Forward–backward semiclassical dynamics for systems of indistinguishable particles

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Abstract

Forward–backward semiclassical dynamics (FBSD) in conjunction with an accurate path integral (PI) description of the density operator provides an accurate, yet practical methodology for simulating important quantum mechanical effects in the dynamics of many-particle systems. In this paper we extend the FBSD methodology to systems of indistinguishable bosons or fermions. Test applications on model systems solvable by numerically exact basis set methods demonstrate that FBSD allows accurate descriptions of the dynamics in fluids characterized by quantum statistics. Specifically, the PI-FBSD methodology successfully captures the frequency shift and spectral narrowing associated with Bose–Einstein condensation. The methodology is also applied to a Lennard-Jones fluid of identical bosons.

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1. Introduction

Time-dependent semiclassical theory [1,2] is emerging as a promising tool for capturing quantum mechanical effects using classical trajectory input in systems which are too large to be treated by other means. Recent advances that made this possible include the development of semiclassical initial value representations (SC-IVR) [3–17,70], filtering techniques [18–20], and forward–backward semiclassical approaches [21–43]. Forward–backward treatments aim at overcoming the problem associated with the oscillatory semiclassical phase. This is achieved by combining the forward and reverse time semiclassical propagators into one. This way the full semiclassical expression for a time-dependent observable or correlation function, which has the form of a double IVR,

\[
\int \, dx_f \int \, dp_f e^{iS_f/\hbar} \cdots \int \, dx_b \int \, dp_b e^{-iS_b/\hbar}
\]

(where \( S_f \) and \( S_b \) are the actions along classical trajectories corresponding to the forward and backward branches of the time contour) is replaced by a single phase space integral with a phase given by the net action along a forward–backward trajectory

\[
\int \, dx_0 \int \, dp_0 e^{iS_0/\hbar}.
\]

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The resulting cancellation of action integrals leads to smoother integrands that can be evaluated efficiently by Monte Carlo integration methods. Just as the semiclassical approximation itself neglects quantum fluctuations associated with highly non-classical paths, forward–backward semiclassical dynamics (FBSD) ignores the interference between distinct trajectories that enter the double IVR expression, leading to loss of quantum interference. FBSD methods are most practical for condensed phase calculations since they can benefit from forward–backward cancellation to the largest extent possible. Fortunately, dephasing processes in many-particle systems tend to suppress quantum interference effects, and thus FBSD approximations can be essentially quantitative in such situations. Miller and coworkers [33] have also obtained generalized forward–backward semiclassical expressions that can interpolate between the double IVR and full FBSD limits, and which therefore can capture some quantum interference (albeit at a higher computational cost).

The present paper aims at extending the FBSD methodology to systems of indistinguishable particles that obey Bose–Einstein or Fermi–Dirac statistics. Such systems exhibit a host of unusual quantum phenomena, which include Bose–Einstein condensation, exclusion, and superfluid behavior. In particular, recently there has been a growing interest in spectroscopy of atoms or molecules embedded in helium nanodroplets and its implication for superfluidity at the molecular level [44,45]. Equilibrium effects associated with particle exchange in systems of identical particles have been thoroughly investigated via imaginary time path integral calculations [46–48], although fermionic systems are much harder to simulate by Monte Carlo methods because the terms entering with negative coefficients lead to severe cancellation [49]. Since real time simulations in many-particle systems have remained out of reach until recently, dynamical calculations on systems of identical particles have been very scarce. To date, dynamical calculations on these systems have been limited to a model of three interacting bosons [50] treated via one of the identical particle extensions of the centroid molecular dynamics method [51–54] and a simulation of superfluid helium [55] using the maximum entropy method to invert imaginary time information.

In Section 2 we review the FBSD methodology and generalize it to systems of indistinguishable particles. The extent to which the FBSD approximation can describe the dynamics of such quantum fluids is not obvious a priori, so we present in Section 3 calculations on model non-interacting systems whose quantum dynamics can be evaluated via accurate basis set methods. The results of these test calculations are very encouraging, demonstrating that FBSD is just as accurate in systems obeying quantum statistics as it has been found to be in systems of distinguishable particles described by the Boltzmann statistics. Based on this success of FBSD, we present in the same section the first PI-FBSD calculation on a fluid of interacting bosons using the identical particle generalization of the pair product (PP) propagator FBSD methodology we developed in a recent paper [42]. Finally, some concluding remarks are given in Section 4.

2. Theory

In this section we review the FBSD methodology for time correlation functions and extend it to systems of identical particles that obey Bose–Einstein or Fermi–Dirac statistics. Our focus in this paper is on the velocity autocorrelation function [56] at finite temperature

\[
C_V(t) = \frac{1}{m^2} C_P(t) = \frac{1}{nm^2 Z} \sum_{i=1}^{n} \text{Tr} \left\{ e^{-\beta \hat{H}_i} \hat{p}_i(t) \cdot \hat{p}_i(0) \right\}_{\text{sym}} = \frac{1}{nm^2 Z} \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{P} \cdot \hat{P}(t) \right\}_{\text{sym}}.
\]  

(2.1)

