

Influence of Carbon Curvature on Molecular Adsorptions in Carbon-Based Materials: A Force Field Approach

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A general force field methodology is developed for description of molecular interactions in carbon-based materials. The method makes use of existing parameters of potential functions developed for sp^2 and sp^3 carbons and allows accurate representation of molecular forces in curved carbon environment. The potential parameters are explicitly curvature and site dependent. The proposed force field approach was used in molecular dynamics (MD) simulations for hydrogen adsorption in single-walled carbon nanotubes (SWNTs). The results reveal significant nanotube deformations and the calculated energies of adsorption are comparable to the reported experimental heat of adsorption for H_2 in SWNTs.

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Recent progress in the preparation of novel carbons has led to the investigation of molecular hydrogen adsorption in these materials. A number of groups have reported the effective storage of H_2 in single-walled carbon nanotubes (SWNTs) [1–3]. Despite these optimistic experimental reports, several theoretical studies [4–8] based upon classical physisorption simulations of rigid and structureless (nonatomistic) tube models suggest that the heat of adsorption and the storage capacities fall far short of the reported experimental values [1]. Very recently, we performed quantum-mechanical *ab initio* molecular dynamics simulations [9] of hydrogen adsorption in SWNTs, revealing significant distortions of the nanotubes and a considerable enhancement of adsorption energy upon interaction of instantaneously distorted carbon atoms in the SWNT wall and H_2 molecules.

What should make carbon nanotubes and fullerenes distinctively different from other graphitic carbons in their ability to adsorb gas molecules is the curvature (i.e., C-C-C bond angles) of the carbon surface. The carbon atoms must adopt a quasi- sp^2 hybridization due to the imposed highly curved structure. The degree of the valence orbital hybridization depends upon the radius (r) of the material: a large radius leads to a hybridization close to pure sp^2 while a small radius yields a hybridization towards sp^3 . Interactions with H_2 under a pure sp^2 hybridization ($r \rightarrow \infty$) give a very weak adsorption energy as in the case of graphite (~ 1.0 kcal/mol). In contrast, small radius fullerenes and/or nanotubes with a hybridization closer to sp^3 can even be hydrogenated [10–13].

In classical simulations, interactions between molecules and carbon materials are described by empirical potential functions. Unfortunately, to date, none of the available force fields, which generally employ potential functions derived for graphite, have explicitly accounted for the effect of curvature on the adsorption properties,

limiting the accuracy of these simulations. The recently developed reactive empirical bond-order (REBO) potential by Brenner [14], the generalized extended empirical bond-order dependent force fields by Goddard and co-workers [15,16], and the adaptive intermolecular REBO potential (AIREBO) by Stuart and co-workers [17] can be potentially useful for molecular adsorption in a curved carbon environment, but the accuracy of their force fields on the adsorption energetics is yet to be tested.

In this Letter, we propose a description of molecular potential functions in carbon-based materials that is explicitly dependent upon the curvature of graphitic nanostructures. Our method does not create a novel force field, but makes use of the existing force fields for interatomic potential functions developed for carbon atoms with sp^2 and sp^3 hybridizations and derives new parameters for quasi- sp^2 - or sp^3 -like carbons. While we focus our current discussion on molecular hydrogen in SWNTs, the method is readily applicable to other molecules in materials with curved carbon surfaces, such as fullerenes, nanocones, and multiwalled nanotubes.

Common force fields include bonding interactions contributed by forces due to deformations of bond distances, bond angles and torsion angles, out-of-plane interactions, as well as the couplings between deformations of internal coordinates and nonbonding interactions describing van der Waals forces and electrostatic interactions. These terms are usually represented by well-behaved analytic functions with parameters derived from fitting either experimental or *ab initio* results. The forces between H_2 and graphite (pure sp^2 hybridization) have been represented by a number of highly accurate potential functions [18–20]. However, for three-coordinate carbon atoms with near- sp^3 hybridization in highly curved carbon materials, such as small radius fullerenes and nanotubes, parameters used in conventional force fields are not suitable; these potential functions were created to model

saturated tetrahedral single bonds, while in the curved carbon materials there is a dangling bond (empty valence) associated with the carbon atoms.

