PHYSICAL REVIEW B **79**, 033403 (2009)

Diffusion through a molecular ball check valve composed of a C_{60} molecule and a nanotube cap

D. Y. Sun,[1,2] H. Y. Chen,[2] J. W. Liu,[1] X. G. Gong,[3] and Zhi-Feng Liu[1,*]
[1]*Department of Chemistry and Centre for Scientific Modeling and Computation, Chinese University of Hong Kong, Shatin, Hong Kong, China*
[2]*Department of Physics and Key Laboratory of Optical and Magnetic Resonance Spectroscopy, East China Normal University, Shanghai 200062, China*
[3]*Department of Physics and Surface Physics Laboratory, Fudan University, Shanghai 200433, China*

(Received 2 November 2008; published 7 January 2009)

A nanostructure, consisting of C_{60} enclosed within a carbon nanotube near its cone shaped cap, is shown to behave like a ball check valve, a pressure-driven device for the storage of fluid. The van der Waals force acts like a spring that traps C_{60} near the cap section with a potential well around 1 eV. The restricted interstitial space around the valve produces a volume difference that forces C_{60} near the top center of the cap and therefore blocks the outward diffusion. It is estimated that such a mechanism can produce nanocapsules with internal pressure up to 40 GPa or above.

DOI: 10.1103/PhysRevB.79.033403 PACS number(s): 85.65.+h, 61.46.−w, 62.50.−p

Pressure, as an experimental variable, can now be tuned up to millions of atmosphere, thanks to the development of diamond-anvil cells and shock wave methods.[1–4] Under such extreme conditions, the structures and properties of condensed matters can change dramatically, revealing not only a variety of physical phenomena but also prospects for different materials.[5–7] However, both techniques have their limits that largely restrict high-pressure studies to the states of matters. In the case of diamond anvil, the amount of sample is small, typically in the microgram range. In the case of shock wave methods, high pressure is produced only for a short instant. To take advantage of property changes induced by high pressure, other types of containers must be designed. For this purpose, carbon nanotubes offer interesting prospects due to their two well-known structural features. First, inside their curved walls, there is a lot of empty space[8] into which molecules as big as C_{60} can be inserted.[9,10] Second, they have remarkable mechanical strengths.[11,12] It has recently been demonstrated that a single-walled carbon nanotube could already stand internal pressure as high as 40 GPa.[13] What is needed to make them into functional high-pressure containers is a workable design for a nanosized valve, through which gases could be let in, and inside which gases could be securely locked.

The inspiration for the design reported here comes from a mechanical device, known as the "ball check valve," which is often used in pumps and spray devices. As shown in Fig. 1(a), the valve is open or closed by a ball which is attached to a loaded spring and pushed against the inlet so that the valve is shut from inside. The application of external pressure through a compressed fluid can push the ball inward and open the inlet to fill the container. Upon equilibrium between the external and internal pressures, the ball is pushed back to close the valve and the fluid is locked inside. As a nanolevel analogy, we have recently proposed a molecular valve, with a C_{60} molecule as the ball [similar to Fig. 1(b)].[14] It is enclosed in a carbon nanotube near its end section where a bowl shaped calixarene[15] caps the tube. The calixarene molecule must be stitched to the tube and the leaks on the bowl wall must also be patched up, both of which are synthetically very challenging. As it is proposed in the context of hydrogen storage, a calixarene bowl offers structural features that make it easier to manipulate the leaks on the bowl for storing and releasing hydrogen.

