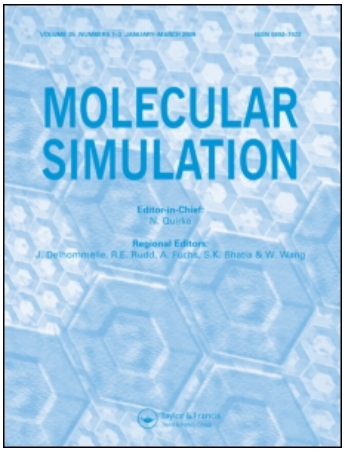

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Movement of hydrogen molecules in pristine, hydrogenated and nitrogen-doped single-walled carbon nanotubes

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Carbon nanotubes (CNT) are considered promising nano-scale materials because of their unique structural, mechanical and electronic properties. Due to their long seamless cylindrical shaped structures they could be applied as effective nano-channels for mass transfer and relevant storages for hydrogen molecules. We study hydrogen transport mechanisms in CNTs for various chiral indices and different peculiarities, using the molecular dynamics simulation and quantum mechanical approach. Various CNT models such as pristine, hydrogenated and doped by nitrogen atoms of zigzag (10,0), chiral (7,5) and armchair (6,6) types with hydrogen molecules diffusing inside are simulated at 300 K. The behaviour of hydrogen molecules inside CNTs is analysed using mean-square displacements and velocity autocorrelation functions. From the quantum mechanical approach, the electronic density distribution of CNT is calculated to verify the smooth characteristics of inner surfaces of nanotubes.

Keywords: carbon nanotube; self-diffusion coefficient of hydrogen molecules; velocity autocorrelation function; molecular dynamics simulation; density functional theory

Nomenclature

α	diffusion exponent
D	diffusion coefficient (cm^2/s)
H_2	hydrogen molecule
MSD	mean-square displacement (Å/ps)
VAF	velocity autocorrelation function
$R_i(t)$	position of molecule
t	time (ps)
$\mathbf{v}_i(t)$	velocity of molecule

1. Introduction

Since the great challenge taken by Iijima [1], research from various fields has been conducted into the properties and applications of the carbon nanotubes (CNT). CNTs are now drawing attention from industrial areas, due to their unique peculiarities in mechanical, thermal and electronic aspects.

Among the many distinctive characteristics of CNTs, the very long shape, similar to that of bamboo, with uniform diameter and hollow inner space, could be used for mass or energy transport without additive devices in a nano-scale system, analogous to pipes in a macro-scale system. Because, of the smooth surface inside CNTs there is, especially, the possibility of many applications for efficient channels of fluid delivery in membranes, micro- and nano-pipes and sensors [2–10].

Tuzun et al. [11] simulated the behaviour of fluid in a confined space, such as argon and helium flowing in CNTs, and concluded that the structural movement of CNTs is one important factor affecting the mechanisms of fluid flows in CNTs. It was ascertained by Skoulidas et al. [12] and Ackerman et al. [13] that fluid flows in CNTs become much faster than those in conventional porous materials. Comparing armchair (10,10) and (6,6) CNTs, ZSM-12 and Silicalite types, they proposed that the reason for the higher flow rates in CNTs is that the inner surfaces of CNTs are extremely smooth. This proposal has been proved by indirect experiments on CNTs [14]. For gases or liquids, the smoothness of carbon nanotubes can be one of the very important factors for efficient transportation [15].

For movements of methane and ethane in CNTs, if the diameters of CNTs become smaller, the molecules collide more frequently with the inside walls of CNTs. Being more interactive between CNTs and the fluid molecules, kinetic energies in the fluid can be transformed into those of vibrational and rotational motions and the fluid molecules do a 'wagging' motion [16]. That is, the external energy taken by the fluid molecules from the surroundings is transformed into the internal energy by the interaction between the fluid and CNTs. It is still not clear if the

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smooth inner surface of CNTs is the only reason of the high flow velocity and the wagging motion of fluid in CNTs. Therefore, the present study focuses not only on the structural feature of CNTs but also on the actual behaviour of fluid molecules in CNTs in order to clarify the interactive mechanisms between the fluid and CNTs.

