# Chapter 3

# Statistical Description of Thermodynamic System

- **Aim**

    The aim of statistical mechanics is to derive all the equilibrium properties of a macroscopic system from the fundamental law(classical mechanics or quantum mechanics) plus some statistical postulates.

    It merely states what the equilibrium situation is for a given system. That is, it does not describe the nonequilibrium properties of the system.

- **Thermodynamic System**

    A macroscopic system composed of a large number of particles occupying a large volume $V$.

    Thermodynamic limit: $N \to \infty, V \to$ s.t. $N/V = n =$ finite const.
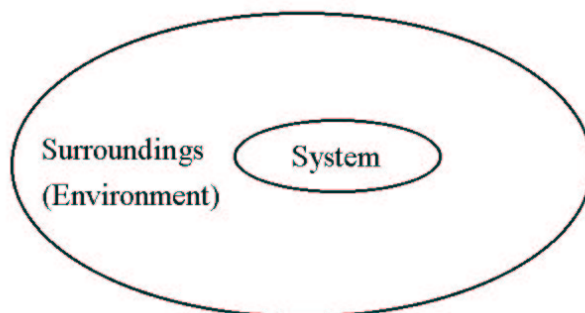


(1) Isolated System

    No exchange of energy and particles between the system and it's surroundings

(2) Closed System

Exchange of only energy between the system and it's surroundings

(3) Open System

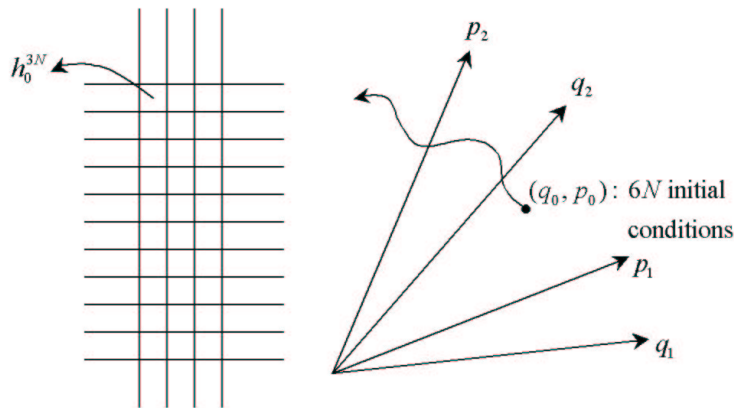Exchange of energy and particles between the system and it's surroundings

- **Specification of the state of a system**

  Let's consider a Hamiltonian system of $3N$ degrees of freedom.

  **Classical Approximation**

$$H = H(q, p), \text{where } (q, p) = (q_1, \cdots, q_{3N}, p_1, \cdots, p_{3N}) \qquad (3.1)$$

$$\dot{q}_i = \frac{\partial H}{\partial P_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}, i = 1, \cdots, 3N \qquad (3.2)$$



*6N-D* Phase Space

$(q(t), p(t))$: a microscopic state (microstate) of the system

Divide the phase space into small cells of equal volume:

$$\delta_{qi}\delta_{pi} = h_0 \rightarrow \prod_{i=1}^{3N} \delta_{qi}\delta_{pi} = h_0^{3N} : \text{Countable state.}$$

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## Partial Information

However, it is practically impossible to obtain $6N$ initial conditions for large $N$. We have usually only macroscopic quantities which can be obtained from experiment.

Macroscopic quantities: $N$, $V$, $E \sim E + \Delta (\Delta \ll E)$.

A macroscopic condition of the system is characterized by macroscopic quantities $(N,\ V,\ E)$. Therefore, all the microstates on the energy surface $(H(q,p) = E)$ are accessible (or possible) states:



$H = E$
$(6N-1)D$
hypersurface
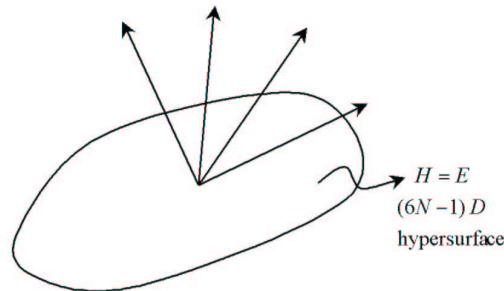
## Ensemble

To describe the system statistically, let us consider an infinite number of systems satisfying the same macroscopic condition. Such a collection of systems is called an "ensemble." The systems in the ensemble are distributed over the various accessible states.

## 3.1  Microcanonical Ensemble

**Fundamental Statistical Postulate (Equal A Priori Weight)**

When an isolated system is in the thermodynamic equilibrium, its state is equally likely to be in any microstate subject to the given macroscopic conditions.

