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Critical Films on Graphene Substrates

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CRITICAL FILMS ON GRAPHENE SUBSTRATES

A Thesis Presented

by

Renee Beneski

to

The Faculty of the Honors College

of

The University of Vermont

In Partial Fulfillment of the Requirements
for the Degree of Bachelor of Science
Specializing in Physics

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ABSTRACT

When depositing a substance onto a surface, it follows that as one adds more of the substance, the thickness of the film formed on the surface will grow. However, a particle's ability to adsorb onto the surface is dependent on the interaction potential and geometry. For atomically flat two-dimensional materials such as graphene, it is predicted that the interactions between the graphene sheet and light atoms in a nearby gas are so weak that film growth may become arrested at a critical thickness. We report on molecular dynamics simulations of nitrogen near graphene to explore the existence and properties of the predicted critical film.

*To my parents,
who instilled in me that education is the greatest gift a person can receive
and for supporting me on my long and continuing journey to get one*

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CHAPTER 1

INTRODUCTION

1.1 WETTING

Wetting refers to a fluid's ability to maintain contact with a surface. It is driven by competition between particle-particle and particle-substrate van der Waals interactions, where van der Waals interactions refers to weak forces that arise due to uneven charge distributions, leading to momentary attraction or repulsion between molecules. Wetting is traditionally broken down into three cases: no wetting, partial wetting, and complete wetting [1]. The case of no wetting refers to when the particle-particle interactions are significantly stronger than the particle-substrate interactions, resulting in the deposited particles forming a well-defined droplet on the substrate. As consequence, no wetting is extremely uncommon. Conversely, when the particle-substrate interactions dominate the system, the deposited particles adsorb across the substrate, forming a macroscopically thick film. This is the case of complete wetting. Lastly, partial wetting is the case where the particle-particle interactions are on par with the particle-substrate interactions, resulting in a coexistence between the well-

defined droplet of no wetting and the thin film of complete wetting. These three cases are shown schematically in Figure 1.1.

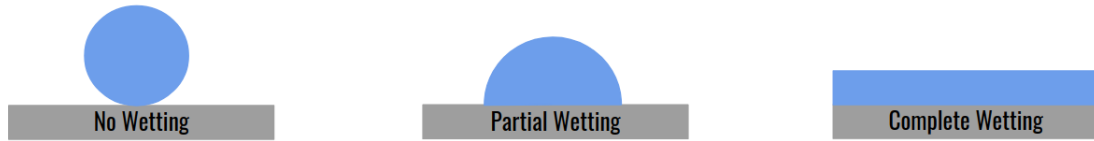


Figure 1.1: Visualization of the three traditional forms of wetting

Understanding wetting goes beyond the question of droplet or thin film. If a thin film does form across the substrate, one must look then at the growth of that thin film. In the case of complete wetting, as one adds more particles to be deposited onto the substrate, the thickness of the layer continues to grow. This follows traditional logic- add more material to the layer, the layer gets bigger. However, it is theorized that for some substrates, there is a point in the film growth where it is no longer energetically favorable to adsorb another molecule, resulting in a finite, or critical, film distance. This strange phenomenon is known as critical wetting. The growth of the film for complete versus critical wetting can be seen in Figure 1.2.

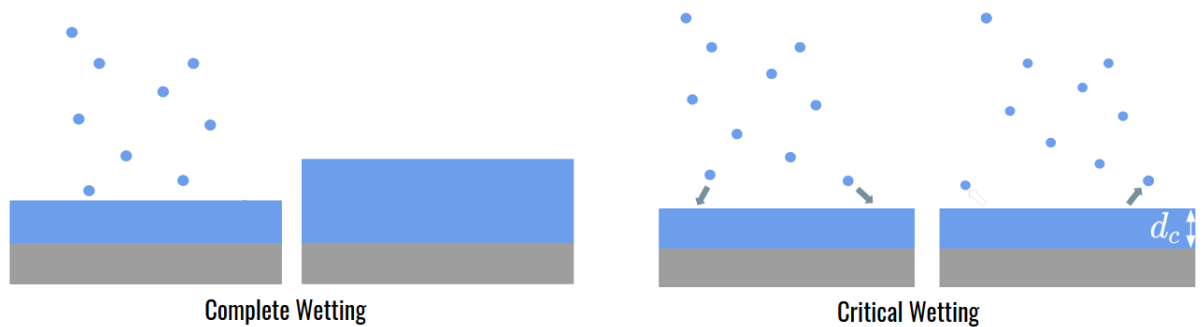


Figure 1.2: Film growth in complete versus critical wetting

1.2 SUBSTRATE DIMENSION AND INTERACTION POTENTIAL

Critical wetting falls in the regime between the microscopic and the macroscopic. In order to observe this critical film distance, the film growth must be greater than a few angstroms. Yet if the critical film height is above a couple nanometers, leading to an effect on emergent properties, the overall system result is the same as if complete wetting had occurred. Light molecules depositing onto a weakly interacting surface offer the best chance to observe wetting in this narrow regime. Two dimensional (2D) materials offer promise in allowing critical wetting compared to many three dimensional (3D) substrates. This can be seen via a basic calculation comparing the potential between a particle suspended above a 3D or 2D surface. In one dimension, the van der Waals potential, or force that determines attraction over long ranges is proportional to r^{-6} , where r is the distance between particles. When generalizing from the interactions between two point particles to the interactions between a point particle and a surface, the potential is found by integrating over the dimensions of the surface.

2D:

$$V(z) = \int \int \frac{C}{r^6} dx dy = \int \int \frac{C}{(x^2 + y^2 + z^2)^3} dx dy \sim \frac{C'}{z^4}$$

3D:

$$V(z) = \int \int \int \frac{C}{r^6} dx dy dz' = \int \int \int \frac{C}{(x^2 + y^2 + |z - z'|^2)^3} dx dy dz' \sim \frac{C''}{z^3}$$

where \sim refers to the behavior in the long distance $z \gg 1$ limit which can be inferred from dimensional analysis.

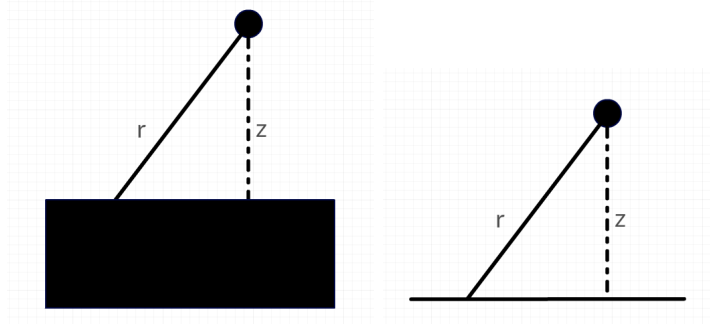


Figure 1.3: Diagrams of a particle above a surface. In three-dimensional space, the particle is at a distance of r above the surface. The left represents a 3D surface, such as graphite, while a 2D surface, such as graphene, is on the right.

When comparing the potentials for the 2D and 3D case, depicted in Figure 1.3, the potential between a 2D sheet and particle decays faster by one power of inverse distance than the potential between a 3D surface. The thinness of the 2D substrate interaction will allow light, weakly interacting gases to stick to the surface but only to a certain point; after which, the substrate will no longer be able to hold the gas particles into the film layer. Ergo, the weak interaction of particles above 2D materials is believed to lead to a finite film thickness.

1.3 LIFSHITZ THEORY OF WETTING AND GRAPHENE SUBSTRATES

A more formal understanding of critical wetting can be gained from the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory [2], which relates the variation of the chemical po-

tential with film thickness to the stability of its growth. Mathematically, the theory is written as:

$$\mu(d) - \mu(d = \infty) = \Delta\mu = \frac{\delta U(d)}{\delta d}$$

$$U(d) = \frac{\hbar}{n(2\pi)^3} \int d^2q \int_0^\infty d\omega \ln \varepsilon(\mathbf{q}, i\omega)$$

Where $\mu(d)$ is the chemical potential at height d above the substrate, and $U(d)$ is the van der Waals interactions between surface boundaries separated by distance d . DLP Theory states that long as $\Delta\mu < 0$, the film will grow. In the paper “Theory of liquid film growth and wetting instabilities on graphene,” Sengupta, Nichols, Del Maestro, and Kotov [3] expand upon the DLP theory, placing a monolayer of graphene onto the substrate. With the addition of graphene, the contributions of the substrate (\mathcal{U}_d) and graphene (\mathcal{U}_g) can be seen directly in the correlation energy:

$$U(d) \simeq \frac{\hbar}{n(2\pi)^3} \int d^2q \int_0^\infty d\omega (\mathcal{U}_d + \mathcal{U}_g)$$

Where \mathcal{U}_g is dependent on the polarization function Π :

$$\mathcal{U}_g = \ln(1 - V_2\Pi)$$

$$\Pi(\bar{q}, i\omega) = -\frac{1}{4v_x v_y \sqrt{v_x^2 q_x^2 + v_y^2 q_y^2 + \omega^2}}$$

V_2 is defined as the Coulomb potential of the deposited liquid layer, and v_x and v_y are the x and y-components of the anisotropic Fermi velocity. Using this expanded DLP theory, Sengupta *et al* explores three different graphene geometries named “substrate,” “submerged,” and “suspended.” The substrate geometry places a layer of

graphene on top of an insulating substrate, and a macroscopic liquid film grows to a thickness d where it is in equilibrium with its vapor. The submerged geometry places graphene on top of a liquid, and the macroscopic film that grows on the graphene is made of the same substance. The suspended geometry places graphene above a vacuum [3].

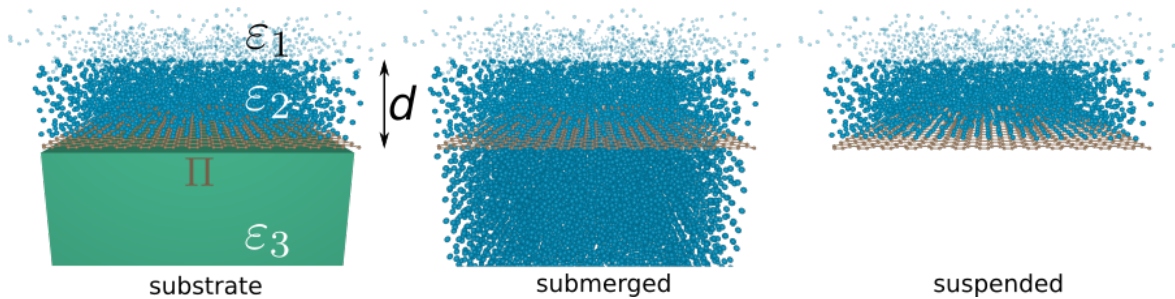


Figure 1.4: Three unique geometries studied in “Theory of liquid film growth and wetting instabilities on graphene” by Sengupta et al [3]

The suspended and submerged geometries offer the opportunity to study adsorption for purely 2D systems. Comparing van der Waals interactions (Γ) to film height (d) for each 2D geometry and the traditional 3D graphite substrate [4], the paper states “For suspended graphene ..., we observe a novel physical effect for all elements: there is a critical distance d_c at which graphene’s (always positive) contribution becomes so weak it can no longer compensate the negative dielectric part and $\Gamma(d_c) = 0$.” Plainly stated, the suspended graphene exhibits critical wetting. This is seen in Figure 1.5, the plot crossing the zero line for the suspended graphene curve.

Referring back to the idea that the value of $\Delta\mu$ determines film growth, critical wetting is predicted in the textbook “Statistical Physics- Part 3” by E.M. Lifshitz and L.P. Pitaevskii [5]. Shown in Figure 1.6, the textbook states “...if the function $\mu'(\gamma)$ passes through zero and has a maximum (Fig. 76c) we have a case of wetting but with

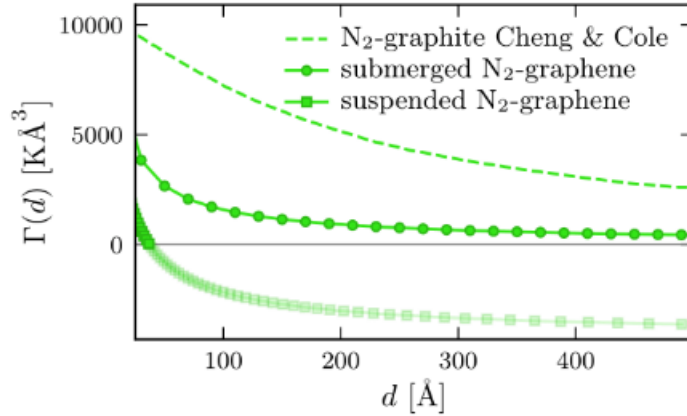


Figure 1.5: Thickness dependence of van der Waals interaction $\Gamma(d)$ for nitrogen films formed on submerged, suspended and traditional 3D graphite geometry (taken from the Cheng & Cole paper [4]). The crossing of the zero line by the suspended graphene curve indicates critical wetting.[3]

a formation of a film stable only at thickness below a certain limit.” Point A indicates a film thickness where the liquid film is in equilibrium with vapor [5]. Looking at the nitrogen film formed on the suspended geometry from the Sengupta *et al* paper (Figure 1.7), the change in chemical potential vs film thickness curve matches the predicted textbook curve almost exactly. Reflecting the prediction in Lifshitz’s and Pitaevskii’s work, along with predicting critical wetting in comparing van der Waals interactions to film height, Sengupta *et al* suggests nitrogen on vacuum suspended graphene is a good system in which to study this phenomenon.

1.4 CURRENT WORK

This thesis aims to use atomistic simulations to validate the continuum Lifshitz theory of critical film thickness. Using molecular dynamics (MD) simulations, the case of nitrogen on vacuum suspended graphene is explored, allowing for additional, com-

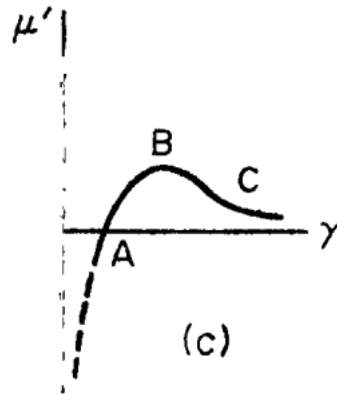


Figure 1.6: The change in chemical potential vs film growth for critical wetting, from E.M. Lifshitz and L.P. Pitaevskii “Statistical Physics- Part 3.” [5]

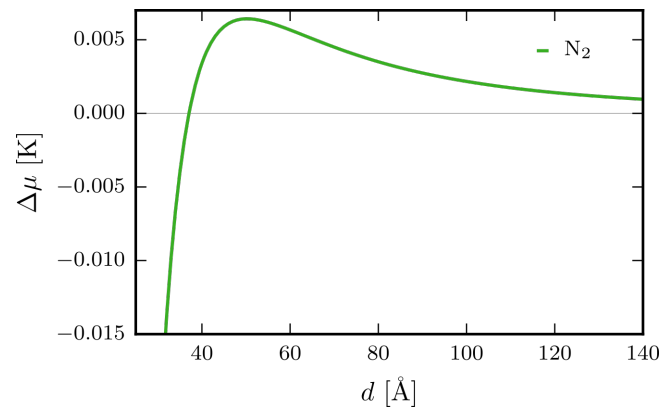


Figure 1.7: The change in chemical potential vs film growth for critical wetting for the nitrogen film on graphene in the suspended geometry from “Theory of liquid film growth and wetting instabilities on graphene” by Sengupta et al.[3]

putational evidence in studying and predicting critical wetting.

