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On Hardware Benchmarking of First Principles Calculations for Predicting Lattice Thermal Conductivity of Monolayer Graphene

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***Abstract*— Graphene is a 2D material obtained from exfoliation of Graphite and possesses exotic electrical and thermal properties in the form of high electrical conductivity, high lattice thermal conductivity and several folds anisotropy between in-plane and cross-plane lattice thermal conductivities. Studying these transport properties requires high throughput first principles calculations and computationally intensive simulations which enable predictive design of materials for applications like energy conversion, heat dissipation in electronic systems and sensors. The following work aims to predict the lattice thermal conductivity of Monolayer Graphene (MLG) by the direct solution of linearized phonon-Boltzmann Transport Equation (LBTE) using phono3py code, integrated with first principles calculations implemented in Quantum ESPRESSO. All first principle calculations are accelerated on an NVIDIA GeForce RTX 4090 GPU and BTE computation is parallelized using an Intel Core i9-13900K processor. Hardware benchmarking of scf calculation of a single displacement file for various wave-vector grid sizes is performed. GPU proves to be a faster computational hardware with computing time ≈2 orders of magnitude lower than that of the CPU.**

***Index Terms*— Graphene, Boltzmann Transport Equation, first principles calculations, Graphics Processing Unit (GPU).**

ABBREVIATIONS

BTE – Boltzmann Transport Equation
CPU – Central Processing Unit
DOS – Density of States
GGA – Generalized Gradient Approximation
GPU – Graphics Processing Unit
IFC – Interatomic Force Constant
LBTE – Linearized Boltzmann Transport Equation
LO – Longitudnal Optical
MLG – Monolayer Graphene
PDOS – Projected Density of States
PW – Plane Wave

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RTA – Relaxation Time Approximation
SCF – Self-Consistent Field
TBG – Twisted Bilayer Graphene
TO – Transverse Optical

I. INTRODUCTION

Graphene is a 2D material with a hexagonal layered structure, and is obtained from exfoliation of Graphite. It possesses unique electronic, electrical and thermal properties. At room temperature, the electrical conductivity of Graphene is reported to be around 10^8 Sm^{-1} [1] due to high electron mobility, and the thermal conductivity is in the range 1500 – 5000 W/mK [2]. These properties render Graphene suitable for a wide range of applications which include electronic heat dissipation, thermoelectric energy conversion, and sensors. Investigating thermal transport properties of Graphene has a lot of significance, for instance, lattice thermal conductivity of Graphene exhibits several folds anisotropy between in- and cross-plane components which can be effectively utilized for conflicting objectives like heat dissipation in electronic devices (requiring extremely high thermal conductivity) and thermoelectric energy conversion (requiring extremely low thermal conductivity). Investigating energy and charge transport properties requires high throughput first principles calculations and computationally intensive simulations for the predictive design of novel materials, which can be enabled by using state-of-the-art computational hardware with suitable architecture to speed-up/parallelize the computations. Hence, studying the capabilities of various computational hardware and benchmarking them for different numerical solvers/tools forms a significant aspect of any first principles study. A lot of research work focused on energy and charge transport in Graphene has been carried out in recent years [2-8]. Shadab Alam et. al [2] proposed an alternative framework of thermal snapshot technique to extract temperature dependent 2^{nd} and 3^{rd} order interatomic force constants (IFCs), and compared it with conventional Finite Displacement and Molecular Dynamics methods. Thermal snapshot technique was helpful in analyzing thermal transport in bilayer Graphene due to its temperature dependent IFCs. Its major drawback is dependency on computational cell size for some materials like single layer Graphene. Rafiq Mulla et al. [3] highlighted the scope of Graphene and its composites as a potential thermoelectric material and enumerated various avenues for future research, which include exploring various types of Graphene (like bilayer), effects of heterostructuring and nanostructuring. Jeong Yun Kim et. al [4] discussed the effects of patterning of Graphene on thermoelectric efficiency. Patterning imparted quasi-1D effect to Graphene resulting in a decrease in its thermal conductivity, in turn increasing its Figure of Merit by 2 orders of magnitude (≈3 at 300 K). Shahid Ahmed et. al [5] investigated thermal transport in twisted bilayer Graphene (TBL) and performed a comparative study for various twisted configurations. They reported that the thermal conductivities of 13.2° and 21.8° twisted configuration were 56% and 36% lower than the untwisted configuration which has thermal conductivity of 2260 W/mK, which was attributed to reduced contributions from flexural phonon modes owing to increased phonon anharmonicity due to larger spread of cubic IFCs of flexural modes in TBL. The following study aims to predict the lattice thermal conductivity of Monolayer Graphene (MLG) by the direct solution of linearized phonon-BTE (LBTE) using phono3py [9, 10] code, integrated with first principles calculations implemented in Quantum ESPRESSO. All first principles calculations are accelerated on an NVIDIA GeForce RTX 4090 GPU, and numerical computations for phonon-BTE solution are parallelized on an Intel Core i9-13900K processor. Hardware benchmarking of first principles scf calculations is performed by comparing computing times on both the hardware for various wave-vector grid sizes.

