A Monte Carlo computer simulation algorithm in classical phase space is given for the treatment of quantum systems. The non-commutativity of position and momentum is accounted for by a mean field approach and instantaneous effective harmonic oscillators. Wave function symmetrization is included at the dimer and double dimer level. Quantitative tests are performed against benchmarks given by Hernando and Vanček (2013) for spinless neon–parahydrogen, modeled as interacting Lennard-Jones particles in a one dimensional harmonic trap. The mean field approach is shown to be quantitatively accurate for high to moderate temperatures $\beta \omega_{1J} \lesssim 7$, and moderate densities, $\rho \sigma \approx 1$. Results for helium show that at the lowest temperature studied, the average energy is about 4% lower for bosons than for fermions. It is argued that the mean field algorithm will perform better in three dimensions than in one, and that it will scale sub-linearly with system size.

The present algorithm consists of classical Metropolis Monte Carlo, combined with umbrella sampling for the commutation function and symmetrization function weight. The commutation function is evaluated in mean field, analytic, harmonic oscillator approximation, as defined by the instantaneous local curvature of the potential energy. This mean field quantum harmonic oscillator approach differs from an unrelated perturbation method that estimates quantum corrections to a classical system by using the spectrum of the classical velocity auto-correlation function as the density of states for a distribution of effective quantum simple harmonic oscillators.

The major purpose of this paper is to establish the regime of validity of the mean field approximation by comparison with the benchmark results. The symmetrization function is evaluated in a loop expansion that retains the monomer, dimer, and double dimer terms. Results are presented for both fermions and bosons. Although the differences between them are small for neon-parahydrogen (but more noticeable for helium), they nevertheless justify the conclusion that the symmetrization loop expansion is rapidly converging, and that the additional computational burden in accounting for particle statistics is not prohibitive in the present phase space formulation of quantum statistical mechanics.
II. PHASE SPACE FORMULATION OF QUANTUM STATISTICAL MECHANICS

A. Exact Formulation

The fundamental formulae upon which the simulation algorithm is based is summarized here; a full derivation is given in Ref. 3. For a canonical equilibrium quantum system, the statistical average in phase space is

$$\langle \hat{A} \rangle_{N,V,T}^{\pm} = \frac{1}{Z^{\pm}} \text{Tr}' \left\{ e^{-\beta H} \hat{A} \right\}$$

$$= \frac{1}{Z^{\pm} h^{2N} N!} \int d\Gamma \times e^{-\beta H(\Gamma)} W_p(\Gamma)\eta^\pm(\Gamma). \quad (2.1)$$

Here \( \beta = 1/k_B T \) is the inverse temperature of the reservoir, with \( k_B \) being Boltzmann’s constant and \( T \) being the temperature, \( N \) is the number of particles, assumed identical, \( V \) is the volume, and \( d \) is the dimensionality, all for the sub-system. Also \( h \) is Planck’s constant, \( \Gamma = \{ p, q \} \) is a point in classical phase space, with the position vector being \( q = \{ q_1, q_2, \ldots, q_N \} \), and \( q_i = \{ q_{ix}, q_{iy}, \ldots, q_{id} \} \), and similarly for the momentum vector \( p \), and \( H(\Gamma) = K(p) + U(q) \) is the classical Hamiltonian or total energy function, with \( K(p) = p^2/2m \) being the kinetic energy \((m\text{ is the mass of the particles})\), and \( U(q) \) being the potential energy. Finally, \( Z^{\pm} \) is the normalizing canonical partition function, with the superscript designating the type of particle: the upper sign is for bosons and the lower sign is for fermions.

The commutation function \( W \) arises from the non-commutativity of the position and momentum operators.\1\2\3\4 It is essentially the same as the function introduced by Wigner,\1\2 and analyzed by Kirkwood.\3\4\5 and is defined by

$$e^{-\beta H(\Gamma)} W_p(\Gamma) = \frac{\langle q | e^{-\beta H} | p \rangle}{\langle q | p \rangle}$$

$$= \frac{1}{\langle q | p \rangle} \sum_n e^{-\beta E_n} \langle q | n \rangle \langle n | p \rangle. \quad (2.2)$$

One has \( W_p(p, q)^* = W_p(-p, q) \), where the asterisk denotes the complex conjugate. High temperature expansions for the commutation function have been given.\1\2\3\4\5 The second equality invokes the sum over the energy eigenstates of the sub-system, with the energy eigenfunctions in the position and momentum representations appearing. The present simulations are based on the commutation function in this form, as will be discussed below.

In general the commutation function is specific to the function being averaged. But for functions that are linear combinations of functions purely of momenta or purely of position, this generic form is valid.\1\2 Energy and density, which are the two major quantities sought in the simulations reported below, fall into this category.

