

# Coherent state semiclassical initial value representation for the Boltzmann operator in thermal correlation functions

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A semiclassical methodology for evaluating the Boltzmann operator entering semiclassical approximations for finite temperature correlation functions is described. Specifically, Miller's imaginary time semiclassical approach is applied to the Herman–Kluk coherent state initial value representation (IVR) for the time evolution operator in order to obtain a coherent state IVR for the Boltzmann operator. The phase-space representation gives rise to exponentially decaying factors for the coordinates and momenta of the real time trajectories employed in the dynamical part of the calculation. A Monte Carlo procedure is developed for evaluating dynamical observables, in which the absolute value of the entire exponential part of the integrand serves as the sampling function. Numerical tests presented show that the methodology is highly accurate as well as stable over the temperature range relevant to chemical applications. © 2002 American Institute of Physics.

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## I. INTRODUCTION

The last few years have witnessed a rebirth of interest in using semiclassical (SC) theory<sup>1,2</sup> as a practical way for adding quantum mechanical effects to classical molecular dynamics (MD) simulations of complex molecular processes.<sup>3–51</sup> The appeal of this approach is evident, for classical MD simulations are widely used to describe a vast array of complex molecular phenomena, and SC theory—which only requires classical trajectories (plus their stability properties) for its implementation—has been demonstrated to provide a very good description of essentially all types of quantum effects in molecular systems (at least for low-dimensional examples for which the accuracy can be verified by comparison to quantum calculations).

For complex systems, i.e., those with many degrees of freedom, the physical observables of interest are almost always expressed in terms of some kind of time correlation function, and in most cases the system is in a Boltzmann (i.e., thermal) distribution with respect to some Hamiltonian. A standard *A-B* correlation function, for example, is given by the expression

$$C(t) = Z^{-1} \text{Tr}(e^{-\beta H} A e^{iHt/\hbar} B e^{-iHt/\hbar}). \quad (1.1)$$

The flux–flux autocorrelation function<sup>52</sup> that determines thermally averaged chemical reaction rates, for example, corresponds to  $\hat{A} = \hat{B} = \hat{F}$  (the flux operator). Another case is a thermal distribution with respect to one Hamiltonian and time evolution by another (as in photoexcitation to an excited electronic state),

$$\langle B(t) \rangle = Z_0^{-1} \text{Tr}(e^{-\beta \hat{H}_0} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}), \quad (1.2)$$

where  $Z = \text{Tr} e^{-\beta H_0}$ . A third example is the golden rule rate for transitions from electronic state *i* to *f*, which is given by

$$k_{f \leftarrow i}(T) = Z_i^{-1} \hbar^{-2} \int_{-\infty}^{\infty} dt \times \text{Tr}(e^{-\beta \hat{H}_i} V_{if} e^{i\hat{H}_f t/\hbar} V_{fi} e^{-i\hat{H}_i t/\hbar}), \quad (1.3)$$

where  $V_{fi}$  is the electronic coupling. For simplicity, the methodology developed below is presented for correlation functions of the type shown in Eq. (1.1), but it is understood that observables of the type given in Eq. (1.2) or Eq. (1.3) are obtained by using appropriate Hamiltonians in the real time evolution operators.

Current implementations of SC theory are based on various initial value representations<sup>3,6,13–19</sup> (IVRs), which express the quantum time evolution operator as a phase-space average over the initial conditions of classical trajectories; see, for example, the Herman–Kluk<sup>13,14</sup> (HK) or coherent state IVR below [Eqs. (2.1)–(2.4)]. At a more approximate level, there exist “forward–backward” IVRs<sup>29–42</sup> that combine the two propagators in the Heisenberg time-evolved operator  $\hat{B}$ ,

$$\hat{B}(t) = e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \quad (1.4)$$

into one IVR, and the still more approximate “linearized” SC-IVR<sup>27,28</sup> that leads to the “classical Wigner” model (see, for example, Ref. 53).

