Relative stability of some graphene layered structures

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Abstract. Molecular dynamics simulations were used to study realative stability of graphene. The formulation of the Tersoff bond-order potential was used to investigate the energetic stabilities and thermodynamics properties of graphene through a range of temperature. The structural properties were studied using the radial distribution functions effects and the thermodynamics effects were studied using the energy-temperature. Similarities and differences in graphene 64 atoms and graphene 256 atoms are discussed.

1. Introduction

Graphene was discovered in 2004 and has since 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. This rippling makes graphene a nearly perfect two dimensional crystal in three dimensional spaces which is not forbidden. 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 [2].

The carbon-carbon bond length of graphene is 0.142 nanometres with an interplanar spacing of 0.335 nm. 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. In particular, it has been recently demonstrated that high speed graphene devices were achieved with a cutoff frequency reaching up to 100 GHz, demonstrating the significant potential of graphene devices for radio frequency (RF) applications [8]. Graphene, being a zero gap semiconductor is not suitable for the preparation of digital FET devices because of the missing energy band. To make such devices from graphene, one must open a bandgap in the graphene band structure. One possible solution for this is based on the quantum confinement effect in graphene ribbons of a few nanometers in width and with well-defined crystallographic orientation. The other solution is the introduction of a double layer graphene structure with a tunable interplanar spacing. The functionality of graphene nanodevices strongly depends on the structure of the edges. Because of its special chemical character, large scale processing of graphene in a future device technology possibly implies the use of ion beam and plasma based etching techniques [9].

In this paper, two surface area dimensions of double layered graphene are being studied through structural and thermodynamic properties. Using the structural optimization and radial distribution functions some equilibrium properties of these layered graphene are noted. Thermodynamic properties will be investigated to understand the behaviour at high temperatures.

2. Computational details

In this paper structural and thermodynamics properties of double layered graphene are being explored. 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 carbon atoms of which 32 atoms make one layer (graphene64); the other model has 256 carbon atoms with 128 atoms per layer (graphene256). Both models have interplanar spaicng of 15 Å. The hexagonal sheets have a two carbon atom unit cell with a lattice constant a_0 = 2.461 Å [10]. Each carbon atom per sheet has three nearest neighbors, six next-nearest neighbors, and three second-nearest neighbors.

The scope of the simulations is to investigate the energetics with varying temperature and radial distribution effects that govern the nano-size effects and atomic distribution in a given structure. In order to fully understand these effects, it is essential to perform molecular dynamics (MD) simulations at an atomistic level and a sequential resolution in the scale of the Debye frequency for thermodynamic properties. The Tersoff potential [11] used has been the most successful model to replicate much of the semiconducting properties in carbon structures. Atomistic interactions are tackled by the potential energy function in the form of an interactive empirical bond-order potential.

The MD simulation is performed within a canonical NVT ensemble, using DL_POLY software [12]. In order to investigate the thermal expansion coefficient some strain has been exerted along the sheet plane on the models. 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. 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. The MD cells in this report are made of 64 and 256 in graphene double layered structure. For structural optimization the simulation temperature is 300 K at zero pressures. Real space cut off and primary neighbour cut off is 2.68 angstroms.

3. Results and discussion

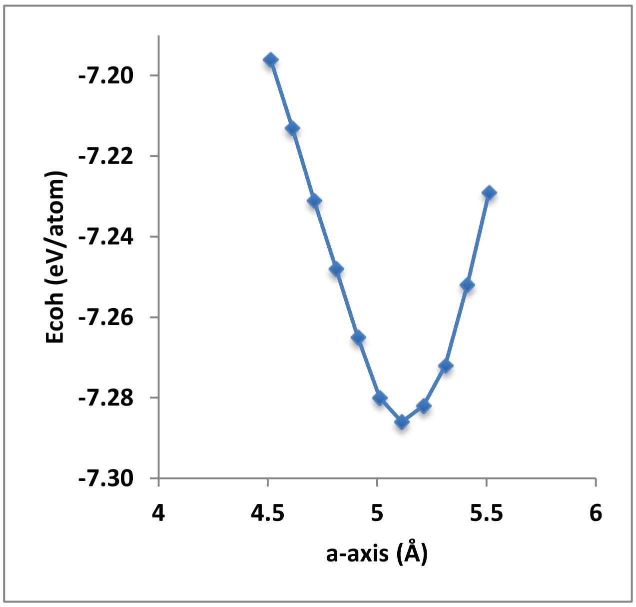

Figure 1. Cohesive energy as a function of volume for graphene64.

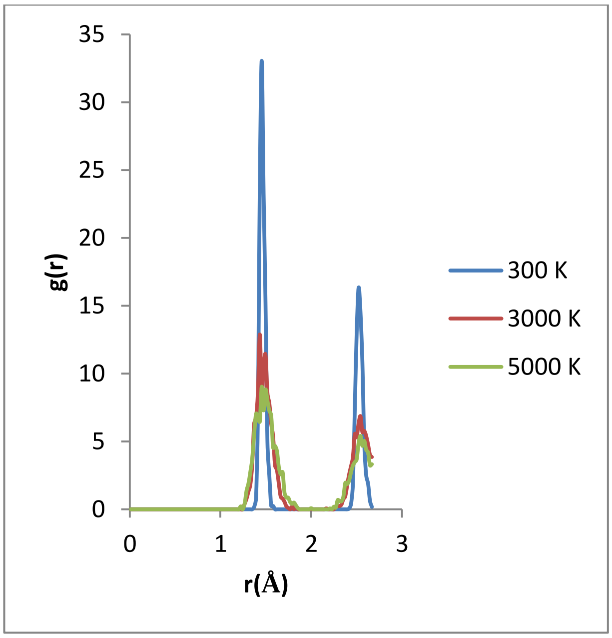

Figure 2. Radial distribution function for graphene64 at 300, 3000, and 5000 K.