CHAPTER 2

METHODOLOGY

2.1 MOLECULAR DYNAMICS

MD describes computer simulations where a multiparticle system is studied via determining the positions and velocities of each particle using Newton's second law. At each time step, each particle experiences a force due to the interaction potential between particles. The force creates an acceleration, thus creating a velocity, and a new position for each particle. With each new position of the particle, the interaction between particles differs, and thus the total force on each particle changes, and by extension, a new resultant position. As the name "molecular dynamics" would imply, MD simulations are limited to the scale of atoms and molecules. The use of Newton's second law to calculate the new positions at each time step makes this a classical system. While some atomistic experiments require quantum mechanics, classical mechanics can account for many phenomenon on the atomtic scale, and thus allow for the use of MD simulations. For many systems, electrons are bound so tightly to the nucleus of atoms that the energy required to promote an electron or remove it from

the atom is far greater than the energy associated with the center of mass motion of the atom. Thus, when looking at collisions between atoms, the energy scale does not warrant the need to look at electron configurations, and “each atom can be treated as a simple structureless particle” [6]. Additionally, the scale of atomic de Broglie wavelength is far smaller than the actual particle separation in the simulation, thus allowing for the atoms to be treated as simple particles, and supporting the use of classical mechanics. The classical approach of MD provides the necessary physics to see how particles move over time, without the computational difficulty and time cost of a quantum simulation. This does come with some drawbacks. MD does not work for all atomistic simulations, and has a finite scale for which it works. However, in general MD provides a step by step view into how the system develops.

Having this step by step view of how particles move over time may seem a trivial exercise, but MD can provide the connection “between microscopic length and time scales and the macroscopic world of the laboratory” [7]. While lab bench experiments can give us a view into an overall process, comparing the initial and resultant bulk properties of a system, MD simulations can a look at what is happening between particles, and thus an idea of why such properties arise. MD can also provide a method of testing theory. The results of the simulation can then be tested against real world experimental values to test the validity of the model, or the model provides a means of testing the theory for situations that are unreasonable for bench top experiments, such as extreme temperatures, and/or pressures [7]. MD has been used to model complicated biomolecular systems, such as conformational changes in proteins allowing for allostery [8], explore behavior of nanowires containing experimentally observed microstructure [9], and study the properties of graphene, a single atom thick material.

With its ability to connect the microscopic and the macroscopic, MD simulations are useful in studying critical wetting. This MD experiment utilizes the open code GROMACS [10].

GROMACS' Global MD Algorithm follows a general scheme of four steps. First, each run requires an input set of initial conditions, including positions and velocities of all particles involved in the system, and the potential interaction as a function of particle positions. Next, the force on any particle is computed by calculating the sum of the force between non-bonded particle pairs, the forces due to bonded-interactions, and the restraining and/or external forces. The movement of each particle is then simulated by solving Newtons' equations of motion, and the final positions, velocities, energy, temperature, etc. are written. These last three steps are repeated for the number of time steps in the simulation run [10].

2.2 SIMULATION CREATION

The simulation cell is designed as a sheet of graphene with a deposited layer of liquid nitrogen, followed by a vacuum above it, a secondary layer of liquid nitrogen, and graphene at the top of the box (see Figure 2.1). Analyzing the evaporation of liquid nitrogen off the graphene studies the same phenomenon as the deposition of nitrogen gas onto the substrate, but in much less time. Having the depicted dual layer system allows for control of the pressure within the system. If there was only vacuum above the nitrogen layer, the liquid would all evaporate. Creating the overall simulation can be broken down into several steps.

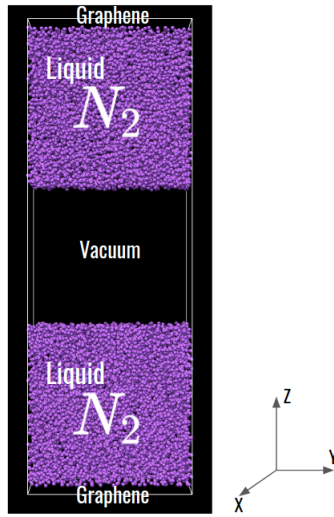


Figure 2.1: Experimental setup

2.2.1 SIMULATING LIQUID NITROGEN

In creating the dual layer system, the first stage was simulating the liquid nitrogen. This was done in four steps: creation of the particle, adjustment of space around the particle, multiplying the single particle to create the cubic system, and minimizing the energy. The first three steps are depicted in Figure 2.2.

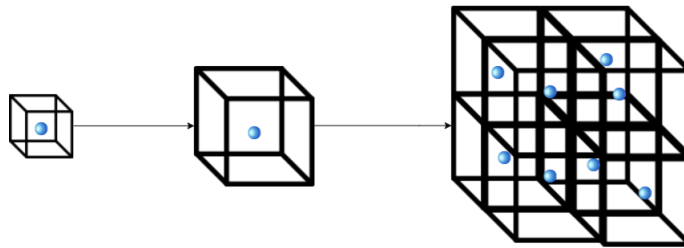


Figure 2.2: Diagram depicting the creation of coarse grain liquid nitrogen

A single particle can be created via visualization software; for this coarse grain

dinitrogen simulation, UCSF Chimera[11] was used. A particle can be created via the Build Structure feature found under tools and then structure editing. By selecting the x,y,z position option for the atom, and setting each one equal to zero, an atom is placed at origin. When a particle is created in the simulation, an invisible box surrounds it, showing how much space the particle takes up. When more particles are added to the simulation, the particles (each in their individual boxes) create the overall system volume. The specific type of atom or molecule is indicated via the topology file [10]. The topology file names the type of molecules in the simulation and lists the atomic number of the atoms in the molecule, the mass of the atom/molecule, charges, and the Lennard-Jones parameters. The Lennard-Jones potential is a mathematical model that approximates the interaction potential between neutral molecules:

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

Where r is the distance between molecules, σ is the distance in which the potential between particles is zero, and ε is the depth of the potential well. For this experiment, nitrogen's Lennard-Jones parameters were determined from the 2016 paper "Free Energy-Based Coarse-Grained Force Field for Binary Mixtures of Hydrocarbons, Nitrogen, Oxygen, and Carbon Dioxide" by F. Cao, J. Deetz, and H. Sun [12], in which a temperature dependence is applied to ε : $\sigma = 0.3611$ nm, $\varepsilon(T) = 0.8508$ kJ/mol at 65K. A plot of this Lennard-Jones potential can be seen in Figure 2.3, and for more information on temperature-dependent Lennard-Jones parameters, see Appendix A.

Once the single particle box is created, the size of the box can be adjusted using `editconf` [10], which adjusts the lengths of the box in the x, y, and z directions to

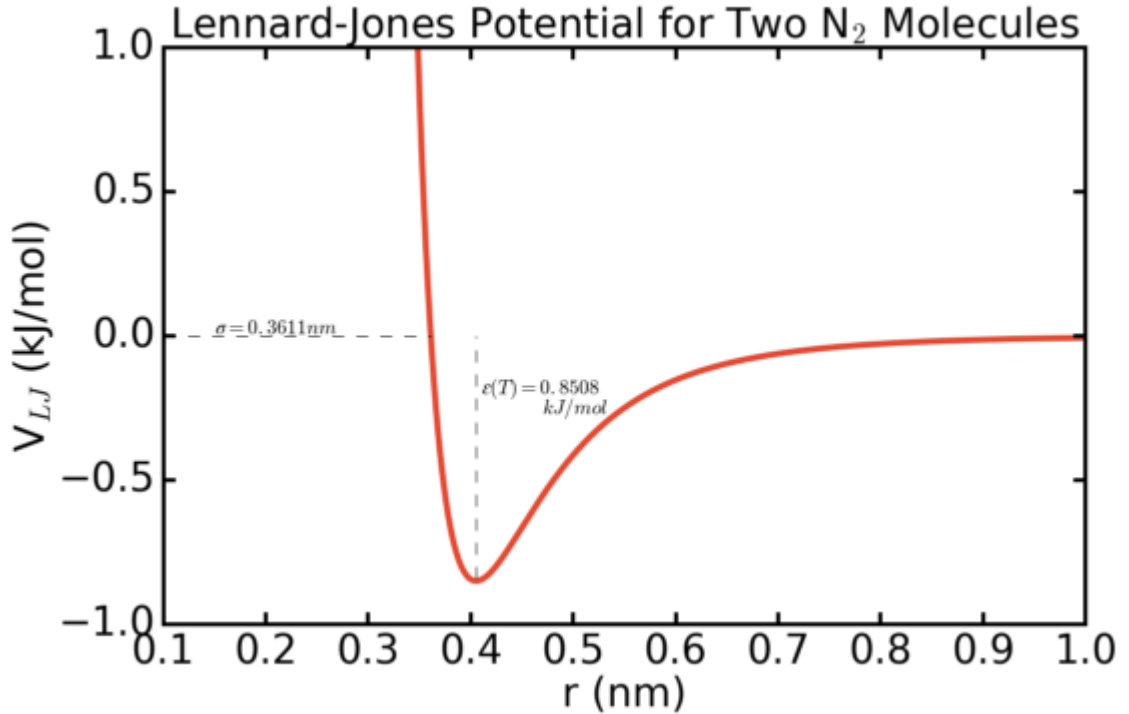


Figure 2.3: Lennard-Jones potential for two nitrogen molecules, determined from Cao et al

specified values to give a new structure file. For systems with a specified density and number of particles, the new single particle box size, and therefore the needed x, y, z inputs, are determined by taking the cube root of the overall system volume, given by:

$$V = \frac{N}{\rho}$$

where N = number of particles, ρ = density, and V = volume. For more information on determining of the overall system volume, see Appendix B. Having the single particle box is the desired size, the box needs to be multiplied to create the overall cubic system. GROMACS uses the command `genconf`[10], taking a structure file and multiplying it by specified values in the x, y, and z directions to create a new, larger structure file. By setting the x, y, and z multipliers to be the cube root of

the total number of particles, the resulting structure file will be a cube of the right number of particles at the desired density.

To ensure there is no unnatural stress occurring, such as two particles being placed too close together, an energy minimization must be done on the system. To relax the structure and minimize the energy, one first needs to create a run-input file (.tpr) by using the line of code `grompp` (GROMACS preprocessor)[10]. `grompp` creates a .tpr file by taking a .mdp topology file and a structure file and expanding the topology file to match the molecular description in the structure file. The .mdp file is where one sets up many properties of the simulation beyond just particles, such as temperature, run time, and periodic boundary conditions. Setting the integrator in the .mdp file to `steep` and running `grompp`, the resulting .tpr file will have the correct minimal energy state. The final trajectory file is created by running `grompp` again, this time with the input .pdb file set to the file created by the energy minimization and the integrator set to `md`. With that, the simulation for liquid nitrogen is fully set up and able to run, allowing for the positions and trajectories of the particles to be known.

With nitrogen simulated, it is necessary to check the simulation's validity. While the experiment uses liquid nitrogen, the validity of nitrogen was checked in the gaseous phase; this allows for smaller and faster simulations. Nitrogen's validity was checked by creating a simulation of 1000 particles at 1 atm over a temperature range of 78-98 K. The density of each simulation at each temperature was then plotted against experimental values from the C++ library CoolProp[13]. Shown in Figure 2.3, the experimental values align with the simulation, proving this is an accurate representation of nitrogen.

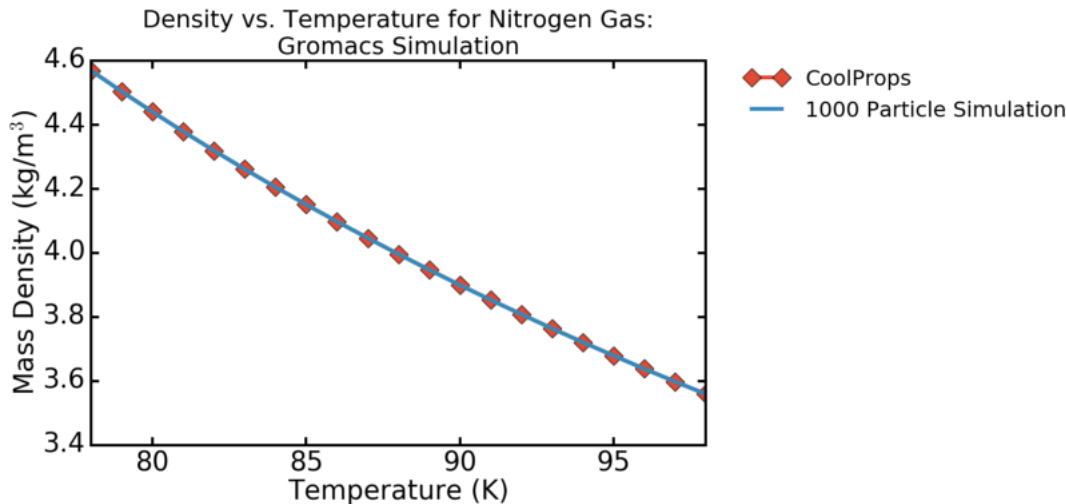


Figure 2.4: Comparison Plot between simulated nitrogen and experimental values from Cool-Prop

2.2.2 GENERIC CARBON WALLS

The creation of properly simulated nitrogen allows for attention to be turned to creating the desired system layout. Before inserting the graphene sheet, the dual layer system can be created using the GROMACS code `Wall`. `Wall` creates a smooth wall at specific z-axis value. The wall has specified Lennard-Jones parameters, but does not function the same as a sheet of molecules with the same Lennard-Jones parameters. For the initial set-up, the wall is set to have CH_4 Lennard-Jones parameters, as they were parameterized along with the coarse-grain nitrogen and give the wall the resemblance of carbon: $\sigma = 0.3723$ nm, $\varepsilon(T) = 1.26001$ kJ/mol at 65K. To begin creating the layout, use `gmx editconf -box[10]` to expand the unit cell of the newly formed nitrogen simulation along z-axis. The full length along the z-axis will be the height of each molecule layer ($2 \times$ z-dimension of molecule cube), the space between the molecule layers and each wall, and height of the vacuum. To prevent growth

from the center of the box, it is important to include in the command line `-noc`. Once the total box size is determined, one needs to determine the location of the top layer of nitrogen. This can be done by using `gmx editconf -translate` to shift the molecules to the top of the box. The total amount of shift is equal to the height of molecules + height of vacuum + space between molecules and wall. The output (`-o`) will be a file containing the location of all of the molecules in the top layer. In an empty text file, the initial nitrogen `.pdb` file and the new `.pdb` file can be combined to create a record of all initial nitrogen molecule location for both layers. Once the files have been combined, the molecules must be renumbered using `gmx editconf -resnr 1`, where 1 sets the first number to 1 and counts upwards. Once the files are combined and renumbered, it is useful to check that the layers are positioned correctly by looking at the combined `.pdb` file in Chimera. It should appear as two masses of particles, clearly separated, and the small separation between each layers and the top and bottom of the unit cell appearing equal to the eye, see Figure 2.1.

