Ab initio simulation of helium inside carbon nanotubes

D B Timerkaeva$^{1,2}$, V Stutzmann $^1$, B Minisini $^1$, D A Tayurskii $^2$

$^1$ Institut Supérieur des Matériaux et Mécaniques Avancés du Mans, 44 Av. Bartholdi, Le Mans, 72000, France
$^2$ Institute of Physics, Kazan Federal University, 18 Kremlevskaya st., Kazan, 420018, Russia

E-mail: dtimerkaeva@gmail.com

Abstract. In present work we consider the complex behaviour of quantum liquids like liquid He-4 inside carbon nanotubes. Interactions between helium atoms and carbon atoms of the short-length atomistic model and model with periodical boundary conditions of carbon nanotube were studied via ab initio quantum simulations. Effects of geometrical confinement of the tube on the He behaviour inside CNT (13,0) have been explored. Nanotubes with typical average diameter of 10 angstroms are under consideration.

1. Introduction

Nowadays various nanostructures like carbon nanotubes (CNT’s), fullerenes, quantum dots and others continue to be one of the hottest research areas in the world of science [1]. CNT’s were first observed by soviet scientists Radushkevich and Lukyanovich in 1950 and the first transmission electron microscopy pictures of the hollow structures of the carbon filaments were published in 1952 [2]. The work remained basically unknown and in 1991 carbon nanotubes have been rediscovered by Iijima [3]. The chain of investigations in this sphere lasts until our days. The interest is driven by the possibility of variety commercial applications [1], [4]-[5]. Among them, the storage of hydrogen inside nanotubes and nanotube bundles was extensively studied [6]-[9] and opened an important branch of investigations in the field of gas-nanotube interacting systems. The previous works have revealed that the gases in confined geometry are ruled by new physics and new effects [10]-[20].

The natural quasi one-dimensional system is realized via atoms encapsulation inside small radius nanotubes, inside the interstitial channels of nanotube bundles and via their adsorption on the grooves of the bundle surface. Two-dimensional systems can be formed on the inner and outer surface of freestanding nanotubes and on the outer surface of nanotube bundles whereas three-dimensional anisotropic condensed phase was considered as a result of interaction of helium atoms between neighboring interstitial channels [10].

In the confined geometry conditions, helium atoms $^4$He and $^3$He form bound states, so-called dimers, trimers and so on [14]-[16]. It is known, that such dimers should be bound extraordinarily weak in unconfined space. The binding energy value is up to four times smaller than the interatomic potential well [17]-[18]. This leads to the uncommon high length of the bond of the order of several van der Waals radiuses and can open a new branch of quantum chemistry, where giant molecules with practically destroyed bonds act as a building material [19]. In addition, lots of fundamental questions dealing with the general problem of existing He$_n$ clusters appear. Finally, there is a category of interesting problems, which deal with the existence possibility of n-mers in helium liquids including...
thin films. This is a huge field remains largely unexplored even if several examples, discussed by Ghassib [20], have illustrated that such clusterization can lead to interesting results.

In this context the problem of a correct description of helium in the confined geometry at nanoscale length has been emerged. So far the experimental studies face significant difficulties, the majority of studies dealing with helium inside nanotubes [21]-[22] use theoretically calculated Stan and Cole adsorption potential [23] based on the van der Waals interaction between helium atom and nanotube. Stan and Cole [23] in their study proposed a smooth walls nanotube model with van der Waals parameters extracted from the experiments on helium adsorption on planar graphite [24]. They can be used to evaluate for example the binding energies [25]-[26] or the adsorption coverage [27] but most of all these methods can provide a powerful tool to have an opportunity to “look inside” the nanotube and analyze gas and liquid behavior whereas experiments are difficult to carry on.

In present work we consider the complex behavior of quantum liquids like liquid He-4 and liquid He-3 inside carbon nanotubes. Interaction between helium atoms and carbon atoms of the short-length atomistic model of CNT and the model with periodical boundary conditions are studied via \textit{ab initio} quantum simulations. Effects of geometrical confinement of the tube on the He behavior as well as effects of helium presence on the various electronic properties of the tube are explored. Nanotubes with typical average diameter of 10 angstroms are under consideration.

