

DEVELOPMENT OF FORCE FIELDS FOR NOVEL 2D MATERIALS FOR TEMPERATURE DEPENDENT VIBRATIONAL PROPERTIES

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DEVELOPMENT OF FORCE FIELDS FOR NOVEL 2D MATERIALS FOR TEMPERATURE DEPENDENT VIBRATIONAL PROPERTIES

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ABSTRACT

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A new era of nanodevice engineering has been started after fabricating graphene. This motivated vast number of researches for predicting, fabricating and utilizing 2D materials. Temperature dependent properties are essential for device applications. Although rigorous density functional theory based approaches are able to predict electronic and mechanical properties accurately, but they are mostly limited to zero temperature and ab initio based molecular dynamics are computationally very demanding. Classical molecular dynamics is a very powerful alternative, however its accuracy is basically depend on the interatomic potential used for describing the considered system and therefore constructing accurate force fields is always an open problem, especially for the emerging 2D materials with extra ordinary properties. Single-layer transition metal dichalcogenides (TMDs) are new class of 2D materials which are shown to be good candidates for thermoelectric applications, flexible electronic and optoelectronic devices. In order to investigate thermal properties of TMDs, Stillinger-Weber type potentials are developed using particle swarm optimization method. These potentials are validated by comparing the resulted phonon dispersion curves and thermal conductivities with available first principle and experimental results. In addition, for understanding the anharmonic effects imposed by the generated force fields the trends of the shifts of the optical phonon frequencies at Γ point with variation in the temperature are compared with available experimental data. In all cases, optimized potentials generate results which are in agreement with the target data. In the second step, spectral energy density method together with phonon mode decomposition is used for obtaining temperature dependent phonon frequencies and lifetimes in entire Brillouin zone. The contribution of each phonon branch in thermal conductivity is predicted utilizing the obtained phonon lifetimes and group velocities within the framework of relaxation time approximation. Eventually, with the aim of constructing transferable potentials for describing 2D

and bulk structures, a very fast and reliable optimization method is presented. Combining local and global optimization methods and utilizing the energy curves obtained from first principle method, novel Stillinger-Weber type potentials for graphene, silicene and group III nitrides are developed. The proposed approach provides a solid framework for parameter selection and investigating the role of each parameter in the resulted phonon dispersion curves.



Keywords: 2D materials, Molecular dynamics, Interatomic potentials, Stillinger-Weber potential, Spectral energy density method, Thermal conductivity .

ÖZET

YENİ 2B MALZEMELER İÇİN ETKİLEŞİM POTANSİYELLERİNİN GELİŞTİRİLMESİ: SICAKLIĞA BAĞLI TİTREŞİM ÖZELLİKLERİ

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Grafen üretimi sonrası yeni bir aygıt mühendisliği dönemi başlamıştır. Bu, 2B malzemeleri öngörmek, üretmek ve kullanmak için yapılan çok sayıda araştırmayı tetiklemiştir. Sıcaklığa bağlı özellikler cihaz uygulamaları için önemlidir. Hassas yoğunluklu fonksiyonel teori temelli yaklaşımlar, elektronik ve mekanik özellikleri doğru bir şekilde tahmin edebilmelerine rağmen, yoğunlukla sıfır derece sıcaklıkla sınırlıdır ve ab initio bazlı moleküler dinamik hesaplamalar hala pahalıdır. Klasik moleküler dinamik çok güçlü bir alternatiftir, ancak doğruluğu temel olarak, dikkate alınan sistemi tanımlamak için kullanılan atomlar arası potansiyelle bağlıdır ve bu nedenle doğru kuvvet alanları oluşturmak, özellikle ekstra sıradan özelliklere sahip yeni çıkan 2B malzemeler için her zaman açık bir problemdir. Tek katmanlı geçiş metali diklorojenitler (TMD), termoelektrik uygulamalar, esnek elektronik ve optoelektronik aygıtlar için iyi aday olduğu gösterilen 2B malzeme sınıfıdır. TMD'lerin termal özelliklerini araştırmak için, ilk olarak, parçacık sürüsü optimizasyonu kullanılarak Stillinger-Weber tipi potansiyeller geliştirilmiştir. Bu potansiyeller, elde edilen fonon dağılım eğrileri ve termal iletkenliklerin mevcut ilk prensip ve deneysel sonuçlarla karşılaştırılmasıyla doğrulanmıştır. Ek olarak, oluşturulan kuvvet alanlarının dayattığı anharmonik etkileri anlamak için, sıcaklık değişimleri ile Γ noktasındaki optik fonon frekanslarının kayma eğilimleri mevcut deneysel verilerle karşılaştırılmıştır. Her durumda, optimize edilmiş potansiyellerin ürettiği sonuçlar, hedef verilerle uyumludur. İkinci adımda, fonon modu ayrışımı ile birlikte spektral enerji yoğunluğu metodu, Brillouin bölgesinin tamamında sıcaklığa bağlı fonon frekansları ve ömürleri elde etmek için kullanılmıştır. Her fonon dalının ısı iletkenliğe katkısı, elde edilen fonon yaşam süreleri ve gevşeme süresi yaklaşımı çerçevesinde grup hızları kullanılarak tahmin edilmiştir.

Sonunda, 2B ve hacimsel yapıları tanımlamak için aktarılabılır potansiyeller oluşturmak amacıyla çok hızlı ve güvenilir bir optimizasyon yöntemi sunulmaktadır. Yerel ve küresel optimizasyon yöntemlerini birleştirerek ve ilk prensip yönteminden elde edilen enerji eğrilerini kullanarak grafen, silisen ve grup III nitridler için yeni Stillinger-Weber tipi potansiyeller geliştirilmiştir. Önerilen yaklaşım, parametre seçimi ve elde edilen fonon dağılım eğrilerindeki her parametrenin rolünün araştırılması için sağlam bir çerçeve sunmaktadır.



Anahtar sözcükler: 2B malzemeler, Moleküler dinamik, Atomlararası potansiyeller, Stillinger-Weber potansiyel, Spektral enerji yoğunluğu yöntemi, Termal iletkenlik .

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Contents

1	Introduction	1
1.1	Lattice Structures of 2D Materials	2
1.1.1	Planar 2D Materials	2
1.1.2	Buckled Single Layer 2D Materials	2
1.1.3	Layered 2D Materials	3
1.2	Why MD?	4
1.3	Diversity in the Reports of Thermal Properties of TMDs	4
1.4	Thesis Organization	6
2	Basics and Theory of Computational Methods	7
2.1	Equations of Motion	7
2.1.1	Thermostats	8
2.2	Force Fields	12
2.2.1	SW Potential	14
2.2.2	Tersoff and Brenner Potentials	16
2.2.3	Vashishta Potential	18
2.3	Particle Swarm Optimization	19
2.4	Methods for Evaluating Thermal Conductivity	20
2.4.1	Direct Method	20
2.4.2	Green-Kubo Method	21
2.4.3	Boltzmann Transport Equation	22
2.5	Determining Phonon Lifetimes and Group Velocities	23
2.6	Spectral Energy Density Method	24
3	Thermal Conductivity of TMDs	25

3.1	Validation of Interatomic Potential for WS ₂ and WSe ₂	25
3.1.1	Computational Details for DFT Calculations	26
3.1.2	Optimizing SW Potential for WS ₂ and WSe ₂	26
3.1.3	Computational Details of the SED Analysis	28
3.1.4	Phonon Frequencies and Lifetimes at Γ Point as a Function of Temperature	30
3.2	Evaluating Thermal Conductivity of TMDs	33
3.2.1	Thermal Conductivity using Green-Kubo Method	33
3.2.2	SED Thermal Conductivity of TMDs	34
4	Optimized Stillinger-Weber Potential for Sample 2D Materials	56
4.1	Isolating Three-body Term of the SW Potential	57
4.2	SW Potential for Graphene	58
4.3	SW Potential for Silicene	63
4.4	SW Potential for Graphene Revisited	70
4.5	SW Potential for Group III Nitrides	74
4.5.1	SW Potential for GaN	76
4.5.2	SW Potential for AlN	83
4.5.3	SW potential for BN	87
5	Conclusions	92

List of Figures

2.1	Two body energies for N-N, Ga-Ga and Ga-N interactions of available SW potential	15
2.2	Phonon dispersions of MoS ₂ obtained from DFT (black lines) and REBO potential	18
3.1	Schematic representations (top and side views) of single layer WS ₂ and WSe ₂ structures.	27
3.2	Vibrational phonon frequencies of WS ₂ and WSe ₂ structures along the high-symmetry paths of the Brillouin zone.	29
3.3	Normalized SEDs and Lorentzian fits for WS ₂	30
3.4	Ratio of phonon frequencies to frequencies at 300 K and linewidths at Γ point as function of temperature for WS ₂ and WSe ₂	31
3.5	Phonon frequencies of WS ₂ and WSe ₂ at Γ as a function of temperature	32
3.6	Full SEDs and mode decomposed SEDs of MoS ₂ at 500 K	35
3.7	Full SEDs and mode decomposed SEDs of MoSe ₂ at 500 K	35
3.8	Full SEDs and mode decomposed SEDs of WS ₂ at 500 K	36
3.9	Full SEDs and mode decomposed SEDs of WSe ₂ at 500 K	36
3.10	Phonon dispersions of 2D WS ₂ , WSe ₂ , MoS ₂ and MoSe ₂ structures calculated at different temperatures.	37
3.11	The calculated phonon lifetimes by SED approach at 300 K.	38
3.12	Phonon lifetime of as function of frequency for MoS ₂	40
3.13	Phonon lifetime of as function of frequency for MoSe ₂	41
3.14	Phonon lifetime of as function of frequency for WS ₂	42
3.15	Phonon lifetime of as function of frequency for WSe ₂	43

3.16	The magnitude of the group velocities at 300 K.	44
3.17	Contribution of different modes to the room temperature lattice thermal conductivity.	45
3.18	Temperature dependence of the contribution of acoustic modes to the lattice thermal conductivity.	46
3.19	The lattice thermal conductivity values as a function of temperature	47
3.20	The calculated phonon lifetimes by SED approach at 100 K . . .	48
3.21	The magnitude of calculated phonon group velocities by SED approach at 100 K	49
3.22	The calculated phonon lifetimes by SED approach at 200 K . . .	50
3.23	The magnitude of calculated phonon group velocities by SED approach at 200 K.	51
3.24	The calculated phonon lifetimes by SED approach at 400 K. . . .	52
3.25	The magnitude of calculated phonon group velocities by SED approach at 400 K	53
3.26	The calculated phonon lifetimes by SED approach at 500 K. . . .	54
3.27	The magnitude of calculated phonon group velocities by SED approach at 500 K	55
4.1	Results of the fitting of DFT data for graphene.	59
4.2	Phonon dispersion curves obtained from the SW potential parametrized by fitting energy curves compared with DFT results and experimental data.	60
4.3	Effect of the change of the $\cos \theta_{0,ijk}$ on phonon dispersion.	61
4.4	Phonon dispersion curves obtained from SW potential with optimized $\cos \theta_{0,ijk}$	62
4.5	Results of the fitting of DFT data for silicene.	64
4.6	Phonon dispersion curves for silicene obtained from the SW potential parametrized by fitting energy curves and available SW potential.	65
4.7	Effect of variation of the three-body parameter λ on the phonon dispersion in silicene.	67
4.8	Effect of variation of the two-body parameter A on the phonon dispersion in silicene.	68

4.10	Phonon dispersion curves for silicene obtained from the optimized SW potential and available SW potential.	68
4.9	Energy curves obtained from the optimized parameters and DFT for silicene.	69
4.11	Phonon dispersion curves for silicene obtained from the SW potential parametrized using valence force field and Terssof potential.	70
4.12	Effect of variation of the three-body parameter λ on phonon dispersion in graphene.	71
4.13	Phonon dispersion curves for graphene obtained from the optimized SW potential and Terssof potential.	72
4.14	Phonon dispersion curves for graphene obtained from the optimized SW potential and LCBOP potential.	73
4.15	Unit cell of the zinc blende structure.	75
4.16	Results of the fitting the DFT data and phonon dispersion curves of monolayer GaN.	76
4.17	Effect of selecting different three-body parameter λ for Ga-N-N and N-Ga-Ga interactions on the phonon dispersion curves of GaN.	77
4.18	Phonon dispersion curves of monolayer GaN obtained from SW potential.	78
4.19	Phonon dispersion for bulk GaN from different potentials.	79
4.20	Results of particle swarm optimization for energy curves of monolayer and bulk GaN.	80
4.21	Phonon dispersions for bulk and monolayer GaN obtained from optimized SW potential.	81
4.22	Results of the fitting of DFT data and phonon dispersion curves of monolayer AlN.	84
4.23	Results of particle swarm optimization for the energy curves of monolayer and bulk AlN.	85
4.24	Phonon dispersion for bulk and monolayer AlN obtained from optimized SW potential.	85
4.25	Results of the fitting of DFT data and phonon dispersion curves of monolayer BN.	87

4.26	Phonon dispersions for bulk and monolayer BN obtained from SW potential optimized for monolayer.	88
4.27	Results of particle swarm optimization for energy curves of monolayer and bulk BN.	89
4.28	Phonon dispersion for bulk and monolayer BN obtained from optimized SW potential.	90



List of Tables

1.1	Available temperature coefficients for the E_g^1 mode of TMDs from different experiments are presented($\text{cm}^{-1}\text{K}^{-1}$).	5
3.1	Two-Body Stillinger-Weber parameters in GULP format.	27
3.2	Three-Body Stillinger-Weber parameters in GULP format.	28
3.3	Lattice parameters and mechanical properties of WS_2 and WSe_2 obtained from optimized SW potential	28
4.1	Lattice constant(a (Å)) and buckling value (B (Å)) of silicene obtained from different SW potentials.	66
4.2	Two sets of optimized SW parameters for silicene.	67
4.3	Three sets of optimized SW parameters for graphene.	74
4.4	Lattice constants of bulk and monolayer GaN obtained from optimized SW compared with DFT.	82
4.5	Sets of the optimized SW parameters for GaN.	82
4.6	Defect energies obtained from optimized SW potential for monolayer GaN.	83
4.7	Sets of the optimized SW parameters for AlN.	86
4.8	Lattice constants of bulk and monolayer AlN obtained from optimized SW compared with DFT.	86
4.9	Sets of the optimized SW parameters for BN.	90
4.10	Lattice constants of bulk and monolayer BN obtained from optimized SW compared with DFT.	91

Chapter 1

Introduction

Isolation of single layer of carbon atoms arranged in honeycomb structure named as graphene [1] followed by experimental and theoretical confirmations of its distinguished properties from the bulk phases [2, 3] has opened new door in nano device engineering. Thereafter, many of two dimensional materials are predicted theoretically [4] and some of them are already synthesized. Most of the 2D materials are proven to be promising candidates for device applications. These materials can be categorized by considering the number and type of elements or according to their lattice structures. The main aim of this chapter is clarifying the importance of the molecular dynamics (MD) simulations. Since the force fields used in MD are mostly depend on the lattice structures, here we first categorize 2D materials based on their topography. Then, we elaborate the importance of MD simulations. Finally, by giving a brief review of previous studies on transition metal dichalcogenides we illustrate the necessity of the present work.

1.1 Lattice Structures of 2D Materials

1.1.1 Planar 2D Materials

Planar two dimensional structures are mostly formed by single layer of atoms in hexagonal lattice similar to graphene. Hexagonal Boron Nitride (h-BN) is another planar two dimensional (2D) material, contrary to the graphene it has an intrinsic band gap, however being an insulator restricts its applications especially for electronics. Its band gap can be controlled by different methods such as changing the number of layers or doping, but due to large band gap it is more suitable for dielectric applications [5, 6]. The other examples of planar 2D hexagonal materials are experimentally synthesized bismuthene [7] and theoretically predicted Si_2BN [8]. Due to spin orbit coupling bismuthene possesses a band gap about 800 meV and is a good candidate for a high-temperature quantum spin Hall application. Metallic Si_2BN is a promising candidate for hydrogen storage because Si makes the surface more reactive than graphene.

1.1.2 Buckled Single Layer 2D Materials

Fabrication of graphene motivated the researches for searching single layers from the elements of the same group. A theoretical study showed the stability of buckled hexagonal 2D Si and Ge structures [9] and also fluorinated graphene-like sheets from group IV [10]. Despite of theoretical prediction, there were arguments against fabrication of such structure because contrary to carbon Si does not have layered allotrope like graphite. Afterwards, the formation mechanism of silicite [11] is theoretically explained by dumbbell reconstruction in silicon [12]. The silicene field-effect transistors operating at room temperature are already fabricated [13]. 2D allotrope of germanium is also fabricated [14, 15]. All of the aforementioned materials have honeycomb structures. Single layer of black phosphorus named as phosphorene is an example of different type of 2D material which is already fabricated [16]. This material has a band gap and high electron

mobility and therefore is more promising than graphene for semiconductor applications. There are many other fabricated or predicted buckled 2D structures such as predicted monolayers from group II-VI semiconductors [17].

1.1.3 Layered 2D Materials

The other possible class of 2D structures are layered structures mostly consisted of three layers with low thickness. Transition metal dichalcogenides (TMDs), MX_2 (where M stands for transition metal atom, and $X = S, Se, Te$), consist of a metal layer sandwiched between two layers of chalcogen atoms. They are proven to possess properties such as low thermal conductivity [18–21], intrinsic band gap and chemical versatility [22] that makes them ideal candidates for vast range of applications such as thermoelectric [23, 24], field effect transistors [25, 26], catalysis [22] and optoelectronic devices [27]. Thermal and mechanical properties are crucial in any device applications and they fundamentally depend on phonon properties. A part of this thesis is devoted to investigation of phonon properties of TMDs based on classical molecular dynamics where the accuracy of the force field used to describe inter-atomic interactions plays an important role. Therefore, optimizing potentials for MD is the other target of the thesis. The other emerging layered 2D structures are transitional metal carbide and nitrides which are named MXenes (M stands for transition metal and X is carbon or nitrogen). They are fabricated by etching from the layered bulk MAX phases where A is an element commonly from the group IIIA or IVA. MXenes are proven to be good candidates in applications such as: photo-catalyst for water splitting [28] and field effect transistors [29]. MABs (B stands for bor) phases are ternary borides similar to MAX phases and series of these types of materials are fabricated by arc-melting [30]. Thereafter, stability of series of MBenes are theoretically predicted and it is shown that MnB is a 2D ferromagnet with high Curie temperature [31]. The monolayer MoB as the first synthesized MBene is recently reported [32].

1.2 Why MD?

Density functional theory(DFT) facilitates accurate investigation of phonon properties but it is basically limited to zero temperature. Apart from the phonon dispersion, before the recent work [33] the evaluation of thermal conductivity based on Green-Kubo method was assumed to be impossible based on DFT methods. Besides, DFT based MDs are computationally very expensive and it is almost impossible to use such techniques in studying systems consisted of large number of atoms.

First principle methods based on iteratively solving the Boltzmann equation are mainly dealing with perfect crystal lattice well below the melting point and neglecting the repelling behavior that stabilize 2D structures.

From the experimental point of view, there are many factors that can affect experimental results for thermal conductivity such sample size, supporting material, sample quality and even laser spot size [34] in commonly used Raman methods. Classical molecular dynamics (MD) simulation is a powerful alternative that is capable of solving all of the aforementioned problems. Within this framework and utilizing a fairly accurate inter-atomic force field, it is possible to study anharmonic effects, defected structures and the role of the substrates which are not easily accessible in experiments or other theoretical methods. Furthermore, utilizing spectral energy density (SED) method [35] incorporated with phonon mode decomposition, it is possible to access contribution of each phonon modes in thermal conductivity and the distribution of phonon life times in the Brillouin zone which provides basis for controlling thermal conductivity.

1.3 Diversity in the Reports of Thermal Properties of TMDs

Single and multilayer of TMDs as well as their heterostructures are already fabricated [25, 36–41]. All of them are proven to possess band gap and being a semiconductor contrary to gapless graphene and insulator h-BN. Furthermore,

semiconductor to metal transitions caused by substrates [42], indirect-to-direct band gap with number of layers [43] and tunable spin and valley degrees of freedom [44] in TMDs are already pointed out. These flexibilities make TMDs capable of being used in vast range of devices which motivated many studies of their mechanical and thermal proprieties. It is already shown that TMDs have small thermal conductivities, for example the reported values for single and double layers of WS_2 are $32.0 \text{ Wm}^{-1}\text{K}^{-1}$, and $53.0 \text{ Wm}^{-1}\text{K}^{-1}$ [20] respectively and ultra-low cross-planar thermal conductivity is reported for disordered WSe_2 [45]. The other reports show the same behavior in other TMDs [18, 19, 21, 46]. The main issue is diversity of the reports in the experiments. For instance, the thermal conductivity of MoS_2 using confocal micro-Raman method is reported as $34.5 \text{ Wm}^{-1}\text{K}^{-1}$ [18] but other study in vacuum condition gives this value as $13.3 \text{ Wm}^{-1}\text{K}^{-1}$ [47]. The other important quantity is the temperature coefficient which shows the amount of the shift in phonon frequencies with variation of temperature. Some of the reports for this quantity obtained from different experiments for E_g^1 are summarized in Table 1.1.

Table 1.1: Available temperature coefficients for the E_g^1 mode of TMDs from different experiments are presented ($\text{cm}^{-1}\text{K}^{-1}$).

MoS₂	-0.014 ^a	-0.016 ^b	-0.013 ^c	-0.008 ^d
MoSe₂	-0.012 ^a	-0.005 ^c		
WS₂	-0.006 ^e	-0.0121 ^f		
WSe₂	-0.003 ^c	-0.009 ^a		

^a Reference [48].

^b Reference [49].

^c Reference [50].

^d Reference [51].

^e Reference [52].

^f Reference [53].

From the Table 1.1 it is clear that different experimental conditions highly affect the reported values. From the theoretical point of view one of the main issues in first principle based studies on Boltzmann equation is the sample size which is systematically investigated for vast types of TMDs [46]. The studies of TMDs based on classical MD are limited in the literature mainly because of the lack of accurate force fields for TMDs. This issue is explained in details and

resolved in chapter three of the thesis by presenting optimized parameters for TMDs. Although, there are some works on optimizing potentials and evaluating thermal conductivities that will be mentioned during the next chapters of the thesis, but there is only one report based SED which only considers the phonon shifts at Γ point [54]. In this work phonon lifetimes and frequencies in entire Brillouin zone is considered which leads to results that shed more light on the thermal properties of these 2D crystals.

1.4 Thesis Organization

In this chapter, we illustrated the capability of classical MD in investigation of 2D structures. The forthcoming chapters are organized as follows. In the second chapter the backbones of classical MD are described by explaining methods of coupling the system with external pressure and temperature, methods of integrating resulted equation of motions, the interatomic interaction descriptors, methods for the optimization of the potential parameters and methods for evaluating the thermal conductivity. In chapter three the results of evaluated lifetimes and phonon frequencies at different temperatures as well as contribution of each phonon mode in thermal conductivity for TMDs are presented. Chapter four is devoted to parametrization of Stillinger-Weber (SW) type potential by an approach which combines local and global optimizations. In the final chapter all results of this research are summarized.

Chapter 2

Basics and Theory of Computational Methods

2.1 Equations of Motion

The basic formulation of the classical mechanics is the Newton's second law. For a system of N interacting particles, it generates N second order differential equations which are reducible to $2N$ first order equations. This set of equations can be obtained using Lagrangian or Hamiltonian approaches as well. By setting a proper set of initial conditions and using suitable method for integration, the energy of the system will be preserved during the time evolution resulting a microcanonical (NVE) ensemble. However, in the realistic situations where experiments are carried on, usually the temperature of the environment is adjusted. Therefore, constructing formalism for creating a canonical (NVT) ensemble was the one the first problems of this field. In the canonical ensemble the volume of the system is fixed, but in most cases external pressure plays a crucial role, especially in the case of solids where the cell shape can be variable. Therefore, controlling the pressure of the system is the other important task. These are achieved by introducing thermostats and barostats. There are several methods presented in the literature for considering the effect of the external pressure and

temperature. Here we briefly explain the main and widely used approaches in classical MD.

2.1.1 Thermostats

One of the main properties of any method used for controlling temperature is the ability of preserving the ergodicity. In the Langevin method, this is achieved by using a stochastic approach [55]. A heat bath is considered to be consisted of fictitious particles and the kinetic energy of the actual particles are controlled by their collision with heat bath particles. The equation of motions are:

$$\begin{aligned}\dot{\vec{r}}_i &= \frac{\vec{p}_i}{m_i} \\ \dot{\vec{p}}_i &= \vec{F}_i - \gamma \vec{p}_i + \vec{F}_{L_i}(t)\end{aligned}\tag{2.1}$$

Where, $\dot{\vec{r}}_i$, $\dot{\vec{p}}_i$ and m_i are the position, momentum and the mass of the the i 'th particle, respectively. The viscous damping is considered by parameter γ . $\vec{F}_i$ is the external force and $\vec{F}_{L_i}(t)$ is the force exerted on particle in collision with heat bath particles and has the following properties:

$$\begin{aligned}\left\langle \vec{F}_{L_i}(t), \vec{F}_{L_i}(t') \right\rangle &= 2k_B T \gamma m_i \delta(t - t') \\ \left\langle \vec{F}_{L_i}(t) \right\rangle &= 0\end{aligned}\tag{2.2}$$

Here, k_B is the Boltzmann constant and T is the temperature. The first approach for generating canonical approach in deterministic and time reversible manner is presented by Nosé [56] and later improved by Hoover [57]. The main idea is to introduce explicitly extra degrees of freedom to the system. For a system with d spatial dimensions, the equation of motions of Nosé -Hoover chain (NHC) [58]

are:

$$\begin{aligned}
\dot{\vec{r}}_i &= \frac{\vec{p}_i}{m_i} \\
\dot{\vec{p}}_i &= -\vec{F}_i - \frac{p_{\chi_1}}{Q_1} \vec{p}_i \\
\dot{\chi}_j &= \frac{p_{\chi_j}}{Q_j} \quad j = 1, \dots, M \\
\dot{p}_{\chi_1} &= \left[\sum_i^N \frac{p_i^2}{m_i} - dNk_B T \right] - \frac{p_{\chi_2}}{Q_2} p_{\chi_1} \\
\dot{p}_{\chi_j} &= \left[\frac{\dot{p}_{\chi_{j-1}}^2}{Q_{j-1}} - k_B T \right] - \frac{p_{\chi_{j+1}}}{Q_{j+1}} p_{\chi_j} \quad j = 2, \dots, M \\
\dot{p}_{\chi_M} &= \left[\frac{\dot{p}_{\chi_{M-1}}^2}{Q_{M-1}} - k_B T \right]
\end{aligned} \tag{2.3}$$

Where χ_j and p_{χ_j} are the position and momentum of the heat bath. Q is called heat bath mass and must be chosen carefully, because it controls the time required for temperature to equilibrate. In the cases where the time scale of the system is known as t_s , the optimum choice for heat bath masses are [58]:

$$\begin{aligned}
Q_1 &= dNk_B t_s \\
Q_j &= k_B T t_s^2
\end{aligned} \tag{2.4}$$

Otherwise, a reasonable choice is $t_s > 20\Delta t$, where Δt is the time step. The chaining scheme is imposed in order to assure the canonical behavior of the system. A single thermostat fails to establish NVT ensemble correctly.

2.1.1.1 External Pressure and Stress

As it is mentioned before, it is desired to consider variable volume and shape for simulation cell. In the later work by Hoover [59], he tried to use the similar method of thermostating to construct a barostat. But he failed to generate isothermal-isobaric (NPT) partition function. Motivated by this, Martyna et

al [60] introduced a set of equations for generating NPT ensemble considering the most general case of the anisotropic fluctuations of volume. In their method, a cell matrix h is defined using three cell vectors $\vec{A}$, $\vec{B}$ and $\vec{C}$ which form a complete right handed basis. Explicitly h is given by:

$$h = \begin{pmatrix} A_x & B_x & C_x \\ A_y & B_y & C_y \\ A_z & B_z & C_z \end{pmatrix} \quad (2.5)$$

There are only six parameters required to define all elements of the matrix h . They are the lengths of the three lattice vectors and three angles between them. The volume of the cell can be obtained from:

$$\Omega = \det(h) \quad (2.6)$$

A momentum is assigned to volume which is given by:

$$\frac{p_g}{W_g} = \dot{h}h^{-1} \quad (2.7)$$

Where W_g is the time scale parameter. Using these arguments they showed that the internal pressure of the system can be obtained as follows:

$$P_{\alpha\beta}^{\text{int}} = \frac{1}{\Omega} \sum_{i=1}^N \left(\frac{p_{i\alpha} p_{i\beta}}{m_i} + F_{i\alpha} r_{i\beta} \right) \quad (2.8)$$

There are cases where the interatomic potential might explicitly depend on the cell volume. One important example is the potentials with long range interactions where the interactions beyond the first nearest neighbors are considered. In such cases this correction must be added to equation:

$$-\frac{1}{\Omega} \sum_{\gamma=1}^3 \frac{\partial \phi(\vec{r}, h)}{\partial h_{\alpha\gamma}} \gamma_\beta \quad (2.9)$$

In another work, the effect of the external stress is taken into account by Parrinello and Rahman [61]. These two approaches are combined with NHC approach by Shinoda et al [62]. For a system with N_d degrees of freedom the resulted equations

of motion are:

$$\begin{aligned}
\dot{\vec{r}} &= \frac{\vec{p}_i}{m_i} + \frac{p_g}{W_g} \vec{r}_i, \\
\dot{\vec{p}}_i &= \vec{F}_i - \frac{p_g}{W_g} \vec{p}_i - \frac{1}{N_d} \frac{Tr(p_g)}{W_g} \vec{p}_i - \frac{p_x}{Q} \vec{p}_i \\
\dot{h} &= \frac{p_g}{W_g} h \\
\dot{p}_g &= \Omega (P^{int} - IP^{ext}) - h \Sigma h^T + \left(\frac{1}{N_d} \sum_{i=1}^N \frac{p_i^2}{m} \right) I - \frac{p_{x1}}{Q_1} p_g \\
\dot{\chi}_k &= \frac{p_{\chi k}}{Q_k} \quad k = 1, \dots, M \\
\dot{p}_\chi &= \sum_{i=1}^N \frac{p_i^2}{m} + \frac{1}{W_g} Tr [p_g^T p_g] - (N_f + d^2) k_B T^{ext} - p_{\chi 1} \frac{p_{\chi 2}}{Q_2} \\
\dot{p}_{\chi k} &= \left[\frac{\dot{p}_{\chi k-1}^2}{Q_{k-1}} - k_B T^{ext} \right] - \frac{p_{\chi k+1}}{Q_{k+1}} p_{\chi k} \quad k = 2, \dots, M \\
\dot{p}_{\chi M} &= \left[\frac{\dot{p}_{\chi M-1}^2}{Q_{M-1}} - k_B T^{ext} \right]
\end{aligned} \tag{2.10}$$

Where, I is the identity matrix and the effect of external stress, S , is taken into account by the term Σ which is given by:

$$\Sigma = (h_0^{-1}) (S - IP^{ext}) \left((h_0^T)^{-1} \right) \tag{2.11}$$

Where h_0 is the reference cell matrix. All NVE, NVT and NPT ensembles can be obtained from this set of equations. The internal pressure has the same expressions as equations 2.8 and 2.9. All MD calculations of this work have been carried out using the LAMMPS program [63, 64] which uses equations of motion of Equation 2.10.

2.1.1.2 Verlet Algorithm

The integration method used in this work is velocity Verlet algorithm [65] where the positions and velocities of the particles are obtained by:

$$\begin{aligned}\vec{r}_i(t + \Delta t) &= \vec{r}_i(t) + \vec{v}_i(t) \Delta t + \frac{\vec{F}_i(\vec{r}_i(t), t)}{2m} (\Delta t)^2 \\ \vec{v}_i(t + \Delta t) &= \vec{v}_i(t) + \frac{\Delta t}{2m} \left(\vec{F}_i(\vec{r}_i(t), t) + \vec{F}_i(\vec{r}_i(t + \Delta t), t + \Delta t) \right)\end{aligned}\tag{2.12}$$

In this from, the potential is assumed to be only explicitly depend on the positions, which is the case for empirical potentials used in this study. An explicit velocity Verlet integrator for 2.10 without applied stress is presented in [60].