The symmetrization function \( \eta^\pm \) arises from the fact that the wave function must be fully symmetric (bosons, upper sign) or fully anti-symmetric (fermions, lower sign) with respect to particle permutation.\1\2\1\3\1\4\1\5 Formally it is

$$\eta^\pm(\Gamma) \equiv \frac{1}{(p|q)} \sum_p (\pm 1)^p \langle \hat{p} p | q \rangle$$

$$= e^{p \cdot q / i\hbar} \sum_p (\pm 1)^p e^{-\langle \hat{p} p | q \rangle / i\hbar}. \quad (2.3)$$

Here \( \hat{p} \) is the permutation operator and \( p \) is its parity. The second equality invokes the momentum eigenfunctions in the position representation, \( |p\rangle \equiv e^{-p \cdot (r - q) / i\hbar} / \sqrt{N/2} \), with the position eigenfunctions being Dirac delta functions, \( |q\rangle \equiv \delta((r - q) \cdot \cdot \cdot q) \). Evidently, \( \eta^\pm(p, q)^* = \eta^\mp(-p, q) \).

Because of the exponential terms, the symmetrization function is highly oscillatory, which means it cancels to zero unless the particles involved in any given permutation are close together in phase space. This gives rise to a rapidly converging loop expansion which is discussed and exploited below.

B. Mean Field Harmonic Oscillator Approximation

In the simulations reported below, a mean field approximation is used that exploits the analytic form of the commutation function in the case of independent simple harmonic oscillators.\1\2\3\1\4\1\5 This approximation is now described.

1. Mean Field Approximation

In general, the particles of the sub-system interact via the potential energy, which is the sum of one-body, two-body, three-body terms, etc.,

$$U(q) = \sum_{j=1}^{N} u^{(1)}(q_j) + \sum_{j<k}^{N} u^{(2)}(q_j, q_k)$$

$$+ \sum_{j<k<l}^{N} u^{(3)}(q_j, q_k, q_l) + \ldots \quad (2.4)$$

Distributing the energy equally, the energy of particle \( j \) can be defined as

$$U_j(q_j, q) = u^{(1)}(q_j) + \frac{1}{2} \sum_{k=1}^{N} u^{(2)}(q_j, q_k)$$

$$+ \frac{1}{3} \sum_{k<l}^{N} u^{(3)}(q_j, q_k, q_l) + \ldots \quad (2.5)$$

The total potential energy is just \( U(q) = \sum_{j=1}^{N} U_j(q_j; q) \). The argument \( (q_j; q) \) means that \( q_j \) is here separated out from \( q \).
The potential energy of particle $j$ in configuration $\mathbf{q}$
may be expanded to second order about its local minimum at $\mathbf{q}_j$,
\begin{equation}
U_j(\mathbf{q}_j; \mathbf{q}) = U_j(\mathbf{q}) + \frac{1}{2}[\mathbf{q}_j - \mathbf{q}_j(\mathbf{q})] \cdot \mathbf{\nabla}'' U_j(\mathbf{q}) \cdot [\mathbf{q}_j - \mathbf{q}_j(\mathbf{q})], \quad (2.6)
\end{equation}
where the minimum value of the potential is $U_j(\mathbf{q}_j; \mathbf{q}) \equiv \nabla_j U_j(\mathbf{q}_j; \mathbf{q})$. The gradient, $\nabla_j U_j(\mathbf{q}_j; \mathbf{q})$, vanishes at $\mathbf{q}_j = \mathbf{q}_j(\mathbf{q})$. The $d \times d$ second derivative matrix for particle $j$ at the minimum, $\mathbf{\nabla}'' U_j = \nabla_j \nabla_j U_j(\mathbf{q}_j; \mathbf{q})|_{\mathbf{q}_j = \mathbf{q}_j} = \mathbf{\Sigma}_j$, is assumed positive definite. Computationally, it is convenient to iterate Newton’s method to locate the local minimum,
\begin{equation}
\mathbf{q}_j^{(n+1)} = \mathbf{q}_j^{(n)} - [\mathbf{\nabla}''(\mathbf{q}_j^{(n)})]^{-1} \mathbf{\nabla} U_j(\mathbf{q}_j^{(n)}). \quad (2.7)
\end{equation}

For configurations $\mathbf{q}$ that have no local minimum in the potential, or that have too large a displacement $|\mathbf{q}_j - \mathbf{q}_j|$, the corresponding single particle commutation function can be set to unity, $W_j(\mathbf{q}) = 1$. This is justified by analytic results for the simple harmonic oscillator. The positive definite second derivative matrix has $d$ eigenvalues $\lambda_j(x; \mathbf{q}) > 0$, and orthonormal eigenvectors, $\mathbf{\Sigma}_j^{\dagger} \mathbf{X}_j = \lambda_j \mathbf{X}_j$, $\alpha = x, y, \ldots, d$. As $d$ is typically 1, 2, or 3, it is trivial numerically to find the eigenvalues and eigenvectors and to diagonalize $\mathbf{\Sigma}_j''$. For molecule $j$ in configuration $\mathbf{q}$ the eigenvalues define the frequencies
\begin{equation}
\omega_{j\alpha}(\mathbf{q}) = \sqrt{\lambda_{j\alpha}(\mathbf{q})/m}, \quad \alpha = x, y, \ldots, d. \quad (2.8)
\end{equation}