Here \( n \) is the number of atoms (each of which is assumed to have \( d \) degrees of freedom) with mass \( m \), \( \hat{H} \) is the Hamiltonian operator, which is separated into kinetic and potential energy terms

\[
\hat{H} = \hat{H}_0 + V(Q), \quad \hat{H}_0 = \sum_{i=1}^{n} \hat{H}_0^{(i)}, \quad \hat{H}_0^{(i)} = \frac{\hat{p}^{(i)}_i^2}{2m}, \quad \beta = \frac{1}{k_B T}
\]

(2.2)

\( \beta = 1/k_BT \) is the reciprocal temperature in units of the Boltzmann constant,

\[
Z = \text{Tr} \{ e^{-\beta \hat{H}} \}_{\text{sym}}
\]

(2.3)

is the partition function, and the \( d \)-dimensional vector \( \hat{p}^{(i)} \) denotes the momentum of the \( i \)th atom. The momenta of all the atoms are collected in the \( nd \)-dimensional vector \( \hat{P} \) and the subscript \( H \) denotes the Heisenberg time-dependent form of the corresponding operator

\[
\hat{A}_H(t) = e^{i\hat{H}/\hbar} \hat{A} e^{-i\hat{H}/\hbar}.
\]

(2.4)

Finally, the symbol \( \text{Tr}\{ \}_{\text{sym}} \) denotes the trace over states of the appropriate exchange symmetry. In the description that follows the \( d \)-dimensional Cartesian position vectors for the \( i \)th atom are denoted \( \vec{r}^{(i)} \), while the coordinates of all the particles are collected in the \( nd \)-dimensional vector \( \vec{Q} \).
2.1. Forward–backward semiclassical dynamics and pair product approximation

Consider first a system of distinguishable particles obeying Boltzmann statistics. In this case no particular symmetrization is required, and the time correlation function of interest takes the form

$$C_{VV}(t) = \frac{1}{nmZ} \sum_{i=1}^{n} \text{Tr} \left\{ e^{-i\hat{H}t} \hat{P} \cdot \hat{P}_i(t) \right\} = \frac{1}{nm^2Z} \text{Tr} \left\{ e^{-i\hat{H}t} \hat{P} \cdot \hat{P}_i(t) \right\}. \quad (2.5)$$

The key idea in the FBSD formulation is to combine the forward and backward time evolution operators into a single propagator, which is then evaluated using the semiclassical approximation of time-dependent quantum mechanics [21]. Alternatively, FBSD can be thought of as the $\hbar \rightarrow 0$ (stationary phase) limit of a time-dependent observable or correlation function. In a series of recent papers, our group has focused on the FBSD formulation of Shao and Makri [26,27], which uses a derivative identity for the operator $A$ in conjunction with the coherent state representation of the semiclassical propagator developed by Herman and Kluk [5]. This formulation leads to a rigorous quasiclassical approximation to the correlation function that is practical for systems with hundreds of atoms. For simplicity, we resort to the Cartesian decomposition of the inner product in Eq. (2.1) and treat the time dependence of each scalar operator separately. The starting point of the FBSD formulation is the use of an exponential derivative identity for the Heisenberg operator

$$\hat{A}_H(t) = -\frac{i}{\hbar} \delta_{\hat{A}} \left| \hat{A} \right|_{\mu=0} e^{|\hbar A|/\hbar} e^{-iHt/\hbar} \left| \mu=0 \right>. \quad (2.6)$$

The exponential operators on the right- and left-hand side of this equation describe time evolution in the forward and backward time directions. These events are interrupted by an infinitesimal (delta-function in time) propagation step arising from the action of $\exp(i\mu \hat{A})$. By combining all three exponential operators into a single time evolution for the relevant time-dependent Hamiltonian, applying the semiclassical propagator in the coherent state representation, and performing some algebra, it can be shown that the Heisenberg operator takes the following prefactor-free form [26,27,37,39]

$$\hat{A}_H(t) \approx -i(2\pi \hbar)^{-nd} \frac{\delta}{\delta \mu} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \exp \left( \frac{i}{\hbar} \mathbf{S}(\mathbf{Q}_0, \mathbf{P}_0) \right) \langle \mathbf{G}(\mathbf{Q}, \mathbf{P}_f) \rangle \langle \mathbf{G}(\mathbf{Q}_0, \mathbf{P}_0) \rangle \bigg|_{\mu=0}. \quad (2.7)$$

Here the ket in Eq. (2.7) represents an $nd$-dimensional coherent state [57], i.e., a product of $d$-dimensional coherent states for each particle, and is described in the coordinate representation by the wavefunction

$$\langle \mathbf{Q}\mathbf{G}(\mathbf{Q}_0, \mathbf{P}_0) \rangle = \prod_{j=1}^{n} \langle \mathbf{r}^{(j)} | g(\mathbf{r}^{(j)}_0, \mathbf{P}^{(j)}_0) \rangle = \left( \frac{2}{\pi} \right)^{nd/4} |\det \Gamma|^1/4 \exp \left[ - (\mathbf{Q} - \mathbf{Q}_0) \cdot \Gamma \cdot (\mathbf{Q} - \mathbf{Q}_0) + \frac{i}{\hbar} \mathbf{P}_0 \cdot (\mathbf{Q} - \mathbf{Q}_0) \right], \quad (2.8)$$

