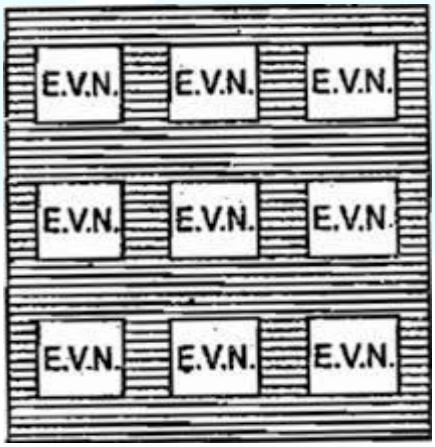
Statistical Ensemble

Microcanonical Ensemble

Microcanonical ensemble is a collection of independent systems of constant volume separated from the neighbourhood with rigid impermeable adiabatic walls. N, V and E remains constant, N is the total number of particles in the system. V and E are the volume and energy of the system respectively.

Consider a system for which the total energy H(q, p) = E is conserved.
i . e E (q_1 ..... . q_f, p_1 ..... p_f)= a constant

The locus of all the phase points having the same value for energies in the phase space is called an energy surface or ergodic surface. A number of such energy surfaces can be constructed in the phase space. Each energy surface divides the phase space into two parts, one of lower energy and the other of higher energy. Since the two are of different energies they do not intersect each other.



Let E and E + δE be the two neighbouring ergodic surfaces. The phase volume in between the two surfaces encloses a certain number of phase points and will be a constant. Let us assume the density to be zero for all values of energy except in a arrow range of energy between E and E + δE . Then the ensemble specified in terms of ρ as,

$$\rho = \begin{cases} a\ constant, in\ the\ region\ between\ \mathrm{E}\ \text{and}\ \mathrm{E}\ +\ \delta\mathrm{E} \\ 0, outside\ this\ region \end{cases}$$

Is called a micro canonical ensemble.

ρ is a function of energy. Here ρ is constant and hence E is also constant. So the ensemble is in statistical equilibrium. Since ρ is a constant within the energy shell, the distribution of phase points is also uniform, by Lioville's theorem. As the ensemble is in statistical equilibrium, the average properties predicted will not change with time.

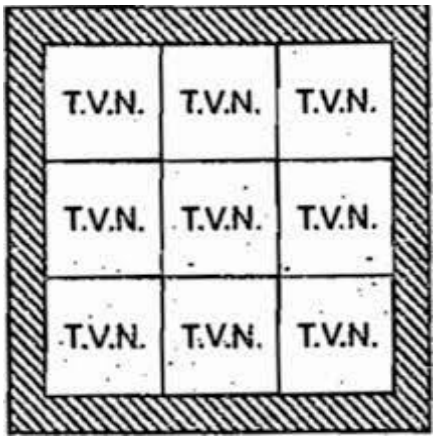
A microcanonical ensemble can be obtained from uniform ensemble by neglecting those systems whose phase points do not lie within the phase space corresponding to the energy range between E and E + δE.

A microcanonical ensemble is an idealised concept and hence cannot exist in practice because the systems which we come across always interact with their surroundings, either thermally or mechanically.

In a microcanonical ensemble there is exchange of neither energy nor particles among the systems.

Canonical Ensemble

Canonical ensemble is a collection of independent systems of constant volume separated from the neighbourhood by **rigid impermeable, diathermic** walls so that the system are in thermal equilibrium. The particles can exchange energy and hence all the systems will attain the same temperature. The systems have the same temperature T and constant volume v . The number of particles N is also constant. In **canonical ensemble systems can exchange energy and not particles.**



Grand Canonical Ensemble

Grand canonical ensemble is a collection of independent systems of constant volume but open and separated from its neighbours by diathermic permeable membrane so that both material and energy can be exchanged between the neighbours. Since there is exchange of energy, the energy of each system E is not a constant. Also there is exchange of particles, so the total number of particles in each system do not remain constant. The temperature T, volume V and chemical potential μ of each system remain constant.