

# Nanoscale Tubular Vessels for Storage of Methane at Ambient Temperatures

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Novel carbon nanostructures can serve as effective storage media for methane, a source of “clean energy” for the future. We have used Grand Canonical Monte Carlo Simulation for the modeling of methane storage at 293 K and pressures up to 80 MPa in idealized bundles of (10,10) armchair-type single-walled carbon nanotubes and wormlike carbon pores. We have found that these carbon nanomaterials can be treated as the world’s smallest high-capacity methane storage vessels. Our simulation results indicate that such novel carbon nanostructures can reach a high volumetric energy storage, exceeding the US FreedomCAR Partnership target of 2010 (5.4 MJ dm<sup>-3</sup>), at low to moderate pressures ranging from 1 to 7 MPa at 293 K. On the contrary, in the absence of these nanomaterials, methane needs to be compressed to approximately 13 MPa at 293 K to achieve the same target. The light carbon membranes composed of bundles of single-walled carbon nanotubes or wormlike pores efficiently physisorb methane at low to moderate pressures at 293 K, which we believe should be particularly important for automobiles and stationary devices. However, above 15–20 MPa at 293 K, all investigated samples of novel carbon nanomaterials are not as effective when compared with compression alone since the stored volumetric energy and power saturate at values below those of the bulk, compressed fluid.

## Introduction

Recent reports on the large quantities of naturally occurring methane hydrates have encouraged the U.S. and Japanese governments to invest in research associated with the use of methane as an important source of “clean energy” for the future.<sup>1</sup> In fact, hydrogen and natural gases are commonly considered to be suitable nonpolluting alternatives to fossil fuel. However, in addition to the technological and economical problems associated with methane production or mining, efficient storage and transportation appear to be major obstacles for widespread use of this source of clean energy. One of the most significant problems to be addressed in this regard is that methane (like hydrogen) is in a supercritical state near room temperature. To enhance the storage efficiency of methane, three general methods are commonly used, namely: liquefaction, compression, and adsorption in a host material.<sup>1</sup> Due to its supercritical state, it is impossible to liquefy methane at room temperatures. Moreover, lowering the temperature appears to be impractical for applications in the automobile industry or stationary vessels due to the high cost involved.<sup>1</sup> The second method, which involves compression of the bulk fluid, is characterized by extreme conditions (i.e., very high pressures typically more than 20–30 MPa<sup>1</sup>). Under these conditions, compression of methane would require a high-pressure-resistant, bulky, and heavy vessel that would generally be difficult to integrate within the limited space of an automobile.<sup>1</sup>

As a result, the compression method seems to be impractical in terms of cost and safety both for mobile and stationary applications. Adsorption of methane in new generation nanoporous materials would appear to be a very attractive and promising method due to the possibility of obtaining high storage near room temperature and at moderate pressures.<sup>2–7</sup> The strong enhancement of the solid–fluid interaction potential results in an efficient packing of the fluid molecules in nanospaces<sup>2</sup> and, while excluded volume effects resulting from Pauli’s restriction always lowers the stored amount of the supercritical fluid, especially in pores of molecular dimensions,<sup>8</sup> it is important to note that of most significance is the influence of the solid–fluid cohesive potential of physical adsorption since it moderates the pressure and temperature required for the respective uptake and release of the fluid.<sup>9</sup>

Methane is recognized as an alternative source of clean energy due to its high heat of combustion<sup>1</sup> (for details, see Supporting Information). Moreover, combustion of methane liberates the smallest amount of carbon dioxide per unit of heat produced among fossil fuels. This fact is of primary importance for the protection of the environment. Among the known greenhouse gases, carbon dioxide is the most important contributor, and it

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is responsible for over 60% of current global warming effects.<sup>10</sup> Like carbon dioxide, methane is also an important greenhouse gas, and therefore the capture and subsequent sequestration of methane is also important for the reduction of the greenhouse effect.

