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Calculation of quantum mechanical free energy at low temperature

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Abstract. The path integral method is used to calculate the quantum mechanical free energy at low temperature. Based on the variational harmonic reference system and implemented by the partial averaging technique, the path integral can be cast into the form of a classical configurational integral with the original potential replaced by an effective one. We compared this approach with other related methods and found that it gave better results than the others considered in this paper. Furthermore, the multidimensional implementation of this method is discussed.

Key words: Path integral – Free energy

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1 Introduction

Feynman path integral methods have proved to be quite useful in the calculation of thermodynamic functions such as the density matrix element, the partition function and other equilibrium thermodynamical properties [1–10]. To evaluate the Feynman path integral, one approximation is to discretize the quantum path such that the quantum particle becomes isomorphic to a chain of p classical beads connected with each other through a temperature-dependent harmonic force [2–5, 11]. Another equivalent approximation is to expand the quantum path in a Fourier series [1, 12] and to use only the first p low-order terms in numerical calculations. Both approximations share the common feature of "truncating" the terms or beads presumed to represent a negligible contribution. These approximations have been shown to give accurate and converged results for cases at relatively high temperature, where small p will usually suffice. However, at low temperatures these approximations start to suffer from slow convergence, because larger p is required to account for the increasing quantum effects at low temperature. Various schemes [10, 13–17] have been devised to overcome the need for large p at low temperature. Feynman introduced an effective potential approach [1] to evaluate the path integral without the need for discretizing the quantum paths. This approach incorporates quantum effects by averaging the potential over the quantum paths, and thus generates a new effective potential, with which the quantum mechanical partition function can be conveniently calculated using a modified classical configurational integral. Unfortunately, this effective potential approach is unsatisfactory at low temperature. One way to improve the effective potential approach is to use the "partial averaging" technique [17], where the original potential is averaged only over the high-order Fourier terms, while the low-order ones are calculated explicitly by numerical schemes such as the Monte Carlo method. Another way to improve the effective potential approach is to find a better reference system; Feynman's original effective potential can be shown to be derived from a free particle reference system. Different reference systems such as the local harmonic [9] or the variational harmonic [6, 7] reference systems have been proposed to improve the effective potential approach. In this paper we introduce a path integral approach based on the variational principle and the partial averaging technique. We compare this approach with other related methods [9, 10] in the calculation of quantum mechanical free energy.

2 Methods

The quantum mechanical partition function is written in terms of the Feynman path integral [1],

$$Z = \int \exp\left\{ -\frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \left[\frac{p^2}{2m} + V(x(\tau)) \right] \right\} Dx(\tau) \qquad (1)$$

where p, m and V are momentum, mass and the potential function of the system, respectively. β is $1/kT$, where k is the Boltzmann constant and T, temperature. The path $x(\tau)$ is expanded in the Fourier series, i.e.,

$$x(\tau) = x_0 + \sum_{n=1}^{\infty} 2a_n \cos \Omega_n \tau + 2b_n \sin \Omega_n \tau \qquad (2)$$

where $x_0 = \int_0^{\hbar\beta} x(\tau)d\tau$ and $\Omega_n = 2n\pi/\hbar\beta$.

By separating the terms with $n > p$ and the terms with $n \leq p$, we can write Eq. (1) in the following form:

$$\begin{aligned} Z = & \int \frac{dx}{\sqrt{2\pi\hbar\beta/m}} \int \prod_{n=1}^{p} \frac{da_n\, db_n}{\pi/\beta\Omega_n^2 m} \\ & \times \exp\left[-\beta \sum_{n=1}^{p} m\Omega_n^2\left(a_n^2 + b_n^2\right)\right] \times \int \prod_{n=p+1}^{\infty} \frac{da_n\, db_n}{\pi/\beta\Omega_n^2 m} \\ & \times \exp\left[-\beta\left(\sum_{n=p+1}^{\infty} m\Omega_n^2\left(a_n^2 + b_n^2\right) + \frac{1}{\hbar\beta}\int_0^{\hbar\beta} V_{hmo}[x(\tau)]\; d\tau\right)\right] \\ & \times \exp\left(-\frac{1}{\hbar}\int_0^{\hbar\beta} \left(V[x(\tau)] - \tfrac{1}{2}m\omega^2 x(\tau)^2\right) d\tau\right) \end{aligned} \tag{3}$$

