Finite Temperature Correlation Functions via Forward−Backward Semiclassical Dynamics[†]

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The forward−backward semiclassical treatment of ensemble averaged quantities is combined with a discretized path integral description of the Boltzmann operator describing the initial density. We present a practical Monte Carlo methodology for calculating time-dependent expectation values and time correlation functions, applicable to polyatomic systems.

I. Introduction

Semiclassical theory, in particular its time-dependent version,[1,2] offers an intuitive picture of quantum mechanics near the classical limit. The semiclassical approximation arises naturally as the small $\hbar$ limit of the path integral in Feynman's formulation of quantum mechanics[3,4] and, as such, contains no ad hoc assumptions. Unlike its time-independent counterpart, time-dependent semiclassical theory encounters no conceptual difficulties in multidimensional systems exhibiting classically chaotic dynamics. As shown in the pioneering work of Miller,[5,6] the semiclassical propagator retains all fundamental features of quantum mechanics in most regimes of chemical interest: it preserves unitarity, uncertainty products and zero-point energy, captures phase interference phenomena semiquantitatively, and also allows (at least to some extent) tunneling. A number of studies have shown that the semiclassical approximation can offer a semiquantitative description of small molecule reaction dynamics and that it is sufficiently accurate even in strongly chaotic systems.[7−9] Miller has shown[10] that the semiclassical expression for the survival amplitude or a time correlation function can be cast in an initial value representation which involves trajectories that are specified in terms of their initial phase space values, thus avoiding solution of double-ended boundary value problems, and several variants of this idea have been suggested and applied with success.[11−23] The major obstacle that has in the past hindered routine use of semiclassical methods in polyatomic simulations is the oscillatory character of the integrand. As in the case of the real time path integral, Monte Carlo methods suffer from the "sign problem" and generally fail to converge, although filtering techniques have proven quite successful in certain cases.[24,25] Several excellent articles and books have reviewed the foundations and recent progress in this field.[26,5,6,27,28]

Forward−backward semiclassical dynamics (FBSD) methods[29−39] have emerged as a practical approach to the quantum dynamics of polyatomic systems. The main appeal of these methods is the joint treatment of the time evolution operator and its adjoint (a structure common to all ensemble averaged expressions) as a *single* operator whose dynamics are approximated by the semiclassical method. This treatment results in trajectories that are integrated along a forward−backward time contour. As a result, the combined action integral is small,

implying that the forward−backward semiclassical propagator is a smooth function of the integration variables and thus can be handled successfully by Monte Carlo methods.

The present paper focuses on the forward−backward treatment of expectation values and time correlation functions at finite temperature. We work with a particular version of FBSD that offers the additional advantage of allowing rigorous elimination of the semiclassical prefactor.[35,36] The absence of a prefactor from these expressions leads to enormous computational savings, since its evaluation generally scales as the third power of the number of degrees of freedom. While practical for large scale simulation, FBSD is not as accurate as a full semiclassical calculation. The combined treatment of the dynamics along a forward−backward time contour excludes combinations of different forward and backward paths that are largely responsible for quantum interference.[32] As a result, the method is often accurate for short or intermediate times, and is indeed very similar in spirit to the quasiclassical Wigner method[40,41] which can also be viewed as the linearized limit of a semiclassical treatment.[42] In practice, extensive dephasing in systems of many degrees of freedom leads naturally to decoherence, and FBSD (as well as the quasiclassical Wigner method) can be essentially quantitative in such cases.[35]

Sampling of initial conditions for a classical trajectory requires knowledge of a weight factor determined by the prescribed initial condition. In the present version of FBSD,[35,36] this factor is given by the matrix element of the initial density with respect to coherent states.[11] If the initial wave function corresponds to a pure state of Gaussian form this matrix element can be evaluated analytically. However, more general initial conditions require a numerical treatment of the density. The most common situation is that of a canonical ensemble where the initial condition describes Boltzmann statistics. The most general and accurate methodology for evaluating matrix elements of the Boltzmann operator is the path integral formulation of quantum statistical mechanics.[3,4,43] In this paper we adopt the discretized path integral to develop a Monte Carlo methodology for calculating the coherent state matrix element entering the prefactor-free FBSD expression for time correlation functions or expectation values. A path integral treatment of the canonical density in conjunction with the Wigner approximation has recently been developed by Ciccotti et al.[46]

Section II describes the theoretical formulation and develops a procedure that can be used in conjunction with a Metropolis

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random walk.[44] Because the sampling factor arising from the path integral treatment of the Boltzmann operator is not normalized a priori, one has to find a way of evaluating its norm. Fortunately, we are able to express the normalization integral in terms of one additional integral which is easily evaluated by a separate Monte Carlo procedure. Section III illustrates the methodology with numerical calculations of the average position and correlation functions in one-dimensional anharmonic systems. Finally, section IV concludes.