2.2 Force Fields

The main reason of using classical MD is simplifying the quantum mechanical problem and designing the mathematical form for describing inter-atomic interactions which is the most important problem in this field. The force field must be able to give a fairly accurate results in reasonably less time than it is required for solving the exact problem. In the case of crystal structures there is an additional requirement that the force field should have some level of flexibility in order to be used for different phases of considered material. The current state-of-art in designing force descriptors are machine learning potentials that are parametrized by considering many crystal phases of a material so they generate almost exact results for phonon properties and consequently mechanical and thermal properties. The main concern of machine learning potentials is modeling the Born-Oppenheimer potential energy surface of a set of atoms without explicitly considering electrons [66]. With this aim, the total energy of atoms is considered as the sum over atomic energies:

$$E = \sum_i^{atoms} \varepsilon(\vec{r}_i)\tag{2.13}$$

Which gives a direct relation between the atomic configuration and its energy without any approximation apart from those included in obtaining ab-initio data [67]. In the first step of constructing machine learning potentials, the atomic positions need to be transformed to a set of coordinates suitable as input for the machine learning method. The atomic energy function is invariant under translation, rotation and the permutation of atoms. One of the key issues is to represent atomic neighborhoods in a transformed system of coordinates that accounts for these symmetries. There are different methods to this, such as neural network representation [68], bispectrum of the neighbor density [66] and smooth overlap of atomic positions [69]. There are different type machine learning potentials used in the literature such as Gaussian approximation potential (GAP) [66, 70], artificial neural networks [71] and spectral neighbor analysis potential [72]. A recent study used GAP for silicon [73] and obtained results for many properties including phonon dispersions for both acoustic and optical modes in very good agreement with DFT results. However, applications of machine learning potentials are very limited. The main reasons are the amount of the required target data and most importantly the complexity of the used potentials. Empirical(analytical) potentials are good alternatives to aforementioned approach. The main idea of empirical potentials is considering the total energy as the result of two-body and three-body or higher order interactions which all of them can be written as function of distances between pairs of atoms and usually predefined cutoff distances are assumed. In this framework, there are three main categories of potentials. The first types are those which are consisted of the separated two and there body interactions such as SW [74] and Vashishta potentials [75–77]. The second types are those that consider a pairwise interactions which are affected by the neighboring atoms in the distance less than the assumed cutoff. These potentials are known as the bond order potentials (BOP). The broadly used BOPs are Tersoff [78–80] and Brenner potentials [81]. The third types, consider many body interactions in a collective manner and usually are functional of the electronic density and therefore are more suitable for describing metals [82, 83]. The initial motivation in constructing empirical potentials was describing vast range of configurations in crystalline forms as well as their melting behaviors. However, after emerging 2D materials, the demand for thermal and mechanical properties

inspired the researchers to optimize the parameters of the potentials for this new class of materials to consider the near equilibrium configurations which are more related to phonon dispersion and mechanical properties. SW potential is used in this research, but in the fourth chapter we present an optimizing method for SW potential which can be generalized to other potentials with similar forms. Therefore, here we give basic formulation of these kinds of potentials.

2.2.1 SW Potential

SW potential is initially designed in order to describe solid and liquid phases of Si [74]. The main idea was to consider a two-body term ϕ_2 , which describes the bond stretching and a three-body term ϕ_3 , which describes bond bending, together to span the entire configuration space. The simple form of this potential and its ability in giving good description of thermal properties makes it very favorable and there are many works based on this potential which will be mentioned in forthcoming chapters. The general form of SW potential can be written as:

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad (2.14)$$

$$\phi_2(r_{ij}) = A_{ij} \left(\frac{B_{ij}}{r_{ij}^4} - 1 \right) \exp \left[\frac{\rho_{ij}}{r_{ij} - r_{ij}^{max}} \right] \quad (2.15)$$

$$\begin{aligned} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = & K_{ijk} \exp \left[\frac{\rho_{ij}}{r_{ij} - r_{ij}^{max}} \right. \\ & \left. + \frac{\rho_{ik}}{r_{ik} - r_{ik}^{max}} \right] (\cos \theta_{ijk} - \cos \theta_{0,ijk})^2 \end{aligned} \quad (2.16)$$

Where the radius r^{max} restricts the number of the atoms which are considered in the summation. This cutoff value plays an important role in the simulation time and by increasing the cutoff more neighbors will be considered so the computation time will be increased. Usually, this value is selected to be slightly smaller than the second nearest neighbor atom. Furthermore as it is shown in [84], the actual

cutoff of the SW potentials falls even before the theoretically introduced cutoff r^{max} . Since a part of the results of the current research is optimizing parameters for nitrides here we give further explanation for the effect of cutoff. With this aim in Figure 2.1 the two body terms of the widely used SW potential of GaN [85] are shown.

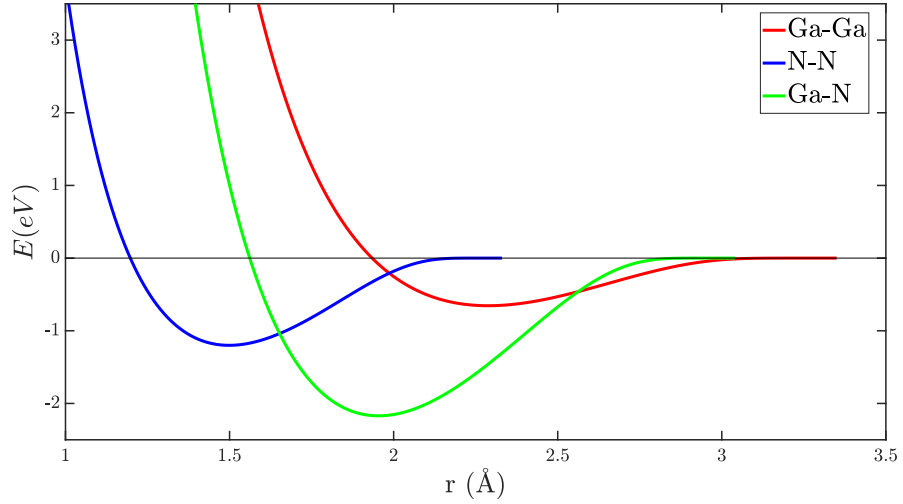


Figure 2.1: Two body energies for N-N, Ga-Ga and Ga-N interactions of SW potential [85].

The lattice constant of the relaxed structure using this potential is 3.19 Å and as it is clear from Figure 2.1 that at equilibrium N-N and Ga-Ga interactions do not contribute in the energy. These interactions are included to study point defects. Therefore, it is possible to neglect these interactions in parameterizing potentials for studying the phonon properties. The other important factor in this potential is the $\cos \theta_{0,ijk}$. In the original work this value is selected as $-\frac{1}{3}$ to consider ideal tetrahedron angle as the most favorable bond angle. This causes the diamond structure to be the ground state of Si. Following this, authors use the same angle in parameterizing or they use the equilibrium angle of the considered structures. This choice works in most cases. A recent work shows that within this scope SW is not able to describe the simple planar materials such graphene and h-BN [86]. This issue is resolved in the fourth chapter of this thesis by presenting a method for deducing three-body term independently. In addition, we show that even in

the case of tetrahedron structures the equilibrium angle is not the best choice.

2.2.2 Tersoff and Brenner Potentials

Tersoff potential [78–80] is a bond order potential and introduced to describe wide range of covalent bonding geometries of silicon where three body potentials were not able to give accurate results. The main argument in constructing this potential is that the bonds become weaker by increasing the number of neighbors. Therefore, this is taken into account in the potential by introducing a bond order term and the interatomic potential is given by:

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} V_{ij} \quad (2.17)$$

$$V_{ij} = f_C(r_{ij}) (f_R(r_{ij}) + b_{ij} f_A(r_{ij})) \quad (2.18)$$

Where f_C is the cutoff function given by:

$$f_C(r) = \begin{cases} 1 & \text{if } r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2} \frac{r-R}{D}\right) & \text{if } R - D < r < R + D \\ 0 & \text{if } r > R + D \end{cases} \quad (2.19)$$

The value of R is selected to consider only the first nearest neighbor. The cutoff function has continuous derivatives for all r . The f_R and f_A are repulsive and attractive two body potential and have the following forms:

$$f_R(r) = A \exp(-\lambda_1 r) \quad (2.20)$$

$$f_A(r) = B \exp(\lambda_2 r) \quad (2.21)$$

The bond order is introduced by b_{ij}

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-\frac{1}{2n}} \quad (2.22)$$

The function ζ_{ij} counts the number of bonds to atom i and considers three body term by flowing expression:

$$\zeta_{ij} = \sum_{k \neq i, j} f_C(r_{ik}) g(\theta_{ijk}) \exp(\lambda_3^m (r_{ij} - r_{ik})^m) \quad (2.23)$$

$$g(\theta) = \gamma_{ijk} \left(1 + \frac{c^2}{d^2} - \frac{c^2}{(d^2 + (\cos(\theta_{ijk}) - \cos(\theta_0)))} \right) \quad (2.24)$$

Tersoff potential is one of the widely used potentials and it is parameterized for SiC and SiGe by Tersoff [79, 80]. Later it is parametrized for describing phonon dispersions and thermal conductivity of graphene [87]. Also, this potential is available for h-BN [88]. The other widely used bond order potential is adaptive intermolecular reactive empirical bond order potential (AIREBO) which is designed for describing hydrocarbons [89, 90]. The general form of this potential is given by:

$$E = \frac{1}{2} \sum_i \sum_{j \neq i} \left(E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k \neq i} \sum_{l \neq i, j, k} E_{kijl}^{TORSION} \right) \quad (2.25)$$

Where E_{ij}^{REBO} is the reactive empirical bond order (REBO) potential which is initially introduced by Brenner [91] based on Tersoff approach and later generalized for correctly describing bond creating and breaking in hydrocarbons [81], E_{ij}^{LJ} is a 12-6 Lennard-Jones potential multiplied by universal switching function added to give better description of intermolecular interactions. The torsion term is dependent on dihedral angles and added for putting a barrier to rotation about single bonds and simulating saturated hydrocarbons larger than methane. Later, it is shown that the singular LJ potential fails to describe the systems at high pressure due to unphysical divergent power law repulsion and the LJ potential replaced by Morse potential [90]. Recently, REBO potential is optimized for describing graphene [92]. A REBO type potential is introduced for Mo-S systems [93] and used for investigating anharmonicity of optical modes in MoS₂ [54]. In Figure 2.2 the phonon dispersion obtained from this potential are compared with the DFT results.

From Figure 2.2 it is clear that the potential fails to describe the phonon dispersions accurately and can not give sufficient description for thermal conductivity.

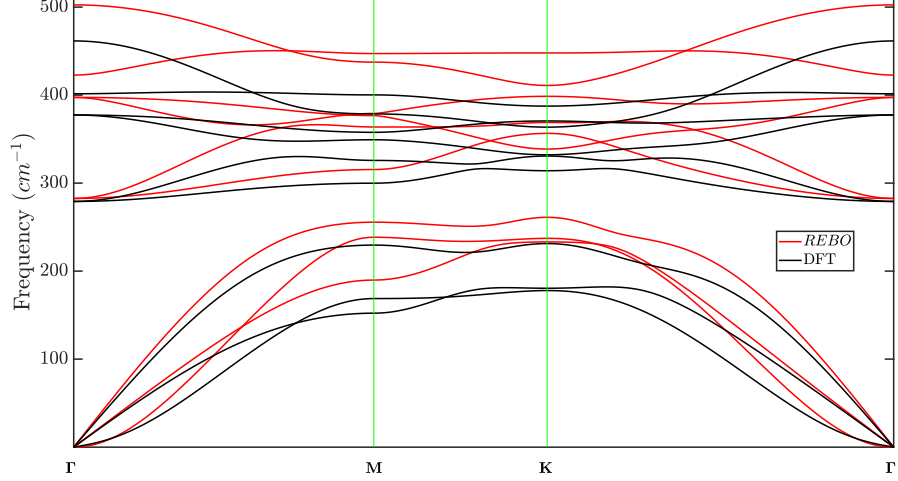


Figure 2.2: Phonon dispersions of MoS₂ obtained from DFT (black lines) and REBO potential [93] (red lines).

2.2.3 Vashishta Potential

All of the previously described potentials are designed for materials with covalent bonds. In materials such SiO₂ there is also ionic nature of bonds because of the charge transfer between the atoms which gives rise to long range Coulomb interactions between the atoms. Furthermore, there is a short range repulsion due to size of atoms known as steric repulsion which is proportional to inverse of distance between the atoms. In addition, because of atomic polarizability of ions dipole-dipole attractions become important. These are taken into account by Vashishta et al [75, 94] in the two-body term of the potential. Similar to SW potential, two-body and three-body terms of the Vashishta potential are written as separate sums over neighbors:

$$E = \sum_{i < j}^N \phi_2(r_{ij}) + \sum_{i, j < k, j \neq i, k \neq i}^N \phi_3(r_{ij}, r_{jk}, \theta_{ijk}) \quad (2.26)$$

The two-body and three body terms are given by:

$$\phi_2(r_{ij}) = \frac{H_{ij}}{r_{ij}^{\eta_{ij}}} + \frac{Z_i Z_j}{r_{ij}} \exp\left(-\frac{r_{ij}}{\lambda_1}\right) - \frac{D_{ij}}{r_{ij}^4} \exp\left(-\frac{r_{ij}}{\lambda_4}\right) - \frac{w_{ij}}{r_{ij}^6} \quad r_{ij} < r_{c2} \quad (2.27)$$

Where the last term describes van der Waals interaction.

$$\begin{aligned} \phi_3(r_{ij}, r_{jk}, \theta_{ijk}) = \\ B_{ijk} \frac{(\cos(\theta_{ijk}) - \cos(\theta_0))^2}{1 + (C_{ijk}(\cos(\theta_{ijk}) - \cos(\theta_0))^2)} \exp\left(\frac{\lambda_{ij}}{r_{ij} - r_{c3}}\right) \exp\left(\frac{\lambda_{ik}}{r_{ik} - r_{c3}}\right) \end{aligned} \quad (2.28)$$

The three body term is similar to SW potential. Apart from charge interaction terms, the main difference between SW and Vashishta potential is the different cutoff values for two and three body terms. The two-body term of Vashishta potential is shifted to give zero force and energy at the cutoff. Mathematically:

$$\phi_2(r_{ij}) = \begin{cases} \phi_2(r_{ij}) - \phi_2(r_{c2}) - (r_{ij} - r_{c2}) \frac{d\phi_2(r_{ij})}{dr_{ij}} & r_{ij} \leq r_{c2} \\ 0 & r_{ij} > r_{c2} \end{cases} \quad (2.29)$$

This potential is used for AlN [94] which is investigated using SW potential in the fourth chapter of this thesis.

2.3 Particle Swarm Optimization

Optimizing force-field parameters for complex functional forms requires a systematic training procedure, which allows efficient sampling of the entire parameter space. Traditionally employed least-squares methods are sensitive to initial guesses and are not sufficient for fitting problems with large number of parameters. Global optimization methods start with large number of random guesses in the phase space and then evolve them to new solutions to get best minimum considering desired constraints. There are different approaches for generating new solutions from the random initial guess. The mostly used algorithms are particle swarm (PSO) [95, 96], genetic algorithm and simulated annealing [97]. In this research we use PSO to parametrize SW potential. The method is inspired from flocking motion of birds in swarm. Each point in the phase space of the parameters is called a particle. For each problem, a function which is called cost function is defined as the weighted sum of the differences between the target values and values obtained by each particle and the main aim is minimizing the cost function. After generating initial particles which are randomly placed in the phase space, the algorithm evolves them by assigning a n_p dimensional velocity

vector at each step of the evaluation. Where n_p is the number of the parameters in the problem. This velocity vector is the resultant of three different vectors. The first one is in the direction of the previous velocity vector. The second vector is in the direction from previous position of each particle to position of the global minimum ($\vec{g}_{iB}$) at the previous step of the evaluation. The third vector is in the direction from position of each particle to the particles own best measurement ($\vec{p}_{iB}$). Mathematically the equations of the motions of the particles are given as follow:

$$\vec{x}_i(t+1) = \vec{x}_i(t) + \vec{v}_i(t+1) \quad (2.30)$$

$$\vec{v}_i(t+1) = w\vec{v}_i(t) + r_1c_1(\vec{p}_{iB}(t) - \vec{x}_i(t)) + r_2c_2(\vec{g}_{iB}(t) - \vec{x}_i(t)) \quad (2.31)$$

Where w , c_1 and c_2 are predefined constants. r_1 and r_2 are random variables between 0 and 1.

2.4 Methods for Evaluating Thermal Conductivity

There are different methods for predicting thermal conductivity. In this section the main approaches are briefly explained.

2.4.1 Direct Method

The direct method is a non-equilibrium method [98, 99] and relies on direct application of the Fourier's law:

$$\vec{J} = -\kappa \vec{\nabla} T \quad (2.32)$$

Where, $\vec{J}$ is the heat current and κ is the thermal conductivity tensor. In such methods a heat flux is introduced to the system by considering two fixed boundaries as hot and cool boundaries and they are kept at fixed temperatures during

the simulation. After the steady state is established, the velocity of the particle must obey the Maxwell-Boltzmann distribution:

$$P_{MB}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(-\frac{mv^2}{2k_B T} \right) \quad (2.33)$$

In the steady state the system can be divided into small segments and then the temperature of each part can be obtained using equipartition for energy which results the temperature gradient profile and the thermal conductivity can be obtained from Fourier's law. The direct method is completely classical method and doesn't use the concept of quasiparticles. The most important disadvantage of this method is that it is highly depend on the considered length. In addition, by increasing the system size, the time required for getting the steady state will be increased.

2.4.2 Green-Kubo Method

From the equilibrium point of view, the most reliable results are obtained by Green-Kubo method [100, 101]:

$$k = \frac{1}{k_B T^2 \Omega} \int_0^\infty \langle \vec{J}(t) \vec{J}(0) \rangle dt \quad (2.34)$$

$$\vec{J}(t) = \frac{d}{dt} \sum_{i=1}^N E_i \vec{r}_i \quad (2.35)$$

Similar to direct method Green-Kubo method doesn't uses phonons as carries. However, it is shown that in order to get reliable results the system size must be large enough to excite enough phonons [102]. Also, the convergence of the autocorrelation function must be assured. The final results of this method is only the tensor of the thermal conductivity.

2.4.3 Boltzmann Transport Equation

The general form of the Boltzmann transport equation (BTE) for a distribution function f is given by:

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t} \right)_{force} + \left(\frac{\partial f}{\partial t} \right)_{diff} + \left(\frac{\partial f}{\partial t} \right)_{scatt} \quad (2.36)$$

The terms in the right hand side of the equation are due to external force, diffusion, and the collision between particles. In the case of phonons and in the presence of temperature gradient which imposes the explicit dependence of temperature on position and using the fact that phonons can not experience external force and considering the steady state where the total time derivative of the distribution is zero, the BTE for phonons can be written as:

$$\vec{v}_g \cdot \vec{\nabla} T \frac{\partial n}{\partial T} = \left(\frac{\partial n}{\partial t} \right)_{scatt} \quad (2.37)$$

Where the v_g is the phonon group velocity and is given by:

$$\vec{v}_g(\vec{q}, \nu) = \frac{\partial \omega(\vec{q}, \nu)}{\partial \vec{q}} \quad (2.38)$$

Here ω is the phonon frequency of the branch ν . The equation 2.37 is an integro-differential equation because of the scattering term in left hand side and since its solution is far from trivial. The scattering term can be simplified by assuming up to three phonon scattering. Then the resulted equation must be solved iteratively [103–105]. At the equilibrium condition phonons obey Bose–Einstein distribution which is given by :

$$n_{eq} = \frac{1}{\exp\left(\frac{\hbar\omega(\vec{q})}{k_B(T)}\right) - 1} \quad (2.39)$$

Letting n' to be the fluctuation about the equilibrium, a possible simplification is the relaxation time approximation which is based on the following assumptions:

$$\begin{aligned} n &= n_0 + n' \\ \left(\frac{\partial n}{\partial t} \right)_{scatt} &= -\frac{n'}{\tau} \\ \frac{\partial n'}{\partial T} &= 0 \end{aligned} \quad (2.40)$$

Here τ is the phonon relaxation time. The heat flux is given by [98]:

$$J = \frac{1}{\Omega} \sum_{\vec{q}} \sum_{\nu} \hbar \omega \vec{v}_g n' \quad (2.41)$$

and using the equations 2.39 and 2.37 the thermal conductivity can be obtained by:

$$\kappa = \sum_{\vec{q}} \sum_{\nu} c_{ph} \vec{v}_g \vec{v}_g \tau \quad (2.42)$$

Where c_{ph} is the phonon specific heat:

$$c_{ph} = \frac{\hbar \omega}{k_B T} \frac{\exp\left(\frac{\hbar \omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right)^2} \quad (2.43)$$

2.5 Determining Phonon Lifetimes and Group Velocities

Equation 2.42 is the fundamental equation for determining thermal conductivity under relaxation time approximation. But it is necessary to find the lifetimes and group velocities. The first method for obtaining phonon group velocities is simply using harmonic or quasi harmonic approximation in the framework of lattice dynamics. By same methodology and considering the third order force constants it is possible to find the lifetimes as well. However, this actually imposes another approximation on top of the previously considered ones. This method is based on expanding the potential up to third order, so it neglects anharmonic effects beyond those considered terms which are only negligible at low temperatures. One improvement to this method is taking group velocities from lattice dynamics and obtaining the lifetimes from autocorrelation function of the time dependent energy of the normal-mode which is an exponentially decaying function of phonon lifetimes [98, 106]. There is another approach based on Green's function that facilitates evaluating phonon frequencies directly from MD [107, 108]. This method

considers anharmonic effects, but it is shown that this method might fail to produce stable results near the Γ point [109].

2.6 Spectral Energy Density Method

In the spectral energy density method which is a frequency domain method, considering a simulations cell consisted of N_c unit cell with n_b basis atom in each unit cell, a function is defined as [35, 110, 111]:

$$\psi(\vec{q}, j | t) = \sum_{\alpha, b} \left[\sum_{i=1}^{N_c} v_{\alpha}(i, b | t) \exp(i\vec{q} \cdot \vec{r}_{eq_{i,n}}) \right] e^{\dagger}(b | \vec{q}, j) \quad (2.44)$$

Where $v_{\alpha}(i, b | t)$ is the component of the velocity of the b 'th basis in the i 'th unit cell in the Cartesian direction α and $\vec{r}_{eq_{i,n}}$ is the corresponding equilibrium position. $e(b | \vec{q}, j)$ is the time independent phonon eigenvector. It is shown that the power spectrum of the function $\psi(\vec{q}, j | t)$ is sharply picked at the position of the phonon frequency and phonon lifetime and frequency can be obtained by fitting a Lorentzian function:

$$\frac{I}{1 - \left(\frac{\omega - \omega_0}{\lambda}\right)^2} \quad (2.45)$$

Where ω_0 is the phonon frequency, I is the peak amplitude and λ is the phonon linewidth and the phonon lifie time is given by $\tau = \frac{1}{2\lambda}$. This method provides a robust framework for analyzing anharmonic effects and evaluating thermal conductivity as well as contribution of each phonon mode in thermal conductivity. There is another equivalent but simplified approach which gives the spectral energy density without directly using phonon mode eigenvectors [35]:

$$\Psi(\vec{q}, j | t) = \sum_{\alpha=1}^3 \sum_{b=1}^{n_b} \frac{m_b}{4\pi t_s N_c} \left| \int_0^{t_s} \sum_{l=1}^{N_c} v_{\alpha}^{b,l} \exp(i\vec{q} \cdot \vec{r}_{eq_{l,b}} - i\omega t) dt \right|^2 \quad (2.46)$$

Where m_b is the mass of b 'th basis of the unit cell and t_s is the simulation time. The only disadvantage is that the final result is $3m_b$ Lorentzian function and this makes fitting process difficult, especially when phonon branches cross each other. Therefore, its application is mainly restricted to Γ point optical phonons.

Chapter 3

Thermal Conductivity of TMDs

The SW potential is optimized for Mo based materials in [112]. Therefore, the first step of this work is optimizing parameters of SW potential for WS_2 and WSe_2 [113]. Equipped with fairly accurate potentials, a systematic study of temperature dependent phonon lifetimes and frequencies of MoS_2 , MoSe_2 , WS_2 and WSe_2 based on SED approach is presented [114].

3.1 Validation of Interatomic Potential for WS_2 and WSe_2

In optimization of the force fields for properties far from equilibrium, such as melting and thermal expansion and phase transitions, the target data are mostly taken from experiments. Ab-initio calculations are basically limited to ground state at zero temperature. However, the near equilibrium properties such as phonon dispersion are accurately described by DFT method. The objective values of this study are taken from first-principles pseudopotential plane-wave calculations based on DFT by using the Vienna ab initio simulation package (VASP) [115–117].

3.1.1 Computational Details for DFT Calculations

In order to eliminate interactions with periodic images a vacuum of 20 Å is considered above the layer. The core valence electrons are described by projector augmented wave type pseudopotentials (PAW) [118, 119]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) is used for the exchange correlation potential. The parameters are selected after performing convergence test for total energy and forces. Accordingly, 500 eV kinetic energy cutoff is considered for plane wave basis. The Γ centered $26 \times 26 \times 1$ Monkhorst-Pack q-point mesh is used for sampling the Brillouin zone. For obtaining the phonon frequencies a $4 \times 4 \times 1$ supercell and $8 \times 8 \times 1$ qpoint mesh is used. First the force constants are determined utilizing the density functional perturbation theory as implemented in the VASP code then the frequencies are calculated using phonopy code.

3.1.2 Optimizing SW Potential for WS₂ and WSe₂

In Figure 3.1 the lattice structure of TMDs are schematically presented. In order to describe these structures by SW potential three stretching terms, M-M, M-X and X-X, are required. Here M is the transition metal and X is the chalcogen atom.

In the case of bond bending which described by three-body term the chalcogen atoms must be distinguished to describe the asymmetric chalcogen polyhedra around M. Therefore, as it is depicted in Figure 3.1 subscripts u and d are used to show the chalcogen atoms above and below the metal layer and We defined three bond bending terms: $X_{u,(d)}-W-X_{u,(d)}$, $W-X_{u,(d)}-W$ and X_u-W-X_d , where the first atom is the center atom in the configuration. In Figure 3.1 the corresponding angles are shown as θ_1 , θ_2 , and θ_3 respectively. In LAMMPS code the cutoff values for three body and two body terms are assumed to be same, therefore these cutoffs are distinguished by modifying the *pair_sw.cpp* module of the LAMMPS code. The PSO is implemented for minimizing the cost function which is defined

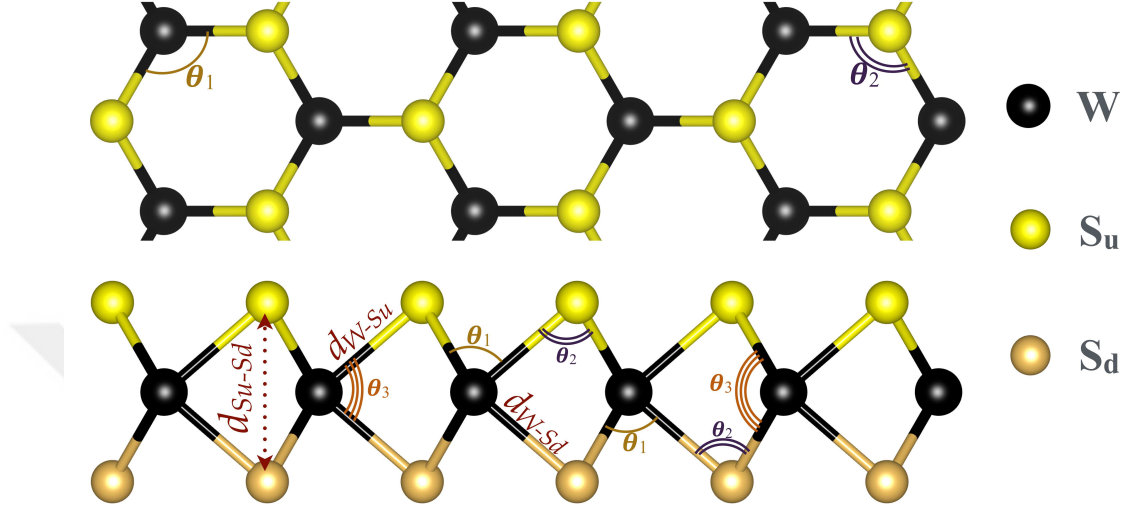


Figure 3.1: Schematic representations (top and side views) of single layer WS_2 and WSe_2 structures.

as a normalized sum of the objectives. The assumed target data are phonon frequencies, lattice parameters (a_0), distance between two chalcogen atoms (one above and one below the W layer (d_{X_u, X_d})), elastic constants (C_{11} and C_{12}), Young's moduli (Y) and Poisson's ratio (ν). The obtained parameters are given in the GULP [120] format in Table 3.1 and Table 3.2.

Table 3.1: Two-Body Stillinger-Weber parameters in GULP format.

	A	ρ	B	r_{min}	r_{max}
S-S	0.7701	0.1284	17.7001	0.00	3.80
W-S	8.8208	1.3972	16.1615	0.00	3.21
W-W	1.4797	0.7340	66.9509	0.00	4.35
Se-Se	1.6103	0.1000	20.0000	0.00	4.02
W-Se	10.0106	1.7403	19.2854	0.00	3.36
W-W	0.6120	0.1098	100.0000	0.00	4.53

In Table 3.3, mechanical and structural properties obtained from DFT and SW are compared.

In Figure 3.2 the phonon frequencies obtained from lattice dynamics using the optimized SW potentials and DFT are presented. The dispersion curves of both

Table 3.2: Three-Body Stillinger-Weber parameters in GULP format.

	K	θ_0	ρ_{12}	ρ_{13}	r_{12}^{max}	r_{13}^{max}	r_{23}^{max}
W-S _{u,d} -S _{u,d}	19.5209	82.3451	1.054	1.054	3.21	3.21	3.80
S _{u,d} -W-W	19.5209	82.3451	1.054	1.054	3.21	3.21	4.35
W-S _u -S _d	0.1000	81.0412	1.054	1.054	3.21	3.21	3.80
W-Se _{u,d} -Se _{u,d}	20.0000	81.2948	1.3007	1.3007	3.36	3.36	4.02
Se _{u,d} -W-W	20.0000	81.2948	1.3007	1.3007	3.36	3.36	4.53
W-Se _u -Se _d	0.1000	82.4418	1.3007	1.3007	3.36	3.36	4.02

Table 3.3: The lattice parameter (a_0), the distance between two chalcogen atoms above and below the W layer (d_{X_u, X_d}), elastic constants (C_{11} and C_{12}), Young's modulus (Y), and Poisson's ratio (ν) of WS₂ and WSe₂ evaluated with both DFT and the generated potential parameters set.

	a_0 (Å)	$d_{S,Se}$ (Å)	C_{11} (N/m)	C_{12} (N/m)	Y(N/m)	ν
WS₂						
DFT	3.18	1.57	146.5	31.8	139.6	0.22
SW	3.21	1.49	136.4	37.4	126.1	0.27
WSe₂						
DFT	3.32	1.50	120.4	23.1	116.0	0.19
SW	3.37	1.54	112.5	33.2	102.7	0.29

of the considered materials have similar behavior, except that WS₂ has higher frequencies. The phonon frequencies are in well agreement with DFT results, especially acoustic modes are perfectly captured.

In order to assess the ability of the optimized parameters sets in capturing anharmonic effects the mode independent version of SED [35] is used to compare the effect of the temperature on optical modes at the Γ point with experimental results.

