The formulation of quantum statistical mechanics based on the Feynman path centroid density. III. Phase space formalism and analysis of centroid molecular dynamics

Jianshu Cao and Gregory A. Voth
Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

(Received 29 March 1994; accepted 14 June 1994)

The formulation of quantum statistical mechanics based on the path centroid variable in Feynman path integration is generalized to a phase space perspective, thereby including the momentum as an independent dynamical variable. By virtue of this approach, operator averages and imaginary time correlation functions can be expressed in terms of an averaging over the multidimensional phase space centroid density. The imaginary time centroid-constrained correlation function matrix for the phase space variables is then found to define the effective thermal width of the phase space centroid variable. These developments also make it possible to rigorously analyze the centroid molecular dynamics method for computing quantum dynamical time correlation functions. As a result, the centroid time correlation function as calculated from centroid molecular dynamics is shown to be a well-defined approximation to the exact Kubo transformed position correlation function. This analysis thereby clarifies the underlying role of the equilibrium path centroid variable in the quantum dynamical position correlation function and provides a sound theoretical basis for the centroid molecular dynamics method.

I. INTRODUCTION

In two papers[1,2] (hereafter referred to as paper I and paper II) and a Communication,[3] the formulation of quantum statistical mechanics based on the Feynman path centroid was extensively studied. These efforts originated from the notion that the path centroid variable[4] in equilibrium quantum systems is the most direct analog to a classical variable and should therefore possess both formally interesting and computationally useful properties. Paper I developed the formal "cornerstone" for the centroid-based formulation of equilibrium properties, introducing many of the mathematical tools necessary for subsequent theoretical developments. For example, a formally exact theory was developed for the equilibrium density[4] associated with the centroid variable (the so-called "centroid density"). This analytical theory goes well beyond the Feynman–Hibbs variational theory[4] for the partition function by employing an infinite-order diagrammatic perturbation expansion along with resummation and renormalization techniques. The analysis also explores the diagrammatic representation of various approximation schemes[4,5] for the centroid density and then systematically improves upon those schemes. In addition to the analytical theory for the centroid density in paper I, the quantum expressions for equilibrium operator averages and imaginary time correlation functions were reformulated so that the centroid density occupies the role of the underlying statistical distribution function. Taken together, the developments in paper I represent a unified view of *equilibrium* quantum statistical mechanics from the centroid perspective.

In paper II and the Communication, the path centroid perspective was significantly extended to address the challenge of calculating quantum *dynamical* time correlation functions. The most intriguing and promising result of the dynamical centroid analysis is a method called *centroid molecular dynamics* (centroid MD).[2,3] Motivated by the appeal of the centroid perspective, it was argued that the quantum position correlation function can be related to a time correlation function for the centroid variable with the centroid "trajectories" generated by classical-like dynamical equations on an effective, temperature-dependent, centroid potential energy surface. A number of strategies were then developed in paper II to compute the time correlation functions of *general* coordinate-dependent operators. By virtue of the centroid MD approach, time correlation functions can, in principle, be computed for quantum many-body systems with a numerical effort that scales with system size in the same manner as a classical molecular dynamics (MD) simulation. In the companion paper,[6] some numerical algorithms are presented for centroid MD calculations in general physical systems which obey Boltzmann quantum statistics.

The formal analysis in the earlier papers[1–3] was based on the Feynman path integral formulation in coordinate space.[7] Though it can be argued that momentum dependent quantities can in principle be obtained by taking time derivatives of the position coordinate, complications arise due to the time ordering of quantum operators, especially when mixed position and momentum terms appear in those operators. A better treatment, therefore, requires a path integral centroid formulation in phase space which not only generalizes the earlier position centroid-based formulation,[1–3] but also provides a remedy to the time ordering problem. Such a formulation is contained in the present paper [see also Refs. 5(b)–5(d)]. In a fashion similar to paper I, the imaginary time-correlated operators are reformulated as Gaussian averaged functions which are then to be averaged over the centroid phase space density. The final formulas resemble those in coordinate space, although they are defined here in phase space through a compact vector-matrix notation. For completeness, the expressions are also formulated for many degrees-of-freedom which is simply an extension of a one-dimensional treatment.

 0021-9606/94/101(7)/6157/11/$6.00

In terms of the *dynamical* centroid variable perspective for quantum time correlation functions, a complete analysis of centroid MD, and its justification, again requires a path integral formulation in phase space[8] so that momentum can be treated as an independent dynamical variable. Indeed, the phase space centroid formulation in the present paper has its most important application in the analysis of centroid MD presented in Sec. III. At the time when centroid MD was proposed,[2,3] a relationship between the Fourier transform of the real time position correlation function and the centroid time correlation function was identified. This relationship is based on the analytical continuation of the variationally optimized local quadratic approximation[1,5(a)] to the centroid-constrained imaginary time position correlation function.[1] Since the Fourier relationship holds exactly if the centroid correlation function is replaced by the Kubo transformed[9] position correlation function, it was speculated that the centroid correlation function must therefore be an approximation to the Kubo transformed position correlation function. Through the phase space centroid formulation developed herein, the relationship between the centroid correlation function and the Kubo transformed position correlation function is found to be unique and cannot be obtained unless the centroid is taken as the dynamical variable. In the end, centroid MD turns out to be exact for the first two terms in the Taylor expansion of the correlation function in time, and the systematic error in the method can be identified at all subsequent orders. The deviation from the exact quantum time correlation function is directly proportional to the average thermal width of the centroid "particle," as well as higher-order derivatives of the mean centroid force. Centroid MD is thereby shown to capture the leading quantum dynamical behavior of the position correlation function to within a well-defined error.

As a direct extension of the centroid MD theory in phase space, three strategies are also presented in the present paper to calculate time correlation functions of general operators which may depend on both position and momentum. The derivations are relatively straightforward given the similar results for the correlation functions of general coordinate dependent operators published in paper II. Nevertheless, the demonstration that the momentum can be incorporated into the theory in the same fashion as the position is significant both from the formal point of view and for actual numerical applications.

The present paper is organized as follows: In Sec. II, the equilibrium formulation of the Feynman path centroid density, operator averages, and imaginary time correlation functions in multidimensional phase space is described. In Sec. III, the phase space centroid perspective is then used to analyze and more completely justify the dynamical centroid MD method for the real time position correlation function. This theory is then extended in Sec. IV to formulate three approaches for computing general quantum time correlation functions. Some numerical examples are given in Sec. V, and concluding remarks appear in Sec. VI.

II. FEYNMAN PATH CENTROID FORMULATION IN PHASE SPACE

In paper I, general imaginary time correlation functions were expressed in terms of the coordinate space centroid density $\rho_c(q_c)$ and the centroid-constrained imaginary time position correlation function $C_c(\tau,q_c)$. Here, the formalism of paper I will be extended by a phase space path integral formulation[8] so that the momentum appears as an independent variable. The development will first involve the specification of the phase space centroid density, then the definition of the centroid-constrained position, momentum, and cross-correlation functions, and finally the formulation of the expressions for equilibrium operator averages and general imaginary time correlation functions. Unless specified otherwise, the analysis will be presented for an N-dimensional system with the position and momentum variables described by the N-dimensional column vectors $\mathbf{q}$ and $\mathbf{p}$, respectively. The generalized vector ζ is defined as the collection of the $2N$ degrees of freedom in phase space, i.e., $\zeta\equiv(\mathbf{p},\mathbf{q})$.

