An enhanced sampling approach to the simulation of electrons in quantum dots

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An enhanced sampling approach to the simulation of electrons in quantum dots

A study of the fermionic sign problem in Path Integral Molecular Dynamics simulations

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Abstract

The numerical simulation of quantum matter is an important part of modern computational physics. Methods based on Feynman’s path integral description of quantum mechanics have been used since the 1980s to map the quantum system to a classical system that can be readily simulated with standard molecular dynamics techniques. A major difficulty in such simulations is the indistinguishability of identical particles. In particular for fermions at low temperatures the quantum symmetry of the particles leads to severe cancellation effects. This is referred to as the fermionic sign problem.

In this thesis we treat the fermionic sign problem as a sampling problem and apply it to electrons confined in nanometer-sized quantum dots. We observe that configurations in which an exchange of the particles would lead to a decrease in the configurational energy have large impact on the measured observables but are only rarely sampled. The modern enhanced sampling method Metadynamics is used to increase the sampling probability of such configurations. This significantly improves the numerical accuracy of simulations with two particles at low temperatures. We also show that the energy difference between fermionic and bosonic particles can be approximated by their free energy difference, which can be calculated with Bennett’s acceptance ratio method, and that this approach gives more robust energy calculations than Metadynamics alone.

The methods are applied to two electrons in quantum dots, for which we calculate thermal averages of singlet and triplet energies, probability densities and pair correlation functions. We investigate the impact of different ratio between the interaction strength and the confinement energy, and different anisotropy. With Metadynamics we are able to obtain results in agreement with experimental values and other numerical methods in literature.

We also propose how the methods can be generalised to higher particle numbers.
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Chapter 1

Introduction

In our everyday experience, we know that even if we see objects that look identical to us, we can always invent a method to label them. For instance identical items in the shop can still be distinguished by their different bar codes. However in the quantum world, this labelling procedure is not always possible. One of the most fundamental results of quantum physics is that identical particles are truly indistinguishable. In a system of identical particles ‘A’ and ‘B’, we should get the same outcome in all experiments if ‘B’ took the place of ‘A’ and vice versa. As a consequence, even if the particles are not interacting, the system cannot be described as a sum of two independent one-particle systems. Instead we need a many-body theory that is able to capture the effects of this quantum symmetry.

Luckily, the quantum symmetry is only realized in two different ways. In a wavefunction description, the many-body wavefunction $\Psi(x_A,x_B)$ needs to be either symmetric or antisymmetric with respect to a permutation of the particles ‘A’ and ‘B’. The same is true for a general number of particles under pairwise permutations. Particles which are symmetric under exchange are called bosons, and particles with the antisymmetric exchange symmetry are called fermions. Bosons have a higher probability to be found together than distinguishable particles, which gives rise to phenomena like superfluid $^4$He or photon bunching. Fermions on the other hand follow the Pauli principle and have zero probability to be found in the same state. Since electrons are fermions, they avoid each other not only because of their electrostatic repulsion but also because of quantum symmetry.

Most many-particle systems of interest are too complicated to be described analytically, but can still be sufficiently well described with numerical methods. A widely used class of methods is based on Feynman’s path integral formulation of quantum mechanics [1]. With path integrals it is possible to map a quantum problem to a classical problem of higher dimensionality [2]. Observables of the quantum system can then be calculated by sampling the corresponding classical system. This approach is formally exact and as we will see in section [2.2] it is possible to include quantum exchange effects in a comprehensive manner. To sample a property of a bosonic system, contributions from the permuted and non-permuted system
are added up. However, for a fermionic system, contributions from different permutations partly cancel out. One can show that the cancellation decreases the signal-to-noise ratio exponentially with inverse temperature and with the number of particles \[3\]. This is called the fermionic sign problem.

The fermionic sign problem limits the possibilities to simulate systems of many fermions, for example electrons. Ways to solve it have been attempted for several decades, but one can show that no polynomially scaling algorithm exists for a classical computer \[4\]. To improve computational efficiency, many attempts are described in literature on how to soften the sign problem by various approximations \[3,5\]. In this thesis we will explore another method to improve the performance in simulations of few-particle quantum systems, based on enhanced sampling with Metadynamics. Metadynamics is a general tool to enhance the sampling of arbitrarily chosen collective variables in classical Monte Carlo or Molecular Dynamics simulations \[6,7\], and will be described in more detail in chapter 3. We will investigate if Metadynamics can be used to efficiently sample contributions from all the permutations of a quantum system.

To allow for comparison with analytical results, we will first study the simple case of two non-interacting particles in a harmonic potential (section 4.1). Different choices of collective variables will be considered and compared with each other. We will also investigate how a generalisation to higher particle numbers could be realised.

The harmonic potential is not only a hypothetic example, but also makes a good approximation of a semiconductor quantum dot. Quantum dots are isolated islands of electrons on the length-scale of a few nanometers and have a range of applications including solar cells and quantum computing \[8–10\]. These have been investigated both experimentally and theoretically for several decades \[11\]. Because of the strong confinement, the effect of quantum exchange often needs to be included to correctly describe the system, which is a major difficulty when performing numerical simulations. In chapter 5.3 we will study a realistic system of two electrons and compare with experimental results and other computational methods.
Chapter 2

Path Integral Molecular Dynamics

In this chapter we will describe how to simulate a quantum system at finite temperature by mapping it to a classical system of higher dimensionality, using Feynman’s path integral formalism [1]. Before we discuss the complication of quantum symmetry, we derive the theory for a single quantum particle, and then show how this can be generalised to several particles. When the theoretical foundations have been established, we will show how to calculate thermodynamic estimators of properties like energy, probability distribution and pair correlation functions. In the last section of this chapter, we will provide more detail on how to perform the simulations at constant temperature.

2.1 Classical isomorphism

Consider a single quantum particle in an external potential $V(r)$ at inverse temperature $\beta = 1/k_B T$, where $r$ is its $d$-dimensional coordinate vector. The density matrix of this system is given by

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}$$

where $Z = \text{Tr} e^{-\beta \hat{H}}$ is the canonical partition function and $\hat{H}$ the Hamiltonian. In a coordinate basis $\{|r\rangle\}$ the trace can be written as an integral, $Z = \int dr |r\rangle e^{-\beta \hat{H}} |r\rangle$. The expectation value of an operator $\hat{O}$ can then be calculated as

$$\langle \hat{O} \rangle = \frac{\text{Tr} [\hat{O} e^{-\beta \hat{H}}]}{Z}.$$  

If $\hat{O}$ is local in the coordinate representation, this can be written $\langle \hat{O} \rangle = \int dr O(r) \rho(r)$. In general the Hamiltonian is not diagonal in the coordinate basis, to that the traces...
cannot be easily computed. The Hamiltonian has one kinetic and one potential part:

\[ \hat{H} = \hat{T} + V(\hat{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\hat{r}), \]

where the kinetic energy is diagonal in the momentum basis and the potential energy is diagonal in the coordinate basis. To compute the trace, we would like to factorize \( e^{-\beta \hat{H}} \) into its kinetic part and potential part. However, since \( \hat{T} \) and \( \hat{V} \) do not in general commute, this will introduce an error term. A common factorization\(^1\) is the so-called Trotter decomposition

\[ e^{-\beta(\hat{T} + \hat{V})} = e^{-\beta \hat{T}} e^{-\beta \hat{V}} + O(\beta^2). \]

For high temperatures, this is a feasible approximation; however for low temperatures, when quantum effects become important, it is necessary to make the error smaller. We can use the fact that the Hamiltonian commutes with itself:

\[ e^{-\beta(\hat{T} + \hat{V})} = e^{-\beta \hat{T}} e^{-\beta \hat{V}}. \]

By introducing a complete set of states, the partition function can be written

\[ Z = \int d\mathbf{r}_1 d\mathbf{r}_2 \langle \mathbf{r}_1 | e^{-\beta \hat{H}} | \mathbf{r}_2 \rangle \langle \mathbf{r}_2 | e^{-\beta \hat{H}} | \mathbf{r}_2 \rangle \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1, \mathbf{r}_2; \beta_1) \rho(\mathbf{r}_2, \mathbf{r}_1; \beta_2), \]

where \( \rho(\mathbf{r}_2, \mathbf{r}_1; \beta) = \langle \mathbf{r}_2 | e^{-\beta \hat{H}} | \mathbf{r}_1 \rangle \) is a Green’s function for the propagation of a particle from \( \mathbf{r}_1 \) to \( \mathbf{r}_2 \). Repeating this decomposition we divide \( \beta \) into \( P \) equal steps \( \tau = \beta/P \):

\[ Z = \int d\mathbf{r}_1 \cdots d\mathbf{r}_P \rho(\mathbf{r}_1, \mathbf{r}_2; \tau) \rho(\mathbf{r}_2, \mathbf{r}_3; \tau) \cdots \rho(\mathbf{r}_{P-1}, \mathbf{r}_P; \tau) \rho(\mathbf{r}_P, \mathbf{r}_1; \tau). \] (2.1)

If \( P \) is sufficiently large, we can now apply the Trotter-Suzuki decomposition on each high-temperature Green’s function:

\[ \langle \mathbf{r}_{i+1} | e^{-\tau(\hat{T} + \hat{V})} | \mathbf{r}_i \rangle = \langle \mathbf{r}_{i+1} | e^{-\tau \hat{T}} e^{-\tau \hat{V}} | \mathbf{r}_i \rangle + O(\tau^2) \approx \int d\mathbf{r}' \langle \mathbf{r}_{i+1} | e^{-\tau \hat{T}} | \mathbf{r}' \rangle \langle \mathbf{r}' | e^{-\tau \hat{V}} | \mathbf{r}_i \rangle. \]

Since the potential energy is diagonal in the coordinate basis, this simply gives

\[ \int d\mathbf{r}' \langle \mathbf{r}' | e^{-\tau \hat{V}} | \mathbf{r}_i \rangle = \int d\mathbf{r}' e^{-\tau \hat{V}(\mathbf{r}_i)} \delta(\mathbf{r}' - \mathbf{r}_i). \]

The kinetic part can be computed by switching to the momentum basis

\[ \langle \mathbf{r}_{i+1} | e^{-\tau \hat{T}} | \mathbf{r}_i \rangle = \int d\mathbf{k}' d\mathbf{k}'' \langle \mathbf{r}_{i+1} | \mathbf{k}' \rangle \langle \mathbf{k}' | e^{-\tau \hbar^2 \nabla^2/2m} | \mathbf{k}'' \rangle \langle \mathbf{k}'' | \mathbf{r}_i \rangle = \]

\[ = \frac{1}{2\pi} \int d\mathbf{k}' e^{\mathbf{k}' \cdot (\mathbf{r}_{i+1} - \mathbf{r}_i)} e^{-\tau \hbar^2 k^2/2m} = \]

\[ = \left( \frac{m}{2\pi \hbar^2 \tau} \right)^{d/2} \exp \left( \frac{m}{2\hbar^2 \tau} (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 \right) \equiv \rho_0(\mathbf{r}_{i+1}, \mathbf{r}_i; \tau). \)

\(^1\)Higher order decompositions exist (see for example [12]) but are not considered in this thesis.
This will be referred to as the *free-particle propagator*. We have now ended up with the following expression for the partition function:

\[
Z_P = \left( \frac{mP}{2\pi\hbar^2\beta} \right)^{Pd/2} \int \mathcal{D}r_1 \cdots \mathcal{D}r_P \exp \left( -\beta V_{\text{eff}}(r_1, \ldots, r_P) \right)
\]

with the effective potential

\[
V_{\text{eff}}(r_1, \ldots, r_P) = \sum_{i=1}^{P} \left( \frac{mP}{2\hbar^2\beta^2} (r_{i+1} - r_i)^2 + \frac{1}{P} V(r_i) \right),
\]

where we are using periodic indices, so that \(r_{P+1} \equiv r_1\). In the limit of infinite \(P\) this equals the exact partition function, \(Z = \lim_{P \to \infty} Z_P\). In practice we shall work with a large finite \(P\) rather than taking the limit.

Now we are ready to make an important observation \[1\]: the partition function in equation (2.2) can be interpreted as a configurational integral of a cyclic polymer of \(P\) beads. Each bead is interacting with its neighbours with harmonic springs with spring constant \(mP/\hbar^2\beta^2\) and is under the effect of a reduced external potential \(V/P\).

The classical polymer system is said to be *isomorphic* to the quantum one-particle system \[2\]. We can therefore calculate properties (see sec. 2.3) of the quantum system by sampling configurations from the classical distribution \(e^{-\beta V_{\text{eff}}}\).

There are several ways to perform such a sampling. In this thesis we will use *Path Integral Molecular Dynamics* (PIMD) in which we assign fictitious momenta \(\{p_i\}\) and masses \(m'_i\) to the polymer beads \[13,14\]. We will take \(m'_i = m\) for all \(i\), although other choices are possible. The extended partition function is

\[
Z_P = \int \mathcal{D}p_1 \cdots \mathcal{D}p_P \int \mathcal{D}r_1 \cdots \mathcal{D}r_P \exp(-\beta H_{\text{eff}}),
\]

with the effective Hamiltonian

\[
H_{\text{eff}} = \sum_{i=1}^{P} \frac{p_i^2}{2m} + V_{\text{eff}}(r_1, \ldots, r_P).
\]

The extended system can be evolved with Hamilton’s equations of motion \[14\]

\[
\begin{cases}
\dot{r}_i = \partial H_{\text{eff}} / \partial p_i \\
\dot{p}_i = -\partial H_{\text{eff}} / \partial r_i
\end{cases}
\]

which can be numerically integrated in numerous different ways. In this thesis a velocity-Verlet scheme has been used; its implementation is described in Appendix D.1.

Another common procedure is *Path Integral Monte Carlo* (PIMC), using Monte Carlo techniques to generate a trajectory in configuration space \[14\]. This thesis uses PIMD instead of PIMC since Metadynamics has been more thoroughly developed for MD simulations.
2. Path Integral Molecular Dynamics

Note that the dynamics is only fictitious; the classical trajectories of the beads are not intended here to represent the quantum dynamics in real time (we refer the reader who is interested in real time quantum dynamics to Ref. [15]). However, the statistical operator $e^{-\beta \hat{H}}$ can be interpreted as a quantum time evolution operator $e^{-i\hat{H}/\hbar}$ with the substitution $it/\hbar \rightarrow \beta$. The configurations $\{r_i\}$ can thus be interpreted as paths in imaginary time [1]. We will refer to $i$ as an index for the imaginary time slice and $\tau = \beta/P$ as an imaginary time step.

