

Accelerated Quantum-to-Macro Scale Simulations with Machine Learning and Parallel Replica Dynamics for Mass and Thermal Transport

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Degree

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This dissertation is dedicated to my parents and grandparents, who are always loving me and supporting me unconditionally!

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Abstract

Mass and thermal transport significantly affect the performance of engineering systems. Since various parameters in transport can be systematically controlled and investigated, multiscale simulations have been employed as powerful tools for transport analyses. Among them, quantum-scale *ab initio* molecular dynamics (AIMD), atomic-scale classical molecular dynamics (CMD), and macro-scale finite element method (FEM) simulations, can provide comprehensive system analysis and design by addressing electronic structures, atomic dynamics, and engineering-scale properties, respectively. However, each approach has its own limitations to overcome for more accurate analyses of mass and thermal transport. Specifically, AIMD calculation is too expensive to produce sufficient atomic data for accurate analysis due to complicated force field evaluation. Besides AIMD, CMD can also require significant resources to examine the slow transport processes. Moreover, efficient identification of reliable interatomic potential has always been a major challenge for CMD. For FEM, effective processing of large volume of data and identification of accurate material properties for simulations are imperatives.

Aiming to overcome the limitations of those simulation methodologies, novel simulation and data processing algorithms with acceleration approaches have been proposed. Firstly, the feasibility of accelerating atomic data production in AIMD is demonstrated through recurrent neural network (RNN). The RNN training and prediction is found about one order of magnitude faster than the ground-truth AIMD. Secondly, parallel replica dynamics is implemented with CMD for investigating the deformation and transformation and diffusion properties of θ' -Al₂Cu precipitate in aluminum (Al) matrix for up to 133 ns with reasonable computational resources. Thirdly, machine learning (ML) technique is employed for rapid developments of interatomic potentials. A comprehensive Buckingham potential of Al is successfully developed, which can excellently reproduce the structural, mechanical, and thermodynamic properties. Lastly, ML

technique with FEM analysis is successfully employed for quick prediction of microscopic thermal transport properties and identification of the effect of various microstructures on thermal transport of Al-based alloy.

The successful implementation and further improvement of the proposed acceleration and data processing methodologies will advance the mass and thermal transport research with improved efficiency and accuracy, and ultimately contribute to the innovation of various engineering systems and processes.

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Nomenclature

a	lattice parameter a
$\mathbf{a}$	acceleration
a_{Al}	lattice constant of aluminum
a_{Ni}	lattice constant of nickle
A	parameter in Buckingham potential
Al	aluminum
Al'	aluminum atom in θ' -Al ₂ Cu precipitate
A_{p}	surface area of θ' -Al ₂ Cu precipitate
$A_{\text{p},i}$	surface area of i th θ' -Al ₂ Cu precipitate
$A_{\text{p,tot}}$	total surface area of θ' -Al ₂ Cu precipitates
b	lattice parameter b
c	lattice parameter c
c_p	specific heat capacity
$c_{\theta'}$	lattice parameter c of θ' -Al ₂ Cu precipitate
C	parameter in Buckingham potential

Cr	chromium
Cu	copper
$\langle d^2 \rangle$	mean square displacement
$dn(r_{i,j})$	number of atoms within atomic distance ranging from $r_{i,j}$ to $r_{i,j}+dr$
dr	atomic spacing for calculation of radial distribution function
D_m	average precipitate diameter
D_p	phonon density of states
D_{self}	self-diffusivity
D_{std}	standard deviation of precipitate diameter
$D_{\theta'}$	diameter of θ' -Al ₂ Cu precipitate
D_0	pre-factor of jump attempt frequency
D_1	long diameter of θ' -Al ₂ Cu precipitate
D_2	short diameter of θ' -Al ₂ Cu precipitate
e	electric charge
E	energy
E_a	activation energy
E_k	kinetic energy
E_p	potential energy
E_{ph}	phonon energy
E_{total}	total energy
$E_{\langle 100 \rangle}$	Young's modulus along $\langle 100 \rangle$ orientation

f_V	volume fraction of total precipitates
f_α	nonlinear activation function
F	embedding energy
$\mathbf{F}$	force vector
Fe	iron
$\langle g(r) \rangle$	radial distribution function
g_β	nonlinear activation function
G_{int}	interfacial thermal conductance
$\hbar$	reduced Planck constant
h_t	hidden layer in recurrent neural network
H	enthalpy
$\mathcal{H}$	many-body Hamiltonian
$\mathcal{H}_e$	electronic Hamiltonian
H_L	enthalpy of system in liquid state
H_S	enthalpy of system in solid state
ΔH_f	latent heat of fusion
k_{Al}	thermal conductivity of aluminum
$k_{\text{Al}_2\text{Cu}}$	thermal conductivity of θ' -Al ₂ Cu
k_B	Boltzmann constant
k_{eff}	effective thermal conductivity
$k_{\text{eff,FEM}}$	finite element method calculated effective thermal conductivity

$k_{\text{eff,ML}}$	machine learning model predicted effective thermal conductivity
k_{int}	thermal conductivity of interfacial region
k_{tot}	total rate constant of hopping event
k^{TST}	rate constant from the transition state theory
K	number of time steps used for training
l	side dimension of simulation domain
l_i	simulation dimension in i th direction
$l_{\theta'}$	side dimension of $\theta' - \text{Al}_2\text{Cu}$ precipitate
L	window size
L1	layer 1
L2	layer 2
L3	layer 3
m	mass
m_i	mass of an electron
M	prediction gap
M	number of processor or replica
M_I	mass of a nucleus
n	index
n_{dim}	dimensionality
n_e	number of electron orbital
n_p	precipitate number density

n -PB	non-periodic boundary
n_{rep}	number of replica
n_t	number of time instant
N	number of atom
N_a	number of atom
N_p	number of precipitate
N_{prop}	number of propertie
N_s	number of time step
Ni	nickle
O	an observable of interest
p	probability distribution of waiting time during transition event
P	pressure
$P_{\text{CMD},n}$	n -th property calculated by classical molecular dynamics
$P_{\text{EXP/FP},n}$	n -th property from experiment or first-principles calculations
P1	potential 1 for Fe-Ni-Cr system
P2	potential 2 for Fe-Ni-Cr system
q	heat flux
r	interatomic distance
$\mathbf{r}$	position vector
$\mathbf{r}_{\text{com}}$	position vector of center of mass
$\mathbf{r}_i$	coordinates of all electrons

r_m	equilibrium interatomic distance at energy minimum
R	universal gas constant
R_{int}	interfacial thermal resistance
$\mathbf{R}_I$	coordinates of all nuclei
R^2	coefficient of determination
s	specific time step in <i>ab initio</i> molecular dynamics simulation
Si	silicon
t	time
t_{clock}	total simulation time
t_{int}	thickness of interfacial region
t_m	average precipitate thickness
t_{rep}	simulation time on each replica
t_s	simulation timestep
t_{std}	standard deviation of precipitate thickness
$t_{\theta'}$	thickness of $\theta' - \text{Al}_2\text{Cu}$ precipitate
t_0	time origin
T	temperature
T_e	electronic kinetic energy operator
T_m	melting temperature
$T_{m,\text{Al}}$	melting temperature of aluminum
T_L	liquidus temperature

$T_{L,P1}$	liquidus temperature of Fe-Cr-Ni alloy determined by potential 1
$T_{L,P2}$	liquidus temperature of Fe-Cr-Ni alloy determined by potential 2
T_N	nuclear kinetic energy operator
$T_{NP,P1}$	melting temperature of nickle nanoparticle determined by potential 1
$T_{NP,P2}$	melting temperature of nickle nanoparticle determined by potential 2
T_S	solidus temperature
$T_{S,P1}$	solidus temperature of Fe-Cr-Ni alloy determined by potential 1
$T_{S,P2}$	solidus temperature of Fe-Cr-Ni alloy determined by potential 2
$\mathbf{u}$	velocity vector
u_{ij}	angular dependent force function for dipole distortion
$u^{2*}(t)$	velocity autocorrelation function
V	volume
V_{ee}	electron-electron potential energy operator
V_{eN}	electron-nuclear potential energy operator
V_{NN}	nuclear-nuclear potential energy operator
$V_{p,i}$	volume of i th θ' -Al ₂ Cu precipitate
$V_{p,tot}$	total volume of θ' -Al ₂ Cu precipitates
w_{ij}	angular dependent force function for quadruple distortion
x_i	original atomic data in <i>ab initio</i> molecular dynamics
$x_{\max}$	maximum of original atomic data in <i>ab initio</i> molecular dynamics
$x_{\min}$	minimum of original atomic data in <i>ab initio</i> molecular dynamics

x_t	input layer in recurrent neural network
y_i	normalized atomic data in <i>ab initio</i> molecular dynamics
$\tilde{y}_i$	predicted atomic data by recurrent neural network
y_n	actual value of mean square displacement
$\hat{y}_n$	mean square displacement value obtained from linear regression
y_t	output layer in recurrent neural network
Z	atomic number

Acronyms

ABAQUS	finite-element computer code
ACNA	adaptive common neighbor analysis
ADP	angular dependent potential
AGNI	adaptive, generalizable, neighborhood informed
AIMD	<i>ab initio</i> molecular dynamics
AR	aspect ratio
AVE	average
BCC	body-centered cubic
BR	Bayesian ridge
BUCK	Buckingham
CG	conjugate gradient
CHM	constant heating method
CI	coherent interface

CMD	classical molecular dynamics
CPU	central processing unit
DICTRA	diffusion controlled transformation
DL	deep learning
EAM	embedded atom method
EXP	experiment/experimental
FCC	face-centered cubic
FEA	finite element analysis
FEM	finite element method
FP	first-principles
FTD	finite-temperature dynamics
GPU	graphics processing unit
GRU	gated recurrent unit
HCP	hexagonal close packed
KR	kernel ridge
KS	Kohn-Sham
LAMMPS	large-scale atomic/molecular massively parallel simulator
LR	linear regression
LSTM	long short-term memory
MATLAB	matrix laboratory
MD	molecular dynamics

MEAM	modified embedded atom method
MEV	maximum edge value
MIC	maximal information coefficient
ML	machine learning
MPD	melting point depressant
MSE	mean squared error
NN	nearest neighbor
NP	nanoparticle
NPT	isobaric-isothermal ensemble
NVE	microcanonical ensemble
NVT	canonical ensemble
PB	periodic boundary
PCC	Pearson's correlation coefficient
PRD	parallel replica dynamics
PRE	prediction
RDF	radial distribution function
RF	random forest
RMSE	root mean square error
RNN	recurrent neural network
SCI	semi-coherent interface
TEM	transmission electron microscopy

TLP	transient liquid phase
TST	transition state theory
VACF	velocity autocorrelation function
VASP	Vienna <i>ab initio</i> simulation package

Greek Symbols

α	parameter set of nonlinear activation function f_α , i.e., $\{W, U, b\}$
α_h	heat diffusivity
α_L	linear thermal expansion coefficient
α_s	parameter measuring the steepness of the exponential
β	parameter set of nonlinear activation function g_β , i.e., $\{P, c\}$
γ	Cartesian component
δ	Dirac delta function
Δ	difference
ε	depth of energy minimum
ε_T	temperature difference
ε_0	eigenvalue of ground-state energy
η	simulation efficiency of parallel replica dynamics
θ	θ phase of Al_2Cu
θ'	θ' phase of Al_2Cu
$\lambda_i^{\gamma\chi}$	quadruple distortion in angular dependent potential
μ	micro ($\times 10^{-6}$)

μ_i^γ	dipole distortion in angular dependent potential
ν_i	trace of quadruple term $\lambda_i^{\gamma\chi}$ in angular dependent potential
ρ	ionic-pair dependent length parameter in Buckingham potential
$\bar{\rho}_i$	host electron density at the site of atom i
ρ_j	electron density assigned to atom j
ρ_m	mass density
σ	sigmoid function
σ_u	ultimate tensile strength
τ	time
τ_{corr}	correlation time
φ	potential energy
φ_1	one-body potential energy
φ_2	two-body potential energy
φ_3	three-body potential energy
Φ	pair interaction energy
χ	Cartesian component
ψ	single-particle electron orbital
Ψ	wave function
ω	phonon frequency

Other Symbols

+	point-wise addition in recurrent neural network
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$\times$	point-wise multiplication in ecurrent neural network
$\langle \rangle$	ensemble and/or time average
♥	label of selected parameter set for Buckingham potential
'	prime phase of Al_2Cu
∂	partial differential
∞	infinity
$^{\circ}\text{C}$	degree Celsius
∇	position operator, $= \frac{\partial}{\partial r}$

Chapter 1

Introduction

1.1 Motivations and Objectives

Mass and thermal transport (i.e., movement of mass from one place to another [1] and flow of energy in the form of heat [1]) analyses are essential for understanding the physics of various engineering applications and processes, such as joining of nanomaterials, precipitate deformation and transformation in alloy, and heat dissipation in microelectronics [2, 3, 4, 5], for more effective and efficient design and control of engineering applications and processes.

Multiscale computer simulations (shown in Figure 1.1), including *ab initio* molecular dynamics (AIMD), classical molecular dynamics (CMD), and finite element method (FEM), which can address quantum-scale, atomic-scale, and macro-scale engineering problems respectively, have been broadly employed in analysis of mass and thermal transport [6, 7, 8, 9, 10]. Compared with experiment, the simulations are much more flexible (e.g., easy manipulation of simulation subject and simulation parameters), less expensive, and have no strict requirement of human presence in a specific lab. However, the aforementioned multiscale simulations have their own limitations and deficiencies. Specifically, in AIMD, the electronic structure is evaluated within each ionic step by quantum mechanics, rendering it very expensive to simulate a large system ($> 1,000$ atoms) or long simulation time (> 100 ps). Although the CMD does not involve quantum mechanics for deriving the energy and force, it can still require a tremendous amount of computational resources for obtaining accurate results, especially when the simulated system is large (e.g., $> 10^6$ atoms); or

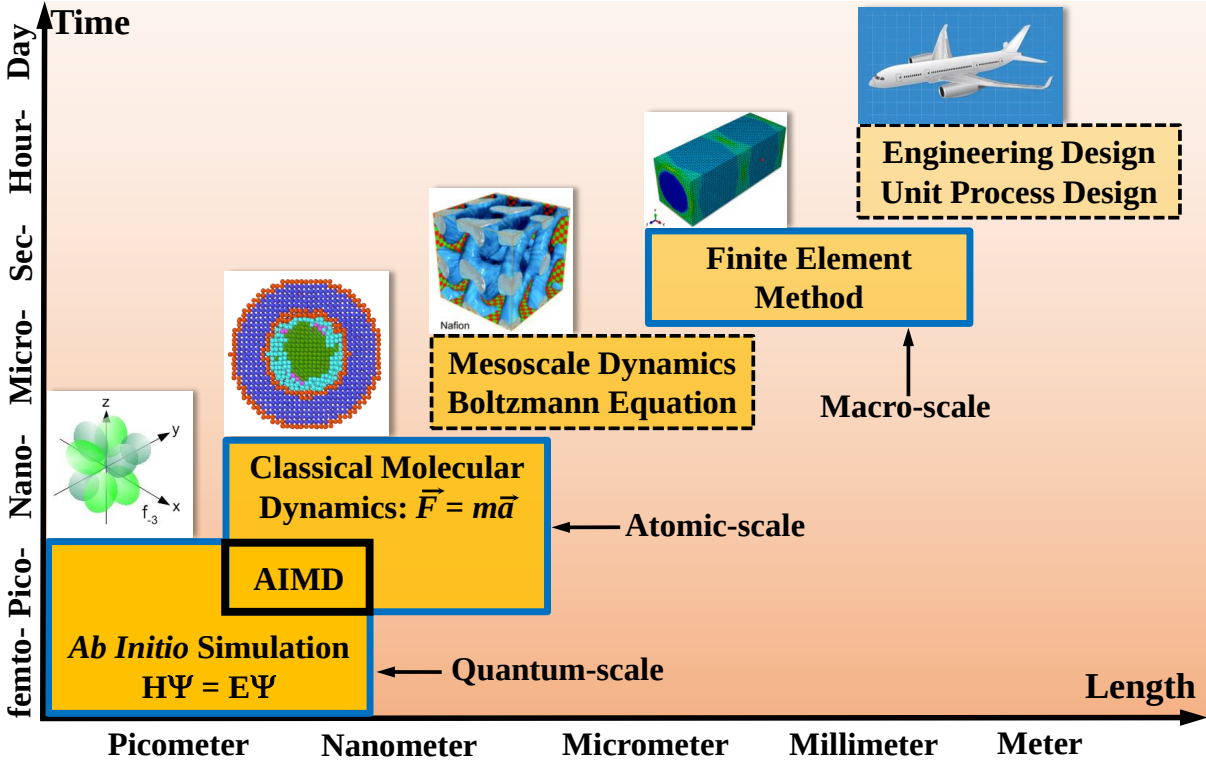


Figure 1.1: Multiscale computer simulations from quantum-to-macro scale. In this work, I employ quantum-scale *ab initio* molecular dynamics (AIMD), atomic-scale classical molecular dynamics (CMD), and macro-scale finite element method (FEM) as simulation tools with assistance of deep learning (DL) algorithm of recurrent neural network (RNN), parallel replica dynamics (PRD), and traditional machine learning (ML), to overcome the challenges and limitations of those computational approaches in the research field of mass and thermal transport.

when the interatomic potential is complicated (e.g., reactive force field); or due to the intrinsic nature of the problem investigated (e.g., solid-state atomic diffusion).

In this work, I aim to improve the efficiencies and effectiveness of these simulation approaches for enhanced understanding of mass and thermal transport, by 1) accelerating the production of atomic data in AIMD; 2) advancing the simulation clock of CMD up to 133 ns with reasonable computational time; 3) expediting the development and improving the accuracy of interatomic potentials for CMD; and 4) accelerating the calculation and analysis of FEM simulations, with assistance of acceleration algorithms such as deep learning (DL) of recurrent neural network (RNN), parallel replica dynamics (PRD), and machine learning (ML). The general background, motivation, and novel methodologies we adopt to address the current challenges in each task will be given in the following subsections.

1.2 Summary of Four Tasks

This dissertation is comprised of six chapters. Chapter 1 states the motivations, objectives, and summary of four tasks completed. Chapter 2 to 5 are detailed introduction, methodology, and achieved outcome of each task. Figure 1.2 illustrates the summary of the four tasks, including the scale of each simulation approach, system tested, challenges of each task, and the achieved outcome. Chapter 6 states the conclusions, impacts, and recommendations for further studies in the field of mass and thermal transport with multiscale simulations.

1.2.1 Chapter 2. Accelerated Atomic Data Production in AIMD with RNN

AIMD employs quantum mechanics to calculate the potential energy of the system and the Newtonian classical mechanics to update the position and velocity of atoms. Due to the quantum-level accuracy, AIMD has been employed in the sciences of physics, chemistry, and biology, for unravelling the relevant mechanisms as well as for property calculations. However, the temporal (up to hundreds of picoseconds) and spatial scale (up to hundreds of atoms) of AIMD simulation have restricted its broad applications, since accurate simulation results would demand a sufficient simulation time and size. For example, accurate harvest of diffusion properties requires the system to reach steady state, while solid-state diffusion normally takes tens of nanosecond to reach a stea-

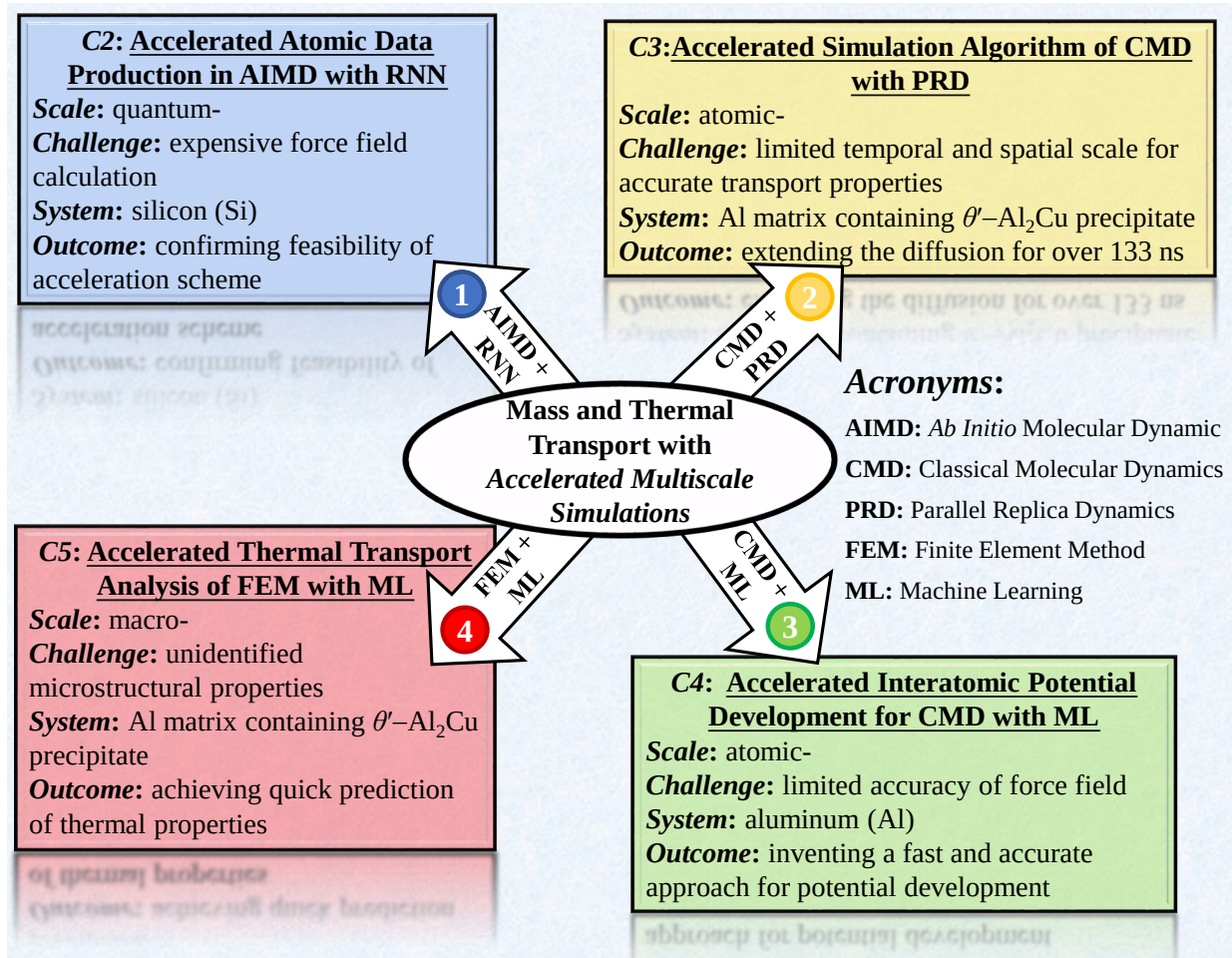


Figure 1.2: Summary of the four tasks [in chapter 2 (C2) to 5(C5)], including scale of each simulation approach, challenge, system tested, and achieved outcome.

dy state, which cannot be achieved within AIMD. Thus, in this research, I attempt to develop an acceleration scheme for atomic data production in AIMD coupled with DL algorithm, i.e., RNN. In the proposed scheme, I first proceed the ground-truth AIMD simulation for N_s step (output every step), and then use 80% of the N_s step data to train a RNN model (the rest 20% is used for testing) for prediction of the next several steps until a specific error threshold is reached, to replace the ground-truth AIMD steps. Through this way, the AIMD simulation will be accelerated by the predicted steps which only take several seconds, while the ground-truth AIMD steps could take up to hours. In addition, the error accumulation will be diminished since the prediction decouples the update of position and velocity data from Newtonian mechanics, proved by that the calculated material properties with the predicted atomic data present a quantum-level accuracy. In this task, I present the feasibility of accelerating the production of atomic data in AIMD with DL algorithm of RNN, and the RNN training and prediction is confirmed to be approximately one order of magnitude faster than the ground-truth AIMD itself. This work opens the door for implementing the DL into AIMD algorithm, and may motivate the algorithm realization of AIMD with DL in the future, for significantly enhancing the efficiency of AIMD while maintaining its accuracy.

1.2.2 Chapter 3. Accelerated Simulation Algorithm of CMD with PRD

Although CMD is capable of simulating systems with even over one million atoms, and can reach a simulation time of more than $1\ \mu\text{s}$, it depends on the complexity of the interatomic potential and system size. Qualitatively speaking, it is still quite challenging to achieve a long simulation time with a large system or a complicated interatomic potential (such as reactive force field or bond order potential). However, for solid-state diffusion, a single atom may take up to 10 ns or more to finish a hopping event (i.e., atom jumping from one atomic site to another). Therefore, to harvest accurate diffusion properties of solid-state diffusion and its corresponding diffusion mechanisms, a much longer simulation time is required than the liquid-phase diffusion. To extend the time scale of the CMD for investigating the solid-state diffusion of θ' -Al₂Cu precipitate in aluminum (Al) matrix with an advanced interatomic potential, i.e., angular dependent potential (ADP), I embed PRD algorithm with CMD, in which identical replica of the system can run simultaneously and parallelly without modification of dynamics, so that the simulation time can add up while only

costing a single-replica computational wall time. The simulation time has been extended to 133 ns with reasonable amount of computational resources, and the deformation and transformation mechanisms of the θ' -Al₂Cu precipitate at high temperatures ($> 200^\circ\text{C}$) via atomic diffusion have been unravelled. Diffusion properties, such as self-diffusivity of each element at different interfaces, activation energy, and diffusion pre-factors have been successfully calculated, which can contribute to the phase field modelling of precipitate growth. The implementation of PRD in CMD has been proven to effectively extend the temporal scale of CMD, for more accurate evaluations of material properties and the underlying dynamics.

1.2.3 Chapter 4. Accelerated Interatomic Potential Development for CMD with ML

Differing from AIMD in force calculation by solving Schrödinger equation, CMD employs mathematical forms of force field to describe the interactions between atoms. Thus, the interaction potential plays a dominant role in determining the accuracy of simulation results. Development of accurate interatomic potential serving general simulation purposes is not a trivial work, especially for multiple-element systems, where the number of interatomic potential parameters increases exponentially with the number of element. The traditional development of interatomic potentials employs first-principles or experimental data, for either fitting the potential energy surface or the material properties by minimizing errors. However, the traditional approach is always suffering from time-consuming quantum-mechanical simulations or lack of comprehensive experimental data. As a result, the developed potentials are often biased to specific simulation purposes or conditions as what are considered in the parameterization. To expedite the development of a comprehensive interatomic potential without quantum-mechanical simulations and is suitable for general-purpose CMD simulations, a finite temperature dynamics machine learning (FTD-ML) technique is proposed and demonstrated through the case of Buckingham-type potential with Al. The developed Al potential can work well under various ensembles, i.e., NVT (constant number of atom, volume, and temperature), NPT (constant number of atom, pressure, and temperature), and NVE (constant number of atom, volume, and energy), and it can reproduce the structural, thermodynamic, and mechanical properties with satisfying agreement with experimental

or first-principles data. Since the FTD-ML approach does not involve any quantum-mechanical simulation, and the ML algorithm is employed for quick prediction, this approach is expected to significantly expedite the development of interatomic potential with enhanced accuracy.

1.2.4 Chapter 5. Accelerated Thermal Transport Analysis of FEM with ML

Thermal transport analysis is critical for achieving thermal stability and reducing operational stresses in alloys. The thermal energy in metallic alloys is transmitted by electron and phonons, so it is necessary to investigate the contributions of both electrons and phonons with various microstructural features such as grain boundary. Particularly, the first-principles simulation can be employed for investigating electron thermal transport properties. However, due to the complexity and the time-consuming issues of first-principles calculation, only a few theoretical researches have been reported. Instead, FEM simulation can be used for thermal transport simulations. FEM simulation is a macro-scale approach using continuum models serving various research fields such as heat transfer, fluid flow, and structural analysis. The accuracy of FEM simulation results is highly dependent on the “mesh” size, which is the number of the “finite element”. To achieve higher accuracy, a larger “mesh” size is normally required, but also more computational cost is demanded. Additionally, various thermal transport properties of the materials have to be defined as input, part of which are sometimes unknown beforehand. To expedite the FEM simulations and to predict the thermal transport properties of materials, the ML technique is employed. Extensive data of effective thermal conductivity of Al alloy are generated with various microstructural features (such as precipitate diameter) and thermal transport properties (such as interfacial thermal conductance between the θ' -Al₂Cu precipitate and Al matrix). ML models are then trained for predicting the effective thermal conductivity with new input set of microstructural features and thermal transport properties, enabling determination of the real thermal transport properties and identification of microstructural effect on the effective thermal conductivity of the Al alloy. This work provides an innovative solution for calculating thermal transport properties in complicated alloy structure and identifying the effect of various microstructure parameters on the final effective thermal conductivity, which contributes to the alloy design with enhanced thermal stability and life-span.

1.3 Theories of Multiscale Simulations

1.3.1 Quantum-Scale - *Ab Initio* Molecular Dynamics

The basic idea of AIMD is to compute the energies [i.e., quantum-mechanical potential energy for the nuclei (ions) of a system] and thus the forces acting on the nuclei, from electronic structure calculations that are performed “on-the-fly” as the molecular dynamics trajectory is updated. Simply saying, the position and velocity of each nucleus are updated based on the Newtonian classical mechanics, but the forces deriving from electrons are calculated by quantum mechanics, via solving Schrödinger equation using particular approximations.

In this dissertation, I only formulate the most fundamental and essential theories relating to the limited temporal and spatial scales of AIMD. The detailed theories, including the basis set, pseudopotential, implementation of AIMD and so on, can be found in the literatures of [11, 12, 13, 14, 15, 16, 17].

The foundation of AIMD is the time-dependent Schrödinger equation, characterized by the wave function $\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$ and Hamiltonian $\mathcal{H}$ [18]:

$$i\hbar \frac{\partial}{\partial t} \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = \mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t). \quad (1.1)$$

The standard many-body Hamiltonian $\mathcal{H}$ with position representation is:

$$\begin{aligned} \mathcal{H}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) &= - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I<J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \\ &= T_N + T_e + V_{ee}(\{\mathbf{r}_i\}) + V_{eN}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) + V_{NN}(\{\mathbf{R}_I\}) \\ &= T_N + \mathcal{H}_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}), \end{aligned} \quad (1.2)$$

where $i = \sqrt{-1}$, $\hbar$ is the reduced Planck constant, M_I is the mass of a nucleus and m_i is the mass of an electron. The $\mathbf{r}_i$ represents the coordinates of all electrons, while $\mathbf{R}_I$ denotes the coordinates of all nuclei. e is the electric charge, and Z is the atomic number, i.e., the number of protons in a given nucleus. T_N , T_e , V_{ee} , V_{eN} , V_{NN} , is nuclear and electronic kinetic energy operators, and electron-electron, electron-nuclear, and nuclear-nuclear interaction potential operator, respectively.

Inside the Equation 1.2, the electronic Hamiltonian $\mathcal{H}_e$ cannot be solved analytical, instead, approximation approach for electronic structure is required, which normally takes tremendous amount of computational resources. Nowadays, the Kohn-Sham (KS) formulation of density functional theory [19] is the most commonly used approximation for electronic structure, in which the total energy is expressed as a functional of n_e mutually orthonormal single-particle electron orbitals $\psi_i(\mathbf{r})$ (i.e., $\langle \psi_i(\mathbf{r}) | \psi_j(\mathbf{r}) \rangle = \delta_{ij}$), $i = 1, \dots, n_e$. There are four terms in the KS energy functional, including the kinetic energy of a non-interacting reference system, Hartree energy (the classical electrostatic energy of two charge clouds which stems from the electronic density), exchange-correlation energy, and the energy from fixed external potential. Among them, the exchange-correlation energy has to be approximated for solving the total energy.

In AIMD, the dynamics of the nuclei is given by the Newtonian mechanics [18]:

$$M_I \{\ddot{\mathbf{R}}_I\} = -\nabla_I [\varepsilon_0(\{\mathbf{R}_I\}) + V_{NN}(\{\mathbf{R}_I\})], \quad (1.3)$$

where $\varepsilon_0(\{\mathbf{R}_I\})$ is the corresponding ground-state energy eigenvalue at the nuclear configuration of $\mathbf{R}_I$.

There are two types of commonly used approach for solving the energy terms, i.e., $\varepsilon_0(\{\mathbf{R}_I\}) + V_{NN}(\{\mathbf{R}_I\})$, in Equation 1.3. One is termed as Born-Oppenheimer dynamics [20], in which energy is calculated by minimization of the KS energy functional with the nuclear configuration in each time step. Another is called Car-Parrinello dynamics [21], in which the energy is calculated by using the Car-Parrinello extended Lagrangian approach. The Equation 1.3 can then be solved straightforwardly by numerical integration using a symplectic integrator (such as Verlet algorithm).

Although the fundamentals and algorithms of AIMD have been much advanced over last several decades, however, the progress in solving the limited temporal and spatial scales of AIMD has not been achieved, due to the intrinsic complexity of electronic structure calculation. Motivated by this challenge, I attempt to overcome the temporal and spatial limitations by avoiding addressing electronic structure, i.e., expediting the simulation clock using the DL algorithm of RNN. My approach has shown great promise in accelerating the simulation clock of AIMD, while maintaining the quantum-level accuracy in material properties calculation.

1.3.2 Atomic-Scale - Classical Molecular Dynamics

CMD serves as a powerful atomic “microscope”, for unravelling the nanoscale dynamics which is challenging to harvest in real-world experiments. CMD has been broadly employed in chemistry, physics, and biology due to its much larger time and length scale (can reach up to μs and μm) compared with AIMD.

The underlying physics of CMD is quite straightforward, that is, the Newtonian physics (as shown in Equation 1.3). Different from that in AIMD, the electronic and nuclear contribution to the interatomic potential in CMD is not separately derived. Instead, the potential energy is calculated by a given empirical or semi-empirical mathematical formula considering nucleus only. For simplicity, we can rewrite the Equation 1.3 as [22]:

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I[\varphi(\{\mathbf{R}_I\})], \quad (1.4)$$

where $\varphi(\{\mathbf{R}_I\})$ is the interatomic potential energy and is normally split into 1-body, 2-body, 3-body...terms as [22]:

$$\varphi(\{\mathbf{R}_I\}) = \sum_I \varphi_1(\mathbf{R}_I) + \sum_I \sum_{J>I} \varphi_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_I \sum_{J>I} \sum_{K>J>I} \varphi_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots \quad (1.5)$$

Here φ_1 is the 1-body term, arising from an external field or boundary condition. φ_2 is the 2-body term, or termed as pair potential, determined only by the atomic spacing and is not affected by the presence of other atoms. The 3-body term φ_3 stems from the presence of a third atom which modifies the interaction of a pair of atoms.

In general, there are two categories of interatomic potential: two-body and many-body. The two-body potential, such as Lennard-Jones [23], Morse [24], and Buckingham potential [25], assumes a functional form of atomic interaction and fits the function parameters to reproduce a set of experimental data of material properties. The many-body potential is normally derived from quantum-mechanical simulations by fitting potential energy surface, and may not have a parameter-based analytical form, such as embedded atom method (EAM) potential [26] and bond order potential (BOP) [27]. After determining the interatomic potential, the forces acting on atoms can be calculated, and the dynamics of the simulation system will evolve correspondingly. Thus, the

interatomic potential is extremely critical for CMD since it determines the accuracy of simulation results. For more information of interatomic potential such as development and recent advances, one can refer to [28, 29, 30, 31, 32].

There is a trade-off between simulation speed and accuracy regarding the interatomic potential. To keep up the accuracy while improving the CMD simulation speed, I propose to employ the PRD algorithm for evolving the dynamics and consuming computational resources as minimum as possible, with the many-body ADP potential [33]. Additionally, developing accurate two-body interatomic potential is also of great benefit for improving the simulation speed. Thus, the FTD-ML approach is invented to accelerate the development of a comprehensive two-body potential suitable for general simulation purposes, which can also be extended to development of many-body potentials.

Besides interatomic potential, there are several other critical parameter settings in CMD (and AIMD as well) which can possibly affect the simulation speed and accuracy, such as integration algorithm, timestep, boundary condition, and ensemble. They will be introduced briefly in the following paragraphs:

(1) Integration algorithm. The potential energy $\varphi(\{\mathbf{R}_I\})$ is a function of $3N$ (N is number of atom) coordinates of all atoms in the system. Due to the complicated nature of equations of motion, no analytic solution can be found, therefore, they have to be solved numerically. Several integration algorithms have been developed, such as Verlet [34], velocity Verlet [35], and leapfrog [36], etc. Among them, the velocity Verlet algorithm is the most commonly used nowadays, due to its improved accuracy over traditional Verlet algorithm.

(2) Timestep. For simulating a longer time trajectory with minimum computational resources, timestep should be maximized in CMD. However, the integration algorithm, such as the Verlet algorithm, becomes unstable due to the large truncation errors in the integration process with larger timestep, leading the total energy of the system to increase rapidly. Thus, the timestep determines the numerical accuracy of CMD as well. One typically picks a timestep that is between $0.5 \sim 2$ fs [37]. One of the explanations is that the selected timestep should be comparable to the period of the highest vibrational frequency of molecules or atoms. To maximize the computational efficiency while ensuring accuracy, a testing of timestep in NVE ensemble should always be carried out before any implementation of simulations.

(3) Boundary condition. In CMD, there are two types of boundary which are commonly used, one is periodic boundary (PB) condition, and another one is non-periodic boundary (n -PB) condition [22]. The PB condition enables the macroscopic properties to be calculated from fewer number of atoms, so it is mostly used for simulating the “bulk” materials. The primary cell in PB condition [blue cell in Figure 1.3(left)] is replicated in all dimensions, rendering the primary cell and image cells have identical system size and shape, as well as position and momentum of atoms. The atoms in primary cell with PB condition can interact with the atoms in the neighboring images if their distance are within the interaction cutoff. Once the atoms migrate across the boundary, they will reenter the simulation box from another side, as shown in Figure 1.3(left). Although the PB is employed for simulation of “bulk” material, a size test on the primary cell is still necessary, to ensure the convergence of the calculated results.

The n -PB condition is normally used for simulating nanomaterials, in which atoms can only interact with the ones within the primary cell. Also, atoms cannot migrate over the boundary, but the movement of atoms is not prescribed by the boundary, if the boundary is not set to be fixed at certain position (so that it can move with the atoms). The Figure 1.3(right) illustrates that the atoms can migrate over a long distance, even larger than the original cell size, and the boundary can correspondingly expand (or shrink) with the atoms (i.e., the solid n -PB boundary can move to the dashed-line position with the movement of atoms). Since the n -PB creates free surface and sharp corner with dangling bonds, the chemistry of the simulated system may be alternated in a dramatic manner. Scrutiny should be applied when simulating with n -PB to ensure that the basic physics is correct. It should be noted that the pressure control through barostat cannot be implemented in n -PB condition.

(4) Ensemble. An ensemble is a collection of all possible system states which have different microscopic features but have an identical macroscopic or thermodynamics state. There exist several ensembles with different attributes: (1) microcanonical ensemble (NVE) [38], which corresponds to an isolated system with fixed number of atom N , volume V , and energy E ; (2) canonical ensemble (NVT) [39], which is a collection of all system states which have a fixed number of atom N , volume V , and temperature T ; (3) isobaric-isothermal ensemble (NPT) [39], which is a collection of system states with a fixed number of atom N , pressure P , and temperature T . In this work, the NVE ensemble is employed for timestep testing, as well as extracting data for

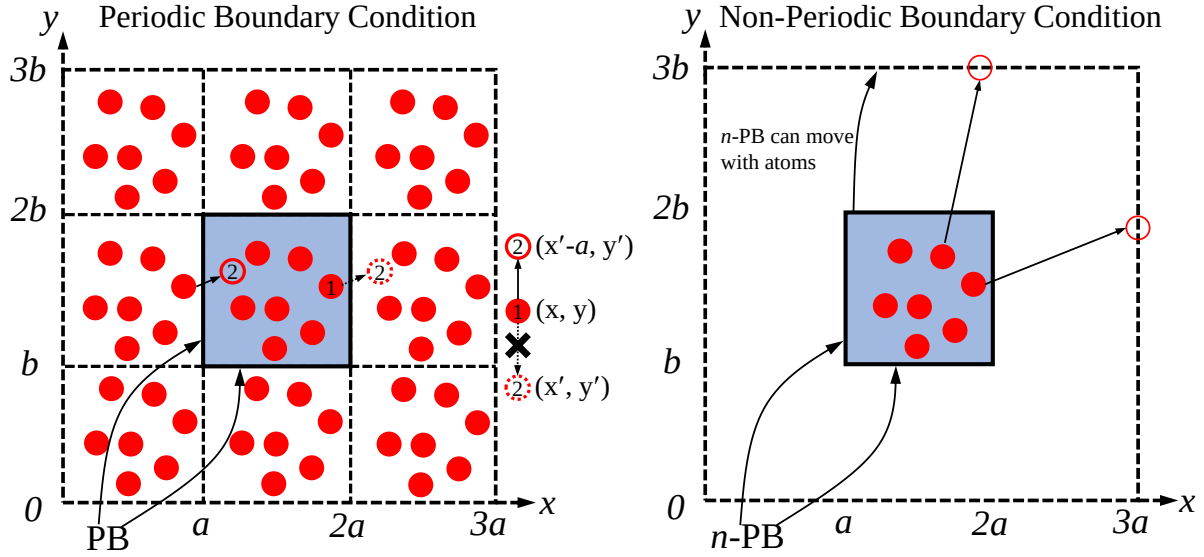


Figure 1.3: Illustration of periodic boundary (PB) condition (left) and non-periodic boundary (n -PB) condition (right). In PB condition, primary cell (blue) and neighboring images have identical atomic environment, and atoms can interact with the ones within the interaction cutoff in the neighboring images. Atoms can migrate over the boundaries, however, they will not actually locate to the neighboring images, instead they will reenter the primary cell from another side (the atom 1 in primary cell will not locate to the atom 2 position indicated by dashed-line red circle, but instead will be in the position of atom 2 indicated by solid-line red circle). In n -PB condition, atoms cannot migrate over the boundaries and atoms cannot interact across the boundary, but the boundary can be set to move with the atoms (or fixed position boundary), no matter how far the atoms move.

calculations of diffusion properties and phonon density of states. NPT is normally used with PB condition, and the author would think the NPT ensemble is the most accurate one for systems under different temperatures, since the volume would always change according to temperature (so that NVT may yield some accuracy). The NVT is used for investigating the temperature effect where the NPT ensemble cannot work, such as the temperature effect on the sintering dynamics of nanoscale systems.

An experimental observable is usually determined on a macroscopic sample that contains a tremendous amount of atoms or molecules. In statistical mechanics, average, a counterpart to the experimental observable is defined in terms of ensemble average. To obtain the accurate ensemble average, theoretically, CMD has to pass through all possible states of the system, which is extremely challenging. However, time average of an observable of interest is quite easy to obtain, and the ensemble average is taken as the time average of an observable of interest in CMD, i.e., the ergodic hypothesis [40, 41]:

$$\langle O \rangle_{ensemble} = \langle O \rangle_{time}, \quad (1.6)$$

where O is an observable of interest, which can be expressed as a function of momenta and positions of the system. The basic idea is that if the system in CMD evolves in time indefinitely, the system will eventually pass through all possible states. Thus, to obtain accurate simulation results, the simulation time should be long enough to generate a sufficient amount of phase space.

1.3.3 Macro-Scale - Finite Element Method

FEM is a powerful engineering analysis tool, and has been widely utilized in structural engineering, heat transfer physics, fluid mechanics and so on, since it was introduced in the 1950s [42].

FEM is an alternative numerical method used for obtaining approximate solutions of boundary value problems (also called field problems), since many engineering problems do not have close-up form solutions due to complicated geometry and boundary condition [43]. Differing from AIMD and CMD, FEM employs continuum simulation models, which rendering the FEM a macro-scale simulation approach. The solutions in FEM are achieved by either eliminating the differential equations completely (steady-state problems), or by rendering the partial differential equation into an equivalent ordinary differential equation, which is then solved using standard techniques such

as finite difference. There are several quantities have to be defined to implement a FEM simulation, such as domain, governing equation, boundary condition, element, node, and mesh (grid). Among them, the mesh, which is formed by elements and nodes, is the critical one to achieve accurate results [43, 44], and more refined mesh normally can generate more accurate results but also consume more computational resources.

In solving the mass and thermal transport problems in FEM, the material properties have to be input as simulation parameters. However, this is quite challenging when investigating new materials since some of the properties are unknown. Coupled with ML algorithm in this research, a prediction of material properties becomes possible, and also the effect of various microstructure details on the thermal transport is identified.

1.4 Acceleration Approaches

1.4.1 Parallel Replica Dynamics

For some mass transport problems, such as solid-state diffusion and grain-boundary sliding, the dynamics can be characterized by extended residence time in a potential basin, with an occasional transition to a new basin [45]. Since CMD is normally limited to nanoseconds, it is thus necessary to accelerate CMD for running up to more than hundreds of nanoseconds even to microsecond with reasonable computational resources, while retaining full atomistic details for investigating the long-time dynamical evolution.

The theoretical foundation of PRD is the transition state theory (TST) [46], in which the TST rate constant k^{TST} is defined as the equilibrium outgoing flux through the total dividing surface, an equilibrium property of the canonical (thermal) system. In PRD, the only assumption is that the infrequent events obey the first-order kinetics (exponential decay). For any time greater than τ_{corr} after entering a new state, the probability distribution function p of waiting time t for the next escape is give by [47]:

$$p(t) = k_{\text{tot}} \exp(-k_{\text{tot}} t), \quad (1.7)$$

where k_{tot} is the total rate constant for escape. τ_{corr} is correlation time (typically a few picoseconds), during which the system remembers how it enters the new state, and recrossing back to original

state or sending it to another state may occur. If the system does not exhibit any correlated crossing event, k_{tot} is exactly the k^{TST} . In more general cases, i.e., the correlated crossings occur, k_{tot} is smaller than k^{TST} .

Here, I will not derive the PRD theorem, since it has been proved in literature of [48]. Instead, the implementation of PRD will be introduced briefly, since it is critical to understand the algorithm and thus set up correct parameters for CMD simulations.