With this the potential energy is
\begin{equation}
U(\mathbf{q}) = \sum_{j=1}^{N} U_j + \frac{1}{2} \sum_{j=1}^{N} \langle \mathbf{q}_j - \mathbf{q}_j | \mathbf{q}_j - \mathbf{q}_j \rangle \cdot \mathbf{\Sigma}_j'.
\end{equation}
\begin{equation}
= \sum_{j=1}^{N} U_j + \frac{1}{2} \sum_{j,\alpha} \hbar \omega_{j\alpha} Q_j^2. \quad (2.9)
\end{equation}
Here $Q_{j\alpha} \equiv \sqrt{\hbar \omega_{j\alpha}/\hbar} Q_{j\alpha}$, and $Q_j' = \mathbf{X}_j^T | \mathbf{q}_j - \mathbf{q}_j |$.\[2.9\]

2. Harmonic Oscillator Analysis

The mean field approximation combined with the second order expansion about the local minima maps each configuration $\mathbf{\Gamma}$ to a system of $dN$ independent harmonic oscillators with frequencies $\omega_{j\alpha}$ displacements $Q_{j\alpha}$, and momenta $P_{j\alpha} = \sqrt{\hbar \omega_{j\alpha}} \left\{ \mathbf{X}_j^T | P_j \right\}$. With this harmonic approximation for the potential energy, the effective Hamiltonian in a particular configuration can be written
\begin{equation}
\mathcal{H}^{\text{SHO}}(\mathbf{p}, \mathbf{q} - \mathbf{q}) = \sum_{j=1}^{N} U_j + \frac{1}{2} \sum_{j,\alpha} \hbar \omega_{j\alpha} \left[ P_{j\alpha}^2 + Q_{j\alpha}^2 \right]. \quad (2.10)
\end{equation}

\begin{equation}
The commutation function for the interacting system for a particular configuration can be approximated as the product of commutation functions for effective non-interacting harmonic oscillators which have the local displacement as their argument. With this the mean field commutation function is
\begin{equation}
W_p^m(\mathbf{\Gamma}) = W_{p,j\alpha}(\mathbf{q} - \mathbf{q})
= e^\beta \mathcal{H}^{\text{SHO}}(\mathbf{p}, \mathbf{q} - \mathbf{q})
= \prod_{j,\alpha} W_{p,j\alpha}(P_{j\alpha}, Q_{j\alpha}). \quad (2.11)
\end{equation}

The harmonic oscillator commutation function for a single mode is
\begin{equation}
W_{p,j\alpha}(P_{j\alpha}, Q_{j\alpha})
= \sqrt{2} e^{-\frac{1}{2} P_{j\alpha} \mathcal{H}_{j\alpha} P_{j\alpha} + \frac{1}{2} Q_{j\alpha}^2} e^{-\frac{1}{2} P_{j\alpha}^2 + \frac{1}{2} Q_{j\alpha}^2}
\times \sum_{n_{j\alpha} = 0}^{\infty} \frac{i^n_{j\alpha} e^{-n_{j\alpha} \mathcal{H}_{j\alpha} (1+1/2)} H_n_{j\alpha} (P_{j\alpha}) H_{n_{j\alpha}} (Q_{j\alpha}). \quad (2.12)
\end{equation}

The prefactor $e^{-\frac{1}{2} P_{j\alpha} \mathcal{H}_{j\alpha} P_{j\alpha} + \frac{1}{2} Q_{j\alpha}^2}$ corrects the prefactor $e^{-\frac{1}{2} P_{j\alpha} \mathcal{H}_{j\alpha} P_{j\alpha} + \frac{1}{2} Q_{j\alpha}^2}$ given in Eq. (5.10) of Ref. [12]. Here $H_n(z)$ is the Hermite polynomial of degree $n$. The imaginary terms here are odd in momentum. As mentioned, for configurations such that $\mathbf{\Sigma}_j''$ is not positive definite, or that the displacement $Q_{j\alpha}$ is too large, the commutation function can be set to unity, $W_{p,j\alpha} = 1$. For the averages, the momentum integrals can be performed analytically, both here and in combination with the symmetrization function. This considerably reduces computer time and substantially increases accuracy.

C. Symmetrization Function

The symmetrization function can be written as a series of loop products\[2.9\]
\begin{equation}
\eta_{l}^+/(\mathbf{\Gamma}) = 1 + \sum_{jk} \eta_{l;j,k}^+ + \sum_{jkl} \eta_{l;j,k,l}^+ + \sum_{jklm} \eta_{l;j,k,l,m}^+ + \ldots \quad (2.13)
\end{equation}
Here the superscript is the order of the loop, and the subscripts are the atoms involved in the loop. The prime signifies that the sum is over unique loops (ie. each configuration of particles in loops occurs once only) with each index different (ie. no particle may belong to more than one loop). The $l$-loop symmetrization factor is
\begin{equation}
\eta_{l;1,\ldots,l}^+ = (\pm 1)^l e^{Q_{l;1,\ldots,l}/i\hbar} \prod_{j=1}^{l-1} e^{Q_{j+1,j+1}/i\hbar}, \quad (2.14)
\end{equation}
where $Q_{jk} \equiv Q_j - Q_k$.\[2.9\]
In the series loop expansion above, the first term of unity is for monomers. The second term is a dimer loop, the third term is a trimer loop, and the fourth term shown is the product of two dimers. The monomer term, \( \eta_{q;1}^{(1)} = 1 \), is obviously the classical one, and it is the only term present for so-called distinguishable particles. This is the dominant term when \( \rho \Lambda_{\text{th}}^d \ll 1 \), which is the low density, high temperature limit. Here \( \rho = N/V \) is the number density and \( \Lambda_{\text{th}} = (2\pi h^2 / \beta m)^{1/2} \) is the de Broglie thermal wave length.

