

# AN ABSTRACT OF THE THESIS OF

Cade W. Trotter for the degree of Bachelor of Science in Physics presented on May 28, 2019.

Title:

Multi-Grand, Multi-Canonical, Flat Histogram, Monte Carlo Simulations for the Square Well Fluid

Abstract approved: \_\_\_\_\_

David Roundy

## **Multi-Grand, Multi-Canonical Flat Histogram Simulations for the Square Well Fluid.**

Currently multi-canonical, and grand canonical Monte Carlo simulations exist, but do not always give all of the necessary information of the system. When using a 1-D (only changing in one variable) broad histogram Monte Carlo method a user would need to run a range of simulations in order to get the data necessary for generating the equation of state. In our multi-grand, multi-canonical approach we demonstrate the effectiveness of a “2-D” broad histogram simulation. The M-G, M-C Monte Carlo allows for both a change in the energy and the number of atoms in a square well fluid. The multiple degrees of change allow for the calculation of the entire equation of state from only one simulation.

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OREGON STATE UNIVERSITY

**Multi-Grand, Multi-Canonical, Flat  
Histogram, Monte Carlo Simulations for  
the Square Well Fluid**

AN UNDERGRADUATE THESIS  
ADVISED BY DR. DAVID ROUNDY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
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Bachelor of Science Thesis of Cade W. Trotter presented on May 28, 2019.

APPROVED:

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major professor

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dean of college

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Cade W. Trotter, Author

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# I Introduction:

## I.I Fundamentals:

Monte Carlo simulations use several steps to model stochastic systems: make a pseudo-random move, accept or deny the move, and analyze the results. The name Monte Carlo comes from the famous city of gambling. The randomness of gambling is what gave way to the name Monte Carlo. Our Monte Carlo is multi-grand, and multi-canonical meaning that it allows a simulation to vary in both number and energy of particles in a system at a range of temperatures. Allowing for atoms to be both moved, added, or removed closely represents what is happening in most physical systems than the typical Monte Carlo approach that only varies one aspect of the system.

### I.I.1 Monte Carlo Background:

In general to model random processes, we use a stochastic method. In the case of interactions at atomic level this also remains true. To model the seemingly random actions of particles in a fluid Monte Carlo methods are used. Using a set of rates and probabilities adjustments are made to the physical system in question (the fluid). The rates and probabilities in Monte Carlo simulations affect various physical parameters depending on the simulation. A common use of a Monte Carlo simulation is varying the positions of atoms in the system given by the rates set in the simulation. Depending on whether or not the simulation decides to make a move, it then decides which atom to move, and the affect on the energy of the system is then noted. One of the key early Monte Carlo methods was the Metropolis Monte Carlo (after Nicholas Metropolis). This method consisted of a system of  $N$  particles with known positions. Knowing the positions allows for an easy calculation of the energy given by:

$$E = \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^N \sum_{j=1}^N V(d_{i,j}) \quad (1)$$

Where  $V$  is the potential between particles, and  $d$  is the minimum distance between particles  $i$ , and  $j$ . [1].

### I.I.2 Flat Histogram:

The term flat histogram applies to the Stochastic Approximation Monte Carlo (SAMC) method used in our computation. SAMC was chosen due to the fact that it is guaranteed to reach convergence given the right initial parameters. SAMC functions by using a SA factor  $\gamma^{SA}$  that can be represented by the equation below:

$$\gamma^{SA} = \frac{t_0}{\max(t_0, t)} \quad (2)$$

where  $t$  is the total number of moves done so far, and  $t_0$  corresponds to the expected number of moves to reach convergence [2]. The potential downside of SAMC is that if a user picks an unsuitable  $t_0$  then the system will have trouble reaching convergence [3]. To combat the issue of a bad  $t_0$ , we simulate for a variety of  $t_0$  values to determine which has the best convergence.

### I.I.3 Square Well Fluid:

The square well (SW) fluid acts as an improvement upon the hard sphere fluid by behaving as a hard sphere fluid that accounts for both the attractive, and repulsive forces. The SW fluid is commonly used system to test the results of a Monte Carlo simulation. The reason for choosing a square well is the level of accuracy achieved compared to the work to compute physical properties of the fluid. Computationally the SW fluid is convenient in that it allows for the potential energy to be in integer values. Having integer value bins ensures there will be no round off error when storing the values. The square well fluid can be described by the piece-wise function depicted below:

$$V_{sw}(r) = \begin{cases} \infty & r \leq \sigma \\ -\epsilon & \sigma < r \leq \lambda\sigma \\ 0 & r \geq \lambda\sigma \end{cases}$$

where  $r$  is the distance between two atoms,  $\sigma$  is the radius of an atom,  $\epsilon$  is the well energy, and  $\lambda$  is the factor that determines the well width. [4].

