Presented at the DLSU Research Congress 2016
De La Salle University, Manila, Philippines
March 7-9, 2016

A DFT-based calculation of equilibrium lattice parameter of (6,0) SWCNT for adsorption of CO, NO, and NO_2 gases

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Abstract: We report in this paper the results of our investigation on the equilibrium lattice parameters of (6,0) SWCNT as well as CO, NO and NO_2 gases in preparation for our study of the adsorption mechanisms of these pollutant gases on SWCNT. Using first-principles calculations, we found that the equilibrium C-C bond lengths in (6,0) SWCNT is 1.5573 Å while the equilibrium bond lengths for CO, NO and NO_2 gases are 1.122 Å, 1.1562 Å and 1.232 Å, respectively. All calculations were performed in the framework of plane-wave basis set adopting the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional. The results are in good agreement with experimental values.

Key Words: air pollution; gas sensing; density functional theory; SWCNT; gas adsorption

1. INTRODUCTION

The discovery of carbon nanotube by Iijima in the early 1990's sparked multitude of studies on its adsorption properties toward pollutant gases (Azizi, Majid Hashemianzadeh, & Bahramifar, 2011). The importance of this type of researches is accentuated by the increasing production of cars where copious exhaust gases heavily pollute the atmosphere (Annenberg Foundation, 2007). Several technologies were implemented in the past to address the issue but efforts seem to be unviable in the long run. For instance, the use of automotive catalytic converters successfully catalyzes the exhaust gases from cars into more environment-friendly products (Ozhan, Fuster, & Da Costa, 2014). However, the device itself is composed of heavy metal that is so expensive and hard to find.

Previous studies were already successful in revealing interesting information about the adsorption of gases onto CNTs. It was already shown that the zigzag chirality of CNT is most effective for the adsorption of gases and that the smaller the diameter of the CNT, the higher the binding energy (Mittal & Kumar, 2014). Other studies have also shown that molecular orientation of gases towards the adsorbing medium gives favorable adsorption energy (Yue, Shao, Chang, & Li, 2013). The nanotube size, specifically its surface curvature, was also established to significantly affect adsorption of gases in CNTs as it was shown that larger curvature enhanced both the adsorption energy and charge transfer due to the greater strain on the carbon atoms resulting better interaction of the gas and the CNT (Moreno, Aspera, David, & Kasai, 2015).

On the same note, we attempted to understand the adsorption of pollutant gases (specifically the most harmful motor vehicle emissions

– CO, NO and NO_2) on (6,0) single wall carbon nanotubes, a CNT configuration with zigzag chirality. The Density Functional Theory, as implemented in the Vienna Ab-initio Simulation Package (VASP), was used in the calculations since previous studies have proven that it is a powerful and economic method of studying gas adsorption (Borówko, 2002).

We report in this paper the result of our investigation of the equilibrium parameters of the SWCNT and the CO, NO and NO_2 molecules. The equilibrium parameters provide the initial conditions and are therefore deemed vital in the simulation of the adsorption process of the gas molecules on SWCNT.

2. METHODOLOGY

The VASP program was used to perform an iterative solution of the Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}) \quad \text{(Eq. 1)}$$

where:

$v_{eff}(\mathbf{r})$ = Kohn-Sham potential
ε_i = the orbital energy of the corresponding Kohn–Sham orbital

based on residuum-minimization and optimized charge-density mixing routines that calculates the total energy E_{tot} of some collection of atoms (Kresse & Furthmüller, 1996a; Kresse & Furthmüller, 1996b). These E_{tot} values were plotted against position r (that is, the carbon-carbon-distance in the SWCNT and the bond length among the gas molecules) in order to reveal a single minimum value that can be used to calculate the equilibrium parameters (Sholl & Steckel, 2009). These parameter values were derived from the calculations by expressing the total energy as a truncated Taylor expansion then fitted to the Birch-Murnaghan equation of state (Birch, 1978).

In this study, the calculations were performed using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional (Perdew, Burke, & Ernzerhof, 1996), a non-empirical generalized gradient approximation (GGA). These calculations were performed using spin-polarized density functional theory as implemented in the VASP computer codes. Ionic cores were described by the projector augmented wave (PAW) method (Blochl, 1994). The surface Brillouin zone integration was performed using the special-point sampling technique of Monkhorst and Pack (Monkhorst & Pack, 1976).

