Van der Waals forces and Confinement in Carbon Nanopores: Interaction between CH₄, COOH, NH₃, OH, SH and Single-Walled Carbon Nanotubes

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Abstract

Interactions between CH₄, COOH, NH₃, OH, SH and armchair (n, n) ($n = 4, 7, 14$) and zigzag ($n, 0$) ($n = 7, 12, 25$) single-walled carbon nanotubes (SWCNTs) have been systematically investigated within the framework of dispersion-corrected density functional theory (DFT-D2). Endohedral and exohedral molecular adsorption on SWCNT walls is energetically unfavorable or weak, despite the use of C_6/r^6 pairwise London-dispersion corrections. The effects of pore size and chirality on the molecule/SWCNTs interaction were also assessed. Chemisorption of COOH, NH₃, OH and SH at SWCNT edge sites was examined using a H-capped (7, 0) SWCNT fragment and its impact on electrophilic, nucleophilic and radical attacks was predicted by means of Fukui functions.

Keywords: Nanotubes, carbon nanopores, density functional theory

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1. Introduction

Since the seminal work of Rice and Whitehead on electrolyte solutions confined in capillaries with nanometer-scale diameters (1), nanofluidics has emerged among the fastest growing research fields, owing to the rapid development of nanotechnologies and the wider availability of tools and techniques to interrogate and manipulate fluids/materials systems at the nanoscale (2, 3). Because physical scaling lengths (e.g. Debye radius) of confined fluids closely match the dimensions of their host nanostructured materials, the properties of nanoconfined fluids – whether liquid, gas or plasma – depart significantly from their bulk counterparts. Such fascinating properties have drawn attention, for example, in nanofluidic electronics (4, 5), lab-on-a-chip (6) and nanomaterials storage technologies (7, 8, 9), biotechnology (10) and nanogeochemistry (11).

In geologic environments, a precise knowledge of the interaction of gas with kerogen, a naturally occurring carbon-rich polymer material resulting from the condensation of organic residues, is of crucial importance to understanding nanofluidic processes underlying natural gas extraction. In addition to carbon,

kerogen is composed predominantly of hydrogen, oxygen, nitrogen, and sulfur. After undergoing successive transformations during the diagenesis, catagenesis, and metagenesis maturation stages, polynuclear aromatic (PNA) units in kerogen eventually combine to form sp^2 -hybridized graphitic flakes as components of a complex network of carbon nanopores. Due to inherent complexity of the post-catagenesis kerogen morphology, single-walled carbon nanotubes (SWCNTs) can serve as useful model hosts to predict the intricate properties of gas confined in nanoporous carbon (7, 8, 9, 12). Indeed, since SWCNT diameter is related to the chiral vector (n, m) (through the relationship $d_t = (a/\pi) \sqrt{n^2 + m^2 + nm}$, where $a = 0.246$ nm and n and m are integers), SWCNTs can be viewed as intrinsically well-defined carbon nanopores.

In this Letter, interactions between CH₄, COOH, NH₃, OH, SH and armchair (n, n) ($n = 4, 7, 14$) and zigzag ($n, 0$) ($n = 7, 12, 25$) SWCNTs have been systematically investigated within the framework of dispersion-corrected density functional theory (DFT-D2). Long-range dispersion interactions were previously found to play an important role in molecular aggregation under confinement and SWCNT filling (9, 13). Endohedral and exohedral adsorption on SWCNT walls was studied using explicit C_6/r^6 pairwise London-dispersion corrections and the impact of

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pore size and chirality on the molecule/SWCNTs interaction for SWCNTs diameters of $\approx 5, 10$ and $20 \text{ \AA}$ was systematically assessed. Chemisorption of COOH, NH_3 , OH, and SH at SWCNT edge sites was also examined using a H-capped (7, 0) SWCNT fragment. The impact of edge-site chemisorption on potential electrophilic, nucleophilic and radical attacks was predicted by means of Fukui functions.

Details of our computational approach are given in the next section, followed by a discussion of our results for structural and electronic properties.

2. Computational methods

First-principles total energy calculations were performed using DFT, as implemented in the Vienna *ab initio* simulation package (VASP) (14). The exchange-correlation energy was calculated using the generalized gradient approximation (GGA), with the parameterization of Perdew, Burke, and Ernzerhof (PBE) (15). Standard functionals such as the PBE or PW91 functionals were found in previous studies to correctly describe structures and properties of atom adsorption on graphitic surfaces (16, 17).

