Path integral formulation of centroid dynamics for systems obeying Bose–Einstein statistics

Nicholas V. Blinov and Pierre-Nicholas Roy
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

Gregory A. Voth
Department of Chemistry and Henry Eyring Center for Theoretical Chemistry, University of Utah, Salt Lake City, Utah 84112-0850

(Received 4 May 2001; accepted 20 June 2001)

This paper presents a formal foundation for the recent extension [J. Chem. Phys. 110, 3647 (1999)] of the centroid molecular dynamics (CMD) method to systems obeying Bose–Einstein statistics. It is shown that the introduction of centroid phase space coordinates corresponding to individual physical particles allows one to obtain (exact) canonical averages within the framework of the bosonic CMD method. It is also shown that formally exact expressions for quantum mechanical Kubo transformed correlation functions can be written in terms of individual particle centroids and that a CMD approximation can be introduced. Calculations for a bosonic trimer are used as an illustration of the new concepts introduced in this work. © 2001 American Institute of Physics. [DOI: 10.1063/1.1392355]

I. INTRODUCTION

Statistical mechanics provides many powerful theoretical methods to treat many-particle systems, but a nonperturbative description of the quantum dynamics of real systems taking into account finite temperature and exchange effects still remains a great challenge. Recent experimental results on the spectroscopy of molecules embedded in ultra cold helium nanodroplets, have stimulated extensive theoretical development aimed at the understanding of the observed phenomena. The theoretical analysis of the equilibrium properties of such extremely quantum systems mostly involves diffusion and path integral Monte Carlo calculations. A direct use of the Monte Carlo method for dynamical calculations is precluded by the so-called sign problem arising from the oscillatory nature of the quantum mechanical real time propagator. One can nevertheless take advantage of microscopic calculations within the Monte Carlo method combined with a classical-like approximation for dynamics in the framework of the centroid molecular dynamics (CMD) method. This approach is based on the concept of the centroid of a Feynman path. This quantity corresponds to the center of mass of an isomorphic classical cyclic polymer representing a quantum mechanical particle obeying Boltzmann statistics in the discretized path integral picture. The effective potential, defined on the basis of the centroid density, incorporates finite temperature and quantum effects and allows one to express the equilibrium averages of physical observables in a classical-like form.

As shown by Cao and Voth, the dynamics of the centroid in the field of the effective potential can also be used to extract approximate information on the real time dynamics of quantum systems. More precisely, quantum mechanical Kubo transformed correlation function can be approximated by the centroid correlation function if one of the observables entering in the correlation function is a linear operator in position and/or momentum. The CMD method has recently been rigorously analyzed using the operator formalism suggested by Jang and Voth. It has also been shown that the CMD method for correlation function can be extended to the case of such functions involving nonlinear operators. The application of the CMD approach to real systems exhibiting strong quantum effects has yielded very encouraging results compared to experiment. It should be noted that the CMD approach can also be used in conjunction with the maximum entropy method to describe quantum mechanical real time dynamics under conditions when the CMD approximation fails at long times. The extension of the CMD method to systems obeying Bose–Einstein and Fermi–Dirac quantum statistics allows one to take into account quantum exchange effects within the framework of classical-like molecular dynamics calculations. This very attractive feature has generated considerable interest in the development of a Bose–Einstein centroid molecular dynamics (BECMD) and Fermi-Dirac centroid molecular dynamics (FDCMD). The first definition of the centroid density for many-particle systems consisting of bosons or fermions has been introduced by Roy and Voth. They also demonstrated that the bosonic and fermionic CMD methods provides accurate results for a model system consisting of two identical bosons or fermions in an anharmonic potential. An analogous definition of the centroid density was later used in the context of path integral molecular dynamics (PIMD) calculations based on the concept of the so-called permutation potential.

Although important steps have been taken towards a usable BECMD framework, several questions remain to be addressed regarding the formulation of the method in a way that is amenable to the computer simulation of complex problems of chemical and physical interest. From a theoretical point of view, it is important to introduce the BECMD
method starting from an exact quantum mechanical formulation that will allow one to clarify the nature of the BECMD approximations. From the standpoint of the numerical implementation, one needs to develop efficient algorithms for the calculation of the centroid force entering into the BECMD equations of motion.

The main goals of this work are: (i) to prove that centroid variables corresponding to physical observables can be introduced for a bosonic system in the same way as for Boltzmann statistics; (ii) to show that equilibrium averages of operators can be expressed in terms of the bosonic centroid dynamics; (iii) to show that quantum mechanical Kubo transformed correlation functions can be approximately expressed in terms of the bosonic centroid density; (iv) to justify the BECMD method based on a set of physical assumptions regarding the exact quantum dynamics.

This paper is organized as follows: In Sec. II, the path integral formulation of the centroid molecular dynamics method is briefly outlined. Centroid variables corresponding to physical observables are introduced in Sec. III and the bosonic CMD method is used to express the equilibrium average of quantum mechanical operators. It is shown in Sec. IV that quantum mechanical Kubo transformed correlation functions can be approximately written in terms of centroid coordinates associated with individual bosonic particles. Details on numerical implementation and results for a trimer system are presented in Sec. V. Concluding remarks are presented in Sec. VI.

II. CENTROID VARIABLES AND THE CMD METHOD

The theoretical basis for both the regular (Boltzmann) CMD and bosonic (Bose–Einstein) CMD methods is Feynman’s formulation of statistical mechanics in terms of imaginary time path integrals. In this approach, a matrix element of the density operator corresponding to a quantum mechanical system obeying Boltzmann statistics can be written in the coordinate representation as a sum over all (open) imaginary time paths \( q(\tau) \) connecting the points \( q \) and \( q' \) in configuration space (units with \( \hbar = 1 \) are used throughout this paper)

\[
\rho(q,q';\beta) = \int_{q(0)=q}^{q(\beta)=q'} Dq(\tau) \exp \{-S[q(\tau)]\},
\]

where

\[
S[q(\tau)] = \int_{0}^{\beta} \left\{ \frac{m}{2} \dot{q}(\tau)^2 + V[q(\tau)] \right\} d\tau
\]

is the Euclidean imaginary time action functional, \( \beta = (\hbar \kappa T)^{-1} \) is the inverse temperature, \( m \) is the mass of the particle, and \( V(q) \) is the interaction potential. It should be noted that both \( \beta \) and \( \tau \) have dimensions of time when \( \hbar = 1 \). The partition function is the trace of the density operator and is given in the path integral representation as the sum of weighted exponents of the imaginary time action over all closed \( [q(\beta)=q(0)] \) paths,

\[
Z = \int Dq \rho(q,q;\beta) = \int_{q(\beta)=q(0)} Dq(\tau) \exp \{-S[q(\tau)]\}.
\]

