H$_2$ in the interstitial channels of nanotube bundles

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The equation of state of H$_2$ adsorbed in the interstitial channels of a carbon nanotube bundle has been calculated using the diffusion Monte Carlo method. The possibility of a lattice dilation, induced by H$_2$ adsorption, has been analyzed by modeling the cohesion energy of the bundle. The influence of factors such as the interatomic potentials, the nanotube radius, and the geometry of the channel on the bundle swelling is systematically analyzed. The most critical input is proved to be the C-H$_2$ potential. Using the same model than in planar graphite, the dilation is smaller than in previous estimations or even inexistent. H$_2$ is highly unidimensional near the equilibrium density, the radial degree of freedom appearing progressively at higher densities.

I. INTRODUCTION

Theoretical and experimental research in carbon nanotubes (CN's) is nowadays a very active field in which new avenues are opening continuously, all related to its particular structure at the nanometer-scale level. Besides their singular electrical and mechanical properties, CN's are able to adsorb some atoms and molecules offering a real possibility for quasi-one-dimensional environments. These are mainly the inner part of the nanotubes and the interstitial channels (IC's) among them due to their natural bundle arrangement. When CN's are formed, they appear as long capped cylinders which only can adsorb a given substance if their caps are removed by chemical means. Instead, IC's are always present offering very narrow channels, distributed according to an hexagonal lattice, and with a sizable adsorption capability in comparison with adsorption in planar graphite. Recently, Talapatra *et al.*[1] studied experimentally the binding energies of Xe, CH$_4$, and Ne on close-ended nanotube bundles and concluded that none of them is adsorbed in the intersites. Probably, the size of these atoms and molecules is too large compared with the radius of the interchannel ($r_{IC} \simeq 3$ Å) to fit into them. However, the situation for lighter species such as He or H$_2$ seems different. There are several experiments which claim that both of them can be adsorbed in the IC's due to their small radius.[2–4] H$_2$ is certainly the most interesting system since a CN bundle could be one of the best options to reach the target energy densities for a lightweight hydrogen-storage system usable for transportation.[5,6]

In a recent theoretical work, Calbi *et al.*[7] have studied the adsorption of H$_2$, and other molecules and atoms, in the IC's of a CN bundle. Introducing in the formalism a possible dilation of the bundle, by means of a harmonic approximation, they concluded that in equilibrium the bundle can swell. The dilation is observed in all cases, with different intensity depending on the particular system. In the geometry there

considered, corresponding to (10,10) tubes in the standard terminology, and when the gas adsorbed is H$_2$, the swelling amounts approximately to 1%. This is the result of a delicate balance between two competing effects when the lattice is expanded: a decrease in the CN bundle cohesion energy and an increase in the H$_2$-nanotube binding energy. Obviously, this prediction for H$_2$ acquires special relevance since it would imply a significant increase of the CN bundle storage power. However, at present there is not any experimental confirmation of this possible adsorption-induced dilation. Probably, even if such effect is indeed present, its manifestation could be hardly observed due to the present experimental uncertainties. Raman spectroscopy seems a promising method for a better insight. In a recent work, this method was applied successfully by Williams *et al.*[3] to discriminate the different adsorption sites of H$_2$ in CN bundles.

In the present work, we present a diffusion Monte Carlo (DMC) study of H$_2$ adsorbed in IC's of a (10,10) CN bundle. In the past, and using the same methodology, we characterized the ground-state properties of ^{4}He and H$_2$ inside a single CN (Refs. 8,9) and of ^{4}He adsorbed in an IC.[10] In this paper, our aim is to determine the equation of state of H$_2$ using microscopic theory, with special attention to the possibility of an adsorption-induced bundle dilation. To this end, the influence on swelling of inputs such as the nanotube radius, the molecule-molecule and CN-molecule interactions, the geometry of the intersite, and the transversal degree of freedom are thoroughly discussed. Our results agree somehow with the ones of Ref. 7, but the magnitude of a possible swelling is seen to be comparatively smaller or even inexistent.

