

# Chapter 4

## Statistical Thermodynamics

- **Maximum Entropy Principle**

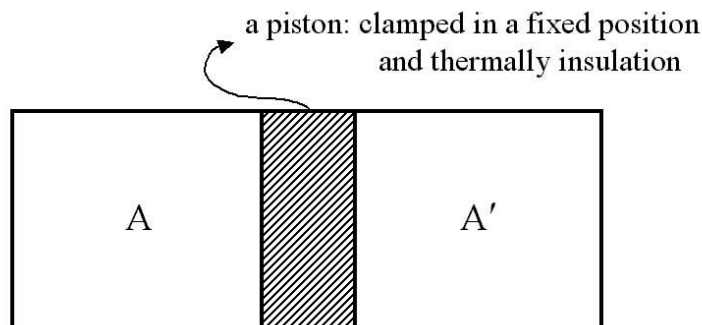
Consider an isolated thermodynamic system in equilibrium which satisfies a given macroscopic condition characterized by a set of macroscopic quantities  $\{y_i\}$  [=  $(E_t, N_t, \{x_i, i = 1, \dots, n\})$ ], where  $y$  is a macroscopic quantity of the total system or its subsystem and a kind of constraints to the isolated system.

$\Omega_t$  : No. of accessible microstates which satisfy the given macroscopic condition.

$$\Omega_t = \Omega_t(\{y_t\})$$

$$i(\text{microstates}) : 1, \dots, \Omega_t$$

e.g.,  $y = E$  or  $V$  of some subsystem



$$E : \text{fixed}, E' : \text{fixed}, E_t = E - E' \tag{4.1}$$

$$N : \text{fixed}, N' : \text{fixed}, N_t = N - N' \tag{4.2}$$

$$V : \text{fixed}, V' : \text{fixed}, V_t = V - V' \tag{4.3}$$

The entropy of the system is given by

$$S_t = k_B \ln \Omega_t \longrightarrow S_t = S_t(\{y_t\}) \quad (4.4)$$

Fundamental Statistical Postulate: Equal A Priori Weight

$$P_i = 1/\Omega_t \quad i = 1, \dots, \Omega_t \quad (4.5)$$

Let us consider a process in which some constraints of an isolated system in equilibrium are removed. Then, after a sufficiently long time, the isolated system will approach to a new equilibrium state. Let's denote the number of accessible states of the initial equilibrium state and the final equilibrium state as  $\Omega_t^{(i)}$  and  $\Omega_t^{(f)}$ , respectively. Then, generally  $\Omega_t^{(f)} \geq \Omega_t^{(i)}$ , since some constraints are removed. If  $\Omega_t^{(f)} > \Omega_t^{(i)}$ , then the process is said to be irreversible, while if  $\Omega_t^{(f)} = \Omega_t^{(i)}$ , then the process is said to be reversible. For example, let us consider the simplest case in which a constraint  $y$  is removed. Then  $y$  can now change, and the (new) equilibrium probability distribution is given by  $P(\hat{y}) = \frac{\Omega_t(\hat{y})}{\sum_y \Omega_t(y)}$  from the fundamental statistical postulate.

The state in which  $P(\hat{y})$  is max. is most probable.

$$P(\hat{y}) : \max \longrightarrow \Omega_t(\hat{y}) : \max \longrightarrow S_t(\hat{y}) : \max \quad (4.6)$$

That is, the value of  $y$  in the final equilibrium state will be statistically  $\hat{y} (S_t(\hat{y}) : \max)$ .