For a high-pressure container that could stand internal pressure of few dozens of gigapascal, such a design can be significantly improved and simplified by replacing the calixarene with a carbon nanocone that typically caps carbon nanotubes. Synthetically, inserting C_{60} into open ended carbon nanotubes to form "peapod" structures is now a standard procedure,[9,10] after which the two open ends can be easily capped by heating around 1000 K. After cooling down, a small hole must be etched on the top of the cap. The top of such a nanocone is typically the region with the highest curvature and therefore chemically the most active.[16] By using the appropriate oxidant and controlling factors such as concentration, acidity, and temperature, the underlying equilibrium and therefore the extent of the etching can be controlled, which is best explored by chemistry rather than by

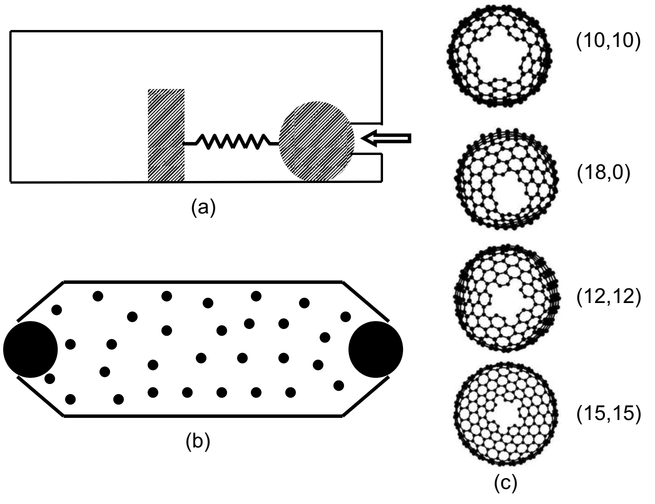

FIG. 1. (a) A ball check valve for the storage of compressed fluids. (b) A nanoanalogy to the ball check valve with a C_{60} molecule near an end cap for a carbon nanotube. (c) The shapes of the leak holes used in our models for MD simulations.

TABLE I. Results for the model containers. Diameter: the diameter of the tube; Length: the total length for each container from one cap to the other. E_{tube}: the adsorption energy of C_{60} in the tube section. E_A: the adsorption energy of C_{60} at the symmetric site A near the cap. E_B: the adsorption energy of C_{60} at the asymmetric site B near the cap. ΔV: the difference between the hydrogen volumes at sites A and B, computed with a threshold of 2.3 Å for $H_2 \cdots C$ distance. ΔD: the distance of inward movement for C_{60} from sites A to B.

Tube index	Diameter (Å)	Length (Å)	E_{tube} (eV)	E_A (eV)	E_B (eV)	ΔV (Å^3)	ΔD (Å)
(10,10)	13.5	65.5	3.65	4.61			
(18,0)	14.0	52.0	3.07	4.22			
(12,12)	16.2	58.0	2.20	3.17	3.21	~126	1.4
(15,15)	27.0	65.0	1.45	2.19	2.32	~193	2.6

modeling. The overall procedure is much easier to implement than that for the calixarene caps.[14] However, conceptually, a number of questions arise regarding the physical and dynamical behaviors of such a structure. Will C_{60} move to the cap section after its formation? Where would C_{60} be when gases are pushed into the tube through such a valve? When external pressure is withdrawn, can it block the hole before gases escape?

To answer these questions, we build several models for molecular-dynamics (MD) simulations. The pressure-transmitting gas is molecular hydrogen because it is highly compressible and diffusive even at cryogenic temperature and in solid state.[17] The ball part is C_{60}. A single-walled carbon nanotube is used as the container, the index of which takes the values listed in Table I. With the interactions determined by van der Waals potentials, the chirality of a tube matters less than the tube diameter, which varies from 13.5 Å for (10,10) to 27.0 Å for (15,15).[18] A carbon nanotube is capped by two carbon nanocones, each at one end. A nanocone is cut so that the radius of its bottom matches that for a tube of a particular index. When necessary, one or two more carbon atoms near the joint are removed so that only hexagon and pentagon are present and no two pentagons are connected. After attaching a nanocone to a tube, the top of the nanocone is opened by removing a few carbon atoms, which produces a hole with a diameter around 7 Å at each end as a gas filling window, as shown in Fig. 1(c). The length of such a container is listed in Table I.

