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Effective classical partition functions with an improved time-dependent reference potential

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The original Feynman-Kleinert [Phys. Rev. A **34**, 5080 (1986)] variational approach to Euclidean path integrals is improved by introducing a reference harmonic potential whose center is allowed to change with time. The motion of the center of the potential is varied such that the "effective potential" of Feynman and Kleinert is minimized and leads to an equation of motion for the classical path in the reference system that closely reproduces the "exact" average path. The formalism is applied to the double-well potential $V(x)=-x^2/2+gx^4/4+1/4g$. This modification improves the accuracy of the approximate quantum-mechanical distribution function and, to a larger extent, the density matrix.

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I. INTRODUCTION AND THEORY

A remarkably accurate variational treatment of Euclidean path integrals was first proposed by Feynman and Kleinert some years ago [1] and the accuracy of the method was investigated in detail in Ref. [2]. Kleinert [3] extended the basic approach to obtain a uniformly convergent variational perturbation theory, and the method has been applied, in its original or modified form, to quantum crystal lattices [4], to calculate excited state energies [5], density matrices [6], and much more. In this paper, we suggest a modification to the first-order, original, Feynman-Kleinert method and show that it improves the calculation of the partition function and the density matrix for a particle in a one-dimensional double-well potential.

The quantum-mechanical partition function Z for a general potential $V(x)$, expressed as a path integral [7], is

$$\begin{aligned} Z &= \int \mathcal{D}[x(\tau)] e^{-\mathsf{A}} \\ &= \int \mathcal{D}[x(\tau)] \exp\left(-\int_0^\beta d\tau\left[\frac{1}{2}\dot{x}(\tau)^2 + V(x(\tau))\right]\right), \end{aligned} \tag{1.1}$$

where $\beta=1/T$, A is the Euclidean action, and the mass and Planck's ($\hbar$) and Boltzmann's constants have been set to unity. To make a connection with classical statistical mechanics, the partition function can be written as

$$Z = \int \frac{dx_0}{\sqrt{2\pi\beta}} e^{-\beta W_{eff}(x_0)}, \tag{1.2}$$

where $W_{eff}(x_0)$ is called an "effective classical potential." Clearly, $W_{eff}(x_0)$ can be obtained from

$$\frac{e^{-\beta W_{eff}(x_0)}}{\sqrt{2\pi\beta}} = Z_{x_0}, \tag{1.3}$$

where

$$Z_{x_0} \equiv \int \mathcal{D}[x(\tau)]\delta(\bar{x}-x_0)e^{-\mathsf{A}}, \tag{1.4}$$

and where $\bar{x}$ is some functional of the path variable $x(\tau)$.

In the original Feynman-Kleinert paper [1], a variational approach was used to approximate $W_{eff}(x_0)$, based on a harmonic reference problem with an analytic solution. Their reference Euclidean action was

$$\mathsf{A}_{x_0} \equiv \int_0^\beta d\tau\left(\frac{\dot{x}(\tau)^2}{2} + \frac{\omega^2(x_0)}{2}[x(\tau)-x_0]^2\right), \tag{1.5}$$

where the oscillator frequency depends on x_0. They also chose $\bar{x}=\frac{1}{\beta}\int_0^\beta d\tau\, x(\tau)$, such that the harmonic oscillator is centered around the time average of each individual path. The partition function was then rewritten as

$$\begin{aligned} Z &= \int dx_0 \int \mathcal{D}[x(\tau)]\delta(\bar{x}-x_0)e^{-\mathsf{A}_{x_0}}e^{-(\mathsf{A}-\mathsf{A}_{x_0})} \\ &= \int dx_0 Z_{x_0}^{(0)}\langle e^{-(\mathsf{A}-\mathsf{A}_{x_0})}\rangle_{x_0}, \end{aligned} \tag{1.6}$$

