PATH INTEGRAL QUANTUM MONTE CARLO STUDY OF COUPLING AND PROXIMITY EFFECTS IN SUPERFLUID HELIUM-4

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Abstract

When bulk helium-4 is cooled below $T = 2.18$ K, it undergoes a phase transition to a superfluid, characterized by a complex wave function with a macroscopic phase and exhibits inviscid, quantized flow. The macroscopic phase coherence can be probed in a container filled with helium-4, by reducing one or more of its dimensions until they are smaller than the coherence length, the spatial distance over which order propagates. As this dimensional reduction occurs, enhanced thermal and quantum fluctuations push the transition to the superfluid state to lower temperatures. However, this trend can be countered via the proximity effect, where a bulk 3-dimensional (3d) superfluid is coupled to a low (2d) dimensional superfluid via a weak link producing superfluid correlations in the film at temperatures above the Kosterlitz-Thouless temperature. Recent experiments probing the coupling between 3d and 2d superfluid helium-4 have uncovered an anomalously large proximity effect, leading to an enhanced superfluid density that cannot be explained using the correlation length alone. In this work, we have determined the origin of this enhanced proximity effect via large scale quantum Monte Carlo simulations of helium-4 in a topologically non-trivial geometry that incorporates the important aspects of the experiments. We find that due to the bosonic symmetry of helium-4, identical particle permutations lead to correlations between contiguous spatial regions at a length scale greater than the coherence length. We show that quantum exchange plays a large role in explaining the anomalous experimental results while simultaneously showing how classical arguments fall short of this task.
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CHAPTER 1

INTRODUCTION

This work is intended to be a complete account of my journey thus far into the world of research in the condensed matter theory community. This document did not start its life as a thesis, rather its original purpose was to be a complete set of notes that someone unfamiliar with quantum fluids and/or path integral Monte Carlo could read and use as reference along the journey to this corner of condensed matter enlightenment. The aim of this work was to study proximity effects in superfluid helium-4, and much background information had to be ingested and digested in order to fully grasp how to do this with the tools available. It is the hope of the author that the information presented in this work will assist other researchers with tackling the undeniably challenging and fulfilling subjects presented herein.

1.1 IMPACT

At the time of this work, there are open questions related to enhanced proximity effects and coupling between weakly linked regions of superfluid helium that have different transition temperatures. These enhanced proximity effects cannot be explained with mean field approaches or other analytical methods and cannot be fully attributed to critical fluctuations.
1.1. IMPACT

This means that there is potentially new physics to learn from studying and understanding these confined systems. Studies of helium-4 confined to porous materials, packed powders, and various other confined geometries [1, 2] have been done and the proximity effects are not always easily quantifiable. This is the primary reason we, as a theoretical condensed matter research group, are interested in this problem.

This work may also help aid in the realization or improvement of new devices. Superfluids have a good deal in common with superconductors, and just as a superconducting quantum interference device (dc-SQUID) [3] may be used to measure small changes in current, researchers are working on a device known as a superfluid helium quantum interference device (SHeQUID) [4] which will measure very small changes in rotation. Both types of interferometers exploit the fact that applying a chemical potential difference $\Delta \mu$ between two weakly coupled samples of material which exhibit macroscopic quantum behavior results in oscillation at the Josephson frequency $f_J = \Delta \mu / h$ where $h$ is Planck’s constant. What is oscillating depends on the material, so if the materials are superconducting then we get an oscillating electrical current and if the materials are in the superfluid phase we get oscillating total mass current.

It has been proposed that the SHeQUID could be used as a Sagnac interferometer, which is a device built for detecting changes in rotation. These devices work by detecting Sagnac phase shifts [5], and may be constructed as optical devices or matter wave interferometers. Those that exploit the Sagnac phenomena in matter waves can detect phase changes that are many orders of magnitude smaller than the optical devices, which can lead to the fabrication of devices of much higher sensitivity. Extensive studies of superfluid helium in confined and weakly linked geometries is essential for full control of these devices.

From a methods standpoint, application of path integral Monte Carlo is important by itself. Quantum Monte Carlo methods are becoming increasingly more popular within the computational materials science community, as they provide benefits that other current
1.2. OUTLINE AND NOTES TO READER

analytical and numerical methods are simply not capable of providing. When simulating bosonic systems, path integral Monte Carlo is second to none because it is stochastically exact unlike methods such as density functional theory which are only exact when supplied with an exact trial wave function. For fermionic systems, there are strategies to get around what is known as the ‘sign problem’, but these cause the method to no longer be exact. These methods are out of the scope of this thesis.

An understanding of when QMC methods are useful, or sometimes even essential, to studying a physical system seems necessary for practicing computational materials scientists. The work presented herein is therefore important for both the knowledge gained about coupled superfluid helium systems, but also the proof of principle that quantum Monte Carlo is broadening its applicability to new exciting systems.

1.2 Outline and Notes to Reader

An overview of each chapter is now given as a roadmap of sorts.

2. A brief historical account of helium from the standpoint of a condensed matter physicist is supplied. This includes the commonly used interaction potential for helium-4 atoms and some early experimental findings. Next, some properties of Bose Einstein Condensates are discussed, and the argument for the necessity of quantum Monte Carlo simulations of quantum fluids is presented by discussing the shortcomings of other methods. From here, some common properties of superfluids are presented that have been deemed of interest to the reader who is new to the quantum fluids community. The chapter ends with discussion of how helium-4 behaves when confined to certain geometries. This includes a presentation of results that are currently unexplained, which stands as the motivation for this work.

3. A brief overview of the Feynman path integral formulation of quantum mechanics is
1.2. OUTLINE AND NOTES TO READER

supplied where a kernel is defined that contains knowledge about the probability of quantum mechanical events occurring. We start by defining the classical action and show why it is important to extremize this quantity, and then show why one should care about this in the context of quantum mechanics. Then, the Schrödinger equation is derived from the path integral formalism in order to touch base with the differential form of quantum mechanics. From this result, it is shown that steady state solutions to the Schrödinger equation may be expressed as sums over linear combinations of some orthonormal basis set, which leads to defining the kernel in terms of these linear combinations of orthonormal functions.

A very brief overview of statistical mechanics is then supplied, where physical systems in thermal equilibrium are considered. The partition function and density matrix are defined and it is shown that expectation values of physical observables for a system may be computed given knowledge of these quantities. Then, a very important connection between the partition function and the kernel is made in which the two are shown to be formally equivalent.

4. This is where some of the basic aspects of path integral Monte Carlo are presented, including but not limited to the density matrix decomposition, the imaginary time propagator, and a couple of different ways to approximate the action along with motivation for why this must be done. Following this, two energy estimators are presented rigorously. One of these, called the centroid virial energy estimator, was added to the production code by the author, and evidence is provided that shows this to be a superior way to compute the energy of a quantum system. Using the centroid virial energy estimator, it is then shown how one may compute the specific heat. Finally, a new estimator called the local permutation number estimator is presented. This provides a novel method of measuring how locally ‘connected’ the quantum particles in a simulation cell have become and may provide a way of viewing
1.2. OUTLINE AND NOTES TO READER

the local superfluid density within a simulation cell. An estimator for the superfluid density is referenced, along with a method of computing the pressure of a system.

5. This chapter contains most of the novel work that has been done. As a note to the reader who wants to understand what is undocumented in the literature at the time of this writing, it is recommended that this chapter be read first and the previous chapters be referenced as needed. A new simulation cell is presented which provides a way to study quantum systems confined to contiguous spatial regions with different superfluid transition temperatures. Next, a new type of non-trivial topological winding is discussed, along with a way of measuring it in path integral Monte Carlo simulations. This winding helps explain how weakly coupled spatial regions are coupled at relatively large distances. This winding is discussed in depth, and results are presented for a film region connecting two 3d regions.

6. Provides some background and motivation for possible avenues of future research based on or related to the work done here.
CHAPTER 2

HELIUM-4 AS A QUANTUM FLUID

2.1 GENERAL PROPERTIES OF HELIUM-IV

The existence of $^4$He was first reported on Earth in 1895 by William Ramsay and it was first liquified in 1908 by Kamerlingh Onnes [6]. It has some truly remarkable properties, some of which are shared only with its fermionic isotope $^3$He. A glance at the phase diagram will make some of these properties readily apparent. To begin with it has no triple point, which is a rather uncommon feature. More strikingly, it does not undergo a transition to a solid phase under standard atmospheric pressure and requires application of at least 25 bars of pressure at ultracold temperatures to solidify. The poten-

Figure 2.1: Helium-4 Phase Diagram
2.1. GENERAL PROPERTIES OF HELIUM-IV

tential well depth for a helium atom is rather shallow compared to most any other atomic species of comparable atomic mass. This is a trait belonging to the noble gases and can be accredited to a full outer valence shell. The full valence shell, along with the lack of polarizability (from spherical symmetry of the full 1s shell) and neutral charge make Van der Waals forces the overwhelming contributors to the interaction potential in $^4$He, which are known to be weaker forces than other types of interatomic interaction forces. The reason why $^4$He doesn’t solidify under atmospheric pressure can be understood qualitatively by considering the zero-point motion. If there exists a lattice, then this implies that there is some knowledge of at least the average position of its constituent atoms. With this knowledge, the uncertainty principle says that there will be some uncertainty in the momentum as well. Since momentum is directly proportional to kinetic energy, this will also be present to some degree. It turns out that the kinetic energy due to the zero-point motion is actually great enough to overcome the weak bonding due to the shallow potential well of each $^4$He atom. It has been shown that this argument is not sufficient [7], and it turns out that the indistinguishability of the helium-4 atoms contributes to this lack of crystallization also. The potential well for helium-4 may be seen in Figure 2.2, and is given by an expression that was determined semi-empirically by R. Aziz in 1979. The expression, along with its first and second derivatives will be given in the next section.

So far, we have given arguments that are somewhat classical in nature (other than the fact that the uncertainty principle was used) but part of the
2.1. GENERAL PROPERTIES OF HELIUM-IV

reason why \(^4\text{He}\) does not solidify is due to completely quantum mechanical considerations. Matter has wave-like properties and can be described by its de Broglie wavelength,

\[
\lambda_{dB} = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}. \tag{2.1}
\]

When this wavelength is on the order of the interatomic spacing between neighboring atoms, quantum mechanical effects become strongly influential on the properties of the system as single particle wave function overlap begins to occur and exotic behavior such as Bose-Einstein condensation and superfluidity may be observed. These phenomena can be described by a macroscopic wave function or off-diagonal long range order, to be discussed shortly. Inspection of Equation (2.1) shows that the de Broglie wavelength is inversely proportional to the square root of the temperature, so lowering the temperature of a physical system will make quantum effects more prominent as this wavelength grows larger. Because the mass of helium is the second smallest of any element on the periodic table and \(\lambda_{dB} \sim \sqrt{1/m}\), helium already has a larger de-Broglie wavelength than most other substances.

Shortly after \(^4\text{He}\) was liquified in the early 1900s, it was experimentally brought to temperatures around 1 K, well into the superfluid regime. Although the superfluid phase of \(^4\text{He}\) was attained this early on in the century, its exotic properties were not known to actually exist for almost 30 more years. In 1938, two papers [8, 9] were published that reported experimental realizations of superfluidity in \(^4\text{He}\). Right about the same time, Fritz London published an article [10] on the theory of an ideal Bose-Einstein gas which helped to explain Bose-Einstein condensation and related it to superfluidity.

As an important note, one may see that as the mass of an object becomes smaller, \(\lambda_{dB}\) becomes larger. This may lead the informed reader to ask the question: Why does hydrogen form a solid at low enough temperatures under standard atmospheric pressure? The answer to this lies in the fact that hydrogen, left to its own devices, will exist as \(H_2\) due to its energy being lowered by forming a covalent bond between two atoms. Molecular hydrogen is highly
2.2. AZIZ POTENTIAL

polarizable and as such can form dipole-dipole bonds which are much stronger than bonds
due to Van der Waals forces. Therefore, it becomes energetically favorable at some point
for hydrogen to form a solid rather than staying liquid [11].

Due to the unique properties of $^4$He, it is the quintessential test-bed for those studying
quantum fluids both theoretically and experimentally. Those studying helium-4 from a
theoretical standpoint must know the interatomic interaction potential, so the standard
form of this is presented next.

2.2 AZIZ POTENTIAL

2.2.1 INTERATOMIC INTERACTION POTENTIALS

Interatomic interaction potentials have features which must be accounted for when writing
out their functional form. To begin with, at large distances (compared to the atomic radius)
neutral atoms tend to attract one another. This is due to the fact that all atoms are at least
slightly polarizable since there is a positively charged nucleus surrounded by a negatively
charged electron cloud. When one atom ‘feels’ the presence of another, there is spontaneous
polarization of both atoms and hence an attractive force. Of course, at very large distances
($d \gg a$, where $a$ is loosely the radius of the atom) the interaction potential should tend
to zero. Another feature that must be incorporated into the functional form is the fact
that when two atoms are brought too close to one another there is a repulsive force. The
most basic form of a potential which can be written that incorporates this physics is the
Lennard-Jones 6-12 potential:

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2.2)$$
2.2. AZIZ POTENTIAL

where \( r \) is the distance between atoms, \( \sigma \) is the distance at which the interatomic potential becomes zero, and the minimum well depth is given by \( \epsilon \). The 6\(^{th}\) order term accounts for the attractive part of the potential and the 12\(^{th}\) order term accounts for the repulsive part. The attractive term may be derived from perturbation theory, but the repulsive term is phenomenologically constructed. This repulsive part is also commonly approximated using an exponential function. Either way one approximates it, these types of potentials will roughly take the form as in Figure 2.2. Of course, over the years there has been much work done to come up with more accurate potentials for given atomic species. These will often have more terms and scaling constants/exponents which are determined by collecting experimental data and then applying fitting techniques. This type of method leads to what are called semi-empirical interaction potentials.

2.2.2 1979 AZIZ FUNCTIONAL FORM

A semi-empirical intermolecular potential for \(^4\)He, first presented in [12], is

\[
V(r) = \epsilon \left[ Ae^{-\alpha r/r_m} - \left( C_6 \left( \frac{r_m}{r} \right)^6 + C_8 \left( \frac{r_m}{r} \right)^8 + C_{10} \left( \frac{r_m}{r} \right)^{10} \right) \cdot F(x) \right],
\]

(2.3)

where \( x = r/r_m \) and \( r \) is the interatomic spacing between two helium atoms while \( r_m \) is the distance from the nucleus to the minimum of the potential well. This may be seen in Figure 2.2. The \( F \) term is given as

\[
F(x) = \begin{cases} 
\exp \left( - \frac{D}{x} + 1 \right)^2 & : x < D \\
1 & : x \geq D
\end{cases},
\]

(2.4)

and the constants are chosen such that: \( C_6 = 1.3732, C_8 = 0.42538, C_{10} = 0.1781, D = 1.2413, \alpha = 13.353, \epsilon = 10.8K, A = 0.5449 \cdot 10^6 \), and \( r_m = 2.9673\text{Å} \). In order to perform numerical studies of \(^4\)He using the 1979 Aziz interaction potential, the first and second
2.2. AZIZ POTENTIAL

derivatives are required. With foresight, we first compute the first and second derivatives of the function \( F(x) \). The first derivative, for \( x < D \), is seen to be

\[
\frac{d}{dx} F(x) = \frac{2D}{x^2} \left( \frac{D}{x} - 1 \right) \exp \left( -\frac{D}{x} + 1 \right)^2,
\]

and the second derivative is

\[
\frac{d^2}{dx^2} F(x) = \frac{2D}{x^3} \left( \frac{2D^3}{x^4} - 4\frac{D^2}{x^2} - \frac{D}{x} + 2 \right) \exp \left( -\frac{D}{x} + 1 \right)^2.
\]

Putting \( V(r) \) into the form \( V(x) \) and differentiating is now in order. The substituted form of the interatomic potential is

\[
V(x) = \epsilon \left[ A e^{-\alpha x} - \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot F(x) \right],
\]

and as such, the first derivative with respect to \( r \) is

\[
\frac{d}{dr} V(x) = \frac{1}{r_m} \frac{d}{dx} V(x) = \epsilon \frac{d}{dx} \left[ A e^{-\alpha x} - \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot F(x) \right]
\]

\[
= -\frac{\epsilon}{r_m} \left[ A e^{-\alpha x} - \left( 6 C_6 \left( \frac{1}{x} \right)^7 + 8 C_8 \left( \frac{1}{x} \right)^9 + 10 C_{10} \left( \frac{1}{x} \right)^{11} \right) \cdot F(x) \right]
\]
\[
+ \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot \frac{d}{dx} F(x) \].
\]
2.2. AZIZ POTENTIAL

Now, the second derivative may be taken:

\[
\frac{d}{dr} \frac{d}{dr} V(x) = 1 \frac{d}{dr} \frac{d}{dx} V(x) = \\
= \frac{\epsilon}{r_m^2} \left[ A \alpha^2 e^{-\alpha x} - \left( 42C_6 \left( \frac{1}{x} \right)^8 + 72C_8 \left( \frac{1}{x} \right)^{10} + 110C_{10} \left( \frac{1}{x} \right)^{12} \right) \cdot F(x) \\
+ 2 \left( 6C_6 \left( \frac{1}{x} \right)^7 + 8C_8 \left( \frac{1}{x} \right)^9 + 10C_{10} \left( \frac{1}{x} \right)^{11} \right) \cdot \frac{d}{dx} F(x) \\
- \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot \frac{d^2}{dx^2} F(x) \right].
\]

The exact reason that these derivatives are needed will become clear to the reader during the section on path integral Monte Carlo energy estimators.

2.2.3 POTENTIAL TAIL CUTOFF CORRECTION

In simulations of bulk systems, one may choose to only compute the interaction potential up until some cutoff distance, \( r_c \). This cutoff length is chosen such that the efficiency of the code is maximized while minimizing the error that comes from not considering the full interaction potential. This error must be accounted for by adding a tail correction to the observed potential energy.

In general, for a particle at \( \vec{r}_1 \) interacting with one at \( \vec{r}_2 \) one needs to compute an integral of the form

\[
V_{\text{tail}} = \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \rho(\vec{r}_1) \rho(\vec{r}_2) V(|\vec{r}_1 - \vec{r}_2|),
\]

where \( \rho(\vec{r}_i) \) is the density around the \( i^{\text{th}} \) particle and the integral must be done from one particle out to the next, where the second particle moves from the cutoff radius out to infinity. The \( 1/2 \) is to avoid double-counting. Of course, in bulk we have translational invariance so we can set one of the particles at the origin and just integrate out to the next. We can also consider the probability density of finding a particle, and our expression
2.2. AZIZ POTENTIAL

becomes

\[ V_{\text{tail}} = \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 (\rho(\vec{r}_1)\rho(0))V(|\vec{r}_1|) = \frac{\ell}{2} \int d\vec{r}_1 (\rho(\vec{r}_1)\rho(0))V(|\vec{r}_1|), \]  

(2.11)

where \( \ell \) is the volume in 3d, the area in 2d, and the length in 1d. The quantity in angled brackets is proportional to the pair correlation function (radial distribution function \( g(r) = \rho^{-2}(\rho(\vec{r})\rho(0)) \)), where \( \rho \) is the average density, gives us the probability of a particle being a distance \( r \) away given that there is a particle at the origin), and for homogeneous fluids at a large enough distance we assume this to be approximately one. Our expression for the potential tail correction then becomes

\[ V_{\text{tail}} = \frac{N^2}{2\ell} \int d\vec{r} V(r). \]  

(2.12)

We now specifically consider the 3d case. The potential here is spherically symmetric, so the integral becomes

\[ V_{\text{tail}} = 2\pi \rho N \int_{r_c}^{\infty} dr \ r^2 \ V(r). \]  

(2.13)

When Equation (2.3) is inserted into the above, the result is

\[ V_{\text{tail}} = 2\pi \rho N \ell \left[ \frac{Ar_m}{\alpha^3} (2r_m^2 + 2r_c^2 \alpha + r_m^2 \alpha^2) \exp(-r_c \alpha/r_m) \right. \\
\left. - r_m^3 \left( \frac{C_6}{3} \left( \frac{r_m}{r_c} \right)^3 + \frac{C_8}{5} \left( \frac{r_m}{r_c} \right)^5 + \frac{C_{10}}{7} \left( \frac{r_m}{r_c} \right)^7 \right) \right], \]  

(2.14)

which gives the potential tail correction for the 1979 Aziz potential for helium-4 in 3d. Note that in the case of no pre-set potential cutoff, due to the mirror image convention, one must take \( r_c \) to be half of the distance of the longest simulation cell wall.
2.3. BOSE EINSTEIN CONDENSATES

2.2.4 Pressure Tail Cutoff and Impulse Corrections

In examining the estimator for the thermodynamic pressure, given in Equation (4.103), one may notice that the virial of Clausius appears, which depends upon the radial derivative of the potential action (hence potential). Therefore, we need to account for a possible tail correction to the pressure. This correction is

\[ P_{\text{tail}} = -\frac{1}{d\ell \tau M} \left\langle \sum_{\alpha=1}^{M} \vec{R}_{\alpha} \cdot \nabla_{\alpha} U(\vec{R}_{\alpha}) \right\rangle \]  

(2.15)

for all particles outside of a cutoff radius \( r_c \), where \( d \) is the dimensionality and \( \ell \) is the volume in 3d, area in 2d and length in 1d. The expression for this tail correction is written out explicitly in Appendix A.

Since we consider interaction potentials up to a cutoff \( r_c \) and then let the potential be zero past this point, there is a correction due to the derivative of this step function. We call this correction the pressure impulse term. This term is not considered here because unless the cutoff length is very small, this term is negligible.

2.3 Bose Einstein Condensates

Ultimately, the aim of this work is to study the superfluid properties of \(^4\)He, but any in-depth discussion of superfluidity benefits greatly by first discussing Bose-Einstein condensation. This is not by any means an exhaustive discussion of Bose-Einstein condensation, and the reader is urged to read textbooks such as the ones by Annett [13], Pethick and Smith [14], and Pitaevskii and Stringari [15]. The Bose-Einstein condensate (BEC) is a macroscopic manifestation of quantum mechanics and is a state in which the amount of atoms within a sample that have fallen into the ground state (the zero-momentum state) is on the same order at the total number of atoms in the system.
2.3. **BOSE EINSTEIN CONDENSATES**

Unlike in classical mechanics, it may not be assumed that quantum mechanical entities are distinguishable from one another. The two main types of quantum mechanical particles are bosons, which can have the same set of quantum numbers, and fermions, which may not share the same quantum numbers due to the Pauli Exclusion principle [16]. Because bosons may share a set of quantum numbers, there may be multiple particles in the ground state for a single quantum mechanical system. This concept of indistinguishability has consequences in statistical mechanics, where probability comes into play in estimating observables for physical systems. It turns out the BEC is a result of a Bose gas undergoing a thermodynamic phase transition which is driven by particle statistics rather than interactions. Past the critical point, some finite number of atoms within the gas will be a part of the BEC and some will not. These atoms will not actually be separated in position space as would be a liquid-gas mixture, but rather they are separated in Fourier space into zero (condensate) and non-zero (‘normal’) momentum states.

2.3.1 **OFF-DIAGONAL LONG RANGE ORDER**

In order to come up with a rigorous definition of a BEC, first recall the general form of the one-body density matrix (OBDM):

\[
\rho_1(\vec{r} - \vec{r'}) = \left\langle \hat{\Psi}^\dagger(\vec{r})\hat{\Psi}(\vec{r'}) \right\rangle, \quad (2.16)
\]

where \(\hat{\Psi}^\dagger(\vec{r})\) and \(\hat{\Psi}(\vec{r})\) are the quantum field operators which create and destroy (respectively) a particle at position \(\vec{r}\) in space. In this case, these operators satisfy the bosonic commutation relations, given by

\[
[\hat{\Psi}(\vec{r}), \hat{\Psi}^\dagger(\vec{r'})] = \delta(\vec{r} - \vec{r'}) ; \quad [\hat{\Psi}^\dagger(\vec{r}), \hat{\Psi}^\dagger(\vec{r''})] = 0. \quad (2.17)
\]
2.3. Bose Einstein Condensates

If we are considering a homogeneous system of bosons (as is the case in purified, bulk $^4$He), then the OBDM takes the form

$$\rho_1(\vec{r} - \vec{r}') = N \int d\vec{r}_2 \cdots d\vec{r}_N \Psi_0^*(\vec{r}, \vec{r}_2, ..., \vec{r}_N) \Psi_0(\vec{r}', \vec{r}_2, ..., \vec{r}_N),$$  \hspace{1cm} (2.18)

which tells us about the correlation between the many body quantum states $\Psi_0(\vec{r}, \vec{r}_2, ..., \vec{r}_N)$ and $\Psi_0(\vec{r}', \vec{r}_2, ..., \vec{r}_N)$ at spatial position $\vec{r}$ and $\vec{r}'$. The OBDM can tell us important information about a quantum system. It is Hermitian, and therefore may be expanded in a complete orthonormal basis set of single particle wave functions, $\zeta_i(\vec{r})$ as

$$\rho_1(\vec{r} - \vec{r}') = \sum_i N_i \zeta_i^*(\vec{r}) \zeta_i(\vec{r}'),$$  \hspace{1cm} (2.19)

where it turns out that these expansion coefficients may be interpreted as occupation numbers subject to the normalization condition $\sum_i N_i = N$ for an $N$ particle system. A condensate will be observed if $O(N_0) \sim O(N)$, and the quantum state denoted as $\zeta_0(\vec{r})$ is then called a BEC. It is convenient in this case to separate out the condensate from the rest of the sample, as

$$\rho_1(\vec{r} - \vec{r}') = N_0 \zeta_0^*(\vec{r}) \zeta_0(\vec{r}') + \sum_{i \neq 0} N_i \zeta_i^*(\vec{r}) \zeta_i(\vec{r}').$$  \hspace{1cm} (2.20)

As it turns out, one can compute the momentum distribution

$$n(\vec{p}) = \left\langle \hat{\Psi}^\dagger(\vec{p}) \hat{\Psi}(\vec{p}) \right\rangle$$  \hspace{1cm} (2.21)

from the off-diagonal terms of the OBDM, which in effect gives a nice way to compute the BEC fraction. Above,

$$\hat{\Psi}^\dagger(\vec{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int d\vec{r} e^{-i\vec{p} \cdot \vec{r}/\hbar} \hat{\Psi}^\dagger(\vec{r})$$  \hspace{1cm} (2.22)
2.3. BOSE EINSTEIN CONDENSATES

is the quantum field operator in reciprocal space. If this definition is inserted into the expression for the momentum distribution, it is easily shown that it yields

\[ n(\vec{p}) = \frac{1}{(2\pi\hbar)^3} \int d\vec{r} d\vec{r}' e^{i\vec{p} \cdot (\vec{r} - \vec{r}')/\hbar} \left\langle \hat{\Psi}^\dagger (\vec{r}) \hat{\Psi} (\vec{r}') \right\rangle. \] (2.23)

One should notice that this momentum distribution tends to zero when the separation \(|\vec{r} - \vec{r}'|\to \infty\), except for the case where \(\vec{p} = 0\). This fact can be combined with Equation (2.20) to show that the OBDM tends to a constant value in the large distance limit. In order to see this, recall that in the thermodynamic limit the eigenfunctions of the OBDM are plane waves with \(\vec{p} = 0\) in the case of the non-interacting ground state:

\[ \psi_0 (\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{p} \cdot \vec{r}/\hbar}. \] (2.24)

This may be inserted into Equation (2.20) to give an expression for the one body density matrix for a homogeneous system of bosons in the thermodynamic limit:

\[ \rho_1 (\vec{r} - \vec{r}') = \frac{N_0}{V} + \frac{1}{V} \sum_{\vec{p} \neq 0} N\vec{p} e^{i\vec{p} \cdot (\vec{r} - \vec{r}')/\hbar}. \] (2.25)

As can be seen, it turns out that the value of the OBDM approaches a constant when the separation between \(\vec{r}\) and \(\vec{r}'\) is sufficiently large because all terms in this sum tend to zero. This behavior is known as off-diagonal long range order due to the fact that we have off-diagonal elements of the OBDM (different particles) correlated in such a way as to yield a non-zero OBDM in the long-range limit. The expectation value of the ground state wave function \(\Psi\) is non-zero in this long-range limit, further defining the off-diagonal long-range order.
2.3. BOSE EINSTEIN CONDENSATES

2.3.2 BEC IN THE IDEAL BOSE GAS

Before moving on to discussion of superfluidity, we derive results for the BEC fraction and critical temperature in the case of a non-interacting Bose gas. As it turns out, much can be learned from this simplified example. If we use the Bose-Einstein distribution for this system of non-interacting bosons, it is true that

\[ N = \sum_{k} \frac{1}{\exp(\beta(\epsilon_k - \mu)) - 1} = \sum f_k \]  \hspace{1cm} (2.26)

is the total number of particles in the system, where \( \epsilon_k \) is the energy of the boson with momentum \( k \), \( \mu \) is the chemical potential, and \( \beta \) is the inverse temperature. If we consider the thermodynamic limit, this sum may be approximated as an integral and the total number of particles in 3d inside of a volume \( \ell \) becomes

\[ N = \frac{\ell}{(2\pi)^d} \int d^3k \frac{1}{\exp(\beta(\epsilon_k - \mu)) - 1}, \]  \hspace{1cm} (2.27)

where \( d \) is the dimensionality of the system. It is desirable to then write this in terms of the density \( (n = N/\ell) \) as an integral over momentum states and then convert to the density as an integral over energy states using the density of states per unit volume. In the case of free bosons here, we have plane wave solutions and the allowed wave vectors are

\[ \vec{k} = \left( \frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right), \]  \hspace{1cm} (2.28)

and the number of quantum states in an infinitesimal volume in momentum space is \( d\vec{k}/(2\pi)^3 \), each having energy \( \epsilon_{\vec{k}} = h^2 k^2/2m \). Therefore, for \( d = 3 \), a shell of radius \( k_s \) and thickness \( \delta k_s \) contains

\[ N_s = \frac{\ell}{(2\pi)^{d-1}} 4\pi k_s^2 \delta k_s \]  \hspace{1cm} (2.29)
2.3. **BOSE EINSTEIN CONDENSATES**

quantum states. Using the relationship between the wave number and the energy given above, one may trivially show that the number of states in this shell can be expressed as

\[ N_s = \frac{\ell m^{3/2}}{\pi^2 \hbar^3} \sqrt{\frac{\epsilon}{2}} \delta_{\epsilon_s}. \]  

(2.30)

This gives the density of states per unit volume for a boson of mass \( m \):

\[ D(\epsilon) = \frac{m^{3/2}}{\pi^2 \hbar^3} \sqrt{\frac{\epsilon}{2}}. \]  

(2.31)

Using this, one may write the density as

\[ n = \frac{m^{3/2}}{\sqrt{2} \pi^2 \hbar^3} \int_0^\infty d\epsilon \frac{\sqrt{\epsilon}}{\exp(\beta(\epsilon_k - \mu))} - 1. \]  

(2.32)

The integral above may be solved by writing it in terms of \( x = \beta \epsilon \) and the fugacity \( z = e^{\mu \beta} \), leaving it in the form

\[ n = \frac{m^{3/2}}{\sqrt{2} \pi^2 \hbar^3 \beta^{3/2}} \int_0^\infty dx \sqrt{x} \frac{z e^{-x}}{1 - z e^{-x}}. \]  

(2.33)

Upon inspection, this integrand contains a power series

\[ \frac{z e^{-x}}{1 - z e^{-x}} = z e^{-x} \sum_{p=0}^\infty z^p e^{-px} = \sum_{p=1}^\infty z^p e^{-px}, \]  

(2.34)

meaning that the the expression for the density of the system becomes

\[ n = \frac{m^{3/2}}{\sqrt{2} \pi^2 \hbar^3 \beta^{3/2}} \sum_{p=1}^\infty z^p \int_0^\infty dx \sqrt{x} e^{-px}. \]  

(2.35)

The integral above is a Gamma function of argument \( 1/2 \), which has a known solution. This brings us to a final expression for the density:

\[ n = \left( \frac{m}{2 \beta \pi \hbar^2} \right)^{3/2} \sum_{p=1}^\infty \frac{z^p}{p^{3/2}}. \]  

(2.36)
2.3. BOSE EINSTEIN CONDENSATES

The series in Equation (2.36) converges when the absolute value of the fugacity is less than one, \( |z| < 1 \), and when \( z = 1 \) the series converges to a value of 2.612. When \( |z| > 1 \), the sum does not converge. This means that relatively good results may be obtained from this method for free bosons with a negative chemical potential.

