Quasi-one-dimensional ^{4}He inside carbon nanotubes

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We report results of diffusion Monte Carlo calculations for both ^{4}He absorbed in a narrow single walled carbon nanotube ($R = 3.42$ Å) and strictly one-dimensional ^{4}He. Inside the tube, the binding energy of liquid ^{4}He is approximately three times larger than on planar graphite. At low linear densities, ^{4}He in a nanotube is an experimental realization of a one-dimensional quantum fluid. However, when the density increases the structural and energetic properties of both systems differ. At high density, a quasicontinuous liquid-solid phase transition is observed in both cases.

Since their discovery by Ijima[1] in 1991, carbon nanotubes have received a great deal of attention. Basically, they are the result of the seamless rolling up of one or several graphite sheets over themselves.[2–4] Depending on the relative orientation of the rolling axis with respect to underlying graphite structure, one can have different types of nanotubes:[5] armchair, zig-zag, and chiral with different radii and different mechanical and electrical properties. Nowadays, it is possible to obtain high yields of nanotubes (single and multiple walled), with a variety of diameters ranging from 7 to 40 Å (Ref. 6) and lengths up to ~ 1000 times larger.

One of the most attractive features of carbon nanotubes is the possibility of filling with different materials both their inner cavities and the interstitial channels among them.[7,8] The interest in this field is twofold. On one hand, the expected increase in the particle-substrate potential energy with respect to a flat carbon surface has suggested the use of nanotubes as storage devices for molecular hydrogen in fuel cells.[9,10] On the other, more theoretical hand, nanotubes provide a reliable realization of one-dimensional systems in the same way that a substance adsorbed on graphite manifests trends that are characteristic of a two-dimensional medium. If the nanotubes are filled with light atoms (He) or molecules (H_2) and the temperature is low enough, one is dealing with quasi-one-dimensional quantum fluids. Such an experimental realization has been carried out for the first time by Yano *et al.*[11] in a honeycomb of FSM-16. This is a mesoporous substrate with tubes approximately 18 Å in diameter. Using a torsional oscillator, this group proved the existence of superfluidity of the ^{4}He atoms absorbed in the pores below a critical temperature of ~ 0.7 K. More recently, Teizer *et al.*[12] have studied experimentally the desorption of ^{4}He previously absorbed in the interstitial sites of carbon nanotube bundles. In this case, the data points unambiguously to the one-dimensional nature of the helium inside the nanotubes.

From a theoretical point of view, it has been recently established using both the hypernetted-chain (HNC) variational approach [13] and the diffusion Monte Carlo (DMC) method[14] that strictly one-dimensional (1D) ^{4}He is a self-bound liquid at zero temperature. However, contrary to the situation for dilute classical gases,[14–16] there are no many-body calculations of quantum fluids inside nanotubes yet. In this work, we address the question of the quasi-one-dimensionality of ^{4}He absorbed in a tube by a direct com-

parison between the results of DMC for strictly 1D ^{4}He and ^{4}He inside a nanotube of radius equal to 3.42 Å, which corresponds to a (5,5) armchair tube in the standard nomenclature.[2]

The DMC method[17,18] solves stochastically the N-body Schrödinger equation giving results that are *exact* for bosonic systems as liquid ^{4}He, provided that the interatomic potential is known. In the present calculation, we have used the HFD-B(HE) Aziz potential for the He-He pair interaction,[19] and the potential given by Stan and Cole[15] in their study of Lennard-Jones fluids in tubes for the He-tube one. Basically, they consider the nanotubes as smooth cylinders by making a z average of the corresponding sum of all the C-He interactions. Thus, the potential felt by a particle only depends on its distance to the center of the cylinder. This is a simplification, but one would expect the error involved to be small since the helium atoms are much larger than the C-C distance. In fact, the differences in energy and position between a ^{4}He atom in the smooth cylinder model and the same particle considering its interaction with the surrounding individual carbons are about 1% for the tube considered here.[20]

The efficiency of the DMC method is greatly enhanced by introducing a trial wave function $\Psi(\mathbf{R})$ that acts as an important sampling auxiliary function. In 1D ^{4}He we have used a two-body Jastrow wave function

$$\Psi^{1D}(\mathbf{R}) = \Psi_J(\mathbf{R}) \tag{1}$$

with $\Psi_J(\mathbf{R}) = \Pi_{i<j} \exp[-\frac{1}{2}(b/r_{ij})^5]$, whereas liquid ^{4}He inside nanotubes requires the additional introduction of a one-body term