The present paper deals with evaluation of the Boltzmann operator in semiclassical thermal correlation functions such as Eqs. (1.1)–(1.3), which is clearly a necessary ingredient no matter what level of approximation is used to treat the time evolution. In some cases, too, an accurate treatment of the Boltzmann operator may be the most important con-

sideration, for in complex systems quantum coherence effects may often be quenched. One possibility is to evaluate the Boltzmann operator by an imaginary time Feynman path integral<sup>54</sup> procedure. That approach<sup>38</sup> is feasible in many cases and has the advantage that it can be pushed to (numerical) exactness with sufficient numerical effort. In this paper, however, we explore the use of a semiclassical approximation for the Boltzmann operator, of the same character as the approximation for the real time dynamics, namely an SC-IVR. This is esthetically appealing, i.e., to treat the Boltzmann operator and the propagator at the same level of approximation, and it should also be easier to apply than a full Feynman path integral treatment.

Finally, we note that the high dimensionality of the phase-space averages involved in an IVR necessitates use of Monte Carlo methods. The coherent state IVR for the Boltzmann operator that we develop here is ideally suited for this purpose, providing a natural sampling function for the initial conditions for the real and imaginary time (*vide infra*) trajectories.

Section II first presents the development of the coherent state IVR for the Boltzmann operator and then describes the Monte Carlo procedure, which requires evaluation of the normalization integral of the sampling function. In Sec. III we test the method of equilibrium and dynamical calculations in one-dimensional anharmonic oscillators, and Sec. IV concludes.

## II. SEMICLASSICAL BOLTZMANN OPERATOR

### A. Theory

Recall the HK or coherent state IVR for the propagator,

$$e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-1} \int dx_0 \int dp_0 D_t(x_0, p_0) \times e^{iS_t(x_0, p_0)/\hbar} |x_t, p_t\rangle \langle x_0, p_0|, \quad (2.1)$$

where  $|x_0, p_0\rangle$  is a standard coherent state (“minimum uncertainty wave packet”), the coordinate space wave function for which is

$$\langle x | x_0, p_0 \rangle = \left( \frac{\gamma}{\pi} \right)^{1/4} \exp \left( -\frac{\gamma}{2} (x - x_0)^2 + \frac{i}{\hbar} p_0 (x - x_0) \right), \quad (2.2)$$

$S_t$  is the classical action along the trajectory with initial conditions  $x_0, p_0$ , i.e.,

$$S_t = \int_0^t \left( \frac{1}{2} m \dot{x}(t')^2 - V(x(t')) \right) dt' \quad (2.3)$$

and  $D_t(x_0, p_0)$  the Herman–Kluk prefactor,

$$D_t(x_0, p_0) = 2^{-1/2} \left( \frac{\partial x_t}{\partial x_0} + \frac{\partial p_t}{\partial p_0} + \frac{\hbar\gamma}{i} \frac{\partial x_t}{\partial p_0} + \frac{i}{\hbar\gamma} \frac{\partial p_t}{\partial x_0} \right)^{1/2}. \quad (2.4)$$

(Throughout this paper we assume that the Boltzmann operator in the expression of interest involves a simple one-dimensional Cartesian Hamiltonian of the type

$$H = \frac{p^2}{2m} + V(x);$$

the multidimensional generalization of the methodology developed below is straightforward.)

It is easy to see that the propagator becomes the Boltzmann operator with the formal replacement  $t \rightarrow i\hbar\beta$ , and this trick has been used in many different contexts. One of us<sup>55</sup> used it first semiclassically within the Van Vleck approximation<sup>1</sup> for the propagator, and here we generalize this to the coherent state IVR. One thus considers classical trajectories in pure imaginary time  $t = -i\tau$ , where  $\tau$  is a real-valued parameter that increments from 0 to  $\hbar\beta$ . The classical momentum is therefore purely imaginary,

$$p \equiv m \frac{dx}{dt} = im \frac{dx}{d\tau} \equiv i\bar{p}(\tau), \quad (2.5)$$