Equation (2.36) is an interesting result, because at low temperatures and fixed density, it helps to define the critical temperature at which the phase transition to BEC occurs. This is due to the fact that when the system is cooled, eventually the chemical potential becomes zero and the value of \( z \) reaches unity, and no energy is required to add a particle with zero momentum \((k = 0)\) to the ground state. This gives our critical temperature a value of

\[
T_c = \frac{2\pi \hbar^2}{k_B m} \left( \frac{n}{2.612} \right)^{2/3}.
\]  

The astute reader will now take a step back and think to themselves that if the chemical potential goes to zero, then the number of bosons in the ground state \((\varepsilon_k = 0)\) will become infinite:

\[
N_0 \rightarrow \frac{1}{e^0 e^0 - 1}.
\]  

This is alright though, since we are working in the thermodynamic limit where \( V \rightarrow \infty \) while \( N \rightarrow \infty \) and the density is kept constant. Turns out, when we go below the critical temperature, the \( N_0 \) term (corresponding to \( \vec{k} = 0 \)) from Equation (2.26) needs to be treated separately. Going through the same procedure for determining the density before, one can write out the density (recalling \( z = 1 \) below \( T_c \)) as

\[
n = n_0 + \frac{m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \frac{\beta^{3/2}}{2\beta \pi \hbar^2} \int_0^\infty dx \sqrt{x} \frac{e^{-x}}{1 - e^{-x}}.
\]  

As before, the above integral is soluble and the result can be seen to be

\[
n = n_0 + 2.612 \left( \frac{m}{2\beta \pi \hbar^2} \right)^{3/2}.
\]
2.3. **BOSE EINSTEIN CONDENSATES**

Equations (2.37) and (2.40) may be combined to express the ratio of the number of bosons in the condensate over the number of bosons not in the condensate for an ideal Bose gas. This is called the condensate fraction and is expressed as

\[
\frac{n_0}{n} = 1 - \left( \frac{T}{T_c} \right)^{3/2}.
\]  

(2.41)

2.3.3 **ON DETERMINING THE BEC FOR REAL SYSTEMS**

If one takes Equation (2.37) and inserts the low temperature bulk density of $^4\text{He}$ under saturated vapor pressure and the corresponding mass of $^4\text{He}$, one will find that the predicted critical temperature is 3.1 kelvin. Although this is assuming an ideal gas, it is actually pretty close to the temperature at which the onset of the superfluid phase begins, 2.17 kelvin (see Figure 2.1). Turns out, $^4\text{He}$ atoms interact strongly and so the number of atoms actually in the ground state is quite small even near absolute zero [14].

So far, the ideal Bose gas has been discussed and it has been shown that treating low temperature systems of bosons in this approximation is not as bad of an approximation as one may expect. Of course, any real system being studied in a laboratory will have interactions and so another framework needs to be presented to predict the properties of the condensate in the presence of interactions. The Gross-Pitaevskii equation is a non-linear partial differential equation that has the basic form of the Schrödinger equation but with a second order term added to account for the mean-field produced by interacting bosons. It gives a mean-field approach to tackling problems related to quantum fluids by allowing one to numerically solve for the condensate wave function and has eigenvalues that are the chemical potential rather than the energy. This method can be read about in the references given earlier, in particular [14]. The Gross-Pitaevskii approach works quite well in the case of weakly interacting Bose gases at low densities, such as those created from atomic gases in laboratories. It does not work for $^4\text{He}$ for anything other than qualitative predictions.
2.4. SUPERFLUIDITY

due to the strong repulsive interactions when the $^4$He atoms get close to one another.

In practice, quantum Monte Carlo techniques have yielded the best results for computing the physical properties of strongly interacting quantum fluids. These will be discussed in depth in the chapters to come.

2.4  SUPERFLUIDITY

So far, we have dealt with the exotic phase of matter known as BEC. As mentioned, this is a macroscopic manifestation of quantum mechanics that can be understood through the off-diagonal long range ordering in the one-body density matrix. It would seem that this is a static property of a quantum fluid, but there exist other strange phenomena when one starts to examine the dynamics of certain quantum fluids. The superfluid phase emerges as one such exotic phenomenon, as it is a phase of matter which exhibits flow without viscosity. A superfluid emerges when there are a macroscopic number of particles within a system in the ground state, all characterized by the same macroscopic wave function but having a spatially varying complex phase. It is this spatially varying phase that results in superflow and primarily distinguishes a superfluid from a BEC. Here, we discuss some properties of the superfluid phase.

2.4.1  SUPERFLUID TRANSMITION AND SUPERFLOW

As previously mentioned, there is a critical temperature at which atoms begin to fall into the ground state for $^4$He, and this is the temperature at which a thermodynamic phase transition occurs. For bulk 3d $^4$He, this is $T_\lambda=2.172$K. This transition is characterized by a power law singularity in the specific heat, which can be see in Figure 2.3. The specific heat
2.4. *SUPERFLUIDITY*

around this transition in bulk $^4$He has been determined [13] to take the form

$$C_V = \begin{cases} 
C(T) + A_+ |T - T_c|^{-\alpha} : T > T_\lambda \\
C(T) + A_- |T - T_c|^{-\alpha} : T < T_\lambda 
\end{cases},$$

(2.42)

where $A_\pm$ are constants that differ depending upon whether the temperature is less than or greater than the critical temperature, $C(T)$ is a non-singular smooth function of the temperature, and the critical exponent $\alpha$ is roughly 0.009, which puts this transition into the 3d XY-model universality class [13]. The XY-model is characterized by $O(2)$ symmetry and consists of a d-dimensional lattice of spins, each having rotational symmetry. Each spin is characterized by a unit vector $\vec{n}(r) = [\cos \theta, \sin \theta]$ for an angle $\theta$ at every point in space, $\vec{r}$. The meaning of the unit vector $\vec{n}(r)$ is quite obvious for spins, but is less obvious in
2.4. SUPERFLUIDITY

the case of the superfluid. If one imagines that there is a macroscopic wave function that describes all of the atoms which have fallen into the zero momentum state, then this wave function may be written out generally as

$$\psi_0(\vec{r}) = \sum_n n_0(\vec{r}) e^{i\theta(\vec{r})}, \quad (2.43)$$

where $n_0(\vec{r}) = |\psi_0(\vec{r})|^2$. This wave function is similar to the wave function which describes the BEC, but one must be careful in thinking about this because we can have a BEC in the case of no interactions. Therefore a condensate wave function may be defined for the non-interacting case, however superfluidity requires that there be some interaction between constituent particles so the many-body wave function for most systems cannot actually be defined using mean-field approaches. This is one way to see where the Gross-Pitaevskii approach fails to completely describe a system of strongly interacting atoms within a quantum fluid.

It turns out that this macroscopic wave function $\psi_0$ is the order parameter used to characterize the superfluid transition, as it is only non-zero below $T_\lambda$. For the case of a BEC wave function, the phase at every point in $\mathbb{R}^3$ should be the same, but in order to get a superflow, this phase $\theta(\vec{r})$ must vary in space. If we decide to insert the general form of our wave function in Equation (2.43) into the standard expression for the probability density current (which for a non-relativistic, homogeneous system corresponds to the mass density current),
2.4. SUPERFLUIDITY

density current), the result is

\[ \vec{j}_0 = -\frac{i\hbar}{2m} \left[ \psi_0^*(\vec{r}) \nabla \psi_0(\vec{r}) - \psi_0(\vec{r}) \nabla \psi_0^*(\vec{r}) \right] = \frac{\hbar}{m} n_0 \nabla \theta. \quad (2.44) \]

One can write, by definition, that the direct contribution that the condensate makes to the current is \( \vec{j}_0 = n_0 \vec{v}_s \) and therefore the superfluid velocity is

\[ \vec{v}_s = \frac{\hbar}{m} \nabla \theta. \quad (2.45) \]

There have been many experiments which have confirmed that this type of behavior actually exists. Before looking at the consequences of the superfluid velocity being directly proportional to the gradient of the phase, we state the criteria to actually observe superflow.

2.4.2 QUANTIZATION OF CIRCULATION

From looking at Equation (2.45), it is immediately apparent that the superfluid flow should be irrotational due to the fact that the probability density (and mass) must be conserved in this velocity field:

\[ \nabla \times \vec{v}_s = \frac{\hbar}{m} \nabla \times \nabla \theta = 0. \quad (2.46) \]

Consider a container filled with helium-4 where some fraction of the sample is in the superfluid phase. Now imagine tracing out some closed path inside of our container in real space. According to Stokes theorem, the integral along this path in real space should be zero if the space enclosed by the path is simply connected. Any singularities in the enclosed space will result in a potentially different value for this closed path integral.

In order for our proposed wave function given by Equation (2.43) to be single valued, a full trip along this closed path must yield either the same wave function once we return to the same spot we started, or the phase must have changed by an integer multiple of \( 2\pi \),

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2.4. SUPERFLUIDITY

meaning

\[ \Delta \theta = \oint \nabla \theta \cdot d\vec{l} = 2\pi l \]  \hspace{1cm} (2.47)

where \( l \in \mathbb{Z} \). From this argument, one can predict that there can be singularities inside of the system. It turns out that these correspond to superfluid vortices, which can be thought of as the carriers of angular momentum within a superfluid fraction. We call them singularities because their cores consist of atoms in the normal fluid phase. These can form when a sample of normal fluid is given some angular momentum and then cooled below the critical temperature such that the sample ‘stores’ the momentum in these vortices. These have been observed experimentally [17].

By examining Equation (2.45), one sees that this phase change is proportional to the flow circulation \( \Gamma \) around the closed contour:

\[ \Gamma = \frac{\hbar}{m} \oint \nabla \theta \cdot d\vec{l} = l \frac{\hbar}{m}. \]  \hspace{1cm} (2.48)

This quantization of flow was actually first proposed for liquid \(^4\)He by Lars Onsager [18] in 1949. The quantum number \( l \) in this case is known as the topological winding number and it corresponds to the number of times that the phase \( \theta \) winds around in the complex plane while going around the closed path in real space. These windings are often referred to as phase slips when dealing with low-d systems. It turns out that one can measure the winding number in Quantum Monte Carlo simulations in order to gain knowledge about the superfluid fraction. This discussion is put off until the end of the chapter about path integral Monte Carlo.

2.4.3 SUPERFLUID RESPONSE UNDER ROTATION

Superfluidity is characterized in experiments by moving the boundaries of a system and observing the response to those movements. Landau discussed a rotating bucket experiment
2.4. SUPERFLUIDITY

[19] where it was predicted that a superfluid should have a non-classical relationship between the work required to rotate a bucket of superfluid and its moment of inertia. If one rotates a bucket with a normal fluid, the work done to rotate the bucket with angular velocity \( \omega \) is \( E = \frac{1}{2} I \omega^2 \), where \( I \) is the moment of inertia of the bucket filled with fluid. If the contents of the bucket are superfluid however, they will not move when the bucket rotates, meaning that the moment of inertia measured will be less than that of the bucket filled with normal fluid. This lesser (non-classical) moment of inertia was experimentally verified by Andronikashvili in 1946 [20].

In order to formally develop this idea of superfluid density as measured through the non-classical moment of inertia, we consider a cylinder (bucket) of height \( h \), inner radius \( R \) and wall thickness \( d \) where \( d \ll R \) and \( h \gg d \). Let this cylinder be filled with a quantum fluid composed of \( N \) identical bosonic particles each having mass \( m \). Assume that most of the particles are not in contact with the walls and that the walls behave classically. Under these and our previous assumptions about the bucket, the classical moment of inertia of this system, when rotated about the cylindrical axis is \( I_0 = N m R^2 \). If this bucket is rotated slowly then we may approximate that there is no redistribution of mass. If we assume that the ground state of this system has some free energy \( F_0 \), then we may write out the free energy of our system as

\[
F(\omega) = F_0 + \frac{1}{2} [N m R^2] \omega^2 + \Delta F(\omega),
\]

(2.49)

where \( \Delta F(\omega) \) is the change in free energy due to the fact that some of the system is superfluid. If we work under the assumption that there exists a finite superfluid density \( \rho_s \equiv \rho - \rho_n \), where \( \rho_n \) is the normal fluid density and \( \rho \) is the total density of the system,
2.5. **CONFINED HELIUM-4**

then we may write out this change in free energy as

\[ \Delta F(\omega) = -\frac{1}{2} \frac{\rho_s}{\rho} [NmR^2] \omega^2. \]  
(2.50)

One may write the free energy of the system in terms of the full quantum moment of inertia, yielding \( F(\omega) = F_0 + I \omega^2/2 \). Inserting Equation (2.50) into our previous expression for the free energy and equating it with that using the quantum moment of inertia gives

\[ F(\omega) = F_0 + \frac{1}{2} I_0 \omega^2 - \frac{1}{2} \frac{\rho_s}{\rho} I_0 \omega^2 = F_0 + \frac{1}{2} I_0 \omega^2 \]

\[ \Rightarrow \frac{\rho_s}{\rho} = 1 - \frac{I}{I_0}. \]  
(2.51)

This final expression gives us a way of determining the superfluid fraction experimentally for the cylindrical case being discussed, as one can measure the classical moment of inertia at temperatures above the critical point and then measure the moment of inertia below the critical point.

Much is known about the superfluid phase of matter, but there is still a lot of research to be done to understand certain properties. Among the active studies being done is that of superfluid helium-4 in confined geometries, which will be discussed next.

**2.5 CONFINED HELIUM-4**

Over the course of the last 25 years, an extensive body of work has been accumulated that quantifies the behavior of uniformly confined \(^4\)He near the superfluid transition temperature. Experimental data for dimensional crossover from 3 dimensions to 2d, 1d, and 0d have been collected, as well as data for the crossover from a 2d film to a 1d channel. Gasparini et. al. published a thorough review [21] of this work.

When helium is confined in contiguous regions having different superfluid transition
2.5. CONFINED HELIUM-4

temperatures it exhibits coupling and proximity effects. The difference in critical temperatures results from the regions being of different dimensionality. One such geometry is given by bulk 3d regions of helium coupled weakly by 2d regions, which is an example of a superfluid Josephson junction. It has been shown experimentally [22] that changing the spacing between these bulk regions has a larger effect on the superfluid fraction than would be predicted by current theory. Mean field approaches [23–25] have been unsuccessfully used [26] to try to explain some of the experimental results. Fisher et al. have shown that alternating semi-infinite Ising strips exhibit qualitatively similar proximity effects [27], however quantitatively this classical system behaves much different than does the confined superfluid system [21,26]. Here, we provide a summary of the experimental data then briefly summarize the work done by Fisher et al. and motivate a numerical study of these proximity and coupling effects on a helium-4 system similar to those that have been probed experimentally.

2.5.1 Correlation Length

The film regions in these experiments are not strictly 2 dimensional, so in order to understand what is meant by calling these regions 2d one must consider the spatial correlation length of the superfluid phase.

Dimensional crossover occurs when a bulk sample of $^4$He with dimensions $\infty \times \infty \times \infty$ is confined to a film with dimensions $L \times \infty \times \infty$, a channel with dimensions $L_1 \times L_2 \times \infty$ or a box with dimensions $L_1 \times L_2 \times L_3$. Here, $\infty$ means that we are working in the thermodynamic limit in that particular dimension, i.e. the extent of the system in that dimension is much greater than the temperature-dependent bulk correlation length $\xi(t)$, given by

$$\xi(t) = \xi_0 t^{-\nu}, \quad (2.52)$$

where $t = |1 - T/T_\lambda|$ is referred to as the reduced temperature. As mentioned, the exponent
2.5. **CONFINED HELIUM-4**

\( \nu = 0.6705 \) was shown [28] to belong to that of the classical 3d XY-model. The correlation length of \(^4\)He far away from the critical temperature, \( \xi_0 \), differs whether the system is above or below \( T_\lambda \). The values are given [26] as

\[
\xi_0 = \begin{cases} 
0.143 \text{ nm} & : T > T_\lambda \\
0.352 \text{ nm} & : T < T_\lambda 
\end{cases} .
\tag{2.53}
\]

When the system is below \( T_\lambda \), we call \( \xi_0 \) the zero temperature correlation length. For a continuous transition, the correlation length can be understood as the distance to which order propagates [29]. When this distance approaches the size of the system in one of its extents (say, in the \( x \) direction) we say that the system 'feels' the system size and a dimensional crossover occurs. In Figure 2.6 one may see a comparison of the de Broglie

![Figure 2.6: Plot of bulk 3d correlation length and de Broglie wavelength, both as a function of temperature.](image-url)


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2.5. CONFINED HELIUM-4

wavelength (see Equation 2.1) and bulk correlation lengths for bulk 3d helium-4.

In the case of confined systems, this correlation length becomes dependent upon the confinement geometries and we denote it as \( \xi(t, L) \). This dependence has been studied [21] in detail and it has been shown that \( \xi(t, L) < \xi(t) \) near the critical temperature and \( \xi(t, L) \approx \xi(t) \) far away.

2.5.2 ENHANCED COUPLING AND PROXIMITY EFFECTS

Contiguous regions of helium with different dimensionality exhibit coupling and proximity effects. In this case, these phenomena are associated with macroscopic wavefunctions, and were realized in superconductors [30,31] some time ago but have only recently been realized experimentally in superfluids [32].

In superconductors, the Josephson effect occurs when two superconductors are separated by a thin insulator and the two superconductors have a difference in phase. This difference in phase results in an electrical current across the junction. These two superconducting materials act together despite being separated in space. This is possible for superconductors at reasonable experimental distances (thickness of the insulator separating the superconducting regions) because the correlation length for most superconducting materials is generally between 10-1500 nm [33]. These lengths are determined experimentally and can be many orders of magnitude larger than the superfluid correlation length of \( ^4 \text{He} \). Because of this, one has to take advantage of the growth in the correlation length near the critical temperature in order to see coupling between regions of superfluid helium for separations larger than the atomic scale.

In recent work [22], Perron et al. fabricated confinement cells from \( \text{SiO}_2 \) in which Josephson effects may be observed for weakly coupled arrays of ‘dots’ (boxes) of superfluid \( ^4 \text{He} \). The boxes are of size \( (2 \ \mu \text{m})^3 \), and the weak coupling is achieved via a 2-dimensional film connecting all of the boxes. A schematic of such a cell may be seen in Figure 2.7. The
2.5. **CONFINED HELIUM-4**

darkest spots are the boxes, the light spots are supports for the cell, and the film region is that which covers the boxes and their connecting regions, seen in darker gray. These type of cells have also been developed and tested that do not contain indented boxes [34], which are used to study the 3d-2d crossover. Measurements of certain thermodynamic quantities such as heat capacity [35] and superfluid fraction [36] can be obtained experimentally from samples in these cells.

Two separate experimental cells like the one in Figure 2.7 were created, one with the boxes spaced 2 µm apart and another with the boxes spaced 4 µm apart. Each cell was exactly the same otherwise in that they held the same thickness films. The superfluid fraction from these two cells with boxes and also from a completely planar cell (no boxes) may be see in Figure 2.8 on the left. The open circles correspond with the case of the film with no boxes, and the open/closed triangles are for the film plus the boxes separated by 2 µm and 4 µm respectively. The filled circles are thought to be a signal from the border regions of the cell where no boxes exist, so they are effectively signal from an isolated film region where no proximity effects exist. The line marked ‘Expected KT jump’ marks where the Kosterlitz-Thouless jump should occur. The Kosterlitz-Thouless transition marks the onset of superfluid stiffness in a 2d system [37,38], and as expected the superfluid transition occurs right at this point for the film regions not in contact with the boxes.
2.5. CONFINED HELIUM-4

There are two things that are particularly interesting about Figure 2.8. The first is that the cell with boxes that are of closer proximity (2 µm spacing) yields a superfluid fraction closer to that of 3d helium-4 than does the cell whose boxes are separated by twice the distance. Those separated by more distance have more 2d character. This means that the superfluid fraction of the entire sample inside of the cell is being enhanced, and it can only be assumed that this is through the coupling of the boxes through the film region. As the boxes move further apart, the coupling is decreased and hence the enhancement decreases.

This by itself is interesting, but what is more fascinating is that this coupling occurs at distances that are at least an order of magnitude larger than the correlation length $\xi(t)$. Using Equation (2.52), one sees that for $t = 10^{-4}$ (closer to the critical temperature than any data point shown in Figure 2.8) that the correlation length is about 170 Å. The well spacing is on the order of microns, and this correlation length is merely on the order of tens of nanometers! If one looks to Figure 2.8 and thinks about this fact, it is astonishing that the cell with 4 µm well spacing has so much more 2d character than the one with 2 µm well spacing, since both of these distances far exceed the correlation length anyway.

As mentioned, mean field approaches do not work which implies that critical fluctuations must be important here but these alone cannot explain why the boxes are coupled at
2.5. **CONFINED HELIUM-4**

distances larger than the correlation length. Next, we briefly introduce classical Monte Carlo simulations done by Fisher et al. [27] that probe coupling and enhanced proximity effects in a classical system of Ising spins.

### 2.5.3 CLASSICAL PROXIMITY EFFECTS

The 2d Ising model [39] consists of a square lattice where each lattice site hosts a single spin that may be oriented ‘up’ or ‘down’ ($\pm \sigma_i$). These spins only interact with nearest neighbors via a Hamiltonian $\mathcal{H} = \sum_j \sum_i J_{ij} \sigma_i \sigma_j$ where $J_{ij}$ is the coupling constant for spins on neighboring sites $i, j$. Michael Fisher and coworkers have taken this basic setup and partitioned the lattice into alternating regions of semi-infinite Ising strips [27], differing in their coupling constants $J_1$ and $J_2$ as well as their relative widths $m_1$ and $m_2$. They performed classical Monte Carlo simulations on these systems in order to probe the physics of coupling and proximity effects in classical systems. Their simulations were run such that $J_1 > J_2$ in all cases. Such a configuration can be seen in Figure 2.9. This is a great example of a classical system that exhibits coupling and proximity effects. It is somewhat similar to the 3d to low-d coupled regions in that the strips have inherently different transition temperatures $T_{1c}$ and $T_{2c}$, due to the different coupling constants. If we had just a uniform Ising lattice, there would be a critical temperature at which one would observe a logarithmic divergence in the specific heat. This critical temperature changes as the value of the coupling constant changes. The different transition temperatures of

![Figure 2.9: Alternating semi-infinite Ising Strips of coupling constants $J_1, J_2$ and widths $m_1, m_2$.](image-url)
2.5. **CONFINED HELIUM-4**

The different strips lead to two separate peaks in the specific heat, near \( T_{1c} \) and \( T_{2c} \). As these regions become more strongly coupled the lower temperature peak moves to a higher temperature and the higher temperature peak moves to a lower temperature. This can be attributed to coupling of the regions, just as in the experiments where the wells of helium were coupled via a 2d film.

Qualitatively, these simulations mimic the proximity effects seen in the specific heat experimental data [26]. They do not, however, address the modified superfluid fraction observed nor do they explain why coupling occurs over distances so much larger than the correlation length. It was shown that varying the weakness ratio \( r = J_2/J_1 \) and the lattice spacing ratio \( s = m_2/m_1 \) had substantial effects on the properties of the system. The values of \( r \) and \( s \) that gave the best agreement between the simulations and the experiments were determined, and while the \( s \) values (lattice spacing ratio) were comparable to the relative spacing in the experiments, the strength ratios \( r \) were limited to \( r < 0.9 \) where they should have been closer to unity in order to properly reflect the real system.

In Figure 2.10, one can see that the closer that \( r \) gets to one, the less the system displays the two peaks that are a signature of a coupled system. To this point, these simulations do

![Figure 2.10: Classical simulation results from coupled Ising strips. Figure taken from [27].](image)
2.5. CONFINE HELIUM-4

not fully reflect the experiments so there is much more work to be done to understand the coupling and proximity effects.

The intention of the next two chapters is to provide the background needed to understand how path integral quantum Monte Carlo, a stochastically exact numerical method, can provide insight to these proximity effects that is not possible with any other method.
Chapter 3

PIMC Background

3.1 Path Integrals

3.1.1 Classical Action

The trajectory of a classical particle in motion may be determined by whichever of its possible paths minimizes a certain quantity, $S$, which we call the action,

$$ S[x(t)] = \int_{t_1}^{t_2} dt \ L(x(t), \dot{x}(t); t). \tag{3.1} $$

Here, $L$ is the Lagrangian for a physical system:

$$ L = T(\vec{x}, t) - V(\vec{x}, t), $$

where $T$ is the kinetic energy and $V$ is the potential energy of the entire system. We employ the calculus of variations to determine the functional form of the path which minimizes the action. The basic problem of the calculus of variations, in terms of the action integral, is to determine some $x(t)$ such that the action is an extremum. The idea is to vary $\dot{x}(t)$ until an extremum is found for the quantity $S$. So, let’s represent all possible functions, $x$,
3.1. PATH INTEGRALS

parametrically as

\[ x = x(\alpha, t) = y(0, t) + \alpha \eta(t), \]  

(3.2)

where \( \alpha \) is some variational parameter and \( \eta(t) \) has a continuous first derivative and vanishes at \( t_1 \) as well as \( t_2 \). Now, since \( x(\alpha, t) = x(t) \) at the endpoints of the path, we may see that \( \eta(t_1) = \eta(t_2) = 0 \). This leads us to

\[ S[\alpha] = \int_{t_1}^{t_2} dt \mathcal{L}(x(\alpha, t), \dot{x}(\alpha, t); t). \]  

(3.3)

A necessary, but insufficient, condition for an extremum to result for the action is

\[ \left. \frac{\delta S}{\delta \alpha} \right|_{\alpha=0} = 0 \quad \forall \ \eta(t). \]  

(3.4)

Substituting the right hand side of Equation (3.3) into Equation (3.4), then using the chain rule yields

\[ \frac{\delta S}{\delta \alpha} = \int_{t_1}^{t_2} \left( \frac{\partial \mathcal{L}}{\partial x} \frac{\partial x}{\partial \alpha} + \frac{\partial \mathcal{L}}{\partial \dot{x}} \frac{\partial \dot{x}}{\partial \alpha} \right) dt. \]  

(3.5)

Then, we use Equation (3.2) to see that \( \partial_\alpha x = \eta(t) \) and \( \partial_\alpha \dot{x} = \partial_\alpha \eta \). Appropriate substitution of these expressions into Equation (3.5), followed by integration by parts of the second term will yield results that appear as

\[ \frac{\partial S}{\partial \alpha} = \int_{t_1}^{t_2} dt \left( \frac{\partial \mathcal{L}}{\partial \dot{x}} \eta(t) + \frac{\partial \mathcal{L}}{\partial \dot{x}} \frac{\partial \eta(t)}{\partial \alpha} \right) \]

\[ = \int_{t_1}^{t_2} dt \frac{\partial \mathcal{L}}{\partial x} \eta(t) + \int_{t_1}^{t_2} dt \frac{\partial \mathcal{L}}{\partial \dot{x}} \frac{\partial \eta(t)}{\partial \alpha} \]

\[ = \int_{t_1}^{t_2} dt \frac{\partial \mathcal{L}}{\partial x} \eta(t) + \left. \frac{\partial \mathcal{L}}{\partial \dot{x}} \eta(t) \right|_{t_1}^{t_2} - \int_{t_1}^{t_2} dt \left( \frac{\partial \mathcal{L}}{\partial \dot{x}} \frac{\partial \eta(t)}{\partial \alpha} \right) \]

\[ = \int_{t_1}^{t_2} dt \left( \frac{\partial \mathcal{L}}{\partial x} - \frac{\partial \mathcal{L}}{\partial \dot{x}} \frac{\partial \eta(t)}{\partial \alpha} \right). \]  

(3.6)
3.1. PATH INTEGRALS

The integrand of Equation (3.6) is what supplies us with the Euler-Lagrange equation, since it must equal zero whenever our variational parameter \( \alpha \) goes to zero:

\[
\frac{\partial L}{\partial x_i} - \frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{x}_i} = 0.
\] (3.7)

Not only is the minimum value of \( S \) important in classical mechanics, but the functional form of the action integral is also of great interest. This statement applies in quantum mechanics as well. In classical mechanics, it is sufficient to consider only the one path which minimizes the action when determining the space time trajectory of a particle. This is not the case in quantum mechanics.

3.1.2 ENTERING THE QUANTUM REGIME

It is of utmost importance that the laws of physics in different regimes be consistent when one regime meets another. There is no case where this is more true than when considering the transition from treating a system classically versus having to treat it with the laws of quantum mechanics. Consider the set of space-time trajectories in Figure 3.1. Assume that the path labelled \( \bar{x}(t) \) (red, dotted line) is that which corresponds with the minimum action. In a classical system, the value of the action, \( S \) will be much greater than the value of \( \hbar \). We can assign some phase to each path, call it \( S/\hbar \), and in the classical case this phase corresponds with some large

*Figure 3.1: Space-time diagram of possible paths*
3.1. PATH INTEGRALS

angle. It will be apparent just what this phase is in the next section. If we perturb this path by some arbitrarily small distance \( \delta x(t) \), then the phase corresponding to this path will likely change by a large amount in the classical regime. This new phase is as likely to be positive as negative, so if we consider many possible paths, then each will be cancelled by the others except for the one which is labelled \( \bar{x}(t) \). This is what we expect classically, but the quantum case is different. For a system which must be considered quantum mechanically, the action, \( S \), may be on the same order of magnitude as \( \hbar \). This means that a small perturbation may only change the phase slightly, meaning that many paths must be considered as a likely path for the particle to traverse.

3.1.3 Summing Over All Paths

Let us consider non-relativistic quantum mechanics. The probability of a particle to go from \( x_a \) to \( x_b \) at times \( t_a \) to \( t_b \) is given by

\[
P(b, a) = |K(b, a)|^2, \tag{3.8}
\]

where the amplitude (often called the kernel), \( K \), is given as

\[
|K(b, a)| = \sum_{\text{all paths}} \phi[x(t)].
\]

These paths may be given by something like those that appear in Figure 3.1. This function, \( \phi \) looks like

\[
\phi[x(t)] = Ae^{iS[x(t)]/\hbar}. \tag{3.9}
\]

Here, \( A \) is some normalization constant to be discussed shortly, and \( S \) is the classical action, as defined by Equation (3.1). Now, let’s slice the function \( \phi \) up into many time intervals.
3.1. **PATH INTEGRALS**

such that each slice has a width $\tau$. Then we may write out the amplitude, $K$, as

$$K(b, a) = \lim_{\tau \to 0} \int \ldots \int e^{iS[b,a] / \hbar} \frac{dx_1}{A} \ldots \frac{dx_{M-1}}{A}. \quad (3.10)$$

Notice that this is the sum over all possible paths, but we have let the sum go to an integral, where $M$ is the number of slices, each having a width $\tau$. This means that we may write $\tau = |x_{i+1} - x_i|$. For the sake of the elegance of our equations and simplicity, we will write this kernel using the product of all differentials, $Dx(t)$. There exist situations where Equation (3.10) isn’t adequate and the integration must be redefined. For a more complete discussion, see Feynman’s original text [40]. However, redefining an integration method (or in this case, the sum over all paths), should not completely discredit the concept of integration itself, so it seems logical to get rid of the normalization and write Equation (3.10) in a less restrictive form:

$$K(b, a) = \int Dx(t)e^{iS[b,a] / \hbar}. \quad (3.11)$$

It is very important to note that this only samples a subset of the paths unless the time step goes to zero, so for finite $\tau$, a more accurate value of the integral is obtained by making $\tau$ smaller, but no limit may ever be reached because no limit actually exists. This is what gives rise to the need for the normalization constant $A$ that depends upon $\tau$ itself. This normalization factor will be different depending on the Lagrangian. The action integral, $S$, may be approximated in a number of increasingly accurate ways, as will be discussed in a later chapter.

### 3.1.4 Successive Events

Let us imagine a sequence of successive quantum mechanical events, $a$, $c$, $b$, such that $c$ occurs in time between $a$ and $b$. Then due to the fact that the Lagrangian doesn’t depend on derivatives higher than the velocity, the action for this sequence of events may be stated...
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as

\[ S[b,a] = S[b,c] + S[c,a]. \] (3.12)

This allows us to write out the kernel as

\[ K(b,a) = \int Dx(t)e^{i(S[b,c]+S[c,a])/\hbar}. \] (3.13)

Now, we want to integrate over all paths from \( a \) to \( c \) then over all paths from \( c \) to \( b \), then integrate the result of those integrations over all possible values of the spatial point corresponding to the event \( c \), call it \( x_c \). Note that \( x_c \) could be placed anywhere, since we are the ones choosing how to divide our paths, so it’s range is from \(-\infty \) to \( \infty \). Thus

\[ K(b,a) = \int_{-\infty}^{\infty} dx_c \int_{x_2}^{x_1} \int_{x_1}^{x_2} K(b,M-1)K(M-1,M-2)\cdots K(1,a)dx_1dx_2\cdots dx_{M-1}. \] (3.15)

This leads to the idea of the multiplicative property for the amplitudes of successively occurring events. Note that this may be generalized to an arbitrary number of events. Let us divide our time scale into \( M \) intervals. Then

\[ K(b,a) = \int_{-\infty}^{\infty} dx_c \int_{a}^{c} \int_{c}^{b} Dx(t)e^{i(S[b,c]/\hbar, iS[c,a])/\hbar} \]

\[ = \int_{-\infty}^{\infty} dx_c \int_{c}^{b} Dx(t)e^{i(S[b,c]/\hbar}K(c,a) \]

\[ = \int_{-\infty}^{\infty} dx_c K(b,c)K(c,a). \] (3.14)

According to the definition stated above, if we examine just one of the kernels in the integrand, let’s say, the one going from the \( j^{th} \) to the \((j+1)^{th} \) slice, separated by an infinitesimal time \( \tau \), it will look like (to first order in \( \tau \)):

\[ K(j+1,j) = \frac{1}{A} \exp \left( i \frac{\tau}{\hbar} \mathcal{L} \left( \frac{x_{j+1} - x_j}{\tau}, \frac{x_{j+1} + x_j}{2}, \frac{t_{j+1} + t_j}{2} \right) \right). \] (3.16)
This is an important result, as it will be employed in converting this path integral formalism into one in which differential equations are examined.

3.1.5 Reclaiming the Schrödinger Equation

It can be rather convenient to reduce the path integrals describing a quantum system down to differential equations. This is not always possible, but is desirable because most of the time it is easier to solve the relevant differential equation than it is to solve the integral equation. Consider a path integral with action given by Equation (3.12). If we let each time occur sequentially with an arbitrarily small time step in between, then we can often obtain a well behaved differential equation from the related path integral.

