Quantum Monte Carlo Simulations: From Few to Many Species

by

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ABSTRACT

QUANTUM MONTE CARLO SIMULATIONS: FROM FEW TO MANY SPECIES

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We study systems of particles with varying numbers of distinguishable species ranging from 4-species to the $N$-species limit, where $N$ is the number of particles in the system itself. We examine these systems using various powerful simulation techniques that belong to the quantum Monte Carlo (QMC) family. The $N$-species limit is studied via Path Integral Monte Carlo (PIMC), which is a finite temperature, non-perturbative technique. At this limit, we explore the viability of two different thermal density matrices for systems that interact via hard-sphere, hard-cavity potentials. We then study the impact of finite-size effects on calculations of the energy, pressure and specific heat of the system when reaching the thermodynamic limit under periodic boundary conditions. We then move to studying a 4-species fermionic system using Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC), which are ground state techniques. We apply these methods to the clustering problem of 4-particle and 8-particle systems. While the 4-particle, 4-species system is relatively simple to calculate as it is physically identical to a bosonic system of 4-particles, the 8-particle fermi system is more complicated. We detail the process of simulating a bound 8-particle state with respect to decay into two independent 4-particle clusters with DMC for the first time.
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Chapter 1

Introduction

The study of cold atomic systems has been of great interest over the past century or so and has given great insight into fundamental quantum phenomena. More recently, experimentalists have been able to probe cold Fermi gases and even tune the interaction between two atoms via the use of Feshbach resonances. This allowed unprecedented access to detailed features or novel aspects of quantum many-body physics, leading to confrontation of theory with experiment [1]. The specific systems probed include homogeneous and trapped Fermi gases beyond $^3$He, polarons, optical lattices, Fermi-Fermi and Bose-Fermi mixtures, lower-dimensional systems, spin-orbit coupled gases, among several related settings [1, 2, 3, 4, 5, 6, 7].

In the study of quantum many-body physics an important feature of the system is the type of statistics that the particles obey. When the temperature is low enough such that the thermal de Broglie wavelength of the particles is of the same order as the interparticle spacing the particles are said to be indistinguishable. When this occurs in systems consisting of one species of particles, Fermi-Dirac statistics, in which quantum states can only be occupied by one particle and the wave function
is antisymmetric under two-particle exchange, are needed for fermions and Bose-
Einstein statistics, in which there is no limit to the number of particles occupying a
state and the wave function is symmetric under two-particle exchange, for bosons.
At larger temperatures, such systems follow Maxwell-Boltzmann statistics [8].

A current frontier in cold-atom physics is the study of many-component gases:
the leading contenders have been $^{173}$Yb and $^{87}$Sr [9, 10, 11, 12, 13, 14, 15, 16, 17,
18, 19, 20]. The motivation behind such experiments is to use a large number of
atoms $N$, distributed among different states. The natural extension of this approach
is to keep increasing the number of possible states among which the total number
of particles is distributed. The extreme case of this scenario is when the number of
states equals the number of particles, namely each component/species is placed in
a distinct state: the particles may still be strongly interacting with each other, but
the fermionic (or bosonic) nature of the underlying atom is no longer relevant. This
is the problem we are interested in in the first half of this thesis, namely the study
of quantum Boltzmannons, where quantum mechanics plays a significant role but
quantum statistics doesn’t. Since each particle is taken to be in a different quantum
state, the particles are distinguishable, so they follow Maxwell-Boltzmann statistics
even at low temperature.

Cold atomic systems are also valuable to study as they can be used as a model
for other areas of Physics as well. Cold atoms have proven to be a good laboratory
for studying nucleonic matter [21, 22, 23, 24] Thus, experiments with two species of
cold Fermi gases probe the physics of strong pairing, which is very similar to that
of low-density neutron matter, found in the inner crusts of neutron stars. Similarly,
the three-species quantum problem and the related area of Efimov physics have been
of interest to both nuclear and atomic physicists [25, 26]. The obvious extension,
the four-species problem, is of direct relevance to all of nuclear physics, since nuclei on earth and nucleonic matter in astrophysical settings are all made up of neutrons and protons (with two spin-projection states each). As more species are added to the problem, one can attempt to disentangle the effect of interactions from that of statistics. This is somewhat analogous to the large species limit of Quantum Chromodynamics, as studied in previous work [27]. Importantly, one can expect that the many-species cold-atom problem may be experimentally probed in the not too distant future.

The second half of this thesis focuses on simulations of systems containing a fixed number of four species. In these simulations we are now forced to consider the fermionic nature of the system. As stated previously these calculations are relevant to the nuclear problem, as well as closer to what can be experimentally probed. A main focus within this thesis is the ability of Quantum Monte Carlo to successfully simulate the four-species fermi gas.

Quantum Monte Carlo (QMC) is a term describing a family of powerful theoretical simulation techniques applied to several different physical systems, including cold-atomic gases. QMC methods are typically non-perturbative and can probe both weak coupling and strong coupling, at both zero temperature [28, 29, 30, 31, 32, 33, 34, 35] and finite temperature [36, 37, 38, 39, 40, 41, 42, 43]. The particular QMC methods used in this work are Path Integral Monte Carlo (PIMC), Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC). The Path integral Monte Carlo simulation techniques described and utilized in this work are suited to systems that obey Maxwell-Boltzmann statistics (Boltzmannons) and can be used to calculate thermodynamic properties of systems composed of distinguishable particles in the quantum regime. With this technique it is possible to calculate quantities such as
the energy, pressure and specific heat (to name a few) of interacting particles at finite temperatures. The interactions focussed on in this work are those of hard spheres and hard cavities. These interactions have been a topic of interest in the past in PIMC simulations, and other computational studies, due to the fact that they can be handled with relative computational ease, and they provide a standard form for repulsive interactions between atoms [44]. VMC and DMC are used to calculate the ground state \( (T = 0) \) of systems that obey Fermi-Dirac and Bose-Einstein. In these techniques we begin with the Hamiltonian we wish to study and a trial wave function that we believe is suitable for the particular system. In this work we focus on central potentials with 2- and 3-body components.
Chapter 2

Quantum Boltzmannons

An important aspect of studying statistical mechanical properties is the evaluation of the partition function. However, for a large system of interacting particles it is extremely difficult to evaluate the partition function directly. In PIMC, the partition function is evaluated using a path integral approach where thermal density matrices can be thought of as propagators over discretized imaginary time slices that form a path in coordinate space. Approximations are utilized to evaluate the thermal density matrices for the specific interactions found in the system being studied. For hard-sphere and hard-cavity interactions two approximations are commonly used, the Image Approximation (IA) [45] and another derived by Cao & Berne (CB) [46]. These approximations become more accurate as the path becomes more discretized and the number of imaginary time-slices increases, becoming exact in the limit of infinite time slices. However, increasing the number of time-slices causes an increase in computational time. Thus, a good measure for the effectiveness of an approximation is how quickly its simulation results converge as a function of number of

The work presented in this chapter is adapted from the article *Path-integral Monte Carlo study of particles obeying quantum mechanics and classical statistics*, published in Physics Review A. by the same author as this thesis with Alexandros Gezerlis.
time-slices. Crucially, Boltzmannons do not suffer from the fermion-sign problem, so a non-perturbative PIMC calculation for this system is in principle exact (of course, one must still carefully study finite-size effects, time slice errors, and so on, as we do below).

In this chapter, we perform an analytic calculation of the energy for a two-body system interacting via a hard-sphere, hard-cavity interaction and perform PIMC simulations for the same system using both the IA and the CB approximations at varying temperatures. We study the convergence of both approximations to the analytic value as a function of number of time-slices. Additionally, we carry out calculations of the energy, pressure, and specific heat of a system of $N$ hard-sphere particles under periodic boundary conditions using the CB density matrix. We investigate finite-size effects and at what value of $N$ do these finite-size effects drop away and the thermodynamic limit can be said to have been reached.

