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Diffusion of single alkane molecule in carbon nanotube studied by molecular dynamics simulation

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Abstract

Full atomistic molecular dynamics simulations have been used to study the diffusion of alkane molecule in single wall carbon nanotube (SWCNT), with different alkane chain lengths and nanotube diameters. In this paper, we calculated the self-diffusion coefficient, mean-square gyration and bond-orientation order parameter of alkane molecule and the average intermolecular interaction energy per segment between SWCNT and alkane. Furthermore, structure of alkane in SWCNT was characterized through the radial distribution function, with results showing that the self-diffusion coefficient is related to the nanotube diameter. The component of mean-square gyration in *z*-direction scales with alkane chain length in SWCNT(9,9) like $N^{1.07\pm0.04}$, which is in good agreement with the prediction from scaling theory for polymers. The obtained results show that nanotube diameter and alkane chain length are important factors affecting the behavior of one-dimensional confined alkanes.

Keywords: Molecular dynamics simulation; Alkane; Nanotube

1. Introduction

The behavior of confined polymers has been continuing to be a subject of considerable excitement and interest [1–10], with polymers confined on molecular length scales showing different static and dynamic properties from bulk systems. The properties of polymers adsorbed on surfaces, which are in the two-dimensional (2D) confined condition, have received much more attentions [11–24]. In these studies, it is showed that, for a certain temperature, a polymer chain changes its properties from three-dimensional (3D) direction to two-dimensional direction [25,26]. With further confinement on polymer chain, such as putting polymer chain in a nanochannel, the polymer will be in quasi one-dimension (1D). Nanochannels have been found in various solid states or biological systems [27,28]. Carbon nanotube (CNT), formed by rolling graphene planes into tubular structures, can provide structurally perfect and stable nanochannels with variable size [29], which can be incorporated in the macroscopic structure of separation devices [30–32]. Therefore, it is practical of interest to understand the diffusive behavior of molecules adsorbed on it. Previous investigations [33–43] showed that water or gas molecules, etc. could be encapsulated inside nanotubes. To the best of our knowledge, the diffusion of single polymer chain in CNT has rarely been investigated, only Wei and Srivastava [29] reported that there are two processes in the transport of polyethylene to pass through carbon nanotubes (transport from surrounding solutions into CNT and diffusion inside CNT).

In the present study, molecular dynamics (MD) simulations were carried out in order to study the diffusion of single alkane molecule in single wall carbon nanotube (SWCNT) in vacuum. This means that we tried to look into the effect of an ideal bad solvent. Relations between the alkane chain length (N), or diameter of SWCNT and the self-diffusion coefficient (D) are covered in our studies. It was found that the solvent could also affect the self-diffusion coefficient of alkane, which needs

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to be studied further in future. From the comparison of static and dynamics properties of 1D polymer in SWCNT with those of 2D confined polymer, we hope that our investigation results may enrich the understanding of the behavior of confined polymers, particularly on the diffusion of 1D polymer in the nanochannel.

2. Simulation method

There were five models 9-9-40C, 9-9-50C, 9-9-60C, 9-9-70C, and 9-9-80C, with different alkane chain lengths ($N = 40$, 50, 60, 70, 80) to be used to study the effect of N to D in our simulations. Another four models were built in order to obtain the relation between nanotube diameter and D. They are denoted as 10-10-80C, 11-11-80C, 12-12-80C and 13-13-80C. The initial model used in each simulation is an extended alkane chain in SWCNT with the periodical boundary condition, parameters of periodical box are $a = b = 30$ Å, $c = 193.99$ Å, and carbon–carbon bond length is 1.4 Å and bond angle is 120° in SWCNT [33]. The length of SWCNT c is chosen to be long enough as compared to the size of alkane to avoid edge effects. Both a and b are much longer than the maximum nanotube diameter 17.38 Å of SWCNT(13,13). This is to ensure that the alkane cannot be affected by the periodic image. In this way, the alkane chain diffuses in the 1D infinite nanochannel.