A. Phase space Feynman path centroid density

The phase space centroid density can be straightforwardly defined as

$$\rho_c(\zeta_c)=\int\cdots\int \mathscr{D}\zeta(\tau)\,\delta(\zeta_c-\zeta_0)\exp\{-S[\zeta(\tau)]/\hbar\}, \tag{2.1}$$

where the path centroid vector in phase space is given by

$$\zeta_0=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\zeta(\tau). \tag{2.2}$$

The action functional for the imaginary time phase space path integral is given by[8]

$$S[\zeta(\tau)]=\int_0^{\hbar\beta} d\tau\left\{\frac{1}{2}\,\mathbf{p}\cdot(\tau)\mathbf{m}^{-1}\cdot\mathbf{p}(\tau)-i\mathbf{p}(\tau)\cdot\dot{\mathbf{q}}(\tau)+V[\zeta(\tau)]\right\}, \tag{2.3}$$

where $\mathbf{m}$ is the diagonal particle mass matrix and $\dot{\mathbf{q}}(\tau)$ is understood as the imaginary time velocity vector. The quantum partition function is related to Eq. (2.1) such that $Z=\int d\zeta_c\rho_c(\zeta_c)$. The phase space centroid-constrained correlation functions[1,2] are defined by the $2N\times 2N$ matrix

$$\mathbf{C}_c(\tau,\mathbf{q}_c)=\frac{\int\cdots\int\mathscr{D}\zeta(\tau)\,\delta(\zeta_c-\zeta_0)[\zeta(\tau)-\zeta_0][\zeta(0)-\zeta_0]\exp\{-S[\zeta(\tau)]/\hbar\}}{\int\cdots\int\mathscr{D}\zeta(\tau)\,\delta(\zeta_c-\zeta_0)\exp\{-S[\zeta(\tau)]/\hbar\}}. \tag{2.4}$$

Each element of this matrix with the indices i,j is given explicitly by the 2×2 block

$$[\mathbf{C}_c(\tau,\mathbf{q}_c)]_{ij}=\begin{Bmatrix} C_c[\tilde{p}_i(\tau)\tilde{p}_j(0),\mathbf{q}_c] & C_c[\tilde{p}_i(\tau)\tilde{q}_j(0),\mathbf{q}_c] \\ C_c[\tilde{q}_i(\tau)\tilde{p}_j(0),\mathbf{q}_c] & C_c[\tilde{q}_i(\tau)\tilde{q}_j(0),\mathbf{q}_c] \end{Bmatrix}, \tag{2.5}$$

where $\tilde{\boldsymbol{\zeta}}(\tau)$ is the quantum path fluctuation with respect to the centroid position $\boldsymbol{\zeta}_c$, i.e., $\boldsymbol{\zeta}(\tau)=\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}}(\tau)$. The elements of the centroid-constrained correlation function matrix in Eq. (2.5) can also be obtained by adding linear field terms of the form $-\mathbf{f}(\tau)\cdot\tilde{\mathbf{q}}(\tau)$ and $-\mathbf{g}(\tau)\cdot\tilde{\mathbf{p}}(\tau)$ to the action functional in Eq. (2.3) and by then taking the appropriate second-order functional derivatives of $\exp\{-\beta F_c[\mathbf{f}(\tau),\mathbf{g}(\tau)]\}$ and dividing by $\hbar^2/\rho_c$ in the limit $\mathbf{f}(\tau)\to0$ and $\mathbf{g}(\tau)\to0$, where $-\beta F_c[\mathbf{f}(\tau),\mathbf{g}(\tau)]\equiv\ln\{\rho_c[\mathbf{f}(\tau),\mathbf{g}(\tau)]\}$ is the centroid free energy as functional of the two external fields. The centroid-constrained correlation function matrix in Eq. (2.5) is independent of the momentum centroid $\mathbf{p}_c$ if the potential V is independent of the momentum variable. This fact can be proven by considering the Fourier mode representation[2,3] of the phase space action functional in Eq. (2.3).

B. Operator averages

It proves informative to first formulate the expression for the equilibrium average of a general operator in the phase space centroid perspective. This simple analysis identifies the centroid-constrained correlation function matrix in Eqs. (2.4) and (2.5) as providing the effective centroid "width" factors in phase space. In the phase space path integral perspective,[8] the equilibrium average of an operator A is given by the expression

$$\langle A\rangle=Z^{-1}\int\cdots\int\mathscr{D}\boldsymbol{\zeta}(\tau)A[\boldsymbol{\zeta}(0)]\exp\{-S[\boldsymbol{\zeta}(\tau)]/\hbar\}. \tag{2.6}$$

Due to the cyclic invariance of the trace, the operator can be evaluated at any point along the cyclic imaginary time path $\boldsymbol{\zeta}(\tau)$. The average in Eq. (2.6) is first re-expressed so that the centroid variable appears explicitly in the statistical averaging, i.e.,[1,10]

$$\langle A\rangle=Z^{-1}\int d\boldsymbol{\zeta}_c\left\{\int\cdots\int\mathscr{D}\boldsymbol{\zeta}(\tau)\,\delta(\boldsymbol{\zeta}_c-\boldsymbol{\zeta}_0)\times A[\boldsymbol{\zeta}(0)]e^{-S[\boldsymbol{\zeta}(\tau)]/\hbar}\right\}. \tag{2.7}$$

The operator $A(\boldsymbol{\zeta})$ is then represented in $2N$-dimensional Fourier space, i.e.,

$$A(\boldsymbol{\zeta})=\frac{1}{(2\pi)^{2N}}\int d\mathbf{k}\,\hat{A}(\mathbf{k})e^{i\mathbf{k}\cdot\boldsymbol{\zeta}}, \tag{2.8}$$

where $\hat{A}(\mathbf{k})$ is the Fourier transform of the operator, $\mathbf{k}$ denotes the $2N$-dimensional k-vector $(\mathbf{k}_p,\mathbf{k}_q)$, and $\mathbf{k}\cdot\boldsymbol{\zeta}$ represents the contraction $\mathbf{k}\cdot\boldsymbol{\zeta}=\sum_{i=1}^{N}(k_{p_i}p_i+k_{q_i}q_i)$. Equation (2.6) can then be rewritten as

$$\langle A\rangle=Z^{-1}\int d\boldsymbol{\zeta}_c\rho_c(\boldsymbol{\zeta}_c)\int\frac{d\mathbf{k}}{(2\pi)^{2N}}\hat{A}(\mathbf{k})e^{i\mathbf{k}\cdot\boldsymbol{\zeta}_c}\times\left\{\frac{\int\cdots\int\mathscr{D}\tilde{\boldsymbol{\zeta}}(\tau)e^{i\mathbf{k}\cdot\tilde{\boldsymbol{\zeta}}(\tau)}e^{-S[\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}}(\tau)]/\hbar}}{\int\cdots\int\mathscr{D}\tilde{\boldsymbol{\zeta}}(\tau)e^{-S[\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}}(\tau)]/\hbar}}\right\}, \tag{2.9}$$

where the notation for the action functional $S[\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}}(\tau)]$ is understood to mean path integration over the fluctuations around a fixed phase space centroid at $\boldsymbol{\zeta}_c$. At this point, a cumulant average of the term $\exp[i\mathbf{k}\cdot\tilde{\boldsymbol{\zeta}}(\tau)]$ in the brackets in Eq. (2.9) can be performed in terms of the path fluctuation variable $\tilde{\boldsymbol{\zeta}}(\tau)$. The cumulant average, for the present purposes, is truncated at second-order, but it need not be, and it is assumed that the variable $\tilde{\boldsymbol{\zeta}}(\tau)$ exhibits symmetric fluctuations about the centroid. After performing the inverse Fourier transformation by integrating over $\mathbf{k}$ in Eq. (2.9), the final result for the operator average in the phase space centroid picture is given by[5(b)]

$$\langle A\rangle\simeq\langle A_c(\boldsymbol{\zeta}_c)\rangle_{\rho_c}, \tag{2.10}$$

where the effective centroid-dependent quasiclassical operator A_c is given by

$$A_c(\boldsymbol{\zeta}_c)=\langle A(\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}})\rangle_{\mathbf{C}_c(0,\boldsymbol{\zeta}_c)}=\frac{1}{\sqrt{\det[2\pi\mathbf{C}_c(0,\mathbf{q}_c)]}}\int d\tilde{\boldsymbol{\zeta}}\,A(\boldsymbol{\zeta}_c+\tilde{\boldsymbol{\zeta}})\times\exp[-\tilde{\boldsymbol{\zeta}}\cdot\mathbf{C}_c^{-1}(0,\mathbf{q}_c)\cdot\tilde{\boldsymbol{\zeta}}/2]. \tag{2.11}$$

Here, the vector variable $\tilde{\boldsymbol{\zeta}}$ is obviously a Gaussian vector associated with a width matrix given by $\mathbf{C}_c(0,\mathbf{q}_c)$. The above result is a generalization of an expression obtained previously[1,10] for coordinate-dependent operators. This expression reveals the role played by the centroid-constrained correlation function matrix [Eq. (2.5)] in defining the effective width factor in phase space for the centroid quasiparticle.