II. RESULTS

Phonon dispersion curve and density of states, lattice thermal conductivity of MLG and the time taken by scf calculation on various computational hardware are presented in the following sections.

A) *Phonon Dispersion Curve and Density of States*

Phonon dispersion curve and density of states of MLG are shown in Fig. 1 and Fig. 2 respectively. From Fig. 1, it can be observed that there are no negative modes indicating dynamic stability of the structure. Phonon frequency range is 0 – 48 THz. The topmost LO and TO branches are degenerate at 47.24 THz (1575 cm^{-1}),
which is in well agreement with the value of 1587 cm^{-1} reported by Ransell D' Souza and Sujata Mukherjee [6].

B) *Lattice Thermal Conductivity*

Lattice thermal conductivity of MLG at 300 K for various q-point grid configurations is shown in Fig. 3. The value of κ_l obtained by directly solving LBTE for 200x200x1 sized q-point grid is 826.579 W/mK, which is a

severe under-prediction compared to the experimental values reported in literature [1, 2, 7, 8]. One of the main reasons for this is the dependence of anharmonic IFCs on the sizes of supercell, wave-vector and q-point grids.

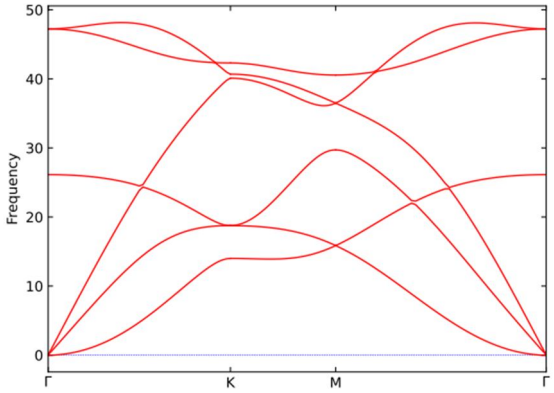

Figure 1: Phonon dispersion curve (frequency in THz) of MLG

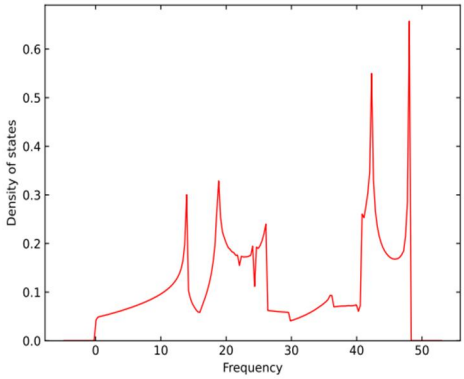

Figure 2: Phonon DOS of MLG

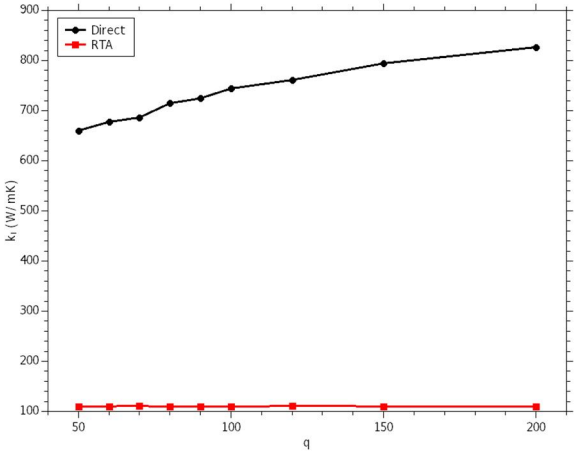

Figure 3: Lattice thermal conductivity of MLG for various q-point grid sizes (qxqx1)

C) *Computing Time on the CPU and GPU*

The problem of under-prediction of κ_l can be addressed by using a larger supercell and denser wave-vector and q-point grids, which would require state-of-the-art computational hardware offering a large memory and a high speedup. This section highlights the capabilities of an NVIDIA GeForce RTX 4090 GPU and an Intel Core i9-13900K CPU by comparing the time taken by them to perform a single scf calculation for various wave-vector grid sizes, as shown in Table I.

