

G25.2651: Statistical Mechanics

Notes for Lecture 16

I. THE HARMONIC OSCILLATOR – EXPANSION ABOUT THE CLASSICAL PATH

It will be shown how to compute the density matrix for the harmonic oscillator:

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2$$

using the functional integral representation. The density matrix is given by

$$\rho(x, x'; \beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'} \mathcal{D}x(\tau) \exp \left[-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left(\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 \right) \right]$$

As we saw in the last lecture, paths in the vicinity of the classical path on the inverted potential give rise to the dominant contribution to the functional integral. Thus, it proves useful to expand the path $x(\tau)$ about the classical path. We introduce a change of path variables from $x(\tau)$ to $y(\tau)$, where

$$x(\tau) = x_{\text{cl}}(\tau) + y(\tau)$$

where $x_{\text{cl}}(\tau)$ satisfies

$$m\ddot{x}_{\text{cl}} = m\omega^2 x_{\text{cl}}$$

subject to the conditions

$$x_{\text{cl}}(0) = x, \quad x_{\text{cl}}(\beta\hbar) = x'$$

so that $y(0) = y(\beta\hbar) = 0$.

Substituting this change of variables into the action integral yields

$$\begin{aligned} S &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 \right] \\ &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m(\dot{x}_{\text{cl}} + \dot{y})^2 + \frac{1}{2}m\omega^2 (x_{\text{cl}} + y)^2 \right] \\ &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}_{\text{cl}}^2 + \frac{1}{2}m\omega^2 x_{\text{cl}}^2 \right] + \int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\omega^2 y^2 \right] \\ &\quad + \int_0^{\beta\hbar} d\tau \left[m\dot{x}_{\text{cl}}\dot{y} + m\omega^2 x_{\text{cl}}y \right] \end{aligned}$$

An integration by parts makes the cross terms vanish:

$$\int_0^{\beta\hbar} d\tau \left[m\dot{x}_{\text{cl}}\dot{y} + m\omega^2 x_{\text{cl}}y \right] = m\dot{x}_{\text{cl}}y|_0^{\beta\hbar} + \int_0^{\beta\hbar} d\tau \left[-m\ddot{x}_{\text{cl}} + m\omega^2 x_{\text{cl}} \right] y = 0$$

where the surface term vanishes because $y(0) = y(\beta\hbar) = 0$ and the second term vanishes because x_{cl} satisfies the classical equation of motion.

The first term in the expression for S is the classical action, which we have seen is given by

$$\int_0^{\beta\hbar} d\tau \left[\frac{1}{2}m\dot{x}_{\text{cl}}^2 + \frac{1}{2}m\omega^2 x_{\text{cl}}^2 \right] = \frac{m\omega}{2\sinh(\beta\hbar\omega)} \left[(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx' \right]$$

Therefore, the density matrix for the harmonic oscillator becomes

$$\rho(x, x'; \beta) = I[y] \exp \left[-\frac{m\omega}{2\sinh(\beta\hbar\omega)} \left((x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx' \right) \right]$$

where $I[y]$ is the path integral

$$I[y] = \int_{y(0)=0}^{y(\beta\hbar)=0} \mathcal{D}y(\tau) \exp \left[-\frac{1}{\hbar} \int_0^{\beta\hbar} \left(\frac{m}{2} \dot{y}^2 + \frac{m\omega^2}{2} y^2 \right) \right]$$

Note that $I[y]$ does not depend on the points x and x' and therefore can only contribute an overall (temperature dependent) constant to the density matrix. This will affect the thermodynamics but not any averages of physical observables. Nevertheless, it is important to see how such a path integral is done.

In order to compute $I[y]$ we note that it is a functional integral over functions $y(\tau)$ that vanish at $\tau = 0$ and $\tau = \beta\hbar$. Thus, they are a special class of periodic functions and can be expanded in a Fourier sine series:

$$y(\tau) = \sum_{n=1}^{\infty} c_n \sin(\omega_n \tau)$$

where

$$\omega_n = \frac{n\pi}{\beta\hbar}$$

Thus, we wish to change from an integral over the functions $y(\tau)$ to an integral over the Fourier expansion coefficients c_n . The two integrations should be equivalent, as the coefficients uniquely determine the functions $y(\tau)$. Note that

$$\dot{y}(\tau) = \sum_{n=1}^{\infty} \omega_n c_n \cos(\omega_n \tau)$$

Thus, terms in the action are:

$$\int_0^{\beta\hbar} d\tau \frac{1}{m} \dot{y}^2 = \frac{m}{2} \sum_{n=1}^{\infty} \sum_{n'=1}^{\infty} c_n c_{n'} \omega_n \omega_{n'} \int_0^{\beta\hbar} d\tau \cos(\omega_n \tau) \cos(\omega_{n'} \tau)$$

