

# Conditions for H<sub>2</sub> adsorption in the interstitials of a bundle of carbon nanotubes

M. C. Gordillo

*Departamento de Sistemas Físicos, Químicos y Naturales, Universidad Pablo de Olavide,  
Carretera de Utrera, km 1, 41013 Sevilla, Spain*

(Received 16 February 2007; revised manuscript received 26 March 2007; published 5 September 2007)

The influence of corrugation, impurities, heterogeneity of tube diameters, shape of the interchannels, and carbon vacancies in the H<sub>2</sub> uptake by a bundle of carbon nanotubes was studied. It was found that both the existence of tubes of different chiralities and the presence of vacancies in narrow interstitials could prevent the hydrogen adsorption, making the system less useful as a reservoir in fuel cells than previously thought.

DOI: 10.1103/PhysRevB.76.115402

PACS number(s): 68.90.+g, 05.30.-d

## I. INTRODUCTION

In 1997, Dillon *et al.*<sup>1</sup> predicted that carbon nanotubes could adsorb enough hydrogen to make them useful as storage devices in fuel cells. Their findings were the beginning of a series of studies both from the theoretical<sup>2</sup> and the experimental point of view aimed at understanding the underlying mechanisms of gas adsorption in bundles of carbon nanotubes. In this last quarter, thermodynamical and diffraction data are starting to show a coherent picture, at least in the case of the light gases adsorbed in bundles of closed capped tubes: at low coverages, one finds a set of high binding energy sites that several techniques characterize as forming one-dimensional (1D) arrangements, at least in the case of <sup>4</sup>He (Refs. 3–7) and H<sub>2</sub> (Refs. 8–10). When the coverage increases, the atoms or molecules tend to form two-dimensional phases on the exposed outer surfaces of the cylinders. With an additional gas uptake, multilayers are formed.<sup>10</sup> Obviously, there is an additional adsorbing site inside the carbon nanotubes when their caps are removed.

There are at least two candidates to be the locations of the 1D arrangements. One is the valley formed between every two carbon nanotubes located in the surface of a bundle, usually termed a groove. The other is the set of adsorption sites existing every three (or more, if the bundle is not very regular) cylinders located in the inner positions in the bundle. Those places are usually termed interstitials or interchannels (IC's). In the most simple case of a complete ordered bundle of identical open (10,10) tubes with a minimum separation between centers of 17 Å, a naive geometrical calculation renders that the IC's comprise up to 15% of the total space available for adsorption excluding the surface sites. However, to enter those places, the adsorbed species should be small enough, being He, H<sub>2</sub>, and Ne the only possibilities.<sup>11</sup> Unfortunately, there is not a direct experimental way to determine if the adsorption in the 1D arrangements, if any, was produced in the outside grooves or in the inside interstitial. The data available in the case of Ne (Ref. 12) suggest that the last possibility is forbidden. In the other two cases, there are indications supporting the adsorption<sup>4,8</sup> or denying it.<sup>3</sup>

On the other hand, full quantum mechanical calculations indicate that even in the case of the small triangularly shaped IC's between three carbon nanotubes in a (10,10) bundle, the very high binding energies should guarantee the entrance of

<sup>4</sup>He,<sup>13</sup> H<sub>2</sub>,<sup>14</sup> and Ne (Ref. 15) in the interstitials. However, as mentioned above, at least part of the experimental results deemed that impossible, or resorted to irregularly shaped interstitials<sup>16</sup> to explain some of the results.<sup>8</sup> The aim of this work is to clarify the feasibility of H<sub>2</sub> adsorption inside the IC's of a bundle of carbon nanotubes. H<sub>2</sub> was chosen because of the technological implications that a detailed knowledge of its interaction with this particular substrate could have in the building of fuel cells. To do that, all the conceivable scenarios were considered: the influence of corrugation, impurities, heterogeneity of tube diameters, different IC shapes, and carbon vacancies in the carbon nanotubes. It was found that the introduction of some impurities in corrugated environments, the difference of chirality in the tubes, or the existence of vacancies in narrow IC's were the only way to avoid hydrogen adsorption.

