the second potential is referred to as Ni_{EAM2} (published in 2004). In all the models considered, a two-stage decay in the heat current autocorrelation function was observed. After the first stage of decay, the heat current autocorrelation function showed a peak in the low temperature range. The intensity of the peak decreased as the temperature increased. Furthermore, it transformed to a shoulder which diminished at high temperatures. It was revealed that the lattice thermal conductivity of a monatomic lattice can be decomposed into two contributions due to the acoustic short- and long-range phonon modes. These two contributions can be presented in the form of simple kinetic formulas consisting of the products of the heat capacity, the square of the average phonon velocity and the average relaxation time of the acoustic short- and long-range phonon modes, respectively. In addition, this analysis allowed for numerical evaluations of all these quantities, in a self-consistent manner, from the heat current autocorrelation function. In particular, it was shown that the average phonon velocities of the acoustic short- and long-range phonon modes must be equal to each other and can be expressed via second-order fluctuations of the heat current vector.

This was followed by an extensive consideration of the spectral representation of the analytical model for the heat current autocorrelation function. This has the potential to be used to efficiently decode the generic information on the lattice thermal conductivity and phonon dynamics from spectroscopic measurements, with no gradients imposed on the studied crystal, if a proper resolution of the frequency range of approximately 1 - 20 THz is accessible. In this research, the contribution to the lattice thermal conductivity determined by the phonon-electron scattering processes was intentionally ignored, and

only the contribution due to the phonon-phonon scattering processes was considered. However, during comparisons of the data with the experiments, an estimation of the first contribution was made. Moreover, it is also of great interest, for practical applications, to have simple scaling relations between the lattice thermal conductivity and the other lattice properties readily accessible in experiments, such as the thermal expansion and elasticity. In this context, the scaling relations of the lattice thermal conductivity with the coefficient of the thermal expansion and the bulk modulus were estimated.

Chapter 1: Introduction

1.1 Motivation and Problem Statement

Over the past two decades, thermal conductivity predictions have only been made for a very limited range of materials. For example, McGaughey and Kaviany used molecular dynamics (MD) simulations combined with the Lennard-Jones pair potential to define the phonon transport and to predict the thermal conductivity of f.c.c. Ar [1, 2]. Also, Kaburaki et al. calculated the thermal conductivity of f.c.c. Ar over a wide temperature range, showing that the MD method combined with the Lennard-Jones pair potential has a good accuracy for the prediction of the thermal conductivity of argon [3]. Both the mentioned groups used equilibrium MD along with the Green-Kubo method. He et al. [4] compared the performance of equilibrium and non-equilibrium molecular dynamics (EMD and NEMD) and the Boltzmann transport equation for bulk crystalline Si_{0.5}Ge_{0.5} alloys at room temperature. They found that MD simulations can provide a valuable insight into the thermal properties of materials [4].

The appropriate candidates for this research are Cu, Ni, Al and Ag as:

- (i) Very high-quality embedded-atom method (EAM) potentials [5-8] are available for these elements.
- (ii) The calculated phonon thermal conductivity can be compared to the previous non-equilibrium MD calculations [9] of the phonon thermal conductivity of f.c.c. Cu, as a case study, under a large temperature gradient with an older EAM potential [10].
- (iii) The results obtained for f.c.c. Cu, Ni, Al and Ag can be compared with each other to estimate the scaling relations between the lattice thermal conductivity and the other lattice properties.
- (iv) The results can be compared with the experimental data on the thermal conductivity of the above mentioned metals [11].

Thus, the motivation for the present research was to investigate the temperature dependency of the phonon thermal conductivity and the phonon dynamics of the elemental f.c.c. crystals, using Cu, Ni, Al and Ag models as case studies. The Green-Kubo formalism was applied to examine, in greater detail, the heat current autocorrelation function (HCACF) and to gain an important insight into the phonon scattering processes. The results from this research are then compared with previous related theoretical and experimental studies, with the goal of bridging the experiment and the theory [12].

1.2 Research Objectives and Research Significance

In this work, the thermal transport properties of crystal Cu, Ni, Al and Ag are considered. The main objectives of this study were:

- To use molecular dynamics simulations in conjunction with the Green-Kubo formalism to investigate the heat current auto-correlation functions of those metals in detail.
- (ii) To investigate the temperature dependence of phonon thermal conductivity and the phonon dynamics of Cu, Ni, Al and Ag in detail.
- (iii) To investigate, in detail, the power spectra of equilibrium fluctuations, which are characterized by the HCACF.
- (iv) To compare the results obtained for the f.c.c. Cu, Ni, Al and Ag with each other, and to estimate scaling relations between the lattice thermal conductivity and the other lattice properties, such as the coefficient of thermal expansion and the bulk modulus.
- (v) To use the obtained results for Cu, Ni, Al and Ag to compare them with previous simulation studies and the available experimental data on thermal conductivity.

The outcome of this research will enhance our understanding on how the phonon thermal conductivity of metals can be predicted by using MD simulations, within the framework of the EAM, in conjunction with the Green-Kubo formalism. Another advantage of MD simulations is that testing thermal properties is faster and less expensive than by synthesising and characterizing in real experiments. Moreover, MD simulations provide some details of atomic-level information that would not be accessible in experiments. The results will also be compared with previous related theoretical and experimental data on thermal conductivity.

1.3 Thesis Structure

In this thesis, the temperature dependence of the lattice thermal conductivity and phonon dynamics of the f.c.c. Cu, Ni, Al and Ag models are investigated with the most reliable EAM potentials [5-8] by treating the HCACF extracted from the equilibrium MD simulations within the framework of the analytical model. For this purpose, the thesis begins with an introductory chapter which provides an outline of the topics covered by the thesis.

The first section of Chapter 2 focuses on the fundamental concepts of heat transfer in materials, including the thermal conductivity and structures of materials. As the two main contributors to thermal conductivity, lattice vibrations and free electrons are discussed in detail. The next section of this chapter discusses the MD simulations and details related to the simulations. The Green-Kubo method and the direct method for predicting thermal conductivity and the Lennard-Jones potential are then discussed. A general review of the related literature on the topic of this research study is presented.

In Chapter 3, the Green-Kubo formalism, which is based on a system at equilibrium, is discussed in detail. The MD method and the general details of the simulations will be described. The various parameters, such as the elastic properties, the Debye wavelength, the average speed of sound, the Debye frequency and the Debye temperature of f.c.c. Cu, Al, Ni and Ag, will also be presented in this chapter.

Chapter 4 begins with a description of the analytical model used for the HCACF. The temperature dependence of the lattice thermal conductivity and the phonon dynamics of the MD models of f.c.c. Cu, Ni, Al and Ag are investigated in detail, and show that the HCACF has a two-stage decay for a monoatomic lattice. Moreover, it was demonstrated that the HCACF calculated for wide temperature ranges for the *NPT*, *NVT* and *NVE* ensembles, as well as the averages over the three ensembles, can be universally modelled by this analytical function.

Chapter 5 focuses on the decomposition model for lattice thermal conductivity. In particular, it is shown that the lattice thermal conductivity for a monoatomic crystal can be decomposed into two contributions due to the acoustic short- and long-range phonon modes. Furthermore, the contributions from the acoustic short- and long-range phonon

modes to the total phonon thermal conductivity will be presented in the form of simple kinetic formulas, consisting of the product heat capacity, the average phonon velocity and the average relaxation time.

Chapter 6 presents the spectral representations of the analytical models for the HCACF. This can be used in the future to extract information on the lattice thermal conductivity and the phonon dynamics from the scattering and absorption spectroscopic measurements, with no gradients imposed on the crystal studied, if a proper resolution in the frequency range of approximately 1 - 20 THz is accessible.

Chapter 7 compares the results obtained for the MD models of f.c.c. Cu, Ni, Al and Ag with each other. In addition, the objective was to compare the results obtained to those for the Lennard-Jones pair potential model of f.c.c. Ar. Estimations were made of scaling relations between the lattice thermal conductivity and other lattice properties readily accessible in experiments, such as the coefficient of the thermal expansion and the bulk modulus [1-3].

In the final chapter of this thesis, the important outcomes of the study are presented and a number of interesting possibilities for future work are recommended.

Chapter 2: Background and Literature Review

2.1 The Fundamental Concepts of Heat Transfer in Materials

Thermal conductivity is one of the fundamental physical properties of materials, and it is very important for heat exchange calculations and the evaluation of thermal insulation performance. In general, thermal conductivity has considerable impact on a wide range of technical applications containing the thermal management¹ of mechanical, electrical and chemical sensors and transducers. Furthermore, the investigation of the fundamental physics of the heat conduction process can provide a detailed understanding of the nature of the structure dynamics in materials. The last two decades have seen dramatic improvements in experimental techniques and theoretical studies of thermal conductivity [13].

2.1.1 The Kinetic Theory of Thermal Conductivity

Heat is transferred by three basic mechanisms: conduction, convection, and radiation. Conduction is the transmission of heat from one molecule to another through a substance and thermal conductivity is the ability of a material to transfer heat through the conduction process. Fourier's Law is shown in Equation 2.1:

$$Q = -k\frac{dT}{dx},$$
(2.1)

where, Q is the heat flux $[W/m^2]$, $\frac{dT}{dx}$ is the temperature gradient [K/m], k is the thermal conductivity [W/mk], and the negative sign shows that the heat flows from the hot side area to the colder side. The rate of heat transfer is usually quantified in terms of the thermal conductivity coefficient k. The thermal conductivity of materials can be influenced by a number of factors, such as the molecular bonding, structure and density

¹ Thermal management provides cooling solutions to protect electronic devices from damage by heat generation.

of materials [14]. Figure 2.1 illustrates the heat transfer process in materials through the conduction process.



Figure 2.1: The conduction heat transfer process from high temperature (T_1) to low temperature (T_2) surfaces. A is the area perpendicular to the heat flow, Q is the rate of the conduction heat transfer and Δx is the distance of the heat transfer.

The lattice vibrations $(phonons)^2$ and the free electrons are the two main contributors to the transportation of heat in materials, as shown in Equation 2.2:

$$k = k_{el} + k_{ph},\tag{2.2}$$

where, k_{ph} and k_{el} are the phonon and electronic contributions to the thermal conductivity, respectively [15]. While phonon thermal conductivity is defined by the vibrations of atoms around their equilibrium positions (crystal lattice) in solids, the electron contribution to the thermal conductivity is defined by the free electrons transfer of the thermal energy when the free electrons migrate from a high temperature area to a lower temperature area (see Figure 2.2) [15].



Figure 2.2: Schematic illustration of electronic contribution to the thermal conductivity in metal crystal structures.

² Phonons are collective vibrations of the crystal lattice.

In particular, phonon thermal conductivity is defined by the kinetic theory expression:

$$k_{ph} = \frac{1}{3} C_V s_{ph} \Lambda, \tag{2.3}$$

where, C_V is the phonon specific heat per unit volume, s_{ph} is the phonon velocity and Λ^3 is the mean free path of the phonons, which is defined as the average distance between two collisions, so $\Lambda = s_{ph}\tau$, where τ is the relaxation time⁴ or the collision time (a similar expression is used for electron thermal conductivity) [14].

2.1.2 The Wiedemann-Franz Law

Usually, the Wiedemann-Franz law can be used to estimate the electron thermal conductivity k_{el} , which predicts k_{el} to scale linearly with the product of the electrical conductivity and the temperature $\sigma_{el}T$. The electron thermal conductivity can be presented as:

$$k_{el} = L_0 \sigma_{el} T \tag{2.4}$$

where, σ_{el} is the electric conductivity, L_0 is the Lorenz constant (2.45×10⁻⁸ WΩ/K²) and *T* is the absolute temperature [16]. As a result, the phonon contribution to the total thermal conductivity can be explained as:

³ The average distance travelled between collisions.

⁴ The time required for a system to return to equilibrium after perturbation.

$$k_{ph} = k - L_0 \sigma T \tag{2.5}$$

The derivation of the law assumes that the relaxation times appropriate to thermal and electrical conduction are identical. However, the form of the departure of the electron distribution from equilibrium due to an electric field can be different from the departure produced by a temperature gradient [17]. As a result, the details of the assessment of k_{el} (and subsequently k_{ph}), according to the Wiedemann-Franz law, can be incorrect [14, 17-21]. Aside from the use of the Wiedemann-Franz law, the electronic and lattice contributions may be separated by measuring the magnetic-field dependence of the thermal conductivity [14, 22-24]. The method is based on the assumption that the electronic contribution to the thermal conductivity, as the electrical conductivity, can be sufficiently reduced by the application of a large magnetic field, so that one can isolate or extrapolate the lattice thermal conductivity, presuming it is field independent [14]. This technique requires very high electron mobility, so it was applied for semiconductors and semimetals [22, 24], while in ordinary metals this approach would not work [14]. Furthermore, it was shown in [23] that the utilization of thermal fluctuations or Johnson/Nyquist noise has the potential to be used as a spectroscopic technique to measure multiple transport properties, including the k_{el} , of conductors and semiconductors through the fluctuation spectra of the intrinsic conduction electrons without the application of [14] electrical potentials or thermal gradients.

In general, a fundamental understanding of the factors affecting the electronic and lattice contributions to thermal conductivity is highly desirable for the development of advanced energy conversion devices that utilise the thermoelectric effect [25]. Indeed, the thermoelectric performance of a material is expressed by its dimensionless figure of merit⁵:

Figure of merit =
$$\frac{S^2 \sigma_{el} T}{k} = \frac{S^2 \sigma_{el} T}{k_{el} + k_{ph}}$$
 (2.6)

⁵ A quantity used to define the performance of a device or method.

where *S* is the Seebeck coefficient.⁶ It is straightforward to see from Equation 2.6 that the combination of low thermal conductivities with large values of *S* and σ_{el} are required in order to achieve large values of the figure of merit. Since k_{el} is supposed to scale approximately linearly with $\sigma_{el}T$, according to the Wiedemann-Franz law [14, 17, 19-21, 25], researchers have generally focused on ways to decrease the lattice thermal conductivity k_{ph} in order to enhance the figure of merit of a thermoelectric material [25-27]. In this context, considerable effort for reducing the k_{ph} has been made by managing the structure of the materials in order to increase the phonon blocking and phonon scattering by structural imperfections. This concept of engineering k_{ph} employs different strategies, such as building up superlattices [28, 29] and nanostructures [30, 31], incorporating suitable filler atoms into structural cages [32, 33], introducing point defects and their complexes by alloying with isoelectronic elements [34-39], and so on.

Another conceptual approach for lowering the k_{ph} can be based on an understanding of the interrelations between the lattice thermal conductivity and the other lattice properties readily accessible in experiments, such as thermal expansion and elasticity. With this understanding, guidelines for managing the structure in combination with the basic lattice properties can be formulated in designing new thermoelectric materials which have an exceptionally low phonon mediated contribution to the thermal conductivity. A methodological procedure which, in contrast to experimental methods, straightforwardly allows for a systematic study of the interrelations of the lattice thermal conductivity with the other properties of a perfect lattice can be based on the MD method. However, the complexity of typical thermoelectric materials makes both the accurate MD description of the materials and the evaluation of the interrelations between their lattice properties fairly difficult and not transparent. Meanwhile, a fundamental understanding of the scaling relations of the lattice thermal conductivity with other lattice properties can be achieved using a systematic MD study of a set of high-quality models of isostructural crystals (i.e., crystals which have the same structure but different lattice properties) which have a relatively simple cubic lattice.

⁶ A measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across the materials.

2.1.3 The Debye Model

The Debye model is a method for estimating the phonon contribution to the heat capacity in a solid, introduced by Peter Debye in 1912. The thermal energy is determined as $U = \int D(\omega) \langle n(\omega) \rangle \hbar \omega \, d\omega$, where $D(\omega)$ is the density of state⁷ ($D(\omega) = \frac{V\omega^2}{2\pi^2 s^3}$), (where *s* is the speed of sound, ω is the frequency and *V* is the volume) and the thermal equilibrium occupancy of the phonons is described by the Planck distribution as $\langle n \rangle = \frac{1}{\exp(\hbar\omega/T)-1}$. As a result, the thermal energy is given by:

$$U = \int_0^{\omega_D} \left(\frac{V\omega^2}{2\pi^2 s^3}\right) \left(\frac{\hbar\omega}{e^{\hbar\omega/T} - 1}\right) d\omega = \frac{3Vk_B^4 T^4}{2\pi^2 s^3 \hbar^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx,$$
 (2.7)

where, $x \equiv \hbar \omega / T \equiv \hbar \omega / k_{\rm B} T$ and $x_D \equiv \hbar \omega_D / k_{\rm B} T \equiv T_D / T$ that Debye Temperature⁸ (T_D) is defined as $T_D = \frac{\hbar s}{k_B} \cdot \left(\frac{6\pi^2 N}{V}\right)^{1/3}$, so that the total phonon energy is defined by:

$$U = 9nk_BT\left(\frac{T}{T_D}\right)\int_0^{x_D} \frac{x^3}{e^x - 1}dx,$$
(2.8)

where, $x_D = T_D/T$ and *n* is the number of atoms in the specimen [20].

Heat capacity is the measure of the amount of energy the system needs to increase the temperature by one degree. There are two types of heat capacity: the heat capacity at constant volume C_V , $C_V = \left(\frac{\partial E}{\partial T}\right)_V$ (where *E* is the energy and *T* is the

⁷ Which describes the number of states per interval of energy at each energy level.

⁸ Which estimates the phonon contribution to the specific heat in a solid.
temperature) and the heat capacity at constant pressure C_P ⁹. The contribution of the phonons to the heat capacity of a crystal is called the lattice heat capacity [20]. The heat capacity of solids, according to the Debye approximation, can also be calculated using the following equation. In this equation, ω_D is the Debye frequency. It is close to the maximum frequency derived from the interatomic force constant [19]:

$$C_{\nu,p}(T) = 9 \frac{k_B}{m} \left(\frac{k_B T}{\hbar \omega_D}\right)^3 n \int_0^{\hbar \omega_D / k_B T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \qquad \frac{k_B T}{\hbar \omega_D} \equiv \frac{T}{T_D}$$
(2.9)

$$C_{\nu,p}(T) = 9 \frac{k_B}{m} \left(\frac{T}{T_D}\right)^3 n \int_0^{\hbar\omega_D/k_B T} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$
(2.10)

where, *n* is the number of atoms in the specimen, T_D is the Debye Temperature, k_B is the Boltzmann constant, *m* is the mass of atom and \hbar is the reduced Planck constant ($\hbar = h/2\pi$).

2.1.4 The Grüneisen Parameter

The effect of changing the volume and temperature on the vibrational properties and size of the lattice is described by the Grüneisen parameter. The thermodynamic Grüneisen parameter is defined by:

$$\gamma = V \left(\frac{dP}{dE}\right)_V = \frac{\alpha_P}{C_V \beta_T} \tag{2.11}$$

⁹ A thermodynamic relation gives $C_P - C_V = V_{atom}T \frac{\alpha_P^2}{\beta_T}$, where *V* is the atomic volume, α_P is the coefficient of thermal expansion, *T* is the temperature, and β_T is the isothermal compressibility.

where, *V* is the volume, *E* is the energy, α_P^{10} is the coefficient of thermal expansion, C_V^{11} is the heat capacity at a constant volume, and β_T^{12} is the isothermal compressibility.

2.1.5 Structure and Elastic Properties

This research considers the crystal (solid) phase of Copper (Cu), Nickel (Ni), Silver (Ag) and Aluminium (Al).

The crystal structures of atoms and molecules in solids are unique formations that can be described in terms of a lattice. The simple cubic (sc) lattice, the body-centred cubic¹³ (b.c.c.) lattice and the face-centred cubic¹⁴ (f.c.c.) lattice are three lattices in the cubic system. Table 2.1 gives the essential information on these crystal structures [20]. In the f.c.c. crystal, the atomic displacement is isotropic and all of the atoms are at equivalent positions [19].

	Simple	Body-centred	Face-centred
Unit cell volume*	a^3	a^3	a^3
Number of atoms in one unit cell	1	2	4
Primitive cell volume	a^3	$a^{3}/_{2}$	$a^{3}/_{4}$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	а	$3^{1/2}a/2$	$a/_{2^{1/2}}$

Table 2.1: Basic information about lattice structures

*In terms of the lattice parameter a

In crystal the state, Cu, Ni, Ag and Al have f.c.c. lattices. Figure 2.3 shows the f.c.c. lattice structures.

¹⁰ Characterizes how the size or volume of an objective changes with a change in temperature.

¹¹ The amount of heat required to enhance the temperature of a system by one degree.

¹² Describes how the volume of a system changes as a function of the pressure at a constant temperature.

¹³ Body-centred cubic is a cube where atoms are arranged at the corners of the cube with an atom situated in the middle of the unit cell.

¹⁴ Face-centred cubic is a cube where atoms are arranged at the corners and centre of each face of the unit cell.



Figure 2.3: (a) Face-centred cubic lattice structure (f.c.c.); (b) In the f.c.c. crystal, the centre atom has 12 nearest neighbours and it is an isotropic structure [2].

Phonons are the collective vibrations of the crystal lattice which make a significant contribution to many of the physical properties of materials, including the heat capacity and thermal conductivity [19]. In solids, atoms join up with each other through bonds that can be modelled as springs (see Figure 2.4). The temperature difference causes the vibrations of the hot region to be transmitted through the springs to the cooler region. As a result, all the atoms start to vibrate and transfer the thermal energy. There are two types of phonons: acoustic and optical phonons [19]. Monoatomic solids can demonstrate only one type of phonon, namely, acoustic phonons. In contrast to monoatomic solids, the smallest unit cell of binary alloys exhibits two types of phonons: acoustic and optical mode, two neighbouring atoms move opposite to each other but in the acoustic mode they move together, as shown in Figure 2.5:



Network of atoms

Vibrate hot side

Whole structure vibrating

Figure 2.4: Schematic diagram of conduction by lattice vibration



Figure 2.5: Schematic diagram of optical and acoustic phonons. (a) Dispersion curves in the linear diatomic chain, where *k* is the wave-vector (related to wavelength $k=2\pi/\lambda$) and ω is the frequency; (b) Optical and acoustic vibrations in the linear diatomic chain. m₁ and m₂ are the atomic masses that are repeated periodically at a distance a.

The elastic properties of a solid are defined by interatomic forces when the atoms are moved from their equilibrium position. The general form of Hooke's law is:

$$\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}, \qquad (2.12)$$

where, C_{ijkl} is the tensor of elastic constants, which has $3 \times 3 \times 3 = 81$ components, with only 36 being independent elastic constants. In cubic crystals $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{21} = C_{23} = C_{32} = C_{13} = C_{31}$, $C_{44} = C_{55} = C_{66}$ and the other components are zero, with $C_{11} = \frac{\sigma_{xx}}{\varepsilon_{xx}}$, $C_{12} = \frac{\sigma_{xx}}{\varepsilon_{yy}}$ and $C_{44} = \frac{\sigma_{xy}}{\varepsilon_{xy}}$ describing the longitudinal compression, transverse expansion and shear modulus, respectively. In these equations, σ_{xx} and σ_{xy} present the compression and shear stress, respectively. Also, ε_{xx} and ε_{yy} show the compression strain and ε_{xy} shows the shear strain. The elastic properties have an important effect on the thermal conductivity of materials [40].

2.1.6 The Normal and Umklapp Processes

In an anharmonic crystal, the lattice vibrations (lattice waves or phonons) are not independent, but interact with each other. In particular, the dynamical effects due to this interaction, such as the three phonon-phonon scattering processes, give rise to the phenomenon of intrinsic lattice (phonon) thermal conductivity [17, 41, 42]. The theoretical description of the lattice thermal conductivity is rather more complicated than an analytical treatment of the anharmonic effects in relation to other lattice properties, such as thermal expansion, elasticity and heat capacity. The problem arises from the fact that the thermal conductivity, in contrast to other lattice properties, cannot be readily expressed using the lattice sums. Instead, one first has to solve the Boltzmann equation for the phonon distribution function, originally formulated by Peierls [41, 42]. Furthermore, a mechanism for establishing a local thermal equilibrium distribution of the phonons needs to also be elucidated. This research, however, is not concerned with the interactions of phonons with the crystal boundaries, lattice imperfections and electrons. These contributions to the lattice thermal conductivity can be neglected in comparison with the phonon-phonon interactions for sufficiently large and perfect crystals at sufficiently high temperatures.