Since the cosines are orthogonal between $\tau = 0$ and $\tau = \beta\hbar$, the integral becomes

$$\int_0^{\beta\hbar} d\tau \frac{1}{m} \dot{y}^2 = \frac{m}{2} \sum_{n=1}^{\infty} c_n^2 \omega_n^2 \int_0^{\beta\hbar} d\tau \cos^2(\omega_n \tau) = \frac{m}{2} \sum_{n=1}^{\infty} c_n^2 \omega_n^2 \int_0^{\beta\hbar} d\tau \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega_n \tau) \right] = \frac{m\beta\hbar}{4} \sum_{n=1}^{\infty} c_n^2 \omega_n^2$$

Similarly,

$$\int_0^{\beta\hbar} \frac{1}{2} m \omega^2 y^2 = \frac{m\beta\hbar}{4} \omega^2 \sum_{n=1}^{\infty} c_n^2$$

The measure becomes

$$\mathcal{D}y(t) \rightarrow \prod_{n=1}^{\infty} \frac{dc_n}{\sqrt{4\pi/m\beta\omega_n^2}}$$

which, is not an equivalent measure (since it is not derived from a determination of the Jacobian), but is chosen to give the correct free-particle ($\omega = 0$) limit, which can ultimately be corrected by attaching an overall factor of $\sqrt{m/2\pi\beta\hbar^2}$.

With this change of variables, $I[y]$ becomes

$$I[y] = \prod_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{dc_n}{\sqrt{4\pi/m\beta\omega_n^2}} \exp \left[-\frac{m\beta}{4} (\omega^2 + \omega_n^2) c_n^2 \right] = \prod_{n=1}^{\infty} \left[\frac{\omega_n^2}{\omega^2 + \omega_n^2} \right]^{1/2}$$

The infinite product can be written as

$$\prod_{n=1}^{\infty} \left[\frac{\pi^2 n^2 / \beta^2 \hbar^2}{\omega^2 + \pi^2 n^2 / \beta^2 \hbar^2} \right] = \left[\prod_{n=1}^{\infty} \left(1 + \frac{\beta^2 \hbar^2 \omega^2}{\pi^2 n^2} \right) \right]^{-1}$$

the product in the square brackets is just the infinite product formula for $\sinh(\beta\hbar\omega)/(\beta\hbar\omega)$, so that $I[y]$ is just

$$I[y] = \sqrt{\frac{\beta\hbar\omega}{\sinh(\beta\hbar\omega)}}$$

Finally, attaching the free-particle factor $\sqrt{m/2\pi\beta\hbar^2}$, the harmonic oscillator density matrix becomes:

$$\rho(x, x'; \beta) = \sqrt{\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}} \exp \left[-\frac{m\omega}{2\sinh(\beta\hbar\omega)} \left((x^2 + x'^2) \cosh(\beta\hbar\omega) - 2xx' \right) \right]$$

Notice that in the free-particle limit ($\omega \rightarrow 0$), $\sinh(\beta\hbar\omega) \approx \beta\hbar\omega$ and $\cosh(\beta\hbar\omega) \approx 1$, so that

$$\rho(x, x'; \beta) \rightarrow \sqrt{\frac{m}{2\pi\beta\hbar^2}} \exp \left[-\frac{m}{2\beta\hbar^2} (x - x')^2 \right]$$

which is the expected free-particle density matrix.

II. THE STATIONARY PHASE APPROXIMATION

Consider the simple integral:

$$I = \lim_{\lambda \rightarrow \infty} \int_{-\infty}^{\infty} dx e^{-\lambda f(x)}$$

Assume $f(x)$ has a global minimum at $x = x_0$, such that $f'(x_0) = 0$. If this minimum is well separated from other minima of $f(x)$ and the value of $f(x)$ at the global minimum is significantly lower than it is at other minima, then the dominant contributions to the above integral, as $\lambda \rightarrow \infty$ will come from the integration region around x_0 . Thus, we may expand $f(x)$ about this point:

$$f(x) = f(x_0) + f'(x_0)(x - x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2 + \dots$$

Since $f'(x_0) = 0$, this becomes:

$$f(x) \approx f(x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2$$

Inserting the expansion into the expression for I gives

$$\begin{aligned} I &= \lim_{\lambda \rightarrow \infty} e^{-\lambda f(x_0)} \int_{-\infty}^{\infty} dx e^{-\frac{\lambda}{2}f''(x_0)(x-x_0)^2} \\ &= \lim_{\lambda \rightarrow \infty} \left[\frac{2\pi}{\lambda f''(x_0)} \right]^{1/2} e^{-\lambda f(x_0)} \end{aligned}$$

