The formulation of quantum statistical mechanics based on the Feynman path centroid density. II. Dynamical properties

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The formulation of quantum dynamical time correlation functions is examined within the context of the path centroid variable in Feynman path integration. This study builds on the centroid-based approach to equilibrium properties developed in the companion paper. The introduction of the centroid perspective into the calculation of real time position correlation functions is outlined and an intriguing quasiclassical role for the centroid variable in real time position correlation functions is identified. This quasiclassical perspective is developed in terms of general interaction potentials, and the computational effort in implementing the method should scale with the size of the system in the same fashion as a classical molecular dynamics calculation. The centroid-based theory is also implemented in several different approaches to calculate general time correlation functions. The theoretical results are illustrated and tested by representative numerical applications.

I. INTRODUCTION

In the preceeding paper[1] (hereafter referred to as "paper I"), a formulation of quantum equilibrium statistical mechanics was discussed which is based on the path centroid density in Feynman path integration.[1–4] The centroid density $\rho_c(q_c)$ is expressed as the path integral[1–3]

$$\rho_c(q_c)=\int\cdots\int \mathscr{D}q(\tau)\,\delta(q_c-q_0)\exp\{-S[q(\tau)]/\hbar\}, \quad (1.1)$$

where $S[q(\tau)]$ is the imaginary time action functional. The path centroid variable q_0, defined by

$$q_0=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\, q(\tau), \quad (1.2)$$

and its corresponding density function are particularly useful classical-like quantities in statistical mechanics. It seems accurate to characterize the path centroid in equilibrium quantum systems as being the most direct analog to a classical degree of freedom. Indeed, this property forms the basis for the well-known Feynman–Hibbs quasiclassical theory of the partition function.[5]

In paper I, a formally exact theory for the centroid density was presented which goes well beyond the Feynman–Hibbs theory by using a diagrammatic perturbation expansion along with resummation and renormalization techniques. The latter analysis reveals the relationship between different variational approaches[5–7] and the perturbation series and thus enables one to improve upon the variational approximation. In addition, in paper I the usual quantum expressions for equilibrium quantities such as operator averages and imaginary time correlation functions were reformulated so that the centroid density is cast as the central statistical distribution in the computation of such quantities. Taken together, these two developments present a systematic formulation of equilibrium quantum statistical mechanics from the centroid density perspective.

A natural component of the formalism developed in paper I is the theory for quantum imaginary time correlation functions $\langle A(\tau)B(0)\rangle$. As in the other aspects of the formalism, the correlation function theory is expressed so that the path centroid variable and its corresponding density function [Eqs. (1.1) and (1.2)] occupy a central role. As shown in paper I, accurate analytic expressions can be obtained for such correlation functions through the use of general quadratic action functionals, a diagrammatic perturbation theory, and renormalization techniques. An important quantity in this theory is the centroid-constrained position correlation function which describes the correlations of imaginary time paths with respect to the constrained centroid variable. This correlation function acts as the imaginary time propagator in the diagrammatic theory and is also related to the effective thermal width (i.e., localization) of quantum particles.

In the present paper, an analysis is presented of perhaps one of the most challenging problems in condensed matter theory—the efficient and accurate computation of general real time quantum correlation functions $\langle A(t)B(0)\rangle$. Consistent with the theme of paper I, the properties of dynamical correlation functions are explored using the centroid-based perspective of quantum statistical mechanics.[1] To be more specific, real time dynamical information is first extracted with the help of the centroid-constrained formalism for imaginary time correlation functions developed in paper I. This procedure involves the analytic continuation of imaginary time position correlation functions $\langle q(\tau)q(0)\rangle$ via the inverse Wick rotation $\tau\rightarrow it$. It will be shown in Sec. II below that there is a dual outcome from this exercise. First, an approximate, but mathematically rigorous, analytical approach to real time position correlation functions is derived which is a direct outgrowth of the formalism in paper I. In essence, this theory turns out to be a quantum mechanical generalization of the classical "instantaneous normal mode" perspective,[8] which expresses the time correlation as the centroid density-weighted superposition of locally optimized linear harmonic oscillator (LHO) time correlation functions. The second, and in our opinion more important, outcome of the analysis is the development of a less mathematically rigorous, but far more computationally promising, "centroid molecular dynamics (MD)" perspective for the computation of real time position correlation functions.[9] Both approaches

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are then extended in Sec. III to treat general correlation functions.

Of the two approaches to time correlation functions mentioned above, the centroid MD approach is the most promising because it can be applied to general systems and the numerical effort of such an application scales with the number of particles in the same way as a classical molecular dynamics calculation. Furthermore, the centroid MD method is accurate and stable when compared to numerically exact results, and it holds considerable promise for future applications. Centroid MD is motivated by the results of mathematical analysis and can be supported by several reasonable physical arguments. Simply put, centroid MD "feels right." Nevertheless, it must be stated very clearly that the centroid MD approach, which is the main focus of the present paper, has not yet been completely justified in a rigorous mathematical sense. Rather, centroid MD is a theoretical construct which is based in part on rigorous analysis and in part on physical reasoning and intuition. Although the results obtained thus far are both intriguing and promising, the present paper should be considered more of a progress report on evolving research than a definitive statement on the computation of quantum time correlation functions.

The sections of this paper are organized as follows: In Sec. II, the real time position correlation function is analyzed from the centroid perspective and the centroid MD method is described. Next, various centroid-based approaches are described in Sec. III for calculating general time correlation functions. Numerical applications are then presented in Sec. IV and concluding remarks are given in Sec. V.

II. POSITION CORRELATION FUNCTIONS

To begin the analysis, it proves useful to first describe the centroid-constrained imaginary time position correlation function[1]

$$C_c(\tau,q_c)=\frac{\int\cdots\int \mathscr{D}q(\tau)\,\delta(q_c-q_0)[q(\tau)-q_0][q(0)-q_0]\exp\{-S[q(\tau)]/\hbar\}}{\int\cdots\int \mathscr{D}q(\tau)\,\delta(q_c-q_0)\exp\{-S[q(\tau)]/\hbar\}}. \tag{2.1}$$

This correlation function, which describes the correlations of the imaginary time paths about the centroid variable, is related to the usual position correlation function $C(\tau)\equiv\langle q(\tau)q(0)\rangle$ by the relationship

$$C(\tau)=\langle C_c(\tau,q_c)+q_c^2\rangle_{\rho_c}, \tag{2.2}$$

where the subscript "ρ_c" denotes averaging with the normalized centroid distribution $\rho_c(q_c)/\int dq_c\rho_c(q_c)$ [cf. Eq. (1.2)].