2.2 Quantum symmetry in many-body systems

Now we will generalise the theory of the previous section to systems of several particles. In particular we will focus on how to include quantum symmetry effects of indistinguishable particles.

Let us begin with the case of $N$ distinguishable particles. The generalization of equation (2.2) is straightforward [16]:

$$Z_P = \left( \frac{mP}{2\pi\hbar^2\beta} \right)^{NPd/2} \int dR_1 \cdots dR_P \exp \left( -\beta V_{\text{eff}}(R_1, \ldots, R_P) \right)$$

(2.5)

where $R_i = (r_{i,1}, \ldots, r_{i,N})$ are the $Nd$ coordinates of bead $i$ and

$$V_{\text{eff}}(R_1, \ldots, R_P) = \sum_{n=1}^{N} \sum_{i=1}^{P} \left( \frac{mP}{2\hbar^2\beta^2} (r_{i+1,n} - r_{i,n})^2 + \frac{1}{P} V_1(r_{i,n}) + \frac{1}{P} \sum_{l<n} V_2(r_{i,n}, r_{i,l}) \right).$$

The last term is a two-particle interaction in which beads are only interacting if they belong to the same imaginary time-slice, see Figure 2.1a. To emphasise the difference between two-body and one-body interactions, we have added subscripts 1 and 2 on the potentials.

Identical quantum particles are however indistinguishable, and the distinguishable treatment can only be used as an approximation in Quantum mechanics. Multi-particle systems are described by many-body states $\Psi(R)$ which are either symmetric (bosons) or antisymmetric (fermion) under the exchange of any two particles. For the moment we shall consider only spinless particles (spin will be treated in section 5.2) so that by exchange of two particles we mean exchange of their spatial coordinates.

If $P$ is the permutation operator of the particle labels and $(-1)^P$ its sign we thus have

$$\Psi(PR) = (\pm 1)^P \Psi(R)$$

with positive sign for bosons and negative for fermions. The eigenstates $\{\Psi_k(R)\}$ are related to the Green’s function through [3]

$$\rho(R,R'; \beta) = \sum_k e^{-\beta E_k} \Psi_k(R)\Psi_k(R')$$

2The sign of a permutation $P$ is $-1$ if the number of pair exchanges is odd and $+1$ if even.
so that, using the notation $\rho_B$ for bosons and $\rho_F$ for fermions, we have \[3\]
\[
\begin{cases}
\rho_B(R,R'; \beta) = \rho_B(P R, R'; \beta) = \rho_B(P R, R; \beta) \\
\rho_F(R,R'; \beta) = (-1)^P \rho_F(P R, R'; \beta) = (-1)^P \rho_F(R, PR; \beta).
\end{cases}
\tag{2.6}
\]

Eq. (2.6) shows that the Green’s functions inherit the symmetry of the wavefunctions on both its arguments. As a generalization to equation (2.1) the total bosonic (fermionic) partition function can now be written in terms of (anti)symmetrized distinguishable Green’s functions $\rho_D$ as \[3\]
\[
Z_B/F = \frac{1}{N!} \sum_{P} (\pm 1)^P \int dR_1 \cdots dR_P \rho_D(R_1, R_2; \tau) \cdots \rho_D(R_P, PR_1; \tau). 
\tag{2.7}
\]

Note that we have only applied the permutation operator to the end point. It is possible to (anti)symmetrize anywhere along the path as many times as we wish, but once is enough \[3\]. In appendix \[A\] we motivate in the case of two particles that the fully antisymmetrised propagator must give the same statistics as equation (2.7).

Equation (2.7) might look complicated but in the path integral representation it has an easy interpretation: the permuted terms correspond to polymers connecting to each other, forming new closed polymers of larger length, see Figure 2.1b. In this thesis we will emphasize this picture by introducing the notation

\[
Z_{B/F} = \frac{1}{N!} \sum_{P} (\pm 1)^P Z_{\nu_1(P), \nu_2(P), \ldots, \nu_N(P)},
\]
2. Path Integral Molecular Dynamics

where \( Z_{\nu_1(\mathcal{P}),\nu_2(\mathcal{P}),...,\nu_N(\mathcal{P})} \) denotes the partition function for a classical system with \( \nu_j \) chains of length \( j \) which is created by the permutation operator \( \mathcal{P} \). We will call a set of \( \{\nu_j\} \) a diagram (although note that this is not diagrams as in the Feynman diagram expansion of partition functions in quantum field theory).

Let us look at the example of two particles. Then there are two diagrams, which were shown in Figure 2.1: the disconnected one has two chains, each of length one, which in our notation has the partition function \( Z_{2,0} \). The connected diagram has one chain belonging to two particles, with the partition function \( Z_{0,1} \). To emphasise the pictorial representation of polymer rings, we will write \( Z_{\infty} \equiv Z_{2,0}^2 \), \( Z_{oo} \equiv Z_{0,1} \) and only keep the notation \( Z_{\nu_1,\nu_2,...,\nu_N} \) for \( N \geq 3 \).

In our configuration sampling scheme we now have to make sure to include contributions from all permutations. One way (suitable for Monte Carlo simulations) would be to introduce trial moves in which the permutation is changed. In this thesis, we will only simulate one permutation and include the contributions from all other permutations as a weight (this approach has been used by Ref. [17]).

Let us begin with the case of two particles. Then the partition function can be written

\[
Z_{B/F} = \frac{1}{2} \int \, dR_1 \cdots dR_P \left( 1 \pm e^{-\beta(U_O - U_{oo})} \right) e^{-\beta U_{oo}},
\]

where \( U_O \) is the energy of the connected polymer and \( U_{oo} \) is the energy of the disconnected polymers. The simulation is performed in the permutation \( oo \), which is why exponential \( e^{-\beta U_{oo}} \) has been factorised out.

For a general number of particles, the partition function is

\[
Z_{B/F} = \frac{1}{N!} \int \, dR_1 \cdots dR_P \left( \sum_{\mathcal{P}} (\pm 1)^{\mathcal{P}} e^{-\beta \Delta U_{\mu_1,...,\mu_N}} \right) e^{-\beta U_{\nu_1,...,\nu_N}},
\]

where \( \Delta U_{\mu_1,...,\mu_N} \equiv U_{\mu_1,...,\mu_N} - U_{\nu_1,...,\nu_N} \) and the simulation is performed in the diagram with chain lengths \( \{\nu_j\} \). Most commonly we shall choose \( \nu_1 = N, \nu_j > 1 = 0 \), i.e. disconnected polymers. We will refer to \( W \) as the exchange factor. The exchange factor can be interpreted as a weight that contains contributions from other diagrams.

An advantage of this method is that many permutations give rise to the same diagram. They have the same set of chain lengths \( \{\nu_j\} \) and only differ in the enumeration of the chains. Such diagrams belong to the same permutation group and have the same sign and the same contribution to the exchange factor [17]. The number of nonenumerated diagrams grows much slower than the number of enumerated diagrams \( N! \). We can thus rewrite equation (2.8) as

\[
Z_{B/F} = \frac{1}{N!} \int \, dR_1 \cdots dR_P \left( \sum_{G'} (\pm 1)^{G'} e^{-\beta \Delta U_{G'}} \right) e^{-\beta U_{G'}},
\]
where the simulation is performed in diagram $G$ and the sum is taken over all nonenumerated diagrams $G'$, each of which has multiplicity $c_{G'}$.

### 2.2.1 Fermionic sign problem

The sampling of fermionic path integrals is particularly difficult, because the negative sign creates large cancellation errors. One can show that the average sign obtained from a direct summation of permutations decreases exponentially with both $N$ and $\beta$ \[3\].

There are a number of methods to handle this, for example the fixed-node approximation \[18\], the restricted path integral method \[3\], multilevel blocking \[5\] and exchange truncated grand canonical PIMC \[19\]. These methods are approximate but give reliable results for some sufficiently small systems. Another strategy is to antisymmetrize over each time-slice propagator $\rho_D(R_i, R_{i+1}; \tau)$ in equation (2.7), which softens the sign problems if $N$ is small \[16,20\], and removes all negative signs in one-dimensional systems because the positions of the nodes are known \[16,21,22\].

On the other hand, in higher dimensions the improvement vanishes for higher $N$ \[3\].

One can show that the fermionic sign problem belongs to the complexity class NP (nondeterministic polynomial), which means it would scale exponentially on a deterministic classical computer \[4\]. Since we (so far) only have classical deterministic computers at our disposal, we will need to live with an exponentially vanishing average sign, and rather try to improve the accuracy with which the average sign can be computed on each specific system.

In this thesis we will investigate two methods to improve the sampling of fermionic systems. The first one will be to identify a suitable collective variable to be enhanced by Metadynamics, see section 3.2. The second one is to calculate the difference in free energy between the fermionic and bosonic system with Bennett’s acceptance ratio method, see section 3.3.2.

### 2.3 Thermodynamic estimators

In the previous sections we have found expressions for the partition function of systems of one and several particles. We will now show how to obtain thermal averages of various equilibrium properties from these expressions.

The thermodynamic energy estimator is defined by \[23\]

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}.$$  

Using expression (2.5) this gives

$$E = \left\langle \frac{NPd}{2\beta} - \frac{mP}{2\hbar^2\beta^2} \sum_{i,n} (r_{i+1,n} - r_{i,n})^2 + \frac{1}{P} \sum_{i,n} \phi(r_{i,n}) \right\rangle, \quad (2.10)$$
where $\phi(r_{i,n}) = V(r_{i,n}) + \sum_{l<n} V(r_{i,n}, r_{i,l})$ and $\langle O \rangle$ denotes the thermal average of the observable $O$, defined as

$$\langle O \rangle \equiv \frac{\int d\Omega \, O e^{-\beta V_{\text{eff}}}}{\int d\Omega \, e^{-\beta V_{\text{eff}}}},$$

where $d\Omega$ denotes a generic infinitesimal phase-space volume element. In the coordinate representation, this would be $d\Omega = d\mathbf{R}_1 \cdots d\mathbf{R}_P$. The thermal averages are calculated as an average of samples taken from a Molecular Dynamics simulation, as was described in section 2.1. We can interpret the last term in equation (2.10) as the potential energy

$$E_{\text{pot}} = \frac{1}{P} \sum_{i,n} \phi(r_{i,n}),$$

and the first terms as the kinetic energy

$$E_{\text{kin}} = \left\langle \frac{NPd}{2\beta} - \frac{mP}{2\hbar^2 \beta^2} \sum_{i,n} (r_{i+1,n} - r_{i,n})^2 \right\rangle.$$

From a computational point of view, the kinetic energy estimator is inconvenient since its variance grows with $P$ [24], making it difficult to converge to a fixed value in the limit of low $\tau = \beta/P$. Luckily, the kinetic energy can be recast to other mathematically equivalent expressions, that give a more robust energy estimator. One common choice is the centroid virial estimator [12] which for one particle is given by

$$E_{\text{vir}} = \left\langle \frac{d}{2\beta} + \frac{1}{2P} \sum_i (r_i - \bar{r}) \cdot \frac{\partial \phi}{\partial r_i} + \frac{1}{P} \sum_i \phi(r_i) \right\rangle,$$

where $\bar{r} \equiv \frac{1}{P} \sum_i r_i$ is the centroid of the polymer. The details on how to derive this expression are given in Appendix B, where we also generalise it to a general set of permutations of $N$ particles.

Two other important observables are the probability density

$$\langle p(r) \rangle = \left\langle \frac{1}{P} \sum_{i,n} \delta(r_{i,n} - r) \right\rangle$$

and the radial pair correlation function

$$\langle g(r) \rangle = \left\langle \frac{1}{P} \sum_{n \neq m} \sum_i \delta(|r_{i,n} - r_{i,m}| - r) \right\rangle.$$

The pair correlation function can in also be computed as a function of the distance vector $r = r_n - r_m$:

$$\langle g(r) \rangle = \left\langle \frac{1}{P} \sum_{n \neq m} \sum_i \delta(r_{i,n} - r_{i,m} - r) \right\rangle.$$
In practice, these are calculated by generating a histogram with a finite resolution, normalized to one. In the case of two dimensions, this includes a normalization over the spherical shell for the radial pair correlation function.

So far we have been working in the ensemble of distinguishable particles. If the particles are indistinguishable, the partition function contains an exchange factor \( W \) defined by equation \( ^{2.9} \). For diagonal operators like potential energy or probability densities this can easily be included as a weighted average:

\[
\langle O_{B/F} \rangle = \frac{\langle OW_{B/F} \rangle}{\langle W_{B/F} \rangle}.
\]

For the total energy (we will only consider the virial estimator) the estimator needs to include an extra term from the derivative \( \partial W/\partial \beta \); see Appendix \( ^{B} \) for a full derivation. For fermions we can also compute the average sign

\[
\langle \text{sign} \rangle \equiv \left\langle \frac{W_+ - W_-}{W_+ + W_-} \right\rangle = \frac{W_F}{W_B},
\]

where \( W_+ \) and \( W_- \) are the positive and negative weights, respectively. In section \( ^{3.3} \) we will present an alternative method to compute the average sign.

Samples generated from a Molecular Dynamics simulation will in general be correlated. A way to estimate the statistical error is to divide the samples in blocks and calculate a separate average in each block. Each block is assumed to be much longer than the autocorrelation time of the observable we are interested in. According to the Central limit theorem, the statistical error of \( N_{\text{blocks}} \) independent blocks can then be computed as

\[
\Delta O = \sqrt{\frac{\langle O^2 \rangle - \langle O \rangle^2}{N_{\text{blocks}}}}.
\]

where \( \langle \cdot \rangle \) is in this case to be understood as an average over blocks, see Figure \( ^{2.2} \). We found that 10 blocks were enough to obtain a sufficiently small statistical error.

<table>
<thead>
<tr>
<th>( O_1 )</th>
<th>( O_2 )</th>
<th>( O_3 )</th>
<th>...</th>
<th>( O_{N_{\text{blocks}}} )</th>
</tr>
</thead>
</table>

Figure 2.2: Schematic representation of the block averaging process.

### 2.4 Constant temperature – Generalised Langevin equation thermostat

In a PIMD simulation the beads are assigned fictitious masses and momenta, as was done in equation \( ^{2.3} \) in section \( ^{2.1} \). The extended system should then be evolved...
in time to produce samples distributed according to the canonical ensemble, i.e.
at a constant temperature $T$. However, the equations of motion in equation (2.4) conserve total energy, while a constant temperature simulation should allow for the total energy to fluctuate. This will be achieved by coupling the system to a \textit{thermostat}.

