

## Prediction of the hydrogen storage capacity of carbon nanoscrolls

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Classical grand-canonical Monte Carlo simulations were performed to investigate the equilibrium hydrogen storage capacity of carbon nanoscrolls. The results show that hydrogen molecules can be absorbed in the internal cavity as well as on the external surface of the scroll when the interlayer spacing is less than 4.4 Å. When the interlayer spacing is increased to 6.4 Å, by assuming spacing increase due to intercalation of other species, the hydrogen molecules can also be incorporated in the interlayer galleries, doubling the gravimetric storage capacity and reaching 5.5 wt % hydrogen per weight carbon at 150 K and 1 MPa. Our results showed that intercalated carbon nanoscrolls may be a promising material for hydrogen storage.

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### I. INTRODUCTION

Hydrogen (H<sub>2</sub>) has recently been the object of intense research as a secondarily derived energy source. It would be ideal as a synthetic fuel because it is lightweight, conveniently produced, and its oxidant product (water) is environmentally benign. Unlike petroleum, it can be easily generated from renewable energy sources. Of the problems to be solved for the utilization of hydrogen energy, the most important one is how to store H<sub>2</sub> easily and cheaply. The target of the U.S. Department of Energy (DOE) for hydrogen storage is a gravimetric capacity (weight of stored H<sub>2</sub>/system weight) of 6.5 wt % and a volumetric density of 62 kg H<sub>2</sub> m<sup>-3</sup>.<sup>1</sup> The development of hydrogen-fueled vehicles and portable electronics will require new materials that can store large amounts of hydrogen at ambient temperature and relatively low pressures, and provide small volume, low weight, and fast kinetics for recharging.<sup>2,3</sup>

Graphite, carbon nanotubes, and nanofibers have been both theoretically and experimentally investigated as potential adsorbent structures.<sup>1,4-22</sup> Though some reports claim very high storage capacity, these have not been supported by other investigators.<sup>23</sup> For instance, while the highest capacity of hydrogen storage (67.55 wt %) reported by Chambers *et al.* with the so-called herringbone graphite fibers<sup>4</sup> could not be confirmed in any laboratory up to now,<sup>23</sup> Ahn *et al.* measured for comparable carbon nanofibers a storage capacity less than 0.2 wt % using the same method and under comparable conditions.<sup>24</sup> A rough estimate of about 1 wt % can be obtained from volumetric measurements for carbon nanostructures at room temperature and 10 MPa when the surface area is about 500 m<sup>2</sup>/g.<sup>23</sup> Panella *et al.* investigated different carbon nanostructures optimized for hydrogen storage obtaining the highest storage capacity of 4.5 wt % at 77 K for activated carbon with a specific area of 2564 m<sup>2</sup>/g.<sup>25</sup> Alkali-doped nanotubes have also been investigated. While Chen *et al.* report adsorption of 20 and 14 wt % for Li-doped and K-doped carbon nanotube,<sup>7</sup> respectively, these extraordinarily high values appear to be a result of an artifact. Yang obtained adsorption of 2.5 and 1.8 wt % for the same materials, respectively.<sup>8</sup> In those hydrogen storage experiments

where the results have been confirmed by subsequent investigators, the major percentage of hydrogen is stored by physisorption of H<sub>2</sub> molecules, in contrast to chemisorption observed for metal hydrides.<sup>3</sup> The differences observed in the experimental data reflect how sensitive the reported hydrogen storage capacity is to the details of the experimental procedures, such as nanotube synthesis and pretreatment processes, hydrogen charging techniques, and storage capacity measurement methods.

Theoretical investigations on nanotubes as hydrogen storage materials include Monte Carlo calculations,<sup>9-16</sup> classical molecular-dynamics simulations,<sup>17,18</sup> first-principles calculations,<sup>19,20</sup> and geometry-based estimates.<sup>21,22</sup> The investigations revealed that the adsorption process depends on structural parameters such as size, geometry (tubular or slit pores), distance between pores, and storage temperature and pressure. Furthermore, studies involving finite-diameter ropes of single-walled carbon nanotubes have demonstrated the important role of the external surface of the rope in the hydrogen storage capacity.<sup>11</sup> Like the experimental results, the theoretical predictions by different groups also disagree. The range of the storage capability of carbon nanotube adsorption predicted by molecular simulations varies from ~2% in a tube of 12.2 Å diameter [133 K, 10 MPa, and intertube distance of 3.2 Å (Ref. 10)] to ~12% in a tube of 22 Å diameter [77 K, 10 MPa, and intertube distance of 1.1 Å (Ref. 12)].

