

- Microstate, Macrostate, Multiplicity
 - Idea of Boltzmann Entropy
 - Temperature scale by entropy
 - Temperature of non ideal gas system
 - What is negative temperature?
-

Macro state, Microstate, Multiplicity

- Thermodynamics describe physics by macrostate

= Describe by statistical properties of a system

E.g. P, V, T are statistical average

if no container
what is the volume?

$P \propto$ Avg. collision force



$V \sim$ Avg. Volume occupied



$T \sim$ Avg. velocity

- Classical mechanics describe physics by microstate

= Describe by exact behavior of every object in the system.

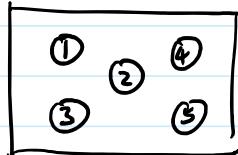
E.g. Mechanical state is like $(\vec{x}_1, \vec{v}_1, \vec{x}_2, \vec{v}_2 \dots \vec{x}_N, \vec{v}_N)$

6 parameters per particle
= $6N$ parameters in total

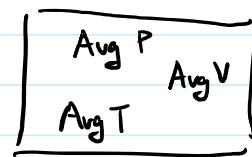
- Multiplicity = No. of microstate corresponding to a macrostate

E.g. Box of gas

Label every particle



Only look at the average quantities



Need $6N$ parameters

Only need 3 parameters

If we exchange the particles' label

Description of microstate changes

Same macrostate

Classification to 5 macrostates		All 16 microstates														
4L-0R	LLLL	$C_0^4 = 1$														
3L-1R	RLLL	LRLL	LLRL	LLRR	$C_1^4 = 4$											
2L-2R	LLRR	RLRL	RLLR	LRRL	LRLR	LLRR	$C_2^4 = 6$									
1L-3R	LRRR	RLRR	RRRL	RRRR	$C_3^4 = 4$											
0L-4R	RRRR	$C_4^4 = 1$														

Boltzmann Entropy

Question : If the particles are allowed to move freely between boxes

Which macrostate has the highest prob. to be observed ?

Prior assumption : Each microstate has the same probability to occur

~ Throw 4 balls. The box entered is random.

⇒ All 16 microstates have equal probability.

⇒ Probability of macrostate is proportional to its multiplicity

$$\boxed{\begin{smallmatrix} \bullet & \bullet \\ \bullet & \circ \end{smallmatrix}} = \frac{1}{16} \quad \boxed{\begin{smallmatrix} \bullet & \bullet & \bullet \\ \bullet & \circ & \circ \end{smallmatrix}} = \frac{4}{16} \quad \boxed{\begin{smallmatrix} \bullet & \bullet & \bullet \\ \circ & \circ & \circ \end{smallmatrix}} = \frac{6}{16} \quad \dots$$

Scenario : Whatever the initial positions of the balls

if they are allowed to move freely for long enough time

⇒ Macrostate of the highest multiplicity ($2L - 2R$)

has the highest chance to be observed.

More extreme case : 100 particles

- No. of microstate of $[100 \text{ in L}, 0 \text{ in R}] = 1$

- No. of microstate of $[50 \text{ in L}, 50 \text{ in R}] = C_{50}^{100} \approx 1 \times 10^{29}$

i.e. Observe the system for $\sim 10^{29}$ times, we get

$$1 \times 10^{29} \text{ observation} = 50L - 50R$$

$$1 \text{ observation} = 100L - 0R$$

⇒ In reality we only see $100L - 0R$ evolves into $50L - 50R$

But almost impossible to see $50L - 50R$ evolves into $\rightarrow 100L - 0R$

⇒ ~ Physically an irreversible process!

Idea of Boltzmann Entropy

- Entropy change of a close system $\Delta S \geq 0$ for any process
- A physical system (almost) always evolves from a macrostate of low multiplicity to high multiplicity

Proposal : Entropy is a function of multiplicity

$$S = \phi(W)$$

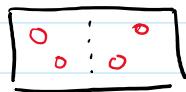
↑ ↑ ←
 entropy some relation multiplicity
 to be determined

Mathematical requirement of $\phi(\dots)$?