where

$$\langle F(x(\tau))\rangle_{x_0} \equiv \frac{1}{Z_{x_0}^{(0)}}\int \mathcal{D}[x(\tau)]\delta(\bar{x}-x_0)e^{-\mathsf{A}_{x_0}}F(x(\tau)) \tag{1.7}$$

is a restricted average relative to the reference problem and $Z_{x_0}^{(0)}$ is defined by Eq. (1.4) with A replaced by A_{x_0}. Using the Gibbs-Bogoliubov-Jensen-Peierls inequality

$$\langle e^{-(\mathsf{A}-\mathsf{A}_{x_0})}\rangle_{x_0} \geq e^{-\langle \mathsf{A}-\mathsf{A}_{x_0}\rangle_{x_0}}, \tag{1.8}$$

the final approximation for the effective potential is obtained from the bound

$$\beta W_{eff}(x_0) \leq \int_0^\beta d\tau \left\langle V(x(\tau)) - \frac{\omega^2(x_0)}{2}[x(\tau)-x_0]^2\right\rangle_{x_0} - \ln Z_{x_0}^{(0)} - \frac{1}{2}\ln(2\pi\beta). \tag{1.9}$$

This bound is then minimized with respect to $\omega^2(x_0)$ to give

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*Author to whom correspondence should be addressed. Email address: David.Ronis@McGill.ca a better estimate of $W_{eff}(x_0)$. Note that Eqs. (1.6) and (1.8) are essentially the starting point of Zwanzig's classical statistical mechanical perturbation theory [8] and that variational perturbation theories have been developed by Mansoori and Canfield [9] for simple liquids and by Ronis and co-workers [10,11] for colloidal suspensions. As was shown in Refs. [1,2,6], this procedure gives remarkably good results for potentials where the restricted average of the potential makes sense. In particular, this averaging is problematic for singular potentials. Kleinert [6] later introduced a series of systematic improvements of the method that include higher-order corrections. In this short paper, we will suggest a simple way of improving this first-order procedure by modifying the reference potential.

The choice of $\bar{x}$ described above, without being completely arbitrary [it makes sense physically and conveniently makes $\langle V(x(\tau))\rangle$ independent of time], can certainly be relaxed. In fact, when the Feynman-Kleinert formalism is used to obtain density matrices, one cannot use this choice and $\bar{x}$ simply becomes another parameter that is varied to minimize $W(x_a,x_b)$, a two-point function that is defined by

$$\begin{aligned}
Z &= \int dx_a dx_b \delta(x_a - x_b) \\
&\quad\times \int \mathcal{D}[x(\tau)]\delta(x_a - x(0))\,\delta(x_b - x(\beta))e^{-\mathsf{A}} \\
&= \int dx_a dx_b \delta(x_a - x_b) Z\rho(x_a,x_b) \\
&= \int \frac{dx_a dx_b}{\sqrt{2\pi\beta}}\delta(x_a - x_b)e^{-\beta W(x_a,x_b)}, \qquad (1.10)
\end{aligned}$$

where $\rho(x_a,x_b)$ is the density matrix [13]. As above, the two-point function is bounded as

$$\begin{aligned}
\beta W(x_a,x_b) \le& \int_0^\beta d\tau \langle \Delta V(x(\tau))\rangle_{x_a,x_b} - \ln[Z^{(0)}\rho_0(x_a,x_b)] \\
&- \frac{1}{2}\ln(2\pi\beta), \qquad (1.11)
\end{aligned}$$

where $\rho_0(x_a,x_b)$ and $Z^{(0)}$ are, respectively, the density matrix and the unrestricted partition function of the reference problem and $\langle \Delta V(x(\tau))\rangle_{x_a,x_b}$ is a conditional average in a reference system where all trajectories start at x_a and end at x_b.