## II. MODEL AND SIMULATION DETAILS

The calculations performed were of the diffusion Monte Carlo (DMC) type. DMC is a standard technique to solve the Schrödinger equation.<sup>17</sup> What we obtain, then, is the ground state of the system, strictly valid at 0 K. However, one expects the results to be fully valid at low enough temperatures. The Schrödinger equation we had to solve was the corresponding to one H<sub>2</sub> molecule modeled by a single sphere inside a three-dimensional interchannel formed by three or four carbon nanotubes of different diameters and/or chiralities. The carbon atoms were kept fixed, while the H<sub>2</sub> molecule was allowed to move. Impurities, when present, were readily included in this description. Modeling H<sub>2</sub> by a single sphere was repeatedly found to be an accurate description of the molecule, at least in this kind of simulations.<sup>18</sup>

One of the fundamental ingredients of any DMC calculation is the so called *trial function*, in which all the information known *a priori* is introduced. In this set of calculations, the carbon nanotubes were modeled by taking into account all the carbon atoms, both in the H<sub>2</sub>-C potential and in the trial function  $\Phi(R)$ . To do so, we considered it to be of the Jastrow form:

$$\Phi(R) = \prod_{\text{H}_2,i} \exp\left[-\frac{1}{2}\left(\frac{b}{r_{\text{H}_2-i}}\right)^5\right], \quad (1)$$

where the *i* index indicates all the carbon atoms present in the cylinders surrounding the considered IC. The *b* parameter

was obtained in a previous variational Monte Carlo calculation and found to be 2.30 Å. When impurities are present, an additional term of the same kind was added to the product. In this case, the  $b$  parameter was considered to be 3.57 Å for all three possibilities (Ne, He, and D<sub>2</sub>).

As indicated above, the carbon-H<sub>2</sub> potential was considered as a sum of the corresponding C-H<sub>2</sub> interactions and was taken from Ref. 19. The hydrogen-impurity interactions were modeled by Lennard-Jones expressions, whose parameters were taken from Ref. 11, the only exception being the H<sub>2</sub>-D<sub>2</sub> pair, for which a Silvera and Goldman potential was used.<sup>20</sup> To see if a H<sub>2</sub> molecule adsorbed in the IC's, it was placed at the beginning of the tube at the simulation starting point and let to evolve until no change in the density profile in the  $z$  direction (the tube axis) was observed (see below). This profile was taken to represent the equilibrium distribution of the system. That means that when a H<sub>2</sub> molecule stops at one point for whatever reason, that is supposed to be the real configuration.

The simulation cell comprised 20 cells (49.2 Å) in the case of arrangements of  $(n,n)$  tubes and was 51.12 Å long for the mixture of two (10,10) and one (18,0) cylinders. As for the vacancies, the single ones (in which only a C atom is removed) were taken to be of the asymmetric 5-1DB type, in which two of the dangling bonds recombine to form a pentagon.<sup>21,22</sup> We considered also an asymmetric two-atom vacancy (5-8-5, the most stable of this kind of defects, according to Ref. 22) for the wider interstitials.

### III. RESULTS

The first question one has to address is if the hydrogen molecule really adsorbs inside the IC's of a bundle of pristine and defectless carbon nanotubes. Obviously, that would depend on the characteristics of the interchannel, basically on its shape and on the presence of corrugation. We started with the simplest case, in which three perfectly formed (10,10) nanotubes separated by 17 Å (Ref. 23) produced a symmetrical interstice. This arrangement is slightly different from that discussed in Ref. 24, in which the smoothed-out carbon nanotubes have a radius of 6.9 Å. This modifies the C-H<sub>2</sub> potential outside the tube to create a potential energy barrier that impedes hydrogen to enter, a barrier that we do not see. Our results are displayed in Fig. 1. The full line represents the equilibrium density of one H<sub>2</sub> molecule when the three tubes are located in such a way as to reduce the corrugation to a minimum (displaced 0.82 Å with respect to each other). We can see that the H<sub>2</sub> distribution is regular, i.e., the molecule enters the IC without problems. The same can be said of the situation in which the corrugation is maximum (tubes located with their carbon rings sharing the same  $z$  coordinate), as can be inferred from the dashed line. Clearly, corrugation is not an issue here: H<sub>2</sub> should readily enter the IC in any case. To see the influence of the IC shape in the adsorption, we performed two additional series of calculations, one for an IC formed by two (10,10) and one (11,11) tubes, and the other with a (10,10), a (9,9), and an (11,11) tube with different corrugations. The tubes were located at distances that were the sum of their diameters plus