Recently, Viculis *et al.*<sup>26</sup> have reported that a low-temperature synthesis method produces a different type of carbon structure, named carbon nanoscroll (CNS).<sup>26,29</sup> These structures are formed by the jelly roll-like wrapping of a graphite sheet to form a nanotube. The synthetic route for carbon nanoscrolls involves intercalation of graphite flakes with potassium metal followed by exfoliation with ethanol to make a dispersion of carbon sheets. After sonication to assist exfoliation and spiral wrapping of the graphite sheets, carbon nanoscrolls are formed.<sup>26</sup> Theoretical studies of the structural and dynamical properties of carbon nanoscrolls revealed that the carbon nanoscroll formation is a self-sustained curling process after a critical overlap area is reached.<sup>27</sup> Depending on the initial shape and dimensions of the graphite sheet, the lowest-energy activated state for self-rolling can have a chi-

ral angle that differs from that developed during the rolling process. Also, conical scrolls can be trapped as metastable states<sup>27</sup> that are thermodynamically less stable than parallel-packed graphene sheets. Stankovich *et al.* have recently described a method for producing large amounts of graphene embedded in a polymer matrix.<sup>28</sup> This work suggests routes for producing large quantities of carbon nanoscrolls.

Almost any sheetlike material can self-assemble into scrolls as long as the lateral sheet dimension is sufficiently large that the energy gain from noncovalent binding between layers of the scroll is sufficient to compensate for the elastic energy cost of forming the scroll. Compositions experimentally demonstrated to form scrolls include, for example, graphite,<sup>26,29</sup>  $V_2O_5$ ,<sup>30</sup> and  $H_2Ti_3O_7$ .<sup>31</sup> Since scrolls can be possibly made industrially by simply exfoliating materials that are presently made in high volume, the use of such structures for hydrogen storage is potentially low cost. Also very important, rapid uptake and release of hydrogen is enabled by the existence of a side entry path all along the length of the scroll.

Because of the scroll topology, scroll properties should differ from those of either single or multiwalled carbon nanotubes. For example, in contrast to single and multiwalled carbon nanotubes, CNSs provide interlayer galleries that can be intercalated with donors and acceptors, and the CNS diameter can expand to accommodate the volume of the intercalant. This feature is potentially important for hydrogen storage where, in principle, these nanoscrolls can store hydrogen between layers of the sheet, on the external surface of the scroll, at the center of the scroll, and in interstitial space between scrolls. These nanoscrolls can act like expanding suitcases—increasing in diameter with increasing hydrogen pickup. Classical molecular-dynamics simulations have shown that significant hydrogen incorporation is possible at 77 K for nanoscrolls, while at higher temperature (300 K), thermal energy drastically reduces this storage capability.<sup>32,33</sup> However, studies to determine the gravimetric capacity of hydrogen storage in nanotube scrolls have not yet been conducted.

In this work, we have used grand-canonical Monte Carlo (GCMC) simulations to estimate the hydrogen storage capacity of carbon nanoscrolls. The simulations were performed for three nanoscroll configurations: isolated, crystal packed, and bundled nanoscrolls. We explored the scroll adsorption capacity by changing the space between scroll layers. The use of expanded interlayers mimics the presence of intercalants between the layers without the necessity of taking them into account explicitly. This work does not address the hydrogen release and thermodynamics of hydrogen binding as the method used in the present investigation is not adequate for studying these issues. They can be addressed by a more suitable approach (e.g., molecular dynamics), where the dynamical aspects of uptake and/or releasing can be explicitly taken into account.

## II. METHODOLOGY

In order to study the storage capability of nanoscrolls, we performed constant-gas-pressure GCMC calculations.<sup>34</sup> We