2.1 Path Integral Monte Carlo Method

2.1.1 Partition Function in the Path Integral Monte Carlo Formalism

A fundamental quantity in a statistical mechanical description of a system is the thermal density matrix. The thermal density matrix is defined as:

$$\hat{\rho} = e^{-\beta \hat{H}} = \sum_i |\psi_i\rangle \langle \psi_i| e^{-\beta E_i} \quad (2.1)$$

Where $\beta = 1/k_B T$, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\psi_i$ are the eigenstates of the system, and $E_i$ are the associated eigenenergies.
One often wishes to compute the partition function because of its usefulness in deriving other thermodynamic quantities. The partition function is defined as the trace of the thermal density matrix. In the PIMC formalism the trace is performed in the position basis:

\[ Z = Tr(\hat{\rho}) = \int dR \langle R | e^{-\beta \hat{H}} | R \rangle \]  

(2.2)

where \( R \) represents the set of positions of all \( N \) particles in the system, \( R = (r_1, r_2, \ldots, r_N) \). The matrix element in the above integration cannot in general be calculated exactly for Hamiltonians of interacting many-body systems. To continue with the evaluation of the partition function one can expand the above integral using the two following relations:

\[ e^{-\beta \hat{H}} = e^{-\frac{\beta}{2} \hat{H}} e^{-\frac{\beta}{2} \hat{H}} \]  

(2.3)

By using these relations \( M - 1 \) times, the partition function can be written as:

\[ Z = \int \ldots \int dR dR_1 dR_2 \ldots dR_{M-1} \langle R | e^{-\frac{\beta}{M} \hat{H}} | R_1 \rangle \times \]  

\[ \langle R_1 | e^{-\frac{\beta}{M} \hat{H}} | R_2 \rangle \ldots \langle R_{M-1} | e^{-\frac{\beta}{M} \hat{H}} | R \rangle \]  

(2.4)

It can now be seen where the analogy to the Feynman path integral can be made. The operator \( e^{-\frac{\beta}{M} \hat{H}} \) is analogous to the time-evolution operator that evolves the system between subsequent states \( |R_i\rangle \), except \( it/\hbar \) is replaced with \( \beta/M \). As a result, \( \beta/M \) is the so-called ‘imaginary time’ and Eq. (2.4) can be thought of as a path integral with \( M \) imaginary time slices.
To continue the derivation it is necessary to evaluate the intermediate density matrix elements that are being integrated over. To do this, the Trotter-Suzuki formula is used:

$$e^{(\hat{A}_1 + \hat{A}_2)/M} \approx e^{\hat{A}_1/M}e^{\hat{A}_2/M}$$  \hspace{1cm} (2.5)

where $M$ is taken to be large. Here, $\hat{A}_1$ and $\hat{A}_2$ are operators that do not necessarily commute. Applying this formula to the intermediate density matrices yields:

$$\langle \mathbf{R}'' | e^{-\tau \hat{H}} | \mathbf{R}' \rangle \approx \langle \mathbf{R}'' | e^{-\tau \hat{K}} e^{-\tau \hat{V}} | \mathbf{R}' \rangle$$  \hspace{1cm} (2.6)

where $\tau = \beta/M$ and, again, $M$ is taken to be large. Also, $\hat{H} = \hat{K} + \hat{V}$ where $\hat{K}$ is the kinetic operator, $\hat{V}$ is the potential operator. From Trotter-Suzuki we see $M$ must be taken to be very large in order for this expression to be near exact. It is now possible to evaluate the matrix element of both the exponentiated kinetic and potential operators separately:

$$\langle \mathbf{R}'' | e^{-\tau \hat{K}} | \mathbf{R}' \rangle = \left( \frac{Mm}{2\pi \hbar^2 \beta} \right)^{3N/2} \exp \left[ -\frac{Mm}{2\hbar^2 \beta} (\mathbf{R}'' - \mathbf{R}')^2 \right]$$  \hspace{1cm} (2.7)

$$\langle \mathbf{R}'' | e^{-\tau \hat{V}} | \mathbf{R}' \rangle = \exp \left[ -\frac{\beta}{M} V(\mathbf{R}') \right] \delta(\mathbf{R}'' - \mathbf{R}')$$  \hspace{1cm} (2.8)

Now the path integral form of the partition function can be written as:

$$Z = \int \cdots \int d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_M \left( \frac{Mm}{2\pi \hbar^2 \beta} \right)^{3N_M/2} \times$$

$$\times \exp \left[ -\frac{Mm}{2\hbar^2 \beta} \sum_{l=1}^{M} (\mathbf{R}_l - \mathbf{R}_{l+1})^2 \right] \exp \left[ -\frac{\beta}{M} \sum_{l=1}^{M} V(\mathbf{R}_l) \right]$$  \hspace{1cm} (2.9)

which is exact in the limit of $M$ going to infinity. It is important to realize that in
the above expression the position state $R_M$ is the original state of which the trace in Eq. (2.2) is being performed over. Additionally, the path integral in the above expression begins and ends at the same state since the partition function is an integral over the diagonal thermal density matrix elements. As a consequence, $R_{M+1} = R_1$.

It should also be noted that the manner with which the potential operator component of the density matrix is handled here is called the ‘primitive approximation’. The present work does not use this approximation in calculations, but it is convenient for introducing and deriving the PIMC technique [47, 48].

2.1.2 Calculating Thermodynamic Averages

As mentioned above, the previous derivation of the partition function uses the primitive approximation to evaluate thermal density matrices. In practice, we evaluate density matrices as follows:

$$\langle R'' | e^{-\tau \hat{H}} | R' \rangle = \langle R'' | e^{-\tau \hat{K}} | R' \rangle \prod_{i,j} \tilde{\rho}(r''_{i,j}, r'_{i,j}, \tau)$$

(2.10)

where $r''_{i,j} = r''_i - r''_j$, $r'_{i,j} = r'_i - r'_j$ and $\tilde{\rho}(r''_{i,j}, r'_{i,j}, \tau)$ is the two-body density matrix, which has replaced the exponentiated potential operator. The two-body density matrix contains information about the interactions between the particles in the system. For the hard sphere and hard cavity interactions that are of interest in this work, there are well-known two-body density matrices (See Secs. 2.2 and 2.3).

Now that the partition function of the system has been found (with the use of the appropriate two-body density matrix) thermodynamic observables can be calculated.
In general, these observables are calculated as:

$$
\langle \hat{O} \rangle = \frac{1}{Z} \text{Tr}(\hat{O}\rho)
$$

(2.11)

In the PIMC formalism Eq. (2.11) becomes:

$$
\langle \hat{O} \rangle = \int d\mathcal{R}O(\mathcal{R})W(\mathcal{R})
$$

(2.12)

where $\mathcal{R} = \{\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_M\}$, which is referred to as the path, and $W(\mathcal{R})$ can be thought of as a probability distribution of all possible paths written as:

$$
W(\mathcal{R}) = \frac{1}{Z} \left( \frac{Mm}{2\pi\hbar^2\beta} \right)^{3NM/2} \exp \left[ \frac{-Mm}{2\hbar^2\beta} \sum_{l=1}^{M} (\mathbf{R}_l - \mathbf{R}_{l+1})^2 \right] \times
$$

$$
\times \prod_{l=1}^{M} \prod_{i,j} \tilde{\rho}(\mathbf{r}_{l,(i,j)}, \mathbf{r}_{l+1,(i,j)}, \tau)
$$

(2.13)

where $\mathbf{r}_{l,(i,j)} = \mathbf{r}_{l,i} - \mathbf{r}_{l,j}$ and $\mathbf{r}_{l+1,(i,j)} = \mathbf{r}_{l+1,i} - \mathbf{r}_{l+1,j}$.

For the calculation of specific observables the functional form of $O(\mathcal{R})$ must be known. These functions are referred to as estimators and can be derived from the appropriate derivatives of the partition function. As an example, the energy of a system is given by:

$$
\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}
$$

(2.14)

Carrying out this derivative gives the energy estimator:

$$
E(\mathcal{R}) = \frac{3NM}{2\beta} - \frac{Mm}{2\hbar^2\beta^2} \sum_{l=1}^{M} (\mathbf{R}_l - \mathbf{R}_{l+1})^2 -
$$

$$
- \sum_{l=1}^{M} \sum_{i,j} \frac{\partial \ln (\tilde{\rho}(\mathbf{r}_{l,(i,j)}, \mathbf{r}_{l+1,(i,j)}, \tau))}{\partial \beta}
$$

(2.15)
An estimator for pressure can be derived in a similar manner. The average pressure of a system is given by:

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \Omega}$$  \hspace{1cm} (2.16)$$

leading to:

$$P(\mathcal{R}) = \frac{NM}{\beta \Omega} - \frac{Mm}{3h^2 \beta^2 \Omega} \sum_{l=1}^{M} (R_l - R_{l+1})^2 + $$

$$+ \frac{1}{\beta} \sum_{l=1}^{M} \sum_{i,j} \frac{\partial \ln (\tilde{\rho}(r_{l,(i,j)}, r_{l+1,(i,j)}, \tau))}{\partial \Omega}$$  \hspace{1cm} (2.17)$$

Where $\Omega$ is the volume of the simulation box. With these estimators the average energy and pressure can be calculated by plugging Eqs. (2.15) and (2.17) into the integral of Eq. (2.12). However, these integrals cannot be evaluated analytically. Instead, a standard Metropolis algorithm is used to sample configurations from the set $\{ \mathcal{R} \}$ according to the probability distribution $W(\mathcal{R})$ (see Sec. 3.3.1 for an outline of the metropolis algorithm). The estimators are then evaluated at each sampled configuration and the average is taken. Therefore the final expressions for the average energy and pressure of a system are:

$$\langle E \rangle = \langle \frac{3NM}{2\beta} - \frac{Mm}{2h^2 \beta^2} \sum_{l=1}^{M} (R_l - R_{l+1})^2 - $$

$$- \sum_{l=1}^{M} \sum_{i,j} \frac{\partial \ln (\tilde{\rho}(r_{l,(i,j)}, r_{l+1,(i,j)}, \tau))}{\partial \beta} \rangle$$  \hspace{1cm} (2.18)$$

$$\langle P \rangle = \langle \frac{NM}{\beta \Omega} - \frac{Mm}{3h^2 \beta^2 \Omega} \sum_{l=1}^{M} (R_l - R_{l+1})^2 + $$

$$+ \frac{1}{\beta} \sum_{l=1}^{M} \sum_{i,j} \frac{\partial \ln (\tilde{\rho}(r_{l,(i,j)}, r_{l+1,(i,j)}, \tau))}{\partial \Omega} \rangle$$  \hspace{1cm} (2.19)$$
where $\langle \cdots \rangle$ denotes an average over configurations sampled with the Metropolis algorithm. As mentioned previously, the number of time slices, or $M$, in the above expressions is an arbitrary parameter that can be set to any positive integer value. However, as discussed, the approximations that were required to derive these expressions require large $M$ to be accurate. As a result, calculations of the energy and pressure in PIMC simulations will converge, over increasing $M$, to the correct value [47, 48].