As mentioned, these loop symmetrization factors are highly oscillatory, and so the only non-zero contribution from them comes from configurations such that successive particles around a loop are close neighbors in phase space. In previous work the compact nature of the loops was used to argue that in the thermodynamic limit \( (V \to \infty) \) at constant fugacity or density \( (\Gamma) \) the grand partition function factorizes and yields a series of loop grand potentials.

Although that result appears both useful and formally exact, in the present work a related but arguably more practical approach is developed that is well-suited for computer simulation. Since the non-zero contributions come only from compact loops, one can restrict each of the sums above to configurations where the consecutive particles around a loop are actual spatial (or more generally phase space) neighbors. This can be defined by some arbitrary cut-off whose quantitative effect can be ascertained a posteriori. That is, in any configuration the symmetrization function is unity plus the contributions from, and only from, loops that are compact by the imposed criterion.

1. One-Dimensional Example

In order to illustrate the idea concretely, consider the case of four particles in one-dimension. For four particles the symmetrization function in full is

\[
\eta_{q;a}^{\pm}(\Gamma) = 1 \pm \left[ \eta_{q;q_{12}}^{(2)} + \eta_{q;q_{23}}^{(2)} + \eta_{q;q_{34}}^{(2)} \right] + \left[ \eta_{q;q_{123}}^{(3)} + \eta_{q;q_{234}}^{(3)} \right] \pm \left[ \eta_{q;q_{13}}^{(2)} + \eta_{q;q_{14}}^{(2)} + \eta_{q;q_{24}}^{(2)} \right] \\
\pm \left[ \eta_{q;q_{124}}^{(3)} + \eta_{q;q_{143}}^{(3)} + \eta_{q;q_{234}}^{(3)} \right] \pm \left[ \eta_{q;q_{1234}}^{(4)} + \eta_{q;q_{1342}}^{(4)} + \eta_{q;q_{2341}}^{(4)} + \eta_{q;q_{3421}}^{(4)} \right].
\]

There is one monomer. There are \( 4 \times 3/2 = 6 \) single dimers. There are \( 3 \) double dimers. There are \( 4 \times 3 \times 2 / 3 = 8 \) trimers. There are \( 4 \times 3 \times 2 \times 1/4 = 6 \) tetramers. This gives \( 4! = 24 \) terms altogether.

As mentioned above, this idea that the symmetrization function is dominated by transpositions of neighbors carries over to two or more dimensions.

In simulations reported below only the three groups corresponding to the first line will be included. For \( N \) particles define the monomer term,

\[
\eta_{q;1}^{(1)}(\Gamma) = 1,
\]

the nearest neighbor dimer,

\[
\eta_{q;2}^{(2)}(\Gamma) = \sum_{j=1}^{N-1} \eta_{q;j,j+1}^{(2)} = \sum_{j=1}^{N-1} e^{-q_{j,j+1}/\hbar},
\]

and the double nearest neighbor dimer,

\[
\eta_{q;3}^{(2)}(\Gamma) = \sum_{j=1}^{N-3} \sum_{k=j+2}^{N-1} \eta_{q;j,j+1}^{(2)} \eta_{q;k,k+1}^{(2)} = \sum_{j=1}^{N-3} \sum_{k=j+2}^{N-1} e^{-q_{j,j+1}/\hbar} e^{-q_{k,k+1}/\hbar}.
\]

Accordingly, here the \( a \)th order approximation to the symmetrization function is defined as

\[
\eta_{q,a}^{\pm}(\Gamma) = \sum_{b=1}^{a} (\pm)^{b-1} \eta_{q;b}^{(b)}(\Gamma), \quad a = 1, 2, 3.
\]

The case \( a = 1 \) is for monomers, also known as distinguishable particles. This is the classical case in the event that the commutation function is set to unity. In some of the results below including the single nearest neighbor dimer, \( a = 2 \), makes a measurable difference. In almost no case was the additional contribution from the double nearest neighbor dimer, \( a = 3 \), measurable.

As mentioned above, including these symmetrization functions does not preclude the momentum integrals from being performed analytically.