II. Theoretical Description

The goal is to calculate correlation functions of the type

$$C(t) = \text{Tr}(\rho(0)Ae^{iH_{\text{dyn}}t/\hbar}Be^{-iH_{\text{dyn}}t/\hbar}) \qquad (2.1)$$

where H_{dyn} is a Cartesian Hamiltonian generating the dynamics, $\rho(0)$ is the density operator of the initial ensemble, and A, B are general operators. To keep the presentation simple we use one-dimensional notation, noting that the multidimensional generalization of the theory presented below is straightforward. The FBSD formulation of Shao and Makri,[35] expresses the correlation function as

$$C(t) = -i\frac{\partial}{\partial\mu}\text{Tr}(\rho(0)Ae^{iH_{\text{dyn}}t/\hbar}e^{i\mu B}e^{-iH_{\text{dyn}}t/\hbar})|_{\mu=0} \quad (2.2)$$

Regarding all three exponentials in this expression as the time evolution operator for an appropriate Hamiltonian along a forward−backward time contour and applying the semiclassical approximation in the coherent state representation[11] brings eq 2.2 to the form

$$C(t) = -i(2\pi\hbar)^{-1}\frac{\partial}{\partial\mu}\int dx_{\text{in}}\int dp_{\text{in}}\, D(x_{\text{in}}, p_{\text{in}}) \times$$
$$\exp\left(\frac{i}{\hbar}S(x_{\text{in}}, p_{\text{in}})\right)\langle g(x_{\text{in}}, p_{\text{in}})|\rho(0)A|g(x_f p_f)\rangle|_{=0} \quad (2.3)$$

Here the classical trajectories with initial conditions x_{in}, p_{in} experience a discontinuity at the end of the forward time evolution and subsequently continue in the backward time direction, reaching eventually the phase space point x_f, p_f. The prefactor D is the forward−backward Herman-Kluk determinant given by the expression

$$D(x_{\text{in}}, p_{\text{in}}) =$$
$$2^{-1/2}\sqrt{\frac{\partial x_f}{\partial x_{\text{in}}} + \frac{\partial p_f}{\partial p_{\text{in}}} - 2i\hbar\gamma\frac{\partial x_f}{\partial p_{\text{in}}} - \frac{1}{2i\hbar\gamma}\frac{\partial p_f}{\partial x_{\text{in}}}} \quad (2.4)$$

and $|g\rangle$ are coherent states described by the wave functions

$$\langle x|g(x_{\text{in}}, p_{\text{in}})\rangle =$$
$$\left(\frac{2\gamma}{\pi}\right)^{1/4}\exp\left(-\gamma(x - x_{\text{in}})^2 + \frac{i}{\hbar}p_{\text{in}}(x - x_{\text{in}})\right) \quad (2.5)$$

Shao and Makri have shown that eq 2.3 can also be written in a prefactor-free form,

$$C(t) = -i(2\pi\hbar)^{-1}\frac{\partial}{\partial\mu}\int dx_{\text{in}}\int dp_{\text{in}}\exp\left(\frac{i}{\hbar}S(x_{\text{in}}, p_{\text{in}})\right) \times$$
$$\langle g(x_{\text{in}}, p_{\text{in}})|\rho(0)A|g(x_f, p_f)\rangle|_{\mu=0} \quad (2.6)$$

Here the trajectories follow the classical equations of motion with the Hamiltonian H_{dyn} up to the time t, at which point the coordinate and momentum jump by the values[34]

$$\delta p_t = \frac{1}{2}\pi\mu\frac{\partial B_t}{\partial x_t}, \quad \delta x_t = -\hbar\mu\frac{\partial B_t}{\partial p_t} \qquad (2.7)$$

Note that the momentum jump amounts to *one-half* of that dictated by Hamilton's equations. At the same time the action increments by the full amount prescribed by the generalized forward−backward Hamiltonian,[35,36,39]

$$\delta S_t = \hbar\mu B(t) + p_t\delta x_t \qquad (2.8)$$

Subsequent evolution takes place in the negative time direction and the integrand is evaluated when the time parameter reaches zero once again, at which time the trajectory has reached the phase space values x_f, p_f. The derivative with respect to the parameter μ is evaluated by a two-point finite difference method. Miller and co-workers have shown that eq 2.6 can also be cast in a derivative-free form involving only initial values of the classical trajectories.