**Macroscopic Conditions:** $N, V, E \sim E + \Delta(\Delta \ll E)$.

From the fundamental law (Classical or Quantum Mechanics), we can obtain accessible microstates of the thermodynamic system which satisfy the given macroscopic conditions:

**Accessible Microstates:** $1, 2, \cdots, \Omega$

Then, by the statistical postulate, we can obtain the probability distribution $P_i$ for the isolated system in equilibrium:

$$P_i = \frac{1}{\Omega} \text{ for all } i, i = 1, \cdots, \Omega. \tag{3.3}$$

**Entropy $S$ of the system**

$$S \equiv k_B \ln\Omega(E), \tag{3.4}$$

where $k_B$ is the Boltzman's constant. Note that the macroscopic quantity $S$ is obtained from the microscopic information $\Omega$.

## Summary

How to study the thermodynamic system statistically?

1. Find all the accessible microstates which satisfy the given macroscopic condition from the fundamental laws of the Classical or Quantum mechanics.

   Accessible Microstates: $1, \ldots, \Omega$

2. Consider a statistical ensemble in which any system satisfies the given macroscopic condition.

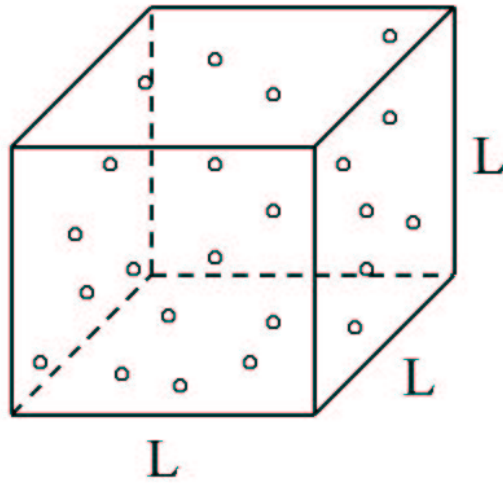   Fundamental Postulates (Equal A priori Weight): $P_i = 1/\Omega$

   Entropy: $S = k_B \ln \Omega$

3. Thermal Average (Ensemble Average)

   $f$ : a thermodynamic quantity, $f = f(i)$.

   $< f >= \sum_i f(i) P_i = \left( \sum_i f(i) \right) / \Omega$

# Classical Ideal Gas



Isolated System

$$H \;=\; \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} \tag{3.5}$$

$$\dot{\vec{q_i}} \;=\; \frac{dH}{d\vec{p_i}}, \quad \dot{\vec{p_i}} = -\frac{dH}{d\vec{q_i}}, \quad i = 1, \cdots, N. \tag{3.6}$$

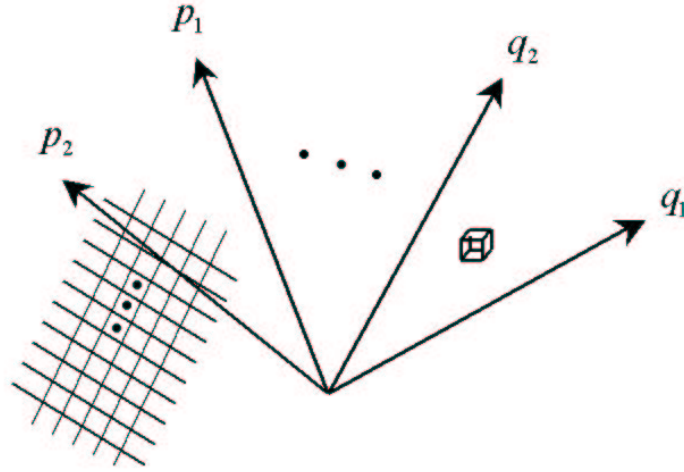isolated system $\longrightarrow E = \text{const.}$

$$\therefore \sum_{i=1}^{N} \frac{\vec{p_i}^2}{2m} \;=\; E \tag{3.7}$$

$$\downarrow$$

$$\sum_{i=1}^{N} \vec{p_i}^2 \;=\; 2mE = (\sqrt{2mE})^2$$

$$\vec{p_i} \;=\; (p_{i,x}, p_{i,y}, p_{i,z}) \tag{3.8}$$

$f(\text{degrees of freedom}) = 3N \longrightarrow$ dimension of the phase space $= 6N$

Partition the phase space into small cells of equal volume $h_0^{3N}(= \prod_{i=1}^{3N} \delta q_i \delta p_i)$ to specify the state of the system.

Assume that we can measure the energy of the system $E$ with the precision $\Delta(\Delta \ll E)$.

$\Omega$ (E) : No. of states whose energy lie between $E$ and $E + \Delta$ = No. of accessible states satisfying the macroscopic condition.

