

Classical molecular dynamics simulation on the dynamical properties of H₂ on silicene layer

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Abstract. This study investigates the diffusion of hydrogen molecule physisorbed on the surface of silicene nanoribbon (SiNR) using the classical molecular dynamic (MD) simulation in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The interactions between silicon atoms are modeled using the modified Tersoff potential, the Adaptive Intermolecular Reactive Empirical Bond Order (AIREBO) potential for hydrogen – hydrogen interaction and the Lennard – Jones potential for the physisorbed H₂ on SiNR. By varying the temperatures (60 K - 130 K), we observed that the Δx displacement of H₂ on the surface SiNR shows a Brownian motion on a Lennard-Jones potential and a Gaussian probability distribution can be plotted describing the diffusion of H₂. The calculated mean square displacement (MSD) was approximately increasing in time and the activation energy barrier for diffusion has been found to be 43.23 meV.

1 Introduction

The search for novel materials is widespread nowadays in response to the advancing world of science and technology. As the field of research goes nanotechnology, many materials, those that are experimentally impossible in the past, have been synthesized at present. These materials are able to adapt and are technologically fit for what is required of them.

One of these materials is graphene [1], a two-dimensional (2-D) honeycomb structure material composed of carbon atoms, which exhibits properties that are very unique and exceptional. Since the production of graphene [1-2], many single-layered materials have been synthesized and theorized over the years. Some of the recent researches investigate the interaction of hydrogen on the surface of these 2-D materials. Due to the increasing demand for energy, most of the studies focuses on finding an efficient hydrogen storage material [3-6] which requires a binding energy of 0.2 ~ 0.6 eV. Applications to microelectronics using these materials are also considered since these materials are semimetals and can have a tunable band gap when saturated with hydrogen.

Studies on the interaction of the hydrogen atom on the surface of graphene were conducted through MD simulation and density functional theory (DFT) [5]. Furthermore, an investigation using classical MD simulation on the static and dynamical properties of molecular hydrogen on the surface of graphene presented the

calculation of the activation energies for the diffusion and desorption of H₂ [6].

One of the recent discoveries is silicene [7], an allotrope of silicon with a pure sp² hybridization, one-atom thick, honeycomb structure material similar to that of graphene. Since it has a graphene-like structure, it is thought to possess properties that resemble that of graphene. Since silicene is a silicon-based material, it can easily be integrated with the present silicon industry. Unlike graphene with a planar structure, silicene structure is slightly buckled and due to this buckling, silicene exhibits properties that are unique and different from graphene [8]. The interaction of hydrogen on silicene and other 2-D materials has attracted many since hydrogenation is thought to affect the properties of the material like band gap tuning and gas sensing. While most of the studies relating to the H₂ interaction focuses mainly on graphene [7-9], only few have considered the hydrogen interaction on silicene [10] and most of it uses the first principle approach, although has higher accuracy as compared to classical approaches but a computationally intensive simulation.

In the present work, we investigated the interaction of H₂ molecule on the surface of the silicene nanoribbon (SiNR). Using classical MD simulation, at varying temperatures, the H₂ Δx displacement shows a Brownian motion on a Lennard-Jones potential and by employing the Δx displacement, the diffusing H₂ molecule is described by the plot of a Gaussian probability distribution. From the MSD calculations, the diffusion coefficients have increased in time and the

diffusion barrier energy has been found to be 43.23 meV. The interaction of molecular hydrogen on silicene is an on-going study at present and this study has its intent to pave more ways, shedding new light for more technological applications of silicene.

2 Computational Method

Dynamical properties of H₂ on silicene were investigated using classical molecular dynamics (MD) simulation [11] through LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The interactions between silicon atoms were modeled using the modified Tersoff potential [12] and the interaction between the two hydrogen atoms were modeled using the AIREBO potential [6]. The hydrogen molecule is considered to be physisorbed on the surface of silicene and thus modeled with Lennard-Jones potential. The Lennard – Jones potential for the diffusing H₂ on silicene is given by the equation [13],

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad r < r_c \quad (1)$$

where r is the distance between H₂ and silicene, r_c is the cut off distance, ϵ is the measurement on how strongly the H₂ and silicene attract, and the distance where there is no intermolecular potential is given by $\sigma = 2.5 \text{ \AA}$.

The simulation box for the silicene has a periodic boundary condition. The dimension of SiNR is $50 \text{ \AA} \times 50 \text{ \AA}$, a square nanoribbon which contains 418 atoms which lie flat on the simulation box and placed at $z = 5 \text{ \AA}$ due to its buckled structure. The hydrogen atoms were placed 2.454 \AA [13] at the top of the hollow site as shown in Fig. 1. The distance of H₂ from the surface of silicene in the hollow site is shorter when compared to the other adsorption sites. This is due to the stronger binding energy on the other sites as compared to the hollow site [14].