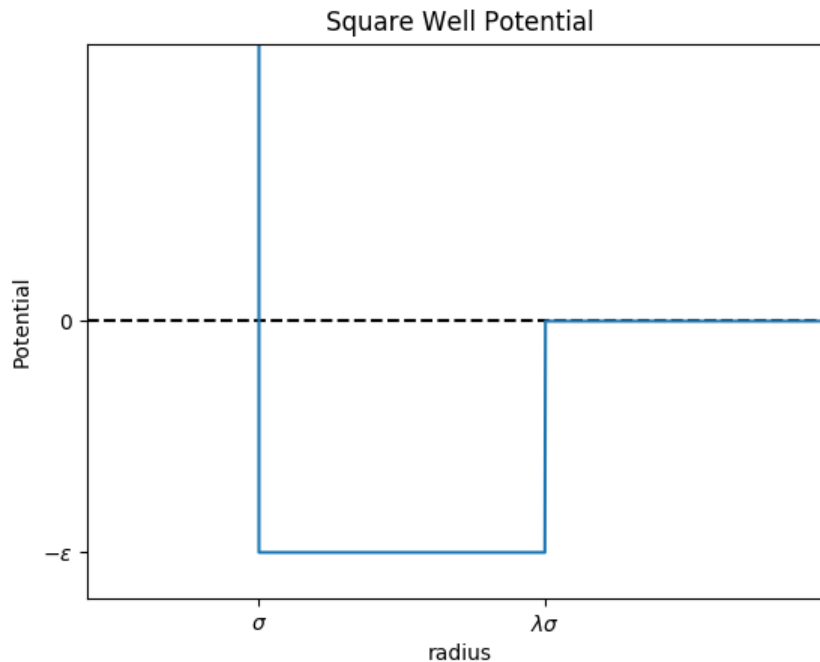


Figure 1: ***Square Well Fluid Potential:***

The figure represents the potential of the square well fluid as function of radius.

## I.II Defining Relevant Statistical Mechanics:

### I.II.1 The Partition Function:

The partition function behaves as a normalization constant in statistical mechanics. In our analysis we consistently use the excess partition function. The canonical partition function can be mathematically split into excess and ideal components:

$$\begin{aligned}
 Z &= \sum_{\text{all micro-states } i} e^{-\beta E_i} [5], \\
 &= \frac{1}{N!} \int d^3 \vec{r}_1, d^3 \vec{r}_2, \dots, d^3 \vec{r}_N \int d^3 \vec{p}_1 d^3 \vec{p}_2 \dots d^3 \vec{p}_N e^{-\beta(u(\vec{r}_1, \vec{r}_2, \dots) + \sum_i p_i^2/2m)} \\
 &= \frac{1}{N!} \int d^3 \vec{r}_1 \dots d^3 \vec{r}_N (e^{-\beta u}) \int d^3 \vec{p}_1 \dots d^3 \vec{p}_N (e^{-\beta \sum_i p_i^2/2m}) \\
 Z_{\text{ideal}} &= \frac{1}{N!} V^N \left( \int d^3 \vec{p}_1 \dots e^{-\beta \sum_i p_i^2/2m} \right) \quad V^N \text{ is a phase-space volume} \\
 Z_{\text{excess}} &= \frac{Z}{Z_{\text{ideal}}} = \frac{1}{V^N} \int d^3 \vec{r}_1 \dots d^3 \vec{r}_N e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)}
 \end{aligned}$$

### I.II.2 Multiplicity:

The multiplicity or  $g$  can be described as the number degeneracy of micro-states that result in a redundant state. To define the excess multiplicity we can work from the definition of the excess partition function to arrive at something in a similar form:

$$g(E, N)_{\text{exc}} \equiv \frac{1}{V^N} \int \int \dots \int d^3 \vec{r}_1 d^3 \vec{r}_2 \dots d^3 \vec{r}_N \delta(E - V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)) \quad (4)$$

The  $\delta$  in this case is used to represent a Dirac delta function due to the fact that we are taking this with respect to 3 N-dimensions.

### I.II.3 Excess Vs. Ideal:

In the code I needed to address the fact that the system does not behave exactly as an ideal fluid and that needs to be compensated for. The total energy in the system is made up of a contribution from the ideal gas (ideal) terms and terms referred to as excess (exc). Excess in the case of the simulation corresponds to the difference from the idealized case. A quick and interesting geometric proof can be used to validate the excess approach:

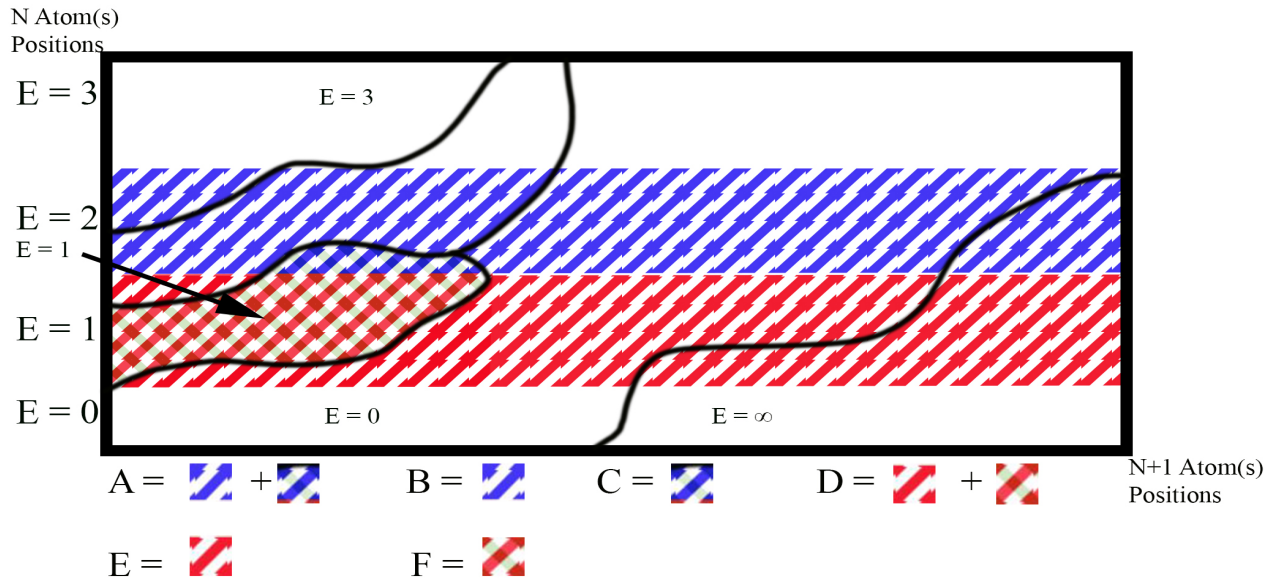


Figure 2: **Geometric Proof of Excess:**

The figure depicts the probabilities of a change in energy vs. the multiplicity ( $g$ ).