$\Phi$ (E) : No. of states whose energy lies below E.

$$\Phi(E) = \int \cdots \int \prod_{i=1}^{3N} dq_i \cdot dp_i / h_0^{3N}$$

$$0 \leq q_i \leq L, H \leq E \longrightarrow \sum_{i=1}^{3N} p_i^2 \leq 2mE \quad \text{(Macroscopic condition)}$$

$$= V^N \cdot \int \cdots \int \prod_{i=1}^{3N} dp_i / h_0^{3N} \quad (\sum_{i=1}^{3N} p_i^2 \leq 2mE) \qquad (3.9)$$

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m} = E \longrightarrow \sum_{i=1}^{3N} p_i^2 = (\sqrt{2mE})^2 \qquad (3.10)$$

$\therefore$ Sphere of radius $\sqrt{2mE}$ in the *3N-D* space

Sphere in the 2-$D$ space $\longrightarrow$ circle $x^2 + y^2 = R^2 \longrightarrow$ Vol $= \pi R^2$ (3.11)

Sphere in the 3-$D$ space $\longrightarrow x^2 + y^2 + z^2 = R^2 \longrightarrow$ Vol $= \dfrac{4}{3}\pi R^3$ (3.12)
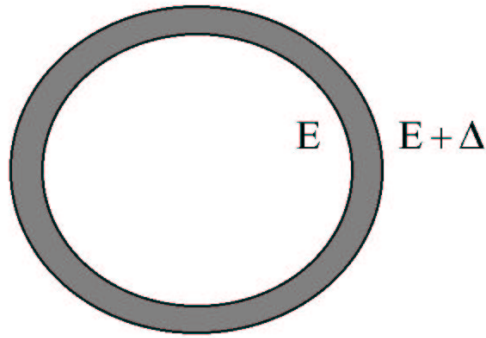
$$\vdots$$

In general, the volume of the sphere of radius $R$ in the $n$-$D$ space $\propto R^n$

$$\therefore \Phi(E) \propto V^N \cdot (\sqrt{2mE})^{3N} \tag{3.13}$$

$$= C \cdot V^N \cdot E^{3N/2} \tag{3.14}$$

$$C : \text{const. indep. of } V \& E \tag{3.15}$$



No. of accessible states:

$$
\begin{aligned}
\Omega(E) &= \Phi(E + \Delta) - \Phi(E) \\
&= \frac{d\Phi}{dE} \cdot \Delta \\
&= C \cdot N \cdot V^N \cdot E^{3N/2 - 1} \cdot \Delta \tag{3.16}
\end{aligned}
$$

Entropy $S$ :

$$
\begin{aligned}
S &= k_B \cdot \ln \Omega(E) \\
&= k_B[\ln C + \ln N + N \ln V + (\frac{3N}{2} - 1)\ln E + \ln \Delta] \\
&\simeq N k_B[\ln V + \frac{3}{2}\ln E + \frac{\ln N}{N} + \frac{\ln(C \cdot \Delta)}{N}]
\end{aligned}
$$

$$= N \cdot k_B[\ln V + \frac{3}{2}\ln E] \quad \text{in the thermodynamic limit} \quad (3.17)$$

$$S = \frac{S}{N} = k_B[\ln V + \frac{3}{2}\ln E] \qquad (3.18)$$

## Spin System

Consider $N$ free localized spins
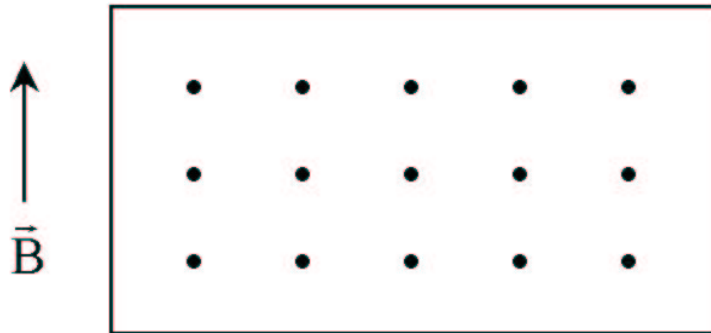


**isolated system**

each spin : $h = -\vec{\mu} \cdot \vec{B}$



$$\varepsilon \equiv -\mu \cdot B \qquad (3.19)$$

- **Macroscopic condition** : $N = n_+ + n_-, E = \varepsilon n_+ - \varepsilon n_-$

$n_+$: no. of spins up, $n_-$: no.of spin down

$$\longrightarrow n_+ = \frac{1}{2}(N + \frac{E}{\varepsilon}), \quad n_- = \frac{1}{2}(N - \frac{E}{\varepsilon})$$

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- **No. of accessible states :**

$$\Omega(E) = {}_N C_{n_+} = \frac{N!}{n_+! \cdot n_-!} \qquad (3.20)$$
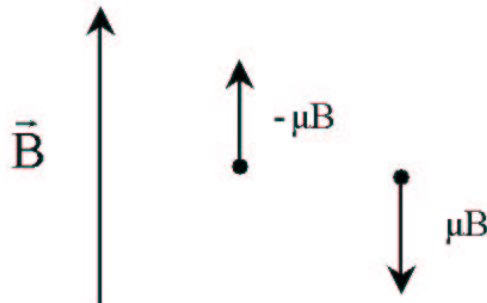
- **Entropy :**

