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Fourier Path-Integral Monte Carlo Methods: Partial Averaging

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Monte Carlo Fourier path-integral techniques are explored. It is shown that fluctuation-renormalization techniques provide an effective means for treating the effects of high-order Fourier contributions. The resulting formalism is rapidly convergent, is computationally convenient, and has potentially useful variational aspects.

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Classical Monte Carlo methods[1,2] have played an important role in the development of the theory of condensed-phase systems. Recently, a number of approaches have been suggested[3–15] for extension of these methods to problems in which quantum mechanical features are significant. A typical vehicle for this extension is the use of Monte Carlo techniques to estimate relevant path-integral expressions for the desired thermodynamic or dynamical[8,16–18] quantities. Path-integral approaches suggested to date generally involve either iterated "short-time" approximations or the use of Fourier expansions of the paths involved.

The present Letter considers a Fourier path-integral Monte Carlo method[4,14,15,17] which appears to offer a number of advantageous features. The method is rapidly convergent, is computationally straightforward to implement, and has potentially useful variational features. In its simplest form the present method is related to the Feynman-Hibbs[19,20] effective-potential method. The present approach, however, can be improved systematically to any desired extent. In what follows we will use a one-dimensional notation for simplicity, since the generalization to many degrees of freedom is straightforward.

We begin by considering the path-integral expression[19,20] for the quantum Boltzmann density matrix $\rho(x',x)$. We have

$$\rho(x',x)=\langle x'|e^{-\beta H}|x\rangle \tag{1}$$

$$=\int Dx(u)\,e^{-S(x(u))/\hbar}, \tag{2}$$

where

$$S(x(u))=\int_0^{\beta\hbar}[m\dot{x}^2+V(x(u))]\,du. \tag{3}$$

The paths in Eq. (2) begin at $x(u=0)=x$ and end at $x(u=\beta\hbar)=x'$. An effective procedure to enumerate the paths in Eq. (2) is to expand each about a "reference" path in a Fourier series.[19,20] For simplicity, we assume here that we expand about a "direct" path and write

$$x(u)=x+\frac{(x'-x)u}{\beta\hbar}+\sum_{k=1}^{\infty}a_k\sin\left(\frac{k\pi u}{\beta\hbar}\right). \tag{4}$$

With this description of the paths, it is a simple matter to rewrite the ratio of the path integral for $\rho(x',x)$ to its free-particle value, $\rho_{\mathrm{FP}}(x',x)$, in terms of integrals over the Fourier coefficients:

$$\frac{\rho(x',x)}{\rho_{\mathrm{FF}}(x',x)}=\frac{\int(\Pi\, da_n)\exp(-\Sigma a_k^2/2\sigma_k^2)\exp[-\int_0^{\beta\hbar}du\; V(x(u))/\hbar]}{\int(\Pi\, da_n)\exp(-\Sigma a_k^2/2\sigma_k^2)}, \tag{5}$$

where

$$\sigma_k^2=2\beta\hbar^2/(m\pi^2k^2). \tag{6}$$

For general applications, Eq. (5) (or related integral expressions for various thermodynamic properties) is evaluated by numerical Monte Carlo methods in which only a finite number of Fourier coefficients in the description of the paths are retained. For arbitrary potentials, the one-dimensional $(0,\beta\hbar)$ "time" integral must be evaluated numerically.

On the basis of specific examples,[14,15,17,21] the convergence of this "direct" Fourier method is good. We note here, however, that with little additional effort it is possible to estimate the effects of the higher-order Fourier coefficients ignored in this direct method. From Eq. (6) we note that the length scale associated with the higher-order Fourier coefficients decreases with increasing k. Hence, beyond a sufficiently large value of that Fourier index, it is reasonable to view these coefficients as describing detailed, short-ranged "fluctuations" about the path described by the lower-order ones. If these higher-order fluctuations are in fact short ranged, then it is plausable to imagine that they are essentially free-particle-like. This suggests replacing the effect of all of the high-order Fourier coefficients ($k > k_{\max}$) by a single Gaussian random process whose statistical properties are determined from free-particle results. Mathematically, this is equlavent to replacing the average of the exponential in Eq. (5) over a_k values for $k > k_{\max}$ by the exponential of the average.[19,20] This "partial averaging" gives (after reducing the multidimensional Gaussian integral involved to a single Gaussian variable)

$$\frac{\rho(x',x)}{\rho_{\mathrm{FP}}(x',x)}=\frac{\int d^{k_{\max}}a\,\exp(-\Sigma\, a_k^2/2\sigma_k^2)\exp[-\int_0^{\beta\hbar}du V_{\mathrm{eff}}(x',x,\mathbf{a},u)/\hbar]}{\int d^{k_{\max}}a\,\exp(-\Sigma a_k^2/2\sigma_k^2)}, \tag{7}$$