The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method (18, 19). The $\text{C}(2s^2, 2p^2)$, $\text{N}(2s^2, 2p^3)$, $\text{O}(2s^2, 2p^4)$ and $\text{S}(3s^2, 3p^4)$ electrons were treated explicitly as valence electrons in the Kohn-Sham (KS) equations and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equation was solved using the blocked Davidson iterative matrix diagonalization scheme (20). The plane-wave cutoff energy for the electronic wavefunctions was set to 500 eV, ensuring the total energy of the system to be converged to within 1 meV/atom.

Although structural features of graphitic carbon systems are usually well reproduced within the local density approximation (LDA) due to fortuitous error cancellation, popular density functionals are unable to describe correctly van der Waals interactions resulting from dynamical correlations between fluctuating charge distributions. A pragmatic method to work around this problem has been given by density functional theory corrected for dispersion (DFT-D), which consists in adding a semi-empirical dispersion potential to the conventional Kohn-Sham GGA total-energy functional, E_{DFT} , i.e.,

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}, \quad (1)$$

In the DFT-D2 method of Grimme (21) utilized in this study, the van der Waals interactions are described

via a simple pairwise London-type force field, which is optimized for DFT functionals. The dispersion energy for periodic systems is defined as:

$$E_{\text{disp}} = -\frac{s_6}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_L' \frac{C_6^{ij}}{|\vec{r}_{i,0} - \vec{r}_{j,L}|^6} f(|\vec{r}_{i,0} - \vec{r}_{j,L}|), \quad (2)$$

where the summation are over all atoms N and all translations of the unit cell $L = (l_1, l_2, l_3)$, with the prime sign indicating that cell $i \neq j$ for $L = 0$, s_6 is a global scaling factor, C_6^{ij} is the dispersion coefficient for the atom pair ij , and $\vec{r}_{j,L}$ is a position vector of atom j after performing L translations of the unit cell along lattice vectors. In practice, terms corresponding to interactions over distances longer than a certain suitably chosen cut-off radius contribute only negligibly to the dispersion energy and can be ignored. The term $f(r^{i,j})$ is a damping function:

$$f(r^{i,j}) = \frac{1}{1 + e^{-d(r^{i,j}/R_0^{i,j}-1)}}, \quad (3)$$

whose role is to scale the force field such as to minimize contributions from interactions within typical bonding distances. Combination rules for dispersion coefficients C_6^{ij} and van der Waals radii R_0^{ij} are:

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \quad \text{and} \quad R_0^{ij} = R_0^i + R_0^j. \quad (4)$$

The global scaling parameter s_6 has been optimized for several different DFT functionals and corresponds to a value of $s_6 = 0.75$ for the PBE functional used in this study. The parameters used in the empirical force-field of Grimme are summarized in Table 1.

Table 1: Parameters used in the semi-empirical force field of Grimme for the present study.^a

Parameters	C	H	N	O	S
$R_0(\text{\AA})$	1.452	1.001	1.397	1.342	1.683
$C_6(\text{Jnm}^6\text{mol}^{-1})$	1.75	0.14	1.23	0.70	5.57

^a[Ref. (21)].

In this study, 3-D periodic unit cells were optimized along the z direction of the armchair (n, n) ($n = 4, 7, 14$) and zigzag $(n, 0)$ ($n = 7, 12, 25$) SWCNTs axis. Those nanotubes were selected to study the impact of pore size and chirality on the molecule/SWCNTs interaction for SWCNTs diameters of *ca.* 5, 10 and $20 \text{ \AA}$. Ionic relaxation was carried out using the quasi-Newton method and the Hellmann-Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV/ $\text{\AA}$. Structural optimizations and properties calculations were carried out using the Monkhorst-Pack special

k -point scheme (22), using a $3 \times 3 \times 5$ k -point mesh for integrations in the Brillouin zone (BZ). The tetrahedron method with Blöchl corrections was used for BZ integrations (23). Ionic and cell relaxations were performed simultaneously, without symmetry constraints. The lattice parameter c of armchair SWCNTs was taken to be twice the lattice constant, while both parameters were identical for zigzag SWCNTs. In addition, adsorption of COOH, NH₃, OH, and SH at SWCNT edge sites was investigated using a H-capped (7, 0) SWCNT fragment.

3. Results and discussion

Figure 1: Interaction energies between endohedrally-confined CH₄, COOH, NH₃, OH and SH molecules and the walls of armchair (n, n) ($n = 4, 7, 14$) and zigzag ($n, 0$) ($n = 7, 12, 25$) SWCNTs calculated at the DFT-D/PBE level of theory. Negative ΔE values correspond to binding interaction.