C. General imaginary time correlation functions

A general imaginary time correlation function is defined as

$$C_{AB}(\tau)=\langle A(\tau)B(0)\rangle=Z^{-1}\int\cdots\int\mathscr{D}\boldsymbol{\zeta}(\tau)A[\boldsymbol{\zeta}(\tau)]B[\boldsymbol{\zeta}(0)]\times\exp\{-S[\boldsymbol{\zeta}(\tau)]/\hbar\}, \tag{2.12}$$

where the operators A and B are general functions of the $2N$ variables $(\mathbf{p},\mathbf{q})$ and the imaginary time interval is bounded such that $0\leq\tau\leq\hbar\beta$. The goal here is to reformulate the correlation function $C_{AB}(\tau)$ in terms of the phase space centroid density and the centroid-constrained correlation function matrix $\mathbf{C}_c(\tau,q_c)$ of Eq. (2.4). Following the analysis of paper I, one first factorizes the expression to expose the integration over the centroid density and then expresses the operators A and B as Fourier transforms, giving

$$C_{AB}(\tau)=Z^{-1}\int d\zeta_c \rho_c(\zeta_c)\int \frac{d\mathbf{k}_1}{(2\pi)^{2N}}\int \frac{d\mathbf{k}_2}{(2\pi)^{2N}} \times\hat{A}(\mathbf{k}_1)\hat{B}(\mathbf{k}_2)e^{i(\mathbf{k}_1+\mathbf{k}_2)\cdot\zeta_c} \times\left[\frac{\int\cdots\int\mathscr{D}\tilde{\zeta}(\tau)e^{i[\mathbf{k}_1\cdot\tilde{\zeta}(\tau)+\mathbf{k}_2\cdot\tilde{\zeta}(0)]}e^{-S[\zeta_c+\tilde{\zeta}(\tau)]/\hbar}}{\int\cdots\int\mathscr{D}\tilde{\zeta}(\tau)e^{-S[\zeta_c+\tilde{\zeta}(\tau)]/\hbar}}\right], \tag{2.13}$$

where $\mathbf{k}$ and $\mathbf{k}\cdot\zeta$ are as defined following Eq. (2.8). The centroid-constrained average in the bracketed term can be expressed as a cumulant expansion which, for the present purpose, is truncated at the second order. The result is given by

$$\langle\exp[i\mathbf{k}_1\cdot\tilde{\zeta}(\tau)+i\mathbf{k}_2\cdot\tilde{\zeta}(0)]\rangle_c \simeq\exp\left\{-\frac{1}{2}[\mathbf{k}_1\cdot\mathbf{C}_c(0,\mathbf{q}_c)\cdot\mathbf{k}_1+\mathbf{k}_1\cdot\mathbf{C}_c(\tau,\mathbf{q}_c)\cdot\mathbf{k}_2 +\mathbf{k}_2\cdot\mathbf{C}_c(\tau,\mathbf{q}_c)\cdot\mathbf{k}_1+\mathbf{k}_2\cdot\mathbf{C}_c(0,\mathbf{q}_c)\cdot\mathbf{k}_2]\right\}, \tag{2.14}$$

where the contractions can be explicitly written as

$$\mathbf{k}_n\cdot\mathbf{C}_c(\tau,\mathbf{q}_c)\cdot\mathbf{k}_m=\sum_{i=1}^{N}\sum_{j=1}^{N}(k_{n,p_i},k_{n,q_i})\begin{pmatrix} C_c[\tilde{p}_i(\tau)\tilde{p}_j(0),\mathbf{q}_c] & C_c[\tilde{p}_i(\tau)\tilde{q}_j(0),\mathbf{q}_c]\\ C_c[\tilde{q}_i(\tau)\tilde{p}_j(0),\mathbf{q}_c] & C_c[\tilde{q}_i(\tau)\tilde{q}_j(0),\mathbf{q}_c]\end{pmatrix}\begin{pmatrix}k_{m,p_j}\\ k_{m,q_j}\end{pmatrix}. \tag{2.15}$$

In order to carry out the integrals over $\mathbf{k}_1$ and $\mathbf{k}_2$ in Eq. (2.13), a phase space vector rotation is first performed such that

$$\zeta_+(\tau)=[\zeta(\tau)+\zeta(0)]/\sqrt{2}$$
$$\zeta_-(\tau)=[\zeta(\tau)-\zeta(0)]/\sqrt{2}, \tag{2.16}$$

and new centroid-constrained correlation function matrices are defined as

$$\mathbf{C}_c^+(\tau,\mathbf{q}_c)=\mathbf{C}_c(0,\mathbf{q}_c)+\mathbf{C}_c(\tau,\mathbf{q}_c)$$
$$\mathbf{C}_c^-(\tau,\mathbf{q}_c)=\mathbf{C}_c(0,\mathbf{q}_c)-\mathbf{C}_c(\tau,\mathbf{q}_c). \tag{2.17}$$

After performing the integrals in Fourier space, one arrives at the following result for the imaginary time correlation function in the phase space centroid density picture:

$$C_{AB}(\tau)\simeq\langle\wp_{AB}(\tau,\zeta_c)\rangle_{\rho_c}, \tag{2.18}$$

where the centroid-dependent imaginary time-correlated operator product $\wp_{AB}(\tau,\zeta_c)$ is defined as the multiple Gaussian average

$$\wp_{AB}(\tau,\zeta_c)=\langle A(\zeta_c+\zeta_1)B(\zeta_c+\zeta_2)\rangle_{\mathbf{C}_c^+,\mathbf{C}_c^-}. \tag{2.19a}$$

Here, the vectors ζ_1 and ζ_2 are related to the two Gaussian vectors ζ_+ and ζ_-, such that

$$\zeta_{1,2}=\frac{1}{\sqrt{2}}(\zeta_+\pm\zeta_-), \tag{2.19b}$$

where ζ_+ and ζ_- have Gaussian width matrices given by $\mathbf{C}_c^+(\tau,\mathbf{q}_c)$ and $\mathbf{C}_c^-(\tau,\mathbf{q}_c)$, respectively. It should be noted that if the cumulant expansion is carried out beyond quadratic order in Eq. (2.14), a more complicated analytical form of Eq. (2.19) would be obtained. On the positive side, however, the expression in Eq. (2.19) simplifies considerably if the operators A and B depend only on the coordinates and/or momenta of a single particle of the system (i.e., almost all of the Gaussian integrals can be "integrated out" of the expression).

Due to the compact notation adopted in the preceding analysis, the final expressions in Eqs. (2.18) and (2.19) resemble those appearing in paper I. Nonetheless, complications arise when cross terms appear because of the noncommutation of position and momentum operators. In fact, the two off-diagonal terms in the matrix $\mathbf{C}_c(\tau,\zeta_c)$ are complex functions and, in turn, complex conjugates of each other. In the expression for operator averages in Eq. (2.10) and for the time correlated operator product in Eq. (2.19), different operator orderings may lead to different values. Though the operator ordering is not explicitly taken into consideration in the Fourier transforms in Eq. (2.13), the final expressions in terms of the Gaussian averages should always be consistent with the original choice of the operator ordering.

The multiple Gaussian average in the centroid-constrained operator product [Eq. (2.19)] may not be easy to evaluate, particularly if the operators A or B are not polynomials or exponentials in the phase space variables. However, if one has an analytical or numerical representation of the centroid density $\rho_c(\zeta_c)$, a quadrature procedure can be employed to evaluate Eq. (2.19) if the Gaussian averages cannot be evaluated analytically. Alternatively, if a good approximation for the width matrix $\mathbf{C}_c(0,\mathbf{q}_c)$ is in hand, a Monte Carlo procedure can be adopted for evaluating Eq. (2.18) simultaneously with Eq. (2.19) by using a combined importance sampling function based on both the centroid density and the multiple Gaussian distribution of Eq. (2.19).

