G25.2651: Statistical Mechanics

Notes for Lecture 14

I. EXPECTATION VALUES OF OBSERVABLES

Recall the basic formula for the expectation value of an observable A:

$$\langle A \rangle = \frac{1}{Q(\beta)} \text{Tr}(Ae^{-\beta H})$$

Two important cases pertaining to the evaluation of the trace in the coordinate basis for expectation values will be considered below:

A. Case 1: Functions only of position

If $A = A(X)$, i.e., a function of the operator X only, then the trace can be easily evaluated in the coordinate basis:

$$\langle A \rangle = \frac{1}{Q} \int dx \langle x | A(X) e^{-\beta H} | x \rangle$$

Since $A(X)$ acts to the left on one of its eigenstates, we have

$$\langle A \rangle = \frac{1}{Q} \int dx \, A(x) \langle x | e^{-\beta H} | x \rangle$$

which only involves a diagonal element of the density matrix. This can, therefore, be written as a path integral:

$$\langle A \rangle = \frac{1}{Q} \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P A(x_1) \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i) \right) \right]$$

However, since all points $x_1, .., x_P$ are equivalent, due to the fact that they are all integrated over, we can make P equivalent cyclic renaming of the coordinates $x_1 \to x_2$, $x_2 \to x_3$, etc. and generate P equivalent integrals. In each, the function $A(x_1)$ or $A(x_2)$, etc. will appear. If we sum these P equivalent integrals and divide by P, we get an expression:

$$\langle A \rangle = \frac{1}{Q} \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P \frac{1}{P} \sum_{i=1}^{P} A(x_i) \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i) \right) \right]$$

This allows us to define an *estimator* for the observable A. Recall that an estimator is a function of the P variables $x_1, ..., x_P$ whose average over the ensemble yields the expectation value of A:

$$a_P(x_1, ..., x_P) = \frac{1}{P} \sum_{i=1}^{P} A(x_i)$$

Then

$$\langle A \rangle = \lim_{P \to \infty} \langle a_p \rangle_{x_1, ..., x_P}$$

where the average on the right is taken over many configurations of the P variables $x_1, ..., x_P$ (we will discuss, in the nex lecture, a way to generate these configurations).

The limit $P \to \infty$ can be taken in the same way that we did in the previous lecture, yielding a functional integral expression for the expectation value:

$$\langle A \rangle = \frac{1}{Q} \oint \mathcal{D}x(\tau) \left[\frac{1}{\beta\hbar} \int_0^{\beta\hbar} d\tau A(x(\tau)) \right] \exp\left[-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left(\frac{1}{2} m\dot{x}^2 + U(x(\tau)) \right) \right]$$

B. Case 1: Functions only of momentum

Suppose that $A = A(P)$, i.e., a function of the momentum operator. Then, the trace can still be evaluated in the coordinate basis:

$$\langle A \rangle = \frac{1}{Q} \int dx \langle x | A(P) e^{-\beta H} | x \rangle$$

However, $A(P)$ acting to the left does not act on an eigenvector. Let us insert a coordinate space identity $I = \int dx | x \rangle \langle x |$ between A and $\exp(-\beta H)$:

$$\langle A \rangle = \frac{1}{Q} \int dx dx' \langle x | A(P) | x' \rangle \langle x | e^{-\beta H} | x \rangle$$

Now, we see that the expectation value can be obtained by evaluating *all* the coordinate space matrix elements of the operator and *all* the coordinate space matrix elements of the density matrix.