$$
\begin{aligned}
S &= k_B \ln \Omega(E) \\
&= k_B \ln \frac{N!}{n_+! n_-!} \\
S &= k_B[\ln N! - \ln n_+! - \ln n_-!] \\
&\simeq k_B[N \ln N - N - n_+ \ln n_+ + n_+ - n_- \ln n_- + n_-] \\
&= -k_B[n_+ \cdot \ln \frac{n_+}{N} + n_- \ln \frac{n_-}{N}] \\
&= -N k_B[\frac{n_+}{N} \cdot \ln \frac{n_+}{N} + \frac{n_-}{N} \cdot \ln \frac{n_-}{N}]
\end{aligned}
$$

$$p_+ \equiv \frac{n_+}{N} = \frac{1}{2}[1 + \frac{E}{N\varepsilon}], \quad p_- = \frac{n_-}{N} = \frac{1}{2}[1 - \frac{E}{N\varepsilon}] \qquad (3.21)$$

$$\therefore \ S = -N k_B[p_+ \cdot \ln p_+ + p_- \cdot \ln p_-]$$

$$\downarrow$$

$$\mathcal{S} = \frac{S}{N} = -k_B[p_+ \cdot \ln p_+ + p_- \cdot \ln p_-] \qquad (3.22)$$

## 3.2 Interaction Between Thermodynamic Systems

**Def. External parameter** $\{x_i, \ i = 1, \ \cdots, \ n\}$

Macroscopically measurable independent parameters $x_1, \ x_2, \ \cdots$ and $x_n$ which appear in the Hamiltonian $H = H(q, \ p; \ \{x_i\})$ of the system ; $(q, \ p) = (q_1, \ \cdots, \ q_{3N}, \ p_1, \ \cdots, \ p_{3N})$

**e.g.,** $V, \ \vec{B}, \ \vec{E}, \ \cdots$

$$\text{Gas system}: \quad \triangle p_i \cdot \triangle q_i \sim h_0 \longrightarrow \triangle p_i \sim \frac{h_0}{L}$$

$$\text{Spin system}: \quad \mu B$$

$$-\mu B$$

$$H \longrightarrow \quad \text{energy levels: } \varepsilon_1, \ \varepsilon_2, \ \cdots, \ \varepsilon_r, \ \cdots$$

$$\varepsilon_r = \varepsilon_r(\{x_i\}, \ N)$$

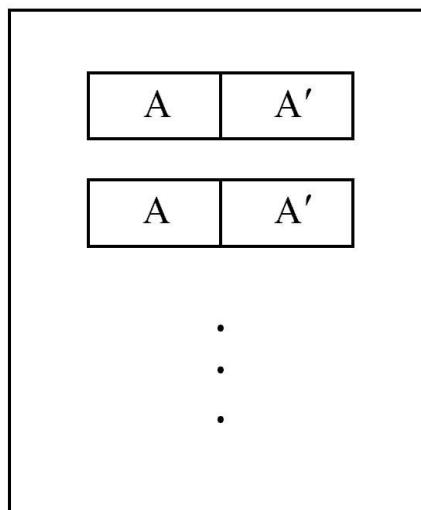$$\therefore \text{ Macroscopic quantities}\{y_i\} = \{E, \ \{x_i\}, \ N\} \qquad (3.23)$$

**Def. Macrostate**

A state which satisfies the macroscopic condition characterized by the given macroscopic quantities

$$\Omega(\text{No. of the accessible states}) = \Omega(E, \ \{x_i\}, \ N) \qquad (3.24)$$

Let's consider the case that two thermodynamic systems exchange energy without particle exchange:

Statistical Ensemble

$$n: \text{ No. of total subsystems}$$

$$^\exists \text{energy exchange between } A \ \& \ A'$$

$$A_t = A + A' : \text{ isolated}$$

$$\downarrow$$

$$E + E' = E_t : \text{ fixed}$$

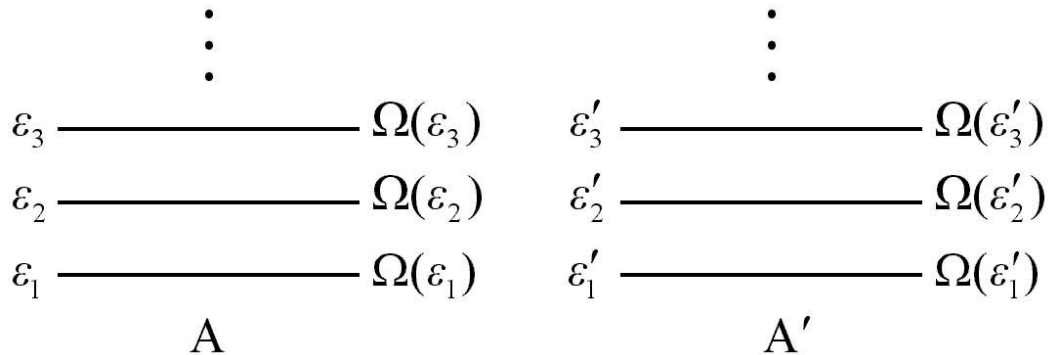$$N + N' = N_t : \text{ fixed}$$

### 3.2.1  Thermal Interaction

**Def.  Thermal Interaction**

Energy exchange with all the external parameters fixed

$$\downarrow$$
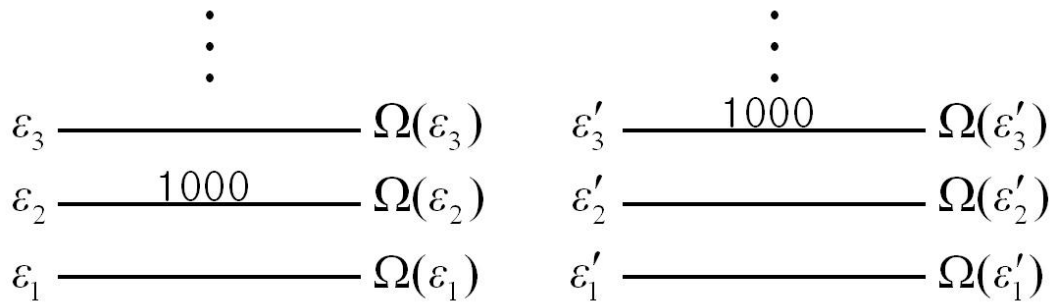
Energy levels of each system are unchanged.



$n_i$: No. of subsystems in the ith energy level

- **Initial equilibrium state**

$$A \ \& \ A' : \text{ isolated, } n = 1,000$$
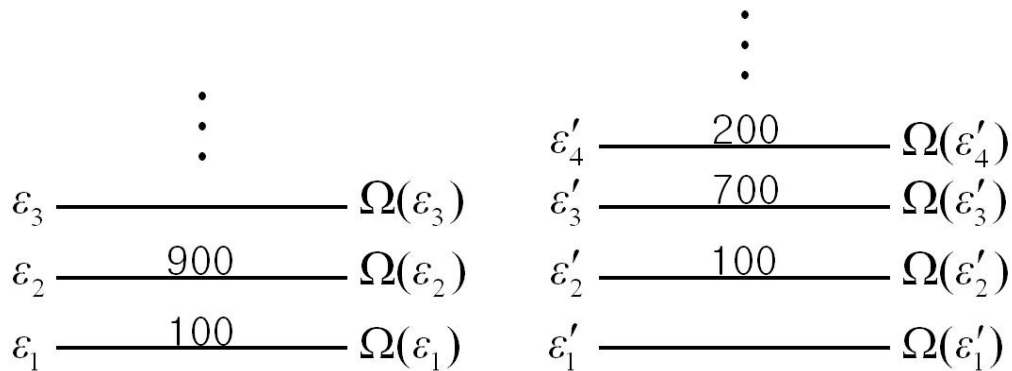
$$A : E_i = \varepsilon_2, \quad A' : E'_i = \varepsilon'_3$$

$$\varepsilon_3 \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_3) \qquad \varepsilon_3' \,\underline{\phantom{xx}1000\phantom{xx}}\, \Omega(\varepsilon_3')$$

$$\varepsilon_2 \,\underline{\phantom{xx}1000\phantom{xx}}\, \Omega(\varepsilon_2) \qquad \varepsilon_2' \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_2')$$

$$\varepsilon_1 \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_1) \qquad \varepsilon_1' \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_1')$$

Each subsystem is equally likely to be in each accessible microstate.

$$E_t = \varepsilon_2 + \varepsilon_3'$$

$$\Downarrow \quad \text{Thermal Interaction}$$

● **Final equilibrium state**

$$\varepsilon_4' \,\underline{\phantom{xx}200\phantom{xx}}\, \Omega(\varepsilon_4')$$

$$\varepsilon_3 \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_3) \qquad \varepsilon_3' \,\underline{\phantom{xx}700\phantom{xx}}\, \Omega(\varepsilon_3')$$

$$\varepsilon_2 \,\underline{\phantom{xx}900\phantom{xx}}\, \Omega(\varepsilon_2) \qquad \varepsilon_2' \,\underline{\phantom{xx}100\phantom{xx}}\, \Omega(\varepsilon_2')$$

$$\varepsilon_1 \,\underline{\phantom{xx}100\phantom{xx}}\, \Omega(\varepsilon_1) \qquad \varepsilon_1' \,\rule{4cm}{0.4pt}\, \Omega(\varepsilon_1')$$

Each subsystem whose energy is $\varepsilon_i$ is equally likely to be in the microstates which satisfy the macroscopic condition $E = \varepsilon_i$.