3.1.3 Computational Details of the SED Analysis

All MD simulations in this work are carried out using LAMMPS code. In all cases reported in this study, a 70×70 triclinic computational cell which consists of 14700 atoms is used. The system is relaxed using conjugate gradient approach.

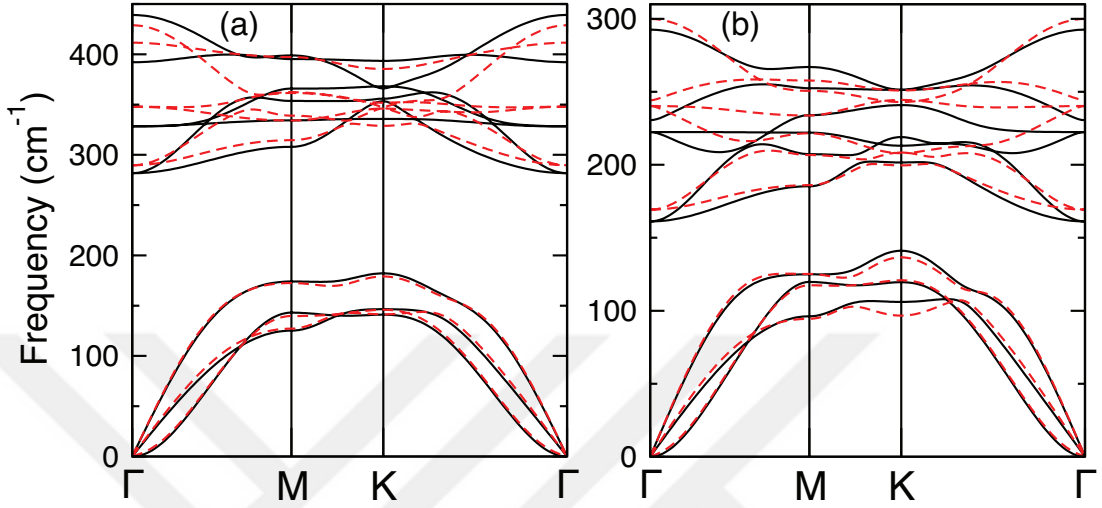


Figure 3.2: Vibrational phonon frequencies of (a) WS_2 and (b) WSe_2 structures along the high-symmetry paths of the Brillouin zone. Here red dashed lines represent the data calculated with density functional perturbation theory and black solid lines are generated using optimized potential parameters sets, respectively.

A vacuum of 30 Å is considered above the layer. Periodic boundary conditions are considered in all three dimensions. In the first step, system is allowed to evolve at desired pressure and temperature for 500 ps using a fine time step of 0.5 fs. The lattice parameters are obtained by averaging over the corresponding values during the NPT run and the lattice is reconstructed using obtained average values. Then velocities are created at desired temperature. In order to eliminate the undesired excitations due to creating velocities the system is allowed to evolve for 200 ps in NVE ensemble. The data are collected in the next 2^{20} time steps of the simulation. A power of 2 is used to utilize fast Fourier transform more efficiently. In order to reduce the memory usage all spatial Fourier transforms of the SED are calculated inside the LAMMPS code.

3.1.4 Phonon Frequencies and Lifetimes at Γ Point as a Function of Temperature

In Figure 3.3 the SEDs of the optical modes of WS_2 at $T=300$ K and the Lorentzian fits are depicted. The lineshapes of SEDs are perfectly match the Lorentzian function.

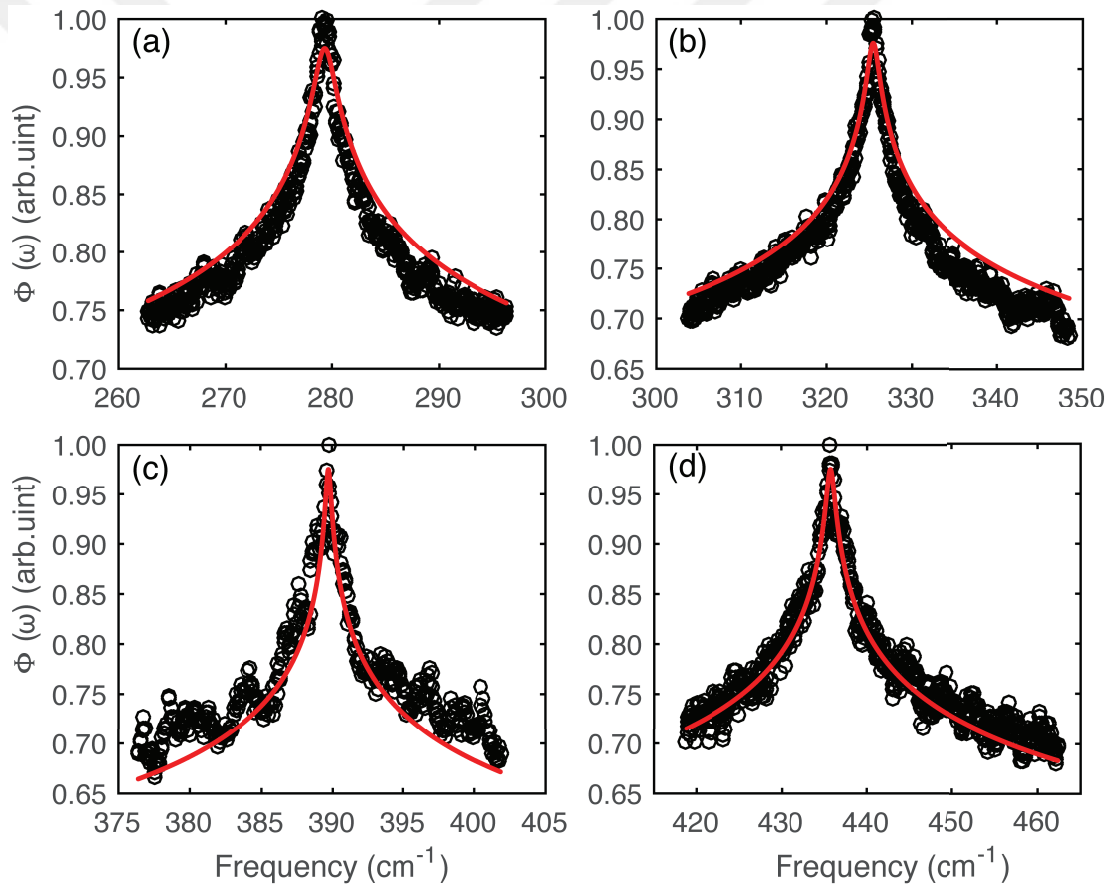


Figure 3.3: Normalized SEDs (black circles) and Lorentzian fits (red lines) for WS_2 (a) E_{1g} , (b) E_{2g}^1 , (c) A_{1g} and (d) A_{2g} modes at $T = 300$ K.

The ratio of the Γ point frequencies to corresponding values at 300 K and the calculated linewidths are shown in Figure 3.4. The frequencies show a linear decreasing behavior with increasing the temperature (red shift). The same behavior is reported in the case of MoS_2 [54].

The melting temperature of the bulk WS₂ and WSe₂ are around 1200 K and BTE is valid only at temperatures well below the melting point. The quantum effects become dominant below the Debye temperature, T_D , which can be obtained from the maximum frequencies of longitudinal and transverse acoustic modes using the following equations [121, 122]:

$$\frac{1}{T_D} = \frac{1}{2} \left(\frac{1}{T_{LA}^3} + \frac{1}{T_{TA}^3} \right) \quad (3.1)$$

$$T_{LA(TA)} = \frac{\hbar \omega_{\max LA(TA)}}{k_B}$$

The Debye temperatures obtained from the maximum frequencies corresponding to the LA and TA modes for WS₂ and WSe₂ are approximately 205 K and 150 K respectively. Therefore, we restricted our study to temperatures from 200 K to 600 K.

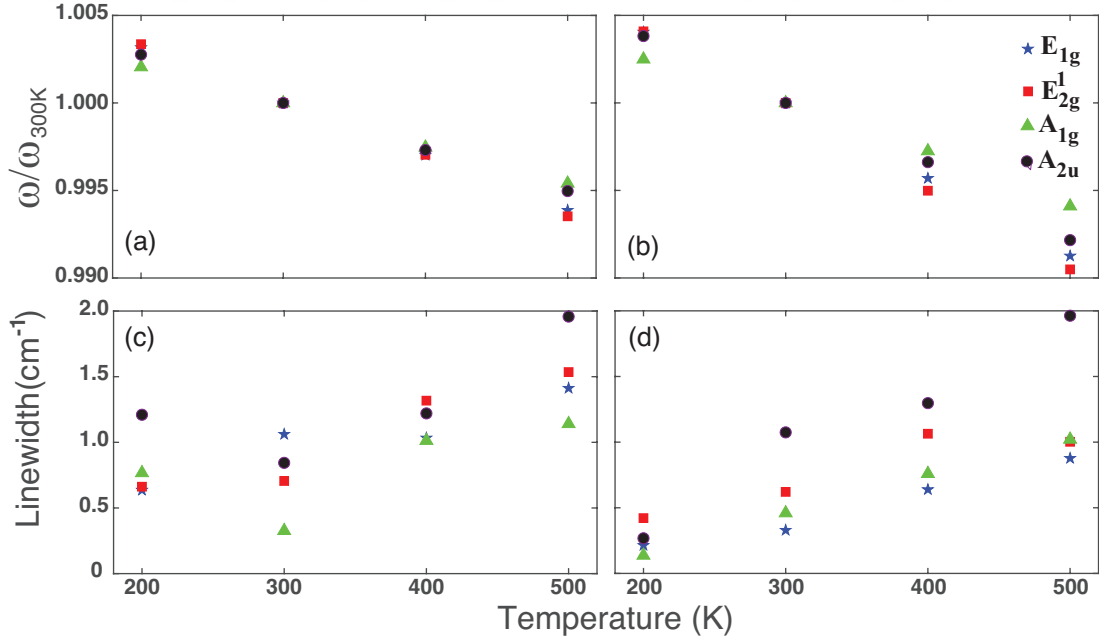


Figure 3.4: Ratio of phonon frequencies to frequencies at 300 K and linewidths at Γ point as function of temperature for: WS₂ (a) and (c), WSe₂ (b) and (d).

Although, frequencies of the optical modes are not exactly match with the DFT results, as it is shown in Figure 3.5, where the frequencies are shifted to

match previously reported experimental values [50, 52], the trend in phonon frequency with increasing temperature is in perfect agreement with previously reported experimental results for WS_2 .

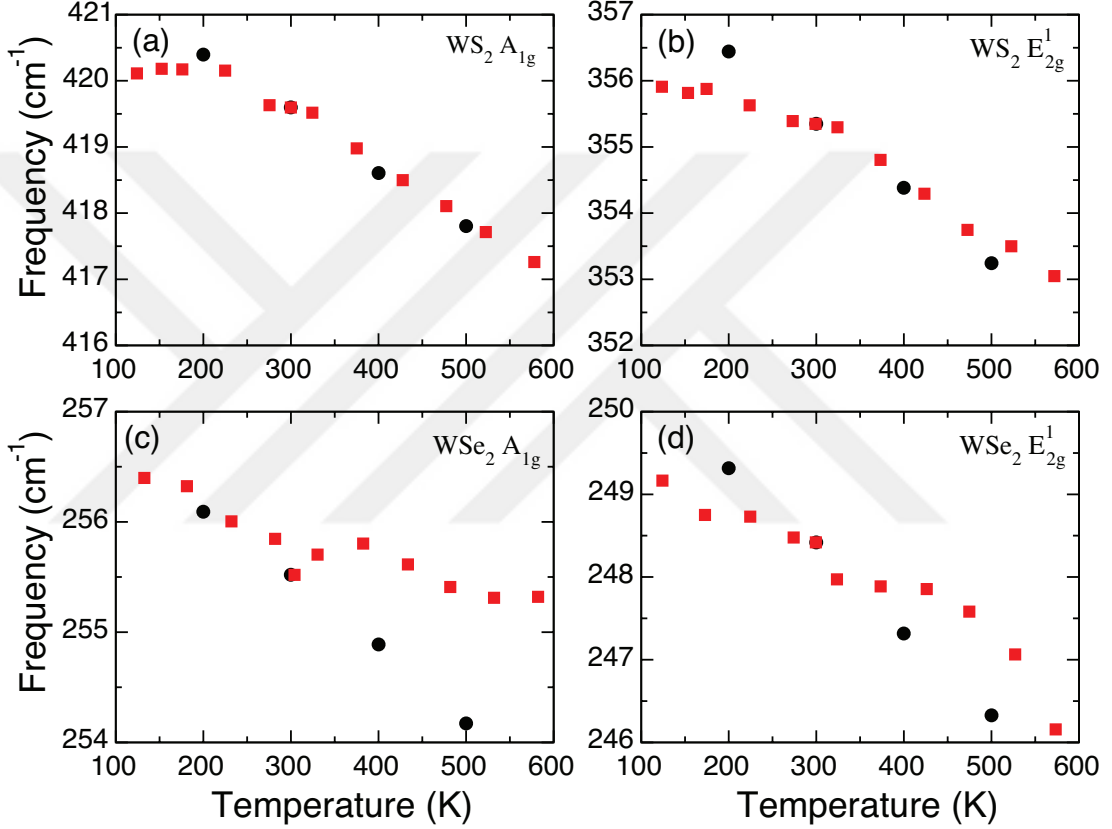


Figure 3.5: Phonon frequencies at Γ as a function of temperature; both experimental data (red squares) and MD results (black circles) are shown. Experimental data taken from [50, 52].

In the case of WSe_2 there are deviations from experimental results, especially for the A_{1g} . However, there are remarkable fluctuations in the experimental data and they do not follow the linear trend. The results presented in this section indicate the accuracy of the optimized SW potentials.

3.2 Evaluating Thermal Conductivity of TMDs

Equipped with the potentials that their accuracies are assessed in the previous section, now it is possible to study thermal transport properties.

3.2.1 Thermal Conductivity using Green-Kubo Method

The Green-Kubo method in its original form which is presented in the previous chapter is proportional to ensemble average of the heat current autocorrelation. The heat current becomes:

$$\vec{J}(t) = \frac{d}{dt} \sum_{i=1}^N E_i \vec{r}_i = \sum_{i=1}^N E_i \vec{v}_i + \sum_{i=1}^N r_i \frac{dE_i}{dt} \quad (3.2)$$

The time derivative of the total energy of each atom is not the direct output of the integrator of the MD simulation and must be evaluated at each time step considering the form of the potential function used in the simulation. Such expressions of heat currents for commonly used many-body potentials are presented in [118]. The other possible approach, which is used in the current study, is using the Einstein relation to convert the Green-Kubo equation into the form that can be directly evaluated in each step of the MD simulation. The infinite time integral of the form:

$$\gamma = \int_0^\infty \langle \dot{A}(t) \dot{A}(0) \rangle dt \quad (3.3)$$

considering very large t can be written as:

$$2t\gamma = \langle (A(t) - A(0))^2 \rangle \quad (3.4)$$

Using equation 3.4 and considering isotropic case, the Green-Kubo thermal conductivity can be written as:

$$\kappa_{\alpha\alpha} = \frac{1}{K_B T^2 \Omega} \lim_{t \rightarrow \infty} \frac{1}{2t} \langle (R_\alpha(t) - R_\alpha(0))^2 \rangle \quad (3.5)$$

Where R_α is given by:

$$R_\alpha = \sum_{i=1}^N r_{i\alpha} E_i \quad (3.6)$$

All variables in equations 3.5 and 3.6 are easily accessible during each step of MD. The time interval of the integrations in all Green-Kubo results presented here is 5 ns. In previous studies it is shown that this value is sufficient for graphene [123] and h-BN [124], both of these materials have much larger thermal conductivities than TMDs and so the larger autocorrelation tail. Therefore the time range used here is justified. The other issue in evaluating thermal conductivity is defining the volume for a 2D system. The volume is defined by multiplying the area of the layer by the mean van der Waals distance in the corresponding hexagonal bulk structure (0.612 nm for WS₂, 0.648 nm for WSe₂, 0.615 nm for MoS₂ and 0.65 nm MoSe₂).

3.2.2 SED Thermal Conductivity of TMDs

The computational details of SED analysis are previously explained. In order to generalize the approach to entire Brillouin zone the mode decomposition method is used considering a $35 \times 35 \times 1$ qpoint mesh. The eigenvectors are taken from lattice dynamics approach using GULP code. It is shown that at very high temperatures the harmonic modes are not able to decompose power spectrum correctly therefore the maximum considered temperature in this study is 500 K. In order to justify this, examples of the full SED, mode decomposed SED and the Lorentzian fits at highest considered temperature are presented in Figures 3.6, 3.7, 3.8 and 3.9.

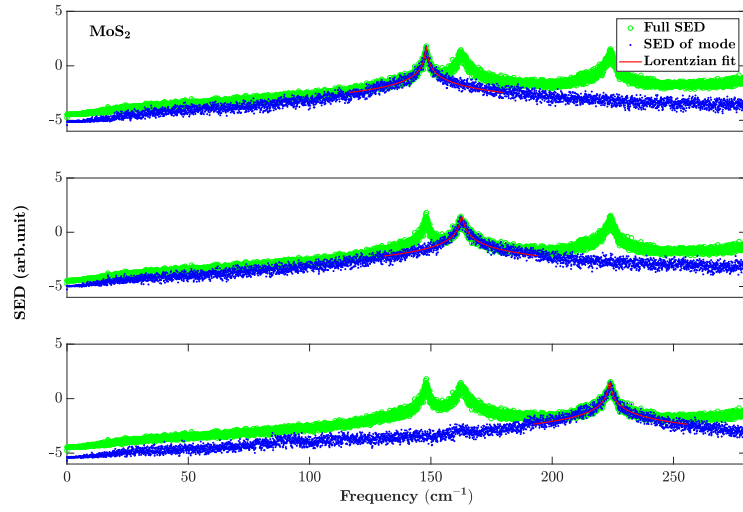


Figure 3.6: Full SEDs and mode decomposed SEDs of MoS₂ at 500 K

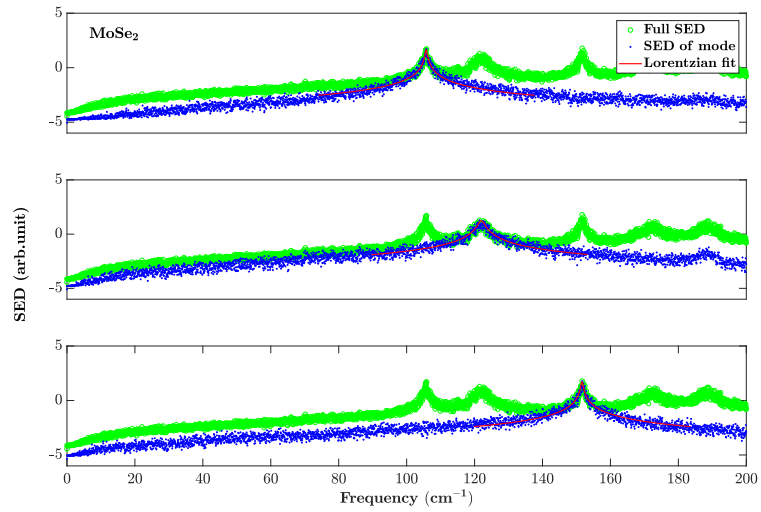


Figure 3.7: Full SEDs and mode decomposed SEDs of MoSe₂ at 500 K

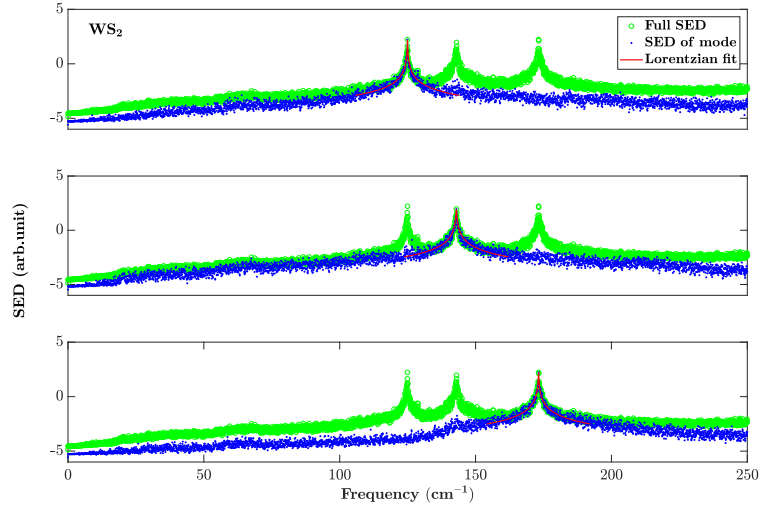


Figure 3.8: Full SEDs and mode decomposed SEDs of WS_2 at 500 K

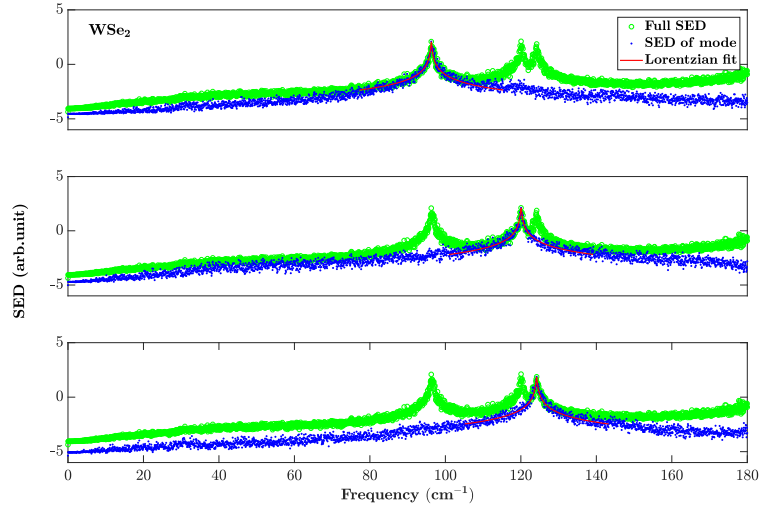


Figure 3.9: Full SEDs and mode decomposed SEDs of WSe_2 at 500 K

These results show that the harmonic modes are able to perfectly decompose the SEDs of all considered materials. It must be mentioned that correct decomposition is not possible with small number of qpoints therefore, a very dense mesh of $140 \times 140 \times 1$ qpoint mesh is used to find the phonon eigenvectors and modes

are sorted utilizing the orthogonality condition for eigenvectors. The obtained temperature depended phonon frequencies are presented in Figure 3.10.

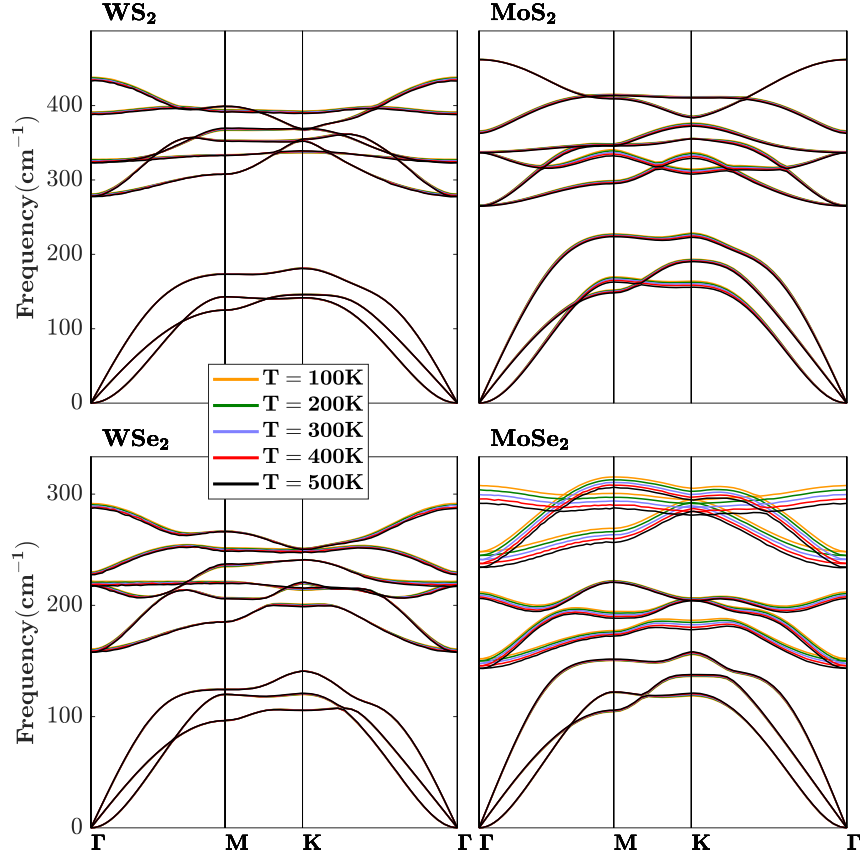


Figure 3.10: Phonon dispersions of 2D WS_2 , WSe_2 , MoS_2 and MoSe_2 structures calculated at different temperatures.

The results, particularly for acoustic frequencies, are in very good agreement with those previously predicted by first-principles approaches. As it is clearly seen from Figure 3.10 the acoustic modes are not notably affected by the change of the temperature. However, there are clear redshifts in the optical phonon frequencies.

These shifts can be considered as constant shifts such that the group velocities do not vary with temperature and therefore can be taken from lattice dynamics, where much finer sampling for taking the derivatives is possible. Figure 3.10 shows the most prominent change with temperature appears in the optical modes of the MoSe_2 and indicates that the strongest anharmonicity belongs to this material among the other considered TMDs.

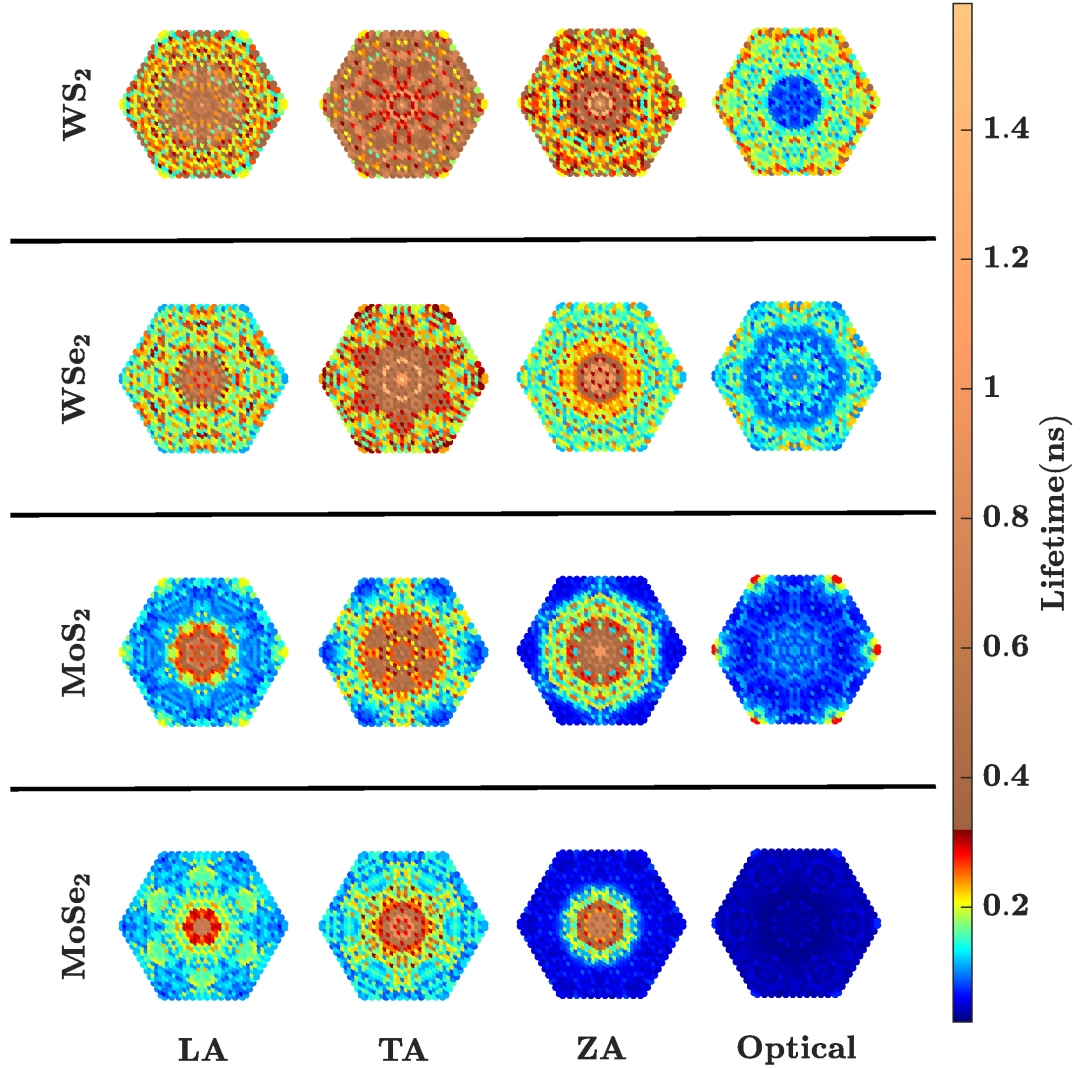


Figure 3.11: The calculated phonon lifetimes by SED approach at 300 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

The calculated phonon lifetimes at room temperature for the acoustic mode and the optical mode which have more contribution in the thermal conductivity are present in Figure 3.11. From Figure 3.11 it is clear that lifetimes of acoustic modes are one order of magnitude larger than the optical mode with largest contribution in the thermal conductivity. There is an apparent decrease in the lifetimes from zone center to zone border. These variations have narrower range in the W based materials than the Mo based materials. In addition, lifetimes have smaller values in Mo based materials than the W based materials. However, as it shown in 3.19, calculated thermal conductivities from different methods indicates comparable κ values for heavier W based and lighter Mo based materials. This unusual behavior can be interpreted by the aforementioned properties of the lifetimes. The phonon lifetimes at other considered temperatures are presented in Figures 3.20, 3.22, 3.24 and 3.26. The considered materials can be ordered as: WS₂, WSe₂, MoS₂ and MoSe₂ according to increasing of the anharmonicity. By increasing the temperature the distribution of the lifetimes according to q points is changing and the only trend is the decreasing the mean value of lifetimes. In order to give a furtherer illustration, the phonon lifetimes as function of frequencies are presented in Figures 3.12, 3.13, 3.14 and 3.15. In these figures the modes are distinguished by different colors. The decreasing trend in lifetimes with variation of the temperature becomes more evident.