where $\Gamma$ is generally an $nd \times nd$ matrix. Throughout the rest of the paper we express the latter as a diagonal matrix with elements $\gamma$ representing the width parameter of the coherent state, which is assumed to have the same value for all particles. The phase space variables $\mathbf{Q}_0$ and $\mathbf{P}_0$ evolve according to Newton’s equations of motion corresponding to the product of three exponential operators, and $\mathbf{Q}_f$, $\mathbf{P}_f$ are the phase space variables at the end of the forward–backward evolution. At the end of the forward propagation trajectories incur position and momentum jumps [22] (originating from the exponential of the operator $A$) according to the relations

$$\delta \mathbf{Q}_f = -\frac{1}{2} \hbar \mu \frac{\delta}{\delta \mathbf{P}_f} A(\mathbf{Q}, \mathbf{P}_f), \quad \delta \mathbf{P}_f = \frac{1}{2} \hbar \mu \frac{\delta}{\delta \mathbf{Q}_f} A(\mathbf{Q}_f, \mathbf{P}_f). \quad (2.9)$$

Here $A(\mathbf{Q}, \mathbf{P})$ is the classical analogue of the operator $\hat{A}$. Note [26,27] that the position and momentum jumps in Eq. (2.9) are equal to one half of the values dictated by the actual classical equations of motion, while the action is incremented by the full amount:

$$\delta S_t = \hbar \mu A(\mathbf{Q}_t, \mathbf{P}_t) + \mathbf{P}_t \cdot \delta \mathbf{Q}_t. \quad (2.10)$$

It has been shown [26,27] that this rescaling of the position and momentum jumps compensates for the contribution of the semiclassical prefactor. The elimination of the prefactor implies that evaluation of the classical stability matrix entering the semiclassical propagator is avoided, leading to linear scaling with the number of degrees of freedom.
In the $\mu \to 0$ limit the difference between forward and backward trajectories is infinitesimal, and in this sense the derivative-FBSD expression differs from the full (double SC-IVR) semiclassical representation of the correlation function. This means that interference between distinct forward and backward trajectories is neglected. Because of this, the derivative version of FBSD cannot account for long-time quantum interference effects such as wave packet rephasing [26]. However, such long-time quantum interference is often naturally suppressed in systems with many degrees of freedom, and thus the FBSD method can provide a very accurate description of quantum dynamics in condensed phases.

The above remarks can also be used to arrive at a derivative-free form with a quasiclassical appearance. Performing some algebra brings the Heisenberg operator to the form [33,39]

$$\hat{A}_H(t) = (2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \mathcal{A}(\mathbf{Q}_0, \mathbf{P}_0) \times \left[ \frac{1 + \frac{d}{2}}{2} \right] \langle G(\mathbf{Q}_0, \mathbf{P}_0) \rangle - 2\Gamma \cdot (\hat{\mathbf{Q}} - \mathbf{Q}_0) \langle G(\mathbf{Q}_0, \mathbf{P}_0) \rangle \langle G(\mathbf{Q}_0, \mathbf{P}_0) \rangle (\hat{\mathbf{Q}} - \mathbf{Q}_0) \right].$$

(2.11)

Here dynamical information enters exclusively via the classical function $\mathcal{A}$ at the phase space point reached by a trajectory at the time $t$ of interest. Using Eq. (2.11) and regrouping vector components, the velocity autocorrelation function becomes

$$C_{VV}(t) = n^{-1} m^{-2} Z^{-1} (2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \left[ 1 + \frac{d}{2} \right] \langle G(\mathbf{Q}_0, \mathbf{P}_0) \langle e^{-\beta\mathbf{P}^2/2} \mathcal{A}(\mathbf{Q}_0, \mathbf{P}_0) \rangle \cdot \mathbf{P}_t, \right.$$

$$- 2n^{-1} m^{-2} Z^{-1} (2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \langle G(\mathbf{Q}_0, \mathbf{P}_0) \langle \hat{\mathbf{Q}} - \mathbf{Q}_0 \rangle e^{-\beta\mathbf{P}^2/2} \mathcal{A}(\mathbf{Q}_0, \mathbf{P}_0) \rangle \cdot (\hat{\mathbf{Q}} - \mathbf{Q}_0) \mathcal{A}(\mathbf{Q}_0, \mathbf{P}_0) \rangle .$$

(2.12)

According to this expression, one must propagate classical trajectories selected from a distribution obtained from the coherent state transform of an operator related to the initial density. It has been shown that the FBSD expressions are related to the Wigner quasiclassical expression [58,59] (which has also been derived by linearizing the full semiclassical expression for the correlation function [60,61]).