Methane is abundant in nature. It is a primary component of natural gas. For example, the natural gas supplied by Air Liquide SA, Greece, has the following composition: CH<sub>4</sub> (84.84 mol %), C<sub>2</sub>H<sub>2</sub> (8.40 mol %), C<sub>3</sub>H<sub>8</sub> (0.50 mol %), N<sub>2</sub> (5.60 mol %), and CO<sub>2</sub> (0.66 mol %).<sup>11</sup> Coal beds are natural methane reservoirs.<sup>12</sup> Methane is trapped in coal deposits, and it is released during mining operations in both underground and surface mines. Handling of coal after mining also results in methane emissions. Clathrate compounds are also important future sources of methane.<sup>13</sup> In these crystalline solids, the ice has a characteristic cubic structure, rather than the usual hexagonal structure.<sup>1</sup> The “guest molecule” (i.e., methane, chlorine, carbon dioxide, and hydrogen sulfide) is trapped at the center of this structure via van der Waals forces. The clathrate compounds are found in two geographic locations: in the permafrost of continental polar regions and deep in the beds of the world’s oceans.<sup>13</sup> The conditions for stability of methane hydrates are low temperature (broadly below 0 °C) and high pressure (> 5 MPa).<sup>13</sup> Since such chemical compounds are in a metastable state, any changes in temperature or pressure could cause a release of trapped molecules. Dell and Rand<sup>1</sup> pointed out that the estimates of the amount of methane available as methane hydrate in the United States range from 3 × 10<sup>15</sup> to 19 × 10<sup>15</sup> m<sup>3</sup>. This is sufficient to supply the energy needs in the United States for more than 300 years.

The key cost factor, and the one that bears most heavily on methane mining or production, is transport. Depending on the distances and the natural obstacles involved (especially relating to sea transport), natural gas is transported either by pipeline or by methane tankers. In the former case, the methane is compressed to 80 bar when it enters the pipeline and then recompressed roughly every 100 km over a distance that can be as much as 6000 km (as in the case of the pipeline linking Siberia to Western Europe).<sup>1</sup> The future expansion of natural gas consumption, especially in Asia, cannot be entirely met using pipelines, and this will make increased use of methane tankers inevitable. The economic transport and distribution of methane near ambient temperatures is a key problem to solve. The cost of transporting equivalent amounts of energy via methane tankers is 10 times the cost of a conventional oil tanker.<sup>1</sup> Inevitably, new types of nanomaterials, which could serve as storage cells to enhance methane load capacity within the transport vessels, would be very appropriate in this case. Novel carbon-based nanomaterials, such as single-walled carbon nanotubes (SWNTs),<sup>14</sup> wormlike SWNTs,<sup>15</sup> double-walled carbon nanotubes (DWNTs),<sup>16</sup> single-walled carbon nanohorns (SWNHs),<sup>17</sup> stacked-cup carbon

nanofibers (SCCNT),<sup>18</sup> doped fullerenes,<sup>19</sup> wormlike graphitic carbon nanofibers,<sup>20</sup> bamboo-type multiwalled carbon nanotubes,<sup>21–23</sup> and ordered porous carbons<sup>24</sup> have been regarded as promising media for efficient reversible storage of fluids via the physisorption mechanism. It is worthwhile noting that they are lightweight, cheap, chemically inert, thermally stable, and environmentally friendly.<sup>25,26</sup> Moreover, progress in the synthesis of novel carbon nanomaterials is unprecedented. On the other hand, metal hydride or chemical carriers appear to be alternative methods for effective storage of supercritical fluids, especially hydrogen.<sup>1</sup> However, while hydride storage beds are feasible in theory, there are a number of complex heat- and mass-transfer problems that need to be solved. Furthermore, while chemical carriers provide very interesting possibilities for storage of supercritical fluids, they suffer from technical obstacles and economy. Other promising materials for storing supercritical fluids are highly porous metal–organic coordination networks (MOCNs).<sup>27,28</sup> Porous solids of this kind, which are based on metal–ligand coordination linkages, are now available, and their storage capacity has been reported.<sup>29,30</sup> The shape, size, and functions of the pores in MOCNs can be tailored to achieve a desired property via “reticular synthesis”, for example, storage of methane near room temperature.<sup>29,30</sup> However, compared to microporous carbon nanomaterials, MOCNs are built with weaker metal–ligand coordination bonds and are inherently less stable. Another issue of concern is that, while carbon is friendly to both humans and the environment, MOCNs are composed of inorganic–organic building blocks, so the recycling of harmful elements (such as metals) should be taken into account for practical applications of these nanomaterials.