III. PHASE SPACE ANALYSIS OF CENTROID MOLECULAR DYNAMICS

In the earlier papers,[2,3] the development of the centroid MD method was guided in part by a variational analysis and, in part, by physical reasoning and intuition. In this section, a more satisfactory analysis and justification will be provided. Centroid MD is essentially a classical MD method defined on a quantum mechanical effective potential energy surface. While the deterministic nature of a classical-like MD algorithm seems to be at odds with the uncertainty inherent in

quantum mechanics, this paradox is partially resolved in centroid MD by the introduction of the centroid mean force which is obtained by first averaging over the quantum thermal path fluctuations. Moreover, the quasiclassical form in centroid MD arises from a kind of quantum "preaveraging" procedure which is *specifically suited* for the computation of the position time correlation function. The evidence to date strongly suggests that centroid MD captures the major features of the ensemble averaged correlations of the quantum dynamical position operator. However, two important questions deserve some further attention. These are (1) Can centroid MD be shown to *always* give a well-defined approximation to quantum position correlation functions? and (2) Why does the *equilibrium* path centroid variable occupy such an important role in *dynamical* correlation functions?

Important progress on the first question can be found in paper II. In that paper, the analogy of the equilibrium path centroid variable to a classical dynamical degree of freedom was motivated within the context of a variational theory based on effective quadratic action functionals in imaginary time.[1,5(a)] Unfortunately, it is not possible to estimate the absolute accuracy of the centroid MD method using the variational approach alone. Fortunately, the hint of a different approach is found in the Appendix of paper II where the analysis of a centroid MD approximation for general correlation functions is presented in the context of the Kubo transformed time correlation function.[9] A similar approach will be developed here to demonstrate that the centroid MD time correlation function is, in fact, always a well-defined approximation to the exact Kubo transformed position correlation function. For notational simplicity, the analysis is restricted to a two-dimensional phase space, but it can be readily generalized through the vector-matrix notation of the previous section.

In centroid MD, the centroid variable evolves according to the classical-like equation of motion,[2,3]

$$\begin{aligned} \dot{q}_c(t) &= p_c(t)/m, \\ \dot{p}_c(t) &= F_c(t), \end{aligned} \tag{3.1}$$

where the instantaneous centroid force is defined by[2,3]

$$F_c(q_c) = \langle f(q_c+\tilde{q})\rangle_c . \tag{3.2}$$

Here, the $f=-dV/dq$ and the symbol $\langle\cdots\rangle_c$ denotes the centroid-constrained average with the phase space imaginary time path integral or, as an approximation, the effective operator representation in Eq. (2.11). With trajectories in hand obtained from the above equations, the centroid MD time-correlation function is given by[2,3]

$$C^*(t) = \langle q_c(t) q_c(0)\rangle_{\rho_c}, \tag{3.3}$$

where the bracket with superscript ρ_c means that the initial conditions of the centroid trajectories are averaged with the phase space centroid density in Eq. (2.1). The companion paper[12] is devoted to the development of several algorithms for evaluating centroid dynamics [Eq. (3.1)] in general many-body systems.

After expanding $C^*(t)$ as a Taylor series in terms of t, and by taking into consideration the time reversibility of correlation function, one obtains

$$C^*(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} C^{[2n]}, \tag{3.4}$$

where the expansion coefficients are expressed as

$$C^{[2n]} = \langle q_c \mathscr{L}_c^{2n} q_c\rangle_{\rho_c}. \tag{3.5}$$

The operator $\mathscr{L}_c$ is the classical Poisson bracket

$$\mathscr{L}_c A = \{A, H_c\} \tag{3.6}$$

for a classical-like centroid Hamiltonian defined by $H_c = p_c^2/2 + V_c(q_c)$ with the effective centroid potential given by $V_c(q_c) = -k_B T \ln[\rho_c(q_c)/(m/2\pi\hbar^2\beta)^{1/2}]$.

At this point, it proves to be particularly informative to similarly analyze the Kubo transformed position correlation function[9]

$$\psi(t) = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \langle q(0) q(t+i\tau)\rangle \tag{3.7}$$

which is directly related to the quantum response function (cf. the Appendix of paper II) and the quantum dynamical position, momentum, and cross correlation functions. For example, by making use of the Kubo transformation and the commutator relation $p/m = [q,H]/i\hbar$, one can derive the following Fourier relations:

$$\tilde{C}_{qq}(\omega) = (\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{\psi}(\omega); \tag{3.8}$$

and

$$\begin{aligned} \tilde{C}_{pq}(\omega) &= i\omega m \tilde{C}_{qq}(\omega), \\ \tilde{C}_{pp}(\omega) &= \omega^2 m^2 \tilde{C}_{qq}(\omega), \end{aligned} \tag{3.9}$$

where p and q stand for any two elements of the multidimensional vectors $\mathbf{p}$ and $\mathbf{q}$. Equation (3.7) can also be written as a Taylor expansion, giving

$$\psi(t) = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} \psi^{[2n]}, \tag{3.10}$$

where the expansion coefficients are expressed as

$$\psi^{[2n]} = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \langle q(\tau) \mathscr{L}^{2n} q(0)\rangle. \tag{3.11}$$

Here, $\mathscr{L}$ is a commutator, the quantum analog of the Poisson bracket, i.e.,

$$\mathscr{L} A = \frac{1}{i\hbar}[A,H]. \tag{3.12}$$

After making use of the definition of the centroid variable in Eq. (2.2) and the invariance of trace, ones obtains

$$\psi^{[2n]} = \langle q_c \langle \mathscr{L}^{2n} q\rangle_c\rangle_{\rho_c}. \tag{3.13}$$

The centroid correlation function and the Kubo transformed correlation function take a similar analytical form [cf. Eqs. (3.5) and (3.13)], the difference being between the

terms $\mathscr{L}_c^{2n} q_c$ and $\langle \mathscr{L}^{2n} q \rangle_c$ in Eqs. (3.5) and (3.13), respectively. These terms can be determined explicitly and compared term-by-term. The first few terms are

$$n=0, \quad \langle q \rangle_c = q_c ; \tag{3.14}$$

$$n=1, \quad \langle \mathscr{L}^2 q \rangle_c = \langle f/m \rangle_c = F_c/m; \tag{3.15}$$

$$n=2, \quad \langle \mathscr{L}^4 q \rangle_c = \frac{1}{4m^3} \langle [f^{(2)} p^2 + 2p f^{(2)} p + p^2 f^{(2)}] \rangle_c + \frac{1}{m^2} \langle f^{(1)} f \rangle_c \tag{3.16}$$

for the Kubo correlation function [Eq. (3.13)], but for the centroid correlation function [Eq. (3.5)],

$$\mathscr{L}_c^4 q_c = \frac{1}{m^3} F_c^{(2)} p_c^2 + \frac{1}{m^2} F_c^{(1)} F_c . \tag{3.17}$$

Therefore, the two leading terms of the Taylor expansions for the centroid and Kubo correlation functions are the same, the difference between them beginning with the third term (i.e., at order t^4). The latter term will now be taken as an example to show how to evaluate the leading correction term to the centroid correlation function (i.e., to demonstrate that the centroid correlation function is a well-defined approximation to the Kubo correlation function). The Gaussian representation of operators in phase space [Eq. (2.11)] proves to be useful, though not essential, in the following analysis.

It is first noted that the centroid average of a product of operators can be written as a product of the centroid averages of operators and a leading correction term, i.e.,

$$\langle AB \rangle_c \simeq A_c B_c + A_c' B_c' C_c , \tag{3.18}$$

where terms higher order in the phase space width factor C_c [Eq. (2.4)] have been omitted. By virtue of the cyclic property of the trace, it can be shown in general that

$$C_c[\tilde{p}(0)\tilde{q}(0), q_c] + C_c[\tilde{q}(0)\tilde{p}(0), q_c] = 0. \tag{3.19}$$

It is also noted that the application of the commutator $\mathscr{L}$ of Eq. (3.12) four times in Eq. (3.16) leads to a symmetrized arrangement of momentum and coordinate operators. Combining this fact with Eqs. (3.18) and (3.19), it is seen that there will exist no centroid-constrained correlation functions mixing momentum and coordinate operators—at least to the order of the leading correction term. Thus, Eq. (3.16) becomes

$$\langle \mathscr{L}^4 q \rangle_c = \frac{1}{m^3} f_c^{(2)} \langle p^2 \rangle_c + \frac{1}{m^2} \langle f^{(1)} f \rangle_c , \tag{3.20}$$

where $f_c^{(n)}$ stands for the centroid-constrained operator average $f_c^{(n)} \equiv \langle f^{(n)} \rangle_c$. Equation (3.18) is useful when comparing the second term on the right-hand side of Eq. (3.20) with the second term of Eq. (3.17), i.e., $\langle f^{(1)} f \rangle_c \simeq F_c^{(1)} F_c$. The correction factor for this term contains the width factor and second- or higher-order derivatives of the force. The focus of the analysis can now shift to a comparison of the first term on the right-hand sides of Eqs. (3.17) and (3.20).

