PART II

$$S = k \ln W$$

- All of Statistical Mechanics
- $$\underbrace{S(E,V,N)}_{\text{Entropy}} = k \ln \underbrace{W(E,V,N)}_{\substack{\#\ \text{microstates} \\ \text{for given macrostate}}}$$

- What are these quantities?
- What are the conditions of validity?
- What does it mean?
- Applications

III. Basic Ideas of Statistical Mechanics.

A. Types of Equilibrium Systems

In equilibrium stat. mech., we are mostly interested in the following three situations.

(i) Isolated Systems

- Do NOT exchange energy OR particles with the surroundings
- Have definite energy, define volume, and definite number of particles

- We shall see that the postulates of stat. mech. are often stated with respect to isolated systems.
- Corresponding Ensemble: Microcanonical Ensemble

Remarks:
- useful in developing the theory
- not so convenient in carrying out calculations

(ii) Systems in thermodynamic equilibrium with a heat bath

- there is heat (energy) exchange between the system and the surroundings
- instead of a definite energy, the system is characterized by a temperature T (that of the heat bath). The number of particles is fixed.
- since no definite energy, we can talk about average or mean energy of the system AND fluctuations in the energy

• We shall see that this is a more convenient way to calculate thermodynamic quantities in stat. mech.

• Corresponding Ensemble: Canonical Ensemble

(iii) Open Systems

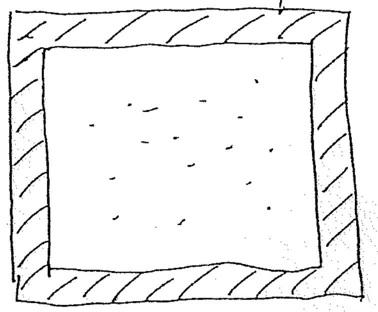
- can exchange heat (energy) with a bath AND exchange particles with the bath
- Equilibrium: thermal + Diffusive (chemical)

  thermal: $T_{system} = T_{bath}$; Diffusive (chemical): $\mu_{system} = \mu_{bath}$
- instead of a definite energy and a definite number of particles, the system is characterized by a temperature T and a chemical potential μ (both of that of the bath).
- E, N not fixed, we can talk about mean energy and mean number of particles and their fluctuations

• We shall see that this is a convenient way of doing stat. mech. calculations, especially when dealing with quantum statistics (fermions / bosons)

