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Research Paper

Diffusion of gas molecules on multilayer graphene surfaces: Dependence on the number of graphene layers

Chengzhen Sun, Bofeng Bai *

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, China

HIGHLIGHTS

- Diffusion coefficients on multilayer graphene surface are calculated.
- Gas diffusion on multilayer graphene surface is controlled by molecular collisions.
- Diffusion coefficient decrease gradually with increasing layer-number.
- Probability distribution of jump length confirms the variations of diffusion coefficient.

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ABSTRACT

The diffusion of gas molecules on multilayer graphene surfaces is of great importance for a wide range of applications in gas-related industries. This study calculates diffusion coefficients for gas diffusion on single layer or multilayer graphene surfaces based on molecular dynamics simulations with a major emphasis on the effect of the number of graphene layers. The results show that the gas diffusion on these graphene surfaces is mainly controlled by molecular collisions in the adsorption layer; because the contributions of the gas adsorption energy and the gas collision energy are always comparable with the gas adsorption energy becoming slightly stronger with increasing number of graphene layers. Therefore, the surface diffusion coefficient decreases gradually with increasing number of graphene layers owing to the larger number of adsorbed molecules on graphene surfaces with more layers. Notably, the diffusion coefficients do not depend strongly on the number of graphene layers when there are a large number of graphene layers due to the limited interaction distance between the gas molecules and the graphene atoms. Furthermore, the variations of the surface diffusion coefficient with the number of graphene layers and the gas species are confirmed from the probability distributions of the molecular jump length on the graphene surface in a given time period.

1. Introduction

Graphene [1,2], as a representative two-dimensional material, has many applications in chemical engineering, thermal engineering and other fields [3–6]. Gas-related applications are especially important, such as graphene-based gas separation membranes [7–9], graphene-based gas sensors [10,11], thermal chemical-vapor-deposition processes for graphene production [12], and the thermal treatment of graphene oxide films in air [13,14]. In these applications, the gas diffusion characteristics on the graphene surface are very important. For example, the gas diffusion on the graphene surface restricts the permeation abilities of graphene-based membranes [15,16] and the surface diffusion characteristics determine the sensitivities of graphene-based gas sensors [10].

The surface diffusion rates reflect the mass transport characteristics on a solid surface, with the diffusion related to the molecular adsorption ability, molecular kinetic parameters and molecular collision energy [17–19]. The surface diffusion phenomena occur along the molecular adsorption layer on the solid surface where the characteristic height is on the order of nanometers. Thus, the gas diffusion phenomenon on a solid surface must be investigated at the molecular level. The relative contributions of the molecular adsorption energy and the molecular collision energy determine the surface diffusion patterns. If the molecular adsorption energy is far greater than the molecular collision energy, the surface diffusion can be described by the hopping mechanism [20–23]; otherwise, the surface diffusion would be governed by the gas behavior and would be mainly controlled by the collisions among

* Corresponding author.
E-mail address: bfbai@mail.xjtu.edu.cn (B. Bai).

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Nomenclature

C	electrostatic constant ($N\,m^2\,C^{-2}$)
d	molecular kinetic diameter (m)
D	diffusion coefficient (m^2/s)
E_r	bond stretch energy (J)
E_θ	angle deformation energy (J)
K_r	bond stretch parameter ($J\,m^{-2}$)
K_θ	angle deformation parameter ($J\,rad^{-2}$)
M	molecular mass (kg)
P	pressure (Pa)
q_i, q_j	charges on atoms i and j (e)
r_0	equilibrium bond length (m)
t	time (s)
t_0	initial time (s)
Δt	time interval (s)
x, y	x and y coordinates of a molecule (m)
x_0, y_0	x and y coordinate at the initial time (m)

Greek symbols

ε	energy parameter (J)
σ	length parameter (m)
χ	dielectric constant ($F\,m^{-1}$)
θ_0	equilibrium bond angle (rad)

adsorbed gas molecules. For graphene, the gas adsorption energy is comparable with the gas collision energy owing to the graphene being several atoms thick. Sun and Bai [24] demonstrated that gas diffusion on graphene surfaces has a gas-like behavior, mainly controlled by molecular collisions. The variation of the surface diffusion coefficient as a function of the molecular concentration is similar to that for the bulk diffusion, but the surface diffusion coefficients are lower than the bulk diffusion coefficients due to the restrictions of the molecular motion on the graphene film.

