

Finding the arbitrary parameter L in Renormalization Group Theory

VIA fitting Monte Carlo simulations to Statistical
Associating Fluid Theory

Billy Edward Geerhart III

A project presented for the degree of
Masters of Science



Department of Physics
Oregon State University
June 18, 2016

Exploring Phase Equilibrium with Statistical non-Associating Fluid Theory:

A Generalized Renormalization Group Theory Approach.

Ryan M. Scheirer

Abstract

Abstract goes hereeee!

Contents

1	Introduction	5
1.1	Introduction	5
2	Methods	8
2.1	Partition function seperation	8
2.2	Free Energy via Monte Carlo Simulations	9
2.2.1	ideal gas free energy	9
2.2.2	hard sphere free energy	10
2.2.3	dispersive free energy	10
2.3	SAFT	11
2.3.1	$S_{exc.\infty}$	11
2.3.2	Normalized Free Energy	11
3	GRG Theory	12
3.1	GRG Theory	12
4	Data	13
4.1	Computation	13
5	Conclusion	14
5.1	Conclusion	14

List of Figures

4.1	Caption for this image.	13
4.2	Caption for all three.	13

Chapter 1

Introduction

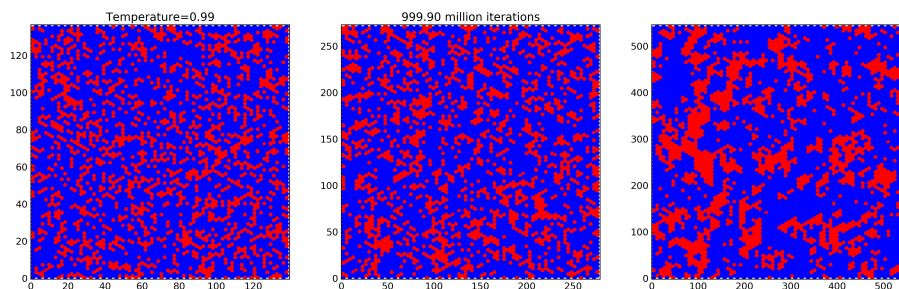
1.1 Introduction

Outline: Introduction to liquid vapor coexistence Demonstrate the problem Fix the problem what I did

The liquid-vapor phase coexistence can be found by just depositing some liquid into a sealed container. Some of the liquid will evaporate into the jar creating a vapor pressure. Provided there is enough liquid to create the necessary vapor pressure, the system will now contain both a liquid and a vapor at the same time. By sealing the liquid into a jar, we have forced the pressure of the liquid to be the same as the pressure of the gas. By allowing the atoms in the liquid to evaporate into a gas, we have also allowed the chemical potential of the liquid to be the same as the chemical potential of the gas.

Although we can find the phase coexistence by physically sealing a liquid in a jar, another method is to model the liquid using an experimentally derived model. The benefit to this method is a few observations can be used to find the parameters, and the parameters can then be used in simulations to find the rest of the coexistence curve.

To find the coexistence curve computationally, the liquid phase is usually considered to be separate from the vapor phase. This is a perfectly reasonable assumption since the surface tension normally keeps the liquid phase separate from the vapor phase. Unfortunately as the liquid approaches the critical point, the density of the liquid approaches the density of liquid. This means the surface tension decreases towards zero as the liquid approaches the critical point. This is unfortunate since the classical behavior of liquid separate from the vapor is no longer valid (see figure 1).



Although figure 1 shows an extreme example of liquid completely mixing with vapor, even under normal circumstances there exist natural fluctuations in the density of either phase. The most basic theory will deal with interactions at the shortest wavelength simply because fluctuations happen at the shortest wavelength first. The problem is that as we approach the critical point, the fluctuations grow in length scale. Fortunately there exists a method called renormalization group theory to deal with interactions on the longer length scale.

Renormalization group theory deals with the variations in density by finding the energy associated with each wavelength and each amplitude. The idea is the partition function will now sum over wavelengths and amplitudes. Forte et al. simplify the sum, but the problem is RGT contains an arbitrary initial wavelength. This initial wavelength is usually fit to the observables, but this introduces yet another free parameter since we can already change the potential used to characterize the fluid.

