Quantum Fluids in Nanotubes: a Quantum Monte Carlo Approach

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Abstract We review quantum Monte Carlo results on energetic and structure properties of quantum fluids adsorbed in a bundle of carbon nanotubes. Using realistic interatomic interactions the different adsorption sites that a bundle offer are accurately studied and compared in some cases with strictly one-dimensional geometries. The study is performed quite extensively for $^4$He and restricted to the inner part of a single nanotube for $H_2$ and $D_2$. From a theoretical point of view, nanotubes open the real possibility of a quasi-one-dimensional confinement where to study quantum fluids in extremely reduced dimensionality. The results obtained show that in the narrowest configurations the system is nearly one-dimensional reinforcing the interest on the physics of one-dimensional quantum fluids. Experimental confirmation of the theoretical results obtained is still not in a satisfactory situation due to the difficulties on extracting from the data the dominant adsorption sites.

Keywords Nanotubes, Adsorption, Quantum Monte Carlo

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1 Introduction

Carbon nanotubes were discovered by Iijima [1] in 1991. They are the result of taking one or several graphene sheets and roll them up to form hollow seamless tubes whose common characteristic is to have a very large aspect ratio [2, 3]. When a single graphene layer is used, we have what it is called Single Walled

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Carbon Nanotubes (SWCN) in opposition to the Multiple Walled Carbon Nanotubes (MWCN) that are structures formed by two or more nanotubes nested with each other. In this work, we will be concerned with the absorption properties of SWCN, since the corresponding to MWCN tubes are expected to be similar. The typical form of obtaining a single walled tube is by laser ablation, high pressure CO conversion or with an arc-discharge technique. With those, one can obtain a Gaussian distribution in the diameters of the tubes, the average being between 1 and 1.5 nm [4, 5, 6]. Single walled tubes tend to associate to each other to form bundles of triangular lattice-like sections.

The previous prescription to create a nanotube indicates that its main properties are the diameter and what it is called the chiral angle. This angle is related to the relative orientation of the graphene sheet, that is used to form the nanotube, and the main axis of the tube formed. Given the close relations between a graphene sheet and a carbon nanotube, those are defined in terms of the graphene vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. These are the shortest ones connecting the center of any given hexagon to the center of two other neighboring hexagons. This definition implies that $|\mathbf{a}_1| = |\mathbf{a}_2| = 2.46 \text{ Å}$ with an angle between them of $60^\circ$. In the unit cell so defined, we have two carbon atoms at the positions $\frac{1}{3}(\mathbf{a}_1 + \mathbf{a}_2)$ and $\frac{2}{3}(\mathbf{a}_1 + \mathbf{a}_2)$. To form a nanotube, we need what it is called a chiral vector $\mathbf{c}$ of the type $\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2$ and identify its length with the circumference of the desired tube, that in turn will be named $(n, m)$.

A bundle of carbon nanotubes offers a variety of adsorption places that hardly can be found in other structures. Apart form the inner part of a single nanotube, that can have different diameters, more room for adsorption appears in the narrow interchannels between three neighboring tubes and in the grooves that appear in the external surface of the bundle [7]. It is particularly interesting from a fundamental point of view the possibility of playing with a nearly one-dimensional confinement. If, in addition, one is interested in quantum fluids then nanotubes afford the unique and fascinating possibility of the theoretical study of nearly one-dimensional quantum fluids. In some sense, this is similar to the new physics that emerged thirty years ago from the experimental observation of films of quantum fluids (quasi two dimensions) adsorbed on graphite and other planar substrates.

In this article, we review recent theoretical results on the physical adsorption of $^4\text{He}$, $\text{H}_2$, and $\text{D}_2$ on the different sites that a bundle makes possible. The study has been carried out using realistic interactions and the diffusion Monte Carlo method that allows for a very accurate description of the ground state of the system. Unfortunately, a great deal of our theoretical results cannot be trusted with available experimental data due to the difficulties of a reliable identification of the dominant adsorption places. However, there is some agreement on the fact that the gases are predominantly adsorbed on the external surface of the bundle. As we report in Section 3, the presence of defects in the carbon nanotube may partially explain the low adsorption rate of helium or hydrogen in its inner surface.

The rest of the work is organized as follows. In Sec. 2, we present the diffusion Monte Carlo method used in our microscopic study and describe the interactions present in the Hamiltonian and the trial wave functions used for importance sampling. Results of $^4\text{He}$ adsorbed in different sites of a nanotube bundle are presented in Sec. 4 and the ones for $\text{H}_2$ and $\text{D}_2$ are comprised in Sec. 5. Finally, some concluding remarks are contained in Sec. 6.
2 Method

Our goal in this study was to obtain the ground state of different quantum liquids when they are confined inside a nanotube or close to the external surface of both a single nanotube and a bundle of them. To do so, we employed a quadratic diffusion Monte Carlo method (DMC) [8]. Nowadays, this is a standard technique to solve the Schrödinger equation of a many-body system using a stochastic approach. The starting point is the equation written in imaginary time \( t \) (in units of \( \hbar \)),

\[
- \frac{\partial \Psi(R, t)}{\partial t} = (H - E) \Psi(R, t)
\]

(1)

where \( \Psi(R, t) \) is the wave function of the \( N \)-particle system, and \( R \) stands for a set of \( 3N \) coordinates for all the \( N \) atoms considered in the simulation. Written in that way, and taking into account that

\[
H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + V(R)
\]

(2)

the above Eq. 1 can be considered as a diffusion equation and treated as such. However, the variance of the results is greatly reduced when an importance sampling scheme is introduced. To do so, one solves the Schrödinger equation for the wave function

\[
f(R, t) = \Psi(R, t) \Phi(R),
\]

(3)

where \( \Phi(R) \) is a time-independent trial function. In this function one introduces relevant information known \textit{a priori} about the system. For instance, if we expect the system to be confined in a given portion of space, \( \Phi(R) \) should have a maximum around that region and be close to zero elsewhere. The Schrödinger equation for the wave function \( f(R, t) \) turns out to be

\[
- \frac{\partial f(R, t)}{\partial t} = -D \nabla^2 f(R, t) + D \nabla (F f(R, t)) + (E_L(R) - E) f(R, t) \equiv (A_1 + A_2 + A_3) f(R, t),
\]

(4)

where \( D = \hbar^2 / 2m \), and \( A_1, A_2 \) and \( A_3 \) are the three operators acting on \( f(R, t) \) in the sum (first line of Eq. 4) in the same order as they appear. The local energy,

\[
E_L(R) = \Phi(R)^{-1} H \Phi(R)
\]

(5)

serves as an estimator for the energy of the considered system, and the term

\[
F(R) = 2 \Phi(R)^{-1} \nabla \Phi(R)
\]

(6)

is the drift force introduced by the importance sampling. In practice, this term allows for sampling mainly the regions in which the trial function has greater values and thus the efficiency of the method is increased.

