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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.
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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].

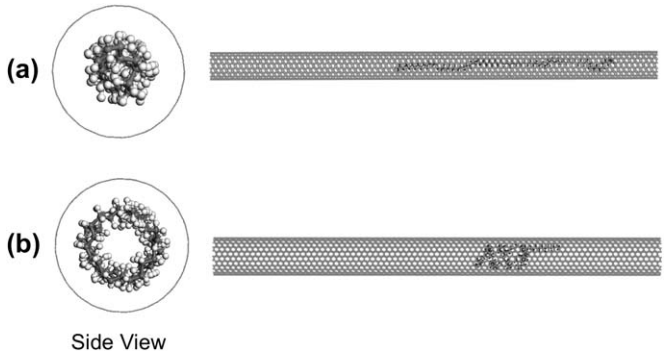

Fig. 1. The snapshots of 80C-alkane diffusion in SWCNT after 1000 ps MD simulation: (a) in SWCNT(9,9); (b) in SWCNT(12,12).

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 ($D_\parallel$), 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:

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

where $r_\parallel(t)$ is the coordinate of the atoms of alkane molecules along the SWCNT axis. The calculated $(D_\parallel)$ is shown in Table 1. $(D_\parallel)$ 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, $(D_\parallel)$ of 80C-alkane increases. The $(D_\parallel)$ 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 $E_{int} = [E_{tot} - (E_{polymer} + E_{CNT})]/N$, 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

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