Simulating Fluids: Testing a New Grand Canonical Histogram Method on the Square-Well Fluid

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Abstract

Monte Carlo methods are used to explore vapor-liquid phase transitions. However, current models are computationally expensive when identifying these phase transitions. Traditionally, Monte Carlo simulations are run across a range of temperatures at a fixed number of atoms/molecules. The Number Monte Carlo method (NMC), our proposed Monte Carlo method, runs simulations at a constant temperature across a range of atoms/molecules. In this thesis, NMC was run using a modified version of Stochastic Approximation Monte Carlo (SAMC).

NMC was able to simulate the square-well fluid at a reduced volume of 100 across a range of four reduced temperatures (0.8, 0.9, 1, 1.1). The liquid-to-vapor phase transition was observed at all temperatures except the reduced temperature of 0.8. Using the NMC phase transitions, a phase diagram was constructed and compared to one built from National Institutes of Standards and Technology (NIST) data. The comparison revealed that the two phase diagrams roughly agree. The simulations demonstrate the validity of NMC as a faster method of finding a single-phase transition. However, simulations with a higher volume are needed to test the accuracy of the model. Additionally, NMC is not found to yield any improvement in constructing a phase diagram.

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Introduction

1.1 Objective

A theoretical upper bound for deliverable gas was discovered at Oregon State in 2019. The upper bound shows how much hydrogen or natural gas could fit into take (such as for a car)[1].

Simulations, like the one above, work by find the thermodynamic properties of a system. The most common method to finding these properties is Monte Carlo Simulations. Many different types of Monte Carlo simulations exist, such as canonical MC Wang-Landu, SAD, and Stochastic Approximation Monte Carlo (SAMC) [2]. To find an isotherm, SAMC simulates a gas or liquid across a range of temperatures at a constant number of particles. The simulation is repeated multiple times, each time changing the number of particles simulated. Once enough simulations have been run the phase transitions can be pulled from the data. Identifying single phase transitions is computationally expensive. Instead, consider a code that can find an isotherm with one simulation.

This 'new' style of simulation is Number Monte Carlo. Number Monte Carlo simulation changes the number of atoms in the system at constant volume and temperature. This type of simulation is useful because it can explore all the pressures at a certain temperature in a single simulation. The simulation was ran on the square-well fluid across a range of temperatures. From the simulations, isotherms were used to construct a phase diagram and compared against data from the National Institutes of Standards and Technology (NIST).

1.2 Monte Carlo Simulations

An ideal simulation would explore every microstate of a system. However, this is not feasible. Monte Carlo simulations remedy this problem by using random sampling. Monte Carlo simula-

tions find the energy of random microstates and use it to represent the entire system. With a large enough random samples, all relevant thermodynamic properties can be pulled from a system [3].

1.2.1 SAMC

In 2007, a modified version of the Wang-Landau algorithm was introduced that was guaranteed to converge regardless of energy – Stochastic Approximation Monte Carlo (SAMC). Previous methods could get stuck at certain energies and never converge[2]. SAMC overcame this problem by introducing the stochastic approximation factor (γ). The factor is defined as

$$\gamma = \frac{t_0}{max(t_0, t)}. \tag{1.1}$$

t_0 is the minimum number of moves the simulation needs to converge and t is the number of moves the simulation has done. To properly estimate the fluid, the gamma factor needs to approach 0. If the factor is not 0, then the simulation has not explored all the necessary micro states. The more complex or larger the system, the higher t_0 has to be. If the correct t_0 is chosen, the simulation will converge. The challenge with SAMC is picking the correct t_0. An improper t_0 results in either a system that takes a long time to converge or will not converge at all [4]. In this thesis, the t_0 used was found by playing with the simulation and seeing what gave the fastest and best results.

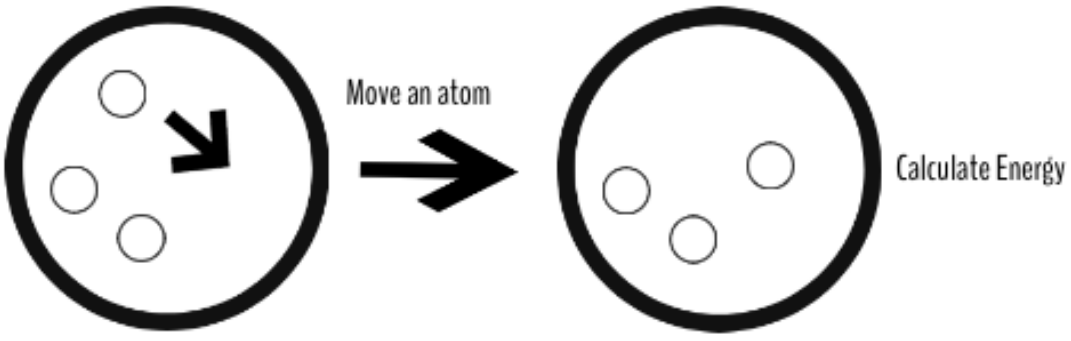

Figure 1.1: **Normal SAMC Methods**
The figure depicts how normal SAMC methods work. An atom is picked by the simulation to be moved. Once moved the thermodynamic properties of the micro state are calculated. Each micro state is explored at a chosen range of temperatures