To solve Eq. 4 it is transformed to integral form,

\[
f(R', t + \Delta t)) = \int G(R', R, \Delta t) f(R, t) dR,
\]

(7)
with \( G(R', R, \Delta t) = \langle R' | \exp(-\Delta t H) | R \rangle \) the Green function. When \( \Delta t \to 0 \), it can be well approximated by the short-time approximation
\[
f(R', t + \Delta t) = \int \exp[-\frac{\Delta t}{2} A_3] \exp[-\frac{\Delta t}{2} A_2] \exp[-\Delta t A_1] \exp[-\frac{\Delta t}{2} A_2] \exp[-\frac{\Delta t}{2} A_3] f(R, t) dR
\]

The partition described in the equation above is not unique, but this form assures that the errors due to the short-time approximation for the Green function are of the order \( (\Delta t)^2 \).

In the diffusion Monte Carlo method, \( f(R, t) \) is not represented by an analytical function, but by \( M \) sets of \( N \) particle coordinates, \( R \). Any of those sets is called a walker. This means that to apply the equation above to \( f(R, t) \), we have to modify any of the \( N \) coordinates of the \( M \) walkers by means of the following prescription:

(a) Change the coordinates of the particles in each walker by means of the drift force an interval \( \Delta t/2 \), i.e.,
\[
R' = R + DF(R)(\Delta t)/2
\]

(b) Change again the coordinates by adding to each of them a random number \( \chi \) drawn from a gaussian distribution in three dimensions \( \exp[-\chi^2/(4D\Delta t)] \)
\[
R'' = R' + \chi
\]

(c) Repeat step (a)
(d) Calculate the factor
\[
n_s = \exp[-\Delta t (E_k(R) - E)]
\]

for each walker \( R \) and replicate it \( n_s \) times. This produces a new set of \( M' \) walkers in which to perform the whole process again. The procedure is repeated as many times as needed to reach convergence to the limit \( t \to \infty \). Once that limit is reached, the expectation values of any of the observables could be obtained from the set of walkers derived from the process outlined above. In particular, as already mentioned, the estimator for the energy is the local energy (Eq. (5)). The quality of the results could be judged by the variance of the local energy, that depends directly on the trial wave function. If \( \Phi(R) \) is the exact solution of the Schrödinger equation for the system under consideration, the variance of the energy is exactly zero. If not, the DMC technique is able to obtain the exact ground state for a system of bosons within some statistical noise.

To apply the diffusion Monte Carlo method to a particular system, we need then a set of walkers \( R \), a trial function, and an interaction potential between the particles. As indicated above, the trial function incorporates information known \textit{a priori} about the system. In particular, \( \Phi(R) \) avoids configurations with two particles (in our case two atoms or molecules in the quantum liquid) sharing the same position. This is traditionally made with a Bijl-Jastrow wave function,
\[
\Phi_J = \prod_{i<j} f(r_{ij})
\]
where $r_{ij}$ is the distance between two $^4$He atoms or two $\text{H}_2$ or $\text{D}_2$ molecules, depending on the case. The two-body correlation function $f(r)$ goes to zero when the distance between particles is very small and approaches one in bulk systems at large interparticle separations. A simple and very efficient model for $f(r)$ is provided by the McMillan function

$$f(r) = \exp \left[ -\frac{1}{2} \left( \frac{b}{r} \right)^5 \right],$$

(13)

with a parameter $b$ that can be optimized in a separate variational Monte Carlo (VMC) calculation, and that is different for each species adsorbed in the nanotubes.

When a quantum liquid is adsorbed on a surface one has also to include in the Hamiltonian interactions between the atoms and the substrate. Also, the trial wave function for importance sampling has to avoid situations in which the adsorbed species is too close to the nanotube. This is usually made by multiplying the Jastrow factor $\Phi_J$ (12) by another function, $\Phi_C$. For that, we have several possibilities. One of them is to consider the nanotube as a confining structure that interacts with a given particle as a whole. In that case, we can use

$$\Phi_C = \prod_i \Phi_i,$$

(14)

$\Phi_i$ being the result of solving the Schrödinger equation for a single particle ($^4$He,$\text{H}_2$ or $\text{D}_2$) under the potential defined by the entire nanotube. A second option consists in using an educated guess. For instance, if the tube is narrow enough (as in a (5,5) case), $\Phi_i$ could be taken as a Gaussian

$$\Phi_i = \exp[-a(x_i^2+y_i^2)]$$

(15)

where $a$ is a variational parameter to be properly optimized, and $x_i$ and $y_i$ are the coordinates of the $i$-atom or molecule with respect to the center of the tube. The use of this expression in a (5,5) case, with a proper $a$, provides a trial function of high quality, as can be seen in the corresponding energy variance (see below).

The third possibility is to use a Jastrow model similar to $\Phi_J$ (12) but with a value for $b$ adapted to the C-He interaction. In this case,

$$\Phi_i = \prod_j \exp \left[ -\frac{1}{2} \left( \frac{b}{r_{ij}} \right)^5 \right]$$

(16)

where $j$ indicates here the positions of all the carbons in the corresponding nanotube or bundle. In any case, the whole trial wave function is the product $\Phi_J \Phi_C \Phi_S$ where

$$\Phi_S = \prod_i \exp \left[ -a_s(x_i-x_{\text{site}})^2 - a_s(y_i-y_{\text{site}})^2 - b_s(z_i-z_{\text{site}})^2 \right].$$

(17)
The coordinates $x_{\text{site}}$, $y_{\text{site}}$, and $z_{\text{site}}$ are the lattice positions in the crystal structure, and are different for each atom or molecule in the quantum solid. The parameters $a_s$ and $b_s$ can be optimized in the same way than the ones in previous $\Phi$'s. This form of the trial function (Nosanow-Jastrow) can also be used when we want to localize the adsorbed species in some way, not necessarily according to a crystal pattern.

The last required microscopic input to describe the systems we are dealing with is the interaction potential between the different species inside or around the nanotube. This whole interaction is the $V(R)$ term in the Schrödinger equation (2), and consists of two parts. The first one is the interaction between any pair of adsorbate atoms or molecules. In all cases described in the present work, the He-He potential was taken from Ref. [9], while the $\text{H}_2-\text{H}_2$ interaction was described by the Silvera potential [10]. The second part is the tube (or set of tubes)-adsorbate potential. To define it, we can consider the nanotube as a whole, or simply sum up all the individual carbon-adsorbate contributions. The former case is simply the result of averaging over the latter, and has the advantage of being computationally less expensive than to take into account all the carbon atoms in their particular positions. However, it has the important drawback of considering as equal tubes that have the same radius but different $(n,m)$ indexes. The most common choice for the individual C-He [11] and C-H$_2$ interactions [12] is the Lennard-Jones (LJ) model. The averaged potential using LJ for a single tube-adsorbate interaction has the form [13]

\[
3\pi\theta\varepsilon\sigma^2 \left[ \frac{21}{32} \left( \frac{\sigma}{R} \right)^{10} M_{11}(x) - \left( \frac{\sigma}{R} \right)^{4} M_{5}(x) \right],
\]

where $\theta$ is the surface carbon density in a graphene sheet ($0.38\ \text{Å}^{-2}$), $R$ is the radius of the cylinder, and $x = r/R$ with $r$ the distance to the center of the tube. The functions $M_n(x)$ are of the form

\[
M_n(x) = \int_0^\pi d\phi \frac{1}{(1 + x^2 - 2x\cos\phi)^{n/2}}.
\]

In the remaining of this review, we report results obtained by applying the diffusion Monte Carlo method to the problem of adsorption of $^4\text{He}$, $\text{H}_2$ and $\text{D}_2$ inside or outside carbon nanotubes of different radii.