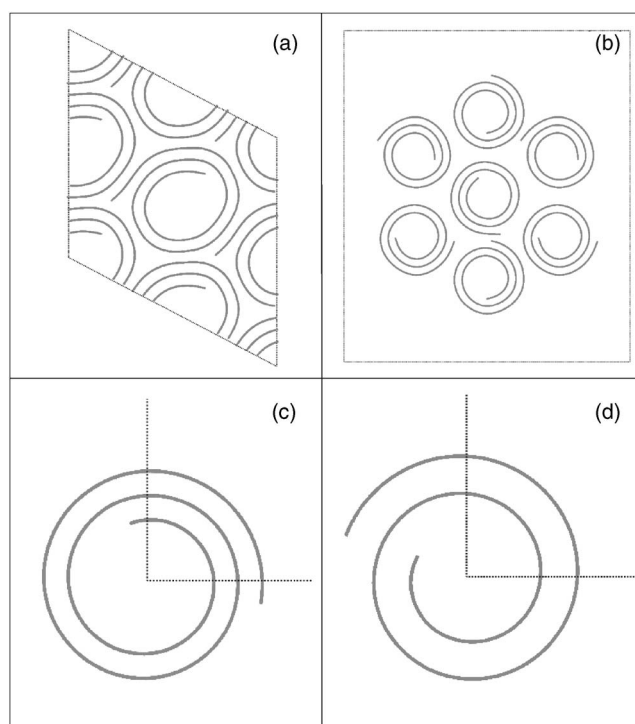


FIG. 1. Configurations used in the simulations of the hydrogen storage in carbon nanoscrolls. (a) crystalline arrangement, (b) bundled, and [(c) and (d)] isolated scrolls. The isolated scrolls shown in (c) and (d) present scrolls with different interlayer spacings, 0.34 and 0.64 nm, respectively.

have used the GCMC method to simulate hydrogen storage for scrolls that are in thermodynamic equilibrium with respect to adsorbed hydrogen gas and hydrogen gas in a large tank at a given temperature and pressure. CERIU<sup>2</sup> software<sup>35</sup> was used to perform the calculations. Exploiting energy dependencies employed by Williams and Eklund<sup>11</sup> for calculating hydrogen storage in carbon nanotube ropes, we used a simplified three-parameter “exponential-6” potential,  $U(r) = A \exp(-\alpha r) - B/r^6$ , for  $H_2$ - $H_2$  interactions, where  $r$  is the internuclear distance, which was obtained by fitting the seven-parameter potential of Silvera and Goldman.<sup>36</sup> The parameters used were  $A = 4.621 \times 10^6$  K,  $\alpha = 3.457 \text{ \AA}^{-1}$ , and  $B = 1.037 \times 10^5 \text{ K \AA}^6$ .<sup>6</sup> This simplified potential reproduces experimental  $H_2$  density values both at 80 K and 10 MPa and at 300 K and 0.1 MPa.<sup>11</sup>

As the available experimental data for carbon nanoscrolls are still very limited and structural details are unavailable,<sup>26,29</sup> we investigated three possible configurations. The first configuration [Fig. 1(a)] is a close-packed pseudo-hexagonal arrangement of scrolls in which each scroll is generated from a single graphite sheet having approximate dimensions of  $34 \times 200 \text{ \AA}^2$  (totalizing 10 496 carbon atoms). These scrolls were generated using an Archimedean spiral having an internal diameter of 20  $\text{\AA}$  and a distance between sheet layers in the scroll of 0.34 nm. The crystal packing arrangement of these scrolls was derived by geometrical optimization using the UNIVERSAL force field,<sup>37</sup> where both atom positions and cell parameters were allowed to vary. The resulting simulation box has the following dimensions: 68.5,

66.3, 33.9, 88.9°, 88.7°, and 117.4° for the lattice parameters  $a$ ,  $b$ , and  $c$  (in Å) and the unit-cell angles  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively.

In order to estimate the hydrogen storage capacity in scroll bundles, we considered a second configuration [Fig. 1(b)] composed of seven hexagonally coordinated scrolls having the same dimension as for the first model, placed in a simulation box of  $147 \times 127 \times 34 \text{ \AA}^3$  (totalizing 18 368 carbon atoms).<sup>38</sup> The angular orientations of the scrolls were randomly chosen before the geometrical optimizations. The third configuration represents an isolated scroll model generated from a single graphite layer with approximate dimensions of  $36 \times 197 \text{ \AA}^2$  (2934 carbon atoms). For this configuration, we simulated the effect of external intercalants on the scroll diameter expansion by calculating the hydrogen storage in isolated scrolls with different interlayer spacings  $a$  (0.34, 0.44, 0.54, and 0.64 nm). The scroll configurations for  $a=0.34$  and  $a=0.64$  nm are shown in Figs. 1(c) and 1(d), respectively. The use of intercalants (e.g., alkaline ions) can lead to the doping of a carbon substrate. First-principles calculations for the hydrogen adsorption in Li-doped porous carbon,<sup>39</sup> graphene layers, and carbon nanotubes<sup>40</sup> have been performed and showed no tendency for dissociation of the hydrogen molecule. This suggests molecular physisorption as the main mechanism responsible for the hydrogen adsorption on Li-doped carbon environments. Furthermore, results from calculations for porous carbon<sup>39</sup> indicated that hydrogen adsorption is facilitated by an interlayer distance of about 0.55 nm. Periodic boundary conditions were imposed in all directions for the simulation box. The interlayer distance expansion from 0.34 to 0.54 nm has been observed in potassium-intercalated graphite.<sup>41</sup> Since the intercalant is not explicitly present in our calculations, the derived storage capacity is an upper limit for the allowed capacity in these structures unless intercalant-hydrogen interactions are strong. Guay *et al.*<sup>16</sup> have found that the presence of metallic particles, which could act as intercalants in scroll structures, can enhance the hydrogen uptake in a single-walled nanotube (SWNT) network.