Because the centroid force F_c is a function and f is a *quantum* operator, the nth order derivative of the centroid force, $F_c^{(n)}$, and the centroid-constrained average of the nth order derivative of the force, $f_c^{(n)}$, are different even though the centroid force is equal to the centroid-constrained average of the force, i.e., $F_c = \langle f \rangle_c$. Application of the chain rule to $F_c^{(n)}$ reveals the difference between the force derivative terms as

$$\delta f_c^{(n)} = f_c^{(n)} - F_c^{(n)} = -\frac{1}{2} f_c^{(1+n)} C_c^{(1)}[\tilde{q}(0)\tilde{q}(0), q_c] + \cdots , \tag{3.21}$$

where the derivative of the width factor appears here instead of the width factor itself. This observation is particularly significant because it shows that an expression in terms of the centroid force or its derivatives agrees with its quantum counterpart $f_c^{(n)}$ to *all orders* in the width factor C_c, with corrections coming only in the spatial derivatives of that factor. From Eqs. (3.5) and (3.13), it is seen that the latter correction is then to be averaged over the centroid density, so large deviations will occur only if the width experiences large fluctuations which persist in the *average* sense.

Returning to the first term in the right-hand side of Eq. (3.20), the quantum fluctuations in momentum will contribute a further deviation from the similar term in the centroid correlation function [Eq. (3.17)]. The difference between the two terms for all powers of n is given by

$$\delta p_c^n = \langle p^n \rangle_c - p_c^n = \frac{n}{2} p_c^{n-2} C_c[\tilde{p}(0)\tilde{p}(0), q_c] + \cdots , \tag{3.22}$$

where $C_c[\tilde{p}(0)\tilde{p}(0), q_c]$ is the width factor for the momentum path fluctuations. The terms associated with this correction have a value of n no smaller than 2. The average of the term p_c^{n-2} over the phase space centroid density will simply factorize and give a constant since the distribution of the momentum centroid is the classical Boltzmann distribution and independent of the higher-order path Fourier modes.[2,3]

Taking into account all of the preceding considerations and generalizing them to terms of higher order, one can sum up in general the difference between the Kubo transformed position correlation function [Eq. (3.11)] and the centroid MD correlation function [Eq. (3.3)] to give

$$\psi(t) - C^*(t) = \sum_{n=2}^{\infty} \frac{t^{2n}}{(2n)!} \Delta^{[2n]}, \tag{3.23}$$

with Δ being the difference between the two sets of coefficients, given by

$$\Delta^{[2n]} = \psi^{[2n]} - C^{[2n]} \propto \left\langle q_c C_c \prod_l F_c^{(n_l)} \right\rangle_{\rho_c} , \tag{3.24}$$

where at least one n_l is no smaller than 2 and terms which involve the spatial derivatives of the width factor C_c have been neglected. The above result can be confirmed by dimensional analysis.

The preceding analysis confirms that the apparent success of centroid MD is by no means incidental and is, in fact, both physically and mathematically understandable. A few comments on the implications and significance of the analysis are as follows:

(a) At first glance, Eq. (3.24) confirms two properties of centroid MD which are already obvious.[2,3] Namely, the method is clearly exact if the potential contains no global anharmonicity [i.e., $F_c^{(n_l)} = 0$] or if the system is near the classical limit (i.e., C_c is small). However, upon closer inspection Eq. (3.24) also reveals why centroid MD is a good approximation in other, less straightforward, situations. To be specific, the centroid force F_c [Eq. (3.2)] at the centroid position q_c is computed by *averaging* the classical force over the imaginary time Feynman paths around the centroid. This averaging tends to smooth out rather dramatically any "kinks" in the potential energy function, at least over the length-scale of the particle's thermal width. The more "quantum" the particle, the more the averaging occurs. This behavior is very important and is one reason an effective *quadratic* action functional can be so accurate in describing, e.g., the equilibrium properties of the polaron[11] and the hydrated electron.[12] Given that such local "smoothing" occurs, the higher-order derivatives of the centroid force in Eq. (3.24) will tend to be small, giving a small correction factor in Eq. (3.24) even though the quantum thermal width C_c may be sizable. In order for centroid MD to become inaccurate, the preceding argument suggests that the locally nonlinear features of the effective *centroid* potential (i.e., the effective anharmonic terms) must be large. Such behavior occurs if the local anharmonicities in the physical potential near the centroid are large in the *average* sense and persist on a length-scale greater than the thermal width factor of the centroid quasiparticle. Moreover, since any correction terms are then *averaged* in Eq. (3.24) over the centroid distribution, the effective anharmonic behavior must also be present to a significant degree in the regions of greatest centroid density. Interestingly, as the system becomes more classical the effective anharmonicities (i.e., the higher derivatives of the centroid force) will indeed become larger, but this effect will be *compensated for* by a greater reduction in the thermal width factor C_c in Eq. (3.24). (Recall that centroid MD always yields the exact classical limit.)

(b) The definition of the centroid force captures the major contribution of quantum fluctuations and predicts the right quantum dynamics to within a tolerance proportional to the *averaged* higher-order derivatives of the centroid force and the centroid thermal width factor C_c. Though many semiclassical approximations are expanded in terms of $\hbar$, the centroid MD correlation function already contains terms which are infinite order in $\hbar$. The leading corrections to the centroid dynamics depend on the thermal width factor for the potential at hand (i.e., not just the free particle width which is of order $\hbar^2$).

(c) In general, the Kubo transformed position correlation function [Eq. (3.7)] is a well-defined quantum quantity which is an ideal candidate for any type of a classical-like approximation. This property arises because the integration over the imaginary time τ eliminates the imaginary part of the correlation function and also averages out certain quantum fluctuations.

(d) To shed some light on the unique role of the centroid in formulating a classical-like approach to the position correlation function, one can apply the Taylor expansion to the symmetrized position correlation function $\tilde{C}(t)$, giving

$$\tilde{C}(t)=\frac{1}{2}\langle[q(t),q(0)]_+\rangle=\sum_{n=0}^{\infty}\frac{t^{2n}}{(2n)!}\langle q\mathscr{L}^{2n}q\rangle, \tag{3.25}$$

where $[\cdots]_+$ is the anticommutator. If one attempts to carry out a term-by-term analysis as was done for the Kubo transformed position correlation function, complications arise with the first few terms because it is more difficult to define the effective momentum distribution and mass in the general case.[13] (Note again that the *centroid* momentum distribution is simply the Boltzmann distribution.[2,3]) Focusing instead on the Kubo transformed position correlation function [Eq. (3.7)] reveals the factorization of the centroid variable which, in turn, leads one to the factorization of the centroid constrained average in Eq. (3.13). The subsequent identification of the centroid force in the Taylor expansion terms of the correlation function supports the conclusion that the centroid variable can indeed be viewed as a *dynamical* variable at a well-defined level of approximation.

(e) To improve its accuracy, it seems certain that centroid MD should be augmented by an additional quantum factor. Because the correction to the centroid force begins at the t^4 term in the Taylor series expansion, such a term will not add linearly to the deterministic centroid force, but it might instead be constructed as some kind of time convolution reflecting the nondeterministic nature of quantum mechanics. Apparently, this "quantum memory function" would depend locally on the width factor and the anharmonicity and still yield a time-reversible dynamics. Of course, this argument is purely speculation.

IV. GENERAL TIME CORRELATION FUNCTIONS

In paper II, three different centroid-based approaches were proposed for calculating time correlation functions consisting of operators which depend on the coordinate variables. In this section, these strategies are modified to allow the computation of correlation functions of *general* operators which may depend on *both* position and momentum.[5(c)] The phase space centroid perspective, developed in Sec. I, will be employed to extend the formulations of paper II to general operators. The results in the present case will also be given for a multidimensional phase space using the notation in accord with that introduced in Sec. II. In addition, the companion paper[6] describes several algorithms for computing centroid MD trajectories.

