The effect of temperature and pressure on nitrogen adsorption in amorphous silica

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Abstract. Nitrogen is an element that is widely found in nature can be used as a gas that is absorbed to help characterize materials, especially on the surface of the material. According to Brunauer–Emmet–Teller (BET) is a theory where nitrogen is used as a gas characterizing material because of its ability to high purity and can interact with solid elements and inert. BET can only produce quantitative data and does not show adsorption phenomena. Molecular dynamics simulation is conducted to observe the phenomena during nitrogen adsorption in amorphous silica, a porous material with a large surface area. In this study, the molecular dynamics simulations are arranged in a state of isotherm, where the temperature used is three variables: 77 K, 100 K, and 150 K in the variation of pressure used 1, 3, 5, 7, and 10 atm for each equilibrium. In molecular dynamics simulation to simulate the interaction between atoms based on Coulomb force is using Lennard-Jones Potential. Based on the simulation results obtain, it was found that at 77 K temperature had the optimal ability to adsorb nitrogen compared to 100 K and 150 K. The higher the pressure given in the system, it will increase the amount of nitrogen adsorbed.

1. Introduction

The Brunauer Emmet Teller (BET) method is still used to calculate porous materials surface area despite of advanced developments in computer simulation like adsorbent design, and density functional theory [1, 2]. This method is originated from the work of Brunauer, Emmet, and Teller in the 1930s, they determined the surface area of materials by adopted gas adsorption at 77 K [3, 4]. The adsorption of monolayer gas is in solid state, according to their assumption. Kelvin equation with a correction underlie the use of Nitrogen adsorption. However, it is found that, rather than monolayer coverage, the isotherm that is determined by the BET method is associated with the completion of pore filling [5]. Nevertheless, despite some limitations, the BET method is still used as a method to determine surface area, while understanding of phenomena of adsorption should still be investigated.

Molecular dynamics is a technique that is used to observe the movements of molecules that interact with each other [6, 7]. The movement of this molecule will be affected by the potential formed by the force field of other particles around it. In this study, molecular dynamics simulations can make it easier to see and determine the optimal temperature and pressure where nitrogen can be adsorbed into solids. The solid selected in this study is silica material which is a porous material with a large surface area so that the nitrogen can be adsorbed properly.
Physical adsorption and chemical adsorption are still considered within the framework of density functional theory and quantum mechanics [8]. However, noble gas adsorption (Ar, Ne, Xe) has been investigated successfully using molecular dynamics simulation on graphite surfaces using two-body potentials [9]. In that paper, three body expressions were used along with two body potentials, however three-body calculation is not required. In this paper, we investigate the Nitrogen adsorption of silica which has not been performed before. Our objective is to reproduce the BET method isotherm using molecular dynamics simulation on silica.

The aim of this research is to understand the principle of molecular dynamics that occurs during nitrogen adsorption, finding the ideal temperature for nitrogen adsorption to determine the optimal BET value, studying the effect of temperature variations on the amount of nitrogen adsorbed, and knowing the quantity of nitrogen adsorbed on silica.

2. Research Method

In this study, we are using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). Amorphous silica was built by the inorganic builders, and the nitrogen molecules were modelled in round particles in the Visual Molecular Dynamics (VMD). The Lennard-Jones equation was used to define all interactions that occur in this process. The LJ parameters are used in this study are shown in table 1. The placement of the nitrogen is done randomly but remains close together. At the same time, the placement of amorphous silica particles is carried out regularly in all parts of the cube wall. Weight percent will be obtained as the results. The simulation results that shown from LAMMPS can be visualized to see how many atoms are adsorbed on silica.

| Atom | σ (Å) | ε (kJ/mol) |
|------|-------|------------|
| N    | 3.250 | 0.170      |
| Si   | 3.385 | 0.586      |
| O    | 3.170 | 0.155      |

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

Cross parameter that used to identify the pair coefficient of different atom, that each particle is termed as i and j is known with Lorentz-Berthelot mixing function.

\[ \varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \]  
(2)

\[ \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \]  
(3)

In this study, the simulation conditions were set in some variations in pressure and fixed temperature. The temperature was set to 77 K, 100 K, and 150 K with the variation of the pressure at 1 atm, 3 atm, 5 atm, 7 atm, and 10 atm, and nitrogen was condensed into gaseous form. Equation 4 can calculate the gravimetric calculation of adsorbed nitrogen in silica.

\[ \rho_w = \frac{N_Km_N}{N_{Si}m_{Si}+N_Om_O+N_Km_N} \]  
(4)

N is the number of atoms or molecules, and m is atomic relative masses. In this simulation, to find the amount of nitrogen needed at the specific pressure, we used pressure variations to calculate it by modifying the ideal gas equation.
\[(P + a \left(\frac{n}{V_m}\right)^2)(V_m - n_b) = nRT\] (5)

Van der Waals coefficient for nitrogen is represented in \(a\) and \(b\), while \(R\) is universal gas constant and \(V_m\) is volume of a nitrogen molecule [11]. We can assume that the system is in or near equilibrium, in the way of using equilibrium equations since no non-conservative forces are taken place [12, 13, 14].