2. Method

The average diameter of experimentally produced CNTs has a value around 1 nm [28]. Several possible chiralities with theoretically calculated diameter close to 1nm can be considered. Among them we have chosen a single-walled (13,0) zigzag nanotube. This choice was motivated by the small periodicity of the zigzag nanotubes compare to chiral ones. We have performed the calculations on the models with and without periodic boundary conditions presented on the Fig. 1, 2 and Fig. 3 respectively. Dangling bonds on the edges of short models were closed by the hydrogen atoms. Short atomistic nanotube models were employed to perform Hartree-Fock, post-Hartree-Fock and ONIOM calculations, while the periodic structure was used in DFT calculations.

2.1. Hartree-Fock, post-Hartree-Fock and ONIOM methods.

Gaussian03W [29] software was used for the Hartree-Fock and Post-Hartree-Fock method calculations. Compare to the DFT, Hartree-Fock method deals with the wave functions of electrons. The later allows to compute the exchange coulomb interaction precisely, and post-Hartree-Fock method allows to take into account the electron correlations accurately. The DFT method due to handling the density distribution function in the calculations leads to approximate calculations of both exchange and correlation interactions and doesn’t take into account van der Waals interactions properly. However, post-HF method are time consuming and consequently gives reliable values but only for small size systems. In our case this disadvantage forces us to reduce the length of nanotube model.

One helium atom was situated inside the tube. As a trial locations we have chosen a central helium location ($r = 0\text{Å}$) and a location at a distance $r = 3.33\text{Å}$ away from CNT center. The influence of the method and the basis set on the results of calculations was studied. The two-layers ONIOM technique [30] allows to perform the calculations of the subsystem with a cheaper cost. Here helium atom is related with “higher layer” and is treated with HF or post-HF methods, whereas the CNT is treated with DFT-LDA method with various basis sets. Performing the full DFT method in this software is associated with difficulties: some parameters for helium atom are absent. The obtained results are presented in Table 1.

The difference in energies between two helium-CNT configurations gives qualitative information about the adsorption potentials calculated with various methods.
Figure 1. Short tube model CNT(13,0) \( l = 9.22\AA \).

Figure 2. Short tube model CNT(13,0) \( l = 4.96\AA \).

Figure 3. Periodic cell corresponding to infinite CNT model.

According to obtained results increasing the basis set for the helium atom hasn’t an influence on the energy difference in ONIOM calculations, however, it is clear that the basis set 6-31+G(d) applied to nanotube walls provide a higher energy difference value \( \Delta E \) than 3-21G. The Moller-Plesset second order perturbation theory (MP2) \[31\] in case of low basis set for “lower level” doesn’t improve the values. An almost zero difference (0.00008Ha) is obtained in the case of 6-31+G(d) basis set for “lower layer”. The comparison between the ONIOM and pure HF results confirms the importance of taking into account the correlation interaction between carbon atoms in such calculations. ONIOM calculations lead to a greater energy difference in comparison with the results obtained with only HF method.

Table 1. Comparison the total energy of the system for two trial helium atom dispositions:

| Methods (CNT b.s./He b.s.) | \( E_{\text{border}} \) (Ha) | \( E_{\text{center}} \) (Ha) | \( \Delta E \) (Ha) |
|---------------------------|-------------------------------|-------------------------------|--------------------|
| DFT-LDA(3-21G)/HF(3-21G)  | -1977.502014                  | -1977.520270                  | -0.018256          |
| DFT-LDA (6-31+G(d))/HF(3-21G) | -1988.478964                 | -1988.501593                  | -0.022629          |
| DFT-LDA (3-21G)/HF(6-31+G(d)) | -1977.521495                 | -1977.539751                  | -0.018256          |
| DFT-LDA (3-21G)/MP2(3-21G)  | -1977.513511                 | -1977.531767                  | -0.018256          |
| DFT-LDA (3-21G)/HF(6-31+G(d)) | -1977.521495                 | -1977.539751                  | -0.018256          |
| DFT-LDA (3-21G)/MP2(6-31+G(d)) | -1977.532695                 | -1977.550951                  | -0.018256          |
| DFT-LDA (6-31+G(d))/HF(6-31+G(d)) | -1988.498445                 | -1988.521074                  | -0.022629          |
| DFT-LDA (6-31+G(d))/MP2(6-31+G(d)) | -1988.509645                 | -1988.532354                  | -0.022709          |
| DFT-LDA (3-21G)/HF(3-21G)  | -1977.502014                  | -1977.520270                  | -0.018256          |
| HF 3-21 G                  | -1975.557694                 | -1975.594138                  | -0.036444          |
| HF 6-31 + G (d)            | -1986.770631                 | -1986.811064                  | -0.040433          |