Examining Equation (3.8), it is noticed that the kernel has the same utility as a wave function. Let’s call this wave function $\psi(\vec{x}, t)$. So, we may say that the kernel $K(b, a)$ is equal to the wave function, $\psi(b)$. Written more carefully, this is $K(x_b, t_b; x_a, t_a) = \psi(x_b, t_b)$. It may be noticed that the kernel actually contains information about the evolution of the system from $a$ to $b$, whereas the wave function only tells us something about the system at time $t_b$. However, in situations where nothing is gained through knowledge of the evolution of the system before the time of measurement, then it is beneficial to view this as a wave function rather than a kernel. So, if we want to express the wave function at a time $t_b$ in terms of the wave function at some previous time $t_a$, then we may make a substitution into Equation (3.14) to obtain

$$\psi(x_b, t_b) = \int_{-\infty}^{\infty} dx_a K(b, c) \psi(x_a, t_a).$$  \hspace{1cm} (3.17)

As a side note, this actually has a profound physical interpretation. If we disregard all knowledge about some particle except for its wave function at some particular time, then everything about that particle may be calculated at any future time.

If the same conditions leading up to Equation (3.16) are imposed, then combining Equa-
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Equation (3.16) with (3.17) allows the wave function to be written as

\[
\psi(x,t + \tau) = \frac{1}{A} \int_{-\infty}^{\infty} dz \exp \left( \frac{i}{\hbar} \tau \mathcal{L} \left( \frac{x - z}{\tau}, \frac{x + z}{2} \right) \right) \psi(z,t). \tag{3.18}
\]

This \( z \) state is one that occurs at a time infinitesimally close (\( \tau \), to be precise) to the state \( x \). Let us consider, as a case study, a particle moving in one dimension that feels a time dependent potential \( V(x,t) \) such that the corresponding Lagrangian looks like

\[
\mathcal{L} = \frac{m}{2} \dot{x}^2 - V(x,t). \tag{3.19}
\]

Then its wave function will look like

\[
\psi(x,t + \tau) = \frac{1}{A} \int_{-\infty}^{\infty} dz \exp \left( \frac{i}{\hbar} \tau \frac{m(x - z)^2}{2\tau} \right) \exp \left( - \frac{i}{\hbar} \tau V \left( \frac{x + z}{2}, t \right) \right) \psi(z,t) \\
= \frac{1}{A} \int_{-\infty}^{\infty} dz \exp \left( \frac{im\xi^2}{2\tau\hbar} \right) \exp \left( - \frac{i}{\hbar} \tau V \left( x + \frac{\xi}{2}, t \right) \right) \psi(x + \xi,t). \tag{3.20}
\]

Here, the substitution \( \xi = z - x \) was made. The exponential functions in the integrand above are oscillatory, so for large arguments, they will oscillate rapidly as \( z \) varies, and as such, the value of the integral over \( z \) will be quite small. However, if \( \xi \) is very small, then the first exponential function will not oscillate as rapidly, so we expect that only smaller values of \( \xi \) will contribute. We know that only the paths which are close in phase to the classical path will contribute, so this means that those which oscillate wildly will be cancelled by others which also oscillate wildly. Next, the wave function \( \psi \) is expanded in a power series, where only the first order terms of \( \tau \) are kept. In looking at the potential term, the one present, \( \tau V(x + \tau/2, t) \) may be replaced by \( \tau V(x, t) \) since the error associated with the former term is of higher order than \( \tau \). An expansion of the left-hand side to first order in
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\( \tau \) leads to

\[
\psi(x, t+\tau) + \tau \partial_t \psi = \frac{1}{A} \int_{-\infty}^{\infty} d\xi e^{im\xi^2/2\hbar\tau} \left( 1 - \frac{i}{\hbar} \tau V(x, t) \right) \left( \psi(x, t) + \xi \partial_x \psi + \frac{\xi^2}{2} \partial_x^2 \psi \right). \tag{3.21}
\]

It is important to note (for clarity) that an expansion to order \( \tau \) is equivalent to an expansion to order \( \xi^2 \). Taking the highest order term on either side of the above expression, the expression becomes

\[
\psi(x, t) = \frac{1}{A} \int_{-\infty}^{\infty} d\xi \exp \left( \frac{im\xi}{2\hbar\tau} \right) \psi(x, t), \tag{3.22}
\]

which implies

\[
1 = \frac{1}{A} \int_{-\infty}^{\infty} d\xi \exp \left( \frac{im\xi}{2\hbar\tau} \right) = \frac{1}{A} \sqrt{\frac{2\pi i\hbar\tau}{m}}, \tag{3.23}
\]

giving us back an expression for the normalization constant, \( A \). This looks like

\[
A = \sqrt{\frac{2\pi i\hbar\tau}{m}}. \tag{3.24}
\]

This normalization constant could have been obtained in a slightly simpler fashion for our test case, but this method gives a more general way to determine how to normalize problems that could potentially be more complicated. We require for these types of problems that \( A \) be chosen in such a way that the kernel (or wave function) is correct to zeroeth order in \( \tau \). If not for this, then no limit will exist as the time step \( \tau \) goes to zero.

With this solution, we may now evaluate the right hand side of Equation (3.21). Integrating both the first and second order terms in \( \xi \) (we already evaluated the zeroeth order) yields

\[
\psi + \tau \partial_t \psi = \psi - \frac{i}{\hbar} \tau V(x, t) \psi + \frac{i\hbar\tau}{2m} \partial_x^2 \psi,
\]

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which may be simplified to give us back the time dependent Schrödinger equation:

\[ i \hbar \partial_t \psi = V(x,t)\psi - \frac{\hbar^2}{2m} \partial_x^2 \psi = \mathcal{H}\psi. \]  

(3.25)

This is the differential equation we would expect a single particle in one-dimension experiencing a potential \( V(x,t) \) to obey. This is good news, because we have started with a completely different formulation of quantum theory and reclaimed the one we all know and love. Beginning with Equation (3.25), we may often assume a separable solution of the form

\[ \psi(x,t) = f(t)\phi(x). \]  

(3.26)

Substitution into Equation (3.25) yields an equation that appears as

\[ i\hbar \frac{f'(t)}{f(t)} = \mathcal{H}\phi(x) = E, \]  

(3.27)

where \( E \) is the separation constant to be used in the separation of variables technique. This leads to two different equations, one for space and one for time. These may be solved simultaneously to yield an expression for the wave function:

\[ \psi(x,t) = \phi(x)e^{-iEt/\hbar}. \]  

(3.28)

Here, \( \phi \) satisfies the time independent Schrödinger equation. Any eigenfunction \( \psi \) that takes this form will oscillate in space with some definite frequency, which corresponds to it’s energy classically. It may also be said that this function will decay in \( \tau = it \) imaginary time. This concept will become quite important for our path integral formalism.
3.1. PATH INTEGRALS

3.1.6 Steady State Wave Functions

Let us consider some quantum system with a set of energy levels \( E_j \). Assume that we know the wave functions which correspond to these energy levels, and that these functions are part of an orthonormal basis set such that

\[
\int_{-\infty}^{\infty} dx \, \phi_j^*(x) \phi_k(x) = \delta_{j,k}. \tag{3.29}
\]

There exist many sets of functions that may be expressed as linear combinations of such functions. Such basis sets are the Fourier series, the spherical harmonics, Bessel functions, etc... The choice of these depends upon such things as symmetry and simplicity of working in one coordinate system versus another, but for the sake of generality these issues are not currently discussed. The general form we seek here is

\[
f(x) = \sum_{j=1}^{\infty} a_j \phi_j(x). \tag{3.30}
\]

These coefficients \( a_j \) tell us something about how much each individual \( \phi_j \) goes into constructing the function \( f(x) \) and may be obtained by multiplying each side of Equation (3.30) by \( \phi_k^*(x) \) and integrating over all space to yield

\[
a_j = \int_{-\infty}^{\infty} dx \, \phi_j^*(x) f(x). \tag{3.31}
\]

Plugging this result back into Equation (3.30) gives us a new identity:

\[
f(x) = \sum_{j=1}^{\infty} \phi_j(x) \int_{-\infty}^{\infty} dx' \, \phi_j^*(x') f(x') = \int_{-\infty}^{\infty} dx' \left( \sum_{j=1}^{\infty} \phi_j(x) \phi_j^*(x') \right) f(x'). \tag{3.32}
\]
3.1. PATH INTEGRALS

Now, the only way for \( f(x) = f(x') \) to be true is if the bracketed expression in Equation (3.32) is equal to the Dirac delta function. We may actually write an expression for the kernel \( K(b, a) \) in terms of an orthonormal basis set of eigenfunctions \( \phi_j(x) \) and corresponding eigenenergies \( E_j \). Using Equation (3.28) and Equation (3.30), we can write a time dependent wave function at an arbitrary time \( t_a \) as

\[
\psi(x, t_a) = \sum_{j=1}^{\infty} c_j e^{-iE_j t_a / \hbar} \phi_j(x). \tag{3.33}
\]

But, using the idea that any well behaved function may be expressed as a linear combination of an orthonormal basis set, as in Equation (3.30), we notice

\[
\psi(x, t) = \sum_{j=1}^{\infty} a_j \phi_j(x), \tag{3.34}
\]

which leads to the conclusion that \( c_j = a_j e^{iE_j t_a / \hbar} \). If an equation is constructed of the same form as Equation (3.33), but for another time \( t_b \neq t_a \), then one may see

\[
\begin{align*}
\psi(x, t_b) &= \sum_{j=1}^{\infty} c_j e^{-iE_j t_b / \hbar} \phi_j(x) = \sum_{j=1}^{\infty} a_j e^{-iE_j (t_b - t_a) / \hbar} \phi_j(x) \\
&= \sum_{j=1}^{\infty} \left( \int_{-\infty}^{\infty} dx' \phi_j^*(x') f(x') \right) e^{-iE_j (t_b - t_a) / \hbar} \phi_j(x) \\
&= \int_{-\infty}^{\infty} \sum_{j=1}^{\infty} \phi_j^*(x') \phi_j(x) e^{-iE_j (t_b - t_a) / \hbar} f(x') dx'. \tag{3.35}
\end{align*}
\]

Looking back at Equation (3.17), we see that an expression for the kernel may be had in terms of a linear combination of orthonormal functions:

\[
K(x_b, t_b; x_a, t_a) = \theta(t_b - t_a) \sum_{j=1}^{\infty} \phi_j^*(x') \phi_j(x) e^{-iE_j (t_b - t_a) / \hbar}, \tag{3.36}
\]
3.2. STATISTICAL MECHANICS

where $\theta(t_b - t_a)$ is the Heaviside step function, which means that our kernel is zero up until when $t_b > t_a$. This result is really quite remarkable, because the kernel, which was once expressed in terms of an integral, is now expressed in terms of the solution to a wave equation. The idea of a steady state wave function will become important when talking about quantum systems in equilibrium, because these systems will be described by such a wave function. There is quite a leap to be made if one wants to study many body systems, as this will require using a different framework than what has been developed so far. This framework is statistical mechanics, and it can be related beautifully to what has been discussed in this first section.

3.2 STATISTICAL MECHANICS

3.2.1 PARTITION FUNCTION AND DENSITY MATRIX

In most physical systems of interest, the initial state of the system is not known, but rather the probability of the system being in various states is known. We may be interested in the probability of the system transitioning from one state to any number of other degenerate or non-degenerate states rather than just being concerned with the transition to one single state. This now enters into the realm of statistical mechanics. Quantum statistical mechanics shows that for a quantum system in thermal equilibrium at some definite temperature $T$, the probability of the system being in a state with total energy $E$ is directly proportional to $e^{-E/k_B T}$. This decaying exponential function is known as a Boltzmann factor, where $k_B$ is the Boltzmann constant which has a value of $1 \, eV$ per $11605 \, K$. This knowledge is not yet useful to us because it cannot be used as a probability distribution without normalizing it. Let us then write out our normalization factor as $1/Z$, and define the term $1/k_B T$ as $\beta$. 

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3.2. STATISTICAL MECHANICS

This means that we may state the probability of finding our system with energy \( E_j \) as

\[
p_j = \frac{1}{Z} e^{-\beta E_j}.
\]  
(3.37)

The value of \( Z \) that normalizes our probability distribution is given as

\[
Z = \sum_j e^{-\beta E_j}.
\]  
(3.38)

Suppose that \( O \) is the value of some physical observable for a system in thermal equilibrium and that it’s mean value in the \( j^{th} \) state is

\[
O_j = \int d\Gamma \phi_j^* O \phi_j,
\]  
(3.39)

where this integral is taken over the entire configuration space, \( \Gamma \). Then the statistical average for the observable will be given by

\[
\langle O \rangle = \frac{1}{Z} \sum_j O_j e^{-\beta E_j}.
\]  
(3.40)

It may be quite easily shown that knowledge of a systems partition function allows the calculation of many thermodynamic properties, by simply differentiating \( Z \). However, some physical properties of the system will actually require more knowledge than just the partition function. Suppose that we have a quantum system in some configuration basis, and we want to know the probability of finding the system in the coordinate \( x \). The probability of finding this quantum system in \( x \) is given by

\[
p(x) = \frac{1}{Z} \sum_j \phi_j^*(x) O \phi_j(x) e^{-\beta E_j}.
\]  
(3.41)
3.2. **STATISTICAL MECHANICS**

If we need to calculate some observable $O$ of a quantum system in thermal equilibrium, we may calculate the expectation value as

$$
\langle O \rangle = \frac{1}{Z} \sum_j \int dx \phi_j^*(x) \hat{O} \phi_j(x) \ e^{-\beta E_j}
$$

$$
= \frac{1}{Z} \int dx \ \hat{O}' \sum_j \phi_j(x') \phi_j^*(x) \ e^{-\beta E_j}
$$

$$
= \frac{1}{Z} \int dx \ \hat{O}' \rho(x', x). \quad (3.42)
$$

Since the operator $\hat{O}$ acts only to the right, it doesn’t act on the complex conjugated $\phi^*$ in the top line of Equation (3.42). So, we may imagine that the operator $O$ only acts on functions of $x'$ (hence the $\hat{O}'$ in the second line of Equation (3.42)) and after it operates then we switch all $x'$ back to $x$ since these are dummy variables anyway. This procedure is simply that of finding the trace of $O \rho$. This mathematical entity which we have called $\rho$ is known as the statistical density matrix and has the general form:

$$
\rho(x', x) = \sum_j \phi_j(x') \phi_j^*(x) \ e^{-\beta E_j}. \quad (3.43)
$$

The relationship between the partition function and thermal density matrix may be seen in Appendix B. It should be obvious that the expectation values of any physical observable we want to know for the system would be within reach if the density matrix is known. Relating Equation (3.42) to Equation (3.41), we obtain an expression for finding our quantum system in some state characterized by the coordinate $x$ in terms of the density matrix:

$$
p(x) = \frac{1}{Z} \rho(x, x). \quad (3.44)
$$

Taking into account that we want our probability distribution $p(x)$ to be normalized to unity such that the integral over all of the configuration space is equal to one, we come up
with a nice expression for the partition function:

\[ Z = \int dx \, \rho(x, x) = \text{Tr}\{\rho(x, x)\}. \] (3.45)

This expression for the partition function along with the density matrix will prove to be extremely useful in solving problems in statistical mechanics. This can actually be related to the path integral formulation from the previous section.

### 3.2.2 Path Integrals in Statistical Mechanics

If we examine Equation (3.36) at a time \( t_b > t_a \), we notice that it looks a great deal like Equation (3.43). The difference lies in the argument of the exponential function. These can be shown to be formally identical in the following way. Start by defining a new variable, the imaginary time \( \tau \equiv it \). This turns the form of the kernel to

\[ K(x_b, \tau_b; x_a, \tau_a) = \theta(\tau_b - \tau_a) \sum_{j=1}^{\infty} \phi_j^*(x') \phi_j(x) e^{-E_j(\tau_b - \tau_a)/\hbar}. \] (3.46)

From now on, we shall drop the Heaviside function, because it is assumed that we are going forward in time and are measuring at a time \( t_b > t_a \). It is also assumed that the system is in equilibrium, hence the Hamiltonian, \( \mathcal{H} = T + V \) is not changing with time, where \( T \) is the full kinetic energy of the system and \( V \) is the potential energy of the system including both interaction potentials and external potentials. Also, since we have the freedom to set the starting imaginary time \( \tau_a \) to whatever we want, we set it to zero for convenience. Our kernel takes the form:

\[ G(x_b, \tau_b; x_a, \tau_a) = \sum_j \phi_j^*(x') \phi_j(x) e^{-E_j(\tau_b)/\hbar}. \] (3.47)
Note that the notation change for our kernel from $K \rightarrow G$ is in light of the fact that it can be shown that this is a Green function for the imaginary time dependent Schrödinger equation. Differentiating $G$ with respect to $\tau$ yields:

$$\frac{\partial G(b,a)}{\partial \tau_b} = -\frac{1}{\hbar} \sum_j E_j \phi_j^*(x') \phi_j(x) e^{-E_j(\tau_b)/\hbar} = -\frac{1}{\hbar} \mathcal{H}_b G(b,a).$$

This last step has used the fact that $\phi_j$ is a solution to the time independent Schrödinger equation, i.e. $\mathcal{H} \phi_j(x_b) = E_j \phi_j(x_b)$. As such, a Hamiltonian has been written that operates only on functions that exist at time $t_b$ as $\mathcal{H}_b$. However, it can be noted that if we allow $\tau_b = \hbar \beta$ in Equation (3.47), then it will look exactly like our density matrix. Hence, we can divide each side of the previous equation by $\hbar$ to obtain

$$\frac{\partial \rho(b,a)}{\partial \beta} = -\mathcal{H}_b \rho(b,a).$$

This is an important result, because for systems with simple Hamiltonians that involve only position and momentum coordinates, we can express the kernel as a path integral. We build up a product of many kernels, sum over paths, and let the imaginary time step go to zero. This is the important connection between path integrals and statistical mechanics that is necessary to express the formalism of path integral Monte Carlo.

The sums and integrals that give us expectation values for physical observables here are often huge and one should not expect to evaluate them without the help of special tools. The next chapter will discuss quantum Monte Carlo methods, which are just the tools we need to evaluate observables stochastically.
4.1 Monte Carlo

Monte Carlo algorithms are used to numerically evaluate integrals of high dimensionality without the error that is involved with other numerical techniques. Chapter 3 presented a framework for computing physical observables for quantum systems given knowledge of the partition function. However, determining values for these observables requires computing integrals of high dimensionality, so we desire a method which reduces the error involved in numerically solving these integrals. When faced with this problem, one may look to Quantum Monte Carlo (QMC), a class of computer algorithms designed to stochastically evaluate observables for quantum systems.

4.1.1 Why QMC?

For every accessible microstate, $\mu$ of a physical system, there may be assigned a weight, $w_\mu$, where there is a normalisation condition defined such that $\sum_\mu w_\mu = 1$. This is a very general statement, but is exactly related to what was mentioned in the beginning of the previous statistical mechanics section, in particular Equation (3.37). These weights correspond to the relative probability of finding the system in that microstate. With this in mind, we may
4.1. **MONTE CARLO**

find the expectation value of any observable for the system can be calculated as:

\[
\langle \hat{O} \rangle = \sum_{\mu} O_\mu w_\mu.
\]

Statistical mechanics tells us that the number of microstates pertaining to any real physical systems can be enormous, so it is not practical to believe that we should be able to evaluate these sums exactly. We need a more efficient way to calculate observables from the system. Enter Monte Carlo. Monte Carlo simulations are capable of stochastically sampling the random fluctuations of a many-body physical system without the unwanted error scaling of most other numerical integration techniques. The errors associated with Monte Carlo integration are completely independent of the dimensionality of the integral being taken. This is just what is needed, since the integrals encountered in statistical mechanics are often of very high dimensionality. Fundamental to the development of any MC method is the concept of importance sampling, which exists to improve the efficiency of the algorithm. The Metropolis algorithm is such a method, and it allows for sampling of an arbitrary probability distribution of any complexity or dimensionality. If we may assume that each time a measurement is taken for the value of a physical observable, \(O\), that the measurement is statistically independent of the previous measurement, then the error is

\[
\sigma = \sqrt{\frac{\langle O^2 \rangle - \langle O \rangle^2}{n - 1}},
\]  

(4.1)

where \(n\) is taken to be the number of measurements. This is a gross approximation for most cases, and more advanced methods of error analysis must be adopted. Such methods include data binning (only keeping a data point after so many MC iterations) and calculating a autocorrelation function.
4.1. MONTE CARLO

4.1.2 IMPORTANCE SAMPLING

Consider a probability distribution, \( p(x) \) of the evolution of some Markov transition matrix \( \Pi(x|y) \) which satisfies \( p(x) \). This probability distribution is comprised of all of the possible microstates of the system, just as in Equation (3.41). The Metropolis-Hastings algorithm [41] samples this distribution by making use of the detailed balance condition:

\[
\Pi(x|y)p(y) = \Pi(y|x)p(x). \tag{4.2}
\]

Detailed balance is basically a statement saying that it is equally likely for the system to transition from one state \( x \to y \) as to go from the state \( y \to x \). It is convenient to decompose these stochastic transition probabilities as

\[
\Pi(x|y) = T(x|y)A(x|y), \tag{4.3}
\]

where \( T(x|y) \) is a stochastic process able to be sampled and \( A(x|y) \) gives the probability of acceptance of a move from microstate \( y \) to \( x \) according to \( T(x|y) \). We are free to choose these probabilities however we want, but certain choices result in efficiency gains. In the Metropolis algorithm, we fix \( A \) according to

\[
A(x|y) = \min\left(1, \frac{T(y|x)p(x)}{T(x|y)p(y)}\right). \tag{4.4}
\]

This comes from inserting Equation (4.3) for \( x \to y \) and for \( y \to x \) into Equation (4.2), setting \( A(y|x) = 1 \), and solving the resulting expression for \( A(x|y) \). We take the minimum of the resulting value and 1 because if the value exceeds 1 then we cannot interpret it as a probability.

This type of sampling in these simulations generally seeks to extremize the classical action of the system, but also allows for the system to move to higher energy states with
some probability. This is in order to allow for the system to climb out of relative minima in energy and seek a global minimum for the supplied thermodynamic parameters. Before proceeding, it is pertinent that the action be discussed.

4.2 THE ACTION

4.2.1 Trotter Formula

There exist quite a few methods for solving the Schrödinger equation numerically which are of mean-field type and do not take into account correlation effects. Most of the time, however, these correlations are what gives rise to the most interesting, exotic behavior. In general, we want to simulate  \( N \) quantum mechanical particles in the continuum, which means the full Hamiltonian for this problem may be expressed as

\[
\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i \hat{V}_{\text{ext}}(\vec{r}_i) + \sum_{i<j} \hat{V}_{\text{int}}(\vec{r}_i - \vec{r}_j).
\]

(4.5)

For a given system of particles, we may use the notation of first quantization to express the state of the system as

\[
|\vec{r}_1, \vec{r}_2, ..., \vec{r}_N\rangle = |R\rangle,
\]

(4.6)

where the required normalization condition is

\[
\int dR |R\rangle \langle R| = 1.
\]

(4.7)

As discussed in the previous chapter, knowledge of the partition function for this quantum system will give us the weights of each state and hence many observables may be known.
4.2. THE ACTION

Here, we restate Equation (3.45) in a slightly different way:

\[ Z = \int d\vec{r}_1 \ldots \int d\vec{r}_N \langle R | e^{-\beta \hat{H}} | R \rangle = \int dR \langle R | e^{-\beta \hat{H}} | R \rangle. \]  

(4.8)

If we examine our Hamiltonian operator, we know that the kinetic and potential pieces do not commute with one another, \([\hat{T}, \hat{V}] \neq 0\), which means that the exponential piece being sandwiched between the bra and ket vectors in Equation (4.8) may not be decomposed as would be the case if the two operators did commute;

\[ e^{-\beta \hat{R}} \neq e^{-\beta \hat{T}} e^{-\beta \hat{V}}. \]  

(4.9)

However, an important insight that is accredited to Feynman is that the full Hamiltonian does commute with itself, hence our density matrix may be broken up as

\[ \hat{\rho} = e^{-\beta \hat{R}} = e^{-(\beta/2+\beta/2) \hat{H}} = e^{-(\beta/2) \hat{H}} e^{-(\beta/2) \hat{H}}. \]  

(4.10)

Substitution of the above results into Equation (4.8) will yield a new expression for our density matrix:

\[
\rho(R, R; \beta) = \langle R | e^{-\beta \hat{R}} | R \rangle \\
= \langle R | e^{-(\beta/2) \hat{H}} e^{-(\beta/2) \hat{H}} | R \rangle \\
= \int dR' \langle R | e^{-(\beta/2) \hat{H}} | R' \rangle \langle R' | e^{-(\beta/2) \hat{H}} | R \rangle \\
= \int dR' \rho(R, R'; \beta/2) \rho(R', R; \beta/2).
\]  

(4.11)
4.2. THE ACTION

This means we now have two density matrices, and each is at a higher effective temperature since $\beta$ is inversely proportional to temperature. This is fantastic, since

$$e^{-\beta \hat{H}} \xrightarrow{T \to \infty} e^{-\beta T} e^{-\beta \hat{V}}.$$ \hfill (4.12)

So, if we split up this exponential a large number of times, then it turns out that it becomes a better and better approximation to say that the potential and kinetic energy operators commute with one another. This means that the partition function may be written as:

$$Z = \int dR_0 \cdots \int dR_{M-1} \langle R_0 | e^{-\beta/M \hat{H}} | R_1 \rangle \langle R_1 | e^{-\beta/M \hat{H}} | R_2 \rangle \cdots \langle R_{M-1} | e^{-\beta/M \hat{H}} | R_0 \rangle.$$ \hfill (4.13)

Notice that the density matrix has been broken up $M$ times, where $M \in \mathbb{Z}^+$. This is exactly what was done in the first chapter when the kernel was divided up into many different slices, each of duration $\tau$. We define this value as

$$\tau \equiv \frac{\beta}{M}.$$ \hfill (4.14)

As a side note, if this is to be done for a zero temperature system, one requires $M$ be an odd integer in order to make sure that there is always an odd number of slices. So, more often than not, in the literature on finite temperature path integral Monte Carlo (PIMC), $M$ is used as the total number of imaginary time slices. This is not seen to be the case in the zero temperature literature, where $2M + 1$ is generally the number of time slices.

4.2.2 POLYMER ISOMORPHISM

We have defined this exponential function that involves the Hamiltonian operator and shown that the commutative properties of the kinetic and potential energy operators complicate the decomposition of this function, but that we may divide up $\beta$ in order to get a higher
4.2. **THE ACTION**

effective temperature. Another important leap to make in order to form some sort of useful numerical technique is that we may define an imaginary time propagator as

\[
\langle R_{\alpha-1} | e^{-\tau \hat{H}} | R_{\alpha} \rangle = \langle R_{\alpha-1} | \hat{U}(-i\hbar \tau) | R_{\alpha} \rangle,
\]

where \( | R_{\alpha} \rangle = | \vec{r}_{\alpha,1}, \vec{r}_{\alpha,2}, ..., \vec{r}_{\alpha,N} \rangle \) represents the state of the entire \( N \)-body system at imaginary time slice \( \alpha \). This is also due to Feynman, and simply comes from the fact that our real time evolution of the system is given to us by \( \exp \left( -it \hat{H} / \hbar \right) \), and making the substitution \( \tau = it \) will then give us the definition of the imaginary time propagator \( \hat{U} \). One can imagine how this works by picturing a quantum system fluctuating in time and taking snapshots of the system throughout different stages of its evolution. For finite temperature PIMC, these worldlines are periodic in imaginary time, and hence we may view the first and the last imaginary time step as being connected. We call the nodes of these worldlines ‘beads’, and allow for the beads to be connected by ‘links’, which tell us something about the kinetic energy of the particles. Each one of these worldlines corresponds to a different particle. It will be formally shown that the partition function for this system is equivalent to that of a system of classical polymers, but one can see the resemblance right away by looking at the worldlines themselves. We may map a system of \( N \) quantum particles onto a system of \( N \) classical polymers. For the case of finite-temperature simulations (PIMC), these are cyclic chain
4.2. THE ACTION

polymers. For the zero-temperature case, the path integral ground state (PIGS) method is used, and these polymers are open-chain polymers because the periodic boundary conditions are not imposed in imaginary time. A brief overview of PIGS is given in Appendix D.

The formalism needs to be developed a bit more before this is fully presented, but it is helpful when seeing the mathematics to have this image of beads as slices in imaginary time. These worldlines may ‘mix’, which tells us many fascinating things about a system. When the number of beads and worldlines is kept fixed, this corresponds with working in the canonical ensemble, however PIMC (be it finite or zero temperature) is not limited to working in this ensemble due to the worm algorithm [42,43].

4.2.3 PRIMITIVE APPROXIMATION

The zeroeth order thing to do when writing a path integral code is to assume that the potential and kinetic energy operators do in fact commute with one another. This can be a decent approximation, as seen in Equation (4.12), if we define enough imaginary time propagators (i.e. enough imaginary time steps such that the Trotter error is small). In this approximation the density matrix element corresponding to going from state (time slice) \(R_\alpha\) to \(R_{\alpha+1}\), for a system of \(N\) particles is

\[
\rho(R_\alpha, R_{\alpha+1}; \tau) = \langle R_\alpha | e^{-\tau \hat{T}} e^{-\tau \hat{V}} | R_{\alpha+1} \rangle + O(\tau^2)
\]

\[
\approx \int DR'D \langle R_\alpha | e^{-\tau \hat{T}} | R' \rangle \langle R' | e^{-\tau \hat{V}} | R_{\alpha+1} \rangle
\]

\[
= \int DR'D \langle R_\alpha | e^{-\tau \hat{T}} | R' \rangle e^{-\tau V} \langle R' | R_{\alpha+1} \rangle
\]

\[
= \int DR'D \langle R_\alpha | e^{-\tau \hat{T}} | R' \rangle e^{-\tau V} \delta^N(R' - R_{\alpha+1})
\]

\[
= \langle R_\alpha | e^{-\tau \hat{T}} | R_{\alpha+1} \rangle e^{-\tau V}.
\]

(4.16)
4.2. THE ACTION

This quantity tells us about the $3N$ degrees of freedom (in 3 spatial dimensions for a spinless system) of the system between time slice $\alpha$ and $\alpha + 1$. The matrix element above containing the free propagator may be evaluated by using an eigenfunction expansion of the kinetic energy operator. Consider the 3-dimensional case where our free particles are in a cube of volume $\ell = L^3$. Then our wave functions are

$$|R_\alpha\rangle = \frac{1}{\sqrt{\ell}} \sum_n e^{i k_n R_\alpha} |k_1, k_2, \ldots, k_N\rangle,$$  \hspace{1cm} (4.17)

where $k_n R_\alpha$ is the wave vector for the $n^{th}$ particle projected onto the state vector $R_\alpha$. We know that when the kinetic energy operator acts on these states it yields the eigenvalues $\lambda k_n^2$ where $k_n = 2\pi n/L$ and $\lambda = \hbar^2/2m$. Hence, we may write out the matrix element as

$$\langle R_\alpha| e^{-\tau \hat{T}} |R_{\alpha+1}\rangle = \sum_n L^{-3N} e^{-\tau \lambda k_n^2} e^{ik_n R_{\alpha+1}} e^{-ik_n R_\alpha}.$$  \hspace{1cm} (4.18)

The next step is to approximate the sum as an integral:

$$\langle R_\alpha| e^{-\tau \hat{T}} |R_{\alpha+1}\rangle \to L^{-3N} \int d\vec{k} e^{-\tau \lambda k_n^2} e^{ik_n R_{\alpha+1}} e^{-ik_n R_\alpha} \hspace{1cm} (4.19)$$

This integral is a $3N$ dimensional Gaussian integral that has a solution of the form:

$$\langle R_\alpha| e^{-\tau \hat{T}} |R_{\alpha+1}\rangle \to \left(\frac{1}{2\pi}\right)^{3N} \int d\vec{k} e^{-\tau \lambda k_n^2} e^{ik_n R_{\alpha+1}} e^{-ik_n R_\alpha} \hspace{1cm} (4.20)$$
4.2. THE ACTION

Hence, the thermal density matrix describing the link between time slice $\alpha$ to $\alpha + 1$ looks like:

\[
\rho(R_\alpha, R_{\alpha+1}; \tau) = (4\pi\lambda\tau)^{-3N/2} \exp\left(-\frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda\tau}\right) \exp\left(-\tau V(R_\alpha)\right). \tag{4.21}
\]

The partition function for this system is then written out as an integral over the configuration space of the product of all density matrices of the time slices. When we take this product, the indistinguishability of the bosons and the periodicity in imaginary time require that we divide the partition function by $N!$. Ignoring permutations of the worldlines, the general partition function in the primitive approximation for $N$ particles in $d$ dimensions, each having $M$ time slices is

\[
Z^{pr} = \frac{1}{N!} \prod_{\alpha=0}^{M-1} \int dR_\alpha \rho(R_\alpha, R_{\alpha+1}; \tau)
\]

\[
= \frac{1}{N!} \int dR_0 \cdots dR_{M-1} \rho(R_0, R_1; \tau) \cdots \rho(R_{M-1}, R_0; \tau)
\]

\[
= \frac{1}{N!} (4\pi\lambda\tau)^{-3NM/2} \int dR_0 \cdots dR_{M-1} \exp\left(-\frac{(R_0 - R_1)^2}{4\lambda\tau}\right) \exp\left(-\tau V(R_0)\right)
\]

\[
\times \cdots \times \exp\left(-\frac{(R_{M-1} - R_0)^2}{4\lambda\tau}\right) \exp\left(-\tau V(R_{M-1})\right)
\]

\[
= \frac{1}{N!} (4\pi\lambda\tau)^{-3NM/2} \prod_{\alpha=0}^{M-1} \prod_{i=1}^{N} \int d\vec{r}_{\alpha,i} \exp\left(-\frac{(\vec{r}_{\alpha,i} - \vec{r}_{\alpha+1,i})^2}{4\lambda\tau}\right) \exp\left(-\tau V(\vec{r}_{\alpha,i})\right)
\]

\[
= \frac{1}{N!} (4\pi\lambda\tau)^{-3NM/2} \prod_{\alpha=0}^{M-1} \prod_{i=1}^{N} \int d\vec{r}_{\alpha,i} \exp\left(-\tau \left[\frac{(\vec{r}_{\alpha,i} - \vec{r}_{\alpha+1,i})^2}{4\lambda\tau^2} + V(\vec{r}_{\alpha,i})\right]\right), \tag{4.22}
\]

where

\[
V(\vec{r}_{\alpha,i}) = V_{ext}(\vec{r}_{\alpha,i}) + \sum_{i<j} V_{int}(\vec{r}_{\alpha,i} - \vec{r}_{\alpha,j}). \tag{4.23}
\]

This is slightly different if we allow for permutations, but this discussion is put off for now. It may actually be seen that permutations need not be considered for zero temperature systems when the path integral ground state technique is implemented. This will be com-
4.2. **THE ACTION**

mented on in the appendix on zero temperature QMC. The main problem with the primitive approximation is that often one needs to take many, many time steps in order to get good results, which leads to decreased efficiency of the PIMC algorithm, which scales as $MN^2$. There exist higher order approximations which help address this problem.