As far as we are aware of, there have been no reports on the effective application of nanoporous carbon materials as a powerful medium for storage of hydrogen near room temperature.<sup>9,31,32</sup> Both physisorption and encapsulation of molecular hydrogen in tailored nanoporous materials near room temperature has not achieved the U.S. Department of Energy goals of 6.0% mass ratio and 45 kg/m<sup>3</sup> volume density for 2010.<sup>33</sup> Dell and Rand<sup>1</sup> concluded, “We are pessimistic about fuel cells for cars, less so for buses and trucks. It should also be noted that automobiles (particularly diesels) are becoming increasingly efficient. Clearly, the fuel cell is aiming at a moving target.” In contrast to hydrogen

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the interaction of methane with carbon surfaces is stronger due to its higher binding energy. Indeed, the densification of methane near room temperature is more efficient than that of hydrogen. Yang et al.<sup>34</sup> reported that methane can be efficiently stored in modified single-walled carbon nanohorns (SWNHs). Highly ultramicroporous samples of SWNHs were prepared by intercalation with nitric acid and successive heat treatments. The high methane uptake of modified SWNHs was attributed to the enlargement of interstitial pores due to intercalation of nitric acid molecules. Bekyarova et al.<sup>35</sup> repeatedly compressed open SWNTs at 50 MPa to generate a nanocarbon material of high bulk density. The nanostructured, disordered carbon fabricated in this manner exhibits a high methane storage capacity at 303 K and 3.5 MPa. The high methane uptake in compressed samples resulted from widening the interstitial channels between individual tubes of the SWNHs dahlia-flower spherical aggregate. On the basis of these recent experimental studies, it can be seen that widening of the quasi one-dimensional interstitial channels of the SWNH colloidal aggregates influences the efficient packing of methane in nanospaces. Lee et al.<sup>36</sup> reported measurements of methane adsorption on wide-pore, multiwalled carbon nanotubes (MWNTs) and two samples of synthetic zeolites (HSZ-320 and DAY) at 303, 313, and 323 K and pressures up to 3 MPa. Even though the carbon nanotubes in these studies are characterized by wide pores (i.e., internal pore diameter 40–60 nm), the methane uptakes and binding energies of the MWNTs exceed those measured for microporous zeolites.

Studies of the storage capacity for methane in carbons have a long history. Here, we have focused on recent simulations.<sup>37–42</sup> Cao et al.<sup>43</sup> applied Grand Canonical Monte Carlo Simulation (GCMC) for optimization of the SWNT arrays for methane storage at room temperature. Optimized triangular arrays of the SWNTs were found to be capable of storing 215 g CH<sub>4</sub>/kg C at 4.1 MPa. However, the optimized van der Waals gap of 8 Å between the individual carbon nanotubes forming the bundle structure is much greater than that reported experimentally (i.e., intertube spacing 3–4 Å),<sup>17,44,45</sup> and the storage of methane in the interstitial channels formed by the adjacent SWNTs was almost 60% of the total uptake. Irrespective of where the binding takes place, one point is clear from each of these experimental and simulation studies: storage of methane in appropriately configured bundles of SWNTs by physical adsorption near room temperature is much more effective than compression of methane fluid. Bhatia and Myers<sup>46</sup> predicted optimum conditions for adsorptive storage using phenomenological and statistical thermodynamics. For methane, an optimum enthalpy change of 18.8 kJ mol<sup>-1</sup> is found, with the optimum temperature for carbons being 254 K. For a bundle of SWNTs placed in square array and spaced 9 Å apart,

the researchers predicted an optimum temperature of approximately 233 K for the largest nanotube examined, having a 13.6-Å diameter, and decreases to about 213 K for three other tubes of smaller size. Moreover, Bhatia and Myers concluded that energetic heterogeneity in any form is detrimental to adsorptive storage of the gas.

