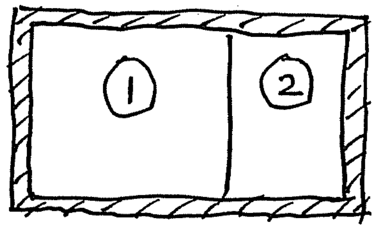
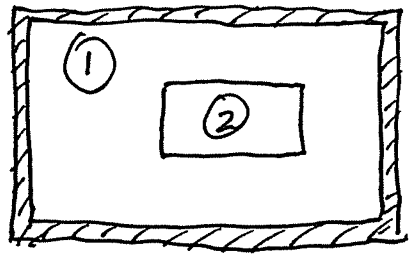
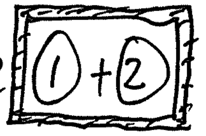
- Now, we go back to the remarks at the end of. Sec. B
- We will discover thermodynamics by considering two systems in thermal contact



Same as



The composite  system is an isolated system

↑

Important!

The only thing we know applies to isolated system in equilibrium!

C. Thermal Contact between Two macroscopic systems[†]

System ①: N_1, V_1 fixed
System ②: N_2, V_2 fixed

①+② forms an isolated system
(N, V, E) fixed

∴ For ①+②:

$$\begin{cases} V = V_1 + V_2 \ ;\ N = N_1 + N_2 \\ E = \text{constant} \end{cases}$$

- Each system (① and ②) is in internal thermodynamic equilibrium
- They may NOT be in equilibrium with each other.
- Assuming the interaction between ① and ② is weak

[ignore interaction energy, but it will mean we have to wait for a long time for ① and ② to reach equilibrium, but that's OK as we don't care about waiting]

$$E = E_1 + E_2$$ (true for any partition of E into E_1 and E_2)

OR $E_2 = E - E_1$

$W(E_1)$ = # accessible microstates of combined system for the partition (E_1, V_1, N_1) and (E_2, V_2, N_2)

$$= W_1(N_1, V_1, E_1) \cdot W_2(N_2, V_2, E_2)$$

[†] Important section on concepts!

- The total energy E could, in principle, be partitioned in any possible way between ① and ②

When <u>the systems reach equilibrium</u> with each other (and hence the isolated system $\boxed{1|2}$ <u>as a whole reaches equilibrium</u>), the total number of accessible microstates is:

$$W_{total} = \sum_{E_1=0}^{E} W_1(N_1, V_1, E_1)\cdot W_2(N_2, V_2, E_2) = \underbrace{\text{some number}}_{\text{a constant}}$$

- From <u>postulate of equal a priori probabilities</u>:

> Prob. of finding $\boxed{1|2}$ in the partition of E into E_1 and $E-E_1$
>
> $$= \frac{W_1(N_1,V_1,E_1)\cdot W_2(N_2,V_2,E_2)}{W_{total}}, \quad E_2 = E - E_1$$

- For macroscopic systems ① and ②, W_1 increases sensitively with E_1 (thus W_1 also drops sensitively with E_1).