$$\Psi^T(\mathbf{R}) = \Psi_J(\mathbf{R})\Psi_c(\mathbf{R}) \tag{2}$$

with $\Psi_c(\mathbf{R}) = \Pi_i^N \exp(-c\, r_i^2)$ (r_i being the radial distance of the particle to the center), that accounts for the hard core of the helium-nanotube interaction. Using the variational Monte Carlo method (VMC) we have optimized the parameters b and c at low densities around the equilibrium. The values obtained, $b = 3.067$ Å and $c = 2.679$ Å^{-2}, show a negligible dependence with the density and therefore they have been used everywhere in the DMC calculations. In all the simula-
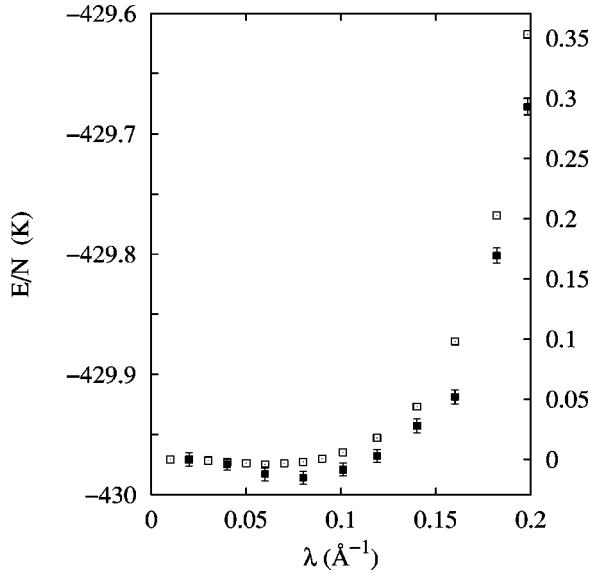
FIG. 1. Energy per particle (E/N) versus the linear concentration (λ), for the two systems we have studied: a strictly one-dimensional system (open squares, right energy scale), and a (5,5) armchair tube (full squares, left energy scale). In the first case, the error bars are less than the size of the symbols. Both energy scales are in K.

tions $N = 30$ atoms have been used, a number that has proved to be large enough to reduce the size effects to the level of the statistical errors reported.

The variational HNC equation of Krotscheck and Miller[13] on 1D liquid ^{4}He points to the existence of a liquid-solid phase transition at high density. We have explored this feature, that is only possible at zero temperature, by using a solid trial function which results from the product of $\Psi^{1D}(\mathbf{R})$ and $\Psi^T(\mathbf{R})$ by a z-localized factor $\Psi_s(R) = \Pi_i^N \exp[-a(z_i - z_{is})^2]$. The solid sites z_{is} are equally spaced points along the z direction which is both the longitudinal axes of the tube and the line of the 1D system. In both solid systems, a VMC optimization at high densities leads to values $b = 2.939$ Å and $a = 0.612$ Å^{-2}, with $c = 2.908$ Å^{-2} in the tube case.

The energy per helium atom versus the linear coverage, λ, for the 1D (open squares, energy scale on the right) and the tube (full squares, energy scale on the left) is shown in Fig. 1. The two curves have have been drawn for the full square with the lowest λ to coincide with the open symbol for the same He density. One observes that for $\lambda < 0.05$ Å^{-1}, both curves are similar, but for larger concentrations the tube curve is located below the other one. A similar phenomenology appears in the comparison between the energies of purely 2D ^{4}He and ^{4}He adsorbed in graphite. As for this system, the difference in energy between ^{4}He in a nanotube and 1D ^{4}He is always negative with an absolute value that increases with the density. Both in graphite and in nanotubes this increase with respect to the 2D and 1D systems is mainly due to the emergence of their actual 3D nature. Beyond this qualitative agreement between ^{4}He adsorbed on graphite and inside carbon nanotubes, there are significant differences in the values of the binding energies in the two systems. The binding energy of a single ^{4}He atom in graphite is $E_B^G = 140.74$ K,[21] whereas in the nanotube we are studying is roughly three times larger, $E_B^T = 429.97$ K, a

TABLE I. Parameters of Eq. (4) for the two systems studied.

Parameter	1D ^{4}He	^{4}He in a tube
λ_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
χ^2/ν	2.2	0.24

significant difference that has been dramatically observed in the desorption experiment of Teizer et al.[12] On the other hand, the departure of the real 3D systems (^{4}He in graphite or a nanotube) from the idealized 2D or 1D liquids can be quantified by means of the parameter

$$\Delta^{T(G)} = \frac{(E^{T(G)} - E_B^{T(G)}) - E_{1(2)D}}{(E^{T(G)} - E_B^{T(G)})}, \quad (3)$$

where T stands for the tube and G for the graphite adsorbents and E is the energy per particle in the system under consideration. Around the respective equilibrium densities one obtains $\Delta^T = 90\%$ and $\Delta^G = 6\%$, a large difference that indicates that the 1D representation of ^{4}He inside the nanotube is worse than the 2D modelization of ^{4}He in planar graphite.