There are generally five steps in one PRD procedure, denoted by A to E in Figure 1.4 [48, 49]. Firstly, the initial system is replicated in M processors, to create M replicas. Secondly, the velocity and the momentum of each replica are randomized independently. Thirdly, a dephasing is run to eliminate the correlation between each replica. In the fourth step of searching for transition event, the simulation clock starts to count, until a transition event occurs. The CMD simulation clock is advanced by adding up all the time of searching for transition event in each replica. In the last step of searching for correlation event, only the correlation time on event replica is counted. The procedure is then repeated from A to E with the new state. For running PRD with CMD, the number of velocity randomization, dephasing time, time step interval for event check, and also correlation time have to be set with great care.

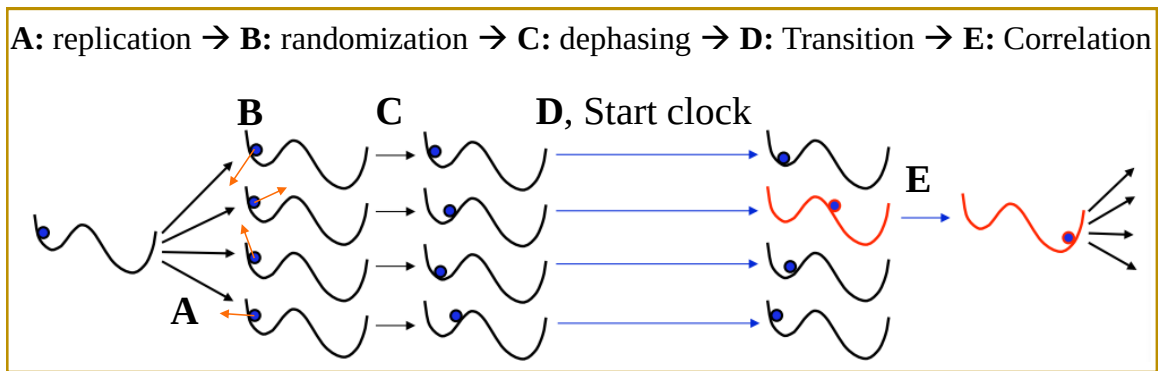


Figure 1.4: Procedure of parallel replica dynamics, which includes five steps: (A) replication of initial system, (B) randomization of velocity/momentum, (C) dephasing for eliminating correlation, (D) searching for transition event, (E) searching for correlation event.

1.4.2 Machine Learning

ML approaches, including both traditional ML and more advanced DL, are revolutionizing computer simulations and material science. ML has been recently implemented for the fast development of interatomic potentials [50, 51, 52] and accelerating the simulation clock of quantum-mechanical simulations [53, 54]. The basic idea of ML is quite simple, although the involved training algorithms may be complicated. A machine does not have a human brain, so it is not able to learn actively, however, the machine is able to learn from the existed patterns. This pattern is trained from the algorithms such as neural network and support vector machine, by using the massive multiple-dimensional data including feature and target. The machine is then able to predict outcome by applying the patterns already acquired in machine “brain”, with feed of new set of feature data [55]. The workflow and essential explanations of ML are show in Figure 1.5. For accurate prediction, the data used for training patterns should have high volume and reliability. In this research, I demonstrate the feasibility of employing the traditional ML and a more advanced DL algorithm of RNN for accelerating the development of interatomic potential for CMD and production of atomic data in AIMD.

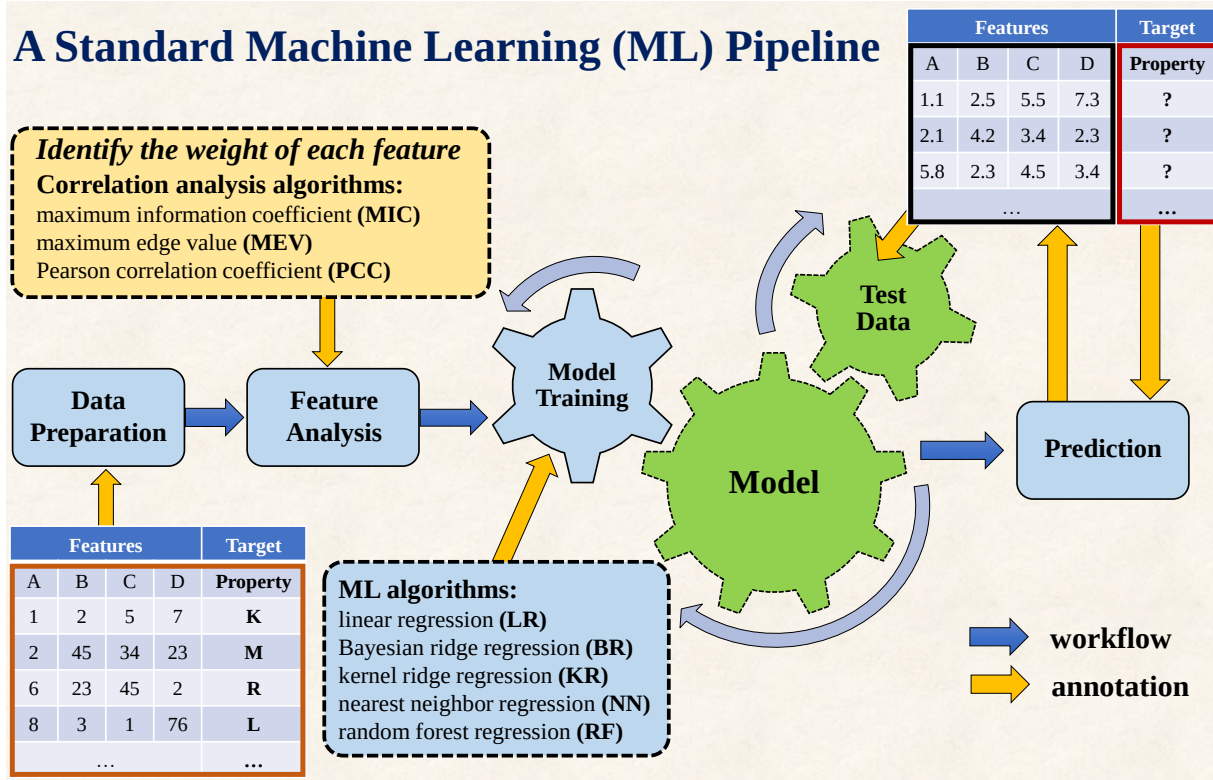


Figure 1.5: A standard workflow of machine learning (ML). The first step is generation of training data. The training data are consisted of various features and targets. For example, in the potential development work, the features are the potential parameters, and the targets are various material properties. Secondly, analyzing the significance of each feature using specific algorithm such as maximum information coefficient or Pearson correlation coefficient. This feature analysis provides a reference for setting a suitable increment for the feature data in the prediction stage. For example, if parameter A has a significant impact on the targets, then the increment of parameter A has to be decreased, since a small difference of A can yield very different value of targets. Thirdly, performing ML training using multiple algorithms such as linear regression and random forest regression, and the most accurate ML model from those algorithms is chosen for prediction. Lastly, performing prediction with new sets of feature data without target. Through the prediction of the model, we will then be able to obtain the targets, and suitable sets of feature data can be sorted out by comparing with the experimental values of the targets. The key of a successful ML work is reliable and massive training data.

Chapter 2

Accelerated Atomic Data Production in *Ab Initio* Molecular Dynamics with Recurrent Neural Network

Note: Chapter 2 is a modified version of the submitted work: **Jiaqi Wang**, Chengcheng Li, Seungha Shin*, and Hairong Qi, “Accelerated Atomic Data Production in *Ab Initio* Molecular Dynamics with Recurrent Neural Network for Materials Research”, *The Journal of Physical Chemistry C*, in revision, (2020). This manuscript is reprinted with permission from ACS Publications. The dissertation author listed in this manuscript directed and supervised the research which forms the basis for this manuscript.

2.1 Introduction

As various material properties can be characterized by analyzing ensemble of atomic data (position, velocity, force, and so on), molecular dynamics (MD), which provides the required data using Newton’s equations of motion, is a broadly utilized computational approach in materials research. Two main MD schemes, which are commonly employed, are referred as classical molecular dynamics (CMD) and *ab initio* molecular dynamics (AIMD). CMD updates atomic information, using approximated mathematical models of interatomic potential [22], while AIMD employs the first-principles calculation for atomic interactions at each time step [17, 56]. Since AIMD does

not rely on approximated models, it is generally regarded as a more accurate simulation approach than CMD. However, the spatial and temporal scales of AIMD are limited to at most hundreds of atoms and hundreds of picoseconds in general, due to significant computational costs of electronic structure calculation at each time step [57, 58, 59, 60]. These limitations have hindered further applications of AIMD to materials research because reliable calculations of material properties (e.g., diffusion properties [58]) demand a sufficient simulation size and time.

In the previous attempts of extending the spatial and temporal scales of AIMD, learning-based algorithms {e.g., traditional machine learning (ML) [61, 53, 62, 63, 64] and deep learning (DL) [65, 66, 67, 68, 69]} have been adopted to learn and predict the force field for more universal applications. Although promising, since atomic data (i.e., position and velocity data) still need to be derived through the Newtonian mechanics using the predicted force field [53, 70, 71], the prediction errors can be propagated or accumulated to the atomic data calculation. In this work, because atomic positions and velocities are determined by those in the previous time step (or steps), direct mapping between previous and future simulation data can be modeled, without the force field prediction. This direct mapping decouples the update of velocity and position in future time steps from the Newtonian mechanics, allowing for more efficient and accurate predictions of atomic data by elimination of error propagation through several procedures (e.g., force and acceleration calculation, and position and velocity update through the Newtonian mechanics).

Here, the direct mapping is examined to generate atomic data for the AIMD acceleration. The velocity and position data of silicon (Si) at 300 K from actual AIMD simulations are used as training data, and recurrent neural network (RNN) is selected as training algorithm for prediction of future simulation data. Si is an intensively studied semiconductor material, which facilitates the validation and comparison with other approaches. Among various ML algorithms, RNN is a family of neural networks that specializes in processing a sequence of values, where the time dependence information is better utilized, as compared with traditional neural networks which assume that all inputs are independent of each other. In recent years, RNN has shown great promise in many tasks, for example, natural language processing [72, 73] and time series prediction [74]. The RNN algorithm is expected to demonstrate similar success in the time-series prediction of atomic velocity and position.

Through this study, we ultimately pursue the application of adaptive AIMD scheme (i.e., alternative run of ground-truth AIMD and RNN prediction) for materials research, in which the RNN model predictions would accelerate the atomic data production. Thus, the performance of the material property calculations with the RNN-predicted atomic data can be examined. Although the errors of predicted velocity and position data are unavoidably accumulated, the calculated material properties from ensemble or time dependence of atomic data can exhibit good performance with accurate description of correlation between atomic data at different time steps or optimal data processing conditions. Therefore, the objectives of this research are to confirm the reliability of the property calculations with RNN-predicted data and to provide data processing conditions for the calculation improvement of various material properties.

2.2 Methodology

In conventional AIMD scheme, the position and velocity vectors of each atom i at time t [$\mathbf{r}_i(t)$ and $\mathbf{u}_i(t)$] are updated based on Newton’s equations of motion, with the force evaluated using first-principles calculations (Figure 2.1). Here, we study the replacement of the conventional AIMD process of atomic data production with RNN prediction for materials research. RNN models predict the position and velocity vectors after M time steps [i.e., $\mathbf{r}_i(t + Mt_s)$ and $\mathbf{u}_i(t + Mt_s)$; t_s is a simulation timestep, and M is a prediction gap] using the atomic position and velocity at time t [$\mathbf{r}_i(t)$ and $\mathbf{u}_i(t)$]. We then evaluate various material properties based on the RNN predicted data. In the following subsections, we describe the methodologies of AIMD data generation for RNN model training and validation, RNN model development, and calculation of material properties using the atomic data.

2.2.1 Generation of AIMD Atomic Data

Atomic data are generated for RNN model training and validation by conducting AIMD simulations with a $3 \times 3 \times 3$ Si supercell (i.e., 216 atoms) at 300 K, with Vienna Ab initio Simulation Package (VASP) [75]. In the ground-truth AIMD simulations, atomic position and velocity data are updated with a timestep of 1 fs, employing the Verlet algorithm [34] to integrate Newton’s equations of motion. The canonical ensemble of NVT (constant number of atoms, volume, and te-

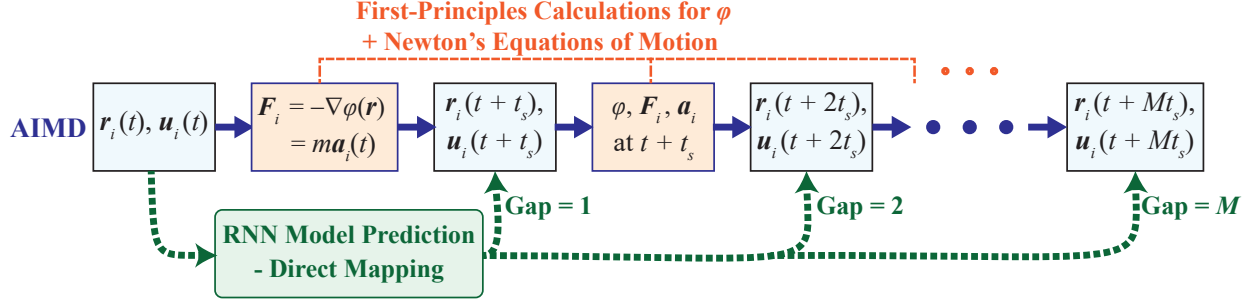


Figure 2.1: The blue-arrow flow indicates that, in conventional AIMD, the position and velocity vectors $[r_i(t)$ and $u_i(t)]$ are updated using Newton’s equations of motion $[F_i = -\nabla\varphi(\mathbf{r}) = m\mathbf{a}_i(t)]$ with potential energy (φ) obtained from first-principles calculations; the green-arrow flow is a scheme adopted in this research that the position and velocity vectors in future time steps $[r_i(t + Mt_s)$ and $u_i(t + Mt_s)]$ are updated with RNN model prediction. Direct mapping between current and future atomic data is achieved without evaluation of potential energy φ , force $\mathbf{F}$, and acceleration $\mathbf{a}$, which is the key for acceleration of AIMD simulation clock and reduction of error accumulation.

temperature) is adopted with the Nosé algorithm for velocity (i.e., temperature) control. It is worth noting that the temperature fluctuation is particularly sensitive to the Nosé mass, and here, we select the Nosé mass (unitless) of 6.28×10^{-3} to ensure that the induced frequency of temperature fluctuation resembles the typical phonon frequency of Si (~ 14 THz) [76]. A projected augmented wave pseudopotential is employed, and the Perdew-Burke-Ernzerhof type generalized gradient approximation is used for the exchange-correlation. The energy cutoff for the plane wave expansion of 500 eV and a single k -point are selected after the convergence test.

2.2.2 Development of RNN Models for Atomic Data Prediction

A fundamental structure of a vanilla RNN includes an input layer ($x_1, \dots, x_t$), an output layer ($y_1, \dots, y_t$), and multiple hidden layers ($h_1, \dots, h_t$), as described in Figure 2.2(a). In the context of this work, x_s is the atomic position and velocity at time step s , $s = 1, \dots, t$. Using the RNN, the next time step x_{s+1} in the sequence of given $x_1, \dots, x_s$ is predicted as:

$$h_s = f_\alpha(h_{s-1}, x_s) = \sigma(Wx_s + Uh_{s-1} + b), s = 1, \dots, t, \quad (2.1)$$

$$x_{s+1} = g_\beta(h_s) = \sigma(Ph_s + c), s = 1, \dots, t, \quad (2.2)$$

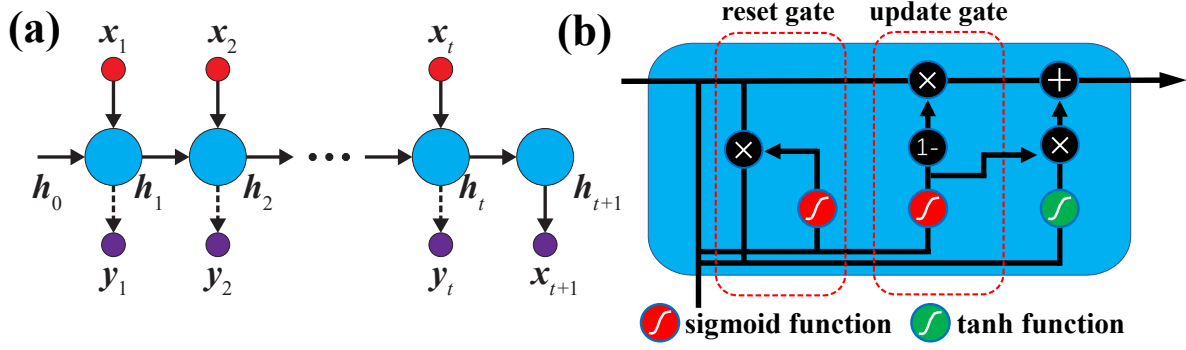


Figure 2.2: (a) Schematic of vanilla RNN. The circles and the arrows represent matrices and functions (e.g., matrix multiplication), respectively. Sequential input, output, and RNN’s states are denoted as red (x), violet (y), and blue (h), respectively, where the subscript t represents a time step. (b) One RNN unit with gated recurrent unit (GRU). A GRU cell consists of two modules, which are reset gate and update gate. Black circles with $\times$ and $+$ represent point-wise multiplication and addition, respectively.

where f_σ and g_β are nonlinear activation functions, e.g., the sigmoid function σ , and the network weights are parameterized by $\alpha = \{W, U, b\}$ and $\beta = \{P, c\}$, respectively.

The potential issue of the conventional RNN-based learning is the “short-term memory” problem [77]. It has been demonstrated that the original vanilla RNN [Figure 2.2(a)] has difficulty in capturing long-term dependencies (e.g., dependencies between steps that are far apart) because the gradients tend to either vanish or explode. In recent years, researchers have developed more sophisticated types of RNN to overcome the shortcomings. The long short-term memory (LSTM) [77] network and the gated recurrent unit (GRU) [78] are two instances of sophisticated RNN that are capable of remembering long-term dependencies over sequences. Figure 2.2(b) illustrates the details of a GRU-based RNN cell, where the “update gate” decides what information to erase and what to keep through training, and the “reset gate” is another gate to decide what past information need to forget or carry along. In this way, although the RNN network uses a long sequence of simulation steps during training, it selectively “remembers” most relevant information to pass through to the next node and “forgets” the irrelevant information. In this work, we choose to apply the GRU-based RNN structure for training and testing due to a relatively fewer number of parameters involved as compared to LSTM-based RNN to train the parameters (i.e., α and β) of RNN.

There are a couple of parameters that can possibly affect the convergence speed of the training process and the accuracy of trained models:

(1) Number of training and testing data sets. Specifically, in this study, the simulation data consist of 50,000 steps (50 ps AIMD simulation with a timestep of 1 fs) in total, and the first 40,000 steps are employed as training data, while the rest 10,000 steps as testing data. Within 50,000 steps, we should be able to achieve accurate training model while consuming reasonable computational resources for generating the data with AIMD.

(2) Batch size, i.e., the number of training sample used for upgrading the parameters of the model per iteration. The batch size is chosen as 32, considering the model and computer configurations used.

(3) Window size (L), which indicates how many previous simulation steps are included as an input for prediction purpose. Four window sizes of 1, 2, 5, and 10 are tested in experiments (as shown in Figure 2.3), and the window size of 1 is selected as the optimal one for prediction. The detailed discussions can be found on Section 2.3.2.

(4) Prediction gap size (M), the step distance between the current step and predicted step. Gap size is a critical parameter indicating how far the RNN prediction can proceed within the error threshold. Namely, it determines how many steps of AIMD can be replaced by RNN prediction. Therefore, the acceleration efficiency is determined by the gap size. In this research, four gap sizes of 1, 2, 5, and 10 are tested, and detailed discussions can be found on Sections 2.3.2 and 2.3.3.

(5) Number of unit in the GRU cell. In this research, the number of unit in the GRU cell is $1296 = 6 \times 216$, which is the dimension of the feature (3 for position and 3 for velocity) times atom number.

After we select the parameters of (1) – (5), RNN model is then trained by minimizing the mean squared error (MSE) of the ground-truth step and corresponding predicted step. The MSE is calculated as [79]:

$$\text{MSE} = \frac{1}{N_a} \sum_{i=1}^{N_a} (y_i - \tilde{y}_i)^2, \quad (2.3)$$

where y_i is a normalized ground-truth AIMD result, $\tilde{y}_i$ is the corresponding predicted data, i.e., atomic position and velocity data in this research, and N_a is the number of atoms ($= 216$). It should be noted that, before training, all the atomic data have been rescaled into $[0, 1]$ through

normalization [i.e., $y_i = (x_i - x_{\min})/(x_{\max} - x_{\min})$], where x_i is the original atomic data in AIMD]. The MSE's presented in this research are averaged over position and velocity data in 3 dimensions.

Since we employ a 40,000 – 10,000 split for training and testing in this research, the RNN model training starts from taking the first K steps as input to predict the $(K + M)^{\text{th}}$ time step for $K = 1, 2, \dots, (40,000 - M)$. The MSE between the predicted $(K + M)^{\text{th}}$ time step and the ground-truth $(K + M)^{\text{th}}$ time step from the AIMD is back propagated through the network, to refine on the estimation of parameters of the model. The training continues by shifting the $(K + M - L + 1)$ window to the right by gap M , when the window size is L for the prediction of the $(K + M + 1)^{\text{th}}$ time step. This process continues until the estimation of parameters converges. The trained model can then be utilized to predict the position and velocity information of a future step when given the position and velocity input from a current simulation step or the steps inside a window.

2.2.3 Evaluation of Material Properties Using Atomic Data

We first calculate the properties with actual AIMD simulations to confirm the validity of the property calculation codes and to provide benchmarks for the calculation using the RNN data. Five properties, including radial distribution function [RDF, $\langle g(r) \rangle$], temperature (T), velocity autocorrelation function [VACF, $u^{2*}(t)$], phonon density of states [$D_p(\omega)$], and specific heat capacity (c_p) are calculated with our in-house MATLAB codes, based on position and velocity data.

(1) Step-averaged radial distribution function [RDF, $\langle g(r) \rangle$] is calculated as follow:

$$\langle g(r) \rangle = \frac{1}{N_s N_a} \sum_{i=1}^{N_s} \sum_{j=1}^{N_a} \frac{V \cdot dn(r_{i,j})}{N_a \cdot 4\pi r_{i,j}^2 dr}, \quad (2.4)$$

where N_a is the number of atoms ($N_a = 216$), and N_s is the number of time steps ($N_s = 9,000$ out of the last 10,000 datasets for testing, i.e., the RDF is averaged over the last 9,000 time steps), V is the system volume, $dn(r_{i,j})$ is the number of atom within atomic distance ranging from $r_{i,j}$ to $r_{i,j} + dr$. For a numerical calculation, dr is selected as 0.02 Å, and $4\pi r^2 dr$ is used as the volume of the shell spanning from $r_{i,j}$ to $r_{i,j} + dr$.

(2) The temperature (T) is calculated by the equipartition theorem [80]:

$$T = \frac{2E_k}{n_{\text{dim}}N_a k_B} = \frac{\sum_{i=1}^{N_a} m(u_{i,x}^2 + u_{i,y}^2 + u_{i,z}^2)}{3N_a k_B}, \quad (2.5)$$

where E_k is the total kinetic energy, n_{dim} is the dimensionality ($n_{\text{dim}} = 3$), N_a is the total number of atom, k_B is the Boltzmann constant ($= 8.617 \times 10^{-5} \text{ eV K}^{-1}$), m is the atomic mass of Si ($m = 28.0855 \text{ amu}$), and $u_{i,x}$, $u_{i,y}$, and $u_{i,z}$ is the velocity vector component of atom i in x , y , and z direction, respectively.

(3) Velocity autocorrelation function [VACF, $u^{2*}(t)$] [81] is calculated as:

$$u^{2*}(t = n\Delta t) = \frac{\sum_{i=1}^{N_s} \langle \mathbf{u}_i(t = t_0) \cdot \mathbf{u}_i(t = t_0 + n\Delta t) \rangle}{\sum_{i=1}^{N_s} \langle \mathbf{u}_i(t = t_0) \cdot \mathbf{u}_i(t = t_0) \rangle}, \quad (2.6)$$

where $\mathbf{u}_i(t)$ [$u_{i,x}(t)$, $u_{i,y}(t)$, $u_{i,z}(t)$] is the velocity vector of atom i at time t , and angle brackets indicate ensemble averages, n denotes the index of time step, N_s is the time step used for calculating the VACF ($= 3,000$), and t_0 is the time origin.

(4) Phonon density of states [$D_p(\omega)$] is calculated from the Fourier transform of the VACF [81], given as:

$$D_p(\omega) = \int_0^\tau u^{2*}(t) \cos(\omega t) dt, \quad (2.7)$$

where ω is phonon frequency, and τ is taken as 1 ps based on the $\Delta\omega$ resolution of π/τ (i.e., $\pi \times 10^{12} \text{ rad s}^{-1}$).

(5) Specific heat capacity (c_p) is calculated using the $D_p(\omega)$ by differentiating the phonon energy (E_{ph}) with respect to T [81]:

$$c_p = \frac{\partial \langle E_{ph} \rangle}{\partial T} = \int_0^\infty \hbar \omega \frac{\hbar \omega}{k_B T^2} \frac{\exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2} D_p(\omega) d\omega, \quad (2.8)$$

where $\hbar$ is the reduced Planck constant ($\hbar = 1.05 \times 10^{-34} \text{ J}\cdot\text{s}$).

2.3 Results and Discussion

2.3.1 Time Consumption of AIMD Simulations and RNN Prediction

According to our study, actual AIMD simulation using the VASP code for 216 Si atoms, running on 4 cores (tested as optimal core number) for 2,000 time steps (i.e., 2 ps with a timestep of 1 fs) takes about 59 hours (i.e., 236 core-hours) with the high-performance computing resources [82]. It should be noted that the exact computing speed is dependent on simulation conditions and machine specification, however, the computing speed does not vary too much based on the suggested optimal number of running cores. In contrast, the RNN predictions for 2,000 time steps takes only 0.8 – 1.0 second (with one GPU) with TensorFlow [83] on NVIDIA Quadro P6000 and Intel(R) Xeon(R) CPU E5-1650 v3 @ 3.50GHz with 64G memory. This implies that successful prediction will be very effective for accelerating AIMD with a close-to-CMD efficiency (i.e., the RNN prediction itself is 5 orders of magnitude faster than ground-truth AIMD). However, the training time should also be taken into account for clarifying the acceleration efficiency. The average training time per epoch is 8 seconds, and totally 3,000 epochs have been run; therefore, the training takes 24,000 seconds (6.67 hours) with one set of selected parameters (i.e., batch size, L , M , etc.) in this research. Considering the training time, the data production of 2,000 time steps with RNN prediction is ~ 8.85 times faster than the ground-truth AIMD, even though this efficiency is also highly dependent on the number of epochs, number of time steps predicted, and selected parameters.

2.3.2 MSE Loss during Training Processes

To construct a RNN model with a high accuracy (i.e., small MSE), we first test four window sizes ($L = 1, 2, 5$, and 10) and calculate the MSE loss of each case during the training process. As shown in Figure 2.3, L clearly influences the testing loss (the minimum testing loss is achieved with the smallest L), while L has a negligible effect on the training loss. Therefore, we apply the L of 1 in all other training processes with different prediction gaps.

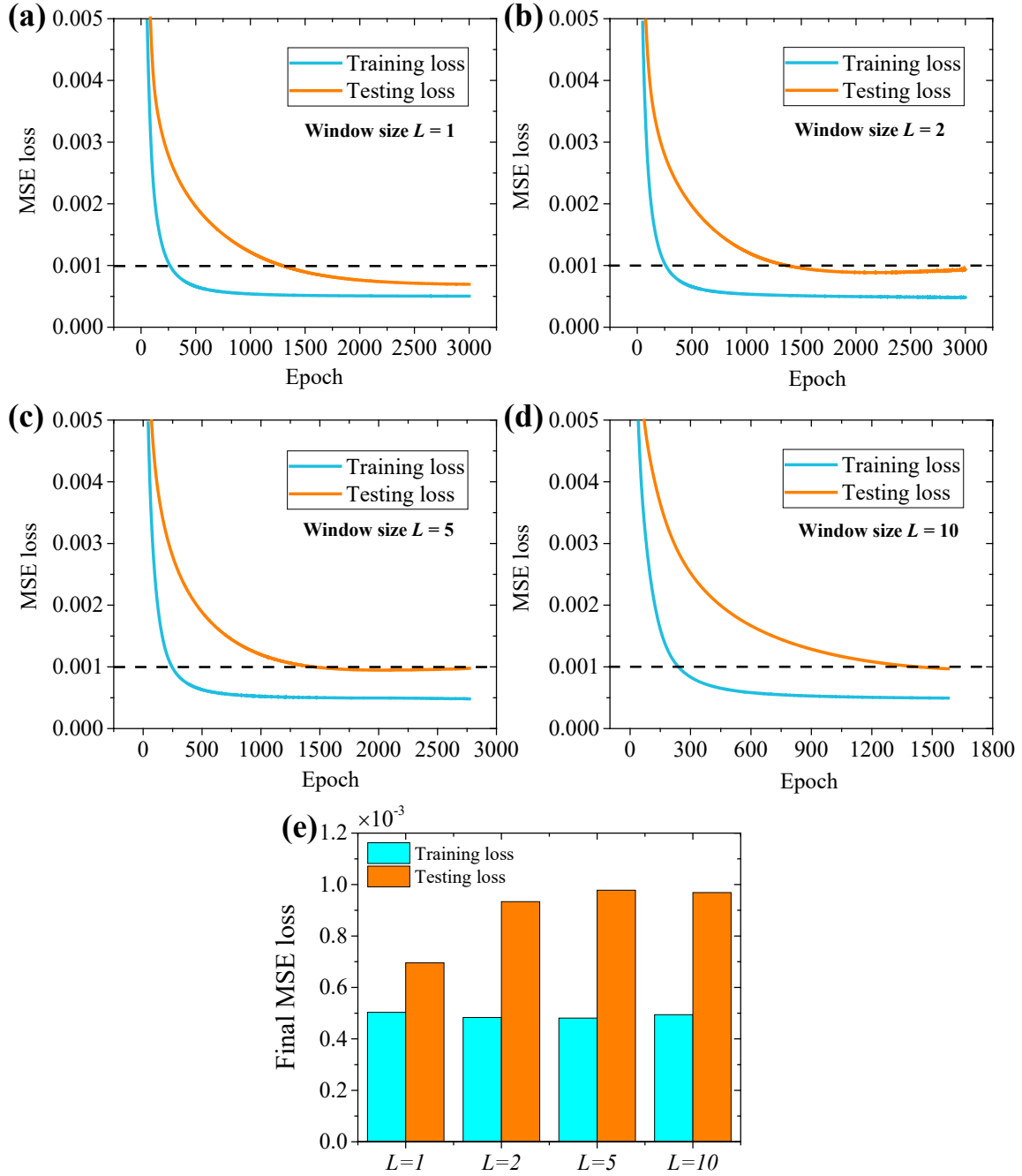


Figure 2.3: (a) – (d) Mean squared error (MSE) losses averaged over position and velocity during training and testing processes with different window size L ; (e) Last-step averaged MSE loss on L .

Secondly, four prediction gaps ($M = 1, 2, 5$, and 10) are tested, with a fixed window size ($L = 1$). Gap size M is a critical parameter indicating how far the RNN prediction can proceed within the error tolerance, which determines the acceleration efficiency of adaptive AIMD scheme with RNN prediction. Figure 2.4 shows that the MSE losses increase as the gap increases. This is attributed to that, with larger prediction gap, the correlation between the current step(s) and predicted step becomes weaker, so that the RNN passes through less relevant information of input step(s) [current step(s)] to the output step (predicted step), leading to increased errors. Although the absolute value of the loss is increasing with gap M , still it is within the range of error tolerance and it does not deteriorate the practice of calculation of material properties, which is further discussed in Section 2.3.3.

It is a critical and interesting topic to investigate how to enhance the long-term memory of RNN to enlarge the prediction gap for increasing the acceleration efficiency while maintaining the quantum-level accuracy. The prediction accuracy can be further enhanced by adding more physical constraints (e.g., energy conservation, minimum and maximum interatomic distance, etc). In this research, we also test different coordinate setups, and the training results are identical, which confirms the rotational and translational invariance.

2.3.3 Properties Evaluated from AIMD and RNN-Predicted Data

The RDFs and atomic configurations are evaluated using atomic position data from the last 9,000 steps of a ground-truth AIMD simulation and RNN predictions with different gaps and compared in Figures 2.5(a) and 2.5(b), respectively. The RDFs from RNN predicted data exhibit overall satisfying agreement with the ground-truth AIMD simulations (the major peaks coincide with each other), although we can discern that as the gap size M increases, more noise peaks occur between the major peaks, such as the small peaks between the r of $2 - 4$ Å. This indicates that the number of atom deviating from the original lattice sites increases with increasing prediction gap, leading to increased prediction errors. Figure 2.5(b) illustrates directly that as the gap size increases, more atoms are deviated from the original lattice sites ($\sim 10\%$ for gap $M = 10$). However, majority of the atoms still remain at their original lattice sites, which implies that material properties can be calculated with a reasonable accuracy using RNN-predicted data even with gap $M = 10$.

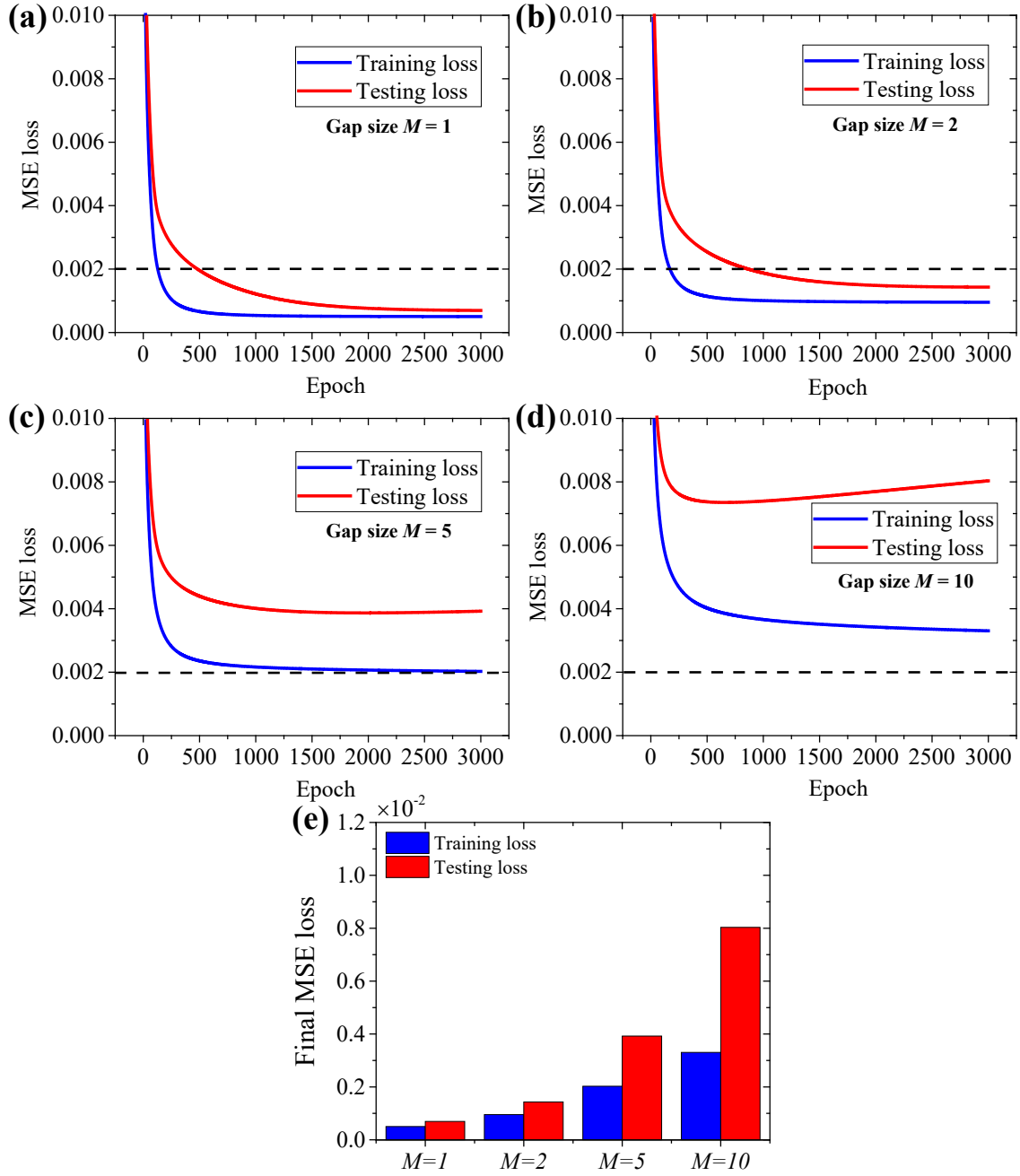


Figure 2.4: (a) – (d) Mean squared error (MSE) losses averaged over position and velocity during training and testing processes with different gap size M ; (e) Last-step averaged MSE loss on M .

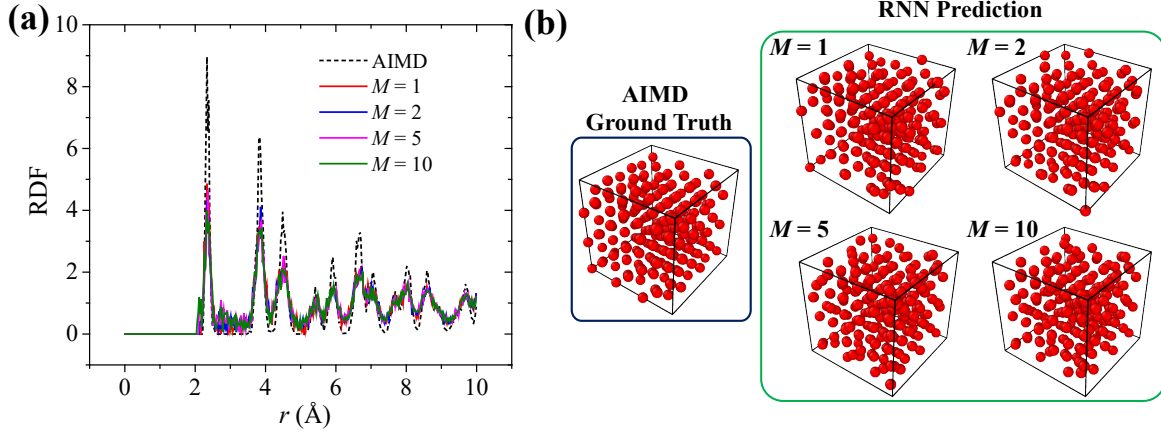


Figure 2.5: (a) Radial distribution functions (RDF's) and (b) atomic configurations of the ground-truth AIMD simulation and predictions with different prediction gap M ($M = 1, 2, 5$, and 10).

Figure 2.6 shows the properties calculated from the last 10,000 steps velocity data from a ground-truth AIMD simulation and RNN predictions with different gaps. As Figure 2.6(a) shows, although a thermostat is not applied and the energy conservation is not considered in training and prediction, RNN predicted data maintains the system temperature quite in consistence with that of the ground-truth AIMD. As the gap increases, the deviation of predicted temperature slightly increases, but even with gap of 10 (skipping 9 steps in AIMD), the average system temperature is still around 300 K.

Three dynamic properties, VACF, D_p and c_p , which are determined based on time correlations, are calculated using the RNN-predicted data and compared with those from the ground-truth data [Figures 2.6(b)-(d)]. All three properties are in excellent agreements with the ground-truth AIMD, indicating that the properties based on time correlations can be well reproduced with RNN prediction even with a 10% of the position prediction error.

2.4 Conclusions

This is an original study to accelerate the computational calculations of material properties with quantum-level accuracy (i.e., similar level of accuracy of AIMD) employing RNN training and prediction. Direct mapping of atomic data through RNN algorithms is examined not only to accel-

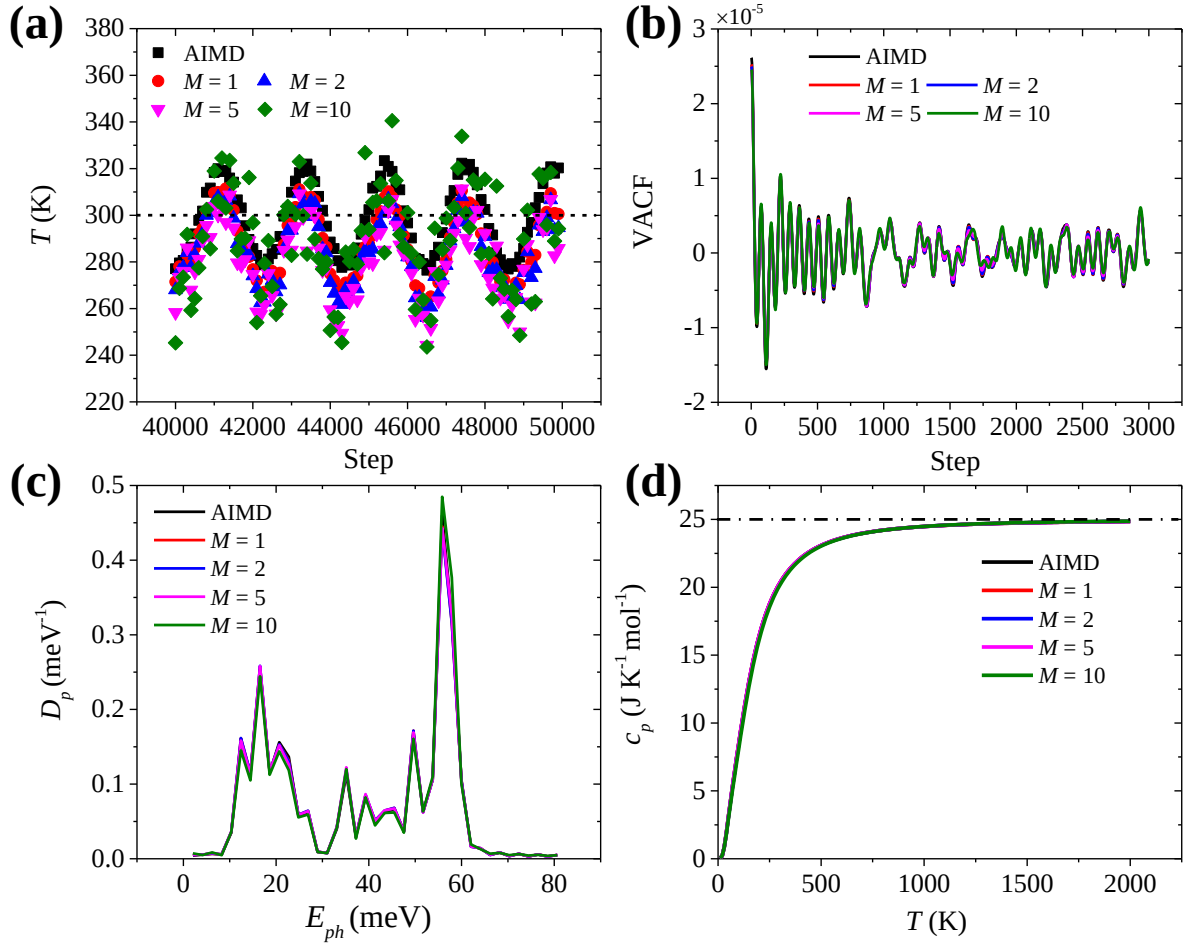


Figure 2.6: Material properties calculated from ground-truth AIMD simulation and RNN predictions with different prediction gap M : (a) temperature (T); (b) velocity autocorrelation function (VACF); (c) phonon density of States (D_p); (d) specific heat capacity (c_p).

erate the AIMD simulation clock but also to reduce the error accumulation by eliminating the force evaluation process. This research with crystalline Si demonstrates that the RNN prediction is approximately one order of magnitude faster than the ground-truth AIMD simulation, even including the time spent on RNN model training process. In this research, the RNN models are trained using AIMD simulation results with different window and gap sizes. The RNN-predicted atomic data have more deviation from the ground-truth AIMD with a larger gap size, but material properties calculated using the RNN-predicted data show reasonable agreements with the AIMD calculations; especially, dynamic properties based on time correlations between atomic data are very accurately reproduced even with largest gap size of 10.

This research shows the promise and feasibility of the application of RNN prediction in computational materials research. For broader applications of this approach, future research can address different material systems (metallic alloys and composites) or processes, such as sintering [84] and diffusion [85], which involve significant atomic displacements. Also, RNN training should include more diverse training conditions (e.g., different batch size and number of unit in GRU cell) in addition to window and gap sizes or include physical constraints (e.g., energy conservation, minimum interatomic distance, etc), to improve the overall prediction accuracy and efficiency.

Chapter 3

Accelerated Simulation Clock of Diffusion Kinetics via Parallel Replica Dynamics in Classical Molecular Dynamics

Note: Chapter 3 is a modified version of the publication: **Jiaqi Wang**, Ali Yousefzadi Nobakht, Seungha Shin*, and Amit Shyam, “Structural Deformation and Transformation of θ' -Al₂Cu Precipitate in Al Matrix via Interfacial Diffusion”, *Computational Materials Science*, 156, 111-120 (2019). This publication is reprinted with permission from Elsevier. The dissertation author listed in this publication directed and supervised the research which forms the basis for this publication.

3.1 Introduction

Aluminum (Al) alloys have a high strength-to-weight ratio and are heavily utilized in automotive and aerospace industries [86, 87]. The high strength of an Al alloy is attributed to spatially distributed fine precipitates, which impede the movement of dislocations, thus enhancing the strength [88, 89]. Specifically, the plate-like θ' -Al₂Cu precipitate is known as the most important strengthener for several commercially available Al alloys [90, 91]. It has a tetragonally-distorted fluorite structure, and presents two types of interfaces to the Al matrix, i.e., coherent and semi-coherent interface with relative orientation of $(001)_{\theta'} // (001)_{\text{Al}}$ and that of $(100)_{\theta'}$ or $(010)_{\theta'} // \{100\}_{\text{Al}}$, respectively [92, 93, 94, 95]. However, θ' -Al₂Cu is metastable over 200 °C, which will

transform to θ -Al₂Cu phase, evidenced by both first-principles calculations and experiments, and the thermodynamically stable θ -Al₂Cu phase leads to degraded mechanical properties [92, 96, 97]. Therefore, understanding the structural deformation and phase transformation of θ' -Al₂Cu precipitate at high temperatures is a prerequisite for achieving Al alloys with stable and superior mechanical properties, and the study of atomic diffusion will contribute to the enhanced understanding as it characterizes the mobility and structural evolution during the transformation and deformation processes. However, no research has been performed on the atomic mobility in the θ' -Al₂Cu/Al system via classical molecular dynamics (CMD) until now, which can provide detailed atomic-scale insights into structural deformation and phase transformation at the interface.