Summary: If some constraints of an isolated system are removed, the parameters of the system readjust themselves in such a way that its entropy  $S_t(\{y_i\})$  is max.;  $S_t^{(f)} \geq S_t^{(i)}$ ; Entropy Maximum Principle

Removal of some constraint  $y : \Omega_t^{(i)}$

New Equilibrium State :  $\Omega_t^{(f)}$

$$\Omega_t^{(f)} \geq \Omega_t^{(i)} \quad (4.7)$$

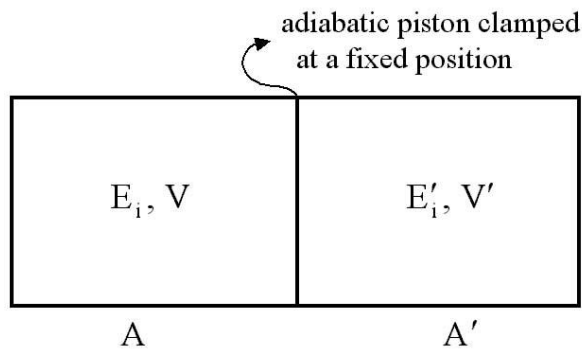
$$P(\hat{y}) \propto \Omega_t(\hat{y}) \quad (4.8)$$

Most Probable State :  $P(\hat{y}) : \text{Max}$

$$\longrightarrow \Omega_t(\hat{y}) : \text{Max} \longrightarrow S_t(\hat{y}) : \text{Max} \quad (4.9)$$

## 4.1 Thermal Interaction

Initial equilibrium state:

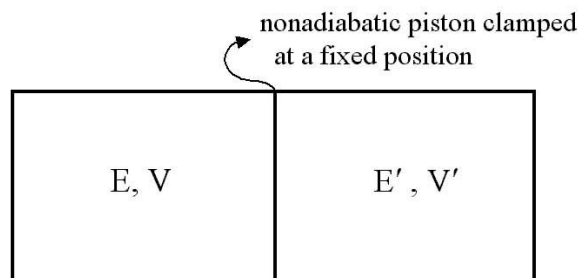


$$A_t = A + A' : \text{isolated} \quad (4.10)$$

$$E_i = \text{fixed}, E'_i = \text{fixed} \longrightarrow E_t = E_i + E'_i : \text{fixed} \quad (4.11)$$

$$V = \text{fixed}, V' = \text{fixed} \longrightarrow V_t = V + V' : \text{fixed} \quad (4.12)$$

⇓ Thermal Int. between  $A \& A'$



$$\Omega_t(E) = \Omega(E) \cdot \Omega'(E_t - E) \quad (4.13)$$

↓

$$\underline{P}(E) = C \cdot \Omega_t(E) = C \cdot \Omega(E) \cdot \Omega'(E_t - E) \quad (4.14)$$

**What is the most probable state?**

$$\underline{P}(E) : \max, \Leftrightarrow \Omega_t(E) : \max \Leftrightarrow S_t(E) : \max \quad (4.15)$$

$$S_t(E) = k_B \cdot \ln \Omega_t(E) \quad (4.16)$$

$$= S(E) + S'(E_t - E) \quad (4.17)$$

$$S = S(E, \{x_i\}, N) \quad (4.18)$$

$$S_t(E) : \max \longrightarrow \frac{\partial S_t}{\partial E} = 0, \quad \frac{\partial^2 S_t}{\partial E^2} < 0. \quad (4.19)$$

$$\frac{\partial S_t}{\partial E} = \frac{\partial S(E)}{\partial E} + \frac{\partial S'(E')}{\partial E'} \cdot \frac{\partial E'}{\partial E} \quad (4.20)$$

$$= \frac{\partial S}{\partial E} - \frac{\partial S'}{\partial E'} = 0 \quad (4.21)$$

$$\therefore \frac{\partial S}{\partial E} = \frac{\partial S'}{\partial E'} : \text{thermal equilibrium condition} \quad (4.22)$$

• **Def. Temperature  $T$**

$$T \equiv \left[ \frac{\partial S(E, \{x_i\}, N)}{\partial E} \right]^{-1} \quad (4.23)$$

$$\therefore T = T' : \text{thermal equilibrium condition} \quad (4.24)$$

e.g. Classical ideal gas

$$S = Nk_B \ln V + \frac{3}{2}Nk_B \ln E \quad (4.25)$$

$$\frac{\partial S}{\partial E} = \frac{3}{2}Nk_B \cdot \frac{1}{E} = \frac{1}{T} \quad (4.26)$$

$$\therefore E = \frac{3}{2} N k_B T \longrightarrow e = \frac{E}{N} = \frac{3}{2} k_B T \quad (4.27)$$

