G25.2651: Statistical Mechanics

Notes for Lecture 3

I. THE CLASSICAL VIRIAL THEOREM (MICROCANONICAL DERIVATION)

Consider a system with Hamiltonian $H(x)$. Let $x_i$ and $x_j$ be specific components of the phase space vector. The classical virial theorem states that

$$ \langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij} $$

where the average is taken with respect to a microcanonical ensemble.

To prove the theorem, start with the definition of the average:

$$ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C}{\Omega(E)} \int dx x_i \frac{\partial H}{\partial x_j} \delta(E - H(x)) $$

where the fact that $\delta(x) = \delta(-x)$ has been used. Also, the $N$ and $V$ dependence of the partition function have been suppressed. Note that the above average can be written as

$$ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int dx x_i \frac{\partial H}{\partial x_j} \theta(E - H(x)) $$

$$ = \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x) < E} dx x_i \frac{\partial H}{\partial x_j} $$

$$ = \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x) < E} dx x_i \frac{\partial (H - E)}{\partial x_j} $$

However, writing

$$ x_i \frac{\partial (H - E)}{\partial x_j} = \frac{\partial}{\partial x_j} [x_i(H - E)] - \delta_{ij}(H - E) $$

allows the average to be expressed as

$$ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x) < E} dx \left\{ \frac{\partial}{\partial x_j} [x_i(H - E)] + \delta_{ij}(E - H(x)) \right\} $$

$$ = \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \left[ \int_{H - E} x_i(H - E) dS_j + \delta_{ij} \int_{H - E} dx (E - H(x)) \right] $$

The first integral in the brackets is obtained by integrating the total derivative with respect to $x_j$ over the phase space variable $x_j$. This leaves an integral that must be performed over all other variables at the boundary of phase space where $H = E$, as indicated by the surface element $dS_j$. But the integrand involves the factor $H - E$, so this integral will vanish. This leaves:

$$ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{C \delta_{ij}}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(x) < E} dx (E - H(x)) $$

$$ = \frac{C \delta_{ij}}{\Omega(E)} \int_{H(x) < E} dx $$

$$ = \frac{\delta_{ij}}{\Omega(E)} \Sigma(E) $$
where $\Sigma(E)$ is the partition function of the uniform ensemble. Recalling that

$$\Omega(E) = \frac{\partial}{\partial E} \Sigma(E)$$

we have

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} \frac{\Sigma(E)}{\delta(E)\Sigma(E)}$$

$$= \delta_{ij} \frac{1}{\frac{\partial \ln \Sigma(E)}{\partial E}}$$

$$= k\delta_{ij} \frac{1}{\frac{\partial S}{\partial E}}$$

$$= kT\delta_{ij}$$

which proves the theorem.

**Example:** $x_i = p_i$ and $i = j$. The virial theorem says that

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = kT$$

$$\langle \frac{p_i^2}{m_i} \rangle = kT$$

$$\langle \frac{p_i^2}{2m_i} \rangle = \frac{1}{2} kT$$

Thus, at equilibrium, the kinetic energy of each particle must be $kT/2$. By summing both sides over all the particles, we obtain a well known result

$$\sum_{i=1}^{3N} \langle \frac{p_i^2}{2m_i} \rangle = \sum_{i=1}^{3N} \langle \frac{1}{2} m_i v_i^2 \rangle = \frac{3}{2} NkT$$

**II. LEGENDRE TRANSFORMS**

The microcanonical ensemble involved the thermodynamic variables $N$, $V$ and $E$ as its variables. However, it is often convenient and desirable to work with other thermodynamic variables as the control variables. Legendre transforms provide a means by which one can determine how the energy functions for different sets of thermodynamic variables are related. The general theory is given below for functions of a single variable.

Consider a function $f(x)$ and its derivative

$$y = f'(x) = \frac{df}{dx} \equiv g(x)$$

The equation $y = g(x)$ defines a variable transformation from $x$ to $y$. Is there a unique description of the function $f(x)$ in terms of the variable $y$? That is, does there exist a function $\phi(y)$ that is equivalent to $f(x)$?

