Chapter 8
Canonical Ensemble (E,V,N)

2. What is Canonical ensemble?

The reservoir in contact with the system consists of an infinitely large number of imaginary copies of the given system. So, there is an ensemble of systems. But this time it is an ensemble in which the microstate of the systems is defined through the parameters *N*, *V*, and *T*. (unlike microcanonical). Such an ensemble is referred to as a **canonical** ensemble (**NVT ensemble**).

In statistical mechanics, a **canonical ensemble** is the statistical ensemble that represents the possible states of a mechanical system in thermal equilibrium with a heat bath at a fixed temperature. The system can exchange energy with the heat bath, so that the states of the system will differ in total energy.

Properties of Canonical Ensemble

Uniqueness: The canonical ensemble is *uniquely* determined for a given physical system at a given temperature, and does not depend on arbitrary choices such as choice of coordinate system (classical mechanics), or basis (quantum mechanics), or of the zero of energy.

Statistical equilibrium (steady state): A canonical ensemble does not evolve over time, despite the fact that the underlying system is in constant motion. This is because the ensemble is only a function of a conserved quantity of the system (energy).

Thermal equilibrium with other systems: Two systems, each described by a canonical ensemble of equal temperature, brought into thermal contact will each retain the same ensemble and the resulting combined system is described by a canonical ensemble of the same temperature.

Maximum entropy: For a given mechanical system (fixed N, V), the canonical ensemble average $-\langle \log P \rangle$ ($S = -k_B \sum_i P_i \log P_i = -k_B \langle \log P \rangle$, the entropy) is the maximum possible of any ensemble with the same $\langle E \rangle$.

Minimum free energy: For a given mechanical system (fixed N, V) and given value of T, the canonical ensemble average $\langle E + k_B T \log P \rangle$ (the Helmholtz free energy $F = E - TS$) is the lowest possible of any ensemble. This is easily seen to be equivalent to maximizing the entropy.

Example: In a thermodynamic system in equilibrium, each molecule can exist in three possible states with probabilities $1/2, 1/3$ and $1/6$ respectively. The entropy for N molecules is given by?

Solution: $S = -k_B \sum_i P_i \log P_i$ Entropy for one molecule.

$P_1 = \frac{1}{2}$, $P_2 = 1/3$ and $P_3 = 1/6 \cdot$

$$S = -k_B \left(\frac{1}{2} \ln 1/2 + 1/3 \ln 1/3 + 1/6 \ln 1/6 \right) \cdot$$

$$= -k_b \left(\frac{1}{2}(\ln 1 - \ln 2) + \frac{1}{3}(\ln 1 - \ln 3) + \frac{1}{6}(\ln 1 - \ln 6) \right)$$

$$= k_B \left[\frac{1}{2}\ln 2 + \frac{1}{3}\ln 3 + \frac{1}{6}\ln 2 + \frac{1}{6}\ln 3 \right] = k_B \left[\frac{1}{2}\ln 2 + \frac{1}{6}\ln 2 + \frac{1}{3}\ln 3 + \frac{1}{6}\ln 3 \right]$$

$$S = k_B\left[\frac{3\ln 2+\ln 2}{6}+\frac{2\ln 3+\ln 3}{6}\right] = k_B\left(\frac{4\ln 2}{6}+\frac{3\ln 3}{6}\right) = k_B\left[\frac{2}{3}\ln 2+\frac{1}{2}\ln 3\right]$$

For N molecules, $S = Nk_B\left[\frac{2}{3}\ln 2+\frac{1}{2}\ln 3\right]$

Examples of Canonical Ensemble

(a) Boltzmann distribution (separable system)

(b) Ising model (strongly interacting system)

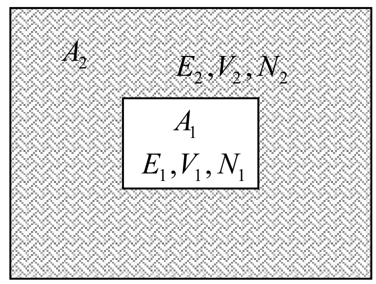
(c) Quantum mechanics (ex. Harmonic Oscillator)

(d) Classical Mechanics (ex. Harmonic Oscillator)

Mathematical Expressions for Canonical Ensemble

(a) System in contact with a heat reservoir

We consider a small system A_1 characterized by E_1, V_1 and N_1 in thermal interaction with a heat reservoir A_2 characterized by E_2, V_2 and N_2 in thermal interaction such that $A_1 \ll A_2$, A_1 has hence fewer degrees of freedom than A_2. Ex: A water bottle (A_1 small macroscopic system) in a pond (A_2 heat reservoir).



$E_2 \ll E_1$ $N_1 =$ constant

$N_2 \gg N_1$ $\quad N_2 =$ constant

with $E_1 + E_2 = E =$ constant

Both systems are in thermal equilibrium at temperature T. The wall between them allows interchange of heat but not of particles.

Distribution of energy states	The question we want to answer is the following: "Under equilibrium conditions, what is the probability of finding the small system A_1 in any particular microstate r of energy E_r? In other words, what is the distribution function $\rho = \rho(E_r)$ of the system A_1?"

We note that the energy E_1 is not fixed, only the total energy $E = E_1 + E_2$ of the combined system is fixed.

Hamilton Function

The Hamilton function of the combined system A is

$$H(q,p) = H_1(q(1), p(1)) + H_2(q(2), p(2))$$

Or

$$\boxed{H(q,p) = H_1 + H_2}$$

were we have used the notation,

$$q = (q(1), q(2)), \qquad p = (p(1), p(2))$$