Molecular dynamics simulations of bilayer graphene structures

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Abstract

In this paper, the formulation of the Tersoff bond-order potential was used to study the structural and thermodynamics properties of bilayer graphene (BLG). The simulations were performed within a canonical (NVT) ensemble for structural properties and isothermal–isobaric ensemble (NPT) for thermodynamic properties. Each double layer is a hexagonal arrangement of carbon atoms at the corners to make up a two dimensional honeycomb sheet. One model consists of 64 carbons (graphene64); the other model has 256 carbon atoms (graphene256). Using the structural optimization and radial distribution functions, some equilibrium properties of these layered graphene structures are noted. Thermodynamic properties will be investigated to understand the behaviour of graphene at high temperatures.

Introduction

Graphene has sparked much interest in the field of condensed matter physics. It is atomically thin sheet of carbon arranged in a two dimensional honeycomb crystal [1]. The existence of graphene has since been explained by the idea that graphene has intrinsic roughness. The rippling of graphene makes it to be a nearly perfect two dimensional crystal in three dimensional spaces which is not forbidden [2]. Graphene is not only important new testing ground for fundamental physics such as relativistic quantum mechanics and low dimensional thermodynamics, but also have potential applications to nano-scale technology [3]. The carbon-carbon bond length of graphene is 1.42 Å with an interplanar spacing of 3.35 Å for bilayer graphene. Because of its unique structural, mechanical and electronically properties, it has stirred many scientists involved in the field to look forward to making a breakthrough in some new research areas. Up to date research has revealed many possible applications in solar cell technology [4], sensors, liquid device and the fabrications of nanosized prototype transistors [5]. Similar to carbon nanotube [6], graphene is also a good candidate for usage as gas sensor materials to detect various molecules, ranging from gas phase molecules to some small bioactive molecules [7]. These desirable properties promise graphene to offer excellent short-circuit current-gain cutoff frequency for high frequency applications. Figure 1 and 2 shows two structures of bilayer graphene64 and bilayer graphene256. Both structures were varied at 300 K temperature using DL-POLY software and a program that is called a Viewer life.

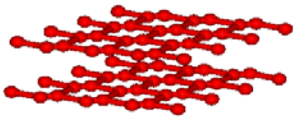


Fig 1: Bilayer graphene 64 atoms

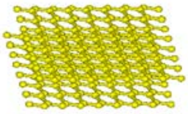


Fig 2: Bilayer graphene 256 atoms

Molecular dynamics

Molecular dynamics (MD) is a form of computer simulation in which atoms and molecules are allowed to interact for a period of time by approximations of known physics, giving a view of the motion of the particles. The leapfrog verlet method and Tersoff potential for molecular dynamics was used. Leapfrog integration is a simple method for integrating equations, particularly in the case of a dynamical system [4]. In this method position ($\vec{r}$) and force ($\vec{F}$) at time t are needed while the velocities ($\vec{v}$) are half a time step behind. We first advance the velocities to $t + \frac{\Delta t}{2}$ by

$$\vec{v}(t + \frac{\Delta t}{2}) = (\vec{v}t - \frac{\Delta t}{2})\vec{r}(t) + \Delta t\frac{\vec{f}(t)}{m}\ , \qquad (1)$$

$$\vec{r}(t + \Delta t) = \vec{r}(\mathrm{t}) + \ \Delta t\vec{v}(t + \frac{\Delta t}{2}), \qquad (2)$$

The velocity equation is executed first and generates a new mid-step velocity. This velocity is then used to calculate the new position. The velocity is calculated from

$$\vec{v}(t) = \left(\frac{1}{2}\right)\vec{v}\left(t + \frac{1}{2}\Delta t\right) + (\frac{1}{2})\vec{v}(t - \frac{1}{2}\Delta \mathrm{t}). \qquad (3)$$

This leapfrog method also has the advantage that temperature scaling by velocity scaling is feasible [4]. The family of potentials developed by Tersoff are based on the concept of bond order: the strength of a bond between two atoms is not constant, but depends on the local environment (11). At first sight, a Tersoff potential has the appearance of a pair potential:

$$E = \sum_i E_i \ = \ \frac{1}{2}\sum_{i \neq j} V_{ij} \qquad (4)$$

$$= \frac{1}{2}\sum_{ij} \emptyset_R\left(\vec{r}_{ij}\right) + \cdots + \frac{1}{2}\sum_{ij} B_{ij}\emptyset_A\left(\vec{r}_{ij}\right) + \cdots \qquad (5)$$

