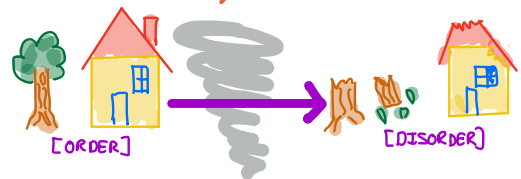


Heat Death, The Fimbulwinter



41. Fills the foreshore with dead men, reddens reigns abode with red gore; black was sunshine the summer after, the weather unsafe. Understand ye yet, or what?

-Völuspá, Poetic Edda, Odin visits a seeress who narrates the events before Ragnarök

54. "First, there is a winter called the Fimbulwinter, when snow drives from all quarters, the frosts are so severe, the winds so keen and piercing, that there is no joy in the sun. There are three such winters in succession, without any intervening summer."

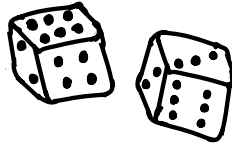
-Gylfaginning, Prose Edda, Hár replies to Gangleri's questions on preludes to Ragnarök (extract)

Entropy

Entropy is often introduced as a measure of "disorder". Let us explore a less "classical" definition of entropy as a measure of the number of microstates consistent with a given macrostate. $[S = k_B \ln \Omega]$

Let's play a game where 2 dice are tossed and we are told only the sum of the 2 faces after a throw. The possible sums 2, 3, 4, 5, ..., 12 would be the macrostates and the combinations possible to get a sum, the microstates. e.g. We can get a sum of 3 for (1, 2) and (2, 1).

The macrostate corresponds to the "large-scale" and observable part of the system and the microstate, the small-scale configurations which we can only infer.



SUM CONFIGURATIONS

2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		

Macrostate 7 has highest entropy. The microstates are more "spread out" in the probability space for 7. The notion of disorder comes from this. There are many ways to get 7.

Note: The mean corresponds with 7.

: The microstates are equiprobable.

2 and 12 have minimum entropy by this definition. Only one possible configuration leads to either 2 or 12.

Interpretation for a gas.

Consider a box containing an ideal gas. It has a specific pressure, volume, temperature and number of molecules. This is the picture of the gas as a whole. The (macrostate of the) gas is defined by the variables (P, V, T, N).

Zooming in on the gas, in the microscopic picture, we see a huge number of molecules constantly bumping into the walls of the container and into themselves. One important attribute of these molecules is their velocities. The distribution of molecular velocity resembles a normal distribution. Few with very low or very high and most at the mean.

The moving molecules make up the internal energy U of the gas. By elasticity of molecular collisions (and conservation of Energy), 2 molecules knocking into each other simply exchange their velocities. -1ϵ for 1 molecule and $+1\epsilon$ for another does not change the average.

→ The temperature of the gas is a measure of the average velocity of molecules.

While fixing a given state, (P, V, N, T), we now ask ourselves how many such different configurations are possible which leave the state fixed.



The number of microscopic configurations (microstates) consistent with ONE macrostate is the entropy of the system!

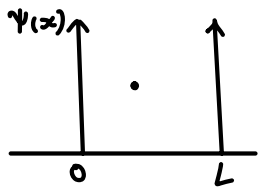
If we slowly cause a small disturbance to the gas by changing (P, V, N, T), eventually the gas will stabilise at a new equilibrium. We will again see the typical behaviour of gases. The equilibrium position corresponds to max entropy for that state.

Microscopic View

Classical Thermodynamics originally started as an investigation on Steam Engines. The birth of this field led to the industrial era. Analysis of macroscopic behaviour of systems was enough for engineers to improve engines. Watt refined the steam engine, Otto and Diesel pioneered the first model of automobile engines.

For the engineers, the classical model was enough to work with. However for scientists, many concepts remained unexplained. When considering atoms in the microscopic view, the Classical Mechanics started to be somehow lacking. A new mechanics was needed for the small particles; Quantum Mechanics.

