

First principles calculation of thermoelectric parameters of Monolayer- and Bilayer-Graphene and Heterostructures of Graphene and h -BN

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Abstract. Electrical conductivity and Seebeck coefficient were calculated using Boltzmann transport theory based on first-principles bandstructure calculations for the monolayer- and bilayer-graphene. We also present calculations of the thermoelectric parameters of Graphene/ h -BN/Graphene sandwiched heterostructures. These results will be discussed in the light of existing experimental data.

1. Introduction

Study of the thermoelectric properties of nanomaterials has become a topic of great interest in the recent past [1, 2, 3]. Electrical conductivity (σ) and Seebeck coefficient (S) of monolayer graphene (MLG) was measured in great detail by Kim and coworkers [4, 5] and others [6]. The conductivity measurements established its dependence with the square root of the carrier density, $\sigma \sim \sqrt{n}$, and the resistivity (ρ) showed the Bloch-Grüneisen type of behaviour with temperature [7]. Similar results were obtained also for the bilayer graphene (BLG) [8], where S showed slightly different behaviour than in MLG.

On the other hand, multilayers of graphene (G) and hexagonal boron nitride (h -BN), which is semiconducting with band gap depending on the degree of mixing of its constituents, have attracted a lot of attention for device application. Recently thermoelectric parameters of multiple layers of h -BN sandwiched between graphene were measured in a series of experiments by Chen et al [9, 10, 11]. Thermal conductivity (κ) of G/ h -BN/G heterostructure and that of multilayer and bulk h -BN was reported and based on these measurements, the Figure of merit, $ZT = S^2\sigma T/\kappa$ was estimated.

In this paper we report theoretical calculations of thermoelectric parameters of MLG, BLG and in G/ h -BN/G heterostructure. Our calculations of electrical transport were carried out using Boltzmann transport theory applied to band electrons, with band structure calculated from first-principles DFT based plane wave method. We have also compared our DFT based calculations with a tight-binding bandstructure based calculation of σ and S in MLG and BLG. The thermal transport in G/ h -BN/G and in multilayer and bulk h -BN was carried out using equilibrium Green-Kubo theory based MD simulations performed at constant temperature and

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finally Z was calculated. Our results show very good agreement with available experimental data.

2. Method of Calculation

2.1. First-principles Bandstructure Calculation

Electronic structure calculations were carried out using density functional theory (DFT) with plane-wave pseudopotential based method as implemented in Quantum Espresso code [12]. Hexagonal unit cells were used for both MLG and BLG calculations and orthogonal unit cells for G/*h*-BN/G heterostructures. Ultrasoft pseudopotentials [13] were used to describe the core electrons and the generalized gradient approximation (GGA) [14] for the exchange-correlation potential. Monkhorst-Pack k -point grid [15] of $150 \times 150 \times 1$ and $70 \times 70 \times 4$ were used for MLG and BLG in the self-consistent calculations, while $48 \times 48 \times 2$ k -point grid was used for the G/*h*-BN/G heterostructures; respectively. All self-consistent calculations were performed with a 40Ry kinetic energy cutoff and a 160Ry charge density energy cutoff. For two-dimensional samples, we have kept the vacuum spacing in the unit cell to be 22Å along the z -direction which is large enough to avoid interaction between the cells. As it has been shown that the AB stacking is the most stable [16], the two monolayers in BLG and *h*-BN layers in G/*h*-BN/G heterostructures were arranged in the AB stacking, with bond lengths calculated self-consistently. We have

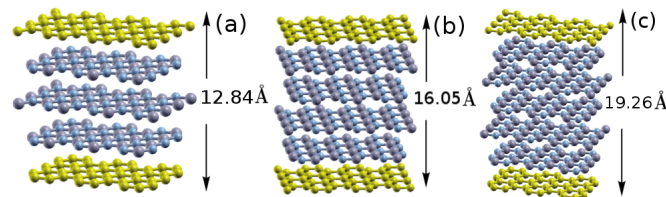


Figure 1. Ball-stick model of G/*h*-BN/G heterostructures with (a) three-, (b) four- and (c) five *h*-BN layers sandwiched between Graphene layers. Thickness of the heterostructures are indicated.

included the van der Waals interactions [17] for systems involving multiple layers.