The rest of the paper is organized as follows. In Sec. II, the influence of the several parameters of the model on a possible dilation of the bundle is studied using a one-dimensional approximation. The accuracy of this model is then tested in Sec. III by means of a three-dimensional DMC calculation. Finally, Sec. IV comprises a brief summary and the main conclusions.

II. ONE-DIMENSIONAL APPROXIMATION: TESTING THE MODEL

As in Ref. 7, we study H_2 adsorbed in the IC of a (10,10) CN bundle. The bundle is disposed in such a way that, in the plane perpendicular to the CN long axis, a triangular lattice is formed. The lattice constant, i.e., the distance between adjacent centers, is $D_0 = 17$ Å. D_0 corresponds to the equilibrium position and there is an overall agreement on its value. Therefore, we consider it as a fixed parameter in all the calculations.

Having established the value of D_0, the radius of a single nanotube is directly related to the C-C minimum separation between two neighbors. In a theoretical calculation, Tersoff and Ruoff[11] concluded that this distance is 3.4 Å, in agreement with the most accepted value for the Lennard-Jones σ_{C-C}. In fact, this value coincides with the experimentally accepted distance between graphite sheets. Considering this C-C distance, the radius of a (10,10) tube is 6.8 Å. It is worth mentioning that this radius is the same as one obtains constructing the same nanotube by rolling up a graphitic surface with a C-C distance of 1.42 Å. However, there is not a general agreement on those values. Recently, Charlier *et al.*[12] carried out a density functional calculation of a CN bundle and obtained an equilibrium geometry corresponding to a C-C intertube distance of ~ 3.2 Å. The CN radius is then 6.9 Å, a value which was used in Ref. 7. At present and to our knowledge, there are no experimental data on the C-C distance, which could help to choose between different theoretical models. Therefore, we consider in the present calculation two possible CN radii 6.8 and 6.9 Å.

The interstitial channel between three adjacent nanotubes in a (10,10) bundle can lodge a hard sphere with radius 2.9 or 3 Å, corresponding to CN's with radii 6.8 and 6.9 Å, respectively. Since the σ parameter for the C-H_2 Lennard-Jones potential is around 3 Å, one can reasonably assume a one-dimensional (1D) approximation for hydrogen adsorption in IC's. In this approximation, the H_2 energy per particle ($e = E/N$) can be written as[7]

$$e(\lambda,D) = \epsilon_0(D) + e_{1D}(\lambda) + h(\lambda,D) + \frac{1}{\lambda}\frac{3}{4}k(D-D_0)^2,$$

$$(1)$$

with λ the linear density of the H_2 molecules and D the lattice parameter. In Eq. (1), $\epsilon_0(D)$ is the binding energy of a single molecule in the IC, $e_{1D}(\lambda)$ is the 1D H_2 energy per particle, $h(\lambda,D)$ corresponds to the interaction energy with H_2 in neighboring IC's, and the last term takes into account the cohesion energy of the bundle when it is dilated from the equilibrium lattice distance D_0. In the following, we analyze the several terms entering Eq. (1) to disentangle which are the relevant inputs influencing a possible dilation of the bundle.

Both $\epsilon_0(D)$ and $e_{1D}(\lambda)$ are calculated using the DMC method.[13,14] The DMC method solves in a stochastic way the N-body Schrödinger equation in imaginary time for the wave function $f(\boldsymbol{R},t) = \psi(\boldsymbol{R})\Psi(\boldsymbol{R},t)$,

$$-\frac{\partial f(\boldsymbol{R},t)}{\partial t} = -D\nabla^2 f(\boldsymbol{R},t) + D\nabla[\boldsymbol{F} f(\boldsymbol{R},t)]$$

$$+ [E_L(\boldsymbol{R}) - E]f(\boldsymbol{R},t), \qquad (2)$$

with $\psi(\boldsymbol{R})$ a trial wave function introduced for importance sampling. In Eq. (2), $D = \hbar^2/2m$, $E_L(\boldsymbol{R}) = \psi(\boldsymbol{R})^{-1}H\psi(\boldsymbol{R})$ is the local energy, and $\boldsymbol{F}(\boldsymbol{R}) = 2\psi(\boldsymbol{R})^{-1}\nabla\psi(\boldsymbol{R})$ is the so-called drift force which guides the diffusion movement to regions where $\psi(\boldsymbol{R})$ is large.

