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THERMAL RECTIFICATION IN GRAPHENE AND CARBON NANOTUBE SYSTEMS USING MOLECULAR DYNAMICS SIMULATIONS

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ABSTRACT

We investigate the thermal rectification phenomena in asymmetric graphene and carbon nanotube systems using molecular dynamics (MD) simulations. The effects of various parameters, including mean temperature, temperature difference, and system size on rectification factor have been studied. In homogenous triangular graphene nanoribbons (T-GNR), the heat current is normally higher from wide to narrow end than that in the opposite direction, resulting in a positive rectification factor. The rectification factor increases further for a double layered T-GNR. It is also found that varying the parameters like mean temperature can result in reverse of the sign of thermal rectification factor. In the case of carbon nanotube (CNT) - silicon system, the heat current is higher when heat flows from CNT to silicon. The thermal rectification factor is almost independent of the diameter of CNT. In both cases, the rectification factor increases with the imposed temperature difference.

NOMENCLATURE

η	Thermal Rectification factor
J	Heat current (W)
T	Temperature (K)
v	Velocity (Å/ps)
m	Mass of atom (g/mol)
E	Kinetic energy (eV)
t_s	Simulation time (ns)
κ	Thermal conductance (nW/K)
Δ	Ratio of temperature difference to twice of mean temperature

INTRODUCTION

Thermal rectification is the phenomena where heat flow in two opposite directions under same temperature difference is not identical. This property is measured in terms of rectification factor (η) which is defined as

$$\eta = \frac{J_+ - J_-}{J_-} \times 100\,(\%) \tag{1}$$

where J_+ is the heat current when heat is flowing from larger cross sectional area to small cross sectional area and J_- is the heat current in the opposite direction. This phenomenon has potential applications in nanoscale thermal management such as on-chip cooling and energy conversion by controlling the heat transport. It is also fundamental in several recently proposed novel schemes of "thermal circuits" or information processing using phonons[1, 2] . Recently, it was found that phonons are able to carry and process information just like electrons [3]. This gave scope to the area of control and manifestation of phonons which in turn leads to theoretical design of thermal devices like thermal diodes, thermal transistors and thermal logic gates analogous to the electronic counterparts [4].

Terraneo *et al.* has proposed the first theoretical model of thermal rectifier based on a non linear 1D chain [5]. Later, Li and his coworkers has proposed another model with two 1D nonlinear lattices which acts as a conductor in one direction and insulator in the opposite [1]. Experiments done by Chang *et al.* recently on externally mass loaded CNT's demonstrating the phenomena of thermal rectification, gave much needed impetus to the theoretical work [6]. We have studied this effect in T-GNRs and estimated the effect of mean temperature, degree of asymmetry on rectification factor using MD simulations in a previous work [7]. Based on our results, it was concluded that boundary scattering could affect the magnitude of η considerably as perfect T-GNRs with smooth edges exhibit larger η than those with rough edges and with defects. A similar work by Yang *et al*. showed the characteristics of variation of heat current (J) with temperature difference (ΔT) in an asymmetric GNR along with the dependence of η on geometry [8]. This phenomenon was also studied in various homogenous systems like nanohorns [6], nanocones [9], carbon nanotubes [10, 11] using MD simulations.

Studies on inhomogeneous systems like CNT - silicon and silicon – polyethylene systems using MD simulations [12-14] are also been reported estimating the thermal boundary resistance, (defined in terms of conductance in some cases) also known as Kapitza resistance [15]. This thermal conductance is also dependent on the direction of heat flow leading to thermal rectification. Lan *et al.* has shown that strong temperature dependence of vibration spectra of atoms near the interface leads to thermal rectification [16]. To the best of our knowledge, no one has estimated the rectification factor in the case of CNT – silicon system.

In this work, non equilibrium molecular dynamics simulations are used to study this phenomenon in homogenous system with asymmetric geometry like single layered and double layered T-GNR and in an inhomogeneous system with two different materials like CNT - silicon interface. In T-GNRs, we had studied the size and temperature dependence of η. Based on our results, we speculate that ballistic transport is the key for thermal rectification in T-GNR and also η is a strong function of temperature. Also in CNT – silicon system, we had calculated η and studied the effect of size (diameter of CNT) on thermal rectification factor.

