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Shape-dependent collective diffusion coefficient of multi-layers graphene nanopores

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Using non-equilibrium molecular dynamics, we study the particle transport in graphene membrane nanopores. The dependences of collective diffusion coefficient on the shape, the length, the cross sectional area of nanopore and the environmental temperature are discussed. Compared with carbon nanotubes, multi-layers graphene membrane has much lower collective diffusion coefficient. It is suggested that the interfacial and intracrystalline resistance can suppress particles transport in nanopores. Our research provides valuable advice for controlling the particle transport through nanoscale channels.

Gaseous diffusion in nanopores has attracted considerable attentions in recent years, due to rapid development of porous membrane materials and their comprehensive applications. Molecular dynamics (MD) simulations demonstrated that diffusivity of gases in carbon nanotube membrane could be extremely high compared with other known porous materials.¹⁻⁴ It is proved that the almost frictionless surface of carbon nanotubes (CNTs) is the main reason.⁵⁻⁷ In particular, according to theoretical studies, graphene membrane could be a potential candidate for porous materials for the mechanical strength, the chemical stability and the essential two-dimensional structure. Graphene membrane has enormous potential in application of gas barrier,⁸ the selectivity of particles,^{2, 9-13} the purification of water,^{14, 15} and the characterization of DNA.¹⁶ Indeed, graphene oxide sheet is utilized to the experimental study of gas selectivity and water

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purification in recent years.¹⁷⁻²¹ Usually, artificial nanopores can be created by electron beam sculpting on suspended multi-layers graphene sheets.^{22, 23} However, the technology of sculpting on graphene today is not perfect to ensure that a nanopore is always standard. The nanopores of all shapes and sizes are inevitably produced. Therefore, it is necessary to know how the shape of nanopore affects the diffusion.

In this paper, we will build three typical shapes, roundness, triangle and square, to investigate the influence of the nanopore's shape on the collective diffusion coefficient. The distribution of particle in the nanopore is provided to explain the interfacial and intracrystalline resistance, which may influence the particle transport in nanochannels. Our results are also compared with those of the carbon nanotubes.

We build a non-equilibrium molecular system, and use MD and Monte Carlo methods to simulate the process of molecular diffusion. As shown in Figure 1, noble gaseous atoms (helium or neon) are divided by stationary multi-layers graphene membranes into two particle reservoirs at a certain chemical potential. A nanopore perpendicular to the surface of multi-layers graphene connects these two particle reservoirs. The distance between two adjacent graphene layers is small enough (3.4 Å) so that the gaseous atoms would not leak from that interspace. We investigate the relationship of the diffusion coefficient D with the area, the shape of nanopores, the length of nanochannel, and the temperature. Here the van der Waals interactions of gas-gas and gas-carbon are described by the Lennard-Jones (LJ) potential^{24, 25}

$$V_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where “ σ ” and “ ε ” refer to distance and energy parameters of LJ interaction, respectively. The collective diffusion coefficient is defined by Fick’s law

$$J = -D \frac{\partial c}{\partial L}, \quad (2)$$

where D is the collective diffusion coefficient, which shows the transport ability of the nanochannel. J , c and L refer to the gas flux of unit area, the concentration of gas particles and the length of nanochannels, respectively. We use Metropolis algorithm to control the concentration of gas in both of the particles reservoirs by creating or deleting a particle as a probability

$$P_{cr} = \min\left[1, \frac{zV}{N+1} \exp(-\beta\Delta U)\right] \quad (3)$$

$$P_{del} = \min\left[1, \frac{N}{zV} \exp(-\beta\Delta U)\right], \quad (4)$$

where P_{cr} and P_{del} refer to the probability of creating and deleting a particle, respectively. V and N are the volume of particles reservoir and the quantity of particles in it. ΔU refers to the change of chemical potential when creating or deleting a particle, z refers to absolute activity described as $z = \exp(\beta\mu) / \Lambda^3$, in which $\beta = 1 / k_B T$, μ is chemical potential, and Λ is De Broglie wavelength. In our research, all the carbon atoms are fixed, temperature is controlled by Langevin heat baths,²⁶ and the equations of motion are integrated by using Verlet algorithm²⁷ with a time step 0.55 fs. Environmental temperature is 300 K if not mentioned particularly.

