An optimized harmonic reference system for the evaluation of discretized path integrals

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A harmonic reference system for Monte Carlo evaluation of discretized path integrals is developed. Various equilibrium averages are calculated for a one-dimensional quartic oscillator, and compared to converged basis set results; it is shown that use of the reference system substantially decreases the number of discretized points (relative to the free particle reference system) necessary to compute accurate quantum mechanical expectation values.

I. INTRODUCTION

Recently there has been great interest in the use of discretized path integral (DPI) methods to compute equilibrium quantum ensemble averages.[1–4,16] A number of specific implementations have been proposed and applied to a wide variety of systems. The results which have been obtained for large, nontrivial systems[3] are encouraging, and suggest that optimal development of this approach may lead to a qualitative improvement in our ability to calculate, quantum mechanically, properties of anharmonic condensed phase systems.

The advantages of DPI methods have been discussed extensively in the literature.[1,2] The procedure is systematically improvable by adding more quadrature points, and is exact in the classical limit for the smallest number of points. Powerful numerical methods (Monte Carlo, molecular dynamics) can be used to evaluate the many-dimensional configuration integrals; all the techniques of classical simulations can be brought to bear on the quantum problem when cast in this form. As compared to basis set methods, the size of the problem grows much more slowly with increasing numbers of degrees of freedom.

The original formulation of the path integral for a many-boson system (to which we restrict consideration here) partitions the Hamiltonian into its kinetic (T) and potential energy (V) parts, and defines the zeroth order (reference) part of the Hamiltonian H_0 to be T. For application of DPI methods to complex molecular and condensed phase systems, this scheme can clearly be improved on quantitatively. In Ref. 2, the use of a reference system (other than that of the free particle) was suggested and implemented for a specific model, yielding quite good results. In this paper, we develop a generalized, temperature-dependent harmonic reference system which can be easily applied to anharmonic boson potentials. Such a method will lead to accurate results in the low temperature limit (where a harmonic Taylor series expansion about the potential minimum will be valid) as well as the high temperature, classical limit, for a small number of path integral points; it is reasonable to expect sensible results in the interpolated region as well. This approach is in the same spirit as one proposed by Doll,[4] but differs considerably in its details.

An immediate problem arises if the system under study contains more than one potential minimum. In this work we will assume that use of a single minimum will generate an efficient sampling algorithm (note that the formalism is still exact in the limit that the number of points increases; the presence of multiple minima simply renders the single harmonic reference system less useful). For condensed systems with many minima (e.g., liquids), it is probably best to treat the intramolecular degrees of freedom harmonically and the translational and rotational ones in standard fashion. This (and other) constructions of more complex reference systems are straightforward, but will not be pursued further here.

A useful harmonic reference system can be obtained using recently developed classical simulation techniques.[5–9] Essentially a classical molecular dynamics (or Monte Carlo) simulation is performed, and the ensemble averages $\langle x_i \rangle$, $\langle x_i x_j \rangle$ (at temperature T) for all sites i, j are computed. These quantitites uniquely define a set of "quasiharmonic" normal modes (eigenvectors), frequencies (eigenvalues), and equilibrium positions; the resulting effective harmonic Hamiltonian reproduces the first and second moment averages of the full anharmonic potential exactly. We can therefore expect that $V(\mathbf{x}) = V_{\text{anharmonic}}(\mathbf{x}) - V_{\text{quasiharmonic}}(\mathbf{x})$ will be small in the most important regions of $\mathbf{x}$ space at temperature T. It is also possible to improve on the classical quasiharmonic reference system and obtain an *optimized* quasiharmonic reference system. This requires some preliminary calculations, but can greatly reduce the number of quadratic points required for convergence at low temperatures. Optimization is particularly valuable if the reference system is to be used for other calculations (e.g., dynamics).

In this paper, a practical Monte Carlo scheme for calculating equilibrium ensemble averages using the above harmonic reference systems is presented. The harmonic path integral formalism is developed, and efficient numerical algorithms are discussed. As a simple example, we treat the one-dimensional quartic oscillator, comparing calculation of averages of various functions of the coordinate to converged basis set calculations. Comparison with primitive reference calculations display the substantial improvement obtained by using our formalism. Umbrella sampling techniques[10] are used to compute the partition function it-

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self, and to obtain an optimized reference system by minimizing the fluctuation of the renormalized potential energy. Calculations employing optimzied quasiharmonic frequencies yield the most rapid convergence (as a function of the number of quadrature points) for all quantities studied.