The main advantage of the FBSD result given in Eq. (2.12) is the possibility of evaluating the factor describing the initial preparation of the system by full quantum mechanics, leading to an exact result at zero time. A fully quantum treatment of this time-independent part is essential to capture the effects of zero-point energy and reproduce the imaginary part of a correlation function. For systems of distinguishable particles at finite temperature, the relevant density is given by the Boltzmann operator, whose discretized path integral (PI) representation [62] has been used to arrive at a PI-FBSD methodology [36]. The starting point is an expression of the Boltzmann operator $e^{-\beta H}$ as a product of $N$ exponential operators with imaginary time steps of length $\Delta \beta = \beta/N$,

$$e^{-\beta H} = \langle e^{-\Delta \beta H} \rangle^N.$$  

(2.13)

By implementing the Trotter factorization [63] of the exponential operator $e^{-\Delta \beta H}$ for sufficiently small $\Delta \beta$,

$$e^{-\Delta \beta H} \simeq e^{-\Delta \beta H_0/2} e^{-\Delta \beta H_1/2},$$  

(2.14)

and using the closure relation, one arrives at the following expression for the coherent state representation of the Boltzmann operator:

$$\langle G(\mathbf{Q}_0, \mathbf{P}_0) | e^{-\beta \hat{H}} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle = \int d\mathbf{Q}_1 \int d\mathbf{Q}_2 \cdots \int d\mathbf{Q}_N \langle G(\mathbf{Q}_0, \mathbf{P}_0) | e^{-\Delta \beta H_0/2} \mathcal{Q}_1 \rangle e^{-\Delta \beta \mathbf{P}^2/2} \mathcal{Q}_1 \rangle \times \langle \mathcal{Q}_1 | e^{-\Delta \beta H_1/2} | \mathcal{Q}_2 \rangle \cdots \langle \mathcal{Q}_N | e^{-\Delta \beta H_N/2} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle.$$

(2.15)
\[ C_{VV}(t) = n^{-1} m^{-2} (2\pi\hbar)^{nd} \int dQ_0 \int dP_0 \int dQ_1 \cdots \int dQ_N \Theta(Q_0, P_0, Q_1, \ldots, Q_N) A(Q_0, P_0, Q_1, Q_N), \]  

(2.16)

where

\[ \Theta(Q_0, P_0, Q_1, \ldots, Q_N) = Z^{-1} \langle G(Q_0, P_0) | e^{-\Delta\beta H_0/2} | Q_1 \rangle e^{-\Delta\beta V(Q_1)} \langle Q_1 | e^{-\Delta\beta H_0/2} | Q_2 \rangle \cdots e^{-\Delta\beta V(Q_N)} | G(Q_0, P_0) \rangle \]

\[ \times \langle Q_N | e^{-\Delta\beta H_0/2} | G(Q_0, P_0) \rangle \]

\[ = Z^{-1} \left( \frac{2^N}{\pi} \right) \frac{m}{m + \hbar^2 \Delta\beta} \left( \frac{m}{2\pi\hbar^2 \Delta\beta} \right)^{nd(N-1)/2} \]

\[ \times \exp \left\{ -\frac{m}{m + \hbar^2 \Delta\beta} \left( \gamma |Q_1 - Q_0|^2 + |Q_N - Q_0|^2 + \frac{i}{\hbar} \langle P_0 | (Q_1 - Q_N) + \frac{\Delta\beta}{2m} |P_0|^2 \right) \right\} \]

\[ - \frac{m}{\hbar^2 \Delta\beta} \sum_{k=2}^N |Q_k - Q_{k-1}|^2 - \Delta\beta \sum_{k=1}^N V(Q_k) \}

(2.17)

is the integrand in the Trotter-discretized path integral representation of the coherent state transform of the Boltzmann operator alone, and the function \( A \) was given in [40].

The multidimensional integral appearing in Eq. (2.16) must be performed by Monte Carlo methods. In the past we have used the modulus of the entire exponential part as the sampling function. Since the integral of this sampling function is not necessarily proportional to the partition function, one has to perform a separate Monte Carlo calculation to obtain normalized results. These procedures are detailed in [40]. A molecular dynamics sampling technique that provides efficient sampling of initial phase space and path integral variables was recently developed in our group [41].

Although the operators that enter the function \( \Theta \) (i.e., the integrand in the path integral representation of the coherent state matrix element of the Boltzmann operator) do not carry real time information, numerical evaluation of the PI-FBSD expression is complicated by the presence of slowly varying, yet oscillatory phase factors of the type

\[ \prod_{i=1}^n \exp \left[ -\frac{i}{\hbar} \frac{m}{m + \hbar^2 \Delta\beta} (r_i^{(0)} - r_N^{(0)}) \right] \]

(2.18)

that arise from the coherent state functions. For this reason, the PI-FBSD methodology based on the Trotter approximation for the short imaginary time (high temperature) propagator [36,40,65] is not so practical for condensed phase systems at low temperatures, where many path integral variables are necessary for convergence. We recently obtained an improved propagator for simple fluids based on the pair-product approximation which was developed mainly in the context of liquid helium at low temperatures [48,66]. The pair product path integral (PP-PI) approximation is accurate over larger imaginary time steps and it is found to be the most efficient method for a system with pairwise additive interactions. By allowing larger imaginary time steps, phase cancellation originating from the coherent state functions can be diminished significantly (see (2.18)) and together with the reduction in the number of path integral variables it extends the applicability of FBSD to much larger systems at very low temperature [42]. The PP relations are summarized below.