3. RESULTS AND DISCUSSION

3.1. Equilibrium Parameters of (6,0) SWCNT

For the purpose of calculations, a supercell composed of 18 Carbon atoms was used to form the SWCNT model, as shown in Figure 1.

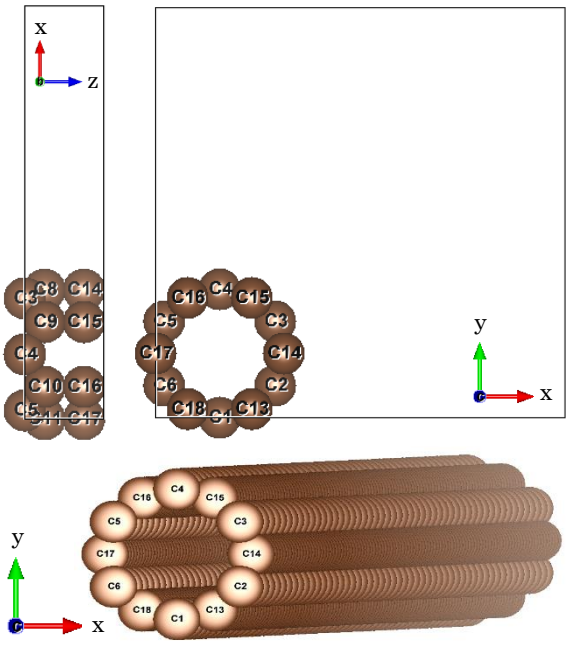

Fig. 1. The supercell geometry showing the vacuum layers inserted along the x and y axes in the model to avoid interaction in the CNTs when periodically repeated.

The diameter of the carbon nanotube was calculated from the carbon-carbon distance and the chiral indices using the formula

$$d = 0.55133\, r\sqrt{n^2 + m^2 + nm} \quad \text{(Eq. 2)}$$

where:

$n = 6$
$m = 0$
r = distance between nearest carbon neighbor.

On the other hand, the volume of the unit cell is calculated using the formula

$$V = 0.14513\,\pi\,r^3\,(n^2 + m^2 + nm). \qquad \text{(Eq. 3)}$$

The results of the total energy calculations for different values of C-C distance are summarized in Figure 2.

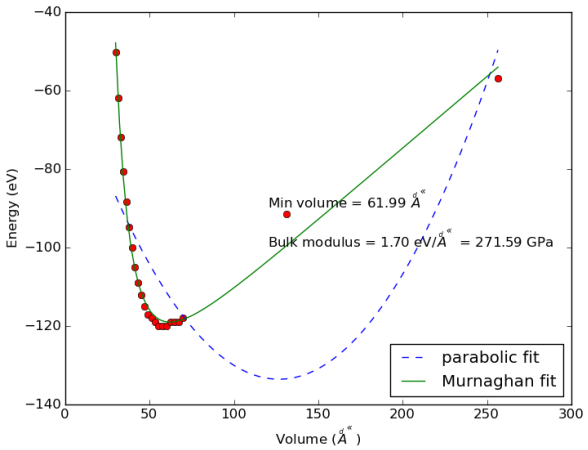

Fig. 2. Birch-Murnaghan Fit for SWCNT based on data from VASP Calculations

The Birch-Murnaghan Fit revealed that the equilibrium C-C distance in (6,0) single wall carbon nanotube is 1.5573 Å and that its bulk modulus is 271.59 GPa. These values are in good agreement with accepted values, as shown in Table 1.

Table 1. Equilibrium Parameters of SWCNT

Parameter	Calculated	Accepted	% Difference
C-C distance	1.5573 Å	1.42 Å [a]	9.22%
Bulk Modulus	271.59 GPa	~200-500 GPA [b]	---

[a] O'Connell, 2006
[b] Wan, 2008

The agreement of the calculated values and the accepted values of the equilibrium parameters of (6,0) SWCNT ensures that the pseudopotential and calculation parameters used gave reasonable values and therefore justifies the use of such parameters in the succeeding calculations.

3.2. Equilibrium Parameters of the Gas Molecules

Shown in Figure 3 are the respective supercell configurations used in this study to determine the equilibrium lattice parameters of the gas molecules.

