

# Thermal expansion coefficient of graphene using molecular dynamics simulation: A comparative study on potential functions

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**Abstract.** In this paper, we studied the thermal expansion coefficient (TEC) of pristine graphene sheets (GSs) using molecular dynamics (MD) simulation. We validated our model with previous studies employing AIREBO potential function and repeated the same simulation with the optimized Tersoff potential function. We also discussed the differences of the results and the corresponding reasons: evaluating the negative TEC of graphene by measuring the C-C bond length and out-of-plane vibrations of the GS. We finally showed that the ripples and wrinkles are more represented over the GS during the simulation with the AIREBO potential function rather than the optimized Tersoff. Comparing the results of both potential functions; it is seen that the results obtained by AIREBO potential function are in better agreement with those reported by previous scholars.

## 1. Introduction

Graphene has exceptional physical properties[1]–[3]; high thermal conductivity[4]–[9] and high mechanical strength make it an ideal candidate in order to control heat transfer in high-speed, high-density developed electronic and thermoelectric devices. Electronic devices usually experience wide ranges of temperature. Thermal deformations (expansion or contraction) caused by temperature differences in GSs are more significant comparing to other carbon structures: carbon nanotubes and diamonds[10], [11]. An exceptional characteristic of graphene is its negative TEC which has attracted many attentions. Therefore, studying thermal properties of graphene (especially TEC due to its interesting behaviour) over various temperatures is critical in optimizing the designs of novel graphene-based electronic devices. Many scientists have reported a negative TEC in the temperature range of 200–400 K[12]–[18]. Several authors assume that the negative TEC of GSs is due to competitions of two factors: bond length stretching and in-plane contraction due to existence of ripples and wrinkles over the GSs[15]–[17]. The prior causes a positive TEC and the later leads to an opposite effect. Although there are many experimental reports and literatures for calculating the TEC of GSs, the use of computer simulations is much less usual.

Mounet[15] used density-functional theory (DFT) and Zacharchenko[18], [19] used atomistic Monte-Carlo simulations to find TEC. Islam et al.[20] examined the effects of vacancies on the TEC of GSs. They made a comparison and found that the TEC differs less than 9% between the armchair and zigzag directions; two vacant atoms (about 1.56% by volume) increase the negative TEC nearly 40%.



Newton et al.[21] studied the thermal expansion behaviour of holes in graphene nanomeshes (GNMs). Using MD simulations, they exhibited that the GNMs behave in an opposite way: while the entire structure contracts (expands), the nano-holes expand (contract) under thermal excitation. Hu et al. [21] used lattice dynamics analysis to demonstrate that at low temperatures, ripples and negative thermal expansion, are both intrinsic characteristics of any 2D crystals with a honeycomb structure (or any monatomic 2D crystals). Based on their calculations, using self-consistent phonon theory, the negative TEC is largely affected by the “vibrational elongation” or in other words by large out-of-plane fluctuations at finite temperatures.

In this paper, we utilized MD simulations to show the effect of two popular potential functions: AIREBO and optimized Tersoff to obtain TEC and some other parameters (bond length stretching and out-of-plane fluctuations) of a GS. We explained the differences of the results and discussed the reasons. We also showed that the AIREBO potential function considers more parameters than the optimized Tersoff and maybe this is the reason of its accurate prediction of TEC.

## 2. Molecular dynamics simulation

MD simulations are implemented in this paper to study TEC's dependency of a GS to the temperature. A molecular dynamics simulation is based on the explanation of a potential function, or a description of the relations by which the particles in the simulation will interact. Here, we utilize two potential functions mostly used for carbon based materials: nanotubes, graphene, and graphite. LAMMPS package[22], [23] was hired in this study, using the two mentioned potential functions: optimized Tersoff and AIREBO.

### 2.1. Interatomic molecular dynamics potentials

**2.1.1. Optimized Tersoff.** The optimized Tersoff potential function predicts the interatomic interactions as follows:

$$V_{ij} = f_{ij}^C (a_{ij} f_{ij}^R - b_{ij} f_{ij}^A) \quad (1a)$$

$$f_{ij}^R = A e^{-\lambda_1 r_{ij}} \quad (1b)$$

$$f_{ij}^A = B e^{-\lambda_2 r_{ij}} \quad (1c)$$

where,  $r_{ij}$  is the distance between atoms  $i$  and  $j$  and  $f_{ij}^C$  shows the truncation function that limits nearest neighbors atomic interactions;  $f_{ij}^R$  and  $f_{ij}^A$  represent mutual attractive and repulsive terms respectively, and  $a_{ij}$  relates to the range-limiting repulsive potential term which is typically equal to one as we do here.  $b_{ij}$  is the term depends on the bond angle and local coordination of atoms around atom  $i$ . The corresponding parameters for the optimized Tersoff-2010 potential function are represented by Lindsay et al[24].

