

## A nanocontainer for the storage of hydrogen

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### Abstract

Molecule hydrogen is known to have a weak van der Waals potential, which makes it difficult to raise its storage efficiency for physisorption based methods. In this report, we explore the other side of such a weak potential, the well-known compressibility of hydrogen. A (20, 0) single wall carbon nanotube based nanocontainer is designed, in which a C<sub>60</sub> “peapod” at the cap section of the nanotube serves as a molecular valve. Diffusion barriers through such a valve is examined by molecular dynamics simulations under various conditions. It is demonstrated that H<sub>2</sub> can first be filled into the container upon compression at low temperature, and then be locked inside it after the release of external pressure. The internal pressure that can be achieved in this design is in the GPa range at room temperature, which is much higher than the typical pressure of a few hundred bar currently employed for hydrogen storage. At 2.5 GPa, the storage weight ratio approaches a promising 7.7%.

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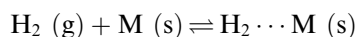
### 1. Introduction

Storage of hydrogen is a crucial link between hydrogen production and its use as a clean fuel for transportation [1]. To achieve better efficiency than simply storing H<sub>2</sub> in a gas tank, there have been extensive searches for adsorbent materials that could bind H<sub>2</sub> by either chemical [2] or physical (van der Waals) [3,4] forces. Physisorption based storage has the advantages of higher energy efficiency and fast adsorption/desorption cycling [3,4]. The initial reports of impressive weight ratio achieved by the sorption of H<sub>2</sub> in carbon nanotubes have attracted much attention [5–7]. Although these results were later called into question [8,9], such efforts have ignited interests in the search for materials with large surface areas, such as zeolites [10], metal–organic frameworks [11], and especially various forms of carbon [4], as storage media. Furthermore, these results also highlight the great potentials of nanostructures, with their unique physical and chemical properties, for the

solution of this challenging problem. Nonetheless, the storage weight ratio achieved so far is still less than the commonly accepted threshold of 6.5% [1]. Promising results were reported in carbon micropores, but the temperature at 77 K was too low for real application [10].

Many theoretical studies on the adsorption of H<sub>2</sub> have been reported, often using the most sophisticated techniques in molecular modeling [12–14], and sometimes producing conflicting assessments [15–17]. However, a clear description of the physics governing the physisorption process can actually be obtained by an analysis of the underlying thermodynamic variables, which also illustrates the great difficulty in raising the storage efficiency.

The physisorption can be treated as an equilibrium process,



where M stands for the storage media. At constant temperature and pressure, the process is governed by the Gibbs free energy,  $\Delta G = \Delta E + p\Delta V - T\Delta S$ . A good estimate can be made for both the pressure/volume ( $p\Delta V$ ) and the temperature/entropy ( $T\Delta S$ ) terms. The change in volume is defined as  $\Delta V = V_{\text{H}_2 \cdots \text{M}} - V_{\text{H}_2} - V_{\text{M}}$ . With H<sub>2</sub> in the

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gas phase and both  $M$  and  $H_2 \cdots M$  in the solid state,  $V_{H_2}$  is much larger than the other two items. Treating  $H_2$  as ideal gas under ambient conditions, we have  $p\Delta V \simeq -pV_{H_2} = -nRT$ . The change in entropy,  $\Delta S = S_{H_2 \cdots M} - S_{H_2} - S_M$ , is a bit more complicated, as it contains contributions from translational, vibrational and rotational motions. However for a gas like  $H_2$ , the vibrational and rotational parts change little upon physisorption and are very small compared to the translational part. The entropy change in the solid material should also be very small.  $\Delta S$  is thus dominated by the much reduced space for the translational motion of  $H_2$  upon physisorption, so that we have  $-T\Delta S \simeq TS_{H_2 \text{ Translation}}$ . By the Sack–Tetrode equation,  $S_{H_2 \text{ Translation}}$  can be calculated explicitly as