Before we present the thermostat, note that there is also another problem of the equations of motion (2.4). The polymers are closed chains of harmonic oscillators, which can be decomposed into a set of normal modes. These modes are in general only weakly coupled by the interacting potential, which means that the energy distribution over the modes depends strongly on the initial configuration, making the sampling non-ergodic \cite{13}. To obtain an ergodic sampling, we will choose a thermostat that is able to dissipate energy between the normal modes.

A widely used thermostat is based on the Langevin equation \cite{25}

$$
\begin{aligned}
\dot{q} &= p \\
\dot{p} &= -\frac{\partial V}{\partial q} - \gamma p + \xi(t)
\end{aligned}
$$

which consists in the equations (2.4) supplemented by a friction force $\gamma p$ and a random force $\xi(t)$. We assume $\xi(t)$ to be uncorrelated and Gaussian-distributed with average zero, and have set the mass to one for simplicity. The magnitude of $\xi$ and the friction coefficient $\gamma$ can be chosen such that the generated samples are canonically distributed.

This kind of thermostat can dissipate energy between different normal modes, but is unfortunately only efficient for a rather narrow range of frequencies \cite{26}. Instead we use a generalisation of the Langevin thermostat, where a memory kernel $K$ features in the equation of motion:

$$
\dot{p} = -\frac{\partial V}{\partial q} - \int_{-\infty}^{t} K(t-t')p(t') \, dt' + \zeta(t).
$$

(2.14)

Here $\zeta(t)$ is another Gaussian random process. A thermostat based on this \textit{generalised Langevin equation} is efficient for a much wider frequency range \cite{26}. It can however be computationally inconvenient to store the past trajectory of $p$. One can show that the equations (2.14) can be converted to a form that is not history-dependent, by coupling the momenta to a set of additional degrees of freedom. This is fully described in Ref. \cite{27} and we summarise the most important details in Appendix \ref{app:optimal}. In short, this \textit{optimal sampling GLE thermostat} has parameters that can be tuned to optimise the coupling between the normal modes. Since the thermostat is rotationally invariant, it can be applied directly in the coordinate representation, such that no transformation to normal mode coordinates is needed.
Chapter 3

Enhanced sampling techniques

In the previous chapter we described how to simulate quantum particles with Path Integral Molecular Dynamics. For systems of several indistinguishable particles we saw that the simulation needs to include an (anti-)symmetrization over all possible permutations of the particles. The effects of this quantum exchange are most important when the particles are close to each other and the polymers overlap. However, in section 4.1 we will see that configurations with strongly overlapping particles are only rarely sampled.

To enhance the sampling of such configurations, we will introduce a bias potential, which pushes the system towards regions in phase-space which would otherwise be difficult to reach. In the case of a fixed, pre-determined bias, this method is called umbrella sampling and is described in section 3.1. However, often we have too little a priori knowledge about the system to choose a good bias. This is our case and in fact we will use a more general method called Metadynamics, in which one creates a bias potential on the fly. This is described in section 3.2. The last part of this chapter, section 3.3 covers the problem of sampling free energy differences between systems.

3.1 Umbrella sampling

Umbrella sampling is one of the oldest enhanced sampling methods. It was historically invented to enhance the sampling of free energy differences, but it can be used to enhance also the sampling of other properties [28]. To begin with, consider an unbiased simulation, where we acquire samples according to a canonical distribution

\[ p(q) = \frac{\exp(-\beta U(q))}{\int dq \exp(-\beta U(q))}. \]

Here \( U(q) \) is the energy of a configuration with coordinates \( q \). If \( U(q) \) has a region which is difficult to reach from a pure canonical sampling (for example if it is separated by a large potential barrier), the probability of sampling in this region
will be very low. However, samples from this region may still have important contributions to observables of our interest. To change the sampling probability we introduce a weight

\[ w(q) = \exp(-\beta V_{\text{bias}}(q)) \]

where \( V_{\text{bias}} \) is called a bias potential. In the weighted ensemble samples are acquired from the distribution

\[ \pi(q) = \frac{w(q) \exp(-\beta U(q))}{\int dq \ w(q) \exp(-\beta U(q))} = \frac{\exp(-\beta U(q) + V_{\text{bias}}(q))}{\int dq \ \exp(-\beta U(q) + V_{\text{bias}}(q))}. \] (3.1)

In a Molecular Dynamics simulation, the bias generates additional forces \( -\nabla V_{\text{bias}} \) on the particles. To obtain unbiased ensemble averages \( \langle O \rangle \) from a biased simulation, we can reweight the samples taken in the biased ensemble according to \[ 28 \]

\[ \langle O \rangle = \frac{\int dq \ O \exp(-\beta [U(q) + V_{\text{bias}}(q)]) \exp(+\beta V_{\text{bias}}(q))}{\int dq \ \exp(-\beta [U(q) + V_{\text{bias}}(q)]) \exp(+\beta V_{\text{bias}}(q))} \]

\[ = \frac{\langle O \exp(+\beta V_{\text{bias}}) \rangle_V}{\langle \exp(+\beta V_{\text{bias}}) \rangle_V}, \]

where

\[ \langle O \rangle_V = \frac{\int dq \ O \exp(-\beta [U(q) + V_{\text{bias}}(q)])}{\int dq \ \exp(-\beta [U(q) + V_{\text{bias}}(q)])} \]

is a thermal average taken in the biased ensemble.

Pure umbrella sampling is not the main enhanced sampling method used in this thesis, so we will not go into details on this topic. Instead let us continue with the more general method Metadynamics.

3.2 Metadynamics

In the previous section we described how a bias potential can be used to change the sampling distribution of an MD simulation. It is in general difficult to guess a suitable bias potential without detailed pre-knowledge about the system. Metadynamics generalises umbrella sampling by using a history-dependent bias which adapts depending on the measured sampling distribution.

The first question we need to ask ourselves is what we want to enhance. From the theoretically or experimentally available information we choose a set of so-called collective variables

\[ s = s(R_1, \ldots, R_P). \]

These are functions of some many-body coordinates, which should be able to distinguish between different types of physically relevant configurations. In this thesis we shall only use a single CV. In theory any number of CVs is possible but Metadynamics scales exponentially with the number of CVs \[ 7 \]. From the CV we can define the free energy surface (FES)

\[ F(s) = -\frac{1}{\beta} \log p(s) \] (3.2)
3. Enhanced sampling techniques

Figure 3.1: Sketch of the Metadynamics algorithm, reprinted with permission from Ref. [30]. The free energy surface (solid dark line) has two energy minima separated by an energy barrier which is only very rarely crossed by thermal fluctuations. A bias potential (solid light line) is deposited with time, which creates a new free energy surface (dashed line). When enough bias has been deposited to the left basin, the system can cross the energy barrier and sample configurations in the right basin. Eventually the free energy surface converges to a flat landscape.

where \( p(s) \) is the sampled distribution of \( s \). In a typical situation, the FES consists of several minima separated by high barriers, which are only rarely crossed thermally. The bias added with Metadynamics will with time fill the minima and enhance the crossing of the energy barriers [29], see Figure 3.1.

There are many choices on how to construct such a bias. A common and general choice is as a sum of Gaussian functions of the form

\[
G(s,s') = H e^{-((s-s')^2)/2\sigma^2}.
\]

Such a Gaussian is added after every constant time interval \( \tau_G = N_G \Delta t \), i.e. every \( N_G \) MD steps. Each bias update is done as [7]

\[
V_n(s) = V_{n-1}(s) + H_n e^{-((s-s_n)^2)/2\sigma^2}.
\]

We would like the bias to eventually converge to a final function. One may think of a simulation in the converged biased system as a simulation at a higher temperature \( T + \Delta T \equiv \gamma T \), where \( \gamma \) is called the bias factor. The effect of the bias factor is to

\[\footnote{The usual notation in literature for the Gaussian height is \( W \) but has been replaced by \( H \) to avoid confusion with the exchange factor \( W \).} \]

\[\footnote{1} \]
3. Enhanced sampling techniques

smoothen out $p(s)$ to $p(s)^{1/\gamma}$, which enhances the fluctuations of the system. One can show \[6,7\] that this can be achieved by adapting the heights of the Gaussians according to

$$H_n = H \exp \left( -\frac{1}{\gamma - 1} \beta V_{n-1}(s_n) \right).$$

Such an approach is called well-tempered Metadynamics and has been proven rigorously in Ref. \[31\]. The biased simulation asymptotically generates samples distributed as \[7\]

$$p_V(q,t) = \frac{e^{-\beta[U(q)+V(s(q),t)]}}{\int dq e^{-\beta[U(q)+V(s(q),t)]}} = p(q)e^{-\beta[V(s(q),t)-c(t)]},$$

with

$$c(t) = \frac{1}{\beta} \log \frac{\int ds \exp \left( \frac{\gamma}{\gamma - 1} \beta V(s,t) \right)}{\int ds \exp \left( \frac{1}{\gamma - 1} \beta V(s,t) \right)}. \quad (3.3)$$

The function $c(t)$ is an estimator for the reversible work done by the bias \[31\]. Even though both $V(s(q),t)$ and $c(t)$ grow with time, their difference remains comparatively small \[32\]. Just as for umbrella sampling, unbiased expectation values can be obtained through the reweighting relation \[32\]

$$\langle O \rangle = \frac{\langle O e^{\beta[V(s(q),t)-c(t)\rangle_V}}{\langle e^{\beta[V(s(q),t)-c(t)\rangle_V}}. \quad (3.4)$$

For example, the unbiased distribution over $s$ can be computed with $O = \delta(s-s(q))$. From this the FES can be computed with equation \[3.2\]. Alternatively, one can obtain the FES from the bias through \[31\]

$$F(s) = -\frac{1}{\gamma - 1} V(s) + \text{const.}$$

When the number of Gaussians becomes large, their explicit computation becomes very slow. Practical details on how this was handled numerically are given in appendix \[D.3\].

3.3 Free energy methods

Metadynamics can be used to enhance the sampling of many different properties. One of the most common observables to measure is the total energy, and we will now consider this in more detail. We saw in chapter \[2\] that the simulation of fermions is associated to harder numerical issues than the simulation of bosons. Because of this, it is interesting to ask ourselves if the fermionic energy can be computed through the difference in energy from the bosonic system. If so, we would be able to replace the difficult problem of computing the fermion energy by an easier boson energy calculation and an apparently less difficult energy difference calculation.
One can show \(33,34\) that the average sign is related to the free energy difference as
\[
\langle \text{sign} \rangle = \frac{Z_F}{Z_B} = \frac{Z_+ - Z_-}{Z_+ + Z_-} = e^{-\beta(F_F - F_B)}. \tag{3.5}
\]
In the limit of low temperatures only the ground states (with energies \(E_F\) and \(E_B\)) contribute to the partition function, so that one can approximate
\[
F_F - F_B \approx E_F - E_B. \tag{3.6}
\]
In our simulation we do not have access directly to the ensembles with partition functions \(Z_F\) or \(Z_B\) but rather to the individual permutation terms. For example for two particles, the positive part is the diagram of disconnected polymers, \(Z_+ = Z_{oo}\), and the negative part is the diagram of connected polymers, \(Z_- = Z_O\). This notations was introduced in section \(2.2\). Since
\[
\frac{Z_B}{Z_F} = \frac{1}{2} \int dR_1 \cdots dR_P (e^{-\beta U_{oo}} \pm e^{-\beta U_O})
\]
the ratio of the partition functions can be written
\[
\frac{Z_F}{Z_B} = \frac{\int dR_1 \cdots dR_P (e^{-\beta U_{oo}} - e^{-\beta U_O})}{\int dR_1 \cdots dR_P (e^{-\beta U_{oo}} + e^{-\beta U_O})} = \frac{e^{-\beta F_{oo}} - e^{-\beta F_O}}{e^{-\beta F_{oo}} + e^{-\beta F_O}} = \frac{1 - e^{-\beta(F_O - F_{oo})}}{1 + e^{-\beta(F_O - F_{oo})}}. \tag{3.7}
\]
This means that knowledge of the free-energy difference \(F_O - F_{oo}\), i.e. between the connected and the disconnected polymers, is enough to compute the free energy difference \(F_F - F_B\).

The computation of free energy differences between two ensembles is a delicate task and many methods are described in literature. In section \(3.3.1\) we describe the simple approach of averaging the exponentials \(e^{-\beta \Delta F}\) in only one ensemble, and in section \(3.3.2\) we will show how measurements from both ensembles can be weighted together to create a more accurate estimate. Another common approach is thermodynamic integration \(35\), based on numerical integration of free energy differences along a continuously changing path between the two ensembles, but it is not applied in this case since the transition between disconnected and connected polymers is not continuous.

### 3.3.1 Exponent average

This method (also called the Free energy perturbation method) was first derived by Zwanzig in 1954 \(36\), and is thereby one of the oldest methods to compute free-energy differences. Let us start with the identity
\[
\frac{Z_0}{Z_1} = e^{-\beta(F_0 - F_1)}
\]
for two states 0 and 1. Then
\[
\frac{Z_0}{Z_1} = \frac{1}{Z_1} \int dq e^{-\beta U_0(q)} = \frac{1}{Z_1} \int dq e^{-\beta[U_0(q) - U_1(q)]} e^{-\beta U_1(q)} = \langle e^{-\beta \Delta U} \rangle_1
\]
3. Enhanced sampling techniques

with $\Delta U \equiv U_0 - U_1$. Note that such a sampling is only ergodic if $U_0(q)$ and $U_1(q)$ are mostly overlapping and $U_1(q)$ is ergodically sampled. If this is the case, the free energy difference can be computed by

$$F_0 - F_1 = -\frac{1}{\beta} \langle e^{-\beta(E_0 - E_1)} \rangle_1.$$  

3.3.2 Bennett’s acceptance ratio method

If the ensembles of the states 0 and 1 have a small overlap, the procedure in section 3.3.1 is doomed to fail, because the simulation of system 0 will not be able to sample a large part of the ensemble 1. Instead, Bennett argued in a paper from 1976 [37] that samples need to be acquired from both ensembles in order to efficiently sample their overlap.

