Quantum statistics and classical mechanics: Real time correlation functions from ring polymer molecular dynamics

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We propose an approximate method for calculating Kubo-transformed real-time correlation functions involving position-dependent operators, based on path integral (Parrinello-Rahman) molecular dynamics. The method gives the exact quantum mechanical correlation function at time zero, exactly satisfies the quantum mechanical detailed balance condition, and for correlation functions of the form $\tilde{C}_{Ax}(t)$ and $\tilde{C}_{xB}(t)$ it gives the exact result for a harmonic potential. It also works reasonably well at short times for more general potentials and correlation functions, as we illustrate with some example calculations. The method provides a consistent improvement over purely classical molecular dynamics that is most apparent in the low-temperature regime. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1777575]

I. INTRODUCTION

A number of potentially practical methods have been proposed for including short-time quantum mechanical effects in classical molecular dynamics simulations, all of which combine what is in principle an exact treatment of the quantum Boltzmann operator with an approximate treatment of the real-time evolution based on classical mechanics.[1–7] The short-time limit is of particular interest because quantum interference effects are often rapidly quenched in condensed phase systems, and an exact treatment of the Boltzmann operator is essential if one wants to get this limit correctly. The neglect of quantum phase information in the subsequent dynamics is clearly undesirable, but it seems (at present) to be essential if the method is to be applied to truly complex problems. As a rule of thumb, the most one can reasonably expect of such a method is that it will give an accurate approximation to the quantum mechanical correlation function for times on the order of the thermal time ($\beta\hbar$), after which the results will only be accurate if quantum mechanical interference effects have died away.[8]

The purpose of the present paper is to demonstrate that, if this level of description is all one is after, it can be obtained in a comparatively straightforward way using well-established molecular dynamics techniques. In particular, we shall show that existing path integral molecular dynamics codes can be adapted in a simple way to calculate approximate Kubo-transformed real-time correlation functions involving position-dependent operators. The resulting correlation functions are consistently better than those given by purely classical molecular dynamics, and they coincide with the exact quantum mechanical result in the limit as $t\to 0$. In fact, they are only marginally less accurate than those given by the centroid molecular dynamics method,[1,2] which is somewhat related to what we are proposing but which requires a great deal more computational work.

The basic idea of the method is to make an appropriate choice of the fictitious masses of the ring-polymer beads introduced by Parrinello and Rahman,[9] and then to focus on the Kubo-transformed correlation function[10] as the object of interest. This idea is described in Sec. II. The appeal of the Kubo-transformed correlation function is that it has the same symmetries as a classical correlation function and gives the same result for the position autocorrelation function in the harmonic limit, as we discuss in Secs. III and IV. Section V provides some numerical tests to illustrate what one should (and should not) expect of the present method, and Sec. VI contains some concluding remarks.

II. THE BASIC IDEA

The exact calculation of quantum real-time correlation functions is still "a very difficult problem"[11] that no one has yet solved in a completely general way. However, it is well known that the static equilibrium properties of a quantum mechanical system can be computed comparatively easily, by exploiting the isomorphism between the path integral representation of the quantum mechanical partition function[12,13] and the classical partition function of a fictitious ring polymer.[14–16]

As a result of this isomorphism, the canonical partition function at inverse temperature $\beta = 1/k_B T$,

$$Z = \mathrm{tr}[e^{-\beta\hat{H}}] \tag{1}$$

can be calculated exactly as $Z = \lim_{n\to\infty} Z_n$, where for a one-dimensional system with Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{x})$ (the generalization to more dimensions is straightforward)

$$Z_n = \frac{1}{(2\pi\hbar)^n} \int d\mathbf{p} \int d\mathbf{x}\, e^{-\beta_n H_n(\mathbf{p},\mathbf{x})}. \tag{2}$$

Here $\beta_n = \beta/n$, and $H_n(\mathbf{p},\mathbf{x})$ is the classical Hamiltonian of a harmonic ring polymer with an external potential of $V(x)$ on each polymer bead,

$$H_n(\mathbf{p},\mathbf{x}) = \sum_{j=1}^{n} \frac{p_j^2}{2m} + \frac{m}{2\beta_n^2\hbar^2} \sum_{j=1}^{n} (x_j - x_{j-1})^2$$

$$+ \sum_{j=1}^{n} V(x_j), \tag{3}$$

subject to the cyclic boundary condition $x_0 = x_n$. For $n=1$, Eq. (2) is simply the classical partition function, and for any finite n the equation provides an upper bound on the exact quantum mechanical result $(Z_n > Z)$.[17]

