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

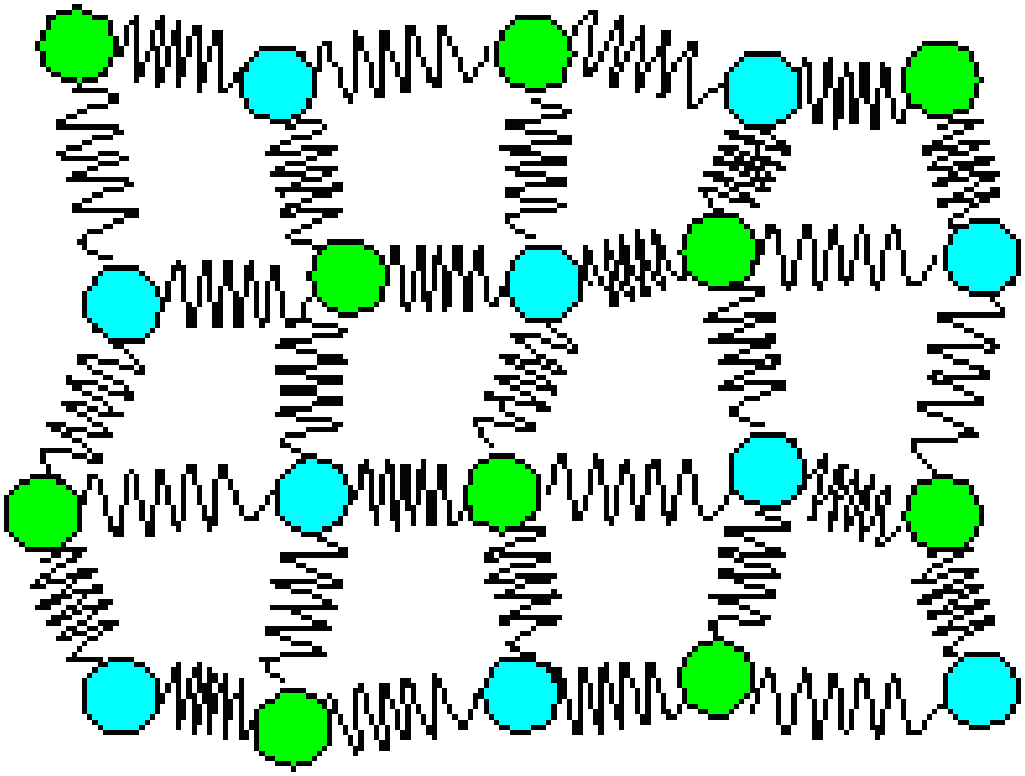
This is to certify that the thesis entitled “Prediction of Phonon Thermal Conductivity of Materials by Molecular Dynamics Simulation” submitted by Mrs Leila Momenzadeh contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution 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

List of Publications and Awards

Awards

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

Invited Talks

2014 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.

1. **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.
2. 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.
3. 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.
4. 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.
5. A.V. Evteev, E.V. Levchenko, **L. Momenzadeh**, I.V. Belova, and G.E. Murch, *Molecular Dynamics Study of Phonon-Mediated Thermal Transport in $Ni_{50}Al_{50}$ Melt: case analysis of the influence of the process on the kinetics of solidification.* Philosophical Magazine, 2015. 95: p. 90-111.
6. 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.
7. 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 7.1: (a_1), (b_1), (c_1), (d_1) and (e_1) 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 $k_{ph} = \left(k_{ph-ph}^{-1} + k_{ph-el}^{-1}\right)^{-1}$, 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 electron scattering. (a_2), (b_2), (c_2), (d_2) and (e_2) 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.. 164

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.…...169

List of Tables

List of Symbols

Arabic Symbols	
Symbol	**Description**
a	Lattice parameter, Lattice constant
$\overrightarrow{a_i}$	Acceleration
A	Constant number
A_1	Strength (1, refer to acoustic short-range phonons)
A_2	Strength (2, refer to acoustic long-range phonons)
B_T	Isothermal bulk modulus
C_1	Partial heat capacity of acoustic short-range phonon modes
C_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_{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-th atom
E	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
$\boldsymbol{g}$	Reciprocal lattice vector
$g(\omega, T)$	Density of phonon modes
$g_1(\omega, T)$	Density of the acoustic short-range phonon modes

