

G25.2651: Statistical Mechanics

Notes for Lecture 4

I. THE CLASSICAL VIRIAL THEOREM (MICROCANONICAL DERIVATION)

Consider a system with Hamiltonian $H(\mathbf{x})$. 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:

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

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

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int d\mathbf{x} x_i \frac{\partial H}{\partial x_j} \theta(E - H(\mathbf{x})) \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(\mathbf{x}) < E} d\mathbf{x} x_i \frac{\partial H}{\partial x_j} \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(\mathbf{x}) < E} d\mathbf{x} x_i \frac{\partial(H - E)}{\partial x_j} \end{aligned}$$

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

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(\mathbf{x}) < E} d\mathbf{x} \left\{ \frac{\partial}{\partial x_j} [x_i(H - E)] + \delta_{ij}(E - H(\mathbf{x})) \right\} \\ &= \frac{C}{\Omega(E)} \frac{\partial}{\partial E} \left[\oint_{H=E} x_i(H - E) dS_j + \delta_{ij} \int_{H < E} d\mathbf{x} (E - H(\mathbf{x})) \right] \end{aligned}$$

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:

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{C \delta_{ij}}{\Omega(E)} \frac{\partial}{\partial E} \int_{H(\mathbf{x}) < E} d\mathbf{x} (E - H(\mathbf{x})) \\ &= \frac{C \delta_{ij}}{\Omega(E)} \int_{H(\mathbf{x}) < E} d\mathbf{x} \\ &= \frac{\delta_{ij}}{\Omega(E)} \Sigma(E) \end{aligned}$$

where $\Sigma(E)$ is the partition function of the uniform ensemble. Recalling that

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

we have

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \delta_{ij} \frac{\Sigma(E)}{\frac{\partial \Sigma(E)}{\partial E}} \\ &= \delta_{ij} \frac{1}{\frac{\partial \ln \Sigma(E)}{\partial E}} \\ &= k \delta_{ij} \frac{1}{\frac{\partial S}{\partial E}} \\ &= kT \delta_{ij} \end{aligned}$$

which proves the theorem.

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

$$\begin{aligned} \left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle &= kT \\ \left\langle \frac{p_i^2}{m_i} \right\rangle &= kT \\ \left\langle \frac{p_i^2}{2m_i} \right\rangle &= \frac{1}{2} kT \end{aligned}$$

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 know result

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

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.