Supple et al. [17] showed that decane molecules move ballistically in armchair (13,13) CNTs. Bhide et al. [18] indicated that the molecular motion in armchair (9,9) CNTs seems to be ballistic in early simulation time (less than 1–2 ps) and that it becomes super-diffusive after the initial period. This is due to the fact that the frictional force inside CNTs is almost diminished after an early simulation time because of the uniform pore diameter and smooth surface. The transition to super-diffusion could not be explained only by the geometrical characteristics of CNTs, since the dynamics of the molecules could be affected by the interaction with carbon atoms of CNTs.

As another factor influencing the molecular movement in CNTs, Lee and Sinnott [10] pointed out the diameter of CNTs. They argued that if the diameters of CNTs decrease, molecular flows in CNTs experience anomalous transport phases of the ballistic or super-diffusive motion, while molecular transports become normal-mode diffusion if the diameters increase. The reason for this transition is that larger diameter CNTs reach near-steady-state conditions more quickly than smaller ones do. The anomalous transport in smaller CNTs implies that the system is still in transition mode and the molecules in the system move ballistically. This could explain why self-diffusion coefficients are generally large in CNTs in many applications [19,21,22].

High diffusion in small diameter CNTs can be influenced in other aspects of thermal fluctuation. Real CNTs fluctuate thermally, being influenced by interactions with carbon atoms and sorbates in CNTs. In low density flows this fluctuation might enhance ballistic motions of sorbates, while it would rather reduce their ballistic motions for much higher density flows. These cannot be understood by theoretical models for CNTs assuming a perfect smooth surface [19,20]. Furthermore, the chiral index of CNT might not have considerable effects on the self-diffusion coefficients of fluids in CNTs [12,23], compared to the major factors discussed previously.

The goal of this work is to investigate the influence of various CNT types (zigzag, chiral and armchair) and states (pristine, hydrogenated and nitrogen-doped) on the behaviour of molecules in CNTs, especially hydrogen molecules. Their movements are analysed using mean-square displacements (MSDs) and velocity autocorrelation functions (VAFs) to determine the diffusive characteristics in CNTs. From the quantum mechanical approach, the electronic density distributions of CNTs are calculated to verify the inner surface characteristics of inner surfaces of nanotubes. Since CNTs are still promising efficient storage systems for hydrogen molecules, transport properties for hydrogen in CNTs are still required for the optimal design of the storage system. The transport of low density fluids in nano-channels is one of essential functions for the bio/nano-mechanical engineering as well.

2. Theory and models

2.1 Theoretical models for diffusion

When a molecule diffuses, generally its path length is proportional to time. Therefore, if time goes to infinite, the MSD of that molecule usually grows linearly in time, as described by the Fickian diffusion. The MSD is a measure of the average distance, defined as,

$$\left\langle \sigma_i^2(t) \right\rangle = \left\langle (r_i(t) - r_i(0))^2 \right\rangle, \tag{1}$$

where $r_i(t) - r_i(0)$ is the distance travelled by molecule i over time interval t. The slope of the MSD is related to the self-diffusion constant, D, given by

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \sum_{i=1}^{N} \left\langle (r_i(t) - r_i(0))^2 \right\rangle, \tag{2}$$

where N is the number of diffusing molecules and the summation on the right-hand side is for the MSDs of all diffusing particles. It is crucial that Equation (2) is reasonable only when the motion of the diffusing particle follows a random path. In other words, the moving path of a molecule is not related to its route at previous time.

In specific situations, however, where some spatial or temporal factors can have a critical effect on the behaviour of molecules, the molecules do not follow the Fickian diffusion process. In general, diffusion of molecules can be depicted by the relation between MSD and time, given as

$$\left\langle \sigma^2(t) \right\rangle \sim D t^{\alpha}. \tag{3}$$

The exponents α in Equation (3) have different values depending on the types of the transport mechanisms: $\alpha = 0.5$ for single-file motion, $0.5 < \alpha < 1$ for sub-diffusion (known as inhibited diffusion), $\alpha = 1$ for the Fickian diffusion (normal-mode diffusion), $1 < \alpha < 2$ for super-diffusion (known as accelerated diffusion), and finally $\alpha \geq 2$ for ballistic motion [24–28].