1.3 Square-Well Fluid

The simplest method to model fluids is the hard sphere. The potential of a hard sphere fluid is infinite outside the sphere and zero inside the sphere. The fluid is modeled in Equation 1.1 where V(r) is the potential, σ is the diameter and r is distance from the center of sphere [5, 6],

$$V(r) = \begin{cases} \infty & r > \sigma \\ 0 & r < \sigma \end{cases}. \tag{1.2}$$

However the hard sphere model has it's pitfalls - it has only one fluid phase. The problem can be remedied by introducing the square-well fluid. The square well-fluid is defined with the potential seen in Equation 1.2. ϵ is the well-depth energy, σ is the length scale, and λ is the well-width,

$$V(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}. \tag{1.3}$$

The square-well fluid is a well known and well tested fluid, making it a good benchmark to check new code. The potential is visualized in Figure 1.2.

1.3.1 Statistical Associating Fluid Theory (SAFT)

While the square-well fluid is an ideal fluid, it has real world application. One such application is Statistical Associating Fluid Theory (SAFT)[7]. SAFT uses the square-well fluid to predict properties of real substances. SAFT was developed in the 1980s by Chapman, et.al at Cornell University [8]. Industry needs accurate models of thermophysical properties, but these properties are hard to come by so other models are needed. Using ideal fluids, such as the square-well fluid, properties of these complex fluids, especially for mixtures, can be modeled. This makes SAFT a very useful method for chemical engineers and those working in industry.

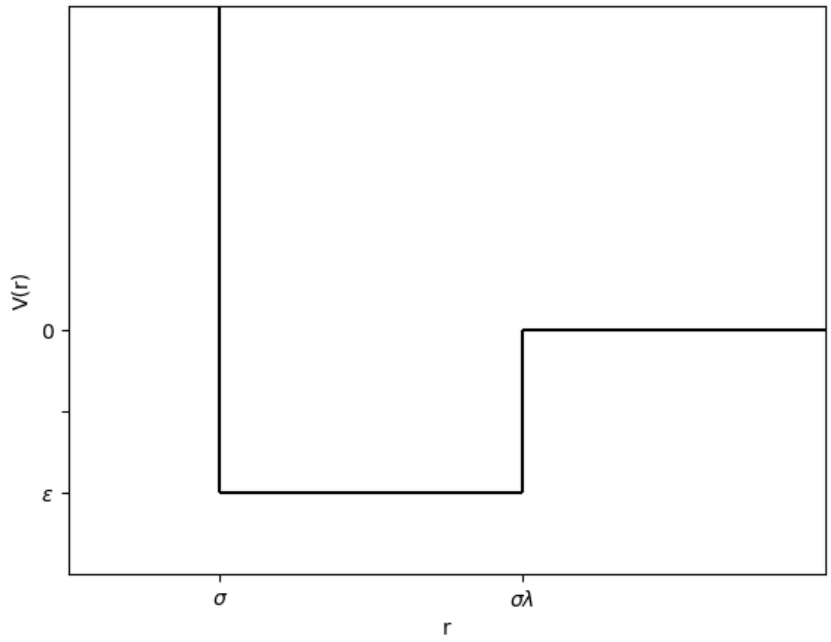

Figure 1.2: **Square-Well Fluid**
The figure displays the potential of the square well fluid. The potential is infinite outside the well and set to a certain energy inside the well. Then the potential goes to zero to the right side of the well.

1.4 Statistical Mechanics

In this section all relevant statistical mechanic terms are defined.

1.4.1 Canonical Ensemble

All the analysis of the data was done with the canonical ensemble. The canonical ensemble partition function, which works as a normalization in statistical mechanics is defined as:

$$Z = \sum_{i}^{\text{all microstates}} e^{-\beta E_i}[9]. \tag{1.4}$$

1.4.2 Excess vs Ideal

The partition function (Z) can be split into Excess and ideal parts. Z can be rewritten as,

$$Z = \frac{1}{N!}\int d\vec{r}_1 \int d\vec{r}_2 ... \int d\vec{r}_N \int d\vec{p}_1 \int d\vec{p}_2 ... \int d\vec{p}_N e^{-\beta(U(\vec{r}_1,\vec{r}_2...\vec{r}_N)+\sum_i^N \frac{p_i^2}{2m})}. \tag{1.5}$$