Note that the frequency ω is not yet specified and will be determined variationally, as will be shown later. Making use of the first-order cumulant inequality for the free energy [1], and integrating out the Fourier terms with $n > p$, we obtain

$$\begin{aligned} Z = & \int \frac{dx_0}{\sqrt{2\pi\hbar^2\beta/m}} \prod_{n=1}^{p} \frac{da_n db_n}{\pi/\beta\Omega_n^2 m} \\ & \times \exp\left[-\beta W\left(x_0, a_1, b_1, \ldots, a_p, b_p\right)\right] \end{aligned} \tag{4}$$

where W, the generalized effective potential, is given by

$$\begin{aligned} W\left(\omega, \alpha; x_p(\tau)\right) = & \sum_{n=1}^{p} m\Omega_n^2\left(a_n^2 + b_n^2\right) - \tfrac{1}{2}m\omega^2\alpha^2 \\ & - \tfrac{1}{\beta}\ln\left(\frac{\hbar\omega\beta/2}{\sinh \hbar\omega\beta/2} \prod_{n=1}^{p} \frac{\Omega_n^2 + \omega^2}{\Omega_n^2}\right) \\ & + \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \tilde{V}\left[x_p(\tau)\right] \end{aligned} \tag{5}$$

where $x_p(\tau)$ is the approximate path retaining the Fourier coefficients up to $n = p$, and the function $\tilde{V}(x_p(\tau))$, called the "smeared potential" [6], is given by

$$\tilde{V}\left(x_p(\tau)\right) \equiv \int \frac{dx}{\sqrt{2\pi\alpha^2}} \exp\left(-\frac{x^2}{2\alpha^2}\right) V\left(x + x_p(\tau)\right) \tag{6}$$

The Gaussian width, or the "quantum spread", α, and the frequency ω are determined by minimizing W and are given by the following iterative equations:

$$\alpha^2 = \frac{1}{\beta m\omega^2}\left[\frac{\hbar\beta\omega}{2}\coth(\hbar\beta\omega/2) - 1\right] - \sum_{n=1}^{p} \frac{2}{\beta m(\Omega_n^2 + \omega^2)} \tag{7}$$

$$\omega^2\left(x_0, a_1, b_1, \ldots, a_p, b_p\right) = \frac{1}{m\hbar\beta}\int_0^{\hbar\beta} d\tau \tilde{V}^{(2)}\left[x_p(\tau)\right] \tag{8}$$

where the superscript 2 denotes the second derivative.

Equations (5), (7) and (8) are the main equations of the paper. For convenience, we will refer to this approach as the "variational harmonic" (VH) method.

A similar approach [9] based on the local harmonic reference system was previously introduced and the equations in their original forms are given below:

$$\begin{aligned} W_{LH}\left(\omega, \alpha; x_p(\tau)\right) & \\ = & \sum_{n=1}^{p} m\Omega_n^2\left(a_n^2 + b_n^2\right) - \tfrac{1}{2}V''(x_0)\alpha^2 \\ & - \tfrac{1}{\beta}\ln \prod_{n=p+1}^{\infty} \frac{\Omega_n^2}{\Omega_n^2 + V''(x_0)/m} + \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \tilde{V}\left[x_p(\tau)\right] \end{aligned} \tag{9}$$

and

$$\alpha_{\mathrm{LH}}^2 = \sum_{n=p+1}^{\infty} \frac{2}{\beta m(\Omega_n^2 + V''(x_0)/m)} \tag{10}$$

Equations (9) and (10) are referred to as the local harmonic (LH) approximation. The major difference between the VH and LH approaches lies in the way that the frequency ω is evaluated. The VH approach uses the optimized frequency (Eqs. 7 and 8) obtained by minimizing Eq. (5) through a variational principle, while the LH approach approximates it by a local harmonic frequency, i.e., $\omega^2 = V''(x_0)/m$. Note that the infinite sums appearing in Eqs. (9) and (10) can be shown to be equivalent to the corresponding terms in Eqs. (5) and (7). The LH approach has been used to calculate thermodynamic averages at low temperature [9].