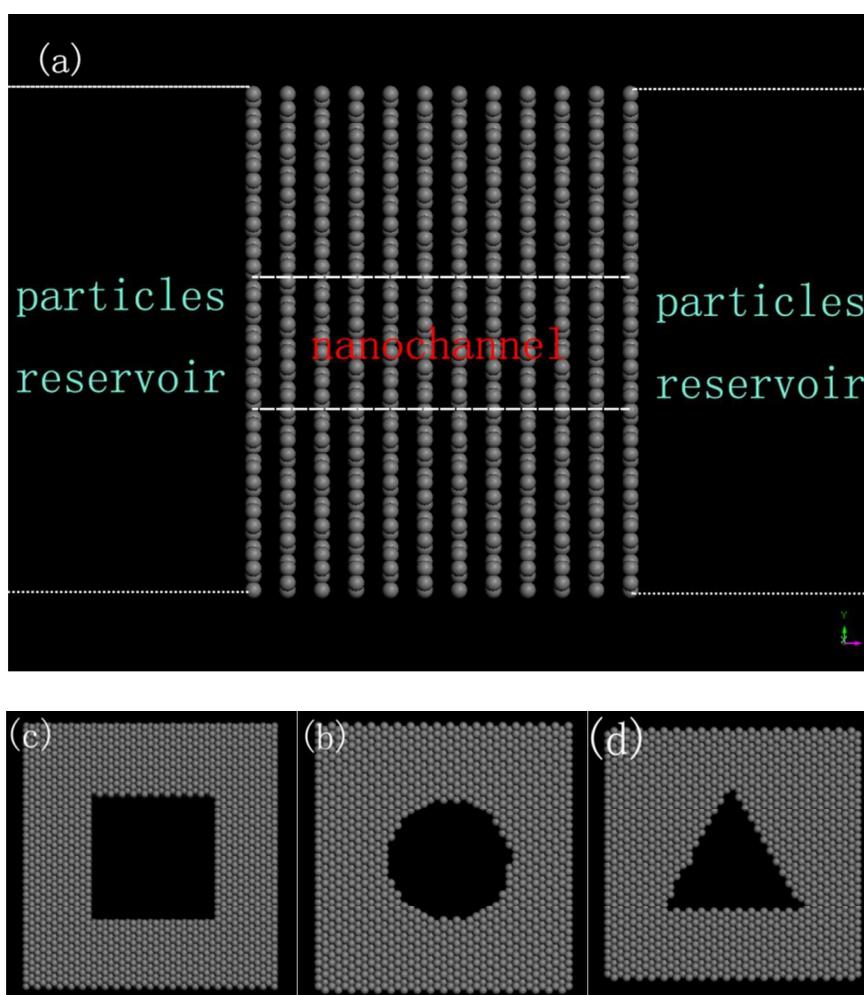


FIG. 1. The structure of graphene membranes, with a nanopore connecting two particle reservoirs. (a) side view of the construction (b) round nanopore (b) square nanopore (c) triangle nanopore

Firstly, we investigate the relationship between the collective diffusion coefficients (D) and the environmental temperature. As shown in Figure 2, D of helium in graphene membranes nanopores are almost linear with the environmental temperature, just as theoretical research predicted.²⁸ Moreover, D increases with the length of nanochannel.