Suppose there is a system with number of atoms given by  $N_{atoms}$ , and an energy given by:  $E_i$ . What is the probability of getting energy  $E_f$ ? Well this can be solved by a comparison of the energy levels/areas of the regions in 2, and the probability of adding or removing given by  $P_{Add}$ , and  $P_{Remove}$  respectively:

$$P_{N,2 \rightarrow N+1,1} = \frac{C}{A} * P_{Add}$$

$$P_{N,1 \rightarrow N+1,1} = \frac{F}{D} * P_{Add}$$

$$P_{N+1,1 \rightarrow N,2} = \frac{C}{C + F} * P_{Remove}$$

$$P_{N+1,1 \rightarrow N,1} = \frac{F}{C + F} * P_{Remove}$$

To find the multiplicity of a given energy value we can divide the probability of an  $N$  particle system with energy 2 that is transitioning to a  $N+1$  particle system with energy 1 by the opposite

of that:

$$\begin{aligned}\frac{P_{N,2 \rightarrow N+1,1}}{P_{N+1,1 \rightarrow N,2}} &= \frac{\frac{C}{A} * P_{Add}}{\frac{C}{C+F} * P_{Remove}} \\ \frac{P_{N,2 \rightarrow N+1,1}}{P_{N+1,1 \rightarrow N,2}} &= \frac{C + F}{TotalArea} \\ g_{exc}(N + 1, 1) &= \frac{C + F}{TotalArea}\end{aligned}$$

This returns the total shape in the  $E = 1$  region divided by the total area.

### I.III Ensembles:

#### I.III.1 Micro-Canonical Ensemble:

The micro-canonical ensemble (sometimes NVE ensemble) is used to represent a system that does not allow for a change in energy. Such a system can be thought of as an entirely isolated system unable to vary in energy. This ensemble allows for simplified explanations of what is physically occurring in the system. We can represent the internal energy of the system as:

$$U = \sum_i^{\text{all micro-states}} E_i P_i = \langle E \rangle \quad (5)$$

Where  $E_i$ ,  $P_i$ , and  $k_B$  represent the energy, probability, and Boltzmann's constant respectively. The equation to find the probability at that given micro-state is represented by:

$$P_i = \frac{1}{W} \quad (6)$$

Where  $W$  is the number of micro-states with that given energy [6].

#### I.III.2 Canonical Ensemble:

The canonical ensemble (sometimes NVT ensemble) is used to represent a system that does allow for a change in energy, this energy can be thought of as an exchange in energy between the system in question, and an additional one with a different temperature. In our canonical Monte Carlo code we start with a micro-state, and we chose a random move to do it. Once the move has been made we calculate the change in energy, and then we compare it to the probability of the accepting the move. The probability can be given as:  $P_{\text{accept}} = e^{-\beta \Delta E}$ . In this representation if the energy were to be increasing the probability would then be less than one, and the code would reject the move (meaning the system would tend to be in the lower energy states). Going through randomly sampled micro-states allows for finding the range of probabilities negating the need to sample all micro-states. The representation of excess internal energy in this ensemble can be represented as:

$$U_{\text{exc}} = \sum_i^{\text{all states}} \frac{e^{-\beta E_i} E_i}{Z_{\text{exc}}} \quad (7)$$

Where the partition function here can be represented as:

$$Z_{\text{exc}} = \sum_i^{\text{all states}} e^{-\beta E_i} \quad (8)$$

### I.III.3 Grand-Canonical Ensemble:

The grand-canonical ensemble (sometimes  $\mu VT$ ) is used to represent a system in contact with another system with a different temperature that not only allows for an exchange of energy, but also an exchange of atoms. Internal energy in the grand canonical ensemble can be represented as:

$$U_{\text{exc}}(\mu, T) = \sum_i^{\text{all states}} \frac{E_i e^{-\beta(E_i + \mu N_i)}}{Z(\mu, T)} \quad (9)$$

Where the grand partition function is represented as:

$$Z_{\text{exc}} = \sum_i^{\text{all states}} e^{-\beta(E_i + \mu N_i)} \quad (10)$$

[7].

### I.III.4 Multi-Grand, Multi-Canonical (M-G, M-C):

As previously mentioned our new proposed Monte Carlo allows for both the energy and number of atoms to vary. It can be thought of as varying in energy, temperature, and number of atoms. When compared to the standard Monte Carlo it allows for much more versatility in one simulation. To achieve an equation of state using a standard Monte Carlo, the user must run several simulations. In the case of our M-G, M-C Monte Carlo one simulation is enough to find the equation of state of a system.

## I.IV Thermodynamic Relationships:

Starting with a well known thermodynamic equation:

$$dU = TdS - PdV + \mu dN \quad (11)$$

[8], from this we can take several partial derivatives while holding variables constant.

### I.IV.1 Entropy:

In the simulation we find the entropy from multiplying a Boltzmann factor by the log of the multiplicity:

$$S = K_B \ln(g) \quad (12)$$

[9]

**I.IV.2 Temperature:**

Knowing the internal energy we can take a quick derivative of it with respect to entropy while holding number, and volume fixed we arrive at:

$$\frac{1}{T} = \left(\frac{\delta S}{\delta U}\right)_{V,N} \quad (13)$$

**I.IV.3 Chemical Potential:**

Taking a similar approach to the temperature we can take a derivative of the internal energy, but this time with respect to number while holding entropy and volume constant:

$$\mu = \left(\frac{\delta U}{\delta N}\right)_{S,V} \quad (14)$$

Chemical potential describes a system's ability to hold or release an amount of energy per unit volume. Chemical potential can be thought of as the amount of material that can be put into a container as well as the amount of that same material that one could get out of the container. In the same way that temperature can be thought of as controlling the flow of energy, chemical potential can analogously be thought as controlling the flow of particles [10].