A particle in a 1D box

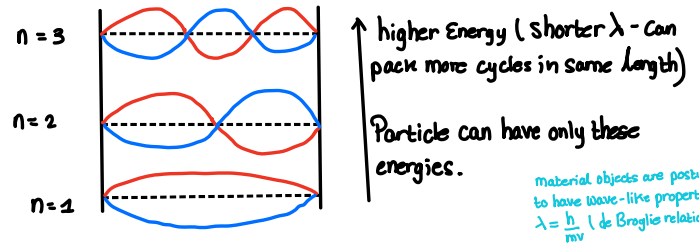


Principal quantum number n

$$E_n = \frac{n^2 h^2}{8 m L^2} \quad (n = 1, 2, 3, \dots)$$

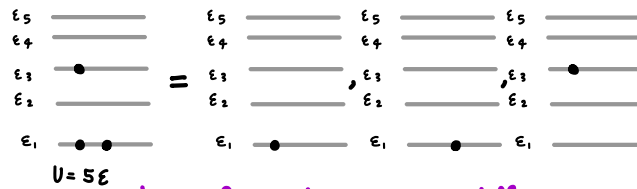
Length of box L

Energy of the particle E_n

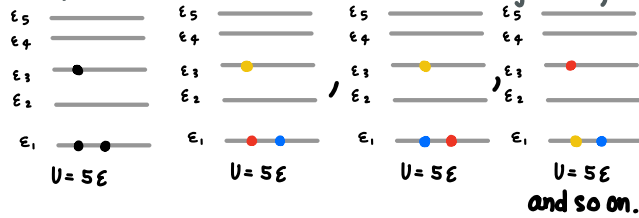


We shall simplify our diagram as follows :

- 1) Consider only 2 particles
- 2) Abstract the energy levels



Now, this state of 5ε can have different configurations,



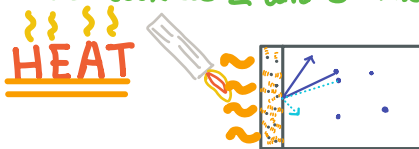
and so on...

The configurations represent different permutations. Classically, we see this as particles of same mass hitting into each other (elastically) and simply exchanging velocities (kinetic energy). 20 ml of water contains more than 10^{26} particles. If we got so many arrangements with 3 particles, think about one billion billion billion billion particles! Imagine for a glass of water.

Adding Energy to the System

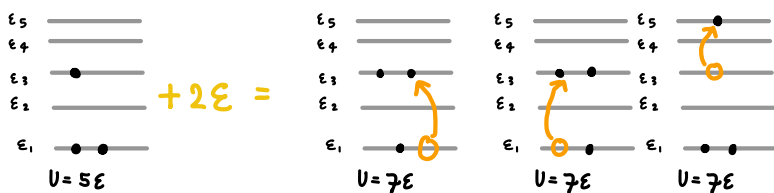
- There are a lot of ways to do so :
- 1) Pumping more particles into the system
 - 2) Crushing the system
 - 3) Placing the system over a candle
 - 4) Passing a force field through

Let's look at 2 and 3. They represent energy transfer as Work (2) and Heat (3).



Heating up the walls cause the molecules there to vibrate VIOLENTLY in a RANDOM fashion. The gas molecules moving randomly too, knock into the wall molecules. They bounce back with additional energy but randomly attributed. Vibrations in wall are too wild to give all colliding molecules same energy. Some that collide may get a lot while others, little.

Let's transfer 2ε of Energy as heat and see the result



The absorption of energy by gas molecules is random. Each has a chance of catching 2ε. Each separate state has its own set of permutations.

We see that after heating, we have access to more permutations.

This is why heat is associated with Entropy.

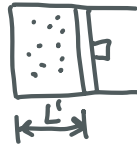
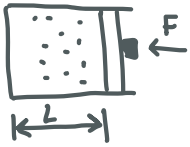
Cooling is heating another object. The system particles drop down restricting no. of microstates accessible.

This is same as the dice game. When we got a 5, it could have been (2+3), (3+2), (1+4) or (4+1). 5 has a higher entropy than 3 which could only be (1+2) or (2+1).