Because the forward and backward trajectories join at the time t almost continuously, this formulation of FBSD neglects the quantum interference that arises from combinations of distinct forward and backward classical paths. The neglect of such interference terms may result in large error if eq 2.6 is applied to highly anharmonic Hamiltonians. Numerical tests on model one-dimensional systems with Gaussian initial conditions have shown that the method generally produces semiquantitative results for the first few periods of motion, while failing to capture wave packet rephasing at later times.[35] These observations are very similar to the findings of Sun et al.[45] on the behavior of a linearized semiclassical approximation of Miller and co-workers,[42] equivalent to the quasiclassical Wigner method.[40,41] Since long-time phase coherence is often suppressed when many degrees of freedom are involved, all these methods may offer satisfactory accuracy for simulating the dynamics of polyatomic systems and thus can be very valuable.

Since the semiclassical dynamics prescription is well posed, the purpose of the present section is to develop a computational framework for calculating the coherent state matrix element of the density operator describing the initial state of the system. Earlier papers by our group have focused on specific cases where the initial density is given by a Gaussian function[36] or by the Boltzmann factor in its high-temperature limit.[30] Here we focus on initial conditions corresponding to Boltzmann statistics at finite temperatures in anharmonic systems where the Gaussian approximation does not apply, while the high-temperature factorization is too crude. The initial density operator is given by

$$\rho_0 = \frac{e^{-\beta H}}{Z} \qquad (2.9)$$

where Z is the partition function and, depending on the situation,

$$H = H_0 + V$$

where H_0 is the kinetic energy operator, may be the Hamiltonian generating the dynamics (i.e., the Born−Oppenheimer potential surface that governs the motnion of the nuclei, as in the case of vibrational spectroscopy) or that describing a different electronic potential surface in which the system is prepared.

Feynman's path integral formulation of quantum statistical mechanics provides the only accurate, yet practical prescription for calculating matrix elements of the Boltzmann operator for systems described in terms of arbitrary Hamiltonians. To apply it to the coherent state matrix element entering eq 2.6 we

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partition the Boltzmann operator in a product of n factors, i.e.,

$$e^{-\beta H} = (e^{-\Delta\beta H})^n, \quad \Delta\beta \equiv \frac{\beta}{n} \qquad (2.10)$$

and write

$$\langle g_{x_{in},p_{in}}|e^{-\beta H}A|g_{x_f p_f}\rangle =$$
$$\int dx_1 \dots \int dx_n \langle g_{x_{in},p_{in}}|e^{-\Delta\beta H_0/2}|x_1\rangle e^{-\Delta\beta V(x_1)}$$
$$\langle x_1|e^{-\Delta\beta H_0}|x_2\rangle \dots e^{-\Delta\beta V(x_n)}\langle x_n|e^{-\beta H_0/2}A|g_{x_f p_f}\rangle \quad (2.11)$$

If the operator A has a simple form, e.g., if it is given by a low order polynomial in position or momentum, the last factor in the above equation can be evaluated in closed form. We consider this situation first in the specific cases of expectation values ($A = 1$), position correlation functions ($A = x$), or velocity correlation functions ($A = p/m$). In other cases the matrix element involving A may not be obtainable in closed form. It is then necessary to evaluate this factor numerically, and this procedure introduces an additional integration variable in eq 2.11. While requiring more work, this case also lends itself to a robust numerical procedure presented in the last part of this section.

(a) Expectation Values and Correlation Functions of Linear Operators. Perhaps the simplest case arises in the calculation of expectation values, where $A = 1$. Further, it is often of interest to calculate position or velocity correlation functions, which are obtained from eq 2.1 by setting $A = x$ or $A = p/m$, respectively. Using the well-known result for the propagator of a free particle and performing the resulting Gaussian integrals, one can obtain closed form expressions for the factors involving coherent states. In the particular cases of interest we find

$$\langle x_n|e^{-\Delta\beta H_0/2}|g_{x_f p_f}\rangle = \left(\frac{2\gamma}{\pi}\right)^{1/4}\sqrt{\frac{m}{m+\hbar^2\Delta\beta\gamma}} \times$$
$$\exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\left(\gamma(x_n - x_f)^2 + \frac{\Delta\beta}{4m}p_f^2 - \frac{i}{\hbar}p_f(x_n - x_f)\right)\right\}$$
$$(2.12)$$

$$\langle x_n|e^{-\Delta\beta H_0/2}x|g_{x_f p_f}\rangle = \left(\frac{2\gamma}{\pi}\right)^{1/4}\left(\frac{m}{m+\hbar^2\Delta\beta\gamma}\right)^{3/2}\left[x_n + \right.$$
$$\frac{\hbar^2\Delta\beta}{m}\left(\gamma x_f + \frac{i}{2\hbar}p_f\right)\right]\exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\left(\gamma(x_n - x_f)^2 + \right.\right.$$
$$\left.\left.\frac{\Delta\beta}{4m}p_f^2 - \frac{i}{\hbar}p_f(x_n - x_f)\right)\right\} \quad (2.13)$$

$$\langle x_n|e^{-\Delta\beta H_0/2}p|g_{x_f p_f}\rangle = \left(\frac{2\gamma}{\pi}\right)^{1/4}\left(\frac{m}{m+\hbar^2\Delta\beta\gamma}\right)^{3/2}[p_f +$$
$$2i\hbar\gamma(x_n - x_f)] \times \exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\left(\gamma(x_n - x_f)^2 + \frac{\Delta\beta}{4m}p_f^2 - \right.\right.$$
$$\left.\left.\frac{i}{\hbar}p_f(x_n - x_f)\right)\right\} \quad (2.14)$$