To create a wall in a GROMACS Simulation, the `.mdp` file is edited. First periodic boundary conditions are changed to only be `xy` rather than `xyz`. The number of walls inserted into the system is then set with `nwall`, followed by the wall type. The default for `nwall` is 0, but when `nwall = 2`, a wall is placed at $z = 0$ and on the opposite end of the box, which is desired for this experiment. As for the wall type, `wall-atomtype` specifies what particles create the wall, with all particles and properties for the whole system specified in the topology (`.top`) file, while `wall-type` determines the interaction potential exhibited by the wall, with 12-6 being the standard Lennard-Jones Potential. Once the `.mdp` file is edited to include a wall, the energy minimization is run in the same manner described for creating the bulk nitro-

gen simulation: setting the integrator to **steep**, keeping **nsteps** low (~ 100), running **grompp** to create a **.tpr** file, and then performing an **mdrun** to create the **.pdb** file as the input for the actual simulation. Again, creating the final simulation is similar to that of creating the final version of nitrogen. Using the energy minimized **.pdb** file, **gmx grompp** is used to create the trajectory **.tpr** file, being sure to set the integrator in the **.mdp** file to **md** and increase **nsteps** to the proper amount of time steps for the simulation. With the **.tpr** file, **mdrun** can be performed and the result will be a final **.pdb** and **.xtc** files. The **.tpr** and **.xtc** files show the positions and trajectories of all the particles within the system and therefore can be used to examine and visualize the model.

2.2.3 INSERTING GRAPHENE SHEETS

With the determination that the system can be set up with dual layers of nitrogen separated by a vacuum, focus shifts to the important task of inserting simulated graphene sheets, rather than using smooth CH_4 walls. The following describes the process to create the dual-layer liquid nitrogen and graphene sheet simulation, as depicted in the model in Figure 2.1. However, at this point, the simulation fails to realistically portray the interactions between nitrogen and graphene. This will be further discussed within the Results chapter, Section 3.3: Graphene Simulation and Nitrogen Solidification.

To begin, like simulating nitrogen, one can create a **.pdb** file for a graphene sheet by visualizing the system inside Chimera. For this experiment, Dr. Juan Vanegas provided the graphene **.pdb** file. With the atom locations of the graphene sheet, the next step is to create the initial system layout by combining nitrogen and graphene

.pdb files. The nitrogen layers were already created when creating the dual layer system with smooth CH₄ walls, so the atom locations can be copied from the existing .pdb file. The initial graphene sheet generated places the sheet along the (0,0) xy plane. The top graphene sheet can be generated by using `gmx editconf -translate` to shift the molecules to the top of the box again. The atom locations from each graphene and nitrogen .pdb file can be copied into one text file to create an overall list of atom locations.

Following the establishment of the full atom location list, the corresponding topology file must be created. In addition to providing Lennard-Jones parameters, the topology file allows for the creation of groups of molecules. These groups can then be acted upon and/or studied individually rather performing an action on the entire system. This helps to further distinguish the nitrogen and graphene sheets within the simulation. As for Lennard-Jones parameters of the graphene sheet, this experiment uses the graphene-graphene values from the L. A. Girifalco, Miroslav Hodak, and Roland S. Lee paper "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential" [14]: $\sigma = 0.34148$ nm and $\varepsilon = 0.23059988$ kJ/mol.

To access the groups specified in the topology file, GROMACS requires an index file. The index file (.ndx) lists the atom number for each atom in each group. For this experiment, the two groups are N2 and GRP, standing for nitrogen and graphene. N2 contains all nitrogen molecules while the GRP groups contains carbon atoms. Rather than looking for molecules marked N2 or C each time a group is called, by setting up an index file, it creates a list of which molecules in the .pdb file are in each group.

After the creation of an index file for the proper creation of groups, creating the full simulation follows the same process of first running an energy minimization to to

prevent unnatural stress and then using those output files as the inputs for the full simulation run. However, as the graphene sheets are fixed at the top and bottom of the box, in each .mdp file, one must include the line `freezegrps = GRP`. This tells the simulation to not move any molecules listed within the GRP group, which would be the case for atoms inside graphene sheets.

Following this process, one should end with simulation depicting graphene sheets at the top and bottom of the simulation cell, each with a layer of deposited liquid nitrogen, separated by vacuum. As stated, current issues facing this experiment will be discussed later in the paper. For example code on creating the simulation up to creating the dual layer system with the smooth walls, see Appendix C.

CHAPTER 3

RESULTS

3.1 STUDYING SYSTEM LAYOUT WITH GROMACS WALLS

Creating the dual layer system with smooth, generic carbon walls gives important insights before studying specifically the phenomenon of critical wetting. By using GROMACS generated walls, the focus is purely on creating two layers of liquid nitrogen separated by vacuum.

To study the separation of layers, the system was simulated with vacuum heights varying between 2-10 nm, and the average density of particles in the z-direction was created for each simulation. In the overview of the results, the 6 nm vacuum example will be used, but all density-histograms are available in Appendix D. Each liquid nitrogen layer consists of 8,000 particles at 65K at 1 atm, starting in an initial configuration of a cube of length 7.5645 nm for each side.

The histograms plot the density of nitrogen along the z-axis. `gmx density` calculates density across the box and then generates an accompanying text file [10]. Traditionally, in calculating the density of the box, `gmx density` divides the box

into 50 slices. However, as each box will be a different height with the variable vacuum height, the number of slices ($-sl$) is set to match the height of each box in angstroms, thus keeping each slice a constant 1 Å across all simulations.

Plotting the density of nitrogen along the z-axis for the 6 nm vacuum case results in Figure 3.1. Near the locations of each wall, the density shows sharp peaks, indicating solidification. This is expected close to the the solid wall, as particles are pulled strongly and tightly to the wall. After this section of solidification, the density evens off and then drops off sharply. After a section of the density appearing close to zero, it sharply increases back to the same value as before the initial drop, and then shows the peaks indicating solidification near the wall at the top of the box. This density curve is characteristic of two bulk liquid layers separated by vacuum - confirming the proposed system layout.

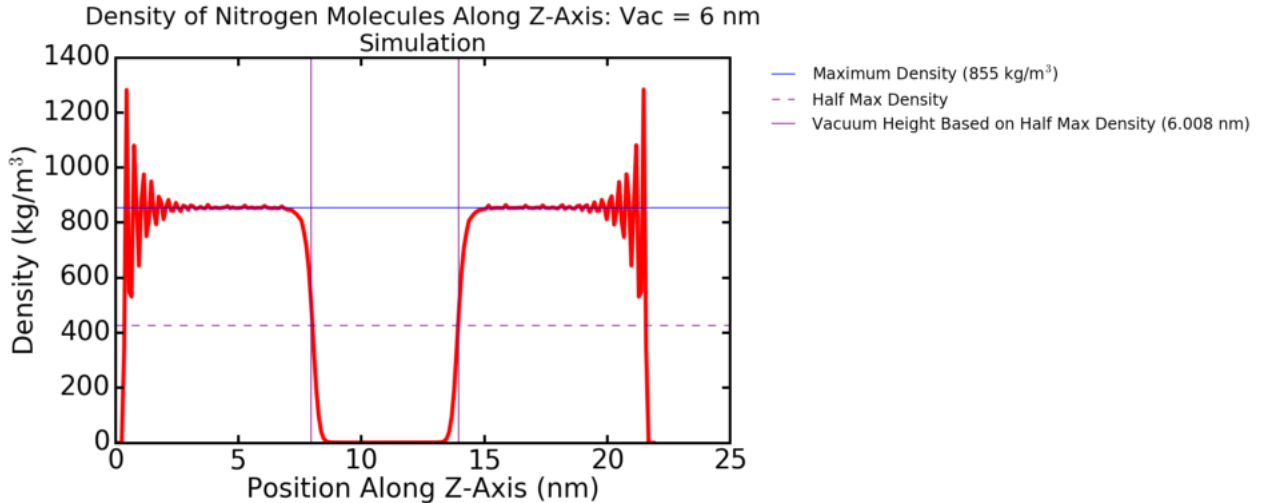


Figure 3.1: Density-histogram for simulation of nitrogen on GROMACS smooth walls. The simulation was run for 10 ns, with 16,000 N_2 particles (8,000 in each layer), at a temperature of 65 K, and a vacuum height of 6 nm.

While setting up the system, the vacuum was created by shifting the nitrogen

layers to be 6 nm apart. The actual height of the vacuum is calculated by determining the two locations along the z-axis in which the density of nitrogen is half that of the average bulk liquid density, and subtracting the difference between them. For this trial, the calculated vacuum height is 6.008 nm, again confirming this is a good method to create the desired system layout.

Looking through the histograms in Appendix D, they all display this same curve indicating bulk liquid separated by vacuum with solidification near the system walls. Differences between the proposed and measured vacuum heights are all, again, within the thousandths of nanometers. Thus the histograms confirm the method described in Section 2.2.2 Generic Carbon Walls creates the desired simulation.

In addition to the histograms showing a distinct drop in density, the presence of vacuum can be confirmed by comparing the minimum density within each vacuum region for each trial. Shown in Figure 3.2, the approximate leveling off of density within the vacuum as vacuum height increases validates the true existence of vacuum within the simulations.

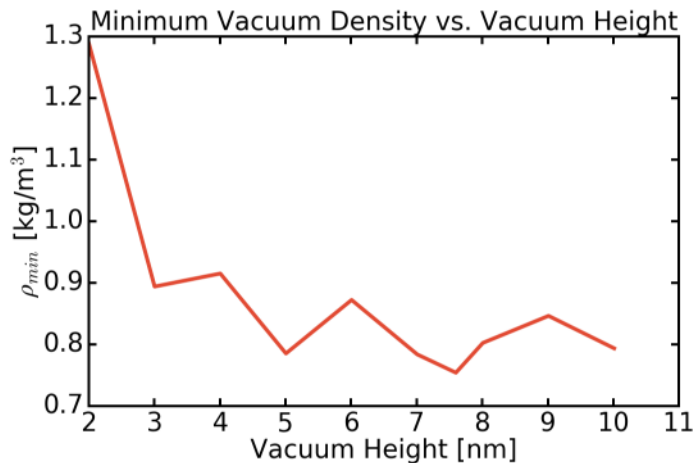


Figure 3.2: Minimum density versus vacuum height for each dual layer nitrogen simulation with GROMACS walls.

3.2 VACUUM-LIQUID INTERFACE

Looking at the histograms in Appendix D, there is a distinct curve between the vacuum and bulk liquid in each simulation. By characterizing this curve, one can study this interface between the vacuum and bulk liquid nitrogen.

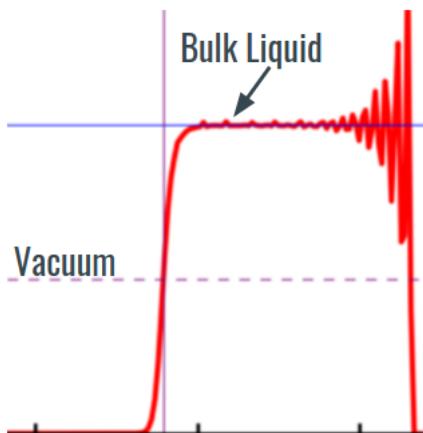


Figure 3.3: Curve between vacuum and bulk liquid from the histogram for simulation of nitrogen on GROMACS smooth walls in Figure 3.1.

A strong candidate for fitting this interface is the the cumulative distribution function (CDF):

$$\Phi\left(\frac{x - \mu}{\sigma}\right) = \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{x - \mu}{\sigma\sqrt{2}}\right)\right]$$

Where in terms of curve fitting, μ can be defined as the interface location, and a multiple of σ can define the interface width. For this experiment, the interface width is defined as 2σ .

Plotting the CDF function and the normalized data from the dual-layer GROMACS wall simulations, the curves fit together nicely. Thus, the interface between

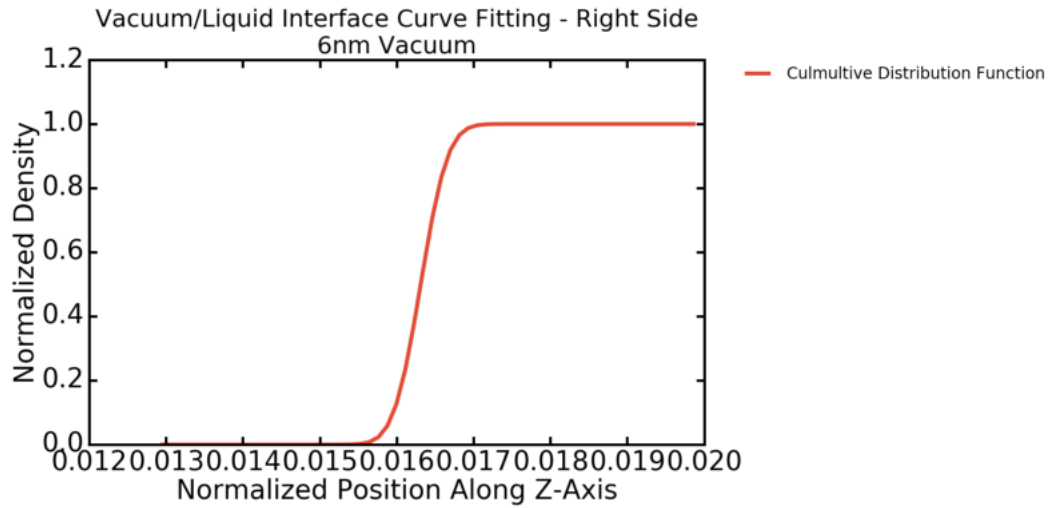


Figure 3.4: CDF curve with $\sigma = 0.000276$ and $\mu = 0.0163$

vacuum and bulk liquid can be characterized by this curve. For the 6 nm vacuum trial, the interface width is approximately 0.473 nm. Plots showing the curve fitting and respective interface widths for all trials can be found in Appendix E.