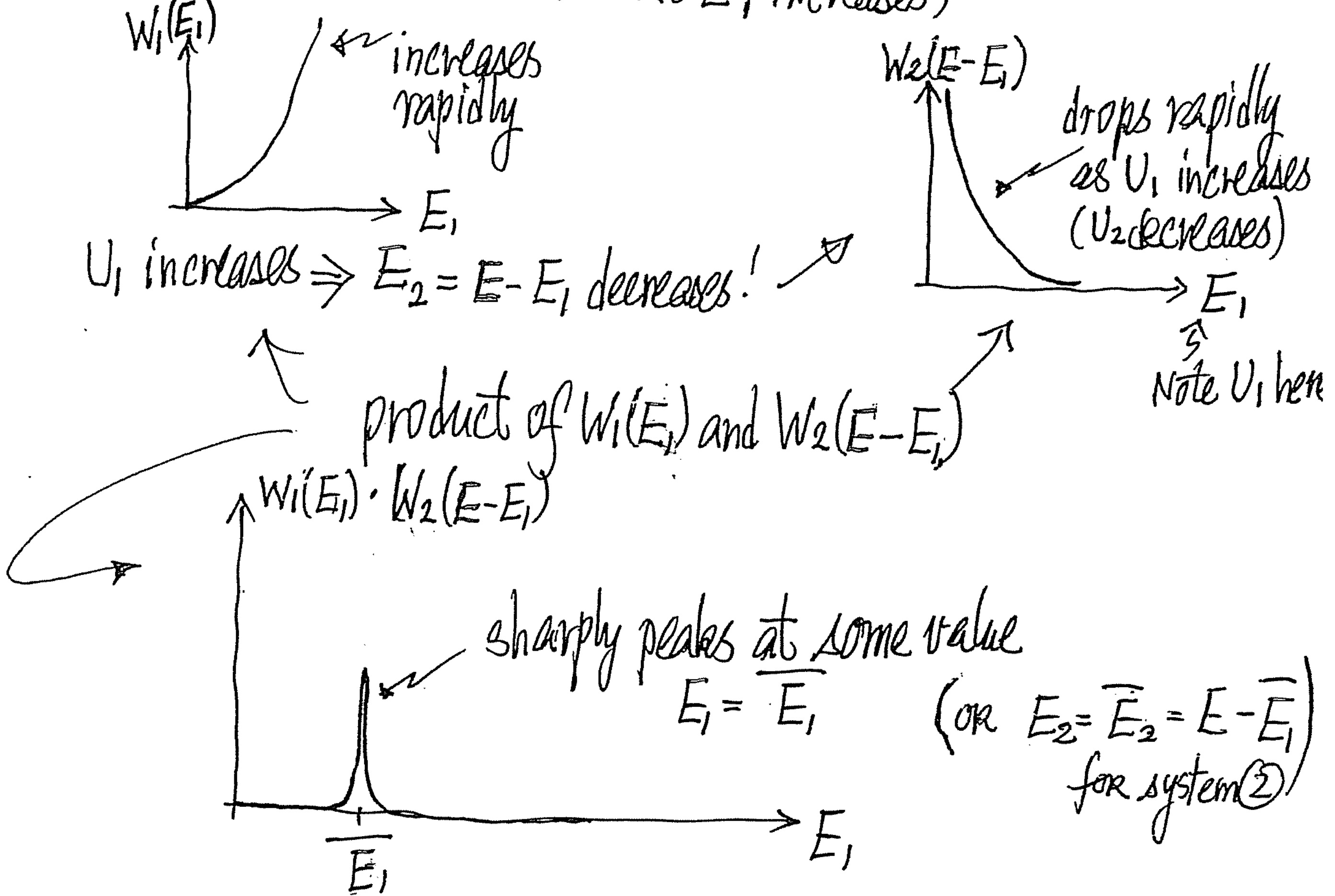
$\therefore$ There exists a particular partition $E_1 = \overline{E_1}$ and $E_2 = E - \overline{E_1}$ that $W(\overline{E_1}) = W_1(N_1, V_1, \overline{E_1})\cdot W_2(N_2, V_2, E-\overline{E_1})$ is a <u>maximum</u> and dominates all other terms in W_{total}. [This is thermodynamics]

Look at $\dfrac{W_1(N_1,V_1,E_1)\cdot W_2(N_2,V_2,E_2)}{W_{total}}$

$$= \frac{W_1(E_1)\cdot W_2(E-E_1)}{W_{total}} \qquad (E \text{ is fixed})$$

Typically, for a system that we consider its thermodynamics, the number of microstates increases rapidly with energy.

Let's consider $W_1(E_1)$. As E_1 increases,



i.e. a division of E into $\overline{E_1}$ and $E-\overline{E_1}$ <u>dominates other divisions</u>!!

At equilibrium, (almost) <u>always observe this division</u> because it carries the largest number of microstates!

- In <u>thermodynamics</u>, this is the description being used. For example, when ① becomes in equilibrium with ②, we say ① has an energy $U_1 = \overline{E_1}$.

The main points are...

- Starting from a particular division of energy E, say u and $E-u$, the systems are not in equilibrium and $W_1(u)\cdot W_2(E-u)$ is just one term in W_{total}
- Wait (relax the enforced division of u and $E-u$) and let the systems exchange energy, the composite system at equilibrium becomes accessible to all microstates in $W_{total}=\sum_{E_1} W_1(E_1)\cdot W_2(E-E_1)$

  [so, connects to increasing S as systems go towards equilibrium and S is a maximum at equilibrium (∵ ALL microstates are accessible)]
- For the many terms in W_{total}, one particular division of E into $\bar{E}_1$ and $E-\bar{E}_2$ dominates, i.e.