It is also possible to use the free particle as the reference state for evaluation of Eq. (1), and the resultant equations for the effective potential W_{FP} and the Gaussian width α_{FP} are given as

$$W_{FP}\left(\omega, \alpha; x_p(\tau)\right) = \sum_{n=1}^{p} m\Omega_n^2\left(a_n^2 + b_n^2\right) + \frac{1}{\hbar\beta}\int_0^{\hbar\beta} d\tau \tilde{V}\left[x_p(\tau)\right] \tag{11}$$

and

$$\alpha_{FP}^2 = \frac{\beta\hbar}{12m}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{p}\frac{1}{n^2}\right] \tag{12}$$

This method will be referred to as the free particle (FP) approximation. These equations can be shown to be equivalent to the one proposed by Doll and Freeman [12] for the density matrix element. It should be noted that, in the case of $p = 0$, Eqs. (11) and (12) reduce to the original effective classical potential method introduced by Feynman [1]. The multidimensional implementation of our method, as in the case of the LH method, is rather straightforward. The N-dimensional version of the smeared potential $\tilde{V}(\mathbf{x}_p(\tau))$ is written as

$$\tilde{V}(\mathbf{x}_p(\tau)) = \int \prod_{i}^{N} \frac{dx_i}{\sqrt{2\pi\alpha_i^2}} \exp\left(-\sum_{j=1}^{N} \frac{\xi_j^2}{2\alpha_j^2}\right) V(\mathbf{x} + \mathbf{x}_p(\tau)) \tag{13}$$

where the mass-weighted coordinates x_i are used. Consider an $N \times N$ matrix $\mathbf{F}$ defined by

$$F_{ij} = \frac{1}{\hbar\beta\sqrt{m_i m_j}} \int\limits_0^{\hbar\beta} d\tau \tilde{V}_{x_i x_j}\left[\mathbf{x}_p(\tau)\right] \tag{14}$$

where $V_{x_i x_j} = \partial^2 V/\partial x_i \partial x_j$, then the quantities ξ_j and α_j^2 in Eq. (13) are given, respectively, by

$$\xi_j = \sum_{k=1}^{N} x_j C_{jk}$$

$$\alpha_j^2 = \frac{1}{\beta\omega_j^2}\left[\frac{\hbar\beta\omega_j^2}{2}\coth\left(\hbar\beta\omega_j^2/2\right) - 1\right] - \sum_{n=1}^{p}\frac{2}{\beta(\Omega_n^2 + \omega_j^2)} \tag{15}$$

where ω_j and C_{jk} are the j^{th} eigenvalue and its corresponding k^{th} eigenvector of **F**. As in the case of the LH method, we need to construct and diagonalize the **F** matrix in the multidimensional calculations. The difference between the VH and LH methods lies in the way that ω_j and α_i are calculated. Our approach involves the non-linear optimization of the frequency factor. This presents no problem, however, since the optimization involves only trivial iterative calculations of Eqs. (14) and (15), which quickly converge after a few steps. Actually, the most time-consuming part of both approaches is the calculation of the effective potential, i.e., Eq. (13). However, this could be remedied to some degree by approximating the effective potential by the following expression:

$$\tilde{V}\left[\mathbf{x}_p(\tau)\right] \approx V[\mathbf{x}_p(\tau)] + \tfrac{1}{2}\mathrm{Tr}\left\{\left[\mathbf{C}^T\mathbf{F}\mathbf{C} - \mathbf{W}\right]\mathbf{A}\right\} \tag{16}$$

where **W** and **A** are the diagonal matrices of ω_i and α_i^2, respectively.