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 cohesive energy, bulk modulus and its derivative were calculated using Figure 1 and least squares fitted to the Murnaghan's equation of state. In Table 1, results achieved are listed together with some measured [14] and computational results [10,13]. 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 interplanar planar spacing of 15 Å could also play a crucial role. Graphene64 and graphene256 equilibrium properties results are the same.

In both models, the radial distribution functions (rdf's) were studied at 300, 3000, and 5000 K as shown in Figure 2. In all temperature range first peak appear at 1.4 Å and the second peak appear at 2.5 Å. 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 ~2.5 Å [10]. This is another way the mechanical hardness of graphene manifest at extreme temperatures. The structural properties through rdf's are in total agreements with the measurements and calculations [10, 13, 14].

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 ref[10,13]	graphite ref[13,14]
a (Å)	2.551	2.571	2.461	2.603
B_0 (GPa)	130	130	700	33.8
B'	3.5	3.5	1	8.9
E_0 (eV)	-7.279	-7.300		
V_0 (Å^3)	9.682	20.74	6.076	35.12

Up to this point, ordinary temperature (300 K) properties of double layered models have been considered. The thermodynamics properties of the systems were also 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. The graphite Debye temperature of 2500 K along the a-axis has been considered [14].

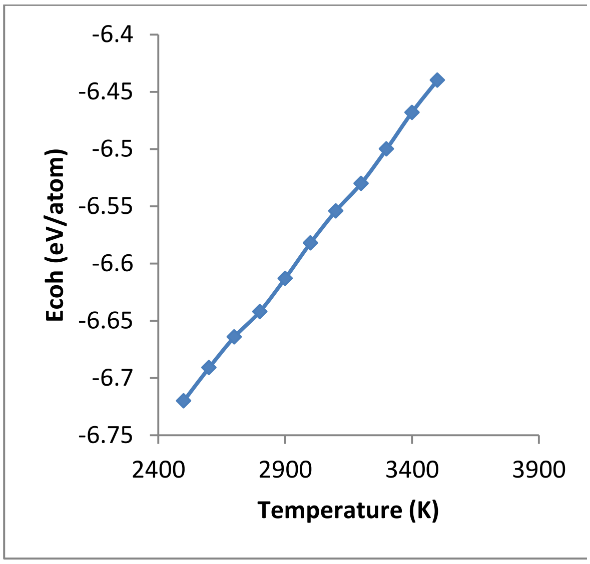

Figure 3. The energy as function of temperature for graphene256 system.

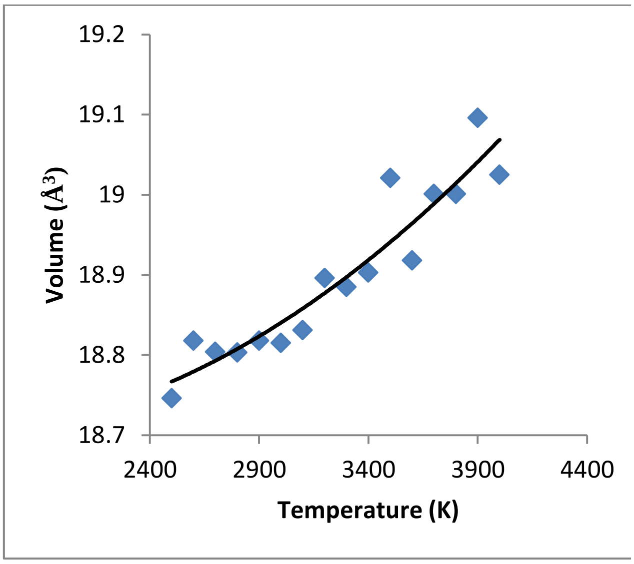

Figure 4. The volume as function of temperature for single layer graphene72 system.

The specific heat capacities of graphene64 and graphene256 at constant volume have also been calculated. This is obtained from temperature derivative of the total energy of the system. Figure 3 shows the total energy versus temperature for the 256 atom system. The specific heat capacity calculated for both systems is $3.42k_B$. This differs by 12% from the Dulong –Petit's law ($3k_B$) of solids at high temperatures, although no experimental data on this has been considered.

The thermal expansion coefficient for the systems was also calculated. It must be reported that due to disordered nature of the volume-temperature double layered structure relation, a single sheet consisting of 72 carbon atoms (graphene72) was taken into account. Graphene72 also experienced the turbulent behaviour of volume with temperature as shown in Figure 4, though tolerable. This behaviour could be attributed to the thermal contraction causing bending modes which produce negative values as argued by Mounet and Marzaris quasiharmonic approximation [15]. The thermal expansion coefficient was found to be -9.04×10^{-6} K^{-1}, which agrees well with other calculations [15] and experiments [14].

4. Conclusion

The Tersoff bond-order potential was proposed for graphene, and tested the validity of our parameters by calculating the structural and thermodynamics properties of graphene. The results 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. Lastly, surface area has no notable effects on the properties of graphene layers.

5. Acknowledments

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6. References

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