$g_2(\omega, T)$	Density of the acoustic long-range phonon modes
$\boldsymbol{J}$	Microscopic heat current vector per unit volume
$\boldsymbol{J}_1$	Heat current due to acoustic short-range phonon modes
$\boldsymbol{J}_2$	Heat current due to acoustic long-range phonon modes
k	Thermal conductivity
k_1	Thermal conductivity (1, refer to acoustic short-range phonons)
k_2	Thermal conductivity (2, refer to acoustic long-range phonons)
k_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*
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
N	Number of atoms
N_1	Acoustic short-range phonon modes
N_2	Acoustic long-range phonon modes
P	Pressure
p_1 and p_2	Probabilities
$\mathbf{p}_i$	Momentum vectors
P_{set}	Pressure
$\boldsymbol{q}$	Wave vector
Q	Heat flux
$\boldsymbol{r}_i$	Position vectors, radius-vector of the *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
$s_{\boldsymbol{e},b}$	Speed of sound in the direction of $\boldsymbol{e} = \frac{\boldsymbol{q}}{\lvert\boldsymbol{q}\rvert}$ 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
T	Absolute temperature
T_D	Debye temperature
T_m	Melting temperature
T_{set}	Desired temperature
$\boldsymbol{u}$	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
$v_{i\alpha}$ or $v_{i\beta}$	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 $\boldsymbol{r}_i$
$x_{ij\alpha}$ or $x_{ij\beta}$	Components of the vectors $\boldsymbol{r}_{ij}$

$\boldsymbol{X}$	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*
β_{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
ε_{xy}	Shear strain
ϵ	Time history of parameter
φ_1	Contribution of the acoustic short-range phonon modes into the lattice heat capacity
φ_2	Contribution of the acoustic long-range phonon modes into the lattice heat capacity
$\emptyset_{\alpha\beta}$	Pair-wise potential function
γ	Gruneisen parameter
$\hbar$	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
$\bar{\rho}_i$	Host electron density

ρ_β	The electron density from one atom of type β at location of the other atom
$\rho_{\mu_j}(r_{ij})$	Electron density induced by an atom *j* at the location of atom *i*
σ	Finite distance, Entropy
σ_{el}	Electrical conductivity
$\sigma_{i\alpha\beta}^{(p)}$	Potential energy contribution to the components of the stress tensor of atom *i*
σ_{xx} and σ_{yy}	Compression stress
σ_{xy}	Shear stress
τ	Relaxation time
τ_1	Time constant (1, refer to acoustic short-range phonons)
τ_2	Time constant (2, refer to acoustic long-range phonons)
τ_1'	Average relaxation time
$\tau_{2\mathrm{N}}$	Relaxation time for a given acoustic long range phonon mode to restore the same perturbed phonon distribution $n(\boldsymbol{q}, b, T)$ to the displaced distribution $n_0'(\boldsymbol{q}, b, \boldsymbol{u}, T)$ via N-processes
$\tau_{1\mathrm{U}}$	Relaxation time for a given acoustic short-range phonon mode to restore a perturbed phonon distribution $n(\boldsymbol{q}, b, T)$ to the equilibrium distribution $n_0(\boldsymbol{q}, b, T)$ via U-processes
$\tau_{2\mathrm{U}}$	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 $n_0(\boldsymbol{q}, b, T)$ via U-processes
τ_{c}	Characteristic time constant
τ_C	Combined relaxation time
τ_M	Effective relaxation time for a given phonon mode
τ_N	Mode-dependent relaxation time for N-processes
τ_P	Barostate time constant
τ_T	Reservoir-system time constant
τ_U	Mode-dependent relaxation time for U-processes
τ^*	Phonon relaxation time
$\boldsymbol{v}_i$	Velocity vector of the *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 b
ω_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 $\lvert Z_1(\omega)\rvert$, where $Y_1(\omega)$ passes via zero value
ω_{02}	Minimum location of impedance $\lvert Z_2(\omega)\rvert$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.