In Equation 1.5, N is the number of atoms, dr is the integral with respect to the position of an atom, and dp is the integral with respect to the momentum of the atom. When considering an ideal gas, the potential energy is assumed to be 0. The dr integrals then equal V^N(where V is volume). From here we can find the ideal gas partition function,

$$Z_{\text{ideal}} = \frac{1}{N!} V^N \int d\vec{p}_1 ... d\vec{p}_N e^{-\beta \sum_i^N \frac{p_i^2}{2m}}. \tag{1.6}$$

The total partition function can then be rewritten it terms of the ideal partition function,

$$Z = Z_{\text{ideal}} \frac{1}{V^N} \int d\vec{r}_1 ... d\vec{r}_N e^{-BU(\vec{r}_1, \vec{r}_2 ... \vec{r}_N)}. \tag{1.7}$$

The simulation did not specify a momentum for each atom, only a position. Only the excess quantities were found; the ideal quantities were solved for by hand.

1.4.3 Internal Energy

The internal energy is the sum of all energy in a system. The differential of internal energy is defined as

$$dU = TdS - pdV + \mu dN, \tag{1.8}$$

Where U is internal energy, T is temperature, S is entropy, p is pressure, μ is chemical potential and N is number. These quantities will be explained later as necessary. The excess internal energy was computed by the simulation.

Free Energy

Free energy can be thought of as the amount of work required to create a system out of nothing. The total free energy is defined as

$$F = U - TS, \tag{1.9}$$

where F is the free energy. When temperature and volume are held constant, the free energy becomes much easier to solve for and can be described as the maximum amount of work a system can do. Since both temperature and volume are fixed in our simulation, the excess free energy is computed.

The total free energy can be found by adding the excess and ideal free energies. The ideal free

energy,

$$F = NkT(ln(\frac{n}{n_Q}) - 1). \tag{1.10}$$

Where N is the number of atoms, T is the reduced temperature, n = $\frac{N}{V}$, and

$$n_Q = (\frac{mkT}{2\pi\hbar^2})^{3/2}. \tag{1.11}$$

In Equation 1.11, m is the mass. The trouble with ideal free energy is that it relies on quantum mechanics. Classically, phase transitions do not worry about the quantum mechanics occurring in a system. However, since ideal free energy is calculated, there are notable quantum mechanical effects. For now, the effects are mostly ignored and will be resolved in the future.

1.4.4 Chemical Potential

In this thesis, the chemical potential was necessary for finding phase transitions. A common way to find phase transitions is to plot the Gibbs free energy vs pressure. However, since the number of atoms changes, the chemical potential (Gibbs free energy per number) is found. This is advantageous in terms of calculations because the free energy can be used to find the chemical potential. The differential of Equation 1.9 can be taken to yield

$$dF = -SdT - pdV + \mu dN. \tag{1.12}$$

The chemical potential is then solved for to get

$$\mu = (\frac{\partial F}{\partial N})_{V,T}. \tag{1.13}$$

Equation 1.13 simplifies the calculation greatly since the free energy and number of atoms are quantities solved for in the simulation.

1.4.5 Pressure

The pressure was used to find the density of the phase transition and packing fraction was used to describe the density of the fluid. Pressure was computed using the thermodynamic identity and free energy. Combining both gives,

$$p = \frac{-F + n\mu}{V}. \tag{1.14}$$

Equation 1.14 is found applying Euler's homogeneous function theorem to the differential and the internal energy and free energy and combing both. The graph of pressure versus packing fraction is used to find the density of each phase transition.

1.4.6 Phase Diagram

The objective of these simulations was to find phase transitions via chemical potential vs pressure plots. The plot will cross itself and the pressure at this point of intersection is the pressure of the phase transition. Only vapor-to-liquid phase transitions were found. The pressure is then used to find the densities at which the phase transitions occur. In turn, these densities can be used to construct a phase diagram when plotted against temperature. At each temperature, there are two