  $W_1(\bar{E}_1)\cdot W_2(E-\bar{E}_1)$ is a large part of W_{total} and the dominance becomes more pronounced as the systems get bigger ($N\sim 10^{26}$)

∴ Observe system ①, (almost) always see $\bar{E}_1$

Observe system ②, (almost) always see $\bar{E}_2$

[These are what we referred to as the energies U_1 and U_2 of the systems in thermodynamics when they are in equilibrium]

(Strictly speaking, E_1 fluctuates a bit around $\bar{E}_1$
E_2 fluctuates a bit around $\bar{E}_2$)

Question:
When ① and ② are at equilibrium, is there a common quantity that they share?

Remark

- The physical idea here will be used in deriving the Boltzmann distribution and the partition function in the canonical ensemble theory. [See next chapter]

- Let $\bar{E}_1$ and $E-\bar{E}_1$ be the energy partition that has the largest # microstates, i.e.

$$W_1(E_1)\cdot W_2(E-E_1) \text{ is maximized.}$$

- This means

$$\begin{cases} \ln[W_1(E_1)\cdot W_2(E_2)] = \ln W_1(E_1) + \ln W_2(E_2) \\ \text{is maximized when } E_1 = \bar{E}_1 \quad (\text{recall } E_2 = E - E_1) \end{cases}$$

↳ Write this statement in Math...

$$\underbrace{\frac{\partial \ln W_1}{\partial E_1} + \frac{\partial \ln W_2}{\partial E_1}}_{} \text{ evaluated at } E_1 = \bar{E}_1 \text{ is zero}$$

$$\Rightarrow \left.\frac{\partial \ln W_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} + \left.\left(\frac{\partial \ln W_2(E_2)}{\partial E_2}\cdot\frac{\partial E_2}{\partial E_1}\right)\right|_{E_1=\bar{E}_1} = 0$$

$$\Rightarrow \left.\frac{\partial \ln W_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} - \left.\frac{\partial \ln W_2(E_2)}{\partial E_2}\right|_{E_2=\bar{E}_2 = E-\bar{E}_1} = 0$$

$$\Rightarrow \boxed{\left.\frac{\partial \ln W_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial \ln W_2(E_2)}{\partial E_2}\right|_{E_2=\bar{E}_2}} \quad (*)$$

Indeed, there is something $\left(\frac{\partial \ln W}{\partial E}\right)$ in common.
["Discovered" a quantity in common]

- Thermodynamics: that "something in common" is temperature
- Microscopically: that "something in common" is $\frac{\partial \ln W}{\partial E}$

Define absolute temperature T of a system characterized by (N, V, E) as

$$\boxed{\frac{1}{kT} \equiv \left(\frac{\partial \ln W(E,V,N)}{\partial E}\right)_{V,N}}$$

OR

$$\boxed{\frac{1}{T} = \frac{\partial(k \ln W)}{\partial E} = \left(\frac{\partial S}{\partial E}\right)_{V,N}} \qquad (**)$$

Then Eq.(*) (microscopic consideration) ⇒ ↗ equilibrium condition when energy exchange is allowed

$$\boxed{T_1(\bar{E}_1, V_1, N_1) = T_2(\bar{E}_2, V_2, N_2)}$$

which is zeroth law! (We discovered zeroth law by a microscopic theory.)

From (**), we have $\underbrace{dE = TdS}$ $\underbrace{(\text{constant } V \,\&\, N)}$ vanish!

which is one term in $dE = TdS - \overbrace{pdV + \mu dN}$

(∴ also "derived" one term in the thermodynamic identity)

A sense on "Temperature"

- In microcanonical ensemble, T is a derived quantity

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

What is "low" temperature?

Add ΔE to system (fixed N, V), if adding ΔE allows system to access many more microstates then ΔW increases by much, thus ΔS increases a lot, thus $\frac{\Delta S}{\Delta E}$ is big, so $\frac{1}{T}$ is big, and thus T is low temperature. (Following me?)