The trial wave function ψ used in the calculation of 1D H_2 is a Jastrow one,

$$\psi^{1D}(\boldsymbol{R}) = \prod_{i<j} f(r_{ij}), \qquad (3)$$

with $f(r_{ij}) = \exp[-0.5(b/r_{ij})^5]$ a McMillan two-body correlation factor. The parameter b in $f(r)$ has been determined by means of a variational Monte Carlo (VMC) optimization. Near the equilibrium density the optimal value is $b = 3.996$ Å, and it increases gradually with the density λ (at $\lambda = 0.358$ Å^{-1}, $b = 4.026$ Å).

The trial wave function used in the calculation of $\epsilon_0(D)$ includes two-body correlations with the three nanotubes surrounding the IC. They are also of McMillan type,

$$\psi^{IC}(\boldsymbol{R}) = \prod_{n=1}^{3} \exp\left[-\frac{1}{2}\left(\frac{a}{r_n}\right)^5\right], \qquad (4)$$

r_n being the distance of the hydrogen molecule to the center of any of the three tubes. The parameter a, optimized using VMC, varies from $a = 22.5$ Å for zero dilation to $a = 21.5$ Å for $D - D_0 = 0.2$ Å. On the other hand, the optimal values for the parameter a present a negligible dependence with the particular C-H_2 potential chosen in the calculation. The IC is so narrow that one can approximate the sum of individual CN-molecule potentials by a new one which is only a function of the radial distance r to the center of the IC. This simplified model is obtained by an azimuthal average of the three individual potentials.[7] In this case, the trial wave function is simpler than the previous model (4). We have chosen a Gaussian

$$\psi_c(\boldsymbol{R}) = \exp(-c r_n^2), \qquad (5)$$

the parameter c varying from 7.6 Å^{-2} to 11.5 Å^{-2}, depending on the radius of the tube and on the dilation. The greater the radius, the smaller the value of c.

Para-hydrogen is spherical to a large extent. As usual, in most of molecular hydrogen calculations, the intermolecular interaction is considered purely radial and described by the Silvera and Goldman (hereafter SG) model.[15] In addition, and to make comparisons with previous work (Ref. 7), we have also made some calculations with the potential proposed by Kostov, Cole, Lewis, Diep, and Johnson.[16] This H_2-H_2 potential (hereafter KCLDJ) incorporates, in a rather crude way, three-body corrections to the pair potential coming from the triplets H_2-C-H_2.

Much more critical for estimating a possible bundle dilation is the model for the CN-H_2 interaction. As in our previ-

ous work on the equation of state of H$_2$ adsorbed inside a nanotube,[9] we use the CN-H$_2$ potential proposed by Stan and Cole.[17] This potential results from an average over all the C-H$_2$ interactions between the C of an infinite CN and a single molecule located at a radial distance r. The interaction is thereby independent of z (corrugation effects are neglected) and can be used for adsorption both inside and outside the nanotube. The resulting CN-H$_2$ potential depends explicitly on the σ and ϵ parameters of the Lennard-Jones potential between C and H$_2$. At present, there is no overall agreement about which are the best set of parameters (σ,ϵ) describing this interaction. In order to study the influence of this choice on the calculations, two different sets have been studied. The first one (used, for example, in Refs. 7 and 18) is derived with the Lorentz-Berthelot combining rules

$$\sigma_{C\text{-}H_2} = \frac{\sigma_{H_2\text{-}H_2} + \sigma_{C\text{-}C}}{2},$$

$$\epsilon_{C\text{-}H_2} = \sqrt{\epsilon_{H_2\text{-}H_2}\epsilon_{C\text{-}C}} \ . \tag{6}$$