Peierls was the first to point out [41, 42] that the three-phonon scattering process is of the form:

$$q_1 + q_2 = q_3, (2.13)$$

Consisting of the interaction of two phonons with wave vectors q_1 and q_2 to produce a third phonon with a wave vector q_3 within the first Brillouin zone¹⁵ cannot establish equilibrium. This is because the scattering process given in Equation 2.13 conserves the phonon momentum (which is $\hbar q$ for a phonon with a wave vector q). Such non-resistive scattering processes are called normal processes or N-processes. To enable a way for restoring the non-equilibrium phonon distribution to the equilibrium, Peierls suggested [41, 42] a three-phonon scattering process which does not conserve the total phonon momentum:

$$q_1 + q_2 = q_3 + g, \tag{2.14}$$

where, \boldsymbol{g} is a reciprocal lattice vector. Equation 2.14 reflects the fact that if a wave vector of the produced phonon is outside the first Brillouin zone then it can be transformed into

¹⁵ The Brillouin Zone is determined as a primitive cell in the reciprocal lattice.

a physically equivalent wave vector inside the first Brillouin zone by the addition of a reciprocal lattice vector \boldsymbol{g} . Such resistive scattering processes are called Umklapp processes or U-processes. It follows on from Equation 2.14 that the wave vectors of phonons suitable for the Umklapp processes must satisfy the following condition:

$$|\boldsymbol{q}_1 + \boldsymbol{q}_2| > \frac{1}{2} |\boldsymbol{g}_{min}|.$$
 (2.15)

In other words, at least one of the two initial phonons suitable for a U-process must have a wave vector which exceeds $\frac{1}{4}|\boldsymbol{g}_{\min}|$ in magnitude, where \boldsymbol{g}_{\min} is the shortest reciprocal lattice vector [42]. Both the N-processes and the U-processes conserve the phonon energy (which is $\hbar\omega$ for a phonon with angular frequency ω), since it can be expressed by:

$$\omega_1 + \omega_2 = \omega_3, \tag{2.16}$$

where, ω_1 , ω_2 and ω_3 are the angular frequencies of the phonons participating in the scattering processes. It should also be noted that in the crystal, the phonon scattering processes clearly exist; the reverse of the processes is given by Equations 2.13, 2.14 and 2.16. In addition, despite the N-processes themselves not tending to restore the phonon equilibrium distribution and not contributing to the thermal resistance, the N-processes may still have a profound influence on the lattice thermal conductivity. These processes have the significant effect of transferring energy between the different phonon modes, thus preventing large deviations from the equilibrium distribution.



Figure 2.6: In Figures (a) and (b), the squares demonstrate the first Brillouin zone. (a) The N-processes show two incoming phonons with wave-vectors q_1 and q_2 (blue) generating one outgoing phonon with a wave vector q_3 (red). (b) The U-Processes illustrate that the sum of the two wave-vectors q_1 and q_2 might point to outside the Brillouin zone (q'_3). As shown in Figure 2.6(b), the q'_3 outside the first Brillouin zone are physically equivalent to the vectors inside it and can be mathematically transformed into each other by the addition of a reciprocal lattice vector g.

2.1.7 The Boltzmann Equation

In the presence of a temperature gradient, when steady state is established, the Boltzmann equation can be written as [17, 41, 42]:

$$\boldsymbol{\nu}_{\rm G} \boldsymbol{\nabla} T \frac{\partial n}{\partial T} = \left(\frac{\partial n}{\partial t}\right)_{\rm scatt.},\tag{2.17}$$

where, the left- and right-hand sides represent the balanced rates of change of a perturbed phonon distribution n of a given phonon mode due to the temperature gradient ∇T (transport term) and due to the phonon scattering processes (collision term), respectively, while $v_{\rm G}$ denotes the group velocity of the phonon mode. Each phonon mode can be characterised by an angular frequency $\omega = \omega(q, b)$ which is a function of the phonon wave vector q and the phonon polarization b (branch index), so that n = n(q, b) and:

$$\boldsymbol{v}_{\rm G}(\boldsymbol{q}, b) = \frac{\partial \omega(\boldsymbol{q}, b)}{\partial \boldsymbol{q}}.$$
(2.18)

In the case of a monatomic lattice (i.e., a Bravais lattice) consisting of N atoms, which will be considered in the present work, there are 3N possible phonon modes with b = 1, 2 and 3 enumerating the three acoustic branches, one longitudinal and two transverse. Furthermore, if the deviation of n from the equilibrium phonon distribution n_0 is assumed to be small, in the transport terms of Equation 2.17 one can replace n by n_0 by keeping only the first order in the temperature gradient. Considering that the equilibrium phonon distribution is given by Bose-Einstein statistics [17, 41, 42]:

$$n_0 = \left[\exp\left(\frac{\hbar\omega}{k_{\rm B}T}\right) - 1 \right]^{-1},\tag{2.19}$$

one can readily obtain:

$$\frac{\partial n}{\partial T} \approx \frac{\partial n_0}{\partial T} = \frac{c}{\hbar \omega},$$
(2.20)

where, $k_{\rm B}$ is the Boltzmann constant, \hbar is the Planck constant divided by 2π , while:

$$c = \frac{\hbar^2 \omega^2}{k_{\rm B} T^2} (1 + n_0) n_0 \tag{2.21}$$

is the phonon specific heat.

However, a rigorous theoretical construction of the collision term that leads to a satisfactory solution of Equation 2.17 is much more difficult [43]. The main point here is to understand in detail how to precisely evaluate the collision term in order to make it applicable for a reliable description of the phonon-phonon scattering processes spanning the entire frequency range, from the low-frequency domain to the Debye frequency. Indeed, despite both the low- and high-frequency domains being experimentally accessible at present using ultrasonic and light scattering techniques and neutron scattering techniques, respectively, because of experimental difficulties, very little is known about the intermediate frequency region [44-47]. Future progress in this context might be expected with the development of modern laser and cold neutron based scattering techniques. At the same time, it should be noted that the different phenomenological models have been intensively studied for approximate treatments of the collision term of Equation 2.17 [17]. One of the most widely used treatments for analysing the experimental data on lattice thermal conductivity is the treatment attributed to Callaway [36].

Callaway's treatment is based on the so-called relaxation-time approximation [17] of the collision term in Equation 2.17 by an expression of the following form:

$$\left(\frac{\partial n}{\partial t}\right)_{\text{scatt.}} \approx -\frac{n-n_0}{\tau_{\text{U}}} - \frac{n-n_0'}{\tau_{\text{N}}},$$
 (2.22)

where, $n'_0 = n_0 \left(\frac{\hbar\omega - \hbar q u}{k_B T}\right)$ is the so-called displaced phonon distribution which can be viewed as the equilibrium phonon distribution relative to a coordinate system which moves with velocity u (u is the drift velocity in the direction of the heat flow), $\tau_U = \tau_U(q, b, T)$ is the mode-dependent relaxation time for the U-processes (in the presence only of the phonon-phonon scattering process) to restore a perturbed phonon distribution to an equilibrium phonon distribution, and $\tau_N = \tau_N(q, b, T)$ is the mode-dependent relaxation time for the N-processes to restore a perturbed phonon distribution to a displaced phonon distribution. This phenomenological approximation of the collision term is qualitatively in line with the abovementioned reasoning that the non-resistive scattering N-processes should have an effect on the lattice thermal conductivity, but not the same as the resistive scattering U-processes, which tend to restore the true thermal equilibrium [17]. Then, assuming that the magnitude of the drift velocity u is noticeably smaller than the magnitude of the phonon phase velocity $v_P(q, b) = \omega(q, b)/q$ for all acoustic phonon modes ($u \ll v_P(q, b)$), one can expand n'_0 to the first order in $v_P u/v_P^2$ as:

$$n_0' \approx n_0 + \frac{\boldsymbol{\nu}_{\mathrm{P}} \boldsymbol{u}}{\hbar \omega \boldsymbol{\nu}_{\mathrm{P}}^2} T c, \qquad (2.23)$$

and readily find the solution of the Boltzmann equation as:

$$n = n_0 - \frac{c}{\hbar\omega} \tau_{\rm M} \boldsymbol{\nu}_{\rm G} \boldsymbol{\nabla} T , \qquad (2.24)$$

where, $\tau_{\rm M} = \tau_{\rm M}(\boldsymbol{q}, \boldsymbol{b}, T)$ is an effective relaxation time for a given phonon mode. It is relatively simple to see that $\tau_{\rm M}$ can be expressed as:

$$\tau_{\rm M} = \tau_{\rm C} + \frac{\tau_{\rm C}}{\tau_{\rm N}} \frac{\mu}{v_{\rm P} v_{\rm G}},\tag{2.25}$$

where, $\tau_{\rm C} = \tau_{\rm C}(\boldsymbol{q}, \boldsymbol{b}, T)$ is a combined relaxation time determined as:

44

$$\frac{1}{\tau_{\rm C}} = \frac{1}{\tau_{\rm U}} + \frac{1}{\tau_{\rm N}},\tag{2.26}$$

and μ can be interpreted as the phonon mobility, since it is the coefficient of the proportionality between the drift velocity \boldsymbol{u} and the thermodynamic force $\boldsymbol{X} = -\frac{1}{T} \nabla T$ due to the temperature gradient:

$$\boldsymbol{u} = \boldsymbol{\mu} \boldsymbol{X}.\tag{2.27}$$

The phonon mobility can be determined from the condition that the rate of changing the total phonon momentum due to the N-processes must be zero:

$$\sum_{q,b}^{3N} \hbar q \frac{n(q,b) - n_0'(q,b)}{\tau_N(q,b)} = 0.$$
(2.28)

For a cubic crystal (isotropic case), this leads to (see also Equations 2.23 - 2.27):

$$\mu = \sum_{\boldsymbol{q},b}^{3N} \frac{c(\boldsymbol{q},b)\boldsymbol{v}_{\mathrm{G}}(\boldsymbol{q},b)\tau_{\mathrm{C}}(\boldsymbol{q},b)}{\boldsymbol{v}_{\mathrm{P}}(\boldsymbol{q},b)\tau_{\mathrm{N}}(\boldsymbol{q},b)} \bigg/ \sum_{\boldsymbol{q},b}^{3N} \frac{c(\boldsymbol{q},b)\tau_{\mathrm{C}}(\boldsymbol{q},b)}{\boldsymbol{v}_{\mathrm{P}}^{2}(\boldsymbol{q},b)\tau_{\mathrm{U}}(\boldsymbol{q},b)\tau_{\mathrm{N}}(\boldsymbol{q},b)}.$$
(2.29)

Once the Boltzmann equation is solved for n(q, b), either from first principles, or by using different approximate approaches, one can find the microscopic heat current vector per unit volume V (the heat flux) in the form first derived by Peierls [41, 42]:

$$\boldsymbol{J} = \frac{1}{V} \sum_{\boldsymbol{q}, b}^{3N} \hbar \omega(\boldsymbol{q}, b) \boldsymbol{n}(\boldsymbol{q}, b) \boldsymbol{v}_{\rm G}(\boldsymbol{q}, b).$$
(2.30)

It is important to note that J = 0 when $n = n_0$, since ω and n_0 are even functions of q while v_G is an odd function of q. In particular, it is straightforward to see from Equations 2.24, 2.25 and 2.30 that the expression for the lattice thermal conductivity of a cubic

crystal, which follows from Callaway's treatment of the collision term, can be written as:

$$k = -\frac{J}{\nabla T} = k_1^{\text{Callaway}} + k_2^{\text{Callaway}}, \qquad (2.31)$$

where

$$k_{1}^{\text{Callaway}} = \frac{1}{3V} \sum_{\boldsymbol{q}, b}^{3N} c(\boldsymbol{q}, b) v_{\text{G}}^{2}(\boldsymbol{q}, b) \tau_{\text{C}}(\boldsymbol{q}, b), \qquad (2.32)$$

$$k_{2}^{\text{Callaway}} = \frac{\mu}{3V} \sum_{q,b}^{3N} \frac{c(q,b)v_{\text{G}}(q,b)\tau_{\text{C}}(q,b)}{v_{\text{P}}(q,b)\tau_{\text{N}}(q,b)}.$$
(2.33)

Despite the purely phenomenological inclusion of the contribution of the N-processes in the collision term, without clear physical elucidation of their role in the restoring of the equilibrium phonon distribution, Callaway's treatment had great success in interpreting experimental results over the simplest (single) relaxation-time approximations which neglect the second term on the right-hand side of Equation 2.22 [17]. Even using the simplifying assumptions of the Debye theory, Callaway's expression for the lattice thermal conductivity [36], consisting of two terms, is able to reproduce the experimental data with a reasonably good accuracy [17]. Thus, Callaway's treatment remarkably demonstrates that in order to properly fit the experimental data on lattice thermal conductivity, one needs to construct the collision term in the Boltzmann equation in such a reasonable way that underlines the roles of the U-processes and the N-processes in restoring equilibrium and the displaced phonon distributions, respectively. As a result, this can be considered as a strong indication that a relevant solution of the Boltzmann equation should eventually lead to the decomposition of the lattice thermal conductivity into two distinct contributions.

2.1.8 Real Space and Phonon Space

The analysis of the phonon heat conduction in crystal structures is usually done in the phonon or wave-vector spaces. Thermal conductivity is influenced by the phonon's characteristics, such as mean free path, velocity, etc. The design and synthesis of new materials are realized in real space, while the phonon space is more convenient for the analysis of their thermal properties [48]. Hence, defining a relationship between the real space and the phonon space is essential for the effective application of information on lattice dynamics. In this research, molecular dynamics simulation is considered where the Newton laws of motion have been used to predict the position and momentum space trajectories of a classical particles system. The atomic structures and suitable interatomic potentials are inputs that can be achieved from experimental data or *ab initio*¹⁶ results. Molecular dynamics simulation can also provide an opportunity to investigate the phonon dynamics in greater detail [2].

2.2 The Molecular Dynamics Method

Thermal transport phenomena have been an attractive research topic for many years, and as a result many methods, such as Molecular Dynamics [49], Monte Carlo [18] and the Boltzmann transport equation, have been used to investigate thermal transport numerically [50]. MD is a computer simulation method where the time evolution of a set of interacting atoms is followed by numerically integrating their equations of motion. It has two different types: the first type is *ab initio* molecular dynamics and the second type is classical molecular dynamics¹⁷ [1]. At high temperatures (approximately above the Debye temperature) classical MD simulations have been successfully used to calculate thermal conductivity [1].

During phase transformations or recrystallization processes, latent heat gives rise to a thermal gradient in the local region surrounding an interface. As a result, the interface mobility, which is one of the most important properties of an interface, can be

¹⁶ The term *ab initio* means that from first principles one can make a rational approximation of the solution of the Schrödinger equation.

¹⁷ Classical molecular dynamics calculates the time dependent behaviour of a molecular system.

affected [51]. Despite the importance of interface mobility in understanding the physics underlying the kinetics of phase transformation or recrystallization, there are only a few successful experimental measurements of interface mobility [52, 53]. Currently, much of our understanding of the kinetic properties of interfaces has been derived from MD simulations [51, 54, 55]. However, one would expect that the classical MD simulations of metals underestimate the magnitude of the thermal conductivity due to the absence of the free-electron contribution [9]. Accordingly, without an accurate knowledge of the thermal conductivity it is difficult to assess how well classical MD simulations of metals, together with EAM interatomic potentials [40], are able to predict the kinetic properties of interfaces. Indeed, there is a concern in predicting non-equilibrium flows in the local region surrounding an interface, since the free-electron contribution to the thermal conductivity can outweigh the phonon contribution [9].

2.2.1 Thermodynamic Ensembles and Equations of Motion

MD uses the classical equation of motion, which comes from the second law of Newton, and is expressed as $\vec{F}_i = m_i \vec{a}_i$, where \vec{F}_i is the force [kgm/s²], m_i is the mass [kg], and \vec{a}_i is the acceleration [m/s²]. The integration of Newton's equation in MD simulations is usually achieved through several algorithms, including the velocity Verlet, Verlet leapfrog, and Gear predictor-correction algorithms, that are dependent on the thermodynamic ensembles [12]. The most natural ensemble¹⁸ is the *NVE* (micro canonical) in which the number of atoms *N*, the system volume *V* and the total energy *E*, are all fixed quantities, while the temperature and pressure of the system fluctuate around their average values. In other ensembles, the temperature and pressure of the system can be set through the application of different thermostats¹⁹ and barostats.²⁰ In the *NVE* ensemble, the equation of motion for particle *i* is expressed as $\mathbf{F}_i = \frac{d\mathbf{p}_i}{dt}$. In this study, the Verlet leap-frog algorithm has been used, where the positions and momenta are offset by a half time step [56], as shown in Equations 2.34 and 2.35:

¹⁸ The most natural ensemble is the *NVE* since Newton's equations of motion lead naturally to the conservation of energy.

¹⁹ A thermostat is a part of a control system which adjusts the system's temperature near a selected set point.

²⁰ A barostat is a device used to preserve constant pressure in a closed chamber.

$$\boldsymbol{r}_{i}(t+\Delta t) = \boldsymbol{r}_{i}(t) + \boldsymbol{p}_{i}\left(t+\frac{\Delta t}{2}\right)\frac{\Delta t}{m_{i}},$$
(2.34)

$$\boldsymbol{p}_{i}\left(t+\frac{\Delta t}{2}\right) = \boldsymbol{p}_{i}\left(t-\frac{\Delta t}{2}\right) + \boldsymbol{F}_{i}\Delta t, \qquad (2.35)$$

where, m_i is the mass of atom *i*, whereas r_i and p_i are the position and momentum vectors for atom *i*, respectively.

When the MD simulations run with a thermostat, the system is said to be in the *NVT* (canonical) ensemble where the equation of motion is modified with the damping parameter η as: $\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \eta \mathbf{p}_i$ [2]. The authors of [2] described that the damping parameter changes in time according to the following ordinary differential equation: $\frac{d\eta}{dt} = \frac{1}{\tau_T^2} \left(\frac{T}{T_{set}} - 1\right)$, where τ_T is the reservoir-system time constant and T_{set} is the desired temperature. When the independent variables are the system mass, pressure and temperature, the system is said to be in the *NPT* (isobaric-isothermal) ensemble. In this case, the equation of motion is expressed as $\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i - \eta \mathbf{p}_i - \epsilon \mathbf{p}_i$ with the time history of parameter ϵ being specified as: $\frac{d\epsilon}{dt} = \frac{1}{\tau_P^2} \left(\frac{P}{P_{set}} - 1\right)$, where τ_P is the pressure [56]. The Nosé-Hoover thermostat is used to generate suitable temperature fluctuations for the *NPT* and *NVT* ensembles. The Nosé-Hoover barostat can produce the appropriate pressure fluctuations for the *NPT* ensemble [2].

2.2.2 Periodic Boundary Condition

MD simulations consist of thousands of atoms in a small system. As a result, a periodic boundary condition is used to prevent problems with boundary effects due to the finite size of the simulation cell. This ensures that the number density of the atoms in the simulation domain and the momentum of the whole system are preserved [57]. In this case, when a particle moves in the central cell, its periodic image particles in each of the neighbouring cells move in the same direction, as shown in Figure 2.7.



Figure 2.7: Schematic illustration of the effect of the periodic boundary conditions in a three dimensional system.

2.2.3 The Limitations of the MD Method

As with any simulation technique, MD simulations have some limitations:

- (i) The time limitation is the most common problem in MD simulations. It is usually within 1 μ s. The simulation time should be much longer than the relaxation time of the quantities as systems tend to become slower around phase transitions [58].
- (ii) The size limitation is the second important limitation. It should be within the length scales ranging between 1 nm and 1 μ m. Because the correlation lengths may increase or even diverge around phase transitions, the results are not reliable when they become equivalent with the size of the MD cell [59].
- (iii) In MD simulations, the temperature should be above the critical temperature where the classical description of the atomic dynamics is applicable. In this case, at low temperatures the quantum effects become important in any system [58].

2.2.4 The Interaction Model: Lennard-Jones Potential

The Lennard-Jones pair potential model is a mathematical model that describes the potential energy U_{ij} between two particles. The potential energy changes with the distance between the interacting bodies r_{ij} [19, 60]:

$$U_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \qquad (2.36)$$

where, r_{ij} is the distance between the centres of two particles, σ is the finite distance and ε is the depth of the potential well. Figure 2.8 shows the Lennard-Jones potential versus the separating distance (r_{ij}) . The parameters ε and σ are chosen to fit the physical properties of the material [60]. The first and second terms in the right-hand side of Equation 2.36, $\left(\left(\frac{1}{r_{ij}}\right)^{12}, \left(\frac{1}{r_{ij}}\right)^{6}\right)$, are dominated by short and large distances, respectively. This potential is strongly repulsive as two uncharged atoms come too close to each other; however, this potential is weakly attractive when they approach one another from a distance. Also, at the minimum of the Lennard-Jones potential, when the pair of atoms tend to go into a separation, distance is at equilibrium. Nevertheless, the depth of the well increases with the intensity of the force [19].



Figure 2.8: Lennard-Jones potential (U) versus separating distance. It shows regions of attraction and repulsion. R is the distance between the centres of two particles, σ is the chosen finite distance and ε is the depth of the potential well.

2.2.5 The Embedded-Atom Method (EAM)

Introduced by Daw and Baskes in 1984 [40], the EAM is a semi-empirical method²¹ that describes the energy between atoms. As each atom embeds in a host lattice including all other atoms, they nominated the theory of the embedded-atom method [40]. The EAM is generally used in several different types of calculations, such as MD, Monte Carlo, and energy minimization [61].

In the EAM formalism, the potential energy of an atom *i*, is defined as: $E_i = F_{\alpha} \left[\sum_{i \neq j} \rho_{\beta} (r_{ij}) \right] + \frac{1}{2} \sum_{i \neq j} \phi_{\alpha\beta} (r_{i,j})$, where $r_{i,j}$ is the distance between atom *i* and *j*, $\phi_{\alpha\beta}$ is a pair-wise potential function, ρ_{β} is the electron density from atom *j* of type β at location of atom *i*, F_{α} is the embedding function for type α , and α and β are the element types of atoms *i* and *j*, respectively [62]. This equation describes that the interaction energy between two atoms depends on the distance between them and the environment around them [63].

In the form of embedding energy, $F_{\alpha}[\sum_{i\neq j} \rho_{\beta}(r_{ij})]$, the EAM presents a proper definition of the volume dependent energy that is added in the pair-potential theory to define the elastic properties of metals [63].

2.2.6 The Direct Method

The direct method is a non-equilibrium method that calculates the thermal conductivity from the ratio of a heat flux and temperature gradient $(k = -Q / (\partial T / \partial x))$. In this method, two types of simulation cell can be used: with either fixed or periodic boundary conditions. A fixed end boundary is divided into N_s equal slabs and it is suitable for finite-sized structures where heat flows in one direction from the hot slab to the cold slab. For periodic boundary conditions, the simulation cell is broken into N_s equal slabs perpendicular to the x direction and they are repeated periodically. As shown in Figure 2.9, the hot slab is located at the centre part of this box (0) and cold slabs are located at

²¹ Semi-empirical methods are based on the Hartree-Fock formalism by introducing functions with empirical data.

 $N_s/2$ and $-N_s/2$. Thermal energy is transferred from the hot slab to the cold slab [4]. The simulation cells consist of tens or hundreds of thousands of atoms that need a hundred thousand time steps for converging. The direct method predicts the thermal conductivity directly from the simulation in one direction and is an appropriate method for studying finite structures such as thin films [2].