$N \sim 10^{24}$ particles, each is a 2-state system

$T=0$: All particles in lower state ($W=1$) [ground state]

Say, $\Delta E = \varepsilon$, then one particle can be in upper state

$W \sim 10^{24}$ (any one can be in upper state)

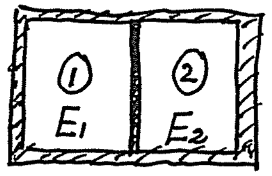
ΔW is huge! [Of course, $T \approx 0$ is low temperature]

What is "high" temperature?

Ex.

A bit deeper (Optional)

- Direction of process
- Beginning



kept out of equilibrium — thermodynamics $T_1 \neq T_2$

[thus NOT accessing many microstates and definitely NOT the optimum partition $\bar{E}_1$ & $E-\bar{E}_1$]

- Let ① and ② be in contact for a short while

Naturally (spontaneously), δE_1 of energy gets into ① and $\delta E_2 = -\delta E_1$ gets out of ②

This happens because the composite system can access more microstates (Stat. Mech.)

Meaning: $\delta(W_1 \cdot W_2) > 0$

$$\Rightarrow \delta(\ln W_1 + \ln W_2) > 0$$

$$\Rightarrow \frac{\partial \ln W_1}{\partial E_1} \cdot \delta E_1 + \frac{\partial \ln W_2}{\partial E_2} \cdot \delta E_2 > 0$$

$$\Rightarrow \left(\frac{\partial \ln W_1}{\partial E_1} - \frac{\partial \ln W_2}{\partial E_2}\right) \cdot \delta E_1 > 0$$

$$\Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \delta E_1 > 0$$

right direction!

ⓘ If $T_2 > T_1$, $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0$ and thus $\delta E_1 > 0$ (energy goes from hotter to colder)

ⓘⓘ If $T_2 < T_1$, $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0$ and thus $\delta E_1 < 0$ (energy goes from hotter to colder)

D. More than thermal contact – Movable Walls between ① & ②

- ① and ② can exchange volume

  ⇒ V_1 and V_2 can change, but $V_1+V_2=V=\text{constant}$

  [in addition to exchanging energy]

- Repeat the argument in Sec. B and define the pressure by

$$\frac{p}{T} \equiv \left(\frac{\partial S(U,V,N)}{\partial V}\right)_{U,N} \quad \text{OR} \quad \frac{p}{kT} \equiv \left(\frac{\partial \ln W}{\partial V}\right)_{N,U}$$

  to get that in equilibrium[+]

$$\left.\begin{array}{l} p_1 = p_2 \\ T_1 = T_2 \end{array}\right\} \text{ movable, diathermal wall}$$

  [Do this as an exercise]

- More generally, for initially non-equilibrium situations, movable wall moves toward region of lower pressure

  [Ex: Show this using $\delta S \geq 0$ for the combined system]

[+] These are the equilibrium conditions in thermodynamics when two systems are allowed to exchange energy and volume. We also found the term $dS = \frac{p}{T}dV$ in thermodynamic identity.

More than thermal contact – Porous Walls between ① & ②

- ① and ② can exchange particles

  ⇒ N_1 and N_2 can change, but $N_1+N_2=N=\text{constant}$

  [in addition to exchanging energy]

- Repeat argument in Sec. B and define the chemical potential μ by

$$\frac{\mu}{T} \equiv -\left(\frac{\partial S(U,V,N)}{\partial N}\right)_{U,V} \quad \text{OR} \quad \frac{\mu}{kT} \equiv -\left(\frac{\ln W}{\partial N}\right)_{U,V}$$

  to get that in equilibrium[+]

$$\left.\begin{array}{l} \mu_1 = \mu_2 \\ T_1 = T_2 \end{array}\right\} \text{ porous, diathermal wall}$$

  [Do this as an exercise]

- More generally, for initially non-equilibrium situations, particles move toward regions of smaller μ.

[+] These are the equilibrium conditions in thermodynamics when two systems are allowed to exchange energy and particles. We also found the term $dS = -\frac{\mu}{T}dN$ in the thermodynamic identity.

E. Thermodynamic Identity

Putting the cases in Secs. B, C, D together, we have

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{\frac{p}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\frac{\mu}{T}} dN$$

$$= \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

OR $dU = TdS - pdV + \mu dN$

as in thermodynamics

This completes the formal connection of statistical mechanics with thermodynamics within the microcanonical ensemble.