SIMULATION PROCEDURE

Homogenous systems (T-GNR):

In this study of thermal rectification in homogenous systems, we had chosen a system with single material having geometric asymmetry. For this, a finite length T-GNR with vertex angle of 30^0 which has a smooth armchair effect along the hypotenuse edge as shown in Fig. 1A is considered. The end layers on both ends along the length are fixed to avoid the GNR from rotating where as atoms along the top and bottom edges are left free to move. Two regions which are approximately 5% of the length are defined at the ends adjacent to the fixed layers act as thermal reservoirs (T_L and T_R) to maintain the temperature difference. The interatomic interactions between carbon atoms are modeled using second generation REBO [17] potential. For multi layered T-GNR's, vander Waals interactions between different layers are modeled using Lennard Jones potential. First the T-GNR is equilibrated at desired temperature in NVT ensemble using Nose Hoover thermostat for 100 ps using a time step of 0.5fs. Then the ensemble is shifted to micro canonical ensemble (NVE) where the total energy, volume and number of atoms are kept constant. Now, the velocity scaling algorithm which will be described below is applied to create temperature difference at both ends for a time period of 2.5 ns and heat current is calculated.

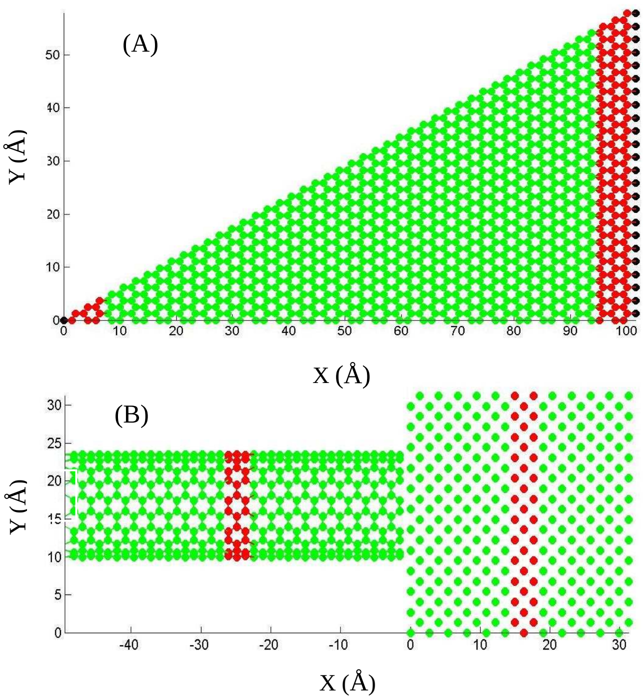

FIGURE 1. (A) T-GNR SHOWING FIXED REGIONS (BLACK) AND THERMAL RESERVOIRS (RED). (B) CNT SILICON INTERFACE.

Heterogeneous systems:

In addition to homogenous system with geometric asymmetry, a heterogeneous system (CNT-Silicon interface) consisting of two different types of atoms is also considered. Here an interface is formed by placing a 5nm long carbon nanotube along (100) faces of silicon of size 6×6×6 unit cells. All the interatomic interactions in this case (C-C, Si-Si, C-Si) are modeled based on Tersoff bond order potential [18]. This potential has been used successfully for predicting the thermal properties of CNT and silicon [19, 20]. Periodic boundary conditions are used in all three directions. The system is initially equilibrated in a NPT ensemble to atmospheric pressure and room temperature (300K) using a Nose Hoover thermostat for a period of 1 ns to reach the minimum energy configuration. Following this energy minimization process, the process of velocity scaling is applied in an NVE ensemble where volume and total energy of the system are maintained constant. Then the heat current is calculated as per the procedure discussed below. All the MD simulations shown here are performed using LAMMPS [21] simulation package.

As can be seen in the expression for thermal rectification factor, heat currents in both directions of heat flow are needed to obtain η. Different methods are available in literature to accomplish this. Li *et al.* applied Nose-Hoover thermostat at both ends to maintain a constant temperature and calculated heat current as a function of thermostat relaxation time and kinetic energy of atoms [10]. Alternatively Muller-Plathe *et al.* used the reverse non equilibrium molecular dynamics simulations (RNEMD) based on Muller - Plathe algorithm to calculate heat current [11]. In our work, we employed a direct velocity scaling of atoms to control the temperatures of the two plates [22]. The velocity scaling factor is obtained as