Figure 2.9: (a) Schematic diagram of the periodic simulation cell used in the non-equilibrium method. Hot slab (0) and cold slabs (at $N_s/2$ as well as at $-N_s/2$) are shown in red and blue colours, respectively. There is a heat flow out from both sides of the hot slab. (b) Schematic diagram of the fixed boundary condition.

2.2.7 The Green-Kubo Method

Equilibrium MD simulations can also be used to compute the thermal conductivity of materials [1, 3, 64, 65]. It has been demonstrated that equilibrium MD, combined with the Green-Kubo formalism, is an effective method to estimate thermal conductivity and to also calculate the phonon transport properties of materials. A brief overview of the application of this method is given below.

In the Green-Kubo method, which is based on an equilibrium system for an isotropic material, the thermal conductivity, k, is given in terms of the time integral of the HCACF, $\langle J(t)J(0) \rangle$ by Equation 2.37 [66]:

$$k = \frac{1}{3Vk_BT^2} \int_0^\infty \langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle dt, \qquad (2.37)$$

53

where, V is the volume of the simulation cell, $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, J is the heat current vector and t is the time. In general, the heat current vector is described by the following equation:

$$J = \frac{d}{dt} \left(\sum_{i} e_{i} \boldsymbol{r}_{i} \right) = \sum_{i} e_{i} \boldsymbol{v}_{i} + \sum_{i} \boldsymbol{r}_{i} \frac{de_{i}}{dt}, \qquad (2.38)$$

where, the summations are over the atoms in the system, and e_i , r_i , v_i are the total energy, radius-vector and velocity vector of the *i*-th atom, respectively. The first term in Equation 2.38 on the right side is associated with convection, whilst the second is associated with conduction. The implementation of the Green-Kubo method has no effect on the atomic dynamics and the system temperature is uniform and constant. In addition, this elegant but time consuming method allows for the calculation of the temperature dependence of the thermal conductivity. Furthermore, one can use equilibrium MD simulations to investigate the phonon dynamics, for example, by analysing the HCACF [2].

2.2.8 Overview of Previous Works

MD simulation was introduced by Alder and Wainwright at Lawrence Livermore National Laboratory [67]. They used a "hard sphere"²² model that described their dynamic properties without approximations. This was the first time the molecular simulation technique was used [67]. Rahman then used the Lennard-Jones potential function to define the potential interaction in argon (Ar) particles, and this algorithm has been used in many molecular dynamic simulation codes [68]. It was clearly shown that the phase space trajectories of atoms or molecules can be computed by molecular dynamics [69].

The Green-Kubo method has been successfully used to calculate the thermal conductivity of some materials during the last decades [1-3, 65]. Ladd et al. [65]

²² The hard sphere model is a perfect model of atoms motions in a container.

considered a f.c.c. crystal model that used MD and the Green-Kubo method to compute thermal conductivity. They also calculated the lifetimes of all the phonons using MD and developed a harmonic perturbation theory²³ in order to determine the thermal conductivity. They found that the results of the Green-Kubo method complied with the phonon perturbation theory at low temperature. It was also the first time that the Green-Kubo method was used to calculate thermal conductivity in three dimensional solids. In addition, He et al. [4] investigated the heat transport in bulk silicon (Si), germanium (Ge) and silicon germanium (SiGe) alloys using equilibrium molecular dynamics and the Boltzmann Transport Equation, with $10^5 - 10^6$ atoms in the temperature range close to or above the Debye temperature. Consequently, their results showed that the equilibrium MD was a strong method to describe the thermal transport at high temperature conditions close to the Debye temperature [4]. Moreover, equilibrium MD simulations also provide a detailed atomistic interpretation of the different contributions to the conductivity. In addition, Tretiakov and Scandolo [64] and Sellan et al. [70] studied the system size effects in the MD thermal conductivity predictions. They found that the size effects in the thermal conductivity were negligible. Schelling et al. [71] used non-equilibrium and equilibrium MD simulations to predict the thermal conductivity of silicon. They found that there is a good agreement between the two techniques at a temperature of 1000K.

In the last decade, McGaughey and Kaviany [1] investigated the thermal conductivity of Ar by using MD simulations with the Green-Kubo method. Their results showed that, at low temperature, the HCACF has two stages of decay. This was first observed in the HCACF in MD simulations [65]. McGaughey and Kaviany [1, 2] fitted the HCACF to a sum of two exponential functions as suggested by Che et al. [72]:

$$\frac{1}{3}\langle \boldsymbol{J}(t)\boldsymbol{J}(0)\rangle = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right),\tag{2.39}$$

where, $\langle ... \rangle$ means an average taken at the thermodynamic equilibrium, J is the microscopic heat current vector per unit volume, t is the time, τ_1 and τ_2 are the time

²³ Perturbation theory is a set of approximation schemes that are related to mathematical perturbation for describing a complicated quantum system in a simpler condition.

constants, and A_1 and A_2 are the strengths, while the subscripts "1" and "2" refer to the acoustic short- and long-range phonons, respectively. McGaugey and Kaviany [1, 2] interpreted the two-stage behaviour of the HCACF of f.c.c. Ar in the context of the phonon mean free path (or its temporal representation – the mean phonon relaxation time). The first and second terms on the right side of Equation 2.39 describe two time scales of the decay, which are associated with the acoustic short- and long-range phonons respectively (optical phonons cannot be present, as the unit cell is monatomic). Physically, the lower bound on the mean free path is given by half of the phonon wavelength, known as the Cahill and Pohl limit [1, 2, 73]. Hence, according to [1, 2], the first time scale in the HCACF decomposition, described by the mean phonon relaxation time τ_1 , corresponds to those phonons with a mean free path equal to one half of their wavelength. The second time scale, described by the mean phonon relaxation time τ_2 , is longer, and corresponds to the acoustic phonons with mean free paths longer than one half of their wavelength [10,14]. With Equations 2.37 and 2.39 in hand, the thermal conductivity is given by:

$$k_{ph} = \frac{1}{Vk_B T^2} (A_1 \tau_1 + A_2 \tau_2) = k_1 + k_2, \qquad (2.40)$$

McGaughey and Kaviany [1, 2] pointed out that in the decomposition given by Equation 2.40, all of the temperature dependence of the thermal conductivity is contained in k_2 , while the short-range component, k_1 , shows little temperature dependence. These authors also argued [1, 2] that phonons with a mean free path of the order of their wavelengths (as assumed for the acoustic short-range phonons) should have wavelengths of the order of a few atomic spacing, i.e., they are supposed to be in the higher frequency range of the acoustic branches. This suggests that τ_1 and k_1 should be strong functions of the coordination of the atoms [1, 2]. Thus, the small temperature dependence of k_1 is a result of the coordination of the atoms remaining constant as the density changes with temperature. Overall, the predicted temperature dependence of the thermal conductivity of the MD model of the f.c.c. Ar was found to be in agreement with the trend and magnitude of the experimental data [1, 2].

Using the Lennard-Jones pair potential with a longer cut-off radius, Kaburaki et al. [3] also demonstrated that the temperature dependence of the experimentally measured thermal conductivity of f.c.c. Ar can be reproduced with good accuracy by the equilibrium MD simulation in conjunction with the Green-Kubo method. In addition, the authors [3] found that the absolute values of the thermal conductivity and the twostage relaxation of the HCACF are in agreement with the results reported by McGaughey and Kaviany [1, 2]. However, Kaburaki et al. [3] differ from the previous authors [1, 2] in the interpretation and analysis of the HCACF. They attribute the first-stage of relaxation to the single-particle motions sampling the local environment of the system, whereas McGaughey and Kaviany [1, 2] regard this relaxation to be associated with the short wavelength acoustic phonons, as mentioned above. Furthermore, Kaburaki et al. [3] pointed out that the first stage of relaxation is not properly described by a single exponential function. Indeed, they observed a slight plateau (shoulder) for short times at low and intermediate temperatures, which had not been noted previously. The authors [3] suggested that it may be associated with the collective oscillations, possibly of a transverse or shear nature, and highly damped. Nonetheless, Kaburaki et al. [3] also expect that, overall, the first stage of the relaxation of the HCACF will be relatively insensitive to temperature because the local environment surrounding a particle does not change much, even when the system goes from a low-temperature solid to the liquid phase and loses long-range ordering. Regarding the second stage of the relaxation of the HCACF, Kaburaki et al. [3] are in agreement with McGaughey and Kaviany [10,14] that the underlying process is the lattice vibrations or the phonons. According to [3], this part is also expected to be sensitive to temperature variations because long-range ordering is needed to sustain the collective motions.

Thus, the commonly accepted main feature of the HCACF of f.c.c. Ar predicted by the equilibrium MD simulation with the Lennard-Jones pair potential is a two-stage decay (relaxation) [1-3]. This was in contrast to the Peierls theory of thermal conductivity, which is consistent with a single-stage decay of the HCACF [1-3, 65]. Ladd et al. [65] quantitatively examined the approximations involved in deriving the Peierls phonon-transport expression for the lattice thermal conductivity. They demonstrated that the Peierls expression of the heat current is only an approximation to the full atomistic Irving-Kirkwood expression [74], which disregards the short-time contribution to the HCACF. Unfortunately, no results could be found in the literature regarding phonon thermal conductivity calculations in metals within the framework of the EAM using equilibrium MD simulations in conjunction with the Green-Kubo formalism. However, aside from the aforementioned importance of knowledge of the phonon thermal conductivity in problems dealing with predicting the kinetics properties of interfaces in metals using classical MD simulations, it is of fundamental interest to investigate the phonon dynamics in an EAM potential model by analysing its HCACF in comparison with the HCACF of the Lennard-Jones pair potential model of argon.

Chapter 3: Research Methodology

Following on from the discussion in Chapter 1, a fundamental understanding of the generic features of the lattice thermal conductivity and phonon dynamics can be advanced, in particular, by a systematic MD study of the HCACF of a set of high-quality models of isostructural materials with a simple crystal lattice. An appropriate choice for this study is a set of MD models of f.c.c. metals such as Cu, Ni, Al, and Ag. The choice was mostly determined by the availability of state-of-the-art first principles-based many body potentials developed for these metals within the framework of the EAM [5-8]. In this research, the interaction between the atoms in the MD model of f.c.c. Ni are described by using two different EAM interatomic potentials developed by Mishin et al.. The first one nominated was Ni_{EAM1} (published in 1999) [7], and the second was Ni_{EAM2} (published in 2004) [6].

In general, the total energy of an atom *i* is represented in the EAM model [5]as:

$$e_{i} = \frac{1}{2}m_{i}v_{i}^{2} + F_{\mu i}(\bar{\rho}_{i}) + \frac{1}{2}\sum_{j(\neq i)}V_{\mu_{i}\mu_{j}}(r_{ij}), \qquad (3.1)$$

in this equation the $\frac{1}{2}m_iv_i^2$ describes the kinetic energy, where m_i is the mass of the atom, v_i is the absolute value of the velocity vector of the atom, $F_{\mu_i}(\bar{\rho}_i)$ is the embedding energy of the atom as a function of the host electron density $\bar{\rho}_i$ induced at site *i* by all other atoms in the system, and $V_{\mu_i\mu_j}(r_{ij})$ is the pair interaction potential as a function of the distance r_{ij} between atoms *i* and *j* (μ_i and μ_j indicate whether the functional form for the species of atom *i* or atom *j* are used). The host electron density $\bar{\rho}_i$ is given by:

$$\bar{\rho}_i = \sum_{j(\neq i)} \rho_{\mu i}(r_{ij}), \tag{3.2}$$

where, $\rho_{\mu_j}(r_{ij})$ is the electron density induced by an atom *j* at the location of atom *i*. In particular, for a monatomic system this model involves three potential functions, $F(\bar{\rho})$, V(r) and $\rho(r)$, which can be treated as some fitting functions that have to be reasonably parameterized. In this work, the interactions between atoms in the MD model of f.c.c. metals are described by using an EAM potential developed by Mishin et al. [5-8]. The potential functions were obtained by fitting to the experimental and first principles data. This potential accurately reproduced the lattice parameter, cohesive energy, elastic constants, phonon frequencies, thermal expansion, lattice-defect energies, and other relevant properties of the metals. The melting temperature of Cu, Al, Ni_{EAM2} and Ag predicted by this potential were 1327 K, 1042 K, 1701 K and 1267 K, which were in good agreement with the experimental values of 1357 K, 933 K, 1728 K and 1235 K, respectively [75].

Following on from Equations 2.38, 3.1 and 3.2, the Cartesian components of the heat current vector in a system using an EAM Potential model can be represented as [76, 77]:

$$J_{q\alpha} = \frac{1}{V} \frac{d}{dt} \left(\sum_{i} e_{i} x_{i\alpha} \right) = \frac{1}{V} \sum_{i} e_{i} x_{i\alpha} - \frac{1}{V} \sum_{i} \Omega_{i} \sigma_{i\alpha\beta}^{(p)} v_{i\beta}, \qquad (3.3)$$

where:

$$\sigma_{i\alpha\beta}^{(p)}\Omega_{i} = \sum_{j(\neq i)} \left[\frac{\partial F_{\mu j}(\bar{\rho}_{i})}{\partial \bar{\rho}_{i}} \frac{\partial \rho_{\mu i}(r_{ij})}{\partial r_{ij}} + \frac{1}{2} \frac{\partial V_{\mu i\mu j}(r_{ij})}{\partial r_{ij}} \right] \frac{x_{ij\alpha} x_{ij\beta}}{r_{ij}},$$
(3.4)

 Ω_i is the volume of atom *i*, the symbols α and β enumerate the Cartesian components of the vectors and tensors: $x_{i\alpha}$, $x_{ij\alpha}$ (or $x_{ij\beta}$) and $v_{i\alpha}$ (or $v_{i\beta}$) are the components of the vectors \mathbf{r}_i , \mathbf{r}_{ij} and \mathbf{v}_i , respectively, while $\sigma_{i\alpha\beta}^{(p)}$ denotes the potential energy contribution to the components of the stress tensor of atom *i*. For symbols that enumerate the Cartesian components of the vectors and tensors, the Einstein summation notation is implied.

In this study, a wide temperature range for each metal was considered (see Table 3.1 for details). It has previously been argued [72] that the dominant contributors to the thermal transport in crystals are the long wavelength phonons which are active even at low temperatures. Moreover, there is no evidence to support the use of quantum corrections with the classical MD thermal conductivity predictions at relatively low temperatures, up to around one-tenth of the Debye temperature [2]. This is in contrast to the specific heat, where the high-frequency (short wavelength) modes become excited as the temperature of the quantum system is increased, leading to a significant temperature dependence up to the Debye temperature [2, 72].

All the reported data were averaged over the MD simulations in the *NPT* (isothermal-isobaric), *NVT* (canonical) and *NVE* (microcanonical) ensembles at zero pressure. A Nosé-Hoover thermostat was used for the *NPT* and *NVT* ensembles and a Nosé-Hoover barostat was used for the *NPT* ensemble. The cubic simulation block was composed of 4000 atoms with periodic boundary conditions in all three directions. The MD simulations were started in the *NPT* ensemble. The obtained equilibrium (zero pressure) value of the system volume at each temperature was subsequently used as an input for the MD simulations in the *NVT* and *NVE* ensembles. The obtained temperature dependences of the equilibrium (zero pressure) atomic volumes $\Omega = V/N$ of the f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag models are shown in Figure 3.1. The atomic volume versus temperature data can be satisfactorily fitted by the equation:

$$\Omega = \Omega_0 + \alpha_\Omega T + \beta_\Omega T^2, \qquad (3.5)$$

with the parameters introduced in Table 3.2.

Metals	Temperature (K)	Temperature Step	
Cu	40,1300	10 K in temperature range 40-100 K	
Cu	40-1300	100 K in temperature range 100-1300 K	
Ni _{EAM1} , Ni _{EAM2}	100-1700	100 K	
Al	100-1000	100K	
Ag	40,1200	10 K in temperature range 40-100 K	
	40-1200	100 K in temperature range 100-1200 K	

Table 3.1: Temperature range	s for f.c.c. Cu,	, Al, Ni _{EAM1} , I	Ni _{EAM2} and Ag.
------------------------------	------------------	------------------------------	----------------------------

Table 3.2: Atomic volume parameters for the quadratic equations (see Equation 3.5) in the cases of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag.

Parameters	Ω_0	$lpha_\Omega$	eta_Ω
Metals	$\left(\frac{nm^3}{atom}\right)$	$\left(\frac{nm^3K^{-1}}{atom}\right)$	$\left(\frac{nm^3K^{-2}}{atom}\right)$
Cu	11.81×10 ⁻³	4.8×10 ⁻⁷	1.6×10 ⁻¹⁰
Ni_{EAM1}	10.92×10 ⁻³	3.1×10 ⁻⁷	5.7×10 ⁻¹¹
Ni _{EAM2}	10.9×10 ⁻³	1.97×10 ⁻⁷	1.03×10 ⁻¹⁰
Al	16.61×10 ⁻³	5.01×10 ⁻⁷	4.04×10 ⁻¹⁰
Ag	17.1×10 ⁻³	9.64×10 ⁻⁷	2.18×10 ⁻¹⁰







(b)



(d)



(e)

Figure 3.1: Temperature dependence of the equilibrium atomic volumes of the EAM potential models [5-8] of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1} , (d) Ni_{EAM2} , and (e) Ag according to the MD simulations of the *NPT* ensemble. The solid line shows the fit of the MD data by Equation 3.5.

After the equilibration of the system at a given temperature by performing a run of 150 ps ($10^5\Delta t$, Δt =1.5fs is the time-step), the HCACF was calculated during a production run. The length of the production run, as well as the correlation length and the number of time origins used in the HCACF calculations, were varied depending on the temperature (see Table 3.3 for details). This is because the time of the HCACF decay increases as the temperature decreases. It should be noted that, in order to set a given temperature for the *NVE* ensemble, the first 75ps ($5 \times 10^4 \Delta t$) of the equilibration run were always done in the *NVT* ensemble.

Metals	Temperature (K)	Length of production run (ps)	Correlation length (ps)	Number of time origins
	40 - 90	15000	150	$\sim 10^{6}$
Cu	100 - 200	15000	75	~10 ⁶
Cu	300	3000	30	~2×10 ⁵
	400 - 1300	1500	15	~10 ⁵
Al	100	15000	75	~107
	200-300	15000	30	~107
	400-1000	15000	15	~107
NT:	100-300	15000	30	~107
INIEAM1	400-1700	15000	15	~107
	100	15000	150	~107
NI:	200-300	15000	60	~107
N1EAM2	400-600	15000	30	~107
	700-1700	15000	15	~107
Ag	40-90	15000	150	~10 ⁷
	100-300	15000	30	~107
	300-1200	15000	15	~107

Table 3.3: Details of the HCACF calculations.

According to the Debye theory, the shortest wavelength λ_D that can be propagated through a lattice is $(4\pi\Omega/3)^{1/3}$, where Ω is the atomic volume [21]. For an f.c.c. lattice with a lattice constant (*a*), we have $\Omega = a^3/4$, so that:

$$\lambda_D = \left(\frac{\pi}{3}\right)^{1/3} a \tag{3.6}$$

Then, the Debye frequency can be estimated as:

$$\omega_D = \frac{2\pi s}{\lambda_D} \tag{3.7}$$

where *s* is the average speed of sound (or phonon speed). Next, in the Debye approximation, the average speed of sound s_{δ} in a given direction δ of a crystal can be assessed as the harmonic mean of both the cubes and squares (see Equations 3.8 and 3.9 [21]) of the speeds of sound for longitudinal and transvers polarizations.

$$\frac{3}{s_{\delta}^{3}} = \frac{1}{s_{l,\delta}^{3}} + \frac{1}{s_{t_{1},\delta}^{3}} + \frac{1}{s_{t_{2},\delta}^{3}},$$
(3.8)

$$\frac{3}{s_{\delta}^2} = \frac{1}{s_{l,\delta}^2} + \frac{1}{s_{t_1,\delta}^2} + \frac{1}{s_{t_2,\delta}^2},\tag{3.9}$$

where $s_{l,\delta}$, $s_{t_1,\delta}$ and $s_{t_2,\delta}$ are the phonon speeds of the longitudinal mode and the two transverse modes, respectively, in the given direction δ . Normally, the longitudinal mode has the highest speed, while the two transverse modes have lower speeds. This reflects the fact that the longitudinal mode is essentially a compression wave, for which the elastic restoring forces are stronger than for the transverse (or shear) waves [21]. The phonon speeds of the three modes in three low-index directions [100], [110] and [111] in a cubic crystal are given by [21]:

$$s_{l,[100]} = \sqrt{\frac{C_{11}}{\rho}}, \quad s_{t_1,[100]} = s_{t_2,[100]} = \sqrt{\frac{C_{44}}{\rho}}$$
 (3.10)

in the [100] direction:

$$s_{l,[110]} = \sqrt{\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}}, \qquad s_{t_1,[110]} = \sqrt{\frac{C_{44}}{\rho}}, \qquad s_{t_2,[110]} = \sqrt{\frac{C_{11} - C_{12}}{2\rho}}$$
(3.11)

in the [110] direction, and

$$s_{l,[111]} = \sqrt{\frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho}}, \quad s_{t_1,[111]} = s_{t_2,[111]} = \sqrt{\frac{C_{11} - C_{12} + C_{44}}{3\rho}}$$
(3.12)

in the [111] direction. In Equations 3.10 – 3.12, C_{11} , C_{12} and C_{44} are the elastic constants and ρ is the mass density. The following calculations estimate the average phonon speed in the f.c.c. Cu, Al, Ni and Ag models as:

$$s = \frac{1}{3} \left(s_{[100]} + s_{[110]} + s_{[111]} \right), \tag{3.13}$$

where $s_{[100]}$, $s_{[110]}$ and $s_{[111]}$ are the average phonon speeds in the three low-index directions [100], [110] and [111], respectively, as determined by Equations 3.8 and 3.9, using Table 3.4. Finally, using Equations 3.6, 3.4 and 3.13, we can estimate the Debye temperature of the MD models for f.c.c. Cu, Al, Ni and Ag as:

$$T_D = \frac{\hbar\omega_D}{k_B},\tag{3.14}$$

where, \hbar is the Planck constant divided by 2π (reduced Planck constant) (see details in Table 3.5).

Table 3.4: The elastic properties of f.c.c. Cu, Al, Ni and Ag according to Mishin et al. [5-8],
Debye wavelength and the phonon speeds of the longitudinal mode and two transverse modes
in three direction for f.c.c. Cu, Al, Ni and Ag.

Parameters	Units	Cu	Al	Ni	Ag
а	Å	3.615	4.05	3.52	4.09
<i>C</i> ₁₁	GPa	169.9	114	247	124.2
<i>C</i> ₁₂	GPa	122.6	61.6	148	93.9
C ₄₄	GPa	76.2	31.6	125	46.4
λ_D	Å	3.671	4.113	3.575	4.153
$S_{l,[100]}$	km/s	4.36	6.501	5.26	3.44
$S_{t_1,[100]}$	km/s	2.92	3.42	3.74	2.11
$S_{t_2,[100]}$	km/s	2.92	3.42	3.74	2.11
$S_{l,[110]}$	km/s	4.99	6.65	6.01	3.85
$S_{t_1,[110]}$	km/s	2.92	3.42	3.74	2.11
$S_{t_2,[110]}$	km/s	1.63	3.12	2.35	1.203
$S_{l,[111]}$	km/s	5.18	6.703	6.24	3.98
$S_{t_1,[111]}$	km/s	2.15	3.22	2.89	1.56
$S_{t_2,[111]}$	km/s	2.15	3.22	2.89	1.56

Table 3.5: The average speed of sound, Debye frequency and Debye temperature of f.c.c. Cu, Al, Ni and Ag for the first and second cases. All quantities presented in this table are introduced in the text.