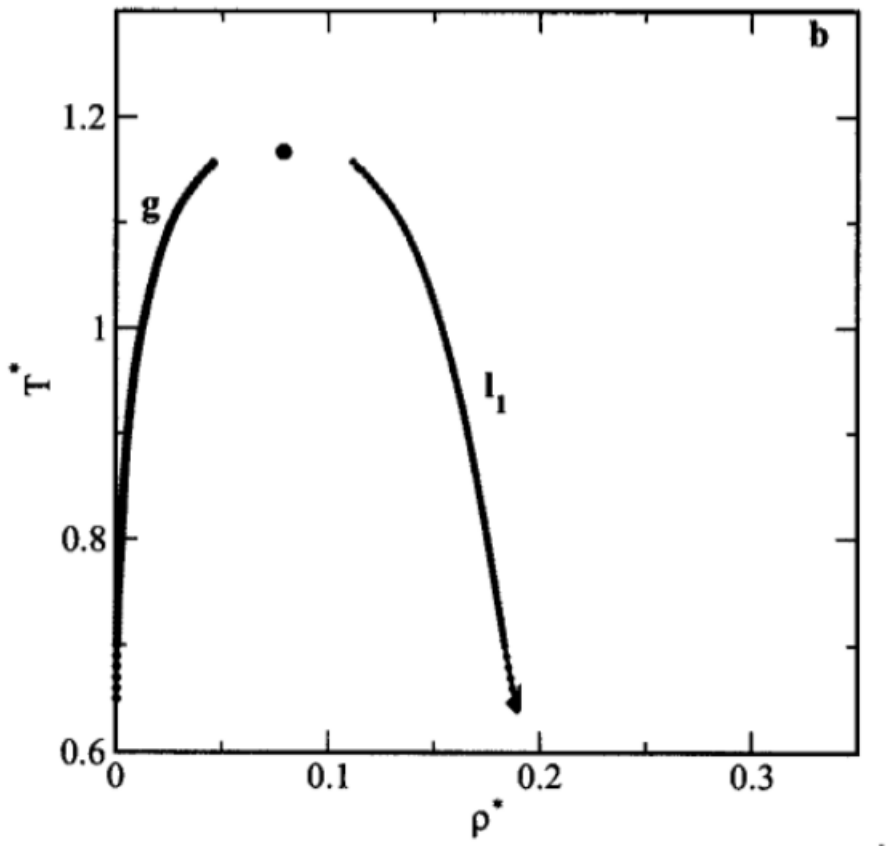

Figure 1.3: **Sample Phase Diagram**
The figure displays a phase diagram for the square well-fluid. Places inside the curve on the diagram are not allowed and the fluid cannot occupy this region.

different densities a square-well fluid can have as a result of coexistence (Figure 1.3). The region inside the curve in Figure 1.3 is the forbidden region that the fluid cannot occupy. Along the curve is the region of coexistence. The peak of the curve, marked with the dot, is the critical temperature

where the fluid is both a gas and a liquid with the same density and temperature.

Methods

2.1 Number Monte Carlo

Number Monte Carlo (NMC) method, written and developed by Dr. David Roundy, was used for the simulations. NMC simulates a fluid across a range of number of atoms and at a constant temperature (i.e. a constant energy). NMC differs from normal SAMC by varying the number of atoms instead of the temperature. The advantage of NMC is it allows an isotherm to be found with one simulation instead of multiple simulations [10]. The simulation works by taking a cube of an inputted volume and adding in one atom. From there, the simulation will decide whether to add, remove, or move an atom. This is all done statistically. First the probability to remove or add an atom is calculated. Then the simulation decides, based off the probability, whether to add or remove the atom. The other way to explore more micro states is to move an atom. The probability to move an atom is calculated and then the simulation decides whether or not to move the atom. Atoms can arrange themselves in any fashion inside the sphere as long as there is no overlap. The simulation wants to explore as many random micro states as possible to build the full picture of a square well fluid with the chosen parameters.

2.1.1 Internal and Free Energy

The excess Internal and Free energy were found by the simulation. The internal energy was found simply as a by product of how the simulation is run. The energy of the system was specified so the internal energy is known. The excess free energy was found as it is a by product of the weights of the system. The weights are simply how likely a certain microstate is. The weights (w) are specified in the simulation by:

$$\ln(w(F,N)) = -\frac{F_{\text{excess}}}{kT} \tag{2.1}$$

Since w is known the simulation can compute F without further analysis.

