

Monte Carlo Simulations for a Soft Sphere Fluid

PATRICK KREITZBERG
Advisor: DR. DAVID ROUNDY

May 8th, 2015

Contents

1	Abstract	3
2	Introduction	4
3	Methods	4
4	Results and Discussion	6
5	Conclusion	8
6	Acknowledgments	8
7	References	9

1 Abstract

In this paper I present the results of Monte Carlo simulations for a soft sphere fluid with a Weeks-Chandler-Anderson (WCA) pair potential. The results are compared to Soft Fundamental Measure Theory (SFMT) results obtained by our research group. One of the research group's goals was to show that our SFMT is accurate over a wide range of reduced temperatures and densities. The radial distribution function and pressure calculations were accurate at temperatures below freezing and higher than room temperature as well as reduced densities ranging from 0.3 to 1.0. Experimental data for the radial distribution function of argon was matched very well using a soft-sphere fluid surrounding a sphere with a Leonard-Jones pair potential.

2 Introduction

The hard-sphere fluid model is commonly used in statistical mechanics. Yaakov Rosenfeld derived a classical density functional (cDFT) theory called Fundamental Measure Theory in 1989 which is able to calculate the free energy of a hard-sphere fluid^[1]. Impenetrable hard spheres are not physical as they have an infinite potential. In 2000, Matthias Schmidt developed a Soft Fundamental Measure Theory (SFMT) based on Rosenfelds classical density functional theory which allowed the spheres to become soft and penetrate one another^[2]. Rosenfeld and Schmidt have since worked together and tested Schmidt’s SFMT, but not very extensively^[3].

Dr. Roundy and Ph.D. candidate Eric Krebs of Oregon State University have created a simplified approximation for the SFMT that we believe will be easy to work with and relatively easy to compute. There is little experimental data on a soft sphere fluid so the SFMT data has to be compared to computer simulations; in this case Monte Carlo simulations. The Monte Carlo simulations will approach the exact answers, if allowed to run for a sufficient amount of time, which can be used to test the accuracy of the new SFMT. I created Monte Carlo simulations that can calculate the density, pressure, and the radial distribution function of a soft sphere fluid to compare against the SFMT results. The radial distribution function describes the density of the fluid as a function of distance from a reference sphere. Similar Monte Carlo simulations have been used to find similar properties for a hard sphere fluid in the past^[4].

The Monte Carlo method relies on random sampling to provide numerical answers to problems which otherwise might not be solvable through more traditional mathematical techniques^[5]. The downfall of the Monte Carlo method is that the inferences made based upon the Monte Carlo results have inherent uncertainty. The uncertainty stems from the fact that the data obtained from the Monte Carlo method represents only some possible outcomes of the system and in most cases does not represent all outcomes. To reduce uncertainty, at least for the experiments represented in this thesis, the Monte Carlo simulations need to run for a sufficient amount of time so that the results can be deduced from a large amount of observations of the fluid.

The discovery and introduction of the Monte Carlo method to the scientific community is credited to the mathematicians and physicists Stanislaw Ulam, John von Neumann, and Enrico Fermi. Ulam and von Nuemann used random sampling while working on the atomic bomb during the Second World

War to study the “random neutron diffusion in fissile material”^[6]. Following the war, the three scientists helped popularize the Monte Carlo method, in part, when Fermi, Ulam, and Nicholas Metropolis used Monte Carlo Methods to estimate the eigenvalues of the Schrödinger equation.

The oldest paper I could find that used the Monte Carlo method for a soft-sphere fluid was from 1970^[7]. However, the 1970 paper does not estimate the same properties of a soft-sphere fluid that I do in this thesis so the results cannot be compared. Since there has not been much work done in the past in improving Schmidt’s SFMT there are very few papers which cover Monte Carlo methods for soft spheres.