**2.1.2. AIREBO.** The AIREBO model originated from a REBO one with extra LJ and torsional terms

$$V_{ij} = V_{ij}^{\text{REBO}} + V_{ij}^{\text{LJ}} + \sum_{k \neq i,j} \sum_{l \neq i,j,k} V_{ij}^{\text{TORSION}} \quad (2a)$$

$$V_{ij}^{\text{LJ}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right], r_{ij} < r_c \quad (2b)$$

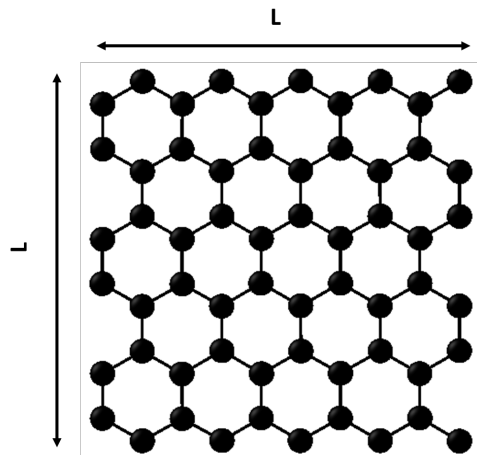
where,  $\epsilon$  is the energy parameter,  $\sigma$  is the distance one and  $r_c$  is the cutoff distance. All mentioned parameters are represented by Stuart et al[25].

### 2.2. Simulation details

In solids, thermal expansion dependency to pressure is ignored and is simply given by the following relation

$$\alpha = \frac{1}{L} \frac{dL}{dT} \quad (3)$$

where,  $L$  is the equilibrated length of the graphene as a function of equilibrium temperature  $T$ ; it is recorded for each value of temperature from 50K to 1000K along  $x$  and  $y$  directions separately. We did the simulation within the NPT ensemble imposing periodic boundary conditions along  $x$  and  $y$  directions. The Newton's equations of motion were integrated with the velocity-Verlet integrator with the time step of 0.5 fs, for a total of 3 900 000 time steps (or 1.95 ns) to ensure full equilibration of the structure. Then, we made an average on length:  $L = \frac{L_x + L_y}{2}$  and plotted the length values versus the temperature. Using try and error to reach the best fitted polynomial, we fitted a fourth order polynomial to the length values. According to the above equation, we obtained the TEC in each temperature. Each simulation was repeated four times in order to report the statistical uncertainties.



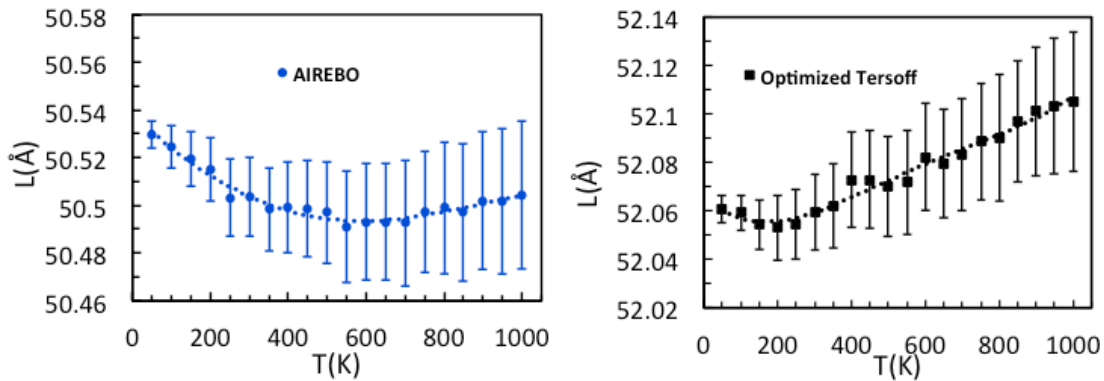
**Figure 1.** The schematic view of a GS.

We studied three GS lengths; 1nm, 5nm and 10nm and calculated the TEC of each size twice, once running the simulation for AIREBO potential function and then for the optimized Tersoff. Obtaining TEC values for each size, we were able to see how the size of the GS affects the TEC.

Looking for the reason of the odd behaviour – negative values in some temperatures- of the GS, we studied changing of bond length of the GS with increasing the temperature. Another important factor for this behaviour is existence of intrinsic wrinkles and ripples over the GS surface. So, we analysed how much theses ripples and wrinkles affect TEC. Finally, these two factors were compared for both optimized Tersoff and AIREBO potential functions. Then, we discussed which potential function would be a better choice in order to calculate the TEC.