Chemically, an sp^3 carbon atom with a dangling bond behaves as a radical, with the free electron located in an sp^3 orbital in a tetrahedral framework. The tetrahedral bonding arrangement orients the dangling bonds towards the outside surface, giving rise to a stronger interaction with H_2 at the exohedral site [9]. At the endohedral site, the interaction with H_2 is primarily the van der Waals force. We propose here a simple procedure that explicitly includes both the curvature of the carbon surface and the H_2 orientation relative to the surface in the parameters, both bonding and nonbonding, of potential functions, assuming that the parameters for pure sp^2 and sp^3 carbons are known. For carbon nanotubes or fullerenes, an arbitrary bond parameter X is introduced as a function of the radius, r . Introducing a curvature parameter, $f(r)$, and using the corresponding sp^2 and sp^3 values of the bond parameter, X^{sp^2} and X^{sp^3} , respectively, we can define a new bond parameter of the “mixed” state as the following linear combination:

$$X(r) = f(r)X^{sp^2} + [1 - f(r)]X^{sp^3}, \quad (1)$$

where the curvature parameter $f(r)$ is defined as

$$f(r) = \left(1 - \frac{r_0}{r}\right)^\lambda, \quad (2)$$

where r_0 is the reference constant and λ is a positive number. The reference constant is chosen to be the radius of the SWNT (armchair, zigzag, or chiral) or fullerene which has C-C-C bond angles and orbital hybridization closest to sp^3 (C-C-C = 109.5°). It is therefore obvious that

$$0 \leq f(r) \leq 1. \quad (3)$$

From Eqs. (1)–(3), if the radius of a carbon-based material is close to the reference constant, then $f(r) \rightarrow 0$ and $X(r) \rightarrow X^{sp^3}$, subscribing a set of sp^3 bond parameters. In contrast, if the material is planar, we then have $f(r) \rightarrow 1$ and $X(r) \rightarrow X^{sp^2}$. The existing sp^2 bond parameters, based upon graphite, would work well in this case. Equations (1) and (2) are explicitly radius dependent and allow new bond parameters for curved carbons to be developed based upon the existing parameters of sp^2 and sp^3 types.

While geometric bond parameters can be derived in the same way as described above, the energy term must be managed in a slightly different fashion to reflect the adsorption site dependence. We assume that the nonbonding interaction can be described with the Lennard-Jones potential using parameters σ_{CH} and ε_{CH} . While σ_{CH} is derived from Eqs. (1) and (2), we propose to use the following linear combination to estimate the nonbonding well depth ε_{CH} :

$$\varepsilon_{CH}(r) = \begin{cases} f(r)\varepsilon^{sp^2} + [1 + f(r)]\varepsilon_{\text{head-on}}^{sp^3}, & \text{exohedral,} \\ f(r)\varepsilon^{sp^2} - [1 - f(r)]\varepsilon_{\text{side-on}}^{sp^3}, & \text{endohedral,} \end{cases} \quad (4)$$

where $\varepsilon_{\text{head-on}}^{sp^3}$ and $\varepsilon_{\text{side-on}}^{sp^3}$ are the well depths of an sp^3 hybridized carbon atom with a dangling bond interacting with a H_2 molecule on the exohedral end-on and the endohedral side-on orientations, respectively. Since for an individual C- H_2 pair the end-on orientation is energetically more favorable than the side-on orientation, as shown later in our *ab initio* calculation, the value of $\varepsilon_{\text{head-on}}^{sp^3}$ is generally larger than that of $\varepsilon_{\text{side-on}}^{sp^3}$. Furthermore, based on the previous arguments, $\varepsilon_{\text{head-on}}^{sp^3}$ is considerably larger than ε^{sp^2} and thus for exohedral adsorption, the value of ε_{CH} is significantly enhanced. On the other hand, for endohedral adsorption, the well depth will be smaller than ε^{sp^2} . From Eqs. (2) and (4) it can be readily shown that, if

$$r < \frac{1}{1 - \left(\frac{\varepsilon_{\text{side-on}}^{sp^3}}{\varepsilon^{sp^2} + \varepsilon_{\text{side-on}}^{sp^3}}\right)^{1/\lambda}} r_0, \quad (5)$$

then the endohedral well depth $\varepsilon_{CH} < 0$. Thus, the interaction between H_2 and the inner tube wall becomes repulsive.