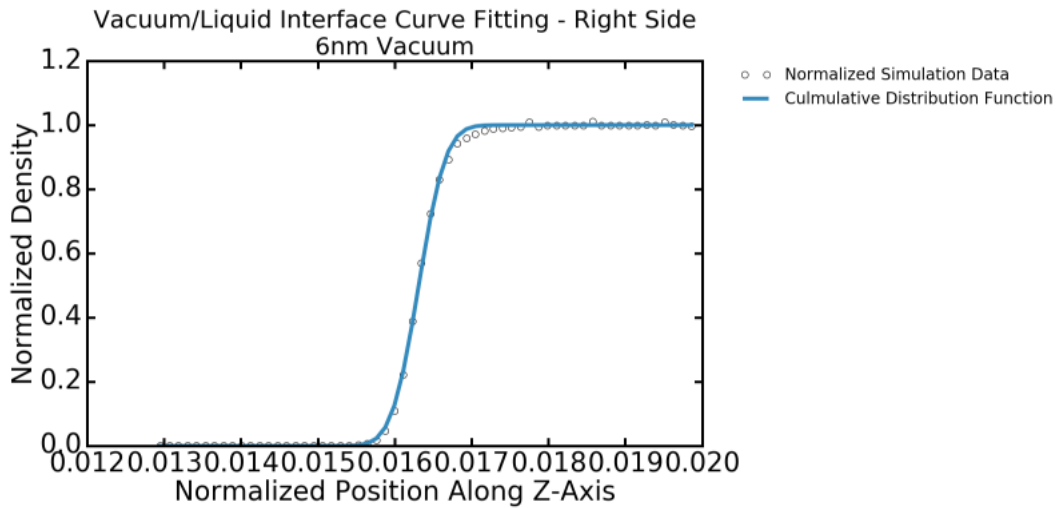


Figure 3.5: CDF curve overlaid on normalized data of the interface between vacuum and bulk liquid nitrogen from the dual-layer GROMACS wall simulation with a 6nm vacuum height

3.3 GRAPHENE SIMULATION AND NITROGEN SOLIDIFICATION

As mentioned in the Methodology chapter, at this point, the simulation containing graphene fails to realistically portray the interactions between nitrogen and graphene. At the time of this thesis's publication, each nitrogen layer completely solidifies on top of each graphene sheet, see Figure 3.6. Even if this experiment failed to simulate critical wetting, nitrogen molecules placed about a single layer of graphene at a temperature of 65 K should not solidify. Initial analysis suggests an error with the code's Lennard-Jones parameters. However, for this simulation, the code is calling the Lennard-Jones parameters $\sigma = 0.3611$ nm, $\varepsilon(T) = 0.8508$ kJ/mol for nitrogen at 65K, and $\sigma = 0.34148$ nm and $\varepsilon = 0.23059988$ kJ/mol for graphene. The similarity between σ values does not suggest that the particles are becoming too close together, leading to the formation of a solid.

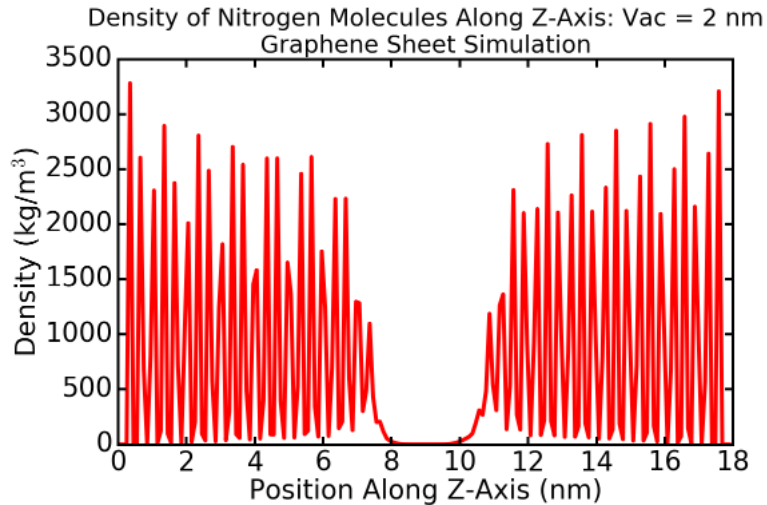


Figure 3.6: Histogram showing the complete solidification of nitrogen on each graphene sheet

Additionally, when substituting the Lennard-Jones parameters of graphene with CH_4 parameters ($\sigma = 0.3723$ nm, $\varepsilon(T) = 1.26001$ kJ/mol at 65K), as used with the smooth walls, the problem still arises.

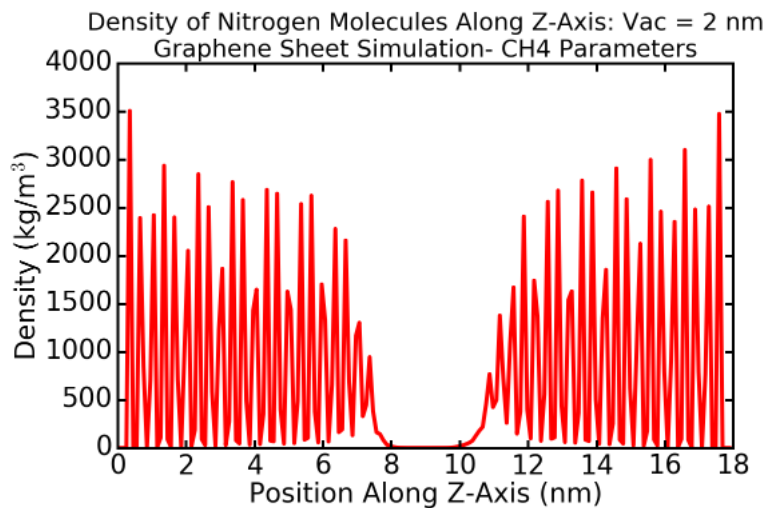


Figure 3.7: Histogram for simulation of nitrogen on graphene sheets, with the graphene sheets having the same Lennard-Jones parameters as the previously used GROMACS smooth walls. The histogram of the modified simulation still shows the solidification problem.

Determining the cause of this solidification issue is the main hurdle in creating an accurate computational experiment, and thus being able to study critical wetting for nitrogen on monolayer graphene.

CHAPTER 4

CONCLUSION AND FUTURE WORK

This thesis is an ongoing project. Its goal, to use atomistic simulations to validate the continuum Lifshitz theory of critical film thickness, is unfulfilled. Yet, in the process of creating the simulation to study the critical wetting phenomenon, one has learned about the theory behind critical wetting, how to create a molecular dynamics simulation, and measure the interface width between bulk liquid nitrogen and vacuum. Immediate work is focused on properly simulating graphene sheets, solving the nitrogen solidification error. Once these issues are fixed, and the experiment can be properly simulated, the actual studying of critical wetting can begin. In each trial, the density of the overall system will vary, and in response, one can measure the effect on film height. Additionally, in studying critical wetting, one can measure the forces on particles at different heights within the nitrogen layers. While there is much exciting work still left in this project, the work presented within this paper provides a solid foundation for the project, as well as for other projects involving molecular dynamics simulations and phenomena related to two-dimensional materials.

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APPENDIX A

LENNARD-JONES PARAMETERS

For the simulation of nitrogen, this work calculated the Lennard-Jones parameters using the 2016 F. Cao, J. Deetz, and H. Sun paper "Free Energy-Based Coarse-Grained Force Field for Binary Mixtures of Hydrocarbons, Nitrogen, Oxygen, and Carbon Dioxide" [12]. In the paper, ε is temperature dependent:

$$\varepsilon(T) = \varepsilon^U + \varepsilon^S(T) = \varepsilon^U + \varepsilon_0^S + T\delta\varepsilon$$

Table 1 within the F. Cao paper (recreated below) lists the different ε variables needed, along with σ for eight different molecules.

Optimized FE-12-6 Force Field Parameters				
	σ (Å)	ε^U (kcal/mol)	ε_S^0 (kcal/mol)	$\delta\varepsilon$ (cal/mol*K)
CH ₄	3.725	0.2851	0.018	-0.03
C ₂ H ₆	4.233	0.5315	0.015	-0.23
C ₃ H ₈	4.690	0.6780	0.022	-0.35
<i>n</i> - C ₄ H ₁₀	5.087	0.8309	0.020	-0.43
<i>i</i> - C ₄ H ₁₀	5.102	0.7678	0.037	-0.40
CO ₂	3.650	0.5634	0.077	-0.57
N ₂	3.611	0.1951	0.018	-0.15
O ₂	3.378	0.2385	0.013	-0.10

Using a temperature of 65K, and adjusting the ε values to have units of kJ/mol (the units used by GROMACS), the Lennard-Jones parameters for N₂ were determined.

This method was also used for determining CH₄ parameters, which were used as the Lennard-Jones parameters for the smooth walls created by GROMACS in place of simulated graphene sheets.

For the Lennard-Jones parameters for the graphene sheets, "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential" by L. A. Girifalco, Miroslav Hodak, and Roland S. Lee was used [14]. The paper uses the AB form of the Lennard Jones Potential:

$$V_{LJ}(x) = -\frac{A}{x^6} + \frac{B}{x^{12}}$$

Where A and B are the attractive and repulsive constants respectively. For graphene-graphene system:

$$A = 15.2 \text{ eV} \times \text{\AA}^6$$

$$B = 24.1 \times 10^3 \text{ eV} \times \text{\AA}^{12}$$

$$x_0 = 3.83 \text{ \AA}$$

$$|\varepsilon| = 2.39 \text{ meV}$$

Using the equations:

$$\sigma = \left(\frac{B}{A}\right)^{\frac{1}{6}}$$

$$\epsilon = \frac{A^2}{4B}$$

one can calculate σ and confirm ε values

In summary:

Lennard-Jones Parameters Used		
	σ (nm)	ε (kJ/mol))
N_2	0.3611	0.8508 (at 65K)
CH_4	0.3725	1.26001 (at 65K)
Graphene-Graphene	0.34148	0.23059988

APPENDIX B

DETERMINING SIMULATION VOLUME

To determine the box size, one can use the equation:

$$V = \frac{N}{\rho}$$

where N = number of particles, ρ = density, and V = volume. The number of particles is arbitrary, but the density is dependent on the number of particles, temperature and pressure of the system. CoolProp is a C++ library containing the equation of state and experimental values for over 122 fluids [13]. Using CoolProp, the density of the fluid can be determined over a temperature range.

```
Tt = [65,66,67,68,69,70,71,72,73,74,75]
T = np.asarray(Tt)
Nn = [100,250,500,750,1000]
N = np.asarray(Nn)

from CoolProp.CoolProp import PropsSI
rho = np.zeros_like(T)
for i in range(T.size):
    rho[i] = PropsSI('Dmolar','P',101325, 'T', T[i], 'Nitrogen')
    rho[i] = rho[i]*NA*(1E-27)
print('rho = ', rho)
```

Figure B.1: Code displaying how to determine the density within a box using CoolProp

From there, to determine the size of each unit cell surrounding a molecule, it is a matter of taking the cube root of the overall box volume, and dividing it by the cube root of the number of particles within the box.

APPENDIX C

SIMULATION CODE

This section presents code for a simulation of 16,000 N₂ molecules in two layers (8,000 particles per layer) separated by 6 nm of vacuum; each layer rests on smooth wall. The simulation is at a temperature of 65K.

C.1 SINGLE PARTICLE CREATION

The creation of a single particle in Chimera does not involve specific code. In place of example code, Figure C.1 shows the process.

C.2 BULK NITROGEN

Creation of the bulk nitrogen layer

```
1 gmx editconf -f N2CG_single.pdb -box 0.37822326 0.37822326 0.37822326 -o  
   ↪ T65single.pdb  
2  
3 gmx genconf -f T65single.pdb -nbox 20 20 20 -o N8000T65box.pdb
```

The first line sets the size around the particle, while the second line multiples the

number of particles to create an 8000 N₂ box.

Energy minimization

```
1 gmx grompp -f gromppsteep.mdp -c N8000T65box.pdb -o eminN8000T65.tpr
2
3 gmx mdrun -s eminN8000T65.tpr -c eminN8000T65.pdb -x eminN8000T65.xtc
```

By setting the integrator inside the .mdp file to **steep**, the system is set up to run a short simulation, minimizing the energy within the system.

Final nitrogen simulation

```
1 gmx grompp -f gromppmd.mdp -c N8000T65.pdb -o N8kT65.tpr
2
3 gmx mdrun -s N8kT65.tpr -c N8kT65.pdb -x N8kT65.xtc
```

Using the minimized energy particle locations and trajectories, and by setting the integrator in the .mdp file to md, the bulk N₂ MD simulation is created.

C.3 DUAL LAYER SYSTEM WITH SMOOTH WALLS

Creating the dual layer system

```
1 gmx editconf -f N8kT65.pdb -translate 0 0 0.4 -o N8kT65shift_original.pdb
2
3 gmx editconf -f N8kT65shift_original.pdb -box 7.5645 7.5645 21.929 -noc -o
   ↪ N8kT65zexpand.pdb
4
5 gmx editconf -f N8kT65zexpand.pdb -translate 0 0 13.9645 -o N8kT65shift.pdb
```

The first line shifts the existing bulk liquid nitrogen layer up 0.4 nm to create space for the wall to be placed on the (0,0) xy plane. Then, this simulation cell is expanded to create space for the top layer and the vacuum space. The liquid nitrogen layer in this expanded box is shifted up to the top, giving the atom locations for the top

nitrogen layer. N8kT65shift.pdb and N8kT65zexpand.pdb are combined into one file., creating a dual layer system of nitrogen. In this example, this combined file is named N8kT65systemcombine.pdb.

```
1 gmx editconf -f N16kT65systemcombine.pdb -resnr 1 -o N16kT65doublesystem.pdb
```

The atom locations in this combined system .pdb file are renumbered.