Notice in particular that, as we have written it, Eq. (2) corresponds to one special choice for the fictitious masses of the polymer beads introduced by Parrinello and Rahman.[9] With this choice, the equation has the correct form for a phase space average of a classical equilibrium density in a system with n degrees of freedom, albeit at an effective classical temperature of nT.

The thermal expectation value of a position-dependent operator $A(\hat{x})$,

$$\langle A \rangle = \frac{1}{Z} \text{tr}[e^{-\beta\hat{H}}\hat{A}], \tag{5}$$

can also be calculated within the isomorphism as $\langle A \rangle = \lim_{n\to\infty} \langle A \rangle_n$, where

$$\langle A \rangle_n = \frac{1}{(2\pi\hbar)^n Z_n} \int d\mathbf{p} \int d\mathbf{x} \, e^{-\beta_n H_n(\mathbf{p},\mathbf{x})} A_n(\mathbf{x}) \tag{6}$$

with

$$A_n(\mathbf{x}) = \frac{1}{n} \sum_{j=1}^{n} A(x_j). \tag{7}$$

This expectation value is therefore again given by a purely classical expression for the fictitious ring polymer system (as is well known).

More interesting, however, is what happens when we try to generalize this result to a product of two coordinate-dependent operators $\hat{A}$ and $\hat{B}$. Consider, in particular, the following generalization of Eq. (6):

$$\langle AB \rangle_n = \frac{1}{(2\pi\hbar)^n Z_n} \int d\mathbf{p} \int d\mathbf{x} \, e^{-\beta_n H_n(\mathbf{p},\mathbf{x})} A_n(\mathbf{x}) B_n(\mathbf{x}), \tag{8}$$

where $A_n(\mathbf{x})$ is defined in Eq. (7) and $B_n(\mathbf{x})$ is defined similarly as an average over the beads of the polymer necklace. This does not correspond (in the limit as $n\to\infty$) to the thermal average of the operator product $\hat{A}\hat{B}$, but rather to the $t\to 0$ limit of the Kubo-transformed real-time correlation function of the operators $\hat{A}$ and $\hat{B}$[10]

$$\tilde{C}_{AB}(t) = \frac{1}{\beta Z} \int_0^{\beta} d\lambda \, \text{tr}[e^{-(\beta-\lambda)\hat{H}}\hat{A}e^{-\lambda\hat{H}}e^{+i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}]. \tag{9}$$

What makes this interesting is that the Kubo-transformed correlation function arises in a natural way in a variety of approximate treatments of real-time quantum dynamics, including in particular the centroid molecular dynamics method.[1,2] (The reason why it arises so naturally is

that it has the same symmetries as a classical correlation function, as we shall discuss in more detail in Sec. III.) The above observation shows that this correlation function can be calculated exactly at time $t=0$ via an integral over a classical phase space, albeit an artificial one with more dimensions than are present in the quantum mechanical problem. So what happens if we take this phase space literally and use its classical dynamics to extend Eq. (8) to times $t>0$?

A good reason for not even attempting this is that the classical dynamics generated by the artificial Hamiltonian in Eq. (3) has no obvious connection (in general) with the true quantum dynamics embodied in the evolution operators $e^{\pm i\hat{H}t/\hbar}$ in Eq. (9).[9,11] However, there are some reasons to believe that such an approach may nevertheless give a reasonable short-time approximation to the quantum mechanical correlation function $\tilde{C}_{AB}(t)$, as we shall see in this paper.

