

# Analyzing Adsorption Behavior Using Grand Canonical Monte Carlo (GCMC)

Bridget Ferris

November 2024

## 1 Introduction

We are a chemical company that produces ammonia using the Haber-Bosch process. The company is interested in understanding the competitive adsorption of nitrogen and hydrogen on the catalyst surface to optimize the reaction conditions. The goal of this study is to simulate the adsorption behavior of nitrogen and hydrogen on a 2D lattice and analyze the effects of varying chemical potentials and interaction energies.

Grand Canonical ensemble is defined as an open system in thermal and chemical equilibrium. That is, there is an exchange of energy and particles present; however, chemical potential, volume, and temperature are kept constant. Grand Canonical Monte Carlo (GCMC) simulations will be used to model the competitive adsorption of nitrogen and hydrogen on a 2D square lattice. While varying the chemical potential of hydrogen ( $\mu_H$ ), the chemical potential of nitrogen ( $\mu_N$ ) will be held constant because nitrogen is in excess in the reaction. The exact values of the adsorption and interaction energies are currently unknown, a range of parameters will be explored in this study to understand the system's behavior. Phase diagrams and coverage plots showing the overall and precise coverage of nitrogen and hydrogen on the surface are presented and the affects of different parameters on adsorption behavior will be analyzed. This report summarizes these findings and discusses the implications of the results on the ammonium synthesis process.

## 2 Adsorption Behavior of Nitrogen & Hydrogen Under Different Conditions: Results

Since the system's behavior regarding adsorption is unknown, a series of different tests were run to explore several different parameters, changing adsorption and interaction energies between the molecules. Variables that were held between all simulations are listed below.

Variable	Value/Range
$\mu_H$	-0.2 - 0 eV
$\mu_N$	-0.1 eV
$T$	11.6 - 220.5 K
Lattice Size	4 * 4
# of steps	1000

Values that are ranges sample over a set of values and provided graphs show the range of sampling as stated above. To state again  $\mu_H$  is varied while  $\mu_N$  is held constant because nitrogen exist in excess during the ammonium production. In the lattice model, total energy is given as:

$$E = \sum_i (n_i^H \epsilon_H + n_i^N \epsilon_N) + \frac{1}{2} \sum_{i,j} (n_i^H n_j^H \epsilon_{HH} + n_i^N n_j^N \epsilon_{NN} + H n_i^H n_j^N \epsilon_{HN} + n_i^H n_j^N \epsilon_{HN}) \quad (1)$$

where  $\epsilon$  represents adsorption and interactions energies of the species (specified in simulations). When analyzing figures shown, coverage plots show an example of what one specific phase diagram would look like at a given  $\mu_H$  and  $T$ . Blue dots represent nitrogen coverage and red dots represent hydrogen coverage. Though phase diagrams give a better understanding of the overall system, coverage plots are important to understand where on a surface a molecule is binding in comparison to other molecules on the surface rather than just a percentage of coverage over the whole space. This gives important insight in relation to interaction energies.

## 2.1 Ideal Mixture of Nitrogen & Hydrogen

First, an ideal mixture of hydrogen and nitrogen on the surface was considered. Thus, the adsorption energies for both hydrogen and nitrogen are -0.1 eV and there are no interaction energies between the molecules. These energies are tabulated below. Results of this simulation are shown in Figure 1.

Energy	Value
$\epsilon_H$	-0.1 eV
$\epsilon_N$	-0.1 eV
$\epsilon_{HH}$	0 eV
$\epsilon_{NN}$	0 eV
$\epsilon_{HN}$	0 eV

In this scenario, when  $\mu_H$  is less than -0.1 eV there is no coverage on the surface and nitrogen covers between 30-40% of the surface space. When the chemical potentials are equal, there is approximately equal coverage of both species, leading to a total coverage of 70%. It is clear once  $\mu_H$  is larger than  $\mu_N$  it quickly covers the entire surface. This happens more quickly at lower temperature because the nitrogen is more adsorbed onto the surface, versus at high temps the hydrogen can more easily desorb from the surface allowing nitrogen to take its place. Based on coverage plots, there does not seem to be a pattern of where the particles are more or less likely to adsorb to.

