SIMULATING CO₂ ADSORPTION AND DIFFUSION ON A GRAPHITE SURFACE

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ABSTRACT

We performed classical molecular dynamics (MD) simulation to understand the mechanism of CO₂ adsorption and transport on graphite surface. The temperature of the system in our simulation was in the range 300-500K. The simulation data show that there are two layers of CO₂ molecules absorbed on the surface. These two layers have a different behavior. The first CO₂ layer is isolated as it does not exchange molecules with the second layer and is liquid-like, while the second layer exchanges molecules with the gas phase. The layers are separate thermodynamic systems. We use the simple Langmuir model to fit the adsorption isotherm for the second layer. The enthalpy of adsorption is calculated \( \Delta H^0 = -16 \text{ kJ/mol} \). This value is in good agreement with experimental data of adsorption of CO₂ on activated carbon. Along the graphite surface, the diffusion coefficient of CO₂ in the first layer and the second layer are roughly of \( 10^{-11} \text{ m}^2/\text{s}, 10^{-10} \text{ m}^2/\text{s} \) respectively. These values are much smaller than for H₂.

INTRODUCTION

The production of cheap membranes for CO₂ separation is of primary importance for the realization of carbon capture and sequestration technologies. Nano-porous, fibrous, carbonaceous materials are promising candidates from an experimental point of view. In order to make further progress to produce molecular sieve membranes, better knowledge of several issues is needed. Central for good membrane functionality are pore size, surface binding, surface wall transport, pore inlet control, carbon structure and composition.

There are many experimental works and simulations devoted to understand the adsorption of CO₂ on carbon based material such as activated carbon and graphite. The adsorption isotherm of CO₂ on active carbon is well described by several models such as Langmuir, Tóth, Dubinin-Astakhov (D-A), reported values for iso-steric enthalpy of adsorption differ a lot and depend on the sorbent used and the condition of adsorption. Saha et al. reported that heats of adsorption of CO₂ in Maxsorb II and ACF (A-20) material were around -20 kJ/mol. If one uses another untreated activated carbon C3345 material, the heat of adsorption was -14 kJ/mol. Guo et al. reported that the heat of adsorption can vary in the range of (-10 - -28 kJ/mol) depending on the modification condition of the activated carbon material. Himeno et al. also reported an adsorption enthalpy which was in range -16 - -25 kJ/mol) of pure CO₂ on five different commercial activated carbons.

Several theories have motivated the adsorption isotherm of CO₂ on graphite surface and in the slit pores of graphite. Lim et al. presented a Langmuir adsorption model and diffusion coefficient \( (D_s = 10^{-9} - 10^{-10} \text{ m}^2/\text{s}) \) of CO₂ in a narrow pore width \( (H=0.65 - 0.75 \text{ nm}) \) and for temperatures \( T=298 - 318\text{K} \). While Zhou et al. reported these value in wider range of slit pore size \( (H=0.7 - 3.4 \text{ nm}) \) and the values were comparable with Lim et al., Levesque et al. calculated the heat of CO₂ adsorption on activated carbon using Monte-Carlo simulations. The authors discussed the dependence of adsorption enthalpy on the distribution of pore sizes. These works had no distinct CO₂ layers in the pores or on the surface.

This work aims to establish a thermodynamic model for the layers of CO₂ on the graphite surface and find diffusion coefficient for the surface. We use molecular dynamics simulation (see Figure 1) for wide range of temperatures \( (T=300-500K) \)

THEORY AND MODEL

Isotherm adsorption

The reaction between the gas phase and the adsorbed phase on the surface can be written:

\[ \text{CO}_2 \text{(gas)} + \text{graphite} \rightleftharpoons \text{CO}_2 \text{(graphite)} \]  

At equilibrium, the gas chemical potential is equal to the surface chemical potential:

\[ \mu_s = \mu_i \]  

\[ \mu_g = \mu_g^0 + RT \ln \left( \frac{P}{P_0} \right) \]  

where \( \mu_g^0 \) is the standard chemical potential of the gas phase, \( i.e., \) the chemical potential at the reference pressure \( P_0 \).

We may also write the chemical potential for surface as

\[ \mu_s = \mu_s^0 + RT \ln a_s \]  

where \( a_s \) is the activity of the adsorbed phase:
\[ a_i = \frac{C_i}{C_s} \]  
\[ \mu_s^0 = \text{the standard state chemical potential at standard state. It follows from equation 2 that} \]  
\[ \mu_s^0 - \mu^0 = RT \ln \left( \frac{p}{p^0 a_i} \right) \]  
\[ \text{Hence the adsorption equilibrium constant is given by} \]  
\[ K = \left( \frac{p^0 a_i}{p} \right) \]  
\[ \text{If we choose the standard state such that } p^0 = 1 \text{ atm }, \]  
\[ C_s^{'max} = \frac{K_p}{1 + K_p} \]  
\[ K \text{ is the Langmuir equilibrium constant. The van’t Hoff relationship to describe the temperature dependence of } K \]  
\[ K = K_0 \exp \left( \frac{-\Delta H^0}{RT} \right) \]  
\[ \text{where } K_0 \text{ is the pre-exponential factor, and } \Delta H^0 \text{ is the constant iso-steric enthalpy of adsorption. Plotting } K \text{ semi-logarithmically versus } 1/T \text{ gives a linear fit from which the slope } -\Delta H^0 / R \text{ is extracted.} \]