		Cu		Al		Ni		Ag	
Quantities	Units	Cube	Square	Cube	Square	Cube	Square	Cube	Square
		Eq	Eq	Eq	Eq	Eq	Eq	Eq	Eq
<i>s</i> _[100]	km/s	3.19	3.23	3.83	3.93	4.05	4.09	2.32	2.37
<i>S</i> _[110]	km/s	2.2	2.37	3.66	3.77	3.1	3.27	1.62	1.75
<i>S</i> _[111]	km/s	2.43	2.52	3.62	3.74	3.25	3.36	1.77	1.84
S	km/s	2.61	2.71	3.7	3.81	3.47	3.58	1.91	1.99
ω_D	THz	44.6	46.34	56.6	58.2	61	62.9	28.8	30
T_D	Κ	341	354	432	445	466	481	220	229

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used in this work to carry out the molecular dynamic simulations. The fundamental structure of the MD simulation is shown in the following flowchart (see Figure 3.2):



Figure 3.2: Basic structure of the MD simulation.

As a sensitivity test of the system size, calculations were also performed with the cubic simulation block composed of 32,000 atoms (it has a two times longer side length) at various temperatures. The results will be explained in the following chapters.

Chapter 4: The Heat Current Autocorrelation Function (HCACF)

Figure 4.1 shows, as an example, the HCACF calculated over wide temperature ranges (see Table 3.1) for the *NPT*, *NVT* and *NVE* ensembles, as well as averaged over the three ensembles. Each curve was normalized by its zero time value to allow for a comparison between the different temperatures. It can be seen that all four curves sit very close to each other at all temperatures. This fact is reassuring that the calculations in all three ensembles are equivalent.

The temporal decay of the HCACF of the f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1} , (d) Ni_{EAM2} and (e) Ag models (see Figure 4.1) at low and intermediate temperatures showed a more complex behaviour than the two-stage decay observed in [1, 2] for the HCACF of the f.c.c. Ar model, which was described by two exponential functions (see Equation 2.39).

In Figure 4.1(a), the first stage of the HCACF of the f.c.c. Cu model is an initial rapid decay of up to 0.2 - 0.25 ps, which is similar to the first stage of the HCACF decay of the f.c.c. Ar model [1, 2]. This stage was followed by a peak of around 0.5 ps in the temperature range 40 - 800 K. The intensity of the peak decreased as the temperature increased. At 900 K, it transformed to a shoulder which diminished almost entirely at 1200 K. Thus, at very high temperatures, of above 1200 K, the first stage decay was directly followed by a longer second stage decay. As a result, in the temperature range 900 - 1100 K, indicating a shoulder after the first decay, the HCACF of the f.c.c. Cu model is similar to the HCACF of the f.c.c. Ar model in [3] at low and intermediate temperatures. It was surmised that the peak found in the f.c.c. Cu model was related to the transition between the two stages of the heat dissipation. It may be activated by the influence of the positive (non-zero) Cauchy pressure $C_{12} - C_{44} \approx 46.4$ GPa in f.c.c. Cu [5] on the phonon dynamics. As mentioned above, the longitudinal phonons are essentially compression waves, so that the positive Cauchy pressure may affect their scattering whilst not affecting (or affecting much less) the scattering of the transverse phonons which are shear waves. In any case, since a rise of the HCACF after the first stage of the heat dissipation was observed, it was assumed that due to the positive
Cauchy pressure, either the scattering of the acoustic long-range phonons slows down or the scattering of the acoustic short-range phonons accelerates, or both processes take place. This is stated here simply as a suggestion without any justification. A verification of the proposition can be carried out during a systematic MD study of the HCACF of a monatomic f.c.c. crystal with a pair potential which uses an accompanying volumedependent energy to manage the elastic properties of the model [40]. By varying the volume-dependent energy, one can find the dependence of the HCACF on the Cauchy pressure. Another approach would be to carry out a systematic MD study of the HCACF of a monatomic f.c.c. crystal with an EAM potential. It is known that for an elemental crystal, the Cauchy pressure is determined by the curvature of the embedding energy at equilibrium [40]. Hence, by varying the curvature, one can also find the dependence of the HCACF on the Cauchy pressure. These types of studies could provide a more scientific grounding for the proposition. These areas are expected to be the subjects of future work in this direction but lie beyond the scope of the present research.

A two-stage decay of the HCACF of the f.c.c. Al model (see Figure 4.1(b)) was also observed. Namely, an initial rapid decay of the HCACF of up to 0.17 - 0.2 ps was followed by a peak of around 0.29 - 0.34 ps. The intensity of the peak decreased as the temperature increased. This peak persisted up to temperatures close to the melting temperature of the f.c.c. Al model, while a similar peak on the HCACF of the f.c.c. Cu model was observed to transform to the shoulder at high temperatures.

As observed for the f.c.c. Cu and Al models, a two-stage decay of the HCACF of the f.c.c. Ni_{EAM1} and Ni_{EAM2} models (for two EAM interatomic potentials [6, 7]) was found (see Figures 4.1(c) and 4.1(d)). At low and intermediate temperatures, an initial rapid decay of the HCACF of up to 0.2 - 0.22 ps was followed by a peak of around 0.45 - 0.5 ps below 1300 K. The intensity of the peak decreased as the temperature increased. At high temperatures, above 1300 K, it transformed to a shoulder which tended to gradually diminish at higher temperatures. Furthermore, in the f.c.c. Ag model (see Figure 4.1(e)), an initial rapid decay of the HCACF was followed by a peak of around 0.6 - 0.75 and that the intensity of the peak decreased as the temperature increased which almost diminished at very high temperatures.



(a)



(b)



(c)



(d)



(e)

Figure 4.1: Normalized HCACF of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1} , (d) Ni_{EAM2} and (e) Ag at different temperatures for the *NPT* (thin solid line), *NVT* (dashed line), and *NVE* (dot-dashed line) ensembles, as well as averaged over the three ensembles (red solid line).

In additional studies, an effect of the size of the simulation cell on the shape of the HCACF was observed. In particular, Figure 4.2 gives the comparison of the HCACFs of the f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag models at temperatures predicted from the simulation blocks containing 4,000 and 32,000 atoms. As can be seen in Figure 4.2, in both cases a good agreement between the calculations can be observed. This comparison is an additional confirmation of the reliability of the results.







(b)







(d)



Figure 4.2: Comparison of the normalized HCACF of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1} , (d) Ni_{EAM2} and (e) Ag calculated at three different temperatures with the simulation blocks containing 4,000 (black solid line) and 32,000 (blue dashed line) atoms.

Chapter 5: The Decomposition Model for Lattice Thermal Conductivity

As mentioned in Chapter 4, a more complex behaviour was observed for the temporal decay of the HCACF of the models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag at low and intermediate temperatures in comparison to the two exponential functions (see Equation 2.39). Taking into account the observed shape of the HCACF of the MD models of the f.c.c. for the four metals investigated at different temperatures (see Table 3.1), it was found that the HCACF of the models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag can be satisfactorily modelled with the following analytical function of the form (as shown in Figure 5.1):

$$C_{JJ}(t) = \frac{1}{3} \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle = A_1 \exp\left(-\frac{t}{\tau_1}\right) \cos(\omega_c t) + A_2 \left(-\frac{t}{\tau_2}\right), \tag{5.1}$$

where $\langle ... \rangle$ means an average taken at the thermodynamic equilibrium, J is the microscopic heat current vector per unit volume, τ_1 and A_1 are the time constant and strength of the first-stage relaxation, respectively. This stage is associated with the acoustic short-range phonons, and τ_2 and A_2 are the time constant and the strength of the long-time decay of the HCACF associated with the acoustic long-range phonons, respectively. Finally, the $cos(\omega_c t)$ model in this equation is the transition between these two stages of the heat dissipation, so that the parameter ω_c can be described as the characteristic angular frequency of the phonon modes at which the crossover between the first and second stages of the HCACF relaxation occurs. In compliance with McGaughey and Kaviany [1, 2], τ_2 and τ_1 , as well as A_2 and A_1 , have the same meaning as in Equation 2.39. The decomposition model, introduced by Equation 5.1 (page 81), can capture all the characteristics of the HCACF behaviour for a monatomic f.c.c. lattice, as discussed in the literature. Only the acoustic phonon modes are considered in this study. Thus, the first and second exponential terms in Equation 5.1 (page 81) describe the two time scales of the decay, while the $\cos(\omega_c t)$ term models the transition between the two stages of the heat dissipation.

Such an interpretation of the observed HCACF relaxation is in accordance with Klemens' idea [78], which suggests that for a U-process linking a low-frequency phonon mode ω_1 with the two high-frequency phonon modes ω_2 and ω_3 in the vicinity of the zone boundary, the requirements of energy conservation given by $\omega_1 + \omega_2 = \omega_3$ can be satisfied only for the phonon modes with frequencies higher than a minimum (critical or threshold) frequency ω_c , i.e. $\omega_1 \ge \omega_c$.

Klemens also suggested that ω_c is approximately equal to the difference in frequency of the two different polarization branches (longitudinal and transverse) in the vicinity of the zone boundary. Thus, the low-frequency modes $\omega < \omega_c$ cannot directly undergo the three-phonon U-processes. Hence, the transfer of phonon momentum from the low-frequency modes $\omega < \omega_c$ must proceed in two steps (otherwise, a direct transfer of phonon momentum from the low-frequency modes can be realised only through their participation in much less feasible fourth and higher order U-processes). The first step is a N-process, which is always possible [79]. Such a N-process links the low-frequency mode to the modes of frequency ω_c or higher. The second step is an U-process linking the later intermediate-frequency modes ($\omega \gtrsim \omega_c$) to the high-frequency (zoneboundary) modes. This implies that the low-frequency modes $\omega < \omega_c$ can reach equilibrium only by these two steps, and that their effective relaxation time can be seen as a superposition of the relaxation time for the N-processes which link the lowfrequency modes to the intermediate-frequency modes and the average relaxation time for the U-processes (only possible if $\omega \gtrsim \omega_c$) [78, 80]. Meanwhile, the intermediateand high-frequency modes $\omega \gtrsim \omega_c$ can reach equilibrium in one step, and their relaxation time is just the relaxation time for the U-processes. Furthermore, one can suppose that, because of the two steps, the relaxation of the low-frequency modes $\omega < \omega$ ω_c (referred to as a slow relaxation process) should be separated in time from the onestep relaxation of the intermediate- and high-frequency modes $\omega \gtrsim \omega_c$ (referred to as a fast relaxation process). Additionally, because ω_c is supposed to be small (ω_c is about 4 - 5 times less than ω_D , according to both the assumption attributed to Klemens [78, 80] and the analysis of the simulation data presented here), the relative fraction of the low-frequency modes $\omega < \omega_c$ itself can be seen as a very small quantity, of the order of ω_c^3/ω_D^3 (it can be roughly estimated about 10⁻² or even less). However, to reach equilibrium the low-frequency modes $\omega < \omega_c$ need to interact with the intermediateand high-frequency modes $\omega \gtrsim \omega_c$, so that the total fraction of the phonon modes contributing towards the slow relaxation process (which is described by the second term in Equation 5.1 (page 81)) may be comparable with the fraction of the phonon modes contributing towards the fast relaxation process (which is described by the first term in Equation 5.1 (page 81)).

In other words, the acoustic short- and long-range phonon modes are those phonon modes that contribute towards the fast and slow relaxation processes, respectively. According to the recently explored two-fluid nature of phonon heat conduction in a monatomic lattice [81], the fluctuating microscopic heat current in a given direction of a large enough local volume of a crystal lattice can be decomposed into two parts, as:

$$\boldsymbol{J} = \boldsymbol{J}_1 + \boldsymbol{J}_2, \tag{5.2}$$

where, J_1 and J_2 are the heat currents (in the same direction) due to the acoustic shortand long-range phonon modes, respectively ($\langle J \rangle = 0$, $\langle J_1 \rangle = 0$ and $\langle J_2 \rangle = 0$, where the average is taken in thermal equilibrium on the time scale of $t \gg \tau_2$). Furthermore, if one assumes that there is no transfer of either energy or momentum (or it is strictly limited) between these two thermal motions associated with the acoustic short- and long-range phonon modes, then it follows that the HCACF should consist of two terms [81]:

$$C_{JJ}(t) = C_{JJ_1}(t) + C_{JJ_2}(t), (5.3)$$

where, $C_{JJ_1}(t) = \frac{1}{3} \langle J(0)J_1(t) \rangle$ and $C_{JJ_2}(t) = \frac{1}{3} \langle J(0)J_2(t) \rangle$ describe the contributions into the HCACF decay due to the acoustic short- and long-range phonon modes, respectively. Otherwise, the decomposition of the HCACF into these two contributions would not be possible. A simple comparison of Equations 5.1 (page 81) and 5.3 shows that:

$$C_{JJ_1}(t) = A_1 \exp(-t/\tau_1) \cos(\omega_c t),$$
 (5.4)

$$C_{JJ_2}(t) = A_2 \exp(-t/\tau_2).$$
 (5.5)

Thus, the frequency ω_c can be considered as the lower bound of the frequency range of the acoustic short-range phonon modes. This means that the density of the acoustic shortrange phonon modes $g_1(\omega, T)$, goes to zero around ω_c , so that the frequency range of the acoustic short-range phonon modes can be estimated as $\omega_c \leq \omega \leq \omega_D$. Meanwhile, the density of the acoustic long-range phonon modes $g_2(\omega, T)$, is assumed to be spread out over the whole frequency range $0 < \omega \leq \omega_D$. This also suggests that all lowfrequency phonons with $\omega < \omega_c$ belong to the acoustic long-range phonon modes. Hence, the acoustic short-range phonon modes can be characterized as intermediate- and high-frequency phonon modes with $\omega \gtrsim \omega_c$ that reach equilibrium in one step by directly undergoing a U-process (fast relaxation process). Consequently, the acoustic long-range phonon modes include the low-frequency phonon modes with $\omega < \omega_c$ and those intermediate- and high-frequency phonon modes which interact with the lowfrequency phonon modes to produce two-step relaxations, as suggested by Klemens (slow relaxation process). Perhaps, the best way to view $g_1(\omega, T)$ and $g_2(\omega, T)$ is through $p_1(\omega, T) = g_1(\omega, T)/g(\omega, T)$ $p_2(\omega,T) =$ the probabilities and $g_2(\omega,T)/g(\omega,T)$ (where $g(\omega,T) = g_1(\omega,T) + g_2(\omega,T)$ is the density of all the phonon modes, so that $p_1(\omega, T) + p_2(\omega, T) = 1$ to find the phonon modes between ω and $\omega + d\omega$ at a given temperature T among the acoustic short- and long-range phonon modes respectively.



(a)



(b)



(c)



(d)



(e)

Figure 5.1: The normalized HCACF averaged over the *NPT*, *NVT* and *NVE* ensembles of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag at different temperatures (black solid line) and its fit by Equation 5.1 (blue dashed line).

5.1 Thermal Conductivity Decomposition

In the framework of this model for HCACF, this study has demonstrated that the thermal conductivity k can be represented as a sum of two contributions (see Equation 5.6) (Figure 5.2). In accordance with McGaughey and Kaviany [1, 2], the first part of the thermal conductivity k_1 takes into account the acoustic short-range phonons that have mean free paths equal to one half of their wavelength, while the second part of the thermal conductivity k_2 takes into account the acoustic long-range phonons with mean free paths longer than one half of their wavelength.

$$k_{ph} = \frac{1}{Vk_B T^2} \left(A_1 \frac{\tau_1}{1 + \tau_1^2 \omega_c^2} + A_2 \tau_2 \right) = k_1 + k_2,$$
(5.6)

where:

$$k_1 = \frac{VA_1\tau_1}{k_B T^2 (1 + \tau_1^2 \omega_c^2)},\tag{5.7}$$

$$k_2 = \frac{VA_2\tau_2}{k_B T^2}.$$
 (5.8)

The first term in Equation 5.6, given by Equation 5.7, is characterized by the average relaxation time:

$$\tau_1' = \frac{\tau_1}{1 + \tau_1^2 \omega_c^2},\tag{5.9}$$

Furthermore, it can be seen in Figure 5.2, the temperature dependence of the phonon thermal conductivity, k, of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag can be well fitted by linear functions in different temperature ranges in the double-logarithmic scale. The linear fits in Figure 5.2 show that the data varies approximately as: (a) $T^{-0.93}$ at 40 - 200 K and $T^{-1.36}$ at 300 - 1300 K, (b) $T^{-1.19}$ at 100 - 500 K, and $T^{-1.49}$ at 500 - 1000 K, (c) $T^{-0.65}$ at 100 - 500 K, and $T^{-1.25}$ at 600 - 1700 K, (d) $T^{-1.2}$ at 100 - 500 K, and $T^{-1.85}$ at 600 - 1700 K, and (e) $T^{-1.15}$ at 40 - 200 K, and T^{-1} at 200 - 1200 K. These trends correlate well with classical phonon perturbation theory (it takes into account the effect of anharmonicity in the atomic interactions to describe the three-phonon scattering processes) which predicts that the lattice thermal conductivity should be inversely proportional to temperature $k_{ph} \sim T^{-1}$ at sufficiently high temperatures (according to some estimations above $T_D/4$ [43]).

The data on thermal conductivity collected in this study are also in agreement with the above mentioned calculations of the phonon thermal conductivity of f.c.c. Cu under a large temperature gradient (using heat baths at 300 and 850 K at the ends of the simulation cell) [9] with an older EAM potential [10]. In particular, the numerical value of the thermal conductivity found in [9], 5.7 W/mK (which probably should be related to the temperature 575 K at the middle of the simulation cell), is between the thermal conductivities of 6.22 and 4.65 W/mK calculated in the present work at 500 and 600 K, respectively.

As can be seen in Figure 5.2, at low temperatures $k_1 \ll k_2$ so that we have $k \approx k_2$. This means that at low temperatures, the second term in Equation 5.6, which is related to the second stage of the HCACF relaxation, dominates and contains most of the temperature dependence of the lattice thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag.



(a)



(b)





(c)



(d)



(e)

Figure 5.2: Double-logarithmic plot of the temperature dependence of the thermal conductivity, k_{ph} , of the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag calculated by using Equation 5.6 at different temperatures (diamonds) (see Table 3.1). The solid lines show the linear fits of the data in the different temperature ranges. The upward facing triangles (k_1) and downward facing triangles (k_2) show the decompositions of the thermal conductivity given by Equations 5.7 and 5.8.

5.2 Time Constant

Figure 5.3 illustrates the interrelation between all the discussed time constants τ_1 , τ_2 and τ'_1 for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag. Also in this figure is shown the time constant $\tau_c = \pi/\omega_c$ (one half of the period of oscillations with characteristic frequency ω_c) which according to Einstein [82] is the minimum time needed for a vibrational mode with frequency ω_c to lose or gain thermal energy, i.e., to undergo either a N-process or an U-process. It can be seen in Figure 5.3 that, at low

temperatures, τ_1 approaches τ_c . This means that the apparent contribution of the low frequency phonon modes to τ_1 in the case $\omega_c \rightarrow 0$ should be the most significant at low temperatures. As a result, the difference between τ_1 and τ'_1 , due to the cut-off of the density of the acoustic short-range phonon modes at ω_c , is the most remarkable at low temperatures. In contrast, at high temperatures $\tau_1 \ll \tau_c$, so that the cut-off of the density of the acoustic short-range phonon modes at ω_c leads to a smaller difference between τ_1 and τ'_1 . In addition, it is important to point out that $\tau'_1 \ll \tau_2$ at all temperatures.



(a)













Figure 5.3: Double-logarithmic plots of the temperature dependences of the time constants τ_1 (upward facing solid triangle), τ_2 (downward facing solid triangle), τ'_1 (upward facing open triangle) and $\tau_c = \pi/\omega_c$ (open diamonds) calculated within the framework of the HCACF decomposition given by Equation 5.6 as applied to the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag.

5.3 Analysis of the Phonon Thermal Conductivity Decomposition

In general, the lattice thermal conductivity of an isotropic solid can be derived from the Boltzmann transport equation in the form [17]:

$$k = \frac{1}{3} \int_0^{\omega_D(T)} c(\omega, T) v_G^2(\omega, T) \tau^*(\omega, T) g(\omega, T) d\omega, \qquad (5.10)$$

where:

$$c(\omega,T) = \frac{\hbar^2 \omega^2}{k_B T^2} \frac{exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2}$$
(5.11)

is the phonon-specific heat, $v_G(\omega, T)$ is the phonon group velocity, $\tau^*(\omega, T)$ is the phonon relaxation time, $g(\omega, T)d\omega$ is the number of phonon modes between ω and $\omega + d\omega$ per unit volume of crystal ($g(\omega, T)$) is the density of phonon modes) and $\omega_D(T)$ is the Debye (maximum) frequency, such that there are in total 3N distinguishable phonon modes (*N* is the number of atoms in the crystal):

$$\frac{3N}{V} = \int_0^{\omega_D(T)} g(\omega, T) d\omega$$
(5.12)

It should be noted that for every given pair of ω and T, the product $v_G^2(\omega, T)\tau^*(\omega, T)g(\omega, T)$ inside the integral in Equation 5.10 should be considered as an appropriately weighted average over the different reciprocal lattice directions and the different phonon polarizations (one longitudinal and two transverse).

Next, using the concept described above on the two-stage decay of the HCACF of a crystal with a monatomic unit cell, the general expression for the lattice thermal conductivity given by Equation 5.10 can be decomposed (by way of analogy with Equation 5.6) into two contributions k_1 and k_2 associated with the acoustic short- and long-range phonon modes, respectively:

$$k_{1} = \frac{1}{3} \int_{0}^{\omega_{D}(T)} c(\omega, T) v_{G}^{2}(\omega, T) \tau_{1}^{*}(\omega, T) g_{1}(\omega, T) d\omega, \qquad (5.13)$$

$$k_{2} = \frac{1}{3} \int_{0}^{\omega_{D}(T)} c(\omega, T) v_{G}^{2}(\omega, T) \tau_{2}^{*}(\omega, T) g_{2}(\omega, T) d\omega, \qquad (5.14)$$

where, $\tau_1^*(\omega, T)$ and $\tau_2^*(\omega, T)$ are the relaxation times of the acoustic short- and long-range phonon modes, respectively, while $g_1(\omega, T)d\omega$ and $g_2(\omega, T)d\omega$ are the numbers of the acoustic short- and long-range phonon modes, respectively, between ω and $\omega + d\omega$ per unit volume of crystal ($g_1(\omega, T)$ and $g_2(\omega, T)$ are the partial densities of the acoustic short- and long-range phonon modes, respectively). By this definition, it follows that:

$$\tau^{*}(\omega, T)g(\omega, T) = \tau_{1}^{*}(\omega, T)g_{1}(\omega, T) + \tau_{2}^{*}(\omega, T)g_{2}(\omega, T),$$
(5.15)

$$g(\omega, T) = g_1(\omega, T) + g_2(\omega, T).$$
 (5.16)

Thus, there are in total N_1 and N_2 acoustic short- and long-range phonon modes, respectively $(N_1 + N_2 = N)$:

$$\frac{N_1}{V} = \int_0^{\omega_D(T)} g_1(\omega, T) d\omega, \qquad (5.17)$$

$$\frac{N_2}{V} = \int_0^{\omega_D(T)} g_2(\omega, T) d\omega, \qquad (5.18)$$

As a result, the average relaxation times of the acoustic short- and long-range phonon modes can be defined as:

$$\tau_1^* = \frac{V}{N_1} \int_0^{\omega_D(T)} \tau_1^*(\omega, T) g_1(\omega, T) d\omega,$$
 (5.19)

$$\tau_{2}^{*} = \frac{V}{N_{2}} \int_{0}^{\omega_{D}(T)} \tau_{2}^{*}(\omega, T) g_{2}(\omega, T) d\omega, \qquad (5.20)$$

so that the average relaxation time of all the phonon modes is given by:

$$\bar{\tau}^* = f_1 \bar{\tau}_1^* + f_2 \bar{\tau}_2^* = \frac{V}{3N} \int_0^{\omega_D(T)} \tau^*(\omega, T) g(\omega, T) d\omega,$$
(5.21)

where $f_1 = N_1/3N$ and $f_2 = N_2/3N$ are the fractions of the acoustic short- and long-range phonon modes, respectively $(f_1 + f_2 = 1)$. Moreover, the partial heat capacities of the acoustic short- and long-range phonon modes, respectively, are:

$$C_1 = \int_0^{\omega_D(T)} c(\omega, T) g_1(\omega, T) d\omega, \qquad (5.22)$$

$$C_2 = \int_0^{\omega_D(T)} c(\omega, T) g_2(\omega, T) d\omega, \qquad (5.23)$$

so that the total heat capacity of all the phonon modes is given by:

$$C = C_1 + C_2 = \int_0^{\omega_D(T)} c(\omega, T) g(\omega, T) d\omega, \qquad (5.24)$$

It should also be noted that in the decomposition of the lattice thermal conductivity given by Equations 5.13 and 5.14, it was assumed that the phonon group velocity $v_G(\omega, T)$ depends mainly on the frequency, while it is much less sensitive to the type (short or long range) of the phonon modes. Hence, it is treated identically for both the short- and long-range phonon modes.