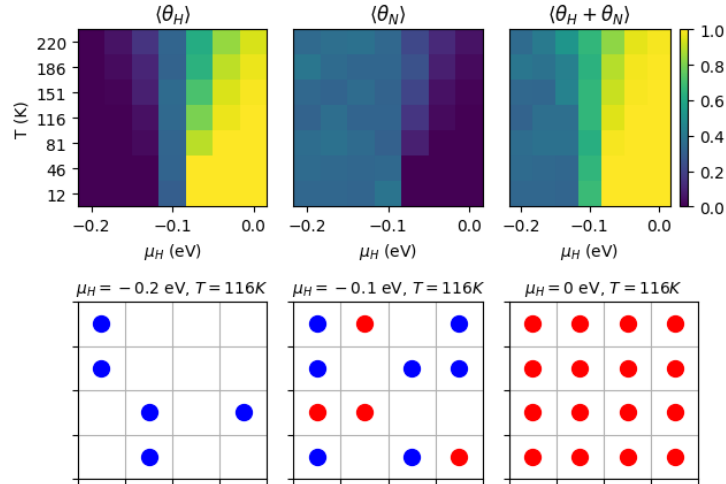


Figure 1: Phase diagrams and coverage plots under ideal mixture conditions

## 2.2 Repulsive Interactions between Nitrogen & Hydrogen

Next, we considered a model in which the nitrogen and hydrogen particles repel each other. To do this, adsorption energies were kept the same, but the interaction energies were made to be slightly positive, repelling the molecules from each other. These values are tabulated below. Results of this simulation are depicted in Figure 2.

Energy	Value
$\epsilon_H$	-0.1 eV
$\epsilon_N$	-0.1 eV
$\epsilon_{HH}$	0.05 eV
$\epsilon_{NN}$	0.05 eV
$\epsilon_{HN}$	0.05 eV

First, consider the coverage plots. Due to the repulsive forces between the molecules, when a molecule is present in a specific position on the lattice, there appears to be no scenario when another molecule appears in one of the 4 neighboring positions. Because of this, total coverage does not surpass 50%. Otherwise, a similar pattern follows the ideal mixture results, which is only nitrogen coverage at low  $\mu_H$ , approximately equal coverage at  $\mu_H = \mu_N$  and only hydrogen coverage at high  $\mu_H$ ; however, all coverage percentages are cut in half.

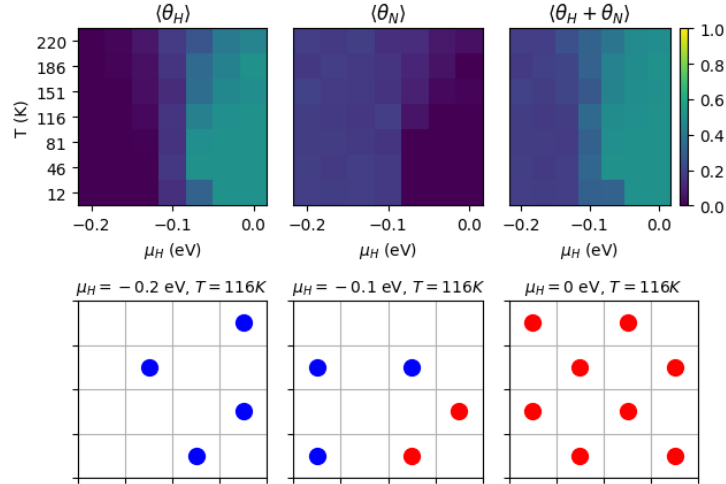


Figure 2: Phase diagrams and coverage plots with repulsive interactions present between nitrogen and hydrogen.

### 2.3 Attractive Interactions between Nitrogen & Hydrogen

In the next model, the signs of the interaction energies were swapped to determine what would occur under attractive forces between hydrogen-hydrogen, and nitrogen-nitrogen, and hydrogen-nitrogen. Values used are tabulated below and the results are shown in Figure 3.

Energy	Value
$\epsilon_H$	-0.1 eV
$\epsilon_N$	-0.1 eV
$\epsilon_{HH}$	-0.05 eV
$\epsilon_{NN}$	-0.05 eV
$\epsilon_{HN}$	-0.05 eV

The first evident difference between this scenario and the previous 2 is that there is always fully coverage of the surface. Additionally, in this model there is an overall equal coverage of both hydrogen and nitrogen over multiple temperatures and chemical potentials. There does seem to be a slightly lower coverage of hydrogen at low  $\mu_H$ , which is as to be expected considering  $\mu_N$  is higher. The coverage plots show a full coverage in every state and there is no pattern in what is likely to be in the neighboring positions of a certain molecule since interactive energies between the the same molecule and a different molecule is the same.