A. Analytically continued effective harmonic theory

Clearly, the centroid variable plays a central role in the behavior of the centroid-constrained correlation function in Eq. (2.1). The issue of interest here, however, is the role of the centroid variable in the *real time* quantum position correlation function. This information can in principle be extracted from the exact centroid-constrained correlation function $C_c(\tau,q_c)$ through the analytic continuation $\tau\rightarrow it$. Such a procedure, however, is generally not tractable unless there is some prior simplification of the problem. One such simplification is achieved through the use of an optimized reference quadratic action functional given by[1,7]

$$S_{\rm ref}[q(\tau)]=\int_0^{\hbar\beta} d\tau\left\{\frac{m}{2}\,\dot{q}(\tau)^2+\frac{1}{2}\,m\tilde{\omega}^2[q(\tau)-q_c]^2\right\}, \tag{2.3}$$

where $\tilde{\omega}$ is the centroid-dependent optimized effective LHO frequency. In paper I, it was shown that the effective frequency $\tilde{\omega}$ can be determined from summation and renormalization of the single vertex diagrams in the perturbation expansion of the centroid density or, equivalently, through the use of the Gibbs–Bogoliubov–Feynman (GBF) variational principle[6] with $\tilde{\omega}$ treated as the variational parameter.[7] The value for the optimized frequency $\tilde{\omega}$ is determined from the solution of the transcendental equation

$$m\tilde{\omega}^2=\frac{1}{\sqrt{2\pi\tilde{\alpha}}}\int d\tilde{q}\; V''(q_c+\tilde{q})\exp(-\tilde{q}^2/2\tilde{\alpha}), \tag{2.4}$$

where the effective thermal width factor $\tilde{\alpha}$ for a particular position of the path centroid is given by

$$\tilde{\alpha}=\frac{1}{m\beta\tilde{\omega}^2}\left[\frac{\hbar\beta\tilde{\omega}/2}{\tanh(\hbar\beta\tilde{\omega}/2)}-1\right]. \tag{2.5}$$

The imaginary time correlation function in Eq. (2.2) can be determined analytically for the optimized LHO reference system giving[1,9]

$$C_{\rm ref}(\tau)=\frac{1}{Z}\int dq_c\;\rho_c(q_c)\,\frac{\hbar}{2m\tilde{\omega}}\,\frac{\cosh[\tilde{\omega}(\tau-\hbar\beta/2)]}{\sinh(\hbar\beta\tilde{\omega}/2)} -\langle(m\tilde{\omega}^2\beta)^{-1}\rangle_{\rho_c}+\langle q_c^2\rangle_{\rho_c}, \tag{2.6}$$

where $Z=\int\rho_c(q_c)dq_c$ is the partition function. The second term in Eq. (2.6) is the effective LHO representation of the centroid mean squared fluctuation, i.e.,

$$\langle(m\tilde{\omega}^2\beta)^{-1}\rangle_{\rho_c}=\langle(q_c-\langle q_c\rangle_{\rho_c})^2\rangle_{\rho_c}. \tag{2.7}$$

Now one can make use of the equality

$$\langle q_c^2\rangle_{\rho_c}-\langle(q_c-\langle q_c\rangle_{\rho_c})^2\rangle_{\rho_c}=\langle q_c\rangle_{\rho_c}^2.$$

In turn, $\langle q_c\rangle_{\rho_c}^2$ can be easily shown to exactly equal $\langle q\rangle^2$. Since this term is a simple factor and not the focus of the dynamical analysis, the last two terms in Eq. (2.6) and related equations will hereafter be replaced by $\langle q\rangle^2$ or $\langle q_c\rangle_{\rho_c}^2$ interchangeably.

By using the expression in Eq. (2.6), it is now possible to analytically continue the above function to obtain the optimized LHO representation of the real time position correlation function[9]

$$C_{\rm ref}(t)=\frac{1}{Z}\int dq_c\ \rho_c(q_c)\ \frac{\hbar}{2m\bar{\omega}}\left[\frac{1}{\tanh(\hbar\beta\bar{\omega}/2)}\ \cos(\bar{\omega}t)-i\ \sin(\bar{\omega}t)\right]+\langle q\rangle^2. \tag{2.8}$$

The real time correlation function at this level of theory is just the superposition of centroid correlation functions for effective harmonic oscillators defined at each centroid position q_c. Each centroid correlation function is then weighted by the centroid density for the given value of q_c. The expression for the correlation function in Eq. (2.8) represents a quantum mechanical generalization of the classical "instantaneous normal mode" perspective for condensed phase correlation functions.[8]

One intriguing feature of Eq. (2.8) is the factorization into the centroid density (i.e., the centroid statistical distribution) and a dynamical part *which depends on the centroid frequency* $\bar{\omega}$. It is by no means obvious that such a factorization should occur. Furthermore, a rather different factorization occurs when the conventional formalism for computing time correlation functions is used [i.e., a double integration in terms of the *off-diagonal* elements of the thermal density matrix and Heisenberg operator $q(t)$ are required]. This result is considered as being significant, particularly in view of the physical insight it provides regarding the role of the centroid variable in real time position correlation functions.[9]

B. The centroid molecular dynamics method

In this section, the centroid MD method is first motivated by analyzing the result of the previous section. To do this, it is beneficial to introduce another real time correlation function given in terms of the centroid variable by

$$C^*_{\rm ref}(t)=\frac{1}{Z}\int dq_c\ \rho_c(q_c)\ \frac{1}{m\bar{\omega}^2\beta}\ \cos(\bar{\omega}t)+\langle q_c\rangle^2_{\rho_c}. \tag{2.9}$$

This correlation function is the exact analog of a classical correlation function for an effective LHO with the centroid "frequency" $\bar{\omega}$, and it is related to the quantum correlation function in Eq. (2.8) by the Fourier relation given in Eq. (2.15) below.[9] By noting that the first term on the right-hand side of Eq. (2.9) describes the correlation of fluctuations about the mean value $\langle q_c\rangle_{\rho_c}=\langle q\rangle$, Eq. (2.9) can then be rewritten as

$$C^*_{\rm ref}(t)=\frac{1}{Z}\int dq_c\ \rho_c(q_c)\langle q_c(t)q_c(0)\rangle_{\bar{\omega}}, \tag{2.10}$$

where $\langle q_c(t)q_c(0)\rangle_{\bar{\omega}}$ is a position correlation function calculated for *quasiclassical centroid dynamics* on the optimized LHO centroid potential. The dynamical centroid "trajectories" for this correlation function are given by the classical-like equations

$$q_c(t)=q_c(0)\cos\{\bar{\omega}[q(0)]t\}+\frac{p_c(0)}{m\bar{\omega}[q(0)]}\ \sin\{\bar{\omega}[q(0)]t\}. \tag{2.11}$$

The symbol $\langle\cdots\rangle_{\bar{\omega}}$ in Eq. (2.10) denotes initial condition averaging using the optimized LHO approximation to the phase space centroid density, which is given in the general case by

$$\rho_c(p_c,q_c)=\int\cdots\int \mathscr{D}p(\tau)\mathscr{D}q(\tau)\,\delta(p_c-p_0)\,\delta(q_c-q_0)\times\exp\{-S_E[p(\tau),q(\tau)]/\hbar\}. \tag{2.12}$$

The Euclidean phase space action functional in this expression is given by[10]

$$\begin{aligned}S_E[p(\tau),q(\tau)]&=\int_0^{\hbar\beta}d\tau\left\{\frac{p(\tau)^2}{2m}+V[q(\tau)]-ip(\tau)\dot{q}(\tau)\right\}\\&=\hbar\beta\,\frac{\tilde{p}_0^2}{2m}+\hbar\beta\sum_{n\neq 0}\left(\frac{\tilde{p}_n^2}{2m}+\frac{2\pi n}{\hbar\beta}\ \tilde{p}_n\tilde{q}_{-n}\right)\\&\quad+\int_0^{\hbar\beta}d\tau\ V[q(\tau)],\end{aligned} \tag{2.13}$$

where the Fourier modes $\{\tilde{p}_n,\tilde{q}_n\}$ are for the momentum and position paths, respectively. It seems particularly significant that the momentum centroid $\tilde{p}_0$ is always decoupled from position coordinates and is *precisely the same* as the classical Boltzmann momentum distribution. It should also be noted that Eq. (2.9) turns out to be the optimized LHO representation of the Kubo transformed[11] position correlation function given by

$$\psi(t)=\frac{1}{\hbar\beta}\int_0^{\hbar\beta}d\tau\langle q(t+i\tau)q(0)\rangle. \tag{2.14}$$

The latter connection is apparently significant for a centroid-based approach to general correlation functions (see the Appendix).