A combination of first-principles calculations, mixed-space cluster expansion approach, and mesoscale phase-field modeling, have been employed to study the growth and coarsening of θ' -Al₂Cu [92, 98, 99]. The first two approaches generate input quantities for the phase-field modeling, such as the precipitate/matrix interfacial free energies, lattice parameters, and elastic properties. However, other input parameters, such as tracer diffusivity (self-diffusivity, D_{self}), cannot be obtained from the first-principles calculations due to its temporal limit. If the diffusivities on both sides of the interface have a large discrepancy, artificial non-equilibrium effects, such as extra surface diffusion, solute trapping, and interface stretching, will affect the microstructure [100, 101]. In addition, the parameter of “atomic mobility” in the phase-field modeling can have a dominant effect on the microstructure, and it is significantly dependent on D_{self} [102]. DICTRA (Diffusion Controlled TRAnsformation) software is developed to obtain the temperature and composition-dependent atomic mobility [103]. However, due to the limited experimental data of D_{self} , only a few systems are optimized and accessible in DICTRA. Therefore, determining the D_{self} with a more accurate and convenient approach than experiment facilitates the development of DICTRA software and phase-field modeling, which will contribute to development of higher temperature Al alloys for the automotive and aerospace industries.

CMD is a proper approach to examine D_{self} , but its short timestep (usually, order of femtosecond) for numerical stability hinders investigation of long temporal scale phenomena, such as phase transformation. Accelerated CMD approach is employed to extend the simulation time, even up to a few microseconds [49, 48], which allows for more insightful and realistic investigation. Among various acceleration methods, the parallel replica dynamics (PRD), which has been widely

applied to study infrequent events [104, 105, 106, 107], is selected to monitor the interfacial atomic diffusion, determine the D_{self} of each element, and unravel possible diffusion mechanisms in this research. In PRD, the probability distribution of transition event is assumed to follow the first-order kinetics, while modified dynamics is involved in other acceleration methods, such as “hyper-dynamics” [47], “meta-dynamics” [108], and “temperature accelerated dynamics” [49] methods. From that perspective, the PRD is regarded as the most powerful and accurate algorithm to advance the simulation clock with full atomistic details [104].

The PRD has been reported to calculate the mean square displacement ($\langle d^2 \rangle$) as accurate as CMD [109]; thus, the accuracy of D_{self} calculated by using the $\langle d^2 \rangle$ from the PRD, is also expected to be similar to full CMD, which has been employed in the diffusion simulations [110, 111]. Therefore, the PRD is expected to capture D_{self} of Al and Al' atoms adjacent to the θ' -Al₂Cu/Al matrix interfaces correctly and efficiently (especially for low temperature solid-state diffusion; the detailed discussions on the enhanced efficiency at low temperatures are elaborated in Section 3.3.1 “Diffusion Simulation Performance”), and it can be extended to study diffusion properties of other intermetallic systems.

3.2 Simulation Methodology

3.2.1 Interaction Potential - Angular Dependent Potential

Interatomic interactions of Al-Al, Al-Cu, and Cu-Cu pairs are modeled using the angular dependent potential (ADP) [33], which can reproduce lattice parameters, elastic constants, and formation energies very well for both θ and θ' phases. In addition, the ADP provides a reasonable description of the phase stability across the Al-Cu phase diagram, dilute heat of formation, vacancy-impurity binding, and other thermodynamic properties, demonstrating its superiority for atomic simulations of precipitation hardening in Al-Cu alloys to other potential models {such as embedded atom method (EAM) potential [112]}. Total energy (E_{total}) of the atom ensemble described by the ADP model is represented as:

$$E_{total} = \frac{1}{2} \sum_{i,j(j \neq i)} \Phi_{ij}(r_{ij}) + \sum_i F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{i,\gamma} (\mu_i^\gamma)^2 + \frac{1}{2} \sum_{i,\gamma,\chi} (\lambda_i^{\gamma\chi})^2 - \frac{1}{6} \sum_i v_i^2, \quad (3.1)$$

where i and j are atom indices, and superscripts γ and χ refer to Cartesian components of vectors and tensors. The first two terms (Φ_{ij} and F_i) in the right-hand side comprise a regular EAM potential [113], which is independent of angles between interatomic bonds. $\Phi_{ij}(r_{ij})$ represents a pair interaction potential, determined by chemical species and atomic distance r_{ij} of atoms i and j , and $F_i(\bar{\rho}_i)$ is the embedding energy summed over all atoms. Here, $\bar{\rho}_i$ is the host electron density at the site of atom i induced by all other atoms in the system, defined as:

$$\bar{\rho}_i = \sum_{j \neq i} \rho_j(r_{ij}), \quad (3.2)$$

where $\rho_j(r_{ij})$ is the electron density function assigned to atom j .

The third and fourth terms (μ_i^γ and $\lambda_i^{\gamma\chi}$) depend on the dipole vectors and quadrupole tensors, respectively, which are given by:

$$\mu_i^\gamma = \sum_{j \neq i} u_{ij}(r_{ij}) r_{ij}^\gamma \text{ and} \quad (3.3)$$

$$\lambda_i^{\gamma\chi} = \sum_{j \neq i} w_{ij}(r_{ij}) r_{ij}^\gamma r_{ij}^\chi. \quad (3.4)$$

The last term ν_i , in Equation 3.1 is the trace of $\lambda_i^{\gamma\chi}$, given as:

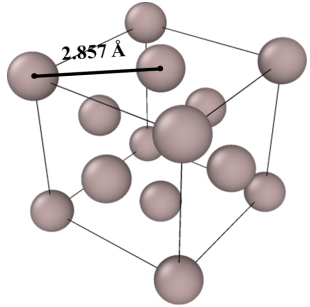
$$\nu_i = \sum_{\gamma} \lambda_i^{\gamma\gamma}. \quad (3.5)$$

$u_{ij}(r_{ij})$ and $w_{ij}(r_{ij})$ are two additional pairwise functions, representing angular dependent forces. The angular terms, which are introduced for the deviation of atomic structure from cubic symmetry, can alter various material properties, such as melting point, defect formation energy, and elastic constants. Detailed description and parameterization of this ADP model can be found in the literatures [33, 114].

3.2.2 Atomic Structure for Diffusion Simulations

Using the crystallographic information of Al and θ' -Al₂Cu unit cells summarized in Table 3.1 [93, 115, 116], the atomic structure for the diffusion simulations is prepared, that is, θ' -Al₂Cu precipitate enclosed by Al matrix. The nearest neighbor distance (2.857 Å for Al, and 2.487 Å for

Table 3.1: Crystallographic information of Al and θ' -Al₂Cu unit cells. The nearest neighbor distances (2.857 Å for Al, and 2.487 Å for θ' -Al₂Cu) in crystallographic structures are used to determine a threshold distance for detection of transition event.

Property	Al	θ' -Al ₂ Cu
Lattice constants	$a = b = c = 4.04 \text{ Å}$	$a = b = 4.04 \text{ Å}, c = 5.08 \text{ Å}$
Space group	$Fm-3m$ (225), Cubic	$I-4m2$ (119), Tetragonal
Fractional coordinates	Al (0.0, 0.0, 0.0)	Al (0.0, 0.0, 0.0) Al (0.5, 0.5, 0.5) Cu (0.5, 0.0, 0.75)
Crystallographic structure		
Al 		
Cu 		

θ' -Al₂Cu) is annotated in the crystallographic structure, which provides a basis for selecting a suitable threshold distance for detection of transition event. The θ' -Al₂Cu has a plate-like morphology with high aspect ratios: typically, 1 – 10 nm in thickness and 100 – 1000 nm in diameter [93]. In our simulations, θ' -Al₂Cu is shaped as a rectangular cuboid ($l_{\theta'} \times l_{\theta'} \times t_{\theta'}$) with a thickness ($t_{\theta'}$) of 2.42 nm ($= 6a_{\text{Al}}$, close to median thickness of θ' -Al₂Cu in 319 alloy [117]) and a side dimension ($l_{\theta'}$) of 6.46 nm ($= 16a_{\text{Al}}$), as shown in Figure 3.1.

Since the side dimension $l_{\theta'}$ employed in this study is much smaller than that in the experiment [93], to justify the simulated dimension, additional simulations are performed with two larger side dimensions ($24a_{\text{Al}}$ and $32a_{\text{Al}}$) at 900 K. The difference in the calculated mean square displacement $\langle d^2 \rangle$ (Figure A.1) of Al atoms in the first layer of precipitate near both the coherent and semi-coherent interfaces, among three cases with different side dimensions, is almost indiscernible, which demonstrates that the interfacial atomic diffusion is not significantly affected by the side dimension, when it is larger than the employed dimension ($16a_{\text{Al}}$). In contrast, the thickness dimension is expected to be more influential on interfacial structure and diffusion properties, as the diffusion of corner atoms will play a more significant role in overall diffusion. Although the atomic diffusion properties depend on precipitate geometry especially with small dimensions and their geometrical dependence needs to be further studied, we expect that the simulated precipitate dimension is suitable to reasonably reproduce experimental behaviors while saving computational cost; thus, we employed a θ' -Al₂Cu precipitate with a dimension of 6.46 nm $\times$ 6.46 nm $\times$ 2.42 nm ($l_{\theta'} \times l_{\theta'} \times t_{\theta'}$) for all temperature simulations.

As shown in Figure 3.1, after generating a $28 \times 28 \times 12$ supercell of Al matrix (37,632 atoms), θ' -Al₂Cu precipitate replaces the $16 \times 16 \times 6$ Al supercell. The generated θ' -Al₂Cu plate structure has a supercell dimension of $16 \times 16 \times 4.5$ (i.e., $4.5c_{\theta'} = 6a_{\text{Al}}$, shown in the side view), containing 6,912 atoms (4,608 Al' and 2,304 Cu atoms, respectively. Al' denotes the Al atoms in θ' -Al₂Cu, and this notation is used subsequently). Periodic boundary conditions are applied to all three directions, and interaction with precipitates in neighboring images can be excluded due to a sufficient distance between θ' -Al₂Cu precipitates ($= 6a_{\text{Al}} = 24.24 \text{ \AA}$, approximately three times larger than the potential cut-off distance of $8.29 \text{ \AA}$). As in the front and side views, the coherent interface is normal to the z direction with a relative orientation of $(001)_{\theta'} \parallel (001)_{\text{Al}}$, while the semi-coherent interface is normal to the x or y direction as reported [118].

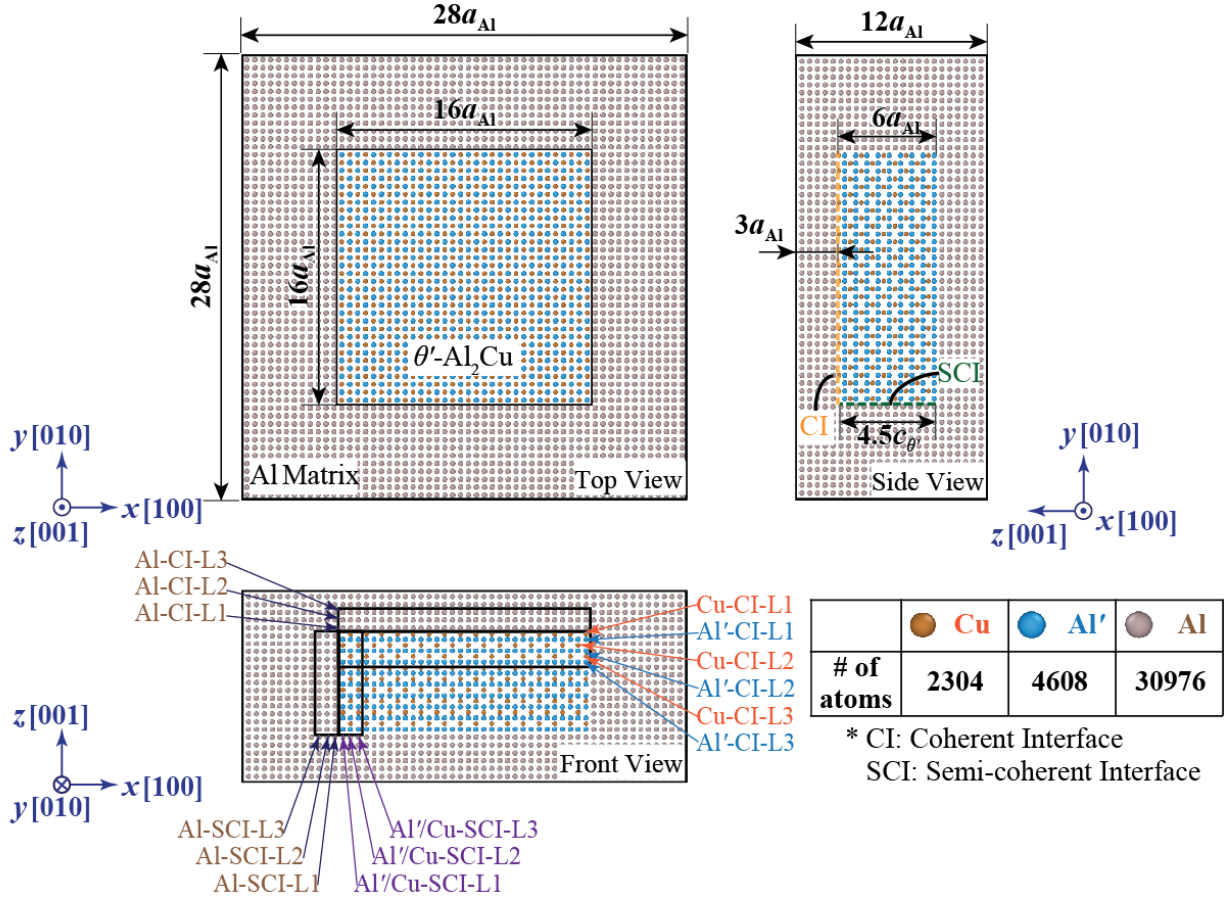


Figure 3.1: Simulated cell structure: $16 \times 16 \times 4.5$ θ' - Al_2Cu supercell enclosed in a $28 \times 28 \times 12$ Al matrix with an interfacial configuration of $3c_{\theta'} : 4a_{\text{Al}}$ ($= 4.5c_{\theta'} : 6a_{\text{Al}}$). The coherent interface (CI) is normal to the z direction while the semi-coherent interface (SCI) is perpendicular to the x or y direction. The front view illustrates first three atomic layers of CI and SCI interfaces. L1, L2, and L3 indicate layer 1, layer 2, and layer 3, respectively. The atoms in each layer are counted as L1, L2 or L3 layer atoms depending on which layer they belong to in this initial structure, regardless of their migration during later diffusion period.

3.2.3 Molecular Dynamics with Parallel Replica Dynamics for Diffusion Properties

All simulations in this research are performed using an open-source package of LAMMPS [119]. The velocity Verlet algorithm [35] and a timestep of 2 fs are employed for the integration of Newton's equations of motion in both configuration equilibration and PRD simulations. Five temperatures (700, 750, 800, 850, and 900 K) below the melting point of Al ($T_{m,Al} = 933.5$ K) are employed for solid-state atomic diffusion of θ' -Al₂Cu/Al system. These temperatures are selected for kinetic reason, i.e., to accelerate diffusion within the selected time scale, and it is recognized that most of these temperatures are above the solvus temperature for the dissolution of precipitate phases. Here, it is assumed that D_{self} of each element at lower temperatures (< 600 K) can be estimated by extrapolating the simulation results at higher temperatures (employed in this study, i.e., 700, 750, 800, 850, and 900 K) with the Arrhenius expression [120], on the presumption that the activation energy does not change with temperature.

Prior to allocating the initial configuration (Figure 3.1) to each partition for executing PRD, it is equilibrated at each diffusion temperature for 200 ps to achieve a quasi-equilibrium. Figure A.2 shows that the initial diffusion structure has been stabilized after 20 ps of equilibration at each temperature. NVT ensemble [constant atom number (N), volume (V) and temperature (T)] is employed during the equilibration for maintaining a constant temperature with Nosé-Hoover thermostat.

Dephasing is then performed by running momentum randomization at the same temperature of equilibration. For choosing an appropriate dephasing time, velocity autocorrelation function (VACF) is computed (Figure A.3). The system loses its memory about its initial momentum state within 2 ps at all temperatures, i.e., the VACF decays to 0 within 2 ps; thus, the dephasing time is chosen as 2 ps with 10 dephasing repetitions.

Afterwards, each replica runs dynamics to check whether a transition event has occurred, by energy-minimizing the system through the conjugate-gradient algorithm [121] and comparing the resulting atomic configuration with the counterpart in the previous minimum-energy basin. If any atom moves further than the threshold distance of 3 Å (chosen based on nearest neighbor distances as shown in Table 3.1), then a transition event is counted. After a transition event is

detected, only the event replica advances the simulation clock while searching for correlated event, and other replicas stop making contributions to the total simulation time (t_{clock}), although they are still searching for transition or correlated event. Thus, t_{clock} is smaller than the production of the number of replicas ($n_{rep} = 40$ in this research) and the time simulated on each replica (r_{rep}), and the efficiency (η) of PRD is defined as [104],

$$\eta(\%) = \frac{t_{clock}}{n_{rep} \times t_{rep}} \times 100\%. \quad (3.6)$$

The atomic trajectory of the minimum-energy configuration is output whenever a transition event occurs. The atomic trajectories of the first three layers are then processed with our in-house MATLAB code to obtain the mean square displacement of each atomic species j ($\langle d^2 \rangle_j$, $j = \text{Cu, Al}', \text{ or Al}$), which is given by [84]:

$$\langle d^2 \rangle_j = \langle \{ [\mathbf{r}(t_0 + \tau) - \mathbf{r}_{com}(t_0 + \tau)] - [\mathbf{r}(t_0) - \mathbf{r}_{com}(t_0)] \}^2 \rangle, \quad (3.7)$$

where τ is the elapsed observation time (maximum τ is selected as the half of total simulation time) and t_0 is the time origin (the number of time origin is equal to the half of event number). $\mathbf{r}(t_0 + \tau)$ and $\mathbf{r}(t_0)$ is the atomic position at observation time τ and at time origin t_0 , respectively. Angle brackets $\langle \rangle$ indicate an ensemble average over all atoms of species j and over all time origins as well. Effect of random motion of center-of-mass caused by Nosé-Hoover thermostat or barostat is eliminated by subtracting the coordinate of center-of-mass at observation time τ and time origin t_0 [$\mathbf{r}_{com}(t_0 + \tau)$ and $\mathbf{r}_{com}(t_0)$, respectively].

The self-diffusivity (D_{self}) is calculated by the Einstein relation [122], based on $\langle d^2 \rangle_j$, as shown below:

$$D_{self} = \frac{1}{2n_{dim}} \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \langle d^2 \rangle, \quad (3.8)$$

where n_{dim} is the diffusion dimensionality (3 for bulk diffusion, and 1 for directional diffusion along x , y , or z axis). As Figures A.4 – A.13 show, after a few tens nanoseconds, $\langle d^2 \rangle$ curves display a linear increase versus time, and we used the linear $\langle d^2 \rangle$ regime to calculate the D_{self} to exclude the time dependence. Although the linear relationship is not confirmed by the slope of the $\log(t)$ and $\log(\langle d^2 \rangle)$ curve, however, the D_{self} obtained should be satisfying enough to compare the relative

mobility. Figures A.14 – A.18 show the $\langle d^2 \rangle$ of Cu, and it can be observed that the Cu atoms are actually vibrating around the equilibrium position, i.e., no diffusion can be observed, so that the D_{self} of Cu is not calculated.

The activation energy (E_a) is then obtained by fitting the T -dependence of D_{self} to the Arrhenius expression as [120]:

$$D_{self} = D_0 \exp\left(-\frac{E_a}{RT}\right), \quad (3.9)$$

where D_0 is a frequency pre-factor, and R is the universal gas constant ($= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

3.3 Results and Discussion

3.3.1 Diffusion Simulation Performance

During a PRD simulation, once any replica detects a transition event, other replicas will stop accumulating the simulation time, while only the event replica advances the simulation clock during subsequent searching for correlated events. At higher temperatures, the transition events occur more frequently, and the simulation clock is mostly advanced only by event replica, and thus the total simulation time and efficiency will generally decrease with increasing temperature, as shown in Table 3.2. Note that the decrease in PRD efficiency at high temperatures has no influence on the accuracy of CMD-calculated diffusivity. The enhanced PRD efficiency at low temperatures renders it more effective than conventional CMD in metallic diffusion, since conventional CMD requires much longer time to smooth a $\langle d^2 \rangle$ curve and obtain accurate D_{self} at low temperatures.

Table 3.2: Total simulation time and efficiency of PRD at each temperature.

T (K)	n_{rep}	t_{rep} (ns)	t_{clock} (ns)	η (%)
700	40	3.90	133.08	85.31
750	40	4.36	136.22	78.11
800	40	3.24	98.91	76.32
850	40	3.59	92.17	64.19
900	40	2.59	64.53	62.25

3.3.2 Initial and Final Atomic Configurations of Diffusion

The structures after energy minimization and equilibration for diffusion at each temperature are shown in first column of Figure 3.2, all of which share a similar atomic configuration, since diffusion is at an initial stage after a short initial equilibration time of 200 ps. These structures display distorted Al lattice sites (highlighted in the black ellipses at 700 K), especially in the z direction, and the extent of distortion is mitigated as the distance of lattice sites from the interface increases. This confirms that the initial diffusion structures after equilibration have not reached complete equilibrium, but it is observed that a stable diffusion is initiated after the equilibration [i.e., diffusion has excluded undesired fluctuations from initial CMD process, displaying smooth $\langle d^2 \rangle$ curves]. Thus, atomic trajectories are then recorded from this point to extract D_{self} and E_a .

The distorted lattice sites in Al matrix are gradually recovered during the diffusion simulation by atomic rearrangement, which is induced by system inclination of locating in the minimum energy state, as shown in second column of Figure 3.2, with a highlight in top figure of second column using black ellipses. However, at semi-coherent interfaces and corners of coherent interfaces, crystalline structure of Al matrix is deformed (circled with yellow ellipses), and this deformation grows along the x and $+z$ direction with temperature. For instance, at 900 K, the deformation at 64.53 ns is even severer than that of 700 K at 133.08 ns, which is induced by higher atomic mobility. The third column of Figure 3.2 shows the displacement vectors between the initial and final diffusion configurations. It is observed that the corner atoms and the atoms in the semi-coherent interfaces exhibit longer and more circuitous trajectories than those in the coherent interfaces, which suggests that the corner atoms and those in semi-coherent interfaces have higher mobility and thus induces significant deformation/possible transformation at semi-coherent interfaces and corners of coherent interfaces. The detailed mechanisms of structural deformation and transformation will be elaborated in the next section of 3.3.3.

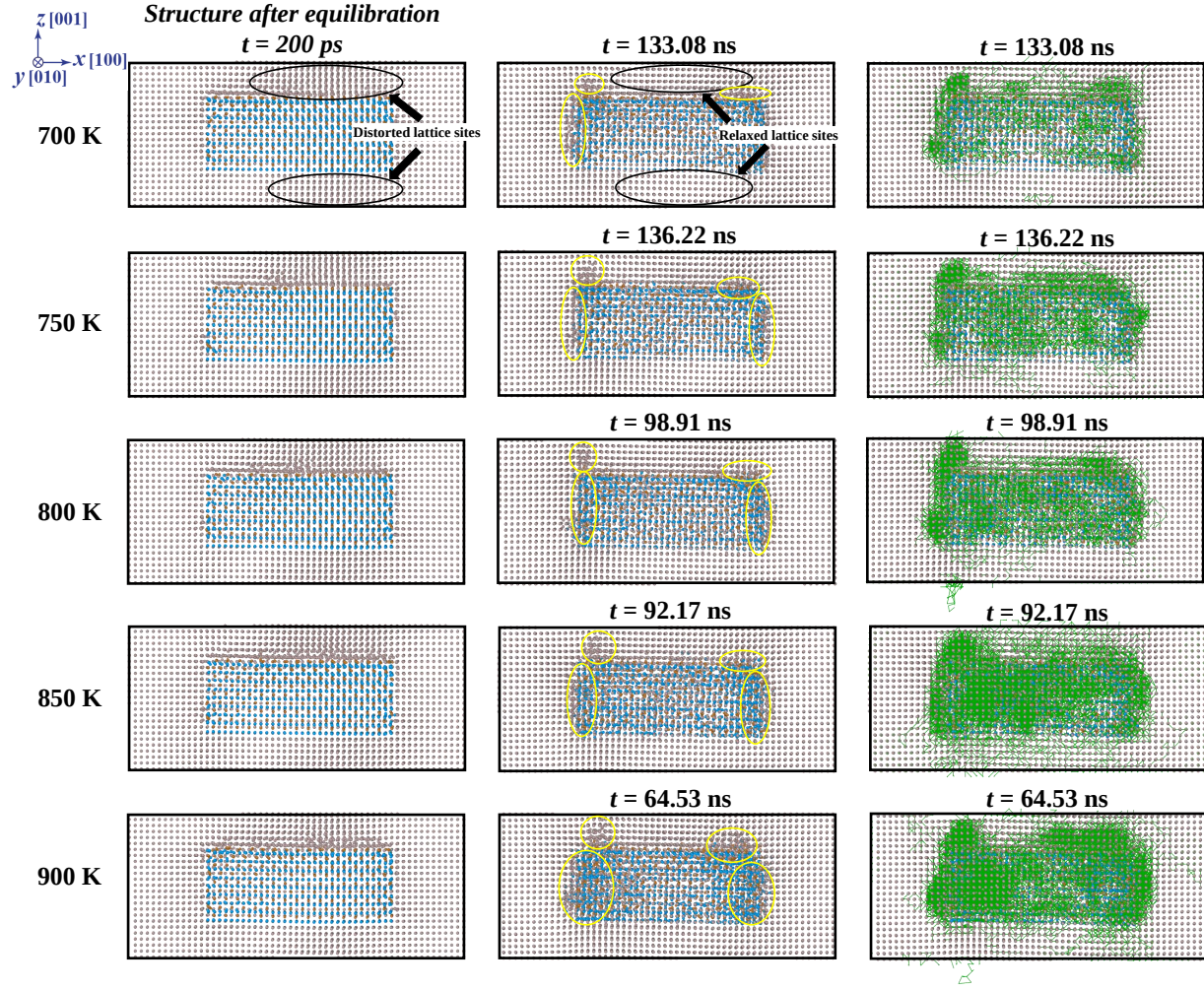


Figure 3.2: First column: structures after energy minimization and 200 ps equilibration for diffusion simulations at specific diffusion temperature (as shown in the second column). Second column: atomic configurations after diffusion at each temperature. The yellow ellipses highlight the regions where significant deformation and possible phase transformation occur. Third column: displacement vectors (green lines) between the initial and final configurations after diffusion at each temperature.

3.3.3 Structural Deformation and Transformation through Interfacial Diffusion

The semi-coherent interfaces exhibit a drastic structural deformation during isothermal heating, while coherent interfaces remain relatively stable, except for the corners intersecting with semi-coherent interfaces. The crystalline structure of the semi-coherent interface evolves into an amorphous state, while structural transformation into another ordered structure occurs at the edges of the coherent interfaces at high temperatures. Therefore, analysis of structural deformation is concentrated on semi-coherent interfaces, while interfacial transformation is on coherent interfaces.

At 700 K, the Al' and Cu atoms tend to move into and out of the space between the lattice sites of Al matrix at semi-coherent interfaces, causing the deformation of structure on both sides of the interface. Due to insufficient temperature and short time scale, Al' or Cu atoms are rarely found to hop to the lattice sites in Al matrix, and Al' and Cu atoms in the first three layers aggregate along the semi-coherent interfaces. The first-layer mean square displacement $\langle d^2 \rangle$ and atomic trajectories of Al' and Cu at 700 K (Figure 3.3) consolidate this finding. Maximum $\langle d^2 \rangle_{\text{Cu}}$ at 700 K is found less than $0.35 \text{ \AA}^2$ in Figure 3.3(a), demonstrating that most of Cu atoms only vibrate around their equilibrium positions. Additionally, the complete trajectory of Cu further proves that a very small number of Cu atoms exhibit diffusion behavior [the diffusive Cu atom is indicated in the trajectory of Figure 3.3(a)]. The square root of the maximum $\langle d^2 \rangle_{\text{Al'}}$ in the first semi-coherent layer is $1.5 \text{ \AA}$ at 700 K, demonstrating that the average travelling distance of Al' atoms is a half of the threshold distance ($\sim 3 \text{ \AA}$). Note that this is an averaged value, and even with this short travelling distance, as in Figure 3.3(e), the edge atoms ($\sim 25\%$ of all atoms) exhibit a long-range diffusion, which mostly contribute to the structural deformation and transformation, although the inner-plane atoms are not activated for diffusion at 700 K. Since a definite linear increase trend can be observed in $\langle d^2 \rangle_{\text{Al'}}$ at 700 K, and with a longer simulation time or higher temperature, an overall long-range diffusion of Al' is expected.

In the complete trajectory of Al' (in Figure 3.3b), more diffusive atoms can be detected than Cu, inducing a higher maximum $\langle d^2 \rangle_{\text{Al'}}$ than $\langle d^2 \rangle_{\text{Cu}}$. Examining the diffusion process of Al' at 700 K, diffusion distance toward the Al matrix is found to be longer than that toward the $\theta' - \text{Al}_2\text{Cu}$ (Figure

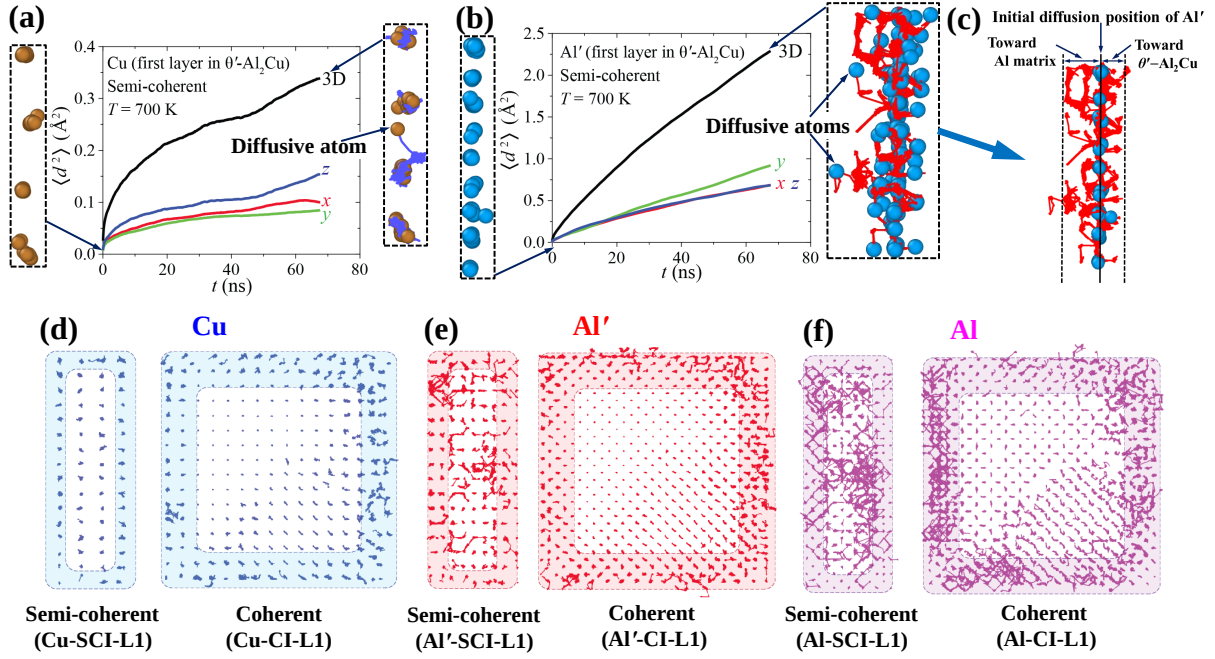


Figure 3.3: Mean square displacement ($\langle d^2 \rangle$) of (a) Cu and (b) Al' atoms in the first layer from the semi-coherent interface at 700 K. For (a) and (b), the initial diffusion configuration after equilibration for 200 ps (front view) is shown on the left, while the final diffusion configuration with trajectories is shown at right. (c) Initial diffusion position of first-layer semi-coherent interface Al' atoms and its complete trajectories. The average trajectory of diffusion toward Al matrix is longer than that toward the θ' -Al₂Cu. (d)-(f) are atomic diffusion trajectories of Cu, Al' and Al at semi-coherent interfaces and coherent interfaces at 700 K. The edge atoms (shaded regions) have a larger diffusivity than the inner-plane atoms (center regions) at the coherent interfaces, while for semi-coherent interfaces, inner-plane atoms have similar (in case of Cu) or even larger (in cases of Al' and Al) mobility than the edge atoms.

3.3c). While Al' atoms diffused into the Al matrix easily form metallic bonding with other Al atoms after breaking the Al-Al bonding, angular dependent Al-Cu bonding in θ' -Al₂Cu is more difficult to form and the dissociation for further diffusion of Al' atoms requires a higher energy (the bonding dissociation energy of Al-Cu is 216 kJ mol⁻¹, which is 30 kJ mol⁻¹ higher than the Al-Al bonding energy [123]); this explains more limited diffusion (or shorter diffusion distance) in θ' -Al₂Cu. Figures 3.3d – 3.3f exhibit the atomic trajectories of Cu, Al', and Al atoms near the semi-coherent (left) and coherent interfaces (right). At semi-coherent interfaces, not only edge atoms but also inner-plane atoms participate in the diffusion. For Cu at the semi-coherent interfaces, the mobility of the inner-plane atoms is similar to the edge atoms, and the inner-plane Al' atoms have even higher mobility than that at the edges, evidenced by the longer and more circuitous trajectories. Thus, uniform structural deformation of Al matrix and θ' -Al₂Cu precipitate spans over the semi-coherent interfaces (circled in the yellow ellipses near the semi-coherent interfaces in the second column of Figure 3.2), not only at the edges. However, at the coherent interfaces, the edge atoms have a larger mobility than the inner-plane atoms in blue (Figure 3.3d), red (Figure 3.3e), and magenta (Figure 3.3f) rectangles for Cu, Al', and Al, respectively. This explains the local growth of amorphization at the corners of the coherent interfaces (circled in the yellow ellipses at coherent interfaces in second column of Figure 3.2).

The differences of diffusion behaviors between semi-coherent and coherent interfaces in terms of location (i.e., edge or center region of interface) can be attributed to the interfacial atomic arrangement. At the semi-coherent interfaces, atoms located on both sides are dislocated, i.e., atoms in θ' -Al₂Cu could be aligned with the vacancies between the Al matrix atoms or edge dislocations, which lowers energy barrier for diffusion, activating the diffusion even for the inner-plane atoms. In contrast, interfacial atoms in θ' -Al₂Cu are aligned with Al matrix atoms at the coherent interfaces, and the alignment leads to less disturbance in atomic bonding and lowers interfacial energy (strain energy is also minimized due to improved lattice match of Al matrix and θ' -Al₂Cu in *z* direction), stabilizing the structure. Average potential energies of Al, Al', and Cu atoms at the semi-coherent ($E_{p,SCI,Al}$, $E_{p,SCI,Al'}$, and $E_{p,SCI,Cu}$) and those at the coherent interfaces ($E_{p,CI,Al}$, $E_{p,CI,Al'}$, and $E_{p,CI,Cu}$) are -3.37, -3.58, -3.00 eV atom⁻¹ and -3.46, -3.75, -3.02 eV atom⁻¹, respectively; these values support larger diffusion at the semi-coherent interface. The deformation

near the semi-coherent interfaces induces diffusion at the edges of coherent interfaces, initiating the phase transformation.

The atomic configurations and complete trajectories of Cu and Al' atoms in the first layer from the semi-coherent interface confirm that, as expected, atomic mobility increases at higher temperatures (Figure 3.4). The diffusion of Cu is not significantly enhanced even at 900 K in the time scales considered (Figure 3.4a), illustrated by the maximum root mean square displacement of Cu (in the order of 0.95 Å). Compared with Cu, Al' atoms generally have a longer diffusion distance; e.g., at 900 K, Al' has an order-of-magnitude larger $\langle d^2 \rangle_{\text{Al'}}$ than that of Cu, as shown in Figure 3.4b. The difference of $\langle d^2 \rangle$ can be attributed to atomic mass and availability of metallic bonding with Al matrix. As temperature increases, both the $\langle d^2 \rangle$ of Al' and Cu atoms increase along with more metallic bonds being broken, and thus the amorphous structure grows along the semi-coherent interfaces and near the corners of coherent interfaces, mainly by the diffusion of Al' atoms.

For detecting the structural transformation of θ' -Al₂Cu, the first three-layer structures of coherent interfaces (Cu-Al'-Cu, shown in Figure 3.1) are examined in detail from an energetic perspective. Figures 3.5a, 3.5b, and 3.5c are initial structures of Cu (Cu-CI-L1), Al' (Al'-CI-L1), and Cu (Cu-CI-L2) before diffusion, respectively, and Figures 3.5d, 3.5e, and 3.5f are corresponding final configurations after diffusion for 92.17 ns. As can be observed, not only the deformation occurs at the upper edges of the coherent interfaces, but also structural transformation occurs at the left and right edges. The Cu atoms in the red rectangle of the first Cu layer (Figure 3.5d) have even migrated over the next Al' layer, and bonded with third-layer Cu atoms (Figure 3.5f). The Cu atoms in the black rectangle of Figure 3.5d adopt an atomic structure similar to that of the next Al' layer, and bond with both the Al' layer (circled in black rectangle of Figure 3.5e) and the first-layer Al matrix atoms (not shown here) of the coherent interface.

The potential energy (E_p) of each atom is lowered by the formation of a new atomic structure. It is well-known that the θ' -Al₂Cu will transform to θ -Al₂Cu at high temperatures, but confirmation of the θ -Al₂Cu formation requires further validation by longer simulations for nucleation and growth of the new phase, which will be conducted in our future simulations up to 1 μ s. It has been experimentally demonstrated that the θ phase nucleates at the interfaces of the θ' phase and Al matrix during high temperature exposure [124]. However, the new phase generated in our simulat-

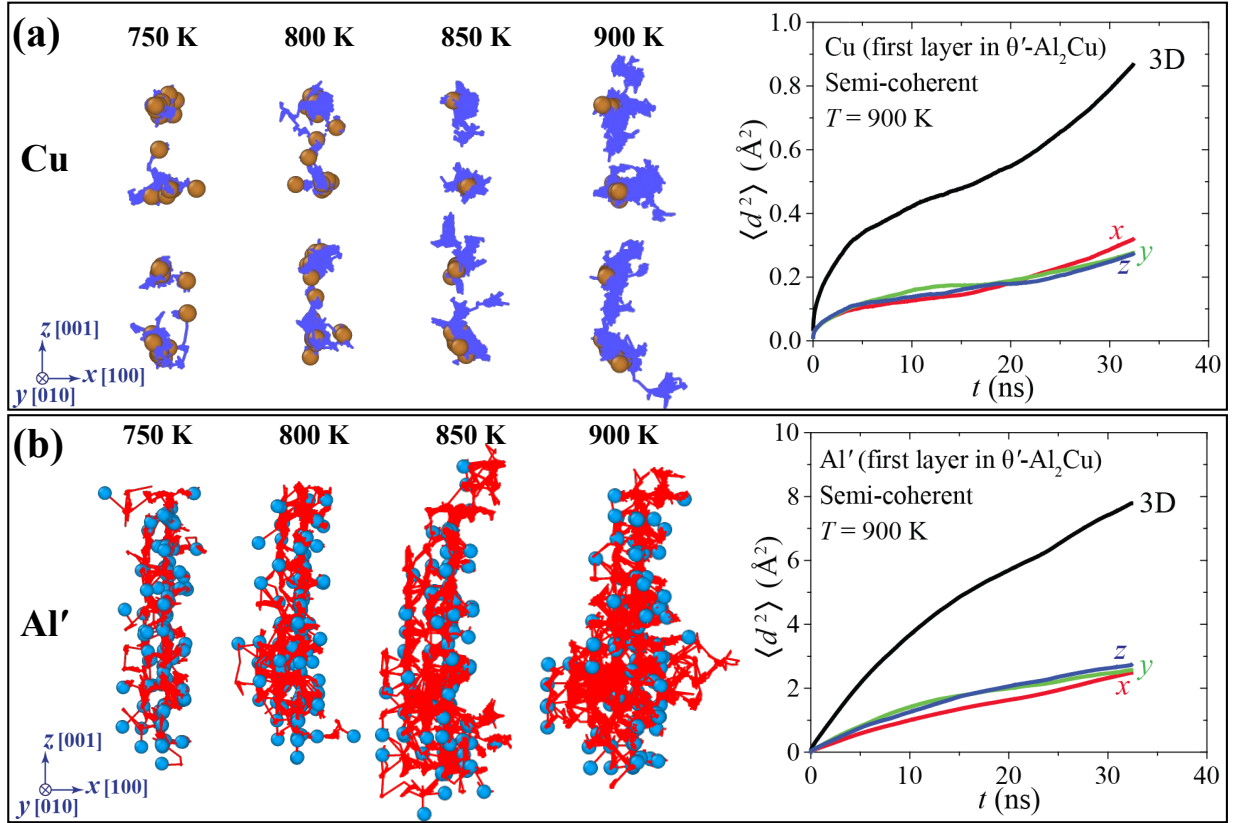


Figure 3.4: Last-frame atomic configurations and complete trajectories (front view) at 750 - 900 K, and mean square displacement ($\langle d^2 \rangle$) at 900 K of the first semi-coherent layer of (a) Cu and (b) Al' atoms (3D: total; x , y , and z : each direction).

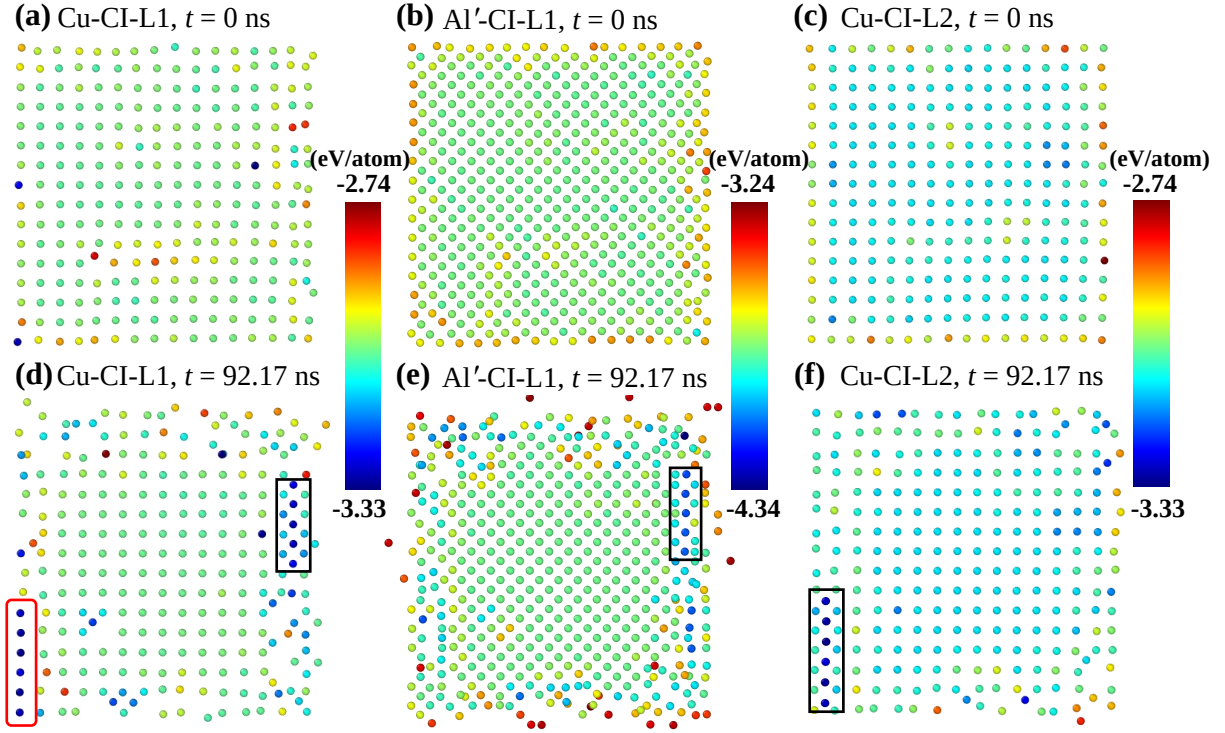


Figure 3.5: (a), (b), and (c) represent the initial atomic configurations of the first three coherent layers in θ' -Al₂Cu (Cu, Al', and Cu atoms, respectively) at 850 K. (d), (e), and (f) describe the final atomic configurations of (a), (b), and (c) at 92.17 ns. The color of each atom represents the magnitude of potential energy in unit of eV atom⁻¹, and should be referred to the color legend on the right side. The black rectangles in (d), (e) and (f) indicate the formation of new structure in both Al' and Cu layers. The red rectangle in (d) indicates that the atoms located originally in the first Cu layer have migrated to the third Cu layer (black rectangle in L2 layer), and have formed a new structure with the third layer Cu atoms.

ion could be an intermediate product (i.e., nucleus of θ -Al₂Cu) during the phase transformation to θ -Al₂Cu since the Cu atoms are found to adopt a similar arrangement in θ -Al₂Cu, which coincides with previous reporting that a good atomic fit exists between the θ and the θ' planes in some orientations [125]. In terms of structural transformation at other temperatures, a more densified atomic packing similar to Al' (or Al) is commonly observed at the edges of coherent interfacial Cu layer through 700 K to 900 K. These observations suggest that the atomic motion results in both deformation and transformation of θ' -Al₂Cu at high temperatures.

3.3.4 Directional Dependence of Diffusion

To quantitatively analyze the directional dependence of interfacial atomic mobility, D_{self} 's of Al and Al' atoms in the first layers (defined in Figure 3.1) at the semi-coherent (in the y - z plane, perpendicular to the x direction) and coherent interfaces in the x , y , and z direction, are calculated and shown in Figure 3.6. As discussed in the previous sections, Cu atoms are much less mobile than Al and Al' and do not display a sufficient displacement for a reliable D_{self} calculation, due to their large atomic mass and strong angular bonding with neighboring Al' atoms. Most of Cu atoms thermally vibrate around their equilibrium positions, and their vibrations are almost isotropic, as indicated by the $\langle d^2 \rangle$ in Figures A.14 – A.18. Thus, D_{self} and its directional dependence are analyzed with Al and Al' only.