### 3 $^4\text{He}$ adsorbed in carbon nanotubes

Bulk helium is the paradigm of a quantum liquid, basically because it remains liquid at zero pressure all the way to 0 K. This is the reason why the studies of how a quantum liquid behaves when confined inside or close to a nanotube have been made primarily with $^4\text{He}$. In this section, we will describe many-body DMC calculations performed in those environments.

The most extreme form of confinement that one can impose upon a set of particles is to force them into a one-dimensional (1D) array. Since, as mentioned above, a nanotube is essentially a long cylinder, this is easily obtained by choosing a tube with small enough radius. Obviously, the nanotube should be opened in
some way, say mechanically or chemically. Since curving the graphene sheet to create a nanotube imposes a certain degree of tension upon the C-C bonds the narrowest stable isolate nanotube of the (n,n) type is the (5,5) one, with a radius of 3.42 Å. This is the distance between the center of the carbon atoms in the rolled up graphene layer and the center of the structure. Since the Lennard-Jones \( \sigma \) parameters for the He-He and C-He interaction are 2.556 and 2.74 Å, respectively, this means that inside a (5,5) tube there is not room enough to have two He atoms sharing the same plane perpendicular to the tube axis, i.e., \(^4\)He should behave in this environment as a (quasi) 1D system.

In Fig. 1, we report DMC results for the equation of state of \(^4\)He in a purely 1D environment and inside a (5,5) tube at low densities. For the pure 1D array of atoms, the trial function was of Jastrow type. When the nanotube was included, it was modeled as a smooth cylinder with an averaged over C-He potential and a trial function that was the result of multiplying \( \Phi_j \) for a set of as many Gaussians as helium atoms in the simulation cell (see previous Section) \[14\].

In that figure, we observe two \( y \) scales, corresponding to the energies per atom \( (E/N) \) for \(^4\)He in a pure 1D system (right) and inside a smooth (5,5) tube (left). The abscissa is the number of atoms per unit length (\( \lambda \)). The curves have been drawn to make the lowest density point inside the tube to coincide with the 1D value for the same linear density. This is basically similar to subtract from all the tube energies the binding energy for a single \(^4\)He in a tube (429.97 K). From Fig. 1 we can infer two main results. First, helium inside this narrow tube is not a pure

![Fig. 1](image-url)  
**Fig. 1**  Energy per particle \( (E/N) \) versus the linear concentration \( (\lambda) \), for a strictly one dimensional system (open squares, right energy scale), and a (5,5) nanotube (full squares, left energy scale).
Table 1 Parameters of Eq. 18 for 1D helium and helium inside a (5,5) smooth tube.

| Parameter       | 1D $^4$He | $^4$He in a tube |
|-----------------|-----------|------------------|
| $\lambda_0$ (Å$^{-1}$) | 0.062 ± 0.001 | 0.079 ± 0.003 |
| $e_0$ (K)       | -0.0036 ± 0.0002 | -429.984 ± 0.001 |
| $A$ (K)         | 0.0156 ± 0.0009  | 0.048 ± 0.006   |
| $B$ (K)         | 0.0121 ± 0.0008  | 0.0296 ± 0.009  |
| $\chi^2/\nu$   | 2.2         | 0.24             |

1D system since the equation of state is different in both cases. Second, the many-body ground state is a liquid in both situations since both curves present an energy minimum corresponding to a density greater than zero. A third-order polynomial fit to DMC energies,

$$e = e_0 + A \left( \frac{\lambda - \lambda_0}{\lambda_0} \right)^2 + B \left( \frac{\lambda - \lambda_0}{\lambda_0} \right)^3,$$

allows us to obtain the parameters $\lambda_0$ (the equilibrium density) and $e_0$ (the energy per particle at equilibrium). These parameters are given in Table I. The minimum in the equation of state is so shallow that its location and value is much dependent on the He-He interatomic potential: using the HFFHDE2 Aziz potential [15] the equilibrium point of 1D $^4$He is $\lambda_0 = 0.036$ Å$^{-1}$ and $e_0 = -0.0017$ K [16].

The comparison between $\lambda_0$ and $e_0$ ($-0.018$ K in the tube case, subtracting the infinite dilution limit) indicates that the energy minimum is deeper and located at a bigger linear density in a tube than in a pure 1D system. The reason is that even though the distance between first neighbors is similar in both environments, it is possible for the second neighbors inside the nanotube to be close to each other by creating a zig-zag structure. This small effect would increase both $\lambda_0$ and $e_0$ and serve to create a quasi-one-dimensional array of atoms instead of a pure 1D one. A behavior completely similar to this for $^4$He was found in the cases of $^{2}$H [18] and $^{2}$D [19], the only difference being that these latter ones are closer to the corresponding 1D systems. Compared with $^4$He, $\lambda_0$ and $e_0$ in $^2$H and $^2$D are larger and deeper, respectively, both in pure 1D systems and inside narrow tubes (see Sec. 4). This trend also follows for Ne, of which a purely 1D DMC calculation is reported in Ref. [20].

Considering a carbon nanotube as a smooth cylinder is clearly an approximation [21]. To check how good it is, we can make use of Fig. 2. There, we report the equation of state for the same (5,5) tube, but now considering the real nanotube by taking into account all the C-He interactions, both in the trial function and in the potential, i.e., we consider a fully corrugated carbon nanotube. As in the case of Fig. 1, the infinite dilution limits are subtracted in both curves to work in the same scale. This is necessary since that binding energy is appreciably different in the smooth (429.97 K) and corrugated (429.51 K) tubes. There is also another difference with Fig. 1: the density in the x axis is taken to be the volume density, i.e., $\lambda/(\pi R^2)$. The results of a fit similar to that of Eq. 20 indicates that in a corrugated structure $\lambda_0$ is nearly the same (0.077 versus 0.079 Å$^{-1}$ in the smooth tube), but $e_0$ is reduced $\sim 25\%$ ($-0.013$ versus $-0.018$ K). This means that to include the corrugation makes the system closer to a pure 1D one.
Fig. 2 Difference between the total adsorption energy and the binding energy for a single helium atom in a (5,5) tube. Full line, results for a smooth C-He potential, full squares and dashed line, same for a corrugated C-He interaction.

Another aspect to be taken into account in this (5,5) tube is the possibility of having a phase transition from a liquid to a solid phase when the density (and the pressure) increases, just like in the bulk case. Evidences of a phase transition of this kind, only possible in 1D at zero temperature, appear in a variational calculation of 1D $^4$He\cite{17}. A solid phase is defined, as indicated above, as one in which the atoms are confined close to particular positions. In quasi-one-dimensional systems, these positions were chosen as regularly spaced in the $z$ direction (the one of the long axis of the nanotube). A comparison between the DMC energies for the liquid and solid phases is given in Table 2. One can see that in both systems, the energy per particle when localization is imposed ($a_s = 0, b_s \neq 0$ in Eq. 17) is below the corresponding to a liquid structure ($a_s = b_s = 0$) for lineal densities greater than 0.358 Å$^{-1}$. Unfortunately, the energy differences between the liquid and the solid structures at very high densities are not big enough to allow us to perform a Maxwell double-tangent construction to obtain the limits of the coexistence region. This probably means that the change is quasi continuous. In any case, this transition is only possible at 0 K.