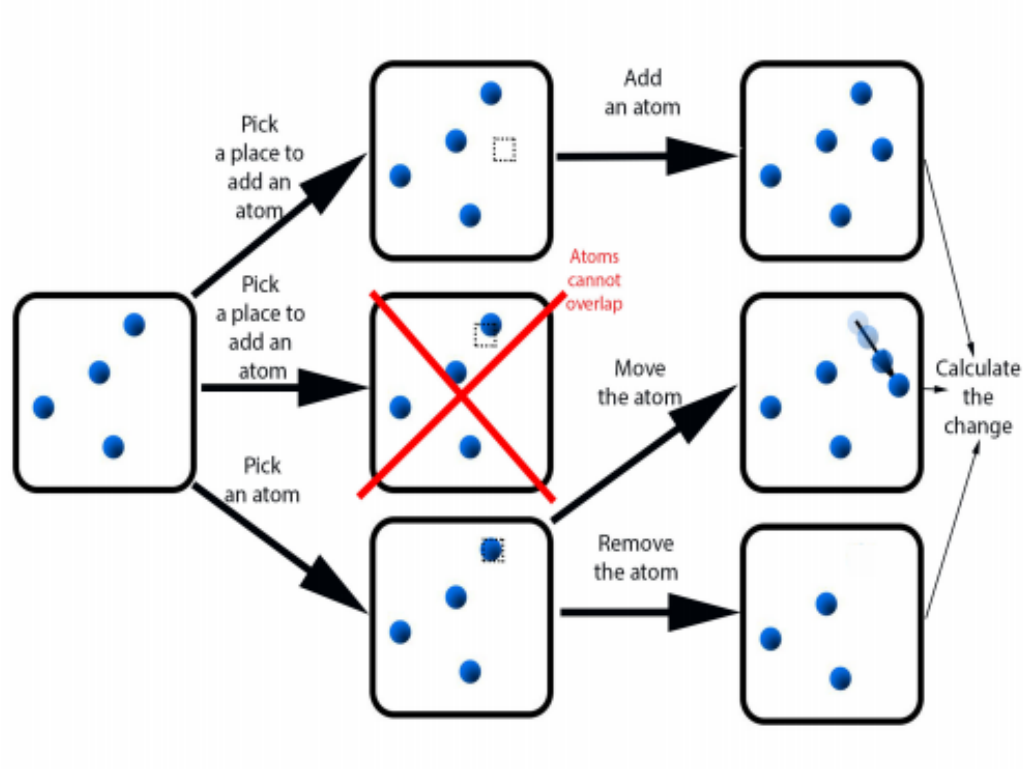

Figure 2.1: **Number Monte Carlo Method**
The figure display how the number SAMC method works. An atom is added, removed, or moved. Once the change is made the thermodynamic properties of the micro state is made. Any micro state can be introduced as long no atoms over lap with each other. Figure reproduced from thesis by Cade Trotter[9]

2.2 Chosen Parameters

2.2.1 Well-Width

The simulation was ran with a well width of $\lambda = 1.5$. The well-width was chosen because the density of states from the NIST database was used with a well-width of 1.5. Using the same well-width, allows for NMC to be checked against a benchmark.

2.2.2 Volume and Atoms

The simulation was ran with volume of 100 and a maximum of 90 atoms. The volume of 100 was chosen arbitrarily to give a sufficiently large volume and an easy to work with number. The maximum number atoms was put in to avoid higher densities. Avoding higher densities, allowed for faster simulations because the liquid the solid phase transition did not occur. Equation 2.2

shows how the maximum of atoms was solved for, where N is the number and V is the volume.

$$\eta = \frac{N_{\text{atoms}} V_{\text{atom}}}{V_{\text{unit cell}}}. \tag{2.2}$$

The packing fraction needed to be below .494 to avoid a vapor to solid phase change [5].

2.2.3 Temperature

The temperature was inputted for each simulation. Four simulations were ran at a reduced temperature of 0.8, 0.9, 1.0, and 1.1 (in units of $\frac{k_B T^*}{\epsilon}$).

2.3 Analysis

Analysis of the simulation was done using the flat histogram method. Flat histogram method method works by weighting the amount each number of atoms is explored against each other [3]. The simulation converges when all number of atoms have been explored equally. Once the system is converged the thermodynamic properties and phase transition of the square-well fluid can be found. A canonical analysis was used to find the phase transitions in the fluid.

2.3.1 The Crossing

Once the canonical analysis was complete, the phase transitions were pulled from the data. First the crossing from the chemical potential versus pressure was found. The crossing was found by using the Langrangian definition of a line,

$$y = y_1 \frac{x - x_2}{x_1 - x_2} + y_2 \frac{x - x_1}{x_1 - x_2}. \tag{2.3}$$

Describing a line with this method is beneficial when you only know 4 points. From equation 2.2 you get take 2 different sets of x_1 and x_2 to get a crossing point. The crossing point is then location of the phase transition. From here the pressure, chemical potential, and packing fraction of the phase transition can be found.

2.4 Github Link

The code used in this thesis can be found at: https://github.com/vandegja/sad-monte-carlo.

Results and Discussion

3.1 Histograms

Figure 3.1 shows the histograms from the simulations run with the parameters specified in the methods section. These histograms were used to evaluate the convergence of a simulation. In a converged simulation, each number of atoms has the same number of moves. A widely varying histogram indicates a simulation has not converged while a flat histogram indicates a simulation has converged. The temperatures are all in units of $\frac{k_B T^*}{\epsilon}$, where T^* is the temperature in kelvin. Although Figure 3.1 differs in appearance from a typical histogram, it still displays the same in-