For semi-coherent interfaces normal to the x direction, the D_{self} of Al in the x direction is smaller than that in the y and z directions. Diffusion of Al atoms into the precipitate (in the x direction) is reduced due to a higher potential energy barrier to form an Al-Cu angular-dependent bonding in the precipitate, while the diffusion in the directions (y and z) parallel to the semi-coherent interfaces results in the same metallic bonding formation; thus, atoms can be more easily dislocated in the y or z direction. However, the smaller dimension of z direction enables the corner atoms to play a dominant role in diffusion, which contributes to a large D_{self} in the z direction. As temperature increases to 900 K close to the melting temperature of Al (i.e., $T_{m,Al} = 933.5$ K), the significantly enhanced mobility covers the corner atom effects, contributing to similar D_{self} in y and z directions. Therefore, at temperature far below $T_{m,Al}$, the $D_{self,x} < D_{self,y} < D_{self,z}$ for Al, while $D_{self,x} < D_{self,y} \approx D_{self,z}$ near $T_{m,Al}$ as in Figures 3.6(a)-3.6(c).

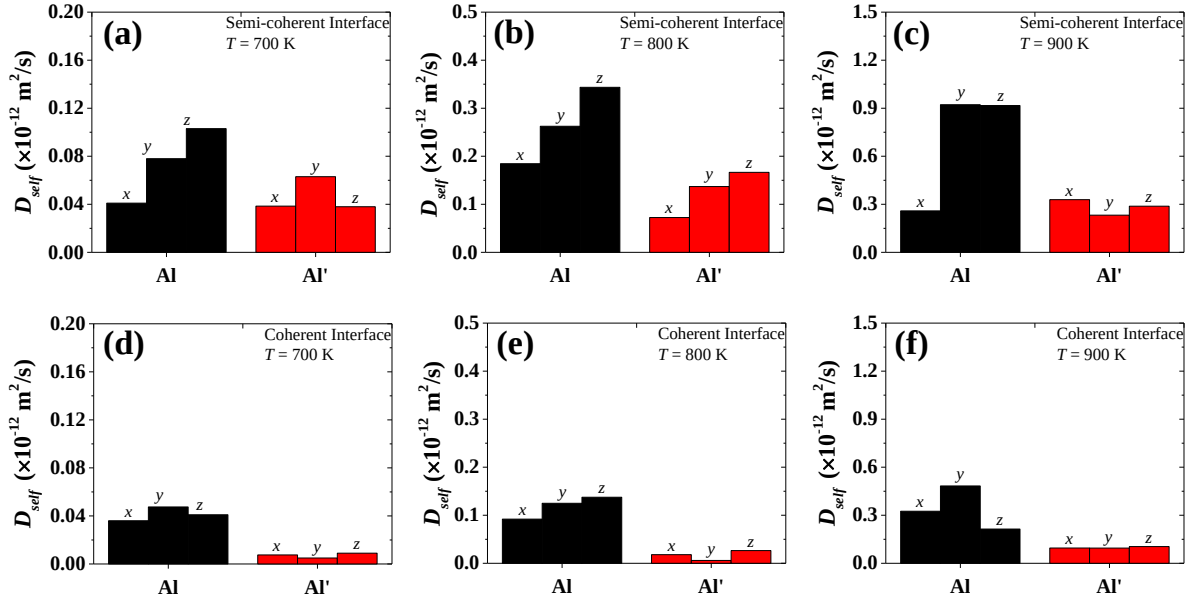


Figure 3.6: Self-diffusivity (D_{self}) of Al and Al' atoms in the first layer from the semi-coherent (parallel to the y-z plane, perpendicular to the x direction) and coherent interfaces (parallel to the x-y plane) at 700 K [(a) and (d)], 800 K [(b) and (e)], and 900 K [(c) and (f)], respectively.

In contrast, with a smaller diffusivity, the anisotropy is not obvious as atoms randomly move around the equilibrium positions. As aforementioned, the root mean square displacements of Al' at the semi-coherent interface are 1.5, 2.1, and 2.8 Å in the final step of diffusion simulations at 700, 800, and 900 K, respectively, all of which are smaller than those of Al matrix atoms at each temperature (2.29, 3.32, and 4.48 Å at 700, 800 and 900 K). These results indicate that most of Al' atoms still maintain their bonding with neighboring atoms, while only a few atoms have migrated over the threshold distance. The formation energy, calculated using the ADP model, is -0.203 eV atom⁻¹ for θ' -Al₂Cu [33] using reference state (face-centered cubic crystal) of pure Al and Cu. The formation energy suppresses the dissociation of Al'-Cu bonding for further diffusion of Al' atoms.

Due to the refined atomic arrangement in coherent interface, diffusivity of Al matrix atoms decreases; thus, significant diffusion anisotropy in coherent interface is not observed. However, the formation energy in θ' -Al₂Cu causes the $D_{self,Al'}$ larger than $D_{self,Al}$ as well. $D_{self,Al'}$ and $D_{self,Al}$ in coherent interfaces are much smaller than those of Al and Al' in semi-coherent interfaces.

3.3.5 Atomic Diffusivity (D_{self}) and Activation Energy (E_a)

The D_{self} values (obtained from linear fitting of mean square displacement $\langle d^2 \rangle$ curves in Figures A.4-A.13 using the Einstein relation) of Al and Al' in first three layers (shown in Figure 3.1) of both semi-coherent and coherent interfaces are reported in Table 3.3. The standard errors of linear fitting in obtaining each D_{self} are added in the parentheses after each D_{self} in Table 3.3 as well, which is calculated as [126]:

$$Error = \sqrt{\frac{\sum_1^{n_t} (y_n - \hat{y}_n)^2}{n_t - 2}}, \quad (3.10)$$

where n_t is the number of time instant, y_n is the actual value of $\langle d^2 \rangle$ value, and $\hat{y}_n$ is the $\langle d^2 \rangle$ value obtained from the linear regression. The standard errors are typically in the order of 10^{-2} to 10^{-3} Å², demonstrating a strong linear relationship between time and $\langle d^2 \rangle$, so they confirm that the D_{self} 's are not dependent on time in this research. As discussed, D_{self} of Al and Al' is larger near the semi-coherent interfaces than the coherent interfaces ($D_{self,SCI} > D_{self,CII}$), and Al in the matrix has larger D_{self} ($D_{self,Al} > D_{self,Al'}$). D_{self} in θ' -Al₂Cu of the semi-coherent interfaces increases as the distance from the interface decreases ($D_{self,SCI,L1} > D_{self,SCI,L2} > D_{self,SCI,L3}$); however, as

Table 3.3: Self-diffusivities of Al' ($D_{self,Al'}$) and Al ($D_{self,Al}$) in the first three layers of both semi-coherent (SCI) and coherent interfaces (CI). The number in the parenthesis is the standard error of linear regression calculated by Equation 3.10. The average (AVE) of the D_{self} is an estimation of the overall D_{self} for all three layers.

T (K)	Layer	SCI ($\times 10^{-14} \text{ m}^2 \text{ s}^{-1}$)		CI ($\times 10^{-14} \text{ m}^2 \text{ s}^{-1}$)	
		$D_{self,Al'}$	$D_{self,Al}$	$D_{self,Al'}$	$D_{self,Al}$
700	L1	4.650 (0.004)	7.383 (0.051)	0.733 (0.004)	4.133 (0.010)
	L2	0.933 (0.010)	9.167 (0.019)	1.083 (0.003)	7.767 (0.020)
	L3	0.417 (0.005)	5.683 (0.017)	0.733 (0.003)	9.350 (0.018)
	AVE	2.000 (0.006)	7.411 (0.029)	0.849 (0.003)	7.083 (0.016)
750	L1	6.467 (0.014)	15.617 (0.005)	1.800 (0.002)	7.600 (0.037)
	L2	2.383 (0.007)	16.300 (0.031)	0.783 (0.003)	11.367 (0.040)
	L3	0.400 (0.001)	6.417 (0.014)	0.933 (0.004)	11.150 (0.012)
	AVE	3.083 (0.007)	12.778 (0.017)	1.172 (0.003)	10.039 (0.030)
800	L1	12.550 (0.008)	26.367 (0.011)	1.700 (0.003)	11.783 (0.073)
	L2	2.700 (0.004)	28.083 (0.054)	1.067 (0.004)	14.117 (0.030)
	L3	1.183 (0.001)	17.033 (0.057)	0.983 (0.006)	27.400 (0.152)
	AVE	5.478 (0.004)	23.828 (0.040)	1.250 (0.004)	17.767 (0.085)
850	L1	18.683 (0.025)	21.067 (0.063)	3.833 (0.003)	17.550 (0.012)
	L2	10.883 (0.012)	37.833 (0.084)	2.267 (0.002)	22.017 (0.045)
	L3	8.250 (0.008)	26.133 (0.043)	5.950 (0.006)	21.067 (0.010)
	AVE	12.605 (0.015)	28.344 (0.063)	4.017 (0.004)	20.211 (0.022)
900	L1	28.300 (0.032)	69.933 (0.174)	9.833 (0.006)	34.083 (0.034)
	L2	24.433 (0.010)	107.717 (0.177)	4.483 (0.003)	50.033 (0.019)
	L3	9.300 (0.007)	69.433 (0.098)	3.617 (0.007)	47.583 (0.013)
	AVE	20.678 (0.016)	82.361 (0.150)	5.978 (0.005)	48.900 (0.022)

interfaces impede the diffusion by energy barrier in addition to inducing the diffusion by interfacial dislocation, the second layer can have a higher D_{self} than the first layer, especially for atoms in Al matrix and coherent interfaces.

The D_{self} 's are typically in the order of $10^{-13} - 10^{-15} \text{ m}^2 \text{ s}^{-1}$, however, some phase field modeling work [92, 99, 116] used a D_{self} in the order of $10^{-18} \text{ m}^2 \text{ s}^{-1}$ or even $10^{-20} \text{ m}^2 \text{ s}^{-1}$ obtained from experiments. The discrepancy among the reported D_{self} 's spans over several orders of magnitude; moreover, all previous phase field modeling studies employed a single D_{self} value regardless of temperature, interface type, and atom location. Therefore, it is imperative to adopt an accurate and convenient approach for calculating D_{self} , in order to minimize the error in phase field modeling work.

Using the Arrhenius plots (Figure A.19) of the resulting D_{self} 's, activation energy (E_a) and diffusion pre-factor (D_0) are calculated. E_a and D_0 of Al' and Al in the first three layers from the semi-coherent and coherent interfaces are summarized in Table 3.4. Despite the large variations in D_{self} , the activation energy (E_a) is similar to each other, implying that the variation is attributed to the jump attempt frequency, or pre-factor D_0 . No experimental value is available for comparison of E_a of Al' and Al as the same conditions adopted in this research. Using E_a and D_0 with the Arrhenius equations [Equation 3.9], D_{self} at lower temperatures can be estimated and used to improve the accuracy of future phase field modeling of precipitate growth.

Table 3.4: Activation energy (E_a) and diffusion pre-factor (D_0) of Al and Al' in the first three layers from the semi-coherent and coherent interfaces.

Element	Semi-coherent		Coherent	
	$E_{a,SCI} \text{ (kJ mol}^{-1}\text{)}$	$D_0 (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$	$E_{a,CI} \text{ (kJ mol}^{-1}\text{)}$	$D_0 (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$
Al	58.263	15.012	47.272	2.140
Al'	63.217	8.901	52.783	0.587

3.4 Conclusions

This is the first investigation of interfacial atomic diffusion in a θ' -Al₂Cu/Al system at high temperatures. Structural deformation and phase transformation through diffusion are analyzed with a focus on semi-coherent and coherent interface, respectively. Structural deformation is extensively observed near the semi-coherent interface while diffusion is suppressed at the coherent interfaces due to structural alignment. Deformation at the semi-coherent interface induces atomic diffusion at the corner of the coherent interfaces, and this corner diffusion initiates the structural transformation, similar to the transformation observed experimentally on phase boundaries. Directional diffusivity calculation demonstrates a lower self-diffusivity of Al atoms in the direction perpendicular to semi-coherent interface than the other directions, but this anisotropy is not obvious in other elements and near coherent interfaces. Understanding of interfacial atomic diffusion near θ' -Al₂Cu/Al interfaces at high temperatures enables the development of technique for controlling the precipitate stability [127] (for instance, solute atoms, which energetically favor the edges of coherent interface and inner-plane positions of semi-coherent interface, can be added for an effective control of diffusion), so as to advance the theories in phase transformation and precipitate growth, and finally improve the elevated temperature mechanical strength of Al-Cu-based alloy. We have also reported self-diffusivity, activation energy, and diffusion pre-factor of Al and Al' at both coherent and semi-coherent interfaces. These information can be applied to phase field modeling of precipitate growth for the improved accuracy of precipitate growth modeling.

As an initial attempt to study θ' -Al₂Cu precipitate diffusion using PRD, we do not consider some factors which could alter the diffusion kinetics, such as the effect of misfit strain in semi-coherent interface. Also, much longer simulation time is required (probably $\sim 1 \mu s$) to achieve accurate self-diffusivity of Cu and observe the complete structural transformation at semi-coherent interface. Future work will also focus on computational and experimental investigation of solute atom effects on the interfacial diffusion at high temperatures ($> 200^\circ C$) with a much longer time scale. Precise understanding and control of structural deformation and phase transformation is expected to be enhanced through these studies, and finally contribute to the effective design of Al alloys for high-temperature applications.

Chapter 4

Accelerated Interatomic Potential Development for Classical Molecular Dynamics: Finite-Temperature Dynamics Machine Learning

Note: Chapter 4 is a modified version of the publication: **Jiaqi Wang**, Seungha Shin*, Sangkeun Lee, “Interatomic Potential Model Development: Finite-Temperature Dynamics Machine Learning”, *Advanced Theory and Simulations*, 3, 1900210, (2019). This publication is reprinted with permission from John Wiley & Sons. The dissertation author listed in this publication directed and supervised the research which forms the basis for this publication.

4.1 Introduction

Over the past two decades, classical molecular dynamics (CMD) simulation has been extensively utilized as a powerful tool to investigate atomic-scale sciences. The ever-increasing utilization of CMD is attributed to the advances of accelerating algorithms [49, 128] and computing processing power (Moore’s law) [129]. The CMD employs empirical or semi-empirical analytical models to describe interatomic interactions, which extends the temporal and spatial scales of atomistic simulations from nano to micro [104, 130, 131, 132]. These interatomic potential models play a

dominant role in determining the accuracy of the CMD simulation results. Therefore, development of reliable potential model is critical to generating CMD results with scientific robustness.

Two approaches have been widely used for deriving an interatomic potential model [133]. One of them is fitting a potential energy surface to that from first-principles calculations. Although this fitting is possibly ideal on periodic solid or perhaps a gas phase cluster [134], precise fitting, especially for multi-component systems, can be infeasible or computationally expensive and may not ensure accurate reproduction of material properties due to the approximations of first-principles calculations. Another approach is that the parameters of potential model are empirically fitted to reproduce material properties (measured by experiments or first-principles calculations) by minimizing errors. However, developed models by these two approaches are often biased to specific domain of chemistries or chemical environments intended or considered during parameterization, losing the predictive capability under different environments (e.g., introduction of defects, phases, or different species) [51, 135]. Aiming at achieving a potential model without bias and high computational cost, we propose a finite temperature dynamics machine learning (FTD-ML) approach, and demonstrate its processes and effectiveness through developing a Buckingham type potential of aluminum (Al). Al is one of the elements the CMD can describe reasonably, and several interatomic potential models have been developed. Thus, Al is an appropriate element to test and validate the suggested FTD-ML approach by comparing with results using different potential models (developed by traditional method of density functional theory) and other machine-learned potential of Al (e.g., adaptive, generalizable, neighborhood informed (AGNI) potential [51]).

In recent years, there has been a significant upsurge in the application of machine learning (ML) approach to the development of interatomic potential models [136]. Various physical quantities (e.g., configuration, energy, force, and stress tensor) calculated by first-principles simulations at 0 K are normally employed in the ML model training [137, 138]. However, tremendous computational cost of first-principles method limits atomic configurations and conditions employed in training data. As a result, achieved interatomic potentials cannot fully address the complexity of configurational (e.g., with different defects and phases) and conditional space (e.g., different temperature and pressure set) in CMD, that is, machine-learned potentials may yield accurate results only on configurations and conditions that they have been fitted to [52, 139]. Additionally,

the first-principles approach has its own limitations, for example, approximations, such as local-density approximation and generalized gradient approximation, are made to solve the exchange-correlation functionals [140], which degrade the accuracy and reliability of generated data used in ML model training. In summary, the machine learned potential has conspicuous deficiencies in transferability and reliability.

To address the drawbacks of conventional first principles-ML approach, we employ FTD-ML approach, in which the training data are generated directly from CMD simulations and the final potential parameter set is selected on the basis that it can reproduce experimental results instead of first-principles data. By employing CMD instead of first-principles calculations for generating training data, the computational cost can also be significantly reduced, resulting that more configurational and conditional data can be included for training. In this research, training data are generated at various finite temperatures (300, 500, and 700 K) with a much larger system ($> 2,000$ atoms) than in first-principles calculation. Comprehensive properties including structural, thermodynamic, and mechanical properties are employed in the data trimming, model training, and validation processes, to minimize the bias of the developed potential.

One FTD-ML Buckingham potential of Al is successfully developed, and it can reproduce structural, thermodynamics, and mechanical properties of Al with a satisfying agreement with experiments or first-principles simulations (where experimental data are not available). This FTD-ML potential of Al can also work well under various ensembles, such as NVT, NVE, and NPT, however, one of the machine-learned Al potentials, that is, the AGNI potential [51], is not capable of generating meaningful results in NPT ensemble due to limited first-principles training data employed; instead, the system is highly unstable and keeps squeezing until the simulation stops (detailed benchmark methodology on AGNI potential of Al is elaborated in Section B.1 of “Detailed Benchmark Methodology of Machine-Learned Al AGNI Potential”). The proposed workflow of FTD-ML can be extended to develop unbiased interatomic potentials for various materials (e.g., multi-component systems) without limitation of model type, and the CMD simulation society is expected to benefit from this easily accessible and fast development approach.

4.2 Finite-Temperature Dynamics Machine Learning Approach

4.2.1 Workflow of FTD-ML Approach

The proposed FTD-ML follows the below four-step workflow as illustrated in Figure 4.1:

(1) Generating training data by performing CMD at various finite temperatures. Structural property of lattice constant, thermodynamics properties of thermal expansion coefficient and heat capacity, and mechanical property of Young's modulus are calculated as training data, using the output information of CMD simulations (detailed simulation and calculation methodologies for various properties are elaborated in Section B.2 of "Simulation and Calculation Methodology of Various Properties for Verification"). The data of thermal expansion coefficient, heat capacity, and Young's modulus are used for data trimming purpose, and the data of lattice constant at different temperatures are employed in the subsequent steps of correlation analysis and ML training. Due to the uncertainty of calculated properties by the selected potential parameters, the reproduced properties can deviate more than $7 \times 10^4\%$ from experiments, for example, the calculated heat capacity within the selected parameter ranges in training (in Table 4.1 of Section 4.2.2) can reach up to $735 \text{ kJ kg}^{-1} \text{ K}^{-1}$ at 300 K, while the experimental heat capacity of Al is $0.9 \text{ kJ kg}^{-1} \text{ K}^{-1}$ [141], and moreover, unrealistic negative values of properties can be generated with unsuitable parameter sets. Thus, it is necessary to trim the training data by selecting the potential parameter sets which generate properties within a reasonable range, and 30% deviation from experiments is used as a criterion for the training data trimming (i.e., if a calculated value falls out of the 30% deviation, it will be trimmed).

(2) Correlation analysis by three algorithms, which are the maximum information coefficient (MIC) [142], maximum edge value (MEV) [142], and Pearson correlation coefficient (PCC) [143]. The purpose of using three algorithms is for crosschecking the consistency of the correlation analysis results. The correlation analysis can identify the sensitivity of each potential parameter in determining the target properties. According to the order of sensitivity, a suitable increment of each potential parameter can be chosen in the ML prediction process. In a qualitative sense, a higher sensitivity indicates a larger change in target properties by a slighter change of the parameter. Thus, a smaller increment in prediction (compared with the increment used in training process) should be set for a parameter with a higher sensitivity on a target property, while a larger increment

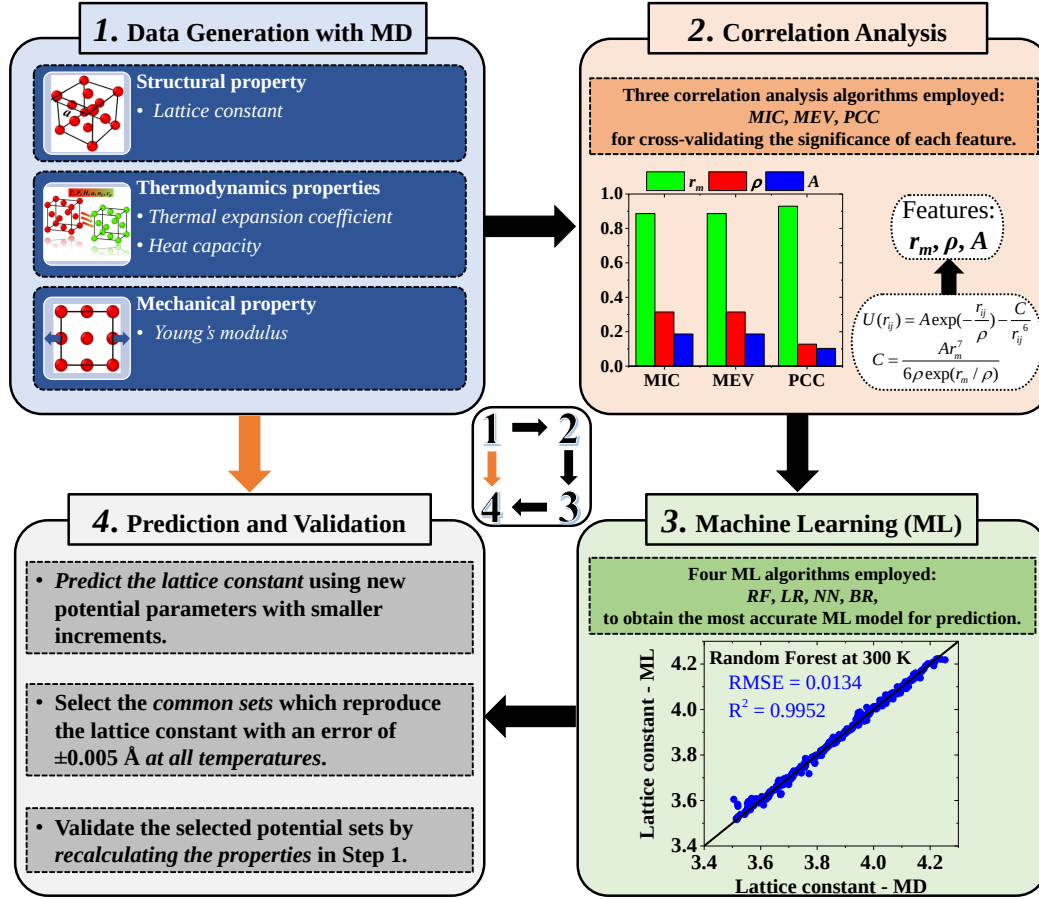


Figure 4.1: Four-step workflow for the proposed finite temperature dynamics machine learning (FTD-ML) approach. In the first step, classic molecular dynamics (CMD) is employed to generate training data which are structural, thermodynamics, and mechanical properties at three temperatures of 300, 500, and 700 K. In the second step, correlation analysis is performed by three different algorithms, i.e., maximum information coefficient (MIC); maximum edge value (MEV); and Pearson correlation coefficient (PCC), to identify the sensitivity of each parameter in determining the material properties and to provide a reference for setting reasonable increment of each parameter in prediction. In the third step, ML training is performed to find the most accurate model for prediction, among four models trained by algorithms of random forest (RF), linear regression (LR), nearest neighbor (NN), and Bayesian ridge (BR). In the last step, lattice constant is predicted using the potential parameters with smaller increment, and the potential parameter sets which reproduce the lattice constant within $\pm 0.005 \text{ \AA}$ of error range are selected. Finally, we validate the selected potential parameter sets by calculating various properties, as in the first step.

can be used for a potential parameter with a lower sensitivity. The selected values, including the increment of each parameter in data generation and prediction, are discussed in the next section (Section 4.2.2).

(3) Training of ML models for prediction. Due to the simplicity of the selected Buckingham potential model (three parameters only), relatively simple (quasi-linear) relationships are presented between the potential parameters and target properties (has been investigated but not shown here). These relationships can be effectively predicted by ML models trained by traditional algorithms, such as random forest (RF) [144], linear regression (LR) [145], nearest neighbor (NN) [146], and Bayesian Ridge (BR) [147]. Thus, this research employs these algorithms for ML model training. Additionally, these models are widely and readily used, which can facilitate further applications of this approach by other researchers. The performance of the trained models is evaluated by the root mean square error (RMSE, smaller is better, minimum = 0) [148] and coefficient of determination (R^2 , larger is better, maximum = 1) [149], and a model with the best performance is then selected for prediction based on these two assessments.

(4) Prediction using the selected model. Prediction is performed with the selected best-performance model, using the potential parameter sets with smaller increments as input. We then select potential parameter sets which reproduce the lattice constant within a small error range (± 0.005 Å used in this study), and validate the selected parameter sets by calculating the structural, thermodynamic and mechanical properties.

The correlation analysis, ML model training, and prediction with the trained ML models, are conducted via our in-house code [150], which employs a Python-based open source data analytic toolkit, scikit-learn [151].

4.2.2 Relation of Buckingham Potential Parameters

In a conventional form of the Buckingham model, interatomic potential energy φ is given as:

$$\varphi(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}, \quad (4.1)$$

where the A (eV), ρ (Å), and C (eV-Å⁶) are three tunable parameters, and r_{ij} is the distance between two atoms of i and j . The first and second terms on the right-hand side represent the repulsive and

attractive interaction between atoms i and j , respectively, leading that A and C should not be negative values. To obtain a reasonable range for data population, it is beneficial to identify the physical meaning of each parameter, which can be readily deduced from the expanded version of Equation 4.1 [152]:

$$\varphi(r) = \frac{\varepsilon}{1 - \frac{6}{\alpha_s}} \left[\frac{6}{\alpha_s} \exp\left(\alpha_s - \frac{\alpha_s r}{r_m}\right) - \left(\frac{r}{r_m}\right)^{-6} \right]. \quad (4.2)$$

Here, ε is the depth of the energy minimum, r_m is the corresponding interatomic distance at the energy minimum, and α_s is a parameter measuring the steepness of the exponential. Through comparison of Equations 4.1 and 4.2, we can obtain the expressions of A , ρ and C using ε , r_m and α_s as:

$$A = \frac{\varepsilon}{1 - \frac{6}{\alpha_s}} \frac{6}{\alpha_s} \exp(\alpha_s), \quad (4.3)$$

$$\rho = \frac{r_m}{\alpha_s}, \text{ and} \quad (4.4)$$

$$C = \frac{\varepsilon}{1 - \frac{6}{\alpha_s}} r_m^6. \quad (4.5)$$

From Equations 4.3 and 4.5, it can be deduced that α_s should be larger than 6 since parameters A and C are non-negative values. Also, according to Equations 4.3-4.5, a physical relation between A , ρ , and C can be derived as:

$$C = \frac{A r_m^7}{6 \rho \exp(r_m / \rho)}. \quad (4.6)$$

The original three parameters of A , ρ , and C then become A , ρ , and r_m . By transforming the third parameter C to parameter r_m , one can easily estimate the reasonable range of the parameter C as the interatomic distance at energy minimum (r_m) should be close to the nearest neighbor distance of the lattice structure (e.g., for face-centered cubic lattice, the nearest neighbor distance is $a/\sqrt{2}$, where a is the lattice constant). After selecting suitable ranges for parameters, i.e., A , ρ , and r_m , we then calculate the corresponding C for each set according to Equation 4.6, and all the simulations are then implemented by the LAMMPS code directly [119].

The range and the increment of potential parameters used in the model training and prediction are listed in Table 4.1. Currently, there is no available Buckingham potential parameters for Al. After an exhaustive search, it is found that the parameter A mostly falls into the range of 10^3 to 0.5×10^5 eV [153, 154, 155], thus, a broad range from 2,500 to 47,500 eV with an increment of 5,000

Table 4.1: Buckingham potential parameters A , ρ , and r_m used in model training and prediction processes.

	Parameters	Minimum	Maximum	Increment	Number
Training	A (eV)	2,500	47,500	5,000	10
	ρ (Å)	0.14	0.32	0.02	10
	r_m (Å)	2.6	3.05	0.05	10
Prediction	A (eV)	2,500	47,500	2,500	18
	ρ (Å)	0.2	0.32	0.01	12
	r_m (Å)	2.6	3.05	0.01	45

eV is employed for parameter A . With this broad range, we also expect to include the global minimum of the potential energy surface of Al. The nearest neighbor distance in Al lattice is $a_{\text{Al}}/\sqrt{2} = 2.863$ Å (where a_{Al} is the lattice constant of Al at 300 K, = 4.0495 Å [156]), and the energy minimum distance r_m should be close to the nearest neighbor distance, then a range from 2.6 Å to 3.05 Å with an increment of 0.05 Å is selected for r_m . Since $\alpha_s > 6$, according to Equation 4.4, $\rho = r_m/\alpha_s < 2.6$ Å/6 (= 0.43 Å), thus a range of 0.14 Å to 0.32 Å with an increment of 0.05 Å is chosen for ρ . A total of 1,000 (= $10 \times 10 \times 10$) training datasets are examined as the number of data points for each parameter is 10; however, some potential parameter sets cannot generate results in CMD simulations, leading to less than 1,000 datasets. The number of CMD simulations, which generate results without simulation errors (not the measurement errors of the properties with respect to the experiment, but errors stopping execution of CMD simulations), are 599, 558, and 522 at 300, 500, and 700 K, and after data trimming by the thermodynamic and mechanical properties within $\pm 30\%$ of discrepancy from experiments, the number of applied training dataset is reduced to 354, 344, and 316, respectively.

The parameters used in the prediction, with a smaller increment compared with that in the training process, is also shown in Table 4.1. The range and increment of the parameters are chosen based on the training data and the correlation analysis. For instance, the range of ρ is set from 0.2 Å to 0.32 Å, instead of from 0.14 Å to 0.32 Å, because the potential parameter sets with ρ smaller than 0.2 Å cannot produce physically meaningful simulation results (i.e., significantly deviated

from the experimental value or negative; or the simulation cannot even execute due to unstable structure). The increment of r_m in prediction is selected as 0.01 Å, while that in the training is 0.05 Å (five times larger than that in prediction), and the increments of other two parameters in prediction is set as half as that in training. The reasons for setting such increments of parameters in prediction are explained in Section 4.3.1 “Correlation Analysis”.

4.3 Results and Discussion

4.3.1 Correlation Analysis

Correlation analysis is performed at each temperature (300, 500, and 700 K) to identify the sensitivity of each parameter (i.e., A , ρ , and r_m) in determining the lattice constant of Al, as shown in Figure 4.2. The lattice constant at each temperature is an important property determining several other properties, such as density and thermal expansion coefficient. The results show that all three algorithms (i.e., MIC, MEV, and PCC) generate similar results at all temperatures, that is, r_m has the most significant effect on the lattice constant, while A has the least impact. As a result, we can set appropriate increment of each parameter in the prediction stage according to this order ($r_m > \rho > A$), to populate the data of lattice constant as comprehensive as possible, in order to predict a more accurate lattice constant. Although it has been mentioned that a smaller increment should be set for parameter with higher sensitivity to the materials properties, the absolute value of increment for higher sensitivity parameter does not necessarily have to be smaller. Here, the “smaller” means that for a higher-sensitivity parameter, the increment of that parameter set in prediction is reduced by a larger time of that in training, compared with lower-sensitivity parameters. For example, the increment of r_m (the most sensitive parameter) is set as 0.01 Å in prediction, and that in the training is 0.05 Å (five times larger than that in the prediction); the increment of ρ (the second-most sensitive parameter) is set as 0.01 Å in prediction, and that in the training is 0.02 Å (only two times larger than that in the prediction); however, the absolute value of the increment of r_m and ρ in prediction is the same, as shown in Table 4.1.

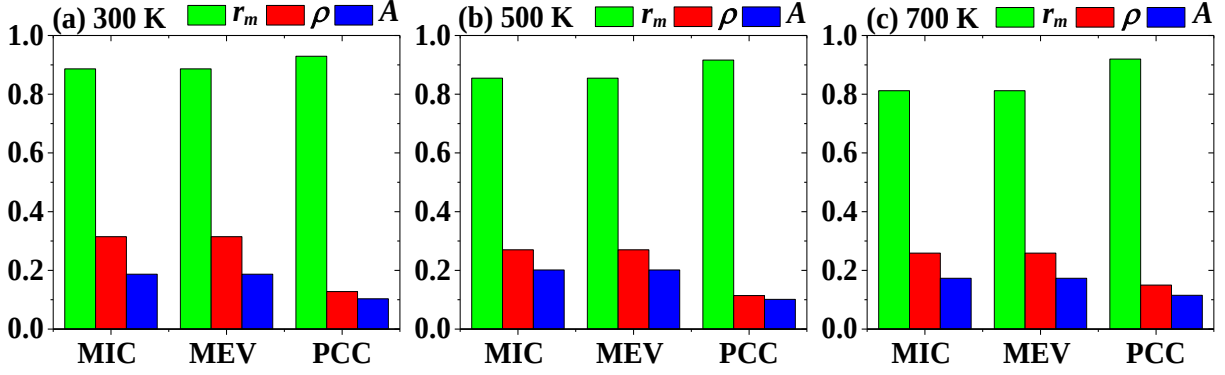


Figure 4.2: Correlation coefficients between the lattice constant a and the potential parameters A , ρ , and r_m at (a) 300, (b) 500, and (c) 700 K, using three correlation analysis algorithms. The order of significance of each parameter is determined as $r_m > \rho > A$, indicating that the r_m is the most sensitivity potential parameter in determining the lattice constant, while A is the least one.

4.3.2 Model Training and Prediction

Four ML models at each temperature of 300, 500, and 700 K, using the algorithms of RF, LR, NN, and BR are trained and evaluated by the RMSE and R^2 , as shown in the Figure 4.3(a)-(l). For all temperatures and training algorithms, we achieve a RMSE less than 0.04 and a R^2 value higher than 0.95, demonstrating notably high accuracy of trained models in property prediction. At 300, 500, and 700 K, the performance order of each algorithm is RF > LR > BR > NN, LR > BR > RF > NN, and LR > BR > RF > NN, respectively. Since LR demonstrates the best performance overall, we select the LR-trained models for prediction. Figure 4.4 shows the predicted lattice constant with an error of ± 0.005 Å, at 300, 500, and 700 K. Ten common sets are found and labeled by the symbol of “♥”. The potential parameter values of the ten common sets at various temperatures are listed in Table 4.2. Although a high prediction accuracy of the selected model is expected according to the performance (RMSE and R^2), it is not 100% guaranteed that the predicted lattice constants equals to the CMD calculated ones. Therefore, CMD simulations are also performed to find the lattice constants for the ten labelled potential parameter sets, and calculate the RMSE of the CMD-calculated lattice constants with respect to the experimental values. The lattice constants at each temperature obtained by the prediction and CMD simulation using the ten parameter sets, and the RMSE’s are also listed in Table 4.2. The set “ $A = 17,500$ (eV), $\rho = 0.25$ (Å), and $r_m = 2.94$

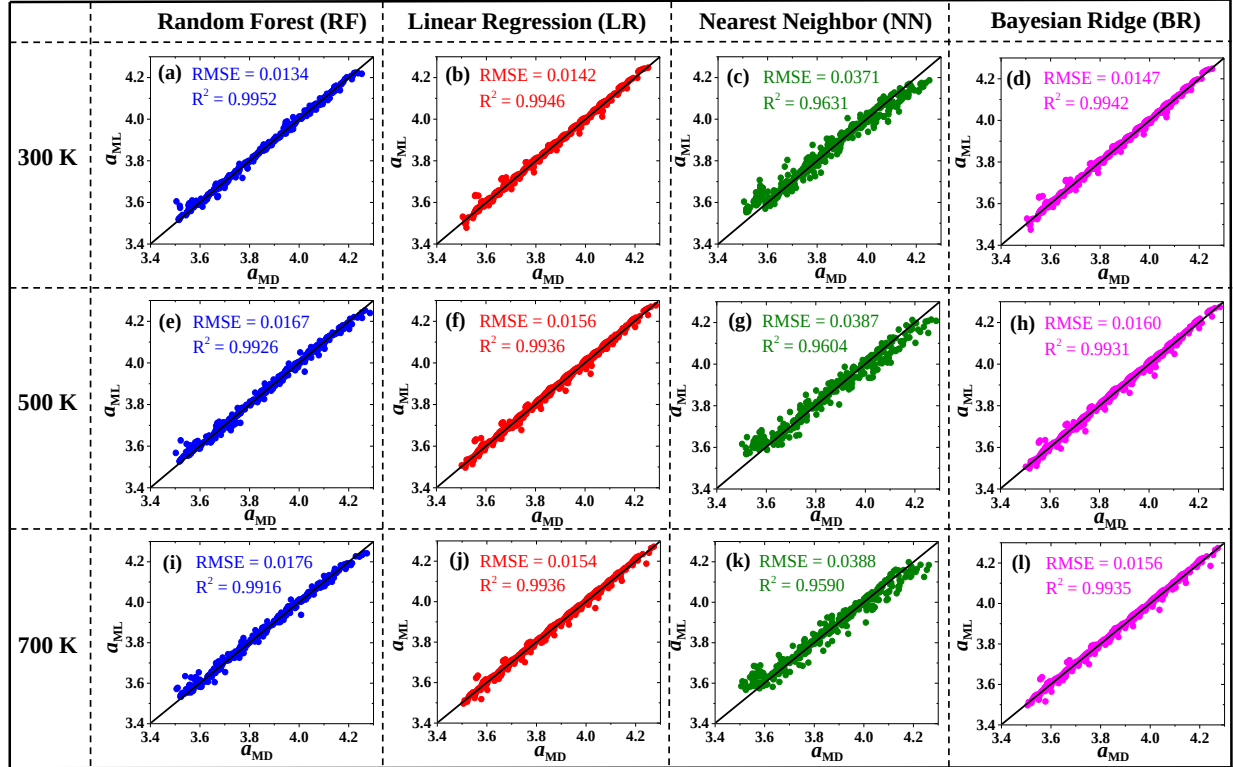


Figure 4.3: ML model training results of lattice constant a (in unit of Å) of Al using four different algorithms [i.e., random forest (RF), linear regression (LR), nearest neighbor (NN), Bayesian ridge (BR)] at 300 K [(a)-(d)], 500 K [(e)-(h)], and 700 K [(i)-(l)]. The x -axis represents the CMD-calculated results and y -axis represents the ML model-generated results. The root-mean-square error (RMSE) and coefficient of determination R^2 values are also displayed in each figure, demonstrating the accuracy of each model.

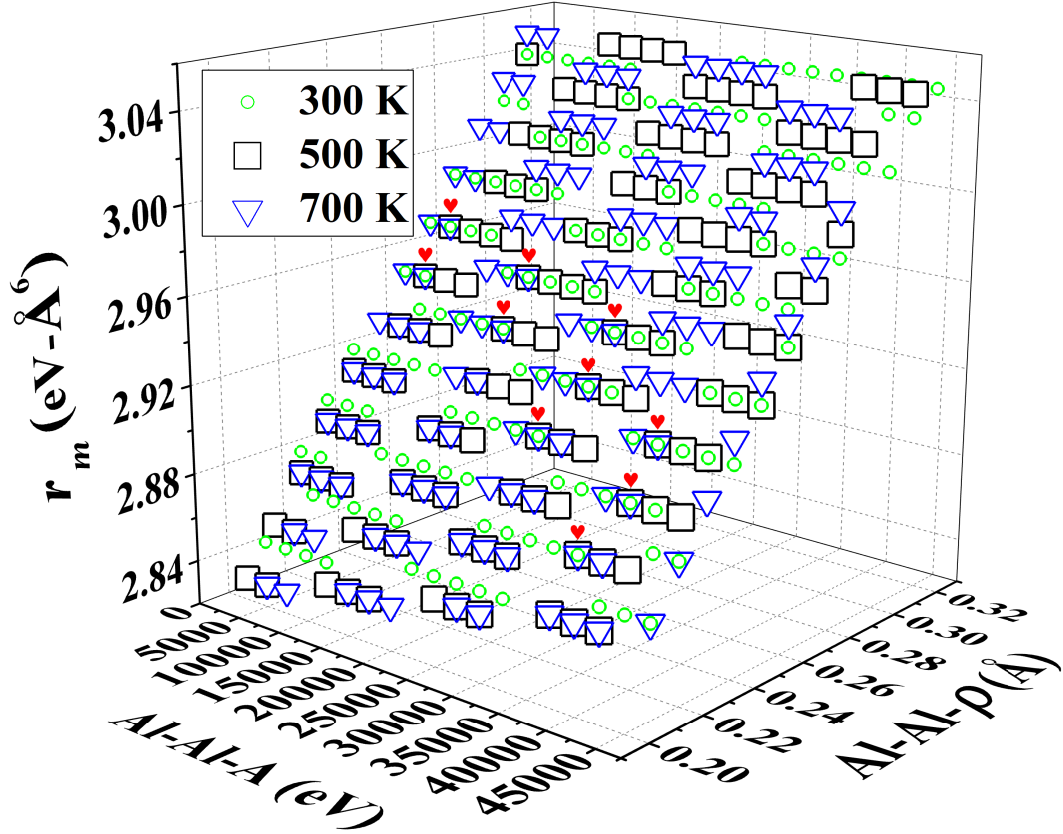


Figure 4.4: Potential parameter sets which reproduce lattice constant of Al within the error range of $\pm 0.005 \text{ \AA}$ at each temperature. Ten common sets for all temperatures (300, 500, and 700 K) are found and labelled by “♥”. The parameters of each set with “♥” label are listed in Table 4.2.

Table 4.2: List of the ten sets of common potential parameters for all temperatures of 300, 500, and 700 K. Here “common” means the potential parameter set works well for all three temperatures. “PRE” denotes the lattice constant predicted by the machine-learned LR models, “CMD” denotes the lattice constant calculated by classic molecular dynamics simulations with the same parameter set used in prediction, while “EXP” represents experimental values.

A (eV)	ρ (Å)	C (eV·Å ⁶)	r_m (Å)	T (K)	Lattice constant (Å)			
					PRE	CMD	EXP	RMSE
5,000	0.26	73.6257	2.95	300	4.0443	4.1114	4.0495	0.4144
				500	4.0736	4.4005	4.0698	
				700	4.0911	4.7270	4.0929	
5,000	0.27	105.0778	2.97	300	4.0484	4.0940	4.0495	0.2075
				500	4.0748	4.1661	4.0698	
				700	4.0904	4.4362	4.0929	
17,500	0.25	173.0115	2.94	300	4.0462	4.0428	4.0495	0.0072
				500	4.0729	4.0710	4.0698	
				700	4.0900	4.1034	4.0929	
17,500	0.26	253.9114	2.96	300	4.0506	4.0427	4.0495	0.0085
				500	4.0744	4.0618	4.0698	
				700	4.0897	4.0827	4.0929	
27,500	0.23	112.7034	2.91	300	4.0454	4.0348	4.0495	0.0225
				500	4.0738	4.0760	4.0698	
				700	4.0928	4.1285	4.0929	
30,000	0.24	192.6734	2.93	300	4.0477	4.0317	4.0495	0.0156
				500	4.0719	4.0544	4.0698	
				700	4.0885	4.0797	4.0929	
30,000	0.25	291.8161	2.95	300	4.0522	4.0383	4.0495	0.0174
				500	4.0734	4.0536	4.0698	
				700	4.0883	4.0700	4.0929	
37,500	0.21	54.1218	2.88	300	4.0447	4.0659	4.0495	0.4814
				500	4.0746	4.4117	4.0698	
				700	4.0955	4.8533	4.0929	
40,000	0.22	98.5110	2.90	300	4.0467	4.0365	4.0495	0.1257
				500	4.0725	4.0828	4.0698	
				700	4.0911	4.3099	4.0929	
40,000	0.23	160.7719	2.92	300	4.0510	4.0378	4.0495	0.0075
				500	4.0739	4.0647	4.0698	
				700	4.0906	4.0952	4.0929	

(Å)” yields the minimum RMSE (i.e., 0.0072); thus, this set is selected as the final potential parameter set for Al, and it is applied in the following verification simulations by comparing the structural, thermodynamic, and mechanical properties with experiments or first-principles results (when the experimental results are not available).

4.3.3 Verification of Selected Potential Parameter Set

For verifying the accuracy of potential parameter set of “ $A = 17,500$ (eV), $\rho = 0.25$ (Å), and $C = 173.0115$ (eV·Å⁶)” (parameter C is calculated by Equation 4.6), structural property of mass density (ρ_m); thermodynamic properties including linear thermal expansion coefficient (α_L), constant-pressure specific heat capacity (c_p), and melting temperature (T_m); mechanical properties of Young’s modulus along $\langle 100 \rangle$ orientation ($E_{\langle 100 \rangle}$) and ultimate tensile strength (σ_u), are calculated as shown in Table 4.3 (detailed simulation and calculation methodologies for various properties are elaborated in Section B.2 of “Simulation and Calculation Methodology of Various Properties for Verification”. Except T_m , all other properties are measured at temperature of 300 K. The RMSE of the properties calculated by each potential, including Buckingham (BUCK) potential developed in this work, modified embedded atom method (MEAM) potential [157], embedded atom method (EAM) potential [158], and angular dependent potential (ADP) [33] are shown as the last column in Table 4.3. The RMSE is calculated as:

$$\text{RMSE} = \sqrt{\frac{1}{N_{prop}} \sum_{n=1}^{N_{prop}} \left(1 - \frac{P_{\text{CMD},n}}{P_{\text{EXP/FP},n}} \right)^2}, \quad (4.7)$$

where N_{prop} denotes the number of property ($N_{prop} = 6$, including ρ_m , α_L , c_p , T_m , $E_{\langle 100 \rangle}$, and σ_u). For each potential set, $P_{\text{CMD},n}$ is the n -th property calculated by CMD and $P_{\text{EXP/FP},n}$ is corresponding experimental data or first-principles data.