Using $\sigma_{C\text{-}C} = 3.4$ Å, $\epsilon_{C\text{-}C} = 28$ K, $\sigma_{H_2\text{-}H_2} = 3.05$ Å, and $\epsilon_{H_2\text{-}H_2} = 37.0$ K, the first set is $\epsilon_{C\text{-}H_2} = 32.2$ K and $\sigma_{C\text{-}H_2} = 3.23$ Å (hereafter LB). The second option is to consider the optimal parameters which describe the interaction of H$_2$ with planar graphite. This set from Wang, Senbetu, and Woo[19] is probably more realistic than the first one and it has also been used in the past.[3,9,20] The values are $\epsilon_{C\text{-}H_2} = 42.8$ K and $\sigma_{C\text{-}H_2} = 2.97$ Å (hereafter WSW). Notice the sizable difference between both sets, which will generate significant differences in the final results.

Dilation and compression of the lattice constant in the CN bundle have an energetic cost. Following Refs. 21 and 7, that contribution is assumed to be harmonic in the displacement around the equilibrium position D_0 [see Eq. (1)]. This approximation is expected to hold for small $D - D_0$ values but the uncertainty in the real value of k is rather large. From compression modes measured in graphite by Nicklow et al.,[22] Mizel et al.[21] estimated a value $k = 1740$ K Å^{-3}. The constant k can also be obtained from the bulk modulus B. Considering that any deformation of the tube takes place only in a direction perpendicular to its long axis, $k = 2/\sqrt{3}B$.[11] From the experimental measure of B by Tang et al.[23] ($B = 41.66$ GPa) one obtains $k = 3015$ K Å^{-3}, a figure much larger than the one from Ref. 21. Part of the difference can somehow emerge from the fact that the experimental data for B were obtained for CN's with wider radius (7.04 Å). In the results presented below, we have used $k = 1740$ K Å^{-3} everywhere, but the influence on the final results of the particular k value is analyzed in selected cases.

Finally, the term $h(\lambda,D)$ in Eq. (1) sums the interaction energy between the H$_2$ molecules of a given IC and the ones of its neighboring channels. This contribution may be readily obtained assuming a mean-field approximation,

$$h(\lambda,D) = \frac{\lambda}{2}\int_{-\infty}^{\infty} dx\, V_{H_2\text{-}H_2}(\sqrt{x^2 + D^2}), \tag{7}$$

TABLE I. Binding energy of a single H$_2$ molecule adsorbed in the interstitial channels of a (10,10) CN bundle for different CN radii, IC geometries, and C-H$_2$ potentials. Figures in parentheses are statistical errors.

Radius (Å)	IC	$V_{C\text{-}H_2}$	ϵ_0 (K)
6.9	T	WSW	$-1020.69(8)$
6.9	T	LB	$-278.02(8)$
6.8	T	WSW	$-1096.02(2)$
6.8	T	LB	$-668.39(9)$
6.9	R	WSW	$-965.93(7)$
6.9	R	LB	$-207.59(5)$
6.8	R	WSW	$-1044.49(2)$
6.8	R	LB	$-576.56(2)$

which considers the neighboring channels as uniform arrays without correlation effects that could modify the H$_2$ kinetic energy. The calculation in Eq. (7) is extended to the nearest neighbors, the next-nearest neighbors, and then on up to the desired accuracy. Obviously, $h(\lambda,D)$ changes when the bundle swells. In Ref. 24, we have verified the high accuracy of Eq. (7) by comparing its estimation with an exact DMC calculation.