After Fourier transforming Eq. (2.9) and using the properties of the Dirac delta function, the relationship of $C^*_{\rm ref}(t)$ to the optimized LHO representation of the quantum position correlation function $C_{\rm ref}(t)$ can be shown to be[9]

$$\tilde{C}_{\rm ref}(\omega)=(\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{C}^*_{\rm ref}(\omega). \tag{2.15}$$

For general systems, the analytically continued result for the position correlation function in Eq. (2.10) must be considered a short time approximation to the actual quantum correlation function. In particular, the LHO approximation for the time evolution can and will break down at long times. It is then reasonable to assert that Eq. (2.10) must actually be an approximation to a more accurate expression. In a preliminary communication,[9] we have argued that, in fact, a more accurate representation of the quantum position time correlation function is related to a general centroid position correlation function

$$C^*(t)=\langle q_c(t)q_c(0)\rangle_{\rho_c}, \tag{2.16}$$

where the centroid trajectories are now generated by the effective classical equations of motion

$$m\ddot{q}_c(t) = -\frac{dV_c(q_c)}{dq_c}, \tag{2.17}$$

and the centroid potential is the *exact* excess quantum free energy of the centroid, i.e.,

$$V_c(q_c) = -k_B T \ln[\rho_c(q_c)/(m/2\pi\hbar^2\beta)^{1/2}]. \tag{2.18}$$

The centroid force $-dV_c(q_c)/dq_c$ defined in the right-hand side of Eq. (2.17) is the quantum mechanical potential of mean force for the centroid given by

$$-\frac{dV_c(q_c)}{dq_c} = -\frac{\int\cdots\int \mathcal{D}q(\tau)\delta(q_c-q_0)\{dV[q(0)]/dq\}\exp\{-S[q(\tau)/\hbar]\}}{\int\cdots\int \mathcal{D}q(\tau)\delta(q_c-q_0)\exp\{-S[q(\tau)]/\hbar\}}. \tag{2.19}$$

In the centroid MD correlation function [Eq. (2.16)], the notation $\langle\cdots\rangle_{\rho_c}$ means that the exact (normalized) phase space centroid density in Eq. (2.12) is used to average the initial conditions of the centroid trajectories. After the centroid correlation function $C^*(t)$ in Eq. (2.16) is calculated, the exact quantum position correlation function $C(t)$ can be estimated through the Fourier transform relationship

$$\tilde{C}(\omega) = (\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{C}^*(\omega). \tag{2.20}$$

An alternative route to these expressions is to use the fact that $C^*(t)$ is an approximation to the Kubo transformed position correlation function in Eq. (2.14). The relationship of the Kubo function to $C(t)$ is always given by the expressions in Eq. (2.20).

There is no doubt that the centroid MD prescription has *ad hoc* elements to it since the expressions in Eqs. (2.16) and (2.17) have not yet been rigorously derived. Yet, there are a number of strong arguments in favor of the centroid MD approach. First, it is noted that the analytically continued effective LHO theory in Eqs. (2.9)–(2.11) *has been* rigorously developed. The notion of classical-like centroid trajectories and a statistical averaging of initial conditions using the phase space centroid density has its basic origin to that theory. On the other hand, the analytically continued effective LHO theory must be taken for what it is—a short time approximation to some more accurate expression. By analogy with the classical instantaneous normal mode picture[8] and its connection to exact classical correlation function theory, the centroid MD perspective seems to provide the natural improvement of the optimized LHO theory. Furthermore, once the notion of a centroid trajectory is accepted, it seems quite evident that the force on a centroid trajectory at some later time and position in space should be no different from the force experienced by a different centroid trajectory which is *initiated* at $t=0$ at that same point in space. The centroid MD expression in Eqs. (2.16) and (2.17) satisfies this condition, while the analytically continued optimized LHO theory does not. Furthermore, centroid trajectories should be derived from the same effective potential which gives the *exact* centroid statistical distribution so that a "centroid ergodic theorem" will hold. Again, the centroid MD approach satisfies this condition, while the analytically continued optimized LHO theory may not. Finally, one would wish to have an approach which recovers the exact limiting expressions for globally harmonic potentials and for general classical systems. The centroid MD procedure in Eqs. (2.16)–(2.19) satisfies this criterion in each case.

Having made the above statements, it must again be stressed that centroid MD is *approximate* for nonlinear quantum systems. It seems clear that further research is needed to justify and/or improve on the approach. However, the numerical results presented in Ref. 9 and in Sec. IV suggest that centroid MD already provides an accurate and stable approximation to quantum position correlation functions. Based on this result, in the next section, the extension of the theory to treat general quantum time correlation functions is explored.

III. GENERAL CORRELATION FUNCTIONS

In this section, three strategies are presented to calculate general time correlation functions within the centroid dynamics perspective. While none of the three should be viewed as being completely satisfactory, it seems clear that each approach has promising and useful aspects to it. Moreover, these three approaches have different computational strengths and weaknesses which will become apparent in the numerical applications discussed in Sec. IV.

A. Analytical continuation of centroid-constrained correlation functions

One of the primary results from paper I is the expression for general imaginary time correlation functions in the centroid-based perspective given by

$$C_{AB}(\tau) = \langle \rho_{AB}(\tau, q_c)\rangle_{\rho_c}, \tag{3.1}$$

where the centroid-dependent imaginary time-correlated operator product $\rho_{AB}(\tau, q_c)$ is defined in the centroid density picture by the double-Gaussian average

$$\rho_{AB}(\tau, q_c) = \langle A(q_c+\tilde{q}_1)B(q_c+\tilde{q}_2)\rangle_{C_c^+, C_c^-}. \tag{3.2}$$

Here, the variables $\tilde{q}_1$ and $\tilde{q}_2$ are expressed as linear combinations of the two Gaussian variables q_+ and q_- such that

$$\tilde{q}_{1,2} = \frac{1}{\sqrt{2}}(q_+ \pm q_-). \tag{3.3}$$

The variables q_+ and q_- have the respective centroid-dependent Gaussian width factors

$$C_c^+(\tau,q_c)=C_c(0,q_c)+C_c(\tau,q_c),$$
$$C_c^-(\tau,q_c)=C_c(0,q_c)-C_c(\tau,q_c), \tag{3.4}$$

and the centroid-constrained imaginary time position correlation function $C_c(\tau,q_c)$ is defined in Eq. (2.1).

In principle, the double-Gaussian average in Eq. (3.2) can be performed for certain forms of the general operators A and B. The resulting expression will then involve an average of functions which depend on $C_c(\tau,q_c)$ over the normalized centroid density. An example is for the correlation function $\langle q^3(t)q^3(0)\rangle$, which is given by

$$\begin{aligned}\langle q^3(t)q^3(0)\rangle=\langle q_c^6+3q_c^4[2C_c(0,q_c)+3C_c(t,q_c)]\\ +9q_c^2[C_c^2(0,q_c)+2C_c^2(t,q_c)\\ +2C_c(t,q_c)C_c(0,q_c)]+3C_c(t,q_c)\\ \times[3C_c^2(0,q_c)+2C_c^2(t,q_c)]\rangle_{\rho_c}.\end{aligned} \tag{3.5}$$

This equation is exact in the case of a globally harmonic potential.