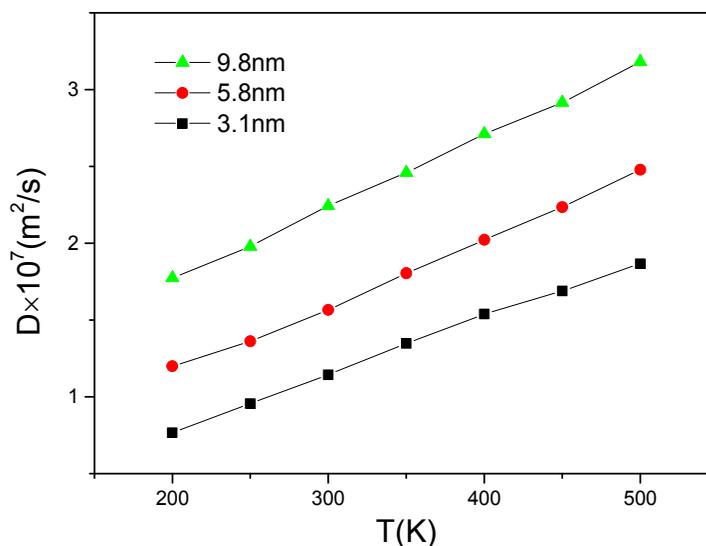


FIG. 2. Temperature dependence of collective diffusion coefficient. The lengths of nanopores are 9.8, 5.8 and 3.1 nm, respectively. The diameter of nanopore is 1.6 nm.

Then we make a further research on the dependence of D on the cross sectional area (CSA) of different shapes nanochannels. Fixing the length of graphene membranes nanopore as 3.1 nm, we simulate the transport of helium in three different shapes (roundness, square and triangle) of nanochannels. Adjusting the CSA of these nanochannels, we can find that, as shown in Figure 3, D grows as the diameter increases no matter what shape the nanopore is, and then tends to a constant. Furthermore, as displayed in the inset of Figure 3, the collective diffusion coefficient of neon (Ne) shows the same tendency with that of helium. However, D of neon is 1 order of magnitude less than that of helium.

This phenomenon can be explained that a small CSA nanochannel will create a high potential barrier for helium atoms in the entrance and exit of nanochannel, shown as the interfacial resistance, which will prevent those particles without enough momentum entering or leaving nanochannels, so that a small CSA for nanochannel would lead to a small D value. And the huge

difference of the D between He and Ne could be explained that the mass of neon atoms is much larger than helium.

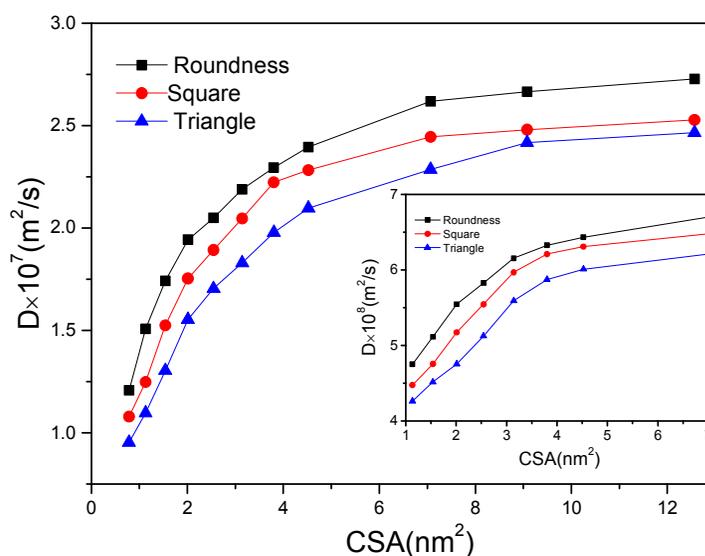
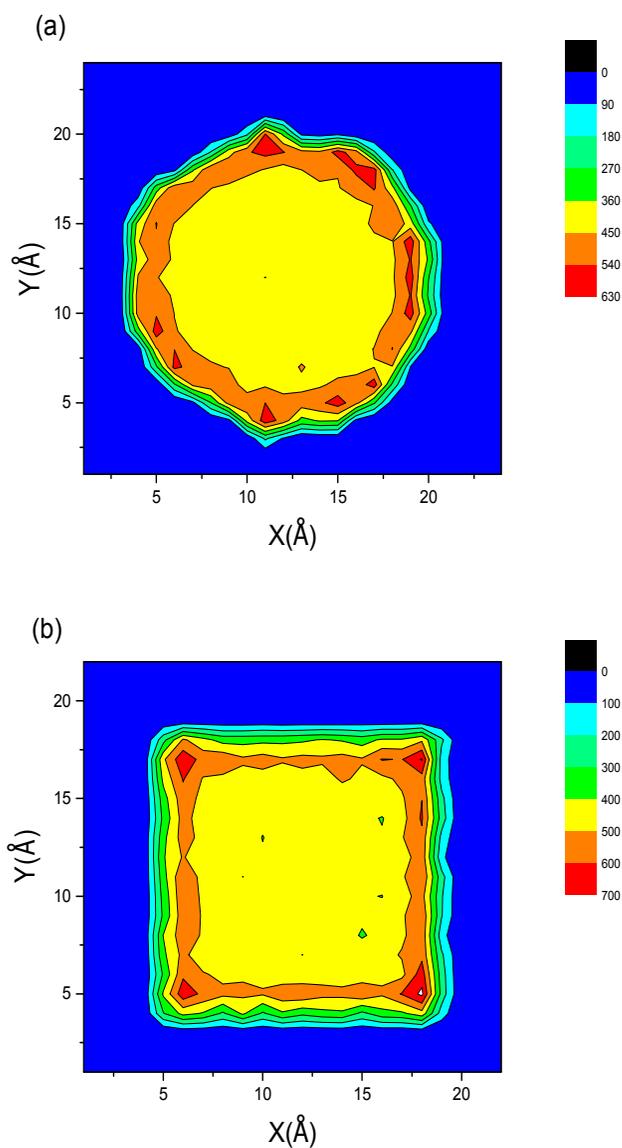