Notwithstanding the encouraging results reviewed above, there are still considerable obstacles to be overcome in applying novel carbon nanomaterials for efficient storage of supercritical fluids such as methane and hydrogen because of the difficulty in preparing homogeneous, well-defined, pure and reproducible samples. As a guide to the development of optimized nanostructures, computer simulations offer an alternative tool for the investigation of the storage of supercritical fluids in these novel nanomaterials. When the underlying physical conditions and the intermolecular potentials are known, computer simulations are a convenient vehicle for extrapolating experimental results to conditions difficult to access experimentally (i.e., well-defined samples of carbon nanomaterials, high purity of nanomaterial, etc.). Thus, in the current work we consider the storage of methane at 293 K and pressures up to 80 MPa in idealized bundles of the (10,10)-armchair SWNTs and carbon wormlike pores by molecular simulation techniques. For the simulations of methane storage in the bundle of SWNTs near room temperature by molecular simulation techniques, we selected the idealized bundle of (10,10)-armchair SWNTs since this kind of nanotube is the most abundant and has been used in many theoretical studies.<sup>14,47,48</sup> Our idealized model of a SWNTs bundle consists of eleven individual tubes arranged in an infinitely long hexagonal lattice with a van der Waals gap of 4 Å (for details, see Supporting Information). Similarly, we have built an idealized bundle of single-walled wormlike carbon pores which imitate recently observed stable periodic tubular nanotubes synthesized via a process of fullerene fusion in the interior of the SWNTs.<sup>49,50</sup> The fascinating coalescence of fullerenes encapsulated in SWNTs is driven by thermal annealing or electron irradiation. Wormlike carbon pores are also characteristic for graphitic carbon nanofibers.<sup>20</sup> Moreover, stable periodic pores of this type can be produced by carbonization and activation of carbon precursors (e.g., furfuryl alcohol, phenol-resin monomers, acetylene, sucrose solution) inside novel wormlike silica-type materials used as a template.<sup>51</sup> To the best of our knowledge, no studies have been reported (either experimental or theoretical) dealing with the application of such novel tubular nanoporous carbon materials as media for storage of supercritical fluids. We wish to emphasize that recent experimental modifications of SWNTs by oxidation, compression, thermal annealing, electron radiation, and so forth deformed the bundle structure of SWNTs. The defects and undulations introduced in these studies change the tube diameter along the tube length or cause tube coalescence. Our model of the idealized bundle of wormlike carbon pores captures the main properties of such novel nanomaterials.

## Simulation Methods

The potential models with the description of the experimental equation of state for methane at 293 K, computational methodol-

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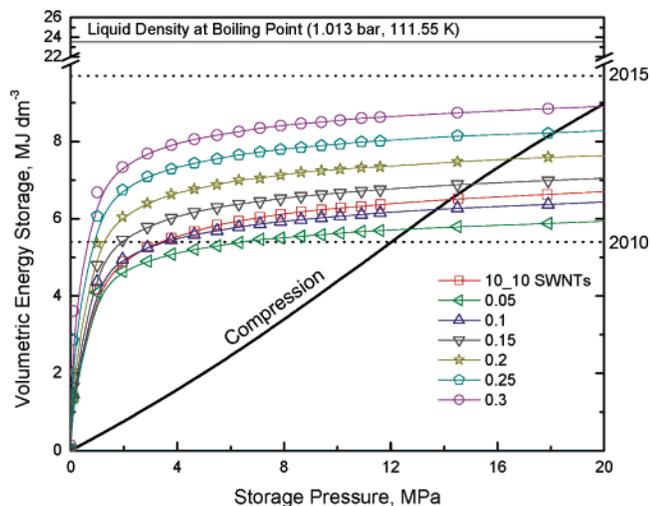
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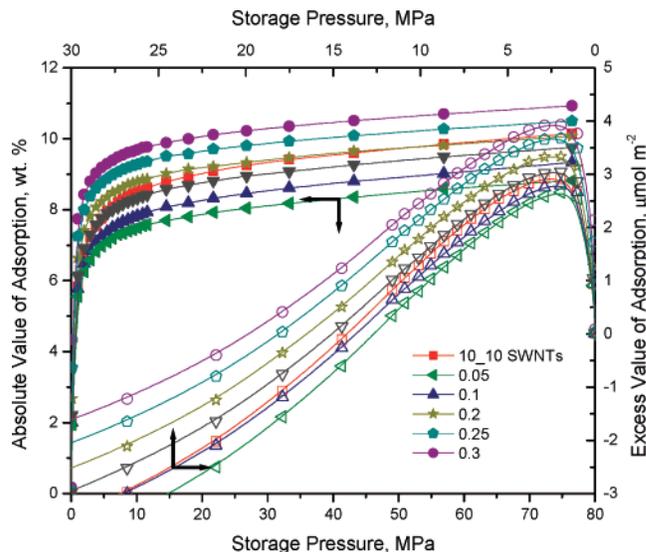


