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A molecular-dynamics simulation study of diffusion of a single model carbonic chain on a graphite (001) surface

Abstract Molecular-dynamics simulations have been used to study the diffusion of a short single model carbonic chain on the graphite (001) surface. The calculated diffusion coefficient (D) first increases, then decreases with increasing chain length (N). This abnormal behavior is similar to polymer lateral diffusion at the solid–liquid interface. Furthermore, we have studied the relation between the mean-square gyration radius and N.

Keywords Molecular dynamics · Surface diffusion · Graphite surface

Introduction

Diffusion of confined polymers is always fundamental, yet difficult to obtain at a surface [1–6]. This problem has already attracted attention for decades. A special case is that when the polymers are sufficiently constrained, they are almost two-dimensional (2D). Experiments and theoretical considerations show that, for a certain temperature, a polymer chain changes its properties from three-dimensional (3D) to 2D [3–6]. Recently, Granick and coworkers have studied polyethylene glycol molecules adsorbed on a solid surface by fluorescence microscopy [7–9]. They found that the diffusion coefficient (D) of such chains scales with chain length (N) like $N^{-3/2}$, which is characteristic for 2D chain models. On the other hand, Maier and Rädler found much weaker scaling, namely N^{-1}, when studying adsorbed DNA in a lipid bilayer [10, 11]. Computer simulations of the mechanism for a single polymer chain adsorbed on a surface are important, as experimental studies of the adsorption of isolated polymer chains are difficult. Many simulations have been performed for different systems with the chains (or a single chain) adsorbed on surfaces [12–16]. Milchev and Binder [12] showed that D scales with the chain length as N^{-11}, Azuma and Takayama [14] obtained $D \sim N^{-3/2}$, but Falck et al. [15]. found that D scaled as N^0. Therefore, diffusion of confined polymers on surfaces is still an interesting problem.

In this study, we focus on the diffusion behavior of a single chain on a surface. We carry out molecular dynamics (MD) simulations to study the diffusion of 2D single model carbonic chain with different lengths on a graphite (001) surface in vacuum. An accurate and common force field is used. A provocative nonmonotonic dependence of D on N is found. As the chain length increases, the concentration of carbonic chain on the surface increases. This behavior is quite similar to the concentration dependence of polymer lateral diffusion at the solid-liquid interface found by Zhao and Granick [17].

Models and simulation details

The MD simulation was carried out in a simulation box (x=24.6 Å, y=24.6 Å, z=40 Å) with periodical boundary conditions. The single model carbonic chain studied is embedded into the simulation box with a fixed graphite (001) surface. Similar to polyethylene, the carbonic atoms are connected through a single bond in the model carbonic chain. The chain lengths are 10, 14, 20, 50 and 100 and they are denoted as C10, C14, C20, C50 and C100, respectively. As an example, the initial model of C20 on the surface is shown in Fig. 1. The thickness of the graphite surface is 12 Å with four layers. z=40 Å is chosen large enough so that the interactions between the adsorbed carbonic chain and the periodic images of graphite in the top plane can be ignored. In this way the 3D-periodicity inherent in the model is transformed into an actual 2D periodicity, thus simulating an infinitely extended surface.

The COMPASS [18–20] force field was used in the simulation. Energy calculations with COMPASS are a com-