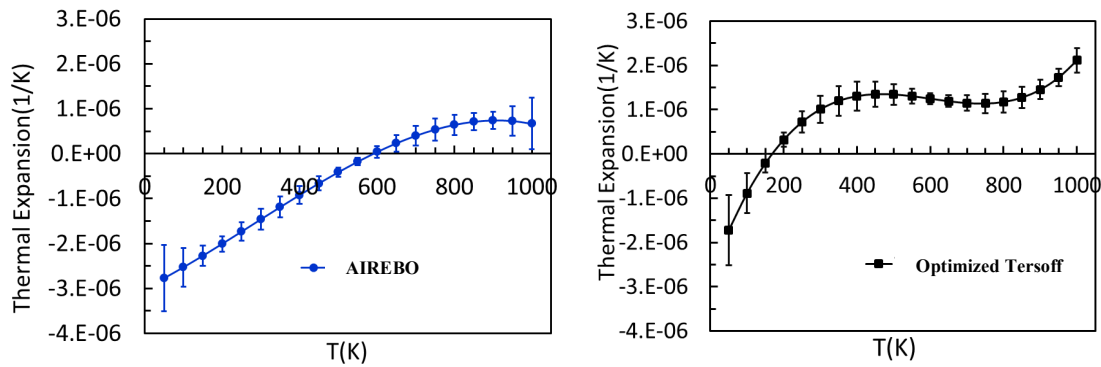
### 3. Results and discussion

In this section, we represent our results and figures. Then, we discuss in details why the GS has this interesting behaviour by increasing the temperature. Figure 2 shows how the length of the 5 nm GS changes with increasing the temperature. It is seen that, GS has an interesting behaviour by increasing the temperature. For the simulation running with AIREBO, the length of the GS decreases as long as the temperature reaches to nearly 600 K. In another simulation with optimized Tersoff, the GS's odd behaviour does not last long; just nearly the temperature of 200K, the length starts to get increased.



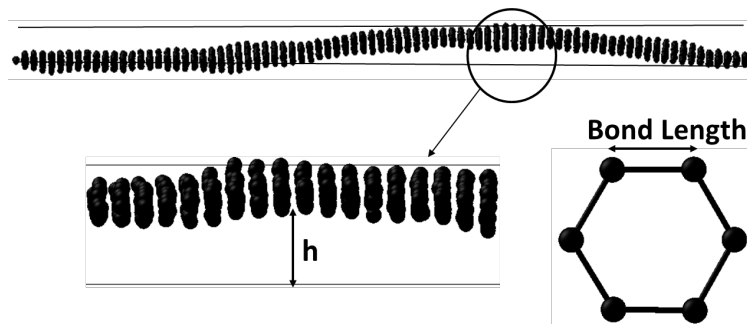
**Figure 2.** The length of the 5 nm GS with increasing the temperature using AIREBO potential function (Left) and optimized Tersoff potential function (Right).

The TEC results are shown in figure 3; it is seen than in AIREBO potential function, the TEC has a negative value under 600K and then changes to positive above that temperature.



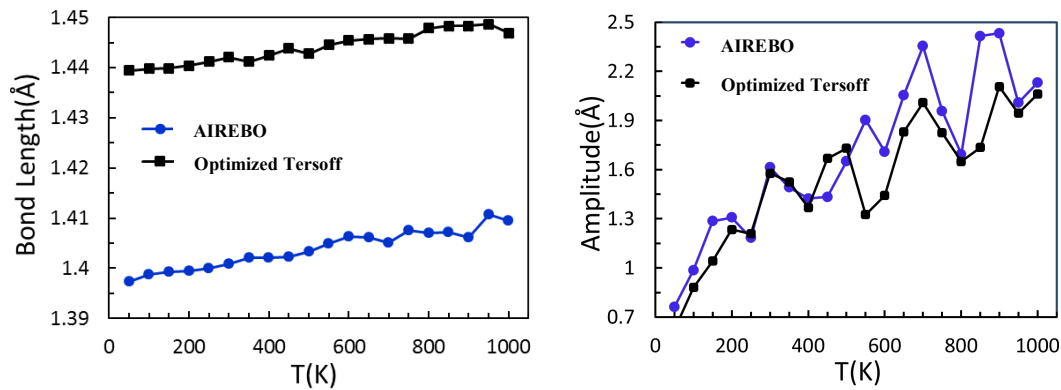
**Figure 3.** The TEC of the 5 nm GS with increasing the temperature using AIREBO potential function (Left) and optimized Tersoff potential function (Right).

Actually, what we have measured and called as out-of-plane fluctuations and bond length have been shown in figure 4.