3 Results and discussion

The model system comprises a harmonic potential coupled to an anharmonic term, i.e.,

$$V(x) = \tfrac{1}{2}x^2 + \gamma x^4 \tag{17}$$

For this system, both the smeared potential and the frequency can be solved analytically, and we obtain $m = 1, \hbar = 1$),

$$\bar{V}\left(\bar{x}_p\right) = \gamma\bar{x}_p^4 + \tfrac{1}{2}(1 + 12\gamma\alpha^2)\bar{x}_p^2 + 3\gamma\alpha^4 + \tfrac{1}{2}\alpha^2 \tag{18}$$

and

$$\omega^2 = 12\gamma\left(\bar{x}_p^2 + \alpha^2\right) + 1 \tag{19}$$

where $\bar{V}(\bar{x}_p) = \frac{1}{\beta}\int_0^\beta d\tau\tilde{V}[x_p(\tau)]$ and $\bar{x}_p = \frac{1}{\beta}\int_0^\beta x_p(\tau)d\tau$.

It is usually difficult to obtain the analytical solutions for the smeared functions, and the following series should be useful for practical applications:

$$\tilde{V}(\bar{x}_p) = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{\alpha^2}{2}\right)^n V^{(2n)}(\bar{x}_p) \tag{20}$$

In the model system we have deliberately used the relatively large coupling, $\gamma = 250$, to enhance the anharmonic effects, in order to check to what extent our approach can be applied to the anharmonic systems, since the LH and VH approach give exact results for harmonic systems.

Figure 1 shows the calculated free energy, i.e., $F = \frac{1}{\beta}\ln Z$, as a function of β for $p = 6$. The VH approach gives quite accurate free energies throughout the temperature range considered, while the other approaches, especially the FP method, start to deviate from the exact results when the temperature is lowered. In Fig. 2a, we compare the calculated free energies ($\beta = 5$) by the VH, LH and FP approaches as a function of number of the Fourier terms. Again, the VH method gives the fastest convergence in the calculations of the quantum free energy, while the FP method gives the slowest convergence. In Fig. 2a it is hard to discern the improvement due to increasing p by the VH approach because of the scale used in the figure. In a scale-up of Fig. 2a, i.e. Fig. 2b, we can clearly see that the increase of p will indeed improve the calculated free energy and only relatively small p is needed to achieve high accuracy. Our results indicate that our approach not only accounts for large anharmonicity, but also gives very accurate quantum mechanical free energy at low temperature.

It is instructive to examine the relation between the local and the variational harmonic frequencies: Fig. 3 compares both in the model system, with $p = 0$. At high temperature ($\beta = 0.1$), the harmonic frequency is similar to its counterpart, but at low temperature ($\beta = 5$), significant deviations become obvious, especially in the region near the potential well. This result suggests that the LH approach could be used as an approximation to the VH approach at high temperature. This could be useful in realistic applications when more complex potential surfaces are involved.

In summary, we have introduced a path integral method to evaluate the quantum mechanical free energy. This method, using the variational harmonic reference system and implemented by the partial averaging technique, recasts the quantum mechanical free energy into a modified classical configurational integral, which can be

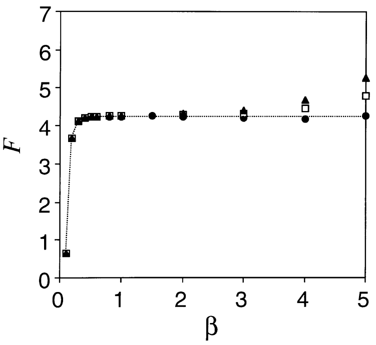

Fig. 1. The calculated free energies F of the model system with the anharmonic coupling $\gamma = 250$ (see Eq. 17), plotted as a function of β for $p = 6$ (β is $1/kT$, where k is the Boltzmann constant and T is temperature; p is the number of terms in the Fourier expansion of the path). The free energies calculated by the VH, LH and FP approaches are denoted by *filled circles*, *open squares* and *filled triangles*, respectively. The exact values are plotted as a *dotted line*