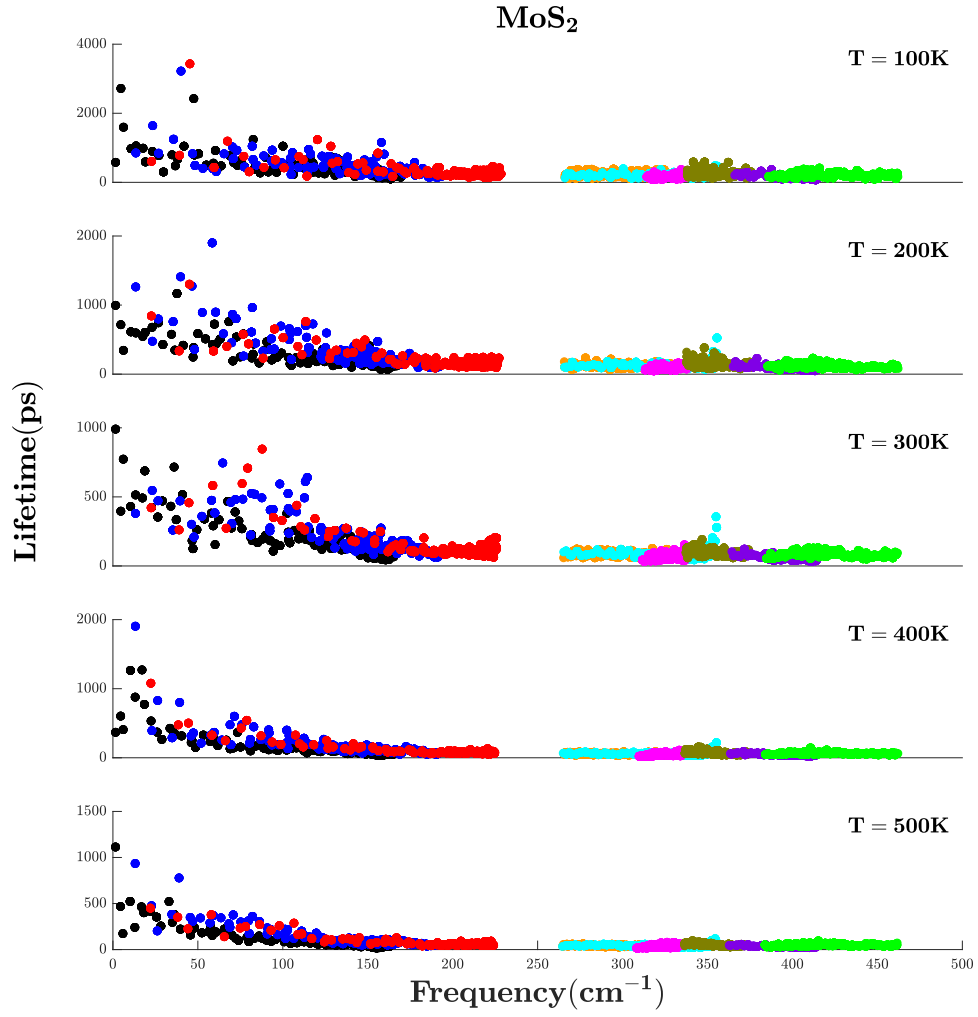


Figure 3.12: Phonon lifetime of as function of frequency for MoS₂

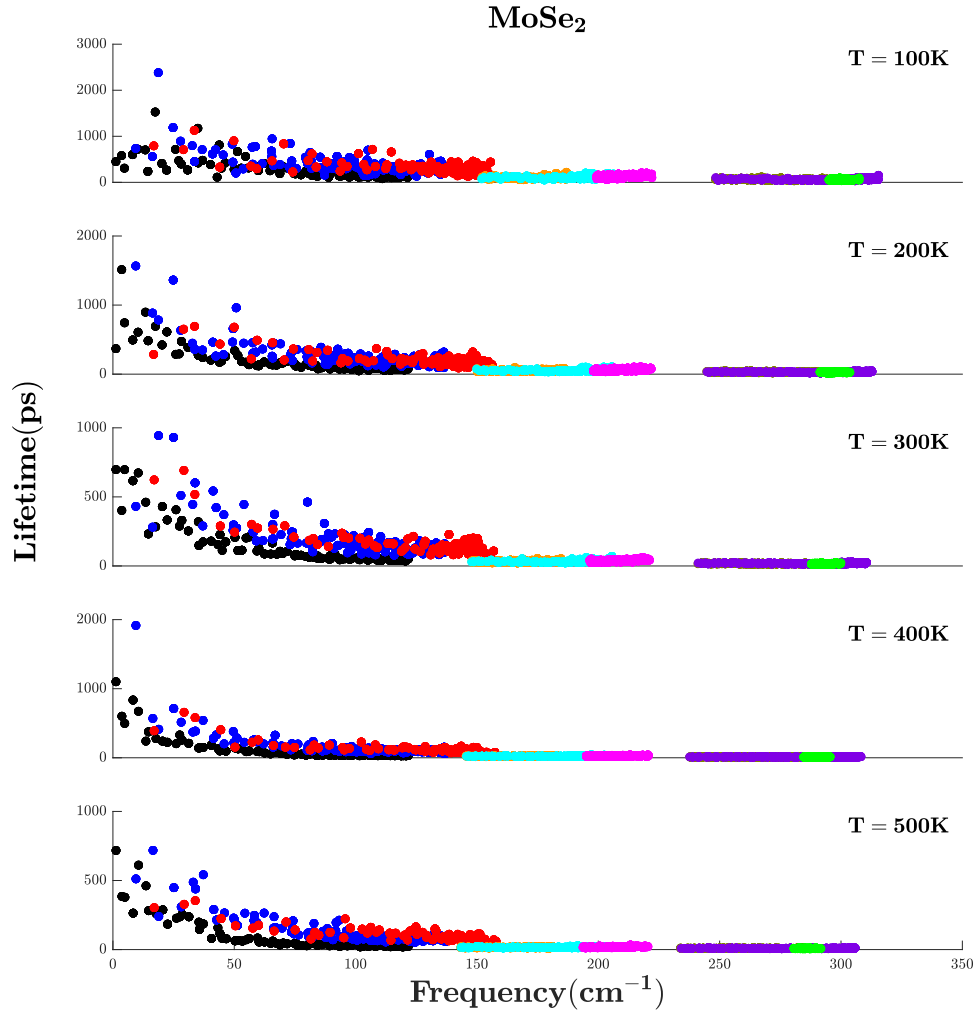


Figure 3.13: Phonon lifetime of as function of frequency for MoSe₂

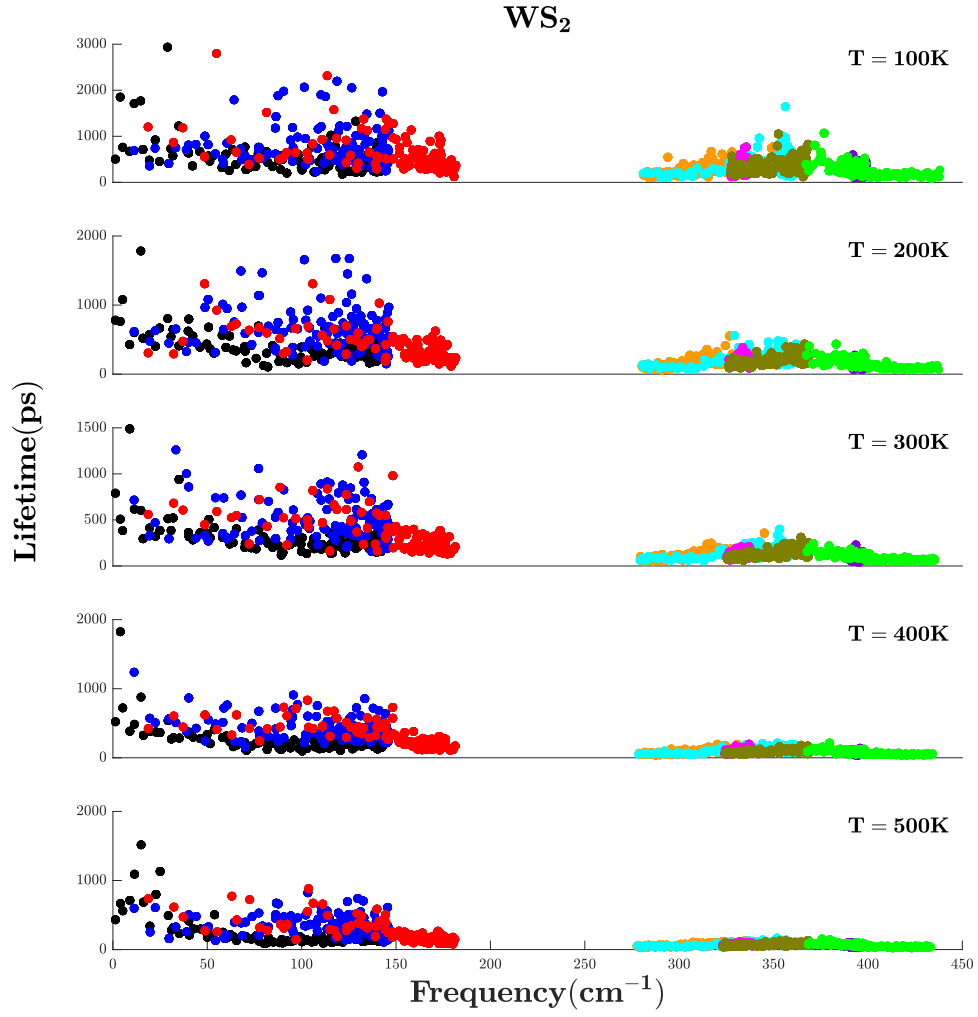


Figure 3.14: Phonon lifetime of as function of frequency for WS_2

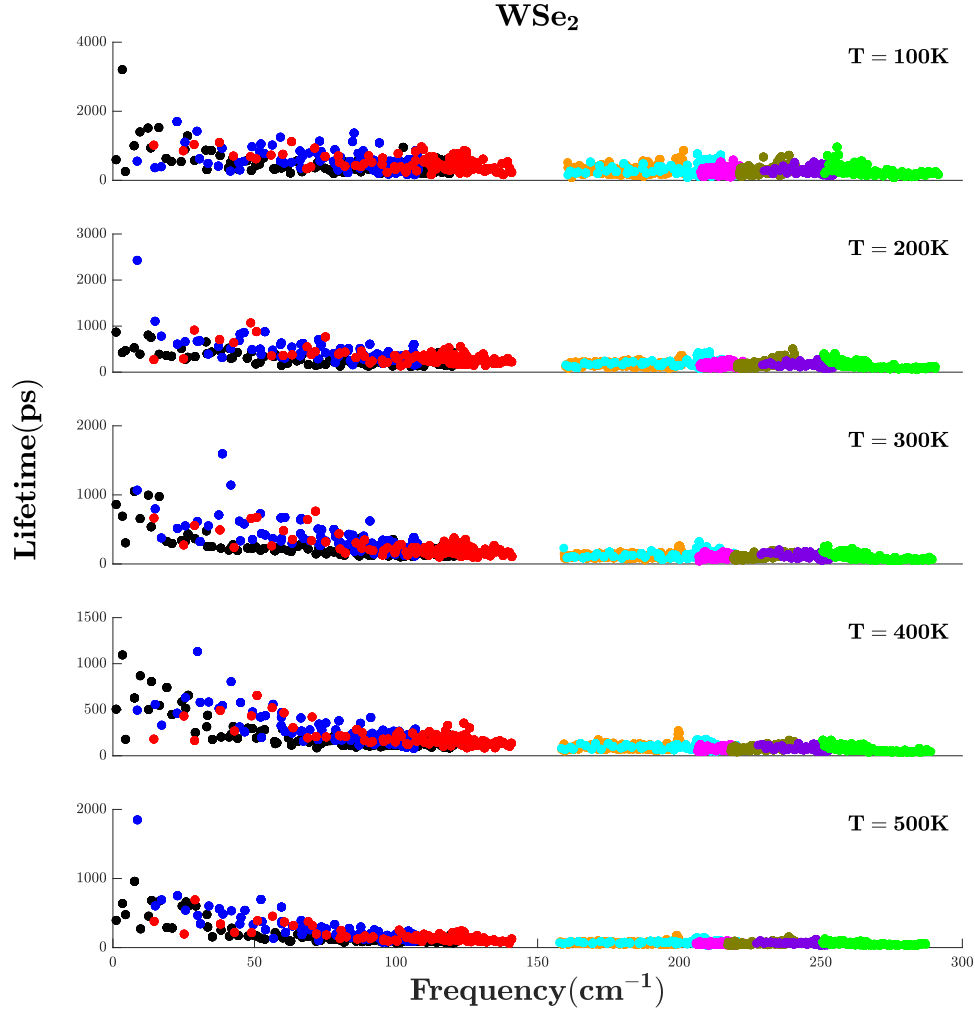


Figure 3.15: Phonon lifetime of as function of frequency for WSe_2

The other quantity which appears in the equation for thermal conductivity is the group velocity. In Figure 3.16 group velocities obtained from lattice dynamics using the lattice parameters calculated from MD at room temperature is presented.

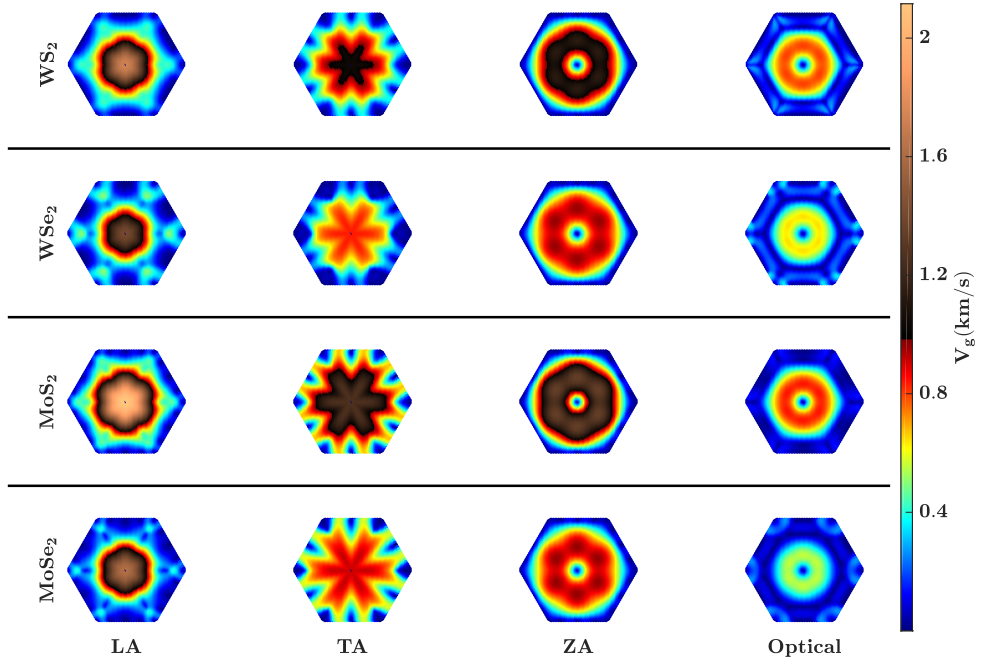


Figure 3.16: The magnitude of the group velocities at 300 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

In contrast to lifetimes where transition metal atoms are dominant, behavior of the group velocities are dictated by chalcogen atoms. In order to explain this behavior, it must be noted that total ionic mass in the unit cell is one of the factors that determines the maximum frequencies. The quadratic behavior of ZA mode is one the features of the 2D materials. From Figure 3.16 this feature is observable from the circularly symmetric increasing group velocity from the Γ point.

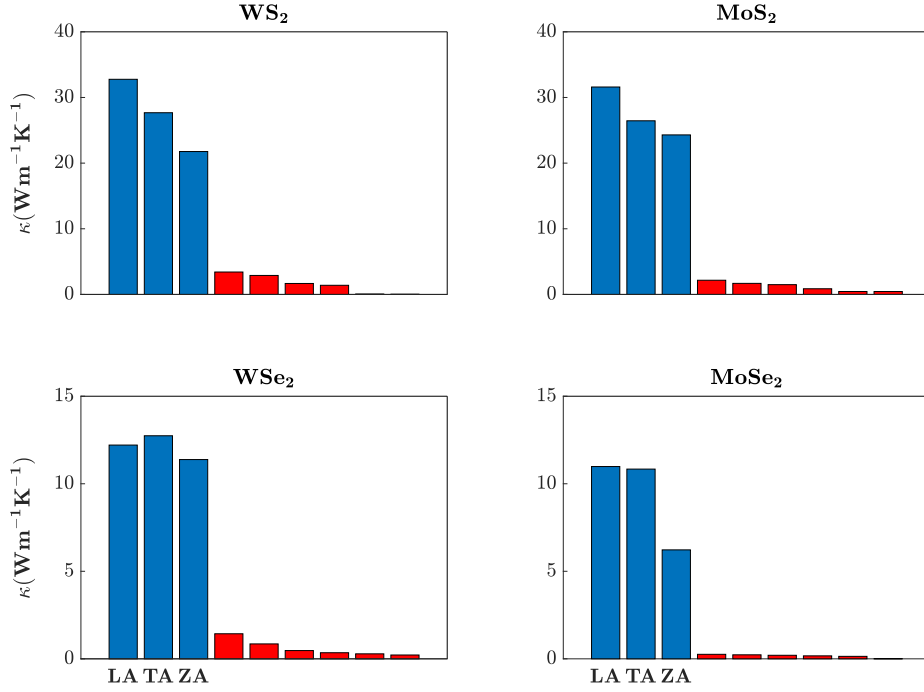


Figure 3.17: Contribution of different modes to the room temperature lattice thermal conductivity. The contributions of optical modes are shown by the red bars.

Accurately calculated lifetimes, group velocities for distinguished modes enables us to determine the thermal conductivity as well as the contribution of each mode in thermal conductivity. In Figure 3.17 the contribution of each mode in thermal conductivity at room temperature is presented. The expected high contribution of acoustic modes can be seen from this figure. There are small contribution from optical modes in WS₂, WSe₂ and MoS₂, however for MoSe₂ the optical modes have negligible contribution. Furthermore, the contribution of ZA mode is the smallest in MoSe₂. This trend is observable for ZA mode of MoSe₂ in all considered temperatures as it is shown in Figure 3.18 where temperature dependence of the contribution of acoustic modes to the lattice thermal conductivity is depicted. This factor might be other evidences for larger anharmonicity in MoSe₂.

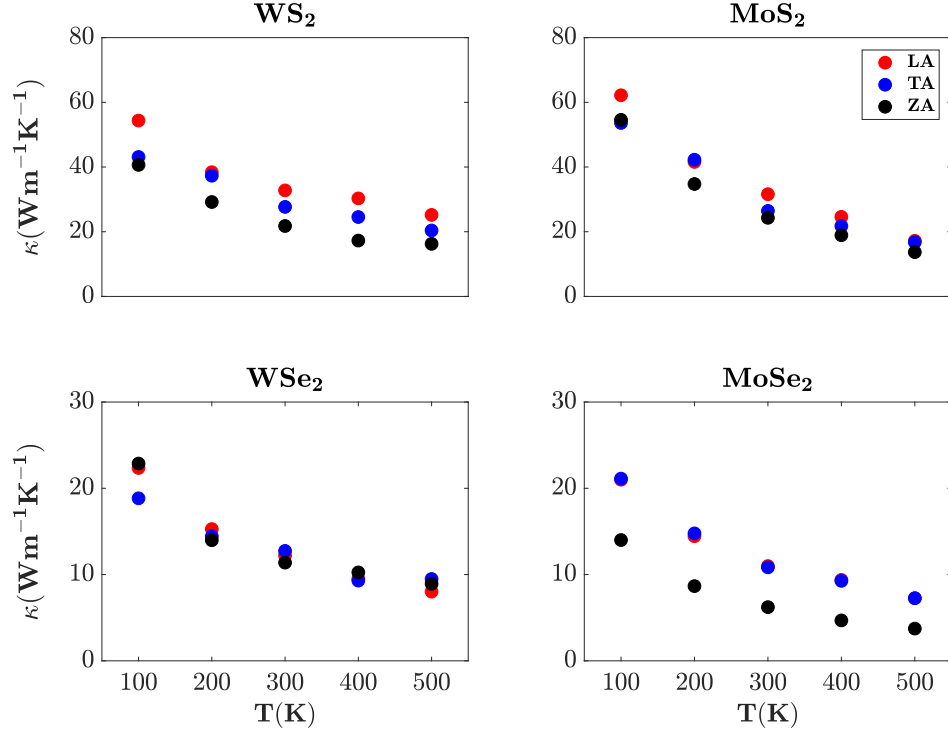


Figure 3.18: Temperature dependence of the contribution of acoustic modes to the lattice thermal conductivity.

In final step, the obtained thermal conductivities from SED are presented in Figure 3.19 and are compared to those predicted by Green-Kubo and other theoretical methods as well as available experimental data. The calculated thermal conductivities at room temperature are 91.66, 89.43, 39.94, and 29.05 $\text{Wm}^{-1}\text{K}^{-1}$ for WS_2 , MoS_2 , WSe_2 and MoSe_2 respectively. These results indicate the dominant role of the chalcogen atom in the thermal conductivity.

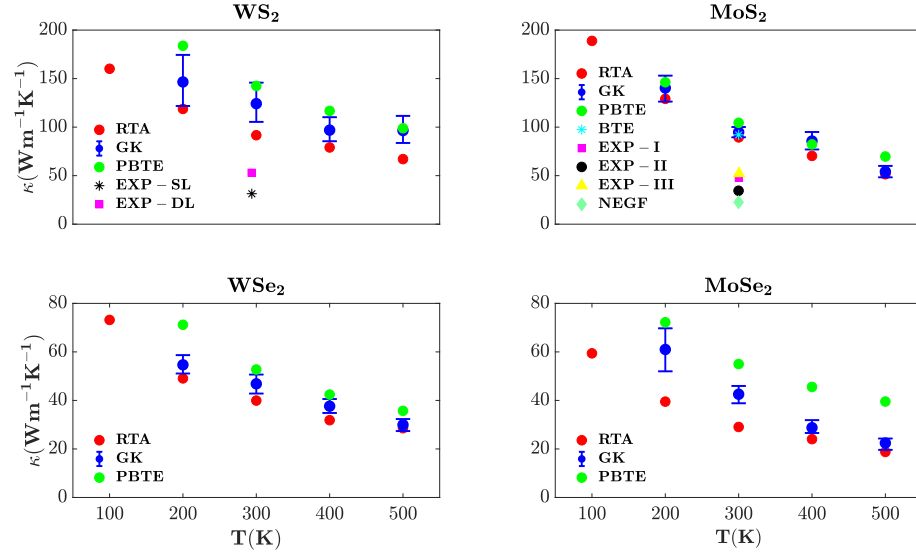


Figure 3.19: The lattice thermal conductivity values as a function of temperature. Here, solid red circles are the values calculated in this study, and the values represented by GK, PBTE, BTE, NEGf, EXP-SL, EXP-DL, EXP-I, EXP-II, EXP-III are extracted from [18–21, 112, 113, 125–127], respectively.

The rest of the figures presented in this chapter are the group velocities and lifetimes at other temperatures considered in this study rather than room temperature.

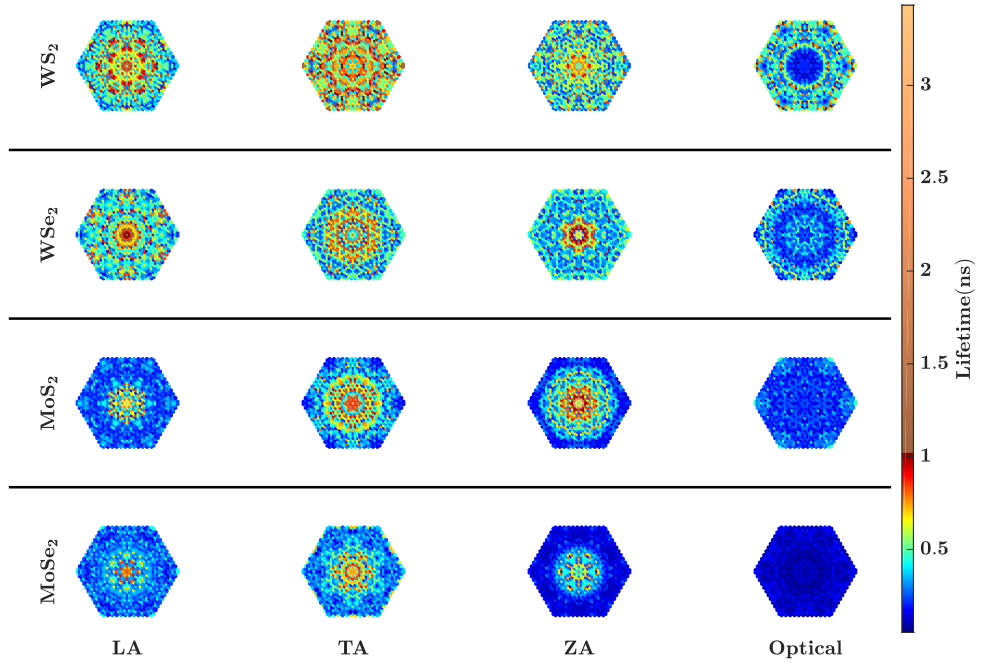


Figure 3.20: The calculated phonon lifetimes by SED approach at 100 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

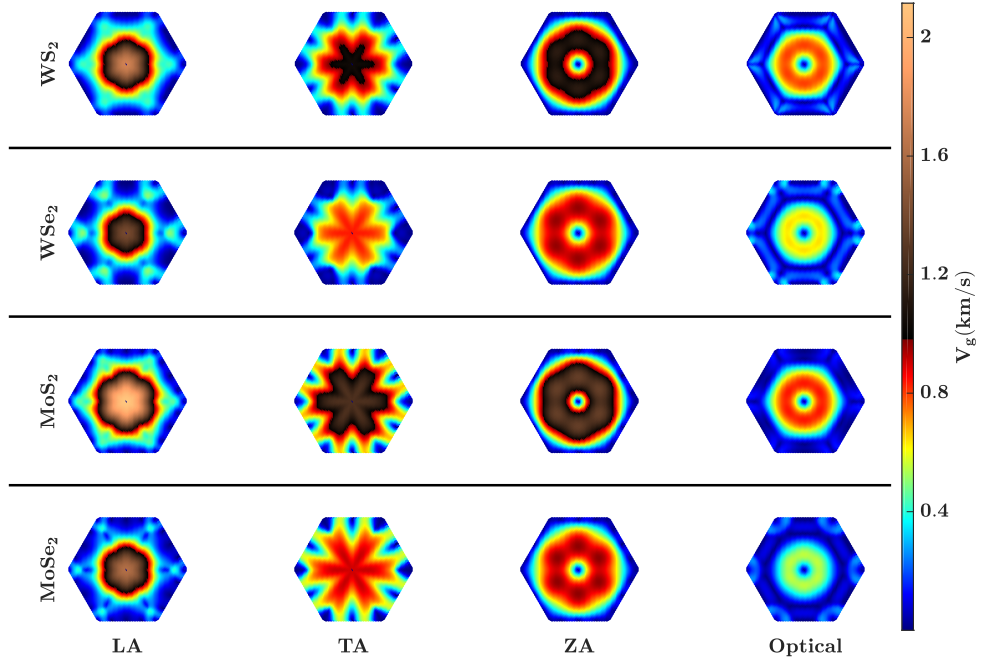


Figure 3.21: The magnitude of calculated phonon group velocities by SED approach at 100 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

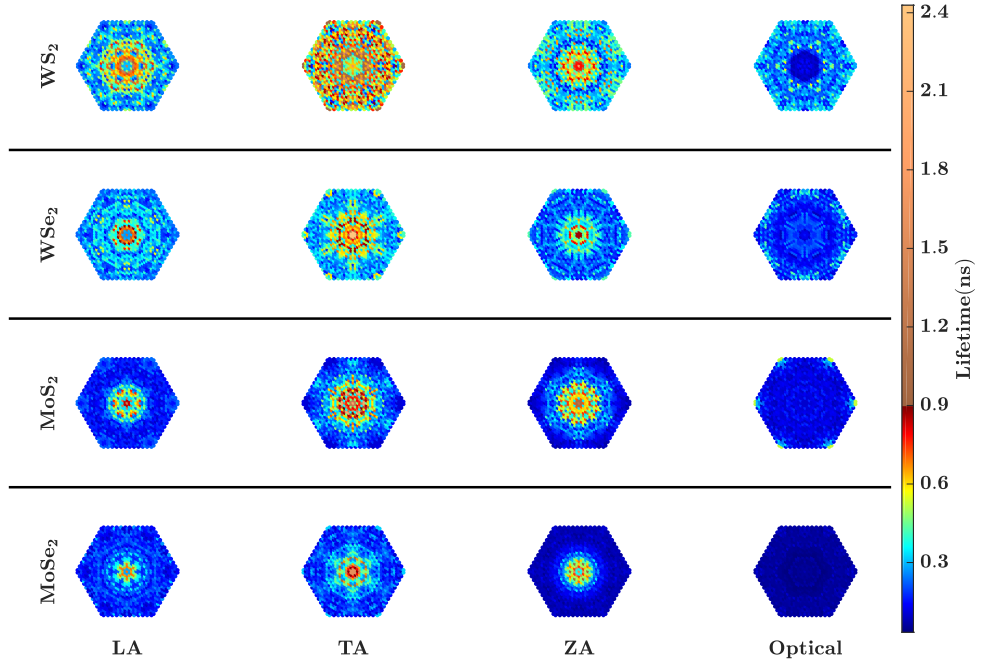


Figure 3.22: The calculated phonon lifetimes by SED approach at 200 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

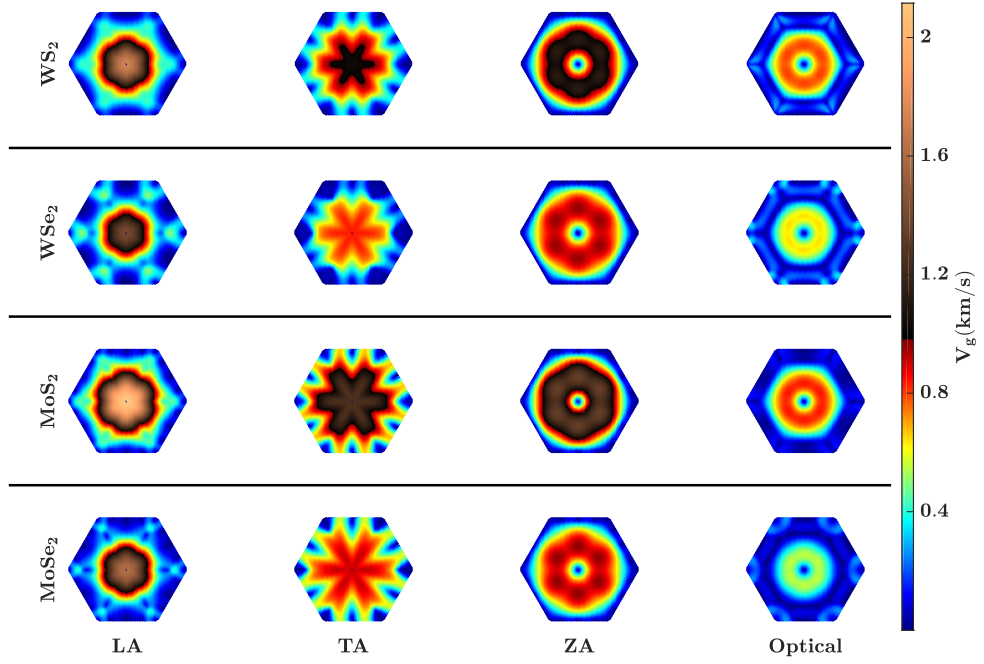


Figure 3.23: The magnitude of calculated phonon group velocities by SED approach at 200 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

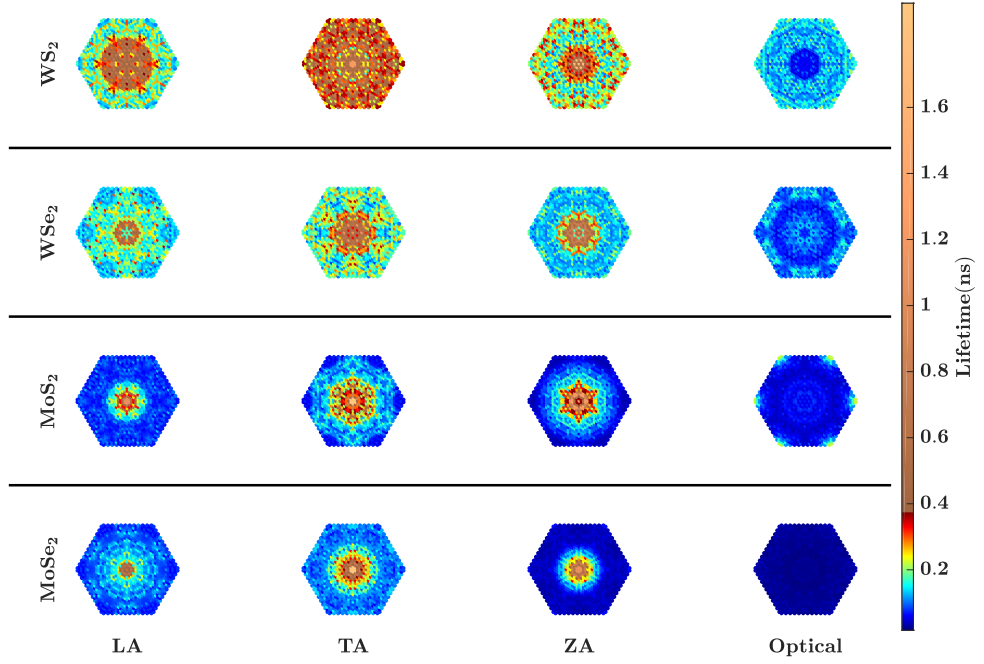


Figure 3.24: The calculated phonon lifetimes by SED approach at 400 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