The key modification introduced here is the use of the following reference Euclidean action:

$$\mathsf{A}_0(x_a,x_b) = \int_0^\beta d\tau\left(\frac{\dot{x}(\tau)^2}{2} + \frac{\omega^2(x_a,x_b)}{2}[x(\tau) - \bar{x}(\tau)]^2\right), \qquad (1.12)$$

where $\bar{x}$ now depends on time. In other words, for each (x_a,x_b) pair, we will minimize $\beta W(x_a,x_b)$ with respect to $\omega^2(x_a,x_b)$ and $\bar{x}(\tau)$ for all time in the interval $[0,\beta]$ which means that the center of the reference potential will "move" and, hopefully, better describe the true paths. This is the unique difference between this work and what is done by Kleinert in Ref. [6] (there, $\bar{x}$ is a parameter that is varied, but it is independent of time) and, as we show below, gives rise to an interesting equation for the classical path.

Of course, our method is guaranteed to improve the Feynman-Kleinert original first-order method. However, since the earlier work already gave very good estimates for $\beta W_{eff}(x)$ and for the free energy, we will not be able to do much better there. On the other hand, we expect $\rho(x_a,x_b)$ to be estimated more accurately using our reference potential, especially for cases where the off-diagonal correlations are important.

For our reference potential, the path that minimizes the action (the classical path) satisfies

$$\ddot{x}_{cl}(\tau) = \omega^2(x_a,x_b)[x_{cl}(\tau) - \bar{x}(\tau)] \qquad (1.13)$$

and the reference density matrix is (for example, see Ref. [12])

$$Z^{(0)}\rho_0(x_a,x_b) = \sqrt{\frac{\omega(x_a,x_b)}{2\pi\sinh[\beta\omega(x_a,x_b)]}}e^{-\mathsf{A}_{cl}^{(0)}}, \qquad (1.14)$$

where

$$\mathsf{A}_{cl}^{(0)} = \int_0^\beta d\tau\frac{1}{2}\{\dot{x}_{cl}(\tau)^2 + \omega^2(x_a,x_b)[x_{cl}(\tau) - \bar{x}(\tau)]^2\}. \qquad (1.15)$$

In order to make comparison with Feynman and Kleinert, we will work with the following double-well potential:

$$V(x) = -\frac{x^2}{2} + \frac{gx^4}{4} + \frac{1}{4g}, \qquad (1.16)$$

where $g > 0$. By Taylor expanding $V(x(\tau))$ around the classical trajectory $x(\tau) = x_{cl}(\tau) + \delta x(\tau)$, and noting that only even powers of $\langle[\delta x(\tau)^n]\rangle_{x_a,x_b}$ are nonzero, Eq. (1.11) can be rewritten as

$$\begin{aligned}
\beta W(x_a,x_b) \le& \int_0^\beta d\tau\Bigg(\frac{\dot{x}_{cl}(\tau)^2}{2} - \frac{x_{cl}^2}{2} + \frac{gx_{cl}^4}{4} \\
&+ \frac{3gx_{cl}^2(\tau) - 1 - \omega^2(x_a,x_b)}{2}a(\tau) + \frac{3g}{4}a(\tau)^2\Bigg) \\
&+ \frac{\beta}{4g} - \frac{1}{2}\ln\left(\frac{\beta\omega(x_a,x_b)}{\sinh\beta\omega(x_a,x_b)}\right), \qquad (1.17)
\end{aligned}$$

where it can easily be shown that

$$a(\tau) = \langle[\delta x(\tau)]^2\rangle_{x_a,x_b} = \frac{\sinh[\omega(x_a,x_b)\tau]\sinh[\omega(x_a,x_b)(\beta - \tau)]}{\omega(x_a,x_b)\sinh[\omega(x_a,x_b)\beta]} \qquad (1.18)$$

accounts for fluctuations around the classical path.