Apart from the corrugation, there are other influences we should take into account to describe the adsorption of gases in quasi 1D systems such as (5,5) tubes. For instance, carbon nanotubes are known to have a certain amount of defects\cite{22,23,24}, single carbon vacancies being among the simplest of them. In principle, the most stable structure when a carbon atom is removed from the carbon layer conforming a nanotube is the so-called 5-1DB defect. This is the result of
two of the possible dangling bonds recombining with each other to form a pentagon and leaving the third one unchanged. There are two forms of doing this, termed symmetric and asymmetric. It appears that for \((n,n)\) nanotubes the last one is the most stable \([25, 26, 27, 28]\). Diffusion Monte Carlo calculations were carried out to check if \(^4\)He atoms are allowed to enter this narrow system when a single vacancy is present \([29]\). To check that, a single atom of the gas was placed at \(z=0\) (the beginning of a simulation cell of length 49.2 Å) and left to evolve until no appreciable change in the density profiles (see Fig. 3) was found. The case of \(^{20}\)Ne is also contemplated. In both cases, the analysis of Fig. 3 indicates that, while there is no problem for those atoms to enter and explore all space inside a defect-less (5,5), the presence of a single vacancy of any kind would bar the loading of those tubes.

A (5,5) tube is not the only environment narrow enough to produce a quasi-one-dimensional system. Another possibility is the interstitial channel (IC) located among every three carbon nanotubes when they associate to create a bundle. A section of a bundle of three tubes is shown schematically in Fig. 4. This channel is even narrower than a (5,5) tube, and its conformation depends on the particular nanotubes that surrounds it \([30]\). If a perfect (with no defects) IC formed by three (10,10) nanotubes is considered, the same type of calculations made for a (5,5) tube can be performed in order to know if it is possible to have helium inside those IC’s. However, in this case it should taken into account the fact that the carbon nanotubes could be displaced with respect to each other, creating different potential energy landscapes to be felt by the helium atoms.

The results are shown in Fig. 5. There, two different density profiles were considered for a defect-less tube. The smoother one is the corresponding to the minimum corrugation (the configuration of the carbon nanotubes in which the helium atoms feel the potential along the \(z\) direction to be smoothest) and it is similar to the one of a (5,5) tube. The profile with more structure corresponds to the opposite case of maximum corrugation. In any case, one can observe that a \(^4\)He atom has no problem to enter an IC located among three (10,10) tubes. The same behavior was found for \(\text{H}_2\) \([30]\), for which several others possibilities were checked (4-tube IC’s, and IC’s formed by 3 different \((n,n)\) tubes).

Obviously, once helium atoms enter the defect-less IC, they can form a quasi-one-dimensional arrangement in a similar way to the one already considered for the (5,5) tube \([31, 32]\). In principle, the details of the equation of state should depend on the particular kind of tubes that form the IC, and on their positions with respect to each other. However, in the same way than in the narrow tube considered above, a smooth averaged tube could be considered, in the hope that the interaction with the \(^4\)He atoms is at least qualitatively similar to that of the

| \(\lambda (\text{Å}^{-1})\) | \(E/N\) (1D, liquid) | \(E/N\) (1D, solid) | \(E/N\) (T, liquid) | \(E/N\) (T, solid) |
|---|---|---|---|---|
| 0.406 | 123.726 ± 0.012 | 123.361 ± 0.012 | -350.155 ± 0.030 | -350.20 ± 0.02 |
| 0.380 | 67.070 ± 0.011 | 67.000 ± 0.009 | -382.282 ± 0.016 | -382.321 ± 0.012 |
| 0.358 | 37.602 ± 0.008 | 37.596 ± 0.007 | -401.873 ± 0.013 | -401.844 ± 0.010 |
| 0.338 | 21.881 ± 0.007 | 21.904 ± 0.005 | -413.091 ± 0.014 | -413.041 ± 0.012 |
| 0.320 | 13.240 ± 0.005 | 13.258 ± 0.006 | -419.551 ± 0.011 | -419.493 ± 0.010 |

Table 2 Energies per particle at large \(\lambda\) for the quasi one dimensional systems considered in the text. All the energies are in K.
corrugated structures. The trial function for a set of three smooth (10,10) tubes is also qualitatively different from the ones considered in Sec. 2,

\[ \Psi(R) = \prod_{i<j}^{N} \exp \left[ -\frac{1}{2} \left( \frac{b}{r_{ij}} \right)^5 \right] \prod_{i}^{N} \prod_{n=1}^{3} \exp \left[ -\frac{1}{2} \left( \frac{a}{r_{in}} \right)^5 \right] \] (21)

i.e., it has a Jastrow-type term (the one with the double productory) that takes care of the interaction of \(^4\)He with the walls of the three tubes forming the interchannel.

The equation of state in the low density regime is shown in Fig. 6. There, we can see the comparison between the results of an IC, a (5,5) tube and a pure 1D system. We can see that the energies per helium atom in the IC are a bit closer to a 1D line than in the case of a cylindrical environment. A least-squares fit to the DMC energies in this environment with the same equation considered previously (Eq. 20), renders \( \lambda_0 = 0.076 \pm 0.004 \, \text{Å}^{-1} \), and \( (E - E_B)/N = 0.010 \pm 0.001 \, \text{K} \). This means that the atoms inside an interchannel formed by three tubes form a quasi-one-dimensional arrangement that is similar to that of a (5,5) tube.

In the case of interchannel adsorption there is still another issue to consider. A bundle of carbon nanotubes is rarely formed by three tubes, what means that it is virtually impossible to have an isolated IC in the same way that we can have an isolated (5,5) tube [33]. For instance, we can expect a certain influence in the equation of state of helium atoms adsorbed in neighboring channels of the same

![Graph showing probability density of single atom positions in (5,5) tube](image)
Fig. 4 Sketch of a section of a bundle including three nanotubes together with a depiction of the location of an interstitial and a groove adsorption locations.

bundle. In a regular bundle made of (10,10) carbon nanotubes, a simple geometrical calculation indicates that the minimum distance between a pair of these channels is about 9.8 Å, implying that the influence of filled neighboring tubes could be accurately described by a mean field approximation of the type

$$V_{mf} = \lambda \int_{-\infty}^{\infty} dx V_{He-He} \left( \sqrt{x^2 + d^2} \right), \quad (22)$$

with $d$ the distance between one channel and one of its neighbors and $\lambda$ the helium linear density. The total energy correction is obtained by summing up the contribution for channels with increasing $d$ values until the desired accuracy. Thus, the total energy per $^4$He atom in the bundle is of the form $E(\text{IC})/N + V_{mf}$. The mean-field approach assumes that the correlation effects between interchannels are negligible, the net influence being only the increase of binding energy due to the van der Waals attractive tails. This has been checked to be essentially correct [19]. The difference between the equations of state of a single IC and a set of them is given in Fig. 7. We can see that the overall effect is to increase the binding energy and the equilibrium density of the system. This behavior was also observed in H$_2$ [35] and Ne [20, 36].