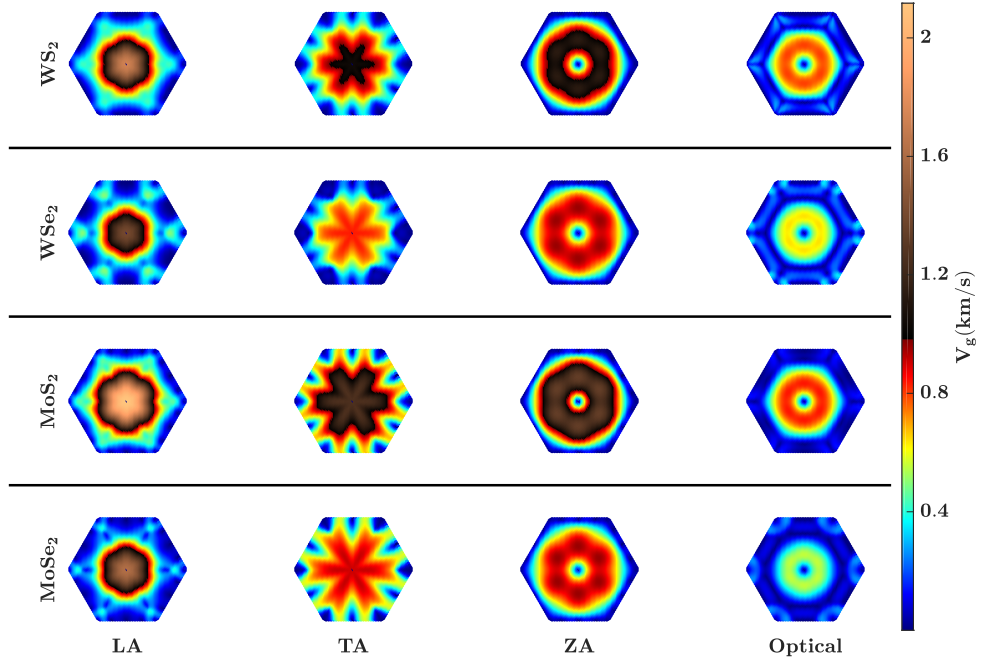


Figure 3.25: The magnitude of calculated phonon group velocities by SED approach at 400 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

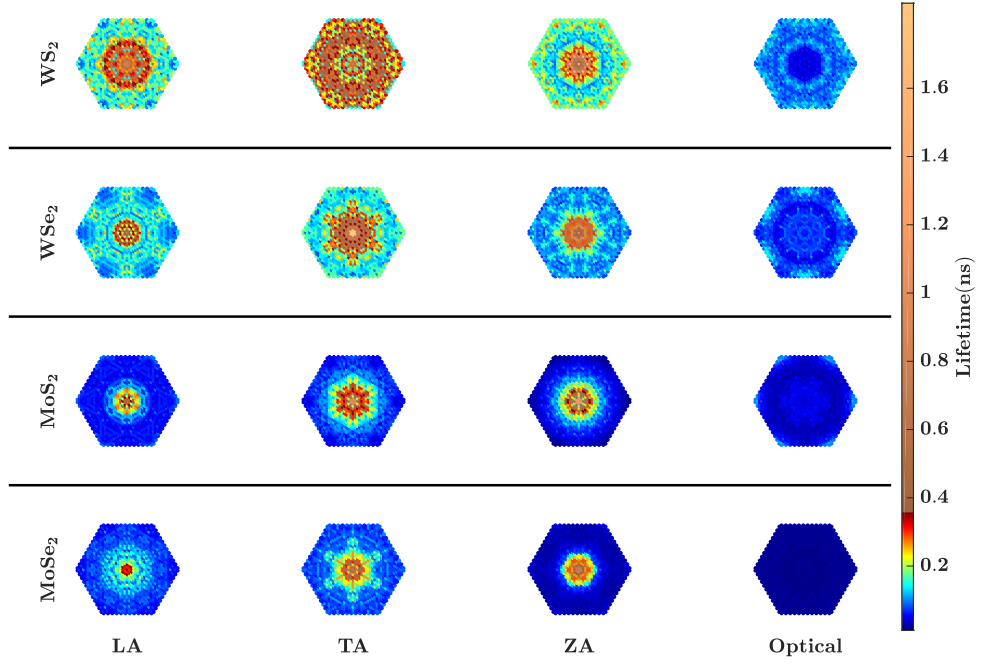


Figure 3.26: The calculated phonon lifetimes by SED approach at 500 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

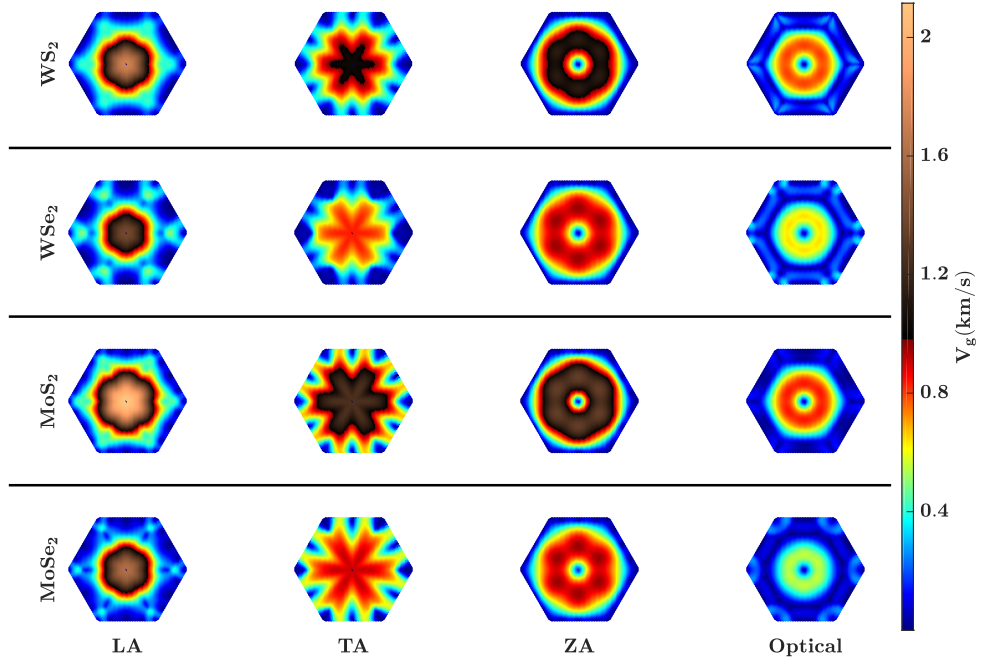


Figure 3.27: The magnitude of calculated phonon group velocities by SED approach at 500 K. The represented optical mode is the optical phonon branch, which has a greater contribution to thermal conductivity.

Chapter 4

Optimized Stillinger-Weber Potential for Sample 2D Materials

As it is explained in chapter 2 and utilized in chapter 3 the general approach in optimizing parameters for the pairwise potentials is using a global optimization method targeting the experimental or first principle results. Dealing with constant target functions such as lattice constant or cohesive energy is not very expensive, however the most important objective function is the error in phonon frequencies which makes the optimization very expensive. This approach becomes more expensive when the properties of different phases considered as the target values. On the other hand, in the case of the SW potential it was thought that it is unable to describe the bond bending in the simple planar 2D materials such as graphene or h-BN [86]. In this chapter by distinguishing three body and two body parameters using the energies taken from DFT calculations, we presented a method for optimizing this potential and novel SW potentials for graphene and silicene and planar 2D structures of GaN, BN and AlN are obtained. Furthermore, we investigated the capability of SW potential in describing both bulk and monolayer structures using single set of parameters. The method presented here provides a very fast and reliable framework for parameter selection and can be used for any analytic potential with similar form as SW potential.

4.1 Isolating Three-body Term of the SW Potential

Based on the main assumptions in selecting the parameters of SW potential which are described in chapter 2 and using two sets of displacements of atoms it is possible to obtain an energy curve which can be described by only the three-body parameters of the SW potential. In the cases of graphene-like structures which have two basis atoms in the unit cell, assuming that one of the basis atoms is fixed at the origin the first set of displacements are perpendicular to the lattice plane and the position of the second atom in each step can be written as:

$$x = \left(\frac{b_e\sqrt{3}}{2}, \frac{b_e}{2}, n_d D \right) \quad (4.1)$$

Where D is the constant magnitude of the displacement at each step n_d and b_e is the equilibrium bond length. In each step, three bond lengths between the displaced atom and its nearest neighbors are same and corresponding angles are also equal and given by:

$$\theta = 2\sin^{-1} \left(\frac{b_e\sqrt{3}}{2\sqrt{(b_e^2 + n_d^2 D^2)}} \right) \quad (4.2)$$

Therefore, the total energy at each step can be written as an explicit function of the bond length.

In the second set of displacements, the bond length of the equilibrium structure is gradually increased according to the values which are considered at the first set of displacements. Therefore, the two-body energies of the first and second displacements are equal and their energy difference can be written in the terms of the three-body potentials:

$$E_{d_1} - E_{d_2} = \phi_3(b, b, \cos(\theta)) - \phi_3(b, b, -0.5) \quad (4.3)$$

Where E_{d_1} and E_{d_2} are the total energies obtained from the first and second

sets of displacements, b is the bond length and θ is given by equation 4.2. Because only the increasing of the lattice constant is considered previously, another set of displacements is required to describe the change of the energy with decreasing the lattice constant. In LAMMPS notation two-body and three-body terms of the SW potential are given by:

$$\begin{aligned}\phi_2(r_{ij}) &= A_{ij}\varepsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}} \right) \\ \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) &= \lambda_{ijk}\varepsilon_{ij} [\cos(\theta_{ijk}) - \cos(\theta_{0_{ijk}})]^2 \exp \left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}} \right)\end{aligned}\tag{4.4}$$

The parameters σ and ϵ have the units of distance and energy respectively. The rest of the parameters are unitless.

By using the aforementioned method the problem of parametrization of the SW potential is reduced to fitting two energy curves obtained by the described displacements. Equation 4.3 is described only by three parameters. Therefore, by using Equation 4.3 it is possible to investigate the effect of the parameter $\theta_{0_{ijk}}$ which is usually selected as the equilibrium angle.

4.2 SW Potential for Graphene

In determining the three-body parameters using the method which is described in previous section if we select the angle manually the number of the parameters would be reduced to two. Therefore, it is possible to fit the obtained curve using nonlinear least squares. As it shown figure 4.1, applying the presented method to graphene reveals that by using the equilibrium angle ($\cos \theta_{0_{ijk}} = -0.5$) it is not possible to fit the obtained energy curve. Therefore, we let this value to vary within the range of $[-1 \ 1]$. We tested particle swarm method and nonlinear least squares fit for selecting three-body parameters and both of the methods give ($\cos \theta_{0_{ijk}} = -1$) as the best value for angle term in the potential.

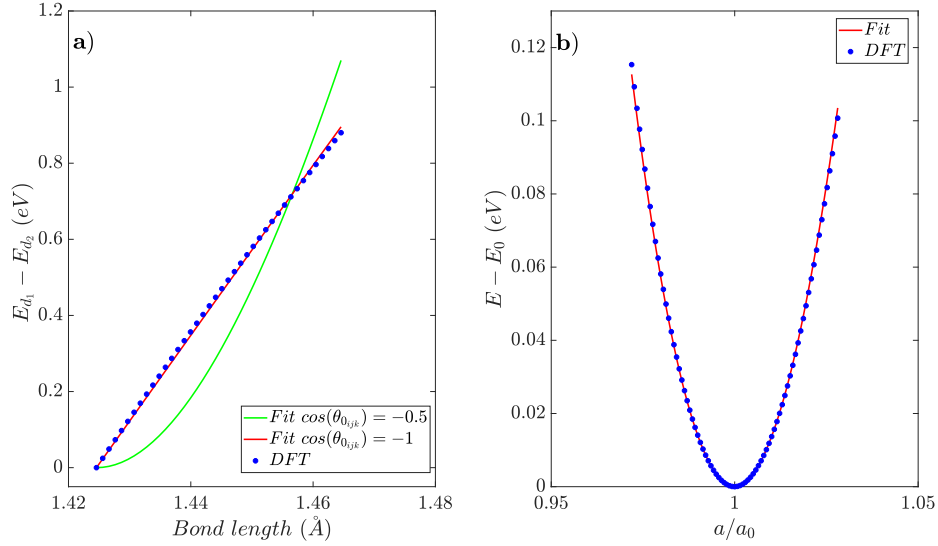


Figure 4.1: a) Energy difference between the second and first displacements obtained from DFT (blue dots), fitted curves by using the equilibrium angle (green line) and the best fit (red line) which gives the $\cos\theta_{0,ijk} = -1$ as the best angle. b) Difference between the total energy and minimum energy versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data and red line is the fit obtained using the three-body parameters obtained from the best fit of the a).

Using the obtained three-body parameters the energy versus bond length curve is also fitted. Obtained parameters are presented in Table 4.3. In order to justify the resulted potential in Figure 4.2 the obtained phonon dispersion curves are compared with those obtained from Tersoff potential [87], DFT-GGA, and available experimental data.

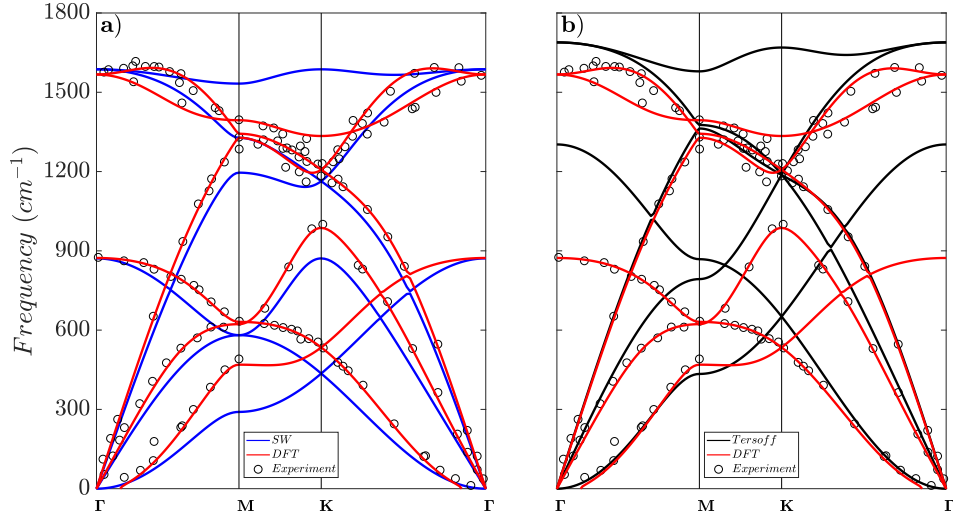


Figure 4.2: a) Phonon dispersions obtained from SW (blue lines) compared with DFT (red lines) and the experimental results (black circles) for graphite [128, 129]. b) Phonon dispersions obtained from Tersoff potential [87] compared with DFT.

The new SW potential gives more accurate description near Γ point, especially for the ZO mode (optic mode with the lowest frequencies) where Tersoff potential fails to generate the desired results. In addition, SW accurately describes the crossing points of phonon branches, whereas Tersoff potential fails. However, SW potential gives lower phonon frequencies than the DFT at points far from the Γ point. This can be interpreted as the result of the first nearest neighbor approach. It is shown that without considering the long range interactions it is not possible to describe the behavior of LO-TO phonons near the center of the Brillouin zone and the flatting of the TA mode at the zone boundary [130]. The Tersoff potential is optimized by giving more weight to the acoustic phonon frequencies therefore the acoustic phonon frequencies near the Γ points are match to experimental data. However, near the zone boundaries specially the K point it gives much higher frequencies than DFT and group velocities are overestimated. One way for improving the potential is adjusting the value of $\cos \theta_{0,ijk}$. The effect of the change of this value is shown in Figure 4.3.

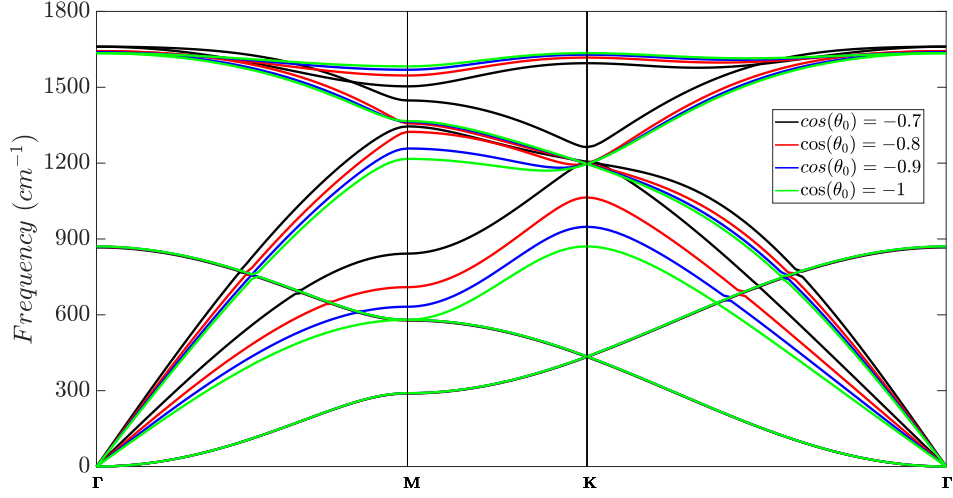


Figure 4.3: Effect of the change of the $\cos \theta_{0,ijk}$ on phonon dispersion.

From Figure 4.3 it is clear that by decreasing $\cos(\theta_0)$ LA and TA modes shift to higher frequencies, but the ZA mode remains unchanged. In order to obtain better behavior of acoustic phonon frequencies we combined particle swarm optimization with nonlinear least squares method. The particle swarm optimization has only the $\cos \theta_{0,ijk}$ as the variable and the total error in the phonon frequencies is considered as the cost function. Each particle of particle swarm optimization generates a SW potential as the LAMMPS input by taking a $(\cos \theta_{0,ijk})$ value then fitting the energy curves. The parameters obtained from this approach are given in Table 4.3 and the the phonon dispersion curves compared with the result of the DFT in Figure 4.4.

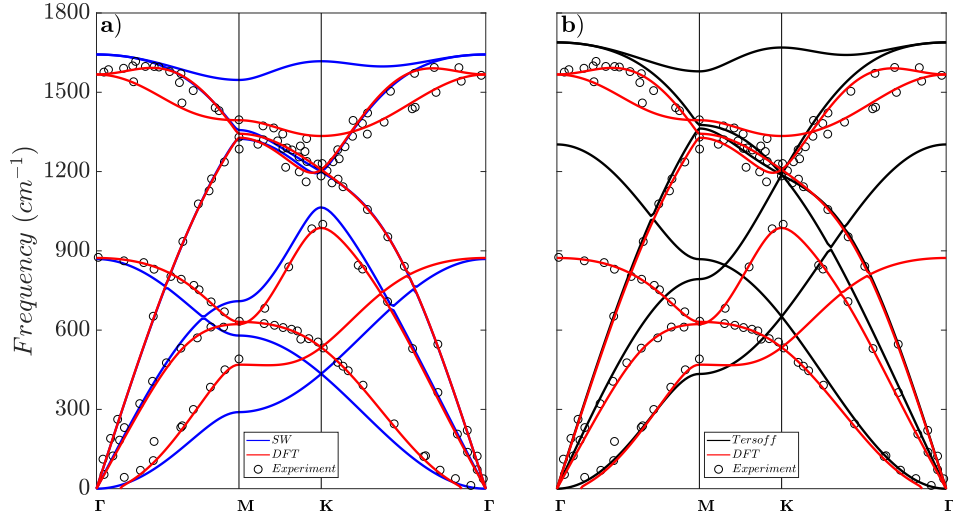


Figure 4.4: a) Phonon dispersion obtained from SW potential with optimized $\cos \theta_{0,ijk}$ compared with DFT and experiment. b) Phonon dispersion obtained from Tersoff potential compared with DFT and experiment (black circles) [128, 129].

It is clear that all of the acoustic branches and all near Γ frequencies are in good agreement with the DFT data. However, in this case the crossing points of the ZO mode and acoustic modes are shifted. Also the ZA mode is still underestimated. It is shown that by considering the second nearest neighbors in the potential, a good agreement with the DFT results can be achieved. Since the magnitude of the long range forces are usually much smaller than the short range forces, the main effect of considering the second nearest neighbor interactions is the correcting the directions of the forces on the atoms. Here this correction is partially achieved by the change in $\cos \theta_{0,ijk}$. In the next section we show that it is possible to improve the dispersion curves by adjusting the potential parameters and then the SW potential for graphene will be revisited.

4.3 SW Potential for Silicene

Silicene has hexagonal lattice similar to graphene, but there is a small buckling in this case. Considering the primitive unit cell with two basis atoms the positions of the displaced atom in the first set of displacements is given by:

$$x = \left(\frac{b_e\sqrt{3}}{2}, \frac{b_e}{2}, n_d D + B \right) \quad (4.5)$$

Where D is the constant magnitude of the displacement at the step n_d of the displacements and B is the buckling value. The bond angles are equal in each step of the displacements and they can be written as a function of the bond length. In this case, by using a negative value for D it is possible to decrease the bond length in the first set of displacements. Therefore, only two sets of displacements are enough for obtaining three-body parameters. The second set of displacement are simply moving the lower plane upward or downward according to the bond lengths obtained in the first set of displacements. This keeps the bond angle constant and equal to equilibrium angle. The results of the fittings are presented in Figure 4.5. Unlike the graphene, both particle swarm optimization and fit give the equilibrium angle as the best value for the angle term in the SW potential. The parameters of the DFT calculation are selected according to dose described in reference [9].

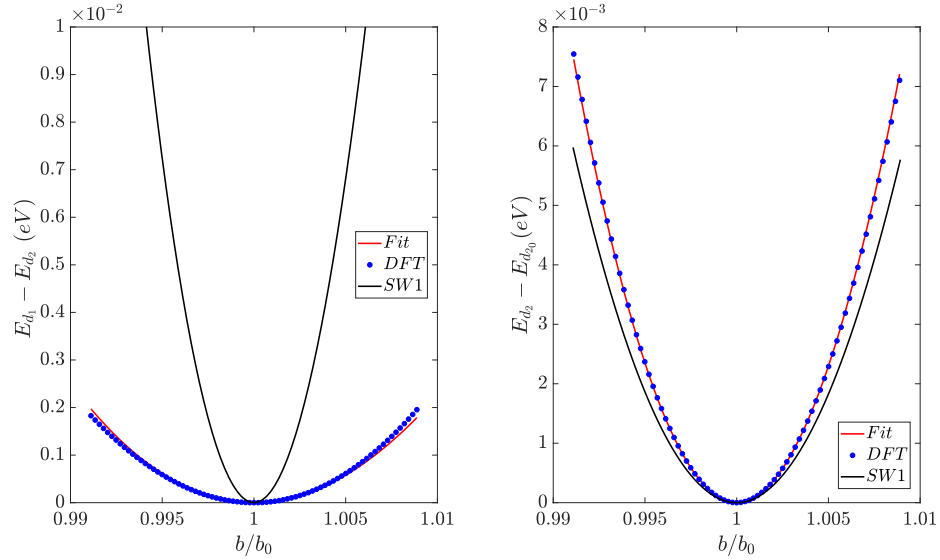


Figure 4.5: a) Energy difference between the second and first displacements obtained from DFT (blue dots), the best fit (red line) and the resulted curve using the three-body parameters of [131]. b) Difference between the total energy obtained in second sets of the displacements and its minimum versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data, red line is the fit obtained using the three-body parameters obtained from the best fit of the a) and the black line is the result of reference [131].

In Figure 4.6 the phonon dispersion curves obtained from the fit are compared with the results obtained using available SW potential [131]. From Figure 4.6 it can be seen that unlike the graphene the parameters obtained from fit are not able to describe none of the acoustic modes correctly. This shows that within the framework of the SW potential and using the first nearest neighbor approach it is not possible to describe phonon dispersion curves correctly. One possible solution is considering a two-body interaction with larger cutoff between the second nearest neighbor atoms. It is exactly the same approach which is used in the previous chapter for optimizing SW potential for TMDs. Although it is possible to utilize the approach which is described in this chapter for including the second nearest interactions as well, but we move in another direction to find possible ways for improving the results based on the first nearest neighbor approach.

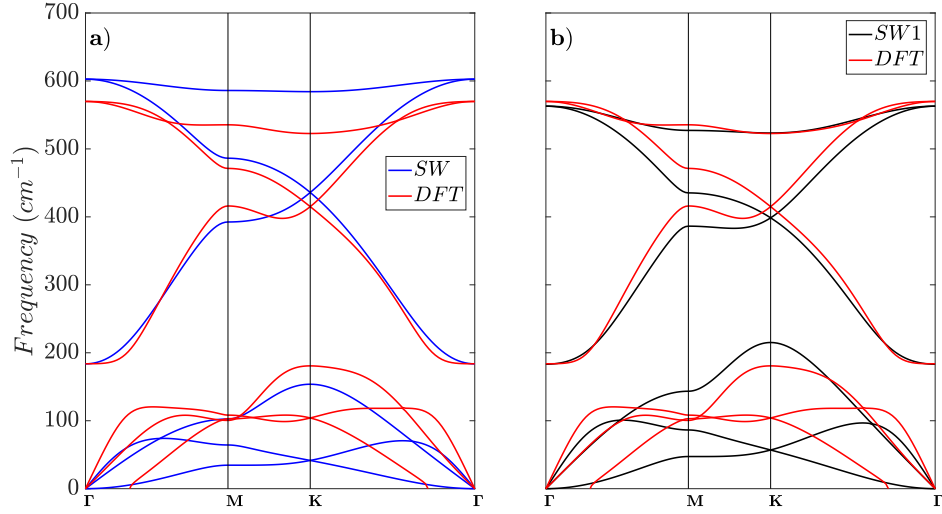


Figure 4.6: a) Phonon dispersion curves obtained from the SW potential parametrized by fitting energy curves (blue lines) and DFT (red lines). b) Black lines are the phonon dispersion curves for silicene obtained from the SW potential of the reference [131] and red lines are DFT results.

Comparing the results of the SW potentials in Figure 4.6 reveals that the acoustic modes have similar behaviors but SW potential obtained from the fit gives smaller frequencies. Although, the DFT approach used for generating target data for optimizing parameters in [131] is not exactly same as our approach, but as it shown in Table 4.1 the resulted lattice parameters are close. Therefore, the resulted energy curves from the two sets of the displacements can be compared as it is done in Figure 4.5. This reveals that the energy difference curve obtained from parameters of reference [131] deviates from DFT results. As it is illustrated in Figure 4.7 such deviation can be generated by adjusting the three-body parameter λ and keeping the rest of the three-body parameters same.

From Figure 4.7 it is clear that the phonon frequencies are increasing by increasing λ . There is also deviation from DFT results in second set of the displacements using the parameters of the reference [131] which can be generated by tuning the two-body parameter A and keeping other two-body parameters fixed.

Table 4.1: Lattice parameters obtained from two sets of SW potential. Here SW_{fit} is the potential parametrized by fitting energies obtained from DFT and SW_1 and DFT_1 are the potential optimized and the result of the DFT calculation in reference [131].

	SW_{fit}	SW_1	DFT	DFT_1
$\mathbf{a}$ (Å)	3.826	3.812	3.826	3.812
$\mathbf{B}$ (Å)	0.438	0.427	0.438	0.427

In 4.8 the effect of the variation of parameter A on the phonon dispersion curves is shown. The acoustic modes remain same by variation of A and only optical frequencies are increasing by increasing the parameter A . These results clarify the the difference between the phonon dispersion from the fitting energy curves and the results of the reference [131] where the phonon frequencies are used as target data in optimization.

Using these results, it is possible to improve the phonon dispersion by particle swarm optimization approach in two steps. In the first step, acoustic modes are optimized by tuning parameter λ and in the second step optical modes are optimized by adjusting the parameter A . In Figure 4.9 the resulted energy curves are shown and the obtained phonon dispersion is shown in Figure 4.10 and the obtained parameters from the fit and final optimized parameters are given in Table4.2. The optimized potential has better agreement with DFT for acoustic modes near the Γ point but still is far from the DFT results near the Brillouin zone boundaries.

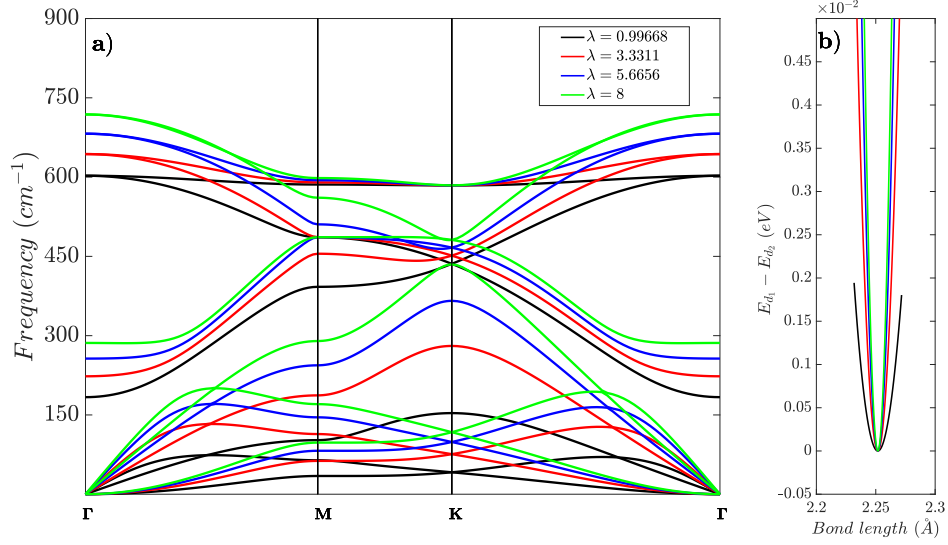


Figure 4.7: a) Effect of variation of the three-body parameter λ on the phonon dispersion of the silicene. b) Effect of variation of the three-body parameter λ on the energy difference curve.

Table 4.2: Two sets of optimized SW parameters for silicene. SW_{fit} is obtained by directly fitting and SW_{opt} is obtained by optimizing parameters λ and A using particle swarm optimization method.