The interaction energies between endohedrally-confined CH₄, COOH, NH₃, OH and SH molecular species and (n, n) ($n = 4, 7, 14$) and ($n, 0$) ($n = 7, 12, 25$) SWCNTs were calculated using the formula:

$$\Delta E = E_{\text{SWCNT+mol}} - E_{\text{SWCNT}} - E_{\text{mol}}, \quad (5)$$

where $E_{\text{SWCNT+mol}}$, E_{SWCNT} and E_{mol} are the total energies of the SWCNT and molecule system, the isolated SWCNT, and the isolated molecular species, respectively. As shown in Figure 1, only endohedrally-confined CH₄ can weakly physisorb to the walls of the largest SWCNTs, with binding energies of $E_b = -0.21$ and -0.23 eV for (7, 7) and (12, 0) SWCNTs, and less than -0.01 eV for (14, 14) and (25, 0) SWCNTs. Electron charge density maps depicting the interaction

Figure 2: Cross-sectional charge density maps (normal to SWCNT axis) of a endohedrally-confined CH₄ molecule interacting with the walls of armchair (n, n) ($n = 4, 7, 14$) and zigzag ($n, 0$) ($n = 7, 12, 25$) SWCNTs calculated at the DFT-D/PBE level of theory. Maps boundaries correspond to the limits of the periodic cells used.

between CH₄ and zigzag and armchair SWCNTs are shown in Figure 2. While COOH is also close to form bonds inside those SWCNTs, OH, SH and NH₃ do not adsorb to walls ($\Delta E > 0$); NH₃ is the least susceptible to interact with carbon walls inside SWCNTs, followed by OH and SH. Only minor differences are observed between nanotubes with distinct chirality (i.e. armchair vs. zigzag). Results also show that a confinement effect, manifested by an increase or decrease in ΔE relative to larger SWCNTs with diameters in the range $\approx 1 - 2$ nm, appears for SWCNTs with the smallest diameters, i.e. ≈ 0.5 nm [(4, 4) and (7, 0)]. This stems from the fact that the minimum distance separating outermost atoms of the molecule and the adjacent C atoms of the (4, 4) and (7, 0) SWCNT walls is shorter than the sum of their van der Waals radii R_0 (cf. Table 1).

In addition, exohedral interaction between CH₄, COOH, NH₃, OH, SH and (n, n) ($n = 4, 7, 14$) and ($n, 0$) ($n = 7, 12, 25$) SWCNTs was investigated (cf. Figure 3). Let us note that exohedral is defined here as in the space in-between SWCNTs in a close-packed array. CH₄ only binds to the largest (14, 14) and (25, 0) SWCNTs, with $E_b = -0.25$ eV, and COOH can physisorb to (4, 4)

Figure 3: Interaction energies between exohedral CH_4 , COOH , NH_3 , OH and SH molecular species and the walls of armchair (n, n) ($n = 4, 7, 14$) and zigzag $(n, 0)$ ($n = 7, 12, 25$) SWCNTs calculated at the DFT-D/PBE level of theory. Negative ΔE values correspond to binding interaction.

($E_b = -0.40$ eV), (14, 14) ($E_b = -0.61$ eV), (7, 0) ($E_b = -0.36$ eV), (12, 0) ($E_b = -0.02$ eV), and (25, 0) SWCNTs ($E_b = -0.59$ eV). Charge density maps of exohedral CH_4 and COOH physisorption to (25, 0) SWCNT walls are displayed in Figure 4. Similar to endohedral interaction, OH , SH and NH_3 do not adsorb exohedrally to SWCNT walls ($\Delta E > 0$). In the equilibrium close-packed array, SWCNTs of diameter d_t are separated by an approximate distance $d \simeq d_t + 0.35$ nm. In the exohedral space in-between the nanotubes, the largest distance to any SWCNT wall is $d/\sqrt{3} - d_t/2$. The exohedral inter-tube space is sufficiently large for small molecules, whereas it is too small for large molecules. The wall-molecule repulsion explains the unfavorable binding of very large molecules. The computed tube-tube separation distances with (without) van der Waals correction are (in Å): 3.10 (3.46) for (4,4); 3.52 (3.75) for (7,7); 3.11 (3.53) for (14,14); 3.41 (3.47) for (7,0); 3.46 (3.53) for (12,0); 3.42 (3.55) for (25,0).

Finally, chemisorption of COOH , NH_3 , OH and SH functional groups at the edge of a H-capped (7,0) SWCNT fragment was studied (cf. Figure 5). The computed bond distances between the functional groups and the non-hydrogen terminated, dangling C atom at the edge of the (7,0) SWCNT are: $d_{\text{C-COOH}} = 1.49$ Å, $d_{\text{C-SH}} = 1.76$ Å, $d_{\text{C-OH}} = 1.36$ Å, $d_{\text{C-NH}_3} = 1.48$ Å. The functional groups are covalently binding the SWCNT edge, with computed binding energies of -3.88 eV for COOH , -0.67 eV for NH_3 , -4.07 eV for OH and

Figure 4: Cross-sectional charge density maps of exohedrally-confined CH_4 (left) and COOH (right) molecules interacting with the walls of (25, 0) SWCNTs (top) and corresponding equilibrium structures with their charge density (isosurface corresponding to $0.16 \text{ e}/\text{\AA}^3$) (bottom) calculated at the DFT-D/PBE level of theory. Maps boundaries correspond to the limits of the periodic cells used.