The α_L and c_p are calculated from the centered finite difference method [81], the T_m is determined from the volume-temperature curve [Figure 4.5(a)], and the $E_{\langle 100 \rangle}$ and σ_u are obtained from the strain-stress curve [Figure 4.5(b)]. The phonon density of states (D_p) of Al is also calculated by CMD [Figure 4.5(c)], processed by our in-house MATLAB code. The developed Buckingham potential can well reproduce all properties, especially the D_p . Comparing the D_p , ex-

Table 4.3: Properties of Al calculated by the set of 17,500 (A), 0.25 (ρ), and 173.0115 (C) using a $20 \times 20 \times 20$ supercell, and comparison with corresponding experimental (EXP) or first-principles (FP) results when the experimental results are not available. Except the melting temperature (T_m), all other properties are calculated at temperature of 300 K.

Potential model	ρ_m (g cm ⁻³)	α_L ($\times 10^{-6}$)	c_p (J mol ⁻¹ K ⁻¹)	T_m (K)	$E_{\langle 100 \rangle}$ (GPa)	σ_u (GPa)	RMSE
EXP/FP	2.70 [159]	23.60 [160, 161]	24.45 [162]	933.5 [141]	49.18 [161]	4.67 [161]	-
BUCK (this work)	2.71	32.96	26.44	930.0	47.52	4.29	0.169
MEAM	2.64	28.91	27.29	1,050.0	56.73	5.91	0.170
EAM	2.69	27.00	25.96	870.0	57.81	4.94	0.102
ADP	2.67	15.44	24.43	1,150.0	62.80	7.53	0.323

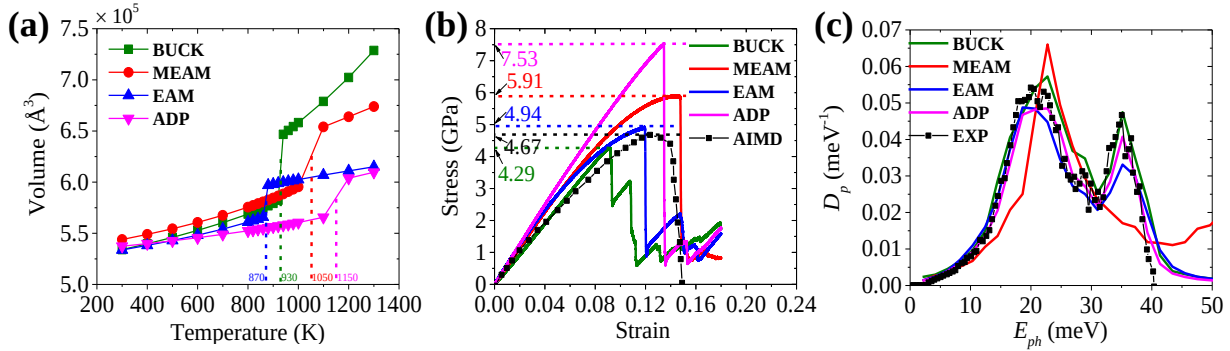


Figure 4.5: (a) Evolution of volume during the isothermal heating process from 300 K to 1,300 K. The melting temperature (T_m) is determined at which the volume exhibits a sharp increase. More accurate T_m can be determined as the increment of temperature decreases. However, the selected increment of temperature has been proven enough for comparison of determined T_m . (b) Strain-stress curve during uniaxial tensile testing along the $\langle 100 \rangle$ orientation at 300 K. The Young's modulus is calculated based on the strain data up to 0.01. The ultimate strength is determined as the highest point of the strain-stress curve. (c) Phonon density of states (D_p) of Al at 300 K.

cept the MEAM potential, all other potentials generally produce similar-contour D_p as experiment, and our developed Buckingham potential has the best agreement with experiments. It can be observed that the Buckingham potential can well reproduce the peak position at phonon energy of ~ 22 and ~ 36 meV, demonstrating an enhanced accuracy in reproducing thermodynamic properties.

As aforementioned, the Al AGNI potentials [51] developed by ML approach cannot work properly in NPT ensemble to calculate the temperature-dependent properties since the system becomes extremely unstable with exertion of additional pressure constraint. We attribute this to that the configurations used in training data of AGNI potential do not include pressure as a possible feature (although pressure has minimal effect on configurations of Al), thus the AGNI potential cannot work under conditions with pressure constraint. In contrast, the developed Buckingham potential can generate physically meaningful results in NVE, NVT, and NPT ensembles since the development employs data generated directly from CMD simulations at NPT ensemble. Also, the developed Buckingham potential exhibits an unbiasedness in reproducing all properties since the development incorporates structural, thermodynamic, and mechanical properties in the data trimming and model training processes. Furthermore, the Buckingham potential demonstrates high transferability to high-temperature simulations, evidenced by the accurate melting temperature.

4.4 Conclusions

An unbiased Buckingham potential of Al is successfully developed through the proposed finite-temperature dynamics machine learning (FTD-ML) approach. Compared with traditional ML method for potential development which employs first-principles calculated data, we employ the training data, i.e., various properties including structural, thermodynamic, and mechanical properties, directly calculated by the CMD with a large number of atoms (2,048) and a longer simulation time (50 ps for data production) at various finite temperatures. The generated training data intrinsically incorporate much larger configurational and conditional space compared with first-principles data, enhancing the transferability of the developed potential to various simulation configurations and conditions. The proposed FTD-ML approach is much simpler and thus more effective compared with conventional ML parameterization, since no first-principles calculation is

involved: no hands-on experience or knowledge of first-principles simulations is required for FTD-ML approach, and it takes much less computational time. Therefore, the FTD-ML is expected to significantly accelerate development of interatomic potentials and should benefit the whole CMD society with developing an interatomic potential with high transferability, without limitation of model type. One can include more training data such as more types of properties and data at more temperatures for developing a comprehensive potential fitting general simulation purpose. For more accurate prediction of other metallic systems (e.g., transition metals) or multi-component alloys, using a more complicated interatomic potential such as MEAM potential, support vector regression and neural network can also be implemented in the future work.

Chapter 5

Accelerated Thermal Transport Analysis of Aluminum Alloys with Finite Element Method and Machine Learning

Note: Chapter 5 is a modified version of the publication: **Jiaqi Wang**, Yousefzadi Nobakht, James Dean Blanks, Dongwon Shin, Sangkeun Lee, Amit Shyam, Hassan Rezayat, and Seungha Shin*, “Machine Learning for Thermal Transport Analysis of Aluminum Alloys with Precipitate Morphology”, *Advanced Theory and Simulations*, 2, 1800196 (2019). This publication is reprinted with permission from John Wiley & Sons. The dissertation author listed in this publication directed and supervised the research which forms the basis for this publication.

5.1 Introduction

Enhanced requirements in engineering applications lead to an increased demand of advanced materials, especially metallic alloys [163]. To improve their properties, composition and structure of alloys have been intensively studied in the recent decades [164, 165, 166, 167]. Mechanical properties, among various properties, of solid-solution alloys are significantly influenced by microstructures, such as grains, phases, and boundaries; thus, solutes or precipitates, which impede movement of dislocation, are introduced for mechanical strength of alloys [168]. A high density of interfaces, while good for mechanical properties, degrades the thermal transport due to the

increased scatterings of thermal energy carriers by the same interfaces [169, 170, 171, 172, 173, 174, 175]. To achieve thermal stability and to reduce residual or operational thermal stress inside components, we need to design alloys with enhanced thermal conductivity, which induces a rapid heat dissipation from high-temperature regions.

Despite the significance, thermal transport in metallic alloys considering microstructures has been less extensively explored compared to mechanical properties due to technical challenges [176]. Heat in metallic alloys is transferred by electron and vibration propagation, and their transport behaviors depend on atomic structure. Thus, for a fundamental understanding of thermal transport, we need to investigate contributions of electrons and vibrations to thermal transport and their behaviors at various microstructural features, such as grain boundary, solute, and precipitate. In particular, to address electronic thermal transport, which is dominant in most of metallic materials, electron dispersion relation (i.e., band structure for effective mass, energy spectrum, and propagation speed) and scattering kinetics should be identified. First-principles calculations can be employed for electronic thermal transport as reliable approaches [177, 178, 179, 180]; however, due to their expensive computational cost, there has been limited theoretical research on thermal conductivity of alloys [179, 181]. To the best of our knowledge, thermal transport in metallic alloys with detailed microstructural features has not been studied via the first-principles approaches. In practice, finite element method (FEM) is widely used for thermal transport simulations including microstructures of larger size systems [182, 183, 184, 185]. However, even in FEM simulations, thermal properties of the materials must be defined as the simulation input parameters. Additionally, structural modeling and adequate mesh definition precede the FEM calculations, and these procedures and FEM calculations are more complicated, time-consuming, and resource-intensive when all the microstructural details are incorporated.

In this study, we propose data-driven approach, that is, machine learning (ML) and correlation analysis, for thermal transport analysis of metallic alloys to overcome the aforementioned challenges in calculation of elementary thermal transport properties and inclusion of many microstructural features. Lightweight aluminum (Al) alloys with strengthening precipitates are selected as an example, and their microstructural information on precipitate geometry for computational modeling is obtained from experimental measurements (Section 5.2.1). We generate data of effective thermal conductivity (k_{eff}) of Al alloys with various precipitate geometries

and thermal transport properties using FEM simulations (Section 5.2.2). ML, as an effective prediction and optimization tool, is being widely used to reduce the computational costs in different material science and engineering applications [186, 187, 188, 189, 190]; here, it is employed to extract elementary thermal properties without performing intensive microscopic analysis (Section 5.2.3 and Section 5.3.1). Using the correlation analysis between precipitate features (related to morphology and thermal transport) and alloy effective thermal conductivity, the significance of precipitate features in thermal transport of Al alloy is evaluated (Section 5.2.4 and Section 5.3.2). In addition, several ML models are trained to predict effective thermal conductivities of Al alloys and their prediction accuracies are evaluated (Section 5.3.2). This research is schematically summarized in Figure 5.1. Through this research, the feasibility and effectiveness of data-driven approach for thermal transport analysis in alloy systems are confirmed.

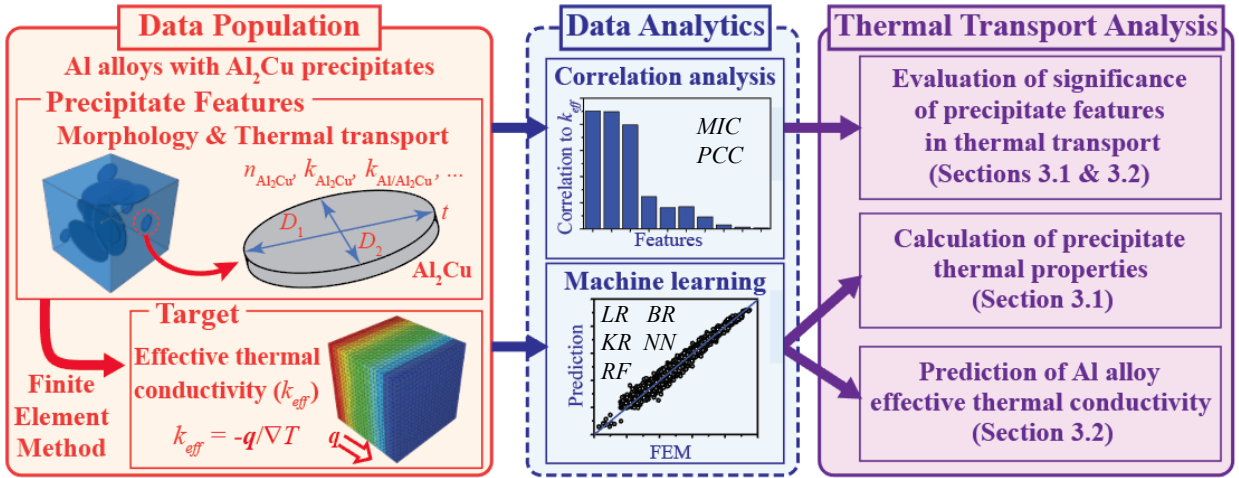


Figure 5.1: Schematic diagram of this research. Data of precipitate features (morphology and thermal transport properties) and effective thermal conductivity (calculated using the FEM) are processed using data science techniques, such as correlation analysis and machine learning, for alloy thermal transport analysis.

5.2 Experimental Section

5.2.1 Modelling of Aluminum Alloys

Increasing use of lightweight Al alloys in engineering applications can bring many advantages (e.g., high fuel efficiency in vehicles), but their lower mechanical strength and high cost limit their applications [191, 192]. Copper (Cu) alloying has been introduced to enhance mechanical strength as Cu forms strengthening precipitates (θ' -Al₂Cu), which impede the motion of dislocations [193]. However, as the θ' phase of Al₂Cu is metastable, the θ' -Al₂Cu precipitates are transformed to a more thermodynamically stable θ -phase at high temperatures, degrading the mechanical properties [194]. Effective heat dissipation by high thermal conductivity can delay the transformation [3], and thus, the development of Al alloys with high thermal conductivity as well as high mechanical strength is important for more prevalent application of Al alloys. Since thermal transport properties, like mechanical properties, depend on alloy microstructural information, it is imperative to comprehensively examine the precipitate effects on both mechanical and thermal properties for alloy design. Therefore, with an interest in θ' -Al₂Cu precipitate-hardened Al alloy development, Al alloys are selected and studied to test data science methodologies, with their thermal transport properties and precipitate morphologies.

In this research, RR350 and 319 among θ' -Al₂Cu precipitate-hardened Al alloys are prepared, and their thermal transport properties and microstructural information are obtained from experimental measurements at Oak Ridge National Laboratory. These experimental data allow for the reasonable selection of feature ranges in data generation and the validation of our analysis. Transmission electron microscopy (TEM) identifies that θ' -Al₂Cu precipitates in Al matrices of RR350 (Figure 5.2a) and 319 (Figure 5.2b) have elongated hexagonal and oblong disc shapes, respectively, and they form in (001) planes in the α -Al matrix lattice. Although these alloys contain other microstructural features, such as grain boundaries or solute atoms, which also affect thermal properties, we confine our scope to the effects of the precipitate morphology, focusing on the development and application of new data-driven methodologies for thermal transport analysis. Thus, RR350 and 319 are modeled as alloys with disc-shaped θ' -Al₂Cu precipitates contained in Al matrix, simplifying Al alloy structures, as Figure 5.2c shows.

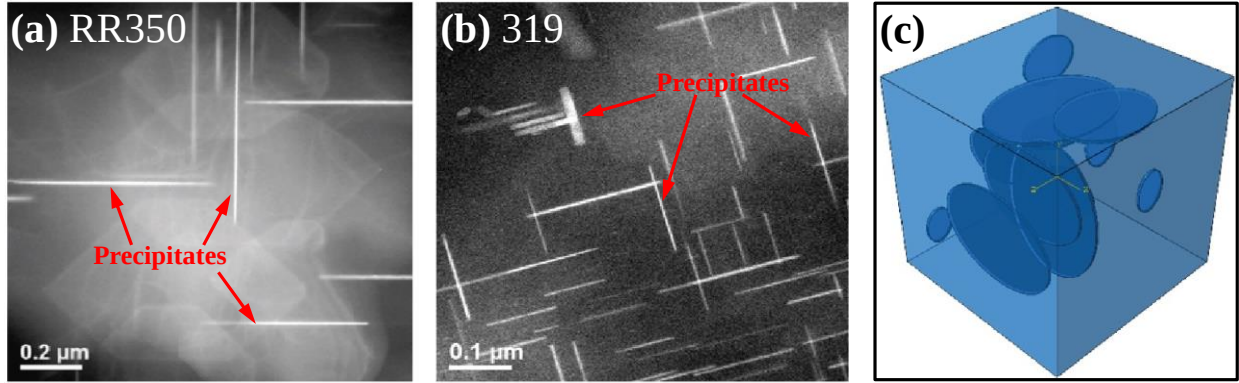


Figure 5.2: Transmission electron microscopy (TEM) micrographs of (a) RR350 and (b) 319 Al alloys, and (c) a modeled alloy structure with disc-shaped precipitates.

Statistical information of precipitates in RR350 and 319 is extracted from the analysis of TEM micrographs. Larger θ' -Al₂Cu precipitates, but a smaller number of precipitates, are observed in RR350, and overall volume fraction of the precipitate is larger in 319 (1.9 %) than RR350 (1.1 %). Due to small dimensions of thickness comparable to the TEM resolution, the precipitate thickness measurement induces a large error [195]; however, in this study, no thickness correction is performed on the precipitates. Effective thermal conductivities (k_{eff}) of RR350 and 319 at 300 K are 139 W m⁻¹ K⁻¹ and 141 W m⁻¹ K⁻¹, respectively, which are calculated using the density (ρ_m , kg m⁻³), specific heat capacity (c_p , J kg⁻¹ K⁻¹), and heat diffusivity (α_h , m² s⁻¹) in experiments (i.e., $k_{\text{eff}} = \rho_m c_p \alpha_h$ [196]). The statistical information of the precipitate shape (median diameter and thickness: D_m and t_m ; standard deviation of diameter and thickness: D_{std} and t_{std}), precipitate number density (n_p), and effective thermal conductivity (k_{eff}) of the two Al alloys are summarized in Table 5.1.

5.2.2 Finite Element Method for Thermal Transport

Thermal transport is characterized by effective thermal conductivity (k_{eff}), and for calculation of k_{eff} , the FEM is employed. In FEM, a modeled Al alloy structure is subdivided into small and simple elements (or finite elements) and solutions to energy equations of finite elements are integrated for the whole system. According to experimental results [195, 197, 198] and our measurements, the shapes of θ' -Al₂Cu precipitates are mostly elongated hexagonal or oblong dis-

Table 5.1: Summary of the experimental values of θ' -Al₂Cu precipitate distribution and effective thermal conductivity in two Al alloys (i.e., RR350 and 319). D_m : median diameter; t_m : median thickness; n_p : number density; D_{std} : standard deviation of diameter; t_{std} : standard deviation of thickness; and k_{eff} : effective thermal conductivity of alloy at 300 K.

Alloy	D_m , nm	t_m , nm	n_p , ppts μm^{-3}	D_{std} , nm	t_{std} , nm	k_{eff} , W m ⁻¹ K ⁻¹
RR350	321	6.62	20.4	145	1.25	139
319	127	2.85	466	29	0.22	141

cs, but for effective parameterization, each precipitate is modeled as an elliptical disc.

In addition to a modeled structure, elementary thermal properties are required for the k_{eff} calculation. Since a transient behavior of heat transfer is not of interest in this study, our FEM calculations employ the thermal transport properties only (not including density and heat capacity). It is assumed that thermal conductivities of Al matrix and θ' -Al₂Cu precipitate (k_{Al} and k_{Al_2Cu}) are uniform and constant, and k_{Al} includes all other microstructural effects, displaying a lower conductivity than that of pure Al ($\approx 237 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K [199, 200]). Due to the structural mismatch between Al matrix and θ' -Al₂Cu precipitate, additional resistance, termed as interfacial thermal resistance (R_{int} , m²·W K⁻¹; the inverse of interfacial thermal conductance, $1/G_{int}$), is imposed on the thermal transport across their interfaces. To incorporate the interfacial thermal resistance, as in Figure 5.3a, a shell region with a lower thermal conductivity (k_{int}) and constant thickness (t_{int} , 1 nm in this study) is introduced surrounding each precipitate disc ($R_{int} = t_{int} / k_{int}$).

The modeled Al alloy structures in this study include 1.75 to 2.43 million of C3D4 (4-node linear tetrahedron) heat transfer elements (Figure 5.3b), and the number of elements depends on the number, shape, and size of the precipitates. An appropriate mesh size is determined by additional FEM calculations with different element sizes, through which it is confirmed that heat flux and temperature distribution are captured adequately and independent of element size.

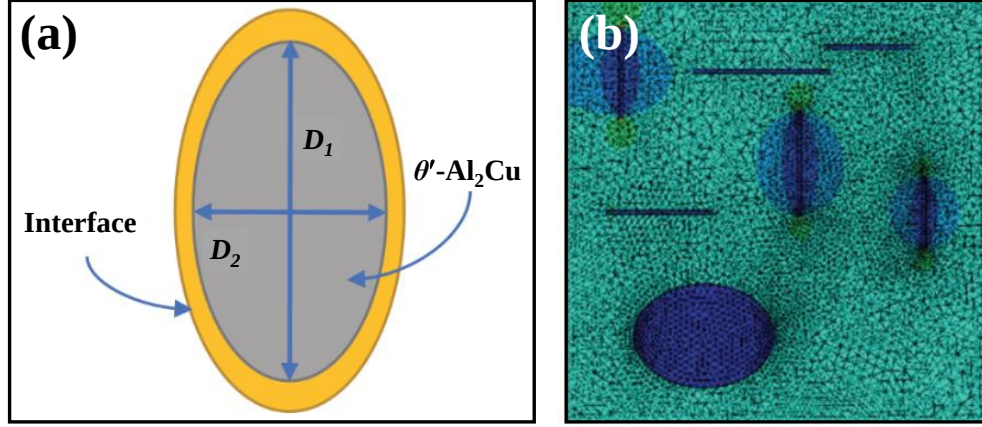


Figure 5.3: (a) Model of θ' -Al₂Cu precipitate and (b) mesh grid of Al alloy for a FEM simulation.

To calculate an effective thermal conductivity of the alloy (k_{eff} , W m⁻¹ K⁻¹), a temperature difference (ΔT , K) between opposing faces of the simulation block (in the x -, y -, or z -direction each time) is prescribed. While simulating a steady-state heat transfer with the given temperature difference, an overall heat flux through the block (q , W m⁻²) is calculated in the direction of temperature difference by solving the energy equation of all mesh elements and integrating the solutions. Using q and ΔT with the Fourier law, the effective thermal conductivity of Al alloy (k_{eff}) is calculated as follows:

$$k_{\text{eff},i} = q_i / (\Delta T / l_i), \quad (5.1)$$

where i is the direction of interest for thermal transport ($i = x, y, \text{ or } z$), $k_{\text{eff},i}$ is the effective thermal conductivity in the i -direction, ΔT is the prescribed temperature difference, and l_i is the dimension of simulation domain in the i direction. For all the FEM simulations and thermal transport analysis, ABAQUS FEA is employed [201].

5.2.3 Data Generation and Processes for Elementary Thermal Properties

Elementary thermal transport properties in θ' -Al₂Cu precipitate-hardened Al alloys, that is, k_{Al} , $k_{\text{Al}_2\text{Cu}}$, and k_{int} , are identified by using the data from FEM simulations and ML models. While using the FEM simulations to generate data, modeled structures with different geometrical details are prepared based on the microstructural information, discussed in Section 5.2.1. A modeled domain

with a cubic box includes 16 precipitates ($N_p = 16$), and the side dimension of modeled domain (l) is determined by the precipitate number density (n_p), i.e., $l = (N_p/n_p)^{1/3}$. Random values from the standard normal distributions with the median values and standard deviations of precipitate diameter (D_m and D_{std}) and thickness (t_m and t_{std}) are used to decide diameter ($D_{\theta'}$) and thickness ($t_{\theta'}$) of each precipitate. The orientation (the direction perpendicular to the disc surface; either x -, y -, or z - direction) and the center location (c_x , c_y , c_z) of precipitate are also randomly determined, but intersection or overlap between precipitates and that between precipitate and domain boundaries are avoided.

Based on the microstructural information of two Al alloys (RR350 and 319), 10 different modeled structures are constructed for each Al alloy and their heat transfer behaviors are analyzed in all three directions (x , y , and z) for all the constructed structures using the FEM simulations. Averaging the thermal conductivities from the FEM simulations with different structures and directions ($= 3 \times 10$ cases), the effective thermal conductivity of Al alloy (k_{eff}) with a specific combination of elementary thermal transport properties (k_{Al} , k_{Al2Cu} , and k_{int}) is obtained. Varying k_{Al} , k_{Al2Cu} , and k_{int} independently, data of k_{Al} , k_{Al2Cu} , and k_{int} , and k_{eff} are generated and variations of the thermal properties are summarized in Table 5.2.

For the efficiency and scalability of this approach, the input preparation, running, and postprocessing of the FEM simulations are automated by in-house MATLAB and Python codes. Our MATLAB code creates various modeled structures using random number generating functions and microstructural information, prescribes thermal transport properties, and generates a Python script. The Python script generated by MATLAB creates the ABAQUS input files, prescribing me-

Table 5.2: Chosen values of elementary thermal transport properties (k_{Al} , k_{Al2Cu} , and k_{int} , in unit of $W\ m^{-1}\ K^{-1}$) in FEM calculations for the thermal conductivity data generation.

	Minimum	Maximum	Increment	# points
k_{Al}	140	155	5	4
k_{Al2Cu}	40	60	10	3
k_{int}	0.5	2.0	0.5	4

shing and boundary conditions, for the FEM simulations. More Python scripts are written to run multiple cases of the FEM simulations in ABAQUS and to extract the thermal conductivity data from the ABAQUS output files.

Correlations between k_{eff} and elementary thermal transport properties are examined by various data analysis techniques, such as the maximal information coefficient (MIC) and conventional Pearson's correlation coefficient (PCC) analysis [142], to evaluate the significance of thermal transport features in k_{eff} . The PCC is a linear quantification of correlation between input features and target properties, while the MIC can identify nonlinear correlations. These two approaches are intended to be complementary to each other, while examining the consistency of the correlations.

The generated data are used to train ML models, and here, five different models are tested, which are the linear regression (LR) [202], Bayesian ridge regression (BR) [147], kernel ridge regression (KR) [203], nearest neighbor regression (NN) [146], and random forest regression (RF) [144]. These five models represent different types of ML models: LR and BR are generalized linear models, KR is a kernel method, NN is a non-parametric nearest neighboring method, and RF is an ensemble method. During the model training process, k -fold cross-validation (at $k = 5$) has been performed for controlling the potential overfitting of the trained model. The trained ML models are then used to predict k_{eff} (without the FEM) with more combinations of thermal transport properties using smaller increments. Through the prediction, combinations of k_{Al} , k_{Al2Cu} , and k_{int} , which can reproduce experimental thermal conductivities of RR350 and 319, are identified.

The correlation analysis, ML model training, and prediction with the trained ML models are conducted via our in-house code, which employs a Python-based open source data analytic toolkit, scikit-learn [151]. Here, its default hyperparameter setting is used for the models. This code was employed in the previous work [186] on Al alloy design study with the density function theory, and more detailed descriptions on the ML models and correlation analysis are also available in reference [186].

5.2.4 Data Generation and Processes for Effects of Precipitate Morphology

For analysis of precipitate morphological effects in Al alloy thermal transport, another thermal conductivity data set is generated with respect to various precipitate morphological features as well

as elementary thermal transport properties (k_{Al2Cu} and k_{int}). The controlled morphological features of precipitates are the average disc diameter and thickness of modeled precipitate (D_m and t_m), aspect ratio of elliptical disc surface (AR), and number density of precipitates (n_p). Here, the aspect ratio AR is the ratio of long diameter (D_1) to short diameter (D_2) of disc, i.e., $\text{AR} = D_1/D_2$, and since D_1 and D_2 are $\text{AR}^{0.5}$ and $\text{AR}^{-0.5}$ of a desired diameter ($D_{\theta'}$), AR does not change the surface area of ellipse ($A_p = 0.25\pi D_1 D_2 = 0.25\pi D_{\theta'}^2$). The ranges of D_m , t_m , and n_p are selected based on the median values of precipitates in RR350 in Table 5.1; for example, $(D_{m,\text{RR350}} - 0.3D_{m,\text{RR350}})$, $(D_{m,\text{RR350}} - 0.1D_{m,\text{RR350}})$, $(D_{m,\text{RR350}} + 0.1D_{m,\text{RR350}})$, and $(D_{m,\text{RR350}} + 0.3D_{m,\text{RR350}})$ are employed for the variation of D_m . D_{std} and t_{std} of RR350 are also used in random number generation to determine diameter ($D_{\theta'}$) and thickness ($t_{\theta'}$) of each precipitate. All the controlled features and their value ranges for data generation are summarized in Table 5.3.

Modeled structures and thermal transport properties required for the FEM simulations are prepared by varying the controlled features for precipitate geometrical and thermal transport properties in the FEM input-generating codes. Using the same MATLAB and Python codes described in Section 5.2.3, a large number of FEM simulations are conducted in three different heat flow directions, and data of effective thermal conductivity (k_{eff}) of Al alloys are obtained. Through total 9,216 FEM runs [= 3 (k_{Al2Cu}) $\times$ 4 (k_{int}) $\times$ 4 (n_p) $\times$ 4 (AR) $\times$ 4 (D_m) $\times$ 4 (t_m) $\times$ 3 (heat

Table 5.3: List of controlled features and the chosen values for the FEM data generation for analysis of precipitate morphological effects in Al alloy thermal transport. The percentages in parentheses of “Increment” column represent the ratio of increment to the RR350 value.

Controlled features	Minimum	Maximum	Increment	# points
k_{Al2Cu} , W m ⁻¹ K ⁻¹	40	60	10	3
k_{int} , W m ⁻¹ K ⁻¹	0.5	2.0	0.5	4
n_p , ppts μm^{-3}	17.34	23.46	2.04 (10%)	4
AR	1.05	1.95	0.3	4
D_m , nm	224.7	417.3	64.2 (20%)	4
t_m , nm	4.634	8.606	1.324 (20%)	4

flow directions)], 3,072 data points are generated by averaging three directional k_{eff} 's in each parametric combination.

Since random functions are employed to determine the shape, size, orientation, and location of precipitates, D_m , D_{std} , t_m and t_{std} of precipitates in a created modeled structure can be different from the setting values; i.e., each modeled structure has different distributions (average and standard deviation) of $D_{\theta'}$ and $t_{\theta'}$. Average and standard deviation of precipitate diameter and thickness (D_m , D_{std} , t_m and t_{std}) in a modeled structure are calculated when the structure is created. Our data analysis and ML model training employ the calculated average and standard deviation values instead of the setting values. In addition to the controlled features, the volume fraction of total precipitates (f_V) and total surface area of precipitates ($A_{p,\text{tot}}$) are calculated by analyzing modeled structures and also used for the data process. Here, the volume fraction is given as $f_V = V_{p,\text{tot}}/V$, where $V_{p,\text{tot}}$ is the total volume of precipitates ($V_{p,\text{tot}} = \sum_i V_{p,i}$, where $V_{p,i}$ is the volume of the i th precipitate) and V is the volume of modeled structure ($= l^3$). $A_{p,\text{tot}}$ is the summation over all precipitate surface area, i.e., $A_{p,\text{tot}} = \sum_i A_{p,i}$, where $A_{p,i}$ is the surface area of the i th precipitate).

Using the correlation analysis on the produced data, the effects of various microstructural features on k_{eff} are evaluated. Depending on elementary thermal transport properties (k_{Al2Cu} and k_{int}), the correlations of morphological features are expected to change, and the changes of correlations are also investigated. ML models are trained using the data of various microstructural features (precipitate morphology, thermal properties, etc.), and the training performances are examined. Our study on alloy microstructural effects employs the two correlation analysis approaches (MIC and PCC) and five ML models (LR, BR, KR, NN, and RF), as introduced in Section 5.2.3.

5.3 Results and Discussion

5.3.1 Extraction of Thermal Transport Properties via Machine Learning Models

FEM simulations of modeled structures (generated based on structural information in Table 5.1) with different combinations of k_{Al} , k_{int} , and k_{Al2Cu} identify k_{eff} with respect to k_{Al} , k_{int} , and k_{Al2Cu} in

RR350 and 319 Al alloys. The correlation analysis of the RR350 and 319 data demonstrates that the thermal conductivity of Al matrix, k_{Al} , has the most significant effect on alloy thermal transport or k_{eff} while k_{Al2Cu} has the least correlation to k_{eff} . This order ($k_{Al} > k_{int} > k_{Al2Cu}$) is identical in both MIC (Figure 5.4a) and PCC analysis (Figure 5.4b) for both RR350 and 319 alloys.

Due to a large volume fraction of matrix ($> 98\%$), a strong correlation of k_{Al} is expected and confirmed with our data analysis. However, a larger precipitate volume fraction (f_v) or a larger surface area of precipitates ($A_{p,tot}$) does not ensure more significant influence of precipitate-related thermal transport properties (i.e., k_{int} and k_{Al2Cu}) on overall alloy thermal transport (k_{eff}), as k_{int} and k_{Al2Cu} have stronger correlations in RR350 than 319 even though the 319 alloy has a larger f_v and $A_{p,tot}$ in our modeled structures. We attribute the stronger correlations in the RR350 modeled structures to its larger average diameter of precipitates. Heat flow is diverted to a high conductivity (low thermal resistance) region when it faces a high thermal resistance component [204]. Thus, interfacial resistance between matrix and precipitate and a lower precipitate conductivity lead to the heat flow diversion around precipitates; however, a large area (or diameter) of precipitate in a direction perpendicular to heat flow results in a longer detour, undermining the thermal resistance reducing effect. Precipitates whose disc surfaces are perpendicular to a heat flow direction have a larger influence on thermal transport than those with a disc surface parallel to heat flow, and the in-

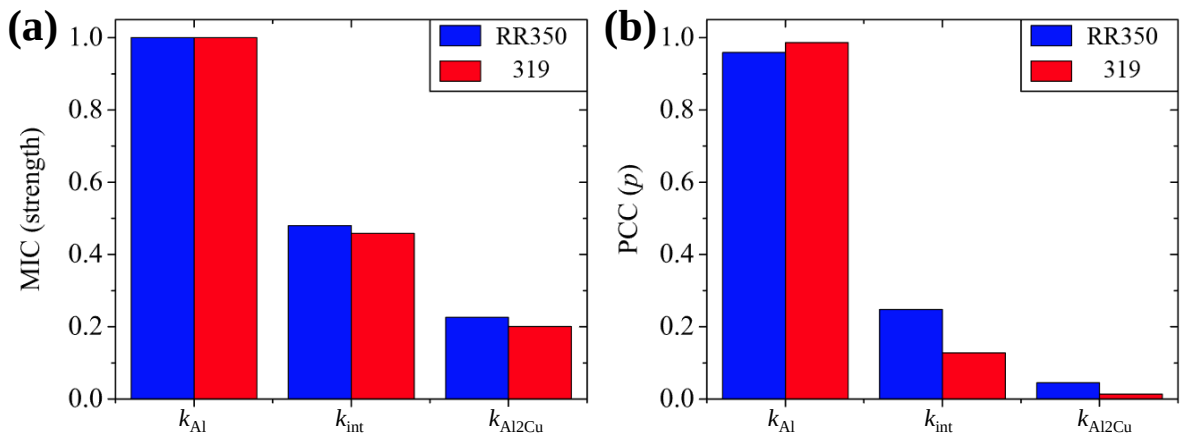


Figure 5.4: Correlation coefficients between effective thermal conductivities (k_{eff}) of RR350 (blue) and 319 (red) from the FEM simulations and thermal conductivities of alloy components (k_{Al} , k_{Al2Cu} , and k_{int}) using (a) maximal information coefficient (MIC) and (b) Pearson's correlation coefficient (PCC) analysis.

fluence will increase with a disc diameter. In thermal transport along a thickness direction, considering the dimension of precipitate thickness (< 10 nm), interfacial thermal transport property is more important than that of precipitates (k_{Al2Cu}), which supports a stronger correlation of k_{int} than k_{Al2Cu} in both alloys and both correlation analysis approaches.

The five ML models described in Section 5.2.3 (LR, BR, KR, NN, and RF) are trained using the created database, and their performances are evaluated using the coefficient of determination (R^2) and root mean square error (RMSE) as in Figure 5.5a. R^2 closer to the unity and smaller RMSE represent a better performance; thus, among the examined models, the linear regression (LR) model (Figure 5.5b) presents the best accuracy for both RR350 and 319.

The trained LR models for RR350 and 319 are used to find combinations of k_{Al} , k_{Al2Cu} , and k_{int} , which produce the experimental thermal conductivities, $139 \text{ W m}^{-1} \text{ K}^{-1}$ for RR350 and $141 \text{ W m}^{-1} \text{ K}^{-1}$ for 319. Prediction of effective thermal conductivity (k_{eff}) using the trained models is much faster than FEM simulations, and thus it allows for test of a larger number of k -value combinations (k_{Al} , k_{Al2Cu} , and k_{int}). While increments of 5, 10, and $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ for k_{Al} , k_{Al2Cu} , and k_{int} are em-

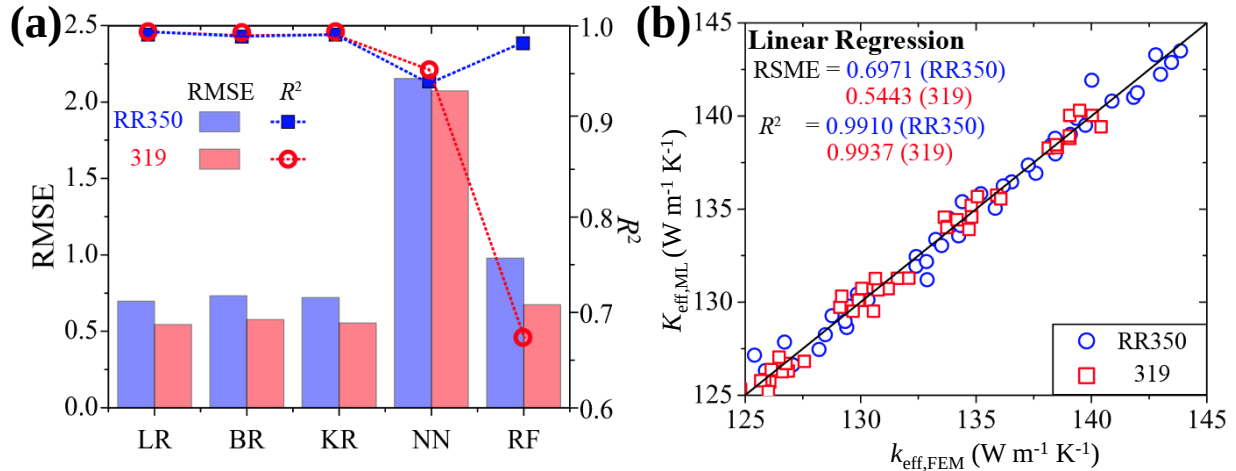


Figure 5.5: (a) Comparison of the RMSE (bars; left y-axis) and R^2 (dotted lines with symbols; right y-axis) in training of the five ML models (LR: linear regression; BR: Bayesian ridge; KR: kernel ridge; NN: nearest neighbor; RF: random forest) for effective thermal conductivity of RR350 (blue) and 319 (red). (b) Scatter plot for the LR models trained with RR350 (blue) and 319 (red) data. The x- and y-axes represent the FEM calculation results ($k_{\text{eff,FEM}}$) and model-predicted thermal conductivities ($k_{\text{eff,ML}}$).

ployed for the FEM data production, five times smaller increments and wider ranges of conductivity values are tested in the prediction with the trained ML (LR) models as seen in Table 5.4.

From the ML prediction, we identified combinations of k_{Al} , k_{Al_2Cu} , and k_{int} , which reproduce k_{eff} of RR350 and 319 within $0.1 \text{ W m}^{-1} \text{ K}^{-1}$ of accuracy compared with the experimental values (i.e., $139 \pm 0.1 \text{ W m}^{-1} \text{ K}^{-1}$ for RR350 and $141 \pm 0.1 \text{ W m}^{-1} \text{ K}^{-1}$ for 319). Several k-value combinations exist for RR350 and 319, respectively, but as we assume that both RR350 and 319 contain the same type of precipitates resulting in identical thermal transport properties related to said precipitates in both alloys, we select k_{Al_2Cu} and k_{int} values which satisfy the k_{eff} reproduction criterion for both RR350 and 319 (Figure 5.6). In contrast, different k_{Al} values in two alloys are allowed because their other microstructural details (e.g., solute atom, grain boundary, etc.) affecting the matrix thermal conductivity are different.

Table 5.5 lists the top ten combinations for the k_{eff} of RR350 and 319 among the examined combinations. The calculated k_{Al_2Cu} ranges from 54 to $70 \text{ W m}^{-1} \text{ K}^{-1}$ and k_{int} from 0.8 to $2.3 \text{ W m}^{-1} \text{ K}^{-1}$. With t_{int} set as 1 nm, the interfacial thermal conductance between θ' - Al_2Cu and Al (G_{int}) is calculated as $0.8 - 2.3 \text{ GW m}^{-2} \text{ K}^{-1}$. To the best of our knowledge, k_{Al_2Cu} and G_{int} have not been reported; however, the interfacial thermal conductance between Al and Cu was measured as $4 \text{ GW m}^{-2} \text{ K}^{-1}$ at room temperature [205], which we expect to be similar to that of θ' - Al_2Cu /Al interface due to material similarity. Compared with the experiment, the G_{int} calculated from the ML models for k_{eff} can be regarded as reasonable. With microstructural information on more Al alloys, possible combinations of elementary thermal transport properties can be further reduced, or

Table 5.4: Ranges and increments of the tested elementary thermal transport properties (k_{Al} , k_{Al_2Cu} , and k_{int} , in unit of $\text{W m}^{-1} \text{ K}^{-1}$) for the effective thermal conductivity (k_{eff}) prediction with the trained ML models.

	Minimum	Maximum	Increment
k_{Al}	145	165	1
k_{Al_2Cu}	40	80	2
k_{int}	0.5	3.5	0.1

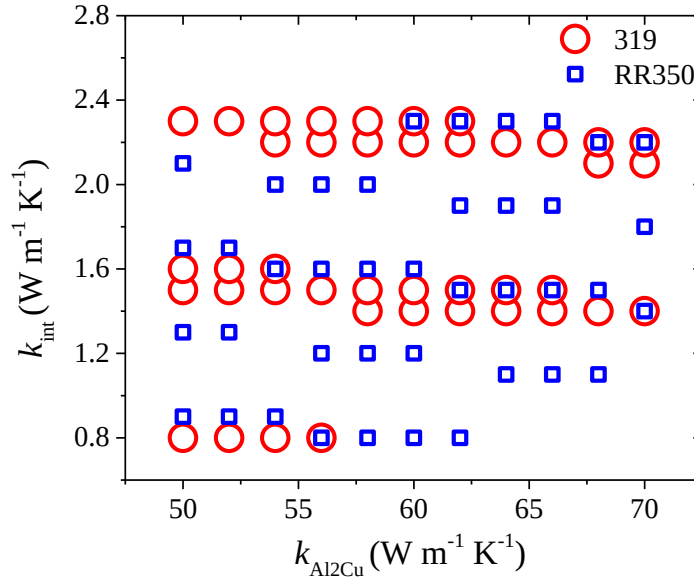


Figure 5.6: k_{Al2Cu} and k_{int} values which reproduce k_{eff} of RR350 (blue squares) and 319 (red circles) within $0.1 \text{ W m}^{-1} \text{ K}^{-1}$ of accuracy.

Table 5.5: Ten combinations of k_{Al} , k_{Al2Cu} , and k_{int} which reproduce experimental thermal conductivity of 319 and RR350 with the smallest errors among the whole examined combinations. $k_{\text{eff, ML}}$ represents the model predicted value, and all thermal conductivity values in this table are in unit of $[\text{W m}^{-1} \text{ K}^{-1}]$. Error: addition of difference between ML-predicted and experimental value for 319 and that for RR350.

k_{Al2Cu}	k_{int}	319		RR350		Error
		k_{Al}	$k_{\text{eff, ML}}$	k_{Al}	$k_{\text{eff, ML}}$	
70	2.2	158	141.037	149	138.979	0.058
70	1.4	159	141.006	151	138.921	0.085
64	1.5	159	141.069	151	138.977	0.092
68	2.2	158	141.020	149	138.922	0.098
62	2.3	158	141.084	149	138.978	0.106
66	1.5	159	141.086	151	139.034	0.120
62	1.5	159	141.053	151	138.920	0.132
60	2.3	158	141.067	149	138.922	0.146
56	0.8	160	141.086	153	138.919	0.167
54	1.6	159	141.100	151	138.920	0.180

exact properties can be found. Additionally, using this data process with other microstructural details, more thermal transport properties related to microstructures can be identified.

5.3.2 Effects of Precipitate Morphology on Thermal Transport in Al Alloys

As discussed in Section 5.3.1, the matrix conductivity (k_{Al}) has the largest influence on thermal conductivity of Al alloy, and its effect dominates over other thermal transport properties; therefore, to focus on the effects of precipitate morphology, while fixing k_{Al} as $150 \text{ W m}^{-1} \text{ K}^{-1}$, a data set of alloy thermal conductivity (k_{eff}) and various precipitate morphological features as well as their thermal properties (k_{Al2Cu} and k_{int}) is generated. Data include the calculated features (e.g., precipitate area and volume fraction). Although the derived features are dependent on controlled precipitate features (D_m , t_m , n_p , AR, etc.), we analyze all the data to identify more descriptive features and to train more accurate training models.

Correlations between FEM thermal conductivity and various precipitate features are analyzed via the MIC and PCC models as shown in Figure 5.7. Both analyses demonstrate that total precipitate area ($A_{p,tot}$), average disc diameter (D_m), and volume fraction (f_v) show strong correlations to k_{eff} . Precipitate-related thermal transport properties (k_{Al2Cu} and k_{int}) have less influence than these three morphological features ($A_{p,tot}$, D_m , and f_v). Although $A_{p,tot}$ and f_v are dependent on the number density (n_p) and thickness (t_m) of precipitate, their influence on k_{eff} is minor, different from D_m on which $A_{p,tot}$ and f_v also depend ($\propto D_m^2$). Rather, the standard deviation of disc diameter (D_{std}) has a larger correlation. This indicates that the large effect of $A_{p,tot}$ and f_v originates mainly from the disc diameter rather than other geometrical features, and this agrees with the discussion on the heat flow diversion in Section 5.3.1. This analysis also agrees with the fact that among the cast aluminum alloys, the 356 type alloys with needle shaped precipitates have the highest thermal conductivity.

