CHAPTER IV

EARLIER APPROXIMATIONS TO STATISTICAL PATH INTEGRALS

In Chapter III we have discussed the path integral approach to quantum statistical systems. After having expressed the partition function of a general system in path integral form, we have shown the exact calculation for a harmonic oscillator. In this present chapter, and also in the next one, we shall review and study some methods of approximation to deal with statistical systems for which the path integral cannot be solved exactly. We shall find that the variational path integral approach is an excellent way of approaching to the correct results. Here we are interested in a simple system of one particle of mass M moving in one dimension within the one-dimensional potential $V(x)$. We want to find the optimal partition function Z of that system.

Approximation in the Classical Limit

If the temperature is not too low, i.e., $T \to \infty$ or $\beta \to 0$, the time $\beta\hbar$ as a period of motion is very small. Thus, in calculating the partition function for which the initial point x_a and the final point x_b are the same, over the time interval $[0, \beta\hbar]$, each path starts from x_a and comes back to x_a again in a very short time. In this case the particle requires a high velocity or a large kinetic energy for a path far form x_a. For such a path the exponential function appearing in the expression

$$Z \equiv e^{-\beta F} = \int_{-\infty}^{\infty} \mathcal{D}x \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left[\frac{M}{2}\dot{x}^2 + V(x)\right]\right\} \qquad (4.1)$$

becomes negligibly small, and it will contribute a negligible amount to the sum over all paths. Under this assumption, the path we will consider in evaluating the potential $V(x)$ never move far from the initial point. Thus we can assume [Feynman and Hibbs 1965, Feynman 1972]

$$V(x) \approx V(x_a) \tag{4.2}$$

and we have

$$Z = \int_{-\infty}^{\infty} dx_a\, e^{-\beta V(x_a)} \int_{x_a}^{x_a} \mathcal{D}x \, exp \left\{ -(1/\hbar) \int_{0}^{\beta\hbar} d\tau\, M\dot{x}^2/2 \right\}. \tag{4.3}$$

The path integral in (4.3) can be performed as a case of free particle in Chapter II, Eq. (2.83). By setting $x_a = x_b$ and $t_b - t_a = -i\beta\hbar$, then we are reduced to

$$Z = \sqrt{\frac{M}{2\pi\hbar^2\beta}} \int_{-\infty}^{\infty} dx_a\, e^{-\beta V(x_a)}. \tag{4.4}$$

This is the well known partition function of classical statistical mechanics recovered for $\beta\hbar \to 0$ in the classical or high temperature limit. We see that,for example, for a harmonic oscillator with potential $M\omega^2 x^2/2$, the partition function in this case can be represented by the Gaussian integral,

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}} \qquad \text{for } a > 0. \tag{4.5}$$

so that we have the partition function

$$Z = \frac{1}{\beta\hbar\omega} \tag{4.6}$$

and then the free energy is

$$F = \frac{1}{\beta} \ln \beta\hbar\omega \ . \tag{4.7}$$

Remember that these results were obtained from the classical approximation.

Approximation with Quantum Corrections

There are some cases in which the classical approach is not adequate. It therefore is necessary to include the change in the potential along the path. Then, instead of approximating $V(x)$ by the constant $V(x_a)$, we might try a Taylor expansion for $V(x)$ around x_a. However, to increase our accuracy, we should choose to expand it about the average position of any particular path defined by [Feynman and Hibbs 1965, Feynman 1972]

$$x_0 = \frac{1}{\beta\hbar} \int_0^{\beta\hbar} x(\tau)\, d\tau \ . \tag{4.8}$$

We then have

$$\int_0^{\beta\hbar} V(x)\, d\tau = \beta\hbar V(x_0) + \int_0^{\beta\hbar} (x - x_0)\, V'(x_0)\, d\tau$$

$$+ \frac{1}{2} \int_0^{\beta\hbar} (x - x_0)^2\, V''(x_0)\, d\tau + \dots \ , \tag{4.9}$$

Notice that the second term of (4.9) is zero by virtue of (4.8). The path integral expression of a partition function becomes, keeping terms up to V'',

$$Z \approx \int_{-\infty}^{\infty} dx_0\, e^{-\beta V(x_0)} \int_{x_a}^{x_a} \mathcal{D}x \exp\left\{ -\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left[\frac{M}{2} \dot{x}^{\,2} + \frac{(x - x_0)^2}{2} V''(x_0) \right] \right\} . \tag{4.10}$$

This path integral must be evaluated under the constraint

$$\int_0^{\beta\hbar} (x - x_0)d\tau \;=\; \int_0^{\beta\hbar} y d\tau \;=\; 0. \tag{4.11}$$

We now apply the Fourier transform of the delta function

$$\delta\left(\int_0^{\beta\hbar} y d\tau\right) \;=\; \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik\int_0^{\beta\hbar} y d\tau} \tag{4.12}$$

in order to manipulate the constraint within the path integral.