where  $\bar{p}(\tau)$  is real. The classical equations of motion for the trajectory  $\{x(\tau), \bar{p}(\tau)\}$  are thus given by

$$\dot{x}(\tau) = \frac{\bar{p}(\tau)}{m}, \quad \dot{\bar{p}}(\tau) = + \frac{\partial V(x(\tau))}{\partial x(\tau)}, \quad (2.6)$$

which can be interpreted as real time motion on the inverted ( $V \rightarrow -V$ ) potential-energy surface. The coherent state IVR for the Boltzmann operator is obtained by making these replacements in Eqs. (2.1)–(2.4),

$$e^{-\beta\hat{H}} = (2\pi\hbar)^{-1} \int d\bar{x}_0 \int d\bar{p}_0 \bar{D}(\bar{x}_0, \bar{p}_0) \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} |\bar{x}_{\hbar\beta}, i\bar{p}_{\hbar\beta}\rangle \langle \bar{x}_0, i\bar{p}_0|, \quad (2.7)$$

where we have added a “bar” over the coordinate variable  $x$  for notational convenience, the imaginary action is

$$\bar{S}(\bar{x}_0, \bar{p}_0) = \int_0^{\hbar\beta} \left\{ \frac{1}{2} M \dot{x}(\tau)^2 + V(x(\tau)) \right\} d\tau, \quad (2.8)$$

and the imaginary time prefactor is given by

$$\bar{D}(\bar{x}_0, \bar{p}_0) = 2^{-1/2} \left( \hbar\gamma \frac{\partial \bar{x}_{\hbar\beta}}{\partial \bar{p}_0} + \frac{1}{\hbar\gamma} \frac{\partial \bar{p}_{\hbar\beta}}{\partial \bar{x}_0} - \frac{\partial \bar{x}_{\hbar\beta}}{\partial \bar{x}_0} - \frac{\partial \bar{x}_{\hbar\beta}}{\partial \bar{p}_0} \right)^{1/2}. \quad (2.9)$$

Below we will also, for convenience in the applications, utilize the symmetry of the Boltzmann operator, i.e.,

$$\langle x | e^{-\beta\hat{H}} | x' \rangle = \langle x' | e^{-\beta\hat{H}} | x \rangle,$$

to write Eq. (2.7) equivalently as

$$e^{-\beta\hat{H}} = (2\pi\hbar)^{-1} \int d\bar{x}_0 \int d\bar{p}_0 \bar{D}(\bar{x}_0, \bar{p}_0) \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} |\bar{x}_0, -i\bar{p}_0\rangle \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta}|. \quad (2.10)$$

We now apply the coherent state IVR of the Boltzmann operator, Eq. (2.10), to evaluate the canonical expectation value in Eq. (1.2). The Heisenberg time-evolved operator  $\hat{B}(t)$  defined in Eq. (1.4) will be evaluated via a real-time coherent state IVR,

$$e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-1} \int dx_0 \int dp_0 (\dots) \times |x_f, p_f\rangle \langle x_0, p_0|, \quad (2.11)$$

where the quantity  $(\dots)$  depends on the specific IVR that is used (e.g., derivative FB-IVR,<sup>35,37</sup> integral FB-IVR,<sup>33–36</sup> generalized FB-IVR,<sup>41</sup> etc.). Utilizing this together with Eq. (2.10) for the Boltzmann operator thus gives the following result for the correlation function:

$$C(t) = (2\pi\hbar)^{-2} \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \dots \bar{D}(\bar{x}_0, \bar{p}_0) \\ \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} \langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle \langle \bar{x}_{\hbar\beta}, \\ -i\bar{p}_{\hbar\beta} | \hat{A} | x_f, p_f \rangle. \quad (2.12)$$