At this point, two approaches can be taken to calculate the real time correlation function $\langle A(t)B(0)\rangle$. The first is to seek an *exact numerical* analytical continuation of the centroid-constrained correlation function $C_c(\tau,q_c)$ in Eqs. (3.1)–(3.4) to real time. Numerical analytical continuation of correlation functions is a subtle issue[12] which will be reserved for future research. The second approach, which is discussed here, is to analytically continue the optimized LHO expression for the centroid constrained propagator $C_c(\tau,q_c)$ by replacing τ with *it* and to then use the resulting expression in Eqs. (3.1)–(3.4). In this case, the real time version of $C_c(\tau,q_c)$ is given by

$$C_c(t,q_c)\simeq\frac{\hbar}{2m\bar{\omega}}\left[\frac{1}{\tanh(\hbar\beta\bar{\omega}/2)}\cos(\bar{\omega}t)-i\sin(\bar{\omega}t)\right]-\frac{1}{m\bar{\omega}^2\beta}, \tag{3.6}$$

where the optimized frequency $\bar{\omega}$ depends on the centroid position via Eq. (2.4). The next step is to replace $C_c(\tau,q_c)$ with the approximate $C_c(t,q_c)$ in the closed-form expression for $\rho_{AB}(\tau,q_c)$, resulting in the real-time centroid constrained correlated operator product $\rho_{AB}(t,q_c)$. This function is then calculated for each value of the centroid variable and averaged over the centroid density [cf. Eq. (3.1)].

As will be shown in Sec. IV, the result obtained from this procedure is not completely satisfactory for the following two reasons: (1) The accuracy of the analytically continued version of Eq. (3.2) is only as good as the accuracy of the analytically continued centroid constrained propagator $C_c(t,q_c)$. While the effective LHO version of this function given in Eq. (3.6) is good at short times, anharmonicities in the real potential will cause it to deviate from the exact behavior at long times even in the classical limit. (2) The operator representation in Eq. (3.1) is expressed at the level of a second-order cumulant expansion [cf. Eqs. (2.14)–(2.19) of paper I]. Though this approximation is an excellent one for imaginary time calculations, real time correlation functions are more sensitive to nonlinear interactions and hence less predictable in their behavior. In principle, however, the cumulant average discussed in paper I could be carried out to higher order.

B. Cumulant expansion combined with centroid MD

In Sec. II B, the centroid MD method was described which is based on the propagation of quasiclassical centroid trajectories $q_c(t)$ derived from the mean force on the centroid as a function of position [cf. Eqs. (2.17)–(2.19)]. This method, combined with Eq. (2.20), generally provides an accurate representation of the exact quantum real time position correlation function $\langle q(t)q(0)\rangle$. It is therefore advantageous to first introduce the position time correlation function directly into the formulation of the general correlation function $\langle A(t)B(0)\rangle$ and to then use centroid MD to calculate $\langle q(t)q(0)\rangle$.

To begin, the general imaginary time correlation function $C_{AB}(\tau)=\langle A(\tau)B(0)\rangle$ is expressed as

$$C_{AB}(\tau)=\int\frac{dk_1}{2\pi}\int\frac{dk_2}{2\pi}\,\hat{A}(k_1)\hat{B}(k_2)\langle\exp[ik_1q(\tau)+ik_2q(0)]\rangle, \tag{3.7}$$

where

$$\langle\cdots\rangle\equiv\frac{\int\cdots\int\mathscr{D}q(\tau)(\cdots)\exp\{-S[q(\tau)]/\hbar\}}{\int\cdots\int\mathscr{D}q(\tau)\exp\{-S[q(\tau)]/\hbar\}}. \tag{3.8}$$

The cumulant average of the exponential term in Eq. (3.7) can be performed and truncated at second order giving

$$\begin{aligned}\langle\exp[ik_1q(\tau)+ik_2q(0)]\rangle\simeq\exp\Big\{ik_1\langle q\rangle+ik_2\langle q\rangle\\ -\frac{1}{2}[k_1^2C_\delta(0)+2k_1k_2C_\delta(\tau)\\ +k_2^2C_\delta(0)]\Big\},\end{aligned} \tag{3.9}$$

where now the imaginary time position fluctuation correlation functions are defined by

$$C_\delta(\tau)=\langle\delta q(\tau)\delta q(0)\rangle, \tag{3.10}$$

where $\delta q=q-\langle q\rangle$. In order to perform the integrals over k_1 and k_2 in Eq. (3.9), new imaginary time correlation functions are defined as

$$C_\delta^\pm(\tau)=C_\delta(0)\pm C_\delta(\tau). \tag{3.11}$$

After performing the k integrals in Eq. (3.9), the expression for the general imaginary time correlation function is given by the double-Gaussian average

$$C_{AB}(\tau)=\langle A(\langle q\rangle+\tilde{q}_1)B(\langle q\rangle+\tilde{q}_2)\rangle_{C_\delta^+,C_\delta^-}, \tag{3.12}$$

where the variables $\tilde{q}_1$ and $\tilde{q}_2$ are related to the two Gaussian variables q_+ and q_- such that

$$\tilde{q}_{1,2}=\frac{1}{\sqrt{2}}(q_+\pm q_-). \tag{3.13}$$

The Gaussian variables q_+ and q_- have width factors given by $C_\delta^+(\tau)$ and $C_\delta^-(\tau)$, respectively, defined in Eq. (3.11).

At this point, the above imaginary time expression for $C_{\delta}^{\pm}(\tau)$ can be continued analytically via the inverse Wick rotation $\tau \rightarrow it$. The resulting expression for the real time correlation function $C_{AB}(t)$ is given by

$$C_{AB}(t)=\langle A(\langle q\rangle+\tilde{q}_1)B(\langle q\rangle+\tilde{q}_2)\rangle_{C_{\delta}^{+}(t),C_{\delta}^{-}(t)}, \quad (3.14)$$

where the time-dependent Gaussian width factors are given by

$$C_{\delta}^{\pm}(t)=C_{\delta}(0)\pm C_{\delta}(t). \quad (3.15)$$

Since $C_{\delta}(t)$ equals $\langle q(t)q(0)\rangle-\langle q\rangle^2$, the correlation functions in Eq. (3.15) can be calculated with the help of the centroid MD method for real time position correlation functions outlined in Sec. II B. It should be noted that both the real and imaginary parts of $C(t)=\langle q(t)q(0)\rangle$ are required in the above expression. The centroid MD position correlation function $C^*(t)$ defined in Eq. (2.16) can be used to calculate the real and imaginary parts of $C(t)$ through the Fourier transform relation in Eq. (2.20).

Equation (3.14), which is the central result of this subsection, has two particularly appealing characteristics. Namely (a) it involves only the real time position correlation function $\langle q(t)q(0)\rangle$ which can be determined from centroid MD; and (b) the double-Gaussian average in Eq. (3.14) does not have to be expressed in closed form [i.e., it can be evaluated numerically at each time point using the values of the complex Gaussian width factors $C_{\delta}^{\pm}(t)$ computed from the centroid MD algorithm]. On the negative side, Eq. (3.14) is exact only in the globally harmonic limit due to the truncation of the cumulant expansion in Eq. (3.9). Furthermore, Eq. (3.14) may disagree with the exact classical limit for highly anharmonic systems at elevated temperatures. Nevertheless, Eq. (3.14) represents a promising first step towards the calculation of general real time correlation functions using the centroid MD method. This method is expected to be particularly useful for studying the quantum dynamics of high frequency molecular vibrations in condensed phases.

C. Centroid MD with semiclassical operators

In this subsection, a third algorithm is proposed for calculating general correlation functions. This procedure employs centroid MD along with a semiclassical representation of the quantum operators. While this approach is less mathematically direct than the ones developed in the previous two subsections, the goal here is one of utility. That is, the algorithm proposed below is easy to use and is capable of recovering the exact classical limit of general correlation functions. This approach, therefore, may be the method of choice for studying many problems in chemistry which are nearly classical in nature. The basic equations underlying the algorithm are simply stated below—the reader is referred to the Appendix for some supporting mathematical analysis.