The influence of the CN radius and the C-H$_2$ potential in the equation of state of adsorbed H$_2$ is clearly observed in the value of ϵ_0. Table I contains results for the H$_2$ binding energy considering two CN radii (6.8 and 6.9 Å), the two C-H$_2$ potentials discussed above (LB and WSW), and two geometries for the IC, the real one with the triangular composition of the tubes surrounding the IC (T) and the radial (R) model from an azimuthal average. The narrowness of the IC makes the differences between the T and R results not to be larger than 15%. The dominant effect is unquestionably the C-H$_2$ potential. The significant differences between the pairs (σ,ϵ) for the two models generate a big discrepancy in the value of ϵ_0. The largest binding energies correspond to the most accurate WSW potential due to its larger parameter ϵ. The different behavior of ϵ_0 with the CN radius is also noticeable, and will be discussed below in connection with dilation; it strongly depends on the radius for LB, whereas it remains nearly unchanged for WSW. This last feature is a consequence of the larger σ value of the LB potential, which effectively reduces the space available inside the IC to accommodate the H$_2$ molecule.

In order to determine if a dilation of the bundle is energetically preferred, a series of calculations using Eq. (1) has been carried out. As commented before, our aim is to quantitatively determine the influence of the potentials, the CN radius, the elastic constant k, and the geometry model for the IC on a possible dilation. The direct output of Eq. (1) is the energy per particle as a function of the linear density λ and D. For a given dilation $D - D_0 \geq 0$ (with fixed $D_0 = 17$ Å), $e(\lambda)$ can be obtained, and from it the equilibrium point (λ_0, e_0) corresponding to zero pressure. Illustrative outputs of this procedure are shown in Figs. 1 and 2. Figure 1 contains the H$_2$ equation of state in the IC for values of the lattice dilation $D - D_0 = 0.18$, 0.17, 0.16, and 0.15 Å. All the curves have been calculated assuming a CN radius of 6.9 Å, the SG
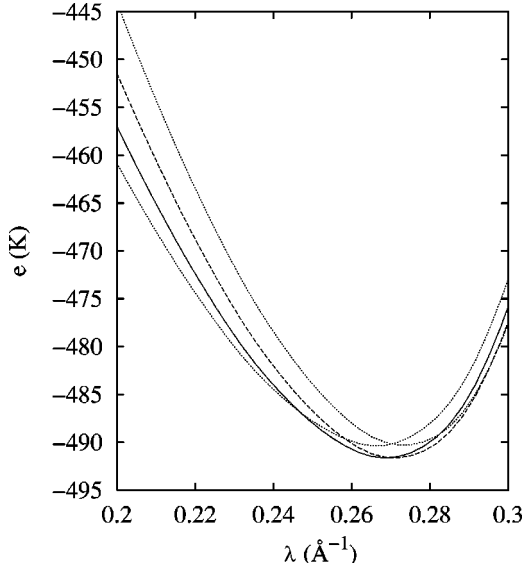
FIG. 1. Energy per hydrogen molecule for CN radius 6.9 Å, T geometry, SG H_2-H_2 potential, and LB C-H_2 potential. From top to bottom in $\lambda = 0.2$ Å^{-1}, $D - D_0 = 0.18$, 0.17, 0.16, and 0.15 Å.

H_2-H_2 potential, $k = 1740$ K Å^{-3}, the LB C-H_2 potential, and a T channel. The lowest energy per particle at the minimum is obtained for a dilation 0.16 Å, nearly coincident with the result reported in Ref. 7 (0.166 Å) obtained with the H_2-H_2 KCLDJ potential and an R channel. If the C-H_2 potential is the WSW model, the H_2 equation of state changes dramatically and the dilation becomes much smaller. This is shown in Fig. 2, which differs from Fig. 1 in the C-H_2 potential, the other inputs being unchanged. The curves now correspond to dilations $D - D_0 = 0.06$, 0.05, and 0.04 Å. The minimum corresponds to a swelling of 0.05 Å. The equilibrium density is $\lambda_0 = 0.232$ Å^{-1}, slightly inferior to the one obtained with the LB potential, $\lambda_0 = 0.268$ Å^{-1}. The magnitude of the energy per particle is very different in the two cases: going from LB to WSW the energy increases by a factor of 2. The major part of this increment comes from the differences in the binding energies of a single molecule (ϵ_0) [Table I].