-3.01 eV for SH . The smaller binding energy for NH_3 stems in part from the repulsion between H atoms of NH_3 and adjacent H atoms terminating the SWCNTs.

Since functionalization of SWCNT edges is energetically more favorable than endohedral and exohedral addend adsorption, predicting the chemical reactivity of functionalized SWCNT fragments, such as in Figure 5, can be of particular interest. This can be achieved by invoking Pearson's hard/soft acid-base (HSAB) principle (26) in a local sense, in combination with a graphical representation of Fukui functions to identify preferential sites for nucleophilic, electrophilic and radical attacks. The Fukui function (24, 25) is defined for nucleophilic attack as,

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}), \quad (6)$$

where $\rho(\vec{r})$ is the electron density at a point $\vec{r}$ in space, and N and $N + 1$ correspond the number of electrons of the neutral molecule and its anion (i.e. with an electron added to the lowest-unoccupied molecular orbital (LUMO) of the neutral molecule). For electrophilic attack, the Fukui function is expressed as,

$$f^-(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}), \quad (7)$$

where $N - 1$ is the number of electrons of the cation (i.e. with an electron removed from the highest-occupied molecular orbital (HOMO) of the neutral molecule). The Fukui function for radical attack is given by:

$$f^0(\vec{r}) = (1/2) [f^+(\vec{r}) + f^-(\vec{r})]. \quad (8)$$

As shown in Figure 5, chemisorption of the SH moiety at the SWCNT edge does not impact significantly

Figure 5: Optimized structures showing covalent bonding between COOH, NH₃, OH and SH functional groups and the edge of a H-capped (7,0) SWCNT fragment calculated at the DFT/PBE level of theory. The Fukui functions for electrophilic (f^-), nucleophilic (f^+), and radical (f^0) attacks are represented by the blue, green and pink isosurfaces, respectively. Color legend: C, brown; H, white; N, purple; O, red; S, yellow.

the reactivity of H-capped SWCNT fragments with respect to the three types of attacks: chemically softer regions are present at the H-decorated edges (large Fukui function), while a chemically harder region exists between both edges (small Fukui function). For COOH-, NH₃- and OH-functionalized SWCNT fragments, larger Fukui functions are predicted at the chemisorbed edge for radical attacks, while more complex regioselectivity is suggested for nucleophilic and electrophilic attacks. Indeed, for the latter two types of attacks, the functionalized edge tends to become chemically harder, except for electrophilic attacks with NH₃ chemisorption where a softer chemical character is induced on the adjacent side.

4. Conclusions

In summary, interactions between CH₄, COOH, NH₃, OH, SH and (n, n) ($n = 4, 7, 14$) and ($n, 0$) ($n = 7, 12, 25$) SWCNTs have been investigated using DFT-D2 dispersion-corrected density functional theory. Despite the use of C_6/r^6 pairwise London-dispersion corrections, only endohedrally-confined CH₄ molecules can weakly physisorb to the walls of the largest (7, 7), (12, 0), (14, 14) and (25, 0) SWCNTs. Minor differences are observed for the interaction between guest molecules and nanotubes with distinct chirality. Results also show that a confinement effect appears when the distance separating the confined molecule from the

SWCNT walls is less than the sum of their respective van der Waals radii. Regarding exohedral interaction, CH₄ and COOH are the only species that can physisorb to SWCNT walls. Chemisorption of COOH, NH₃, OH and SH at SWCNT edge sites of a H-capped (7, 0) SWCNT fragment was found to be energetically more favorable than endohedral or exohedral interaction with SWCNTs. The chemical reactivity of this functionalized system was investigated based on Fukui functions and Pearson's hard/soft acid-base principle. Chemisorption of the SH moiety at the SWCNT edge does not modify the reactivity of H-capped SWCNT fragments with respect to electrophilic, nucleophilic and radical attacks: chemically softer regions are located at H-decorated edges, while a chemically harder region exists between both edges. For COOH-, NH₃- and OH-functionalized SWCNT fragments, chemically softer regions are predicted at the chemisorbed edge for radical attacks, while more complex regioselectivity is suggested for nucleophilic and electrophilic attacks.

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Graphical abstract