Let us start with the identity

$$Z_0 Z_1 = Z_0 \int dq w(q) e^{-\beta[U_0(q) + U_1(q)]} = \langle w e^{-\beta U_0} \rangle_1$$

This is true for any everywhere-finite function $w(q)$ [37]. A simple example would be $w = \exp(\min\{U_0, U_1\})$, giving

$$Z_0 Z_1 = \langle M(U_0 - U_1) \rangle_1$$

where $M(x) = \min\{1, e^{-x}\}$ is the Metropolis function. Physically this would correspond to the ratio of acceptance probabilities for a Metropolis step in different directions [37], giving the method its name (however note that the Metropolis steps are never carried out). This is however not the optimal choice. Bennett derived the optimal weighting function (giving the estimate with minimum variance) to be the Fermi function $f(x) = 1/(1 + e^x)$ and additionally introduced a shift to the origin of the potential functions in order to increase their overlap: [37]

$$Z_0 Z_1 = \langle f(\beta(U_0 - U_1) + C) \rangle_1 \exp(C).$$ (3.8)

This is true for any $C$, but the optimal choice is

$$C = \ln(Z_0 n_1 / Z_1 n_0)$$ (3.9)

where $n_i$ is the number of samples taken from ensemble $i$ [37]. Since we don’t know $Z_0 / Z_1$ yet, this gives two equations (3.8) and (3.9) which need to be solved self-consistently. Practical details on how this was done are given in Appendix D.4.

Bennett’s acceptance ratio method (often abbreviated as BAR) is known to be much more powerful than exponent averaging (see for example Ref. [38,39]). It will however fail to give a good estimation if the overlap between $U_1$ and $U_0$ becomes
too small. In this case, one would need to create a set of intermediate ensembles and calculate the free-energy difference stepwise \cite{37}.

The idea of using BAR in path integral simulations has previously been used by Ceperley \cite{23,40} to compute exchange frequencies in helium crystals, and by Kono et al. \cite{41} to compute ratios of partition functions between systems of different potentials. We have however not found previous work in literature which uses BAR to directly calculate energy differences between systems of different quantum symmetry.
3. Enhanced sampling techniques
Chapter 4

Two non-interacting particles in a harmonic potential

We will now apply the methods presented in the previous chapter on PIMD simulations. To test the methods, we begin by studying a simple model system for which we can compare with exact analytic solutions, namely two noninteracting particles in a harmonic oscillator. We will compare distinguishable particles with bosons and fermions and analyse the severity of the sign problem.

4.1 Introduction

Consider two spinless particles in the harmonic potential

\[ V(r) = \frac{1}{2} m\omega_0^2 r^2, \]

and in the absence of inter-particle interaction. From elementary quantum mechanics we know that the eigenenergies of a one-dimensional harmonic potential are \( E_n = \hbar \omega_0 \left( n + \frac{1}{2} \right), \) \( n = 0, 1, 2, \ldots \). In two dimensions, the states are labelled by two quantum numbers \( n_x \) and \( n_y \) with energies \( E_{n_x,n_y} = \hbar \omega_0 (n_x + n_y + 1) \) (for the moment we consider only a circular potential; the elliptic case will be treated in section 5.3.3).

If the particles are distinguishable, they can be treated completely independently and will fill up the states according to Boltzmann statistics. For example in 1D we have for two particles

\[ Z = \left( \sum_n e^{-\beta E_n} \right)^2, \quad E_D = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{2}{\sum_n e^{-\beta E_n}} \sum_n E_n e^{-\beta E_n} = 2\hbar \omega_0 \left( \frac{1}{2} + \frac{1}{e^{\hbar \omega_0 \beta} - 1} \right). \]

In the low-temperature limit, both particles occupy the ground state, \( E_D = 2E_0 \). If the particles are bosons, they will also both occupy the ground state in the low-temperature limit, but for finite temperatures the average energy will be lower than
in the distinguishable case, because bosons have a higher probability of being found in the ground state. Fermions however follow the Pauli principle, so that in the low temperature limit on average one of them will be in the first excited single-particle state. Table 4.1 summarizes the exact zero temperature energies, which can be used as a validity check of values that we calculate later in this chapter. Expressions for the exact energies at arbitrary temperature in a general number of dimensions are derived in Appendix C.1.

Having found a set of target values, we now turn our attention to the choice of simulation parameters. The harmonic oscillator will in the next chapter be used to model quantum dots, which typically have $\hbar \omega_0$ in the order of a few meV. Since we are in this chapter only interested in testing the method rather than calculating measurable results, the exact choice is unimportant. We have chosen $\hbar \omega_0 = 3$ meV and $m = m_e$, the electron mass. The timestep was chosen as $\Delta t = 5$ fs; see Appendix D.1 for a justification.

To identify a suitable number of beads for PIMD, we need to make sure that the imaginary time step $\tau$ is small enough (recall that $P = \beta / \tau$, see section 2.1). Several simulations of distinguishable particles were performed for different $\tau$ at constant $\beta$ until the energy converged. As can be seen in Figure 4.1, convergence is reached at about $1/\tau \approx 10$ meV$^{-1}$. Thus $\tau = 0.1$ meV$^{-1}$ is sufficiently small; a smaller value would increase the simulation time but not significantly change the results. At $\beta = 1$ meV$^{-1} (T = 11.6 \text{ K})$ this corresponds to $P = 10$ beads. It was assumed that convergence occurs at the same $\tau$ for bosons and fermions as for distinguishable particles.

### 4.2 Motivation for using enhanced sampling

Let us begin with non-biased simulations, using the parameter settings described in the previous section. In Figure 4.2, we show two of the most important observables: total energies calculated at different temperatures, and radial pair correlation functions at low temperature, in one- and two-dimensional potentials. Recall that the radial pair correlation function is defined in equation 2.12.

It is clear that distinguishable particles gives results consistent with theory for both high and low temperatures. This is true also for bosons, although the pair correlation in 1D is slightly inaccurate at small distances. Fermions however, can be decently simulated at high $T$, but the calculated energies are wrong at low $T$. As for the pair correlations at low $T$, the calculated results are clearly inconsistent.

<table>
<thead>
<tr>
<th>Particle</th>
<th>1D</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distinguishable</td>
<td>$\hbar \omega_0$</td>
<td>$2\hbar \omega_0$</td>
</tr>
<tr>
<td>Boson</td>
<td>$\hbar \omega_0$</td>
<td>$2\hbar \omega_0$</td>
</tr>
<tr>
<td>Fermion</td>
<td>$2\hbar \omega_0$</td>
<td>$3\hbar \omega_0$</td>
</tr>
</tbody>
</table>
4. Two non-interacting particles in a harmonic potential

Figure 4.1: Convergence of the energy estimator with $1/\tau = P/\beta$ in one dimension. The dashed line indicates the theoretical low-temperature limit.

with theory: for example they do not converge to 0 at low distances. Here we see a demonstration of the fermionic sign problem.

To figure out what needs to be done, let us have a look at Figure 4.3, which shows the distribution of the exchange factor $W$ for fermions at low temperature. It is clear that very large negative values are insufficiently sampled. Since the exchange factor spans over several orders of magnitude, it is more appropriate to look at the corresponding distribution of the exponent $\beta(U_0 - U_{oo})$. Let us denote this exponent $s$. First see in Figure 4.4 a that $p(s)$ is poorly sampled for low $s$. Then recall that each configuration is weighted by the exchange factor $W = 1 \pm e^{-s}$, which is large for negative $s$ and comparatively small for positive $s$. If we look at the weighted distribution $(1 \pm e^{-s})p(s)$ in Figure 4.4 b–c, we observe poor sampling at negative $s$ for both bosons and fermions. For fermions this has much more severe consequences, since the thermodynamic averages are computed as a fraction of two small quantities $\langle W_F E \rangle$ and $\langle W_F \rangle$, with $W_F = 1 - e^{-\beta(U_0 - U_{oo})}$. Thus we need to enhance the probability of sampling these rare configurations.

To enhance the sampling, we used Metadynamics with the collective variable $s = \beta(U_0 - U_{oo})$. The physical meaning of this CV is the difference in energy between the connected and the disconnected polymers, measured in units of $k_B T$.

In terms of bead coordinates the CV can be written as

$$s = \frac{Pm}{\hbar^2 \beta} (r_{P,A} - r_{P,B}) \cdot (r_{1,A} - r_{P,B}),$$  \hspace{1cm} (4.1)$$

where the particles have been labelled A and B. The scalar product is taken between two vectors, which are shown as blue arrows in Figure 4.5. When the particles are far away, the blue arrows are parallel so that the CV is positive and large. If the particles are overlapping the blue arrows can be antiparallel, making $s$ negative. If
we do not want to choose which bead pair can exchange, we can symmetrise over
the bead pairs as
\[ s = -\log \left( \frac{1}{P} \sum_{i=1}^{P} \exp \left( \frac{-Pm}{\hbar^2 \beta} \cdot (r_{i,A} - r_{i,B}) \cdot (r_{i+1,A} - r_{i+1,B}) \right) \right) \] (4.2)
again remembering that \( r_{P+1,n} \equiv r_{1,n} \) for \( n \in \{A,B\} \). This formula effectively serves
to pick the bead pair with the lowest value of the scalar product between the blue
arrows. After having checked that both formulas give the same result, we have used
eq (4.1) since it is faster to compute than eq. (4.2).

Use of enhanced sampling gives distributions shown in Figure 4.3–4.4 together
with the non-enhanced distributions. It can clearly be seen that the enhanced
distributions are smoother than the non-biased distributions and are well characterised
in a much wider range.

Figure 4.2: Left: Energy as a function of temperature in one and two dimensions
calculated in non-biased simulations. Theoretical values are shown by dashed
curves, that from top to bottom indicate fermions, distinguishables and bosons,
respectively. Note that fermions deviate from theory at low temperature; other-
wise all energies are consistent with theory. Right: Pair correlation functions
in one and two dimensions calculated in non-biased simulations at \( T = 11.6 \) K.
Solid lines indicate theoretical curves. The discrepancy to theory is particularly
large for fermions. In 2D the coordinate is radial and the functions have been
normalized over the circular shell.
4. Two non-interacting particles in a harmonic potential

Figure 4.3: Distribution of the exchange factor $W$ for two fermions at $\beta = 1 \text{meV}^{-1}$ in 1D (with logarithmic scale). Very large (negative) values are insufficiently sampled without Metadynamics.

Figure 4.4: (a) Free energy surface of $s = \beta(U_O - U_{oo})$ without and with Metadynamics. Right panels: Distribution of the exchange factor plotted against $s$ for bosons (b) and fermions (c). The inset shows a magnification of the low-$s$ region. Note that there is a division into a positive and negative domain for fermions. The simulations were performed at $\beta = 1 \text{meV}^{-1}$ in 1D.
4. Two non-interacting particles in a harmonic potential

Figure 4.5: The CV we used is the difference in energy between the disconnected and the connected diagrams. It can be written as a scalar product between the two blue vectors shown in this sketch. The scalar product is always positive if the particles A and B are well separated (upper polymers), giving small exchange effects, and can be negative if A and B overlap (lower polymers), giving large exchange effects. With Metadynamics we enhance the sampling of the scalar product so that both the upper and the lower types of configurations are sufficiently sampled.

4.3 Results and discussion

After having motivated the use of enhanced sampling and chosen a collective variable in the previous section, we are now ready to study the accuracy of our approach to quantum symmetry. We will in turn present the calculated low-temperature energies, probability densities and pair correlation functions.

4.3.1 Average energy at different temperatures

A comparison between simulations without and with Metadynamics is shown in Figure 4.6. The direct computation method with $\langle WE \rangle / \langle W \rangle$ is reliable down to about 10 K, but also fails when at lower temperatures, because both numerator and denominator become small compared to their statistical errors. However, the bosonic low-temperature energies are consistent with theory with good precision.

Because of this, Bennett’s acceptance ratio method (BAR) was used to calculate the fermionic energies as a sum of the boson energy and the free energy difference between the bose and the fermi states, with equations (3.6)–(3.7). With BAR the energy could be computed at even lower temperatures. Typical free energy surfaces for the disconnected and connected polymers are shown in Figure 4.7. One can see that the curves only partly overlap, which motivates the use of BAR, since then the overlap region is sampled from ‘both directions’ in the $s$-space. Note that also BAR
cannot be used at arbitrarily low temperatures; it only works as long as the average sign is larger than its statistical error, see Figure 4.8.

In addition to calculating the free energy differences at different temperatures, we can fit $\log \langle \text{sign} \rangle$ to a first order polynomial and estimate $\Delta F$ from its slope. This was done in the right panel of Figure 4.8 and the result with BAR is 2.98 meV (the theoretical value is $\hbar \omega_0 = 3$ meV. As a comparison, the result with the exponent average method (still using Metadynamics) is 3.06 meV. The number of points is too low to compute an uncertainty of the fit, but qualitatively we can see that the points for BAR are less spread out from the line than for exponent averaging. As a conclusion, BAR gives a more accurate estimate than the exponent average method.

### 4.3.2 Density functions

Metadynamics also gives significant improvement for the density functions. We expect from theory that at low temperature two bosons are both in the ground state and two fermions fill up the two lowest states, i.e.

\[
\begin{align*}
|p_B(r)| &\approx |\psi_0(r)|^2 + |\psi_1(r)|^2 \\
|p_F(r)| &\approx |\psi_0(r)|^2 + |\psi_1(r)|^2
\end{align*}
\]

Figure 4.6: Metadynamics improves the simulation of fermion energies down to about 10 K. Bennett’s method is more accurate and can be used to reach even lower temperatures, at least in the 1D case. Dashed lines indicate theoretical solutions (from up to down: fermion, distinguishable, boson).
4. Two non-interacting particles in a harmonic potential

\[ F(s) = -\log p(s) \]

Figure 4.7: Free energy surfaces of the CV \( s = \beta(U_O - U_{oo}) \) for \( \beta = 1\,\text{meV}^{-1} \) in 1D. The FES of the connected polymer is almost (but not completely) a mirrored version of the FES of the disconnected polymers. The limited overlap motivates the use of Bennett’s acceptance ratio method.