where only a_1 through $a_{k_{\max}}$ are explicitly included in Eq. (7), and where

$$V_{\mathrm{eff}}(x',x,\mathbf{a},u)=\int_{-\infty}^{\infty}dp\,\exp[-p^2/2\sigma^2(u)]\,V(x(u)+p)/[2\pi\sigma^2(u)]^{1/2}, \tag{8}$$

with $x(u)$ specified by

$$x(u)=x+\frac{(x'-x)u}{\beta\hbar}+\sum_{k=1}^{k_{\max}}a_k\sin\left(\frac{k\pi u}{\beta\hbar}\right), \tag{9}$$

and with $\sigma^2(u)$ given in terms of the statistical properties of the previously ignored Fourier coefficients by

$$\sigma^2(u)=\sum_{k=k_{\max}+1}^{\infty}\sigma_k^2\sin^2\left(\frac{k\pi u}{\beta\hbar}\right)=\left(\frac{\beta\hbar^2}{m}\right)\left(\frac{u}{\beta\hbar}\right)\left(1-\frac{u}{\beta\hbar}\right)-\left(\frac{2}{\pi^2}\right)\sum_{k=1}^{k_{\max}}\sigma_k^2\sin^2\left(\frac{k\pi u}{\beta\hbar}\right). \tag{10}$$

We note in passing that the concavity of the exponential function can be used to verify that the $\rho(x',x)$ produced by Eqs. (7)–(10) for a finite number of explicit Fourier coefficients is everywhere a lower bound to the exact results.[19,20]

The simplest implementation of the above results would correspond to the retaining of no explicit Fourier coefficients whatsoever [i.e., dropping of the k-dependent terms in Eqs. (7)–(10)]. At that level of approximation, the present results resemble the Feynman-Hibbs Gaussian-transform effective-potential formalism,[19,20] except that the transform width is "time dependent." Here, however, the results can be improved systematically by explicit inclusion of more Fourier coefficients. As more coefficients are included, the magnitude of the Gaussian noise decreases [cf. Eq. (10)]. This in turn means that the transform variable in Eq. (8) has a "small" range, implying that gradient expansions of Eq. (8) about $x(u)$ [as opposed to gradient expansions about x or x' in Eq. (2)] are likely to be useful in the present context. By using such gradient expansions or by fitting the actual potential to simple functional forms for which Gaussian transforms are analytically available, we can readily adapt the above procedure to situations in which the actual potential cannot be analytically transformed.

Below we present a numerical example which demonstrates the rapidity of convergence of the present method. Before we do so it is worth noting that the partial averaging procedure described above can also be implemented with a harmonic-oscillator reference system. The results are entirely analogous to those stated in Eqs. (7)–(10), except that the various free-particle quantities are replaced by the appropriate oscillator results. The oscillator reference version may prove valuable in the study of systems characterized by nearly harmonic vibrations (e.g., crystals). It also serves as a starting point for variational procedures in which the characteristics of the harmonic reference are adjusted to give optimal results for a fixed number of Fourier coefficients. For example, at the crudest level (i.e., choice of $k_{\max}=0$ and use of the concavity inequality to simplify further the coordinate-space integration), the standard Gibbs-Boguliobov lower bound on the partition function is recovered. The present approach gives a clear prescription for systematically improving upon this bounding formula.

While the possibilities of variational optimization are esthetically attractive, we have found that direct (nonvariational) implementation of Eqs. (7)–(10) is generally satisfactory. To demonstrate this we have computed the configuration-space density, $\rho(x,x)$ [or, for notational simplicity, $\rho(x)$], for the one-dimensional double-well potential displayed in Fig. 1. This model potential consists of a simple oscillator potential plus a Gaussian "mound" at the origin. Specifically,

$$V(x)=A\exp[-\alpha\nu_{\text{ho}}(x)]+\nu_{\text{ho}}(x), \tag{11}$$

where

$$\nu_{\text{ho}}(x)=m\omega^2x^2/3. \tag{12}$$

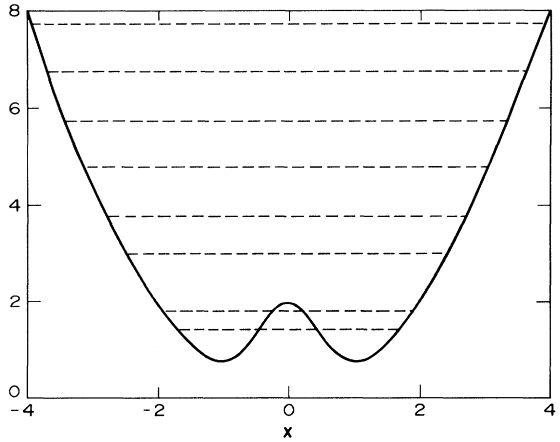

FIG. 1. The model double-well potential [Eq. (11)]. The dashed lines are the (numerically determined) exact energy levels for the parameters used in the present study.