The centroid MD method with semiclassical operators involves the computation of a general real time centroid correlation function $C_{AB}^{*}(t)$ given by

$$C_{AB}^{*}(t)=\langle A_c(t)B_c(0)\rangle_{\rho_c}, \quad (3.16)$$

where the initial condition averaging is performed with the (normalized) phase space centroid density defined in Eq. (2.12), and the semiclassical operators $O_c[q_c(t)]$ are given by the time-dependent analog of Eq. (2.11) in paper I, i.e.,

$$O_c[q_c(t)]=\langle O[q_c(t)+\tilde{q}]\rangle_{C_c[0,q_c(t)]}. \quad (3.17)$$

Here, $q_c(t)$ is the centroid trajectory which obeys the quasiclassical equation motion in Eq. (2.17), and the time dependent Gaussian width factor $C_c[0,q_c(t)]$ for the variable $\tilde{q}$ is given by the zero-time value of the centroid constrained correlation function in Eq. (2.1) with its centroid q_0 located at $q_c(t)$. It should be noted that Eq. (3.17) reduces to the centroid MD expression in Eq. (2.16) in the case of a position correlation function. As will be shown in Sec. IV B, the numerical results on general correlation functions indicate that for such problems, the Gaussian "smeared" representation of the operators in Eq. (3.17) will be superior to a simpler classical representation in terms of the centroid variables [cf. Eq. (4.3) below]. Schenter *et al.*[13] have employed the latter procedure to estimate the dynamical corrections to the path integral quadratic transition state theory (QTST) rate constant,[14] although their approach will be exact[15] in the globally quadratic limit for the barrier potential and orthogonal nonreactive modes.

As shown in the Appendix, the general centroid correlation function in Eq. (3.16) is actually an approximation to the Kubo transformed version[11] of the exact correlation function $C_{AB}(t)$. Therefore, in order to calculate $C_{AB}(t)$, one must make use of the general Fourier relationship

$$\tilde{C}_{AB}(\omega)=(\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{C}_{AB}^{*}(\omega). \quad (3.18)$$

The expression in Eq. (3.16) emphasizes the appealing characteristics of the centroid MD method in a fairly transparent fashion, but, as will be shown in the next section, it is somewhat lacking in its description of certain features of low temperature nonlinear vibrational correlation functions.

IV. APPLICATIONS

In this section, the accuracy of the centroid MD method is tested. In order to do this, two nonlinear oscillator models have been employed. The first model is an asymmetric potential given by

$$V(q)=\tfrac{1}{2}q^2+cq^3+gq^4 \quad (4.1)$$

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 in terms of values of the dimensionless parameter $\beta\hbar\omega$. The potential in Eq. (4.1) has a single minimum at $q=0$, exhibiting a cubic anharmonicity for small deviations from the minimum and a quartic anharmonicity for larger deviations from the minimum. At low temperatures where mode quantization effects are operational, the cubic anharmonicity is therefore the dominant perturbation. The potential in Eq. (4.1) shifts the energy gap between the ground and first excited vibrational states downward by 6% compared with the harmonic limit of the energy spectrum. This anharmonic shift is equivalent to, e.g., a 180 cm^{-1} shift of a 3000 cm^{-1} C–H stretching mode or a 60 cm^{-1} shift of a 1000 cm^{-1} C–C stretching mode.

This magnitude of the anharmonic energy shift is somewhat on the large side for realistic molecular vibrations. Two temperatures are employed in the calculations $\beta=3$ and 10. The first system is typical of a C–Cl single bond at 300 K, while the second is more like a C=C double bond at the same temperature.

A second model potential used to test the centroid-based theory is the quartic potential given by

$$V(q)=\tfrac{1}{2}q^2+gq^4 \tag{4.2}$$

with the parameters $g=0.03$, $m=1.0$, and $\hbar=1.0$. For this model, the energy gap between the ground and first excited states *increases* by 8%. The eigenvalue spacing of the quartic potential in Eq. (4.2) exhibits a nonlinear growth as $n^{4/3}$ with the quantum number n. This behavior might be typical of certain molecular bending vibrations which "stiffen" as the amplitude increases.

For both potential models, the exact results were obtained by first diagonalizing the nonlinear Hamiltonian in a harmonic oscillator basis set to find its eigenvalues and eigenvectors. Then, 100 of the eigenstates were employed to calculate the time correlation functions. The centroid molecular dynamics calculations for the two potential models required accurate centroid forces and centroid potential. These quantities were calculated from the optimized harmonic reference centroid density which 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 $[-10,10]$. As specified by the centroid MD algorithm, initial positions were generated by Metropolis importance sampling from the centroid distribution, while the initial momenta were directly sampled from the Gaussian centroid momentum distribution function. The dynamics of 10^5 centroid trajectories were then calculated using the leapfrog algorithm with a time step of 0.05. Because the correlation functions are always even functions of time, a discretized cosine Fourier transformation was employed to process the centroid correlation functions via Eq. (3.18). The classical MD simulations were performed in the same fashion except that the real potential and force were used instead of centroid quantities.

In the application of the direct analytical continuation method from Secs. II A and III A, the effective centroid frequency $\tilde{\omega}$ was determined self-consistently from Eq. (2.4) and the centroid constrained correlation function in Eq. (3.6) was calculated for that centroid position. The integration over the centroid density was then performed on a 200-point grid from $q=-2.0$ to 2.0.

In all figures below, the real part of the time correlation functions is plotted.

A. Position correlation functions

In Fig. 1, the position correlation function is shown for the nonlinear oscillator in Eq. (4.1) at $\beta=10$. The solid circles are the exact quantum results, the solid line is the centroid MD result from Eq. (2.16) with Eq. (2.20), the dashed line is the analytically continued effective harmonic result from Eq. (2.8), and the dotted–dashed line is the classical MD result. The centroid MD formalism is clearly the superior approach. The analytically continued result is also reasonably accurate, but it dephases somewhat too rapidly. The classical correlation function is in poor agreement with the exact quantum result. In Fig. 2, similar results are plotted, but for the higher temperature of $\beta=3$. In this case, the classical correlation function is in better agreement with the exact result, but the centroid MD is still superior. The analytically continued theory again dephases too quickly. (This anomalous dephasing seems to be a characteristic of the latter method.) It should be noted that in Ref. 9, similarly encouraging results were reported on the position correlation function for the quartic potential in Eq. (4.2)

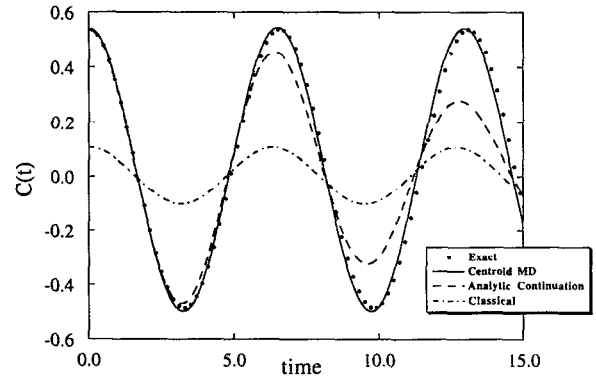

FIG. 1. A plot of the real time position autocorrelation function for the nonlinear oscillator described in Eq. (4.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the centroid MD result from Eq. (2.16), the dashed line is the analytically continued effective harmonic result from Eq. (2.8), and the dotted–dashed line is the classical MD result.

