He on the outside of a bundle of (10,10) carbon nanotubes

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Abstract. Diffusion Monte Carlo calculations were performed on the subject of $^4$He adsorbed on the external surface of (10,10) carbon nanotube bundles. The carbon nanotubes were considered to be defectless and perfectly parallel cylinders in which all individual carbon-helium interactions were considered. This corrugation makes this substrate a very inhomogeneous one, with a range of $^4$He binding energies in the infinity dilution limit between $\sim 227$ and $202$ K. On increasing the helium density, we go from a quasi one-dimensional phase on the grooves between two tubes, to a liquid monolayer, with a three-line arrangement in between. No stable solid helium monolayer at high density was found. Instead, helium atoms are promoted to a second quasi-one dimensional phase on top of the liquid first layer. On increasing the helium intake, a two layer structure is formed in which the helium directly in contact with the carbon surface solidifies.

1. Introduction
Carbon nanotubes have been the subject of much work both theoretical and experimental since their discovery back in 1991 [1]. Among their especial properties are their use as gas adsorbents. In this quarter, it is well known that an open ended carbon nanotube can admit inside species of adequate size [2]. However, since these tubes are usually syntetised as closed-capped structures, the only surface accessible by default is their external one. Besides, carbon nanotubes are usually grouped together to form what is called a bundle, meaning that the only place in which a gas can be adsorbed is on the external surface of the tubes located at fringes of the bundles. The aim of this work is to study $^4$He adsorption on these accessible surfaces of a bundle of (10,10) carbon nanotubes. That was made by means of Diffusion Monte Carlo (DMC) calculations [3]. The idea is to compare the results with that of the experiments for the same system [4, 5, 6]. From classical gases [7], we know that, on increasing the density of the helium atoms, we should see a quasi one dimensional (1D) phase on between every two cylinders, a three stripes phase, and an homogeneous liquid one. This would complete the first layer. We also considered what happens on the second layer.

2. Method
To perform a DMC calculation, one should define first the so-called trial wave function. This takes into account all the physical information known a priori about the system, in particular, its phase (one dimensional, two dimensional, solid, liquid, and so on). In the present case, all
trial functions have a common part given by:

$$\Phi_J = \prod_{i<j} \exp \left[ -\frac{1}{2} \left( \frac{b_{He-He}}{r_{ij}} \right)^5 \right] \prod_{i} \exp \left[ -\frac{1}{2} \left( \frac{b_{C-He}}{r_{C-i}} \right)^5 \right]$$  \hspace{1cm} (1)

which has a contribution for all the He-He and C-He pairs. Then, depending on the phase, the trial is multiplied by one of the two following forms:

$$\Phi_1 = \prod_{i} \exp \left[ -a_1(x - x_{site})^2 - a_1(y - y_{site})^2 - b_1(z - z_{site})^2 \right]$$  \hspace{1cm} (2)

or

$$\Phi_2 = \prod_{i} \exp \left[ -a_2(r - r_{centre})^2 \right]$$  \hspace{1cm} (3)

All the necessary parameters were obtained variationally. $\Phi_1$ serves both for the one dimensional (1D) phase every two carbon nanotubes (what it is usually termed a groove; there $b_1 = 0$) and for the different phases in which the atoms are located at particular positions ($x_{site}$, $y_{site}$, $z_{site}$), like in the three stripes or solid phases. $\Phi_2$ is the trial function for an homogeneous two dimensional liquid wrapped around the external surface of the bundles. There, $r_{centre}$ is the distance of this liquid layer to the centre of the closest carbon cylinder. To complete the description of the simulations, we should say that the Aziz helium-helium potential was used [8], and that the carbon-helium interaction was modelled by a Lennard-Jones potential [9]. The simulation cell comprised two carbon cylinders when the phase considered was confined to a single groove (1D and three stripes). In other cases, it was made of three parallel nanotubes.

Since all the carbon atoms were considered individually the influence of corrugation was checked, and found quite important. To test it, the binding energy of a single helium atom on top of of a groove in between two carbon cylinders was calculated. All the possible relative rotations of a nanotube with respect to each other were considered, finding a minimum energy of $227.54 \pm 0.01$ K, versus the least favourable case of $201.85 \pm 0.01$ K [10]. These values compares favourably with the experimental data [5, 6]. All the data discussed here will correspond to the systems with the minimum energy of adsorption for each given density.

3. Results

In the first of the figures we show the equation of state of the 1D phase of helium on top of the grooves. Full squares represent the results for the system with a lowest energy per helium atom
in the infinite dilution limit. That infinite dilution binding energy was subtracted from all the data displayed in Fig. 1. The dotted line shows the result of a third order polynomial fit to the simulation results. This fit is to be compared with the one represented by the full line, that is the corresponding to a pure 1D system with the same He-He interaction [11]. The density in the $x$ axis is the linear density of helium atoms on top of the groove.

One observes a sizeable difference between the two curves: the energy minimum is much greater in the groove, and the linear density at zero pressure is smaller. This could be only due to the corrugation of the substrate, a conclusion supported by the comparison with the results for a (5,5) tube, also a quasi 1D system [11]. When the orientation of the tubes is different, the position and depth of the energy minimum change, but in any case the energy minimum exceeds the infinite dilution limit by more than 0.1 K.

![Figure 2. Energy per helium atom for the different phases considered. Lines are guides-to-the-eye. From bottom to top of the energy scale we have quasi 1D system (open squares), three stripes phase (full squares), homogeneous one layer liquid (open circles) and a second 1D phase (full circles) of helium on top of a liquid layer. Open triangles represent the unstable two stripes phase.](image)

Fig. 2 shows the energy per helium atom versus the density for all the systems considered. The density displayed is a surface density, i.e., the number of helium atoms divided by the accessible surface on the outer surface of the bundles. That surface was the one located at 9.5 Å of the closest cylinder. We observe that on increasing the density, the system undergoes different phase changes. Fig. 2 display the energy per He atom of all the possible phases in the density range displayed. This phases are, from bottom to top: quasi 1D, three stripes, a two dimensional liquid, and a second quasi 1D on a second layer of helium. The hypothetical two stripes phase was found to be unstable. A series of Maxwell constructions gives us the stability ranges of all those phases. The 1D phase will be stable up to $1.4 \times 10^{-2}$ Å$^{-2}$, the three stripes phase around $3.9 \times 10^{-2}$ Å$^{-2}$ and the liquid one from $6.2 \times 10^{-2}$ Å$^{-2}$ to $9.8 \times 10^{-2}$ Å$^{-2}$. The second 1D phase is stable around a density of $0.103$ Å$^{-2}$ [10].

After the second 1D phase on top of a liquid monolayer, we should have a two-layer phase. Here, we have two possibilities: two liquid layers (full squares on Fig. 3) and a liquid layer on top of a solid monolayer (dashed line in the same figure, corresponding to a splines fit to the simulation results). The lowest energy of this last phase was obtained with an underlying solid layer of density $0.110$ Å$^{-2}$. A close observation of Fig 3 shows that this last second possibility is slightly more favourable, but not by much. This means that after the second 1D layer phase, on increasing the helium density what we have is a liquid on top of a solid monolayer. The corresponding Maxwell construction between these two arrangements gives us that the lowest equilibrium density for this phase is $0.116$ Å$^{-2}$. 

4. Conclusions
We presented the results of DMC calculations on the subject of $^4\text{He}$ adsorbed on the external surfaces of a bundle of (10,10) carbon nanotubes. Several phases were identified until the second layer of helium, that was found to be a double layer made of a solid + liquid arrangement.

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5. References
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