PHYS 3014: Statistical Mechanics

Lecture Notes
Part 5

Canonical Ensemble: Partition Function

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Canonical Ensemble

The microcanonical ensembles with natural variables E, V and N are suitable for isolated systems. For microcanonical ensemble postulate of equal a priori probability is strictly applied.

Practically, it is very difficult to maintain a constant value of energy for a system. The total energy of system is hardly ever measured and as well as impossible to control its value. other difficulty is how to specify the width of ergodic shell between E and E+Δ in any case.

So we define new ensemble whose physical parameters could easily be controlled.

If we consider a system at constant temperature T, then temperature could easily be measured as well as controlled by placing a heat reservoir in contact with the system. The reservoir should have large heat capacity so that irrespective of the energy exchange between system and reservoir, the overall constant temperature can be maintained.

We can now construct an ensemble of systems. If the reservoir consists of infinitely large no. of mental copies of a given system then such collections of many systems have same N, V and T defines an ensemble called as **Canonical Ensemble**.

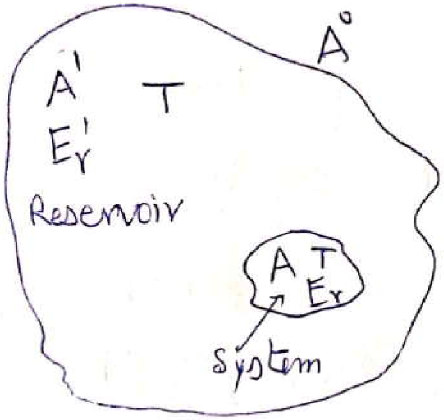
In canonical ensemble, energy E of the system is variable. It can take any value between zero and infinity.

We can find out the probability P_r at any time t, that a system in the ensemble is found to be in one of the state characterized by energy value E_r.

This can be calculated by two ways. In first we can regard the system as in equilibrium with the heat reservoir at a common temperature T and study the statistics of the energy exchange between the system and heat reservoir.

In second we regard the system as member of a canonical ensemble defined by N, V and T in which energy E is shared among N identical systems consisting the ensemble and studying the statistics of sharing process.

Equilibrium between a system and a heat reservoir



Consider a given system A is in contact with a very large heat reservoir A'. At equilibrium both are at common temperature T.

The total energy of the A^0 i.e composite system $(A+A')$ is E^0 which is constant. So the energies of the system and reservoir can have any value between 0 and E° at any time. If at any instant, system is in a state characterized by energy E_r then reservoir must have an energy E_r' such that

$$E_r + E_r' = E^\circ = \text{Constant}$$

Since the reservoir is larger than the given system, so the practical value of E_r is very small in comparison to E°. So we must have

$$\frac{E_r}{E^\circ} = \left(1 - \frac{E_r'}{E^\circ}\right) << 1$$

If A is in one definite state r, then the no. of states accessible to the composite system A° is equal to the no. of states $\Omega'(E^\circ - E_r)$ accessible to A' with the energy E_r'. Larger is the no. of states available to the reservoir assuming the particular value E_r', larger will be its probability to assume that energy E_r' and hence larger will be the probability of the system A to assume corresponding energy E_r.

The probability of occurence of a situation where A is in state r is proportional to the number of states accessible to A^0

$$P_r = C' \Omega'(E^0 - E_r)$$

C' is constant of proportionality independent of r.

Since $E_r << E^0$, we can expand $\Omega'(E^0 - E_r)$

around the value $E'_r = E^\circ$ i.e around $E_r = 0$

Due to reasons of convergence, we expand $\ln \Omega'(E'_r)$ about $E'_r = E^\circ$.

$$\ln \Omega'(E'_r) = \ln \Omega'(E^\circ - E_r)$$

$$= \ln \Omega'(E^\circ) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E^\circ} \cdot (E'_r - E^\circ) + \cdots$$

$$\simeq \text{Constant} + \beta'(-E_r)$$

$$\because \left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} = \beta$$

In equilibrium.

$\beta' = \beta = \frac{1}{KT}$ and $\Omega'(E^\circ)$ is a constant independent of r.

$$\therefore \quad \Omega'(E'_r) = \Omega'(E^\circ) \exp(-\beta E_r)$$

$$\therefore \quad P_r = C \exp(-\beta E_r)$$

On normalization, we get $C = \dfrac{1}{\sum_r \exp(-\beta E_r)}$

where summation goes over all states accessible to the system A.

$$\therefore \quad P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$$

It shows that the probability of occurrence of a situation when the system A is in a state defined by E_r decreases with increasing E_r. The exponential factor $e^{-\beta E_r}$ is called the Boltzmann factor. The probability distribution $P_r = C e^{-\beta E_r}$ is called as canonical distribution.