The movement of heat goes on for a while. At a point both bodies have access to the same number of microstates. (The energy levels are universal). This must mean that the 2 bodies become indistinguishable in a thermodynamic sense. The 2 bodies are said to be in thermodynamic equilibrium and this occurs at a certain temperature. Heat flow stops.

WORK

Let's now look at Work. Consider a simple gas - piston setup. We expend energy as we make a macroscopic force F act on the gas to compress it. By conservation of energy, the gas must store this added energy (which disrupts its initial equilibrium).



We see that expended energy to compress the gas.

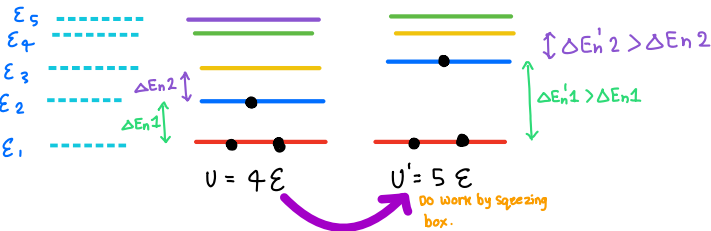
$$\uparrow E_n = \frac{n^2 h^2}{8 m L^2}$$

We see that decreasing the length increases the gap between the energy levels.

$$(E_n - E_{n-1}) = \frac{n^2 h^2}{8 m} \left(\frac{1}{L^2} - \frac{1}{L'^2} \right) \Rightarrow \Delta E_n \propto \frac{1}{\Delta L}$$

Work is a little different. It **BROADENS** the gaps between the energy levels.

population distribution



We see that work cause no change in the energy distribution when the particles collide with each other and exchange velocities. The number of permutation is same at initial and final equilibrium. Work causes no change in entropy.

In our 3D world, we are not limited to only length. The wave function for the particle in a box becomes:

$\Psi_{n_x, n_y, n_z} = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$. It is the product of 3 1D considerations. It is a 3D standing wave.

The 3 terms (for ideal particle) represent the 3 degrees of freedom for kinetic energy in x, y, z .

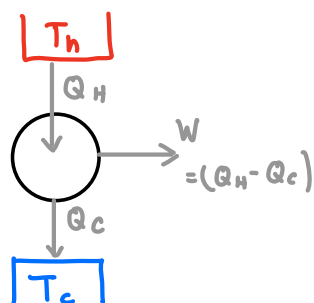
When we do work on a system, we exert a macroscopic force in a particular direction ($W = F \cdot ds$) e.g. the x direction. Transferring this energy to the gas corresponds to energizing the x d.o.f in all particles. To reject back the work, all particles, get rid of the energy added in their x d.o.f. The reverse occurs. The piston which pushed the gas in the x direction is pushed back by the gas particles. The energy released from the x d.o.f corresponds to a macroscopic force which push back the piston.

Owing to its intrinsic mechanism, heat transfers energy randomly. A particle getting energy in the x d.o.f could as likely get it in y or z degrees of freedom. Real gases are not restricted to these, they can rotate or vibrate too. When we want work done (in a particular direction), we most likely desire all particles to give up Energy in the concerned d.o.f to get a macroscopic force out put. But heat does not energize only one kind of degree of freedom (unlike work).

There is a certain number of energized x d.o.f, certain number of y and same for z . If our piston needs to move in the x direction, we can only use energy from the (few) x degree of freedom. The rest (y and z d.o.f) represent unavailable work. There is still energy which we got from heat, but by its nature a portion of it cannot push the piston. This is why thermal energy is seen as a LOW GRADE energy form. When it is injected into a system, not all of it can be used to do useful work. Work when injected into a system can be used by the system to do other work. Work from electrical, kinetic and Chemical is seen as HIGH GRADE.

LEAD to (some) GOLD

Trying to turn low grade stuff to high grade seems like the work of engineers. The French army engineer Sadi Carnot proposed an (ideal) mechanism nowadays known as the Carnot Cycle. It is a cycle built to get work from heat.



Even operating in ideal conditions, the engine does not reach full efficiency. Some of the energy unavailable to do work must be rejected in the cold reservoir, decreasing efficiency.

$$\eta_{\text{Carnot}} = 1 - \frac{Q_C}{Q_H}$$

The Arrow of Time

There are many processes in nature which seems to occur in only one direction despite the reverse being in accord with the laws of physics.