**I.V Equation of State:**

The equation of state is a means of describing the physical phase that the system is in. Using state variables such as temperature, pressure, volume, and energy the phase the system is in can be known. In the case of the M-G, M-C Monte Carlo, varying the number and energy provides all the required information to solve the equation of state in just one simulation. To represent the equation of state one can use what is referred to as a phase diagram, in the case of our Monte Carlo we will frequently plot pressure with respect to temperature.

## II Methods:

### II.I Changing in Two Directions:

In our Monte Carlo atoms are either chosen to be moved or removed/added at random. In a fluid atoms are always moving, and occasionally they can be removed from the system -think evaporation in a fluid. To stay accurate to a physical system we are using a physically 3-D simulation. In the simulation it first chooses an atom at random, and then decides whether or not it will be moved, or removed. Another possible outcome is that the simulation chooses to add an atom to a location where it does not violate the hard sphere potential. The case of being removing an atom is easy to deal with. Adding an atom is based upon whether or not it will overlap with another atom in the same location. When deciding whether or not it will be moved or the simulation has to look where it is moving the atom and decide if it overlap with another atom in the system. Since we are using a hard sphere potential for the atoms they cannot occupy the same space as one another. If the simulation tries to move a ball or add a ball into a space where there is already a ball occupying it will reject the move and proceed to the next. To illustrate the difference between the standard Monte Carlo approach M-G, M-C two figures are included below:

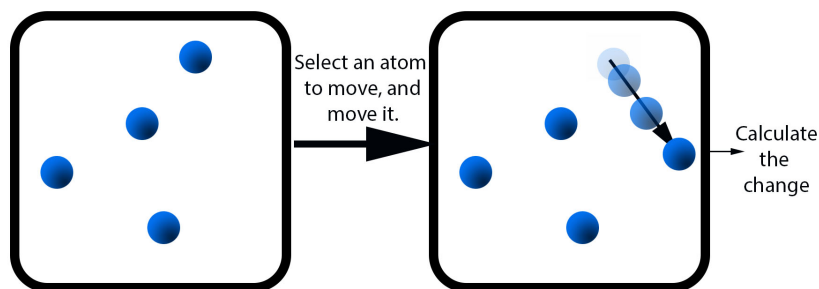


Figure 3: *Typical Monte Carlo:*

The figure depicts the process of a typical Monte Carlo simulation. The code picks an atom in the system, moves it, and then calculates the change in the thermodynamic properties of the system.



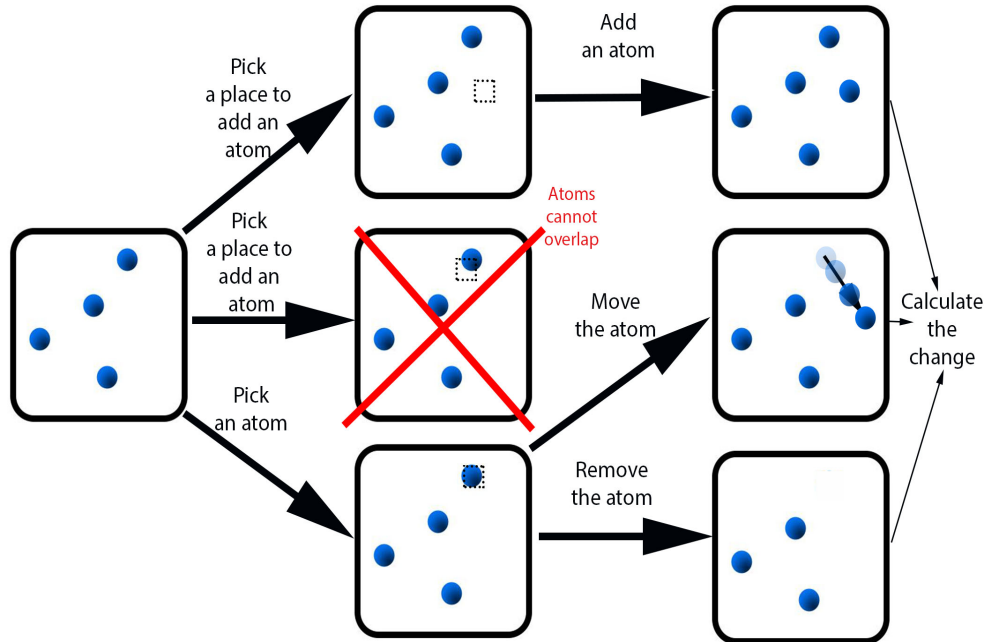


Figure 4: *M-G, M-C, Flat Histogram Monte Carlo Flow Chart:*

The figure depicts the process of our Monte Carlo. The simulation picks an atom to move, or it adds/removes an atom. When a change has been made the simulation then calculates the entropy of the system.

## II.II Crystallization/Volume Choice:

cy in thermal physics

If the atoms in the system are aligned in a lattice structure then a crystal will appear. Given a certain volume and number of atoms it almost guaranteed this configuration will occur.

### II.II.1 Detailed Balance:

In the simulation a concept of detailed balance must be obeyed. Detailed balance essentially states that the opposite of any move that is proposed needs to be equally probable. Meaning removing an atom needs to be as probable as adding one.

## II.III Histogram Entropy:

Due to the multi-variable nature of the simulation, the output needs to be capable of modeling the specific energy and number the values correspond to. In order to do this 2-D arrays are used. The output of our simulation comes in the form of 2-D arrays whose magnitude depicts either the histogram data or the excess entropy of the system. The method of visualization comes in

the form of 2-D colour plots to illustrate the magnitude of each output at the specific energy and number combinations.