Energy minimization

```
1 gmx grompp -f gromppsteepwall2.mdp -c N16kT65doublesystem.pdb -o  
  ↪ eminN16kT65Wall2.tpr  
2  
3 gmx mdrun -s eminN16kT65Wall2.tpr -c eminN16kT65Wall2.pdb -x eminN16kT65Wall2.  
  ↪ xtc
```

Inside the .mdp file, the line `nwall = 2` is added, adding a smooth wall to the top and bottom of the simulation cell. Again, with a short run, the energy within the system is minimized.

Final dual layer simulation

```
1 gmx grompp -f gromppmdwall2.mdp -c eminN16kT65Wall2.pdb -o N16kT65Wall2.tpr  
2  
3 gmx mdrun -s N16kT65Wall2.tpr -c N16kT65Wall2.pdb -x N16kT65Wall2.xtc
```

By switching the integrator back to `md`, the dual layer system is processed, and the final simulation is created and run with `mdrun`.

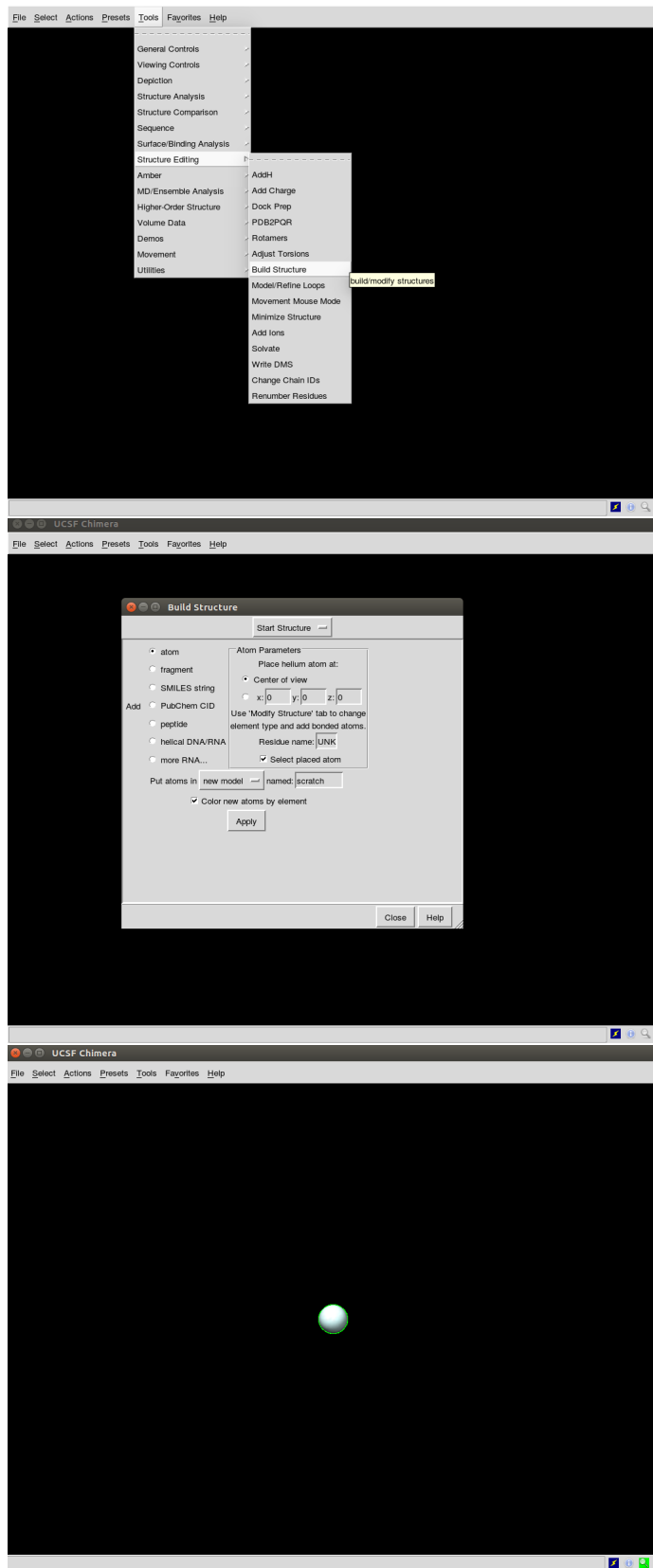


Figure C.1: Creation of a single particle in Chimera [11]

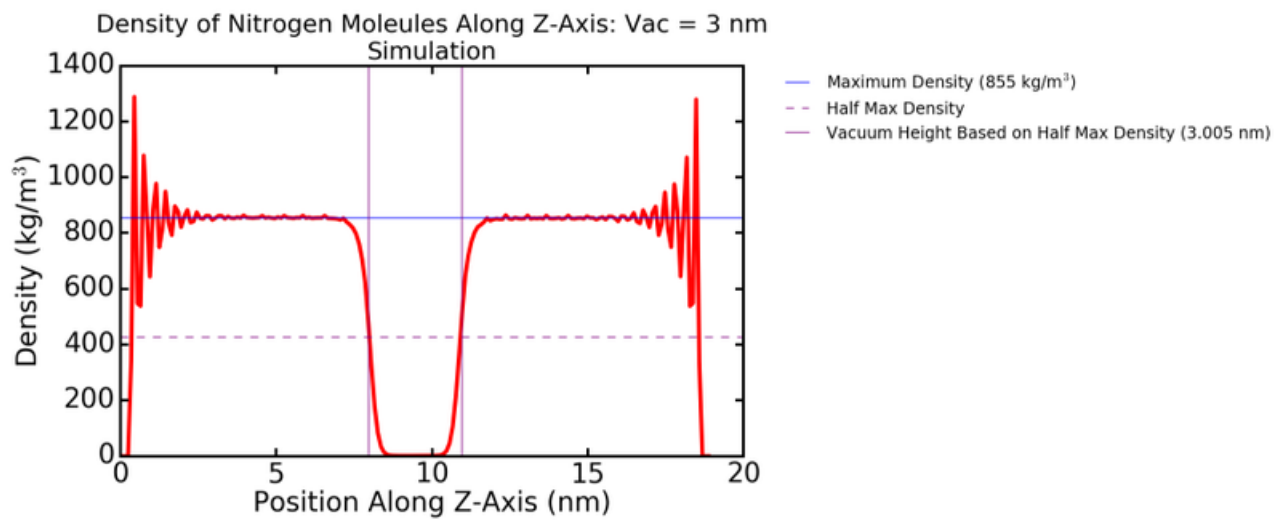
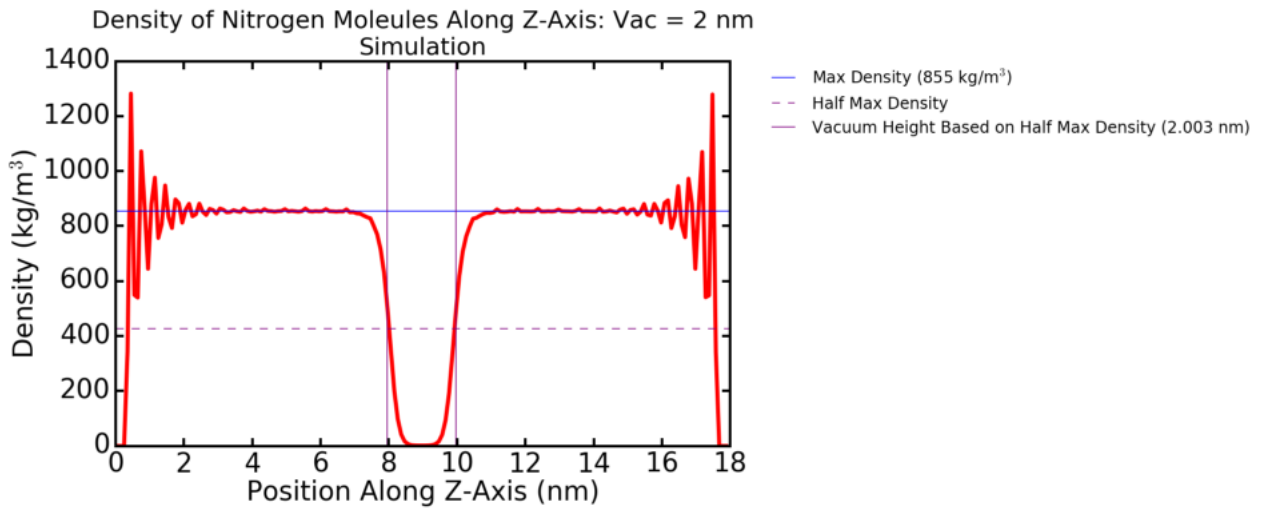
APPENDIX D

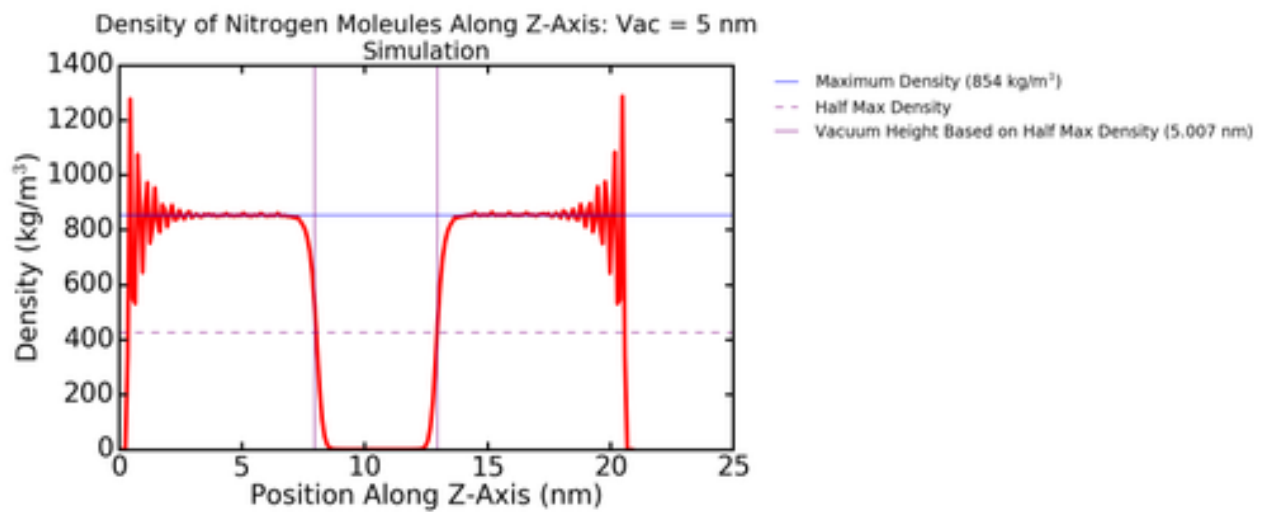
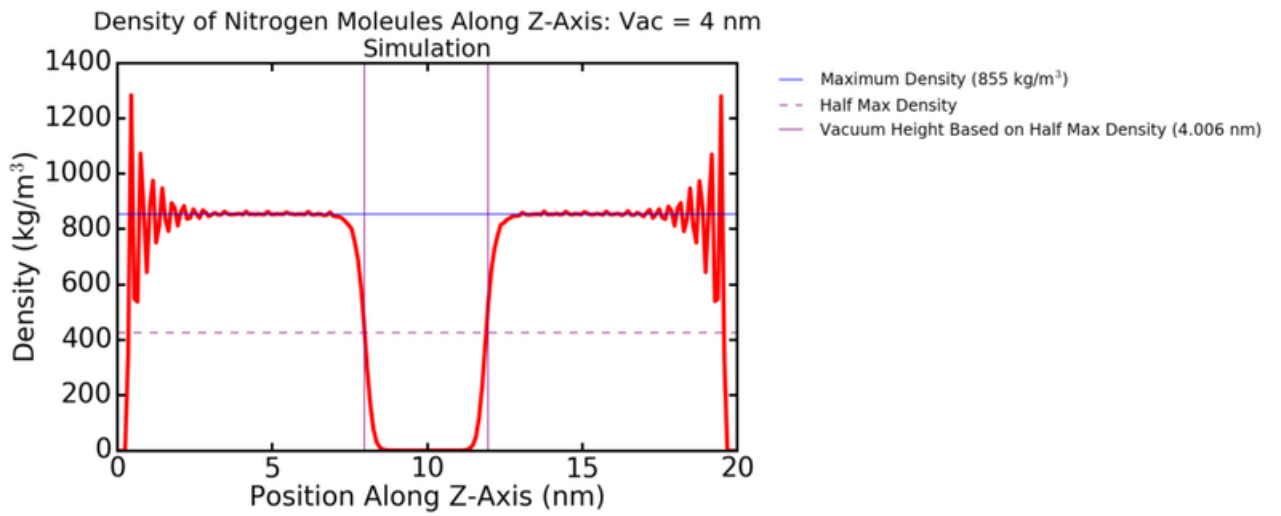
HISTOGRAMS FOR SIMULATIONS WITH CH₄ WALLS