II. HARMONIC PATH INTEGRAL

We consider a many-body boson Hamiltonian:

$$H=\sum_{i=1}^{N} -\frac{h^2}{2m_i}\nabla_{x_i}^2+V(\mathbf{x}), \tag{1}$$

where N is the total number of particles in the system, and V is the exact potential. The coordinatex $\mathbf{x}$ in this representation are the $3N$ Cartesian coordinates of the N particles.

It is easiest to proceed on the assumption that the system under study has a well-defined potential minimum at each temperature, and that the center of mass (translational) and rotational degrees of freedom can be separated from H. This description will apply nonproblematically to small molecules and solids, and reasonably well to some large molecules (e.g., proteins[5-8]) in specific conformations. A detailed discussion of these considerations will appear in forthcoming publications.

We will henceforth work in the quasiharmonic normal mode basis set $\mathbf{z}=(\mathbf{z}_1\ldots\mathbf{z}_M)$, where $M=3N-6$. The generalized coordinates $\mathbf{z}$ are ordinarily linear combinations of *internal* coordinates (e.g., angular and radial displacements) $\mathbf{y}$, i.e.,

$$\mathbf{z}=\mathbf{Sy}\,. \tag{2}$$

The quasiharmonic minimum $\mathbf{z}_0$ can be taken to be at 0 without loss of generality. The Hamiltonian is then

$$H=H_0+V_{\mathrm{QH}}(\mathbf{z}), \tag{3}$$

where H_0 is most conveniently expressed in second quantized notation as

$$H_0=\sum_{i=1}^{M}\omega_i b_i^+ b_i\,, \tag{4}$$

where $b_i^+(b_i)$ creates (destroys) a vibrational excitation of the ith quasiharmonic mode. This mixed representation of the Hamiltonian is quite suitable for development of the harmonic path integral formulation.

The canonical partition function Q is, in the normal coordinate basis set

$$Q=\int d\mathbf{z}_1\langle\mathbf{z}_1|\exp(-\beta H)|\mathbf{z}_1\rangle\,. \tag{5}$$

We set

$$\exp(-\beta H)=[\exp(-\beta H/P)]^P, \tag{6}$$

and insert complete sets of (many-body) coordinate states $\mathbf{z}_i$ to obtain

$$\begin{aligned}Q=\int d\mathbf{z}_1\cdots d\mathbf{z}_P&\langle\mathbf{z}_1|\exp(-\beta H/P)|\mathbf{z}_2\rangle\\ &\times\langle\mathbf{z}_2\exp(-\beta H/P)|\mathbf{z}_3\rangle\cdots\langle\mathbf{z}_{P-1}|\exp(-\beta H/P)|\mathbf{z}_P\rangle\\ &\times\langle\mathbf{z}_P|\exp(-\beta H/P)|\mathbf{z}_1\rangle\,,\end{aligned} \tag{7}$$

a discretized path integral with P points.

It is now necessary to separate H into H_0 and V. The traditional approach chooses $H_0=\Sigma(h/2m_i)\nabla_i^2$, $V=V(\mathbf{x})$, i.e., H_0 is that of a free particle. We instead set $H_0=\Sigma\omega_i b_i^+ b_i$ [Eq. (4)] to obtain

$$\begin{aligned}\langle\mathbf{z}_j|&\exp(-\beta H/P)|\mathbf{z}_{j+1}\rangle\\ &\approx\langle\mathbf{z}_j|\exp(-\beta\Sigma\omega_i b_i^+ b_i)/P|\mathbf{z}_{j+1}\rangle\\ &\qquad\times\exp[-\beta V_{\mathrm{QH}}(\mathbf{z}_j)/2P]\exp[-\beta V_{\mathrm{QH}}(\mathbf{z}_{j+1})/2P]\,.\end{aligned} \tag{8}$$

This will be an improvement over the free particle H_0 if (roughly) the commutator of H_0 and V is substantially smaller; the trivial case, of course, is when the full $V(\mathbf{x})$ is harmonic, whereupon $V_{\mathrm{QH}}=0$.