2.2 Two-Particle Hard-Sphere & Hard-Cavity System

2.2.1 Analytic Calculation of Energy

An objective of this work was to test the effectiveness of two well-known approximations for two-body density matrices used in hard-sphere and hard-cavity interactions. To do this, we first analytically calculate the energy of a system in contact with a heat bath at temperature $T$, consisting of two particles that have a hard-sphere radius of $\sigma$ and cannot be separated by a distance greater than a specified hard-cavity radius $r_{\text{cav}}$. Once this calculation was performed for various temperatures, PIMC simulations were also performed for the same system using both of the two-body density matrix approximations. The convergence of these simulations to the analytic results as a function of $M$ was then observed.
The two-body Schrödinger equation when the potential is a function of the distance between the particles can be separated into the following differential equations:

\[-\frac{\hbar^2}{2M} \nabla^2_R \psi = E_M \psi \]  

\[- \frac{\hbar^2}{2\mu} \nabla^2_r \psi + V(|r_1 - r_2|) \psi = E_\mu \psi \]  

(2.20)

(2.21)

where we use $|r_1 - r_2|$ and $r$ interchangeably. Our task has now been separated into two problems: one is a free particle of mass $M = 2m$ in the centre of mass position Eq. (2.20), and the other is a particle of reduced mass $\mu = m/2$ whose radial component is that of the separation distance in the original problem Eq. (2.21). $E_M$ denotes the centre of mass energy, and $E_\mu$ is the separation distance energy.

To solve for the expectation value of the energy at a finite temperature, the energy levels of the system must be solved for and then averaged using Boltzmann statistics.

The centre of mass energy is continuous since it is a free particle and can be calculated as:

\[
\langle E_M \rangle = \frac{\Omega m^{3/2}}{\sqrt{2\pi} \hbar^3} \int_0^\infty E^{3/2} e^{-\beta E} dE 
\]

\[
Z = \frac{\Omega m^{3/2}}{\sqrt{2\pi} \hbar^3} \int_0^\infty E^{1/2} e^{-\beta E} dE 
\]

(2.22)

which can now be solved for a general inverse temperature $\beta$.

The potential for the two-particle system we are studying, $V(|r_1 - r_2|)$, is defined
in the following way:

\[
V(|\mathbf{r}_1 - \mathbf{r}_2|) = \begin{cases} 
0 & \text{if } \sigma \leq |\mathbf{r}_1 - \mathbf{r}_2| \leq r_{cav} \\
\infty & \text{otherwise}
\end{cases}
\]

This leads to the following differential equation for the radial component of the wavefunction in the separation distance:

\[
\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \left( k^2 - \frac{l(l+1)}{r^2} \right) R = 0
\]

\[k = \frac{\sqrt{2mE_\mu}}{\hbar}\]

The solutions to this differential equation are the spherical Bessel functions of the first and second kind, therefore the radial wavefunctions are taken to be:

\[
R_l(r) = A j_l(kr) + B n_l(kr)
\]

where the \(j_l\)’s are the first kind and the \(n_l\)’s are the second. The \(k\) values are solved for by imposing the boundary conditions of the problem: \(R(\sigma) = 0\) and \(R(r_{cav}) = 0\). This results in the following transcendental equation that \(k\) must satisfy:

\[
j_l(r_{cav}k) - \frac{j_l(\sigma k)}{n_l(\sigma k)} n_l(r_{cav}k) = 0
\]

Once the solutions for \(k\) have been determined, the energy levels for the reduced mass component of the energy are given by:

\[
E_{\mu,l,i} = \frac{\hbar^2 k_{l,i}^2}{2\mu}
\]
where \( l \) is the \( l \)'th spherical Bessel function and \( i \) is \( i \)'th \( k \) value associated with the \( l \)'th spherical Bessel function. According to Boltzmann statistics, the expectation value of the energy becomes:

\[
\langle E_{\mu} \rangle = \frac{1}{Z} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \sum_{i=1}^{\infty} E_{\mu,l,i} e^{-\beta E_{\mu,l,i}}
\]

\[
Z = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} \sum_{i=1}^{\infty} e^{-\beta E_{\mu,l,i}}
\]  

(2.27)

where \( m_l \) is the regular magnetic quantum number introduced in the 3D Schrödinger equation solved in spherical coordinates. Since the potential has no angular dependence \( m_l \) introduces a \( 2l + 1 \) degeneracy in the energy levels.

Now the total energy can be calculated as:

\[
\langle E \rangle = \langle E_M \rangle + \langle E_{\mu} \rangle
\]  

(2.28)

### 2.2.2 PIMC Calculation of Energy

The two-body density matrices used in this work are the IA and the CB density matrix. The Image Approximation is a simple way of meeting the requirement of going to zero as \( r \) goes to \( \sigma \) or \( r_{cav} \). On the other hand, the CB two-body density matrix is based on the partial-wave scattering solution of hard-sphere potentials and is a more general formula (which reduces to the IA one under specific conditions). Because of this, it is expected the CB density matrix will yield better convergence. The functional forms of the two-body density matrices used in this work are given as: [46]
Figure 2.1: PIMC results for the two particle hard-sphere, hard-cavity system using both the IA and CB density matrix approximations compared to analytic results. The temperature of the system is $T = (\hbar^2/m\sigma^2 k_B)^{-1} = 1.0$ and $r_{cav}/\sigma = 6$. Convergence of the PIMC results to the analytic energy occurred at approximately the same rate for both density matrices.
Figure 2.2: PIMC results of the energy for two particle hard-sphere, hard-cavity interaction for both Image Approximation and CB thermal density matrices.
\[
\tilde{\rho}_{IA}(\mathbf{r}, \mathbf{r}') = (1 - \exp[-(Mm/\beta \hbar^2)(\mathbf{r} - \mathbf{\sigma})(\mathbf{r}' - \mathbf{\sigma})]) \times \\
(1 - \exp[-(Mm/\beta \hbar^2)(\mathbf{r}_{cav} - \mathbf{r})(\mathbf{r}_{cav} - \mathbf{r}')]])
\]

\[
\tilde{\rho}_{CB}(\mathbf{r}, \mathbf{r}') = (1 - \frac{\sigma(r + r') - \sigma^2}{rr'}) \times \\
\exp[-(Mm/2\beta \hbar^2)(\mathbf{r} - \mathbf{\sigma})(\mathbf{r}' - \mathbf{\sigma})(1 + \cos \chi)]) \times \\
(1 - \frac{2\mathbf{r}_{cav} - \mathbf{r}}{\mathbf{r}}) \times \\
\exp[-(Mm/4\beta \hbar^2)((\mathbf{r}_{-1} + \mathbf{r}')^2 - (\mathbf{r} - \mathbf{r}')^2)]
\]

\[
\mathbf{r}_{-1} = (\mathbf{r} - 2\mathbf{r}_{cav})\hat{\mathbf{r}}
\]

where we have defined \( r \) to always be the larger of the two vector magnitudes, i.e. \( r \geq r' \) and \( \chi \) is the angle between \( \mathbf{r} \) and \( \mathbf{r}' \). Both \( \tilde{\rho}_{IA} \) and \( \tilde{\rho}_{CB} \) are set to zero if \( r \) or \( r' \) are less than \( \sigma \) or greater than \( r_{cav} \).

Calculations of the energy of the system were performed at five different temperatures for increasing number of time slices. The results are presented in reduced units where \( \sigma \) is the unit of length and \( \hbar^2/m\sigma^2 \) is the unit of energy.

Convergence studies for the two density matrices using the two-particle calculation were carried out at varying temperatures, \( T(\hbar^2/m\sigma^2k_B)^{-1} = 0.5, 1.0, 1.6, 2.0, 2.5 \). The results for the convergence study at \( T(\hbar^2/m\sigma^2k_B)^{-1} = 1.0 \) are presented in Fig. 2.1. It was found that in all cases of varying temperature the general behaviour of the PIMC results vs temperature as a function of time slices remains fairly constant. For this system, PIMC simulations converge rather quickly to the analytic result.
regardless of the density matrix approximation that is used. It could be argued the Image Approximation density matrix gives slightly quicker convergence over the CB density matrix, but the difference is fairly insignificant.

PIMC results for the energy vs temperature for both thermal density matrices and analytic results are plotted in Fig. 2.2. Both sets of results are in close agreement with each other and both agree very well with the analytic results given by the calculations outlined in Sec. 2.2.1 over the entire range of temperatures studied.