TABLE I: COMPUTING TIME ON THE CPU AND GPU

Size of wave-vector grid	No. of k-points	Time taken by the CPU (s)				Time taken by the GPU (s)
		1 core	4 cores	8 cores	24 cores	
Gamma	1	36.84	14.03	29.92	191.03	3.83
2x2x1	4	246.17	86.28	157.58	756.24	17.96
4x4x1	10	597.77	203.23	354.22	1831.67	46.64
6x6x1	20	1238.49	421.06	730.02	3900	90.7
8x8x1	34	1949.31	712.92	1168.08	6000	137.68
10x10x1	52	3205.92	1092.37	1871.93	9960	223.64
12x12x1	74	4140	1522.93	2674.88	13440	288.18

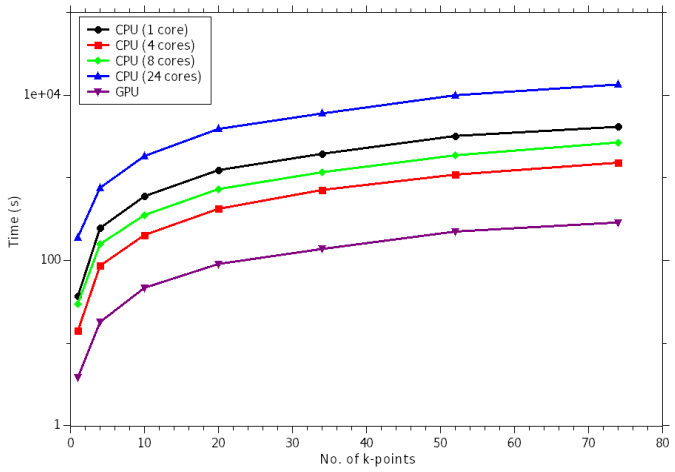

Figure 4: Variation of time taken by the CPU and GPU to perform a single scf calculation with the no. of k-points

Time taken for an scf calculation increases with the wave-vector grid size/no. of k-points as shown in Fig. 4. In case of the CPU, maximum acceleration is achieved by using 4 cores, whereas the computation is slowest when 24 cores are used. This is due to the optimized distribution strategy in the former case. For a given size of wave-vector grid, computing time decreases with the no. of cores upto 4 cores, and after that, it increases with any further increase in the no. of cores. Time taken by the GPU is ≈2 orders of magnitude lower than that of the CPU, proving it a better alternative of the CPU to accelerate first principles calculations.

III. COMPUTATIONAL DETAILS

The methods to calculate phonon dispersion curve and DOS, and lattice thermal conductivity are presented below. For all DFT calculations, the Plane-Wave (PW) based algorithm and the Generalized Gradient Approximation (GGA) are employed together with Perdew–Burke–Ernzerhof (PBE) using Troullier-Martins (MT) pseudopotential. The energy cutoffs for wave functions and charge density are set to 45 Ry and 360 Ry respectively, with Marzari-Vanderbilt smearing for electrons. Experimental lattice parameters obtained from crystallographic materials database [11-13] are used as input for structure optimization. The convergence threshold for all first principles calculations is set to 10^{-12}.

A. Simulation Experimental Setup

The simulation experimental setup consists of NVIDIA GeForce RTX 4090 GPU to accelerate first principles calculations carried out in Quantum ESPRESSO, and Intel Core i9-13900K processor to parallelize computations involving phonopy/phono3py code. Their specifications are given below,

TABLE II: SIMULATION EXPERIMENTAL SETUP

GPU/CPU	No. of cores	Base clock (GHz)	Memory
NVIDIA GeForce RTX 4090	16384 CUDA cores	2.73	24 GB GDDR6X
Intel Core i9-13900K CPU	24	3.00	128 GB

B. Crystal Structure Optimization

First, the structure is optimized to a stable intermediate with minimum energy and interatomic forces. The convergence criteria for energy and forces are set to 10^{-12} Ry and 10^{-7} Ry/bohr respectively. All parameters of the cells (x-y-components and angles) are optimized and the atomic positions are adjusted accordingly. Automatically generated k-points grid of size 32x32x1 is used for this purpose. After the structure is relaxed, the final cell parameters and atomic positions are used as inputs for the following calculations.