The interaction between H_2 molecules is modeled by the well-known Silvera-Goldman potential,[17,19] with a cutoff of 8 Å. The Tersoff-type many-body potential[20] with the parameters given by Brenner[21] is used for the covalent interactions between carbon atoms.[12,22] The van der Waals interaction between atoms on the tube and on the fullerenes are modeled by a Lennard-Jones potential,[23,24] also with a cutoff of 8 Å. The interaction between H_2 and C is described by the recently fitted potential in Ref. 25, which reproduces the results over a wide range of repulsive and attractive regions as calculated by high level *ab initio* methods.[26,27] The potential energy for moving C_{60} inside a tube or pushing it through a nanocone cap is calculated as a function of the distance between the mass centers of the tube and of C_{60}, varied stepwise by 0.2 Å. At each step the system is fully relaxed for 100 ps using the steepest descent method with this distance constrained. The diffusion of H_2 molecules is calculated by MD simulations in which the distance between H_2 and the mass center of the tube is constrained. The MD simulations are performed in canonical ensemble with the temperature controlled by a Nosé-Hoover thermostat.[28,29] The equations of motion are solved by using the predictor-corrector algorithm with a time step of 1 or 2 fs.[30]

Energetically, it is favorable for C_{60} to stay close to the cap section. The calculated adsorption energy of C_{60} ranges from 2.2 to 4.6 eV, as listed in Table I, which is a substantial amount of energy for the typically weak van der Waals interaction. A good geometric match between cap and C_{60} makes it possible for favorable interactions between many a pair of C atoms on cap and on C_{60}. In other words, the strength of van der Waals interaction is favored by good contact between C_{60} and tube cap/body. When C_{60} is moved to the body section of the tube, such contacts are limited to the equatorial region of C_{60} in proximity to the tube and the adsorption energy is reduced by ~1 eV. A potential well for C_{60} is produced near the cap, as shown in Fig. 2(c). In analogy to a ball check valve, the van der Waals interaction acts like a loaded spring that forces C_{60} to stay near the cap.

The best fit is achieved in the (10,10) tube, which produces the largest adsorption energy. Unfortunately, it also makes the diffusion of hydrogen into the container difficult, with a calculated barrier of 0.8 eV. The C_{60} ball must be pushed inward as H_2 is squeezed through the opening between cap and C_{60} by as much as 1.2 Å from the equilibrium position. In simulation at 300 K with a 1 GPa difference between the external and internal pressures, C_{60} is pushed into the tube section where the potential surface is flat. In such a situation, there is no force to move C_{60} back to the cap section fast enough to block the leaking of hydrogen once the external pressure is withdrawn. This problem is alleviated for a (18,0) tube. The diffusion barrier for H_2 to enter the container is now reduced to 0.4 eV while C_{60} is still pushed inward by 0.6 Å.

Further increase in the tube diameter results in a qualitative change in the adsorption curve as shown in Fig. 2(c) for (12,12) and (15,15) tubes: there are now two adsorption sites. The first, labeled as A, is a symmetric site observed in all tubes as shown in Fig. 2(a). For the larger tubes, there is an additional asymmetric site, labeled B, in which C_{60} moves sideway and inward relative to the hole, as shown in Fig.

