Chapter 7

Microcanonical Ensemble (E,V,N)

2. Entropy

The expectation value of a classical observable $O(q,p)$ can be obtained by averaging over the probability density $\rho(q,p)$ of the Microcanonical ensemble,

$$\langle O\rangle = \iint d^{3N}q d^{3N}p\ O(q,p) = \frac{1}{\Gamma(E,V,N)} \iint_{E<H(q,p)<E+\Delta} d^{3N}q d^{3N}p\, O(q,p)$$

$$= \frac{\iint_{E<H(q,p)<E+\Delta} d^{3N}q d^{3N}p\, O(q,p)}{\iint_{E<H(q,p)<E+\Delta} d^{3N}q d^{3N}p}$$

For 1D and one particle N=1,

$$= \frac{\iint_{E<H(q,p)<E+\Delta} dx dp_x\, O(x,p_x)}{\iint_{E<H(q,p)<E+\Delta} dx dp_x}$$

The entropy can however not been be obtained as an average of a classical observable. It is instead a function of the overall number of available states.

POSTULATE The entropy is, according to Boltzmann, proportional to the

Logarithm of the number of available states, as measured by the phase space volume Γ:

$$S = k_B \ln\left(\frac{\Gamma(E,V,N)}{\Gamma_0(N)}\right) = S = k_B \ln \omega$$

The number of accessible microstates $\omega(E,V,N) = e^{\frac{S}{k_B}}$ Is equivalent to "micro canonical partition function"

Normalization factor. The normalization constant $\Gamma_0(N)$ introduced in (5) has two functionalities.

– $\Gamma_0(N)$ cancels the dimensions of $\Gamma(E,V,N)$. The argument of the logarithm is consequently dimensionless.

– The number of particles N is one of the fundamental thermodynamic variables. The functional dependence of $\Gamma_0(N)$ on N is hence important.

Incompleteness of classical statistics. It is not possible to determine $\Gamma_0(N)$ correctly within classical statistics. We can derive that $\Gamma_0(N)$) takes the value

$$\boxed{\Gamma_0(N) = h^{3N} N!},$$

in quantum statistics, where h = 6.63 · 10^{-34} m^2kg/s is the Planck constant. We consider this value also for classical statistics.

– The factor h^{3N} defines the reference measure in phase space which has the dimensions $[q]^{3N}[p]^{3N}$. Note that $[h] = m(kgm/s) = [q][p]$

– $N!$ is the counting factor for states obtained by permuting particles.

The factor $N!$ arises from the fact that particles are indistinguishable.

Even though one may be in a temperature and density range where the motion of molecules can be treated to a very good approximation by classical mechanics, one cannot go so far as to disregard the essential indistinguishability of the molecules;

one cannot observe and label individual atomic particles as though they were macroscopic billiard balls.

Example: The energy of Einstein oscillator is given by $E_i = n_i h\nu$ if there is N no of oscillator in the 3D system which has total energy E at temperature T.

(a) Write down micro canonical partition function Ω .

(b) What is entropy of the system?

Solution: (a) Ω is no. of microstate which is equivalent to $\Omega = \sum_1^{3N} n_i \Rightarrow \sum_1^{3N} \frac{E_i}{h\nu}$

$\Omega = \sum_1^{3N} \frac{E_i}{h\nu} \Rightarrow \frac{E}{h\nu}$ where $\sum_1^{3N} E_i \Rightarrow E$

Example: If there is N no. of particle which have spin $\frac{3}{2}$ which will interact with magnetic field B which are in equilibrium at temperature T .

(a) How many no. of microstate for each particle

(b) What is entropy of the system.

Solution: (a) if $s = \frac{3}{2}$ then z component of spin i.e. $s_Z = \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$ so there is 4 microstate for each particle

For the *N* number of particle there will be 4^N number of state.

(b) $S = k_B \ln \Omega$, where $\Omega = 4^N$ for given system. So $S = Nk_B \ln 4$

Example: A solid contain N magnetic atoms having spin $\frac{1}{2}$. At sufficiently high temperature each spin is completely random oriented .at sufficiently low temperature all the spin become oriented in same direction let the heat capacity as a function of temperature T by

$$c(T) = a\left(\frac{2T}{T_1} - 1\right) \qquad \text{if } \frac{T_1}{2} < T < T_1$$
$$= 0 \qquad \text{otherwise}$$

Find the value of "a".

Solution: At very low temperature all spins are oriented in only one direction, so there is only one possible microstate for each atom. Hence entropy is $S_1 = 0$ at high temperature all the spins are randomly oriented and they can be either in up or down microstate so there are two microstate for each atom, hence for N number of atom entropy is given by $S_2 = Nk_B \ln 2$. So $S_2 - S_1 = Nk_B \ln 2$, which is determined by theoretical calculation.

Now from the given expression of heat capacity, we have relation $c = \frac{Tds}{dT}$.

$$S(\infty) - S(0) \Rightarrow S_2 - S_1 = \int_0^{\infty} \frac{c}{T} dT = \int_{\frac{T_1}{2}}^{T_1} a\left(\frac{2T}{T_1} - 1\right)\frac{dT}{T}$$

So $a = \frac{Nk \ln 2}{1 - \ln 2}$