Corrections can be obtained by further expansion of higher order terms. For example, consider the expansion of $f(x)$ up to fourth order:

$$f(x) \approx f(x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2 + \frac{1}{6}f'''(x_0)(x - x_0)^3 + \frac{1}{24}f^{(iv)}(x_0)(x - x_0)^4$$

Substituting this into the integrand and further expanding the exponential would give, as the lowest order nonvanishing correction:

$$I = \lim_{\lambda \rightarrow \infty} e^{-\lambda f(x_0)} \int_{-\infty}^{\infty} dx e^{-\frac{\lambda}{2}f''(x_0)(x-x_0)^2} \left[1 - \frac{\lambda}{24}f^{(iv)}(x_0)(x - x_0)^4 \right]$$

This approximation is known as the *stationary phase* or *saddle point* approximation. The former may seem a little out-of-place, since there is no phase in the problem, but that is because we formulated it in such a way as to anticipate its application to the path integral. But this is only if λ is taken to be a real instead of an imaginary quantity.

The application to the path integral follows via a similar argument. Consider the path integral expression for the density matrix:

$$\rho(x, x'; \beta) = \int_{x(0)=x}^{x(\beta\hbar)=x'} \mathcal{D}[x] e^{-S_E[x]/\hbar}$$

We showed that the classical path satisfying

$$\begin{aligned} m\ddot{x}_{\text{cl}} &= \left. \frac{\partial U}{\partial x} \right|_{x=x_{\text{cl}}} \\ x(0) &= x \quad x(\beta\hbar) = x' \end{aligned}$$

is a stationary point of the Euclidean action $S_E[x]$, i.e., $\delta S_E[x_{\text{cl}}] = 0$. Thus, we can develop a stationary phase or saddle point approximation for the density matrix by introducing an expansion about the classical path according to

$$x(\tau) = x_{\text{cl}}(\tau) + y(\tau) = x_{\text{cl}}(\tau) + \sum_n c_n \phi_n(\tau)$$

where the correction $y(\tau)$, satisfying $y(0) = y(\beta\hbar) = 0$ has been expanded in a complete set of orthonormal functions $\{\phi_n(\tau)\}$, which are orthonormal on the interval $[0, \beta\hbar]$ and satisfy $\phi_n(0) = \phi_n(\beta\hbar) = 0$ as well as the orthogonality condition:

$$\int_0^{\beta\hbar} d\tau \phi_n(\tau) \phi_m(\tau) = \delta_{mn}$$

Setting all the expansion coefficients to 0 recovers the classical path. Thus, we may expand the action $S[x]$ (the ‘‘E’’ subscript will henceforth be dropped from this discussion) with respect to the expansion coefficients:

$$S[x] = S[x_{\text{cl}}] + \sum_j \left. \frac{\partial S}{\partial c_j} \right|_{\{c\}=0} c_j + \frac{1}{2} \sum_{j,k} \left. \frac{\partial^2 S}{\partial c_j \partial c_k} \right|_{\{c\}=0} c_j c_k + \dots$$

Since

$$S[x] = \int_0^{\beta\hbar} d\tau \left[\frac{1}{2} m \dot{x}^2 + U(x(\tau)) \right]$$

the expansion can be worked out straightforwardly by substitution and subsequent differentiation:

$$\begin{aligned} S[x] &= \int_0^{\beta\hbar} d\tau \left[\frac{1}{2} m \left(\dot{x}_{\text{cl}} + \sum_n c_n \dot{\phi}_n \right)^2 + U(x_{\text{cl}} + \sum_n c_n \phi_n) \right] \\ \frac{\partial S}{\partial c_j} &= \int_0^{\beta\hbar} d\tau \left[m(\dot{x}_{\text{cl}} + \sum_n c_n \dot{\phi}_n) \dot{\phi}_j + U' \left(x_{\text{cl}} + \sum_n c_n \phi_n \right) \phi_j \right] \\ \left. \frac{\partial S}{\partial c_j} \right|_{\{c\}=0} &= \int_0^{\beta\hbar} d\tau \left[m \dot{x}_{\text{cl}} \dot{\phi}_j + U'(x_{\text{cl}}) \phi_j \right] \\ &= m \dot{x}_{\text{cl}} \phi_j \Big|_0^{\beta\hbar} + \int_0^{\beta\hbar} d\tau [-m \ddot{x}_{\text{cl}} + U'(x_{\text{cl}})] \phi_j \\ &= 0 \\ \frac{\partial^2 S}{\partial c_j \partial c_k} &= \int_0^{\beta\hbar} \left[m \dot{\phi}_j \dot{\phi}_k + U'' \left(x_{\text{cl}} + \sum_n c_n \phi_n \right) \phi_j \phi_k \right] \end{aligned}$$