3 Methods

For the data represented in this thesis the simulations were carried out on the physics computer cluster at Oregon State University. The cell for most Monte Carlo simulations is a 30x30x30 cube. The size of the cell is in units of σ which is the distance between two spheres when the pair potential is zero; in these simulations σ the same as the radius of the spheres. All six walls of the cube have periodic boundaries which enable the fluid to be treated as homogeneous. The size of the cell is not of great importance and was chosen to be large enough that our fluid was interesting. The cell also had to be small enough that the time to perform the simulations would give us rough data within a few hours and smooth data within a few days. The number of spheres in the cell, N , is given by the user as a reduced density. N is then calculated using the equation:

$$N = \frac{(2 * ReducedDensity)^{-5/2}}{CellVolume} \quad (1)$$

One by one, the simulation proposes a random direction for each sphere to move. If the proposed move means that two spheres overlap, they create a potential energy equal to the Weeks-Chandler-Anderson pair potential. The WCA pair potential is a modified Lennard-Jones potential where the attractive force is offset by the $+\epsilon$ so that it is only repulsive. This potential is what separates the soft sphere fluid from the hard sphere fluid (where $V(r) = \infty$ for $0 < r < 2R$). A graph and the equation for the WCA pair potential:

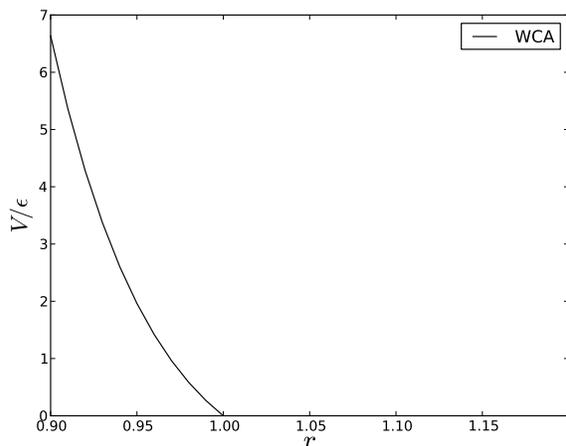


Figure 1: Weeks Chandler Anderson Pair Potential

$$v_{wca}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \epsilon, & 0 < r < 2R \\ 0, & \text{otherwise} \end{cases} \quad (2)$$

The probability of a proposed move being accepted is the Boltzmann factor

$$e^{\frac{E_f - E_i}{T^*}} \quad (3)$$

where E_i and E_f are the potential energy (sum of the pair potentials) of the system before and after the proposed move, respectively. In equation 4, k is the Boltzmann constant and T^* is the reduced temperature. The reduced temperature is defined by the user and the relation to “regular” temperature is

$$T^* = \frac{kT}{\epsilon} \quad (4)$$

If the move does not create overlap between spheres or reduces the total potential energy of the fluid then it is automatically accepted. When a simulation is initially created it is possible that all the randomly placed spheres are in an unrealistic arrangement which creates an unusually high potential energy. If they are in an unrealistic arrangement, the moving of spheres should almost always lower the potential energy. Once the spheres are in a more realistic arrangement we should see some movement of spheres that raises the potential energy, if this happens twice we are done initializing and can start taking data.

To calculate the radial distribution function of the fluid the cell must first be divided into “shells.” The

shells are three dimensional spherical shells of roughly 0.01 thickness. Figure 2 shows a two dimensional cutout of a homogeneous fluid with a spherical shell which is represented by the two unfilled red circles. The graph is not from the actual Monte Carlo code and the units are arbitrary with the radius of each sphere set to one. The simulation has an array of values for each shell. The shells move so that each sphere is put into the center then the distance between this reference sphere and all other spheres is calculated. When the simulation observes a sphere that is not the reference sphere that sphere will have its center inside of one of the shells surrounding the reference sphere so the array value for that shell is incremented by one. Every few hours, roughly 60,000 iterations depending on the density, when the data is printed the number of spheres in a shell is multiplied by the volume of the cell then divided by the volume of the shell. This is then averaged over the number of spheres and the amount of times each sphere has been counted. This gives the radial distribution for the value of the radius of the shell (the distance from the center of the reference sphere).