An ensemble of systems all of which are in contact with a heat reservoir at constant temperature T & are distributed over energy states in accordance with $P_r = Ce^{-\beta E_r}$ is called a Canonical Ensemble.

The quantity $\sum_r e^{-\beta E_r} = Z$ is called the canonical partition function. It is "sum over states". It reflects the way in which Z measures how energy is partitioned among states of the system.

For classical system, one has to integrate over the phase space. A microstate is represented by (q_r, p_r) and summation $\sum_r \rightarrow \frac{1}{h^{3N}} \int dq^{3N} dp^{3N}$

$\therefore$ partition function $Z = \frac{1}{h^{3N}} \int dq^{3N} dp^{3N} \exp\{-\beta H(q_r, p_r)\}$

and probability distribution function (Canonical phase space density)

$$P_c(q_r, p_r) = \frac{\exp\{-\beta H(q_r, p_r)\}}{Z}$$

These are for distinguishable particles. For non-distinguishable particles, partition function is given by

$$Z = \frac{1}{\lfloor N \, h^{3N}} \int dq^{3N} dp^{3N} \exp\{-\beta H(q_r, p_r)\}.$$

A System in the Canonical Ensemble

Consider an ensemble of $\mathcal{N}$ identical systems sharing a total energy E. $\mathcal{N}$ is different than N which is the total no. of particle in a system. E_r are the energy eigen values of the systems.

If n_r is the no. of systems in the ensemble which have energy eigen values E_r at any time t, then for the set of numbers $\{n_r\}$ we must have

$$\left.\begin{aligned} \sum_r n_r &= \mathcal{N} \\ \sum_r n_r E_r &= E = \mathcal{N}U \end{aligned}\right\} \quad \text{---} \; (1)$$

where U denotes the average energy per

system in the ensemble.

Any set $\{n_r\}$ satisfying the Condition (1) can be Considered as a possible mode of distribution of total energy E among N systems in the ensemble.

The no. of different ways for occurence of such mode is

$$W\{n_r\} = \frac{\lfloor N}{\lfloor n_0 \lfloor n_1 \lfloor n_2 \cdots \lfloor n_r \cdots} \quad \text{---} \quad (2)$$

subjected to the condition (1), there are many possible states of ensemble which are equally likely to occur. The frequency with which distribution set $\{n_r\}$ may appear will be proportional to the number $W\{n_r\}$. For most probable distribution, the number $W\{n_r\}$ is maximum.

For finding most probable distribution, we have to maximize

$$\ln W = \ln(\lfloor N) - \sum_r \ln(\lfloor n_r) \quad — ③$$

In the limit when $N \to \infty$, n_r also tends to ∞ then using Stirling formula

$$\ln W = N \ln N - N - \sum_r (n_r \ln n_r - n_r)$$

$$= N \ln N - \sum_r n_r \ln n_r \quad — ④$$

$\because N = \sum_r n_r$

If we shift the set $\{n_r\}$ to a slightly different set $\{n_r + \delta n_r\}$ then the change in $\ln W$ will be

$$\delta(\ln W) = - \sum_r (\ln n_r + 1)\, \delta n_r \quad --- ⑤$$

The variation δn_r also satisfies $\sum_r \delta n_r = 0 \quad -- ⑥$

$$\sum_r E_r \delta n_r = 0 \quad -- ⑦$$

If set $\{n_r\}$ is maximal, then $\delta(\ln W) = 0$. By using Lagrange multiplier method, we have

$$\sum_r \{-(\ln n_r + 1) - \alpha - \beta E_r\} \delta n_r = 0 \quad --- (8)$$

δn_r is arbitrary, so for set $\{n_r\}$ to be maximal we have for each r

$$\ln n_r = -(\alpha+1) - \beta E_r$$

$$\Rightarrow \quad n_r = c \exp(-\beta E_r) \quad --- (9)$$

where $c = e^{-(\alpha+1)}$ is another constant

$\therefore$ probability of finding a system with energy E_r in the ensemble is

$$P_r = \frac{n_r}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad --- (10)$$

Equation (9) shows the most probable distribution of energy among the various systems of the ensemble.

The statistical mean value of all energy E_r which are assumed in the ensemble is

$$U = \frac{E}{\mathcal{N}} = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad \cdots \quad (11)$$

Ensemble average of a thermodynamic quantity A is defined as

$$\bar{A} = \frac{\sum_r A_r P_r}{\sum_r P_r} = \frac{\sum_r A_r n_r}{\sum_r n_r}$$

$$= \sum_r A_r P_r$$ If probability P_r is normalized to unity.

References:

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Thank You

For any questions/doubts/suggestions and submission of assignments

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