The term $\langle\mathbf{z}_j|\exp[-(\beta/P)\Sigma\omega_i b_i^+ b_i]|\mathbf{z}_{j+1}\rangle$ is easily evaluated as a product of harmonic propagators, the form of which is known exactly. We will use units such that the coordinates $\mathbf{z}$ are mass weighted, and set $\hbar=1$. The harmonic propagator for a single mode of frequency ω is[11]

$$\begin{aligned}G_0(z,z',\beta/P)&\\ =\left\{\frac{m\omega}{2\pi h\sinh(\beta\hbar\omega/P)}\right\}^{1/2}&\exp\left(\frac{-m\omega}{2\sinh(\beta\hbar\omega/P)}\right.\\ &\left.\times\{[z^2+(z')^2]\cosh(\beta\hbar\omega/P)-2zz'\}\right),\end{aligned} \tag{9}$$

which, under the above scaling conventions, becomes

$$\begin{aligned}G_0(z,z',\gamma)=\left(\frac{\omega}{2\pi}\sinh\gamma\right)^{1/2}&\\ \times\exp&\left(\frac{\omega}{2}\sinh\gamma\{[z^2+(z')^2]\cosh\gamma-2zz'\}\right),\end{aligned} \tag{10}$$

where we have defined $\gamma=\beta\hbar\omega/P$. The discretized path integral is now compactly written as

$$Q=\int\prod_{i=1}^{P}\overline{G}_0(\mathbf{z}_i,\mathbf{z}_{i+1},\boldsymbol{\gamma})\exp\left[-\beta\sum_{i=1}^{P}V(\mathbf{z}_i)/P\right]d\mathbf{z}_1\cdots d\mathbf{z}_P\,. \tag{11}$$

Here $\boldsymbol{\gamma}=(\gamma_1\cdots\gamma_M)$ is the set of M reduced parameters for the M quasiharmonic degrees of freedom with $\gamma_j=\beta h\omega_j/P$; ω_j is the effective reference frequency for mode j; then

$$\overline{G}_0(\mathbf{z}_i,\mathbf{z}_{i+1},\boldsymbol{\gamma})=\prod_{j=1}^{M}G_0(z_i^{(j)},z_{i+1}^{(j)},\gamma_j) \tag{12}$$

[note that the superscripts on the z's in Eq. (12) refer to *modes*, while the subscripts denote *quadrature points*]. Also, $\mathbf{z}_{P+1}$ is defined to be $\mathbf{z}_1$.

Defining the integrand of Eq. (11) to be $K(\mathbf{z}_1\cdots\mathbf{z}_P)$, we have for the ensemble average of $A(\mathbf{z})$,

$$\overline{A}=\frac{\int d\mathbf{z}_1\cdots d\mathbf{z}_P A(\mathbf{z}_1)K(\mathbf{z}_1\cdots\mathbf{z}_P)}{\int d\mathbf{z}_1\cdots d\mathbf{z}_P K(\mathbf{z}_1\cdots\mathbf{z}_P)}\,. \tag{13}$$

We shall call the resulting expressions [Eqs. (10) and (11)] the quasiharmonic discretized path integral (QHDPI) formulation. The discretized path integral utilizing a free particle reference system will be referred to as the FPDPI.

III. MONTE CARLO ALGORITHM

A. Ensemble averages

Equation (13) is now in the usual form for application of the Metropolis Monte Carlo algorithm,[10] with $K(\mathbf{z}_1\cdots\mathbf{z}_P)$ as the weighting function. Moves are chosen in the normal coordinate basis set; within a particular mode, the optimal choice of independent random variables will depend upon γ_j. For $\gamma_j \ll 1$, $z_i^{(j)} - z_{i+1}^{(j)}$ will be constrained to be small, and the optimized set will be $z_1^{(j)}, z_2^{(j)} - z_1^{(j)}, z_3^{(j)} - z_2^{(j)}, \ldots, z_P^{(j)} - z_{P-1}^{(j)}$. For $\gamma_j \gg 1$, the set $z_1^{(j)} \cdots z_P^{(j)}$ itself if preferrable. A reasonable interpolation is to define the effective coordinates $q_i^{(j)}$,

$$q_1^{(j)} = z_1^{(j)} ,$$
$$q_i^{(j)} = z_i^{(j)} - \exp(-\gamma_j) z_{i-1}^{(j)} \quad \text{for } i \neq 1 . \tag{14}$$

This formulation is used in the numerical results that follow. Each $q_i^{(j)}$ is updated in turn, and Eq. (14) is solved for the set of coordinates $\{z^{(j)}\}$.

For the one-dimensional application in this paper, no conversion between normal and other sets of coordinates is necessary. For larger systems, one must choose a coordinate system in which to evaluate V_{QH}, and obtain the relevant set of coordinate from the quasiharmonic normal set. This procedure will be described elsewhere.