One can now include the integration over the ends of the path in the definition of the path integral and denote the sum over all (closed) imaginary time paths as \( \int_{q(\beta)=q(0)} Dq(\tau) \). In the high temperature limit, the closed paths collapse to a point (the position of the classical particle). They correspond to the quantum mechanical spreading of the particle at finite temperatures. Based on this property of imaginary time paths, Feynman suggested that a quantum system could be described in a classical-like manner using the centroid (“center of mass”) of the imaginary time trajectory of a particle.

\[
q_0 = \frac{1}{\beta} \int_{0}^{\beta} d\tau q(\tau).
\]

A formally exact expression for the partition function in terms of the centroid coordinates, \( q_c \), can be obtained by integrating Eq. (3) over all paths with a fixed centroid first, and then over all possible centroid configurations, i.e.,

\[
Z = \int dq_c \int_{q(\beta)=q(0)} Dq(\tau) \delta(q_c - q_0) \exp \{-S[q(\tau)]\} \rho_c(q_c)
\]

\[
= \int dq_c \rho_c(q_c),
\]

where the \( \delta \)-function in the above equation sets the centroid constraint on the imaginary time paths, and the path integral in this expression defines the centroid density. Using the above result, one can rewrite the equation for the partition function in the following classical-like manner,

\[
Z = \left( \frac{m}{2 \pi \beta} \right)^{1/2} \int dq_c e^{-\beta V_{\text{eff}}(q_c)},
\]

where the effective potential has been introduced by the definition \( V_{\text{eff}}(q_c) = -\ln[(2\pi\beta/m)^{1/2} \rho_c(q_c) \beta] \). In the high temperature limit, \( V_{\text{eff}} \) coincides with the classical potential energy. At finite temperatures, very accurate approximations for \( V_{\text{eff}} \) can be obtained. In connection with the classical limit, it is convenient to include the free particle normalization factor from the above equation in the definition of the configurational centroid density \( \rho_c(q_c) \), and such a normalization will be used throughout this paper.

An important extension of Feynman’s ideas is the concept of centroid dynamics. This provides a way to evaluate quantum mechanical real time correlation functions for systems obeying Boltzmann statistics. Indeed, the quantum mechanical Kubo transformed correlation function for the operators \( \hat{A} \) and \( \hat{B} \) can be expressed in terms of the centroid coordinates as,

\[
\langle \hat{B}(\hat{A}(t)) \rangle_{\text{Kubo}} = \frac{1}{Z} \int_{0}^{\beta} d\tau \text{Tr} \left\{ e^{-\alpha \hat{H}} \hat{B} e^{-\beta \hat{H}} e^{i\beta\hat{H}} \hat{A} e^{-i\alpha\hat{H}} \right\}
\]

\[
= \int_{-\infty}^{+\infty} dp_c dq_c \frac{\rho_c(p_c,q_c)}{Z} B_c A_c(t),
\]

where \( A_c \) and \( B_c \) are the centroid variables of the corresponding quantum mechanical operators, and the phase space centroid distribution function is given by \( \rho_c(p_c,q_c) \).
\[ e^{-\beta \hat{H}/2m} \rho_s(q_s) \]. If the physical observable \( \hat{B} \) is a linear function of the position and/or momentum operators, Eq. (7) is exact if \( A_s(t) \) is propagated exactly. For a nonlinear operator \( \hat{B} \), the concept of centroid dynamical correlation functions has been extended in a recent publication.19

Within the framework of the CMD approximation, the nonstationary centroid variables coincide with their stationary counterparts, and depend on time through the centroid momenta and positions only. Their dynamics are governed by classical equations of motion with the effective potential \( V_{eff} \) defined above. The explicit expression for the stationary centroid variable corresponding to the operator \( \hat{A} \) is

\[
A_s(p_c, q_c) = \frac{2 \pi}{\rho_s(p_c, q_c)} \int Dp_0 Dq_0 \delta(p_c-p_0) \delta(q_c-q_0) \times \left[ \frac{1}{\beta} \int_0^\beta A(q(\tau)) d\tau \right] \exp\{-S[p(\tau), q(\tau)]\}. \tag{8}
\]

where the momentum centroid is defined as \( p_0 = (1/\beta) \int_0^\beta d\tau p(\tau) \), \( S[p(\tau), q(\tau)] \) is the phase space Euclidean action (see Appendix A), and the path integral is taken over all closed paths in phase space. An analogous equation exits for \( B_c \). It should be noted that the equilibrium average of physical observables can be expressed in terms of the centroid density defined in configuration space, but it is important to introduce the centroid dynamics in phase space to correctly treat quantum mechanical real time correlation functions.17

III. THE BOSONIC CMD METHOD: EQUILIBRIUM AVERAGES

In this section, centroid variables corresponding to quantum mechanical operators are defined in terms of the centroid coordinates associated with individual particles, and it is shown that equilibrium averages of physical observables can be written in terms of the centroid density for systems obeying Bose–Einstein statistics.

Introducing the centroid coordinates for systems consisting of identical particles, and extracting the contribution of the paths with fixed centroid in the path integral representing the partition function, will allow one to define the bosonic centroid density. This, in turn, allows one to define an effective potential that includes finite temperature and quantum exchange effects. The definition of the centroid variables in the case of non-Boltzmann statistics is, however, not straightforward. Moreover, different definitions coinciding with the obvious symmetry requirement are possible. For Bose–Einstein systems which are the focus of the present work, all physical observables are symmetric with respect to the permutation of particle labels, and the definition of the centroid density should reflect this symmetry. Nevertheless, from the point of view of both a theoretical description and of numerical implementation of the bosonic CMD method, it is important to define the centroid density in terms of centroid coordinates corresponding to individual physical particles.

For quantum mechanical systems consisting of identical particles, only symmetrized (in the case of Bose–Einstein statistics) or antisymmetrized (Fermi–Dirac statistics) states contribute to the density matrix. For the particular case of bosonic particles, the density matrix can be obtained as a result of a symmetrization of the density matrix \( \rho(q, q'; \beta) \) corresponding to distinguishable particles

\[
\rho^B(q, q'; \beta) = \frac{1}{N!} \sum_p \rho(q, \mathcal{P} q'; \beta), \tag{9}
\]

where the sum is taken over all possible permutations of the \( N \) identical particles. For simplicity, vector notation is used hereafter whenever possible; for the general case of a many-particle system consisting of \( N \) atoms, \( q \) and \( p \), for example, will denote the vectors of the positions and momenta of all particles: \( q = (q_1, q_2, \ldots, q_N) \) and \( p = (p_1, p_2, \ldots, p_N) \). The partition function is obtained from the expression

\[
Z = \int dq \rho^B(q, q; \beta) = \frac{1}{N!} \sum_p \int_{q(\beta) = \mathcal{P} q(0)} Dq(\tau) \exp\{-S[q(\tau)]\}, \tag{10}
\]

where the path integral representation has been used for the matrix elements of the density matrix in the position representation. Every term in the above sum corresponds to a fixed permutation of the end point of the imaginary time paths. As a result, not only closed paths corresponding to each individual particle contribute to the density matrix, but also the paths connecting any combination of particles depending on the particular type of permutation.