3. Result and Analysis

In this molecular dynamic’s simulation, the temperature variations are 77 K, 100 K, 150 K, with variations in pressure at each nitrogen adsorption temperature of 1 atm, 3 atm, 5 atm, 7 atm, and 10 atm. Figures 1, 2 and 3 is showing the mechanism of nitrogen adsorption in 500000 timesteps at various pressure. The red atom represented nitrogen while silica molecules were shown by the blue and white atoms, where the silicon is blue, and the oxygen is a white atom.
Figure 1. Simulation at temperature 77 K (a) Start condition at 1 atm (b) Finish condition at 1 atm (c) Start condition at 3 atm (d) Finish condition at 3 atm (e) Start condition at 5 atm (f) Finish condition at 5 atm (g) Start condition at 7 atm (h) Finish condition at 7 atm (i) Start condition at 10 atm (j) Finish condition at 10 atm
Figure 2. Simulation at temperature 100 K (a) Start condition at 1 atm (b) Finish condition at 1 atm (c) Start condition at 3 atm (d) Finish condition at 3 atm (e) Start condition at 5 atm (f) Finish condition at 5 atm (g) Start condition at 7 atm (h) Finish condition at 7 atm (i) Start condition at 10 atm (j) Finish condition at 10 atm
Figure 3. Simulation at temperature 150 K (a) Start condition at 1 atm (b) Finish condition at 1 atm (c) Start condition at 3 atm (d) Finish condition at 3 atm (e) Start condition at 5 atm (f) Finish condition at 5 atm (g) Start condition at 7 atm (h) Finish condition at 7 atm (i) Start condition at 10 atm (j) Finish condition at 10 atm
The amount of nitrogen in the initial conditions of each pressure varies according to equation 5. From equation 5, we can calculate the amount of nitrogen for the initial condition where the result was in table 2. The nitrogen concentration was calculated in different pressure at every 500000 timesteps. The total running time in each simulation is 500000.

**Table 2.** The initial amount of nitrogen molecules in various pressure.

|     | 1 atm | 3 atm | 5 atm | 7 atm | 10 atm |
|-----|-------|-------|-------|-------|--------|
| 77 K| 33    | 98    | 163   | 229   | 327    |
| 100 K| 25   | 75    | 126   | 176   | 252    |
| 150 K| 16   | 50    | 84    | 117   | 168    |

In table 2, it is shown that the amount of initial nitrogen molecules will increase by the increasing of pressure and shows that the greater the temperature in the simulation will reduce the number of nitrogen molecules involved. This is in accordance with theory of ideal gas equation.

**Table 3.** The nitrogen concentration at 77 K, 100 K, and 150 K on 450000 timestep.

|     | 1 atm | 3 atm | 5 atm | 7 atm | 10 atm |
|-----|-------|-------|-------|-------|--------|
| 77 K| 0.0435499 | 0.152259 | 0.173972 | 0.195676 | 0.48776 |
| 100 K| 0     | 0.087062 | 0.0979341 | 0.119671 | 0.173972 |
| 150 K| 0.0653107 | 0.0761875 | 0.0761875 | 0.0979341 | 0.1522259 |

The capacity of silica in adsorbing nitrogen in this simulation is shown in table 3. We also take a value in each pressure at the same timestep to know the trend at each pressure that were given in table 3. The results were also plotted in figure 4, 5, and 6.

**Figure 4.** Graph of simulation results at the temperature of 77 K (a) Amount of nitrogen concentration (b) Amount of nitrogen concentration at timestep 450000
Figure 5. Graph of simulation results at the temperature of 100 K (a) Amount of nitrogen concentration (b) Amount of nitrogen concentration at timestep 450000

![Figure 5](image1.png)

Figure 6. Graph of simulation results at the temperature of 150 K (a) Amount of nitrogen concentration (b) Amount of nitrogen concentration at timestep 450000

![Figure 6](image2.png)

Figure 7. Total Nitrogen concentration at 77 K, 100 K, 150 K with Pressure at Timestep 450000

![Figure 7](image3.png)

Figure 4 shows the nerve simulation results of the nitrogen concentration advertised at a temperature of 77 K at a pressure of 1, 3, 5, 7 and 10. In figure 7 (a), the amount of nitrogen concentration to timestep is 0 to 50000. It appears that nitrogen adsorbed increasingly large along with the running timestep, which is getting longer. Based on the image, there is an area that shows stable adsorption that occurs on a running timestep indicating material has a maximum capacity to absorb gas or fluid depending on the interactions between the two. The saturation point at a temperature of 77 K occurred at timestep 450000. Figure 7 (b) shows the optimum point of nitrogen concentration that is absorbable in amorphous silica at timestep 450000 where, the most considerable nitrogen concentration adsorption at 10 atm is 0, 48776% Wt.