To compare the hydrogen storage determined by Monte Carlo simulations with experiment, we computed the excess gravimetric storage<sup>11</sup> wt % of a carbon host defined by

$$\text{wt \%} = \frac{m_{\text{H}} - m_{\text{H}}^0}{m_{\text{H}} - m_{\text{H}}^0 + m_{\text{C}}}, \quad (1)$$

where  $m_{\text{C}}$  ( $m_{\text{H}}$ ) is the total mass of carbon (hydrogen) in the simulation cell, and  $m_{\text{H}}^0$  is the total mass of hydrogen present in the occupiable volume due only to  $\text{H}_2$ - $\text{H}_2$  interactions. The value of  $m_{\text{H}}^0$  was computed by Monte Carlo loading of  $\text{H}_2$  in a simulation cell without scrolls with the same accessible volume for the  $\text{H}_2$  molecules. This volume was determined using the maximum number of spherical probes of diameter<sup>11</sup> 2.8 Å (comparable to the kinetic diameter of  $\text{H}_2$  under the conditions of interest) that can be loaded in the simulation box containing the scrolls, considering 1.7 Å as the van der Waals radius for the carbon atoms.<sup>11</sup> In our simulations, up to  $10^7$  configurations were used to achieve total energy convergence. The final  $10^4$  configurations were used

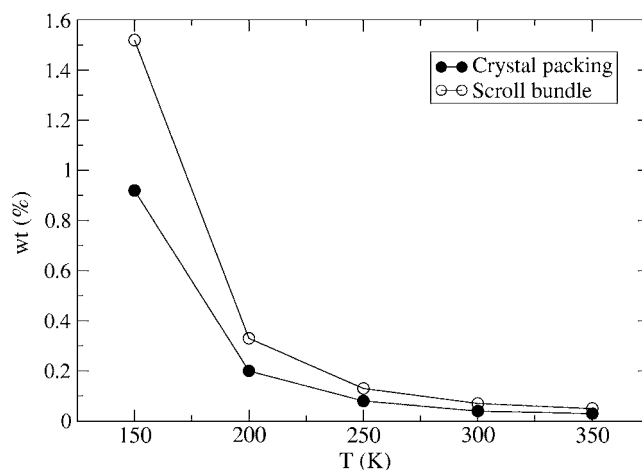


FIG. 2. Excess gravimetric storage for different temperatures at 1 MPa for the cases of crystal packing and scroll bundle.

to compute the average hydrogen loading. We determined the storage capacity of the scroll configurations for temperatures in the range of 150–350 K for the low-pressure regime. A pressure of 1 MPa (145 psi) was used in all simulations.

### III. RESULTS AND DISCUSSION

Figure 2 shows the dependence of the hydrogen storage on temperature for close-packed bundles without intercalants ( $a=0.34$  nm). We can see the expected behavior, i.e., higher values of wt % hydrogen for lower temperatures. At high temperatures, thermal energy overcomes van der Waals interactions and thus the hydrogen molecules are not very effectively captured by the scroll structure. However, when the temperature is lowered to 150 K, there is a significant increase in the hydrogen storage, reaching values of 0.9% and 1.5% hydrogen for the crystal packing and scroll bundle cases, respectively. Furthermore, we can see that the scroll bundle configuration presents a higher absorption than the crystal packing case, specially at 150 K. This result is consistent with the case of SWNT ropes investigated by Williams and Eklund,<sup>11</sup> which indicates that small diameter ropes are preferable for hydrogen storage than the larger diameter ones. This is due to the higher specific areas, mainly due to the outer adsorption sites, presented by the small diameter SWNT ropes. Similar gravimetric storage was obtained by Levesque *et al.*<sup>15</sup> for a crystal packing of single-walled carbon nanotubes with the distance between tubes artificially increased to 6 Å (at 150 K and 1 MPa).