A particularly useful form for the expectation value can be obtained if a momentum space identity is inserted:

$$\langle A \rangle = \frac{1}{Q} \int dx dx' dp \langle x | A(P) | p \rangle \langle p | x' \rangle \langle x' | e^{-\beta H} | x \rangle$$

Now, we see that $A(P)$ acts on an eigenstate (at the price of introducing another integral). Thus, we have

$$\langle A \rangle = \frac{1}{Q} \int dp A(p) \int dx dx' \langle x | p \rangle \langle p | x' \rangle \langle x' | e^{-\beta H} | x \rangle$$

Using the fact that $\langle x | p \rangle = (1/2\pi\hbar) \exp(ipx/\hbar)$, we find that

$$\langle A \rangle = \frac{1}{2\pi\hbar Q} \int dp A(p) \int dx dx' e^{ip(x-x')/\hbar} \langle x' | e^{-\beta H} | x \rangle$$

In the above expression, we introduce the change of variables

$$r = \frac{x + x'}{2} \qquad s = x - x'$$

Then

$$\langle A \rangle = \frac{1}{2\pi\hbar Q} \int dp A(p) \int dr \, ds \, e^{ips/\hbar} \langle r - \frac{s}{2} | e^{-\beta H} | r + \frac{s}{2} \rangle$$

Define a distribution function

$$\rho_{\mathrm{W}}(r, p) = \frac{1}{2\pi\hbar} \int ds \, e^{ips/\hbar} \langle r - \frac{s}{2} | e^{-\beta H} | r + \frac{s}{2} \rangle$$

Then, the expectation value can be written as

$$\langle A \rangle = \frac{1}{Q} \int dr dp A(p) \rho_{\mathrm{W}}(r, p)$$

which looks just like a classical phase space average using the "phase space" distribution function $\rho_{\mathrm{W}}(r, p)$. The distribution function $\rho_{\mathrm{W}}(r, p)$ is known as the Wigner density matrix and it has many interesting features. For one thing, its classical limit is

$$\rho_{\mathrm{W}}(r, p) = \exp\left[-\beta \left(\frac{p^2}{2m} + U(r) \right) \right]$$

which is the true classical phase space distribution function. There are various examples, in which the exact Wigner distribution function is the classical phase space distribution function, in particularly for quadratic Hamiltonians. Despite its compelling appearance, the evaluation of expectation values of functions of momentum are considerably more difficult than functions of position, due to the fact that the entire density matrix is required. However, there are a few quantities of interest, that are functions of momentum, that can be evaluated without resorting to the entire density matrix. These are thermodynamic quantities which will be discussed in the next section.

II. THERMODYNAMICS FROM PATH INTEGRALS

Although general functions of momentum are difficult (though not intractable) to evaluate by path integration, certain functions of momentum (and position) can be evaluated straightforwardly. These are thermodynamic quantities such as the energy and pressure, given respectively by

$$E = -\frac{\partial}{\partial \beta} \ln Q(\beta, V)$$

$$P = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q(\beta, V)$$

We shall derive estimators for these two quantities directly from the path integral expression for the partition function. However, let us work with the partition function for an ensemble of 1-particle systems in three dimensions, which is given by

$$Q(\beta, V) = \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3P/2} \int d\mathbf{r}_1 \cdots d\mathbf{r}_P \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} U(\mathbf{r}_i) \right) \right]$$

Using the above thermodynamic relation, the energy becomes

$$
\begin{aligned}
E &= -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \\
&= \frac{1}{Q} \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3P/2} \int d\mathbf{r}_1 \cdots d\mathbf{r}_P \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} U(\mathbf{r}_i) \right) \right] \\
&\quad \times \left[\frac{3P}{2\beta} - \sum_{i=1}^{P} \frac{1}{2} m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} \sum_{i=1}^{P} U(\mathbf{r}_i) \right] \\
&= \lim_{P \to \infty} \langle \varepsilon_P(\mathbf{r}_1, ..., \mathbf{r}_P) \rangle
\end{aligned}
$$

where

$$\varepsilon_P(\mathbf{r}_1, ..., \mathbf{r}_P) = \frac{3P}{2\beta} - \sum_{i=1}^{P} \frac{1}{2} m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} \sum_{i=1}^{P} U(\mathbf{r}_i)$$

is the thermodynamic estimator for the total energy.