Of course, the perfect outcome can be obtained with the best parameters set. In our case it should be the post-HF method with basis set 6-31+G(d) applied to the whole system. But the limitation in resources forces us to use less powerful techniques. During the testing of the methods, serial calculations were performed using HP Z600 workstations only for two configurations, and some of them took important time period (up to two weeks). It is not acceptable for the important quantity of calculations we have to perform in order to have some information concerning the interactions.
between Helium atom and nanotube. That is the reason why we perform the following calculations on the short model tube with the simple 3-21G basis set.

2.2. DFT method.
A full DFT method was realized using VASP (Vienna Ab-initio Simulation Package) software in MedeA [32] interface, which allows to use the periodic boundary conditions, and consequently we can use an atomistic infinite model. The nanotube structures were created with Materials Studio 4.4 software [33]. The energy cutoff of plane wave basis set is chosen up to 500eV. For the exchange and the correlation contributions the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (PBE-GGA) [34] was used. Number of k-points is a critical parameter in that kind of simulations, but increasing leads to higher price of the simulations. On the other hand, the high symmetry of the system allows to decrease the value of this parameter. Depending on the periodic cell parameter along the tube axis k-mesh 1×1×3 or k-mesh 1×1×2 were used. As a convergence criterion for the SPE calculations 10⁻⁵ eV on the total energy was used.

The cell parameters were taken to correspond to an intertube distance of 5.45 Å. We were interested in the freestanding tube, but higher intertube distance is incompatible with our computing resources. After the first 3 optimization steps (containing two steps of cell volume, cell shape and atomic position optimization and as a third step only atomic position optimization), we doubled the cell size in the axis direction and perform optimization again. Nanotube size and cell parameters are presented in the Table 2. Increasing of the cell was performed to exclude the helium-helium interaction while adsorption potential curves calculations. The periodic boundary conditions being used, it is necessary that the cell size be much larger than parameter σ=2.57 Å [20]. Larger size of the cell also permits to reduce number of k-points in axis directions from three to two. Other parameters were kept without changes.

### Table 2. Parameters of the CNT models after optimization.

| Model       | D (Å) | Nₙₙ | a (Å) | b (Å) | c(Å) | α(°)  | β(°)  | γ(°)  |
|-------------|-------|-----|-------|-------|------|-------|-------|-------|
| 1 CNT(13,0) initial | 10.180 | 52  | 15.640 | 15.640 | 4.260 | 90.000 | 90.000 | 120.000 |
| 1 CNT(13,0) final   | 10.247 | 52  | 15.732 | 15.737 | 4.285 | 89.998 | 89.995 | 119.981 |
| 2 CNT(13,0) initial | 10.247 | 104 | 15.732 | 15.737 | 8.570 | 89.998 | 89.995 | 119.981 |
| 2 CNT(13,0) final   | 10.250 | 104 | 15.735 | 15.740 | 8.561 | 89.998 | 89.996 | 119.982 |

3. Results and discussion
On the Fig. 4 the potential curves for helium atom inside carbon nanotube (13,0) (R=5.13 Å) as a function of the distance from nanotube center are presented. Set of energy calculations were performed for the helium-CNT system with different methods. The results were compared with the Stan and Cole potential [23]. Values for the DFT methods were rescaled to obtain the same tube radius as in the MP2 calculations. The obtained depth of potential well (~3K) in the case of MP2 method isn’t as deep as in theoretical calculations (~100K) and the minimum position is shifted to the axis direction (1.5 Å compare to 2.3 Å [23]). The same tendency can be noticed in the DFT results. Moving helium atom along the radius from the center to the wall directions, three adsorption sites were studied: adsorption to the center of hexagonal ring, named “hole”-site, adsorption to the node center, “node”-site, and finally to the carbon atom, “edge”-site. It should be mentioned that only short-range (chemical) interactions were taken into account, and the dispersion interactions are badly represented due to the limitation of the functional.