The sub-diffusion shows that diffusing molecules undergo anomalously long waiting times between successive walks, while the super-diffusion indicates that the molecules take anomalously long random walks [28].

The VAF is a time dependent correlation function, revealing the underlying nature that is the sequence of correlated collisions of the dynamical processes operating

on a molecular system, defined as

$$F_{\mathrm{VAF}} = \frac{1}{N}\sum_{i=1}^{N}(\mathbf{v}_i(t_0)\cdot\mathbf{v}_i(t_0+\Delta t)), \tag{4}$$

where $\mathbf{v}_i(t)$ is the velocity of diffusing molecule i. Using the VAF, the self-diffusion coefficient is correlated as

$$D = \frac{1}{3}\int_0^{\infty}\langle\mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle\,\mathrm{d}t. \tag{5}$$

This equation is an example of the Green–Kubo formalisms for calculating transport coefficients from time correlation functions measured on an equilibrium system [29–32].

2.2 Simulation models

Structurally, CNTs can be modelled by rolling up a graphene sheet into a seamless cylinder with a constant radius [33] and can be characterised by considering a lattice point as the origin in a graphene sheet. Then, any other lattice point can be reached by using the lattice vector of the two-dimensional graphene sheet, i.e. the Bravais lattice [34].

Using a pair of integers (n, m) for definition of the carbon nanotube, the lattice vector is represented as $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ where $\mathbf{a}_1$ and $\mathbf{a}_2$ are two unit-cell basis vectors. The vector $\mathbf{C}_h$ is referred to as the chiral vector and the pair of integers (n, m) are referred to as chiral indices. If the sheet is rolled by chiral angle θ, $\mathbf{a}$ (n, m) tube is specified. If the chiral angle corresponds to $\theta = 0$, a zigzag tube is generated and its chiral index is (n, 0). When the chiral angle corresponds to $\theta = \pi/6$, it makes the armchair tube and its chiral index is (n, n). If a tube has any other value of θ between these two limits, i.e. $0 < \theta < \pi/6$, it is referred to as the chiral tube and its chiral index is (n, m).

In this study, the behaviour of molecules in CNTs influenced by chemical adjustment is investigated using molecular models with different peculiarities: pristine, adsorbed hydrogen (chemisorption) and doped by nitrogen. If hydrogen atoms are adsorbed on the CNT wall or some other elements are doped to CNTs, their properties are significantly varied, compared to pure CNTs [35–41], especially for reactivity. The interaction among molecules in CNTs is also changed according to the degree of chemical adjustments and thus molecular behaviour can be differed accordingly.

For hydrogenated CNTs, hydrogen atoms are adsorbed to carbon atoms on the outside of CNTs as in the case of chemisorption [37] and for nitrogen-doped CNTs, the doping density of nitrogen is set to 10% [41]. The numbers of hydrogen molecules diffusing in a CNT are five and twenty for current simulations. Figure 1 shows the molecular models for pristine armchair (6,6), hydrogenated chiral (7,5) and nitrogen-doped zigzag (10,0) CNTs, whose diameters are around 8 Å and lengths are around 45 Å, as given in Table 1.

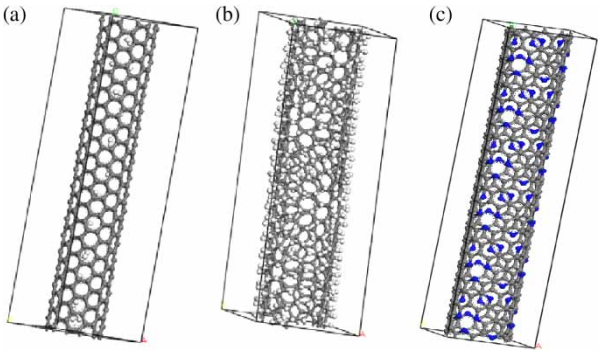

Figure 1. Simulation models for (a) pristine armchair (6,6), (b) hydrogenated chiral (7,5), and (c) nitrogen-doped zigzag (10,0) CNT.