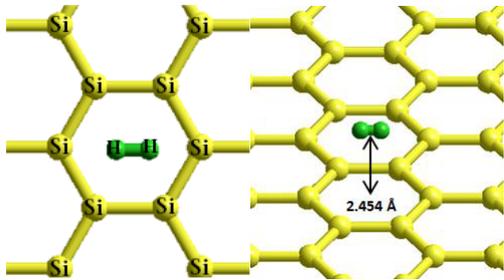


Figure 1. Top view of the silicene structure (yellow) topped with the hydrogen molecule (green) on the hollow site (left) and the distance between silicene and H₂ molecule (right).

The simulation uses an NVT ensemble and a Brendsen thermostat to regulate the

temperature of the system during the simulations. A timestep of 0.2 fs was used to investigate the dynamical properties of H₂ on silicene during the simulation. In this study, low temperatures were used ranging from 60K to 130K, with a total number of 1×10^5 steps to equilibrate the system and another 1×10^8 steps to take the averages. For low temperatures, simulation times were increased to minimize statistical errors [6]. Since the boundaries on every side of the simulation box are periodic, the adsorption, diffusion and desorption of H₂ from the surface of silicene were observed and were tracked during the simulation. The displacement of the H₂ atoms in three dimensions was tracked.

The calculation of the diffusion coefficient, D at any given temperature is calculated through the mean square displacement (MSD), $\langle r^2 \rangle$ [15-16],

$$D = \frac{1}{4} \lim_{t \rightarrow \infty} \frac{\langle r^2 \rangle}{t} \quad (2)$$

where the mean square displacement in two dimensions calculated in every temperature is given as [15],

$$\langle \Delta r^2(t) \rangle = \langle (x(t + t_0) - x(t_0))^2 + (y(t + t_0) - y(t_0))^2 \rangle \quad (3)$$

The coordinates x and y corresponds to the center of mass of the H₂ molecule.

The activation energy, E_a was calculated using the relationship of the temperature and the diffusion coefficient, D through the empirical formula: [15-16]

$$D = D_0 e^{\frac{-E_a}{k_B T}} \quad (4)$$

The plot of the logarithm of the diffusion coefficient versus the inverse of the temperature gives a linear fit from which the activation energy [17] is calculated.

The probability of finding the H₂ molecule from its original position on the SiNR surface is calculated using the Gaussian probability density distribution function [18], employing the Δx displacement as the random variable representative to the H₂ coordinate,

$$f(x) = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (5)$$

where σ is the standard deviation and μ is the mean.

3 Results and Discussion

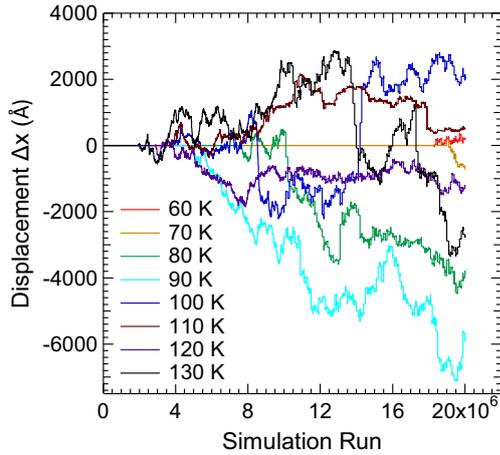


Figure 2. The Δx displacement of H_2 on SiNR with a time step of 0.2 fs per simulation run.

In Figure 2, the Δx displacement, a representative of the H_2 coordinate, shows the Brownian motion behavior on a Lennard-Jones potential as H_2 moves on the SiNR surface with varying temperatures. The probability of finding the H_2 molecule from its original position is shown in Figure 3. Through the Δx displacement, a Gaussian probability distribution from equation (5) can be plotted describing a diffusing molecule. At lower temperatures, there is a high probability that H_2 can be found at its original position, and with increasing temperatures, there is a low probability that H_2 can be found and diffuses randomly away from its original position. This only demonstrates that the energy of the H_2 molecule has increased with temperature causing it to be more diffusive on the surface.

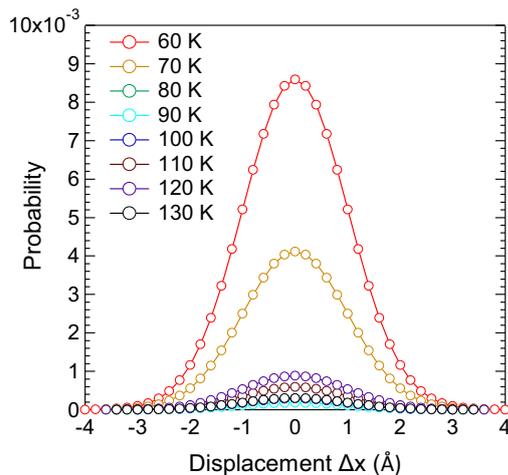


Figure 3. Gaussian distribution calculations of the displacement of H_2 at various temperatures.

The mean square displacement (MSD) for H_2 on the surface of SiNR was recorded during the simulation for the calculation of the diffusion

coefficient at each temperature. The plot in Figure 4 shows the MSD evolution over time at each temperature to calculate the average diffusion coefficient for a temperature range of 60 K to 130 K. By calculating the average MSD and plotting a linear fit, it is observed that the MSD significantly increases in time, a characteristic of a diffusing molecule in Brownian motion.