First, the coordinate matrix element of the Boltzmann operator is approximated by the relation [48,66]

\[ \langle Q_{k+1} | \exp(-\tau\hat{H}) | Q_{k+1} \rangle \approx \prod_{i=1}^n \langle r_i^{(0)} | \exp \left( -\tau\hat{H}_0^{(0)} \right) | r_i^{(0)} \rangle \prod_{i<j}^n \exp \left( -\varphi(r_i^{(0)}, r_j^{(0)}) \right). \]

(2.19)

Here \( r^{(0)} = r^{(0)} - r^{(0)} \) is the relative position vector and \( \varphi \) is an effective pair potential that produces the exact imaginary time propagator for a pair of atoms:

\[ \exp \left( -\varphi(r_i^{(0)}, r_j^{(0)}) \right) = \frac{\langle r_i^{(0)} | \exp \left( -\tau\hat{H}_{\text{int}}^{(0)} \right) | r_j^{(0)} \rangle}{\langle r_i^{(0)} | \exp \left( -\tau\hat{p}_{\text{int}}^{(0)} \right) | r_j^{(0)} \rangle}. \]

(2.20)

In the last equation \( \hat{H}_{\text{int}}^{(0)} \) and \( \hat{p}_{\text{int}}^{(0)} \) are the internal Hamiltonian and kinetic energy operators for the given pair of atoms:

\[ \hat{H}_{\text{int}}^{(0)} = \hat{T}_{\text{int}}^{(0)} + \hat{V}^{(0)}(r^{(0)}), \quad \hat{T}_{\text{int}}^{(0)} = \frac{\hat{p}^{(0)}_i^2}{2\mu}, \]

(2.21)

where \( \hat{p}^{(0)}_i \) is the momentum conjugate to \( r^{(0)}_i \) and \( M = m \) are the total and reduced mass, respectively. Also needed is the mixed coordinate-coherent state propagator. This is approximated by the relation
where the effective potential \( u \) is the coherent state analogue of \( \varphi \) and is given by the expression

\[
\exp \left( -u(r^{(j)}, r_0^{(j)}, p_0^{(j)}) \right) = \frac{\int dr^{(j)} \langle r^{(j)} | \exp \left( -\hat{H}_{\text{int}}^{(j)} \right) G(r^{(j)}, p^{(j)}) \rangle}{\langle r^{(j)} | \exp \left( -\hat{H}_{\text{int}}^{(j)} \right) G(r^{(j)}, p^{(j)}) \rangle}. \tag{2.23}
\]

The kinetic energy matrix element in the denominator of this expression is available analytically. The density matrix appearing in Eqs. (2.20) and (2.23) can be evaluated accurately by the matrix-squaring method. The reader can refer to [48] for details.

Using Eq. (2.22) we obtained in [42] a single-bead PP-FBSD expression for the momentum correlation function for an isotropic fluid. Inserting a complete set of coordinate states in Eq. (2.12), the correlation function for the total momentum vector becomes

\[
C_{\mathbf{P}}(t) = Z^{-1}(2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \int d\mathbf{Q}_1 \times \left[ \left( 1 + \frac{d}{2} n \right) \langle G(\mathbf{Q}_0, \mathbf{P}_0) | e^{-\beta \hat{H}/2} | \mathbf{Q}_1 \rangle \langle \mathbf{Q}_1 | e^{-\beta \hat{H}/2} \hat{P} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle \cdot \mathbf{P}_t \right. \\
- 2 \langle G(\mathbf{Q}_0, \mathbf{P}_0) | (\mathbf{Q} - \mathbf{Q}_0) e^{-\beta \hat{H}/2} | \mathbf{Q}_1 \rangle \cdot \langle \mathbf{Q}_1 | e^{-\beta \hat{H}/2} (\hat{P} \cdot \mathbf{P}_t) \Gamma \cdot (\mathbf{Q} - \mathbf{Q}_0) | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle \big]. \tag{2.24}
\]

The various matrix elements in this expression can be written in terms of matrix elements of the Boltzmann operator alone. For example,

\[
\langle \mathbf{Q}_1 | e^{-\beta \hat{H}/2} \hat{P} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle = i\hbar \frac{\partial}{\partial \mathbf{Q}_0} \langle \mathbf{Q}_1 | e^{-\beta \hat{H}/2} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle. \tag{2.25}
\]

The Monte Carlo sampling function is chosen as the absolute value of the exponential factor in the PP-FBSD expression.

2.2. Extension to systems of indistinguishable particles

Below we extend the FBSD method to systems of indistinguishable particles. For particles that obey Bose–Einstein or Fermi–Dirac statistics, the velocity autocorrelation function at finite temperature defined in Eq. (2.1) has the form

\[
C_{\mathbf{v}}(t) = \frac{1}{nm^{2}Z} \text{Tr} \left\{ e^{-\beta \hat{H}} \hat{\mathbf{P}} \cdot \hat{\mathbf{P}}_{\text{int}}(t) \right\}_{\text{sym}} = \frac{1}{nm^{2}Z} \text{Tr} \left\{ \hat{\mathcal{P}} e^{-\beta \hat{H}} \hat{\mathbf{P}} \cdot \hat{\mathbf{P}}_{\text{int}}(t) \right\}. \tag{2.26}
\]