The expression for the partition function can be written in terms of the centroid density, generalized to the case of Bose–Einstein statistics, after explicitly pulling out an integration over fixed centroid in Eq. (10). The result is given by the equation similar to Eq. (5), but with the conventional centroid density replaced with its Bose–Einstein statistics analog defined as

\[
\rho^B_c(q_c) = \left( \frac{2 \pi \beta}{m} \right)^{3N/2} \lim_{\epsilon \to 0^+} \sum_p \int_{q(\beta) = \mathcal{P} q(0)} Dq(\tau) \times \delta(q_c - q^c) e^{-\beta S[q(\tau)]}, \tag{11}
\]

where \( q^c_0 = (1/\beta) \int_0^\beta d\tau q(\tau) \) is the centroid of the imaginary time path and the normalization factor is chosen for compatibility between the phase space formulation of bosonic centroid dynamics and the classical limit. It should be noted that taking the limit \( \epsilon \to 0^+ \) in Eq. (11) after evaluating the path integral guarantees that the centroid position corresponds to the unpermuted paths of the physical particles.

It is demonstrated below that the equilibrium average of any physical observable can be written as an average of the corresponding centroid variable over the phase boson centroid density \( \rho^B_c(p_c, q_c) = e^{-\beta \hat{H}/2m} \rho^B_c(q_c) \). It should be noted that the description of real time dynamics in terms of centroid variables is essentially based on the concept of the phase space centroid, while equilibrium averages can be en-
tirely expressed in terms of position centroids. However, the phase space formulation is used here even for the equilibrium case. This is done to highlight the fact that the BECMD method can be used to calculate the equilibrium properties of bosonic systems.

The standard expression for the thermal average value of the quantum mechanical observable \( \hat{A} \) is given by,

\[
\langle \hat{A} \rangle = \text{Tr} \{ \hat{A} \rho \} / Z = \frac{1}{Z} \int dq \int dq' \rho^B(q,q';\beta) \langle q | \hat{A} | q' \rangle ,
\]

(12)

where \( \langle q | \hat{A} | q' \rangle \) is a matrix element of the operator \( \hat{A} \), and the subscript \( s \) denotes that the trace is taken over totally symmetric states only. Using the phase space path integral representation for the bosonic density matrix and pulling out the integration over position and momentum centroids yields

\[
\langle \hat{A} \rangle = \frac{1}{ZN!} \int \frac{dp_c dp_{c'}}{(2 \pi)^{3N}} \int dq \int dq' \rho^B(p_c,q_c;q,q') 
\times \langle q | \hat{A} | q' \rangle ,
\]

(13)

where the bosonic reduced density matrix is introduced as

\[
\rho^B(p_c,q_c;q,q') = (2 \pi)^{3N} \sum_p \lim_{e \to 0+} \int_{q(0)=q}^{q(\beta)=p q' - q} \mathcal{D}p(\tau) \mathcal{D}q(\tau) 
\times \delta(p_c - p_0) \delta(q_c - q_0^c) e^{-S[p(\tau),q(\tau)]},
\]

(14)

This expression is a Bose–Einstein statistics generalization of the centroid-constrained conventional reduced density matrix, and corresponds to a matrix element of the unnormalized quasidensity operator, also known as a static-force density matrix or constrained propagator. The dependence of the reduced density matrix on the centroid momentum can be found in explicit form. The result is (see Appendix A for details)

\[
\rho^B(p_c,q_c;q,q') = \sum_p \exp \left\{ -\beta \left[ p_c - \frac{m}{\beta} (p q' - q) \right]^2 / 2m \right\} 
\times \rho(q_c;q,p q'),
\]

(15)

where \( \rho(q_c;q,p q') \) is the position reduced density matrix. An explicit relationship between this expression and the quasidensity operator is given in Appendix A.

For the case of Boltzmann statistics, one can define the phase space centroid density as a sum of the diagonal matrix elements of the reduced density matrix. As can be seen from Eq. (15), the direct generalization of this approach to Bose–Einstein statistics leads to an expression for the density matrix which does not factorize into parts depending on position and momentum centroids only. The consequence of such a definition will be addressed in future work, but one can show that Eq. (13) can be written in terms of the phase space centroid density matrix. Indeed, substituting the expression for the reduced centroid density from Eq. (15) into Eq. (13), changing variables according to \( p_c \to p_c - i (m/\beta) (p q' - q) \), and taking into account the fact that shifting the path of integration over the new centroid momentum back to the real axis does not change the result of integration, allows one to express the average of the operator \( \hat{A} \) in the following form

\[
\langle \hat{A} \rangle = \frac{1}{N!} \int \frac{dp_c dp_{c'}}{(2 \pi)^{3N}} \rho^B(p_c,q_c) \int dq(f) \mathcal{D}q(f) 
\times \delta(\tilde{q}_c - \tilde{q}_0^c) A_c(q_c) e^{-S[q(\tau)]},
\]

(16)

where, for the particular case of physical observables depending on the position operator, the centroid variable is given by the following equation:

\[
A_c(q_c) = \frac{1}{\rho^B(q_c)} \left( \frac{2 \pi \beta}{m} \right)^{3N/2} \sum_f \lim_{e \to 0+} \int_{q(\beta)=p q' - q}^{q(0)=q} \mathcal{D}q(\tau) 
\times \delta(q_c - \tilde{q}_0^c) A(q(0)) e^{-S[q(\tau)]},
\]

(17)

In contrast with the case of distinguishable particles, the matrix elements of the operator in this definition should be evaluated at the starting-point of the path \( q(0) \) and cannot be replaced by the path average \( (1/\beta) \int A(q(\tau)) d\tau \). This is a direct consequence of the centroid definition for bosonic systems introduced above. It is also quite different from the case of regular averages of physical observables in the path integral picture, where permutations can be applied to the path at every imaginary time slice as a result of the translational symmetry along the paths. It should also be noted that if one applies Eq. (17) to the particle position or momentum operator, the result is not the position or momentum centroid of the individual particle. Rather, it is an admixture of the particle centroids due to the permutation operation. The centroid variables corresponding to physical observables depending on momentum operators can also be found as a function of the centroid positions and momenta. As an example, the expression for the centroid kinetic energy is derived in Appendix B.