2.2. Boltzmann Transport Theory: Electrical Transport Calculations

To calculate the transport properties, we have used the semi-classical Boltzmann transport theory applied to band electrons as implemented in the Boltztrap code [18]. The transport parameters are obtained from the group velocity, $v_\alpha(i, \mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon_{i, \mathbf{k}}}{\partial k_\alpha}$, of the band electrons, referring to the i -th energy band and α -th component of the wavevector $\mathbf{k}$.

The electrical conductivity tensor is then written, in the relaxation time approximation, as,

$$\frac{\sigma_{\alpha\beta}(T, \mu)}{\tau} = \frac{1}{V} \int e^2 v_\alpha(i, \mathbf{k}) v_\beta(i, \mathbf{k}) \left[\frac{-\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon \quad (1)$$

Here, f_μ is the Fermi-Dirac distribution function, V is the sample volume and τ is the electron relaxation time, which depends on the electron-electron interaction, and e is the electronic charge. Detailed studies [19, 20] have shown that τ does not depend on both the band index and $\mathbf{k}$ and is isotropic to a good approximation. Above relation was used to calculate temperature dependent resistivity of two-dimensional CBN nanomaterials recently [21]. The Seebeck coefficient tensor is expressed as,

$$S_{\alpha\beta}(T, \mu) = \frac{1}{eT} \frac{\int v_\alpha(i, \mathbf{k}) v_\beta(i, \mathbf{k}) (\epsilon - \mu) \left[\frac{-\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon}{\int v_\alpha(i, \mathbf{k}) v_\beta(i, \mathbf{k}) \left[\frac{-\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon} \quad (2)$$

ML- and BL- graphene are both gapless while calculated bandstructure of G/*h*-BN/G heterostructure [22] exhibits a small band gap ~ 0.05 eV which changes very little for three-, four- and five-layers of *h*-BN in the sample. The electrical transport around the Fermi energy can be expressed in the Mott formula [23] as,

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{d}{dE} [\ln \sigma(E)]. \quad (3)$$

Here k_B is the Boltzmann constant. The Power factor is defined as, $P = S^2 \sigma$ and the Figure of merit is defined as, $ZT = PT/\kappa$ where κ is the temperature dependent total thermal conductivity.

2.3. Thermal Transport Calculations

The thermal conductivity is calculated from the correlation function of the heat current ($\mathbf{J}$) using equilibrium molecular dynamics simulations. One can calculate the thermal conductivity κ by applying the Green-Kubo method [24, 25] or the Einstein relation [26]. There have been detailed calculations on two-dimensional stripes of Graphene and *h*-BN [27, 28, 29, 30, 31] using the latter method. We adopt the equilibrium Green-Kubo method as implemented in the code LAMMPS [32]. Thermal conductivity is expressed as,

$$\kappa = \frac{1}{3Vk_B T^2} \int_0^\infty \langle \mathbf{J}(0) \mathbf{J}(t) \rangle dt, \quad (4)$$

where V and T are the volume and equilibrated temperature. The factor 3 accounts for averaging over the 3 dimensions and the angular brackets refers to the average over time. The macroscopic heat current is given by,

$$\mathbf{J}(t) = \sum_i \mathbf{v}_i \varepsilon_i + \frac{1}{2} \sum_{i < j} \mathbf{r}_{ij} (\mathbf{F}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)), \quad (5)$$

where $\mathbf{v}_i$ and ε_i are the velocity and site energy of particle i . $\mathbf{F}_{ij}$ is force on the atom i due to its neighbor j calculated from the interatomic potential.

Molecular dynamics (MD) simulations were performed first in microcanonical ensemble (*NVE*) and then in the Nosé-Hoover (*NVT*) ensemble at constant T . The constant temperature *NVT* ensemble requires an additional frictional term [33] to be introduced in Eq 5. As MD simulations requires an ensemble of initial velocities chosen using random number generator with a specified seed, we have used five different seeds for different sets of MD runs and the value of κ was obtained after the system was equilibrated at constant T by taking average over these runs with the standard deviation as the error bar. In all MD runs we used a large simulation cell containing around 40000 atoms to have a small error bar and a time step of 1fs. The Tersoff potential based force field [34] was used in our calculations, parameters of which were taken, for *h*-BN from Sevik et al. [28], for graphene from Lindsay et al. [35] and those for the B-C and N-C bonds from Kinaci et al [36], respectively. The calculated κ for two-dimensional striped Graphene and *h*-BN with different strip-widths [22] were found in excellent agreement with earlier simulation results [36].