Where the potential energy is decomposed into a site energy E_{ij} and a bonding energy V_{ij}, $\vec{r}_{ij}$ is the distance between atoms *i* and *j*, $\emptyset_R$ and $\emptyset_A$ means ``repulsive'' and ``attractive'' pair potential respectively.

$$\emptyset_R\left(\vec{r}_{ij}\right) = Ae^{\left(-\lambda_1\vec{r}_{ij}\right)} \qquad (6)$$

$$\emptyset_A\left(\vec{r}_{ij}\right) = -Be^{(-\lambda_2\vec{r}_{ij})}, \qquad (7)$$

Methodology

The molecular dynamics (MD) simulation is performed within a canonical NVT and NPT ensembles, using DL_POLY software [7]. The Newtonian equations of motion are integrated with a routine based on the leapfrog verlet algorithm with the time step of 1.0 x 10^{-3} s at a 0.0atm pressure. The temperature was varied from 300 K to 5000 K for calculating the radial distribution functions. For equilibrium properties we varied only the lattice constant at 300 K. All the equilibrium calculations were made at 300 K temperature. After 400 000 iterations, different average properties are separated. This step is very important and aims to calculate for each atom and generate at each time step, a new positions and velocities. After that a frequency distribution of atomic separations is produced to compute the pair distribution function, and other various properties which are computed along the trajectory of the system in the phase space. Real space cut off and primary neighbour cut off was 2.68 Å. The structures were optimized at 300 K, by allowing the atomic positions, cell shape, and volume to relax.

Results and discussion

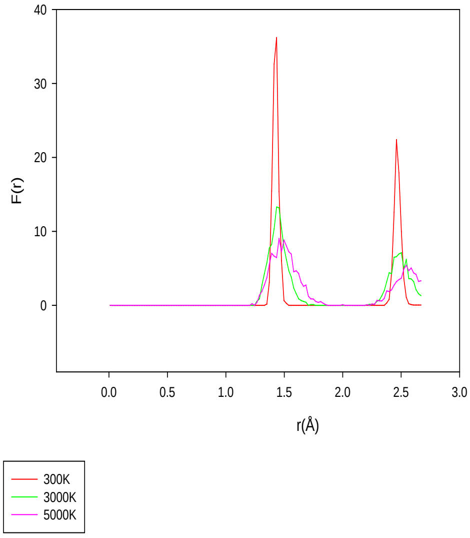


Figure 3: The radial distribution functions of graphene64.

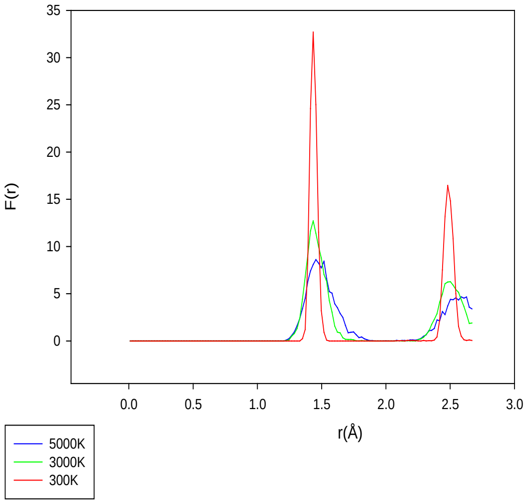


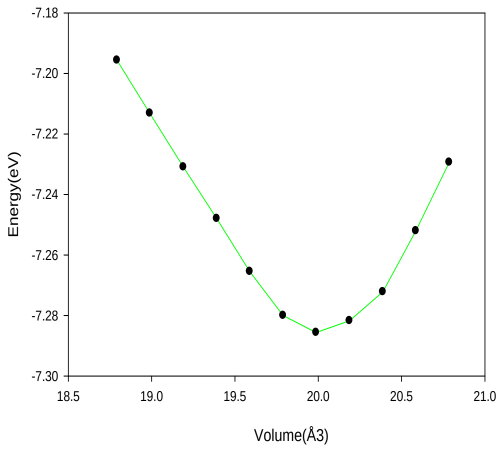
Figure 4: The radial distribution functions of graphene256.