B. Umbrella sampling

The quasiharmonic reference system is ideally suited to evaluating the quantum partition function via standard umbrella sampling techniques. The function

$$K_0 = \prod_{i=1}^{P} \bar{G}_0(\mathbf{z}_i, \mathbf{z}_{i+1}, \gamma) \tag{15}$$

is taken to be the Monte Carlo weight function, and we evaluate the average of

$$R(\hat{\mathbf{z}}) \equiv \exp\left\{ -(\beta/P) \sum_j V_{\mathrm{QH}}(\mathbf{z}_j) \right\} , \tag{16}$$

(where $\hat{\mathbf{z}}$ designates the entire set of $\mathbf{z}_1 \cdots \mathbf{z}_P$) over this weight function. The resultant quantity

$$F(\beta) = \frac{\Sigma_{\hat{\mathbf{z}}} K_0(\hat{\mathbf{z}}) R(\hat{\mathbf{z}})}{\Sigma_{\hat{\mathbf{z}}} K_0(\hat{\mathbf{z}})} \tag{17}$$

will converge to the P point approximation to the quantum partition function divided by the partition function for a set of harmonic oscillators with frequencies $\omega_{\mathrm{eff}}^{(1)} \cdots \omega_{\mathrm{eff}}^{(M)}$; thus

$$Q(\beta) = F(\beta) \prod_{i=1}^{M} \frac{\exp(-\beta\omega_{\mathrm{eff}}^{(i)}/2)}{[1 - \exp(-\beta\omega_{\mathrm{eff}}^{(i)})]} . \tag{18}$$

The method is useful because the fluctuations of V_{QH} will be much less drastic than that of V. A similar approach (use of a harmonic reference system for umbrella sampling) has been applied to evaluation of the *classical* partition function of anharmonic crystal lattices.[15]

An optimized quasiharmonic frequency can be estimated by varying the parameters ω_{eff} so as to minimize the quantity

$$\langle \delta R(\hat{\mathbf{z}}) \rangle = \frac{\langle [R(\hat{\mathbf{z}}) - \langle R(\hat{\mathbf{z}}) \rangle]^2 \rangle}{\langle R(\hat{\mathbf{z}}) \rangle^2} , \tag{19}$$

where the angled brackets denote an average in the (trial) optimized reference system. For one dimension, the procedure is straightforward; one chooses a value of ω_{eff}, computes $\langle R(\hat{\mathbf{z}}) \rangle$ as described above, and then uses $K_0(\hat{\mathbf{z}})$ to sample $\langle \delta R(\hat{\mathbf{z}}) \rangle$ in identical fashion. A small number of trial points are sufficient to ascertain the location of the minimizing value of ω_{eff}.

For a multidimensional problem, there will obviously be a tradeoff between the amount of computation necessary to optimize the set of ω_{eff}'s and that needed for a larger number of quadrature points. This issue must be explored in the context of calculations on an actual system.

IV. QUARTIC OSCILLATOR

A. Basis set calculations

The quartic oscillator has been studied by many authors using a variety of different methods.[12] We will consider only parameter values where the potential has a single minimum, so that the classical Hamiltonian is

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} + a x^4 , \tag{20}$$

where $a > 0$.

The essential properties (for purposes) of the wave functions and eigenvalue spectrum of H are easily summarized. As $a \to 0$, the lowest eigenvalues and eigenstates approach those of a harmonic oscillator. As the quantum number $n \to \infty$, the separation of the neighboring levels grows larger and larger, for any fixed value of a. Thus the averaged effective quasiharmonic frequency will *increase* as the temperature rises, a simple reflection of the narrowing (relative to the pure harmonic system) of the potential well as $x \to \infty$.

This type of situation is one in which the choice of reference system can be important, because the rise in effective frequency means that, even at "high" temperatures the classical limit may not be rapidly reached. The relevant quantity for evaluating the importance of quantum effects is really $\beta\hbar\omega_{\mathrm{eff}}(\beta)$; which may decrease more slowly than $\beta\hbar\omega$. Hence, the primitive algorithm will require a larger number of points to converge than at the corresponding temperature for a harmonic oscillator.