### 4.2.4 Generalized Suzuki Factorization

We want the partition function, which is the trace of the density matrix. This may be expressed as in Equation (4.13). We can write this out as

$$
Z = \prod_{\alpha=0}^{M-1} \int dR_\alpha \langle R_\alpha | e^{-2\tau\hat{H}} | R_\alpha \rangle. \quad (4.24)
$$

This is exact, but since the kinetic and potential operators do not commute with one another, approximation schemes are necessary. There exist higher order schemes, one of which is the generalized Suzuki factorization (GSF) for the action, which is good to fifth order in the time step, $\tau$. Notice that the action has a time step of length $2\tau$. The significance of this will be discussed shortly. This approximation ends up taking the form

$$
\rho(R_\alpha, R_{\alpha+1}; 2\tau) = \langle R_\alpha | e^{-\tau\hat{V}_e/3} e^{-\tau\hat{T}} e^{-4\tau\hat{V}_m/3} e^{-\tau\hat{T}} e^{-\tau\hat{V}_e/3} | R_{\alpha+1} \rangle + O(\tau^5), \quad (4.25)
$$

where we have defined:

$$
V_e = V + \frac{C}{3} \sum_{i=1}^{\tilde{N}} \tau^2 \lambda_i [\partial_i V]^2 \quad (4.26)
$$

$$
V_m = V + \frac{(1-C)}{6} \sum_{i=1}^{\tilde{N}} \tau^2 \lambda_i [\partial_i V]^2. \quad (4.27)
$$

The above expressions are those for the effective potential and are as general as can be due to the fact that they are written out for $\tilde{N}$ general degrees of freedom, meaning the total number of beads from all particles in the system [44]. The constant $C \in [0,1]$ is a scaling
4.2. THE ACTION

factor that is dependent upon whether the current time slice is even or odd. This can be simplified in the case where all of the atoms in the system are of the same type, and then our expressions look like:

\[ V_e(\vec{r}_{\alpha,i}) = \frac{1}{M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}) + \frac{C \tau^2 \lambda}{3} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} [\partial_{\alpha,i} V(\vec{r}_{\alpha,i})]^2 \]  

(4.28)

\[ V_m(\vec{r}_{\alpha,i}) = \frac{1}{M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}) + \frac{(1-C) \tau^2 \lambda}{6} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \partial_{\alpha,i} V(\vec{r}_{\alpha,i})^2. \]  

(4.29)

From here on, we will work under the assumption that all atoms being studied are of the same type. The density matrix can be evaluated by inserting complete basis sets between all exponential functions. For the GSF action,

\[ \rho(R_\alpha, R_{\alpha+1}; 2\tau) \approx \langle R_\alpha | e^{-\tau \hat{V}_e/3} e^{-\tau \hat{T}} e^{-4\tau \hat{V}_m/3} e^{-\tau \hat{T}} e^{-\tau \hat{V}_e/3} | R_{\alpha+1} \rangle 
\]

\[ = \int dR' dR'' \langle R_\alpha | e^{-\tau \hat{V}_e/3} | R' \rangle \langle R | e^{-\tau \hat{T}} e^{-4\tau \hat{V}_m/3} e^{-\tau \hat{T}} | R'' \rangle \langle R'' | e^{-\tau \hat{V}_e/3} | R_{\alpha+1} \rangle 
\]

\[ = \int dR' dR'' e^{-\tau \hat{V}_e/3} \delta N(R_\alpha - R') \langle R | e^{-\tau \hat{T}} e^{-4\tau \hat{V}_m/3} e^{-\tau \hat{T}} | R'' \rangle e^{-\tau \hat{V}_e/3} \delta N(R'' - R_{\alpha+1}) 
\]

\[ = e^{-\tau \hat{V}_e/3} \langle R_\alpha | e^{-\tau \hat{T}} e^{-4\tau \hat{V}_m/3} e^{-\tau \hat{T}} | R_{\alpha+1} \rangle e^{-\tau \hat{V}_e/3}. \]  

(4.30)

The potential energy terms were pulled out of the matrix elements above because they are diagonal in the position basis and therefore commute with our eigenstates in position space.
4.2. THE ACTION

Now, we insert two more complete basis sets:

\[
\rho(R_\alpha, R_{\alpha+1}; 2\tau) \approx e^{-\tau V_e/3} \langle R_\alpha | e^{-\tau T} e^{-4\tau V_m/3} e^{-\tau T} | R_{\alpha+1} \rangle e^{-\tau V_e/3}
\]

\[
= \int dR' dR'' e^{-\tau V_e/3} \langle R_\alpha | e^{-\tau T} | R' \rangle \langle R' | e^{-4\tau V_m/3} | R'' \rangle \langle R'' | e^{-\tau T} | R_{\alpha+1} \rangle e^{-\tau V_e/3}
\]

\[
= \int dR' dR'' e^{-\tau V_e/3} \langle R_\alpha | e^{-\tau T} | R' \rangle e^{-4\tau V_m/3} \delta_\alpha \langle R' | e^{-\tau T} | R_{\alpha+1} \rangle e^{-\tau V_e/3}
\]

\[
= \int dR' e^{-\tau V_e/3} \langle R_\alpha | e^{-\tau T} | R' \rangle e^{-4\tau V_m/3} \delta_\alpha \langle R' | e^{-\tau T} | R_{\alpha+1} \rangle e^{-\tau V_e/3}. \tag{4.31}
\]

This means that the partition function for the GSF action may be written out as

\[
Z = \int dR \prod_{\alpha=0}^{M-1} \rho_0(R_\alpha, R_{\alpha+1}) \rho_\nu(R_\alpha), \tag{4.32}
\]

where the first density matrix above is the kinetic piece which was determined in the section discussing the primitive action. Recall:

\[
\rho_0(R_\alpha, R_{\alpha+1}) = (4\pi \tau \lambda)^{-3NM/2} \exp \left[ -\tau \sum_{i=1}^{N} \frac{(r_{\alpha,i} - r_{\alpha,i+1})^2}{4\tau^2 \lambda} \right], \tag{4.33}
\]

and the second term is that which corresponds to the potential:

\[
\rho_\nu(\vec{r}_{2\alpha-1}) = \exp \left[ -\frac{2}{3} \tau V_e \right] \tag{4.34}
\]

\[
\rho_\nu(\vec{r}_{2\alpha}) = \exp \left[ -\frac{4}{3} \tau V_m \right]; \quad k \in \mathbb{Z}. \tag{4.35}
\]

Now, one may notice that the sampling done in Equation (4.31) measures the potential action then steps from time slice \(\alpha\) to another ‘time slice’ via the kinetic part of the density matrix, then measures the potential action again and makes one more step through to time slice \(\alpha+1\). This extra step in the middle is an unphysical time slice that is necessary to allow for this GSF decomposition of the density matrix to be possible. It is necessary for
4.3  **MONTE CARLO SAMPLING UPDATES**

sampling but one must be careful not to measure any observables on this unphysical time slice.

4.3  **MONTE CARLO SAMPLING UPDATES**

With knowledge of the sampling/acceptance criteria as well as how the polymer isomorphism works, we are in the position to discuss how one goes about sampling configurations. Thorough documentation for many different types of path integral Monte Carlo updates are readily accessible in the literature [45], so here we simply supply an overview without going into too much detail.

4.3.1  **DIAGONAL UPDATES**

When all of our worldlines in a simulation are closed, we say that we are working in a diagonal ensemble. The worldlines can be moved about in such a way that none of the links are broken between beads. One can imagine many types of updates to perform that will allow for sampling of the full density matrix.

The simplest type of diagonal update is just bead-per-bead sampling. Here, we first compute the action of the system, then a single bead is displaced by a random amount and the action is measured again. The Metropolis algorithm is then called upon to either accept or reject the move. This is simple, but turns out to be terribly inefficient due to what is referred to as critical slowing down.

To combat the inefficiency of single bead displacement updates, one needs to look to moving multiple beads at once. Of course, one could move an entire worldline at once by the same displacement across all beads. This is referred to as a center-of-mass move, and it is easy to imagine that these are not accepted very often for a well equilibrated system.

The most efficient types of diagonal updates that one can use in sampling the configura-
4.3. MONTE CARLO SAMPLING UPDATES

The configuration space of a quantum system are bisection and staging moves. The reason for the critical slowing down is that the kinetic term in the action tends to dominate the potential term, so we wish to separate the kinetic and potential terms and include the kinetic term in our sampling scheme. This is exactly what is done in both bisection and staging moves. Both take advantage of the fact that the solution to the kinetic part of the action is exactly given by the free particle density matrix. A full account of both of these estimators is given in the thesis by Brualla [46], so the reader is referred to this work for details and implementation.

4.3.2 OFF-DIAGONAL UPDATES

The introduction of the worm algorithm [43] means that path integral Monte Carlo is capable of even more efficient sampling schemes and also that one can work in the grand canonical ensemble. With this comes a whole new set of ergodic local updates, some of which are referred to as off-diagonal. We refer to these moves as such because their occurrence either brings us to or from an off-diagonal ensemble, effectively meaning that our worldlines are not all closed.

There exist three complementary pairs of updates which preserve detailed balance: open/close, insert/remove, and advance/recede. If a worldline is closed, we can open it. This effectively brings us from a diagonal ensemble to an off-diagonal ensemble. Furthermore, we can close an open worldline, changing the ensemble back to diagonal. Another way to go into an off-diagonal ensemble is to seed a new open worldline composed of some number of beads. This is referred to as an insert move. We call the resulting worldline a worm, hence the name ‘worm algorithm’. Complementary to the insert update, we can remove a worm from the configuration. The advance update is similar to insert, except it adds a random number of beads to an already existing open worldline. The recede move removes a random number of beads from an existing worldline.

Another very important move is called a swap update. This is strictly off-diagonal, and
4.4. **THERMODYNAMIC ENERGY ESTIMATOR**

is self-complimentary in that it preserves the number of links and beads. An example of how a *swap* move might work is given in Figure 4.2. This update generates all possible many-body permutations and exhibits a high acceptance rate. It allows permutations of identical particles automatically, which is part of the reason why a worm algorithm path integral Monte Carlo code can more efficiently sample all possible configurations than a conventional PIMC code.

The *swap* update exploits the indistinguishable nature of the bosonic particles being studied. If one wishes to simulate distinguishable particles, called Boltzmannons, then these moves must not be performed.

![Figure 4.2: Illustration of swap Monte Carlo update.](image)

4.4 **Thermodynamic Energy Estimator**

Arguably one of the most important, desirable physical observables for a quantum system is the total energy of the system. It turns out that this happens to be one of the more challenging observables to measure and there are multiple schemes that have been devised
4.4. THERMODYNAMIC ENERGY ESTIMATOR

in order to do so. The first we will discuss is the thermodynamic energy estimator, which is based on standard statistical mechanics. The second to be discussed is one which has less variance than the thermodynamic estimator, and is known as the virial energy estimator.

Thermodynamic energy estimators can be determined using standard statistical mechanics:

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z. \quad (4.36)$$

The partition function for a system of \( N \) indistinguishable particles, each having \( M \) beads per worldline has the form

$$Z = \frac{1}{N!} (4\pi \lambda \tau)^{-3NM/2} \prod_{\alpha=0}^{M-1} \prod_{i=1}^{N} d\tilde{r}_{\alpha,i} \exp \left( -\tau \left[ \frac{(r_{\alpha,i} - r_{\alpha+1,i})^2}{4\lambda \tau^2} + V_{\text{eff}}(\tilde{r}_{\alpha,i}, \tilde{r}_{\alpha,i+1}; \tau) \right] \right), \quad (4.37)$$

where \( V_{\text{eff}} \) is called the effective potential and will be different depending upon which approximation is used for the action. Often in the literature this is multiplied by \( \tau \) and called the potential action, denoted as \( U = \tau V_{\text{eff}} \). For simplicity, let us define

$$V_{\text{eff}} = \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V_{\text{eff}}(\tilde{r}_{\alpha,i}, \tilde{r}_{\alpha,i+1}; \tau). \quad (4.38)$$

Then, defining

$$\int \mathcal{D}R = \prod_{\alpha=0}^{M-1} \int dR_{\alpha} = \prod_{\alpha=0}^{M-1} \prod_{i=1}^{N} d\tilde{r}_{\alpha,i}, \quad (4.39)$$

we may write the general partition function in a form more suitable for manipulation:

$$Z = \frac{1}{N!} (4\pi \lambda \tau)^{-3NM/2} \int \mathcal{D}R \exp \left( -\tau \left[ \frac{(R_{\alpha} - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} \right] \right). \quad (4.40)$$

Recognizing that \( d\beta = Md\tau \), this may be inserted into Equation (4.36) to come up with a general expression for the thermodynamic energy estimator. For simplicity, when \( R_{\alpha} - R_{\alpha+1} \) is written, it is assumed that this must be averaged over all time slices. The thermodynamic
4.4. THERMODYNAMIC ENERGY ESTIMATOR

Energy becomes

\[ \langle E \rangle_T = -\frac{1}{Z} \frac{\partial}{\partial \beta} \frac{1}{N!} (4\pi \lambda \tau)^{-3NM/2} \int \! DR \exp \left( -\tau \left[ \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} \right] \right) \]

\[ = \frac{(4\pi \lambda)^{-3NM/2}}{MZ} \frac{1}{N!} \int \! DR \tau^{-3NM/2} \exp \left( -\tau \left[ \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} \right] \right) \]

\[ \times \left\{ \frac{3NM}{2\tau} - \left( M \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} \right) - MV_{\text{eff}} - M\tau \frac{\partial}{\partial \tau} V_{\text{eff}} \right\} \]

\[ = \frac{(4\pi \lambda \tau)^{-3NM/2}}{Z} \frac{1}{N!} \int \! DR \exp \left( -\tau \left[ \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} \right] \right) \]

\[ \times \left\{ \frac{3N}{2\tau} - \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} + \tau \frac{\partial}{\partial \tau} V_{\text{eff}} \right\} \]

\[ = \left\langle \frac{3N}{2\tau} - \frac{1}{M} \sum_{\alpha=0}^{M-1} \frac{(R_\alpha - R_{\alpha+1})^2}{4\lambda \tau^2} + V_{\text{eff}} + \tau \frac{\partial}{\partial \tau} V_{\text{eff}} \right\rangle \] \quad (4.41)

This means that the thermodynamic energy estimator is known as long as \( V_{\text{eff}} \) is known as a function of \( \tau \). To be consistent with other literature, notice by the product rule that \( \partial_\tau U = V_{\text{eff}} + \tau \partial_\tau V_{\text{eff}} \).

4.4.1 PRIMITIVE THERMODYNAMIC ENERGY

Looking back to the expression for the partition function of a general system in the primitive approximation, one may see that the effective potential is given by

\[ V_{\text{eff}}^{pr} = \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}). \] \quad (4.42)

Therefore, the derivative with respect to \( \tau \) in the thermodynamic energy estimator for this approximation is given as

\[ \frac{\partial}{\partial \tau} V_{\text{eff}}^{pr} = \frac{\partial}{\partial \tau} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}) = 0. \] \quad (4.43)
4.4. THERMODYNAMIC ENERGY ESTIMATOR

Inserting this into Equation (4.41), we have the expression for the thermodynamic energy estimator in the primitive approximation:

\[
\langle E \rangle_{pr}^{T} = \frac{3N}{2\tau} - \frac{1}{4\lambda M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left( \frac{\bar{r}_{\alpha,i} - \bar{r}_{\alpha+1,i}}{\tau} \right)^2 + \frac{1}{M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \hat{V}(\bar{r}_{\alpha,i}).
\] (4.44)

4.4.2 GSF THERMODYNAMIC ENERGY

It becomes convenient here to recognize that the terms \(V_e\) and \(V_m\) are the effective potential:

\[
V_{\text{eff}}^{\text{GSF}} = \begin{cases} 
\frac{2}{3} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\bar{r}_{\alpha,i}) + \frac{2C\tau^2\lambda}{9} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\bar{r}_{\alpha,i}) \right]^2 : \text{odd } \alpha \\
\frac{4}{3} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\bar{r}_{\alpha,i}) + \frac{2(1-C)\tau^2\lambda}{9} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\bar{r}_{\alpha,i}) \right]^2 : \text{even } \alpha
\end{cases}
\] (4.45)

which allows one to express the partition function for a general system in the GSF approximation as

\[
Z = (4\pi\tau\lambda)^{-3NM/2} \int \mathcal{D}R \exp \left( - \tau V_{\text{eff}} + \frac{1}{4\lambda} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left( \frac{\bar{r}_{\alpha,i} - \bar{r}_{\alpha+1,i}}{\tau} \right)^2 \right).
\] (4.46)

To get the thermodynamic energy estimator, we first need to take the derivative of this effective potential with respect to \(\tau\), which will need to be taken for even and odd time slices:

\[
\tau \frac{\partial}{\partial \tau} V_{\text{eff}} = \begin{cases} 
\frac{4C\tau^2\lambda}{9} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\bar{r}_{\alpha,i}) \right]^2 : \text{odd } \alpha \\
\frac{4(1-C)\tau^2\lambda}{9} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\bar{r}_{\alpha,i}) \right]^2 : \text{even } \alpha
\end{cases}
\] (4.47)
4.5. CENTROID VIRIAL ENERGY ESTIMATOR

and then this and the effective potential in Equation (4.45) can be inserted back into Equation (4.41) to show the expression for the thermodynamic energy estimator:

$$\langle E \rangle_{GSF, T} = \frac{3N}{2\tau} - \frac{1}{4\lambda M} \left[ \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left( \vec{r}_{\alpha,i} - \vec{r}_{\alpha+1,i} \right)^2 \right] + \begin{cases} \frac{2}{3M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}) + \frac{2C\tau^{2}\lambda}{3} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) \right]^2 & : \text{odd } \alpha \\ \frac{4}{3M} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} V(\vec{r}_{\alpha,i}) + \frac{2(1-C)\tau^{2}\lambda}{3} \sum_{\alpha=0}^{M-1} \sum_{i=1}^{N} \left[ \nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) \right]^2 & : \text{even } \alpha \end{cases}$$

(4.48)

This is the same result as is presented in the article [44] by Jang, Jang, and Voth. The first two terms in the above expression compute the kinetic energy. The second fluctuates quite a bit, especially at lower temperatures where a bead in one time slice may be farther away the bead it is linked to in imaginary time.

4.5 CENTROID VIRIAL ENERGY ESTIMATOR

Fluctuations in one of the kinetic terms of the thermodynamic energy estimator cause it to be accompanied by a large statistical variance that makes it inefficient to converge the average with reasonable certainty. Therefore, it is desirable to come up with another way to estimate the energy of a quantum system that reduces these statistical variances and the virial energy estimators do just that.

There are a couple of ways to write a virial estimator, which is a fact that seems overlooked in even the most cited of PIMC literature [45]. The expression with the smallest variance is known as the centroid virial estimator. Most of the derivation is given in full in the thesis [47] by Rota, so the work here has included some of the possibly more challenging intermediate steps and left out much of the tedious (but trivial) algebra.
4.5. CENTROID VIRIAL ENERGY ESTIMATOR

4.5.1 CENTROID VIRIAL ENERGY DERIVATION

Recall that the thermal density matrix may be broken up as in Equation (4.11). Consider breaking it up \( L \) times, such that it takes the form:

\[
\rho(\vec{R}_{\alpha+L}, \vec{R}_{\alpha}; L\tau) = \int \prod_{\gamma=1}^{L-1} dR_{\alpha+\gamma} \rho(\vec{R}_{\alpha+\gamma}, \vec{R}_{\alpha+\gamma-1}; \tau)
\]

\[
= \frac{1}{(4\pi\lambda\tau)^{3N/2}} \int \prod_{\gamma=1}^{L-1} dR_{\alpha+\gamma} \exp \left(-S(\vec{R}_{\alpha+\gamma}, \vec{R}_{\alpha+\gamma-1}; \tau)\right),\]  

(4.49)

where \( S \) is the action and is most generally broken into a kinetic part and an effective potential part. In order to come up with a new estimator for the energy, consider the term

\[
E_{1;L+1} = -\frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} \frac{\partial}{\partial \tau} \rho(\vec{R}_1, \vec{R}_{L+1}; L\tau).
\]  

(4.50)

This term is considered first due to the foresight that it leads us towards an expression for the virial energy estimator. The fact that we chose to start at the 1st time slice here is completely arbitrary and is for the sake of making this derivation easier. As will be seen at the end of this derivation, it is beneficial to average over all time slices anyway. Taking the derivative of this density matrix with respect to the time step is started by recognizing

\[
\frac{\partial}{\partial \tau} \rho(\vec{R}_1, \vec{R}_{L+1}; L\tau) = \frac{\partial}{\partial \tau} \int \prod_{\gamma=1}^{L-1} dR_{1+\gamma} \rho(\vec{R}_{1+\gamma}, \vec{R}_{\gamma}; \tau)
\]

\[
= \int \left( \prod_{\gamma=1}^{L-1} dR_{1+\gamma} \right) \frac{\partial}{\partial \tau} \prod_{\gamma=1}^{L-1} \rho(\vec{R}_{1+\gamma}, \vec{R}_{\gamma}; \tau),\]  

(4.51)
4.5. CENTROID VIRIAL ENERGY ESTIMATOR

and then seeing that

\[
\frac{\partial}{\partial \tau} \prod_{\gamma=1}^{L-1} \rho(\vec{R}_{1+\gamma}, \vec{R}_\gamma; \tau) = \frac{\partial}{\partial \tau} \left[ \rho(\vec{R}_2, \vec{R}_1; \tau) \rho(\vec{R}_3, \vec{R}_2; \tau) \cdots \rho(\vec{R}_{L+1}, \vec{R}_L; \tau) \right]
\]

\[
= \rho(\vec{R}_3, \vec{R}_2; \tau) \cdots \rho(\vec{R}_{L+1}, \vec{R}_L; \tau) \frac{\partial}{\partial \tau} \rho(\vec{R}_2, \vec{R}_1; \tau)
\]

\[
+ \rho(\vec{R}_2, \vec{R}_1; \tau) \cdots \rho(\vec{R}_{L+1}, \vec{R}_L; \tau) \frac{\partial}{\partial \tau} \rho(\vec{R}_3, \vec{R}_2; \tau)
\]

\[
+ \rho(\vec{R}_2, \vec{R}_1; \tau) \rho(\vec{R}_3, \vec{R}_2; \tau) \cdots \frac{\partial}{\partial \tau} \rho(\vec{R}_{L+1}, \vec{R}_L; \tau).
\]

(4.52)

Now, we need a general expression for the derivative with respect to \(\tau\) of one of these reduced density matrices. So, we take the derivative for a thermal density matrix linking time slice \(\gamma + 1\) to time slice \(\gamma\):

\[
\frac{\partial}{\partial \tau} \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) = \frac{1}{(4\pi \lambda \tau)^{3N/2}} \exp \left( - S(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right) \left[ - \frac{3N}{2\tau} - \frac{\partial}{\partial \tau} S(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right]
\]

\[
= -\rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \left[ \frac{3N}{2\tau} + \frac{\partial}{\partial \tau} S(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right].
\]

(4.53)

This could be left in this form and substituted back in, but since we generally decompose the action into a kinetic and effective potential piece, we shall do this here and write the imaginary time derivative of the action in a more useful form:

\[
\frac{\partial}{\partial \tau} S(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) = \frac{1}{4\lambda \tau} \left[ \frac{1}{4\lambda \tau^2} (\vec{R}_{\gamma+1} - \vec{R}_\gamma)^2 + U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right]
\]

\[
= -\frac{1}{4\lambda \tau^2} (\vec{R}_{\gamma+1} - \vec{R}_\gamma)^2 + \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau).
\]

(4.54)

Inserting this back into the previous result yields

\[
\frac{\partial}{\partial \tau} \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) = \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \left[ \frac{3N}{2\tau} + \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right].
\]

(4.55)
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Inserting this result back into Equation (4.52), one may notice that the result is

\[ \frac{\partial}{\partial \tau} \prod_{\gamma=1}^{L-1} \rho(\vec{R}_{1+\gamma}, \vec{R}_\gamma; \tau) \]

\[ = \prod_{\gamma=1}^{L-1} \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \sum_{\gamma=1}^{L} \left[ \frac{3N}{2\tau} - \frac{1}{4\lambda \tau^2} (\vec{R}_{\gamma+1} - \vec{R}_\gamma)^2 + \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right] \]

\[ = \prod_{\gamma=1}^{L-1} \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \left[ \frac{3NL}{2\tau} - \frac{1}{4\lambda \tau^2} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma+1} - \vec{R}_\gamma)^2 + \sum_{\gamma=1}^{L} \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right], \]

(4.56)

which may be combined with Equation (4.51) to give us back the expression for \( E_{1;L+1} \) we originally sought:

\[ E_{1;L+1} = \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; \tau)} \int \left( \prod_{\gamma=1}^{L-1} dR_{\gamma+1} \rho(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right) \]

\[ \times \left[ \frac{3NL}{2\tau} - \frac{1}{4\lambda \tau^2} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma+1} - \vec{R}_\gamma)^2 + \sum_{\gamma=1}^{L} \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) \right]. \]

(4.57)

If we integrate this quantity over the coordinates \( \vec{R}_1 \) and \( \vec{R}_{L+1} \) then we get the virial energy estimator:

\[ E_L = \frac{1}{L} \int dR_{L+1} dR_{1} E_{1;L+1}. \]

(4.58)

In order to evaluate this integral, we first need to evaluate the expression for \( E_{1;L+1} \). We begin this by first defining

\[ G = \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; \tau)} \int dR_2 \cdots dR_L \frac{1}{L} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma} - \vec{R}_1) \cdot \nabla \gamma \exp \left( -\sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right), \]

(4.59)

which can be expanded by first evaluating the gradient in the integrand. This is done with foresight, as it turns out that the expression for \( E_{1;L+1} \) can be extracted from this integral.
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This gradient looks like

\[ \nabla \gamma \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \]

\[ = \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \sum_{\beta=1}^{L} \nabla \gamma \left[ \frac{1}{4\lambda \tau} (\vec{R}_{\beta+1} - \vec{R}_{\beta})^2 + U(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right]. \]

(4.60)

The summand may be evaluated (carefully) as

\[ \nabla \gamma \left[ \frac{1}{4\lambda \tau} (\vec{R}_{\beta+1} - \vec{R}_{\beta})^2 + U(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right] \]

\[ = \left[ - \frac{2}{4\lambda \tau} (\vec{R}_{\beta+1} - \vec{R}_{\beta}) + \nabla \gamma U(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right] \delta_{\beta, \gamma}, \]

(4.61)

where \( \delta_{\beta, \gamma} \) is a Kronecker delta function. Inserting this summand back into its sum, we see

\[ \nabla \gamma \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \]

\[ = \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \sum_{\beta=1}^{L} \left[ - \frac{1}{2\lambda \tau} (\vec{R}_{\beta+1} - \vec{R}_{\beta}) + \nabla \gamma U(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right] \delta_{\beta, \gamma} \]

\[ = \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \left[ \frac{1}{2\lambda \tau} (\vec{R}_{\gamma} - \vec{R}_{\gamma+1}) + \nabla \gamma U(\vec{R}_{\gamma+1}, \vec{R}_{\gamma}; \tau) \right. \]

\[ + \left. \frac{1}{2\lambda \tau} (\vec{R}_{\gamma} - \vec{R}_{\gamma-1}) + \nabla \gamma U(\vec{R}_{\gamma}, \vec{R}_{\gamma-1}; \tau) \right]. \]

(4.62)

Therefore, our Green function becomes

\[ G = \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_{1}; L \tau)} \int dR_2 \cdots dR_L \frac{1}{\tau} \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \sum_{\gamma=1}^{L} (\vec{R}_{\gamma} - \vec{R}_{1}) \cdot \left[ \frac{1}{2\lambda \tau} [(\vec{R}_{\gamma} - \vec{R}_{\gamma+1}) + (\vec{R}_{\gamma} - \vec{R}_{\gamma-1})] + \nabla \gamma \left( U(\vec{R}_{\gamma+1}, \vec{R}_{\gamma}; \tau) + U(\vec{R}_{\gamma}, \vec{R}_{\gamma-1}; \tau) \right) \right]. \]

(4.63)
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This expression may be simplified by examining the term

\[ \alpha \equiv \sum_{\gamma=1}^{L} (\vec{R}_{\gamma} - \vec{R}_{1})[(\vec{R}_{\gamma} - \vec{R}_{\gamma+1}) + (\vec{R}_{\gamma} - \vec{R}_{\gamma-1})] \]

\[ = (\vec{R}_{L+1} - \vec{R}_{1}) \cdot (\vec{R}_{L} - \vec{R}_{L+1}) + \sum_{\gamma=1}^{L} (\vec{R}_{\gamma+1} - \vec{R}_{\gamma})^2. \quad (4.64) \]

The algebra for this is done out in detail in [47], so it was omitted in this work because it is trivial but rather tedious. Inserting this result back into our expression for our integral equation \( G \) yields

\[
G = \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_{1}; L\tau)} \int dR_{2} \cdots dR_{L} \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_{\beta}; \tau) \right) \]

\[ \times \left[ \frac{1}{2\lambda\tau^2} (\vec{R}_{L+1} - \vec{R}_{1}) \cdot (\vec{R}_{L} - \vec{R}_{L+1}) + \frac{1}{2\lambda\tau^2} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma+1} - \vec{R}_{\gamma})^2 \right. \]

\[ + \left. \frac{1}{\tau} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma} - \vec{R}_{1}) \cdot \nabla_{\gamma} \left( U(\vec{R}_{\gamma+1}, \vec{R}_{\gamma}; \tau) + U(\vec{R}_{\gamma}, \vec{R}_{\gamma-1}; \tau) \right) \right]. \quad (4.65) \]
In order to proceed, one must go back to Equation (4.59) and solve the integral using integration by parts. It is fairly straightforward to show that this has a simple solution:

\[
G = \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} \int dR_2 \cdots dR_L \frac{1}{\tau} \sum_{\gamma=1}^{L} (\vec{R}_\gamma - \vec{R}_1) \cdot \nabla \gamma \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right)
\]

\[
= \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} \left[ \frac{1}{\tau} \sum_{\gamma=1}^{L} (\vec{R}_\gamma - \vec{R}_1) \cdot \nabla \gamma \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right) \right]
\]

\[
+ \int dR_2 \cdots dR_L \frac{1}{\tau} \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right) \sum_{\gamma=1}^{L} \nabla \gamma (\vec{R}_\gamma - \vec{R}_1)
\]

\[
= \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} \int dR_2 \cdots dR_L \frac{1}{\tau} \exp \left( - \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right) 3N
\]

\[
= \frac{3N}{\tau} \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} (L - 1) \rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)
\]

\[
= \frac{3N(L - 1)}{\tau}.
\]

(4.66)

This boundary term tends to zero only if the imaginary time step is small enough. This means that it would seem that the derivation of this estimator requires that the PIMC simulations use a small enough time step. One can now equate the two expressions for \(G\). This is just algebra and recognizing that Equation (4.57) appears when one looks hard enough. These fairly trivial steps are omitted here, but done out in detail in the thesis by Rota [47]. Finally, we may state

\[
E_{1;L+1} = \frac{3N}{2\tau} + \frac{1}{\rho(\vec{R}_{L+1}, \vec{R}_1; L\tau)} \int dR_2 \cdots dR_L \exp \left( \sum_{\beta=1}^{L} S(\vec{R}_{\beta+1}, \vec{R}_\beta; \tau) \right)
\]

\[
\times \left[ (\vec{R}_{L+1} - \vec{R}_1) \cdot (\vec{R}_L - \vec{R}_{L+1}) \right] + \sum_{\gamma=1}^{L} \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau)
\]

\[
+ \frac{1}{\tau} \sum_{\gamma=1}^{L} (\vec{R}_\gamma - \vec{R}_1) \cdot \nabla \gamma \left( U(\vec{R}_{\gamma+1}, \vec{R}_\gamma; \tau) + U(\vec{R}_\gamma, \vec{R}_{\gamma-1}; \tau) \right)
\]

(4.67)
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Once one plugs this into Equation (4.58), we notice that the first term is a constant and all other terms are thermal averages, hence our expression becomes

\[
E_L = \frac{3N}{2\tau L} + \left\langle \frac{1}{4\tau^2\lambda L} \sum_{\gamma=1}^{L} \frac{\partial}{\partial \tau} U(\vec{R}_{\gamma+1}, \vec{R}_{\gamma}; \tau) \right\rangle + \left\langle \frac{1}{\tau L} \sum_{\gamma=1}^{L} (\vec{R}_{\gamma} - \vec{R}_1) \cdot \nabla_{\gamma} \left( U(\vec{R}_{\gamma+1}, \vec{R}_{\gamma}; \tau) + U(\vec{R}_{\gamma}, \vec{R}_{\gamma-1}; \tau) \right) \right\rangle. \tag{4.68}
\]

As mentioned, it is beneficial to average over all time slices here. We chose the 1st time slice corresponding to positions \( \vec{R}_1 \) as the reference configuration, and it shows up in the equation above. To further reduce the variance, we choose to average over all imaginary time slices. This is what actually distinguishes the centroid virial energy estimator from other virial estimators. As a note, this includes letting the imaginary time derivative of the potential action be across all time slices instead of just over the ‘virial window’ size.