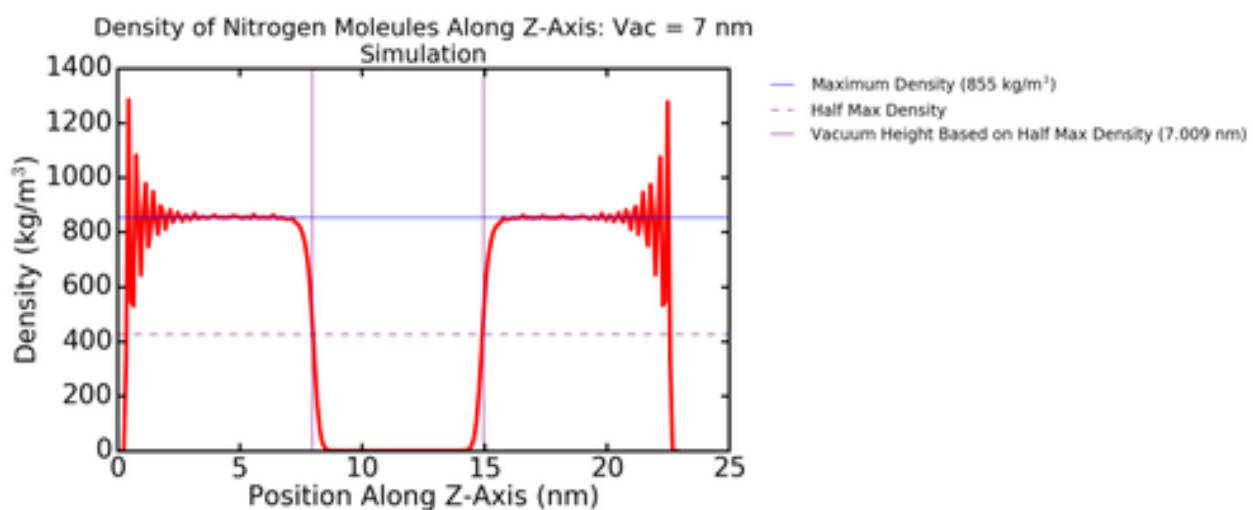
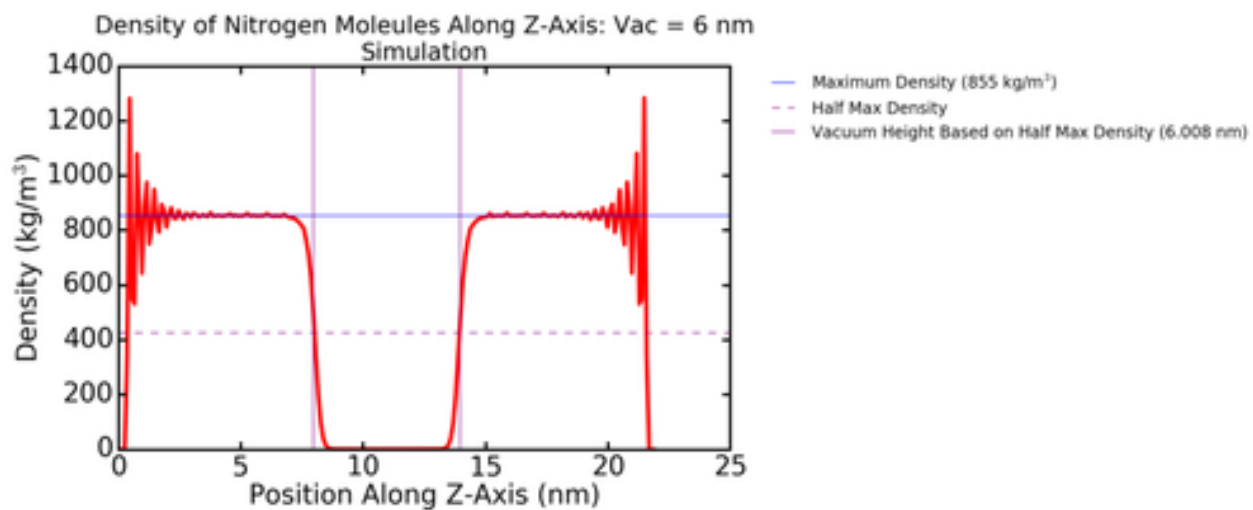
Below are histograms for simulations of nitrogen on GROMACS smooth walls. The simulations were each run for 10 ns, with 16,000 N_2 particles (8,000 in each layer), and at a temperature of 65 K. The box was 7.5645 nm along the x and y axes, while the z axis varied with vacuum height. Vacuum ranged from 2-10 nm.

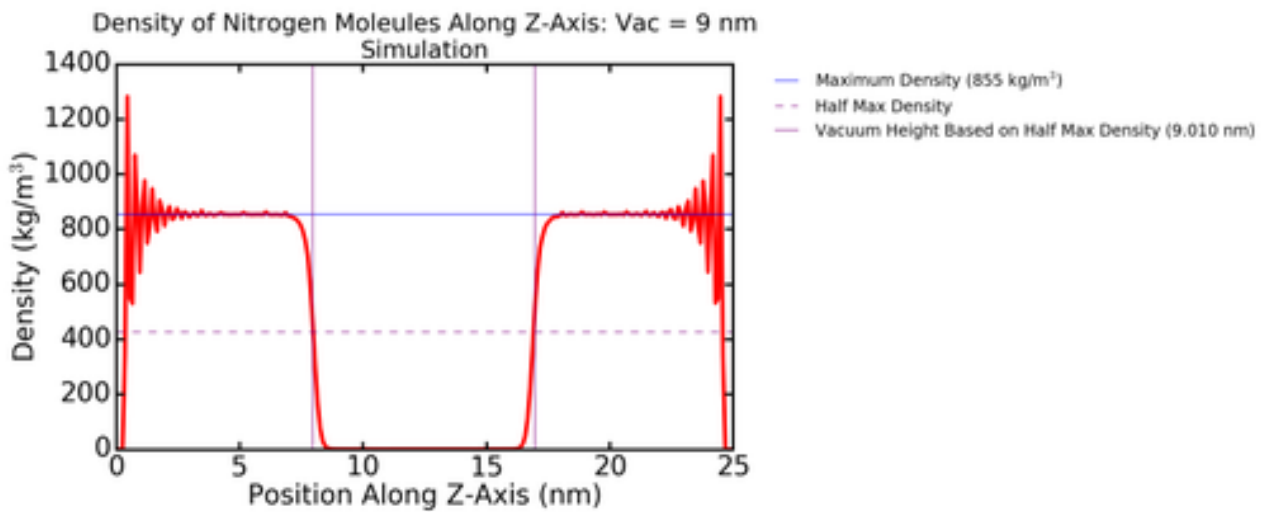
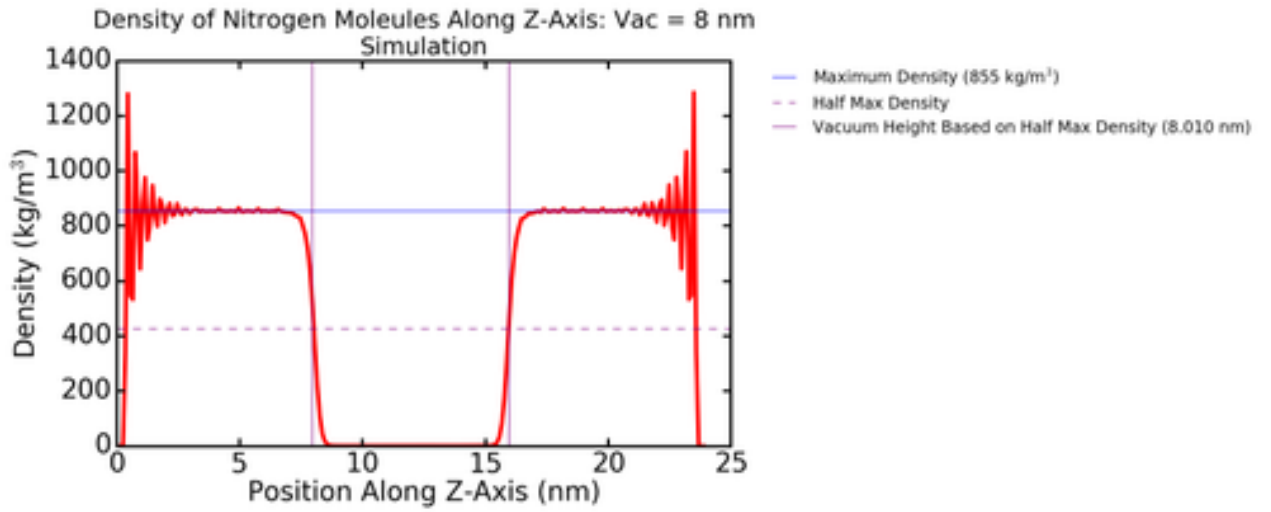
Each proposed vacuum height was coded by the amount the top layer of nitrogen was shifted to reach the top of the simulation cell. The actual height of the vacuum is calculated by determining the two locations along the z-axis in which the density of nitrogen is half that of the average bulk liquid density, and subtracting the difference between them. Differences between the proposed and measured vacuum heights are all, again, within the thousandths of nanometers.

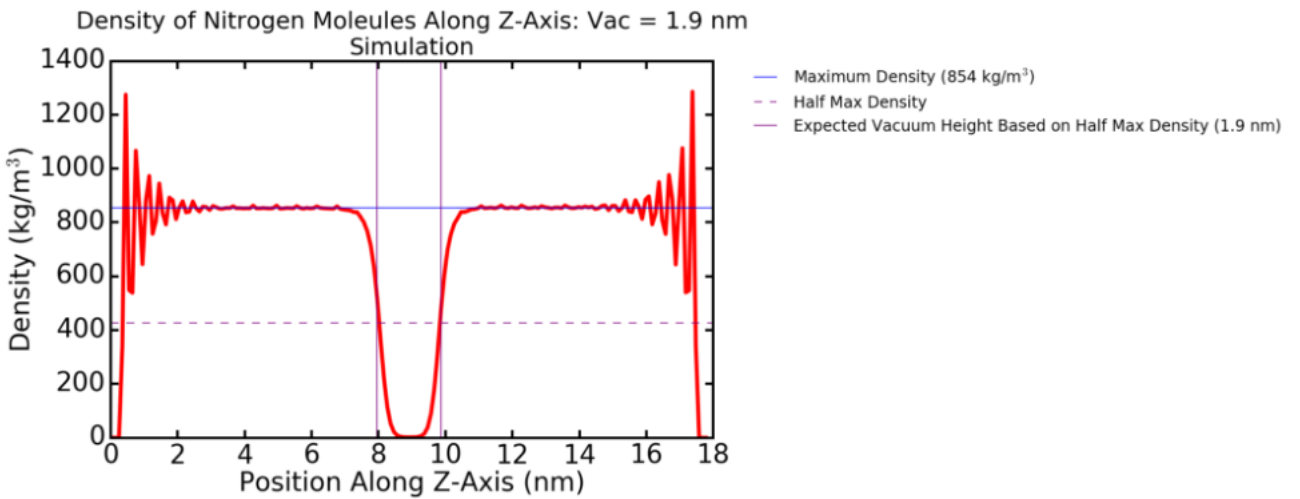
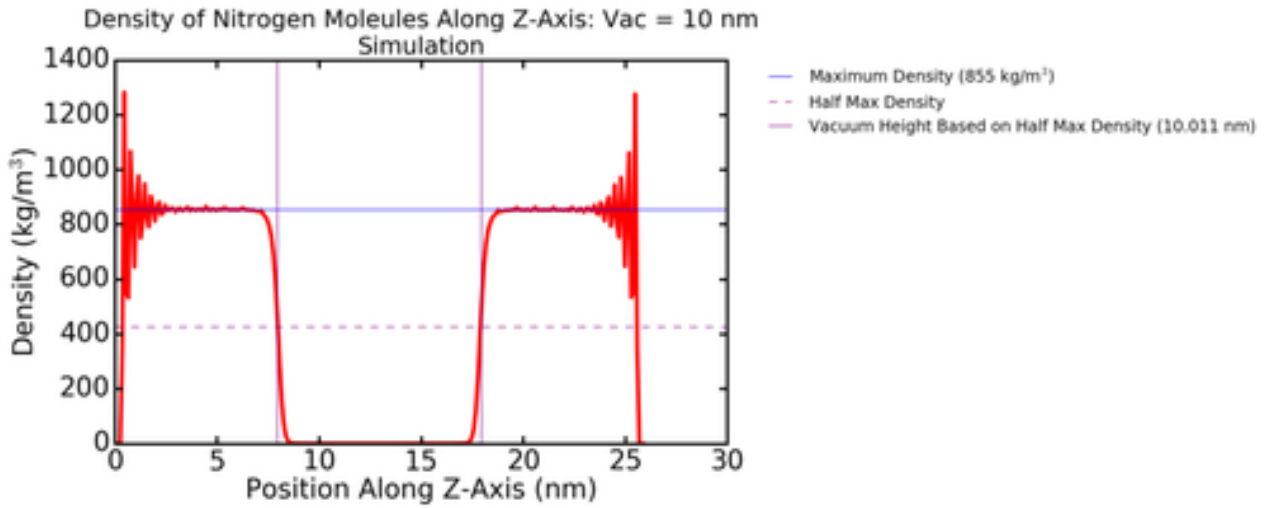
In addition to validating the system set up by seeing well defined bulk liquid layers separated by vacuum, the point in which distinct liquid layers disappears can be seen by creating histograms for vacuums starting at 1.9 nm and decreasing by 0.1 nm.

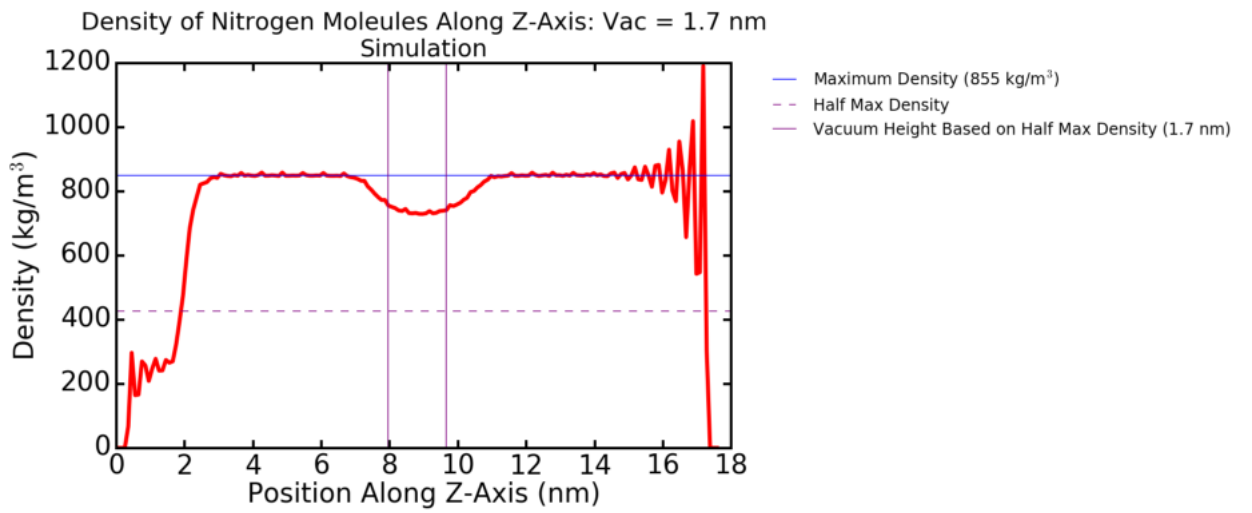
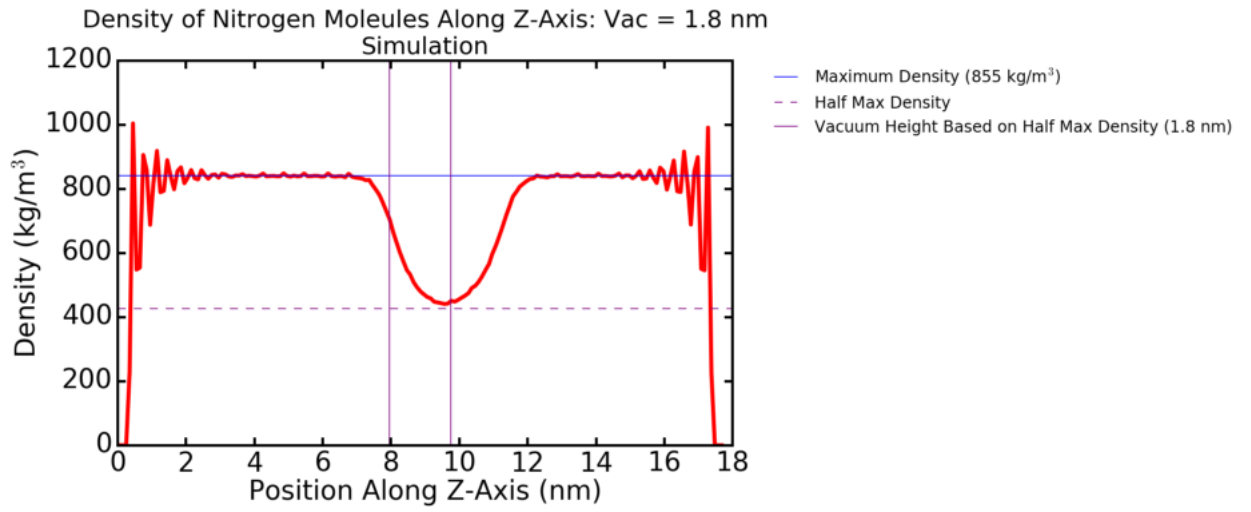