Given a point $x_0$, can one determine the value of the function $f(x_0)$ given only $f'(x_0)$? No, for the reason that the function $f(x_0) + c$ for any constant $c$ will have the same value of $f'(x_0)$ as shown in the figure below.
However, the value \( f(x_0) \) can be determined uniquely if we specify the slope of the line tangent to \( f \) at \( x_0 \), i.e., \( f'(x_0) \) and the \( y \)-intercept, \( b(x_0) \) of this line. Then, using the equation for the line, we have

\[
f(x_0) = x_0 f'(x_0) + b(x_0)
\]

This relation must hold for any general \( x \):

\[
f(x) = x f'(x) + b(x)
\]

Note that \( f'(x) \) is the variable \( y \), and \( x = g^{-1}(y) \), where \( g^{-1} \) is the functional inverse of \( g \), i.e., \( g(g^{-1}(x)) = x \). Solving for \( b(x) = b(g^{-1}(y)) \) gives

\[
b(g^{-1}(y)) = f(g^{-1}(y)) - yg^{-1}(y) \equiv \phi(y)
\]

where \( \phi(y) \) is known as the Legendre transform of \( f(x) \). In shorthand notation, one writes

\[
\phi(y) = f(x) - xy
\]

however, it must be kept in mind that \( x \) is a function of \( y \).

III. THE CANONICAL ENSEMBLE

A. Basic Thermodynamics

In the microcanonical ensemble, the entropy \( S \) is a natural function of \( N, V \) and \( E \), i.e., \( S = S(N, V, E) \). This can be inverted to give the energy as a function of \( N, V \), and \( S \), i.e., \( E = E(N, V, S) \). Consider using Legendre transformation to change from \( S \) to \( T \) using the fact that
\[ T = \left( \frac{\partial E}{\partial S} \right)_{N,V} \]

The Legendre transform \( \hat{E} \) of \( E(N,V,S) \) is

\[
\hat{E}(N,V,T) = E(N,V,S(T)) - S \frac{\partial E}{\partial S} \\
= E(N,V,S(T)) - TS
\]

The quantity \( \hat{E}(N,V,T) \) is called the Helmholtz free energy and is given the symbol \( A(N,V,T) \). It is the fundamental energy in the canonical ensemble.

The differential of \( A \) is

\[
dA = \left( \frac{\partial A}{\partial T} \right)_{N,V} dT + \left( \frac{\partial A}{\partial V} \right)_{N,T} dV + \left( \frac{\partial A}{\partial N} \right)_{T,V} dN
\]

However, from \( A = E - TS \), we have

\[
dA = dE - TdS - SdT
\]

From the first law, \( dE \) is given by

\[
dE = TdS - PdV + \mu dN
\]

Thus,

\[
dA = -PdV - SdT + \mu dN
\]

Comparing the two expressions, we see that the thermodynamic relations are

\[
S = - \left( \frac{\partial A}{\partial T} \right)_{N,V} \\
P = - \left( \frac{\partial A}{\partial V} \right)_{N,T} \\
\mu = \left( \frac{\partial A}{\partial N} \right)_{V,T}
\]

**B. The partition function**

Consider two systems (1 and 2) in thermal contact such that

\[
N_2 \gg N_1 \\
E_2 \gg E_1 \\
N = N_1 + N_2; \quad E = E_1 + E_2
\]

and the total Hamiltonian is just \( H(x) = H_1(x_1) + H_2(x_2) \)

Since system 2 is infinitely large compared to system 1, it acts as an infinite heat reservoir that keeps system 1 at a constant temperature \( T \) without gaining or losing an appreciable amount of heat, itself. Thus, system 1 is maintained at canonical conditions, \( N, V, T \).

The full partition function \( \Omega(N,V,E) \) for the combined system is the microcanonical partition function

\[
\Omega(N,V,E) = \int dx_1 \delta(H_1(x_1) + H_2(x_2) - E) = \int dx dx_2 \delta(H_1(x_1) + H_2(x_2) - E)
\]

Now, we define the distribution function, \( f(x_1) \) of the phase space variables of system 1 as
\[ f(x_1) = \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E) \]

Taking the natural log of both sides, we have

\[ \ln f(x_1) = \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E) \]