3. Results and Discussions

3.1. σ and S of MLG and BLG:

The conductivity (σ), calculated from the semiclassical Boltzmann transport theory by Eq. 1 is plotted in Fig. 2(c & d) as a function of the chemical potential (μ) for temperature $T=300$ K. In

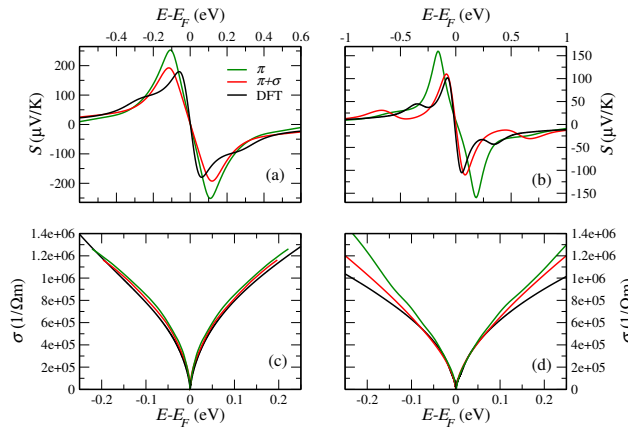


Figure 2. Calculated Seebeck coefficient (a,b) and electrical conductivity (c,d) of ML- and BL-graphene as a function of μ at $T = 300\text{K}$, respectively. Results from DFT based bandstructure are shown as black line, those from the tight-binding bandstructure with only π bands as green, and with both π and σ bands as red lines, respectively.

Fig. 2(c) we observe σ of ML graphene to be proportional to $\sqrt{n}$ where n is the charge carrier density. This $\sqrt{n}$ behavior can be explained using a tight binding model with an expansion of energy around the k point to get $\epsilon_F = \hbar v_F k_F$, where $\hbar$ is the reduced Planck constant, v_F is the Fermi velocity and k_F is the Fermi wavenumber. For a 2-dimensional sample,

$$n = \frac{k_F^2}{\pi} = \frac{\epsilon_F^2}{\pi(\hbar v_F)^2} \quad (6)$$

Therefore the MLG's density of states $D(\epsilon_F)$,

$$D(\epsilon_F) = \frac{dn}{d\epsilon} = \frac{2\sqrt{n}}{\hbar v_F \sqrt{\pi}} \quad (7)$$

Substituting this in the Einstein relation $\sigma \propto D(\epsilon_F)$, we obtain $\sigma \propto \sqrt{n}$. This behavior has been experimentally confirmed for pristine graphene [4].

The Seebeck coefficient was calculated for both ML and BL graphene using the Mott relation Eq 3 numerically and shown in Fig. 2(a & b) as a function of chemical potential μ . Our calculated S is in very good agreement with Zuev et al's [5] measurement of Seebeck coefficient for ML graphene. Using a back-gated field effect transistor, the Fermi energy can be tuned by adjusting the gate voltage V_g . Zuev et al [5] have used this method for mesoscopic graphene sample using the relation,

$$S = -\frac{\pi^2 k_B^2 T}{3e} \frac{1}{\sigma} \frac{d\sigma}{dV_g} \frac{dV_g}{dE} \Big|_{E=E_f}. \quad (8)$$

It can be easily seen that this expression is exactly same as eq. 3. Therefore there is a direct correspondence between the gate voltage and chemical potential.

We find the resistivity of ML and BL graphene when plotted as a function of carrier density shows ρ is maximum at $n = 0$ and rapidly decreases for larger values $|n|$, which can be understood from the $\sqrt{n}$ behavior of conductivity. This has been experimentally confirmed [8, 4]. In Fig 3 we plot ρ as a function of T . This behavior of ρ at certain values of μ having the same form has

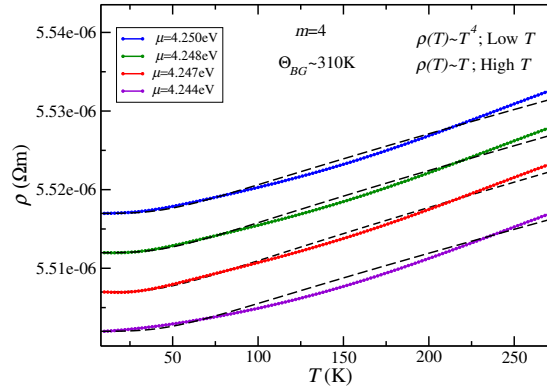


Figure 3. Calculated resistivity (ρ) of MLG as a function of T . The dashed black lines show the best fit to the Bloch-Grüneisen formula for different μ , Eq (9). Points represent results of ρ calculated from the Boltzmann Transport theory for different chemical potential μ . For clarity, the data corresponding to $\mu = 2.247$ eV, 2.248 eV and 2.25 eV are shifted by 5×10^{-9} , 10×10^{-9} and 15×10^{-9} in the y -axis, respectively.