In Fig. 3 we show the  $\text{H}_2$  molecule distribution over the structures of the crystal-packed and scroll bundle configurations. We can see for both configurations  $\text{H}_2$  molecules on the internal surface of scrolls (endohedral sites) as well as in the spacing between adjacent scrolls (interstitial sites), covering all the scroll axis extension. Moreover, in the case of a scroll bundle,  $\text{H}_2$  molecules are also found physisorbed on the outer layer of the bundle. However, due to the orientational disorder of scrolls in the scroll bundle, the spacing between adjacent scrolls is larger in some internal regions than others, and, therefore, more  $\text{H}_2$  are seen on the intersti-

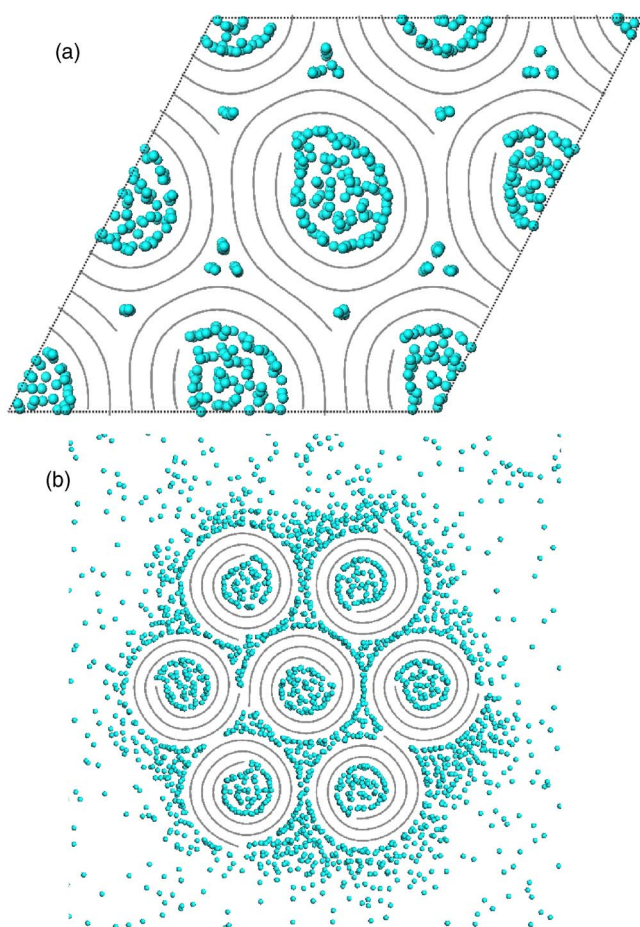


FIG. 3. (Color online) Top-view snapshots of the equilibrium state at 150 K and 1 MPa for the (a) crystal-packed and (b) scroll bundle arrangements. The balls represent H<sub>2</sub> molecules.

tial sites in comparison to the crystallographically packed arrangement. The same disorder can contribute to scroll deformation to elliptical-like shapes in scroll bundles. Further studies focusing into these thermal aspects are necessary to clarify this aspect and are currently in progress. The common aspect of both configurations is that no H<sub>2</sub> molecules are observed in the interlayer galleries of individual scrolls. This result indicates that hydrogen storage in carbon scrolls arranged in configurations similar to the ones shown in Figs. 1(a) and 1(b) is not efficient and cannot reach the DOE target if a 3.4 Å spacing is maintained. It is worth mentioning that different arrangements, for instance, scroll with conical shapes or multilayered scrolls, can lead to different storage capacities.

In order to determine the contribution of interlayer galleries on the hydrogen storage in carbon scrolls, we have analyzed single, isolated scroll models with different interlayer spacings. Figure 4 shows the storage capacity of scroll models with  $a=0.34\text{--}0.64$  nm for different temperatures. Similar to the previous considered configurations, lower temperatures also lead to larger values of gravimetric capacity reaching values of about 2.6% hydrogen for the models with  $a=0.34$  and 0.44 nm, and 5.5% for the model with  $a=0.64$  nm at 150 K. For bundle configurations, one could expect even higher values due to the possibility of H<sub>2</sub> storage

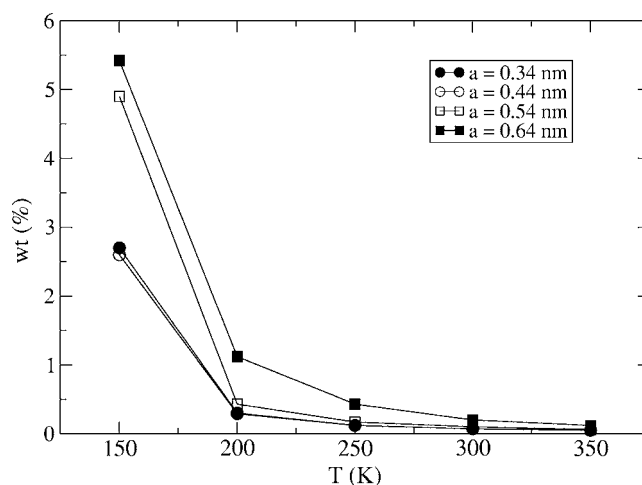


FIG. 4. Excess gravimetric storage for different temperatures at 1 MPa for the isolated scroll models with different interlayer spacings.