The classical Hamiltonian in Eq. (3) generates the equations of motion

$$\dot{p}_j = -\frac{m}{\beta_n^2\hbar^2}[2x_j - x_{j-1} - x_{j+1}] - \frac{\partial V(x_j)}{\partial x_j} \tag{10}$$

and

$$\dot{x}_j = \frac{p_j}{m}, \tag{11}$$

for $j=1,\ldots,n$, and what we are proposing is to use these equations to evolve the initial phase space variables $(\mathbf{p},\mathbf{x}) \equiv (\mathbf{p}_0,\mathbf{x}_0)$ for time t and hence extend Eq. (8) to

$$\langle A(0)B(t) \rangle_n = \frac{1}{(2\pi\hbar)^n Z_n} \int d\mathbf{p}_0 \int d\mathbf{x}_0 e^{-\beta_n H_n(\mathbf{p}_0,\mathbf{x}_0)}$$

$$\times A_n(\mathbf{x}_0) B_n(\mathbf{x}_t), \tag{12}$$

where $\mathbf{x}_t \equiv \mathbf{x}_t(\mathbf{p}_0,\mathbf{x}_0)$. This will obviously give the same result as $\tilde{C}_{AB}(t)$ in the limit as $t\to 0$ (for sufficiently large n), and the following two sections discuss some other reasons why it may not be such a bad idea.

III. SYMMETRY CONSIDERATIONS

The standard form for a real-time correlation function is not that given in Eq. (9) but rather

$$C_{AB}(t) = \frac{1}{Z} \text{tr}[e^{-\beta\hat{H}}\hat{A}e^{+i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}], \tag{13}$$

the $t\to 0$ limit of which is simply the thermal average of the operator product $\hat{A}\hat{B}$. The two correlation functions are of course related: if $\tilde{G}_{AB}(\omega)$ is the Fourier transform of $\tilde{C}_{AB}(t)$,

$$\tilde{G}_{AB}(\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \tilde{C}_{AB}(t), \tag{14}$$

and $G_{AB}(\omega)$ that of $C_{AB}(t)$, then it is easy to show by working in the basis of eigenstates of $\hat{H}$ that

$$G_{AB}(\omega) = \frac{\beta\hbar\omega}{(1-e^{-\beta\hbar\omega})} \tilde{G}_{AB}(\omega). \tag{15}$$

However, the Kubo-transformed correlation function $\tilde{C}_{AB}(t)$ has considerably more symmetry than $C_{AB}(t)$.

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In particular, one can show by rearranging the order of the operators within the trace in Eq. (9) and then changing the integration variable to $\lambda' = \beta - \lambda$ that

$$\widetilde{C}_{AB}(t) = \widetilde{C}_{BA}(-t), \tag{16}$$

and by exploiting the hermicity of $\hat{H}$, $\hat{A}$, and $\hat{B}$ that

$$\widetilde{C}_{AB}(t) = \widetilde{C}_{AB}(t)^*. \tag{17}$$

Furthermore, since the matrix representations of $A(\hat{x})$ and $B(\hat{x})$ can both be chosen to be real in the basis of eigenstates of $\hat{H} = \hat{p}^2/2m + V(\hat{x})$, it is clear from Eq. (9) that

$$\widetilde{C}_{AB}(t) = \widetilde{C}_{AB}(-t)^*. \tag{18}$$

Combining all three symmetries, we see that $\widetilde{C}_{AB}(t) = \widetilde{C}_{BA}(t)$ is a real and even function of t. Only the last of these results [Eq. (18)] holds for the more standard correlation function $C_{AB}(t)$.

All three results do hold, however, for the classical ring-polymer correlation function in Eq. (12), and under exactly the same circumstances as in the quantum case. The detailed balance condition in Eq. (16) follows in the classical context from Liouville's theorem $[\int d\mathbf{p}_0 \int d\mathbf{x}_0 = \int d\mathbf{p}_t \int d\mathbf{x}_t]$ and from the fact that the dynamics in Eqs. (10) and (11) conserves the classical equilibrium density $[e^{-\beta_n H_n(\mathbf{p}_0,\mathbf{x}_0)} = e^{-\beta_n H_n(\mathbf{p}_t,\mathbf{x}_t)}]$:

$$\langle A(0)B(t)\rangle_n = \langle B(0)A(-t)\rangle_n. \tag{16'}$$

The reality of the classical quantity $\langle A(0)B(t)\rangle_n$ is also completely general,