The above definitions of the centroid density and centroid representations of operators allow one to replace the phase space average over the centroid position and momentum configurations with the time average along centroid "trajectories." Indeed, one can rewrite Eq. (16) in a classical-like form,

\[
\langle \hat{A} \rangle = \frac{1}{Z} \int \frac{dp_c dp_{c'}}{(2 \pi)^{3N}} e^{-\beta(p_{c'}^2/2m + V_{\text{eff}}(q_c))} A_c ,
\]

(18)

where the effective centroid potential is defined by the equation \( V_{\text{eff}}(q_c) = -\ln \rho^B(q_c) / \beta \). With the additional assumption of ergodicity, one obtains

\[
\langle \hat{A} \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A_c(p_c(t),q_c(t)) dt ,
\]

(19)

where \( q_c(t) \) and \( p_c(t) \) are the centroid positions and momenta calculated along the centroid trajectories. In order that Eqs. (18) and (19) are equal in the ergodic limit, the equations of motion for the centroids are assumed to be given by

\[
p_c(t) = F_c(q_c(t)) / m , \quad p_c(t) = F_c(q_c(t))
\]

(20)
with the centroid force $F_c(q_c)$ given by the following equation:

$$
F_c(q_c) = \frac{1}{\beta} \frac{\partial \ln \rho^B_c}{\partial q_c} = \frac{1}{\rho^c_c(q_c)} \left( \frac{2 \pi \beta}{m} \right)^{3N/2} \sum_{q} \lim_{\varepsilon \to 0} \int_{q(q) = \varepsilon_0 + q} Dq(\tau) 
\times \beta \delta(q_c - q_0) \left[ - \frac{1}{\beta} \int_0^\beta \delta S[q(\tau)] \frac{d\tau}{\beta} \right] e^{-S[q(\tau)]} 
= - \left( \frac{\partial S[q(\tau)]}{\partial q_c(\tau)} \right) \rho^c_c, \quad (21)
$$

where $\delta S[q(\tau)] / \partial q_c(\tau)$ denotes the functional derivative with respect to particle position along the imaginary time path. Note that proper thermostating has to be applied during the dynamical calculations to guarantee the correct sampling of the canonical-like distribution given in Eq. (18). In contrast with the case of Boltzmann statistics, $\delta S[q(\tau)] / \partial q_c(\tau)$ does not reduce to the derivative of the potential energy, but also includes additional terms arising from the kinetic part of the imaginary time action and from the effects of particle exchange (see Appendix C). It should be noted that Eq. (20) is not derived from the quantum Liouville equation as in the case of Boltzmann statistics [i.e., Eqs. (41) and (42) of Ref. 17].

Equations (20) and (21) will be referred to as Bose–Einstein centroid molecular dynamics (BECMD) equations. It should be noted that no approximations have yet been made as long as one is only concerned with equilibrium averages. Of course, there are no simplifications of the original quantum mechanical problem of the calculation of such averages of physical observables for many-particle systems because the evaluation of the centroid force according to Eq. (21) involves an exact quantum mechanical calculation. This formalism has, however, very attractive features regarding its amenability to computer simulations and can be used as a basis for different numerical implementations, including Monte Carlo calculations (centroid force) and dynamical calculations (centroid dynamics).

Recently, a path integral molecular dynamics method (PIMD) taking into account the effects of quantum statistics through the so-called permutation potential has been proposed. In its exact formulation, the approach developed by Kinugawa et al. gives the same result as the BECMD method first suggested in Ref. 28 and being the topic of the present work. The approach developed in Ref. 39 is also based on the concept of a permutation potential. Besides the technical details and approximations made, this approach differs from the former one by the symmetrization of the permutation potential over the imaginary time slices. Of course, in the absence of a centroid constraint, these approaches are equivalent due to the invariance of the path integral expression of the partition function with respect to the translations along the imaginary time axis, but the applicability of the symmetrized version of the permutation potential for dynamical calculations within a centroid framework has yet to be demonstrated.

IV. THE BOSE–EINSTEIN CMD METHOD: REAL TIME CORRELATION FUNCTIONS

In this section, it is shown that in the case of Bose–Einstein statistics, an exact quantum mechanical Kubo transformed correlation function can be approximately expressed in terms of centroid coordinates corresponding to individual physical particles. A further approximation to the time evolution of the centroid coordinates analogous to the CMD method for Boltzmann statistics can then be made although some additional restrictions due to the permutation symmetry must be taken into account.

The Kubo transformed correlation function for a bosonic system is given by the following equation:

$$
\langle \hat{A}(t) \rangle_{Kubo} = \frac{1}{Z} \int_0^\beta da \ Tr[\hat{e}^{-\beta (\hat{H} - \hat{B})} \hat{A} e^{-\beta \hat{H} / 2} e^{-i \hat{H} t}], \quad (22)
$$

where the subscript $s$ denotes that the trace is taken over totally symmetric states only. Evaluating the trace from the above equation in the coordinate representation, using the path integral expression for the matrix elements of the density matrix, and after some algebra, gives

$$
\langle \hat{A}(t) \rangle_{Kubo} = \frac{1}{Z} \int dq \int dq' \langle q|\hat{A}(t)|q'\rangle 
\times \frac{1}{N!} \sum_p \int_q \frac{d\rho}{(2\pi)^{3N}} \frac{d\rho}{(2\pi)^3} \int \frac{d\tau}{\beta} \int_0^\beta d\tau B(q(\tau)) e^{-S[p(\tau),q(\tau)]}, \quad (23)
$$

where for the sake of simplicity it is assumed that the physical observable $\hat{B}$ depends only on position, but no restrictions were imposed to the operator $\hat{A}(t) = e^{i \hat{H} t} e^{-i \hat{H} t}$.

Decomposing the path integral in this equation into a sum over the phase space centroids corresponding to individual particles and over all paths with fixed centroids, yields

$$
\langle \hat{A}(t) \rangle_{Kubo} = \frac{1}{ZN!} \int \frac{dp_c dq_c}{(2\pi)^{3N}} \int dq \int dq' \langle q|\hat{A}(t)|q'\rangle 
\times \rho^B(p_c, q_c; q, q'), \quad (24)
$$

where $\rho^B(p_c, q_c; q, q')$ is the reduced density matrix for individual centroids since Eq. (14) and the physical observable $\hat{B}$ is an arbitrary linear combination of the position and momentum operators. In contrast with the equilibrium case, one could replace the operator $\hat{B}$ with the corresponding centroid variables even though introducing individual centroid constraints breaks the translation invariance along the imaginary time axis. This is an advantage of using Kubo transformed correlation functions which allows one to replace $\hat{B}$ with its matrix element averaged over imaginary time paths even in the absence of the symmetry mentioned above.
Using the same argument as in the equilibrium case, one can write the correlation function in terms of individual centroid coordinates as