Consider 2 boxes of close system

① If look at them independently

$$S_A = \phi(W_A)$$



$$\text{state} = (2, 2)$$

$$S_B = \phi(W_B)$$



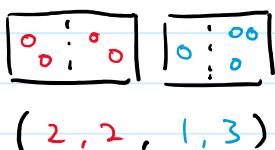
$$\text{state} = (1, 3)$$

② Consider them as 1 combined system

$$\text{Total entropy} = S_{\text{tot}} = S_A + S_B \quad (\text{Entropy} \sim \Delta Q \propto \text{no. of particle})$$

$$\text{Total multiplicity} = W_{\text{tot}} = W_A \times W_B \quad (\text{Total combination} \Rightarrow \text{multiplication})$$

E.g. A B



No. of ways to construct state (2, 2, 1, 3)

$$= \left(\begin{array}{l} \text{No. of ways to construct} \\ (2, 2) \text{ in box A} \end{array} \right) \times \left(\begin{array}{l} \text{No. of ways to construct} \\ (1, 3) \text{ in box B} \end{array} \right)$$

\Rightarrow Basically the only choice of $\phi(\cdot)$ $\propto \ln(\cdot)$, such that

$$S_{\text{tot}} = S_A + S_B = \phi(W_A) + \phi(W_B) = \phi(W_A \times W_B)$$

$$\Rightarrow \boxed{S = k \ln W}$$

k = Some proportionality constant = Boltzmann constant

What is the value of Boltzmann constant?

\Rightarrow By Ideal gas entropy

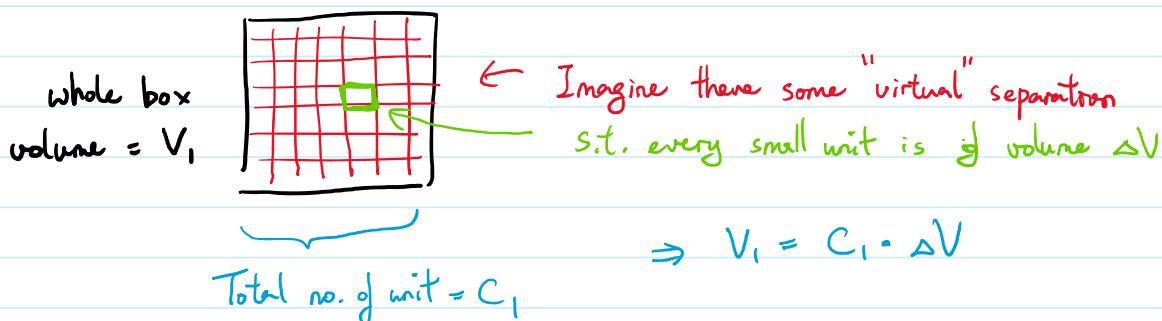
① Entropy change along an isothermal path is calculated as

$$\Delta S = \int \frac{dQ}{T} = \int \frac{dW}{T} = \frac{1}{T} \int pdV = nR \ln\left(\frac{V_2}{V_1}\right)$$

$dQ = dT$ in isothermal
 $T = \text{const.}$

② Change in multiplicity on isothermal path can be modelled by

① Divide the volume into grids of (arbitrary) size ΔV



② Put n particles in the box

- No. of ways to put 1 particle = $C_1 = \frac{V_1}{\Delta V}$

- No. of ways to put N particles = $C_1^N = \left(\frac{V_1}{\Delta V}\right)^N$

$$\Rightarrow \text{Multiplicity } \underline{W_1 \propto \left(\frac{V_1}{\Delta V}\right)^N}$$

③ Let the system undergo isothermal process. Assume the volume of the whole box change to V_2

(Unit volume ΔV is unchanged \therefore It is chosen arbitrarily)

$$\Rightarrow \text{No. of small unit becomes } C_2 = \frac{V_2}{\Delta V}$$

\Rightarrow New multiplicity of putting N particles become

$$W_2 \propto C_2^N = \underline{\left(\frac{V_2}{\Delta V} \right)^N}$$

③ Finally plug everything in the relation $S = k \ln W$

$$\begin{aligned} \Delta S &= nR \ln \left(\frac{V_2}{V_1} \right) = S_2 - S_1 \\ &= k \ln W_2 - k \ln W_1 \\ &> k \ln \left[\frac{\left(\frac{V_2}{\Delta V} \right)^N}{\left(\frac{V_1}{\Delta V} \right)^N} \right] \end{aligned}$$

$$n = \text{no. of mole of particles.} \quad = Nk \ln \left(\frac{V_2}{V_1} \right)$$

$$\Rightarrow \underline{nR} = \underline{Nk} \quad N = \text{no. of particle.}$$