If the operator  $\hat{A}$  has a simple form, its matrix element can be evaluated analytically. For example, if  $\hat{A}$  is a polynomial, one can show that

$$\langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | \hat{A} | x_f, p_f \rangle = f(x_f, p_f, \bar{x}_{\hbar\beta}, \bar{p}_{\hbar\beta}) \\ \times \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x_f, p_f \rangle, \quad (2.13)$$

where the function  $f$  has a polynomial form. The coherent state overlaps in Eq. (2.12) are given by standard formulas, which here yield

$$\langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle = \exp\left(-\frac{\gamma}{4}(x_0 - \bar{x}_0)^2 - \frac{1}{4\gamma\hbar^2}(p_0 + i\bar{p}_0)^2\right. \\ \left. + \frac{i}{2\hbar}(x - \bar{x}_0)(p_0 - i\bar{p}_0)\right). \quad (2.14)$$

## B. Monte Carlo procedures

The integrals in Eq. (2.12) are to be evaluated by Monte Carlo procedures. Note that the use of a coherent state basis for the Boltzmann factor has introduced Gaussian factors for the position and momentum of the real-time trajectory that can serve as parts of a sampling function. Since the semiclassical expression to be computed contains small oscillatory components, it is important to use a sampling function that includes as much of the integrand as possible. The best choice involves the entire part of the integrand of Eq. (2.12) that does not depend on the final coordinates of the real-time trajectory. We assume that the forward-backward treatment employed for the dynamical factor ensures  $x_f \approx x_0$ ,  $p_f \approx p_0$  and choose a sampling function that depends only on the initial conditions of the real-time trajectory:

$$\rho(x_0, p_0, \bar{x}_0, \bar{p}_0) = (2\pi\hbar)^{-1} \bar{D}(\bar{x}_0, \bar{p}_0) \\ \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} |\langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle \\ \times \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x_0, p_0 \rangle|. \quad (2.15)$$

In general the final positions and momenta of the thermal trajectory differ considerably, and Eq. (2.15) is chosen to depend on these final phase-space coordinates in order to provide optimal sampling.

To be used in a Metropolis random walk, the sampling function must be normalized. The procedure described below is similar in spirit to that employed for the path integral representation of the Boltzmann operator.<sup>38</sup> To this end, note

that if the phase factors arising from the coherent state overlaps are reinserted in Eq. (2.15), its integral would be proportional to the partition function. This is seen by contracting the semiclassical representation of the Boltzmann operator in the coherent state basis along with the overcompleteness relation of coherent states, i.e.,

$$(2\pi\hbar)^{-1} \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \bar{D}(\bar{x}_0, \bar{p}_0) \\ \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} \langle x_0, p_0 | \bar{x}_0 - i\bar{p}_0 \rangle \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x_0, p_0 \rangle \\ = \int dx_0 \int dp_0 \langle x_0, p_0 | e^{-\beta H} | x_0, p_0 \rangle \\ = 2\pi\hbar \text{Tr} e^{-\beta H} = 2\pi\hbar Z. \quad (2.16)$$

The integrand of Eq. (2.16) differs from the sampling function by the phase of the coherent state overlap factors, i.e.,

$$(2\pi\hbar)^{-1} \bar{D}(\bar{x}_0, \bar{p}_0) e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} \langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle \langle \bar{x}_{\hbar\beta}, \\ -i\bar{p}_{\hbar\beta} | x_0, p_0 \rangle = \rho(x_0, p_0, \bar{x}_0, \bar{p}_0) e^{iw(x_0, p_0, \bar{x}_0, \bar{p}_0)}, \quad (2.17)$$

where

$$w(x_0, p_0, \bar{x}_0, \bar{p}_0) = \frac{1}{2\hbar} p_0 \left( \bar{x}_f - \bar{x}_0 + \frac{1}{2\gamma\hbar} (\bar{p}_f - \bar{p}_0) \right). \quad (2.18)$$

Thus, Eq. (2.16) reads

$$\int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \rho(x_0, p_0, \bar{x}_0, \bar{p}_0) \\ \times e^{iw(x_0, p_0, \bar{x}_0, \bar{p}_0)} = 2\pi\hbar Z. \quad (2.19)$$