$$S_{H_2 \text{ Translation}} = nR \cdot \ln \left( \frac{e^{5/2} kT}{p(h/\sqrt{2\pi mkT})^3} \right) = A(p, T) \cdot nR$$

with  $k$  and  $h$  being the Boltzmann and Planck constant respectively, and  $m$  being the molecular mass of  $H_2$ . The free energy  $\Delta G$  can thus be written as  $\Delta G \simeq \Delta E + [A(p, T) - 1]nRT$ . The positive value of the latter term, as listed in Table 1 under various conditions, must be overcome by the  $\Delta E$  term, to achieve exothermic free energy for the adsorption process.

Unfortunately, the van der Waals potential for  $H_2$  is weak. The binding energy in a hydrogen dimer,  $H_2 \cdots H_2$ , is a negligible amount of only 0.07 kcal/mol [18], and for the physisorption based storage, there could only be the adsorption of a  $H_2$  monolayer, with  $\Delta E \simeq -E_{\text{ads}}$  and with  $E_{\text{ads}}$  being the adsorption energy of  $H_2$  on the surface of the solid material. On graphite,  $E_{\text{ads}}$  is only 1.2 kcal/mol [19,20], which is not large enough to produce negative free energy for physisorption even at 100 K and 500 bar, as shown in Table 1. It should be pointed out that such weak adsorption energy is due to the intrinsic nature of  $H_2$ . The van der Waals interaction is caused by the instantaneous polarization of the electron cloud. There are only two electrons on  $H_2$ , and the bonding orbital is formed by the combination of two compact 1s orbitals. Therefore, the van der Waals interaction, both between  $H_2$  molecules and between  $H_2$  and solid surfaces are the weakest among all gaseous atoms and molecules, with the only exception of He.

Table 1  
The  $(p\Delta V - T\Delta S)$  contribution to  $\Delta G$ :  $(A - 1)RT$

$T$ (K)	$P$ (bar)	$A(p, T)$	$(A - 1)RT$ (kcal/mol)
298	1	14.3	7.87
	100	9.52	5.04
	500	7.91	4.09
200	1	13.1	7.18
	100	8.53	4.46
	500	6.92	3.50
100	1	11.4	6.16
	100	6.79	3.43
	500	5.19	2.48

It has been argued that the curved surface of a carbon nanotube could enhance the storage capacity because it increases the adsorption energy, as the curvature brings more carbon atoms into interactions with a  $H_2$  molecule [1,21]. Recent high level ab initio calculations put the maximum value at 2.1 kcal/mol [22]. A more favorable value of 4.5 kcal/mol was previously reported in an experimental study [23], although it was still smaller than the value of  $(A - 1)RT$  at 298 K and 100 bar, shown in Table 1. Moreover, there is a serious problem with such an approach. To scale up  $E_{\text{ads}}$  by a factor of  $\alpha$  (with  $\alpha > 1$ ), the number of carbon atoms around the adsorption site should be scaled up approximately by the same factor, since the curvature does not fundamentally change the orbital extent for either  $H_2$  or carbon. With a carbon atom being considerably heavier than a H atom, it means that the storage weight ratio should be scaled down by a factor of  $1/\alpha$ . In other words, the curved surface of a carbon nanotube could make it easier to form a monolayer on nanotube surface, at the expense of reducing the storage weight ratio. Current search for adsorbent materials is often motivated by finding porous materials with large surface areas [10,11]. But how to increase the adsorption energy without reducing the weight ratio is actually the more difficult problem, which has been the focus of recent studies on hydrogen storage [24,25].