\[
\langle \hat{B} \hat{A}(t) \rangle_{\text{Kubo}} = \frac{1}{N!} \int \frac{dp_c dq_c}{(2\pi)^3} \rho^B(p_c, q_c) \frac{1}{Z} B A_c(p_c, q_c, t),
\]

where the time dependent centroid variable \( A_c(p_c, q_c, t) \) is defined by the equation

\[
A_c(p_c, q_c, t) = \frac{1}{\rho^B(p_c, q_c)} \int dq dq' \langle q | \hat{A}(t) | q' \rangle \times \rho^B(p_c, q_c; q, q')
\]

\[
= \frac{1}{\rho^B(p_c, q_c)} \int dq dq' \langle q | \hat{A}(t) | q' \rangle \times \rho^B(p_c, q_c; q, q', t),
\]

and the (exact) time dependence of this reduced density matrix is given by the standard expression,

\[
\rho^B(p_c, q_c; q, q', t) = \int dq'' dq''' e^{-iHt}|q'' \rangle \rho^B(p_c, q_c; q'', q''') |q''' \rangle \times \rho^B(p_c, q_c; q'''', q''''') |q''''\rangle.
\]

It should be noted that no approximation has been made yet and Eqs. (25)–(27) are exact for any linear (in position and momentum) operator \( \hat{B} \) as long as the time dependent centroid variable is propagated exactly. Of course, the direct use of the above equations is precluded by the oscillatory behavior of the propagators entering in the definition of the (exact) centroid variable, but they form a very convenient starting point for developing approximations which lead to simple classical-like equations for correlation functions taking into account both finite temperature and quantum exchange effects.

In terms of the operator formalism developed in Refs. 17 and 18, the classical-like assumption consists of replacing the exact quasidensity operator with an approximate one that depends on time only through the centroid coordinates. This results in the following approximation for the time dependent centroid variable \( A_c(p_c, q_c, t) \approx A_c(p_c(t), q_c(t)) \). The dynamics of the centroid positions and momenta are governed by classical equations of motion in the field of the effective potential. For Boltzmann statistics, this approximation is the CMD method, and its extension here to the case of bosonic statistics is the Bose–Einstein CMD (BECMD) method. In terms of the reduced centroid density matrix approach, the above assumption is equivalent to the following approximation for the normalized centroid-constrained reduced density matrix;

\[
\frac{1}{\rho_c} \rho^B(p_c, q_c; q, q', t)
\]

\[
\approx \frac{1}{\rho_c^B(p_c(t), q_c(t))} \rho^B(p_c(t), q_c(t); q, q').
\]

In contrast to the case of Boltzmann statistics where this approximation actually leads to the CMD equations [cf. Eqs. (1)–(3) of Ref. 18], here it is an additional ansatz that the centroid trajectories in phase space are given by the BECMD equations of motion for individual centroids, Eqs. (20)–(21), with initial conditions \( p_c(t)|_{t=0} = p_c, q_c(t)|_{t=0} = q_c \). Also, the BECMD approximation above can not be related directly to the exact quantum mechanical equations of motion for the individual position and momentum centroids. This is a consequence of breaking the permutation symmetry as a result of introducing centroid constraints associated with individual physical particles. In the path integral picture, this appears as a breaking of the translation symmetry along the imaginary time path. As it has been shown in Sec. III, however, one can use boson centroid molecular dynamics to evaluate exact equilibrium averages, and it is now suggested that this approach can be used in approximate dynamical calculations. However, the basis for this approach requires additional assumptions.

V. NUMERICAL IMPLEMENTATION AND RESULTS

One of the most important results of the CMD (BECMD) method is the connection between a centroid correlation function and a Kubo transformed quantum mechanical one, and, as a consequence, the possibility to find approximate quantum mechanical correlation functions using classical-like calculations. Another interesting result is that the CMD (BECMD) method can be used in the exact calculation of equilibrium properties for quantum mechanical systems. In this case, this approach comprises the benefits of both path integral Monte Carlo and molecular dynamics calculations. In particular, using Monte Carlo sampling along the centroid trajectories may help one to avoid some problems connected with ergodicity in systems having some deep local minima in the potential energy surface.

The numerical implementation of the BECMD method is quite straightforward and consists of three well defined problems: (i) calculating the effective centroid force taking into account quantum (including exchange) and finite temperature effects; (ii) obtaining the trajectories in the centroid phase space in the framework of classical molecular dynamics (MD) calculations using the effective centroid force; (iii) analyzing the resulting trajectories and extracting information about quantum mechanical dynamics. For example, approximate quantum real time correlation functions can be found from the equations connecting the CMD/BECMD correlation functions and Kubo transformed quantum mechanical ones. In this work the so-called “on-fly” method first proposed by Cao and Voth and then widely used in the different implementations of the CMD method is adopted. In this approach, the centroid force is calculated along the trajectory at each MD step. In contrast with conventional implementations of CMD for real systems where this technique is often combined with path integral molecular dynamics (PIMD) calculations, the path integral Monte Carlo (PIMC) method is used here to compute the effective centroid force.

For the numerical implementation of algorithms based on path integral techniques, one needs a proper discretized
representation. To describe exchange effects in path integral calculations, it is important to reduce the number of discretizations such that the thermal length corresponding to the high temperature density matrix (used to construct the actual density matrix) is of the order of the interparticle distance. This can be achieved, for example, by using an accurate expression for the high temperature density matrix in the discrete-time PIMC calculations, or by applying partial averaging techniques in the framework of the Fourier PIMC method.

At the same time, one needs to increase the number of time slices in the discretized picture to fix the centroid constraint in the proper way. It is therefore important to investigate the accuracy of the definition of the centroid constraint as a function of the number of imaginary time slices and that will be a subject of forthcoming work. In the present paper, however, the primitive approximation will be used for the high temperature density matrix. As a result, one needs to introduce some additional approximations to sample permutations in the proper way.

The explicit expression for the discretized counterpart of the centroid force entering into the BECDM equations of motion can be found from Eq. (21). Substituting in this equation the discretized version of the bosonic centroid density, Eq. (11), gives for the bosonic centroid force (see Appendix C for details),
cal observables. As a result, the positions of the beads (particle coordinates along the imaginary time path) are separated by a length scale characteristic of the effective potential. This allows one to use the following approximate procedure in the PIMC calculations. The staging algorithm is first used to sample configuration space for the identity permutation with additional restrictions to the possible configurations due to the centroid constraint. The permutation space is then sampled using the renormalized free particle approximation for the centroid constrained density matrix. The effective mass is chosen to reproduce the results of the equilibrium calculation of Ref. 42.

The calculations of the centroid force is the most time-consuming step of the above algorithm. To increase the efficiency of the numerical implementation of the PIMC calculations, the computer code was parallelized. The calculation were performed on a Beowulf-type cluster configured with 16 nodes.