Figure 4.8: Left panel: The average fermionic exchange factor as well as the average sign approaches 0 with decreasing temperature. EA (Exponent average method) was computed as \( W_F/W_B \) and BAR (Bennett’s acceptance ratio method) with eq. (3.5). When the average sign becomes smaller than its uncertainty, Bennett’s method cannot be used anymore. Right panel: if \( \log(\text{sign}) \) is fitted to a line in \( \beta \), the slope is an estimation of \( -\Delta F \). All simulations were done in 1D and Metadynamics was used for \( \beta \geq 0.5\,\text{meV}^{-1} \).
Two non-interacting particles in a harmonic potential

where in 1D

\[
\begin{align*}
|\psi_0(x)|^2 &\propto e^{-m\omega_0 x^2/\hbar} \\
|\psi_1(x)|^2 &\propto x^2 e^{-m\omega_0 x^2/\hbar}.
\end{align*}
\] (4.3)

Note that the first excited state has a node at \( x = 0 \). We can obtain the density of the first excited single-particle state from our simulations through

\[ |\psi_1(r)|^2 = p_F(r) - \frac{1}{2} p_B(r). \]

We will call this state ‘partial’ rather than the excited state, in order not to confuse it with an excited two-particle state. The densities for bosons, fermions and the partial are shown in Figure 4.9 for the 1D potential and Figure 4.10 for the 2D potential. The partial has a node in the center, as expected from equation 4.3. A gaussian filter has been applied to Figure 4.10 to eliminate noise, as well as to the other 2D plots in this thesis.

![Figure 4.9: Normalised density function for two particles in a 1D harmonic potential with \( \hbar \omega_0 = 3 \text{meV} \) at inverse temperature \( \beta = 1 \text{meV}^{-1} \). The curve ‘partial’ denotes the density of the first excited state, computed from \( p_F(r) - \frac{1}{2} p_B(r) \). Dashed curves indicates theoretical (zero-temperature) densities.](image)

4.3.3 Pair correlation functions

Lastly we take a look at the pair correlation functions (defined in equation (2.12) and (2.13)). Theoretically we expect bosons to have an increased probability of being found close to each other compared to distinguishable particles, since they form a Bose-Einstein condensate at low \( T \), and that fermions have zero probability of being found at the same spatial coordinate, because of the Pauli principle. Analytical expressions for the pair correlation functions are derived in Appendix C.2.

Calculated results with and without Metadynamics are shown in Figure 4.11. In particular, the fermionic pair correlation at zero distance reaches zero, \( g(0) = 0 \), when simulated with Metadynamics.
4. Two non-interacting particles in a harmonic potential

Figure 4.10: Probability density for two particles in a 2D harmonic oscillator with $\hbar \omega_0 = 3 \text{meV}$ at inverse temperature $\beta = 1 \text{meV}^{-1}$. "Partial" (right panels) denote the density of the first excited state, computed from the left and the middle panels. Note that there is a node in the center for the first excited state. Colouring is in arbitrary units and has been rescaled by 0.6 for bosons and 2.5 for partial in order to fit into the same scale.

Also in two dimensions the fermionic pair correlation approaches 0 much clearer than without Metadynamics. See as well Figure 4.11 where the pair correlation has been plotted as a function of two coordinates (equation (2.13)); also in this case the pair correlation approaches zero in the center.

Figure 4.11: Pair correlation functions for a harmonic oscillator with $\hbar \omega_0 = 3 \text{meV}$ at $\beta = 1 \text{meV}^{-1}$ ($T = 11.6 \text{K}$), calculated with Metadynamics. Solid lines indicate theoretical curves. In 2D the coordinate is radial and the functions have been normalized over the circular shell. Units are arbitrary.
4. Two non-interacting particles in a harmonic potential

**Figure 4.12:** Two-dimensional pair correlation function obtained with Metadynamics, for a harmonic potential with $\hbar \omega_0 = 3$ meV at $\beta = 1$ meV$^{-1}$. Note the clear ring shape in the fermion case.

### 4.4 Choice of collective variable

We have seen that enhancement of the CV $s = \beta(U_O - U_{oo})$ does significantly improve the results. It is also the natural variable to enhance when using the BAR method. It has however a fundamental problem: the Metadynamics bias takes very long time to converge. In fact, for many simulations in this thesis, we could not converge the bias completely. For example for the simulation of the disconnected polymers at $\beta = 1$ meV$^{-1}$, the Gaussian heights decayed as in Figure 4.13. We see that high Gaussians continue to be deposited also late in the simulation. These are however for very high or very low $s$, where the weight has zero contribution (see Figure 4.3). We made however sure that the bias converged within the region with non-negligible weight contribution.

The convergence could be improved by using a higher Gaussian height scale $H_0$, but this would on the other hand lead to noisy distribution functions. Another strategy could be to increase the Gaussian width $\sigma$, but then fine details of the FES might no longer be resolved, and the theory of Metadynamics is only strictly proven in the limit of small (delta-like) Gaussians [7].

Let us ask ourselves why the bias takes so long time to converge with the current CV? First, from Figure 4.7 we see that the disconnected polymers have a much steeper FES towards negative $s$ than the connected. This means that in order to reach out deep enough into the negative $s$-region (from the right panel of Figure 4.3 we can estimate this to be $s \geq -20$), we need to fill up the FES to a high level, so that a high bias factor $\gamma$ is necessary. A high $\gamma$ implies a long convergence time.

Second, note that we enhance both positive and negative values of the exponent $s = \beta(U_O - U_{oo})$. In the simulation with the disconnected polymers, the exchange factor $1 \pm e^{-s}$ vanishes for large positive $s$, but the simulation is spending more time
4. Two non-interacting particles in a harmonic potential

![Diagrams](image)

Figure 4.13: The bias does not converge completely: even though most deposited Gaussians have a small height, there are still Gaussians at late times with almost maximum height. The simulation was done with $\sigma = 4$ and $\gamma = 4$.

on enhancing positive $s$ than negative $s$ (see Figure 4.7). For the connected polymers, the same reasoning applies for $-s$. In this way, a large part of the simulation is spent on enhancing unimportant parts of the CV-space.

We are now ready to ask if there is a better choice of CV, which would solve one or more of the problems mentioned above. We will speak about the CV used so far as the energy-difference CV, $s = \beta(U_O - U_\infty)$. What we actually want to enhance is the sampling of the weight $W$, but directly using $W$ as a CV does not work for two reasons: first, it spans over many orders of magnitude and is sharply peaked around 1, meaning that it is difficult to choose a good $\sigma$; second, it is very sensitive to small changes in the coordinate positions and thereby leads to very large forces. This motivated us to use the exponent $\beta(U_O - U_\infty) = -\log(W - 1)$ (for the disconnected polymers), but it might also be possible to use the logarithm directly, $s = \log W$. However, for fermions $W$ can be close to 0 or even negative. If we use $\log |W|$ we remove the negative arguments of the logarithm, but the divergence at 0 remains. Some authors (for example [17]) interpret $-\frac{1}{\beta} \log |W|$ as an effective potential, so that this approach is somewhat analogous to using the potential energy as a CV as in Ref. [42].

Some attempts were made to regularise the divergence with $\log(|W| + \eta)$ for a small constant $\eta$, but these have not been successful. A fundamental problem with this CV is that it is not separating the two domains. The transition from the positive to negative domain will go from low $s$ to high $s$ and then back to low $s$. We might also introduce some error through the regularisation $\eta$, but without this the domain barrier becomes infinitely high.

A slightly different CV following the same idea is $\log(W_+ + W_-)$, which is always positive. For two particles simulated from the disconnected ensemble this is $s = \log \left( 1 + e^{-\beta \Delta U} \right)$. The unbiased distribution of this CV is sharply peaked around 0 and has a second maximum close by. Metadynamics can give a smoother sam-
Two non-interacting particles in a harmonic potential

pling distribution, but the calculated energies are incorrect. At the temperature $T = 23.2\,\text{K}$, slightly above the quantum regime (by which we mean $T \lesssim 15\,\text{K}$), the simulation without Metadynamics gives $E_F = (2.36 \pm 0.02)\hbar\omega_0$ and with Metadynamics $(2.20 \pm 0.01)\hbar\omega_0$ (the exact result is $2.36\hbar\omega_0$). This error might occur because it is hard to choose a $\sigma$ which is both small enough to resolve the peaks and large enough to fill up the FES up to $s \approx 10$ within a reasonable time.

Another choice of CV which could be easily generalised to many particles is the expression for the average sign

$$s_{\text{sign}} = \frac{W_+ - W_-}{W_+ + W_-}.$$  

This is physically intuitive and we are able to distinguish between the two domains for two particles. However, it is not able to distinguish between weights of the same sign but different magnitude, for example $W = -100$ and $W = -1000$ for fermions. This makes it rather useless since it does not improve the sampling of the tails of the distribution $p(W)$. Instead, we would like to enhance a function of the sign which better resolves values close to $s_{\text{sign}} = \pm 1$. A natural choice of such a function would be $\tanh^{-1}(s_{\text{sign}})$. A short algebraic manipulation shows that this is in fact the same as the energy-difference CV (up to an unimportant factor 2). Thus a possible generalisation of the energy-difference CV to several particles is

$$s = \tanh^{-1} \frac{W_+ - W_-}{W_+ + W_-},$$

which could be investigated further in future studies.
4. Two non-interacting particles in a harmonic potential
Chapter 5

Two electrons in a quantum dot

In the previous chapter we have investigated systems of noninteracting particles in a harmonic potential. Now we shall add a Coulomb interaction to our particles to provide a model for electrons in parabolic quantum dots. The usefulness of this model will be demonstrated by comparison with experimental data. Then we will investigate the influence on changing different parameters characterising the quantum dot.

5.1 Quantum dot model

A quantum dot (QD) is an isolated island of electrons in a semiconductor, with a lateral size small enough to make its quantum mechanical energy levels observable \[43\]. Quantum dots have been investigated experimentally and theoretically for several decades. Their energy spectra remind in many aspects those of atoms and they are therefore sometimes called artificial atoms.

A common way to fabricate a quantum dot is to use heterostructures: different materials are layered on top of each other, forming a two-dimensional electron gas (2DEG) at their interface. This electron gas can be locally depleted if a negative potential is applied to a nearby conductor. By adding a conducting structure called a split gate the 2DEG can be limited to a certain region, for example a circular disc shape, see Figure 5.1 for a side view. Two further electrodes, called plunger gates, can be used to tune the number of electrons in the quantum dot and to perform various measurements. We will not go into further details on the experimental techniques used in the fabrication of quantum dots or in their measurements, but refer the interested reader to various work in literature \[11\][3][44].

Many quantum dots can be modelled as electrons confined in a parabolic potential. The difference to the system in the previous chapter is the inclusion of the coulomb interaction between the electrons,

\[ V(r_1,r_2) = \gamma_{\text{screen}} \frac{e^2}{\kappa |r_1 - r_2|}, \]
where $e$ is the electronic charge, $\kappa$ is the dielectric constant of the material and $\gamma_{\text{screen}}$ is a dimensionless screening factor. This introduces a new energy scale, the interaction energy $e^2/\kappa l_0$, in addition to the confinement energy scale $\hbar \omega_0$ and the thermal energy scale $k_B T$. Here $l_0 \equiv \sqrt{\hbar/m^* \omega_0}$ is a typical length scale of the system. The ratio between the interaction energy and the confinement energy is called the Wigner parameter

$$R_W = \gamma_{\text{screen}} \frac{e^2}{\kappa l_0 \hbar \omega_0}. \quad (5.1)$$

The value $R_W = 0$ corresponds to ideal particles, as in the previous chapter, and $R_W \gg 0$ means strong Coulomb interaction.

It is now important to note that by mass we now mean the effective mass $m^*$ in the material rather than the bare electron mass. This is a material parameter just like the dielectric constant $\kappa$. For example, for GaAs we have $m^* = 0.067 m_e$ and $\kappa / 4\pi \epsilon_0 = 12.9$ [43]. The interaction is also screened by experimental contacts and by effects originating from the finite width of the third dimension of the dot [45]. These effects are included the screening constant $\gamma_{\text{screen}} < 1$, which reduces the Wigner parameter. Apart from screening, we will not explicitly consider the third dimension.

We will also study confining potentials that are elliptic rather than circular:

$$V(x,y) = \frac{1}{2} m^*(\omega_x^2 x^2 + \omega_y^2 y^2).$$

The degree of anisotropy will be measured by the parameter $\eta \equiv \omega_y/\omega_x$. The effective confinement energy scale of an elliptic dot is defined as $\hbar \omega_0 = \hbar \sqrt{(\omega_x^2 + \omega_y^2)/2}$.

In our model we will assume that the quantum dot is well isolated from the environment so that the number of electrons is constant. Magnetic field, as well as spin-orbit coupling, will not be considered in this work.
5. Two electrons in a quantum dot

5.2 Spin

So far we have neglected the intrinsic spin of the particles. To provide a realistic description of few-electron quantum dots we need to include the electron spin $S = 1/2$. The spin can have projection $S_z = \pm 1/2$ along an axis $z$, which we take to be along the thickness of the quantum dot. The total wavefunction of an electron system can be written as a product of the spatial wavefunction $\varphi$ and a spin wavefunction $\chi$. In the case of two particles

$$\Psi(r_1,\sigma_1; r_2,\sigma_2) = \varphi(r_1,r_2)\chi(\sigma_1,\sigma_2),$$

where $\sigma_i = \uparrow$ or $\downarrow$ is another notation for the spin projection $s_z$. In order for the total wavefunction to be antisymmetric, we can either let $\varphi$ be symmetric and $\chi$ antisymmetric, or let $\varphi$ be antisymmetric and $\chi$ symmetric. A full analysis yields the symmetric spin function

$$\chi(\sigma_1,\sigma_2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle),$$

and total spin $S_{\text{tot}} = 0$. This is called the singlet state. The antisymmetric spin function can be realised in three ways:

$$\chi(\sigma_1,\sigma_2) = \begin{cases} 
|\uparrow\downarrow\rangle \\
\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\
|\downarrow\downarrow\rangle 
\end{cases},$$

with total spin $S_{\text{tot}} = 1$. These are called the triplet states. The triplet states have spin projection $S_z = +1/2, 0, -1/2$. We assume for simplicity that the Hamiltonian is spin-independent. If also the spatial part of the wavefunction is radially symmetric, which is the case in circular dots, the triplet states are degenerate. For elliptic dots however, the lack of radial symmetry lifts this degeneracy.

The singlet state has a symmetric spatial wavefunction and can therefore be simulated as spinless bosons, as done in in the previous chapter; the only difference is the Coulomb interaction. By the same reasoning, the triplet state can be simulated in the same way as spinless fermions. The ground state will always be the singlet state. The triplet state energy is the sum of the two lowest singlet-particle energies plus an interaction term. Note that in the low temperature limit we only get the singlet and triplet states with the lowest energy in our PIMD simulations; the simulation of specific excited states is more complicated (one method is given in Ref. [22]).