This project explores if it is possible fix this initial wavelength by comparing theory to Monte Carlo simulations. A Monte Carlo simulation involves putting atoms within a box and finding the density of states. The idea is that a Monte Carlo simulation at a small box size only incorporates interactions at the shortest wavelength, yet a simulation with a large box size will incorporate interactions at both short wavelengths and long wavelengths. This corresponds with how the most basic theory incorporates only short wavelength interactions, while renormalization group theory incorporates both short and long wavelength interactions. By changing the size of the box in a Monte Carlo simulation, we should be able to transition from SAFT to renormalization group theory; it is this transition that should represent the arbitrary parameter L within renormalization group theory.

Test of fancyhdr page.

Chapter 2

Methods

Outline: SAFT
liquid-vapor+run-absolute
How comparisons were made

2.1 Partition function seperation

The Monte Carlo simulations can be partitioned into high and low temperature regimes. At low temperature the interactions dominate, while at high temperatures the entropy dominates. Both regimes can be partitioned yet again by seperating the kinetic energies into an ideal gas term. In terms of equations, we start with the partition function and seperate the summation into the three partitions:

$$Z = \frac{1}{N!} \sum_i e^{-\beta \cdot E_i} Z = \frac{1}{N!} \int \dots \int e^{-\beta \cdot [\{P_1^2/2m + P_2^2/2m + \dots\} + V(\vec{R}_1, \vec{R}_2, \dots)]} d\vec{P}_1 \cdot d\vec{P}_2 \dots d\vec{P}_N \cdot d\vec{R}_1 \cdot d\vec{R}_2 \dots d\vec{R}_N$$

The momentum integrals are independent of the position integrals, so we seperate the momentum integrals which we then incorporate into an ideal gas term by multiplying by V^N/V^N .

$$Z = Z_{ideal} \cdot \frac{1}{V^N} \cdot \int \dots \int e^{-\beta \cdot V(\vec{R}_1, \vec{R}_2, \dots)} d\vec{R}_1 \cdot d\vec{R}_2 \dots d\vec{R}_N$$

where

$$Z_{ideal} = V^N \cdot \frac{1}{N!} \int \dots \int e^{-\beta \cdot [P_1^2/2m + P_2^2/2m + \dots]} d\vec{P}_1 \cdot d\vec{P}_2 \dots d\vec{P}_N$$

The remaining potential energy term is seperated into the low temperature and high temperature regime. At high temperatures, the atom energies are much higher than the potential well; this means the finite potential well can be considered zero. However; even at infinite temperature the atoms are assumed to be a hard sphere. This hard sphere behavior is incorporated into the partition function by multiplying by Z_{HS}/Z_{HS} .

$$Z = Z_{ideal} \cdot Z_{HS} \cdot \frac{1}{Z_{HS}} \cdot \frac{1}{V^N} \cdot \int \dots \int e^{-\beta \cdot V(\vec{R}_1, \vec{R}_2, \dots)} d\vec{R}_1 \cdot d\vec{R}_2 \dots d\vec{R}_N$$

where $Z_{HS} = \frac{1}{V^N} \int \dots \int e^{-\beta \cdot V_{HS}(\vec{R}_1, \vec{R}_2, \dots)} d\vec{R}_1 \cdot d\vec{R}_2 \dots d\vec{R}_N$

The last part is just the ratio between the interaction and the hard sphere partition function; we call this the dispersive term.

$$Z = Z_{ideal} \cdot Z_{HS} \cdot \frac{Z_{interaction}}{Z_{HS}} = Z_{ideal} \cdot Z_{HS} \cdot Z_{disp}$$

where $Z_{interaction} = \frac{1}{V^N} \cdot \int \dots \int e^{-\beta \cdot V(\vec{R}_1, \vec{R}_2, \dots)} d\vec{R}_1 \cdot d\vec{R}_2 \dots d\vec{R}_N$
and $Z_{disp} = \frac{Z_{interaction}}{Z_{HS}}$

2.2 Free Energy via Monte Carlo Simulations

Given the separated partition function, the free energies are just the sum of the free energies due to the ideal term, the hard sphere term, and the dispersive term. The ideal term is ignored because it stays the same between theory and the Monte Carlo simulations. Due to the finite nature of the Monte Carlo simulations, the hard sphere term in the simulations aren't exactly the hard sphere terms in theory. Although we can make some corrections due to the finite nature, ultimately we have to enforce the boundary condition that at high temperature the atoms behave like hard spheres. Given this boundary condition, we are then able to define what the dispersion term should be based on estimation of the density of states.