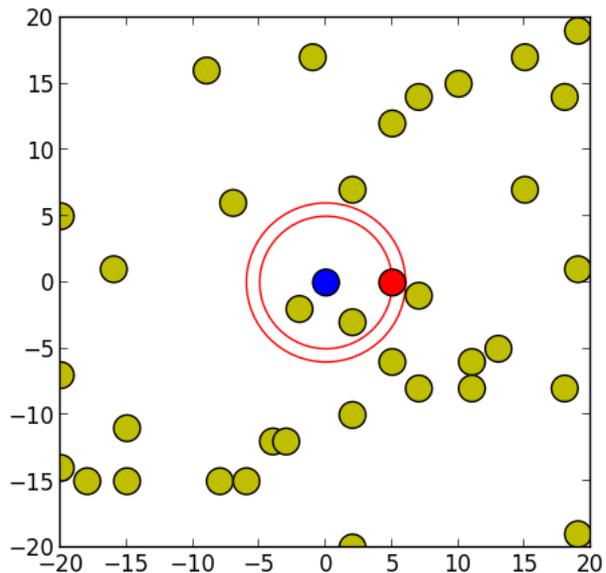


Figure 2

Calculating the density is similar to calculating the radial distribution function. For the density the cell is divided into the same shells. The difference is that there is no reference sphere, the distance measured is instead from the origin to each sphere. The density is just the number of spheres in each shell divided by the shell volume and averaged over the number of moves each sphere has taken. The density for a homogeneous is not very interesting but is help-

ful for making sure the fluid is not in some unrealistic high energy state.

The pressure for the homogeneous fluids was also calculated using the following formula:

$$\frac{N}{VolumeOfEnvironment} * kT - \frac{\sum V(r)}{3 * VolumeOfEnvironment} \quad (5)$$

There is experimental data for the radial distribution function of argon which we wanted to check against the new SFMT^[8-10]. To create a Monte Carlo simulation to compare against the argon data a static sphere was placed in the center of the cell with a Lennard-Jones potential. Lennard-Jones potential is often used because it “provides a realistic description of rare-gas interactions at pressures up to a few kilobars^[7].” The Lennard-Jones potential is the WCA potential in equation 2 without the $+\epsilon$. The Lennard-Jones parameters for argon are $\sigma = 3.405\text{\AA}$ and $\epsilon = 119.8K$ ^[11]. The process for the simulation is essentially the same as the homogeneous fluid except that the one center particle is always the reference particle.

4 Results and Discussion

Figure 3 shows the pressure of a homogeneous fluid as a function of reduced density, n^* , and reduced temperature, T^* . The Monte Carlo simulations can compute the pressure for only one reduced temperature and reduced density at a time so the data is represented by the dots. The dashed lines connecting the dots are not from real data but are there to help visually compare Monte Carlo to SFMT data.

Reduced room temperature is about 2.48 kelvin so it is important that the Monte Carlo and SFMT agree near this temperature. For a reduced density of 0.7, the filling fraction (volume of spheres divided by cell volume) is about 0.55. Considering that a sphere of radius one inside a cube that has all sides with a length of two has a filling fraction of 0.52 this is a very dense fluid so it is acceptable that the SFMT and Monte Carlo results are not a perfect match at such a high density. What is important is that the Monte Carlo and SFMT data match for very low reduced temperatures, lower than the freezing point of water.

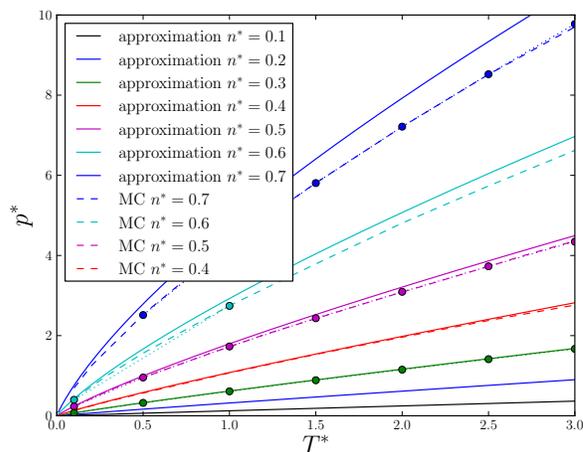


Figure 3: Reduced pressure versus reduced temperatures for homogeneous fluids.

Figures 4 and 5 show the Monte Carlo data versus the SFMT data for a homogeneous fluid at two different reduced densities, both with different reduced temperatures. For all different reduced densities the data matches almost perfectly.

Figure 4 shows the best range for the data to match. A reduced density of 0.6 is a filling fraction of about 0.47 which is on the low end of the experiments. However, the temperature range is quite large covering from four times room temperature to below the freezing point of water of roughly $T^* = 2.28$.

The data in figure 5 has a much higher reduced density than the data in figure 4 so it is acceptable for the SFMT data to not match the Monte Carlo data. The Monte Carlo data has strange bumps for reduced temperature of 1, this is most likely due to the temperature being low enough that the spheres begin to crystallize. If the simulations were not able to run long enough or got stuck then we should expect this strange behavior. However, since room temperature is roughly 2.48 the fact that the data at reduced temperature of 2.5 is off is slightly disconcerting.