FIG. 3. CSA dependence of helium's collective diffusion coefficient for different shapes. The inset is the CSA dependence of neon's collective diffusion coefficient for different shapes. The length of nanochannels is 3.1 nm.

Additionally, Figure 3 shows that the shape of the nanopore influences the D value obviously. With the same CSA, round nanopore has the highest D value, while the D of triangle nanopores is the smallest. To address the different dependence of D on the shape, we investigate the distribution of helium atoms in different shapes nanochannels. For each nanochannel shape, 1×10^5 helium atoms are projected to a plane perpendicular to the axis of nanopore, which have the same CSA (3.1 nm^2). The particles distributional density is counted in every $1 \text{ \AA} \times 1 \text{ \AA}$ region. Obviously, as shown in Figure 4, the density of helium atoms near the boundary of nanochannels is much higher (generally 30% or more) than that in the center, especially when the corner of triangular and square nanochannel are noticed. This phenomenon, similar to the work given by Skoulidas et al.,²⁹ could be explained by the van der Waals interactions of gas-carbon. When the

distances between gas and carbon atoms are beyond the equilibrium position (about 2.98 Å) of Lennard-Jones potential, the carbon atoms will attract gaseous atoms. Because of larger specific surface area, the boundary of nanochannels affects the flow more seriously than that of macroscopic size. Therefore, the velocity of gas particles nearby the boundary of nanochannel may decrease due to gas-carbon and gas-gas interaction, so that a longer perimeter such as triangle brings greater intracrystalline resistance at the same CSA, which induces a low D.



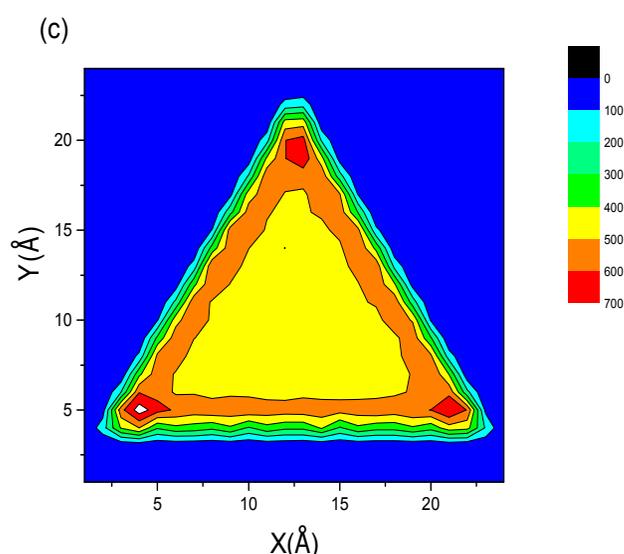


FIG.4. Distribution projection density of 10^5 helium atoms on a plane perpendicular to the axis of nanochannels in different shapes. (a) Roundness (b) Square (c) Triangle