To identify the robustness of our correlation analysis results, the correlations between precipitate features and k_{eff} are examined with different thermal transport properties of precipitate (k_{Al2Cu} and k_{int}). To observe the changes in the correlations more clearly, we employ the minimum and maximum values of k_{Al2Cu} and k_{int} in the data producing FEM simulations; those are 40 and 60 $\text{W m}^{-1} \text{ K}^{-1}$ for k_{Al2Cu} , and 0.5 and 2.0 $\text{W m}^{-1} \text{ K}^{-1}$ for k_{int} , respectively. Both the MIC and PCC an-

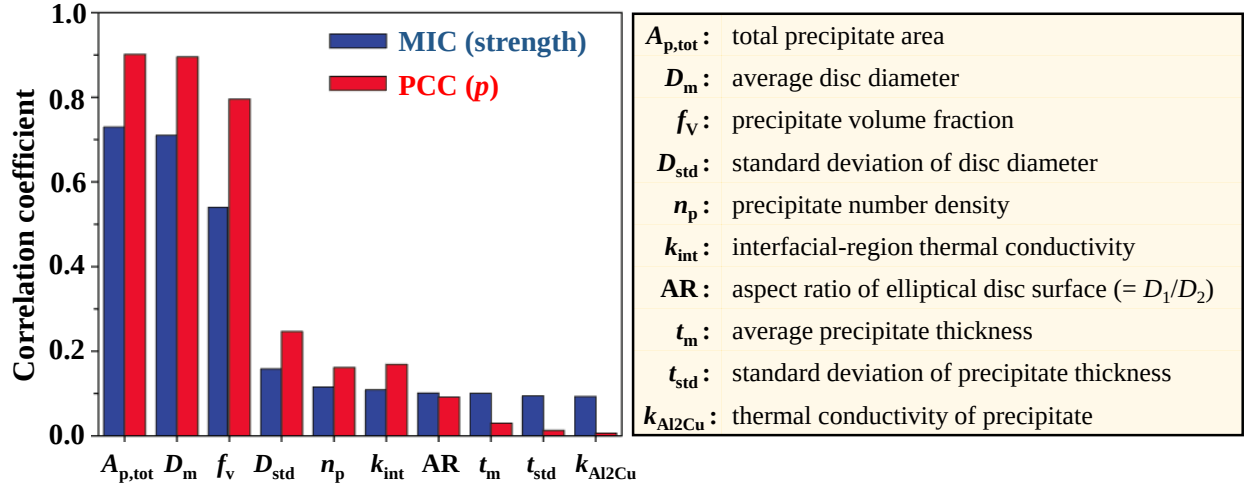


Figure 5.7: Correlation coefficients between effective thermal conductivity from the FEM simulations (k_{eff}) and various alloy features, including precipitate thermal transport and morphological properties, using the MIC and PCC analysis.

analyses show that a larger precipitate thermal conductivity ($k_{Al2Cu} = 60 \text{ W m}^{-1} \text{ K}^{-1}$) slightly reduces the correlations of features related to surface area and diameter (i.e., $A_{p,tot}$, D_m , and D_{std}), while the correlations of precipitate volume and thickness (f_v and t_θ) increase (Figure 5.8a and 5.8b). In contrast, lowering an interfacial-region conductivity ($k_{int} = 0.5 \text{ W m}^{-1} \text{ K}^{-1}$) or increasing a larger thermal resistance between precipitate and matrix leads to different correlations of $A_{p,tot}$, n_p , and t_m in the MIC and PCC; however, both show reduced correlations of f_v and the increase in D_{std} (Figure 5.8c and 5.8d). Overall, even with different k_{Al2Cu} and k_{int} , the correlation analysis results do not change significantly.

The five ML models are trained using the generated database on precipitate morphological and thermal transport properties. All the trained ML models demonstrate small RMSE and large R^2 (close to the unity), especially the RF, LR, and BR models, as shown in Figure 5.9. Prediction using the trained ML models in our code requires several orders-of-magnitude smaller computing resources than the same number of the FEM simulations; in this research, the examined data of 3,072 cases are created by FEM simulations for more than 150 hours with 20 CPU cores, while the ML training and prediction take only a few tens of seconds. This implies that k_{eff} of Al alloy can be accurately predicted by using a well-trained ML model with microstructural information and without FEM simulations, which will enable more efficient thermal transport analysis.

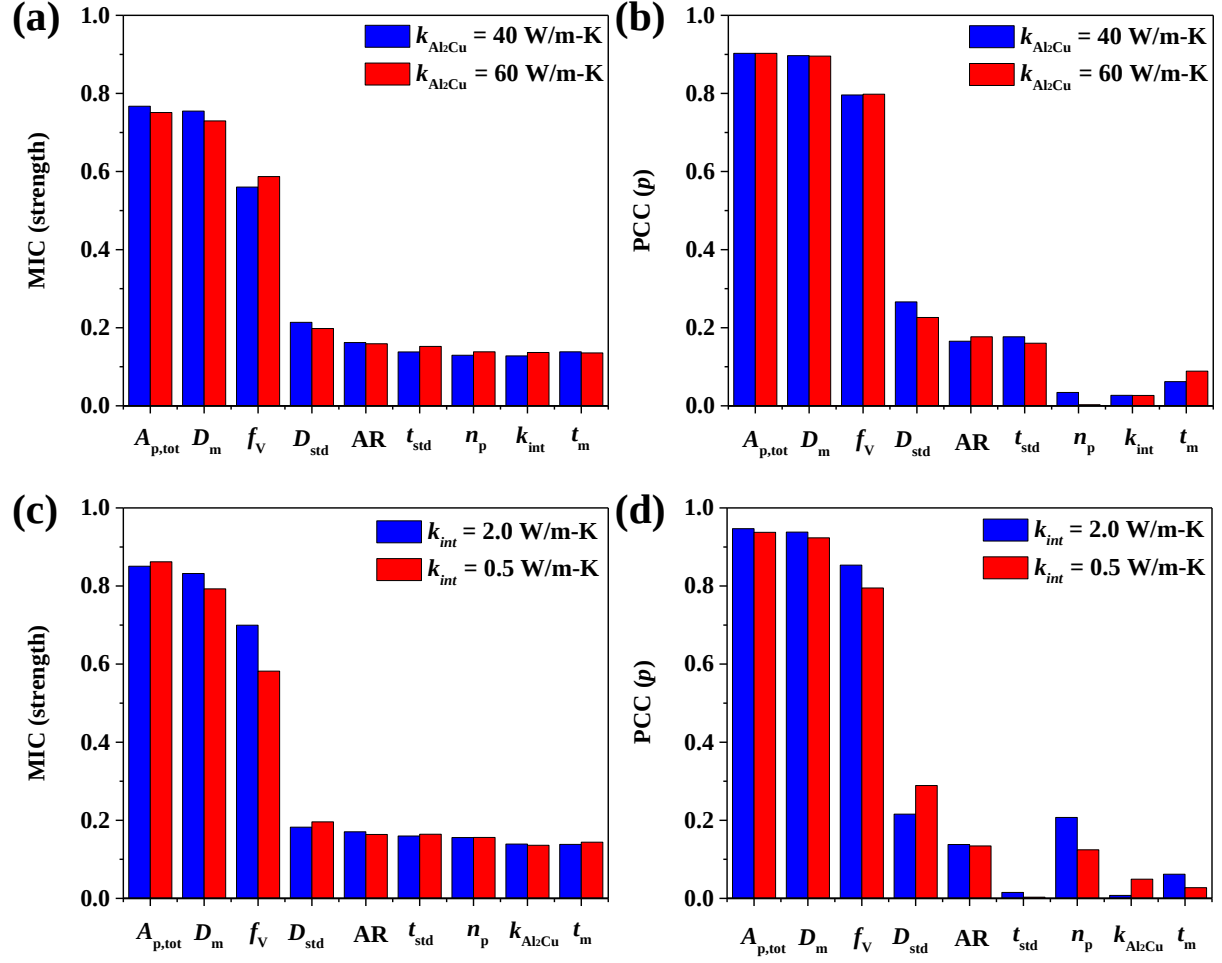


Figure 5.8: Correlation coefficients between effective thermal conductivity from the FEM simulations (k_{eff}) and various alloy properties with different k_{Al2Cu} values using (a) MIC and (b) PCC analysis, and with different k_{int} values using (c) MIC and (d) PCC analysis.

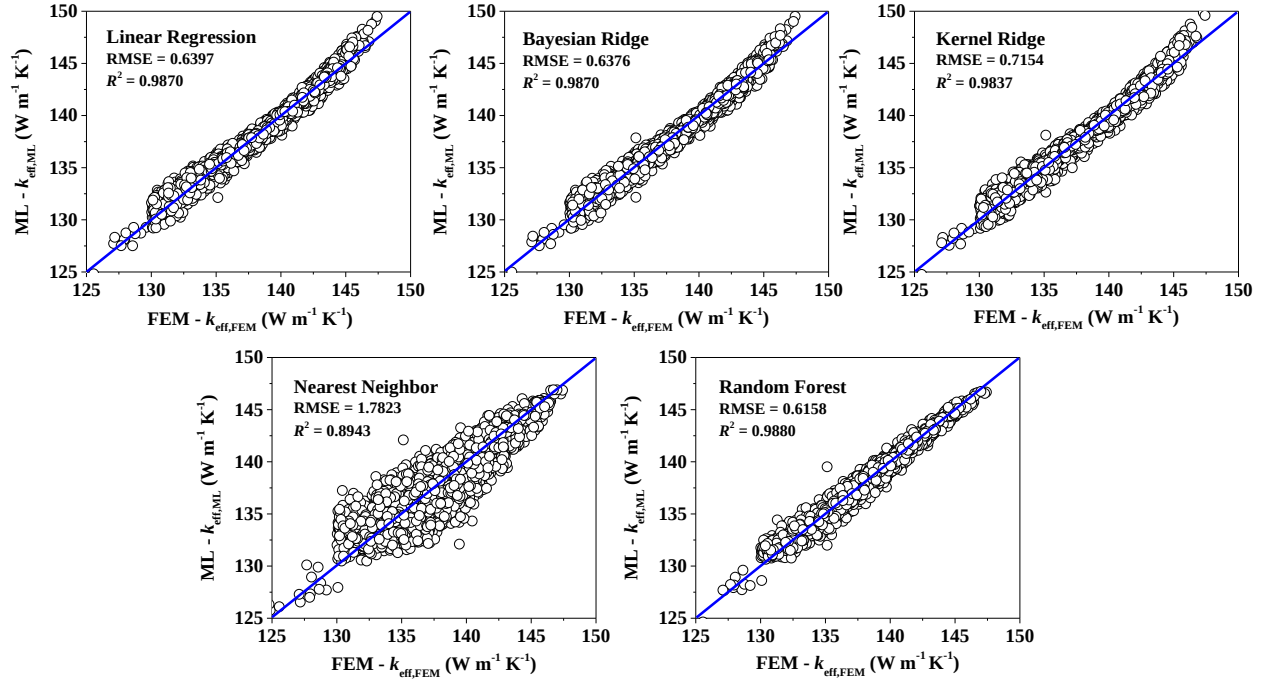


Figure 5.9: Scatter plots for the five different ML models trained using the FEM data. The x - and y -axes represent the FEM calculation results ($k_{\text{eff,FEM}}$) and model-predicted thermal conductivities ($k_{\text{eff,ML}}$).

5.4 Conclusions

We apply modern data analytics approach, consisting of the correlation analysis and machine learning, to thermal transport analysis of θ' -Al₂Cu precipitate-hardened aluminum alloys. We generate data of precipitate features (morphology and thermal transport properties) and effective thermal conductivity using the FEM. The correlation analyses of the data evaluate the significance of various precipitate features in effective thermal conductivity of the modeled alloys. According to our data analysis, the diameter of precipitates should be a key parameter in alloy precipitate design for effective heat dissipation (a smaller precipitate diameter leads to a larger heat transfer due to easier heat flow diversion). Several ML models are trained to predict the effective thermal conductivity of the modeled Al alloy structures and the trained ML models exhibit excellent accuracy. Using the best trained model (linear regression), we identify possible precipitate thermal transport properties which can accurately reproduce experimental alloy thermal conductivities with the experimental precipitate morphological features. The high accuracy of the trained ML models indicates that a quick and precise calculation of alloy thermal conductivity is enabled without FEM when precipitate features are available.

This research demonstrates the feasibility of various data-driven approaches in thermal transport analysis. The suggested approaches with sufficient data are expected to enable the scientific and engineering community 1) to accurately predict the overall thermal transport of alloys, 2) to identify challenging microscopic thermal transport properties without performing intensive atomistic simulations, and 3) to effectively guide thermal transport analysis and design. To further enhance the thermal transport prediction and analysis, we can perform additional ML model parameter tuning or use other possible algorithms such as support vector machines [206] or neural networks [207]. Although this study only focuses on the effective thermal conductivity considering precipitate morphology, if mechanical properties or other microstructural features are included, this approach could allow for more comprehensive and optimal evaluation of metallic alloys and enhanced design of alloy microstructure.

Chapter 6

Conclusions and Future Work

6.1 Conclusions and Impacts

Through my Ph.D. research, I have demonstrated the approaches and the feasibility of embedding acceleration algorithms such as ML and PRD with multiscale simulations of AIMD, CMD, and FEM, for elucidating the fundamental physics of mass and thermal transport with enhanced efficiency and accuracy. Respectively, 1) the production of atomic data in AIMD is advanced by RNN with a speed of one order of magnitude faster than the ground-truth AIMD; 2) the time scale of CMD simulation is propagated through PRD up to 133 ns with cost of reasonable amount of computational resources; 3) additionally, a fast and accurate potential development scheme (i.e., FTD-ML) without involving quantum-mechanical simulations is innovated, which can generate interatomic potentials for general CMD simulation purposes; 4) the application of ML is also extended to FEM simulations for predicting thermal transport properties and identifying the microstructure effect on the effective thermal conductivity of alloy.

The conclusions and impacts of each chapter are summarized below:

- *Chapter 2: Accelerated Atomic Data Production in AIMD with RNN.* This research presents a pioneer attempt in accelerating the simulation clock of AIMD with RNN. By employing RNN algorithm, atomic data (i.e., atom position and velocity) is directly predicted with quantum-level accuracy based on trained RNN models, without evaluation of force and acceleration. Therefore, error accumulation is effectively and significantly reduced

by decoupling the update of atom position and velocity through Newtonian mechanics. Additionally, the prediction of AIMD step through RNN is found one order of magnitude faster than the ground-truth AIMD simulation, which bears the great potential to accelerate the AIMD simulation clock. The material properties calculated with the RNN predicted data, including RDF, T , VACF, D_p , and c_p , present excellent agreement with ground-truth AIMD data. In summary, the presented approach can effectively advance the simulation clock of AIMD while maintaining its quantum-level accuracy. It is expected that the acceleration of AIMD with RNN algorithm would have a significant impact on computational materials research, by extending the temporal scale for harvesting more accurate properties and underlying physics.

- *Chapter 3: Accelerated Simulation Algorithm of CMD with PRD.* This is the first research on diffusion-induced structural deformation and phase transformation of θ' -Al₂Cu precipitate in Al matrix, investigated by CMD and PRD, allowing for more accurate capturing of diffusion kinetics due to its extended temporal scale. This research suggests and discusses i) structural deformation activated at the semi-coherent θ' -Al₂Cu/Al interfaces, ii) phase transformation initiated at the edge of the coherent θ' -Al₂Cu/Al interface, and iii) directional dependence of diffusion properties on the semi-coherent and coherent interfaces. These findings are expected to be employed in a larger scale phase-field modeling of precipitate growth, and to contribute to the development of alloys with θ' -phase retained to higher temperatures (> 500 K). Since θ' -Al₂Cu precipitate is known as the most important strengthener for several commercially available Al alloys, development of effective control of θ' -Al₂Cu precipitate deformation and transformation will lead to great improvements in various technologies, such as automobile engine and power generation.
- *Chapter 4: Accelerated Interatomic Potential Development for CMD with ML.* This research proposes a new ML approach for developing interatomic potentials serving CMD simulations, i.e., finite-temperature dynamics machine learning (FTD-ML). Compared with conventional ML approaches employing first-principles calculated data for potential model development, the proposed FTD-ML exhibits three distinguished features: (1) FTD-ML approach intrinsically incorporates more extensive configurational and conditional space

for enhancing the transferability of developed potential models; (2) FTD-ML approach employs various properties (structural, thermodynamic, and mechanical properties), which are calculated directly and consistently from CMD, for ML model training and prediction validation against experimental data, instead of force or energy data obtained from first-principles calculations; (3) FTD-ML approach is much more computationally cost-effective than first-principles simulations, especially when the system size increases over 10^3 atoms as employed in this research for ensuring reliable training data. This FTD-ML approach is expected to significantly accelerate development of interatomic potentials and should benefit the whole CMD society by developing interatomic potentials with high transferability and speed without limitation of model and material type.

- *Chapter 5: Accelerated Thermal Transport Analysis of FEM with ML.* This research applies the ML technique with combination of FEM simulation for the enhancement of thermal transport analysis. The FEM simulation is employed to create a database of effective thermal conductivity of hypothetical aluminum (Al) alloy with varying precipitate morphological and thermal transport features. The significance of various precipitate features in determining the effective thermal conductivity of Al alloy is then identified by the correlation analysis, and various ML models are trained to accurately predict thermal transport of aluminum alloys. The research broadens the predictive power of ML to thermal transport properties of complicated alloys, which is challenging to harvest in first-principles calculations. Therefore, it is expected that this approach should benefit the thermal transport analysis and design in alloy system by prediction with a quantum-level accuracy.

The successful implementation of acceleration algorithms in multiscale simulations will improve the overall accuracy and efficiency of mass and thermal transport analysis, by addressing quantum-scale electronic structure calculations, atomic-scale dynamics, and engineering-scale properties. The reliability, performance, and life-span of various engineering applications and processes will be improved by the enhanced understanding of fundamental physics of mass and thermal transport physics eventually.

6.2 Recommendations for Further Studies

The presented works in this dissertation initialize the implementation of acceleration algorithms in multiscale simulations in mass and thermal transport analysis. For more efficient, accurate, and comprehensive analysis and solutions for mass and thermal transport challenges, here, possible extensions of this research are suggested.

6.2.1 Algorithms for Acceleration of AIMD with RNN

A variety of parameters and conditions are involved in the predictions of atomic data in AIMD, such as the window size, gap size, number of training data set, batch size, number of unit in GRU cell [as shown in Figure 6.1(a)], and the effects of these parameters on the prediction accuracy should be further comprehensively investigated for further efficiency enhancement. Among them, the gap size determines how many steps would replace the ground-truth AIMD steps. Thus, enhancing the long-term memory, which is indicated by prediction gap, is promising to improve the efficiency of acceleration. Also, adding more physical constraints during the training processes [as shown in Figure 6.1(a)], such as energy conservation, minimum and maximum interatomic distance, and system temperature, should also be beneficial for improving the prediction accuracy.

The current research employs a solid-state Si system with lattice vibration only, i.e., no atomic diffusion involved. For further validation and border applications of this approach, various material systems (such as carbon-based materials, metallic alloys, molecules, etc) or dynamic processes (diffusion, sintering, chemical reaction, etc) [as shown in Figure 6.1(b)], should be addressed more rigorously in the future studies.

In this research, the ground-truth AIMD and RNN model training and prediction are executed separately. For broad applications of this approach and eventually advancing the scientific discoveries in atomic world, automating the “adaptive” AIMD scheme [as shown in Figure 6.1(c)], in which ground-truth AIMD, RNN model training, and prediction by trained models can execute without human intervention, is imperative.

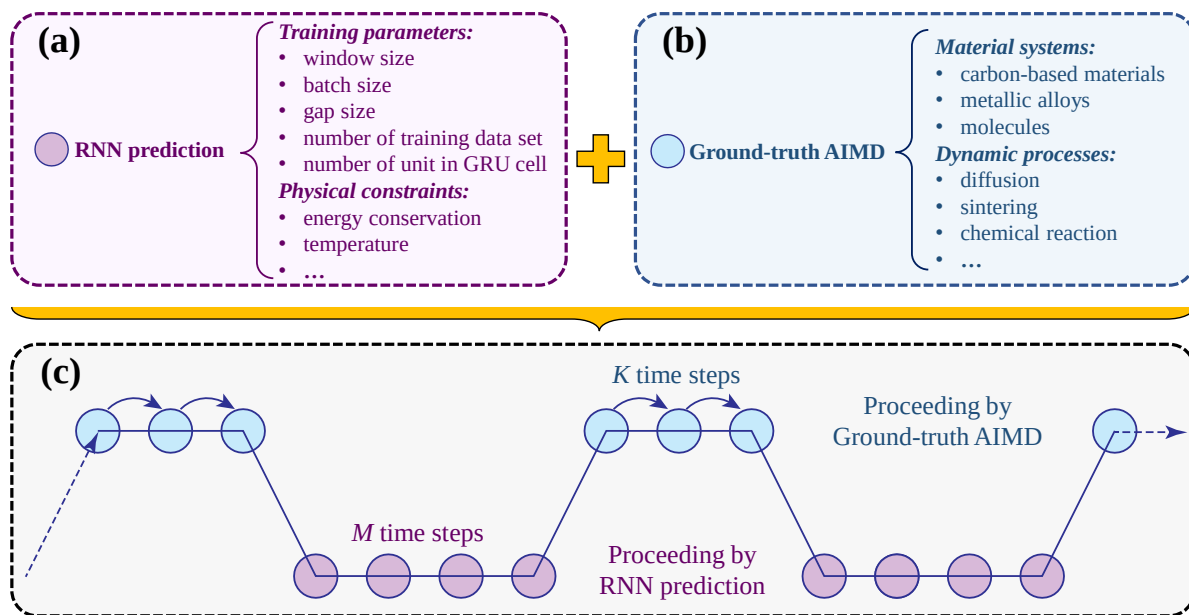


Figure 6.1: (a) Training parameters and physical constraints in the training process of RNN. The effect of each parameter and physical constraint on the prediction accuracy should be investigated in the future studies. (b) Besides of lattice vibration of Si, various materials and dynamic processes should be investigated to corroborate the proposed approach. (c) An “adaptive” AIMD scheme, during which the ground-truth AIMD and RNN training and prediction would proceed automatically without human intervention.

6.2.2 Formation and Transformation of θ' -Al₂Cu Precipitate

Although the time scale in CMD with PRD has been extended to 133 ns, within this time scale, several critical problems have not been rigorously addressed, such as the calculation of self-diffusivity of Cu atom and the complete transformation mechanisms of θ' -Al₂Cu precipitate to θ -Al₂Cu phase, which should be further investigated {as shown in Figure 6.2(a); the atomic-resolution annular dark field image of θ' -Al₂Cu is from reference [208]}.

Additionally, finite-temperature interfacial energetics such as the interfacial energy between the semi-coherent interface of θ' -Al₂Cu and Al matrix [as shown in Figure 6.2(b)], the solute segregation energies of various elements are rarely reported [as shown in Figure 6.2(c)], which are critical for the interfacial stability at higher temperatures. It should be noted that, the interfacial energy and the solute segregation energy depend on temperature, interface type, misfit strain, as well as the size of the system, and their effect should be addressed by both simulations and experiments. For experimental and engineering side, more stability control approaches should be invented for improving the performance of Al alloy under extreme working conditions, based on the fundamental physics unravelled by simulations.

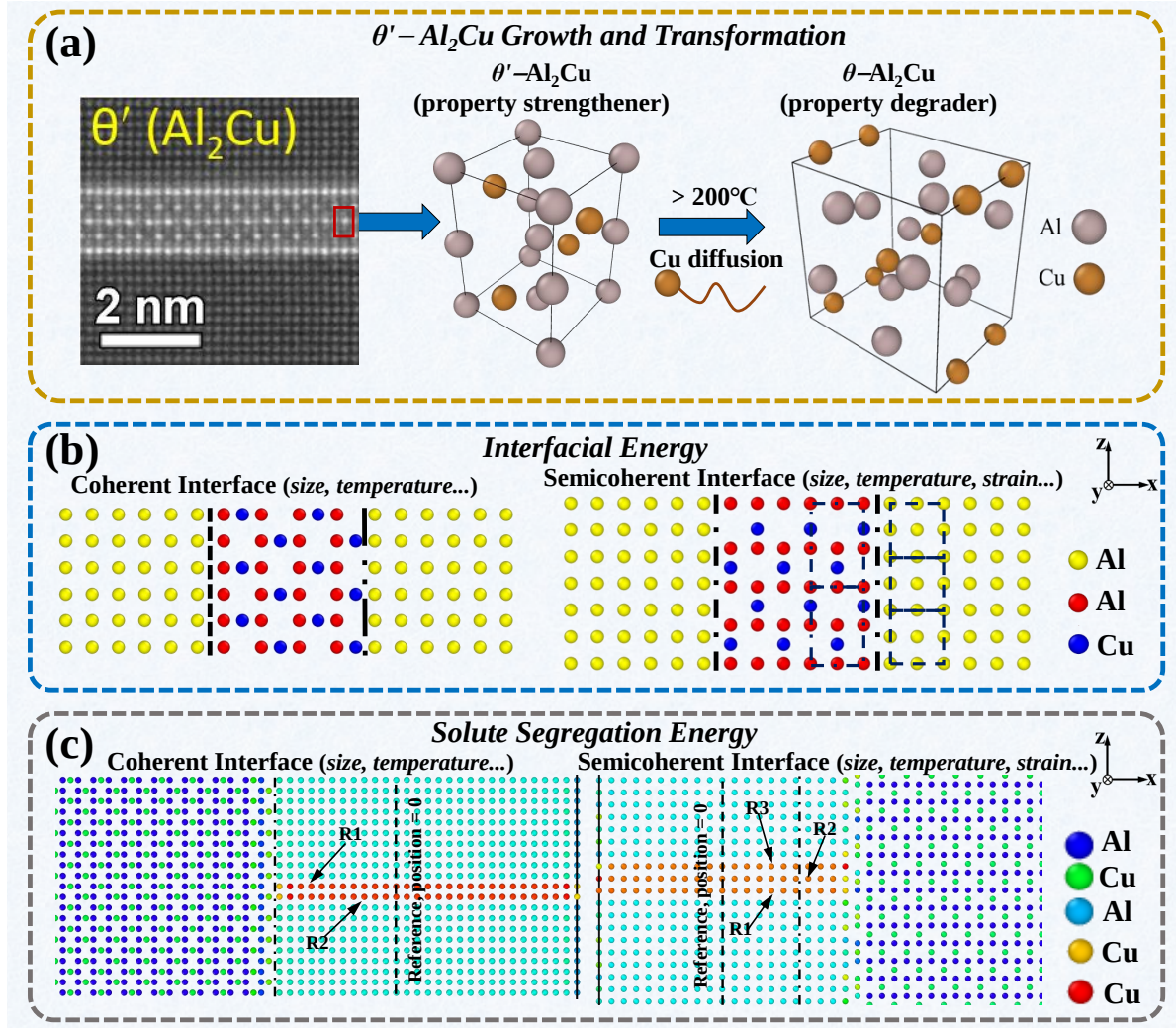


Figure 6.2: (a) Formation (growth) and transformation of θ' -Al₂Cu. Future simulations should extend the time scale for a complete observation of atomic scale growth and transformation mechanisms and calculating accurate self-diffusivity of Cu. (b) Interfacial energy of the θ' -Al₂Cu and Al matrix system at finite temperatures has not been comprehensively reported, and the effect of system size, orientation, temperature, and misfit strain should be investigated in future studies. (3) Same as interfacial energy, solute segregation energy of various elements should be reported with respect to size, temperature, orientation, and misfit strain, for thermal stability control of θ' -Al₂Cu precipitate at high temperatures.

6.2.3 Fast Development of Interatomic Potentials

It is a prerequisite to generate reliable training data for any ML work. In the potential development work with ML and CMD, it should be noted that the data acquired from energy minimization may not be suitable for finite-temperature CMD simulation, thus, the data from energy minimization at 0 K may not be considered as reliable data, instead, the time averaged data at finite temperatures should be promising for ML model training.

A good initial guess of the potential parameters is challenging, and how to find the suitable range of potential parameters for training reliable ML models should be studied more. Currently, there exist three general schemes for initial guess: 1) certain potential parameters represent a specific physical property of materials, such as bulk modulus or thermal expansion coefficient. Based on the physical meaning of the potential parameters, one can easily determine a suitable range; 2) based on the published potential parameters, a suitable range may also be determined; 3) for the potential parameters which do not represent a physical meaning or have no reference value reported, the trial and error process can be experimented, however, there is no guarantee for a good initial guess, and it would be time-consuming and less efficient. Inventing the algorithms, such as the genetic algorithm, in which the initial guess has negligible effect on final results, should be a promising alternative way for training reliable ML models.

For generating an accurate and comprehensive interatomic potential, more properties and conditions (such as various temperatures) should be included. Depending on the number of properties and conditions included, various ML models will be generated, but the final goal is to generate only one set of potential parameters from all ML models through prediction. Thus, how to guarantee that one final potential set can be found which fits all ML models should also be addressed.

To expand the application of this FTD-ML approach and to benefit the CMD society, scheme of development of interatomic potential for multi-element system, using the Al-Cu-Zr as an example, is provided here for reference (as shown in Figure 6.3).

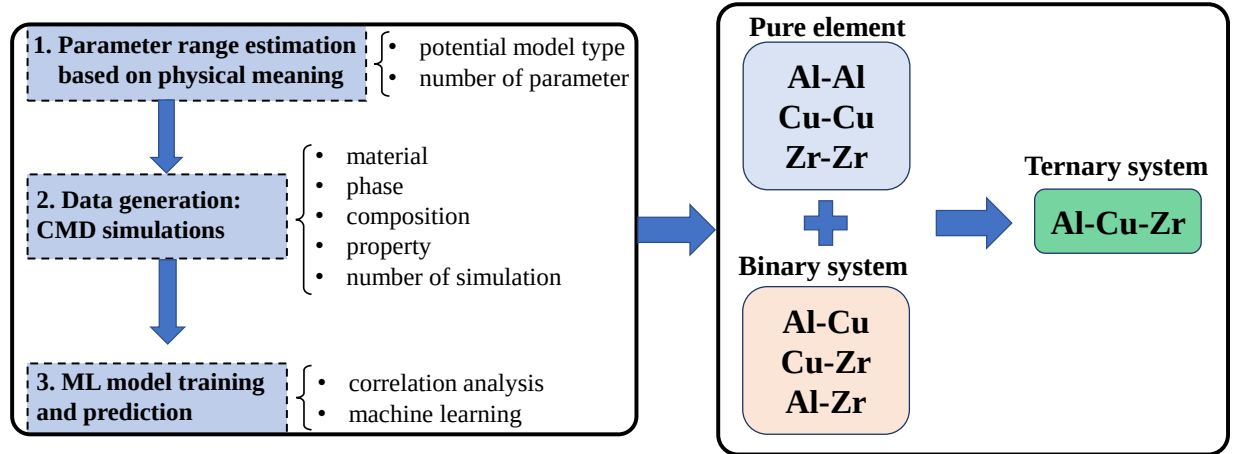


Figure 6.3: Scheme of development of interatomic potential for ternary Al-Cu-Zr system. For developing an interatomic potential of ternary system, the starting point is developing interatomic potential for pure element, and then the binary system. For some potential types, such as MEAM, additional bond order term has to be developed for the ternary system, otherwise, after obtaining the full pure element and binary interatomic potentials, a ternary potential is achieved. In the FTD-ML approach, several factors have to be considered before performing the simulation for generating training data, for example, in the parameter range estimation, the type of interatomic potential model and the number of potential parameter have to be sorted out. The factors for data generation using CMD and ML model training and prediction are also listed.

6.2.4 Enhanced Accuracy of Analysis of FEM with ML

FEM simulation is a powerful simulation approach for calculations of various properties and unravelling underlying transport physics, using continuum models without complications of involving electronic structure. For improving the accuracy of thermal transport analysis of FEM simulation with ML, various microstructure features, such as defects and grain boundaries should be included in the modelling. Furthermore, various external conditions and intrinsic properties, such as temperature and pressure, mechanical properties, respectively, should be included when necessary. For consolidating the ML prediction results, more ML algorithms such as support vector machine and neural network should be implemented in the future work.

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Appendices

A Supplementary Materials for Chapter 3

The additional figures for Chapter 3 are listed below:

Figure A.1: Mean square displacement ($\langle d^2 \rangle$) of Al' atoms in the first layer of coherent (upper) and semi-coherent (lower) interfaces at 900 K, with different side dimensions;

Figure A.2: Potential energy evolution of θ' -Al₂Cu/Al matrix system during equilibration;

Figure A.3: Velocity autocorrelation function (VACF) profile at different temperatures;

Figures A.4–A.8: $\langle d^2 \rangle$ of the first three Al layers at semi-coherent and coherent interfaces at 700 (Figure A.4), 750 (Figure A.5), 800 (Figure A.6), 850 (Figure A.7), 900 K (Figure A.8);

Figures A.9–A.13: $\langle d^2 \rangle$ of the first three Al' layers at semi-coherent and coherent interfaces at 700 (Figure A.9), 750 (Figure A.10), 800 (Figure A.11), 850 (Figure A.12), 900 K (Figure A.13);

Figures A.14–A.18: $\langle d^2 \rangle$ of the first three Cu layers at semi-coherent and coherent interfaces at 700 (Figure A.14), 750 (Figure A.15), 800 (Figure A.16), 850 (Figure A.17), 900 K (Figure A.18);

Figure A.19: Arrhenius plots of total self-diffusivity (D_{self}) of the first three layers of Al and Al' in both semi-coherent (left) and coherent interfaces (right).

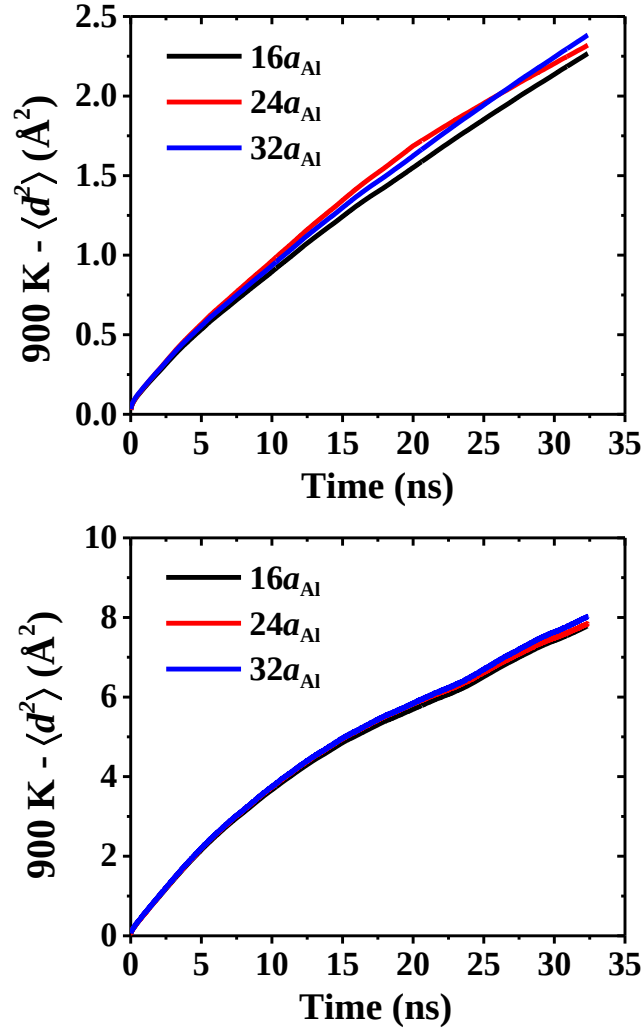


Figure A.1: Mean square displacement ($\langle d^2 \rangle$) of Al' atoms in the first layer of coherent (upper figure) and semi-coherent (lower figure) interfaces at 900 K, with different side dimensions. The difference of $\langle d^2 \rangle$ is almost indiscernible, indicating the weak dependence of diffusion properties on the side dimension and justifying our selection of the side dimension in this research.

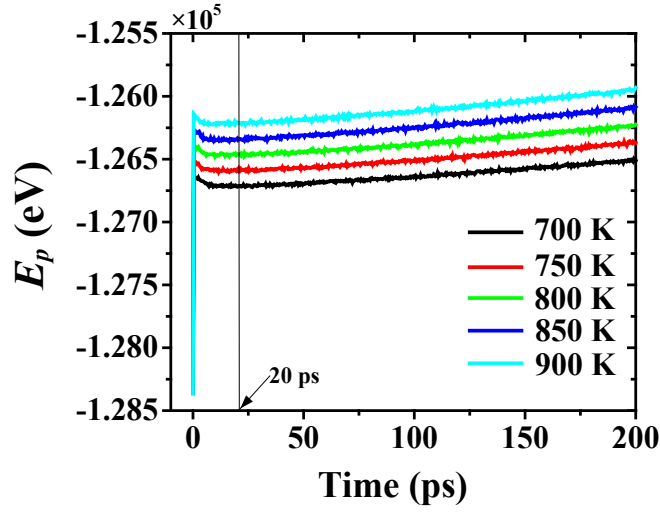


Figure A.2: Potential energy (E_p) evolution of θ' -Al₂Cu/Al system during equilibration. After 20 ps, the system has achieved quasi-equilibrium.

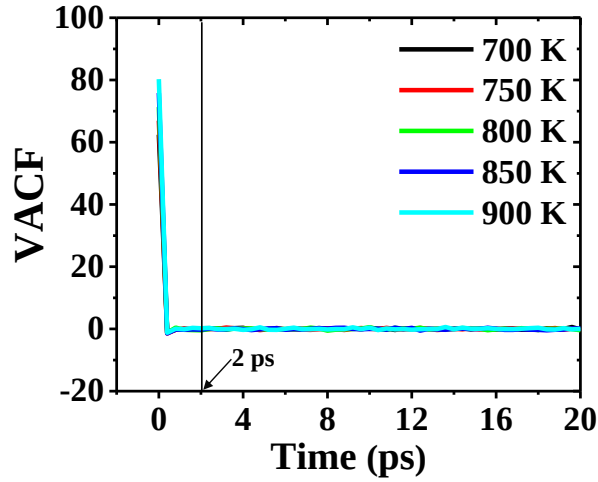


Figure A.3: Velocity autocorrelation function (VACF) profile at different temperatures. The system has been relaxed for 200 ps before running for VACF. As can be seen, the VACF converges within 2 ps at all temperatures.

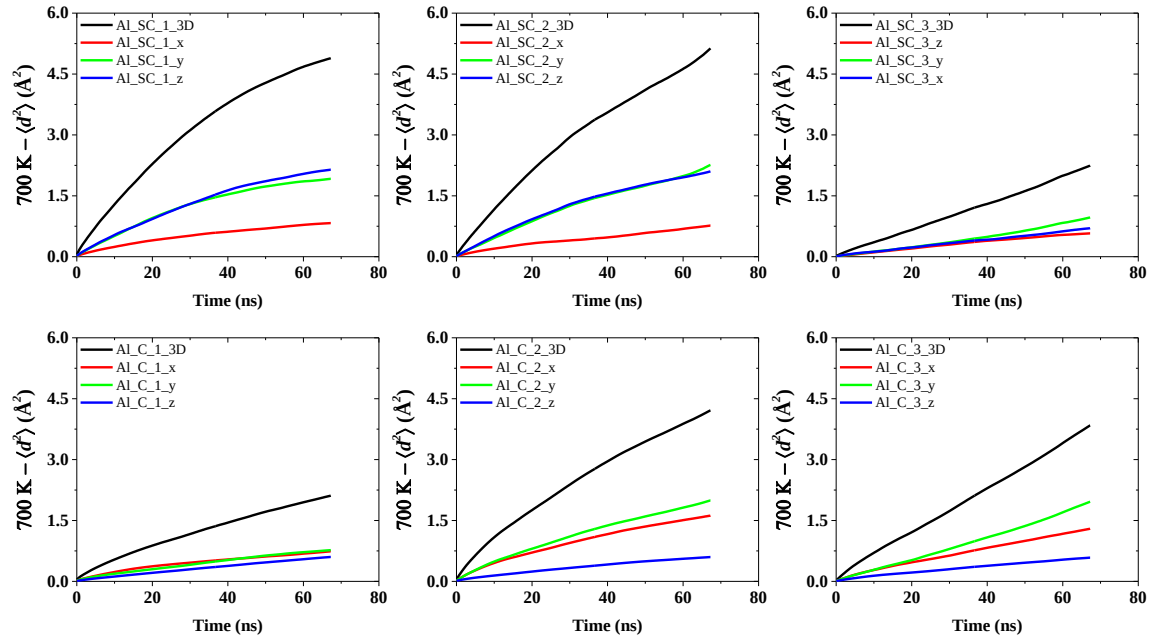


Figure A.4: Mean square displacement ($\langle d^2 \rangle$) of the first three Al layers at semi-coherent and coherent interfaces at 700 K.

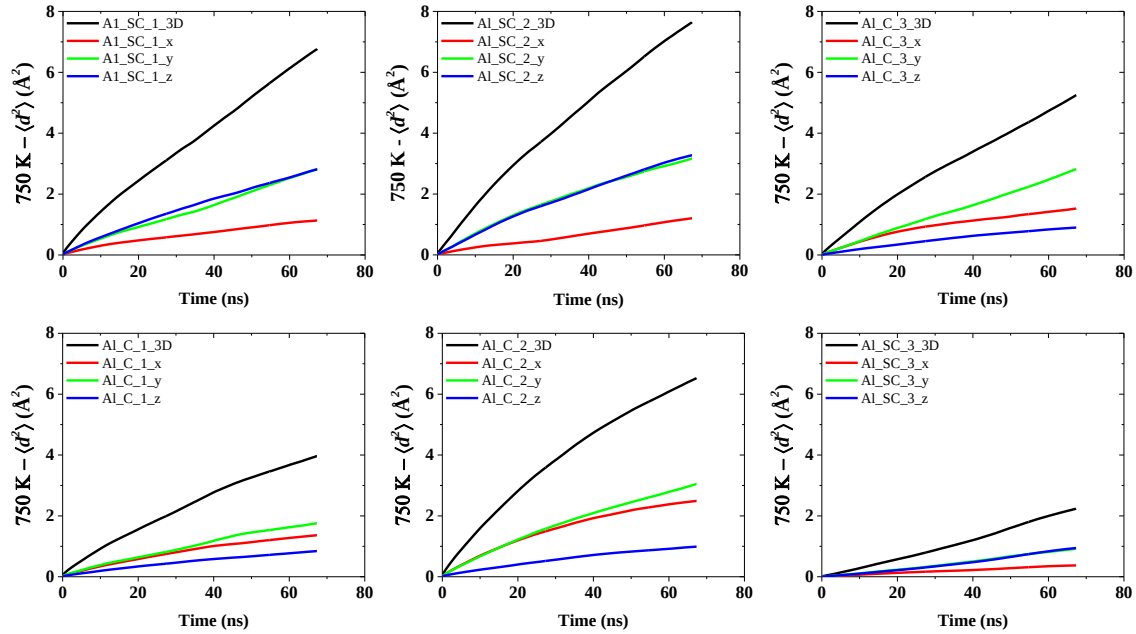


Figure A.5: Mean square displacement ($\langle d^2 \rangle$) of the first three Al layers at semi-coherent and coherent interfaces at 750 K.

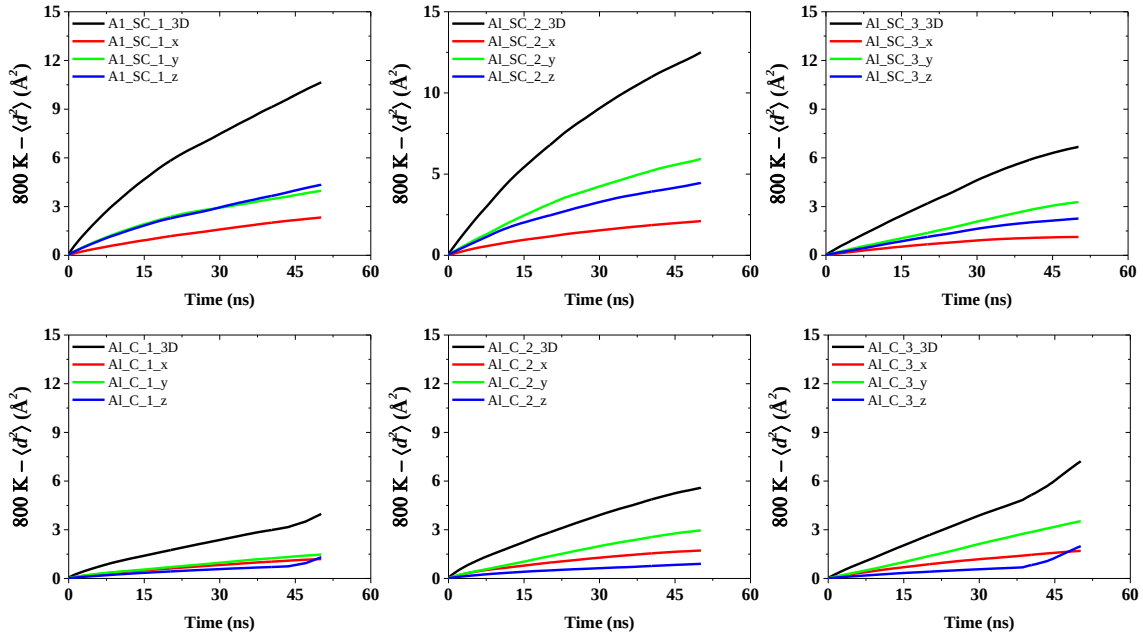


Figure A.6: Mean square displacement ($\langle d^2 \rangle$) of the first three Al layers at semi-coherent and coherent interfaces at 800 K.

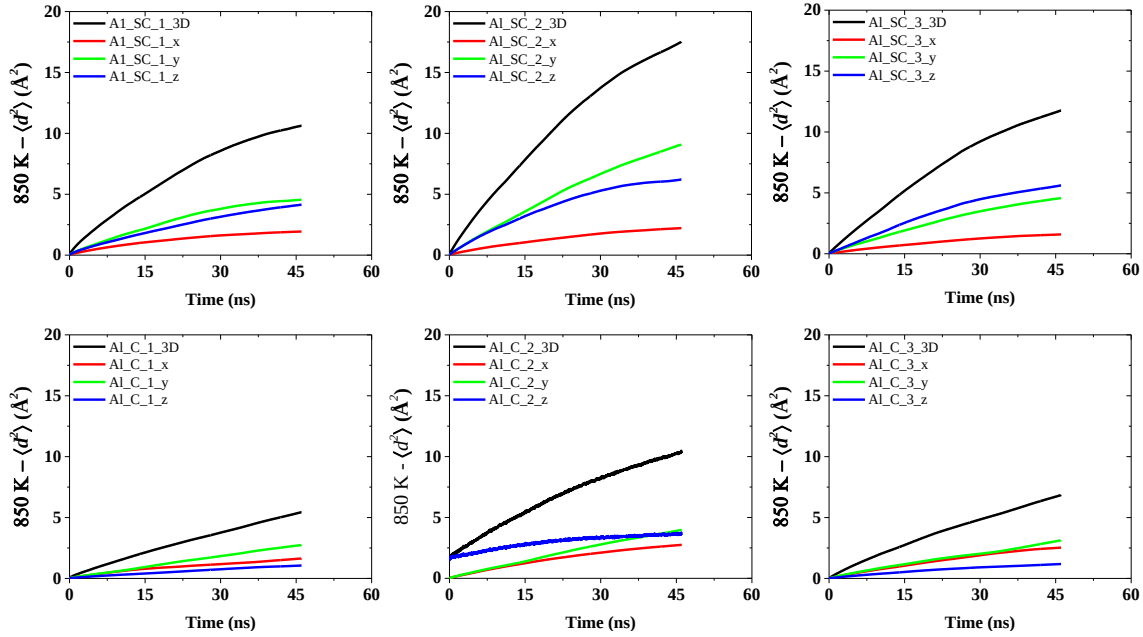


Figure A.7: Mean square displacement ($\langle d^2 \rangle$) of the first three Al layers at semi-coherent and coherent interfaces at 850 K.