Let us consider the case where

$$\Omega(E) = C(\{x_i\}, N) \cdot E^{\alpha f} \quad (4.28)$$

$\alpha$  : some positive const. ( $O(\alpha) = 1$ ),  $f$  : degrees of freedom

$$S(E) = k_B \ln \Omega \quad (4.29)$$

$$= k_B \ln C + k_B \cdot \alpha f \cdot \ln E \quad (4.30)$$

$$\frac{\partial S}{\partial E} = k_B \cdot \frac{\alpha f}{E} = \frac{1}{T} \longrightarrow E = f(\alpha k_B T). \quad (4.31)$$

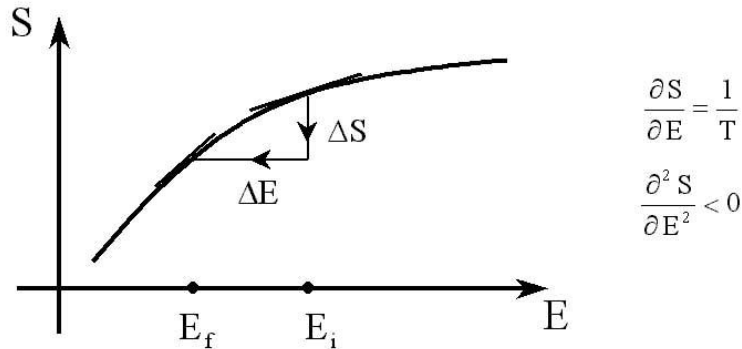
$$\frac{\partial^2 S}{\partial E^2} = -\frac{\alpha k_B f}{E^2} < 0, \quad \frac{\partial^2 S'}{\partial E'^2} < 0 \quad (4.32)$$

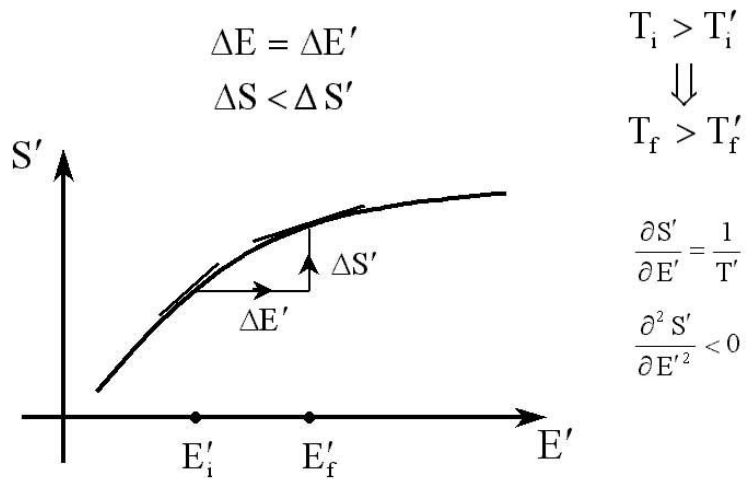
$$\therefore \frac{\partial^2 S_t}{\partial E^2} = \frac{\partial^2 S}{\partial E^2} + \frac{\partial^2 S'}{\partial E'^2} < 0 \quad (4.33)$$

$$\frac{\partial^2 S}{\partial E^2} < 0 \iff \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = -\frac{1}{T^2} \frac{\partial T}{\partial E} < 0 \quad (4.34)$$

$$\therefore \left( \frac{\partial E}{\partial T} \right)_v > 0 \longrightarrow C_v \left( \equiv \frac{\partial E}{\partial T} \right) > 0 \quad (4.35)$$