$$\langle A(0)B(t)\rangle_n = \langle A(0)B(t)\rangle_n^*, \tag{17'}$$

whereas the time-reversal symmetry in Eq. (18) relies on the reversibility of classical mechanics $[\mathbf{x}_t(\mathbf{p}_0,\mathbf{x}_0) = \mathbf{x}_{-t}(-\mathbf{p}_0,\mathbf{x}_0)]$ and the fact that the classical Boltzmann factor $e^{-\beta_n H_n(\mathbf{p}_0,\mathbf{x}_0)}$ is symmetric with respect to replacing $\mathbf{p}_0$ with $-\mathbf{p}_0$,

$$\langle A(0)B(t)\rangle_n = \langle A(0)B(-t)\rangle_n^*. \tag{18'}$$

As in the quantum case, this last symmetry is therefore connected with the fact that $A = A_n(\mathbf{x})$ and $B = B_n(\mathbf{x})$, although it also applies more generally to autocorrelation functions as is evident from Eq. (16') [and indeed from Eq. (16)].

This close correspondence between the symmetries of the Kubo-transformed quantum correlation function and the classical correlation function in Eq. (12) is of course already well known in the context of classical molecular dynamics ($n = 1$ polymer bead). In that context, the correspondence suggests that one should identify the classical correlation function $\langle A(0)B(t)\rangle_1$ with $\widetilde{C}_{AB}(t)$ rather than $C_{AB}(t)$, and then multiply the resulting spectrum by $\beta\hbar\omega/(1-e^{-\beta\hbar\omega})$ to obtain $G_{AB}(\omega)$ [see Eq. (15)]. This is precisely the so-called "harmonic correction factor" that is widely used to correct classical molecular dynamics results for detailed balance.[18–20]

What is more interesting, however, is the fact that the correspondence is maintained for any number of polymer beads n. This is a consequence of the fact that the classical ring-polymer dynamics in Eqs. (10) and (11) is consistent with the equilibrium density $e^{-\beta_n H_n(\mathbf{p},\mathbf{x})}$. Hence nothing has

been lost in going from classical molecular dynamics to ring-polymer molecular dynamics, and something might just have been gained: if $\langle A(0)B(t)\rangle_n$ provides a closer approximation to $\widetilde{C}_{AB}(t)$ than does $\langle A(0)B(t)\rangle_1$, we are guaranteed to do better with this approximation than we would by applying the harmonic correction factor to the results of a purely classical molecular dynamics simulation.

IV. THE HARMONIC LIMIT

A further justification for Eq. (12) is that it gives the exact quantum mechanical result $\widetilde{C}_{AB}(t)$ for all t in the limit of a harmonic potential $V(x) = 1/2 m\omega^2 x^2$, at least in the special case where $A(x)$ and/or $B(x)$ is a linear function of x.

The key thing that makes this case special is that the operator $\hat{x}$ only connects harmonic oscillator eigenstates differing by one quantum number. Hence the exact Kubo-transformed correlation function $\widetilde{C}_{Ax}(t)$ (for example) contains just a single frequency component in this case, at the natural frequency ω of the harmonic oscillator. Since $\widetilde{C}_{Ax}(t)$ is a real and even function of t, we must have

$$\widetilde{C}_{Ax}(t) = \widetilde{C}_{Ax}(0)\cos \omega t. \tag{19}$$

Now consider what happens in Eq. (12). When $B(x) = x$ we have

$$\langle A(0)x(t)\rangle_n = \frac{1}{(2\pi\hbar)^n Z_n} \int d\mathbf{p}_0 \int d\mathbf{x}_0 e^{-\beta_n H_n(\mathbf{p}_0,\mathbf{x}_0)} \times A_n(\mathbf{x}_0)x_n(\mathbf{x}_t), \tag{20}$$

where

$$x_n(\mathbf{x}) = \frac{1}{n}\sum_{j=1}^{n} x_j \tag{21}$$

is the centroid of the ring-polymer coordinates. Defining the corresponding momentum centroid

$$p_n(\mathbf{p}) = \frac{1}{n}\sum_{j=1}^{n} p_j, \tag{22}$$

we obtain the following equations of motion for p_n and x_n from Eqs. (10) and (11)