The full set of results combining CN radius, C-H_2 and H_2-H_2 interactions, and IC geometry is reported in Table II. λ_0 corresponds to the H_2 equilibrium density at the energetically preferred swelling, also reported in the table. Due to the large uncertainty in the value of k, we only report the influence of its change (3015 K Å^{-3} instead of 1740 K Å^{-3}) in the most favorable cases for the bundle swelling. Inspection of the data shows that neither the H_2-H_2 potential nor the detailed form of the IC, R, or T are relevant in the swelling process. Maintaining the radius fixed to a value 6.9 Å and the LB C-H_2 interaction, the dilation comes out to be 0.16–0.17 Å, in overall agreement with Calbi *et al.*[7] However, if the LB interaction is substituted by the WSW one, the swelling observed is reduced by a factor of 3 (from 0.17 Å to 0.05 Å), and the equilibrium density λ_0 decreases by 15%.

The second part of Table II contains a similar analysis for a CN radius of 6.8 Å. A general trend arising from the comparison between the first half of the Table (6.9 Å) and the second one (6.8 Å) is the increase of the dilation with the CN radius when the rest of the inputs are kept fixed. This seems quite obvious since, with a smaller nanotube and the same CN-CN distance, the room for adsorption increases. Thus, the swelling decreases from 0.17 to 0.11 Å with the LB C-H_2 interaction, whereas it turns absolutely negligible in case of using the probably most accurate WSW potential. On the other hand, λ_0 is observed to systematically decrease when the radius is moved from 6.9 to 6.8 Å. Finally, the influence of the value of k appears in the table marked with an asterisk for a particular case in which the dilation is one of the largest values. As it could be expected, $D - D_0$ decreases if k increases: using $k = 3015$ K Å^{-3} instead of 1740 K Å^{-3} the dilation is reduced by 30%. Similar reductions would be obtained in the other cases.

III. FULL DMC CALCULATION

In the preceding section it has been assumed that radial and longitudinal degrees of freedom of H_2 inside IC's are not coupled. The correlations between H_2 molecules were purely longitudinal and the interaction with the surrounding walls was solved only for the one-body problem. In this section, we check the validity of that approximation by making an exact three-dimensional DMC calculation of H_2 in the IC. The CN bundle cohesion term and the mean-field contribution $h(\lambda, D)$ are summed up to the DMC energy as in Eq. (1).

The trial wave function for importance sampling is written as

$$\psi(\boldsymbol{R}) = \psi^{1D}(\boldsymbol{R}) \psi^{IC}(\boldsymbol{R}), \tag{8}$$

where $\psi^{1D}(\boldsymbol{R})$ and $\psi^{IC}(\boldsymbol{R})$ are the same than in the 1D calculation, Eqs. (3) and (4), respectively. The optimal values
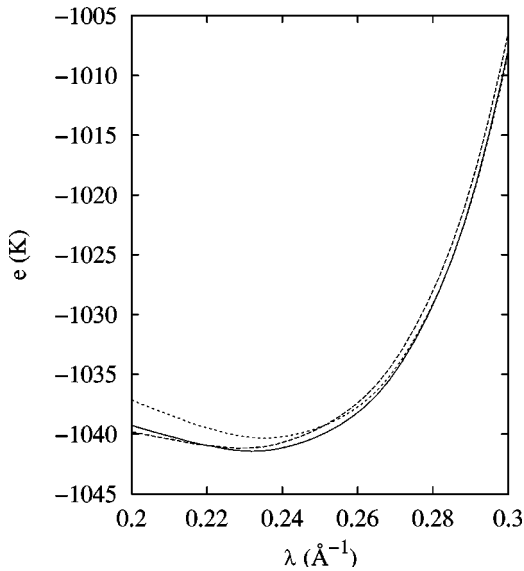

FIG. 2. Same as in Fig. 1 but changing the LB C-H_2 potential by the WSW one. From top to bottom at $\lambda = 0.2$ Å^{-1}, lattice dilations of 0.06, 0.05 and 0.04 Å.