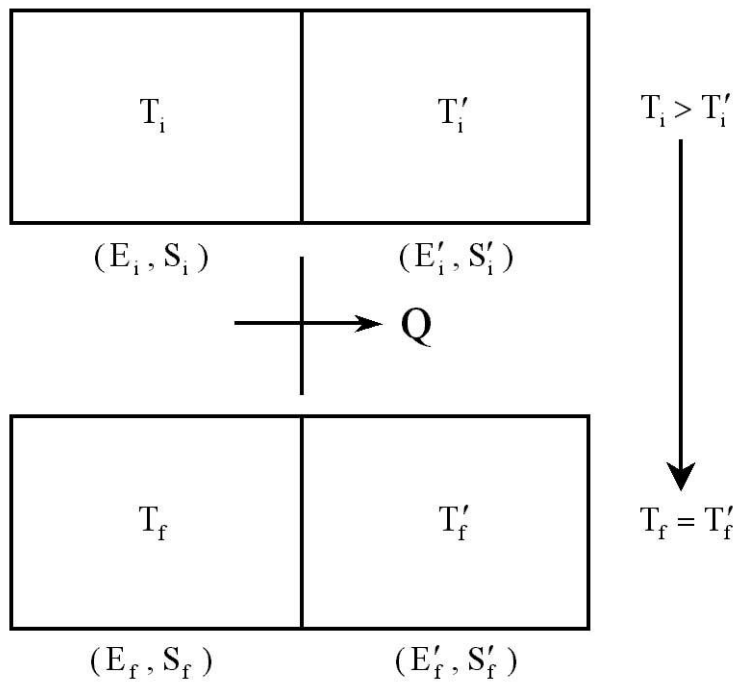
↑ Heat capacity





$$\Delta S = S_f - S_i \quad , \quad \Delta S' = S'_f - S'_i \quad (4.36)$$

$$Q = \Delta E = E_f - E_i \quad , \quad Q' = \Delta E' = E'_f - E'_i \quad (4.37)$$



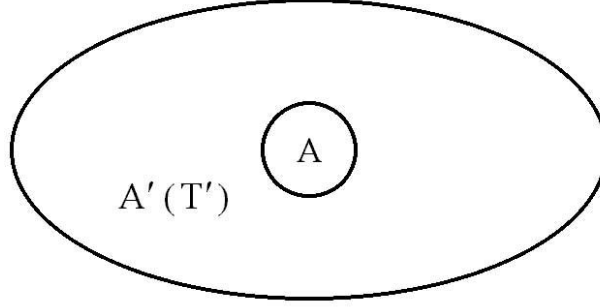
$$\left. \begin{aligned} Q = E_f - E_i < 0 \\ Q' = E'_f - E'_i > 0 \end{aligned} \right) \longrightarrow Q + Q' = 0 \quad (4.38)$$

$$\Delta S < 0, \Delta S' > 0 \longrightarrow \Delta S + \Delta S' > 0 \quad (4.39)$$

$$Q < 0 \implies S(\downarrow), \quad Q' > 0 \implies S'(\uparrow) \quad (4.40)$$

$$\Delta S_t > 0 \quad (4.41)$$

## 4.2 Heat Reservoir (heat bath)



- Def. Heat Reservoir

$\frac{\bar{E}}{\bar{E}'} \ll 1 \implies$  The system  $A'$  is said to act as a heat reservoir with respect to the smaller system  $A$ .

Suppose that the heat reservoir absorbs a heat  $Q'$ .