For the simulations, we set up the models for three types of flexible CNTs: zigzag (10,0), armchair (6,6) and chiral (7,5) by the MS Visualizer and MS Amorphous Cell [42] with the periodic boundary condition in each direction. Here, the chiral indices of CNTs are carefully selected to avoid the influence from the difference in diameters of each CNT type and thus CNT in present simulation models has almost the same diameter around 8 Å.

Before the main simulation starts, the first minimisation process is carried out to attain the initial equilibrium state, until maximum derivatives of conjugate gradients reach the value of 1.0×10^{-5} kcal/(mol × Å). After the first minimisation process, each system undergoes the equilibration process at 300 K during 500 ps with time step of 1 fs. Finally, self-diffusion coefficients of hydrogen molecules in CNTs at 300 K are calculated during 500 ps dynamic times with a time step of 1 fs using the molecular dynamics simulation tool.

The COMPASS force field [43] has been used for all simulations and the system temperature is controlled by the Nose–Hoover method [44–47] under the NVT ensemble condition. The summation method of non-bonded interactions is the atom based method with 15.5 Å cutoff distance.

In order to understand the electron structure of pristine, hydrogenated and nitrogen-doped CNTs, we calculate the electron density distribution of CNTs in each system by

Table 1. The geometry of carbon nanotubes for current simulations.

Type	Chiral index	Diameter [Å]	Length [Å]
Zigzag	(10,0)	7.83	46.86
Armchair	(6,6)	8.14	46.73
Chiral	(7,5)	8.17	44.48

density functional theory (DFT) with the generalised gradient approximation (GGA) using the plane-wave pseudo potential CASTEP code [42]. The revised Perdew–Burke–Ernzerh (RPBE) functional proposed by Hammer et al. [48] has been applied for the exchange-correlation potential. The ultrasoft pseudopotential proposed by Vanderbilt [49] is employed in the calculation, and the energy cutoff for plane-wave basis is set to be 300 eV. The software used here is the Amorphous Cell program and the Discover molecular modelling system in Materials Studio® [42].

It is possible to simulate the molecular behaviour in most systems by using molecular dynamics simulation tools. Where electron contributions are significant, however, the consequences of simulation are not understood readily. In such case, the combination of classical molecular dynamics and DFT calculation will be excellent for predicting such a system because both methods complement each other.

3. Results and discussion

Hydrogen molecules in CNTs move along the hollow inner space and experience the major intrinsic characteristics of CNTs. Here, we calculated the electron density distribution of CNTs by DFT to explore the precise inner space of CNTs.

Figure 2 shows the distribution of 20 hydrogen molecules in a chiral (7,5) CNT whose size is given in Table 1. Dotted lines imply the position of carbon atoms on the CNT, dashed ones represent the boundary of electron clouds of the CNT. The distance from carbon atoms to the edge of electron clouds in the chiral (7,5) CNT is approximately 0.83 Å. The solid line indicates the distribution of hydrogen molecules at equilibrium. Because

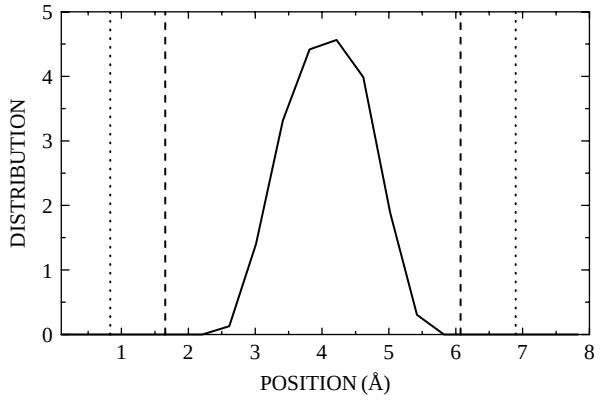

Figure 2. Distributions of hydrogen molecules in a chiral (7,5) CNT. Dotted lines describe the wall of the CNT, dashed lines represent the electronic fields of carbon atoms on the CNT, and the solid line implies the distribution of hydrogen molecules in the CNT.

of repulsive forces, hydrogen molecules are keeping a certain distance from carbon atoms and thus they have to stay in the central region of carbon atoms in the CNT. On the contrary, Skoulidas et al. [22] indicated that CO_2 molecules in CNTs can move near the CNT wall and this is due to the fact that CO_2 molecules and carbon atoms of the CNT interact with weak attraction owing to the partial double-bond of carbon atoms. This situation can explain the transport of H_2O molecules [21] as well. However, hydrogen molecules do not have this polarity and can move along the central region of CNTs, as shown in Figure 2.