$$\dot{p}_n = -\frac{1}{n}\sum_{j=1}^{n} \frac{\partial V(x_j)}{\partial x_j} \tag{23}$$

and

$$\dot{x}_n = \frac{p_n}{m}. \tag{24}$$

Note in passing that the first term in Eq. (10), which results in high-frequency oscillations in the individual ring-polymer trajectories for high n, exactly cancels in the Ehrenfest-like average of Eq. (23), and so the phase-space centroid variables p_n and x_n evolve in a less oscillatory fashion than the individual ring-polymer beads [regardless of whether or not the potential $V(x)$ is harmonic]. Since the time-dependence of $\langle A(0)x(t)\rangle_n$ in Eq. (20) only depends on the motion of the

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coordinate centroid, it too is expected to vary smoothly, as indeed is the exact quantum mechanical correlation function $\tilde{C}_{Ax}(t)$.

In the case of the simple harmonic potential $V(x) = 1/2\,m\omega^2 x^2$, Eq. (23) simplifies to $\dot{p}_n = -m\omega^2 x_n$, which in conjunction with Eq. (24) gives

$$x_n(\mathbf{x}_t) = x_n(\mathbf{x}_0)\cos\omega t + \frac{p_n(\mathbf{p}_0)}{m\omega}\sin\omega t. \tag{25}$$

Thus all of the coordinate centroids that are integrated over in Eq. (20) exhibit simple harmonic motion in this case, at the natural frequency ω of the oscillator. And since $\langle A(0)x(t)\rangle_n$ is a real and even function of t (or equivalently, since $\int d\mathbf{p}_0 e^{-\beta_n H_n(\mathbf{p}_0,\mathbf{x}_0)} p_n(\mathbf{p}_0) = 0$) we must have

$$\langle A(0)x(t)\rangle_n = \langle Ax\rangle_n \cos\omega t. \tag{26}$$

But we also know quite generally, from the discussion following Eq. (8), that $\lim_{n\to\infty}\langle Ax\rangle_n = \tilde{C}_{Ax}(0)$, and hence from Eq. (19) that

$$\lim_{n\to\infty}\langle A(0)x(t)\rangle_n = \tilde{C}_{Ax}(t). \tag{27}$$

This completes the proof that Eq. (12) will give the exact result for a correlation function of the form $\tilde{C}_{Ax}(t)$ in a harmonic potential, and the fact that the same is true for $\tilde{C}_{xB}(t)$ follows from the symmetry considerations in Sec. III.

In the special case of the position autocorrelation function, one can show further (with a bit more effort) that Eq. (12) gives the exact result for a harmonic potential, namely $\tilde{C}_{xx}(t) = [1/(\beta m\omega^2)]\cos\omega t$, for any n. The purely classical limit of $n=1$ polymer bead is therefore exact in this case, which explains why the factor of $\beta\hbar\omega/(1-e^{-\beta\hbar\omega})$ in Eq. (15) is called a harmonic correction factor. When one or other of the operators $\hat{A}$ and $\hat{B}$ is not a linear function of x, the classical result is no longer exact, but Eq. (12) still is (in the limit as $n\to\infty$).

Of course all of the competing methods that have been proposed for including quantum mechanical effects in short-time correlation functions are also exact in the harmonic limit.[1–7] In cases where the method is based on semiclassical mechanics, such as the classical Wigner model (or linearized semiclassical initial value representation[3,4]), this is true in principle for any two operators $\hat{A}$ and $\hat{B}$. The present method bears a closer resemblance to centroid molecular dynamics,[1,2] which is also only exact in the harmonic limit if one or other of the correlated observables is a linear function of the coordinates (or momenta).[2]

V. EXAMPLE CALCULATIONS

So far, we have established that Eq. (12) gives the exact result as $n\to\infty$ in two important special cases: in the limit as $t\to 0$ and for a certain class of correlation functions in a harmonic potential. The key remaining question, therefore, is how well the method works when we move away from these special regimes.