**Figure 4.** The schematic amplitude and bond length of a GS.

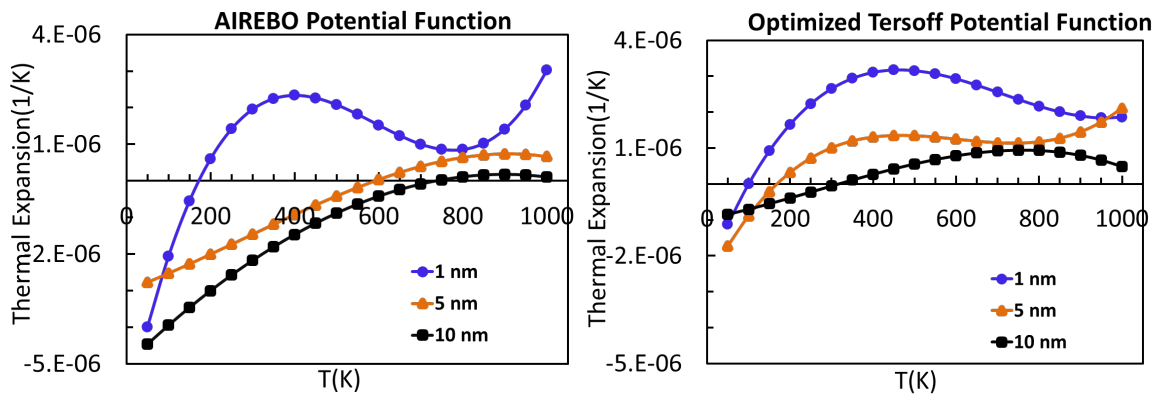
In order to calculate the amplitude (out-of-plane vibrations) of the graphene, we used a simple definition called, the standard deviation of height component of atoms.



**Figure 5.** a) The bond length changes of carbon atoms with both AIREBO and optimized Tersoff potential functions. b) Amplitude fluctuations of carbon atoms with both AIREBO and optimized Tersoff potential functions of the 5nm sample.

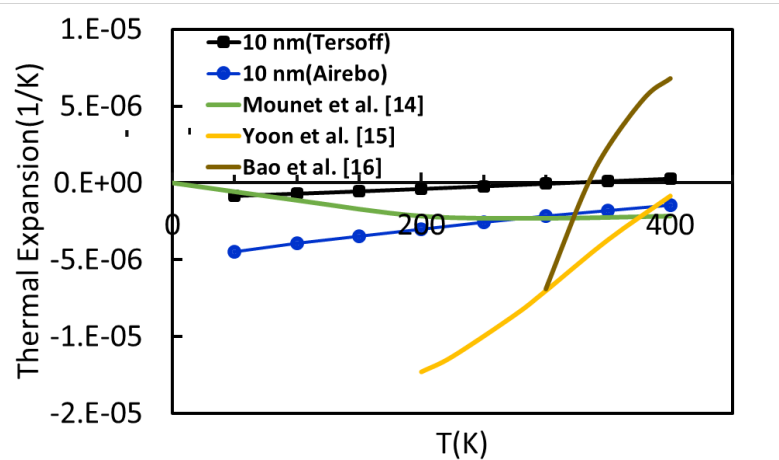
The bond length changes of carbon atoms are shown in figure 5a. It is seen that, in both interaction functions, the bond length increases by increasing the temperature. So, there might be another reason for odd negative behaviour of TEC. It also means that we can have a regular (positive) behaviour for the TEC of the GS with imposing the sheet to an initial strain in order to avoid intrinsic ripples and wrinkles.

Figure 5b represents the amplitude fluctuations of the GS in different temperatures with both AIREBO and optimized Tersoff potential functions. It is clearly seen that, the overall trend of the figure is additive. Figure 6 shows the thermal expansion of graphene for various lengths. It is seen that, by increasing the temperature both potential functions predict a converging behaviour



**Figure 6.** The effect of length on TEC of GSs.

Now, we are going to evaluate if there is an agreement between our results with those predicted by other scientists. In figure 7, we showed that our 10 nm sample which its atoms have interacted with AIREBO potential function have a better agreement with the DFT results reported by Mounet et al.[15] at temperatures higher than 200K. However, the results of classical molecular dynamics should not be compared to DFT results at low temperatures wherein quantum effects are important.



**Figure 7.** Comparison the results of the current study with some previous reports.

#### 4. Conclusion

In this paper, we tried to have a review on effective reasons on interesting behaviour of TEC of pristine sheets using molecular dynamics simulations employing two interatomic potential functions: AIREBO and optimized Tersoff; we observed that by increasing the length of the graphene, the TEC shows better converging performance. On the other side, we showed how selecting a proper potential function in predicting the TEC could be important; AIREBO has a better behaviour in comparison to optimized Tersoff. It was found that the results of a 10 nm long sheet has a good agreement with those predicted by previous scholars.

#### 5. References

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