Gas-related graphene applications always involve multilayer graphene. For example, multilayer graphene is used in gas separation membranes to eliminate the effects of defects in the graphene films [8,25]. For multilayer graphene, the interactions between the graphene atoms and the gas molecules then depend on the number of graphene layers which affects the number of interacting carbon atoms. Therefore, the gas adsorption on multilayer graphene surfaces changes with the number of graphene layers and the surface diffusion characteristics then vary depending on the molecular number density on the graphene surface. These nanoscale transport phenomena are normally analyzed using molecular dynamics (MD) simulations which can accurately capture the movements of atomic particles to investigate the transport characteristics on the molecular level [26–30]. In this paper, we dedicate to study the gas diffusion characteristics on multilayer graphene surfaces by statistically calculating the surface diffusion coefficients using the Einstein equation. The surface diffusion coefficients are calculated for gaseous CH_4, H_2S, CO_2 and N_2 molecules for monolayer graphene and multilayer graphene with up to four layers. The results show the dependence of the diffusion coefficients on the number of graphene layers and the underlying mechanisms. These results have significant implications to a broad community investigating graphene materials in gas-related industries.

2. Simulation method

The MD simulations modeled a cubic box with 50 gas molecules on top of a $3 \times 3\,nm^2$ multilayer graphene surface, as shown in Fig. 1(a). The simulation box height was related to the system pressure. The initial system pressure was set to 25 bar with the box height then based on the ideal gas equation for each gas set to approximately 9 nm. The simulation box height was sufficient for efficient simulations of the molecular motions on the graphene surface and avoiding the computational costs of extensive simulations of the molecular motions in the gas phase. Periodic boundary conditions were applied in the x and y directions with reflective boundary conditions in the z direction. The graphene carbon atoms were fixed during the simulations. The simulations used the NVT ensemble with a small time step of 0.134 fs, so that the system temperature equilibrated at 300 K with small fluctuations. Fig. 1 (b) and (c) display snapshots of the multilayer graphene and atomic models of the gas molecules (CH_4, H_2S, CO_2 and N_2).

The simulations modeled the CH_4 atomic interactions using the popular AIREBO potential model [31], which can be used to accurately model both chemical reactions and intermolecular interactions in hydrocarbon systems. Comparisons also show small differences between the results obtained using the AIREBO potential model and the Lennard-Jones (L-J) potential model. The other interactions were modeled using the L-J potential model coupled with Coulomb interactions:

$$\phi(r_{ij}) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{Cq_iq_j}{\chi r_{ij}} & (r_{ij} < r_{cut}) \\ 0 & (r_{ij} \geqslant r_{cut}) \end{cases} \quad (1)$$

where q_i and q_j are the charges on atoms i and j, σ is the length parameter, ε is the energy parameter, χ is the dielectric constant, and C is the electrostatic constant. The relative dielectric constants for all the gases were set to 1 with the normal values listed in Table 1 used for the L-J potential parameters and the atomic charges. The parameters ε and σ for crossing atoms were estimated by the Lorentz-Berthelot mixing rule. The cutoff distances for the van der Waals interactions and the short-range Columbic interactions were both set to 10 Å. The bond stretch energy, E_r, and the bond angle deformation energy, E_θ, within a gas molecule were defined based on the Harmonic model as:

$$E_r = K_r(r - r_0)^2$$
$$E_\theta = K_\theta(\theta - \theta_0)^2 \quad (2)$$

where r_0 is the equilibrium bond length, θ_0 is the equilibrium bond angle, K_r is the bond stretch parameter, and K_θ is the angle deformation parameter. These parameters for H_2S, CO_2 and N_2 are listed in Table 2. The bond information in CH_4 molecules is already included in the AIREBO potential model.

The surface diffusion occurs in the molecular adsorption layer on the graphene surface. The Einstein equation was used to calculate the statistics for the gas diffusion coefficients on the graphene surface based on the coordinates of the molecules moving in the adsorption layer. The Einstein equation is:

$$D = \frac{\langle (x - x_0)^2 + (y - y_0)^2 \rangle}{4\Delta t} \quad (3)$$

where D is the gas diffusion coefficient (m^2/s), x and y are the x and y coordinates of the molecule at time, t, x_0 and y_0 are the x and y coordinates at time t_0 (the initial time for the molecules entering the adsorption layer), and Δt equals t–t_0. The model for calculating the diffusion coefficient on multilayer graphene surface is illus-