Ideal gas const.

$$k = \frac{R}{N_A} \quad \text{Avogadro no.} = 6.02 \times 10^{23}$$

$$\simeq \underline{1.38 \times 10^{-23}} \quad (\text{Easy to remember by } R = 8.31)$$

Example of change in multiplicity in reality

$$\underline{\Delta S} = k \ln \underline{\Delta W} \quad \Rightarrow \quad \Delta W = e^{\frac{\Delta S}{k}}$$

By subtraction By ratio

Suppose we have 2 objects having the same heat capacity C

Object A's temp = 300.1 K

Object B's temp = 299.9 K

After allowing heat exchange, expect reaching eqm. Temp = 300 K

Entropy change by $S = \int \frac{dQ}{T}$

$$\Delta S_A = \int_{300.1}^{300} \frac{CdT}{T} = C \cdot \ln\left(\frac{300}{300.1}\right)$$

$$\Delta S_B = \int_{299.9}^{300} \frac{CdT}{T} = C \cdot \ln\left(\frac{300}{299.9}\right)$$

$$\Rightarrow \Delta S_{\text{tot}} = C \cdot \ln\left(\frac{300}{300.1} \times \frac{300}{299.9}\right) \simeq 1.11 \times 10^{-7}$$

$$\Rightarrow \Delta W = \frac{W_{\text{final}}}{W_{\text{initial}}} = e^{\frac{\Delta S}{k}} = e^{8.05 \times 10^{-15}} \simeq 10^{10^{15.54}}$$

= A number with 10^{15} digits.

\Rightarrow Physically the reverse process will never occur spontaneously.

Defining temperature by entropy

① The very first idea of temperature: Want to quantify hot/cold

↪ Calculus scale: Scale by material expansion

② How to quantify hotness from $\sim -273^\circ\text{C}$ to ∞ in 1 theory?

↪ Kelvin scale: Scale by engine efficiency

③ Any physics exist below -273°C ? Why temp scale is such weird?

↪ With Boltzmann's proposal what entropy physically means

↪ Define temperature by entropy

$$\text{By 1st Law : } dU = \delta Q - \delta W$$

by $dS = \frac{\delta Q}{T}$

$$= \boxed{T} dS - \boxed{P} dV$$

is a relation completely written in state functions

But we can view U as a multivariable function of S & V
such that under chain rule :

$$dU(S,V) = \boxed{\left(\frac{\partial U}{\partial S}\right)} dS + \boxed{\left(\frac{\partial U}{\partial V}\right)} dV$$

Comparing the terms .

$$\Rightarrow T = \frac{\partial}{\partial S} U(S,V) , P = -\frac{\partial}{\partial V} U(S,V)$$

i.e. If we plot U as a function of S & V

We can define temperature as the rate of change along S at const. V .

In practice, we use the reciprocal of temperature as definition.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{\text{const. } V}$$

$\therefore U$ is usually some simple functions

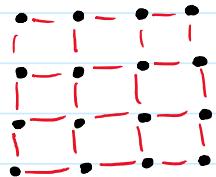
Counting multiplicity
is very annoying

But S is usually a complicate function

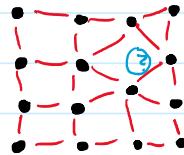
So doing differentiation of $\frac{\partial S}{\partial U}$ is easier than $\frac{\partial U}{\partial S}$

Example 1: Crystal vacancy

Perfect Crystal



Crystal with defect
E.g. Vacancy = missing atoms



Energy stored in the form of bonding
Regular arrangement = same energy everywhere

New bonding form + stretch
⇒ Cost extra energy

① Suppose we have a crystal with N atoms & n vacancy

i.e. No. of positions that we can put the atom = $N+n$

⇒ Multiplicity = No. of ways to arrange N atoms into $N+n$ positions

$$\begin{aligned} &= C_N^{N+n} \\ &= \frac{(N+n)!}{N! n!} \end{aligned}$$

② Calculating Boltzmann Entropy

$$S = k_B \ln \left(\frac{(N+n)!}{N! n!} \right)$$

$$= k_B \left[\ln(N+n)! - \ln N! - \ln n! \right]$$

$$\approx k_B \left[\underline{(N+n) \ln(N+n)} - \underline{N \ln N} - \underline{n \ln n} \right]$$