In order to answer this question, we have performed a series of numerical calculations on some simple one-
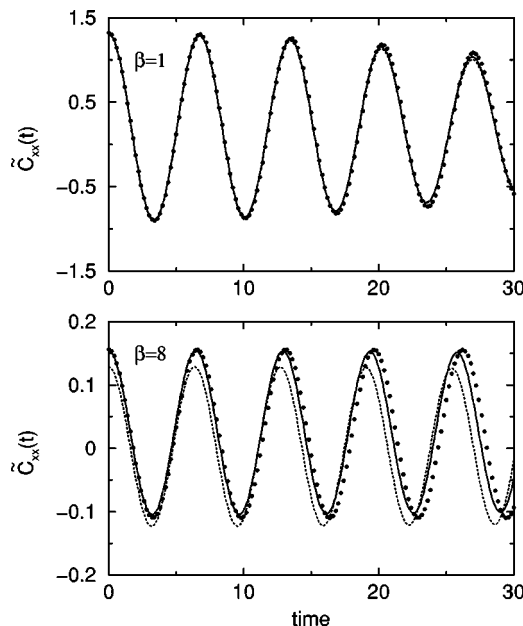

FIG. 1. Kubo-transformed position autocorrelation functions for the mildly anharmonic potential in Eq. (28), at two different temperatures. Dashed line: the classical result $\langle x(0)x(t)\rangle_1$. Solid line: the ring-polymer result $\langle x(0)x(t)\rangle_n$ with $n=4\beta$. Filled circles: the exact quantum mechanical result $\tilde{C}_{xx}(t)$.

dimensional problems, two of which have been used previously to test various adaptations of the centroid molecular dynamics method.[2] Throughout these calculations, we used standard path integral molecular dynamics techniques to evaluate Eq. (12). The only difficulties we encountered were the well-known ones associated with the stiffness of the polymer necklace for high n. This leads to a problem of nonergodicity[21] which can be avoided[11] by periodically resampling the momenta from the Maxwell distribution contained in $e^{-\beta_n H_n(\mathbf{p},\mathbf{x})}$. It also leads to the need to use a small time step in a standard classical trajectory integrator, which we avoided by using a symplectic integrator based on alternating free harmonic ring-polymer and external force steps. Let us now discuss the results of these calculations.

First, in order to explore how well Eq. (12) works away from the harmonic regime, we have used it to calculate the position autocorrelation function $\tilde{C}_{xx}(t)$ for both the mildly anharmonic potential

$$V(x) = \tfrac{1}{2}x^2 + \tfrac{1}{10}x^3 + \tfrac{1}{100}x^4, \tag{28}$$

and the strongly anharmonic quartic oscillator, $V(x) = x^4/4$, considered by Jang and Voth,[2] with $\hbar=1$ and $m=1$ in both cases. The results are shown at two different temperatures in Figs. 1 and 2, where they are compared with the purely classical results and the exact quantum mechanical (Kubo-transformed) correlation functions. In the path integral molecular dynamics calculations, $n=4$ polymer beads were found to suffice for $\beta=1$, and $n=32$ for $\beta=8$. We used a time step of 0.05 in our symplectic integrator and time averaged the correlation function for a large number of dif-
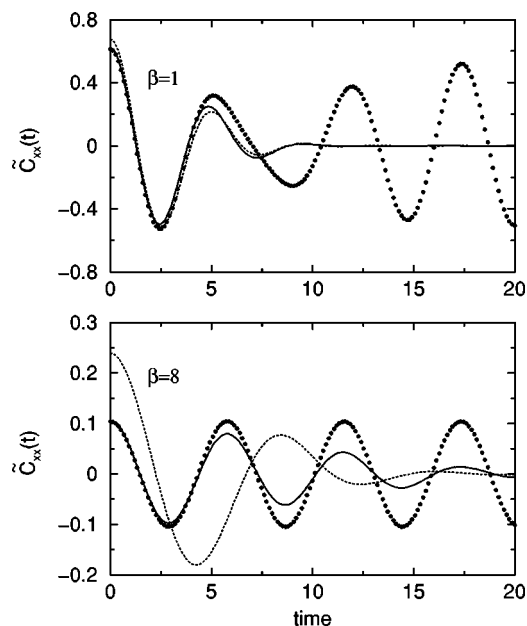
FIG. 2. As in Fig. 1, but for the strongly anharmonic potential $V(x)$ $= 1/4\,x^4$.

ferent ring-polymer trajectories, with a resampling of the momenta between each one. The classical results were obtained in the same way, but with $n=1$.