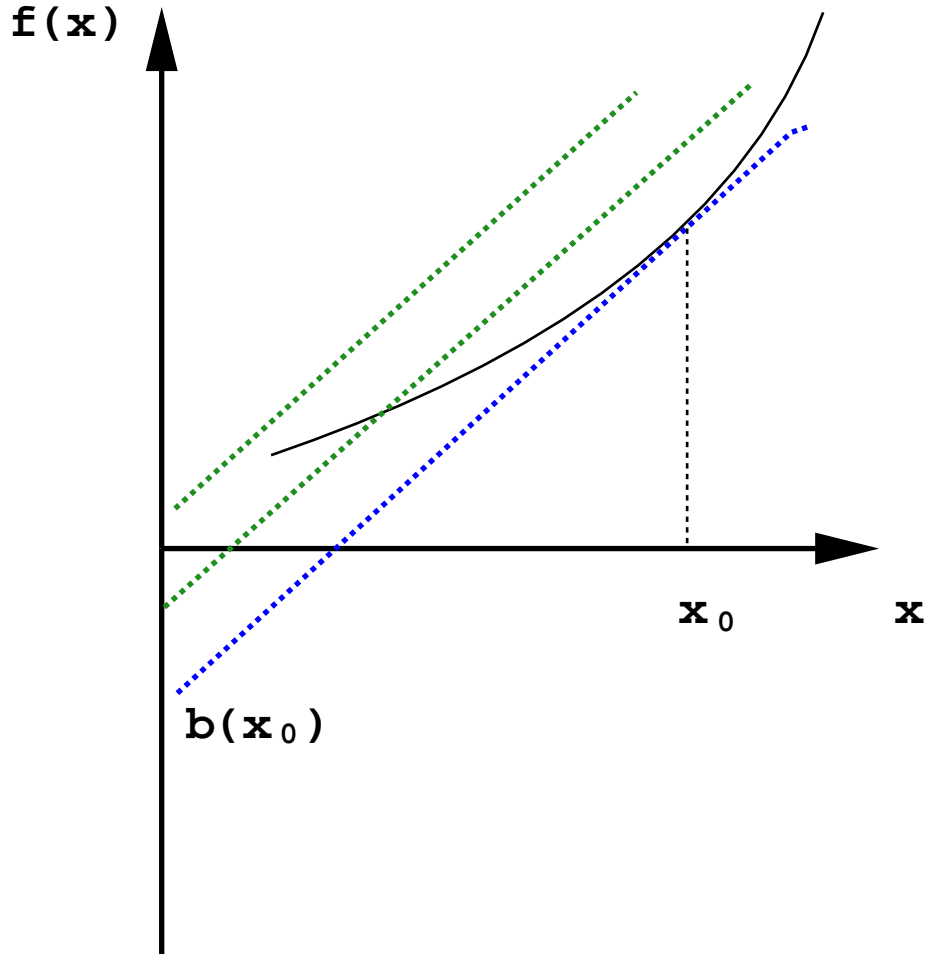


FIG. 1.

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

$$b(g^{-1}(y)) = f(g^{-1}(y)) - y g^{-1}(y) \equiv \phi(y)$$

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 \tilde{E} of $E(N, V, S)$ is

$$\begin{aligned} \tilde{E}(N, V, T) &= E(N, V, S(T)) - S \frac{\partial E}{\partial S} \\ &= E(N, V, S(T)) - TS \end{aligned}$$

The quantity $\tilde{E}(N, V, T)$ 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

$$\begin{aligned} S &= - \left(\frac{\partial A}{\partial T} \right)_{N,V} \\ P &= - \left(\frac{\partial A}{\partial V} \right)_{N,T} \\ \mu &= \left(\frac{\partial A}{\partial N} \right)_{V,T} \end{aligned}$$

B. The partition function

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

$$\begin{aligned} N_2 &\gg N_1 \\ E_2 &\gg E_1 \\ N &= N_1 + N_2; & E &= E_1 + E_2 \\ \dim(\mathbf{x}_1) &\gg \dim(\mathbf{x}_2) \end{aligned}$$

and the total Hamiltonian is just $H(\mathbf{x}) = H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2)$

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

$$\Omega(N, V, E) = \int d\mathbf{x} \delta(H(\mathbf{x}) - E) = \int d\mathbf{x}_1 d\mathbf{x}_2 \delta(H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2) - E)$$

Now, we define the distribution function, $f(\mathbf{x}_1)$ of the phase space variables of system 1 as

$$f(\mathbf{x}_1) = \int d\mathbf{x}_2 \delta(H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2) - E)$$

Taking the natural log of both sides, we have

$$\ln f(\mathbf{x}_1) = \ln \int d\mathbf{x}_2 \delta(H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2) - E)$$

Since $E_2 \gg E_1$, it follows that $H_2(\mathbf{x}_2) \gg H_1(\mathbf{x}_1)$, and we may expand the above expression about $H_1 = 0$. To linear order, the expression becomes

$$\begin{aligned} \ln f(\mathbf{x}_1) &= \ln \int d\mathbf{x}_2 \delta(H_2(\mathbf{x}_2) - E) + H_1(\mathbf{x}_1) \left. \frac{\partial}{\partial H_1(\mathbf{x}_1)} \ln \int d\mathbf{x}_2 \delta(H_1(\mathbf{x}_1) + H_2(\mathbf{x}_2) - E) \right|_{H_1(\mathbf{x}_1)=0} \\ &= \ln \int d\mathbf{x}_2 \delta(H_2(\mathbf{x}_2) - E) - H_1(\mathbf{x}_1) \frac{\partial}{\partial E} \ln \int d\mathbf{x}_2 \delta(H_2(\mathbf{x}_2) - E) \end{aligned}$$

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

$$\begin{aligned} \ln \int d\mathbf{x}_2 \delta(H_2(\mathbf{x}_2) - E) &= \frac{S_2(E)}{k} \\ \frac{\partial}{\partial E} \ln \int d\mathbf{x}_2 \delta(H_2(\mathbf{x}_2) - E) &= \frac{\partial}{\partial E} \frac{S_2(E)}{k} = \frac{1}{kT} \end{aligned}$$

