Fourier Path Integral Monte Carlo Method for the Calculation of the Microcanonical Density of States

David L. Freeman

Department of Chemistry, University of Rhode Island, Kingston, RI 02881

J.D. Doll

Department of Chemistry, Brown University, Providence, RI 02912

Abstract

Using a Hubbard-Stratonovich transformation coupled with Fourier path integral methods, expressions are derived for the numerical evaluation of the microcanonical density of states for quantum particles obeying Boltzmann statistics. A numerical algorithm is suggested to evaluate the quantum density of states and illustrated on a one-dimensional model system.
Over the past decade there has been considerable progress in the development of path integral approaches to computational quantum statistical mechanics. With few exceptions, the application of path integral methods have been restricted to simulations in the canonical ensemble. Canonical simulations are amenable to path integral treatments because the canonical density matrix is formally identical to the quantum propagator in imaginary time. The purpose of this note is to show that path integral methods can provide an algorithmic basis for microcanonical simulations as well.

We let $\Omega(E) dE$ represent the number of energy states between $E$ and $E + dE$. Throughout this paper we will suppress the dependence of the density of states on the number of particles in the system $N$ and the system volume $V$ for notational convenience. For $N$ indistinguishable particles obeying Boltzmann statistics, we begin with the Fourier path integral expression for the canonical partition function:

$$Q(\beta) = \frac{1}{N!} \left( \frac{m}{2\pi \beta \hbar^2} \right)^{3N/2} \left( \prod_{k=1}^{\infty} \prod_{j=1}^{3N} \frac{1}{\sqrt{2\pi \sigma^2_{k,j}}} \right) \int d\mathbf{r} d\mathbf{a} \exp\left[ - \sum_{k,j} a^2_{k,j}/2\sigma^2_{k,j} - \beta \langle \Phi \rangle_{a} \right].$$

(1)

In Eq. (1) we have suppressed the dependence of the partition function on $N$ and $V$, $\beta = 1/k_B T$ with $T$ the temperature and $k_B$ the Boltzmann constant, $\mathbf{r}$ is a collective $3N$-dimensional vector representing the coordinates of all the particles in the system,

$$\sigma^2_{j,k} = \frac{2\beta \hbar^2}{m(k\pi)^2},$$

(2)

$m$ is the mass of the constituent particles, $a_{k,j}$ is Fourier coefficient $k$ for particle $j$, and for the potential energy $\Phi(\mathbf{r})$ we define

$$\langle \Phi \rangle_{a} = \int_{0}^{1} du \Phi[\mathbf{r}(u)]$$

(3)

as the average of the potential energy over a particular path. As discussed elsewhere, each path is parameterized by a Fourier sine series. In practice a finite number, $k_{max}$, of Fourier coefficients are actually included in Eq.(1).

The connection between the canonical partition function and the microcanonical density of states is given by
\[ Q(\beta) = \int dE \Omega(E) e^{-\beta E} \]  

which is just a Laplace transform relation. Equation (4) can be inverted using the Mellin inversion integral

\[ \Omega(E) = \frac{1}{2\pi i} \int_C d\beta e^{\beta E} Q(\beta) \]  

where the subscript \( C \) on the integral in Eq. (5) implies integration along a contour to the right and parallel to the imaginary axis in the complex plane. The inversion in the present application is not simple, because of the inverse \( \beta \)-dependence in the exponent of Eq. (5). The \( \beta \)-dependence in Eq.(4) can be altered using a Hubbard-Stratonovich transformation [5].

Writing

\[ \exp(-\sum_{k,j} a_{k,j}^2/2\sigma_{k,j}^2 = \prod_{k,j} \left( \frac{\sigma_{k,j}^2}{\pi} \right)^{1/2} \int d\phi \exp(-\sum_{k,j} \sigma_{k,j}^2 \phi_{k,j} + i\sqrt{2} \sum_{k,j} a_{k,j} \phi_{k,j}) \]  

the expression for the partition function becomes

\[ Q(\beta) = \frac{1}{N!} \left( \frac{1}{\sqrt{2\pi}} \right)^{3Nk_{max}} \left( \frac{m}{2\pi \hbar^2} \right)^{3N/2} \frac{1}{\beta^{3N/2}} \times \int d\mathbf{a} d\mathbf{r} d\phi \cos(\sqrt{2} \sum_{k,j} a_{k,j} \phi_{k,j}) \Theta[E - \langle \Phi \rangle_a - \sum_{k,j} \sigma_{k,j}^2 \phi_{k,j}^2][E - \langle \Phi \rangle_a - \sum_{k,j} \sigma_{k,j}^2 \phi_{k,j}^2]^{3N/2-1}, \]

where

\[ \sigma_{k,j}^2 = \beta \bar{\sigma}_{k,j}^2. \]  