5.3 Results and discussion

We will now investigate quantum dots with $N = 2$ electrons using PIMD simulations with Metadynamics. Two electrons are enough to observe quantum exchange and the spin combinatorics is easier than for higher electron numbers. As mentioned
in the previous section, we can obtain the singlet state by simulating two spinless electrons with Bose symmetry, and Fermi symmetry for the triplet states. We will start with a set of parameters for which we can compare with previous experimental and theoretical results. Then we will investigate the impact of changing, in turn, the interaction strength, the anisotropy and the temperature. The simulation parameters used in this section are given in Appendix D.5, unless they are already stated in the main text.

5.3.1 Comparison with experiment

In a study from 2006 [45], Ellenberger et al. investigated the excitation spectrum of two electrons in an elliptic quantum dot both experimentally and numerically with exact diagonalisation, and found that the theoretical model agrees well with experiments for the lowest energy levels. The experimental device, consisting of Ga[Al]As (an alloy between GaAs and AlAs with varying aluminium concentration), was designed to have a small effective Landé factor for electrons, so that the spin-orbit coupling could be ignored. The material constants were estimated to be $m^* = 0.07m_e$ and $\kappa = 12.5$. In their simulations, the authors obtained results consistent with theory for $\hbar \omega_x = 4.23\text{meV}$, $\hbar \omega_y = 5.84\text{meV}$ and $\gamma_{\text{screen}} = 0.862$. This means that the Wigner parameter was $R_W = 1.34$ and the anisotropy $\eta = 1.38$. The temperature was below 300 mK, which is in the deep quantum regime.

The system described above was used as a benchmark for Metadynamics-enhanced PIMD simulations. A quantum dot was simulated with the same parameter settings, except for $\gamma_{\text{screen}}$ which was allowed to vary slightly (it was noted in Ref. [45] that this did not influence their fit). Figure 5.3 shows the calculated low-temperature energies for $\gamma_{\text{screen}} = 0.9$ ($R_W = 1.40$). It is clear that Bennet’s method gives a much more robust estimate of the singlet-triplet energy gap than direct simulation of the triplet energy. The calculated energies are slightly below the ones in Ref. [45], although the uncertainties of the literature values are not stated, making it difficult to quantify how large the difference is. If we assume that the uncertainty of the lit-
Figure 5.3: Singlet and triplet energies for a wide temperature range. Inset: magnification of the low temperature regime. Energies below 20 K are calculated with Metadynamics-enhanced simulations. Experimental values from [45] are indicated with circles. The simulations were performed with \( \tau = 0.067 \text{ meV}^{-1} \), corresponding to \( P = 15 \) beads at \( T = 11.6 \text{ K} \).

Figure 5.3 also shows that the temperature \( T = 11.6 \text{ K} \) (\( \beta = 1.0 \text{ meV}^{-1} \)) is low enough to be in the quantum regime. At this temperature, the density distribution of the electrons was simulated, see Figure 5.4. In contrast to Figure 4.10, the partial state has a nodal plane instead of a nodal point, because of the anisotropy. This will be investigated further in section 5.3.3.

The pair correlation function was calculated at the same temperature and is shown together with its projection onto the axes of the elliptic potential in Figure 5.5. To demonstrate the impact of the enhanced sampling, the corresponding simulation without Metadynamics is shown in the same figure. The electrons have zero probability of being at the same spatial position also for the singlet state, because of the Coulomb repulsion. The central minimum is however much wider for the triplet than for the singlet state. Note that the maximum of the projected pair correlation is further out in the \( x \)-than in the \( y \)-direction because the repulsion compared to the confinement is stronger.

### 5.3.2 Exchange effects for different Wigner parameters

As was mentioned in section 5.1, the two most important energy scales in a parabolic quantum dot are the Coulomb interaction energy and the confinement energy. A
5. Two electrons in a quantum dot

5.3.2 Impact of anisotropy

As was seen in section 5.3.1 the anisotropy of the quantum dot caused the partial state (the first excited single-particle state) to have a nodal plane rather than a nodal point (compare Figure 5.4 and 4.10). Another simulation was done in an even higher anisotropy $\eta \equiv \omega_y/\omega_x = 3.0$, keeping the effective confinement energy scale $\hbar \omega_0 = \hbar \sqrt{(\omega_x^2 + \omega_y^2)/2}$ constant. The density distribution of this quantum dot is shown in Figure 5.8. It is possible to see a clear separation of the electrons. The separation is even clearer in the pair correlation function in Figure 5.8. If the pair correlation is projected onto the axes of the ellipsis, one observes that the singlet...
Figure 5.5: Pair correlation for two electrons in a parabolic quantum dot with anisotropy $\eta = 1.38$, without Metadynamics (upper panels) and with Metadynamics (middle and lower panels). The lower panel shows the projection onto the axes of the elliptic potential. Note that the pair correlation does not go to zero for $r_i = 0$ because it is a projection, $g(x) = \int dy g(x,y)$. 

5. Two electrons in a quantum dot
and triplet states look the same in the $y$-direction but are still different in the $x$-direction. One could say that the electrons are effectively distinguishable in the $y$-direction and effectively indistinguishable in the $x$-direction.

Having investigated the case of high anisotropy, we now consider the opposite case: what happens when we go to low anisotropies? We have already seen that at $\eta = 1$ the 2D-density plot of the partial state has a nodal point but for $\eta = 1.38$ it has a nodal plane. If one could continuously change $\eta$ towards 1, would then the transition from nodal plane to nodal point be smooth or abrupt? In Figure 5.10 we show density plots for $\eta = 1.2$ and $\eta = 1.1$. The transition look more smooth than abrupt. This is a finite-temperature effect: the ellipticity causes the triplet energy level in Figure 5.2 to split up into two levels $T^+$ and $T^-$, so that the $E_{ST}$ we measure is the energy difference between $S$ and the lowest $T$ state, that we call $T^-$. The two levels correspond to a single-electron excitation along the two different half-axes of the ellipsis. When the ellipsis becomes more circular, the energy levels $T^+$ and $T^-$ become closer and closer in energy. At exactly zero temperature the system would be stuck in the lowest energy level, so that the transition from nodal plane to nodal point would be abrupt. Since we are working at a low but finite temperature, the partial state we measure will always be a mix between $T^-$ and $T^+$, and the closer they become in energy the more circular the partial state will look like. Thus we observe a smooth rather than a sharp transition.
5. Two electrons in a quantum dot

Figure 5.7: Pair correlation function for circular dots with different interaction strength. A higher interaction strength causes the particles to be on average on a higher distance.
5. Two electrons in a quantum dot

Figure 5.8: Density distribution for a quantum dot with anisotropy $\eta = 3.0$ at inverse temperature $\beta = 1\text{ meV}^{-1}$. The confinement energies are $\hbar\omega_x = 2.28\text{ meV}$, $\hbar\omega_y = 6.84\text{ meV}$ and the Wigner parameter $R_W = 1.4$. 

Figure 5.8: Density distribution for a quantum dot with anisotropy $\eta = 3.0$ at inverse temperature $\beta = 1\text{ meV}^{-1}$. The confinement energies are $\hbar\omega_x = 2.28\text{ meV}$, $\hbar\omega_y = 6.84\text{ meV}$ and the Wigner parameter $R_W = 1.4$. 

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Figure 5.9: Pair correlation function for a quantum dot with the same parameters as in Figure 5.8. The particles are more separated than for $\eta = 1.38$ in Figure 5.5. The projections onto the axes of the elliptic potential (lower panel) show that the particles are effectively distinguishable in the $y$-direction (almost no difference between singlet and triplet) and effectively indistinguishable in the $x$-direction (singlet and triplet are clearly different).
Figure 5.10: Density plots for slightly elliptic dots. The transition between a nodal plane and a nodal point for the partial states is smooth rather than abrupt because of the finite temperature (also compare with Figures 5.4 and 4.10).
Chapter 6

Conclusions

In this work we have treated the fermionic sign problem as a sampling problem and investigated how this sampling problem can be addressed by enhanced sampling techniques. We have shown that Metadynamics can be used to significantly improve the sampling of PIMD simulations of two particles in a parabolic potential. The method can be used to calculate various properties of parabolic quantum dots with two electrons and the results are consistent with experiment and other theoretical methods. In particular we have studied the influence of temperature, ratio between interaction strength and confinement energy, and ellipticity. Further, we have shown that we can calculate fermion energies at low temperatures by approximating the energy gap between bosons and fermions with their free energy difference, and that this approach is more robust than using pure Metadynamics.

The method is so far limited to two-electron systems. It could potentially be generalised to more electrons by using a suitable CV.

6.1 Future prospects

Here we will discuss other ideas which would be interesting to investigate, but which have not been tried in this project.

**Sampling methods** First, note that we are by no means enforced to keep the polymers in the same diagram during the full simulation. For example in the Worm algorithm [49], one also performs permutation switches. A possible perspective is to add additional Monte Carlo steps which try such permutation switches. With the help of Metadynamics we should then be able to recover a FES which follows the lowest curves in Figure 4.7 (up to a global constant).

Another approach would be to use a *replica exchange method* [50,51] to improve the sampling of the overlap regions between different diagrams. In this approach all diagrams would be simulated in parallel, with their Hamiltonians differing only in the bead connections. The configuration of a simulation of diagram $G$ can then be switched to a configuration of a parallel simulation of diagram $G'$ with probability
6. Conclusions

\[
\min \left(1, e^{-\beta \Delta}\right),
\]

\[
\Delta = [U_G(q_G) - U_G'(q_G)] - [U_G(q_G) - U_G'(q_G')].
\]

This approach could improve the sampling of the overlap regions but requires parallelisation of the code.

Also note that the shape of the FES in Figure 4.1 is relatively simple: it has a cusp close to \( s = 0 \) and quickly converges to two straight lines for high and low \( s \). A general approach to fill this FES with a bias would be to use variationally enhanced sampling \[52,53\]. In this method, one introduces a functional of the bias, which is constructed such that the bias that minimises the functional is directly related to the free energy surface. The bias is then written as a sum of basis functions with coefficients that are varied to minimise the functional. Because of the simple shape of our \( F(s) \) it should be possible to construct a bias from a relatively low number of (suitably chosen) basis functions, meaning that this method would converge faster than Metadynamics.

If we limit ourselves to energy calculations, an alternative possibility is to use BAR pairwise on the different diagrams to calculate the free energy difference between fermionic and bosonic particles. For example for three particles

\[
e^{-\beta(F_F - F_B)} = \frac{1 - 3e^{-\beta(F_{1,1,0} - F_{3,0,0})} + 2e^{-\beta(F_{0,0,1} - F_{3,0,0})}}{1 + 3e^{-\beta(F_{1,1,0} - F_{3,0,0})} + 2e^{-\beta(F_{0,0,1} - F_{3,0,0})}},
\]

where \( F_{3,0,0} \) is the free energy of disconnected polymers, \( F_{1,1,0} \) the free energy of the diagram where two polymers are connected together, and \( F_{0,0,1} \) the free energy of the diagram where all three polymers are connected. In this case there are two free energy differences needed to be computed, \( F_{1,1,0} - F_{3,0,0} \) and \( F_{0,0,1} - F_{3,0,0} \). Each difference can be obtained with BAR, collecting data from both ensembles and enhancing the corresponding energy difference between two ensembles with Metadynamics. This means that in total four runs need to be performed. One can use the results not only to obtain the free energy difference between fermions and bosons, but also between states with different spin, since they differ only by the coefficients of the diagrams. Also note that for non-interacting particles \( F_{1,1,0} - F_{3,0,0} = F_O - F_{oo} \) since the contribution from an extra single polymer has no influence, so that one of the differences has already been calculated. Alternatively to using pairwise BAR, one can use a multistate BAR method \[54\] to calculate all free energies simultaneously up to an additive constant, which could be advantageous for high particle numbers.

Applications Since the enhanced sampling methods are independent on the external potential, it should be possible to use more complex potentials. Our only condition is that it should be differentiable to allow for the use of the virial energy estimator. In particular, it would be interesting to study two electrons in a double-well, which serves as a model of two quantum dots close to each other. Such coupled
quantum dots have been proposed as an implementation of a quantum gate in a quantum computer \cite{9}. Each quantum dot is then a two-level system that can be used as a quantum bit. A possible approach to simulate coupled quantum dots with our method would be to use one CV for the exchange effects, as in this thesis, and a second CV to enhance the tunnelling probability between the wells.

Lastly it would be interesting to include a magnetic field in the method, since many experiments study the influence of magnetic field on the singlet–triplet energy gap. The magnetic field is also used when performing operations on quantum bits. In PIMD a magnetic field would introduce complex phases, modifying the estimators in a non-trivial way. This would make the implementation more involved but should in principle be possible to do without major modifications of the enhanced sampling methods. The generalisation of $s$ would be complex but this can be handled as a two-dimensional CV.
6. Conclusions
Bibliography


Bibliography


Appendix A

Symmetrisation of the propagator

In section 2.2 we stated that a fully (anti)symmetrised propagator gives the same statistics as the propagator where we have only (anti)symmetrised after one imaginary time slice. We will motivate this only for two particles. Each bead exchange causes the two polymers either to connect or disconnect, so that the partition function must be on the form $Z_{B/F} = c_1 Z_F^P + c_2 Z_2 P$. If we (anti)symmetrise at all imaginary time slices, the right-hand side of equation (2.7) is a product of determinants of the kind

$$
\begin{vmatrix}
\rho_D(r_{i,1},r_{i+1,1};\tau) & \rho_D(r_{i,1},r_{i+1,2};\tau) \\
\rho_D(r_{i,2},r_{i+1,1};\tau) & \rho_D(r_{i,2},r_{i+1,2};\tau)
\end{vmatrix}
\equiv
\begin{vmatrix}
\rho_{Di}(1,1) & \rho_{Di}(1,2) \\
\rho_{Di}(2,1) & \rho_{Di}(2,2)
\end{vmatrix}.
$$

When this product is expanded, all terms either contribute to $c_1$ or $c_2$. Each factor $\rho_{Di}(1,2)\rho_{Di}(2,1)$ corresponds to a switch between the disconnected and the connected topology. All terms that contribute to $c_1$ thus contain an even number of such factors. The number of ways an even number of factors can be chosen is

$$
\binom{P}{0} + \binom{P}{2} + \cdots = c_1
$$

and the number of ways an odd number of factors can be chosen is

$$
\binom{P}{1} + \binom{P}{3} + \cdots = c_2.
$$

Then we must have $c_1 = c_2$ since

$$
c_1 - c_2 = \binom{P}{0} - \binom{P}{1} + \binom{P}{2} - \cdots = (1 - 1)^P = 0.
$$

An overall numerical prefactor to the partition function is irrelevant. Thus this is equivalent to $Z_{B/F} = Z_F^P \pm Z_2 P$, i.e. to only (anti)symmetrise at one imaginary time slice.