III. COMPUTATIONAL DETAILS

A. Model

Results from the present mean field simulation approach are tested against benchmark results given by Hernando and Vanícek. These are based on the first 50 energy eigenvalues, which, apart from the discretization of time and space, are numerically exact. The model used by these authors consists of spinless Lennard-Jones particles in one-dimension trapped by a harmonic potential. The latter is the harmonic oscillator potential

\[
U_1(q) = \frac{1}{2} m \omega^2 \sum_{j=1}^{N} q_j^2.
\]
The Lennard-Jones pair potential is

$$U_2(q) = \epsilon \sum_{j<k}^N \left[ \left( \frac{r_e}{q_{jk}} \right)^{12} - 2 \left( \frac{r_e}{q_{jk}} \right)^6 \right], \quad (3.2)$$

where $q_{jk} = q_j - q_k$. Note that all particle pairs interact, not just nearest neighbors. The equilibrium separation $r_e$ is related to the more usual Lennard-Jones diameter $\sigma$ by $r_e = 2^{1/6}\sigma$.

Hernando and Vančel̆ková give results at the de Boer quantum delocalization length $L_{db} = 2^{1/6}h/(r_0\sqrt{\epsilon m}) = 0.16$. They state that this corresponds to hypothetical particles between parahydrogen and neon. They also use $\omega_{r_e}\sqrt{m/\epsilon} = 1/2$. Unless stated otherwise, parameters corresponding to these two values are used below.

In SI units, for this case I used the neon mass, $m = 3.351 \times 10^{-26}$ kg, and Lennard-Jones diameter, $r_e = 2^{1/6}\sigma_{Ne} = 3.13055 \times 10^{-10}$ m. These give $\omega = 2^{1/6}\sqrt{2}/(2L_{db}\sigma_{Ne}^2 m) = 1.1264 \times 10^{11}$ s$^{-1}$, and $\epsilon = 14.03 \ h\omega = 1.6666 \times 10^{-22}$ J. This last value is about one third of the Lennard-Jones well-depth parameter for neon, $\epsilon_{Ne} = 4.93 \times 10^{-22}$ J.$^1$

The temperature below is reported in terms of the frequency corresponding to the Lennard-Jones pair potential at the equilibrium spacing, $\omega_{LI} \equiv \sqrt{\epsilon} \langle r_e \rangle/m = \sqrt{72\epsilon/m_{\alpha^2}} = 16.97\omega$, (since in the present simulations $\omega_{r_e}\sqrt{m/\epsilon} = 1/2$).

### B. Simulation Algorithm

The Metropolis Monte Carlo algorithm was used in classical phase space with umbrella sampling.$^2$ The statistical average in the form of the final phase space integral in Eq. (2.1) was written

$$\langle A \rangle_T|_{W\eta^z} = \frac{\langle AW\eta^z \rangle_T}{\langle W\eta^z \rangle_T}. \quad (3.3)$$

The right hand side consists of the ratio of two canonical averages in classical phase space, which are well-suited to the Metropolis Monte Carlo algorithm.

For the product of single particle commutation functions, Eq. (2.12), with or without the symmetrization function, Eqs (2.17) or (2.18), and with the kinetic energy part of the Maxwell-Boltzmann factor, it is evident that the momentum integrals may be evaluated analytically. The integrals are of the type

$$\int_{-\infty}^{\infty} dP \ e^{-\alpha P^2/2} e^{iPQ} p^n = \sqrt{2\pi\alpha}^{(n+1)/2} e^{-Q^2/2\alpha} \times \sum_{m=0}^{[n/2]} \frac{n! (iQ/\sqrt{\alpha})^{n-2m}}{(2m)! [n-2m]!} (2m-1)!! \quad (3.4)$$

(Note here only, $(-1)!! \equiv 1$.) Comparison between Monte Carlo in the full phase space, and Monte Carlo in position space with the analytic quadratures, showed agreement between the two, with the latter method being the most reliable and by far the most computationally efficient. The results reported below use the analytic momentum quadrature.

For the single particle commutation function, Eq. (2.12), most results reported below used up to the sixth Hermite polynomial, although tests with up to 12 terms were carried out. Generally 6 iterates of Newton’s method was used to locate each local minimum, which is probably a factor of 2 too many. No effort was made to optimize these parameters or to adjust them for different temperatures or models. A potential cut-off, generally $u_{cut} = 5\hbar\omega$, was used so that $W_j(p,q) = 1$ whenever $U_j(q) - \mathcal{U}_j(q) \geq U_{cut}$. This was also done if $\mathcal{U}_j \leq 0$. The results were not sensitive to the value of the cut-off, except that at the highest temperatures large displacements $Q_j$ made a smaller value necessary, $u_{cut} \approx 2\hbar\omega$. In retrospect it might possibly have been better to apply the cut-off criterion directly to the displacement $Q_j$.

High temperature expansions for the commutation function were also implemented.$^2, 12$ These involved up to the fourth tensor gradient of the potential. The results were a little disappointing in that their regime of validity, $\beta\hbar\omega_{LI} \lesssim 1$, is not easily resolved in the figures below. These results are not reported here.

The implementation of the Metropolis algorithm for a classical canonical system was standard and need not be repeated here. The simulation was broken into 500 blocks, and the statistical error was estimated from the fluctuations in the ratio of the averages of each block. The error reported below is twice the standard deviation divided by the square root of the number of blocks, which corresponds to the 96% confidence level. This calculated error was consistent with the error calculated from the fluctuations between independent repeat runs.