We shift the time slice indices by \( \alpha - 1 \) because we end up touching them all anyway, and this makes our expression match Rota’s. This results in the final general expression for the centroid virial energy estimator, given by

\[
E_{CV} = \frac{3N}{2\tau L} + \left\langle \frac{1}{4\lambda M L^2} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha+L} - \vec{R}_{\alpha}) \cdot (\vec{R}_{\alpha+L-1} - \vec{R}_{\alpha+L}) \right\rangle + \left\langle \frac{1}{2M \tau} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha} - \vec{R}_{\alpha}^C) \cdot \nabla_{\alpha} \left( U(\vec{R}_{\alpha+1}, \vec{R}_{\alpha}; \tau) + U(\vec{R}_{\alpha}, \vec{R}_{\alpha-1}; \tau) \right) \right\rangle + \left\langle \frac{1}{M} \sum_{\alpha=1}^{M} \frac{\partial}{\partial \tau} U(\vec{R}_{\alpha+1}, \vec{R}_{\alpha}; \tau) \right\rangle, \tag{4.69}
\]

where

\[
\vec{R}_{\alpha}^C = \frac{1}{2L} \sum_{\gamma=0}^{L-1} (\vec{R}_{\alpha+\gamma} + \vec{R}_{\alpha-\gamma}) \tag{4.70}
\]

helps compute the average distance that a given bead is from its worldline. We shall henceforth refer to \( L \) as the ‘virial window’. One may notice that in the second term above, the vector \( \vec{R}_{\alpha+L} - \vec{R}_{\alpha+L+1} \) could be substituted for \( \vec{R}_{\alpha} - \vec{R}_{\alpha+1} \) without affecting
the result. We make this substitution and write the full expression for the centroid virial energy estimator as

\[
E_{CV} = \frac{3N}{2\tau L} + \left\langle \frac{1}{4\lambda ML^2} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\vec{r}_{\alpha+L,i} - \vec{r}_{\alpha,i}) \cdot (\vec{r}_{\alpha+L-1,i} - \vec{r}_{\alpha+L,i}) \right\rangle \\
+ \left\langle \frac{1}{2M} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\vec{r}_{\alpha,i} - \vec{r}_{\alpha,i}^C) \cdot \nabla_{\alpha,i} \left( U(\vec{r}_{\alpha+1,i}, \vec{r}_{\alpha,i}; \tau) + U(\vec{r}_{\alpha,i}, \vec{r}_{\alpha-1,i}; \tau) \right) \right\rangle \\
+ \left\langle \frac{1}{M} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} \frac{\partial}{\partial \tau} U(\vec{r}_{\alpha+1,i}, \vec{r}_{\alpha,i}; \tau) \right\rangle ,
\]

It is important when implementing this estimator that one carefully treats these terms, especially the second and third. The first term is a constant of the simulation, and the fourth term may be averaged over entire time slices when actually measuring it. The second and third can be tricky.

For example, most often in PIMC simulations, some form of periodic boundary conditions are implemented. One must take care to properly compute all terms of this estimator when particle exchange and periodic boundary conditions are present. Imagine that one wants to compute \( \vec{r}_{\alpha,i}^C \) for the circled bead in Figure 4.3 by starting at the circled bead and stepping forward in imaginary time by \( L \) steps and backward in imaginary time by \( L \) steps, averaging as you go. This can be complicated when the minimum image convention is used in the PIMC code. This convention is a way of simulating the thermodynamic limit with a small number of parti-
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cles by allowing particles to interact with other particles within a simulation cell only up
to half of the length of the cell. In looking at Figure 4.3, it should be fairly obvious for
someone used to thinking about periodic boundary conditions that the circled bead will

Figure 4.4: Picture of how a given bead interacts with other beads in a simulation cell when the
minimum image convention is used.

‘see’ the other beads in the cell as they appear in Figure 4.4. However, in computing the
average distance that a bead is from its given worldline, the picture that one needs to have
is actually given in Figure 4.5.

If one were to compute the average distance between the circled bead and the other
members of its worldline, the result would be different between Figure 4.4 and Figure 4.5
if one simply took the distance between beads. This same consideration must be taken
when computing terms like \( \vec{R}_{L+\alpha} - \vec{R}_\alpha \), because a small enough system size at a low enough
temperature may cause these beads to be farther apart than half of the simulation cell size.
Therefore this term (in the second term of the centroid virial energy estimator) must only
have boundary conditions enforced between subsequent imaginary time slices. Also, when
computing the third term, one must not use periodic boundary conditions in computing
\( \vec{r}_{\alpha,i}^C \), but periodic boundary conditions must be enforced when computing \( \vec{r}_{\alpha,i} - \vec{r}_{\alpha,i}^C \).
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Figure 4.5: Picture of the spatial configuration that one should have in mind when computing the average separation of a bead from the next four beads and previous four beads in its worldline.

4.5.2 Primitive Centroid Virial Energy

Here, we show the explicit form of the centroid virial energy expression in the case of the primitive action. Looking at Equation (4.69), one may notice that the gradient of the potential action across two links is taken, from $\alpha \rightarrow \alpha + 1$ and from $\alpha - 1 \rightarrow \alpha$. This is useful for the case of non-local actions that are not diagonal in $\tau$. These are those in which neighboring time slices interact with one another, such as the hard-sphere or hard-rod propagators. However, for local actions, such as the primitive, Takahashi-Imada, and GSF, one only needs to compute the gradient of the potential action on one time slice because the other is zero here.

Note that from now on, we drop the angled brackets denoting a thermal average. All energy estimator terms are to be considered a thermal average. So, for local actions, Equation
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(4.69) becomes

\[ E_{CV} = \frac{3N}{2\tau L} + \frac{1}{4\lambda M L^2} \sum_{a=1}^{M} (\vec{R}_{a} + L - \vec{R}_{a}) \cdot (\vec{R}_{a} + L - \vec{R}_{a} + L) \]
\[ + \frac{1}{2\tau} \sum_{a=1}^{M} (\vec{R}_{a} - \vec{R}_{a}^C) \cdot \nabla_{a} U(\vec{R}_{a}, \vec{R}_{a-1}, \tau) \]
\[ + \frac{1}{M} \sum_{a=1}^{M} \frac{\partial}{\partial \tau} U(\vec{R}_{a+1}, \vec{R}_{a}, \tau). \tag{4.72} \]

We choose the notation which is consistent with Ceperley [45], \( U^a = U(\vec{R}_a, \vec{R}_{a-1}, \tau) \). Now insert the potential action \( U = \tau V_{\text{eff}} \) from Equation (4.42) to show the expression reduces to

\[ E_{CV} = \frac{3N}{2\tau L} + \frac{1}{4\lambda M L^2} \sum_{a=1}^{M} (\vec{R}_{a} + L - \vec{R}_{a}) \cdot (\vec{R}_{a} + L - \vec{R}_{a} + L) \]
\[ + \frac{1}{2\tau} \sum_{a=1}^{M} (\vec{R}_{a} - \vec{R}_{a}^C) \cdot \nabla_{a} V(\vec{R}_{a}) + \frac{1}{M} \sum_{a=1}^{M} \frac{\partial}{\partial \tau} V(\vec{R}_{a}), \tag{4.73} \]

and since the potential is not dependent upon the imaginary time step, this simply becomes

\[ E_{CV}^{pr} = \frac{3N}{2\tau L} + \frac{1}{4\lambda M L^2} \sum_{a=1}^{M} (\vec{R}_{a} + L - \vec{R}_{a}) \cdot (\vec{R}_{a} + L - \vec{R}_{a} + L) \]
\[ + \frac{1}{2\tau} \sum_{a=1}^{M} (\vec{R}_{a} - \vec{R}_{a}^C) \cdot \nabla_{a} V(\vec{R}_{a}) + \frac{1}{M} \sum_{a=1}^{M} V(\vec{R}_{a}). \tag{4.74} \]

This makes sense, because the leading term is just the classical kinetic energy (seen explicitly when one lets \( L = M \)) and the second term is the quantum correction to the kinetic energy and is zero for the case of no particle exchange if one lets \( L = M \). The third term is also a part of the kinetic energy, and for the case of higher temperatures it will be somewhat close to zero because of the fact that \( R_{a} - R_{a}^C \) will be approximately zero because the worldlines do not ‘spread’ out at higher temperatures very much. This is a statement that the higher temperature systems will have a nearly classical kinetic energy, which is what we expect. It
is important to note that this will still be the case for the GSF or other known higher-order action approximations.

4.5.3 GSF Centroid Virial Energy

In order to see the expression for the centroid virial energy in the case of the GSF action, one needs to combine Equations (4.69) and (4.45) to yield

\[
E_{CV} = \frac{3N}{2\tau L} + \frac{1}{4\lambda ML\tau^2} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha+L} - \vec{R}_{\alpha}) \cdot (\vec{R}_{\alpha+L-1} - \vec{R}_{\alpha+L}) \\
+ \frac{1}{2M\tau} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha} - \vec{R}_{\alpha}^C) \cdot \nabla_{\alpha} \left( C_1 \tau V(\vec{R}_{\alpha}) + C_2 \frac{2\tau^3 \lambda}{9} [\nabla_{\alpha} V(\vec{R}_{\alpha})]^2 \right) \\
+ \frac{1}{M} \sum_{\alpha=1}^{M} \frac{\partial}{\partial \tau} \left( C_1 \tau V(\vec{R}_{\alpha}) + C_2 \frac{2\tau^3 \lambda}{9} [\nabla_{\alpha} V(\vec{R}_{\alpha})]^2 \right),
\]

(4.75)

where

\[
C_1 = \begin{cases} 
2/3 & : \text{odd slices} \\
4/3 & : \text{even slices}
\end{cases}, \quad C_2 = \begin{cases} 
C & : \text{odd slices} \\
(1 - C) & : \text{even slices}
\end{cases} \quad (4.76)
\]

This may be rewritten as

\[
E_{CV} = \frac{3N}{2\tau L} + \frac{1}{4\lambda ML\tau^2} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha+L} - \vec{R}_{\alpha}) \cdot (\vec{R}_{\alpha+L-1} - \vec{R}_{\alpha+L}) \\
+ \frac{1}{2M\tau} \sum_{\alpha=1}^{M} (\vec{R}_{\alpha} - \vec{R}_{\alpha}^C) \cdot \left( C_1 \tau \nabla_{\alpha} V(\vec{R}_{\alpha}) + C_2 \frac{2\tau^3 \lambda}{9} \nabla_{\alpha} [\nabla_{\alpha} V(\vec{R}_{\alpha})]^2 \right) \\
+ \frac{1}{M} \sum_{\alpha=1}^{M} \left( C_1 V(\vec{R}_{\alpha}) + C_2 \frac{6\tau^2 \lambda}{9} [\nabla_{\alpha} V(\vec{R}_{\alpha})]^2 \right) \\
\equiv T_1 + T_2 + T_3 + T_4 + T_5, \quad (4.77)
\]

where the terms have been assigned names in order and the last two terms (the final summand) collectively correspond with \(T_5\). This is the final analytical expression for the centroid virial energy in the GSF action case, but some of these terms are obviously not in
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a suitable form for coding, so we must tackle this problem now. We begin by evaluating the square of the gradient of the potential, which exists as a part of $T_4$ and $T_5$. We write it out in the most explicit form as

$$\left[ \nabla_{\alpha i} V(\vec{r}_{\alpha i}) \right]^2 = \left[ \nabla_{\alpha i} V_{\text{ext}}(\vec{r}_{\alpha i}) + \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1 \{k \neq j\}}^{N} \nabla_{\alpha i} V_{\text{int}}(\vec{r}_{\alpha j} - \vec{r}_{\alpha k}) \right]^2. \quad (4.78)$$

In order to successfully evaluate this, we first need

$$\nabla_{\alpha i} V_{\text{int}}(\vec{r}_{\alpha j} - \vec{r}_{\alpha k}) = \left. \frac{d}{dr} V_{\text{int}}(r) \right|_{r=\vec{r}_{\alpha j} - \vec{r}_{\alpha k}} \frac{\vec{r}_{\alpha j} - \vec{r}_{\alpha k}}{|\vec{r}_{\alpha j} - \vec{r}_{\alpha k}|} (\delta_{ij} - \delta_{ik}). \quad (4.79)$$

Inserting this into the previous expression and using the delta functions, we find

$$\frac{1}{2} \sum_{j=1}^{N} \sum_{k=1 \{k \neq j\}}^{N} \nabla_{\alpha i} V_{\text{int}}(\vec{r}_{\alpha j} - \vec{r}_{\alpha k}) = \sum_{j=1 \{j \neq i\}}^{N} \left. \frac{d}{dr} V_{\text{int}}(r) \right|_{r=\vec{r}_{\alpha j} - \vec{r}_{\alpha i}} \frac{\vec{r}_{\alpha j} - \vec{r}_{\alpha i}}{|\vec{r}_{\alpha j} - \vec{r}_{\alpha i}|}, \quad (4.80)$$

meaning

$$\left[ \nabla_{\alpha i} V(\vec{r}_{\alpha i}) \right]^2 = \left[ \nabla_{\alpha i} V_{\text{ext}}(\vec{r}_{\alpha i}) + \sum_{j=1 \{j \neq i\}}^{N} \left. \frac{d}{dr} V_{\text{int}}(r) \right|_{r=\vec{r}_{\alpha j} - \vec{r}_{\alpha i}} \frac{\vec{r}_{\alpha j} - \vec{r}_{\alpha i}}{|\vec{r}_{\alpha j} - \vec{r}_{\alpha i}|} \right]^2 \quad (4.81)$$

Let's define the unit vector in the above equation as $\hat{r}_{ij}$. We also need to evaluate the gradient of this last term and we do so without explicitly separating the external and interaction pieces of the potential:

$$\nabla_{\alpha} \left[ \nabla_{\alpha} V(\vec{R}_\alpha) \right]^2 = \sum_{i=1}^{N} \nabla_{\alpha,i} \left[ \nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) \right]^2$$

$$= \sum_{i=1}^{N} \nabla_{\alpha,i} \left[ \left( \sum_{j=1 \{j \neq i\}}^{N} \left. \frac{d}{dr} V(r) \right|_{r=|\vec{r}_{ij}|} \right) \cdot \left( \sum_{k=1 \{k \neq i\}}^{N} \left. \frac{d}{dr} V(r) \right|_{r=|\vec{r}_{\alpha,i,k}|} \right) \right]. \quad (4.82)$$
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From here, we drop the time slice index since we know we act only on time slice \(\alpha\) in the case of local actions, and we switch to tensor notation, meaning our expression for the summand above now looks like

\[
\nabla_\alpha [\nabla_\alpha V(\vec{R}_\alpha)]^2 = \frac{\partial}{\partial r^a} \left[ \sum_{j=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{r_{ij}^a}{r_{ij}} \right]_{r=|\vec{r}_{ij}|} \cdot \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|}
\]

\[
= \sum_{j=1}^{N} \frac{\partial}{\partial r^a} \left( \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{r_{ij}^a}{r_{ij}} \right)_{r=|\vec{r}_{ij}|} \cdot \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|} + \sum_{j=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{r_{ij}^a}{r_{ij}} \right]_{r=|\vec{r}_{ij}|} \cdot \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|}
\]

\[
= 2 \left[ \sum_{j=1}^{N} \frac{\partial}{\partial r^a} \left( \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{r_{ij}^a}{r_{ij}} \right)_{r=|\vec{r}_{ij}|} \right] \cdot \left[ \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|}
\]

\[
= 2 \left[ \sum_{j=1}^{N} \left( \frac{\partial}{\partial r^a} \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{r_{ij}^a}{r_{ij}} + \frac{\partial}{\partial r} V(\vec{r}_{ij}) \frac{\partial}{\partial r^a} \frac{r_{ij}^a}{r_{ij}} \right)_{r=|\vec{r}_{ij}|} \right]
\]

\[
\cdot \left[ \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|}
\]

\[
= 2 \left[ \sum_{j=1}^{N} \left( \frac{r_{ij}^a r_{ij}^a}{r^2} \frac{\partial^2}{\partial r_j^a \partial r} V(\vec{r}_{ij}) + \left( \frac{\delta_{ab}}{r} - \frac{r_{ij}^a \delta_{ij}}{r^3} \right) \frac{\partial}{\partial r} V(\vec{r}_{ij}) \right)_{r=|\vec{r}_{ij}|} \right]
\]

\[
\cdot \left[ \sum_{k=1}^{N} \frac{\partial}{\partial r} V(\vec{r}_{ik}) \frac{r_{ik}^a}{r_{ik}} \right]_{r=|\vec{r}_{ik}|}
\]

(4.83)

This is practically finished, so we reclaim our sum over particles and explicitly write out all of the values of \(r\) in terms of their inter-particle indices, and recognize that the second term in large square brackets is simply the gradient of the potential. This gives us a final
4.6. COMPARISON OF ENERGY ESTIMATORS

form of

\[
\left[ \nabla_{\alpha} \nabla_{\alpha} V(\vec{R}_{\alpha}) \right]_{b}^{2} = 2 \sum_{i=1}^{N} \nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) \cdot \sum_{\substack{j=1 \atop j \neq i}}^{N} \frac{r_{ij}^{b} r_{ij}^{a}}{|\vec{r}_{ij}|^2} \frac{\partial^2}{\partial r_{ij}^a \partial |\vec{r}_{ij}|} V(\vec{r}_{ij}) + \left( \frac{\delta_{ab}}{|\vec{r}_{ij}|^3} - \frac{r_{ij}^{b} r_{ij}^{a}}{|\vec{r}_{ij}|^3} \right) \frac{\partial}{\partial |\vec{r}_{ij}|} V(\vec{r}_{ij})
\]

\[
\equiv 2 \sum_{i=1}^{N} \nabla_{\alpha,i} V(\vec{r}_{\alpha,i})^{a} \cdot T(\vec{r}_{\alpha,i})^{b}_{a}, \tag{4.84}
\]

where \( b = 1, \ldots, d \). This tensor quantity \( T(\vec{r}_{\alpha,i}) \) is very useful, as it is the key to being able to put this estimator into a PIMC code. With this, one has everything they need to be able to implement this estimator in a PIMC code for the GSF action, which is given as

\[
E_{CV} = \frac{3N}{2\tau L} + \frac{1}{4\lambda M L^2} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\vec{r}_{\alpha+L,i} - \vec{r}_{\alpha,i}) \cdot (\vec{r}_{\alpha+L-1,i} - \vec{r}_{\alpha+L,i})
\]

\[
+ \frac{1}{2M\tau} \left( C_{1\tau} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\vec{r}_{\alpha,i} - \vec{r}_{\alpha,i}^{C}) \cdot \nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) + C_{2} \frac{4\tau^3 \lambda}{9} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\vec{r}_{\alpha,i} - \vec{r}_{\alpha,i}^{C}) \cdot [\nabla_{\alpha,i} V(\vec{r}_{\alpha,i}) \cdot T(\vec{r}_{\alpha,i})] \right)
\]

\[
+ C_{2} \frac{4\tau^2 \lambda}{9} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} C_{1} V(\vec{r}_{\alpha,i}) + C_{2} \frac{6\tau^2 \lambda}{9} [\nabla_{\alpha,i} V(\vec{r}_{\alpha,i})]^2 \right]. \tag{4.85}
\]

Here we express Equation (4.85) explicitly in terms of the position of each bead because one cannot compute all terms across an entire imaginary time slice. Also note that one may shift the time slice indices on the second term above by \(-L\) for ease of computation. This term is implemented in the code this way.

4.6 Comparison of Energy Estimators

As mentioned, the reason for implementing the centroid virial energy estimator in a PIMC code is to reduce the variance associated with the highly fluctuating terms in the thermo-
4.6. COMPARISON OF ENERGY ESTIMATORS

dynamic energy estimator. Here, some results are shown that emphasize how this variance is reduced for some test cases.

4.6.1 CONVERGENCE OF ERROR BARS

The first test one may want to perform is to check whether the variance is actually reduced for the centroid virial estimator versus the thermodynamic estimator. First, we look at the raw output of the energy for a test case of 3d $^4$He. This data was generated for a system of 4 particles in the canonical ensemble at $T=5K$, a density of $0.02198 \text{ Å}^{-3}$ in a cubic container with walls sized at $5.67 \text{ Å}$, and an imaginary time step size of $\tau=0.004 \text{ K}^{-1}$. The instantaneous energy measurements as a function of Monte Carlo bin number may be seen in Figure 4.6.

![Graph of energy vs. MC bin number](image)

Figure 4.6: Testing centroid virial energy estimator. Shown is the instantaneous energy vs. MC bin number for 3d bulk He-4.

4.6. The data plotted is just the last 2000 binned data points from a run which performed
4.6. **COMPARISON OF ENERGY ESTIMATORS**

10^6 measurements. One may see how much closer the instantaneous measurements of the energy are to each other for the centroid virial energy versus the thermodynamic estimator. Clearly the centroid virial energy estimator fluctuates less than does the thermodynamic energy estimator. To see just how much this reduces the variance, we can observe the accumulated average of this data, which may be see in Figure 4.7. One can immediately see how the variance is reduced for the centroid virial energy estimator versus the thermodynamic energy estimator and they agree to within error bars, as they should. This provides support for the centroid virial estimator being a superior way to measure the energy of a quantum system. The next obvious course of action was to investigate the relationship between the virial window size and the variance.

![Figure 4.7: Testing centroid virial energy estimator. Shown is the accumulated average of the energy vs. MC bin number for 3d bulk He-4.](image)

The variance is reduced for the centroid virial energy estimator versus the thermodynamic energy estimator and they agree to within error bars, as they should. This provides support for the centroid virial estimator being a superior way to measure the energy of a quantum system. The next obvious course of action was to investigate the relationship between the virial window size and the variance.
4.6. COMPARISON OF ENERGY ESTIMATORS

4.6.2 Virial Window Scaling

If one looks at the centroid virial energy estimator, it can be seen upon inspection that if we let the virial window size \( L = 1 \), then this estimator reduces simply to the thermodynamic energy estimator. So the next test is to see how the variance acts as a function of this window size for 3d bulk (periodic boundary conditions in all three dimensions) \(^4\text{He}\). First, a system size of \( N = 4 \) (in a cubic cell with wall size of 5.67Å and \( \tau = 0.004K \)) was examined in the canonical ensemble for temperatures \( T = 2 \) kelvin and \( T = 5 \) kelvin. These had the density which corresponds to when \(^4\text{He}\) is under saturated vapor pressure.

![Figure 4.8: Energy vs. virial window (L) size for 3d He-4 with a system size of N=4 particles at a temperature of 5 kelvin.](image)

In Figure 4.8 we see that the variance shrinks with increasing virial window size by a
4.6. **COMPARISON OF ENERGY ESTIMATORS**

noticeable amount up until around $L = 5$ or 6. The next figure shows roughly this same scaling when the temperature is lowered below the critical point. These average values agree to within errorbars.

Next, this same analysis was performed for a system of 16 $^4$He atoms in a cubic cell with wall size of 8.99Å under the same physical conditions in the canonical ensemble, at a temperature of $T=5$ K. The results from this may be seen in Figure 4.10.

As can be seen, the variance is reduced substantially under an increase in virial window size from $L=1$ to roughly $L=5$, but past that there is no noticeable reduction. This is an important analysis to perform each time that one wants to study a new quantum system. The reason being that this window size can be as large as the number of imaginary time slices.
4.7. SPECIFIC HEAT ESTIMATOR

Figure 4.10: Energy vs. Virial Window (W) size for 3d He-4 with a system size of N=16 particles at a temperature of 5 kelvin.

and the larger that one makes this window size, the less efficient the PIMC code becomes. For larger system sizes, this scaling can drastically slow down the energy estimator. It has been deduced here that for $^4$He systems, a value of $L=5$ will sufficiently lower the variance in the energy estimator.

4.7 SPECIFIC HEAT ESTIMATOR

Using the specific heat estimator

$$\frac{\langle C_V \rangle}{k_B \beta^2} = \langle E_T E_{cv} \rangle - \langle E_{cv} \rangle^2 - \langle \frac{dE_{cv}}{d\beta} \rangle,$$  \hspace{1cm} (4.86)
the error estimation is less trivial than some estimators due to the fact that the expected values of correlated data are summed. For compound estimators, one must propagate the errors correctly to get meaningful error bars. Alternatively, methods such as jackknife and bootstrap may be used. These methods are outlined in the Appendix E.

A test system for this estimator is one boson in a 1d quantum harmonic oscillator since this model is exactly soluble. If the fundamental frequency of the oscillator is $\omega_0$ then the eigenenergies are $E_n = (n + 1/2)\hbar\omega_0$ where $n \in \mathbb{Z}$, and therefore the partition function is

$$Z = \frac{1}{2\sinh(\beta\hbar\omega_0/2)}.$$  \hfill (4.87)

Differentiating the partition function with respect to $\beta$ yields the expectation value of the energy:

$$\left\langle E \right\rangle = -\frac{\partial}{\partial \beta} Z = \frac{\hbar\omega_0}{2} \coth\left(\frac{\beta\hbar\omega_0}{2}\right).$$  \hfill (4.88)

We generally wish to work with a system of units where energy is given in kelvin and $\hbar\omega_0 = k_B$. Note that for this to be true, one must set the mass of the particle to $m = 48.48$ amu. To get energy in terms of kelvin we divide by the Boltzmann constant and therefore the energy becomes

$$\left\langle E \right\rangle_{k_B} = \frac{\hbar\omega_0}{2k_B} \coth\left(\frac{\beta\hbar\omega_0}{2}\right) = \frac{1}{2} \coth\left(\frac{1}{2T}\right).$$  \hfill (4.89)

Then, the expected value of the specific heat is given by

$$\left\langle C_V \right\rangle_{k_B} = -\frac{\partial}{\partial T} \left\langle E \right\rangle_{k_B} = \frac{1}{4T^2} \text{csch}^2\left(\frac{1}{2T}\right).$$  \hfill (4.90)

Below are plots of both energy and specific heat as a function temperature for a single particle in the 1d quantum harmonic oscillator. The numerical results agree with the exact results to within error bars.
4.8. LOCAL PERMUTATION NUMBER ESTIMATOR

When looking at the superfluid properties of quantum fluids in certain geometries, one may wish to gain knowledge of how the superfluid fraction changes as a function of position within the cell. In PIMC simulations of quantum fluids, the worldlines begin to permute
4.8. LOCAL PERMUTATION NUMBER ESTIMATOR

with one another below the temperature at which the sample begins to become superfluid. Here, we present a new estimator containing information about how 'linked' worldlines are with one another as a function of spatial position. This type of permutation occurs through moves such as the swap move discussed previously. One worldline may link up with another in such a way that they become a single worldline with $2M$ beads. This example would mean that there is a permutation number of 2.

As mentioned, we desire knowledge of how the worldlines are entangled as a function of spatial position, so naturally we would like to generate a histogram showing this information. Just such a histogram may be generated using the expression

\[ \rho_{\text{perm}} = \frac{1}{N_{\text{beads}}} \sum_{\text{beads}} \sum_i (P_i - 1) \delta(\vec{r}_i \in \Delta V), \]  

(4.91)

where $N_{\text{beads}}$ is the number of beads in volume $\Delta V$, $P_i$ is the permutation number associated with a given worldline at bead position $\vec{r}_i$ inside of the grid index $i$. Algorithmically, what this estimator does is start at a bead in a given worldline and sequentially loop over all other beads in the worldline, counting the number of beads in the worldline, until it returns to that from which it started. This is done for all worldlines in the simulation cell, which effectively assigns a permutation number, $P$ to each worldline. In the case that there is no linking present, the value of $P$ will be unity, and for each additional $M$ beads that are added to a worldline this increases the value of $P$ by one. Once the permutation number of a worldline is known, a tensor may be constructed that holds the sum of $P_i - 1$ for each grid point $i$ in space.

This estimator returns zero for all spatial gridpoints in the classical limit, which makes sense due to the fact that we expect to observe no superfluidity at higher temperatures. However, it is unclear exactly how to interpret the lower temperature case other than as a qualitative estimator that would tell us the relative amount of particles which are a part of the superfluid fraction in one spatial position versus another spatial position.
4.9 WINDING ESTIMATOR FOR SUPERFLUID FRACTION

One way of measuring the superfluid fraction of a sample within a PIMC method is to measure the winding number, $W$. The winding number is defined as the flux of paths that wind out of the cell via periodic boundary conditions times the length of the cell in that particular winding direction [45,48].

To picture this winding, notice how as we step through increasing imaginary time, the worldline in Figure 4.3 winds out of the right side of the cell in the $x$ direction and back in on the left to reconnect with where it started. If the cell was of length $L_x$ in the $x$ direction, then this would return a value of $L_x$ for $W$. If the worldline did this twice before returning to its starting position in imaginary time, then we would have $W = 2L_x$. Using this winding number, the superfluid fraction for a $d$-dimensional system is

$$\frac{\rho_s}{\rho} = \frac{\langle W^2 \rangle}{2d\beta\lambda N} = \frac{1}{2d\beta\lambda N} \sum_{j=1}^{d} \langle W_j^2 \rangle,$$ (4.92)

where $N$ is the number of particles in the simulation cell, $d$ is the dimensionality of the system, $\beta=1/T$ is the inverse temperature, $\lambda=\hbar^2/2mk_B$, and $W$ is the winding number. One may do a quick dimensional analysis and notice that this quantity is dimensionless, as it should be.

4.10 THERMODYNAMIC PRESSURE ESTIMATOR

One may measure the pressure of a quantum system with the thermodynamic pressure estimator. It is worth documenting this here because it has a term closely relating to one of the terms of the virial energy estimator, specifically the dot product of the bead positions of a worldline with the gradient of the potential action. Since this term was added to the group’s production code in adding the virial energy estimator, the pressure estimator has
4.10. THERMODYNAMIC PRESSURE ESTIMATOR

also been implemented.

4.10.1 Pressure Derivation

The general form of the pressure estimator, for local actions, is derived from the definition:

\[ \langle P \rangle = \frac{1}{\beta Z} \frac{\partial}{\partial \ell} Z, \]  

(4.93)

where \( \ell \) is the volume in 3\( d \), the area in 2\( d \), and the length in 1\( d \). In our simulations, the partition function, \( Z \), is of the form

\[ Z = c_1 \int \prod_{i=1}^{N} \prod_{\alpha=1}^{M} dr_{i,\alpha}^{d} \exp \left[ - \beta \sum_{\alpha=1}^{M} \left( c_2 \sum_{i=1}^{N} (\vec{r}_{i,\alpha+1} - \vec{r}_{i,\alpha})^2 + \frac{1}{\tau M} U(\vec{R}_\alpha) \right) \right], \]  

(4.94)

where \( U \) is the potential action defined earlier, \( d \) is the dimensionality of the system, and the previously undefined constants are

\[ c_1 = \frac{1}{N!} (4\pi \lambda \tau)^{-dNM/2} \]  

(4.95)

and

\[ c_2 = \frac{1}{4\lambda \beta \tau}. \]  

(4.96)

We begin by making the substitution \( \bar{s}_{i,\alpha} = \ell^{-1/d} \bar{r}_{i,\alpha} \), meaning \( ds_{i,\alpha}^{d} = \ell^{-1}dr_{i,\alpha}^{d} \) and \( \bar{\sigma}_\alpha = \ell^{-1/d} \bar{R}_\alpha \). Substituting this into our expression for the partition function, we get

\[ Z = c_1 \ell^{NM} \int \prod_{i=1}^{N} \prod_{\alpha=1}^{M} ds_{i,\alpha}^{d} \exp \left[ - \beta \sum_{\alpha=1}^{M} \left( c_2 \ell^{2/d} \sum_{i=1}^{N} (\bar{s}_{i,\alpha+1} - \bar{s}_{i,\alpha})^2 + \frac{1}{\tau M} U(\ell^{1/d} \bar{\sigma}_\alpha) \right) \right]. \]  

(4.97)
4.10. THERMODYNAMIC PRESSURE ESTIMATOR

Now, we take the derivative of this with respect to the volume (or equivalent $\ell$ for $d < 3$):

$$
\frac{\partial}{\partial \ell} Z = \frac{NM}{\ell} Z + c_1 \ell^{NM} \int \prod_{i=1}^{N} \prod_{\alpha=1}^{M} d\vec{s}_{i\alpha} \frac{\partial}{\partial \ell} \exp \left[ -\beta \sum_{\alpha=1}^{M} \left( c_2 \ell^{2/d} \sum_{i=1}^{N} (\vec{s}_{i,\alpha+1} - \vec{s}_{i,\alpha})^2 + \frac{1}{\tau M} U(\ell^{1/d} \vec{\sigma}_{\alpha}) \right) \right].
$$

This second term is evaluated using the chain rule. The result is

$$
\frac{1}{Z} \frac{\partial}{\partial \ell} Z = \frac{NM}{\ell} Z + \frac{c_1 \ell^{NM}}{Z} \int \prod_{i=1}^{N} \prod_{\alpha=1}^{M} d\vec{s}_{i\alpha} \exp \left[ -\beta \sum_{\alpha=1}^{M} \left( c_2 \ell^{2/d} \sum_{i=1}^{N} (\vec{s}_{i,\alpha+1} - \vec{s}_{i,\alpha})^2 + \frac{1}{\tau M} U(\ell^{1/d} \vec{\sigma}_{\alpha}) \right) \right] \left[ -\beta \sum_{\alpha=1}^{M} \left( \frac{2}{d} c_2 \ell^{2/d} \sum_{i=1}^{N} (\vec{s}_{i,\alpha+1} - \vec{s}_{i,\alpha})^2 + \frac{1}{\tau M} \frac{\partial}{\partial \ell} U(\ell^{1/d} \vec{\sigma}_{\alpha}) \right) \right].
$$

Notice that this second term is the integral of the probability distribution multiplied by the argument of the exponential function, all divided by the partition function. This is an expectation value of the argument of the exponential function. This leaves the expression for the pressure as

$$
P = \frac{NM}{\ell \beta} - \left\langle \sum_{\alpha=1}^{M} \left( \frac{2}{d} c_2 \ell^{2/d} \sum_{i=1}^{N} (\vec{s}_{i,\alpha+1} - \vec{s}_{i,\alpha})^2 + \frac{1}{\tau M} \frac{\partial}{\partial \ell} U(\ell^{1/d} \vec{\sigma}_{\alpha}) \right) \right\rangle.
$$

We may convert the third term into a more useful form by noticing that $U = U(\vec{R}_\alpha(\ell))$ where $R_\alpha$ keeps track of all bead positions at time slice $\alpha$. We let our dimensionless variable $\vec{s}$ now stand for all reduced variables at time slice $\alpha$, as we will get rid of this variable anyway.