B. General correlation functions

In order to test the methods outlined in Sec. III for calculating general correlation functions, the correlation function $\langle q^3(t)q^3(0)\rangle$ was calculated for the nonlinear potential defined in Eq. (4.1). This correlation function presents a serious test for the approximate methods because of its nonlinearity and the fact that its amplitude is highly quantum mechanical in nature at lower temperatures. In Fig. 3, the results

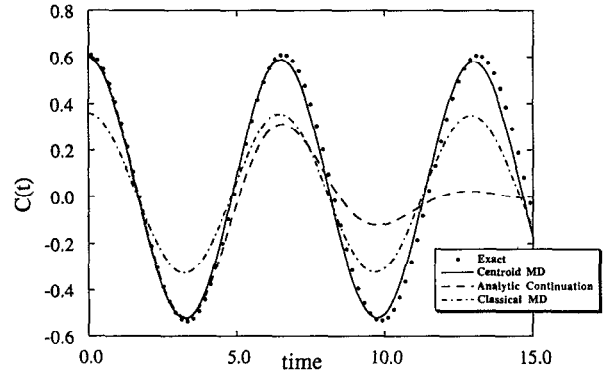

FIG. 2. The same as Fig. 1, but for a higher temperature of $\beta=3$.

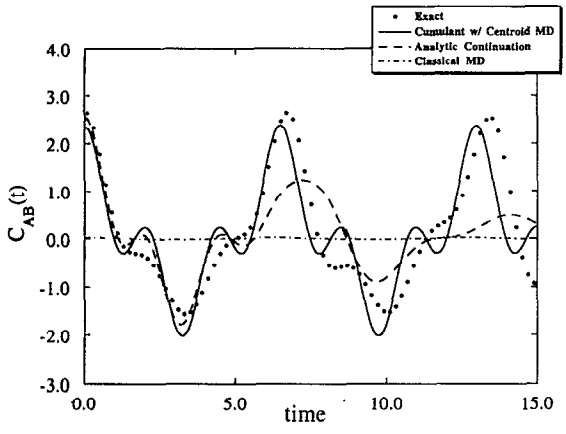

FIG. 3. A plot of the correlation function $\langle q^3(t)q^3(0)\rangle$ for the nonlinear potential in Eq. (4.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the cumulant expansion with centroid MD theory of Sec. III B, the dashed line is the analytically continued effective harmonic result from Sec. III A, and the dotted–dashed line is the classical MD result.

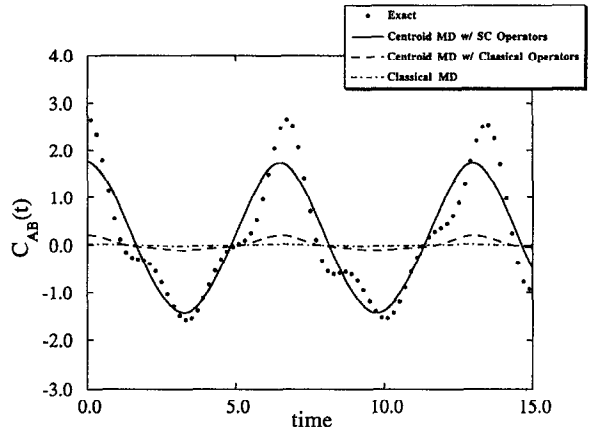

FIG. 4. A plot of the correlation function $\langle q^3(t)q^3(0)\rangle$ for the nonlinear potential in Eq. (4.1) at a temperature of $\beta=10$. The centroid MD with semiclassical operators method of Sec. III C is shown by the solid line, the exact result is given by the solid circles, and the classical result shown by the dotted–dashed line. Also shown by the dashed line is a centroid MD result, but one obtained by using the classical form of the operators as in Eq. (4.3).

for a temperature of $\beta=10$ are shown. The solid circles are the exact quantum results, the solid line is the cumulant expansion with the centroid MD theory of Sec. III B, the dashed line is the analytically continued effective harmonic result from Sec. III A, and the dotted–dashed line is the classical MD result. The correlation function from the cumulant expansion theory is in best agreement with the exact result, although there is too much structure and symmetry in the oscillations. Again the analytically continued result dephases much too quickly, being accurate only at short times, while the classical result is extremely inaccurate. One should bear in mind that while the accuracy of the cumulant expansion method combined with centroid MD is encouraging, this method may not reproduce the exact high temperature limit of correlation functions for very nonlinear potentials. The cumulant method should thus be viewed as being best suited for vibrational systems in which $\hbar\beta\omega>1$.

In Fig. 4, the centroid MD with semiclassical operators approach of Sec. III C (solid line) is compared to the exact result (solid circles) and to the classical result (dotted–dashed line) at $\beta=10$ for the potential in Eq. (4.1). Also shown is a centroid MD result (dashed line), but one calculated without using the Gaussian averaged operators defined in Eq. (3.17), i.e., by instead using the classical form of the operators expressed in terms of the centroid variables such that

$$C^*_{AB}(t)\approx\langle A_{\rm cl}[q_c(t)]B_{\rm cl}[q_c(0)]\rangle_{\rho_c}, \tag{4.3}$$

where $A_{\rm cl}$ and $B_{\rm cl}$ are the classical limits of the operators A and B (cf. Sec. III C). The centroid MD with semiclassical operators result does not completely capture the high frequency oscillation of the exact result, but it is clearly superior to both the classical and approximate centroid MD results. Evidently, the Gaussian representation of the effective operators is an essential component of this particular approach.

Calculations were also performed for the correlation function $\langle q^3(t)q^3(0)\rangle$ for the quartic potential in Eq. (4.2) at $\beta=10$. These results are shown in Fig. 5. The solid circles depict the exact quantum results, the solid line is the cumulant with centroid MD method of Sec. III B, the dashed line is the centroid MD with semiclassical operators approach of Sec. III C, while the dotted–dashed line is the classical MD result. The general level of agreement between the various approximate approaches and the exact result is similar to that for the potential in Eq. (4.1) and depicted in Figs. 3 and 4, although the beat pattern of the exact case is not as well reproduced.

In Fig. 6, the correlation function $\langle q^2(t)q^2(0)\rangle$ is shown for the nonlinear potential in Eq. (4.1) at $\beta=10$. The symbols and lines are the same as in Fig. 5. This correlation function is another serious test of the various methods because, classically, it can have no negative values, while quantum mechanically, it can be negative due to interference effects. Clearly, only the cumulant method can describe those effects, but its oscillation amplitude is not perfect. The classical result is extremely poor for this correlation function at such a low temperature. The centroid MD with semiclassical operators method also cannot give a correlation function with negative values in this case. This feature of the 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 quantum real time interference of the two operators and may thus fail to provide the finer dynamical details of some general time correlation functions at low temperatures. On the other hand, the accuracy of the centroid MD/semiclassical operator method is already far superior to a classical calculation and will rapidly improve as the temperature is increased. It also provides a simple and intuitive semiclassical algorithm to evaluate general quantum time correlation functions.