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

$$\begin{aligned} \ln f(\mathbf{x}_1) &= \frac{S_2(E)}{k} - \frac{H_1(\mathbf{x}_1)}{kT} \\ f(\mathbf{x}_1) &= e^{S_2(E)/k} e^{-H_1(\mathbf{x}_1)/kT} \end{aligned}$$

Thus, the distribution function of the canonical ensemble is

$$f(\mathbf{x}) \propto e^{-H(\mathbf{x})/kT}$$

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:

$$\int d\mathbf{x} e^{-H(\mathbf{x})/kT} \equiv Q(N, V, T)$$

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 *ad hoc* quantum corrections to the classical result to give

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int d\mathbf{x} e^{-\beta H(\mathbf{x})}$$

The thermodynamic relations are thus,

Hemlholtz 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 :

$$A = E - TS = \langle H(\mathbf{x}) \rangle - TS$$

But we saw that

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

Substituting this in gives

$$A = \langle H(\mathbf{x}) \rangle - T \frac{\partial A}{\partial T}$$

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

$$A = \langle H(\mathbf{x}) \rangle + \beta \frac{\partial A}{\partial \beta}$$

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

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

Substituting in gives, therefore

$$A = \langle H(\mathbf{x}) \rangle + A - \langle H(\mathbf{x}) \rangle = A$$

so this form of A satisfies the differential equation.

Other thermodynamics follow:

Average energy:

$$\begin{aligned} E = \langle H(\mathbf{x}) \rangle &= \frac{1}{Q} C_N \int d\mathbf{x} H(\mathbf{x}) e^{-\beta H(\mathbf{x})} \\ &= - \frac{\partial}{\partial \beta} \ln Q(N, V, T) \end{aligned}$$

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:

$$\begin{aligned} S &= - \frac{\partial A}{\partial T} = - \frac{\partial A}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{1}{kT^2} \frac{\partial A}{\partial \beta} \\ &= k\beta^2 \frac{\partial}{\partial \beta} \left(- \frac{1}{\beta} \ln Q(N, V, T) \right) = -k\beta \frac{\partial \ln Q}{\partial \beta} + k \ln Q \\ &= k\beta E + k \ln Q = k \ln Q + \frac{E}{T} \end{aligned}$$

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 :

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

Using the δ -function to do the integral over E :

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

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 $\mathbf{x} = (p_1, \dots, p_{3N}, q_1, \dots, q_{3N})$. Consider the canonical average

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$$

given by

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \frac{1}{Q} C_N \int dx x_i \frac{\partial H}{\partial x_j} e^{-\beta H(\mathbf{x})} \\ &= \frac{1}{Q} C_N \int dx x_i \left(-\frac{1}{\beta} \frac{\partial}{\partial x_j} \right) e^{-\beta H(\mathbf{x})} \end{aligned}$$

But

$$\begin{aligned} x_i \frac{\partial}{\partial x_j} e^{-\beta H(\mathbf{x})} &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(\mathbf{x})} \right) - e^{-\beta H(\mathbf{x})} \frac{\partial x_i}{\partial x_j} \\ &= \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(\mathbf{x})} \right) - \delta_{ij} e^{-\beta H(\mathbf{x})} \end{aligned}$$

Thus,

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= -\frac{1}{\beta Q} C_N \int dx \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(\mathbf{x})} \right) + \frac{1}{\beta Q} \delta_{ij} C_N \int dx e^{-\beta H(\mathbf{x})} \\ &= -\frac{1}{\beta Q} C_N \int dx' \int dx_j \frac{\partial}{\partial x_j} \left(x_i e^{-\beta H(\mathbf{x})} \right) + kT \delta_{ij} \\ &= \int dx' x_i e^{-\beta H(\mathbf{x})} \Big|_{x_j=-\infty}^{\infty} + kT \delta_{ij} \end{aligned}$$

Several cases exist for the surface term $x_i \exp(-\beta H(\mathbf{x}))$:

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 $U \rightarrow \infty$ as $q_i \rightarrow \pm\infty$, thus representing a bound system. Then, $\exp(-\beta H)$ also vanishes at $q_i = \pm\infty$.
3. $x_i = q_i$ and $U \rightarrow 0$ as $q_i \rightarrow \pm\infty$, 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 $U \rightarrow \infty$ at the boundary and $\exp(-\beta H) \rightarrow 0$ at the boundary.

Thus, we have the result

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

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).