Dmitriy Kats
Monte Carlo Simulations of Hydrogen on Surface of Palladium
05/22/2018

The objective of this project is to use the simple two-dimensional Ising model to explore and visualize many of the aspects of phase transformations.

Energy Model:
A Monte Carlo simulation accepts a trial perturbation if the energy decreases due to the perturbation, and accepts the perturbation that increases energy with probability (p) proportional to exp(-energy/kT). Thus, all Monte Carlo simulations need an energy model. The Ising model will be used.

Configuration of lowest energy: $\theta = \frac{1+<\sigma>}{2}$ $E = \frac{1}{2}\sum_{ij}^{NN} V_1\sigma_i\sigma_j + \frac{1}{2}\sum_{ij}^{NNN} V_2\sigma_i\sigma_j - \mu\sigma_i$

Consider the 6x6 grid as a representative case study of the optimal configuration.

+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+
+	-	+	-	+	-
-	+	-	+	-	+

The energy will be calculated based off the middle point with $\mu = 0, V_1 = 1, \& V_2 = -2$ to ease analysis. Only the sign of the spin is drawn below.

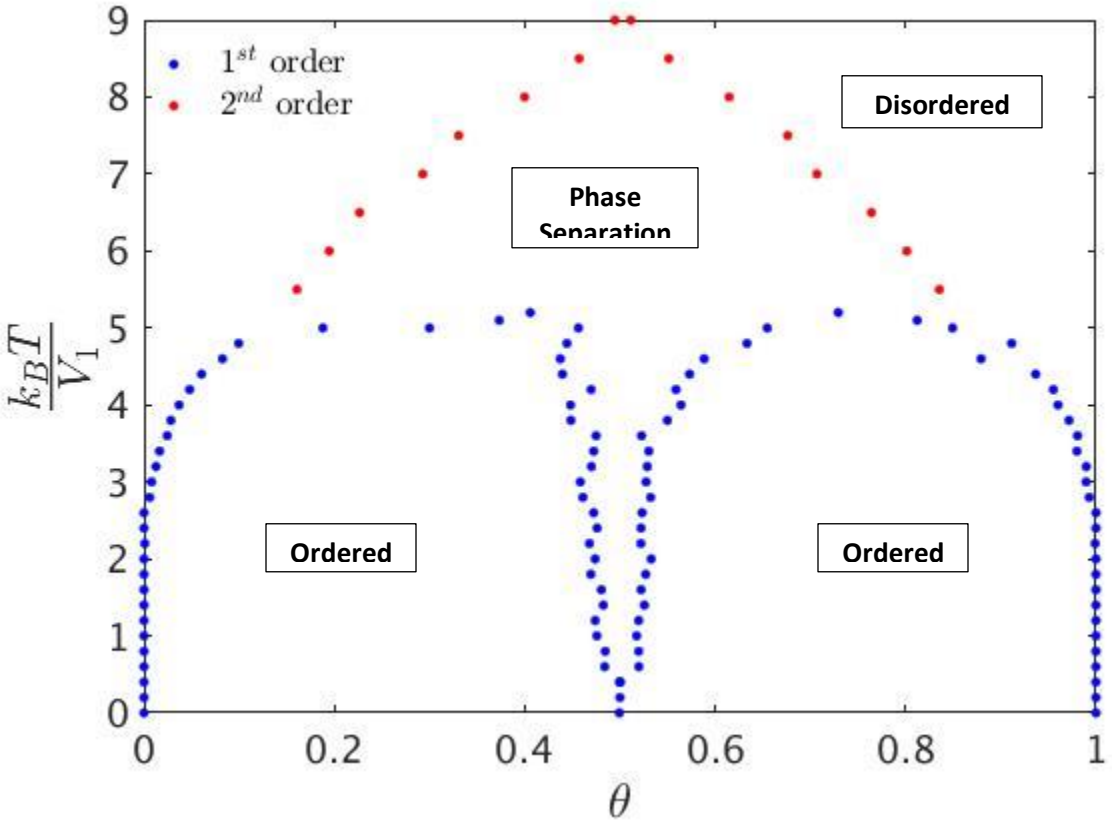
$$\theta = \frac{1}{2} \quad E = \frac{1}{2}(-4) - (4) = -6$$

In order to minimize the energy, the nearest neighbors need to be all negative since the sign of V_1 is positive and the next-nearest neighbors need to be positive since the sign of V_2 is negative. Flipping a positive and negative sign from the optimal configuration will lead to an energy higher than -6. To show how the energy cannot get any smaller, the signs can be flipped. As an extreme case, all the signs are flipped below and energy is no longer minimized.

$$\begin{matrix} - & + & - \\ + & + & + \\ - & + & - \end{matrix} \quad \theta = \frac{1}{2} \quad E = \frac{1}{2}(4) - (-4) = 6$$