Consider first the results for the mildly anharmonic potential in Fig. 1. In the high-temperature regime ($\beta=1$), all three results are in good agreement even for fairly long times (several oscillation periods). This is to be expected for a mildly anharmonic problem in the classical regime because classical mechanics gives the exact Kubo-transformed position autocorrelation function for a harmonic oscillator (see Sec. IV). At lower temperatures ($\beta=8$), there is, however, a more noticeable departure between the classical and quantum mechanical results with regard to both the frequency and the amplitude of the oscillation, and it is encouraging to see that the present ring-polymer method corrects both deficiencies of the classical result rather well.

Now consider the results for the more strongly anharmonic potential in Fig. 2. In this case, the classical result is way off the exact quantum mechanical result even at high temperatures, except for the duration of the first oscillation. It is also clear that the classical ring-polymer generalization does not do much to correct this, and nor should one expect it to. The long-time oscillations in the quantum result arise from the coherent collisions of a broad thermal wave packet with a quartic wall, and Eq. (12) is missing the phase information that would be needed to capture this. However, as stressed in the Introduction, an accurate description of long-time quantum coherences is not what we are looking for. Such coherences are at their most extreme in anharmonic one-dimensional problems like the quartic oscillator, but they are typically far less important in the sort of condensed phase problems to which one would ultimately like to apply the present approach.

The classical result for the quartic oscillator is of course even worse in the low-temperature regime, as can be seen from the lower panel of Fig. 2. In this regime, the classical result does not even agree with the quantum result for the first oscillation, because the classical statistics are completely wrong. This *is* something that one would expect the present ring-polymer method to correct, and it can be seen from the figure that it does so rather well: the ring-polymer result follows the quantum mechanical result with the correct frequency for several periods, although without maintaining the full amplitude of the coherent quantum oscillation.

It can also be seen from Fig. 2 that the ring-polymer method does rather better at low temperatures than high temperatures for this quartic problem. This is simply because the thermal time $\beta\hbar$ is longer (i.e., quantum statistical effects are more important than quantum dynamical effects for longer) at lower temperatures. The classical ring-polymer method gets the quantum statistical effects right while missing the quantum dynamical effects, as is quite evident from the two panels of the figure. Let us therefore reiterate that the method will only work well in situations where quantum effects in the dynamics are comparatively unimportant.

As we have already mentioned, the problems considered in Figs. 1 and 2 have been studied previously by Jang and Voth using a number of different variations of the centroid molecular dynamics method.[2] These authors considered the real part of the correlation function $C_{AB}(t)$ in Eq. (13), rather than the more natural Kubo-transformed version we have considered here. However, the behaviors of the two correlation functions are sufficiently similar to allow one to make a qualitative comparison between the present results and those in Figs. 2 and 6 of their paper.[2]

The upshot of this comparison is that the present ring-polymer molecular dynamics method seems to do almost as well as centroid molecular dynamics for these simple problems. [The one situation where centroid molecular dynamics does slightly better is for the quartic oscillator in the low-temperature regime (the lower panel of Fig. 2), where it seems to capture more of the amplitude of the long-time quantum oscillation. As discussed by Jang and Voth,[2] their method works especially well in this case because the centroid potential is nearly harmonic.] Given the simplicity of the present method when compared with centroid molecular dynamics, we find this very encouraging.