Calling upon the chain rule for gradients,

$$
\frac{\partial}{\partial \ell} U(\vec{R}_\alpha(\ell)) = \nabla U(\vec{R}_\alpha) \cdot \frac{\partial}{\partial \ell} \vec{R}_\alpha = \nabla U(\vec{R}_\alpha) \cdot \frac{\partial}{\partial \ell} \ell^{1/d} \vec{\sigma}_\alpha = \frac{1}{d} \nabla U(\vec{R}_\alpha) \cdot \ell^{(1-d)/d} \vec{\sigma}_\alpha = \frac{1}{d} \nabla U(\vec{R}_\alpha) \cdot \vec{R}_\alpha.
$$
4.10. THERMODYNAMIC PRESSURE ESTIMATOR

Inserting this into our latest expression for the pressure and grouping like terms, we obtain

\[
P = \frac{1}{d\ell \tau} \left[ dN - \left\langle 2\tau c_2 \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\tilde{r}_{i,\alpha+1} - \tilde{r}_{i,\alpha})^2 + \frac{1}{M} \sum_{\alpha=1}^{M} \tilde{R}_{\alpha} \cdot \nabla U(\tilde{R}_{\alpha}) \right\rangle \right].
\] (4.102)

Now, we can insert the constant \(c_2\) back in to get to the final expression, given as

\[
P = \frac{1}{d\ell \tau} \left[ dN - \left\langle \frac{1}{2\lambda^3} \sum_{\alpha=1}^{M} \sum_{i=1}^{N} (\tilde{r}_{i,\alpha+1} - \tilde{r}_{i,\alpha})^2 \right\rangle - \left\langle \frac{1}{M} \sum_{\alpha=1}^{M} \tilde{R}_{\alpha} \cdot \nabla U(\tilde{R}_{\alpha}) \right\rangle \right].
\] (4.103)

Notice that the third term above also exists in the expression for the virial energy estimator in Equation (4.69). As for the energy estimator, the above expression can probably be extended to a centroid virial term, but this is not done here at this time. So far, this is for local actions (those interacting only across a single time slice). It is likely very easy to extend this pressure estimator to work for non-local actions.

4.10.2 PRESSURE IN ENGINEERING UNITS

Here, we convert from the pressure in our units \(K/\AA^3\) to atmospheres (atm). Looking at the boundary term, we convert the units to Pascals as follows:

\[
\begin{bmatrix} N \\ \tau V \end{bmatrix} = \frac{K}{\AA^3} = \frac{K}{\AA^3} \cdot 10^{30} \cdot \frac{\AA^3}{m^3} \cdot k_B \cdot J = k_B \cdot 10^{30} \cdot \text{Pa}.
\] (4.104)

Then, noting that 1 atm = 101325 Pa, we end up with

\[
\frac{K}{\AA^3} = \frac{k_B 10^{30}}{101325} \text{ atm} \approx 136.259 \text{ atm}.
\] (4.105)

100
Chapter 5

PIMC Studies of Confined He-4

There has been much interest in confined $^4$He systems which exhibit coupling and enhanced
proximity effects, both in the theoretical and experimental condensed matter community.
The experimental data [22] is not amenable to any classical explanation [27] so there is
much work to be done to fully explore the physics of these systems. The superfluid tran-
sition of $^4$He falls into the classical 3d XY universality class, however the existence of the
superfluid phase is attributed to quantum mechanical effects. Due to the shortcomings of
the theoretical work done so far, path integral Monte Carlo is a necessary tool for studying
systems which exhibit enhanced coupling and proximity effects.

Here, we present a path integral Monte Carlo study of proximity effects in superfluid
helium. We begin by defining a simulation cell that allows for the study of 3d spatial
regions coupled to contiguous 2d spatial regions. A new estimator is presented that has
never before been presented in any literature. This estimator, referred to as the angular
winding estimator, explicitly shows how coupling of regions may occur at distances larger
than the helium correlation length. The angular winding estimator also allows us to see
that the enhanced proximity effects are due in large part to the indistinguishable nature of
helium-4, thus showing that the work done thus far [27] falls short of being able to fully
explain the experimental results obtained by Gasparini et al.
5.1 CONFINEMENT SIMULATION CELL

In order to study a system with contiguous regions having different transition temperatures, a special type of simulation cell was devised. One such cell may be imagined where there is some spatial region that is inaccessible to the atoms within the cell. This excluded region could be positioned within the cell so that the inhabitants of the cell are confined to certain geometries. The implementation of this exclusion is possible by either making the potential inside of the spatial region arbitrarily high so that no Monte Carlo moves into the region are ever accepted or by creating a cell which actually has walls with a surface potential. Either way, the cell will look like that in Figure 5.1. For our purposes, the excluded region is kept empty by setting the potential inside of that region arbitrarily high so that no proposed
5.1. **CONFINEMENT SIMULATION CELL**

Monte Carlo moves will result in any beads being moved into that region. It is important to note that this cell has periodic boundary conditions in all three spatial dimensions in order to alleviate some of the dependence on the finite size of the system. Because of this, one may view the simulation cell given in Figure 5.1 as being identical to that in Figure

![Diagram](image)

Figure 5.2: Another way to view PIMC simulation cell with excluded volume. Due to PBC this is the same as when the volume is excluded from the center.

5.2. The lengths $L_x$, $L_y$, $L_z$ define the size of the cell while $a_y$, $a_z$, and $S$ will be discussed shortly.

The atoms are never to enter the excluded region, so it is imperative that we carefully check that this doesn’t happen. As such, it was helpful to generate histograms of average particle positions as the PIMC simulations were performed. The histograms generated were done as projections into either the $xy$, $xz$, or $yz$ planes, where the normalization is such that the values are read as particle per cubic angstrom.

It turns out that this way of excluding volume has one particular benefit that was
5.1. CONFINEMENT SIMULATION CELL

unexpected. In surface physics, often one will see what is called a ‘wetting’ layer when a fluid is adsorbed onto a surface. Directly on the surface, we see a layer of adsorbed atoms or molecules, then there will be a lower density region followed by the bulk substance. This is generally attributed to the integrated Lennard Jones 6-12 potential of the constituent atoms of the surface. Here there is no surface potential defined, yet we still observe the wetting layer.

It may be seen from Figures 5.3 and 5.4 that the volume exclusion works with the method we have chosen, and as mentioned a somewhat artificial wetting layer contributes to making this excluded volume act more like it has an attractive surface potential, as would be the case for an experimental setup.

This simulation cell may be used to study both planar confinement in the case that $a_z = 0$ and two bulk regions connected by a film in the case that $a_z$ is larger than the correlation length and $a_y$ is close to the magnitude of the correlation length. In this work we choose to study the latter case.

5.1.1 Modified Insert Update

In order to preserve detailed balance in our Monte Carlo sampling for a simulation cell such as the one proposed here, one must modify the insert worm move discussed in Section 4.3. If proposed insert moves randomly sample all coordinates of the simulation cell without regard to whether they are part of the excluded volume or not, this makes the probability of successfully inserting a worm less than it actually should be. This violates detailed balance, and must be accounted for when performing these simulations. This problem is fixed by simply never attempting an insert move in the excluded volume region.

Assume that we are working with the excluded volume cell in the regime where we have $a_z$ and $a_y$ set up to have two bulk regions connected by a film. If we want to perform an insert move, we will randomly choose whether to insert the worm into the film region
5.1. CONFINEMENT SIMULATION CELL

Figure 5.3: Spatial density histograms projected into the $xy$ and $xz$ planes for bulk helium-4 at SVP in a simulation cell with volume excluded from the center. This was for $T = 5$ K, time step $\tau = 0.004$ K$^{-1}$. 
5.2. COUPLED 3D AND 2D REGIONS

Figure 5.4: Spatial density histogram projected into the \(yz\) plane for bulk helium-4 at SVP in a simulation cell with volume excluded from the center.

with probability \(P_{\text{film}} = V_{\text{film}}/V\), where \(V = V_{\text{film}} + V_{\text{bulk}}\), or into the bulk region with probability \(P_{\text{bulk}} = V_{\text{bulk}}/V\). This makes it equally probable to try an insert into any region of accessible space in the cell. Once a region is chosen to try to insert a worm, the spatial coordinates of this worm are randomly generated to place the worm somewhere inside of the chosen spatial region.

5.2 COUPLED 3D AND 2D REGIONS

If we want to study a system with contiguous 3d and 2d regions, then we could examine the case of a thin film connecting 3d bulk regions. We refer to the separation between the 3d regions as the bulk separation, and define it as \(S = |L_z - 2a_z|\), as in Figures 5.1 and 5.2.

It is of interest to study how changing this bulk separation affects physical observables such as energy, specific heat, and superfluid density. If these observables are to be measured in some meaningful manner then one must carefully consider how to set up the simulations to make sure that changes in observables are caused by changing things such as temperature and bulk separation rather than other parameters which are not of interest.
5.2. COUPLED 3D AND 2D REGIONS

5.2.1 Scaling of the Density with Chemical Potential

In order to study this system near experimental conditions, we require that the bulk region have roughly the 3d bulk density and the film region have roughly the 2d density, both under saturated vapor pressure (SVP). We choose to work in the grand canonical ensemble rather than the canonical because this more closely resembles experimental conditions where there is some reservoir of $^4$He that is allowed to come into or out of the simulation cell. In this case, the chemical potential generally stays fixed and as the temperature changes the density of the sample may fluctuate slightly. Therefore, if one is working in the grand canonical ensemble then it is necessary to determine a chemical potential which will allow this to

![Graph showing bulk and film density vs chemical potential scaling for different values of bulk separation. This was done at $T = 1K$ for a system with $a_z = 47.5\text{Å}, a_y = 4\text{Å}$, and $L_y = L_x = 12\text{Å}$.]

Figure 5.5: Bulk and film density vs chemical potential scaling for different values of bulk separation. This was done at $T = 1K$ for a system with $a_z = 47.5\text{Å}, a_y = 4\text{Å}$, and $L_y = L_x = 12\text{Å}$. 

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be so over a range of $S$ as well as a range of temperatures. The initial scaling performed was that of spatial density as a function of chemical potential. In this scaling, the bulk density was measured separately from the film density. The film density is reported as the 3d density in the film region projected down onto the film ‘area’. It is clear from Figure 5.5 that the chemical potential that gives the correct bulk density for all $S$ values of interest is $\mu \approx -3$K. However, at this chemical potential, the 2d regions are practically empty for all values of $S$. This means that a different value of chemical potential is necessary in the film region to achieve the 2d SVP density. It is well known that 2d helium has a higher chemical potential at SVP than does 3d helium at SVP [49]. In order to fix this problem, one may simply introduce a lower potential in the film region.

### 5.2.2 Lower Potential in the Film Region

Since we are working in the grand canonical ensemble, the energy of our system with chemical potential $\mu$ is given by

$$
\mathcal{H} = \left( \sum_{i=1}^{N} T_i \right) + \left( \sum_{i=1}^{N} V_i \right) - \mu N = \left( \sum_{i=1}^{N} T_i \right) + \sum_{i=1}^{N} \left( V_i - \mu \right),
$$

where $N$ is the number of particles and we have averaged over all time slices for each particle in the case of quantum Monte Carlo. The sum over potentials actually needs to be a double sum for the case of interaction potentials, but for clarity we assume that this sum will be performed for each individual particle indexed by $i$. In the previous section, we determined a value of chemical potential which gives the desired 3d density, so we denote this value as $\mu$ here and refer to it as the bulk chemical potential. This means that the energy in the bulk region is given by Equation (5.1).

From Figure 5.5 it is clear that the chemical potential in the film region must be higher than that of the bulk region. This means that we desire a chemical potential of the form...
5.2. COUPLED 3D AND 2D REGIONS

\[ \mu_{\text{film}} = \mu + \mu_{\text{extra}}. \]

This means that the energy of the film will become

\[ \mathcal{H}_{\text{film}} = \left( \sum_{i=1}^{N} T_i \right) + \sum_{i=1}^{N} \left( V_i - (\mu + \mu_{\text{extra}}) \right) = \left( \sum_{i=1}^{N} T_i \right) + \sum_{i=1}^{N} \left( (V_i - \mu_{\text{extra}}) - \mu \right), \quad (5.2) \]

which tells us that this value \( \mu_{\text{extra}} \) is exactly equal to the amount that needs to be subtracted from the potential energy of each particle in order to supply the correct chemical potential to the film region.

5.2.3 SCALING OF THE DENSITY WITH FILM POTENTIAL ENERGY

Upon becoming convinced that lowering the potential in the film region is a suitable way to account for the difference in chemical potential, one may see from Figure 5.5 that as \( S \) increases, the potential must be lowered. There is a physical justification for this, as can be

![Figure 5.6: Bulk and film density vs film potential shift scaling for different values of bulk separation. This was done at \( T = 1\text{K} \) for a system with \( a_z = 47.5\text{Å}, a_y = 4\text{Å}, \) and \( L_y = L_x = 12\text{Å}. \)]
5.2. **COUPLED 3D AND 2D REGIONS**

seen by considering a surface consisting of atoms possessing Lennard-Jones type interaction potentials. If you consider the Lennard-Jones semi-infinite half-space, and then trim down one of the dimensions to create an object which is infinite in one direction, semi-infinite in another direction, and having width $S$ in the third direction (see Appendix F) then you find that as $S$ increases, the potential well minimum decreases. This means that as our bulk separation increases, we are justified in decreasing the potential in the film region. The data showing suitable values of the potential shift for the film region is displayed in Figure 5.6.

As is customary for scaling analyses, the first range of jobs submitted for locating the correct potential shifts were over a wide range of potential shift values ($V = -5K \rightarrow -1K$) in relatively low resolution ($\Delta 1K$) and then data was collected at a higher potential shift

![Figure 5.7: Bulk and film density vs film potential shift scaling for different values of bulk separation for bosonic systems. This was done for a system with $a_z = 47.5\,\text{Å}, a_y = 4\,\text{Å},$ and $L_y = L_x = 12\,\text{Å}$. Temperatures above, near, and below the bulk critical transition temperature were tested.](image)
5.2. **COUPLED 3D AND 2D REGIONS**

resolution ($\Delta 0.1K$) around the corresponding shifts of interest for each bulk separation. After this scaling was done at temperature $T = 1K$, it was necessary to check that the same potential shift yields constant bulk and film densities as $S$ changes for higher temperatures. The data in Figure 5.7 shows that there exist film potential shift values for $S = 5, 10, 20, 40 \text{ Å}$. This was done for a system with $a_z = 47.5 \text{ Å}, a_y = 4 \text{ Å}$, and $L_y = L_x = 12 \text{ Å}$. Temperatures above, near, and below the bulk critical transition temperature were tested.

![Graph showing bulk and film density vs film potential shift scaling for different values of bulk separation for Boltzmann systems](image)

Figure 5.8: Bulk and film density vs film potential shift scaling for different values of bulk separation for Boltzmann systems. This was done for a system with $a_z = 47.5 \text{ Å}, a_y = 4 \text{ Å}$, and $L_y = L_x = 12 \text{ Å}$. Temperatures above, near, and below the bulk critical transition temperature were tested.

which allow for us to report $\rho_{\text{film}} = 0.043 \pm 0.006 \text{ Å}^{-2}$ and $\rho_{\text{bulk}} = 0.0220 \pm 0.0007 \text{ Å}^{-3}$, which are within 7% and 3% of 2d SVP and 3d SVP densities respectively. These values are given in Table 5.1. It is important to note that the film or bulk densities do not change noticeably

<table>
<thead>
<tr>
<th>$S$ [Å]</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{\text{film}}$ [K]</td>
<td>-0.3</td>
<td>-2.9</td>
<td>-4.5</td>
<td>-4.9</td>
</tr>
</tbody>
</table>

Table 5.1: Film potential values, $V_{\text{film}}$, that give desired film and bulk densities for different bulk separations, $S$. Note that these are the same for bosons and Boltzmannons.
between simulations of distinguishable or indistinguishable particles. To see this, refer to Figure 5.8, where we have considered it sufficient to show that the densities are constant for the $S = 5, 10$ cases independently, and so the densities for all other bulk separations should not depend upon the quantum statistics of the particles outside of error bars.

5.3 Non Trivial Topological Winding

One may look to see whether any worldlines wrap entirely around the excluded volume to form a non-trivial topological winding that will be referred to as the angular winding. This would cause the projection into the $yz$ plane of the region enclosed by the worldline to no longer be a simply connected region, as the worldline could never shrink to a point because it winds around a spatial region that it cannot enter. Such a configuration would look like that shown in Figure 5.9.

Figure 5.9: Snapshot of worldline winding around excluded volume, taken from an actual PIMC simulation below the critical temperature. The worldline configurations were written to disk and this data was converted to a visual Python scene, which was then converted into a POVray image. The beads belonging to the winding worldline are seen in blue, while all beads belonging to non-winding worldlines may be seen in white.
5.3. **NON TRIVIAL TOPOLOGICAL WINDING**

The way to measure this winding is to integrate over the projected angle from somewhere inside the excluded volume to each bead of a worldline. In practice, the excluded volume is centered at the origin and this integration is actually a sum since our worldlines are discrete. The angular winding estimator for one particle then takes the form

$$W_\theta = \frac{1}{2\pi} \int_0^{\hbar \beta} d\tau \left( \frac{d\theta}{d\tau} \right) \approx \frac{1}{2\pi} \sum_{\alpha=1}^{\tilde{M}} \Delta_\alpha, \quad (5.3)$$

where the sum is over $\tilde{M}$ beads in a worldline and $\Delta_\alpha \equiv \theta_\alpha - \theta_{\alpha-1}$. This estimator will return $W_\theta = n$ where $n \in \mathbb{Z}$. Notice that if a given worldline is not entangled with any others, $\tilde{M}$ is simply the $M$ that has been discussed throughout this work, but otherwise it will be an integer multiple of this value. One must also notice that periodic boundary conditions in imaginary time must be enforced such that $\Delta_{\tilde{M}} = \theta_0 - \theta_{\tilde{M}}$.

Note that spatial periodic boundary conditions must be disregarded when computing this estimator by allowing for the position of a particle to be located outside of the cell.

![Figure 5.10: Schematic of the components of the summand for the winding number estimator for a worldline winding around the excluded volume (left) where $W_\theta=1$ and a worldline not enclosing the excluded volume (right) where $W_\theta=0$. Excluded volume shown as the dark rectangular box.](image-url)
5.3. NON TRIVIAL TOPOLOGICAL WINDING

Figure 5.10 gives an illustration of what a worldline would look like in the case that it wound around the excluded volume once and in the case that it did not wind around the excluded volume at all. It is obvious that integration of the projected angle from the origin around this closed path will yield zero for the non-winding case, as $\Delta_0$ through $\Delta_5$ are exactly cancelled by $\Delta_6$ through $\Delta_8$, as seen on the right in Figure 5.10. The winding case on the left in Figure 5.10 clearly evaluates to one.

This angular winding is the primary novel contribution of this work and will ultimately be used to quantify the nature of the enhanced proximity effects. It helps identify the extent to which particles exist simultaneously in the regions of different dimension. The fact that it shows this through the quantum paths provides strong evidence for the fact that the enhanced proximity effects are truly of quantum mechanical origin.

5.3.1 NORMALIZATION OF ANGULAR WINDING

We choose to report this estimator similar to the way that the superfluid fraction is computed in Equation (4.92). The normalization for the superfluid fraction is chosen such that the value limits to one as we simultaneously approach the thermodynamic limit and the temperature approaches zero.

Imagine the limit where $a_y$ and $a_z$ become small enough that the excluded volume leaves only enough room for one layer of atoms on any side of it, as in Figure 5.11. In this case the number of particles in the cell, $N$, will be called $N_{\text{layer}}$, so as not to confuse this quantity with the number of...
5.3. NON TRIVIAL TOPOLOGICAL WINDING

particles in our film region or with the total number of particles in the cell. This configuration is topologically equivalent to a 2d film, as can be seen in Figure 5.12. The

transformation from one to the other is done by ‘unrolling’ our cell as displayed in Figure 5.12. This is possible due to the spatial periodic boundary conditions. Our normalization is chosen such that in the limit that the accessible space inside of the excluded volume cell becomes 2d, our estimator matches the component of $\rho_s/\rho$ in the unrolled direction. Once unrolled, our transformed 2d cell now has a length $L_{cell} = 2(S + L_y)$ in the unrolled direction.
5.3. NON TRIVIAL TOPOLOGICAL WINDING

so the standard winding estimator returns $L_{\text{cell}}$. The normalized angular winding estimator is normalized by taking the denominator of Equation (4.92) and replacing $N$ with $N_{\text{layer}}$ then inserting $L_{\text{cell}}^2 = 4(S + L_y)^2$ into the numerator, giving it the form

$$\Omega = \frac{L_{\text{cell}}^2}{\beta \lambda N_{\text{layer}}} \langle W_\theta^2 \rangle,$$

(5.4)

where $N_{\text{layer}}$ is the number of particles contained within a distance $a_y$ of the excluded volume (this includes those in the ‘corners’), $\beta = 1/k_B T$, and $\lambda = \hbar^2/2m$.

5.3.2 SCALING OF ANGULAR WINDING WITH BULK REGION SIZE

In reporting the normalized angular winding number estimator for a system, it is important to first determine how scaling of the size of the bulk region affects this winding. Schematically, this scaling is done as in Figure 5.13. The reason this scaling is necessary is that we want to work in a regime where the bulk regions are large enough that finite size effects are minimized. As our main interests lie within a temperature range below $T_\lambda$, we report this scaling for temperatures, $T=2K$ and $T=1.5K$. The results of this scaling for a simulation cell size of $L_x=L_y=12$ Å and $S = 5$ Å showed that the finite size effects have a significant impact on our winding estimator. The smallest $L_z$ values, 20 Å, corresponds with bulk regions of size 7.5 Å and the largest $L_z$ value, 150 Å, corresponds with bulk regions of size 72.5 Å. Figure 5.14 shows that the angular winding number converges as a function of $L_z$ (hence bulk size) at around $L_z=100$ Å, corresponding with a bulk size of 47.5 Å. This convergence was then seen again when the scaling was performed for a system with
5.3. NON TRIVIAL TOPOLOGICAL WINDING

Figure 5.14: Scaling of Normalized Angular Winding number with the bulk region size. This was for a cell size of $L_x=L_y=12$ Å and $S=5$ Å at a temperature $T=2K$.

Figure 5.15: Scaling of Normalized Angular Winding number with the bulk region size for a cell size of $L_x=L_y=12$ Å and $S=20$ Å at a temperature $T=1.5K$. 
5.3. NON TRIVIAL TOPOLOGICAL WINDING

bulk separation $S = 20$ Å at $T=1.5K$. Results for this may be seen in Figure 5.15. This convergence of winding as a function of increasing bulk extent helped identify a cell size that would minimize finite size effects while still working with a number of particles that would give data in a reasonable amount of time.

5.3.3 SCALING OF ANGULAR WINDING WITH BULK SEPARATION

Here we present how the angular winding is affected as the bulk separation varies while keeping the bulk regions the same size. This scaling was done at $S = 5,10,20$ Å for bosons and for $S = 5$ Å for Boltzmannons. These simulations were done for time step $\tau = 0.004$

![Figure 5.16: Scaling of Normalized Angular Winding number with the bulk region separation for a cell size of $L_x=L_y=12$ Å.](image)

Figure 5.16: Scaling of Normalized Angular Winding number with the bulk region separation for a cell size of $L_x=L_y=12$ Å.
5.3. NON TRIVIAL TOPOLOGICAL WINDING

K$^{-1}$. The average film densities may be seen in Figure 5.17. It can be seen that all film densities are within about 7% of the 2d film density under saturated vapor pressure. This is critical because we know that any differences we see in the winding as a function of varying

![Figure 5.17: Film density as a function of temperature for various values of bulk separation.](image)

$S$ from Figure 5.16 are not due to the particle density in the film region. When looking at the angular winding signal as a function of temperature for various values of bulk separation, many important points may be noted. First of all, the signal becomes non-zero remarkably close to the superfluid transition temperature and that its slope starts to decrease by around $T = 0.75$ K. For systems with a larger bulk separation, this transition occurs at a lower temperature. This is not all that surprising, as going below the transition temperature causes the worldlines to ‘expand’, which gives way to the standard type of winding with
5.3. *NON TRIVIAL TOPOLOGICAL WINDING*

which the superfluid fraction is measured. In looking at Figure 2.6, one notices that this winding occurs at $S$ values greater than either the de Broglie wavelength or the correlation length.

Another point of interest lies in looking at the angular winding signal as a function of increasing bulk separation. Experimentally, when the bulk regions were farther apart the superfluid response was decreased. This angular winding is also suppressed whenever the bulk regions are separated by a larger distance. In the path integral representation of quantum mechanics, we may understand quantum fluctuations by visualizing particle worldlines spreading out and fluctuating in imaginary time. When these worldlines wind around the excluded volume they are contributing to the enhanced proximity effects of the system due to the fact that we have individual particles simultaneously fluctuating between 2d and 3d regions, even across a distance much greater than the correlation length. These fluctuations are known to stabilize the superfluid phase of matter, and here it appears that they also contribute to enhanced proximity effects in confined systems.

One feature that is certainly not to be overlooked here is the difference between the indistinguishable (boson) particles and the distinguishable (Boltzmannon) particles. These particles were treated as Boltzmannons by not performing any *swap* moves, which were depicted in Figure 4.2. Treating the particles as distinguishable resulted in a drastic difference in the angular winding signal. When particles are allowed to be truly indistinguishable, they are allowed exchange. This exchange occurs quantum mechanically through these swap moves where one particle may swap links with another. This results in much greater fluctuations and hence a larger angular winding signal. This provides more support for the fact that the enhanced proximity effects truly are a quantum mechanical effect and cannot be attributed to classical phenomena [27].
5.3. NON TRIVIAL TOPOLOGICAL WINDING

5.3.4 Superfluid Fraction of Confined Systems

Just as the angular winding varied as a function of changing bulk separation, so did the superfluid fraction. The same systems studied in the previous section had their superfluid response measured, and the results may be seen in Figure 5.18. It is interesting to note that the superfluid response is muted as the bulk separation is increased. This is also to be expected, as the larger excluded volume greatly inhibits the worldlines from winding in the two spatial dimensions in which translational symmetry has been broken. It would be ideal to be able to perform simulation very close to the critical temperature, as in Figure 2.8, however it would take a great deal of time to get converged data due to the critical fluctuations near the transition point so this study was not performed at this time.

Figure 5.18: Scaling of superfluid fraction as a function of temperature for a cell size of $L_x=L_y=12$ Å.

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Chapter 6

Prospects for Future Research

Here, a few possible avenues of interest are outlined that either stem directly from or are related to the work presented in this thesis.

6.1 Specific heat for our confined system

The experimental work that initially inspired the work presented in this thesis included enhanced specific heat measurements [26]. As a function of temperature, the specific heat for coupled systems shows a two-peak structure that is due to the different character of each coupled region. These plots were not generated in the current work, but if one were to want to study the specific heat of these confined systems then some of the preliminary work has been done, mainly in section 4.7.

6.1.1 Specific Heat of 3d Bulk Helium-4

To see how the specific heat changes in the confined cases, it is necessary to have knowledge of the specific heat for helium-4 in the bulk case.

A semi-empirical form for the specific heat of bulk $^4$He has been determined [50] by
6.2. PLANAR CONFINEMENT

Mehta et. al. from data collected above and below $T_\lambda$. The semi-empirical form is given by

$$C(t, \infty) = \left(\frac{A}{\alpha} t^{-\alpha} (1 + D t^{0.5}) + B\right) \left[1 + E \frac{t}{\ln t} + F \left(\frac{t}{\ln t}\right)^2\right],$$  \hspace{1cm} (6.1)

where the fitting parameters are dependent upon whether the temperature is above or below $T_\lambda$ and are given in Table 6.1.

<table>
<thead>
<tr>
<th>$T &lt; T_\lambda$</th>
<th>$A$ [J/ mol K]</th>
<th>$\alpha$</th>
<th>$B$ [J/ mol K]</th>
<th>$D$</th>
<th>$E$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8422</td>
<td>0.0134188</td>
<td>447.33</td>
<td>-0.023310</td>
<td>12.9425</td>
<td>138.719</td>
<td></td>
</tr>
<tr>
<td>$T &gt; T_\lambda$</td>
<td>6.1674</td>
<td>0.0134322</td>
<td>447.44</td>
<td>-0.02014</td>
<td>-20.566</td>
<td>-60.234</td>
</tr>
</tbody>
</table>

Table 6.1: Fit parameters for semi-empirical form of specific heat for bulk Helium-4.

These parameters were determined by analyzing multiple data sets of bulk data from various experimental groups. The data range over $10^{-8} < t < 0.07$, there $t$ is the reduced temperature previously defined. A plot of this fitting function can be seen in Figure 2.3, and this is exactly what is used as $C(\infty, t)$ in Equation (6.4). In order to properly use this equation along with the semi-empirical form of the specific heat to analyze the finite-size scaling, one needs to know the exponent $\alpha$. As mentioned in [51], the values of $\alpha$ between 0.011 and 0.014 will affect the scaling locus by only a few percent. As such, these exponents may be taken to be variables and one needs to choose a value that makes the data best follow Equation (6.4).

6.2 PLANAR CONFINEMENT

Bulk $^4$He has been experimentally confined from 3d to 2d in silicon wafers [21]. Far from the critical temperature, the specific heat behaves as if the sample were bulk 3d $^4$He, but as the temperature gets closer to the critical point (approaching from above), the specific heat hits a plateau where it deviates from bulk behavior. The larger the film width, the closer one must come to the critical point to see this plateau effect. It is believed that we can
6.2. PLANAR CONFINEMENT

reproduce this same type of result using PIMC simulations. In order to make this possible
with the simulation cell in Figure 5.1, we simply need to let \( a_z = 0 \) and our film width will
then vary as we vary \( a_y \).

6.2.1 SCALING OF THE SPECIFIC HEAT

The scaling of the specific heat and the superfluid density have been well studied both
theoretically and experimentally for a number of geometric confinements. For simplicity we
consider our system to have \( L_1 = L_2 = L_3 \equiv L \), and recognize that the bulk correlation
length \( \xi \) need be the only relevant length scale for the confined system. Then, the critical
part of the Gibbs free energy per atom [51], known as the scaling ansatz, may be expressed
as

\[
f(t, L) = t^{2-\alpha} Y(L/\xi),
\]

where \( t = |1 - T/T_\lambda| \) will hereby be referred to as the reduced temperature and \( \xi = \xi_0 t^{-\nu} \),
where \( \xi_0 \) is the correlation length amplitude in the confined case. The critical exponent is
given by \( \alpha \), just as in Equation (2.42), and the exponent \( \nu \) is related to \( \alpha \) by \( \alpha = 2 - 3\nu \).
The function \( Y \) will have a different form depending upon which type of confinement under
consideration. One may use the definition of the specific heat in terms of the second
derivative of free energy with respect to temperature to obtain

\[
C(l, T) = t^{-\alpha} g(l t^\nu)
\]

where \( l = L/\xi_0 \) and the function \( g(l t^{-\nu}) \) is a function of \( Y \) as well as its first and second
derivatives. If one wants to examine the case of \( l \to \infty \), then we expect to reclaim the bulk
specific heat, \( C(t, \infty) \). With this term being considered we may come up with a scaling
function for the specific heat, defined as the difference between the bulk and confined systems.
multiplied by some scaling function $t^\alpha$. This function has the form

$$\Delta C t^\alpha \equiv [C(t, \infty) - C(t, l)]t^\alpha = g_1(l t^{\nu}),$$

and is useful in comparing dimensional crossover data to what is predicted by theory.

It would be interesting to see that $C(l, t)$ of the confined systems studied in this thesis gave results which matched (after scaling) the experimental results that have been obtained.
Chapter 7

Conclusions

There has been much interest among members of the quantum fluids community in providing an explanation for the existence of enhanced proximity effects in helium confined to contiguous spatial regions having different superfluid transition temperatures. Beginning with the empirical evidence presented by the Gasparini group, researchers have been working towards understanding the underlying physics which drives this exotic behavior. There are those whom ascribe to the notion that because the superfluid transition falls into the classical 3d XY universality class, that these proximity effects are susceptible to a classical explanation. Although the transition falls into this universality class, it is actually quantum fluctuations which stabilize the superfluid phase of matter, and as such we feel that one must certainly take quantum mechanics into consideration when constructing a theory.