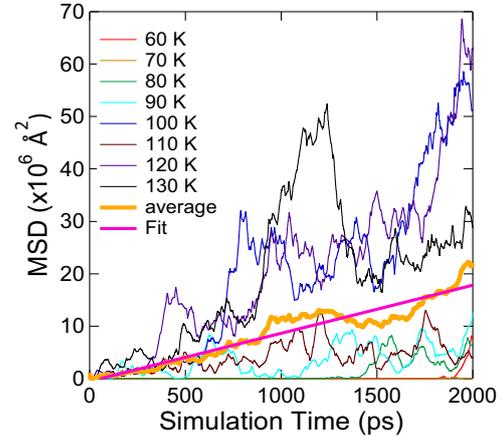


Figure 4. The mean square displacement of H_2 on SiNR for the calculation of the average diffusion coefficient of various temperatures.

In Table 1, the diffusion coefficients were calculated from the MSD. The plot of the logarithm of the calculated diffusion coefficient versus the reciprocal of the temperature is shown in Figure 5. This shows the temperature dependence of the diffusion of the H_2 on the surface of SiNR. Based on equation (4), the activation energy barrier for diffusion which was calculated from the slope of the graph is 43.23 meV with the calculated pre-exponential $D_0 = 1.942 \times 10^5 \text{ Å}^2/\text{ps}$.

Table 1. The data of the diffusion coefficient for the hydrogen diffusion on SiNR at various temperatures.

Temperature(K)	Diffusion Coefficient ($\text{Å}^2/\text{ps}$)
60	43.76
70	91.99
80	296.35
90	550.0449
100	1286.91
110	1587.634
120	2392.27
130	5324.11

The activation energy barrier for the diffusion of H_2 on SiNR is greater compared to the diffusion barrier calculated for H_2 on graphene[6] which has the value of 9.8 meV. Factors affecting the diffusivity of H_2 on these materials are also considered. The structure of silicene is buckled, unlike graphene with a planar structure, affects the

behavior of H_2 on its surface. This buckling breaks the symmetry of the silicene causing ripples on the surface [19]. The difference in the binding energy of both materials may affect the diffusivity of H_2 . Silicene has shown a greater binding energy of 94 meV [20] than that of graphene, 25 meV per H_2 molecule.

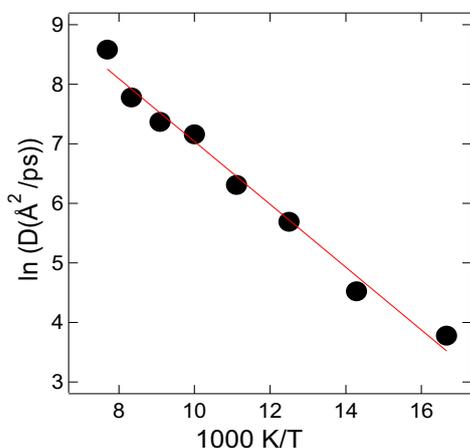


Figure 5. The temperature dependence of the diffusion coefficient of H_2 on SiNR.

Based on our calculations, H_2 tends to be more stable on silicene than in graphene. H_2 is less likely to be diffused on the SiNR surface perhaps due to its buckled structure which may affect the interaction by increasing the activation energy barrier for diffusion through the change in the parameters of the Lennard-Jones potential. This calculation may be of help to some possible applications of silicene like hydrogen sensor since it has higher sensitivity on H_2 as compared to other gases or a hydrogen separator[21]. This could also be seen in the anomalous increase of the thermal conductivity of silicene as the number of hydrogen increases on the surface of silicene.[22]

Since the production of a free-standing silicene is still experimentally impossible, it is now a challenge as to how will we unlock more properties of silicene that will support its production and application when the time comes when all the impossibilities become a possibility.

4 Summary

The diffusion of H_2 molecule on the surface of silicene was investigated using the classical molecular dynamics simulation in LAMMPS. Various temperatures ranging from 60K-130K were introduced during the simulation to record of the Δx displacement of H_2 on the SiNR surface. The Δx displacement shows the Brownian motion on a Lennard-Jones potential. Through the Δx displacement, a Gaussian probability distribution can be plotted describing the diffusion of the H_2 molecule. At lower temperatures, there is a high probability that H_2 can found at its original

position, and with increasing temperatures, there is a low probability that H_2 can be found and diffuses randomly away from its original position. A linear fit is plotted from the average MSD showing that it increases in time. The diffusion coefficients were calculated and the activation energy barrier for diffusion has been found to be 43.23meV. With this investigation, a need arises as to till more ground in the study of H_2 interaction on silicene for its future applications considering that the production of a free-standing silicene is still experimentally impossible at present.

Acknowledgment

The authors would like to acknowledge the Department of Science and Technology (DOST) of the Republic of the Philippines through the Accelerated Science and Technology Human Resource Development Program (ASTHRDP) for the financial support and Dr. Eli Christopher Enobio of Tohoku University for his scholastic support.

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