Substitution of this expression in eq 2.11 brings the coherent state matrix element of the initial density into the form

$$\langle g_{x_{in},p_{in}}|e^{-\beta H}A|g_{x_f,p_f}\rangle = \left(\frac{2\gamma}{\pi}\right)^{1/2}\frac{m}{m+\hbar^2\Delta\beta\gamma} \times$$
$$\left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{(n-1)/2}\int dx_1 \dots \int dx_n\, \sigma(x_n, x_f, p_f) \times$$
$$\exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\left(\gamma(x_1 - x_{in})^2 + \frac{\Delta\beta}{4m}(p_{in}^2 + p_f^2) + \right.\right.$$
$$\frac{i}{\hbar}p_{in}(x_1 - x_{in}) + \gamma(x_n - x_f)^2 - \frac{i}{\hbar}p_f(x_n - x_f)\right) -$$
$$\frac{m}{2\hbar^2\Delta\beta}\sum_{k=2}^{n}(x_k - x_{k-1})^2 - \Delta\beta\sum_{k=1}^{n}V(x_k)\right\} \quad (2.15)$$

where

$$\sigma(x_n, x_f, p_f) =$$

$$1 \qquad\qquad\qquad\qquad\qquad \text{if } A = 1$$

$$\frac{m}{m+\hbar^2\Delta\beta\gamma}\left[x_n + \frac{\hbar^2\Delta\beta}{m}\left(\gamma x_f + \frac{i}{2\hbar}p_f\right)\right] \quad \text{if } A = x$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (2.16)$$

$$\frac{m}{m+\hbar^2\Delta\beta\gamma}[p_f + 2i\hbar\gamma(x_n - x_f)] \qquad \text{if } A = p$$

Noting that the remaining semiclassical integrand in eq 2.6 consists of a pure phase, we must extract a sampling function solely from eq 2.15. Taking into consideration the fact that the initial and final phase space coordinates of each trajectory differ only by an infinitesimal amount determined by the magnitude of the finite difference parameter μ, we construct a sampling function R from the entire real valued part of the exponent in eq 2.15, replacing x_f, p_f by x_{in}, p_{in}:

$$R(x_{in}, p_{in}, x_1, \dots, x_n) = \exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\left(\gamma(x_1 - x_{in})^2 + \right.\right.$$
$$\left.\gamma(x_n - x_{in})^2 + \frac{\Delta\beta}{2m}p_{in}^2\right) - \frac{m}{2\hbar^2\Delta\beta}\sum_{k=2}^{n}(x_k - x_{k-1})^2 -$$
$$\Delta\beta\sum_{k=1}^{n}V(x_k)\right\} \quad (2.17)$$

In terms of this, the correlation function (or expectation value) is given by the expression

$$C(t) = -i\lambda\frac{\partial}{\partial\mu}\int dx_{in}\int dp_{in}\int dx_1 \dots \int dx_n \times$$
$$\exp\left(\frac{i}{\hbar}S(x_{in}, p_{in})\right)R(x_{in}, p_{in}, x_1, \dots, x_n) \times \sigma(x_n, x_f, p_f) \times$$
$$\exp\left\{-\frac{m}{m+\hbar^2\Delta\beta\gamma}\frac{i}{\hbar}[p_{in}(x_1 - x_{in}) - p_f(x_n - x_f)] - \right.$$
$$\left.\frac{m}{m+\hbar^2\Delta\beta\gamma}\left[\frac{\Delta\beta}{4m}(p_f^2 - p_{in}^2) + \gamma(x_n - x_f)^2 - \gamma(x_n - x_{in})^2\right]\right\}\bigg|_{\mu=0}$$
$$(2.18)$$

where λ combines the constants entering eqs 2.6 and 2.15 along with the normalization integral, i.e., the integral of the sampling function with respect to all variables:

$$\lambda = (2\pi\hbar)^{-1}\left(\frac{2\gamma}{\pi}\right)^{1/2}\frac{m}{m+\hbar^2\Delta\beta\gamma}Z^{-1}\left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{(n-1)/2} \times$$
$$\int dx_{in}\int dp_{in}\int dx_1 \dots \int dx_n R(x_{in}, p_{in}, x_1, \dots, x_n) \quad (2.19)$$

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Because the sampling function contains potential terms which correspond in general to nonlinear functions, evaluation of its integral by purely analytic manipulations is not possible. Below we describe a procedure for obtaining that integral.

