

Thermal transport properties of bulk and monolayer MoS₂: an ab-initio approach

Amreen Bano^a, Preeti Khare and N K Gaur

Department of Physics, Barkatullah University, Bhopal-462026, M.P. INDIA

E-mail: ^abanoamreen.7@gmail.com

Abstract. The transport properties of semiconductors are key to the performance of many solid-state devices (transistors, data storage, thermoelectric cooling and power generation devices, etc). In recent years simulation tools based on first-principles calculations have been greatly improved, being able to obtain the fundamental ground-state properties of materials accurately. The quasi harmonic thermal properties of bulk and monolayer of MoS₂ has been computed with *ab initio* periodic simulations based of density functional theory (DFT). The temperature dependence of bulk modulus, specific heat, thermal expansion and gruneisen parameter have been calculated in our work within the temperature range of 0K to 900K with projected augmented wave (PAW) method using generalized gradient approximation (GGA). Our results show that the optimized lattice parameters are in good agreement with the earlier reported works and also for thermoelastic parameter, i.e. isothermal bulk modulus (B) at 0K indicates that monolayer MoS₂ (48.5 GPa) is more compressible than the bulk structure (159.23 GPa). The thermal expansion of monolayer structure is slightly less than the bulk. Similarly, other parameters like heat capacity and gruneisen parameter shows different nature which is due to the confinement of 3 dimensional structure to 2 dimension (2D) for improving its transport characteristics.

1. Introduction

Molybdenum disulfide MoS₂ is a 'layered' transition metal dichalcogenide (TMD) in its bulk state with an indirect band gap has attracted many of the researchers for its various electronic and catalytic applications [1-5]. The crystal structure of MoS₂ is similar to graphene, having Mo and S atoms stacked together forming a sandwich where S-Mo-S sandwiches are bonded with weak Van-der-Waals forces. The 2D materials possess unique properties. Hexagonal boron nitride (h-BN), graphene, MoS₂, MoSe₂, WSe₂, WS₂ etc TMDs offered promising candidature for novel nanoelectronics, large band gap insulators, semiconductors and semimetals [6-10]. In particular, 2D semiconductors show high bendability, high on-off current ratio that offers low power consumption and flexible electronics for future generations [11-15]. The confinement of bulk MoS₂ from ploy layer to monolayer has shown drastic improvements in its transport mechanism as its monolayer gives a direct semiconducting band gap which makes it an efficient candidate for thermoelectric, optical, and many other application areas. However, a great amount of work has been carried out in the research filed for its electronic, optical and vibrational properties but very less is available regarding its thermodynamic properties under the temperature change. In the present work, we have explored the temperature dependent thermodynamic nature of MoS₂ in bulk and monolayer both. In the following sections, the results obtained in our study for isothermal bulk modulus (B), specific heat (C_p), thermal expansion coefficient (α) and gruneisen parameter with temperature variation has been discussed.



2. Computational details

In the present work, all the calculations are performed using PWSCF code [15] based on DFT. Using the plane-wave pseudopotential method and employing the generalized gradient approximation (GGA) [16]. The all electron projector augmented wave (PAW) method [17] was employed with a plane-wave cutoff energy of 55 Rydberg. The k-point samplings with 11x11x7 for bulk and 9x9x1 for monolayer structures has been used after convergence test in the Brillouin zone using the Monkhorst-Pack scheme [18]. The total energy convergence tests showed that convergence to within 1 meV/atom was achieved with the above calculation parameters. To simulate the monolayer of a vacuum of 20 Å is included along Z direction to avoid any interactions between the periodic images. In order to investigate the thermodynamic properties, we have used quasi harmonic approximation (QHA) as implemented in Phonopy code [19], which includes the phononic effects. This model is very quick and easy, and it has been successfully applied to predict the thermodynamic properties of some materials [20, 21].