Since $\bar{x}(\tau)$ appears only implicitly through $x_{cl}(\tau)$ in Eq. (1.17), minimizing the bound to $\beta W(x_a,x_b)$ with respect to $\bar{x}(\tau)$ is accomplished by taking a functional derivative of Eq. (1.17) and setting the result to zero, i.e.,

$$\frac{\delta(\beta W(x_a,x_b))}{\delta(\bar{x}(s))} = \int_0^\beta d\tau\Big[-\ddot{x}_{cl}(\tau) - x_{cl} + g x_{cl}^3 + 3ga(\tau)x_{cl}(\tau)\Big]\frac{\delta(x_{cl}(\tau))}{\delta(\bar{x}(s))} = 0. \tag{1.19}$$

The factor $\delta(x_{cl}(\tau))/\delta(\bar{x}(s))$ of the last equation is proportional to the Green's function that solves the classical equation of motion for $x_{cl}(\tau)$, Eq. (1.13). Hence, acting on Eq. (1.19) with $d^2/ds^2 - \omega^2(x_a,x_b)$ shows that

$$\ddot{x}_{cl}(\tau) = -[1 - 3ga(\tau)]x_{cl}(\tau) + g x_{cl}^3(\tau), \tag{1.20}$$

with $x_{cl}(0)=x_a$ and $x_{cl}(\beta)=x_b$, minimizes $\beta W(x_a,x_b)$. Equations (1.20) and (1.13) trivially determine $\bar{x}(\tau)$; namely,

$$\bar{x}(\tau) = \frac{[\omega^2(x_a,x_b) + 1 - 3ga(\tau)]x_{cl}(\tau) - g x_{cl}^3(\tau)}{\omega^2(x_a,x_b)}. \tag{1.21}$$

Equation (1.20) describes the motion of a particle in an unstable potential where the harmonic force constants are time dependent. In fact, the time-dependent term in Eq. (1.20), $3ga(\tau)$, is nothing more than the one-loop correction to the equation of motion, albeit with a variationally determined $\omega^2(x_a,x_b)$.

In order to implement the theory numerically we proceed as follows. For every pair (x_a,x_b), the differential equation Eq. (1.20) is solved numerically as a boundary value problem for a predetermined grid of ω's, and the resulting $x_{cl}(\tau)$ are used in Eq. (1.17) to find the frequency that gives the smallest $\beta W(x_a,x_b)$. This frequency is further refined with a one-dimensional minimization routine, thereby giving the best approximation to $\beta W(x_a,x_b)$, which is then used to calculate $\rho(x_a,x_b)$.

If $a(\tau)$ is set to zero in Eq. (1.20), it is well known that the boundary value problem can have multiple solutions if x_a and x_b both lie between the two minima at $x=\pm\sqrt{1/g}$. This can also happen for nonzero $a(\tau)$ when g is small and β is large. In such cases, we use the solution that gives the smallest $\beta W(x_a,x_b)$.

II. RESULTS AND DISCUSSION

We now compare our results against those of Kleinert [6] where $\bar{x}$ is not a function of time, hereafter referred to as the "original" calculation. In Fig. 1, we compare the free energy $A=-\ln(Z)/\beta$ when $g=0.4$ for both approximate cases against the exact answer that we obtained by solving Schrödinger's equation using 170 harmonic oscillator basis functions for an oscillator having unit frequency and centered at $x=0$. At the level of the free energy, the improvement that our method gives is small.

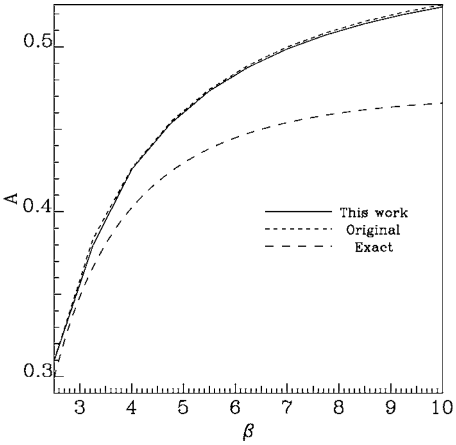

FIG. 1. The free energy $A=-\ln(Z)/\beta$ in the two approximate cases is compared with the exact answer.