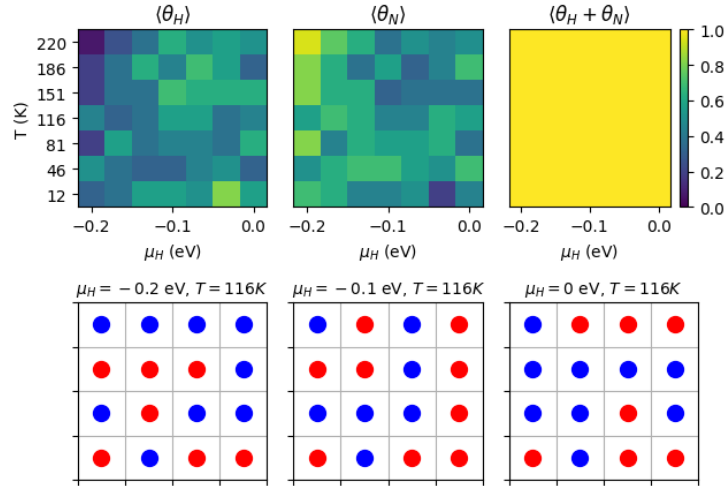


Figure 3: Phase diagrams and coverage plots with attractive interactions present between nitrogen and hydrogen.

## 2.4 Immiscible Nitrogen & Hydrogen

Immiscible is defined as not being able to form a homogeneous mixture of the nitrogen and hydrogen. That being said, there is an attractive interaction between nitrogen-nitrogen and hydrogen-hydrogen; however, the nitrogen-hydrogen interaction is repulsive. These values are tabulated below. The phase diagrams and coverage plots for this simulation are shown in Figure 4.

Energy	Value
$\epsilon_H$	-0.1 eV
$\epsilon_N$	-0.1 eV
$\epsilon_{HH}$	-0.05 eV
$\epsilon_{NN}$	-0.05 eV
$\epsilon_{HN}$	0.05 eV

It is clear from the coverage plots a homogeneous mixture of both hydrogen and nitrogen is not achieved, following the definition of immiscible. Similar to the attractive interactions, full coverage of nitrogen is over all 3 values of  $\mu_H$  due to the positive values for  $\epsilon_{HH}$  and  $\epsilon_{NN}$ . At equal chemical potentials, however, there continues to be full coverage of nitrogen on the surface at the temperature measured on the coverage plots. This is because the interaction between the same atoms is much stronger than between hydrogen and nitrogen reactions, which is repulsive. Finally, when the chemical potential for hydrogen is higher, there is a chance that coverage fully changes to hydrogen, or as shown in this simulation there is half coverage of both. The pattern occurs by rows where the rows are all the same color because it is more favored to have more neighbors that are the same molecule versus different.

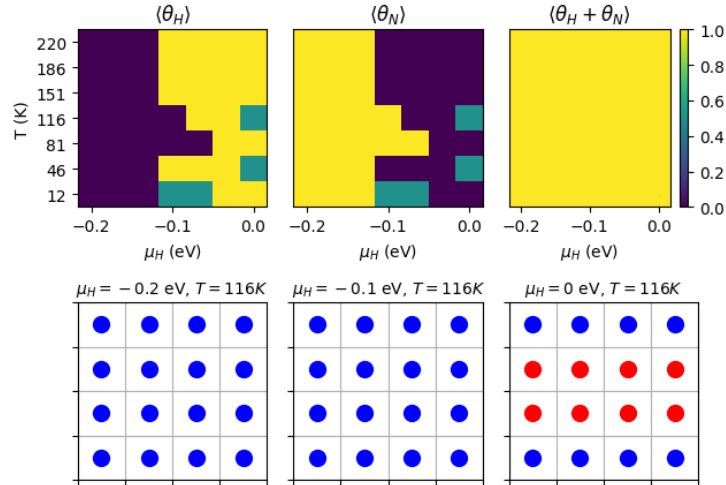


Figure 4: Phase diagrams and coverage plots under immiscible conditions.