As an illustration, results for the kinetic and potential energy are given in Fig. 1 for the triatomic cluster. Both distinguishable (Boltzmann statistics) and bosonic (Bose–Einstein statistics) particles are treated using the CMD and BECMD methods, respectively. Results from Ref. 42 are also included for comparison purposes. As a result, the positions of the beads (particle coordinates along the imaginary time path) are separated by a length scale characteristic of the effective potential. This allows one to use the following approximate procedure in the PIMC calculations. The staging algorithm is first used to sample configuration space for the identity permutation with additional restrictions to the possible configurations due to the centroid constraint. The permutation space is then sampled using the renormalized free particle approximation for the centroid constrained density matrix. The effective mass is chosen to reproduce the results of the equilibrium calculation of Ref. 42.

The calculations of the centroid force is the most time-consuming step of the above algorithm. To increase the efficiency of the numerical implementation of the PIMC calculations, the computer code was parallelized. The calculation were performed on a Beowulf-type cluster configured with 16 nodes.

As an illustration, results for the kinetic and potential energy are given in Fig. 1 for the triatomic cluster. Both distinguishable (Boltzmann statistics) and bosonic (Bose–Einstein statistics) particles are treated using the CMD and BECMD methods, respectively. Results from Ref. 42 are also included for comparison purposes. To implement the CMD/BECMD methods, the numerical algorithm described above was used, the temperature was 3 K, and the effective mass of the particle was chosen to be $m_{\text{eff}}=2.5$ m based on the results of equilibrium PIMC calculations. It is found that in the case of Boltzmann statistics, canonical equilibrium averages of physical observables can be converged using the regular Monte Carlo calculations for the number of discretization $K=30$. The same number of discretizations was also used in PIMD calculations. The effect of quantum statistics are clearly seen in this figure as a decrease in the kinetic energy of the cluster. From the point of view of the centroid dynamics perspective, this is the manifestations of two factors: (i) alteration of the kinetic energy at every molecular dynamics step as a result of incorporating the effects of statistics in the estimator of the centroid kinetic energy; (ii) the change in the dynamics of the bosonic particles in comparison with the case of Boltzmann statistics. The last factor is mainly due to the term in the expression for the centroid force Eq. (29) which depends on permutations and results in an additional attraction between bosonic particles.

We also present results for the velocity autocorrelation function in Fig. 2. The conditions are the same as for the equilibrium calculations presented above. The quantum correlation functions have been obtained from the following relationship in frequency space; $C(\omega)=\beta \omega/2[\coth(\beta \omega/2)+1]C_{\text{Kubo}}(\omega)$, connecting the Fourier transforms of the real time $C(\omega)$ and Kubo transformed $C_{\text{Kubo}}(\omega)$ quantum mechanical correlation functions. The Kubo transformed correlation functions have been calculated in the framework of the BECMD (for the case of Bose–Einstein statistics) and CMD (Boltzmann statistics) methods. To compare with the classical case, we plot only the real part of the correlation functions. As seen from this figure, the quantum correlation functions for both bosonic and distinguishable particles reveal a considerable lowering of the fre-
quency in comparison with the classical calculations. This is a direct consequence of the application of the BECMD/CMC methods where the dynamics of the quantum particles is defined by the effective potential incorporating quantum effects. The difference between CMD and BECMD correlation function is more subtle. Nevertheless, a change in the frequency spectrum is observed for the bosonic case. The shift to the higher frequency for the bosonic system can be explained by the additional attraction arising from taking into account the effects of quantum statistics in the definition of the centroid force. This has also been discussed above in the context of the equilibrium calculations.

VI. CONCLUDING REMARKS

A path integral formulation of the BECMD method has been presented along with further developments regarding the centroid representation of operators for systems obeying Boson–Einstein statistics. It had been demonstrated in earlier work\textsuperscript{28} that the BECMD method could provide very accurate results for the center of mass position autocorrelation functions for a model system consisting of two noninteracting particles.\textsuperscript{28,29} In the present work, it was shown that the BECMD method can be used in equilibrium calculations giving formally exact results. This work also provides the first numerical implementation of the BECMD method as a hybrid approach incorporating the molecular dynamics method for the centroid coordinates and PIMC calculations for the rest of degrees of freedom. Such an approach can include the benefits of both dynamical and Monte Carlo calculations for systems where exchange effects are present.

One of the most attractive features of BECMD is the possibility of performing approximate dynamical calculations. As for regular Boltzmann CMD, quantum mechanical Kubo transformed correlation functions can be related to the centroid ones. It was shown here that this connection is formally exact for bosons in the case of centroid coordinates associated with individual particles and that the BECMD approximation can then introduced as an additional ansatz.

From a computational point of view, it is very important to use accurate approximations for the density matrix to decrease the number of discretizations in order to describe correctly the effects of quantum statistics, while the definition of the centroid in the discretized picture is based on the so-called primitive approximation for the density matrix. This problem will require future attention for the application of the method to complex low temperature systems. Effective estimators for the effective centroid force and physical observables depending on the momentum operator also need to be developed. It is finally very important for the application of the BECMD method to many-particle systems to develop numerical implementations allowing one to control the statistical and systematic errors of the Monte Carlo calculations along the molecular dynamics centroid path, and to investigate the contributions of these errors to the final result.

We finally note that the formalism presented here also applies to the case of Fermi–Dirac statistics with the important exception of an alternating sign in all expressions involving sums over permutations. This feature of fermionic systems leads the “fermion sign problem” when attempting a calculation of the centroid force using Monte Carlo methods. A better understanding of this difficulty will be required before one can apply Fermi–Dirac CMD (FDCMD) to complex systems. A first step in this direction was presented in Ref. 29, and approaches such as the Restricted Path Integral Method\textsuperscript{36} could be used to render FDCMD simulations possible.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the University of Alberta (P.-N. R.) and the United States National Science Foundation (G.A.V.).

APPENDIX A: REDUCED DENSITY MATRIX FOR BOSE–EINSTEIN SYSTEMS

To express equilibrium averages of physical observables and quantum mechanical real time correlation functions in terms of centroid coordinates, one needs the matrix elements of a centroid-constrained reduced density matrix. In the operator formalism developed recently,\textsuperscript{17,18} these are matrix elements of the unnormalized quasidensity operator.

To correctly treat dynamics in the centroid formalism, it is important to define the centroid in phase space. One can start from the expression for the matrix elements of the density matrix in terms of the phase space imaginary time path integral,\textsuperscript{12,32,47}

\[
\rho(q,q';\beta) = \int_{q(0)=q}^{q(\beta)=q'} Dp(\tau) Dq(\tau) e^{-\mathcal{S}[p(\tau),q(\tau)]},
\]

(A1)

where \( \int_{q(0)=q}^{q(\beta)=q'} Dp(\tau) Dq(\tau)\{ \cdots \} \) denotes the measure of the integration over paths in phase space with fixed end points \( q(0)=q \) and \( q(\beta)=q' \),

\[
\mathcal{S}[p(\tau),q(\tau)] = -\int_0^\beta \left[ i p(\tau)\dot{q}(\tau) - H(p(\tau),q(\tau)) \right] d\tau
\]

(A2)

is the imaginary time (Euclidean) action.