First, notice that the integrals with respect to the trajectory initial conditions are of the Gaussian type and can be evaluated analytically. This brings the normalization integral to the form

$$\int dx_{in} \int dp_{in} \int dx_1 \ldots \int dx_n R(x_{in}, p_{in}, x_1, \ldots, x_n) =$$
$$\pi \frac{m + \hbar^2 \Delta\beta\gamma}{\sqrt{m\gamma\Delta\beta}} \int dx_1 \ldots \int dx_n f(x_1, \ldots, x_n) \quad (2.20)$$

where

$$f(x_1, \ldots, x_n) = \exp\left\{ -\frac{m\gamma/2}{m + \hbar^2 \Delta\beta\gamma} (x_1 - x_n)^2 - \right.$$
$$\left. \frac{m}{2\hbar^2\Delta\beta} \sum_{k=2}^{n} (x_k - x_{k-1})^2 - \Delta\beta \sum_{k=1}^{n} V(x_k) \right\} \quad (2.21)$$

It is thus sufficient to calculate the normalization integral of this function. To proceed, we note that the canonical partition function at the same level of approximation (i.e., expressed as a discretized path integral with n imaginary time slices) takes the form

$$Z = \text{Tr} e^{-\beta H} = \left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{n/2} \int dx_1 \ldots \int dx_n \times$$
$$\exp\left\{ -\frac{m}{2\hbar^2\Delta\beta}\left[\sum_{k=2}^{n} (x_k - x_{k-1})^2 + (x_1 - x_n)^2\right] - \right.$$
$$\left. \Delta\beta \sum_{k=1}^{n} V(x_k) \right\} \quad (2.22)$$

The partition function is now expressed in terms of the function entering the normalization integral:

$$Z = \left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{n/2} \int dx_1 \ldots \int dx_n f(x_1, \ldots, x_n) \times$$
$$\exp[-\alpha(x_1 - x_n)^2] \quad (2.23)$$

where

$$\alpha \equiv \frac{m}{2\pi\hbar^2\Delta\beta} - \frac{m\gamma/2}{m + \hbar^2\Delta\beta\gamma} \quad (2.24)$$

is a positive constant.

Using f as the weight function, we sample the function $\exp[-\alpha(x_1 - x_n)^2]$ in a Metropolis random walk. This procedure yields the integral

$$\kappa \equiv \xi^{-1} \int dx_1 \ldots \int dx_n f(x_1, \ldots, x_n) \exp[-\alpha(x_1 - x_n)^2]$$
$$(2.25)$$

where

$$\xi = \int dx_1 \ldots \int dx_n f(x_1, \ldots, x_n) \quad (2.26)$$

is the desired integral. In terms of these, the partition function takes the form

$$Z = \left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{n/2} \xi \kappa \quad (2.27)$$

Finally, we find

$$Z^{-1} \int dx_{in} \int dp_{in} \int dx_1 \ldots \int dx_n R(x_{in}, p_{in}, x_1, \ldots, x_n) =$$
$$\pi \frac{m + \hbar^2\Delta\beta\gamma}{\sqrt{m\Delta\beta\gamma}} \left(\frac{m}{2\pi\hbar^2\Delta\beta\gamma}\right)^{n/2} \kappa^{-1} \quad (2.28)$$

Combining this relation with the remaining constants in eq 2.19 gives the overall prefactor λ in eq 2.18; the result is extremely simple:

$$\lambda = k^{-1} \quad (2.29)$$

To summarize the procedure developed above, we calculate by Monte Carlo the integral κ of the function $\exp[-\alpha(x_1 - x_n)^2]$ using a sampling function proportional to f. The result is the inverse of the overall prefactor in the FBSD expression for an expectation value. The generalization to systems with many degrees of freedom is straightforward.

(b) Correlation Functions of General Position Space Operators. Next we consider the general case, where the operator A is sufficiently complex that evaluation of its matrix element is not possible by analytic means. For example, the dipole moment operator whose correlation function encodes important spectroscopic information is often available in terms of a complicated function or even in numerical form. Inserting an additional complete set of position states, eq 2.11 becomes

$$\langle g_{x_{in} p_{in}} | e^{-\beta H} A | g_{x_f p_f} \rangle =$$
$$\int dx_1 \ldots \int dx_{n+1} \langle g_{x_{in} p_{in}} | e^{-\Delta\beta H_0/2} | x_1 \rangle e^{-\Delta\beta V}(x_1) \times$$
$$\langle x_1 | e^{-\Delta\beta H_0} | x_2 \rangle \ldots e^{-\Delta\beta V(x_n)} \langle x_n | e^{-\beta H_0/2} | x_{n+1} \rangle A(x_{n+1}) \langle x_{n+1} | g_{x_f p_f} \rangle$$
$$(2.30)$$