By multiplying the whole path integral with the delta function expressed in (4.12), we finally obtain the partition function

$$Z \;=\; \int_{-\infty}^{\infty} dx_0\, e^{-\beta V(x_0)} \int_{-\infty}^{\infty} \frac{dk}{2\pi} \int_{x_a - x_0}^{x_a - x_0} \mathcal{D}y$$

$$\times \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left[\frac{M}{2}\dot{y}^2 + \frac{1}{2}V''(x_0)\, y^2 - iky\right]\right\}. \tag{4.13}$$

This last expression has the same form as the path integral for a forced harmonic oscillator, as described in Chapter II, if we interpret $-ik$ as the current j and $V''(x_0)$ as the factor $-M\omega^2$. We make use of the result in (2.155), by replacing $x_a = x_b$ and $t_b - t_a = -i\beta\hbar$, to get the approximate partition function

$$Z \;=\; (\text{Const.}) \times \int_{-\infty}^{\infty} dx_0 \exp\left\{-\beta\left[V(x_0) + \frac{\beta\hbar^2}{24M} V''(x_0)\right]\right\}. \tag{4.14}$$

Here we get Const. $= \sqrt{M/2\pi\beta\hbar^2}$ by comparison with the classical case (4.4) and now we have the correction term, $(\beta\hbar^2/24M)\, V''(\bar{x})$, which is clearly quantum mechanical in nature.

For the case of a harmonic oscillator we have its partition function

$$Z = \sqrt{\frac{M}{2\pi\beta\hbar^2}} \int_{-\infty}^{\infty} dx_0 \exp\left\{-\frac{\beta M\omega^2 x^2}{2} - \frac{\beta^2\hbar^2\omega^2}{24}\right\}, \qquad (4.15)$$

from the gaussian integral we obtain

$$Z = \frac{1}{\beta\hbar\omega} e^{-\beta^2\hbar^2\omega^2/24} , \qquad (4.16)$$

and then the free energy can be expressed as

$$F = \frac{1}{\beta} \ln \beta\hbar\omega + \frac{\beta\hbar^2\omega^2}{24} \qquad (4.17)$$

This free energy is different from the classical one in (4.4) by the quantum mechanical term, $\beta\hbar^2\omega^2/24$.

Feynman Variational Approximation

The method based on variational principle for the approximate evaluation of path integrals was firstly introduced by Feynman [Feynman and Hibbs 1965 , Feynman, 1972]. In this section we review some basic ideas of his method which may be useful later. For the partition function Z in path integral expression in Lagrangian form

$$Z = e^{-\beta F} = \int_{-\infty}^{\infty} \mathcal{D}x(\tau) e^{-S/\hbar} , \qquad (4.18)$$

where the path integral is calculated over all closed paths and S is the euclidean action. For the case of a particle with potential $V(x)$, the action is

$$S = \int_0^{\beta\hbar} d\tau\left[\frac{M}{2}\dot{x}^2 + V(x)\right]. \tag{4.19}$$

Now we wish to evaluate the energy F of a system with potential $V(x)$, which cannot be done directly. Let us suppose a trial action S_0 of another simple system of potential V_0 for which the path integral can be solved exactly. If F_0 and Z_0 are the free energy and the partition function, respectively, corresponding to the trial action S_0, then

$$Z_0 = e^{-\beta F_0} = \int_{-\infty}^{\infty} \mathcal{D}x\, e^{-S_0/\hbar}, \tag{4.20}$$

and

$$S_0 = \int_0^{\beta\hbar} d\tau\left[\frac{M}{2}\dot{x}^2 + V_0\right]. \tag{4.21}$$

To connect the original Z with the trial Z_0 we rewrite (4.18) is

$$Z = \int \mathcal{D}x\; e^{-S_0/\hbar} e^{-(S-S_0)/\hbar} \tag{4.22}$$

and

$$Z = Z_0 \left\langle e^{-(S-S_0)/\hbar}\right\rangle_0 \tag{4.23}$$

where $\langle \ldots \rangle_0$ denotes the expectation value with the trial probability distribution $exp\ \{-S_0/\hbar\}$. For an arbitrary functional $O[x]$ of the path $x(\tau)$ we define

$$\langle O[x]\rangle_0 = Z_0^{-1}\int \mathcal{D}x\, e^{-S_0/\hbar}\, O[x]. \tag{4.24}$$