### II.III.1 Numerical Derivatives:

When doing manipulations of the thermodynamic properties, derivatives often come up. To do derivatives on the 2-D array centered finite difference numerical derivatives are used. Numerical derivatives represent the change in a specific finite variable with respect to another finite variable in the data.

### II.III.2 Computing averages (or analyzing results)

When dealing with large sums of exponentials computers can become limited by overflow error (this occurs when numbers exceed  $\simeq 10^{300}$ ) To computationally avoid this, we break up any equations with a potential overflow, and split them into a numerator and denominator that are calculated separately. The maximum of the thing being calculated can be subtracted from both the numerator and denominator of the function, thus keeping it mathematically correct while fixing the overflow issue. To illustrate this an arbitrary equation is manipulated using the described process:

$$\frac{e^x}{e^y + e^z} = \frac{e^x}{e^y + e^z} \left( \frac{e^{x-xmax}}{e^{-xmax}} \right) \quad (15)$$

## II.IV Simulation Parameters:

To run the simulations we need to specify some physical parameters of the system. When looking at Fig. 1 it is obvious that we need to specify a well width. To stay consistent with the convention in common Monte Carlo simulations we chose a well width of 1.3. The volume was chosen to be approximately 30.

## III Results:

### III.I Histogram Data:

When doing a flat histogram simulation, the results of the simulation are valid when the system has explored all of the energies. We know that a simulation has explored all of the energies when the histogram data displays that the simulation has been to all of the energy number combination the same number of times.

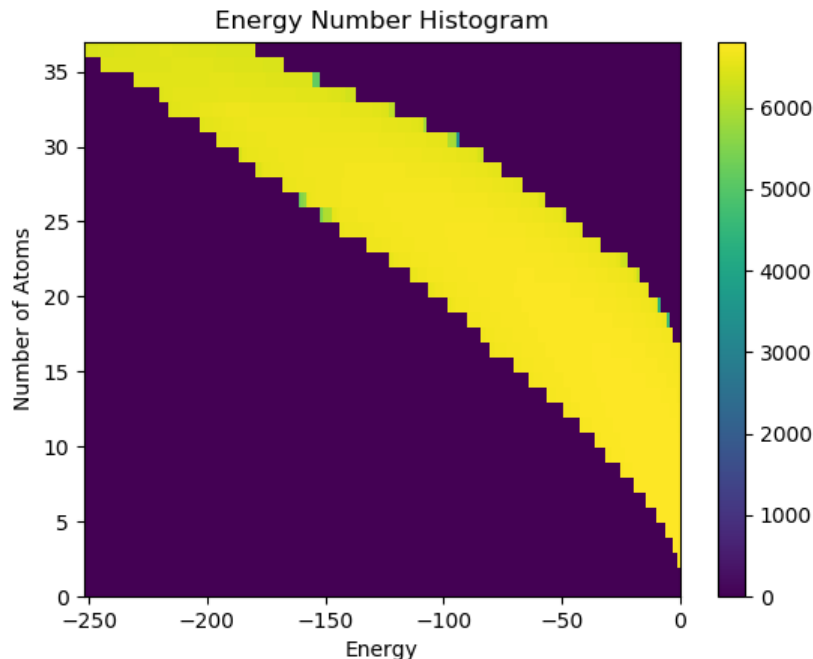


Figure 5: *Histogram Plot:*

The figure depicts the flat aspect of the histogram data. The uniform spread of color illustrates that the simulation has reached convergence.

The uniformity of yellow data points is indicative of having reached or nearly reached convergence. The standard flat histogram method knows that a simulation has reached convergence when the histogram reaches a broad distribution. When analyzing a 2-D case, we are not able to represent all of the combinations of energy and number with just a simple histogram. To represent it we use a color plot, and flatness is described by the uniformity of the color across the region in question. When looking at the graph it can be seen that there is a yellow band-diagonal structure going through the center. The region where physically possible energy number combinations is indicated by this yellow band, whereas the purple represents regions that cannot be visited. To justify this region we can look at the number of atoms. As the number of atoms decreases from its maximum of 36 atoms, we observe the energy in the system decrease in magnitude. Using Eq. 5 it can be seen that as the number of micro-states decrease the sum will be over a smaller range, thus decreasing

the magnitude of the energy.

### III.II Micro-Canonical Excess Entropy:

The entropy can be thought of as the log weight of the simulation. From this entropy the rest of the thermodynamic properties can be found. The entropy can be observed as plotted below:

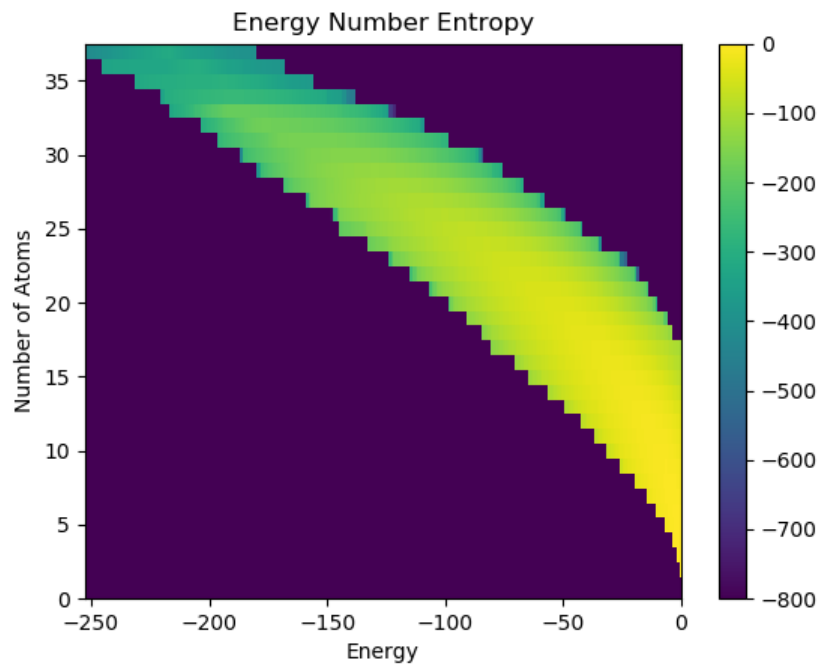


Figure 6: *Canonical Entropy Plot:*

The entropy can be seen to increase as the number of atoms in the system increase.