This can be viewed clearly through the electron density of CNTs calculated by the DFT. In Figure 3, carbon atoms in CNTs are arranged regularly and thus the electron density distribution has a strong regularity and CNTs have an extremely smooth inner surface due to the uniform electron density distribution, as expected.

If foreign elements are adsorbed or doped to CNTs, the interaction between hydrogen molecules and carbon atoms in CNTs can vary from that for pristine CNTs. As shown in Figure 4, if hydrogen atoms are adsorbed to CNTs, electron clouds would be shifted to the outside of CNTs caused by adsorbed hydrogen, and then the inner volume could be enlarged slightly. In addition, the roughness of inner surface will increase and this explains the rugged inner surface of hydrogenated CNTs.

If nitrogen atoms are doped to CNTs, there occurs a kind of large hole on the CNT wall due to the strong bond between nitrogen and carbon atoms. This implies an irregular electron density distribution inside CNTs. Namely, the strong gradient of energy level occurs in the energy surface inside of CNTs and has a significant effect on the molecular transport in the CNTs.

As already discussed, the behaviour of fluids in CNTs differs from that of bulk fluid, since CNTs are confined systems with nearly the same diameter along the tube axis. To understand the specific movement of hydrogen molecules in CNTs, we analysed the MSDs of hydrogen molecules.

Generally, the MSD of bulk hydrogen molecules is clearly linear with time, following Fick's law. The MSD of hydrogen molecules in CNTs, however, is non-linear with time, as discovered by Mukherjee et al. [50]. It would be helpful to utilise the relationship between the MSD and time, Equation (3), in order to understand the non-linear behaviour. As shown in Figure 5, the slope of MSD of hydrogen molecules in CNTs is steeper than that for pure hydrogen molecules. The value of diffusion exponent α for pure hydrogen molecules shows 0.95 which means the normal-diffusion (Figure 5(a)). The α of hydrogen molecules in (6,6) CNTs ranges from 1.07 to 1.44, implying the accelerated diffusion. It tells us that the hydrogen molecules in CNTs move more actively than the pure ones.

Table 2 shows that the exponents α are greater than one and that hydrogen molecules in CNTs undergo

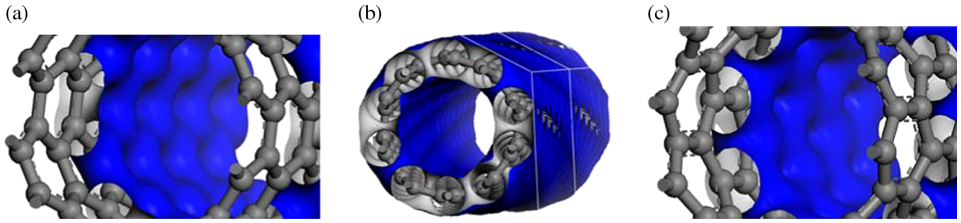

Figure 3. Electron density distributions of (a) armchair, (b) chiral, and (c) zigzag CNTs calculated by DFT.