$$\alpha = \sqrt{T_t / T_c}\,; v_{i,new} = \alpha v_{i,old} \qquad (2)$$

where T_t is the target temperature of the plate and T_c is the current temperature of the plate. The energy added to the hot plate or removed from the cold plate is calculated by summing the difference of kinetic energies before and after scaling over all the atoms in the plate (N). i.e.,

$$\Delta E = \frac{1}{2}\sum_{i=1}^{N} m_i (v_{i,new}^2 - v_{i,old}^2)$$

Now the heat current is obtained by

$$J = \frac{\sum_{j=1}^{n} \Delta E_j}{t_s} \qquad (3)$$

Here t_s is total simulation time, n is the number of velocity rescaling performed during the simulation. Typically this scaling process is carried out in micro canonical (NVE) ensemble. This method is effective in reducing the fluctuations in temperature when there are few atoms in the thermostat (like the narrow end of T-GNR). Also calculating heat current in this case is independent of any thermostat parameters like relaxation time (for Nose-Hoover thermostat).

RESULTS AND DISCUSSION

Homogenous systems:

The temperature difference with respect to the mean temperature is defined by $\Delta = (T_L - T_R) / (2T_0)$ where T_0 is the mean temperature of the whole system. Figure 2 shows the typical nonlinear temperature profile in T-GNR for Δ=0.2. The temperature profile is obtained by dividing the entire simulation box into plates of 4 Å along the direction of heat flow and averaging the temperature of all the atoms in that particular plate over 500 ps. The nonlinear shape is a direct consequence of geometrical asymmetry in the structure. The variation of heat current with temperature difference at room temperature 300K in a 10nm long T-GNR is demonstrated in Fig. 3A. The positive temperature difference (Δ) corresponds to heat flow from wide (right) side to narrow (left) side whereas negative Δ corresponds to the opposite. The gradient of the curve in these two regions are not exactly same which demonstrates the nonlinear behavior of the device. Figure 3B shows the variation of rectification factor (η) with Δ which is increasing as expected at room temperature for the same case. It shows that larger the difference in temperatures between the two ends,

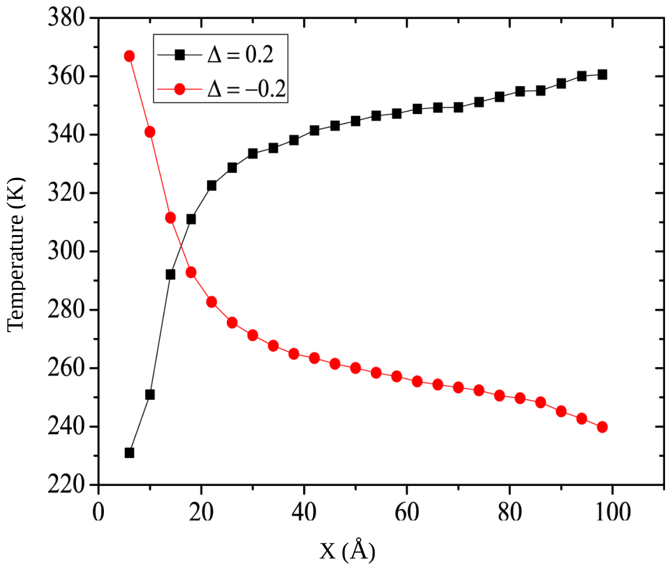

FIGURE 2. NONLINEAR TEMPERATURE PROFILE IN A T-GNR

larger is the nonlinearity *i.e.*, the rectification factor. In all the cases, η is positive implying that heat current is high when heat flows from wide end to narrow end. Figure 4A shows the effect of η on mean temperature of the system for temperature difference equal to 20% of the mean temperature (T_0) in a 10nm long T-GNR. It can be seen that as T_0 increases, the rectification factor (η) decreases gradually and crosses zero to reach a value of -6% at 500K. Though the exact origin for this behavior is not known, it will be interesting to study the role of thermal conductivity in this behavior.