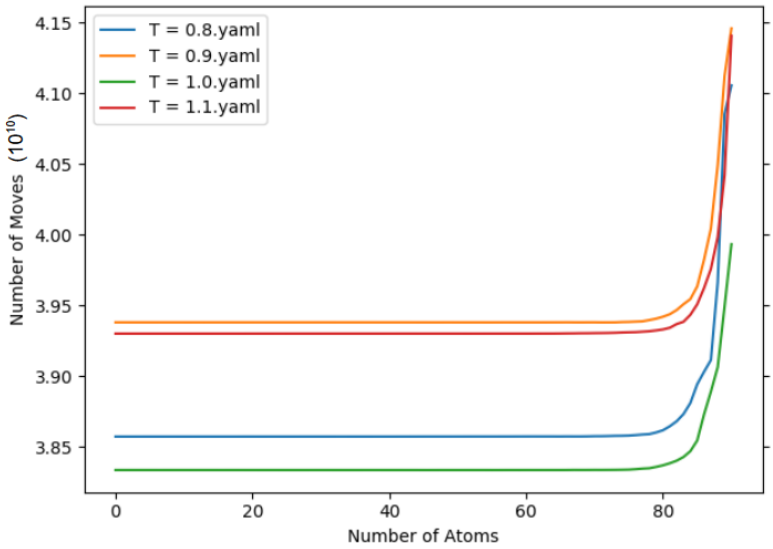

Figure 3.1: **Histogram**
The figure is of the histogram from all the simulations. The relative flatness of the histogram implies a converged system.

formation. The spike in number of moves at high numbers of atoms in Figure 3.1 means the simulation has not equally explored all states. However, the convergence of the simulation is adequate for calculation because the number of moves is so great that the slight variation is negligible

3.2 Free Energy

The free energy displayed in Figure 3.2 was found by the simulation and the ideal free energy was calculated by hand. The smooth curve is indicative of a converged simulation, as expected. Additionally, the cubic shape of each curve is indicative of the phase transitions. Pressure and

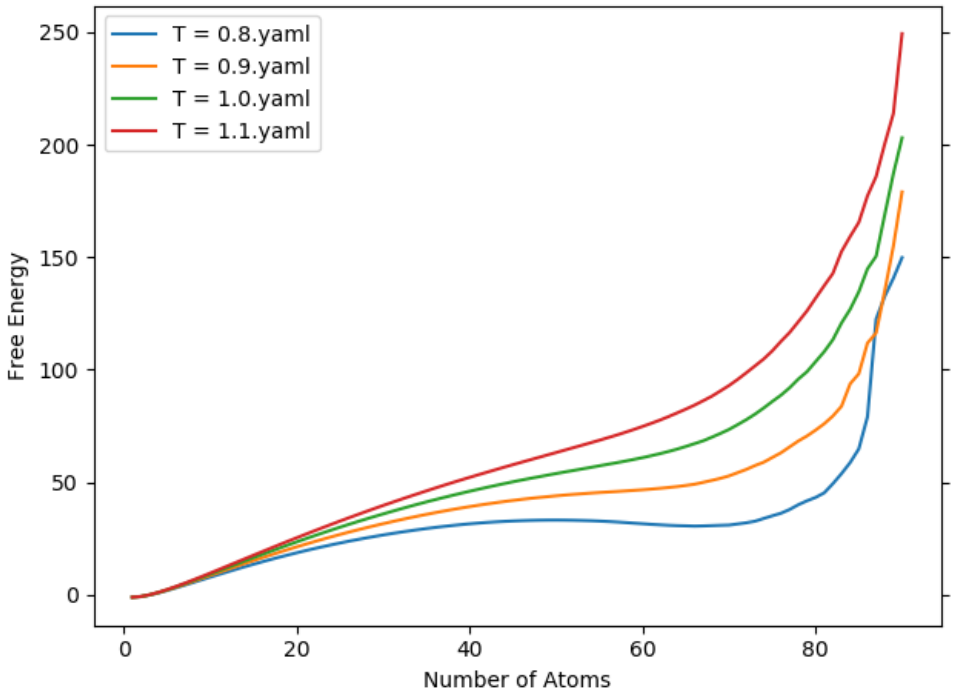

Figure 3.2: **Free Energy**
The Figure displays the free energy at across all temperatures. The curve behaves as expected. The cubic shape of the curve is indicative of a phase transition.

chemical potential can be determined from the free energy and number of atoms. Therefore, each phase transition was found from the data in Figure 3.2.

3.3 Chemical Potential

The chemical potential was found via the method described in the Introduction. To find the phase transitions, chemical potential was plotted against pressure. Figure 3.3 shows the chemical potential versus pressure at a reduced temperature of 1.1. The crossing was found in Figure 3.3 using the method described in section 2.3.1. The cross did not occur at a reduced temperature of 0.8 due to the small size of the system. The Volume of 100 system has trouble modeling reduced pressures due to the small number of atoms in the sphere. A higher volume system would have an increase