Even though a significant difference between the convergence of the density matrices was not observed, it was decided that the CB density matrix should be used in the many body system calculations moving forward. This is because, as mentioned earlier, the CB form was more rigorously derived based on the partial-wave scattering solution for the hard-sphere interaction.

2.3 Many Hard-Sphere Particle System

2.3.1 Non-Interacting Boltzmannon Gas

In this section we discuss the calculation of the energy and specific heat of a system composed of many non-interacting Boltzmannons under periodic boundary conditions. Periodic boundary conditions (PBC) in simulations are meant to approximate an infinite system in which a relatively small simulation box is repeated in all directions, and particles that leave one side of the box re-enter from the opposite side. PBC can be mathematically expressed as:

\[ \psi(x, y, z) = \psi(x \pm L_x, y \pm L_y, z \pm L_z) \]  \hspace{1cm} (2.32)
Figure 2.3: Energy per particle of non-interacting gas of distinguishable particles vs temperature for increasing particle number. At small values of $N$ finite-size effects cause a deviation from the expected $E/N = \frac{3}{2} k_B T$; as $N$ is increased, the expected behaviour is observed at lower $T$. Inset: Energy per particle of non-interacting gas vs $N$ at $T(\hbar^2/m\sigma^2 k_B)^{-1} = 0.1$, $n\sigma^3 = 0.2063$. As the particle number rises, $E/N$ approaches a constant value.
Figure 2.4: Specific heat of non-interacting gas of distinguishable particles vs temperature for increasing particle number, \( n_\sigma^3 = 0.2063 \). At small values of \( N \) a spike observed in \( c_v \) at lower temperatures; as \( N \) is increased, this spike becomes smaller and is seen at lower \( T \) as finite-size effects fall away.

where \( L_{x,y,z} \) are the lengths of the simulation box in the \( x, y, z \) directions. Often times, and in the case of our simulations, the geometry of the simulation box is taken to be a cube, therefore \( L_x = L_y = L_z = L \).

PBC are useful as a simulation can be performed with a computationally manageable number of particles (10-1000), but can simulate properties of macroscopic systems at the thermodynamic limit when \( N \to \infty \) and \( \Omega \to \infty \), while the number density \( n = N/\Omega \) is a constant. An issue with PBC is inaccuracies which are a result of finite-size effects. Finite-size effects are a result of the system within the simulation box being too small (i.e. too few particles). Finite-size effects can be observed by
increasing the particle number and volume while maintaining a constant density and observing if intensive properties (i.e. independent of particle number) change. An example of finite-size effects can be seen in calculations of energy per particle and specific heat of a system of non-interacting Boltzmannons. To begin, the eigenvalues of energy for a system of non-interacting particles under PBC are given as:

\[ E_n = \frac{\hbar^2}{2m} |\mathbf{k}_n|^2 \]

\[ \mathbf{k}_n = \frac{2\pi}{L} (n_x \hat{x} + n_y \hat{y} + n_z \hat{z}) \]  

(2.33)

where \( L \) is the length of our simulation box and \( n_x, n_y, n_z \) are integers. The energy of the system at a specific temperature is calculated by averaging the eigenenergies over the usual Maxwell-Boltzmann factor \( e^{-\beta E_n} \). This calculation was performed at a constant density of \( n_\sigma^3 = 0.2063 \) at increasing particle number values. The results are plotted in Fig. 2.3. The expected behaviour of a non-interacting gas that obeys Boltzmann statistics is given by the equipartition theorem. For a 3D system where particles only have translational degrees of freedom, energy is related to temperature by:

\[ \frac{E}{N} = \frac{3}{2} k_B T \]  

(2.34)

In Fig. 2.3 it can be seen that as the particle number is decreased, finite-size effects cause a deviation from the equipartition theorem at increasingly higher temperatures. \( E/N \) is plotted against \( T \) for \( N = (60, 100, 250, 500, 1000, 10000) \) and it can be seen that as \( N \) increases, finite-size effects fall away and the results eventually converge. Finite-size effects are more prominent at lower \( T \). For \( N = 100 \) the results only begin to match what is expected at \( T \approx 0.3 \), which is drastically improved by the increase of the system size to \( N = 250 \), and as \( N \) is further increased, the expected result
is found at lower and lower temperatures. The inset in Fig. 2.3 shows the reduction of finite-size effects at $T(\hbar^2/m\sigma^2k_B)^{-1} = 0.1$ as $N$ is increased and $E/N$ eventually reaches the expected 0.15 ($\hbar^2/m\sigma^2$), and then stays constant as $N$ is further increased.

The specific heat of this system was calculated by the derivative of $E/N$ with respect to $T$ at all values of $N$ previously used. Fig. 2.4 again shows the convergence to the equipartition theorem at lower and lower $T$ as $N$ is increased. At lower $T$, $c_v$ increases from the expected values of 1.5 $k_B$, as predicted by the equipartition theorem, and then quickly decreases as $T$ is further decreased. This behaviour becomes less and less prominent as $N$ is increased, and $c_v$ eventually converges to the expected value.

Because of finite-size effects, care must be taken to ensure simulations are being performed with an adequate system size such that the results are representative of the thermodynamic limit. In the next section we explore at what system size the thermodynamic limit is reached for simulations of hard-sphere Boltzmannons using the CB thermal density matrix.

2.3.2 Hard-Sphere Boltzmannons

In this section we study systems of hard sphere particles using the PIMC methods described in the previous sections. As opposed to the two-particle calculation, this system does not have hard-cavity interactions present, as a result the CB two-body density matrix takes the form:

$$
\rho_{CB}(\mathbf{r},\mathbf{r}') = (1 - \frac{\sigma(r + r') - \sigma^2}{rr'} \times \\
\times \exp\left[-\frac{(Mm/2\beta\hbar^2)(r - \sigma)(r' - \sigma)(1 + \cos\chi)}{\sigma^2}\right]
$$

(2.35)
Figure 2.5: Energy of 20-particle system produced by PIMC vs the number of steps in the Metropolis algorithm. When taking the average of these results equilibration time must be taken into account. This calculation was performed at $T(h^2/m\sigma^2k_B)^{-1} = 1.0$, $n\sigma^3 = 0.2063$ and $M = 41$. Inset: A closer look at the equilibration of the system over the early steps.
Fig. 2.5 shows the energy for a simulation of a 20-particle system with \( T(\hbar^2/m\sigma^2k_B)^{-1} = 1.0, \ n\sigma^3 = 0.2063 \) and \( M = 41 \) at each configuration sampled by the Metropolis algorithm. An important detail of these simulations is to account for the equilibration time, which can be seen in the inset of Fig. 2.5. When evaluating averages, one should only include values taken after the system has equilibrated.

We perform our calculations for the energy per particle and pressure using the PIMC method at varying temperatures and particle numbers while maintaining a constant density. As stated earlier, intensive properties such as the energy per particle or pressure are not affected by the number of particles in the system, but rather the number density \((N/\Omega)\), that is, a system of varying particle number, but constant density, will have a constant \( E/N \) and \( P \). In our simulations it is expected that as the number of particles in our simulation box increases, \( E/N \) and \( P \) will vary at small values of \( N \), but will eventually reach a constant value, analogously to the non-interacting case.

In our PIMC calculations, particle number was increased until the results for energy per particle and pressure reached a final value. These calculations were performed at varying temperatures \( (T(\hbar^2/m\sigma^2k_B)^{-1} = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0) \) and varying particle numbers \((N = 20, 60, 108, 200, 300, 400)\) at a density \( n\sigma^3 = 0.2063 \). This density was chosen such that the Wigner-Seitz radius \((3/4\pi n)^{1/3}\) is equal \(1.05\sigma\), which ensures the system is strongly interacting via the hard-sphere potential. At all the above listed points in the \((N, T)\) plane, simulations were performed where \( M \) was increased in steady increments until the results no longer varied by a statistically significant amount. When the converged values of \( E/N \) and \( P \) at specific values of \( N \) no longer vary with increasing \( N \), the thermodynamic limit has been reached.