in the regions between scrolls. The distribution of H<sub>2</sub> molecules are shown in Fig. 5 for a temperature of 150 K. We can see that for interlayer spacing of 0.34–0.44 nm the H<sub>2</sub> molecules are distributed mainly in the endohedral sites and on the outer scroll surface. When the interlayer spacing reaches 0.54 nm, H<sub>2</sub> molecules can now reside in the interlayer galleries. This incorporation in the galleries together with the increase in the adsorption in the outer scroll layer double the gravimetric capacity. In addition, the sites in the galleries provide a preferable location for the H<sub>2</sub> molecules.

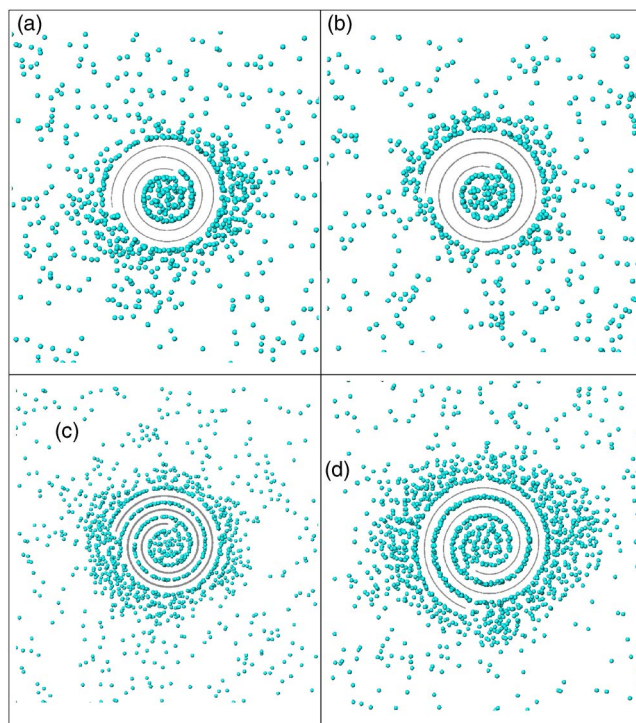


FIG. 5. (Color online) Top-view snapshots of the equilibrium state at 150 K and 1 MPa for the isolated scroll models with interlayer spacings of (a) 0.34, (b) 0.44, (c) 0.54, and (d) 0.64 nm.

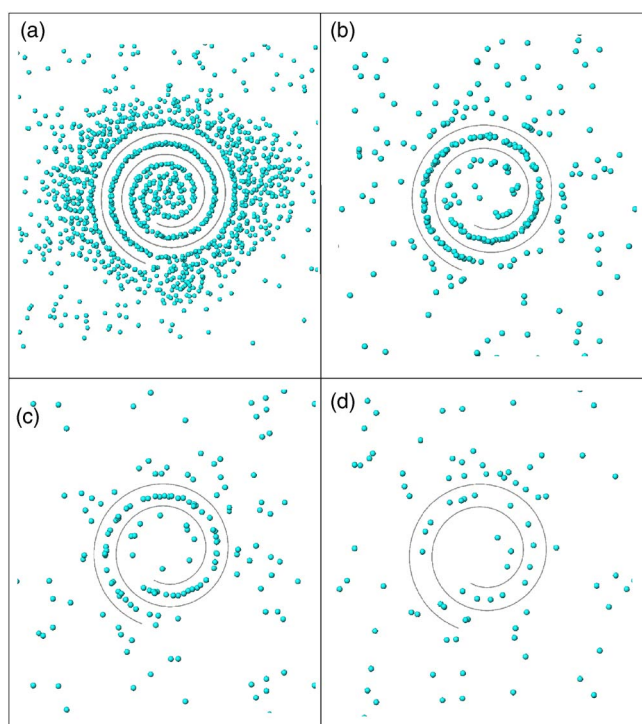


FIG. 6. (Color online) Top-view snapshots of the equilibrium state for the isolated scroll with an interlayer spacing of 0.64 nm at (a) 150, (b) 200, (c) 250, and (d) 300 K.

