Collective diffusion in carbon nanotubes: Crossover between one dimension and three dimensions*

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Using non-equilibrium molecular dynamics and Monte Carlo methods, we study the collective diffusion of helium in carbon nanotubes. The results show that the collective diffusion coefficient (CDC) increases with the dimension of the channel. The collective diffusion coefficient has a linear relationship with the temperature and the concentration. There exist a ballistic transport in short carbon nanotubes and a diffusive transport in long carbon nanotubes. Fick's law has an invalid region in the nanoscale channel.

Keywords: transport, carbon nanotube, fluid

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1. Introduction

Fourier's law and Fick's law are two important laws describing the thermal and mass transport in nature. When the dimension of the physical structure approximates to the mean free path of the carrier or the duration of the physical process is shorter than the relaxation time of the carrier, Fourier's law cannot describe some thermal behaviors correctly in microscopic systems.[1] Similarly, it is reported when the mean free path of the carrier is far shorter than the size of the channel's structure, Fick's law cannot describe collective diffusion very well either.[2]

Recently, many theoretical and experimental investigations about Fick's law and the related diffusion behavior have been extensively performed. In 1991, Alley and Alder[3] took into account the effect of time memory and proposed that Fick's law should be improved. Later on, Brogioli and Availati[4] put forward that the local density and the fluctuation of the velocity might affect the feasibility of Fick's law and provided a revised formula. In 1995, Cracknel *et al.*[5] constructed the three-dimensional (3D) box of nanoscale and studied the non-equilibrium system of particles with the concentration gradient. Through the calculation of the relation between mass flow and the concentration gradient of the particles, they found that Fick's law was still applicable. In 2006, Haibin Chen *et al.*[6] studied the transport diffusions of gases in flexible carbon nanotubes and found that the transport diffusivities are still large in flexible carbon nanotubes compared with those of other materials. In the same year, Arora and Sandier[7] proposed that they used single wall carbon nanotubes to separate air. They found that good kinetic selectivity can be achieved for air separation by fine-tuning the upstream and downstream pressures. In 2010, Malek and Sahimi[8] used silicon–carbide nanotubes to study the molecular dynamics simulations of adsorption and diffusion of gases. In 2011, Liu *et al.*[9] came up with an efficient method to compute Fick's diffusivities from equilibrium molecular dynamics (MD) simulations, the method does not need additional knowledge such as the equation of state of the system. In 2013, Noy[10] studied the kinetic model of gas transport in carbon nanotube (CNT) channels. It should be noted that in the same year, Becker *et al.*[11] proposed the correlation between the self-diffusion constant of interacting particles and the diffusion coefficient of Fick's Law through the investigation of the hybrid behavior of two mixed gases. It was explained by the difference between transport diffusion and self-diffusion. It was declared that the transport diffusion has more physical meanings than the self-diffusion. Apart from the theoretical studies, many experimental researches have addressed the transport behaviors of molecular sieves,[12–14] biological channels,[15,16] porous medium,[17–20] etc., and further explanations of the microscopic mechanisms have been proposed. Liu and Zhu[21] studied the diffusion model for ion conduction with micro-channel and found that channel charges play a key role in current rectification rather than geometric asymmetry. In 2015, Siems and Nielaba[22] studied the diffusion model of colloidal particles with a periodic potential in a two-dimensional (2D) microscopic system. Wen *et al.* reported the shape-dependence of the channel on the transport diffusion.[23] All these studies above still unsettled the question on the physical mechanism of collective diffusion in nanoscale channels. Especially, it is still not clear how the collective diffusion changes when the channel crosses from one-dimensional (1D) to 3D system. In

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other words, it is unknown whether Fick's Law is still valid in a nanoscale.

In this work, we will investigate the collective diffusion behavior from 1D to 3D system. Since CNTs with different diameters and lengths can be synthesized easily, here we use CNTs to model this system. As shown in Fig. 1, when we use the (4, 4) CNTs, the atom can only move forth and back. That means the atom moves in 1D space. When the diameter is increased, such as (32, 32) CNTs, the channel can be regarded as 3D space. Then the channel from one to three dimensions will be built up. It is expected that our result will present a new perspective to understand its microscopic mechanism.