Fig. 2.6 shows our calculation of \( E/N \) for \( T(\hbar^2/m\sigma^2k_B)^{-1} = 2.0 \). The general
Figure 2.6: PIMC results of energy for a system of hard-sphere particles under periodic boundary conditions at varying particle number for $T(\hbar^2/m\sigma^2 k_B)^{-1} = 2.0$ and $n\sigma^3 = 0.2063$. For each value of $N$ the value of $M$ was increased until $E/N$ sufficiently converged. $N$ was increased until the thermodynamic limit was reached; this was found to be in the $N = 300 – 400$ range. Inset: The converged values of $E/N$ for all values of $N$ at $T(\hbar^2/m\sigma^2 k_B)^{-1} = 2.0$, averaged over values at converged $M$. 
Figure 2.7: PIMC results of pressure for a system of hard-sphere particles under periodic boundary conditions at varying particle number for $T(h^2/m\sigma^2 k_B)^{-1} = 2.0$ and $n\sigma^3 = 0.2063$. For each value of $N$ the value of $M$ was increased until $P$ was sufficiently converged. $N$ was increased until the thermodynamic limit was reached, this was found to be in the $N = 300 – 400$ range. Inset: The converged values of $P$ for all values of $N$ at $T(h^2/m\sigma^2 k_B)^{-1} = 2.0$, averaged over values at converged $M$. 
Figure 2.8: Energy per particle of system of hard-sphere particles at the thermodynamic limit for density $n\sigma^3 = 0.2063$. At higher temperatures $E/N$ is linear in $T$, while this relationship does not hold as temperature is decreased. This shows that at high $T$ this system reaches the classical limit, while at low $T$ quantum effects take over.
Figure 2.9: Specific heat of system of hard-sphere particles at the thermodynamic limit with density $n \sigma^3 = 0.2063$. As $T$ is raised $c_v$ approaches the $1.5 \ k_B$ limit predicted by the equipartition theorem. In the range plotted $c_v$ decreases with $T$, as a consequence of the third law of thermodynamics.

trends observed at $T(\hbar^2/m\sigma^2k_B)^{-1} = 2.0$ are seen at all temperature values we studied. As the particle number is increased, $E/N$ decreases monotonically at all numbers of time slices, eventually settling at a constant value. It was also observed that convergence in $M$ was slower at lower values of $N$. This can be be seen in Fig. 2.6 where the value $M$ needed to be taken to 81 in order to observe convergence in $N = 20, 60$ and only $M = 61$ was needed for the larger values of $N$. The inset of Fig. 2.6 shows the final converged values of $E/N$ at varying $N$ for $T(\hbar^2/m\sigma^2k_B)^{-1} = 2.0$, where the monotonic decreasing of the energy to a constant value can be clearly observed.

The pressure of the same system is plotted in Fig. 2.7. The pressure also follows
the general trend of decreasing as the number of particles is increased, eventually converging to a final value, however unlike $E/N$, this does not occur monotonically at all temperatures, as can be seen in the higher time slice values of $N = 20$ and $60$ for the $T(h^2/m\sigma^2k_B)^{-1} = 2.0$ case where the pressure increases between the two values of $N$. It can also be observed that convergence in $M$ is slower at smaller particle numbers, similar to the $E/N$ calculations. The converged values of $P$ for each value of $N$ are shown in the inset of this plot. Again, unlike the $E/N$ case we do not see a monotonically decreasing convergence to a final value, but instead an oscillatory convergence. After the above analysis was performed at each of the previously listed temperatures, it was found that a system size of $N = 300 - 400$ was sufficient to have reached the thermodynamic limit at all temperatures studied.

The results for $E/N$ at all values of $T$ that were studied are plotted in Fig. 2.8. These values are for $N = 400$ as this well approximates the thermodynamic limit. At larger $T$, $E/N$ becomes linear, as would be expected from a classical system. At lower values of $T$ the system moves away from this classical behaviour as the curve begins to flatten and the slope decreases. This behaviour is expected as $T$ becomes smaller causing the thermal de Broglie wavelength to grow and quantum effects begin to dominate the system’s behaviour.

Fig. 2.9 shows the specific heat of the system which was calculated via the numerical derivative of $E/N$ at many values of $T$ for $N = 300$, which was still verified to be within the thermodynamic limit for $T > 0.5$. At high $T$ we again observe classical behaviour as $c_v$ approaches 1.5, given by the equipartition theorem. At low $T$ we can again observe behaviour that deviates from classical expectations as $c_v$ begins to decrease. By the third law of thermodynamics we expect $c_v$ to go to 0 as $T$ goes to 0, however, $c_v$ was calculated at values in the $T < 0.5$ range and a rapid increase in $c_v$
Figure 2.10: Pressure of system of hard-sphere particles at the thermodynamic limit for density $n\sigma^3 = 0.2063$. Similar to results for $E/N$, at higher temperatures $P$ is linear in $T$, while this again stops being the case as $T$ is decreased.
was observed as the temperature was decreased in this lower range. Given the third law of thermodynamics, these results appear to be unphysical and could be the result of finite-size effects. This is considered a strong possibility due to the fact that an increase in $c_v$ as the temperature was lowered was also seen for the non-interacting case in Fig. 2.4, which was also shown to be the result of finite-size effects.

The pressure results plotted against temperature are shown in Fig. 2.10. These results are also for the $N = 400$ system. In a similar manner to the $E/N$ results, at high $T$ the pressure is shows a linear relation to the temperature, as expected from a classically behaving system. As temperature is lowered we again see the linear relation begin to flatten and move away from the classical behaviour.
Chapter 3

4-Species Fermion Clusters

3.1 Quantum Monte Carlo

Quantum Monte Carlo (QMC) refers to a family of powerful \textit{ab initio} simulation methods applied to the quantum many-body problem. As seen previously in this thesis, Monte Carlo techniques in general are used to evaluate complicated integrals. In this section we will look specifically at variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC), which are employed to find the ground state of strongly interacting many-body problems.

3.1.1 Variational Monte Carlo

Variational Monte Carlo is a method that is utilized in this work to give an upper bound on the ground state energy of a complicated system. The VMC method is based on sampling from a $dN$-dimensional configuration space, where $d$ is the dimensionality of the system and $N$ is the number of particles present. Specifically, we are sampling position vectors of the system $\mathbf{R} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Both VMC and DMC (discussed in
the next section) are very easily parallelizable and as such a simulation will make use of several hundreds or thousands of copies of the system being studied, referred to as ‘walkers’, and sample configuration vectors from all of these.

Begin with a general probability distribution \( P(\mathbf{R}) \) that satisfies \( P(\mathbf{R}) \geq 0 \) and \( \int d\mathbf{R} P(\mathbf{R}) = 1 \). Imagine there is a general integral \( I \) that we wish to calculate with the form:

\[
I = \int d\mathbf{R} f(\mathbf{R}) P(\mathbf{R}) \quad (3.1)
\]

Where, \( d\mathbf{R} = dr_1...dr_N \) and the integration limits cover the entire \( P(\mathbf{R}) \) function. In the above integration \( I \) is equal to the mean value of \( f(\mathbf{R}) \) when averaged over the probability distribution \( P(\mathbf{R}) \). In this case, it is possible to evaluate the integral in the following way:

\[
I \approx \frac{1}{M} \sum_{i=1}^{M} f(\mathbf{R}_i) \quad (3.2)
\]

Where the configurations \( \mathbf{R}_i \) have been sampled according to the probability distribution \( P(\mathbf{R}) \) and \( M \) is the number of sampled configurations. The evaluated integral will also have an associated standard deviation given by:

\[
\delta = \frac{1}{\sqrt{M}} \left[ \int d\mathbf{R} (f(\mathbf{R}) - I)^2 P(\mathbf{R}) \right]^{\frac{1}{2}} \quad (3.3)
\]

We can use the above formalism to calculate expectation values found in quantum mechanics, by calculating weighted averages over the probability distribution provided by the wave function of the system. In VMC since we often do not know the true wave function that describes our system we use our best guess in the form of a trial wave function, therefore we calculate the following variational estimate of the energy:
\[ E_V = \frac{\int dR \psi_T^*(R) \hat{H} \psi_T(R)}{\int dR \psi_T^*(R) \psi_T(R)} \] (3.4)

Where \( \psi_T(R) \) is the trial wave function and \( \hat{H} \) is the Hamiltonian of the system that we are studying. We are able to rewrite this expectation value in the form of Eq. (3.1):

\[ E_V = \frac{\int dR \psi_T^*(R) \hat{H} \psi_T(R) |\psi_T(R)|^2}{\int dR |\psi_T(R)|^2} = \int dR E_L(R) P_T(R) \] (3.5)

Where \( E_L(R) = [\psi_T^{-1}(R) \hat{H} \psi_T(R)] \) is the local energy and \( P_T(R) = |\psi_T(R)|^2 / \int dR |\psi_T(R)|^2 \) is the probability distribution given by the trial wave function. By analogy to Eq. (3.2) we can evaluate this expectation value as:

\[ E_V \approx \frac{1}{M} \sum_{i=1}^{M} E_L(R_i) \] (3.6)

To evaluate the expectation value in this way we need a large sample set of \( R \) vectors, distributed according to \( P_T(R) \). In practice, the Metropolis algorithm is utilized to achieve this sampling [49, 50]. The Metropolis algorithm uses a Markov process which is a sequence of sampled states which will equilibrate to a desired distribution, in our case \( P_T(R) \), if certain conditions are met. The first condition that must be met is that of detailed balance. Given some configuration \( R \), a transition to a new configuration \( R' \) is governed by a transition probability \( T(R \rightarrow R') \). The transition probability obeys the detailed balance condition if:

\[ P(R)T(R \rightarrow R') = P(R')T(R' \rightarrow R) \] (3.7)

That is, it is equally probable to exist at a state \( R \) and transition to \( R' \) as it is
to do the opposite and $P(R)$ is some general probability distribution. The Markov process must also be ergodic:

- All states are accessible by a finite number of steps
- $T(R \rightarrow R) > 0$, i.e. staying at the same configuration is possible
- The number of steps to return to the current configuration is finite

The above requirements ensure that the sampled states will equilibrate to form a distribution described by $P(R)$.