To compute accurate quantum averages we first obtain the eigenvalues E_n and eigenvectors ψ_n of H by performing a matrix diagonalization using a truncated harmonic oscillator basis set $\{\phi_n\}$. The Hamiltonian in this basis factors into two blocks, those with n even, and those with n odd, because x^4 connects only states of the same parity. The matrix elements are easily evaluated from the relation

$$\sqrt{2} x \phi_n(x) = \sqrt{n} \phi_{n-1}(x) + \sqrt{n+1} \phi_{n+1}(x) , \tag{21}$$

200 basis functions were used for each block; convergence was checked by comparing the averaged quantities obtained using a 250 function basis set. Three quantities are computed for each value of β and a; $\langle x^2 \rangle$, $\langle x^4 \rangle$, and the canonical partition function Q, where

$$Q = \sum_{n=0}^{\infty} e^{-\beta E_n} ,$$
$$\langle x^2 \rangle = \sum_{n=0}^{\infty} \langle \psi_n | x^2 | \psi_n \rangle \frac{e^{-\beta E_n}}{Q} ,$$
$$\langle x^4 \rangle = \sum_{n=0}^{\infty} \langle \psi_n | x^4 | \psi_n \rangle \frac{e^{-\beta E_n}}{Q} . \tag{22}$$

We set $\hbar$, m and ω equal to one, and express all ensemble average quantities as functions of β and a [now scaled to have units of $(\hbar\omega)^{-1}$ and $\hbar\omega$, respectively]. The zero of energy is taken to be at $+\frac{1}{2}\beta\hbar\omega$ ($\frac{1}{2}\beta$ in reduced units), i.e., the ground state energy of the unperturbed oscillator is set to 0. The quartic perturbation raises the ground state energy, and the partition function at low temperature ($\beta = 10$) is essentially $\exp\{-\beta E_0\}$, where E_0 is the (positive) energy shift of the ground state from the harmonic value.

The basis set results, listed in the first row of Tables I–IV, are in accordance with the picture of the quartic oscillator described above. As a increases, Q, $\langle x^2\rangle$, and $\langle x^4\rangle$ each decrease for fixed temperature. This behavior has two sources: (1) the increased spacing between levels, noted above, and (2) the averages of x^2 and x^4 for a given level decrease (this is most apparent at very low temperature, where $\langle x^2\rangle$, $\langle x^4\rangle$ essentially measure the expectation values in ground state). The latter effect parallels the expected classical result (the quartic potential confines the particle near $x = 0$) but is mitigated by uncertainty effects. Comparison with the classical (primitive algorithm, $P = 1$) shows that even for $\beta\hbar\omega = 0.5$, there are noticeable discrepancies between the two calculations, especially for $\langle x^4\rangle$ and Q. The problem is therefore a substantive test of the QHDPI method at both low and high temperature.

B. Monte Carlo path integral calculations

Three types of path integral calculations have been performed; a FPDPI calculation ($\omega_{\text{eff}} = 0$), a quasiharmonic calculation, and an optimized quasiharmonic calculation. For the second of these, ω_{eff} is obtained by requiring the quasiharmonic second moment to equal the classical value, i.e.,

$$\frac{\int_{-\infty}^{\infty} x^2 \exp(-\beta\omega_{\text{QH}}^2 x^2/2)}{\int \exp(-\beta\omega_{\text{QH}} x^2/2)} = \frac{\int x^2 \exp(-\beta\{x^2/2 + ax^4\})}{\int \exp(-\beta\{x^2/2 + ax^4\})} = \langle x^2\rangle_{\text{Cl}} \,. \tag{23}$$

Carrying out the integrals on the left yields

$$\omega_{\text{QH}}(\beta,a) = \{\langle x^2\rangle_{\text{Cl}}\,\beta\}^{-1/2}\,. \tag{24}$$

Table I lists values of ω_{QH} as a function of β and a.

The optimization procedure described in Sec. III B was carried out for $P = 4$. It was found that, for $\beta = 1.0$ or 0.5, the quasiharmonic classical values yielded as good (or better) results when there was any difference (the latter occurred only for $a = 5.0$), so optimized results are given only for the three lowest temperatures. While the FPDPI and classical quasiharmonic moments start at smaller values than the exact results and increase as P increases (corresponding to a smearing of the coordinate by quantum effects), the optimized values in some cases decrease or oscillate. This is because the reference system can be chosen to be more diffuse (in some sense) than the actual system. Other optimization procedures could easily be constructed, and would perhaps yield somewhat better results for calculation of particular quantities at a particular level of quadrature. It is clear, however, that the actual method employed does lead to substantial improvement, especially for large values of β and a.

TABLE I. Quasiharmonic frequencies.