Finally, in order to illustrate what to expect of the present method for more general correlation functions, we have calculated the (Kubo-transformed) autocorrelation function of $A(x)=x^3$ for a simple harmonic potential $V(x)$ $= 1/2\,x^2$. (Recall from Sec. IV that there is no guarantee that the ring-polymer method will give the exact result in this case, even though the potential is harmonic.) The computed results are shown in Fig. 3, again at two different temperatures. One sees, as in the previous two figures, that the present method provides a consistent improvement over purely classical molecular dynamics that becomes most apparent in the low-temperature regime.
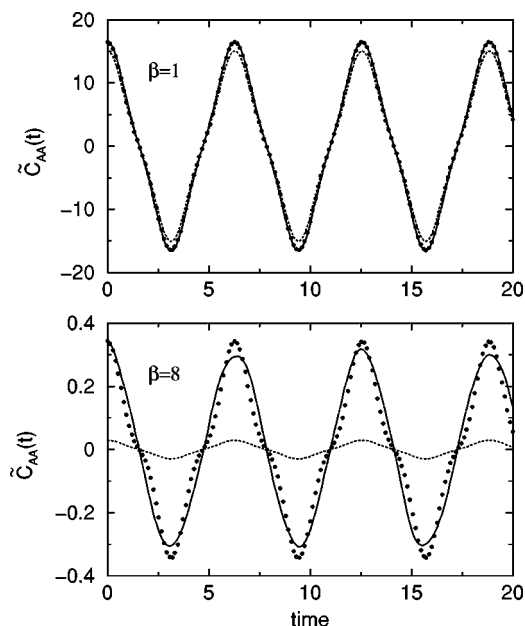
FIG. 3. Kubo-transformed harmonic oscillator autocorrelation functions with $A(x)=x^3$. Dashed line: the classical result $\langle A(0)A(t)\rangle_1$. Solid line: the ring-polymer result $\langle A(0)A(t)\rangle_n$ with $n=4\beta$. Filled circles: the exact quantum mechanical result $\tilde{C}_{AA}(t)$.

VI. SUMMARY

In this paper, we have demonstrated that the standard path integral molecular dynamics method can be used to calculate approximate (Kubo-transformed) real-time correlation functions.

The results are not perfect, and in particular the method misses the long-time quantum coherence effects that arise in simple one-dimensional anharmonic systems. However, the short-time quantum effects that stem from the Boltzmann operator are correctly included, and the method has been shown to provide a consistent improvement over classical molecular dynamics.

It will be interesting in future work to see how well this ring-polymer molecular dynamics method does in condensed phase applications, such as a calculation of the infrared absorption spectrum of liquid water. The one thing we can be confident about on the basis of the present results (and the discussion at the end of Sec. III) is that it will do better than applying the harmonic detailed balance correction factor to the classical dipole autocorrelation spectrum, which is an approach that already works rather well.[22]

[1] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5106 (1994).
[2] S. Jang and G. A. Voth, J. Chem. Phys. **111**, 2371 (1999).
[3] H. Wang, X. Sun, and W. H. Miller, J. Chem. Phys. **108**, 9726 (1998).
[4] X. Sun, H. Wang, and W. H. Miller, J. Chem. Phys. **109**, 7064 (1998).
[5] J. Shao and N. Makri, J. Phys. Chem. A **103**, 9479 (1999).
[6] Q. Shi and E. Geva, J. Phys. Chem. **107**, 9059 (2003).
[7] J. A. Poulsen, G. Nyman, and P. J. Rossky, J. Chem. Phys. **119**, 12179 (2003).
[8] W. H. Miller, J. Phys. Chem. A **105**, 2942 (2001).
[9] M. Parrinello and A. Rahman, J. Chem. Phys. **80**, 860 (1984).
[10] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[11] B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. **37**, 401 (1986).
[12] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[13] R. P. Feynman, *Statistical Mechanics* (Addison-Wesley, New York, 1972).
[14] D. Chandler and P. G. Wolynes, J. Chem. Phys. **74**, 4078 (1981).
[15] K. S. Schweizer, R. M. Stratt, D. Chandler, and P. G. Wolynes, J. Chem. Phys. **75**, 1347 (1981).
[16] D. Chandler, J. Phys. Chem. **88**, 3400 (1984).
[17] M. F. Trotter, Proc. Am. Math. Soc. **10**, 545 (1959).
[18] P. H. Berens and K. R. Wilson, J. Chem. Phys. **74**, 4872 (1981).
[19] J. S. Bader and B. J. Berne, J. Chem. Phys. **100**, 8359 (1994).
[20] S. A. Egorov, K. F. Everitt, and J. L. Skinner, J. Phys. Chem. A **103**, 9494 (1999).
[21] R. W. Hall and B. J. Berne, J. Chem. Phys. **81**, 3641 (1984).
[22] H. Ahlborn, B. Space, and P. B. Moore, J. Chem. Phys. **112**, 8083 (2000).