$$|Q'|_{\max} = \bar{E} \longrightarrow |Q'| \ll \bar{E}' \quad (4.42)$$

$$\Omega(E') = C \cdot E'^{\alpha' \cdot f'} \longrightarrow \frac{1}{T'} = \frac{\partial S'}{\partial E'} = \frac{\alpha' \cdot f'}{E'} \cdot k_B \quad (4.43)$$

$$A' : \bar{E}' \longrightarrow E' = \bar{E}' + Q' \simeq \bar{E}' : \text{unchanged} \quad (4.44)$$

$$\frac{\partial^2 S'}{\partial E'^2} = -\frac{1}{T'^2} \cdot \frac{\partial T'}{\partial E'} = -k_B \cdot \frac{\alpha' \cdot f'}{E'^2} = -\frac{1}{T' E'} \quad (4.45)$$

$$\therefore \left. \frac{\partial T'}{\partial E'} \right|_{\bar{E}'} = \frac{T'}{\bar{E}'} \quad (4.46)$$

$$T'(E') \cong T'(\bar{E}') + \left. \frac{\partial T'}{\partial E'} \right|_{\bar{E}'} Q' \quad (4.47)$$

$$= T'(\bar{E}') + T'(\bar{E}') \cdot \frac{Q'}{\bar{E}'} \quad (4.48)$$

$$= T'(\bar{E}') \left[ 1 + \frac{Q'}{\bar{E}'} \right] \quad (4.49)$$

$$\simeq T'(\bar{E}') \quad (4.50)$$

$$\frac{\bar{E}}{\bar{E}'} \ll 1 \implies T' : \text{unchanged} \quad (4.51)$$

$$S'(\bar{E}' + Q') \cong S'(\bar{E}') + \left. \frac{\partial S'}{\partial E'} \right|_{\bar{E}'} \cdot Q' + \frac{1}{2} \left. \frac{\partial^2 S'}{\partial E'^2} \right|_{\bar{E}'} \cdot Q'^2 \quad (4.52)$$

$$\Delta S' = S'(\bar{E}' + Q') - S'(\bar{E}') \quad (4.53)$$

$$= \frac{1}{T'} \cdot Q' - \frac{1}{2} \cdot \frac{1}{T'^2} \cdot \left. \frac{\partial T'}{\partial E'} \right|_{\bar{E}'} \cdot Q'^2 \quad (4.54)$$

$$= \frac{Q'}{T'} - \frac{k_B}{2} \alpha' f' \left( \frac{Q'}{\bar{E}'} \right)^2 \quad (4.55)$$

$$\simeq \frac{Q'}{T'} \quad (4.56)$$

A similar relation holds for any system whose temperature is  $T$  and which absorbs an infinitesimal amount of heat  $dQ$  from other system at a slightly different temperature by an infinitesimal quasi-static process.

$$\ln \Omega(\bar{E} + dQ) - \ln \Omega(\bar{E}) = \left. \frac{\partial \ln \Omega(E)}{\partial E} \right|_{\bar{E}} \cdot dQ \quad (4.57)$$

$$\therefore dS = \frac{dQ}{T} \text{ for an infinitesimal quasi-static process.} \quad (4.58)$$

### 4.3 Equilibrium Conditions



$$A_t = A + A' : \text{isolated} \quad (4.59)$$

$$\therefore E_t = E + E' : \text{fixed} \quad (4.60)$$



$$S = S(\bar{E}, \{X_\alpha\}) \quad (4.61)$$

Recall that

$$\bar{X}_\alpha = - \left( \frac{\partial \bar{E}}{\partial X_\alpha} \right)_S \quad (4.62)$$

$$dS = \frac{\partial S}{\partial \bar{E}} \cdot d\bar{E} + \sum_\alpha \frac{\partial S}{\partial X_\alpha} \cdot dX_\alpha \quad (4.63)$$

Consider an infinitesimal adiabatic quasi-static process.  $\longrightarrow dS = 0$

$$d\bar{E} = - \sum_\alpha \left( T \cdot \frac{\partial S}{\partial X_\alpha} \right) \cdot dX_\alpha = - \sum_\alpha \bar{X}_\alpha \cdot dX_\alpha \quad (4.64)$$

$$= -dW \quad (4.65)$$

$$\therefore \frac{\partial S}{\partial X_\alpha} = \frac{X_\alpha}{T} \quad (4.66)$$

e.g. Classical ideal gas

$$S = Nk_B(\ln V + \frac{3}{2} \ln E) \quad (4.67)$$

$$\frac{\partial S}{\partial V} = \frac{Nk_B}{V} = \frac{P}{T} \longrightarrow PV = Nk_B T \quad (4.68)$$