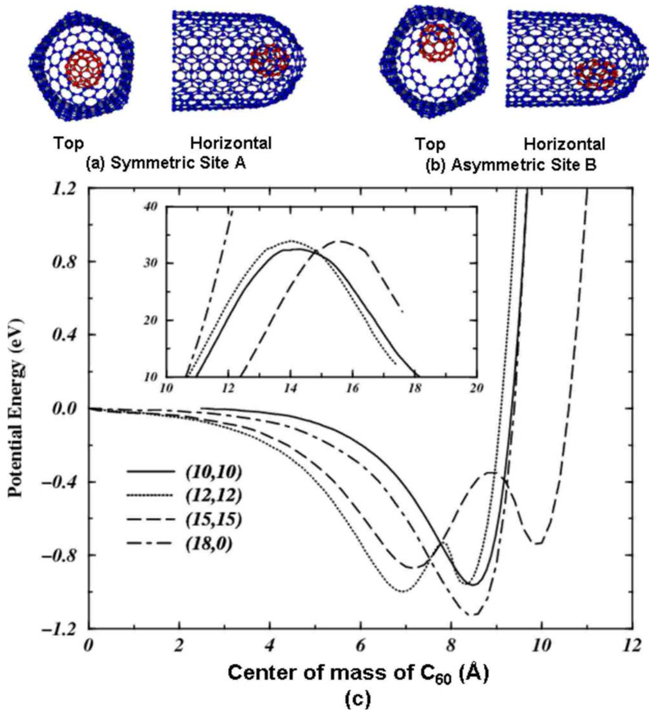

FIG. 2. (Color online) (a) The top and side views for a symmetric adsorption site. (b) The top and side views for an asymmetric site. (c) The potential energy for a nanovalve as the distance between the mass center of C_{60} and the tube is varied. The dramatic increase in the potential energy between 8 and 10 Å is due to the repulsive interaction between C_{60} and nanocone cap. For the (12,12) and (15,15) tubes, the curve shows two wells, corresponding to symmetric and asymmetric sites. The latter is in an inward position, with a smaller value for the position of C_{60}. The inset shows the details of energy change when C_{60} is pushed through the hole in the nanocone cap. The potential energy is relative to the energy when C_{60} is in the middle of the tube section.

2(b). Moreover, the adsorption energy at site B is more favorable. When the tube diameter is large enough, it is preferable to move C_{60} away from the hole for better contact with the nanocone, as in site B. The adsorption energy difference between these two sites is 0.04 eV for (12,12) and 0.13 eV for (15,15), and in both cases the barrier separating these two adsorption sites is small, 0.23 eV for (12,12) and 0.41 eV for (15,15). The presence of site B makes it much easier for the filling of H_2 into the nanocontainer. Even when C_{60} is at site A initially, the diffusion of H_2 into the container through the nanovalve will push C_{60} to site B. The diffusion barrier is almost zero while C_{60} is securely situated in site B with a potential depth around 1 eV.

While this is ideal for filling the container, it however raises a serious problem: if C_{60} stays at site B, hydrogen cannot be trapped inside the container once the external pressure is withdrawn. There must be a way to move C_{60} back to site A. Our simulations indicate that such a reversal will take place automatically once the hydrogen pressure is raised. To understand such a change, we notice another important difference between the two sites: for the asymmetric site B C_{60} is around 2 Å inward (Table I). For a macrodevice, such a movement produces no net change in the container volume. However, this is not true for a nanodevice. For the symmetric site A, the distance between the nanocone wall and C_{60} is only around 4.5 Å. The equilibrium distance between a hydrogen molecule and a graphene surface is around 3 Å,[25] and to open up space for H_2, the separation between carbon surfaces should be around 6 Å. Even when C_{60} moves inward by 1–2 Å as in site B, the interstitial space is still too restricted for hydrogen except for a narrow passage in the diffusion process. In other words, the inward movement of C_{60} reduces the available volume for hydrogen, which is not fully compensated in the interstitial region.

Quantitatively, such a change in volume can be evaluated numerically. The valve region is first divided into very small cubes with a side length of 0.01 Å. The distance of such a cube to its nearest carbon atom is then calculated. When the distance is larger than a certain threshold, say 2.6 Å, the cube is collected and added to the sum of the total volume available for hydrogen. The difference between the calculated volumes at sites A and B provides the change in hydrogen volume. As listed in Table I, the changes are −126 Å^3 for the (12,12) tube and −193 Å^3 for the (15,15) tube when the threshold is set at 2.3 Å. The larger change for the (15,15) tube is due to its larger inward movement (2.6 Å) from site A to site B. We have also calculated the volume change using threshold values ranging from 2.0 to 2.6 Å, which produces only small changes in the results (around 10%). Upon compression of hydrogen into the container, C_{60} will be pushed to the symmetric site A, which increases the available volume for hydrogen and reduces the free energy largely through the entropy factor. This conclusion is verified by MD simulations with pressures at gigapascal range, which all demonstrate that C_{60} will stay at the symmetric site A at high pressure.