The COMPASS [44–46] force field was used in the simulation. Energy calculations with COMPASS are a combination of bonding and nonbonding terms. The bonding terms include stretching, bending, and torsion energies as well as the diagonal and off-diagonal cross-coupling terms. The van der Waals interactions were calculated with a direct cutoff $R_c = 10$ Å. There is no charge in our system, so Coulombic interactions are not calculated. The interaction between the alkane molecule and the SWCNT is controlled by the van der Waals interactions. We did some calculations on the effect of the SWCNT to the results and found that the result of system with confined SWCNT atoms is similar to that of system without confined SWCNT atoms, thus we fixed the atoms of SWCNT in their initial positions. Canonical (*NVT*) MD simulations of 1000 ps were performed for all systems. Each simulation was repeated to ensure the reliability of the results. The equations of motion were integrated with a time step of 0.5 fs. A temperature of 300 K was maintained with a Hoover thermostat [47], using a relaxation time of 0.1 ps. All the simulations were performed using *Cerius*^{2} and *Material Studio* software packages from Accelrys Inc.

3. Results and discussion

A polymer molecule adsorbed into a nanotube is energetically favorable through the energy gain due to van der Waals interactions [29]. We will only discuss the effects of alkane chain length and the nanotube diameter on the diffusion of polymer in SWCNT. Fig. 1 shows the snapshots of 9-9-80C and 12-12-80C after 1000 ps MD simulation, in which alkane molecules are adsorbed on the internal wall of SWCNT. The shape of alkane molecule is cylinder, different from that confined in 2D (“pancake”) or bulk system (coil). This result is consistent with the reports of Wei and Srivastava [29].

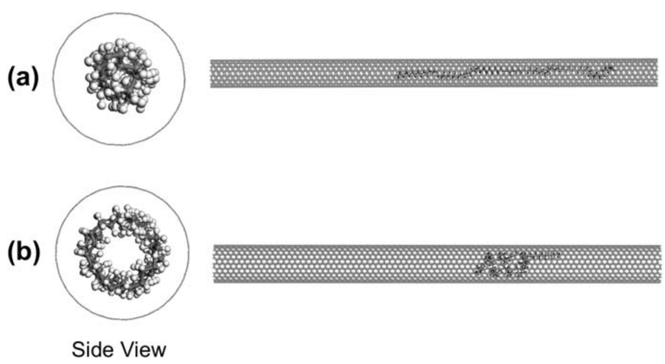

Fig. 1. The snapshots of 80C-alkane diffusion in SWCNT after 1000 ps MD simulation: (a) in SWCNT(9,9); (b) in SWCNT(12,12).

In our study the alkane molecules are all adsorbed on the internal wall of SWCNT, and diffuse along the SWCNT axis (z-direction). Therefore, the diffusion can be characterized by the self-diffusion coefficient of alkane molecules along SWCNT axis ($D_\|$), which can be extracted from the slope of mean-square displacement (MSD) averaged over the trajectories of the individual atoms. The calculation function is as follows:

$$D_\| = \lim_{t\to\infty} \frac{1}{2t}\left\langle \left| r_\|(t+t_0) - r_\|(t_0) \right|^2 \right\rangle, \tag{1}$$

where $r_\|(t)$ is the coordinate of the atoms of alkane molecules along the SWCNT axis. The calculated $(D_\|)$ is shown in Table 1. $(D_\|)$ of alkane molecules with different N in SWCNT(9,9) is close to each other, ranging from 6 to 10 Å^2/ps. This is different from the 2D confined polymers, whose self-diffusion coefficient was found to obey Rouse dynamics, $D \sim N^{-1}$ [14–16], or Reptation model, $D \sim N^{-3/2}$ [11–13,19]. With nanotube diameter increasing, $(D_\|)$ of 80C-alkane increases. The $(D_\|)$ of 80C-alkane in SWCNT(10,10) is a little smaller than that determined by Wei and Srivastava [29].

The sizes of alkane molecule and nanochannel are comparable, therefore, the interaction between them could play a significant role in the dynamics of such kind of systems. The average intermolecular interaction energy per segment E_{int} is calculated by $E_{\text{int}} = [E_{\text{tot}} - (E_{\text{polymer}} + E_{\text{CNT}})]/N$, where E_{polymer} is the potential energy of the adsorbed alkane molecule on SWCNT, E_{CNT} the potential energy of SWCNT, E_{tot} the potential energy of alkane molecules and SWCNT after adsorption. The calculated E_{int} is shown in Table 1. As E_{int} increases, the interaction between alkane and SWCNT decreases. An identical nanotube diameter will help to stabilize E_{int} of different alkanes in SWCNT(9,9), with variations of about 3.35 Kcal/mol per segment. When the alkane chain length N is same (80C), E_{int} of 80C-alkane decreases as nanotube diameter increases. This is consistent with the result of hydrogen adsorption in SWCNT obtained by Cheng et al. [48].