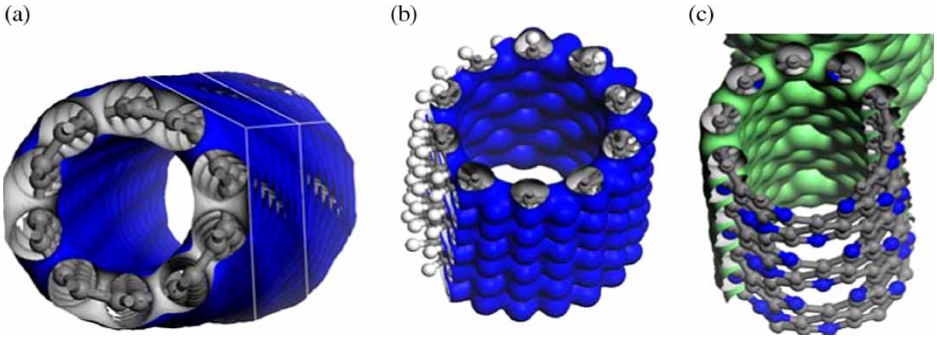

Figure 4. Electron density distributions of (a) pristine (7,5), (b) hydrogenated (6,6), and (c) nitrogen-doped (10,0) CNT models calculated by DFT.

the super-diffusion process in general, as already discussed by Lee et al. [24] who note that hydrogen molecules in CNTs undergo the anomalous transport.

The values of α for hydrogenated CNTs are close to those of pristine CNTs for some types of CNTs denoted in Table 2. Thermal fluctuation of hydrogenated CNTs enhanced by the rugged electron structure as shown in Figure 4(b) causes the 'bouncing' motion of molecules in the radial direction [10, 24], while the inner volumes of the hydrogenated CNTs for molecular diffusion are enlarged slightly due to outward shifts of electrons. As a result, these two effects cancel each other and thus the overall diffusion in hydrogenated CNTs is close to that in pristine CNTs.

In the case of nitrogen-doped CNTs, α is close to one, which implies the normal-mode diffusion, as expected from the electron structure shown in Figure 4(c). The gradient of potential energy in nitrogen-doped CNTs results in irregular inner surface structures and interrupts the movement of hydrogen molecules. The molecular behaviour becomes less super-diffusive than in the pristine CNT.

To clarify current findings, we compare the VAFs of the CNT models. As shown in Figure 6, the magnitude of VAF oscillation in nitrogen-doped CNTs is smaller than those for other CNT models. This explains why the flow is less super-diffusive and slightly restricted in nitrogen-doped CNT. Figure 7 shows that the VAF

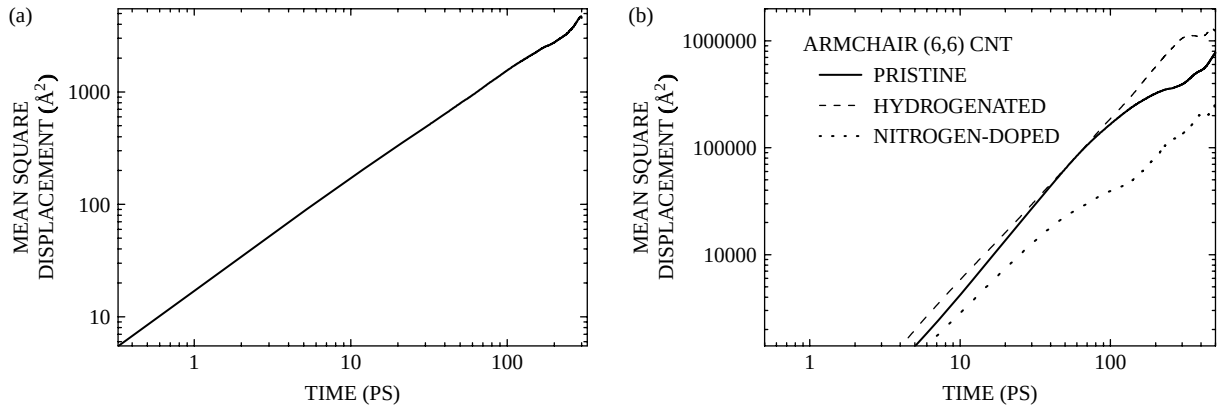

Figure 5. The MSDs of (a) bulk hydrogen molecules and (b) hydrogen molecules in armchair (6,6) CNTs.

Table 2. Values of diffusion exponent α in Equation (3) estimated from the MSDs of hydrogen molecules in various types CNTs.