The computations were performed on a teen-aged personal computer. Typically a given simulation for five particles took between two minutes and two hours, depending on the temperature and the accuracy sought. Turning off the calculation of the symmetrization function reduced the computation time by about a factor of two in one typical case.

Some relatively short tests were carried out for the system size dependence. With $4 \Rightarrow 8 \Rightarrow 16 \Rightarrow 32 \Rightarrow 64$ particles, the computer time increased consecutively by factors of 1.9, 2.2, 2.7, and 3.9 respectively. The case of $N = 64$ took 303 seconds for a relative statistical error in the total energy of 0.03%. In these five cases only nearest and next nearest neighbors were included in the Lennard-Jones potential calculation, which corresponds to a cut-off of $R_{cut} \approx 2.5-3r_e$. (No cut-off was used in any other results reported in this paper.) These particular tests used the same number of trial position cycles (a cycle is one attempted move of every particle), and hence the number of trial positions increased linearly with particle number. With the cut-off and effective neighbor
table, the cost of a trial move of one particle is independent of system size. In the simulations, after every six cycles of trial moves, the commutation function and the symmetrization function were calculated, and the quantities to be averaged were accumulated. The costs of evaluating a single particle commutation function and a nearest neighbor dimer symmetrization function, are independent of the size of the system.

There are $\sim N$ nearest neighbor dimers, and $\sim N^2/2$ double nearest neighbor dimers. Therefore the cost of evaluating the instantaneous weighted potential energy at these two levels scales as $N$ and $N^2$, respectively. The cost of evaluating the instantaneous weighted kinetic energy scales as $N^3$ and $N^3$, respectively, because of the momentum integrals. These are the dominant costs of the simulation; the cost of a run is the number of cycles times these.

This assumes an inhomogeneous system in which each particle makes a distinct contribution that has to be explicitly accounted for, which is what is done here. In principle, for a homogeneous system, the kinetic energy could be obtained by calculating one representative term of each type that can occur, and simply multiplying it by an appropriate combinatorial factor, which would mean that the cost of evaluating the instantaneous weighted kinetic energy would not depend on $N$. Of course this would mean that one would have to increase the number of cycles of trial configurations in order to obtain statistical accuracy comparable to the present case when each contribution is evaluated explicitly and accumulated.

The relative statistical error in the total energy in the present specific tests at constant number of trial position cycles was 8.7%, 2.7%, 0.20%, 0.11%, and 0.03%, respectively. In general the statistical error scales inversely with the square root of the computer time, all other things being equal. These values mean that one would have to run the present $N = 4$ system 2,700 times as long a time as the present $N = 64$ system was run in order to get the same statistical error.

IV. RESULTS

1. Neon–Parahydrogen

Results for the average energy of $N = 4$ Lennard-Jones particles are shown in Fig. 1. These are for $L_{1B} = 0.16$ and $\omega r_0 \sqrt{m/\epsilon} = 1/2$, which correspond to neon–parahydrogen. The Lennard-Jones frequency used as a scale is much larger than that of the harmonic potential, $\omega_{LJ} = 16.97 \omega$. The exact results were derived by computing the canonical average of the first 50 energy eigenvalues obtained by Hernando and Vaníček. Since originally an unknown constant has been applied to shift the eigenvalues to the Lennard-Jones potential minimum, here the exact average energy curve has been shifted into coincidence with the classical result at the highest temperature studied.

It can be seen that the classical results remain accurate for temperatures $\beta \hbar \omega_{LJ} \lesssim 2$. The high temperature expansion (not shown) is close to the classical result. The mean field quantum theory has a larger regime of validity, and it remains accurate for temperatures $\beta \hbar \omega_{LJ} \lesssim 7$.

Interestingly enough, the classical equipartition theorem for the kinetic energy is not satisfied in a quantum system. It increasingly underestimates the actual kinetic energy as the temperature is lowered. For example, at $\beta \hbar \omega_{LJ} = 17$, for $N = 4$ the mean field theory for indistinguishable particles gives the kinetic energy as $\beta K/N = 1.83 \pm 0.03$.

In the present model symmetrization effects were practically negligible. For example, at $\beta \hbar \omega_{LJ} = 17$, adding the single nearest neighbor dimer to the symmetrization function decreased the average energy for bosons by about 0.2%, and increased that for fermions by the same amount. Adding to this the double nearest neighbor dimer contribution increased the energy by about 6 parts in $10^6$. At this temperature, the thermal wave length is only slightly larger than the equilibrium spacing, $A_{th} = 1.34 r_0$, and so one expects symmetrization effects to be small.

(The momentum integrals for a dimer applied to the classical case $W = 1$ yield Gaussians $\exp -2\pi q_j^2 / A_{th}^2$, which is why symmetrization effects are negligible unless the typical particle spacing is somewhat smaller than the thermal wavelength.)