This can be verified for the distributions of  $H_2$  molecules in the scroll model with  $a=0.64$  nm for the different temperatures considered here as shown in Fig. 6. While for 300 K only a few  $H_2$  molecules are in the galleries, for 250 and 200 K they represent the major part of adsorbed molecules. At 150 K,  $H_2$  molecules in the endohedral site and on the outer surface are also presented in addition to the molecules in the galleries. This result indicates that the sorption and/or desorption cycle on carbon scrolls can be controlled by thermal cycles. Practically all adsorbed molecules (5.5% by weight hydrogen at 150 K and 1 MPa) can be released for the specific case of  $a=0.64$  nm when the scroll is heated up to 350 K. Similar to what was observed in Monte Carlo calculations<sup>11</sup> for carbon nanotubes and in molecular-dynamics simulations<sup>32</sup> for carbon nanoscrolls, it seems that no saturation would occur while accessible sites are present.

The kinetics of the sorption and/or desorption of hydrogen is an important issue to select good candidates for hydrogen

storage. The uptake and/or release cycle of hydrogen in carbon nanoscrolls has been simulated by classical molecular dynamics.<sup>33</sup> The system (carbon nanoscroll and hydrogen molecules) was initially thermalized at 80 K, leading to some amount of hydrogen to be adsorbed in the carbon nanoscroll. Then, the system was heated up and cooled down a couple of times. The results indicated that the amount of adsorbed hydrogen is reduced when the temperature is increased ( $\approx 400$  K) and it is approximately recovered when the temperature is decreased.

Besides equilibrium hydrogen storage capability, hydrogen transport through the carbon nanoscrolls is also critically important for practical applications. Further investigations, using molecular-dynamics simulations, for example, are needed to quantify rate aspects.

#### IV. CONCLUSIONS

In this work, we investigated the hydrogen storage capacity of carbon nanoscrolls using classical grand-canonical Monte Carlo calculations. At equilibrium geometries, i.e., when the interlayer spacing is about 3.4 Å, the scroll storage capacity can reach 2.5 wt %, which is higher than the values obtained for crystallographically packed single walled carbon nanotubes at a 150 K and 1 MPa.<sup>15</sup> Higher capacities were reached when increased interlayer spacings within scrolls were explored. The maximum value of 5.5 wt % hydrogen was obtained when the interlayer spacing was 6.4 Å. This is in agreement with the general proposition that adsorption is strongly influenced by the structure porosity. While all the present simulations were performed at low pressure (1 MPa) and relatively high temperatures (150–350 K), we expect an increase in the storage capacity of carbon nanoscrolls for pressures available in experimental setups ( $\sim 10$  MPa),<sup>4,6</sup> as in the case of carbon nanotubes and carbonaceous materials. Therefore, our simulations suggest that carbon nanoscrolls can be promising systems for hydrogen storage especially when intercalants are present.

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<sup>1</sup>A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kalng, D. S. Bethune, and M. J. Heben, *Nature* (London) **386**, 377 (1997).

<sup>2</sup>R. H. Baughman, A. A. Zakhidov, and W. A. de Heer, *Science* **297**, 787 (2002).

<sup>3</sup>L. Schlapbach and A. Züttel, *Nature* (London) **414**, 353 (2001).

<sup>4</sup>A. Chambers, C. Park, R. Terry, K. Baker, and N. M. Rodriguez,

*J. Phys. Chem. B* **102**, 4253 (1998).

<sup>5</sup>Y. Ye, C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith, and R. E. Smalley, *Appl. Phys. Lett.* **74**, 2307 (1999).

<sup>6</sup>C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, *Science* **286**, 1127 (1999).

<sup>7</sup>P. Chen, X. Wu, J. Lin, and K. L. Tan, *Science* **285**, 91 (1999).

<sup>8</sup>R. T. Yang, *Carbon* **38**, 623 (2000).