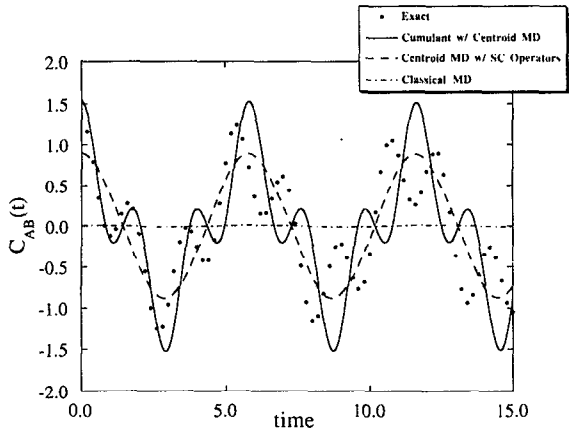

FIG. 5. A plot of the correlation function $\langle q^3(t)q^3(0)\rangle$ for the quartic potential in Eq. (4.2) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the cumulant expansion with the centroid MD theory of Sec. III B, the dashed line is the centroid MD with semiclassical operators result from Sec. III C, and the dotted–dashed line is the classical MD result.

C. Quantum self-diffusion constants

Thus far, the numerical applications have focused on the nonlinear vibrational dynamics of one-dimensional systems. However, the centroid MD formalism is by no means restricted to such systems. For example, the diffusion constant is a transport coefficient often computed by computer simulation. Naturally, one would like to include quantum effects in these calculations in a straightforward manner. If a system of quantum particles is assumed to evolve under the laws of centroid dynamics, then the diffusion constant can be calculated from the centroid velocity time correlation function via a Green–Kubo-like formula[16]

$$D=\frac{1}{3}\int_0^\infty dt\langle \mathbf{v}_c(t)\cdot\mathbf{v}_c(0)\rangle, \tag{4.4}$$

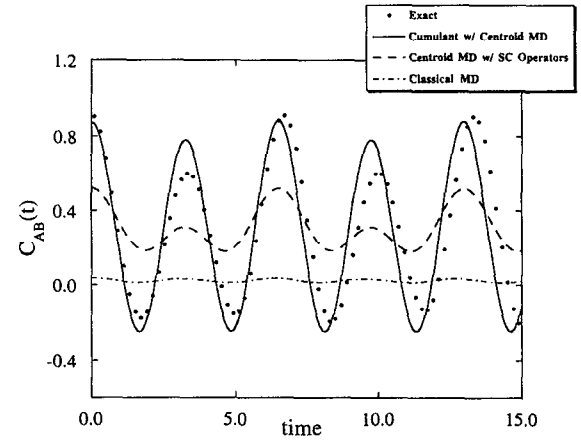

FIG. 6. A plot of the correlation function $\langle q^2(t)q^2(0)\rangle$ for the nonlinear potential in Eq. (4.1) at a temperature of $\beta=10$. The solid circles are the exact quantum results, the solid line is the cumulant expansion with the centroid MD theory of Sec. III B, the dashed line is the centroid MD with semiclassical operators result from Sec. III C, and the dotted–dashed line is the classical MD result.

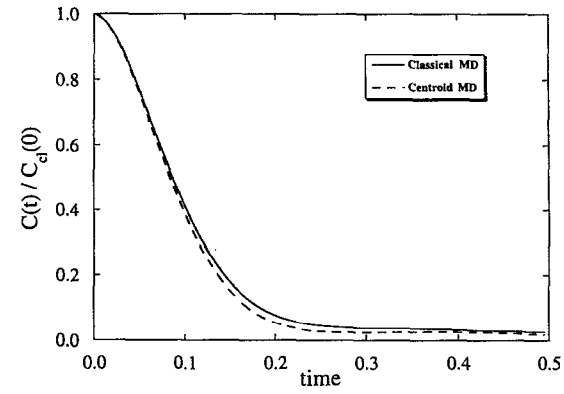

FIG. 7. The centroid velocity autocorrelation function from Eq. (4.4) for neon is shown here by the dashed line. The classical MD result is given by the solid line. The results are plotted as the ratio $C(t)/C_{cl}(0)$.

where $\mathbf{p}_c=m\mathbf{v}_c$ and the average is over all particles and initial configurations according to the phase space centroid density. While the centroid dynamics should formally be computed according to Eqs. (2.17)–(2.19), in a homogeneous nearly classical system, the leading quantum correction in the centroid potential is given by

$$V_c(q)=V(q)+\frac{\hbar^2\beta}{12m}\,V^{(2)}(q). \tag{4.5}$$

This expression, which can be easily generalized to N particles in three dimensions, simplifies the implementation of the centroid MD algorithm considerably in nearly classical systems.

The above algorithm to compute diffusion constants was applied to liquid argon and neon as described by a pairwise Lennard-Jones interaction potential. In Fig. 7, the velocity time correlation function is plotted for liquid neon as described by the parameters listed in Table I. The quantum and classical diffusion constants were calculated from the velocity correlation function using Eq. (4.4) and its classical limit. In Table I, the classical and quantum diffusion constants computed in this way are listed for Ne and Ar liquids.

When the quantum mechanical nature of the noble gas atoms is taken into account, the diffusion constant is reduced by a small fraction. In the gas phase and to some degree in liquids, the diffusion process can be viewed as a sequence of two-body collisions, the frequency of which depends on the collision cross section. Because the quantum centroid cross section is larger than the corresponding classical value, the quantum diffusion constant is found to be smaller. In addition, it has been suggested[8] that the magnitude of the unstable instantaneous normal modes in liquids reveals the "fluidity" of the liquid and thus relates directly to the diffusion process. In a subsequent paper, it will be demonstrated that the quantum instantaneous phonon spectrum for Lennard-Jones fluids shows a less prominent peak in the imaginary frequency region than in the classical limit. This result supports the conclusions drawn from the present centroid MD simulation.

TABLE I. Diffusion constants[a] for Lennard-Jones fluids.[b]

Fluid	D_{cl}	D_{qt}	D_{qt}/D_{cl}
Ar	6.34	6.27	0.99
Ne	4.38	4.08	0.93

[a]D_{cl} and D_{qt} are the classical and quantum diffusion constants, respectively, as calculated from Eq. (4.4). The units of D are 10^{-5} cm^2 s^{-1}.
[b]The parameters for the argon fluid are σ=3.4 Å, ϵ=120 K, m=40 a.u., T=156 K, and $\rho\sigma^3$=0.75, while the parameters for the neon fluid are σ=2.75 Å, ϵ=35.8 K, m=20 a.u., T=40 K, and $\rho\sigma^3$=0.68.

V. CONCLUDING REMARKS

In the present paper, the role of the path integral centroid variable in quantum real time correlation functions has been explored. Based on the analytical continuation of centroid constrained position correlation functions, the concept of a classical-like centroid trajectory was formulated. A "centroid molecular dynamics" method was then proposed which improves upon the analytically continued expression and also builds into the theory several desirable features of condensed phase correlation functions. Three strategies were then elaborated for using the centroid MD algorithm in the calculation of general correlation functions. The results of the various formulations were tested on nonlinear vibrational systems with varying degrees of success. The position correlation functions calculated with centroid MD are highly accurate, but none of the approaches for general correlation function gives completely satisfactory results. On the other hand, the test cases were stringent tests of the methods (i.e., low dimensional, highly quantum mechanical systems). Higher temperatures and/or condensed phase dissipative effects should tend to enhance the accuracy of the centroid MD approaches.

The future holds several challenges for the improvement and application of the centroid MD method. Above all, a more rigorous mathematical justification of the method is needed. It seems almost certain that the centroid force as specified by Eq. (2.19) should be augmented by other, more "quantum mechanical", terms. These terms must depend on the nonlinearity of the potential since centroid MD is exact for globally harmonic systems. Second, a completely general and reliable centroid MD formalism is certainly needed for computing general correlation functions, although good progress on this issue has been achieved in the present paper. Finally, efficient algorithms will be required in order to evaluate the centroid forces for the centroid trajectories in general many-body systems. Future publications will be devoted to these challenges, as well as to the application of the centroid MD method to a variety of condensed matter systems.