	SW_{fit}	SW_{opt}
$\epsilon(\text{eV})$	1	1
$\sigma(\text{\AA})$	1.701074	1.701074
a	2.14451	2.124116
λ	2.098841	2.90
γ	0.293932	0.293932
$\cos(\theta_0)$	-0.443227	-0.443227
A	15.165689	11.5
B	0.582054	1.059419
p	4	4
q	0	0

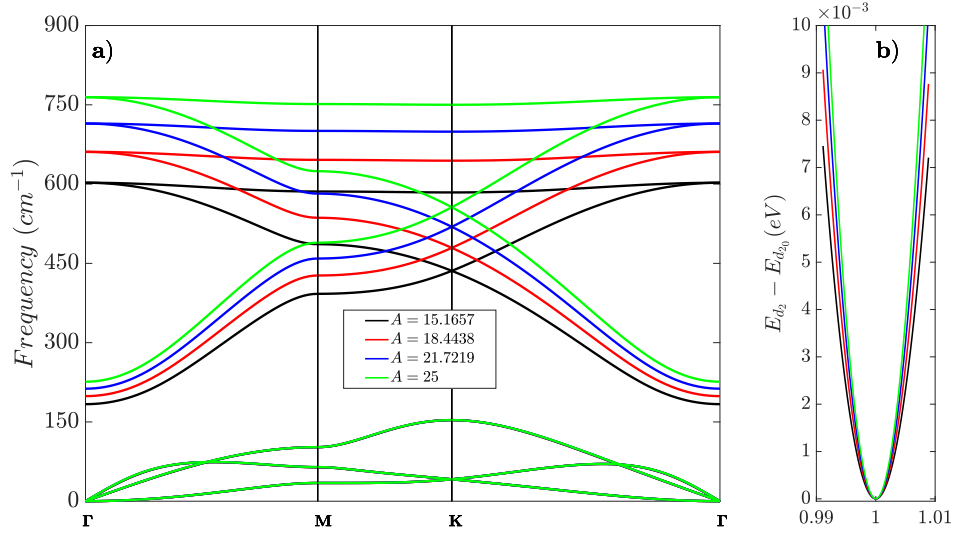


Figure 4.8: a) Effect of the variation of the two-body parameter A on the phonon dispersion of the silicene. b) Effect of the variation of the two-body parameter A on the energies obtained from second set of the displacements.

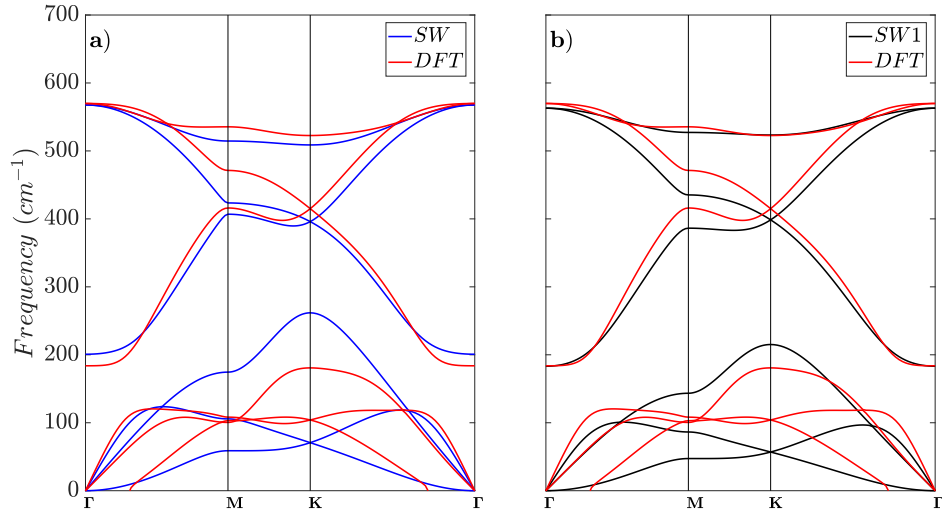


Figure 4.10: a) Phonon dispersion curves obtained from optimized SW potential (blue lines) and DFT (red lines). b) Black lines are the phonon dispersion curves for silicene obtained from the SW potential of the reference [131] and red lines are DFT results.

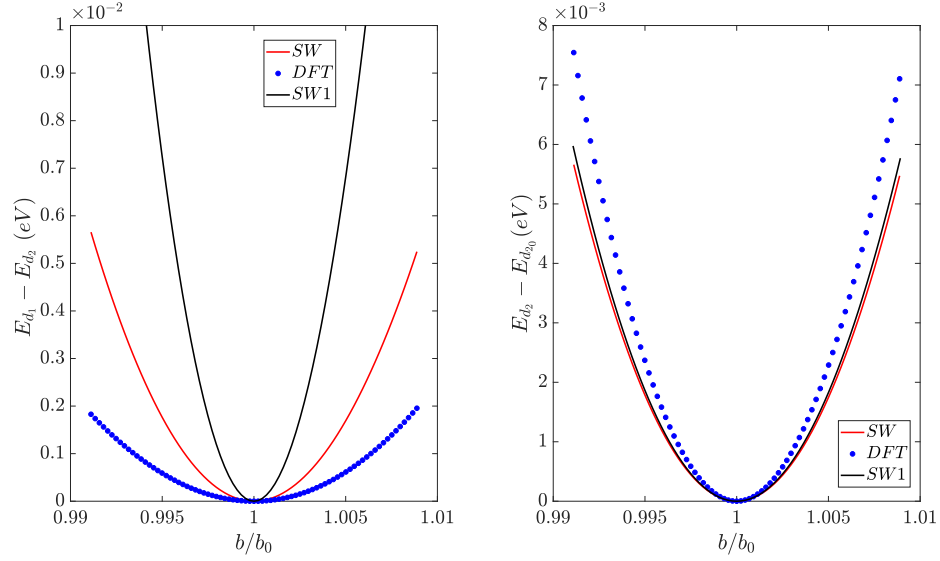


Figure 4.9: a) Energy difference between the second and first displacements obtained from DFT (blue dots), optimized λ (red line) and the resulted curve using the three-body parameters of [131] (black line). b) Difference between the total energy obtained in second sets of the displacements and its minimum versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data, red line is obtained using the three-body parameters of a) and black line is the result of reference [131].

There has been other attempts for generating interatomic potential for silicene. In reference [86] the parameters of the SW potential are analytically driven from the valence force field model. In another work Tersoff potential is optimized for silicon and thermal stability of the silicene is investigated and it is predicted that the single layer is not stable at room temperature [132]. The phonon dispersions obtained from these potentials are shown in Figure 4.11.

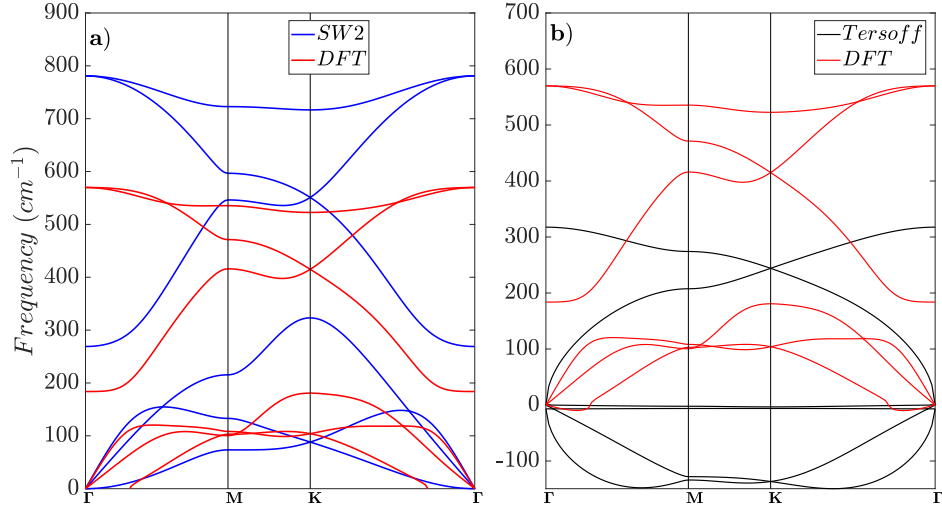


Figure 4.11: a) Blue lines are the phonon dispersion curves obtained using SW potential parametrized using valence force field [86]) and DFT (red lines). b) Black lines are the phonon dispersion curves for silicene obtained from the Tersoff potential [132] and red lines are DFT results.

The SW potential obtained from valence force field predicts much higher optical frequencies and the Tersoff potential gives negative frequencies which clarify the reason of the reported collapse during the MD simulation.

4.4 SW Potential for Graphene Revisited

Using the results of the previous section, it is possible to improve the behavior of phonon dispersion curves of graphene. Here the angle term in three-body potential is selected as the best predicted angle which is equal to π rad. Therefore the parameters λ and A are not decoupled and the selection of parameter λ changes all other two-body parameters. The effect of the variation of λ is shown in Figure 4.12.

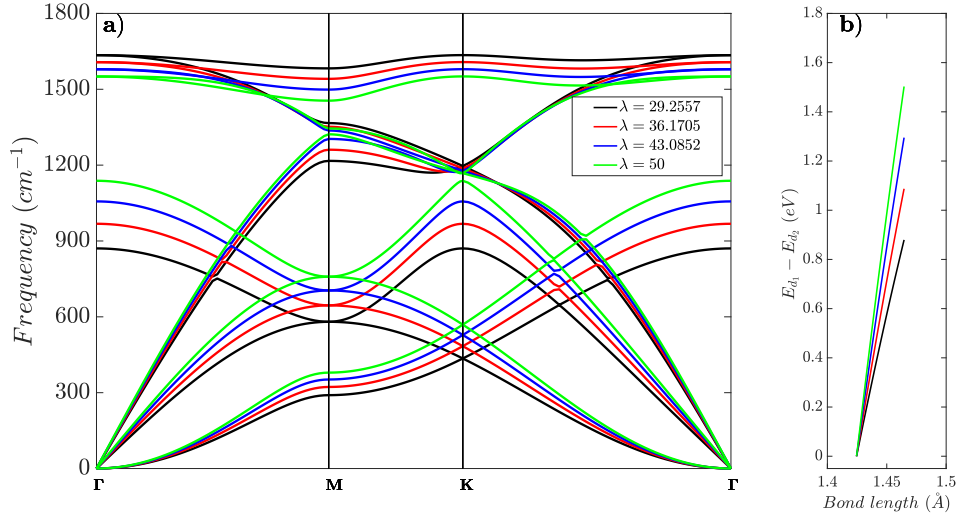


Figure 4.12: a) Effect of variation of the three-body parameter λ on the phonon dispersion of the graphene. b) Effect of variation of the three-body parameter λ on the energy difference curve.

From Figure 4.12 it is clear that all acoustic phonon frequencies are increasing by increasing λ . In order to improving the results, the parameter λ is adjusted to minimize the error in phonon dispersion curves. The resulted phonon dispersion of this last step is presented in Figure 4.13 and the obtained parameters are presented in Table 4.3.

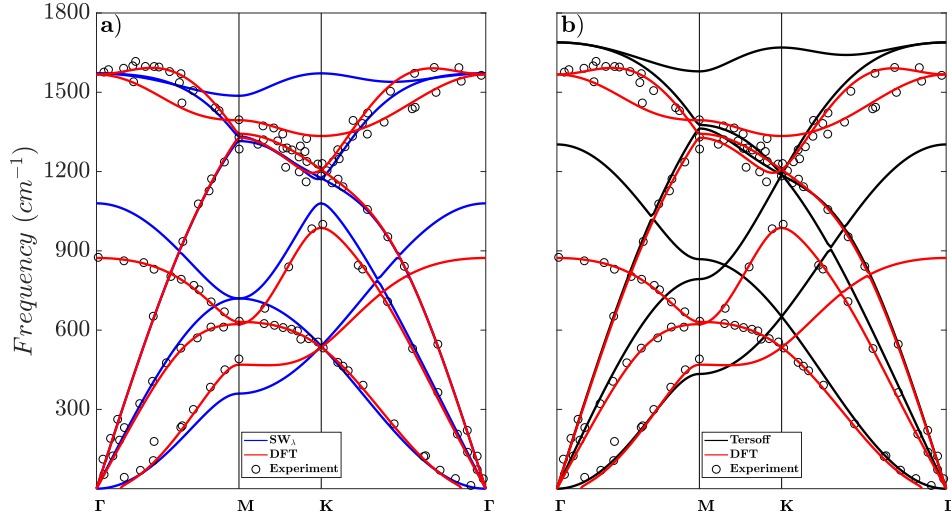


Figure 4.13: a) Blue lines are the phonon dispersion curves obtained using SW potential parametrized according to parameter λ , DFT (red lines) and experimental data (black circles) taken from . b) Black lines are the phonon dispersion curves for obtained from the Tersoff potential [87].

As it can be seen in Figure 4.14 the resulted potential generates acoustic modes much more accurately than the Tersoff potential. The LA mode (acoustic mode with highest frequency) is completely captured and the behavior of other acoustic modes are become more similar to DFT results. Also the position of the degenerate optical modes at Γ point is correctly obtained. Although, the behavior of the ZO mode (optical mode with lowest frequencies) is deviated from DFT results, but the obtained potential is still the best among those potentials based on first nearest neighbor approaches. We conclude this section by comparing the result of the optimized potential with the results of long-range bond-order potential for carbon (LCBOP) [133]. From Figure 4.14 it can be seen that the optimized SW potential gives better description for phonon dispersions. The more accurate phonon dispersion curves are obtained using machine learning potential which has a cutoff equal to $4\text{\AA}$ [134].

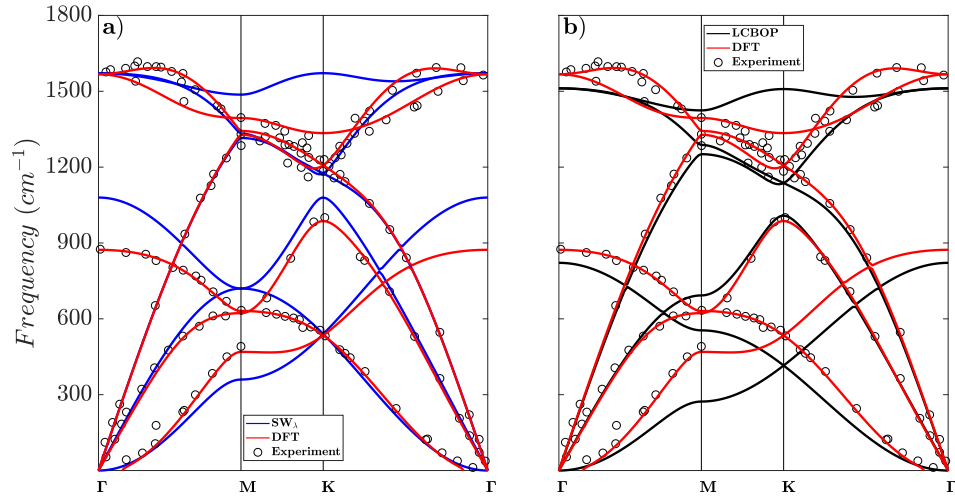


Figure 4.14: a) Blue lines are the phonon dispersion curves obtained using SW potential parametrized according to parameter λ , DFT (red lines) and experimental data (black circles) taken from [128, 129]. b) Black lines are the phonon dispersion curves for obtained from the LCBOP potential [133].

Table 4.3: Three sets of optimized SW parameters for graphene. SW_{fit} is obtained by directly fitting, $SW_{cos(\theta_0)}$ is obtained by optimizing $cos(\theta_0)$ using the particle swarm optimization method and SW_λ is obtained by optimizing λ using the particle swarm optimization method.

	SW_{fit}	$SW_{cos(\theta_0)}$	SW_λ
$\epsilon(\text{eV})$	1	1	1
$\sigma(\text{\AA})$	1.119137	1.129882	1.218292
a	2.14451	2.124116	1.969971
λ	29.242514	140.921647	45
γ	1.194453	1.642945	1.097401
$cos(\theta_0)$	-1	-0.8	-1
A	28.729826	27.951552	33.551116
B	0.582054	0.592305	0.391605
p	4	4	4
q	0	0	0

4.5 SW Potential for Group III Nitrides

In order to generalize the presented parameter selection approach to materials with more than one atom types and investigate the possibility of constructing transferable potentials, in this section we investigate GaN, AlN and BN monolayers and their bulk zinc blende structures. The stability of the graphene like monolayers of these structures are predicted theoretically [135] and they are already fabricated [136–139]. There are available force fields for bulk structures of these systems. In the case of monolayers widely used potential is Tersoff potential for h-BN [88]. The available SW potential for GaN [85] predicts negative phonon frequencies for monolayer.

The sets of displacements used for monolayers are exactly same as the case of the graphene.

The zinc blende structure considered for bulk systems is not the ground state

structure for all cases, for example at ambient condition AlN has wurtzite structure and under high pressure it transforms to zinc blende. The reason for selecting the zinc blende structure is that it has two basis atoms in the unit cell which simplifies the calculations. The unit cell of zinc blende structure is shown in Figure 4.15.

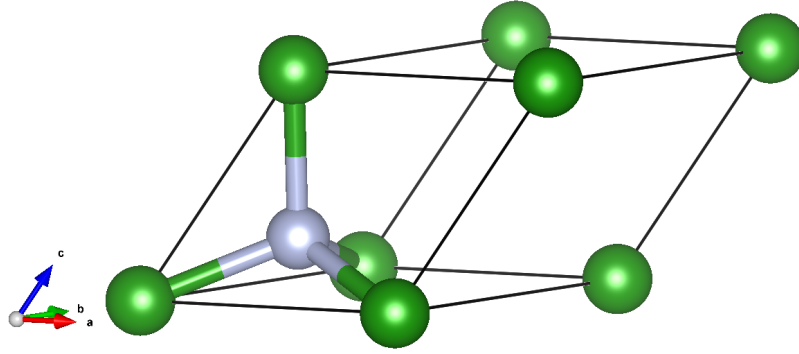


Figure 4.15: Unit cell of the zinc blende structure.

For the bulk case, in order to isolate the three-body interaction term the first set of the displacements is obtained by increasing or decreasing the angles between the three lattice vectors and moving the atom which is inside the parallelepiped on the diameter of the parallelepiped which passes from both of the considered basis atoms. This displacement makes the length of the bonds between the atoms equal. The angles between the three lattice vectors of primitive unit cell of the zinc blende structure are equal to $\frac{\pi}{3}$. In the first set of displacements this angle can be written as function of bond length:

$$\theta = 2\sin^{-1} \left(\frac{\sqrt{3}}{2} \sin \left(\cos^{-1} \left(\frac{a_e}{2bl} \right) \right) \right) \quad (4.6)$$

Where a_e is the equilibrium lattice constant. In each step of the displacement each atom has two different bond angles and they can be written in terms of bond

angle. The second set of the displacements are obtained by changing the lattice constant according to the bond lengths obtained from the first displacements.

4.5.1 SW Potential for GaN

In a first principle study it is shown that because of the large difference in electron negativity between Ga and N atoms the covalent bond in monolayer GaN is strongly polarized [140]. Therefore, the effect of the neglecting the long range interactions in designing the potential is predictable. The results of the fitting the energy curves and obtained phonon dispersion curves are presented in Figure 4.16.

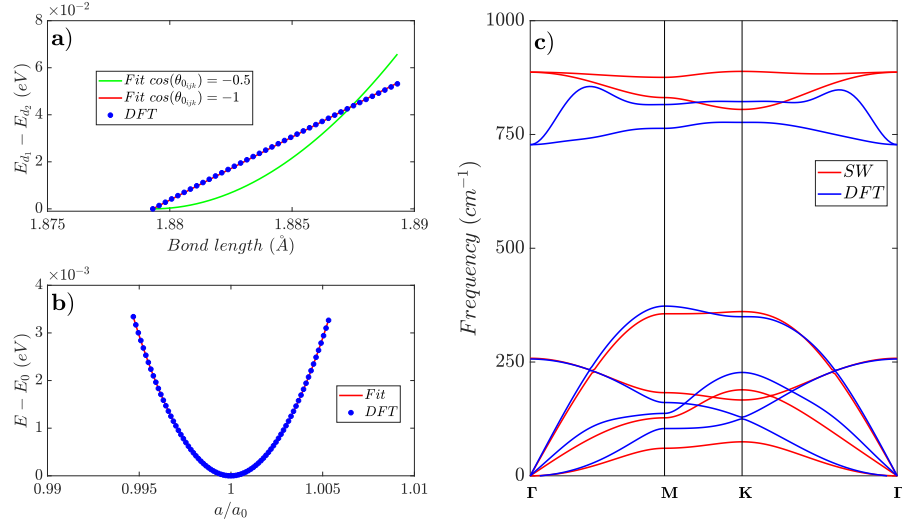


Figure 4.16: a) Energy difference between the first and second displacements obtained from DFT (blue dots), fit obtained using the equilibrium angle (green line) and the best fit (red line) which gives the $\cos \theta_{0,ijk} = -1$ as the best angle. b) Difference between the total energy and minimum energy versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data and red line is the fit obtained using the three-body parameters obtained from the best fit of the a). c) Calculated phonon dispersion curves for GaN by using SW potential (red lines) and DFT (blue lines).

From Figure 4.16, the effect of the neglecting long range interactions are evident. The LO-TO modes are not described correctly and the ZA and TA modes

are below the DFT results. Furthermore, there is a gap between ZO and ZA branches in the results obtained from SW potential. Here, the three-body terms $Ga - N - N$ and $N - Ga - Ga$ (the first atom is the center atom) are considered to be same. However, it is possible to distinguish these two terms and partially include the long range interaction of N-N and Ga-Ga atoms. As it shown in Figure 4.17, this can be achieved by using different three-body parameter λ for aforementioned three-body interactions.

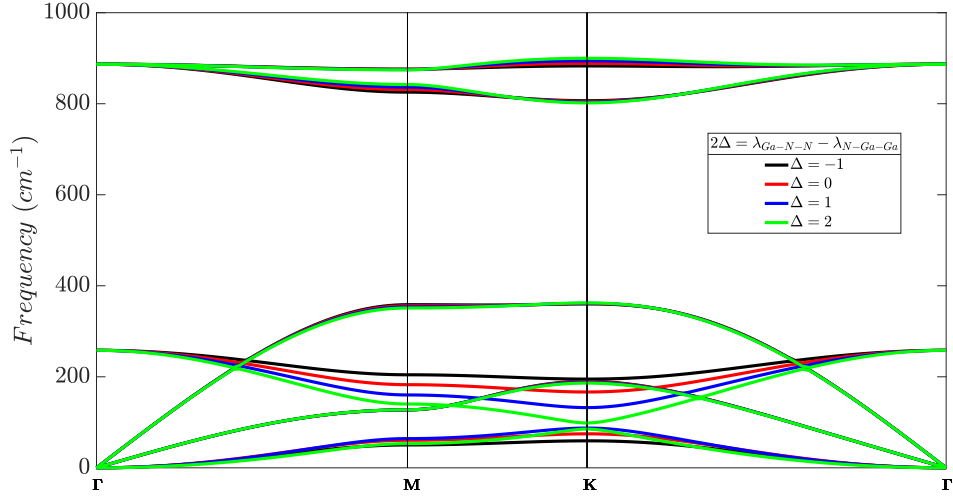


Figure 4.17: Effect of selecting different three-body parameter λ for Ga-N-N and N-Ga-Ga interaction on phonon dispersion curves of GaN. Here, the sum of two three-body parameters is equal to parameter λ which is obtained by fitting energy curves.

From Figure 4.17, it can be seen that by using the described approach it is possible to adjust the gap between the ZO and ZA modes. In order to obtain a better result the parameter λ is initially optimized using the same method used for graphene and then different λ values are selected utilizing particle swarm optimization. The resulted phonon dispersion curves are presented in Figure 4.18 and obtained parameters from this approach and the fitting the energy curves are presented in Table 4.5. The final optimization gives fairly accurate description for acoustic phonons but the behavior of optical phonons are not captured correctly.

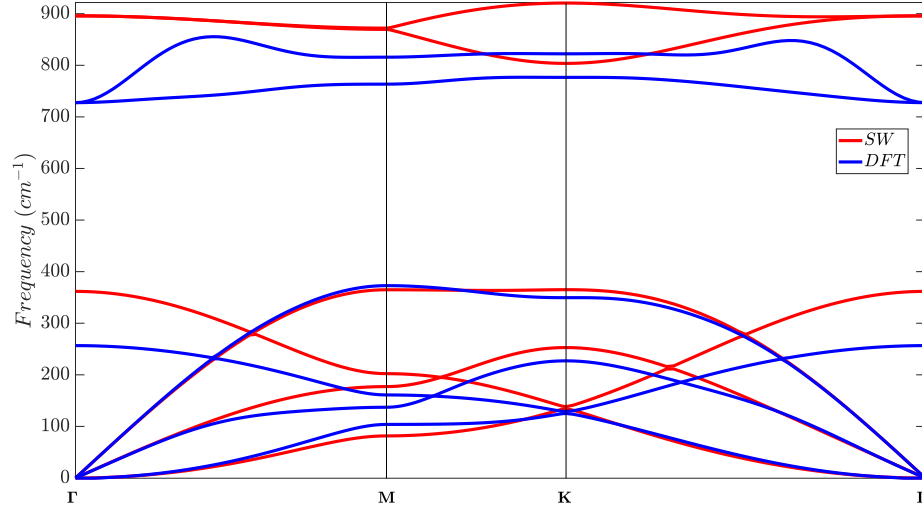


Figure 4.18: Calculated phonon dispersion curves from SW (red lines) optimized according to parameter λ and DFT (blue lines).

In the case of bulk structure, the energy difference curve can be fitted with wide range of the angles including the equilibrium angle as well. However, the equilibrium angle generates optical phonon frequencies higher than the DFT results. The phonon dispersion curves obtained by using SW potential which is optimized according to parameter λ and using the equilibrium angle is presented in Figure 4.19 (SW_1 in Figure 4.19). This potential generates acoustic modes accurately but fails in describing the optical modes but still can be used for investigating thermal and mechanical properties. In the same figure the result of another set of SW potential which is optimized according to three-body parameter $\cos(\theta_0)$ is presented (SW_2 in Figure 4.19). In this case all phonon frequencies are considered as the target data. These results are compared with the available SW potential [85] (SW_3 in Figure 4.19) and Tersoff potential [141]. It is clear that SW_3 is the less accurate one and SW_1 gives the best results for acoustic phonon frequencies.

In order to construct a potential for monolayer and bulk structure, all of the obtained curves must be fitted simultaneously. In this case, nonlinear least square

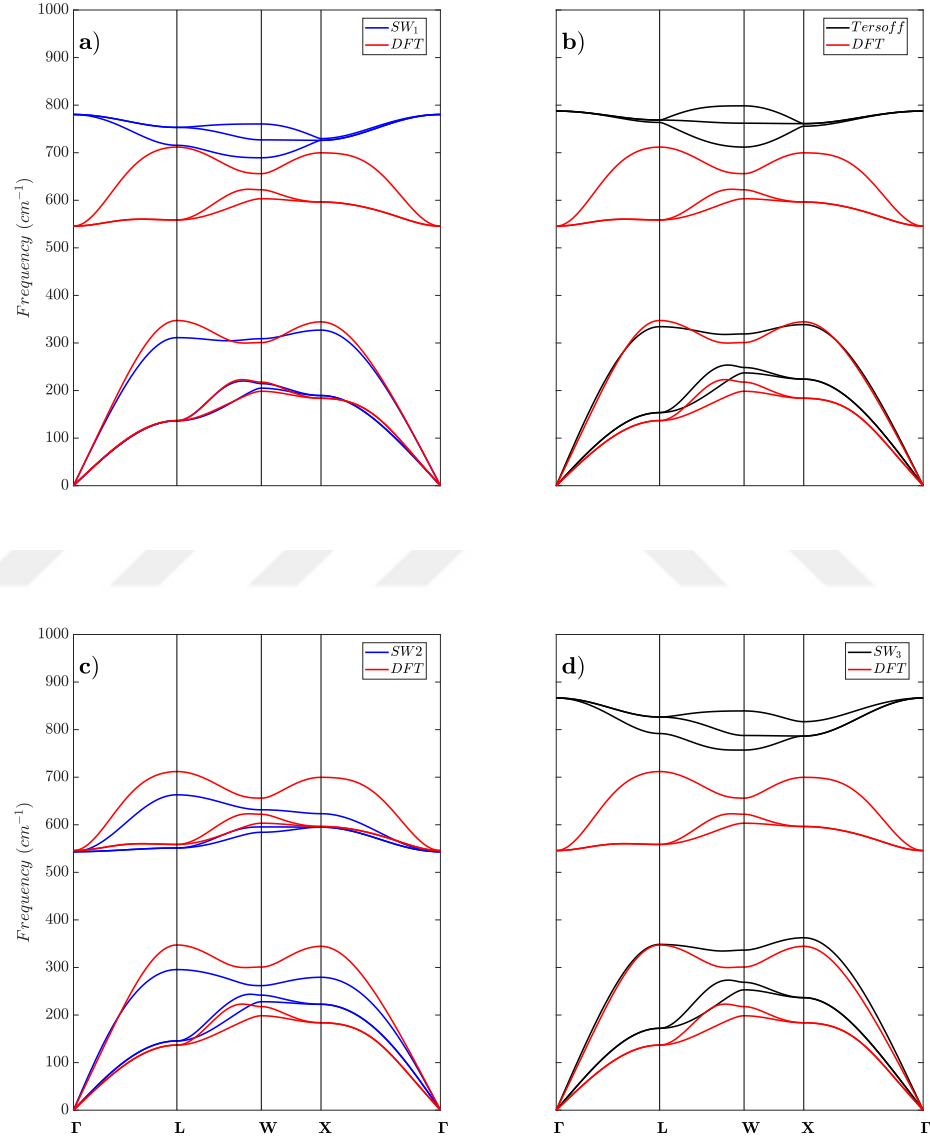


Figure 4.19: a) Phonon dispersion curves obtained from SW using equilibrium angle (blue lines) and DFT (red lines). b) Results using Tersoff potential [141](black lines). c) Calculated phonon dispersion curves from SW optimized according to $\cos(\theta_0)$ (blue lines) d) Results of SW potential parametrized in reference [85] (black lines).

fit is not applicable and particle swarm optimization method is used. In all of the results presented before, all of the obtained lattice parameters are exactly match with the DFT results. But in this case the deviation from the DFT data are possible. Therefore, in the particle swarm optimization function an extra condition is imposed on the cost function according to the obtained lattice constant. The cost function has been set to very large number for the predicted lattice constants $0.05 \text{ \AA}$ larger or smaller than the target value. The results of particle swarm optimization for energy curves are presented in Figure 4.20. From the Figure 4.20 it clear that for the bulk structure a perfect match is obtained and there are small deviation from the DFT data for monolayer.

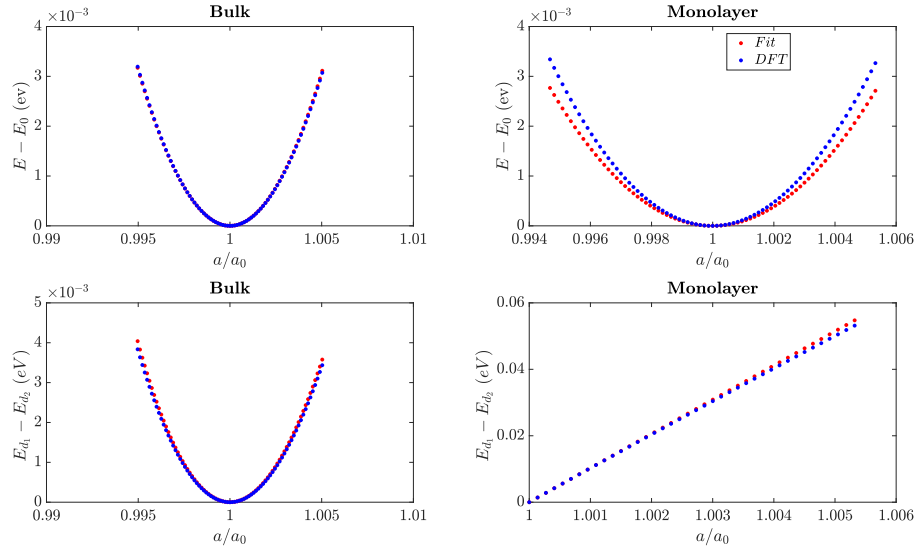


Figure 4.20: Result of fitting energy curves of monolayer and bulk GaN.

The other particle swarm optimization step is performed to for selecting three-body parameter λ for the different three-body terms. The resulted phonon dispersion curves are compared with the results of the Tersoff potential [141] in Figure 4.21 and the obtained parameters are presented in Table 4.5. The SW potential of the reference [85] predicts negative phonon frequencies for monolayer and therefore is not compared with final results.