The Metropolis algorithm depends on constructing a Markov process that satisfies the above requirements. In our case, we wish to sample the $P_T(R)$ distribution, therefore our detailed balance requirement becomes:

$$P_T(R)T(R \rightarrow R') = P_T(R')T(R' \rightarrow R)$$ (3.8)

This can be rewritten:

$$\frac{T(R \rightarrow R')}{T(R' \rightarrow R)} = \frac{P_T(R')}{P_T(R)}$$ (3.9)

Next, we will break down the transition probability $T(R \rightarrow R')$ into two terms. The first will be the proposal probability $\Lambda(R, R')$, this is the probability that a move to $R'$ from $R$ will be proposed in the first place. The second term is the acceptance probability $A(R, R')$, which is simply the probability of the move being accepted. We can rewrite Eq. (3.9) using these terms as:

$$\frac{A(R, R')}{A(R', R)} = \frac{P_T(R')\Lambda(R', R)}{P_T(R)\Lambda(R, R')}$$(3.10)

At this point we must pick an acceptance probability that we are to use in our algorithm that satisfies Eq. (3.10). The common choice is:
\[ A(R, R') = \min \left( 1, \frac{P_T(R')A(R', R)}{P_T(R)A(R, R')} \right) \]

Therefore either \( A(R, R') = 1 \) or \( A(R', R) = 1 \), but either way Eq. (3.10) is satisfied. The proposal probabilities can also be chosen to be symmetrical, such that a move to \( R' \) from \( R \) will have the same probability of being proposed as the opposite move. Therefore when we are sampling configurations for the VMC calculation, we accept moves with a probability given by:

\[ A(R, R') = \min \left( 1, \frac{P_T(R')}{P_T(R)} \right) \]

As mentioned at the start of this section, VMC can only give an upper bound to the ground state energy of the system being studied. It is possible to lower this variational limit by adjusting parameters in \( \psi_T(R) \) and lowering \( E_V \), but in general \( E_V \geq E_0 \).

### 3.1.2 Diffusion Monte Carlo

In DMC we are still sampling configuration space with a set of walkers, similar to what was done with VMC. However, now rather than evaluating a variational estimate of the ground state energy, we are propagating through imaginary time in order to project to the ground state \( \phi_0 \). In this method, we begin from the trial wave function, provided by the VMC method and apply the usual time propagation seen in quantum mechanics:
\[
|\Psi(\tau)\rangle = e^{-(\hat{H} - E_T)\tau} |\Psi(0)\rangle = e^{-(\hat{H} - E_T)\tau} |\Psi(0)\rangle = c_0 e^{-(E_0 - E_T)\tau} |\psi_0\rangle + c_1 e^{-(E_1 - E_T)\tau} |\psi_1\rangle + c_2 e^{-(E_2 - E_T)\tau} |\psi_2\rangle + \ldots
\]

where we have used imaginary time \( \tau = it \) and have decomposed the trial wave function into the energy eigenstates using the completeness relation: \( |\Psi_T\rangle = \sum_i c_i |\psi_i\rangle \). \( E_T \) is the trial energy and is added as an offset to the Hamiltonian. If we are able to set \( E_T \) such that it is approximately equal to the ground state energy we find that at the large \( \tau \) limit we are left with:

\[
|\Psi(\tau \to \infty)\rangle = c_0 |\psi_0\rangle \lim_{\tau \to \infty} e^{-(E_0 - E_T)\tau}
\]

Here we see that if \( E_T \approx E_0 \), the exponential terms associated with the higher energy states cause those contributions to the wave function to go to 0, while the exponential in the ground state term remains finite. This means that if we project this system for large enough \( \tau \) values we will find the ground state.

The evolution of the system is performed in configuration space using short-time propagators in small steps of \( \Delta \tau \):

\[
\langle \mathbf{R}\Psi(\tau + \Delta \tau)\rangle = \langle \mathbf{R}| e^{-(\hat{H} - E_T)\Delta \tau} \left[ \int |\mathbf{R}'\rangle \langle \mathbf{R}'| d\mathbf{R}' \right] |\Psi(\tau)\rangle
\]

\[
= \int d\mathbf{R}' \langle \mathbf{R}| e^{-(\hat{H} - E_T)\Delta \tau} |\mathbf{R}'\rangle \langle \mathbf{R}'|\Psi(\tau)\rangle = \int d\mathbf{R}' G(\mathbf{R} \leftarrow \mathbf{R}') \langle \mathbf{R}'|\Psi(\tau)\rangle
\]

\[
\Psi(\mathbf{R}, \tau + \Delta \tau) = \int d\mathbf{R}' G(\mathbf{R} \leftarrow \mathbf{R}') \Psi(\mathbf{R}', \tau)
\]

38
Where $G(R \leftarrow R')$ is the short-time propagator that evolves the system from $R'$ to $R$.

In order to implement the DMC method we must evaluate $G(R \leftarrow R')$:

$$
G(R \leftarrow R') = \langle R | e^{-(\hat{H} - E_T) \Delta \tau} | R' \rangle \\
= \langle R | e^{-\frac{\hat{V}}{2} e^{-\hat{K} \Delta \tau} e^{-\frac{\hat{V}}{2}}} + O(\Delta \tau^3) | R' \rangle e^{E_T \Delta \tau} \\
\approx e^{-V(R) \frac{\Delta \tau}{2}} \langle R | e^{-\hat{K} \Delta \tau} | R' \rangle e^{-\frac{1}{2} \Delta \tau (V(R) + V(R') - 2E_T)} \\
= \langle R | e^{-\hat{K} \Delta \tau} | R' \rangle e^{-\frac{\Delta \tau}{2} (V(R) + V(R') - 2E_T)}
$$

(3.16)

The above evaluation uses the Trotter-Suzuki formula, as seen in Eqs. (2.5) and (2.6). The remaining matrix element can be evaluated as:

$$
\langle R | e^{-\hat{K} \Delta \tau} | R' \rangle = \left[ \frac{m}{2\pi \hbar^2 \Delta \tau} \right]^{\frac{3N}{2}} \exp \left[ -\frac{m (R - R')^2}{2 \hbar^2 \Delta \tau} \right]
$$

(3.17)

Giving the full propagator as:

$$
G(R \leftarrow R') = \left[ \frac{m}{2\pi \hbar^2 \Delta \tau} \right]^{\frac{3N}{2}} \exp \left[ -\frac{m (R - R')^2}{2 \hbar^2 \Delta \tau} \right] \\
\times \exp \left[ -\frac{\Delta \tau}{2} (V(R) + V(R') - 2E_T) \right]
$$

(3.18)

As seen in the derivation, the results of the DMC method require a sufficiently small $\Delta \tau$ to be accurate. In practice however, this parameter can be made arbitrarily small in calculations in order to make this error negligible. The trade-off for this is requiring more computational time to reach a large enough total $\tau$ to ensure you have projected to the ground state.

As seen in the expressions above, the matrix element produced by the exponentiated kinetic energy operator produces a Gaussian with a standard deviation of
\(\sqrt{\hbar^2 \Delta \tau/m}\). In simulations this is the term that causes the \(R'\) vector to shift to a new \(R\). This new position vector is selected from a normal distribution centered at \(R'\) with the same standard deviation as in the propagator. In the full propagator, this Gaussian is multiplied by a weight \(P = \exp\left[-\frac{\Delta \tau}{2}(V(R) + V(R') - 2E_T)\right]\), which is referred to as the branching probability. When a certain walker makes the move \(R' \rightarrow R\) there is a possibility that this walker will be duplicated or destroyed. If \(P \geq 1\) the walker is duplicated with probability \(P - 1\), if \(P < 1\) the walker is destroyed with a probability \(1 - P\). This birth/death process ensures large numbers of walkers form in areas of small potential energy, and are more scarce in areas of high potential energy.