The parameters used in the present study were $m=\omega=\hbar=1$, $\alpha=4$, and $A=2$. Exact eigenfunctions and eigenvalues were computed by matrix diagonalization using the harmonic-oscillator basis functions corresponding to $\nu_{\text{ho}}(x)$. From these results the exact density, $\rho(x)$, was constructed for the inverse temperature $\beta=5$. At this temperature approximately 87% and 13% of the population are in the ground and first excited states, respectively. The exact density is displayed as the solid line in each of the four panels of Fig. 2. Also displayed in Fig. 2 are the results of various Monte Carlo path-integral calculations. Metropolis sampling[1] was used to do the appropriate multidimensional integrations. Each filled circle in Fig. 2 is the average of four independent Monte Carlo runs of 2000 passes (one attempted move for each integration variable) each. The error bars correspond to one rms deviation. Figures 2(a) and 2(c) display the results of "direct" Fourier path-integral $\rho(x)$ calculations which include three and five Fourier coefficients explicitly. The corresponding partial averaging results are shown in Figs. 2(b) and 2(d). In both cases the improvement produced by inclusion of the higher-order Fourier coefficients is significant. Figure 2(b) illustrates the bounding propety of the partial averaging method.

The accuracy of this method of calculation is sufficient that the splitting between the ground and first excited energy levels can be extracted in a manner

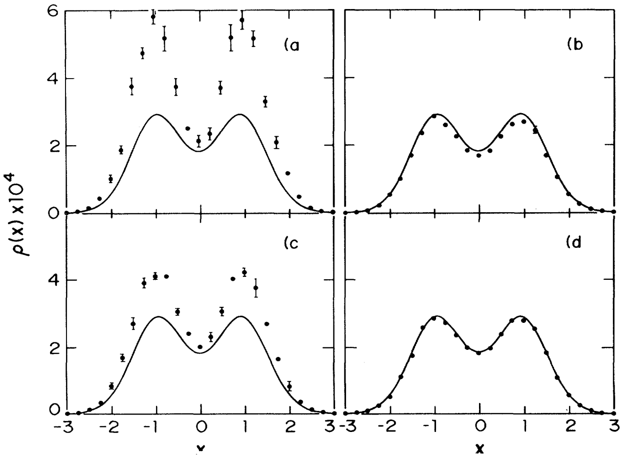

FIG. 2. Plots of $\rho(x)$ for the double-well potential of Fig. 1. In each case the solid line is the exact result obtained by summing over the numerically determined eigenfunctions while the points and error bars are the Fourier Monte Carlo results. The temperature corresponds to approximately 87% and 13% of the population in the ground and first excited states, respectively. Panels (a) and (c) represent the direct Fourier result ($k_{\max}=3$ and 5, respectively), while panels (b) and (d) represent the Fourier results with partial averaging ($k_{\max}=3$ and 5, respectively). [Note the lower bound to $\rho(x)$ in (b).]

which is both straightforward and implementable in many spatial dimensions. Specifically, let us set,

$$Z_\beta^{(\pm)} = \int dx\, \rho(x, \pm x). \tag{13}$$

Then, as a result of the inversion symmetry of the potential under study,

$$E_1 - E_0 = \lim_{\beta \to \infty} \log[(Z_\beta^{(+)} + Z_\beta^{(-)})/(Z_\beta^{(+)} - Z_\beta^{(-)})/\beta]. \tag{14}$$

With the free-particle reference propagator with $k_{\max} = 3$ and the partial averaging prescription plus a Gaussian reference density for the x integration, $Z_\beta^{(\pm)}$ were evaluated by Metropolis sampling. With approximately 5000 passes the exact splitting $E_1 - E_0 = 0.39$ was obtained to two-significant-figure accuracy. It is hoped that enhancement and/or quenching mechanisms which arise when a tunneling coordinate is coupled to a bath of (say, oscillator) coordinates can be studied by multidimensional generalizations of this technique.

In addition to the Gaussian-mound potential discussed here, we have found a similar dramatic increase in the rapidity of convergence of the partial averaging method relative to either the direct Fourier or discretized methods for a variety of model potentials. Preliminary studies also indicate that the present approach is of use for complex as well as real temperatures, suggesting possible utility in the calculation of finite-temperature time-correlation functions.

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