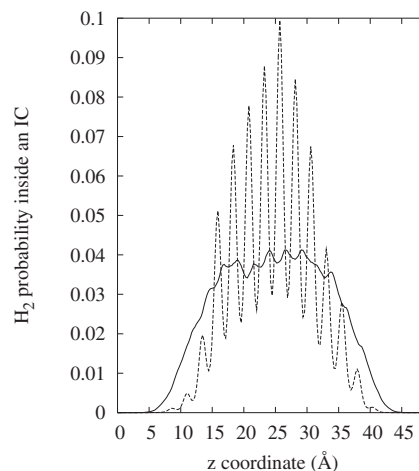


FIG. 1. Probability distribution in the  $z$  axis of a H<sub>2</sub> molecule inside an interchannel formed by three (10,10) tubes with no defects. Full line, minimum corrugation; dashed line, maximum corrugation.

3.4 Å.<sup>23</sup> The results, shown in Fig. 2, were similar to the ones already displayed: the hydrogen molecule had no problem entering the irregular interchannels. The same can be said of the other symmetrical IC considered: the square shape formed by four (10,10) tubes separated 17 Å from their closest neighbor (not shown for simplicity) is something not surprising considering that this IC has a bigger section than the others already considered. The corresponding binding energies for the minimum corrugation cases are given in Table I. The first case [three (10,10) tubes] can also be compared with the smooth average potential of Ref. 14. From all these results, one can conclude that neither the form of the interstices nor the inhomogeneity of the tubes diameters are relevant in the hydrogen adsorption since there is no obstacle for the IC's to be filled with as many H<sub>2</sub> molecules as they could bear.

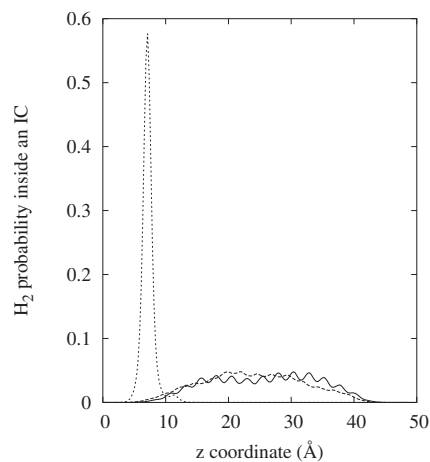


FIG. 2. Probability distribution in the  $z$  axis of a H<sub>2</sub> molecule inside an interchannel formed by a (10,10), an (11,11), and a (9,9) carbon nanotube (full line), two (10,10) and one (11,11) tubes (dashed line), and two (10,10) and one (18,0) cylinders (dotted line) with no defects. In all the cases displayed, the corrugation is minimum.

TABLE I. Binding energies in K for a single H<sub>2</sub> inside different kinds of interstices in a bundle of carbon nanotubes with no defects. The numbers indicate the cases for minimum corrugation. Error bars are given in parentheses.

IC type	
Three (10,10) tubes	1058.5(7)
Three (10,10) tubes (averaged potential) <sup>a</sup>	1096.02(2)
Two (10,10) and one (11,11) tubes	1106.2(7)
(10,10), (11,11), and (9,9) tubes	1054.1(5)
Four (10,10) tubes	709.6(7)

<sup>a</sup>Reference 14.