TABLE II. Dilation $D-D_0$, equilibrium densities λ_0, and energies e_0 for different radii, H$_2$-H$_2$ and C-H$_2$ interactions, and geometries (T and R). Figures in parentheses are statistical errors.

Radius (Å)	IC	$V_{C\text{-}H_2}$	$V_{H_2\text{-}H_2}$	$(D-D_0)$(Å)	λ_0 (Å^{-1})	e_0 (K)
6.9	T	WSW	KCLDJ	0.04	0.2087(3)	$-1032.98(1)$
6.9	T	LB	KCLDJ	0.16	0.2667(1)	$-481.42(2)$
6.9	T	WSW	SG	0.05	0.2322(2)	$-1041.41(1)$
6.9	T	LB	SG	0.17	0.2685(1)	$-491.64(1)$
6.9*	T	LB	SG	0.11	0.276(12)	$-300.35(1)$
6.9	R	WSW	KCLDJ	0.05	0.2252(1)	$-980.07(1)$
6.9	R	LB	KCLDJ	0.16	0.2662(1)	$-422.29(2)$
6.9	R	WSW	SG	0.05	0.2323(3)	$-988.59(1)$
6.9	R	LB	SG	0.16	0.2685(1)	$-432.17(1)$
6.8	T	WSW	KCLDJ	0.01	0.1311(6)	$-1096.35(1)$
6.8	T	LB	KCLDJ	0.10	0.2472(1)	$-731.55(2)$
6.8†	T	WSW	SG	0.01	0.2194(5)	$-1102.31(2)$
6.8	T	LB	SG	0.01	0.2514(2)	$-740.64(2)$
6.8	R	WSW	KCLDJ	0.01	0.1315(2)	$-1045.85(1)$
6.8	R	LB	KCLDJ	0.11	0.2501(5)	$-679.27(1)$
6.8	R	WSW	SG	0.02	0.223(1)	$-1047.39(2)$
6.8	R	LB	SG	0.10	0.2502(9)	$-679.53(3)$

for the parameters entering Eq. (8) are the same than the ones in the preceding section. The DMC calculation has been carried out for a selected case which we consider contains the most reasonable model. The CN radius is 6.8 Å and the IC is of T type. The H$_2$-H$_2$ interaction is SG and the parameter set for C-H$_2$ is the WSW one.

In Fig. 3, the total energy per particle of H$_2$ in the IC is shown as a function of λ and for different bundle lattice values, $D-D_0=0$, 0.05, 0.10, and 0.15 Å. The minimum of the energy is achieved with $D=D_0$, what implies an absence of dilation in the bundle of nanotubes. This is in agreement

with the corresponding case in Table II, marked by a dagger. In the full 3D calculation the equilibrium density is $\lambda_0 = 0.2184(12)$ Å^{-1}, to be compared with 0.2194(5) Å^{-1} from Table II. The second value is within the error bar of the first one. The energy per hydrogen molecule at the equilibrium density is also very similar in both cases, $e_0 = -1101.43(1)$ K and $e_0^{1D} = -1102.31(2)$ K. This clear overlap means that the 1D model (1) is a very good approximation to the physics of H$_2$ inside the interchannels of a bundle of nanotubes around the equilibrium density.

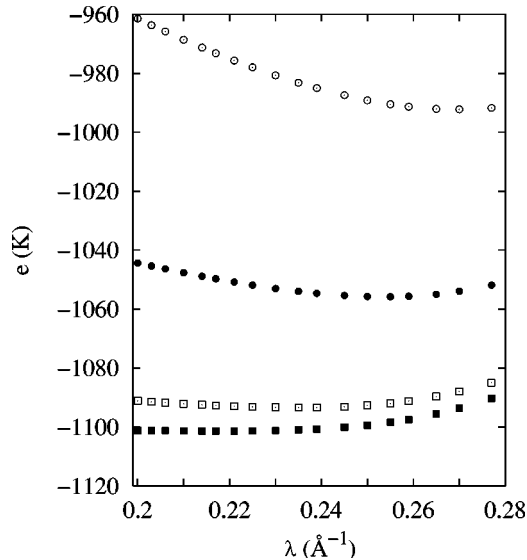Finally, in Fig. 4 the comparison between both calculations is extended to higher densities. In the energy scale, the