**Surface Excess Densities**

In a thermodynamic description, the surface excess concentration \( C_s \) is determined. From that we can describe the adsorption isotherm by plotting the surface excess density versus the gas pressure. We use the Gibbs surface excess for systems in global equilibrium as described in the book of Kjelstrup and Bedeaux. An interface is considered as a thin layer between phases. We restrict ourselves to surfaces parallel to the graphite surface, so
\[ C_s = \int \left( C_{2nd} - C_{gas} \right) dz \]  
\[ \text{where } C_s \text{ is the surface excess concentration, and } C_{gas}, C_{2nd} \text{ are the concentration of CO}_2 \text{ in the gas and in the second layer, respectively.} \]

**Simulation details**

We performed classical molecular dynamic (MD) simulation with the DL_POLY classic package to understand the mechanism of CO\(_2\) adsorption and transport on the graphite surface. The system consists of a sheet of crystalline graphite and CO\(_2\) molecules. The graphite has hexagonal structure with P63/mmc without any defects. The crystal is constructed from 5 sheets of graphene and contains 4284 carbon atoms. We orient graphene sheets in our simulation box such that the surfaces of the sheets are perpendicular to the \( z \) direction. The size of the box is around 42x51x84 Å\(^3\). We use periodic boundary conditions in all directions. At least ten systems with different number of CO\(_2\) molecules ranging from \( N_{CO2}=50-700 \) were simulated. For each \( N_{CO2} \), simulations were performed at different 10 temperatures in the range 300-500K.

The MD simulation had time steps of 0.001ps. The initial configuration was constructed by randomly distributing of CO\(_2\) molecules above the graphite surface. The system was stabilized during 1000 ps by NVT runs with the Nose-Hoover thermostat. When the system was in the thermal equilibrium, we performed another 1000 ps run with microcanonical ensemble (NVE) to study adsorption and transport properties. The trajectory is printed every 100 time step and stored for further analysis.

**Potential energy interaction**

We fix the graphite layer and use the rigid body model TraPPE for CO\(_2\). The intermolecular potential consist of the long range Columbic interactions handled using the Ewald sum technique\(^{13}\) and the shifted and truncated 12-6 Lennard-Jones (LJ) potential.\(^{13}\)
\[ V_{ij}^{nb} = V_{ij}^{LJ} + V_{ij}^{coulomb} \]  
\[ V_{ij}^{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \]  
\[ V_{ij}^{coulomb}(r_{ij}) = \begin{cases} V_{ij}(r_{ij}) - V_{ij}(r_c), & r_{ij} < r_c \\ 0, & r_{ij} > r_c \end{cases} \]  
\[ \varepsilon_{ij} = \frac{1}{2} \left( \sigma_{ii} + \sigma_{jj} \right) \]
The parameters is taken from the DREIDING and TraPPE force field are listed on Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(\sigma) (Å)</th>
<th>(\epsilon/k_B) (K)</th>
<th>charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (in CO(_2))</td>
<td>2.80</td>
<td>27</td>
<td>0.7</td>
</tr>
<tr>
<td>O (in CO(_2))</td>
<td>3.05</td>
<td>79</td>
<td>-0.35</td>
</tr>
<tr>
<td>C (graphite)</td>
<td>3.34</td>
<td>26</td>
<td>0</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

Two distinct CO\(_2\) surface layers

Figure 2 depicts the distribution of CO\(_2\) molecules along the surface of graphite with system \(N_{CO_2}=700\) at different temperatures. It is shown that there are different regions of CO\(_2\) on the surface. The first adsorption layer is located around 0-5Å, the second adsorption layer is located around 5-12Å and the CO\(_2\) gas above 12 Å. The first layer is well separable from the second, see bar indicated with \(\alpha\). The separation between the second layer and the gas \(\beta\) is less precise. In the first layer, there are two peaks, the higher one is big and correspond to the CO\(_2\) molecule that are parallel to the surface. The second small peak corresponds CO\(_2\) molecules that do not touch completely the surface (the angle surface-C-O is around 30°).

Figure 3. Radial distribution function of CO\(_2\)-CO\(_2\) in different layers

Figure 4. Trajectory plot of CO\(_2\) movement in different layers in time scale of 100ps. Only carbon atom is shown. The dark color is the adsorbed first layer. There is only the second layer exchange molecule with gas phase.