However, things are different when we consider the case of two (10,10) tubes forming a channel with an (18,0) one. Although their radii are similar [6.8 Å in the first case and 7 Å in the second, a smaller difference than for the (10,10) and (11,11) tubes], the incommensurability of the cylinder potentials makes the H<sub>2</sub> molecule stop in the first minimum of the potential energy, as can be seen in Fig. 2. That probably means that to adsorb in the IC's, all the nanotubes should be of the same chirality, since once the first molecule is stopped, the rest of the possible adsorbates could not enter inside the IC's.

The second source of problems can be the impurities of the right size entering the IC's before the H<sub>2</sub> molecules can do it, and blocking the way. As mentioned above, the only species able to do it are <sup>4</sup>He, D<sub>2</sub>, and Ne. However, the calculations show that this is a minor problem: if the impurity itself enters the IC, the H<sub>2</sub> would readily follow. This is exactly what we can see in Fig. 3: from top to bottom, we have the cases of Ne, D<sub>2</sub>, and <sup>4</sup>He. The full lines display the impurity probability profiles, while the dashed ones correspond to the hydrogen molecule. In all cases, we have low enough corrugation to allow the impurities to enter. We ob-

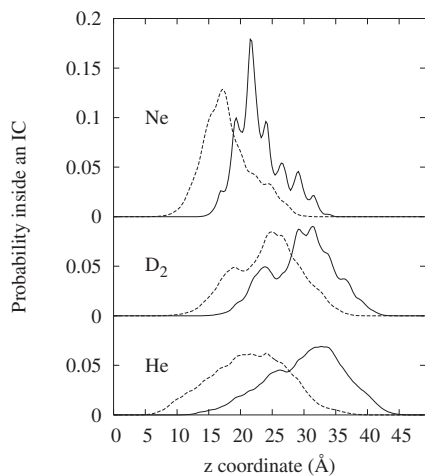


FIG. 3. Probability distribution in the z axis of some impurities (full lines) and following a H<sub>2</sub> molecule (dashed lines) inside an interchannel formed by three (10,10) tubes with no defects and minimum corrugation. From top to bottom, we have the cases of Ne, D<sub>2</sub>, and <sup>4</sup>He impurities.

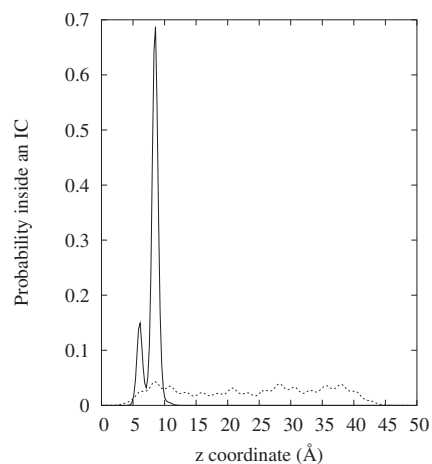


FIG. 4. Probability distribution in the z axis of a Ne impurity (full line) and a H<sub>2</sub> molecule (dashed line) inside an interchannel formed by four regularly disposed (10,10) tubes with no defects.

serve that the H<sub>2</sub> spreads almost uniformly throughout the IC, even though its distribution follows closely that of the impurities. Obviously, when the corrugation is big enough to prevent the impurity to enter (the case of Ne, see Ref. 25), the hydrogen does not go inside either. However, this only happens for the narrow environment of the triangularly shaped IC's. In Fig. 4, we can see that even when the Ne atom gets stuck due to corrugation, the H<sub>2</sub> is able to “jump over” the impurity and roams freely in the IC's with square sections. According to these series of results, the impurities that are able to enter the channel are not an obstacle to hydrogen adsorption in the IC's.