The dimension of alkane molecules may be helpful to describe the diffusion behavior, so we also did calculation

Table 1
Summary of simulation results for nanotube diameter, alkane molecule dimension, average intermolecular interaction energy per segment E_{int}, bond-orientation order parameter along z-direction $P(\theta)$ and self-diffusion coefficient along z-direction $\langle D_{\parallel} \rangle$ for the nine studied systems[a]

System	Diameter (Å)	R_g (Å)			E_{int} (Kcal/mol)	$P(\theta)$	$D_{\parallel}$ (Å^2/ps)
		R_{gx}	R_{gy}	R_{gz}			
9-9-40C	12.03	1.03	1.05	12.69	−3.40	0.81	9.96
9-9-50C	12.03	1.00	1.02	16.98	−3.32	0.84	8.90
9-9-60C	12.03	1.05	1.06	19.91	−3.31	0.82	6.18
9-9-70C	12.03	1.10	1.09	23.53	−3.35	0.83	6.77
9-9-80C	12.03	1.11	1.12	26.97	−3.31	0.82	7.82
10-10-80C	13.37	1.64	1.59	25.60	−2.76	0.80	9.69
11-11-80C	14.71	1.61	1.62	24.74	−2.46	0.74	10.09
12-12-80C	16.04	2.63	2.62	8.87	−2.29	0.53	12.78
13-13-80C	17.38	2.94	2.88	8.22	−2.22	0.54	13.76

[a] These data are calculated from the trajectories 201–1000 ps.

on the three components of mean-square gyration radius R_{gx}, R_{gy}, and R_{gz} of alkane molecule (Table 1). R_{gx} and R_{gy} are different for alkane in different SWCNTs while R_{gx} almost equals R_{gy} for each system. R_{gz} shows the trend of increasing when N increases for alkane molecule in SWCNT(9,9), and the trend of decreasing when the diameter of SWCNT increases.

The radius of gyration of one coil depends on the degree of polymerization. From Flory we have

$$R_g = (\text{constant})aN^{\nu}, \tag{2}$$

where ν is close to 3/5 for bulk polymers, 3/4 for 2D confined polymers, and 1 for 1D confined polymers [1]. Our systems are confined in 1D, which means that the dimension of alkane molecule can be characterized by R_{gz}. Fig. 2 shows a log–log plot of R_{gz} for alkane in SWCNT(9,9) as a function of N. The straight line is the least-square linear fit for different N, with scaling exponent ν is 1.07 ± 0.04. This is in good agreement with the prediction from the scaling theory for polymers [1]. Increase of N only leads to increase of R_{gz}. Combining Fig. 2 with Fig. 1, shows that the alkane molecule is in an extended configuration as compared to the case in a free space or in a 2D confinement. This may be the reason why $\langle D_{\parallel} \rangle$ of systems with different alkanes in SWCNT(9,9) changes a little. As nanotube diameter increases, 80C-alkane molecules change from long and thin cylinder structure to short and thick cylinder structure.

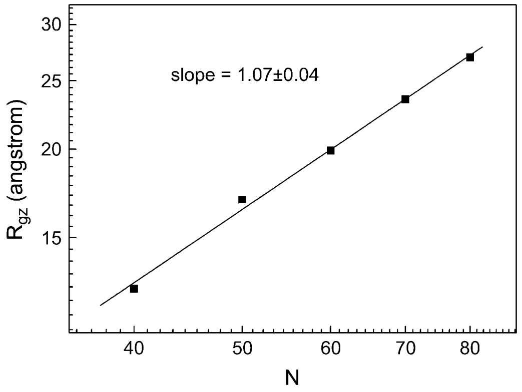

Fig. 2. Log–log plot of R_{gz} of alkane molecules in SWCNT(9,9) as a function of chain length N.