## 2. Computational model and details

The weak van der Waals potential of  $H_2$  therefore poses a serious challenge for physisorption based storage methods. However, there is another side of such a weak potential: the repulsive part of the van der Waals interaction of  $H_2$  is also much weaker than usual [18]. For example, although the intermolecular distance at the energy minimum of  $H_2 \cdots H_2$  dimer is 3.3 Å, the repulsive energy at 2.4 Å is only 1.0 kcal/mol. It is well known that even solid  $H_2$  is highly compressible [26]. In fact, it was observed in experiment that  $H_2$  could be first squeezed into the interstitial space of ice by high pressure and trapped there even after the release of pressure at a temperature of 140 K [27], although the temperature was too low for mobile applications.

It thus seems hard to take advantage of the compressibility of  $H_2$  because it requires very high pressure, while the  $H_2$  storage on board of a vehicle must be maintained at room temperature and at a pressure of a few hundred bar. The challenge is to identify structures that could trap  $H_2$  in a compressed state even after the withdrawal of external pressure. Shown in Fig. 1(a) is such a structural design for a nanocontainer that meets this requirement. It has three parts. First, the container itself is made of a single-walled carbon nanotube. Then, two fullerene molecules are put inside the tube as blockers. Similar “peapods” structures have already been extensively studied, with fullerenes and other molecules easily introduced into a nanotube [28,29]. Finally, there are two cap sections at the two ends. Initially  $H_2$  gas at high pressure could be squeezed into the tube through the leaks on the cap sections. After filling the tube, the external pressure is withdrawn, and the pressure inside the tube pushes the two fullerenes against the cap sections, which blocks the leaks and traps hydrogen. Essentially, the fullerene and the cap together serve as a nanovalve, in a fill-and-lock mechanism.

To explore the feasibility of such a design, we have built an actual model and performed molecular dynamics simulation to calculate the barriers for hydrogen diffusion, using the Tinker program [30] with the MM3 force field [31]. For molecular hydrogen, this means a Lennard-Jones potential, fitted from experimental data. Good agreements with the results of accurate ab initio calculations on the interactions between two  $H_2$  molecules have been obtained in a previous study [32], although the MM3