A. Analytical continuation of centroid-constrained correlation functions

One of primary results from Sec. II is the expression for general imaginary time phase space correlation functions in the centroid-based perspective [Eqs. (2.12)–(2.19)]. In principle, the double Gaussian average in Eq. (2.19) can be performed for any functional form and the resulting expression

will then involve an average of functions which depend on $\mathbf{C}_c(\tau,\mathbf{q}_c)$ over the normalized centroid density. At that point, the centroid-constrained propagator can be analytically continued into real time ($\tau \rightarrow it$) to yield an approximation to the real time correlation function $C_{AB}(t)$. Within the framework of the approximate locally optimized effective harmonic theory,[1,5] the real time version of the centroid-constrained correlation function matrix can be obtained by replacing τ with it and the resulting expressions used in Eqs. (2.18) and (2.19).

As was pointed out in paper II, this analytical continuation method may not be completely satisfactory for two reasons: (1) The effective harmonic version of Eq. (2.4) is dynamically accurate only for relatively short times. The anharmonicities in the real potential will cause the analytically continued effective quadratic correlation function to deviate from the exact behavior at long times even in the classical limit. (2) The correlated operator representation in Eq. (2.18) is expressed at the level of a second-order cumulant expansion. Though this approximation may be an excellent one for imaginary time calculations, approximate real time correlation functions can be more sensitive to nonlinear interactions and thus less stable in their behavior at long times.

B. Cumulant expansion combined with centroid MD

As has been shown in Sec. III, the centroid MD correlation function [Eq. (3.3)] generally provides an accurate representation of the exact Kubo transformed position correlation function which, in turn, yields the real time correlation functions $\langle \dot{\boldsymbol{\zeta}}(t)\boldsymbol{\zeta}(0)\rangle$ through the Fourier relations in Eqs. (3.8) and (3.9) after replacing $\tilde{\psi}(\omega)$ with $C^*(\omega)$. Another strategy for computing *general* correlation functions is therefore to first introduce the phase space variable correlation functions directly into the expression for the general correlation function $\langle A(t)B(0)\rangle$ and to then use centroid MD to calculate $\langle \dot{\boldsymbol{\zeta}}(t)\boldsymbol{\zeta}(0)\rangle$ in that expression. Though many of the following expressions in this approach are similar to those given in paper II, the derivation in phase space is included here for completeness.

To begin the derivation, one considers the general imaginary time correlation function $C_{AB}(\tau)=\langle A(\tau)B(0)\rangle$ and expresses it as

$$C_{AB}(\tau)=\int \frac{d\mathbf{k}_1}{(2\pi)^{2N}}\int \frac{d\mathbf{k}_2}{(2\pi)^{2N}}\hat{A}(\mathbf{k}_1)\hat{B}(\mathbf{k}_2) \times\langle \exp[i\mathbf{k}_1\cdot\boldsymbol{\zeta}(\tau)+i\mathbf{k}_2\cdot\boldsymbol{\zeta}(0)]\rangle, \tag{4.1}$$

where the canonical path integral average in phase space is explicitly given by

$$\langle\cdots\rangle\equiv\frac{\int\cdots\int\mathscr{D}\boldsymbol{\zeta}(\tau)(\cdots)\exp\{-S[\boldsymbol{\zeta}(\tau)]/\hbar\}}{\int\cdots\int\mathscr{D}\boldsymbol{\zeta}(\tau)\exp\{-S[\boldsymbol{\zeta}(\tau)]/\hbar\}}. \tag{4.2}$$

The cumulant average of the exponential term in Eq. (4.1) can be performed and, for simplicity, truncated at second order, giving

$$\langle \exp[i\mathbf{k}_1\cdot\boldsymbol{\zeta}(\tau)+i\mathbf{k}_2\cdot\boldsymbol{\zeta}(0)]\rangle \simeq\exp\{i\mathbf{k}_1\cdot\langle\boldsymbol{\zeta}\rangle+i\mathbf{k}_2\cdot\langle\boldsymbol{\zeta}\rangle-\tfrac{1}{2}[\mathbf{k}_1\cdot\mathbf{C}_\delta(0)\cdot\mathbf{k}_1+\mathbf{k}_1\cdot\mathbf{C}_\delta(\tau)\cdot\mathbf{k}_2+\mathbf{k}_2\cdot\mathbf{C}_\delta(\tau)\cdot\mathbf{k}_1+\mathbf{k}_2\cdot\mathbf{C}_\delta(0)\cdot\mathbf{k}_2]\}, \tag{4.3}$$

where the imaginary time fluctuation correlation functions constitute a Hermitian matrix, defined by the elements

$$[\mathbf{C}_\delta(\tau)]_{ij}=\begin{bmatrix}\langle\delta p_i(\tau)\delta p_j(0)\rangle & \langle\delta p_i(\tau)\delta q_j(0)\rangle\\ \langle\delta q_i(\tau)\delta p_j(0)\rangle & \langle\delta q_i(\tau)\delta q_j(0)\rangle\end{bmatrix}, \tag{4.4}$$

where $\delta\boldsymbol{\zeta}=\boldsymbol{\zeta}-\langle\boldsymbol{\zeta}\rangle$. In order to perform the integrals over $\mathbf{k}_1$ and $\mathbf{k}_2$ in Eq. (4.1), new imaginary time correlation function matrices are defined as

$$\mathbf{C}_\delta^{\pm}(\tau)=\mathbf{C}_\delta(0)\pm\mathbf{C}_\delta(\tau). \tag{4.5}$$

After performing the k-integrals in Eq. (4.3), the expression for the general imaginary time correlation function is given by the double-Gaussian average

$$C_{AB}(\tau)\simeq\langle A(\langle\boldsymbol{\zeta}\rangle+\boldsymbol{\zeta}_1)B(\langle\boldsymbol{\zeta}\rangle+\boldsymbol{\zeta}_2)\rangle_{\mathbf{C}_\delta^+,\mathbf{C}_\delta^-}, \tag{4.6}$$

where the vectors $\boldsymbol{\zeta}_1$ and $\boldsymbol{\zeta}_2$ are related to the two Gaussian vectors $\boldsymbol{\zeta}_+$ and $\boldsymbol{\zeta}_-$ such that

$$\boldsymbol{\zeta}_{1,2}=\frac{1}{\sqrt{2}}(\boldsymbol{\zeta}_+\pm\boldsymbol{\zeta}_-). \tag{4.7}$$

The Gaussian vectors $\boldsymbol{\zeta}_+$ and $\boldsymbol{\zeta}_-$ have width matrices given by $\mathbf{C}_\delta^+(\tau)$ and $\mathbf{C}_\delta^-(\tau)$, respectively, as defined in Eq. (4.5).

The imaginary time expressions for $\mathbf{C}_\delta^{\pm}(\tau)$ can now be analytically continued via the inverse Wick rotation $\tau\rightarrow it$. The resulting approximate expression for the real time correlation function $C_{AB}(t)$ is given by

$$C_{AB}(t)\simeq\langle A(\langle\boldsymbol{\zeta}\rangle+\boldsymbol{\zeta}_1)B(\langle\boldsymbol{\zeta}\rangle+\boldsymbol{\zeta}_2)\rangle_{\mathbf{C}_\delta^+(t),\mathbf{C}_\delta^-(t)}, \tag{4.8}$$

where the real time-dependent Gaussian width matrices are given by

$$\mathbf{C}_\delta^{\pm}(t)=\mathbf{C}_\delta(0)\pm\mathbf{C}_\delta(t). \tag{4.9}$$

The correlation function elements of Eq. (4.9) can be calculated using the centroid MD position correlation function $C^*(t)$ defined in Eq. (3.3) and the Fourier transform relations in Eqs. (3.8) and (3.9) with $\tilde{\psi}(\omega)$ replaced by $\tilde{C}^*(\omega)$. Equation (4.8), with Eq. (4.9), is the central result of this subsection. It should be noted that Eq. (4.8) simplifies considerably if the operators A and B depend on only one phase space coordinate (i.e., most of the Gaussian integrals can be integrated out of the expression).