The calculation of radial distribution functions (rdf's) from molecular dynamics trajectory data is a common and computationally expensive analysis task. To test the reliability of the tersoff potential in describing graphene, we calculate the pair distribution function of $F(r)$ for graphene. From peak positions of $F(r)$, we can know the probable distance between the atoms. Figure 3 and 4 are rdf's of graphene64 and graphene256 respectively, the first peak which is the first nearest neighbour parameter appears at 1.43 Å for 300 K and 3000 K. At 5000 K which is above melting point of graphene, the first nearest neighbour parameter increases to 1.46 Å for graphene64 and 1.48 Å for graphene256. The second peak which is the second nearest neighbour parameter appears at 2.48 Å for 300 K and 3000 K. At 5000 K the second nearest neighbour parameter increases to 2.50 Å for graphene64 and 2.56 Å for graphene256. When the temperature increases, the base of the peaks increases and the height decreases. The first peak is associated with the bond length of graphene which is 1.42 Å, and the second peak is associated with the lattice parameter of graphene which is 2.46 Å [10]. The results for both models at 5000 K, shows that, above the melting point of

BLG the bond length and lattice constant changes. These results of the rdf's of graphene are in agreement with both the theoretical calculations and the experimental [10, 13, 14].

Equilibrium properties of bilayer of graphene (BLG)

The two graphs are for energy as a function of volume and energy as a function of lattice constant for graphene64 and graphene256 respectively. Since the two graphs behave similar and we can calculate the same things using them, we decided to take one for lattice constant and one for volume.



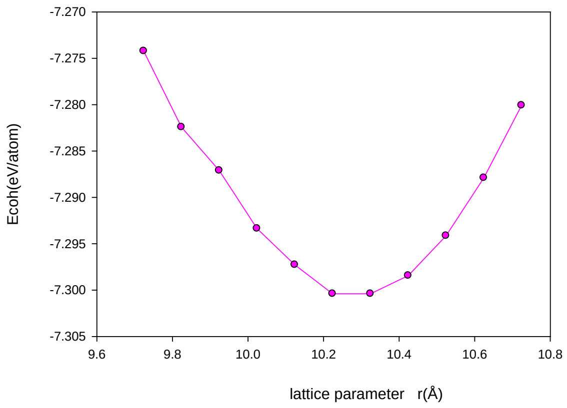


Figure 5: Energy as a function of volume

Figure 6: energy as a function of lattice constant

In order to find the most favourable structural configuration for the double layer graphene the relaxed 64 and 256 atom double layered graphene are optimized in order to obtain some notable equilibrium properties of the material. In so doing the lattice constant, the minimum energy, bulk modulus and its derivative were calculated using figure 5 (energy as a function of volume) and figure 6 (energy as a function of lattice constant), least squares fitted to the Murnaghan's equation of state. Again, $E(a)$ is found to be [13]:

$$E(a) = a_0 + \frac{9V_0B_0V_0}{16}\left[\left(\frac{a_0}{a}\right)^2 - 1\right]^2 + A\left[\left(\frac{a_0}{a}\right)^3 - 1\right]^3 + B\left[\left(\frac{a_0}{a}\right)^2 - 1\right]^4 + 0\left[\left(\frac{a_0}{a}\right)^2 - 1\right]^5 \qquad (8)$$

Where B_0 is the bulk modulus, V_0 the primitive volume and A and B are fit parameters.

Table 1: Calculated and measured lattice constant *a*, bulk modulus *(B_0)*, its derivative *(B')*, minimum energy *(E_0)*, and minimum volume *(V_0)*.

	Graphene64 this work	Graphene256 this work	Graphene[10,13]	Graphite[13,14]
a(Å)	2.551	2.571	2.461	2.603
E_0(eV/atom)	-7.279	-7.300		
B_0(GPa)	130.000	130.000	700.000	33.800
B'	35.000	35.000	1.000	8.900
V_0(Å^3/atom)	19.987	20.088	6.076	35.120

The lattice constants are in good agreement with the measured [14] and calculated values [10, 13]. Although the bulk modulus is totally disagreeing with other calculations and experiments, it should also be noted that the model used here is a double layered structure (i.e graphene64 and graphene256), whereas calculations used a single sheet graphene. The vacuum distance of 15 Å used to minimized interactions between the models with their periodic images could also play a crucial role. Graphene64 and graphene256 equilibrium properties results are the similar.

Thermodynamics properties of a bilayer of graphene

Up to this point, ordinary temperature (300 K) properties of double layered models have been considered. Quantum mechanics effects are very important in understanding the thermodynamics properties below the Debye temperature. Since the molecular dynamics method treats the motion of the atoms classically, we only consider the thermodynamics properties above the Debye temperature, where the quantum effect can be neglected [16]. The graphite Debye temperature of 2500 K along the a-axis has been considered [17].

Specific heat capacity and coefficient thermal expansion of bilayer of graphene 256 and 64 atoms

The specific heat capacity of a material represents the change in energy density E when the temperature changes by 1 K,

$$C_v = \frac{d\,U}{dT}\,. \qquad (9).$$

The specific heat and heat capacity are sometimes used interchangeably, with units of joules per kelvin mass, per unit volume, or per mole. The specific heat does not determine the thermal energy stored within a body only but also how quickly the body cools off or heats up [18].