Entropy behaves as to be expected. As the number of atoms in the simulation increases, so does the entropy. Adding more atoms allows for potentially more disorder, and the entropy data reflects that.

### III.III Micro-Canonical Excess Chemical Potential:

As mentioned in Sec. I.IV.3 the chemical potential can be thought as how much material can be added or removed from its container on specific conditions. The chemical potential at several energy number combinations can be observed in the figure below:

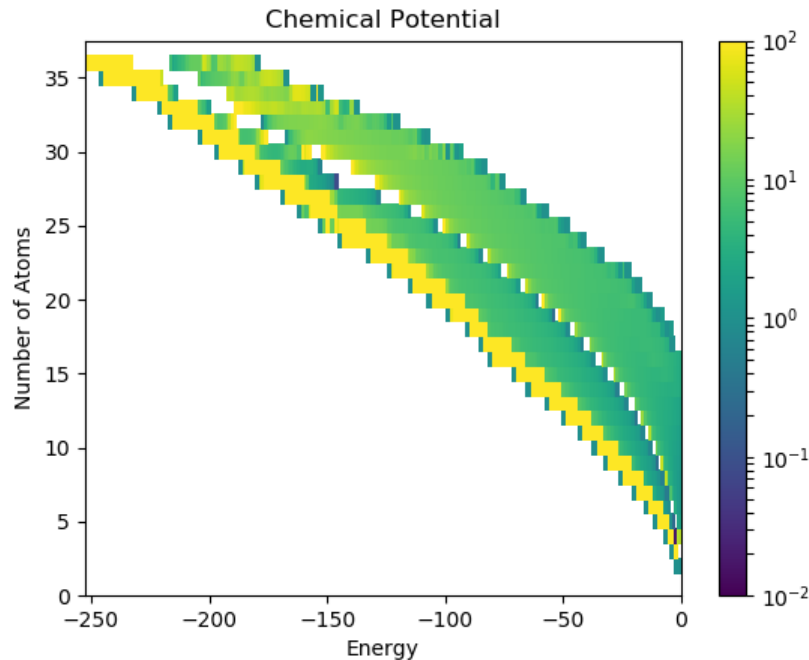


Figure 7: *micro-canonical Excess Chemical Potential Plot:*

In the figure, chemical potential can be observed to have data in a band like structure.

Looking at the chemical potential we observe the same physical region as Sec. II.III. The figure is micro-canonical in that each energy number combination represents a chemical potential at that given combination. Due to the use of numerical derivatives, there is a yellow region on the left hand side of the band that can be ignored. Looking at the rest of the plot further, it can be seen that when the number is higher there is a larger chemical potential than when the number is smaller. To justify the trend in chemical potential we can use Eq.14.

### III.IV Micro-Canonical Temperature:

Due to the fact that the simulation sweeps through all numbers and energies for a system without constraining temperature we can find the temperature at any given energy number combination. A depiction of the temperature can be seen in the figure depicted below:

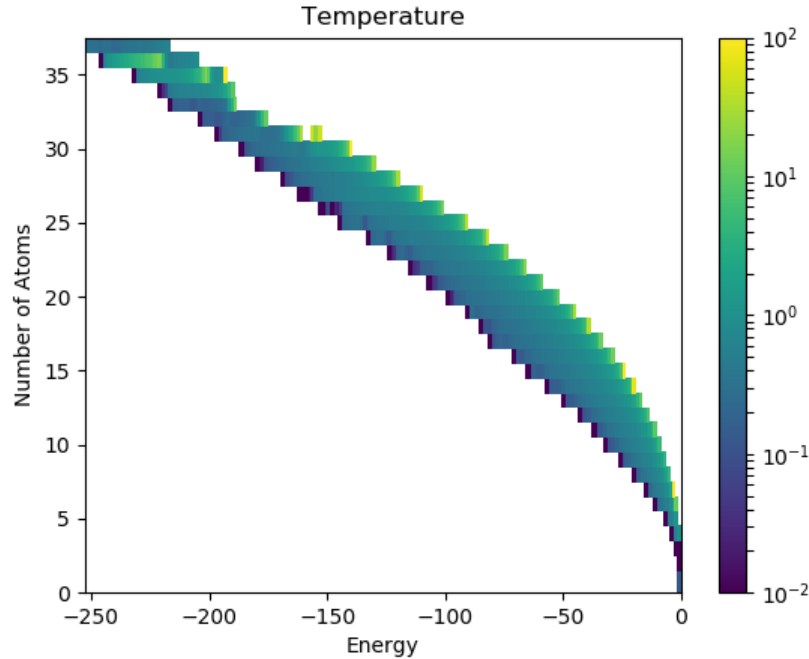


Figure 8: *Micro-Canonical Temperature Plot:*

In the figure, Temperature is observed to have a band-diagonal-like structure with maximum temperature in the region associated with the lowest number of atoms at a given energy.