C. Centroid MD with semiclassical operators

A third algorithm is discussed in this subsection for calculating general time correlation functions with centroid MD. This procedure, which is more approximate than the previous ones, assumes a semiclassical representation of the quantum operators, the goal here being one of computational utility.

The method called "centroid MD with semiclassical operators," introduced in paper II, centers around the computation of the real time correlation function $C^*_{AB}(t)$, given by

$$C^*_{AB}(t)=\langle A_c(t)B_c(0)\rangle_{\rho_c}, \tag{4.10}$$

where the initial condition averaging is performed with the (normalized) phase space centroid density defined in Eq. (2.1). The semiclassical operators $O_c[q_c(t)]$ in Eq. (4.10) are given by the time-dependent analog of Eq. (2.11), i.e.,

$$O_c[\zeta_c(t)]=\langle O[\zeta_c(t)+\tilde{\zeta}]\rangle_{\mathbf{C}_c[0,\mathbf{q}_c(t)]}. \tag{4.11}$$

Here, $\zeta_c(t)$ is the phase space centroid trajectory which obeys the centroid MD equation of motion in Eq. (3.3), and the time dependent Gaussian width matrix $\mathbf{C}_c[0,\mathbf{q}_c(t)]$ for the vector $\tilde{\zeta}$ is given by the centroid-constrained correlation function matrix in Eq. (2.4) with the position centroid $\mathbf{q}_0$ located at $\mathbf{q}_c(t)$.

As shown in the Appendix of paper II, the general centroid correlation function in Eq. (4.10) is an approximation to the Kubo transformed version of the exact correlation function $C_{AB}(t)$. Therefore, in order to calculate $C_{AB}(t)$ one makes use of the Fourier relationship[2]

$$\tilde{C}_{AB}(\omega)\simeq(\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{C}^*_{AB}(\omega). \tag{4.12}$$

The expression in Eq. (4.10) is intended to maximize the utility of the centroid MD method in a transparent, though approximate, fashion for general correlation functions. The reader is referred to paper II for further analysis and comments.

V. NUMERICAL EXAMPLES

In this section, the accuracy of the centroid MD formulation is tested for correlation functions other than the position correlation function. In these studies, a nonlinear oscillator model is employed which is the same as one studied in paper II. The potential for this model is given by

$$V(q)=\frac{1}{2}q^2+cq^3+gq^4 \tag{5.1}$$

with the parameters $c=0.10$, $g=0.01$, $\hbar=1.0$, and $m=1.0$. In these units, the inverse temperature β is given as values of the dimensionless parameter $\beta\hbar\omega$. The single minimum of the potential in Eq. (5.1) is located at $q=0$. The cubic anharmonicity is operational for small deviations from the minimum, while the quartic anharmonicity influences the larger deviations from the minimum. At low temperatures, the cubic anharmonicity is the dominant perturbation. The energy gap between the ground and first excited vibrational state for the potential in Eq. (5.1) is shifted to the red by 6% compared with the harmonic limit of the energy spectrum. Such an anharmonic shift is equivalent to a (rather large) shift of 180 cm^{-1} for a 3000 cm^{-1} C–H stretching mode or a 60 cm^{-1} shift of a 1000 cm^{-1} C–C stretching mode. A temperature of $\beta=10$ was employed in the calculations which is equivalent to a C=C double bond at 300 K.

The exact correlation functions for the potential in Eq. (5.1) were obtained by diagonalizing the nonlinear Hamiltonian in a harmonic oscillator basis and employing 100 of the eigenstates in the dynamics calculations. The centroid forces and centroid potential in the centroid MD calculations were calculated from the optimized harmonic reference centroid density.[1,5] This approximation was shown in paper I to be an extremely good representation of the exact result. The centroid potential and forces were interpolated from a 1000-point grid within the range $[-10,10]$. The centroid MD initial positions were generated by Metropolis importance sampling from the position centroid distribution, while the initial momenta were directly sampled from the Gaussian centroid momentum distribution function. The evolution of 10^5 centroid trajectories were then calculated using the leapfrog algorithm with a time step of 0.05. The classical MD simulations were performed in the same fashion except that the real potential and force were used instead of centroid quantities.

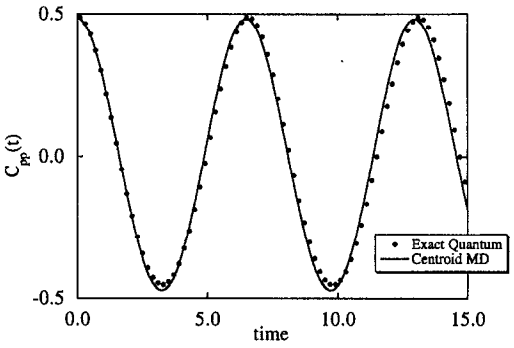

FIG. 1. A plot of the real time momentum autocorrelation function for the nonlinear oscillator described in Eq. (5.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, while the solid line is the centroid MD result (Ref. 14).

A. Momentum correlation functions

In Fig. 1, the momentum correlation function is shown for the nonlinear oscillator in Eq. (5.1) at $\beta=10$. The solid circles are the exact quantum results, while the solid line is the centroid MD result.[14] The latter method is clearly very accurate. It should be noted that results of similar accuracy were reported in paper II for the position correlation function.

B. General correlation functions

In order to test the methods outlined in Sec. IV for calculating general correlation functions in the phase space centroid perspective, the correlation function $\langle p^3(t)p^3(0)\rangle$ was calculated for the nonlinear potential defined in Eq. (5.1). This correlation function is a serious test for the approximate methods because of its nonlinearity and the fact that its classical amplitude is almost completely negligible at lower temperatures. In Fig. 2, the results for a temperature of $\beta=10$ are shown. The solid circles are the exact quantum results, the solid line is the cumulant expansion with centroid MD theory of Sec. IV B, the dashed line is the centroid MD with semiclassical operators result from Sec. IV C, and the dot–dashed line is the classical MD result. The correlation function from the cumulant expansion theory probably obtains the best

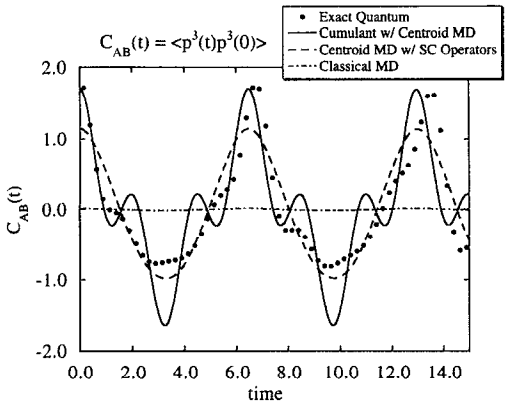

FIG. 2. A plot of the correlation function $\langle p^3(t)p^3(0)\rangle$ for the nonlinear potential in Eq. (5.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the cumulant expansion with centroid MD theory of Sec. IV B, the dashed line is the centroid MD with semiclassical operators method of Sec. IV C, and the dot–dashed line is the classical MD result.

agreement with the exact result, although there is too much structure and symmetry in the oscillations. The centroid MD with semiclassical operators method is also accurate, but it does not seem to reproduce the higher frequency oscillation. By comparison, the classical MD result is extremely inaccurate. Qualitatively similar results were obtained in paper II for the correlation function $\langle q^3(t)q^3(0)\rangle$. A discussion of the strengths and weaknesses of the cumulant with centroid MD method was provided in paper II, and this discussion is also applicable to the phase space centroid formulation of this method.

In Fig. 3, the correlation function $\langle A(t)B(0)\rangle$, where $A=pq$ and $B=qp$, is shown for the nonlinear potential in Eq. (5.1) at $\beta=10$. The symbols and lines are the same as in Fig. 2. This correlation function presents another serious test of the various methods because of the noncommutation of the position and momentum operators. Again, the classical

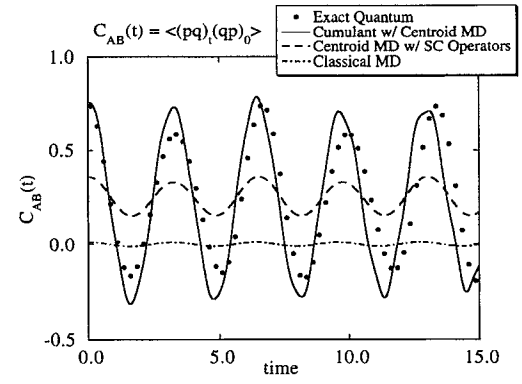

FIG. 3. A plot of the correlation function $\langle A(t)B(0)\rangle$, where $A=pq$ and $B=qp$, for the nonlinear potential in Eq. (5.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the cumulant expansion with centroid MD theory of Sec. IV B, the dashed line is the centroid MD with semiclassical operators result from Sec. IV C, and the dot–dashed line is the classical MD result.