$p_i$: probability that the energy of the system $A$ is $\varepsilon_i$

$$p_i = \lim_{n \to \infty} \frac{n_i}{n} \tag{3.25}$$

$$\therefore p_1 = \frac{1}{10}, \ p_2 = \frac{9}{10}. \tag{3.26}$$

$$\overline{E_f} = \sum_i p_i \cdot \varepsilon_i = \frac{9}{10}\varepsilon_2 + \frac{1}{10}\varepsilon_1 \tag{3.27}$$

**Def. Heat $Q$**

$Q \equiv \overline{E_f} - E_i = \triangle \overline{E}$ : the change $\triangle \overline{E}$ of the average energy of the system $A$ is called the heat $Q$ absorbed by this system.

$$\text{Likewise} \quad, \quad \overline{E'_f} = \sum_i p'_i \cdot \varepsilon'_i = \frac{1}{10}\varepsilon'_2 + \frac{7}{10}\varepsilon'_3 + \frac{2}{10}\varepsilon'_4$$

$$\therefore \; Q' = \triangle E' = \overline{E'_f} - E'_i$$

However, the total system $A_t \, (= A + A')$ is isolated.

$$\therefore E_{t,\,i} = E_i + E'_i = E_{t,\,f} = \overline{E_f} + \overline{E'_f}$$

$$\downarrow$$

$$(\overline{E_f} - E_i) + (\overline{E_f}' - E'_i) = Q + Q' = 0$$
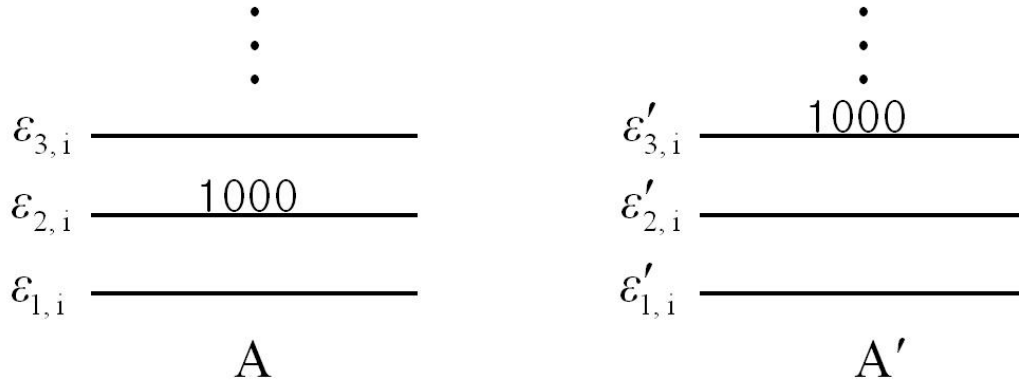
$$\therefore \; Q = -Q'$$

Note that for thermal interaction, the energy levels and $\Omega(\varepsilon_i)$ of each subsystem are unchanged, but $n_i$'s or equivalently $P_i$'s are changed.

### 3.2.2  Mechanical Interaction

- **A system which cannot interact thermally with any other system is said to be "thermally insulated (or isolated)."**

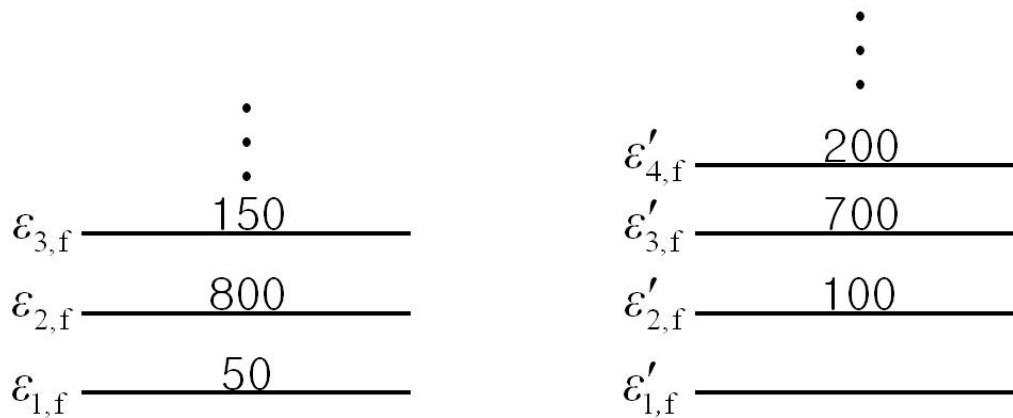- **A process in which there is no thermal interaction is said to be "adiabatic."**

Let's consider an adiabatic process in which external parameters change. Since external parameters change, energy levels, $\Omega$ & $n_i$'s can generally change.

- **Initial equilibrium state**

$$\varepsilon_{3,i} \underline{\hspace{4cm}} \qquad \varepsilon'_{3,i} \underline{\quad 1000 \quad}$$

$$\varepsilon_{2,i} \underline{\quad 1000 \quad} \qquad \varepsilon'_{2,i} \underline{\hspace{4cm}}$$

$$\varepsilon_{1,i} \underline{\hspace{4cm}} \qquad \varepsilon'_{1,i} \underline{\hspace{4cm}}$$

$$\text{A} \qquad\qquad\qquad \text{A}'$$

$$E_{t,i} = \varepsilon_{2,i} + \varepsilon'_{3,i}$$

$$\Downarrow \quad \text{Mechanical Interaction}$$

$$\varepsilon'_{4,f} \underline{\quad 200 \quad}$$

$$\varepsilon_{3,f} \underline{\quad 150 \quad} \qquad \varepsilon'_{3,f} \underline{\quad 700 \quad}$$