which involves an additional integration with respect to the auxiliary variable x_{n+1}. Substituting the various factors we write eq 2.30 in the form

$$\langle g_{x_{in} p_{in}} | e^{-\beta H} A | g_{x_f p_f} \rangle = \left(\frac{2\gamma}{\pi}\right)^{1/2} \sqrt{\frac{m}{m + \hbar^2\Delta\beta\gamma}} \times$$
$$\left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{(n-1)/2} \left(\frac{m}{\pi\hbar^2\Delta\beta}\right)^{1/2} \int dx_1 \ldots \int dx_{n+1} \times$$
$$\exp\left\{ -\frac{m}{m + \hbar^2\Delta\beta\gamma}\left(\gamma(x_1 - x_{in})^2 + \frac{\Delta\beta}{4m}p_{in}^2 + \frac{i}{\hbar}p_{in}(x_1 - \right.\right.$$
$$\left. x_{in}\right) - \gamma(x_{n+1} - x_f)^2 + \frac{i}{\hbar}p_f(x_{n+1} - x_f) - \frac{m}{2\hbar^2\Delta\beta}\left(\sum_{k=2}^{n+1} (x_k - \right.$$
$$\left. x_{k-1})^2 + (x_{n+1} - x_n)^2\right) - \Delta\beta \sum_{k=1}^{n} V(x_k) \right\} A(x_{n+1}) \quad (2.31)$$

Proceeding as before, we choose the sampling function

$$R(x_{in}, p_{in}, x_1, \ldots, x_{n+1}) = \exp\left\{ -\frac{m}{m + \hbar^2\Delta\beta\gamma}\left(\gamma(x_1 - x_{in})^2 + \right.\right.$$
$$\left. \frac{\Delta\beta}{4m}p_{in}^2\right) - \gamma(x_{n+1} - x_{in})^2 - \frac{m}{2\hbar^2\Delta\beta}\left(\sum_{k=2}^{n+1} (x_k - x_{k-1})^2 + \right.$$
$$\left. (x_{n+1} - x_n)^2\right) - \Delta\beta \sum_{k=1}^{n} V(x_k) \right\} \quad (2.32)$$

Following similar steps as in the previous subsection, we define

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the function

$$f(x_1, ..., x_{n+1}) = \exp\left\{ -\frac{c\gamma}{1+c}(x_1 - x_n)^2 - \Delta\beta \sum_{k=1}^{n} V(x_k) - \frac{m}{2\hbar^2\Delta\beta}\left(\sum_{k=2}^{n+1} (x_k - x_{k-1})^2 + (x_{n+1} - x_n)^2\right) \right\} \quad (2.33)$$

where

$$\alpha \equiv \frac{m}{m + \hbar^2\Delta\beta\gamma}$$

and its normalization integral

$$\xi = \int dx_1 ... \int dx_n f(x_1, ..., x_n) \quad (2.34)$$

Once again, one can show that the partition function at the same level of approximation becomes

$$Z = \left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{(n-1)/2} \frac{m}{\pi\hbar^2\Delta\beta} \int dx_1 ... \int dx_{n+1} f(x_1, ..., x_{n+1}) \times$$
$$\exp\left\{ -\frac{2m^2}{\hbar^2\Delta\beta\,(2m + \hbar^2\Delta\beta\gamma)}(x_1 - x_{n+1})^2 \right\} =$$
$$\left(\frac{m}{2\pi\hbar^2\Delta\beta}\right)^{(n-1)/2}\left(\frac{m}{\pi\hbar^2\Delta\beta}\right)\xi\kappa \quad (2.35)$$

where κ is the Monte Carlo average of the exponential function in the last equation with respect to the normalized distribution $\xi^{-1} f(x_1, ..., x_{n+1})$, i.e.,

$$\kappa = \int dx_1 ... \int dx_{n+1} \xi^{-1} f(x_1, ..., x_{n+1}) \times$$
$$\exp\left\{ -\frac{2m^2}{\hbar^2\Delta\beta\,(2m + \hbar^2\Delta\beta\gamma)}(x_1 - x_{n+1})^2 \right\} \quad (2.36)$$

Combining these results, the overall normalization factor for the correlation function becomes

$$\sqrt{\frac{2}{1+\alpha}}\,\kappa^{-1} \quad (2.37)$$

III. Numerical Tests

We test the methodology presented in section II by applying it to calculate the position correlation functions in a model one-dimensional system. The system is a nonlinear oscillator of the form

$$H_{\text{dyn}} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - 0.1x^3 + 0.1x^4$$

with $m = 1$, $\omega = \sqrt{2}$. As discussed in ref 35, the potential in this system is very anharmonic, leading to nearly complete dephasing of a pure state within a few oscillation periods. It was found that even though the forward−backward treatment of the dynamics is incapable of accounting for the coherence effects that lead later to wave packet rephasing at zero temperature, it captures the initial several oscillations semi-quantitatively.