been observed experimentally [7, 4]. In order to understand the behavior, we fit our calculated values of ρ to the Bloch-Grüneisen formula,

$$\rho(T) = \rho(0) + A \left(\frac{T}{\Theta_{BG}} \right)^m \int_0^{\frac{\Theta_{BG}}{T}} \frac{x^m}{(e^x - 1)(1 - e^{-x})} dx, \quad (9)$$

with m and Θ_{BG} as fitting parameters. Our best fit resulted in $m = 4$ and $\Theta_{BG} \approx 310K$ as plotted in Fig 3 as dashed lines. This suggests that at low temperatures, resistivity scales as T^4 and smoothly scales to linear T behavior at higher temperatures. This behavior has been theoretically predicted by Hwang [37] and experimentally observed by Efetov et al [7]. Our best fitted value of Θ_{BG} is in the same order of magnitude as estimated from the experimental measurements [7] and much lower than the Debye temperature $\Theta_D \approx 2100K$ for MLG [38].

3.2. Electrical Conductance and Thermopower of G/h-BN/G

Our calculations of electrical conductance were carried out in the relaxation time approximation assuming τ to be isotropic and independent of directions in the reciprocal lattice space. We have assumed $\tau \sim 10^{-14}s$, which is reasonable. In Fig. 4 results of the Seebeck coefficient (S) of G/h-BN/G heterostructure having 5 BN layers are shown.

As h -BN has a gap between the conduction and valence bands, the electric conduction is essentially controlled by Graphene layers at the top and bottom of the heterostructure film. Due to this, the features in S is essentially similar to that of Graphene, except at the low temperatures when the effect of the presence of a small band gap becomes evident. For $T \sim 40K - 300K$ the conductivity decreases as T increases, thereby increasing S with T as seen in the inset of Fig 4, where we plot S as a function of T at constant chemical potential. The linear dependence of S on T suggests that the mechanism for thermoelectricity is diffusive [39].

In order to compare our calculations with experimental measurements, which were performed at a constant gate voltage, we fix the chemical potential (μ) to obtain the experimental Seebeck coefficient, as indicated by the horizontal line in Fig 4. We then use the same μ in the plot of the Power factor ($S^2\sigma$) and obtain this parameter for G/h-BN/G heterostructure [22]. Our estimated value of S^2G , where G refers to the electrical conductance depending on the thickness of the sample, compares very well with the experimental data, presented in the final section.

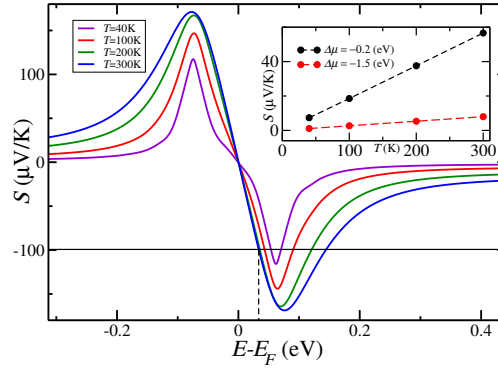


Figure 4. Calculated Seebeck coefficient of G/h-BN/G plotted against energy at various temperatures. The black horizontal line refers to the experimental value at $T=300\text{K}$ [9]. The inset shows the Seebeck coefficient plotted against Temperature at a constant chemical potential. Taken from [22].

3.3. Thermal Conductivity of Bulk and multilayers of h-BN

The calculated κ of multilayer and bulk h-BN using the equilibrium Green-Kubo theory based MD simulation, performed at constant temperature in the Nosé-Hoover thermostat, is shown in Fig 5 for $T \sim 25\text{K}-400\text{K}$ together with the experimental data of Jo et al [11]. For each simulation run, the system was thermalized at the desired temperature first for each set of initial uniform distribution of velocities. κ was calculated for five different sets of initial velocities and the error bar was estimated from the standard deviation.