Next we compare the effective potential obtained in both approaches for $g=0.4$ and $\beta=10$. Note that $\beta=10$ is well into the quantum regime. In addition, in the classical limit, i.e., when β is small, both methods approach the exact answer. In Fig. 2, we compare $\beta[W_{eff}(x)-A]$, where A is the corresponding energy for each approach, and where $\beta W_{eff}(x_a) = \beta W(x_a,x_a)$ and where $\beta W_{eff}(x_a)$ is then used to calculate the quantum-mechanical distribution function $\rho(x_a,x_a)$. Also shown is the exact effective potential and the one obtained within the WKB semiclassical approximation.

Recall that, in the WKB approximation,

$$\beta W_{eff}(x_a) = -\int_0^\beta d\tau\left(\frac{\dot{y}_{cl}(\tau)^2}{2} - \frac{y_{cl}^2}{2} + \frac{g y_{cl}^4}{4}\right) + \frac{\beta}{4g} - \ln[\beta/f(\beta)], \tag{2.1}$$

where $y_{cl}(\tau)$ is the solution of the Euler-Lagrange equation with the full potential (the boundary condition is that the trajectory starts and ends at x_a) and $f(\tau)$ is the solution of the Jacobi equation

$$\ddot{f}(\tau) = [-1 + 3g y_{cl}(\tau)^2]f(\tau), \tag{2.2}$$

with $f(0)=0$ and $\dot{f}(0)=1$.

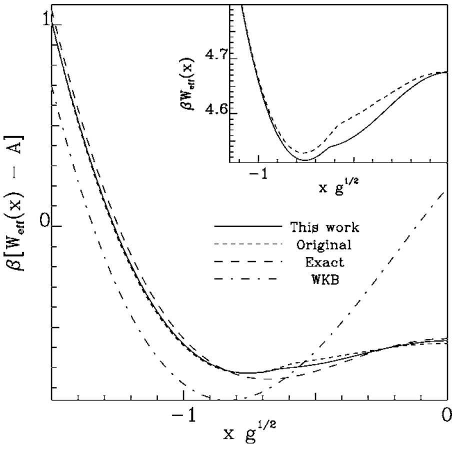

FIG. 2. $\beta[W_{eff}(x)-A]$ for $g=0.4$ and $\beta=10$. Only $x<0$ is shown because $\beta W_{eff}(x)=\beta W_{eff}(-x)$. In the inset, $\beta W_{eff}(x)$ is shown for the region where our method differs most compared to the original case.

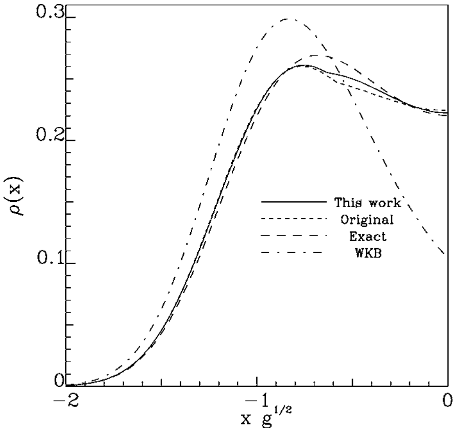

FIG. 3. The quantum-mechanical distribution function $\rho(x)$ for $g=0.4$ and $\beta=10$.

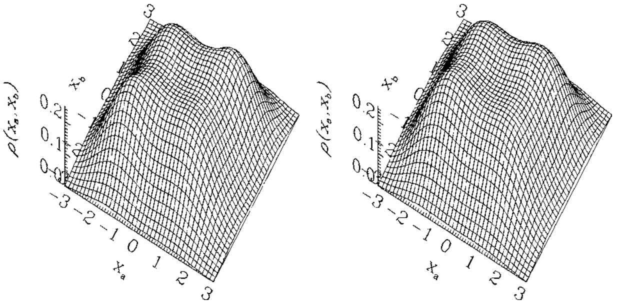

FIG. 4. The density matrix $\rho(x_a,x_b)$ for $g=0.4$ and $\beta=10$. The figure on the left is our calculation while that on the right is the exact answer.