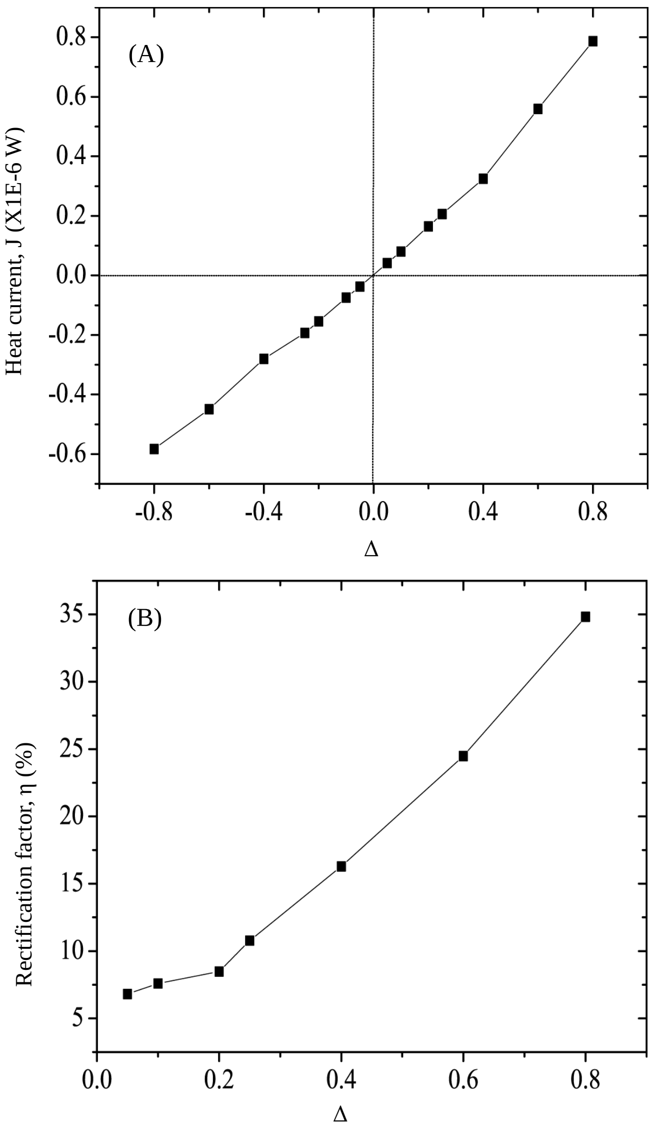

FIGURE 3. THERMAL RECTIFICATION IN 10 nm LONG T-GNR AT 300K: (A) HEAT CURRENT VS Δ, (B) η VS Δ

The authors have also studied the effect of rectification factor on the length of the T-GNR. It was found that as length increases, η decreases as shown in Fig. 4B for Δ=0.2. We speculate that this trend highlights the role of ballistic transport in thermal rectification. Since the length scales in our study are much less than the phonon mean free path (MFP ~700nm) [23] the heat transfer is mainly ballistic. We believe that as we move towards the diffusive regime, the thermal rectification properties will slowly diminish. Please note that although η seems to approach zero as the length increases to 25 nm (less than MFP) in Fig. 4B, it will still exhibit thermal rectification for a higher value of Δ as long as it is in the ballistic regime. It will be computationally challenging to prove this in T-GNRs using MD simulations as a 700nm long T-GNR will have atoms in the order of millions. We are currently looking at alternative systems which have lower phonon mean free path which can help in verifying this claim.