Finally, some remarks on the partial densities $g_1(\omega, T)$ and $g_2(\omega, T)$ of the acoustic short- and long-range phonon modes are provided. As discussed in the previous section, the density of the acoustic short-range phonon modes $g_1(\omega, T)$ is supposed to go to zero around ω_c , so that the actual frequency range of the acoustic short-range phonon modes in Equations 5.13, 5.17, 5.19 and 5.22 can be estimated as $\omega_c \leq \omega \leq \omega_D$. The densities of the acoustic long-range phonon modes $g_2(\omega, T)$ are supposed to be spread out over the whole frequency range $0 < \omega \leq \omega_D$, so that $g_2(\omega, T) \equiv g(\omega, T)$ at $\omega \leq \omega_c$. Nonetheless, the actual fraction of the low-frequency phonon modes with $\omega \leq \omega_c$ relative to the total number of all phonon modes is expected to be a very small quantity, in the order of about 10^{-2} or even less, as pointed out in Chapter 1. Thus, the main contributions to both the $g_1(\omega, T)$ and the $g_2(\omega, T)$ are supposed to come from the intermediate- and high-frequency phonon modes with $\omega \geq \omega_c$, so that the partial fractions f_1 and f_2 of the acoustic short- and long-range phonon modes can be expected to be quantities of the same order of magnitude.

At high temperatures $T > T_D$, when all the phonon modes are excited and the phonon specific heat, given by Equation 5.17, is nearly the same for all the phonon

modes and can be approximated by the classical value of k_B . Hence, for high temperatures $T > T_D$, Equations 5.13 and 5.14 can be rewritten as:

$$k_{1} = \frac{k_{B}}{3} \int_{0}^{\omega_{D}(T)} v_{G}^{2}(\omega, T) \tau_{1}^{*}(\omega, T) g_{1}(\omega, T) d\omega, \qquad (5.25)$$

$$k_{2} = \frac{k_{B}}{3} \int_{0}^{\omega_{D}(T)} v_{G}^{2}(\omega, T) \tau_{2}^{*}(\omega, T) g_{2}(\omega, T) d\omega, \qquad (5.26)$$

while from Equation 5.17, 5.18 and 5.22 - 5.24 it follows that:

$$C_1 = \varphi_1 C, \tag{5.27}$$

$$C_2 = \varphi_2 C, \tag{5.28}$$

where φ_1 and φ_2 are the relative contributions of the acoustic short- and long-range phonon modes to the lattice heat capacity, respectively ($\varphi_1 + \varphi_2 = 1$), and *C* is the heat capacity and also:

$$C_{\rm DP} = \frac{3Nk_B}{V} \tag{5.29}$$

is the classical lattice heat capacity, known as the Dulong and Petit value. Finally, the average phonon velocity of the acoustic short- and long-range phonon modes is defined as:

$$v_1^2 = \frac{V}{N_1 \bar{\tau}_1^*} \int_0^{\omega_D(T)} v_G^2(\omega, T) \tau_1^*(\omega, T) g_1(\omega, T) d\omega,$$
(5.30)
102

$$v_2^2 = \frac{V}{N_2 \bar{\tau}_2^*} \int_0^{\omega_D(T)} v_G^2(\omega, T) \tau_2^*(\omega, T) g_2(\omega, T) d\omega,$$
(5.31)

so that the average phonon velocities of all the phonon modes is given by:

$$v^{2} = \varphi_{1} v_{1}^{2} \frac{\bar{\tau}_{1}^{*}}{\bar{\tau}^{*}} + \varphi_{2} v_{2}^{2} \frac{\bar{\tau}_{2}^{*}}{\bar{\tau}^{*}} = \frac{V}{3N\bar{\tau}^{*}} \int_{0}^{\omega_{D}(T)} v_{G}^{2}(\omega, T) \tau^{*}(\omega, T) g(\omega, T) d\omega.$$
(5.32)

Thus, Equations 5.25 and 5.26 can be rewritten in the form of simple kinetic formulas:

$$k_1 = \frac{1}{3} C_1 v_1^2 \bar{\tau}_1^*, \tag{5.33}$$

$$k_2 = \frac{1}{3}C_2 v_2^2 \bar{\tau}_2^*. \tag{5.34}$$

Now, by direct comparison of Equations 5.33 and 5.34 with the results of the classical MD simulations given by Equations 5.7 - 5.9, one can obtain the following relations:

$$\frac{1}{3}C_1 v_1^2 = \frac{A_1}{Vk_B T^2},\tag{5.35}$$

$$\bar{\tau}_1^* = \tau_1' = \frac{\tau_1}{1 + \tau_1^2 \omega_c^2} \tag{5.36}$$

$$\frac{1}{3}C_2 v_2^2 = \frac{A_2}{Vk_B T^2},\tag{5.37}$$

$$\bar{\tau}_2^* = \tau_2'. \tag{5.38}$$

Hence, by combining Equations 5.35 and 5.36, and taking into account Equations 5.1 (page 81) and 5.29, one can find that:

$$\varphi_1 v_1^2 + \varphi_2 v_2^2 = v_J^2, \tag{5.39}$$

where:

$$v_{J} = \frac{1}{k_{\rm B}T} \sqrt{\frac{A_1 + A_2}{N(\frac{C}{C_{\rm DP}})}} = \frac{1}{k_{\rm B}T} \sqrt{\frac{\langle J^2 \rangle}{3N(\frac{C}{C_{DP}})}}$$
(5.40)

can be described as the average phonon velocity determined from the second-order fluctuations of the heat current vector. Then, it follows that:

$$v_1 = \sqrt{\frac{\varepsilon_1}{\varphi_1}} v_j, \tag{5.41}$$

$$v_2 = \sqrt{\frac{\varepsilon_2}{\varphi_2}} v_J, \tag{5.42}$$

where:

$$\varepsilon_1 = \frac{A_1}{A_1 + A_2},\tag{5.43}$$

$$\varepsilon_2 = \frac{A_2}{A_1 + A_2},\tag{5.44}$$

 $(\varepsilon_1 + \varepsilon_2 = 1)$. From Equations 5.41 and 5.42, the following relation can also be obtained:

$$\frac{\varepsilon_1}{v_1^2} + \frac{\varepsilon_2}{v_2^2} = \frac{1}{v_J^2}.$$
(5.45)

At this point, it was assumed that the average phonon velocities of the acoustic short- and long-range phonon modes given by Equations 5.30 and 5.31 may approximately be considered as equal to each other $v_1 \approx v_2$. Indeed, the fraction of the low-frequency phonon modes $\omega \leq \omega_c$, which have higher velocities than other modes, was very small, as discussed above. Consequently, the contribution of the low-frequency phonon modes $\omega \leq \omega_c$ to v_2 was also expected to be small. Meanwhile, the main contributions from the intermediate- and high-frequency phonon modes $\omega \geq \omega_c$ to v_1 and v_2 can be expected to be rather similar. Then, from Equations 5.41 and 5.42, it follows that the fractions (or partial heat capacities) of the acoustic short- and long-range phonon modes can be estimated as $f_1 \approx \varepsilon_1$ and $f_2 \approx \varepsilon_2$, respectively. Thus, the MD calculations of the HCACF of a crystal with a monatomic unit cell, besides the phonon thermal conductivity and its decomposition into k_1 and k_2 , also allow for the numerical decomposition of k_1 and k_2 , according to the simple kinetic formulas (see Equations 5.33 and 5.34), as products consisting of the heat capacity and the average relaxation time of the considered phonon modes as well as the square of the average phonon velocity.

Figure 5.4 shows the average phonon velocity v_J of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag calculated according to Equation 5.40 as a function of the temperature in the temperature range that is above the Debye temperature of the models, as mentioned in Table 3.5. It can be seen in Figure 5.4 that, over the temperature ranges considered, the average phonon velocity changes with temperature in good agreement with the linear law (see Table 5.1):

$$v_I = v_0 + \alpha_v T, \tag{5.46}$$

Table 5.1 shows the details of the average phonon velocities at zero temperature, v_0 , of metals that are in good agreement with the average speed of sound by using zero temperature elastic constants of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag (see Table 3.5).



(a)







(c)




(d)





Figure 5.4: Temperature dependences of the average phonon velocities for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1} , (d) Ni_{EAM2} and (e) Ag calculated according to Equation 5.40 at different temperature ranges above T_D . The lines show the linear fit of the data according to Equation 5.46.

Table 5.1: Details of the linear fits of the average phonon velocities (v_0, α_v), Debye frequencies (ω_D) and Debye temperatures (T_D) at zero temperature.

Metals	$v_0 \left(\frac{\mathrm{km}}{\mathrm{s}}\right)$	$\alpha_v(\times \frac{10^{-4} \text{km}}{\text{sK}})$	ω_D (THz)	<i>T_D</i> (K)
Cu	2.72	4.64	46.7	356
Al	3.68	8.64	56.2	429
Ni _{EAM1}	3.23	4.54	56.7	433
Ni _{EAM2}	3.15	1.98	55.4	423
Ag	2.16	4.39	32.7	250

Figure 5.5 shows the temperature dependences of the total lattice heat capacity *C* as well as the partial heat capacities $C_1 \approx CA_1/(A_1 + A_2)$ (upward facing triangles) and $C_2 \approx CA_2/(A_1 + A_2)$ (downward facing triangles) of the acoustic short range phonon and acoustic long-range phonon modes, respectively, calculated for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag over temperature ranges more than the Debye temperature (see Table 3.5). Firstly, the classical value of the lattice heat capacity at a constant volume in temperature ranges of more than the Debye temperature was verified:

$$C = C_V = \frac{1}{V} \left(\frac{\partial E}{\partial T}\right)_V,\tag{5.47}$$

where *E* is the internal energy of the model. For each temperature considered, and their respective zero-pressure volumes, this was done by linear approximations of the internal energy of the model at five nearby temperatures separated by a 5 K increment at the fixed volume. It can be seen in Figure 5.5 that the data obtained for the temperature ranges considered can be approximated with very good accuracy by the classical value C_{DP} . This reassured us in the use of the classical value C_{DP} in the calculation (in

particular in Equation 5.40). It can be seen in Figure 5.5 that C_1 dominates the whole temperature range. However, with decreasing temperatures the difference between C_1 and C_2 diminishes. Thus, one can conclude that at high temperatures the average contribution of the direct U-processes (the fast relaxation process) in restoring the equilibrium distribution of the high- and intermediate-frequency phonon modes $\omega \gtrsim \omega_{\rm c}$, i.e., the fraction of the acoustic short range phonon modes, prevails over the slow relaxation process, i.e., the fraction of the acoustic long-range phonon modes. This leads to the conclusion that the contribution of the acoustic short range phonon modes to the lattice thermal conductivity is notable at high temperatures and cannot be neglected (see Figure 5.2), despite the considerably shorter average relaxation time τ'_1 of the acoustic short range phonon modes in comparison to the average relaxation time τ_2 of the acoustic long-range phonon modes (see Figure 5.3). The decomposition on the acoustic short- and long-range phonon modes is probably also the reason that the lattice thermal conductivity varies more rapidly than the T^{-1} law at $T > T_D$. In addition, it was noted that in principle, it can be expected that C_2 might be close to zero at some very high temperatures which is, however, likely to be always higher than the melting temperature $T_{\rm m}$. Although such a state of phonon gas, consisting mainly of the acoustic short range phonon modes, is hard to realise in a crystal lattice, it would be of great interest for the development of advanced energy conversion devices that utilize the thermoelectric effect [8].



(b)







(d)



Figure 5.5: Temperature dependences of the partial heat capacities C_1 (upward facing triangles) and C_2 (downward facing triangles) of the acoustic short- and long-range phonon modes for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag over temperature ranges of more than the Debye temperature. Diamonds show the calculated lattice heat capacity $C = C_V$.

At low temperatures $T < T_D$, not all of the phonon modes will be excited in the quantum crystal system. In this case, the classical approximation for the phonon specific heat can no longer be used. However, according to the MD results at low temperatures, one can note in Figure 5.2 that $k_1 \ll k_2$, so that we have [1-3]:

$$k \approx k_2 = \frac{1}{3} \int_0^{\omega_D(T)} c(\omega, T) v_G^2(\omega, T) \tau_2^*(\omega, T) g_2(\omega, T) d\omega, \qquad (5.48)$$

where, $C(\omega, T)$ is the phonon heat capacity (see Equation 5.11), $v_G(\omega, T)$ is the phonon group velocity, $\tau_2^*(\omega, T)$ is the relaxation time of the acoustic long-range phonon modes, $g_2(\omega, T)d\omega$ is the number of the acoustic long-range phonon modes between ω and $\omega + d\omega$ per unit volume of crystal ($g_2(\omega, T)$) is the density of the acoustic long-range phonon modes), and $\omega_D(T)$ is the Debye frequency. At low temperatures, the contributions of the acoustic short range phonon modes can be neglected because their average relaxation time $\bar{\tau}_1^* \equiv \tau_1'$ is approximately one to two orders of magnitude shorter than $\bar{\tau}_2^* \equiv \tau_2$ (see Figure 5.3).

As the temperature goes below T_D , the fraction of excited phonon modes in a real crystal and, consequently, the lattice heat capacity C, start to decrease. It was assumed that the decrease of C should first of all be determined by the decrease of the heat capacity C_1 of the acoustic short range phonon modes, and only then, at sufficiently low temperatures, where $C_1 \ll C$, by a decrease of the heat capacity C_2 of the acoustic longrange phonon modes. Then, it is reasonable to surmise that classical MD simulations could be used to estimate the lattice thermal conductivity (limited by the phonon-phonon interactions) of a real quantum crystal at temperatures $T < T_D$, if the two following conditions were to be satisfied simultaneously: (i) all the low-frequency phonon modes with $\omega \leq \omega_c$ must be entirely excited, i.e., $T \geq T_c$ $(T_c = \frac{\hbar \omega_c}{k_B})$, and (ii) the total number of excited phonon modes must be sufficient to produce a two-step relaxation as suggested by Klemens [78, 80] (slow relaxation process), i.e., $C_2 \ll C$. Indeed, the freezing out of some fraction of the intermediate- and high-frequency phonon modes in a real crystal at temperatures below T_D would produce, in comparison with the classical MD model, an extra decrease of C_1 and, consequently, k_1 , but, even without it, k_1 is negligible compare to k_2 at $T < T_D$ in the classical MD model. Therefore, the thermal transport properties limited by the phonon-phonon interactions in both a real crystal and its classical MD model at $T_c \leq T < T_D$ should be determined by nearly the same contribution of the acoustic long-range phonon modes.

As a first approximation, let us neglect the frequency dependency of $v_G(\omega, T)$, so that its average value v_J can be used. Then, over the temperature range $T_c \leq T < T_D$ we can rewrite Equation 5.48 as:

$$k_{ph} \approx k_2 \approx \frac{1}{3} C_2' v_q^2 \bar{\tau}_2^{*'} + \frac{v_q^2}{3} \int_{\omega_c(T)}^{\omega_D(T)} c(\omega, T) v_G^2(\omega, T) \tau_2^*(\omega, T) g_2(\omega, T) d\omega.$$
(5.49)

where:

$$C_2' \approx k_B \int_0^{\omega_c(T)} g_2(\omega, T) d\omega = k_B \frac{3f_2'N}{V}$$
(5.50)

is the heat capacity of the acoustic long-range phonon modes with $\omega \leq \omega_c (c(\omega, T) \approx k_B \text{ for } T \geq T_c \text{ and } \omega \leq \omega_c), f'_2$ is the fraction of the acoustic long-range phonon modes with $\omega \leq \omega_c$, and:

$$\bar{\tau}_{2}^{*'} = \frac{V}{3f_{2}'N} \int_{0}^{\omega_{c}(T)} \tau_{2}^{*}(\omega, T)g_{2}(\omega, T)d\omega$$
(5.51)

is the average relaxation time of the acoustic long-range phonon modes with $\omega \leq \omega_c$. It also should be recalled that according to the model description, all the low-frequency phonons with $\omega \leq \omega_c$ belong to the acoustic long-range phonon modes, so that $g_2(\omega, T) \equiv g(\omega, T)$ at $\omega \leq \omega_c$ (where $g(\omega, T)$ is the total density of all the phonon modes). Moreover, it is reasonable to assume that the average relaxation time, $\bar{\tau}_2^*$, of the acoustic long-range phonon modes is mostly defined by the average relaxation time, $\bar{\tau}_2^*$, of the acoustic long-range phonon modes with $\omega \leq \omega_c$, because specifically, these phonon modes intrinsically originate the two step slow relaxation process, as described above. As a result, the phonon relaxation time, $\tau_2^*(\omega, T)$, of the acoustic long-range phonon modes with $\omega \geq \omega_c$ should be considered as being closely coupled to $\bar{\tau}_2^{*'} \approx \bar{\tau}_2^*$. For this reason, we can neglect the frequency dependency of $\tau_2^*(\omega, T)$ compared to $c(\omega, T)$ in the second term on the right hand side of Equation 5.49, so that the average relaxation time $\bar{\tau}_2^*$ can be used to replace $\tau_2^*(\omega, T)$. Thus, Equation 5.49 can be evaluated to obtain a simple kinetic formula:

$$k_{ph} \approx k_2 \approx \frac{1}{3} C_2' v_q^2 \bar{\tau}_2^* + \frac{1}{3} C_2'' v_q^2 \bar{\tau}_2^* = \frac{1}{3} C_2 v_q^2 \bar{\tau}_2^*, \qquad (5.52)$$

where:

$$C_2^{\prime\prime} = \int_{\omega_c(T)}^{\omega_D(T)} c(\omega, T) g_2(\omega, T) d\omega$$
(5.53)

is the heat capacity of the acoustic long-range phonon modes with $\omega \gtrsim \omega_c$, so that:

$$C_2 = C_2' + C_2''. \tag{5.54}$$

The simple kinetic formula given by Equation 5.52 allows us to evaluate C_2 in the temperature range $T_c \leq T < T_D$ and, hence, compare it to *C* by employing the Debye approximation [17, 20, 21] for the heat capacity of a crystal, so that the feasibility of the simultaneous satisfaction of the two above mentioned conditions can be directly verified in a self-consistent manner. The total phonon heat capacity of a crystal can be estimated as the Debye heat capacity [17, 20, 21]:

$$C \approx C_D = \frac{9Nk_B}{V} \left(\frac{T}{T_D}\right)^3 \int_0^{T_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$
 (5.55)

Hence, a classical description of the thermal transport properties of the acoustic long-range phonon modes in the temperature range $T_c \leq T < T_D$ can be considered if $C_2 \approx 3k_2/v_I^2 \bar{\tau}_2^*$ (v_I can be estimated by linear extrapolation according to Equation 5.46, and $\bar{\tau}_2^*$ can be taken as approximately equal to τ_2), estimated from Equation 5.52, is less than the Debye heat capacity C_D . Figure 5.6 shows the temperature dependences of both C_2 (including its high temperature values) and C_D (at $T < T_D$). It can be seen that C_D reaches C_2 at a temperature of around 90 K for the f.c.c. Cu model (see Figure 5.6(a)), 100 K for the f.c.c. Al, NiEAM1, NiEAM2 models (see Figure 5.6(b), 5.6(c) and 5.6(d), respectively) and 60 K for the f.c.c. Ag model (see Figure 5.6(e)). Meanwhile, the fitting of the HCACFs of the MD models of f.c.c. Cu, Al, NiEAM1, NiEAM2 and Ag at the mentioned temperatures gave the characteristic frequency (ω_c) of approximately 11.5, 17.4, 12.6, 14.1 and 8.02 THz, respectively. The values of the characteristic temperature $(T_c = \frac{\hbar\omega_c}{k_B})$ of the MD models of f.c.c. of Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag were around 88, 133, 96, 108 and 61 K for those frequencies were in excellent agreement with the mentioned temperatures (90 K for f.c.c. Cu model, 100 K for the f.c.c. Al, NiEAMI, Ni_{EAM2} models and 60 K for the f.c.c. Ag model) found from the condition $C_2 = C_D$ (see Figure 5.6). Consequently, one can conclude that for the MD models of f.c.c. Cu, Al, NiEAM1, NiEAM2 and Ag the temperature range, where both abovementioned conditions are satisfied simultaneously, is $T_c \leq T < T_D$, with T_c estimated to be around one quarter of T_D .





(b)





Temperature (K)





Figure 5.6: Heat capacity of the acoustic long-range phonon modes (downward facing triangles) calculated as $C_2 \approx 3k_2/v_J^2 \tau_2$ for the MD models of f.c.c. (a) Cu, (b) Al, (c) NiEAM1, (d) NiEAM2 and (e) Ag over a wide temperature range (see Table 3.1) using the classical MD simulation data versus the Debye heat capacity C_D (solid line). The solid line shows C_D as a function of the temperature calculated according to Equation 5.55 by using the Debye temperature of 356, 429, 433, 423 and 250 K, respectively (estimated for 2.72, 3.68, 3.23, 3.15 and 2.16 km/s, respectively).

Thus, it has been have demonstrated that despite the freezing out of some fraction of the intermediate- and high-frequency phonon modes at temperatures below the Debye temperature, a classical description of the phonon thermal transport properties in the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag can be used down to around one quarter of the Debye temperature. This is because the acoustic long-range phonon modes, which are the main heat carriers responsible for the phonon thermal transport at low temperatures, are active down to around one quarter of the Debye temperature down to around one quarter of the Debye temperature, and only at lower temperatures do they start to freeze out.

At lower temperatures, $T < T_c$, one can expect that the freezing out of the acoustic long-range phonon modes will result in the interactions among the acoustic long-range phonon modes rapidly becoming less effective in restricting their men-free path. Therefore, the quantum effects on the populations of the acoustic long-range phonons at temperatures $T < T_c$ will affect, in Equation 5.48, not only the heat capacity but also their relaxation times. Thus, at temperatures $T < T_c$, the classical MD simulations data are unlikely to provide valuable insight into the prediction of the phonon thermal transport properties.

Chapter 6: Spectral Representation

In this chapter, it is shown that the information about the parameters of the analytical model for the HCACF given by Equation 5.1 (page 81) (and consequently the lattice thermal conductivity) can, in principle, be obtained experimentally by scattering or absorption measurements. In particular, the power spectrum of the heat flux fluctuations and the spectrum of the power of the heat dissipation in the thermal equilibrium in a crystal with monatomic lattice are analysed. The theoretical ground for the spectral representation of the HCACF, on the basis of Equation 5.1 (page 81), was developed by Dr Alexander Evteev²⁴. The peculiarities of the power spectrums of the heat flux fluctuations predicted below for the f.c.c. metals can, in principle, be observed in a scattering experiment with no gradients imposed on the studied crystal if a proper resolution of the frequency range of approximately 1 - 20 THz is accessible.