Similarly, an estimator for the internal pressure can be derived using $P = kT\partial \ln Q/\partial V$. As we have done in the past for classical systems, the volume dependence can be made explicit by introducing the change of variables:

$$\mathbf{r}_k = V^{1/3} \mathbf{s}_k$$

In terms of the scaled variables $\mathbf{s}_k$, the partition function expression reads:

$$Q(\beta, V) = \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3P/2} V^P \int d\mathbf{s}_1 \cdots d\mathbf{s}_P \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 V^{2/3} (\mathbf{s}_{i+1} - \mathbf{s}_i)^2 + \frac{1}{P} U(V^{1/3}\mathbf{s}_i) \right) \right]$$

Evaluating the derivative with respect to volume gives the internal pressure:

$$
\begin{aligned}
P &= \frac{1}{\beta Q} \frac{\partial Q}{\partial V} \\
&= \frac{1}{Q} \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3P/2} V^P \int d\mathbf{s}_1 \cdots d\mathbf{s}_P \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 V^{2/3} (\mathbf{s}_{i+1} - \mathbf{s}_i)^2 + \frac{1}{P} U(V^{1/3}\mathbf{s}_i) \right) \right] \\
&\quad \times \left[\frac{P}{\beta V} - \frac{1}{3} m\omega_P^2 V^{-1/3} \sum_{i=1}^{P} (\mathbf{s}_{i+1} - \mathbf{s}_i)^2 - \frac{1}{P} \sum_{i=1}^{P} \frac{\partial U}{\partial (V^{1/3}\mathbf{s}_i)} \cdot \frac{1}{3} V^{-2/3} \mathbf{s}_i \right]
\end{aligned}
$$

$$= \frac{1}{Q} \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{3P/2} \int d\mathbf{r}_1 \cdots d\mathbf{r}_P \exp \left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} U(\mathbf{r}_i) \right) \right]$$

$$\times \left[\frac{P}{\beta V} - \frac{1}{3V} m\omega_P^2 \sum_{i=1}^{P} (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 - \frac{1}{3VP} \sum_{i=1}^{P} \frac{\partial U}{\partial \mathbf{r}_i} \cdot \mathbf{s}_i \right]$$

$$= \lim_{P \to \infty} \langle p_P(\mathbf{r}_1, ..., \mathbf{r}_P) \rangle$$

where

$$p_P(\mathbf{r}_1, ..., \mathbf{r}_P) = \frac{P}{\beta V} - \frac{1}{3V} \sum_{i=1}^{P} \left[m\omega_P^2 (\mathbf{r}_{i+1} - \mathbf{r}_i)^2 + \frac{1}{P} \mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} \right]$$

is the thermodynamic estimator for the pressure. Clearly, both the energy and pressure will be functions of the particle momenta, however, because they are related to the partition function by thermodynamic differentiation, estimators can be derived for them that do not require the off-diagonal elements of the density matrix.

III. PATH INTEGRAL MOLECULAR DYNAMICS (OPTIONAL READING)

Consider once again the path integral expression for the one-dimensional canonical partition function (for a finite but large value of P):

$$Q(\beta) = \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{P/2} \int dx_1 \cdots dx_P \exp \left[-\beta \sum_{i=1}^{P} \left(\frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i) \right) \right] \tag{1}$$

(the condition $x_{P+1} = x_1$ is understood). Recall that, according to the classical isomorphism, the path integral expression for the canonical partition function is isomorphic to the classical configuration integral for a certain P-particle system. We can carry this analogy one step further by introducing into the above expression a set of P momentum integrations:

$$Q(\beta) = \int dp_1 \cdots dp_P \, dx_1 \cdots dx_P \exp \left[-\beta \sum_{i=1}^{P} \left(\frac{p_i^2}{2m'} + \frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i) \right) \right] \tag{2}$$