The distribution functions obtained with the various methods are shown in Fig. 3 where we also compare with the "exact" results. As Figs. 2 and 3 show, our choice of reference potential improves the already good results originally obtained, especially for x_a lying between the two minima of $V(x)$. Also note that the error in $\beta W_{eff}(x_a)$, is largely due to the error in the free energy (cf. Fig. 1). Moreover, at this temperature, the WKB approximation is very inaccurate, and, in particular, fails to describe the suppression of the central potential barrier.

The more interesting aspect of this work is to see what type of improvement we get for the full density matrix. After all, it is when the initial and final points of the path are far from each other (when the path is stretched) that we expect our more general potential to pay off, although the distance between the two points should not be too large, since, for large separation, the density matrix vanishes.

In Fig. 4, we compare our method against the exact answer (again, $g=0.4$ and $\beta=10$). On that scale, the difference between the two calculations is small (the original approximation is also very similar). On the other hand, there really are some differences as can be seen from Fig. 3, which focuses on the diagonal of $\rho(x_a,x_b)$. In Fig. 5, we plot the difference $|\rho-\rho_{exact}|$, where ρ is calculated using our formalism or the original one. This figure focuses on the region around the off-diagonal peak and clearly shows that our potential more accurately describes the off-diagonal peaks of the density matrix, since the error is systematically lower. In particular, the small error region near $(0,0)$ is much larger in our case. Also, at the point $(-0.9,0.9)$ (a point close to the top of the off-diagonal peaks), the exact density matrix is 0.243, our calculation gives 0.244, and the original method gives 0.233.

In Fig. 6 we show $\bar{x}(\tau)$ and $x_{cl}(\tau)$ obtained from Eqs. (1.20) and (1.21) at the off-diagonal point ($x_a=0.9$, $x_b=-0.9$). As expected, since the end points are symmetrically placed around zero, $\bar{x}=0$ in the original approach, whereas here, the initial and final $\bar{x}(\tau)$ deviate strongly from zero. As seen in the figure, this difference in $\bar{x}(\tau)$ allows us to better describe the average paths (obtained from Monte Carlo simulations using the full potential and a discretized path containing 1000 points). In the same figure, we also show the $x_{cl}(\tau)$ that minimizes the Euclidean action with the full potential used in the WKB approximation. As seen in Fig. 6, there are two energetically equivalent solutions $y_{cl}(\tau)$ (they should be included in the theory with equal weight), both of them being quite far from the actual exact average path. The average of these two equivalent trajectories is also shown in Fig. 6 and turns out to be farther from the exact result than the other two approximate methods. Figure 6 also shows that the reference potentials used in this work or in the original calculation replace the two equivalent solutions by one that follows the exact average more closely than the mean of the two WKB paths.

In the original and our calculation, the fluctuations around the classical path are included to first order and appear in $a(\tau)$ defined by Eq. (1.18). These fluctuations will differ in our formalism and in the Feynman-Kleinert one only through the numerical value of ω, which is independently chosen in

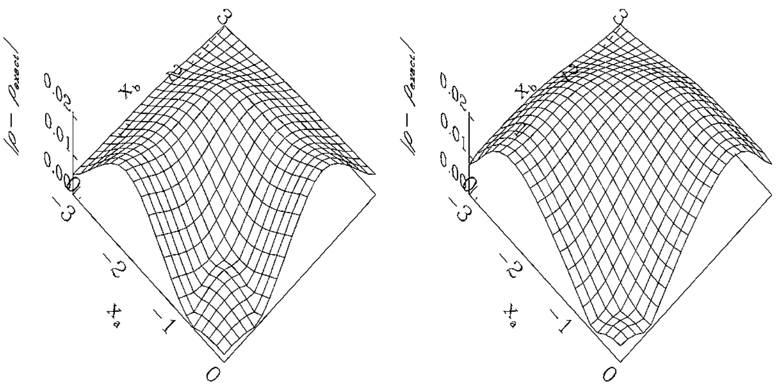

FIG. 5. The difference $|\rho-\rho_{exact}|$ for $g=0.4$ and $\beta=10$. The left figure is our calculation while the right figure is the time-independent reference potential of Kleinert.