In fact, some authors prefer to develop thermodynamics based on statistical mechanics. See, for example, J.R. Waldram, "The theory of Thermodynamics".

F. Recipe : Microcanonical Ensemble

(i) Isolated system (E, V, N) fixed

(ii) Find $W(E,V,N)$, i.e. # accessible microstates as a function of E, V, N.

Practically, often consider E to $E+\delta E$

- more convenient in getting W
- results insensitive to δE
- resolution in energy measurements

(iii) Isolated system in equilibrium, all accessible microstates are equally probable (fundamental postulate)

- an averaging postulate
- time average vs ensemble average
- choosing members of an ensemble

(iv) $S(E,V,N) = k \ln W(E,V,N)$

(v) $dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$

$$\therefore \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} ; \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} ; \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Thermodynamic quantities & Equation of state follow.

Done!

Remarks:

(a) In counting $W(U,V,N)$ or $W(E,V,N)$, often we allow for an energy interval (or uncertainty) ΔE. First of all, the result will not be sensitive to ΔE. And including a ΔE avoids many uneasy problems related to the discreteness of allowed values of E in a quantum (N-particle) system.

Q: How about two choices ΔE_1 and ΔE_2?

$W(E,\Delta E_1)$ = # microstates with energies in $E \to E+\Delta E_1$

$W(E,\Delta E_2)$ = # microstates with energies in $E \to E+\Delta E_2$

Typically, $W(E,\Delta E_1) = w(E)\,\Delta E_1$

$W(E,\Delta E_2) = w(E)\,\Delta E_2$

↑ called "density of states"

$S_1 = k \ln(w\,\Delta E_1)$ ↖ Are they very different? No!

$S_2 = k \ln(w\,\Delta E_2)$ ↙

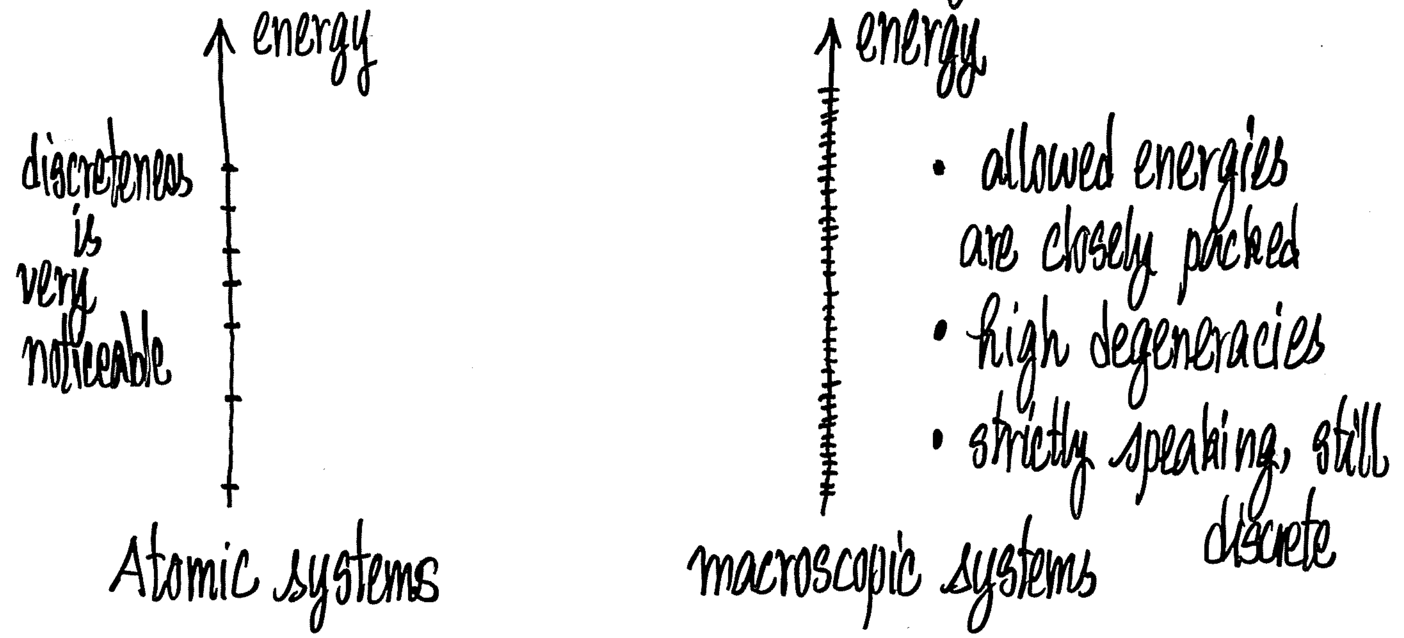
S_1, S_2 are of order $k\,\underbrace{O(N)}$