	Number of H_2 molecules					
	Pristine		Hydrogenated		Nitrogen-doped	
Type	5	20	5	20	5	20
(10,0)	1.39	1.29	1.35	1.3	1.23	1.02
(6,6)	1.4	1.24	1.44	1.3	1.13	1.07
(7,5)	1.6	1.16	1.48	1.22	1.13	1.1

oscillation becomes strong for low density hydrogen flow in CNTs compared to that for higher density flow. This implies that the interaction between the fluid and the wall

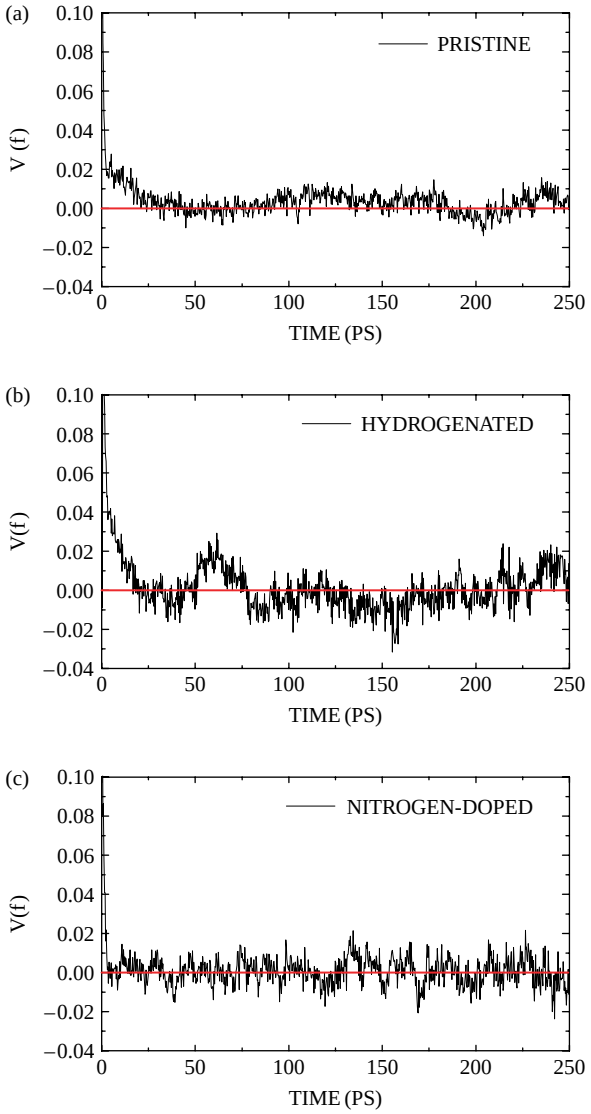

Figure 6. VAF of hydrogen molecules in (a) pristine, (b) hydrogenated, and (c) nitrogen-doped zigzag (10,0) CNT.

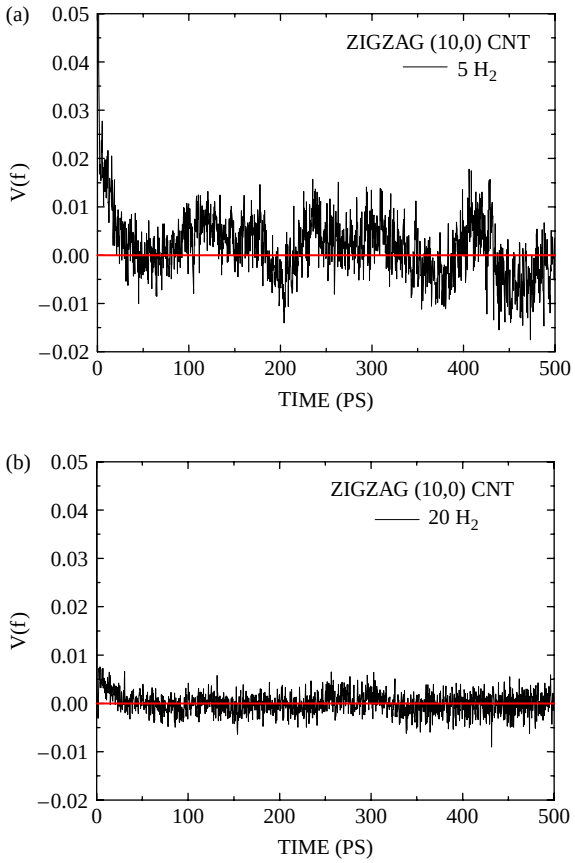

Figure 7. VAF of (a) five hydrogen molecules and (b) 20 hydrogen molecules in zigzag (10,0) CNTs.

