

Response to “Comment on ‘Theoretical evaluation of hydrogen storage capacity in pure carbon nanostructures’” [J. Chem. Phys. 120, 9427 (2004)]

Ju Li^{a)}

Department of Materials Science and Engineering, Ohio State University, Columbus, Ohio 43210

Sidney Yip

Department of Nuclear Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 13 January 2004; accepted 29 January 2004)

[DOI: 10.1063/1.1688318]

In our recent paper,¹ we tried to rationally understand previous results of modeling hydrogen adsorption in pure single-walled carbon nanotubes (SWNTs), including the results of Cheng *et al.*,² by doing simpler calculations that a large percentage of the community can perform and check. For this purpose all the raw data of our calculations were put on the web.¹ Cheng *et al.*'s comments do not seem to object to the technical correctness of our numbers, but rather the interpretation and significance of these numbers. Our calculation setup in Sec. III of Ref. 1 indeed differs from that of Ref. 2—a point that was quite clear in Ref. 1 and further clarified in Cheng *et al.*'s comments—even though the same plane-wave density functional theory (DFT) program under the local density approximation (LDA) and, probably, even the same pseudopotentials were used. Our goal was to understand the nature of isolated nanotube–H₂ molecule interactions when the nanotube is distorted to a degree that is commensurate with thermal fluctuations at $T=300$ K. We avoided SWNT–SWNT coupling and free-energy sampling, which are still challenging to treat to good statistical accuracy in DFT calculations. Due to the differences in setups, our calculation results are not yet in direct conflict with those of Ref. 2. So our reply below may still be somewhat speculative. But we believe it will lead to a good discussion and probably more clarifying evidence later on.

Cheng *et al.* raised two major concerns:

(A) The relevance of the room-temperature and -pressure H₂ physisorption capacity upper bound estimated in our Sec. II based on a rigid SWNT bundle geometry and assuming the binding energy of H₂ to an isolated SWNT is the same as that of H₂ to a graphene sheet, and that the binding energies to multiple tubes are pair additive. The concern here is that the SWNT bundles are not fixed, and the tube–tube separation w can deviate from 3.4 Å significantly to accommodate more hydrogen.

(B) The relevance of our H₂-isolated SWNT “instantaneous” adsorption energy results in Sec. III. We used an isolated, distorted but fixed SWNT [obtained from finite- T molecular dynamics (MD) simulation using the Brenner empirical potential] in the DFT calculation while relaxing the

adsorbed H₂ molecule. The concern is that real SWNTs exist in bundles, so they are not isolated. Also, they are not rigid and the C–C–C angles have thermal fluctuations, and there are also concerns whether the Brenner potential is capable of reproducing the transient thermal fluctuations to a good measure.

Before replying to the comments, we would like to introduce some terminology. (a) Although the experimentally determined binding energy of a H₂ molecule to a flat graphene layer, $E_{\text{H}_2\text{-graphene}}^{\text{experiment}}$, is 30–50 meV/H₂ (Ref. 3), for a self-consistent discussion of the DFT-LDA calculations results, we cite the results of Arellano *et al.*,⁴ who obtained $E_{\text{H}_2\text{-graphene}}^{\text{DFT-LDA}} = 86$ meV/H₂. This gives a large margin of safety for our discussions below. An “abnormal interaction” is said to occur between a H₂ molecule and an isolated SWNT if their binding energy $E_{\text{H}_2\text{-SWNT}}$ is much greater than $E_{\text{H}_2\text{-graphene}}$, with both energies obtained by the same method: that is, if $E_{\text{H}_2\text{-SWNT}}^{\text{DFT-LDA}} \gg E_{\text{H}_2\text{-graphene}}^{\text{DFT-LDA}}$ or $E_{\text{H}_2\text{-SWNT}}^{\text{experiment}} \gg E_{\text{H}_2\text{-graphene}}^{\text{experiment}}$. So if one obtains from a DFT-LDA calculation a binding energy of 120 meV/H₂ between a H₂ molecule and an isolated SWNT, it will not be considered “abnormal” even though 120 meV/H₂ is much greater than 30–50 meV/H₂, since $E_{\text{H}_2\text{-graphene}}^{\text{DFT-LDA}} = 86$ meV/H₂. If, however, $E_{\text{H}_2\text{-SWNT}}^{\text{DFT-LDA}} = 300$ meV/H₂, then we can say abnormal interaction is found at the isolated H₂ and SWNT level, since such a big difference with $E_{\text{H}_2\text{-graphene}}^{\text{DFT-LDA}} = 86$ meV/H₂ cannot be explained by simple steric factors without some novel physics. (b) Another possible kind of “abnormal” interactions would be strong nonadditivity in the reverse-saturation sense: that is, when a H₂ molecule is interacting with multiple SWNTs, the total binding energy is somehow much greater than the sum of binding energies to individual SWNT participants when isolated. This would be considered abnormal because it is well known that van der Waals and ionic bonding are pair additive, while metallic and covalent bonding are nonadditive, but in the saturation sense. It would be quite surprising to find nonadditive interactions in a strong reverse-saturation sense.