In the previous calculations we have assumed that $^4$He atoms can be effectively adsorbed inside the interchannels and, in fact, this would be the case within perfect defect-less tubes. However, in view of Fig. 5, this could be not fully realistic. Besides the already discussed case of a no vacancy tube, in Fig. 5 it is displayed what happens when a 5-1DB asymmetric vacancy (the most stable one) is introduced in the center of a IC of a tube 49.2 Å long. Two cases are considered, one in which the hole is directly below the trajectory of the adsorbed atom, and another in which the defect is the one furthest away of this position. We can see than in
the first case the helium density profile vanishes beyond the place in which the defect is located (see discussion above), what indicates that the adsorption in this case is prohibited. The reason is that once the atom reaches that position, it cannot progress further and blocks the way to other atoms. However, when the defect is further away, the helium atoms are able to pass the potential barrier, leaving a minimum in the density profile close to the vacancy position. Since, as mentioned above, all nanotubes are thought to have a certain fraction of defects, and some of them are just inside an IC, this means than most of the IC’s will be at least partially empty.

Nevertheless, if the tubes are wide enough it is sure that helium can enter inside them. For instance, we can see what happens in the case to a (10,10) tube, whose radius is 6.8 Å. Obviously, we can only consider open-ended tubes, i.e., those whose caps have been removed by chemical or mechanical ways. Intuitively, one can think that $^4\text{He}$ atoms would first go close to the wall of the nanotube forming a cylindrical shell. This layer creates an empty space in the center of the tube in which additional helium atom can then enter. DMC calculations of this system were carried out in Ref. 37. In principle, all the C-$\text{He}$ interactions were taken into account, both in the potential energy and in the trial function, the latter being a product of the forms already described in Eq. 14 and Eq. 16. i.e., a product of C-$\text{He}$ Jastrow functions and the one-body solution of the Schrödinger equation for a smooth tube.
Fig. 6  Energy per $^4\text{He}$ atom inside an IC formed by three smooth (10,10) tubes in the density range between 0 and 0.15 Å$^{-1}$. Open squares, 1D; filled squares, $^4\text{He}$ in a interchannel of (10,10) tubes; open circles, $^4\text{He}$ in a (5,5) tube. The dashed line is a polynomial fit to the IC results. The binding energy of a single $^4\text{He}$ atom to the interchannel (323.41 K) has been subtracted.

Fig. 8 displays results obtained for a single liquid shell (circles) versus a single solid shell close to the wall (full squares). The density in the abscissae is simply the number of atoms divided by the volume of the tube, considering the radius as to be the distance between the center of the tube and the center of the graphene sheet; in this tube, 6.8 Å. As indicated above, a solid is a phase in which the atoms are located around fixed positions. In practice, this means that the trial function for a solid phase includes a set of localized Gaussians of the kind shown in Eq. 17. Fig. 8 suggests that at low densities the most stable phase is a liquid, but this changes at high enough densities. However, to determine if a single solid layer is the most stable structure, all the possibilities have to be considered, in particular the one where one has simultaneously a liquid layer close to the wall and an additional liquid layer on top of it (circles in Fig. 8). From data in Fig 8, we can see that a single solid has very similar energy per atom than a two-layer liquid of the same density. In addition, at higher densities than the ones displayed in Fig. 8, another phase made of a solid layer closer to the wall and a liquid part in the center is observed.

In order to establish rigorously which phases are stable, a double-tangent Maxwell construction should be made. In practice, this means to display the free energies (energies in the 0 K limit) per atom for each considered phase (single
layer, and double layer liquid, single layer solid and single layer solid plus a liquid) versus the inverse of the density and draw a single line that connects zones with the same slope. Since the slope is minus the equilibrium pressure, if there are several possibilities, the line with the minimum slope should be chosen. The phases connected by that line will be the stable ones, and the equilibrium densities will be the ones that share the same slope with the line drawn.

This procedure is shown in Fig. 9 for the (10,10) tube: the dashed line is a double tangent construction between the single-layer liquid and the single-layer solid with a liquid on top. This line implies a transition between a low density phase of $2 \times 10^{-2} \, \text{Å}^{-3}$ and another of $2.7 \times 10^{-2} \, \text{Å}^{-3}$. The transition pressure would be of 430 atm. However, the data cannot allow us to distinguish between this alternative and to draw two transition lines, one between a single-layer liquid and a double-layer liquid, followed by other between this last dense liquid and the solid with a liquid on top. In this scenario, in addition to the already mentioned equilibrium densities, we will have small a window with a two-layer liquid at around $2.5 \times 10^{-2} \, \text{Å}^{-3}$. The one-shell liquid–two-shell liquid transition pressure would be of 420 atm. Our results show that the high-pressure stable phase in the density range considered is a solid with a liquid on top. This one-layer shell liquid in a cylindrical arrangement is unique, since simulations of helium in wider Gelsil pores indicate that the first layer is a 2D solid [38].
As in the previous analysis of the (5,5) tube, it is relevant to take into account the influence of the other nanotubes within a bundle arrangement. Now, for the (10,10) tubes each cylinder is surrounded by six others, with a minimum distance between centers of 17 Å [39]. The influence that the surrounding tubes have in the energy per helium atom in a particular cylinder can be estimated by the mean-field expression

\[
E_{\text{correction}} = 6 \int_{x'} \int_{y'} d(x', y')dx'dy'
\]

\[
\times \int_{0}^{\infty} \int_{x} \int_{y} R(x,y,z)V(x,y,z,x',y')dxdydz ,
\]

where \(d(x', y')\) represents the normalized probability of finding an \(^4\)He atom at coordinates \(x'\) and \(y'\) for any \(z\) position in the first tube. \(R(x,y,z)\) is the radial density function of helium atoms in the second tube \((x,y,z)\) and \(V(x,y,z,x',y')\) is the helium-helium Aziz potential used in our simulations [9]. This integral has been performed for all the helium densities corresponding to stable phases and verified that its net effect was to decrease the energy per atom, but in negligible amounts.

For instance, in the solid + liquid phase, the energy per atom in an isolated tube was \(-98.41 \pm 0.09\) K, with an effect due to the other tubes of \(-0.11\) K. For lower helium densities the effect was even smaller.

Unfortunately, all this theoretical effort cannot be trusted at present by reliable experimental data. One of the main reasons for explaining the difficulties of experiment is that for helium to enter inside a tube this has to be opened. However, there
is a place in which quantum gases are readily adsorbed, i.e., the external surfaces of a bundle of carbon nanotubes. In this case there are a number of experimental measures \[22, 40, 41, 42, 43, 44, 45, 46, 47, 48\] one can compare the theoretical results with. Among the theoretical studies of this particular adsorption, we would mention the case of a single atom or a small cluster in a groove \[49, 50\] and a full DMC calculation on the same subject \[51, 52\]. This last calculation analyzed all the possible phases of \(^4\)He on the outer surface of a (10,10) carbon-nanotube bundle, from a pure 1D one in between two cylinders (what is termed a groove), to a two layers shell in which the helium layer closer to the surface of the tubes is a quasi-two-dimensional solid.