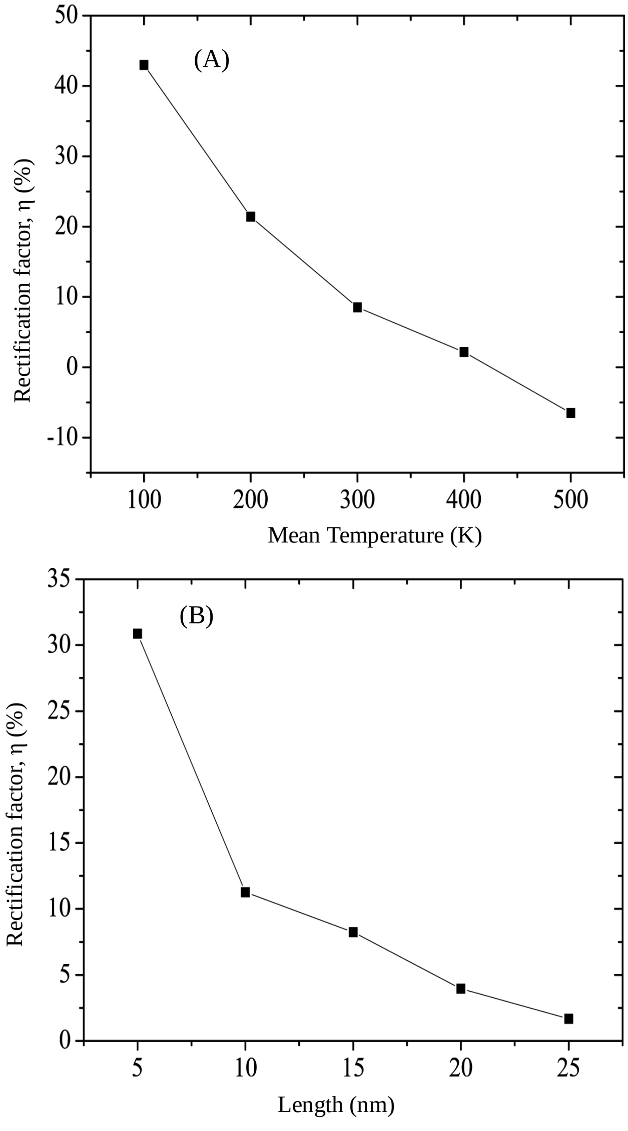

FIGURE 4: VARIATION OF RECTIFICATION FACTOR (η) WITH: (A) TEMPERATURE (B) LENGTH.

The authors have also calculated the rectification factor of a 10nm long double layered T-GNR and found that value of rectification factor increases when compared to a single layer T-GNR as highlighted in Fig. 5. However, further increase in η is not observed if more layers of atoms are included. We are investigating thermal rectification in the case where periodic boundary conditions are applied in Z direction (perpendicular to both in-plane directions) which will be analogous to finite size graphite to see if thermal rectification can be observed.

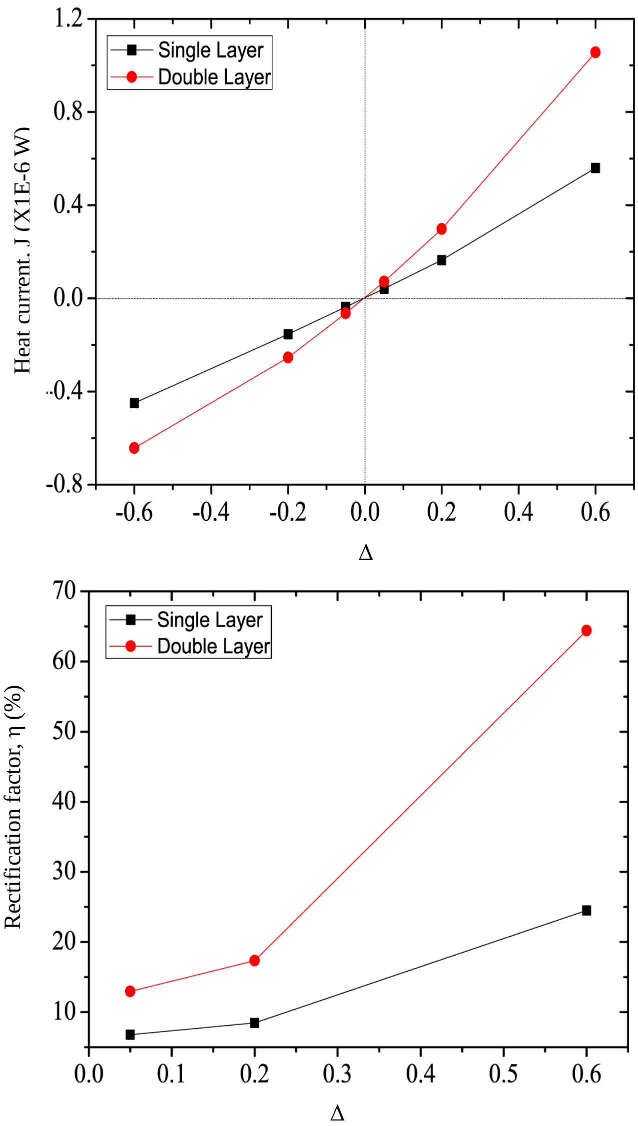

FIGURE 5. THERMAL RECTIFICATION IN MULTI-LAYERED T-GNR: (A) HEAT CURRENT VS Δ, (B) η VS Δ

Heterogeneous systems:

The typical time averaged temperature profile in the case of CNT - Silicon system demonstrating the drop in temperature at the interface for heat flow in both directions is shown in Fig. 6. The temperature variation is quite less in CNT when compared to silicon possibly because of its higher thermal conductivity. It can be observed that the temperature drop at the interface is not the same in both cases (for positive and negative J) demonstrating thermal rectification. In this case, positive J (or Δ) corresponds to heat flow from silicon to CNT where as negative J (or Δ) corresponds to opposite. The variation of heat current with Δ is nonlinear as well similar to that of Fig. 4A. The interfacial thermal conductance (κ) which is defined as the ratio of heat current to temperature difference is of the order 0.6 nW/K. Figure 7 shows the variation of η with Δ for CNTs of different diameters and chiralities.