The path integral quantum Monte Carlo method, a stochastically exact numerical technique that maps a d-dimensional quantum system onto a d+1-dimensional classical system, is an ideal tool to use to probe systems which may exhibit enhanced proximity effects when confined to a similar geometry as the experimental cells. This method also allows us to treat particles as indistinguishable or distinguishable, which makes it even more alluring since this allows us to see the difference in a simulation of a classical particles versus a truly quantum mechanical system.
We began by designing a simulation cell which allows for contiguous 2d and 3d spatial regions of helium-4 to be simulated with the path integral Monte Carlo numerical technique, since 2d and 3d helium have different superfluid transition temperatures. This cell consisted of regions of zero potential and a region of extremely high potential, thus allowing no proposed Monte Carlo moves into this forbidden region to be accepted. The cell was given periodic boundary conditions in all three spatial dimensions in order to alleviate finite size effects. It was thoroughly tested that the inhabitants of the simulation cell were forbidden from entering this region and it was shown that this type of confinement even led to a semi-realistic wetting layer around the excluded volume just as one would see for a material with a long-range attractive surface potential. A chemical potential was chosen that best gave the density of bulk helium under saturated vapor pressure, however this chemical potential gave much too low of a 2d density in the film region. To account for this, the potential was lowered in the 2d spatial region of the simulation cell, with the justification that if the excluded volume were made of a Lennard-Jones type material then the potential actually would be lower in that region than in the bulk region.

With our new cell firmly in place and tested, we introduced a new estimator, called the angular winding estimator, which quantifies the extent to which a particle worldline winds around the excluded volume, extending into both the 2d regions and 3d regions simultaneously. Before we could run simulations measuring this new type of winding, we ran intensive finite-size scaling tests in order to make sure that we were working with a simulation cell that minimized finite size effects while also maximizing efficiency by allowing us to work with as few particles as possible. It was shown that two 3d regions separated by a 2d region start to exhibit angular winding at only a slightly lower temperature than the 3d superfluid transition temperature, and that it increases with temperature until reaching a plateau around a temperature of 0.5K.

It was shown that the angular winding signal, as well as the superfluid response, is
suppressed as a function of increasing separation distance between the 3d superfluid regions. This is consistent with empirical evidence presented in the literature. It was also shown that particles treated as distinguishable had a highly suppressed winding signal. These results lend themselves perfectly to a quantum mechanical explanation of the enhanced proximity effects.

In the path integral representation, superfluidity is driven by indistinguishable particle exchange causing worldlines to link up and eventually span the size of the system. In the presence of periodic boundary conditions, this manifests as a winding of worldlines around the boundaries. When bosonic helium-4 is confined to a volume with a non-trivial topology, where bulk three dimensional regions are coupled through a two dimensional film, winding between the 3d regions enhances the superfluid fraction of the film at length scales larger than the correlation length. This appears to be a profoundly quantum mechanical effect and would not be present for the case of distinguishable particles.

We have demonstrated that enhanced proximity effects observed experimentally were a direct result of the quantum mechanical nature of confined superfluid systems and could not be understood with a purely classical explanation. Treating the helium atoms as indistinguishable, as could only be the case for a quantum system, greatly increased the coupling between contiguous spatial regions of helium-4. This directly shows that the effects are due to quantum exchange, in agreement with our initial predictions.

We set out to show that the enhanced proximity effects observed experimentally were a direct result of the quantum mechanical nature of the confined superfluid systems and could not understood with a classical explanation. Treating the helium atoms as indistinguishable, as could only be the case for a quantum system, greatly increased the coupling between contiguous spatial regions of helium-4. This directly shows that the effects are due to quantum exchange and thus agree with our initial predictions.
APPENDIX A

PRESSURE TAIL CORRECTION FOR 1979 AZIZ POTENTIAL

Here we present the tail correction to the pressure for the 1979 Aziz interaction potential. Starting with Equation (2.15), we may substitute $\tau V_{\text{eff}} = U$ and expand the sum in terms of the explicit particle indices, yielding

$$P_{\text{tail}} = -\frac{\ell}{2d\ell M} \left\langle \sum_{\alpha=1}^{M} \sum_{j=1}^{N'} \bar{r}_{\alpha,j} \cdot \nabla_{\alpha,j} V_{\text{eff}}(\bar{r}_{\alpha,j}) \right\rangle,$$

where the factor of $1/2$ above is to avoid double counting the interaction potential, as the sum over particle labels is actually a double sum over interacting particles. The $\ell$ in the numerator comes the coordinate transform where we place one of the interacting particles at the origin, as in the derivation of the potential tail correction. If one is considering a particle at the origin interacting with a homogenous fluid outside of a sphere of radius $r_c$, then the thermal average may be converted to an integral. First, we see the sum over time slices should just yield $M$ times the sum over particle indices, and in this case the effective
potential is just the actual potential energy since this now looks classical. Hence

\[ P_{\text{tail}} = -\frac{1}{2d} \left\langle \sum_{j=1}^{N'} \vec{r}_j \cdot \nabla_j V(\vec{r}_j) \right\rangle. \quad (A.2) \]

Then, since we are considering a homogeneous fluid, this sum becomes an integral through the mapping

\[ \left\langle \sum_{j=1}^{N'} \vec{r}_j \cdot \nabla_j V(\vec{r}_j) \right\rangle \rightarrow \rho^2 \int d\vec{r} \vec{r} \cdot \nabla V(\vec{r}), \quad (A.3) \]

where the \( \rho^2 \) shows up for the same reason as in the derivation of the potential cutoff. This means that our pressure tail correction takes the form

\[ P_{\text{tail}} = -\frac{\rho^2}{2d} \int d\vec{r} \vec{r} \cdot \nabla V(\vec{r}), \quad (A.4) \]

where the radial part of the integral is from \( r_c \) to \( \infty \). Then, in the case of the 3d helium-4 being modelled with the 1979 Aziz interaction potential, this cutoff potential becomes

\[ P_{\text{tail}} = \frac{2\pi \epsilon \rho^2}{3} \left[ \frac{2r_m^6}{35L^2} (35C_6 L^4 + 28C_8 L^2 r_m^2 + 25C_{10} r_m^4) \right. \\
- \frac{A}{\alpha^3} (6r_m^3 + 6\alpha L r_m^2 + 3\alpha^2 L^2 r_m + \alpha^3 L^3) \exp\left[-\alpha L/r_m\right]. \quad (A.5) \]
APPENDIX B

RELATIONSHIP BETWEEN PARTITION FUNCTION AND DENSITY MATRIX

Here we show why the partition function of a quantum system is the trace of the thermal density matrix. Start with the Schrödinger equation:

$$\hat{H}\psi_j = E_j \psi_j.$$  \hfill (B.1)

Because $\psi_j$ is an eigenfunction of $\hat{H}$, we can write

$$\hat{H}^n \psi_j = E_j^n \psi_j,$$  \hfill (B.2)

and hence an analytic function of $\hat{H}$ acts on $\psi_j$ as

$$e^{-\beta \hat{H}} \psi_j = e^{-\beta E_j} \psi_j.$$  \hfill (B.3)

Now we multiply the entire expression through by $\psi_j^*$ and integrate over all coordinates (expressed by $\tau$, not to be confused with the imaginary time step in the PIMC literature)
with which $\psi_j$ depends. This results in

$$ e^{-\beta E_j} = \int d\tau \psi_j^* e^{-\beta \hat{H}} \psi_j $$  \hspace{1cm} (B.4)

due to the fact that $\psi_j$ is normalized and $e^{-\beta E_j}$ is simply a number. If we sum now over the index $j$, we see that the partition function emerges on the right side of the above expression as

$$ Z = \sum_j e^{-\beta E_j} = \sum_j \int d\tau \psi_j^* e^{-\beta \hat{H}} \psi_j. $$  \hspace{1cm} (B.5)

Notice that the summand on the right side of the above expression may be expressed in matrix notation as

$$ Z = \sum_j \int d\tau \psi_j^* e^{-\beta \hat{H}} \psi_j = \sum_j (e^{-\beta \hat{H}})_{jj}, $$  \hspace{1cm} (B.6)

where this is simply the trace of the full thermal density matrix, $e^{-\beta \hat{H}}$. 

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APPENDIX C

PIMC SAMPLE CODE

C.1 SIMPLE PIMC CODE

The purpose of this section is to outline the path integral Monte Carlo method in general by providing a simple working Python code that measures the average thermodynamic energy, potential energy and position for one particle in the 1d quantum harmonic oscillator at finite temperature. The primitive action is used, and the only MC moves performed are single bead moves and center of mass moves.

Improvements such as using an action more accurate than $O(\tau)$ and implementing multi-bead MC moves such as bisection and staging will make the code more efficient but these are not outlined here. The purpose of this omission is to make the general method as transparent as possible to the reader new to path integral Monte Carlo, in hopes that the information and references supplied throughout the body of this thesis may be used by the reader to write a complete PIMC code.
C.1. SIMPLE PIMC CODE

```python
# Simple PIMC algorithm for finite temperature quantum harmonic oscillator.
#
# Author: Max Graves
# Last Revised: 03.MAR.2014
#
import random
import numpy as np

def SingleBeadMove(beads, M, R, rat):
    'single bead displacement'
    move = rat * (2.0 * random.random() - 1)
    beads[R] += move
    return beads

def CenterOfMassMove(beads, M, R1):
    'function to move entire world line'
    for i in range(M):
        beads[i] += R1
    return beads

def harmonicPotential(m, w, pos):
    'return value for harmonic potential'
    return 0.5 * m * w * w * pos * pos

def thermodynamicEnergy(beads, tau, m, w):
    'thermodynamic energy estimator'
    M = float(len(beads))
    Energy = 0.5 / tau
    t2, t3 = 0.0, 0.0
    for i, bead in enumerate(beads):
        if i == 0:
            t2 += (beads[0] - beads[M - 1]) ** 2
        else:
            t2 += (beads[i] - beads[i - 1]) ** 2
            t3 += harmonicPotential(m, w, bead)
    t2 *= 0.5 * m / (1.0 * M * M * tau * tau)
    t3 /= M
    Energy += (t3 - t2)
    return Energy

def main():
    # --- General Setup -----------------------------------------------
    tau = 0.005  # Imaginary time step length
    T = 5.0  # Temperature [K]
    m = 1.0  # Mass [amu]
```

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C.1. SIMPLE PIMC CODE

```
s = 1000000  # number of MC sweeps
skips = 100  # number of sweeps to make between measurements
equilSteps = 200000  # number of sweeps to make before collecting data

# we work in units where energy is reported in Kelvin.
hbar = 1.0  # Planck constant / 2Pi
k = 1.0  # Boltzmann constant
w = 1.0  # QHO frequency

# Set beta and M (# time slices) based on T and tau.
# NOTE: beta = 1/T = tau*M --> T = 1/(tau*M)
beta = 1.0/(k*T)
M = int(beta/tau)  # Be careful in choosing tau and T.

# constants to scale COM and single bead moves
rat = 1.0  # individual beads
rat2 = 1.0  # entire worldline

# place M beads in an array. This could be generalized for N>1 particles.
beads = np.zeros(M)

# open filestream to write data to disk
fout = open('pimcToyQHOdata.dat', 'w')
fout.write('#%15s	%16s	%16s
' % ('Position', 'Energy', 'Potential'))

# --- Start PIMC method ---------------------------------------------------

# start MC sweeps
accept, reject = 0.0, 0.0  # keep track of acceptance stats
for z in range(s):
    # store old bead positions in an array called tempBeads
    tempBeads = beads.copy()

    # generate random number to decide what type of move
    r = random.random()

    if (r <= 0.25):
        # move an entire worldline
        R1 = rat2*(2.0+random.random())-1
        R = 0
        beads = CenterOfMassMove(beads, M, R1)
    else:
        # move a single bead
        R = random.randint(0, M-1)
        beads = SingleBeadMove(beads, M, R, rat)

    # --- calculate potential action difference ---------------------------
    S_prV = 0  # present potential action
    S_paV = 0  # past potential action
```
C.1. SIMPLE PIMC CODE

for i in range(M):
    # present
    S_prV += tau*harmonicPotential(m,w,beads[i])
    # past
    S_paV += tau*harmonicPotential(m,w,tempBeads[i])
S_V_diff = S_prV - S_paV

# --- calculate kinetic action difference -----------------------------
S_kpr = 0  # present kinetic action
S_kpa = 0  # past kinetic action
for i in range(M):
    # account for periodic boundary conditions
    if (i == 0):
        S_kpr += m/(2.0*beta*hbar**2)*(beads[i]-beads[M-1])**2
        S_kpa += m/(2.0*beta*hbar**2)*(tempBeads[i]-tempBeads[M-1])**2
    else:
        S_kpr += m/(2.0*beta*hbar**2)*(beads[i]-beads[i-1])**2
        S_kpa += m/(2.0*beta*hbar**2)*(tempBeads[i]-tempBeads[i-1])**2
S_k_diff = S_kpr - S_kpa

# calculate the quotient of density matrices
rho = np.exp(-((S_V_diff) + S_k_diff))

# --- Use Metropolis algorithm to accept or reject moves -------------
if (rho >= 1):
    # if energy goes down, accept move.
    accept += 1
    beads = beads
else:
    # otherwise roll the dice and see if we accept move.
    rn = random.random()
    if (rn <= rho):
        beads = beads
        accept += 1
    else:
        beads = tempBeads.copy()
        reject += 1

# --- bin measurements on system --------------------------------------
if (z % skips == 0 and z >= equilSteps):
    # position
    x = np.average(beads)
    # total energy
    E = thermodynamicEnergy(beads,tau,m,w)
C.2. CENTROID VIRIAL ENERGY METHOD

Now, pseudo-code detailing the centroid virial energy estimator method is supplied. This is presented as a blend of Python syntax and comments.
C.2. CENTROID VIRIAL ENERGY METHOD

# Compute the second term, T2
for bead in range(M):
    for ptcl in range(N):
        bead1 = bead, ptcl  # tuple to hold bead and particle numbers

# Function to return nextBeadLocation - beadLocation accounting
# for periodic boundary conditions.
vel2 = getVelocity(bead1)
beadNext0ld = bead1
vel1 = 0.0

# get r_{current + window} - r_{current}
for gamma in range(virialWindow):
    beadNextOld = bead

    # Function to find next bead in worldline. Some schemes left-
    # pack the worldline arrays, so this is not always trivial.
    beadNext = nextBead(bead1, gamma)

    # Function to get spatial separation vector of the next bead
    # and the current bead, accounting for periodic boundary cond.
    vel1 += getSeparation(beadNext, beadNextOld)

    T2 -= dot(vel1, vel2)

# Compute T3, T4, T5
T3 = 0.0
T4 = 0.0
T5 = 0.0
for bead in range(M):
    T3 += deltaDOTgradUterm1(bead)
    T4 += deltaDOTgradUterm2(bead)
    T5 += derivPotentialActionTau(bead)

# scale all terms by their respective correct constants.
T2 *= (m/(4.0*virialWindow*tau*tau*hbar*hbar*M))
T3 /= beta
T4 /= beta
T5 /= M

# NOTE: If a lookup table is used to compute the potential, then
# a 'tail correction' must be made. See the thesis by Brualla.
# Compute total centroid virial energy
totEcv = T1 + T2 + T3 + T4 + T5  # + tailV
return totEcv
C.2. CENTROID VIRIAL ENERGY METHOD

```python
# ----------------------------------------------------------------------------
def computeCOM(bead1, virialWindow):
    '''
    Compute deviation of bead from COM of worldline
    WITHOUT mirror image convention.
    '''

    # Vectors to hold running total of distance from bead1 to
    # beads forward in imaginary time (More) and backwards in
    # imaginary time (Less).
    vector runTotMore = 0.0
    vector runTotLess = 0.0

    # Vector to hold center of mass location of worldline that
    # bead1 belongs to.
    vector COM = 0.0

    # Call function to get spatial location vector of bead1.
    pos1 = beadLocation(bead1)

    beadNextOld = bead1
    beadPrevOld = bead1

    # step forward and backwards in imaginary time simultaneously.
    for gamma in range(virialWindow):

        # move along worldline to next (previous) bead
        beadNext = path.next(bead1, gamma)
        beadPrev = path.prev(bead1, gamma)

        # keep running total of distance from first bead
        # to the current beads of interest
        runTotMore += path.getSeparation(beadNext, beadNextOld)
        runTotLess += path.getSeparation(beadPrev, beadPrevOld)

        # update center of mass of WL
        COM += (pos1 + runTotMore) + (pos1 + runTotLess)

        # store current bead locations
        beadNextOld = beadNext
        beadPrevOld = beadPrev

        COM /= (2.0 * virialWindow)

    return COM

# ----------------------------------------------------------------------------
def deltaDOTgradUterm1(bead, virialWindow):
    '''
    Return (bead distance - COM) vector dotted into the first
term of the gradient of the potential action. This is as outlined
    '''
```

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C.2. CENTROID VIRIAL ENERGY METHOD

in the section on the centroid virial energy estimator.

eo = bead % 2  # determine if current time slice is even/odd

# Vector for the two interacting particles
vector bead1, beadNext, beadPrev, beadNextOld, beadPrevOld
bead1[0] = bead2[0] = bead

vector gVi, gVe, gV, delta
rDotgV = 0.0

# We loop over the first bead.
for bead1[1] in range(N):
    gVi = 0.0  # gradV_interaction vector
    gVe = 0.0  # gradV_external vector
    gV = 0.0   # gradV_total vector
    delta = 0.0  # deviation from center of mass vector

    # Sum potential of bead1 interacting with all other beads at
    # a given time bead.
        # Avoid self interactions
        if (!all(bead1==bead2)):
            gVi += interactiongradV(getSeparation(bead1,bead2))

        # Now add the external component of the gradient of the potential.
        # Here, position returns the position vector of bead1 and
        # externalgradV returns the gradient of the potential at that point.
        gVe += externalgradV(position(bead1))

        # Compute center of mass vector of WL. See above for implementation.
        COM = computeCOM(bead1,virialWindow)
        delta = pos1-COM

        # enforce boundary conditions
        putInBC(delta)

        # total gradient of potential vector.
        gV += (gVe + gVi)

        rDotgV += dot(gV, delta)

return VFactor[eo]*tau*rDotgV
C.2. CENTROID VIRIAL ENERGY METHOD

def deltaDOTgradUterm2(bead, virialWindow):
    eo = bead % 2  # determine if this is an even or odd time bead

    # vectors for two interacting particles
    vector bead1, beadNext, beadPrev, beadNextOld, beadPrevOld
    bead1[0] = bead2[0] = bead

    vector gVi, gVe, gV, g2V, delta

    double term2 = 0.0

    # Some forms of the action (primitive for example) do not
    # require this term be computed. So check this with function
    # gradVFactor that holds this information.
    if (gradVFactor[eo] > EPS):  # EPS is a tiny number (epsilon)
        # constants for tMatrix. See section on CV energy estimator.
        vector rDiff = 0.0
        rmag = 0.0
        d2V = 0.0
        dV = 0.0
        dVe = 0.0
        dVi = 0.0
        g2Vi = 0.0
        g2Ve = 0.0

        # We loop over the first bead.
        for bead1[1] in range(N):
            gV = 0.0  # gradient of potential vector
            g2V = 0.0  # laplacian of potential scalar
            delta = 0.0  #
            tMat = 0.0  # matrix we have called t-matrix
            gVdotT = 0.0

            # Compute external potential 1st and 2nd derivatives.
            # position function returns spatial position vector of bead1,
            # externalgradV and externalgrad2V return gradient and
            # Laplacian at bead1's position in space.
            gVe = externalgradV(position(bead1))
            dVe = sqrt(dot(gVe,gVe))
            g2Ve = externalgrad2V(position(bead1))

            gV += gVe  # update full bead gradient at bead1

            # Sum potential of bead1 interacting with all other beads at
            # a given time bead.
            for bead2[1] in range(N):
# function to return separation vector between bead1 and bead2
rDiff = getSeparation(bead1, bead2)
rmag = sqrt(dot(rDiff, rDiff))

# Avoid self interactions
if (!all(bead1==bead2)):
    # Compute interaction potential gradient and Laplacian.
    gVi = interactiongradV(rDiff)
dVi = sqrt(dot(gVi,gVi))
g2Vi = interactiongrad2V(rDiff)

    # total derivatives between bead1 and bead2 at bead1
dV = dVi + dVe
d2V = g2Vi + g2Ve

    # compute the T-matrix for bead1 interacting with bead2
    for a in range(NDIM):
        for b in range(NDIM):
            tMat(a,b) += (rDiff(a)*rDiff(b)*d2V/(rmag*rmag)
            - rDiff(a)*rDiff(b)*dV/pow(rmag,3))

            if (a == b):
                tMat(a,b) += dV/rmag

    # update full bead gradient at bead1
gV += gVi

    # matrix-vector multiplication
    for j in range(NDIM):
        for i in range(NDIM):
            gVdotT(j) += gV(i)*tMat(j,i)

    # compute center of mass of WL
    COM = computeCOM(bead1,virialWindow)

delta = pos1 - COM

    # enforce periodic boundary conditions on delta
    putInBC(delta)

    term2 += dot(gVdotT, delta)

term2 *= gradVFactor[eo]*tau*tau*hbar*hbar/m

return term2

# derivPotentialActionTau(bead):
    ''' Compute dU/dtau at a given time slice. '''

    dU = 0.0
C.3 COMMENTS ON IMPLEMENTATION

As it would turn out, the PIMC method lends itself particularly well to the Singleton design pattern, which restricts the instantiation of a class to one object. The class which has this restriction is referred to as the Singleton, and in our case the Singleton is the constants class. The class members are constant parameters that are accessed globally through the use of pointers, which in C++ look like constants()->nameOfConstant(), where constants() is the handle for the constants class and nameOfConstant() returns the value of the parameter nameOfConstant. The reason that only one instance may be created at a time is that some of these parameters may change while the code is running, such as the number of particles for a grand canonical simulation, so keeping only one instance at a time ensures that they will not change to conflicting values. These are the main reasons that the Singleton design pattern is the one recommended for the PIMC method.
Appendix D

Zero Temperature QMC

There are subtle differences between finite temperature quantum Monte Carlo (QMC) and zero temperature QMC. This will explain some of those differences and highlight how zero temperature PIMC (PIGS) should be able to give expectation values for physical observables for the ground state of a quantum system in thermal equilibrium within the canonical ensemble. Note that this may be extended to the grand canonical ensemble [47], but this will not be discussed in the current work.

D.1 Trial Functions and Projection Techniques

Before discussing the PIGS method, it is beneficial to consider some properties of the ground state wave function of a quantum system. Consider a quantum system at zero temperature. Let $\psi_0$ be the ground state wave function for said quantum system. It is desirable to know the ground state average of some observable $\hat{O}$ for this system:

$$\langle \psi_0 | \hat{O} | \psi_0 \rangle = \frac{\int d\vec{R} \hat{O}(\vec{R}) \psi_0^2(\vec{R})}{\int d\vec{R} \psi_0^2(\vec{R})}. \quad (D.1)$$
D.1. TRIAL FUNCTIONS AND PROJECTION TECHNIQUES

This expectation value may be calculated by sampling the coordinates of the quantum system according to the probability distribution

\[ p(\vec{R}) = \frac{\psi_0^2(\vec{R})}{\int d\vec{R} \psi_0^2(\vec{R})}. \]

The problem is that we generally don’t know the ground state wave function, \( \psi_0(\vec{R}) \), so it is necessary to define a trial function, \( \psi_T(\vec{R}) \). This trial function must obey the postulates of quantum mechanics, and hence must respect symmetry under particle exchange. So, exchange must be symmetric for bosons and antisymmetric for fermions. Even with these restrictions, the trial wave functions may still be chosen quite arbitrarily. In practice, a few functional forms of \( \psi_T(\vec{R}) \) are proposed and then the variational principle is used to test which function is best. Recall the variational principle, which tells us the ground state is that which minimizes the energy functional

\[ E[\psi] = \langle \psi | \mathcal{H} | \psi \rangle \geq E_0. \tag{D.2} \]

So, the better the trial function, the lower our estimated local energy will be:

\[ E_T = \frac{\int d\vec{R} E_L(\vec{R}) \psi_T^2(\vec{R})}{\int d\vec{R} \psi_T^2(\vec{R})}, \tag{D.3} \]

where, here we have defined the local energy as

\[ E_L(\vec{R}) = \frac{\mathcal{H} \psi_T(\vec{R})}{\psi_T(\vec{R})}. \tag{D.4} \]

Our strategy is to construct a physically motivated trial wave function that involves some free parameters. These free parameters are then to be optimized in order to minimize the trial energy, \( E_T \). When this optimization is done via Monte Carlo methods, this is known as Variational Monte Carlo. Both the efficiency and the reliability of this method relies
on our choice of a trial function. The errors are difficult to quantify for VMC because we really only know $E_T$, which is an upper bound for the ground state energy of the quantum system. An effective way to improve our trial function is found in the solution of the time dependent Schrödinger equation in imaginary time $\tau \equiv it$. Letting $\hbar = 1$, the Schrödinger wave equation is

$$-\frac{\partial}{\partial \tau} \psi(\vec{R}; \tau) = \mathcal{H} \psi(\vec{R}; \tau).$$

(D.5)

Now, we choose to designate our trial function as

$$\psi(\vec{R}; 0) = \psi_T(\vec{R})$$

(D.6)

and we know the solution for $\psi$ at any imaginary time $\tau$ can be trivially found to be

$$\psi(\vec{R}; \tau) = e^{-\tau \mathcal{H}} \psi_T(\vec{R}) = \sum_{i=0}^{\infty} c_i \psi_i(\vec{R}) e^{-\tau E_i},$$

(D.7)

where

$$c_i = \langle \psi_i | \psi_T \rangle.$$  

(D.8)

For sufficiently large $\tau$, only the eigenfunction with the lowest eigenvalue contributes to the sum above. So, if our trial function isn’t orthogonal to the actual ground state wave function, $\psi_0(\vec{R})$, then over time our system should evolve to the ground state:

$$\psi_0(\vec{R}) = \lim_{\tau \to \infty} \psi(\vec{R}; \tau),$$

(D.9)

meaning that up to a normalisation constant:

$$\psi_0(\vec{R}) \sim \lim_{\tau \to \infty} \int d\vec{R}' \, G(\vec{R}, \vec{R}'; \tau) \psi_T(\vec{R}').$$

(D.10)
D.2. PIGS METHOD

Here, \( G(\vec{R}, \vec{R}'; \tau) = \langle \vec{R} | e^{-\tau \hat{H}} | \vec{R}' \rangle \) is the imaginary time propagator. This all means that given a large enough imaginary time, Equation (D.10) above can be used to project a trial initial state onto the ground state. This so-called projection technique is employed in Green Function monte carlo, diffusion monte carlo, and reptation monte carlo. It may be noticed that \( G \) is the thermal density matrix for a finite temperature quantum system at effective temperature \( \beta = 1/k_B T \), and as such we may use the Feynman path integral formalism to write an approximation to the ground state wave function! This is what is known as the PIGS method. So, by definition, the path integral ground state method is a systematic way of improving a trial wave function, and as such effectively drives a quantum system into its ground state.

D.2 PIGS METHOD

PIGS works by constructing an imaginary time propagator, \( G \), for the total imaginary time, \( \tau_{\text{total}} \), as a convolution of \( 2M + 1 \) propagators on some smaller time step, \( \tau = \tau_{\text{total}}/(2M + 1) \). Breaking up the imaginary time into smaller intervals allows for a more reliable estimation of the propagator. This is given to us by the fact that we are raising the effective temperature by increasing the number of imaginary time propagators, as in Equation (4.12). So, our propagator ends up looking like

\[
G(\vec{R}_{2M}, \vec{R}_0; \tau) = \int d\vec{R}_j G(\vec{R}_{j+1}, \vec{R}_j; \tau),
\]

which implies that our projected trial wave function takes the form:

\[
\psi_0(\vec{R}) = \lim_{M \to \infty} \int d\vec{R}_j G(\vec{R}_{j+1}, \vec{R}_j; \tau) \psi_T(\vec{R}_0).
\]
Then, if we fix the number of imaginary time steps at some finite value, we arrive at an analytical expression for the ground state wave function:

$$\psi_{\text{pigs}}(\vec{R}_{2M}) = \int_0^{2M} d\vec{R}_j \psi_T(\vec{R}_0).$$

(D.13)

The larger we make $M$, the better that our approximation of the ground state wave function will be. At sufficiently large $M$, the result is considered a stochastically exact estimation of the ground state energy of the system, $E_0$. This is due to the fact that the estimated energy values become independent of $M$, which is indicative of the systematic error due to the choice of the trial function being lowered below statistical uncertainty. So, like finite temperature PIMC, the zero temperature PIMC is stochastically exact. This PIGS method was mentioned by David Ceperley [45] in 1995 where he called this the variational path-integral (VPI) method. Generally, a certain kind of wave function called a shadow wave function is used to simulate many-body quantum systems. This type of trial function is symmetric and translationally invariant. This, along with the fact that the polymer isomorphism is made to open chain polymers rather than ring polymers means that is not necessary to sample permutations of particles when using PIGS.

D.3 Measuring Observables with PIGS

Once the optimal value of $M$ has been determined for which $\psi_{\text{pigs}}(\vec{R})$ describes the ground state, all relevant observables of the quantum system can be calculated with

$$\langle \psi_0 | \hat{O} | \psi_0 \rangle = \frac{\int d\vec{R}_M \hat{O}(\vec{R}_M) \psi_{\text{pigs}}^2(\vec{R}_M)}{\int d\vec{R}_M \psi_{\text{pigs}}^2(\vec{R}_M)},$$

(D.14)
and substitution of Equation (D.13) into Equation (D.14) yields
\[
\langle \psi_0 | \hat{O} | \psi_0 \rangle = \int \prod_{j=1}^{2M} d\vec{R}_j \psi_T(\vec{R}_{2M}) G(\vec{R}_j, \vec{R}_{j-1}; \tau) \hat{O}(\vec{R}_M) \psi_T(\vec{R}_0) \int \prod_{j=1}^{2M} d\vec{R}_j \psi_T(\vec{R}_{2M}) G(\vec{R}_j, \vec{R}_{j-1}; \tau) \psi_T(\vec{R}_0).
\] (D.15)

This integral above is how PIGS will be used to calculate the values of the observables of these zero-temperature quantum systems. These are computed by sampling the probability distribution:
\[
P(\vec{R}_0, \vec{R}_1, ..., \vec{R}_{2M}) = \frac{\prod_{j=1}^{2M} \psi_T(\vec{R}_{2M}) G(\vec{R}_j, \vec{R}_{j-1}; \tau) \psi_T(\vec{R}_0)}{\int \prod_{j=1}^{2M} d\vec{R}_j \psi_T(\vec{R}_{2M}) G(\vec{R}_j, \vec{R}_{j-1}; \tau) \psi_T(\vec{R}_0)}
\] (D.16)

It is very important to note that the above equation is the Boltzmann distribution for a classical system of polymers, each with \(2M + 1\) beads. Hence, we recognize an isomorphism from a quantum \(N\)– particle system to a classical system of \(N\) polymers, as originally pointed out by David Chandler [52]. The interaction of these polymers will be specified in an appropriate form to approximate our smaller imaginary time propagators, \(G(\vec{R}_j, \vec{R}_{j-1}; \tau)\).

In general, one may take a measurement of a physical observable by simply inserting the operator into the polymer at any arbitrary imaginary time slice. However, it is beneficial to take measurements at the center (\(M^{th}\)) time slice, since the error is smallest near the center. This can be understood qualitatively by imagining this projection technique that has been mentioned. At the ends of the worldlines, the wave functions are simply the trial functions, and as the imaginary time propagators act on each bead sequentially through imaginary time, we can think of the system being less like the trial function and more like the actual ground state wave function. Note that it doesn’t matter if we propagate from the \(2M^{th}\) bead backward or the \(0^{th}\) bead forward, the symmetry of the system means that the same answer should be obtained.
D.4. DIFFERENCES BETWEEN PIGS AND PIMC

D.4 DIFFERENCES BETWEEN PIGS AND PIMC

- At $T = 0$, we need not worry about imposing periodic boundary conditions on the imaginary time worldlines because we are not taking the trace of the propagator. This leads to an isomorphism to a system of open chain polymers instead of closed ring polymers as in finite temperature PIMC.

- $\tau$ has no physical meaning in PIGS, whereas it is related to the temperature of the system in finite temperature PIMC. Here, it is simply taken as a variational parameter.

- If $\psi_T(\vec{R})$ is symmetric and the propagator is the symmetric one of the form of Equation (4.11), then there is no need to sample the permutations between identical particles. The single-polymer movements will sufficiently provide ergodic sampling and will reliably give us back ground state averages. As mentioned, this is due to having open paths [45].
Often in computational physics one desires knowledge of the expectation values of observables along with an estimation of the error bars from data collected from some simulation. Never is this more the case than for quantum Monte Carlo simulations. In QMC, one will generate sets of values $a_i, b_i, \ldots$ where $i \in \mathbb{Z} \cap [1, N]$ is the number of sets of measurements obtained and $a_i, b_i, \ldots$ is the $i^{th}$ measurement for observable $a, b, \ldots$ respectively. Average quantities such as $\langle a \rangle$ and the associated errorbars are trivially computed \cite{53} when one may assume that the measurement $a_i$ is not correlated with the measurement $a_{i+1}$ and will not be discussed here. However, this analysis becomes more complicated when one deals with correlated data and quantities such as $\langle a^2 \rangle - \langle a \rangle^2$. In these cases, one needs to address the average and error bar estimation in a generally more robust fashion.