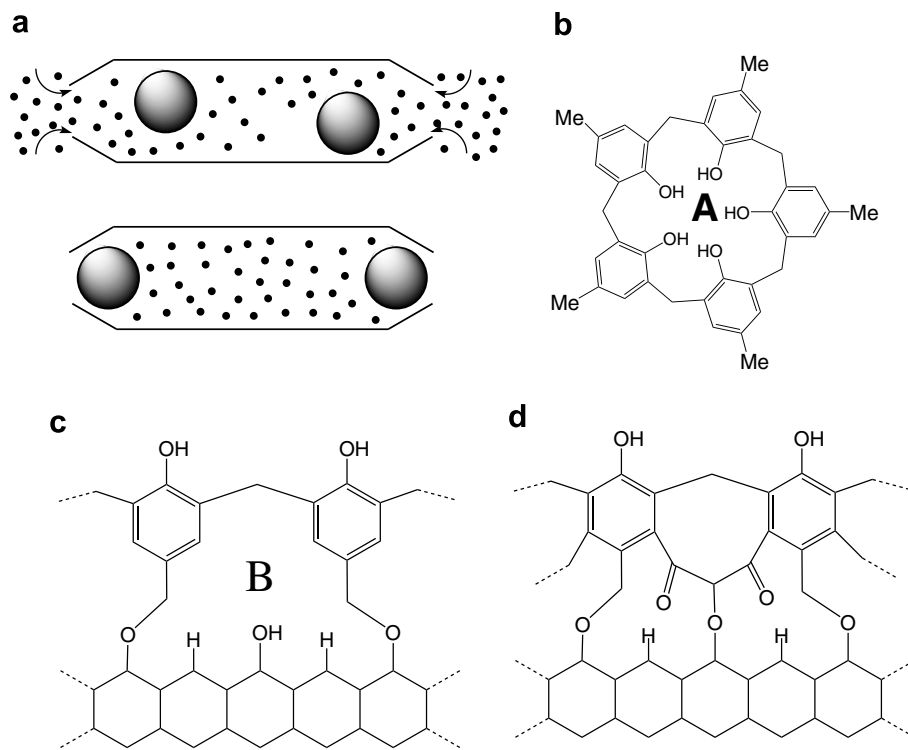


Fig. 1. (a) The design for a nanocontainer, with the cap and the ball ( $C_{60}$ ) together serving as a molecular valve that traps the hydrogen after the release of the external pressure. (b) The bowl-shaped calix[5]arene is used as the cap for the container, with its center, labeled as **A**, being one of the leaks. (c) Side-view of the bonds linking the calix[5]arene to the edge of the carbon nanotube, with **B** being another leak. (d) Additional bonds are added in **B** region to seal it off.

potential is somewhat more repulsive. The body of the container is a (20,0) single-walled carbon nanotube, with a diameter of  $\sim 15$  Å, while the two spherical blockers are fullerene molecules  $C_{60}$ . A carbon nanotube is usually capped by half-fullerenes at its two ends, and by etching the top few atoms away, a hole can be created at each end as a gas leak. In our work, we use a more elaborate design, based on a bowl-shaped calix[5]arene molecule as shown in Fig. 1(b), which is attached to the end of the (20,0) tube. A crystal structure has actually been reported previously with a  $C_{60}$  contained inside the bowl-shaped calix[5]arene as an inclusion complex [33].

There are two leaks on such a valve: one on the top of the cap, labeled as **A** in Fig. 1(b), and the other along the edge of the cap, labeled as **B** in Fig. 1(c). Although **A** is blocked by  $C_{60}$ , **B** must be patched up further to prevent  $H_2$  leakage, by additional links shown in Fig. 1(d). The atomic model for the container, as shown in Fig. 2(a) and (b), is obtained by experimenting with tubes and calix[ $n$ ]arenes of various sizes. A good match is identified between the calix[5]arene cap and the (20,0) tube, as determined by comparing the structural parameters for a free calix[5]arene and for a calix[5]arene attached to the (20,0) tube. The difference is less than 0.01 Å for bond distance and  $0.5^\circ$  for bond angles.

### 3. Results and discussion

To examine the filling of the container, we constrain the distance between a  $H_2$  molecule to a virtual atom within the tube, and minimize the total energy at each distance. The potential energy barrier obtained is 10 kcal/mol through **A**, which is in agreement with the expectation that diffusion into the tube can be easily achieved. The barrier through **B** is much higher at more than 70 kcal/mol, which indicates that the links in **B** region effectively seal it off.

More detailed calculations are performed for the escape of  $H_2$  from the filled tube as shown in Fig. 2(b), in which

the pressure is in the GPa range (1 GPa = 10,000 bar) in the interior and zero in the exterior. The simulations are performed under constant NVT, with the temperature controlled by using a Berendsen thermostat. The equations of motion are solved by using the Beeman algorithm, with a time step of 1.0 fs. As the volume is constant and the  $H_2$  is very compact under high pressure, the pressure value is obtained by calculating the Virial tensor of hydrogen, averaged over the time steps within a simulation period. Leakage of hydrogen through the sidewall is unlikely, since in such a process a hydrogen molecule must exit through the center of a hexagonal carbon ring, when the distance between  $H_2$  and each of the six C atoms is 1.42 Å and the van der Waals potential is in a very steeply repulsive region. The outward diffusion is only possible through the two cap sections of the tube, and the diffusion coordinate is again defined by the distance between a  $H_2$  molecule and a virtual atom inside the tube. While the coordinate is constrained to a constant value, the system is first equilibrated for 100 ps and then run for an additional 100 ps for data collection. The averaged potential energy produces the energy profile along the diffusion coordinate, while the averaged force along the diffusion coordinate is integrated to obtain the free energy profile [34], which also includes the entropy contribution.