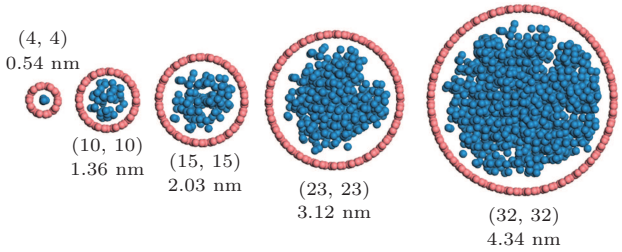


Fig. 1. (color online) Distributions of helium atoms in the carbon nanotubes with different diameters.

2. Model and method

Figure 2 shows the diagram of particle transport in CNTs. The left box (equivalent to the right box) is the left particle reservoir with a volume of $AB \times AE \times AD =$ 4.6 nm×4.6 nm×4.0 nm, the blue balls represent the helium (He) atoms and the green ones denote the carbon atoms. The plane $ABCD$ (or $A'B'C'D'$) is set as the rigid wall. The plane $EFHG$ ($E'F'H'G'$) is graphene wall. The X and Y directions are set as the periodic boundaries. The single-walled carbon nanotubes (SWCTs, represented by the pink balls), acting as the molecular transport channel, connect the left and right atom reservoirs. The dimension of nanochannel changes by adjusting the diameter of the SWCTs.

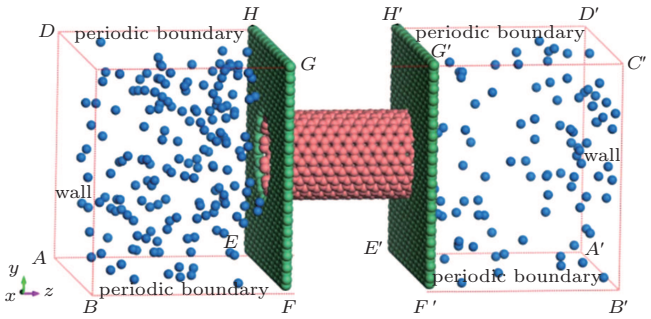


Fig. 2. (color online) A channel for molecular transport. Blue particle is the helium atoms, left and right particle reservoirs are connected by the carbon nanotubes, the green wall is graphene.

We use the Monte Carlo method to control the concentration of atoms in both atom reservoirs. When the absolute activity of the atom reservoir is less (or bigger) than the present value z, an atom will be automatically created (or annihilated). When a creation is accepted, the atom is given a velocity, selected from Maxwell–Boltzmann distribution according to the simulation temperature. Equations (1) and (2) are the acceptance probabilities of creations and annihilations, respectively.

$$P_{\rm cr} = \min\left[1, \frac{zV}{N+1}\exp(-\beta\Delta U)\right], \tag{1}$$

$$P_{\rm dest} = \min\left[1, \frac{N}{zV}\exp(-\beta\Delta U)\right], \tag{2}$$

where $z = \exp(\beta\mu)/\Lambda^3$ is the absolute activity at temperature $kT = 1/\beta$, Λ the de Broglie wavelength, the chemical potential, V the volume of the left or right reservoir, N the number of atoms in the left or right reservoir, and ΔU the variation of inner energy after the creation or annihilation of an atom.

The collective diffusion coefficient is obtained from Fick's law,

$$J = -D\frac{\partial c}{\partial L}, \tag{3}$$

where D is the collective diffusion coefficient, which shows the ability to transport the particles. J, c, and L refer to the mass flux of unit area, the concentration of helium atoms and the length of CNTs, respectively.

In the simulations, a non-equilibrium molecular dynamics method is used, and the two different interactions between He and He, and between He and C are described by the Lennard–Jones potential.[24] In the whole process, the positions of carbon atoms are fixed. The temperature is set according to Langevin random thermal bath. The calculus involved in the calculation is performed by the Verlet algorithm[25] in steps of 0.55 fs. In order to rapidly and accurately collect the diffusion flux, we set different stationary times depending on the length of CNTs and then calculate the unit area diffusion flux after the stationary state.

3. Influence factors of molecular transport

When the system transforms from 1D to 3D system, the collective diffusion behavior will be involved with the influence factors of the transport medium and the transport object. Therefore, to further analyze the nature of the molecular transport, we address the temperature, the density gradient, the chirality of the CNTs, the dimension and length of the channel.