The minimum of the potential wells for the “hole”-site and “node”-site adsorptions have practically the same values. And the minimum position is found at a distance r=1.7 Å, while the minimum position of the potential curve for “edge”-site adsorption shifted towards the axis direction and equal
The depth of the potential well is of 20K smaller than those coming from Stan and Cole calculations [23].

Using various methods potential curves of different depth values and different minimum positions can be obtained. Whatever the method of calculation used, the influence on the results is important and few reasons can be mentioned to explain these discrepancies. For MP2 calculations very short nanotube segment was used. In addition the presence of hydrogen atoms at the end and the edge effects can lead to discrepancy in energy values. It was already mentioned above that basis set strongly influences the energy values, but higher is the basis set and higher are the resources requirements. On the other hand DFT with the lower computational cost leads to reasonable results. The carbon nanotube model with periodical boundary conditions is alike the infinite tube model considered by Stan and Cole. Stan and Cole’s semi-empirical potential is a van der Waals potential summarized over infinite smooth tube walls. The input parameters for [23] were taken from the helium adsorption experiment on graphite plane [24]. Therefore some effects caused by structure rearrangement can be lost.

![Figure 4](image)

**Figure 4.** Adsorption potentials for helium atom inside CNT (13,0) with radius 5,13 Å (black) 3-21G (MP2), (blue, red, green) DFT GGA-PBE, (orange) Stan and Cole potential [23].

Presented on the Fig. 5a and Fig 5b slices of electron density distribution confirm that the helium atoms presence cannot affect the electronic properties of the tube. Here the electronic density distribution is studied for two configurations, the central position and the position close to the border, corresponding to the highest probability. It can be noticed that in both cases we had the same spherical shape for helium and the same shape for the electronic density distribution for the tube. If the helium atom goes closer to the border, then the electronic shells overlap, and this fact tells us about the very strong repulsion. That is the reason why the probability of the helium atom presence closer to the border is very low. The presence of some helium atoms cannot really affect the electronic properties of the tube except in the cases of very high pressure; in particular the HOMO-LUMO gap value of the tube remains the same when helium is situated in the central part up to 2,25Å far away from the center.

Transport properties of the CNT (13,0) were explored using the DFT GGA-PBE scheme. Optimization calculations for the helium atom position inside optimized CNT were performed for two
initial states, presented on the Fig. 3. From the geometrical point of view it is clear, that the helium position He (2) is not at a local minimum, but at an unstable equilibrium position.

![Figure 5a. Electron density distribution: helium atom situated in the centre of CNT (13,0).](image1)

![Figure 5b. Electron density distribution: helium atom situated in the most preferable position inside CNT (13,0).](image2)

To have an idea about the transportation and the energy barriers of helium atoms inside CNTs, helium atom is allowed to flow from He (1) position to He (2) position (see Fig. 3). Set of 10 single point energy calculations were performed with 0.2 Å step from minimum position He (1) to He (2) (see Fig. 6). An energy barrier of 12K which can be treated as activation energy was obtained. This is the energy value required to a linear flow of helium atom. Another flow possibility is a zigzag-motion along the CNT walls. From energetic consideration, this case is more preferable with an energy barrier of about 1K (difference between energy minimums of the adsorption potential curves presented on fig.4). In this case helium moves as a snake that bypasses the carbon atoms.

![Figure 6. Activation energy.](image3)

| Helium atom position | $E_{\text{CNT-He}}$ (eV) | $E_{\text{He}}$ (eV) | $E_{\text{CNT}}$ (eV) | $E_{\text{bind}}$ (eV) | $E_{\text{bind}}$ (K) |
|----------------------|---------------------------|---------------------|-----------------------|-----------------------|-----------------------|
| He (1)               | -950.631                  | 0.0133              | -950.625              | -0.0195               | -225.96               |
| He (2)               | -950.630                  | 0.0133              | -950.625              | -0.0179               | -207.65               |
An important property of interest is the cohesive energy (or binding energy) of helium atom with CNT. This value can be found from the expression: 
\[ E_{\text{bind}} = E_{\text{He+CNT}} - E_{\text{CNT}} - E_{\text{He}} \], where 
- \( E_{\text{He+CNT}} \) – total energy value of carbon nanotube-helium molecule system with helium situated on its energetically most preferable position,
- \( E_{\text{CNT}} \) – total energy of the tube without helium and
- \( E_{\text{He}} \) – the energy of helium atom at the same periodic cell. The binding energy values of this two optimized positions of helium atom inside the CNT are presented in the Table 3. He (1) position corresponds to the minimum of the “hole”-site potential curve, while He (2) corresponds to the minimum of the “node”-site potential curve. Negative values of binding energy indicate that the adsorbed state is more profitable than separated state as well as the “hole”-site adsorption is more preferable than the “node”-site adsorption.