The Langmuir model for the adsorption isotherm

In the previous section we have shown that the first layer and the second layer of adsorbed CO\(_2\) show very different behavior. So we only use the second layer to construct the adsorption isotherm.
Figure 5. CO\textsubscript{2} adsorption isotherm on graphite surface at selected temperatures. The continuous line is the fitted Langmuir model.

Table 2. Langmuir parameters isotherm of CO\textsubscript{2} on graphite

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$C_{\text{max}}^{\text{S}}$ (molecule/nm\textsuperscript{2})</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>13.2</td>
<td>2.48 \times 10^{-1}</td>
</tr>
<tr>
<td>320</td>
<td>12.2</td>
<td>1.53 \times 10^{-1}</td>
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<td>350</td>
<td>10.5</td>
<td>1.08 \times 10^{-1}</td>
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<td>380</td>
<td>9.6</td>
<td>5.74 \times 10^{-2}</td>
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<tr>
<td>400</td>
<td>9.1</td>
<td>4.57 \times 10^{-2}</td>
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<tr>
<td>420</td>
<td>8.7</td>
<td>3.65 \times 10^{-2}</td>
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<td>450</td>
<td>7.9</td>
<td>2.49 \times 10^{-2}</td>
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<tr>
<td>480</td>
<td>6.8</td>
<td>2.06 \times 10^{-2}</td>
</tr>
<tr>
<td>500</td>
<td>6.4</td>
<td>1.82 \times 10^{-2}</td>
</tr>
<tr>
<td>550</td>
<td>5.6</td>
<td>1.27 \times 10^{-2}</td>
</tr>
</tbody>
</table>

The Langmuir model can be fitted quite well to experimental adsorption isotherms for CO\textsubscript{2} on activated carbon.\textsuperscript{2} We extended the number of CO\textsubscript{2} molecules to 2000 in an additional calculation to see if we could obtain more than two adsorbed layers. However the system formed only two layers as in Figure 2. The Langmuir model was chosen to fit our data. The isotherms are presented in Figure 5. The excess surface adsorption of the second layer reaches a plateau when the pressure increases. This type of adsorption is typically for a CO\textsubscript{2} isotherm not only on graphite, activated carbon but also on other material such as zeolite, MOF, COF, etc.

The parameters for Langmuir equation 8 are presented in Table 2. The maximum excess adsorption decreases when the temperature increases (Figure 6).

A plot of the logarithm of the equilibrium constant K versus the inverse temperature is given in Figure 7. The dependence is linear and from the slope, a value of the isosteric enthalpy of adsorption $\Delta H^0 = -16$ kJ/mol is obtained. This value is typical for physisorption and in the range (-10.5, -28.4 kJ/mol) of experimental data of adsorption of CO\textsubscript{2} on activated carbons.\textsuperscript{3,7,15}

Surface self-diffusion

We limited our study to the self-diffusion of adsorbed CO\textsubscript{2} on the surface. This gives an important contribution to the transport of CO\textsubscript{2} inside the slit pores. The self-diffusion coefficient of molecule can be obtained from:

$$D_i = \lim_{t \to \infty} \frac{1}{2dN_i} \sum_{i=1}^{N_i} \left[ \left( \vec{r}_i(t) - \vec{r}_i(0) \right)^2 \right]$$

(16)

where $d$ is the dimensionality (for surface $d = 2$), $N_i$ is the total molecules, $\vec{r}_i(t)$ and $\vec{r}_i(0)$ is the position of molecule at time $t$ and time initial.

By plotting the logarithm of the diffusion coefficients found versus the inverse of temperature, we obtained an Arrhenius plot. This was used to estimate the temperature dependence of the diffusion coefficient according to

$$D(T) = D_0 \exp \left( -\frac{E_{\text{act}}}{k_B T} \right)$$

(17)
where $D_0$ is the pre-exponential factor, $k_B$ is the Boltzmann constant, and $E_{\text{act}}$ is the activation energy.

**CONCLUSION**

In this work, we have used Equilibrium Molecular Dynamics to study the adsorption isotherm and diffusion of CO$_2$ on a graphite surface. The results show that there are two CO$_2$ adsorbed layers. The two layers have very different diffusion and exchange possibilities with the gas phase. A simple Langmuir model was used to fit the isotherm of the second layer. The heat of adsorption was estimated ($\Delta H^\circ = -16$ kJ/mol). The rate of self-diffusion of CO$_2$ on graphite ($\sim 10^{-10}$ m$^2$/s) is small compared to H$_2$ adsorbed ($\sim 10^{-7}$ m$^2$/s) and CO$_2$ dense gas ($\sim 10^{-9}$ m$^2$/s). These results of the equilibrium system form the basis for further studies of non-equilibrium properties of pure CO$_2$ and mixture CO$_2$/H$_2$ systems.

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