↖ number of order $N \sim 10^{22}$

$S_1 - S_2 = k \ln\left(\dfrac{\Delta E_1}{\Delta E_2}\right) \sim k\,O(1)$ ← number of order 1

⇒ difference is negligibly small compared to S_1 and S_2.

Strictly speaking, when we solve a quantum mechanical problem, the allowed energies are discrete.



$W(E,V,N)$ = # states at energy E = degeneracy at E

If we take the discreteness <u>seriously</u>,

$W(E,V,N) \neq 0$ only at the allowed energies E

⇒ $W(E,V,N)$ is wildly fluctuating as a function of E!

Including a δE in the counting, $W(E,V,N)$ becomes a well-behaved function of E, and one can do derivatives without worrying too much!

(b) More than p-V work?

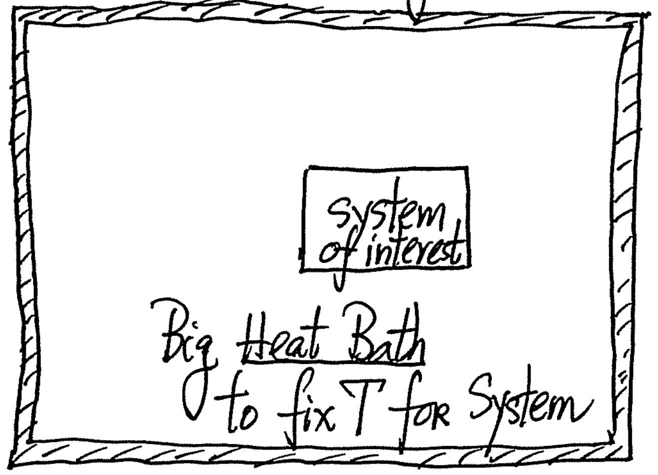
Generally, if $W = W(E, N, x_\nu)$ where $x_\nu = \{x_1, x_2 \cdots, x_n\}$ are external parameters (e.g. $x_1 = V$ = volume), then define generalized force X_ν by

$$\frac{X_\nu}{kT} \equiv \frac{\partial \ln W(E, N, x_\nu)}{\partial x_\nu}$$

(c) The Theory can handle all equilibrium Stat. Mech. problem (in principle)!

(d) But...

- Counting $W(E, V, N)$ is not easy ($N \sim 10^{23}$)
- Experimentally, controlling temperature T is usually the case than controlling E



How to handle this case?

Easy! "Done"

We discussed it in Sec. C.

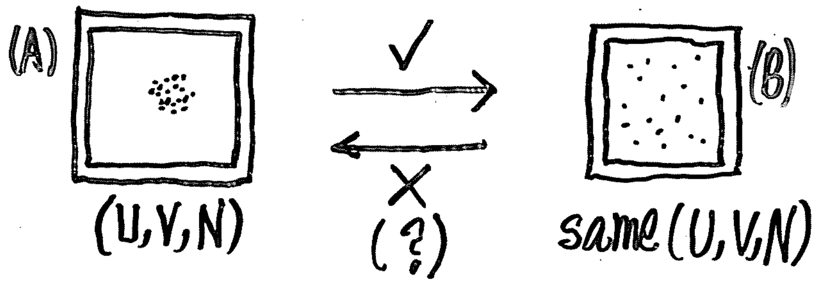
It leads to a new calculation method — canonical ensemble.

