Chapter 3
Statistical Thermodynamics of Microstates

3.1 Microstates:

A state of a system shows how energy levels are occupied. For example, consider a system consists of two distinguishable particles, and this system has three energy levels ε_0, ε_1 and ε_2. The state $(1,1,0)$ of the system means there is a particle in the first energy level ε_0, a particle in the second energy level ε_1, and the third energy level ε_2 is empty. The macrostate $(1,1,0)$ is divided into two microstates: $(B, W, 0)$ and $(W, B, 0)$.

* Example 1. Find the number of microstates for a state $(2,1,0)$ for a system consists of three distinguishable particles.

solution

Consider a system consists of three distinguishable particles u, v, and w. The microstates of the state $(2,1,0)$ are

$(uv, w, 0)$, $(uw, v, 0)$, $(vw, u, 0)$.

The number of microstates $= 3$.

Note: The number of microstates of a given state of a system is the number of wayes of rearranging the distinguishable particles in this state.

* Theorem 1. The number of microstates of the state $(N_1, N_2, \dots, N_M)$ is

$$\omega = \frac{N!}{N_1!\, N_2! \cdots N_M!}, \quad N = \sum_{i=1}^{M} N_i.$$

* Proof.

The number of wayes of selecting N_1 particles for the first energy level from N particles is

$$\omega_1 = \binom{N}{N_1} = \frac{N!}{(N-N_1)!\, N_1!}.$$

The number of wayes of selecting N_2 particles for the second energy level from $N-N_1$ particles is

$$\omega_2 = \binom{N-N_1}{N_2} = \frac{(N-N_1)!}{(N-N_1-N_2)!\, N_2!}.$$

The number of wayes of selecting N_{M-1} particles for the $(M-1)$ th energy level is

$$w_{M-1} = \binom{N-N_1-N_2-\cdots-N_{M-2}}{N_{M-1}}$$

$$= \frac{(N-N_1-N_2-\cdots-N_{M-2})!}{(N-N_1-N_2-\cdots-N_{M-2}-N_{M-1})!\,N_{M-1}!}.$$

The number of wayes of selecting N_M particles for the Mth energy level is

$$w_M = \binom{N-N_1-N_2-\cdots-N_{M-1}}{N_M}$$

$$= \frac{(N-N_1-N_2-\cdots-N_{M-1})!}{(N-N_1-N_2-\cdots-N_{M-1}-N_M)!\,N_M!}.$$

The total number of microstates for the state $(N_1, N_2, \cdots, N_M)$ is

$$w = w_1 \cdot w_2 \cdot \cdots \cdot w_M$$
$$= \frac{N!}{N_1!\ N_2!\ \cdots\ N_M!}$$

* Example 2. Find the number of microstates for the state $(4, 3, 2, 1, 0)$ of a system.

* Definition 1. If ω_k is the number of microstates for the state k, then the total number of microstates of the system is

$$\Omega = \sum_k \omega_k$$

3. 2 The Entropy:

* Definition 2. The entropy is defined as

$$S = k_B \ln \Omega,$$

where k_B is the Boltzmann's Constant.

* Properties of the Entropy:

① $\lim_{T \to 0} S = 0$

* Proof.

As $T \to 0°K$, all particles go to the ground state energy, and the total number of microstates $\Omega = 1$

$$\therefore \lim_{T \to 0} S = k_B \ln 1 = 0$$

② Additive property of the entropy:

* Proof.

Let Ω_1 and Ω_2 be the total number of microstates for two systems. If the

Two systems are combined, then the total number of microstates:

$$\Omega_{total} = \Omega_1 \times \Omega_2$$

$$\therefore S_{total} = k_B \ln \Omega_{total}$$

$$= k_B \ln \Omega_1 + k_B \ln \Omega_2$$

$$= S_1 + S_2$$

* Example 3. Study the distribution of microstates of a system consists of three distinguishable particles, and has four energy levels $\varepsilon_i = i\,\varepsilon$ J, $i = 0, 1, 2, 3$, such that the total energy $U = 3\varepsilon$ J.

Solution

As shown in the following table,

The total number of microstates $= 10$

The state $(1, 1, 1, 0)$ is the most probable distribution.

Macrostates	Microstates				ω_k	P_k
	N_0	N_1	N_2	N_3		
(2,0,0,1)	AB			C	3	0.3
	AC			B		
	BC			A		
(1,1,1,0)	A	B	C		6	0.6
	B	C	A			
	C	A	B			
	A	C	B			
	B	A	C			
	C	B	A			
(0,3,0,0)		ABC			1	0.1

3.3 The Helmholtz Free Energy:

$$F = U - TS$$

* Example 4. A system consists of six distinguishable particles, and has five energy levels $E_i = i \times 10^{-20}$ J, $i = 0,1,2,3,4$, such that the internal energy $U = 4 \times 10^{-20}$ J.

(1) Find the total number of microstates.

(2) Which macrostate minimizes the Helmholtz free energy?

Solution

Macrostates	ω_k	S $\times 10^{-23}$ J/K	F $\times 10^{-20}$ J
(5,0,0,0,1)	6	2.47	3.26
(4,1,0,1,0)	30	4.69	2.6
(4,0,2,0,0)	15	3.74	2.88
(3,2,1,0,0)	60	5.65	2.32
(2,4,0,0,0)	15	3.74	2.88

(1) The total number of microstates:

$$\Omega = 126$$

(2) The macrostate (3,2,1,0,0) minimizes the Helmholtz free energy.