MD result is extremely inaccurate for this low temperature correlation function. The centroid MD with semiclassical operators method does not reproduce the amplitude and negative values of this correlation function. This feature of the latter method arises because the correlation of the two operators at different times is ignored when the Gaussian averages are performed. Consequently, the semiclassical operator approximation underestimates the real time interference of the two quantum operators. On the other hand, the accuracy of the centroid MD with semiclassical operator method is superior to the classical calculation. Apparently, only the cumulant method can describe the quantum interference effects for this correlation function, and it appears to do so quite well.

Though the centroid MD results are quite encouraging and far superior to classical MD, it seems evident that none of the centroid MD approaches developed in Sec. IV for general correlation functions are completely satisfactory under all circumstances. Future research will be devoted to this important issue.

VI. CONCLUDING REMARKS

In the present paper, the formulation of quantum statistical mechanics based on the path centroid variable in Feynman path integration has been generalized to a phase space perspective. By virtue of this perspective, one can express operator averages and imaginary time correlation functions in terms of a classical-like averaging over the multidimensional phase space centroid density. An imaginary time centroid-constrained correlation function matrix for the phase space variables is seen to provide the effective width factors for the phase space centroid variables. The most significant aspect of the phase space analysis is that it facilitates a rigorous analysis and justification of the centroid molecular dynamics method for computing quantum dynamical time correlation functions.[2,3] Specifically, the centroid time correlation function calculated with centroid MD is shown to be a well-defined approximation to the exact Kubo transformed position correlation function. This analysis thereby reveals the important and not completely obvious connection between the equilibrium path centroid variable and the quantum dynamical position correlation function. Several strategies were then be developed for using centroid MD in the computation of general time correlation functions of quantum operators which depend on both position and momentum. In addition, the companion paper[6] describes several algorithms for computing centroid dynamics in realistic many-body systems. Future publications will be devoted to the application of centroid MD in the simulation of real systems, as well as to the continuation of its formal development.

ACKNOWLEDGMENTS

This research was supported by grants from the National Science Foundation and the Office of Naval Research. G.A.V. is a recipient of a National Science Foundation Presidential Young Investigator Award, a David and Lucile Packard Fellowship in Science and Engineering, an Alfred P. Sloan Foundation Research Fellowship, and a Dreyfus Foun-

dation New Faculty Award. The authors are indebted to John Lobaugh for his critical reading of the manuscript.

[1] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5093 (1994).
[2] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5106 (1994).
[3] J. Cao and G. A. Voth, J. Chem. Phys. **99**, 10 070 (1993).
[4] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw–Hill, New York, 1965), see in particular, pp. 279–286; see also Ref. 5.
[5] (a) R. P. Feynman and H. Kleinert, Phys. Rev. A **34**, 5080 (1986); R. Giachetti and V. Tognetti, Phys. Rev. Lett. **55**, 912 (1985); Phys. Rev. B **33**, 7647 (1986); W. Janke and H. Kleinert, Chem. Phys. Lett. **137**, 162 (1987); J. Cao and B. J. Berne, J. Chem. Phys. **92**, 7531 (1990); (b) See also the effective harmonic phase space perspective, in A. Cuccoli, V. Tognetti, P. Verrucchi, and R. Vaia, Phys. Rev. B **45**, 8418 (1992). Equation (2.11) is equivalent to their Eq. (24) if a variational effective quadratic action functional is implemented in the former equation for the width matrix [Eq. (2.5)]; (c) The displacement time correlation function for quantum lattices has been studied using moment expansion techniques and the centroid-based effective quadratic theory of Refs. 5(a) and 5(b) to compute the average moments. [See A. Cuccoli, V. Tognetti, A. A. Maradudin, A. R. McGurn, and R. Vaia, Phys. Rev. B **46**, 8839 (1992); **48**, 7015 (1993); A. Cuccoli, M. Spicci, V. Tognetti, and R. Vaia, *ibid.* **47**, 7859 (1993)]. The latter work makes use of the earlier results of A. Cuccoli, V. Tognetti, and R. Vaia, Phys. Rev. A **44**, 2734 (1991); (d) Phase space centroid density ideas have been used in the field of quantum activated dynamics by M. Messina, G. K. Schenter, and B. C. Garrett, J. Chem. Phys. **98**, 8525 (1993); G. K. Schenter, M. Messina, and B. C. Garrett, *ibid.* **99**, 1674 (1993). The latter ideas build on the path integral quantum transition state theory of G. A. Voth, D. Chandler, and W. H. Miller, J. Chem. Phys. **91**, 7749 (1989); G. A. Voth, Chem. Phys. Lett. **170**, 289 (1990). For a review of the latter, see G. A. Voth, J. Phys. Chem. **97**, 8365 (1993). See also the related work of M. J. Gillan, J. Phys. C **20**, 3621 (1987).
[6] J. Cao and G. A. Voth, J. Chem. Phys. **101**, 6168 (1994), following paper.
[7] See Ref. 4, Chap. 10, and R. P. Feynman, *Statistical Mechanics* (Addison–Wesley, Reading, 1972), Chap. 3. For reviews of path integral methods, both numerical and analytical, see B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. **37**, 401 (1986); J. D. Doll, D. L. Freeman, and T. L. Beck, Adv. Chem. Phys. **78**, 61 (1990); in *Quantum Simulations of Condensed Matter Phenomena*, edited by J. D. Doll and J. E. Gubernatis (World Scientific, Singapore, 1990); D. Chandler, in *Liquides, Cristallisation et Transition Vitreuse, Les Houches, Session LI*, edited by D. Levesque, J. P. Hansen, and J. Zinn-Justin (Elsevier, New York, 1991). For a discussion of the numerical path integral computation of quantum dynamics, see the above reviews as well as N. Makri, Comp. Phys. Commun. **63**, 389 (1990); D. Thirumalai and B. J. Berne, *ibid.* **63**, 415 (1991).
[8] See, e.g., M. S. Swanson, *Path Integrals and Quantum Processes* (Academic, San Diego, 1992), Sec. 4.2.
[9] See, e.g., R. Kubo, N. Toda, and N. Hashitsume, *Statistical Physics II* (Springer, Berlin, 1985), Chap. 4.
[10] A. Cuccoli, V. Tognetti, and R. Vaia, Phys. Rev. A **44**, 2734 (1991); G. A. Voth, *ibid.* **44**, 5302 (1991); see also Refs. 5(b) and 5(c).
[11] See, e.g., R. P. Feynman, *Statistical Mechanics* (Addison–Wesley, Reading, 1972), Chap. 8.
[12] See, e.g., D. Laria, D. Wu, and D. Chandler, J. Chem. Phys. **95**, 4444 (1991), and references cited therein.
[13] An effective set of molecular dynamics equations can be specified to formulate an alternative path integral approach for the calculation of $\tilde{C}(t)$ [G. J. Martyna (unpublished)]. However, for general nonlinear systems the appropriate MD mass in this approach is not the physical mass, but it must instead be a position-dependent effective mass.
[14] The momentum correlation function can be calculated with centroid MD in two ways. The first method is to compute the centroid position correlation function [Eq. (3.3)] and to then use the Fourier relationships in Eqs. (3.8) and (3.9) with $\tilde{\psi}(\omega)$ replaced by $\tilde{C}^*(\omega)$ to obtain the momentum correlation function. The second route is to calculate the centroid *momentum* correlation function and then use its Fourier transform directly in Eq. (4.12) to obtain the momentum correlation function. It can be shown that the two methods are equivalent, although the latter is numerically preferable because the former has a tendency to amplify the high frequency noise in the transform.