Take for example: Dropping an egg on the floor



We never observe the egg magically reconstituting and jumping up from the floor. This is because that process is associated with a decrease in entropy!

When the egg hits the floor, we can see that there is an increase in distribution of mass through space. The mass of the object before falling was concentrated in a small area, the egg. This spreading of mass is an increase in entropy.

Now, when the egg hits the floor, some of its kinetic energy is converted to thermal energy in the floor (heat released). Like we previously saw, heat is associated with Entropy change. Conversion of work to Heat means Entropy increased. Friction between shards and air also releases heat.

Suppose the reverse is to occur; there was no physical laws forbidding the air and ground molecules concentrating to their prior single degree of freedom. Classically, the molecular collisions reverse transferring kinetic energy to molecules in air which push back the shards to the original location. As physical reconstitution reaches completion, the ground molecules align and push the egg back up.

This is very unlikely! Statistics shows this. A new law was needed in physics to account for this. It is the very famous Second Law of Thermodynamics; $dS_{univ} > 0$ (Entropy of universe always increases). Another way of saying this is time progresses in direction of increasing Entropy.

Now, one might sit down and bring all the pieces together. He might even give the reconstituted egg a kick up. But in doing so, the person expends his energy and sweats (releasing heat) and increases S_{univ} even more. He could get a machine which does not sweat; but it releases heat by friction ($\uparrow S_{univ}$ even more). He could also build a heat engine to convert the heat from the egg impact to work to push it up. But inefficiency of these engines release some heat by its operating principle and by internal friction (real case). Realizing the desired reconstituted egg propulsion increases S_{univ} even more. There is no winning from this.

Work can be done to decrease entropy in one area but on the universal scale, entropy increased. This is the principle of the refrigerator, it moves heat from colder region to hotter to keep food cold. Naturally, heat flows from hot to cold as it increases entropy. The friction in compressor and coolant increases entropy more than that movement of heat. $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$. When $\uparrow \Delta S_{surr} > \downarrow \Delta S_{sys} \Rightarrow \Delta S_{univ} > 0$. All processes are limited by the laws of Thermodynamics!

The Heat Death

As we saw, all processes result in the entropy of the universe increasing. Eventually, this reaches a maximum value and we then say that the universe itself is in thermodynamic equilibrium. Everywhere is thermodynamically indistinguishable. The whole universe is at the same temperature. Since it is very large, the even distribution of thermal energy results in a cold, eternal winter.

There is no gradient. Heat exchange is not possible and neither are heat engines to extract work. Everywhere in the universe is uniform

Gravity $\rightarrow$ Entropy?
Bringing Objects together
Non-elastic
Cause Entropy to $\uparrow$.

The universe reaches thermodynamic equilibrium at maximum entropy. Everywhere is even. Everywhere is cold.
All the energy in the universe has been distributed in the large region. All forms of energy become heat.

Work cannot be done as it requires a disturbance. But everywhere is the same. There can be no external work as it is the whole universe which is in equilibrium. There is no heat flow as everywhere is at the same temperature. Heat engines do not work.

Long before the heat death, the following events concerning us would occur.

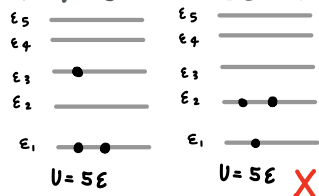
If climate change continues as it does so, ecological catastrophe could ensue. Mass migrations and mass extinctions become more likely.

As the Earth's core cools down, it loses its magnetic shield and Sun coronal mass ejections quickly rip apart our atmosphere.

Then it is the turn of the Sun to cool down and in the process of becoming a white dwarf incinerate us.

The piston simultaneously energises all the gas molecules by the same amount. The disturbance created in the gas represents the energy added. If we give the system enough time, eventually the system will reach a new equilibrium (molecular interactions even out disturbance). Else, the system can return back to its original state by rejecting the work input.