The configuration of alkanes can also be monitored by the bond-orientation order parameter along z-direction $P(\theta)$, which is defined as

$$P_2(\theta) = \left\langle \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle_{\text{bond}} \right\rangle, \tag{3}$$

where θ is the angle between the sub-bond vector and the z-direction. The sub-bond vector is the vector formed by connecting centers of two adjacent carbon–carbon bonds i and $i-1$ of the backbones, $\langle \cdots \rangle_{\text{bond}}$ denotes the average over the sub-bonds in a model, and $\langle \cdots \rangle$ denotes the time average from 201 ps to 1000 ps. The calculated $P(\theta)$ is shown in Table 1. Similar to $\langle D_{\parallel} \rangle$ and E_{int}, $P(\theta)$ of different alkanes in SWCNT(9,9) is close to each other (about 0.82), which means that the alkane molecule prefers to extended structure when the molecule is in a narrow nanochannel, with its backbone parallels to the nanotube axis. Increase of nanotube diameter brings decrease of $P(\theta)$ of 80C-alkane along the z-direction. This shows the whole configuration of the alkane backbone in different confinements.

Information about the structural characteristics of alkane molecule in SWCNT can also be extracted from the radial distribution function $g(r)$. Fig. 3 represents the calculated $g(r)$ of C_{CNT}–C_{alkane} (C_{CNT} is carbonic atom belongs to SWCNT, C_{alkane} is carbonic atom belongs to alkane molecule). $g(r)$ for 9-9-40C, 9-9-50C, 9-9-60C, 9-9-70C, 9-9-80C is similar, therefore, we only show $g(r)$ for 9-9-80C, 10-10-80C, 11-11-80C, 12-12-80C, 13-13-80C. There are two peaks in the $g(r)$ of C_{CNT}–C_{alkane} for the five systems. The position of peak reflects the average position of C_{CNT} and C_{alkane}. Those two peaks show that alkane molecules are of cylindrical structure, and the distance between them reflects the cavity size of the cylinder. The first peak is located around 5 Å, while the second peak is found around 7.5 Å for 9-9-80C, 8.5 Å for 10-10-80C, 10.3 Å for 11-11-80C, 11.5 Å for 12-12-80C, 13 Å for 13-13-80C. The minimum distance between alkane molecule and SWCNT is about 5 Å deduced from the first peak. As the diameter of SWCNT increases, a shift of the second peak position in $g(r)$ toward larger distances is observed, and the distance between the two peaks increases, too. These obviously show that the alkane molecule changes from thin to thick

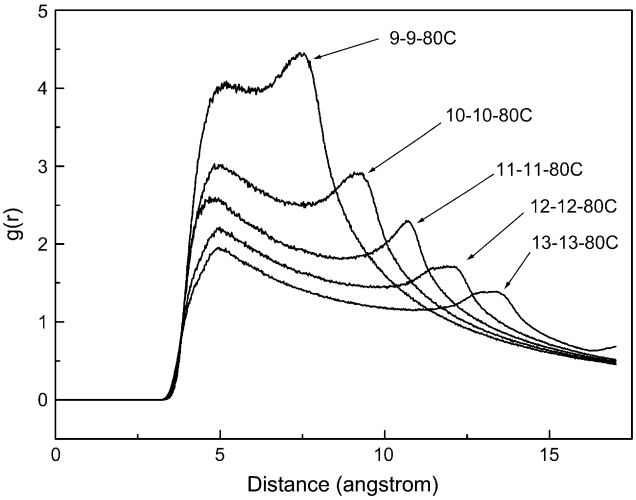

Fig. 3. Radial distribution function $g(r)$ of $C_{\mathrm{CNT}}-C_{\mathrm{alkane}}$ for 9-9-80C, 10-10-80C, 11-11-80C, 12-12-80C, and 13-13-80C.

cylinder structure as nanotube diameter increases. It also shows in Fig. 3 that the decrease of interaction energy of 80C with increasing SWCNT diameter comes from the decease of the effective interaction of C-alkane pair within van der Waals radius.

4. Conclusion

MD simulations have been performed to study the diffusion behavior of single alkane molecule in SWCNT. Nine systems are considered with different alkane chain lengths or different nanotube diameters. The self-diffusion coefficient along z-direction $(D_{\|})$ of alkanes and average intermolecular interaction energy per segment change a little as N increases, and increase as increasing nanotube diameter. The mean-square gyration, bond-orientation order parameter of alkane and the radial distribution function show that the alkane molecules change from the long and thin cylinder structure to the short and thick cylinder structure when nanotube diameter increases. Moreover, R_{gz} of alkane molecules scales with their length in SWCNT(9,9) like $N^{1.07\pm0.04}$, which is in good agreement with the prediction from the scaling theory for polymers. All these results show that the nanotube diameter and the alkane chain length affect the behaviors of one-dimensional confined alkanes.

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