Here the trace must be evaluated with respect to symmetric or antisymmetric states, depending on whether the system is composed of bosons or fermions. This constraint is expressed in the second part of Eq. (2.26) in terms of a projection operator \( \hat{\mathcal{P}} \) which guarantees that only symmetric or antisymmetric states are taken into account. The projection operator is defined as

\[
\hat{\mathcal{P}} = \frac{1}{m!} \sum_{\sigma} \mathcal{P}_{\sigma}(\hat{\sigma} \cdot \mathbf{Q}) \langle \mathbf{Q} \rangle. \tag{2.27}
\]

Here the sum is over all possible permutations \( \sigma \) (where permutation \( \sigma \sigma_{-1} \) is generated from the previous permutation \( \sigma \) by exchanging an additional pair of particles) and \( \xi \) is the parity of the permutation, i.e., \( \xi = +1 \) for bosons and \( \xi = -1 \) for fermions. In a system of bosons all particle permutations enter with the same sign, while for fermions odd permutations enter with a negative sign.

The indistinguishable particle analogue of the FBSD expression for the velocity autocorrelation function is

\[
C_{\mathbf{v}}(t) = n^{-1} m^{-2} Z^{-1} (2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \left( 1 + \frac{d}{2} n \right) \langle G(\mathbf{Q}_0, \mathbf{P}_0) | \hat{\mathcal{P}} e^{-\beta \hat{H}} \hat{\mathbf{P}} | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle \cdot \mathbf{P}_t \\
- 2n^{-1} m^{-2} Z^{-1} (2\pi\hbar)^{-nd} \int d\mathbf{Q}_0 \int d\mathbf{P}_0 \langle G(\mathbf{Q}_0, \mathbf{P}_0) | (\mathbf{Q} - \mathbf{Q}_0) \hat{\mathcal{P}} e^{-\beta \hat{H}} [\hat{\mathbf{P}} \cdot \mathbf{P}_t] \cdot \Gamma \cdot (\mathbf{Q} - \mathbf{Q}_0) | G(\mathbf{Q}_0, \mathbf{P}_0) \rangle. \tag{2.28}
\]
Exchange effects are readily included in the imaginary time path integral representation of the coherent state density. Since the total Hamiltonian commutes with the permutation operator, the latter can be inserted in front of any path integral variable. For example, Eq. (2.15) is extended to systems of identical particles as follows:

$$
\langle G(Q_0, P_0) | e^{-\beta H} | G(Q_0, P_0) \rangle = \frac{1}{n!} \sum_{\sigma} \int dQ_1 \int dQ_2 \cdots \int dQ_N \times \langle G(Q_0, P_0) | e^{-\beta H} | \hat{\sigma}_1 Q_1 ) e^{-\beta V(Q_1)} \rangle \langle Q_1 | e^{-\beta H} | Q_2 \rangle \cdots e^{-\beta V(Q_N)} \times \langle Q_N | e^{-\beta H} | G(Q_0, P_0) \rangle.
$$

The velocity autocorrelation function takes a form similar to Eq. (2.16),

$$
C_V(t) = n^{-1} m^{-2} (2\pi \hbar)^{-nd} \sum_{\ell=1}^{l} \xi_{\ell} \tilde{\theta}(Q_0, P_0, \hat{\sigma}(Q_1, \ldots, Q_N) \tilde{\lambda}(Q_0, P_0, \hat{\sigma}, Q_1, Q_N)
$$

with

$$
\tilde{\theta}(Q_0, P_0, \hat{\sigma}, Q_1, \ldots, Q_N) = Z^{-1} \langle G(Q_0, P_0) | e^{-\beta H}^{1/2} | \hat{\sigma}, Q_1 ) e^{-\beta V(Q_1)} \rangle \langle Q_1 | e^{-\beta H} | Q_2 \rangle \cdots e^{-\beta V(Q_N)} \times \langle Q_N | e^{-\beta H} | G(Q_0, P_0) \rangle
$$

$$
= Z^{-1} \left( \frac{2\gamma}{\pi} \right)^{nd/2} \left( \frac{m}{m + \hbar^2 \Delta \beta} \right)^{nd/2} \left( \frac{m}{2 \pi \hbar^2 \Delta \beta} \right)^{nd(N-1)/2} \times \exp \left\{ -\frac{m}{m + \hbar^2 \Delta \beta} \left( \gamma \| \hat{\sigma} Q_1 - Q_0 \|^2 + \gamma \| Q_N - Q_0 \|^2 + \frac{i}{\hbar} P_0 \cdot (\hat{\sigma}, Q_1 - Q_N) + \frac{\Delta \beta}{2m} | P_0 |^2 \right) - \frac{m}{2 \hbar \Delta \beta} \sum_{k=2}^{N} | Q_k - Q_{k-1} |^2 - \Delta \beta \sum_{k=1}^{N} V(Q_k) \right\}.
$$

The integrals over path integral and coherent state variables and the sum over particle permutations are performed simultaneously using the Metropolis Monte Carlo method. As discussed in the first part of this section, the path integral representation of the Boltzmann operator in a coherent state basis is isomorphic to an open necklace, introducing an oscillatory phase in the integrand of the FBSD expression. In the case of Boltzmann statistics the path integral necklace collapses to a single bead in the $N=1$ (single bead) limit, and thus the oscillatory factor disappears in this case, allowing maximal sampling efficiency. As seen from Eq. (2.31), this is not the case when identical particle exchange effects are taken into account; the imaginary term in the exponential factor does not vanish in this case, leading to phase cancellation even in the single bead limit.