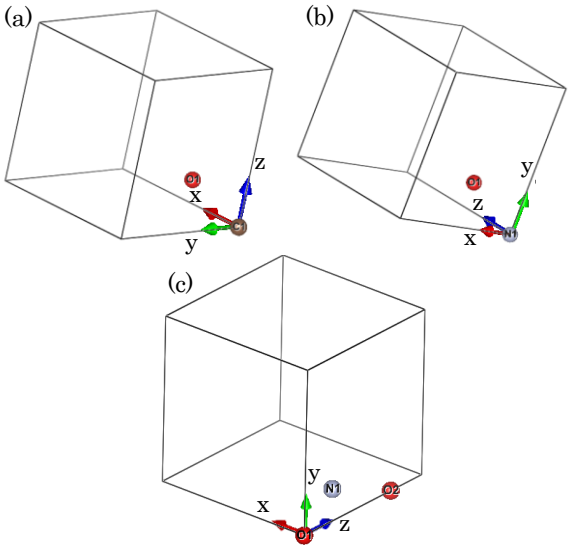

Fig. 3. The supercell geometry showing the vacuum layers inserted in the models of (a) CO, (b) NO, and, (c) NO_2 molecules to avoid interaction when periodically repeated.

The results of the total energy calculations for different bond length values for the molecules are summarized in Figure 4. Shown also in the figure are the Birch-Murnaghan fit on the calculated data for each of the pollutant gas molecules considered in this study.

The identified bond length with minimum energy in the BM fit revealed that the equilibrium bond lengths of CO, NO and NO_2 molecules are 1.122 Å, 1.1562 Å and 1.2143 Å, respectively. These calculated values are as well in good agreement with accepted values, as shown in Table 2.

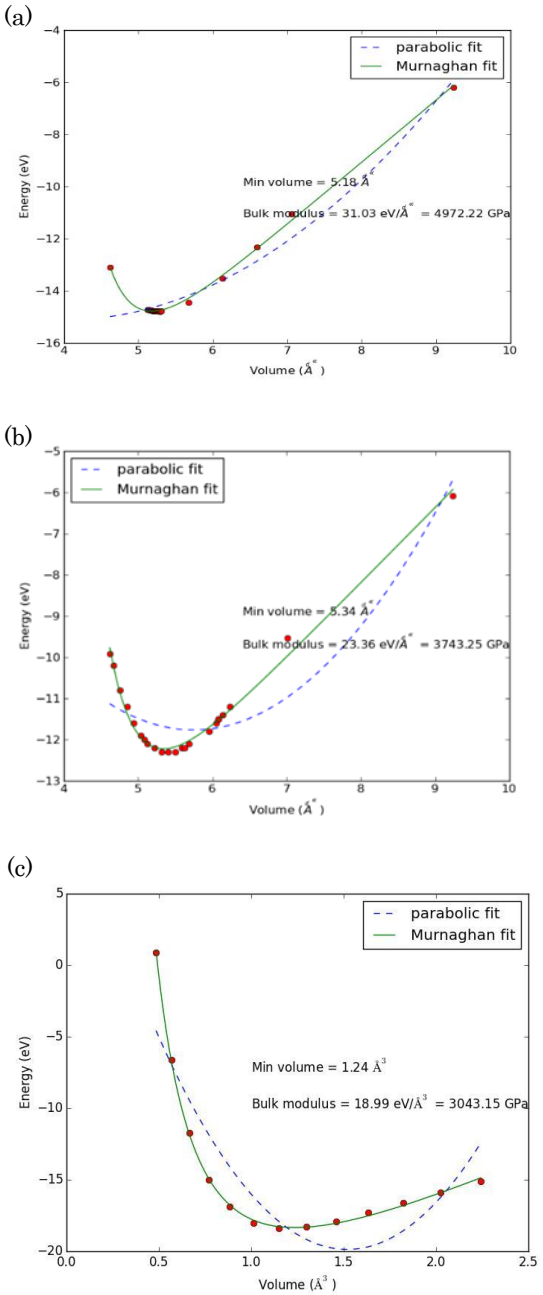

Fig. 4. Birch-Murnaghan Fit for (a) CO, (b) NO, and, (c) NO_2 gas molecules based on data from VASP Calculations