Having seen the influence that the interstitial shape, corrugation, and the presence of impurities have in the adsorption, the only remaining factor is the existence of carbon vacancies. Their influence in the adsorption in regular IC's has already been studied for the quantum noble gases in Ref. 25. There, a single carbon vacancy of the 5-1DB type (a pentagon and a dangling bond) was introduced in one of those interchannels. The result was that the gas atoms were stopped and prevented to go beyond the vacancy as a consequence of the potential barrier created by the absence of the carbon atom. Something similar happens in the case of H<sub>2</sub>, as can be shown with the help of Fig. 5: a vacancy in the center of the IC prevents the H<sub>2</sub> molecule to move further both in the cases in which the vacancy is closest to the tube axis (full line) or furthest away (dashed one). This would imply that when a single carbon atom is missing, the adsorption would stop at the point at which the vacancy is. Since even the purest carbon nanotubes are thought to have a certain measure of defects,<sup>27</sup> a vacancy close to the entrance of the IC would make it an empty place. However, this only holds for narrow interstices. If one considers the wider, square-shaped IC's already mentioned and repeats the calculations with a 5-1DB defect as close as possible to the center of the axis of the channel, it can be seen that the hydrogen molecules have no problem to explore it entirely (full line, Fig. 6). The same can be said of the case in which the defect involves the absence of two carbon atoms (a 5-8-5 vacancy,<sup>22</sup> dashed line in Fig. 6). That would mean that at least some of the hydro-

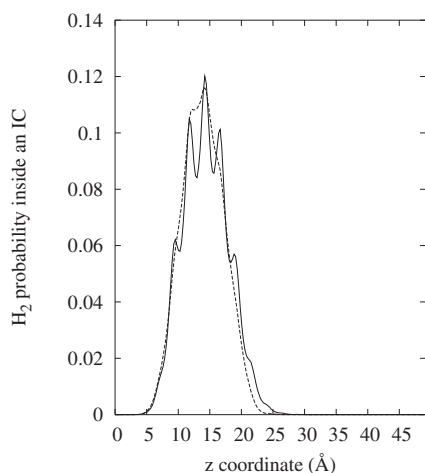


FIG. 5. The same as the previous figures but for a  $H_2$  molecule inside an interchannel formed by three regularly disposed (10,10) tubes with a single 5-1DB defect in the center of the simulation cell closest (full line) or furthest (dashed line) to the IC  $z$  axis.

gen atoms would enter the bigger interstices, increasing the total adsorption capacity of the bundle.

Obviously, this past scenario would hold only if the  $H_2$ -tube interaction is of the physisorption type. According to Ref. 26, a dangling bond is reactive and a  $H_2$  molecule could chemisorb on it after the overcoming of a considerable energy barrier [1.2–1.65 eV, depending on the original orientation of the  $H_2$  (Ref. 26)]. However, that does not invalidate the results discussed above. Even though this kind of DMC calculations is not able to deal with chemisorption, an analysis of the data of Ref. 26 indicates that a chemisorbed  $H_2$  molecule will block an interchannel of the narrow type, since this process will be produced in the outer surface of the carbon nanotube, with or without hydrogen dissociation. Thus, a chemisorbed molecule in a triangular IC would prevent additional hydrogen to enter the IC, just as in the phy-

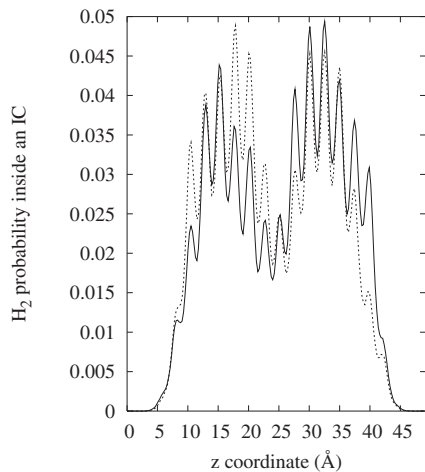


FIG. 6. The same as Fig. 5 but for a  $H_2$  molecule inside an interchannel formed by four (10,10) tubes. The full line indicates the case of a 5-1DB defect closest to the  $z$  axis of the interchannel, while the dashed line displays the adsorption profile of the molecule with a 5-8-5 defect in the same location.