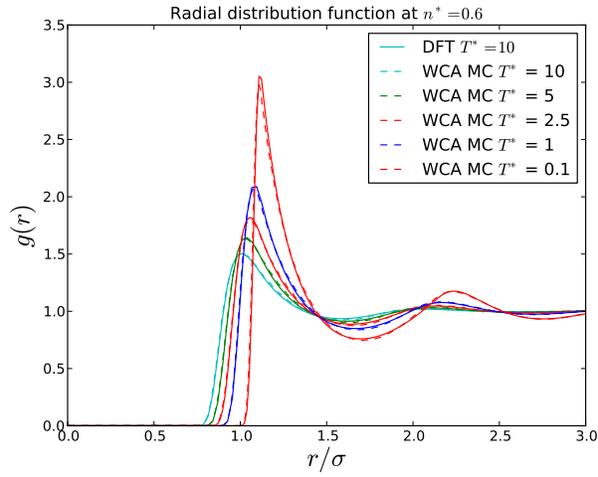


Figure 4: Radial Distribution Function for Homogeneous Fluid

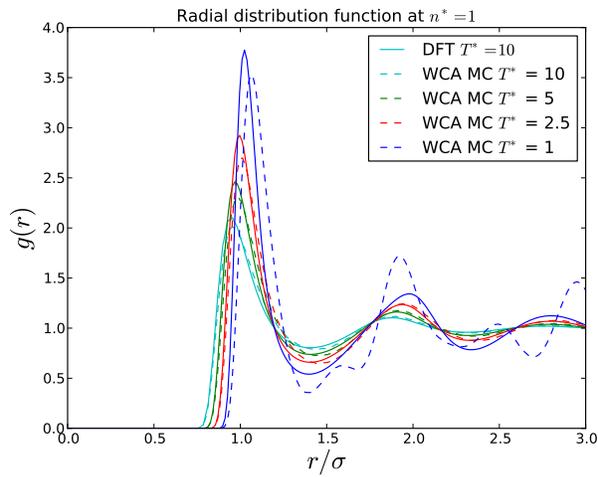


Figure 5: Radial Distribution Function for Homogeneous Fluid

The following figures 6, 7, and 8 are the plots of the argon experimental data versus Monte Carlo and SFMT. The experiment for figure 6 has a very large reduced density compared to the homogeneous data in figure 3. This high density can explain the drastic difference in the first peak between all three sets of data. For the Monte Carlo simulations such a high reduced density has a tendency to make the spheres stick together. Whenever there is such a high density it is hard for the spheres to move since the sphere that wants to move will almost always move into other spheres, creating a higher potential energy and therefore a lower probability of the move being accepted. Also, argon is not a perfect Lennard-Jones

fluid and is certainly not a Weeks-Chandler-Anderson fluid. Because argon is not a Lennard-Jones fluid the potential used in the Monte Carlo program is an estimate so the data that does match well with experiment, figures 7 and 8, is a real accomplishment.

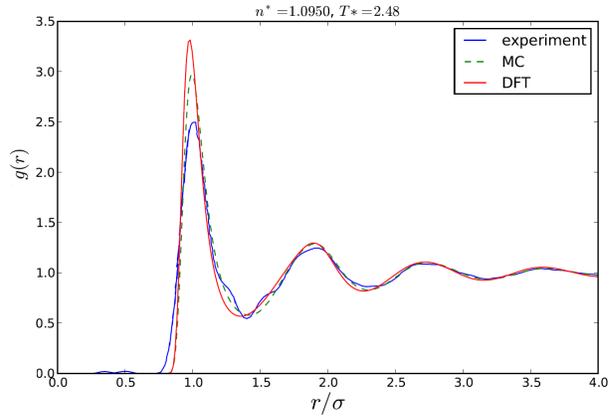


Figure 6: Radial Distribution Function Argon Experimental Data vs Monte Carlo and SFMT

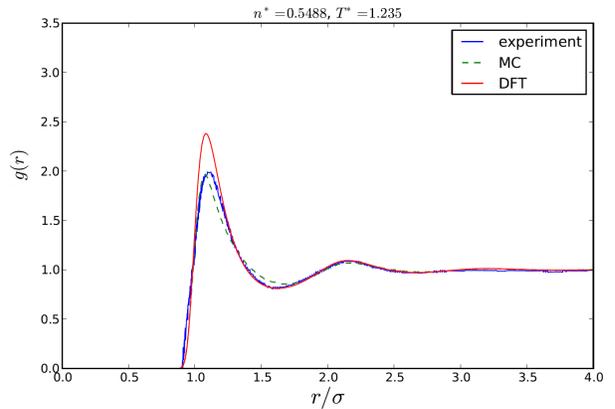


Figure 7: Radial Distribution Function Argon Experimental Data vs Monte Carlo and SFMT