$$\begin{aligned}
\left. \frac{\partial^2 S}{\partial c_j \partial c_k} \right|_{\{c\}=0} &= \int_0^{\beta \hbar} d\tau \left[m \dot{\phi}_j \dot{\phi}_k + U''(x_{\text{cl}}) \phi_j \phi_k \right] \\
&= \int_0^{\beta \hbar} d\tau \left[-m \phi_j \ddot{\phi}_k + U''(x_{\text{cl}}(\tau)) \phi_j \phi_k \right] \\
&= \int_0^{\beta \hbar} d\tau \phi_j(\tau) \left[-m \frac{d^2}{d\tau^2} + U''(x_{\text{cl}}(\tau)) \right] \phi_k(\tau)
\end{aligned}$$

where the fourth and eighth lines are obtained from an integration by parts. Let us write the integral in the last line in the suggestive form:

$$\left. \frac{\partial^2 S}{\partial c_j \partial c_k} \right|_{\{c\}=0} = \langle \phi_j | -m \frac{\partial^2}{\partial \tau^2} + U''(x_{\text{cl}}(\tau)) | \phi_k \rangle = \Delta_{jk}$$

which emphasizes the fact that we have matrix elements of the operator $-m d^2/d\tau^2 + U''(x_{\text{cl}}(\tau))$ with respect to the basis functions. Thus, the expansion for S can be written as

$$S[x] = S[x_{\text{cl}}] + \frac{1}{2} \sum_{j,k} c_j \Delta_{jk} c_k + \dots$$

and the density matrix becomes

$$\rho(x, x'; \beta) = \mathcal{N} \int \prod_j \frac{dc_j}{\sqrt{2\pi\hbar}} e^{-S_{\text{cl}}(x, x'; \beta)} e^{-\frac{1}{2} \sum_{j,k} c_j \Delta_{jk} c_k / \hbar}$$

where $S_{\text{cl}}(x, x'; \beta) = S[x_{\text{cl}}]$. \mathcal{N} is an overall normalization constant. The integral over the coefficients becomes a generalized Gaussian integral, which brings down a factor of $1/\sqrt{\det \Delta}$:

$$\begin{aligned}
\rho(x, x'; \beta) &= \mathcal{N} e^{-S_{\text{cl}}(x, x'; \beta)} \frac{1}{\sqrt{\det \Delta}} \\
&= \mathcal{N} e^{-S_{\text{cl}}(x, x'; \beta)} \frac{1}{\sqrt{\det \left(-m \frac{d^2}{d\tau^2} + U''(x_{\text{cl}}(\tau)) \right)}}
\end{aligned}$$

where the last line is the abstract representation of the determinant. The determinant is called the *Van Vleck-Pauli-Morette* determinant.

If we choose the basis functions $\phi_n(\tau)$ to be eigenfunctions of the operator appearing in the above expression, so that they satisfy

$$\left[-m \frac{d^2}{d\tau^2} + U''(x_{\text{cl}}(\tau)) \right] \phi_n(\tau) = \lambda_n \phi_n(\tau)$$

Then,

$$\Delta_{jk} = \lambda_j \delta_{jk} = \lambda_j(x, x'; \beta) \delta_{jk}$$

and the determinant can be expressed as a product of the eigenvalues. Thus,

$$\rho(x, x'; \beta) = \mathcal{N} e^{-S_{\text{cl}}(x, x'; \beta)} \prod_j \frac{1}{\sqrt{\lambda_j(x, x'; \beta)}}$$

The product must exclude any 0-eigenvalues.

Incidentally, by performing a Wick rotation back to real time according to $\beta = -it/\hbar$, the saddle point or stationary phase approximation to the real-time propagator can be derived. The derivation is somewhat tedious and will not be given in detail here, but the result is

$$U(x, x'; t) = e^{\frac{i}{\hbar} S_{\text{cl}}(x, x'; t)} \frac{1}{\sqrt{\det \left(-m \frac{d^2}{dt^2} - U''(x_{\text{cl}}(t)) \right)}} e^{-i\pi\nu/2}$$

where $x_{\text{cl}}(t)$ satisfies

$$m\ddot{x}_{\text{cl}} = - \left. \frac{\partial U}{\partial x} \right|_{x=x_{\text{cl}}}$$

$$x_{\text{cl}}(0) = x \quad x_{\text{cl}}(t) = x'$$

and ν is an integer that increases by 1 each time the determinant vanishes along the classical path. ν is called the Maslov index. It is important to note that because the classical paths satisfy an endpoint problem, rather than an initial value problem, there can be more than one solution. In this case, one must sum the result over classical paths:

$$U(x, x'; t) = \sum_{\text{classical paths}} e^{\frac{i}{\hbar} S_{\text{cl}}(x, x'; t) - i\pi\nu/2} \frac{1}{\sqrt{\det \left(-m \frac{d^2}{dt^2} - U''(x_{\text{cl}}(t)) \right)}}$$

with a similar sum for the density matrix.