The temperature is something very familiar that can be intuitively explained. Referencing Eq.13 we can see that temperature can be given as a function of internal energy with respect to entropy. Using that notation this is not convenient to calculate, however its inverse is. Inverting the derivative we were quickly able to solve for the temperature. Looking at the temperature it can be seen that the largest regions occur where the greatest number of atoms are at a given energy.

## III.V Grand Canonical:

### III.V.1 Grand Number Representation:

One form of identifying a phase transition is to look for a sudden change in the number of atoms in the system. Using this logic we used the grand canonical ensemble to plot the number of atoms at any chemical potential, and temperature. The graph below depicts the number of atoms present at a range of chemical potentials, and temperatures:

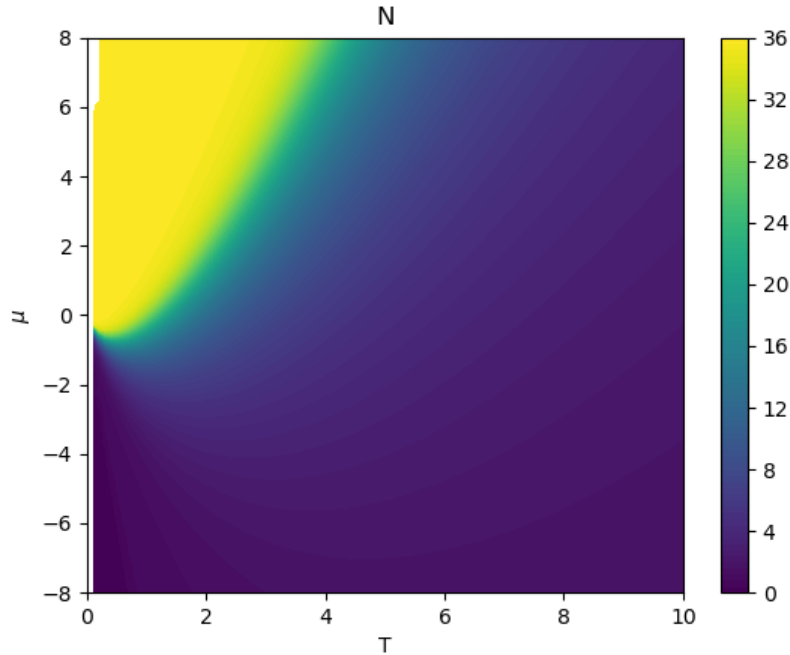


Figure 9: *Grand Number Representation:*

In the figure, it can be seen that there is a region of chemical potential and temperature combinations in which the maximum number of atoms exist.

There is a noticeable region that exists when the temperature is smaller, and the chemical potential is larger. Physically a region with the maximum number of atoms should exist there as this region is indicative of a crystal. As the chemical potential decreases or the temperature increases there is a noticeable phase change that can be observed as the sudden color change from yellow. A phase change at a region like that can be justified by the number of atoms in that region. The yellow can be thought to represent a solid phase, and the purple region can be thought of as a gas. In the case of this figure it can be observed that as the temperature increases after a certain region, the number of atoms at a given chemical potential decreases as to be expected.

### III.V.2 Grand Canonical Internal Energy Representation:

When doing the grand canonical ensemble we can also find a representation of the excess internal energy at any chemical potential, and temperature. The figure below depicts the internal energy of the system at a range of chemical potentials, and temperatures:

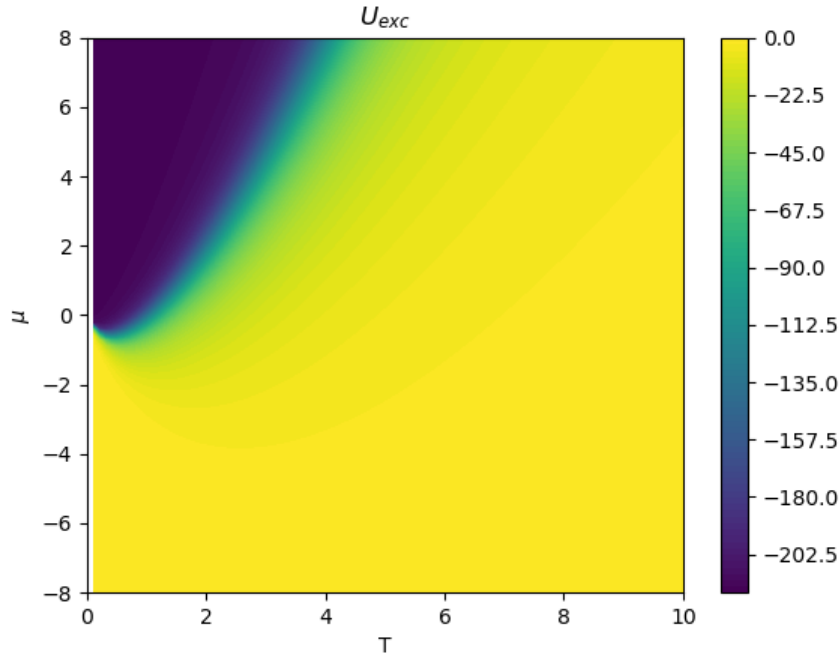


Figure 10: *Grand Internal Energy:*

In the figure, it can be seen that there is a region of chemical potential and temperature combinations in which a local minima of internal energy exists.

It is apparent that there is a region of low temperature, high chemical potential combinations such that a series of local minima exist. This region can be explained by the fact that these combinations occur at a region of low temperature which would result in a low internal energy. When comparing the plot to it is easy to see that this minimized region of internal energy occurs in the exact region that the number of atoms is maximized. A maximization of density is indicative of a crystal, which we would expect to have a low internal energy.