Now, this state of 5ϵ can have different configurations,



It is also worth remembering that each molecule can take the place of another (permutations). This gives rise to a large number of ways to arrange. 20 ml of water has about 10^{26} particles of water. If we got so many arrangements from 3 particles, imagine with one billion billion billion billion particles! Now think for a glass of water.

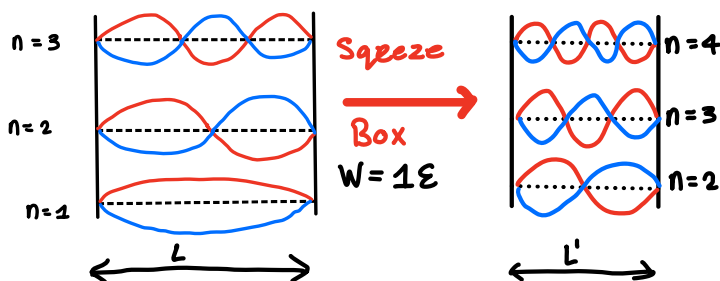
$Q = n\epsilon$ *thermal wavelength wave interference*

Like dice game.

$10\epsilon \rightarrow 3\epsilon, 4\epsilon, 5\epsilon$

Microstate of Possibility.

Some Energy must always be added to disturb the equilibrium.



$$\Psi(x, y, z) = X(x) Y(y) Z(z)$$

$$\Rightarrow \Psi_{n_x, n_y, n_z}(x, y, z) = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 \right)$$

Can heat only activate rotation & Vibration?

What about non-quadratic dof?
Other types of work activate those too.

Link no microstates to random energization of d.o.f in particles.

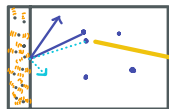
Physical meaning of Entropy

Entropy first appeared as a concept in the field of Thermodynamics. In this, the modes of transfer of Energy in form of heat and work are studied in details. They transfer energy by distinct mechanisms. Heat flow always accompanies entropy change.

For simplicity, consider this 1D box filled with We want to transfer 1 additional unit

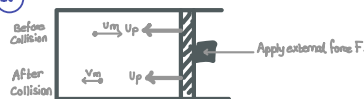
HEAT

$$Q = 1 \text{ J}$$



2 particles close together likely have different fates.

5 ideal gas particles. The particles move randomly and the internal energy U depends solely on the temperature; ultimately on the average velocity of the molecules. ($PV = NkT$, $U = \frac{3}{2} PV$). Assume each particle has 1 J of energy.



WORK

Elastic collisions $V_i = V_f$

$$\begin{aligned} \text{rel. vel before} &= U_p - (-U_m) = U_p + U_m \\ \text{rel. vel after} &= -(U_p - V_m) = V_m - U_p \\ \Rightarrow V_m &= U_m + 2U_p \end{aligned}$$

$$W = 1 \text{ J}$$

- Heating up the box cause the wall molecules to vibrate RANDOMLY.
- Gas particles collide with the wall and receive some energy.

$$\begin{aligned} &\begin{matrix} 1 \text{ J} & 1 \text{ J} & 1 \text{ J} & 1 \text{ J} & 1 \text{ J} \\ + & + & + & + & + \\ 0.3 \text{ J} & 0.1 \text{ J} & 0.05 \text{ J} & 0.2 \text{ J} & 0.35 \text{ J} \end{matrix} = 5 \text{ J} \\ &\hspace{10em} \text{We see the energy gained from heat is more "spread out".} \\ &\begin{matrix} 1.5 \text{ J} & 1.4 \text{ J} & 1.05 \text{ J} & 1.8 \text{ J} & 1.25 \text{ J} \\ + & + & + & + & + \\ 0.3 \text{ J} & 0.1 \text{ J} & 0.05 \text{ J} & 0.2 \text{ J} & 0.35 \text{ J} \end{matrix} = 6 \text{ J} \\ &\hspace{10em} \text{We see more disorder in Energy distribution.} \end{aligned}$$

- Collisions cause random distribution of molecular velocity.

- Energy is spent for an external macroscopic force to act on the system. By conservation of Energy, this external energy is converted to internal energy.
- We see that after collision, the (x-component) velocity increases (+2U_p) for ALL molecules. The higher velocity results in increased internal Energy.