FIG. 3. Full DMC calculation of molecular hydrogen adsorbed in the interchannels of a CN bundle. No dilation, full squares; $D-D_0=0.05$ Å, empty squares; $D-D_0=0.10$ Å, full circles; $D-D_0=0.15$ Å, empty circles.
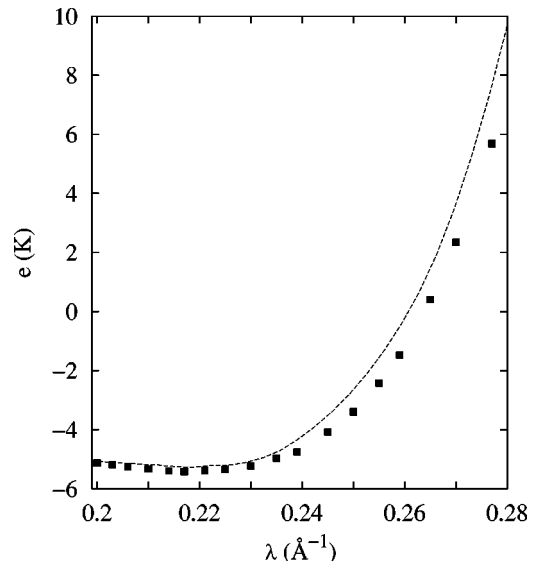

FIG. 4. Comparison between a DMC calculation (full squares) and a 1D approximation (solid line) in a case without dilation. See comments in the text.

binding energy $\epsilon_0 = -1096.02$ K (Table I) is now subtracted. Equation (1) provides un upper bound to the exact result which is very close to the exact energies near λ_0. However, its quality worsens when the density increases due to the emergence of the radial degree of freedom, which is frozen in the 1D model.

IV. SUMMARY AND CONCLUSIONS

The equation of state of H_2 adsorbed in the IC's of a CN bundle has been calculated using microscopic theory. By means of the DMC method, which provides exact results for given model potentials, the possible dilation of the bundle induced by adsorption has been carefully analyzed. The most complete analysis has been done in the 1D model.[7] In spite of its simplicity, this approach (1) has proven to be very accurate when compared with a full 3D calculation, specially near the equilibrium density. Playing with the different alternatives for the parameters entering into the calculation, the influence of each one has been established. Summarizing, the results show that the critical one is the particular C-H_2 interaction. The deeper and probably more realistic WSW potential reduces the swelling predicted by the LB model in a significant way. The same can be concluded about the C-C interaction, represented here by the k parameter, but to a lesser extent. On the other hand, sizable changes in the H_2-H_2 interaction do not modify the physics of the dilation process. Our results do not exclude completely the possibility of some lattice dilation, but if it exists, its value seems clearly smaller than the figures quoted in Ref. 7.

A key point in the discussion is the issue of what C-H_2 potential is more realistic. To this end, one should compare theoretical data with experimental results. However, the latter are really scarce. Recently, Vilches and co-workers[25,26] reported data on H_2 isotherms on bundles of closed-capped carbon nanotubes for several temperatures. At very low coverages, they deduced the existence of H_2 adsorption on the ridges created between two nanotubes in the outer part of the bundle and/or in the IC's. For these sites, they estimated a binding energy ~ 700 K, 1.5 times larger than the one for molecular hydrogen on graphite. Comparison with Table I rules out the case with $R = 6.9$ Å and the LB potential: its ϵ_0 is too small. On the other hand, the value for $R = 6.8$ Å and the LB potential seems to fit the experimental result perfectly well. However, there is a problem: the binding energy (700 K) is supposed to be an average of the energies of hydrogen adsorbed on the ridges and in the IC's. Then, the real binding energy in IC's should be greater than the experimental finding, fitting well with the results obtained with the WSW potential.

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