## 2.5 "Like Dissolves Unlike" Scenario

The final simulation measured was a 'like dissolves unlike' simulation, which is the opposite of immiscible conditions. This means it is more likely more a given molecule to have opposing neighbors. Values are tabulated below. Results (coverage plots and phase diagrams) from the shown in figure 5.

Energy	Value
$\epsilon_H$	-0.1 eV
$\epsilon_N$	-0.1 eV
$\epsilon_{HH}$	0.05 eV
$\epsilon_{NN}$	0.05 eV
$\epsilon_{HN}$	-0.05 eV

In this final simulation, there again is a full coverage of the surface over all chemical potentials for hydrogen. The difference between this simulations is that there always is half coverage of both species no matter the temperature and chemical potential and they all possess a similar pattern. The pattern that arises is that  $\geq 3$  neighbors of a given species is the other species i.e. at least 3 atoms surrounding a nitrogen must be hydrogen and vice versa. This is a believable simulation because 'like dissolves unlike' implies that unlike molecules will be aligned with each other on the surface.

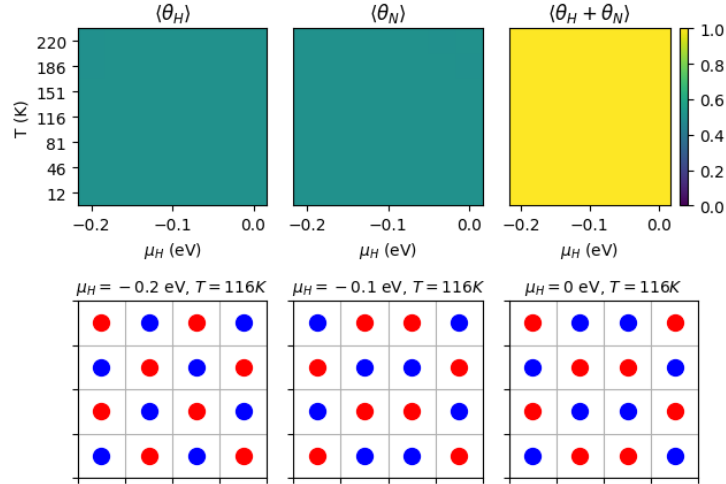


Figure 5: Phase diagrams and coverage plots under a "like dissolves unlike" scenario.

### 3 Adsorption Behavior Analysis

Though hydrogen and nitrogen adsorption is analyzed for each simulation in Section 2, it is important to further analyze why these differences present between the simulations.

#### 3.1 Temperature and Chemical Potential of Hydrogen

Varying temperature and chemical potential of hydrogen affect adsorption in differing ways. First, consider temperature. The probability distribution function for a grand canonical ensemble relates to temperature:

$$P(n_i^H, n_i^N) \propto e^{\frac{-E + \mu_H N_H + \mu_N N_N}{k_b T}} \quad (2)$$

where the number of adsorbates H and N are denoted as  $N_H$  and  $N_N$  respectively. Since there is an inverse temperature value in an exponential, it can be inferred that the probability distribution widens at higher temperatures, thus there is more variation of the possible states at higher temperatures. This follows patterns in simulations 1 and 2 because nitrogen stays adsorbed for longer as  $\mu_H$  increases at higher temperatures compared to lower temperatures.

Next consider chemical potential of hydrogen. Since  $\mu_N$  was kept constant at -0.1 eV and  $\mu_H$  varies between -0.2 eV to 0 eV the affects of having higher, lower, and equal chemical potentials can be examined. First, when  $\mu_N > \mu_H$  there is consistently more coverage on nitrogen on the surface compared to oxygen (with an exception of simulation 5, being always equal and some temperatures for simulation 3). This matches what is expected to minimize the grand potential ( $\Omega$ ) to thermal equilibrium:

$$\Omega = E - \mu_H N_H - \mu_N N_N \quad (3)$$

Similarly, coverage of hydrogen increases for all simulations (excluding 5 and some of 3) once  $\mu_H$  is increased to a value greater than -0.1 eV. This equation can easily explain the trends seen in all simulations; however, it does not always come out exact. For example, Figure 4 shows full coverage of nitrogen when  $\mu_H$  and  $\mu_N$  are equal when it would be expected to have half coverage. This is due to the randomness added into either removing or adding a particle in a given position in GCMC.