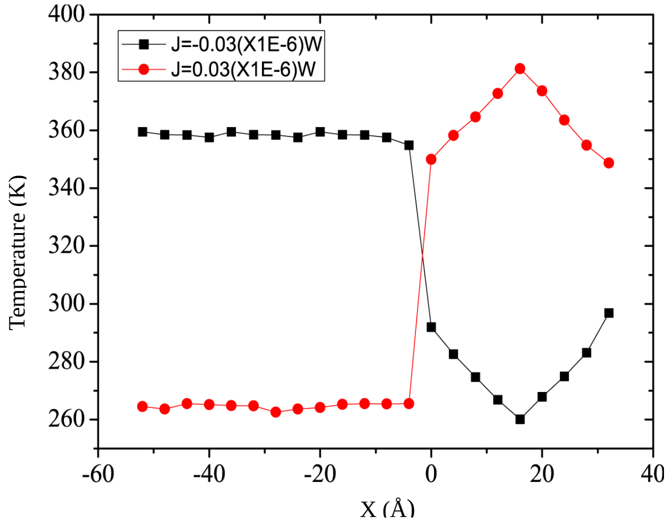

FIGURE 6. TEMPERATURE PROFILE IN CNT-SILICON SYSTEM

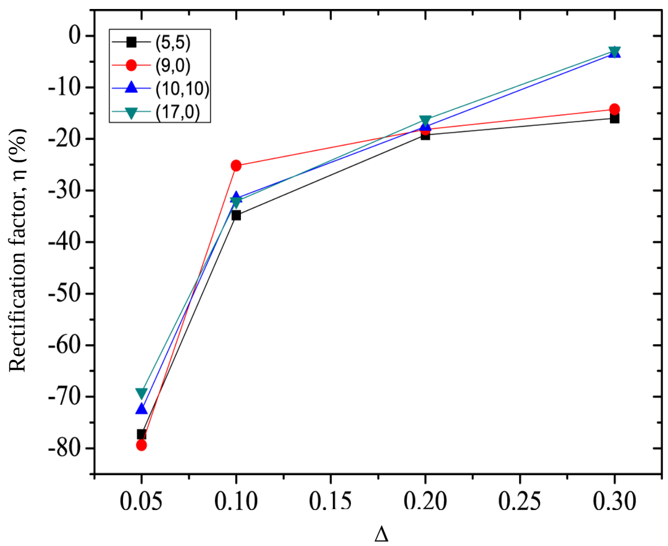

FIGURE 7. RECTIFICATION FACTOR (η) Vs Δ IN CNT - SILICON SYSTEM FOR DIFFERENT DIAMETERS

We had considered two pairs of CNT's with same diameter but with different chirality (one is armchair and the other is zigzag). But both the diameter and chirality of CNT's doesn't seem to have a strong effect on rectification factor. The diameter of (10, 10) CNT (also 17,0) is double that of (5,5) and (9,0) pair. It can be observed that η is negative in all these cases at room temperature which means that heat flow from CNT to silicon is dominating when compared to the heat flow in opposite direction. As temperature difference increases, the rectification factor increases and approaches zero. The effect of size of cross section of silicon is currently under investigation.

SUMMARY

To summarize, we have demonstrated thermal rectification phenomenon in T-GNRs and CNT - Silicon interface using non equilibrium molecular dynamics simulations. The temperature profile and heat current variation with temperature difference in T-GNR demonstrate the nonlinearity of the system. The rectification factor is quite sensitive to the mean temperature and length of the system emphasizing the role of ballistic transport in thermal rectification. Structure with multiple layers could increase the nonlinearity of the device as evident in the increase of rectification factor in double layered T-GNR. The rectification factor in the case of CNT – silicon interface is independent of diameter and chirality of CNT. Although the trends obtained from MD simulations are quite fascinating, more work is warranted on theoretical front to understand the exact origin and mechanism of thermal rectification.

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