	Anharmonicity							
	0.05		0.2		1.0		5.0	
$\beta\hbar\omega$	Classical	Optimized	Classical	Optimized	Classical	Optimized	Classical	Optimized
10.0	1.03	1.09	1.09	1.25	1.27	1.7	1.65	2.4
5.0	1.05	1.11	1.15	1.30	1.41	1.75	1.89	2.6
2.0	1.11	1.14	1.27	1.35	1.65	1.85	2.30	2.9
1.0	1.17		1.41		1.89		2.9	
0.5	1.27		1.58		2.19		3.16	

TABLE II.

(A). $\langle x^2\rangle$, $\beta\hbar\omega = 10$.

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.445	0.370	0.257	0.161
Primitive algorithm QP				
1	0.0939	0.0842	0.0654	0.0359
2	0.262	0.141	0.0959	0.0525
4	0.262	0.223	0.149	0.0845
8	0.358	0.313	0.196	0.110
Quasiharmonic QP				
1	0.320	0.231	0.133	0.0716
2	0.364	0.269	0.158	0.0847
4	0.397	0.303	0.189	0.102
8	0.431	0.346	0.225	0.121
Optimized quasiharmonic QP				
1	0.440	0.389	0.329	0.183
2	0.431	0.367	0.175	0.157
4	···	···	0.254	0.149
8	···	···	···	0.151

(B). $\langle x^2\rangle$, $\beta\hbar\omega = 5$.

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.448	0.370	0.257	0.161
Primitive algorithm QP				
1	0.181	0.151	0.100	0.0558
2	0.284	0.227	0.151	0.0802
4	0.389	0.317	0.193	0.112
8	0.422	0.360	0.235	0.135

TABLE II (*continued*).
(B). $\langle x^2 \rangle, \beta\hbar\omega = 5.$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Quasiharmonic QP				
1	0.389	0.291	0.185	0.100
2	0.421	0.324	0.204	0.112
4	0.441	0.357	0.232	0.129
8	...	...	0.244	0.147
Optimized quasiharmonic QP				
1	0.453	0.410	0.291	0.197
2	0.443	0.380	0.264	0.169
4	...	0.364	0.258	0.160
8	...	...	...	...

(C). $\langle x^2 \rangle, \beta\hbar\omega = 2$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.537	0.412	0.265	0.161
Primitive algorithm QP				
1	0.408	0.367	0.182	0.0944
2	0.486	0.364	0.221	0.122
4	0.526	0.395	0.246	0.143
8	...	...	...	0.159
Quasiharmonic QP				
1	0.533	0.401	0.250	0.140
2	0.540	0.403	0.261	0.149
4	...	...	...	0.155
8	...	...	...	...
Optimized quasiharmonic QP				
1	0.548	0.430	0.296	0.202
2	0.541	0.418	0.271	0.176
4	...	...	...	0.167

(D). $\langle x^2 \rangle, \beta\hbar\omega = 1$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.785	0.550	0.315	0.172
Primitive algorithm QP				
1	0.727	0.502	0.278	0.138
2	0.778	0.535	0.303	0.157
4	0.780	0.543	0.304	0.168
8	...	...	...	...
Quasiharmonic QP				
1	0.788	0.563	0.321	0.173
2	0.788	0.546	0.320	0.172
4	...	...	...	...
8	...	...	...	...

(E). $\langle x^2 \rangle, \beta\hbar\omega = 0.5$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	1.26	0.814	0.431	0.214
Primitive algorithm QP				
1	1.23	0.794	0.416	0.200
2	1.25	0.796	0.429	0.210
4	...	...	...	...
Quasiharmonic QP				
1	1.27	0.828	0.437	0.227
2	1.26	0.805	0.426	0.218
4	...	...	...	...

TABLE III.
(A). $\langle x^4 \rangle, \beta\hbar\omega = 10.$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.578	0.387	0.182	0.0709
Primitive algorithm QP				
1	0.025	0.019	0.0096	0.0032
2	0.0836	0.0536	0.0225	0.0066
4	0.191	0.131	0.0539	0.0166
8	0.371	0.215	0.0961	0.0286
Quasiharmonic QP				
1	0.252	0.117	0.0362	0.0097
2	0.337	0.168	0.0545	0.0144
4	0.422	0.231	0.0810	0.0225
8	0.516	0.314	0.121	0.0335
Optimized quasiharmonic QP				
1	0.437	0.280	0.154	0.0440
2	0.467	0.285	0.132	0.0397
4	0.510	0.306	0.131	0.0416
8	0.535	0.336	0.143	0.0473

TABLE III (*continued*).