Note added in proof. A forthcoming paper will present a phase space centroid analysis of centroid MD, as well as a second justification which is not based on the effective harmonic perspective.

ACKNOWLEDGMENTS

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APPENDIX: THE CENTROID MD METHOD WITH SEMICLASSICAL OPERATORS

In order to analyze the centroid MD method with semiclassical operators (cf. Sec. III C), it is useful to introduce the Kubo transformed time correlation function[11]

$$\psi_{AB}(t)=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\langle A(t+i\tau)B(0)\rangle \tag{A1}$$

and the corresponding response function

$$K_{AB}(t)=\frac{i}{\hbar}\ \langle[A(t),B(0)]\rangle, \tag{A2}$$

where

$$K_{AB}(t)=-\beta\dot{\psi}(t). \tag{A3}$$

Classically, the two correlation functions $\psi_{AB}(t)$ and $C_{AB}(t)=\langle A(t)B(0)\rangle$ are the same, whereas quantum mechanically, they are related through the Fourier transform relations

$$\tilde{C}_{AB}(\omega)=(\hbar\beta\omega/2)[\coth(\hbar\beta\omega/2)+1]\tilde{\psi}_{AB}(\omega). \tag{A4}$$

To relate ψ to the centroid MD correlation function in Eq. (3.16), it proves informative to perform the Taylor expansion

$$\psi_{AB}(t)=\sum_n \frac{t^n}{n!}\ \psi_{AB}^{(n)}$$

$$=\sum_n \frac{t^n}{n!}\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\langle\mathscr{L}^n A(\tau)B(0)\rangle, \tag{A5}$$

where operator $\mathscr{L}$ is defined by a commutator

$$\mathscr{L}A\equiv\frac{1}{i\hbar}\ [A,H], \tag{A6}$$

which is the quantum analog of the Poisson bracket. The notation for purely imaginary time correlation functions $C_{AB}(\tau)=\langle A(\tau)B(0)\rangle$ is used in Eq. (A5) as opposed to the mixed time notation necessary for the Kubo correlation function in Eq. (A1).

The leading order ($n=0$) term in Eq. (A5) is the equilibrium value of the correlation given by

$$\psi_{AB}^{(0)}=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\langle A(\tau)B(0)\rangle. \tag{A7}$$

After representing the operators in Fourier space as in Eq. (2.14) of paper I, one obtains

$$\psi_{AB}^{(0)}=\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\int\frac{dk_1}{2\pi}\int\frac{dk_2}{2\pi}\ \hat{A}(k_1)\hat{B}(k_2)$$

$$\times\langle\exp[ik_1q(\tau)+ik_2q(0)]\rangle, \tag{A8}$$

where, after performing a cumulant average over the quantum path fluctuations through second order, the exponential term is expressed as

$$\langle \exp[ik_1 q(\tau)+ik_2 q(0)]\rangle = \langle \exp\{ik_1 q_c + ik_2 q_c - \tfrac{1}{2}[k_1^2\alpha(0) + 2k_1k_2\alpha(\tau)+k_2^2\alpha(0)]\}\rangle_{\rho_c}. \tag{A9}$$

Here, $\alpha(\tau)$ is the centroid-constrained propagator in Eq. (2.1). Now the integration over τ in Eq. (A8) can be approximated by

$$\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \exp[-k_1k_2\alpha(\tau)] \approx \exp\left[-k_1k_2\frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau\,\alpha(\tau)\right]=1, \tag{A10}$$

where $(\hbar\beta)^{-1}\int_0^{\hbar\beta} d\tau\,\alpha(\tau)=0$ according to the definition of the centroid-constrained correlation function in Eq. (2.1) of the main text. Since the coupling term between k_1 and k_2 in Eq. (A10) vanishes in this approximation after the integration over τ, the equilibrium quantity $\psi_{AB}^{(0)}$ turns out to be

$$\psi_{AB}^{(0)} = \langle A_c(q_c)B_c(q_c)\rangle_{\rho_c}, \tag{A11}$$

where the centroid operators $A_c(q_c)$ and $B_c(q_c)$ are defined as in Eq. (3.17) of the main text and Eq. (2.11) of paper I. Equation (A11) indicates that the initial value of the Kubo correlation function $\psi_{AB}(t)$ can be evaluated using a product of centroid quantities if the imaginary time correlation between the Gaussian averages in the expression is ignored [cf. Eq. (A10)]. This approximation is a good one if the quantum width of the particle is relatively small, leading to the term "semiclassical operator" in this particular implementation of the centroid MD method.

The $\psi_{AB}^{(1)}$ term in Eq. (A5) vanishes because $\psi(t)$ must be an even function of time t. The next term is nonzero, however, and is given by

$$\psi_{AB}^{(2)} = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \langle \mathscr{L}^2 A(\tau)B(0)\rangle = \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \left\langle \left[\frac{1}{m^2}A''(\tau)p^2(\tau) - \frac{1}{m}A'(\tau)V'(\tau)\right]B(0)\right\rangle + \cdots, \tag{A12}$$

where terms of higher order in $\hbar$ are neglected. By using the same approximations as used in deriving Eqs. (A9)–(A11), one obtains

$$\psi_{AB}^{(2)} = \left\langle \left(\frac{1}{m^2}A''p^2 - \frac{1}{m}A'V'\right)_c B_c(q_c)\right\rangle_{\rho_c}, \tag{A13}$$

where the notation $(\cdots)_c$ denotes a momentum and position centroid-constrained average with the phase space path integral and $\langle\cdots\rangle_{\rho_c}$ here denotes an average over the normalized phase space centroid density. Consistent with the semiclassical operator assumption is an approximation for the product of two operators A and B in the centroid representation given by

$$(AB)_c \approx A_c(q_c)B_c(q_c). \tag{A14}$$

[This approximation introduces an error of the order $A'(q_c)B'(q_c)C_c(0,q_c)$, where the centroid-constrained propagator $C_c(0,q_c)$ is the Gaussian width factor of the particle.] After using Eq. (A14) in Eq. (A13), the above expression can be approximated to be

$$\psi_{AB}^{(2)} = \left\langle \frac{1}{m^2}[A''(q_c)]_c p_c^2 - \frac{1}{m}[A'(q_c)]_c[V'(q_c)]_c B_c(q_c)\right\rangle_{\rho_c}, \tag{A15}$$

where the fact has been used that

$$(p^2)_c = p_c^2 + \mathscr{O}(\hbar^2). \tag{A16}$$

The distribution for the centroid momentum p_c is the same as the classical Boltzmann distribution [cf. Eq. (2.13)].

If the centroid MD correlation function $C_{AB}^*(t)$ described in Eqs. (3.16) and (3.17) of the main text is expanded through second order in t, one discovers that the first two expansion terms agree with Eqs. (A11) and (A15). In general, the operator $\mathscr{L}$ always gives the same result as the Poisson bracket if all higher orders in $\hbar^2$ are ignored. With this approximation and the approximations in Eqs. (A10) and (A14), the expansion terms in Eq. (A5) can be expressed in terms of equivalent centroid quantities and the same procedure can in principle be carried out to all orders of $\psi_{AB}^{(n)}$. This analysis suggests that to a reasonable degree of accuracy, the general Kubo time correlation function $\psi_{AB}(t)$ in Eq. (A1) can be approximated by the centroid MD correlation function $C_{AB}^*(t)$ with semiclassical operators. The real time correlation function $\langle A(t)B(0)\rangle$ can then be estimated through the Fourier relation in Eq. (A4) [i.e., Eq. (3.18)].

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