We find that κ increases with T and tends to saturate at $T \sim 220\text{K}$ for each sample of h-BN, with results for 11-layer tending towards the bulk value. For each of the three samples of h-BN multilayered films, κ shows maxima in the temperature region of 200-250K. We observed an overall agreement of our MD simulation results with recent experimental measurements [11]. For 11-layer and bulk h-BN samples the agreement between the simulation and experimental data is better in temperature range 25-300K, whereas for the 5-layer sample the MD results seem to agree only in the temperature range 100-250K.

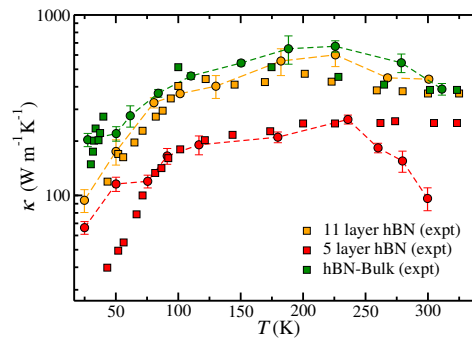


Figure 5. Calculated temperature dependence of the thermal conductivity of multilayer h-BN of different thickness and that of bulk h-BN. Experimental results [11] are shown as squares and present calculations as circles. Taken from [22].

We feel more detailed first-principles phonon based transport calculations are necessary for making a quantitative comparison with experimental data and other available calculations [40, 41, 42]. Phonon-phonon scattering and the lifetime of such processes play in an important

role in thermal conductance and these can be addressed in such models.

3.4. K , S^2G and ZT of $G/h\text{-BN}/G$ Heterostructures

In Fig 6, we show our calculated thermal conductance (K), Power Factor (S^2G) and the Figure-of-merit (ZT) of $G/h\text{-BN}/G$ heterostructures with three-, four- and five-layers of $h\text{-BN}$. K and G were obtained by multiplying the corresponding κ and σ by the thickness of the heterostructures, respectively. The chemical potential (μ) was kept fixed at the experimentally observed value $-99.3 \mu\text{V/K}$ of S as shown in Fig 4. With increasing thickness of $h\text{-BN}$ layers, K decreases whereas S^2G increases with T , thereby increasing ZT with temperature. Our calculated values of these thermoelectric parameters agree well with the experimental data [9] for three-, four- and five-layer $h\text{-BN}$ sandwiched between the Graphene layers.

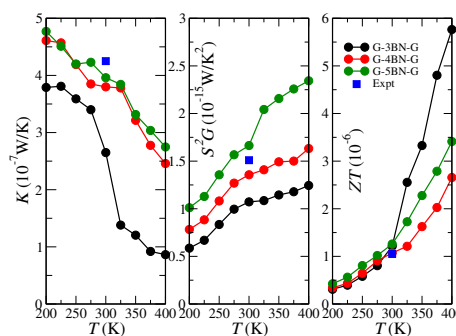


Figure 6. Calculated temperature dependence of Thermal Conductance (K), Power Factor (S^2G) and the Figure-of-merit (ZT) of $G/h\text{-BN}/G$ heterostructure of different thickness shown in the left, middle and right panels; respectively. The available experimental data [9] in each panel at 300K is also indicated. Taken from [22].

We would like to stress on the fact that our calculations involve electrical transport not strictly along the vertical direction, because the Boltzmann transport theory yields smaller contributions to the electron group velocity and thereby electrical conductivity along that direction compared to those along horizontal x - and y -directions. We have calculated the z -component of the Seebeck coefficient (S_z) [22] and found this to be finite and comparable to S_x and S_y close to the Fermi energy. The total Seebeck coefficient S shown in Fig 4, however, shows a quantitative agreement with the experimental data [9]. Thus, we conclude that in the thermoelectric measurements [9] the electrical transport may not be strictly along the z -direction as the upper and lower Graphene contacts with multilayer $h\text{-BN}$ would allow transport channels involving components along x - and y -directions also. A good quantitative agreement with experimental data also supports above conclusion.

In summary, we have presented a detailed computational study of the calculation of the thermoelectric parameters of monolayer- and bilayer-graphene and also of $G/h\text{-BN}/G$ heterostructures with three-, four- and five-layers of $h\text{-BN}$. Our results show quantitative agreement with the available experimental data.

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