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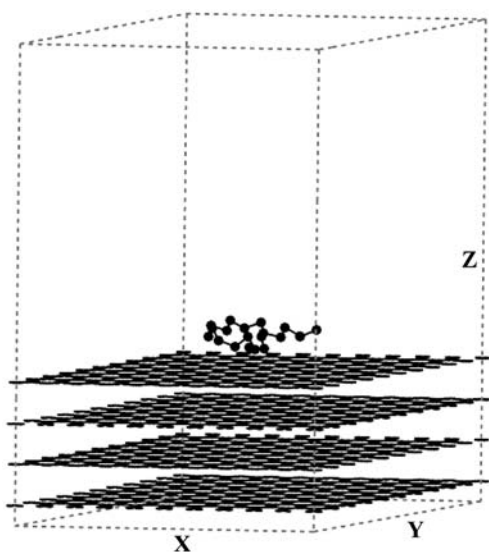e-mail: zeshengli@mail.jlu.edu.cn
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Fig. 1 The initial model of C20 on the graphite (001) surface (x=24.6 Å, y=24.6 Å, z=40 Å)
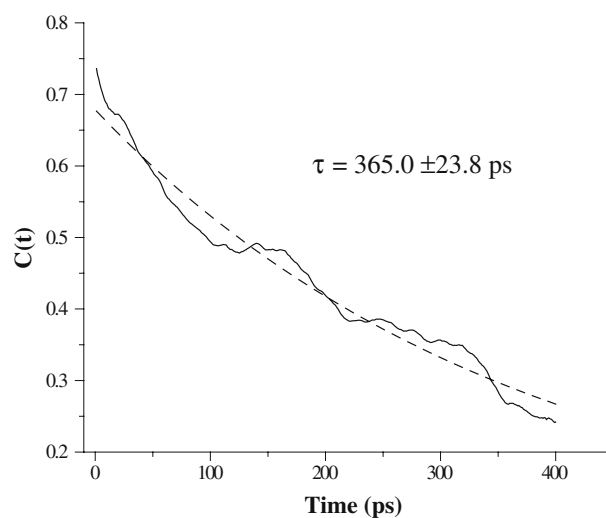

Fig. 2 Plot of the end-to-end correlation function $C(t)$ vs time t for C100. The *dashed line* indicates possible fit to a behavior $C(t) \propto (-t/\tau.)$

bination 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=20Å. Our system is not charged, therefore Coulombic interactions were not calculated throughout. The interaction between the model carbonic chain and the surface is controlled by the van der Waals interactions. Before the MD simulations, energy minimizations were performed to relax the local unfavorable structure of the chains. Subsequently, canonical MD simulations of 1,000 ps were performed. Every simulation was performed three times to ensure the reliability of the results. The equations of motion were integrated with a time step of 0.001 ps. A temperature of 300 K was maintained with a Hoover thermostat [21], using a relaxation time of 0.1 ps.

Results and discussion

We first characterize the relaxation of the chains by the relaxation times. A standard method is to consider the time–displacement correlation function of the end-to-end vector of the chain [22, 23],

$$C(t) = \langle R(0) \cdot R(t) \rangle / \langle R^2 \rangle \quad (1)$$

and since one expects $C(t) \propto \exp(-t/\tau)$ for large enough times, the relaxation time τ can be extracted from a plot of $C(t)$ vs time. We calculate the end-to-end correlation function $C(t)$ vs time t for C100, whose τ is the longest (Fig. 2), and the relaxation of C100 is the slowest one among the systems studied. The relaxation time of C100 is 365.0±23.8 ps. This indicates that our simulation time of 1,000 ps is long enough for these systems.

The self-diffusion coefficient of the adsorbed chain can be extracted from the slope of the mean-square displacement averaged over the trajectories of individual particles. The single model carbonic chain is so strongly adsorbed onto the graphite surface that the chain can only move in the xy plane. Therefore, we calculate the 2D diffusion coefficient by

$$D = \lim_{t \to \infty} \frac{d}{dt} \frac{\left\langle |r(t) - r(t)|^2 \right\rangle}{4} \quad (2)$$

where $r(t)$ denotes the particle position vector in the xy surface.

Figure 3 shows the calculated 2D self-diffusion coefficient versus the chain length N. When N is less than 20, D increases with increasing N, and when N is larger than 20,
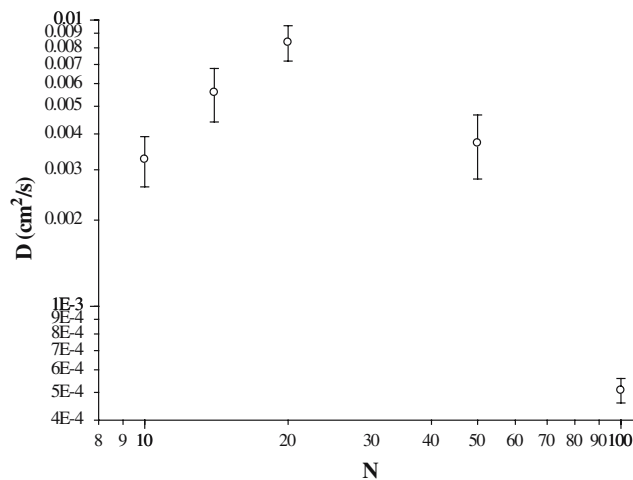