$$\varepsilon_{2,f} \underline{\quad 800 \quad} \qquad \varepsilon'_{2,f} \underline{\quad 100 \quad}$$

$$\varepsilon_{1,f} \underline{\quad 50 \quad} \qquad \varepsilon'_{1,f} \underline{\hspace{4cm}}$$

$$P(\varepsilon_{1,f}) = \frac{1}{20}, \ P(\varepsilon_{2,f}) = \frac{4}{5}, \ P(\varepsilon_{3,f}) = \frac{3}{20} \qquad (3.28)$$

$$\therefore \ \overline{E_f} = \frac{\varepsilon_{1,f}}{20} + \frac{4}{5}\varepsilon_{2,f} + \frac{3}{20}\varepsilon_{3,f} \qquad (3.29)$$

$\triangle \overline{E} = \overline{E_f} - E_i$: the change $\triangle \overline{E}$ of the average energy due to the external

parameter changes.

**Def. Work $W$**

$$W \equiv -\triangle \overline{E} : \text{Work done by the system}$$

$$\text{Likewise, } \triangle \overline{E'} = \overline{E'_f} - E'_i$$

$$\triangle \overline{E} + \triangle \overline{E'} = 0 \quad \longrightarrow \quad W + W' = 0$$

### 3.2.3  General Interaction

thermal interaction + mechanical interaction

$\triangle \overline{E}$ : the change in the average energy due to a general interaction

$\triangle_x \overline{E}$ : the change in the average energy due to external parameter

changes

$$\downarrow$$

$$\triangle \overline{E} \equiv \triangle_x \overline{E} + Q = Q - W; \; W = -\triangle_x \overline{E} \qquad (3.30)$$

Both work and heat are a kind of energy transferred in different ways.

- **1st law of thermodynamics**

    An equilibrium macrostate of a system can be characterized by the average energy $\overline{E}$ (called the "internal energy") which has the following properties:

    (1) For an isolated system, $\overline{E}$ =const.

    (2) Interaction $\longrightarrow$ $\triangle \overline{E} = Q - W$

    ( one macrostate $\longrightarrow$ another macrostate )

- **Infinitesimal general interactions**

    A process is said to be infinitesimal if it takes the system from an initial microstate to a final macrostate which differs from the initial macrostate only infinitesimally.

### 3.2.4  Quasi-Static Process

A process is said to be quasi-static if it is carried out so slowly that it remains arbitrarily close to equilibrium at all stages of the process.
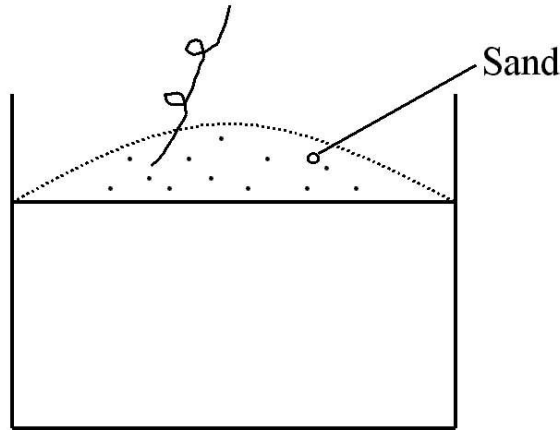


$r$ : a microstate $\longrightarrow$ $\varepsilon_r$ : the energy of the microstate $r$

$$\varepsilon_r = \varepsilon_r(\{x_i\},\ N) \tag{3.31}$$

$p_r$ : the probability that the system is in the state $r$

$$U = \overline{E} = \sum_r p_r \cdot \varepsilon_r \tag{3.32}$$

Consider an infinitesimal adiabatic quasi-static process:

$$\{x_i\} \longrightarrow \{x_i + dx_i\}. \tag{3.33}$$

$$dW = -d\overline{E} = -\sum_r p_r \cdot d\varepsilon_r \tag{3.34}$$

$$\varepsilon_r = \varepsilon_r\left(x_1,\ ,\ \cdots,\ x_n,\ N\right)$$

$$\downarrow$$

$$d\varepsilon_r = \sum_{i=1}^{n} \frac{\partial \varepsilon_r}{\partial x_i} \cdot dx_i \tag{3.35}$$

$$\therefore dW = \sum_{i=1}^{n}\left(-\sum_r p_r \cdot \frac{\partial \varepsilon_r}{\partial x_i}\right) \cdot dx_i \tag{3.36}$$