Stirling Approximation:

If N is very large, then $\ln N! \approx N \ln N - N$

(3) Calculating internal energy

Assume each vacancy increase internal energy by $\underline{\varepsilon}$

which we can determine
by experiment

Total n vacancy = Total extra energy of $n\underline{\varepsilon}$

(4) By definition, $\frac{1}{T} = \frac{\partial S}{\partial U}$.

Since we observe both S & U are functions of n .

$$\Rightarrow \frac{\partial S}{\partial U} = \frac{\frac{\partial S}{\partial n}}{\frac{\partial U}{\partial n}}$$

From Entropy :

$$\begin{aligned}\frac{\partial S}{\partial n} &= k_B \frac{\partial}{\partial n} \left[(N+n) \ln(N+n) - N \ln N - n \ln n \right] \\ &= k_B \left[\ln(N+n) - \ln(n) \right]\end{aligned}$$

From internal energy

$$\frac{\partial U}{\partial n} = \frac{\partial}{\partial n}(n\underline{\varepsilon}) = \underline{\varepsilon}$$

$$\begin{aligned}\Rightarrow \frac{1}{T} &= \left(\frac{\partial S}{\partial U} \right)_{\text{const. } V} = \frac{\left(\frac{\partial S}{\partial n} \right)}{\left(\frac{\partial U}{\partial n} \right)} \\ &= \frac{k_B}{\underline{\varepsilon}} \left[\ln(N+n) - \ln(n) \right]\end{aligned}$$

$$T = \frac{\underline{\varepsilon}}{k_B \ln \left(\frac{N+n}{n} \right)}$$

A temperature scale can be
defined by no. of vacancy

Or by change of variable

$$\frac{n}{N} = \frac{1}{e^{\frac{-\underline{\varepsilon}}{k_B T}} - 1}$$

No. of vacancy can be
estimated by measuring temperature

* Interesting result : $n \rightarrow 0$ only if $T \rightarrow 0$

\Rightarrow Perfect crystal does not exist in real world

*** One of the version of Thermo 3rd Law

Entropy of perfect crystal $\rightarrow 0$ when $T \rightarrow 0$

$\therefore T = 0 \Leftrightarrow$ System at state of lowest energy state

As long as there is only 1 ground state, $W=1 \Rightarrow S=0$

Example 2 : Rubber band

Model : A long chain of particle (polymer)

Expectation :

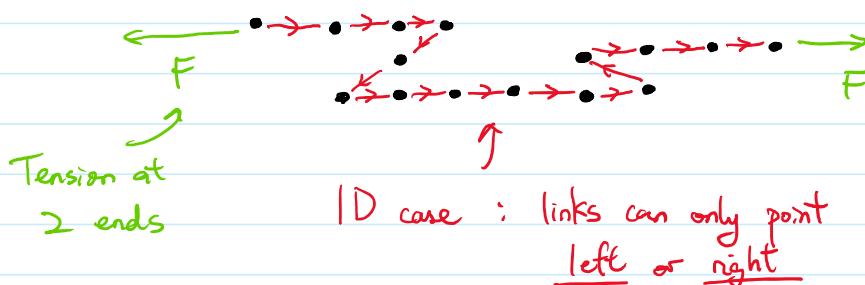


- Low entropy state = Tidy arrangement E.g.

- High entropy state = All tangled together E.g.



Here we only consider a simpler model : 1D chain



(1) Suppose no. of link pointing left = n_L

no. of link pointing right = n_R

with the total no. of link $n_L + n_R = N = \text{const.}$

\Rightarrow Multiplicity = No. of ways to assign n_R left links
to a total of N links

$$= C_{n_R}^N = \frac{N!}{n_L! n_R!}$$

② Calculating Boltzmann Entropy

Take log and then Stirling Approximation

$$S = k_B [N \ln N - n_R \ln n_R - n_L \ln n_L]$$

③ Calculating Internal Energy

A rubber band can store elastic PE, which relates to its length.