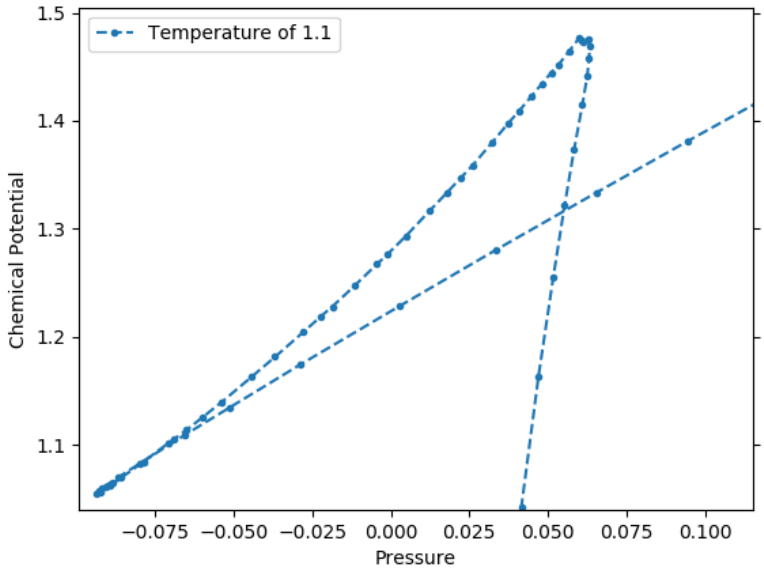

Figure 3.3: **Phase Transition Crossing**
The figure displays the cross between the chemical potential and the pressure at a reduced temperature of 1.1. The pressure at the cross is the phase transition from vapor to liquid.

number of atoms at lower pressures. Therefore, the crossing would occur.

Chemical potential is plotted against pressure in Figure 3.3 because the phase transition and coexistence occur when two different densities have the same pressure and chemical potential values.

3.4 Pressure

Pressure was found using the method described in the introduction. Figure 3.4 displays the pressure from the simulation in units of $\frac{p^*\sigma^3}{\epsilon}$, were p^* is the pressure in units of $\frac{N}{m^2}$. The units are derived from the square-well potential. The pressure was found using,

$$p = \frac{\mu N - F}{V}. \tag{3.1}$$

The quantities in Equation 3.1 have been previously solved for, simplifying the pressure calculation. Figure 3.4 displays the pressure versus packing fraction (density). Figure 3.4 demonstrated the same pressure is possible at two different densities. These two different densities are the vapor and liquid density of the square-well fluid at a certain temperature. The lower density corresponds to vapor while the higher density corresponds to liquid. At the higher densities, the pressure di-

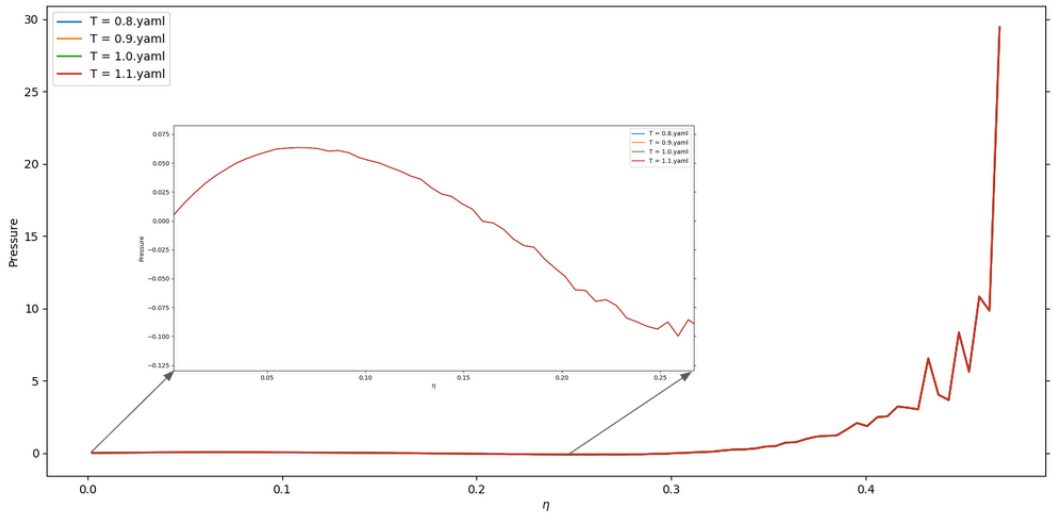

Figure 3.4: **Pressure versus Packing Fraction**
The figure shows the pressure of the system. From the pressure graph the packing fraction of the phase transition were pulled. These packing fractions were then used to make the phase diagram.

verges since the simulation has not fully converged at a high number of atoms (as seen in Figure 3.1). To converge at high density, the simulation would need to run longer. Alternatively, a higher volume or different t_0 can give better results at higher densities.

3.5 Phase Transitions

The phase diagram was constructed from the values in the table above. Temperature was plotted against packing fraction. The three-phase transition gave six data points for the phase diagram. The blue graph is the results from the NMC simulation, and the red graph is the data from NIST. While the results are not consistent with the NIST data, they do show promise in validating NMC..

Temperature($\frac{k_B T^*}{\epsilon}$)	Pressure($\frac{p^* \sigma^3}{\epsilon}$)	Vapor Density(η)	Liquid Density(η)
1.1	0.055	.04	.31
1.0	0.03	0.02	0.33
0.9	0.0053	0.003	0.35

3.6 Phase Diagram

The phase diagram was constructed from the values in the table above. Temperature was plotted against packing fraction. The three-phase transitions gave six data points for the phase diagram.