- **Def. Generalized force**

$$X_{i,\,r} \equiv -\frac{\partial \varepsilon_r}{\partial x_i} : \text{generalized force conjugate to the external}$$

$$\text{parameter } x_i \text{ in the state } r$$

$$\overline{X_i} = \sum_r p_r \cdot X_{i,\,r} : \text{average generalized force conjugate to } x_i$$

$$\therefore dW = \sum_{i=1}^{n} \overline{X_i} \cdot dx_i \tag{3.37}$$

$$dU = d\overline{E} = -\sum_i \overline{X_i} \cdot dx_i \tag{3.38}$$

$$\therefore \overline{X_i} = -(\frac{\partial U}{\partial x_i})_s \tag{3.39}$$
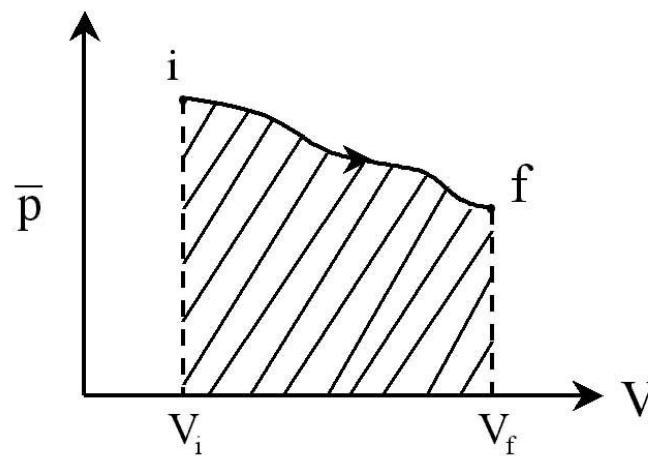
$$\downarrow$$

Consider a finite adiabatic quasi-static process.

$$\triangle W = W_f - W_i = \int_{path\ i}^{f} dW \tag{3.40}$$

**e.g.** $P - V$ work

$$dW = P \cdot dV \tag{3.41}$$

### 3.2.5 Exact and Inexact Differentials

Consider a thermodynamic function $F(x_1, x_2)$;

$$x_1 \text{ and } x_2 \text{ are thermodynamic variables}$$

$$\downarrow$$

- **Infinitesimal change**: $(x_1, x_2) \longrightarrow (x_1 + dx_1, x_2 + dx_2)$

$$
\begin{aligned}
dF &= F(x_1 + dx_1, x_2 + dx_2) - F(x_1, x_2) \\
&= \frac{\partial F}{\partial x_1} \cdot dx_1 + \frac{\partial F}{\partial x_2} \cdot dx_2
\end{aligned}
\tag{3.42}
$$

- **Finite change** $(i \longrightarrow f)$

$$\triangle F = \int_i^f dF = F_f - F_i = \int_i^f \left( \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_2} dx_2 \right) \tag{3.43}$$

$\triangle F$ depends only on the initial & final states.

It does not depend on the process $(i \longrightarrow f)$

Now, consider an arbitrary infinitesimal quantity. $đF$

$$đF = A(x_1, x_2)dx_1 + B(x_1, x_2)dx_2 \tag{3.44}$$

If there is some function $F$ s.t. $A(x_1, x_2) = \frac{\partial F}{\partial x_1}$ & $B(x_1, x_2) = \frac{\partial F}{\partial x_2}$,
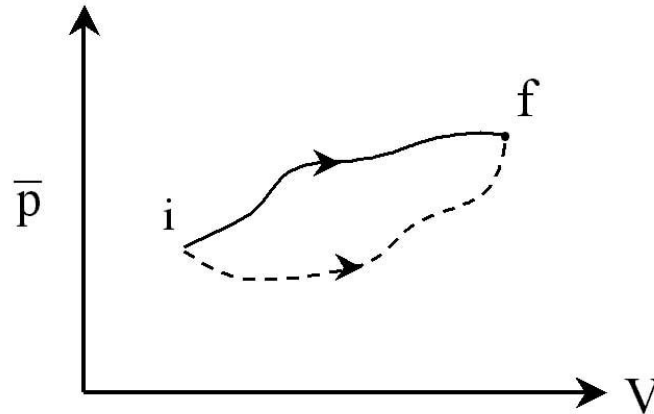then $đF = dF$: exact differential.

Otherwise, $đF$: inexact differential.

For the case of an inexact differential,

$$\triangle F (= \int_i^f đF) \text{ depends on the process } (i \longrightarrow f). \tag{3.45}$$

For this case, the thermodynamic quantity $F$ is not a thermodynamic function.

**e.g.** Quasi-static work for general interaction.



$$\bar{d}W = \bar{p} \cdot dv, \triangle W = \int_i^f \bar{d}W \ \text{ depends on the process}$$

$$dU = \bar{d}Q - \bar{d}W$$

$$\downarrow$$

$$\bar{d}Q = dU + \bar{d}W$$

$$\downarrow$$

$\bar{d}Q$ is generally an inexact differential.

Adiabatic process $\longrightarrow \bar{d}Q = 0$

$$\therefore \ \bar{d}W = -dU : \ \text{exact differential} \tag{3.46}$$

Pure thermal interaction $\longrightarrow \bar{d}W = 0$

$$\therefore \ \bar{d}Q = dU : \ \text{exact differential.} \tag{3.47}$$