**Figure 1.** The stored volumetric energy of methane adsorbed in idealized bundles of SWNTs and wormlike pores at 293 K. The abbreviations connected with the size of the individual wormlike pores and SWNTs are given in the Supporting Information (part SIV entitled Investigated Samples of Carbon Nanomaterials).

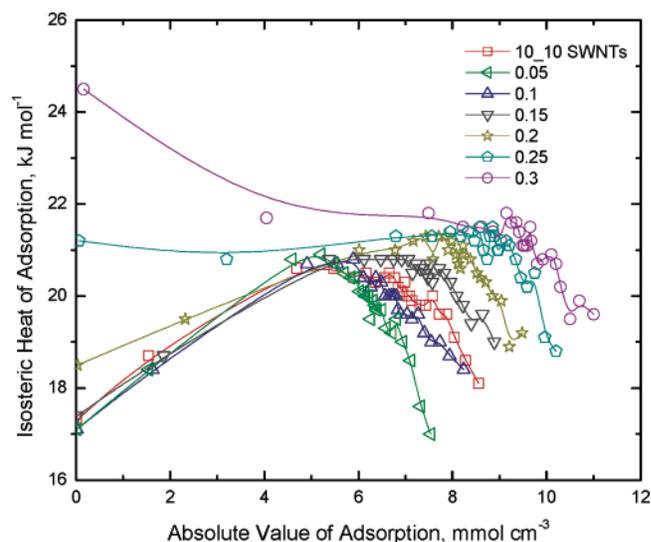
ogy, sample characteristics, and quantities characterizing the efficiency of methane storage are documented in Supporting Information.

### Results and Discussion

The key results of our simulation studies indicate that the storage of methane at 293 K and moderate pressures is significantly more efficient than the compression method (see Figures 1, 2, and Table 1). The idealized bundles of (10,10) armchair-type SWNTs and wormlike pores may be considered to be the world's smallest methane storage vessels. To achieve the 2010 goal for the volumetric energy storage in the absence of the carbon nanomaterials, the methane fluid needs to be compressed to  $\approx 13$  MPa at 293 K. On the contrary, all carbon nanomaterials investigated in the simulations exceed this target at much lower storage pressures (see Figures 1, 2, 7S). Due to the enhanced van der Waals forces, methane molecules are efficiently trapped in the internal pores and interstitial channels of the carbon nanomaterials even at low pressures (see Figures 4–6 and movies attached to Supporting Information). However, the shape of the individual carbon pores forming a bundle seems to be a key parameter to control the efficiency of methane storage (see Figures 1, 2, 7S). It significantly affects the methane packing and density in the carbon nanospaces (see Figures 4–6 and movies attached to Supporting Information). Our computer experiments reveal that even a small variation at the nanoscale can lead to a very significant change in methane densification, favoring idealized bundles of wormlike pores with optimized intertube distance between SWNTs. As an example, for the idealized bundle



**Figure 2.** The stored volumetric energy of methane adsorbed in idealized bundles of SWNTs and wormlike pores at 293 K. The description is the same as that for Figure 1.