Up to $\lambda = 0.15$ Å^{-1} the energies per particle ($e = E/N$) of both 1D ^{4}He and ^{4}He inside the tube may be well fitted by a third-degree polynomial

$$e = e_0 + A\left(\frac{\lambda - \lambda_0}{\lambda_0}\right)^2 + B\left(\frac{\lambda - \lambda_0}{\lambda_0}\right)^3. \quad (4)$$

The optimal values for the parameters A, B, λ_0, and e_0 are reported in Table I. The linear equilibrium densities λ_0 of both systems are close, $\lambda_0^{1D} = 0.062$ Å^{-1} and $\lambda_0^T = 0.079$ Å^{-1}, whereas the energy difference between $\lambda = 0$ and $\lambda = \lambda_0$ is significantly different, 0.00364 and 0.018 K for 1D ^{4}He and ^{4}He inside the tube, respectively. The latter results point again to a large enhancement of the binding energy of ^{4}He inside the tube with respect to the 1D system. On the other hand, the equilibrium density of liquid ^{4}He inside the tube ($\rho_0 = 0.0022$ Å^{-3}) is much smaller than the one in homogeneous 3D liquid ^{4}He ($\rho_0 = 0.022$ Å^{-3}).

In agreement with the DMC calculation of Stan et al.[14] and the variational one of Krotscheck and Miller,[13] ^{4}He self-bounds in a 1D array but with a binding energy (-0.0036 ± 0.0002 K) much smaller than that in 2D (-0.897 ± 0.002 K) (Ref. 22) and 3D (-7.267 ± 0.013 K).[18] It is worth noting that such a small total energy results from a big cancellation between the potential and kinetic energies. At λ_0, we have $T/N = 0.2706 \pm 0.0004$ K and $V/N = -0.2742 \pm 0.0004$ K. In fact, the influence of the ^{4}He interatomic potential in this system is very large. A calculation at the equilibrium density λ_0 for the 1D system using the HFDHE2 Aziz potential[23] indicates that ^{4}He is still a liquid, but the total energy is a factor two smaller (-0.0018 ± 0.0003 K, with a potential energy -0.2724 ± 0.0004 K and the same kinetic energy). This sizeable difference partially explains the discrepancies of our DMC calculation with both the results of Stan et al.[14] and Krotscheck and Miller,[13] who used the HFDHE2 Aziz potential.
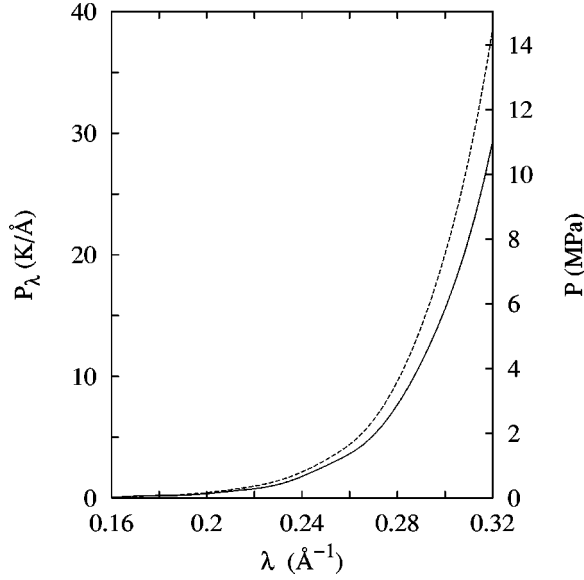
FIG. 2. Pressure at high helium densities for both systems (one-dimensional, dashed line, left scale; nanotube, full line, right scale).

FIG. 3. Pair distribution function along the z coordinate, $g_z^{T(1D)}(r)$. Full lines correspond to the narrow tube at 0.08 Å^{-1} (bottom), 0.182 Å^{-1} (middle), and 0.406 Å^{-1} (top), and dashed lines to the purely linear system at the same densities.

From the values of the energy, one can obtain the linear system pressure, $p_\lambda = \lambda^2 \partial e / \partial \lambda$, and estimate the same property for helium inside the cylinder as $p = p_\lambda / \pi R^2$. Figure 2 displays this observable as a function of the ^{4}He density. The range corresponds to a liquid structure both in the 1D and tube cases (see discussion below). One can see that the pressure increases faster in a pure linear arrangement of atoms than in a tube. This can be understood if one considers that in a narrow nanotube it is possible to avoid the repulsive core of the nearest neighbors by shifting transversely the helium positions, a situation that is obviously not possible in 1D. Also interesting is the comparison between the sound velocity, $c(\lambda) = [1/m(\partial P / \partial \lambda)]^{1/2}$ at their respective equilibrium densities. The values are $c_{1D} = 7.98 \pm 0.07$ m/s and $c_T = 14.2 \pm 0.8$ m/s, in both cases a tiny fraction of the corresponding 2D ($c = 92.8$ m/s) (Ref. 22) and 3D (238.3 m/s) (Ref. 18) ^{4}He liquids. The spinodal point can be obtained as the density at which the speed of sound becomes zero. According to our results, the spinodal points are located at $\lambda_{1D} = 0.047 \pm 0.001$ Å^{-1} and $\lambda_T = 0.059 \pm 0.001$ Å^{-1}.