The expression for the reduced density matrix can be obtained from Eq. (A1) if one takes into account only the contribution from the imaginary time paths with fixed position and momentum centroids defined as \( q_0 = (1/\beta)\int_0^\beta q(\tau) d\tau \) and \( p_0 = (1/\beta)\int_0^\beta p(\tau) d\tau \). This can be achieved by inserting a \( \delta \) function corresponding to the centroid constraint in the latter equation. In the case of Boltzmann statistics the result is,

\[
\rho(p_c,q_c;q,q') = (2\pi)^{3N} \int_{q(0)=q}^{q(\beta)=q'} Dp(\tau) Dq(\tau) \delta(p_c-p_0) \times \delta(q_c-q_0) e^{-\mathcal{S}[p(\tau),q(\tau)]}.
\]

(A3)

It should be noted that this equation gives the path integral representation for the matrix elements of the quasidensity operator \( \hat{\varphi}(q_c,p_c) \) from Ref. 17.
\[ \rho(p_{c},q_{c};q,q') = \langle q'|\phi(q_{c},p_{c})|q \rangle \]
\[ = \lim_{K \to \infty} (2\pi)^{3N} \int \ldots \int \frac{dp_{1}}{(2\pi)^{3N}}dq_{1} \frac{dp_{2}}{(2\pi)^{3N}}dq_{2} \ldots \frac{dp_{K}}{(2\pi)^{3N}}dq_{K} \]
\[ \times \exp\left\{ ip_{1}(q_{2} - q_{1}) + \ldots + ip_{K}(q_{K+1} - q_{K}) \right\} \]
\[ \times \exp\left\{ -\frac{p^{2}}{2m} + \frac{p^{2}}{2m} + 0.5V(q_{1}) + V(q_{2}) \right\} \]
\[ + \ldots + V(q_{K}) + 0.5V(q_{K+1}) \right\}, \]  

(A4)

with \( q_{1} = q \) and \( q_{K+1} = q' \), \( \tau = \beta/K \), and \( K \) is the number of discretizations. The above expression can be written in different forms, but for a Hamiltonian written as a sum of kinetic and potential energy depending only on the momenta and positions of the particles, respectively, the result does not depend on the procedure of discretization.

One can now evaluate the path integral in Eq. (A3) over the momentum variables. It can be done using the Fourier representation for the \( \delta \)-function corresponding to the momentum centroid resulting in the following equation:

\[ \rho(p_{c},q_{c};q,q') = \exp\left\{ -\beta \left[ p_{c} - \frac{m}{\beta}(q' - q) \right]^{2} / 2m \right\} \times \rho(q_{c};q,q'), \]  

(A5)

where \( \rho(q_{c};q,q') = \langle q'|\phi(q_{c})|q \rangle \) is the matrix elements of the configurational part of the quasi-density operator (the position reduced density matrix) given by

\[ \rho(q_{c};q,q') = \left( \frac{2\pi\beta}{m} \right)^{3N/2} \int_{q(\beta) = q'}^{q(\beta) = q} \mathcal{D}'q(\tau)\delta(q_{c} - q_{0}) \]
\[ \times \exp\left\{ -\mathcal{S}[q(\tau)] \right\}, \]  

(A6)

with the Euclidean action in the position representation defined by the equation,

\[ \mathcal{S}[q(\tau)] = \int_{0}^{\beta} \left[ \frac{m}{2} \dot{q}(\tau)^{2} + V[q(\tau)] \right] d\tau, \]  

(A7)

and the volume element in Eq. (A6) being

\[ \mathcal{D}'q(\tau) = \lim_{K \to \infty} \left( \frac{mK}{2\pi\beta} \right)^{3N/2} \prod_{i=1}^{K-1} \left( \frac{mK}{2\pi\beta} \right)^{3N/2} dq_{i}. \]  

(A8)

In the case of Bose–Einstein statistics, one can introduce the reduced centroid density by the following equation:

\[ \rho^{B}(p_{c},q_{c};q,q') = \sum_{p} \rho(p_{c},q_{c};q,p_{c}q') \]
\[ = \sum_{p} \langle q'|\phi(q_{c},p_{c})|q \rangle \]
\[ = (2\pi)^{3N} \int_{q(0) = q}^{q(\beta) = q'} \mathcal{D}'p(\tau)\mathcal{D}q(\tau) \]
\[ \times \delta(p_{c} - p_{0}) \delta(q_{c} - q_{0}) e^{-\mathcal{S}[p(\tau),q(\tau)]}, \]  

(A9)

where the position centroid is defined as \( q_{0} = (1/\beta) \int_{0}^{\beta} p_{0} d\tau \), and a path integral representation for the quasidensity operator is given by Eq. (C1) of Ref. 17. Again, the integration over momentum variables can be done explicitly, but one can also use the results of previous calculations corresponding to the case of Boltzmann statistics, and substituting Eq. (A5) in Eq. (A9), one obtains

\[ \rho^{B}(p_{c},q_{c};q,q') \]
\[ = \sum_{p} \exp\left\{ -\beta \left[ p_{c} - \frac{m}{\beta}(p_{c}q' - q) \right]^{2} / 2m \right\} \times \rho(q_{c};q,p_{c}q'). \]  

(A10)

Using the reduced centroid density defined above allows one to express the equilibrium averages of physical observables in the canonical ensemble and Kubo transformed real time correlation functions in terms of centroid coordinates corresponding to individual physical particles.