Here are our replies to the concerns raised by Cheng *et al.*:

(A) Our Sec. II (Ref. 1) provides a simplified analysis of

^{a)} Author to whom correspondence should be addressed. Electronic mail: lij@mse.eng.ohio-state.edu

previous physisorption simulation results. The tube-tube separations in a SWNT bundle indeed can deviate from 3.4 Å to accommodate more hydrogen. However, this would not help room-temperature storage. Excluding the possibility of abnormal interactions, it was seen that only the triple junction interstices can offer enough binding energy ($3 \times 86 \text{ meV}/\text{H}_2$) for significant room- T, P adsorption. The double-tube adsorption sites ($2 \times 86 \text{ meV}/\text{H}_2$) and the single-tube adsorption sites ($86 \text{ meV}/\text{H}_2$) are simply too weak compared to the 300–400 meV/H_2 needed for room- T, P adsorption.

(i) As explained in Sec. II (Ref. 1), there are too few triple junctions in a SWNT bundle. A conservative estimate of 1.5 wt% is computed as the upper bound of room-temperature and pressure H_2 physisorption in a pure SWNT bundle, based on the triple-junction density.

(ii) Increasing the tube-tube distance w above 3.4 Å will only reduce the number of triple-junction adsorption sites and convert them to double- and single-tube adsorption sites. Indeed, when $w \rightarrow \infty$, all the triple- and double-tube sites will disappear and only the single-tube sites will remain (“trading quality for quantity”). This may be advantageous for increasing the adsorption uptake at very low temperatures, but *not* at room temperature and pressure.

(iii) Decreasing the tube-tube distance w much below 3.4 Å is forbidden, since there is strong repulsion between the tubes when w is decreased significantly, as shown in Fig. 1 of Cheng *et al.*'s comments.

We emphasize that our crude analyses serve only as an aid to understand the results of direct physisorption simulations, and not to replace the simulations. Almost all the physisorption simulations published to date, when assuming H_2 /isolated SWNT binding energy is similar in strength to H_2 /graphite surface binding energy, were not able to achieve >1 wt% H_2 adsorption at room temperature and pressure. Recent simulations of Dodziuk and Dolgonos⁵ and Gordillo *et al.*⁶ allowed for flexible SWNT bundles, but were not able to observe significant difference with rigid-bundle simulations.

(B) In Sec. III of Ref. 1, we tried to address the following question: is there abnormal binding between H_2 and an isolated SWNT with thermally fluctuating C–C–C bond angles? This is obviously a very important question, because if the answer is yes, then the underlying assumption of many previous physisorption simulations (that the binding of H_2 molecule to an isolated SWNT is similar in strength to the binding to a flat graphene sheet) would be wrong, and there would be a straightforward physical basis to rationalize the results of Ref. 2. If the answer is no, it does not automatically mean the result of Ref. 2 is wrong, but in light of the many other physisorption simulations and arguments provided in (A), would be quite puzzling. Indeed, it was postulated in Ref. 2 that “The atomistic quantum mechanical description of SWNT’s used in our *ab initio* MD simulation reveals partial electron-transfer interactions of hydrogen with specific, highly distorted carbon atoms (very acute C–C–C bond angles) in the nanotube walls. ... These enhanced electron-transfer interactions likely contribute to the higher energies of adsorption.” From crude lattice dynamical con-

siderations of the relationship between vibrational amplitudes and (out-of-plane) stiffness, the C–C–C bond angle fluctuations in an isolated SWNT should be close to or even somewhat greater than that in a SWNT bundle, so it seemed highly necessary and appropriate to clarify the nature of interaction between H_2 molecule and an isolated but thermally fluctuating SWNT.

We used the Brenner potential to carry out MD simulations of an isolated (7,7) SWNT (without H_2) at 300 K, took an instantaneous configuration from the MD trajectory, and computed the adsorption energies of H_2 to several binding sites of the distorted nanotube without relaxing the tube. The results suggest that C–C–C bond angle fluctuations, at a level corresponding to $T=300$ K, do not seem to have a significant effect on enhancing the H_2 binding energy. The “instantaneous” adsorption energies we obtained ranged from 54 to 110 meV/H_2 , which are somewhat less than the 114 meV/H_2 we obtained when the H_2 molecule is adsorbed at the endohedral site of an isolated SWNT with no thermal fluctuations. This latter number is in excellent agreement with recent independent DFT-LDA studies by Arellano *et al.*⁷ and Zhao *et al.*⁸

(i) Arellano *et al.*⁷ obtained 120 meV/H_2 and 70 meV/H_2 binding energies for endohedral and exohedral adsorption sites on (6,6) SWNTs, respectively; these should be compared to their prior result of 86 meV/H_2 adsorption energy to a flat graphene layer.⁴ No “abnormal interaction” was found, and the order of exohedral < flat graphene < endohedral binding energies is easily explained by the steric factor caused by the nanotube curvature.