Fig. 10 displays the binding energy of a single \(^4\)He atom on the groove in between two (10,10) carbon nanotubes. Since all the C-He interactions are individually taken into account, that energy depends on the corrugation of the substance, in particular of the relative orientation of the two cylinders that form the groove. The additional trial function apart from the product of Eq. 12 and 14 is that of Eq. 17 with \(b_z = 0\). \(x_{\text{site}}\) and \(y_{\text{site}}\) are here the optimized coordinates for a single atom left to roam freely along the length of the groove (\(z\) coordinate).

The absolute maximum and minimum helium energies at 0 K considering all rotations and translations of both cylinders are indicated by two open squares and correspond to binding energies of \(227.54 \pm 0.01\) and \(201.85 \pm 0.01\) K, respectively. These compare favorably with the experimental results given in Ref. \[22\] (range between 210 and 250 K), and Ref. \[44\] (212 K, to be compared to our aver-
Fig. 10  Energy per helium atom on top of a groove in the infinity dilution limit (full squares). A dashed line joints the results obtaining by fixing the orientation of a cylinder and rotating the other one. Additional rotations and displacements in the $z$ direction (crosses) are considered. Open squares represent the maximum and minimum values of $^4$He binding energies.

The discrepancies of the binding energies for a single atom mean that the equation of state of a full array of atoms on top of a groove is going to be different depending on the particular orientations and displacement of the tubes forming the groove with respect to each other. To study those cases, the same trial function and simulation cell than in the infinite dilution limit was used. Fig. 11. shows the results for three different tube arrangements (full squares, maximum binding energy, $227.54 \pm 0.01$ K; open squares, minimum binding energy, $201.85 \pm 0.01$ K; open circles, an intermediate case). These three calculations are fairly representative of all the simulations done: most cases correspond to a quasi-one dimensional liquid weakly bounded, while the third case represents the minority that is a gas. The system is a liquid or a gas depending on the corrugated structure of the groove, not on the binding energy. The different relative orientations of the tubes imply also that the filling of the grooves will go from the more binding to the less binding ones up to completion. This quasi-one dimensional phase has been detected experimentally [45, 46].

Fig. 12 shows the next step of the absorption process when more helium atoms are introduced. In that figure, the $x$ axis is the inverse of the surface density. The area of the surface was taken to be as all the available space located at 9.5 Å from the center of any of the tubes in the groove. This defined a distance between
any adsorbed particle and the carbon shell which produced the maximum binding energy per particle in all the phases considered. In Fig. 12 those phases are the 1D one on a groove (already considered in the previous figure), what it is called a three-stripes phase (similar to the previous one but with two other lines of atoms forming an approximately triangular section) and a 2D liquid monolayer covering all the external surface of the bundle. The corresponding trial function for the three-stripes phase is the product of the ones given in Eq. 12, 14 and 17 with $b_s = 0$ and adequate elections for $x_{\text{site}}, y_{\text{site}}$, while the corresponding to the 2D liquid substitutes Eq. 17 in the product by

$$
\Phi_L = \prod_i \exp \left[ -a_L (r - r_{\text{center}})^2 \right], \quad (24)
$$

where $a_L$ is a parameter variationally optimized and $r$ is the distance between any of the adsorbed atoms in the liquid phase and the center of the nanotube. On the other hand, $r_{\text{center}} = 9.5 \, \text{Å}$ in agreement with the above comment.

Since the actual binding energies will depend on the particular configuration of the groove, only the most extreme cases of minimum and maximum binding energies per particle were considered for each of the three phases already introduced. Within this frame, and from the energy per particle shown in Fig. 12, one expects the quasi 1D phase to be filled before the three stripes (3S) phase starts to do so. That is the reason why the Maxwell construction line (lower full line) is made from the minimum binding energy of the 1D phase to the maximum binding

Fig. 11  Energy per helium atom for three representative cases of quasi 1D arrangements. In all cases, binding energies for the infinite dilution limit were subtracted to afford an easier comparison.
Fig. 12  Maxwell constructions for different helium phases up to the monolayer limit. Lower set of curves, quasi 1D system; medium set, 3D phase; upper couple of curves, liquid monolayer. In all cases, full squares represent the results for the minimum binding energies per particle and open squares for the maximum ones. Dashed lines are guides-to-the-eye. Open circles correspond to an unstable zigzag phase.

of the 3S one. The corresponding equilibrium densities are $1.4 \times 10^{-2}$ Å$^{-2}$ (1D) to $3.9 \times 10^{-2}$ Å$^{-2}$ (three stripes). This means that the average distance between helium atoms in the 1D phase at complete filling is 3.4 Å, the same result found experimentally for a bundle of (8,8) tubes [46]. It can also be seen that a zigzag phase [53] (two stripes of helium instead of one or three on top of groove) is unstable. The upper full line corresponds to the Maxwell construction between a 2D liquid phase and the three stripes one. The corresponding equilibrium densities are $6.2 \times 10^{-2}$ Å$^{-2}$ and $3.9 \times 10^{-2}$ Å$^{-2}$. The latter one is the same than for the previous transition, indicating a very narrow stability range for the 3S phase. This liquid monolayer is akin to the single layer liquid already described above for helium inside a (10,10) nanotube, being both the only stable ground-state 2D liquids in contact with a carbon monolayer. The other possibility, $^4$He on flat graphene, was found to have a solid ground state [54]. We know that the liquid phase is the stable one with the help of Fig. 13: the full squares (solid monolayer) are always on top (higher energies) than other phases with the same density.

The results for the minimum energy structures are the actually shown in Fig. 13. Open circles correspond to a quasi 1D phase on top of a liquid monolayer of 0.103 Å$^{-2}$. Full circles represent the binding energies of an structure formed by an eight-channel solid monolayer in contact with the carbon shell and density 0.110 Å$^{-2}$ and a 2D liquid monolayer on top of it located at a distance of 12.6 Å to the center of closest tube. No other structure with lower energy in this density range
Fig. 13 Phases of helium in the groove at high densities: open squares, 2D liquid monolayer; full squares, 2D solid monolayer; open circles, 1D phase on top of a liquid; full circles, two layered-phase.

was found. Neither of the following possibilities is found: a double-liquid layer, a three-stripes second-layer phase, and a quasi 1D phase on top of a solid layer. The second layer quasi 1D phase was found experimentally in the case of Ne [48], but has not been identified for helium. There is not any experimental indication of a solid + liquid phase at 0 K. The experimental results on the single monolayer seem to point to a solid, not to the liquid found here [46]. The difference could be due to shortcomings of the simulation, (for instance, a too small simulation cell) or to the fact that the experimental results are for a bundle of (8,8) tubes instead of the (10,10) considered here.