The same trend is observed at finite temperature. The imaginary time path integral converged with $\hbar\omega\Delta\beta \approx 0.5$. The FBSD results are compared to those obtained via a numerically exact basis set representation of the correlation function and
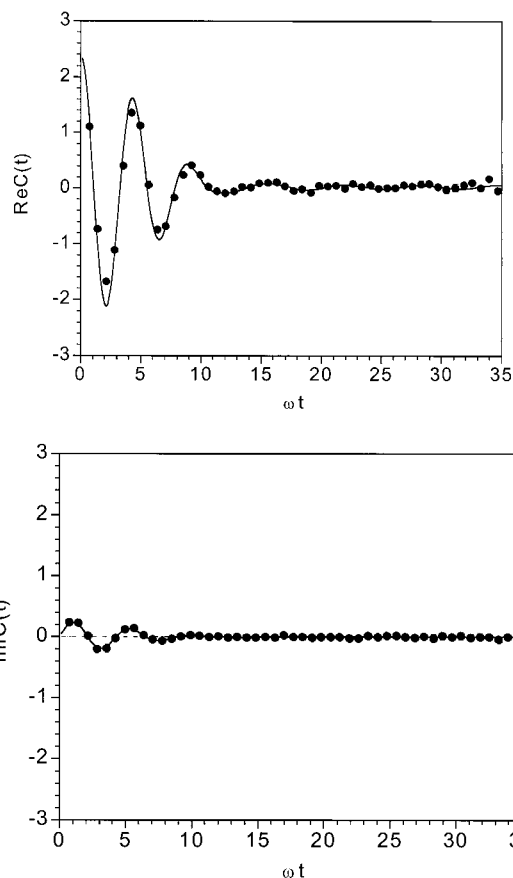

Figure 1. Real and imaginary parts of the position correlation function for the quartic oscillator described in this section at a high temperature, $\hbar\omega\beta = \sqrt{2}/10$. Solid lines: exact quantum mechanical results. Markers: FBSD-path integral results with $N = 1$ and 10 000 Monte Carlo points per integration variable. Dashed lines: classical results.

also to results generated by a purely classical treatment,

$$C_{\text{cl}}(t) = \frac{\int dx_0 \int dp_0\, e^{-\beta H(x_0, p_0)} x_0 x_t}{\int dx_0 \int dp_0\, e^{-\beta H(x_0, p_0)}}$$

where x_t is the classical position of the system at the time t.

Figures 1−3 show the position correlation function in this system at three different temperatures corresponding to $\hbar\omega\beta = \sqrt{2}/10$, $\sqrt{2}$ and $3\sqrt{2}$, respectively. For reference, note that for a molecular vibration of $\omega = 300$ cm^{-1} these temperatures correspond to 3000, 300, and 100 K, respectively. The effects of potential anharmonicity are seen as dephasing of the correlation function, which becomes faster as the temperature is increased. At the highest temperature displayed in Figure 1 the FBSD-path integral results are practically exact. At lower temperatures the FBSD results are still very accurate during the first few oscillation periods but tend to overestimate somewhat the dephasing rate. Note that in all cases the overall magnitude and oscillation frequency of the real and imaginary parts of the correlation function obtained from the FBSD-path integral calculation are in good agreement with the exact results. By contrast, the purely classical calculation is accurate only at very high temperature, and significant discrepancies from the exact results are observed at intermediate and low temperatures. As expected, the classical approximation cannot reproduce the correct magnitude of the correlation function at low temperatures, and the classical oscillation period is larger than that predicted by the quantum mechanical calculation, a consequence
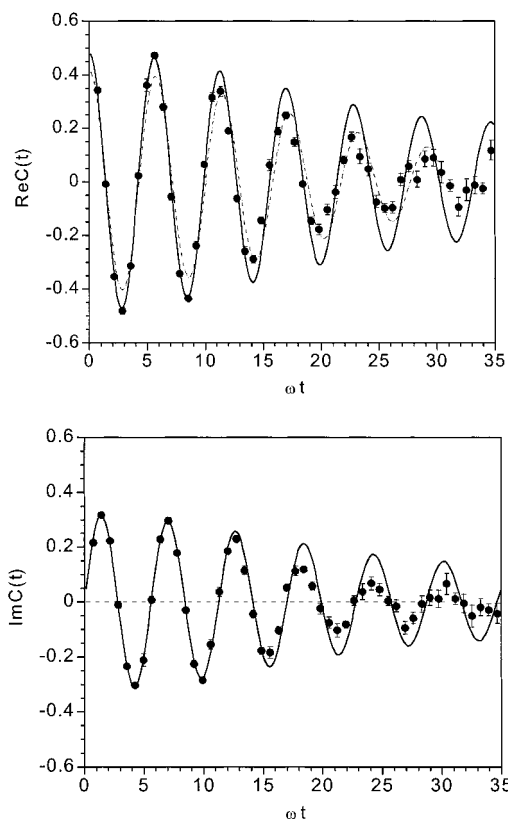
Figure 2. Real and imaginary parts of the correlation function for the quartic oscillator described in this section at an intermediate temperature, $\hbar\omega\beta = \sqrt{2}$. Solid lines: exact quantum mechanical results. Markers: FBSD-path integral results with $N = 3$ and 10 000 Monte Carlo samples per integration variable. Dashed lines: classical results.