G. Arrow of Time?

- Equal a priori probabilities

W = # of accessible microstates (e.g., U,V,N)

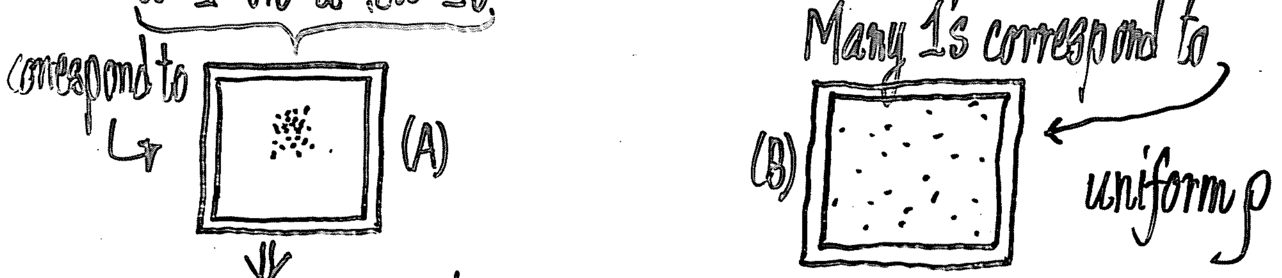
- Each microstate occurs with equal probability $(\frac{1}{W})$



$\rho(\vec{r})$ is non-uniform $\rho(\vec{r}) = \rho = \frac{N}{V}$ = constant

$$W = 1 + \boxed{1} + 1 + \cdots + \underbrace{1+1+1+1+1+\cdots}_{W' \text{ of them}} + 1+1+1$$

a "1" or a few "1's"



⇓ only a tiny fraction of W ⇓ represents a large fraction of W

- Equal a priori probabilities: (A) "could happen" in principle
- But for $N \sim 10^{23}$, W is a huge number (e.g. e^{100})
  - (A) ⇒ only a few cases out of W
  - (B) ⇒ a significant fraction of W

∴ Even if we intentionally start with (A), we need to wait and wait, and there is a chance of $\frac{a}{W}$, where $a \sim O(1)$, that we can eventually get back to (A) [in principle!].

But, since W is huge, the chance is just too small.

∴ When we observe the system again and again and again, we keep on seeing the system being in states corresponding to (B)

the equilibrium situation in thermodynamic sense.

OR we need to wait on average a time of $W \cdot \tau$, where τ is a characteristic time for the system to go from one microstate to another (very short), to get back to (A). Since W is huge, the time $(W\tau)$ is so long that we never observe (A) again, even we started off from (A).

H. $S = k\ln W$ hints at a General Formula for Entropy

Consider members in $\underbrace{\text{a microcanonical ensemble}}_{\text{every accessible microstate is evenly represented}}$

- $i = 1, 2, \cdots, W$ label accessible microstates
- p_i = Probability that microstate i is picked in a random pick from the ensemble

  $= \frac{1}{W}$ (equally probable)

Recall: $S = k\ln W$ is Entropy of a System

Gibbs: $\boxed{S = -k\sum_i p_i \ln p_i}^{+}$ (*)

Average entropy per member in the context of an ensemble

p_i = prob. that a microstate i occurs in ensemble

Eq. (*) turns out to be a general formula of entropy. It can be applied to different ensembles.

Microcanonical Ensemble: $p_i = \frac{1}{W}$ and $i = 1, 2, \cdots, W$

$$S = -k\sum_{i=1}^{W} \frac{1}{W} \ln\frac{1}{W} = -k\frac{1}{W}\cdot W \ln\frac{1}{W} = k\ln W \quad \text{(Boltzmann)}$$

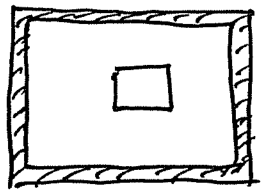
$\therefore S = -k\sum_i p_i \ln p_i$ works!

[+] The quantity $H = -\sum_i p_i \ln p_i$ is the Shannon Entropy in Information Theory.

Summary

You should be able to:

- Make sense out of $S = k\ln W$
- work out standard problems using microcanonical ensemble
- relate spontaneous irreversible processes to "all accessible microstates are equally probable"
- relate Stat. Mech. to thermodynamics based on two systems in contact



Refs:

Yoshioka (Ch. 2)
Bowley/Sanchez (Ch. 4)
Rosser (Ch. 3)
Mandl (Ch. 2)