### III.V.3 Phase Through Internal Energy and Number as a Function of P and $\mu$ :

To represent the equation of state the internal energy was plotted as a function of pressure and temperature:



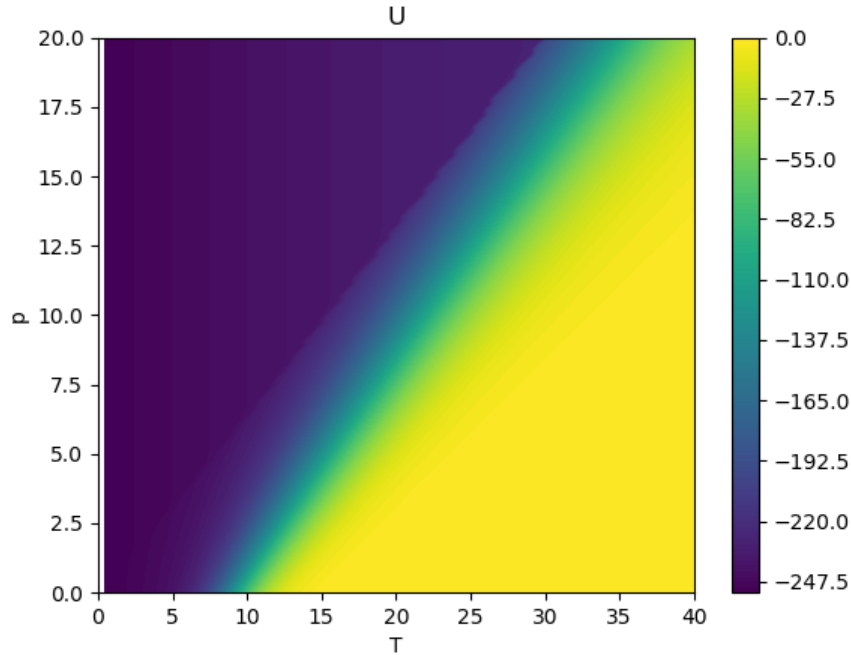


Figure 11: *Internal Energy Phase Representation:*

In the figure, it can be seen that there are three distinct regions of internal energy. The changes between these regions can be used to demonstrate phase transitions.

Looking at the internal energy the three regions act very similarly to Fig.10. The change in color once again represents the difference in internal energy. The region with a large pressure would likely cause a solid, and thus the internal energy would be lower. Looking at a particular pressure and increasing temperature shows a drastic change in internal energy. The change is indicative of a phase change, which is what is to be expected of an increase in temperature. In order to display this phase change further the number was plotted with respect to the same variables:

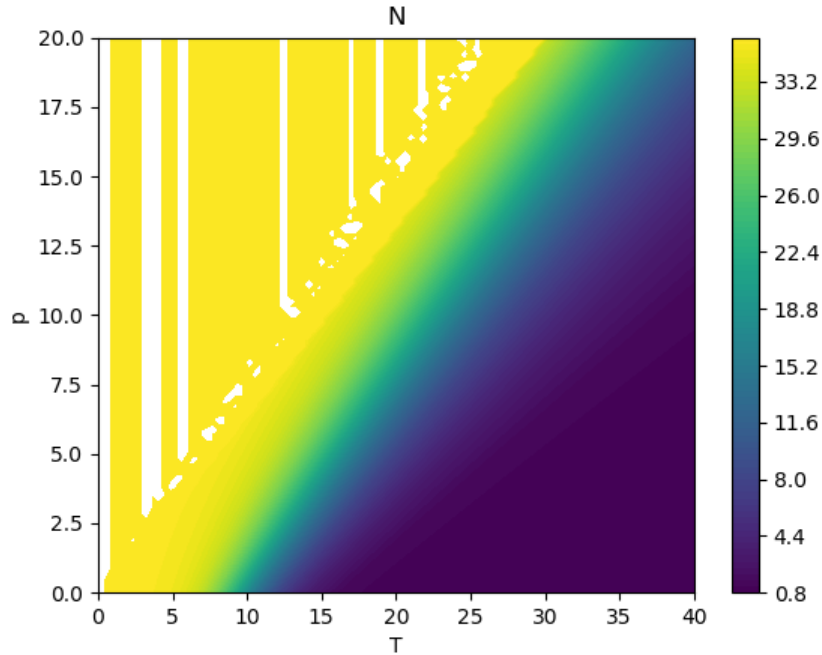


Figure 12: *Number Phase Representation:*

In the figure, it can be seen that there are three distinct regions of internal energy. The changes between these regions can be used to demonstrate phase transitions.

This figure behaves very similarly to Fig.9. When the pressure is high the number can be seen to be larger, indicating that the system is in a solid phase. When the temperature is increased, the number of atoms decreases. This decrease shows a change in phase from a solid, all the way up to a gas.

## IV Conclusion:

Modeling fluids requires complex stochastic methods, and the ability to simplify a method can drastically improve the results. The current state of Monte Carlo methods involves running several simulations and picking which parameters are useful for the user. Having a method that could act as an all in one model of a system drastically decreases the need for any guess work, or tedium.

Our new multi-grand, multi-canonical, flat histogram, Monte Carlo simulation allows for a system to change in both number of particles, and energy of the system while allowing for multiple temperatures. Allowing for these changes, provides the user an ability pick which ensemble they want to analyze. Depending on the requirements of the problem sometimes only a canonical approach is necessary, and sometimes a grand canonical approach is what is needed. Due to this ability to change several things, our new method has been shown to work for finding the entire equation of state from just one simulation. A user simply needs to pick which system to model, and then run our simulation on the system.

Future work will include: applications to real world problems, more representations of the equation of state, and the implementation of this method to other systems such as the Ising model for example. Collaboration with the OSU chemical engineering department to use grand canonical simulations on metal organic frameworks is already underway within our group. Potential improvements in visualization would provide a stronger framework for our equation of state representations.

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