* (All molecules get mU_p^2 additional Energy)

$$\begin{aligned} &\begin{matrix} 1 \text{ J} & 1 \text{ J} & 1 \text{ J} & 1 \text{ J} & 1 \text{ J} \\ +0.2 & +0.2 & +0.2 & +0.19 & +0.21 \end{matrix} = 5 \text{ J} \\ &\begin{matrix} 1.2 \text{ J} & 1.2 \text{ J} & 1.2 \text{ J} & 1.19 \text{ J} & 1.21 \text{ J} \\ + & + & + & + & + \end{matrix} = 6 \text{ J} \\ &\text{We see more order in energy distribution from (reversible) work.} \end{aligned}$$

→ In contrast to heat, there is no dispersion in molecular energy.

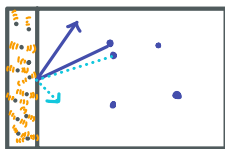
Algebras: The Reunion of Broken Parts.

If an alien sends you travelling through space and time into dark empty space, before dying look at your entropy-meter. Now $S_{\text{univ}} \approx 10^{103} k_B$. By looking at the value, you will know if you are in the past or future. Always keep your entropy-meter on you. Being lost in space does not always need for you to be lost in time!

Transferring Energy: Thermodynamics studies 2 common method of Energy Transfer; Heat & Work.

Heat is generally referred as microscopic Energy transfer while Work is macroscopic. Heat exchange is usually associated with change in System Entropy.

HEAT



When we crank up the heat on one wall of the container, the wall molecules start to vibrate wildly! This jiggling is highly unpredictable (RANDOM).

It must be greater or that process would not be statistically feasible by universe

At thermodynamic equilibrium, the Equipartition Theorem states that all the d.o.f quadratic in energy are equally filled. No work can be done. Imagine pushing a ball up then down, left then right. No net work is done. To get work, we must disturb the equilibrium. We input some energy. To resolve the disturbance, we make it go through a mechanism to take in energy from only one degree of freedom. The machine will take that energy from that particular d.o.f and the system will go back to equilibrium.

↳ It might be a new one as when we changed (disturbed) the sys. we could have changed states.

also, d.o.f

could be electrical

nuclear, magnetic

or rotational

#006FFF

Also, the input Energy could be by heat or work,

Work would be like
2 piston connected to
gas & locking
pushing one energizes the
 $\propto$ microstate
& rejection pushes the other piston.
(No change in state same equilibrium).



Heat like Carnot cycle

Mechanism absorb a particular d.o.f

System returns back to eq.

∴ Carnot cycle Analysis.

D.o.f are independent

Rotating ball does not make it fall
faster.

Projectile Motion: x does not influence
 y .

↳ Usual Parabolic Shape.

All the Energy can be taken by
many machinery

e.g. Piston in x , y & z

Rotating Plane for rotating particles
or something like that

Vibration for something else.

But when we want only x
the others appear useless!

↓ Is there a restriction on this?

Consider case of ideal gas only.
Prove this!

The degrees of freedom all get filled in thermodynamic Equilibrium!

↳ Mechanism of the distribution.

↳ How do degrees of freedom get filled?

Like how does Motional Energy get into the
Electric degree of freedom.

or empty space.
If closed in box, measure
entropy before & after time
travels

$$U = \sum \text{microscopic Energy.}$$

Look for Webpage on

$$W = qV$$

Work, Entropy & Electricity

It looked like Chem Libre text.

egg hit floor.

Work done on floor, U_{floor} increase but is disturbed.

To reach Thermodynamic equilibrium, Since it has NO mechanism to expel the additional Energy as work, it releases it by heat.

Study therm. eq.

again
in terms of work

E. Level Expand, compress

$\sin(\alpha) \sin(\alpha) \sin(\alpha)$ dof & bounce energy.

(or it settles to eq by distributing that random energy $\uparrow \Delta S$)

$$E_k = \text{Work}$$

For heat transfer there must be 2 reservoirs

else the system will absorb heat, reach same T as source & heat (Transfer) will stop!