In order to confirm our consideration about the dependence of helium diffusion coefficient on the intracrystalline resistance, we make further research. As shown in Figure 5, D of graphene membranes nanopore shows clear dependence on the length of nanochannel. It seems that both of the curves reach a stable value at a length of 16 nm. It is a reasonable result that could be explained as that the intracrystalline resistance has a linear relationship with the length of nanochannel,^{30, 31} and the interfacial resistance is neglectable if nanochannel is long enough.⁶ In Figure 5, we also make a comparison between graphene membrane nanopore and CNTs, and find that D of CNTs ($3.8 \times 10^{-7} \text{ m}^2/\text{s}$) is much higher than that of graphene membrane nanopore ($2.1 \times 10^{-7} \text{ m}^2/\text{s}$). Moreover, this trend is the same as the inset of Figure 5.

Different with CNT, owing almost absolutely smooth internal wall, graphene is unfolded in the direction that is perpendicular to the flow. Each of these graphene layers for the transport of particles is a little potential barrier for the transport of particles, so that diffusion in multi-layers graphene nanopore has much more intracrystalline resistance than that in CNTs. The difference

between the transport in CNTs and multi-layers graphene membranes nanopore is the intracrystalline resistance, so we consider that the smooth internal wall of nanochannel is the key point of fast transport diffusion.

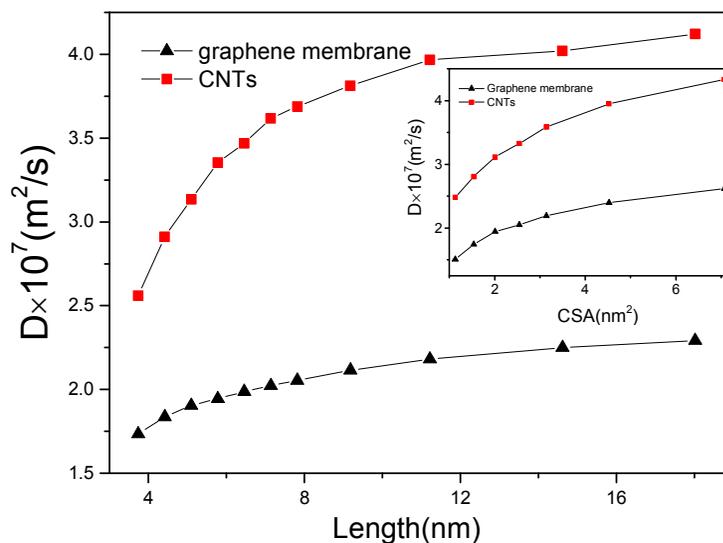


FIG. 5. Length dependence of collective diffusion coefficients for helium transport in graphene membranes nanopores and CNTs,

The CSA of nanopores is 3.1 nm². And the CSA dependence is shown in the inset, the length of nanochannels is 10.6 nm.

In summary, we have studied the collective diffusion coefficient of noble gas in multi-layers graphene membranes nanopores, and discussed some elements that might affect the collective diffusion coefficient such as temperature, the length of nanochannels, the diameter of nanochannels, the shape of nanopores, and the kind of gas particles. It is suggested that the interfacial resistance and intracrystalline resistances are the key points to analyze the transport properties the transport in nanoscale channels. Our research may give some valuable suggestion for the application of multi-layers graphene membranes on gas selectivity.