Note that these momentum integrations are completely uncoupled from the position integrations, and if we were to carry out these momentum integrations, we would reproduce Eq. (1) apart from trivial constants. Written in the form Eq. (2), however, the path integral looks exactly like a phase space integral for a P-particle system. We know from our work in classical statistical mechanics that dynamical equations of motion can be constructed that will generate this partition function. In principle, one would start with the classical Hamiltonian

$$H = \sum_{i=1}^{P} \left[\frac{p_i^2}{2m'} + \frac{1}{2} m\omega_P^2 (x_{i+1} - x_i)^2 + \frac{1}{P} U(x_i) \right]$$

derive the corresponding classical equations of motion and then couple in thermostats. Such an approach has certainly been attempted with only limited success. The difficulty with this straightforward approach is that the more "quantum" a system is, the large the paramester P must be chosen in order to converge the path integral. However, if P is large, the above Hamiltonian describes a system with extremely stiff nearest-neighbor harmonic bonds interacting with a very weak potential U/P. It is, therefore, almost impossible for the system to deviate far harmonic oscillator solutions and explore the entire available phase space. The use of thermostats can help this problem, however, it is also exacerbated by the fact that all the harmonic interactions are coupled, leading to a wide variety of time scales associated with the motion of each variable in the Hamiltonian. In order to separate out all these time scales, one must somehow diagonalize this harmonic interaction. One way to do this is to use normal mode variables, and this is

a perfectly valid approach. However, we will explore another, simpler approach here. It involves the use of a variable transformation of the formed used in previous lectures to do the path integral for the free-particle density matrix.

Consider a change of variables:

$$u_1 = x_1$$
$$u_k = x_k - \tilde{x}_k \qquad k = 2, ..., P$$

where

$$\tilde{x}_i = \frac{(k-1)x_{k+1} + x_1}{k}$$

The inverse of this transformation can be worked out in closed form:

$$x_1 = u_1$$
$$x_k = u_1 + \sum_{l=k}^{P} \frac{(k-1)}{(l-1)} u_l$$

and can also be expressed as a *recursive inverse*:

$$x_1 = u_1$$
$$x_k = u_k + \frac{k-1}{k} x_{k+1} + \frac{1}{k} x_1$$

The term $k = P$ here can be used to start the recursion. We have already seen that this transformation diagonalized the harmonic interaction. Thus, substituting the transformation into the path integral gives:

$$Q(\beta) = \int dp_1 \cdots dp_P \, du_1 \cdots du_P \exp\left[-\beta \sum_{i=1}^{P} \left(\frac{p_i^2}{2m_i'} + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, ..., u_P)) \right) \right]$$

The parameters m_i are given by

$$m_1 = 0$$
$$m_i = \frac{i}{i-1} m$$

Note also that the momentum integrations have been changed slightly to involve a set of parameters m_i'. Introducing these parameters, again, only changes the partition function by trivial constant factors. How these should be chosen will become clear later in the discussion. The notation $x_i(u_1, ..., u_P)$ indicates that each variable x_i is a generally a function of all the new variables $u_1, ..., u_P$.

A dynamics scheme can now be derived using as an effective Hamiltonian:

$$H = \sum_{i=1}^{P} \left[\frac{p_i^2}{2m_i'} + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, ..., u_P)) \right]$$

which, when coupled to thermostats, yields a set of equations of motion

$$m_i' \ddot{u}_i = -m_i \omega_P^2 u_i - \frac{1}{P} \frac{\partial U}{\partial u_i} - \dot{\eta}_i \dot{u}_i$$

$$Q \ddot{\eta}_i = m_i \dot{u}_i^2 - \frac{1}{\beta} \qquad\qquad (3)$$

These equations have a conserved energy (which is not a Hamiltonian):

$$H' = \sum_{i=1}^{P} \left[\frac{1}{2} m_i' \dot{u}_i^2 + \frac{1}{2} m_i \omega_P^2 u_i^2 + \frac{1}{P} U(x_i(u_1, ..., u_P)) + \frac{1}{2} Q \dot{\eta}_i^2 + \frac{1}{\beta} \eta_i \right]$$