• Corresponding Ensemble: Grand Canonical Ensemble

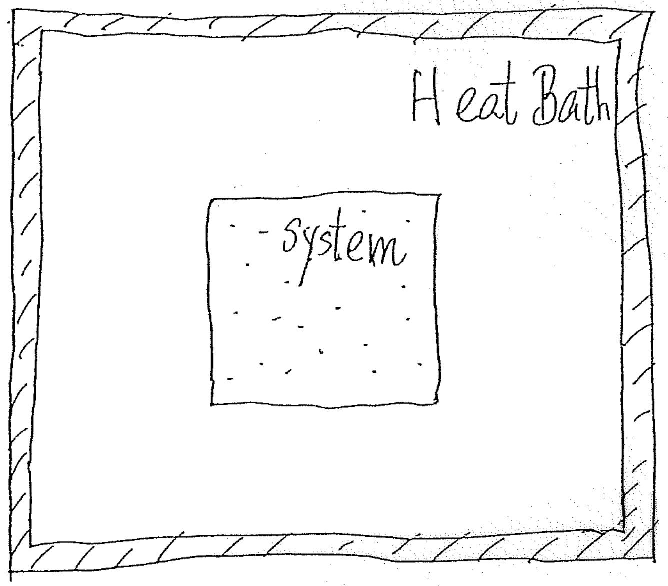
Isolated System



E, V, N fixed

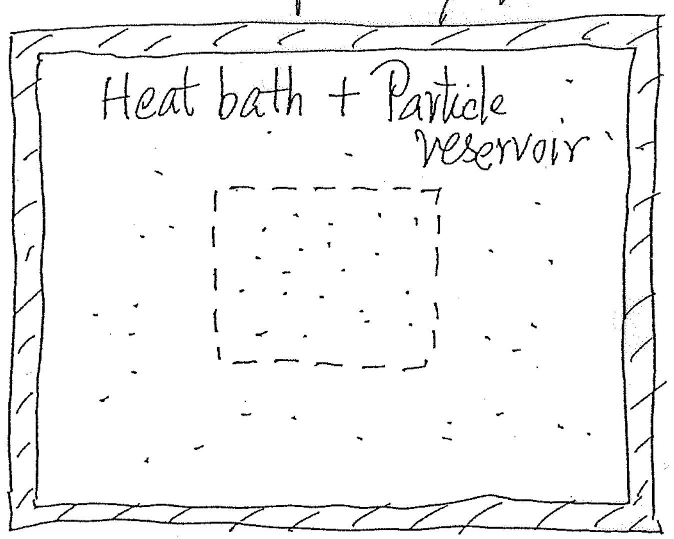
- System to establish principles of Stat. Mech.

[Microcanonical Ensemble]



System has T, V, N fixed
(System in equilibrium with a heat bath)
[Canonical Ensemble]

Open System



System has T, V, μ fixed
(System in equilibrium with a heat bath and a particle reservoir)

[Grand Canonical Ensemble]

Remark

- A fourth system is one with the temperature T and pressure p kept fixed.

Fixed temp. $\Rightarrow$ Energy can be exchanged between system and bath

Fixed pressure $\Rightarrow$ Volume can be exchanged between system and bath

"T-p ensemble"
[useful in chemistry]

B. Different levels of describing a system

- Macrostates (a macroscopic picture)
- Microstates (a very detailed description)
- Distributions (somewhere in between)

Macrostates

- In thermodynamics, we are not concerned with the detailed behaviour of each of the $N (\sim 10^{23})$ particles.
- Instead, system is characterized by a few variables, e.g. volume (V), pressure (p), total energy (U or E), number of particles (N), magnetic dipole moment (for magnetic systems), etc.
- For example, (E, N, V) for an isolated system.
- In large systems, for a given macrostate, there correspond a huge number of microstates.

Microstates / Accessible microstates

- Look at the $N (\sim 10^{23})$ particles and specify the detail of the particles

e.g. particle #1 is in single-particle state of energy ϵ
" #2 " " " " " " energy ϵ'
" #3 " " " " " " energy ϵ''
⋮
[if interactions between particles are weak]

Obviously, whether the particles are distinguishable or indistinguishable is important

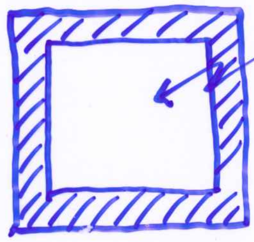
- Accessible microstates for a given macrostate

microstates that are compatible with the few variables (e.g. E, N, V) that specify the macrostate.

↓

imposes constraints on the possible microstates

C. An Example

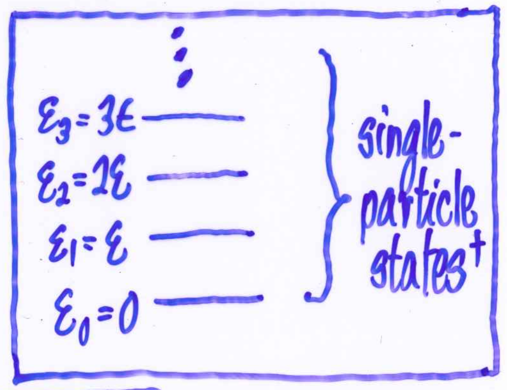


There are 3 distinguishable particles A, B, C
(easier to handle) (for simplicity)

For each particle, the allowed states (or energy levels) are

$\varepsilon_0 = 0$, $\varepsilon_1 = \varepsilon$,

$\varepsilon_2 = 2\varepsilon$, $\varepsilon_3 = 3\varepsilon$, etc.



> Q: Given total energy $E = 3\epsilon$, what are the possible microstates?

- Macrostate: $N=3$, $E=3\epsilon$
- Microstates: particle A in which level, particle B in which level, particle C in which level

  Infinitely many in this case

- Accessible microstates
  - microstates that are compatible with $N=3$, $E=3\varepsilon$

† If the interactions between particles are weak, the 3-body QM problem can be treated as 3 1-body QM problems. The Schrödinger equation gives the allowed single-particle states.

Let's list the accessible microstates

Particles										
A	ϵ	3ϵ	0	0	2ϵ	2ϵ	ϵ	ϵ	0	0
B	ϵ	0	3ϵ	0	ϵ	0	2ϵ	0	2ϵ	ϵ
C	ϵ	0	0	3ϵ	0	ϵ	0	2ϵ	ϵ	2ϵ
	I (1)	II (3 microstates)			III (6 microstates)					

Notes:

(1) Given $E=3\epsilon$ and $N=3$, we have a total of 10 accessible microstates, i.e.

W = number of accessible microstates $= 10$

(2) $N=3$ (very small system), $W=10 \sim$ a few times of N

For $N \sim 10^{23}$, W is a huge number!

Ex: Macrostate is characterized by $N=8$, $E=8\varepsilon$ (same average energy per particle (temperature))

How many accessible microstates are there?

> The counting problem is that of distributing E units of energy among N distinguishable particles. The mathematics of permutation and combinations comes in!

What is this "10"?

$$10 = \frac{(3+3-1)!}{(3-1)!\,3!}$$

- Recall that the problem was to distribute 3 units of energy among 3 distinguishable particles. [3 balls and 2 sticks]

- Ex: Try to make sense of the above expression.
- Ex: Convince yourself that
  - (i) W increases rapidly with E, for fixed N
  - (ii) As we scale up the system, [e.g., N increases and E increases but keeping $\frac{E}{N}$ constant] W increases rapidly.
- In terms of QM, W is the degeneracy of the 3-particle energy level of energy E as allowed by QM, [i.e., number of QM states W with the same energy E]

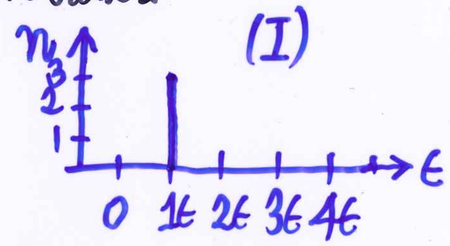
(3) More importantly, the 10 possible microstates divide naturally into 3 groups.

- Each group is characterized by a distribution.

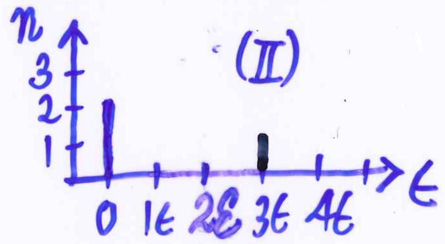
∴ The 10 microstates give 3 different distributions.

In words, these distributions give the ways to share the given E among the particles.

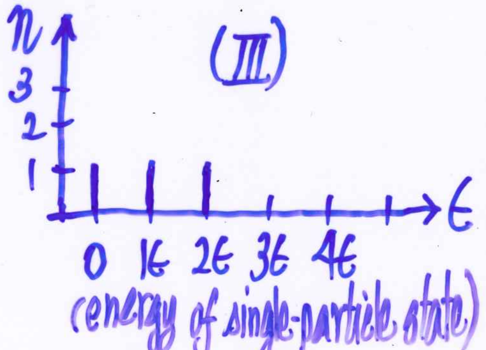
Group I: "3 particles all in $\varepsilon_1 = \varepsilon$ energy level"
[1 corresponding microstate]



Group II: "One particle in level $\epsilon_3 = 3\epsilon$ and the other two in $\epsilon_0 = 0$"
[3 corresponding microstates]



Group III: "One particle in level $\epsilon_2 = 2\epsilon$, one particle in level $\epsilon_1 = 1\epsilon$, and one particle in level $\epsilon_0 = 0$"
[6 corresponding microstates]



- To specific <u>a distribution</u>, we need <u>a string of numbers</u>

$$\{n_0, n_1, n_2, \cdots, n_i, \cdots\}$$

n_0: # particles in level 0 of energy ε_0; n_1: # particles in level 1 of energy ε_1; n_i: # particles in level i of energy ε_i

with these <u>"occupation numbers"</u> satisfying <u>the constraints</u>:

$$\boxed{\begin{cases} \sum_i n_i = N \\ \sum_i \varepsilon_i n_i = E \end{cases}}^{\dagger}$$

specified by <u>macroscopic</u> state

Our example:

- Group I (Distribution I): $\{0, 3, 0, 0, 0, \cdots\}$ (1 microstate)
- Group II (Distribution II): $\{2, 0, 0, 1, 0, \cdots\}$ (3 microstates)
- Group III (Distribution III): $\{1, 1, 1, 0, 0, \cdots\}$ (6 microstates)

† These constraints are important in determining the "most probable distributions".

- <u>Be careful</u>, for a distribution $\{n_0, n_1, n_2, \cdots\}$, one needs to keep in mind that <u>there are a number of microstates</u> behind a distribution.

- Average Distribution?

Weighted average of distributions

∴ Listing out All accessible microstates

$\underbrace{}$

<u>Most microscopic</u> description

$\boxed{W(E,V,N) \text{ in total}}$

Distributions

$\underbrace{}$

- <u>Intermediate</u> between microscopic & macroscopic descriptions
- Useful for <u>non-interacting</u> systems

(E, V, N)

$\underbrace{}$

<u>macroscopic</u> description

D. Microstates, distributions, and number of microstates in a distribution

From the example in Sec. C, we can write:

$$W = \sum_{\text{distributions}} \underbrace{W(\text{distribution})}_{\text{number of microstates for a distribution}}$$

e.g.

$$10 = 1 + 3 + 6$$

$$= W\left(\begin{matrix}\text{Type I}\\ \text{distribution}\end{matrix}\right) + W\left(\begin{matrix}\text{Type II}\\ \text{distribution}\end{matrix}\right) + W\left(\begin{matrix}\text{Type III}\\ \text{distribution}\end{matrix}\right)$$

E.g., $W\left(\begin{matrix}\text{Type III}\\ \text{distribution}\end{matrix}\right)$

What is the skill needed?

"How many ways can we put 3 distinguishable particles into 3 distinguishable levels, with one particle in a level?"

i.e. how to count? $\dfrac{3!}{1!\,1!\,1!} = 6$

same as

"Dividing 3 distinguishable particles into 3 groups, with one in each group."

E. Postulate of equal a priori probabilities for an isolated system in equilibrium

- The most important step in developing stat. mech.
- Postulate ⇒ No proof
- Justified by the results that follow
- Important: a postulate for isolated system in internal thermodynamic equilibrium

Motivation:

- Given E and N, if we inspect a system (at some time), which microstate will we find?

Ans: $\underbrace{\text{Don't know!}}$

ignorance ⟷ probabilistic description⁺

No reason for one microstate to appear with a higher chance than the other microstates!

$\boxed{\text{THEY ARE EQUALLY PROBABLE!}}$

⁺ Think about it! If we are certain about the outcome of a measurement, then we don't need to invoke probability!

A fundamental postulate in stat. mech. is:

> For an isolated system in equilibrium, all accessible microstates are equally probable.

All results of equilibrium stat. mech. follow from this postulate!

- Given E, N, V, count $W(E,N,V)$,
  postulate $\Rightarrow$ Prob. of system being in any one of the accessible states $= \dfrac{1}{W}$

- It is important to realize that the postulate refers to (i) isolated systems and (ii) equilibrium.
- That is to say, if we wait and wait until equilibrium is reached, the system would have visited (will visit) all accessible microstates an equal number of times!
- The postulate is really an averaging postulate, i.e., telling us how to do averages.

E.g. Take the example in Sec. C

- 3 units of energy among 3 particles $\Rightarrow W = 10$

In equilibrium, probability of system being found in any one of the W microstates

$$= \frac{1}{W} = \frac{1}{10}$$

"equally probable" [isolated system in equilibrium]

- Think like a phyicist!

- Everything starts to make sense!

If initially, all $E=3$ goes into one particle [one place is hotter in the box, other places are cold] NOT in equilibrium

Through collisions (exchange energies), energy is continually re-distributed. At equilibrium, all W microstates are equally probable.

For a big system, highly unlikely to go back to the non-equilibrium initial state $\Rightarrow$ spontaneous process!