Consider the integral

$$\kappa \equiv \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \rho_{\text{norm}}(x_0, p_0, \bar{x}_0, \bar{p}_0) \\ \times e^{iw(x_0, p_0, \bar{x}_0, \bar{p}_0)} \quad (2.20)$$

of the phase with respect to the *normalized* sampling function

$$\rho_{\text{norm}}(x_0, p_0, \bar{x}_0, \bar{p}_0) \\ \equiv \frac{\rho(x_0, p_0, \bar{x}_0, \bar{p}_0)}{\int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \rho(x_0, p_0, \bar{x}_0, \bar{p}_0)}. \quad (2.21)$$

It follows that

$$\kappa \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \rho(x_0, p_0, \bar{x}_0, \bar{p}_0) = 2\pi\hbar Z, \quad (2.22)$$

and therefore the desired normalization integral is

$$Z^{-1} \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \rho(x_0, p_0, \bar{x}_0, \bar{p}_0) = 2\pi\hbar \kappa^{-1}. \quad (2.23)$$

To summarize, the procedure consists of two Monte Carlo integrations. In the main part, one performs a Metropolis random walk to evaluate the integral,

$$\kappa C(t) = \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 (\dots) \rho(x_0, p_0, \bar{x}_0, \bar{p}_0) \times \frac{\langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x_f, p_f \rangle}{|\langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle| |\langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x_0, p_0 \rangle|}, \quad (2.24)$$

where the three dots denote the dynamical part of the integrand arising from the particular semiclassical approximation applied to the real-time evolution, using  $\rho$  of Eq. (2.15) as the sampling function. In a separate procedure one evaluates the integral  $\kappa$  of the phase  $w$  arising from the Boltzmann part using the same sampling function. The desired expectation value is given by the first Monte Carlo integral divided by  $\kappa$ .

### III. NUMERICAL TESTS

In this section we test the semiclassical methodology described above by evaluating finite temperature expectation values in two model systems. The first is a one-dimensional symmetric quartic oscillator described by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 + cx^4, \quad (3.1)$$

with  $m = \omega = 1$  and  $c = 0.1$ . We calculate the variance of the thermal distribution in this system, i.e.,

$$\Delta x^2 \equiv \langle x^2 \rangle_\beta - \langle x \rangle_\beta^2 = \frac{\text{Tr} e^{-\beta \hat{H}} x^2}{\text{Tr} e^{-\beta \hat{H}}}, \quad (3.2)$$

because  $\langle x \rangle_\beta = 0$  for symmetric potentials. Using the semiclassical representation of the Boltzmann operator presented in Sec. II, Eq. (3.2) takes the form

$$\Delta x^2 = (2\pi\hbar)^{-1} \int d\bar{x}_0 \int d\bar{p}_0 \bar{D}(\bar{x}_0, \bar{p}_0) e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} \times \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | x^2 | \bar{x}_0, -i\bar{p}_0 \rangle. \quad (3.3)$$

This can be evaluated directly by Monte Carlo methods. However, since the primary use of the semiclassical treatment of the thermal density is in conjunction with semiclassical approximations in real time and the latter employs the coherent state representation, we rewrite Eq. (3.3) in the form

$$\Delta x^2 = (2\pi\hbar)^{-2} \int dx_0 \int dp_0 \int d\bar{x}_0 \int d\bar{p}_0 \bar{D}(\bar{x}_0, \bar{p}_0) \times e^{-\bar{S}(\bar{x}_0, \bar{p}_0)/\hbar} \langle \bar{x}_{\hbar\beta}, -i\bar{p}_{\hbar\beta} | \bar{x}_0, p_0 \rangle \times \langle x_0, p_0 | x^2 | \bar{x}_0, -i\bar{p}_0 \rangle. \quad (3.4)$$

The matrix element of  $x^2$  between a real and an imaginary momentum coherent state is given by the expression

$$\langle x_0, p_0 | x^2 | \bar{x}_0, -i\bar{p}_0 \rangle = \frac{1}{2\gamma} \left( 1 + \frac{1}{2\gamma} (\gamma(\bar{x}_0 + x_0) + \hbar^{-1}(\bar{p}_0 - p_0))^2 \right) \times \langle x_0, p_0 | \bar{x}_0, -i\bar{p}_0 \rangle. \quad (3.5)$$

TABLE I. Exact, semiclassical results for the variance of the thermal density for the quartic oscillator of Eq. (3.1) at various temperatures. The Monte Carlo error bars for the semiclassical calculation are also given.