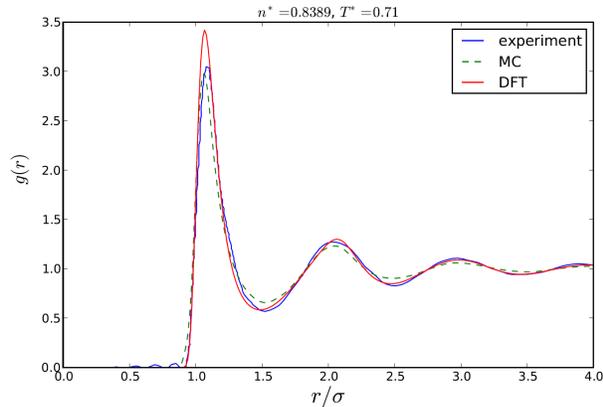


Figure 8: Radial Distribution Function Argon Experimental Data vs Monte Carlo and SFMT

5 Conclusion

We investigated several different homogeneous soft sphere fluids and calculated their density, pressure, and radial distribution function using both Monte Carlo simulations and SFMT. For a wide vari-

ety of reduced temperatures and densities the SFMT data matched the Monte Carlo data very well. This includes temperatures roughly four times the boiling point of water and temperatures below the freezing point of water. The radial distribution function of argon was calculated by the Monte Carlo simulation and SFMT and was found to match very well with experimental data. The comparisons between the SFMT and Monte Carlo data suggests the SFMT is very accurate in these situations and should be used in statistical mechanics where applicable.

6 Acknowledgments

I would like to thank Professor David Roundy and Ph.D. Candidate Eric Krebs of Oregon State University for helping me with my research project as well as providing me with the SFMT data and python scripts to create most of the figures in this paper. Also, I would like to thank all my fellow physics undergrads who edited and provided feedback on earlier drafts of this paper.

7 References

- [1] Y. Rosenfeld, “Free-energy model for the inhomogeneous Hard-Sphere Fluid Mixture and Density-Functional Theory of Freezing,” *Phys. Rev. Lett.* **63**, 980 (1989).
- [2] M. Schmidt, “Fluid structure from density-functional theory,” *Physical Review E* **62**, 4976 (2000).
- [3] Y. Rosenfeld, M. Schmidt, M. Watzlawek, “Fluid of penetrable spheres: Testing the universality of the bridge functional,” and H. Lowen, *Physical Review E* **62**, 5006 (2000).
- [4] J. Schulte, P. Kreitzberg, C. Haglund, and D. Roundy, “Using Fundamental Measure Theory to Treat the Correlation Function of the Inhomogeneous Hard-Sphere Fluid,” *Physical Review E* **86**, 061201 (2012).
- [5] J.P. Hansen and I.R. McDonald. *Theory of Simple Liquids*. Amsterdam: Elsevier, 2006. p 415.
- [6] Hammersley, J. M., and D. C. Handscomb. *Monte Carlo Methods*. S.l.: Springer, 2013. Print.
- [7] W. Hoover, et al., “Soft-Sphere Equation of State,” *The Journal of Chemical Physics* **52**, 4932 (1970).
- [8] P. Mikolaj and C. Pings, “Structure of Liquids. III. An XRay Diffraction Study of Fluid Argon,” *The Journal of Chemical Physics* **46**, 1401 (2004).
- [9] J.H. Eggert, G. Weck, P. Loubeyre, and M. Mezouar, “Quantitative structure factor and density measurements of high-pressure fluids in diamond anvil cells by x-ray diffraction: Argon and water,” *Physical Review B* **65**, 174105 (2002).
- [10] J. Yarnell, M. Katz, R.G. Wenzel, and S. Koenig, “Structure Factor and Radial Distribution Function for Liquid Argon at 85 K,” *Physical Review A* **7**, 2130 (1973).
- [11] L. Verlet, “Computer ”Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules,” *Physical Review* **159**, 98 (1967).