3.1. Temperature effect

According to Fig. 3, it can be seen that collective diffusion coefficient D and the temperature T follow a law $D \propto T$. The results conform with Einstein relation $D_{\rm S} = \mu k_{\rm B} T$, where μ is the mobility. From this law, it can be shown that the temperature has a linear relationship with the collective diffusion constant.

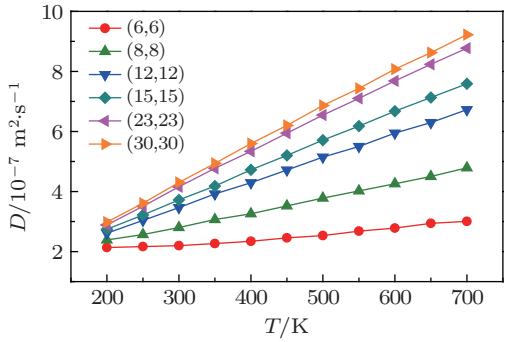


Fig. 3. (color online) Temperature dependences of the diffusion coefficient in carbon nanotubes with different diameters. The density of the left atoms is 0.0042 mol/cm^3, the length of the transport channel is 9.15 nm, and the diameter is set to be between 0.81 nm–4.04 nm.

3.2. Density effect

According to Fig. 4, the collective diffusion constant increases with the concentration gradient increasing no matter what the CNTs are. With the increase of the density, the increasing rate of the unit diffusion flux J_S is bigger than that of the density difference Δc, i.e $J_S/\Delta c$ keeps going up. According to Fick's law, the collective diffusion constant $D_S = (J_S/\Delta c)L_{CNT}$, where L_{CNT} is a constant. Therefore, the collective diffusion constant increases with the density gradient increasing. It can also be shown that the density has an approximately linear influence on the collective diffusion constant.

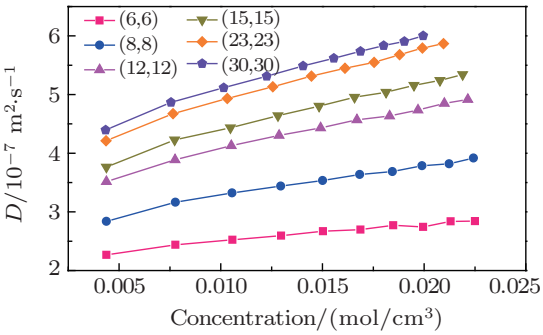


Fig. 4. (color online) Concentration dependences of the collective diffusion coefficient for carbon nanotubes with different diameters. The temperature is 300 K. In the simulation process, the density of the left atoms is fixed at 0.0001 mol/cm^3, while the density of the right atoms can be varied in a range between 0 mol/cm^3–0.0250 mol/cm^3. The remaining parameters are the same as those in Fig. 3.

3.3. Diameter and chirality effects

As shown in Fig. 5, the chirality of the carbon nanotubes has no influence on the collective diffusion constant. This is mainly attributed to the fact that the walls of the carbon nanotubes are almost smooth and the different carbon distribution around the orifice does not affect the entrance of He into the tubes. Considering that the decrease of the diameter, namely the channel changes from a 3D to a 1D channel, the orifice where the He atoms enter into the CNTs will generate a higher potential barrier. Since the potential barrier controls the directions of helium atoms and reduces the unit diffusion flux J_S, as a result, the collective diffusion constant decreases rapidly when the channel changes from the 3D to the 1D channel. The result is opposite to heat transfer: the thermal transport coefficient of 2D graphene is larger than that of 3D multi-layer graphene.

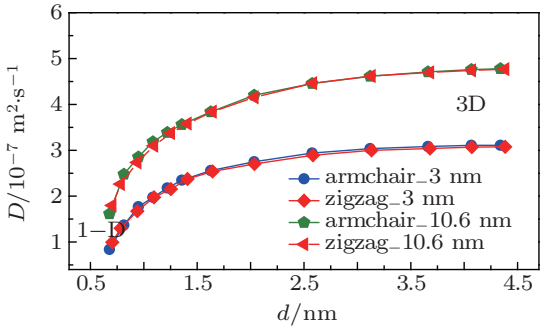


Fig. 5. (color online) Diameter dependence of the collective diffusion constant for two chiralities and lengths. The density of the left atom dictionary is 0.0065 mol/cm^3, the density of the right atom dictionary is 0.0001 mol/cm^3, the lengths are 3 nm and 10.6 nm, respectively. The temperature is 300 K.