We now apply the Jensen - Peierls inequality [Golden 1965, Symanzik 1965], which is based on the first order cumulant expansion [Kubo 1962],

$$\langle e^{O} \rangle \ \geq \ e^{\langle O \rangle} \tag{4.25}$$

for any probability distribution. Then from (4.23) and (4.24) we see that

$$Z \ \geq \ Z_0 e^{-(1/\hbar)\langle S - S_0 \rangle_0} \tag{4.26}$$

or

$$e^{-\beta F} \ \geq \ e^{-\beta F_0 - (1/\hbar)\langle S - S_0 \rangle_0} . \tag{4.27}$$

The inequality (4.27) gives us

$$F \ \leq \ F_0 + \frac{1}{\beta\hbar}\langle S - S_0 \rangle_0 . \tag{4.28}$$

Because the action S and S_0 have the same kinetic part, in case of time independent potential we have

$$\langle S - S_0 \rangle_0 \ = \ \beta\hbar \langle V - V_0 \rangle_0 . \tag{4.29}$$

So that

$$F \ \leq \ F_0 + \langle V - V_0 \rangle_0 . \tag{4.30}$$

If the trial potential V_0 is chose to be the potential $W(x_0)$ at the average point x_0 of any particular path by then $W(x_0)$ becomes a variational parameter to be determined by minimizing the right hand side of (4.28) or (4.30). The physical interpretation is that the particle, constrained to move in one dimension, propagates along the path as a free particle being subjected at the average point x_0 to an *effective potential* $W(x_0)$ which account for the quantum mechanical effects.

By taking into account the particular form of the action (4.19), this condition reads

$$\frac{\delta}{\delta W(x_0)}\left[F_0 + \frac{1}{\beta\hbar}\langle S - S_0\rangle_0\right] = 0 . \tag{4.31}$$

The procedure of calculation can be start with the expectation

$$\langle S - S_0\rangle_0 = \frac{\int \mathcal{D}x\; e^{-S_0/\hbar}(S - S_0)}{\int \mathcal{D}x\; e^{-S_0/\hbar}} \tag{4.32}$$

An equivalent form is derived by considering the average point of each path x_0

$$x_0 = \frac{1}{\beta\hbar}\int_0^{\beta\hbar} d\tau\, x(\tau) \tag{4.33}$$

and firstly integrating over all periodic paths satisfying (4.33) with a fixed x_0 and secondly integrating over all points x_0. Then (4.32) becomes

$$\langle S - S_0\rangle = \frac{\int dx_0\, e^{-\beta W(x_0)}\int_{x_a}^{x_a}\mathcal{D}x\,\exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \frac{M}{2}\dot{x}^2\right\}\left(\int_0^{\beta\hbar} d\tau\,(V(x_a) - W(x_0))\right)}{\int dx_0\, e^{-\beta W(x_0)}\int_{x_a}^{x_a}\mathcal{D}x\,\exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\left[\left(\frac{M}{2}\dot{x}^2\right) + W(x_0)\right]\right\}} . \tag{4.34}$$

The detailed calculation of this path integral can be found in Feynman's books [Feynman and Hibbs 1965, Feynam 1972], which is similar to that in the previous section. The result of (4.34) is

$$\frac{1}{\beta\hbar}\langle S - S_0\rangle = \frac{\int dx_0\, e^{-\beta W(x_0)} \int dx_a\,(V(x_a) - W(x_0))\, e^{-6M(x_a - x_0)^2/\beta\hbar^2}}{\int dx_0\, e^{-\beta W(x_0)} \int dx_a\, e^{-6M(x_a - x_0)^2/\beta\hbar^2}} . \tag{4.35}$$

The integral over x_0 in the demonitor in (4.35) can be easily evaluated as a Gaussian integral to be $\sqrt{\pi\beta\hbar^2/6M}$ and the integral over the $W(x_a)$-term by defining the function

$$K(x_0) = \sqrt{\frac{6M}{\pi\beta\hbar^2}} \int dx_a\, V(x_a)\, e^{-6M(x_a - x_0)^2/\beta\hbar^2} , \tag{4.36}$$

we then have

$$\frac{1}{\beta\hbar}\langle S - S_0\rangle = \frac{\int dx_0\, e^{-\beta W(x_0)}\,(K(x_0) - W(x_0))}{\int dx_0\, e^{-\beta W(x_0)}} \tag{4.37}$$

It should be noticed that $K(x_0)$ is $V(x_a)$ averaged over a Gaussian with a smearing width $a = \sqrt{\beta\hbar^2/12M}$.