**APPENDIX B: ESTIMATORS FOR THE KINETIC ENERGY**

To calculate an equilibrium average of a physical observable using the BECMD method, one needs an estimator of the corresponding centroid variable. The expression for the kinetic energy, for example, can be obtained using a procedure similar to the case of Boltzmann statistics.17

One can start from the expression for the equilibrium average of a quantum mechanical operator in terms of the reduced density matrix given by Eq. (13). Substituting the matrix element of the kinetic energy operator,

\[ \langle q|\hat{K}|q' \rangle = -\frac{1}{2m} \frac{\partial^{2}}{\partial q^{2}} \delta(q - q') \]

in this equation, after integration by parts, leads to the following expression for the equilibrium average of the kinetic energy,

\[ \langle \hat{K} \rangle = \frac{1}{2N^{2}} \int \frac{dp_{c}dq_{c}}{(2\pi)^{2N}} \int dq \]
\[ \times \left[ -\frac{1}{2m} \frac{\partial^{2} \rho^{B}(p_{c},q_{c};q,q')}{\partial q^{2}} \right]_{q' = q}. \]  

(B1)

Taking into account the explicit dependence of the reduced density matrix on the centroid momentum Eq. (15), allows one to write the above expression for the kinetic energy in the following form
\[ \langle K \rangle = \frac{1}{N!} \int \frac{dp_c dq_c}{(2\pi)^n} \frac{\rho_c^B(p_c, q_c)}{Z} K_c(p_c, q_c), \quad (B2) \]

where the centroid kinetic energy defined as

\[ K_c(p_c, q_c) = \left[ \frac{p_c^2}{2m} - \frac{3N}{2\beta} + \frac{1}{\beta} \frac{\partial^2 \rho_c^B(q_c)}{\partial q_c^2} \right] \delta(q_c - q_c') . \quad (B3) \]

Formally, this expression coincides with the corresponding result for Boltzmann statistics,\(^{17}\) incorporating all the effects specific to Bose–Einstein statistics through the coordinate part of the bosonic reduced density matrix. The explicit expression for the centroid kinetic energy in the discretized picture can be easily obtained from the above equation. For example, using the primitive approximation for the path integral representing the reduced density matrix and the semi-closed quadrature method to write down the discretized action, one obtains the following estimator for the kinetic energy,

\[ K_c(p_c, q_c) = \left[ \frac{p_c^2}{2m} - \frac{3N}{2\beta} + \frac{1}{\beta} \frac{m(q_c - Pq_1)^2}{2\tau} \right] \rho_c^B . \quad (B4) \]

It should be noted that the first two terms in the above equation cancel out after the integration over momentum variables in Eq. (B2), and one can use the rest as an estimator for the kinetic energy in actual calculations.

**APPENDIX C: DISCRETIZED REPRESENTATION FOR THE CENTROID FORCE**

To find the general (unsymmetrized) expression for the bosonic centroid force in the discretized picture required for the numerical implementation of the BECMD method, one can substitute the discretized centroid density for a bosonic system given by\(^{28}\)

\[ \rho_c^B(q_c) = \left( \frac{2\pi \beta}{m} \right)^{3N/2} \sum_{p} \int \cdots \int \left( \frac{m}{2\pi \tau} \right)^{3N/2} dq_1 \cdots dq_K \delta(q_c - \frac{1}{K} \sum_{i=1}^{K} q_i) \times e^{-S^T\{q_i\}}, \]

where the discretized counterpart of the action is

\[ S^T\{q_i\} = \frac{(q_1 - q_2)^2}{4\lambda \tau} + \cdots + \frac{(q_K - Pq_1)^2}{4\lambda \tau} + \tau V(q_1) + \cdots + \tau V(q_K), \]

with \( \lambda = 1/2m \), in the equation for the centroid force,

\[ F_c = \frac{1}{\beta} \frac{\partial}{\partial q_c} \ln \rho_c^B = \frac{1}{\beta} \frac{\partial \rho_c^B}{\partial q_c} . \quad (C1) \]

The density \( \rho_c^B(q_c) \) depends on \( q_c \) through the \( \delta \)-function only, and its derivatives with respect to \( q_c \) is

\[ \frac{\partial}{\partial q_c} \delta(q_c - \frac{1}{K} \sum_{i=1}^{K} q_i) = -\sum_{i=1}^{K} \frac{\partial}{\partial q_j} \delta(q_c - \frac{1}{K} \sum_{i=1}^{K} q_i). \]

Substituting the discretized bosonic centroid density in Eq. (C1), taking into account the above equality, integrating by part the resulting expression and setting to zero the surface terms gives

\[ F_c(q_c) = A \frac{1}{\beta} \sum_{p} \int \cdots \int \left( \frac{m}{2\pi \tau} \right)^{3N/2} dq_i \times \delta(q_c - \frac{1}{K} \sum_{i=1}^{K} q_i) \times \left( \frac{m(q_c - Pq_1)^2}{2\tau} \right) e^{-S^T\{q_i\}}. \quad (C2) \]

where the normalization factor \( A = (2\pi \beta m)^{3N/2} \rho_c^B(q_c) \) has been introduced.

Due to particle permutations, some care must be taken when calculating the derivatives of the action from Eq. (C2). One can distinguish three cases:

1. \( j \neq K \)
\[ \frac{\partial S^T\{q_i\}}{\partial q_j} = \left[ -\frac{q_j - 2q_{j-1} + P^{-1}q_K}{2\lambda \tau} + \tau \frac{\partial V(q_j)}{\partial q_j} \right]. \]

2. \( j = 1 \)
\[ \frac{\partial S^T\{q_i\}}{\partial q_1} = \left[ -\frac{q_2 - 2q_1 + P^{-1}q_K}{2\lambda \tau} + \tau \frac{\partial V(q_1)}{\partial q_1} \right]. \]

3. \( j = K \)
\[ \frac{\partial S^T\{q_i\}}{\partial q_K} = \left[ -\frac{q_K - 2q_{K-1} + P^{-1}q_1}{2\lambda \tau} + \tau \frac{\partial V(q_K)}{\partial q_K} \right]. \]

Taking into account this result, one can write Eq. (C2) in the following form

\[ F_c(q_c) = A \frac{1}{\beta} \sum_{p} \int \cdots \int \left( \frac{m}{2\pi \tau} \right)^{3N/2} dq_i \times \delta(q_c - \frac{1}{K} \sum_{i=1}^{K} q_i) \times \left( \frac{m(q_c - Pq_1)^2}{2\lambda \tau} \right) e^{-S^T\{q_i\}}. \]

Then, because of the centroid constraint in the above equation, \( \sum_{j=1}^{K} q_j = Kq_c \), and therefore \( \sum_{j=1}^{K} (q_{j+1} - 2q_j + q_{j-1})/2\lambda \tau = 0 \). The discretized centroid force can now be written as
\[
F_c(q_c) = A \sum_\mathcal{P} \int \cdots \int \prod_{i=1}^K \left[ \frac{m}{2\pi \tau} \right]^{3N/2} dq \delta \left( q_c - \frac{1}{K} \sum_{j=1}^K q_j \right) \left( -\frac{1}{K} \sum_{j=1}^K \frac{\partial V(q_j)}{\partial q_j} \right) e^{-\beta V(q_c)} \\
+ \frac{A}{\beta} \sum_\mathcal{P} \int \cdots \int \prod_{i=1}^K \left[ \frac{m}{2\pi \tau} \right]^{3N/2} dq \delta \left( q_c - \frac{1}{K} \sum_{j=1}^K q_j \right) \left[ \frac{P^{-1} q_K - q_K}{2\lambda \tau} + \frac{P q_1 - q_1}{2\lambda \tau} \right] e^{-\beta V(q_c)}.
\]