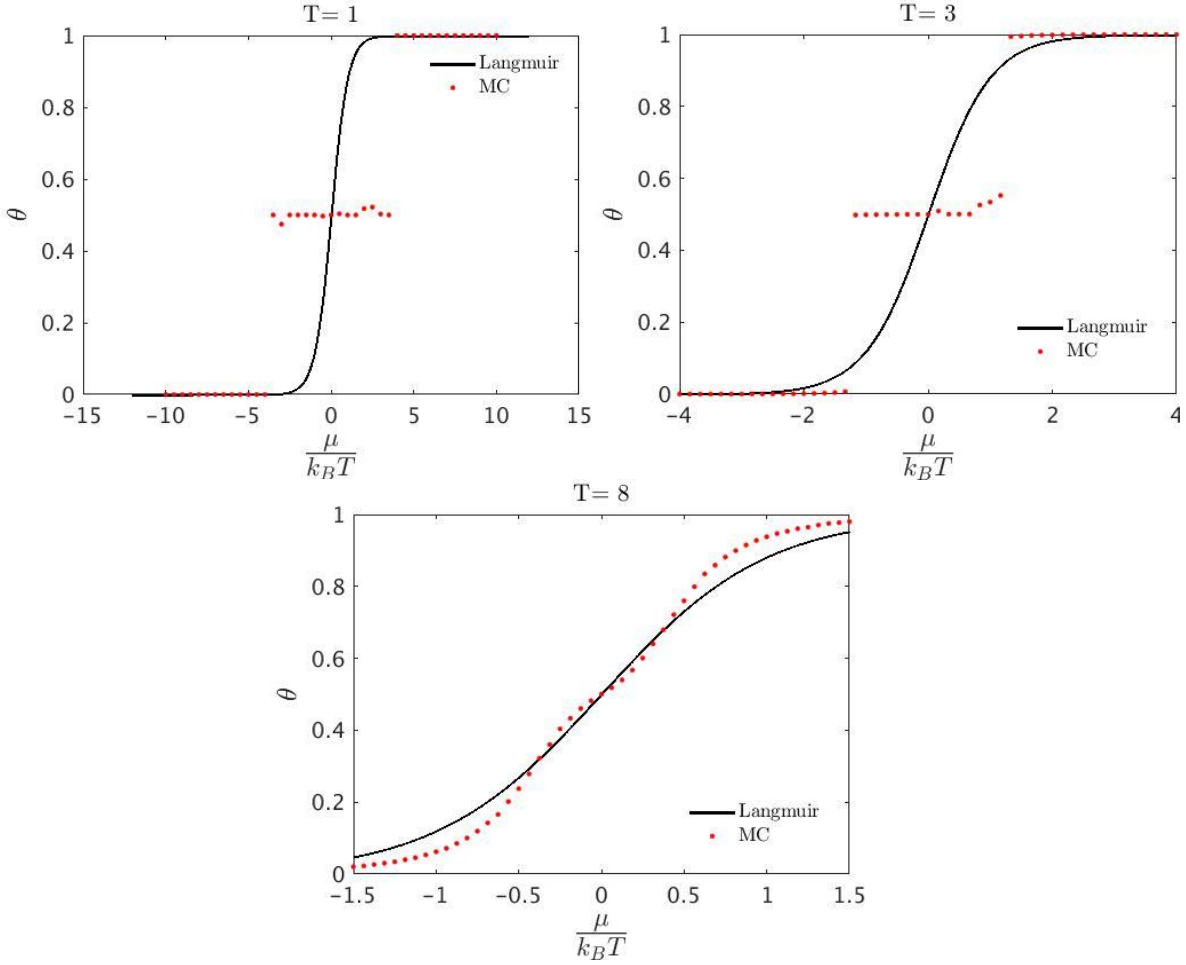
Phase diagram determination:

The phase diagram for the adsorbate system is below. The parameters used for the simulation were $V_1 = 1, V_2 = -2, k_B = 1$. The μ values considered were between [-5, 5] and the temperature values ranged from [0, 9]. The first order transition were detected as discontinuities in the average spin as a function of μ. The second order transition were detected as discontinuities in the plot of Cv vs T. The points determined by first order transitions are in blue and the points determined by second order transitions are in red.



Coverage:

The plot of coverage versus $\frac{\mu}{k_B T}$ for a few interesting temperatures are below. The plot is made for a fixed T value. The comparison to Langmuir's isotherm $\ln\left(\frac{\theta}{1-\theta}\right) = \frac{2\mu}{k_B T}$ is also made. There is some agreement between the Ising model results and the Langmuir's isotherm especially around $\theta = 0.5$ because the mean-field approximation is pretty good here. For higher temperature, the agreement improves. The disagreement is due to the fact that the Langmuir's isotherm uses a mean-field approximation, while the Ising model moves away from this assumption by consider the neighbor interactions.



Improvements of Simulation:

Since experimental evidence indicates that the maximum coverage is below $\theta = 0.5$, this means the Hamiltonian needs to be modified to feature multi-body interactions. This can be done with the cluster expansion to capture the extra relevant terms associated with the more complicated interaction of the Pd atoms and H adsorption sites. Adding a third nearest

neighbor term could also help with capturing the relevant physics. The long-range affects may need to be considered.

Simulating a Disordered State:
As the temperature approaches infinity, the Monte Carlo simulation will just randomly flip between adsorbed and not (or in other words ordered and disorder). This can be justified by the probability formula $\left(P = \exp\left(-\frac{\Delta E}{k_B T}\right)\right)$ going to 1 as the temperature going to infinity. This means the flip is always going to be expected because the random number generated is between 0 and 1. Thus the system will constantly flip at all the potential flip sites and there is disorder.

Code commentary:
The code was written in C for speed and ease of running many Monte Carlo simulations in parallel. It takes an input of a single μ and T value. Thus, a bash script was written to run many test cases all at once. The script worked great on 32 processors to get results very quickly. A matlab post processing code is also included.