The blue graph is the results from the NMC simulation, and the red graph is the data from NIST. While the results are not consistent with the NIST data, they do show promise in validating NMC. The phase diagram from the simulation behaves similarly to the phase diagram constructed with

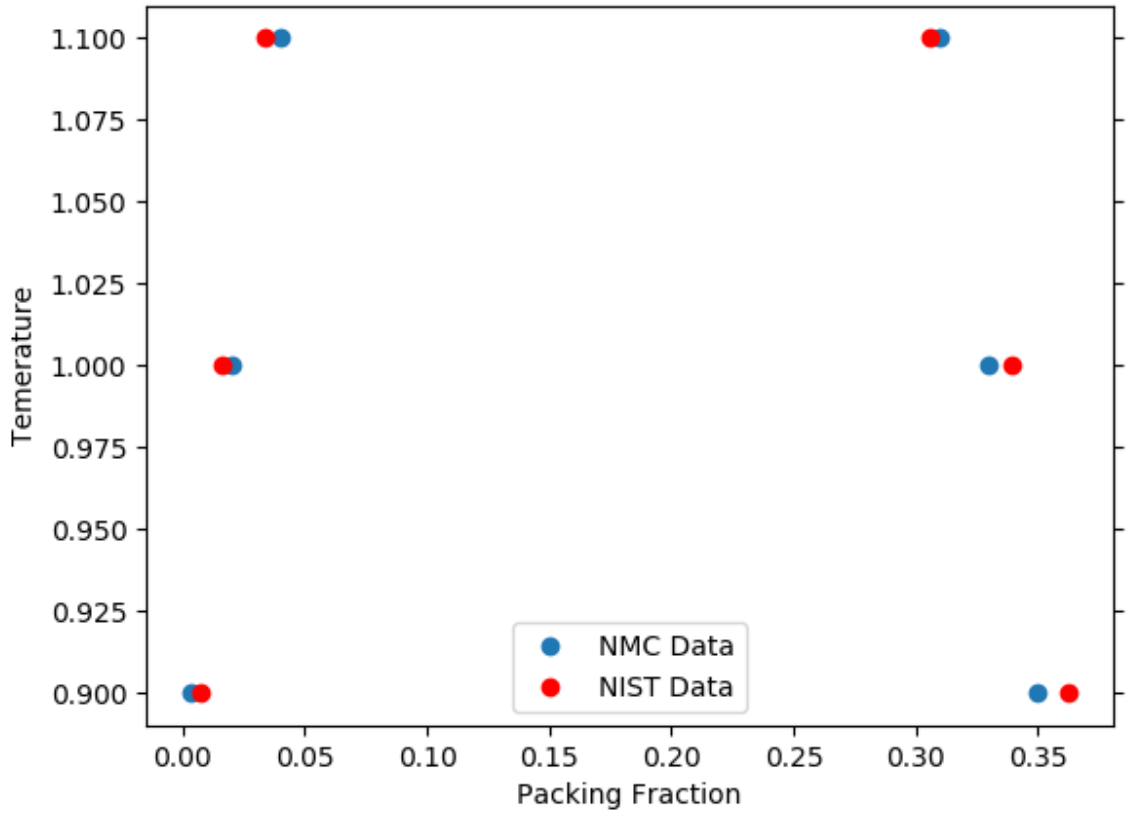

Figure 3.5: **Phase Diagram**
The figure displays the phase diagram of the square-well fluid. The graph shows the NMC data is slightly off from the data from NIST. A larger volume would increase the accuracy of the results.

data from NIST. Densities at a reduced temperature higher than 1.1 would be needed to make the phase diagram complete. Also, a simulation ran at the critical temperature of the square-well fluid is needed to construct the top point on the curve. Figure 3.5 shows potential for the NMC since NMC can find isotherms across a range of temperatures. However, the accuracy of the model still needs to be tested for the method to be used in other applications.

Conclusion

NMC shows promise to be a computationally inexpensive way to swiftly detect single-phase transitions. Thus, NMC has the potential to accelerate research in gas adsorption and SAFT by providing faster simulation turnaround.

Simulations discussed in this thesis detected phase transitions at reduced temperatures of 0.9, 1.0, and 1.1. Although the simulations were well-converged, a reduced volume of 100 hindered the accuracy of the simulations. Additionally, use of a wider range of temperatures would be necessary to construct a complete phase diagram of the square-well fluid..

Going forward, future work must be done to solidify the accuracy and confirm the validity of the Number Monte Carlo method. Such work may include running the code at a larger volume, yielding phase transitions at lower temperatures. Additionally, NMC must be tested on other methods besides SAMC. A potential contender is SAMC with a dynamic update factor (SAD), developed in this group. Similarly, NMC must be tested on other fluids, such as the Leonard Jones fluid.

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