As shown in Fig. 2(c), the barrier is considerably higher than that during the filling of the empty tube. These barriers are mostly calculated at 300 K for various internal pressures, as listed in Table 2. The free energy barrier is actually

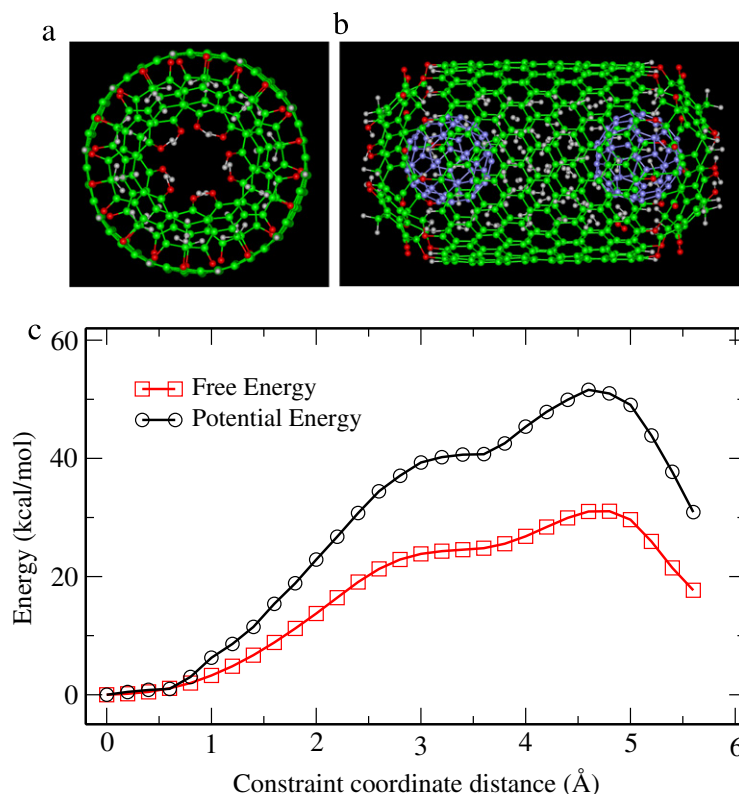


Fig. 2. (a) The nanocontainer, without the two fullerenes, viewed from one end, with the carbon atom in green, oxygen in red, and hydrogen in white. (b) The side view of a filled nanocontainer, with the two C<sub>60</sub> colored in blue. (c) The profiles for the potential energy and the free energy calculated by molecular dynamics simulations at 300 K. The internal pressure is at 2.5 GPa. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

lower than the potential energy barrier, which indicates that the entropy factor makes it easier for the escape of H<sub>2</sub>. The barrier through leak **A** increases significantly with pressure, as the C<sub>60</sub> is pushed against the calix[5]arene cap. On the other hand, the barrier through **B** along the edge of the cap decreases somewhat with increasing pressure, due to the stress on the cap structure, which indicates a limit for the pressure that could be endured by the cap. However, the internal pressure at 2–3 GPa range is two orders magnitude higher than the pressure inside a conventional storage tank, and the corresponding free energy barriers at more than 24 kcal/mol indicate that H<sub>2</sub> molecules are safely trapped inside the container, even though the external pressure is withdrawn. When the temperature is raised to 400 K at 2.5 GPa, the change in barrier is small.