4 Quasi-one-dimensional H\textsubscript{2} and D\textsubscript{2} in carbon nanotubes

The physisorption of hydrogen [12, 55, 56, 57, 58] in the quest for a fuel cell efficient enough to be used as a pollution-free energy carrier has been studied in different environments. Single wall carbon nanotubes (SWCN) with diameters of the order of a nanometer have been proposed as one of the possible candidates to approach the pursued level of packing [55]. Besides its technological relevance, the case study of H\textsubscript{2} adsorbed in carbon nanotubes offers the appealing possibility of the existence of a homogeneous liquid phase at zero temperature. It is worth noticing that both, bulk and two-dimensional H\textsubscript{2}, are solid in the zero-temperature limit.
Molecular para-hydrogen at zero temperature was studied [18] using the DMC method in a one-dimensional (1D) array and inside a single walled carbon nanotube (T) of radius $R = 3.42 \text{Å}$ (a (5,5) armchair tube [59]) that is one of the narrowest experimentally obtained [60]. $\text{H}_2$ molecules interact via the isotropic semiempirical potential from Silvera and Goldman (SG) [61] that has been extensively used in path integral Monte Carlo (PIMC) and DMC calculations [62]. The SG is a pair potential that incorporates to some extent the effect of three-body interactions by means of an effective two-body term of the form $C/\rho^9$. On the other hand, the isotropy of the potential is well justified if one considers that at very low temperatures almost all the $\text{H}_2$ molecules are para-hydrogen species, i.e., they are in the $J=0$ rotational state. In the simulations of $\text{H}_2$ inside a nanotube, we use the cylindrically symmetric potential suggested by Stan and Cole [11]. Considering the Lennard-Jones parameters of the pair $\text{C-H}_2$ interaction $\sigma = 2.97 \text{Å}$ and $\varepsilon = 42.8 \text{K}$, the symmetric potential felt by a $\text{H}_2$ molecule in a (5,5) tube has a depth of $42\varepsilon$, three times larger that the attraction of the same molecule in a flat graphitic surface.

In Table 3, we show DMC results for the energy per particle in both 1D and inside a (5,5) nanotube, and for the liquid and solid phases. The comparison between the energies of both phases at the same density shows that their difference changes sign in going from $\lambda = 0.312 \text{ Å}^{-1}$ to $\lambda = 0.304 \text{ Å}^{-1}$ in 1D and from $\lambda = 0.320 \text{ Å}^{-1}$ to $\lambda = 0.312 \text{ Å}^{-1}$ in the tube. Above these densities, the system prefers to be localized in a solid-like structure with a difference $|E(s) - E(l)|$ that increases with $\lambda$. When the density decreases the liquid phase is energetically preferred and again the size of the difference $|E(s) - E(l)|$ increases when $\lambda$ diminishes. The density value at which this difference becomes zero is estimated to be $\lambda = 0.309 \text{ Å}^{-1}$ in 1D and $\lambda = 0.315 \text{ Å}^{-1}$ in the tube, being not possible to distinguish between freezing and melting densities.

Inside the nanotube (T), the energies are much more negative that in 1D due to the strong attraction of the carbon substrate: the binding energy of a single $\text{H}_2$ molecule in the tube is $E_b = -1539.87 \pm 0.11 \text{ K}$. Looking at the T-energy results contained in Table 3 one realizes that also in this case a transition occurs at a density very close to the 1D one. It is remarkable that both in 1D and T, $\text{H}_2$ remains liquid below the liquid-solid transition density, and thus a homogeneous liquid phase at zero pressure is predicted. That result contrasts with the theoretically and experimentally well established solid phase in 3D [63] and the 2D solid phase predicted by a PIMC calculation [64].

The equations of state of liquid $\text{H}_2$ near the equilibrium density for both the 1D and T systems are shown in Fig. 14. In order to make the energy scales compatible we have subtracted the single binding energy $E_b$ to the T results. The lines in
the figure correspond to third-degree polynomial fits. The equilibrium densities in both systems are the same considering their respective uncertainties but the binding energy $e_0 = e(\lambda_0)$ is larger when $\text{H}_2$ is inside the nanotube.

In Fig. 15, the density dependence of the pressure for both the 1D and T systems is reported from equilibrium up to the liquid-solid transition density. Results for $^4\text{He}$ are also plotted for comparison. Both in $\text{H}_2$ and $^4\text{He}$ the pressure increases faster in the 1D geometry ($P_\lambda$) than in the tube ($P$) due the transverse degree of freedom that particles have in the latter case (notice the proportionality between the scales of $P$ and $P_\lambda$ in Fig. 2, $P_\lambda/P = \pi R^2$). At a given density $\lambda$, the difference between the T and 1D pressures is smaller in $\text{H}_2$ than in $^4\text{He}$. The one-dimensionality of $\text{H}_2$ inside the nanotube is observed in all the liquid regime in contrast with $^4\text{He}$, in which the departure from such an idealized model already appears around the equilibrium density and increases significantly with $\lambda$ (see Section 3). Also apparent from Fig. 15 is a much smaller compressibility in $\text{H}_2$ than in $^4\text{He}$.

The DMC method has also been used to study the influence of both the interparticle potential and mass on the thermodynamic behavior of the isotopes of molecular hydrogen, $\text{H}_2$ and $D_2$, adsorbed inside a carbon nanotube [19]. Since the electronic structure of molecular deuterium and hydrogen is the same, the $D_2$-$D_2$ interparticle potential is identical to the $\text{H}_2$-$\text{H}_2$ one. This is equally true for the particle-tube interactions. Moreover, the mass of the $D_2$ molecule is very similar
Fig. 15 1D ($P_\lambda$, solid line) and T ($P$, dashed line) pressures for $\text{H}_2$ and $^4\text{He}$ as a function of the linear density.

to that of a $^4\text{He}$ atom. Thus, by comparing the deuterium results with those for helium, the effect of the respective potential wells can be inferred. On the other hand, the influence of the zero-point energy in the thermodynamic behavior of a quasi-one dimensional array can be drawn from the comparison between the deuterium and hydrogen results.

At low densities, the dominant effect is due to the binding energy of a single molecule to the nanotube. From our DMC calculations the binding energy of a single molecule inside a carbon tube turns out to be, for the (5,5) tube, $-1539.87 \pm 0.11$ K for $\text{H}_2$, and $-1605.23 \pm 0.01$ K and $-1624.37 \pm 0.01$ K for $^2\text{H}_2$ and $^3\text{He}$, respectively. The increase in the binding energy with the mass comes from the combination of two features: a decrease in the kinetic energy, mainly due to a direct effect of the mass ($m_{^2\text{H}_2}/m_{^4\text{He}} \approx 1/2, m_{^3\text{He}}/m_{^3\text{He}} \approx 2/3$), and a simultaneous increase of the potential energy. Although those energies correspond to the ground state of single molecules at 0 K, they constitute a very good estimation in the limit of infinite dilution at nonzero temperatures. From the above binding energies one can extract information on the selectivity in the adsorption inside the nanotube. Following Ref. 63, the selectivity of isotope 2 with respect to isotope 1 can be defined by the quotient $S = (x_1/x_2)/(y_1/y_2)$ with $x_i$ ($y_i$) the nanotube (bulk) mole fractions. It has been proved that in the limit of zero pressure the selectivity $S_0$ is very well approximated by

$$S_0 = \frac{m_2}{m_1} \exp \left( \frac{E_1 - E_2}{T} \right),$$

(25)
where $E_i$ is the binding energy of isotope $i$. Considering $T = 20$ K, as in Ref. [65], we obtain $S_0(T_2/H_2) = 22.8$ and $S_0(T_2/D_2) = 1.7$ for the (5,5) tube. The selectivity is especially high in the case $T_2/H_2$ due to the sizeable difference in binding energies between the two isotopes, $E_{T_2} - E_{H_2} = -84.5$ K. That large selectivity, which is a purely quantum effect, has been proposed in Ref. [65] to achieve an efficient isotopic sieving.