(B). $\langle x^4 \rangle, \beta\hbar\omega = 5$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.586	0.388	0.1822	0.0708
Primitive algorithm QP				
1	0.0934	0.0692	0.0248	0.0022
2	0.226	0.137	0.0559	0.0147
4	0.434	0.262	0.0944	0.0290
8	0.509	0.338	0.139	0.0441
Quasiharmonic QP				
1	0.382	0.191	0.0709	0.0194
2	0.470	0.2545	0.0918	0.0246
4	0.543	0.329	0.127	0.0360
8	0.569	0.385	0.152	0.0500
Optimized quasiharmonic QP				
1	0.495	0.348	0.146	0.0569
2	0.521	0.338	0.141	0.0516
4	0.571	0.341	0.154	0.0526
8	···	0.354	0.167	0.0565

(C). $\langle x^4 \rangle, \beta\hbar\omega = 2$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.823	0.471	0.192	0.0712
Primitive algorithm QP				
1	0.456	0.240	0.0792	0.0203
2	0.659	0.351	0.120	0.0348
4	0.786	0.427	0.154	0.0498
8	0.805	0.451	0.185	0.0634
Quasiharmonic QP				
1	0.738	0.381	0.135	0.0393
2	0.801	0.425	0.163	0.0486
4	0.787	0.445	0.179	0.0582
8	···	0.473	0.189	0.0662
Optimized quasiharmonic QP				
1	0.773	0.431	0.180	0.0705
2	0.817	0.445	0.169	0.0642
4	···	0.450	0.184	0.0645
8	···	0.464	0.202	0.0689

TABLE III (*continued*).

(D). $\langle x^4 \rangle, \beta\hbar\omega = 1$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	1.670	0.792	0.261	0.0796
Primitive algorithm QP				
1	1.38	0.620	0.180	0.0430
2	1.618	0.727	0.224	0.0586
4	1.645	0.752	0.234	0.731
8	···	0.777	0.249	0.0765
Quasiharmonic QP				
1	1.636	0.725	0.229	0.0629
2	1.674	0.756	0.245	0.0747
4	···	0.776	0.252	0.0776
8	···	···	···	···

(E). $\langle x^4 \rangle, \beta\hbar\omega = 0.5$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	4.071	1.632	0.453	0.115
Primitive algorithm QP				
1	3.842	1.505	0.395	0.0898
2	4.012	1.537	0.438	0.105
4	4.226	1.665	0.452	0.117
Quasiharmonic QP				
1	4.036	1.631	0.426	0.112
2	4.063	1.568	0.428	0.112
4	···	···	0.460	···

TABLE IV.

(A). Partition function, $\beta\hbar\omega = 10$.

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.721	0.359	0.047	0.00071
Classical	0.0985	0.0953	0.0858	0.0698
Optimized quasiharmonic QP				
1	0.755	0.442	0.101	0.0498
2	0.743	0.418	0.0836	0.0349
4	0.734	0.400	0.0700	0.0248
8	···	0.379	0.0612	0.0017

TABLE IV (*continued*).

(B). Partition function, $\beta\hbar\omega = 5$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	0.852	0.600	0.219	0.0267
Classical	0.194	0.184	0.158	0.124
Optimized quasiharmonic QP				
1	0.865	0.644	0.285	0.0558
2	0.859	0.625	0.263	0.0459
4	0.855	0.616	0.245	0.0384
8	...	0.607	0.232	0.0333

(C). Partition function, $\beta\hbar\omega = 2$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	1.046	0.872	0.551	0.235
Classical	0.472	0.428	0.349	0.260
Optimized quasiharmonic QP				
1	1.047	0.890	0.598	0.287
2	...	0.880	0.578	0.265
4	...	...	0.564	0.251
8	...	...	...	0.242

(D). Partition function, $\beta\hbar\omega = 1$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	1.410	1.195	0.854	0.507
Classical	0.908	0.795	0.620	0.450
Quasiharmonic QP				
1	1.414	1.21	0.877	0.548
2	1.412	1.20	0.867	0.525

(E). Partition function, $\beta\hbar\omega = 0.5$

	Anharmonicity parameter			
	0.05	0.2	1.0	5.0
Exact quantum	2.163	1.799	1.313	0.8679
Classical	1.71	1.45	1.09	0.773
Quasiharmonic QP				
1	2.16	1.81	1.33	0.890

C. Numerical results

Monte Carlo results presented here were obtained with 20 000–50 000 steps per discretized point (the precise number used depended on various parameters). The step lengths were varied to yield acceptance rates of between 30% and 70%; the variance did not appear in any case to depend critically on the precise choice of step length. Typical numbers are accurate to ± 5%. A detailed study of this aspect of the problem is not the purpose of this paper, but it can be noted that improvement of the reference system generally yielded improved statistics as well, a not very surprising result.