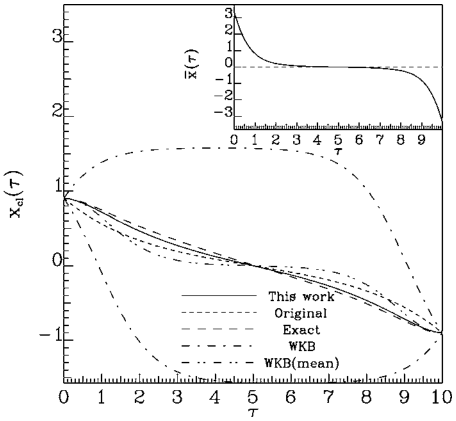

FIG. 6. The classical paths $x_{cl}(\tau)$ defined by our reference potential and the original reference potential are compared with the exact average path linking the points $(0.9,-0.9)$. Here, WKB(mean) is the average of the two energetically equivalent WKB paths (see text). In the inset, $\bar{x}(\tau)$ is compared for both reference potentials.

the two cases to minimize $\beta W(x_a,x_b)$. For example, we have $\omega=0.495\,039$ while, when $\bar{x}$ is independent of time, $\omega=0.460\,409$ (again, with $g=0.4$, $x_a=0.9$, $x_b=-0.9$, and $\beta=10$). This means that the fluctuations around the classical path will be larger in the original method. These fluctuations are compared in Fig. 7 against the exact result where it is seen that both approximate methods underestimate the fluctuations. Remember that the Gibbs-Bogoliubov-Jensen-Peierls inequality (1.8) only guarantees that the two-point function $\beta W(x_a,x_b)$ is bounded below by the exact results and that, consequently, our $\beta W(x_a,x_b)$ is guaranteed to be smaller than the one in the original calculation; nothing else need be improved. For example, as shown in Fig. 2, even though the two quantities $\beta W_{eff}(x)$ and βA are separately bounded by the inequality, their combination $\beta[W_{eff}(x)-A]$ is not.

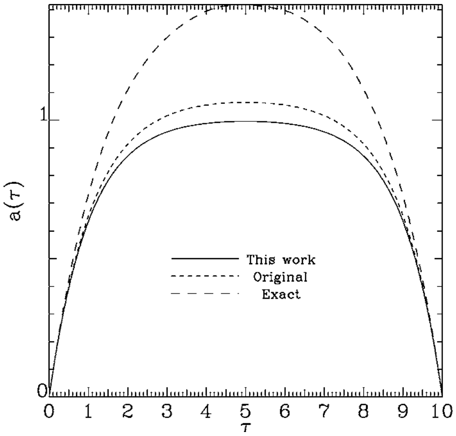

FIG. 7. The fluctuations around the classical paths linking $x_a=0.9$ and $x_b=-0.9$ for $g=0.4$ and $\beta=10$.

In conclusion, the modification to the Feynman-Kleinert method presented in this work improves the results by a small, but non-negligible amount. The improvement that we get becomes more significant when trying to capture information about the microscopic details of the problem. In fact, we get very little improvement in the free energy, but a better description of the density matrix. In general, our method will be particularly useful for potentials containing energy barriers for temperatures where the off-diagonal correlations in the density matrix are large. We also think that the equation of motion defining $\bar{x}$, Eq. (1.20), is, by itself, quite interesting.

ACKNOWLEDGMENT

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[13] Only one $\sqrt{2\pi\beta}$ factor was included in this definition. This was done such that $\beta W(x_a,x_b)$ reduces to $\beta W_{eff}(x_a)$ when $x_b=x_a$.