Now, let us consider a general quasi-static process.

$$dS = \frac{\partial S}{\partial \bar{E}} d\bar{E} + \sum_\alpha \frac{\partial S}{\partial x_\alpha} \cdot dx_\alpha \quad (4.69)$$

$$= \frac{1}{T} (d\bar{E} + \sum_\alpha \bar{X}_\alpha \cdot dx_\alpha) \quad (4.70)$$

$$= \frac{1}{T} (d\bar{E} + dW) \quad (4.71)$$

$$= \frac{dQ}{T} : \text{valid for any infinitesimal quasi-static process} \quad (4.72)$$

**What is the equilibrium condition?**

$$S_t(E, \{X_\alpha\}) = S(E, \{X_\alpha\}) + S'(E', \{X'_\alpha\}) \quad (4.73)$$

$$dS_t = \left( \frac{\partial S}{\partial E} - \frac{\partial S'}{\partial E'} \right) \cdot dE + \sum_\alpha \left( \frac{\partial S}{\partial X_\alpha} - \frac{\partial S'}{\partial X'_\alpha} \right) \cdot dX_\alpha \quad (4.74)$$

In equilibrium,  $S_t : \max \longrightarrow dS_t = 0$

$$\therefore \frac{\partial S}{\partial E} = \frac{\partial S'}{\partial E'} \longrightarrow T = T' \text{ (thermal equilibrium)} \quad (4.75)$$

$$\frac{\partial S}{\partial X_\alpha} = \frac{\partial S'}{\partial X'_\alpha} \longrightarrow \bar{X}_\alpha = \bar{X}'_\alpha \text{ (mechanical equilibrium)} \quad (4.76)$$

#### 4.4 Properties of the Entropy $S$

$$S = S(\bar{E}, \{X_i\}) \quad (4.77)$$

$$= k_B \cdot \ln \Omega(\bar{E}, \{X_i\}) \quad (4.78)$$

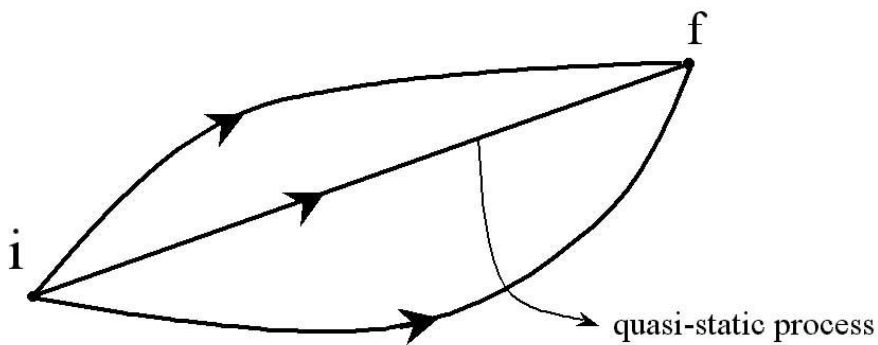
For an infinitesimal quasi-static process,

$$dS = \frac{\partial S}{\partial E} dE + \sum_\alpha \frac{\partial S}{\partial X_\alpha} \cdot dX_\alpha \quad (4.79)$$

$$= \frac{1}{T} dE + \sum_\alpha \frac{\bar{X}_\alpha}{T} \cdot dX_\alpha \quad (4.80)$$

$$= \frac{1}{T} (dE + \delta W) \quad (4.81)$$

$$= \frac{\delta Q}{T} \quad (4.82)$$



$$\Delta S = \int_i^f dS = \int_i^f \frac{\delta Q}{T} = S_f - S_i \quad (4.83)$$