In summary, we have performed first-principle calculations on the adsorption and transport properties of nanotube with helium molecule inside. Adsorption potentials were obtained via post HF MP2 and DFT GGA-PBE calculations. Comparison with the theoretical Stan and Cole potential shows a shift of the minimum position to the center. The straightforward flow requires to overcome an energy barrier around 12K, while the zigzag-type motion requires an energy corresponding to 1K. Obtained binding energy values shows that the adsorbed state is profitable compare to the separated state.

Acknowledgement
The work was supported by the Ministry of Science and Education of Russia. D.B.T. thanks Region Pays de la Loire for partial individual financial support (MOA0021).

References
[1] Bhushan B et al Springer Handbook of Nanotechnology 2010
[2] Radushkevich L and Lukyanovich V Zh. Phys. Khim. 1952 26 88
[3] Iijima S Lett. to Nature 1991 354 56
[4] Maiti A Microelectronic Journal 2008 39-2 208
[5] Jung H Y, Jung S M et al. Applied Physics Letters 2007 90 153114
[6] Nikitin A, Li X., Zhang Z et al. Nano Lett. 2008 8-1 162
[7] Xia Y et al. Phys Rev B 2005 71 075412
[8] Han S S, Lee H M Carbon 2004 42 2169
[9] Du A J and Smith S C Nanotechnology 2005 16 2118
[10] Carraro C Phys. Rev. B 2000 61 R16351
[11] Aichinger M, Kilić S, Krotscheck E and Vranješ L Phys Rev B 2008 70 155412
[12] Stan G J Low Temp Phys 2009 157 374
[13] Mayol R, Ancilotto F, Barranco M, Hernández E S and Pi M J Low Temp Phys 2008 148 851
[14] Kilpatrick J E and Kilpatrick M F J. Chem. Phys. 1951 19 930
[15] Pais A and Uhlenbeck G E Phys. Rev. 1959 116 250
[16] Ghassib H B Z. Phys. B. Condensed Matter 1984 56 91
[17] Feltgen I R, Kirst H, Köhler K A et al. J. Chem. Phys. 1982 76 2360
[18] Uang Y-H and Stwalley W C J. Chem. Phys. 1982 76 5069
[19] Stwalley W C Cont. Phys. 1978 19 65
[20] Ghassib H B Z Phys B Condensed Matter 1984 56 91
[21] M.C. Gordillo, J. Boronat, J Low Temp Phys (2009) 157: 296–323
[22] D. Hirashima ’ K. Yamashita, JOURNAL OF LOW TEMPERATURE PHYSICS, Volume 158, Numbers 1-2, 112-117
[23] Stan G and Cole M W Surf. Sci. 1998 395 280
[24] Cole M W and Klein J R 1983 124 547
[25] Zhao J, Buldum A, Han J and Lu J P Nanotechnology 2002 13 195
[26] Chang H, Lee J D, Lee S M and Lee Y H \textit{Appl Phys Lett} 2001 \textbf{79-23} 3863

[27] Kuznetsova A, Yates J T, Simonyan V V, Johnson J K, Huffman C B and Smalley R E \textit{J Chem Phys} 2001 \textbf{115} 6691

[28] Journet C and Bernier P \textit{Applied physics A: Materials science & processing} 1998 \textbf{67-1} 1

[29] http://www.gaussian.com/

[30] Frisch M O et al. \textit{Gaussian 03 revision C.02 Gaussian Inc.: Wallingford CT} 2004

[31] Møller C. and Plesset M S \textit{Phys. Rev.} 1934 \textbf{46} 618

[32] http://www.materialsdesign.com/medea

[33] http://accelrys.com/events/webinars/materials-studio-44/

[34] Perdew J P, Burke S and Ernzerhof M \textit{Phys Rev Lett} 1996 \textbf{77} 3865