$\hbar\omega\beta$	Exact	Semiclassical	Classical
0.2	1.83	1.81 ± 0.05	1.83
0.5	1.03	1.03 ± 0.04	1.01
1	0.67	0.67 ± 0.02	0.62
1.5	0.54	0.58 ± 0.02	0.45
2	0.48	0.46 ± 0.08	0.36
2.5	0.45	0.47 ± 0.08	0.30

This way, the variance of the thermal density has the form considered in the previous section; it can be evaluated using Eq. (2.15) as the weight function and the factor multiplying the coherent state overlap in Eq. (3.5) as the integrand to be sampled.

Table I shows the results obtained at various temperatures and compares with accurate quantum mechanical and classical predictions. All calculations were performed with  $\gamma$  ranging between 16 and 32 and with  $10^5$  Monte Carlo points. The semiclassical procedure developed in Sec. II is stable and also very accurate over the entire temperature range considered. At very low temperatures some of the imaginary time trajectories tend to “roll downhill” very rapidly in this steep potential, such that the quantity inside the square root of the imaginary time coherent state prefactor turns negative. Since the Boltzmann matrix element is real-valued, proper care must be taken to avoid large Monte Carlo steps that are responsible for this situation. Increasing the value of the coherent state parameter results in narrower sampling and tends to prevent such instabilities. In the zero temperature limit instant on-type trajectories are known to dominate the Boltzmann factor. Obtaining the initial conditions for such trajectories requires a delicate sampling process. The results presented in Table I are in excellent agreement with those of accurate quantum mechanical calculations employing wavepacket propagation techniques and thus capture quantitatively the deviations from classical behavior.

Next, we present numerical results for the average position in an asymmetric quartic oscillator of the form

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2 - cx^3 + cx^4, \quad (3.6)$$

with  $m = 1$ ,  $\omega = \sqrt{2}$  and  $c = 0.1$ . The Hamiltonian describing the initial density in Eq. (1.2) has the same form but is displaced to the right:

$$\hat{H}_0 = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 (x-a)^2 - c(x-a)^3 + c(x-a)^4, \quad (3.7)$$

with  $a = 1$ . The Heisenberg evolved operator was approximated using the derivative form of the forward-backward semiclassical methodology,<sup>38</sup> i.e.,

$$e^{i\hat{H}t/\hbar} B^{-i\hat{H}t/\hbar} = -i \frac{\partial}{\partial \mu} e^{i\hat{H}t/\hbar} e^{i\mu B} e^{-i\hat{H}t/\hbar} \Big|_{\mu=0}. \quad (3.8)$$