The average energy for $N = 5$ is shown in Fig. 2. The relative performance of the classical and mean field quantum results is similar to that in the $N = 4$ case, and their regime of accuracy is about the same. Symmetrization effects were also quantitatively similar to that of the previous case. This is perhaps not surprising since the...
Figure 2 compares the density profiles for \( N = 4 \) and \( \beta \hbar \omega_{LJ} = 6.8 \). The neon–parahydrogen particles are indistinguishable; symmetrization effects on the density profile are almost immeasurable in this case. The exact result for distinguishable particles shows two relatively broad central peaks and two outer shoulders. The peaks in the present mean field monomer quantum calculations are more pronounced than in the exact calculations, as are those in the classical result. It is noticeable how much of the density profile for the neon–parahydrogen particles is purely classical. The quantum density profile spreads out more than the classical profile, and the average density in the region \(-2r_e \leq q \leq 2r_e\) is lower. This indicates that the harmonic trap confines the classical particles to a smaller region than it does the quantum particles.

Figure 3 is for the lower temperature of \( \beta \hbar \omega_{LJ} = 11.9 \). The peaks in the density profile are now quite pronounced in all three approaches. Again one sees that the major contribution to the density profile is classical. The mean field approximation gives quantitatively the quantum deepening of the density minima. At this temperature the mean field theory is in better agreement with the exact results than at the higher temperature of the preceding figure. Indeed, comparing these results to those in Fig. 1, one can conclude that the regime of accuracy for the mean field approximation appears to be greater for structure than it is for energy.

Figure 4 is the density profile for the still lower temperature of \( \beta \hbar \omega_{LJ} = 47.5 \). In this case the mean field quantum result is almost coincident with the classical result. Both magnify the structure that is apparent in the exact results. Including symmetrization effects would make no apparent difference to the mean field quantum results.

The peaks in the density profile are more pronounced at this low temperature than at the higher temperatures of the preceding figures. The spacing of the peaks is about \( r_e \) in all three cases. In this system confined by the harmonic potential, the peak spacing is relatively insensitive to the number of particles since extra particles just spread further in the harmonic potential trap. Even for a relatively high number of particles the average nearest neighbor spacing is not much less than \( r_e \). (For 64 helium particles at \( \beta \hbar \omega_{LJ} = 17 \), the spacing at the ends is about \( r_e \), and the spacing in the center is about \( 0.8r_e \).)
dimers are used (ie. Eq. (3.3), passing through zero when nearest neighbor is due to the denominator in the umbrella average, there is a singularity in the results for fermions. This expansion vanishes, one has to go to otherwise negligible bosons, and fermions. (Of course measurable difference between distinguishable particles, neon–parahydrogen treated above, for helium there is a nearest neighbor dimer cases. Unlike the case of mean field monomer, nearest neighbor dimer, and double closest neighbor dimer cases. The statistical error is about the width of the curves everywhere except in the vicinity of the pole.

2. Helium

Results were also obtained for helium-4, using \( m = 6.65 \times 10^{-27} \text{kg} \), and Lennard-Jones parameters \( \epsilon_{\text{He}} = 1.41 \times 10^{-22} \text{J} \), and \( \sigma_{\text{He}} = 2.56 \times 10^{-10} \text{m} \). These correspond to a de Boer length of \( L_{\text{dB}} = 0.426 \). The dimensionless trap frequency was unchanged, \( \omega_{\text{c}} \sqrt{m/c} = 1/2 \), which corresponds to \( \omega = 2.54 \times 10^{11} \text{Hz} \).

Figure 6 shows the average total energy at a function of inverse temperature in the classical, quantum mean field monomer, nearest neighbor dimer, and double nearest neighbor dimer cases. Unlike the case of neon–parahydrogen treated above, for helium there is a measurable difference between distinguishable particles, bosons, and fermions. (Of course \(^4\text{He} \) is a boson; the fermion results here are used to illustrate the effects of particle statistics rather than as a quantitative application to a real physical system.)

As for neon–parahydrogen, quantum effects in helium increase the energy over its classical value. Further, adding wave function symmetrization decreases the energy for bosons and generally increases the energy for fermions. This effect was not noticeable for Ne–H\(_2\), Fig. 1. At \( \beta \hbar \omega_{\text{LJ},1} = 17 \), the thermal wave-length is 2.2\( r_e \) for He, and 1.3\( r_e \) for Ne–H\(_2\).

At around \( \beta \hbar \omega_{\text{LJ},1} = 28–29 \) (nearest neighbor dimer), there is a singularity in the results for fermions. This is due to the denominator in the umbrella average, Eq. (3.3), passing through zero when nearest neighbor dimers are used (ie. \( \eta_{\text{q},[2]}^{-} \), the upper dashed curve in Fig. 6). Adding double nearest neighbor dimers, (ie. \( \eta_{\text{q},[3]}^{-} \), the upper dash-dotted curve) shifts the singularity to lower temperatures, but does not remove it. Of course in general whenever the dominant term in a convergent expansion vanishes, one has to go to otherwise negligible higher order terms to get reliable results. One might have to include further terms in the symmetrization expansion to delineate the behavior here more reliably.

Just beyond the range of temperatures plotted the quantum energy curves become structured. This seems to arise from the commutation function, and is most likely just a low temperature artifact of the mean field simple harmonic oscillator approximation.