#### 3.2 Comparing Parameter Sets

When comparing parameter sets, it is important to consider overall coverage. It is noticed that simulations 3, 4, and 5 have full coverage over all  $\mu_H$  and  $T$  values, which is not true for an ideal mixture or repulsive interactions (simulations 1 and 2). This is clear for repulsive interactions because it is favored to have empty neighbors to a given particle (all interaction energies are positive). Similarly for the ideal mixture, there is no energy associated with interactions between particles so there is no 'force' making it more likely for particles to adsorb to



the surface, which is present in the other 3 simulations. From this, it can be concluded that any negative interaction energies will lead to full coverage of the surface.

Next, we can also compare the pattern of neighbors in the simulations. For simulations 1 and 3 there is not a pattern in what neighbor is more favored. This is because interaction energies are all the same for both of these simulations. Though simulation 2 also has all the same interaction energies, because they are repulsive there are no neighbors for any of the particles on the surface. For simulations 4 and 5, there are opposing patterns between the neighbors. In simulation 4, particles tend to favor being next to each other so the neighbors are more likely to be itself. Conversely, simulation 5 flips the sign for all interaction energies compared to simulation 4 therefore it is much more likely for the neighboring particles to be of opposing character.

Finally, consider the shift of hydrogen coverage over  $\mu_H$ . Simulations 3 and 5 have no clear pattern of this change and both see a coverage that averages to 50%. This is because the interaction energies between the particles keep them together, allowing hydrogen to adsorb even at low values of  $\mu_H$ . Simulations 1, 2, and 4 all have a clear shift towards increased hydrogen coverage after surpassing  $\mu_N$ . This pattern, in addition to equation (3) show how chemical potential affect the system (see section 3.1).

### 3.3 Implications for Ammonium Synthesis

In the Haber-Bosch process, ammonium is produced by combining nitrogen and hydrogen utilizing a catalyst under high pressure, thus efficient adsorption of both species is vital. Understanding these scenarios can help give insight into what parameters will best fit industrially. We will consider if all simulations were true and what parameters would be best:

- Ideal: any temperature with  $\mu_H = \mu_N$ .
  - This is the only case where there is coverage of both species on the surface.
  - At high  $\mu_H$  the surface can become hydrogen poisoned.
  - At low  $\mu_H$  there is no coverage of hydrogen on the surface.
- Repulsive: any temperature with  $\mu_H = \mu_N$ 
  - Hard to optimize for ammonium synthesis due to the particles not being able to come next to each other on the surface.
  - Only case where both particles adsorb at similar rates is when the chemical potentials are equal.
- Attractive: Any temperature or  $\mu_H$ 
  - Ideal conditions for ammonium production. Approximately equal coverage of both particles over the full simulation.

- Immiscible: N/A
  - There is no ideal situation for this model. Though there are some cases where there is half coverage of both, it is much more likely for the surface to be poisoned by nitrogen or hydrogen no matter  $\mu_H$ .
- "Like Dissolves Unlike": Any temperature or  $\mu_H$ 
  - Ideal conditions for ammonium production. Exactly equal coverage of both particles over the full simulation.

Optimizing certain characteristics can help influence and thus increase the production of ammonium. Specifically, a goal present is to limit poisoning of the surface by one molecule and thus allow for co-adsorption to persist. Poisoning by hydrogen occurs in simulations 1 and 4 and poisoning by nitrogen occurs in simulation 4. Depending on  $\mu_H$ , modifying the catalytic surface to limit hydrogen/nitrogen adsorption to allow for both molecules to adsorb and produce ammonium can increase the production rate. Simply put, if simulation 1 or 4 represent that behavior of hydrogen and nitrogen changing the character of the catalytic surface to represent the like simulations 3 or 5 will greatly increase of production of ammonium.

## 4 Conclusion

Understanding the adsorption characteristics under different interaction energies will help our company determine what simulations best provide for optimizing the Haber-Bosch process. Attractive Interactions and "Like Dissolves Unlike" efficiently achieve co-adsorption. Contrastingly, Ideal Mixture and Immiscible simulations show poisoning of the surface or phase shift patterns, thus adjusting the catalytic surface to more similarly fit co-adsorption will thus increase ammonium production. Implementing different strategies using industrial measures to implement co-adsorption will be important for the company's success.