3.4. Length effect

As shown in Fig. 6, the transport changes from a ballistic shape, which means the relationship between the mean squared displacement and time is $\langle x^2(t)\rangle \propto t^2$,[26] to diffusive mode when the length of CNT increases.

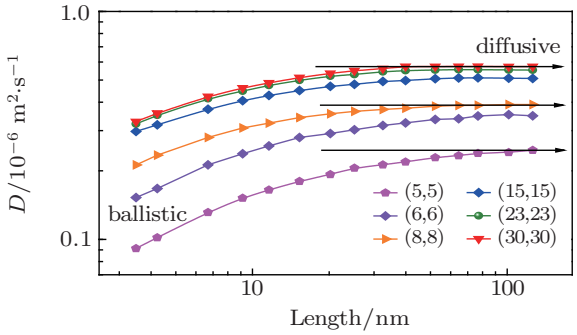


Fig. 6. (color online) Length dependences of the collective diffusion constant for carbon nanotubes with different diameters.

In the ballistic region, the shorter the transport length, the bigger the drive force of the chemical gradient $\nabla\mu$ is under a fast changing nonlinear relationship, i.e., $\nabla\mu \propto 1/L$. Usually, the numbers of atoms in the CNTs (5, 5) remarkably decreases to 1, 2, and 5 for the transport lengths of 3.49 nm, 9.15 nm, and 20.22 nm, respectively. At the same time, the average numbers of atoms in the CNTs (30, 30) are 89, 201, and 458 for the transport lengths of 3.49 nm, 9.15 nm, and 20.22 nm, respectively. Therefore, the collisions happening in short and small CNTs are less than in long and big tubes. Under the influence of the anomalous diffusion behavior, the collective diffusion constant rises up abruptly with the transport length increasing. This can be explained as follows. According to Fick's law, the collective diffusion constant satisfies $D_S = J_S L_{CNT}/\Delta c$, where the density gradient Δc is kept invariable during the simulation. Therefore, D_S is closely associated only with J_S and

L_{CNT}. In this phase, the anomalous diffusion behavior in the CNTs is obvious and the average speed of atoms is relatively high. Although the average number of atoms in the tubes will increase with the increase of the transport length, it will not remarkably change the value of the mass flux J_S. Thus, in the simulation process, the decreasing rate of J_S is lower than the increasing rate of L_{CNT}, then the value of $J_S L_{CNT}$ will increase constantly with the increase of the transport length. Meanwhile, the diffusion constant D_S will increase with the increase of the transport length. In general, the collective diffusion constant is independent of the length, then, Fick's law is invalid in this region.

In a diffusion region, the transport behavior possesses normal transport properties and the mass flux follows the relation of $J_S \propto (L_{CNT})^{-1}$, which means the diffusion coefficient of $D_S \propto J_S L_{CNT}$ remains the same. As a result, the collective diffusion coefficient is independent of the transport length and Fick's law is valid. Comparing these two transport modes, one can observe that there is a transition point between the two transport behaviors. When the diameter of CNT increases from 0.54 nm to 4.34 nm, the length of transition point decreases from 125.97 nm to 25.14 nm. This can be explained as the fact that, within the same transport length, the atoms held by smaller tubes are less than by bigger tubes. These atoms have a more polarized direction of motion as well as more opportunities for collision. As a result, with the increase of the transport length, the collision frequency of all the atoms contained in a carbon nanotube with a large diameter is apparently higher than that with a small diameter. That is to say, within a small change of length the atoms in the large tubes can produce an obvious behavior of disordered collision and the ballistic diffusion characteristics drastically reduce to zero.

4. Conclusions

From 1D to 3D molecular transport system, the collective diffusion constant increases rapidly and finally tends to a plateau constant. The collective diffusion behavior is strongly correlated to the factors such as diameter, temperature, density gradient, transport length, etc. The higher the dimension of the system, the more strongly the temperature and density affect the collective diffusion. As the transport length increases, the transport mode changes from ballistic to normal transport. The transition point length can vary obviously for systems with different dimensions. Anyway, the transition behavior can be attributed to the existence of the anomalous diffusion behavior. The lower the dimension of the system and the shorter the transport length, the more obvious the characteristics of the super diffusion are. Our results suggest that Fick's law may be invalid when the transport length decreases to the nanoscale region.

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