Since \( E_2 \gg E_1 \), it follows that \( H_2(x_2) \gg H_1(x_1) \), and we may expand the above expression about \( H_1 = 0 \). To linear order, the expression becomes

\[
\ln f(x_1) = \ln \left( \int dx_2 \delta(H_2(x_2) - E) + H_1(x_1) \frac{\partial}{\partial H_1(x_1)} \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E) \right)_{H_1(x_1) = 0} \\
= \ln \left( \int dx_2 \delta(H_2(x_2) - E) \right) - H_1(x_1) \frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E)
\]

where, in the last line, the differentiation with respect to \( H_1 \) is replaced by differentiation with respect to \( E \). Note that

\[
\ln \int dx_2 \delta(H_2(x_2) - E) = \frac{S_2(E)}{k}
\]

\[
\frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E) = \frac{\partial}{\partial E} \frac{S_2(E)}{k} = \frac{1}{kT}
\]

where \( T \) is the common temperature of the two systems. Using these two facts, we obtain

\[
\ln f(x_1) = \frac{S_2(E)}{k} - \frac{H_1(x_1)}{kT} \\
f(x_1) = e^{S_2(E)/k} e^{-H_1(x_1)/kT}
\]

Thus, the distribution function of the canonical ensemble is

\[ f(x) \propto e^{-\beta H(x) / kT} \]

The prefactor \( \exp(S_2(E)/k) \) is an irrelevant constant that can be disregarded as it will not affect any physical properties.

The normalization of the distribution function is the integral:

\[
\int dx e^{-\beta H(x) / kT} = Q(N, V, T)
\]

where \( Q(N, V, T) \) is the canonical partition function. It is convenient to define an inverse temperature \( \beta = 1 / kT \). \( Q(N, V, T) \) is the canonical partition function. As in the microcanonical case, we add in the \textit{ad hoc} quantum corrections to the classical result to give

\[
Q(N, V, T) = \frac{1}{N!h^{3N}} \int dx e^{-\beta H(x)}
\]

The thermodynamic relations are thus,

Helmholtz free energy:

\[ A(N, V, T) = -\frac{1}{\beta} \ln Q(N, V, T) \]

To see that this must be the definition of \( A(N, V, T) \), recall the definition of \( A \):

\[ A = E - TS = \langle H(x) \rangle - TS \]
But we saw that

\[ S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \]

Substituting this in gives

\[ A = \langle H(x) \rangle - T \frac{\partial A}{\partial T} \]

or, noting that

\[ \frac{\partial A}{\partial T} = \frac{\partial A}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2} \frac{\partial A}{\partial \beta} \]

it follows that

\[ A = \langle H(x) \rangle + \beta \frac{\partial A}{\partial \beta} \]

This is a simple differential equation that can be solved for \( A \). We will show that the solution is

\[ A = -\frac{1}{\beta} \ln Q(\beta) \]

Note that

\[ \beta \frac{\partial A}{\partial \beta} = \frac{1}{\beta} \ln Q(\beta) - \frac{1}{Q} \frac{\partial Q}{\partial \beta} = A - \langle H(x) \rangle \]

Substituting in gives, therefore

\[ A = \langle H(x) \rangle + A - \langle H(x) \rangle = A \]

so this form of \( A \) satisfies the differential equation.

Other thermodynamics follow:

**Average energy:**

\[ E = \langle H(x) \rangle = \frac{1}{Q} C_N \int dx H(x)e^{-\beta H(x)} = -\frac{\partial}{\partial \beta} \ln Q(N,V,T) \]

**Pressure:**

\[ P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT \left(\frac{\partial \ln Q(N,V,T)}{\partial V}\right)_{N,T} \]

**Entropy:**

\[ S = -\frac{\partial A}{\partial T} = -\frac{\partial A}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{1}{kT^2} \frac{\partial A}{\partial \beta} \]

\[ = k\beta^2 \frac{\partial}{\partial \beta} \left(\frac{1}{\beta} \ln Q(N,V,T)\right) = -k\beta \frac{\partial}{\partial \beta} \ln Q + k \ln Q \]

\[ = k\beta E + k \ln Q = k \ln Q + \frac{E}{T} \]
Heat capacity at constant volume:

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_{N,V} = \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T} = k\beta^2 \frac{\partial}{\partial \beta^2} \ln Q(N,V,T) \]