of CNTs is dominant rather than the interaction between fluid and fluid [51, 52]. On the other hand, a large oscillation in the VAF indicates that hydrogen molecules in CNTs undergo very high confinement process [53]. Jun et al. [54] found that the VAF parallel to the wall shows negative exponential decay trends, but the VAF perpendicular to the wall oscillates considerably in a confined system. In this simulation, the VAF perpendicular to the wall is dominant for low density flows and the VAF parallel to the wall becomes significant in high density flows or flows in nitrogen-doped CNTs.

Finally, the self-diffusion coefficients of hydrogen molecules in CNTs are estimated and compared in Figure 8. Nitrogen-doped CNTs have relatively low diffusivities compared to other types of CNT as expected from the magnitude of the exponent α in Table 2. For low density flows the diffusion coefficients are much larger than those for higher density flow regardless of CNT models. The chiral indices of CNT have minor influences on self-diffusion coefficients as far as the radii of the CNTs are close to each other, which has not been shown here. Skoulidas et al. [12] reported that the self diffusion coefficients of hydrogen molecules in (10,10) CNTs show

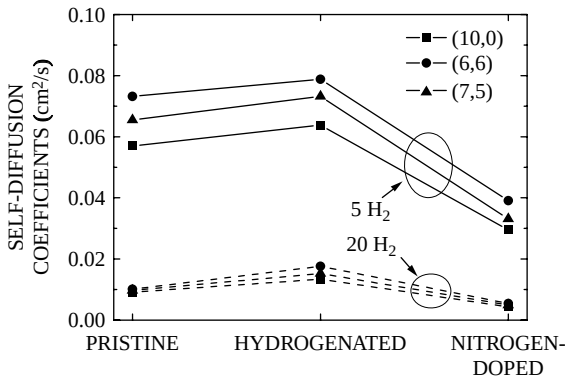

Figure 8. Self-diffusion coefficients of hydrogen molecules under various models of CNTs.

the order of 10^{-2} cm^2/s, which agrees well with our results in Figure 8.

4. Conclusions

We theoretically designed the models for three types of flexible CNTs – zigzag (10,0), armchair (6,6), chiral (7,5) – and models for pristine, hydrogenated and nitrogen-doped CNTs to study the influence of CNT types and electronic states on the behaviour of hydrogen molecules in the CNTs.

We calculated self-diffusion coefficients of hydrogen molecules in CNTs using molecular dynamics simulations. To verify electron structures of each CNT, we calculated the electron density distribution of the CNT by DFT.

For the distribution of hydrogen molecules in CNTs, hydrogen molecules keep a certain distance to carbon atoms. Therefore, most hydrogen molecules flow in the central region of electronic fields of carbon atoms.

The non-linear feature of the MSD of hydrogen molecules in CNTs implies that hydrogen molecules undergo the anomalous diffusion process, which can be clarified by the exponent α for diffusion correlation, the relationship between the MSD and time. The exponents for hydrogenated CNTs are close to those for pristine CNTs and significantly larger than those for nitrogen-doped CNTs. For nitrogen-doped CNTs α is close to one, indicating that the hydrogen molecules diffuse in normal-mode.

The diffusion coefficients are much larger for low density flow than those for higher density flow regardless of CNT models. The chiral index of CNT does not have a strong influence on self-diffusion coefficients and nitrogen-doped CNT has relatively low diffusivities compared to other types of CNT as expected from the magnitude of exponent α.

It is clear that the transport characteristics inside CNTs would be changed if the chemical nature of carbon nanotubes were modified. This can be utilised to control transport properties inside CNTs for effective engineering designs.

Acknowledgements

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