The filling of the (12,12) and (15,15) containers can thus be divided into two stages. In the first stage, C_{60} stays at site B and hydrogen passes through the valve without much hindrance. After the internal pressure is raised, the preferred adsorption site becomes site A. When the external pressure is larger than the internal pressure, the C_{60} ball can still be pushed sideways or even back to site B to let the hydrogen in. However, as the pressure difference decreases toward equilibrium, C_{60} will go back to site A and the nanovalve is thereby closed. It very much behaves in the same way as a check ball valve although its operating mechanism is dependent on the combination of two factors: the van der Waals interaction and the microscopic volume effect.

The crucial parameter that determines the proper functioning of the proposed container is the tube diameter. As a rough estimate, the value of 16.2 Å, which is the diameter of the (12,12) tube, can be taken as the lower limit. The upper limit is likely beyond 27 Å, the diameter of the (15,15) tube. As demonstrated before[14] and verified in current simulations, the barrier for hydrogen to escape from the container, once the external pressure is withdrawn, is high and increases with the internal pressure. Hydrogen can be loaded at cryogenic temperature in their well-known diffusive solid states in gigapascal pressure. Once loaded, the internal pressure can be raised substantially by elevating the temperature.

The maximum pressure for such a container is limited by the breaking of the tube wall or the nanovalve. For the tube wall, the limit is around 40 GPa for single-walled carbon nanotubes.[13] For the valve, C_{60} can be squeezed out of the leak hole, for which the energy barrier is more than 30 eV, although the structural deformation is so large that Tersoff potential can only provide a rough estimate. Based on the potential-energy curves shown in Fig. 2(b), we can calculate the maximum force F_m on C_{60} by the gradient of energy over distance. By requiring $F_m=P_mS$, with S being the effective cross section of C_{60}, πr^2, and, with r taken as 5 Å, calculated P_m ranges from just above 20 GPa for (10,10), (12,12), and (15,15) to just below 50 GPa for (18,0). The large variation is actually due to a small change in the size of the leak hole, which is smaller in the case of (18,0) tube than all the others. The hole structures employed in our models are quite simplistic, leaving some carbon atoms along the edge unsaturated. If they are saturated by OH or carbonyl groups, the P_m would increase significantly. While the barrier for forcing H_2 into the container would also rise, the increase is much smaller due to the weak van der Waals potential. The threshold pressure for the valve could therefore be raised substantially by controlling the size of the leak hole. To raise the threshold of the tube wall, double or multiwalled carbon nanotubes can be used as the container.

In conclusion, we have demonstrated that the van der Waals interaction between C_{60} molecule and cap on a carbon nanotube can produce a double-well potential when the tube diameter is above 16 Å. Such a structure behaves like a check ball valve and makes it possible to fill the tube with pressure as high as 40 GPa. It pushes beyond the requirement envisioned previously for hydrogen storage.[14] Release of hydrogen from such nanocontainers is no longer an important issue because the kind of extreme pressure, previously accessible only in a diamond anvil, opens up interesting opportunities. Such high-pressure capsules could be collected and handled with ease, and as high-density materials, their unique properties induced by compression would become accessible in the real world. They could also be excited to much higher temperature by electric shock and ion-beam/laser irradiation to induce astronomical or fusionlike conditions despite the fact that it would lead to the eventual destruction of these containers.

The work reported was partially supported by an Earmarked grant (Project No. CUHK 4023/05P) from the Research Council of Hong Kong SAR Government, and by a Direct Grant from the Chinese University of Hong Kong. Both D.Y.S. and X.G.G. acknowledge support from the National Science Foundation of China. D.Y.S. also acknowledges support from the Shanghai Project for Basic Research. We are grateful for the generous allocation of computer time on the computer clusters at the Chemistry Department and the Center for Scientific Modeling and Computation and on the high performance computing facilities at the Information Technology Service Center, all located at the Chinese University of Hong Kong.