- Suppose the chain has a natural length L_0
- If we flip an left link to right link , the chain

has an increase in length of $2\Delta n \cdot d$ Let each link be length d

- $\begin{cases} \text{No. of right link : } n_R \rightarrow n_R + \Delta n \\ \text{No. of left link : } n_L \rightarrow n_L - \Delta n \end{cases}$

- PE stored in this extension = $U = F \cdot \Delta L = F \cdot 2\Delta n d$

From these info , we can get these relations :

$$\frac{\partial L}{\partial (\Delta n)} = 2d, \quad \frac{\partial n_R}{\partial (\Delta n)} = 1, \quad \frac{\partial n_L}{\partial (\Delta n)} = -1, \quad \frac{\partial U}{\partial (\Delta n)} = 2Fd$$

④ By definition , $\frac{1}{T} = \frac{\partial S}{\partial U}$

- From entropy ,

$$\frac{\partial S}{\partial (\Delta n)} = \frac{\partial n_R}{\partial (\Delta n)} \frac{\partial}{\partial n_R} [-k_B n_R \ln n_R] + \frac{\partial n_L}{\partial (\Delta n)} \frac{\partial}{\partial n_L} [-k_B n_L \ln n_L]$$

$$= k_B \left[\ln(n_R) - \ln(n_L) \right]$$

Therefore the temperature is

$$\frac{1}{T} = \frac{\left(\frac{\partial S}{\partial \ln(n)} \right)}{\left(\frac{\partial U}{\partial \ln(n)} \right)} = \frac{k_B}{2Fd} \ln \left(\frac{n_R}{n_L} \right)$$

For application, it is more convenient to express in terms of

Total no. of link $N = n_L + n_R$ & Total length $L = (n_R - n_L)d$

$$\Rightarrow n_L = \frac{N - \frac{L}{d}}{2}, \quad n_R = \frac{N + \frac{L}{d}}{2}$$

$$\Rightarrow \frac{1}{T} = \frac{k_B}{2Fd} \ln \left(\frac{Nd + L}{Nd - L} \right)$$

\Rightarrow Tension on a rubber band

$F = \frac{k_B T}{2d} \ln \left(\frac{Nd + L}{Nd - L} \right)$ is an increasing function of T

i.e. The rubber band contract when T increase!

General Rundown of calculation to $\frac{1}{T} = \frac{\partial S}{\partial U}$

① Express S in terms of some state parameter x

(e.g. no. of vacancy, no. of flipped links)

② Express U in terms of the same parameter

③ Using the derivative relation, we get $\frac{1}{T} = \frac{\left(\frac{\partial S}{\partial x} \right)}{\left(\frac{\partial U}{\partial x} \right)}$

Negative Temperature?

If we use $\frac{1}{T} = \frac{\partial S}{\partial U}$ to define temperature, then if a system's entropy decrease when its internal energy increase the slope $\frac{\partial S}{\partial U} < 0$, i.e. temperature is negative!

Requirement of such system to exist:

That system must only have finite no. of microstate

E.g. 2 boxes model with different energy

Suppose particles in the right box has higher energy

$E_R = \varepsilon$ ← Particle in box R has energy ε

$E_L = 0$ ← Particle in box L has energy 0

When total energy = 3ε

4 possible configurations

$$\begin{array}{c} \underline{0} \\ \underline{0} \\ \underline{0} \end{array}$$

Must be 3 in box R
(1 in box L)

Multiplicity = 4

When total energy = 4ε

1 possible configurations

$$\begin{array}{c} \underline{0} \\ \underline{0} \\ \underline{0} \\ \underline{0} \end{array}$$