Figure 3. Real and imaginary parts of the correlation function for the quartic oscillator described in this section at a low temperature, $\hbar\omega\beta = 3\sqrt{2}$. Solid lines: exact quantum mechanical results. Markers: FBSD-path integral results with $N = 6$ and 10 000 Monte Carlo samples per integration variable. Dashed lines: classical results.

of the neglect of zero point energy in the classical treatment. Even more importantly, the classical method can only yield real valued results and thus fails to provide any information about the imaginary part of the correlation function. The latter is as sizable as the real part at low temperatures and plays an important role in determining the shape of the absorption spectrum. The FBSD methodology with a path integral treatment of the Boltzmann factor does not suffer from the above artifacts of the purely classical treatment and thus provides an accurate, yet practical alternative to a full quantum calculation.

IV. Discussion

Classical molecular dynamics simulations offer a valuable picture of the dynamics in polyatomic systems where quantum mechanical treatment remains completely out of reach. By its nature, the classical treatment of nuclear motion is limited to systems where quantum effects are of minor importance. The FBSD methodology combined with a path integral treatment of the Boltzmann operator offers a relatively inexpensive way of impoving the results of classical simulations by incorporating some important quantum effects. As illustrated in the numerical examples presented in section III, the methodology described in this paper captures important effects arising from full quantization of initial conditions: for example, by treating correctly the zero point energy, it produces the correct amplitude of correlation functions, including that of the imaginary part, and the frequency of oscillation, at least for the first few periods of motion. These features are extremely important at low temperatures and/or when light particles are involved. Thus, the present methodology provides a useful, yet practical extension of the conventional molecular dynamics simulation method.
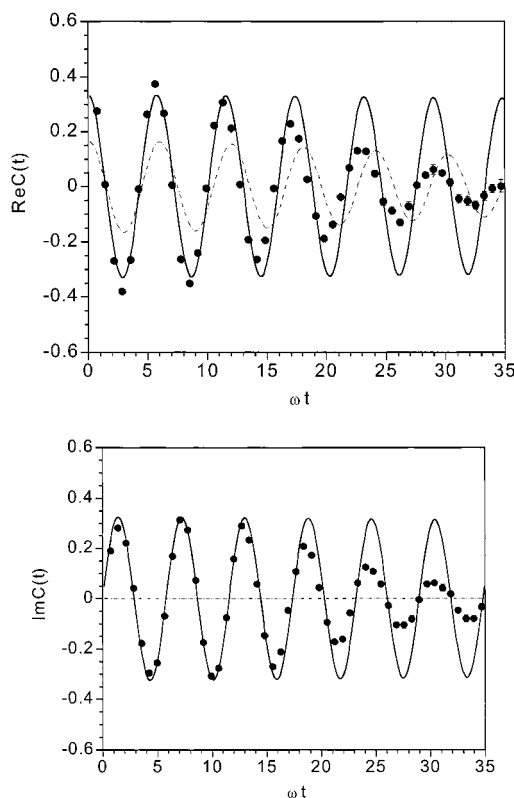
Quantum inteference effects resulting from distinct forward and backward trajectories are neglected by FBSD. Such effects can have dramatic consequences at moderately long times, but usually are not very noticeable during the initial few periods. Thus, FBSD is usually accurate at short times, and generally tends to predict faster dephasing at longer times. Often the presence of many degrees of freedom leads naturally to sufficiently rapid decay of observables or correlation functions. In such cases FBSD can be quantitatively accurate at all times. Nevertheless, at least partial inclusion of quantum intereference effects is very desirable. This is possible by lifting the continuity restrictions imposed by the forward−backward treatment in one or a few important degrees of freedom. Such methods have been formulated and shown to cure the major shortcomings of FBSD in cases where quantum interference is significant, but generally at a much higher computational cost. Progress in this field has been very rapid during the past decade, and improved versions of forward−backward semiclassical dynamics are likely to become practical in the near future.

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