- <sup>9</sup>M. Rzepka, P. Lamp, and M. A. de La Casa-Lillo, *J. Phys. Chem. B* **102**, 10894 (1998).
- <sup>10</sup>Q. Wang and J. K. Johnson, *J. Chem. Phys.* **110**, 577 (1999).
- <sup>11</sup>K. A. Williams and P. C. Eklund, *Chem. Phys. Lett.* **320**, 352 (2000).
- <sup>12</sup>F. L. Darkrim and D. Levesque, *J. Phys. Chem. B* **104**, 6773 (2000).
- <sup>13</sup>C. Gu, G-Hua Gao, Y-Xin Yu, and Z-Qiang Mao, *Int. J. Hydrogen Energy* **26**, 691 (2001).
- <sup>14</sup>F. L. Darkrim, P. Malbrunot, and G. P. Tartaglia, *Int. J. Hydrogen Energy* **27**, 193 (2002).
- <sup>15</sup>D. Levesque, A. Gicquel, F. L. Darkrim, and S. B. Kayiran, *J. Phys.: Condens. Matter* **14**, 9285 (2002).
- <sup>16</sup>P. Guay, B. L. Stansfield, and L. Rochefort, *Carbon* **42**, 2187 (2004).
- <sup>17</sup>Y. Ma, Y. Xia, M. Zhao, R. Wang, and L. Mei, *Phys. Rev. B* **63**, 115422 (2001).
- <sup>18</sup>Y. Ma, Y. Xia, M. Zhao, and M. Ying, *Phys. Rev. B* **65**, 155430 (2002).
- <sup>19</sup>S. M. Lee and Y. H. Lee, *Appl. Phys. Lett.* **76**, 2877 (2000).
- <sup>20</sup>S. M. Lee, K. H. An, Y. H. Lee, G. Seifert, and T. Frauenheim, *J. Am. Chem. Soc.* **123**, 5059 (2001).
- <sup>21</sup>H. Ming Cheng, Q-Hong Yang, and C. Liu, *Carbon* **39**, 1447 (2001).
- <sup>22</sup>A. Zuttel, P. Sudan, Ph. Mauron, T. Kiyobayashi, Ch. Emmenegger, and L. Schlapbach, *Int. J. Hydrogen Energy* **27**, 203 (2002).
- <sup>23</sup>M. Becher, M. Haluska, M. Hirscher, A. Quintel, V. Skakalova, U. Dettlaff-Weglikovska, X. Chen, M. Hulman, Y. Choi, S. Roth, V. Meregalli, M. Parrinello, R. Strobel, L. Jorissen, M. M. Kappes, J. Fink, A. Zuttel, I. Stepanek, and P. Bernierg, *C. R. Phys.* **4**, 1055 (2003).
- <sup>24</sup>C. C. Ahn, Y. Ye, B. V. Ratnakumar, C. Witham, R. C. Bowman, Jr., and B. Fultz, *Appl. Phys. Lett.* **73**, 3378 (1998).
- <sup>25</sup>B. Panella, M. Hirsher, and S. Roth, *Carbon* **43**, 2209 (2005).
- <sup>26</sup>L. M. Viculis, J. J. Mack, and R. B. Kaner, *Science* **299**, 1361 (2003).
- <sup>27</sup>S. F. Braga, V. R. Coluci, S. B. Legoas, R. Giro, D. S. Galvão, and R. H. Baughman, *Nano Lett.* **4**, 881 (2004).
- <sup>28</sup>S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, *Nature (London)* **442**, 282 (2006).
- <sup>29</sup>H. Shioyama and T. Akita, *Carbon* **41**, 179 (2003).
- <sup>30</sup>V. Petkov, P. Y. Zavalij, S. Lutta, M. S. Whittingham, V. Parvanov, and S. Shastri *Phys. Rev. B* **69**, 085410 (2004).
- <sup>31</sup>S. Zhang, L.-M. Peng, Q. Chen, G. H. Du, G. Dawson, and W. Z. Zhou, *Phys. Rev. Lett.* **91**, 256103 (2003).
- <sup>32</sup>V. R. Coluci, S. F. Braga, R. H. Baughman, and D. S. Galvão, *Mater. Res. Soc. Symp. Proc.* **885E**, 0885-A06-07.1 (2006).
- <sup>33</sup>V. R. Coluci, S. F. Braga, R. H. Baughman, and D. S. Galvão (unpublished).
- <sup>34</sup>D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic, San Diego, 1996).
- <sup>35</sup><http://www.accelrys.com>
- <sup>36</sup>I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
- <sup>37</sup>UFF-UNIVERSAL1.02 Molecular Force Field, available from Accelrys, Inc. in CERIU<sup>2</sup> program.
- <sup>38</sup>Bigger simulation boxes were used for 150 K to ensure no interaction between H<sub>2</sub> molecules of neighboring cells.
- <sup>39</sup>O. Maresca, R. J.-M. Pellenq, F. Marinelli, and J. Conard, *J. Chem. Phys.* **121**, 12548 (2004).
- <sup>40</sup>I. Cabria, M. J. Lopez, and J. A. Alonso, *J. Chem. Phys.* **123**, 204721 (2005).
- <sup>41</sup>L. M. Viculis, J. J. Mack, O. M. Mayer, H. T. Hahn, and R. B. Kaner, *J. Mater. Chem.* **15**, 974 (2005).