It can be seen from Figure 4.21 that the optimized SW potential has overall

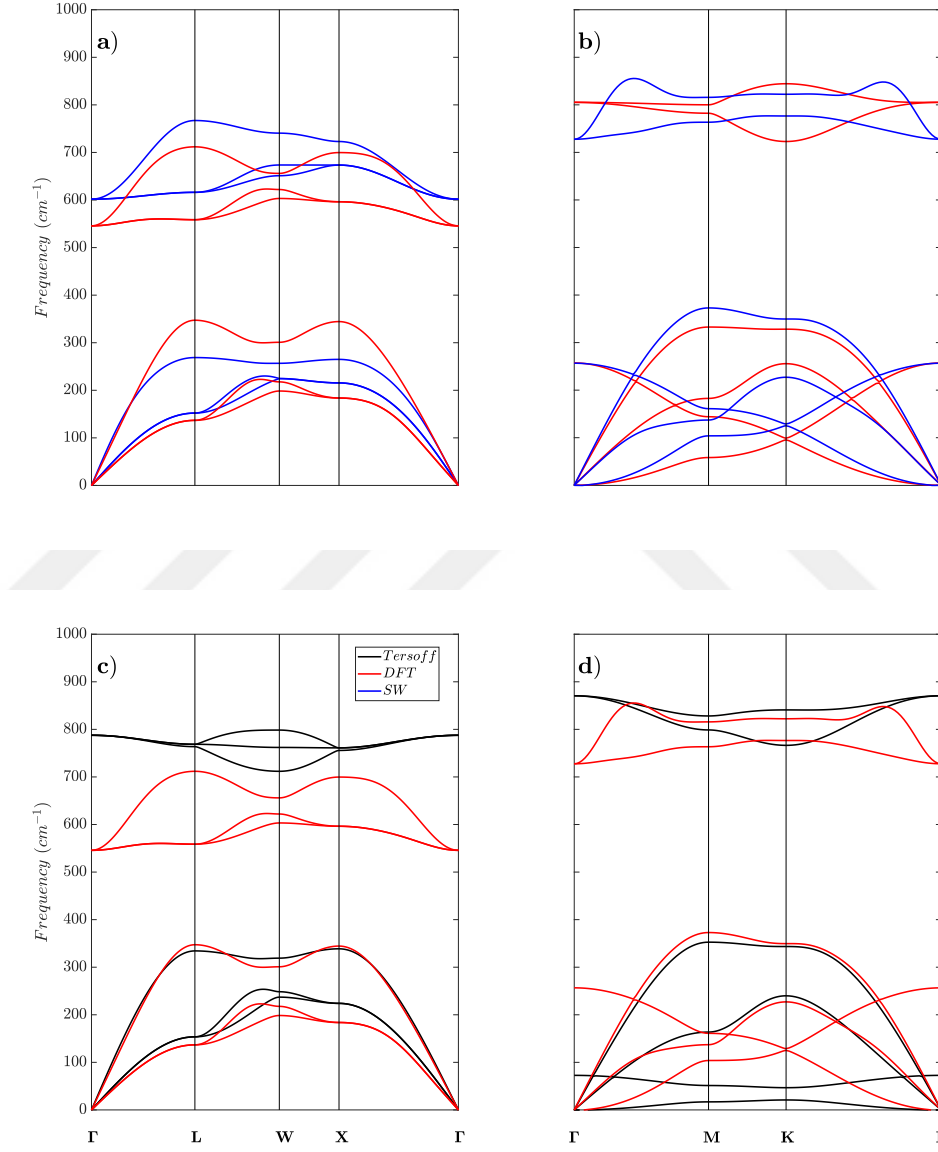


Figure 4.21: a) Phonon dispersion curves for zinc blende GaN obtained from optimized SW potential (blue lines) and DFT (red lines). b) Results for monolayer GaN using optimized SW potential and DFT. c) Calculated phonon dispersion curves of zinc blende GaN obtained from Tersoff potential [141](black lines) compared with DFT d) Calculated phonon dispersion curves of monolayer GaN obtained from Tersoff potential [141] compared with DFT.

better description than Tersoff potential [141]. The results of the Tersoff potential [141] for ZO-ZA modes of the monolayer and optical modes of the bulk structures are far from DFT. The only advantages of this potential is its better description for TA mode of the bulk structure. In Table 4.4 the result of lattice constants and energy differences between the bulk and monolayer structures are compared. The optimized SW potential gives more precise results for lattice constants and energy difference between the monolayer and bulk structure.

Table 4.4: Lattice constants of bulk (a_{bulk} (Å)) and monolayer ($a_{monolayer}$ (Å)) GaN and their energy difference ($\Delta_E = E_{0_{Mono}} - E_{0_{Bulk}}$ (eV)) obtained from optimized SW compared with the results of DFT and Tersoff potential [141].

	a_{bulk} (Å)	$a_{monolayer}$ (Å)	Δ_E (eV)
DFT	3.245	3.255	0.8303
SW	3.230	3.295	0.8305
Tersoff	3.180	3.337	1.8262

Table 4.5: All of the optimized parameters of SW potential for GaN are presented in this table. Here $SW_{m_{fit}}$ and SW_{m_λ} are obtained from fitting the energy curves and optimizing the three-body parameter λ . SW_{b_λ} is optimized according to parameter λ using the equilibrium angle and $SW_{b_{cos(\theta)}}$ is optimized using according to $cos(\theta_0)$. SW_{opt} is the potential optimized for both of the structures.

	$SW_{m_{fit}}$	SW_{m_λ}	SW_{b_λ}	$SW_{b_{cos(\theta)}}$	SW_{opt}
ϵ (eV)	1	1	1	1	1
σ (Å)	1.776988	1.786295	1.333153	1.594306	2.064022
a	1.772663	1.763427	2.36282	1.975781	1.526147
λ_{Ga-N-N}	29.242514	8.765361	6.095828	22.118592	86.82454
$\lambda_{N-Ga-Ga}$	29.242514	1.865361	6.095828	22.118592	18.82454
γ	0.56275	0.559818	0.750102	1.167411	1.089935
$cos(\theta_0)$	-1	-1	-1/3	-0.909695	-0.698925
A	24.262461	25.51868	14.256599	19.76699	21.316873
B	0.40388	0.377685	1.623373	19.76699	0.262144
p	4	4	4	4	4
q	0	0	0	0	0

Table 4.6: Defect energies obtained from optimized SW potential for monolayer GaN (SW_{m_λ}) and final SW potential optimized for bulk and monolayer (SW_{opt}) compared with DFT results. E_N is N defect energy and E_{Ga} is Ga defect energy.

	E_N (eV)	E_{Ga} (eV)
DFT	-7.8191	-11.3848
SW_{m_λ}	-9.1686	-11.0131
SW_{opt}	-6.9775	-7.3777

In Table 4.6 the energy difference between the pristine structure and the relaxed defected structures obtained by single point vacancies are compared. These results show that SW_{m_λ} predicts results close to DFT results. The important future of the point vacancy defect is the final relaxed structure which can be generated using the considered potential model.

4.5.2 SW Potential for AlN

The results of the fitting the energy curves and the and phonon dispersion curves for monolayer AlN are presented in Figure 4.22. The acoustic modes and ZO mode are captured correctly but the LO-TO modes have higher frequencies at Γ point.

With this result the contribution of N-Al-Al and Al-N-N three body interactions in the total energy are same and therefore taking one N atom from system is equivalent to taking one Al atom. The effect of the parameter λ which is investigated in previous part can be used for obtaining more accurate phonon frequencies. Furthermore, similar methods which are used for improving the phonon dispersion of the bulk and monolayer system can be applied in this case as well. Here we presented the SW potential optimized for describing both of the considered phases. The result of applying particle swarm optimization to energy

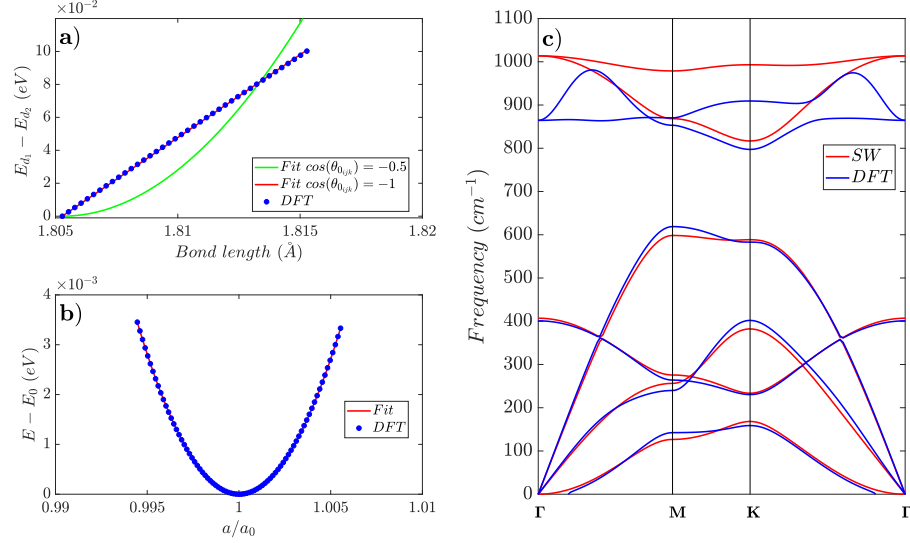


Figure 4.22: a) Energy difference between the first and second displacements obtained from DFT (blue dots), fit obtained using equilibrium angle (green line) and the best fit (red line) which gives the $\cos \theta_{0,ijk} = -1$ as the best angle . b) Difference between the total energy and minimum energy versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data and red line is the fit obtained using the three-body parameters obtained from the best fit of the a). c) Calculated phonon dispersion curves for AlN by using SW potential (red lines) and DFT (blue lines).

curves are presented in Figure 4.23. There are small deviations from DFT data in the energy curves obtained by the variation of lattice constant.

Obtained phonon dispersions are presented in Figure 4.24 and the SW parameters are presented in Table 4.7. The lattice parameters and energy difference between the monolayer and bulks system and the point defect energies are compared with DFT in Table 4.8.

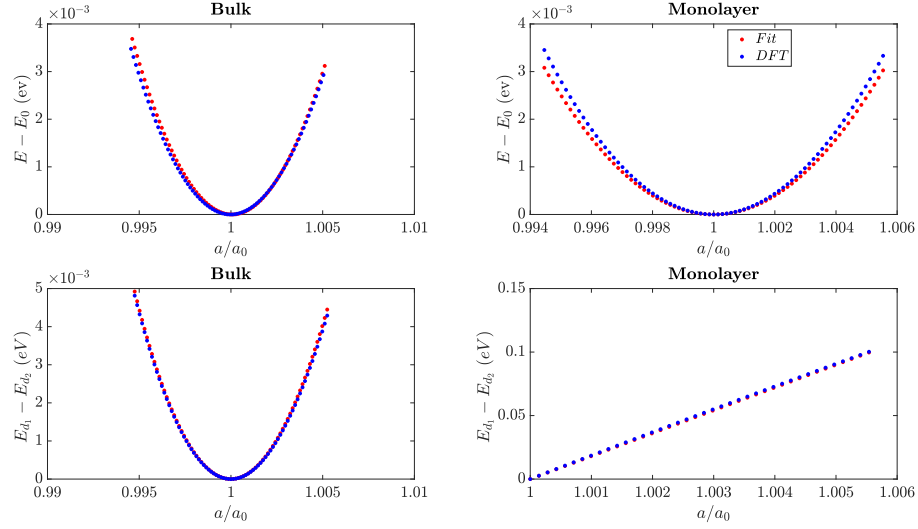


Figure 4.23: Results of particle swarm optimization for the energy curves of monolayer and bulk AlN.

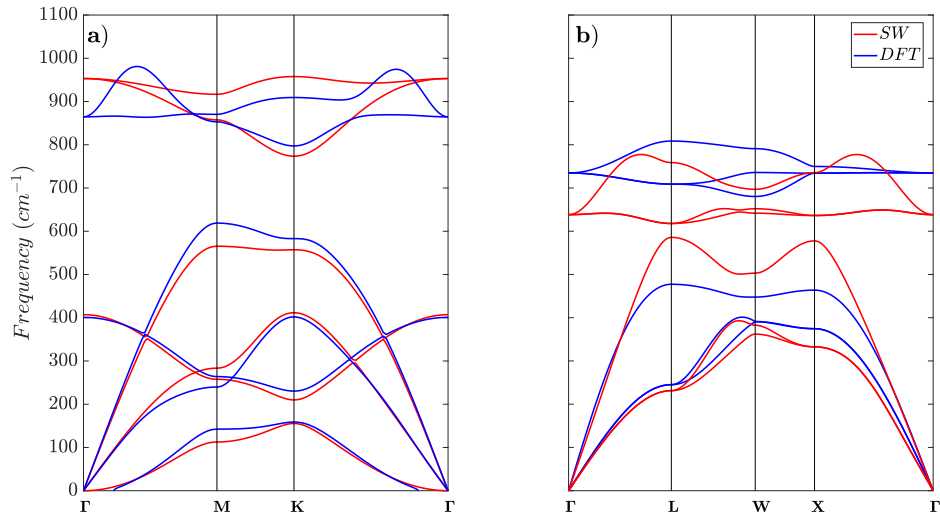


Figure 4.24: a) Phonon dispersion curves for monolayer AlN obtained from optimized SW potential (blue lines) and DFT (red lines). b) Phonon dispersion curves for bulk AlN obtained from optimized SW potential (blue lines) and DFT (red lines).

Obtained phonon dispersions are match to DFT results near Γ point and the deviations of acoustic modes from target data are not large near the zone boundaries. In addition, lattice constants and the energy difference between the monolayer and bulk structures are predicted accurately.

Table 4.7: Two sets of the optimized parameters of SW potential for AlN are presented in this table. Here SW_{mfit} is obtained from fitting the energy curves of monolayer and SW_{opt} is the potential optimized for both of the structures.

	SW_{mfit}	SW_{opt}
ϵ (eV)	1	1
σ (Å)	1.347674	1.477512
a	2.226058	2.03044
λ_{Al-N-N}	5.4249	23.274246
$\lambda_{N-Al-Al}$	5.4249	7.274246
γ	0.742019	0.998737
$\cos(\theta_0)$	-1	-0.882645
A	21.626109	20.264336
B	0.858442	0.596934
p	4	4
q	0	0

Table 4.8: Lattice constants of bulk (a_{bulk} (Å)) and monolayer ($a_{monolayer}$ (Å)) AlN and their energy difference ($\Delta_E = E_{0Mono} - E_{0Bulk}$ (eV)) obtained using optimized SW potential compared with the results of DFT.

	a_{bulk} (Å)	$a_{monolayer}$ (Å)	Δ_E (eV)
DFT	3.112	3.127	0.9785
SW	3.073	3.111	0.9783

4.5.3 SW potential for BN

The results of the fitting the energy curves for monolayer BN are presented in Figure 4.25.

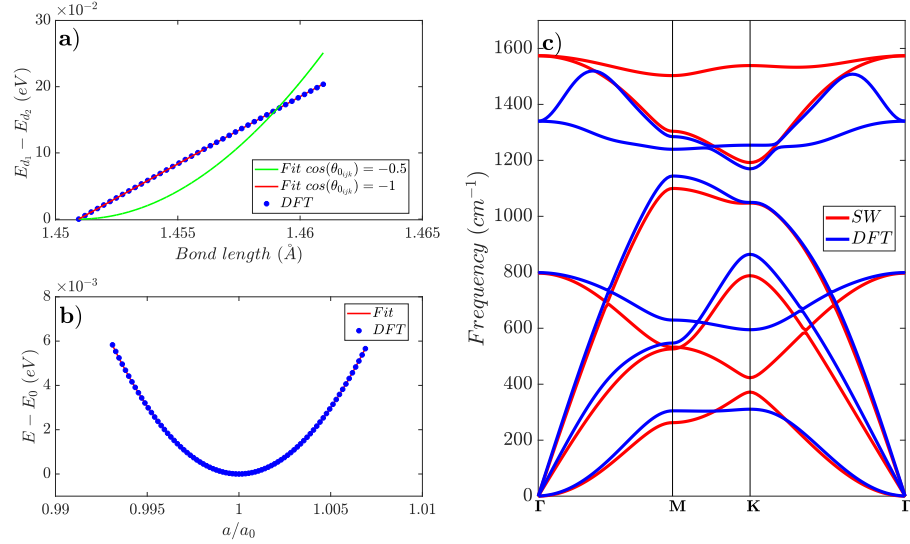


Figure 4.25: a) Energy difference between the first and second displacements obtained from DFT (blue dots), fit obtained using equilibrium angle (green line) and the best fit (red line) which gives the $\cos \theta_{0,ijk} = -1$ as the best angle. b) Difference between the total energy and minimum energy versus lattice constant normalized by its equilibrium value. Here the blue dots are the DFT data and red line is the fit obtained using the three-body parameters obtained from the best fit of the a). c) Calculated phonon dispersion curves for BN by using SW potential (red lines) and DFT (blue lines).

It can be seen from Figure 4.25 that the behavior of the ZO-ZA modes are not generated correctly. As it is done before, this result can be improved by using different λ for different three-body interactions. There are different types of potentials optimized for BN systems. Among them, the most widely used ones are Tersoff potential for h-BN [88] and for cubic boron carbonitrides [142]. An extended version of Tersoff potential with modified bond order term is recently

developed for studying energies and elastic properties of pristine and defected h-BN [143].

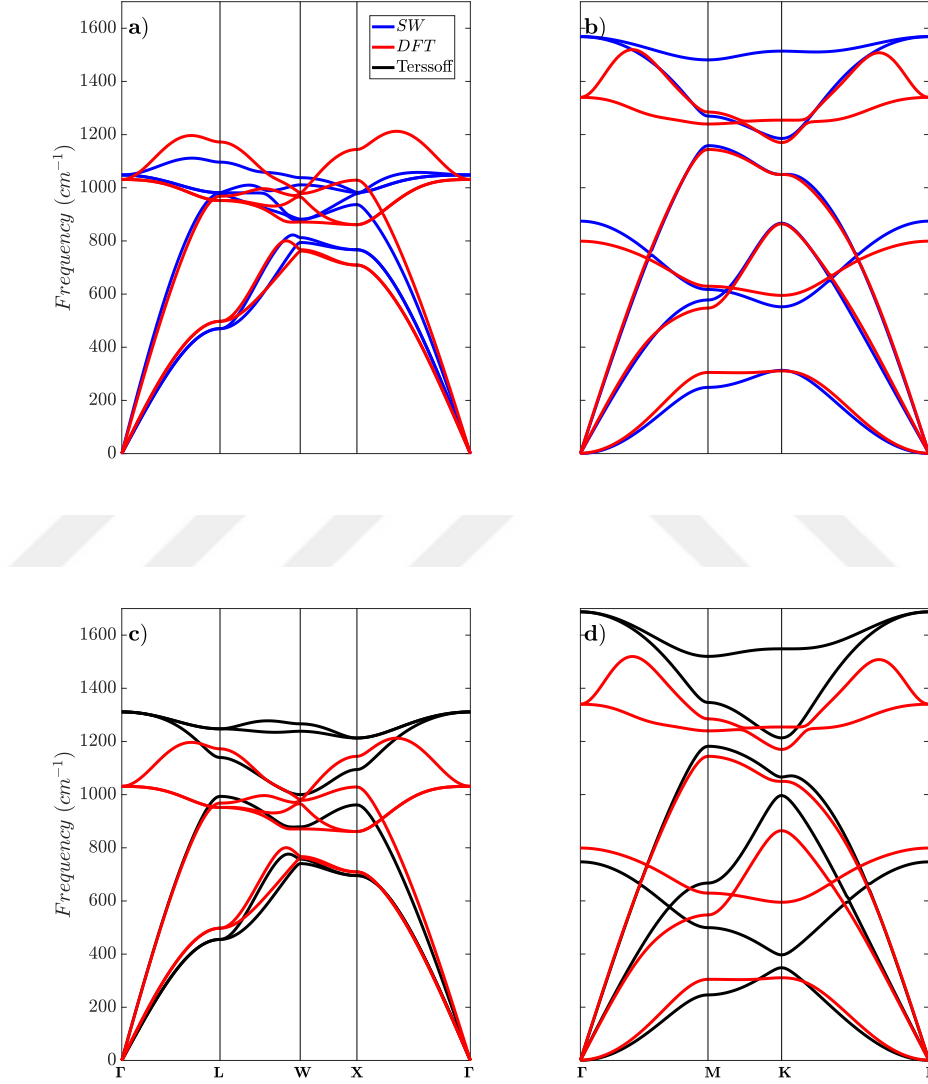


Figure 4.26: a) Phonon dispersion curves for zinc blende BN obtained from optimized SW potential for monolayer (blue lines) and DFT (red lines). b) Results for monolayer BN using optimized SW potential for monolayer and DFT. c) Calculated phonon dispersion curves of zinc blende BN obtained from Tersoff potential [143](black lines) compared with DFT d) Calculated phonon dispersion curves of monolayer BN obtained from Tersoff potential [143] compared with DFT.

In order to illustrate the other capability of the presented method, SW potential is optimized according to parameter λ for monolayer and is used for generating the phonon dispersions for the bulk structure. These results are compared with the results obtained by using extended Tersoff potential [143] in Figure 4.26. One important result which can be deduced from Figure 4.26 is that the parameters optimized for monolayer are able to describe the bulk structure as well. Furthermore, in the case of monolayer the optimized SW potential generated results close to DFT, especially for TA and LA modes.

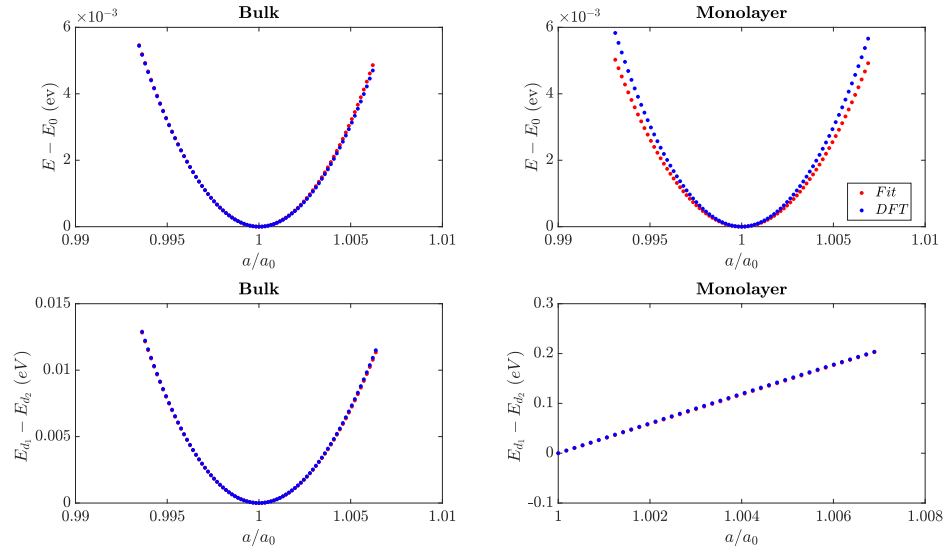


Figure 4.27: Result of fitting energy curves of monolayer and bulk BN using particle swarm optimization.

The results of particle swarm optimization for describing energy curves with single set of parameters are presented in Figure 4.27. There are small deviations from the DFT results in the case of the energy versus lattice constant of the monolayer, however the rest of the energy curves are correctly fitted. The obtained parameters are listed in Table 4.9 and the obtained phonon dispersion curves are shown in Figure 4.28.

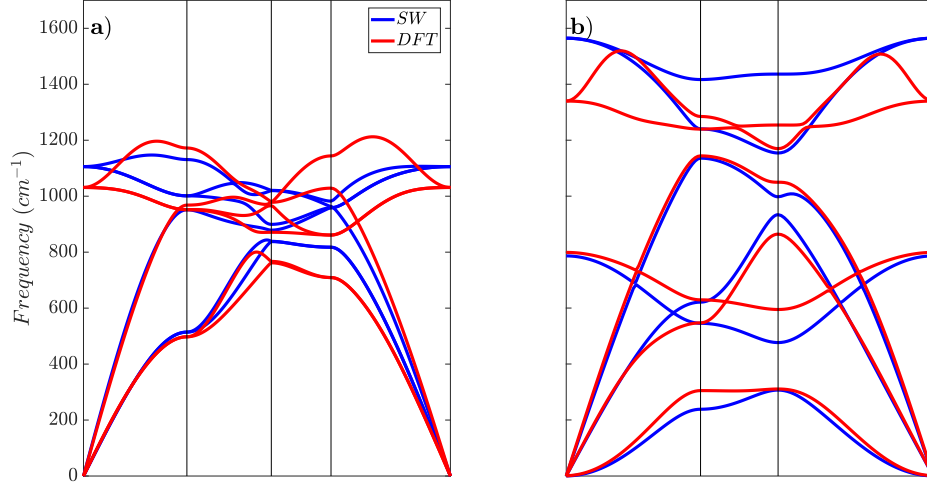


Figure 4.28: a) Phonon dispersion curves for bulk BN obtained from optimized SW potential (blue lines) and DFT (red lines). b) Phonon dispersion curves for monolayer obtained from optimized SW potential (blue lines) and DFT (red lines).

Table 4.9: Two sets of the optimized parameters of SW potential for BN are presented in this table. Here SW_{m_λ} is optimized for monolayer by adjusting parameter λ and SW_{opt} is the potential optimized for both of the structures.

	SW_{opt}	SW_{m_λ}
$\epsilon(\text{eV})$	1	1
$\sigma \text{ (\AA)}$	1.046061	0.99665
a	2.294321	2.408067
λ_{B-N-N}	28.056676	23.3
λ_{N-B-B}	15.056676	9.7
γ	0.955967	1.003361
$\cos(\theta_0)$	-0.816248	-1
A	20.311114	25.215753
B	0.961232	0.993143
p	4	4
q	0	0

Table 4.10: Lattice constants of bulk (a_{bulk} (Å)) and monolayer ($a_{monolayer}$ (Å)) BN and their energy difference ($\Delta_E = E_{0_{Mono}} - E_{0_{Bulk}}$ (eV)) obtained from optimized SW compared with the results of DFT and Tersoff potential [143].

	a_{bulk} (Å)	$a_{monolayer}$ (Å)	Δ_E (eV)
DFT	2.5636	2.5131	-0.1471
SW	2.5401	2.5232	-0.1471

Chapter 5

Conclusions

In this work, first we justified the accuracy of the force fields for WSe_2 and WS_2 by evaluating thermal conductivities utilizing Green-Kubo method and investigating the anharmonic effects imposed by the developed potentials by comparing the trends in the temperature dependent shifts of the Γ point optical phonon frequencies with the available experimental results. The obtained trends are in agreement with experimental reports. Equipped with the force fields that give very accurate description for phonon dispersions, temperature dependent phonon lifetimes of TMDs are systematically investigated utilizing spectral energy density method and phonon mode decomposition. Obtained phonon lifetimes and group velocities are used for determining the contribution of each phonon branch in the thermal conductivity. The most prominent temperature effect is observed in the case of optical phonon frequencies of MoSe_2 . Our results shows that in these binary systems, transition metal atoms drive the phonon lifetimes, whereas chalcogen atoms dictates the group velocity spectrum. Most of the contribution to thermal conductivity arise from the LA and TA acoustic branches, while the contribution of ZA mode is less than the other acoustic modes, particularly in MoSe_2 . Calculated thermal conductivities are in well agreement with the results of the Green-Kubo method and are linearly proportional to inverse temperature. In pursue for developing transferable interatomic analytical potentials based on

SW model a very fast and reliable optimization method is presented. The presented approach uses both local and global optimization methods for fitting the energy curves and by isolating three body term reduces the number of the target parameters. One important advantageous of this method is that it doesn't need the phonon dispersion as the input. Furthermore, it provides a framework for justifying the considered model for describing the interaction between the atoms in the system and therefore can be used for developing the potential models. The limitations of the commonly used first nearest neighbor approach in designing the potential become clear within the presented framework and it facilitates study of the effect of any parameter of the inter-atomic potential and illuminates the dark space of global optimization. All these are illustrated in the steps of constructing novel interatomic potentials for graphene, silicene, and the binary materials of group III nitrides. The presented approach can be directly used for optimizing any potential with distinguishable two-body and three-body terms and even can be generalized for the potentials that treat many-body effects collectively. In addition, in order to improve the results which are already close to DFT results, the interactions beyond the first nearest neighbor can be taken into account with the cost of more terms in analytical description of the energy curves obtained from the displacement of the atoms.

Bibliography

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” *Science*, vol. 306, no. 5696, pp. 666–669, 2004.
- [2] V. Meunier, A. G. Souza Filho, E. B. Barros, and M. S. Dresselhaus, “Physical properties of low-dimensional sp^2 -based carbon nanostructures,” *Rev. Mod. Phys.*, vol. 88, p. 025005, May 2016.
- [3] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, “The electronic properties of graphene,” *Rev. Mod. Phys.*, vol. 81, pp. 109–162, Jan 2009.
- [4] M. Ashton, J. Paul, S. B. Sinnott, and R. G. Hennig, “Topology-scaling identification of layered solids and stable exfoliated 2D materials,” *Phys. Rev. Lett.*, vol. 118, p. 106101, Mar 2017.
- [5] A. Pakdel, C. Zhi, Y. Bando, and D. Golberg, “Low-dimensional boron nitride nanomaterials,” *Materials Today*, vol. 15, no. 6, pp. 256 – 265, 2012.
- [6] Y. Lin and J. W. Connell, “Advances in 2D boron nitride nanostructures: nanosheets, nanoribbons, nanomeshes, and hybrids with graphene,” *Nanoscale*, vol. 4, pp. 6908–6939, 2012.
- [7] F. Reis, G. Li, L. Dudy, M. Bauernfeind, S. Glass, W. Hanke, R. Thomale, J. Schäfer, and R. Claessen, “Bismuthene on a SiC substrate: A candidate for a high-temperature quantum spin hall material,” *Science*, vol. 357, no. 6348, pp. 287–290, 2017.

- [8] D. Singh, S. K. Gupta, Y. Sonvane, and R. Ahuja, “High performance material for hydrogen storage: Graphenelike Si_2BN solid,” *International Journal of Hydrogen Energy*, vol. 42, no. 36, pp. 22942 – 22952, 2017.
- [9] S. Cahangirov, M. Topsakal, E. Aktürk, H. Şahin, and S. Ciraci, “Two- and one-dimensional honeycomb structures of silicon and germanium,” *Phys. Rev. Lett.*, vol. 102, p. 236804, Jun 2009.
- [10] J. C. Garcia, D. B. de Lima, L. V. C. Assali, and J. F. Justo, “Group IV graphene- and graphane-like nanosheets,” *The Journal of Physical Chemistry C*, vol. 115, no. 27, pp. 13242–13246, 2011.
- [11] S. Cahangirov, V. O. Özçelik, A. Rubio, and S. Ciraci, “Silicite: The layered allotrope of silicon,” *Phys. Rev. B*, vol. 90, p. 085426, Aug 2014.
- [12] V. O. Özçelik and S. Ciraci, “Local reconstructions of silicene induced by adatoms,” *The Journal of Physical Chemistry C*, vol. 117, no. 49, pp. 26305–26315, 2013.
- [13] L. Tao, E. Cinquanta, D. Chiappe, C. Grazianetti, M. Fanciulli, M. Dubey, A. Molle, and D. Akinwande, “Silicene field-effect transistors operating at room temperature,” *Nature Nanotechnology*, vol. 10, pp. 227 EP –, Feb 2015.
- [14] M. E. Dávila, L. Xian, S. Cahangirov, A. Rubio, and G. L. Lay, “Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene,” *New Journal of Physics*, vol. 16, p. 095002, sep 2014.
- [15] J. Yuhara, H. Shimazu, K. Ito, A. Ohta, M. Araidai, M. Kurosawa, M. Nakatake, and G. Le Lay, “Germanene epitaxial growth by segregation through Ag(111) thin films on Ge(111),” *ACS Nano*, vol. 12, no. 11, pp. 11632–11637, 2018.
- [16] L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, “Black phosphorus field-effect transistors,” *Nature Nanotechnology*, vol. 9, pp. 372 EP –, Mar 2014.