Notice that each variable is given its *own* thermostat. This is done to produce maximum ergodicity in the trajectories. In fact, in practice, the chain thermostats you have used in the computer labs are employed. Notice also that the

time scale of each variable is now clear. It is just determined by the parameters $\{m_i\}$. Since the object of using such dynamical equations is not to produce real dynamics but to sample the phase space, we would really like each variable to move on the *same* time scale, so that there are no slow beads trailing behind the fast ones. This effect can be produced by choosing each parameter m_i' to be proportional to m_i: $m_i' = cm_i$. Finally, the forces on the u variables can be determined easily from the chain rule and the recursive inverse given above. The result is

$$\frac{1}{P}\frac{\partial U}{\partial u_1} = \frac{1}{P}\sum_{i=1}^{P}\frac{\partial U}{\partial x_i}$$

$$\frac{1}{P}\frac{\partial U}{\partial u_i} = \frac{1}{P}\left[\frac{(k-2)}{(k-1)}\frac{\partial U}{\partial u_{k-1}} + \frac{\partial U}{\partial x_k}\right]$$

where the first $(i=1)$ of these expressions starts the recursion in the second equation.

Later on, when we discuss applications of path integrals, we will see why a formulation such as this for evaluating path integrals is advantageous.

IV. PATH INTEGRALS FOR N-PARTICLE SYSTEMS

If particle spin statistics must be treated in a given problem, the formulation of the path integral is more complicated, and we will not treat this subject here. The extension of path integrals to N-particle systems in which spin statistics can safely be ignored, however, is straightforward, and we will give the expressions below.

The partition function for an N-particle system in the canonical ensemble without spin statistics can be formulated essentially by analogy to the one-particle case. The partition function that one obtains is

$$Q(N,V,T) = \lim_{P\to\infty}\left[\prod_{I=1}^{N}\left(\frac{m_I P}{2\pi\beta\hbar^2}\right)^{3P/2}\int d\mathbf{r}_I^{(1)}\cdots d\mathbf{r}_I^{(P)}\right]\exp\left[-\beta\sum_{i=1}^{P}\left(\sum_{I=1}^{N}\frac{1}{2}m_I\omega_P^2(\mathbf{r}_I^{(i+1)} - \mathbf{r}_I^{(i)})^2 + \frac{1}{P}U(\mathbf{r}_1^{(i)},...,\mathbf{r}_N^{(i)})\right)\right]$$

Thus, it can be seen that the N-particle potential must be evaluated for each imaginary time discretization, however, there is no coupling between separate imaginary time slices due arising from the potential. Thus, interactions occur only between particles in the *same* time slice. From a computational point of view, this is advantageous, as it allows for easily parallelization over imaginary time slices.

The corresponding energy and pressure estimators for the N-particle path integral are given by

$$\epsilon_P(\{\mathbf{r}^{(1)},...,\mathbf{r}^{(P)}\}) = \frac{3NP}{2\beta} - \sum_{i=1}^{P}\sum_{I=1}^{N}\frac{1}{2}m_I\omega_P^2\left(\mathbf{r}_I^{(i)} - \mathbf{r}_I^{(i+1)}\right)^2 + \frac{1}{P}\sum_{i=1}^{P}U(\mathbf{r}_1^{(i)},...,\mathbf{r}_N^{(i)})$$

$$p_P(\{\mathbf{r}^{(1)},...,\mathbf{r}^{(P)}\}) = \frac{NP}{\beta V} - \frac{1}{3V}\sum_{i=1}^{P}\sum_{I=1}^{N}\left[m_I\omega_P^2\left(\mathbf{r}_I^{(i)} - \mathbf{r}_I^{(i+1)}\right)^2 + \frac{1}{P}\mathbf{r}_I^{(i)}\cdot\nabla_{\mathbf{r}_I^{(i)}}U\right]$$