Tables II and III compare the exact quantum results for $\langle x^2\rangle$ and $\langle x^4\rangle$ with the three path integral calculations for various temperatures, anharmonicity, and number of quadrature points. A path integral calculation was considered converged with respect to P (this is indicated by a dash in the next highest level of quadrature) when agreement with the basis set results fell comfortably within the noise level.

Several general observations can be made. First, all three calculations show improvement, as expected, with increasing P. The quantity $\langle x^4\rangle$ shows the slowest convergence, and indeed for large values of β and a is not fully converged even in the best calculations. [The degree of convergence of A is roughly estimated by $(A_{\rm PI}/A_{\rm EXACT})$.] A check was made to determine if some of this effect was due to poor Monte Carlo statistics by using $z_1^2K(z_1\cdots z_n)$ [rather than $K(z_1\cdots z_n)$] as an importance sampling function. This improves the statistics but yields essentially the same results as in Table II and III. It thus appears to be the case that for the path integral calculations quantum corrections to $\langle x^4\rangle$ are more difficult to compute accurately than those to $\langle x^2\rangle$.

The most dramatic effects occur at the lowest temperatures. For $\beta\hbar\omega = 5$, for example, the optimized quasiharmonic calculations yield comparable results for $P = 1$ (for all values of a) to the FPDPI results using $P = 8$. This observation contains the main point of this paper; for a small additional amount of work, convergence of path integral calculations for anharmonic boson systems can be enormously enhanced by use of appropriate harmonic reference potentials. Highly anharmonic systems, of course, will still require many quadrature points to achieve accurate calculation of all quantities (e.g., $\langle x^4\rangle$ for $\beta h\omega = 10$, $a = 5.0$).

Results for the partition function, Q, are presented in Table IV. The Monte Carlo results are obtained using the optimized frequencies for $\beta\omega \geqslant 2$ and the quasiharmonic classical frequencies for $\beta\omega < 2$. As in the previous calculations, convergence is slowest at low temperature and large anharmonicity (where the most important part of the calculation is to obtain the ground state energy). Comparisons are made also with the classical partition function, obtained through numerical one-dimensional integration of the quartic potential. Attempts to evaluate the partition function using a free particle reference system led to extremely poor statistics and inaccurate results.

V. CONCLUSION

It is clear that the quasiharmonic reference system introduces a significant quantitative improvement in the path integral calculation of ensemble averages for suitable problems. Even $P = 1$ ("quasiharmonic classical mechanics") will often yield quite reasonable answers. Furthermore, it is straightforward to implement and involves little additional computer time; the quasiharmonic propagator has a form that is nearly as simple as that for a free particle. The new requirement is the original classical quasiharmonic normal mode analysis; this is also relatively straightforward, even for quite large systems (see Refs. 5–8).

The optimized reference system described above has some common features to that proposed in Ref. 2. In particular, the use of a variational procedure to determine the parametrization of the effective Hamiltonian is employed in both methods. The principal results presented here are a synthesis of these ideas with the classical temperature-dependent effective normal mode analysis of Levy, Karplus, and coworkers; this synthesis enables a straightforward Monte Carlo path integral treatment of many-body systems with complicated anharmonic boson potentials.

As mentioned in the Introduction, it is possible to combine quasiharmonic and free particle propagation, applying each to different degrees of freedom. In principle, there is no reason why one could not also utilize anharmonic reference potentials, although a convenient form for the zeroth order propagator $G_0(x,x',\beta)$ may be difficult to obtain. It is also possible to use a different number of quadrature points for different degrees of freedom.

It seems likely that further optimization of DPI methods will allow routine calculation of quantum equilibrium averages for large, complex systems. The same cannot be said for dynamical problems; there has been considerable work done in this direction recently[13,14] but the difficulties appear to be much greater. Here too, however, use of a reference system can be quite helpful. Application of the QHDPI formalism to calculation of time correlation functions will be presented in a forthcoming paper.

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