isorbed case. This would be independent of the detailed interaction between the hydrogen molecule and the carbon (single or double) defect. It is a simple question of blocking the way. The same could be said of a chemisorbed H atom: experimental accounts on graphite<sup>29</sup> and theoretical on carbon nanotubes<sup>26</sup> indicate that the hydrogen atom would be around 1.2 Å on top of the graphene level, a distance enough to block the IC. However, if the interchannel becomes bigger, the situation could change, since a  $H_2$  chemisorbed molecule will not necessarily stop more molecules to enter. A nondissociated chemisorbed  $H_2$  molecule in a fixed position would have roughly the same effect than a Ne atom stuck by corrugation (their Lennard-Jones parameters are similar<sup>11</sup>), and will not block other  $H_2$  molecules to enter a wide interstice (see Fig. 4). Something similar could be said of a dissociated  $H_2$ : the combined effect of two H atoms close together is quite similar to that of a Ne atom in size (see their respective Lennard-Jones parameters in Refs. 11 and 30, respectively), but with a lesser  $\epsilon$  value. That means that if the interstitial is wide enough, the remaining hydrogen molecules should be able to jump over this single defect; but if the concentration of defects is high enough, the hindrance could be an issue. On the other hand, in the available literature<sup>26</sup> there is no indication of hydrogen chemisorption in a 5-8-5 defect, meaning that our above considerations will hold.

#### IV. CONCLUDING REMARKS

Summarizing, DMC calculations were performed on the possibility of  $H_2$  adsorption on the interstices of a bundle of carbon nanotubes. From the results obtained, it can be stated that at low enough temperatures, hydrogen molecules should readily enter the IC's of a bundle of (10,10) cylinders. Neither the inhomogeneity of the tube diameters nor the presence of small impurities is enough to prevent the uptake, even on the narrower interstices. The only effects that can prevent the adsorption are the presence of nanotubes of different chiralities and the existence of vacancies. This last problem is very important, since all the nanotubes are thought to have a certain amount of them.<sup>27</sup> However, that would be of note only in the case of narrow IC's, since the  $H_2$  molecules will be able to avoid the vacancies in wider environments.

According to our results, the  $H_2$  adsorbing capacity of a bundle of carbon nanotubes can be greatly diminished from the most optimistic estimations, since the presence of vacancies would impede the narrower IC's to store hydrogen. In addition, there are some indications that inhomogeneity is not a key feature of the carbon nanotube bundles,<sup>28</sup> meaning that the amount of hydrogen adsorption in IC's could be negligible. The implications for the use of carbon nanotubes as reservoirs in fuel cells are clear: the adsorption capability of these bundles could be not enough to fulfill the necessary requirements. However, to be sure of that, one would have to make additional calculations about the adsorption of molecular hydrogen in all the remaining accessible positions (outer surfaces and grooves and on the inside of tubes with their caps removed), something that can be done with the help of



additional Diffusion Monte Carlo calculations. Nevertheless, since those are only valid at low temperatures, those simulations could be complemented with some finite temperature results (such as path integral Monte Carlo or molecular dynamics).

#### ACKNOWLEDGMENTS

The Spanish Ministry of Education and Science (MEC) and the Junta de Andalucía are thanked for financial support under Grant No. FIS2006-02356 and FEDER funds and group FQM-205, respectively.