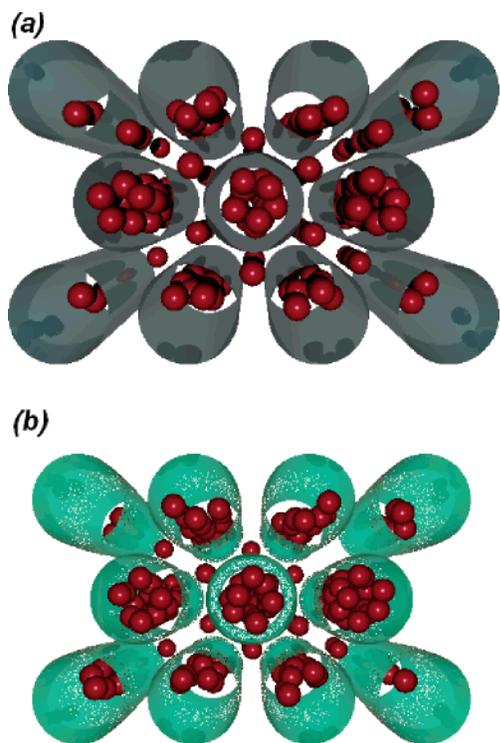
**Figure 3.** The isothermic heat of adsorption versus methane loading in idealized bundles of SWNTs and wormlike pores at 293 K. The description is the same as that for Figure 1.

of (10,10) armchair-type SWNTs, we observe high packing of methane molecules in both internal cylindrical pores and quasi-one-dimensional interstitial channels between neighboring carbon tubes (see Figure 4a and movies attached to Supporting Information). The strong interstitial adsorption centers contribute significantly to the total storage amount of methane fluid. On the contrary, the ratio of the methane molecules adsorbed in the

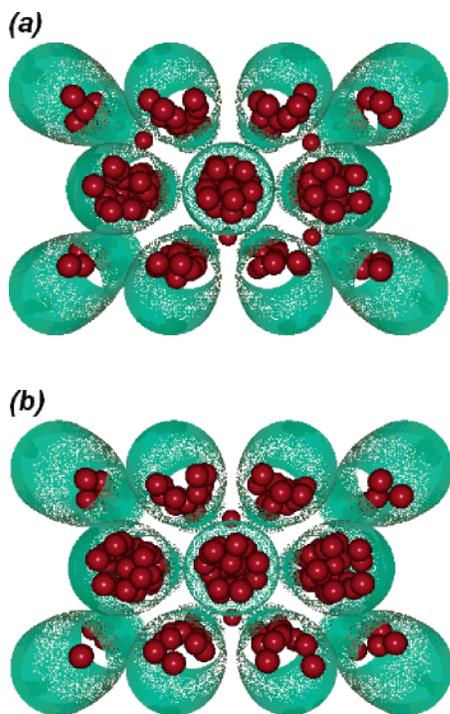
**Table 1. Parameters Characterizing the Storage of Methane in the Idealized Bundles of SWNTs and Wormlike Pores at 293 K at Selected Pressures for Which the 2010 Goal for Volumetric Energy ( $5.4 \text{ MJ dm}^{-3}$ ) Was Achieved**

parameter	storage method <sup>d</sup>						
	10,10 SWNTs	0.05	0.1	0.15	0.2	0.25	0.3
storage pressure, MPa	3.78	7.1	3.78	1.95	1.95	0.99	0.99
volumetric energy, $\text{MJ dm}^{-3}$	5.5	5.47	5.45	5.46	6.04	6.07	6.68
volumetric power, $\text{kWh dm}^{-3}$	1.53	1.52	1.51	1.52	1.68	1.69	1.86
Gibbs excess of adsorption, $\mu\text{mol m}^{-2}$	2.82	1.71	2.64	3.05	3.34	3.49	3.76
absolute value of adsorption, wt %	7.53	7.30	7.09	6.92	7.42	7.26	7.74
isothermic heat of adsorption, $\text{kJ mol}^{-1}$	20.5	20.1	20.4	20.8	21.0	21.3	21.8
constant-volume heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$	19.2	20.0	19.7	19.4	19.9	21.2	22.5

<sup>d</sup> See Supporting Information, part SIV, entitled "Investigated Samples of Carbon Nanomaterials".

