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 displacement of H₂ on the surface SiNR shows a Brownian motion 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 graphenepresented 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−Ax displacement shows a Brownian motion on a Lennard-Jones potential and by employing the Ax displacement, the diffusing H₂ molecule is described by the plot of Gaussian probability distribution. From the MSD calculations, the diffusion coefficients have increased in time and the
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],

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

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

The simulation box for the silicene has a periodic boundary condition. The dimension of SiNR is 50 Å × 50 Å, a square nanoribbon which contains 418 atoms which lie flat on the simulation box and placed at \( z = 5 \text{ Å} \) due to its buckled structure. The hydrogen atoms were placed 2.454 Å[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).](image)

The simulation uses an NVT ensemble and a Brensen 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 \( 1 \times 10^5 \) steps to equilibrate the system and another \( 1 \times 10^8 \) 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), \( \langle r^2(t) \rangle [15-16] \),

\[ D = \frac{1}{4} \lim_{t \to \infty} \frac{\langle r^2(t) \rangle}{t} \quad (2) \]

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

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

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]

\[ D = D_0 e^{-\frac{E_a}{kT}} \quad (4) \]

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 \( \Delta x \) 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 \( \sigma \) is the standard deviation and \( \mu \) is the mean.
3 Results and Discussion

![Graph of Δx displacement](image1)

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 diffuse 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.

![Graph of Gaussian distribution](image2)

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.

![Graph of MSD evolution](image3)

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 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>
<thead>
<tr>
<th>Temperature(K)</th>
<th>Diffusion Coefficient (Å$^2$/ps)</th>
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<tbody>
<tr>
<td>60</td>
<td>43.76</td>
</tr>
<tr>
<td>70</td>
<td>91.99</td>
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<td>2392.27</td>
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<td>130</td>
<td>5324.11</td>
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Table 1. The data of the diffusion coefficient for the hydrogen diffusion on SiNR at various temperatures.

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\textsubscript{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\textsubscript{2}. Silicene has shown a greater binding energy of 94 meV [20] than that of graphene, 25 meV per H\textsubscript{2} molecule.

Figure 5. The temperature dependence of the diffusion coefficient of H\textsubscript{2} on SiNR.

Based on our calculations, H\textsubscript{2} tends to be more stable on silicene than in graphene. H\textsubscript{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\textsubscript{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\textsubscript{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 the \(\Delta x\) displacement of H\textsubscript{2} on the SiNR surface. The \(\Delta x\) displacement shows the Brownian motion on a Lennard-Jones potential. Through the \(\Delta x\) displacement, a Gaussian probability distribution can be plotted describing the diffusion of the H\textsubscript{2} molecule. At lower temperatures, there is a high probability that H\textsubscript{2} can be found at its original position, and with increasing temperatures, there is a low probability that H\textsubscript{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 43.23 meV. With this investigation, a need arises as to till more ground in the study of H\textsubscript{2} interaction on silicene for its future applications considering that the production of a free-standing silicene is still experimentally impossible at present.

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References