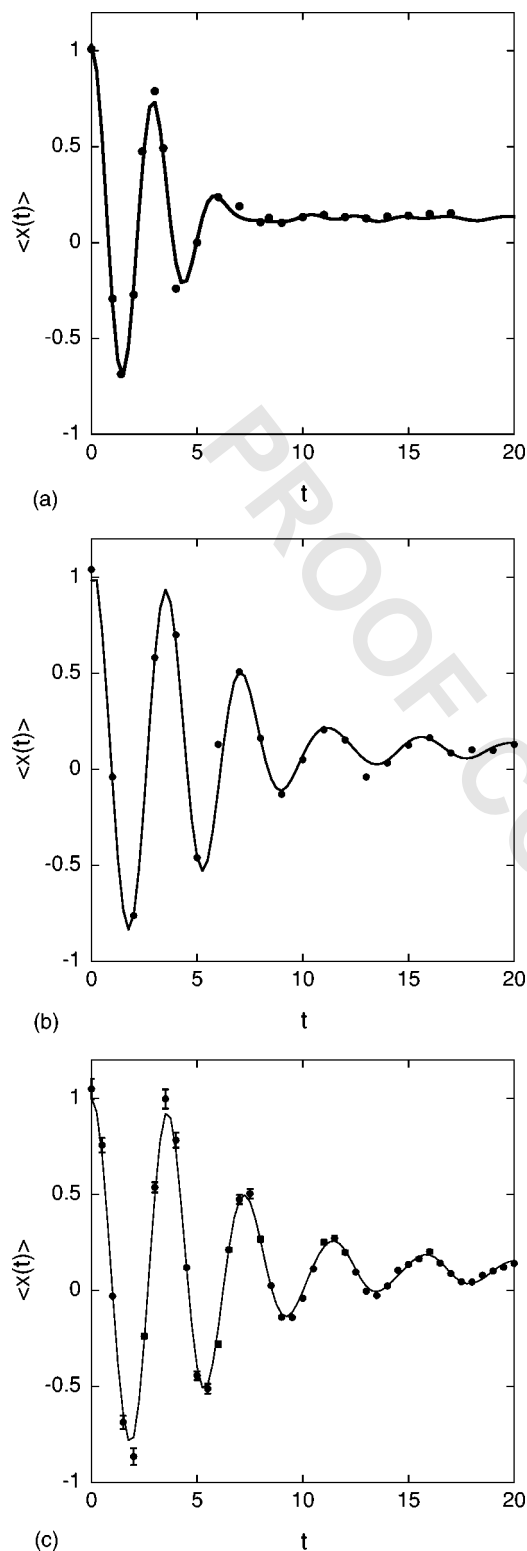


FIG. 1. Position expectation value in the asymmetric quartic potential given by Eq. (3.6) at the temperatures corresponding to (a)  $\hbar\omega\beta=0.1\sqrt{2}$ , (b)  $\hbar\omega\beta=0.5\sqrt{2}$ , and (c)  $\hbar\omega\beta=\sqrt{2}$ . In both cases the real time evolution is approximated by the derivative FBSD methodology (Refs. 35 and 37). The solid line shows results obtained via a path integral description of the Boltzmann operator (Ref. 38), while the markers show the results of the imaginary time semiclassical approximation to the Boltzmann factor described in Sec. II.

The product of exponentials is treated as a single evolution operator and approximated using time-dependent semiclassical theory in the coherent state representation.

Figure 1 shows the average position (i.e.,  $\hat{B} = \hat{x}$ ) at three temperatures corresponding to  $\hbar\omega\beta = 0.1\sqrt{2}$ ,  $0.5\sqrt{2}$ , and  $\sqrt{2}$ . The semiclassical representation of the Boltzmann operator provides an excellent description of the initial conditions, capturing quantitatively the magnitude of the dynamical observable and the frequencies involved. In fact, the results of the present method are nearly identical to those obtained through a path integral discretization of the thermal density<sup>38</sup> within the same quasiclassical treatment of the dynamics.

#### IV. CONCLUDING REMARKS

As has been pointed out in many contexts, the Boltzmann operator  $\exp(-\beta H)$  and the propagator (time evolution operator)  $\exp(-iHt/\hbar)$  are effectively the same operator. It thus seems desirable that equivalent approximations be used for the two. To this end we have shown how to define a coherent state IVR for the Boltzmann operator to be used with such approximations for the propagator. It was seen in some simple test cases to give excellent results, i.e., to be essentially as accurate as using an exact path integral representation for the Boltzmann operator, for the same treatment of the real-time dynamics. This is of course the desired result, so further work will proceed to use this representation of the Boltzmann operator in more serious applications.

A crucial part of SC-IVR calculations is the phase-space average over initial conditions, which must be carried out by Monte Carlo methods for systems with many degrees of freedom. It is thus encouraging to see that use of the coherent state IVR for the Boltzmann operator facilitates this aspect of such calculations, both for the imaginary time trajectory (for the Boltzmann operator) and the real-time trajectory (for the propagator).

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