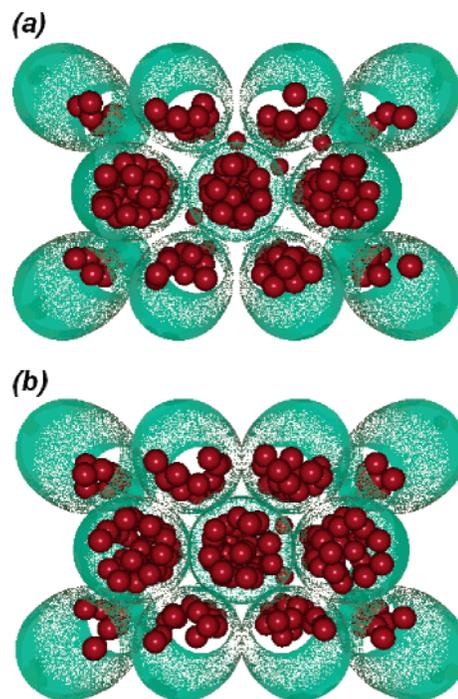


**Figure 4.** Comparison of equilibrium snapshots of methane adsorbed at 293 K in an idealized bundle of (10,10) SWNTs: panel (a)  $R \in [6.78, 8.30]$  Å,  $p = 3.78$  MPa; and carbon wormlike pores: panel (b)  $R \in [6.78, 7.16]$  Å,  $p = 7.10$  MPa. In all of the equilibrium snapshots shown, the stored volumetric energy exceeds the 5.4-MJ/dm<sup>3</sup> 2010 US FreedomCAR Partnership target.



**Figure 5.** Comparison of equilibrium snapshots of methane adsorbed at 293 K in an idealized bundle of carbon wormlike pores of different pore radius: panel (a)  $R \in [6.78, 7.54]$  Å,  $p = 3.78$  MPa; panel (b)  $R \in [6.78, 7.92]$  Å,  $p = 1.95$  MPa. In all of the equilibrium snapshots shown, the stored volumetric energy exceeds the 5.4-MJ/dm<sup>3</sup> 2010 US FreedomCAR Partnership target.

interstitial channels and internal pores of the idealized bundle of wormlike pores can be easily tuned by modulation of the pore



**Figure 6.** Comparison of equilibrium snapshots of methane adsorbed at 293 K in an idealized bundle of carbon wormlike pores of different pore radius: panel (a)  $R \in [6.78, 8.30]$  Å,  $p = 1.95$  MPa; panel (b)  $R \in [6.78, 9.07]$  Å,  $p = 1.00$  MPa. In all of the equilibrium snapshots shown, the stored volumetric energy exceeds the 5.4-MJ/dm<sup>3</sup> 2010 US FreedomCAR Partnership target.

shape (see Figures 4–6 and movies attached to Supporting Information). The variation in internal pore diameters of individual wormlike pores forming a bundle influences the stored energy value, and for small undulations we observe a lowering of the total adsorbed amount of methane in comparison to that of the idealized bundle of (10,10) SWNTs (see Figure 1). This results from a decrease of volume space between the neighboring pores. Increasing the magnitude of the undulation further in the individual wormlike pore diameter leads to an improved packing of methane molecules in the internal pores of the idealized bundle. At the same time, the adsorption in interstitial channels is greatly reduced (see Figures 1–6). Interestingly, the total value of the volumetric storage energy and power is increased with larger undulation of the pore diameter in carbon wormlike pores forming a bundle even though the methane uptake in the interstitial channels is reduced (see Figure 1).

Figure 2 displays the absolute and Gibbs excess values of adsorption versus storage pressure. As expected, the shape of the individual pores forming an idealized bundle of wormlike pores significantly influences both absolute and Gibbs excess values of adsorption. However, the general conclusion is that the storage of methane at 293 K in all of these model carbon nanomaterials above 15–20 MPa is not efficient when compared with compression of methane fluid alone. Above this threshold value, we observe saturation conditions and further accommodation of methane molecules is restricted (see Figure 2). It is seen from Figure 2 that the Gibbs excess value of adsorption passes through a maximum, indicating that the methane density in the bulk phase is continuing to increase while the adsorbed phase density is exhibiting only minor changes. This obvious behavior of the Gibbs excess value of adsorption arises from the presence of a carbon nanostructure, and the slight increase in the absolute value of methane adsorption at higher pressures results primarily from the compression of the adsorbed molecules. It is noted that the

weight percentages of methane for all considered carbon nanostructures are relatively large (i.e., exceeding 6 wt % at moderate pressures). Since these materials are light and achieve reasonable capacity, they are suitable for use in automobile fuel supply tanks to increase the efficiency of methane storage. This property of the carbon nanomaterials is particularly important for mobile applications because the long distance between refueling is known to be a technical barrier to overcome.