- **$S$ : thermodynamic function  $\longrightarrow dS$  : exact differential**

$$S = S(E, \{X_i\}) \longrightarrow dS = \frac{\partial S}{\partial E} dE + \sum_i \frac{\partial S}{\partial X_i} \cdot dX_i \quad (4.84)$$

$$\frac{\partial S}{\partial E} = \frac{1}{T} \quad , \quad \frac{\partial S}{\partial X_i} = \frac{\overline{X_i}}{T} \quad (4.85)$$

- **Maximum entropy principle**

Isolated system

Initial equilibrium state  $\longrightarrow$  Final equilibrium state

↑

$S$  : max

$$\therefore \Delta S = S_f - S_i \geq 0 \quad (4.86)$$

$$\Delta S = 0 \quad : \quad \text{reversible process} \quad (4.87)$$

$$\Delta S > 0 \quad : \quad \text{irreversible process} \quad (4.88)$$

Adiabatic (thermally insulation) quasi-static process:

$$\Delta S = 0 \quad (4.89)$$

$\therefore$  reversible process

- $S = k_B \ln \Omega$

C.M.  $\longrightarrow \delta q_i \cdot \delta p_i = h_0$  (resolution)

$$\Omega = \frac{1}{h_0^f} \int_{E \text{ } E+\delta E} \prod_i dq_i \cdot dp_i \quad (4.90)$$

↓

$$S = k_B \ln \left( \int_{E, E+\delta E} \Pi_i dq_i \cdot dp_i \right) - k_B \cdot f \cdot \ln h_0 \quad (4.91)$$

$$= k_B \ln \left( \int_{E, E+\delta E} \Pi_i dq_i \cdot dp_i \right) + S_0 \quad (4.92)$$

(some const indep. of  $E\delta\{X_i\}$ )

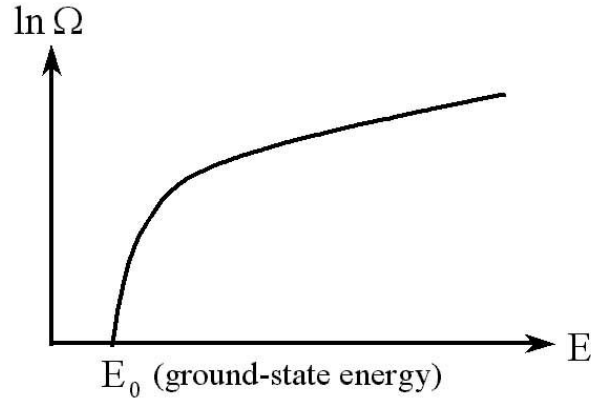
$h_0(S)$  is not uniquely determined in C.M.

Q.M.  $\longrightarrow h_0 = h_0$  (Plank const.)

$S$  is uniquely determined

• **Limiting behavior of  $S$**

$$S = k_B \ln \Omega(E, \{X_i\}) \quad (4.93)$$



$$\Omega(E) \sim (E - E_0)^{\alpha f}, \quad O(\alpha) = 1(\alpha > 0) \quad (4.94)$$

$$\frac{\partial S}{\partial E} > 0 \quad \& \quad \frac{\partial^2 S}{\partial E^2} < 0 \quad \longrightarrow \quad O(S) \sim f(E > E_0) \quad (4.95)$$

$$E(\downarrow) \longrightarrow \Omega(\downarrow) \quad \& \quad T(\downarrow) \quad (4.96)$$

$$E \sim E_0 \longrightarrow \left( \begin{array}{l} T \longrightarrow 0^+ \\ \Omega(E_0) : \text{very small} \end{array} \right) \quad (4.97)$$

$$\longrightarrow \text{at most } O(\Omega(E_0)) \sim f \quad (4.98)$$

$$\therefore T \rightarrow 0^+ \implies E \rightarrow E_0 \text{ (ground state)} \quad (4.99)$$

$$S = k_B \ln \Omega(E_0) = S_0 \quad (4.100)$$

$$\text{nondegenerate} \longrightarrow \Omega(E_0) = 1 \longrightarrow S = 0 \quad (4.101)$$

$$\text{at most } O(S) = \ln f \longrightarrow O(S) = 0 \quad (4.102)$$

$$\frac{S(E_0)}{S(E > E_0)} = 0 \quad (4.103)$$

$$\therefore \text{As } T \longrightarrow 0^+, S \longrightarrow S_0 \quad (4.104)$$

const. indep. of the atomic structure and their interactions of the system.