- 
- <sup>1</sup>A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature (London)* **386**, 377 (1997).
- <sup>2</sup>M. M. Calbi, M. W. Cole, S. M. Gatica, M. J. Bojan, and G. Stan, *Rev. Mod. Phys.* **73**, 857 (2001).
- <sup>3</sup>J. V. Pearce, M. A. Adams, O. E. Vilches, M. R. Johnson, and H. R. Glyde, *Phys. Rev. Lett.* **95**, 185302 (2005).
- <sup>4</sup>J. C. Lasjaunias, K. Biljakovic, J. L. Sauvajol, and P. Monceau, *Phys. Rev. Lett.* **91**, 025901 (2003).
- <sup>5</sup>W. Teizer, R. B. Hallock, E. Dujardin, and T. W. Ebbesen, *Phys. Rev. Lett.* **82**, 5305 (1999).
- <sup>6</sup>W. Teizer, R. B. Hallock, E. Dujardin, and T. W. Ebbesen, *Phys. Rev. Lett.* **84**, 1844 (2000).
- <sup>7</sup>T. Wilson and O. E. Vilches, *Physica B* **329-333**, 278 (2003).
- <sup>8</sup>M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsky, M. Muris, M. R. Johnson, T. Wilson, M. DePies, and O. E. Vilches, *Phys. Rev. B* **70**, 035410 (2004).
- <sup>9</sup>T. Wilson, A. Tyburski, M. R. DePies, O. E. Vilches, D. Becquet, and M. Bienfait, *J. Low Temp. Phys.* **126**, 403 (2002).
- <sup>10</sup>S. Ramachandran, T. A. Wilson, D. Vandervelde, D. K. Holmes, and O. E. Vilches, *J. Low Temp. Phys.* **134**, 115 (2004).
- <sup>11</sup>G. Stan, M. J. Bojan, S. Curtarolo, S. M. Gatica, and M. W. Cole, *Phys. Rev. B* **62**, 2173 (2000).
- <sup>12</sup>S. Talapatra, A. Z. Zambano, S. E. Weber, and A. D. Migone, *Phys. Rev. Lett.* **85**, 138 (2000).
- <sup>13</sup>J. Boronat, M. C. Gordillo, and J. Casulleras, *J. Low Temp. Phys.* **126**, 199 (2002).
- <sup>14</sup>M. C. Gordillo, J. Boronat, and J. Casulleras, *Phys. Rev. B* **68**, 125421 (2003).
- <sup>15</sup>M. C. Gordillo, L. Brualla and S. Fantoni, *Phys. Rev. B* **70**, 245420 (2004).
- <sup>16</sup>W. Shi and J. K. Johnson, *Phys. Rev. Lett.* **91**, 015504 (2003).
- <sup>17</sup>J. Boronat and J. Casulleras, *Phys. Rev. B* **49**, 8920 (1994).
- <sup>18</sup>M. Wagner and D. M. Ceperley, *J. Low Temp. Phys.* **89**, 581 (1992).
- <sup>19</sup>G. Stan and M. W. Cole, *Surf. Sci.* **395**, 280 (1998).
- <sup>20</sup>I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
- <sup>21</sup>A. J. Lu and B. C. Pan, *Phys. Rev. Lett.* **92**, 105504 (2004).
- <sup>22</sup>S. Zhang, S. Meilke, R. Khare, D. Troya, R. Ruoff, G. Schatz, and T. Belytschko, *Phys. Rev. B* **71**, 115403 (2005).
- <sup>23</sup>J. Tersoff and R. S. Ruoff, *Phys. Rev. Lett.* **73**, 676 (1994).
- <sup>24</sup>M. M. Calbi and J. L. Riccardo, *Phys. Rev. Lett.* **94**, 246103 (2005).
- <sup>25</sup>M. C. Gordillo, *Phys. Rev. Lett.* **96**, 216102 (2006).
- <sup>26</sup>A. J. Lu and B. C. Pan, *Phys. Rev. B* **71**, 165416 (2005).
- <sup>27</sup>J. Kotakoski, A. V. Krasheninnikov, and K. Nordlund, *Phys. Rev. B* **74**, 245420 (2006).
- <sup>28</sup>S. Rols, M. R. Johnson, P. Zeppenfeld, M. Bienfait, O. E. Vilches, and J. Schneble, *Phys. Rev. B* **71**, 155411 (2005).
- <sup>29</sup>P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, and R. M. Nieminen, *Phys. Rev. Lett.* **93**, 187202 (2004).
- <sup>30</sup>M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).