Now we seek the best choice of $W(x_0)$ by considering the variation

$$\delta\left(F_0 + \frac{1}{\beta\hbar}\langle S - S_0\rangle\right) = 0 \tag{4.38}$$

and changing

$$W(x_0) \rightarrow W(x_0) + \eta W(x_0) . \tag{4.39}$$

Since the trial partition function

$$
\begin{aligned}
Z_0 &= e^{-\beta F_0} \\
&= \int dx_0\, e^{-\beta W(x_0)} \int \mathcal{D}x \;\exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar} d\tau\, \frac{M}{2}\dot{x}^2\right\} \\
&= \sqrt{\frac{M}{2\pi\beta\hbar^2}} \int dx_0\, e^{-\beta W(x_0)}, \qquad (4.40)
\end{aligned}
$$

then the variation

$$
\delta F_0 = \frac{\int dx_0 \eta\, e^{-\beta W(x_0)}}{\int dx_0\; e^{-\beta W(x_0)}} \qquad (4.41)
$$

and

$$
\begin{aligned}
\delta \frac{1}{\beta\hbar}\langle S - S_0\rangle &= \frac{\int dx_0\, e^{-\beta W(x_0)}\left[-\beta\eta(K(x_0)) - W(x_0)\right]}{\int dx_0\, e^{-\beta W(x_0)}} \\
&+ \frac{\int dx_0\, e^{-\beta W(x_0)}\left(K(x_0) - W(x_0)\right) \int dx_0 \beta\eta\, e^{-\beta W(x_0)}}{\left(\int dx_0\, e^{-\beta W(x_0)}\right)^2}. \qquad (4.42)
\end{aligned}
$$

Thus, (4.38) leads to

$$
W(x_0) = K(x_0), \qquad (4.43)
$$

which is the best choice of $W(x_0)$. Now, the potential in the definition of F_0 has been replaced by the potential $W(x_0)$ defined as $K(x_0)$ in (4.36) so called that the *effective classical potential.*

Let us consider the harmonic oscillator with potential $V(x) = M\omega^2 x^2 / 2$. Eq. (4.36) gives us

$$K(x_0) = W(x_0) = \frac{M\omega^2}{2}\left(x_0^2 + \frac{\beta\hbar^2}{12M}\right), \tag{4.44}$$

and also gives us the approximate partition function

$$Z_0 = \sqrt{\frac{M}{2\pi\beta\hbar^2}} \int dx_0 \exp\left\{-\frac{\beta M\omega^2}{2}\left(x_0^2\right) + \frac{\beta\hbar^2}{12M}\right\}$$

$$= \frac{1}{\beta\hbar\omega} e^{-\beta^2\hbar^2\omega^2/24}. \tag{4.45}$$

Notice that this result has the same form as the quantum mechanical correction to the classical result by expanding the potential about the average position of the path and using terms up through the second order, as shown before. Let us conclude that that approach was a special application of this variational approach.

$\beta\hbar\omega$	1	2	3	4
F_{ex}	0.0827	0.8546	0.9660	0.9906
F_0	0.0833	0.8598	0.9824	1.0264
F_{cl}	0.0000	0.6931	0.9324	0.6931

Table 4.1 A simple numerical comparison is of the free energies calculated by different methods, in unit of $2\beta\hbar\omega$.

Tests of the validity of the approximation when it is applied to a harmonic oscillator can be presented, for which the exact value of the free energy obtained in Chapter III is

$$F_{ex} = \frac{1}{\beta}\ln\left(2\sinh\frac{\beta\hbar\omega}{2}\right). \tag{4.46}$$

Now we have the following approximate free energy for this chapter

$$F_{cl} = \frac{1}{\beta}\ln\beta\hbar\omega \tag{4.47}$$

and the approximate free energy given by the Feynman variational approach

$$F_0 = \frac{1}{\beta}\left(\ln\beta\hbar\omega + \frac{\beta^2\hbar^2\omega^2}{24}\right). \tag{4.48}$$

The numerical comparison is shown in Table 4.1.