At pressures below 10–15 MPa we observe Langmuir-type isotherms, indicating a strong binding energy between the methane molecules and the carbon surfaces (see Figures 2, 3). For all of the carbon nanomaterials investigated in this work, the isosteric heat of adsorption at zero coverage exceeds  $17 \text{ kJ mol}^{-1}$  (see Figure 3 and Figure 5S). However, the shape and the numerical values of the binding energy can be tuned by the shape of the individual carbon pores forming the bundle nanostructure. As seen in Figure 3, the maximum in the isosteric heat of adsorption versus methane loading is characteristic of idealized bundles of SWNTs and wormlike pores with a small variation of the pore diameter. The maximum results from the interplay between the solid–fluid and fluid–fluid interaction energies (see Figure 5S). Indeed, for idealized bundles of SWNTs and wormlike pores with a small variation of pore diameter, the solid–fluid interaction is almost constant versus pore loading. At the same time, due to methane densification the fluid–fluid interactions are progressively increased up to some threshold value. As a result, the total isosteric heat of adsorption progressively increases and passes through a maximum. On the contrary, for idealized bundles of wormlike pores characterized by a larger variation of pore diameter, we observe a monotonically decreasing isosteric heat of adsorption. In fact, the system behaves as a classical heterogeneous material because methane adsorbs onto the highest energetic sites and then onto gradually weaker sites. Obviously, the highest isosteric heat of adsorption is observed for an idealized bundle of wormlike pores with the largest variation in pore diameter (i.e.,  $R \in [6.78, 9.07] \text{ \AA}$ ) due to the decrease in size of the interstitial channels, resulting in the enhancement of the solid–fluid potential. It is also noted that the state of adsorbed methane is far from the corresponding bulk phase. Generally, the constant-volume heat capacity of methane in pores greatly exceeds the value corresponding to the bulk phase (see Figure 6S). At zero coverage and low pressures, the constant-volume heat capacity strongly depends on the variation in the pore diameter of wormlike pores forming a bundle and it can reach  $30 \text{ J mol}^{-1} \text{ K}^{-1}$ . This implies that to raise the temperature of adsorbed methane a greater

amount of energy is required in comparison to the bulk phase due to the additional surface interactions.

From the current computer experiments, we can conclude that at low to moderate pressures both idealized bundles of SWNTs and wormlike pores behave as efficient storage media due to the availability to the methane molecules of a high density of energetic centers located on the carbon surfaces. All of the carbon nanostructures investigated in this work appear to be suitable candidates as future nanoscale storage vessels for methane in contrast to simple compression because of the significantly higher magnitudes of the stored volumetric energy and power, particularly at low pressures (see Table 2S in Supporting Information). Also, since the captured methane is physisorbed, simple manipulation of the temperature may be used to control methane release. Obviously, for automobiles, engines based on fuel-cell technology with stored methane as a fuel would appear to be a major direction for the future due to the high theoretical efficiency of 91.9% (see Table 2S in Supporting Information). In contrast, the efficiency of internal combustion engines is around 30% due to thermodynamic limitations of the Carnot cycle.

In summary, our computational work sheds new light on the problem of methane storage in novel carbon nanomaterials. There is no doubt that idealized bundles of SWNTs and wormlike carbon pores are promising nanomaterials for the future in the area of energy storage despite the idealized models adopted in the current studies (the computational results for which, we should acknowledge, will primarily provide a theoretical upper limit for methane storage). In this regard, from an applications viewpoint, we believe that the production of pure and well-defined bundles of SWNTs and wormlike carbon pores would appear to be a key factor for widespread use of these materials as nanoscopic storage vessels for supercritical gases.

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**Supporting Information Available:** Full details of the simulation techniques, the potential functions, and descriptions of the nanopores investigated in this work as well as supplementary simulation results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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