The same remarks apply to the identical particle generalization of the PP-FBSD methodology. The calculations reported in Section 3 generally required somewhat longer Monte Carlo steps in the case of identical bosons compared to simple Boltzmann statistics. The oscillatory character of the integrand becomes milder at higher temperature, where the identity permutation is dominant.

As is well known, the sign problem is very severe in the case of fermions, even for equilibrium calculations. This feature of alternating sign associated with the interchange of particles can be much more prohibitive than the oscillatory factor originating from the coherent state representation. We note that this FBSD method for fermions can be practical if we employ advanced imaginary time path integral method developed in the equilibrium calculations (e.g. restricted path integral methods [67]).

3. Applications

The accuracy of the FBSD approximation to time correlation functions has been tested extensively on systems obeying Boltzmann statistics. In spite of its inability to capture quantum coherence effects, FBSD (with an accurate evaluation of the coherent state matrix element of the Boltzmann operator) was shown to be essentially quantitative in many-particle systems where quantum interference is naturally suppressed. However, the accuracy of the FBSD methodology in systems that obey quantum statistics, in particular its ability to describe effects associated with
Bose–Einstein condensation or superfluid behavior, must be carefully assessed before the scheme can be applied to real quantum fluids. In the first part of this section we undertake such test calculations using models treatable by numerically exact procedures. In the second part of the section we demonstrate the application of the methodology to Bose fluid with Lennard-Jones interactions.

3.1. Non-interacting models

The model system consists of non-interacting one-dimensional particles \((d=1)\) in an external confining potential given by the form

\[
\hat{H} = \sum_{i=1}^{n} \left[ \frac{\hat{p}_i^2}{2m} + V(\hat{x}_i) \right], \quad V(x) = \frac{1}{2} m \omega^2 x^2 - \frac{1}{10} x^3 + \frac{1}{10} x^4
\]  

(3.1)

with \(m=1\), \(\omega = \sqrt{2}\). Numerically exact results for this system were generated using a basis set procedure. This can be simply done by solving one-dimensional Schrödinger equation for single particle and constructing the eigenstates of many-particle system with the appropriate symmetry. The results of the basis set calculations are presented in Figs. 1–3, where they are also compared to those obtained with the FBSD methodology. The FBSD calculations were

![Figure 1](image1.png)  
(a) (b)

**Fig. 1.** Velocity autocorrelation function for a system of \(n=10\) non-interacting particles with the Hamiltonian given in Eq. (3.1) for \(\hbar\omega = \sqrt{2}/2\). Solid and dashed lines show real and imaginary parts from basis set calculations. Filled and hollow markers show real and imaginary parts of PI-FBSD calculations with \(N=3\). (a) Boltzmann statistics and (b) Bose statistics.

![Figure 2](image2.png)  
(a) (b)

**Fig. 2.** Velocity autocorrelation function for a system of \(n=10\) non-interacting particles with the Hamiltonian given in Eq. (3.1) for \(\hbar\omega = \sqrt{2}\). Solid and dashed lines show real and imaginary parts from basis set calculations. Filled and hollow markers show real and imaginary parts of PI-FBSD calculations with \(N=6\). (a) Boltzmann statistics and (b) Bose statistics.
performed with the Trotter-discretized PI representation of the coherent state matrix element and converged with \( N = 3 \) imaginary time slices for \( \hbar \omega = \sqrt{2}/2 \) and \( N = 6 \) times slices for \( \hbar \omega = \sqrt{2} \). For this system of non-interacting particles the results are independent of the number of particles in the case of Boltzmann statistics. Calculations onbosons employed \( n = 10 \) particles. In this case particle exchange makes phase oscillation only slightly more severe compared to the corresponding system in the Boltzmann statistics, and convergence of the PI-FBSD calculation was relatively straightforward. On the other hand, the PI-FBSD calculations for the fermion system were much more demanding due to the well-known problem associated with terms of alternating signs. Results on fermions are presented for \( n = 3 \). We note that for non-interacting fermions advanced techniques such as that introduced in [46] will help reduce the problem associated with alternating signs, but we do not elaborate on this point in this paper. Fifty million Monte Carlo steps per particle were used for the calculations of 10 bosons and two million steps per particle are used for three fermions.

The results presented in Figs. 1–3 show very clearly the effects of particle exchange. The correlation function of the boson system decays slower. This behavior indicates the onset of Bose condensation; particle exchange causes bosons to prefer a lower energy state, where the dynamics is more heavily dominated by a single frequency corresponding to the difference between ground and first excited levels. This effect also results in a slight red shift in the oscillation pattern of the correlation function with respect to that obtained for Boltzmann particles, as the frequency of this potential has its lowest value near the minimum. The correlation function of the boson system resembles that of the same system under Boltzmann statistics at a lower temperature. The opposite trends are observed for the fermion system in Fig. 3. In this case Pauli exclusion causes the particles to occupy higher energy states, leading to the presence of more frequency components in the correlation function (which are responsible for its faster decay) and a slight blue shift.