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Appendix B

Derivation of the virial estimator

Here we will show how to express the thermodynamic energy estimator (equation (2.10) in section 2.3) as a virial estimator, which is computationally more convenient to use. For simplicity we begin with the single particle case and then generalise it to several particles.

One particle. The main problem is the kinetic part

\[ E_{\text{kin}} = m \frac{\partial Z}{\partial m} = \left\langle \frac{P d}{2 \beta} - \frac{m P}{2 \hbar^2 \beta^2} \sum_i (r_{i+1} - r_i)^2 \right\rangle, \]  

(B.1)

which is a difference between two large quantities for large \( P \), with a variance which also grows with \( P \). Using the notation \( V_{\text{spring}} = \frac{m P}{2 \hbar^2 \beta^2} \sum_i (r_{i+1} - r_i)^2 \) and \( U = V_{\text{spring}} + \frac{1}{P} \sum_i \phi(r) \), this can be written

\[ E_{\text{kin}} = \frac{\int \text{d}r^P \left( \frac{P d}{2 \beta} - V_{\text{spring}} \right) e^{-\beta U}}{\int \text{d}r^P e^{-\beta U}}, \]

where \( \text{d}r^P \) is a shorter notation for \( \text{d}r_1 \text{d}r_2 \cdots \text{d}r_P \). We will now use partial integration to cast this to a form which contains a sum rather than a difference. Note that there are \( Pd \) coordinates, so that the first term can be written

\[ \frac{P d}{2 \beta} = \frac{\int \text{d}r^P \frac{1}{2 \beta} \sum_i \frac{\partial r_i}{\partial r} e^{-\beta U}}{\int \text{d}r^P e^{-\beta U}} = \frac{\int \text{d}r^P \frac{1}{2} \sum_i r_i \cdot \frac{\partial U}{\partial r_i} e^{-\beta U}}{\int \text{d}r^P e^{-\beta U}} = \left\langle \frac{1}{2} \sum_i r_i \cdot \frac{\partial U}{\partial r_i} \right\rangle. \]
We could also do the same for all but one coordinate; a robust choice is the centroid coordinate \( \bar{r} = \frac{1}{P} \sum_j r_j \). Since

\[
\sum_i \frac{\partial}{\partial r_i} \left( r_i - \frac{1}{P} \sum_j r_j \right) = (P - 1)d
\]

we have

\[
\frac{(P - 1)d}{2\beta} = \left\langle \frac{1}{2} \sum_i (r_i - \bar{r}) \cdot \frac{\partial U}{\partial r_i} \right\rangle. \tag{B.2}
\]

Now let us examine the derivative \( \frac{\partial}{\partial r_i} U = \frac{\partial}{\partial r_i} (V_{\text{spring}} + \frac{1}{P} \sum_j \phi(r)) \). The spring term gives

\[
\frac{\partial V_{\text{spring}}}{\partial r_i} = \frac{mP}{2\hbar^2 \beta^2} \frac{\partial}{\partial r_i} \sum_j (r_{j+1} - r_j)^2 = \frac{mP}{\hbar^2 \beta^2} (2r_i - r_{i+1} - r_{i-1}).
\]

If we take the scalar product and sum over \( i \) as in equation (B.2), we can use the cyclicity of the index to write

\[
\left\langle \frac{1}{2} \sum_i (r_i - \bar{r}) \cdot \frac{\partial V_{\text{spring}}}{\partial r_i} \right\rangle = \left\langle \frac{1}{2} \frac{mP}{\hbar^2 \beta^2} \sum_i (r_i - \bar{r}) \cdot (2r_i - r_{i+1} - r_{i-1}) \right\rangle
\]

\[
= \left\langle \frac{mP}{2\hbar^2 \beta^2} \left( \sum_i (r_{i+1}^2 + r_i^2 - 2r_{i+1}r_i) - \bar{r} \cdot \sum_i (2r_i - r_{i+1} - r_{i-1}) \right) \right\rangle
\]

\[
= \left\langle \frac{mP}{2\hbar^2 \beta^2} \sum_i (r_{i+1} - r_i)^2 \right\rangle = \langle V_{\text{spring}} \rangle.
\]

Now note that the same term is subtracted in equation (B.1). Thus the spring energies completely cancel out and we end up with the expression

\[
E_{\text{kin}} = \left\langle \frac{d}{2\beta} + \frac{1}{2P} \sum_i (r_i - \bar{r}) \cdot \frac{\partial \phi(r_i)}{\partial r_i} \right\rangle.
\]

If we sum this with the potential energy estimator, we get the virial estimator in equation (2.11).

**Two particles.** In the case of two particles, the spring part of the kinetic energy estimator depends on the connections of the polymers. With

\[
Z_{B/F} = \frac{1}{2} (Z_{oo} \pm Z_O) = \frac{1}{2} \int d\mathbf{r} 2^P (1 \pm e^{-\beta \Delta U}) e^{-\beta U_{oo}}
\]

we have the kinetic energy

\[
\frac{m}{Z_{B/F} \beta} \frac{\partial Z_{B/F}}{\partial m} = \left\langle \left[ \frac{2P \beta d}{2\beta} - \frac{mP}{2\hbar^2 \beta^2} \sum_{i,n} (r_{i+1,n} - r_{i,n})^2 \right] \right\rangle_{oo} \pm \left\langle \left[ \frac{2P \beta d}{2\beta} - \frac{mP}{2\hbar^2 \beta^2} \sum_{i,n} (r_{i+1} - r_i)^2 \right] e^{-\beta \Delta U} \right\rangle_{oo},
\]
B. Derivation of the virial estimator

where subscripts $\infty$ and $O$ denote index periodicity for disconnected and connected polymers, respectively. In the disconnected part we separate out two centroid co-ordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ and proceed as with one particle. In the connected part we separate out a single centroid coordinate $\mathbf{r}_{12}$. The spring term cancels out also in this case. Thus we get

$$E_{\text{kin}} = \left\langle \frac{d}{2\beta} + \left( \frac{d}{2\beta} + \frac{1}{2P} \sum_{i,n} (r_{i,n} - \mathbf{r}_n) \cdot \frac{\partial \phi(r_{i,n})}{r_{i,n}} \right) (1 \pm e^{-\beta \Delta U}) \right\rangle_{\infty}$$

In the same way, one can derive an estimator expressed in quantities in the $O$-ensemble:

$$E_{\text{kin}} = \left\langle \frac{d}{2\beta} e^{+\beta \Delta U} + \left( \frac{d}{2\beta} + \frac{1}{2P} \sum_{i,n} (r_{i,n} - \mathbf{r}_n) \cdot \frac{\partial \phi(r_{i,n})}{r_{i,n}} \right) e^{+\beta \Delta U} \pm 1 \right\rangle_{O}.$$ 

Many particles. The exchange factor, defined in equation (2.9), can generally be written

$$W = \sum_{\mathcal{G}} (\pm 1)^{G_{\mathcal{G}}} c_{\mathcal{G}} e^{-\beta \Delta U_{\mathcal{G}}}.$$ 

Denote the set of polymer chains in the diagram $\mathcal{G}$ by $\{ G_j \}$ and the number of chains by $N(\mathcal{G})$ If the arguments for one and two particles above are repeated, we get

$$E_{\text{kin}} = \left\langle \frac{1}{2P} \sum_{i,n} \frac{\partial \phi(r_{i,n})}{\partial r_{i,n}} W + (\pm 1)^{G_{\mathcal{G}}} c_{\mathcal{G}} \sum_{\mathcal{G}} \left( \frac{N(\mathcal{G})d}{2\beta} - \frac{1}{2P} \sum_{j} \bar{r}_{G_j} \cdot \sum_{n \in G_j} \frac{\partial \phi}{\partial r_{i,n}} \right) e^{-\beta \Delta U_{\mathcal{G}}} \right\rangle_{\mathcal{G}^\prime},$$

where $\Delta U_{\mathcal{G}} \equiv U_{\mathcal{G}} - U_{\mathcal{G}^\prime}$. 

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Appendix C

Analytic solutions

C.1 Energy as a function of temperature

We shall now derive the thermal average of the energy for two non-interacting particles in a harmonic potential, at arbitrary temperature $T$ and imaginary time step $\tau$.

**One particle.** Let us start with the partition function of a single polymer from equation (2.2):

$$Z_P = \left( \frac{mP}{2\pi \hbar^2 \beta} \right)^{Pd/2} \int \prod_{i=1}^{P} \, dr_i \exp \left[ -\beta \sum_{i=1}^{P} \left( \frac{mP}{2\hbar^2 \beta^2} (r_{i+1} - r_i)^2 + \frac{1}{P} V(r_i) \right) \right].$$

In the case of a harmonic potential, $V(r) = \frac{1}{2} m \omega_0 r^2$, the integral can be evaluated analytically. The effective potential is now

$$V_{\text{eff}} = \sum_{i=1}^{P} \left( \frac{Pm}{2\hbar^2 \beta^2} (r_{i+1} - r_i)^2 + \frac{m \omega_0^2}{2P} r_i^2 \right)$$

and the summation over all $i$ makes it possible to exchange $r_i^2$ with $r_{i+1}^2$. Thus we can write the effective potential in terms of new variables $s_i$,

$$V_{\text{eff}} = \sum_{i=1}^{P} a(r_i - br_{i+1})^2 \equiv a \sum_{i=1}^{P} s_i^2.$$

Using the dimensionless variable $x = \hbar \omega_0 \beta / P$, the two parameters $a$ and $b$ can be written

$$a = \frac{m \omega_0^2 / 2P}{x^2 (1 + \frac{x^2}{2} + \frac{x}{2} \sqrt{4 + x^2})}, \quad b = 1 + \frac{x^2}{2} + \frac{x}{2} \sqrt{4 + x^2}.$$
Now we are ready to carry out the integral: 

\[
Z_P = \left( \frac{Pm}{2\pi\hbar^2\beta} \right)^{Pd/2} \int \prod_{i=1}^{P} ds_i \left| \frac{dr}{ds} \right| \exp \left( -\beta a \sum_{i=1}^{P} s_i^2 \right) = \left( \frac{Pm}{2\hbar^2\beta^2a} \right)^{Pd/2} \left| \frac{ds}{dr} \right|^{-1}
\]

\[
= \left( \frac{b^{P/2}}{b^P - 1} \right)^d.
\]

In the quantum limit, \( P \) is large so that \( x \) is small and \( b \approx 1 + x \). Using the standard limit \( \lim_{P \to \infty} (1 + x/P)^P = e^x \), we can write the partition function

\[
Z_P = \left( \frac{e^{\hbar \omega_0 \beta/2}}{e^{\hbar \omega_0 \beta} - 1} \right)^d
\]

This gives the energy

\[
E = -\frac{\partial}{\partial \beta} \log Z_P = \hbar \omega_0 d \left( \frac{1}{2} + \frac{1}{e^{\hbar \omega_0 \beta} - 1} \right).
\]

In the classical limit, \( P \) is finite but \( \hbar \omega_0 \beta \) is small:

\[
Z_P = \lim_{x \to 0} \left( \frac{(1 + x/P)^P}{(1 + x/P)^P - 1} \right)^d = \left( \frac{1}{x} \right)^d = \left( \frac{k_B T}{\hbar \omega_0} \right)^d
\]

and

\[
E = k_B T.
\]

**Two particles** Two distinguishable particles simply give twice the energy of a single particle, since they are non-interacting. If they are two bosons or fermions, the partition function can be written

\[
Z_{B/F} = 1/2 [Z_{oo} \pm Z_{O}] = 1/2 \left[ \left( \frac{b^{P/2}}{b^P - 1} \right)^{2d} \pm \left( \frac{b^P}{b^{2P} - 1} \right)^d \right].
\]

This gives (after some algebra) the energies

\[
E = \hbar \omega_0 d \frac{1}{b} \frac{\partial b}{\partial x} \left. \frac{b^P + 1}{b^P - 1} \pm \frac{b^{2P} + 1}{b^{2P} - 1} \left( \frac{(b^P - 1)^2}{b^{2P} - 1} \right)^d \right|_{x \to 0} \left. 1 \pm \left( \frac{(b^P - 1)^2}{b^{2P} - 1} \right)^d \right|_{x \to 0}
\]

These energies are plotted in Figure 4.2 and 4.6. Note that fermions and bosons approach the distinguishable energies for high \( T \) in two dimensions, but still keep a fixed distance \( \hbar \omega_0 / 2 \) in one dimension. On the other hand, \( \hbar \omega_0 / E \to 0 \) also in one dimension.
C.2 Pair correlation functions at low temperature

Here we will derive analytic expressions for the pair correlation functions of two non-interacting particles in a harmonic potential. We will limit ourselves to low temperatures, so that we can assume that only the lowest two single-particle states contribute. We assume that the bosons are both in the (single-particle) ground state, fermions have one particle in the first excited state, and that distinguishable particles are distributed according to Boltzmann statistics.

One dimension. Let us start with the case of distinguishable particles. The particles are independent, meaning that the two-particle probability density is the product of the two single particle probability densities. A single particle has probability density

\[ p(x) = p_0 e^{-x^2/a^2} \left( 1 + \frac{x^2}{a^2} e^{-\hbar \omega_0 \beta} \right) \]

where \( a \equiv \sqrt{\hbar/m \omega_0} \) and \( p_0 \) is a normalization constant. Thus for two particles we have the density

\[ p(x_1, x_2) \approx \tilde{p}_0 e^{-\left( x_1^2 + x_2^2 \right)/a^2} \left( 1 + 2 \frac{x_1^2 + x_2^2}{a^2} e^{-\hbar \omega_0 \beta} \right) \]

where \( \tilde{p}_0 \) is a new normalization constant. We have discarded a term proportional to \( e^{-2\hbar \omega_0 \beta} \) since the temperature is low. The pair correlation function can now be obtained by fixing the interparticle distance \( r = |x_1 - x_2| \) and integrating out the remaining degree of freedom. The condition of a fixed distance corresponds in 1D to \( x_1 = x_2 \pm r \), so that

\[ g(r) \propto \int dx_2 e^{-\left( (x_2-r)^2 + x_2^2 \right)/a^2} \left( 1 + 2 \frac{(x_2-r)^2 + x_2^2}{a^2} e^{-\hbar \omega_0 \beta} \right) \]

\[ \propto e^{-r^2/2a^2} \left[ 1 + \left( 1 + \frac{r^2}{2a^2} \right) e^{-\hbar \omega_0 \beta} \right] \]

The overall normalization constant can be determined by inferring that the integral over \( r \) should give 1. This gives the function which has been plotted in Figure 4.11.