It turns out there are methods, known as resampling methods, which automate the errorbar estimation process. In words, resampling methods such as jackknife and bootstrap are those which take subsets of the entire dataset and then average the averages of those subsets to estimate the mean of the entire data set along with the associated errorbars. Before discussing these, we discuss another more traditional method of errorbar estimation that involves expanding in Taylor series. For the current discussion, we will focus on estimating the mean and errorbars for a function $f(\bar{A}, \bar{B}, \bar{C})$ where $\bar{A}$, $\bar{B}$, and $\bar{C}$ are average
E.1 TRADITIONAL METHOD

quantities which have been measured in some simulation. For example, a relevant quantity
is that given for the specific heat in Equation (4.86).

E.1 Traditional Method

For a function of three variables, call it \( T(x_1, x_2, x_3) \), one may perform a Taylor expansion
to second order and obtain

\[
T(x_1, x_2, x_3) = f(a_1, a_2, a_3) + \sum_{j=1}^{3} \frac{\partial}{\partial x_j} f(a_1, a_2, a_3)(x_j - a_j) \\
+ \frac{1}{2} \sum_{j=1}^{3} \sum_{k=1}^{3} \frac{\partial^2}{\partial x_j \partial x_k} f(a_1, a_2, a_3)(x_j - a_j)(x_k - a_k) + \ldots .
\]  

(E.1)

Using this, one will find that the traditional method of estimating the actual mean of a
function from collected, cross-correlated data is given by

\[
f(\bar{A}, \bar{B}, \bar{C}) = f(\mu_A, \mu_B, \mu_C) + \left( \frac{\partial}{\partial A} f \right) (\bar{A} - \mu_A) + \left( \frac{\partial}{\partial B} f \right) (\bar{B} - \mu_B) \\
+ \left( \frac{\partial}{\partial C} f \right) (\bar{C} - \mu_C) + \frac{1}{2} \left( \frac{\partial^2}{\partial A^2} f \right) (\bar{A} - \mu_A)^2 + \frac{1}{2} \left( \frac{\partial^2}{\partial B^2} f \right) (\bar{B} - \mu_B)^2 \\
+ \frac{1}{2} \left( \frac{\partial^2}{\partial C^2} f \right) (\bar{C} - \mu_C)^2 + \frac{1}{2} \left( \frac{\partial^2}{\partial A \partial B} f \right) (\bar{A} - \mu_A)(\bar{B} - \mu_B) \\
+ \frac{1}{2} \left( \frac{\partial^2}{\partial A \partial C} f \right) (\bar{A} - \mu_A)(\bar{C} - \mu_C) + \frac{1}{2} \left( \frac{\partial^2}{\partial B \partial C} f \right) (\bar{B} - \mu_B)(\bar{C} - \mu_C) + \ldots 
\equiv f + (\partial_A f) \delta_A + (\partial_B f) \delta_B + (\partial_C f) \delta_C +
\frac{1}{2} (\partial^2_A f) \delta_A^2 + \frac{1}{2} (\partial^2_B f) \delta_B^2 + \frac{1}{2} (\partial^2_C f) \delta_C^2 \\
+ (\partial_A \partial_B f) \delta_A \delta_B + (\partial_A \partial_C f) \delta_A \delta_C + (\partial_B \partial_C f) \delta_B \delta_C + \ldots ,
\]  

(E.2)

where \( \mu_A \) are meant to denote the exact average of the probability distribution for each
respective observable \( A \) and the variables with overbars \( \bar{A} \) are the mean obtained from the
data. Notice that all first order terms here will average to zero if \( f \) is measured many times,
E.1. TRADITIONAL METHOD

so the leading contribution to the error comes from the second order terms. This is due
to the fact that all of the first order delta terms tend to zero. Also, if we average this
expansion to second order over many iterations, we will notice

\[ \langle \delta_i \delta_k \rangle \rightarrow \langle ik \rangle - \langle i \rangle \langle k \rangle = \sigma_{ik}^2, \quad (E.3) \]

where \( i, k \) are combinations of \( A, B, C \). If we substitute this into our previous expression
and acknowledge that the first order terms vanish, we get

\[
\begin{align*}
f(\bar{\bar{A}}, \bar{\bar{B}}, \bar{\bar{C}}) & \rightarrow f(\mu_A, \mu_B, \mu_C) + \frac{1}{2}(\partial_A f)\sigma_A^2 + \frac{1}{2}(\partial_B f)\sigma_B^2 + \frac{1}{2}(\partial_C f)\sigma_C^2 \\
&+ (\partial_A \partial_B f)\sigma_{AB}^2 + (\partial_A \partial_C f)\sigma_{AC}^2 + (\partial_B \partial_C f)\sigma_{BC}^2 + \ldots ,
\end{align*}
\]

and these \( \sigma^2_{ik} \) terms are given in terms of the average sample variance \( \langle s^2_{ik} \rangle \) for \( i = k \) and
the sample covariance \( s^2_{ik} \) for \( i \neq k \). These terms look like

\[
s^2_{ik} = \frac{1}{N-1} \sum_{\alpha=1}^{N} (i_{\alpha} - \bar{i})(k_{\alpha} - \bar{k})
\]

and \( \sigma^2_{ik} = s^2_{ik}/N \). Therefore, our estimate becomes

\[
\begin{align*}
f(\mu_A, \mu_B, \mu_C) & \approx f(\bar{\bar{A}}, \bar{\bar{B}}, \bar{\bar{C}}) - \frac{1}{N} \left[ \frac{1}{2}(\partial_A^2 f)s_A^2 + \frac{1}{2}(\partial_B^2 f)s_B^2 + \frac{1}{2}(\partial_C^2 f)s_C^2 \\
&+ (\partial_A \partial_B f)s_{AB}^2 + (\partial_A \partial_C f)s_{AC}^2 + (\partial_B \partial_C f)s_{BC}^2 \right]
\end{align*}
\]

Then, the leading error in using \( f(\bar{\bar{A}}, \bar{\bar{B}}, \bar{\bar{C}}) \) to estimate \( f(\mu_A, \mu_B, \mu_C) \) comes from the linear
terms in our original expansion:

\[
\sigma^2_f \equiv \langle f^2(\bar{\bar{A}}, \bar{\bar{B}}, \bar{\bar{C}}) \rangle - (f(\bar{\bar{A}}, \bar{\bar{B}}, \bar{\bar{C}}))^2,
\]

(E.7)
E.1. TRADITIONAL METHOD

where

$$\langle f(\bar{A}, \bar{B}, \bar{C}) \rangle = f(\mu_A, \mu_B, \mu_C)$$

(E.8)

and

$$\langle f^2(\bar{A}, \bar{B}, \bar{C}) \rangle = f^2(\mu_A, \mu_B, \mu_C) + (\partial_A f)^2 \langle \delta_A^2 \rangle + (\partial_B f)^2 \langle \delta_B^2 \rangle + (\partial_C f)^2 \langle \delta_C^2 \rangle$$

$$+ 2(\partial_A f)(\partial_B f)\langle \delta_A \delta_B \rangle + 2(\partial_A f)(\partial_C f)\langle \delta_A \delta_C \rangle + 2(\partial_B f)(\partial_C f)\langle \delta_B \delta_C \rangle,$$

(E.9)

therefore

$$\sigma_f^2 = (\partial_A f)^2 \langle \delta_A^2 \rangle + (\partial_B f)^2 \langle \delta_B^2 \rangle + (\partial_C f)^2 \langle \delta_C^2 \rangle$$

$$+ 2(\partial_A f)(\partial_B f)\langle \delta_A \delta_B \rangle + 2(\partial_A f)(\partial_C f)\langle \delta_A \delta_C \rangle + 2(\partial_B f)(\partial_C f)\langle \delta_B \delta_C \rangle.$$

(E.10)

Now, we may use $$\langle \sigma_i \sigma_k \rangle \approx s_{ik}^2/N$$ to write out a final expression for the approximate traditional error associated with the function \(f\):

$$\sigma_f^2 = \frac{1}{N} \left[ (\partial_A f)^2 s_A^2 + (\partial_B f)^2 s_B^2 + (\partial_C f)^2 s_C^2 + 2(\partial_A f)(\partial_B f)s_{AB} \right.$$

$$\left. + 2(\partial_A f)(\partial_C f)s_{AC} + 2(\partial_B f)(\partial_C f)s_{BC} \right].$$

(E.11)

Notice how one needs to keep track of the derivatives of the function \(f\) with respect to each measurable quantity and also compute the variance and covariance. These steps are not necessary with resampling methods, so we say that the resampling methods automatically give you estimates of the errorbars without having to keep track of any extra terms.
**E.2. JACKKNIFE RESAMPLING**

**E.2 Jackknife Resampling**

Let’s define the $i^{th}$ jackknife estimate of the term $y$ for the dataset already mentioned as

$$y_i^J \equiv \frac{1}{1-N} \sum_{j \neq i} y_j,$$  \hspace{1cm} (E.12)

which is an average over all data except for point $i$. We also want to define the jackknife estimates for a function $f$ as

$$f_i^J = f(A_i^I, B_i^I, C_i^I).$$ \hspace{1cm} (E.13)

With these defined, we acquire the overall jackknife estimate of our function $f(\mu_A, \mu_B, \mu_C)$ as the average over $N$ jackknife estimates $f_i^J$:

$$\bar{f}^J \equiv \frac{1}{N} \sum_{i=1}^{N} f_i^J.$$ \hspace{1cm} (E.14)

It is important to note that a bias will exist in the case that $f$ is nonlinear, but we can compute errorbars and bias in this case anyway. It turns out that we may estimate \[54\] our function as

$$f(\mu_A, \mu_B, \mu_C) = N \langle f(\bar{A}, \bar{B}, \bar{C}) \rangle - (N-1) \langle \bar{f}^J \rangle + \mathcal{O}\left(\frac{1}{N^2}\right),$$

$$\to N \langle f(\bar{A}, \bar{B}, \bar{C}) \rangle - (N-1) \bar{f}^J,$$ \hspace{1cm} (E.15)

which is great because then we do not need to worry about writing extra terms to disk. The variance is simply given by

$$(s_f^J)^2 = (\bar{f}^J)^2 - (\bar{f})^2,$$ \hspace{1cm} (E.16)
E.3. SAMPLE JACKKNIFE SCRIPT

where

$$\overline{(f^J)^2} = \frac{1}{N} \sum_{i=1}^{N} (f^i_J)^2.$$  \hspace{1cm} (E.17)

One may expand these functions once again as for the traditional method (see [54] for details) and obtain

$$\sigma_f \approx \sqrt{N - 1} s_J^f$$  \hspace{1cm} (E.18)

as the expression for the standard error associated with the function $f$. This is a remarkable result because it means that we do not need to worry about correlations amongst subsequent measurements or cross-correlation between different measurements that our function $f$ depends upon.

For completeness, we mention that the bootstrap method works almost exactly as does jackknifing, except instead of taking subsets that are of size $N - 1$, we take randomly sized random samples out of the data and proceed in an analogous fashion to what was discussed here.

E.3 Sample Jackknife Script

Provided here is a function written in Python 2.7 that will perform a jackknife resampling analysis on a dataset. It may be passed one array, in which case it will return the jackknife average as well as the estimated standard error for that array. It may also be passed three arrays, in which case it interprets that the data is that for the specific heat estimator in Equation (4.86). It is assumed that the Python syntax is intuitive enough to understand without prior knowledge of the language. Note that numpy was imported as np in the following script.
E.3. SAMPLE JACKKNIFE SCRIPT

```python
def jackknife(data, data2=None, data3=None):
    
    # Return jackknife average (accounting for bias) and error. This can be passed either
    # a single numpy array or three numpy arrays. If passed a single numpy array it will
    # simply return mean and error for that array. If passed three, it is expected that
    # these are the three arrays for single virial specific heat.
    
    if data2 != None or data3 != None:
        Cv = True
    else:
        Cv = False

    numBins = int(len(data))
    jkTerms = np.zeros(numBins)

    # compute total sums first
    totSum1 = 0.0
    if Cv:
        totSum2, totSum3 = 0.0, 0.0
        for i in range(numBins):
            totSum1 += data[i]
            if Cv:
                totSum2 += data2[i]
                totSum3 += data3[i]

    # create resampled arrays
    for i in range(numBins):
        t1 = (totSum1 - data[i]) / (1.0 * numBins - 1.0)
        if Cv:
            t2 = (totSum2 - data2[i]) / (1.0 * numBins - 1.0)
            t3 = (totSum3 - data3[i]) / (1.0 * numBins - 1.0)
            jkTerms[i] = t1 - t2 * t2 - t3
        else:
            jkTerms[i] = t1

    # compute raw average (no resampling)
    if Cv:
        rawAve = np.mean(data) - (np.mean(data2))**2 - np.mean(data3)
    else:
        rawAve = np.mean(data)

    # compute mean and standard error
    jkAve = np.mean(jkTerms)
    jkVar = np.mean(jkTerms ** 2) - jkAve ** 2
    jkErr = np.sqrt((numBins - 1) * jkVar)

    # account for bias
    ActAve = 1.0 * numBins * rawAve - 1.0 * (numBins - 1) * jkAve

    return ActAve, jkErr
```

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Appendix F

Lennard-Jones Surface

F.1 Semi-Infinite Half-Plane

The potential energy a distance $d$ above a half-plane made up of atoms with a Lennard-Jones type interaction potential, as given in Equation (2.2), may be readily computed. Working in cylindrical coordinates, the integral takes the form

$$
\Phi = 4\epsilon \rho_m \int_0^{2\pi} d\phi \int_{-\infty}^{-d} dz \int_0^{\infty} d\rho \rho \left[ \left( \frac{\sigma}{\sqrt{\rho^2 + z^2}} \right)^{12} - \left( \frac{\sigma}{\sqrt{\rho^2 + z^2}} \right)^6 \right], \quad (F.1)
$$

where we have inserted $\rho_m$ as the density of the material that we are approximating as having a Lennard-Jones interaction potential. The angular integral is done right away, and yields a multiplicative constant $2\pi$. Next, the radial integral is easily done using the substitution $\xi = \rho^2 + z^2$, which leaves

$$
\Phi = 8\pi \epsilon \rho_m \int_{-\infty}^{-d} dz \int_0^{\infty} d\xi \frac{d\xi}{2} \left[ \left( \frac{\sigma^{12}}{\xi^6} \right) - \left( \frac{\sigma^6}{\xi^3} \right) \right] \\
= 4\pi \epsilon \rho_m \int_{-\infty}^{-d} dz \left[ - \left( \frac{\sigma^{12}}{5(\rho^2 + z^2)^5} \right) + \left( \frac{\sigma^6}{2(\rho^2 + z^2)^2} \right) \right]_0^\infty \\
= 4\pi \epsilon \rho_m \int_{-\infty}^{-d} dz \left[ - \left( \frac{\sigma^{12}}{5z^{10}} \right) + \left( \frac{\sigma^6}{2z^4} \right) \right]. \quad (F.2)
$$
This last integral is evaluated to show

\[ \Phi = \frac{4\pi \rho_m}{3} \left[ \frac{\sigma^{12}}{15d^9} - \frac{\sigma^6}{2d^3} \right]. \quad (F.3) \]

**F.2 SEMI-INFINITE HALF-SLAB**

This integral becomes more complicated when one considers only a ‘slab’ of Lennard-Jonesium, as the one seen in Figure F.1. This is similar to one of the ‘faces’ of the film region in our excluded volume simulation cell. Here, we are considering a region of width \( S \) in the \( z \) direction, of infinite extent in the \( x \) direction (hence we have translational invariance in this direction) and of semi-infinite extent in the \( y \) direction. This loss of translational invariance in the \( z \) direction is what makes the resulting integral more challenging than the half-space case. The resulting integral in Cartesian Coordinates is

\[ \Phi = 4\epsilon \rho_m \int_{-S/2}^{S/2} dz \int_{-\infty}^{-d} dy \int_{-\infty}^{\infty} dx \left[ \left( \frac{\sigma}{\sqrt{x^2 + y^2 + z^2}} \right)^{12} - \left( \frac{\sigma}{\sqrt{x^2 + y^2 + z^2}} \right)^{6} \right]. \quad (F.4) \]

The \( x \) component of this integral is easily calculated and is shown to be

\[ \Phi = 4\epsilon \rho_m \int_{-S/2}^{S/2} dz \int_{-\infty}^{-d} dy \left[ \frac{63\pi}{256} \frac{\sigma^{12}}{(y^2 + z^2)^{11/2}} - \frac{3\pi}{8} \frac{\sigma^6}{(y^2 + z^2)^{5/2}} \right]. \quad (F.5) \]

The remainder of this integral is complicated by the finite integration limits, so we opt out of showing the steps here but just state the final result. It is convenient to report this
potential as a dimensionless quantity, scaled by $\epsilon$ and the density $\rho_m$, which gives

$$\frac{\Phi}{\epsilon \rho_m} = 4\pi \left[ \frac{63}{256} \sigma^{12} \mathcal{I}_R - \frac{3}{8} \sigma^6 \mathcal{I}_A \right], \quad (F.6)$$

where $\mathcal{I}_R$ and $\mathcal{I}_A$ are respectively the repulsive and attractive pieces of the potential and have the form

$$\mathcal{I}_R = \frac{256}{2835d^9 S^9 (4d^2 + S^2)^{7/2}} \left( 65536d^{16} + 57344d^{14} S^2 + 17920d^{12} S^4 + 2240d^{10} S^6 ight. \\
+ 70d^8 S^8 + 140d^6 S^{10} + 70d^4 S^{12} + 14d^2 S^{14} + S^{16} \\
\left. - \sqrt{4d^2 + S^2} \left[ 32768d^{15} + 24576d^{13} S^2 + 6144d^{11} S^4 + 512d^9 S^6 \right] \right), \quad (F.7)$$

and

$$\mathcal{I}_A = \frac{4}{9d^3 S^3 \sqrt{4d^2 + S^2}} \left( 16d^4 + 2d^2 S^2 + S^4 - 8d^3 \sqrt{4d^2 + S^2} \right). \quad (F.8)$$

It may readily be shown that this finite $S$ case limits to the infinite $S$ case presented in the previous section. Starting with the repulsive term:

$$\lim_{S \to \infty} \mathcal{I}_R = \frac{256}{2835d^9} \lim_{S \to \infty} \frac{1}{S^9 (4d^2 + S^2)^{7/2}} = \frac{256}{2835d^9}. \quad (F.9)$$

The large $S$ limit of the attractive term is given by

$$\lim_{S \to \infty} \mathcal{I}_A = \frac{4}{9d^3} \lim_{S \to \infty} \frac{S^4}{S^3 \sqrt{4d^2 + S^2}} = \frac{4}{9d^3}. \quad (F.10)$$

Inserting these results into our analytical solution for the potential yields

$$\lim_{S \to \infty} \frac{\Phi}{\epsilon \rho_m} = 4\pi \left[ \frac{63}{256} \sigma^{12} \frac{256}{2835d^9} - \frac{3}{8} \sigma^6 \frac{4}{9d^3} \right] = \frac{4\pi}{3} \left[ \frac{1}{15} \sigma^{12} d^0 - \frac{1}{2} \sigma^6 d^3 \right], \quad (F.11)$$

which is exactly the analytical result obtained in the previous section for the semi-infinite
F.2. SEMI-INFINITE HALF-SLAB

half-space. Knowledge of the scaling of the potential as a function of $S$ is important, so we present this data in Figure F.2. This plot shows convergence of the potential to the

Figure F.2: Scaling of surface potential as a function of $S$. The inset shows the minimum of the potential well as a function of the associated value of $S$.

infinite $S$ limit at a relatively small value of $S$. If the length $S$ were one angstrom, then this convergence happens to a high degree of agreement over the nanometer scale.
APPENDIX G

LENNARD JONES NANOTUBE POTENTIAL AND DERIVATIVES

Measuring the energy of quantum systems with the thermodynamic energy estimator only requires knowledge of the gradient of the potential energy. However, the virial energy estimator requires knowledge of the gradient along with the Laplacian of the potential energy of the system. This second derivative is generally more time-intensive than the first derivative and can also have a much more complicated functional form depending upon which potential is being studied.

PIMC simulations of bosons inside nanotubes with an integrated Lennard-Jones surface potential is of current interest to the Del Maestro research group [55]. Before this work, only the first derivative had been computed in the production PIMC code, but the second derivative has been recently added by the author. Here, the potential along with its first and second derivatives with respect to the distance from the particle of interest to the nanotube wall are supplied.
G.1 Potential

The functional form of the integrated Lennard-Jones potential inside of a cylindrical nanotube may be written out analytically [56]. If we let the cylindrical axis pass through the origin, we may define $x \equiv r/R$ where $r$ is the distance from the atom to the wall and $R$ is the radius of the tube. From here, the potential may be defined as

$$V_{\text{tube}} = \frac{\pi \epsilon \sigma^3 \rho}{3} \left( \frac{a^3 f_1^3}{240 R^9} \left[ (1091 + 11156x^2 + 16434x^4 + 4052x^6 + 35x^8)E_x^2 ight. ight.$$

$$\left. - 8(1 - x^2)(1 + 7x^2)(97 + 134x^2 + 25x^4)K_x^2 \right]$$

$$- \frac{2\sigma^3 f_1^3}{R^3} \left[ (7 + x^2)E_x^2 - 4(1 - x^2)K_x^2 \right), \quad (G.1)$$

where $\sigma$ is the collision diameter and $\epsilon$ is the potential well depth. Both are specific to the material, and are determined empirically. The density of atoms within the nanopore material (outside of the cavity) is given as $\rho$, and the function $f_1 \equiv 1/(1-x^2)$. The functions $E_x^2$ and $K_x^2$ are the complete elliptical integrals of the first and second kind, respectively:

$$K_x^2 = \int_0^{\pi/2} d\theta \frac{1}{\sqrt{1 - x^2 \sin^2 \theta}}, \quad (G.2)$$

$$E_x^2 = \int_0^{\pi/2} d\theta \sqrt{1 - x^2 \sin^2 \theta}. \quad (G.3)$$

For the code, it is nice to have the a small $x$ (hard core limit) of the potential and its radial derivatives. This limit for the potential is

$$\lim_{x \to 0} V_{\text{tube}} = \frac{186766}{R^9} - \frac{2591.78}{R^3}. \quad (G.4)$$
G.2  FIRST RADIAL DERIVATIVE

The first derivative of this nanotube potential with respect to the distance from the particle to the wall is given by:

\[
\frac{d}{dr}V_{\text{tube}} = \frac{\pi \epsilon \sigma^3 \rho}{3R} \left( \frac{\sigma^9 f_1^{10}}{80R^9} \left[ \frac{(1 + x^2)}{x} \left(35 + 5108x^2 + 22482x^4 + 5108x^6 + 35x^8\right)E_x^2 \\
- \frac{(1 - x^2)}{x} \left(35 + 3428x^2 + 15234x^4 + 12356x^6 + 3471x^8\right)K_x^2 \right] \\
- \frac{6\sigma^3 f_1^4}{xR^3} \left[ (1 + 14x^2 + x^4)E_x^2 - (1 + 6x^2 - 7x^4)K_x^2 \right] \right). \tag{G.5}
\]

The small \( x \) limit is

\[
\lim_{x \to 0} \frac{d}{dr}V_{\text{tube}} = -\frac{31127.7}{R^{10}} + \frac{1295.89}{R^4}. \tag{G.6}
\]

G.3  SECOND RADIAL DERIVATIVE

The second derivative of this nanotube potential with respect to the distance from the particle to the wall is given by:

\[
\frac{d^2}{dr^2}V_{\text{tube}} = \frac{\pi \epsilon \sigma^3 \rho}{3R^2} \left( \frac{\sigma^9 f_1^{11}}{120R^9} \left[ (1925x^{10} + 319451x^8 + 2079074x^6 \\
+ 2711942x^4 + 764873x^2 + 20975)E_x^2 \\
- (729400x^{10} + 430024x^8 + 344262x^6 \\
+ 767248x^4 + 386200x^2 + 12712)K_x^2 \right] \\
- \frac{8\sigma^3 f_1^5}{R^3} \left[ (11 + 80x^2 + 5x^4)E_x^2 - 4(1 + 4x^2 - 5x^4)K_x^2 \right] \right). \tag{G.7}
\]

The small \( x \) limit is

\[
\lim_{x \to 0} \frac{d^2}{dr^2}V_{\text{tube}} = \frac{9798390}{R^{11}} - \frac{24189.9}{R^5}. \tag{G.8}
\]
G.4 Testing Virial Energy Estimator

Here we compare the results of the centroid virial energy estimator with those of the thermodynamic energy estimator for a test case for the Lennard-Jones nanopore external potential, just as in Section 4.6. Since the centroid virial energy estimator relies the potential as well as its first and second radial derivatives, agreement of these energy estimators will provide good support for the derivatives being correct.

Figure G.1: Centroid virial energy and thermodynamic energy estimators for Lennard-Jones Nanotube potential. This is for a test system of 4 atoms in the Canonical Ensemble at $T=5K$. 75000 bins were collected but only the last 4500 are shown here.
Appendix H

Ne-Ne HFD-B Interaction Potential

PIMC studies of the noble gas neon may be performed using the semi-empirical Aziz HFD-B [57] potential. Studies of neon have been done in the high temperature, high density regime [58] using a very similar potential (slightly less accurate than the HFD-B) and good agreement is shown between simulation and experiment. The difference between these potentials should only show up in the very high density regime, where the HFD-B potential is reported to yield results more accurately reflecting the experimental data. It seems possible that this interaction potential may also yield good results at lower temperatures. It is worth noting that the values for the fitting parameters and coefficients that follow were already converted to the system of units that we generally use, and can be found in [59].

H.1 Functional Form for the Potential

The functional form found to most closely replicate experimental systems in PIMC simulations is given by

\[
V(x) = \epsilon \left[ Ae^{\beta x^2} e^{-\alpha x} - \left( \frac{C_6}{x^6} + \frac{C_8}{x^8} + \frac{C_{10}}{x^{10}} \right) F(x) \right],
\]  

(H.1)
where \( x = r/r_m \) with \( r \) being the interatomic spacing between two neon atoms and \( r_m \) is the distance from the nucleus to the minimum of the potential well. The \( F \) term is given as

\[
F(x) = \begin{cases} 
\exp \left( - \frac{D}{x} + 1 \right)^2 : x < D \\
1 : x \geq D
\end{cases}
\]

and the constants are chosen such that: \( C_6 = 1.21317545, \ C_8 = 0.53222749, \ C_{10} = 0.24570703, \ D = 1.36, \ \alpha = 13.86434671, \ \beta = -0.12993822, \ \epsilon = 42.25K, \ A = 895717.95, \) and \( r_m = 3.091\text{Å}. \) The first radial derivative of this potential is given by putting \( V(r) \) into the form \( V(x) \) and differentiating, yielding

\[
\frac{d}{dr}V(x) = \frac{1}{r_m} \frac{d}{dx}V(x) = \frac{\epsilon}{r_m} \frac{d}{dx} \left[ Ae^{-\alpha x + \beta x^2} - \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot F(x) \right]
\]

\[
= \frac{\epsilon}{r_m} \left[ A(2\beta x - \alpha)e^{-\alpha x + \beta x^2} - \left( 6C_6 \left( \frac{1}{x} \right)^7 + 8C_8 \left( \frac{1}{x} \right)^9 + 10C_{10} \left( \frac{1}{x} \right)^{11} \right) \cdot F(x) \\
+ \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot \frac{d}{dx}F(x) \right].
\]

Now, the second derivative may be taken:

\[
\frac{d}{dr} \frac{d}{dr}V(x) = \frac{1}{r_m^2} \frac{d}{dx} \frac{d}{dx}V(x) = \frac{\epsilon}{r_m^2} \left[ A(2\beta(1 - \alpha x + 2\beta x^2) - \alpha(2\beta x - \alpha))e^{-\alpha x + \beta x^2} \\
- \left( 42C_6 \left( \frac{1}{x} \right)^8 + 72C_8 \left( \frac{1}{x} \right)^{10} + 110C_{10} \left( \frac{1}{x} \right)^{12} \right) \cdot F(x) \\
+ 2 \left( 6C_6 \left( \frac{1}{x} \right)^7 + 8C_8 \left( \frac{1}{x} \right)^9 + 10C_{10} \left( \frac{1}{x} \right)^{11} \right) \cdot \frac{d}{dx}F(x) \\
- \left( C_6 \left( \frac{1}{x} \right)^6 + C_8 \left( \frac{1}{x} \right)^8 + C_{10} \left( \frac{1}{x} \right)^{10} \right) \cdot \frac{d^2}{dx^2}F(x) \right].
\]

Notice that only the repulsive term and its derivatives are different from those in the Aziz interaction potential used for helium-helium interactions that is discussed in the body of
H.2. TAIL CORRECTIONS

First, we present the potential energy tail correction. For 3 spatial dimensions, this may be found to be

\[ V_{3d}^{\text{tail}} = N\pi \rho \frac{A \epsilon}{4\beta} \exp \left( -\frac{\alpha^2}{4\beta} \right) \left\{ \sqrt{-\pi \beta} (2\beta - \alpha^2) \text{erfc} \left( \frac{\alpha - 2\beta L}{2\sqrt{-\beta}} \right) - 2\beta (\alpha + 2\beta L) \exp \left( \frac{(\alpha - 2\beta L)^2}{4\beta} \right) - 2\epsilon \left( \frac{C_{10}}{7L^7} + \frac{C_8}{5L^5} + \frac{C_6}{3L^3} \right) \right\}. \]  

(H.5)

where \( L = r_c/r_m \) is the reduced cutoff length. In 2d, this may be found to be

\[ V_{2d}^{\text{tail}} = N\pi \rho \frac{A \epsilon}{4\beta^2} \exp \left( -\frac{\alpha^2}{4\beta} \right) \left\{ \sqrt{-\pi \beta} \text{erfc} \left( \frac{\alpha - 2\beta L}{2\sqrt{-\beta}} \right) + 2\beta \exp \left( \frac{(\alpha - 2\beta L)^2}{4\beta} \right) - \epsilon \left( \frac{C_{10}}{8L^8} + \frac{C_8}{6L^6} + \frac{C_6}{4L^4} \right) \right\}. \]  

(H.6)

And in 1d,

\[ V_{1d}^{\text{tail}} = N\rho \left\{ \frac{A \epsilon}{4} \sqrt{-\frac{\pi}{\beta}} \exp \left( -\frac{\alpha^2}{4\beta} \right) \text{erfc} \left( \frac{\alpha - 2\beta L}{2\sqrt{-\beta}} \right) - \frac{\epsilon}{2} \left( \frac{C_{10}}{9L^9} + \frac{C_8}{5L^5} + \frac{C_6}{7L^7} \right) \right\}. \]  

(H.7)

It is apparent that one must choose a suitable library for computing error functions if these tail corrections are to be computed in numerical simulations. Next, we present the pressure tail corrections in all three dimensions. Starting with 3d, we see
APPENDIX I

STARTING JOBS AT DIFFERENT TEMPERATURES FROM THE SAME EQUILIBRATED STATE

Often in large scale path integral Monte Carlo simulations one may have a set of equilibrated state files for a given set of temperatures and desire to have the state files for a different set of temperatures. This may occur if you want to ‘fill in’ data. This section outlines a method that allows you to take a state file for a quantum system at a given temperature, hence a given number of time slices, and quickly find an equilibrated state for a system at a higher or lower temperature.

I.1 UPSAMPLING AND DOWNSAMPLING METHOD

The method implemented is borrowed from signal analysis, and is related to interpolation. Let’s say that you want to go from a worldline that contains \( M_1 \) beads to one that contains \( M_2 \) beads. It doesn’t matter which number of time slices is greater, as this method works the same way regardless.

First, we take the array of \( M_1 \) beads and turn it into an array of \( M_1 \) times \( M_2 \) beads. This is done by placing \( M_2 \) beads evenly spaced between each of the \( M_1 \) existing beads. This is known as upsampling. Next, we choose a starting bead arbitrarily and add it to the
I.1. UPSAMPLING AND DOWNSAMPLING METHOD

new array that will hold our worldline with a different number of beads. Now step along the upsampled worldline in units of \( M_2 \) steps, keeping each one that you land on until you loop back on the first bead, leaving you with an array of size \( M_2 \). This second step is known as downsampling. This method is illustrated in Figure I.1. It should be apparent from this figure that one could decrease or increase the number of time slices using this method. The target number of time slices should be relatively close to the one you are starting from.

This method is particularly nice compared to more primitive methods when studying superfluid systems. In the case of a superfluid system, we see topological winding which stabilizes the superfluid state. If we are well below the critical temperature and want to
I.2. EFFICIENCY GAINS FROM THIS METHOD

start from an equilibrated state at a different temperature that is also below the Lambda point, it is going to be more efficient to start from a state which preserves this winding, as will be done here. The one slight drawback to this method is that we increase the length of the links between beads when going from lower temperatures to higher temperatures (and vice-versa from higher to lower), which is the opposite of what actually happens to these worldlines when the temperature changes. This still turns out to greatly decrease the equilibration time for lower temperatures systems due to the reasons already mentioned.

I.2 EFFICIENCY GAINS FROM THIS METHOD

The way that starting from an equilibrated state of a different number of time slices was implemented before was to simply choose a bead from each worldline and place the new worldline all at this one location. This is what is referred to as a classical configuration. From here, the standard type of equilibration moves were used. Because this state would be pretty close to the classically equilibrated state, it is referred to as loading a classical state. Here, we show the efficiency gained with loading a quantum state via sampling versus this classical method.
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