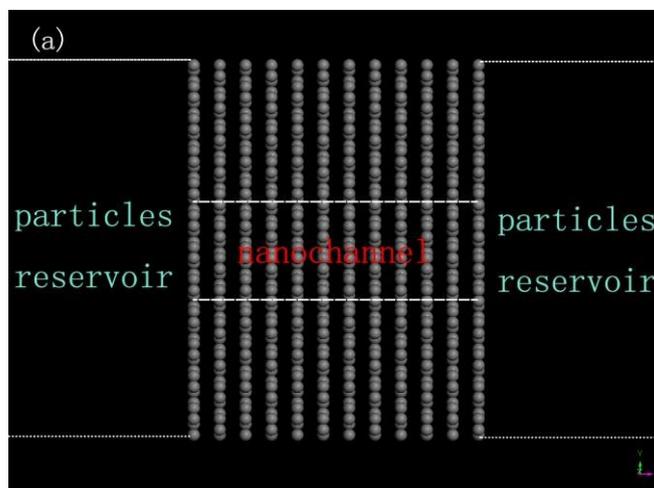
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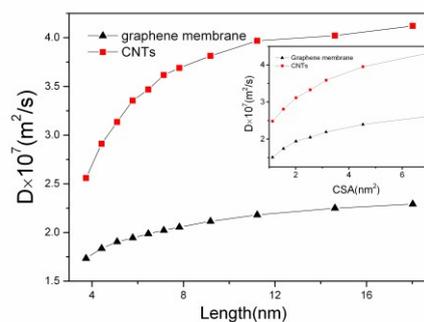
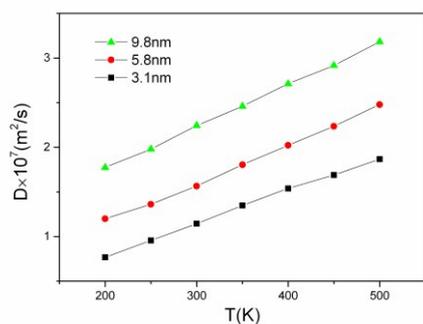
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ABSTRACT

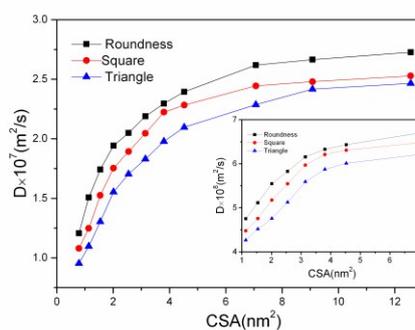
Using non-equilibrium molecular dynamics, we study the particle transport in graphene membrane nanopores. In this paper, our primary works are listed as follow:



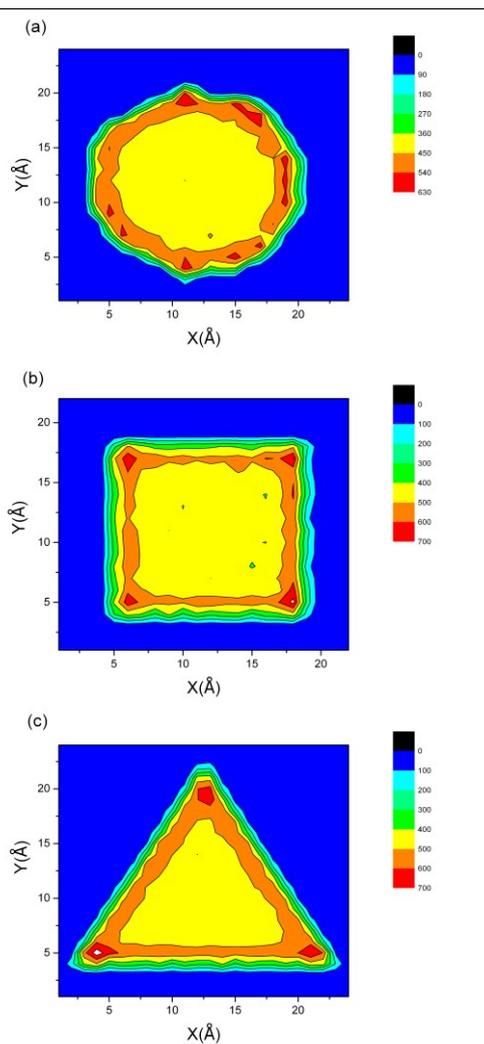
1. We study the temperature, length and cross sectional area dependence of gaseous particles (helium or neon) transport in multi-layers graphene nanopore.



2. We construct three typical shapes (roundness, square and triangle) multi-layers graphene nanopore to study the shape dependence of collective diffusion coefficient.



3. We study the distribution of gaseous particles in nanochannel to explain our result.



4. We compare our result with the transport in carbon nanotubes.

It is suggested that the interfacial and intracrystalline resistance can suppress particles transport in nanopores. Our research provides valuable advice for controlling the particle transport through nanoscale channels.