Using Eqs. (1), (2), and (4) and the existing force field parameters for sp^2 and sp^3 carbons, we have derived a new set of parameters for a range of SWNTs. The main parameters of the force field are summarized in Table I. For the purpose of comparison, the parameters for pure sp^2 and sp^3 carbons are also listed. The reference constant $r_0 = 1.356 \text{ \AA}$ is the radius of a (2, 2) armchair nanotube which has a hybridization relatively close to sp^3 (average bond angle of 112.5°). The values for bonding interactions for sp^2 and sp^3 carbon atoms were obtained from the consistent valence force field (CVFF) [21]. The C-C Lennard-Jones parameters for sp^2 carbon atoms were derived from the properties of crystalline graphite [19,22]. For the interaction between H_2 and an sp^2 carbon, we adopted the values for the C-H parameters used for H_2 on graphite, which gives $\varepsilon^{sp^2} = 2.24 \text{ meV}$ [23]. However, for the interaction between H_2 and an sp^3 carbon with a dangling bond, no experimental data are available. We therefore performed calculations using density functional theory (DFT) and fitted the data with Lennard-Jones parameters for both head-on and side-on orientations at exohedral and endohedral sites. The DFT calculation was conducted by using the hybrid B3LYP functional that combines Becke’s exchange and Lee-Yang-Parr’s correlation functionals with a 6-311++G** basis set. A H_2 molecule was attached to a *t*-butyl radical, used to model the environment of the unsaturated sp^3 carbon, and geometry optimization was performed along the pathway as H_2 approached the carbon atom, yielding the well-depth parameters $\varepsilon_{\text{head-on}}^{sp^3} = 11.01 \text{ meV}$ and

TABLE I. The values of the main force field parameters for sp^2 , sp^3 , and quasi- sp^2 carbon and hydrogen. The bond interaction parameters were taken from Refs. [20,22]; Lennard-Jones parameters were taken from Refs. [19,21]. Here the parameters K_r , r_0 , K_θ , and θ_0 are used to describe the C-C bonding interaction for bond stretch and bond angle deformation. For simplicity, parameters for change in dihedral angles and the coupling terms are not listed. ϵ_{CC} and σ_{CC} are the Lennard-Jones parameters for C-C nonbonding interaction, and $\epsilon_{CH}(\text{end})$ and $\epsilon_{CH}(\text{exo})$ are the Lennard-Jones well depths of the C-H nonbonding interaction for endohedral and exohedral adsorption, respectively. The units of the parameters are K_r in kcal mol $^{-1}$ Å $^{-2}$; r_0 and σ_{CC} in Å; K_θ in kcal mol $^{-1}$, θ_0 in degrees; ϵ_{CC} and ϵ_{CH} in meV.

SWNT	R	K_r	r_0	K_θ	θ_0	ϵ_{CC}	σ_{CC}	$\epsilon_{CH}(\text{end})$	$\epsilon_{CH}(\text{exo})$
(5, 0)	1.96	398.67	1.44	67.5	115.3	2.374	3.49	-0.99 ^a	6.78
(5, 3)	2.74	425.80	1.41	75.0	116.9	2.386	3.46	0.09	5.26
(5, 5)	3.39	437.38	1.39	78.2	117.6	2.391	3.45	0.55	4.62
(9, 0)	3.52	439.12	1.39	78.8	117.7	2.392	3.44	0.62	4.52
(9, 5)	4.81	450.86	1.38	81.9	118.3	2.397	3.43	1.08	3.87
(9, 9)	6.10	457.34	1.37	83.7	118.7	2.400	3.42	1.34	3.50
(10, 0)	3.92	443.62	1.38	79.9	117.9	2.394	3.44	0.79	4.27
(10, 5)	5.18	453.07	1.37	82.6	118.5	2.398	3.43	1.17	3.74
(10, 10)	6.78	459.71	1.36	84.4	118.8	2.401	3.42	1.43	3.37
sp^2	...	480.01	1.34	90.0	120.0	2.410	3.40	2.24	2.24
sp^3	...	323.02	1.53	46.6	111.0	2.340	3.57	4.00	11.0

^aThe negative value of the well depth implies that the interaction becomes purely repulsive and cannot be described by a Lennard-Jones potential.

$\epsilon_{\text{side-on}}^{sp^3} = 4.0$ meV, respectively. The parameter of λ was chosen to be 0.62 so that the van der Waals surface of an endohedral H₂ aligned along the nanotube axis touches the van der Waals surface of the wall. Table I indicates that, for SWNTs with large diameters, the calculated force field parameters have smaller deviation from those developed for sp^2 carbons although the well depth for C-H nonbonding interaction deviates significantly from the sp^2 value for both endohedral and exohedral adsorption. Considerably larger deviations from the sp^2 parameters are observed for small diameter nanotubes, suggesting that using the sp^2 parameters for these materials is inadequate. In particular, the strength of interaction between H₂ and carbon atoms on the exohedral surface increases significantly as the diameter of the nanotubes decreases. At an endohedral site, however, the attractive interaction vanishes very quickly as the nanotube radius shrinks, consistent with the fact that a small nanotube diameter leads to close contacts and steric repulsion between the nanotube wall and H₂ molecules.