Figure 7 shows the density profile at \( \beta \hbar \omega_{\text{LJ},1} = 27 \), near the fermion singularity. As in the earlier density profiles for Ne–H\(_2\), classical effects dominate the structure of the system, even for He. Also like the earlier results, quantum effects spread the overall density profile so that the quantum particles tend to be less confined by the harmonic potential trap than their classical counterparts.

The thermal wavelength here is \( \Lambda_{\text{th}} = 2.8 r_e \), whereas the spacing between density peaks is almost exactly \( r_e \). As mentioned above, an estimate of the magnitude of symmetrization effects is provided by the Gaussian \( \exp -2\pi q_{J,j+1}/\Lambda_{\text{th}}^2 \approx \exp -2\pi/2.8^2 = 0.45 \). One might therefore expect some symmetrization effects here. The fact that in Fig. 7 the profile for bosons is virtually unchanged from that of distinguishable particles suggests that the induced pair attraction due to being able to occupy the same state is weak compared to the short-ranged repulsion of the pair potential. Boson symmetrization has a more noticeable effect on the energy, Fig. 6.

That the results for indistinguishable fermions are distinguishable here is due to the fact that the temperature is close to the fermionic pole that was discussed in conjunction with Fig. 6. The nature of fermion statistics is to reduce the height of the peaks in the density profile and to reduce correspondingly the depth of the valleys. This can be understood from the induced repulsion due to fermions not being able to occupy the same state. This has the effect that two fermions tend not to simultane-

![FIG. 6: Average energy for helium, \( N = 4 \). The dotted curve is the classical result, the solid curve is the mean field quantum result for monomers, the dashed curves include nearest neighbor dimers, and the dash-dotted curves include double nearest neighbor dimers. At high temperatures, the upper pair of curves is for fermions, and the lower (coincident) pair is for bosons. The statistical error is about the width of the curves everywhere except in the vicinity of the pole.](image1)

![FIG. 7: Density profile for helium at \( N = 4 \) and \( \beta \hbar \omega_{\text{LJ},1} = 27 \). The dotted curve is the classical result, the solid curve is the mean field quantum result for monomers, the dashed (fermions) and dash-dotted (bosons) curves both include nearest neighbor and double nearest neighbor dimers. The results for bosons are virtually indistinguishable from those for distinguishable particles.](image2)
ously occupy positions corresponding to adjacent peaks, which would otherwise be their most likely locations. Hence when one fermion is at a peak, the neighboring ones are more likely to be pushed toward the further valley compared with the situation for bosons. The effects of particle statistics on the present density profile of He fermions at $\beta \hbar \omega_{\text{LJ}} = 27$ is qualitatively similar to that for Ne–H$_2$ fermions at zero temperature given by Hernando and Vaněček in their Fig. 1.

The quantum density profiles in Fig. 7 are more noisy than their classical counterpart. This is probably due to the umbrella sampling. In principle it is possible to avoid umbrella sampling by, after the momentum integration, incorporating the magnitudes of the commutation function and the symmetrization function into the Maxwell-Boltzmann phase space weight, and factoring their sign into the function being averaged. (The Metropolis and other algorithms require a positive weight density.)

V. CONCLUSION

This paper has tested the author’s mean field quantum harmonic oscillator algorithm against the benchmark results of Hernando and Vaněček for one-dimensional interacting Lennard-Jones neon-parahydrogen particles. It was found that the mean field approximation was quantitatively accurate down to the relatively low temperatures $\beta \hbar \omega_{\text{LJ}} \lesssim 7$ for the average energy, and $\beta \hbar \omega_{\text{LJ}} \lesssim 12$ for the average density profile. In contrast the classical theory and the high temperature quantum expansion were only valid for the average energy for $\beta \hbar \omega_{\text{LJ}} \lesssim 2$.

It was straightforward to program the method as a modification of existing Monte Carlo simulation algorithms in classical phase space. The computational requirements of the present approach were not high, with most runs being completed in minutes on a personal computer.

It is likely that the present one dimensional tests of the mean field theory are overly pessimistic. Since the fluctuations that are neglected by the mean field decrease with the square root of the number of interacting particles, the theory becomes more accurate as the range and magnitude of the potential is increased, the temperature is decreased, the density is increased, and the dimensionality is increased. Hence one would expect the present theory to perform better in three dimensions than the present one-dimensional results indicate.

The second approximation in the present algorithm was to map each configuration to that of independent harmonic oscillators based on the instantaneous local potential minimum for each individual particle. Modeling each particle as if it were instantaneously trapped by the other particles is reasonable because of the high frequency of the effective oscillator compared to the collective motions of the particles. The independent harmonic oscillator approximation enabled the commutation function for the actual configuration to be written as the product of the exact simple harmonic oscillator commutation functions. The present results indicate that this approach has a larger range of utility than the high temperature expansions.

Finally the present results were in one dimension and for a relatively small number of particles. There is nothing intrinsic in the algorithm that would restrict it to this regime. In particular, both the commutation function and the symmetrization function are readily obtained in three dimensions. With the use of a potential cut-off and neighbor tables, both will likely have favorable scaling properties with system size.

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