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 dimension 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: