

Chapter 1

Fundamentals of Statistical Physics

- **Aim of the Statistical Mechanics**

We will discuss the basic physical concepts and methods appropriate for the description of macroscopic systems consisting of very many particles such as gases, liquids, solids, electromagnetic radiation (photons), and so on. Indeed, most physical, chemical, and biological systems, one is generally not concerned with the detailed behaviors of each constituent (atom or molecule). Instead, one is usually interested in the macroscopic parameters characterizing the macroscopic system as a whole (e.g., volume, pressure, magnetic moment, thermal conductivity, etc.).

The study of macroscopic systems is probably the most active area of modern physics research outside realm of high-energy physics, the main purpose of which is to understand the fundamental interactions in nature. In trying to discuss macroscopic systems, one faces a rather different task which is no less challenging. Even when the interactions between individual atoms (in most cases, electromagnetic interactions) are well known, the task of understanding the macroscopic systems is far from trivial. We must note that even if the interactions between individual atoms are rather simple, quite unexpected macroscopic phenomena may occur due to the collective behavior of the atoms. For example, phase transition (from a gas to a liquid) and biological growth and reproduction. Hence the problem is not just one of carrying out complicated computations (quantitative details). The main aim is, instead, to use one's knowledge

of basic physical laws to develop new concepts which can illuminate the essential qualitative characteristics of such macroscopic systems.

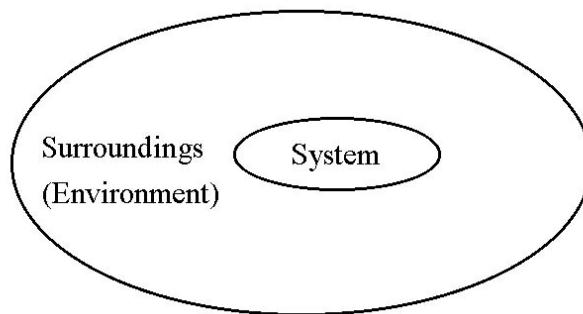
In discussing macroscopic systems, we shall not recapitulate the historical development of the various disciplines dealing with the physical description of such systems. Instead we shall, from the outset, adopt a modern point of view based on the microscopic fundamental laws and some statistical postulates (i.e. Statistical Thermodynamics)

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: $N \rightarrow \infty, V \rightarrow \infty$ s.t. $N/V = n = \text{finite const.}$



(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 its surroundings

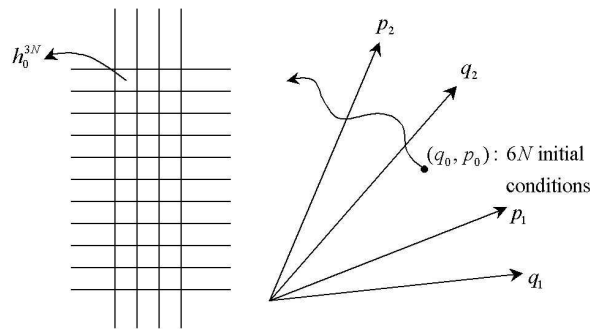
• Specification of the state of a system

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

Classical Approximation

$$H = H(q, p), \text{ where } (q, p) = (q_1, \dots, q_{3N}, p_1, \dots, p_{3N}) \quad (1.1)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \dot{p}_i = -\frac{\partial H}{\partial q_i}, i = 1, \dots, 3N \quad (1.2)$$



$6N$ -D Phase Space

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

Divide the phase space into small cells of equal volume:

$$\delta q_i \delta p_i = h_0 \rightarrow \prod_{i=1}^{3N} \delta q_i \delta p_i = h_0^{3N} : \text{Countable state.}$$

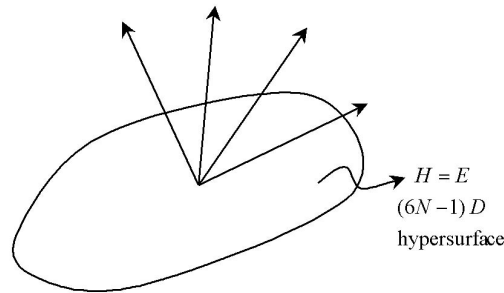
Partial Information

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:



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.

1.1 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: $1, 2, \dots, \Omega$

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

$$p_i = \frac{1}{\Omega} \text{ for all } i, i = 1, \dots, \Omega. \quad (1.3)$$

Entropy S of the system

$$S \equiv k_B \ln \Omega(E), \quad (1.4)$$

where k_B is the Boltzmann's constant. Note that the macroscopic quantity S is obtained from the microscopic information Ω . This entropy S measures the degree of "complexity" (or "randomness") of the system

• **Another Point of View (Maximum Entropy Principle)**

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

→ accessible states : $1, 2, \dots, \Omega$

n_i (occupation number): No. of subsystems in the i th microstate,

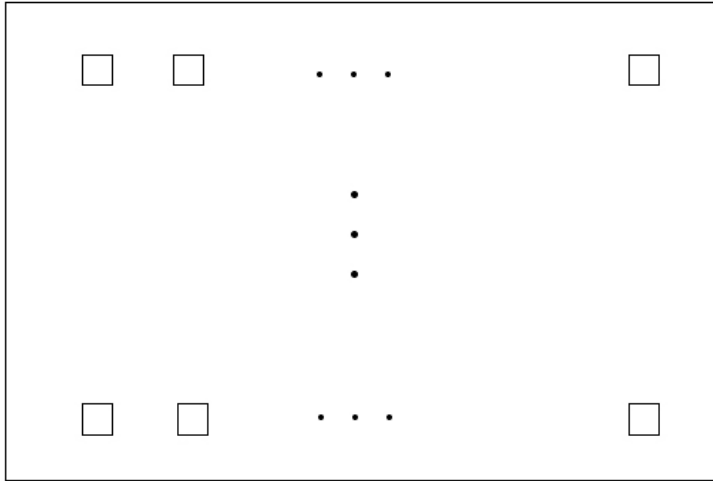
$$i = 1, \dots, \Omega.$$

$$\{n_i\} = (n_1, n_2, \dots, n_\Omega), \quad \sum_{i=1}^{\Omega} n_i = n \quad (1.5)$$

What is the most probable set $\{n_i\}$?

Def. Thermodynamic Probability M of the set $\{n_i\}$

$$M \equiv \frac{n!}{\prod_i n_i!} = {}_n C_{n_1} \cdot {}_{n-n_1} C_{n_2} \cdots \quad (1.6)$$



The subsystems in the M.C.E. are distributed over the accessible states.

Microcanonical Ensemble (M.C.E.)
(n subsystems)

Postulate : $\{n_i\}$ s.t. $M(\{n_i\}) = \max$: most probable set
most probable state = equilibrium state

$$\ln M = \ln n! - \sum_i \ln n_i! \quad (1.7)$$

$$\approx n \ln n - \sum_i n_i \ln n_i \quad (\text{Stirling Formula}) \quad (1.8)$$

$$= \sum_i n_i \ln n - \sum_i n_i \ln n_i \quad (1.9)$$

$$= -n \sum_i \frac{n_i}{n} \ln \frac{n_i}{n} \quad (1.10)$$

$$= -n \sum_i p_i \ln p_i, \quad p_i = \frac{n_i}{n}. \quad (1.11)$$

Def. Entropy S

$$S \equiv k_B \cdot \frac{\ln M}{n} = -k_B \sum_i p_i \cdot \ln p_i, \quad \sum_{i=1}^{\Omega} p_i = 1. \quad (1.12)$$

M : max. \iff S : max.

$$dS = -k_B \sum_i (1 + \ln p_i) dp_i = 0, \quad (1.13)$$

$$\sum_i dp_i = 0. \quad (1.14)$$

Using the undetermined multiplier's method,

$$dS + \lambda \sum_i dp_i = 0, \quad \lambda : \text{some const.} \quad (1.15)$$

$$\therefore \sum_i (1 + \ln p_i + \lambda) dp_i = 0 \quad (1.16)$$

$$\therefore 1 + \ln p_i + \lambda = 0 \longrightarrow p_i = \text{const.} \quad (1.17)$$

$$\sum_{i=1}^{\Omega} p_i = 1 \longrightarrow p_i = 1/\Omega \quad : \text{equal weight for all } i \quad (1.18)$$

$$S = -k_B \sum_i p_i \ln p_i \quad (1.19)$$

$$= -k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} \quad (1.20)$$

$$= k_B \ln \Omega(E). \quad (1.21)$$

Equal a Priori Weight + $S \equiv k_B \ln \Omega(E)$

\Updownarrow

Thermodynamic Prob. M : max

\downarrow

$$S \equiv -k_B \sum_{i=1}^{\Omega} p_i \ln p_i \quad (p_i = \frac{n_i}{n}) \quad : \text{max. under the condition, } \sum_{i=1}^{\Omega} p_i = 1$$

• Summary

How to study the thermodynamic systems statistically?

1. Find all the accessible microstates which satisfy the given

macroscopic condition from the fundamental law (the Classical or Quantum mechanics).

Accessible Microstates: $1, 2, \dots, \Omega$.

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

Fundamental(or basic) Postulate:

Equal a priori Weight ($p_i = 1/\Omega$) + $S \equiv k_B \ln \Omega$

$S \equiv -k_B \sum_i p_i \ln p_i$: max. under the condition

↓

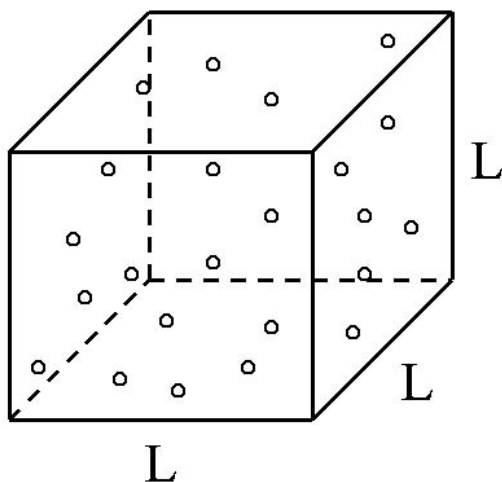
$$p_i = 1/\Omega$$

3. Thermal Average (or Ensemble Average)

f : a thermodynamic quantity $\longrightarrow f = f(i)$.

$$\langle f \rangle = \sum_i f(i)p_i = \sum_i f(i)/\Omega \quad (1.22)$$

Classical Ideal Gas



Isolated System

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} \quad (1.23)$$

$$\dot{q}_i = \frac{dH}{d\vec{p}_i}, \quad \dot{p}_i = -\frac{dH}{dq_i}, \quad i = 1, \dots, N. \quad (1.24)$$

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

$$\therefore \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = E \quad (1.25)$$

\downarrow

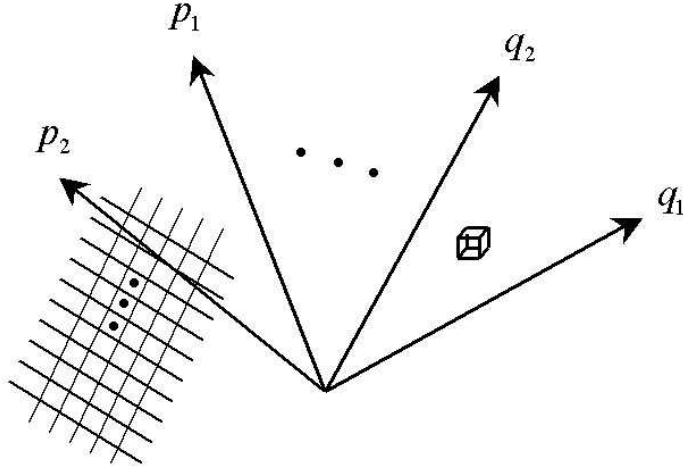
$$\sum_{i=1}^N \vec{p}_i^2 = 2mE = (\sqrt{2mE})^2$$

$$\vec{p}_i = (p_{i,x}, p_{i,y}, p_{i,z}) \quad (1.26)$$

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

6N-D Phase Space

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 .

$$\begin{aligned} \Phi(E) &= \int \cdots \int \prod_{i=1}^{3N} dq_i \cdot dp_i / h_0^{3N} \\ 0 \leq q_i \leq L, H \leq E &\longrightarrow \sum_{i=1}^{3N} p_i^2 \leq 2mE \quad (\text{Macroscopic condition}) \\ &= V^N \cdot \int \cdots \int \prod_{i=1}^{3N} dp_i / h_0^{3N} \quad \left(\sum_{i=1}^{3N} p_i^2 \leq 2mE \right) \quad (1.27) \end{aligned}$$

$$\sum_{i=1}^{3N} \frac{p_i^2}{2m} = E \longrightarrow \sum_{i=1}^{3N} p_i^2 = (\sqrt{2mE})^2 \quad (1.28)$$

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

$$\text{Sphere in the } 2D \text{ space} \longrightarrow \text{circle } x^2 + y^2 = R^2 \longrightarrow \text{Vol} = \pi R^2 \quad (1.29)$$

Sphere in the 3D space $\longrightarrow x^2 + y^2 + z^2 = R^2 \longrightarrow \text{Vol} = \frac{4}{3}\pi R^3$ (1.30)

⋮

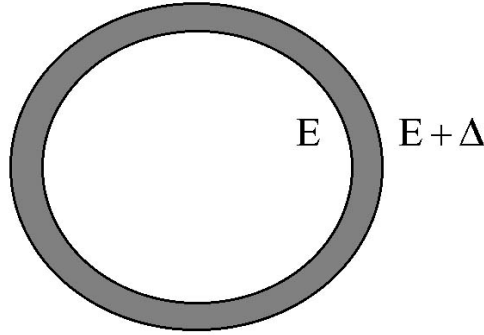
In general, the volume of the sphere of radius R in the n -D space $\propto R^n$

$$\therefore \Phi(E) \propto V^N \cdot (\sqrt{2mE})^{3N} \quad (1.31)$$

$$= C \cdot V^N \cdot E^{3N/2} \quad (1.32)$$

$$C : \text{const. indep. of } V \& E \quad (1.33)$$

No. of accessible states:



$$\begin{aligned} \Omega(E) &= \Phi(E + \Delta) - \Phi(E) \\ &\simeq \frac{d\Phi}{dE} \cdot \Delta \\ &= C \cdot N \cdot V^N \cdot E^{3N/2-1} \cdot \Delta \end{aligned} \quad (1.34)$$

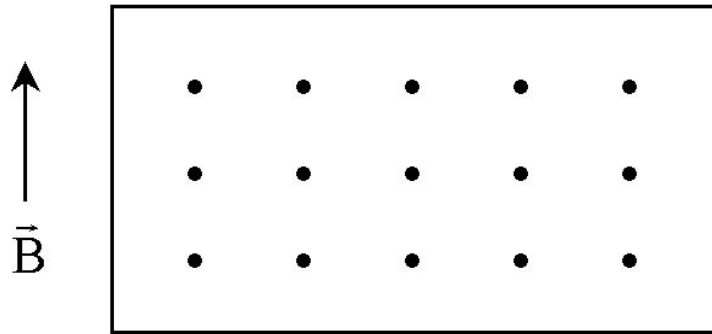
Entropy S :

$$\begin{aligned} S &= k_B \cdot \ln \Omega(E) \\ &= k_B [\ln C + \ln N + N \ln V + (\frac{3N}{2} - 1) \ln E + \ln \Delta] \\ &\simeq N k_B [\ln V + \frac{3}{2} \ln E + \frac{\ln N}{N} + \frac{\ln(C \cdot \Delta)}{N}] \\ &= N \cdot k_B [\ln V + \frac{3}{2} \ln E] \quad \text{in the thermodynamic limit} \end{aligned} \quad (1.35)$$

$$s = \frac{S}{N} = k_B [\ln V + \frac{3}{2} \ln E] \quad (1.36)$$

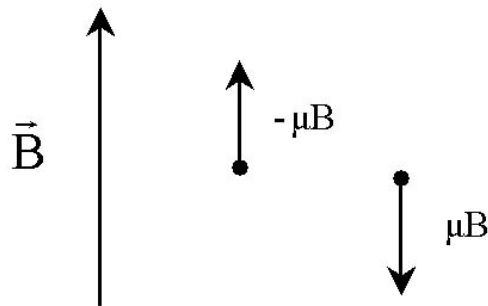
Spin System

Consider N free localized spins



isolated system

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



$$\varepsilon \equiv -\mu \cdot B \tag{1.37}$$

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

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

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

- **No. of accessible states** :

$$\Omega(E) = {}_N C_{n_+} = \frac{N!}{n_+! \cdot n_-!} \tag{1.38}$$

• **Entropy :**

$$\begin{aligned}
S &= k_B \ln \Omega(E) \\
&= k_B \ln \frac{N!}{n_+! n_-!} \\
S &= k_B [\ln N! - \ln n_+! - \ln n_-!] \\
&\simeq k_B [N \ln N - N - n_+ \ln n_+ + n_+ - n_- \ln n_- + n_-] \\
&= -k_B [n_+ \cdot \ln \frac{n_+}{N} + n_- \ln \frac{n_-}{N}] \\
&= -N k_B [\frac{n_+}{N} \cdot \ln \frac{n_+}{N} + \frac{n_-}{N} \cdot \ln \frac{n_-}{N}] \\
p_+ &\equiv \frac{n_+}{N} = \frac{1}{2} [1 + \frac{E}{N\varepsilon}], \quad p_- = \frac{n_-}{N} = \frac{1}{2} [1 - \frac{E}{N\varepsilon}] \tag{1.39}
\end{aligned}$$

$$\begin{aligned}
\therefore S &= -N k_B [p_+ \cdot \ln p_+ + p_- \cdot \ln p_-] \\
&\quad \downarrow \\
s &= \frac{S}{N} = -k_B [p_+ \cdot \ln p_+ + p_- \cdot \ln p_-] \tag{1.40}
\end{aligned}$$

1.2 Interaction Between Thermodynamic Systems

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

Macroscopically measurable independent parameters x_1, x_2, \dots and x_n which appear in the Hamiltonian $H = H(q, p; \{x_i\})$ of the system ;

$(q, p) = (q_1, \dots, q_{3N}, p_1, \dots, p_{3N})$

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

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

Spin system : μB
 $-\mu B$

$H \longrightarrow$ energy levels: $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_r, \dots$
 $\varepsilon_r = \varepsilon_r(\{x_i\}, N)$

$$\therefore \text{Macroscopic quantities } \{y_i\} = \{E, \{x_i\}, N\} \quad (1.41)$$

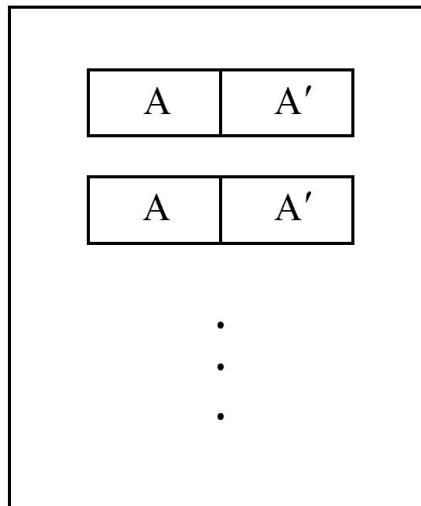
Def. Macrostate

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

$$\Omega(\text{No. of the accessible states}) = \Omega(E, \{x_i\}, N) \quad (1.42)$$

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

Statistical Ensemble



n : No. of total subsystems

\exists energy exchange between A & A'

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

↓

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

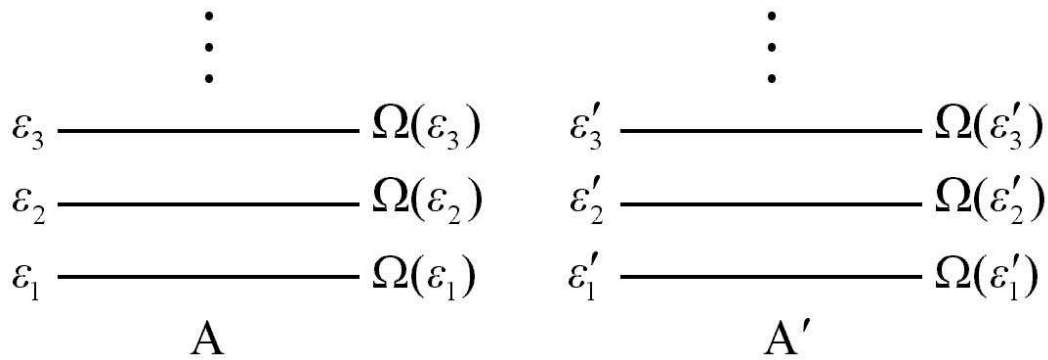
$$N + N' = N_t : \text{fixed}$$

1.2.1 Thermal Interaction

Def. Thermal Interaction

Energy exchange with all the external parameters fixed

↓

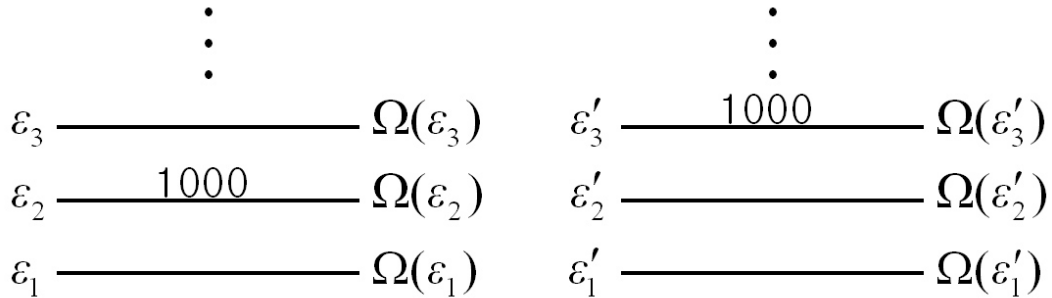


n_i : No. of subsystems in the i th energy level

• Initial equilibrium state

A & A' : isolated, $n = 1,000$

$$A : E_i = \varepsilon_2, \quad A' : E'_i = \varepsilon'_3$$

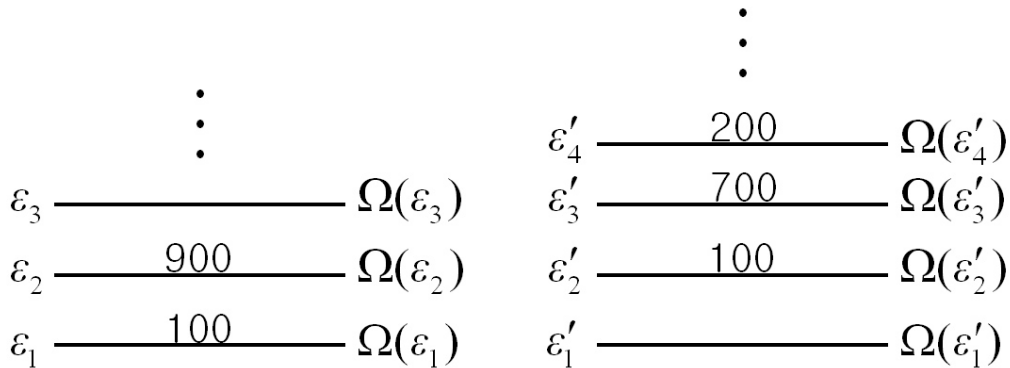


Each subsystem is equally likely to be in each accessible microstate.

$$E_t = \varepsilon_2 + \varepsilon'_3$$

\Downarrow Thermal Interaction

• Final equilibrium state



Each subsystem whose energy is ε_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 ε_i

$$p_i = \lim_{n \rightarrow \infty} \frac{n_i}{n} \tag{1.43}$$

$$\therefore p_1 = \frac{1}{10}, \quad p_2 = \frac{9}{10}. \tag{1.44}$$

$$\overline{E}_f = \sum_i p_i \cdot \varepsilon_i = \frac{9}{10}\varepsilon_2 + \frac{1}{10}\varepsilon_1 \quad (1.45)$$

Def. Heat Q

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

$$\begin{aligned} \text{Likewise , } \overline{E}'_f &= \sum_i p'_i \cdot \varepsilon'_i = \frac{1}{10}\varepsilon'_2 + \frac{7}{10}\varepsilon'_3 + \frac{2}{10}\varepsilon'_4 \\ \therefore Q' &= \Delta E' = \overline{E}'_f - E'_i \end{aligned}$$

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

$$\begin{aligned} \therefore E_{t,i} &= E_i + E'_i = E_{t,f} = \overline{E}_f + \overline{E}'_f \\ &\downarrow \\ (\overline{E}_f - E_i) &+ (\overline{E}'_f - E'_i) = Q + Q' = 0 \\ \therefore Q &= -Q' \end{aligned}$$

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.

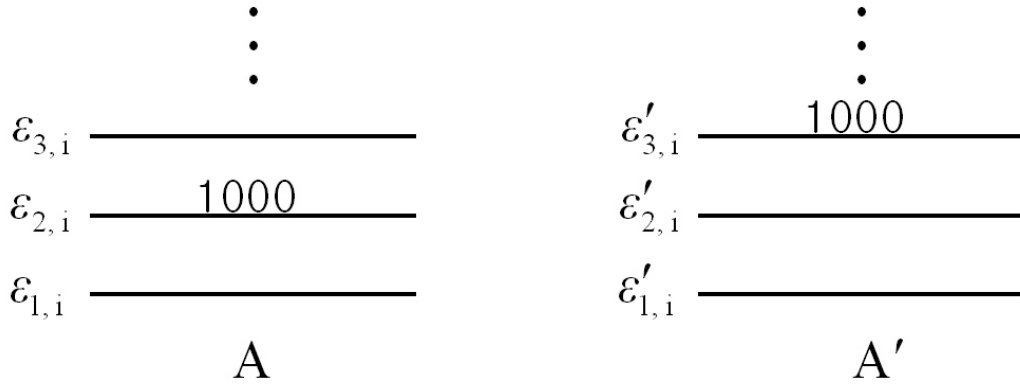
1.2.2 Mechanical Interaction

- 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.

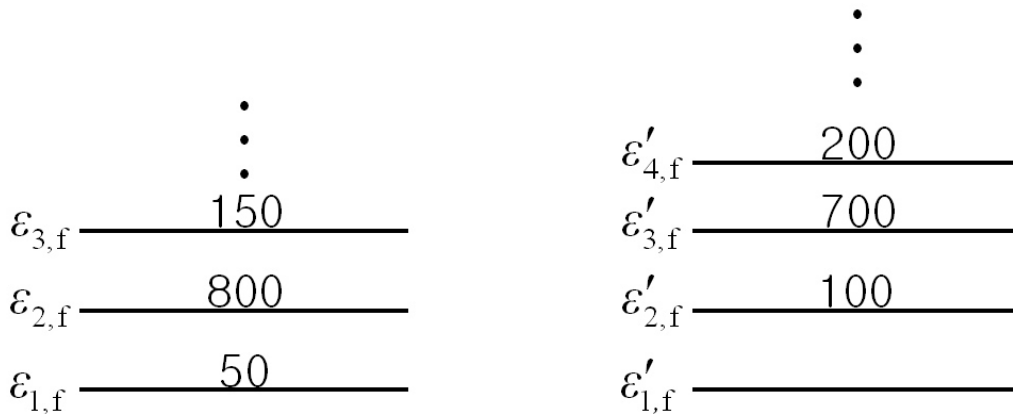
Since external parameters change, energy levels, Ω & n_i 's can generally change.

• **Initial equilibrium state**



$$E_{t,i} = \epsilon_{2,i} + \epsilon'_{3,i}$$

⇓ Mechanical Interaction



$$P(\epsilon_{1,f}) = \frac{1}{20}, \quad P(\epsilon_{2,f}) = \frac{4}{5}, \quad P(\epsilon_{3,f}) = \frac{3}{20} \quad (1.46)$$

$$\therefore \overline{E}_f = \frac{\epsilon_{1,f}}{20} + \frac{4}{5}\epsilon_{2,f} + \frac{3}{20}\epsilon_{3,f} \quad (1.47)$$

$\Delta \overline{E} = \overline{E}_f - E_i$: the change $\Delta \overline{E}$ of the average energy due to the external parameter changes.

Def. Work W

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

$$\begin{aligned} \text{Likewise, } \Delta \bar{E}' &= \bar{E}'_f - E'_i \\ \Delta \bar{E} + \Delta \bar{E}' &= 0 \quad \longrightarrow \quad W + W' = 0 \end{aligned}$$

1.2.3 General Interaction

thermal interaction + mechanical interaction

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

$\Delta_x \bar{E}$: the change in the average energy due to external parameter changes

↓

$$\Delta \bar{E} \equiv \Delta_x \bar{E} + Q = Q - W; \quad W = -\Delta_x \bar{E} \quad (1.48)$$

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 \bar{E} (called the “internal energy”) which has the following properties:

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

(2) Interaction $\longrightarrow \Delta \bar{E} = Q - W$

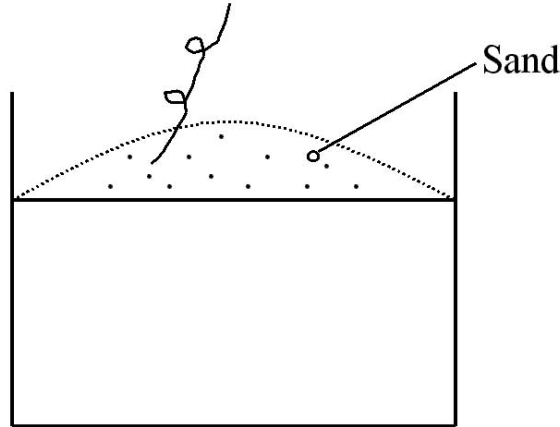
(one macrostate \longrightarrow another macrostate)

- **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.

1.2.4 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

$$\varepsilon_r = \varepsilon_r(\{x_i\}, N) \quad (1.49)$$

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

$$U = \bar{E} = \sum_r p_r \cdot \varepsilon_r \quad (1.50)$$

Consider an infinitesimal adiabatic quasi-static process:

$$\{x_i\} \longrightarrow \{x_i + dx_i\}. \quad (1.51)$$

$$dW = -d\bar{E} = -\sum_r p_r \cdot d\varepsilon_r \quad (1.52)$$

$$\varepsilon_r = \varepsilon_r(x_1, \dots, x_n, N)$$

$$\begin{aligned} & \downarrow \\ d\varepsilon_r &= \sum_{i=1}^n \frac{\partial \varepsilon_r}{\partial x_i} \cdot dx_i \end{aligned} \quad (1.53)$$

$$\therefore dW = \sum_{i=1}^n \left(- \sum_r p_r \cdot \frac{\partial \varepsilon_r}{\partial x_i} \right) \cdot dx_i \quad (1.54)$$

• **Def. Generalized force**

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

$\bar{X}_i = \sum_r p_r \cdot X_{i,r}$: average generalized force conjugate to x_i

$$\therefore dW = \sum_{i=1}^n \bar{X}_i \cdot dx_i \quad (1.55)$$

$$dU = d\bar{E} = - \sum_i \bar{X}_i \cdot dx_i \quad (1.56)$$

$$\therefore \bar{X}_i = - \left(\frac{\partial U}{\partial x_i} \right)_s \quad (1.57)$$

↓

Consider a finite adiabatic quasi-static process.

$$\Delta W = W_f - W_i = \int_{\text{path } i}^f dW \quad (1.58)$$

e.g. $P - V$ work

$$dW = P \cdot dV \quad (1.59)$$