Fig. 3 Log–log plot of the self-diffusion coefficient D versus the chain length N. The *error bars* are the standard deviation measured in three repeated simulations

D decreases with increasing N. This is different to other results, such as a single self-avoiding chain diffusing among regularly-spaced obstacles in 2D [14] and polyethylene glycol on a hydrophobic solid surface [7, 9]. The non-monotonic relation between D and N is quite similar to the concentration dependence of polymer lateral diffusion at the solid–liquid interface found recently by Zhao and Granick experimentally [17].

For an isolated chain $R_g^2 \sim N^{2v}$ (R_g is the mean-square gyration radius), with $v=3/4$ for a reptation model [9], Yethiraj reported that the exponent v decreases as the area fraction is increased [16]. In our simulation process, the carbonic chains are all strongly adsorbed on the surface, the component of R_g in the z-direction is normal to the surface and the other components x- and y-direction parallel to the surface. Therefore, the chain dimensions can be characterized by the parallel component ($R_{g\parallel}$). In this paper, $R_{g\parallel}$ is defined as

$$R_{g\parallel} = (R_{gx}^2 + R_{gy}^2)^{1/2} \tag{3}$$

Figure 4 shows a log–log plot of $R_{g\parallel}$ as a function of chain length N. The straight line is the least-square linear fit for different chain lengths. The scaling exponent is found to be $v=0.59\pm0.05$. This is smaller than the theoretical prediction $v=3/4$ for chains in two dimensions. However, in our simulations, the surface is almost fully covered by C100. Therefore, we omitted the data for C100 and least-square linear fit the other data (the dashed line in Fig. 4). Then a scaling exponent of 0.70 is obtained. This is in good agreement with the theoretical value.

The interaction between the adsorbed chain and the surface may be essential to understand the abnormal dif-
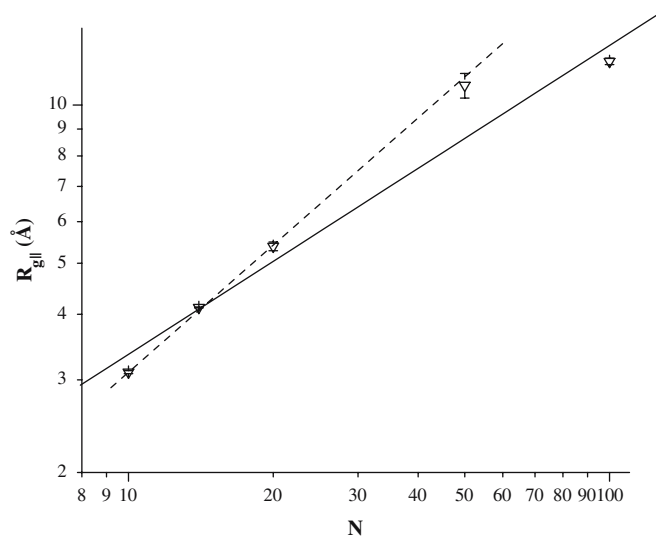

Fig. 5 The average interaction energy per segment E_{int} plotted as a function of chain length N. The *error bars* are the standard deviation measured in three repeated simulations

fusion behavior. Therefore, we show the average interaction energy per segment E_{int} versus chain segment N in Fig. 5. E_{int} is defined as $E_{int} = \left[(E_{frozen} + E_{plane}) - E_{tot}\right]/N$, where E_{frozen} is the potential energy of the adsorbed chain in the frozen geometry adopted upon adsorption, E_{tot} is the potential energy of chain and surface after adsorption, E_{plane} is the potential energy of the surface. As shown in Fig. 5, the interaction between the adsorbed chain and the surface increases when $N<20$. Zhao and Granick found a similar non-monotonic relation between D and N experimentally, and speculated that the chains would diffuse faster and faster with increasing surface coverage as their conformations switched from "pancake" to "loop-train-tail" [17]. The sticking energy per segment is around 0.3 kcal mol^{-1} [7] in their experiments, thus decreasing of the adsorption sites during the transition is possible. However, the interaction energy per segment in our simulation is always as high as 1.1 kcal mol^{-1}, as shown in Fig. 5. For such a strong interaction, the chains cannot change conformation from "pancake" to "loop-train-tail" in