C. Phonon Dispersion and Density of States

Phonon dispersion and density of states are obtained from phonopy code interfaced with Quantum ESPRESSO using finite displacement method. A 4x4x1 sized supercell containing 32 atoms with minute displacements (0.001 Å) about equilibrium atomic positions is employed. 1 supercell configuration is created and sampled using

12x12x1 automatically generated k-points grid, which is later subject to scf calculations in Quantum ESPRESSO. The outputs of scf calculations are used as inputs to compute harmonic interatomic force constants (IFCs) using phonopy code. The phonon dispersion is calculated along high symmetry k-points path and phonon density of states is computed using a dense q-grid of dimension 50x50x1 to ensure accuracy and convergence.
Phonon PDOS is given by,

$$D_{k\alpha}(\omega) = (1/N)\,\Sigma_{\mathbf{q}\nu}\delta(\omega - \omega_{q\nu})|W_{k\alpha}(\mathbf{q}\nu)|^{2} \quad (1)$$

The total DOS is the sum of PDOS given by,

$$D(\omega) = (1/N)\Sigma_{\mathbf{q}\nu}\delta(\omega - \omega_{\mathbf{q}\nu}) \approx (V_c/(2\pi)^3)\int dq\Sigma_{\mathbf{q}\nu}\delta(\omega - \omega_{\mathbf{q}\nu}) \quad (2)$$

where N is no. of unit cells in the crystal, V_c is the volume of the unit cell, W is the periodic function of the crystal lattice, $\mathbf{q}\nu$ is the index of phonon modes, ν is the band index, and ω is the phonon frequency.

C. Calculation of Lattice Thermal Conductivity

Lattice thermal conductivity (κ_l) is calculated by accounting for 3-phonon interactions using phono3py code interfaced with Quantum ESPRESSO. For this, a supercell of size 4x4x1 containing 32 atoms sampled with 12x12x1 automatically generated k-points mesh is used. Similar to the harmonic phonon calculations, atoms are displaced about their equilibrium positions (0.0025 Å) to compute quadratic and cubic IFCs using finite displacement method. 170 supercell configurations are analyzed and subject to scf calculations in Quantum ESPRESSO, following which the force constants are calculated, and κ_l is computed by solving linearized Boltzmann Transport Equation (LBTE).

$$\kappa_{\lambda\lambda'} = (1/4k_BT^2NV_c)\Sigma_{\lambda\lambda'}(\hbar\omega_\lambda v_{\lambda,a}/\sinh(\hbar\omega_\lambda/2\pi k_BT))\Omega^{-1}(\hbar\omega_{\lambda'}v_{\lambda',a}/\sinh(\hbar\omega_{\lambda'}/2\pi k_BT)) \quad (3)$$

where,

$$\Omega_{\lambda\lambda'} = (\delta_{\lambda\lambda'}/\tau_\lambda) + (36\pi/\hbar^2)\Sigma_{\lambda''}|\Phi_{\lambda\lambda'\lambda''}|^2(1/\sinh(\hbar\omega_{\lambda''}/2\pi k_BT))[\delta(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''}) + \delta(\omega_\lambda - \omega_{\lambda'} + \omega_{\lambda''}) + \delta(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''})]$$

$\lambda = \mathbf{q}\nu$ referring to a specific mode, k_B is Boltzmann constant, $\hbar$ is reduced Planck's constant, T is the absolute temperature and Ω is the collision matrix.

IV. Conclusions

In this work, hardware benchmarking of scf calculations for the prediction of lattice thermal conductivity of Graphene was performed, which provided insight on GPU as an alternative of multicore processors to speed up first principles calculations and aid in the discovery of novel materials for applications like energy conversion, sensors, and heat dissipation in electronic devices. Since the value of lattice thermal conductivity strongly depends on supercell, wave-vector and q-grid sizes, exploring all possible combinations of denser wave-vector and q-point grids in a larger supercell becomes imminent and can be achieved by using state-of-the-art computational hardware. GPU proved to be a faster computational hardware with computing time approximately 2 orders of magnitude lower than that of CPU.

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Declarations

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- *Conflict of interest/Competing interests:*- The authors declare no conflict of interest.
- *Data availability:*- The data generated and analyzed during the current study will be made available by the corresponding author on reasonable request.
- *Author contribution*:- Both the authors contributed equally to manuscript development and research work.

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