Although in the previous section it has been shown that the lattice thermal conductivity, k_{ph} , at $T < T_D$ is dominated by the contributions of the acoustic long-range phonon modes (k_2) and, consequently, the temperature range for the MD predictions of k_{ph} can be extended down until $C_2 < C_D$ (i.e., down to T_c), the power spectra discussed in this section are supposed to be spread over the whole frequency range from 0 to ω_D . Therefore, certain corrections to the MD predictions need to be involved in the high-frequency range at $T < T_D$. For this reason, consideration is limited, at the present stage, to only the power spectra of the equilibrium fluctuations at $T > T_D$.

At thermal equilibrium, let us consider a fluctuating heat flux J associated with a spontaneously fluctuating thermodynamic force X which originates from a spontaneously fluctuating temperature gradient:

$$\boldsymbol{X} = -\frac{1}{T} \nabla T. \tag{6.1}$$

The linear response of **J** on **X** can therefore be written in the form [3]:

²⁴ E.V. Levchenko, A.V. Evteev, L. Momenzadeh, I.V. Belova, and G.E. Murch. *Phonon-Mediated Heat Dissipation in a Monatomic Lattice: Case Study on Ni*. Philosophical Magazine, 2015. 95(32): p. 3640-3673.

A.V. Evteev, E.V. Levchenko, L. Momenzadeh, I.V. Belova, and G.E. Murch, *Insight into Lattice Thermal Impedance via Equilibrium Molecular Dynamics: Case Study on Al.* Philosophical Magazine, 2015, **DOI:**10.1080/14786435.2016.1143569.

$$J(t) = \frac{V}{k_{\rm B}T} \int_{0}^{\infty} C_{JJ}(t') X(t-t') dt', \qquad (6.2)$$

where:

$$C_{JJ}(t) = \frac{1}{3} \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle = \langle \boldsymbol{J}(t) \boldsymbol{J}(0) \rangle$$
(6.3)

is the HCACF, and, for simplicity, the vector notation is dropped. It is straightforward to see that the Fourier transformation of Equation 6.2 into the frequency domain can be found as:

$$\tilde{J}(\omega) = TZ^{-1}(\omega)\tilde{X}(\omega), \tag{6.4}$$

where:

$$\tilde{J}(\omega) = \int_{-\infty}^{\infty} J(t)e^{i\omega t}dt, \qquad (6.5)$$

$$\widetilde{X}(\omega) = \int_{-\infty}^{\infty} X(t) e^{i\omega t} dt, \qquad (6.6)$$

are the Fourier transforms of the fluctuating J(t) and X(t), and $Z(\omega)$ is the thermal impedance which can be defined as:

$$Z^{-1}(\omega) = \frac{V}{k_{\rm B}T^2} \int_0^\infty C_{JJ}(t) e^{i\omega t} dt.$$
(6.7)

The lattice thermal impedance $Z(\omega) = R(\omega) + iY(\omega)$ due to the phonon-phonon scattering processes, which is related to the HCACF given by Equation 5.1 (page 81), can be presented as:

$$\operatorname{Re}Z^{-1}(\omega) = \frac{R(\omega)}{|Z(\omega)|^2} = \frac{V}{2k_{\mathrm{B}}T^2} \left[\frac{A_1\tau_1}{1+(\omega+\omega_{\mathrm{c}})^2\tau_1^2} + \frac{A_1\tau_1}{1+(\omega-\omega_{\mathrm{c}})^2\tau_1^2} + \frac{2A_2\tau_2}{1+\omega^2\tau_2^2} \right]$$
(6.8)

$$\operatorname{Im} Z^{-1}(\omega) = \frac{-Y(\omega)}{|Z(\omega)|^2} = \frac{V}{2k_{\rm B}T^2} \left[\frac{A_1 \tau_1^2(\omega + \omega_{\rm c})}{1 + (\omega + \omega_{\rm c})^2 \tau_1^2} + \frac{A_1 \tau_1^2(\omega - \omega_{\rm c})}{1 + (\omega - \omega_{\rm c})^2 \tau_1^2} + \frac{2A_2 \tau_2^2 \omega}{1 + \omega^2 \tau_2^2} \right].$$
(6.9)

where, $R(\omega) = \text{Re}Z(\omega)$ and $Y(\omega) = \text{Im}Y(\omega)$ is the lattice thermal resistance and reactance, respectively, while $|Z(\omega)|^2 = Z(\omega)Z^*(\omega) = R^2(\omega) + Y^2(\omega) (Z^*(\omega) = R(\omega) - iY(\omega))$ is the complex conjugate to $Z(\omega)$). Also, it was noted that from the definition of $Z(\omega)$ given by Equation 6.7 it follows that $Z(-\omega) = Z^*(\omega)$, i.e., $R(\omega) = R(-\omega)$ and $Y(\omega) = -Y(-\omega)$ are even and odd functions of ω , respectively. Furthermore, the lattice thermal impedance can be decomposed into the contributions $Z_1(\omega)$ and $Z_2(\omega)$ associated with the acoustic short and long-range phonon modes, respectively, as:

$$\frac{1}{Z(\omega)} = \frac{1}{Z_1(\omega)} + \frac{1}{Z_2(\omega)},$$
(6.10)

where:

$$Z_1(\omega) = R_1(\omega) + iY_1(\omega), \tag{6.11}$$

$$Z_2(\omega) = R_2(\omega) + iY_2(\omega), \qquad (6.12)$$

so that:

$$R_1(\omega) = \operatorname{Re}Z_1(\omega) = \frac{\tau_1'}{k_1\tau_1} \left[1 + \frac{\omega_c^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \right],$$
(6.13)

$$Y_{1}(\omega) = \operatorname{Im}Z_{1}(\omega) = -\frac{\omega\tau_{1}'}{k_{1}} \left[1 - \frac{\omega_{c}^{2}\tau_{1}^{2}}{1 + \omega^{2}\tau_{1}^{2}} \right]$$
(6.14)

124

are the thermal resistance and reactance of the acoustic short range phonon modes, respectively, while:

$$R_2(\omega) = \text{Re}Z_2(\omega) = \frac{1}{k_2},$$
 (6.15)

$$Y_2(\omega) = \operatorname{Im}Z_2(\omega) = -\frac{\omega\tau_2}{k_2}$$
(6.16)

are the thermal resistance and reactance of the acoustic long-range phonon modes, respectively. Similar to $Z(\omega)$, it can be seen that $Z_1(-\omega) = Z_1^*(\omega)$ and $Z_2(-\omega) = Z_2^*(\omega)$, i.e., $R_1(\omega) = R_1(-\omega)$ and $R_2(\omega) = R_2(-\omega)$ are even functions of ω while $Y_1(\omega) = -Y_1(-\omega)$ and $Y_2(\omega) = -Y_2(-\omega)$ are odd functions of ω .

First, Equation 6.10 implies that for each frequency ω the total impedance $Z(\omega)$ is a parallel combination of the two impedances $Z_1(\omega)$ and $Z_2(\omega)$ associated with the acoustic short- and long-range phonon modes respectively. This means that the following relations should be satisfied:

$$\tilde{J}(\omega)Z(\omega) = \tilde{J}_1(\omega)Z_1(\omega) = \tilde{J}_2(\omega)Z_2(\omega) = T\tilde{X}(\omega),$$
(6.17)

where, $\tilde{J}_1(\omega)$ and $\tilde{J}_2(\omega)$ ($\tilde{J}(\omega) = \tilde{J}_1(\omega) + \tilde{J}_2(\omega)$) are the Fourier transforms of $J_1(t)$ and $J_2(t)$ (see also Equations 6.4 and 6.5). Next, according to the thermodynamics of irreversible processes, at sufficiently small departures from thermodynamic equilibrium the rate of entropy production per unit volume, σ , can be expressed in this case as [83-86]:

$$T\sigma = JX. \tag{6.18}$$

Assuming the isotropy of J and X, taking the inverse Fourier transform of Equations 6.5 and 6.6, and using Equation 6.4, the averaged over time power dissipation in a crystal lattice due to the spontaneously fluctuating thermodynamic force X can be expressed as:

Power =
$$\langle T\sigma \rangle = 3\langle J(t)X(t) \rangle = \frac{3}{(2\pi)^2 T} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle \tilde{J}(\omega)\tilde{J}(\omega') \rangle Z(\omega') e^{-i(\omega+\omega')t} d\omega d\omega'.$$

(6.19)

According to the general theory of fluctuation [83], the averaged over time product $\langle \tilde{J}(\omega)\tilde{J}(\omega')\rangle$ can be related to the power spectrum $S_I(\omega)$ of J(t) as:

$$\langle \tilde{J}(\omega)\tilde{J}(\omega')\rangle = 2\pi S_I(\omega)\delta(\omega+\omega'), \tag{6.20}$$

where, $\delta(\omega + \omega')$ is the Dirac delta function. This definition suggests that $S_J(\omega)$ is the Fourier transform of the HCACF $C_{JJ}(t)$ (as any time autocorrelation function, $C_{JJ}(t)$ must be an even function of time $C_{JJ}(t) = C_{JJ}(-t)$, so that strictly speaking, the absolute value of time |t| should appear instead of t in the first and second exponents of Equation 5.1 (page 81)) and, consequently, is an even function of ω :

$$S_{J}(\omega) = \int_{-\infty}^{\infty} C_{JJ}(t)e^{i\omega t}dt = 2\operatorname{Re}\int_{0}^{\infty} C_{JJ}(t)e^{i\omega t}dt = \frac{2k_{\mathrm{B}}T^{2}\operatorname{Re}Z^{-1}(\omega)}{V} = \frac{2k_{\mathrm{B}}T^{2}R(\omega)}{V|Z(\omega)|^{2}}.$$
(6.21)

Hence, by Equations 6.19 and 6.20 we have:

Power =
$$\langle T\sigma \rangle = \frac{3}{2\pi T} \int_{-\infty}^{\infty} S_J(\omega) Z^*(\omega) d\omega = \frac{3}{\pi T} \int_{0}^{\infty} S_J(\omega) R(\omega) d\omega.$$
 (6.22)

Instead of $S_J(\omega)$, one can alternatively use the power spectra $S_{J_1}(\omega)$ of $J_1(t)$, $S_{J_2}(\omega)$ of $J_2(t)$ or $S_X(\omega)$ of X(t), which are defined similarly to Equation 6.20, along with the relations given by Equation 6.17 to obtain from Equation 6.19 the other expressions for the spectrum of the power dissipation (the integrand in Equation 6.22):

$$S_{\text{Power}}(\omega) = \frac{3}{\pi T} S_J(\omega) R(\omega), \qquad (6.23)$$

so that the following relations between the power spectra can be found:

$$S_{J}(\omega)|Z(\omega)|^{2} = S_{J_{1}}(\omega)|Z_{1}(\omega)|^{2} = S_{J_{2}}(\omega)|Z_{2}(\omega)|^{2} = T^{2}S_{X}(\omega) = \frac{2k_{B}T^{2}R(\omega)}{V}.$$
(6.24)

It is important to point out that the relations given by Equation 6.24 present different forms of the fluctuation-dissipation theorem [83, 87] for the case considered of heat dissipation due to the phonon-phonon scattering processes. The power spectra $S_J(\omega)$, $S_{J_1}(\omega)$, $S_{J_2}(\omega)$ and $S_X(\omega)$ reveal the squared amplitude (intensity, strength or power) of the fluctuations of J(t), $J_1(t)$, $J_2(t)$ and X(t), respectively, at a given frequency ω .

Figure 6.1 shows the normalized power spectrum $VS_X(\omega)/2k_B = R(\omega)$ (in units of thermal resistance) of X(t) calculated according to Equation 6.24. It can be seen in Figure 6.1 that in contrast to the simplest kinetic theory which essentially assumes a single exponential stage of the heat flux relaxation [41], the power spectrum of the randomly fluctuating thermodynamic force is not just a constant equal to the reverse of the lattice thermal conductivity (as an analogy, note that in this case $R_2(\omega) = k_2^{-1} =$ const for all frequencies). It has a peak of an asymmetrical shape with a maximum located at ω_R somewhat below ω_c . Hence, one can conclude that at frequencies near the maximum location the perturbations of the equilibrium phonon distribution due to the spontaneously fluctuating thermodynamic force X(t) should be the most intensive.



(a)



(b)



(c)



(d)



Figure 6.1: Normalized power spectrum $VS_X(\omega)/2k_B = R(\omega)$ of the spontaneously fluctuating thermodynamic force X(t) in thermal equilibrium at different temperatures above T_D for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag predicted on the basis of the analytical model for the heat current autocorrelation function given by Equation 5.1.

Figure 6.2 shows the normalized power spectra $VS_J(\omega)/2k_BT^2 = R(\omega)/|Z(\omega)|^2$, $VS_{J_1}(\omega)/2k_BT^2 = R(\omega)/|Z_1(\omega)|^2$ and $VS_{J_2}(\omega)/2k_BT^2 = R(\omega)/|Z_2(\omega)|^2$ (in units of thermal conductivity) of J(t), $J_1(t)$ and $J_2(t)$ calculated according to Equation 6.24. Meanwhile, Figure 6.3 shows the frequency dependences of the magnitude of the impedances $|Z(\omega)|$, $|Z_1(\omega)|$ and $|Z_2(\omega)|$, along with the resistances $R_1(\omega)$ and $R_2(\omega)$. The magnitude of the impedances determines the responses of J(t), $J_1(t)$ and $J_2(t)$ on X(t) at a given frequency ω , so that:

$$\sqrt{\frac{S_J(\omega)}{T^2 S_X(\omega)}} = |Z(\omega)|^{-1}, \sqrt{\frac{S_{J_1}(\omega)}{T^2 S_X(\omega)}} = |Z_1(\omega)|^{-1}, \sqrt{\frac{S_{J_2}(\omega)}{T^2 S_X(\omega)}} = |Z_2(\omega)|^{-1}.$$
 (6.25)



(a)



(b)



(c)



(d)



Figure 6.2: Normalized power spectra $\frac{VS_J(\omega)}{2k_BT^2} = \frac{R(\omega)}{|Z(\omega)|^2}$ (solid line), $\frac{VS_{J_1}(\omega)}{2k_BT^2} = \frac{R(\omega)}{|Z_1(\omega)|^2}$ (dashed line) and $\frac{VS_{J_2}(\omega)}{2k_BT^2} = \frac{R(\omega)}{|Z_2(\omega)|^2}$ (blue dash dotted line) of the equilibrium fluctuations of the heat fluxes J(t), $J_1(t)$ and $J_2(t)$, respectively, at different temperatures above T_D for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag predicted on the basis of the analytical model for the heat current autocorrelation function given by Equation 5.1.



(a)



(b)



(c)



(d)



Figure 6.3: Magnitude of the impedances $|Z(\omega)|$ (solid line), $|Z_1(\omega)|$ (thick blue dashed line) and $|Z_2(\omega)|$ (thick blue dotted line) along with the resistances $R_1(\omega)$ (thin dashed line) and $R_2(\omega)$ (thin dotted line) at different temperatures above T_D for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag predicted on the basis of the analytical model for the heat current autocorrelation function given by Equation 5.1.
As can be seen in Figure 6.2, at very low frequencies, when $\omega \ll \tau_2^{-1}$ (for example, in the f.c.c. Cu, τ_2^{-1} was approximately 0.6 THz at 400 K (see Table 6.1 for more details)), the amplitude of the fluctuations of J(t) decreased only very slightly from their maximum values as the frequency increased from $\omega = 0$. In this frequency range, the amplitude of the fluctuations of J(t) is mainly determined by the scattering of the acoustic long-range phonon modes. It can be seen in Figures 6.1 – 6.3 that, at $\omega \ll \tau_2^{-1}$, the responses can be estimated as $|Z(\omega)|^{-1} \approx R^{-1}(\omega) \approx k$, $|Z_1(\omega)|^{-1} \approx R_1^{-1}(\omega) \approx$ k_1 , and $|Z_2(\omega)|^{-1} \approx R_2^{-1}(\omega) = k_2$. At $\omega \gg \tau_2^{-1}$, the response $|Z_2(\omega)|^{-1}$ becomes practically independent of the relaxation time (i.e., purely reactive) so that $|Z_2(\omega)|^{-1} \approx$ $|Y_2(\omega)|^{-1} = k_2/\omega\tau_2 = C_2v_j^2/3\omega$. As a result, the temperature dependence of the response $|Z_2(\omega)|^{-1}$ at $\omega \gg \tau_2^{-1}$ is basically controlled by the temperature dependence of the product $C_2v_i^2$.

The impedance $|Z_1(\omega)|$ of the acoustic short-range phonon modes has a minimum at a frequency ω_{01} , which is slightly above ω_c (see Figure 6.3). This frequency ω_{01} can be defined as the undamped resonance frequency of the heat flux $J_1(t)$ driven by hypothetical external periodic temperature perturbations (i.e., this frequency may also be called the driven resonance frequency). Furthermore, it can be noted in Figure 6.2 that $S_{l_1}(\omega)$ has a maximum at a frequency ω_{d_1} , which is located between ω_R and ω_{01} . The frequency ω_{d1} at the location of the maximum on $S_{I_1}(\omega)$ determines the highest amplitude of the fluctuation of the heat flux $J_1(t)$ at thermal equilibrium (i.e., the response on X(t)). As a result, the frequency ω_{d1} can be defined as the damped resonance frequency of the heat flux $J_1(t)$. It is also important to point out that the locations of the minimum of $|Z_2(\omega)|$ and the maximum of $S_{I_2}(\omega)$ of the acoustic longrange phonon modes coincided with each other, so that $\omega_{02} = \omega_{d2} = 0$. Thus, considering that the cut-off of the density of the acoustic long-range phonon modes is at the origin, the matching of ω_{d1} and ω_c is an additional very important piece of evidence of the fact that the cut-off of the density of the acoustic short-range phonon modes occurs in the vicinity of ω_c . In other words, between the lowest energy level of the acoustic short-range phonon modes and the origin there is an energy gap of the order of $\sim \hbar \omega_c$ (or $\sim k_{\rm B}T_{\rm c}$). Figure 6.4 shows the temperature dependences of the frequencies ω_c , ω_R , ω_{01} , and ω_{d1} . In this figure, for comparitive reasons, the data at T < 1 $T_{\rm D}$ is included. Indeed, it is interesting to note that, at high temperatures, $\omega_{\rm c}$ and $\omega_{\rm d1}$ are very well matched with $\omega_c \approx \omega_{d1}$ (strong anharmonic effects), while at low temperatures ω_c tended to approach ω_{01} (quasi-harmonic vibrations).













(d)



	-	7
	ρ	
•	v	۰.
•		

Figure 6.4: Temperature dependences of the characteristic frequencies ω_c (circles), ω_R (diamonds), ω_{01} (solid downward facing triangles), ω_{d1} (squares), and $\omega'_{01} = \omega_c \sqrt{1 - (\omega_c \tau_1)^{-2}}$ (upward facing triangles) for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag in a wide temperature range (see Table 3.1). Open downward facing triangles show an estimation of ω_{01} on the basis of ω_c (via ω'_{01}) and τ_1 according to an approximate relation given by the quartic equation $(\omega_{01}/\omega'_{01})^4 - (\omega_{01}/\omega'_{01})^3 - (\omega_{01}/\omega'_{01})(\omega'_{01}\tau_1)^{-4} - (\omega'_{01}\tau_1)^{-2} = 0$. See text for further details.

Overall, it can be seen in Figure 6.3 that in the frequency range $0 \le \omega \le \omega_{01}$ the impedance $|Z_1(\omega)|$ was practically determined by the resistance $R_1(\omega)$. The resistance $R_1(\omega)$ itself, according to Equation 6.13, decreases from $R_1(\omega) \approx k_1^{-1}$ at low frequencies to $R_1(\omega) \approx \tau'_1/k_1\tau_1$ at high frequencies. Meanwhile, according to Equation 6.14, the reactance $Y_1(\omega)$, increasing from zero, takes positive values at low frequencies, passes via a maximum and then a zero value, and finally changes as $Y_1(\omega) \approx -\omega \tau'_1/k_1 (1 - \omega_c^2/\omega^2)$ at high frequencies $\omega \gg \tau_1^{-1}$ (for example, in the f.c.c. Cu, τ_1^{-1} was approximately 6.4 THz at 400 K (see Table 6.1 for further details)). In this context, it can be noted that in the case if $R_1(\omega)$ were constant, i.e., independent of the frequency, 147

 $|Z_1(\omega)|$ would have a minimum exactly at the frequency where $Y_1(\omega)$ passes via a zero value. Let us denote this frequency as ω'_{01} . This frequency can be readily found from Equation 6.14 as $Y_1(\omega'_{01}) = 0$, so that it is $\omega'_{01} = \omega_c \sqrt{1 - (\omega_c \tau_1)^{-2}}$. In this study, however, $R_1(\omega)$ decreased with a frequency which resulted in the minimum of $|Z_1(\omega)|$ shifting towards a higher frequency $\omega_{01} > \omega'_{01}$. For example, in this case $R_1(\omega'_{01}) =$ $2\tau'_1/k_1\tau_1$ took a value which was two times higher than its high-frequency limit. Thus, if the difference between ω_{01} and ω'_{01} is relatively small, one may use the expansion of $Y_1(\omega)$ to first order in $(\omega - \omega'_{01})$ inside the frequency range between ω'_{01} and ω_{01} to derive an approximate relation for ω_{01} and ω_c (via ω'_{01}). Indeed, noticing from Equations 6.13 and 6.14 a useful relation for $R_1(\omega)$ and $Y_1(\omega)$ of the form $R_1(\omega) =$ $R_1(\omega'_{01}) + Y_1(\omega)/\omega\tau_1$, one may employ the following approximations $Y_1(\omega) \approx$ $-R_1(\omega'_{01})(\omega'_{01}/\omega_c)^2(\omega-\omega'_{01})\tau_1 \quad \text{and} \quad R_1(\omega) \approx R_1(\omega'_{01})(\omega'_{01}/\omega_c)^2(\omega'_{01}/\omega-\omega'_{01})\tau_1$ $(\omega'_{01}\tau_1)^{-2})$ inside the frequency range between ω'_{01} and ω_{01} . Then, using these approximations for $R_1(\omega)$ and $Y_1(\omega)$ in setting the derivative of $|Z_1(\omega)|$ at zero for $\omega =$ ω_{01} , one can readily obtain the following quartic equation for the ratio $\omega_{01}/\omega'_{01} > 1$: $(\omega_{01}/\omega_{01}')^4 - (\omega_{01}/\omega_{01}')^3 - (\omega_{01}/\omega_{01}')(\omega_{01}'\tau_1)^{-4} - (\omega_{01}'\tau_1)^{-2} = 0.$ Figure 6.4, along with ω_c , ω_R , ω_{01} , and ω_{d1} , also show the temperature dependence of ω'_{01} , as well as of ω_{01} , found as a numerical solution of the quartic equation (this study is not concerned with an analytical solution of the quartic equation). It can be seen in Figure 6.4, which as the temperature increases, the difference between ω_{01} and ω'_{01} also increases. For example, in the f.c.c. Cu, their ratio ω_{01}/ω'_{01} was approximately 1.13 and 1.34 at 40 and 400 K, respectively (see Table 6.1 for further details). As a result, the ω_{01} estimated from the quartic equation gave excellent agreement with the actual value of ω_{01} up to the temperatures slightly above the Debye temperature, while such an estimation becomes much less reliable as the temperature approaches the melting temperature.

With increasing frequency at $\omega > \omega_c \sim \omega_{01}$, the ability of the acoustic short-range phonon modes to be scattered for the time of approximately π/ω gradually decreased. As a result, at high frequencies, the response $|Z_1(\omega)|^{-1}$ becomes mainly dominated by the reactance $Y_1(\omega)$. It was noted, for example, that at frequencies close to the Debye frequency the ratio $|Y_1(\omega)|/R_1(\omega)$, in f.c.c. Cu, can be roughly estimated as approximately 5 and 3.5 at 400 and 1300 K respectively (see Table 6.1 for further details). **Table 6.1:** τ_2^{-1} , τ_1^{-1} , ω_{01}/ω'_{01} , $|Y_1(\omega)|/R_1(\omega)$ of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag models at some temperatures. All quantities presented in this table are introduced in the text (see Figures 6.1– 6.4 for further details).