Let's consider an interacting system which consists of  $N$  atoms.

$$H = H(q, p, \{X_i\}) \longrightarrow E_0, E_1, \dots \quad (4.105)$$

$$\text{As } T \longrightarrow 0^+, P(E) = 0(E > E_0) \quad (4.106)$$

↓

All degrees of freedom associated with  $N$  atoms are frozen (ordered state)

**e.g.** Nuclear spin entropy

Let's consider a system which consists of atom having nuclear spin  $\frac{1}{2}$ .

$$\vec{\mu} \propto \frac{\vec{S}}{m} \longrightarrow \underline{\mu_N} \ll \mu_e \quad (4.107)$$

very small

Even at a temp.  $T_0$  ( $\simeq 10^{-3}K$ ), the nuclear spins: randomly oriented.

But, all degrees of freedom not involving nuclear spins: frozen at  $T_0$

$$\therefore \text{total entropy } S_0 \simeq k_B \cdot \ln 2^N \quad (4.108)$$

$$T \rightarrow 0^+ \implies S \rightarrow S_0 \quad (4.109)$$

Note that  $S_0$  depends only on the kinds of the atomic nuclei, but which is completely independent of the spatial arrangement of its atoms, of the nature of their chemical combinations, or of the interactions between them.

**e.g.**  $A$  system: one mole of  $Pb$  & one mole of  $S$

$A'$  system: one mole of  $PbS$

The properties of these two systems are very different, but they consist of the same numbers and kinds of atoms.

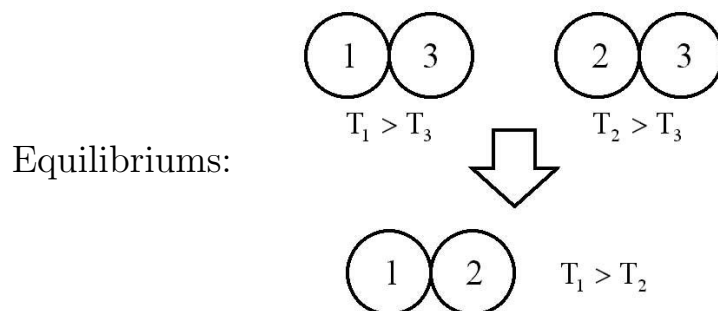
$$\therefore T \rightarrow 0^+, \text{ the two systems have the same entropy } S_0. \quad (4.110)$$

$$T \sim 10^{-6} K, \text{ all the degrees of freedom associated} \quad (4.111)$$

with nuclear spins: frozen (ordered)

## 4.5 Thermodynamic Laws and Statistical Relations

**0th law: Thermal equilibrium and condition ( $T$ )**



**1st law: Internal Energy  $U$**

An equilibrium macrostate can be characterized by its internal energy  $U$ .

- For an isolated system,  $U = \text{const.}$
- Energy exchange  $\longrightarrow dU = \delta Q - \delta W$

### 2st law: Entropy $S$

An equilibrium macrostate can be characterized by its entropy  $S$ .

- For an isolated system,  $\Delta S \geq 0$   
(Entropy maximum principle)
- Quasi-static process,  $dS = \frac{\delta Q}{T}$

### 3st law: Limiting behavior of $S$

As  $T \rightarrow 0^+$ ,  $S \rightarrow S_0$

(some consts. indep. of all external parameters)

#### ◦ Statistical Relations

$$\underline{S} = k_B \ln \underline{\Omega(E, \{X_i\})} \quad (4.112)$$

macroscopic quantities                      microscopic information