Figure 5 shows the nitrogen adsorption mechanism's simulation results at a temperature of 100 K at various pressures. Figure 8 (a) shows that the amount of nitrogen concentration in the 500000 timestep shows that at 1 atm, the absence of nitrogen is adsorbed; this can occur because the pressure does not have a strong tensile force to absorb nitrogen. However, generally, the graph tendency shows running timestep, the longer the amount of nitrogen absorbed increases; based on the image, there is a saturation area at a temperature of 100 K occurs at timestep 450000. While figure 8 (b) shows the optimum point of nitrogen concentration absorbed in amorphous silica at timestep 450000, the graph shows the effect of pressure on the concentration of nitrogen that can be absorbed; the higher the pressure during the
adsorption process, the higher the concentration of absorbed nitrogen—the largest nitrogen concentration at 10 atm at 0.173972% Wt.

Figure 6 shows the nitrogen concentration advertised at a temperature of 150 K at a pressure of 1, 3, 5, 7, and 10. Figure 9 (a) shows the amount of nitrogen concentration in the 500,000 timestep, which shows that the adsorbed nitrogen increases the longer the timestep running. Based on the image, an area shows that the adsorption is stable at a running time; this indicates that the material has a maximum capacity in absorbing gas or fluid depending on the interaction between the two regions is called the saturation point or saturation point. The saturation point at 150 K occurs when the timestep is 450000. Figure 9 (b) shows the optimum point of nitrogen concentration that can be absorbed in amorphous silica at timestep 450000. The graph shows the effect of pressure on the nitrogen concentration that can be absorbed, the higher the pressure at when the adsorption process makes the absorbed nitrogen concentration also more significant, it can also be seen the largest nitrogen concentration at 10 atm at a temperature of 150 K at 0.152259% Wt.

Figure 7 explains the relationship of nitrogen concentration to variations in pressure at 77 K, 100 K, and 150 K. The graph shows that the lower temperature tends to absorb more nitrogen. Where it is seen at a temperature of 77 K, the amount of nitrogen absorbed is more than the other temperatures greater than 100 K and 150 K. Therefore, it can be said that the optimal nitrogen adsorption temperature occurs at 77 K. The simulation results can also influence the pressure on nitrogen adsorption, where pressure increases, nitrogen adsorption will also increase. This is in accordance with the literature, which prefers adsorption at high pressure. However, at a pressure of 1 atm at 150 wt %, the absorbed nitrogen is more significant than at 77K and 100K. This can occur because of the unstable bond at the pressure of 1 atm, which causes a strong force capable of absorbing more nitrogen.

4. Conclusion
We had successfully obtained the value of adsorbed nitrogen on silica using VMD as a builder, OVITO as a visualizer, and LAMMPS. Nitrogen adsorption was influenced by pressure according to what we observed. The nitrogen concentration adsorption becomes higher when pressure increase. Our simulation visualizes the fundamental mechanism of nitrogen adsorption by demonstrating the time dependence of adsorption pressure, adsorption, and saturation. The simulated adsorption phenomena were isotherm adsorption type IV as it was done on the non-porous silica and only monolayer adsorption occurred.

At temperatures of 77 K with a pressure variation of 1 to 10 atm, the absorbed nitrogen ranges from 0.0435499% Wt - 0.48776% Wt. At temperatures of 100 K with a pressure of 1 to 10 atm, the absorbed nitrogen ranges from 0% Wt - 0.173972% Wt. At a temperature of 150 K with a pressure of 1 to 10 atm, the absorbed nitrogen ranges from 0.173972% Wt - 0.152259% Wt.

The optimum temperature for nitrogen adsorption in amorphous silica in this simulation is 77 K, with the highest value of nitrogen is 0.48776% Wt. Temperature and pressure are factors that can influence nitrogen adsorption in amorphous silica. The lower the temperature, the ability to absorb nitrogen will be better. The higher the pressure in the system, the bigger the absorbed nitrogen will be.

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