Metals	Temperature	$ au_2^{-1}$ (THz)	$\tau_1^{-1}(\text{THz})$	$\frac{\omega_{01}}{\omega_{01}'}$	$\frac{ Y_1(\omega) }{R_1(\omega)}$
Cu	40			1.13	
	400	0.6	6.4	1.34	5.0
	1200	2.7			
	1300		11.8		3.5
Al	100			1.06	
	500	1.0	8.3	1.28	6.0
	1000	3.2	12.6	2.32	4.0
Nieami	100			1.15	
	500	0.5	7.6	1.34	7.0
	1700	2.14	15.8		3.8
Ni _{EAM2}	100			1.14	
	500	0.3	6.0	1.19	8.5
	1700	2.2	11.2	3.06	5.0
Ag	40			1.11	
	300	0.5	4.6	1.31	6.0
	1100	2.0	8.8		3.0

Thus, this analysis shows that in a monatomic lattice, especially at sufficiently low temperatures, there might be a frequency "window" $\tau_2^{-1} \ll \omega \ll \omega_c$ for an external periodic temperature perturbation to create a response state in which: (i) the acoustic short-range phonon modes have always enough time to be equilibrated with respect to the lattice; while (ii) the acoustic long-range phonon modes are expected to be equilibrated with respect to each other but do not have enough time to be equilibrated with respect to the lattice. As a result, such an external periodic temperature perturbation can result in thermal waves (so called second sound [87, 88]) being propagated in the lattice via the acoustic long-range phonon modes.

Lastly, by using Equations 6.10 and 6.24, the power spectrum $S_J(\omega)$ of the fluctuations of the total heat flux J(t) and the total impedance $|Z(\omega)|$ can be readily represented via $S_{J_1}(\omega)$ and $S_{J_2}(\omega)$, and via $|Z_1(\omega)|$ and $|Z_2(\omega)|$, respectively, as 149

 $S_{I}(\omega) = S_{I_{1}}(\omega) R_{1}(\omega) / R(\omega) + S_{I_{2}}(\omega) R_{2}(\omega) / R(\omega)$ $|Z(\omega)|^{-2} =$ and $|Z_1(\omega)|^{-2} R_1(\omega)/R(\omega) + |Z_2(\omega)|^{-2} R_2(\omega)/R(\omega)$, or, alternatively, as $S_I(\omega) =$ $S_{J_1}(\omega) Y_1(\omega)/Y(\omega) + S_{J_2}(\omega) Y_2(\omega)/Y(\omega)$ and $|Z(\omega)|^{-2} = |Z_1(\omega)|^{-2} Y_1(\omega)/Y(\omega) + S_{J_2}(\omega) Y_2(\omega)/Y(\omega)$ $|Z_2(\omega)|^{-2} Y_2(\omega)/Y(\omega)$. As a result, it can be seen in Figures 6.2 and 6.3 that $S_J(\omega)$ and $|Z(\omega)|$ represent some appropriately weighted combinations of the features discussed above of $S_{J_1}(\omega)$ and $S_{J_2}(\omega)$, and $|Z_1(\omega)|$ and $|Z_2(\omega)|$, respectively. Meanwhile, Figure 6.5 shows the spectra of the power dissipation for the equilibrium thermal fluctuations for the MD models of f.c.c. Cu, Al, NiEAM1, NiEAM2 and Ag. According to Equations 6.23 and 6.24, this spectrum $S_{Power}(\omega)$ can be defined by the product of $S_I(\omega)$ and $S_X(\omega)$ as $S_{\text{Power}}(\omega) = \frac{3V}{2\pi k_{\text{B}}T} S_{J}(\omega) S_{X}(\omega)$. The spectra $S_{J}(\omega)$ and $S_{\text{Power}}(\omega)$ can, in principle, be obtained experimentally by scattering and absorption measurements. Thus, the considered spectral representation of the analytical model for the HCACF given by Equation 5.1 (page 81) could be used in the future for the interpretation of spectroscopic measurements of phonon dynamics if a proper resolution of the frequency range of approximately 1 - 20 THz is routinely accessible.



(a)



(b)



(c)



(d)



(e)

Figure 6.5: Spectra of the power dissipation $S_{Power}(\omega) = \frac{3V}{2\pi k_B T} S_J(\omega) S_X(\omega)$ for the equilibrium thermal fluctuations at different temperatures above T_D for the MD models of f.c.c. (a) Cu, (b) Al, (c) Ni_{EAM1}, (d) Ni_{EAM2} and (e) Ag predicted on the basis of the analytical model for the heat current autocorrelation function given by Equation 5.1.

Overall, it should be noted that despite having principally restricted the present work to an investigation of the lattice thermal resistance of a cubic (isotropic case) Bravais lattice, using MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag as case studies, the results are not difficult to generalize for other (anisotropic) Bravais lattices in the future, as well as for non-Bravais lattices which also permit optical phonon modes. Furthermore, along with the phonon-phonon interactions, other phonon scattering processes can be included in the considerations. In addition, aside from the steady state Boltzmann equation in the presence of a constant temperature gradient considered (see Chapter 8), the study results in the spectral representation of the heat flux fluctuations in thermal equilibrium to be effectively used to formulate a generalized Boltzmann equation valid for the applied thermal disturbance of an arbitrary finite frequency. In particular, the fundamental understanding of thermal transport on periodic temperature perturbations is of great interest in the intelligent development of electronic devices operating at high frequencies.

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity

Figure 7.1 compares the results for the lattice thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag with a compilation [11] of experimental measurements of the thermal conductivity over wide temperature ranges (see Table 3.1), which obviously also includes contributions due to the electron-phonon and phononelectron scattering processes. Since some confusion may arise here, it is apposite to recall that the quantity calculated in this work is actually the component of the lattice thermal conductivity, k_{ph-ph} , determined by the phonon-phonon scattering processes. As a first approximation, one may estimate the contributions, $k_{el-ph} \approx k_{el}$ and k_{ph-el} , due to the electron-phonon and phonon-electron scattering to the total thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag by using a simplified model of the electron-phonon interactions in a metal [17, 21, 25] along with this study's data for k_{ph-ph} and the experimental data [11] for k. Besides ignoring the effects of the electron-electron scattering, the main simplifications used in the model to evaluate k_{el-ph} and k_{ph-el} include [17, 21, 25]: spherical Fermi surface, electronphonon scattering N-processes only, Thomas-Fermi approximation, etc. Thus, one may employ the following relation [17, 21, 25]:

$$k \approx k_{\rm el-ph} + \left(k_{\rm ph-ph}^{-1} + k_{\rm ph-el}^{-1}\right)^{-1},$$
 (7.1)

with k_{el-ph} and k_{ph-el} given by [17] (for more details, see also [14, 21, 89, 90])

$$k_{\rm el-ph}^{-1} = \frac{A}{L_0 T_{\rm D}} \left(\frac{T}{T_{\rm D}}\right)^4 J_5 \left(\frac{T_{\rm D}}{T}\right) \left\{ 1 + \frac{3}{\pi^2} \left(\frac{n_{\rm e}}{2}\right)^{\frac{2}{3}} \left(\frac{T_{\rm D}}{T}\right)^2 - \frac{1}{2\pi^2} \frac{J_7 \left(\frac{T_{\rm D}}{T}\right)}{J_5 \left(\frac{T_{\rm D}}{T}\right)^2} \right\},\tag{7.2}$$

$$k_{\rm ph-el}^{-1} = \frac{A}{L_0 T_{\rm D}} \frac{\pi^2 n_{\rm e}^2}{27} \left(\frac{T_{\rm D}}{T}\right)^2 \frac{J_5\left(\frac{T_{\rm D}}{T}\right)}{\left[J_4\left(\frac{T_{\rm D}}{T}\right)\right]^2},\tag{7.3}$$

where *A* is a constant which represents the strength of the electron-phonon interactions, $L_0 = 2.445 \text{ W}\Omega\text{K}^{-2}$ is the ideal Lorenz number, n_e is the number of free electrons per atom, and $J_n\left(\frac{T_D}{T}\right)$ is given by:

$$J_n\left(\frac{T_{\rm D}}{T}\right) = \int_{0}^{T_{\rm D}/T} \frac{x^n e^x}{(e^x - 1)^2} dx.$$
 (7.4)

First, it should be noted, as can be seen in Figures 7.1(c₁) and 7.1(d₁), that the total thermal conductivity of f.c.c. Ni_{EAM1} and Ni_{EAM2} above the Curie temperature²⁵ 628 K increased with temperature. In this context, it was noted in [89] that it would seem that abnormal complications are present with the electronic contribution to the thermal conductivity of nickel above the magnetic transformation point. For this reason, this study limits itself to a consideration of only the temperature range of 100 – 600 K (see Figures 7.1(c₁) and 7.1(d₁)). Next, it is known [21] that various experiments indicate that the number of free electrons per atom of Ni is $n_e \approx 0.54$. Then it is straightforward to show that Equation 7.1 can be rearranged to obtain a quadratic equation for the ratio k_{ph-ph}/k_{ph-el} , as:

$$\left(\frac{k_{\rm ph-ph}}{k_{\rm ph-el}}\right)^2 + \left(1 - \frac{k_{\rm ph-ph}}{k} - \frac{k_{\rm ph-ph}}{k} \frac{k_{\rm el-ph}}{k_{\rm ph-el}}\right) \frac{k_{\rm ph-ph}}{k_{\rm ph-el}} - \frac{k_{\rm ph-ph}}{k} \frac{k_{\rm el-ph}}{k_{\rm ph-el}} = 0.$$
(7.5)

²⁵ The Curie temperature is a critical temperature for a ferromagnetic material above which this temperature ferromagnetic material becomes paramagnetic.

Hence, a meaningful positive-root solution of the quadratic equation for the ratio k_{ph-ph}/k_{ph-el} can be readily found as:

$$\frac{k_{\rm ph-ph}}{k_{\rm ph-el}} = \frac{1}{2} \left(\frac{k_{\rm ph-ph}}{k} \frac{k_{\rm el-ph}}{k_{\rm ph-el}} + \frac{k_{\rm ph-ph}}{k} - 1 + \sqrt{D} \right), \tag{7.6}$$

where:

$$D = \left(1 - \frac{k_{\rm ph-ph}}{k} - \frac{k_{\rm ph-ph}}{k} \frac{k_{\rm el-ph}}{k_{\rm ph-el}}\right)^2 + 4 \frac{k_{\rm ph-ph}}{k} \frac{k_{\rm el-ph}}{k_{\rm ph-el}} > 0.$$
(7.7)

Finally, by evaluating numerically the ratio $k_{\rm el-ph}/k_{\rm ph-el}$ from Equations 7.2 – 7.4 ($n_{\rm e}$ is approximately 1, 3, 0.54, 0.54 and 1, for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag, respectively), as well as the ratio $k_{\rm ph-ph}/k$, from the data for $k_{\rm ph-ph}$ and the experimental data [11] for k, the temperature dependence of the ratio $k_{\rm ph-ph}/k_{\rm ph-el}$ and, consequently, the temperature dependences of $k_{\rm ph-el}$, $k_{\rm el-ph}$, and $k_{\rm ph} = k_{\rm ph-ph} (1 + k_{\rm ph-ph}/k_{\rm ph-el})^{-1}$ can be estimated in a wide temperature range.

Thus, the estimations for the temperature dependences of k_{ph-el} , k_{el-ph} , and k_{ph} are shown in Figures 7.1(a₁), 7.1(b₁), 7.1(c₁), 7.1 (d₁) and 7.1(e₁) for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag, respectively, along with the study's data for k_{ph-ph} and the experimental data [11] for k. It can be seen in Figure 7.1 (a₁, b₁, c₁, d₁ and e₁) that the electronic contribution k_{el} ($\approx k_{el-ph}$) to the total thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag dominated the considered temperature ranges. Nonetheless, the phonon thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag increased as the temperature decreased. Furthermore, k_{ph-ph} and k_{ph-el} were calculated for a high temperature range ($T \gg T_D$) that k_{el-ph} and k_{ph-el} for high temperature limits are given by:

$$k_{\rm el-ph}^{-1} = \frac{A}{L_0 T_{\rm D}} \left(\frac{T}{T_{\rm D}}\right)^4 J_5 \left(\frac{T_{\rm D}}{T}\right),$$
 (7.8)

$$k_{\rm ph-el}^{-1} = \frac{A}{L_0 T_{\rm D}} \left(\frac{T_D}{T}\right) J_5 \left(\frac{T_D}{T}\right) \frac{\pi^2 n_{\rm e}^2}{\left(\frac{27}{9}\right) \left(\frac{T_D}{T}\right)^6},\tag{7.9}$$

that at high temperatures $(T \gg T_D)$, $J_5\left(\frac{T_D}{T}\right) = \frac{1}{4}\left(\frac{T_D}{T}\right)^4$, so that Equations 7.8 and 7.9 can be rearranged as:

$$k_{\rm el-ph}^{-1} = \frac{A}{4L_0 T_{\rm D}},\tag{7.10}$$

$$k_{\rm ph-el}^{-1} = \frac{A}{L_0 T_{\rm D}} \frac{\pi^2 n_{\rm e}^2}{12}.$$
(7.11)

Figure 7.1(a₁) shows that the phonon thermal conductivity of f.c.c. Cu increased as the temperature decreased down to 90 K. In addition, it can be seen in Figure 7.1(a₂) that the phonon contribution k_{ph} to the total thermal conductivity of f.c.c. Cu can be estimated as approximately 0.5 % at 1300 K (assuming $k_{ph} \approx k_{ph-ph}$ at $T \gg T_D$), and approximately 7 % at 90 K. Also, it was noted that the use of k_{ph-ph} instead of k_{ph} led to an overestimation of the phonon contribution to the total thermal conductivity by approximately 0.1% and 3% at 1200 and 90 K respectively (see Figure 7.1(a₂)). Figure 7.1 shows that the phonon thermal conductivity of f.c.c. Al increased as the temperature decreased down to 100 K. Moreover, it can be seen in Figure 7.1(b₁) that the phonon

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity

contribution k_{ph} to the total thermal conductivity of f.c.c. Al can be estimated as approximately 1% at 1000 K (assuming $k_{\rm ph} \approx k_{\rm ph-ph}$ at $T \gg T_{\rm D}$), and approximately 8% at 100 K. Also, it was noted that the use of k_{ph-ph} instead of k_{ph} led to an overestimation of the phonon contribution to the total thermal conductivity by approximately 0.3% and 4% at 1000 and 100 K, respectively (see Figure 7.1(b₂)). In f.c.c. Ni_{EAM1} and Ni_{EAM2}, the phonon thermal conductivity contribution to the total thermal conductivity had a maximum at 200 K and started to decrease at 100 K (see Figures 7.1(c_1) and 7.1(d_1)). In addition, it can be seen in Figures 7.1(c_2) and 7.1(d_2) that the phonon contribution k_{ph} to the total thermal conductivity of the MD models of f.c.c. Ni_{EAM1} and Ni_{EAM2} can be estimated as approximately 4% and 4% at 1500 K (assuming $k_{\rm ph} \approx k_{\rm ph-ph}$ at $T \gg T_{\rm D}$), approximately 14.4% and 20.7% at 600 K, approximately 16.8% and 34.1% at 200 K, and approximately 15.6% and 30% at 100 K, respectively. Also, it was noted that the use of k_{ph-ph} instead of k_{ph} led to an overestimation of the phonon contribution to the total thermal conductivity of f.c.c. Ni_{EAM1} by approximately 3%, 4% and 7 % at 600, 200 and 100 K, respectively (see Figure 7.1(c₂)), and this contribution for f.c.c. Ni_{EAM2} is about 3%, 8.3%, 40.5% and 73% at 1400, 600, 200 and 100 K, respectively (see Figure 7.1(d_2)). Figure 7.1(e_1) also showed that the phonon thermal conductivity of f.c.c. Ag increased as the temperature decreased down to 60 K. Furthermore, it can be seen in Figure 7.1(e_2) that the phonon contribution k_{ph} to the total thermal conductivity of f.c.c. Ag can be estimated as approximately 0.2% at 1200 K (assuming $k_{\rm ph} \approx k_{\rm ph-ph}$ at $T \gg T_{\rm D}$), and approximately 4% at 60 K. Also, it was noted that the use of k_{ph-ph} instead of k_{ph} led to an overestimation of the phonon contribution to the total thermal conductivity by approximately 0.04% and 0.6% at 1200 and 60 K, respectively (see Figure $7.1(e_2)$).



(a₁)





(b₁)

(b₂)



(c₁)











Figure 7.1: (a₁), (b₁), (c₁), (d₁) and (e₁) show the decomposition of the total thermal conductivity, k (solid circles), of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag [11], respectively, into the electronic, k_{el} (upward facing open triangles), and phonon, k_{ph} (solid diamonds), components. This decomposition is based on: (i) the relation $k = k_{el} + k_{ph}$; (ii) the calculations of the phonon thermal conductivity, k_{ph-ph} (open squares), limited by the phonon scattering; and (iii) a simplified model of electron-phonon scattering in a metal [14, 17, 21] (see text for details). As a result, it is assumed that $k_{el} \approx k_{el-ph}$ and $k_{ph} = (k_{ph-ph}^{-1} + k_{ph-el}^{-1})^{-1}$, where k_{el-ph} is the electron thermal conductivity limited by the phonon scattering, while k_{ph-el} (downward facing open triangles) is the phonon thermal conductivity limited by the phonon scattering. (a₂), (b₂), (c₂), (d₂) and (e₂) estimate the relative contribution of the phonon component to the total thermal conductivity of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag, respectively. Solid diamonds and open squares show the ratios k_{ph}/k and k_{ph-ph}/k , respectively.

It is very rarely possible to separate the electronic and lattice contributions in an experiment [17]. It is only in some special cases of extrinsic conductors, such as Cd₃As₂,

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity

that the electronic and lattice contributions can be separated by measuring the magneticfield dependence of the thermal conductivity [22]. Nonetheless, a general fundamental understanding of the factors affecting the electronic and lattice contributions to the thermal conductivity is highly desirable for the development of advanced energy conversion devices that utilise the thermoelectric effect [25]. In particular, it is known [25] that, besides a large value of the Seebeck coefficient, combinations of a low thermal conductivity with large electrical conductivity are required to achieve large values of the figure of merit for the thermoelectric performance of a material. It is also known [17] that at a given temperature, the electronic thermal conductivity of different crystals is supposed to scale approximately linearly with the electrical conductivity of the crystals, according to the Wiedemann-Franz law. In other words, this means that a low value of the lattice thermal conductivity is highly desirable to enhance the figure of merit of a thermoelectric crystal. Therefore, besides the spectral representation of the lattice thermal conductivity, which was discussed in the previous section, and which has the potential to be used in the future to enable direct spectroscopic measurements of the lattice thermal conductivity, it is also of great interest for the intelligent development of thermoelectric crystals to have simple scaling relations between the lattice thermal conductivity and other lattice properties readily accessible in the experiment, such as thermal expansion and elasticity.

In this context, it should be noted that MD simulations, in conjunction with the EAM potentials, present a unique opportunity for this type of study. Indeed, a fundamental understanding of the influence of other lattice properties on the lattice thermal conductivity can be achieved by a systematic MD study of a set of high quality models of isostructural crystals (i.e., crystals which have the same structure but different lattice properties). In particular, this study considered the scaling relations of the lattice thermal conductivity with the coefficient of thermal expansion and the bulk modulus estimated by using the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag. It should be highlighted here that one of the main advantages of an EAM potential model, compared to a pair potential model, is the ability to reproduce the elastic anisotropy of a cubic lattice (which results in the three independent elastic moduli) that is one of its well-known generic features [40]. Therefore, as long as a potential model is able to reproduce the fundamental features of a lattice, and all considered lattice properties are calculated for the same potential model, it is not even so important to study the scaling relations

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity

between the lattice properties or how close the considered model can reproduce the actual experimental data for a particular real crystal with the lattice. Indeed, this means that even different EAM models of the same real cubic crystal, which predict slightly different lattice properties of the crystal, can in principle be used for the general study of the scaling relations between the lattice properties of the cubic crystals with the lattice considered. Nonetheless, it should be underlined again that the fitting databases of the employed EAM potentials contained a very extensive set of relevant experimental and first-principles data which guarantee an adequate accounting of the anharmonic effects in the lattice properties of the cubic crystals presenting the isotropic case for the lattice thermal conductivity, this study is a good starting point to gain an initial understanding of the scaling relations. Later, it has the potential to be extended to non-cubic crystals to account for the anisotropy of the lattice thermal conductivity.

In this section, estimations are also given of the simple scaling relations between the lattice thermal conductivity and other lattice properties readily accessible in the experiments, such as the thermal expansion and elasticity. As mentioned in Chapter 1, such simple scaling relations would be of great interest for the intelligent development of thermoelectric crystals. Thus, Table 6.1 shows the lattice thermal conductivity, the coefficient of thermal expansion and the bulk modulus calculated for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag at the three temperatures 500, 700 and 900 K (the chosen temperatures are confined between the Debye and melting temperatures for all the metals, so that we again assume $k_{\rm ph} \approx k_{\rm ph-ph}$). Table 7.1 also shows in brackets the available experimental data: (i) for the coefficient of the thermal expansion of Cu, Al, Ni and Ag [90], and (ii) for the bulk modulus of Cu [91], Al [92], Ni [93] and Ag [91]. The coefficient of thermal expansion α_P was calculated by using the temperature dependence of the atomic volume at zero pressure P = 0 (see Figure 3.1 and Equation 3.5 for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag), and the parameters of Equation 3.5 are: Ω_0 , α_{Ω} and β_{Ω} (see Table 3.2) according to the relation:

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \tag{7.11}$$

Meanwhile, the isothermal bulk modulus B_T was calculated according to the relation:

$$B_T = -V \left(\frac{\partial P}{\partial V}\right)_T. \tag{7.12}$$

For each temperature considered, this was done by using a linear approximation of the pressure of the system at five different volumes in the direct vicinity of the respective zero-pressure volume.

Table 7.1: Lattice properties of the f.c.c. Cu, Al, Ni and Ag models at 500, 700 and 900 K (*k* is the lattice thermal conductivity, α_P is the coefficient of the thermal expansion, and B_T is the isothermal bulk modulus). The available experimental data are shown in brackets: (i) Ref. 90 for the coefficients of the thermal expansion of Cu, Al, Ni and Ag, and (ii) Refs. 91, 92, 93 and 91 for the bulk moduli of Cu, Al, Ni and Ag, respectively.

Temperature (K)	<i>k</i> (W/mK)			$\alpha_P \; (10^{-5} \; \mathrm{K}^{-1})$			B_T (GPa)					
	Cu	Ni	Al	Ag	Cu	Ni	Al	Ag	Cu	Ni	Al	Ag
500	6.22	12.92	5.50	2.05	5.29 (5.47)	3.32 (4.56)	5.34 (7.85)	6.69 (6.18)	127.26 (126.10)	212.21 (179.21)	76.13 (72.01)	95.09 (99)
700	3.82	8.96	3.23	1.45	5.76 (5.81)	3.50 (4.89)	6.22 (9.17)	7.09 (6.78)	121.03 (118.06)	207.16 (173.61)	70.57 (67.69)	88.459 (94)
900	2.59	7.16	2.19	1.18	6.21 (6.32)	3.68 (5.08)	7.07 (10.46)	7.47 (7.44)	114.70 (-)	199.79 (-)	63.61 (62.88)	80.59 (-)

Figures 7.2(a) and 7.2(b) show, in double-logarithmic coordinates, the ratio of the lattice thermal conductivities $k_{\rm ph}(M)/k_{\rm ph}(Cu)$ as a function of the ratio of the coefficients of thermal expansion $\alpha_P(M)/\alpha_P(Cu)$ and the ratio of the isothermal bulk moduli $B_T(M)/B_T(Cu)$, respectively, calculated for the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag at the three temperatures 500, 700 and 900 K (M denotes Cu, Al, Ni_{EAM1}, Ni_{EAM2} or Ag). By analysing the slopes of the linear fits of the data in Figure 7.2, it can be roughly estimated that at a given temperature the lattice thermal conductivity approximately scales as $k_{\rm ph} \propto \alpha_P^{-2}$ and $k_{\rm ph} \propto B_T$. In addition, it can be

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity

seen in Figure 7.2 that in both cases the absolute value of the scaling power changes with temperature only very slightly. This study presents the data for five models so that the scaling relations across a sufficiently large number of MD models of different f.c.c. metals can be investigated. As a result, it can be noted that the lattice component of the thermal conductivity should be smaller in isostructural materials with a higher value of the coefficient of thermal expansion and a lower value of the bulk modulus. Furthermore, one may expect that in materials which exhibit anisotropic lattice properties, the lattice component of the thermal conductivity should be smaller of the thermal conductivity should be smaller at a lower value of the smaller in that direction which has a higher value of the coefficient of thermal expansion and a lower value of the smaller in that direction which has a higher value of the coefficient of thermal expansion and a lower value of the smaller in that direction which has a higher value of the coefficient of thermal expansion and a lower value of the elastic modulus.