(ii) Zhao *et al.*⁸ studied a (10,10) SWNT bundle and found the adsorption energies to be 111 meV/H_2 for an endohedral single-tube (pore) site, 94 meV/H_2 for an exohedral single-tube (surface) site, 114 meV/H_2 for an exohedral double-tube (groove) site, and 174 meV/H_2 for an exohedral triple-junction (interstitial) site. The results above agree with our analyses in two important ways: (a) the triple-junction site is indeed the most favored adsorption site and (b) non-additivity of the binding energies is in the saturation, instead of the reverse-saturation, sense.

In light of the above results, it is hard to understand why Cheng *et al.* obtained 326 meV/H_2 (endohedral) and 293 meV/H_2 (exohedral) binding energies at 300 K (Ref. 2). We would like to emphasize this is independent of whether DFT-LDA is overbinding or not, because^{1,7,8} are all DFT-LDA calculations. We further note that the distinction between isolated SWNTs and bundled SWNTs should matter less to the endohedral H_2 molecule, so more than the 293 meV/H_2 reported for exohedral adsorption, we cannot comprehend the 326 meV/H_2 for endohedral adsorption.

On a separate note, Cheng *et al.* commented that the Brenner potential may not reproduce the C–C–C bond angle fluctuations well. Yet our Fig. 2 (Ref. 1) is in reasonable agreement with Fig. 2 of Ref. 2 when there is no H_2 present, except our distributions are smoother, reflecting better statistics. It is well known that the Brenner potential reproduces the elastic moduli and vibrational spectra of SWNTs quite well.⁹ We did ignore the impact of H_2 /SWNT collisions on the C–C–C bond angles. But in a recent paper,¹⁰ it was

concluded that the Brenner potential did reasonably well describing the redshifts of H₂ vibrational frequencies, in which the H₂/SWNT collisions and the flexibilities of SWNTs had been taken into account.¹¹

Finally, we note that experimentally when the hydrogen in SWNTs is clearly identified to be molecular and adsorbed on the SWNT walls, our computed binding energies do seem to agree with the experimental measurements to within a factor of 2. For instance, Pradhan *et al.* characterized the vibrational spectra of H₂ on SWNTs using Raman spectroscopy and found the isosteric heat of adsorption to be 120 meV/H₂ (Ref. 12).

¹J. Li, T. Furuta, H. Goto, T. Ohashi, Y. Fujiwara, and S. Yip, *J. Chem. Phys.* **119**, 2376 (2003).

²H. S. Cheng, G. P. Pez, and A. C. Cooper, *J. Am. Chem. Soc.* **123**, 5845 (2001).

³K. A. Williams, B. K. Pradhan, P. C. Eklund, M. K. Kostov, and M. W. Cole, *Phys. Rev. Lett.* **88**, 165502 (2002).

⁴J. S. Arellano, L. M. Molina, A. Rubio, and J. A. Alonso, *J. Chem. Phys.* **112**, 8114 (2000).

⁵H. Dodziuk and G. Dolgonos, *Chem. Phys. Lett.* **356**, 79 (2002).

⁶M. C. Gordillo, J. Boronat, and J. Casulleras, *Phys. Rev. B* **68**, 125421 (2003).

⁷J. S. Arellano, L. M. Molina, A. Rubio, M. J. Lopez, and J. A. Alonso, *J. Chem. Phys.* **117**, 2281 (2002).

⁸J. J. Zhao, A. Buldum, J. Han, and J. P. Lu, *Nanotechnology* **13**, 195 (2002).

⁹V. P. Sokhan, D. Nicholson, and N. Quirke, *J. Chem. Phys.* **113**, 2007 (2000).

¹⁰G. Canto, P. Ordejon, H. S. Cheng, A. C. Cooper, and G. P. Pez, *New J. Phys.* **5**, 124 (2003).

¹¹S. J. V. Frankland and D. W. Brenner, *Chem. Phys. Lett.* **334**, 18 (2001).

¹²B. K. Pradhan, G. U. Sumanasekera, K. W. Adu, H. E. Romero, K. A. Williams, and P. C. Eklund, *Physica B* **323**, 115 (2002).