Fig. 4 Log–log plot of the parallel component $R_{g\parallel}$ of the mean-square radius of gyration of the carbonic chains as a function of chain length N. The *straight line* and the *dashed line* are least-square linear fits for all the values of chain length and for the data without C100, respectively. The *error bars* are the standard deviation measured in three repeated simulations
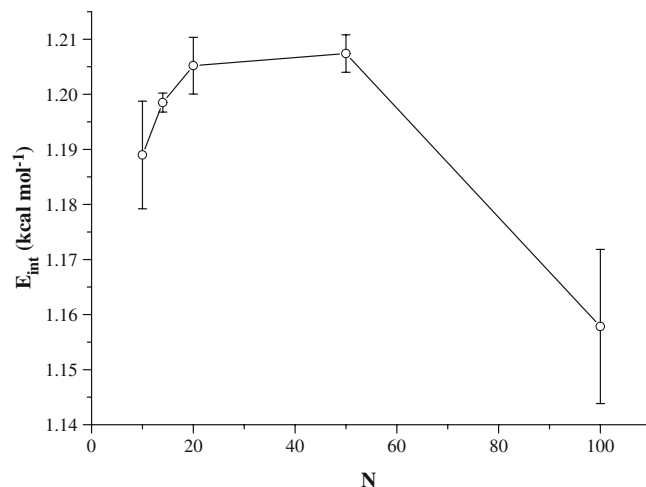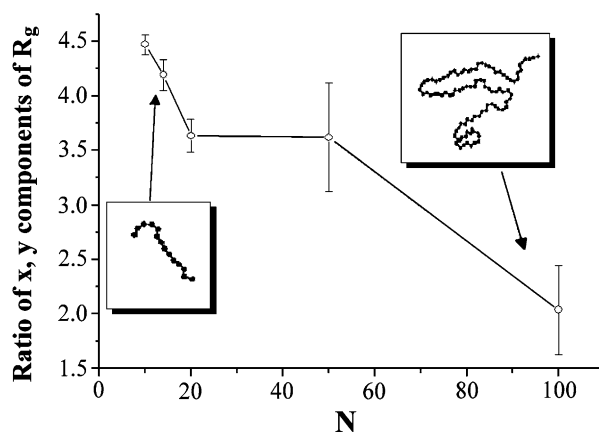

Fig. 6 The ratio between the larger (x or y) and the smaller (y or x) components of R_g versus the chain length N. The *error bars* are the standard deviation measured in three repeated simulation

the present concentrations. When the carbonic chain is adsorbed on a graphite surface, it adopts the "pancake" conformation. The thickness of the "pancake" ranges from 0.88 Å (C10) to 1.34 Å (C100). This shows that the adsorption is strong and no loop configuration can be observed. Zhao and Granick's speculative interpretation is not suitable for our system.

The shape of the "pancake" can be shown by the ratio of the x and y components of the radius of gyration (R_g). Fig. 6 shows the ratio between the larger (x or y) and the smaller (y or x) components of R_g versus the chain length N. The short carbonic chain is extended on the surface. As N increases, the chain starts to bend and forms a circle pan conformation when N is large enough. Thus, we speculate that the chain conformation, which is affected by the concentration and chain length, may be an important factor in determining D. There may be a critical chain length N^*, which is related to the detail conditions. When $N<N^*$, D increases with increasing N; when $N>N^*$, D decreases with increasing N. The enhancement of the mobility at short chain lengths may result from the change of the carbonic chain conformation. When $N<N^*$, the conformations change from rod to circle pan with increasing N. The chain diffuses faster and faster with increasing N as their conformations switch from rod to circle pan. But when $N>N^*$, the circle pan conformations change little with increasing N.

Conclusions

We find a non-monotonic dependence of D on N of single carbonic chain adsorbed on graphite (001) surface by using MD simulations. The mobility of adsorbed chains first increases, then decreases with increasing length of the chain. The scaling relation between R_g and N is in agreement with the theoretical value. The enhancement of mobility with short chain lengths may relate to the chain conformation, which is affected by many conditions.

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