In DMC simulations once the walkers have projected to the ground state wave function mixed estimates of expectation values are taken. For the energy of the system:

\[
\langle \hat{H} \rangle_M = \frac{\langle \Psi_T | \hat{H} | \Psi(\tau) \rangle}{\langle \Psi_T | \Psi(\tau) \rangle} = \frac{\langle \Psi_T | \hat{H} e^{-(\hat{H} - E_T)\tau} | \Psi_T \rangle}{\langle \Psi_T | e^{-(\hat{H} - E_T)\tau} | \Psi_T \rangle} = \frac{\langle \Psi_T | \hat{H} e^{-(\hat{H} - E_T)\frac{\tau}{2}} e^{-(\hat{H} - E_T)\frac{\tau}{2}} | \Psi_T \rangle}{\langle \Psi_T | e^{-(\hat{H} - E_T)\frac{\tau}{2}} e^{-(\hat{H} - E_T)\frac{\tau}{2}} | \Psi_T \rangle} = \frac{\langle \Psi_T | e^{-(\hat{H} - E_T)\frac{\tau}{2}} \hat{H} e^{-(\hat{H} - E_T)\frac{\tau}{2}} | \Psi_T \rangle}{\langle \Psi_T | e^{-(\hat{H} - E_T)\frac{\tau}{2}} e^{-(\hat{H} - E_T)\frac{\tau}{2}} | \Psi_T \rangle}
\]

(3.19)

In the second line we simply pulled out the imaginary time evolution operator from the ket states and show it explicitly, in the third line we divide \(\tau\) by 2 and separate the exponent into two terms, which is exact as \(\tau\) is a scalar. In the next line
the time evolution operator is brought to the other side of the Hamiltonian operator in the numerator, which is allowed since the Hamiltonian commutes with itself, and finally the time evolution operators act on the bras and kets. This shows that even though DMC calculations are evaluating mixed estimates, these mixed estimates are exact as long as the operator you are taking the expectation value of commutes with $\hat{H}$. This can be said to equal the ground state energy if $\tau/2$ is sufficiently large enough to project the system to the ground state, therefore:

$$\langle \hat{H} \rangle_M = \frac{\langle \Psi(\tau/2) | \hat{H} | \Psi(\tau/2) \rangle}{\langle \Psi(\tau/2) | \Psi(\tau/2) \rangle} = \frac{\langle \psi_0 | \hat{H} | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} = E_0$$

(3.20)

As stated previously DMC is completed in practice by evolving the position states of walkers until the distribution of these walkers represent the ground state of the system. Once the ground state has been reached and the system is equilibrated the local energy, introduced in Eq. (3.5), is averaged over the distribution and the ground state energy is calculated.

### 3.2 Simulations of Finite Bosonic Clusters

Previous work done simulating bosonic clustering was the prelude to the study of clustering in 4-species fermionic systems done in this thesis [51, 52, 53, 54, 55, 56, 57].

The Hamiltonian used for the boson system was:

$$H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} V_{i,j} + \sum_{i<j<k} V_{i,j,k}$$

(3.21)

Where:
\[ V_{i,j}(r_{ij}) = (-V_2 \mu_2^2 \frac{\hbar^2}{m}) e^{-0.5(\mu_2 r_{ij})^2} \] (3.22)

\[ V_{i,j,k}(R_{ijk}) = (V_3 \mu_3^2 \frac{\hbar^2}{m}) e^{-0.5(\mu_3 R_{ijk})^2} \] (3.23)

And \( R_{ijk} = \sqrt{r_{ij}^2 + r_{ik}^2 + r_{jk}^2} \).

VMC and DMC were used to calculate the ground state of the boson cluster system. To do this the following trial wave function is used:

\[ \Psi_T = \prod_i f^{(1)}(r_i) \prod_{i<j} f^{(2)}(r_{ij}) \prod_{i<j<k} f^{(3)}(R_{ijk}) \] (3.24)

Where:

\[ f^{(1)}(r_i) = e^{-\alpha_{jas} r_i^2} \]

\[ f^{(2)}(r_{ij}) = \frac{K \tanh(\mu_J r_{ij}) \cosh(\gamma_{jas} r_{ij})}{r_{ij}} \] (3.25)

\[ f^{(3)}(R_{ijk}) = e^{u_o e^{-R_{ijk}^2/(2r_o^2)}} \]

In the two-body function \( f^{(2)} \) the parameters \( K \) and \( \gamma \) are chosen such that \( f^{(2)}(d) = 1 \) and \( f^{(2)'}(d) = 0 \). This value \( d \) is called the 'healing distance'. The parameters \( \alpha_{jas}, \mu_J, d, u_o \) and \( r_o \) are optimized during VMC calculations, such that they are set to give the lowest VMC energy possible. This optimization is performed at every interaction setting studied.

Fig. 3.1 shows energies of 4-particle boson clusters calculated using DMC. These energies are at varying 3-body potential strengths \( V_3 \) with all other potential parameters held constant. We also define a length associated with the binding energy of the least-bound 4-particle cluster in the following plot, \( R_4 \equiv (-2mE_4/\hbar^2)^{-1/2} \).
Figure 3.1: Energy of 4-Particle boson clusters with variable $V_3 = 3.0$, $V_2 = 0.671$, $\mu_2 R_4 = 13.64$ and $\mu_3 R_4 = 3.41$. Parameters $\hbar$ and $m$ are set to 1.0.
3.3 4-Species Fermi system

3.3.1 4-Species Hamiltonian and Trial Wavefunctions

The Hamiltonian used for the 4-species fermi gas is:

\[ H = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} V_{i,j} + \sum_{i<j<k} V_{i,j,k} \]  \hspace{1cm} (3.26)

Where \( V_{i,j} \) is an attractive 2-body potential and \( V_{i,j,k} \) is a repulsive 3-body potential. These potentials are the same as in the bosonic Hamiltonian, seen in the previous section, Eqs. (3.22) and (3.23). The difference however is that \( V_{i,j} \) is only non-zero when the two particles in the argument are of different species, and \( V_{i,j,k} \) is only non-zero when all three particles are of different species.

In this work we use a combination of Variational Monte Carlo and Diffusion Monte Carlo to solve for the ground state energy of this Hamiltonian. Specifically, we study a group of 8 particles distributed evenly between 4 distinct species (i.e. two particles per species). This specific system was focused on for the fermion gas as it is the simplest case where the number of particles can be distributed evenly into all species where the fermionic nature of the particles has an effect (four fermions all belonging to distinct species is physically identical to the four boson system when the system is in the ground state, this is the same calculation performed in Sec. 3.2. In order to carry out the VMC and DMC methods we must develop trial wave functions that are physically appropriate for the 4-species fermi gas system. The fact that the system is now fermionic complicates the form of the trial wave function. As seen in Sec. 3.2 a trial wave function with a relatively simple, nodeless form is sufficient.
for bosonic systems, but a more sophisticated form which incorporates both the anti-
symmetrization and clustering requirements to simulate the ground state is a bit more
tricky. In this section we overview the forms we attempted to simulate this system.

The first trial wave function that was used in calculations of the 4-species fermi
gas problem used the BCS wave function $\Phi_{BCS}$. This form has been used in the
past to study systems of fermions consisting of two species, with pairing between the
species. In the 2-species case, the wave function takes the form:

$$
\Phi_{BCS} = A[\phi(r_{1,1'})\phi(r_{2,2'})...\phi(r_{N,N'})]
$$

$$
\Psi_T = \prod_{i,j'} f_J(r_{i,j'})\Phi_{BCS}
$$

In this notation we differentiate between the two species of fermions by assigning
unprimed indices to one, and primed indices to the other. $\Phi_{BCS}$ is an antisymmetrized
product of pairing functions, $\phi(r)$, and $f_J(r_{i,j'})$ are nodeless functions with correla-
tions between interacting particles referred to as Jastrow terms. Jastrow terms are
used in order to decrease the variance of the simulation.

Since we are dealing with a system of fermions $\Psi_T$ must fulfill the anti-symmetry
requirement. This is accomplished by the $A$ operator. In practice, this operator leads
to a determinant of the $N \times N'$ matrix consisting of pairing functions $\phi(r)$:

$$
\Phi_{BCS} \propto \begin{vmatrix}
\phi(r_{1,1'}) & \phi(r_{1,2'}) & \cdots & \phi(r_{1,N'}) \\
\phi(r_{2,1'}) & \phi(r_{2,2'}) & \cdots & \phi(r_{2,N'}) \\
\vdots & \vdots & \ddots & \vdots \\
\phi(r_{N,1'}) & \phi(r_{N,2'}) & \cdots & \phi(r_{N,N'})
\end{vmatrix}
$$
The form of the pairing functions that has been used traditionally are plane waves in the relative coordinate:

\[
\phi(r) = \sum_n \alpha_n e^{i k_n \cdot r} \quad (3.28)
\]

Where \(\alpha_n\) are variational parameters associated with momentum levels up to \(n\).

When extending the BCS trial wave function to the 4-species system it takes the form:

\[
\Psi_T = f_J \left[ \Phi_{BCS}^{I,II} \Phi_{BCS}^{III,IV} + \Phi_{BCS}^{I,III} \Phi_{BCS}^{II,IV} + \Phi_{BCS}^{I,IV} \Phi_{BCS}^{II,III} \right] \quad (3.29)
\]

Where \(\Phi_{BCS}^{m,n}\) is the BCS function that pairs species \(m\) and \(n\) and we have labeled the four distinct species as I, II, III, IV. The three terms are a result of ensuring each possible pairing between species is accounted for, and since each individual term satisfies anti-symmetry the whole function does as well. The Jastrow used is an adaptation of the nodeless wave function used for the boson clustering case (Eqs. (3.24) and (3.25)), except now \(f^{(2)}(r)\) and \(f^{(3)}(R)\) are only non-zero if the particles in their arguments belong to distinct species, similar to the potential.