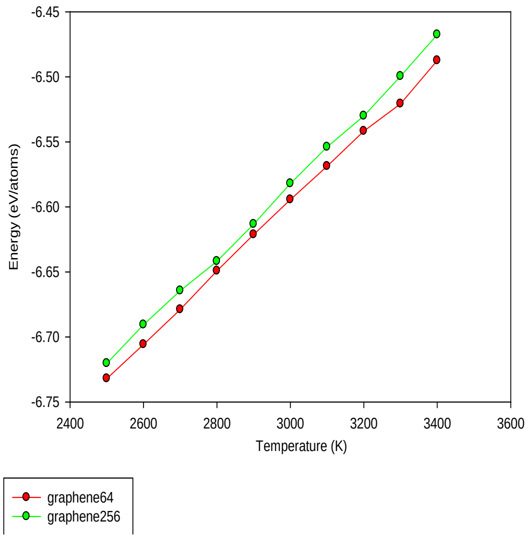


Figure 7: Energy as a function of temperature

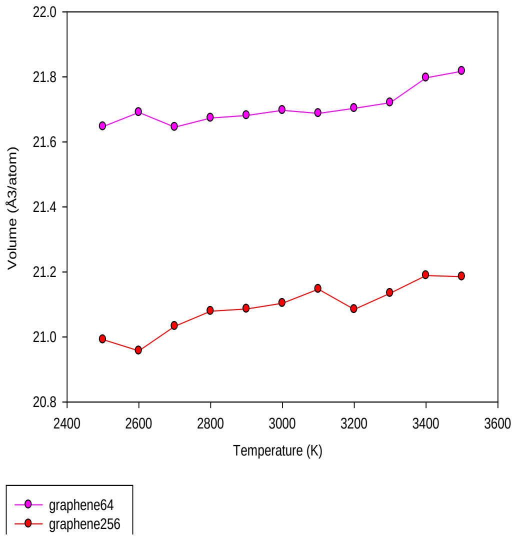


Figure 8: Volume as a function of temperature

Figure 7 was used to calculate the specific heat capacitor of graphene 64 and graphene256. The specific heat capacity calculated for both systems is 3.42 k_B. This differs by 12% from the Dulong –Petit's law (3 k_B) of solids at high temperatures, although no experimental data on this has been considered. Zakharchenko et al [19] found out that the specific heat capacity of a single layer of graphene (SLG) and a bilayer of graphene (BLG) are similar and he also proves that the specific heat capacity at a high and low temperature are not the same. The specific heat of graphene has not been measured directly [20].

The coefficient of thermal expansion is one of the most important nonlinear thermal properties. It is obtained from the temperature derivative of lattice constant or temperature derivative of volume,

This is given by:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{10}$$

The volumetric thermal expansion coefficient of graphene 64 and graphene 256 were calculated using fig 8. At a low temperature, the thermal expansion coefficient of graphene is expected to be negative and positive at high temperature [20, 19]. Most of the people who calculated thermal expansion coefficient at a low temperature used experimental method and those who calculated thermal expansion coefficient at a high temperature used the modelling method. Since our calculation was made at high temperature, we expect our thermal expansion to be positive. The thermal expansion coefficient of graphene 64 atoms is 5.02 $\times 10^{-6}$ K^{-1} and for graphene 256 atoms is 9.76 $\times 10^{-6}$ K^{-1}. Both models have different thermal expansion coefficient but positive. This is because the size effect thermodynamic properties [19,21]. Bao et al [21] calculated the coefficient of thermal expansion of graphene at a low temperature between 200 K -400 K using experimental method and found -7×10^{-6} K^{-1}. Jiang et al [21] calculated the coefficient of thermal expansion of graphene at a low temperature using nonequilibrium Green's function method; he got -6×10^{-6} K^{-1}. Zakharchenko et al [19] calculated the negative thermal expansion coefficient of single layer graphene and found the negative-to positive transition to occur at ∼900 K.

Conclusion

Some of the structural properties are in agreement with the theoretical calculations and experimental data. This agreement shows the ability of Tersoff potential in combination with the molecular dynamics method, to predict the physical properties of various forms graphene. The bulk modulus is totally disagreeing with other calculations and experiments, it should also be noted that the model used here is a double layered structure whereas calculations used a single sheet graphene. The specific heat capacity of graphene64 and graphene256 is the same. The coefficient thermal expansion of both model are positive at a high temperature. Graphene256 is more stable than graphene64 because the minimum energy of Graphene256 is less than the one for graphene64.

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