We applied the calculated force field parameters to canonical molecular dynamics (MD) simulations of H₂ adsorption in (9, 9) armchair SWNT arrays. The MD simulation was conducted by numerically integrating Newton's equations of motion with a Verlet velocity integrator algorithm to track the motion of all atoms with time [24]. Nose's thermostat was used for temperature control and the periodic boundary condition was imposed. With a time step of 1.0 fs, the MD simulation was performed for 100 ps at 300 K. A $1 \times 1 \times 15$ unit cell was selected, which contains 1080 carbon atoms and 0.5 wt% hydrogen. The optimized cell parameters are $a = b = 15.22$ Å, $c = 72.83$ Å; $\alpha = \beta = 90^\circ$, and

$\gamma = 120^\circ$. The nonbonding H-H potential parameters are fitted to the recent high level *ab initio* results reported by Diep and Johnson [25], yielding the center-of-mass separation of 3.4 Å and the Lennard-Jones parameters $\sigma_{CH} = 2.78$ Å and $\epsilon_{CH} = 2.24$ meV.

As expected, the MD simulation yields a strong preference for exohedral adsorption with an average adsorption energy of -4.5 kcal/mol and a calculated energy for endohedral adsorption of only -0.9 kcal/mol, consistent with the respective well depths. In contrast, without introducing the curvature parameter in the standard CVFF force field, the adsorption energy would be considerably underpredicted (-0.51 kcal/mol for exohedral and -0.41 kcal/mol for endohedral, respectively). The MD simulations also reveal significant nanotube deformations, which create nearly planar regions in the SWNT wall and concomitant regions with acute C-C-C bond angles, consistent with the results of *ab initio* MD simulation recently reported [9]. The effect of curvature can also be illustrated in the calculated radial distribution functions (RDF) for exohedral adsorption as shown in Fig. 1, where the dotted lines and the solid lines represent the results calculated with the sp^2 parameters and the newly developed parameters, respectively. While the RDF for H-H distance is seemingly unaffected, considerable deviation in the C-C and C-H RDFs between the two sets of parameters is exhibited. As expected, the sp^2 parameters yield slightly shorter C-C distances due to the overestimation of bonding.

In summary, we have developed a computational scheme to derive more accurate force field parameters for molecular interactions in carbon-based materials with significant curvature. The derived interaction forces

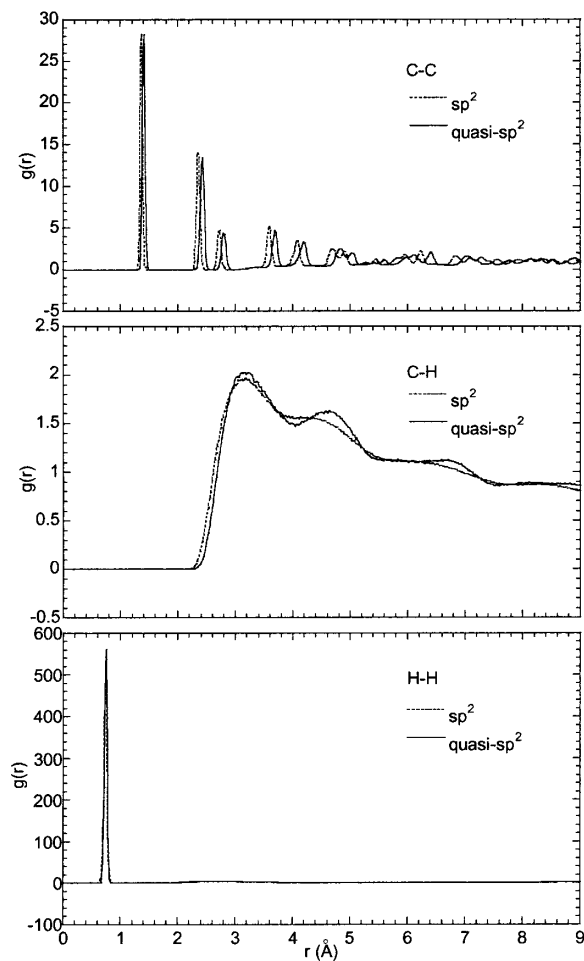


FIG. 1. Radial distribution functions for exohedral H_2 over the 100 000 steps of the 100 ps MD simulation.

are explicitly curvature and site dependent. This is particularly important for carbons with a large curvature, for which conventional force fields are inadequate. Our results suggest that the effect of carbon curvature becomes more pronounced as the nanotube diameters get smaller. The results of our MD simulation give a strong preference for H_2 adsorption on the exohedral surface of SWNTs and reveal significant lattice deformations in agreement with the results of earlier *ab initio* MD simulations.

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