At the expense of the introduction of the auxiliary variables \( \phi \), the \( \beta \)-dependence of the exponent in the expression for the canonical partition function appears entirely in the numerator. Using Eq.(7) the canonical partition function can be introduced in the Mellin inversion integral, and the integration with respect to \( \beta \) can then be evaluated analytically [6]

\[ \Omega(E) = \frac{1}{\Gamma(3N/2)} \frac{1}{N!} \left( \frac{1}{\sqrt{2\pi}} \right)^{3Nk_{max}} \left( \frac{m}{2\pi \hbar^2} \right)^{3N/2} \times \int d\mathbf{a} d\mathbf{r} d\phi \cos(\sqrt{2} \sum_{k,j} a_{k,j} \phi_{k,j}) \Theta[E - \langle \Phi \rangle_a - \sum_{k,j} \sigma_{k,j}^2 \phi_{k,j}^2][E - \langle \Phi \rangle_a - \sum_{k,j} \sigma_{k,j}^2 \phi_{k,j}^2]^{3N/2-1}, \]  

where
where $\Gamma(x)$ is the gamma function and $\Theta(x)$ is the step function. Equation (9) is the principal result of this note. It is easy to verify that Eq.(9) reduces to the proper free particle and classical limits.

A possible approach to evaluate Eq.(9) numerically is based on the existence of methods to compute the classical density of states. We then correct the classical density of states by calculating the ratio of the quantum to classical density. If we specialize Eq.(9) to a one-dimensional system and examine the classical limit, it is easy to show that the ratio of the quantum to classical density of states can be written

$$\frac{\Omega(E)}{\Omega_{cl}(E)} = \left(1 + \sum_{k}\varphi_k^2\right)^{1/2}$$

where $\varphi_k$ are the Fourier coefficients of the wave function.

We present the quantum density of states for a Morse oscillator $\Phi(x) = D_e\{1 - \exp[-a(x - x_e)]\}^2$. The calculations in Figure 1 were evaluated from Eq.(10) and consisted of one hundred million Monte Carlo points with $k_{max} = 2$. The classical density of states was determined from the classical limit of Eq.(9) and was evaluated using Mathematica. For the potential parameters we have chosen $a = 1$, $x_e = 1$, $m = 1822.83$ au, and we have chosen $D_e$ so that the oscillator frequency $\omega = (2a^2D_e/m)^{1/2}$ equals .006 au. The delta functions in Eq.(10) were represented by gaussians with standard deviations of 0.5 au. The path average of the potential energy for the Morse oscillator was evaluated with trapezoid rule quadrature with 16 quadrature points. The peaks in the density of states seen in Figure 1 are in good agreement with the analytic eigenvalues at $E/\hbar\omega = .488, 1.40$ and 2.21. The finite widths of the peaks are a result of the gaussian representation of the delta functions and the finite number of Fourier coefficients used. These preliminary results are encouraging, and the investigation of several methods to evaluate Eq.(9) for more complex systems is in progress.

We would like to thank Professor Robert Topper for helpful discussions. Acknowledgement is made to the Donors of the Petroleum Research Fund of the American Chemical
Society for support of this work. Purchase of the computer equipment used in this work was made possible by NSF grant number CHE-9203498.
REFERENCES

[1] R.P. Feynman and A.R. Hibbs, *Quantum Mechanics and Path Integrals*, (McGraw-Hill, New York, 1965).

[2] B.J. Berne and D. Thirumalai, *Ann. Rev. Phys. Chem.* 37, 401 (1986).

[3] J.D. Doll, D.L. Freeman and T.L. Beck, *Adv. Chem. Phys.* 78, 61 (1990).

[4] D. Thirumalai, B.C. Garrett and B.J. Berne, *J. Chem. Phys.* 83, 2972 (1985).

[5] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group*, (Addison-Wesley, Reading MA, 1992).

[6] R. Kubo, *Statistical Mechanics*, (North-Holland, Amsterdam, 1965) Chapter 2.

[7] A.M. Ferrenberg and R.H. Swendsen, *Phys. Rev. Lett.* 61, 2635 (1988).

[8] P. Labastie and R.L. Whetten, *Phys. Rev. Lett.* 65, 1567 (1990).

[9] S. Wolfram, *Mathematica* (Addison-Wesley, Reading, MA, 1991).
FIGURE CAPTIONS

1. The quantum density of states in atomic units for a one-dimensional Morse oscillator with parameters defined in the text. The error bars are at the double standard deviation level. The maxima in the density of states are in good agreement with the analytic eigenvalues at $E/\hbar\omega = .488, 1.40$ and $2.21$. 
FIGURES

\[ \Omega(E) \] vs. \[ E/\hbar \omega \]