2.2.1 ideal gas free energy

To find the ideal gas free energy we can use previous results based on knowing the entropy of the system which we can then use to find $F_{ideal} = U_{ideal} - T \cdot S_{ideal}$.

$$U_{ideal} = 3/2 \cdot N \cdot k \cdot T$$

$$S_{ideal*} \approx k \cdot N \left(\ln \left[\frac{V}{N} \left(\frac{4 \cdot \pi \cdot m}{3 \cdot h^2} \cdot \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} \right)$$

The Sackur-Tetrode equation with the Stirling approximation actually does not make physical sense as the entropy per particle at constant temperature only depends on density. A simple example can show why this doesn't make sense. Consider two atoms in boxes separated by a partition, and compare the entropy per particle to when the partition in the box has been removed. Once the partition has been removed, the two atoms can explore many more configurations than previously, which means the entropy should have increased once the two atoms were allowed to mix. Unfortunately the Sackur-Tetrode equation with Stirlings approximation would predict the entropy per particle with or without the partition should be the same. This is a bit of a problem since every box in a Monte Carlo simulation will contain exactly N particles, which means the entropy is actually lower than a real ideal gas.

The entropy problem can be fixed by using the Sackur-Tetrode equation without Stirling's approximation. Essentially use a constant density and compare the entropy per particle of a small box to the entropy per particle of a large box. The difference in entropy shows how the ideal gas entropy within a box will deviate from the expected ideal gas entropy.

$$S_{ideal} = k \cdot N \left(\ln \left[V \cdot N!^{-1/N} \left(\frac{4 \cdot \pi \cdot m}{3 \cdot h^2} \cdot \frac{U}{N} \right)^{3/2} \right] + \frac{3}{2} \right)$$

It would be natural to think we can just incorporate this deviation in entropy for the Monte Carlo simulations, unfortunately the simulations contain an intractable problem involving the periodic nature of the simulations. The atoms in the box are repeated in a periodic way to represent the atoms in the entire fluid, however by forcing a periodic boundary condition the entire state of a fluid is now defined by only the atoms within the small box. It is very unlikely that 100 atoms can fully define a system containing an Advogadro's number of atoms, so the entropy should be much less than a realistic system. Rather than incorporate such a change in entropy, we instead must recognize that these Monte Carlo simulations are defining the boundary conditions relative to the smaller sub system; this is basically the equivalent of mean field theory where the boundary is defined by the smaller sub system.

Recognizing that Monte Carlo simulations are a variation of mean field theory, the loss in entropy due to reduced configurations is ignored. Instead the boundary conditions are enforced. At any temperature we expect the kinetic energies to behave like an ideal gas. At high temperatures we expect the system to behave like a hard sphere system.

2.2.2 hard sphere free energy

The hard sphere partition function can be found by calculating the excess entropy at $T \rightarrow \infty$. This can be seen as follows:

$$\begin{aligned}
 Z_{exc} &= Z_{HS} \cdot Z_{disp} \Rightarrow \\
 F_{exc} &= -k \cdot T \cdot \ln(Z_{exc}) = -k \cdot T \cdot \ln(Z_{HS}) - k \cdot T \cdot \ln(Z_{disp}) \Rightarrow \\
 S_{exc.\infty} &= \lim_{T \rightarrow \infty} - \left(\frac{\partial F_{exc}}{\partial T} \right)_{V,N} \quad \text{but} \quad \lim_{T \rightarrow \infty} Z_{exc} = \text{constant} \Rightarrow \\
 S_{exc.\infty} &= -k \cdot \ln(Z_{HS.\infty}) - k \cdot \ln(Z_{disp.\infty}) \\
 \text{but } Z_{HS} &\text{ is constant and } Z_{disp.\infty} = Z_{interaction.\infty} / Z_{HS} = Z_{HS} / Z_{HS} = 1 \Rightarrow \\
 S_{exc.\infty} &= -k \cdot \ln(Z_{HS}) - k \cdot \ln(1) = -k \cdot \ln(Z_{HS}) \Rightarrow \\
 Z_{HS} &= e^{-S_{exc.\infty}/k}
 \end{aligned}$$

To find the hard sphere partition function, we need to find the maximum excess entropy as $T \rightarrow \infty$. The method used to find the maximum excess entropy starts by considering N atoms in an extremely large box. The hard sphere component in

2.2.3 dispersive free energy

The dispersive term is found by estimating the density of states using a * method. The main problem is the density of states is found by sampling the energy levels, but the relative distribution of energy levels is not unique to a single density of states. In other words, the partition function can be changed by an arbitrary factor without actually changing the total energy. This can be seen as follows:

Suppose

$$Z = \sum_i D(E_i) \cdot e^{-\beta \cdot E_i}$$

then

$$U = \sum_i E_i \cdot D(E_i) \cdot e^{-\beta \cdot E_i} / Z$$

Now suppose we let

$$D_2(E_i) = \alpha \cdot D(E_i)$$

then

$$Z_2 = \sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i} = \alpha \cdot Z \Rightarrow$$

$$U_2 = \sum_i E_i \cdot D_2(E_i) \cdot e^{-\beta \cdot E_i} / Z_2$$

$$U_2 = \sum_i E_i \cdot \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i} / (\alpha \cdot Z)$$

$$U_2 = \sum_i E_i \cdot D(E_i) \cdot e^{-\beta \cdot E_i} / Z$$

$$U_2 = U$$

Basically the partition function will define the total energy at all temperatures, but knowing the total energy at all temperatures will not define a unique partition function. Specifically, the partition function up to some arbitrary factor will give the same total energy. This is a bit problematic considering the method to find the density of states makes observations of the total energy to estimate the density of states, which then results in a density of states that is only defined up to some unknown factor.

To get around this problem of an unknown factor in the density of states, note that the dispersive partition function will go towards one as T approaches infinity. This happens because Z_{disp} is the ratio of the interaction term to the hard sphere term, and the interaction term approaches the hard sphere term as the temperature increases. Essentially we can leave the unknown α term alone, and it will show up in both the interaction and hard sphere partition function.

That is:

$$Z_{disp} = \frac{Z_{interaction}}{Z_{HS}} = \frac{\sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}}{\lim_{T \rightarrow \infty} \sum_i \alpha \cdot D(E_i) \cdot e^{-\beta \cdot E_i}} = \frac{\sum_i D(E_i) \cdot e^{-\beta \cdot E_i}}{\sum_i D(E_i)}$$

2.3 SAFT

SW.fid+SW.fdisp+SW.fhs Explain.

2.3.1 $S_{exc.\infty}$

2.3.2 Normalized Free Energy

Chapter 3

GRG Theory

3.1 GRG Theory

Some more splaining.

And also a citation example [1].

And this one too [2]

Chapter 4

Data

4.1 Computation

Provide computation methods and data of what I have done so far.
This is how you can refer to fig 4.1.

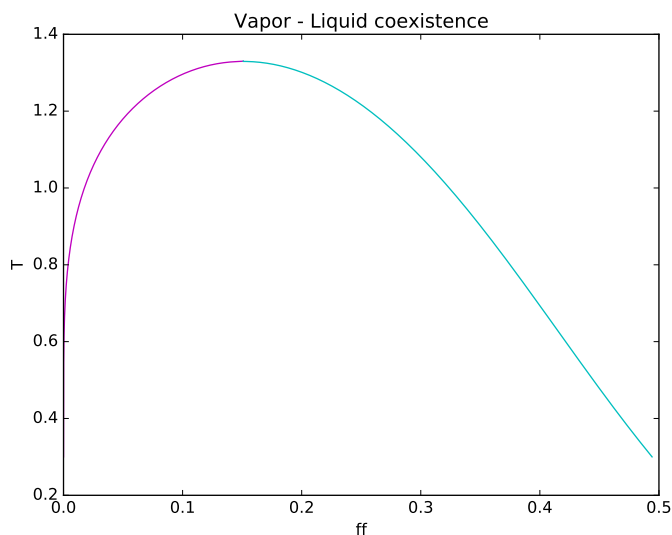
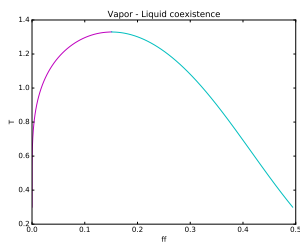
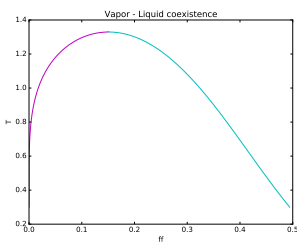


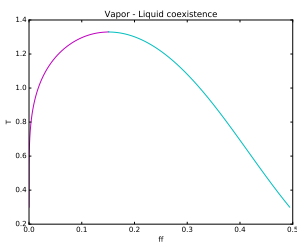
Figure 4.1: Caption for this image.



(a) Caption 01



(b) Caption 02



(c) Caption 03

Figure 4.2: Caption for all three.

Chapter 5

Conclusion

5.1 Conclusion

ta-da!