DMC energy results for both 1D $D_2$ and $D_2$ adsorbed in the (5,5) nanotube are displayed in Fig. 16. In order to show the two equations of state with the same energy scale, we have subtracted to the tube results the adsorption energy of a single molecule. In Fig. 16, the curves are polynomial fits to the DMC data, the optimal parameters for the tube being reported in Table 4. It can be seen that the equilibrium density for 1D $D_2$ and $D_2$ adsorbed in the (5,5) nanotube are almost identical. This is also true for the location of the spinodal points of $D_2$, $\lambda_{s1D}^{D_2} = \lambda_{s1D}^{D_2} = 0.2457 \pm 0.0003$ Å$^{-1}$.
Fig. 17 Two-body distribution function in the nanotube system, and in the $z$ direction. Solid, dashed, and dotted lines correspond to $\text{D}_2$, $\text{H}_2$, and $^4\text{He}$, respectively. All curves are calculated at their respective equilibrium densities $\lambda_0$.

$0.230 \pm 0.001 \ \text{Å}^{-1}$ and $\lambda_{\text{T}}^0 = 0.232 \pm 0.001 \ \text{Å}^{-1}$, which can be derived from the data contained in Table 4.

The energies in the respective equilibrium points ($\langle E/N \rangle_0$) are slightly different: the additional transverse degree of freedom only amounts to an increase of 0.091 K. This increase in the binding energy is nearly a factor two smaller than the one drawn from the DMC calculations for $\text{H}_2$ (0.172 K). In relative terms, the increase of the binding energy is only a 0.85% for $\text{D}_2$ versus a 3.5% for $\text{H}_2$. Therefore, the effects of the additional degree of freedom of the $\text{D}_2$ molecules in the radial direction inside the nanotube, which account for the enhancement of the binding energy, are reduced by the greater mass of the $\text{D}_2$ molecule with respect to the $\text{H}_2$ one. As a matter of comparison, it is illustrative to compare the effects observed in $\text{D}_2$ with the ones previously studied in $^4\text{He}$ using the same methodology and geometry. It is worth noticing that the masses of $\text{D}_2$ and $^4\text{He}$ are nearly the same whereas the interatomic potentials are sizably different. The DMC results show that the latter effect is completely determinant: in $^4\text{He}$ the relative difference mentioned above is 90%, two orders of magnitude larger than in $\text{D}_2$. Another minor effect that contributes to the one-dimensionality of molecular deuterium adsorbed inside the tube, is the larger hard-core size of the C-$\text{D}_2$ interaction ($\sigma_{\text{C}-\text{D}_2} = 2.97 \ \text{Å}$), versus the C-He one ($\sigma_{\text{C}-\text{He}} = 2.74 \ \text{Å}$). The mass versus potential effects can also be seen in the value of the equilibrium density. Inside the tube, $\lambda_0$ goes from $0.079 \pm 0.003 \ \text{Å}^{-1}$ in $^4\text{He}$, to $0.2200 \pm 0.0006 \ \text{Å}^{-1}$ in $\text{H}_2$, to reach $0.2473 \pm 0.0002 \ \text{Å}^{-1}$ in $\text{D}_2$. That sequence clearly indicates that
the main influence in $\lambda_0$ comes from the potential, since the isotopic change varies the location of the energy minimum less than 15%. The features observed in these systems have probably a more general character and one can guess that if the well of the interatomic potential is increased and/or the mass of the particle adsorbed inside a tube is enlarged, the effect would be an increase in the $\lambda_0$ value.

The microscopic study of the spatial structure of the molecules in the array provides additional and useful information on the system. In Fig. 17, results for the radial distribution functions, $g_z(r)$, along the $z$ axis, are shown. They correspond to the quantum fluids adsorbed in the tube at their respective equilibrium densities $\lambda_0$. Being the denser of the three systems, D$_2$ exhibits accordingly the most pronounced oscillations in the $g_z(r)$ function. The shift in the positions of the maxima for the two molecular isotopes arises basically from the difference in their respective $\lambda_0$’s. In the $^4$He case, the much lower equilibrium density, which is direct consequence of the different potential, explains the smoothness of the $g_z(r)$ obtained.

The radial densities inside the (5,5) tube have been also studied. In Fig. 18, the radial densities for $^4$He, H$_2$, and D$_2$ for the same linear density $\lambda = 0.245$ Å$^{-1}$ are shown. The trends shown in the figure are common to all densities studied: the particle with the largest mass (D$_2$) is the one which spends more time in regions closer to the center of the tube, i.e., D$_2$ in the tube is the closest to a one-dimensional system. The change in the mass and in the interatomic potential work in the same direction: the radial densities of H$_2$ and $^4$He are quite similar.

Fig. 18 Radial density of D$_2$ (solid line), H$_2$ (dashed line), and $^4$He (dotted line) inside the (5,5) nanotube.
Both curves show a decrease in the radial localization and larger fluctuations in the transverse direction.

5 Concluding remarks

We have reviewed work carried out mainly in our group on the microscopic description of quantum liquids adsorbed in single nanotubes or in a bundle of them. This theoretical approach has been made by using quantum Monte Carlo, mainly the diffusion Monte Carlo method that allows for a very accurate study of the ground state of the system starting on basic knowledge: the mass, the geometry of the environment and the interatomic potentials. The results here presented correspond to the fully quantum fluids $^4$He, H$_2$, and D$_2$. Apart from some technological applications to come, mainly for hydrogen, the study of quantum fluids and solids in nanotubes offer the real possibility of having nearly one-dimensional quantum systems, extending the previous well-known confining geometry of fluids adsorbed on planar surfaces like graphite which provides a quasi-two-dimensional environment.

A bundle of nanotubes presents the interesting feature of different adsorption places that deserve particularized attention: the inner part of a nanotube, the intersite channels between three neighboring tubes, and the grooves formed in the external surface of the bundle. In the case of $^4$He we have reported results on these different sites taking also into account the effects induced by other atoms filling neighboring tubes. When the atoms or molecules are adsorbed in the inner part of a single tube one observes a quasi-one dimensional system, mainly when the tube is very narrow. The comparison between the equations of state and structural properties of the fluid inside the tube and in a purely 1D geometry allows for a meaningful estimation of the proximity between both systems. In the same narrow tube, we have verified that H$_2$, and mainly D$_2$, approaches better to the 1D geometry than $^4$He due to their stronger interaction with respect to helium. Importantly, our DMC results proved that the ground state of para-H$_2$ inside a (5,5) nanotube is a liquid in contrast with their well-established solid phases in bulk and in 2D.

The experimental confirmation of the results presented in this review is still pending to a big extent. After some preliminary interpretation of experiments carried out with different species about possible adsorption in the inner part of nanotubes or even in the intersites, a more careful analysis concluded the practical impossibility of the actual determination of the dominant adsorption surfaces. Now, it is more generally assumed that the filling of the tubes is quite improbable and that the gases in contact with a nanotube bundle are predominantly adsorbed on the grooves and on the external surface [41, 42]. A possible mechanism that could explain the limited uptake of the tubes is the present of defects in the carbon lattice. We have presented explicit calculations of the influence of this vacancy and proved that this can effectively reduce the adsorption inside a nanotube.

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