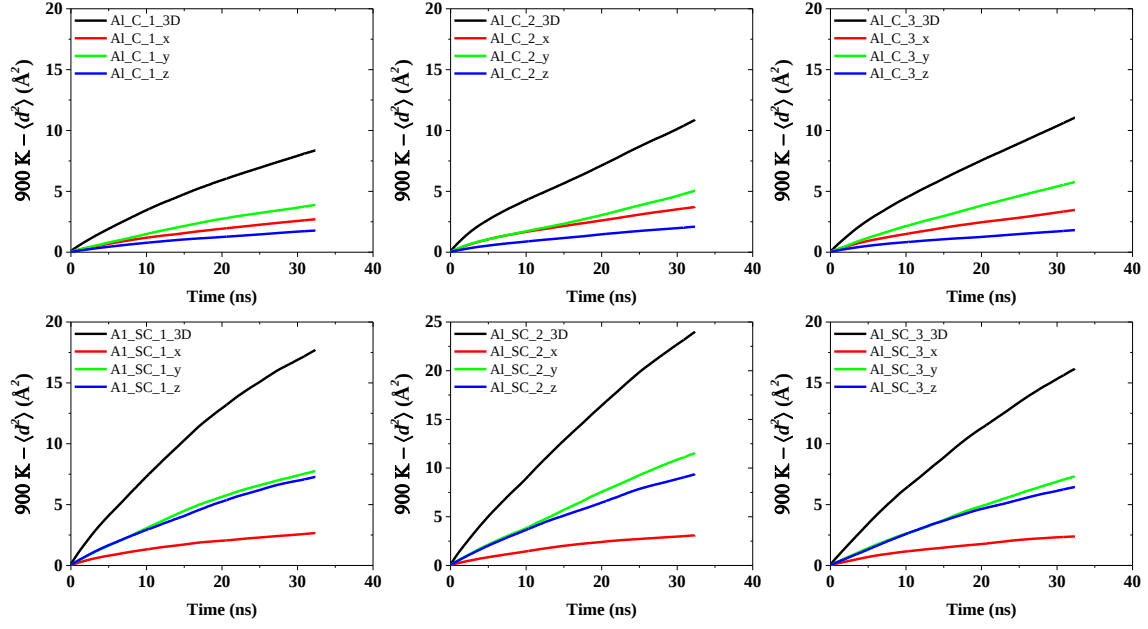


Figure A.8: Mean square displacement ($\langle d^2 \rangle$) of the first three Al layers at semi-coherent and coherent interfaces at 900 K.

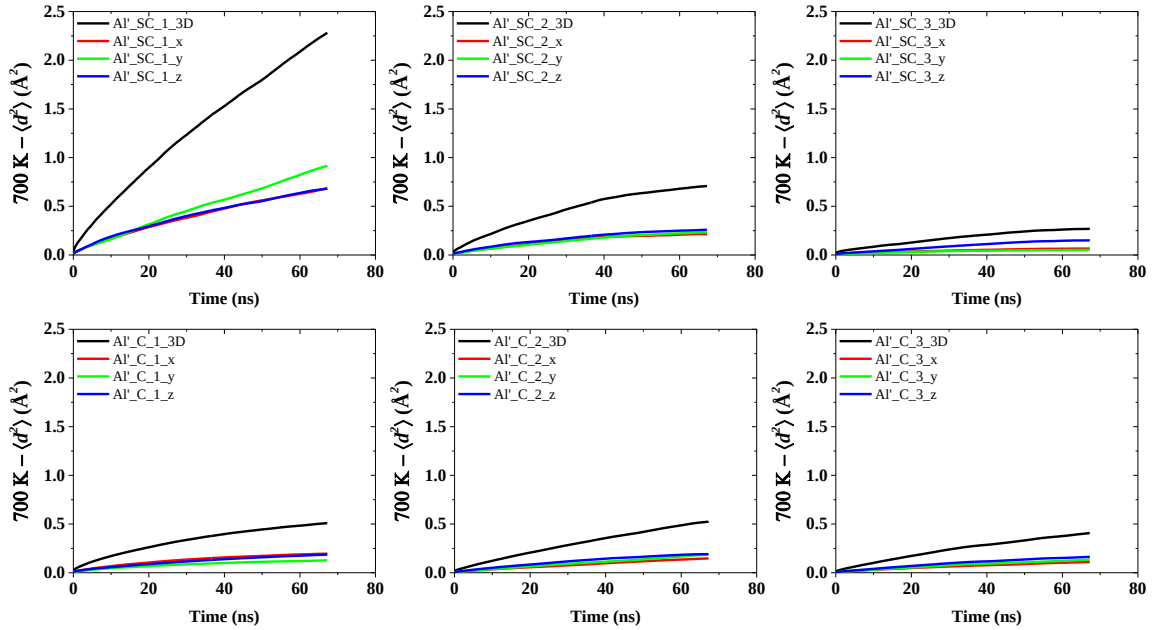


Figure A.9: Mean square displacement ($\langle d^2 \rangle$) of the first three Al' layers at semi-coherent and coherent interfaces at 700 K.

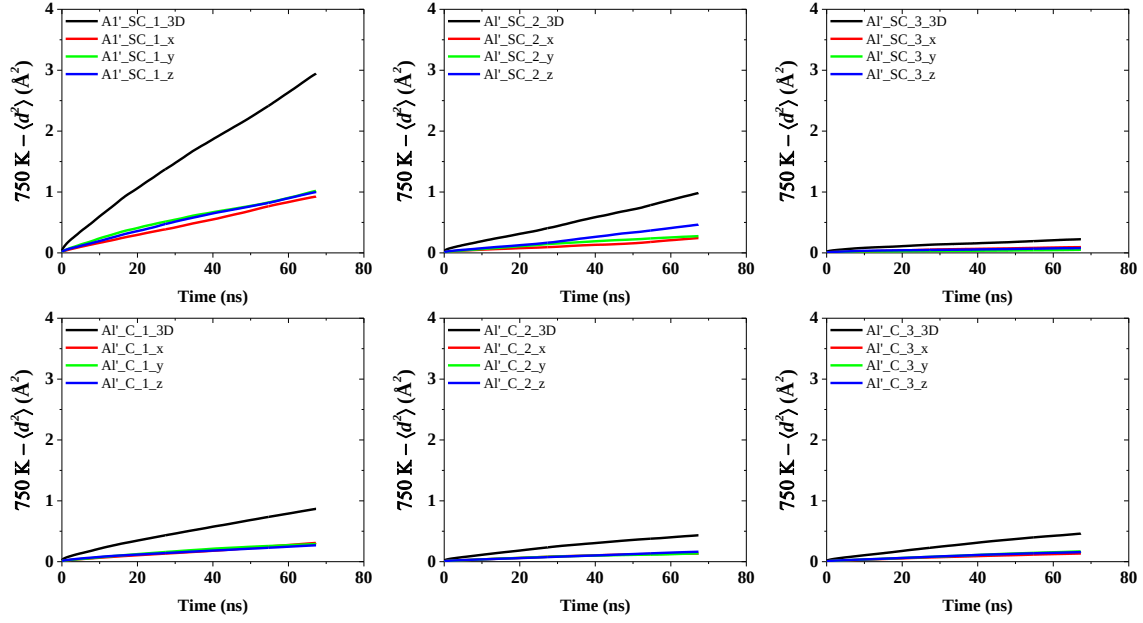


Figure A.10: Mean square displacement ($\langle d^2 \rangle$) of the first three Al' layers at semi-coherent and coherent interfaces at 750 K.

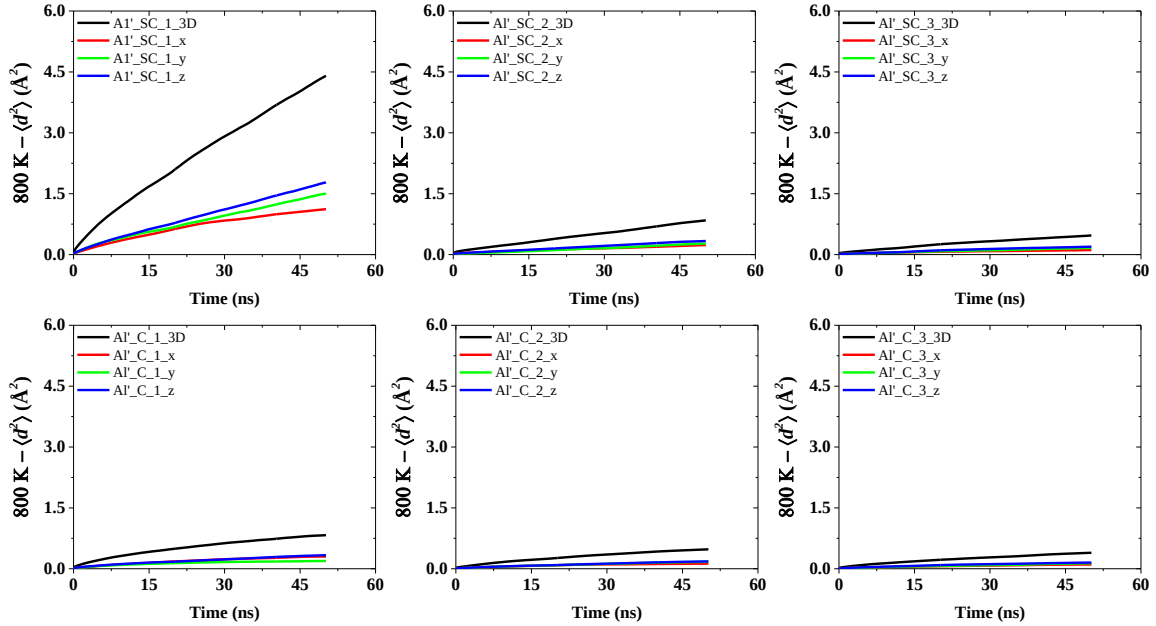


Figure A.11: Mean square displacement ($\langle d^2 \rangle$) of the first three Al' layers at semi-coherent and coherent interfaces at 800 K.

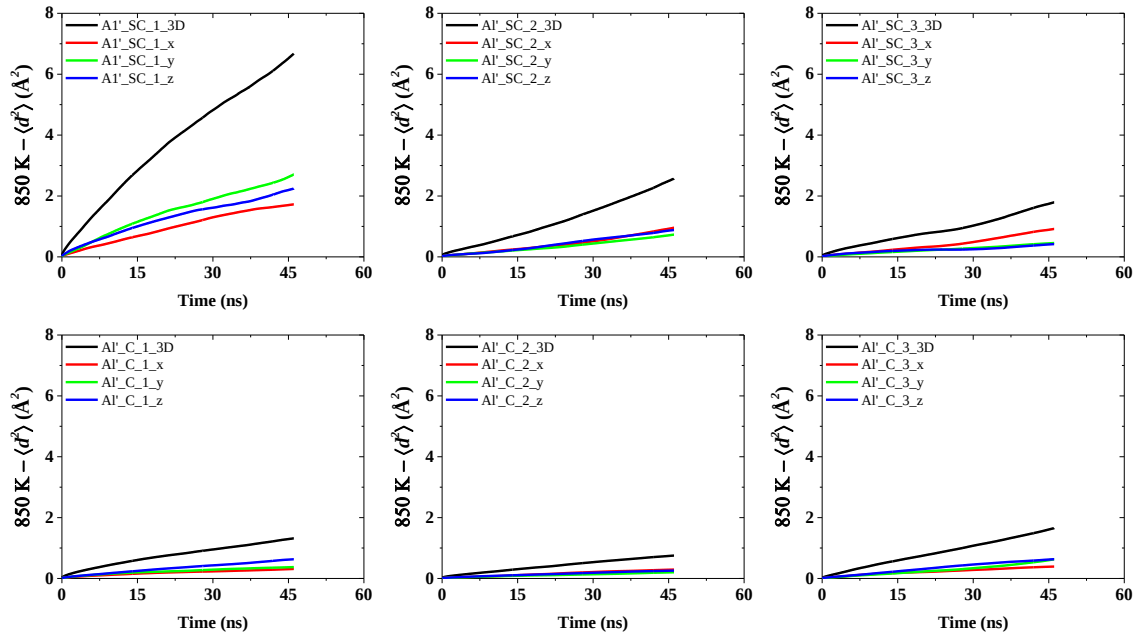


Figure A.12: Mean square displacement ($\langle d^2 \rangle$) of the first three Al' layers at semi-coherent and coherent interfaces at 850 K.

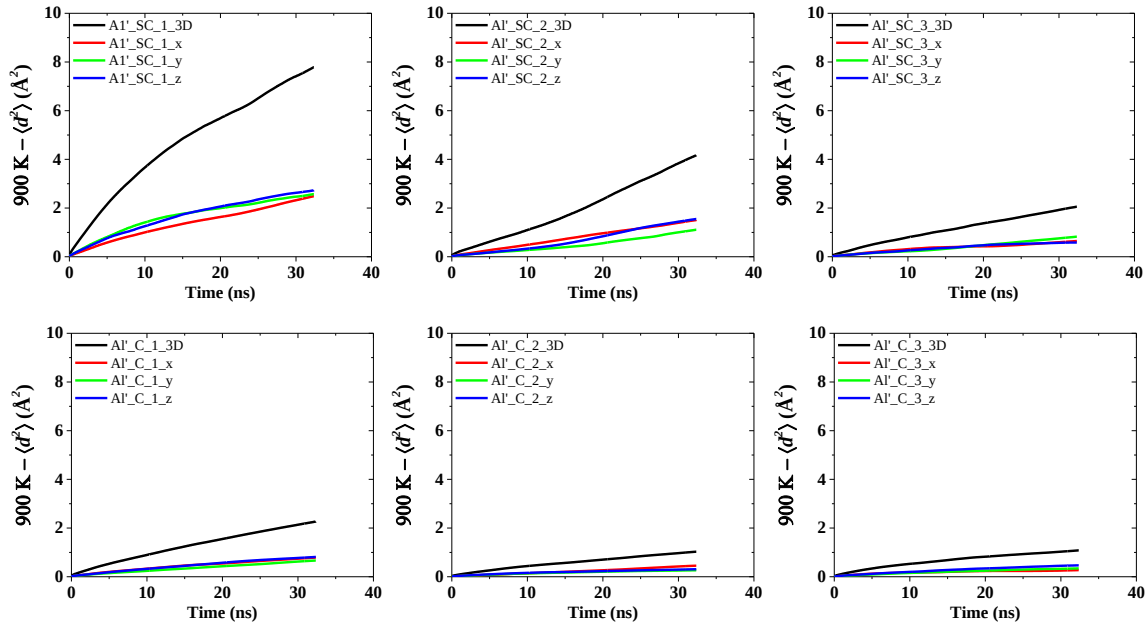


Figure A.13: Mean square displacement ($\langle d^2 \rangle$) of the first three Al' layers at semi-coherent and coherent interfaces at 900 K.

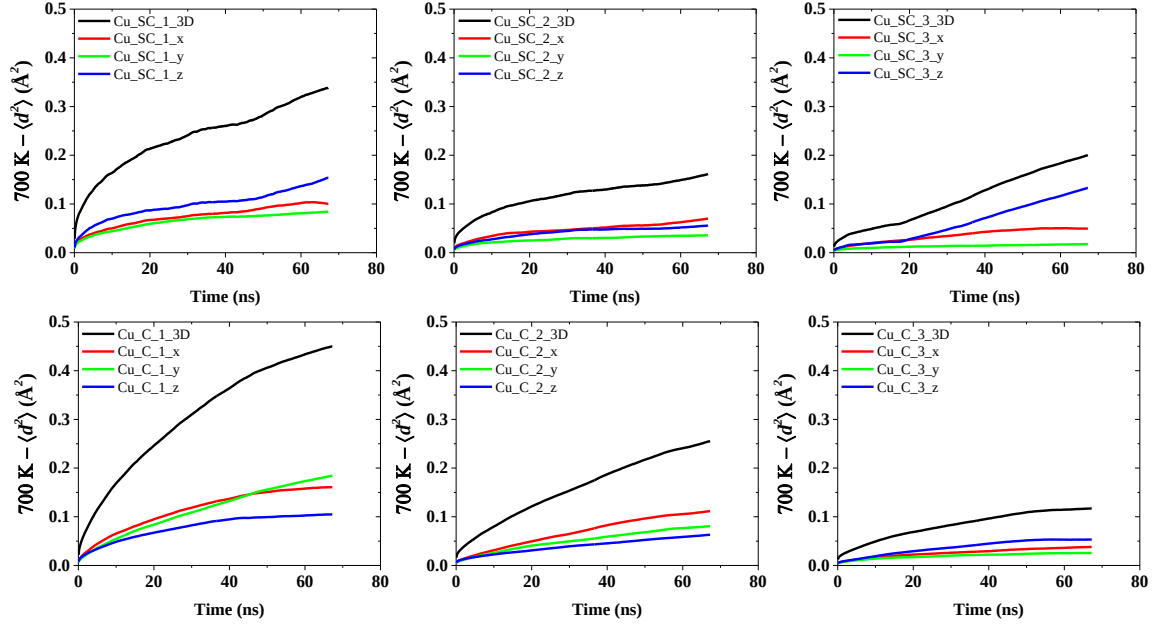


Figure A.14: Mean square displacement ($\langle d^2 \rangle$) of the first three Cu layers at semi-coherent and coherent interfaces at 700 K.

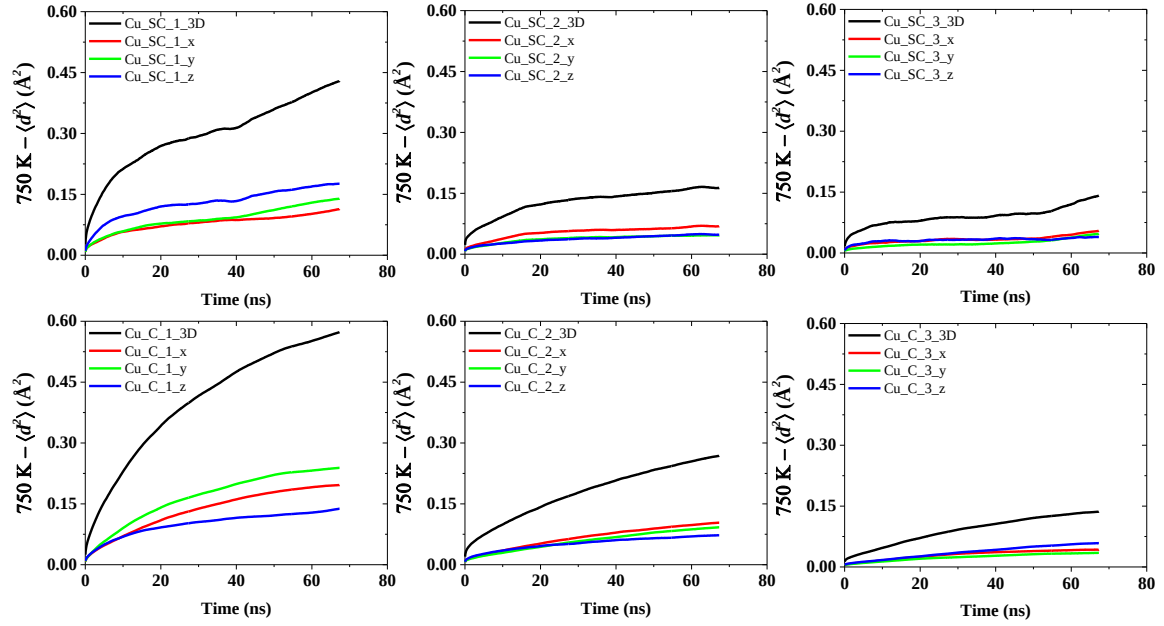


Figure A.15: Mean square displacement ($\langle d^2 \rangle$) of the first three Cu layers at semi-coherent and coherent interfaces at 750 K.

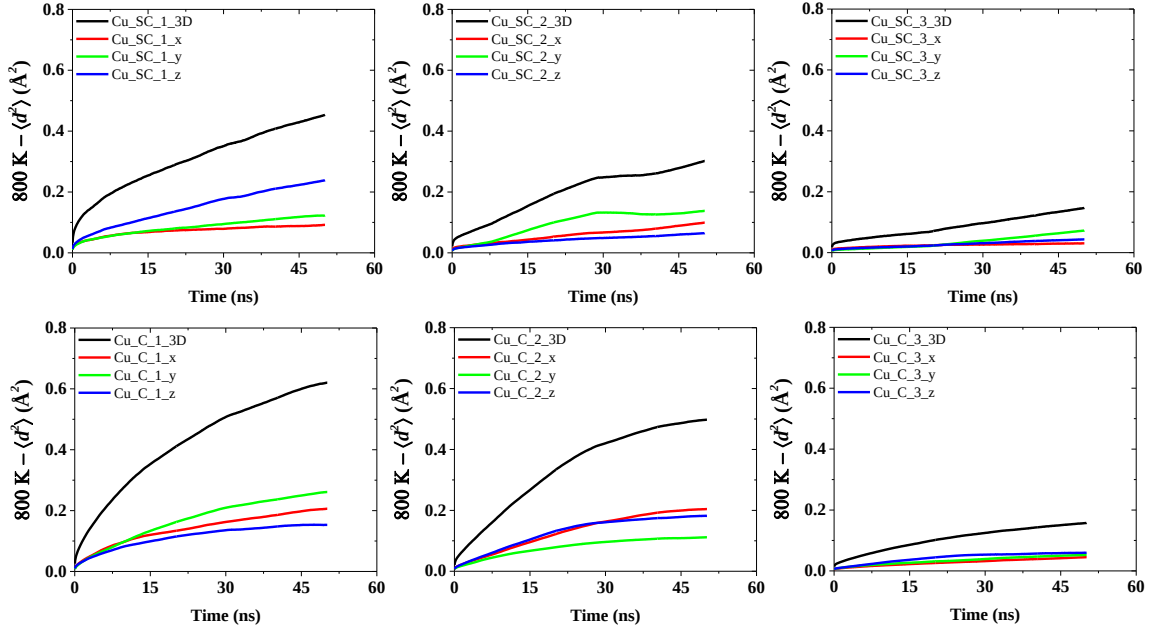


Figure A.16: Mean square displacement ($\langle d^2 \rangle$) of the first three Cu layers at semi-coherent and coherent interfaces at 800 K.

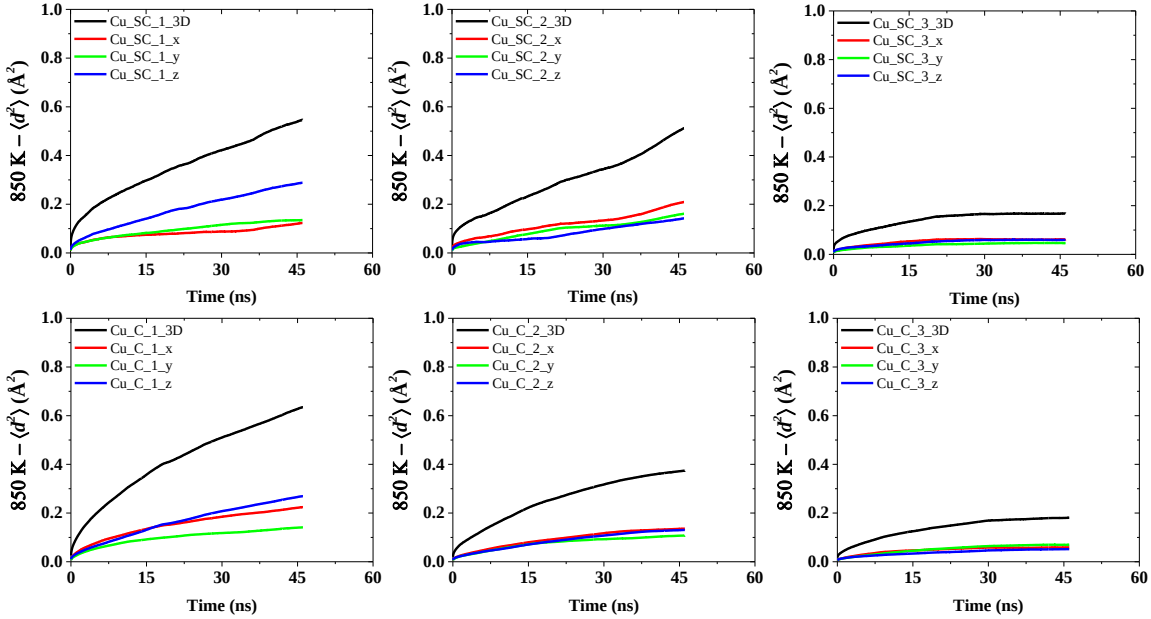


Figure A.17: Mean square displacement ($\langle d^2 \rangle$) of the first three Cu layers at semi-coherent and coherent interfaces at 850 K.

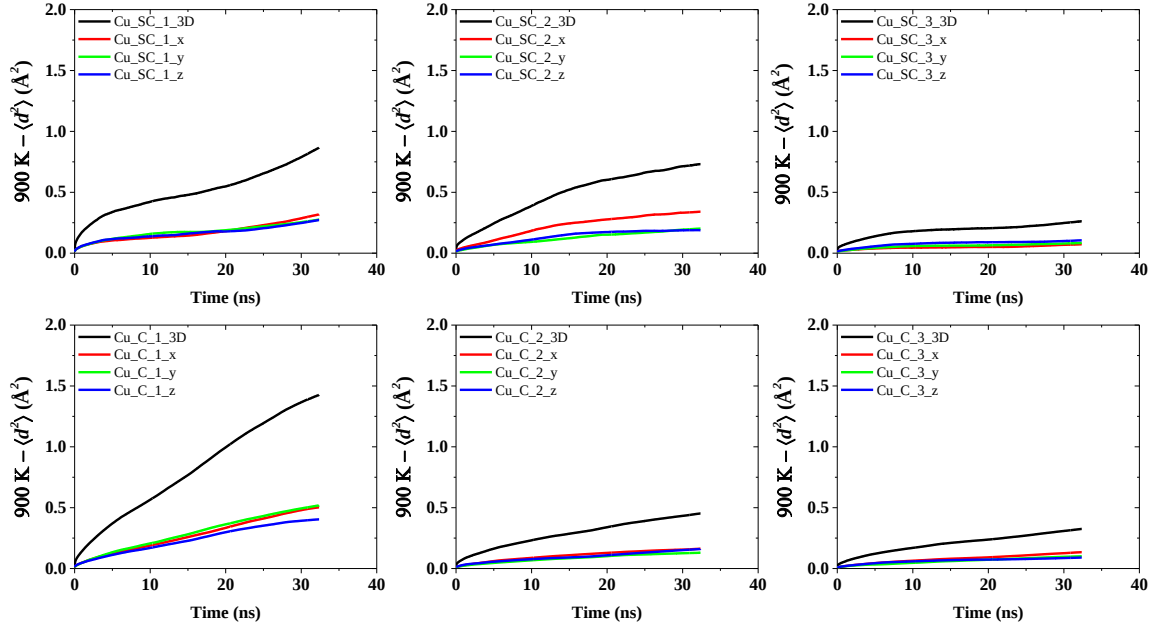


Figure A.18: Mean square displacement ($\langle d^2 \rangle$) of the first three Cu layers at semi-coherent and coherent interfaces at 900 K.

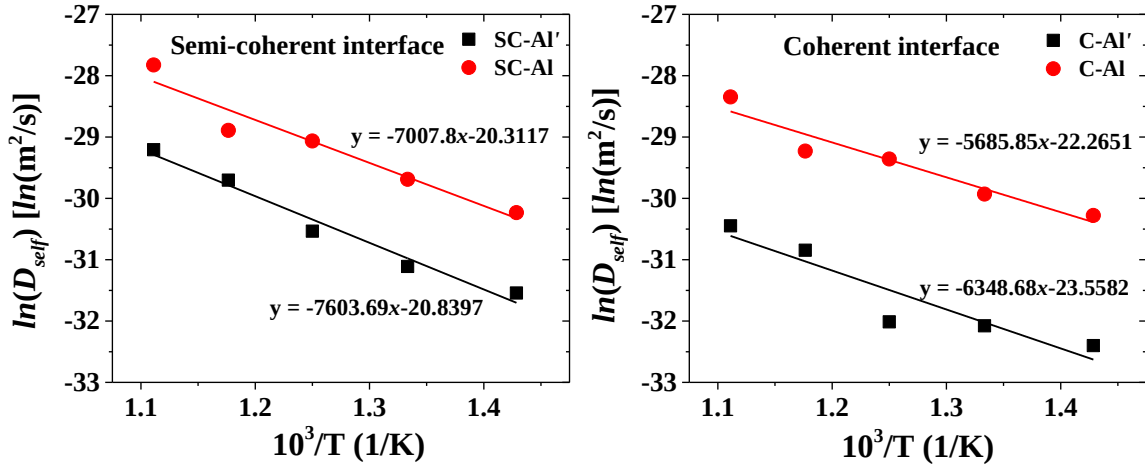


Figure A.19: Arrhenius plots of total self-diffusivity (D_{self}) of the first three layers of Al and Al' in both semi-coherent (left) and coherent interfaces (right). Here, the D_{self} is an averaged one over the D_{self} 's of the three layers.

B Supplementary Materials for Chapter 4

B.1 Detailed Benchmark Methodology of Machine-Learned Al AGNI Potential

All CMD simulations for benchmark of Al AGNI potential [51], generation of training data, and verification of selected potential parameters, are performed with the open-source package of LAMMPS [119]. It should be noted that the AGNI potentials of Al have been deprecated now by the developers. The deprecation information can be found in the AGNI potential file, for example, Al_jpc.agni, in LAMMPS potential repository.

A system of $10 \times 10 \times 10$ supercell of Al is constructed with a lattice constant of 4.04 Å and atom number of 4,000, and the periodic boundary condition is applied in the x -, y -, and z -dimension. The size of the supercell is large enough to exclude the system size effect. 1 fs is chosen as a timestep to update the velocity and force. NPT ensemble (constant number of atom, pressure, and temperature) is applied for maintaining the temperature at 300 K and the pressure at 1 atm. The simulation results show that the initial cell length of 40.4 Å decreases to 20.15 Å after 1,800 steps (1.8 ps), resulting in that density increases from 2.71 to 21.87 g cm⁻³. The simulation stops due to unphysical structure after 1,800 steps. The simulation results demonstrate that the AGNI potential of Al is not capable of generating meaning results under NPT ensemble.

B.2 Simulation and Calculation Methodology of Various Properties for Verification

In the model training process, the data of properties of the lattice constant (a), linear thermal expansion coefficient (α_L), constant-pressure specific heat capacity (c_p), and Young's modulus along $\langle 100 \rangle$ orientation ($E_{\langle 100 \rangle}$), calculated at three finite temperatures of 300, 500, and 700 K, are employed. An $8 \times 8 \times 8$ supercell of Al with 2,048 atoms is constructed as a simulation subject, which ensures that the length of the simulation cell ($L = 8a_{\text{Al}} = 32.396$ Å, where a_{Al} is lattice constants of Al, equal to 4.0495 Å) is at least twice larger than the interaction cut-off distance (10 Å), to exclude the size effect [81]. This initial structure is equilibrated under the NPT ensemble (constant number of atom N , constant pressure P , and temperature T) for 50 ps with a timestep of

1 fs before calculating each property. After the equilibration of the initial structure for 50 ps, the potential energy of the system is converged, demonstrating the equilibrium of the system. Another 50 ps simulation is then performed under the NPT ensemble for generating system data, such as the cell size and enthalpy.

The obtained α_L and c_p at each temperature are calculated based on the averaged data over the second 50 ps period. To calculate the properties of α_L and c_p , the centered finite difference method is employed [209]:

$$\alpha_L = \frac{1}{L(P, T)} \frac{L(P, T + \varepsilon_T) - L(P, T - \varepsilon_T)}{2\varepsilon_T}, \quad (\text{B.1})$$

$$c_p = \frac{H(P, T + \varepsilon_T) - H(P, T - \varepsilon_T)}{2\varepsilon_T}, \quad (\text{B.2})$$

where L is the length of the simulation cell, H is the enthalpy, P is pressure, T is temperature, and ε_T is the temperature difference. P is set as 0, and temperature difference ε_T is set as 10 K. $L(P, T)$ and $H(P, T)$ indicate the length and enthalpy of the system at a specific pressure P and temperature T . In order to obtain the α_L and c_p at one temperature, for instance, 300 K, simulations should be performed at another two temperatures, 290 and 310 K. Therefore, totally nine simulations at (290, 300, 310 K), (490, 500, 510 K), and (690, 700, 710 K) are run for each potential parameter set.

For obtaining $E_{\langle 100 \rangle}$, uniaxial strain is applied in $\langle 100 \rangle$ orientation with a constant engineering strain rate of $1.0 \times 10^{-4} \text{ ps}^{-1}$. Another two engineering rates of 1.0×10^{-5} and $1.0 \times 10^{-6} \text{ ps}^{-1}$ are tested, and it is found that the $E_{\langle 100 \rangle}$ is independent of the engineering rate. To save the computational cost, the largest engineering rate of $1.0 \times 10^{-4} \text{ ps}^{-1}$ is applied. The Young's modulus $E_{\langle 100 \rangle}$ is calculated based on the elastic regime of the strain–stress curve, within a strain ranges from 0 to 0.01, and the ultimate tensile strength (σ_u) is determined as the highest point of the strain–stress curve.

In the verification simulations, α_L , c_p , $E_{\langle 100 \rangle}$, and additional three properties of mass density (ρ_m), melting temperature (T_m), and phonon density of states (D_p) are calculated. The simulation methodology of α_L , c_p , a , and $E_{\langle 100 \rangle}$ for the verification is the same as that for the generation of training data.

The ρ_m is evaluated at the temperature of 300 K and pressure of 0 Pa by measuring volume (i.e., $\rho_m = m/V$, where m is the mass, and V is the volume).

For determining the T_m , the system is subject to isothermal heating [84, 210] from 300 to 1,300 K for 50 ps at each temperature. The increment of temperature is 100 K from 300 to 800 K, 20 K from 800 to 1,000 K (aiming at determining an accurate T_m), and 100 K from 1,000 to 1,300 K. The melting temperature is determined at which a sharp increase occurs in the volume-temperature curve [84, 210].

The D_p is calculated by Equation 2.6, with the Fourier transform of the velocity autocorrelation function $u^{2*}(t)$, which is calculated by Equation 2.7.

C Diffusion Kinetics of Transient Liquid Phase Bonding of Ni-based Superalloy with Ni Nanoparticles

Note: Besides the accelerated multiscale simulations on mass and thermal transport, traditional CMD is also employed in study of the diffusion kinetics of the bonding process of nickel (Ni)-based superalloy with Ni nanoparticles. The detailed introduction, methodology, results and discussions, and conclusions are presented below, with subtle modifications from the published work of: **Jiaqi Wang**, Seungha Shin*, Anming Hu, Jackson K. Wilt, “Diffusion Kinetics of Transient Liquid Phase Bonding of Ni-based Superalloy with Ni Nanoparticles: A Molecular Dynamics Perspective”. *Computational Materials Science*, 152, 228-235 (2018). This publication is reprinted with permission from Elsevier. The dissertation author listed in this publication directed and supervised the research which forms the basis for this publication.

C.1 Introduction

Transient liquid phase (TLP) bonding is a joining technique employing a filler material with low melting temperature for inducing fast atomic diffusion, and subsequent isothermal solidification process of the liquid phase of the filler material, forming strong bonding with the base material [211]. TLP bonding involves minimal microstructure deformation and thermal distortion to the base material, which make it advantageous over traditional joining techniques such as vacuum brazing [212]. The TLP bonding has been widely utilized in joining and repairing of Ni-based superalloys, such as Inconel[®] 718 [213, 214, 215, 216, 217]. Directionally solidified polycrystalline and single crystal Ni-based superalloys possess excellent high-temperature mechanical properties and high corrosion-oxidation resistance [218], allowing for use in various applications, such as turbine engine, blades and vanes, cogeneration, and heat treatment facilities, which are operated under extreme conditions [219, 220]. However, these Ni-based superalloys are expensive and extremely difficult to join and repair, due to challenges in (1) minimization of modification on preexisting precipitates in base materials, (2) remarkable reduction of the bonding time by enhancing the diffusivity, and (3) avoiding formation of undesirable phase, such as Nb-rich Laves phase in Inconel[®] 718 alloy [221, 222].

In traditional TLP bonding, melting point depressants (MPDs), such as carbon, boron, silicon and chromium [219, 223, 224], are added for enhancing diffusion performance of the filler or base materials. However, the addition of such MPDs induces formation of brittle intermetallic phases within the joint, which deteriorate the joint strength and ductility [211]. Nanomaterials are expected to resolve this problem because melting point can be decreased by their fine size without adding such MPDs [225, 84]. Ni nanoparticles (NPs), as a representative example, have been used to braze stainless steel for achieving a high bonding strength [226, 227], which is attributed to their high diffusivity.

Most of experimental studies on joining of Inconel® 718 have addressed the isothermal solidification process [228, 229], microstructures, and mechanical properties of the joint structure [214, 230, 231, 232]; however, the *in situ* diffusion process during joining at atomic scale has been rarely reported by experimental investigations due to challenges in high-resolution structural characterization at high temperatures. Nevertheless, diffusion kinetics affects microstructure formation, and an enhanced understanding of diffusion during joining can suggest possible approaches for achieving excellent mechanical and thermal properties for joints.

Motivated by the advantages of Ni NPs in joining and insufficient understanding of diffusion kinetics, we investigate the atomic-scale TLP bonding of Ni-based superalloy (i.e., modeling Inconel® 718) with Ni NPs, employing classic molecular dynamics (CMD) to enhance fundamental understanding of diffusion kinetics and to facilitate effective processing design of TLP bonding. Bonding with continuous heating method (CHM), i.e., traditional vacuum joining at a uniform temperature, is also studied for comparison. Although the mechanical and thermal properties of joints are not the main focus of this study, potential property-control mechanisms are also discussed.

C.2 Methodology

Interaction Potential

The embedded-atom method (EAM) potential [26] is employed to model interatomic interactions in this work. EAM potential is the most common and accurate interaction model in describing the metallic bonding [233], and has been widely utilized in simulating atomic-scale processes such as

diffusion [234], deformation [235], melting and sintering [84], etc. The total energy (E_{total}) of the EAM potential is formulated as:

$$E_{total} = \frac{1}{2} \sum_{j \neq i, i, j=1} \Phi_{ij}(r_{ij}) + \sum_{i=1} F_i(\bar{\rho}_i), \quad (C.1)$$

where $\Phi_{ij}(r_{ij})$ is a pair interaction energy between atoms i and j with a separation distance of r_{ij} , and a factor of 1/2 is included to avoid duplicated calculation of pair interactions. F_i is the embedding energy of atom i , which is a function of local electron density $\bar{\rho}_i$, given by Equation 3.2.

The Fe-Ni-Cr EAM potential, developed by Bonny et al. in 2013 (potential 1, P1) [236], can reproduce the self-diffusivity (D_{self}) of each element in Fe-Ni-Cr alloys [236]. Thus, it is suitable to simulate the bonding process via atomic diffusion. However, it is parameterized based on properties of Fe₁₀Ni₂₀Cr alloy, whose composition is similar to that of 316L austenitic stainless steel [236]. Whether this potential can be transferred to our simulation subject (i.e., Fe₂₇Ni₅₁Cr₂₂, details of this initial structure will be elaborated in the next subsection) with another composition remains uncertain. In order to verify the robustness of this EAM potential, various thermophysical properties of Fe₂₇Ni₅₁Cr₂₂ (i.e., solidus and liquidus temperatures, linear thermal expansion coefficient at 300 K, constant-pressure specific heat capacity at 300 K, and latent heat of fusion) are calculated and compared with available experimental results. For further verification, melting temperature of Ni NP is also determined. Another Fe-Ni-Cr EAM potential (potential 2, P2) [237], developed by the same group in 2011, is also verified with the same scenario for comparison of the accuracy in describing the metallic bonding. Detailed methodology of potential verification is elaborated in the supplementary information at the end of this appendix.

Construction of Initial Structures

Ni-based superalloy, Inconel® 718 contains more than 10 elements, while almost 90 wt% of the constituent elements are Fe, Ni, and Cr [212]. For simplification of structure model and accuracy of many-body interactions, only the major elements, i.e., Fe, Ni, and Cr, are included in modeling of the Inconel® 718 alloy [238, 239]. In step 1, a $20 \times 40 \times 20$ Ni supercell of face-centered cubic (FCC) lattice is created with periodic boundary conditions, i.e., the dimensions of the supercell in x ,

y, and z directions are $20a_{\text{Ni}}$, $40a_{\text{Ni}}$, and $20a_{\text{Ni}}$, where the a_{Ni} is the lattice constant of Ni ($a_{\text{Ni}} = 3.52$ Å). This supercell contains total 64,000 atoms, and among them, 17,474 Fe and 13,954 Cr atoms are randomly distributed by replacing the Ni atoms in FCC lattice sites. This replacement results in the number percentages of Fe, Ni, and Cr atoms of 27%, 51%, and 22% (the weight percentages are 27.01wt%, 52.91wt%, and 20.08wt%, which are similar to those of realistic Inconel® 718 alloy), and this atomic structure is denoted as $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$.

This initial structure of Ni-superalloy, $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$, for bonding simulations is prepared through three steps: in step 1, the structure created by random replacement is relaxed at 300 K for 1,000 ps; in step 2, the relaxed structure at 300 K is heated to 2,500 K with a heating rate of 11 K ps^{-1} for complete melting, and then relaxed at 2,500 K for 1,000 ps as well; in step 3, the relaxed structure at 2,500 K is quenched to 300 K with a quenching rate of 0.44 K ps^{-1} , followed by another 1,000 ps relaxation at 300 K. In the above three steps, the temperature (T) and pressure ($P = 1 \text{ atm}$ is employed in all steps) are controlled by Nosé-Hoover thermostat and barostat, using the NPT ensemble (constant atomic number, pressure, and temperature).

A Ni NP with a radius of $9a_{\text{Ni}}$ ($= 31.68$ Å) is constructed using non-periodic boundary conditions. Then, an energy minimization is performed using the conjugate gradient (CG) algorithm [240] with a force or energy precision of 1.0×10^{-15} (eV Å^{-1} for force tolerance, unitless for energy tolerance [241]), followed by relaxation at 300 K for 1,000 ps with the NVT ensemble (constant number of atom, volume, and temperature).

Two $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy blocks for base materials and Ni NP fillers are then assembled together for bonding simulations as shown in Figure C.1. The adaptive common neighbor analysis (ACNA) [242] is used to characterize crystalline structures of base and filler materials. To avoid overlapping of atoms while maintaining interaction, two Ni NPs are separated with a distance of $2a_{\text{Ni}}$ in y direction, and the NPs are apart from the alloy blocks with a distance of $1a_{\text{Ni}}$.

TLP and CHM Bonding

In both TLP bonding and CHM bonding simulations, periodic boundary conditions are applied in y and z directions, while a free boundary condition is applied in the x direction (bonding direction), which allows for atomic diffusion without constraint. After energy minimization of the initial configuration, the structure is heated at initial high temperature for 0.1 ns. Five initial temperatures

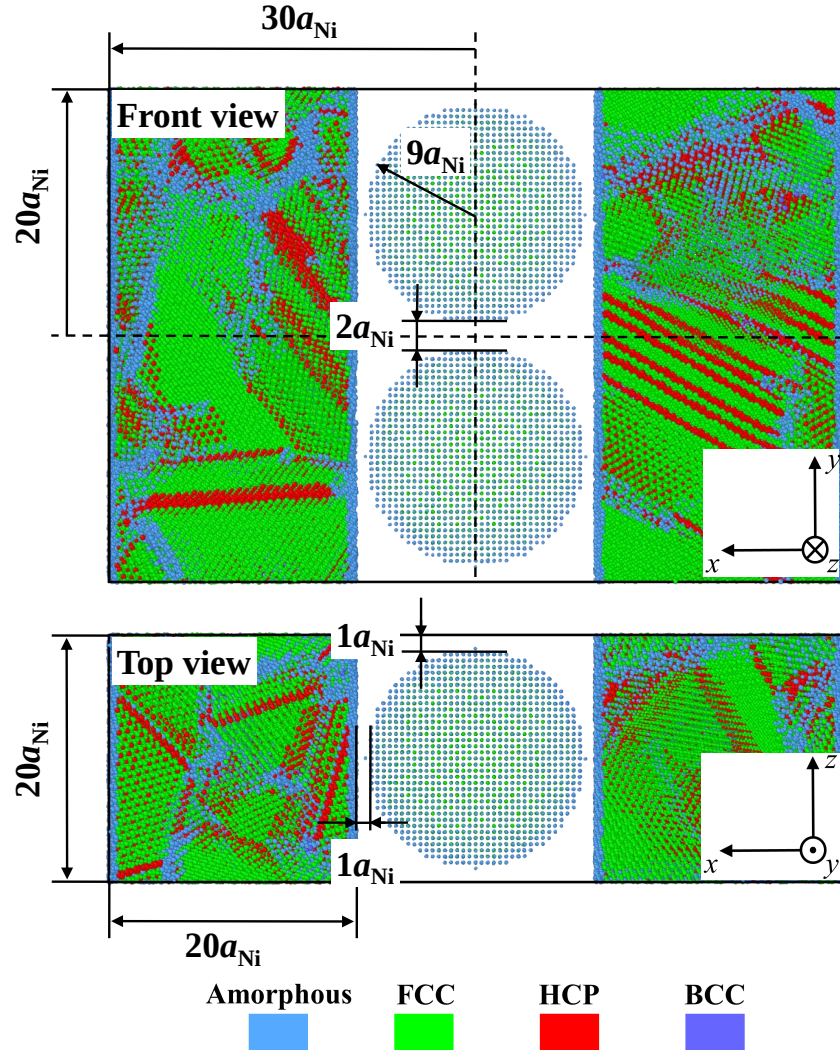


Figure C.1: Front and top views of the simulation configuration for $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ bonding with Ni NPs. Crystalline structure is characterized by the ACNA. The base alloy contains a matrix structure of FCC lattice (60.6%, green) with local orders of hexagonal close packed (HCP, red) of 15.4%, body-centered cubic (BCC, purple) of 0.3%, and amorphous (blue) of 23.8%.

lower than the solidus temperature (1,540 K) of the $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy, i.e., 1,223.15 K, 1,273.15 K, 1,323.15 K, 1,373.15 K, and 1,423.15 K, are employed to activate the surface melting of the NPs while minimizing the heating effect on the base material (the alloy block). Then, in simulations of TLP bonding, the system temperature is lowered to 973.15 K and simulated for 100 ns to examine the diffusion kinetics, while in CHM bonding, the system is maintained at the same initial heating temperature for 5 ns. The joint structure of 1 ns at 973.15 K in TLP bonding is relaxed at 300 K for 0.5 ns, for demonstrating the initial temperature effect. All temperatures in bonding simulations are controlled by the Nosé-Hoover thermostat under the NVT ensemble. The detailed temperature setup in simulations is shown in Figure C.2, with indications of the corresponding time instants of the configurations shown in the subsequent figures.