A natural question arises as to how to fill the carbon nanotubes with H<sub>2</sub> at such high pressures. Compressing

hydrogen gases to a pressure in the GPa range is very difficult. However, hydrogen can be transformed into liquid by applying pressure and cooling at the same time. Liquid nitrogen with a boiling point of 77 K is easily available and can be applied in a large scale in an industrial setting. Pressure up to 2 GPa (20 K bar) has been achieved for the compression of liquid hydrogen in laboratory by using a piston-cylinder apparatus [35,36]. Furthermore, the internal hydrogen pressure achieved at 77 K would be tripled at a room temperature around 300 K [37]. Within such a scheme, a roadside filling station would not store and pump hydrogen. Rather it is a place where filled nanocontainers would be sold and loaded onto a vehicle, while emptied containers would be collected and later transported to an industrial site for processing and refilling. For practical purposes, such an arrangement could actually be advantageous, since it would do away

Table 2  
The diffusion potential barrier and free energy at different internal pressure

Internal pressure (GPa)	C:H	Barrier A (kcal/mol)	Free energy A (kcal/mol)	Barrier B (kcal/mol)	Free energy B (kcal/mol)
0.80	5:3	24.15	16.10	69.00	39.10
1.40	5:4	40.94	26.45	55.89	33.81
2.50	5:5	51.98	31.05	51.06	29.21
2.50 (400 K)	5:5	51.42	30.76	51.23	29.02
3.00	10:11	55.50	32.82	41.75	24.19



with the problem of building hydrogen stations along highways.

It is well known that external pressure at GPa range can induce sectional deformation in a carbon nanotube. This is largely driven by the  $pV$  term, to squeeze out the empty space inside a tube. As shown in previous studies, it is achieved by localized bond buckling so that the tube section is flattened by anisotropic compression [38,39]. In contrast, the pressure in the proposed container is internal, and produces isotropic (i.e. cylindrical) expansion in the radial direction. In such a process, the C–C bond distance is stretched, which requires much more energy than bond buckling. Therefore, carbon nanotubes can endure much higher internal pressure. In a very recent experimental study, it was demonstrated that a (10,10) tube could endure internal pressure up to 40 GPa [40].

At a pressure of 2.5 GPa, the mole ratio between the stored hydrogen atoms and C atoms on the (20,0) tube is an impressive 1:1, corresponding to a weight ratio of 7.7%. The actual weight ratio is lower since the atoms on the caps and on  $C_{60}$  are not included in the calculations. When a long tube is used, the contribution from the cap sections is small and the weight ratio should approach 7.7%, which exceeds the threshold of 6.5% for mobile applications. Since the number of stored hydrogen molecules are proportional to the volume of the cylinder, while the number of carbon atoms is proportional only to its surface area, further increase in the ratio is also possible by using tubes with larger diameter, provided that appropriate caps and blockers can be designed. Such a storage mechanism bears some similarity to the conventional method of storage tanks, made either of steel or composite materials. However, these nanocontainers are much smaller in their sizes and can be carried on board easily under ambient conditions. The internal pressure in nanocontainers are also much higher at the GPa range, which makes it possible to take advantage of the compressibility of  $H_2$  and produces a much needed boost in both volume and weight efficiency. Achieving such a high storage pressure is especially advantageous for  $H_2$ , because of its unique compressibility even in the solid state. In contrast, for other gas such as  $N_2$ ,  $CO$ , or  $CH_4$ , little advantage for storage would be gained by increasing the pressure once the liquid or solid state is reached, due to the typical steep van der Waals repulsion. As for the release of  $H_2$  from these nanocontainers, the functional groups in B region with O–C and C=O bonds can be explored for chemical modification, such as acid/base treatment, so that the bonds are altered to open up the leaks. This is of course one of the problems that need to be addressed in future studies, as the results presented here are a conceptual design, to be improved by more calculations and verified by future experiments. Another important problem is to obtain a more quantitative evaluation of both the internal pressure and the diffusion barrier, for which potential functions must be improved for a better description of the molecular interactions at high pressure.

In summary, we have demonstrated an atomistic model in nanosize for the purpose of hydrogen storage, through a fill-and-lock mechanism, and the correlation between pressure and the diffusion barrier through the molecular valve. Although its actual synthesis is going to be a challenge, it represents a new method to store hydrogen, which takes advantage of the unique and remarkable compressibility of  $H_2$  and shows great potential to achieve high storage efficiency.

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