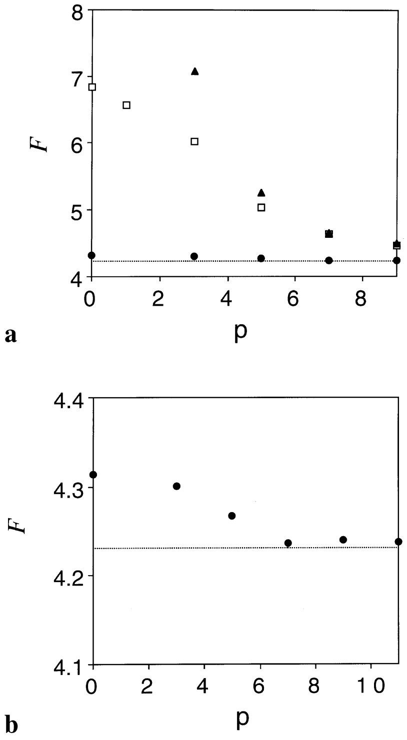

Fig. 2. a Convergence of the calculated free energy F as a function of the number of Fourier terms p at $\beta = 5$. The free energies calculated by the VH, LH and FP approaches are denoted by *filled circles*, *open squares* and *filled triangles*, respectively. The calculated free energies using the FP method with $p < 2$ are off scale and are not plotted. **b** The free energy calculated by the VH approach as a function of the number of the Fourier terms p at $\beta = 5$. This figure is a scale-up of **a** to show the improvement of the calculated free energies with increasing p

conveniently calculated by the usual numerical schemes like the Monte Carlo method. Tognetti and coworkers [18] have recently explored similar implementations of the VH approach. Our results show that the VH approach is superior to other approaches considered in this paper in terms of accuracy and convergence. It should be noted that the difference between the VH and the LH methods lies in the way that the harmonic frequency is calculated, whereby the LH method retains information about the harmonic potential at the centroid, while the VH method includes the correction to the harmonic potential introduced by the fluctuations of the path away from the centroid. It might be argued that the VH method is less practical than the LH method, especially in the N-dimensional applications, since the VH method involves an optimization of the effective harmonic parameters. However, in numerical calculations, the optimization involves only trivial iterative calculations of Eqs. (7) and (8), or Eqs. (14) and (15), which quickly converge after a few steps. Actually, the most CPU-consuming part in both LH and VH methods is the calculation of the effective potential. Hence, the VH method is no less feasible than the LH method in practical applications, but the VH method is obviously superior to the LH method. Since this approach can be applied to cases at rather low temperature, it is also possible to extend this approach to calculate the real-time propagator through a technique of analytical continuation, and this work is now in progress in our laboratory.

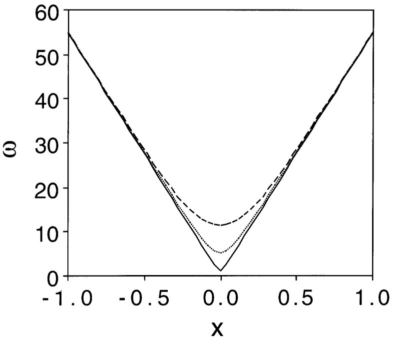

Fig. 3. The variational and local harmonic frequencies ω of the model system as a function of coordinate x. The local harmonic frequency (*solid line*) is similar to the variational harmonic frequency at high temperature ($\beta = 0.1$, *dotted line*), but at low temperature, the variational harmonic frequency ($\beta = 5$, *dashed line*) deviates significantly from the harmonic frequency, especially near the potential well

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