The isothermal bulk modulus (B), specific heat (C_p), thermal expansion coefficient (α) and gruneisen parameter (γ) in QHA are defined by the following relations [22, 23]

$$B(V) = V \left[\frac{d^2 E(V)}{dV^2} \right] \quad (1)$$

$$\alpha_V = \frac{1}{V} \left[\frac{dV}{dT} \right] \quad (2)$$

$$C_p - C_v = \alpha_V^2(T) B_0 V T \quad (3)$$

$$\gamma = \frac{\alpha B T V}{C_v} \quad (4)$$

where, E is the total energy per unit cell, V is the unit cell volume, C_v is the specific heat at constant volume, and T denotes the temperature.

3. Results and discussions

The crystal structure shown in figure 1, of MoS₂ is hexagonal (honeycomb). The space group of bulk MoS₂ is P3m1 (point group D_{6h}) and that is of the single layer is P6m2 (point group D_{3h}). To obtain the ground state structure of both (bulk and monolayer MoS₂), we have fully relaxed the lattice constants and atomic coordinates by using a DFT code Quantum Espresso [16], and obtained a=3.17 Å and c=11.79 Å for bulk and a= 3.15 Å for monolayer structure, which is in good agreement with the available literature [24, 25]. Phonopy [19] based on QHA has been used to calculate the thermodynamic quantities. The variation of isothermal bulk modulus (B) with temperature is shown in figure 2(a). It can be seen that with upto 300K, B is nearly unchanged for both the structures, but on further increasing the temperature, for bulk structure, B start to decrease and in monolayer structure this decreasing trend is very nominal. This is due to the change in the equilibrium volume of the compound. The different variation trends in bulk and monolayer reveals the fact that the rigidity in bulk structure is along the z-direction, where atoms are interacting under Van-der-Waals interactions [26]. This provides hardness to the bulk and high bendability to the monolayer structure of MoS₂. One of the most important thermodynamic properties is specific heat of the material, as it provides information about many applications and vibrational properties. The response of C_p with temperature can be seen in figure 2(b). Upto 400K, C_p increases with increasing temperature and it is noteworthy, for T>400K, it is tending to a converging value which is called as Dulong-Petit limit. For low temperatures i.e. T<100K, it follows the T³ law. In the QHA model, the Gruneisen parameter γ describes the anharmonic effects of the crystal lattice thermal vibration [24, 25]. It is observed from figure 2(c) for both structures, the effect of temperature over γ is not much significant. At T> 150K, γ reaches to a constant value in both structures, i.e. 1.25 for bulk and 1.19 for monolayer. The temperature dependence of thermal expansion α , is presented in figure 2(d). It is observed that it

increases rapidly with T^3 upto 400K. And after that, it gently increases at further high temperatures. The values obtained of each thermodynamic quantity at 300K, is listed in table 1.

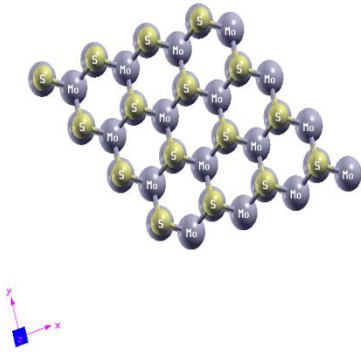


Figure 1. Error! No sequence specified.
crystal structure of MoS₂
(top view)

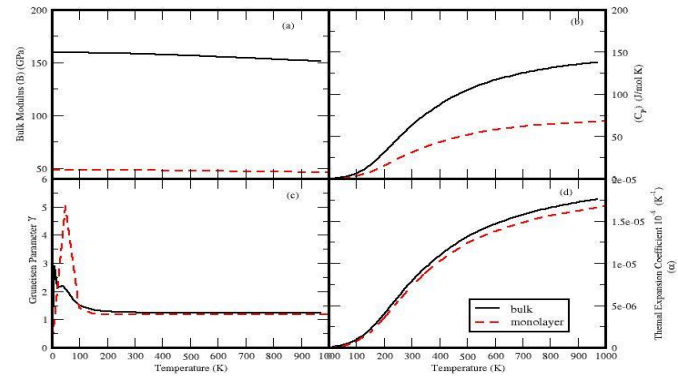


Figure 2. Thermodynamic response of bulk and monolayer of MoS₂ in the temperature range $0K < T < 900K$

Table 1. Thermodynamic quantities of bulk and monolayer MoS₂ at 300 K

Quantities	Bulk	Monolayer
B (GPa)	158.3	47.9
C_p (J/mol K)	62.23	30.76
γ	1.25	1.17
$\alpha(10^{-6} \text{ K}^{-1})$	7.8	7.2

Acknowledgment

The authors highly acknowledge University Grants Commission (UGC) Delhi, for providing financial assistance in our work by Maulana Azad National Fellowship (MANF).