Another aspect that has deserved our attention has been the existence of a liquid-solid phase transition at high densities. Evidences of this phase transition, that is only possible at zero temperature, appear in a variational calculation of 1D ^{4}He.[13] A comparison between the DMC energies for the liquid and solid phases is given in Table II. One can see that in both systems, the energy per particle when localization is
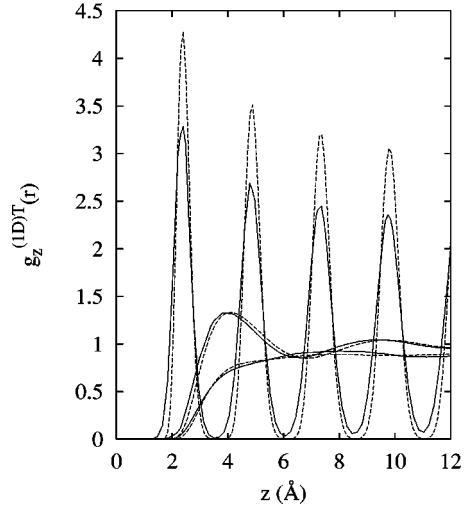
imposed ($a \neq 0$) is below the one corresponding to a liquid structure ($a = 0$) for linear densities greater than 0.358 Å^{-1}. By means of the Maxwell double tangent construction, one would be able in principle to tell the solid from the liquid and to obtain the freezing and melting densities. Unfortunately, the energy differences between the z localized and the liquid structures are too small to allow us to carry out a meaningful calculation. Our results indicate that for large enough densities ($\lambda > 0.358$ Å^{-1}) both the 1D and the tube arrangements have a localized (solid) phase and that the discontinuity in the density (if any) is surely very small. This is in agreement with the results discussed by Whitlock et al.[21] about the reduction of the size of this discontinuity from three to two dimensions: in 3D is fairly large, being considerably smaller in a purely 2D system. In 1D, we observe a further reduction towards a continuous or a quasicontinuous transition. It is also remarkable that ^{4}He inside the carbon tube remains a liquid up to a much larger pressure (around 5 times) than in bulk liquid ^{4}He(~ 2.6 MPa).

Information on the spatial distribution of the ^{4}He atoms may be drawn from the two-body radial distribution function along the z direction, $g_z(r)$. The functions $g_z(r)$ for 1D ^{4}He and ^{4}He in the tube are shown in Fig. 3 at several linear densities. Near the equilibrium density ($\lambda = 0.08$ Å^{-1}, lower part of the figure) $g_z^{1D}(r)$ is quite similar to $g_z^T(r)$, as corresponds to a quasi-one-dimensional system. The same could be said in a broad range of densities, as it can be seen in the

TABLE II. Energies per particle at large λ for the systems studied. All the energies are in K. See text for further details.

λ (Å^{-1})	E/N (1D, $a = 0$)	E/N (1D, $a \neq 0$)	E/N (T, $a = 0$)	E/N (T, $a \neq 0$)
0.406	123.726±0.012	123.561±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	−413.061±0.012
0.320	13.240±0.005	13.258±0.006	−419.551±0.011	−419.493±0.010

curves for $\lambda = 0.182$ Å^{-1} (middle part of the figure). On the other hand, in the solid phase ($\lambda = 0.406$ Å^{-1}), $g_z^{1D}(r)$ and $g_z^T(r)$ are different: in this case, the 3D nature of ^{4}He inside the tubes produces a significant decrease in the localization with respect to the 1D result.

In conclusion, we have compared the properties of strictly 1D ^{4}He with ^{4}He inside a narrow carbon nanotube using the diffusion Monte Carlo method. For a wide range of densities, ^{4}He is a liquid in both systems, and also in both cases a quasicontinuous liquid-solid phase transition has been observed. In accordance with recent experimental determina-

tions, the present calculation evidences a quasi-one-dimensional behavior of ^{4}He inside a nanotube but significant differences with the ideal 1D system appear, especially when the linear density is increased. The origin of these differences is mainly the existence of the additional transverse degree of freedom that helium atoms have inside a nanotube.

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