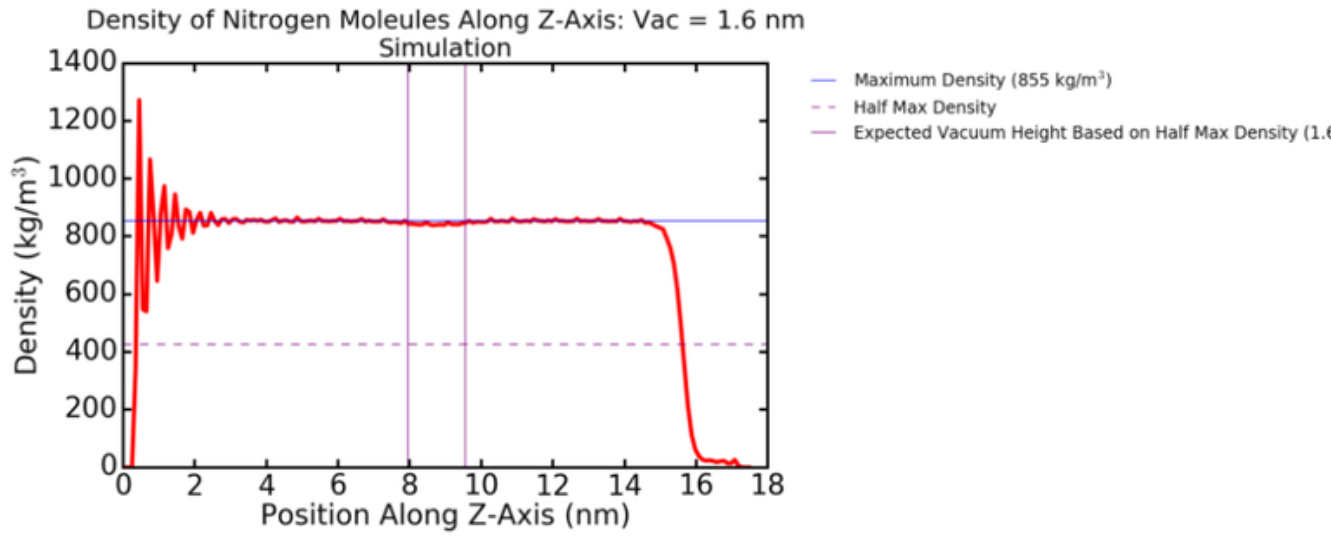












APPENDIX E

CURVE FITTING AND INTERFACE WIDTHS

Below are the curve fitting plots for the liquid-vacuum interface for each varying vacuum height trial (vacuum heights 2-10 nm). The σ , μ , and interface width values (2σ with corrected units) are commented below each plot.

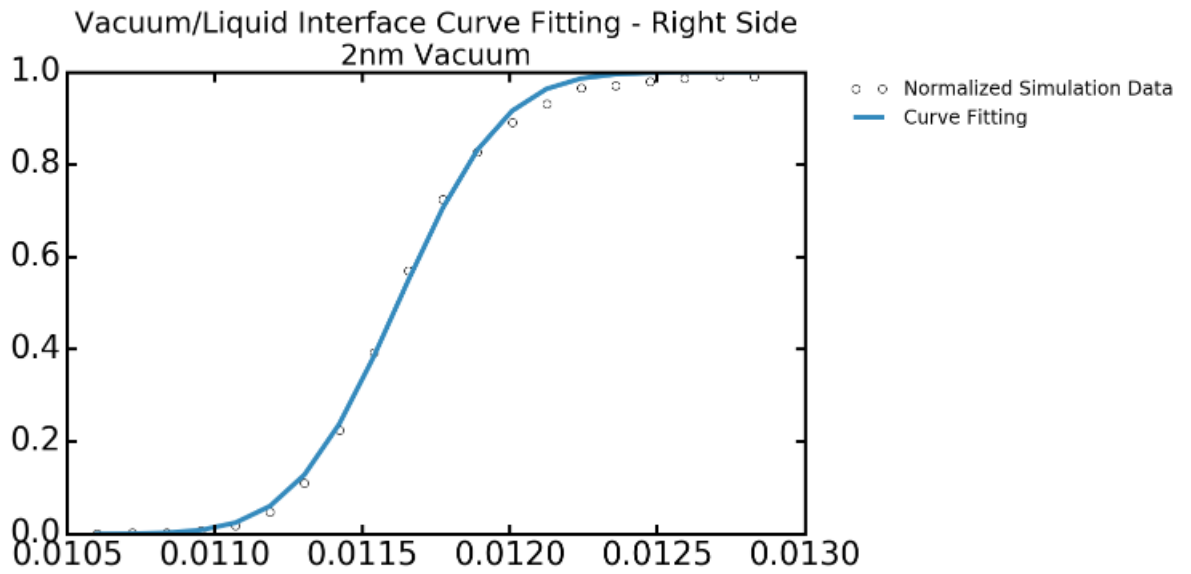


Figure E.1: $Vac = 2 \text{ nm}$: $\mu = 0.0116209970537$, $\sigma = 0.000279684965274$,
Interface width = $0.47829630717595628 \text{ nm}$

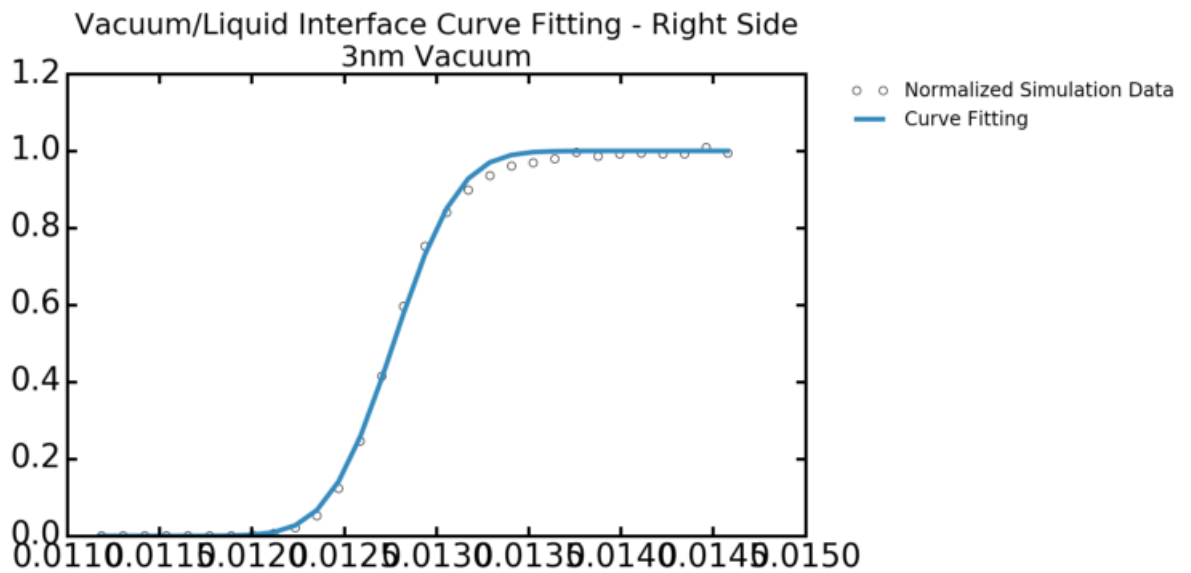


Figure E.2: $Vac = 3 \text{ nm}$: $\mu = 0.0127666512329$, $\sigma = 0.000277108430307$,
Interface width = $0.47410401903445332 \text{ nm}$

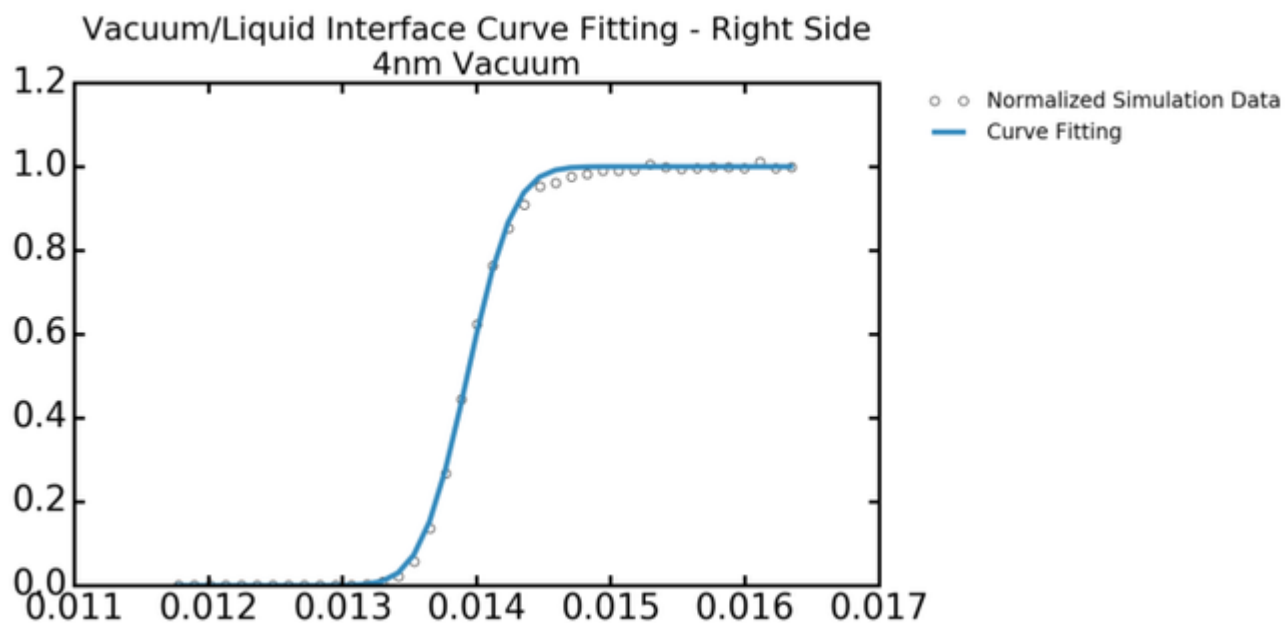


Figure E.3: $Vac = 4 \text{ nm}$: $\mu = 0.0139289632227$, $\sigma = 0.000274055408979$,
Interface width = $0.46856448154715669 \text{ nm}$

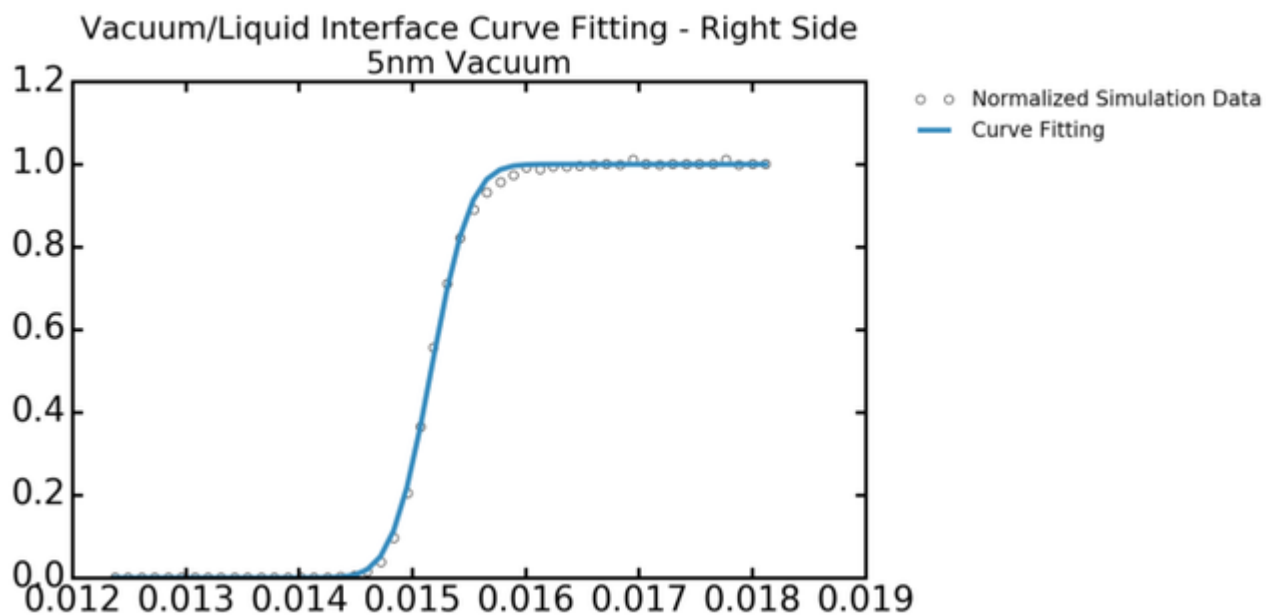


Figure E.4: $Vac = 5 \text{ nm}$: $\mu = 0.015163457968$, $\sigma = 0.000273691894628$,
Interface width = $0.46745581188502044 \text{ nm}$