References

- [1] Byskov L S, Norskov J K, Clausen B S and Topsoe H 2000 *J. Catal.* **187** 109
- [2] Raybaud P, Hafner J, Kresse G, Kasztelan S and Toulhoat H 2000 *J. Catal.* **189** 129
- [3] Galea N M, Kadantsev E S and Ziegler T 2009 *J. Phys. Chem. C* **113** 193
- [4] Vojvodic A, Hinnemann B and Norskov J K 2009 *Phys. Rev. B* **80** 125416
- [5] Li T and Galli G 2007 *J. Phys. Chem. C* **111** 16192
- [6] Kim K K, Hsu A, Jia X, Kim S M, Shi Y, Hofmann M, Nezich D, R-Nieva J F, Dresselhaus M S, Palacios T and Kong J 2011 *Nano Lett.* **12** 161
- [7] Shi Y, Hamsen C, Jia X, Kim K K, Reina A, Hofman M, Hsu A L, Li K, Juang Z Y, Dresselhaus M S, Li L J and Kong J 2010 *Nano Lett.* **10** 4134.
- [8] Chen C H, Wu C L, Pu J, Chiu M H, Kumar P, Takenobu T T and Li L J 2014 *2D Mater.* **1** 034001
- [9] Liu K K, Zhang W, Lee Y H, Lin Y C, Chang M T, Su C Y, Chang C S, Shi Y, Zhang H, Lai C S and Li L J 2012 *Nano Lett.* **12** 1538
- [10] Li X, Cai W, An J, Kim S, Nah J, Yang D, Piner R, Velamakanni A, Jung I, Tutuc E, Banerjee S K, Colombo L and Ruoff R S 2009 *Science* **324** 1312
- [11] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 *Nat. Nanotech.* **6** 147

- [12] Fang H, Chuang S, Chang T C, Takei K, Takahashi T T and Javey A 2012 *Nano Lett.* **12** 3788
- [13] Huang J K, Pu J, C-H.Hsu, Chiu M H, Juang Z Y, Chang Y H, Iwasa Y, Takenobu T and Li L J 2013 *ACS Nano* **8** 923
- [14] Pu J, Yomida Y, Liu K K, Iwasa Y and Takenobu T 2012 *Nano Lett.* **12** 4013
- [15] Baroni S *et al.* see <http://www.pwscf.org/> for more information about the quantum-simulation software
- [16] Perdew P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [17] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [18] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [19] Togo A, Oba F and Tanaka I 2008 *Phys. Rev. B* **78** 134106
- [20] Blanco M A, Francisco E, and Lua-na V 2004 *Comput. Phys. Commun.* **158** 57
- [21] Zhang X, Chen L, Ma M, Zhu Y, Zhang S and Liu R 2011 *J. Appl. Phys.* **109** 113523
- [22] Zhang X, Qin J, Ning J, Sun X, Li X, Ma M and Liu R 2013 *J. Appl. Phys.* **114** 183517
- [23] Zhang X, Chen L, Ma M, Zhu Y, Zhang Sand Riping 2011 *J. Appl. Phys.* **109** 113523
- [24] Grimme S, Antony J, Ehrlich S and Krieg H 2010 *J. Chem. Phys.* **132** 154104
- [25] Kadantsev E S and Hawrylak P 2012 *Solid State Comm.* **152** 909
- [26] Luo F, Cai L C, Chen X R, Jing F Q and Alfe D 2012 *J. Appl. Phys.* **111** 053503