- [17] H. Zheng, X.-B. Li, N.-K. Chen, S.-Y. Xie, W. Q. Tian, Y. Chen, H. Xia, S. B. Zhang, and H.-B. Sun, “Monolayer II-VI semiconductors: A first-principles prediction,” *Phys. Rev. B*, vol. 92, p. 115307, Sep 2015.
- [18] R. Yan, J. R. Simpson, S. Bertolazzi, J. Brivio, M. Watson, X. Wu, A. Kis, T. Luo, A. R. Hight Walker, and H. G. Xing, “Thermal conductivity of monolayer molybdenum disulfide obtained from temperature-dependent Raman spectroscopy,” *ACS Nano*, vol. 8, no. 1, pp. 986–993, 2014.
- [19] S. Sahoo, A. P. S. Gaur, M. Ahmadi, M. J.-F. Guinel, and R. S. Katiyar, “Temperature-dependent Raman studies and thermal conductivity of few-layer MoS₂,” *The Journal of Physical Chemistry C*, vol. 117, no. 17, pp. 9042–9047, 2013.
- [20] N. Peimyoo, J. Shang, W. Yang, Y. Wang, C. Cong, and T. Yu, “Thermal conductivity determination of suspended mono- and bilayer WS₂ by Raman spectroscopy,” *Nano Research*, vol. 8, pp. 1210–1221, Apr 2015.
- [21] I. Jo, M. T. Pettes, E. Ou, W. Wu, and L. Shi, “Basal-plane thermal conductivity of few-layer molybdenum disulfide,” *Applied Physics Letters*, vol. 104, no. 20, p. 201902, 2014.
- [22] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, and H. Zhang, “The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets,” *Nature Chemistry*, vol. 5, pp. 263 EP –, Mar 2013.
- [23] W. Huang, X. Luo, C. K. Gan, S. Y. Quek, and G. Liang, “Theoretical study of thermoelectric properties of few-layer MoS₂ and WSe₂,” *Phys. Chem. Chem. Phys.*, vol. 16, pp. 10866–10874, 2014.
- [24] D. D. Fan, H. J. Liu, L. Cheng, P. H. Jiang, J. Shi, and X. F. Tang, “MoS₂ nanoribbons as promising thermoelectric materials,” *Applied Physics Letters*, vol. 105, no. 13, p. 133113, 2014.
- [25] J.-K. Huang, J. Pu, C.-L. Hsu, M.-H. Chiu, Z.-Y. Juang, Y.-H. Chang, W.-H. Chang, Y. Iwasa, T. Takenobu, and L.-J. Li, “Large-area synthesis of highly crystalline WSe₂ monolayers and device applications,” *ACS Nano*, vol. 8, no. 1, pp. 923–930, 2014.

- [26] A. Dankert, L. Langouche, M. V. Kamalakar, and S. P. Dash, “High-performance molybdenum disulfide field-effect transistors with spin tunnel contacts,” *ACS Nano*, vol. 8, no. 1, pp. 476–482, 2014.
- [27] K. F. Mak and J. Shan, “Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides,” *Nature Photonics*, vol. 10, pp. 216 EP –, Mar 2016.
- [28] Z. Guo, J. Zhou, L. Zhu, and Z. Sun, “Mxene: a promising photocatalyst for water splitting,” *J. Mater. Chem. A*, vol. 4, pp. 11446–11452, 2016.
- [29] S. Lai, J. Jeon, S. K. Jang, J. Xu, Y. J. Choi, J.-H. Park, E. Hwang, and S. Lee, “Surface group modification and carrier transport properties of layered transition metal carbides (Ti₂CTx, T: –OH, –F and –O),” *Nanoscale*, vol. 7, pp. 19390–19396, 2015.
- [30] P. Chai, S. A. Stoian, X. Tan, P. A. Dube, and M. Shatruk, “Investigation of magnetic properties and electronic structure of layered-structure borides AlT₂B₂ (T=Fe, Mn, Cr) and AlFe_{2–x}MnxB₂,” *Journal of Solid State Chemistry*, vol. 224, pp. 52 – 61, 2015.
- [31] Z. Jiang, P. Wang, X. Jiang, and J. Zhao, “MBene (MnB): a new type of 2D metallic ferromagnet with high curie temperature,” *Nanoscale Horiz.*, vol. 3, pp. 335–341, 2018.
- [32] L. T. Alameda, P. Moradifar, Z. P. Metzger, N. Alem, and R. E. Schaak, “Topochemical deintercalation of Al from MoAlB: Stepwise etching pathway, layered intergrowth structures, and two-dimensional MBene,” *Journal of the American Chemical Society*, vol. 140, no. 28, pp. 8833–8840, 2018.
- [33] A. Marcolongo, P. Umari, and S. Baroni, “Microscopic theory and quantum simulation of atomic heat transport,” *Nature Physics*, vol. 12, pp. 80 EP –, Oct 2015.
- [34] J. Liu, G.-M. Choi, and D. G. Cahill, “Measurement of the anisotropic thermal conductivity of molybdenum disulfide by the time-resolved magneto-optic kerr effect,” *Journal of Applied Physics*, vol. 116, no. 23, p. 233107, 2014.

- [35] J. A. Thomas, J. E. Turney, R. M. Iutzi, C. H. Amon, and A. J. H. McGaughey, “Predicting phonon dispersion relations and lifetimes from the spectral energy density,” *Phys. Rev. B*, vol. 81, p. 081411, Feb 2010.
- [36] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, “Single-layer MoS₂ transistors,” *Nature Nanotechnology*, vol. 6, pp. 147 EP–, Jan 2011.
- [37] C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, “Anomalous lattice vibrations of single- and few-layer MoS₂,” *ACS Nano*, vol. 4, no. 5, pp. 2695–2700, 2010.
- [38] J. N. Coleman, M. Lotya, A. O’Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V. Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, and V. Nicolosi, “Two-dimensional nanosheets produced by liquid exfoliation of layered materials,” *Science*, vol. 331, no. 6017, pp. 568–571, 2011.
- [39] H. R. Gutiérrez, N. Perea-López, A. L. Elías, A. Berkdemir, B. Wang, R. Lv, F. López-Urías, V. H. Crespi, H. Terrones, and M. Terrones, “Extraordinary room-temperature photoluminescence in triangular WS₂ monolayers,” *Nano Letters*, vol. 13, no. 8, pp. 3447–3454, 2013.
- [40] S. Tongay, D. Narang, J. Kang, W. Fan, C. Ko, A. Luce, K. Wang, J. Suh, K. Patel, V. Pathak, J. Li, and J. Wu, “Two-dimensional semiconductor alloys: Monolayer Mo_{1-x}W_xSe₂,” *Applied Physics Letters*, vol. 104, 1 2014.
- [41] J. Kang, J. Li, S.-S. Li, J.-B. Xia, and L.-W. Wang, “Electronic structural moiré pattern effects on MoS₂/MoSe₂ 2D heterostructures,” *Nano Letters*, vol. 13, no. 11, pp. 5485–5490, 2013.
- [42] M. Dendzik, A. Bruix, M. Michiardi, A. S. Ngankeu, M. Bianchi, J. A. Miwa, B. Hammer, P. Hofmann, and C. E. Sanders, “Substrate-induced

- semiconductor-to-metal transition in monolayer WS_2 ,” *Phys. Rev. B*, vol. 96, p. 235440, Dec 2017.
- [43] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, “Emerging photoluminescence in monolayer MoS_2 ,” *Nano Letters*, vol. 10, no. 4, pp. 1271–1275, 2010.
- [44] S. Ulstrup, A. G. c. v. a. c. Čabo, D. Biswas, J. M. Riley, M. Dendzik, C. E. Sanders, M. Bianchi, C. Cacho, D. Matselyukh, R. T. Chapman, E. Springate, P. D. C. King, J. A. Miwa, and P. Hofmann, “Spin and valley control of free carriers in single-layer WS_2 ,” *Phys. Rev. B*, vol. 95, p. 041405, Jan 2017.
- [45] C. Chiritescu, D. G. Cahill, N. Nguyen, D. Johnson, A. Bodapati, P. Keblinski, and P. Zschack, “Ultralow thermal conductivity in disordered, layered WSe_2 crystals,” *Science*, vol. 315, no. 5810, pp. 351–353, 2007.
- [46] Z. Zhang, Y. Xie, Y. Ouyang, and Y. Chen, “A systematic investigation of thermal conductivities of transition metal dichalcogenides,” *International Journal of Heat and Mass Transfer*, vol. 108, pp. 417 – 422, 2017.
- [47] J. J. Bae, H. Y. Jeong, G. H. Han, J. Kim, H. Kim, M. S. Kim, B. H. Moon, S. C. Lim, and Y. H. Lee, “Thickness-dependent in-plane thermal conductivity of suspended MoS_2 grown by chemical vapor deposition,” *Nanoscale*, vol. 9, pp. 2541–2547, 2017.
- [48] M. Yang, X. Cheng, Y. Li, Y. Ren, M. Liu, and Z. Qi, “Anharmonicity of monolayer MoS_2 , MoSe_2 , and WSe_2 : A Raman study under high pressure and elevated temperature,” *Applied Physics Letters*, vol. 110, no. 9, p. 093108, 2017.
- [49] N. A. Lanzillo, A. Glen Birdwell, M. Amani, F. J. Crowne, P. B. Shah, S. Najmaei, Z. Liu, P. M. Ajayan, J. Lou, M. Dubey, S. K. Nayak, and T. P. O’Regan, “Temperature-dependent phonon shifts in monolayer MoS_2 ,” *Applied Physics Letters*, vol. 103, no. 9, p. 093102, 2013.

- [50] D. J. Late, S. N. Shirodkar, U. V. Waghmare, V. P. Dravid, and C. N. R. Rao, “Thermal expansion, anharmonicity and temperature-dependent Raman spectra of single- and few-layer MoSe₂ and WSe₂,” *ChemPhysChem*, vol. 15, no. 8, pp. 1592–1598, 2014.
- [51] J. Kutrowska-Girzycka, J. Jadczyk, and L. Bryja, “The study of dispersive ‘b’-mode in monolayer MoS₂ in temperature dependent resonant Raman scattering experiments,” *Solid State Communications*, vol. 275, pp. 25 – 28, 2018.
- [52] T. M and D. J. Late, “Temperature dependent phonon shifts in single-layer WS₂,” *ACS Applied Materials & Interfaces*, vol. 6, no. 2, pp. 1158–1163, 2014.
- [53] X. Huang, Y. Gao, T. Yang, W. Ren, H.-M. Cheng, and T. Lai, “Quantitative analysis of temperature dependence of Raman shift of monolayer WS₂,” *Scientific Reports*, vol. 6, pp. 32236 EP –, Aug 2016.
- [54] P. Anees, M. C. Valsakumar, and B. K. Panigrahi, “Anharmonicity of optic modes in monolayer MoS₂,” *Applied Physics Letters*, vol. 108, no. 10, p. 101902, 2016.
- [55] T. Schneider and E. Stoll, “Molecular-dynamics study of a three-dimensional one-component model for distortive phase transitions,” *Phys. Rev. B*, vol. 17, pp. 1302–1322, Feb 1978.
- [56] S. Nosé, “A unified formulation of the constant temperature molecular dynamics methods,” *The Journal of Chemical Physics*, vol. 81, no. 1, pp. 511–519, 1984.
- [57] W. G. Hoover, “Canonical dynamics: Equilibrium phase-space distributions,” *Phys. Rev. A*, vol. 31, pp. 1695–1697, Mar 1985.
- [58] G. J. Martyna, M. L. Klein, and M. Tuckerman, “Nosé–Hoover chains: The canonical ensemble via continuous dynamics,” *The Journal of Chemical Physics*, vol. 97, no. 4, pp. 2635–2643, 1992.

- [59] W. G. Hoover, “Constant-pressure equations of motion,” *Phys. Rev. A*, vol. 34, pp. 2499–2500, Sep 1986.
- [60] G. J. Martyna, D. J. Tobias, and M. L. Klein, “Constant pressure molecular dynamics algorithms,” *The Journal of Chemical Physics*, vol. 101, no. 5, pp. 4177–4189, 1994.
- [61] M. Parrinello and A. Rahman, “Polymorphic transitions in single crystals: A new molecular dynamics method,” *Journal of Applied Physics*, vol. 52, no. 12, pp. 7182–7190, 1981.
- [62] W. Shinoda, M. Shiga, and M. Mikami, “Rapid estimation of elastic constants by molecular dynamics simulation under constant stress,” *Phys. Rev. B*, vol. 69, p. 134103, Apr 2004.
- [63] S. Plimpton, “Fast parallel algorithms for short-range molecular dynamics,” *Journal of Computational Physics*, vol. 117, no. 1, pp. 1 – 19, 1995.
- [64] “Lammps,” accessed May 25, 2015.
- [65] M. Tuckerman, B. J. Berne, and G. J. Martyna, “Reversible multiple time scale molecular dynamics,” *The Journal of Chemical Physics*, vol. 97, no. 3, pp. 1990–2001, 1992.
- [66] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, “Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons,” *Phys. Rev. Lett.*, vol. 104, p. 136403, Apr 2010.
- [67] J. Behler, “Perspective: Machine learning potentials for atomistic simulations,” *The Journal of Chemical Physics*, vol. 145, no. 17, p. 170901, 2016.
- [68] J. Behler and M. Parrinello, “Generalized neural-network representation of high-dimensional potential-energy surfaces,” *Phys. Rev. Lett.*, vol. 98, p. 146401, Apr 2007.
- [69] A. P. Bartók, R. Kondor, and G. Csányi, “On representing chemical environments,” *Phys. Rev. B*, vol. 87, p. 184115, May 2013.

- [70] A. P. Bartók and G. Csányi, “Gaussian approximation potentials: A brief tutorial introduction,” *International Journal of Quantum Chemistry*, vol. 115, no. 16, pp. 1051–1057, 2015.
- [71] S. Lorenz, A. Groß, and M. Scheffler, “Representing high-dimensional potential-energy surfaces for reactions at surfaces by neural networks,” *Chemical Physics Letters*, vol. 395, no. 4, pp. 210 – 215, 2004.
- [72] A. Thompson, L. Swiler, C. Trott, S. Foiles, and G. Tucker, “Spectral neighbor analysis method for automated generation of quantum-accurate interatomic potentials,” *Journal of Computational Physics*, vol. 285, pp. 316 – 330, 2015.
- [73] A. P. Bartók, J. Kermode, N. Bernstein, and G. Csányi, “Machine learning a general-purpose interatomic potential for silicon,” *Phys. Rev. X*, vol. 8, p. 041048, Dec 2018.
- [74] F. H. Stillinger and T. A. Weber, “Computer simulation of local order in condensed phases of silicon,” *Phys. Rev. B*, vol. 31, pp. 5262–5271, Apr 1985.
- [75] P. Vashishta, R. K. Kalia, J. P. Rino, and I. Ebbsjö, “Interaction potential for SiO₂: A molecular-dynamics study of structural correlations,” *Phys. Rev. B*, vol. 41, pp. 12197–12209, Jun 1990.
- [76] P. Vashishta, R. K. Kalia, A. Nakano, and J. P. Rino, “Interaction potential for silicon carbide: A molecular dynamics study of elastic constants and vibrational density of states for crystalline and amorphous silicon carbide,” *Journal of Applied Physics*, vol. 101, no. 10, p. 103515, 2007.
- [77] P. S. Branicio, J. P. Rino, C. K. Gan, and H. Tsuzuki, “Interaction potential for indium phosphide: a molecular dynamics and first-principles study of the elastic constants, generalized stacking fault and surface energies,” *Journal of Physics: Condensed Matter*, vol. 21, p. 095002, jan 2009.
- [78] J. Tersoff, “New empirical approach for the structure and energy of covalent systems,” *Phys. Rev. B*, vol. 37, pp. 6991–7000, Apr 1988.

- [79] J. Tersoff, “Modeling solid-state chemistry: Interatomic potentials for multicomponent systems,” *Phys. Rev. B*, vol. 39, pp. 5566–5568, Mar 1989.
- [80] J. Tersoff, “Erratum: Modeling solid-state chemistry: Interatomic potentials for multicomponent systems,” *Phys. Rev. B*, vol. 41, pp. 3248–3248, Feb 1990.
- [81] D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott, “A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons,” *Journal of Physics: Condensed Matter*, vol. 14, pp. 783–802, Jan 2002.
- [82] M. S. Daw and M. I. Baskes, “Semiempirical, quantum mechanical calculation of hydrogen embrittlement in metals,” *Phys. Rev. Lett.*, vol. 50, pp. 1285–1288, Apr 1983.
- [83] M. S. Daw and M. I. Baskes, “Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals,” *Phys. Rev. B*, vol. 29, pp. 6443–6453, Jun 1984.
- [84] X. W. Zhou, D. K. Ward, J. E. Martin, F. B. van Swol, J. L. Cruz-Campa, and D. Zubia, “Stillinger-Weber potential for the II-VI elements Zn-Cd-Hg-S-Se-Te,” *Phys. Rev. B*, vol. 88, p. 085309, Aug 2013.
- [85] A. Béré and A. Serra, “On the atomic structures, mobility and interactions of extended defects in GaN: dislocations, tilt and twin boundaries,” *Philosophical Magazine*, vol. 86, no. 15, pp. 2159–2192, 2006.
- [86] J.-W. Jiang and Y.-P. Zhou, “Parameterization of Stillinger-Weber potential for two-dimensional atomic crystals,” *Handbook of Stillinger-Weber Potential Parameters for Two-Dimensional Atomic Crystals*, 2017.
- [87] L. Lindsay and D. A. Broido, “Optimized Tersoff and Brenner empirical potential parameters for lattice dynamics and phonon thermal transport in carbon nanotubes and graphene,” *Phys. Rev. B*, vol. 81, p. 205441, May 2010.

- [88] C. Sevik, A. Kinaci, J. B. Haskins, and T. Çağın, “Characterization of thermal transport in low-dimensional boron nitride nanostructures,” *Phys. Rev. B*, vol. 84, p. 085409, Aug 2011.
- [89] S. J. Stuart, A. B. Tutein, and J. A. Harrison, “A reactive potential for hydrocarbons with intermolecular interactions,” *The Journal of Chemical Physics*, vol. 112, no. 14, pp. 6472–6486, 2000.
- [90] T. C. O’Connor, J. Andzelm, and M. O. Robbins, “AIREBO-M: A reactive model for hydrocarbons at extreme pressures,” *The Journal of Chemical Physics*, vol. 142, no. 2, p. 024903, 2015.
- [91] D. W. Brenner, “Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films,” *Phys. Rev. B*, vol. 42, pp. 9458–9471, Nov 1990.
- [92] G. Dhaliwal, P. B. Nair, and C. V. Singh, “Uncertainty analysis and estimation of robust AIREBO parameters for graphene,” *Carbon*, vol. 142, pp. 300 – 310, 2019.
- [93] J. A. Stewart and D. E. Spearot, “Atomistic simulations of nanoindentation on the basal plane of crystalline molybdenum disulfide (MoS₂),” *Modelling and Simulation in Materials Science and Engineering*, vol. 21, p. 045003, mar 2013.
- [94] P. Vashishta, R. K. Kalia, A. Nakano, and J. P. Rino, “Interaction potential for aluminum nitride: A molecular dynamics study of mechanical and thermal properties of crystalline and amorphous aluminum nitride,” *Journal of Applied Physics*, vol. 109, no. 3, p. 033514, 2011.
- [95] J. Kennedy and R. Eberhart, “Particle swarm optimization,” in *Proceedings of ICNN’95 - International Conference on Neural Networks*, vol. 4, pp. 1942–1948 vol.4, Nov 1995.
- [96] E. Mezura-Montes and C. A. C. Coello, “Constraint-handling in nature-inspired numerical optimization: Past, present and future,” *Swarm and Evolutionary Computation*, vol. 1, no. 4, pp. 173 – 194, 2011.

- [97] H. Aguiar e Oliveira Junior, L. Ingber, A. Petraglia, M. Rembold Petraglia, and M. Augusta Soares Machado, *Adaptive Simulated Annealing*, pp. 33–62. Berlin, Heidelberg: Springer Berlin Heidelberg, 2012.
- [98] J. E. Turney, E. S. Landry, A. J. H. McGaughey, and C. H. Amon, “Predicting phonon properties and thermal conductivity from anharmonic lattice dynamics calculations and molecular dynamics simulations,” *Phys. Rev. B*, vol. 79, p. 064301, Feb 2009.
- [99] Y. Hong, J. Zhang, and X. C. Zeng, “Thermal conductivity of monolayer MoSe₂ and MoS₂,” *The Journal of Physical Chemistry C*, vol. 120, no. 45, pp. 26067–26075, 2016.
- [100] M. S. Green, “Markoff random processes and the statistical mechanics of time-dependent phenomena. II. irreversible processes in fluids,” *The Journal of Chemical Physics*, vol. 22, no. 3, pp. 398–413, 1954.
- [101] R. Kubo, “Statistical-mechanical theory of irreversible processes. i. general theory and simple applications to magnetic and conduction problems,” *Journal of the Physical Society of Japan*, vol. 12, no. 6, pp. 570–586, 1957.
- [102] D. P. Sellan, E. S. Landry, J. E. Turney, A. J. H. McGaughey, and C. H. Amon, “Size effects in molecular dynamics thermal conductivity predictions,” *Phys. Rev. B*, vol. 81, p. 214305, Jun 2010.
- [103] M. Omini and A. Sparavigna, “An iterative approach to the phonon Boltzmann equation in the theory of thermal conductivity,” *Physica B: Condensed Matter*, vol. 212, no. 2, pp. 101 – 112, 1995.
- [104] M. Omini and A. Sparavigna, “Beyond the isotropic-model approximation in the theory of thermal conductivity,” *Phys. Rev. B*, vol. 53, pp. 9064–9073, Apr 1996.
- [105] A. Ward, D. A. Broido, D. A. Stewart, and G. Deinzer, “Ab initio theory of the lattice thermal conductivity in diamond,” *Phys. Rev. B*, vol. 80, p. 125203, Sep 2009.

- [106] T. Feng, B. Qiu, and X. Ruan, “Anharmonicity and necessity of phonon eigenvectors in the phonon normal mode analysis,” *Journal of Applied Physics*, vol. 117, no. 19, p. 195102, 2015.
- [107] C. Campa  a and M. H. M  ser, “Practical Green’s function approach to the simulation of elastic semi-infinite solids,” *Phys. Rev. B*, vol. 74, p. 075420, Aug 2006.
- [108] L. T. Kong, “Phonon dispersion measured directly from molecular dynamics simulations,” *Computer Physics Communications*, vol. 182, no. 10, pp. 2201 – 2207, 2011.
- [109] E. N. Koukaras, G. Kalosakas, C. Galiotis, and K. Papagelis, “Phonon properties of graphene derived from molecular dynamics simulations,” *Scientific Reports*, vol. 5, pp. 12923 EP –, Aug 2015.
- [110] P. Anees, M. C. Valsakumar, and B. K. Panigrahi, “Temperature dependent phonon frequency shift and structural stability of free-standing graphene: a spectral energy density analysis,” *2D Materials*, vol. 2, p. 035014, aug 2015.
- [111] B. Qiu, H. Bao, G. Zhang, Y. Wu, and X. Ruan, “Molecular dynamics simulations of lattice thermal conductivity and spectral phonon mean free path of pbte: Bulk and nanostructures,” *Computational Materials Science*, vol. 53, no. 1, pp. 278 – 285, 2012.
- [112] A. Kandemir, H. Yapicioglu, A. Kinaci, T.   a  m, and C. Sevik, “Thermal transport properties of MoS₂ and MoSe₂ monolayers,” *Nanotechnology*, vol. 27, p. 055703, jan 2016.
- [113] A. Mobaraki, A. Kandemir, H. Yapicioglu, O. G  lseren, and C. Sevik, “Validation of inter-atomic potential for WS₂ and WSe₂ crystals through assessment of thermal transport properties,” *Computational Materials Science*, vol. 144, pp. 92 – 98, 2018.
- [114] A. Mobaraki, C. Sevik, H. Yapicioglu, D.   akır, and O. G  lseren, “Temperature-dependent phonon spectrum of transition metal dichalcogenides calculated from the spectral energy density: Lattice thermal conductivity as an application,” *Phys. Rev. B*, vol. 100, p. 035402, Jul 2019.

- [115] G. Kresse and J. Hafner, “Ab initio molecular dynamics for liquid metals,” *Phys. Rev. B*, vol. 47, pp. 558–561, Jan 1993.
- [116] G. Kresse and J. Furthmüller, “Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set,” *Phys. Rev. B*, vol. 54, pp. 11169–11186, Oct 1996.
- [117] G. Kresse and J. Furthmüller *Comput. Mat. Sci.*, vol. 6, pp. 15–50, 1996.
- [118] Z. Fan, L. F. C. Pereira, H.-Q. Wang, J.-C. Zheng, D. Donadio, and A. Harju, “Force and heat current formulas for many-body potentials in molecular dynamics simulations with applications to thermal conductivity calculations,” *Phys. Rev. B*, vol. 92, p. 094301, Sep 2015.
- [119] G. Kresse and D. Joubert, “From ultrasoft pseudopotentials to the projector augmented-wave method,” *Phys. Rev. B*, vol. 59, pp. 1758–1775, Jan 1999.
- [120] J. D. Gale and A. L. Rohl, “The general utility lattice program (gulp),” *Molecular Simulation*, vol. 29, no. 5, pp. 291–341, 2003.
- [121] B. Peng, H. Zhang, H. Shao, Y. Xu, X. Zhang, and H. Zhu, “Thermal conductivity of monolayer MoS₂, MoSe₂, and WS₂: interplay of mass effect, interatomic bonding and anharmonicity,” *RSC Adv.*, vol. 6, pp. 5767–5773, 2016.
- [122] D. T. Morelli and J. P. Heremans, “Thermal conductivity of germanium, silicon, and carbon nitrides,” *Applied Physics Letters*, vol. 81, no. 27, pp. 5126–5128, 2002.
- [123] J. Haskins, A. Kınacı, C. Sevik, H. Sevinçli, G. Cuniberti, and T. Çağın, “Control of thermal and electronic transport in defect-engineered graphene nanoribbons,” *ACS Nano*, vol. 5, no. 5, pp. 3779–3787, 2011.
- [124] C. Sevik, A. Kinaci, J. B. Haskins, and T. Çağın, “Influence of disorder on thermal transport properties of boron nitride nanostructures,” *Phys. Rev. B*, vol. 86, p. 075403, Aug 2012.

- [125] X. Gu and R. Yang, “Phonon transport in single-layer transition metal dichalcogenides: A first-principles study,” *Applied Physics Letters*, vol. 105, no. 13, p. 131903, 2014.
- [126] W. Li, J. Carrete, and N. Mingo, “Thermal conductivity and phonon linewidths of monolayer MoS₂ from first principles,” *Applied Physics Letters*, vol. 103, no. 25, p. 253103, 2013.
- [127] Y. Cai, J. Lan, G. Zhang, and Y.-W. Zhang, “Lattice vibrational modes and phonon thermal conductivity of monolayer MoS₂,” *Phys. Rev. B*, vol. 89, p. 035438, Jan 2014.
- [128] M. Mohr, J. Maultzsch, E. Dobardžić, S. Reich, I. Milošević, M. Damnjanović, A. Bosak, M. Krisch, and C. Thomsen, “Phonon dispersion of graphite by inelastic x-ray scattering,” *Phys. Rev. B*, vol. 76, p. 035439, Jul 2007.
- [129] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, and P. Ordejón, “Phonon dispersion in graphite,” *Phys. Rev. Lett.*, vol. 92, p. 075501, Feb 2004.
- [130] P. Han and G. Bester, “Interatomic potentials for the vibrational properties of III-V semiconductor nanostructures,” *Phys. Rev. B*, vol. 83, p. 174304, May 2011.
- [131] X. Zhang, H. Xie, M. Hu, H. Bao, S. Yue, G. Qin, and G. Su, “Thermal conductivity of silicene calculated using an optimized Stillinger-Weber potential,” *Phys. Rev. B*, vol. 89, p. 054310, Feb 2014.
- [132] G. P. P. Pun and Y. Mishin, “Optimized interatomic potential for silicon and its application to thermal stability of silicene,” *Phys. Rev. B*, vol. 95, p. 224103, Jun 2017.
- [133] J. H. Los and A. Fasolino, “Intrinsic long-range bond-order potential for carbon: Performance in monte carlo simulations of graphitization,” *Phys. Rev. B*, vol. 68, p. 024107, Jul 2003.
- [134] P. Rowe, G. Csányi, D. Alfè, and A. Michaelides, “Development of a machine learning potential for graphene,” *Phys. Rev. B*, vol. 97, p. 054303, Feb 2018.

- [135] H. Şahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger, and S. Ciraci, “Monolayer honeycomb structures of group-IV elements and III-V binary compounds: First-principles calculations,” *Phys. Rev. B*, vol. 80, p. 155453, Oct 2009.
- [136] Z. Y. Al Balushi, K. Wang, R. K. Ghosh, R. A. Vilá, S. M. Eichfeld, J. D. Caldwell, X. Qin, Y.-C. Lin, P. A. DeSario, G. Stone, S. SubRamanian, D. F. Paul, R. M. Wallace, S. Datta, J. Redwing, and J. A. Robinson, “Two-dimensional gallium nitride realized via graphene encapsulation,” *Nature Materials*, vol. 15, pp. 1166 EP –, Aug 2016.
- [137] T. H. Seo, A. H. Park, S. Park, Y. H. Kim, G. H. Lee, M. J. Kim, M. S. Jeong, Y. H. Lee, Y.-B. Hahn, and E.-K. Suh, “Direct growth of GaN layer on carbon nanotube-graphene hybrid structure and its application for light emitting diodes,” *Scientific Reports*, vol. 5, pp. 7747 EP –, Jan 2015.
- [138] P. Tsipas, S. Kassavetis, D. Tsoutsou, E. Xenogiannopoulou, E. Golias, S. A. Giamini, C. Grazianetti, D. Chiappe, A. Molle, M. Fanciulli, and A. Dimoulas, “Evidence for graphite-like hexagonal AlN nanosheets epitaxially grown on single crystal Ag(111),” *Applied Physics Letters*, vol. 103, no. 25, p. 251605, 2013.
- [139] R. Wang, D. G. Purdie, Y. Fan, F. C.-P. Massabau, P. Braeuninger-Weimer, O. J. Burton, R. Blume, R. Schloegl, A. Lombardo, R. S. Weatherup, and S. Hofmann, “A peeling approach for integrated manufacturing of large monolayer h-BN crystals,” *ACS Nano*, vol. 13, no. 2, pp. 2114–2126, 2019.
- [140] G. Qin, Z. Qin, H. Wang, and M. Hu, “Anomalously temperature-dependent thermal conductivity of monolayer GaN with large deviations from the traditional $1/t$ law,” *Phys. Rev. B*, vol. 95, p. 195416, May 2017.
- [141] J. Nord, K. Albe, P. Erhart, and K. Nordlund, “Modelling of compound semiconductors: analytical bond-order potential for gallium, nitrogen and gallium nitride,” *Journal of Physics: Condensed Matter*, vol. 15, pp. 5649–5662, aug 2003.

- [142] K. Matsunaga, C. Fisher, and H. Matsubara, “Tersoff potential parameters for simulating cubic boron carbonitrides,” *Japanese Journal of Applied Physics*, vol. 39, pp. L48–L51, jan 2000.
- [143] J. H. Los, J. M. H. Kroes, K. Albe, R. M. Gordillo, M. I. Katsnelson, and A. Fasolino, “Extended Tersoff potential for boron nitride: Energetics and elastic properties of pristine and defective *h*-BN,” *Phys. Rev. B*, vol. 96, p. 184108, Nov 2017.