Table 2. Equilibrium Bond Lengths of the Pollutant Gas Molecules

Gas	Calculated	Accepted	% Difference
CO	1.122 Å	1.128 Å [a]	0.53%
NO	1.1562 Å	1.15 Å [b]	0.54%
NO_2	1.232 Å	1.197 Å [b]	2.88%

[a] Raj, 2008
[b] Whitten, Davis, Peck, & Stanley, 2014

4. CONCLUSIONS

We studied the equilibrium parameters of (6,0) SWCNT and three pollutant gas molecules (CO, NO, and NO_2) using Density Functional Theory as implemented in the Vienna Ab-initio Simulation Package. We found that the equilibrium C-C distance in (6,0) SWCNT is 1.5573 Å and its bulk modulus is 271.59 GPa. On the other hand, we found that the equilibrium bond lengths of CO, NO and NO_2 molecules are 1.122 Å, 1.1562 Å and 1.2143 Å, respectively. All calculated values were in good agreement with accepted values. The agreement of the calculated values and the accepted values justifies the use of the pseudopotential and other calculation parameters used in succeeding calculations.

5. ACKNOWLEDGMENTS

The authors would like to thank the High Performance Computing Lab (HPCL) of the Center for Natural Sciences and Environmental Research (CENSER) for allowing them to conduct the calculations using the lab's computing facilities. RRL, DSF, and BZCM would like to express their gratitude to DLSU Physics Department and the Computational Materials Design Research Group for allowing them to conduct their on-the-job training at DLSU.

6. REFERENCES

Annenberg Foundation. (2007). *The Habitable Planet: A System Approach to Environmental Science*. Retrieved January 23, 2016, from Annenberg Learner: https://www.learner.org/courses/envsci/unit/index.php

Azizi, K., Majid Hashemianzadeh, S., & Bahramifar, S. (2011). Density Functional Theory Study of Carbon Monoxide Adsorption on the Inside and Outside of the Armchair Single-Walled Carbon Nanotubes. *Current Applied Physics, 11,* 776-782. doi: 10.1016/j.cap.2010.11.071

Birch, F. (1978). Finite strain isotherm and velocities for single-crystal and polycrystalline sodium chloride at high pressures and 300°K. J. *Geophys. Res., 83,* 1257.

Monkhorst, H. J., & Pack, J. D. (1976, June 15). Special points for Brillouin-zone integrations. *Phys. Rev. B, 13*(12), 5188-5192.

Moreno, J., Aspera, S., David, M., & Kasai, H. (2015). A computational study on the effect of local curvature on the adsorption of oxygen on single-walled carbon nanotubes. *Carbon, 94*, 936-941.

O'Connell, M. (2006). *Carbon nanotubes : properties and applications*. Boca Raton, FL: CRC Press.

Raj, G. (2008). *Advanced Inorganic Chemistry Vol. I (For Honours and Post-Graduate Students of All Indian Universities)*. Meerut, India: GOEL Publishing House.

Sholl, D. A., & Steckel, J. A. (2009). *Density Functional Theory: A Practical Introduction*. Hoboken, New Jersey: John Wiley & Sons, Inc.

Wan, H. (2008). *Mechanics of Carbon Nanotubes (CNTs) and Their Composites*. Retrieved from https://books.google.com.ph/books?id=rx3iH-i-d4UC&pg=PR3&lpg=PR3&dq=Mechanics+of+Carbon+Nanotubes+(CNTs)+and+Their+Composites&source=bl&ots=2bzt7IuJlM&sig=zsIZwG3sBdafpp56QbFPVC--AnQ&hl=en&sa=X&ved=0ahUKEwj_gdLI4NXKAhWBSiYKHWDsAIAQ6AEIKzAC#v=onepage&q=Mec

Whitten, K. W., Davis, R. E., Peck, M. L., & Stanley, G. G. (2014). *Chemistry, Hybrid Tenth Edition*. Belmont, CA: Brooks/Cole Cengage Learning.

Yue, Q., Shao, Z., Chang, S., & Li, J. (2013). Adsorption of gas molecules on monolayer MoS_2 and effect of applied electric field. *Nanoscale Research Letters, 8*, 425-431. doi: 10.1186%2F1556-276X-8-425