The evolutions of atomic trajectories, mean square displacement ($\langle d^2 \rangle$), potential energy (E_p), and displacement vectors are monitored to characterize the diffusion dynamics. $\langle d^2 \rangle$ is given by Equation 3.7 and the D_{self} is correlated with $\langle d^2 \rangle$ by Einstein's relation through Equation 3.8.

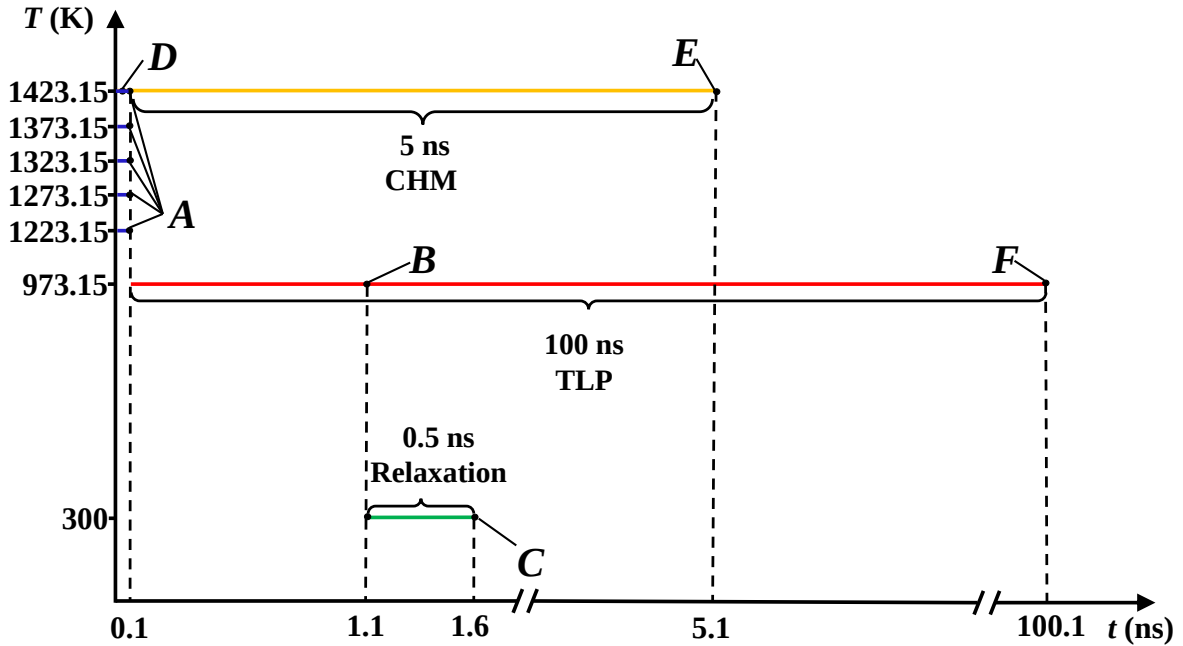


Figure C.2: Temperature setup of transient liquid phase (TLP) and continuous heating method (CHM) bonding. A through F indicate time instants of representative stages for structure characterization in two bonding processes, which are shown in the subsequent figures.

All the simulations in this research are performed using the LAMMPS code [119] and part of the simulations employ the Extreme Science and Engineering Discovery Environment (XSEDE) resources [243].

C.3 Results and Discussion

Selection of Interaction Potential

Table C.1 summarizes the thermophysical properties of $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy calculated using P1 and P2, including solidus (T_S) and liquidus temperatures (T_L), linear thermal expansion coefficient (α_L) at 300 K, constant-pressure specific heat capacity (c_p) at 300 K, and latent heat of fusion (ΔH_f). Potential energy per atom (E_p) is examined for both $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy and Ni NPs at various temperatures to determine the melting temperature or range, which is indicated by the steep jump due to the release of latent heat during phase transition [84], as shown in Figure C.3. The melting temperature of Ni NP determined from CMD with P1 ($T_{NP,P1}$) is 1,520 K, while that with P2 ($T_{NP,P2}$) is 1,490 K; i.e., P1 yields a more accurate melting temperature, compared with the reported melting temperature of Ni NP with the same radius (i.e., 1,550 K) [244]. However, no significant discrepancy is observed in the T_S and T_L of alloy calculated by P1 and P2, i.e., $T_{S,P1} = T_{S,P2} = 1,540$ K and $T_{L,P1} = T_{L,P2} = 1,640$ K, both of which are close to the corresponding experimental values of 1,533 K and 1,609 K [141]. Although P1 overestimates the α_L of $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy by 25.2%, it can reproduce c_p , ΔH_f , and the $T_{NP,P1}$ comparable to experimental data. On the other hand, P2 reproduces α_L and c_p well, but an overestimation of 28.5% is found for ΔH_f . ΔH_f represents bonding energy and accurate melting properties, which are important in bonding process through atomic diffusion. Thus, P1 is employed to investigate the diffusion kinetics at high temperatures (> 973.15 K).

Effects of Initial Temperature on Bonding Products

Mechanical and thermal properties of bonding products are significantly affected by temperature, due to formation of microstructures with different crystallinity, porosity, and phase [245, 246, 247]. As can be observed from the first column in Figure C.4, increasing the initial heating temperature

Table C.1: Thermophysical properties of $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ alloy calculated by potential 1 (P1) and 2 (P2), and are compared with experimental (EXP) results.

	T_S (K)	T_L (K)	α_L ($\times 10^{-6} \text{ K}^{-1}$)	c_p ($\text{J kg}^{-1} \text{ K}^{-1}$)	ΔH_f (J g^{-1})
CMD-P1	1,540	1,640	14.4	462	235
CMD-P2	1,540	1,640	12.2	451	270
EXP	1,533 [141]	1,609 [141]	11.5 [248]	435 [141], 461 [248]	210 [141]

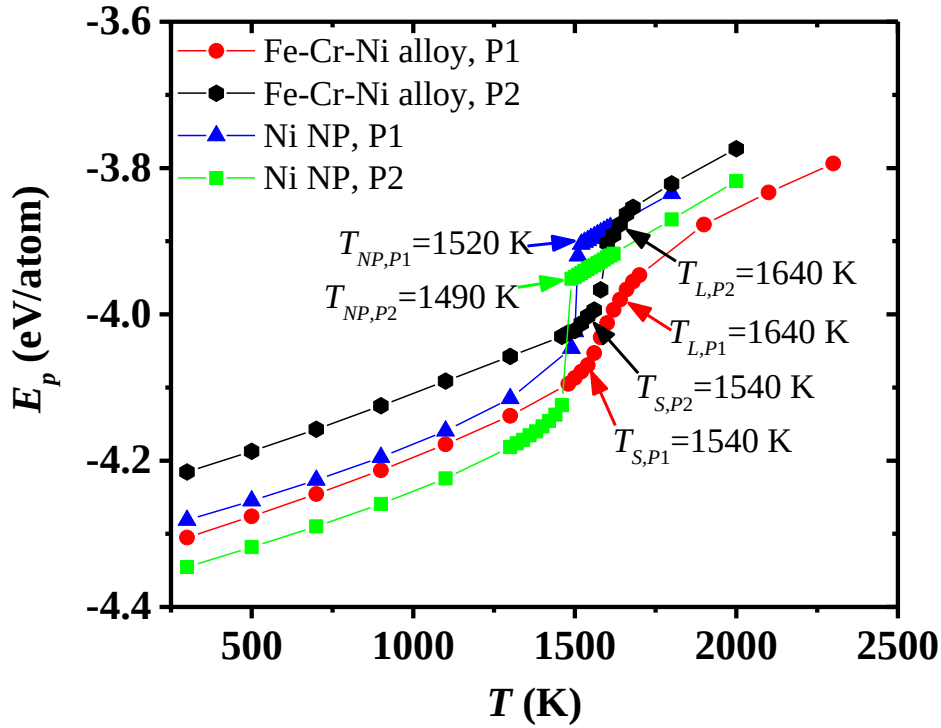


Figure C.3: Evolution of potential energy per atom (E_p) during the isothermal heating processing. The melting points of Ni NP with potential 1 ($T_{NP,P1}$) and potential 2 ($T_{NP,P2}$) are 1,520 K and 1,490 K, respectively. Solidus ($T_{S,P1}$) and liquidus temperatures ($T_{L,P1}$) of $\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$ with both potentials 1 (P1) and 2 (P2) are 1,540 K and 1,640 K, respectively.

decreases the porosity due to a larger atomic mobility from high kinetic energy. Evidenced by the appearance of amorphous atoms (blue atoms) in both surfaces of the NP and alloy structures, activation of surface premelting is confirmed. Atomic trajectories of surface atoms during simulation are shown in Figure C.5, with the first column showing the trajectories of surface atoms in Fe₂₇Ni₅₁Cr₂₂ alloy while the second column showing the surface atoms trajectories in Ni NPs. Longer trajectories are observed at higher temperatures, which also confirms that higher kinetic energy induces a larger mobility at a higher temperature. During the subsequent bonding processes at 973.15 K, crystallization is commonly observed through transformation of amorphous atoms to FCC lattice atoms, while most of atoms in stacking faults remain in the HCP order.

In the following relaxation process at 300 K, further crystallization occurs at the free surfaces and grain boundaries. The evolution of local order percentage (shown in Figure C.6) of the configurations in Figure C.4 confirms the recrystallization during bonding at 973.15 K and relaxation at 300 K. As reported, the existence of pores in bonding joints leads to a poor corrosion resistance and low mechanical strength [249, 250], so an enhanced understanding in diffusion-induced pore elimination is necessary for controlling the porosity and the properties of brazed structures. In this research, pore elimination is only observed at 1,423.15 K, and therefore, diffusion kinetics of initial high temperature bonding at 1,423.15 K and subsequent TLP and CHM bonding processes are analyzed in detail. D_{self} of each element during the joining process is reported and the resulting microstructures induced by the different D_{self} are analyzed accordingly.

Self-Diffusivity (D_{self}) of Each Element during Bonding

It is reported that both insufficient and excessive diffusion lead to weak bonding [211, 251]. Thus, it is imperative to harvest accurate D_{self} quantitatively, and to identify its temperature dependence, which can guide experimentalists to set the optimal temperature for achieving maximum bonding strength. In this research, we calculate the D_{self} of each element in base materials as well as that of the filler material from $\langle d^2 \rangle$, as shown in Figure C.7.

At 1,423.15 K, Ni in the base material has the highest D_{self} while the Cr has the lowest one, depending on their specific bonding situation. The Cr is the most stable element with strong metallic bonding with other Cr atoms because of the previous precipitation during relaxation, while

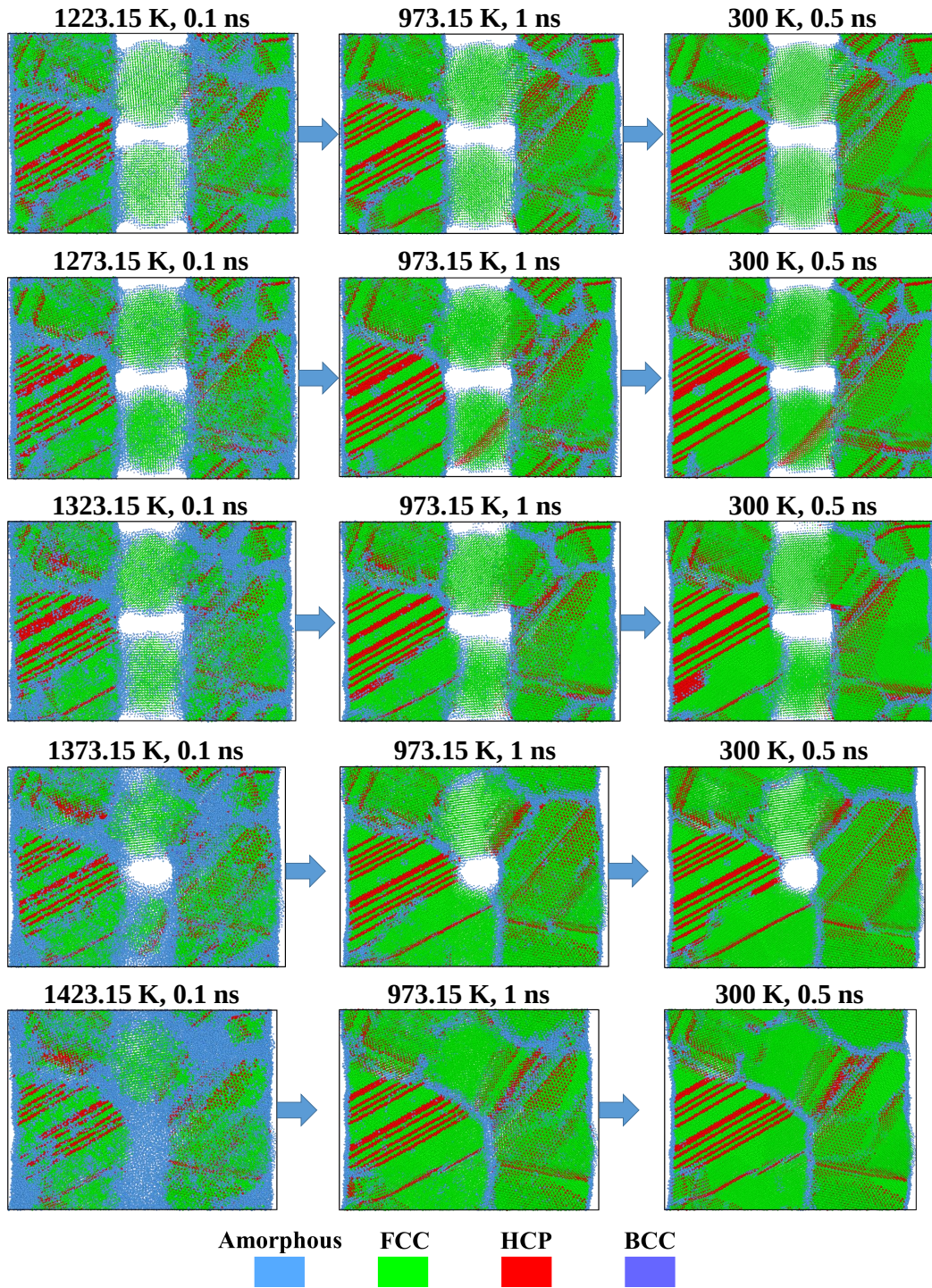


Figure C.4: First column (time instance A in Figure C.2): atomic configurations of joining products of 0.1 ns at five different initial temperatures (1,223.15, 1,273.15, 1,323.15, 1,373.15, and 1,423.15 K); second column (time instance B): bonding products of 1 ns at 973.15 K; third column (time instance C): final structures after 0.5 ns relaxation at 300 K. The atomic configurations of these three columns are cross-sectionals of front views in Figure C.1.

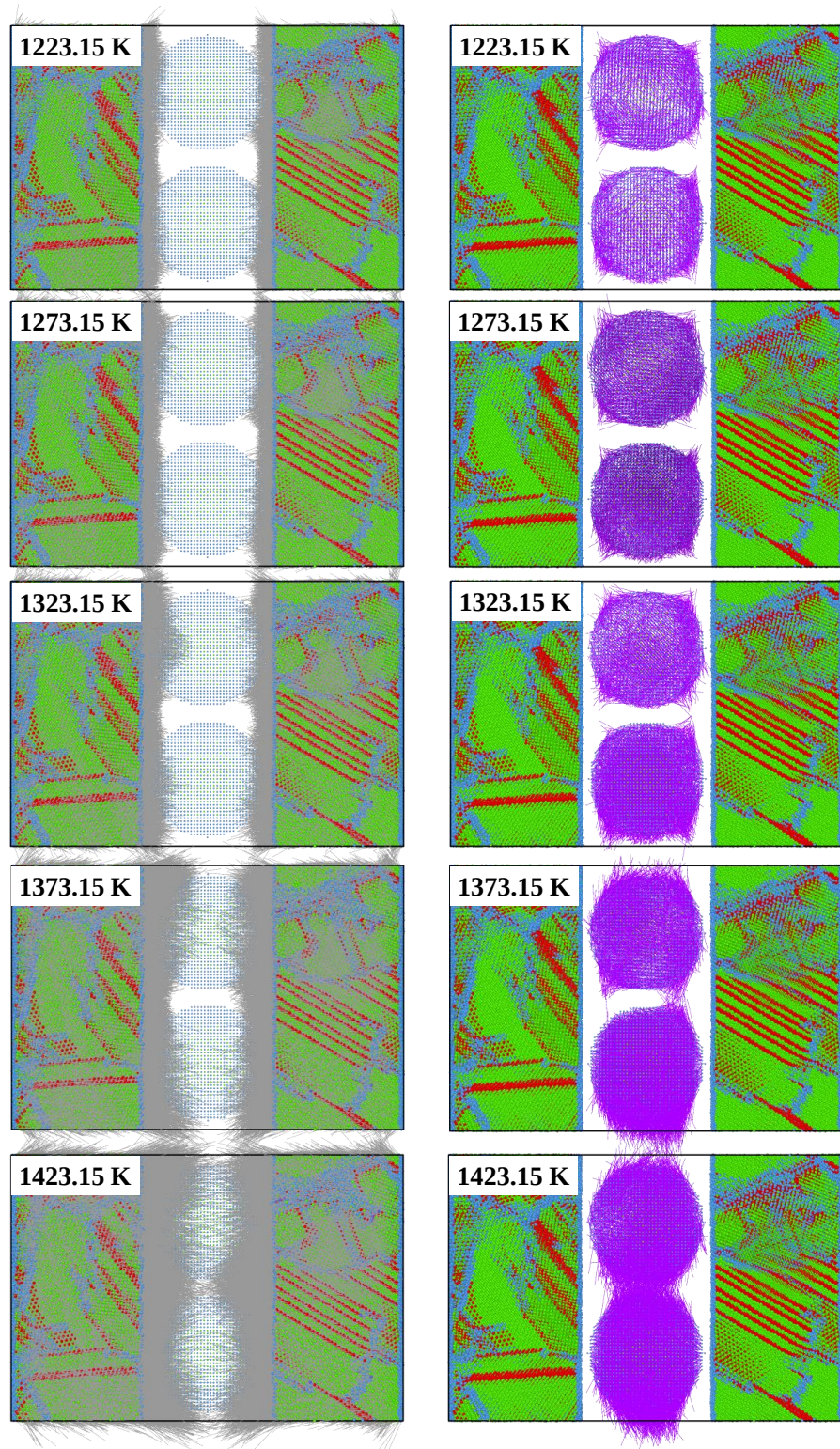


Figure C.5: Atomic trajectories of surface atoms in Fe₂₇Ni₅₁Cr₂₂ alloy (first column, grey color) and Ni NP (second column, purple color), at five different initial temperatures. The initial atomic configuration in Figure C.1 is overlaid with the trajectories, for effective comparison of the trajectories.

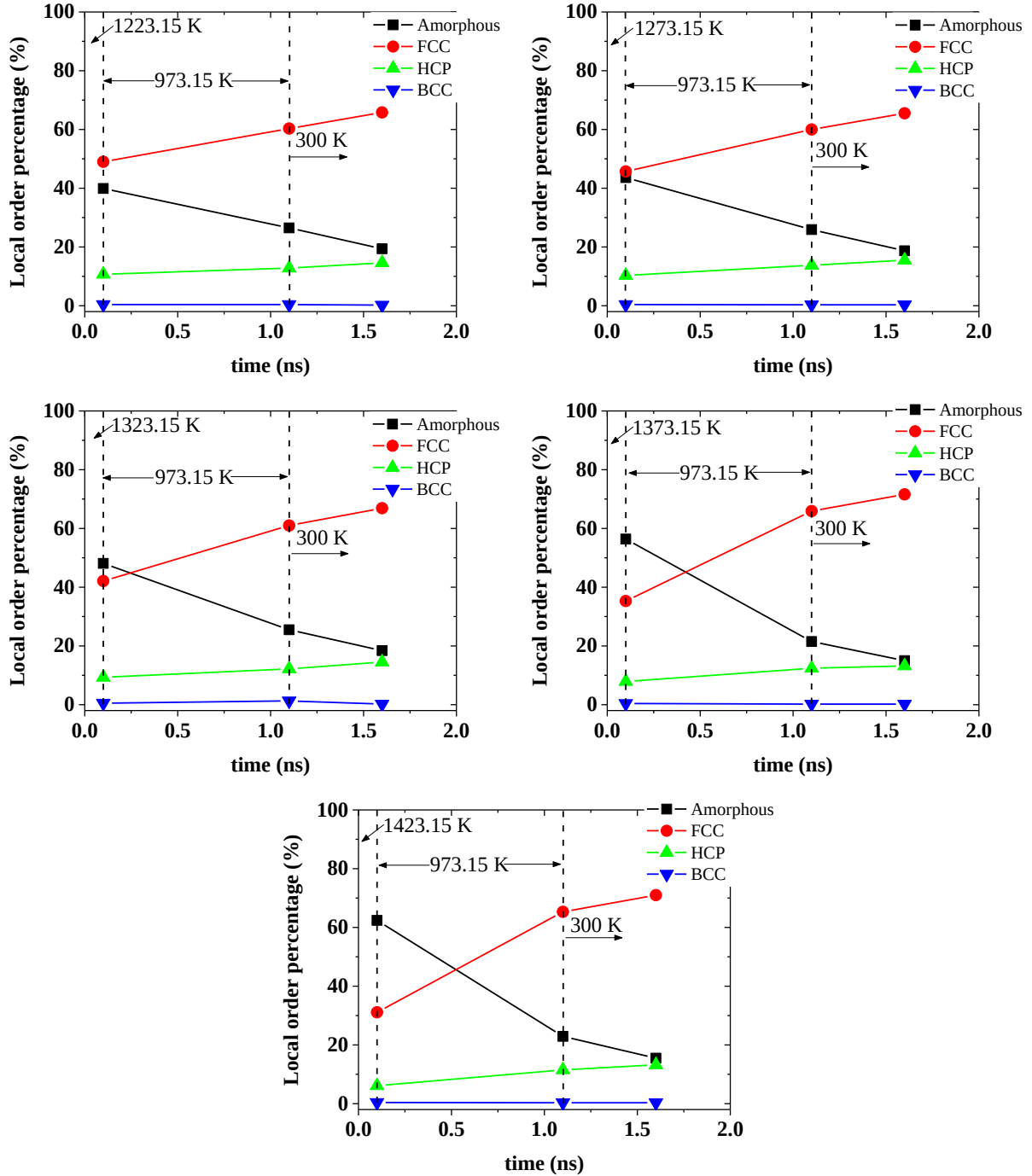


Figure C.6: Local order percentage of final structure (shown in Figure C.4) at different brazing stages in TLP bonding. Diffusion at 973.15 K induces crystallization to the similar degree (~60%), no matter what the initial temperature is, and further relaxation at 300 K contributes to future crystallization to ~75%. Crystallization is mainly contributed by transformation of amorphous order to FCC order.

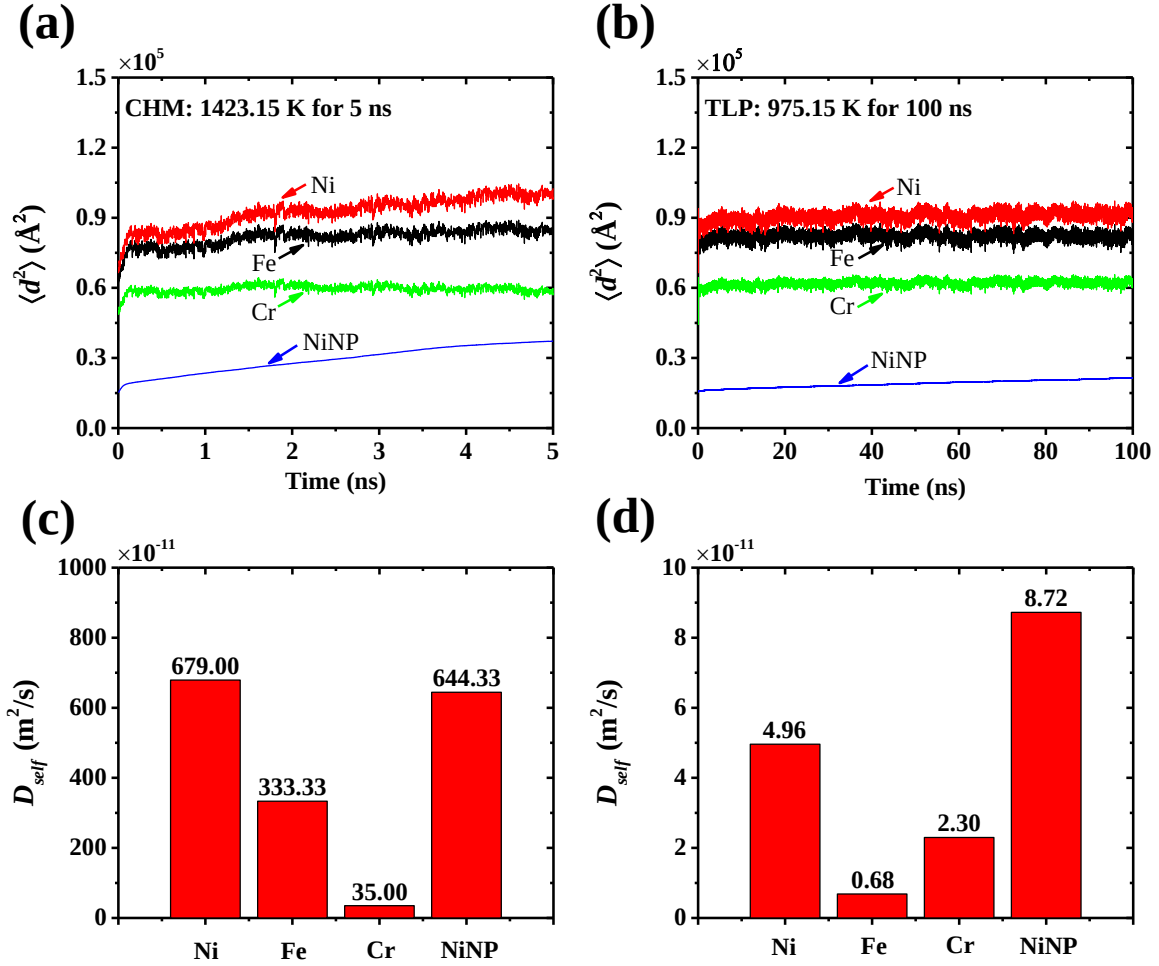


Figure C.7: Mean square displacement ($\langle d^2 \rangle$) of each element and Ni NP during (a) continuous heating method (CHM) and (b) transient liquid phase (TLP) bonding processes. (c) and (d) are self-diffusivities (D_{self} 's) calculated from (a) and (b), respectively.

the Ni and Fe diffuse more readily without lattice constraint. A large D_{self} of Ni NP is found due to the nanoscale size and can possibly contribute to the pore elimination and formation of strong bonding. The D_{self} of Fe is found smaller than that of Cr, i.e., the Fe is the most stable element at 973.15 K, which can be attributed to the high mixing entropy with Ni element in the base material.

The resulting D_{self} of each element at 973.15 K is generally two orders of magnitude smaller than that at 1,423.15 K due to the solid-state diffusion. Thus, diffusion at 973.15 K may be insufficient to achieve high-strength bonding; however, the reduced defects in both base and filler materials at 973.15 K may also improve the mechanical and thermal properties. Therefore, a trade-off between diffusion speed and defects concentration should be compromised, through manipulation of joining temperature, to achieve optimal properties. Arafin et al [229] calculated the D_{self} during brazing of BNi-2 (a Ni-based filler material) to Inconel® 718 at temperatures of 1,325, 1,358, and 1,394 K. Since the temperatures they used are lower than 1,423.15 K, the average D_{self} ($28.20 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 1,395 K) they calculated are smaller than that from this study ($41.50 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), but the values are in the same order of magnitude, and moreover, in this CMD research we report D_{self} of each element, which is very challenging to harvest in experiments.

Microstructure Induced by Different Self-Diffusivities (D_{self} 's)

Due to the discrepancy in D_{self} among the constituent elements, different diffusion scenarios of bonding are expected at different temperatures, which can contribute to formation of various microstructures, and finally affect the mechanical and thermal properties of the joint. Thus, we examine the microstructure and diffusion scenarios at the initial heating stage (time instant D in Figure C.2, 0.06 ns) at a high temperature (1,423.15 K), time instance E after 5 ns of CHM, and time instance F after 100 ns of TLP bonding, as shown in Figure C.8. It is observed that pores have been completely eliminated at 0.06 ns at 1,423.15 K [Figure C.8(a)], due to the high D_{self} of the base material ($\text{Fe}_{27}\text{Ni}_{51}\text{Cr}_{22}$), while the filler material (Ni NPs) does not necessarily contribute to the pore elimination, i.e., especially for the upper Ni NP, only a counter-clockwise rotation is induced by different D_{self} of the surrounding atoms [Figure C.8(b)]. The different diffusion scenarios between the upper Ni NP (counter-clockwise rotation) and lower Ni NP (downwards diffusion) are induced by different D_{self} of surrounding atoms.

The flow-like diffusion of base material mainly contributes to pore elimination; thus, no inter-diffusion of base and filler materials for bonding is observed within 0.06 ns [Figure C.8(c)]. Comparing the subsequent CHM and TLP bonding, clear grain boundaries, which can significantly influence the mechanical and thermal properties, are observed in both final configurations [Figures C.8(d) and C.8(g)]. A nanograin is only left inside the TLP bonding product due to the ordered diffusion (i.e., the atoms diffuse in a specific direction) [Figure C.8(h)], while for CHM, diffusion in the filler region becomes disordered (i.e., the atoms diffuse in random directions) [Figure C.8(e)], resulting that the filler materials share the same crystallographic orientation with the base material [Figure C.8(f)]. The ordered and disordered diffusions are induced by different kinetic energy depending on temperature. For example, at 1,423.15 K, most atoms have sufficient kinetic energy to overcome atomic bonding energy and thus their diffusion is not constrained, i.e., disordered. In contrast, more atoms stay in atomic bonds at 973.15 K; thus, the order in the crystallinity constrains the random diffusion, instead displaying an ordered diffusion. It is also observed in Figure C.8(f) that after 5 ns bonding, the Fe atoms are diffused into the filler material, which could contribute to formation of strong diffusion bonding with the base material; however, inter-diffusion is not clearly observed in the TLP bonding [Figure C.8(i)]. Considering the diffusion properties, crystallinity, defect concentration (grain boundary, amorphization, etc.), and grain size of the joint structure, the mechanical and thermal properties of the joint structures are expected to depend on the bonding conditions, and a more rigorous evaluation of the properties will be conducted in the future.

In addition, understanding of the presented diffusion pathway and joint microstructure in the TLP bonding can be improved by considering the effects of collective diffusion. Relation between tracer diffusion (characterized by D_{self}) and collective diffusion has been studied in recent studies [252, 253, 254] based on the well-known Darken equation [255]. According to the joint atomic structures in Figure C.8, Fe and Ni present more efficient mixing, which reduces a mixing correction factor in the Darken equation [254]. Due to a smaller mixing correction factor, the diffusion of Ni and Fe, both of which possess larger diffusivities than Cr, can be slowed down. However, quantitative analysis of collective diffusion in this ternary system of Fe, Ni, and Cr requires additional, considerable study on thermodynamics with a more elegant design of initial model (including a composition variation) and further extension of the binary Darken equation [253, 254]. Moreover, detailed spatial distribution and gradient of elemental concentration should

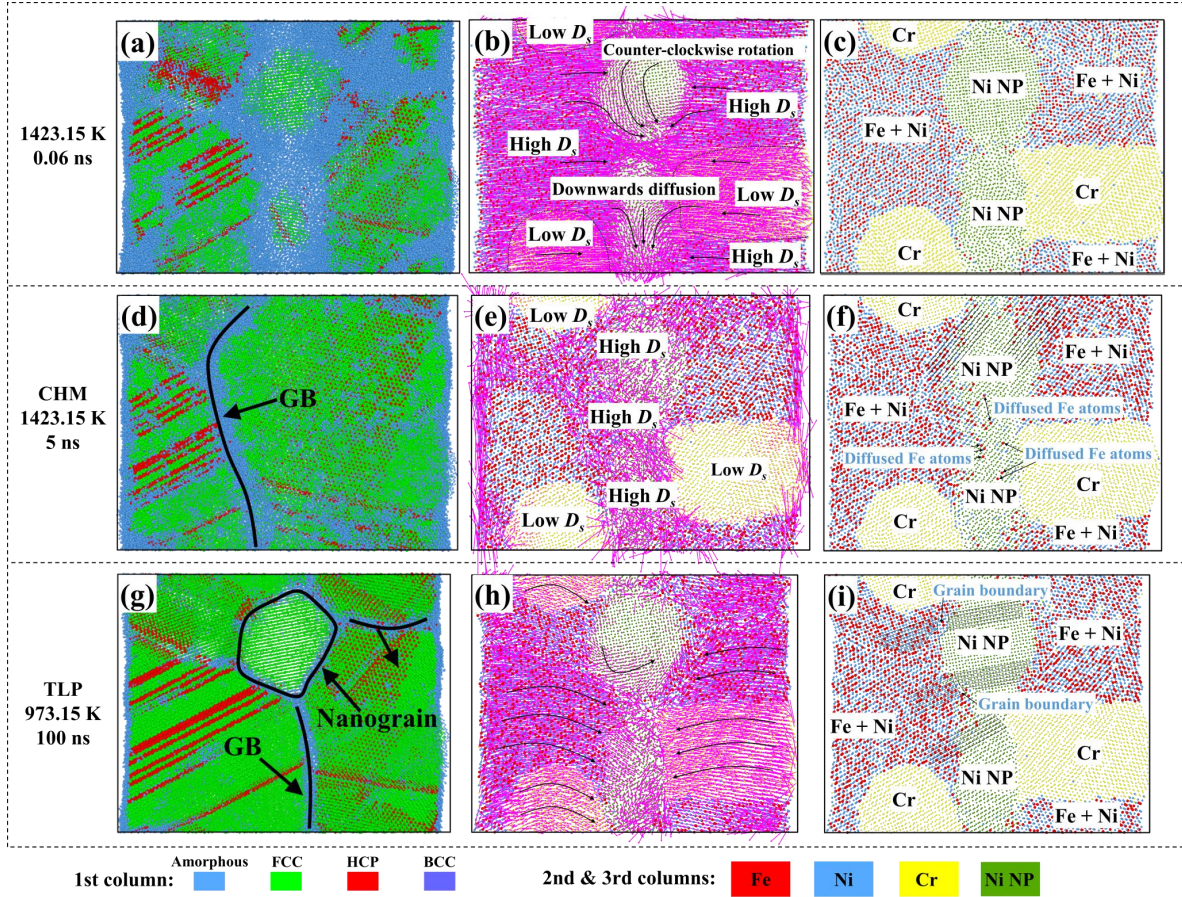


Figure C.8: (a) Microstructure characterized with the ACNA, (b) diffusion scenario, and (c) atomic composition, after initial high temperature joining at 1,423.15 K for 0.06 ns [(a)-(c) are indicated as time instant D in Figure C.2]. (d), (e), and (f) are corresponding microstructure, diffusion scenario, and atomic composition after subsequent continuous heating at 1,423.15 K for 5 ns (at time instant E), while (g)-(i) are those after 100 ns of TLP bonding (at time instant F).

be evaluated to identify the pathway by collective diffusion. Thus, here we suggest the quantitative evaluation of collective diffusion, relation between self- and collective diffusion, and its effects on diffusion pathways as promising future works for more comprehensive understanding of diffusion kinetics in the TLP bonding.

C.4 Conclusions

This research studies the diffusion kinetics of the transient liquid phase bonding of modeled Inconel[®] 718 (Fe₂₇Ni₅₁Cr₂₂, base material) with Ni nanoparticle (NP) filler, employing classic molecular dynamics (CMD) with a reliable interaction potential and simulation methodology. It is confirmed that porosity of brazed structures is reduced as the initial temperature increases, and further joining and relaxation at low temperatures stimulates recrystallization, which would alter the mechanical and thermal properties of joint structure. Self-diffusivity (D_{self}) of each specific element during bonding is calculated in this CMD study, which has not been reported in experiments (only the averaged experimental values are available), and the averaged D_{self} is in a good agreement with the experimental value. The established methodology for D_{self} calculation can be employed in a systematic evaluation of relationship between D_{self} and properties in the future. Diffusion behaviors of filler material are found to be dependent on the diffusivity of surrounding element, which result in different mechanisms of elimination of pores (i.e., by flow-like diffusion of base material or filler material) and formation of joint microstructure (i.e., ordered diffusion forms nanograin, while disordered diffusion induces same crystallographic orientation between the base and filler material). Thus, mechanical and thermal properties of the joint can be tuned by manipulating the atomic surroundings of filler materials. Ni NP and Ni element in the base material are found to have high D_{self} 's in this research, which can contribute to reduce the joining time. A systematical evaluation in effect of temperature and initial alloy structure on the D_{self} , joint microstructure, and mechanical and thermal properties will be further performed in the future to achieve optimal bonding conditions of TLP.

C.5 Supplementary Information

Verification Methodology of Two EAM potentials

In order to verify the robustness of the EAM potentials employed in this research, we calculate thermophysical properties of Inconel® 718 alloy, including solidus (T_S) and liquidus temperature (T_L), linear thermal expansion coefficient (α_L), constant-pressure specific heat capacity (c_p), and latent heat of fusion (ΔH_f). Melting temperature (T_m) of Ni NP with radius of $9a_{\text{Ni}}$ (≈ 3.17 nm, a_{Ni} is lattice constant of Ni, equaling to 0.352 nm) is also calculated. All the verification simulations are implemented with LAMMPS [119], with two different potentials (potential 1 [236] and potential 2 [237]) and identical simulation methodologies are shown as below.

Thermophysical Properties of Inconel® 718 (Base Material)

Constructed Inconel 718 alloy is further relaxed at 300 K for 100 ps, to exclude any effect of structural instability. Then, isothermal heating is applied from 300 K to 2,000 K with increment of 200 K, except from 1,460 K to 1,680 K, an increment of 20 K is applied for accurate determination of ΔH_f , T_S , and T_L using potential energy [84]. The ΔH_f is given by:

$$\Delta H_f = H_L - H_S, \quad (\text{C.2})$$

where H_L and H_S are enthalpy of system in the liquid and solid phase respectively. The enthalpy is obtained by:

$$H = E_{\text{total}} + PV, \quad (\text{C.3})$$

where E_{total} is the total energy of the system, P is the pressure, and V is the volume.

Another two simulations at 280 K and 320 K are run for obtaining averaged enthalpy (H) and cell length in three dimensions (L) over 100 ps, used to determine 300 K c_p and α_L , with the Equation B.1 and B.2, respectively.

Melting Temperature (T_m) of Ni Nanoparticle (Filler Material)

After constructing the Ni NP with radius of $9a_{\text{Ni}}$ using non-periodic boundary condition, the NP is energy-minimized using the conjugate gradient algorithm. Another 100 ps dynamics is run on the

NP after the energy minimization, for further relaxing the NP. Isothermal heating is then applied to NP for 100 ps, in order to achieve the potential energy at each temperature, for determining the T_m . An increment of 200 K is applied from 300 K to 2,000 K (i.e., 300 K, 500 K, 700 K, etc), while for achieving a more accurate identification of T_m , an increment of 10 K is applied from 1,490 K to 1,620 K (1,490 K, 1,500 K, 1,510 K, etc). NVT ensemble (constant atom number, constant volume, constant temperature) is used during the isothermal heating for maintaining a constant temperature.

Journal Publications

- **Jiaqi Wang**, Wenyuan Zhu, Seungha Shin*, “Interfacial Energy and Solute Segregation Energy of θ' -Al₂Cu/Al System”. *In Preparation*, (2020).
- **Jiaqi Wang**, Chengcheng Li, Seungha Shin*, and Hairong Qi, “Accelerated Atomic Data Production in *Ab Initio* Molecular Dynamics with Recurrent Neural Network for Materials Research”. *The Journal of Physical Chemistry C*, in revision, (2020).
- Md Abdullah Al Hasan, **Jiaqi Wang**, Yong Chae Lim, Anming Hu, and Seungha Shin*, “Atomic-scale Concentration Dependence of Hydrogen Diffusion in α -Iron”. *International Journal of Hydrogen Energy*, 44, 27876-27884, (2019).
- **Jiaqi Wang**, Seungha Shin*, Sangkeun Lee, “Interatomic Potential Development: Finite Temperature Dynamics Machine Learning”. *Advanced Theory and Simulations*, 1900210, (2019).
- **Jiaqi Wang**, Ali Y. Nobakht, James Dean Blanks, Dongwon Shin, Sangkeun Lee, Amit Shyam, Hassan Rezayat, Seungha Shin*, “Machine Learning for Thermal Transport Analysis of Aluminum Alloys with Precipitate Morphology”. *Advanced Theory and Simulations*, 1800196, (2019).
- **Jiaqi Wang**, Dongwon Shin, Seungha Shin*, “Comprehensive Evaluation and Parametric Sensitivity of Interatomic Potential Models for Diffusion Kinetics of Cr₂O₃ in Molecular Dynamics”. *AIP Advances*, 9, 015123 (2019).
- **Jiaqi Wang**, Seungha Shin*, Ali Y. Nobakht, Amit Shyam, “Structural Deformation and Transformation of θ' -Al₂Cu Precipitate in Al Matrix via Interfacial Diffusion”. *Computational Materials Science*, 156, 111-120 (2019).

- **Jiaqi Wang**, Seungha Shin*, Anming Hu, Jackson K. Wilt, “Diffusion Kinetics of Transient Liquid Phase Bonding of Ni-based Superalloy with Ni Nanoparticles: A Molecular Dynamics Perspective”. *Computational Materials Science*, 152, 228-235 (2018).
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- **Jiaqi Wang**, Seungha Shin*, “Sintering of Multiple Cu-Ag Core-Shell Nanoparticles and Properties of Nanoparticle-Sintered Structure”. *RSC Advances*, 7, 21607-21617 (2017).
- **Jiaqi Wang**, Seungha Shin*, “Room Temperature Nanojoining of Cu-Ag Core-Shell Nanoparticles and Nanowires”. *Journal of Nanoparticle Research*, 19:53 (2017).
- **Jiaqi Wang**, Seungha Shin*, Anming Hu, “Geometrical Effects on Sintering Dynamics of Cu-Ag Core-Shell Nanoparticles”. *The Journal of Physical Chemistry C*, 120, 17791-17800 (2016).

Conference Presentations/Proceedings

- **Jiaqi Wang**, Seungha Shin*, Ali Y. Nobakht, J. Dean Blanks, Hassan Rezayat, Dongwon Shin, Sangkeun Lee, Amit Shyam, “Thermal Transport Analysis of Aluminum Alloy Using Machine Learning Technique” (presentation). *ASME 2019 Summer Heat Transfer Conference*, Bellevue, Washington, USA, July 14-17, 2019.
- **Jiaqi Wang**, Seungha Shin*, Anming Hu, Jackson K. Wilt, “Molecular Dynamics of Transient Liquid Phase Bonding of Ni-based Superalloy with Ni Nanoparticles” (presentation). *Materials Science & Technology 2018*, Columbus, Ohio, USA, October 14-18, 2018.
- Ali Y. Nobakht, Seungha Shin*, **Jiaqi Wang**, “Asymmetric Thermal Transport by Adjusting Structural Defects” (proceeding). *2018 Joint Thermophysics and Heat Transfer Conference*, Atlanta, Georgia, USA, June 25-29, 2018.
- **Jiaqi Wang**, Seungha Shin*, “Joining of Cu-Ag Core-Shell Nanoparticles and Nanowires at Room Temperature: A Molecular Dynamics study”; “A Molecular Dynamics Study of Geometrical and Temperature Effects on Sintering Dynamics of Cu-Ag Core-Shell Two-Nanoparticles Model”; “Sintering Dynamics and Sintered Structure Properties of Cu-Ag Core-Shell multiple-Nanoparticles Model and Properties of Nanoparticle-Sintered Structures” (presentations), *ASME InterPack 2017*, San Francisco, California, USA, August 29-September 1, 2017.
- **Jiaqi Wang**, Seungha Shin*, “Room Temperature Molecular Dynamics Simulations on the Sintering of Cu-Ag Core-Shell Structures: Nanoparticles and Nanowires” (proceeding). *Materials Science & Technology 2016*, Salt Lake City, Utah, USA, October 23-27, 2016.

- **Jiaqi Wang**, Sheng-Chung Tzeng*, “Experimental Study in Generating Power of Thermo-Electric Conversion System with Novel Porous Medium Heat Absorbers” (proceeding). *The 21st Tri-University International Joint Seminar and Symposium 2014*, Chiang Mai, Thailand, November 2-7, 2014.

Vita

Jiaqi Wang (wftowf@gmail.com) was born in May of 1992, to the parents of Zhujun Wang and Congmei Fu, in Nantong of Jiangsu province in China. He graduated with Bachelor of Science in June of 2015 from Jiangsu University, with a major in Automotive Engineering, and a concurrent Master of Science with a major of Mechanical Engineering from University of Tennessee in May of 2018. He arrived at the United States on July 27, 2015 and initiated his Ph.D. program immediately. His research interest is computational materials science, which primarily employs quantum mechanical simulations and molecular dynamics simulations with assistance of machine learning, for advancing fundamental quantum and nanoscale science. His dream is to become a professor and work on the research field he is or will be interested in for the whole life!