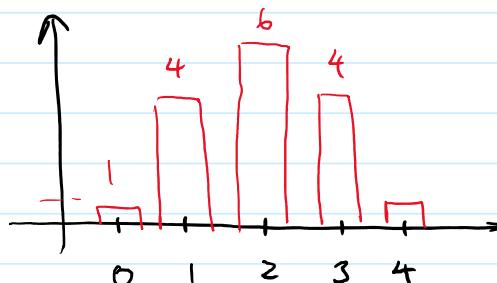
Increase

energy

All must be in box R

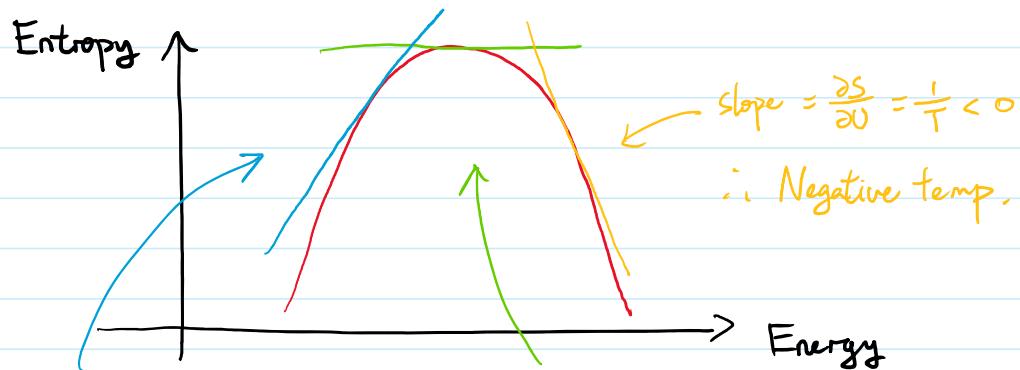
Multiplicity = 1

Multiplicity
~ Entropy



unit of energy, ε

If there are more particles, the chart becomes smooth.



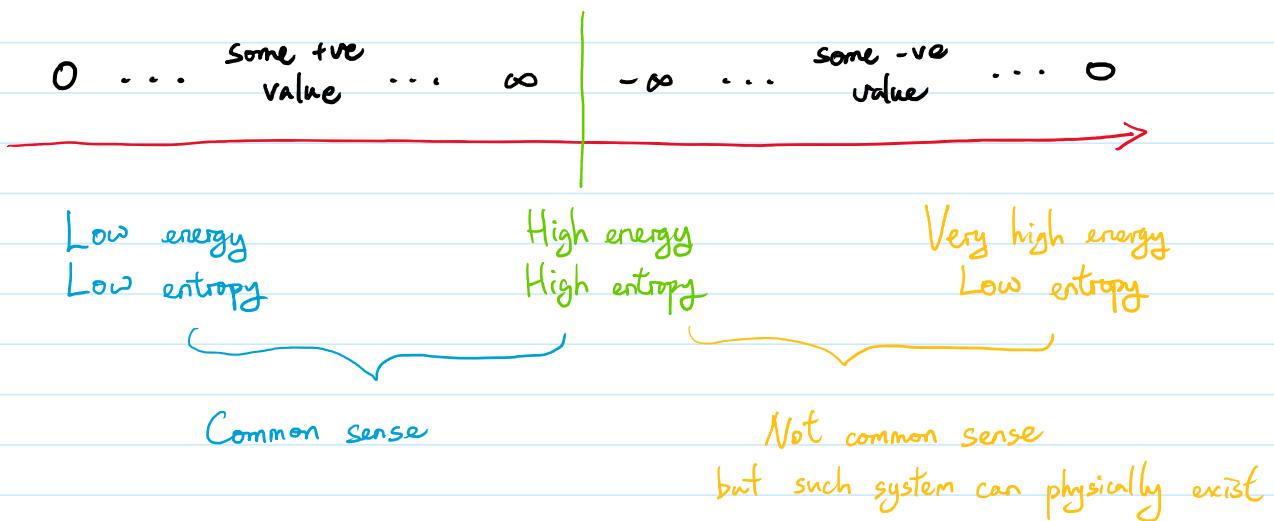
$$\text{slope} = \frac{\partial S}{\partial U} = \frac{1}{T} > 0$$

∴ Positive temp.

$$\text{slope} = \frac{\partial S}{\partial U} = \frac{1}{T} = 0$$

∴ Temp = ∞

⇒ Temperature scale defined by entropy is "weird"



Temperature is not about hot / cold any more

Temperature's history in brief.

- 1600s - 1850s : Celsius, Fahrenheit = By material expansion
- 1850s - 1870s : Kelvin = By heat engine efficiency
- 1870s - Now : Boltzmann, Maxwell = By entropy vs energy