Adsorption

Adsorption is the process where particles, known as adsorbates, attach to a surface, known as an adsorbent, using intermolecular forces. Adsorption is often used for removing impurities from a chemical process, enriching a system with particles extracted from another system, and catalyzing reactions. Due to being a surface phenomenon, adsorption is more effective when the adsorbent has a high surface area relative to its mass or volume. One commonly used adsorbate is activated carbon, which has an extremely high surface area due to its surface containing many pores as small as 2nm. Different adsorbates absorb in different amounts depending on the adsorbent, temperature, and pressure. Many species of adsorbates can attach to the same adsorbent but will often adsorb in different amounts. The amount of adsorption is typically described using a Langmuir Isotherm, which is a chart that relates the amount of adsorbate per amount of adsorbent, temperature, and pressure. Engineers use these Isotherms for designing chemical processes.

[ Picture of Example Isotherm ]

Statistical Thermodynamics

Simulations of thermodynamic systems are only possible by using assumptions and techniques in Statistical Thermodynamics. “Statistical Thermodynamics” is the field of study where macroscopic thermodynamic properties are modeled as the result of microscopic particles’ mechanistic behavior and probability theory. In a more macroscopic approach of Thermodynamics, a non-ideal gas’s thermodynamic properties would be modeled using an equation of state determined by observing these properties in the environment. A statistical thermodynamic approach like the simulations in this paper would model individual gas particles by aggregating their classical and quantum mechanical equations of motion and determine macroscopic properties.

At any given moment, hereafter referred to as a microstate, a thermodynamic system will have thermodynamic properties and discrete locations of the particles within it. One microstate is not enough to describe the behavior of an entire thermodynamic system as particles are always moving and some macroscopic properties are often allowed to change. However, each property can be determined by taking the average of that property across all possible microstates, known as an ensemble, weighted by the probability of that microstate occurring in nature.

Where:

Often thermodynamic systems are described by what properties are forced to be constant and what properties can change. For example, an adsorption system is focused on the amount of particles moving in and out of the system while the layout of the surface being adsorbed to is held constant. These assumptions restrict the number of possible microstates into ones that match this assumption. While still infinite, the number of microstates and the way their thermodynamic properties are described become more manageable. For this study, the Grand Canonical Ensemble is used, which keeps Volume , Temperature , and Chemical Potential constant while notably allowing for the number of particles to change.

To define a Volume for a given system, it is often helpful for simulations to instead define a small but representative chunk of the system known as a “unit cell.”

[Diagram of unit cell]

This unit cell is periodic in two dimensions for a surface, and three dimensions for a bulk fluid or lattice. Intrinsic properties like Pressure and Mole fraction can be calculated directly from this unit cell. Extrinsic properties like number of particles and volume can be determined by multiplying the amount from the unit cell with the total number of unit cells that comprise the studied system. For the purposes of calculating intermolecular interactions, the distance between two particles in a unit cell is the shortest distance between those two particles allowing for those particles to be repeated in adjacent unit cells.

[diagram of periodicity]

For a unit cell periodic across three dimensions, distance of these particles can be described by:

where for each distance with periodicity:

where is the length of one side of a Unit cell. Volume is described by:

Chemical Potential in this study is set by defining the thermodynamic properties of the reservoir and using an equation of state to calculate its fugacity. To do this, we assume that the system is in thermodynamic equilibrium with a reservoir with Temperature Pressure , and mole fractions . Unless otherwise specified in following experiments, Fugacity is calculated using the Peng Robinson Equation of State as shown in Appendix #.