168

Chapter 7: Links to the Experimental Data and Assessment of the Scaling Relations of the Lattice Thermal Conductivity



(b)

Figure 7.2: Double-logarithmic plot for the scaling relations of the lattice thermal conductivity k_{ph} with (a) the coefficient of the thermal expansion α_P and (b) the isothermal bulk modulus B_T . Plots show the ratio of the lattice thermal conductivities $k_{ph}(M)/k_{ph}(Cu)$ as a function of (a) the ratio of the coefficients of the thermal expansion $\alpha_P(M)/\alpha_P(Cu)$ and (b) the ratio of the isothermal bulk moduli $B_T(M)/B_T(Cu)$ calculated for the f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag models at 500, 700 and 900 K (M denotes Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag). The symbols show the calculated data (data for Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag are marked as 1, 2, 3, 4 and 5, respectively) while the lines show the linear fit of the data. The small symbols and solid lines represent data at 500 K, the medium symbols and dashed lines represent data at 700 K, and the large symbols and dotted lines represent data at 900 K.

Chapter 8: Conclusions and Recommendations for Future Research

8.1 Conclusions

In this work, equilibrium molecular dynamics simulations, in conjunction with the Green-Kubo formalism, provided an effective basis to explore the thermal resistance of a crystal lattice with a monatomic unit cell due to phonon-phonon scattering processes. The key role of the equilibrium molecular dynamics simulations is the ability to give unique and direct access to the HCACF, which has been shown for a monatomic lattice, to reveal a consistent two-stage decay. Furthermore, this study has shown that the two-stage decay can be universally modelled by an analytical expression which provides an exceptional basis for the development of a general analytical treatment of the lattice thermal conductivity. The main results of the present study that originated from the treatment are briefly summarized below:

(i) It was found that the HCACFs of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag, as five case studies, exhibited a two-stage temporal decay which can be nicely modelled by the analytical function given by Equation 5.1 (page 81). Namely, an initial rapid decay of the HCACF was followed by a peak in the low temperature range and the intensity of the peak decreased as the temperature increased. It transformed to a shoulder which diminished almost entirely at high temperatures. Thus, only at very high temperatures, the first stage decay of the HCACF was visually and directly followed by a longer second stage decay in accordance with the results reported in [1, 2] for the HCACF of the f.c.c. Ar model. It has been demonstrated that the lattice thermal conductivity of a monatomic lattice can be decomposed into two contributions due to the acoustic short- and long-range phonon modes. Moreover, it has transpired that it is possible to present these two contributions in the form of simple kinetic formulas, consisting of the products of the heat capacity, the square of the average phonon velocity and the average relaxation time of the acoustic short- and long-range phonon modes, respectively. In addition, all these quantities have been numerically evaluated in a self-consistent manner from the HCACF.

- (ii) A HCACF decomposition model was introduced (see Equation 5.1 (page 81)), that can capture all the contributions to the HCACF of a monatomic f.c.c. lattice that were discussed in the literature. In the framework of this model, it has been demonstrated that despite the freezing out of the high frequency phonon modes at temperatures below the Debye temperature, a classical description of the thermal transport properties can be used down to around one quarter of the Debye temperature. This is because the acoustic long-range phonons, which are the main heat carriers responsible for the phonon thermal transport at low temperatures, are active down to around one quarter of the Debye temperature, and only at lower temperatures do they start to freeze out.
- (iii) An analytical treatment of the decomposition of the lattice thermal conductivity allowed for a numerical evaluation of the relaxation times and the partial heat capacity of the acoustic short- and long-range phonon modes from the HCACF extracted from the MD simulations at high temperatures $T > T_D$.
- (iv) It has been demonstrated that the average phonon velocities of the acoustic short- and long-range phonon modes should be equal to each other and can be evaluated via the second-order fluctuations of the heat current vector.
- (v) An extensive analysis of the spectral representation of the calculated HCACF has been carried out. In particular, the power spectra associated with the heat flux fluctuations in thermal equilibrium were predicted and investigated in detail. The power spectra have the potential to be measured in the future by various spectroscopic techniques. Thus, this has allowed for a potential connection between the study's model predictions and experiments
- (vi) Within the framework of a simplified model of the electron-phonon interactions in a metal [14, 17, 21], a comparison of the results was performed for the component of the lattice thermal conductivity, k_{ph-ph} , of the MD models of f.c.c. Cu, Al, Ni_{EAM1}, Ni_{EAM2} and Ag determined by

the phonon-phonon scattering processes with the experimental measurements of the thermal conductivity [11]. It has been demonstrated that: (i) the electronic contribution $k_{\rm el} (\approx k_{\rm el-ph})$ to the total thermal conductivity dominated the considered temperature range; (ii) the phonon thermal conductivity, $k_{\rm ph}$, increased as the temperature decreased; (iii) the use of $k_{\rm ph-ph}$ instead of $k_{\rm ph}$ led to an overestimation of the phonon contribution to the total thermal conductivity.

(vii) The scaling relations of the lattice thermal conductivity with the coefficient of thermal expansion and the bulk modulus have been estimated. As a result, at a given temperature the lattice thermal conductivity scales approximately with the inverse second power of the coefficient of the thermal expansion and are roughly proportional to the bulk modulus.

8.2 Future Research

The following suggestion can be defined for future research:

- (i) In this research, the simulations were performed within the framework of equilibrium MD simulations in conjunction with the Green-Kubo formalism. For this purpose, only five first-principles-based many body potential within the framework of the EAM developed by Mishin et al. were used. Generally, this analysis could be extended by employing other existing and new interatomic potentials, so that more MD models can be investigated.
- (ii) As discussed here, equilibrium MD simulations, along with the Green-Kubo formalism, are an effective method to estimate thermal conductivity and to also calculate the phonon transport properties of materials. Also, *ab initio* MD simulations have become popular in recent years. Consequently, combining the Green-Kubo method with *ab initio* MD simulations might be an interesting and fruitful topic for future work.
- (iii) This thesis focused on monoatomic f.c.c. crystals. Moreover, some alloys exhibit excellent high-temperature physical and mechanical properties.

The techniques developed here can be used in future work for the investigation of the thermal transport properties of alloys.

- (iv) The investigation of scaling relations between the lattice thermal conductivity and other lattice properties can be extended by including the data for models of other metals with different crystal lattices.
- (viii) As shown, the thermal conductivity can be expressed as the sum of two main contributions, one due to the electronic states and the other due to the lattice vibrations. It is normally quite difficult to separate these two contributions directly in an experimental situation. Simulation and experimental work are also important as the simulations provide insight into the nature of the physical phenomena and the experiment makes no assumptions. Furthermore, in this research, the power spectra have been developed. Accordingly, future work can focus on the power spectra that are expected to be accessible for measurements by various spectroscopic techniques. Thus, it can be a potential connection between the theoretical description and experiment.
- (ix) Phononics, like electronics and photonics, is a young branch of physics that is concerned with the behaviour of sound and heat. Understanding how to control sound waves and heat vibrations in materials provides opportunities to develop new ideas and devices for transforming waste heat into electricity.

References

- McGaughey, A.J.H. and M. Kaviany, *Thermal conductivity decomposition and* analysis using molecular dynamics simulations. Part I. Lennard-Jones argon. International Journal of Heat and Mass Transfer, 2004. 47(8–9): p. 1783-1798.
- McGaughey, A.J.H. and M. Kaviany, *Phonon Transport in Molecular Dynamics* Simulations: Formulation and Thermal Conductivity Prediction. 2006. **39**: p. 169-255.
- Kaburaki, H., et al., *Dynamical thermal conductivity of argon crystal*. Journal of Applied Physics, 2007. **102**(4): p. 043514-6.
- He, Y.P., et al., Lattice thermal conductivity of semiconducting bulk materials: atomistic simulations. Physical Chemistry Chemical Physics, 2012. 14(47): p. 16209 - 16222.
- Mishin, Y., et al., Structural stability and lattice defects in copper: Ab initio, tight-binding, and embedded-atom calculations. Physical Review B, 2001.
 63(22): p. 224106.
- Mishin, Y., Atomistic modeling of the γ and γ'-phases of the Ni-Al system. Acta Materialia, 2004. 52(6): p. 1451-1467.
- Mishin, Y., et al., Interatomic potentials for monoatomic metals from experimental data and ab initio calculations. Physical Review B, 1999. 59(5): p. 3393-3407.
- Williams, P.L., Y. Mishin, and J.C. Hamilton, *An embedded-atom potential for* the Cu?Ag system. Modelling and Simulation in Materials Science and Engineering, 2006. 14(5): p. 817.
- 9. Richardson, C.F. and P. Clancy, *Contribution of thermal conductivity to the crystal-regrowth velocity of embedded-atom-method-modeled metals and metal alloys.* Physical Review B, 1992. **45**(21): p. 12260-12268.
- Foiles, S.M., M.I. Baskes, and M.S. Daw, *Embedded-atom-method functions for the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys.* Physical Review B, 1986.
 33(12): p. 7983-7991.
- Ho, C.Y., R.W. Powell, and P.E. Liley, *Thermal Conductivity of the Elements*. Journal of Physical and Chemical Reference Data, 1972. 1(2): p. 279-421.

- 12. Allen, P. and D.J. Tildesley, *Computer Simulation of Liquids*. 1989: Clarendon Press.
- Jeng, M.-S., et al., Modeling the Thermal Conductivity and Phonon Transport in Nanoparticle Composites Using Monte Carlo Simulation. Journal of Heat Transfer, 2008. 130(4): p. 042410-042410.
- 14. Tritt, T.M., *Thermal Conductivity: Theory, Properties, and Applications*. 2004: Springer.
- 15. Shinde, S.L. and J. Goela, *High Thermal Conductivity Materials*. 2006: Springer.
- Plawsky, J.L., *Transport Phenomena Fundamentals, Third Edition*. 2014: CRC Press.
- 17. Berman, R., *Thermal conduction in solids / by R. Berman*. Oxford studies in physics. 1976, Oxford [Eng.]: Clarendon Press.
- Chen, Y., et al., *Minimum superlattice thermal conductivity from molecular dynamics*. Physical Review B, 2005. **72**(17): p. 174302.
- 19. Kaviany, M., Heat transfer physics. 2014: Cambridge University Press.
- 20. Kittel, C., *Introduction to solid state physics*. 1971: Wiley.
- 21. Ziman, J.M., *Electrons and Phonons: The Theory of Transport Phenomena in Solids*. 1960: OUP Oxford.
- Armitage, D. and H.J. Goldsmid, *The thermal conductivity of cadmium arsenide*.
 Journal of Physics C: Solid State Physics, 1969. 2(11): p. 2138.
- Garrity, P.L. and K.L. Stokes, *Thermal noise as a spectroscopic tool to determine transport properties*. Philosophical Magazine, 2009. **89**(25): p. 2129-2147.
- Uher, C. and H.J. Goldsmid, Separation of the Electronic and Lattice Thermal Conductivities in Bismuth Crystals. physica status solidi (b), 1974. 65(2): p. 765-772.
- 25. Slack, G.A., *New materials and performance limits for thermoelecteric coolig*, in *Thermoelecteric Handbook*, D.M. Rowe, Editor. 1995, CRC Press: Boca Raton. p. 407-440.
- 26. Huang, B.L. and M. Kaviany, *Structural metrics of high-temperature lattice conductivity*. Journal of Applied Physics, 2006. **100**(12): p. 123507.

- 27. Toberer, E.S., A. Zevalkink, and G.J. Snyder, *Phonon engineering through crystal chemistry*. Journal of Materials Chemistry, 2011. **21**(40): p. 15843-15852.
- Böttner, H., G. Chen, and R. Venkatasubramanian, Aspects of Thin-Film Superlattice Thermoelectric Materials, Devices, and Applications. MRS Bulletin, 2006. 31(03): p. 211-217.
- 29. Venkatasubramanian, R., et al., *Thin-film thermoelectric devices with high roomtemperature figures of merit.* Nature, 2001. **413**(6856): p. 597-602.
- Ikeda, T., et al., *Nanostructuring of Thermoelectric Mg2Si via a Nonequilibrium Intermediate State*. Small, 2012. 8(15): p. 2350-2355.
- 31. Wu, H.J., et al., *Formation of ordered nano-wire microstructures in thermoelectric Pb–Ag–Sb–Te*. Acta Materialia, 2012. **60**(3): p. 1129-1138.
- 32. Nolas, G.S., et al., *High figure of merit in partially filled ytterbium skutterudite materials*. Applied Physics Letters, 2000. **77**(12): p. 1855-1857.
- Sales, B.C., D. Mandrus, and R.K. Williams, *Filled Skutterudite Antimonides: A New Class of Thermoelectric Materials*. Science, 1996. 272(5266): p. 1325-1328.
- Abeles, B., Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures. Physical Review, 1963. 131(5): p. 1906-1911.
- 35. Ambegaokar, V., *Thermal Resistance due to Isotopes at High Temperatures*. Physical Review, 1959. **114**(2): p. 488-489.
- Callaway, J. and H.C. von Baeyer, *Effect of Point Imperfections on Lattice Thermal Conductivity*. Physical Review, 1960. **120**(4): p. 1149-1154.
- 37. Steigmeier, E.F. and B. Abeles, *Scattering of Phonons by Electrons in Germanium-Silicon Alloys.* Physical Review, 1964. **136**(4A): p. A1149-A1155.
- Yang, J., G.P. Meisner, and L. Chen, Strain field fluctuation effects on lattice thermal conductivity of ZrNiSn-based thermoelectric compounds. Applied Physics Letters, 2004. 85(7): p. 1140-1142.
- 39. Zhou, Z., et al., Influence of point-defect scattering on the lattice thermal conductivity of solid solution Co (Sb 1- x As x) 3. Physical Review B, 2005.
 71(23): p. 235209.

- Daw, M.S. and M.I. Baskes, *Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals.* Physical Review B, 1984. 29(12): p. 6443-6453.
- Peierls, R., Zur kinetischen Theorie der Wärmeleitung in Kristallen. Annalen der Physik, 1929. 395(8): p. 1055-1101.
- 42. Peierls, R.E., *Quantum Theory of Solids*. 1955: Clarendon Press.
- Julian, C.L., *Theory of Heat Conduction in Rare-Gas Crystals*. Physical Review, 1965. 137(1A): p. A128-A137.
- 44. Cowley, R.A., *Zero sound, first sound and second sound of solids*. Proceedings of the Physical Society, 1967. **90**(4): p. 1127.
- 45. Griffin, A., *Brillouin Light Scattering from Crystals in the Hydrodynamic Region*. Reviews of Modern Physics, 1968. **40**(1): p. 167-205.
- 46. Wehner, R.K. and R. Klein, *Scattering of light by entropy fluctuations in dielectric crystals.* Physica, 1972. **62**(2): p. 161-197.
- 47. Koreeda, A., R. Takano, and S. Saikan, *Light scattering in a phonon gas*. Physical Review B, 2009. 80(16): p. 165104.
- 48. Sun, L. and P.U.M. Engineering, *Phonon Transport in Confined Structures and at Interfaces*. 2008: Purdue University.
- 49. Yao, Z., et al., *Thermal conduction of carbon nanotubes using molecular dynamics*. Physical Review B, 2005. **71**(8): p. 085417.
- Mingo, N. and L. Yang, Phonon transport in nanowires coated with an amorphous material: An atomistic Green's function approach. Physical Review B, 2003. 68(24): p. 245406.
- 51. Mishin, Y., M. Asta, and J. Li, *Atomistic modeling of interfaces and their impact* on microstructure and properties. Acta Materialia, 2010. **58**(4): p. 1117-1151.
- 52. Glicksman, M.E. and R.J. Schaefer, *Investigation of solid/liquid interface temperatures via isenthalpic solidification*. Journal of Crystal Growth, 1967. 1(5): p. 297-310.
- 53. Rodway, G.H. and J.D. Hunt, *Thermoelectric investigation of solidification of lead I. Pure lead.* Journal of Crystal Growth, 1991. **112**(2–3): p. 554-562.
- 54. Hoyt, J.J., M. Asta, and A. Karma, *Atomistic and continuum modeling of dendritic solidification*. Materials Science and Engineering: R: Reports, 2003.
 41(6): p. 121-163.

- 55. Monk, J., et al., Determination of the crystal-melt interface kinetic coefficient from molecular dynamics simulations. Modelling and Simulation in Materials Science and Engineering, 2010. 18(1): p. 015004.
- 56. Frenkel, D. and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications*. 2002: Academic Press.
- 57. Landry, E.S., et al., *Droplet evaporation: A molecular dynamics investigation*.Journal of Applied Physics, 2007. 102(12): p. 124301-7.
- 58. Emiliano Ippoliti, Parallel Algorithms for Short-Range Molecular Dynamics, What is Molecular Dynamics? 2011.
- 59. Konstantinos Termentzidis and S. Merabia, Molecular Dynamics Simulations and Thermal Transport at the Nano-Scale, in Molecular Dynamics - Theoretical Developments and Applications in Nanotechnology and Energy, L. Wang, Editor. 2012, InTech, Chapters published
- 60. Furio Ercolessi, *A molecular dynamics primer*. 2004: Spring College in Computational Physics, ICTP, Trieste.
- 61. Daw, M.S., S.M. Foiles, and M.I. Baskes, *The embedded-atom method: a review of theory and applications*. Materials Science Reports, 1993. **9**(7–8): p. 251-310.
- Baskes, M., S. Foiles, and M. Daw, *Application of the Embedded Atom Method* to the Fracture of Interfaces. Journal de Physique Colloques, 1988. 49(C5): p. C5-483-C5-495.
- 63. Luo, N., W. Xu, and S.C. Shen, *Embedded atom method for phonon frequencies in transition metals.* Solid State Communications, 1990. **75**(11): p. 877-880.
- 64. Tretiakov, K.V. and S. Scandolo, *Thermal conductivity of solid argon from molecular dynamics simulations*. The Journal of Chemical Physics, 2004. 120(8): p. 3765-3769.
- Ladd, A.J.C., B. Moran, and W.G. Hoover, *Lattice thermal conductivity: A comparison of molecular dynamics and anharmonic lattice dynamics*. Physical Review B, 1986. 34(8): p. 5058-5064.
- 66. McQuarrie, D.A., *Statistical Mechanics*. 1967: Harper & Row, New York.
- Alder, B.J. and T.E. Wainwright, *Phase Transition for a Hard Sphere System*.
 The Journal of Chemical Physics, 1957. 27(5): p. 1208-1209.
- Rahman, A., Correlations in the Motion of Atoms in Liquid Argon. Physical Review, 1964. 136(2A): p. A405-A411.

- 69. Kubo, R., {Statistical-Mechanical Theory of Irreversible Processes. I. \textit{General Theory and Simple Applications to Magnetic and Conduction Problems}. Journal of the Physical Society of Japan, 1957. 12: p. 570-586.
- 70. Sellan, D.P., et al., *Size effects in molecular dynamics thermal conductivity predictions.* Physical Review B, 2010. **81**(21): p. 214305.
- Schelling, P.K., S.R. Phillpot, and P. Keblinski, *Phonon wave-packet dynamics* at semiconductor interfaces by molecular-dynamics simulation. Applied Physics Letters, 2002. 80(14): p. 2484-2486.
- Che, J., et al., *Thermal conductivity of diamond and related materials from molecular dynamics simulations*. Journal of Chemical Physics, 2000. **113**(16): p. 6888-6900.
- Cahill, D.G., S.K. Watson, and R.O. Pohl, *Lower limit to the thermal conductivity of disordered crystals*. Physical Review B, 1992. 46(10): p. 6131-6140.
- Irving, J.H. and J.G. Kirkwood, *The Statistical Mechanical Theory of Transport* Processes. IV. The Equations of Hydrodynamics. The Journal of Chemical Physics, 1950. 18(6): p. 817-829.
- 75. Massalski, T.B.M.J.L.B.L.H.B.H., *Binary alloy phase diagrams*. 1986, Metals Park, Ohio: American Society for Metals.
- 76. Evteev, A.V., et al., *Molecular dynamics prediction of phonon-mediated thermal conductivity of f.c.c. Cu.* Philosophical Magazine, 2013: p. 1-21.
- 77. Evteev, A.V., et al., Vibrational contribution to thermal transport in liquid cooper: Equilibrium molecular dynamics study. Computational Materials Science, 2015. 96, Part A(0): p. 229-236.
- 78. Klemens, P.G., in *Thermal conductivity 19.* 1988, Plenum: New York. p. 453.
- Herring, C., *Role of Low-Energy Phonons in Thermal Conduction*. Physical Review, 1954. 95(4): p. 954-965.
- 80. Han, Y.J. and P.G. Klemens, *Anharmonic thermal resistivity of dielectric crystals at low temperatures*. Physical Review B, 1993. **48**(9): p. 6033-6042.
- Evteev, A.V., et al., *Two-fluid nature of phonon heat conduction in a monatomic lattice*. Philosophical Magazine, 2015. **95**(23): p. 2571-2595.
- Einstein, A., Elementare Betrachtungen über die thermische Molekularbewegung in festen Körpern Annalen der Physik, 1911. 35(S1): p. 679.
- 83. Lifshits, E.M., et al., *Statistical Physics*. 1980: Elsevier Science & Technology.
- Onsager, L., *Reciprocal Relations in Irreversible Processes. I.* Physical Review, 1931. 37(4): p. 405-426.
- Onsager, L., *Reciprocal Relations in Irreversible Processes. II.* Physical Review, 1931. 38(12): p. 2265-2279.
- 86. De Groot, S.R. and P. Mazur, *Non-Equilibrium Thermodynamics*. 1962, North-Holland, Amsterdam: Dover Publications.
- Callen, H.B. and T.A. Welton, *Irreversibility and Generalized Noise*. Physical Review, 1951. 83(1): p. 34-40.
- Landau, L., *Theory of the Superfluidity of Helium II*. Physical Review, 1941.
 60(4): p. 356-358.
- Powell, R.W., R.P. Tye, and M.J. Hickman, *The thermal conductivity of nickel*. International Journal of Heat and Mass Transfer, 1965. 8(5): p. 679-688.
- 90. Touloukian, Y.S., et al., *Thermal expansion: metallic elements and alloys*. Vol. 12. 1975, New York: IFI/Plenum.
- 91. Chang, Y.A. and L. Himmel, *Temperature Dependence of the Elastic Constants of Cu, Ag, and Au above Room Temperature*. Journal of Applied Physics, 1966.
 37(9): p. 3567-3572.
- 92. Gerlich, D. and E.S. Fisher, *The high temperature elastic moduli of aluminum*.Journal of Physics and Chemistry of Solids, 1969. **30**(5): p. 1197-1205.
- 93. Ledbetter, H.M. and R.P. Reed, *Elastic Properties of Metals and Alloys, I. Iron, Nickel, and Iron-Nickel Alloys.* Journal of Physical and Chemical Reference Data, 1973. 2(3): p. 531-618.