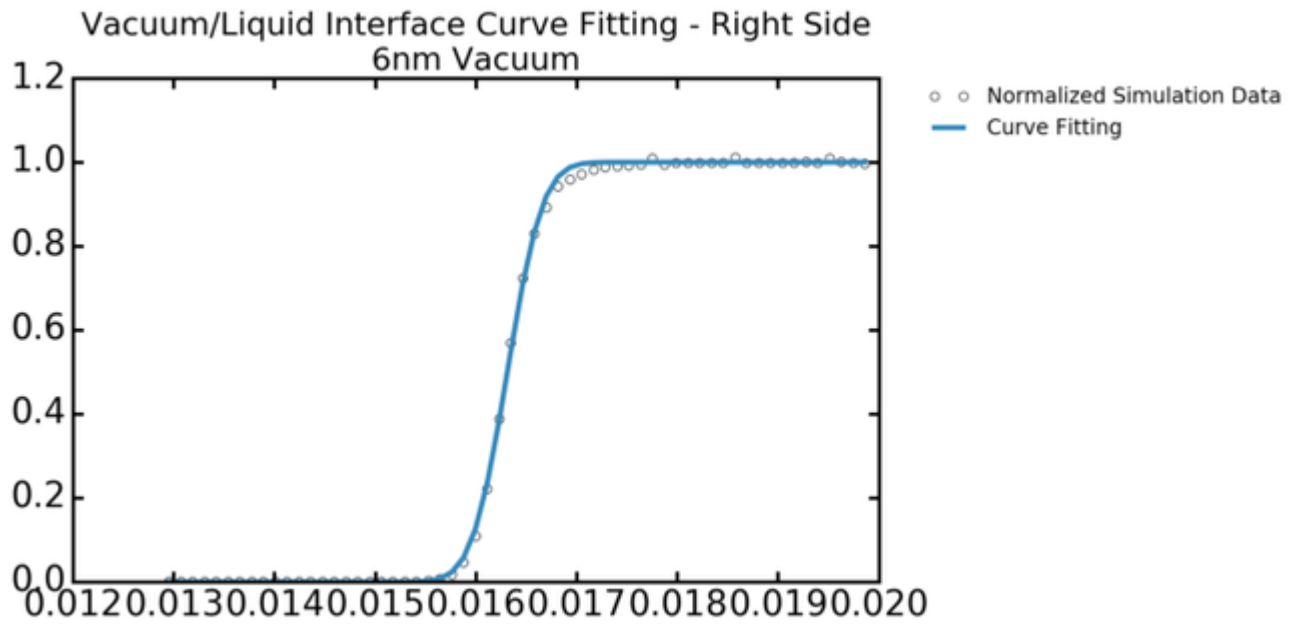


Figure E.5: $Vac = 6 \text{ nm}$: $\mu = 0.0163097473237$, $\sigma = 0.000276299459769$,
Interface width = $0.47227664038778794 \text{ nm}$

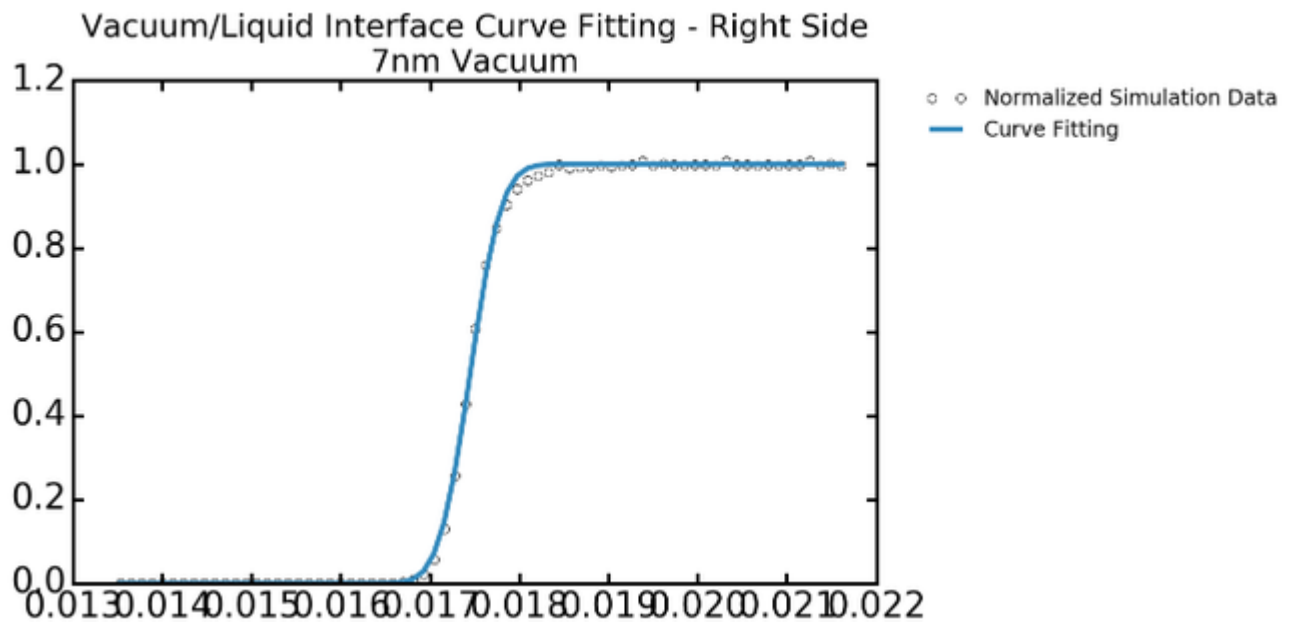


Figure E.6: $Vac = 7 \text{ nm}$: $\mu = 0.0174455553662$, $\sigma = 0.000276445874517$,
Interface width = $0.47274682794978706 \text{ nm}$

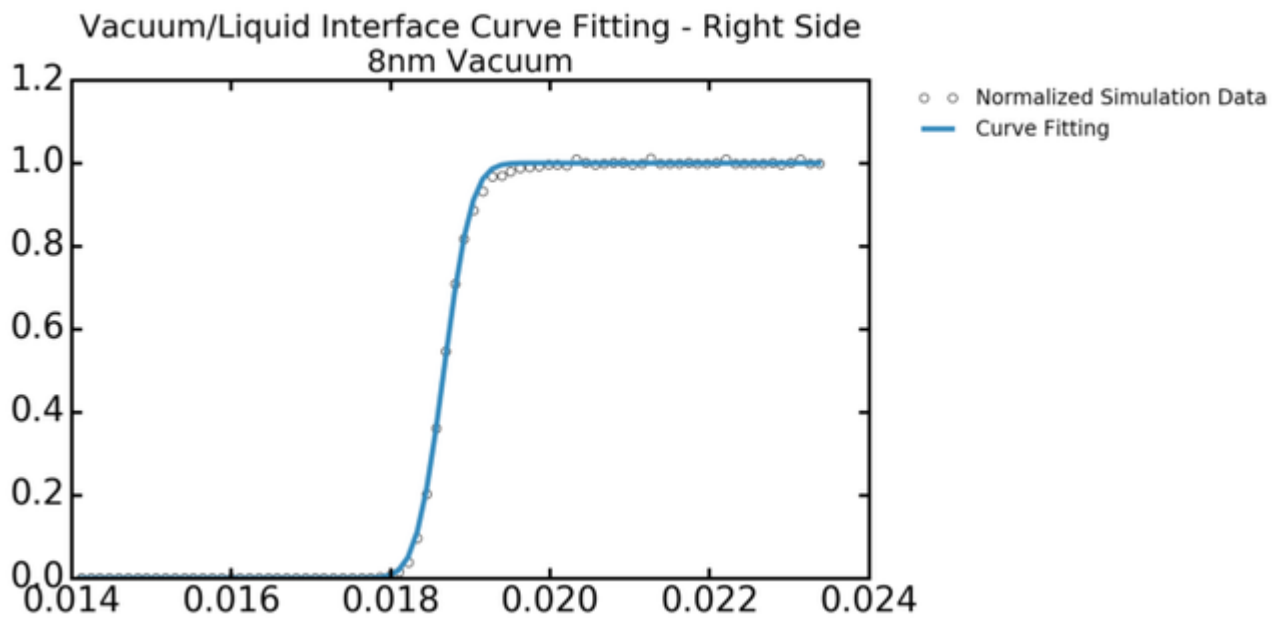


Figure E.7: $Vac = 8 \text{ nm}$: $\mu = 0.0186674236981$, $\sigma = 0.000274861115073$,
Interface width = $0.46981812499405468 \text{ nm}$

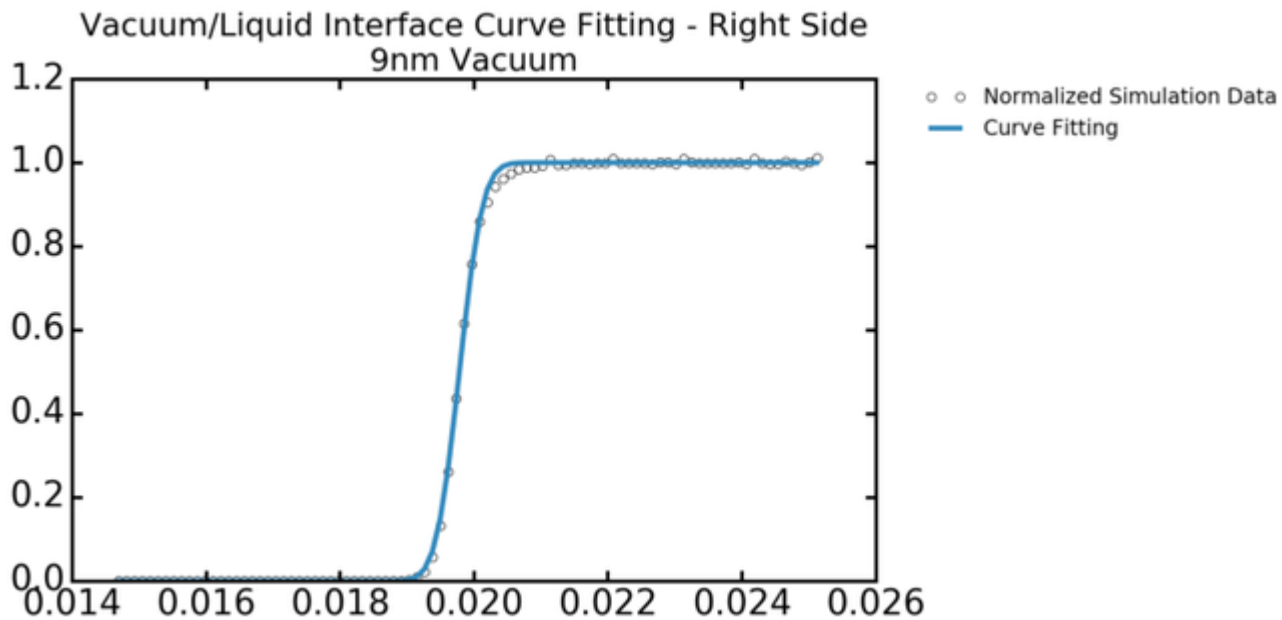


Figure E.8: $Vac = 9 \text{ nm}$: $\mu = 0.0197796938889$, $\sigma = 0.000274217882632$,
Interface width = $0.46897119611470206 \text{ nm}$

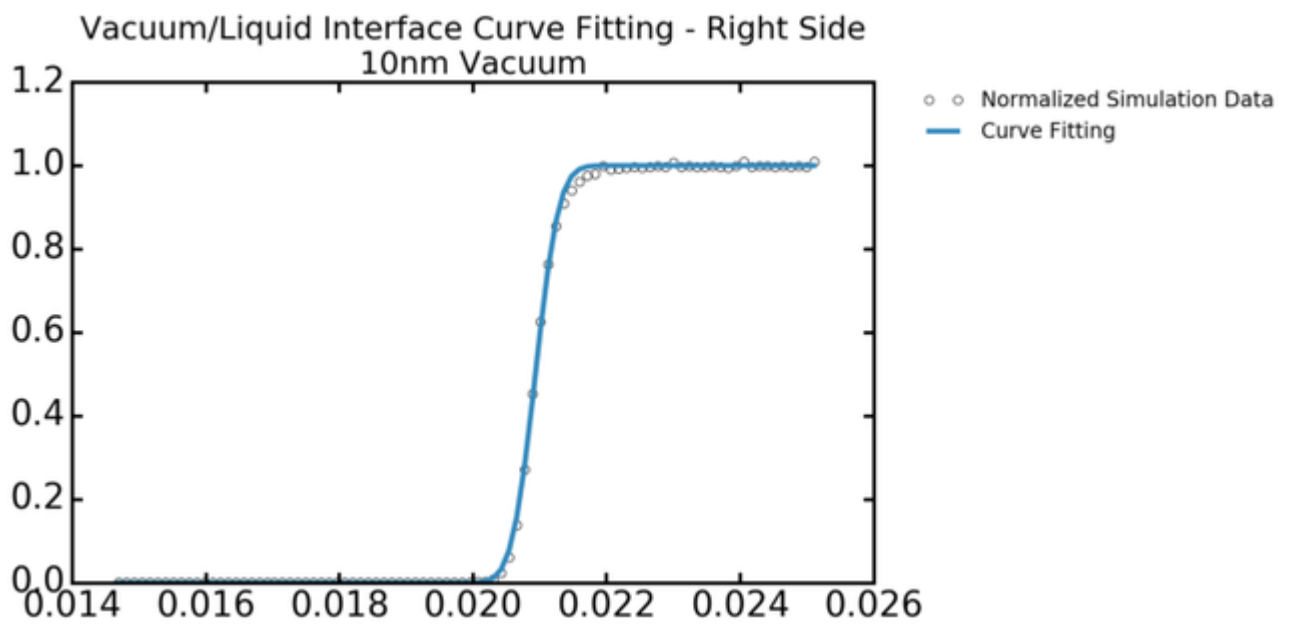


Figure E.9: $Vac = 10 \text{ nm}$: $\mu = 0.0209330322624$, $\sigma = 0.000277613897889$,
Interface width = $0.47498966162200917 \text{ nm}$