---

*Corresponding author. FAX: +852-2603-5057. zfliu@cuhk.edu.hk

[1] R. J. Hemley and N. W. Ashcroft, Phys. Today **51**(8), 26 (1998).
[2] W. Grochala, R. Hoffmann, J. Feng, and N. W. Ashcroft, Angew. Chem., Int. Ed. **46**, 3620 (2007).
[3] H. K. Mao and R. J. Hemley, Proc. Natl. Acad. Sci. U.S.A. **104**, 9114 (2007).
[4] R. Jeanloz, P. M. Celliers, G. W. Collins, J. H. Eggert, K. K. M. Lee, R. S. McWilliams, S. Brygoo, and P. Loubeyre, Proc. Natl. Acad. Sci. U.S.A. **104**, 9172 (2007).
[5] V. V. Struzhkin, B. Militzer, W. L. Mao, H. K. Mao, and R. J. Hemley, Chem. Rev. (Washington, D.C.) **107**, 4133 (2007).
[6] W. L. Mao, H. K. Mao, Y. Meng, P. J. Eng, M. Y. Hu, P. Chow, Y. Q. Cai, J. F. Shu, and R. J. Hemley, Science **314**, 636 (2006).
[7] J. F. Lin, V. V. Struzhkin, S. D. Jacobsen, M. Y. Hu, P. Chow, J. Kung, H. Z. Liu, H. K. Mao, and R. J. Hemley, Nature (London) **436**, 377 (2005).
[8] M. S. Dresselhaus, G. F. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, New York, 1996).
[9] M. Monthioux, Carbon **40**, 1809 (2002).
[10] J. Sloan, A. I. Kirkland, J. L. Hutchison, and M. H. Green, Acc. Chem. Res. **35**, 1054 (2002).
[11] J. Tersoff and R. S. Ruoff, Phys. Rev. Lett. **73**, 676 (1994).
[12] B. I. Yakobson, C. J. Brabec, and J. Bernholc, Phys. Rev. Lett. **76**, 2511 (1996).
[13] L. Sun, F. Banhart, A. V. Krasheninnikov, J. A. Rodriguez-Manzo, M. Terrones, and P. M. Ajayan, Science **312**, 1199 (2006).
[14] X. Ye, X. Gu, X. G. Gong, and Z. F. Liu, Carbon **45**, 315 (2007).
[15] J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston, and C. A. Sandoval, Chem.-Eur. J. **5**, 990 (1999).
[16] Y. F. Zhang and Z. F. Liu, Carbon **44**, 928 (2006).
[17] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).
[18] B. Verberck and K. H. Michel, Phys. Rev. B **74**, 045421 (2006).
[19] I. F. Silvera and V. V. Goldman, J. Chem. Phys. **69**, 4209 (1978).
[20] J. Tersoff, Phys. Rev. Lett. **61**, 2879 (1988).
[21] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[22] D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B **45**, 12592 (1992).
[23] L. Henrard, E. Hernandez, P. Bernier, and A. Rubio, Phys. Rev. B **60**, R8521 (1999).
[24] X. Ye, D. Y. Sun, and X. G. Gong, Phys. Rev. B **72**, 035454 (2005).
[25] D. Y. Sun, J. W. Liu, X. G. Gong, and Z. F. Liu, Phys. Rev. B **75**, 075424 (2007).
[26] A. Ferre-Vilaplana, J. Chem. Phys. **122**, 104709 (2005).
[27] T. Heine, L. Zhechkov, and G. Seifert, Phys. Chem. Chem. Phys. **6**, 980 (2004).
[28] S. Nosé, J. Chem. Phys. **81**, 511 (1984).
[29] W. G. Hoover, Phys. Rev. A **31**, 1695 (1985).
[30] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, UK, 1993).