The potential energy of any given state can be approximated by the sum of all intermolecular potential energies of the particles within it. While many equations are used to calculate this, the Lennard-Jones Potential is by far the most common for simulations of this kind due to its computational simplicity. The potential energy between two particles is described by:

Where is the potential energy between particles and , is the distance between those particles, and are experimentally determined constants for the interactions between the species of those particles.Note that this force-field only applies by assuming each particle as a hard sphere. There are, of course, numerous correction factors and techniques for adapting this assumption that are available for use. Also note that and are particle interaction specific, so Methane-Methane interaction parameters would be different from Carbon-Carbon interaction parameters which would be different from Methane-Carbon interaction parameters. We are approximating these hetero-particle interactions between particles A and B with the Lorenz-Berthelot mixing rules described by:

For a single particle, , the sum of its interactions with other particles in the system is described by:

The sum of all particle interactions is described by:

where .

The total pressure of the system (which is different from the pressure of the reservoir) is often calculated by the Virial Pressure of a system which is defined by:

Where is the intermolecular force exerted on particle from particle . This force can also be determined from the Lennard-Jones potential function:

The probability of a microstate is given by the Boltzmann distribution:

Where is the total energy of the system, is the Boltzmann Constant, and is the Partition Function which is described by:

For a simulation with no time component, kinetic energy can be assumed to be 0. Due to the functionally infinite number of microstates in the Grand Canonical Ensemble, cannot be calculated analytically or estimated. However, since is a constant for a given system, it can be cancelled out when comparing relative probability:

Monte Carlo and the Metropolis Algorithm

For systems too computationally complex to model analytically, simulations can be used instead to model systems empirically. The two most common types of simulations used for Molecular modelling are Monte Carlo (MC) and Molecular Dynamics (MD). For this study of low-density gas particles in an adsorption system at equilibrium, Monte Carlo simulations are the most appropriate. The Monte Carlo method represents a system using a Markov Chain moving from microstate to microstate using stochastic steps. These steps are manifested by minor changes in the system such as the number of particles, position of particles, thermodynamic state variables, and volume for example. An extension of the Monte Carlo method is called the Metropolis Algorithm (later abstracted to the Metropolis-Hastings Algorithm) where each stochastic step is either accepted or declined based on the relative probability of the two states.

For the Grand Canonical Ensemble (Constant the usual moves allowed are movement of a particle to another location in the system, adding a particle to a location within the system, and removing a particle from the system. In this study 50% of trial moves attempted are to move a particle, 25% of moves are attempts to add a particle, and 25% of moves are attempts to remove a particle chosen at random. Similar studies may also incorporate a “swap” move where particles of two different species switch locations within the system.

When attempting to move a particle within the unit cell, an existing particle, i, is chosen at random. Its total potential energy is calculated between it and all other particles and surfaces. A new proposed location is determined by nearby location determined by:

Where is the initial coordinate of the particle, is the new proposed coordinate, is the dimension of the unit cell in that axis direction, is a random number between 0 and 1, and is a measure of distance. may change throughout the simulation to alter the acceptance probability of move actions.

It’s total potential energy is calculated between it and all other particles and surfaces as if it were in the proposed location. The probability of accepting a proposed move action is:

Where , is the potential energy of the particle at the original location, and is the potential energy of the particle at the proposed location.

When attempting to add a particle to the unit cell, a random point anywhere in the unit cell is selected. The total potential energy is calculated as if the particle was at that location between it and all particles and surfaces. The probability of accepting a proposed addition action is:

Where is the fugacity of the species being added.

When attempting to remove a particle from the unit cell, an existing particle is chosen at random. Its total potential energy is calculated between it and all other particles and surfaces. The probability of accepting a proposed removal action is:

For each step of the simulation, one of the above trial moves is proposed at random. For this study, the probability of attempting a move action is 0.5, an addition action is 0.25, and removal action is 0.25.

[ # Swap Move? ]

Assuming the simulation has completed a sufficient enough amount of steps, , where no trends in overall properties are detectable, the steps should occur at the probability described by the Boltzmann distribution (equation ###). This process allows for “Importance Sampling” where microstates are chosen at a relative probability equal to their probability of existing in nature. By using importance sampling, the ensemble average can instead be estimated by:

Where is a sufficiently large number of Markov chain steps taken since equilibration is determined.