The next trial wave function that was used in calculations was a novel form that attempts to capture the clustering we expect to see in our system. This form is specifically designed for use in a system of eight particles, two belonging to each species, where as the BCS form is more general and can be applied to any size system. This clustering wave function takes the form:
\[ \Psi_T = f_J \hat{A} \left[ e^{-\alpha \sum (r_i - R_{\text{Cluster}1})^2} e^{-\alpha \sum (r_j - R_{\text{Cluster}2})^2} e^{-\beta (R_{\text{Cluster}1} - R_{\text{Cluster}2})^2} (R_{\text{Cluster}1} - R_{\text{Cluster}2})^n \right] \]  

(3.30)

Here we attempt to bias the particles to form two clusters, one with position \( R_{\text{Cluster}1} \) and the other with \( R_{\text{Cluster}2} \). The particles that make up the first cluster have positions \( r_i \) and the particles in the second cluster are \( r_j \). Here, all four particles belonging to \( R_{\text{Cluster}1} \) are of distinct species, and therefore the same can be said of \( R_{\text{Cluster}2} \). We are attempting to recreate the clustering we expect to see among four fermions of distinct species, which is the same clustering we see in the four boson case. This clustering is captured in the first two exponential terms where a positive \( \alpha \) causes a decay in the wave function as particles move away from their cluster. Inter-cluster interactions are dictated by the remaining exponential and polynomial terms, and can be tuned with \( \beta \) and \( n \) to probabilistically favour close mixing of the two clusters, or for the two to remain separate. In practice the parameters \( \alpha, \beta \) and \( n \) are variational, and are determined by finding the minimal VMC energy.

The final trial wave function that was used is similar to the previous in that clustering was attempted to be built into it:

\[
\psi = A \left[ F(r_{CM}(r_1, r_3, r_5, r_7) - r_{CM}(r_2, r_4, r_6, r_8)) \right.
\]

\[
\cdot f^c(r_1, r_3, r_5, r_7) \cdot f^c(r_2, r_4, r_6, r_8) \cdot \prod_{m=1,3,5,7}^{n=2,4,6,8} g(r_{nm}) \]  

(3.31)
Where:

\[
F(r_{CM}(r_1, r_3, r_5, r_7) - r_{CM}(r_2, r_4, r_6, r_8)) = \\
(1 - \gamma e^{-((r_{CM}(r_1, r_3, r_5, r_7) - r_{CM}(r_2, r_4, r_6, r_8))/\alpha)^2})^{-1}
\]

(3.32)

\[
g(r_{nm}) = (1 - \gamma g e^{-((r_{nm}/\alpha_g)^2})^{-1}
\]

(3.33)

In this notation we have arbitrarily labelled the particles that belong to species I as \(r_1\) and \(r_2\), species II has \(r_3\) and \(r_4\) and so on.

Here, the \(f^c\) functions are nodeless and are the same as the trial wave functions used in Eqs. (3.24) and (3.25). In this context we are using this function to account for the formation of 4-particle clusters (where each particle in the cluster belongs to each one of the distinct species), that we suspect will occur in the 8-particle case. Eqs. (3.32) and (3.33) attempt to account for cross-cluster correlations, Eq. (3.32) is a function of the distance between the center of masses of the two clusters, while Eq. (3.33) is simply a function of the separation distances between individual particles belonging to different clusters, both go to unity at large distances. The parameters in the trial wave function are again optimized via Variational Monte Carlo.

### 3.3.2 4-Species Fermi Cluster Results and Comparisons to Bosonic System

As stated in the previous section, the calculations carried out in this work focused on obtaining ground state energy of 8-particle clusters. This systems contains eight
fermions, with two fermions each belonging to four species (I,II,III,IV).

A simple benchmark for these calculations is to compare the energy calculated for the 8-particle system to that of a 4-particle bosonic system with the same potential parameters. If our simulations have successfully reached the ground state of the 8-particle system we expect the energy found to be at least two times that of the energy of the corresponding 4-particle system. We expect this upper limit because it should be possible for the system to produce two 4-particle clusters (that are identical to those found in the 4-particle simulation) that do not interact with one another, due to the finite range of our potentials. If this is the case, the energy of the 8-particle system should be exactly two times the 4-particle system, due to the two independent energy contributions of each cluster. It is possible for the energy to be lower than this limit if the two clusters together form a bound state, or if the entire system forms a larger cluster containing all eight particles. This benchmark test was applied using all three trial wave functions covered in Sec. 3.3.1. The results of this test are displayed in Fig. 3.2. In this plot we see the running averages over imaginary time in DMC simulations for all three trial wave functions for a system where $V_3 = 3.0$, $V_2 = 0.671$, $\mu_3 R_4 = 3.41$ and $\mu_2 R_4 = 13.64$, which is the same potential used for the least bound cluster in Fig. 3.1. As can be seen in the figure, the running averages equilibriate over imaginary time and eventually converge to an answer with an acceptable statistical uncertainty. In this test, only the trial wave function form Eq. (3.31) was able to find a bound state with respect to the 4-particle system. This test was carried out for multiple variations of adjusting the potential parameters and in all of these the same outcome was observed. In these tests the BCS trial wave function was found to be the farthest away from obtaining an energy that was bound with respect to the 4-particle system. This is most likely due to the fact that this form is better
Figure 3.2: Running average of all three forms of trial wave functions. Potential parameters set to $V_3 = 3.0$, $V_2 = 0.671$, $\mu_2 R_4 = 13.64$ and $\mu_3 R_4 = 3.41$. Parameters $\hbar$ and $m$ are set to 1.0.

suited for continuous matter simulations, due to the plane waves found within the pairing functions. The first clustering wave function, Eq. (3.30), was found to do a better job than the BCS form, due to the introduction of clustering within the wave functions, but still not good enough to capture the ground state. Finally, the second clustering wave function, given in Eq. (3.31), was able to find a bound state. We can qualitatively observe the behaviour of the system by plotting out the paths of the particles over some number of DMC steps. Fig. 3.2 shows the system from the simulation using Eq. (3.31) over 100 DMC steps. We can see that the system forms two overlapping clusters that form a bound state, rather than a larger single cluster containing all of the particles.
Figure 3.3: Particle positions over 100 DMC time steps, coloured by how the particles have arranged themselves into clusters. Potentials parameters set at $V_3 = 3.0$, $V_2 = 0.671$, $\mu_2 R_4 = 13.64$ and $\mu_3 R_4 = 3.41$. The positions plotted are unitless scaled by $R_4^{-1}$. Parameters $\hbar$ and $m$ are set to 1.0.
Once the testing of the trial wave functions was completed calculations were performed over a set of varying potentials. We are interested in the short-range interaction limit, therefore in our simulations we keep $V_3 = 3.0$ and $V_2 = 0.671$ fixed while increasing $\mu_2$ and $\mu_3$. We also keep the ratio of $\mu_2$ to $\mu_3$ fixed at 4.0. In Fig. 3.4 we plot the ratio of the 8-particle system to the 4-particle system. We can see that as the range of the interactions become smaller, the 8-particle system becomes more bound with respect to the 4-particle system. This is significant as this is the first time a DMC simulation has calculated a bound 8-particle state with respect to decay into two independent 4-particle clusters.
Figure 3.4: Ratio of 8-particle system energy to 4-particle system. $V_3 = 3.0$ and $V_2 = 0.671$ are fixed. $\mu_2$ and $\mu_3$ vary, but the ratio of $\mu_2/\mu_3 = 4.0$ is kept fixed. Parameters $\hbar$ and $m$ are set to 1.0.
Chapter 4

Conclusions

In summary, in the first half of this thesis we discussed Path Integral Monte Carlo simulations for systems of distinguishable particles that interact via hard-sphere and hard-cavity potentials. To begin, we studied a system of two hard-sphere particles trapped inside a hard-cavity. We analytically calculated the energy of the system at varying temperatures by solving the Schrödinger equation and finding the thermodynamic average using the Boltzmann distribution. We calculated the energy of the same system using the PIMC method with two distinct approximations to the thermal density matrix, the Image Approximation, and the CB thermal density matrix. For all temperatures studied, \( T(h^2/m\sigma^2k_B)^{-1} = 0.5, 1.0, 1.6, 2.0, 2.5 \), we found that convergence of the PIMC energy to the analytic energy in number of time slices for both density matrices was approximately the same. We then studied a system of \( N \) hard-sphere particles placed under periodic boundary conditions. We performed calculations of the energy per particle, pressure and specific heat of the system for a range of temperatures. We established when the thermodynamic limit of the system was reached and the finite-size effects caused by the PBC had been eliminated. A range of \( N \approx 300 \) – \( 400 \) was found to be sufficient. We found that \( E/N, P, \) and
$c_v$ approached classical behaviour in the upper limit of the temperature range we studied and deviated from this behaviour at lower $T$. These results constitute non-perturbative microscopic benchmarks for strongly interacting quantum Boltzmannons and can guide further theoretical work as well as comparison with experiment.

Next, the 4-species fermi gas with 2- and 3-body central potentials was studied using Variational Monte Carlo and Diffusion Monte Carlo. In this work three novel forms of trial wave functions were created to attempt to properly capture the physics of 8-particle clustering. It was found that one of these forms was able to successfully simulate the ground state of this system. Further, we studied varying the range of the 2- and 3-body potentials, while keeping the ratio of the two constant, and found that decreasing these ranges caused the 8-particle system to become more bound with respect to decay into 4-particle clusters. In the future it is hoped that this work can be extended to larger systems with higher numbers of particle, such as 12 and upward.
Bibliography