As is seen from Figs. 1–3, the PI-FBSD results are in very good agreement with those obtained through accurate basis set calculations for the initial two or three oscillation periods. Eventually, the FBSD correlation function decays faster than that obtained through quantum mechanical propagation in all cases, in line with observations derived from earlier calculations. We note that the strongly anharmonic system which lacks potential interactions represents the “worst case scenario” for FBSD, as quantum coherence effects are not damped via dephasing processes and thus are most prominent in this system. The fact that the accuracy of the FBSD approximation does not deteriorate when the effects of quantum statistics are included is very encouraging. Based on the demonstrated validity of PI-FBSD for these systems we proceed to a calculation on a system of interacting bosons.

3.2. System of interacting bosons

We consider a two-dimensional (\( d = 2 \)) Lennard-Jones (LJ) Bose fluid whose parameters are set to resemble helium systems (\( \sigma = 2.556 \, \text{Å} \), \( \varepsilon = 10.22 \, \text{K} \), \( m = 6.65 \times 10^{-27} \, \text{kg} \)). Two-dimensional helium films are known to exhibit the effects of Bose statistics, such as superfluidity, at low temperatures [68]. This calculations were performed with the PP-FBSD methodology under minimum image periodic boundary conditions, where each cell consists of 25 Bose particles. In
order to check the convergence with respect to the size of the unit cell we repeated the imaginary time PIMC calculations for a larger system. This calculation concluded that the calculated static properties are well converged for $n = 25$ and that this size of the unit cell is sufficiently large for the calculation of the velocity autocorrelation function. We choose the state point characterized by $T^* = k_B T / e = 0.05$, $\rho^* = \rho \sigma^2 = 0.3$. Around this state point this system is in a liquid phase. Since the thermal de Broglie wavelength at this condition is comparable to the range of interaction, the paths of many particles can be linked together frequently due to the effects of exchange. Fig. 4 shows a snapshot of the typical path configuration. One can observe long paths winding across the unit cell.

Fig. 4. Snapshot of a typical path configuration for the system of Lennard-Jones bosons at $T^* = 0.05$. The red line represents a path winding across the unit cell.

Fig. 5. The normalized velocity autocorrelation function of two-dimensional Lennard-Jones fluid at $T^* = 0.05$. The solid lines show the real and imaginary parts of the correlation function for the boson system, while the dashed lines show results for the same system with Boltzmann statistics.
We employ the pair-product density matrix in the coordinate and mixed coordinate-coherent state representations at $T^* = 2$ as a high temperature form and thus $N = 39$ time steps are used in the calculation. Both the integral over path integral and coherent state variables and the sum over permutations are performed using the Metropolis Monte Carlo method. The equations of motion for classical trajectories were solved using the velocity Verlet algorithm with a time step equal to $\Delta t = \Delta t \sqrt{\hbar / m / \sigma} = 1.4 \times 10^{-3}$. All calculations were performed on an Athlon PC cluster with 16 nodes.

Fig. 5 shows the velocity autocorrelation function for the LJ Bose fluid. The correlation function for a system obeying Boltzmann statistics under the same conditions is also shown for comparison. Due to the strong repulsive interactions, the difference between two statistics is relatively subtle. However, as can be seen, the PP-FBSD correlation function of the Bose fluid exhibits a faster initial decay compared to that of the system obeying Boltzmann statistics. This can be attributed to the additional attractive interaction between particles originating from the Bose statistics.

4. Discussion and concluding remarks

In this paper we extended the PI-FBSD methodology to systems of indistinguishable particles obeying Bose–Einstein or Fermi–Dirac statistics. Even though exchange effects enter as additive terms in the case of bosons, the interchange of coordinates prevents cancellation of the phase associated with the coherent state functions even in the single bead limit. For this reason, PI-FBSD (and also the very efficient single-bead PP-FBSD methodology) generally converges slower if identical particle exchange effects are included. Nevertheless, application to a two-dimensional Lennard-Jones Bose fluid with a unit cell containing 25 atoms showed that such calculations are still feasible in condensed phase systems.

The validity and accuracy of the FBSD approximation in systems with such prominent quantum effects was unclear when we began this project. The comparison of the PI-FBSD results against those given by accurate basis set calculations demonstrated conclusively that the accuracy of FBSD is no worse in these highly quantum mechanical systems than it is in similar systems obeying Boltzmann statistics. This surprising observation can be attributed to the redundancy of particle exchange at various places along a Feynman path. Imagine, for example, performing the calculation using the path integral representation of the real time evolution (rather than a classical trajectory treatment). Although particle exchange may be dramatic, it need to be taken into account only at a single point along each path; thus, coordinates must be interchanged only within a single bead, which may be chosen as the endpoint of the Feynman path representing the Boltzmann operator. Since no particle exchange is necessary within real time paths, it is evident that when the conditions are such the stationary phase (FBSD) approximation to the dynamics is adequate, the present scheme will lead to accurate time evolution.

In conclusion, we hope that the extended PI-FBSD methodology will allow the rigorous and accurate computational modeling of dynamical processes in bosonic fluids. We are currently performing PI-FBSD calculations on liquid helium using accurate interaction potentials [69], attempting to obtain a better understanding of the dynamical manifestations of Bose–Einstein condensation and superfluidity.

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References