For bosons and fermions, there are correlations between the particles, so that we have to start from a wavefunction description rather than the single particle densities. At low temperatures the bosonic and fermionic wavefunctions are

\[
\begin{align*}
\Psi_B(x_1, x_2) &= \frac{1}{\sqrt{2}} \left[ \psi_0(x_1)\psi_0(x_2) + \psi_0(x_2)\psi_0(x_1) \right] \\
\Psi_F(x_1, x_2) &= \frac{1}{\sqrt{2}} \left[ \psi_0(x_1)\psi_1(x_2) - \psi_0(x_2)\psi_1(x_1) \right].
\end{align*}
\]

For the boson case, we find both particles in the ground state. The density is

\[ p_B(x_1, x_2) = |\Psi_B(x_1, x_2)|^2 \propto e^{-\left( x_1^2 + x_2^2 \right)/a^2}, \]
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which is the same as for distinguishable particles at zero temperature. This gives the pair correlation

$$g_B(r) \propto e^{-r^2/2a^2}.$$  

For fermions the density is

$$p_F(x_1,x_2) = |\Psi_F(x_1,x_2)|^2 \propto (x_2 - x_1)^2 e^{-[(x_1^2 + x_2^2)/a^2]}$$

so that with the same integration procedure as above we get the last pair correlation function

$$g_F(r) \propto r^2 e^{-r^2/2a^2}.$$  

Two dimensions. Now the analysis become slightly more complicated since there are in total four coordinates but only one constraint $|r_1 - r_2| = r$, meaning that there are three remaining variables to be integrated over. The constraint is non-trivial to implement in cartesian coordinates, so we switch to use a set of coordinates which includes $r$. Let us thus transform to ‘double polar’ coordinates

$$\begin{align*}
x_1 &= r_1 \cos \phi \\
y_1 &= r_1 \sin \phi \\
x_2 &= r_2 \cos(\phi + \theta) = r_1 \cos \phi + r \cos(\phi + \theta) \\
y_2 &= r_2 \sin(\phi + \theta) = r_1 \sin \phi + r \sin(\phi + \theta),
\end{align*}$$

see Figure C.1. The lowest two single-particle states are

$$\phi_0(r,\phi) = N_0 e^{-r^2/a^2}$$

and

$$\phi_1(r,\phi) = N_1 r e^{-r^2/a^2} e^{\pm i\phi}.$$  

For distinguishable particles the density is thus

$$p(r_1,r_2) \propto e^{-(r_1^2 + r_2^2)/a^2} \left(1 + \frac{r_1^2 + r_2^2}{2a^2} e^{-\hbar \omega_0 \beta}\right),$$

where the second term corresponds to a single-particle excitation (which occurs to any of the particles with probability 1/2 each).

The pair correlation function is obtained through

$$g(r) = \int dr_1 dr_2 d\phi d\theta r_1 r_2 p(r_1,r_2) \delta(|r_1 - r_2| - r).$$

Now we need to rewrite the density in terms of the new coordinates. We have

$$r_1^2 + r_2^2 = 2r_1^2 + r^2 + 2r_1 r \cos \theta$$

so that

$$g(r) \propto \int dr_1 d\theta r_1 r e^{-(2r_1^2 + r^2 + 2r_1 r \cos \theta)/a^2} \left(1 + \frac{1}{2a^2} (2r_1^2 + r^2 + 2r_1 r \cos \theta) e^{-\hbar \omega_0 \beta}\right).$$

To continue, we can make use of the Jacobi-Anger expansion

$$e^{iz \cos \theta} = \sum_{n=-\infty}^{\infty} i^n J_n(z) e^{in\theta} = J_0(z) + 2 \sum_{n=1}^{\infty} i^n J_n(z) \cos n\theta$$

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Figure C.1: We switch to a new set of coordinates which includes the relative distance $r$.

where $J_n(\xi)$ is the $n$-th Bessel function of the first kind. Let’s make the substitution $-iz \equiv \xi \equiv 2r_1r/a^2$. Then we get

$$e^{-\xi \cos \theta} = J_0(-i\xi) + 2iJ_1(-i\xi) \cos \theta + \ldots$$

All higher cosines integrate out to zero. The first excited state has a term with $\cos \theta$, which together with the $\cos \theta$ from the exponential contributes $1/2$ (there is also a factor $2\pi$ from all terms which we discard since we can anyway normalise afterwards). Thus we get

$$g(r) \propto \int dr_1 r_1 e^{-(2r_1^2+r^2)/a^2} \left( J_0(-i\xi) + \frac{(2r_1^2 + r^2)J_0(-i\xi) + 2ir_1rJ_1(-i\xi)}{2a^2} e^{-\hbar\omega_0\beta} \right).$$

This last integral was carried out numerically. The situation is slightly easier for bosons and fermions, where we get

$$g_B(r) = \int dr_1 r_1 e^{-(2r_1^2+r^2)/a^2} J_0(-i\xi)$$

and

$$g_F(r) = \int dr_1 r_1 r^3 e^{-(2r_1^2+r^2)/a^2} J_0(-i\xi).$$
Appendix D

Implementation details

D.1 Velocity-Verlet integration

The equations of motion \(2.4\) can be solved by various numerical integration techniques. We have used the Velocity-Verlet algorithm, which is of second global order in the timestep \(\Delta t\). It gives direct access to the velocities, which will make it easier to include the thermostat (this is described in the next section). It is also a symplectic integrator, which means that it conserves the total energy and the total momentum, apart from small fluctuations arising from the finite timestep. Thus it is commonly used in Molecular Dynamics simulations. The algorithm is

\[
\begin{cases}
  v & \leftarrow v - \nabla V(r) \frac{\Delta t}{2m} \\
  r & \leftarrow r + v \Delta t \\
  v & \leftarrow v - \nabla V(r) \frac{\Delta t}{2m}
\end{cases}
\]

The timestep \(\Delta t\) was chosen in the following way: a trajectory of one of the polymer beads was sampled with a high sampling frequency. This trajectory was Fourier transformed and the highest relevant frequency mode was identified. As an initial timestep we used \(1/20\) of the period of the highest frequency mode of the polymer coupled to an external potential; however we obtained a much better accuracy when further reducing the timestep with a factor of 10. The final timesteps used were 5 fs for the noninteracting particles and 1 fs for the quantum dot (where the effective mass was smaller).

As a check of the algorithm, we show the frequency spectrum of one bead in an unconnected and disconnected polymer in Figure D.1. From the coupled equations of motion consisting of forces from the springs and the external harmonic potential, one can derive the following eigenmodes:

\[
\Omega_l = \frac{\omega_0}{\sqrt{P}} \sqrt{1 + \left(\frac{2P}{\hbar \omega_0 \beta}\right)^2 \sin^2 \left(\frac{l\pi}{P}\right)}, \quad l = 0, 1, \ldots, P - 1.
\]

We see that the measured spectrum agrees with the theory.
D. Implementation details

Figure D.1: Frequency spectrum of the polymers agree with the theoretical peaks (green crosses). Note that the connection of polymers does not influence the highest frequency mode, only the spacing of the modes. The simulation was done with $\beta = 2 \text{meV}^{-1}$, $\Delta t = 0.01 \text{ps}$, $P = 11$ and total time 20 ns.

D.2 Thermostat details

One can show [56] that the generalised Langevin equation (2.14) can be converted to a form that is not history-dependent:

$$
\begin{align*}
\dot{\mathbf{s}} &= \mathbf{a}_p \mathbf{A}_p \\
\dot{\mathbf{p}} &= -\left( \frac{\partial V}{\partial \mathbf{q}} \right)_{\mathbf{0}} - \mathbf{a}_p \mathbf{A}_p \mathbf{p} \\
&\quad + \begin{pmatrix}
\mathbf{b}_p & \mathbf{b}_p^T \\
\mathbf{b}_p & \mathbf{B}_p
\end{pmatrix}
\begin{pmatrix}
\xi \\
\mathbf{0}
\end{pmatrix},
\end{align*}
$$

where $\xi$ are $n + 1$ uncorrelated Gaussian random numbers. A detailed explanation of how to solve the above equations is given in Ref. [56]; here we only state the end results. The Velocity-Verlet algorithm in the previous section was supplemented by a step

$$
(v, s) \leftarrow \mathcal{P}[(v, s), \Delta t/2]
$$

before and after the other steps. This is the reason that the first and last step in the verlet algorithm were not performed together as a single long step. The propagator $\mathcal{P}$ can be written on the form

$$
\mathcal{P}[(v, s), \Delta t]^T = T(\Delta t)(v, s)^T + S(\Delta t)\xi^T
$$

where the matrices $T = e^{-\Delta t \mathbf{A}_p}$ and $SS^T = C_p - e^{-\Delta t \mathbf{A}_p} C_p e^{-\Delta t \mathbf{A}_p^T}$ are computed only once in the beginning of the simulation. The matrix $C_p \equiv \langle (p, s)^T (p, s) \rangle$ is called the static covariance matrix and can be computed from $\mathbf{A}_p C_p + C_p \mathbf{A}_p^T = \mathbf{B}_p \mathbf{B}_p^T$. 
and \( A_p, B_p \) are the matrices in equation (D.1). The last ones where chosen as

\[
A_p = \begin{pmatrix}
322.003 & -0.0727808 & -8162.94 \\
0.788939 & 0.895839 & -10.915 \\
-8054.53 & 10.915 & 204287
\end{pmatrix}
\]

and \( B_p \) from \( B_pB_p^T = \frac{k_B T}{m} (A_p + A_p^T) \). Note that the dimension of \( s \) was thus 2 and that the first row and first column of \( A_p \) is responsible for the coupling to all components of \( v \).

### D.3 Metadynamics details

In section 3.2 we described how to construct a time-dependent bias to enhance the sampling of a collective variable \( s \). The bias at time \( n\tau \) \( G \) is a sum of Gaussians

\[
V_n(s) = \sum_{k=0}^n H_k e^{-\frac{(s-s_k)^2}{2\sigma^2}}.
\]

The bias was stored in the computer as two vectors \( \{H_k\}, \{s_k\} \). When \( n \) becomes large, it becomes very time consuming to evaluate all the gaussians explicitly. In order to speed up the simulation, the bias was approximated by a cubic spline – an interpolating function of piecewise third order polynomials, connected such that the first order derivative is smooth. There are standard numerical methods on how to construct such splines (see for example Ref. [57]). One spline was created for the bias potential and one for its derivative (for force computations). The splines were stored as arrays of polynomial coefficients and were updated only after each new gaussian was added. The polynomials were defined on intervals of \( s \) with width \( \sigma/20 \).

Another quantity that needs to be computed in Metadynamics simulations is the reversible work function \( c(t) \) in equation (3.3). This involves two integrals of the form

\[
\int ds e^{f(s)},
\]

where \( f(s) \propto V(s) \) may become large enough to cause an overflow in the exponential function. Such integrals were therefore first rewritten as

\[
e^{\langle f(s) \rangle} \int ds e^{f(s) - \langle f(s) \rangle},
\]

where \( \langle f(s) \rangle \) is the average of \( f \) along the \( s \)-axis. In this way equation (3.3) can be written

\[
c(t) = \frac{1}{\beta} \log \frac{\exp[\alpha_1(V(s,t))] \int ds \exp[\alpha_1(V(s,t) - \langle V(s,t) \rangle)]}{\exp[\alpha_2(V(s,t))] \int ds \exp[\alpha_2(V(s,t) - \langle V(s,t) \rangle)]} = \langle V(s,t) \rangle + \frac{1}{\beta} \log \frac{\int ds \exp[\alpha_1(V(s,t) - \langle V(s,t) \rangle)]}{\int ds \exp[\alpha_2(V(s,t) - \langle V(s,t) \rangle)]},
\]

where \( \alpha_1 \equiv \frac{\gamma \beta}{\gamma - 1} \) and \( \alpha_2 \equiv \frac{\beta}{\gamma - 1} \).
D. Implementation details

D.4 Bennett’s method details

In Bennett’s acceptance ratio method, we need to solve the two equations (3.8) and (3.9) self-consistently. Since the optimal constant $C$ is not known during the simulation, the Fermi function $f$ was evaluated for several values of $C$. The same number of samples was taken in both states 0 and 1, so that equation (3.8) can be written as

$$
\frac{Z_0}{Z_1} = \frac{\sum_1 f(x) \exp(C)}{\sum_0 f(-x)}
$$

with $x \equiv \beta(U_0 - U_1) + C$. The sums were stored in vectors where each entry corresponded to a value of $C$ between $-2$ and $0$ in intervals of 0.1. The optimal value $C = \log(Z_0/Z_1)$ corresponds to $\sum_1 f(x)/\sum_0 f(-x) = 1$. We found that

$$
h(C) \equiv \log \left( \frac{\sum_1 f(x)}{\sum_0 f(-x)} \right)
$$

can be well fitted to a linear function. The optimal $C$ was calculated as the zero $C_0$ of the linear fit of $h(C)$. Then the free-energy difference between the fermionic and the bosonic system was computed as

$$
F_F - F_B = -\frac{1}{\beta} \log \left( \frac{1 - e^{C_0}}{1 + e^{C_0}} \right),
$$

where $g$ is the degeneracy of the first excited single-particle state.

D.5 Parameter settings in the quantum dot simulations

The parameters used when simulating the quantum dots were, in most cases, $\Delta t = 1$ fs, $\tau = 0.067$ meV$^{-1}$, $\sigma = 10$, $\gamma = 6$ and $H_0 = 0.5k_B T$. The total simulation time was 1 ms, consisting of 0.5 ms building up bias and 0.5 ms sampling time. Samples were acquired in intervals of 5 fs.

For the circular dot with $R_W = 1.9$ and $R_W = 2.0$ the Metadynamics parameters were changed to $\sigma = 12$ and $\gamma = 4$ because $p(s)$ was broader in this case than for weaker interactions. In the case of intermediate interaction strength, the confinement energy scale $\hbar \omega_0$ was almost twice as large for $R_W = 1.0$ than for $R_W = 1.34$. A stronger confinement effectively extends the quantum regime to higher temperatures, so to be able to compare the two results, we kept $\hbar \omega_0 \beta$ constant, meaning that $\beta = 0.5$ meV$^{-1}$ for $R_W = 1.0$ and $\beta = 1.0$ meV$^{-1}$ for $R_W = 1.34$. 

A13
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