C. Relation between canonical and microcanonical ensembles

We saw that the \( E(N,V,S) \) and \( A(N,V,T) \) could be related by a Legendre transformation. The partition functions \( \Omega(N,V,E) \) and \( Q(N,V,T) \) can be related by a Laplace transform. Recall that the Laplace transform \( \tilde{f}(\lambda) \) of a function \( f(x) \) is given by

\[ \tilde{f}(\lambda) = \int_0^\infty dx e^{-\lambda x} f(x) \]

Let us compute the Laplace transform of \( \Omega(N,V,E) \) with respect to \( E \):

\[ \tilde{\Omega}(N,V,\lambda) = C_N \int_0^\infty dE e^{-\lambda E} \int dx \delta(H(x) - E) \]

Using the \( \delta \)-function to do the integral over \( E \):

\[ \tilde{\Omega}(N,V,\lambda) = C_N \int dx e^{-\lambda H(x)} \]

By identifying \( \lambda = \beta \), we see that the Laplace transform of the microcanonical partition function gives the canonical partition function \( Q(N,V,T) \).

D. Classical Virial Theorem (canonical ensemble derivation)

Again, let \( x_i \) and \( x_j \) be specific components of the phase space vector \( x = (p_1, \ldots, p_{3N}, q_1, \ldots, q_{3N}) \). Consider the canonical average

\[ \langle x_i \frac{\partial H}{\partial x_j} \rangle \]

given by

\[ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{Q} C_N \int dx x_i \frac{\partial H}{\partial x_j} e^{-\beta H(x)} \]

\[ = \frac{1}{Q} C_N \int dx x_i \left( \frac{1}{\beta} \frac{\partial}{\partial x_j} \right) e^{-\beta H(x)} \]

But

\[ x_i \frac{\partial}{\partial x_j} e^{-\beta H(x)} = \frac{\partial}{\partial x_j} \left( x_i e^{-\beta H(x)} \right) - e^{-\beta H(x)} \frac{\partial x_i}{\partial x_j} \]

\[ = \frac{\partial}{\partial x_j} \left( x_i e^{-\beta H(x)} \right) - \delta_{ij} e^{-\beta H(x)} \]

Thus,

\[ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta Q} C_N \int dx \frac{\partial}{\partial x_j} \left( x_i e^{-\beta H(x)} \right) + \frac{1}{\beta Q} \delta_{ij} C_N \int dx e^{-\beta H(x)} \]

\[ = \frac{1}{\beta Q} C_N \int dx' \int dx_j \frac{\partial}{\partial x_j} \left( x_i e^{-\beta H(x)} \right) + kT \delta_{ij} \]

\[ = \int dx' x_i e^{-\beta H(x')} \bigg|_{x_j = -\infty}^{\infty} + kT \delta_{ij} \]

Several cases exist for the surface term \( x_i \exp(-\beta H(x)) \):
1. \( x_i = p_i \) a momentum variable. Then, since \( H \sim p_i^2 \), \( \exp(-\beta H) \) evaluated at \( p_i = \pm \infty \) clearly vanishes.

2. \( x_i = q_i \) and \( U \to \infty \) as \( q_i \to \pm \infty \), thus representing a bound system. Then, \( \exp(-\beta H) \) also vanishes at \( q_i = \pm \infty \).

3. \( x_i = q_i \) and \( U \to 0 \) as \( q_i \to \pm \infty \), representing an unbound system. Then the exponential tends to 1 both at \( q_i = \pm \infty \), hence the surface term vanishes.

4. \( x_i = q_i \) and the system is periodic, as in a solid. Then, the system will be represented by some supercell to which periodic boundary conditions can be applied, and the coordinates will take on the same value at the boundaries. Thus, \( H \) and \( \exp(-\beta H) \) will take on the same value at the boundaries and the surface term will vanish.

5. \( x_i = q_i \), and the particles experience elastic collisions with the walls of the container. Then there is an infinite potential at the walls so that \( U \to \infty \) at the boundary and \( \exp(-\beta H) \to 0 \) at the boundary.

Thus, we have the result

\[
\langle x_i \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}
\]

The above cases cover many but not all situations, in particular, the case of a system confined within a volume \( V \) with reflecting boundaries. Then, surface contributions actually give rise to an observable pressure (to be discussed in more detail in the next lecture).